ABSTRACT.

The thesis describes an investigation of the solution photochemistry of nitroalkenes and α-nitroketones. The introduction discusses the general concepts of photochemistry and provides a detailed review of the photochemistry of nitroalkanes, nitroalkenes and nitroaromatics and attempts to relate theoretical studies on the nitro group to the observed photochemistry.

Aliphatic α,β-nitroalkenes have been shown to undergo a photoinduced nitro-to-nitrite rearrangement in a variety of solvents, when steric interactions push the nitro group out of conjugation with the double bond. Nitroalkenes with a secondary or tertiary hydrogen at the γ-carbon from the nitro group undergo a hydrogen abstraction reaction, which competes with the nitro-to-nitrite rearrangement. Planar nitroalkenes do not undergo the nitro-to-nitrite rearrangement, but do undergo photoaddition of methanol, when this is used as the solvent.

α,β-unsaturated nitroalkenes photochemically add to a variety of alkenes. The adducts resulting from β-nitrostyrene are the most stable. The photoreaction is regiospecific with the most nucleophilic carbon of the alkene attached to the α-position of the β-substituted nitroalkene, but gives in every case a mixture of stereoisomers. The mechanism of the photoaddition is either concerted or else involves a short-lived diradical intermediate.

Secondary acyclic α-nitroketones undergo photoreactions in a variety of solvents to give hydroxyiminoketones, where the carbon bearing the oxime group formerly bore the nitro group. This reaction can be rationalized in terms of an initial C-N bond cleavage.

Secondary acyclic α-nitroketones on refluxing in alcohols and ethers give hydroxyiminoketones, solvent oxidation products and fragmentation products. This reaction was again rationalised by an initial C-N bond cleavage. 2-Nitrocyclohexanone undergoes a ring cleavage reaction

on refluxing in alcohols, via a hemi-acetal intermediate.

"None goes so far as he who knows not whither
he is going." Oliver Cromwell

This thesis is dedicated to my wife Sheila, above all else, for her constant encouragement. I also wish to express my thanks for the friendly help and encouragement shown to me by the staff and my fellow students of the Chemistry department which made my stay at Kent so enjoyable.

THE SOLUTION PHOTOCHEMISTRY OF NITROALKENES AND NITROKETONES.

CONTENTS

1. Introduction.

INTRODUCTION

(1) Electronic transitions and excited states.

(2) The photochemistry of the nitro group, a survey of the literature.

ELECTRONIC TRANSITIONS AND EXCITED STATES.

(a) Fundamental concepts.

Photochemistry is the study of the chemical changes which occur in molecules on absorption of ultraviolet or visible radiation. Electromagnetic radiation can be described in terms of either the wavelength λ the frequency ν or the energy E of a quantum of radiation. The relationship between these terms is given by the following expressions:

$\lambda = c/\nu$ where c speed of light,
$E = h\nu$ where h Planck's constant.

The electromagnetic spectrum stretches from 10^{-4} n.m. to 10^{6} n.m. but it is the ultraviolet - visible region that is of principal interest to the photochemist. This lies in the wavelength range 200 - 700 n.m. and corresponds to an energy range of $6 - 1.6 \times 10^{-5}$ J mole^{-1}, hence absorption of light in this region can provide sufficient energy to cause the formation and breakage of chemical bonds.

(b) Orbitals and electronic transitions.

The physical effect of absorption of u.v. or visible radiation is promotion of an electron from a ground state orbital to one of higher energy. Molecular orbitals can be considered to be linear combinations of atomic orbitals which lead to the formation of bonding and anti-bonding orbitals. Bonding orbitals have a high electron density between the nuclei whilst anti-bonding orbitals have a plane of zero electron density between the nuclei; anti-bonding orbitals are always of higher energy than bonding orbitals,

There are three basic types of orbitals commonly found in organic compounds. Sigma (σ) orbitals are formed by the combination of two orbitals (usually s or p) lying along the axis joining the atoms. The energy difference between the σ and σ^* orbitals is such that radiation in the range 100 - 200 n.m. is normally required for a $\sigma \rightarrow \sigma^*$ transition.

Pi (π) orbitals are formed by the sideways overlap of atomic 2p orbitals. Radiation of longer wavelength than in the σ case is required for a $\pi \rightarrow \pi^*$ transition. Non-bonding orbitals are found in molecules containing heteroatoms. These orbitals are not invovled in the bonding system of the molecule. The relative energies for the different types of transitions lie in the following order:

$$\sigma \rightarrow \sigma^* > n \rightarrow \sigma^* > \pi \rightarrow \pi^* > n \rightarrow \pi^*$$

From a practical point of view the majority of photochemical reactions studied result from an initial $n \rightarrow \pi^*$ or $\pi \rightarrow \pi^*$ transition.

The multiplicity of an electronic state is given by the expression $2S+1$, where S is the algebraic sum of the spin quantum numbers of the electrons in the system. Spin quantum numbers can be $\pm 1/2$, and as a consequence of the Pauli exclusion principle, electrons in the same orbital must have their spins paired. In molecules with all the electrons paired, S is zero and the multiplicity is one, and the molecule is in a singlet state (S). On promotion of an electron into a higher energy orbital, the electrons can have their spins paired, which gives an excited singlet state, or their spins unpaired, which gives an excited triplet state.

Promotion of an electron from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) will require the minimum energy uptake consistent with a change in electronic configuration. The resultant state which can either be a singlet or a triplet will be the first excited state and is given the symbol S_1 or T_1 Singlet states are of higher energy than triplets because of greater electron repulsion in the singlet state.

The wide range of intensities observed in absorption spectra is due to different absorptions having different probabilities of occurrence. An intense band is associated with a transition of high probability and is said to be allowed, whilst a weak band is associated with a transition of low probability and is said to be forbidden. It is possible to relate the ε value to a theoretical value known as the oscillator strength.

The probability of an occurrence of an electronic transition depends on various selection rules. Conformity with these rules give intense absorption bands, whilst non-conformity either no or weak absorption. These selection rules take into account changes in the electron spin, orbital symmetry, parity and momentum which occur as a result of the transition.

Changes in spin of an electron during excitation are forbidden, hence transitions from singlet to triplet states and vice versa are forbidden. This selection rule breaks down when a heavy atom or a paramagnetic species is present in the system. If the two orbitals involved in the transition do not simultaneously possess large amplitudes in the same region of space, the transition is forbidden, whilst if both orbitals possess large amplitudes in the same region, the transition is allowed. The selection rule concerning parity requires a definition of wavefunctions. When a wavefunction changes sign on reflection through a centre of symmetry, it is termed ungerade (u), whereas if it does not change sign, it is termed gerade (g). The selection rule states that transitions $g \rightarrow u$ and $u \rightarrow g$ are allowed but that transitions $g \rightarrow g$ and $u \rightarrow u$ are forbidden. The selection rule on momentum states that any transition resulting in a large change in linear or angular momentum is forbidden.

The time required for an electronic transition to occur is very short (10^{-15} sec.) compared with the time for a molecular vibration (10^{-13} sec.). This time difference is embodied in the Franck - Condon principle, which states that the internuclear separation is fixed during the course of an electronic transition.

A molecule in an excited state has a large excess of energy and this may be lost in several ways before chemical reaction can occur. Hence the likelihood of a photochemical reaction depends on the rate of reaction compared with the rates of other energy dissipation processes. There are three types of process by which energy can be dissipated, (a) radiation-less transitions from one excited state to another, (b) radiative transitions ~~between~~ from excited states and (c) electronic energy transfer between molecules.

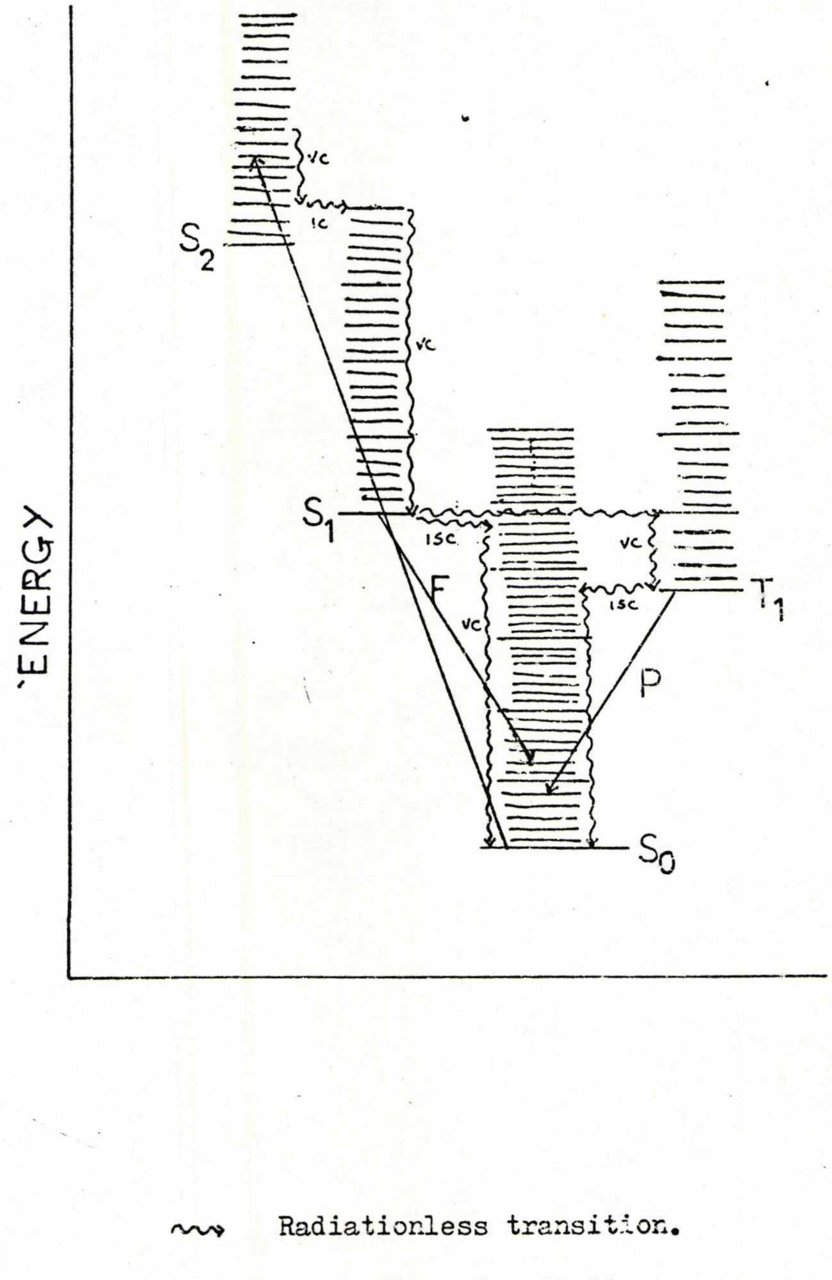
Radiationless transition processes are internal conversion (i.c.) and intersystem crossing (i.s.c.). Internal conversion is the transfer of energy from one excited state to another one of the same multiplicity. Intersystem crossing is the transfer of energy between excited states of different multiplicity (figure 1). The rate of internal conversion between excited and ground state singlets is very fast and hence the life times of upper singlets are very short (10^{-12} sec.). The intersystem crossing process $S_1 \rightarrow T_1$ is slower, due to the spin change ~~invovled.~~ involved

In the case of radiative loss, the emitted radiation is termed fluorescence when the transition is between states of the same multiplicity and phosphorescence when the transition is between states of different multiplicity. In general, the radiative lifetimes of the S_1 states are much shorter than those of the T_1 statas, which has the effect of allowing triplet state molecules to exist for a relatively longer time, greatly enhancing their opportunity to react chemically.

Energy transfer between molecules usually invovles a bimolecular process. The various types of bimolecular collision processes are (a) quenching of the excited state by chemical reaction, (b) deactivation by collision with a substrate molecule, (c) self-quenching of the excited states by bimolecular collision (a rare occurrence) and (d) deactivation of the excited state by donation of electronic energy to another acceptor molecule. Oxygen is a particularly effective quencher of the triplet state and hence has to be removed from the reaction by initial degassing.

Bimolecular reactions invovling radiative transfer of energy from a donor to an acceptor molecule can occur if the intermolecular separation

FIGURE 1



KEY.

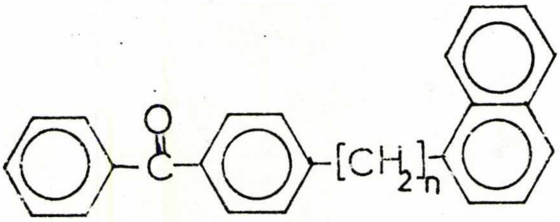
⇝	Radiationless transition.
→	Absorption of radiation.
$\xrightarrow{F}$ or $\xrightarrow{P}$	Emission of radiation.
vc	Vibrational cascade.
ic	Internal conversion.
isc	Intersystem crossing.
F	Fluoresence.
P	Phosphoresence.

between the two species approaches the collision diameter (short-range transfer). It is not necessary for the two species to collide, but for this transfer to occur the multiplicities of the states must agree with the Wigner spin conservation rule, which states that the following transfer reactions are allowed:

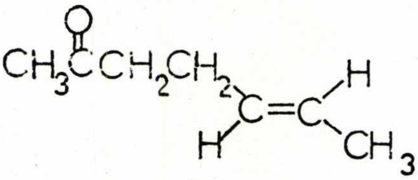
$$D^{*}(S_1) + A(S_0) \longrightarrow D(S_0) + A^{*}(S_1)$$
$$D^{*}(T_1) + A(S_0) \longrightarrow D(S_0) + A^{*}(T_1)$$

A = acceptor, D = donor.

Intramolecular energy transfer by this mechanism is also allowed. It has been shown that in (1), excitation of the benzophenone moiety leads to phosphorescence characteristic of naphthalene.[2] Similarly for (2), excitation of the ketone moiety leads to the formation of the Z-isomer.[3]



[1] n = 1,2,3



[2]

Transfer of electronic energy can also occur when the donor and acceptor molecules are separated by a distance much greater than the donor-acceptor collision diameter. This occurs when the energy differences between the vibrational levels of the ground and first excited states of the donor correspond to the energy differences between the ground and first excited state of the acceptor, here singlet-singlet and triplet-singlet energy transfer processes are allowed.

The quantum yield (∅) is a measure of the efficiency of a photochemical process. The exact process the quantum yield refers to must be defined for the value to have any significance. A general value for the quantum yield is:

$$\phi = \frac{\text{Number of molecules undergoing this process}}{\text{Number of quanta absorbed}}$$

Properties of excited states.

Photochemical reactions are usually concerned with unsaturated systems and the transitions may be classified as either $n \rightarrow \pi^*$ or $\pi \rightarrow \pi^*$; these states can be very different in properties. The initial $n \rightarrow \pi^*$ transition is forbidden and $S_1(n\pi^*)$ is usually of longer lifetime than $S_1(\pi\pi^*)$ as deactivation is forbidden.[1] The probability of conversion to the T_1 state is higher for $S_1(n\pi^*)$ state, than for the $S_1(\pi\pi^*)$ state. This is demonstrated by ketones which upon $n \rightarrow \pi^*$ excitation efficiently form triplet states, whilst alkenes upon $\pi \rightarrow \pi^*$ excitation are not as efficient as ketones in the formation of triplets. Formation of triplet states of alkenes usually requires the use of sensitizers.

Photochemistry of the Nitro group, a survey of the literature.

This literature survey can be divided into four categories: (a) the photochemistry of nitroaromatic compounds, (b) the photochemistry of nitroalkanes, (c) the photochemistry of nitroalkenes and (d) theoretical studies on the nitro group and attempts to relate these studies to photochemical results.

(a) Nitroaromatic photochemistry.

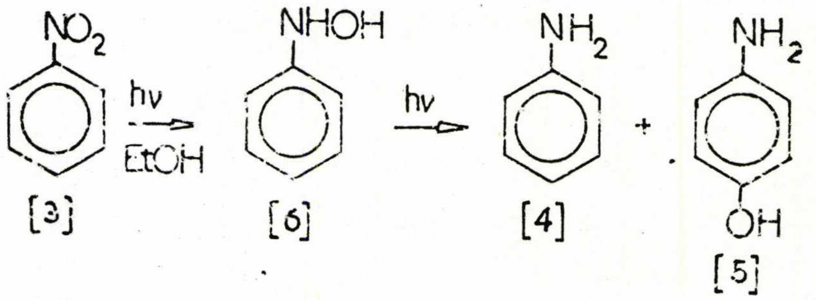
This subject can be divided into five reaction types: (i) hydrogen abstraction reactions, (ii) N-O bond cleavage reactions, (iii) photocycloadditions, (iv) photosubstition reactions and (v) the nitro-to-nitrite rearrangement (which will be discussed in the section on nitroalkenes).

(i) Hydrogen abstraction reactions.

Nitroaromatics can undergo either intermolecular or intramolecular hydrogen abstraction reactions. Intermolecular hydrogen abstraction reactions have been studied using (a) product analysis and (b) electron spin resonance spectroscopy.

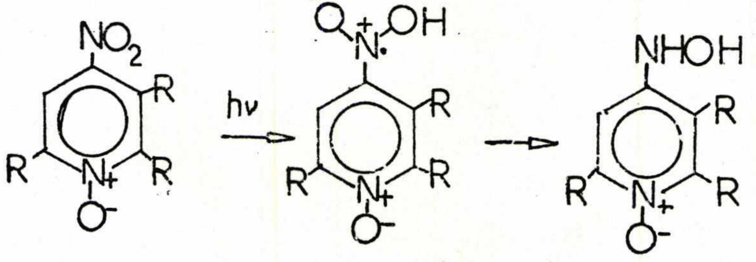
(a) Product analysis:

Nitroaromatics undergo photochemical hydrogen abstraction reactions in hydrogen donor solvents. The earliest report was the photoreduction of nitrobenzene (3) to aniline (4) and p-hydroxyaniline (5) in ethanol.[4] This is now rationalized as the primary photochemical product being phenylhydroxylamine (6) which undergoes further photoreaction to give the observed products.[5] In later work, the phenylhydroxylamine was isolated.



Irradiation of nitrobenzene in propan-2-ol leads to the formation of acetone and phenylhydroxylamine, postulated to arise by an initial hydrogen abstraction by photo-excited nitrobenzene, which is then photochemically converted to the corresponding amine or else reacts with oxygen to form azoxybenzene.[6] This abstraction reaction occurs via the $n\rightarrow\pi^*$ triplet of nitrobenzene, but the quantum yield is low compared with the analogous reaction of benzophenone, due to a rapid radiative deactivation of the nitrobenzene triplet.[7]

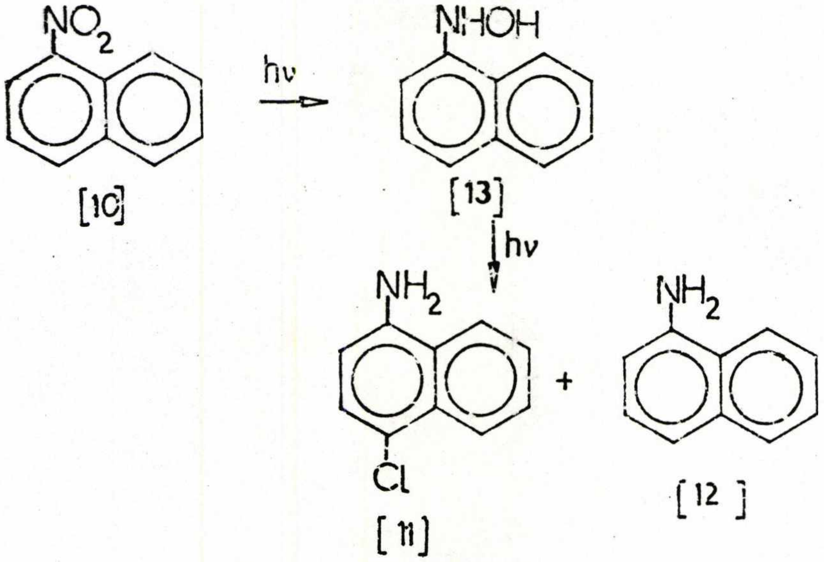
This hydrogen abstraction mechanism has been applied to explain several observations. Irradiation of 4-nitropyridene-N-oxide derivatives (7) in ethanol led to the formation of the corresponding hydroxylamine (8) via (9).[8] This photoreaction is solvent dependant, no reaction being observed in aqueous solution, but it occurs when ethanol or tetrahydrofuran is added. The excited triplet state of the nitroaromatic is considered to be responsible for the initial photochemical reaction.[9]



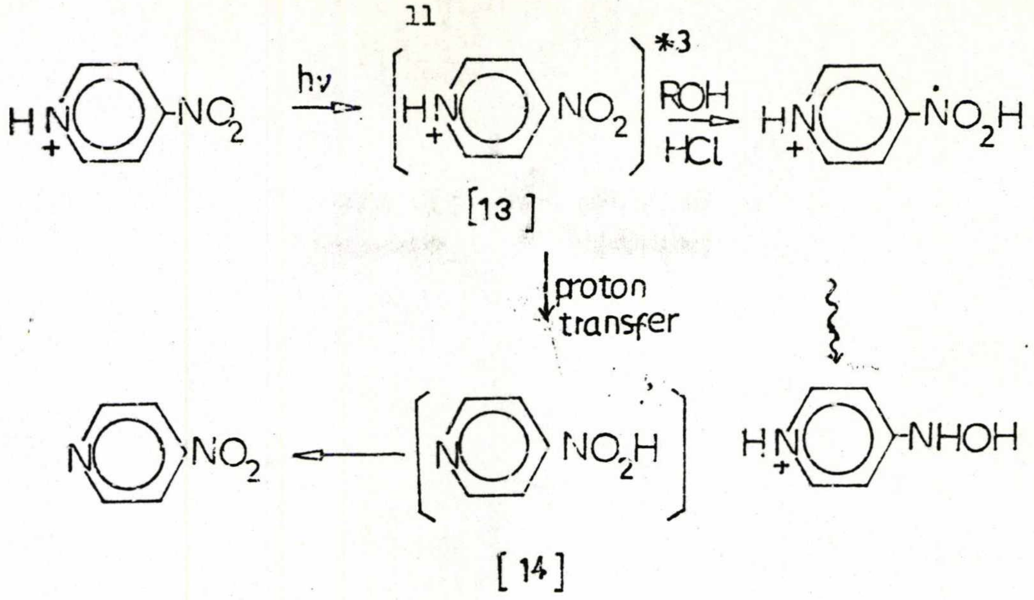
[7] [9] [8]

The photoreduction of 1,3,5-trinitrobenzene and 1,3-dinitrobenzene to azoxybenzene derivatives when ethanol is used as the solvent, has been reported.[10] Aromatic nitroesters are reported to be photoreduced to aminoesters.[11] Irradiation of substituted nitrobenzenes in propan-2-ol gives the substituted amines as products.[12] A study of the irradiation of p-substituted nitrobenzenes in propan-2-ol has shown electron-withdrawing groups give the corresponding amines whereas hydrogen and electron donating groups give phenylhydroxylamines.[13] The observation that nitrobenzenes can undergo either ring attack (photosubstitution) or reduction at nitrogen led to the suggestion that low lying $\pi\pi^*$ states are responsible for ring attack and $n\pi^*$ states for reduction.[14]

Photoreduction of nitroaromatics in alcohols in the presence of acid has been reported. Irradiation of nitrobenzene in propan-2-ol/hydrochloric acid causes protonation of the triplet nitrobenzene which increases its lifetime and enhances the photochemical reactivity by (a) hydrogen abstraction from the solvent and (b) attack of chloride ion on the aromatic ring.[15] Irradiation of 1-nitronaphthalene (10) under these conditions leads to (11) and(12), *via* the hydroxylamine derivative (13).[16,17] The failure of 1-nitronaphthalene to be reduced in neutral media is attributed to it having a $\pi\pi^*$ excited state rather than a $n\pi^*$ excited state[16,17], an analogous explanation to the one used to explain the observed photochemistry of 1-naphthaldehyde.



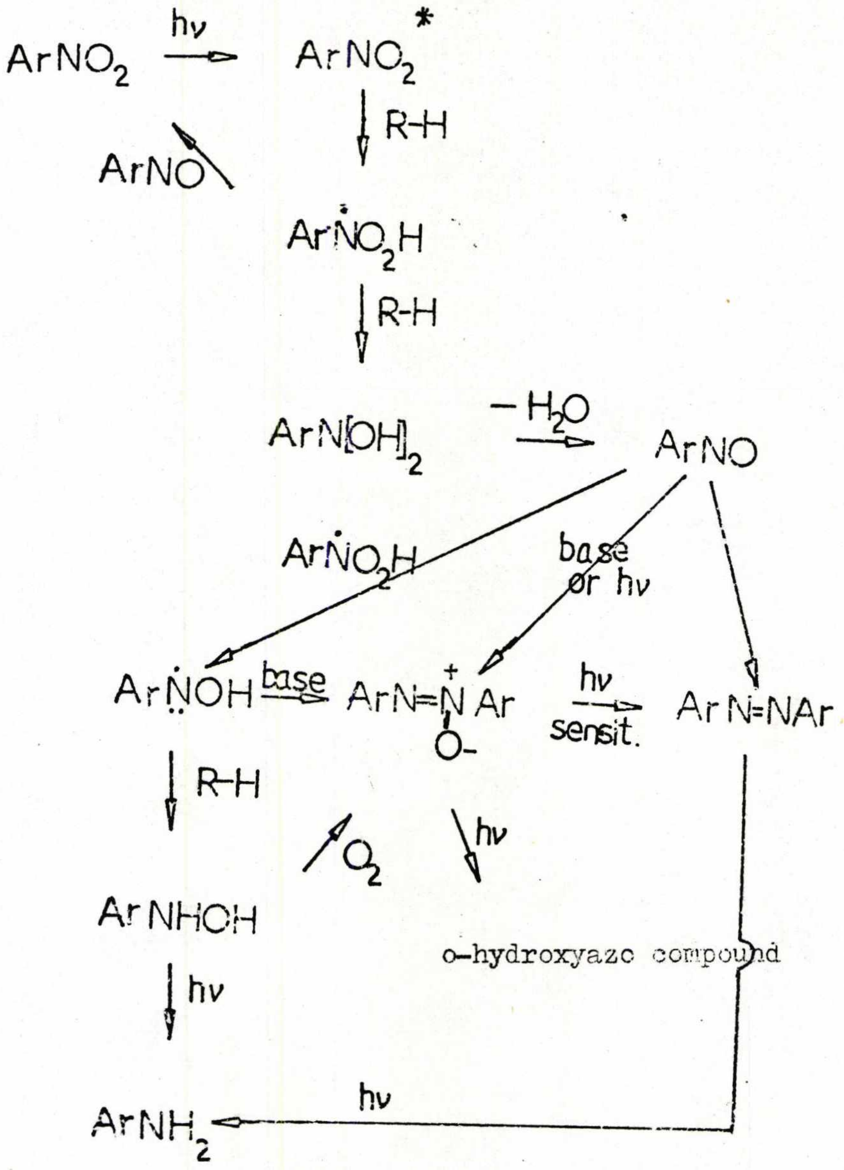
Irradiation of 4-nitropyridine in propan-2-ol/HCl leads to the formation of the corresponding phenylhydroxylamine derivative[18,19]. The triplet state of the 4-nitropyridinium ion (13) is responsible; proton transfer to the nitro group to give structure (14), leads only to deactivation, scheme 1.



Scheme 1.

The role of the chloride ion in these photoreactions has been investigated[20]. Electron transfer from the chloride ion to the nitro group has been observed and the resulting intermediate nitrobenzene anion identified. It was concluded that protons are essential to obtain photoreduction by reaction with the radical anion to give the phenylhydoxylnitroxide radical. The chloride ion can also attack the aromatic nucleus to give chlorine substituted reduction products[21,22].

Photoreduction of the nitro group occurs when amines or ethers are used as the solvent[23,24,25,26,27]. The isolation of amines along with other products was explained by Barltrop in terms of the following mechanism (scheme 2). It was concluded that the photoreaction occured __via__ the $(\pi\pi^*)^3$ state of nitrobenzene and theoretical calculations lend support to this theory[23,24].


ArNO2
hν
ArNO2*
ArNO
R-H
ArṄO2H
R-H
ArN[OH]2
− H2O
ArNO
ArṄO2H
base or hν
ArṄOH
base
ArN=N⁺Ar O⁻
hν sensit.
Ar N=NAr
R-H
O2
hν
ArNHOH
o-hydroxyazo compound
hν
hν
ArNH2

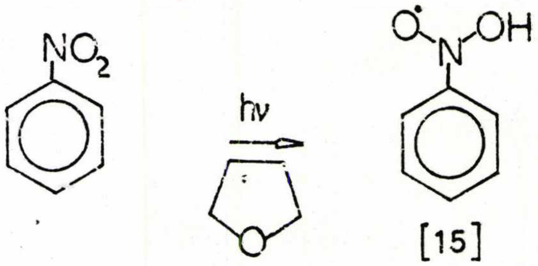
Scheme 2

Tri-n-butylstannane has been used as the source of abstractable hydrogens in the photoreduction of nitroaromatics[28]. It was concluded that the $n\pi^*$ triplet state was responsible for the initial abstraction reaction, in contrast to the work of Barltrop. Abstraction from saturated hydrocarbons has also been observed[29]. Tertiary hydrogens are ~~prefered~~ preferred to secondary and primary ones.

The general conclusion is that the photoreduction of nitroaromatics in hydrogen donor solvents proceeds via an initial hydrogen abstraction process. There is, however, some dispute as to the exact nature of the excited state concerned. Testa suggests that it is a $n\pi^*$ excited triplet whilst Barltrop suggests it is a $\pi\pi^*$ triplet. This will be discussed in more detail later, but it is important to notice that both workers agree that it is a triplet state as opposed to a singlet state that is responsible for the hydrogen abstraction reaction.

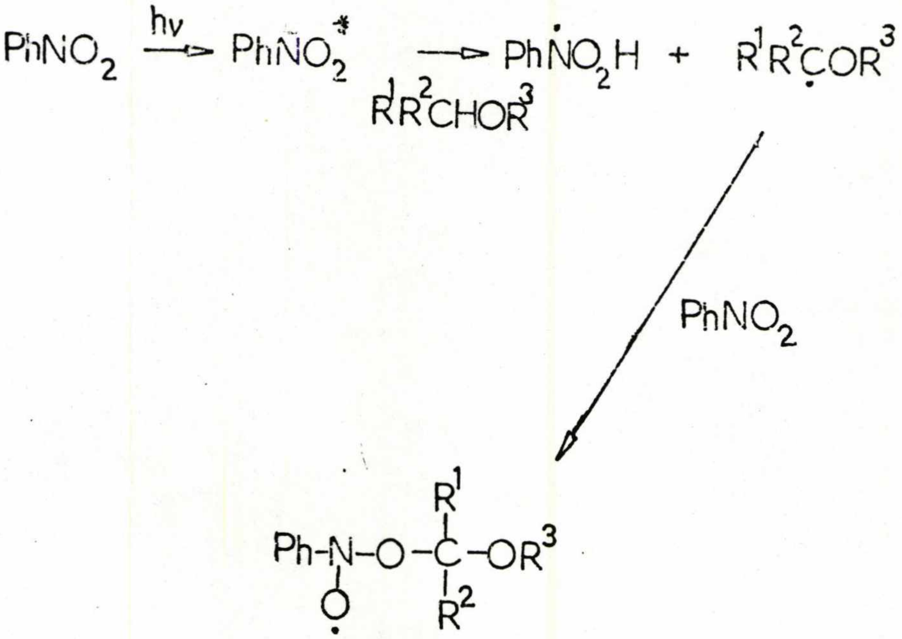
(b) Electron Spin Resonance studies.

The e.s.r. spectrum of 1,3,5-trinitrobenzene in tetrahydrofuran was the first nitroaromatic radical observed[32], and it shown to be a charge transfer complex of three tetrahydrofuran molecules and one 1,3,5-trinitrobenzene[33]. It was originally thought that irradiation of nitrobenzenes in THF gave an e.s.r. spectrum attributable to the phenylhydroxylnitroxide radical (15), formed by photochemical hydrogen abstraction by the excited nitro group from the solvent[34,35,36]. These spectra were reassigned to a



[15]

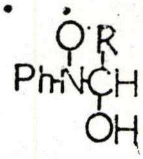
charge transfer complex similar to that postulated for 1,3,5-trinitrobenzene [37,38]. They were reassigned again by Sutcliffe[39] who obtained e.s.r. spectra when substituted nitrobenzenes were irradiated in ethers. These radicals were fairly stable, whereas the decomposition of the phenylhydroxylnitroxide radical (15) has been reported to be very rapid[40]. The observed e.s.r. spectra were attributed to phenylalkoxynitroxide radicals (16), an adduct of the nitrobenzene and a solvent radical, the latter being formed by hydrogen abstraction by excited nitrobenzene from the solvent, as shown in scheme 3. The addition of a radical to nitrobenzene has since been demonstrated[41].



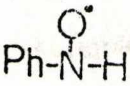
[16]

Scheme 3

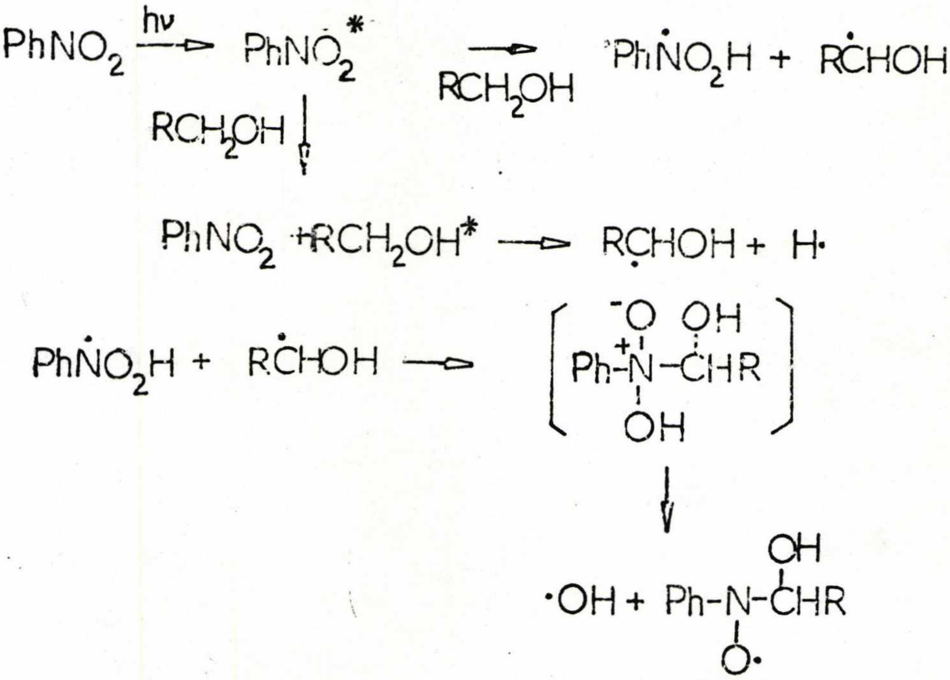
Irradiation of nitrobenzene in alcohols gave e.s.r. spectra assigned to alkylnitroxides (17) when primary alcohols were used, whilst secondary alcohols gave alkylhydronitroxides (18)[42]. The authors presented scheme 4 to account for their observations and claimed that no intermediate radicals were observed due to their low steady state concentration. This mechanism is rather cumbersome and an alternative explanation for the formation of radical (17) may be nitrosobenzene acting as a radical trap, the nitrosobenzene being formed from the breakdown of the phenylhydroxylnitroxide radical[40].



[17]

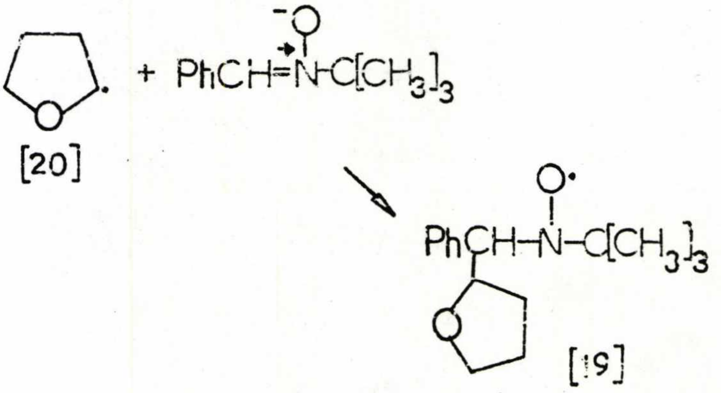


[18]



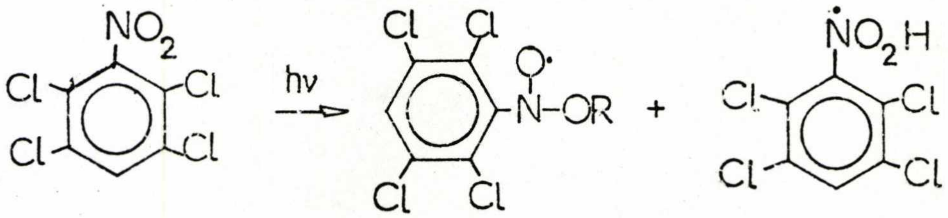
Scheme 4

A reinvestigation into the ~~irradiadiation~~ irradiation of nitrobenzene in THF[43], confirmed previous results[39]. Irradiation in the presence of phenyl t-butyl nitrone (a radical trap), however, gave radical (19), which was taken as evidence for the intermediary tetrahydrofuran radical (20) formed by an initial hydrogen abstraction reaction. Analogous results were found



in molecules containing electron withdrawing substituents whilst molecules containing electron donating groups failed to give any hydrogen abstraction products, explained by analogy with substituted benzophenone by a change from a $n \rightarrow \pi^*$ state to a $\pi \rightarrow \pi^*$ state which is a poor abstractor[43a].

The first report of the elusive phenylhydoxylnitroxide radical came from the irradiation of 2,3,5,6-tetrachloronitrobenzene in a variety of ethers[44]. This gave rise to the normal adduct (21) and a weak signal from a short lived radical attributed to the phenylhydroxylnitroxide radical (22). A detailed report on chloro substituted nitrobenzenes,



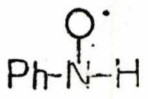
[21]

[22]

showed that only in the case of 2,4,6-trichloronitrobenzene and the case above was a phenylhydroxylnitroxide radical observed[45].

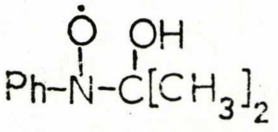
Electron donating groups were found to inhibit this reaction[46], in agreement with previous work[43]. This was explained by a change to a $\pi\pi^*$ excited state from a $n\pi^*$ state or by the substituents hindering the abstraction reaction. Hydrogen abstraction reactions were also shown to occur for nitroheteroaromatics such as 2-nitrofuran and 2-nitrothiophene. Alkoxynitroxide radicals are observed[46,47].

Wong and Wan have studied the photoreductions of nitrobenzene in various solvents[48]. With ethers, the phenylalkoxynitroxide radical was observed, in agreement with earlier results. A spectrum attributed to structure (23) was observed when aqueous tetrahydrofuran was used. Irradiation of nitrobenzene in propan-2-ol led to the observation of radical (24), which



$\mathrm{Ph{-}\overset{O^{\bullet}}{N}{-}H}$

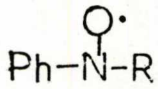
[23]



$\mathrm{Ph{-}\overset{\dot{O}}{N}{-}\overset{OH}{C}[CH_3]_2}$

[24]

is different from previous conclusions [42]. The use of amines and aqueous alkaline solutions as solvents for the irradiation of nitrobenzene led to the formation of radical anions, whilst use of hydrocarbons as solvents led to radicals of type (25) being observed. These results were explained



$\mathrm{Ph-\overset{O\cdot}{N}-R}$

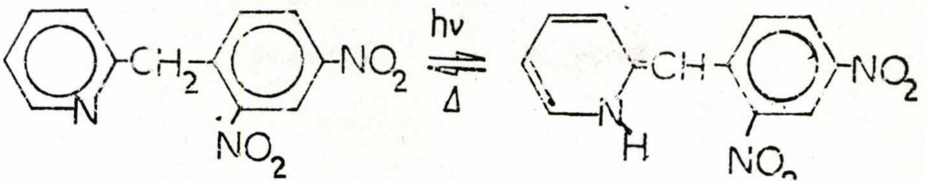
[25]

by the observed radicals being derived from the unstable phenylhydroxyl nitroxide radical. The phenylnitroxide (23) detected in aqueous THF is derived from the reaction of nitrosobenzene and the phenylhydroxylnitroxide radical. In amines and aqueous alkaline solutions, the observed radical anion is postulated to be formed by the breakdown of the phenyl hydroxylnitroxide radical. The radical observed in hydrocarbon solvents is considered to arise by the addition of a solvent radical to nitrosobenzene which is in turn derived from the phenylhydroxylnitroxide radical.

The overall picture presented by these e.s.r. studies is that the initial photochemical step is hydrogen abstraction from the solvent, a proposal which is in agreement with the conclusions drawn from the product analysis studies.

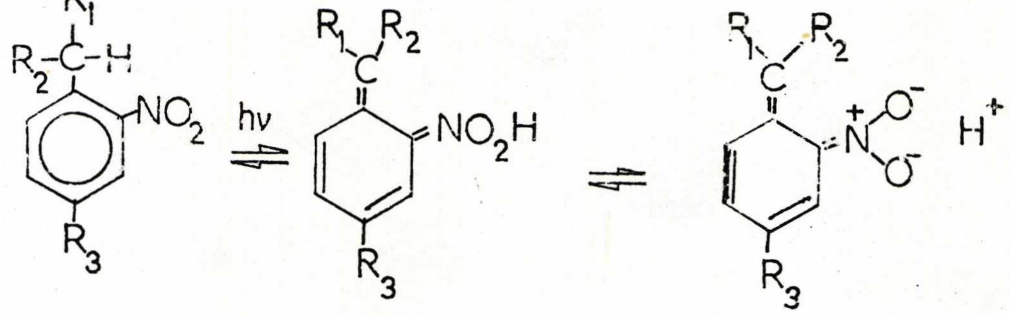
Nitroaromatics also undergo intramolecular hydrogen abstraction reactions, the two best known examples being the photochromism of nitroaromatics and the o-nitrobenzaldehyde rearrangement. These two photoreactions share a common initial reaction of hydrogen abstraction.

The photochromic behaviour of nitroaromatics has been the subject of several reviews[49,50]. The first report of photochromic behaviour of nitroaromatics was by Chichibabin[51] who observed the photochromism of crystalline 2-(2,4-dinitrobenzyl)pyridine (26) and proposed that the effect was due to hydrogen transfer from the methylene bridge to the pyridine nitrogen to give structure (27).



[26] [27]

Hardwich found that both (26) and 4-(2,4-dinitrobenzyl)pyridine were photochromic at low temperatures in solution[52,53]. It was suggested that it was the ortho-nitro group rather than the pyridine nucleus that is the important feature in the molecule. The general mechanism suggested is shown in scheme 5. The initial photochemical reaction is considered to be an intramolecular hydrogen abstraction of one of the benzyl hydrogens via



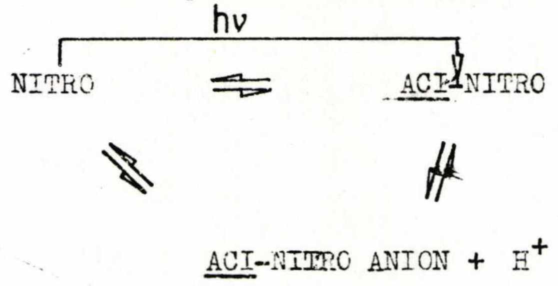
Scheme 5

a six-membered transition state to give an aci-nitro isomer, which being a strong acid will dissociate and the intensity of the observed colour will depend on the extent of the dissociation.

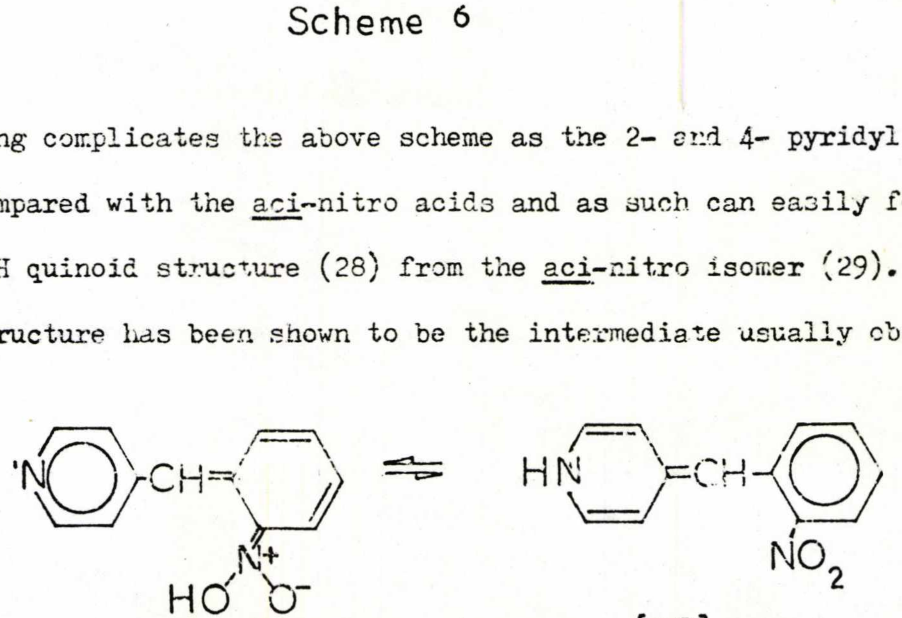
o-Nitrotoluene is the simplest structure that can undergo this intramolecular hydrogen abstraction reaction, and flash-photolysis studies showed that a transient intermediate was formed in aqueous base or acid which was identified as the aci-nitro isomer[54,55,56]. Extra evidence for this hydrogen transfer mechanism was provided by showing that hydrogen-deuterium exchange occured at the methyl group of o-nitrotoluene when it was irradiated in D_2O, whereas *p*-nitrotoluene did not show any exchange[57]. The efficiency of the process is rather low, as the quantum yield, determined by an indirect route, for *aci*-nitro formation from *o*-nitrotoluene, is only 0•01[58].

The formation of coloured species on irradiation of many *o*-nitrobenzyl derivatives has been observed[59,60,61] and this, coupled with the lack of photochromism[59,62] in similar structures containing only *p*- or *m*-nitro groups and in *o*-nitrobenzoyl structures, has provided more evidence for this hydrogen transfer mechanism.

Apart from when strong acid is used as the solvent, the observed absorption spectrum appears to result from the dissociation of the *aci*-nitro isomer. Margerum showed that the colour could be generated in the dark by addition of strong base to an alcoholic solution of these nitro compounds and this was due to the formation of a small equilibrium amount of the *aci*-nitro anion structure[59]. In strong acid, the spectrum of the *aci*-nitro isomer is observed[56,63]. In the absence of pyridine groups a general equilibrium is set up as shown in scheme 6 . The presence of a pyridine ring complicates the above scheme as the 2- and 4- pyridyl groups are basic compared with the *aci*-nitro acids and as such can easily form the tautomeric N-H quinoid structure (28) from the *aci*-nitro isomer (29). The N-H quinoid structure has been shown to be the intermediate usually observed in neutral

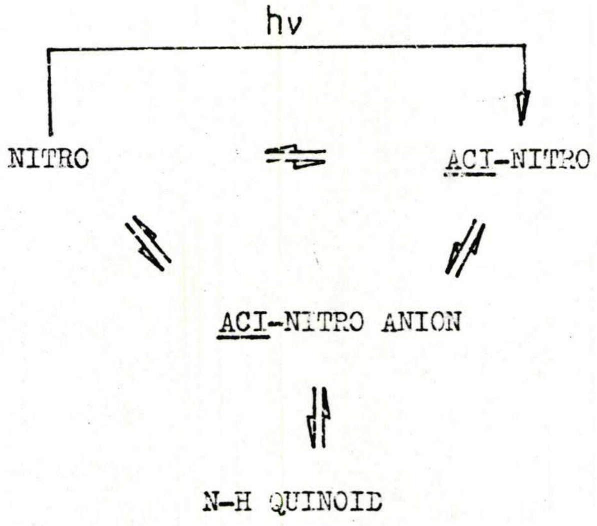


Scheme 6



[29] [28]

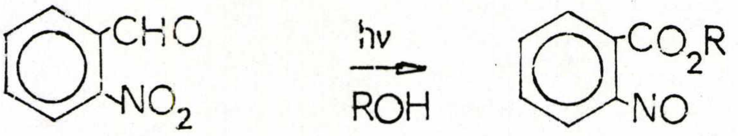
media for pyridine derivatives[64]. Hence the tautomerization initially postulated by Chichibabin[51] is correct but ~~invovled~~ involved an incorrect pathway. The equilibrium set up with 2- or 4- pyridyl derivatives is shown in scheme 7.



Scheme 7

The excited state by which the *aci*-nitro tautomerization occurs is not clearly understood, but a triplet state mechanism has been suggested[50]. These photoreactions have a low quantum yield due to there being competing non-reversible reactions present[59].

The *o*-nitrobenzaldehyde rearrangement has been known since 1901 and examples are shown below. It was found that 3- and 4-nitrobenzaldehydes are relatively light stable[73,74].



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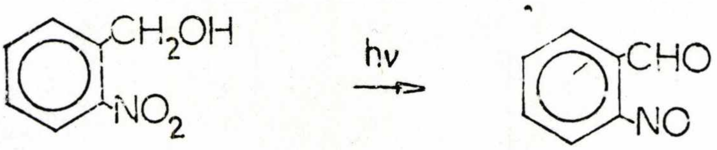

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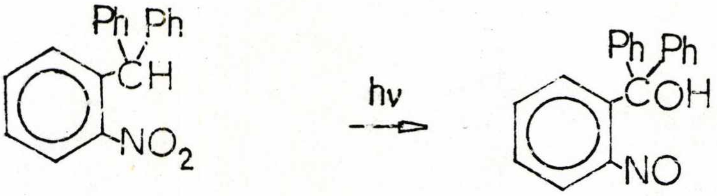

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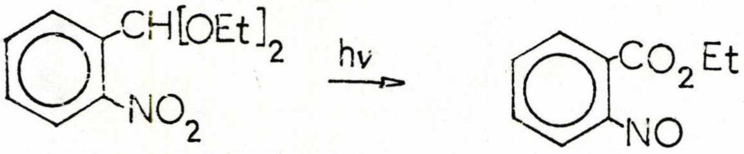

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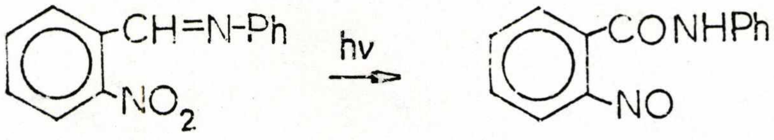

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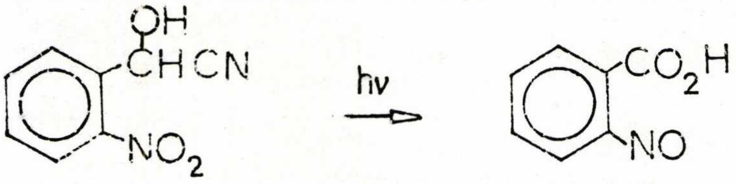

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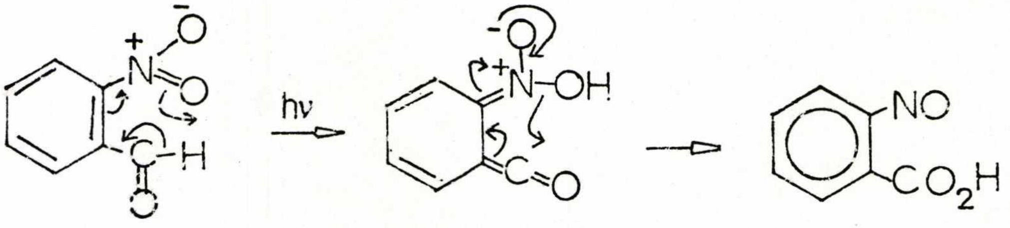
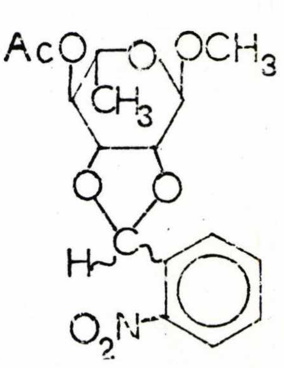
A general mechanism to explain these results was put forward by de Mayo and Reid[75], who postulated an initial photochemical hydrogen abstraction by the excited nitro group <u>via</u> a six-membered transition state leading to a ketene which then gives the observed products (scheme 8). This mechanism in its initial stages is very similar to the one postulated to explain the photochromic behaviour of nitroaromatics. It has, however, been disputed by other workers who suggest that there are heterocyclic intermediates involved ~~invovled~~ after the initial hydrogen abstraction[76]. The first postulation is the one most favoured by subsequent workers.

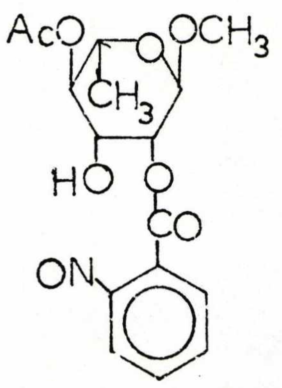


Scheme 8

Attempts have been made to put this rearrangement to synthetic use. Irradiation of an <u>o</u>-nitrobenzylidene pyranoside (30) causes rearrangement to the <u>o</u>-nitrosobenzoate (31), which may provide a potentially useful route to a partially protected carbohydrate <u>o</u>-nitrosobenzoate[77]. Light sensitive nitrobenzyl glucosides were coverted on irradiation into D-glucose which provides a method of protecting hydroxyl groups[78]. 6-Deoxymannose and 6-deoxygalactose can be protected in a similar way[79]. <u>o</u>-Nitrophenylethylene



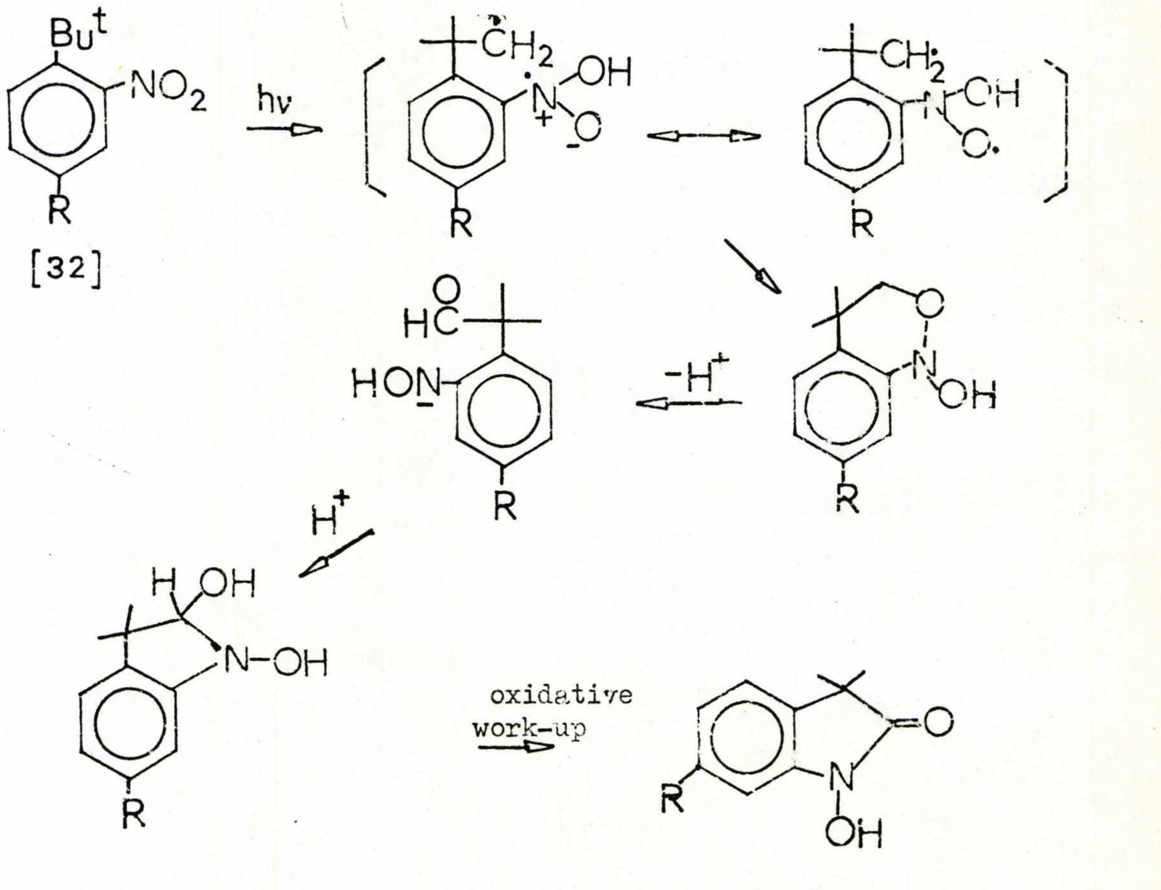
[30]



[31]

glycol has been used as a photosensitive protecting agent for aldehydes and ketones such as testosterone[80], whilst the o-nitrobenzyl group has been employed in the protection of aminosugars[81], in the protection of histidine derivatives[82], and also in peptide synthesis[83]. Little work has been done on the determination of the multiplicity responsible for the photoreaction. Barltrop reported that this rearrangement ~~invovles~~ involves the excited singlet state but no details were given[23].

Recently a number of reports have appeared in the literature that have rationalized product formation by an intramolecular hydrogen abstraction by photoexcited nitrobenzenes but invovling a seven-membered transition state. Dopp has shown that irradiation of a series of substituted o-t-butylnitrobenzenes (32) in various solvents and in the solid state gave indolones (33) as the major product on alkaline oxidative work up[25,84,85,86,87]. The mechanism suggested by Dopp is shown in scheme 9 and ~~invovles~~ involves an



[32]

[33]

Scheme 9

initial hydrogen abstraction by the triplet $n\pi^*$ nitrobenzene. A slightly different mechanism was put forward by another group to explain similar results, but the initial reaction was again postulated to be hydrogen abstraction[88]. Kituara and Matsuura[12] agree in principle with Dopp's mechanism but they favour the participation of an excited singlet state. The photorearrangement of a series of N-aryl-2-nitrobenzamides to 2-(2-hydroxyphenylazo)benzoic acids[89] can also be rationalized by an initial hydrogen abstraction requiring a seven membered transition state.

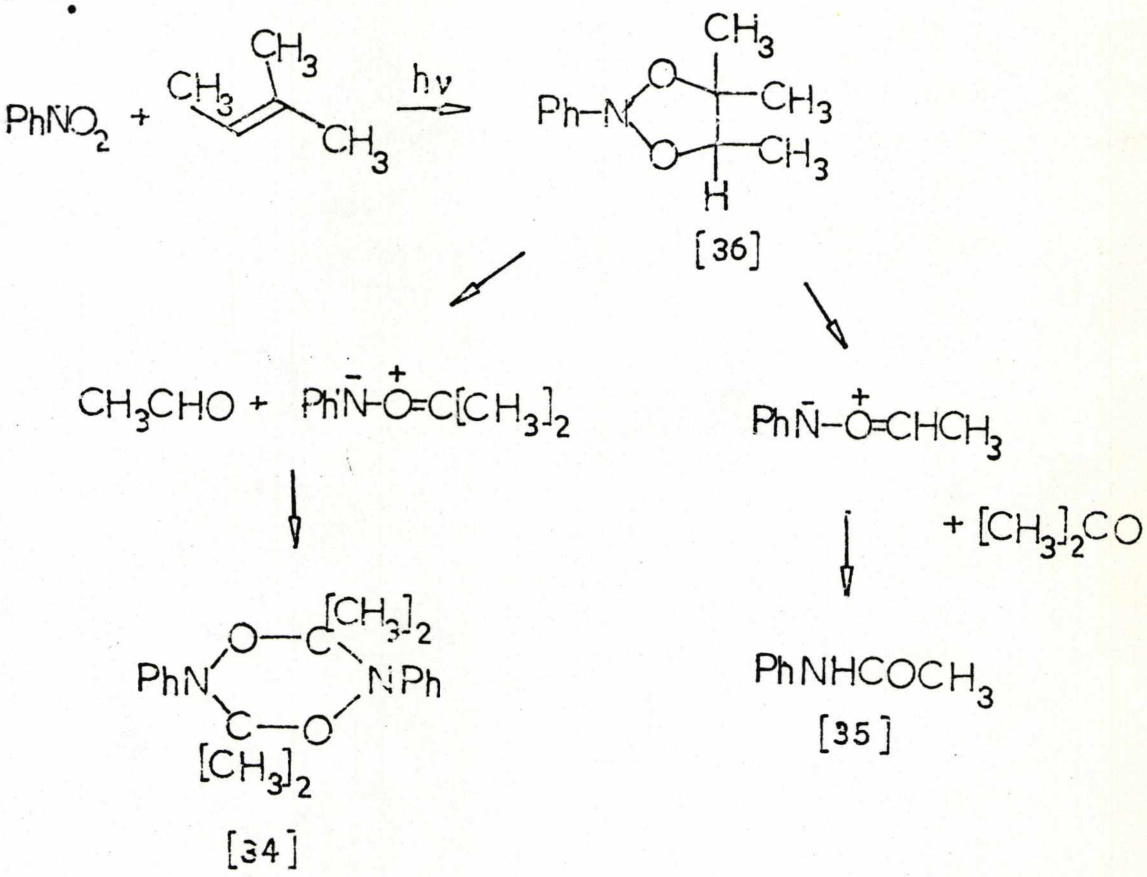
Apart from hydrogen abstraction reactions requiring a six- or seven-membered transition state several examples of remote intramolecular hydrogen abstraction have appeared in the literature. N-2,4-dinitrophenyl-amino-acids, upon irradiation, undergo decarboxylation to yield 4-nitro-2-nitrosoanilines [90,91], and also formation of substituted 6-nitrobenzimidazole-1-oxides[92]. N,N-disubstituted o-nitroanilines on irradiation produce benzimidazoles and benzimidazole-N-oxides[93,94]. Both these reactions occur *via* a nine-membered transition state. Remote intramolecular hydrogen abstraction by an aromatic nitro group has been used to introduce unsaturation in the steriodal D-ring[95].

(ii) N-O bond cleavage photoreactions,

An early report concerns the photodecomposition of nitrobenzene in the gas-phase[96]. The principle products are nitrosobenzene and p-nitrophenol. The production of these products was explained by N-O cleavage of the nitrobenzene to give nitrosobenzene and an oxygen atom which reacts with nitrobenzene, the para isomer being obtained as the nitro group is ortho/para directing for free radical reactions. The primary reaction postulated in this reaction is analogous to the photochemical decomposition of nitrogen dioxide in the gas-phase[97,98]. Photoreduction of nitrobenzene has been observed in the presence of triethylphosphate[30] and borontrichloride[31] where an initial oxygen transfer has been postulated to explain the observed results.

(iii) Nitrophotocycloaddition.

Aromatic nitrocompounds can undergo photoaddition to alkenes across the two oxygen atoms of the nitro group. The first observation was the addition of nitrobenzene to 2-methylbut-2-ene and cyclohexene to give (34) and (35) postulated to occur *via* (36)[99], as shown in scheme 10. de Mayo added evidence for this mechanism by characterizing a 1,3,2-dioxazolidine intermediate (36) in the photoreaction of nitrobenzenes with alkenes[100,101], whilst Saito has shown that the olefinic bond cleaved can be part of an aromatic system[102,103].



Scheme 10

Intramolecular cycloaddition reactions have been postulated. The formation of 2-phenylisatogens from *o*-nitrostilbenes[104] and the formation of benzotriazole-1-oxides from *o*-nitrophenyl-1-pyrazoles[105] are rationalized by an intramolecular 1,3-cycloaddition reaction. A 1,2-intramolecular cycloaddition of a nitro group to a carbonyl double bond has been postulated to explain the conversion of *N*-acyl-2-nitrodiphenylamines into phenazine-*N*-oxides[106].

(iv) Nitroaromatic Photosubstitution.

It was initially observed that nitrophenyl esters and ethers in aqueous solution were stable in the dark but were rapidly hydrolysed in the presence of light; meta-substituted compounds were more reactive than the ortho and para isomers[107,108]. This activation of the meta position by the nitro group was noted by several groups of workers and typical examples are shown below.

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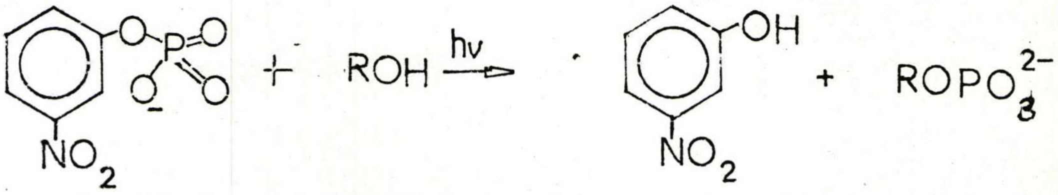

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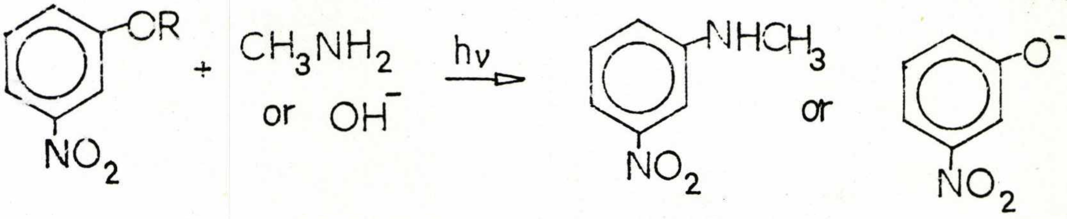

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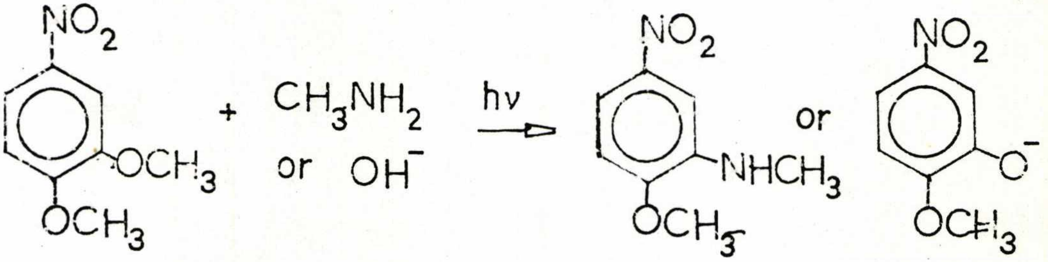


The reaction was found to be bimolecular and invovled the short lived first excited $\pi \; \pi^*$ singlet state. The charge densities for the various sites in the first excited state were calculated and were found to correspond to the site of reaction, hence allowing a certain degree of prediction. In other nitroaromatics the nitro group may undergo substitution as in the 1-nitronaphthalenes[111,112] and 1-nitroazulenes[112]. Nitroheteroaromatics also undergo photosubstitution of the nitro group, as 2-nitrofuran and 2-nitrothiophene are converted to the corresponding cyano-derivatives by irradiation in aqueous potassium cyanide solution[113].

(b) The photochemistry of nitroalkanes and related compounds.

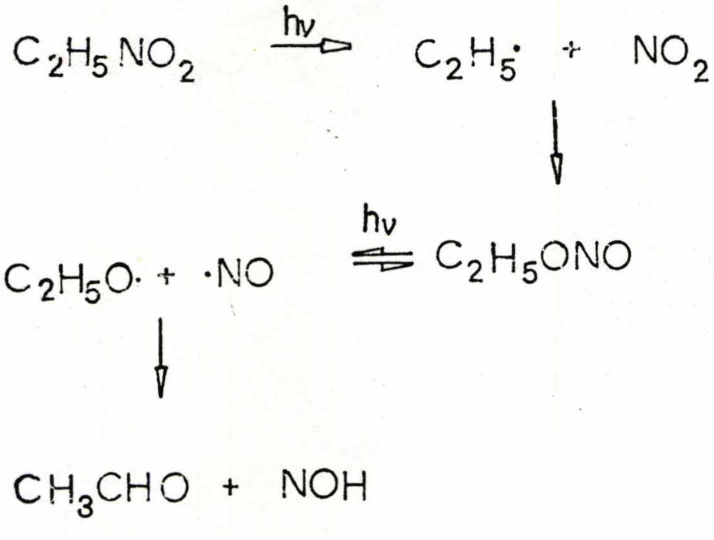
The literature on the photochemistry of nitroalkanes has recently been reviewed by Paszyc[114]. This work concentrated on gas-phase photolyses, with very little mention of solution photochemistry. The conclusions drawn by this reviewer was that the primary photochemical process is C-N homolytic bond cleavage.

The first reports on the photochemistry of nitroalkanes dealt with the gas-phase photolysis of nitromethane and nitroethane[115,116]. On the basis of product analysis the primary photochemical pathway was suggested to be loss of an 'oximino radical' (37), or else primary rearrangement of the nitroalkane to its aci-nitro isomer (38) and the subsequent loss of an 'oximino radical' from this. The possible structure of (37) was, however, not commented upon. The photolysis of nitromethane in an argon matrix at 20 K led to the formation of methyl nitrite as the major product and the primary photochemical process was considered to be C-N homolytic bond cleavage followed by radical recombination within the solvent cage[117,118]. In a reinvestigation of the gas-phase photolysis of nitromethane, using mass spectroscopic analysis, the results were rationalized by an initial homolytic C-N bond cleavage[119]. A detailed account of the photolysis of nitromethane and nitroethane in both gas and liquid phases has been reported

$$C_2H_5NO_2 \xrightarrow{h\nu} CH_3CHO + \underset{[37]}{NOH}$$

$$C_2H_5NO_2 \xrightarrow{h\nu} \underset{[38]}{CH_3CH{=}NO_2H} \longrightarrow CH_3CHO + NOH$$

by Rebbert and Slagg[120]. Irradiation of nitromethane in the gas-phase gave methyl nitrite and nitric oxide as the major products, which were explained by postulating an initial C-N homolytic bond cleavage followed by recombination to give the nitrite and its subsequent decomposition. In the case of nitroethane, ethyl nitrite and acetaldehyde were found to be the major products of gas-phase photolysis and were explained by the following mechanism, scheme 11. Irradiation of nitroethane in the liquid phase gave as the major products, ethyl nitrite, acetaldehyde and ethylene. The observed quantum yields for the production of ethyl nitrite and acetaldehyde were lower in the liquid phase. This could be due to either (a) in the gas-phase initial homolytic C-N bond cleavage gives $C_2H_5\cdot$ and NO_2 which may then separate, but in the liquid phase separation is more difficult and recombination to give the starting nitroalkane may occur, or (b) if recombination occurs in the gas-phase the molecule has enough energy to redissociate whilst in the liquid-phase rapid deactivation *via* the neighbouring ground state nitroalkane molecules can occur. It is very interesting to note that no nitrogen dioxide was observed in the course of this study.



Scheme 11

However, nitrogen dioxide was detected together with the alkyl radical by e.s.r. studies, in the photolysis of nitroalkanes at 77°K in various matrices[121]. It was concluded from these results that the major photochemical pathway for nitroalkanes is homolytic C-N bond cleavage. A similar conclusion was reached by Paszyc to explain formation of nitrogen dioxide, aldehydes and alkyl nitrites in the gas and liquid phase photolyses of nitromethane and nitroethane[122,123]. However, Christie observed nitrosomethane and formaldehyde in the gas-phase photolysis of nitromethane, and the observation that the yield of formaldehyde was not affected by the addition of nitric oxide was intrepreted as evidence for the formation of formaldehyde being a molecular elimination reaction[124]. Flash photolysis studies on nitromethane have indicated methyl radicals and nitrogen dioxide are present[125,126].

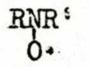
The photolysis of nitromethane in the gas-phase, using light of 313n.m. has been studied in detail[127]. Methyl nitrite, formaldehyde, nitrosomethane and nitrc oxide were obtained. It was observed that the quantum yields for all the products except formaldehyde decreased with an increase in pressure of ethylene or *cis*-but-2-ene. From these results, two primary processes were suggested, firstly cleavage of the C-N bond and secondly a molecular elimination process to give formaldehyde. *Cis*-but-2-ene underwent isomerization to the *trans* isomer and from these results it was concluded that the formation of methyl nitrite and nitric oxide result from a triplet excited state of nitromethane. As addition of ethylene was not as effective, it was suggested that nitromethane had a similar triplet energy to ethylene (328kJ mole^{-1}). Thermal *cis*-*trans* isomerization of but-2-ene, by nitrogen dioxide or nitric oxide require activation energies of 51 kJ mole^{-1} [128], and 109 kJ mole^{-1} [129] respectively and hence these thermal reactions are too slow to account for the measured rate of isomerization.

The vacuum ultraviolet photolysis of 2-methyl-2-nitropropane gives a complex mixture of products which can be explained by a primary homolytic C-N bond cleavage to give a t-butyl radical that undergoes further reaction [130]. The gas-phase photolysis of 1-nitropropane leads to the formation of a large number of products which were explained by two primary photochemical processes, namely homolytic C-N bond cleavage and an intramolecular elimination reaction[131].

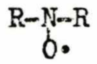
Fairly recently, reports of irradiation of nitroalkanes in solution appeared in the literature. The first report was concerned with an e.s.r. study of the radicals produced upon irradiation of nitroalkanes and β-nitroalcohols in polar solvents[132]. Three types of radicals were detected; for a nitroalkane RNO_2 in a solvent R'H these were:

$R\dot{N}O_2H$

(39)

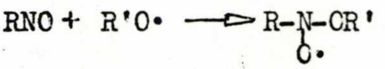

$R\underset{O\bullet}{N}R'$

(40)


$R-\underset{O\bullet}{N}-R$

(41)

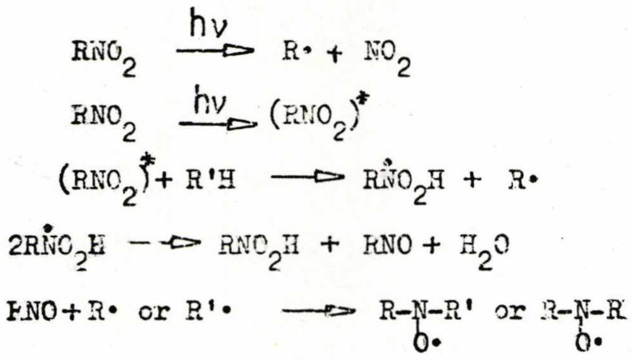
However, the assignment of one of the observed spectra to structure (39) may now be in some doubt as the e.s.r. spectrum of an alkoxyalkylnitroxide radical (42)[133,134], formed by the reaction of an alkoxy radical with a


$$RNO + R'O\bullet \longrightarrow R-\underset{O\bullet}{N}-OR'$$

(42)

nitroso compound, was found to be very similar to the spectrum assigned to the hydroxyalkylnitroxide radical (39).

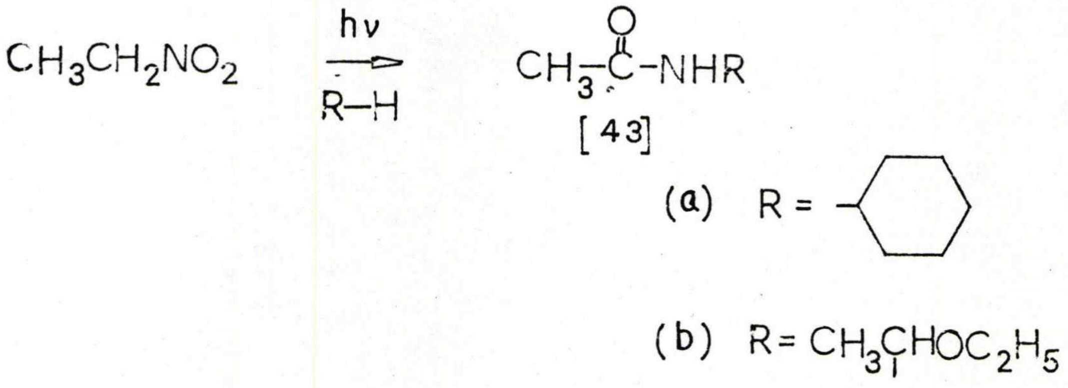
The mechanism suggested to explain these results is shown in scheme 12.


$$RNO_2 \xrightarrow{h\nu} R\bullet + NO_2$$
$$RNO_2 \xrightarrow{h\nu} (RNO_2)^*$$
$$(RNO_2)^* + R'H \longrightarrow R\dot{N}O_2H + R\bullet$$
$$2R\dot{N}O_2H \longrightarrow RNO_2H + RNO + H_2O$$
$$RNO + R\bullet \text{ or } R'\bullet \longrightarrow R-\underset{O\bullet}{N}-R' \text{ or } R-\underset{O\bullet}{N}-R$$

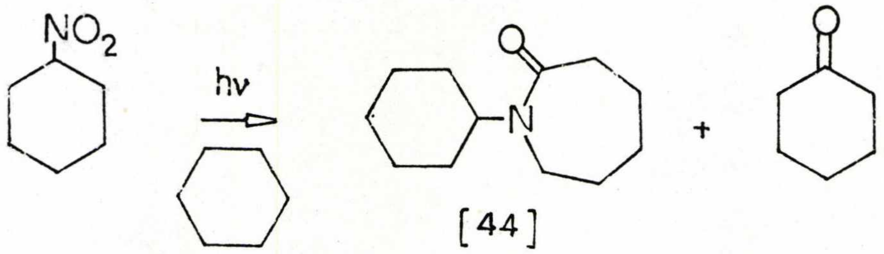
Scheme 12.

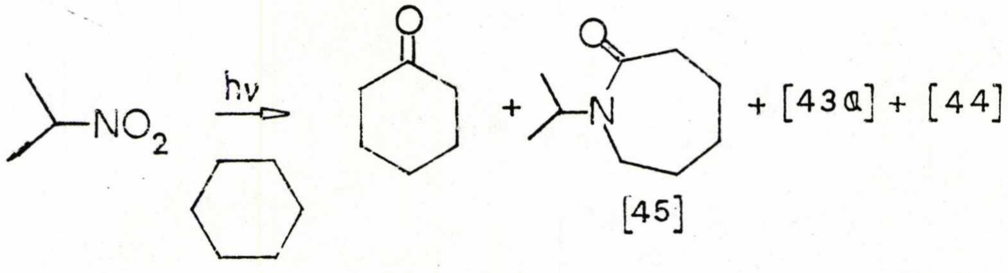
The results and postulated mechanism indicate that in solution two pathways are important, namely homolytic C-N bond cleavage and hydrogen abstraction by the nitro group from the solvent. However, bearing in mind the possible incorrect assignment of the observed e.s.r. spectra, caution must be exercised.

Reid and co-workers studied the products obtained from the irradiation of nitroalkanes in solution. Irradiation of nitroethane in cyclohexane and diethyl ether gave acetamidocyclohexane (43a) and 1-acetamido-1-ethoxyethane (43b) as the respective products[133], whilst irradiation of nitrocyclohexane

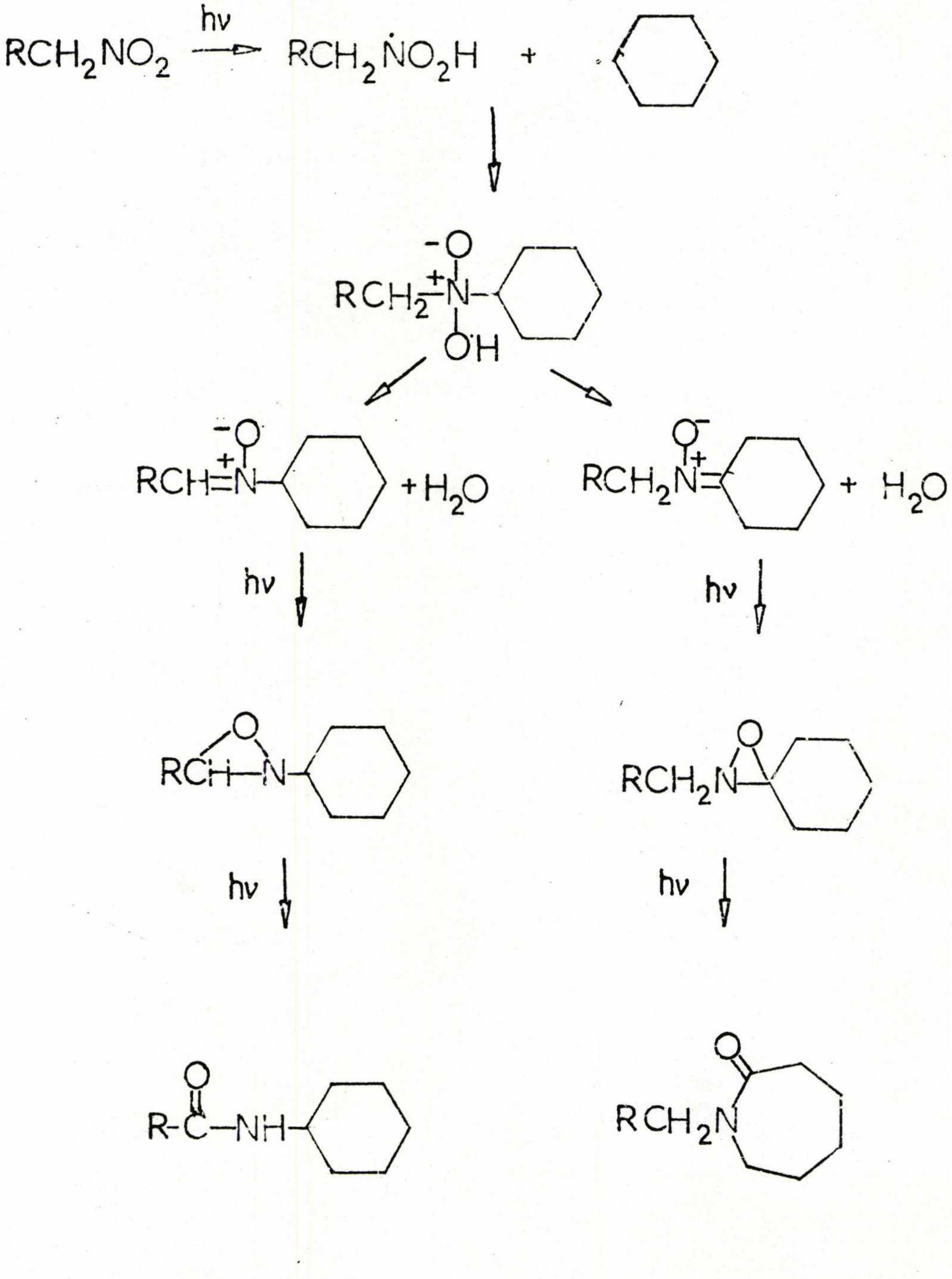


in cyclohexane gave cyclohexanone and N-cyclohexylcaprolactam (44), and irradiation of 2-nitropropane in cyclohexane gave cyclohexanone, N-isopropylcaprolactam (45), acetamidocyclohexane (43a) and N-cyclohexylcaprolactam (44)[134].



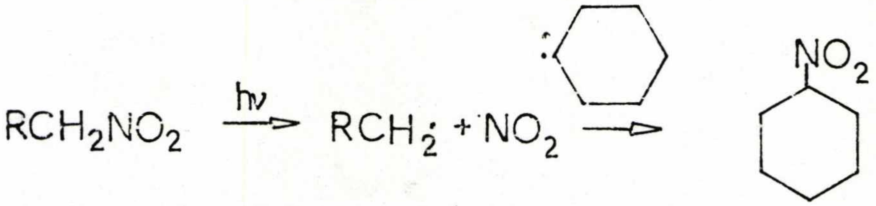


A detailed paper on this subject was published[135]. Cyclohexane as solvent gives three types of product; firstly, solvent oxidation products, cyclohexanol and cyclohexanone, were formed in low yields in all the photoreactions. The second type of product from the irradiation of primary nitroalkanes in cyclohexane are amides and caprolactams, thought to be formed by an initial hydrogen abstraction by the excited nitro group from cyclohexane as in scheme 13. The photorearrangement of nitrones to oxaziridines is well established[136]. In the case of secondary nitroalkanes, cleavage of the oxaziridine ring is accompanied by alkyl migration.



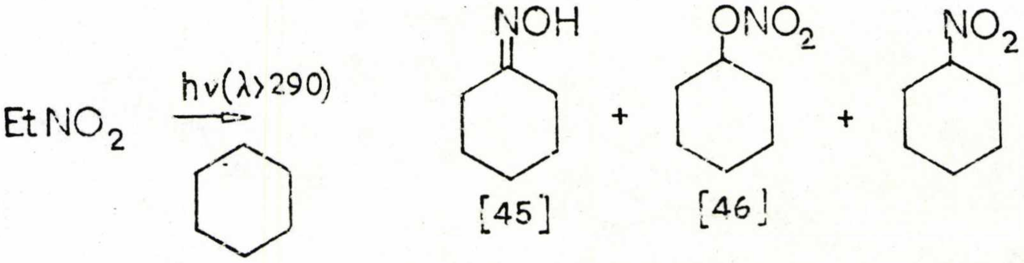
Scheme 13

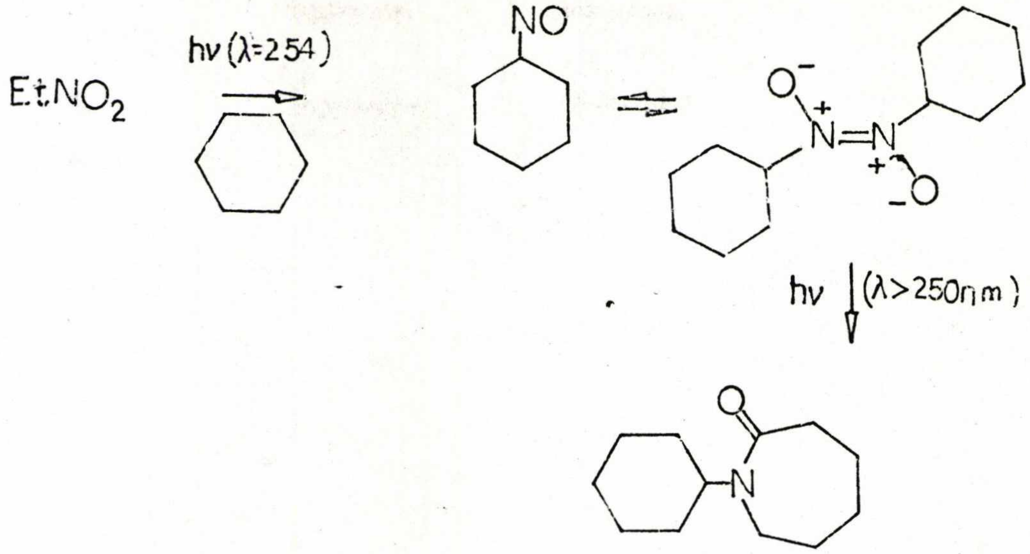
The thrid pathway is the formation of alcohols from the corresponding nitroalkanes. Their formation was rationalized by a photochemical homolytic cleavage of the C–N bond, which gives an alkylnitrite on radical recombination which is then cleaved photochemically to give the alcohols. In all the irradiations in cyclohexane, nitrocyclohexane was present, formed by an initial C–N bond cleavage of the nitroalkane and the reaction of the nitrogen dioxide with cyclohexyl radicals generated by the hydrogen abstraction reaction.



These authors concluded that for nitroalkanes in cyclohexane two competing photochemical pathways exist, namely hydrogen abstraction by the excited nitro group and homolytic cleavage of the C–N bond.

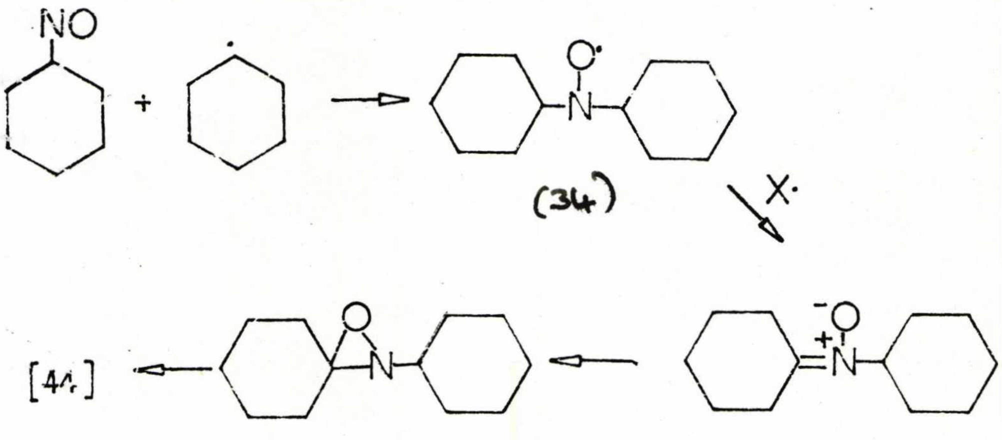
A later report by these authors examined the effect of changing the filter on the photochemistry of nitroethane[137]. A pyrex filter (previous work had used a quartz filter) led to the isolation of hydroxyiminocyclohexane (45), cyclohexylnitrite (46) and nitrocyclohexane. Monochromatic light ($\lambda = 254$n.m.) gave *trans*-azocyclohexanedi-N-oxide (47). This was photochemically stable at this wavelength but is converted into *N*-cyclohexylcaprolactam by use light of longer wavelengths, whilst pyrex filtered light gave the oxime (45), cyclohexyl nitrate (46) and nitrocyclohexane. The interconversion of mono- and bis-nitrosocyclohexane has been reported as well as its conversion to the oxime[138].



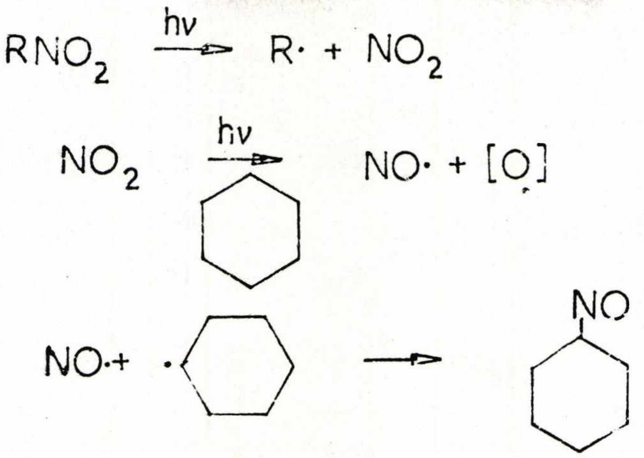


[44]

The formation of the caprolactam was rationalized in terms of an addition of a cyclohexyl radical to nitrosocyclohexane to form a nitroxide radical(47), which decomposes to the nitrone which then rearranges to the caprolactam via the oxaziridine as described before.



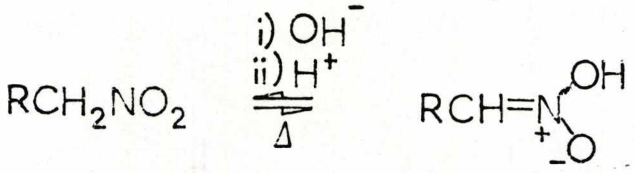
The formation of nitrosocyclohexane when both nitrocyclohexane and nitroethane are irradiated in cyclohexane precludes a direct photochemical deoxygenation. The nitrosocyclohexane seems to arise via an initial homolytic C-N bond cleavage followed by photoconversion of nitrogen dioxide into nitric oxide and radical combination. This mechanism is general and can explain all the previous results on the photochemistry of nitroalkanes in solution[139]. This is an important result as it clear evidence for homolytic



C-N bond cleavage being a primary process in the solution photochemistry of nitroalkanes. It also indicates that the previously postulated hydrogen abstraction pathway may not be as important as supposed.

The photochemistry of some geminal substituted nitroalkanes in solution has been studied and the formation of the α-nitroalkyl radical is the major observed pathway for geminal nitronitrosoalkanes[140,141] and geminal iodonitroalkanes[142,143]. This is due to the carbon-geminal substituent bond being weaker than the C-NO_2 bond.

Nitroalkanes can exist in the isomeric aci-nitro form (48), which is usually unstable, reverting to the parent nitroalkane[144]. The irradiation



[48]

of stable aci-nitro isomers has been reported[145]. The results indicated that the photochemistry of aci-nitro compounds is analogous to the photochemistry of nitrones and is very different from that of nitro compounds.

The photochemistry of α-nitroepoxides has been studied[146, 147]. A marked solvent dependance was noted, the photoreaction ~~occuring~~ occurring in protic or hydrogen-donating solvents. Ring opened oximino derivatives are obtained as products, possibly ~~occuring~~ occurring *via* 1,3-dipolar and α-nitroketone intermediates although an initial C-N bond cleavage cannot be ruled out. A thermal reaction between alcohols and these epoxides , with elimination of the nitro group, to give α-alkoxyketones is also important[148]. Quenching studies suggested that the triplet state of the nitroepoxide was responsible for the product formation[146,147].

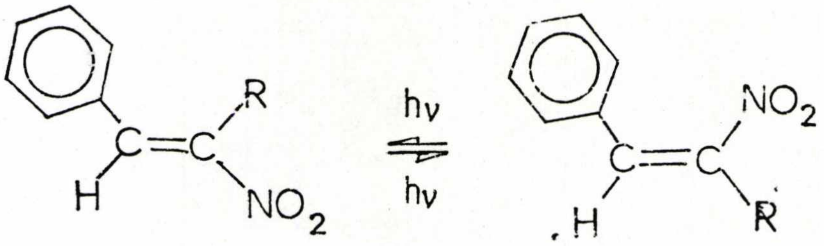
The photochemistry of α-nitroketones has been investigated by various groups and this subject will be discussed when more results on the photochemistry of α-nitroketones are presented.

From the reports on the photochemistry of nitroalkanes and related compounds it would appear that homolytic C-N bond cleavage is a major pathway in solution as well as in the gas-phase. Other photoreactions do occur but their importance is as yet difficult to assess.

(c) The photochemistry of nitroalkenes.

The reported photochemistry of α,β-unsaturated nitroalkenes can be divided into several categories, namely: (i) *Cis*-*trans* (*E*-*Z*) isomerization, (ii) Photochromism, (iii) The nitro-to-nitrite rearrangement, (iv) Intramolecular attack of the nitro group upon the double bond, (v) Photochemical deconjugation, (vi) Dimerizations and photoaddition reactions and (vii) miscellaneous reactions.

(i) The photochemical *cis*-*trans* isomerization of α,β-unsaturated nitroalkenes occurs in many cases, often as a prelude to further reactions. The conversion of *E*-β-nitrostyrene (49a) into the *Z*-isomer (50a) on irradiation in solution has been reported by various groups[150,151,152,153] as well as the conversion of *E*-β-methyl,β-nitrostyrene (49b) into the *Z*-isomer (50b)[154,155]. The conversion of a series of *E*-1-aryl-2-nitroalkenes into the *Z*-isomers on irradiation in solution, prior to the *Z*-isomer exhibiting photochromic properties, has also been reported[156,157]. The conversion of



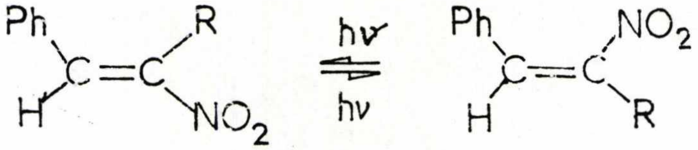
(E) (Z)

[49] [50]

(a) R = H

(b) R = CH_3

E-β-bromo-β-nitrostyrene into the Z-isomer has been suggested but not proven[158], whilst the conversion of E-1-(9-phenanthryl-)2-nitroprop-1-ene into the Z-isomer has been demonstrated[159]. The photolysis of substituted nitrostyrenes causes E-Z interconversion[160]; E-α-nitrochalcone (51a) and ethyl-(Z)-α-nitrocinnamate (51b) were found to undergo conversion into the Z- and E- isomers respectively on irradiation in benzene.

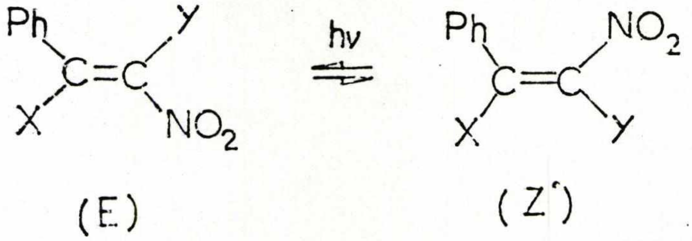


[51]

(a) R = COPh

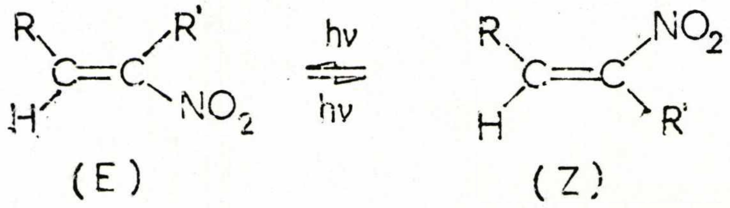
(b) R = CO_2Et

A recent detailed report on the E-Z isomerization of β-nitrostyrenes showed that irradiation of a series E-β-nitrostyrenes in hydrocarbon solvents gives an equilibrium mixture of the E- and Z-isomers, consisting of 60-80 percent of the Z-isomer in the case of (52a-d) and 10-20 percent in the case of (52e)[161].



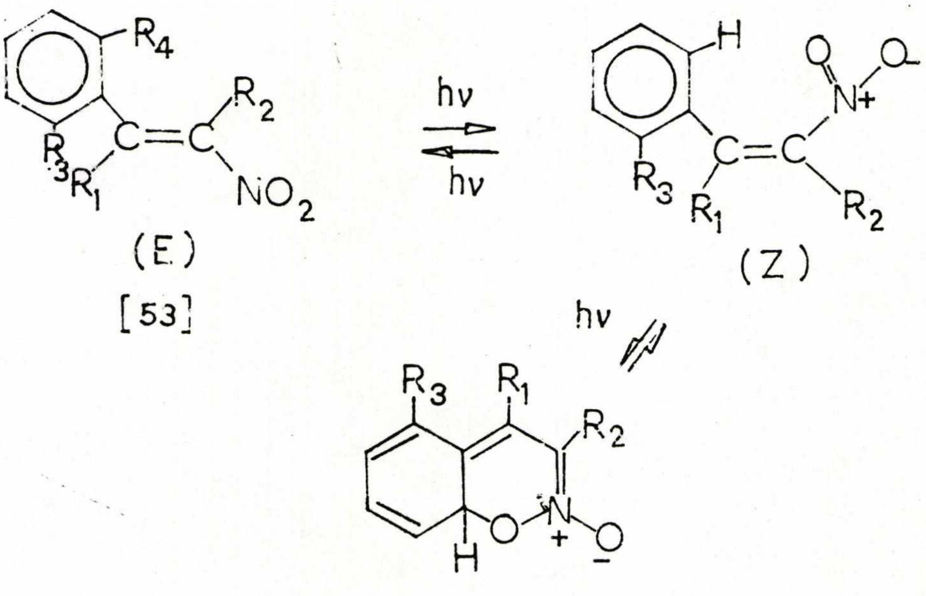
52 (a) X = Y = H.
(b) X = H; Y = CH_3.
(c) X = CH_3; Y = H.
(d) X = H; Y = Cl.
(e) X = H; Y = Br.

The photochemical E-Z isomerization of nitroalkenes is not restricted to nitrostyrenes. Irradiation of the E-isomer of a carbohydrate nitroalkene leads to the formation of the Z-isomer[162]. A comprehensive report on the photochemistry of acyclic nitroalkenes, in diethyl ether and hexane, concluded that nitroalkenes alkyl-substituted at both the α- and β-positions give a photostationary state of the E- and Z-isomers plus sometimes the deconjugated isomer[163]. The equilibrium concentration of the E- and Z-isomers of 3-nitrobut-2-ene was altered by the use of high



triplet energy senstizers; the higher the triplet energy of the sensitizer the more Z-isomer was present in the equilibrium mixture. It was also found that the photostationary state was indifferent to the starting isomer used. The E-Z isomerization of 3-nitrobut-2-ene was also observed when acrolien was used as the solvent^{164}.

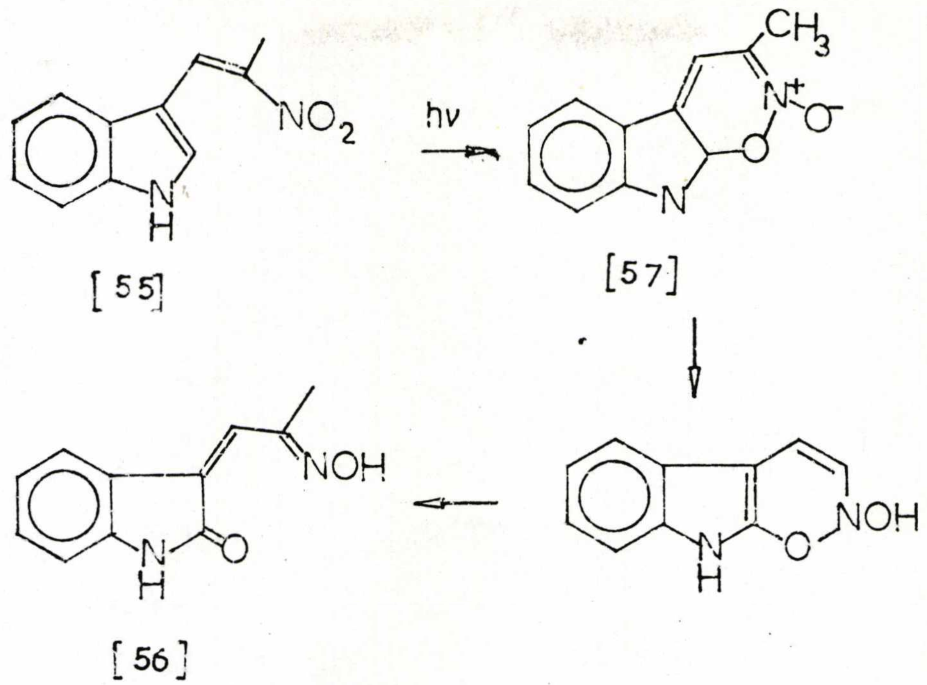
(ii) The photochromic behaviour of nitrostyrenes has been investigated^{156,157}. E-β-nitrostyrenes (53) are not photochromic but isomerize on photolysis in ethanol or cyclohexane to the Z-isomers which are photochromic if R_3 and/or R_4 equals hydrogen. The postulated mechanism invovles attack of the excited nitro group on the benzene ring leading to the coloured isomer, postulated to have structure (54).



[53]

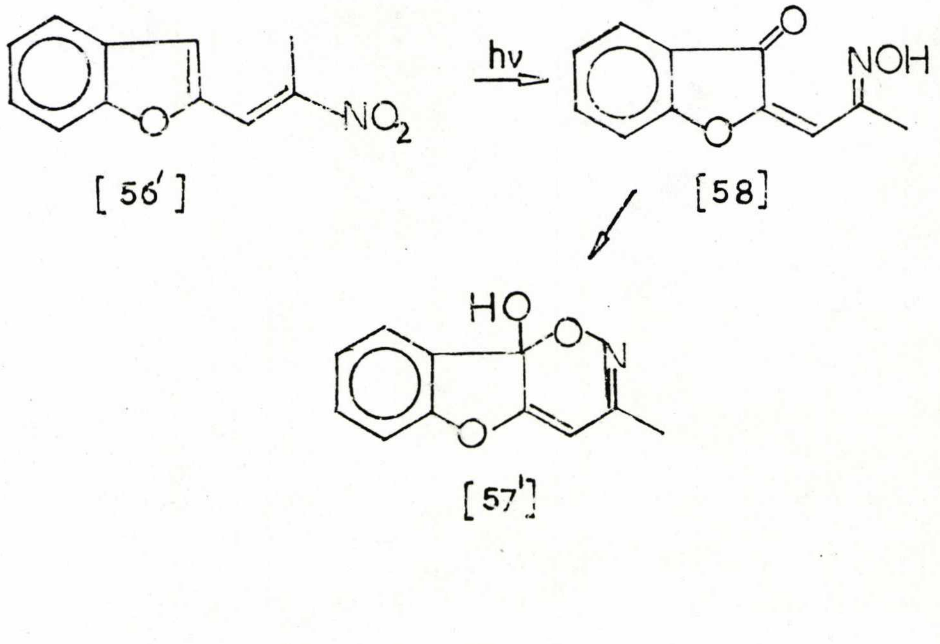
[54]

Several other reports have evoked intermediates of type (54). Irradiation of 3-(2-nitroprop-1-enyl)indole (55) in methanol^{165} leads to the formation of the oxindole derivative (56), via (57) as shown in scheme 14. The initial attack of the nitro group on the aromatic system is analogous to that proposed for the photochromic behaviour of β-nitrostyrenes.

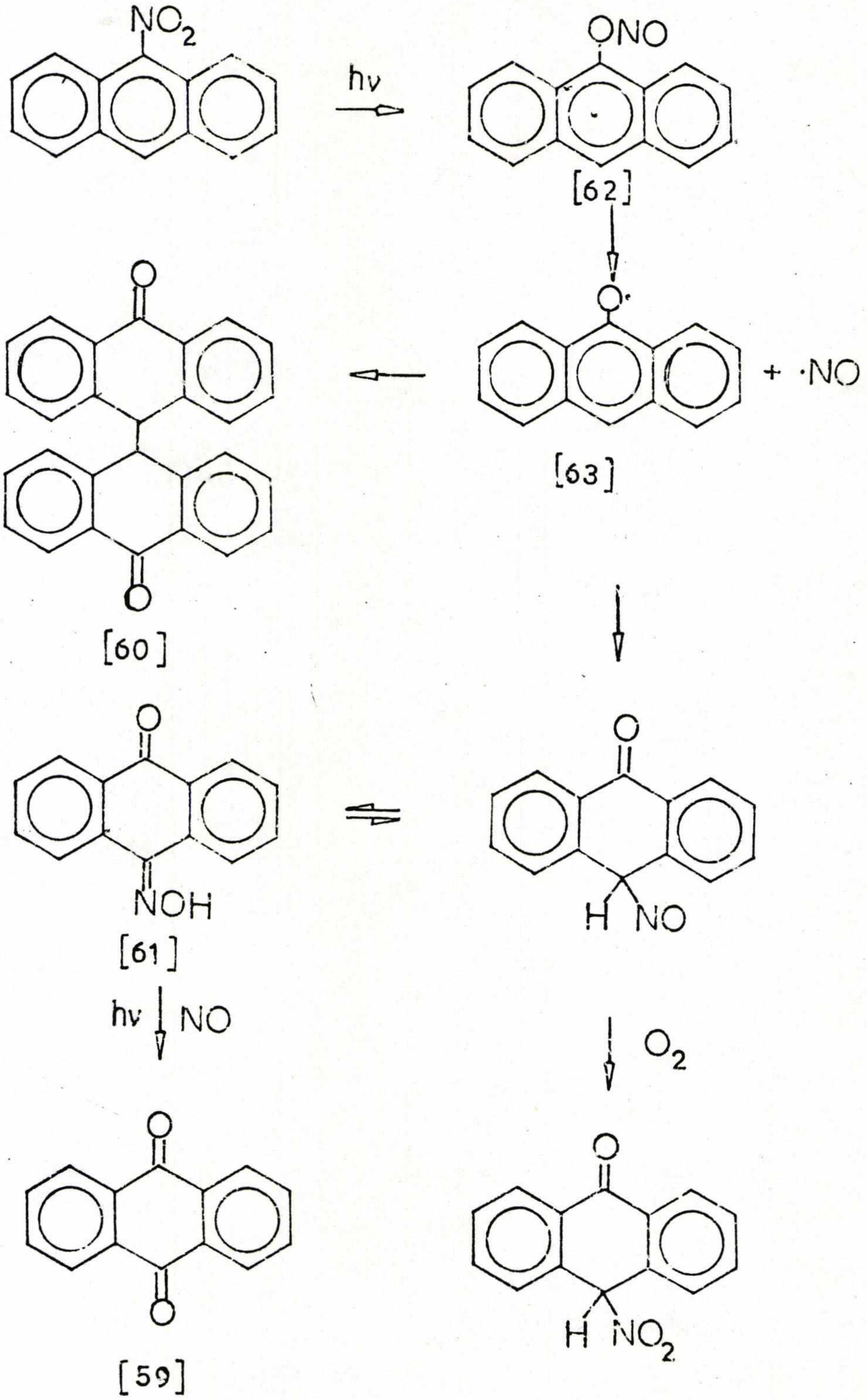


Scheme 14.

It was also observed that irradiation of 2-(2-nitroprop-1-enyl)benzofuran (56$'$) led to the formation of the 6-hydroxy-1,2-oxazine derivative (57$'$), presumably *via* the oxobenzfuran derivative (58)^{166}. Analogous reactions were observed for 2-(2-nitroprop-1-enyl)furan, its 5-methyl derivative and 2-(2-nitroprop-1-enyl)indole.

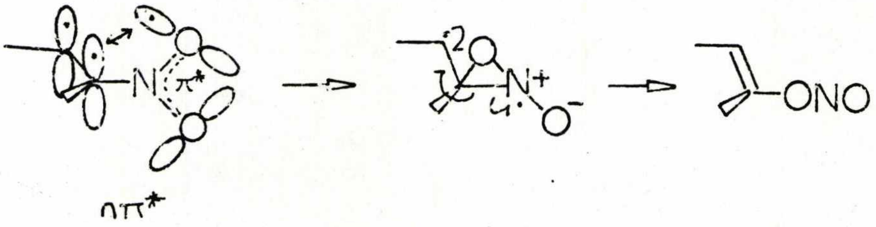


(iii) The nitro-to-nitrite rearrangement was first reported by Chapman in 1964 and since then numerous examples of this particular rearrangement have been reported. This rearrangement is found to be common to nitroaromatics, nitroheteroaromatics, nitrodienes and some nitroalkenes. The early reports were that 2,3-dimethyl-1-nitronaphthalene and 9-nitroanthracene upon irradiation in ethanol or acetone gave 2,3-dimethyl-1,4-naphthaquinone and anthraquinone respectively[154,167]. 9-Nitroanthracene is reported to undergo photo-oxidation to anthraquinone[168,169] and 9-nitroanthrone[168], it being suggested that a peroxide is an intermediate. 4-Nitro-2,6-diphenylphenol upon irradiation gives a quinone derivative[174]. A more recent report on the photochemistry of 9-nitroanthracene showed that there is a wavelength dependance in product formation. When light of 420-530 n.m. is used, a photodimer is obtained whilst light of 370-410 n.m. gave 10,10'bianthrone and nitric oxide[171]. It has since been suggested that this wavelength dependance is due to the photoreaction resulting from an upper $n\pi^*$ triplet state, whilst the dimerization comes from the low lying $\pi\pi^*$ triplet state[172]. The photoreaction was found not to require oxygen, hence excluding a peroxide as an intermediate. Irradiation of 9-nitroanthracene gave anthraquinone (59) and 10,10'bianthrone (60), whilst irradiation for shorter periods with a continous nitrogen flush gave nitric oxide, anthraquinone, 10,10'bianthrone and anthraquinone mono-oxime (61). Irradiation with a nitric oxide flush gave a larger yield of anthraquinone at the expense of 10,10'bianthrone whilst irradiation of anthraquinone mono-oxime in the presence of nitric oxide gave anthraquinone. These and earlier results were rationalized by means of the following mechanism, as shown in scheme 15. The first step is photoisomerization of the nitro compound to the nitrite ester (62) which thermally or photochemically decomposes to the 9-anthroxyl radical (63) and nitric oxide, which can then undergo further reactions. All attempts to prepare 9-anthryl nitrite from 9-hydroxyanthracene failed, a fact which indicated that the nitrite is very unstable and that its breakdown is thermal rather than photochemical. The failure to observe any photodimer in in this work was attributed to a rapid decomposition of the dimer at shorter wavelengths.



Scheme 15.

The initial nitro-to-nitrite rearrangement was considered to occur via a $n\pi^*$ triplet although there was no evidence to support this. The rearrangement was considered to be aided by steric features holding the plane of the nitro group out of the plane of conjugation. In the case of 9-nitroanthracene this is achieved by two peri-hydrogens and in 1-nitro-2,3-dimethylnaphthalene by a peri-hydrogen and an o-methyl group. Two types of mechanism may be considered for this rearrangement, a dissociation-recombination mechanism and an intramolecular rearrangement mechanism. The dissociation-recombination mechanism would require the homolytic cleavage of the C-N bond and subsequent recombination to give the nitrite; as no products derived from these radicals were detected, this mechanism was rejected. The intramolecular mechanism is described in terms of the nitro group being orthoganol to the plane of the anthracene ring, due to steric effects. The excited $n\pi^*$ state with a half-empty non-bonding orbital on oxygen interacts with an adjacent orbital of the aromatic ring to form an oxaziridine ring which collapses to the nitrite, scheme 16.



Scheme 16.

Mass-spectral data provides evidence for the rearrangement being intramolecular. The electron beam in the mass spectrometer removes a non-bonding electron from the nitro group which is of similar effect as the $n\rightarrow\pi^*$ transitio achieved photochemically. The resulting species witha half-empty non-bonding orbital gave a peak at M-30, which became more intense as the ionizing voltage of the electron beam was reduced, and was attributed to the sequence in scheme 17. Due to the low pressures used in the mass-spectrometer, a dissociation-recombination reaction must be excluded, hence demonstrating the rearrangement to be intramolecular.

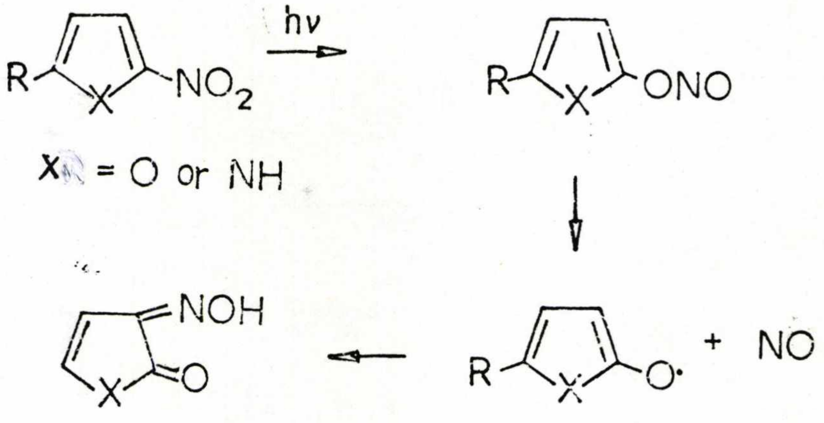
$$[\mathrm{Ar{-}NO_2}]^{+\cdot} \longrightarrow [\mathrm{Ar{-}ONO}]^{+\cdot} \longrightarrow [\mathrm{ArO}]^{+} + \mathrm{NO}\cdot$$

Scheme 17.

There is some precedence in the literature for the oxaziridine intermediates suggested by Chapman. The rearrangement of an aromatic nitro group to an oxaziridine has been suggested by several groups to explain the action of base on nitroaromatics[170,173,174,175].

Several reports on the photochemistry of nitroaromatics have appeared which demonstrate the occurrence of a photochemical nitro-to-nitrite rearrangement. Irradiation of 4-nitropyridine-N-oxide in the presence of oxygen results in the formation of 4-hydroxypyridine-N-oxide nitrate[176]. Irradiation of 3,5-dimethyl-4-nitropyridine-N-oxide in water or alcohol resulted in the formation of 3,5-dimethyl-4-hydroxypyridine-N-oxide, whilst 4-nitroquinoline-1-oxide rearranged to 2,4-dihydroxyquinolone[177]. In these examples, the nitro group is considered to be held out of the plane of conjugation by the ortho substituents, which assists the nitro-to-nitrite rearrangement at the expense of hydrogen abstraction reactions[8]. As oxygen has no effect on the rearrangement, it was suggested the photoreaction occurs *via* a $n\pi^*$ singlet state. Irradiation of 4-nitroanisole gave 4-hydroxy-3-nitroanisole and 4-nitrosoanisole, whilst the 2- and 3-nitroanisoles were unreactive[178]. The postulated mechanism, invovling an initial nitro-to-nitrite rearrangement , however, does not provide an explanation for the lack of reactivity in the 2- and 3-nitro derivatives. 1,4-Di-(t-butyl)-2-nitrobenzene rearranges to a quinone derivative[179]. 7-nitroquinoline derivatives give the hydroxy derivatives on irradiation[180]. Hindered nitrobenzenes undergo a nitro to hydroxyl phototransformation in polar solvents[12]. An initial nitro-to-nitrite rearrangement was postulated; as the nitro group is twisted out of the plane of conjugation by the bulky substituents in the 2- and 6-positions, the nitro-to-nitrite rearrangement is favoured at the expense of the hydrogen abstraction reaction. Quenching experiments indicated that the nitro-to-nitrite rearrangement occurs via an excited triplet state.

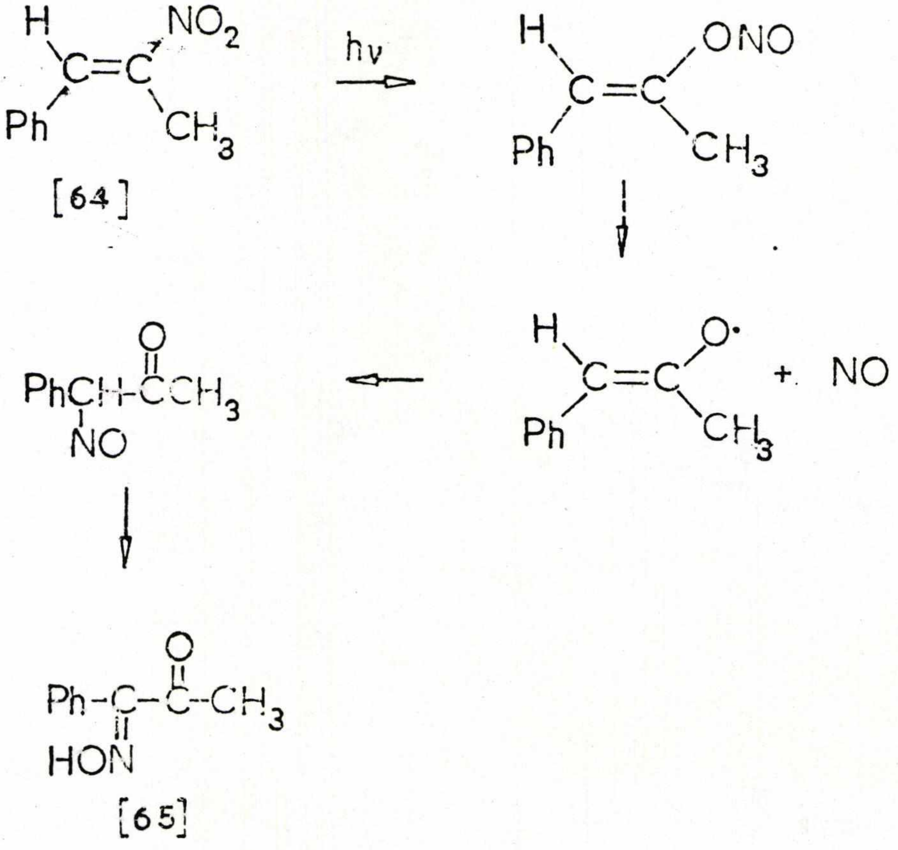
The occurrence of the photoinduced nitro-to-nitrite rearrangement has been postulated in nitroheterocycles. Reid and co-workers[181] have studied the photochemistry of 2-nitrofuran and 2-nitropyrrole and the formation of oximinoketone type products was rationalized via an initial nitro-to-nitrite rearrangement as shown in scheme 18. When the 3-position is blocked, the nitric oxide recombined at the 5-position. This type of photorearrangement is normally judged to be aided by a twisting of the nitro group out of the plane of conjugation. Nitrofuran and nitropyrrole, however, are expected to be planar and these compounds are considered, by these authors, to be an exception to this general rule. Nitrofuran has also been reported to undergo photodecomposition in propan-2-ol after initial hydrogen abstraction by the nitro group[182].



Scheme 18.

Little work on the excited state responsible for the nitro-to-nitrite rearrangement in nitroaromatics has been performed. Kaneko[176] observed oxygen had no effect on the photoreaction of nitropyridine-*N*-oxides and suggested the rearrangement occurred ~~occured~~ *via* a $n\pi^*$ singlet state, whilst Kitaurra and Matsuura[12] on the basis of quenching experiments concluded that the nitro-to-nitrite rearrangement occurred occured *via* an excited triplet state for substituted nitrobenzenes. The later work is more quantitative and more reliance should be placed on its conclusions but the fact that different systems were being investigated should not be ignored.

Photoinduced nitro-to-nitrite rearrangements occuring in nitroalkenes were first reported by Chapman[154,155]. 1-Phenyl-2-nitroprop-1-ene (64), after a rapid equilibration of the *cis* and *trans* isomers, gave 1-hydroxyimnio-1-phenylpropan-2-one (65). The mechanism is considered to involve an initial nitro-to-nitrite photorearrangement followed by either a photochemical or thermal breakdown of the unsaturated nitrite to give the observed product. This rearrangement is analogous in its early stages to the one postulated to explain the photoreactions of 9-nitroanthracene.

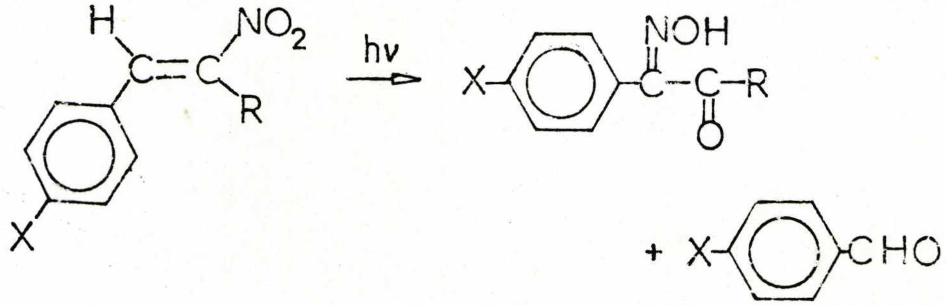


[64]

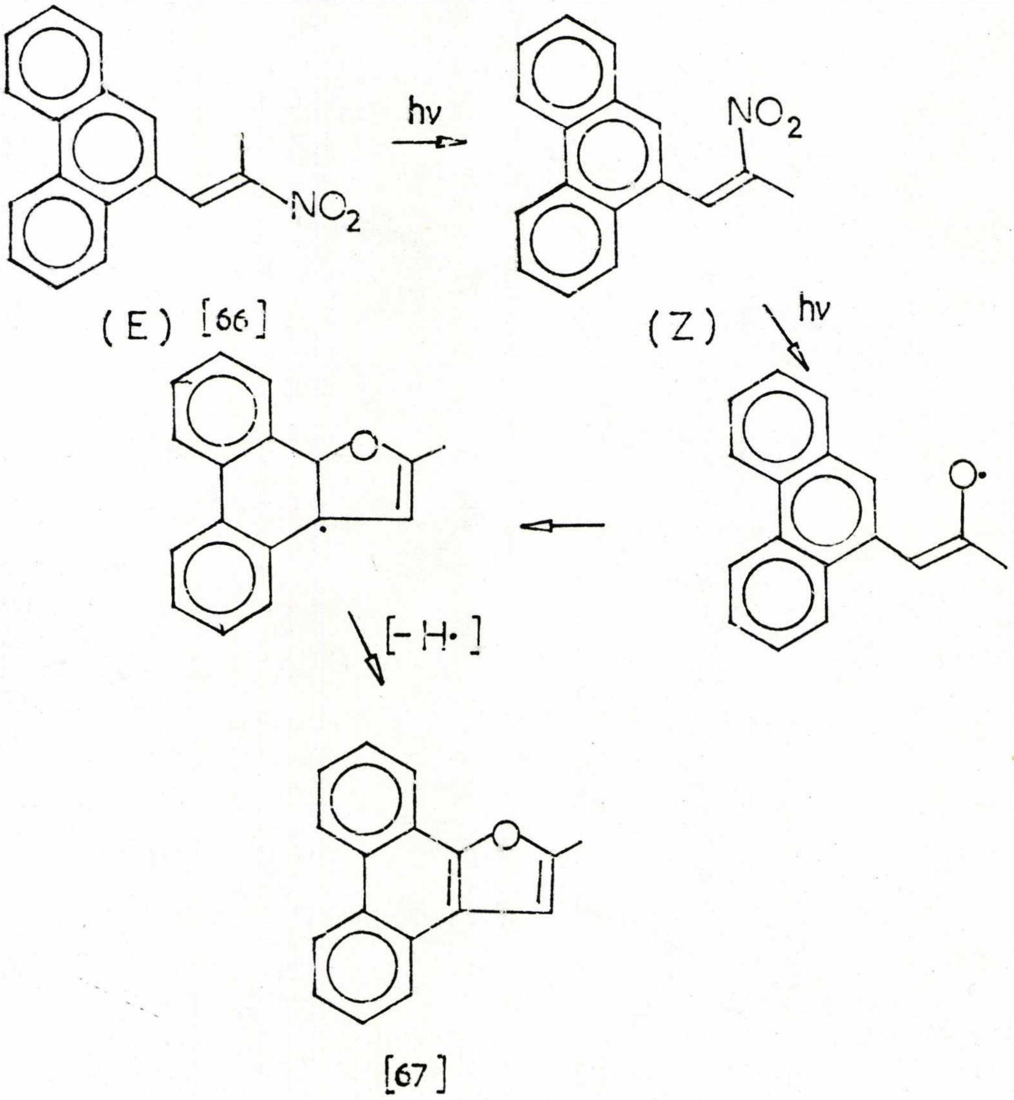
[65]

The solvent is important. Acetone gave the best yields. It was suggested that it may be acting as a sensitizer, but no evidence was presented. The α-methyl group is considered to hold the nitro group out of the plane of conjugation, greatly facilitating the reaction. Additional evidence comes from the observed photochemistry of the β-nitrostyrenes (49), which only undergo E-Z isomerization [152,154.161,183]. Here the steric effect of the α-methyl group has been removed and this causes the rearrangement not to occur.

The effect of substituents in the benzene ring has been investigated[185]. Para-substituted nitrostyrenes give the corresponding oximinoketones. Substituted benzaldehydes were also isolated (the mechanism of their formation will be discussed later). These workers found that the formation of the oximinoketones was unquenchable, indicating the excited state responsible for their formation was either a singlet or a higher triplet state (T_2).



Hunt obtained analogous results when ortho or para substituted β-nitrostyrenes were irradiated in methanol; a reduction in the yield of oximinoketone was noted when the substituent was electron donating[183]. Changing to a heterocyclic nucleus had no substantial effect on the reaction. The photochemistry of nitrostilbenes has been studied and the formation of oximinoketones has been observed[186,147]. Salisbury and co-workers[159] evoke an initial nitro-to-nitrite rearrangement to explain the conversion of *E*-1-(9-phenanthryl)-2-nitroprop-1-ene (66) to the furan derivative (67). It was found that the photoproducts were derived exclusively from the *Z*-isomer. The excited state responsible for the furan derivative was found to be the singlet state by use of quenching studies and use of a heavy atom solvent.

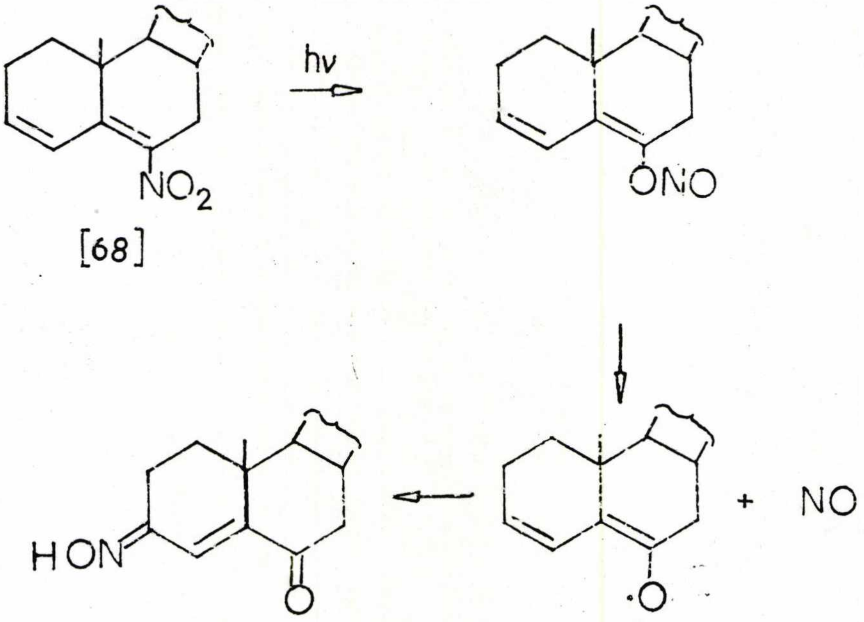


This result is comparable with the results of Saito[185] who found that for nitrostyrenes, the nitro-to-nitrite rearrangement occurred *via* an excited singlet state. The evidence to date points to the rearrangement in nitroalkenes coming from a singlet excited state. This is in comparison with nitroaromatics where to date no definite conclusions as to the excited state responsible for the nitro-to-nitrite rearrangement have been drawn.

A further example of this rearrangement is provided by *E*-β-bromo-β-nitrostyrene, which on irradiation gave alkyl α-isonitrosophenyl acetates[158].

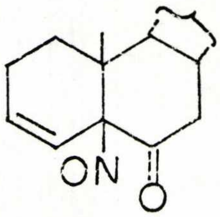
The more sterically strained isomer (Z-isomer) is considered to be responsible for the nitro-to-nitrite rearrangement.

This photoreaction can also occur in steriodal compounds[155]. If a radical recombination centre is blocked a vinylogous rearrangement can occur, subject to there being a correctly placed double bond. Hence irradiation of 6-nitrocholesta-3,5-diene (68) gave 3-oximinocholest-4-ene-6-one (69). Formation of compounds of type (70) are not favoured due to steric reasons.



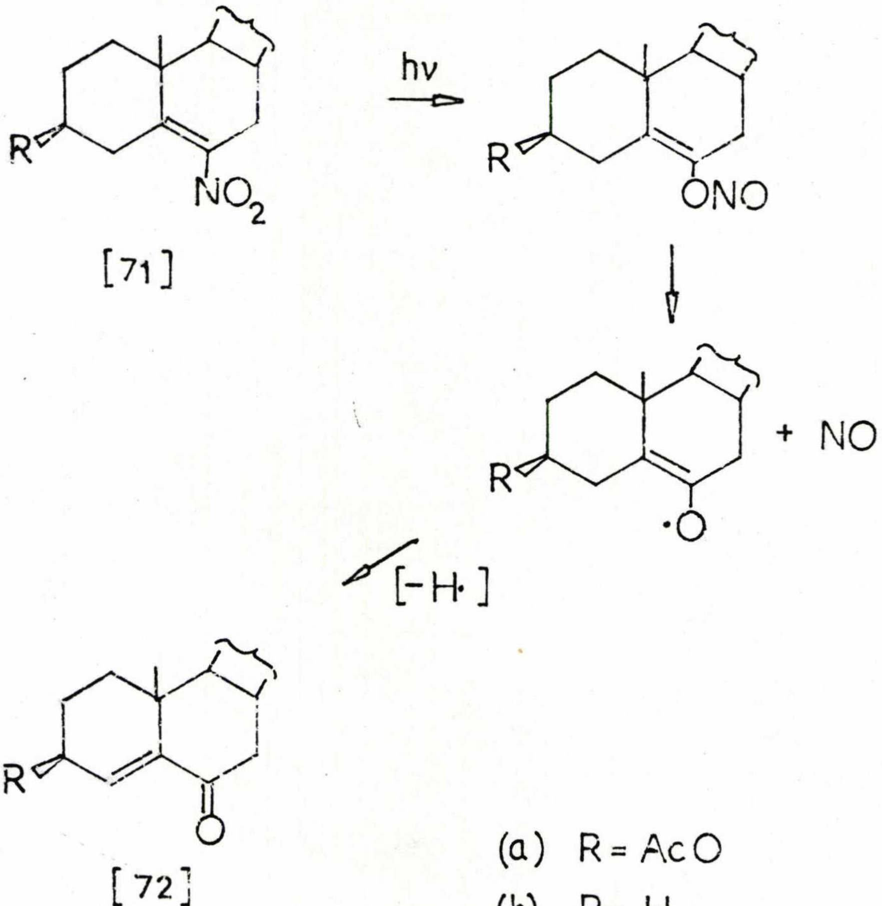
[68]

[69]



[70]

When no double bond is present, α,β-unsaturated ketones are obtained, presumably from the breakdown of the intermediate radical species[155,187,188,189]. This is demonstrated by the isolation of 6-oxo-Δ^4-cholesteryl-3β-acetate (72a) from the irradiation of 6-nitro-Δ^5-cholesteryl-3β-acetate (71a)[155], and 6-oxo-cholest-4-ene from the irradiation of 6-nitrocholest-5-ene (71b)[189].



[71]

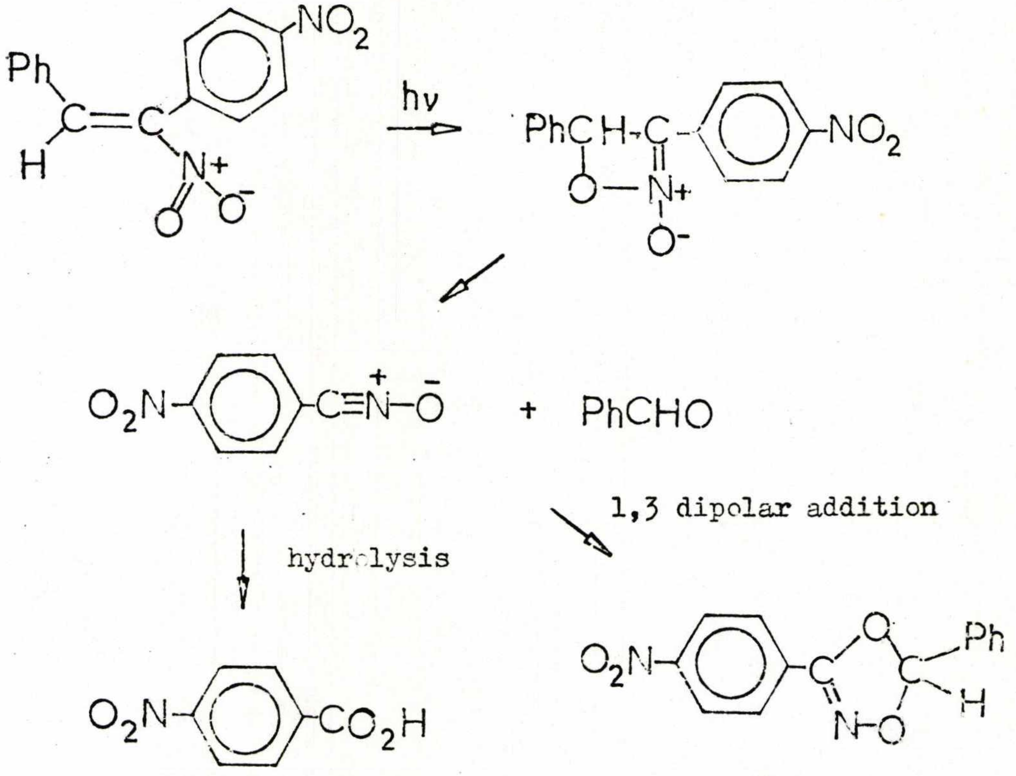
[72]

(a) R = AcO
(b) R = H

It was concluded that the occurrence of the nitro-to-nitrite rearrangement in the photochemistry 6-nitro-$\Delta^{3,5}$-cholestadiene is due to the C-4 hydrogen twisting the nitro group out of the plane of conjugation. Similar steric reasons can explain the observed results in other nitrosteriods.

A carbohydrate E-nitroalkene gave the Z-isomer and the cis-and trans-isomers the corresponding α,β-unsaturated ketones on irradiation. Other products may be present but none could be isolated[162].

(iv) The intramolecular attack of the nitro group on the double bond was first postulated to explain the products, other than oximinoketone, obtained in the photolysis of a substituted nitrostilbene[186], scheme 19. No direct



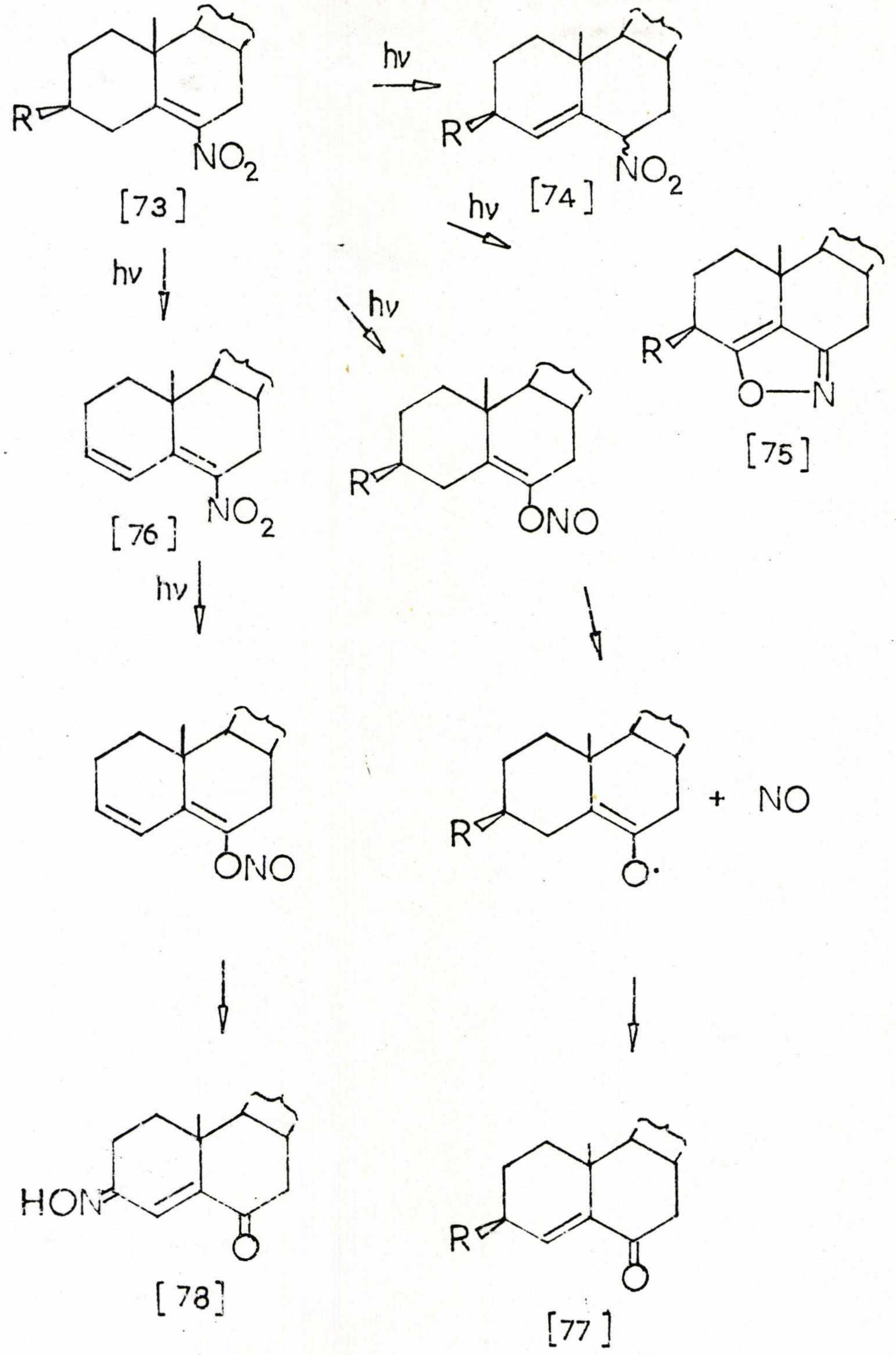
Scheme 19.

evidence for the occurrence of the four membered ring or the nitrile oxide was advanced. Salisbury used this type of mechanism to explain the formation of phenanthrene-9-carboxaldehyde in the irradiation of E-1-(9-phenanthryl-)-2-nitroprop-1-ene (66). The product was shown to occur via a triplet excited state by use of triplet quenchers and heavy atom solvents[159].

This mechanism was also postulated to explain the formation of substituted benzaldehydes in the irradiation of β-nitrostyrenes[185]. These workers succeeded in trapping the intermediate nitrile oxides as isoxazolines, by irradiating in the presence of methyl acrylate. Quenching studies indicated that the reaction occured via the first excited triplet state. This is in complete agreement with Salisbury's results.

(v) A further photochemical pathway open to nitroalkenes is double bond migration from the α,β- to the β,γ-position or photochemical deconjugation. Irradiation of 3β-acetoxy-6-nitrocholest-5-ene (73a) in hexane or dioxane led to the isolation of 3β-acetoxy-6β-nitrocholest-4-ene (74a) as the major product along with the isoxazole (75), the nitrodiene (76) and the unsaturated ketone (77a)[187]. On irradiation in acetone, (73a) gives a mixture of the 6α- and 6β-isomers of (74a) as well as 3-hydroxyimino cholest-4-ene (78) and the α,β-unsaturated ketone (77a)[155]. A detailed study of the photochemistry of several 3-substituted 6-nitrocholest-5-enes was undertaken[188]. It was concluded that the observed photochemical pathways are sensitive to the solvent employed and the nature of the substituent at C-3. In general three photochemical pathways were observed, (a) elimination of the C-3 substituent leading to a nitrodiene and eventually an oximinoketone This process is favoured in ethanol and acetone and when the C-3 group is easily eliminated. (b) Photochemical nitro-to-nitrite rearrangement to give the unsaturated ketone; this is favoured when elimination of the C-3 substituent was difficult and when cyclohexane was used as the solvent. (c) Double bond migration, which occurs when cyclohexane is the solvent and gives a mixture of the 6α-and 6β-isomers of the deconjugated product. This reaction is considered to be analogous to the photochemical deconjugation of α,β-unsaturated ketones.

The photochemistry of a series of aliphatic nitroalkenes has been studied[163]. Irradiation in ether or hexane gives a photostationary state corresponding to an equilibrium between the E- and Z-isomers of the starting material and the deconjugated isomer. It was concluded that β-substituted nitroalkenes give principally the deconjugated isomer whereas α- and β-disubstituted nitroalkenes give a photostationary state consisting of the E- and Z-isomers. Nitroalkenes that are β,β-disubstituted or else are α,β,β-trisubstituted undergo the deconjugation reaction. In these cases, however, as both the E- and Z- isomers are identical, no idea of the amount of *cis/trans* isomerization occurring can be obtained.

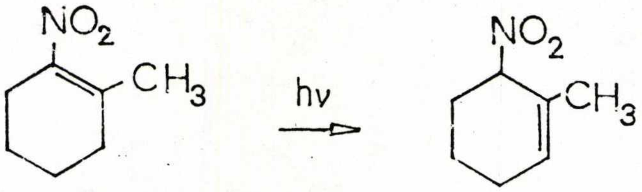


(a) R = AcO

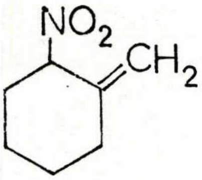
(b) R = CF$_3$CO

(c) R = Cl

Irradiation of a mixture of 3-nitro-2-methylcyclohexene (79) and 1-nitro-2-methylcyclohexene (80) leads to the conversion of (79) to (80)[190]. These authors seemed unaware of any previous work in this field and also failed to present any explanation for this rearrangement. The accepted mechanism for this type of rearrangement involves the abstraction of a γ-hydrogen *via* a six-membered transition state, which should give (81) in this case. An explanation for the formation of (80) by thermal or photochemical conversion of (81) to (80) seems unlikely.

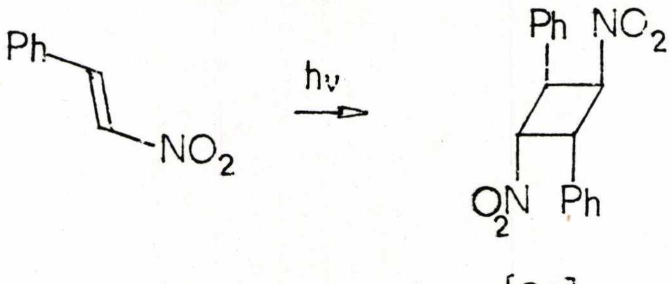


[79] [80]



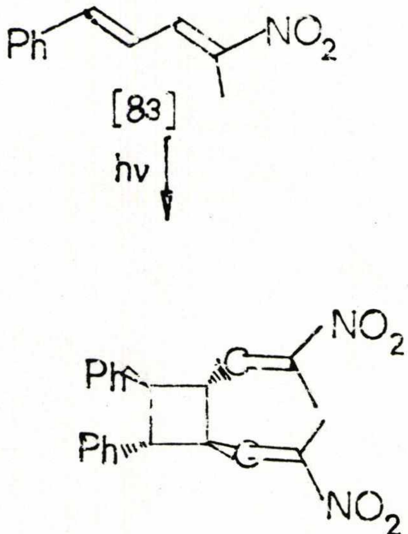
[81]

(vi) Nitroalkenes can also undergo bimolecular photoreactions, namely dimerization and cycloadditions. The solid state dimerization of β-nitrostyrene has been known for many years[191,192], but only recently has the structure of the dimer been fully determined[150,152,153]. The photodimer was shown to be 1-*trans*-3-dinitro-*cis*-2 -*trans*-4-diphenylcyclobutane (82). All attempts to cause the dimerization to occur in solution failed, *cis*-*trans* isomerization occurs instead.



[82]

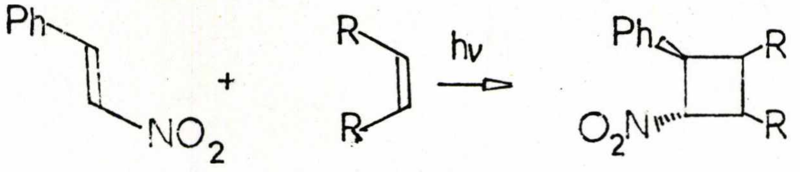
Other nitroalkenes have been dimerized in the solid state, 1-furyl-2-nitroethylene gave the analogous dimer on irradiation[193], and 2-nitrobenzo-1,4-dithiadiene gave either the head-to-head or the head-to-tail dimer[194]. Dimerization in solution has been observed for 1-nitroacenaphthylene which gives the head-to-head and the head-to-tail dimers[195]. Nitrodienes also undergo dimerization in solution, 4-nitro-1-phenylpenta-1,3-diene (83) gives the photodimer (84)[196]. A single stereoisomer resulting from ($\pi^2s + \pi^2s$) addition is obtained even in dilute solution and there is no evidence for $(4+2)\pi$ or $(4+4)\pi$ cycloadditions. The dimerization always



[84]

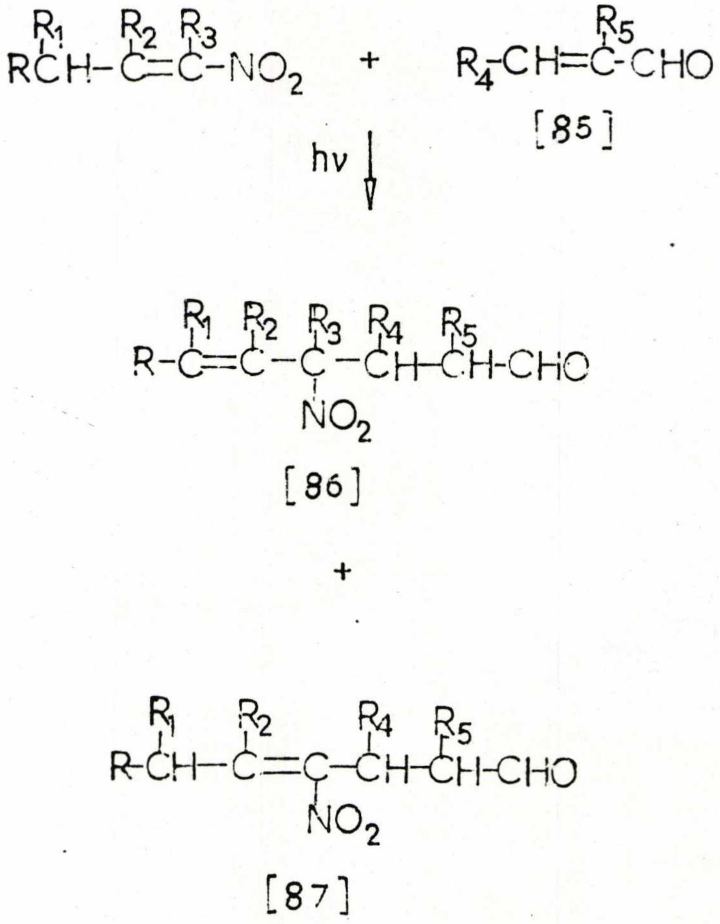
occurs at the 1,2 double bond and not the 3,4 double bond and there is a marked solvent dependance, better yields being obtained in methanol than in acetone whilst no dimer was obtained when cyclohexane was used as the solvent. These results have not as yet been fully rationalized. A related reaction is the dimerization of 9-nitroanthracene in solution, where the head-to-tail dimer is obtained[171]. A marked wavelength dependance was observed, as light in the region of 4200-5300Å gave the dimer whilst light of shorter wavelengths gave anthraquinone as the major product.

Cycloadditions of alkenes to nitroalkenes have recieved attention, Chapman has published a preliminary report and a Thesis containing more details has been published[154,197]. β-nitrostyrene is reported to undergo photoaddition to alkenes to give cyclobutanes. α-Phenyl-β-nitrostyrene



when irradiated in the presence of alkenes gave no reaction, which was attributed to the second phenyl ring causing steric interference. All the photoaddition products are the result of 1,2 additions and when an asymmetrical alkene is used, the resulting adduct has the most nucleophilic carbon attached to the alpha position of the β-nitrostyrene, attributed to the β-nitrostyrene acting as an electrophilic species. Each photoproduct has the phenyl and nitro groups trans to each other. This regiospecificity was attributed to the β-nitrostyrene adding in a trans manner. A mechanism to explain the observed facts has been advanced by Kan[198]. This involves initial attack by the excited nitro group on the double bond of the alkene to give a six-membered ring which then collapses to a four-membered ring. This mechanism is now subject to reappraisal in the light of recent theoretical work.

Nitroalkenes also undergo a so-called photo-Michael addition[164]. Conjugated nitroalkenes on irradiation in the presence of an unsaturated aldehyde (85) gave principally the non-conjugated nitroaldehyde (86) and the conjugated derivative (87). The presence of the double bond was shown not to be critical as nitroethane also underwent this reaction. The reaction seems to involve the photochemical isomerization of the conjugated to the deconjugated nitroalkenes and their subsequent photo-addition, although a photocycloaddition reaction as the first step followed by a breakdown of the cyclobutane ring can explain the results.



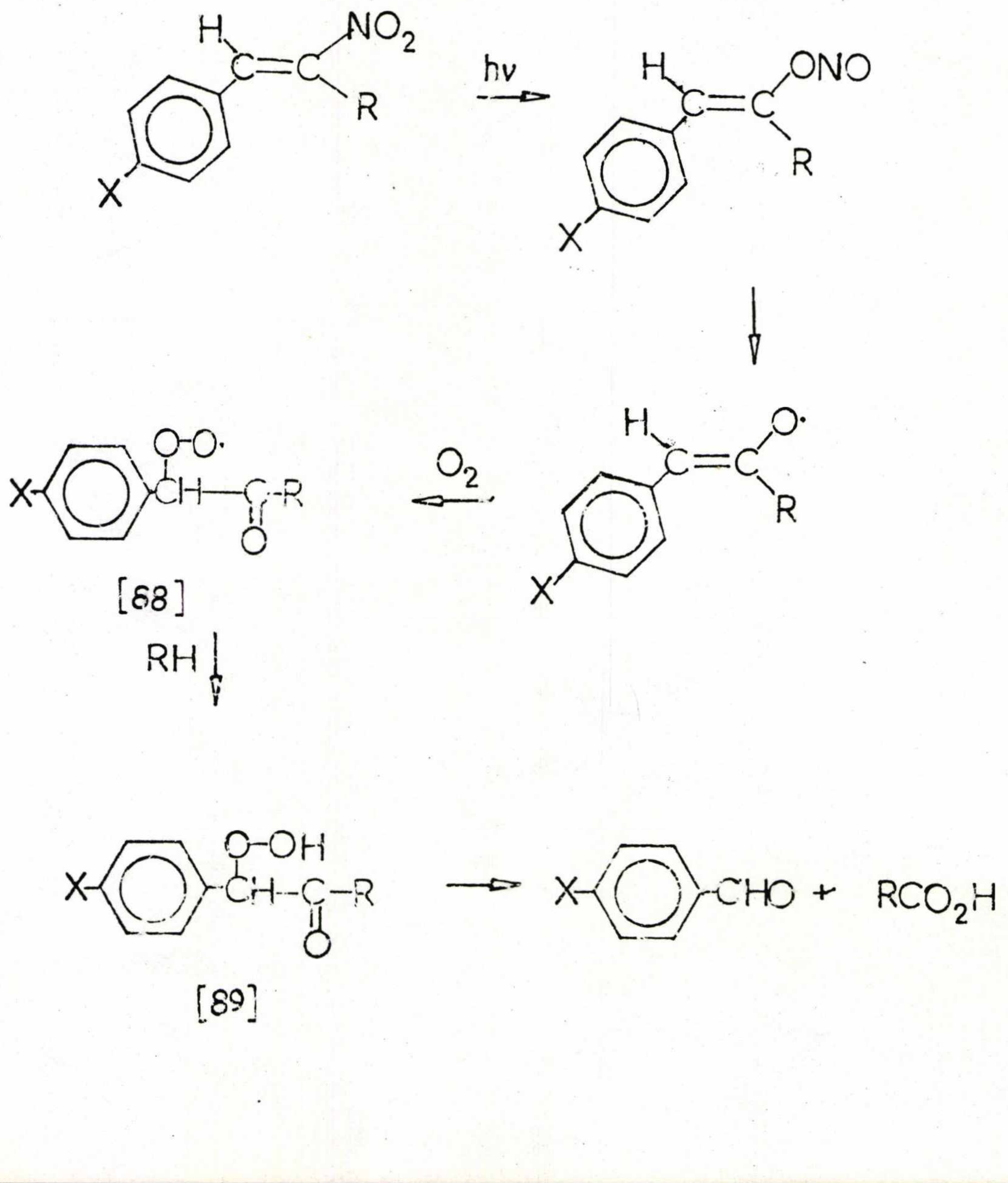
[85]

[86]

[87]

A recent report concerns the photoaddition of alcohols to nitroalkenes. Irradiation of 1-nitrocyclohexene in methanol gave the adduct, *trans*-1-methoxy,2-nitrocyclohexane[189]. No previous examples of this type of photo-addition have been reported but the facile themal addition of ethanol to several substituted nitrostyrenes has been reported[160]. Whether light had any influence on these reactions was not investigated.

(vii) The effect of oxygen on the photoreactions of nitroalkenes has been investigated. Irradiation of para-substituted β-alkyl-β-nitrostyrenes in the presence of oxygen gave substituted benzaldehydes and the corresponding carboxylic acids[165]. The mechanism of the reaction is postulated to involve the attack of oxygen on radical (88), to give an α-ketohydroperoxide (89) which then decomposes to give the observed products. This mechanism may

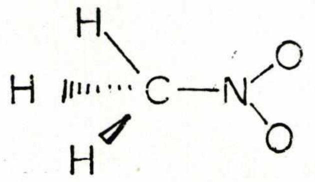


explain earlier results. Irradiation of 3,4-dimethoxy-β-methyl-β-nitrostyrene in acetone gave verataldehyde and veratic acid[199].

A totally different photoreaction is undergone by α-nitro-2'-iodo-cis-stilbene which in cyclohexane gave 9-nitrophenanthrene[200]. This cyclization may be regarded as an example of iodoaromatic photochemistry as opposed to nitroalkene photochemistry.

(d) Theoretical studies on the nitro group.

(i) Nitroalkanes; the following discussion concerns chiefly nitromethane but it is possible to extend the ideas to nitroalkanes in general. Electron diffraction measurements show nitromethane to have the following structure[201];



$r_{CN} = 1{\cdot}46\text{Å}$

$r_{NO} = 1{\cdot}21\text{Å}$

$\angle ONO = 127°$

there is restricted rotation about the C-N bond, but a low energy barrier allows the molecule to attain C_{2V} symmetry[202]. After the formation of the sigma bond framework, there are three p_y orbitals (one on nitrogen and one on each oxygen) perpendicular to the plane of the nitro group, which form an allyl π type system leaving a p_x orbital in the plane on each oxygen to become a lone pair. A better way of considering π orbital system formation is by appyling group theory[203]. Assuming a local symmetry of C_{2V}, the nitrogen $2p_y$ orbital belongs to representation b_2 whilst the two oxygen $2p_y$ orbitals belong to a_2 and b_2. The two b_2 orbitals combine to give the bonding (π) and anti-bonding (π^*) orbitals whilst the a_2 orbital will be non-bonding (π_0) and localized on the oxygens. Each oxygen has a pair of electrons in the plane of the nitro group ($2p_x$). These orbitals belong to representations a_1 and b_2 and are the non-bonding orbitals.

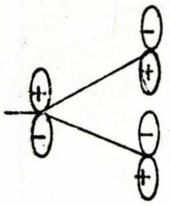
This argument not only allows a picture of the π and n.b.o. systems to be built up, but also allows a prediction as to which electronic transitions are allowed and forbidden. The $\pi_0 \longrightarrow \pi^*$ and $\sigma_{a_1} \longrightarrow \pi^*$ transitions are allowed but the $\sigma_{b_2} \longrightarrow \pi^*$ transition is forbidden. Allocation of these transitions is possible by comparison with the U.V. spectrum of nitromethane. The observed weak long wavelength transition is due to the forbidden $n \longrightarrow \pi^*$ transition whilst the strong shorter wavelength transition is due to either the allowed $n \longrightarrow \pi^*$ or the $\pi_0 \longrightarrow \pi^*$ transition.

Snatzke performed some elementary theoretical studies and assignments, and concluded the long wavelength transition is due to a $n \longrightarrow \pi^*$ transition[204], based on the transition undergoing a blue shift in polar solvents[205].

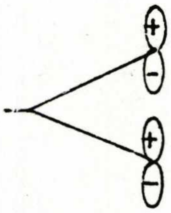
These approaches fail to give the absolute energies of the orbitals. McEwen studied the electronic structure of nitromethane [206]. These calculations show that the π orbitals result entirely from the p_y orbitals on nitrogen and oxygen whilst the non-bonding orbitals result from a combination of many atomic orbitals. The two non-bonding orbitals are nearly degenerate and are lower than the π_0 orbital. The predicted value of the ionization potential is 15·51eV whilst it has been found to be 11·34eV[207]. The calculated electronic transition energies are in good agreement with observed values.

Another attempt at calculation was made by Harris[210]. This treatment indicates there is a contribution from the C_y orbitals in forming the system. The absolute energies are different but the ordering is the same as McEwen. The predicted ionization potential is 12·14eV which is closer to the experimental value. There is good agreement between the calculated and observed transition energies. These results predict two low intensity transitions as the two non-bonding orbitals are very close in energy. The

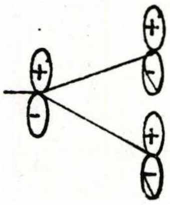
Molecular Orbitals of the Nitro group.



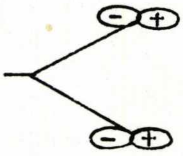
$\pi^* b_1$ (anti-bonding)



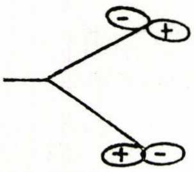
$\pi_o a_2$ (non-bonding)



πa_1 (bonding)



σa_1 (non-bonding)



σb_2 (non-bonding)

observation of only one longer wavelength transition is explained by the two transitions having approximately the same energy. An alternative explanation is that the shorter wavelength, high intensity peak may be due to a $n \rightarrow \pi^*$ transition rather than the $\pi_0 \rightarrow \pi^*$ transition[203].

Molecular orbital drawings and calculated orbital energies of all the orbitals of nitromethane have been produced[211]. The predicted ionization potential is 7·58eV which is so different from the experimental value as to put the calculated energies into some doubt.

An alternative way of obtaining the orbital energies is by studying the photoelectron spectrum of nitromethane. It was observed that photoionization occurred at 11·25eV[212]. Two fuller papers have appeared[213,214] and their results are compared below:

Kobayashi and Nagakura[213]		Rabalais[214]	
Orbital energy	Assignment	Orbital energy	Assignment
11·31eV	σ_{a_1}	11·32eV	σ_{a_1}
11·81eV	$\pi_0 a_2$	11·73eV	π_{a_2}
14·30eV	σ_{b_2}	14·73eV	σ_{b_2}
15·65eV	Not assigned	15·75eV	π_{b_1}
17·35eV	Not assigned	17·45eV	Low lying σ bond

The agreement between the observed values and the assignments is very good Both groups agree that the highest occupied orbital is a non-bonding orbital localized on oxygen. Theory suggested the highest occupied orbital was π_0 and this is clearly shown to be incorrect as is the view that the two non-bonding orbitals are degenerate, experimental work clearly shows they are split by 4·5eV.

Rabalais[214] concluded that the weak band in the U.V. spectrum of nitromethane at 270 n.m. is due to a $\sigma_{a_1} \rightarrow \pi^*$ transition whilst the transition at 198 n.m. is due to a $\pi_{0 a_2} \rightarrow \pi^*$ transition. It was also shown that the $n \rightarrow \pi^*$ transition in nitromethane causes the dipole moment to be decreased in the excited state[205].

From the above discussion it is obvious that theoretical calculations have failed to provide accurate and consistent values for the orbital energies of nitromethane. No attempt has been made to relate theoretical work to the observed photochemistry of nitroalkanes. The fundamental photoreaction undergone by nitromethane is C-N bond cleavage, to explain this, one would expect the excited state to show a decrease in the C-N bond order.

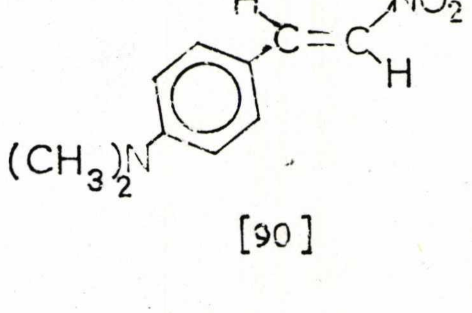
(ii) Nitroaromatics; Nitrobenzene has been shown to be completely planar in the crystaline state[215], and the π electron distribution and bond orders in the ground state have been determined[216]. Calculations of the absolute energies and the L.C.A.O. coefficients of nitrobenzene have been performed[216]. The results indicate that there are bonding, non-bonding and anti-bonding orbitals derived from the nitro group and there are two filled benzene derived orbitals higher in energy than the non-bonding orbitals on the nitro group. These calculations predict the ionization potential to be 10·61eV which is in fair agreement with the experimental value of 10·15eV[217].

Several reports of calculations concerning the excited states of nitrobenzenes have appeared. The transition from the ground to the excited state causes an increase in the dipole moment of nitrobenzene[205]. Calculations on the electron distribution in the ground and excited state of p-nitrophenol showed an increase in the dipole moment in agreement with previous work[218]. The π electron density in the first two $\pi \rightarrow \pi^*$ excited states of nitrobenzene as well as the ground state has been calculated[216]. The charge densities of various substituted nitrobenzenes in the first and second $\pi\pi^*$ states has been calculated[219].

Barltrop attempted to relate the observed photochemistry of nitrobenzene to its electronic structure. Calculations of the π electron charge densities and bond orders for the ground and bottom $\pi\pi^*$ excited singlet and triplet states were performed. These calculations are in good agreement with previous ones[219]. Barltrop[23] explained the photoreduction of nitrobenzene by arguing that the excited singlet state leads to an increase in the electron density on the oxygen atoms which means it should not be easily reduced. The excited triplet state leads to a decrease in the electron density on the oxygen atoms and hence is a more easily reduced state. Barltrop concluded the $\pi \rightarrow \pi^*$ triplet state was responsible from the half-life and the absence of fine structure in the phosphorescence. Testa has claimed on the basis of quenching studies that a $n \rightarrow \pi^*$ triplet state is responsible for the photoreduction[28]. As yet, no firm conclusions have been reached.

Havinga has been very sucessful in relating the site of attack of the nucleophile in aromatic photosubstitution reactions with the charge densities of the excited states[219]. Prediction of reaction pathways is now possible.

(iii) Nitroalkenes; Microwave studies have shown that nitroethylene has a planar structure with a dipole moment of 3.7D[220,221]. The barrier to internal rotation of the C-N bond is 6·51 Kcal mole^{-1}. Theoretical calculations of the dipole moments of E-β-nitrostyrenes are in good agreement with experiment[222]. Nagakura calculated the energy difference between the highest occupied and lowest unoccupied states of several nitroalkenes by studying the interaction of the orbitals of the nitro group and the olefinic system[218]. The results show fair agreement between theory and experiment. Cowley has performed detailed calculations on trans-1-(4-N,N-dimethylaminophenyl)-2-nitroethylene (90)[223]. The lowest energy transition (400 n.m.) was



[90]

assigned to an intramolecular charge transfer excitation, the transfer of the electron being from the aromatic/olefinic system to the nitro group. The absorption at 330 n.m. was assigned to the $n \rightarrow \pi^*$ transition of the nitro group whilst the absorption at 260 n.m. was described as being $\pi \rightarrow \pi^*$ in nature. The effect of substitution on β-nitrostyrenes was then studied[224]. It was concluded that the lowest energy transition involves intramolecular charge transfer. An increase in the electron donating ability of a para-substituent leads to a shift to lower energy of the intramolecular charge transfer transition, whilst the $n \rightarrow \pi^*$ transition was found to remain the same for all the compounds studied, indicating it is an isolated transition, β-methyl substitution was found to lower the triplet lifetime.

No attempts to relate theoretical studies to the photochemistry of nitroalkenes has been made, but the work of Cowley provides a base to build upon.

DISCUSSION

The Photochemistry of Nitroalkenes

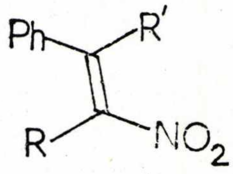
(1) Ultra Violet Spectra of Nitroalkenes.

(2) Photorearrangements of nitroalkenes.

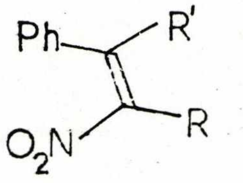
(3) Photoaddition reactions of nitroalkenes.

(1) U.V. spectra of nitroalkenes.

The U.V. spectra of β-nitrostyrenes has been reported. The trans-(E) isomers exhibit strong absorption (ε = 11600–20000) at 304-324 n.m.[161,218,225,226,227,228] due to the nitro group in these isomers being more fully conjugated by achieving a planar configuration[226]. The cis- (Z) isomers



E



Z

show absorption at shorter wavelengths (280-295 n.m.) with greatly reduced maxima (ε = 4000–8000)[161,225,226], attributed to their inability to assume a planar configuration[161].

Trans- (E) aliphatic nitroalkenes exhibit absorption at 220-260 n.m., but the maxima (ε = 5000-16000) are greatly reduced compared to the styrene derivatives[218,227,228]. The cis- (Z) isomers of aliphatic nitroalkenes absorb at about the same wavelength as the trans-isomers but the maxima are reduced in value[227].

The steric effects of substituents in aliphatic nitroalkenes have been investigated[227]. Introduction of substituents at the α - or the β - carbon destroys coplanity leading to a diminution of the conjugation. The molar extinction coefficient of aliphatic nitroalkenes is related to the dihedral angle between the planes of the double bond and the nitro group by the expression:

$$\frac{\varepsilon}{\varepsilon_0} = \cos^2 \phi$$

ε = mol. ext. coef. of compound studied

ε_0 = mol. ext. coef. of planar reference

ϕ = dihedral angle

It was concluded that substitution of an alkyl group in the α - or β - position causes a distortion in planarity of 30-35° ,whilst disubstitution causes a distortion of 40-45° .

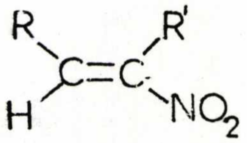
The U.V. spectra of nitrostyrenes has been interpreted by various groups and the lowest energy transition is considered to be an intramolecular charge transfer absorption, the donor being the alkene/phenyl group and the acceptor being the nitro group. The $n \rightarrow \pi^*$ transition of the nitro group is at 300 n.m. and is much weaker[218,223,224].

The U.V. spectrum of nitroethylene has been studied. The lowest energy transition is $n \rightarrow \pi^*$ in character whilst the intramolecular charge transfer transition is at 240 n.m. [229]. The lowest energy transitions in 1-nitropropene and 1-nitropenta-1,3-diene, however have described as intramolecular charge transfer transitions[218]. In a detailed study of conjugated nitroalkenes, Descotes concluded by observing a bathochromic shift in non-polar solvents, that the lowest energy transition is $n \rightarrow \pi^*$ in character whilst the second lowest energy transition by showing a hypsochromic shift is $\pi \rightarrow \pi^*$ in character[227].

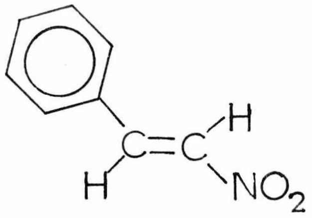
From the work reported in the literature it would seem that there has been little agreement on the interpretation of the U.V. spectra of aliphatic nitroalkenes whilst for nitrostyrene derivatives the agreement is extremely good.

The U.V. spectra of the nitroalkenes used in this study were recorded using methanol as the solvent. The results, which are in good agreement with reported values, are shown in table (1). This table also shows for the aliphatic nitroalkenes studied, the ε value for each nitroalkene at 302•5 n.m., which corresponds to a major emission line of the medium pressure lamp used for this study when a pyrex filter is used. This shows the ability of each nitroalkene to absorb the available light. The figures show that all the aliphatic nitroalkenes have the same ability to absorb the available light, which is as expected.

Table (1)



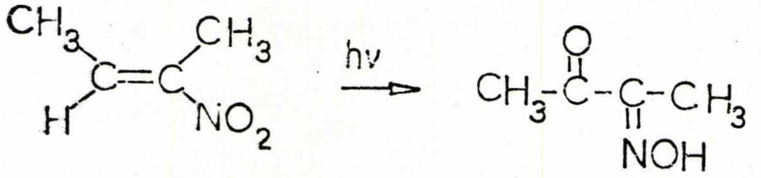
R	R'	λ_{max} (nm) (ε)	Solvent	ε(at 302·5 nm)
CH_3-	CH_3-	250 (6000)	CH_3OH	4400
		250 (6200)	EtOH[227]	
		250 (5600)	EtOH[228]	
CH_3CH_2-	CH_3-	250 (5200)	CH_3OH	2300
		251 (5400)	EtOH[227]	
CH_3-	CH_3CH_2-	249 (5500)	CH_3OH	1900
$[CH_3]_2CH$-	CH_3-	252 (6000)	CH_3OH	2600
		253 (5700)	EtOH[227]	
		258 (6000)	EtOH[228]	
CH_3-	H-	233 (9400)	CH_3OH	1450
		235 (9700)	EtOH[227]	
		235 (9700)	EtOH[228]	



λ max (nm)	ε	solvent
310	16500	CH_3OH

(2) Photorearrangements of nitroalkenes in solution.

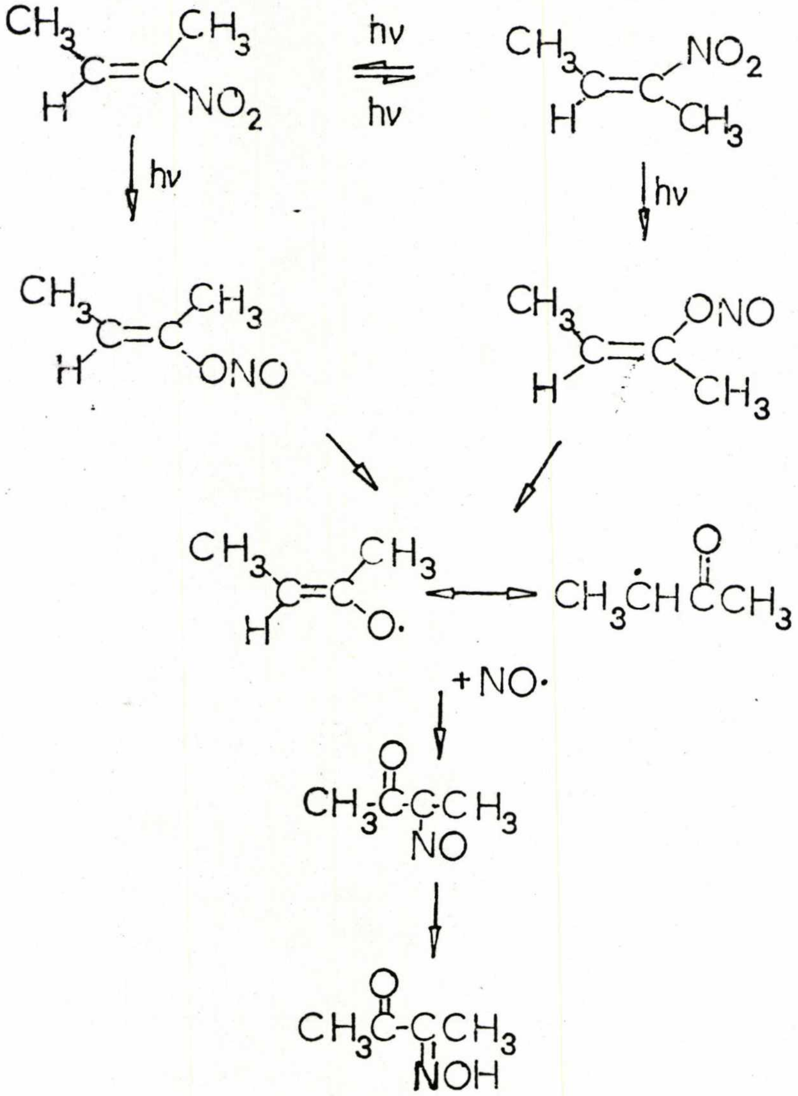
In a preliminary investigation into the photochemistry of aliphatic α-, β-unsaturated nitroalkenes, a 0·126 molar solution of E-3-nitrobut-2-ene (91)[324] in methanol was irradiated under an atmosphere of nitrogen using a pyrex filtered 500 W lamp. The photoreaction was monitored by I.R. and g.l.c. and was continued until no more starting material was evident in the reaction solution. The I.R. spectra of samples, removed after increasing periods of irradiation, showed the appearance of peaks at 3570 (possibly OH) and 1700 cm^{-1} (possibly CO stretch). The appearance of a peak of greater retention time than the starting material in the g.l.c. trace was also noted. When all the starting material had reacted the solvent was removed to give a brown oil ν max. 3570, 3300, 1690, 1360 and 1020 cm^{-1}. This oil was subjected to preparative scale t.l.c. and a white solid was isolated, which was recrystallised to give white crystals which melted at 75-76 °C and had an I.R. spectrum identical to that described above. The material also had δ ($CDCl_3$) 10·02 (1H, singlet), 2·48 (3H, singlet) and 2·02 (3H, singlet). On the basis of this spectral data and the melting point value, the photoproduct was considered to 3-hydroxyiminobutan-2-one (92), which has a reported melting point of 76 °C[230] and reported I.R.[231,232] and n.m.r.[233,234] spectra in close agreement with the values recorded above. The assignment of the oximinoketone structure to the photoproduct was confirmed by a mixed melting point with authentic material. Comparison of the I.R. and n.m.r. spectra and the retention time in the g.l.c. trace of authentic oximinoketone and the photoproduct showed them to be identical in every case. The yield of isolated 3-hydroxyiminobutan-2-one was 21 %.



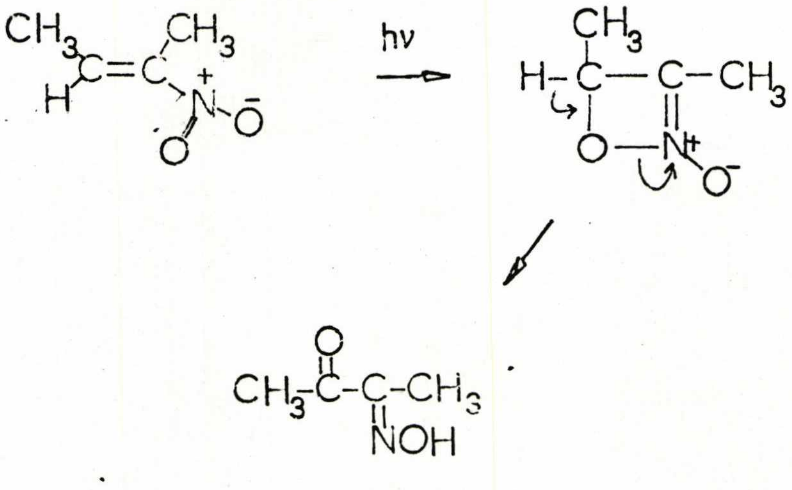
[91] [92]

The formation of the oximinoketone in this photoreaction is important. The formation of oximinoketones is known to occur when 1-aryl-2-nitroprop-1-enes are irradiated in solution[154,155]. This is the first case of this type of rearrangement being observed in non-aryl cases. The oximinoketone could be formed by two different pathways, the first being an aliphatic analogue of the nitro-to-nitrite rearrangement suggested by Chapman[154,155], as shown in scheme (20). This scheme shows E-Z interconversion, occuring on photolysis and both isomers rearranging to unsaturated nitrites to give a common radical intermediate, which recombines with the nitric oxide to give eventually the oximinoketone. Discussion as to whether both the E- and Z-isomers undergo this rearrangement equally well will be delayed until later.

The second possible mechanism is shown in scheme (21). This involves an intramolecular cyclization leading to a system analogous to that postulated previously to account for the formation of aldehydes in the irradiation of some nitroalkenes[186,159,185]. This cyclic species can break down to give the oximinoketone.



Scheme 20.

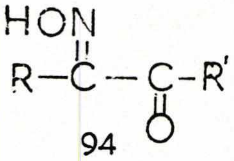


Scheme 21.

In order to differentiate between the nitro-to-nitrite rearrangement (mechanism a) and the intramolecular cyclization (mechanism b), and to see if this rearrangement is general for aliphatic nitroalkenes, a series of these compounds was prepared by the deacylation of the corresponding β-nitroacetates. The purified nitroalkenes were all shown to have the E- configuration by comparison of their spectral data with published data[227].

The table below shows the prepared nitroalkenes and their rearrangement products via mechanism a and mechanism b.

Mechanism (a)



$R-C(=NOH)-C(=O)-R'$

94

hν

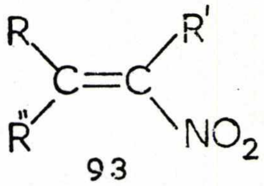
(a) $R = R' = CH_3$

(b) $R = CH_3$; $R' = Et$.

(c) $R = Et$; $R' = CH_3$.

(d) $R = CH(CH_3)_2$; $R' = CH_3$.

(f) $R = CH_3$; $R' = H$.



93

(a) $R = R' = CH_3$; $R'' = H$.

(b) $R = CH_3$; $R' = Et$; $R'' = H$.

(c) $R = Et$; $R' = CH_3$; $R'' = H$.

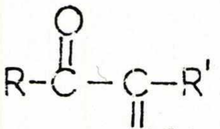
(d) $R = CH(CH_3)_2$; $R' = CH_3$; $R'' = H$.

(e) $R = R' = R'' = CH_3$.

(f) $R = CH_3$; $R' = R'' = H$.

hν

Mechanism (b)



$R-C(=O)-C(=NOH)-R'$

95

(a) $R = R' = CH_3$.

(b) $R = CH_3$; $R' = Et$.

(c) $R = Et$; $R' = CH_3$.

(d) $R = CH(CH_3)_2$; $R' = CH_3$.

(f) $R = CH_3$; $R' = H$.

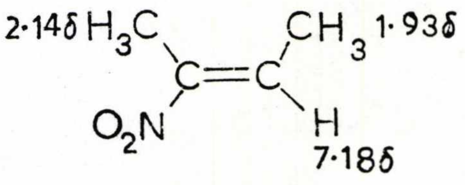
A study of 3-nitropent-2-ene (93b)[236] will differentiate between the two alternative mechanisms, as in this case they will lead to different oximinoketones. A study of 2-nitropent-2-ene [253] (93c) and 4-methyl-2-nitropent-2-ene[325] (93d) will not only help to eluicidate the mechanism of oximinoketone formation, but also show if the intramolecular hydrogen abstraction reaction leading to double bond migration operates. In 93c and d there are secondary and tertiary hydrogen atoms respectively on the γ-carbon, whilst in 93b there are only primary hydrogen atoms, which does not favour the intramolecular hydrogen abstraction reaction[260,261]. 2-Methyl-3-nitrobut-2-ene[227] 93e, if it undergoes the nitro-to-nitrite rearrangement, cannot form an oximinoketone as the final product, it forming a tertiary nitroso compound which cannot undergo tautomerization to the oxime form. This tertiary nitroso compound may then undergo further photoreactions. If mechanism (b) operates, this compound cannot give rise to any oximinoketone as product, unless there is loss of a methyl group. This compound also, only has primary hydrogens on its γ-carbon atom, so photochemical deconjugation would not be expected to be important. 1-Nitroprop -1-ene[227] 93f, has very little steric interaction around its double bond to cause any twisting of the nitro group out of the plane of conjugation. The presence of primary hydrogens on the γ-carbon suggests that photochemical deconjugation should not be favourable.

The irradiation of these nitroalkenes was then studied in detail. All the nitroalkenes studied were shown to be stable in the reaction solvents for long periods of time in the absence of light. A 0·126 molar solution of *E*-3-nitrobut-2-ene was irradiated in methanol under an atmosphere of nitrogen using a pyrex filtered light. The yield of 3-hydroxyiminobutan-2-one was determined to be 27 % by g.l.c. . The reaction mixture was analysed by g.l.c. and the methanol addition product, 2-methoxy-3-nitrobutane and the deconjugated isomer, 3-nitrobut-1-ene were not detected. This was demonstrated by a comparison of retention times, on two different columns, of authentic samples of 2-methoxy-3-nitrobutane[235,236] and 3-nitrobut-1-ene[237].

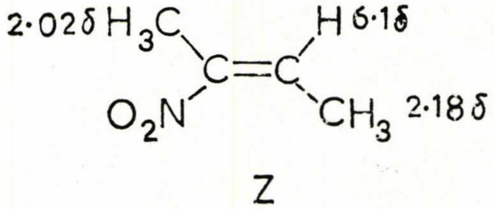
The failure to detect these two compounds means that two possible competing pathways, photochemical addition of methanol and photochemical deconjugation, are not important in the photochemistry of this nitroalkene.

A g.l.c. analysis of samples taken from the irradiation solution after increasing periods of irradiation showed that a peak of shorter retention time appeared very rapidly and became greater in area than the peak due to the E -isomer. The ratio of these two peaks varied little whilst the nitroalkene reacted, once the new peak had formed. An explanation of this observation is that the new peak is due to the Z-isomer, resulting from photochemical E-Z isomerization, as noted by previous workers[163]. The observation that the Z-isomer has a shorter retention time than the E-isomer on a non-polar g.l.c. column is in agreement with published g.l.c. retention times[163]. More evidence for the formation of the Z-isomer was obtained by irradiating a 0•5 molar solution of E-3-nitrobut-2-ene in methanol using pyrex filtered light and following the reaction by g.l.c. and n.m.r. . When a substantial amount of this photoproduct had formed but before substantial rearrangement to the oximinoketone occurred, the reaction mixture was examined by n.m.r..

The n.m.r. spectra of both the E- and Z-isomers of 3-nitrobut-2-ene have been reported[227]. There are significant differences in the chemical shifts of the olefinic proton in the two isomers, and examination of the



E



Z

n.m.r. spectrum of the irradiation solution showed absorption due to the E-isomer at 7•2 δ and absorption at 6•0δ ,the region 1•5–2•5 δ was very complex due to overlaping of the methyl group absorptions. The absorbance at 6•0 δ is due to the Z-isomer and as only one new peak was observed in the g.l.c. trace this peak was attributed to the Z-isomer.

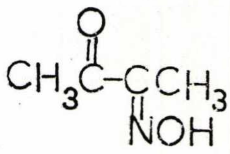
The ratio of the E to the Z-isomers was found to be 0•65, which altered little in the course of the irradiation. This ratio can be compared to the values obtained, for the photostationary state of 3-nitrobut-2-ene in hexane in the presence and absence of sensitizers[163]. The differences in

Sensitizer	E Triplet (Kcalmole^{-1})	Photostationary state (E)/(Z)
Acetophenone	73•6	0•78
Benzophenone	68•5	0•82
Benzil	53•7	1•83
Benzoquinone	50	1•95
None	-	1•32

the value of 1•32 obtained before and the value of 0•65 obtained in this work is attributable to the difference in the solvent. The E-isomer is prefered in hexane whilst in more polar solvents such as methanol the Z-isomer is dominant.

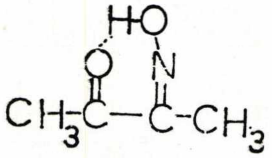
An attempt was made to follow this E-Z isomerization by changes in the U.V. spectrum during the course of the irradiation. The U.V. maxima of the Z and E-isomers of 3-nitrobut-2-ene have their respective values at 254 n.m. and 250 n.m.[227]. However this difference in maxima was not sufficient to allow any conclusive results to be obtained.

Preparative scale t.l.c. isolated the pure oximinoketone and also showed that other, minor, products were present, notably one with I.R. absorption at 1550 cm^{-1} (saturated nitro group) but which was present in such low yield it could not be further characterized. The pure 3-hydroxyiminobutan-2-one isolated from the irradiation was found to be entirely in one geometrical form. The spectral data obtained were the same as the data attributed to the β-isomer^{231,232,233,234}. Previous work using n.m.r.^{233,234} and I.R.^{231,232} has shown that this isomer exists in the β-form rather than the α-form, where intramolecular hydrogen bonding could theoretically stabilize it. No α-isomer was detected in this work by I.R.,n.m.r. or g.l.c. .



$CH_3\overset{\overset{O}{\|}}{C}-\underset{\underset{NOH}{\|}}{C}CH_3$

β



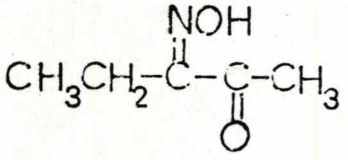
α

To distinquish between the two possible mechanisms, a 0·126 molar solution of E-3-nitropent-2-ene was irradiated in methanol under identical conditions as before. The irradiation was followed by I.R. and g.l.c. . The appearance of peaks at 3560 cm^{-1} and 1690 cm^{-1} in the I.R. spectra of samples removed after increasing periods of irradiation, suggested the formation of an oximinoketone. A g.l.c. comparison of the photoproduct with the two possible oximinoketones that might be formed, was performed. The retention times of 4-hydroxyiminopentan-3-one^{238} (94b) and 3-hydroxyiminopentan-2-one^{239} (95b) were compared with that of the photoproduct in the reaction solution on two different g.l.c. columns, which demonstrated that the photoproduct was 4-hydroxypentan-3-one (94b). The yield of this oximinoketone was calculated to be 31 % by g.l.c. analysis.

Removal of the solvent gave a brown oil which had I.R. absorption at ν max. (CCl_4) 3560 cm^{-1} (strong); 3300 cm^{-1} (strong); 1690 cm^{-1} (strong)

93b

94b



95b

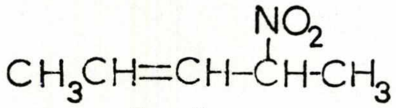
1360 cm^{-1} (strong) and 990 cm^{-1} (strong). This oil was subjected to preparative scale t.l.c. , which led to the isolation of a white solid, which was recrystallized to give white crystals melting at 60-62 °C, and had an I.R. spectrum identical to the one detailed above and ^{1}H n.m.r. absorptions at δ (CDCl$_3$) 1·1 (3H, triplet), 2·05 (3H, singlet), 2·95 (2H, quartet) and 10·1 (1H, singlet). The melting point and spectral data are in complete agreement with those obtained for an authentic sample of 4-hydroxyiminopentan-3-one. This confirmed the assignment of the structure of the photoproduct, as deduced before. The presence of minor products was again noted, but they were present in such low yields that they could not be identified.

An examination, by g.l.c., of samples removed during the course of the irradiation showed the presence of a peak in the g.l.c. trace of shorter retention time than that of E-3-nitropent-2-ene. This peak rapidly became larger than the one due to the E-isomer and once an equilibrium had been established the ratio of the two peaks did not vary. These results are due to the formation of the photostationary state of the E and Z-isomers of 3-nitropent-2-ene, by analogy with 3-nitrobut-2-ene.

The isolation of 4-hydroxyiminopentan-3-one as the photoproduct establishes that the mechanism for the rearrangement is the aliphatic analogue of the one postulated by Chapman[154,155], involving an initial nitro-to-nitrite rearrangement (mechanism (a)).

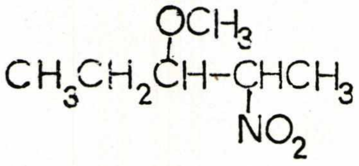
An 0·126 molar solution of E-2-nitropent-2-ene in methanol was irradiated under the same conditions as before, and followed by I.R. and g.l.c This nitroalkene under identical conditions as before reacted very rapidly to give, by I.R., a mixture of an oximinoketone and a compound with a saturated nitro group. A g.l.c. study of samples removed during the course of the irradiation showed the presence of a peak in the g.l.c. trace of shorter retention time than the E-isomer, which by analogy with previous work was assigned to the Z-isomer. After slightly longer periods of irradiation another peak of intermediate retention time was observed which increased in size as the peaks due to the E and Z isomers decreased. In this case the peak due to the E-isomer remained the major peak relative to the Z-isomer.

When the reaction was complete, removal of solvent gave a brown oil which had I.R. absorptions attributable to an oximinoketone and absorptions indicative of a saturated nitro group. The compound containing the saturated nitro group could be either (a) the deconjugated product, 4-nitropent-2-ene (96) or (b) the methanol addition product, 3-methoxy-2-nitropentane (97),



$$CH_3CH{=}CH{-}\underset{}{\overset{NO_2}{CH}}{-}CH_3$$

[96]

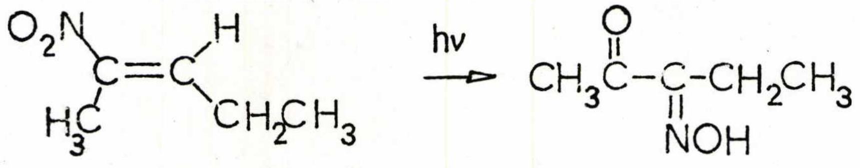


$$CH_3CH_2\overset{OCH_3}{CH}{-}\underset{NO_2}{CH}CH_3$$

[97]

but as absorption due to the C-O stretch of the ether linkage was absent, the formation of the deconjugated product (97) was indicated.

The crude product mixture was then subjected to preparative scale t.l.c. which isolated a solid which on recrystalization gave white crystals melting at 54-56 °C, and had I.R. absorption at 3570 cm^{-1} (strong); 3300 cm^{-1} (broad); 1690 cm^{-1} (strong) and 1360 cm^{-1} (strong) and n.m.r. absorption at δ ($CDCl_3$) 1·0 (3H, triplet), 2·4 (2H, complex), 2·5 (3H, singlet) and 10·0 (1H, singlet). The melting point and spectral data are in complete agreement with those found for an authentic sample of 3-hydroxyiminopentan-2-one[239] (95c). The formation of this oximinoketone is in complete agreement with mechanism (a). The yield of oximinoketone was calculated to be 4 % by g.l.c. analysis.

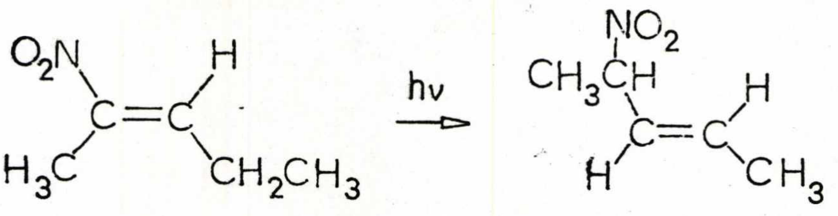


94c

95c

Starting material was also isolated from the t.l.c., and as none was present in the crude product mixture it was concluded that the deconjugated isomer had undergone rearrangement to the conjugated isomer on the silica gel used in the t.l.c. . As this photoproduct was sensitive to normal chromatographic materials the irradiation was repeated and the oil obtained on removal of the solvent was distilled under reduced pressure to give a yellow liquid with I.R. absorption at 2980 cm^{-1} (strong), 2940 cm^{-1} (strong) 1545 cm^{-1} (strong), 1380 cm^{-1} (strong), 1355 cm^{-1} (strong), 960 cm^{-1} (strong) and 860 cm^{-1} (strong) and H^1 n.m.r. absorption at δ ($CDCl_3$) 1·7 (3H, doublet), 1·85 (3H, doublet), 5·2 (2H, complex) and 6·1 (1H, complex).

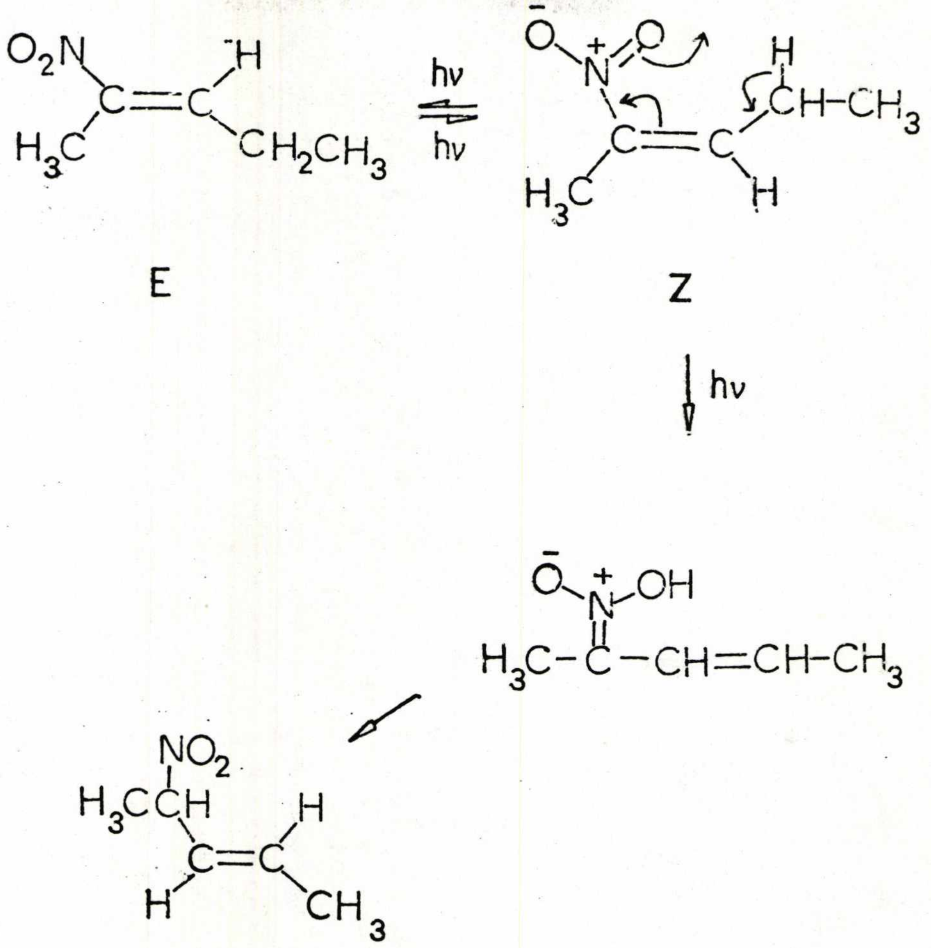
These spectral data are in complete agreement with the reported spectra of 4-nitropent-2-ene^{227}. This photoproduct was obtained in 15 % yield.



E

The deconjugated isomer can exist in either the E or the Z form. The n.m.r. spectrum detailed above is in complete agreement with the one reported for the E-isomer^{227}. No sign of the Z-isomer could be detected by I.R., n.m.r., or g.l.c.. The peak observed in the g.l.c. trace in the study of E - Z equilibrium of the conjugated nitroalkene was identified as the deconjugated isomer. This is in agreement with the published retention times.^{163} Examination of the residues after the distillation revealed that the oximinoketone had undergone decomposition. It was concluded that the isolation of both photoproducts from the same irradiation mixture is rather difficult, but each can be separately isolated at the expense of the other.

The result of the g.l.c. study of the E - Z isomerization in this irradiation is different from the other cases as the E-isomer remains the dominant member of the equilibrium mixture. This is explained by assuming the deconjugated isomer is formed from the Z-isomer, via a six-membered transition state as suggested by previous workers^{188,189}, as shown in scheme (22). This mechanism will be discussed in greater detail later.

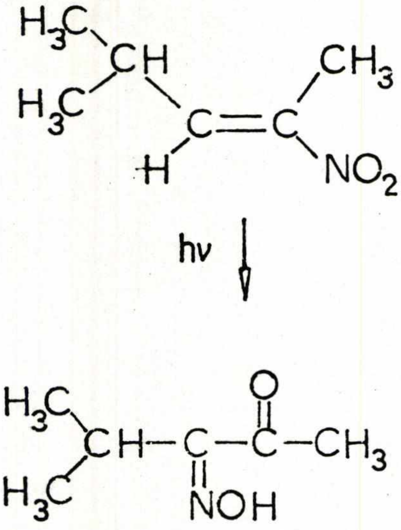


Scheme 22.

The isolation of 4-nitropent-2-ene from the irradiation of 3-nitropent-2-ene, whilst no deconjugated product was detected upon irradiation of 3-nitrobut-2-ene, suggests that going from a primary hydrogen to a secondary hydrogen on the γ-carbon results in the deconjugation reaction becoming a major pathway. Hence going from a secondary to a tertiary hydrogen on the γ-carbon should increase the ease of deconjugation.
A 0·126 molar solution of 4-methyl-2-nitropent-2-ene (93d) in methanol was irradiated under an atmosphere of nitrogen under identical conditions as before. I.R. spectra of samples removed in the course of the irradiation indicated that a complex mixture of products was present, one of them being an oximinoketone. When all the nitroalkene had reacted the solvent was removed to give a brown oil with I.R. absorptions at 3570 cm^{-1} (strong),

3300 cm^{-1} (broad), 2970 cm^{-1} (strong), 1760 cm^{-1} (medium), 1740 cm^{-1} (strong), 1690 cm^{-1} (strong), 1550 cm^{-1} (medium), 1450 cm^{-1} (strong) and 1380 cm^{-1} (strong). On the basis of this I.R. spectrum several conclusions can be drawn. The peaks at 3570, 3300 and 1690 cm^{-1} are indicative of an oximinoketone. The peak at 1550 cm^{-1} may be due to a deconjugated nitroalkene, whilst peaks at 1740 and 1760 cm^{-1} are due to carbonyl absorptions.

The crude product mixture was subjected to preparative scale t.l.c., which isolated a solid that on recrystalization gave crystals melting at 76-77 C, and I.R. absorption at 3570 cm^{-1}, 3300 cm^{-1}, 1690 cm^{-1} and 1360 cm^{-1}. These data are in complete agreement with values obtained for 3-hydroxyimino-4-methylpentan-2-one[240]. The yield of this product was calculated to be 5 %, by g.l.c. analysis. This oximinoketone is the one expected by an initial nitro-to-nitrite rearrangement.



[93d]

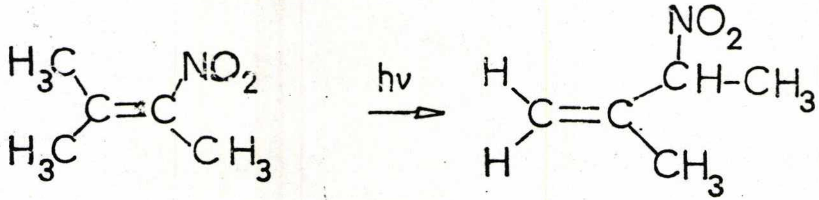
[94d]

Other products were isolated from the t.l.c. but they were present in such small amounts they could not be identified except that one had I.R. absorption at 1740 cm^{-1} and another had I.R. absorption at 1760 cm^{-1}. The isolation of starting material from the t.l.c. indicated that isomerization of the deconjugated isomer to the conjugated isomer had occurred. In an attempt to isolate the β,γ-nitroalkene, the irradiation was repeated and the crude reaction mixture distilled. In this case the distillate was a mixture, showing I.R. absorption at 1760 cm^{-1} and 1550 cm^{-1} which were attributed to an unknown carbonyl compound and the deconjugated nitroalkene respectively. Further attempts to separate these two compounds by careful distillation failed.

A g.l.c. study of samples removed during the course of the irradiation showed no sign of the Z-isomer. This could be due to several reasons, (a) the g.l.c. column in this case failed to separate the two isomers, (b) the physical characteristics of the Z-isomer are such that it does not behave in the way one would predict by analogy with other nitroalkenes or (c) the double bond migration reaction is so facile, no appreciable concentration of the Z-isomer builds up. The g.l.c. retention time for this Z-isomer has been reported and is similar to the other Z-isomers[227]. Failure of the g.l.c. column to separate the isomers in this case is possible, but as good separations were achieved in all the other cases it must be considered a remote possibility. This leaves a facile deconjugation reaction to explain the failure to detect any Z-isomer.

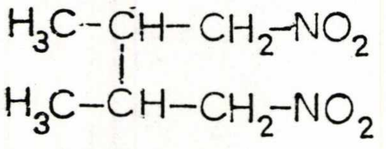
The photochemistry of an α,β-unsaturated nitroalkene which cannot form a stable oximinoketone was next investigated. An 0·063 molar solution of 3-methyl-2-nitrobut-2-ene in methanol was irradiated under identical conditions to before. The reaction was followed by g.l.c. and 2-methyl-3-nitrobut-1-ene was detected by a comparison of retention times, on two different columns, with an authentic sample[237]. Removal of solvent gave an oil which had major I.R. absorptions at 1710 cm^{-1} and 1550 cm^{-1}. This was subjected to preparative scale t.l.c. but no pure compounds could be obtained.

The observation that this nitroalkene, which has a primary hydrogen on the γ-carbon undergoes the deconjugation reaction is at first sight rather odd, as it would appear from previous work a secondary or tertiary hydrogen is normally required. However in this particular nitroalkene there must be steric interaction between the Cis methyl group and the nitro group which are not relieved by isomerization. The movement of a double bond out of conjugation with a nitro group in order to relieve steric interactions is known[241] and may be the cause of this deconjugation reaction. The failure to isolate any other products from this photoreaction apart from the deconjugated isomer does not allow any speculation as to whether a nitrosoketone is a possible intermediate.



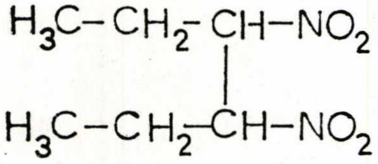
An 0·189 molar solution of E-1-nitroprop-1-ene in methanol was irradiated under an atmosphere of nitrogen under identical conditions to before and was followed by I.R. and g.l.c.. When no more starting material could be detected the solvent was removed to give a brown oil that had I.R. absorption at 1550 cm^{-1}. This oil was subjected to column chromatography using silica gel. Three products were isolated from this chromatography, the first was a white solid, isolated in low yield, which after recrystalization, melted at 52-55 °C. The I.R. spectrum showed absorption at 1550 cm^{-1} and 1370 cm^{-1}. The H^1 n.m.r. spectrum showed absorption at δ ($CDCl_3$) 4·4-4·8 (3H, multiplet), 2·4-2·8 (1h, complex), 1·0-1·3

(5H, complex). Elemental analysis indicated the empirical formula was $C_3H_6NO_2$ and the mass spectrum of this compound showed main fragmentation patterns at m/e 83, 55 and 41. On the basis of this information, two possible structures may be considered, (98) and (99). Structure (98) can be eliminated as 3,4-dinitrohexane has been reported to have different spectra from those reported above[242]. Structure (99), however, fails to explain all the observed spectra and hence the structure of this photoproduct is in some doubt.



$$\begin{array}{l} H_3C-CH-CH_2-NO_2 \\ \qquad\;\; | \\ H_3C-CH-CH_2-NO_2 \end{array}$$

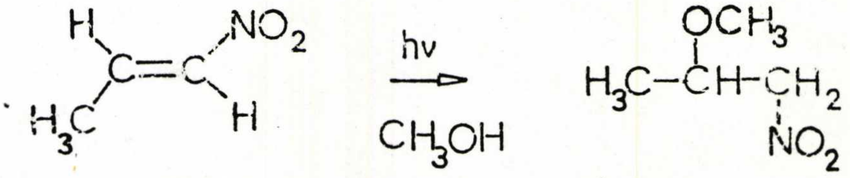
[99]



$$\begin{array}{l} H_3C-CH_2-CH-NO_2 \\ \qquad\qquad\quad\;\; | \\ H_3C-CH_2-CH-NO_2 \end{array}$$

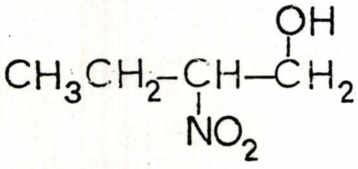
[98]

The second photoproduct to be isolated from the column chromatography was a yellow liquid which had I.R. absorption at 1550 cm^{-1} ,1370 cm^{-1} and 1080 cm^{-1} and H^1 n.m.r. absorption at δ ($CDCl_3$) 4·2-4·7 (3H, complex), 3·5 (3H, singlet) and 1·3 (3H, doublet). These spectral data indicated that the product was 2-methoxy-3-nitropropane resulting from the photochemical addition of methanol. This assignment was confirmed by a comparison with spectra of authentic material[235,236,248]. The yield of this



photoproduct was found to be 29 % .

The third photoproduct to be isolated was a yellow liquid which had I.R. absorption at 3560 cm^{-1} ,3300 cm^{-1} ,1550 cm^{-1} and 1370 cm^{-1} and H^1 n.m.r. absorption at δ ($CDCl_3$) 4•4-4•8 (3H, complex), 1•2-1•4 (5H, complex). Attempts to purify this material by distillation led to its decomposition. The spectral data above is fairly consistent with that of a β-nitroalcohol, as these compounds have OH stretch in the 3300 cm^{-1} region as well as NO_2 assymmetric stretch at 1550 cm^{-1} [243,244]. The I.R. spectrum of 2-nitrobutan-1-ol (100) is extremely similar to that of the photoproduct, but consideration of the two n.m.r. spectra showed thephotoproduct was not this



$$CH_3CH_2-\underset{NO_2}{CH}-\overset{OH}{C}H_2$$

[100]

nitroalcohol. Owing to the decomposition of the photoproduct on attempted purification, the structure could not be fully elucidated but it would appear from the data above to have a β-nitroalcohol type structure.

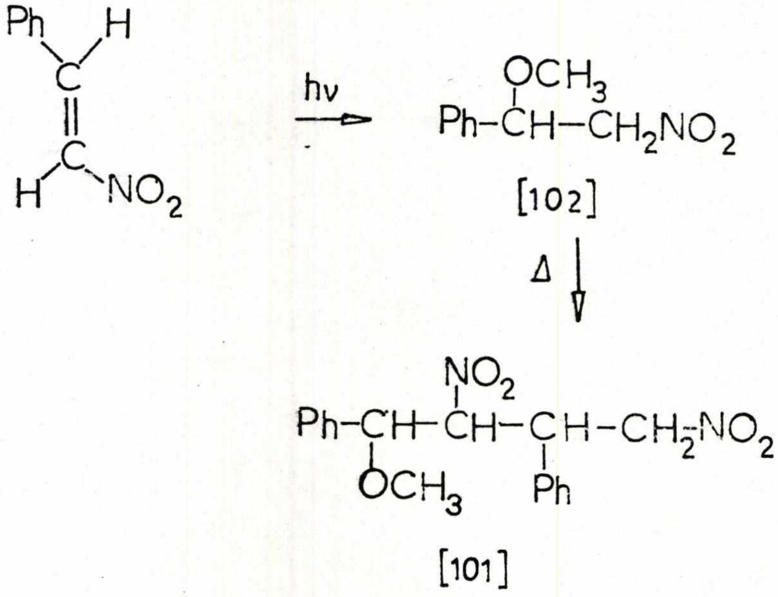
The addition of methanol to this nitroalkene was found to be a very facile reaction, as a solution of the nitroalkene in methanol underwent this photoreaction in normal laboratory light. Refluxing the nitroalkene in methanol also gave the methanol addition product. The photoreaction described above was shown to be photochemical rather than thermal as an 0•189 molar solution of the nitroalkene in methanol when left in a darkened cabinet at the same temperature the irradiation was conducted at, gave no trace of the methanol addition product. This demonstrated that under the conditions used for the irradiation no thermal addition of methanol took place. On refluxing in methanol, thermal addition occurred, as shown by refluxing the nitroalkene in an all black apparatus when a 50 %

yield of the methanol addition product was obtained.

The important point to note from this irradiation is that no products resulting from an initial nitro-to-nitrite rearrangement were obtained. The full implications of this will be considered later.

A nitroalkene with similar steric properties to 1-nitroprop-1-ene is β-nitrostyrene and hence the photochemistry of this nitroalkene in methanol was studied. An 0·27 molar solution of β-nitrostyrene in methanol was irradiated using quartz filtered light and was followed by I.R. and g.l.c. . The g.l.c. trace after a short period of irradiation showed the occurrence of a peak of shorter retention time than the starting <u>E</u>-isomer, which by analogy with previous work was considered to be the <u>Z</u>-isomer. The irradiation was continued until no more nitroalkene was observed in the g.l.c. trace. The I.R. spectrum of the crude product showed a peak at 1550 cm^{-1} (saturated nitro group). Preparative scale t.l.c. separated in low yield, 1-methoxy-2,4-dinitro-1,3-diphenylbutane (101), identified by comparison with an authentic sample[247]. This product was shown to be derived from 1-methoxy-2-nitro-1-phenylethane (102). The reaction of one mole of sodium methoxide with one mole of β-nitrostyrene followed by careful neutralization gave initially a crude product with I.R. absorption at 1535 cm^{-1}, which was attributed to 1-methoxy-2-nitro-1-phenylethane (102) by analogy with previous work[235,245,246]. On standing, however, this material underwent further reaction, as demonstrated by the appearance in the I.R. spectrum of absorption at 1550 cm^{-1}. Recrystallization of this material gave (101), by comparison with an authentic sample[247].

It was concluded that the methanol addition adduct (102) is unstable and undergoes further thermal reaction to give (101) in the absence of any catalyst. Hence it is concluded that the primary photoproduct is (102) resulting from the photoaddition of methanol which then undergoes a thermal reaction to give (101).



Irradiation of β-nitrostyrene in methanol using pyrex filtered light in place of quartz led to the formation of (101), but in this case no E-Z isomerization could be detected by g.l.c. .

The isolation of the methanol addition product is in complete agreement with the results obtained for 1-nitropropene. The observation of E-Z isomerization when quartz but not pyrex filtered light is used suggests fairly high energy is required to cause this isomerization.

The previous irradiations had all used methanol as the solvent. The effect of changing the solvent was investigated. The first solvent used was cyclohexane, which is very similar to hexane, used by Descotes in the investigation of α, β-nitroalkenes[163]. These workers observed E-Z isomerization and double bond migration[163].

Irradiation of a 0·126 molar solution of E-3-nitrobut-2-ene in cyclohexane under an atmosphere of nitrogen using pyrex filtered light led to the slow disappearance of the starting material and the appearance of peaks in the I.R. spectrum attributable to 3-hydroxyiminobutan-2-one. The presence of the oximinoketone was confirmed in the first instance by a comparison of the retention times of the photoproduct in the reaction solution and an authentic sample of the oximinoketone, on two different g.l.c. columns. The yield of oximinoketone was calculated to be 18 % . The photoreaction was not as clean as the methanol case, a brown tar being deposited on the sides of the reaction vessel and lamp. This brown tar was shown by I.R. to contain oximinoketone, but could not be crystalized. The solvent was removed from the reaction mixture and the resulting brown oil was subjected to preparative scale t.l.c. which isolated 3-hydroxyiminobutan-2-one, identified by comparison with authentic material. The reason for the formation of tars in this photoreaction is due to the low solubility of the oximinoketone in cyclohexane, hence the absolute yield of the oximinoketone is somewhat higher than 18 % , which represents the value for a saturated solution.

G.l.c. analysis of the reaction mixture during the course of the irradiation demonstrated that <u>E</u>-<u>Z</u> isomerization was occurring. Once the equilibrium was established it changed little. The equilibrium mixture consisted of about 50 % of each isomer. This is different from the results of Descotes who using hexane as the solvent found the major component to be the <u>E</u>-isomer [163]. The failure of these workers to observe any oximinoketone is due to several reasons. Firstly they report that tars occur, which probably result from the insoluble oximinoketone coming out of solution. Secondly, their work-up procedure involved distillation which has been shown previously to result in the decomposition of the oximinoketone.

The next solvent considered was methylcyanide. A 0·126 molar solution of <u>E</u>-3-nitrobut-2-ene in methylcyanide was irradiated under nitrogen using pyrex filtered light. This led to the formation of 3-hydroxyiminobutan-2-one in 25 % yield, the oximinoketone being identified firstly by comparison of retention times of photoproduct and authentic sample on two different g.l.c. columns and secondly isolation of the crystaline material by preparative scale t.l.c..

It was concluded that the rearrangement of 3-nitrobut-2-ene to the oximinoketone occurs in solvents of widely different polarity and hence it was decided to irradiate this nitroalkene in acetone. In this case energy transfer from the photoexcited solvent to the nitroalkene may be possible. An 0•126 molar solution of 3-nitrobut-2-ene in acetone was irradiated in acetone under exactly the same conditions as before led to the formation of 3-hydroxyiminobutan-2-one in 22 % yield. The oximinoketone was identified by its g.l.c. retention time and its isolation and characterization. after preparative scale t.l.c..

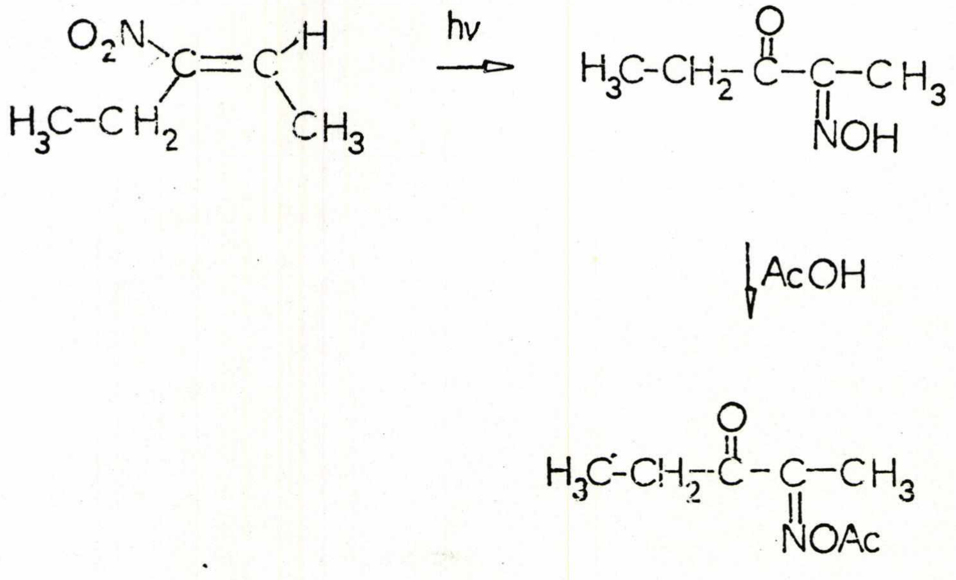
It has been suggested that irradiation of nitroalkenes in acetone gives a higher yield of photoproduct due to energy transfer from the excited acetone[155]. In the present case a lower yield of photoproduct when compared to using methanol as the solvent, was in fact obtained. It was decided to investigate what percentage of the light is being absorbed by the acetone. As a pyrex filter was being employed the major emission lines of the light source that are capable of being absorbed are at 2967 Å, 3025 Å and 3130 Å. The percentages of light absorbed by the nitroalkene and by the acetone at these wavelengths under the conditions of the irradiation are shown below.

Wavelength (Å)	% absorbed by nitroalkene	% absorbed by acetone
2967	45•6	54•4
3025	50•6	49•4
3130	66	34

From these figures it is clear that under the conditions used for the irradiation there is a great deal of light being absorbed by the nitroalkene as compared to the acetone. If energy transfer from acetone occurs, it is only a minor pathway for providing excited state molecules of 3-nitrobut-2ene. These calculations also demonstrate that great care must be taken when discussing the ability of acetone to take part in energy transfer reactions.

In the above case the exact role of the acetone is not clear. The suggestion of Chapman that high yields of oximinoketone in acetone when it is used as the solvent for the irradiation of 1-phenyl-2-nitroprop-1-ene being due to energy transfer[155], cannot be regarded as general.

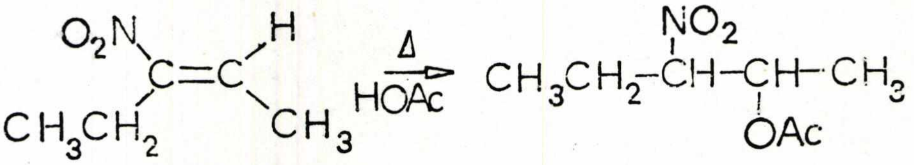
In an attempt to study the effect of acid on the photochemistry of these nitroalkenes, an irradiation in acetic acid was performed. An 0·126 molar solution of E-3-nitropent-2-ene in acetic acid was irradiated under identical conditions to before and the reaction was followed by g.l.c.. When no more starting material was detected the solvent was removed and the crude product mixture subjected to preparative scale t.l.c.. 4-Hydroxyiminopentan-3-one, identified by comparison with an authentic sample, was isolated in 6 % yield. Another photoproduct was isolated in low yield which had I.R. absorption at 2970 cm^{-1}, 1780 cm^{-1}, 1700 cm^{-1}, 1360 cm^{-1} and1170 cm^{-1} and H^1 n.m.r. absorption at δ ($CDCl_3$) 3·1(2H, quartet 2·3 (3H, singlet), 2·1 (3H, singlet) and 1·2 (3H, triplet). These data suggest that the product is the acetate of the oximinoketone (102), as the n.m.r. spectrum is very similar to that of the oximinoketone but with an extra peak at 2·3 δ . The peaks at 1780 cm^{-1} and 1170 cm^{-1} in the I.R. are also suggestive of an acetate. This product is present in low yield and is considered to result from the reaction of the oximinoketone with



the acetic acid. Dissolving some authentic 4-hydroxyiminopentan-3-one in acetic acid and leaving for a similar period of time as the irradiation resulted in the formation of a material with identical spectral properties as the acetate described above.

No product resulting from the photochemical addition of acetic acid was observed in the irradiation and it was concluded that addition is not a favoured pathway, the main photochemical pathway being an initial nitro-to-nitrite rearrangement.

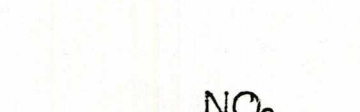
The stability of 3-nitropent-2-ene in acetic acid in the absence of light was studied. A 0•2 molar solution of the nitroalkene in acetic acid was left at room temperature for five days from which the starting material was quantitatively recovered. However, refluxing a 0•2 molar solution of this nitroalkene in acetic acid for 70 hours caused 60 % of the nitroalkene to react (by g.l.c.). Removal of the solvent and distillation gave 2-acetoxy-3-nitropentane in 58 % yield, identified by comparison with an authentic sample[248]. This reaction is interpreted as a thermal



addition of acetic acid to the nitroalkene, acid catalysis being provided by the solvent. To see if this reaction could be extended to other nitroalkenes, a 0•2 molar solution of 2-nitro-1-phenyl prop-1-ene was refluxed in acetic acid for 72 hours, but no reaction was observed. It is interesting to note that no photochemical addition of acetic acid to 3-nitropent-2-ene is observed whilst thermal addition is observed.

As described previously 1-nitropropene when irradiated in methanol does not undergo the nitro-to-nitrite rearrangement, the major photoreaction being the addition of methanol. It was decided to irradiate 1-nitropropene in methyl cyanide, which is a solvent of similar polarity to methanol but one in which any sort of addition of solvent is highly unlikely. Irradiation of a 0•126 molar solution of E-1-nitroprop-1-ene in methyl cyanide under identical conditions to before led to a very slow reaction. Samples removed and examined by g.l.c. during the course of the irradiation showed the occurrence of E-Z isomerization, with the Z-isomer being the major component. When no more starting material could be detected by g.l.c. the solvent was removed to give a brown oil, which had I.R. absorption at 1550 cm^{-1}. The n.m.r. spectrum of the crude product did not contain peaks attributable to the deconjugated isomer 3-nitroprop-1-ene, and hence this was ruled out as a possible product. Subjecting the crude product to preparative scale t.l.c. failed to isolate any pure material. This irradiation demonstrated that 1-nitropropene does not undergo the deconjugation reaction which is what is expected, and again no evidence of products resulting from an initial nitro-to-nitrite rearrangement was obtained.

It is possible that in the rearrangement of an α,β-nitroalkene to an oximinoketone, the deconjugated isomer may be an intermediate, or the deconjugated isomer may be formed in all these reactions but undergo further, rapid, photochemical reactions so it usually fails to be detected. To investigate these points further, a 0•126 molar solution of 3-nitrobut-1-ene in methanol was irradiated under an atmosphere of nitrogen under

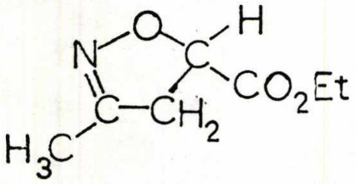


$$CH_2{=}CH{-}\overset{NO_2}{\overset{|}{C}}H{-}CH_3$$

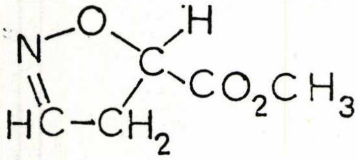
identical conditions to before. The reaction was followed by g.l.c.. 5 % of the β,γ -nitroalkene had reacted in the same amount of time which caused complete reaction of the α,β -nitroalkene. This shows that the β,γ -nitroalkene is relatively light stable, under the conditions used, which is in agreement with previous observations[184,188], and if formed in the course of the reaction it will be detectable at the end. No trace of oximinoketone was found in the reaction solution, hence the β,γ -nitroalkene was ruled out as a reaction intermediate in the formation of the oximinoketone.

The formation of the oximinoketone only at best accounts for about 30 % of the starting nitroalkene. The failure to detect any other products may be due to the nitroalkenes undergoing fragmentation to give volatile products. Recent reports of the isolation of benzaldehydes on irradiation of cis-α,4-dinitrostilbene[159] and para-substituted β-nitrostyrenes[185] have led to the postulation of a four membered cyclic intermediate which can breakdown to an aldehyde and a nitrile oxide. The nitrile oxide has been trapped by performing the irradiation in the presence of methyl acrylate to give isoxazolines[185].

A similar reaction may be possible in the aliphatic series. Detection of any aldehydes is difficult as they are volatile and need to be detected by g.l.c., where masking by solvent can occur. To attempt to trap any nitrile oxide that might be formed, the irradiation was performed in the presence of ethyl acrylate. An 0·126 molar solution of 3-nitrobut-2-ene containing a five molar excess of ethyl acrylate in methyl cyanide was irradiated under identical conditions to before, until no more starting material could be detected by g.l.c.. Removal of the solvent gave a brown oil with I.R. absorption at 1720 cm^{-1} and 1360 cm^{-1} and n.m.r. absorption at δ 4·4(triplet), 2·4(singlet), 2·3-2·1(multiplet), 2·0(singlet) and 1·1-1·5(multiplet). The peaks at 2·4 and 2·0 are due to 3-hydroxyiminobutan-2-one. Distillation of this material gave a 15 % yield of 3-hydroxyiminobutan-2-one, identified by comparison with an authentic sample. The residues in the distillation flask had I.R. absorption at 1720 and 1360 cm^{-1}. Ethyl acrylate has absorption at 1705 and 1290 cm^{-1} which ruled out this material being unreacted ethyl acrylate. The n.m.r. spectrum showed absorption at δ (CDCl$_3$) 4·4 (2H, triplet), 2·2 (2H, doublet), and 1·4 (3H, triplet). If an isoxazoline had been formed in the course of the irradiation it should have structure (103). The H^1 n.m.r. spectrum of (104), an analogous system, has been reported^{249,250}. It has absorption at δ (CDCl$_3$) 6·28 (1H, triplet), 5·0 (1H, triplet), 3·33 (2H, quartet) and 3·8 (3H, singlet). The n.m.r. spectrum of the photoproduct is so



[103]



[104]

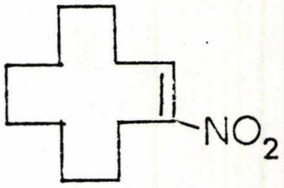
different from (103), it was concluded that the photoproduct was a polymer of ethyl acrylate and hence it was not further investigated.

Failure to trap any nitrile oxide does not rule out its presence, as under the reaction conditions, ethylacrylate underwent polymerization and 1,3-dipolar addition may not have been able to occur.

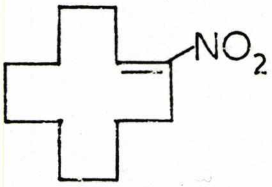
The effect of changing the filter employed from pyrex to quartz was investigated. This has the effect of allowing light of shorter wavelengths through which may lead to $\pi \rightarrow \pi^*$ excitation as well as $n \rightarrow \pi^*$ excitation. An 0·1 molar solution of 3-nitrobut-2-ene was irradiated in methanol under an atmosphere of nitrogen using a quartz filter. The reaction was followed by g.l.c. and when no more starting material could be detected the solvent was removed to show that 3-hydroxyiminobutan-2-one was again the major product. Hence changing the filter does not effect the photochemical behaviour of this compound.

Previous work by Taylor[148] has shown that irradiation of 1-nitrocyclododecane in acetone or methanol causes an intramolecular hydrogen abstraction reaction to occur to give 3-nitrocyclododec-1-ene. Several ambiguities exist about this photoreaction, as the stereochemistries of the starting nitroalkene and the photoproduct were not firmly established. This photoreaction was hence reinvestigated to clarify these points.

1-Nitrocyclododec-1-ene was prepared by an adaption of the method of Steifert[251,252] as developed by Taylor[148]. The stereochemistry of the purified nitroalkene was shown to be E, by a study of its ^{1}H n.m.r. spectrum. From a study of 100MHz ^{1}H n.m.r. spectra of the E-isomers

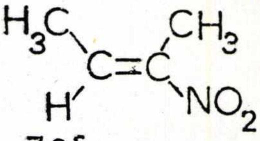
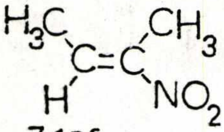
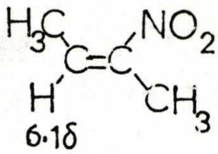
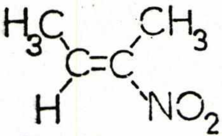
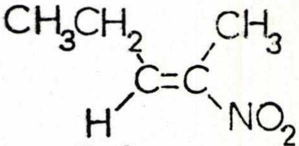
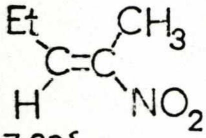
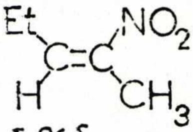
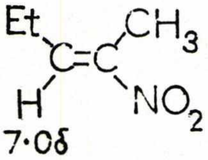
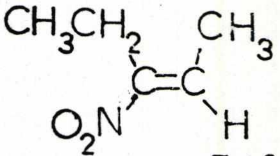
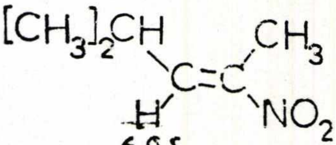
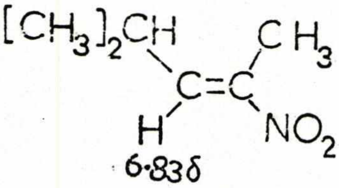
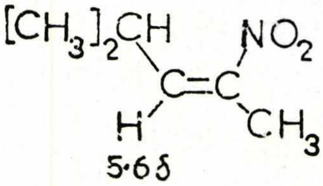


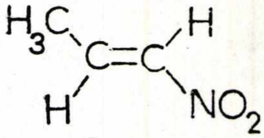
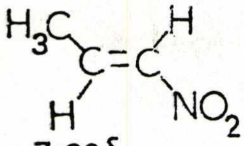
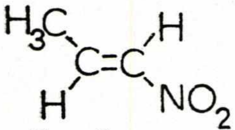
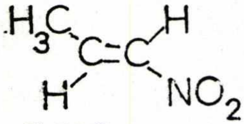
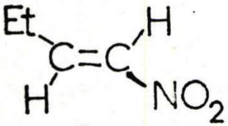
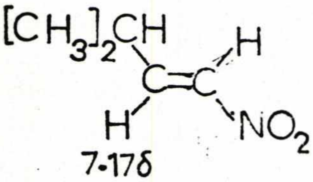
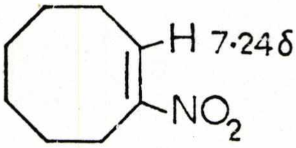
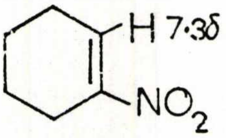
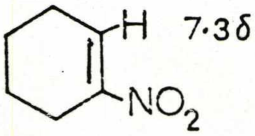
E



Z

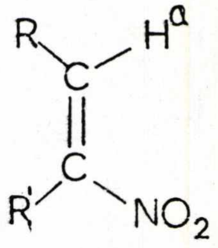
of the nitroalkenes previously prepared, and from a study of the values of E- and Z-isomers of nitroalkenes reported in the literature, the following table was drawn up for the chemical shift of the olefinic

proton. H^1 n.m.r. (100 MHz)$^{(a)}$	Literature values	Ref.
 7·2δ	 7·18δ  6·1δ	$227^{(b)}$
	 7·07δ	$253^{(b)}$
 7·1δ	 7·02δ  5·86δ	$227^{(b)}$
	 7·0δ	$253^{(b)}$
 7·1δ	–	–
 6·9δ	 6·83δ	$227^{(b)}$
	 5·6δ	$227^{(b)}$

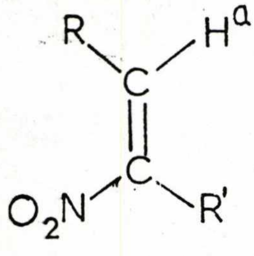
H^1 n.m.r. (100 MHz)$^{(a)}$	Lit. values	Ref.
 7·2δ	 7·22δ	227(b)
	 7·26δ	254(b)
	 7·28δ	255(a)
	 7·24δ	227(b)
	 7·17δ	227(b)
		251(a)
		148(b) 184(b)

NOTES: (a) Recorded in $CDCl_3$.; (b) Recorded in CCl_4

From these results the following generalizations about nitroalkenes can be made; (i) for an E-isomer, H^a lies in the range 6·7–7·2 δ and



E

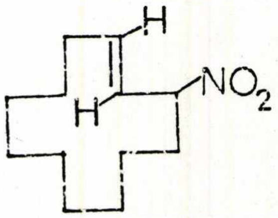


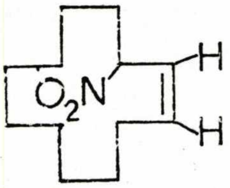
Z

(ii) for the Z-isomer, H^a lies in the range 5·6–6·1 δ . The 100 MHz ^1H n.m.r. spectrum of 1-nitrocyclododec-1-ene has absorption at δ ($CDCl_3$) 7·08 (1H, triplet), 2·65 (2H, multiplet), 2·3 (2H, multiplet) and 1·0–1·8 (16H, multiplet). The chemical shift value of the olefinic proton is in complete agreement with the value predicted for the E-isomer.

An 0·0284 molar solution of E-1-nitrocyclododec-1-ene was irradiated in acetone under an atmosphere of nitrogen using a pyrex filter. The reaction was followed by IR and n.m.r.. The deconjugation reaction was initially observed in the I.R. spectrum by the growth of a peak at 1540 cm^{-1} (saturated nitro group) and the decrease of the peak at 1510 cm^{-1} (unsaturated nitro group). The production of a β,γ-nitroalkene from an α,β-nitroalkene results from an initial rearrangement of the E- to the Z-isomer which then undergoes the deconjugation reaction. The ^1H n.m.r. spectra of samples removed from the irradiation mixture after short periods of irradiation had absorption in the region 6·0–6·2 δ , which is in the range expected for the Z-isomer. The growth of a multiplet in the region 5·4–5·8 δ ,as the irradiation continued was assigned to the deconjugated isomer. The irradiation was continued until no more conjugated nitroalkene could be detected by I.R. . The solvent was removed and the crude product distilled. The distillate was filtered through silica gel and the yellow oil obtained had I.R. absorption at at 2910 cm^{-1}, 1540 cm^{-1}, 1455 cm^{-1} and 1360 cm^{-1} and ^1H n.m.r. absorption at δ ($CDCl_3$) 5·2–5·8 (3H.complex), 1·8–2·6 (4H,complex) and 1·0–1·8 (14H,complex). From these spectral data, the photoproduct was assigned to 3-nitrocyclododec-1-ene, in agreement with earlier observations. No trace of 2-hydroxyiminocyclododecanone, derived from an initial nitro-to-nitrite rearrangement was observed in this photoreaction. Although this oximinoketone is photochemically active[256], under the conditions of this photoreaction it will be stable and if formed should be detectable.

The stereochemistry of the photoproduct was examined by I.R. and n.m.r. The presence, in the I.R. spectrum, of a strong peak at 970 cm^{-1} is in agreement with the C-H out of plane deformation of olefinic protons in an <u>E</u>- substituted alkene. The corresponding peak for the <u>Z</u>-isomer should lie in the range 730–665 cm^{-1}, but in the photoproduct no peak was observed in this range. It has been reported that the <u>E</u> and <u>Z</u>-isomers of cyclododecene are of equal stability[257], but consultation of molecular models of 3-nitrocyclododec-1-ene indicates that the <u>E</u>-isomer suffers less steric interactions than the <u>Z</u>-isomer. The photoproduct should be



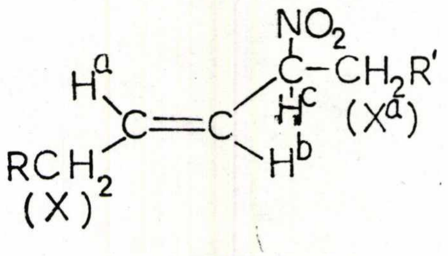


E

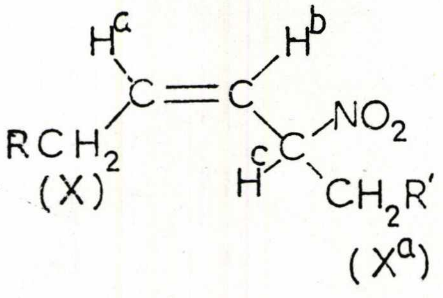
Z

predominantly E, which is confirmed by the I.R. spectrum.

The ^1H n.m.r. spectrum was studied to measure the coupling constants of the olefinic protons in the region 5•2-5•8 δ. The splitting pattern is extremely complex, being due to several effects. Firstly the chemical shifts for the olefinic protons and the proton on the carbon bearing the nitro group are similar in value. Secondly the β, γ -unsaturated nitro compound, whether it is E or Z, will have a three proton coupled system and due to the closeness of the chemical shifts, second order effects will be in operation leading to an ABC type spectrum, which will be further coupled to the protons X and X^a in the diagram below. These types of systems give very complex n.m.r. spectra and no first order analysis can be attempted. From a study of the recorded n.m.r. spectra of analogous nitroalkenes[227,254,255], the olefinic protons absorb in the range 5•08-5•9 δ whilst the proton on the carbon bearing the nitro group absorb in the range 4•8-5•15 δ. Hence the overlapping of the two sets of signals is not unexpected. In an attempt to simplify the spectrum a spin decoupling experiment was performed. Irradiation at the absorption frequencies of the



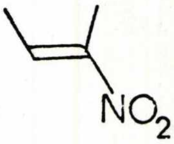
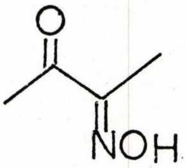
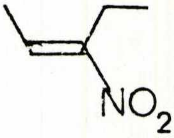
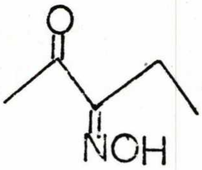
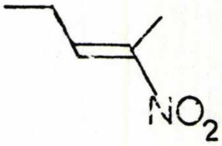
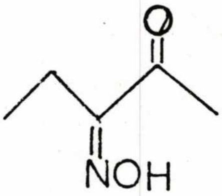
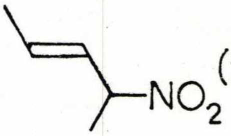
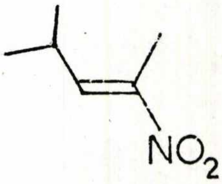
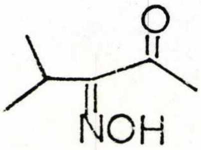
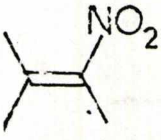
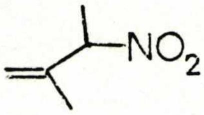
E

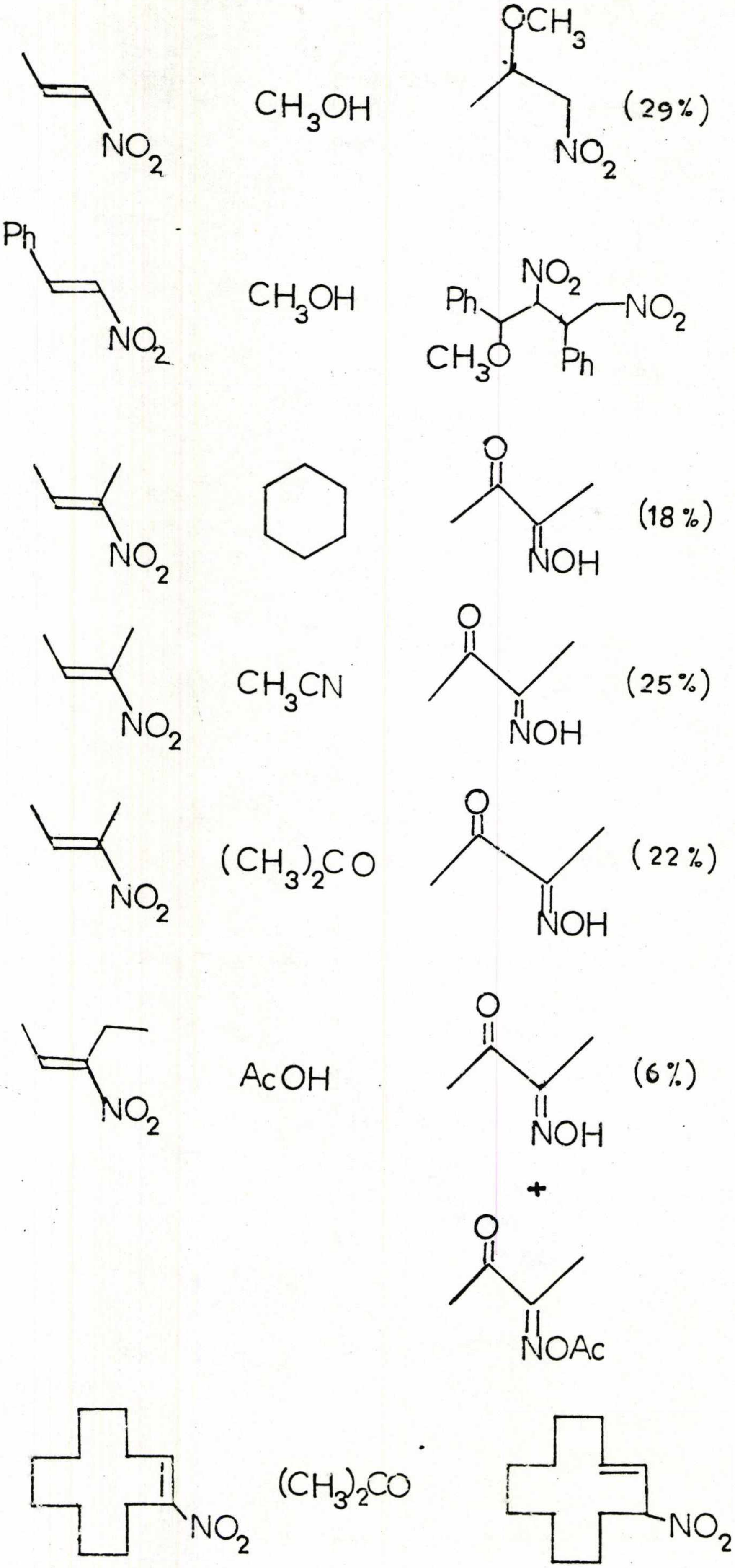


Z

protons X and X^a, which absorb in the region 1·8–2·6 δ, removed their coupling effects, but this still left an ABC pattern. These systems have been analysed[254,255] but are extremely complex. It was therefore concluded that no useful results concerning the stereochemistry of the product could be obtained from this n.m.r. spectrum.

The results of the irradiations are summarised in the table below:

Nitroalkene	Solvent	Products isolated
	CH_3OH	 (27%)
	CH_3OH	 (31%)
	CH_3OH	 (4%)  (15%)
	CH_3OH	 (5%)
	CH_3OH	

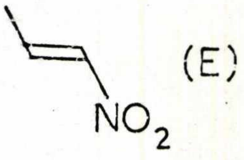
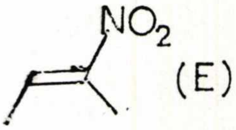
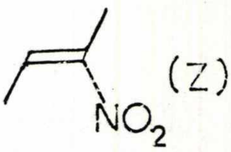
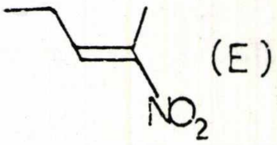
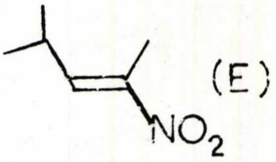
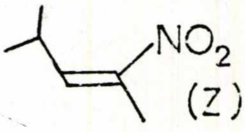
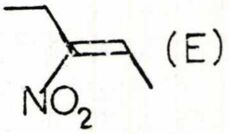
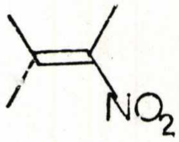

CH3OH
(29%)
CH3OH
(18%)
CH3CN
(25%)
(CH3)2CO
(22%)
AcOH
(6%)
+
(CH3)2CO

The formation of oximinoketones in non-aryl nitroalkenes has not been observed previously. The mechanism of their formation is an aliphatic analogue of the nitro-to-nitrite rearrangement, initially postulated by Chapman to explain the photochemistry of nitrostyrenes[154,155]. This mechanism has to take into account the rapid E-Z isomerization of these α,β-nitroalkenes. Chapman concluded from studies on nitroaromatics and nitroalkenes that an initial nitro-to-nitrite rearrangement is favoured when the nitro group is twisted out of conjugation with the system[167]. A method of estimating the extent of twisting of the nitro group out of conjugation with the double bond in α,β-nitroalkenes has been developed[227], by relating the dihedral angle of the nitroalkene to the ε value of each nitroalkene, as shown on page 67.

The dihedral angle of the E- and Z-isomers of 3-nitrobut-2-ene, were found to be 36° and 44° respectively. These values represent the amount the nitro group is twisted out of conjugation with the π system. It is obvious that the Z-isomer, with the nitro and methyl groups cis to each other is under greater steric constraints than the E-isomer. However, the difference between these figures is not very great and provides justification for assuming both the E and Z-isomers undergo the nitro-to-nitrite rearrangement.

Similar arguments can be used for all the nitroalkenes studied, where an oximinoketone was formed. In the case of 3-nitropent-3-ene, no values for the dihedral angle have been reported but calculations show that for the E-isomer, the dihedral angle is about 39-40° .

Cridland attempted to correlate the yields of α,β-unsaturated ketones, which result from an initial nitro-to -nitrite rearrangement, in the photochemical reactions of steriodal nitroalkenes, to the dihedral angle of the starting material, and concluded that the greater the dihedral angle the greater the yield of photoproduct[184]. In this case the yield of oximinoketone can be compared with the dihedral angle of the starting nitroalkene and the results are shown in the table below;

Nitroalkene	Dihedral angle	Yield of oximino-ketone
 (E)	0°	0[a]
 (E)	36°	27%
 (Z)	44°	
 (E)	37°	4%[b]
 (E)	33°	5%[b]
 (Z)	43°	
 (E)	40°	31%
	40°	0%[a,b]

Notes:

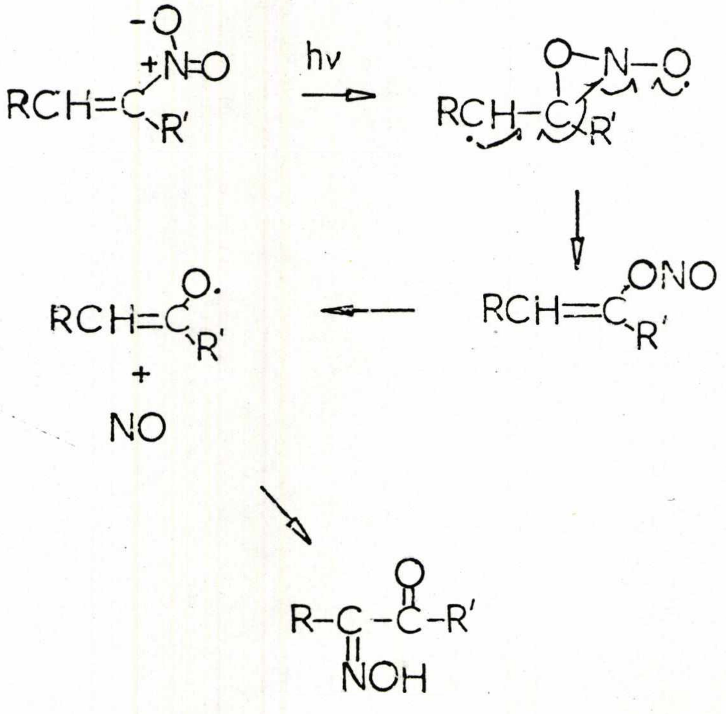
a No products resulting from an initial nitro-to-nitrite rearrangement were isolated.

b Photochemical deconjugation is a competing pathway.

It is difficult to draw many conclusions from these results, as some compounds have a competing reaction pathway open to them, but one can conclude that for nitroalkenes whose major reaction pathway is oximinoketone formation, the greater the dihedral angle the greater the yield of oximinoketone, which is in complete agreement with the work of Chapman and Cridland.

The choice of solvent was found not to be very important. The better results obtained using polar solvents may be due to the oximinoketone being more soluble in these solvents and hence tar formation being kept to a minimum, rather than any solvent stabilization or destabilization of an intermediate excited state or radical.

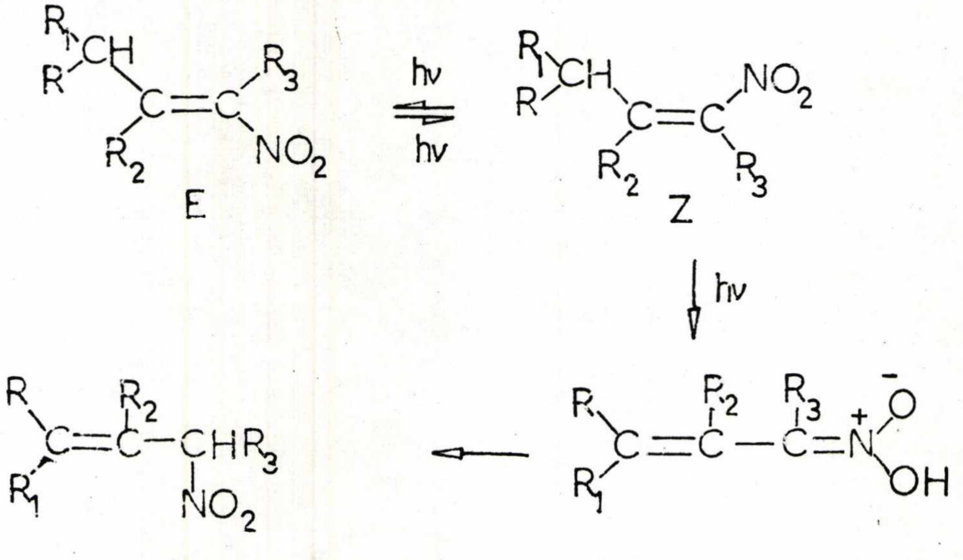
The nitro-to-nitrite rearrangement postulated by Chapman involves an intramolecular attack by the excited nitro group on the olefin system to give an oxiridine intermediate, which then collapses to the nitrite.



This nitrite then breaks down to a radical and nitric oxide. This decomposition may be thermal as unsaturated nitrites have been postulated to be intermediates in the preparation of oximinoketones by the action of alkyl nitrites on ketones, which decompose thermally to give oximinoketones [258,259].

The failure of previous workers[163] to isolate any oximinoketones as reaction products can be attributed to their purification procedure, in which they distilled the crude product. This procedure has now been found to lead to decomposition of the oximinoketone. However, their failure to observe significant decomposition of the nitroalkene and to observe the formation of products by g.l.c. cannot easily be explained.

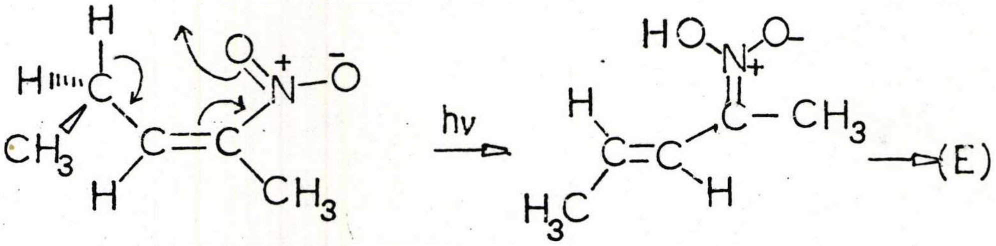
The photochemical formation of β, γ -unsaturated nitroalkenes from α , β -unsaturated nitroalkenes has been noted previously[163]. These results show this rearrangement becomes most facile when R and R_1 are alkyl and least facile when R and R_1 are hydrogen, and it is the Z-isomer which is responsible for the deconjugation reaction. The generally accepted mechanism for this deconjugation reaction is the intramolecular γ-hydrogen abstraction by the Z-isomer followed by rearrangement of the aci-nitro isomer to the nitroalkene[188,189]. This mechanism is analogous to the similar deconjugation reactions of α , β -unsaturated esters[260], ketones[261] and acids[262].



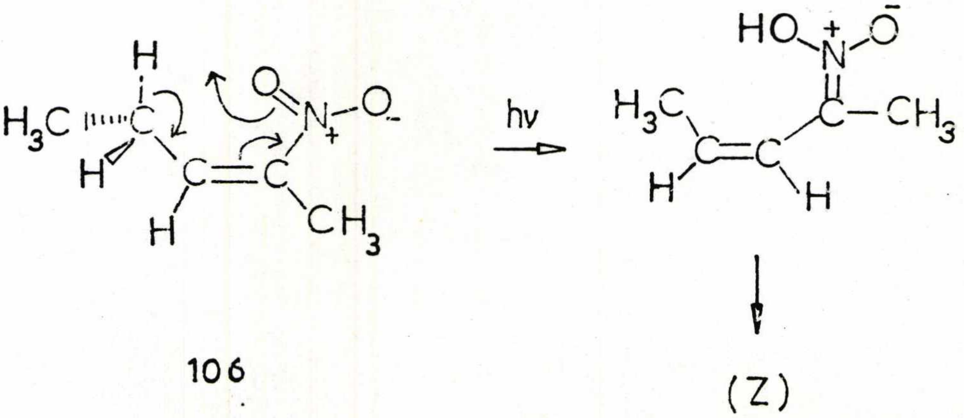
The sample of 4-nitropent-2-ene isolated from the irradiation of

3-nitropent-2-ene was found to be the E-isomer. If any Z-isomer was present it would have been detected. This is not considered unusual as α,β-unsaturated esters[260a] and ketones[261a] give only one isomer of the deconjugated product, also Decotes[227] reports only one example of photochemical deconjugation of α,β-nitroalkenes where a mixture of E- and Z-isomers of the β,γ-nitroalkene is formed.

The reason for the formation of only one isomer of the photoproduct may lie in the stabilities of the various transition states. The transition state arising from (105) has less steric hindrance than the transition



105

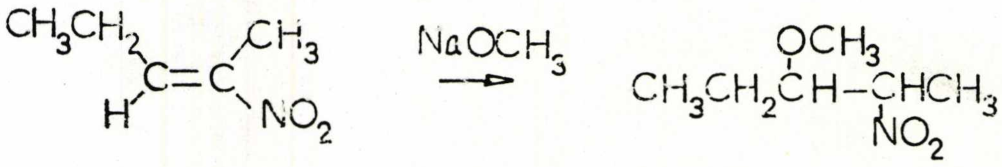


106

state from (106) and as the conversion of (106) to (105) involves only a rotation about a carbon-carbon bond very little energy is required, hence the interconversion of (106) to (105) is energetically easy.

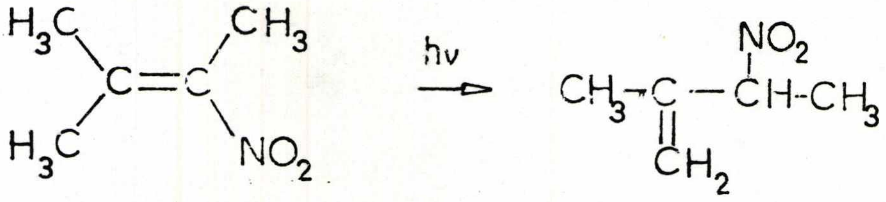
An alternative explanation involves the intermediate *aci*-nitro structure undergoing carbon-carbon bond rotation in its conversion to the nitro compound to give the less sterically hindered isomer. If this second explanation is correct then the formation of an *aci*-nitro structure by another route should result in the formation of the most stable isomer of the resulting β , γ -nitroalkene. The conversion of α , β - to β , γ - nitroalkenes by the action of base *via* an *aci*-nitro intermediate is known[263]. In the case of aliphatic nitroalkenes the systems studied have had both the *E*- and *Z*-isomers of the product identical[237,263,265] or else the product was not identified[264]. In the case of steriodal nitroalkenes the rigid ring system only allows the formation of one isomer of the deconjugated product[266,267,268,269]. The thermal conversion of α , β -nitroalkenes to the β , γ - derivatives *via* an *aci*-nitro intermediate has been reported[163,241]. In every case the least sterically strained isomer was obtained. This constitutes some evidence for the *aci*-nitro structure rearranging to the more stable β , γ -isomer.

In an attempt to generate the β , γ -nitroalkene *via* the *aci*-nitro structure and observe its structure, 3-nitropent-2-ene was treated with sodium hydroxide according to the method of Shechter[263] but on careful acidification only starting material was obtained. Refluxing in excess sodium methoxide failed to cause any isomerization, 3-methoxy - 2-nitropentane (107) being isolated. No definite conclusions concerning the reason why only one isomer of the photoproduct is obtained can be drawn.



107

The formation of 2-methyl-3-nitrobut-1-ene from 3-methyl-2-nitrobut-2-ene is unusual as there are methyl (primary) hydrogens on the γ -carbon atom, but in this case the nitro-to-nitrite rearrangement cannot lead to a stable oximinoketone product and this may cause the deconjugation reaction to become more important. This deconjugation reaction may also be helped by relieving steric interactions in the starting material that are not relieved by E-Z interconversion.



Nitrocyclododecene gives upon irradiation the deconjugated isomer. The n.m.r. spectrum of the photoproduct was too complex to allow any conclusions to be drawn, but the I.R. spectrum indicates that the product is the E-isomer, which is in agreement with previous results.

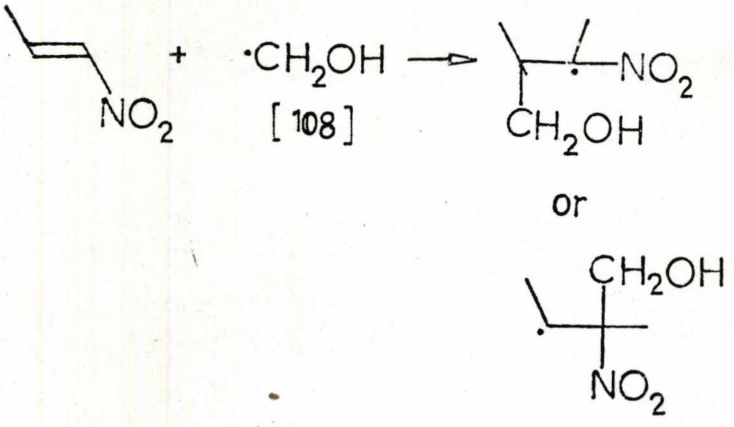
Attempts were made to generate the β , γ -unsaturated nitroalkene by the action of base on 1-nitrocyclododec-1-ene. Treatment with triethylamine or sodium hydroxide or sodium methoxide, however, failed to cause any double bond migration, only starting material being obtained.

The photoaddition of alcohols to nitroalkenes is not a well known reaction. The photoaddition of methanol to nitrocyclohexene to give Trans-2-methoxy-1-nitrocyclohexane has been reported[184,189]. The thermal[270] and base catalysed[235,236,245,246,247] addition of alcohols to nitroalkenes on the other hand is a well known reaction.

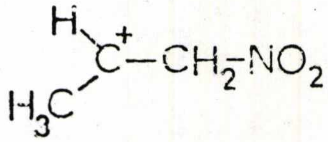
The isolation of 2-methoxy-3-nitropropane and 1-methoxy-2,4-dinitro

-1,3-diphenylethane from the irradiation of 1-nitropropene and β-nitrostyrene in methanol respectively is analogous to the addition of alcohols to unsaturated acids[271], allyl ethers[272] and alcohols[273] and alkenes[274].

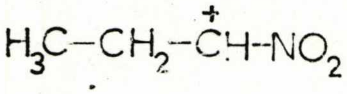
The isolation of a methoxy derivative indicates that the addition is ionic rather than radical in nature. Radical species (108) would be expected to be the most stable radical derived from methanol[275] and radical addition would give a hydroxy nitro compound by analogy with previous work[276,277].



The ionic addition of alcohols to alkenes is postulated to involve an initial protonation to give the most stable carbonium ion and subsequent addition of methanol to give the adduct[277,278,279]. This mechanism explains the observed products for nitroalkenes. The most stable carbonium ion derived from 1-nitroprop-1-ene is (109) rather than (110) and addition of methanol to (109) gives the observed product.



[110]



$H_3C-CH_2-\overset{+}{C}H-NO_2$

[109]

This mechanism explains why only the trans isomer of 2-methoxy-1-nitrocyclohexene was obtained; the intermediate carbonium ion reacts with methanol to give the most stable product. A similar mechanism explains the formation of the methanol adduct when 1-nitroprop-1-ene is refluxed in methanol.

The origin of the proton required for the initial protonation is not however clear. The methanol used in this study may be acidic enough to cause this reaction to occur or else acidic by-products of another photoreaction may be causing this reaction to occur.

No products resulting from an initial nitro-to-nitrite rearrangement were observed. This is in agreement with the postulated mechanism. 1-Nitroprop-1-ene and β-nitrostyrene are planar[227] and as twisting of the nitro group out of the plane of conjugation increases the chances of the nitro-to-nitrite rearrangement occurring, a planar nitroalkene is not expected to undergo this rearrangement.

Chapman[155,167] has suggested that evidence for the nitro-to-nitrite rearrangement in nitroaromatics and nitroalkenes comes from a study of the mass spectra of these compounds. The observation that there is a strong peak at M-30 is attributed to an intramolecular nitro-to-nitrite rearrangement and subsequent breakdown of the unsaturated nitrite. Kiturra and Matsuura however found no such correlation in a series of substituted nitroaromatics[12].

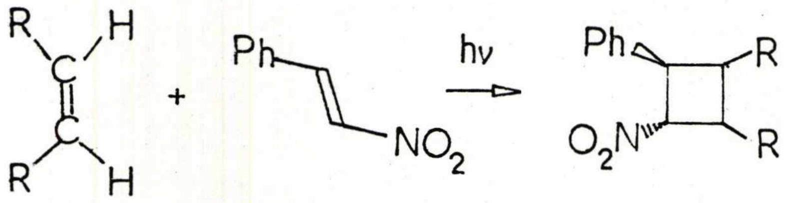
The mass spectra of the nitroalkenes used in this study were determined but no peak at M-30 was observed. The major peak was at M-46, corresponding to loss of NO_2, below this one gets hydrocarbon fragments of little structural value. This is in complete agreement with the work of Taylor[148].

Summary of results.

Aliphatic α,β-nitroalkenes have been shown to undergo a photoinduced nitro-to-nitrite rearrangement in a variety of solvents, when steric interactions push the nitro group out of conjugation with the double bond. Nitroalkenes with a secondary or tertiary hydrogen at the γ-carbon from the nitro group undergo a hydrogen abstraction reaction, which competes with the nitro-to-nitrite rearrangement. Planar nitroalkenes do not undergo the nitro-to-nitrite rearrangement but do undergo photoaddition of methanol, when this is used as the solvent.

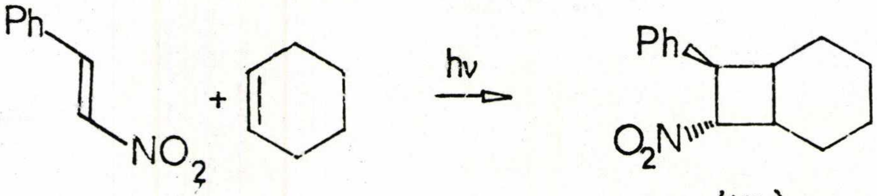
(3) Photoaddition reactions of nitroalkenes.

The photochemical addition of α, β-unsaturated ketones to alkenes is well known[284-289] and has been the subject of several review articles [280-283]. Chapman[154] in a preliminary communication has reported that trans- β-nitrostyrene can be photochemically added to alkenes to give nitrocyclobutanes, whilst Hoganson[197] has added more details about this photoreaction. Trans- β-nitrostyrene undergoes photoaddition to



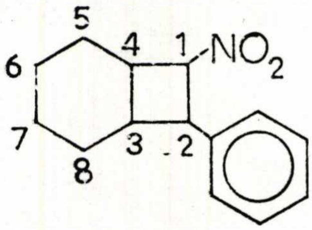
cyclohexene and styrene to give two isomers of the nitrocyclobutane product in each case. Similar cyclobutane derivatives were obtained from cyclopentene, 1,1-diphenylethylene and tetramethylethylene but here only one isomer of the product was isolated[154], and was used by Chapman to argue that the two isomers obtained in the case of cyclohexene and styrene are the result of cis- and trans- fused rings. Hoganson[197] has shown that trans- β-nitrostyrene can also be added to 1,1-diphenylethylene, stilbene, 2-methylprop-1-ene, 2,3-dimethylbutadiene and butadiene. All the photoaddition products are the result of 1,2 additions and when an asymmetrical alkene is used, the resulting adduct has the most nucleophilic carbon attached to the alpha position of the β-nitrostyrene. This is attributed to the nitrostyrene acting as an electrophilic species. Each photoproduct has the phenyl and nitro groups trans to each other. This regiospecificity was attributed to the β-nitrostyrene adding in a trans- manner. To see if this photoreaction could be extended to a more varied range of alkenes and to different nitroalkenes, this photoreaction was investigated.

Trans- β -nitrostyrene was found not to be very soluble in cyclohexene and hence a co-solvent was used. The photoaddition of trans- β -nitrostyrene to cyclohexene was studied in order to obtain the optimum conditions for the photoaddition reaction. The irradiation of β-nitrostyrene and cyclohexene (molar ratio 1:16) in methanol, using pyrex filtered light, was followed by I.R. and the reaction continued until no nitrostyrene could be detected. The solvent was removed to give a brown oil which was distilled under reduced pressure. The I.R. spectrum of the distillate showed absorption at 1535 cm^{-1} and 1360 cm^{-1} (saturated nitro group) and ^{1}H n.m.r. had signals at δ ($CDCl_3$) 7·6 (10H, singlet), 5·3 (0·6H, multiplet) 4·75 (1·4H, multiplet), 4·3 (1·4H, multiplet), 3·9 (0·6H, multiplet) and 1·2-2·2 (20H, complex). These spectra are in agreement with the distillate being the adduct 7-nitro-8-phenylbicyclo(4.2.0)octane (111), reported by Chapman[154] and was a mixture of isomers formed in unequal proportions (67:33). Further evidence for two isomers being present was obtained from g.l.c. and ^{13}C n.m.r. studies. The adduct had two unequal sized peaks in the g.l.c. trace. The ^{13}C n.m.r. spectrum of the adduct is complex (shown overleaf) but signals at 85·42 and 80·32 p.p.m. from T.M.S. are in the range expected for a carbon bearing a nitro group[290]. The occurrence of two signals is in agreement with two isomers being present.



(111)

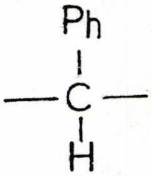
^{13}C n.m.r. spectrum of mixture of isomers of (111)

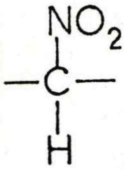


[111]

p.p.m. from T.M.S.	assignment
139·42	Phenyl carbons
137·48	
129·22	
128·62	
127·16	
126·8	
126·5	
85·42	C^1
80.32	
53·75	C^2, C^3; C^4, C^5, C^6, C^7, C^8.
47·44	
46·59	
41.62	
37.23	
30.82	
30.45	
29.24	
25·96	
25·36	
24·38	
22·81	
22·44	
21·96	

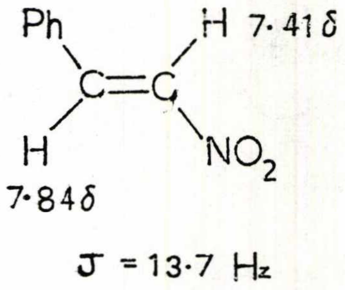
Chapman concluded that the phenyl and nitro groups are *trans* in these cyclobutane adducts[154]. The ^{1}H n.m.r. spectra of a series of nitrocyclobutanes derived from the photodimer of *trans*-β-nitrostyrene have the following ranges when the phenyl and nitro groups are *trans*.[153]


($CDCl_3$) 4·74–6·18δ

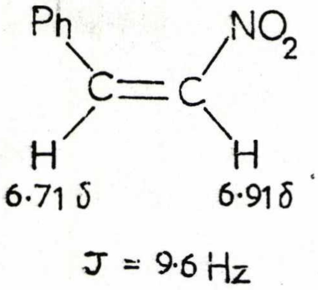

($CDCl_3$) 5·12–6·12δ

The ^{1}H n.m.r. spectrum of the adduct (111) is very complex as it is an ABX_2 system with overlapping due to the two isomers. The relevant chemical shift and integration values for the isomeric adducts are reported above. The absorptions at 5·3δ and 4·75δ were assigned to the proton on the carbon bearing the nitro group and the absorptions at 4·3δ and 5·9δ were assigned to the proton on the carbon bearing the phenyl group. Comparison of these figures with the ranges shown above indicate that the phenyl and nitro groups are *trans* to each other.

The photochemical conversion of the *trans* isomer into the *cis*-isomer has been reported[153,151,150]. To investigate if *trans*-β-nitrostyrene undergoes *trans*-*cis* isomerization under the conditions used for this photoreaction, *trans*-β-nitrostyrene was irradiated in methyl cyanide in the absence of cyclohexene for the same period of time and under exactly the same conditions as those used to obtain the adduct. The solvent was removed and the residue was examined by I.R. and ^{1}H n.m.r. spectroscopy. The I.R. spectrum of the *cis*-isomer has been reported to have absorption at 805 cm^{-1} [150]; this was absent in the I.R. spectrum of these residues. The reported ^{1}H n.m.r. spectra of the *cis* and *trans*-isomers are shown below[161]. Examination of the ^{1}H n.m.r. spectrum of the residues showed there to be very little (less than 5 %) of the *cis*-isomer present. Irradiation in methanol under similar conditions (pyrex filter) has already been shown not to cause any *trans*-*cis* interconversion. From these results it can be concluded that the trans-isomer undergoes the photoaddition

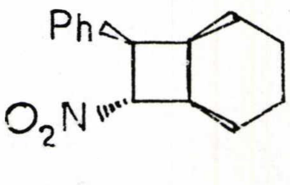


Trans

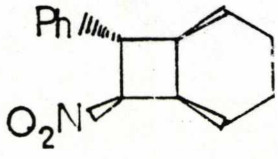


Cis

reaction. If the photoaddition reaction is concerted, this will lead to the phenyl and nitro groups being trans in the cyclobutane adduct. If the photoaddition reaction involves a diradical intermediate, loss of stereochemistry is possible, although trans will be prefered to cis on steric grounds. Chapman[154] explained the formation of two isomers of this adduct by postulating cis and trans ring fusion of the two rings. However, filtration through alumina or silica gel failed to cause any isomerization of either of the two adducts, the occurrence of a trans ring fusion must be considered unlikely, as this should rearrange to the more stable cis ring fusion under these conditions, a process for which there is precedent in the literature[286]. The only two isomers of the bicyclo adduct which have the phenyl and nitro groups trans to each other with the cis ring fusion are (111a) and (111b).



111 a



111 b

The effect of varying the solvent and the ratio of alkene to β-nitrostyrene was investigated. The results are summarized in the table below. From these results it is obvious that the more cyclohexene present, the better the yields and that the solvent used has little effect on the photoreaction. It was concluded therefore that the best conditions for the solvents studied are use of a molar ratio of 1:16 or 1:8 with methanol or methyl cyanide as the solvent.

Solvent	Molar Ratio of β-nitrostyrene to cyclohexene	Percentage yield adduct
Methanol	1:16	78
Methanol	1:8	63
Methanol	1:4	38
Methyl cyanide	1:8	65
Methyl cyanide	1:4	29
Benzene	1:8	48(a)

(a) brown polymer deposited on probe during course of irradiation.

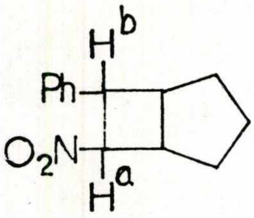
The effect of these changes in concentration and solvent upon the ratio of isomers formed was investigated by ^{13}C and ^{1}H n.m.r. The results are presented in the table below. From these results it is obvious that the ratio is constant in every case investigated and it is concluded that these variations in molar concentrations and solvent have no effect on the ratio of isomer formation.

Experiment	Ratio of peak heights ((^{13}C) of major to minor isomers.	Ratio of areas (^{1}H) of major to minor isomers.	Relative proportions Minor	Relative proportions Major
1:16 Methanol	2·1:1	2·3:1	32 %	68 %
1:8 Methanol	2:1	2·3:1	33 %	67 %
1:4 Methanol	2:1	2·3:1	33 %	67 %
1:8 Methyl cyanide	2:1	2·3:1	33 %	67 %
1:8 Benzene	2:1	2·3:1	33 %	67 %

To establish that this addition is in fact photochemical and not thermal, β-nitrostyrene was refluxed in cyclohexene and methanol for forty hours. No reaction was observed.

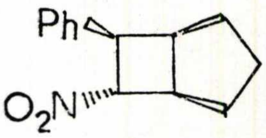
The separation of the two isomeric cycloadducts was attempted. Column chromatography (silica gel) and repeated t.l.c. failed to separate the two isomers. No equilibration of the two isomers in the course of the chromatographies was noted by ^{1}H n.m.r.. The isomeric adducts were stable to dilute acid and base, and acetal formation[291].

Only one isomeric adduct was isolated from the photoaddition of trans-β-nitrostyrene to cyclopentene by Chapman[154]. To confirm this observation, trans-β-nitrostyrene and cyclopentene (molar ratio 1:16) were irradiated in methanol until no more nitrostyrene could be detected. Distillation gave a 81 % yield of the adduct 6-nitro-7-phenylbicyclo (3.2.0)heptane (112), which had ν max 2930 cm^{-1}, 1530 cm^{-1} and 1360 cm^{-1} and n.m.r. absorption at δ ($CDCl_3$) 7·5(10H, multiplet), 5·0 (2H, multiplet), 4·5 (1·6H, multiplet), 3·9 (0·4H, multiplet), 3·4 (2H, multiplet) and 1·3–2·0 (12H, complex).

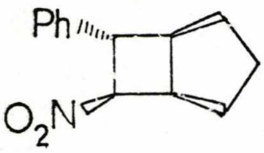


(112)

Evidence was found for the presence of two isomers. The absorption at 5·0 δ is assigned to H^a, with the two isomers overlapping whilst the absorptions at 4·5 and 3·9 δ are assigned to H^b in the two isomers. This shows the relative proportions of the two isomers present (80:20). The ^{1}H n.m.r. spectra of the adduct before and after distillation were identical which rules out a concentration of a lower boiling isomer in the distillate. The initial observation[154] is incorrect, but as the isomer ratio is 80:20, one isomer is being formed predominantly. By analogy with the previous work, the structures were considered to be (112a) and (112b) Attempts to separate these two isomers by chromatography failed.



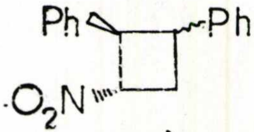
(112a)



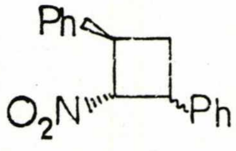
(112b)

The photoaddition of trans- β -nitrostyrene to styrene to give two isomeric adducts has been reported[154]. Irradiation of trans- β -nitrostyrene and styrene (molar ratio 1:16) in methanol gave a 65 % yield of an adduct after distillation. This adduct had a correct elemental analysis for a 1:1 adduct and had ν max 1540 cm^{-1} and 1360 cm^{-1} and ^1H n.m.r. absorption at δ ($CDCl_3$) 7·7 (20H, multiplet), 5·8 (0·8H, quartet), 5·25 (1·2H, quartet), 4·8 (0·8H, triplet), 4·4 (1·2H, triplet) and 2·7-3·7 (6H, complex). The ^{13}C n.m.r. spectrum indicated that there were two isomers present, as there were double the expected number of signals present. From the ^1H n.m.r. spectrum the isomer ratio was calculated to be 45:55.

There are two possible regioisomers, either 2,3-diphenyl-1-nitrocyclo butane (113) or 2,4-diphenyl-1-nitrocyclobutane (114). Chapman[154] claimed that adduct (113) is obtained. A study of the ^1H n.m.r. spectrum of the mixture neither confirms or repudiates this claim, due to second order



(113)

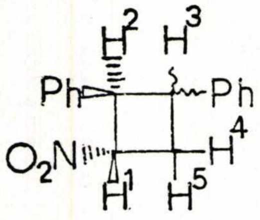


(114)

effects.

A solution of the mixture in petrol was filtered through silica gel which gave an oil, out of which a solid slowly crystalised. The solid was separated from the oil. A study of their respective n.m.r. spectra showed that they were the two isomers. The oil had δ ($CDCl_3$) 7·7(10H, multiplet), 5·25 (1H, quartet), 4·4 (1H, triplet) and 2·7-3·7 (3H, complex), whilst the solid isomer after recrystalization from petrol melted at 104-105 °C and had δ ($CDCl_3$) 7·7 (10H, multiplet), 5·8 (1H, quartet), 4·8 (1H, triplet) and 2·7-3·7 (3H, complex).

These two isomers were then examined by ^{13}C and 100MHz ^1H n.m.r. using spin decoupling techniques. The ^{13}C n.m.r. spectra of both the solid and the oil, as shown below, showed there was only one isomer present in each case, as only the required numbers of signals was present. The 100 MHz ^1H n.m.r. spectra of both isomers were in complete agreement with the values obtained above. The solid isomer had absorption at 5·8 δ (quartet) and 4·8 δ (triplet), by analogy with previous examples these were assigned to H^1 and H^2 respectively. Absorption at 4·0 δ was found to be a triplet, each peak being further split into a doublet and was assigned to H^3. Irradiation at the absorption frequency of H^1



(113)

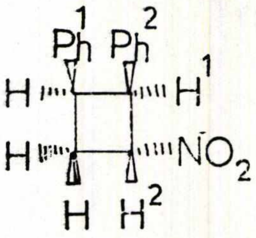
^{13}C n.m.r. spectra of the styrene adduct.

Liquid isomer p.p.m. from T.M.S.	Assignment	Solid isomer p.p.m. from T.M.S.
128·86	Phenyl carbons	128·13
128·37		127·4
128·13		126·92
127·65		126·68
127·28		
126·8		
126·55		
79·11	C^2	79·35
53·99	C^1, C^3, C^4	50·47
38·95		39·31
32·64		30·21

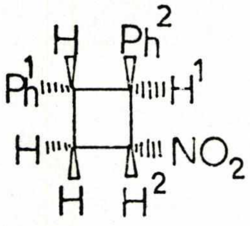
had no effect on the absorption due to H^3, whilst that of H^2 collapsed to a doublet. Irradiation at the absorption frequency of H^2 caused the absorption due to H^1 to become a triplet whilst irradiation at the absorption frequency of H^3 had no effect on the absorption due to H^1. Irradiation at the absorption frequency of H^4 and H^5 caused H^1 to become a doublet whilst H^2 was unaffected. The only regioisomer which satisfies these results is (113). Analogous results were obtained for spin decoupling experiments on the liquid isomer. Irradiation at the absorption frequency of H^1 caused H^2 to become a doublet and had no effect on H^3, whilst irradiation of H^2 caused both H^1 and H^3 to become triplets. The closeness of the other chemical shifts meant that further spin decoupling experiments were not possible. The only regioisomer which satisfies these results is (113). These results show that the solid and liquid are stereoisomers of (113).

These results confirm the structure proposed by Chapman. An attempt was made to determine the relative configuration at the carbon bearing H^3. The two possible isomers are shown below. By a study of molecular models, (115) will have H^1 deshielded strongly by Ph^1 and to a lesser extent by

Ph^2. For isomer (116), H^1 will be deshielded by Ph^1 and to a much lesser



(115)

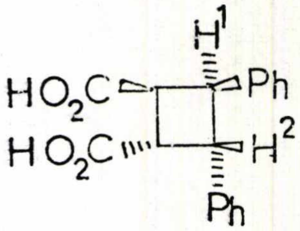


(116)

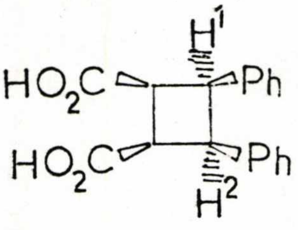
extent by Ph^2, whilst H^2 will be deshielded by Ph^1 and to a much lesser extent by Ph^2. Hence one would expect H^1 and H^2 to be at lower field values in (115) when compared to (116). The solid isomer obtained in this study has absorption for H^1 and H^2 at lower field values than the corresponding absorptions in the liquid isomer. Hence the solid isomer is (115) and the liquid isomer is (116).

This approach is open to question. Firstly the deshielding effects are estimations of the average values and may be incorrect due to secondary steric effects not being taken into account. Secondly the shielding and deshielding effects of the nitro group have not been taken into account, but these should cause little change in the chemical shift values[292,293].

Another approach to this problem involves comparing the ^1H n.m.r. spectra with published values. The coupling constant values for vicinal <u>cis</u> and <u>trans</u> protons in cyclobutanes can vary widely[294]. If systems (117) and (118) are used as models for the two isomers of the photoproduct, $J_{1,2}$(<u>trans</u>) = 4 Hz whilst $J_{1,2}$(<u>cis</u>) = 10 Hz [295]. The values of $J_{1,2}$ for both isomers of the photoproduct were found, by means of the decoupling experiments to be 5 Hz for the solid isomer and 10 Hz for the liquid isomer. This means the solid isomer has a <u>trans</u> structure (116) and the liquid has a cis structure (115).



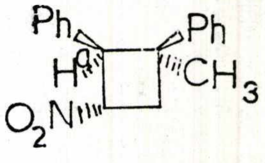
(117)



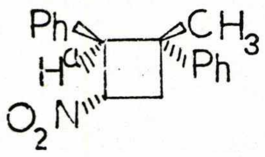
(118)

This is in complete disagreement with the previous assignment. This approach is open to question, as $J_{1,2}$ (cis) and $J_{1,2}$ (trans) can vary widely and not enough data on cyclobutanes exists for accurate analysis[294]. The assignment of relative configuration on the basis of coupling constants must be treated with caution in this case. The use of molecular models is of more use in assigning relative configuration in this case. It is suggested that the solid isomer is (115) and the liquid isomer is (116).

Following the successful isolation of the two isomers of the styrene adduct, the α-methylstyrene adduct was prepared. This adduct has not been described previously and was prepared by irradiating trans-β-nitro styrene and α-methylstyrene (molar ratio 1:16) in methanol until no β-nitrostyrene could be detected. The solvent was removed and the resulting oil was distilled to give an oil, in 81 % yield, which gave a satisfactory elemental analysis for a 1:1 adduct and had ν max 1535 cm^{-1} and 1360 cm^{-1} (saturated nitro group) and δ ($CDCl_3$) 6•9-7•7 (20H, complex), 5•5 (2H, complex), 4•6 (0•8H, doublet), 4•3 (1•2H, doublet), 2•7-3•7 (4H,complex), 1•8 (3H, singlet) and 1•3 (3H, singlet). By analogy with the styrene case the adduct is considered to be a mixture of isomers of 2,3-diphenyl-3-methyl-1-nitrocyclobutane (119a) and (119b). Proof of this was forthcoming from a study of the ^1H n.m.r. spectrum. The absorptions at 4•6 and 4•3 δ were assigned to H^a in the two isomers. In both cases the absorption is a doublet as expected for regioisomers (119a) and (119b) any other regioisomers would have a more complex splitting pattern.



[119a]



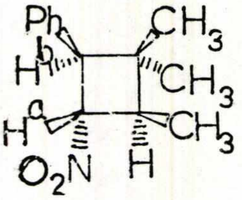
[119b]

Filtering the adduct through silica gel caused no change in the ^1H n.m.r. spectrum, indicating that no isomerization had occurred. Attempts to separate the isomers were unsuccessful.

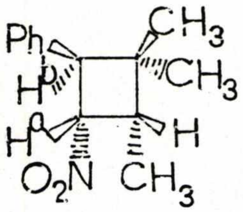
By analogy with the styrene case, (119a) and (119b) would be expected to have ^1H n.m.r. absorption due to H^a at 4·8 δ and 4·4 δ respectively. The actual experimental values were 4·6 δ and 4·3 δ, indicating that this method of assigning stereochemistry of cyclobutanes is of value. These results indicate that (119b) is formed in greater amounts than (119a), in the photoaddition reaction, a point to be considered in more detail later.

The addition of 3-methylbut-2-ene to β-nitrostyrene was studied to allow a simple determination of the mode of addition. A mixture of trans-β-nitrostyrene and the alkene (molar ratio 1:16) was irradiated in methanol until no nitrostyrene could be detected. Removal of the solvent and distillation gave in 65 % yield, a liquid with the correct elemental analysis for a 1:1 adduct and with ν max 1535 cm^{-1} and 1360 cm^{-1} (saturated nitro group) and δ ($CDCl_3$) 7·6(10H, multiplet), 5·5 (0·4H, triplet), 4·9 (1·6H, triplet), 4·2 (0·4H, doublet), 3·85 (1·6H, doublet), 2·4-3·3 (2H, complex), 1·35 (6H, singlet), 1·2 (4.75H, singlet), 1·1 (1·25H, singlet), 0·8 (1·25H, singlet) and 0·6 (4·75H, singlet).

From a study of the ^1H n.m.r. spectrum, the product was found to be the two stereoisomers of 1-nitro-4-phenyl-2,3,3-trimethylcyclobutane (120a) and (120b), formed in the ratio 20:80. The absorption due to H^b (4•2 and 3•85 δ) is a doublet, whilst H^a (5•5 and 4•9 δ) is complex, as expected for adducts (120a) and (120b). All attempts to separate the mixture of isomers failed.



[120a]

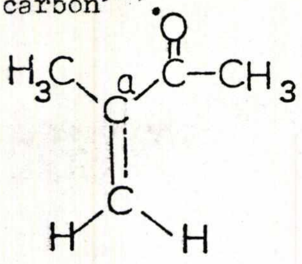


[120b]

Irradiation of trans-β- nitrostyrene and cyclododecene (molar ratio 1:6) in t-butyl alcohol gave a crude product with ν max 1535 and 1360 cm (saturated nitro group), which decomposed on distillation.

Hoganson[197] concluded that the nucleophilic carbon of the alkene attached itself to the α -position of the β -nitrostyrene which suggests that trans- β -nitrostyrene is acting as an electrophilic species. The results with styrene, α -methylstyrene and 3-methylbut-2-ene agree with this conclusion.

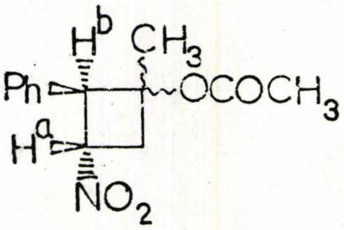
Following the successful addition of trans- β -nitrostyrene to a variety of simple alkenes it was decided to attempt to extend this work to functionally substituted alkenes. Isopropenyl acetate was chosen for this study. With isopropenyl acetate (121), it is not easy to decide which is the most nucleophilic carbon. The methyl group is electron donating and the acetate group electron withdrawing. There is also the back donation of electrons from the acetate which may reduce the electron withdrawing power of the acetate group. From these arguments, C^a is the most nucleophilic carbon^{327}.



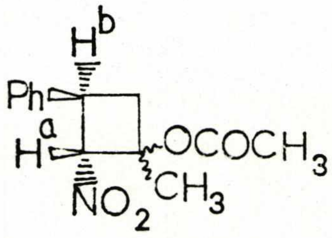
-121

Irradiation of trans- β -nitrostyrene and isopropenyl acetate (molar ratio 1:8) in methanol until no nitrostyrene could be detected, followed by removal of solvent and distillation of the resulting oil gave, in 63 % yield, a yellow oil which had the correct elemental analysis for a 1:1 adduct and had ν max 1740 cm^{-1} (ester), 1540 cm^{-1} and 1360 cm^{-1} (saturated nitro group) and δ (CDCl$_3$)7·3 (10H, singlet), 5·5 (1·5H, quartet) 5·15 (0.5H, quartet), 4·4 (0·5H, doublet), 4·05 (1·5H, doublet), 2·6–3·5 (4H, complex) 2·0(1·8H, singlet), 1·7 (4·2H, singlet), 1·6(4·2H, singlet) and 1·2 (1·8H, singlet).

A study of the ^{1}H n.m.r. spectrum indicates the adduct is amixture of isomers in the ratio 69:31. Irradiation in methyl cyanide gave a 58 % yield of the same adduct mixture with an isomer ratio of 67:33. The ^{13}C n.m.r. spectra of both samples (shown below) confirmed that mixtures of two isomers were present as both had double the number of expected signals. The adducts can be either (122) or (123). A 100 MHz study of the ^{1}H n.m.r.

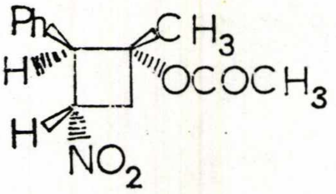


[122]

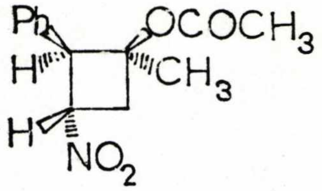


[123]

spectrum showed the peaks at 4•4 and 4•05 δ, assigned to H^b, by analogy with previous examples, [illegible] to be doublets whilst the peaks due to H^a (5•5 and 5•15 δ) were found to be quartets. Structure (122) is the only possible regioisomer to have this splitting pattern. The two isomers observed in this study are stereoisomers of 1-acetoxy-1-methyl-3-nitro-4-phenylcyclobutane (122). The adduct formed has the most nucleophilic carbon of the alkene attached to the a -position of the nitrostyrene and provides evidence for the usefulness of such a postulate.



[122a]

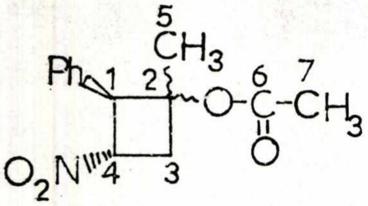


[122b]

An attempt to separate the two isomers by column chromatography failed and no isomerization of the isomers occurred. Use of base in an attempt to convert the acetate into the corresponding [illegible] nitroalcohol caused extensive decomposition. Use of milder basic conditions to stop a Nef reaction[296], led to the recovery of starting material. Attempts to convert the acetate to the nitroalcohol with acid and lithium aluminium hydride[297] were also unsuccessful. The adduct was thermally stable at 160 °C over six hours.

The photoaddition of trans- β -nitrostyrene to vinyl acetate was next studied. Irradiation of trans- β -nitrostyrene and vinyl acetate (molar ratio 1:8) in methanol until no nitrostyrene could be detected followed by removal of solvent and distillation led to an oil with ν max 1730 cm^{-1} (ester), 1540 cm^{-1}, 1360 cm^{-1} (saturated nitro group)

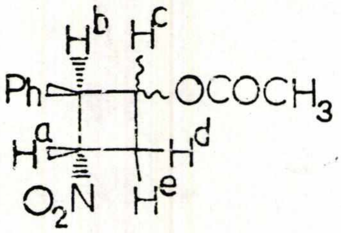
^{13}C n.m.r. spectrum of (122)



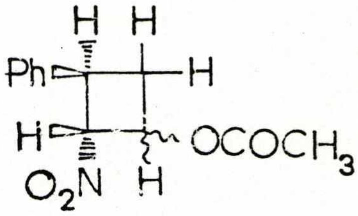
p.p.m. from T.M.S.	Assignment
169.63	C^6
134.44	Phenyl carbons
134.2	
132·02	
129·83	
129·22	
128·74	
128·37	
128·13	
127·77	
127·78	
78·62	C^2
76·93	
56·9	C^4
40·16	C^1, C^3, C^5
37·61	
24·75	
21·23	C^7
20·02	

and δ ($CDCl_3$) 7·5 (10H, singlet), 4-5·8 (6H, complex), 2·3-3·4 (4H, complex), 1·95 (3H, singlet) and 1·55(3H, singlet). From these spectra, it was concluded that the oil was the desired adduct with two isomers being present in equal amounts. On standing, a solid crystallized out of the oil. Recrystallization from ethyl acetate gave a solid melting at 101-103 °C, with the correct elemental analysis for a 1:1 adduct. It was concluded that the solid was one of the isomers mentioned above by a study of its ^1H n.m.r. spectrum which had absorption at δ ($CDCl_3$) 7·8 (5H, singlet), 5·6-6·1 (2H, complex), 4·7 (1H, triplet), 2·5-3·5 (2H, complex) and 1·9 (3H, singlet). The ^{13}C n.m.r. spectrum indicated that there was only one isomer present as there were only the number of signals expected for a 1:1 adduct. The remaining oil was found to be, by n.m.r., predominantly the other isomer, with about 25 % of the solid isomer present. The oil was filtered through celite and distilled under reduced pressure. Both these techniques, however, failed to alter the observed isomer ratio in the oil. A low temperature recrystallization from methanol gave a low melting solid, which by ^{1}H and ^{13}C n.m.r. to be a mixture (3:2) of the liquid and solid isomers. The liquid obtained by removal of the methanol was completely free of the solid isomer. Distillation gave an oil with the correct elemental analysis for a 1:1 adduct and had δ ($CDCl_3$) 7·9 (5H, singlet), 4·9-5·6 (2H, complex), 4·6 (1H, complex) 2·7-3·6 (2H, complex) and 2·2 (3H, singlet).

The 100 MHz ^{1}H n.m.r. spectra of these adducts were obtained. The chemical shift values were in agreement with those reported above. The adducts can be either isomers of 3-acetoxy-1-nitro-4-phenylcyclobutane (124) or 2-acetoxy-1-nitro-4-phenylcyclobutane (125). By analogy with the



[124]

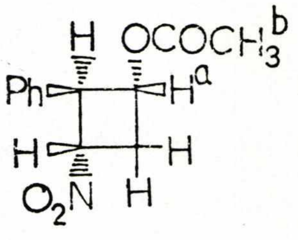


[125]

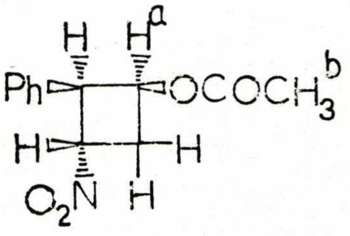
isopropenyl acetate adduct, (124) was considered to be the adduct obtained. The solid isomer has absorption at 5·6-6·1δ , assigned to H^a and H^b, and absorption at $4{\cdot}7\,\delta$, assigned to H^c by analogy with previous results. Spin decoupling experiments were performed. Irradiating at the absorption frequency of H^c had no effect on the splitting pattern of H^d and H^e, whilst irradiation at the absorption frequency of H^a and H^b caused H^c to become a singlet and H^d and H^e to become two sets of doublets. Structure (124) is the only one which fulfils these requirements and it is concluded that vinyl acetate adds in an identical way to isopropenyl acetate.

The chemical shift values of the liquid isomer did not allow a detailed spin decoupling experiment but by analogy with previous cases this isomer was considered to be a stereoisomer of regioisomer (124). This conclusion is supported by a study of the splitting patterns of the ^{1}H n.m.r. spectrum of this isomer. The absorption at $4{\cdot}6\,\delta$, due to H^c, is a triplet which can only be explained by regioisomer (124).

The isolation of the two isomers allowed an attempt to elucidate the relative stereochemistry about the cyclobutane ring of each isomer to be made. Molecular models were used to estimate the relative chemical shift positions of various protons. The shielding and deshielding effects of



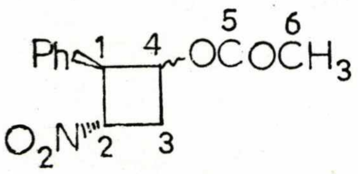
[124a]



[124b]

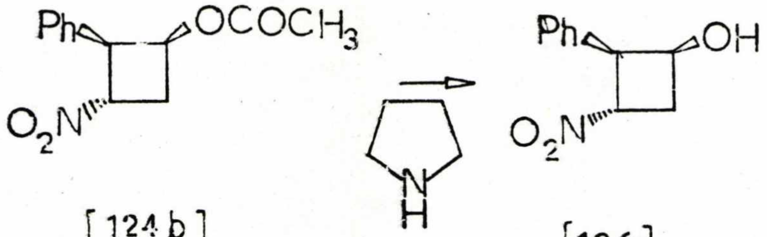
various groups on H^a and CH$_3^b$ were studied. For isomer (124a) the absorptions due to H^a and CH$_3^b$ will be at lower fields than the corresponding absorptions in isomer (124b). This analysis indicates that (124a) is the liquid isomer, whilst (124b) is the solid isomer. These conclusions are subject to the same criticisms as the results obtained for the styrene adduct.

^{13}C n.m.r. spectra of (124)



Solid isomer p.p.m. from T.M.S.	Assignment	Liquid isomer p.p.m. from T.M.S.
169·75	C^5	170·0
134·08	Phenyl carbons	136·87
128·5		133·96
128·01		128·98
127·77		126·55
78·99	C^2	76·8
67·58	C^4	65·64
51·32	C^1, C^3	53·87
32·88		34·09
20·5	C^6.	20.74

Attempts to convert the solid isomer (124b) to the corresponding nitroalcohol by sodium hydroxide and sodium carbonate were unsuccessful. Leaving the adduct to stand with excess pyrrolidine in methanol overnight gave an oil with ν max 3525 cm^{-1}, 3400 cm^{-1}, 1535 cm^{-1} and 1360 cm^{-1}, which indicated that both alcohol and nitro groups were present in the product. T.l.c. indicated that only one product was present. The product was purified by preparative scale t.l.c. and had an I.R. spectrum as detailed above and δ ($CDCl_3$) 7·0(5H, singlet), 5·15 (1H, quartet), 4·2 (1H, triplet), 3·75 (1H, triplet) and 1·4-2·7 (3H, complex). These spectra indicate that the product is the alcohol derived from the acetate, which was confirmed by elemental analysis. The presence of only one isomer was deduced from the n.m.r. spectrum. Hence the nitroalcohol (126) is considered to have the same relative stereochemistry as the nitroacetate.



[124 b] [126]

Refluxing the solid adduct (124b) with methanol containing hydrochloric acid gave the same material as above in 73 % yield. Reluxing the liquid isomer (124a) in methanol containing hydrochloric acid failed to give any characterizable products.

The stereochemistry of the nitroalcohol (126) was confirmed by refluxing this nitroalcohol with acetic anhydride which gave in quantitative yield the original nitroacetate. Attempts to oxidize the nitroalcohol to the ketone using Jones reagent[298], as used by Corey[286] failed.

Passing a solution of the liquid isomer down a silica gel column led to the isolation of trans- β-nitrostyrene. The solid isomer did not undergo this decomposition. This indicates that the liquid isomer (124a) is more easily decomposed than the solid isomer.

Following the successful photoadditions of vinyl acetate and isopropenyl acetate to β-nitrostyrene, other functionally substituted alkenes were tried. Irradiation of β-nitrostyrene and mesityl oxide (molar ratio 1:16) in methanol gave a product with ν max 1540 and 1360 cm^{-1}(saturated nitro group), which was unstable to purification procedures.

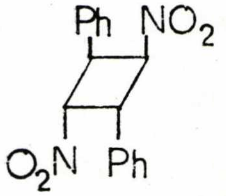
Photoadditions of various courmarins to alkenes have been reported[288]. A solution of trans- β -nitrostyrene and courmarin in methyl cyanide on irradiation, however, led to the recovery of starting materials.

Irradiation of trans- β-nitrostyrene and acrylonitrile in methanol gave a crude product with ν max 1540 and 1360 cm^{-1} (saturated nitro group), which decomposed on distillation. The product resulting from the irradiation of β-nitrostyrene and 1,2-dichloroethylene, which had ν max 1540 and 1360 cm^{-1}, also decomposed on distillation.

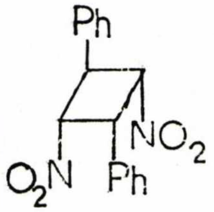
Trans- β-nitrostyrene can easily be added photochemically to enol acetates to give stable cyclobutane adducts. β-Nitrostyrene can be photochemically added to other functionally substituted alkenes, shown by the presence of a saturated nitro group in the crude product, but the product is extremely difficult to isolate. Enol acetates of β-diketones were prepared in order to study the ease of addition to these alkenes and their stabilities.

Irradiation of trans- β-nitrostyrene and the monoenol acetate of dimidone[299] in methanol caused a reaction to occur, as shown by I.R., but there was no sign of a saturated nitro group. T.l.c. of the crude material indicated that there were four products present, but these could not be isolated. Failure to obtain a cyclobutane product may be due to the enol acetate undergoing photoinduced cleavage of the C-O bond[300].

The methods of Bedoukian[301], Filler and Naqui[302] and Murray[303] failed to give the desired monoenol acetate of acetylacetone. The major product, however, which appeared to be the dienol acetate, could not be obtained in an analytically pure state. This meant this enol acetate could not be used in this study. As attempts to prepare the monoenol acetate of acetylacetone failed, the addition of trans- β-nitrostyrene to the enol form of the β-diketone was attempted. de Mayo has shown that cyclohexene can be added to acetyl acetone[284]. Irradiation of a solution of trans- β-nitrostyrene and acetyl acetone in methyl cyanide gave a crude product with ν max 1550 and 1360 cm^{-1} (saturated nitro group), which decomposed on distillation. When methanol was used as the solvent, an identical crude product was obtained which again decomposed on distillation However, during the course of this irradiation a white solid was deposited in very low yield. Recrystallization from acetone-methanol gave a solid which melted at 244-247 °C and had ν max 1550 and 1360 cm^{-1}. Elemental analysis showed this material was a dimer of β-nitrostyrene. This dimer is different from the ones previously reported[153], as (127) and (128) have melting points at 185-187 °C and 192-198 °C respectively. This material



[127]



[128]

was obtained in such low yield and was so insoluble in most organic solvents, an n.m.r. structure determination was not possible.

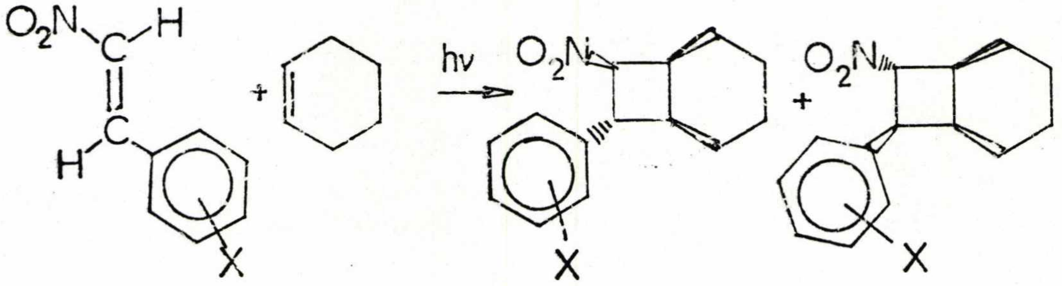
The formation of oxetans resulting from the addition of ketones to alkenes[304], vinyl ethers[305], acrylonitrile[306] and esters of maleic acid[307] have been observed. The possible addition of <u>trans</u>-β-nitrostyrene to ketones was investigated. Irradiation of <u>trans</u>-β-nitrostyrene and benzophenone in benzene failed to cause any addition.

To see if this photoaddition reaction could be extended to substituted β-nitrostyrenes, a series of these compounds was prepared and irradiated in the presence of cyclohexene. The results of this study are shown in table (2). These irradiations all used a molar ratio of the nitrostyrene to cyclohexene of 1:16. Satisfactory elemental analyses were obtained for the 4-methyl and 4-chloro derivatives. Spectroscopic data on these two adducts showed that they were mixtures of stereoisomers. All attempts to separate these stereoisomers by chromatography failed. By analogy with the <u>trans</u>-β-nitrostyrene adduct, these adducts have a <u>cis</u> ring junction.

Spectral evidence was obtained for the formation of cyclobutane adducts for the 4-methoxy, 2-methoxy and 3-nitro derivatives, but these were found to be either thermally unstable or not obtainable in a state of analytical purity.

All these nitroalkenes give a cyclobutane adduct, but the ones with electron donating substituents are more prone to thermal decomposition. This is a function of the stabilities of cyclobutane rings rather than a function of the photoaddition reaction.

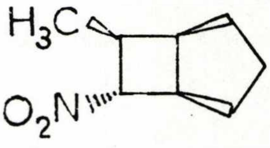
Table (2).



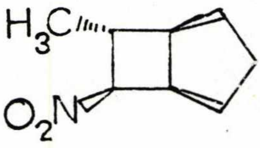
Substituent	Solvent	% yield of adduct	Isomer ratio
4-methyl[308]	CH_3CN	63 %	80:20
4-chloro[309]	CH_3CN	50 %	75:25
4-methoxy[310]	CH_3CN	Decomposed on distillation	
4-methoxy	CH_3OH	Decomposed on distillation	
2-methoxy[310]	CH_3CN	Decomposed on distillation	
3-nitro[309]	CH_3CN	Could not be obtained in a pure state	

The irradiation of 1-furyl-4-nitro-1,3-butadiene[311] and cyclohexene led to the recovery of starting material. The failure to observe addition of the nitrodiene to the alkene is in marked contrast to the other results and the dimerization of nitrodienes[196]. No simple rationalization can be offered, except that _cis_-_trans_ isomerization may be a competing side reaction.

Extending this photoaddition reaction to aliphatic nitroalkenes was then investigated. Irradiation of E-1-nitroprop-1-ene[227] and cyclohexene (molar ratio 1:16) in methyl cyanide until no nitroalkene could be detected followed by removal of solvent gave an oil with ν max 1535 and 1360 cm^{-1} (saturated nitro group). Column chromatography, however, led to decomposition. When cyclopentene was used in place of cyclohexene, a product with ν max 1540 and 1380 cm^{-1} was obtained, but it decomposed on distillation. Repeating the irradiation and subjecting the product to column chromatography gave an oil with ν max 1540 and 1360 cm^{-1} (saturated nitro group) and δ ($CDCl_3$) 6·0(1H, complex), 4·5(1H, complex), 0·8-3·0(8H, complex). These spectra indicate this oil is the cyclobutane adduct but it could not be obtained in a state of analytical purity. This chromatography also isolated an oil with ν max 1780 cm^{-1} , which was not present in the crude product is due to the breakdown of the adduct on the column. By analogy to the nitrostyrene cases, the product was considered to be a mixture of stereoisomers (129a) and (129b).A g.l.c. study of the



[129a]



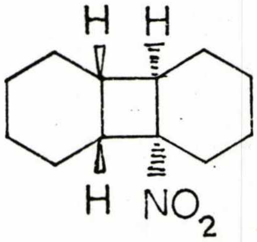
[129b]

reaction mixture during the course of the irradiation indicated that E-1-nitroprop-1-ene was not undergoing E-Z isomerization, hence the E-isomer undergoes the photoaddition.

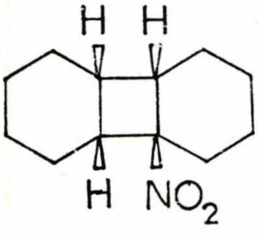
Irradiation of E-1-nitroprop-1-ene and styrene in methyl cyanide gave a product with ν max 1540 cm^{-1} (saturated nitro group), which decomposed on attempted purification. Irradiation of E-1-nitroprop-1-ene and isopropenyl acetate in methanol and methyl cyanide gave a crude product with ν max 1545 cm^{-1} , which decomposed on attempted purification.

A g.l.c. study of these irradiations showed the presence of a peak of shorter retention time than the E-isomer. From the previous work on 3-nitrobut-2-ene and published retention times[163,227], this peak was assigned to the Z-isomer.

Irradiation of 1-nitrocyclohexene[313,312,184] and cyclohexene (molar ratio 1:16) in methanol, gave after distillation an oil with ν max 1525 and 1360 cm^{-1}. Elemental analysis indicated that this was a 1:1 adduct of 1-nitrocyclohexene and cyclohexene. The product was considered to be a mixture of (130a) and (130b) by analogy with previous examples.



[130a]



[130b]

No traces of trans-1-methoxy-2-nitrocyclohexane, the product of prolonged irradiation of 1-nitrocyclohexene in methanol[148,189] were detected.

Irradiation of 1-nitrocyclohexene and vinyl acetate in methanol gave a product with ν max 1720 cm^{-1}, but this could not, however, be purified.

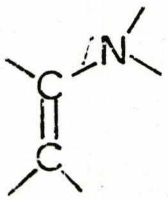
There is often evidence for the photoaddition of aliphatic nitroalkenes to alkenes, but the cyclobutane adduct is often unstable and hence is difficult to isolate. The occurrence of E-Z isomerization when 1-nitroprop-1-ene is irradiated in the presence of isopropenyl acetate is very interesting as no isomerization was noted when 1-nitroprop-1-ene was irradiated in its absence. This may be due to isopropenyl acetate acting as a sensitizer but no detailed conclusions can be drawn.

α-Nitroketones can exist in a nitroenol form and the photoaddition of nitroenols to alkenes was investigated. 2-Nitrocholestan-3-one[314], 2-nitro-4-*t*-butylcyclohexanone, α-nitroacetophenone[315] and the methyl enol ether of α-nitroacetophenone[316], the former two exist to a large extent in the enol form, underwent photoreactions in the presence of cyclohexene and methanol to give a complex mixture of products, but no cyclobutane adduct was detected. It is concluded that additions of the nitroenol system to alkenes do not occur easily, other photoreactions occur.

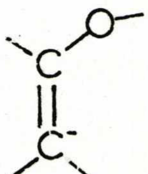
β-Nitrostyrene and its derivatives have been dimerized in the solid state[150,152,153]. An experimental procedure has been published for the large scale preparation of β-nitrostyrene dimer[317]. Repeating this procedure led only to a very small conversion of β-nitrostyrene to its dimer and no dimer was obtained when 1-(4-methoxyphenyl)-2-nitroethylene was used.

The thermal addition of β-nitrostyrene to enamines has been reported[319,320]. When hydrocarbon solvents are used a cyclobutane derivative is formed, which then undergoes a ring opening reaction. To investigate if this thermal reaction is slow enough to enable a photoaddition reaction to compete, the thermal reaction was studied. The reaction between β-nitrostyrene and the morpholine enamine of cyclohexanone in methanol and methyl cyanide was extremely fast. Examining a sample immediately after mixing showed all the β-nitrostyrene had reacted. Hence, the thermal reaction is too fast to allow a photoreaction to compete.

To see if an enol system, which is analogous to an enamine system, undergoes this thermal reaction with β-nitrostyrene; β-nitrostyrene



Enamine.

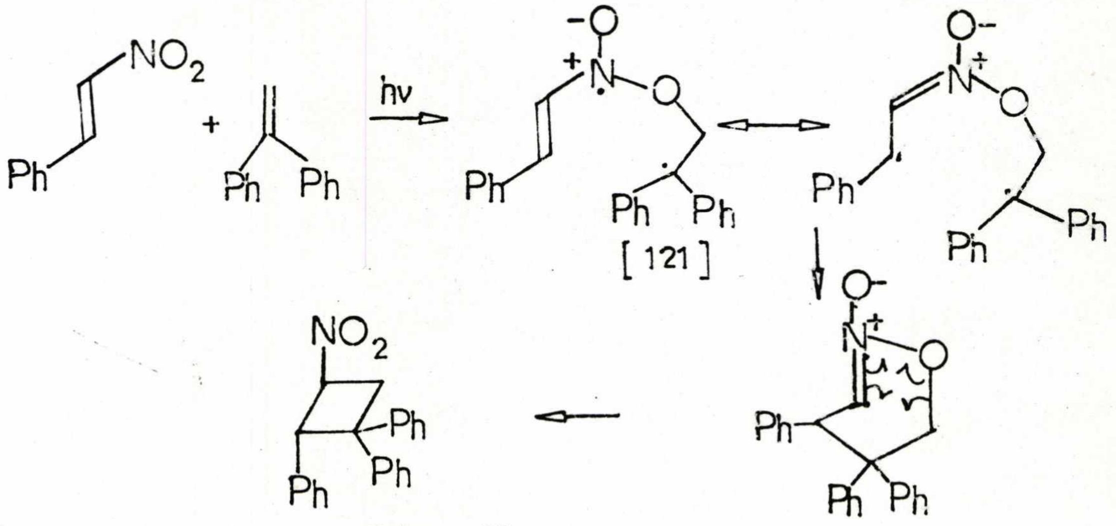


Enol.

and dihydropyran in methanol was refluxed for 120 hours, which caused no reaction to occur. The difference in behaviour between the two systems is interesting as both would be expected to be very similar.

This work shows that cyclobutane adducts are isolatable for a variety of alkenes when β-nitrostyrene is used. Aliphatic nitroalkenes and some substituted nitrostyrenes do add to alkenes but the adduct cannot always be isolated due to their instability.

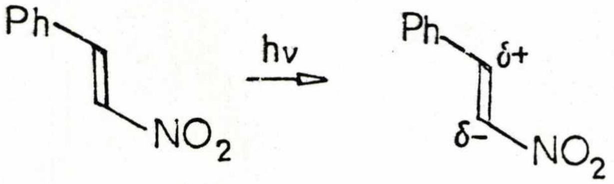
Several attempts at explaining the regiochemistry of this photoaddition reaction have been made. Kan[198] explained the formation of 1-nitro-3,3,4-triphenylcyclobutane, upon irradiation of β-nitrostyrene and 1,1-diphenylethylene by a mechanism involving an initial six-membered ring which collapses to a cyclobutane, scheme (23). This mechanism must be questioned on several counts. The diradical (121) is the most stable possible diradical, but the trans stereochemistry of the nitro and phenyl groups should be lost due to C-C bond rotation. Secondly, the collapse of the six-membered intermediate to a cyclobutane has little precedent and must be regarded with some reservation.



Scheme 23.

Hoganson, on the basis of the regiochemistry of the adducts found the most nucleophilic carbon of the alkene attached itself to the α-position of the β-nitrostyrene, which was regarded as evidence of the β-nitro styrene acting as an electrophilic species[197]. This is also the case for adducts prepared in the course of this study. In these addition reactions this is a general rule for the prediction of the regiochemistry of the resulting adduct.

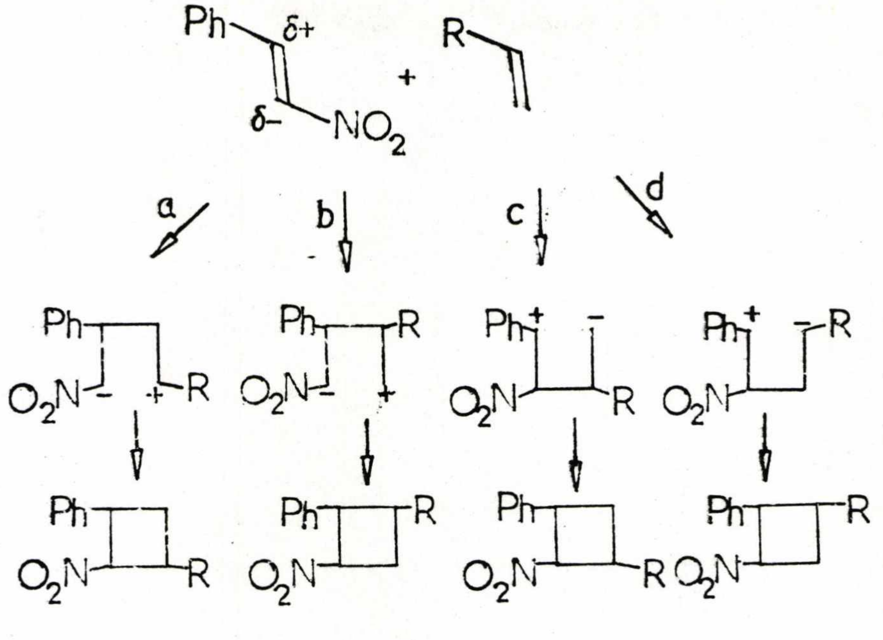
If β-nitrostyrene acts as an electrophile in the excited state, β-nitrostyrene must have charge separation as shown in scheme (24). There is evidence for charge separation in the excited state of β-nitrostyrene



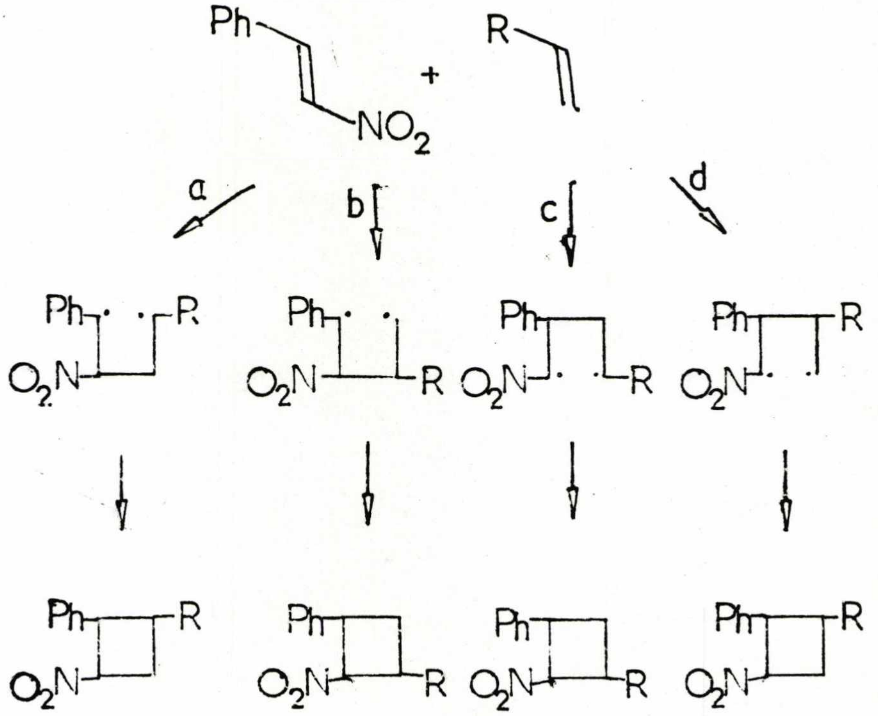
Scheme 24.

from theoretical studies. Irradiation of β-nitrostyrenes and substituted derivatives using pyrex filtered light excites the intramolecular charge transfer absorption in the region 304-324 n.m., which leads to the charge separation above in the excited state[223,224]. Hence on irradiation, trans- β-nitrostyrene is expected to become polar in character and this polar species then reacts. There was found to be no ground state interaction between any of the nitrostyrenes and aliphatic nitroalkenes and any of the alkenes used in this study.

The excited state of β-nitrostyrene with the charge separation as above could react in several different ways with the alkene. If it reacts with the alkene to give a zwitterionic intermediate, this will be one of the species in scheme (25). Path (a) gives a highly stabilized intermediate but a product with the wrong regiochemistry. Path (b) gives a less stabilized intermediate but a product with the correct regiochemistry. Paths (c) and (d) give intermediates that have little stability. Hence, an ionic mechanism, on the basis of stabilities of intermediates, will give the wrong regiochemistry in the product, also free rotation about the



Scheme 25.

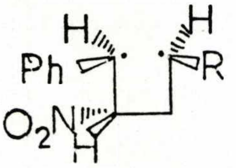


Scheme 26.

C-C bonds in the intermediate will cause the formation of more than two stereoisomers of product. Hence a purely ionic mechanism cannot explain the observed results.

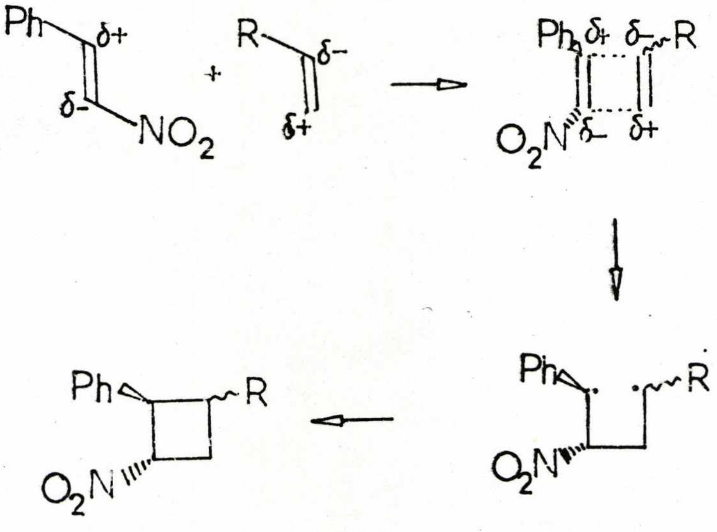
β-Nitrostyrene in its excited state possibly reacts with the alkene by a radical mechanism. This mechanism may lead to the intermediates shown in scheme (26). Path (a) gives the most stable diradical intermediate and also gives a product with the correct regiochemistry. This diradical intermediate can also undergo C-C bond rotation and this should lead to more than the two stereoisomers of the product that are observed. Paths (b) and (c) can be rejected as leading to a product with the wrong regiochemistry whilst path(d) has a diradical intermediate that is far less stabilized than the one from path (a). There is a possibiltiy that a diradical intermediate can breakdown to give <u>cis</u>- β-nitrostyrene, after C-C bond rotation. No <u>cis</u>-isomer is observed and indicates that if this diradical is formed it does not breakdown in this way.

In general a diradical mechanism does not explain the observed facts unless one postulates that the diradical intermediate resulting from path (a), (132), has restricted C-C bond rotation.



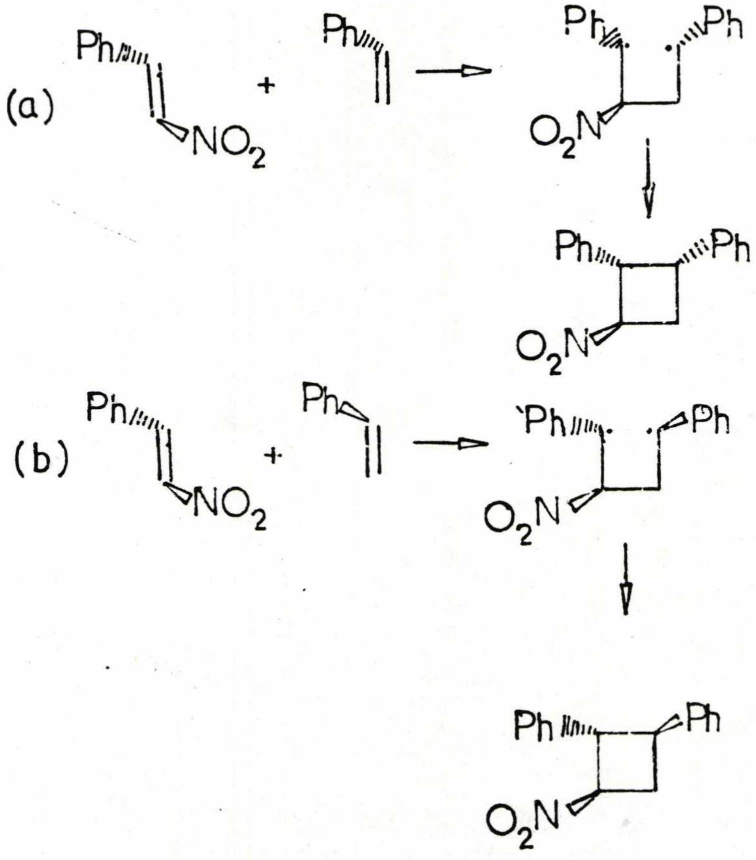
[132]

An alternative explanation is that the β-nitrostyrene and the alkene form the diradical (132), the regiochemistry being decided by the ionic interactions of the excited nitrostyrene and the ground state alkene, as shown in scheme (27). Ionic interactions favour the formation of diradical (132). If this diradical is short lived and undergoes ring closure before bond rotation can occur then there will only be two isomers of the product, the ratio of which will be decided by steric factors.



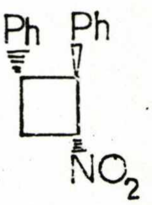
Scheme 27.

This is demonstrated below for the case of styrene, scheme (28).

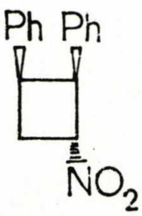


Styrene can approach β-nitrostyrene in two ways. The phenyl groups can either approach (path a) to give a cis system in the cyclobutane or else approach (path b) to give a trans system in the cyclobutane. In path (a) there is more steric interaction than in path (b) and hence path (b), in this case, should be favoured. This means that the isomer with the phenyl groups trans to each other should be present in greater yield, which was found to be the case. In all the adducts studied (except one) there was found to be one isomer of the adduct present in greater amount, as shown in the table below, due to steric interactions on the approach to the reaction intermediate. In the case of the styrene adduct, both isomers were isolated and (133) was found to be present in greater amounts than (134). This shows the isomer with the least steric interactions on approach is formed in greater amounts. Analogous results were found for all the other adducts

Alkene	Percentage of isomers of adduct present	
	Major	Minor
Cyclohexene	67-70	30-33
Cyclopentene	80	20
Styrene	60	40
α-Methylstyrene	60	40
3-Methylbut-2-ene	80	20
Isopropenylacetate	67-69	31-33
Vinyl acetate	50	50



[133]

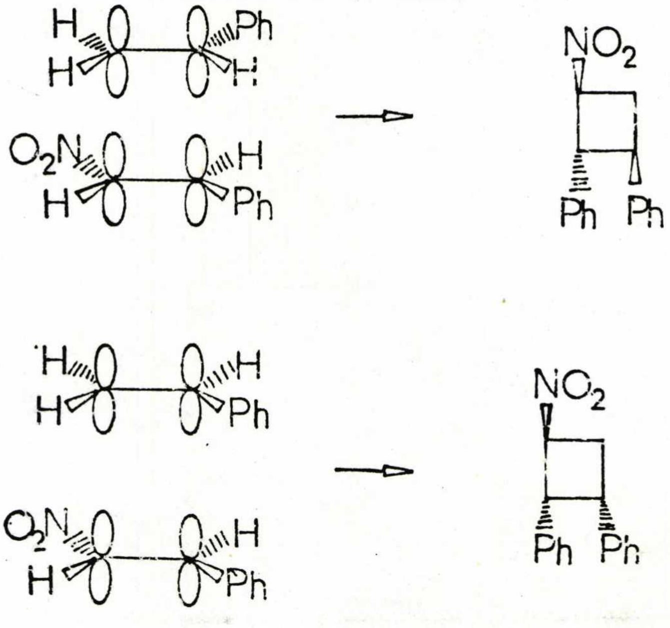


[134]

except in the case of the vinyl acetate adduct, where both modes of approach are equally favoured. A general conclusion that can be drawn is that the predominant isomer results from an approach of least steric interaction.

α -Methylstyrene and styrene have the same ratio of isomers, which indicates the methyl group is of little steric consequence in the photoreaction, the phenyl group is the deciding factor. The difference in isomer ratios between cyclohexene and cyclopentene is due to cyclohexene being more flexible than cyclopentene and providing less steric interaction on the approach to the reaction intermediate. Vinyl acetate is equally favoured on both modes of approach whilst isopropenyl acetate with an extra methyl group has the less sterically hindered isomer formed predominantly. The sterically hindered 3-methylbut-2-ene also has the least hindered isomer formed predominantly.

This mechanism involving a short lived diradical intermediate explains the observed results. It is, however, possible that the reaction is concerted. Photochemical concerted $\pi 2_s$ $\pi 2_s$ cycloadditions are allowed 321,322,323. The reaction may be concerted, the initial mode of approach of the reactants being decided by the ionic interactions discussed before. The two possible modes of reaction are shown in scheme (29). Exactly



Scheme 29.

the same comments about the steric interactions on the approach of the two reagents apply as in the diradical case.

To differentiate between the concerted and the short lived diradical intermediate mechanisms is difficult. The point at which the diradical mechanism becomes concerted is very hard to define. It is worth comparing these conclusions with the case of α , β -unsaturated ketones. The general mechanism involves an initial excited state complex between the unsaturated ketone and the alkene which then proceeds to a diradical intermediate that is usually fairly long-lived, allowing bond rotation to occur[280,281,283]. In some cases the rate of ring closure has been found to be faster than the rate of bond rotation[281]. There is therefore some precedent for a short-lived diradical intermediate in this photoaddition reaction. This does not rule out a concerted mechanism but few cases are known[323].

Summary of results

α , β -unsaturated nitroalkenes photochemically add to a variety of alkenes. The adducts resulting from β-nitrostyrene are the most stable. The photoreaction is regiospecific but gives in every case a mixture of stereoisomers. The mechanism of the photoaddition reaction is either concerted or else involves a short-lived diradical intermediate.

DISCUSSION

The Chemistry of α-Nitroketones

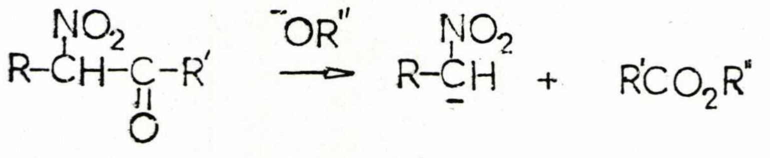
(1) The Photoreactions of α-Nitroketones.

(2) Keto-Enol-Aci-Nitro Tautomerization of α-Nitroketones.

(3) The Thermal Reactions of α-Nitroketones.

The Chemistry of α-Nitroketones.

α-Nitroketones undergo a reverse Claisen condensation with base. This is a general reaction for acyclic[328-331,316], cyclic[332-336] and steriodal α-nitroketones[337]. For α,α'-dinitroketones, the action of

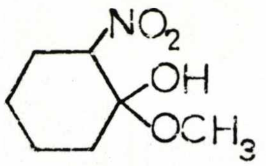


$$R{-}\overset{NO_2}{CH}{-}\underset{O}{\overset{\|}{C}}{-}R' \xrightarrow{^-OR''} R{-}\overset{NO_2}{\underset{-}{C}H} + R'CO_2R''$$

$R'' = H$ or alkyl

base also causes cleavage, often accompanied by decarboxylation[338-344]. This reverse Claisen condensation can also occur in the presence of acids [345-348]. α-Nitroketones undergo other reactions with base; elimination of nitrous acid to give an α,β-unsaturated ketone[349] and displacement of the nitro group by an anion <u>via</u> a radical anion mechanism[350,351]. Primary, secondary and tertiary α-nitroketones react with organocadmium compounds to give either the β-nitroalcohols (primary and secondary) or undergo cleavage to give ketones and nitroalkanes[352].

The action of acids on nitroketones is less well understood. Reaction of acyclic α-nitroketones with concentrated sulphuric, phosphoric and hydrochloric acids gives a hydroxylamine salt and a carboxylic acid, whilst reaction with nitric acid gives nitrogen dioxide and the carboxylic acid[353]. Tertiary α-nitroketones are unaffected by acid reagents[353]. The action of hydrochloric acid on primary α-nitroketones has previously been reported to give hydroximyl chlorides[354]. Heating cyclic α-nitro ketones in methanol/HCl leads to decomposition <u>via</u> a hemi-ketal intermediate (135)[355,333]. α-Nitroketones undergo rearrangement in acidic media. 3-Nitrocamphor (136) gives <u>N</u>-hydroxycamphorimide (137) in the presence of acid[356]. Certain steriodal α-nitroketones undergo this

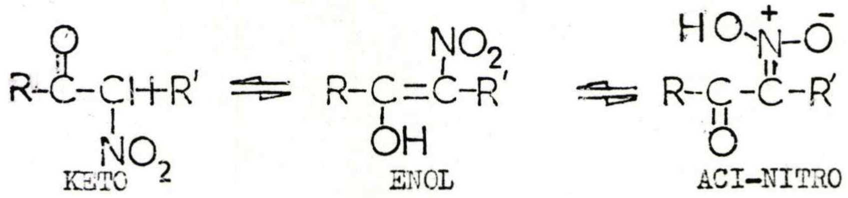


[135]

[136] [137]

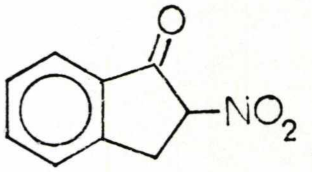
reaction[357], as does 2-nitro-1,3-indanedione[358]. The mechanism of this reaction is subject to some dispute. Cleavage of the aci-nitro form and subsequent recombination[357] and a 1,2 shift with ring expansion[356] have been suggested. 3-Nitrocamphor on heating gives a mixture of three isomeric anhydrides[359,360]. α-Nitroacetophenone derivatives are converted into 3-substituted chromones when reacted with acetic formic anhydride[361]. Complexes of α-nitroketones with nickel (II), colbolt (II), copper (II), iron (III) and aluminum (III) have been reported[362].

For all α-nitroketones there exist three possible tautomeric forms; the keto, the enol or the aci-nitro form. In solution the three forms can exist in tautomeric equilibrium with a common anion, the interconversion being catalysed by bases and acids. The relative concentrations of the



three forms in different systems have been measured by U.V.[333,337,363], I.R.[333] and n.m.r. spectroscopy[333,337,363] and bromine titration[364]. The composition is solvent dependant[333], the keto form being favoured in polar protic solvents and the enol form being favoured in aprotic solvents, suggesting an intramolecular hydrogen-bonded form[333]. Acidification of salts of α-nitroketones can give relatively high concentrations of the aci-nitro form which revert to the nitroketone on standing[365]. The overall conclusion is that the *aci*-nitro form is the least favoured of the equilibrium mixture[363-367]. In cyclic α-nitroketones, ring size affects the enol content in carbon tetrachloride solution, C_6, C_8 and C_{10} α-nitrocycloalkanones having higher enol contents than C_7, C_9 and C_{12} homologs[333]. Spectroscopic evidence supports the presence of an enol form rather than an *aci*-nitro form[333]. The appearance of I.R. absorption bands at 1550 cm^{-1} and 1515 cm^{-1} in the spectrum of an equilibrated sample of 2-nitrocyclohexanone has been interpreted as being due to it being a mixture of unconjugated (1550 cm^{-1}) and conjugated (1515 cm^{-1}) nitro compounds[333]. The percentage enol present for a series of nitroesters indicates that these compounds are more heavily enolized than the corresponding α-nitroketones[368].

Various α-nitroketones have been claimed to exist to a large extent in the enol form. 2-Nitro-1-indanone (138), claimed by early workers to exist entirely in the enol form[369,370], has since been shown to be the isomeric nitroalkene (139)[371-373].



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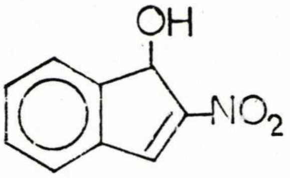
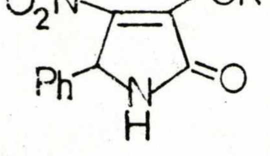


[139]

A series of α-nitroketones (140), which exist entirely in the enol form have been reported[374,375]; the enol form has greater stability than the keto form in this case.



R = H or alkyl

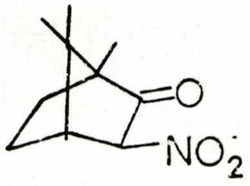
[140]

Nitronic esters and enol ethers of α-nitroketones have been prepared by the action of diazomethane on the α-nitroketone[376,377]. The formation of a nitronic ester of 3-nitrocamphor has been reported[378]. Enol ester derivatives of α-nitroketones have been obtained in a steriodal case[314] and have been postulated as reaction intermediates by various groups[379-381]. 3-Nitrocamphor has been much studied and the isolation of aci-nitro isomers have been claimed[382], but this has since been disputed[383].

Alicyclic α,α'-dinitroketones behave in a similar way to their α-nitroketone counterparts[365,384], although a high percentage enol concentration in aprotic solvents is claimed[384]. Alicyclic α,α'-diketo nitro compounds are often strong acids[365,385], and nitroenol derivatives of these compounds have been reported[386]. 2-Nitro-1,3-indanedione exists mainly in the enol form in water but in the keto form in benzene[385], the reverse of the usual trend.

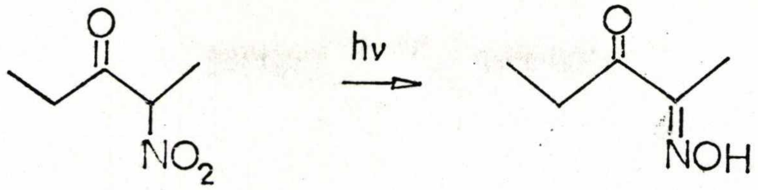
The Photochemistry of α-Nitroketones.

Very little work on the photochemistry of α-nitroketones has been reported. Reid and Tucker[147] reported that 2-nitrocyclohexanone on irradiation gave the ring expanded product N-hydroxy-2,7-dioxoazacycloheptane and 2-nitrocycloheptanone behaved in an analogous way. Irradiation of α-nitrocamphor (141) gave N-hydroxycamphorimide, hydroxyiminocamphor and 4-hydroxyimino-2-oxo-1,8,8-trimethyl-3-oxabicyclo(3,2,1)octane.



[141]

Acyclic α-nitroketones have also been studied[149,387]. Irradiation of 2-nitropentan-3-one (142) gives 2-hydroxyiminopentan-3-one (143) in

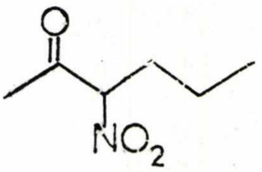


[142] [143]

cyclohexane, ethanol, acetonitrile and acetone. Irradiation of 1-phenylpropan-2-one in propan-2-ol gives 1-phenyl-1,2-propanedione oxime [146,147], whilst 1,2-diphenyl-1-nitroethan-2-one only gave fragmentation products on irradiation in methanol[148]. The irradiation of an α -bromo, α -nitro steriodal ketone has been reported to lead to loss of bromine[338].

The work on acyclic α -nitroketones in the literature indicates that the major photoproduct is an hydroxyiminoketone. Both the nitro and keto groups have U.V. absorption maxima in the 300 n.m. region[390,391], but the reaction products result from the decomposition of the nitro group. Formal energy transfer, however, from theketo to the nitro group is unlikely, in view of the known triplet energies. There are several other possible explanations; (i) nitro group processes are more efficient than carbonyl processes or (ii) the enol form is involved.

In order to investigate the photoreactions of acyclic α -nitroketones further, a series of α -nitroketones were prepared; 3-nitrobutan-2-one[354] (143), prepared by oxidation of 3-nitrobutan-2-ol[354], 3-nitrohexan-2-one[380] (144), prepared by the oxidation of 3-nitrohexan-2-ol[388] and 2-nitroheptan-3-one, a new compound, prepared by oxidation of 2-nitroheptan-3-ol[389], for which a satisfactory elemental analysis was obtained.



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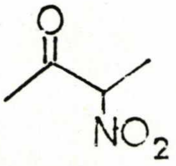

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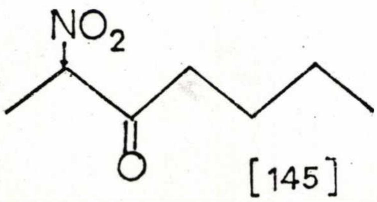
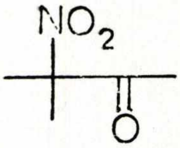


[145]

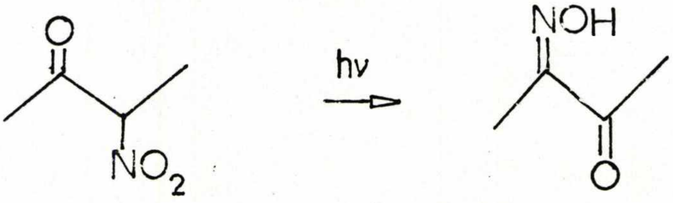
3-Nitrohexan-2-one and 2-nitroheptan-3-one have hydrogen atoms on the γ-carbon from the carbonyl group and hence these compounds may undergo a Norrish type II photoreaction[392]. 3-Methyl-3-nitrobutan-2-one (146)[363] prepared by oxidation of 3-methyl-3-nitrobutan-2-ol[388,389], cannot



[146]

have an enol form.

An 0·1 molar solution of 3-nitrobutan-2-one in methanol was irradiated using a 500W Pyrex lamp with a continous nitrogen flush. After 36 hours the irradiation was discontinued and the solvent removed. The product mixture was chromatographed and unreacted α-nitroketone (20 %) was eluted first followed by a crystaline material with νmax 3570, 3300, 1690 and 1360 cm^{-1} and δ ($CDCl_3$) 10·0 (1H, singlet), 2·48 (3H, singlet) and 2·02 (3H, singlet) and melted at 75-76 °C. On the basis of these spectral data and the melting point value, the photoproduct is 3-hydroxyiminobutan-2-one (which has reported melting point[230], I.R.[231,232] and n.m.r.[233,234] spectra in agreement with the values recorded above. Comparison of g.l.c. retention times again showed the photoproduct to be the hydroxyiminoketone, which was isolated in 20 % yield.

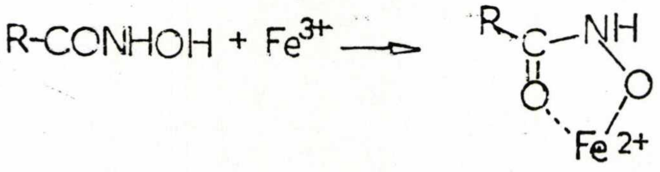


An 0·1 molar solution of 3-nitrobutan-2-one in ethanol was irradiated under identical conditions to before. After 36 hours, the product mixture was chromatographed and unreacted α-nitroketone (10 %) and 3-hydroxyiminobutan-2-one (40 %) were isolated. An 0·1 molar solution of 3-nitrobutan-2-one in propan-2-ol was irradiated for 25 hours under identical conditions to before. Unreacted α-nitroketone (10 %) and 3-hydroxyiminobutan-2-one (40 %) were isolated by preparative scale t.l.c. An 0·1 molar solution of 3-nitrobutan-2-one in butan-1-ol was irradiated for 21 hours under identical conditions to before. 3-Hydroxyiminobutan-2-one (35 %) was isolated using preparative scale t.l.c.. An 0·08 molar solution of 3-nitrobutan-2-one was irradiated in benzene under identical conditions to before, for 24 hours. 3-Hydroxyiminobutan-2-one and phenol were isolated using preparative scale t.l.c. An 0·2 molar solution of 3-nitrobutan-2-one was irradiated in toluene under identical conditions for 40 hours. 3-Hydroxyiminobutan-2-one (35 %) and small amounts of dibenzyl, benzaldehyde and o-, m- and p-cresol were isolated using preparative scale t.l.c. An 0·125 molar solution of 3-nitrobutan-2-one in diethyl ether was irradiated for 24 hours under identical conditions to before. 3-Hydroxyiminobutan-2-one (20 %) was detected by g.l.c. An 0·125 molar solution of 3-nitrobutan-2-one in chloroform was irradiated for 68 hours under identical conditions to before. 3-Hydroxyiminobutan-2-one (5 %) was isolated using preparative scale t.l.c. An 0·125 molar solution of 3-nitrobutan-2-one in acetic acid was irradiated under identical conditions to before, but after 24 hours no reaction had occurred.

The amount of α-nitroketone that reacted in different alcohols under standard, identical, conditions, for the same amount of time was then studied, the reactions being followed quantitatively by g.l.c. The results are shown below, and it can be seen that the α-nitroketone undergoes photoreaction to a greater extent in ethanol and propan-2-ol than in methanol; this may be due to the ethanol and propan-2-ol having more easily abstractable hydrogens α- to the hydroxy group[275].

Solvent	Concentration	Reaction Time	% 3-Nitrobutan-2-one Reacted
Methanol	0·1 Molar	24 hours	36
Ethanol	0·1 Molar	24 hours	78
Propan-2-ol	0·1 Molar	24 hours	81

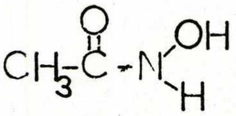
The amount of hydroxyiminoketone formed in the course of these photoreactions was followed using diphenylether as an internal standard. An 0·125 molar solution of 3-nitrobutan-2-one in methanol was irradiated using a 500W pyrex lamp with a nitrogen flush. The amount of 3-hydroxyiminobutan-2-one present after various amounts of time was determined (graph 1). After 36 hours, the irradiation was discontinued and the solvent removed. The crude reaction mixture was shaken with benzene and water. 3-Hydroxyiminobutan-2-one was isolated in 17 % yield, from the benzene layer using t.l.c.. A purple colour was obtained on treatment of the aqueous layer with a solution of ferric chloride. This is indicative of the presence of a hydroxamic acid, due to the formation of a complex (147), rather than $(RCONHO)_3Fe$ as previously thought[393]. An attempt to isolate the hydroxamic acid from the aqueous solution via the formation of the Cu^{2+} complex and reaction with hydrogen sulphide[394], failed.



[147]

The photoreaction was examined in other solvents, to follow the formation of the oximinoketone and to see if a hydroxamic acid could be isolated. An 0·125 molar solution of 3-nitrobutan-2-one in ethanol was irradiated under conditions identical to before. The amount of

3-hydroxyiminobutan-2-one present after various amounts of time was determined (graph 1). After 32 hours the irradiation was discontinued and the solvent removed. The crude reaction mixture was treated with benzene and water. 3-Hydroxyiminobutan-2-one was isolated in 25 % yield by t.l.c.. The aqueous layer gave a positive colour test with $FeCl_3$. Evaporation of the water gave a 7 % yield of acet hydroxamic acid (148), identified by melting point and mass spectral comparison with an authentic sample[395]. Irradiation of an 0·125 molar solution of 3-nitrobutan-2-one in propan-2-ol under conditions identical to before was followed using g.l.c. and the amount of 3-hydroxyiminobutan-2-one present after various amounts of time determined (graph 1). After 32 hours, 3-hydroxyiminobutan-2-one (26 %) and acet hydroxamic acid (5 %) were isolated.



[148]

The previous irradiations using alcohols as solvents , used a nitrogen flush. This could cause the removal of volatile products or intermediates and hence the effect of an atmosphere of nitrogen was studied.

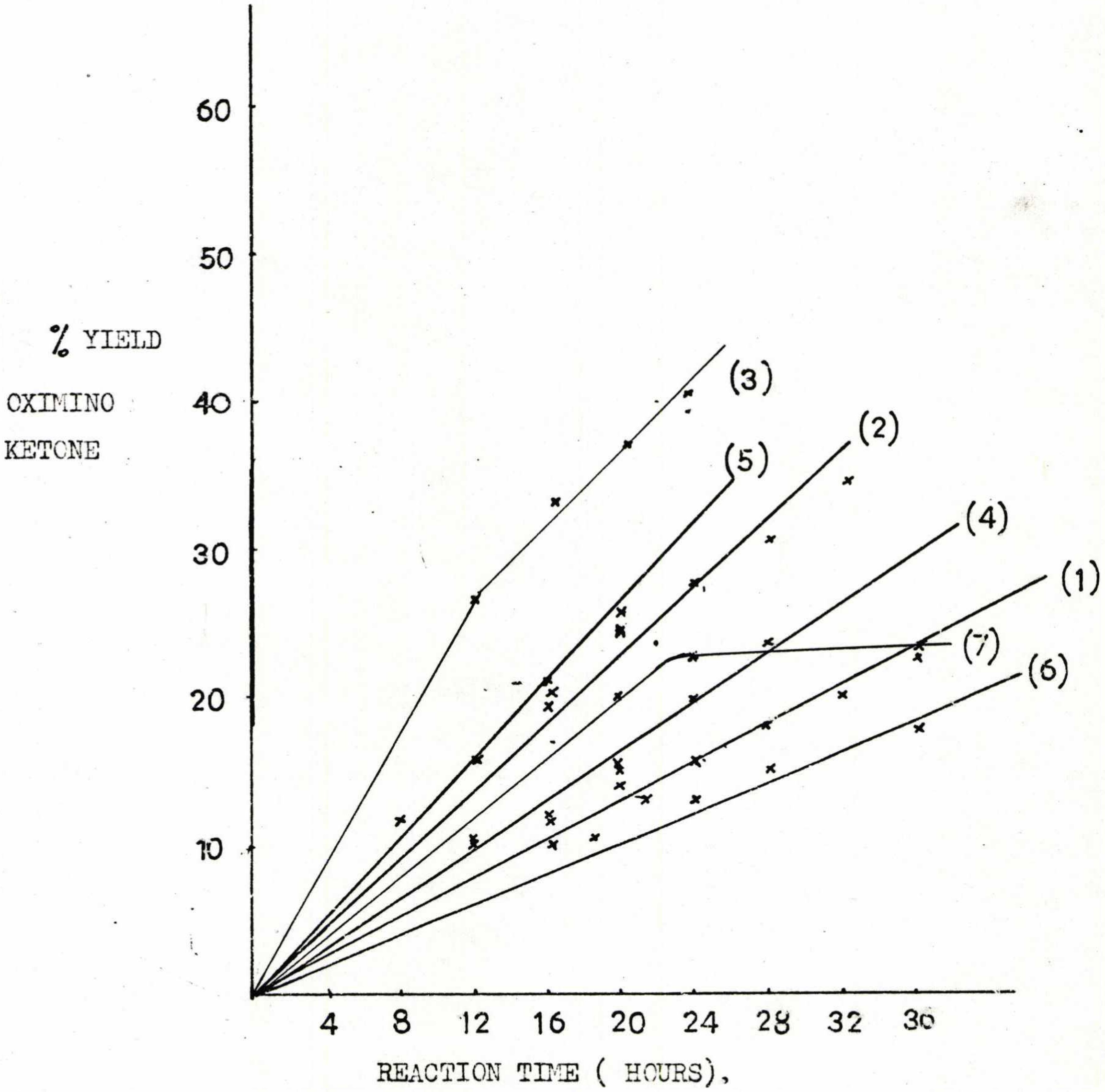
An 0·125 molar solution of 3-nitrobutan-2-one was irradiated in methanol using a 500W pyrex filtered lamp, under an atmosphere of nitrogen. The amount of 3-hydroxyiminobutan-2-one present after various amounts of time was determined (graph 1). After 36 hours, 3-hydroxyiminobutan-2-one (17 %), unreacted α -nitroketone (10 %) and acet hydroxamic acid (4 %) were isolated. An 0·125 molar solution of 3-nitrobutan-2-one in ethanol was irradiated under an atmosphere of nitrogen. The amount of 3-hydroxyiminobutan-2-one after various periods of time was determined using g.l.c.,(graph 1). After 32 hours, 3-hydroxyiminobutan-2-one (25 %) was isolated and a positive colour test indicated the presence of a hydroxamic acid. An 0·125 molar solution of 3-nitrobutan-2-one in benzene was irradiated under an atmosphere of nitrogen. The amount of 3-hydroxyiminobutan-2-one after various amounts of time was determined (graph 1). After 36 hours, 3-hydroxyiminobutan-2-one (5 %), unreacted α-nitroketone (25 %) and phenol were isolated. An 0·125 molar solution of 3-nitrobutan-2-one in toluene was irradiated under an atmosphere of nitrogen and the amount of 3-hydroxyiminobutan-2-one present after various periods of time was determined (graph 1). After 36 hours, 3-hydroxyiminobutan-2-one (20 %), o-, m- and p-cresol were isolated.

These photoreactions indicate that a minor photoproduct is acetohydroxamic acid. The effect of solvent on the yield of oximinoketone can be seen on graph 1 (Page 162). The linear parts of the graphs can be used to judge the ability of the solvent and reaction conditions to aid or hinder the photoreaction. Two immediate conclusions can be drawn; (i) higher yields of oximinoketone are obtained if an atmosphere of nitrogen is used in place of a nitrogen flush and (ii) the solvents which give the best yields can be listed, for an atmosphere of nitrogen, ethanol > toluene > methanol > benzene. For a nitrogen flush propan-2-ol > ethanol > methanol.

An attempt was made to measure accurately the amount of hydroxamic acid present in a reaction mixture by g.l.c. A methanol solution of 3-nitrobutan-2-one after irradiation for 24 hours, gave a [illegible] positive colour test with $FeCl_3$ but no acetohydroxamic acid could be detected by g.l.c. This indicates that acetohydroxamic acid is only a minor photoproduct and the colour test exaggerates the importance of this product. 3-Hydroxyiminobutan-2-one is fairly light stable under the reaction conditions and the hydroxamic acid does not result from this compound.

Changing the filter from pyrex to quartz does not radically alter the photoreaction. 3-Hydroxyiminobutan-2-one was obtained in 13 % yield from the irradiation of 3-nitrobutan-2-one in methanol.

To see if this photoreaction is general and to see if Norrish type II



(1) Solvent: Methanol, N_2 flush.

(2) Solvent: Ethanol, N_2 flush.

(3) Solvent: Propan-2-ol, N_2 flush.

(4) Solvent: Methanol, N_2 atmosphere.

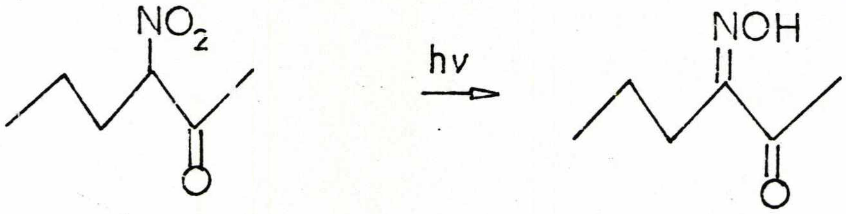
(5) Solvent: Ethanol, N_2 atmosphere.

(6) Solvent: Benzene, N_2 atmosphere.

(7) Solvent: Toluene, N_2 atmosphere.

photoproducts could be obtained from α-nitroketones where there are secondary or tertiary hydrogens on the γ-carbon from the carbonyl group, the photochemistry of 3-nitrohexan-2-one and 2-nitroheptan-3-one was investigated.

An 0·125 molar solution of 3-nitrohexan-2-one was irradiated in methanol using a 500W pyrex lamp and a nitrogen flush. The reaction was followed by g.l.c. and after 55 hours, 90 % of the α-nitroketone had reacted. The solvent was removed and unreacted α-nitroketone (5 %) and a solid with ν max. 3580, 3200, 1690 and 1380 cm^{-1} and δ ($CDCl_3$) 10·1 (1H, broad), 2·5 (2H, triplet), 2·4 (3H, singlet), 1·6 (2H, multiplet) and 0·95 (3H, triplet) were isolated by t.l.c.. The I.R. spectrum is indicative of an oximinoketone[231,232]. Comparison of spectral data with a sample of 3-hydroxyiminohexan-2-one (149), prepared by oximation of hexan-2-one[405], showed this to be the product, isolated in 15 % yield. No Norrish type II photoproducts were obtained. A sample of the reaction mixture gave a red colour with $FeCl_3$ but no hydroxamic could be isolated.

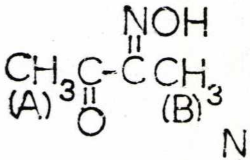
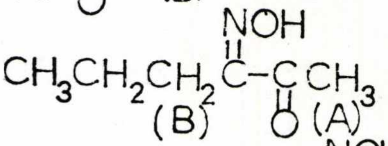
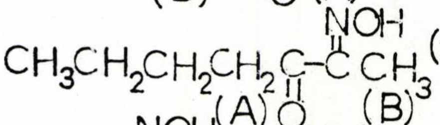
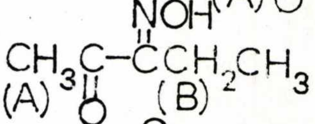
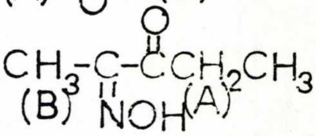
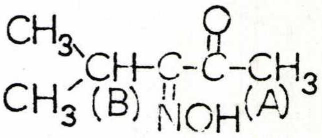


[149]

An 0·07 molar solution of 3-nitrohexan-2-one in ethanol was irradiated under an atmosphere of nitrogen. After 36 hours, 3-hydroxyiminohexan-2-one (40 %) was isolated by t.l.c.. No Norrish type II photoproducts were obtained.

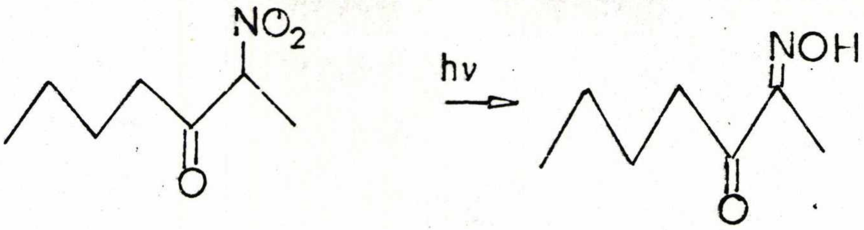
An 0·27 molar solution of 2-nitroheptan-3-one in methanol was irradiated using a 500W pyrex lamp with a nitrogen flush. The reaction was followed by I.R. and after 46 hours the solvent was removed. Unreacted α-nitroketone(10 %), valeric acid (5 %) and an oil with ν max. 3580

3300, 1690, 1365 and 1040 cm^{-1} and δ (CDCl$_3$) 10·0 (1H, broad), 2·9 (2H, triplet), 2·0 (3H, singlet) and 0·8–1·8 (7H, complex) were isolated by t.l.c.. The I.R. spectrum indicated the photoproduct was an oximinoketone and its structure was deduced from the n.m.r. spectrum. In the course of this work the n.m.r. spectra of a series of oximinoketones were obtained, as shown below.

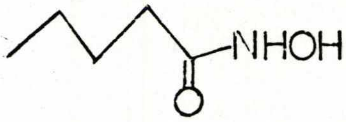
Hydroxyiminoketone	Protons (A)	Protons (B)
 $\underset{(A)}{CH_3}\underset{\overset{\|}{O}}{C}-\overset{NOH}{\overset{\|}{C}}\underset{(B)}{CH_3}$	2·4 δ	2·0 δ
 $CH_3CH_2\underset{(B)}{CH_2}\overset{NOH}{\overset{\|}{C}}-\underset{\overset{\|}{O}}{C}\underset{(A)}{CH_3}$	2·48 δ	2·6 δ
 $CH_3CH_2CH_2\underset{(A)}{CH_2}\underset{\overset{\|}{O}}{C}-\overset{NOH}{\overset{\|}{C}}\underset{(B)}{CH_3}$ (1)	2·84 δ	2·0 δ
 $\underset{(A)}{CH_3}\underset{\overset{\|}{O}}{C}-\overset{NOH}{\overset{\|}{C}}\underset{(B)}{CH_2}CH_3$	2·45 δ	2·6 δ
 $\underset{(B)}{CH_3}-\underset{\underset{NOH}{\|}}{C}-\overset{O}{\overset{\|}{C}}\underset{(A)}{CH_2}CH_3$	2·9 δ	2·1 δ
 $(CH_3)_2\underset{(B)}{CH}-\underset{\underset{NOH}{\|}}{C}-\overset{O}{\overset{\|}{C}}-\underset{(A)}{CH_3}$	2·4 δ	3·7 δ

(1) Prepared by zinc/acetic acid reduction of the corresponding α -nitroketone.

For oximinoketones the methyl protons in the group $-\overset{O}{\overset{\|}{C}}-CH_3$ occur at 2·4 δ and the methyl protons in the group $-\overset{NOH}{\overset{\|}{C}}-CH_3$ occur at 2–2·1 δ . The photoproduct has a methyl group at 2·0 δ which indicates there is a $CH_3-\overset{NOH}{\overset{\|}{C}}-$ group present in the oximinoketone, which indicates the photoproduct is 2-hydroxyiminoheptan-3-one, isolated in 15 % yield. This assignment was confirmed by comparison with an authentic sample of 2-hydroxyiminoheptan-3-one, prepared by zinc/acetic acid reduction of 2-nitroheptan-3-one, a known process[396], for which a satisfactory elemental analysis was obtained.



An 0·125 molar solution of 2-nitroheptan-3-one in ethanol was irradiated under an atmosphere of nitrogen. The reaction was followed by I.R. and after 40 hours the solvent was removed. The crude product mixture was treated with benzene and water. Unreacted α-nitroketone (10 %) and 2-hydroxyiminoheptan-3-one (30 %) was isolated by t.l.c.. The aqueous layer gave a positive colour test with $FeCl_3$. For this α-nitroketone there are two possible hydroxamic acids available from the breakdown of the α-nitroketone, namely valerohydroxamic acid and acethydroxamic acid. Isolation of the hydroxamic acid *via* the acetate was attempted. Acet hydroxamic acid[395], valerohydroxamic acid[397]



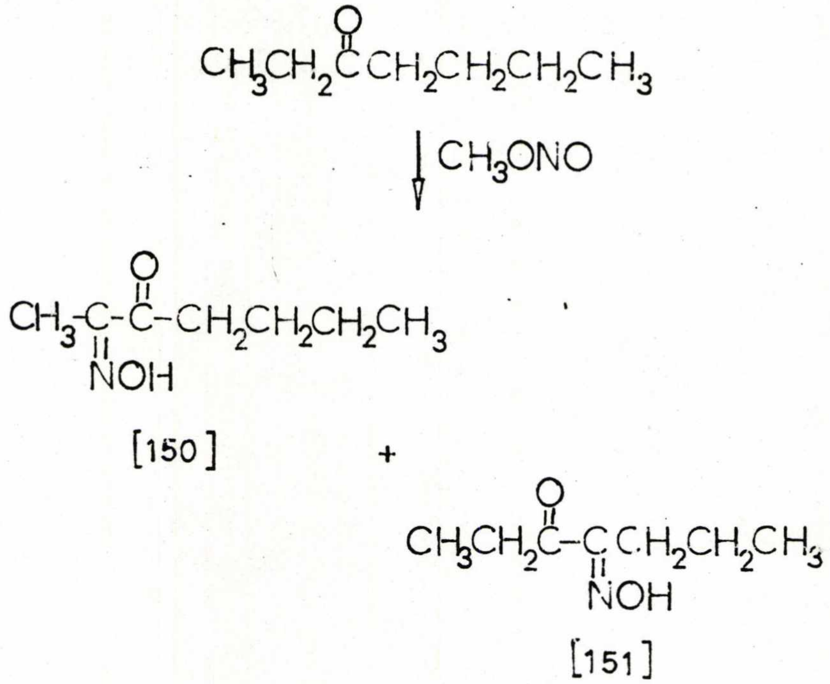
and their acetates were prepared[395]. The residues of the aqueous layer were treated with acetic anhydride and examined by g.l.c. However, the acetates were thermally unstable and no conclusions could be drawn. No Norrish type II photoproducts were isolated.

The photochemistry of an α-nitroketone which cannot have an enol form was investigated. Irradiation of an 0·16 molar solution of 3-methyl-3-nitrobutan-2-one in methanol under an atmosphere of nitrogen was found to a very slow reaction. After 24 hours, only 17 % of the α-nitroketone had reacted. After 140 hours, the solvent was removed and unreacted α-nitroketone (5 %) and a product with ν max. 1720 and 1370 cm^{-1} and δ ($CDCl_3$) 2·35 (1H, doublet) and 1·3 (3H, doublet) using t.l.c.. This photoproduct could not be obtained analytically pure and hence it could not be fully characterized.

Irradiation of an 0·06 molar solution of α-nitroacetophenone[315] in methanol under an atmosphere of nitrogen for 16 hours caused complete reaction of the nitroketone. T.l.c. indicated that at least three components were present in the mixture which could not however be separated.

The photochemistry of 2-nitrocholestan-3-one[314], a heavily enolized nitroketone was studied. An 0·004 molar solution of the α-nitroketone in methanol was irradiated using a 500W pyrex lamp, under an atmosphere of nitrogen, for three hours. T.l.c. indicated that there were at least three products, which could not be separated.

Some general conclusions can be drawn about the photochemistry of acyclic α-nitroketones. Primary α-nitroketones undergo photoreaction to give a multitude of products whilst the photoreaction of tertiary α-nitroketones is very slow. Secondary α-nitroketones undergo a fairly clean photoreaction to give oximinoketones. The synthetic utility of this photoreaction can now be considered. The general method of preparing oximinoketones is by the nitrosation by alkyl nitrites of ketones[398,399], involving the enol form of the ketone[400]. Nitrosation using alkyl nitrites of a ketone with two α-methylene groups can give rise to two isomeric oximinoketones[401], unless the alkyl groups differ significantly in length or one is branched; the shorter or unbranched chain being nitrosated[398]. A recent method involves the addition of nitrosyl chloride to trimethylsilyl enol ethers[402]. This method cannot be used very easily to oximate a specific methylene group. This photoreaction is synthetically useful. In all the examples studied the oximinoketone has the oxime group on the same carbon that originally bore the nitro group. In the case of 2-nitroheptan-3-one, 2-hydroxyiminoheptan-2-one was obtained on irradiation. For comparison purposes the action of methyl nitrite on heptan-3-one was studied. An 0·125 molar solution of heptan-3-one in diethyl ether was treated with an excess of methyl nitrite[399]. Distillation of the reaction mixture recovered the unreacted ketone and on the basis of spectroscopic evidence, an oximinoketone with δ ($CDCl_3$) 3·1-2·4 (complex), 2·1 (singlet) and 1·8-0·7 (complex).The n.m.r. spectrum indicates that the product is a mixture of two isomers (150) and (151).



$$CH_3CH_2\overset{O}{\overset{\|}{C}}CH_2CH_2CH_2CH_3$$

$$\Big\downarrow CH_3ONO$$

$$CH_3\underset{NOH}{\underset{\|}{C}}-\overset{O}{\overset{\|}{C}}-CH_2CH_2CH_2CH_3$$

[150]

+

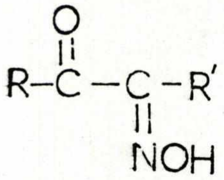
$$CH_3CH_2\overset{O}{\overset{\|}{C}}-\underset{NOH}{\underset{\|}{C}}CH_2CH_2CH_3$$

[151]

G.l.c. indicated there were two isomers present. By a comparison with authentic 2-hydroxyiminoheptan-3-one, the major component of the mixture was shown to be this oximinoketone. The minor product was concluded to be 4-hydroxyiminoheptan-3-one. The isomer ratio was 60:40. All other attempts to separate these isomers by chromatography failed.

A mixture of oximinoketones being obtained in this nitrosation reaction is in agreement with previous workers[401], as is the shorter side chain being preferentially nitrosated[398]. This demonstrates the synthetic utility of the photoreaction, the classical reaction leads to a mixture of isomers whilst the photochemical reaction gives one isomer.

The yields obtained from this photoreaction are good compared to other methods of preparation as shown below:



$$R-\overset{\overset{\displaystyle O}{\|}}{C}-\underset{\underset{\displaystyle NOH}{\|}}{C}-R'$$

R	R'	Method of preparation	% Yield
CH_3	C_3H_7	(1)	35
CH_3	C_3H_7	(2)	16
CH_3	C_3H_7	(3)	40
CH_3	C_2H_5	(1)	28
C_2H_5	CH_3	(1)	37
CH_3	$CH(CH_3)_2$	(1)	30
C_4H_9	CH_3	(2)	12
C_4H_9	CH_3	(3)	35

(1) Action of alkyl nitrite on ketone

(2) Zinc/acetic acid reduction of α -nitroketone

(3) Photochemical reduction of the α -nitroketone in ethanol

The good yields obtained in this photoreaction compared to the alternative methods of preparation coupled with only one isomer of the oximinoketone being obtained mean this photoreaction has definite synthetic utility.

Tautomerization of α-nitroketones.

The tautomerization of α-nitroketones was studied spectroscopically and chemically. The U.V. spectra of a series of α-nitroketones was studied in a variety of solvents to see if there was any sign of a tautomer. Evidence as to whether this tautomer was the enol or the aci-nitro form was also sought.

α-Nitrocycloalkanones have been reported to have absorption at λ max 320-370 n.m. with ε = 1700-4000 with carbon tetrachloride as the solvent[333], assigned to the enol form due to the alkaline salts of these α-nitroketones having a strong band at 340 n.m. in ethanol. For steriodal α-nitroketones, absorption at 370 n.m. was attributed to the enol form[337]. α-Nitroketones have two chromophores present, the carbonyl group in ketones has absorption at 270 n.m. (ε = 16)[391] and aliphatic nitro groups have absorption at 270 n.m. (ε = 19)[390], both being $n \rightarrow \pi^*$ transitions. On simple reasoning absorption at 270 n.m. (ε = 40) for α-nitroketones would be expected, absorption at higher wavelengths being due to the presence of a tautomer. Various groups have concluded that higher wavelength absorption is due to the presence of the enol form.

The U.V. spectra of a series of α-nitroketones were obtained. Running the U.V. spectrum of 3-nitrobutan-2-one in methanol immediately after dissolution showed absorption at 275 n.m. (ε = 160). Leaving the sample solution to stand for up to one hour caused the growth of a new peak at 329 n.m. (ε = 80), as well as the original peak. The time required for an equilibrium condition to be reached was then measured when methanol, ethanol and propan-2-ol were used as the solvents, as shown below.
The U.V. light source of the spectrophotometer does not effect this equilibration.

U.V. spectra of 3-nitrobutan-2one.

Solvent	U.V. maxima immediately after mixing	U.V. maxima after standing	Equilibration time
Methanol	275 n.m. (ε = 100)	276 n.m (ε = 115) 323 n.m. (ε = 85)	36 min.
Ethanol	282 n.m.(ε = 100)	285n.m. (ε = 146) 325 n.m.(ε = 156)	26 min.
Propan-2-ol	285 n.m. (ε = 100)	290 n.m. (ε = 142) 320 n.m. (ε = 156)	23 min.

The use of other solvents was investigated and the results are shown below:

Solvent	U.V. maxima immediately after mixing	U.V. maxima after equilibration
Cyclohexane	297 n.m. (ε = 50)	315 n.m. (ε = 1667)
Benzene	-(1)	327 n.m. (ε = 251)
Toluene	-(1)	327 n.m. (ε = 260)
Methyl cyanide	276 n.m. (ε = 99)	276 n.m. (ε = 99)
Diethyl ether	287 n.m. (ε = 90)	318 n.m. (ε = 194)
Carbon tetrachloride	284 n.m. (ε = 90)	320 n.m. (ε = 282)

(1) Solvent masking.

The U.V. spectra of 3-methyl-3-nitrobutan-2-one, which cannot tautomerize was examined in a variety of solvents, and the results are shown below:

Solvent	U.V. maxima
Methanol	279 n.m. (ε = 89)
Methyl cyanide	278 n.m. (ε = 85)
Cyclohexane	285 n.m. (ε = 151)

These results indicate that this absorption is $n \rightarrow \pi^*$ in character as changing from a non-polar solvent to a polar one causes a shift to shorter wavelengths[1]. For 3-nitrobutan-2-one also the initially observed absorption (due to the carbonyl and nitro groups only) is $n \rightarrow \pi^*$

in character. The U.V. spectra of 3-nitrohexan-2-one and 2-nitroheptan-3-one showed a similar growth of absorption at 325 n.m. in ethanol and methanol. This growth of absorption, common to all these secondary α -nitroketones, may be due to an <u>aci</u>-nitro form or to an enol form. Nitro enol ethers have been reported to have absorption at 285 n.m. and nitronic esters (derivatives of <u>aci</u>-nitro form) have absorption at 310 and 358 n.m.[377]. This indicates that the absorption at 325 n.m. may be due to the <u>aci</u>-nitro form, despite the previous assignments to the enol form.

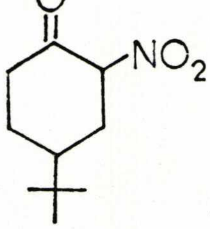
For acyclic α -nitroketones the greatest amount of tautomerization occurs in non-polar solvents, in agreement with previous workers[333], who suggested intramolecular hydrogen bonding stabilized the enol form. An interesting point is the amount of time required for the equilibrium position to be reached. In propan-2-ol and ethanol approimately the same amount of time is required and both these cases are substantially less than when methanol is used.

The ^{1}H n.m.r. spectra of these α -nitroketones were studied to find evidence for the tautomer. The enol form of some cyclic α -nitroketones have been detected by n.m.r.[333,363], but not in the case of acyclic α -nitroketones[333,363]. The n.m.r. spectra of the acyclic α -nitroketones used in this study showed no signs of any tautomer, in agreement with previous workers.

On the basis of these spectral data some general conclusions can be drawn. The U.V. spectra of acyclic α -nitroketones show absorption due to a tautomer at 325 n.m., by analogy with reported values this may be the <u>aci</u>-nitro form. The conclusion that absorption at 325 n.m. in the U.V. spectrum of 2-nitrocyclohexanone being due to the enol form[333], is based on there being absorption at 300-350 n.m. in the U.V. spectrum of the anion and is open to question. Hence there is confusion as to which tautomer is present in solution. For acyclic α -nitroketones the amount of tautomer present in the equilibrium state is very small, it being less than 1 %. The reason for the tautomer (presumed to be the enol) not being favoured has been discussed[363] and it was concluded that any intramolecular hydrogen bonding that might occur between the hydroxyl and nitro groups is very weak and cannot stabilize the enol form relative to the nitroketone form with the nitro and carbonyl groups being <u>trans</u> to each other. Similar comments about the intramolecular hydrogen bonding in the <u>aci</u>-nitro structure apply.

The preparation of enol ethers and acetates of α-nitroketones was studied. The preparation of enol ethers of α-nitroacetophenone <u>via</u> the thermal decomposition of the acetal derivative has been reported[316]. In the case of acyclic α-nitroketones, standard methods of preparing enol ethers failed. Pyrolysis of nitro acetals of these nitroketones also failed, the nitro acetals being very difficult to prepare and purify.

Hassner[314] reported the preparation of 2-nitro-3-acetoxy-2-cholestene from the corresponding α-nitroketone. Campbell[403] failed to prepare enol esters of α-nitroacetophenone, by the action of substituted benzoyl chlorides and pyridine on the α-nitroketone. Standard methods of preparing enol acetates failed to give the desired product in this case. The enol acetate of 2-nitrocholestan-3-one was prepared[314]. This is a very simple procedure and it was considered that a nitroketone with steric properties should form an enol acetate. An α-nitroketone with similar steric properties is 2-nitro-4-<u>t</u>-butylcyclohexanone (152)

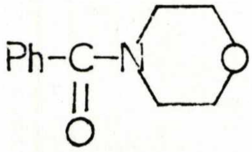


[152]

The tertiary butyl group is bulky enough to cause the cyclohexane ring to remain fixed in one conformation, similar to the situation in steriods. The most stable conformation of this α-nitroketone has the nitro and *t*-butyl groups equatorial. The nitro group can become axial *via* the enol form. This can be compared to the steriod case, which has the nitro group in the α-position[314], which means these two nitroketones are very similar in their steric properties.

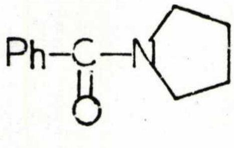
2-Nitro-4-*t*-butylcyclohexanone was prepared by the action of acetyl nitrate on the enol acetate of 4-*t*-butylcyclohexanone, according to the method of Griswold and Starcher[379]. The product melted at 75-79°C, had the correct elemental analysis and ν max. 1735 and 1555 cm^{-1}, indicative of an α-nitroketone[363]. On standing, the I.R. spectrum using carbon tetrachloride as the solvent showed the growth of a peak at 1610 cm^{-1}, attributed to the enol form by analogy with 2-nitrocyclohexanone[333]. The n.m.r. spectrum had δ ($CDCl_3$) 14 (0·7H, singlet), 5·3 (0·3H, doublet of doublets), 2·7-1·2 (7H, complex) and 0·95 (9H, singlet). The absorption at 14 δ is probably due to the enol form, which represents 70 % of the equilibrium concentration. The α-nitroketosteriod exists 30 % in the enol form. The I.R. spectrum can tell whether the nitro group is in the axial or equatorial position. For α-substituted halocycloalkanones, when the halogen is in the equatorial position the carbonyl absorption is at 1735 cm^{-1}, whilst a halogen in the axial position shows carbonyl absorption at 1715 cm^{-1} [404]. The I.R. spectrum of 2-nitro-4-*t*-butylcyclohexanone shows carbonyl absorption at 1735 cm^{-1} indicating the nitro group is in the equatorial position. This α-nitroketone was treated with acetic anhydride, according to the method of Hassner[314]. However, no enol acetate was obtained. The failure of this method to form an enol acetate, even though the nitroketone is so heavily enolized led to the abandonment of this line of research.

The failure of the methods described above to obtain enol derivatives led to an investigation of other derivatives of α-nitroketones. The synthesis of enamines of α-nitroketones, <u>via</u> α-chloro, β-nitroalkenes, has been reported[403]. The simple method of forming enamines by reacting the amine with the α-nitroketone has not been investigated. α-Nitroacetophenone (0·025 moles) in benzene was refluxed with excess morpholine (0·05 moles) and p-toluenesulphonic acid for 40 hours. Removal of the solvent and distillation gave a solid with ν max. 1640, 1420, 1275 and 1110 cm^{-1}, and δ ($CDCl_3$) 7·65 (5H, singlet), 5·7 (8H, singlet), which melted at 74-75° C and had the empirical formula $C_{11}H_{13}NO_2$. This rules out the enamine as the product. Om the basis of the above data, the material was considered to be the amide (153), reported to melt at 74-75° C[406].



[153]

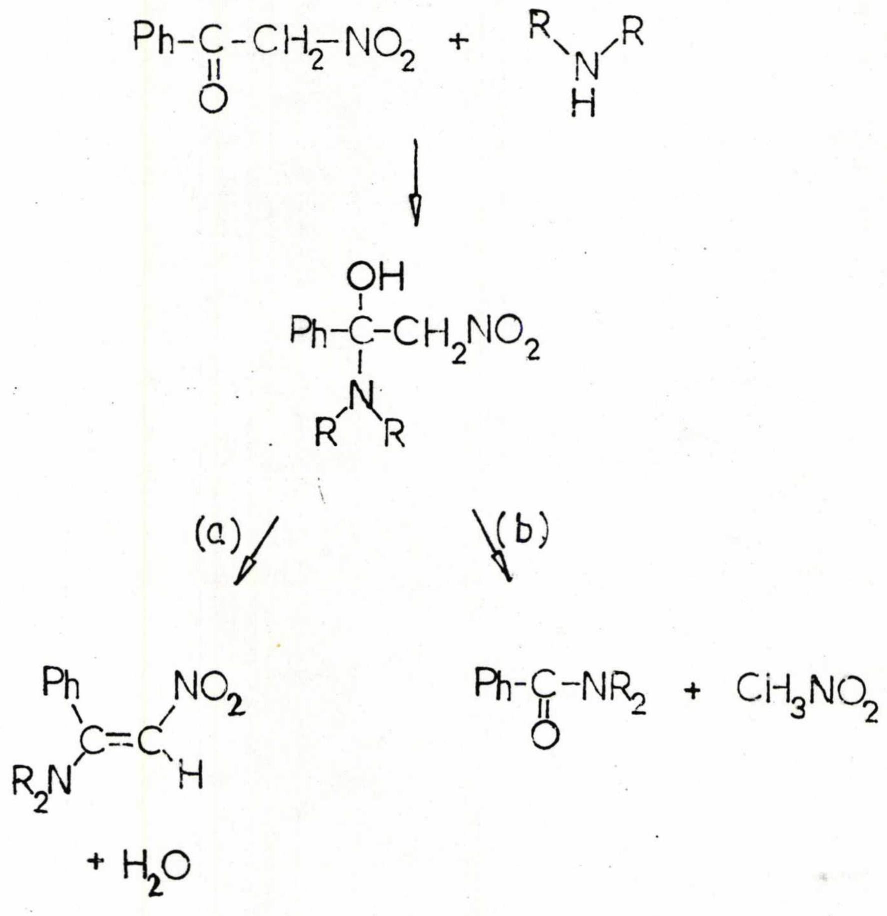
The reaction was repeated using pyrrolidine. Removal of the solvent after 40 hours and distillation gave a product with ν max. 1630 and 1410 cm^{-1} and δ ($CDCl_3$) 7·8 (5H, complex), 3·5-3·8 (4H, complex) and 1·8-2·1 (4H, complex). The mass spectrum of the material showed m/e values at 175, 146, 105 and 77 and elemental analysis indicated an empirical formula of $C_{11}H_{13}NO$. These data indicate the product was the amide (154)[407].



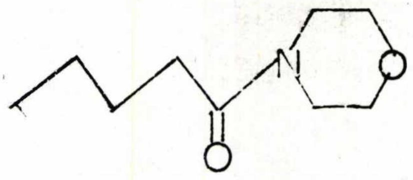
[154]

From these results it would appear that

instead of reacting in the normal way for enamine formation (path a), the α-nitroketone undergoes a cleavage reaction (path b). This cleavage reaction is well known when α-nitroketones are reacted with sodium hydroxide or alkoxides, but it is less well known for amines.



To investigate the mechanism of this reaction, 2-nitroheptan-3-one in benzene was refluxed with morpholine. The crude reaction mixture was examined by g.l.c. and nitroethane was identified. Removal of the solvent and distillation gave the amide (155) with ν max. 1650, 1420 and 1120 cm^{-1} and δ ($CDCl_3$) 3·8 (8H, singlet), 2·2-2·6 (2H, complex), 1·2-1·8 (4H, complex) and 1·0-1·2 (3H, complex).



[155]

Discussion of the tautomerization of α-nitroketones.

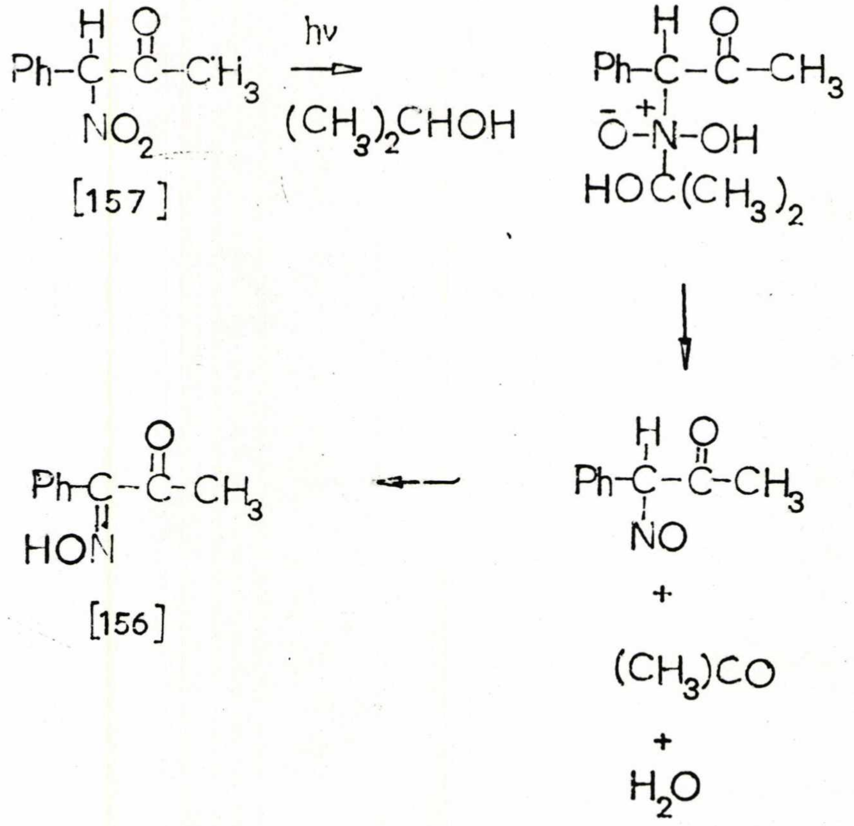
One can conclude that for acyclic α-nitroketones that only U.V. spectroscopy indicates the presence of a tautomer. The amount of tautomer present varies with the solvent. If the ε value for the tautomer is considered to be the same in all the solvents then the amount of tautomer present in each solvent relative to methanol can be estimated by the ratio of the ε values, shown below:

Solvent	Dielectric Constant[408]	Ratio of ε values
CH_3CN	36·2	0
CH_3OH	32·6	1
C_2H_5OH	24·3	1·8
$(CH_3)_2CHOH$	18·3	1·8
$(C_2H_5)_2O$	4·2	2·3
C_6H_6	2·27	2·9
$C_6H_5CH_3$	2·37	3·0
CCl_4	2·22	3·3
cyclo-C_6H_{12}	1·9	12·5

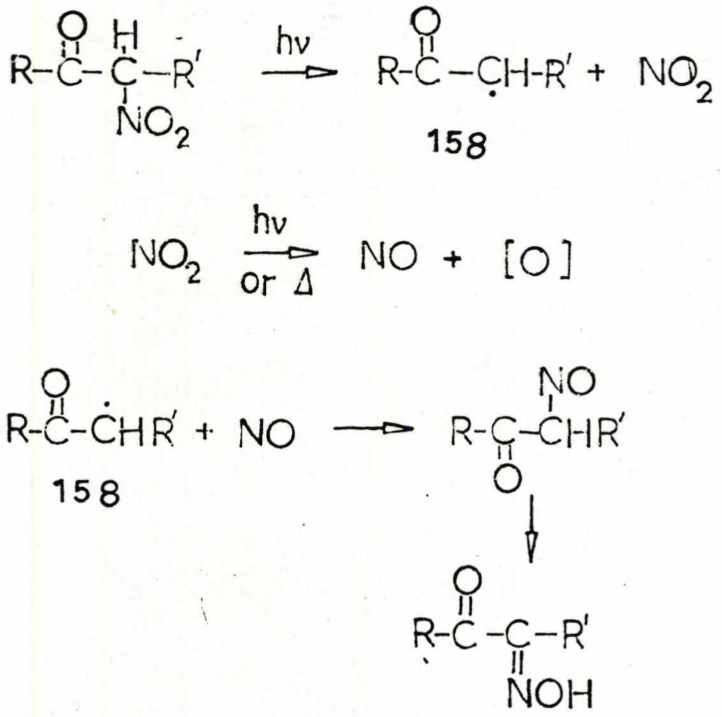
From these results it can be seen that the tautomeric form is most favoured in non-polar solvents. Protic solvents do not favour the tautomer and in aprotic solvents of high dielectric constant no tautomer was detected. This type of behaviour has been noted before. The greater amount of tautomer in non-polar solvents must be due to non-polar solvents stabilizing the tautomer to a greater extent than the polar and aprotic solvents.

Discussion

The major product obtained on irradiation of an acyclic α-nitroketone is an oximinoketone. To explain the formation of 1-hydroxyimino-1-phenylpropan-2-one (156) from 1-nitro-1-phenylpropan-2-one (157), Saito^{146,147} proposed the mechanism in the scheme below, which involves intermediates similar to those proposed by Reid and co-workers to explain the photochemical behaviour of nitroalkanes^{135}. This involves an initial hydrogen



abstraction by the excited nitro group and is based on analogy with early theories on the solution photochemistry of nitroalkanes. It has since been shown, however, that the primary photochemical pathway for nitroalkanes in solution is C-N bond cleavage^{137}. The photochemical conversion of 2-nitropentan-3-one to 2-hydroxyiminopentan-3-one in ethanol, cyclohexane acetonitrile and acetone was explained by an initial C-N bond cleavage. The nitrogen dioxide formed reacting thermally or photochemically to give nitric oxide which then recombines with radical (158) to give a nitroso compound which rearranges to the oximinoketone[149,387]. The cleavage of



the C-N bond as the initial photochemical step is likely. The cleavage of the carbon-substituent bond on irradiation of α-substituted ketones is well known[418]. For a system X-C-C=O, with X being an electronegative substituent, a $n\pi^*$ excited carbonyl group can eject substituents as either radicals or anions[419]. The strength of the C-N bond in α-nitroketones is not known. The C-N bond strength in nitroalkanes is in the region of 50-60 Kcal mole^{-1}. The C-N bond in α-nitroketones might be expected to be slightly stronger due to interactions with the carbonyl group. The energy of U.V. light at 300 n.m. is 95 Kcal mole^{-1}, which means that enough energy is being provided to cleave the C-N bond. This would give nitrogen dioxide, a very reactive species[420]. Nitrogen dioxide is reported to react very rapidly with alcohols in the gas-phase[421-424] to give nitric acid and the nitrite ester. A decrease in reactivity for alcohols in the sequence primary > secondary > tertiary as well as a decrease in reactivity with increasing carbon chain length has been reported[424]. In the liquid phase the formation of nitrites[423,425-427] and nitrates[428] have been reported. Reaction of alcohols with an excess of nitrogen dioxide at low temperatures gives the corresponding carboxylic acid[429], the initial reaction being the formation of the alkyl nitite and nitric acid. Nitrogen dioxide reacts rapidly with ethers to give fragmentation products[430-434] postulated to arise from abstraction of the α -hydrogen atom[430]. Nitrogen dioxide undergoes reaction with aromatic hydrocarons[436]; initially it was reported to be unreactive with toluene[435] but it has since been reported to nitrate both the side chain[437,438] and the benzene nucleus[438] and oxidize the side chain[439,440]. Nitrogen dioxide is photochemically reactive, absorbing over most of the U.V. and visible region[441]. The major photochemical process is loss of an oxygen atom with high quantum yield at 3130 Å [442]. Nitrogen dioxide can undergo reaction with a variety of organic compounds when used as the solvent to give various reaction products, which may then undergo further reaction. When alcohols are used as the solvent the formation of nitrites and in some cases nitrates have been reported. Alkyl nitrites are photochemically reactive, the primary photochemical process being N-O bond cleavage with loss of NO[443-445]. The thermal decomposition of nitrites <u>via</u> the cleavage of the N-O bond is also known[447,448]. Nitrates are photochemically reactive undergoing N-O bond cleavage to give nitrogen dioxide and the alkoxy radical[446]. Nitrates also decompose thermally by the same mechanism[446]. Nitric acid is photochemically reactive, forming nitrogen dioxide[449], this was later rationalized by a primary photoreaction of N-O bond cleavage, with a quantum yield of unity[450]. The conversion of nitrogen dioxide and alcohols to nitrites and nitric acid possibly involves hydrogen abstraction by the nitrogen dioxide. A radical abstraction process would remove a hydrogen α - to the hydroxy group, to give nitrous acid, which reacts with alcohols to produce nitrites.

$$NO_2 + RCH_2OH \longrightarrow HONO + RCHOH$$

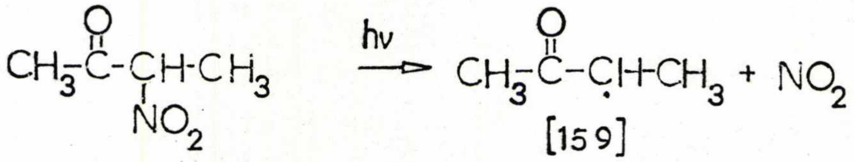
$$HONO + RCH_2OH \longrightarrow RCH_2ONO + H_2O$$

Nitrous acid has two primary photochemical pathways[451].

$$HNO_2 \xrightarrow{h\nu} HO\cdot + \cdot NO$$

$$HNO_2 \xrightarrow{h\nu} H\cdot + \cdot NO_2$$

The proposed scheme for the photodecomposition of α -nitroketones in alcohols is shown below. This scheme does not include the

(1) 

$$CH_3-\overset{\overset{O}{\|}}{C}-\underset{\underset{NO_2}{|}}{CH}-CH_3 \xrightarrow{h\nu} \underset{[159]}{CH_3-\overset{\overset{O}{\|}}{C}-\underset{\cdot}{C}H-CH_3} + NO_2$$

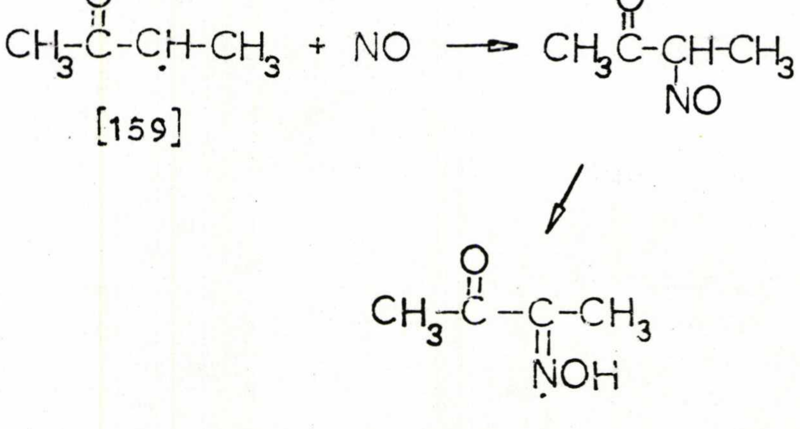
(2) $$NO_2 \xrightarrow{h\nu} NO + [O]$$

(3) $$NO_2 + RCH_2OH \longrightarrow R\underset{\cdot}{C}HOH + HONO$$

(4) $$HONO \xrightarrow{h\nu} HO\cdot + NO$$

(5) $$RCH_2OH + HONO \longrightarrow RCH_2ONO + H_2O$$

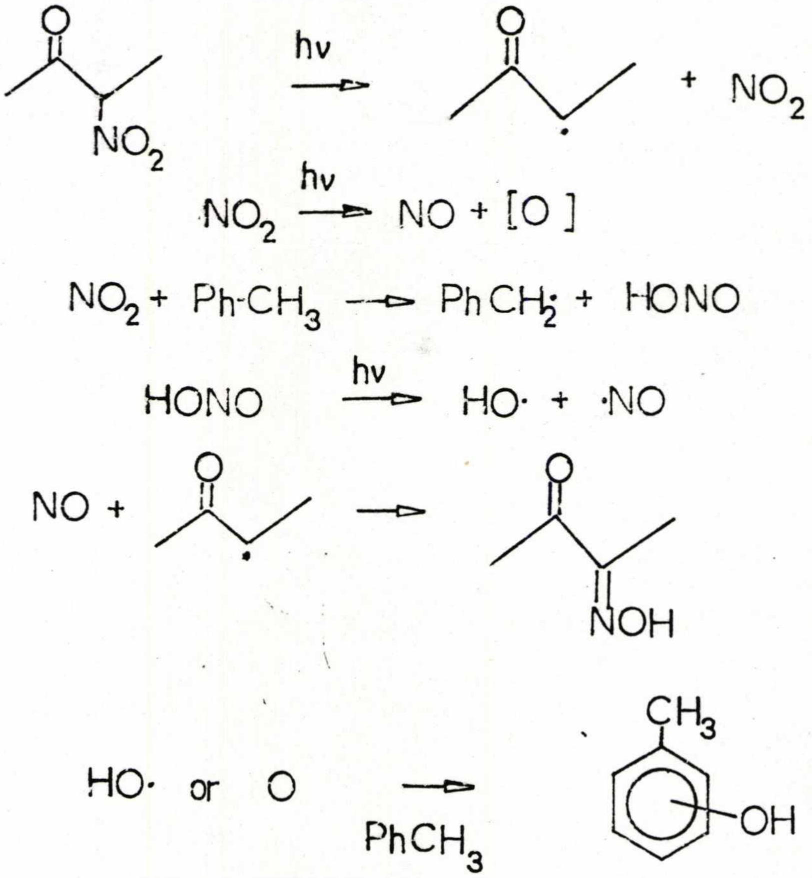
(6) $$RCH_2ONO \xrightarrow{h\nu} RCH_2O\cdot + NO$$

(7) 

$$\underset{[159]}{CH_3-\overset{\overset{O}{\|}}{C}-\underset{\cdot}{C}H-CH_3} + NO \longrightarrow CH_3\overset{\overset{O}{\|}}{C}-\underset{\underset{NO}{|}}{CH}-CH_3 \longrightarrow CH_3-\overset{\overset{O}{\|}}{C}-\underset{\underset{NOH}{\|}}{C}-CH_3$$

photodecomposition of alkyl nitrates and nitric acid which only lead to the regeneration of nitrogen dioxide. The scheme shows that nitrogen dioxide can be converted into nitric oxide, which under the reaction conditions is photochemically stable[452], in a variety of ways. The nitric oxide can recombine with the radical (159) to give a nitroso compound which rearranges to the oximinoketone[453]. A possible deactivating effect is nitric oxide acting as a triplet quencher[452]. Although it is not known if the nitroketone reacts <u>via</u> its triplet state and what the triplet state energy is, this possible source of deactivation cannot be ignored. From performing experiments using alcohols as the solvent, it was found that performing the irradiations under an atmosphere of nitrogen increases the yield of oximinoketone over irradiations where a nitrogen flush is used. This is interpreted as the nitrogen flushing out the intermediate nitric oxide and hence reducing the yield of oximinoketone obtained.

When solvents other than alcohols are used, an adaption of this applies. When benzene or toluene is used as the solvent, nitrogen dioxide is fairly thermally stable and hence photoreaction of the nitrogen dioxide is more probable. Nitrogen dioxide and benzene on photolysis are reported to give nitrobenzene[454] but this was not detected as a reaction product in this study. Phenol was, however, obtained which may result from the reaction of atomic oxygen with the solvent. An alternative explanation is that the hydroxy radical, produced by irradiation of nitrous or nitric acids, reacts with the solvent to give the observed product. The possibility of the phenol resulting from the photodecomposition of nitrobenzene cannot be overlooked. The isolation of <u>o</u>-, <u>p</u>- and <u>m</u>-cresols when toluene is used as the solvent is analogous. Isolation of dibenzyl with toluene as the solvent results from benzyl radicals resulting from hydrogen abstraction by nitrogen dioxide. The benzyl radicals can then react with another benzyl radical or be oxidized to give benzaldehyde the other reaction product. Nitrogen dioxide can react with the benzyl radical to give α -nitrotoluene. This, however, has been shown to be photochemically reactive[139], decomposing via an initial C-N bond cleavage which will regenerate the nitrogen dioxide. For toluene as the solvent, the postulated reaction mechanism is shown below.



When benzene is used as the solvent, the photodecomposition of the nitrogen dioxide is likely to be more important, as there are no easily abstractable hydrogens available.

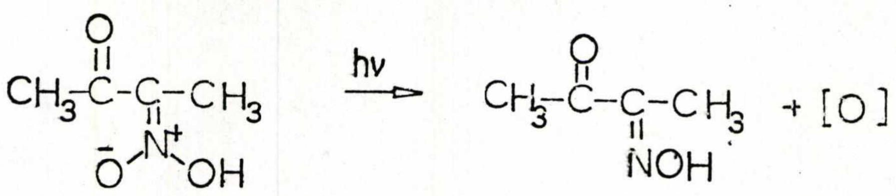
The production of 3-hydroxyiminobutan-2-one from 3-nitrobutan-2-one in a variety of solvents can be explained by the primary photochemical pathway being C-N bond cleavage, which is in agreement with the latest views on the solution photochemistry of nitroalkanes. A variation in the yield of oximinoketone with alcohols used was observed, as shown in the following table. For the α -nitroketone that has reacted, about the same percentage of nitroketone is converted into the oximinoketone, which suggests there is little difference with the solvent used for this part of

Solvent	Reaction time	% Nitroketone reacted	% Yield Oximinoketone	% Yield Oximinoketone, based on nitroketone reacted
CH_3OH	24 hours	36	16	44•5
C_2H_5OH	24 hours	79	28	35•4
$(CH_3)_2CHOH$	24 hours	81	40•5	49•4

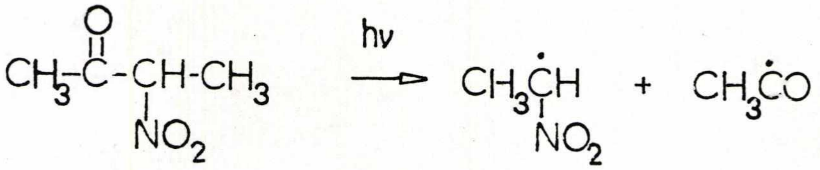
the reaction, the difference lies in the amount of time required for a given yield of oximinoketone to be obtained. For a given amount of time the greatest yields of oximinoketone for irradiations where a nitrogen flush was used are in the solvent order; propan-2-ol > ethanol > methanol and for irradiations where an atmosphere of nitrogen was used, ethanol > toluene > methanol > benzene. These results can be compared with the results of hydrogen abstraction by the triplet state of benzopheone where octan-2-ol > propan-2-ol > ethylbenzene > toluene > t-butylbenzene[455]. This suggests that the amount of oximinoketone obtained after a given amount of time depends on how fast a hydrogen abstraction reaction occurs. The most likely being nitrogen dioxide abstracting from the solvent, which will be favoured when the resultant radical is stabilized.

Alternative mechanisms for the production of the oximinoketone can also be considered. The involvement of a tautomer of the α-nitroketone is considered unlikely as it has been shown to be present in very small amounts. The tautomer was favoured in non-polar solvents but the yields of oximinoketone are, however, related to the ease of hydrogen abstraction from the solvent rather than solvent polarity, hence there is no relationship between the amount of tautomer present and the amount of oximinoketone obtained. U.V. light may cause the rearrangement of the enol to the nitroketone, as has been shown for β-ketoesters[456-458].

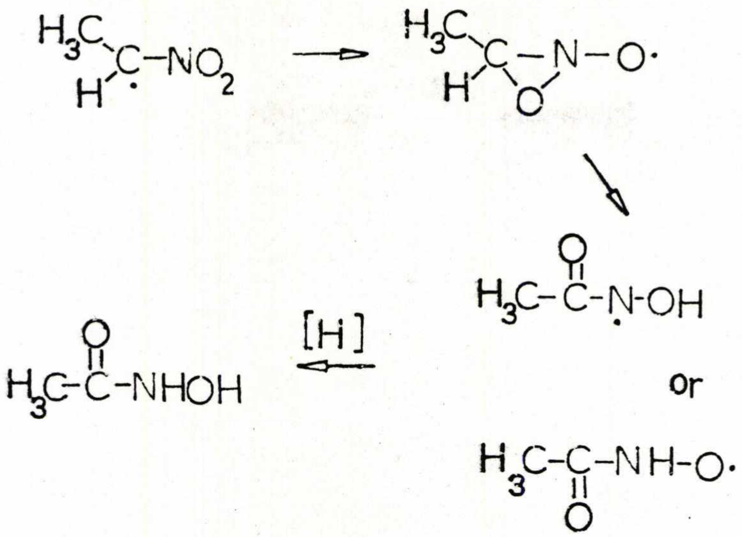
The formation of oximes on irradiation of aci-nitro compounds, by photochemical induced loss of oxygen, is known[145]. The aci-nitro tautomer of the nitroketone could undergo a similar photoreaction but this fails to explain the observed solvent dependence.



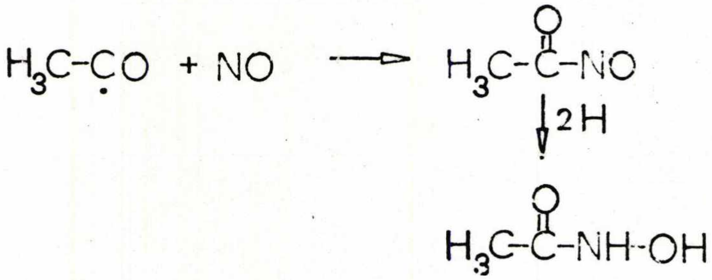
Acet hydroxamic acid was isolated as a minor photoproduct in the irradiation of 3-nitrobutan-2-one in some solvents. This may be the result of a Norrish type I cleavage. Butan-2-one has been reported to undergo a Norrish type I cleavage of the most substituted bond to give the most stable alkyl radical[459,460]. Norrish type I cleavage of 3-nitrobutan-2-one would give the α-nitroethyl radical and the acetyl radical.



Reaction pathways to the hydroxamic acid from both these radicals can be considered. α-Nitroalkyl radicals are known[461-463,142,143]. They decompose to give ketones via an oxaziridine-N-oxyl[142,143]. This oxaziridine radical could also undergo a rearrangement via 1,2 or 1,3 hydrogen migration and abstract another hydrogen from the solvent to the hydroxamic acid. No hydroxamic acid was isolated by these previous workers but they generated secondary nitroalkyl radicals which would not be expected to undergo this type of rearrangement in such a facile manner.



The second pathway to the hydroxamic acid is the acetyl radical reacting with nitric oxide. This nitroso compound could then abstract two hydrogens from the solvent to form the hydroxamic acid. Nitric oxide is known to react with acetyl radicals[464,465].



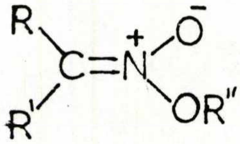
An attempt to differentiate between the two mechanisms by isolating the hydroxamic acid from 2-nitroheptan-3-one, which should give two different hydroxamic acids depending on the radical it comes from, however, failed.

Mass spectra of acyclic α-nitroketones

The major pathway for all the acyclic α-nitroketones used in this study is cleavage to give an acyl ion and a nitroalkyl radical. Compounds that are capable of undergoing an intramolecular rearrangement do not do this. There is no sign of any C-N bond cleavage in these spectra, which is postulated to be a major pathway in the photochemical decomposition of these compounds.

Thermal Reactions of α-Nitroketones

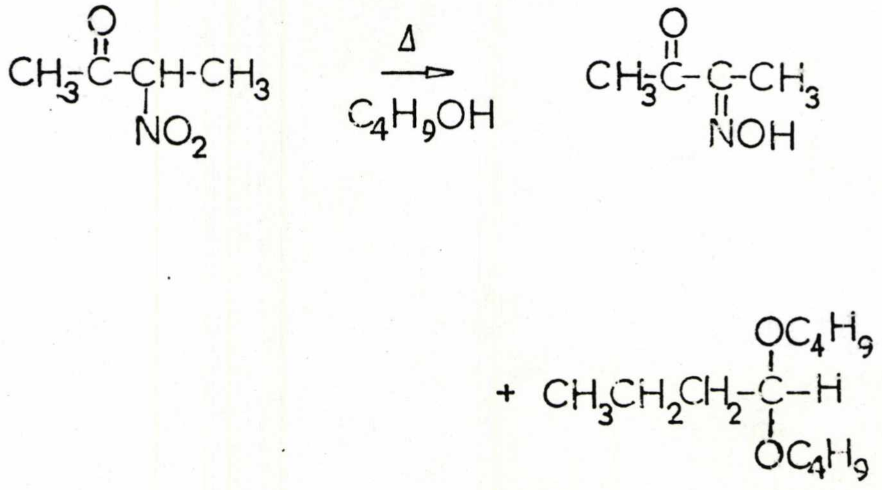
The gas-phase pyrolysis of nitroalkanes has been reviewed[466]. For the pyrolysis of nitroalkanes the primary process is C-N bond cleavage[469,470]. The thermal rearrangement of N-nitropyrazole and its derivatives has been reported and explained in terms of an intramolecular (1,5) sigmatropic shift[467,468]. The action of mineral acids on nitroalkanes gives carboxylic acids via hydroxamic acid intermediates[471]. The reactions of the aci-nitro form of nitroalkanes have been studied. Nitronic esters (160) are unstable species decomposing at room temperature[472]. Nitronic ester derivatives of α-nitrosulphones are reported to undergo thermal decomposition in refluxing dichloromethane to give oximes[473]. Pyrolysis of α-nitroepoxides gives initially the α-nitroketone which then undergoes further reactions. The initial step in the thermal decomposition of the nitroketone is C-N bond cleavage[147]. The pyrolysis of α-nitroketones in the absence of solvent under reduced pressure and in refluxing toluene gives rise to dicarbonyl compounds and fragmentation products[147,148], via an initial C-N bond cleavage. 3-Nitrocamphor undergoes condensation on heating[360]. 3-Nitrocamphor also has a stable nitronic ester which on heating rearranges to an oxaziran[378].



[160]

In an attempt to prepare the butyl- enol ether of an α-nitroketone, an 0•2 molar solution of 3-nitrobutan-2-one in butan-1-ol was refluxed for 24 hours with a trace amount of paratoluenesulphonic acid. Removal of the solvent gave an oil ν max. 3575, 3300, 2960, 1695, 1360, 1125 and 1030 cm^{-1} . This spectrum is not compatible with that of an enol ether. Use of preparative scale t.l.c. separated two products. The product with the greater R$_f$ value was an oil ν max. 2960, 1460 1130, 1080 and 1030 cm^{-1} and δ (CDCl$_3$) 4•8 (1H, triplet), 3•4 (4H, complex) 1•1-1•7 (12H, complex) and 0•9 (9H, triplet). The product with the smaller R$_f$ value was a solid which was recrystallised from petrol to give white crystals melting at 75-76 °C and ν max. 3575, 3300, 1695, 1460, 1125 and 1120 and δ (CDCl$_3$) 10•0 (1H, singlet), 2•0 (3H, singlet) and 2•4 (3H, singlet). The product of smaller R$_f$ value was identified as 3-hydroxyiminobutan-2-one which has a reported melting point[230], I.R [231,232] and n.m.r. spectra[233, 234] in agreement with the values recorded above.

The oil isolated by the use of t.l.c. was considered to be an ether (ν max. 1130 and 1080 cm^{-1}). A possible structure was considered to be the dibutylacetal of butanal (161), by a study of the n.m.r. spectrum. This was confirmed by a spectral comparison of the acetal prepared by literature methods[474] and the oil.



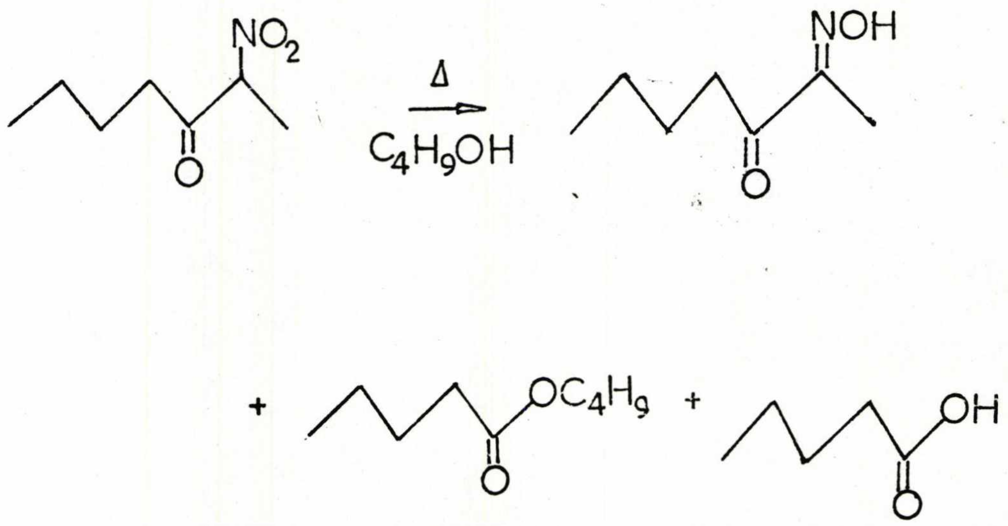
[161]

In order to determine the role of the sulphonic acid, it was om~~m~~itted. An 0·2 molar solution of 3-nitrobutan-2-one in butan-1-ol was refluxed. The reaction was followed by g.l.c. and after 15 hours, 91 % of the nitroketone had reacted and it had reacted completely after 20 hours. 3-Hydroxyiminobutan-2-one was present in 20 % yield and acetic acid in 8 % yield. The dibutylacetal of butanal was also present.

In order to determine whether this reaction is purely thermal 0·2 molar solutions of 3-nitrobutan-2-one were refluxed in solvents of approximately the same boiling point as butan-1-ol (117 °C). Solvents which failed to give any reaction were toluene, acetonitrile, nitroethane and _t_-butylalcohol. The reaction was observed to occur when propan-1-ol, di-n-butyl ether, dioxane and cyclohexanol were used as the solvents. The results are shown in the table below.

Solvent	% Conversion of Nitroketone	Reaction Time (hours)	Products (% yield)
Butan-1-ol (117 °C)	95	15	3-Hydroxyiminobutan-2-one (20 %) Acetic acid (8 %) Dibutylacetal of butanal
Propan-1-ol (97 °C)	75	35	3-Hydroxyiminobutan-2-one (12 %) Acetic acid (5 %) Dipropylacetal of propanal
Di-n-butyl ether (140 °C)	50	27	3-Hydroxyiminobutan-2-one (10 %) Acetic acid (3 %)
Dioxane (101 °C)	20	44	3-Hydroxyiminobutan-2-one (10 %) Acetic acid (2 %)
Cyclohexanol (160 °C)	50	22	3-Hydroxyiminobutan-2-one (5 %)
Toluene (112 °C)	--	70	No reaction
Acetonitrile (82 °C)	-	24	No reaction
Nitroethane (115 °C)	-	20	No reaction
_t_-Butyl alcohol (88 °C)	-	24	No reaction

In order to determine whether this reaction is general for acyclic α-nitroketones, an 0•2 molar solution of 2-nitroheptan-3-one was refluxed in butan-1-ol. After 35 hours the solvent was removed. Use of preparative scale t.l.c. led to the isolation of five bands. Band (1) was the dibutyl acetal of butanal. Band (2) was an oil ν max. 2962, 2940, 1735 and 1375 cm^{-1}, identified as n-butyl pentanoate (14 %). Band (3) was unreacted nitroketone (8 %). Band (4) was an oil ν max. 3500, 3300, 1690 1370 and 1010 cm^{-1}, identified as 2-hydroxyiminoheptan-3-one by a comparison with an authentic sample, prepared by zinc/acetic acid reduction of the 2-nitroheptan-3-one. Band (5) was an oil ν max. 2960-2880, 1710cm^{-1}, identified as pentanoic acid (10 %). The oximinoketone was obtained in 25 % yield.

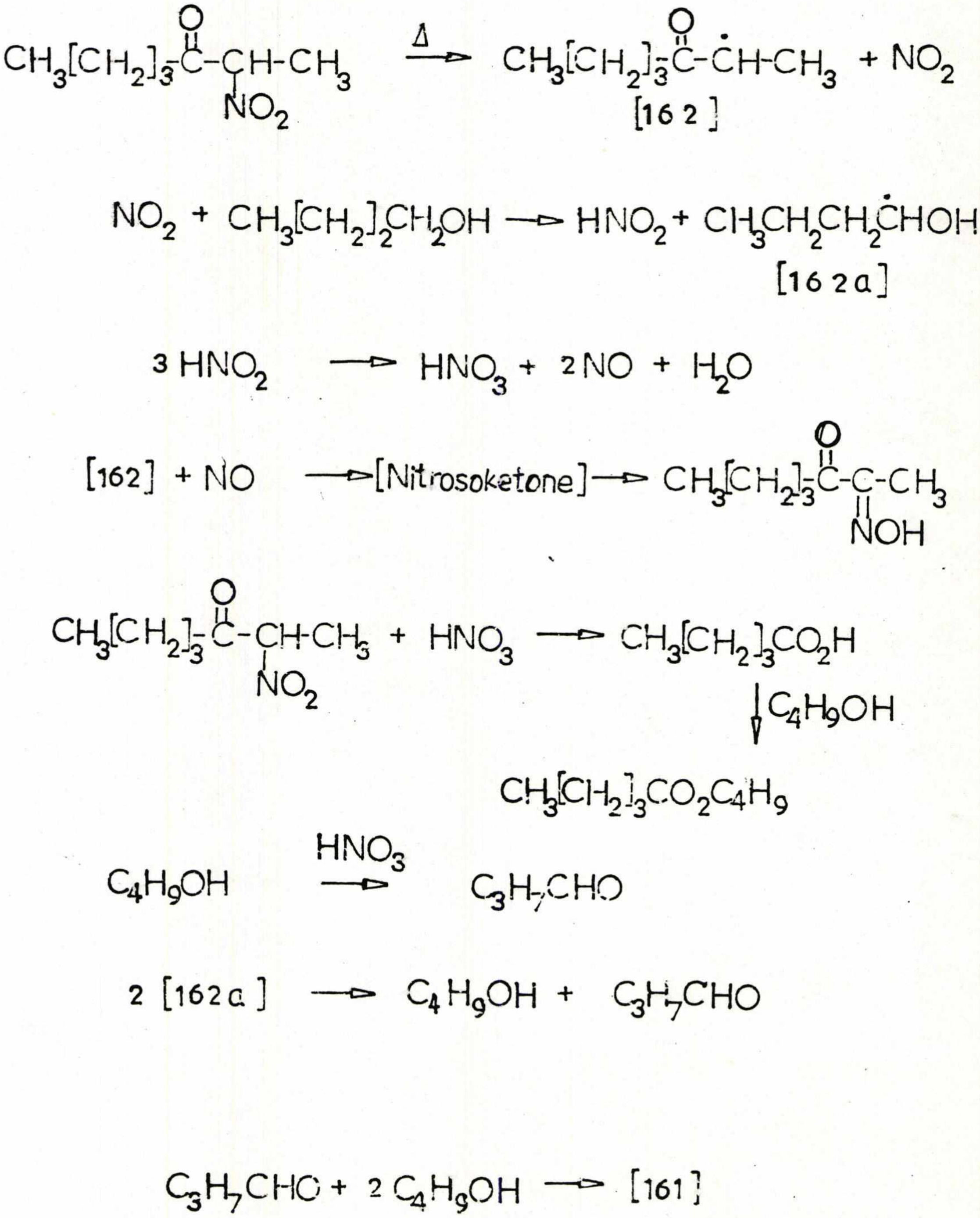


+ [161]

An 0•2 molar solution of 3-methyl-3-nitrobutan-2-one in butan-1-ol was refluxed for 21 hours. After this time 50 % of the nitroketone had reacted, The solvent was removed and preparative scale t.l.c. led to the isolation of the dibutylacetal of butanal.

For acyclic α-nitroketones in butan-1-ol, three types of product are obtained; a formal reduction product the oximinoketone, a carbon-

carbon bond cleavage product, the carboxylic acid and a solvent derived product. A mechanism to explain these products is shown in the scheme below, using 3-nitroheptan-2-one. This requires C-N bond cleavage as the initial step. Thermal reactions of nitro compounds to give C-N bond cleavage are well known in the gas-phase[466] but are unknown in solution. Nitrogen



$$\mathrm{CH_3[CH_2]_3\overset{O}{\overset{\|}{C}}-\underset{NO_2}{\underset{|}{CH}}-CH_3 \xrightarrow{\Delta} \underset{[162]}{CH_3[CH_2]_3\overset{O}{\overset{\|}{C}}-\dot{C}H-CH_3} + NO_2}$$

$$\mathrm{NO_2 + CH_3[CH_2]_2CH_2OH \longrightarrow HNO_2 + \underset{[162a]}{CH_3CH_2CH_2\dot{C}HOH}}$$

$$\mathrm{3\,HNO_2 \longrightarrow HNO_3 + 2\,NO + H_2O}$$

$$\mathrm{[162] + NO \longrightarrow [Nitrosoketone] \longrightarrow CH_3[CH_2]_3\overset{O}{\overset{\|}{C}}-\underset{NOH}{\underset{\|}{C}}-CH_3}$$

$$\mathrm{CH_3[CH_2]_3\overset{O}{\overset{\|}{C}}-\underset{NO_2}{\underset{|}{CH}}-CH_3 + HNO_3 \longrightarrow CH_3[CH_2]_3CO_2H \xrightarrow{C_4H_9OH} CH_3[CH_2]_3CO_2C_4H_9}$$

$$\mathrm{C_4H_9OH \xrightarrow{HNO_3} C_3H_7CHO}$$

$$\mathrm{2\,[162a] \longrightarrow C_4H_9OH + C_3H_7CHO}$$

$$\mathrm{C_3H_7CHO + 2\,C_4H_9OH \longrightarrow [161]}$$

dioxide is known to undergo a very fast reaction with both alcohols[421-429] and ethers[430-434]. The first step in both these cases is hydrogen abstraction to give nitrous acid, which breaks down to nitric oxide and nitric acid. Recombination of the nitric oxide with the radical (162) would give a nitroso compound which under the reaction conditions would isomerize to the more stable oximinoketone.

Evidence to support this part of the postulated mechanism comes from refluxing an 0•2 molar solution of 3-nitrobutan-2-one in butan-1-ol whilst a stream of nitrogen was passed through the solution. After 15 hours, 93 % of the nitroketone had reacted and 3 % of the oximinoketone was present in the reaction mixture. The percentage conversion of the nitroketone in this case is the same as in the standard case, yet the amount of the oximinoketone produced has been drastically reduced. This is due to the nitrogen flushing out the nitric oxide intermediate.

Formation of nitric acid can also explain the other observed products. Nitric acid is known to cleave α-nitroketones to give the corresponding carboxylic acids[353]. Under the conditions of the reaction, esterification would be expected to occur, with the nitric acid as the catalyst. Refluxing an 0•1 molar solution of pentanoic acid in butan-1-ol with a trace of nitric acid present for 20 hours gave a 80 % yield of n-butyl pentanoate as well as the dibutylacetal of butanal. Repeating the experiment without nitric acid gave only a 10 % yield of the ester and no acetal. The formation of the solvent derived product, the dibutylacetal of butanal, requires formation of butanal, formed by either nitric acid oxidizing butan-1-ol or else by disproportionation of two butan-1-ol derived radicals to give butanal and butan-1-ol. Once formed, the butanal undergoes reaction with butan-1-ol to give the dibutylacetal. Evidence to support this mechanism was obtained by refluxing butan-1-ol in the presence of a trace amount of nitric acid for 20 hours which gave the dibutylacetal as the only product. The intermediate was shown to be butanal by refluxing an 0•1 molar solution of butanal in butan-1-ol which gave an 80 % yield of the acetal after 20 hours. This indicates that butan-1-ol can be oxidized to butanal by nitric acid which then undergoes reaction to give the acetal.

According to previous work on the reaction of nitrogen dioxide and alcohols, n-butyl nitrite should be a reaction product[421-427]. However, this product was not observed in this study but refluxing an 0·1 molar solution of n-butyl nitrite in butan-1-ol for 20 hours gave the dibutylacetal of butanal as the only isolated product. An 0·1 molar solution of n-butyl nitrate refluxed in butan-1-ol, which is another possible intermediate[428], gave identical results. This indicates that if either of these compounds is present they react to form the acetal.

The stability of the oximinoketone to the reaction conditions was investigated. 3-Hydroxyiminobutan-2-one was found to be stable to refluxing in butan-1-ol for 20 hours, but refluxing an 0·2 molar solution of the oximinoketone in butan-1-ol with a trace of nitric acid for 20 hours caused 20 % of the oximinoketone to react and the formation of acetic acid (12 %).

To study the effect of nitric acid on the nitroketone, the thermal stability of these compounds in toluene was exploited. Refluxing an 0·1 molar solution of 3-nitrobutan-2-one in toluene with a trace amount of nitric acid caused 23 % of the nitroketone to react and the formation of acetic acid (6 %). These experiments show that the carboxylic acid obtained in this work may result from the cleavage of the nitroketone or the oximinoketone by the nitric acid.

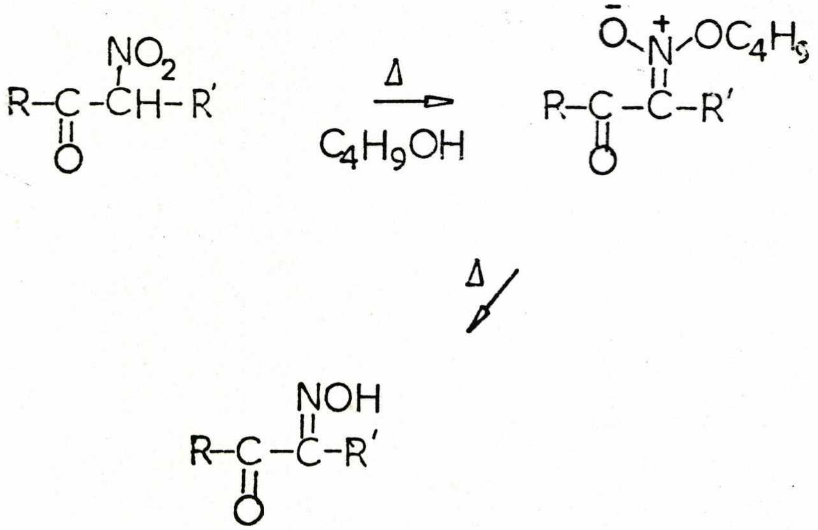
When ethers are used as the solvent a similar mechanism must operate although in these cases no stable solvent derived product is obtained. There is an interesting solvent dependence, the reaction only being observed in alcoholic or etheral solvents. This indicates that solvent polarity is not of prime importance, the important requirement is that the solvent is of type (163). These compounds can give rise to stabilized radicals by

$$RCH_2OR' \qquad R' = H \text{ or alkyl}$$

(163)

abstraction of a hydrogen α to the oxygen. This appears to be the most important feature in deciding whether a reaction will occur. The failure to observe the reaction when toluene is used as the solvent may be due to the abstraction reaction by nitrogen dioxide not being as facile in this solvent. However, refluxing an 0·16 molar solution of dinitrogen tetroxide in toluene for six hours gave rise to phenylnitromethane (50 %), benzaldehyde (5 %), benzylalcohol (4 %) and benzoic acid (3 %), which is are in agreement with previous work on the action of nitrogen dioxide on toluene$^{436-440}$. Hence if there was C-N bond cleavge when toluene is the solvent, one would expect signs of a reaction. Refluxing 3-nitrobutan-2-one in toluene for 70 hours led to the quantitative recovery of starting materials The failure of the nitroketones to undergo C-N bond cleavage in toluene and other solvents may be due to these compunds not having the appropiate abstractable hydrogens or else in the case of the alcohols and ethers there is a solvation effect.

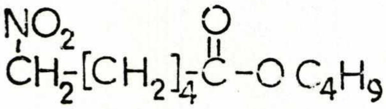
An alternative mechanism to explain the formation of the oximinoketone involves the formation of the nitronic ester derivative of the α-nitroketone. These compounds are known to be thermally unstable^{472,473}. This mechanism does not explain the formation of the other products and must



be treated with caution. It is extremely interesting to compare the thermal decomposition of acyclic α-nitroketones with their photochemical decomposition. This work suggests that they both occur *via* similar mechanisms, in both cases the primary process being C-N bond cleavage.

Thermal reactions of 2-nitrocyclohexanone.

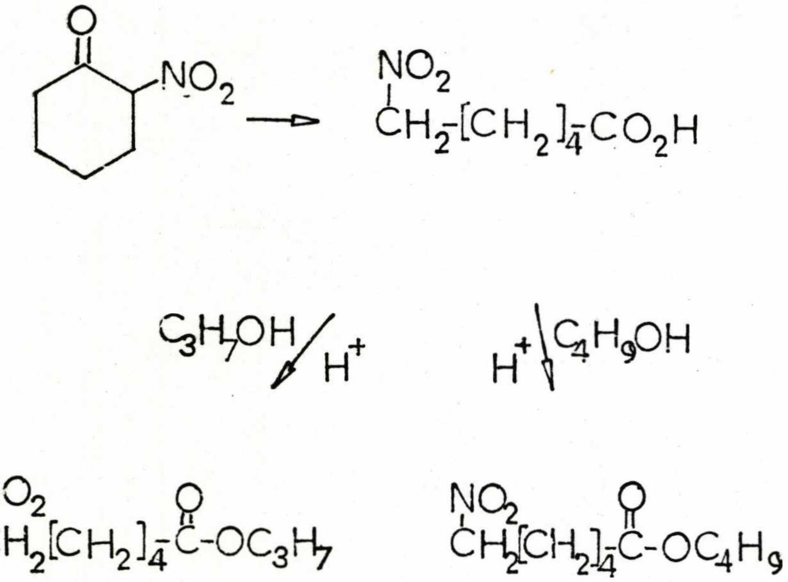
An 0·1 molar solution of 2-nitrocyclohexanone in butan-1-ol was refluxed for 20 hours, after which time the solvent was removed to give a brown oil, ν max. 2960, 2935, 1740, 1558, 1180 and 1160. The oil was examined by t.l.c.. Only one spot was obtained when plates were developed using three different solvents. This indicates that the oil contains one product. Use of preparative scale t.l.c. led to the isolation of one band with the same I.R. spectrum as above. The absorption at ν max. 1740, 1180 and 1160 cm^{-1} is indicative of esters, whilst ν max. 1550 and 1350 cm^{-1} is indicative of a saturated nitro group. As the reaction appears to give only one product, the reaction was repeated and the solvent removed to give a brown oil which was distilled to give a clear oil with an I.R. spectrum identical to the one detailed above and δ ($CDCl_3$) 4·3 (2H, triplet), 3·95 (2H, triplet), 1·1-2·4 (12H, complex) and 0·92 (3H, triplet). On the basis of this spectral data the product was found to be the n-butylester of 6-nitrohexanoic acid (83 %).



$$\overset{NO_2}{\overset{|}{CH_2}}-[CH_2]_4-\overset{O}{\overset{\|}{C}}-O\,C_4H_9$$

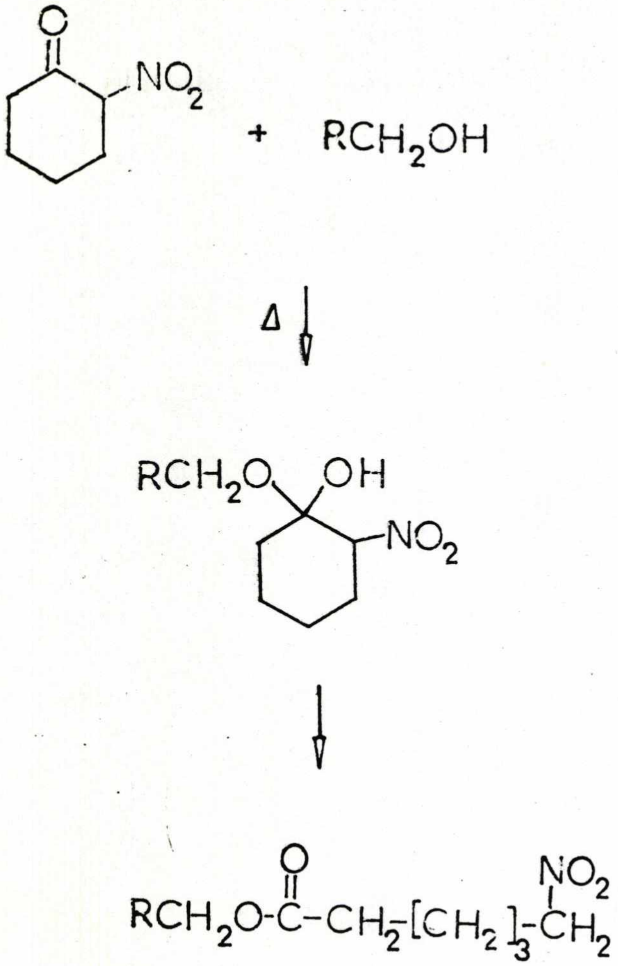
To investigate the generality of this reaction, 2-nitrocyclohexanone was refluxed in propan-1-ol for 20 hours. Removal of solvent gave a brown oil ν max. 2980, 1740, 1555, 1460, 1380, 1180 and 1160 cm^{-1} . Distillation of the oil gave a clear oil with an I.R. spectrum identical with that detailed above and δ ($CDCl_3$) 4·34 (2H, triplet), 3·91 (2H, triplet) 1·2-2·4 (10H, complex) and 0·92 (2H, triplet). On the basis of this spectral data and by analogy with the butan-1-ol case the product was the n-propylester of 6-nitrohexanoic acid, (79 %).

To confirm the assignment of these products as nitroesters, they were independently prepared for comparison purposes. 6-Nitrohexanoic acid was prepared from 2-nitrcyclohexanone[332], and the corresponding esters were prepared by refluxing the appropiate alcohol with a trace of sulphuric acid as a catalyst for 20 hours.



These esters were characterized by their I.R. and n.m.r. spectra and by elemental analysis. Comparison of the I.R. and n.m.r. spectra of the authentic esters with the thermal reaction products showed them to be identical.

The products in this case are derived from a ~~toally~~ totally different mechanism than for the acyclic case. A possible intermediate may be the hemi-ketal previously postulated by Feuer[333], however the possibility of the reaction requiring acid catalysis by nitric acid resulting from C-N bond cleavage cannot be overlooked.


NO2
+
RCH2OH
Δ
RCH2O
OH
NO2
O
NO2
RCH2O-C-CH2-[CH2]3-CH2

EXPERIMENTAL.

1. Instruments, Apparatus and Materials.

1.1. Spectrometers.

Ultraviolet spectra were recorded on a Unicam SP 800 spectrometer, using quartz cells of 1 c.m. pathlength. Infra-red spectra were recorded on either a Perkin-Elmer 237 or a 257 spectrometer using sodium chloride discs or solution cells (0·2 m.m. pathlength). ^{1}H n.m.r. spectra were recorded on a Perkin-Elmer r 10 instrument operating at 60 MHz or a Jeol ps-100 instrument operating at 100 MHz; tetramethylsilane was the internal standard. ^{13}C n.m.r. spectra were recorded on a Joel PS-100 instrument operating at 100 MHz. Mass-spectra were obtained with an A.E.I. MS 902 instrument operating with a 70 eV ionizing beam.

1.2. Melting points and elemental analysis.

Melting points were determined on a Kofler hot-stage apparatus and are uncorrected. Elemental analyses were obtained using an F and M Scientific 185 C, H and N analyser.

1.3. Chromatographic methods.

(a) G.L.C.

G.l.c. analyses were carried out using a Pye 104 gas chromatograph with a katherometer detector, with helium as carrier gas. A Kent Chromalog I integrator was used for quantitative work. Columns (4m) were of glass and packed with the following: PEGA on Chromosorb W, Apeizon L on Chromosorb P, Silicone SE 30 on Chromosorb W, Diisodecyl Phthalate on Chromosorb P and Versamid 930 on Chromosorb W.

(b) T.L.C.

Preparative t.l.c. plates (50 x 20 cm) were coated with GF$_{254}$ in the department and developed by U.V. light.

(c) Column chromatography.

Neutral alumina 100-200 mesh(Fis~~s~~ons) or Silica gel 60-120 mesh (BDH) were used.

1.4. Solvents.

Acetonitrile was refluxed over phosphorus pentoxide (2 x 12 hours) and distilled from fresh phosphorus pentoxide prior to use. Cyclohexene was purified by the following procedure. Peroxides were removed by shaking with freshly prepared ferrous sulphate solution until there was no evidence for further oxidation of the ferrous sulphate. The cyclohexene was then extracted with several portions of water, dried over sodium sulphate and then distilled. Other solvents used for irradiations and chromatography were of AR quality.

2a. Preparation of Nitroalkenes.

2a.1. Preparation of *E*-3-nitrobut-2-ene.

(a) 3-Nitrobutan-2-ol.

The nitroalcohol was prepared from nitroethane and acetaldehyde[389] and was obtained as a colourless liquid (52 %), bp 96-98°C at 6 m.m. Hg (lit.[389] 78°C at 17 m.m. Hg).

(b) 2-Acetoxy-3-nitrobutane.

The nitroacetate was prepared by the action of acetic acid on 3-nitrobutan-2-ol[409] and was obtained as a colourless liquid (70 %), bp 80-84 °C at 2 m.m. Hg (lit[409] 103°C at 10 m.m. Hg).

(c) E-3-Nitrobut-2-ene.

The nitroalkene was prepared by reacting 2-acetoxy-3-nitrobutane with sodium carbonate[410] and was obtained as a pale yellow liquid (50 %), bp 62-64° C at 22 m.m. Hg (lit.[410] 70°C at 30 m.m. Hg).

2a.2. Preparation of *E*-2-nitropent-2-ene.

(a) 2-Nitropentan-3-ol.

The nitroalcohol was prepared from nitroethane and propanal[389] and was obtained as a colourless liquid (61 %), bp 90-92° C at 0·7 m.m. Hg (lit.[389] 79°C at 2 m.m. Hg).

(b) 3-Acetoxy-2-nitropentane.

The nitroacetate was prepared by the action of acetic acid on 2-nitropentan-3-ol[412] and was obtained as a colourless liquid (69 %), bp 82-86°C at 0·6 m.m. Hg (lit.[412] 70-72°C at 0·4 m.m. Hg).

(c) E-2-nitropent-2-ene.

The nitroalkene was prepared by reacting 3-acetoxy-2-nitropentane with sodium carbonate[389] and was obtained as a colourless liquid (52 %), bp 70-72°C at 14 m.m. Hg (lit.[389] 57-58°C at 10 m.m. Hg).

2a.3. Preparation of *E*-3-nitropent-2-ene.

(a) 3-Nitropentan-2-ol.

The nitroalcohol was prepared from 1-nitropropane and acetaldehyde[388] and was obtained as a colourless liquid (66 %), bp 84-88°C at 2 m.m. Hg (lit.[388] 100°C at 10 m.m. Hg).

(b) 2-Acetoxy-3-nitropentane.

The nitroacetate was prepared by the action of acetic acid on 3-nitropentan-2-ol[411] and was obtained as a colourless liquid (71 %), bp 92-96°C at 0·6 m.m. Hg (lit.[411] 80-82°C at 0·4 m.m. Hg).

(c) E-3-nitropent-2-ene.

The nitroalkene was prepared by reacting 2-acetoxy-3-nitropentane with sodium carbonate[410] and was obtained as a pale yellow liquid (46 %) bp 72-74°C at 22m.m. Hg (lit.[411] 59-61°C at 9m.m. Hg)

2a.4. E-2-Methyl-4-nitropent-3-ene.

(a) 2-Methyl-4-nitropentan-3-ol.

The nitroalcohol was prepared from nitroethane and isobutraldehyde[389] and was obtained as a colourless liquid (48 %), bp 92-94°C at 0·4 m.m. Hg (lit.[389] 89°C at 2 m.m. Hg).

(b) 3-Acetoxy-2-methyl-4-nitropentane.

The nitroacetate was prepared by the action of acetic acid on 2-methyl-4-nitropentan-3-ol[411] and was obtained as a colourless liquid (85 %) bp 98-100°C at 0·8 m.m. Hg.

(c) E-2-Methyl-4-nitropent-3-ene.

The nitroalkene was prepared by reacting 3-acetoxy-2-methyl-4-nitropentane with sodium carbonate[389] and was obtained as a pale yellow liquid (53 %) bp 110-112°C at 14 m.m. Hg (lit.[389] 57°C at 1 m.m. Hg).

2a.5. Preparation of E-1-Nitroprop-1-ene.

(a) 1-Nitropropan-2-ol.

The nitroalcohol was prepared from nitromethane and acetaldehyde[409] and was obtained as a colourless liquid (48 %) bp 92-94°C at 3m.m. Hg.

(b) E-1-Nitroprop-1-ene.

The nitroalkene was prepared by heating 1-nitropropan-2-ol with phthalic anhydride[413] and was obtained as a yellow liquid (67 %) bp 96-98°C at 32 m.m. Hg (lit.[413] 54°C at 28 m.m. Hg).

2a.6. Preparation of E-2-Methyl-3-nitrobut-2-ene.

(a) 2-Methyl-3-nitrobutan-2-ol.

The nitroalcohol was prepared from nitroethane and acetone[414] and was obtained as a colourless liquid (9 %) bp 76-78°C at 0·4 m.m. Hg.

(b) 2-Acetoxy-2-methyl-3-nitrobutane.

(i) The action of acetic acid on 2-methyl-3-nitrobutan-2-ol using the method of Tindall[409] gave a brown oil (27 %), with the spectral properties indicating that it was the desired nitroacetate but it could not be obtained in a pure state.

(ii) The nitroacetate was prepared by the action of acetyl nitrate on 2-methylbut-2-ene[415] and was obtained as a colourless liquid (60 %) bp 80-82°C at 4 m.m. Hg (lit.[415] 60-62°C at 1·3 m.m. Hg).

(c) E-2-Methyl-3-nitrobut-2-ene.

The nitroalkene was prepared by reacting 2-acetoxy-2-methyl-3-nitrobutane with sodium carbonate and was obtained as a pale yellow liquid (12 %) bp 70-75°C at 10 m.m. Hg.

2a.7. Preparation of 1-Nitro-2-phenylethylene (β-Nitrostyrene).

The nitroalkene was prepared by reacting together benzaldehyde and nitromethane[318] to give yellow crystals, recrystallized from methanol (70 %) mp 58°c (lit.[318] 58°c).

2b. Photorearrangements of Nitroalkenes.

The photoreactions in this section, unless otherwise specified, were carried out with a 500 W Hanovia medium pressure mercury arc lamp surrounded by a water cooled pyrex jacket, which only allows light of wavelength greater than 300 n.m. to pass. A reactor fitted over the cooling jacket and held 160 mls of solution. Dry oxygen free nitrogen, saturated with solvent vapour was passed through the solution for at least an hour prior to irradiation and the reactor was sealed. The reaction was follwed by observing the reduction in intensity of the assymmetric stretch of the unsaturated nitro group (1510 cm^{-1}) or by following the disappearance of the nitroalkene by g.l.c.

2b.1(i). Irradiation of E-3-Nitrobut-2-ene in methanol.

A solution of E-3-nitrobut-2-ene (0·02 mole) in methanol (160 mls) was irradiated for 15 hours. The solvent was removed under reduced pressure to give a brown oil. Use of preparative scale t.l.c. (using dichloromethane as the developing solvent) led to the isolation of a solid which was recrystallized from 60/80 petrol to give white crystals mp 75-76 °C, ν max. 3570, 3300, 1690, 1360 and 1020 cm $^{-1}$ and δ ($CDCl_3$) 10·02 (1H, singlet), 2·48 (3H, singlet) and 2·02 (3H, singlet). This was identified as 3-hydroxyiminobutan-2-one, isolated in 21 % yield.

2b.1(ii). Irradiation of E-3-nitrobut-2-ene in methanol (quatitatively followed).

A solution of E-3-nitrobut-2-ene (0·02 mole) in methanol (160 mls) was irradiated and the disappearance of the nitroalkene and the appearance of the oximinoketone was quantitatively followed by g.l.c. After 12 hours, the nitroalkene had completely reacted and the yield of 3-hydroxyiminobutan-2-one was determined to be 27 % . A peak in the g.l.c. trace of shorter retention time than the E-isomer was noted. The ratio of the area of the peak due to the E-isomer to that of the peak of shorter retention time (0·65) did not vary greatly as both peaks diminished in value. This new peak was assigned to the Z-isomer. 2-Methoxy-3-nitrobutane and 3-nitrobut-1-ene were not detected in the reaction mixture.

2b.1(iii). Irradiation of E-3-nitrobut-2-ene in methanol; detection of the Z-isomer.

A solution of E-3-nitrobut-2-ene (0·02 mole) in methanol (160 mls) was irradiated. After 3 hours, g.l.c. indicated that the short retention time photoproduct was present and the U.V. spectrum was determined. The maximum at 252 n.m. was not well enough defined, however, to allow assignment of this peak to the Z-isomer.

2b.1(iv). Irradiation of E-3-nitrobut-2-ene in methanol; detection of the Z-isomer.

A solution of E-3-nitrobut-2-ene (0·05 mole) in methanol (100 mls) was irradiated using a 100 W medium pressure lamp, under an atmosphere of nitrogen. After 10 hours, 50 % of the E-isomer had reacted and the new peak (shorter retention time) was present in the g.l.c. trace but little oximinoketone had been formed. The ^{1}H n.m.r. spectrum of the reaction mixture showed absorption due to the E-isomer at 7·2 δ and absorption due to the Z-isomer at 6·0 δ . As the Z-isomer was the only new compound observed in the reaction mixture, the new peak in the g.l.c. trace was assigned to the Z-isomer.

2b.2. Preparation of 2-methoxy-3-nitrobutane.

The nitroether was prepared by the action of sodium methoxide on E-3-nitrobut-2-ene[411] and was obtained as a colourless liquid (30 %) bp 70-72°C at 30 m.m. Hg (lit.[411] bp 96-98°C at 40 m.m. Hg).

2b.3. Preparation of 3-nitrobut-1-ene.

The nitroalkene was prepared by the action of acetyl nitrate on cis-but-2-ene[415] and was obtained as a colourless liquid (16 %) bp 76-78°C at 21 m.m. Hg (lit.[415] 35-40°C at 15 m.m. Hg).

2b.4. Irradiation of E-3-nitropent-2-ene in methanol.

A solution of E-3-nitropent-2-ene (0·02 mole) in methanol (160 mls) was irradiated for 12 hours. The solvent was removed under reduced pressure to leave a brown oil. Using preparative scale t.l.c. (dichloromethane as the developing solvent) led to the isolation of a solid which was recystallized from 60/80 petrol to give white crystals mp 60-62°C, ν max. 3575, 3360, 2980, 1690, 1360, 1040 and 980 cm^{-1} and δ ($CDCl_3$) 2·9 (2H, quartet), 2·05 (3H, singlet) and 1·15 (3H, triplet). This was identified as 4-hydroxyiminopentan-3-one[238]. Comparison of the retention time of the reaction product with an authentic sample on two g.l.c. columns confirmed this assignment. The yield of the product by g.l.c. analysis of the reaction mixture was 31 % . Samples of the reaction solution, removed during the course of the reaction, examined by g.l.c. showed the presence of a peak of shorter retention time than that of the E-isomer. By analogy with E -3-nitrobut-2-ene , this peak was assigned to the Z-isomer. The ratio of the E to the Z-isomer did not vary as the nitroalkene reacted.

2b.5. Preparation of 4-hydroxyiminopentan-3-one.

The hydroxyiminoketone was prepared by the action of amyl nitrite on pentan-3-one[238] and was obtained as white crystals (28 %) mp 60-62° C (lit.[238] 59-62°C).

2b.6(a). Irradiation of E-2-nitropent-2-ene in methanol.

A solution of E-2-nitropent-2-ene (0·02 mole) in methanol (160 mls) was irradiated for five hours. The solvent was removed under reduced pressure to leave a brown oil with ν max. 1550 and 1690 cm^{-1}. Use of preparative scale t.l.c. (dichloromethane as developing solvent) led to the isolation of a solid which was recrystallised from 60/80 petrol mp 54-56°C ν max. 3570, 3300, 1690 and 1360 cm^{-1} and δ ($CDCl_3$) 1·0 (3H, triplet), 2·4 (2H, complex), 2·5 (3H, singlet) and 10·0 (1H, singlet). This product was identified as 3-hydroxyiminopentan-2-one[239] and was confirmed by a g.l.c. comparison with an authentic sample (PEGA/ Chromosorb W). The yield of the product (g.l.c. analysis) was 4 %. Starting material was also isolated (10 %). This was considered to be derived from the rearrangement of a photoproduct on the silica gel. To isolate this photoproduct the irradiation was repeated.

2b.6(b). Irradiation of E-2-nitropent-2-ene in methanol.

A solution of E-2-nitropent-2-ene (0·02 mole) in methanol (160 mls.) was irradiated for five hours. The solvent was removed under reduced pressure to leave a brown oil identical to that obtained above. Distillation under reduced pressure gave an oil bp 80-82°C at 20 m.m. Hg, ν max. 2980, 2940, 1545, 1380, 1355, 960 and 860 cm^{-1} and δ ($CDCl_3$) 1·7 (3H, doublet), 1·85 (3H, doublet), 5·2 (2H, complex) and 6·1 (1H, complex) identified as 4-nitropent-2-ene by the spectral data, which is in complete agreement with published data[227], and obtained in 15 % yield. 3-Hydroxyiminopentan-2-one could not be isolated from the residues of the distillation. G.l.c. examination of samples taken from the reaction mixture during the course of the irradiation showed the presence of two peaks of shorter retention time than E-2-nitropent-2-ene. One was identified as 4-nitropent-2-ene and the other was assigned to the

Z-isomer. The ratio of the E to Z isomers did not vary as the irradiation continued.

2b.7. Preparation of 3-hydroxyiminopentan-2-one.

The hydroxyiminoketone was prepared by the action of amyl nitrite on pentan-2-one and was obtained as white crystals (37 %) mp 53-55°C (lit.[239] 53-55°C).

2b.8(a). Irradiation of 4-methyl-2-nitropent-2-ene in methanol.

A solution of 4-methyl-2-nitropent-2-ene (0·02 mole) in methanol (160 ml) was irradiated for 10 hours. The solvent was removed under reduced pressure to leave a brown oil ν max. 3570, 3300, 2970, 1760, 1740, 1960, 1550, 1450 and 1380 cm^{-1}. Use of preparative scale t.l.c. (using dichloromethane as the developing solvent) led to the isolation of a solid which on recrystallisation from 60/80 petrol gave white crystals mp 76-77°C and ν max. 3570, 3300, 1690 and 1360 cm^{-1}, identified as 3-hydroxyimino-4-methylpentan-2-one[240]. The yield of the photoproduct (g.l.c. analysis) was 5 % . The other photoproducts could not be isolated by t.l.c. and hence the irradiation was repeated.

2b.8(b). Irradiation of 4-methyl-2-nitropent-2-ene in methanol.

4-Methyl-2-nitropent-2-ene was irradiated in methanol under identical conditions to 2b.8(a). The brown oil was this time distilled under reduced pressure. The distillate, bp 30-40°C at 1·0 mm Hg and ν max. 1760 and 1550 cm^{-1}. This was assumed to be a mixture of an unknown compound and the deconjugated nitroalkene. This mixture could not however be separated by chromatography.

2b.9. Preparation of 3-hydroxyimino-4-methylpentan-2-one.

The hydroxyiminoketone was prepared by the action of 4-methylpentan-2-one[240] and was obtained as white crystals (30 %) mp 76-77 C (lit.[240] mp 76-77°C).

2b.10. Irradiation of 3-methyl-2-nitrobut-2-ene in methanol.

A solution of 3-methyl-2-nitrobut-2-ene (0·01 mole) in methanol (160 ml) was irradiated for 16 hours. After this time, all the nitroalkene had reacted and the only product obsrved by g.l.c. (PEGA / Chromosorb W and

Diisodecyl phthalate / Chromosorb P) was 2-methyl-3-nitrobut-1-ene, identified by comparison with an authentic sample. The solvent was removed under reduced pressure to give a brown oil ν max. 1710, but no pure products could be obtained using t.l.c.

2b.11. Preparation of 2-methyl-3-nitrobut-1-ene.

The nitroalkene was prepared by the action of acetyl nitrate on 2-methylbut-2-ene[415] and was obtained as a colourless oil (12 %) bp 35-40°C at 6mm Hg (lit.[415] 54-55°C at 19·5 mm Hg).

2b.12(a). Irradiation of E-1-nitroprop-1-ene.

A solution of E-1-nitroprop-1ene (0·03 mole) in methanol (160 ml) was irradiated for 20 hours. The solvent was removed under reduced pressure to leave a brown oil ν max. 1550 cm^{-1}. Use of column chromatography (silica gel) led to the isolation of three products. The first was a white solid, after recrystallisation from petrol , mp 52-55°C, ν max. 1550 and 1370 cm^{-1} and δ (CDCl$_3$) 4·4-4·8 (3H, multiplet), 2·4-2·8 (1H, complex) and 1·0-1·3 (5H, complex) and m/e 83, 55 and 41. Elemental analysis indicated an empirical formula of $C_3H_6NO_2$, (found C, 41·3; H, 7·1; N, 15·5). This product was not identified.

The second product was a yellow liquid ν max. 1550, 1370 and 1080 cm^{-1} and δ (CDCl$_3$) 4·2-4·7 (3H, complex), 3·5 (3H, singlet) and 1·3 (3H, doublet) identified as 2-methoxy-3-nitropropane by comparison with an authentic sample. This photoproduct was obtained in 29 % yield. The third photoproduct was a yellow liquid ν max. 3500, 1550 and 1370 cm^{-1} and δ (CDCl$_3$) 4·4-4·8 (3H, complex) and 1·2-1·4 (5H, complex). This photoproduct decomposed on distillation and was not identified.

2b.12(b). Stability of E-1-nitroprop-1-ene in methanol.

A sample of 5 mls of (a), before irradiation, when left in normal laboratory light had present after 20 hours 2-methoxy-3-nitropropane.

2b.12(c). Stability of E-1-nitroprop-1-ene in methanol in the absence of light.

A solution of E-1-nitroprop-1-ene (0·03 mole) in methanol (160 mls) was left in the dark in the irradiation chamber for 40 hours. After this time startingnitroalkene was quantitatively recovered.

2b.13(a). Refluxing E-1-nitroprop-1-ene in methanol.

A solution of E-1-nitroprop-1-ene (0·01 moles) in methanol (50 mls) was refluxed for 40 hours in normal laboratory light. The solvent was removed under reduced pressure and the crude product distilled under reduced pressure to give 2-methoxy-3-nitropropane (60 %).

2b.13(b). Refluxing E-1-nitroprop-1-ene in methanol (all black apparatus).

A solution of E-1-nitroprop-1-ene (0·03 moles) in methanol (160 mls) was refluxed for 40 hours in an all black apparatus. The solvent was removed under reduced pressure and the crude product distilled under reduced pressure to give 2-methoxy-3-nitropropane (66 %).

2b.14. Preparation of 2-methoxy-3-nitropropane.

The nitroether was prepared by the action of sodium methoxide on 1-nitroprop-1-ene[235] and was obtained as a colourless liquid (42 %) bp 116-120°C at 24 mm Hg (lit.[235] 62°C at 12 mm Hg).

2b.15(a). Irradiation of E- β -nitrostyrene in methanol.

A solution of β-nitrostyrene (0·015 mole) in methanol (110 mls) was irradiated (100 W lamp, quartz filter, nitrogen flush throughout the irradiation) for 48 hours, after which time all the nitrostyrene had reacted. The solvent was removed under reduced pressure to give a brown oil ν max. 1550 cm^{-1}. Use of preparative scale t.l.c. led to the isolation of an oil ν max. 1550 and 1360 cm^{-1} and δ ($CDCl_3$) 7·8 (10H, singlet), 5·6-4·5 (5H, complex) and 3·25 (3H, singlet), identified as 1-methoxy-2,4-dinitro-1,3-diphenylbutane obtained in 5 % yield, by comparison with an authentic sample. G.L.C. analysis of samples after various periods of irradiation showed a peak of shorter retention time than the E -isomer which was assigned to the Z-isomer.

2b.15(b). Irradiation of E- β -nitrostyrene in methanol.

A solution of E- β -nitrostyrene (0·015 mole) in methanol (110 mls) was irradiated (100 W lamp, pyrex filter, nitrogen flush throughout the irradiation) for 65 hours. 1-Methoxy-2,4-dinitro-1,3-diphenylbutane (5 %) was isolated.

2b.16. Preparation of 1-methoxy-2-nitro-1-phenylethane and its thermal reactions.

β-Nitrostyrene (0·05 mole) in methanol (50 mls) was added to sodium methoxide (0·05 mole) in methanol (50 mls) and stirred at room temperature for two hours. Neutralization with aqueous acetic acid and extraction with ether led to a yellow oil ν max. 1535 and 1360 cm^{-1}, assumed to be the desired 1-methoxy-2-nitro-1-phenylethane. After 12 hours at room temperature the oil solidified and had ν max. 1550 and 1360 cm^{-1}. Recrystallization from methanol gave 1-methoxy-2,4-dinitro-1,3-diphenylbutane (28 %).

2b.17. Preparation of 1-methoxy-2,4-dinitro-1,3-diphenylbutane.

This was prepared by reacting β-nitrostyrene with sodium methoxide and was obtained as white crystals (56 %) mp 151-152°C (lit.[247] 151-152°C).

2b.18. Irradiation of E-3-nitrobut-2-ene in cyclohexane.

A solution of E-3-nitrobut-2-ene (0·02 mole) in cyclohexane (160 mls) was irradiated for 30 hours. The solvent was removed under reduced pressure and t.l.c. isolated 3-hydroxyiminobutan-2-one, previously identified by a g.l.c. comparison with an authentic sample. A brown tar was also obtained which contained the oximinoketone but which could not be purified. The yield of photoproduct (by g.l.c.) was 18 % . The Z-isomer was identified by g.l.c. and the ratio of E- to Z-isomers remaied constant at 1:1.

2b.19. Irradiation of E-3-nitrobut-2-ene in acetonitrile.

A solution of E-3-nitrobut-2-ene (0·02 mole) in acetonitrile (160 mls) was irradiated for 15 hours. 3-Hydroxyiminobutan-2-one was isolated using t.l.c., previously being identified by a g.l.c. comparison with authentic material. The yield of photoproduct (by g.l.c.) was 29 % .

2b.20. Irradiation of E-3-nitrobut-2-ene in acetone.

A solution of E-3-nitrobut-2-ene (0·02 mole) in acetone (160 mls) was irradiated for 10 hours. 3-Hydroxyiminobutan-2-one was isolated using t.l.c. (dichloromethane as developing solvent). The yield of photoproduct (by g.l.c.) was 22 %.

2b.21(a). Irradiation of E-3-nitropent-2-ene in acetic acid.

A solution of E-3-nitropent-2-ene (0·02 mole) in acetic acid (160 mls) was irradiated for 16 hours. The solvent was removed under reduced pressure to give a brown oil. Using preparative scale t.l.c. with dichloromethane as the developing solvent, 4-hydroxyiminopentan-3-one (6 %) was isolated along with an oil ν max. 2970, 1780, 1700, 1360 and 1170 cm^{-1} and δ ($CDCl_3$) 3·1 (2H, quartet), 2·3 (3H, singlet), 2·1 (3H, singlet) and 1·2 (3H, triplet) identified as the acetate of 4-hydroxyiminopentan-3-one.

2b.21(b). Stability of 4-hydroxyiminpentan-3-one in acetic acid.

A solution of 4-hydroxyiminopentan-3-one (0·005 mole) in acetic acid (25 mls) on standing for 48 hours at room temperature led to 80 % recovery of the oximinoketone and 15 % yield of the acetate of 4-hydroxyiminopentan-3-one.

2b.22(a). Stability of E-3-nitropent-2-ene in acetic acid.

A solution of E-3-nitropent-2-ene (0·005 mole) in acetic acid (25 mls) on standing for 120 hours at room temperature led to the quantitative recovery of the nitroalkene.

2b.22(b). Refluxing E-3-nitropent-2-ene in acetic acid.

A solution of E-3-nitropent-2-ene (0·01 mole) in acetic acid (50 mls) was refluxed for 70 hours. After this time 60 % of the nitroalkene had reacted and 2-acetoxy-3-nitropentane (58 %) was isolated by distillation under reduced pressure.

2b.23. Thermal stability of 2-nitro-1-phenylprop-1-ene in acetic acid.

A solution of 2-nitro-1-phenylprop-1-ene (0·01 mole) was refluxed in acetic acid (50 mls) for 72 hours. Starting nitroalkene was quantitatively recovered.

2b.24. Irradiation of 1-nitroprop-1-ene in acetonitrile.

A solution of E-1-nitroprop-1-ene (0·02 mole) in acetonitrile (160 mls) was irradiated for 30 hours. Removal of the solvent under reduced pressure gave a brown oil ν max. 1550 cm^{-1}. Use of t.l.c. failed to give any pure products The Z-isomer was detected by g.l.c. in samples removed during the course of the irradiation, by the appearance of peak, in the g.l.c. trace of shorter retention time than the E-isomer which was in agreement with published data[227].

2b.25. Irradiation of 3-nitrobut-1-ene in methanol.

A solution of 3-nitrobut-1-ene (0·02 mole) in methanol (160 mls) was irradiated for 20 hours, when (by g.l.c.) 5 % of the nitroalkene had reacted. After 40 hours, 15 % of the nitroalkene had reacted.

2b.26. Irradiation of E-3-nitrobut-2-ene and ethyl acrylate in acetonitrile.

A solution of E-3-nitrobut-2-ene (0·02 moles) and ethyl acrylate (0·1 mole) in 150 mls of acetonitrile was irradiated for 16 hours. The solvent was removed under reduced pressure to give a brown oil ν max. 1720 and 1360 cm^{-1} and δ ($CDCl_3$) 4·4 (triplet), 2·4 (singlet), 2·3-2·1 (multiplet), 2·0 (singlet) and 1·1-1·5 (multiplet). This oil was distilled under reduced pressure to give 3-hydroxyiminobutan-2-one (bp 80°C at 2 mm Hg) in 15 % yield. The distillation residue was an oil δ ($CDCl_3$) 4·4 (2H, triplet), 2·2 (2H, doublet) and 1·4 (3H, triplet) which was not identified.

2b.27. Irradiation of E-3-nitrobut-2-ene in methanol (quartz filter).

A solution of E-3-nitrobut-2-ene (0·01 mole) in methanol (110 mls) was irradiated (100 W lamp, quartz filter, nitrogen flush throughout the irradiation) for 6 hours. 3-Hydroxyiminobutan-2-one (15 %) was obtained.

2b.28. Preparation of E-1-nitrocyclododec-1-ene.

The nitroalkene was prepared by the action of nitrogen dioxide on cyclododec-1-ene[148] and was obtained as a pale yellow liquid bp 130°C at 1·0 mm Hg.

2b.29. Irradiation of E-1-nitrocyclododec-1-ene in acetone.

A solution of E-1-nitrocyclododec-1-ene (0·03 mole) in acetone (1000 mls) was irradiated for 9 hours. The reaction was followed by n.m.r.. Peaks in the region 6·7-7·0 δ in the spectra of samples after increasing periods of irradiation were assigned to the Z-isomer. After 9 hours, no starting material (E or Z-isomer) could be detected and the solvent was removed under reduced pressure to give a brown oil which was then distilled under reduced pressure (90°C at 2·5 mm Hg). The distillate was filtered through silica gel to give a yellow oil, ν max. 2910, 1540, 1455 and 1360 cm^{-1}

and δ ($CDCl_3$) 5•2–5•8 (3H, complex), 1•8–2•6 (4H, complex) and 1•0–1•8 (14H, complex), indentified as 3-nitrocyclododec-1-ene[148], obtained in 15 % yield.

2c. Photoaddition reactions of nitroalkenes.

The photoreactions described in this section, unless otherwise specified were carried out with a Hanovia 100 W medium pressure mercury arc lamp surrounded by a water cooled pyrex jacket. Dry, oxygen free nitrogen, saturated with solvent vapour was passed through the solutions for at least an hour prior to and throughout the irradiation. The reaction was followed by observing the reduction in intensity of the assymmetric stretch of the unsaturated group (1510 cm^{-1}).

2c.1(a). Irradiation of β-nitrostyrene and cyclohexene in methanol.

Ratio of cyclohexene to β-nitrostyrene 16:1.

A solution of β-nitrostyrene (0•03 mole), cyclohexene (0•48 mole) and methanol (60 mls) was irradiated for 23 hours. The solvent was removed under reduced pressure to give a brown oil ν max. 1535 and 1360 cm^{-1}, which was distilled under reduced pressure to give a yellow oil bp 150–156 °C at 0•9 mm Hg, ν max. 1535 and 1360 cm^{-1} and δ ($CDCl_3$) 7•6 (10H, singlet), 5•3 (0•6H, multiplet), 4•75 (1•4H, multiplet), 4•3 (1•4H, multiplet), 3•9 (0•6H, multiplet) and 1•2–2•2 (20H, complex). Identified as a mixture of two isomers, ratio 2•3:1, of 7-nitro-8-phenylbicyclo(4.2.0.)octane[150,154] and was obtained in 78 % yield.

2c.1(b). Ratio of cyclohexene to β-nitrostyrene 8:1.

A solution of β-nitrostyrene (0•03 mole), cyclohexene (0•24 mole) and methanol(85 mls) was irradiated for 45 hours. 7-Nitro-8-phenylbicyclo (4.2.0.)octane, a mixture of isomers, ratio 2•3:1, bp 165–170 °C at 1•0 mm Hg was obtained in 63 % yield.

2c.1(c). Ratio of cyclohexene to β-nitrostyrene 4:1.

A solution of β-nitrostyrene (0•03 mole), cyclohexene(0•12 mole) and methanol (98 mls) was irradiated for 90 hours. 7-Nitro-8-phenylbicyclo (4.2.0.)octane, a mixture of isomers, ratio 2·3:1, bp 145-150°C at 0·3 mm Hg and was obtained in 38 % yield.

2c.2(a). Irradiation of β-nitrostyrene and cyclohexene in acetonitrile.

Ratio of cyclohexene to β -nitrostyrene 8:1·

A solution of β-nitrostyrene (0·03 mole), cyclohexene (0·24 mole) and acetonitrile (85 mls) was irradiated for 45 hours. 7-Nitro-8-phenylbicyclo (4.2.0.)octane, a mixture of isomers , ratio 2·3:1 was obtained in 65 % yield.

2c.2(b). Ratio cyclohexene to β-nitrostyrene 4:1.

A solution of β -nitrostyrene (0·03 mole), cyclohexene (0·24 mole) and acetonitrile (98 mls) was irradiated for 168 hours. 7-Nitro-8-phenylbicyclo(4.2.0.)octane, a mixture of isomers, ratio 2·3:1 was obtained in 29 % yield.

2c.3. Irradiation of β -nitrostyrene in benzene.

Ratio of cyclohexene to β-nitrostyrene 8:1.

A solution of β -nitrostyrene (0·03 mole), cyclohexene (0·24 mole) and benzene (85 mls) was irradiated for 105 hours. 7-Nitro-8-phenylbicyclo (4.2.0.)octane, a mixture of isomers, ratio 2·3:1, was obtained in 48 % yield.

2c.4. Irradiation of E- β -nitrostyrene in acetonitrile.

A solution of β-nitrostyrene (0·03 mole) in acetonitrile (110 mls) was irradiated for 20 hours. The solvent was removed under reduced pressure and the crude reaction mixture examined by n.m.r.. Less than 5 % of the Z-isomer (6·7 and 6·9 δ) was present the rest being the E-isomer.

2c.5. Refluxing β-nitrostyrene, cyclohexene and methanol.

A solution of β -nitrostyrene (0·03 mole), cyclohexene (0·48 mole) and methanol (100 mls) was refluxed for 40 hours. The nitrostyrene was quantitatively recovered from the reaction mixture.

2c.6. Attempted separation of isomers of 7-nitro-8-phenylbicyclo(4.2.0.) octane.

(a) 7-Nitro-8-phenylbicyclo(4.2.0.)octane (0·005 mole) was filtered through a column of silica gel using benzene as the elutant. Comparison of n.m.r. spectra before and after the filtration indicated no equilibration of the isomers had occurred.

(b) The cyclohexene adduct (0·001 mole) was applied to a preparative scale t.l.c. plate. Repeated elutions using benzene: petrol (60/80) 1:1, failed to separate the isomers.

2c.7(a). Reaction of 7-nitro-8-phenylbicyclo(4.2.0.)octane with hydrochloric acid.

The adduct (0·001 mole) in methanol (25 mls) and HCl (3 drops) was refluxed for 10 hours. I.R. and n.m.r. spectra indicated no reaction had occurred.

2c.7(b). Reaction of 7-nitro-8-phenylbicyclo(4.2.0.)octane with sodium hydroxide.

The adduct (0·001 mole), sodium hydroxide (0·004 mole) in methanol (50 mls) was refluxed for 6 hours. Neutralization with acetic acid followed by extraction with ether led to the isolation of the adduct, with no change in the isomer ratio.

2c7(c). Nef reaction on 7-nitro-8-phenylbicyclo(4.2.0.)octane.

The adduct 90·05 mole) was added to sodium in methanol (0·05 mole in 50 mls) and stirred for 15 minutes, then poured into excess dilute sulphuric acid and extracted with chloroform[291], which led to the quantitative recovery of the adduct with no change in the isomer ratio.

2c.8. Irradiation of β-nitrostyrene and cyclopentene in methanol.

Ratio of cyclopentene to β-nitrostyrene 16:1.

A solution of β-nitrostyrene (0·03 mole), cyclopentene (0·48 mole) and methanol (67 mls) was irradiated for 20 hours. The solvent was removed under reduced pressure to give a brown oil ν max. 1530 and 1360 cm^{-1} which was distilled under reduced pressure to give a yellow oil bp 150-160 °C at 0·5 mm Hg ν max. 2930, 1530 and 1360 cm^{-1} and δ ($CDCl_3$) 7·5 (10H, multiplet), 5·0 (2H, multiplet), 4·5 (1·6H, multiplet), 3·9(0·4H, multiplet), 3·4 (2H, multiplet) and 1·3-2·0 (12H, complex). Identified as a mixture of two isomers, ratio 4:1, of

6-nitro-7-phenylbicyclo(3.2.0)heptane[154,150] in 81 % yield. Repeated preparative scale t.l.c. using benzene: 60/80 petrol (1:1) as the eluting solvent failed to separate the isomers.

2c.9. Irradiation of β-nitrostyrene and styrene in methanol.

Ratio of styrene to β-nitrostyrene 16:1.

A solution of β-nitrostyrene (0·03 mole), styrene (0·48 mole) and methanol (65 mls) was irradiated for 20 hours. The solvent was removed under reduced pressure to give a brown oil ν max. 1540 and 1360 cm^{-1}, which was distilled under reduced pressure to give a yellow oil bp 190-200°C at 0·4 mm Hg, ν max. 1540 and 1360 cm^{-1} and δ ($CDCl_3$) 7·7 (20H, multiplet), 5·8 (0·8H, quartet), 5·25 (1·2H, quartet), 4·8 (0·8H, triplet), 4·4 (1·2H, triplet) and 2·7-3·7 (6H, complex). Identified as a mixture of two isomers, ratio 3:2, of 2,3-diphenyl-1-nitrocyclobutane[150,154] in 65 % yield. A solution of the adduct (0·02 mole) in 60/80 petrol was filtered through silica gel to give an oil with the same isomer ratio as above. A solid slowly crystalised out of the oil. This solid was separated and recrystalised from 60/80 petrol, mp 104-105°C, δ ($CDCl_3$) 7·7 (10H, multiplet) 5·8 (1H, quartet) , 4·8 (1H, triplet) and 2·7-3·7 (3H, complex). The oil had δ ($CDCl_3$) 7·7 (10H, multiplet), 5·25 (1H, quartet), 4·4 (1 H, triplet) and 2·7-3·7 (3H, complex). The oil and the solid were identified as pure isomers of the adduct.

2c.10. Irradiation of β-nitrostyrene and α-methylstyrene in methanol.

Ratio of α-methylstyrene to β-nitrostyrene 16:1.

A solution of β-nitrostyrene (0·03 mole), α-methylstyrene (0·48 mole) and methanol (50 mls) was irradiated for 20 hours. The solvent was removed under reduced pressure to give an oil ν max. 1535 and 1360 cm^{-1}. This oil was distilled under reduced pressure to give a yellow oil, bp 180-190°C at 1·0 mm Hg ν max. 1535 and 1360 cm^{-1} and δ ($CDCl_3$) 6·9-7·7 (20H, complex), 5·5 (2H, complex), 4·6(0·8H, doublet), 4·3 (1·2H, doublet), 2·7-3·7 (4H, complex), 1·8 (3H, singlet) and 1·3 (3H, singlet). Indentified as 2,3-diphenyl-3-methyl-1-nitrocyclobutane, a mixture of isomers ratio 3:2, obtained in 81 % yield. Found C, 76·5; H, 6·8; N, 5·1,

$C_{17}H_{17}NO_2$ requires C, 76·4; H, 6·4; N, 4·7.

A solution of the adduct (0·01 mole) in petrol was filtered through a column of silica gel (100 g). No change in the observed isomer ratio was observed. Column chromatography (silica gel 100g) of the adduct (0·01 mole) failed to separate the isomers.

2c.11. Irradiation of β-nitrostyrene and 3-methylbut-2-ene in methanol.

Ratio of 3-methylbut-2-ene to β-nitrostyrene 16:1.

A solution of β-nitrostyrene (0·03 mole), 3-methylbut-2-ene (0·48 mole) and methanol (53 mls) was irradiated for 20 hours. The solvent was removed under reduced pressure to give an oil ν max. 1535 and 1360 cm^{-1}. This oil was distilled under reduced pressure to give a pale yellow oil bp 130-136°C at 0·5 mm Hg, ν max. 1535 and 1360 cm^{-1} and δ ($CDCl_3$) 7·6 (10H, multiplet) 5·5 (0·4H, triplet), 4·9 (1·6H, triplet), 4·2(0·4H, doublet), 3·85 (1·6H, doublet), 2·4-3·3 (2H, complex), 1·35 (6H, singlet), 1·2 (4·75H, singlet), 1·1 (1·25H, singlet), 0·8 (1·25H, singlet) and 0·6 (4·75H, singlet). This was identified as 1-nitro-4-phenyl-2,3,3-trimethylcyclobutane, a mixture of isomers ratio 4:1, obtained in 65 % yield. Found C, 71·0, H, 7·6; N, 6·7. Required for $C_{13}H_{17}NO_2$, C, 71·2; H, 7·8; N, 6·4.

Column chromatography (silica gel 150g) of the adduct (0·01 mole) failed to separate the isomers and caused no alteration to the isomer ratio.

2c.12. Irradiation of β-nitrostyrene and cyclododecene in t-butylalcohol.

Ratio of cyclododecene to β-nitrostyrene 16:1.

A solution of β-nitrostyrene (0·015 mole), cyclododecene (0.25 mole) and *t*-butylalcohol (60 mls) was irradiated for 50 hours. The solvent was removed under reduced pressure to give abrown oil ν max. 1535 and 1360 cm^{-1}. Distillation under reduced pressure (200°C at 0·5 mm Hg) led to decomposition, only black tars being obtained.

2c.13. Irradiation of β-nitrostyrene and isopropenyl acetate in methanol.

Ratio of isopropenyl acetate to β-nitrostyrene 8:1.

A solution of β-nitrostyrene (0·03 mole), isopropenyl acetate (0·24 mole) and methanol (82 mls) was irradiated for 50 hours. The solvent was removed under reduced pressure to give a brown oil ν max. 1740, 1540 and 1360 cm^{-1}.

This oil was distilled under reduced pressure to give an oil bp 150-156°C at 0·3 mm Hg, ν max. 1740, 1540 and 1360 cm^{-1} and δ ($CDCl_3$) 7·3 (10H, singlet), 5·5 (1·5H, quartet), 5·15 (0·5H, quartet), 4·4 (0·5H, doublet), 4·05 (1·5H, doublet), 2·6-3·5 (4H, complex), 2·0(1·8H, singlet), 1·7 (4·2H, singlet), 1·6(4·2H, singlet) and 1·2(1·8H, singlet). This was identified as 1-acetoxy-1-methyl-3-nitro-4-phenylcyclobutane, a mixture of isomers, ratio 7:3, obtained in 63 % yield. Found C, 63·0; H, 6·8; N, 5·8. Required for $C_{13}H_{15}NO_4$ C, 62·6; H, 6·1; N, 5·6.

A solution of the adduct (0·01 mole) in petrol was filtered through silica gel (100g). No change in the isomer ratio was noted. Column chromatography (silica gel 100g) of the adduct (0·01 mole) failed to separate the isomers.

2c.14. Irradiation of β-nitrostyrene and isopropenyl acetate in acetonitrile.

Ratio of isopropenyl acetate to β-nitrostyrene 8:1.

A solution of β-nitrostyrene (0·03 mole), isopropenyl acetate (0·24 mole) and acetonitrile (82 mls) was irradiated for 95 hours. The solvent was removed under reduced pressure and the resulting oil distilled under reduced pressure (160-166°C at 0·1 mm Hg) to give 1-acetoxy-1-methyl-3-nitro-4-phenylcyclobutane in 58 % yield.

2c.15. Reaction of 1-acetoxy-1-methyl-3-nitro-4-phenylcyclobutane with base and acid.

(a) Base: A solution of the adduct (0·005 mole) and sodium hydroxide (0·02 mole) in methanol (50 mls) was left to stand at room temperature for 70 hours. The solution was neutralised with acetic acid, diluted with water and extracted with chloroform, 70 % of the adduct was recovered, no other products were obtained.

(b) Base: A solution of the adduct (0·005 mole) and potassium hydroxide (0·005 mole) in methanol (50 mls) was refluxed for 18 hours. The solution was neutralised with acetic acid, diluted with water and extracted with chloroform. No adduct was recovered, an oil ν max. 1700 cm^{-1} was obtained. Preparative scale t.l.c. (dichloromethane as developing solvent) failed to isolate any products.

(c) Base: A solution of the adduct (0•001 mole) in methanol (25 mls) was added to sodium metal (0•005 mole) in methanol (25 mls) and was refluxed for 1 hour. The solution was neutralized with hydrochloric acid, diluted with water and extracted with ether. No adduct was recovered, an oil ν max. 1700 and 1080 cm^{-1} was obtained . No discrete products could be obtained using preparative scale t.l.c. (dichloromethane as developing solvent).

(d) Base: A solution of the adduct and sodium methoxide in methanol as described in (c) was left to stand at room temperature for 18 hours. Work up as detailed above gave identical results.

(e) Base: A solution of the adduct and sodium methoxide in methanol as described in (c) was left to stand at room temperature for 0•25 hours. The solution was neutralised with acetic acid at 0°C, diluted with water and extracted with ether. The adduct was recovered quantitatively and no change in the isomer ratio was noted.

(f) Acid: To a solution of the adduct (0•001 mole) in methanol (25 mls) was added concentrated sulphuric acid (30 mls). The solution went milky and was stirred at room temperature for 1 hour. The solution was diluted with water and extracted with ether. The adduct was recovered quantitatively and no change in the isomer ratio was noted.

2c.16. Reaction of 1-acetoxy-1-methyl-3-nitro-4-phenylcyclobutane with lithium aluminium hydride.

To a solution of the adduct (0•002 mole) in dry ether (25 mls) , lithium aluminium hydride (0•002 mole) was slowly added. The solution was stirred at room temperature for 0•5 hours. Excess hydride was destroyed by the careful addition of water and the resulting solution was extracted to give an oil ν max. 3540, 3350, 1540 and 1360 cm^{-1}. Preparative scale t.l.c. (dichloromethane as developing solvent) failed to provide a pure sample of this material.

2c.17. Attempted pyrolysis of 1-acetoxy-1-methyl-3-nitro-4-phenylcyclobutane.

The adduct (0•002 mole) was heated in the absence of solvent in a current of nitrogen at 250°C at 26 mm Hg for 10 hours. This caused the material to go dark in colour but no change in the I.R. or n.m.r. spectra could be noted.

2c.18. Irradiation of β-nitrostyrene and vinyl acetate in methanol.

Ratio of vinyl acetate to β-nitrostyrene 8:1.

(a) A solution of β-nitrostyrene (0·003 mole), vinyl acetate(0·24 mole) and methanol (86 mls) was irradiated for 100 hours. The solvent was removed under reduced pressure to give an oil ν max. 1730, 1540 and 1360 cm^{-1}. This oil was distilled under reduced pressure to give an oil bp 150-156°C at 0·1 mm Hg, ν max. 1730, 1540 and 1360 cm^{-1} and δ ($CDCl_3$) 7·5 (10H, singlet), 4·0-5·8 (6H, complex), 2·3-3·4(4H, complex), 1·95 (3H, singlet) and 1·55 (3H, singlet). A solid crystalised out of the oil. This was separated and recrystalised from ethyl acetate to give crystals mp 101-103°C, ν max. 1730, 1540 and 1360 cm^{-1} and δ ($CDCl_3$) 7·5 (5H, singlet), 5·6-6·1 (2H, complex), 4·7(1H, triplet), 2·5-3·5 (2H, complex) and 1·9 (3H, singlet). Identified as 3-acetoxy-1-nitro-4-phenylcyclobutane (a pure isomer) obtained in 27 % yield. Found C, 61·2 ; H, 5·5; N, 6·0; Required for $C_{12}H_{13}NO_4$ C, 61·3; H, 5·6; N, 5·9. The ethyl acetate from above was removed under reduced pressure to give an oil δ ($CDCl_3$) 7·5 (6H, complex), 4·0-5·8 (3·5H, complex), 2·3-3·4(2·3H, complex), 1·95(1·75H, singlet) and 1·55(1·75H, singlet) , that was a mixture of isomers (20 % of the solid isomer and 80 % of another isomer). No more solid isomer could be obtained from this mixture by recrystalisation. This oil, dissovled in benzene was filtered through celite but no separation of the isomers or alteration in the isomer ratio was noted. Distillation under reduced pressure (160-170°C at 1·0 mm Hg) failed to separate the isomers. The oil solidified at -10 C and a low temperature recrystallisation from methanol isolated a white solid (a mixture of the solid isomer and the other isomer in the ratio 2:3, obtained in 15 % yield). Removal of the methanol under reduced pressure gave an oil which was distilled under reduced pressure to give an oil bp 150-160°C at 0·9 mm Hg, δ ($CDCl_3$) 7·9(5H, singlet), 4·9-5·6(2H, complex), 4·6(1H, complex), 2·7-3·6(2H, complex) and 2·2 (3H, singlet). This was identified as a pure isomer of the product, obtained in 29 % yield. Found C, 61·2; H, 5·5; N,6·0. Required for $C_{12}H_{13}NO_4$ C, 61·3; H, 5·6; N, 5·9.

(b) A larger scale irradiation was undertaken. A solution of β-nitrostyrene (0·12 mole) and vinyl acetate (0·96 mole) in methanol (350 mls) was irradiated using a 500 W pyrex lamp with a continous nitrogen flush for 42 hours. The solid and liquid isomers were isolated in 28 and 29 % yields respectively.

2c.19. Column chromatography of the isomers of 3-acetoxy-1-nitro-4-phenyl cyclobutane.

(a) Liquid isomer. A solution of the liquid isomer (0·005 mole) in benzene was filtered through a column of silica gel (50g) . β-Nitrostyrene (0·003 mole) was isolated after removal of the solvent under reduced pressure.

(b) Solid isomer. A solution of the solid isomer (0·005 mole) in benzene was filtered through a column of silica gel (50 g). The pure adduct was quantitatively recovered.

2c.20. Reaction of 3-acetoxy-1-nitro-4-phenylcyclobutane with base.

(a) A solution of the solid isomer (0·002 mole) in methanol (50 mls) was added to a solution of sodium hydroxide (0·002 mole) in methanol (25 mls) and water (25 mls) and left to stir for 3 days. The solution was neutralised with acetic acid, diluted with water and extracted with chloroform to give an oil ν max. 3350, 1330 and 980 cm^{-1}. Preparative scale t.l.c. , using dichloromethane as the developing solvent, failed to separate any pure products.

(**b**) A solution of the solid isomer (0·002 mole) in methanol (50 mls) was added to a solution of sodium carbonate (0·002 mole) in water (50 mls) and stirred for 2 hours. The solution was neutralised with acetic acid at 0°C, diluted and extracted with chloroform to give an oil ν max. 3350, 1330 and 980 cm^{-1}. Preparative scale t.l.c. , using dichloromethane as the developing solvent, failed to isolate any pure products.

2c.21. Reaction of 3-acetoxy-1-nitro-4-phenylcyclobutane with pyrolidine.

A solution of the solid isomer (0·002 mole) and pyrolidine (0·002 mole) in methanol (80 mls) was stirred for 16 hours. The solvent was removed under reduced pressure to give an oil ν max. 3525, 3400, 1535 and 1360 cm^{-1}. Preparative scale t.l.c. (2x), using dichloromethane as the developing solvent, gave an oil ν max. 3525, 3400, 1535 and 1360 cm^{-1} and

δ ($CDCl_3$) 7·0(5H, singlet), 5·15(1H, quartet), 4·2(1H, triplet), 3·75(1H, triplet) and 1·4-2·7(3H, complex). Identified as 3-nitro-4-phenylcyclobutan-1-ol (a pure isomer) obtained in 53 % yield. Found C, 62·0; H, 5·8; N, 7·1. Required for $C_{10}H_{11}NO_3$, C, 62·2; H, 5·7; N, 7·3.

2c.22. Reaction of 3-acetoxy-1-nitro-4-phenylcyclobutane with hydrochloric acid.

A solution of the solid isomer (0·0075 mole) in methanol (50 mls) with hydrochloric acid (6 drops) was refluxed for 9 hours. The solvent was removed under reduced pressure to give an oil which was then distilled under reduced pressure to give 3-nitro-4-phenylcyclobutan-1-ol, bp 156-160°C at 0·7 mm Hg, obtained in 73 % yield.

2c.23. Reaction of 3-acetoxy-1-nitro-4-phenylcyclobutane with hydrochloric acid.

A solution of the liquid isomer (0·002 mole) in methanol (80 mls) with hydrochloric acid (6 drpos) was refluxed for 5 hours. The solvent was removed under reduced pressure to give an oil. T.l.c. (dichloromethane as developing solvent) indicated that at least five products were present, but preparative scale t.l.c. failed to isolate any of these products.

2c.24. Reaction of 3-nitro-4-phenylcyclobutan-1-ol with acetic anhydride.

A solution of the nitroalcohol (0·002 mole) and acetic anhydride (0·005 mole) was refluxed for 3 hours. The solvent (excess acetic anhydride) was removed under reduced pressure to yield 3-acetoxy-1-nitro-4-phenylcyclobutane (solid isomer) in quantitative yield.

2c.25. Oxidation of 3-nitro-4-phenylcyclobutan-1-ol.

A solution of the nitroalcohol (0·002 mole) and Jones reagent[298] (0·004 mole) in acetone (20mls) was stirred for 15 minutes. The reaction mixture was diluted with water and extracted with chloroform. The chloroform was removed under reduced pressure to give an oil ν max. 1790, 1700 and 1550 cm^{-1} Preparative scale t.l.c. , using dichloromethane as the developing solvent, failed to isolate any products.

2c.26. Irradiation of β-nitrostyrene and mesityl oxide in methanol.

(a) A solution of β -nitrostyrene (0·03 mole) and mesityl oxide (0·48 mole) in methanol (50 mls) was irradiated for 81 hours. The solvent was removed under reduced pressure to give a brown oil ν max. 1540 and 1360 cm^{-1}, which decomposed on attempted distillation (180°C at 2 mm Hg).

(b) The irradiation was repeated as above but the oil was chromatographed on silica gel (100 g). This led to the decomposition of the crude product.

2c.27. Irradiation of β-nitrostyrene and courmarin in acetonitrile.

A solution of β-nitrostyrene (0·03 mole) and courmarin (0·06 mole) in acetonitrile (100 mls) was irradiated for 20 hours. No reaction had occurred after this time and the irradiation was discontinued.

2c.28. Irradiation of β-nitrostyrene and acrylonitrile in methanol.

A solution of β-nitrostyrene (0·03 mole) and acrylonitrile (0·5 mole) and methanol (78 mls) was irradiated for 250 hours. The solvent was removed under reduced pressure to give an oil ν max. 1540 and 1360 cm^{-1} which decomposed when distilled under reduced pressure (120-130°C at 0·5 mm Hg).

2c.29. Irradiation of β-nitrostyrene and 1,2-dichloroethylene in methanol.

A solution of β-nitrostyrene (0·03 mole) and 1,2-dichloroethylene (0·5 mole) in methanol (72 mls) was irradiated for 40 hours. The solvent was removed under reduced pressure to give an oil 1540 and 1360 cm^{-1} which decomposed under reduced pressure (80-90°C at 0·1 mm Hg).

2c.30. Irradiation of β-nitrostyrene and the enol acetate of dimedone in methanol.

A solution of β-nitrostyrene (0·03 mole) and the enol acetate of dimedone (0·03 mole) in methanol (160 mls) was irradiated for 20 hours. The solvent was removed under reduced pressure to give a brown oil ν max. 1460 cm^{-1}. Using preparatice scale t.l.c. (dichloromethane as developing solvent) failed to isolate any products.

2c.31. Preparation of the enol acetate of dimedone.

The enol acetate was prepared by reacting dimedone with acetic anhydride and was obtained as a colourless liquid (70 %), bp 115-120°C at 0·7 mm Hg (lit.[299] 144°C at 18 mm Hg).

2c.32. Enol acetate of acetyl acetone.

(a) Acetyl acetone (0·5 mole) was heated at 125°C in acetic anhydride (1 mole) with p-toluene sulphonic acid (0·01 mole) as catalyst, for 5 hours according to the method of Bedukian[201]. The reaction mixture was cooled and poured into water and extracted with benzene. The benzene layer was washed with water and sodium bicarbonate solution and the benzene was removed to give a brown oil which was distilled under reduced pressure (80-90°C at 0·8 mm Hg) to give a clear oil ν max. 1755, 1620, 11350 and 1120 cm^{-1} and

δ ($CDCl_3$) 7·1 (1H, singlet), 5·65(1H, singlet), 5·4(1H, singlet) 5·1(1H, singlet) and 1·7 (9H, complex). This oil was not the desired enol acetate and it rapidly decomposed on standing and hence was not identified.

(b) Repeating the reported preparation[302] of this enol acetate failed, the same oil as in (a) was obtained.

(c) Acetyl acetone (0·04 mole.), acetyl chloride (0·04 mole) was dissolved in pyridine (25 mls) and stirred overnight[303]. The solvent was removed under reduced pressure and the oil obtained distilled under reduced pressure to give the same oil as in (a) and (b).

2c.33. Irradiation of β-nitrostyrene and acetyl acetone in acetonitile.

A solution of β-nitrostyrene (0·03 mole) and acetyl acetone (0·48 mole) in acetonitrile (140 mls) was irradiated for 46 hours. The solvent was removed under reduced pressure to give a brown oil ν max. 1550 and 1360 cm^{-1}. Distillation under reduced pressure caused the decomposition of the crude product.

2c.34. Irradiation of β-nitrostyrene and acetyl acetone in methanol.

A solution of β-nitrostyrene (0·03 mole) and acetyl acetone (0·48 mole) in methanol (140 mls) was irradiated for 45 hours using a 100 W lamp with a quartz filter. During the course of the irradiation a white solid was deposited, which was filtered off. The solvent was removed under pressure to give a brown oil, which decomposed under reduced pressure. The solid was recrystallised from acetone-methanol (1:1) to give a crystaline (0·5 %) mp 244-247°C, ν max. 1550 and 1360 cm^{-1}. Found C, 64·2; H, 4·8; N, 9·6. Required for $C_{16}H_{14}N_2O_4$, C, 64·4; H, 4·7; N, 9·4.

2c.35. Irradiation of β-nitrostyrene and benzophenone in benzene.

A solution of β-nitrostyrene (0·3 mole) and benzophenone (0·03 mole) in benzene (160 mls) was irradiated for 108 hours. No reaction had occurred after this time and hence the reaction was discontinued.

2c.36. 2-Nitro-1-(4-chlorophenyl)-ethylene.

The nitroalkene was prepared from 4-chlorobenzaldehyde and nitromethane[309] and was obtained as white crystals, after recrystalisation from ethanol, in 48 % yield, mp 113-114 °C (lit.[309] 113-114 °C).

2c.37. 2-Nitro-1-(3-phenyl)-ethylene.

The nitroalkene was prepared from 3-nitrobenzaldehyde and nitromethane[309] and was obtained as white crystals, after recrystalization from ethanol, in 53 % yield, mp 124-125 °C (lit.[309] 125 °C).

2c.38. 2-Nitro-1-(4-methoxyphenyl)-ethylene.

The nitroalkene was prepared from 4-methoxybenzaldehyde and nitromethane[310] and was obtained as white crystals, after recrystalization from methanol, in 60 % yield, mp 86-87 °C (lit.[310] 86-87 °C).

2c.39. 2-Nitro-1-(2-methoxyphenyl)-ethylene.

The nitroalkene was prepared from 2-methoxybenzaldehyde and nitromethane[310] and was obtained as yellow crystals, after recrystalisation from ethanol, in 43 % yield, mp 48-49 °C (lit.[310] 49 °C).

2c.40. 2-Nitro-1-(4-methylphenyl)-ethylene.

The nitroalkene was prepared from 4-methylbenzaldehyde and nitromethane[308] and was obtained as yellow crystals, after recrystalization from ethanol, in 65 % yield, mp 101-102 °C (lit[308] 102 °C).

2c.41. Furylacrolein.

The unsaturated aldehyde was prepared from furfural, acetaldehyde and para aldehyde[311] and was obtained as yellow crystals, mp 49-51 °C (lit[311] 50-51 °C).

2c.42. 1-Furyl-4-nitrobuta-1,3-diene.

The nitrodiene was prepared from furylacrolein and nitroethane[311] and was obtained as orange crystals in 70 % yield, mp 73-74 °C (lit.[311] 74 °C).

2c.43. Irradiation of 2-nitro-1-(4-methylphenyl)-ethylene and cyclohexene in acetonitrile.

A solution of the nitroalkene (0·015 mole), cyclohexene (0·24 mole) and acetonitrile (85 mls) was irradiated for 20 hours, the solvent was removed under reduced pressure to give a brown oil ν max. 1535 and 1360 cm^{-1}.

This was distilled under reduced pressure to give a yellow oil, bp 190-200° C at 0·1 mm Hg, ν max. 1535 and 1360 cm^{-1} and δ ($CDCl_3$) 7·4 (8H, singlet) 5·3 (0·4H, triplet), 4·7(1·6H, triplet), 3·5-4·4(2H, complex), 2·4(6H, singlet) and 1·3-2·3(20H, complex). This was identified as a mixture of isomers, ratio 4:1, of 7-nitro-8-(4-methyl)-phenylbicyclo(4.2.0.)octane, obtained in 63 % yield. Found C, 73·5; H, 7·8; N, 5·8. Required for $C_{15}H_{19}NO_2$, C, 73·5; H, 7·8; N, 5·71. The adduct (0·005 mole) was chromatographed on silica gel (100 g) but no separation of the isomers was obtained, and no change in the isomer ratio was noted.

2c.44. Irradiation of 2-nitro-1-(4-chlorophenyl)-ethylene and cyclohexene in acetonitrile.

A solution of the nitroalkene (0·015 mole), cyclohexene (0·24 mole) and acetonitrle (85 mls) was irradiated for 25 hours. The solvent was removed under reduced pressure to give a brown oil ν max. 1535 and 1360 cm^{-1}. This oil was distilled under reduced pressure to give a yellow oil, bp 200-206 °C at 0·2 mm Hg, ν max. 1535 and 1360 cm^{-1} δ ($CDCl_3$) 7·65(8H, singlet), 5·3(0·5H, triplet), 4·8(1·5H, triplet), 3.85-4·3(2H, complex) and 1·1-3·3 (20H, complex). Identified as a mixture of isomers, ratio 3:1, of 7-nitro-8-(4-chloro)-phenylbicyclo(4.2.0.)octane, obtained in 50 % yield. Found C, 62.8; H, 5·5; N, 5·3. Required for $C_{14}H_{16}NO_2$ C, 63·3; H, 6·1; N, 5·3. The adduct (0·005 mole) was chromatographed on silica gel (100 g) but no separation of the isomers or change in the isomer ratio was obtained.

2c.45. Irradiation of 2-nitro-1-(3-nitrophenyl)-ethylene and cyclohexene in methanol.

A solution of the nitroalkene (0·015 mole), cyclohexene (0·24 mole) and acetonitrile (85 mls) was irradiated for 20 hours. The solvent was removed under reduced pressure to give a brown oil ν max. 1520 and 1350 cm^{-1}. This was filtered through silica gel to give a yellow oil ν max. 1520 and 1350 cm^{-1}, δ ($CDCl_3$) 8·5(1H, complex), 8·0(8H complex), 7·6(2H, singlet), 3·3-5·4 (2H, complex) and 1·0-2·5(20H, complex). This was tentatively assigned to 7-nitro-8-(3-nitro-)phenylbicycylo(4.2.0.)octane but it could not be obtained in a state of analytical purity.

2c.46. Irradiation of 2-nitro-1-(4-methoxyphenyl)-ethylene and cyclohexene in methanol.

A solution of the nitroalkene (0·015 mole), cyclohexene (0·24 mole) and methanol (85 mls) was irradiated for 40 hours. The solvent was removed under reduced pressure to give a brown oil ν max. 1530 cm^{-1}, which decomposed when distilled under reduced pressure (200°C at 10 mm Hg).

2c.47. Irradiation of 2-nitro-1-(4-methoxyphenyl)-ethylene and cyclohexene in acetonitrile.

A solution of the nitroalkene (0·015 mole), cyclohexene (0·24 mole) and acetonitrile(85 mls) was irradiated for 15 hours. The solvent was removed under reduced pressure to give a brown oil ν max. 1530 cm^{-1}, which decomposed when distilled under reduced pressure (190°C at 8 mm Hg).

2c.48. Irradiation of 2-nitro-1-(2-methoxyphenyl)-ethylene and cyclohexene in acetonitrile.

A solution of the nitroalkene (0·015 mole), cyclohexene (0·24 mole) and acetonitrile (85 mls) was irradiated for 20 hours. The solvent was removed under reduced pressure to give a brown oil ν max. 1535 and 1360 cm^{-1} which decomposed when distilled under reduced pressure (200°C at 9 mm Hg).

2c.49. Irradiation of 1-furyl-4-nitrobuta-1,3-diene and cyclohexene in methanol.

A solution of the nitrodiene (0·01 mole), cyclohexene (0·48 mole) in methanol (160 mls) was irradiated for 40 hours. After this time the nitrodiene was quantitatively recovered from the reaction mixture.

2c.50. Irradiation of 1-nitroprop-1-ene and cyclohexene in acetonitrile.

A solution of the nitroalkene (0·03 mole), cyclohexene (0·24 mole) in acetonitrile (85 mls) was irradiated for 60 hours. The solvent was removed under reduced pressure to give a brown oil ν max. 1535 and 1360 cm^{-1}. This oil was chromatographed on silica gel (100 g) but no pure products were obtained, the photoproduct decomposing on the column.

2c.51. Irradiation of 1-nitroprop-1-ene and cyclopentene in acetonitrile.

(a). A solution of the nitroalkene (0·03 mole), cyclopentene (0·24 mole) and acetonitrile (85 mls) was irradiated for 55 hours. The solvent was removed under reduced pressure to give a brown oil ν max. 1540 and 1380 cm^{-1}. This oil decomposed when distilled under reduced pressure (70-80°C at 0•2 mm Hg).

(b) The irradiation was repeated as above and the brown oil was again obtained. G.l.c. analysis indicated no E/Z isomerisation of the nitroalkene was occurring during the irradiation. The oil was chromatographed on silica gel (100 g). Elution with petrol/benzene (1:1) gave a clear oil ν max. 1540 and 1360 cm^{-1}, δ ($CDCl_3$) 6•0(1H, complex), 4•5(1H, complex), and 0•8-3•0(8H, complex). This oil slowly decomposed at -20°C and could not be obtained in a state of analytical purity. Elution with ethyl acetate, gave a brown oil ν max. 1720 cm^{-1}, which was not identified.

2c.52. Irradiation of 1-nitroprop-1-ene and styrene in acetonitrile.

A solution of the nitroalkene (0•03 mole) and styrene (0•48 mole) in acetonitrile (65 mls) was irradiated for 42 hours. The solvent was removed under reduced pressure to give an oil ν max. 1540 cm^{-1}, which decomposed when distilled under reduced pressure.

2c.53. Irradiation of 1-nitroprop-1-ene and isopropenyl acetate in acetonitrile.

A solution of the nitroalkene (0•03 mole) and isopropenyl acetate (0•24 mole) in acetonitrile (83 mls) was irradiated for 80 hours. The solvent was removed under reduced pressure to give an oil ν max. 1720 and 1545 cm^{-1}. This oil was chromatographed on silica gel (100 g) but no pure products were obtained. A g.l.c. analysis of the reaction solution during the course of the irradiation showed the presence of a compound of shorter retention time than the E-isomer, which by comparison with published retention times was identified as the Z-isomer.

2c.54. Irradiation of 1-nitrocyclohexene and cyclohexene in methanol.

A solution of the nitroalkene (0•03 mole) and cyclohexene (0•24 mole) in methanol (60 mls) was irradiated for 48 hours. The solvent was removed under reduced pressure to give a brown oil ν max. 1525 and 1360 cm^{-1}. This was distilled under reduced pressure to give a clear oil ν max. 1535 and 1360 cm^{-1}, bp 120-130°C at 0•5 mm Hg, identified as the 1:1 adduct of 1-nitrocyclohexene and cyclohexene, obtained in 35% yield. Found C, 68•19

H, 9·37; N, 6·64. Required for $C_{12}H_{19}NO_2$ C, 68·87; H, 9·15; N, 6·69.

2c.55. 1-Nitrocyclohexene.

The nitroalkene was prepared from cyclohexene and nitrogen dioxide[312] and was obtained as a yellow liquid (46 %), bp 75-80°C at 0·8 mm Hg (lit.[312] 60-64°C at 1 mm Hg).

2c.56. Trans-1-methoxy-2-nitrocyclohexane.

The nitroether was prepared from 1-nitrocyclohexene and sodium methoxide in methanol[148] and was obtained as a clear liquid (63 %) bp 70-72°C at 12 mm Hg (lit.[148] 64°C at 9 mm Hg).

2c.57. Irradiation of 1-nitrocyclohexene and isopropenyl acetate in methanol.

A solution of 1-nitrocyclohexene (0·03 mole) and isopropenyl acetate (0·24 mole) in methanol (86 mls) was irradiated for 100 hours. The solvent was removed under reduced pressure to give a brown oil ν max. 1720 and 1360 cm^{-1}, which decomposed on distillation (170-175°C at 0·8 mm Hg)

2c.58. Irradiation of 2-nitrocholestan-3-one and cyclohexene in methanol.

A solution of the nitroketone (0·0014 mole) and cyclohexene (0·24 mole) in methanol (60 mls) was irradiated for 10 hours. The solvent was removed under reduced pressure to give a brown oil ν max. 1710 and 1360 cm^{-1}. Use of preparative scale t.l.c. (using dichloromethane as the developing solvent) failed to isolate any photoproducts.

2c.59. Irradiation of 2-nitro-4-t-butylcyclohexanone and cyclohexene in methanol

A solution of the nitroketone (0·015 mole) and cyclohexene (0·24 mole) in methanol (60 mls) was irradiated for 85 hours. The solvent was removed under reduced pressure to give a brown oil ν max. 1720 and 1360 cm^{-1}. Tho oil was distilled under reduced pressure to give two fractions. The first was a clear oil bp 130-140°C at 0·9 mm Hg, ν max. 1720 and 1360 cm^{-1}. The second fraction was a yellow oil bp 150-160°C at 0·9 mm Hg, ν max. 1710 and 1360 cm^{-1}. Neither fraction was identified.

2c.60. Irradiation of α -nitroacetophenone and cyclohexene in methanol.

A solution of the nitroketone (0·03 mole) and cyclohexene (0·24 mole) in methanol (60 mls) was irradiated for 21 hours. Removal of the solvent under reduced pressure led to the quantiative recovery of the starting material.

2c.61. Irradiation of 1-methoxy-2-nitro-1-phenylethylene and cyclohexene in methanol.

A solution of the enolether (0·01 mole) and cyclohexene (0·24 mole) in methanol (60 mls) was irradiated for 60 hours. Removal of the solvent under reduced pressure gave a brown oil ν max. 1710 and 1270 cm^{-1}, which decomposed on distillation (90-100°C at 2·5 mm Hg).

2c.62. Photodimerization of β-nitrostyrene.

β-Nitrostyrene (0·25 mole) was irradiated according to the published method [317] for 48 hours. After this time only 5 % of the dimer was present.

2c.63. Photodimerization of 1-(4-methoxyphenyl)-2-nitroethylene.

The nitroalkene (0·25 mole) was irradiated under the same conditions as β-nitrostyrene (2c.62) for 50 hours. After this time no dimer was present by I.R. and hence the irradiation was discontinued.

2c.64. Reaction of β-nitrostyrene with the morpholine of cyclohexanone.

(a) Methanol as solvent.

A solution of the enamine (0·01 mole) in methanol (25 mls) was added to a solution of the nitroalkene (0·01 mole) in methanol (25 mls). Examination by I.R. after 0·25 hours, indicated that all the nitroalkene had reacted.

(b) Acetonitrile as solvent.

A solution of the enamine (0·01 mole) in acetonitrile (25 mls) was added to a solution of the nitroalkene (0·01 mole) in acetonitrile (25 mls). Examination, by I.R., after 0·25 hours indicated all the nitroalkene had reacted.

2c.65. Preparation of 1-morpholinocyclohexene.

The enamine was prepared from cyclohexanone and morpholine and was obtained as a clear liquid (59 %), bp 82-86°C at 0·03 mm Hg (lit.[480] 130°C at 18 mm Hg).

2c.66. Reaction of β-nitrostyrene and dihydropyran.

A solution of the nitroalkene (0·01 mole) and dihydropyran (0·01 mole) in methanol (50 mls) was refluxed for 120 hours. No reaction had occurred after this time and hence the reaction was discontinued.

3a. Preparation of α-Nitroketones.

3a.1. 3-Nitrobutan-2-one.

(a) 3-Nitrobutan-2-ol.

The nitroalcohol was prepared as in 2a.1.

(b) 3-Nitrobutan-2-one.

The nitroketone was prepared by sodium dichromate oxidation of 3-nitrobutan-2-ol[354] and was obtained as a colourless liquid (58 %), bp 60-62°C at 4·0 mm Hg (lit[354] 71-75°C at 9 mm Hg).

3a.2. 2,4-Dinitrophenylhydrazone of 3-nitrobutan-2-one.

This derivative was prepared from the nitroketone and the hydrazine[354] and was obtained as yellow crystals mp 124-125°C (lit.[354] 124-125°C). Required for $C_{10}H_{11}N_5O_6$, C, 40·4; H, 3·73; N, 23.56. Found C, 40·23; H, 3·68; N, 23·34.

3a.3. 2-Nitroheptan-3-one.

(a) 2-Nitroheptan-3-ol.

The nitroalcohol was prepared from nitroethane and pentanal[389] and was obtained as a colourless liquid (58 %), bp. 98-100°C at 1·0 mm Hg (lit.[389] 92°C at 2 mm Hg).

(b) 2-Nitroheptan-3-one.

The nitroketone was prepared according to the method of Hurd and Nilson[354] 2-Nitroheptan-3-ol (0·5 mole) was added to sodium dichromate (0·46 mole) in water (80 mls) and was kept at 0°C. A cooled solution of sulphuric acid (0·88 mole) in water (40 mls) was added dropwise over six hours, the temperature being kept below 10°C. The solution was stirred for a further two hours then poured into water (500 mls). This solution was extracted with ether (3x200 mls) washed with water and dried over sodium sulphate. The ether was removed under reduced pressure to give a blackliquid ν max. 1740 and 1550 cm^{-1}. This was distilled under reduced pressure to give a colourless liquid (64 %) bp 106-108°C at 0·8 mm Hg. Identified as 2-nitroheptan-3-one. Required for $C_7H_{13}NO_3$, C, 52·82; H, 8·23; N, 8·8. Found C, 52·64; H, 8·25; N, 8·75.

3a.4. 3-Nitrohexan-2-one.

(a) 1-Nitrobutane.

The nitroalkane was prepared from 1-bromobutane and sodium nitrite[416] and was obtained as a colourless liquid (48 %) bp 56-58°C at 3·0 mm Hg.

(b) 3-Nitrohexan-2-ol.

The nitroalcohol was prepared from 1-nitrobutane and acetaldehyde[388] and was obtained as a colourless liquid (75 %), bp 70-74°C at 0·9 mm Hg (lit.[388] 112°C at 10 mm Hg).

(c) 3-Nitrohexan-2-one.

The nitroketone was prepared by the oxidation of 3-nitrohexan-2-ol according to the method of Hurd and Nilson[354] and was obtained as a colourless liquid (66 %), bp 62-64°C at 0·6 mm Hg (lit.[417] 60°C at 1 mm Hg). Required for $C_6H_{11}NO_3$, C, 45·1; H, 8·33; N, 10·52. Found C, 45·0; H, 8·26; N, 10·31.

3a.5. 2,4-Dinitrophenylhydrazone of 3-nitrohexan-2-one.

This derivative was prepared from the nitroketone and the hydrazine[354] and was obtained as yellow crystals, mp 81-82°C (lit.[417] 82°C).

3a.6. 3-Methyl-3-nitrobutan-2-one.

(a) 3-Methyl-3-nitrobutan-2-ol.

The nitroalcohol was prepared from acetaldehyde and 2-nitropropane[388] and was obtained as a colourless liquid (30 %), bp 74-76°C at 0·8 mm Hg (lit.[388] 90°C at 10 mm Hg).

(b) 3-Methyl-3-nitrobutan-2-one.

The nitroketone was prepared by the oxidation of 3-methyl-3-nitrobutan-2-one and was obtained as a white crystaline material (48 %), mp 29-30°C (lit.[353, 363] mp 30°C).

3a.7. 2,4-Dinitrophenylhydrazone of 3-methyl-3-nitrobutan-2-one.

This derivative was prepared from the hydrazine and the nitroketone according to the method of Hurd and Nilson[354] and was obtained as yellow crystals, mp 158-159°C. Required for $C_{11}H_{13}N_5O_6$, C, 42·45; H, 4·21; N, 22·5. Found, C, 42·17; H, 4·43; N, 22·36.

3a.8. α-Nitroacetophenone.

(a) 1-Phenyl-2-nitroethanol.

The nitroalcohol was prepared from nitromethane and benzaldehyde and was obtained as a colourless liquid [315].

(b) α-Nitroacetophenone.

The nitroketone was prepared by the oxidation of 1-phenyl-2-nitroethanol and was obtained as yellow crystals (67 %) mp 104-105°C (lit.[315] 105°C).

3a.9. 2-Nitrocholestan-3-one.

The nitroketone was prepared by nitration of cholestan-3-one and was obtained as white crystals (70 %), mp 135-136 °C (lit.[314] 135-136 °C).

3a.10. 2-Nitrocyclohexanone.

(a) 1-Acetoxycyclohexene.

The enol acetate was prepared from cyclohexanone and acetic anhydride and was obtained as a yellow oil (78 %), bp 48-52°C at 0·7 mm Hg (lit.[301] 60-62°C at 1·5 mm Hg).

(b) 2-Nitrocyclohexanone.

The nitroketone was prepared by the action of acetyl nitrate on 1-acetoxycyclohexene[379] and was obtained as white crystals (35 %) mp 37-38°C(lit.[379] 38°C).

3a.11. 2-Nitro-4-t-butylcyclohexanone.

(a) 1-Acetoxy-4-t-butylcyclohexene.

The enol acetate was prepared from 4-*t*-butylcyclohexanone and acetic anhydride and was obtained as a yellow oil (46 %.) bp 92-96 °C at 0·6 mm Hg (lit.

(b) 2-Nitro-4-t-butylcyclohexanone.

The nitroketone was prepared by the action of acetyl nitrate on 1-acetoxy-4-*t*-butylcyclohexene according to the method of Griswold and Starcher[379]. Nitric acid (0·3 mole) was added to acetic anhydride (400 mls) with stirring at room temperature and was the cooled to -20 °C. 1-Acetoxy-4-*t*-butylcyclohexene (0·15 mole) was added and the temperature slowly rose to 0°C. This temperature was maintained for 1 hour. The solution was poured into water (500 mls) and was stirred at room temperature for 1 hour. The mixture was extracted with ether (3x100 mls), washed with water and dried (sodium sulphate). The solvent was removed under reduced pressure to give a brown solid which was recrystalized from 60/80 petrol to give white crystals (92 %), mp 75-79°C. Required for $C_{10}H_{17}NO_3$ C, 60·28; H, 8·6; N, 7·03. Found C, 60·7; H, 8·59; N, 6·96.

3b. Solution photochemistry of α-nitroketones.

The photoreactions described in this section, unless otherwise specified, were carried out using a 500 W Hanovia medium pressure mercury arc lamp, surrounded by a water cooled pyrex jacket. Dry oxygen free nitrogen, saturated with the solvent vapour was passed through the solution for at least 1 hour prior to irradiation, some irradiations were performed with a continous flush of nitrogen and others were performed under a sealed atmosphere of nitrogen. The reactions were followed by observing the reduction in intensity of the assymmetric stretch of the saturated nitro group (1550 cm^{-1}) or by following the reaction of the nitroketone by g.l.c.

3b.1. Irradiation of 3-nitrobutan-2-one in methanol.

A solution of the nitroketone (0·15 mole) in methanol (160 mls) was irradiated using a continous nitrogen flush for 36 hours. The solvent was removed under reduced pressure to give an oil , ν max. 1735, 1690,1550 and 1360 cm^{-1}. This oil was chromatographed on silica gel (200 g) . Unreacted nitroketone (20 %) was eluted first followed by a white crystaline material which was recrystalized from 60/80 petrol to give white crystals mp 75-76°C, ν max. 3570, 3300, 1690 and 1360 cm^{-1} and δ ($CDCl_3$) 10·0 (1H, singlet), 2·48(3H, singlet) and 2·02(3H, singlet). This photoproduct was identified as 3-hydroxyiminobutan-2-one, isolated in 20 % yield.

3b.2. Irradiation of 3-nitrobutan-2-one in ethanol.

A solution of the nitroketone (0·015mole) in ethanol (160 mls) was irradiated using a continous nitrogen flush for 36 hours, the solvent was removed under reduced pressure to give a brown oil which was chromatographed on silica gel (200 g). Unreacted nitroketone (10 %) and 3-hydroxyiminobutan-2-one (43 %) were isolated.

3b.3. Irradiation of 3-nitrobutan-2-one in propan-2-ol.

A solution of the nitroketone (0·015 mole) in propan-2-ol (160 mls) was irradiated, using a continous nitrogen flush for 25 hours. The solvent was removed under reduced pressure to give a brown oil which was chromatographed on silica gel (200 g). Unreacted nitroketone (11 %) and 3-hydroxyiminobutan-2-one (40 %) were isolated.

3b.4. Irradiation of 3-nitrobutan-2-one in butan-1-ol.

A solution of 3-nitrobutan-2-one (0•015 mole) in butan-1-ol (160 mls) was irradiated using a continous nitrogen flush for 21 hours. The solvent was removed under reduced pressure to give a brown oil. Preparative scale t.l.c. (dichloromethane as developing solvent) isolated 3-hydroxyiminobutan-2-one (34 %).

3b.5. Irradiation of 3-nitrobutan-2-one in benzene.

A solution of the nitroketone (0•01 mole) in benzene (160 mls) was irradiated using a continous nitrogen flush for 24 hours. The solvent was removed under reduced pressure to give an oil which was chromatographed on silica gel (200g) to give unreacted nitroketone (43 %), 3-hydroxyiminobutan-2-one (3 %) and phenol (1 %).

3b.6, Irradiation of 3-nitrobutan-2-one in toluene.

A solution of the nitroketone (0•03 mole) in toluene (160 mls) was irradiated using a continous nitrogen flush for 40 hours. The solvent was removed under reduced pressure to give a brown oil. Use of preparative scale t.l.c. (dichloromethane as the developing solvent) led to the isolation of 3-hydroxyiminobutan-2-one (33 %) and small amounts (1-2 %) of dibenzyl, benzaldehyde and *o*-,*m*- and *p*-cresol.

3b.7. Irradiation of 3-nitrobutan-2-one in diethyl ether.

A solution of the nitroketone (0•02 mole) in diethyl ether (160 mls) was irradiated using a continous nitrogen flush for 24 hours. 3-Hydroxyimino butan-2-one (20 %) was detected and determined by g.l.c.

3b.8. Irradiation of 3-nitrobutan-2-one in chloroform.

A solution of the nitroketone (0•02 mole) in chloroform (160 mls) was irradiated under an atmosphere of nitrogen for 68 hours. The solvent was removed under reduced pressure to give a brown oil. Use of preparative scale t.l.c. (dichloromethane as the developing solvent) led to the isolation of 3-hydroxyiminobutan-2-one (5%).

3b.9 Irradiation of 3-nitrobutan-2-one in acetic acid.

A solution of the nitroketone (0·02 mole) in acetic acid (160 mls) was irradiated under an atmosphere of nitrogen for 24 hours. After this time no reaction had occurred and the reaction was discontinued.

3b.10. Measurement of the amount of 3-nitrobutan-2-one which had photoreacted in various alcohols.

These reactions were followed by g.l.c., a sample of the solution prior to irradiation was retained in each case. The area of the peak due to the nitroketone was then compared to the areas of the nitroketone peak of samples removed after varying periods of irradiation, equal quantities of the reaction solutions being put on the column.

(a) Methanol.

A solution of the nitroketone (0·015 mole) in methanol (160 mls) was irradiated using a continous nitrogen flush for 24 hours, 36 % of the nitroketone had reacted.

(b) Ethanol.

A solution of the nitroketone (0·015 mole) in ethanol (160 mls) was irradiated using a continous nitrogen flush for 24 hours, 78 % of the nitroketone had reacted.

(c) Propan-2-ol.

A solution of the nitroketone (0·015 mole) in propan-2-ol (160 mls) was irradiated using a continous nitrogen flush for 24 hours, 81 % of the nitroketone had reacted.

3b.11. Measurement of the amount of 3-hydroxyiminobutan-2-one formed in the irradiation of 3-nitrobutan-2-one in various solvents.

These reactions were followed by g.l.c.; diphenyl ether was used as an internal standard. Samples of known volume were removed from the reaction mixtures after varying periods of irradiation, these were mixed with solutions containing known amounts of the standard. These mixtures were analysed by g.l.c. and the ratio of the area of the oximinoketone peak to the area of the diphenyl ether peak was related to ratio of the weights of each component by means of a predetermined calibration curve.

(see 5.1).

(a) Methanol (nitrogen flush).

A solution of the nitroketone (0•02 mole) in methanol (160 mls) was irradiated eventually for 36 hours. The amount of 3-hydroxyiminobutan-2-one was determined after varying periods of time (graph I). The solvent was removed under reduced pressure to give a brown oil. This oil was shaken with benzene and water (10 mls of each). 3-Hydroxyiminobutan-2-one (17 %) and unreacted nitroketone (7 %) were isolated from the benzene layer, after drying over sodium sulphate and removal of the benzene under reduced pressure and preparative scale t.l.c. using dichloromethane as the developing solvent. A sample of the aqueous layer on treatment with ferric chloride solution gave a purple colour, indicative of a hydroxamic acid. The aqueous layer was mixed with cupric acetate (0•01 mole) in water and a green precipitate was obtained. This was filtered off and suspended in ethanol and hydrogen sulphide was passed through for 1 hour, which led to the formation of black precipitate and the disappearance of the green solid. Filtration of this mixture and removal of the ethanol under reduced pressure however failed to give any crystaline material.

(b) Ethanol (nitrogen flush).

A solution of the nitroketone (0•02 mole) in ethanol (160 mls) was irradiated eventually for 32 hours. The amount of 3-hydroxyiminobutan-2-one was determined after varying periods of time (graph I). The solvent was removed under reduced pressure to give a brown oil which was shaken with benzene and water. 3-Hydroxyiminobutan-2-one (25 %) was isolated from the benzene layer, using t.l.c. (dichloromethane as the developing solvent). The water layer was carefully evaporated to give a crystaline material which was recrystalized from ethyl acetate and 60/80 petrol to give white crystals mp 88°C and m/e 43, identified as acet hydroxamic acid obtained in 7 % yield.

(c) Propan-2-ol (nitrogen flush).

A solution of the nitroketone (0•02 mole) in propan-2-ol (160 mls) was irradiated eventually for 32 hours. The amount of 3-hydroxyiminobutan-2-one was determined at varying periods of time (graph I). The solvent was removed under reduced pressure to give a brown oil, which was shaken with benzene and water. 3-Hydroxyiminobutan-2-one (26 %) was isolated from the benzene layer and acet hydroxamic acid (5 %) was isolated from the aqueous layer.

(d) Methanol (nitrogen atmosphere).

A solution of 3-nitrobutan-2-one (0·02 mole) in methanol (160 mls) was irradiated for eventually 36 hours. The amount of 3-hydroxyiminobutan-2-one was determined after varying periods of time (graph I). The solvent was removed under reduced pressure to give a brown oil. This was shaken with benzene and water and 3-hydroxyiminobutan-2-one (17 %) and unreacted nitroketone (10 %) were isolated from the benzene layer and acet hydroxamic acid (4 %) was isolated from the aqueous layer.

(e) Ethanol (nitrogen atmosphere).

A solution of the nitroketone (0·02 mole) in ethanol (160 mls) was irradiated for eventually 32 hours. The amount of 3-hydroxyiminobutan-2-one was determined after various periods of time (graph I). The solvent was removed under reduced pressure to give a brown oil, which was shaken with benzene and water. 3-Hydroxyiminobutan-2-one (25 %) was isolated from the benzene layer using t.l.c. (dichloromethane as developing solvent). The aqueous layer gave a positive colour test with ferric chloride.

(f) Benzene (nitrogen atmosphere).

A solution of the nitroketone (0·02 mole) in benzene (160 mls) was irradiated for eventually 36 hours. The amount of 3-hydroxyiminobutan-2-one was determined after varying periods of time (graph I). The solvent was removed under reduced pressure to give a brown oil, which was shaken with benzene and water. 3-Hydroxyiminobutan-2-one (5%) and unreacted nitroketone (25 %) and phenol (3 %) were isolated from the benzene layer. The aqueous layer gave a positive colour test with ferric chloride.

(g) Toluene (nitrogen atmosphere).

A solution of the nitroketone (0·02 mole) in toluene (160 mls) was irradiated for eventually 36 hours. The amount of 3-hydroxyiminobutan-2-one was determined after varying periods of time (graph I). The solvent was removed under reduced pressure to give a brown oil. This was shaken with benzene and water. 3-Hydroxyiminobutan-2-one (20 %) was isolated along with o-, m- and p-cresol (5 %) from the benzene layer, by use of preparative scale t.l.c. (dichloromethane as developing solvent). The aqueous layer gave a positive colour test with ferric chloride.

3b.12. Acet hydroxamic acid.

The hydroxamic acid was prepared from ethyl acetate and hydroxylamine and was obtained as white crystals (29 %) mp 88°c (lit.[395] 88°c)

3b.13. G.l.c. determination of the amount of acet hydroxamic acid present after irradiation of 3-nitrobutan-2-one in methanol.

A solution of the nitroketone (0·02 mole) in methanol (160 mls) was irradiated under an atmosphere of nitrogen for 24 hours. A sample of the irradiation mixture gave a positive test with ferric chloride, but no acethydroxamic acid could be detected by g.l.c. (PEGA / Chromosorb W).

3b.14. Irradiation of 3-nitrobutan-2-one in methanol (quartz filter).

A solution of the nitroketone (0·02 mole) in methanol (120 mls) was irradiated with a continous nitrogen flush for 9 hours. The solvent was removed under reduced pressure to give a brown oil. 3-Hydroxyiminobutan-2-one (13 %) was isolated using preparative scale t.l.c. (dichloromethane as the developing solvent).

3b.15. Irradiation of 3-nitrohexan-2-one in methanol.

A solution of the nitroketone (0·02 mole) in methanol (160 mls) was irradiated with a continous nitrogen flush for 55 hours. After this time, 90 % of the nitroketone had reacted (by g.l.c.) and the solvent was removed under reduced pressure to give a brown oil, ν max. 3580, 3200, 1735, 1690, 1550 and 1380 cm^{-1}. Use of preparative scale t.l.c., using dichloromethane as the developing solvent, led to the isolation of unreacted nitroketone (5 %), and a solid, which after recrystallization from 60/80 petrol gave white crystals mp 60°C. ν max. 3580, 3200, 1690 and 1380 cm^{-1} and δ ($CDCl_3$) 10·1 (1H, singlet), 2·5 (2H, triplet), 2·4 (3H, singlet), 1·6 (2H, multiplet) and 0·95 (3H, triplet), identified as 3-hydroxyiminohexan-2-one, by comparison with an authentic sample. A sample of the reaction mixture prior to the removal of the solvent gave a positive colour test with ferric chloride.

3b.16 3-Hydroxyiminohexan-2-one.

(a) Direct nitrosation: The hydroxyiminoketone was prepared by the action of methyl nitrite on hexan-2-one[405] and was obtained as white crystals (34 %) mp 60°C, ν max. 3580, 3200, 1690 and 1380 and δ (CDCl$_3$) 10·0(1H, singlet), 2·5(2H, triplet), 2·4(3H, singlet),1·6(2H, multiplet) and 0·95 (3h, triplet).

(b) Reduction of 3-nitrohexan-2-one.: Glacial acetic acid (0·06 mole) was added to a vigorously stirred mixture of zinc dust (0·031 mole) and 3-nitrohexan-2-one (0·03 mole) in water (50 mls) over 0·5 hours and the mixture was stirred for three hours at room temperature. The mixture was extracted with ether (3x200 mls). The ether extracts were washed with water (2x100 mls) and dried over sodium sulphate. The ether was removed under reduced pressure to give a brown oil which was distilled (74-76°C at 0·5 mm Hg) to give a yellow oil which solidified. This was identified as 3-hydroxyiminohexan-2-one.

3b.17. Irradiation of 3-nitrohexan-2-one in ethanol.

A solution of the nitroketone (0·02 mole) in ethanol (290 mls) was irradiated under an atmosphere of nitrogen for 36 hours. 3-Hydroxyiminohexan-2-one (40 %) was isolated using preparative scale t.l.c. (dichloromethane as the developing solvent).

3b.18. Irradiation of 2-nitroheptan-3-one in methanol.

A solution of the nitroketone (0·04 mole) in methanol (160 mls) was irradiated with a continous nitrogen flush for 46 hours. The solvent was removed under reduced pressure to give a brown oil ν max. 3580, 3500, 1740, 1690, 1550, 1365 and 1040 cm^{-1}. Use of preparative scale t.l.c. (dichloromethane as developing solvent) led to the isolation of unreacted nitroketone (10 %), valeric acid (5 %) and an oil ν max. 3580, 3500, 1690, 1365 and 1040 cm^{-1} and δ (CDCl$_3$) 10·0 (1H, broad), 2·9(2H, triplet), 2·0(3H, singlet) and 0·8-1·8(7H, complex), identified as 2-hydroxyiminoheptan-3-one, isolated in 15 % yield.

3b.19. 2-Hydroxyiminoheptan-3-one.

Glacial acetic acid (0·04 mole) was added to a vigorously stirred mixture of zinc dust (0·02 mole) and 2-nitroheptan-3-one (0·019 mole) in water (50 mls) over 0·5 hours and was then stirred for 2 hours. The mixture was extracted with ether (3x200 mls). The ether was washed with water (2x100 mls) and then dried over sodium sulphate. The ether was removed under reduced pressure to give a brown oil ν max. 3580, 1690, 1365 and 1040 cm^{-1}. The oil was chromatographed on silica gel (100 g) and a yellow oil was obtained using 60/80 petrol-diethyl ether (50:50) as the eluting solvent. This oil was then distilled (90°C at 0·2 mm Hg) to give a clear oil ν max. 3580, 3300, 1690, 1365 and 1040 cm^{-1}, δ ($CDCl_3$) 10·0(1H, broad), 2·9(2H, triplet), 2·0(3H, singlet) and 0·8-1·8(7H, complex). Required for $C_7H_{13}NO_2$ C, 58·7; H, 9·1; N, 9·8. Found C, 58·4; H, 8·9; N, 9·6.

3b.20. Irradiation of 2-nitroheptan-3-one in ethanol.

A solution of the nitroketone (0·02 mole) in ethanol (160 mls) was irradiated under an atmosphere of nitrogen for 40 hours. The solvent was removed under reduced pressure to give a brown oil, which was treated with benzene and water. Unreacted nitroketone (10 %) and 2-hydroxyiminoheptan-3-one (30 %) were isolated using preparative scale t.l.c. (dichloromethane as developing solvent). The aqueous layer gave a positive colour test with ferric chloride.

3b.21. Valerohydroxamic acid.

(a) Ethyl valerate: The ester was prepared from pentanoic acid and ethanol and was obtained as a colourless liquid (63 %) bp 144°C (lit.[475] bp 144°C)

(b) Valerohydroxamic acid: The hydroxamic acid was prepared from ethyl valerate and hydroxylamine and was obtained as a pale yellow oil[397] obtained in 52 % yield.

3b.22. Irradiation of 3-methyl-3-nitrobutan-2-one in methanol.

A solution of the nitroketone (0·05 mole) in methanol (290 mls) was irradiated using a continous nitrogen flush. After 24 hours, 17 % of the nitroketone had reacted and after 140 hours 87 % of the nitroketone had reacted. The solvent was removed under reduced pressure to give a brown oil. Use of preparative scale t.l.c. (dichloromethane as developing solvent) led to the isolation of unreacted nitroketone (5%) and an oil ν max. 1720 and 1370 cm^{-1} and δ ($CDCl_3$) 2·35(1H, doublet) and 1·3(3H, doublet). This product was not further identified.

3b.23. Irradiation of α-nitroacetophenone in methanol.

A solution of the nitroketone (0·01 mole) in methanol (160 mls) was irradiated under an atmosphere of nitrogen for 16 hours. The solvent was removed under reduced pressure to give a brown oil ν max. 1700 cm^{-1}. T.l.c. (dichloromethane as developing solvent) indicated that there were three or four photoproducts present, which preparative scale t.l.c. failed to isolate.

3b.24. Irradiation of 2-nitrocholestan-3-one in methanol.

A solution of the nitroketone (0·001 mole) in methanol (250 mls) was irradiated under an atmosphere of nitrogen for 3 hours. The solvent was removed under reduced pressure and the resulting brown solid was examined by t.l.c., using dichloromethane as the developing solvent, which indicated that there were four photoproducts present but preparative scale t.l.c. failed to isolate these products.

3b.25. Oximation of heptan-3-one.

A solution of the ketone (·125 mole) in dry ether (300 mls) and conc. HCl (1 ml) was stirred at 0°C whilst methyl nitrite (0·3 mole), prepared from adding a solution of conc. sulphuric acid (17 mls) in water (10 mls) to a solution of sodium nitrite (0·3 mole) in water (40 mls) and methanol (50 mls), was bubbled in over 1·5 hours. The ether solution was extracted with water (2x100 mls) then dried over sodium sulphate. The ether was removed under reduced pressure to give a brown oil ν max. 1710 and 1690 cm^{-1}. This oil was distilled under reduced pressure to give two fractions. The first, bp 30-35°C at 0·6 mm Hg was unreacted heptan-3-one (13 %) and the second was a yellow oil (45 %), bp 80-90°C at 0·5 mm Hg, ν max. 3560, 3280, 1690 and 1360 cm^{-1} and δ ($CDCl_3$) 3·1-2·4 (complex), 2·1 (singlet) and 1·8-0·7 (complex). G.l.c. analysis indicated that this fraction was a mixture of the isomeric oximinoketones (2-hydroxyiminoheptan-3-one and 4-hydroxyiminoheptan-3-one. Preparative scale t.l.c. (dichloromethane as developing solvent) and column chromatography failed to separate these two isomers.

3c. Tautomerization of α-nitroketones.

3c.1. U.V. spectra of α-nitroketones.

The U.V. spectra were obtained on an Unicam SP 800 spectrophotometer. Solutions were made up in the various solvents and a sample was run immediately, spectra were then run after varying periods of time until an equilibrium situation was reached. The results are shown below, in most cases the growth of another peak was noted.

Nitroketone: 3-nitrobutan-2-one.

Conc. in 25 mls. solvent (10^{-2}g)	Solvent	U.V. Maxima n.m. (ε) Before equilib.	After equilib.
1·73	Methanol	275 (100)	276 (115) 323 (85)
2·93	Ethanol	282 (100)	285 (146) 325 (156)
2·99	Propan-2-ol	285 (100)	290 (142) 320 (156)
0·11	Cyclohexane	297 (50)	315 (1067)
1·1	Benzene	-	327 (251)
0·99	Toluene	-	327 (260)
2·08	Acetonitrile	276 (99)	276 (99)
1·13	Diethyl ether	287 (90)	318 (194)
1·45	Carbon tetrachloride	284 (90)	320 (283)

Nitroketone: 3-Methyl-3-nitrobutan-2-one.

Conc. in 10 mls. solvent (10^{-2}g)	Solvent	U.V. Maxima n.m. (ε)
1·45	Methanol	279 (89)
1·31	Acetonitrile	278 (85)
0·93	Cyclohexane	285 (151)

Nitroketone: 2-nitroheptan-3-one.

Conc. 25 mls. (10^{-2}g)	Solvent	U.V. Maxima Before equilib.	 After equilib.
1·86	Ethanol	280	325
3·15	Methanol	290	330

Nitroketone: 3-nitrohexan-2-one.

Conc. 25 mls. (10^{-2}g)	Solvent	U.V. Maxima Before equilib.	 After equilib.
3·21	Ethanol	285	325
0·95	Methanol	280	325

3c.2. N.M.R. studies on α-nitroketones.

(a) ^{1}H n.m.r. spectra were obtained on the Joel ps-100 machine, to try to detect any signs of a tautomer.

3-Nitrobutan-2-one: δ ($CDCl_3$) 5·4 (1H, quartet), J = 6·8 Hz, 2·3 (3H, singlet) and 1·7 (3H, doublet) J = 6·8 Hz.

3-Methyl-3-nitrobutan-2-one: δ ($CDCl_3$) 4·9 (3H, singlet), and 2·9 (6H, singlet).

2-Nitroheptan-3-one: δ ($CDCl_3$) 5·4 (1H, quartet) J = 7Hz., 2·6 (2H, triplet) J = 7Hz., 1.62 (3H, doublet) J = 7 Hz., 1·2-1·6 (4H, complex) and 0·9 (3H, triplet).

3-Nitrohexan-2-one: δ ($CDCl_3$) 5·3 (1H, doublet of doublets), 2·3 (3H, singlet), 2·1 (2H, complex), 1·4 (2H, complex) and 1·0 (3H, triplet).

2-Nitro-4-t-butylcyclohexanone: δ ($CDCl_3$) 14·0 (0·7 H, singlet), 5·3 (0·3H, doublet of doublets), 2·7-1·2 (7H, complex) and 0·95 (9H, singlet).

2-Nitrocholestan-3-one. δ ($CDCl_3$) 14·0 (0·3 singlet), 0·8-2·6 (48H, complex)

The n.m.r. spectrum of 3-nitrobutan-2-one in CD_3OD was obtained using the Joel machine and it was found to be identical to the one detailed above. Leaving the sample at room temperature for 1 hour failed to show any signs of a tautomer (no change in the integration values).

3c.3. Enol ethers of α -nitroketones and related compounds.

(a) Methyl enol ether of 3-nitrobutan-2-one.

The nitroketone (0·1 mole) was reacted with 2,2-dimethoxypropane (0·3 mole) according to established methods[476]. However, only starting material was recovered.

(b) Dimethoxy acetal of α -nitroacetophenone.

The nitroketone (0·01 mole) in methanol (20 mls.) and trimethylorthoformate (0·02 mole) with 3 drops of conc. sulphuric acid was refluxed for 200 hours. The solvent was removed under reduced pressure to give a brown oil ν max. 1700, 1555 and 1550 cm^{-1}, identified as a mixture of the acetal and nitroketone. Column chromatography failed to separate this mixture.

(c) Diethoxy acetal of 3-nitrobutan-2-one.

The nitroketone (0·01 mole) in ethanol (20 mls.) and triethylorthoformate (0·02 mole) and 3 drops of conc. sulphuric acid were left to stand for 40 hours. The solvent was removed under reduced pressure to give a brown oil ν max. 1735, 1560 and 1550 cm^{-1}, which was distilled under reduced pressure (50-54°C at 0·5 mm Hg), but this distillation failed to separate the unreacted nitroketone from the acetal.

(d) Dimethoxy acetal of 2-nitroheptan-3-one.

The nitroketone (0·01 mole) in methanol (20 mls) and trimethylorthoformate (0·02 mole) with p-toluene sulphonic acid (0·001 mole) was refluxed for 120 hours. After this time no reaction had occured.

(e) Ethylene acetal of 2-nitrobutan-3-one.

The nitroketone was reacted with ethylene glycol using reported conditions[354]. The product was a mixture of the desired acetal and ethylene glycol which three reduced pressure distillations failed to separate.

3c.4. Enol esters of α -nitroketones.

(a) 2-Nitro-3-acetoxy-2-cholestene.

This was prepared from the nitroketone using reported conditions[314], mp 147-148°C (lit.[314] 147-148°C)

(b) Enol acetate of 2-nitro-4-t-butylcyclohexanone.

The nitroketone was reacted with acetic anhydride and pyridine according to the method of Hassner[314]. This led to the recovery of a brown oil from which no pure products could be obtained (t.l.c., using dichloromethane as developing solvent)

(c) Enol acetate of α-nitroacetophenone.

The nitroketone was reacted with acetic anhydride and pyridine according to the method of Hassner[314]. This led to the recovery of the starting material.

(d) Enol acetate of 2-nitrocyclohexanone.

(i) The nitroketone (0•01 mole) in acetic anhydride (20 mls) with p-toluene sulphonic acid (0•001 mole) was refluxed for 6 hours. Removal of the excess anhydride under reduced pressure led to a black oil, which by I.R. , had no compounds with an unsaturated nitro group present.

(ii) The nitroketone was reacted with acetic anhydride and pyridine according to the method of Hassner[314]. This led to a brown oil being recovered which by t.l.c. (dichloromethane as developing solvent) was a mixture of at least four compounds, which could not be separated.

3c.5. Enamines of α-nitroketones.

(a) Reaction between α-nitroacetophenone and pyrrolidine.

The nitroketone (0•025 mole) and pyrrolidine (0•05 mole) in benzene (50 mls) with p-toluene sulphonic acid (0•001 mole) was refluxed for 40 hours using a Dean and Stark trap. No water was obtained in the course of this experiment. The solvent was removed under reduced pressure to give a brown oil, which was distilled (140-146°C at 1•0 mm Hg), ν max. 1630 and 1410 cm^{-1}, δ ($CDCl_3$) 7•8 (5H, complex), 3•5-3•8 (4H, complex) and 1•8-2•1 (4H, complex) and m/e 175, 146, 105 and 77. Found C, 75•8; H, 7•6; N, 7•8.

(b) Reaction between α-nitroacetophenone and morpholine.

The nitroketone (0•025 mole) and morpholine (0•05 mole) in benzene (50 mls) with p-toluene sulphonic acid (0•001 mole) was refluxed for 40 hours. The solvent was removed under reduced pressure to give a brown oil which was distilled under reduced pressure (160-164°C at 1•5 mm Hg) to give a yellow oil which solidified. This was recrystalised from 60/80 petrol to give white crystals mp 74-75°C., ν max 1640 and 1420 cm^{-1}, δ ($CDCl_3$) 7•65 (5H, singlet) and 5•7 (8H, singlet). Found C, 69•55; H, 6•48; N, 7•45.

(c) Reaction between 2-nitroheptan-3-one and morpholine.

The nitroketone (0•02 mole) and morpholine (0•05 mole) in benzene (50 mls) with p-toluene sulphonic acid (0•001 mole) was refluxed for 22 hours. G.L.C. analysis of the crude reaction mixture identified nitroethane as a reaction product. The solvent was removed under reduced pressure to give a brown oil which was distilled under reduced pressure (120-122°C at 1•5 mm Hg) to give a yellow oil ν max. 1650, 1420 and 1120 cm^{-1} and δ (CDCl$_3$) 3•8 (8H, singlet), 2•2-2•6 (2H, complex), 1•2-1•8 (4H, complex) and 1•0-1•2 (3H, complex).

4. Thermal Reactions of α-Nitroketones.

These reactions were carried out by dissolving the nitroketone in the appropiate solvent and refluxing for various amounts of time, with the system being open to the atmosphere. The reactions were followed by I.R. (the reduction in the assymmetric stretch at 1550 cm^{-1}) or g.l.c. (PEGA/Chromosorb W).

4.1. Refluxing 3-nitrobutan-2-one in butan-1-ol.

(a) A solution of the nitroketone (0•02 mole) in butan-1-ol (100 mls) with p-toluene sulphonic acid (0•001 mole) was refluxed for 24 hours. The solvent was removed under reduced pressure to give a brown oil, ν max. 3575, 3300, 2960, 1695, 1360, 1125 and 1030 cm^{-1}. Preparative scale t.l.c. (dichloromethane as the developing solvent) led to the isolation of two products. The product with the greater R$_f$ value was an oil ν max. 2960, 1460, 1130, 1080 and 1030 cm^{-1} and δ (CDCl$_3$) 4•8 (1H, triplet), 3•4 (4H, complex), 1•1-1•7 (12H, complex) and 0•9 (9H, triplet), identified as the dibutyl acetal of butanal, (0•00075 moles isolated). The product with the smaller R$_f$ value was a solid, which was recrystallized from 60/80 petrol to give white crystals mp 75-76°C, ν max. 3575, 3300, 1695, 1460, 1125 and 1120 cm^{-1} and δ (CDCl$_3$) 10•0 (1H, singlet), 2•0 (3H, singlet) and 2•4 (3H, singlet), identified as 3-hydroxyiminobutan-2-one, obtained in 20 % yield.

(b) A solution of the nitroketone (0•02 mole) in butan-1-ol (100 mls) was refluxed eventually for 20 hours. After 15 hours, the reaction mixture was examined by g.l.c. and 91 % of the nitroketone had reacted. After 20 hours, all the nitroketone had reacted. Acetic acid was detected by g.l.c. and determined to be present in 8 % yield. The solvent was removed under reduced pressure to give a brown oil. Use of preparative scale t.l.c. (dichloromethane as developing solvent) led to the isolation of the dibutyl acetal of butanal (0•00074 moles) and 3-hydroxyiminobutan-2-one, obtained in 20 % yield.

4.2. Dibutyl acetal of butanal.

The dibutyl acetal was prepared from butan-1-ol and butanal[474] and was obtained as a colourless liquid bp 100-104°C at 1•0 mm Hg.

4.3. Refluxing 3-nitrobutan-2-one in propan-1-ol.

A solution of the nitroketone (0•02 mole) in propan-1-ol (100 mls) was refluxed for 35 hours. After this time the reaction mixture was analysed by g.l.c., 75 % of the nitroketone had reacted and acetic acid (5 %) and 3-hydroxyiminobutan-2-one (12 %) were detected. The solvent was removed under reduced pressure to give a brown oil. Use of preparative scale t.l.c. (dichloromethane as the developing solvent) led to the isolation of two products. The product of smaller R_f value was identified as the oximinoketone. The product of greater R_f value was an oil, ν max. 2960, 1130 and 1080 cm^{-1}, tentatively identified as the dipropyl acetal of propanal.

4.4 Refluxing 3-nitrobutan-2-one in dibutyl ether.

A solution of the nitroketone (0•02 mole) in di-n-butyl ether (100 mls) was refluxed for 27 hours. The reaction mixture was examined by g.l.c. and 50 % of the nitroketone had reacted and acetic acid (3%) and 3-hydroxyiminobutan-2-one (10 %) were detected.

4.5. Refluxing 3-nitrobutan-2-one in dioxane.

A solution of the nitroketone (0•02 mole) in dioxane (100 mls) was refluxed for 44 hours. The reaction mixture was examined by g.l.c. and 20 % of the nitroketone had reacted and acetic acid (2%) and 3-hydroxyiminobutan-2-one (10 %) were detected.

4.6. Refluxing 3-nitrobutan-2-one in cyclohexanol.

A solution of the nitroketone (0•02 mole) in cyclohexanol (100mls) was refluxed for 22 hours. The reaction mixture was examined by g.l.c. and 50 % of the nitroketone had reacted and 3-hydroxyiminobutan-2-one (5%) was detected.

4.7. Refluxing 3-nitrobutan-2-one in toluene.

A solution of the nitroketone (0·02 mole) in toluene (100 mls) was refluxed for 70 hours, after this time no reaction had occurred.

4.8. Refluxing 3-nitrobutan-2-one in acetonitrile.

A solution of the nitroketone (0·02 mole) in acetonitrile (100 mls) was refluxed for 24 hours, after this time no reaction had occurred.

4.9. Refluxing 3-nitrobutan-2-one in nitroethane.

A solution of the nitroketone (0·02 mole) in nitroethane (100 mls) was refluxed for 20 hours, after this time no reaction had occurred.

4.10. Refluxing 3-nitrobutan-2-one in t-butyl alcohol.

A solution of the nitroketone (0·02 mole) in t-butyl alcohol (100 mls) was refluxed for 24 hours, after this time no reaction had occurred.

4.11. Refluxing 2-nitroheptan-3-one in butan-1-ol.

A solution of the nitroketone (0·02 mole) in butan-1-ol (100 mls) was refluxed for 35 hours. The solvent was removed under reduced pressure to give a brown oil ν max. 3580, 3300, 2960, 1735, 1710, 1690 and 1460 cm^{-1}. Use of preparative scale t.l.c. (dichloromethane as the developing solvent) led to the isolation of five bands. Band (1) was the dibutyl acetal of butanal (0·0005 mole). Band (2) was an oil ν max. 2962, 2940, 1735 and 1375 cm^{-1}, identified as n-butyl pentanoate (14 %). Band (3) was unreacted nitroketone (8%). Band (4) was an oil ν max. 3500, 3300, 1690, 1370 and 1010 cm^{-1}, identified as 2-hydroxyiminoheptan-3-one (25 %). Band (5) was an oil ν max. 2960-2880 and 1710 cm^{-1}, identified as pentanoic acid (10 %).

4.12. n-Butyl pentanoate.

The ester was prepared from pentanoic acid and butan-1-ol[477], bp 187°C (lit.[477] 187°C).

4.13. Refluxing 3-methyl-3-nitrobutan-2-one in butan-1-ol.

A solution of the nitroketone (0·02 mole) in butan-1-ol (100 mls) was refluxed for 21 hours. After this time 50 % of the nitroketone had reacted. The solvent was removed under reduced pressure to give a brown oil. Use of preparative scale t.l.c. (dichloromethane as developing solvent) led to the isolation of unreacted nitroketone (0•005 mole) and the dibutyl acetal of butanal (0•0001 mole).

4.14. Refluxing 3-nitrobutan-2-one in butan-1-ol, in a stream of nitrogen.

A solution of the nitroketone (0•02 mole) in butan-1-ol (100 mls) was refluxed for 15 hours whilst a stream of nitrogen was passed through the solution. After this time, 93 % of the nitroketone had reacted and 3 % of 3-hydroxyiminobutan-2-one had been formed, by g.l.c. analysis.

4.15. Refluxing pentanoic acid in butan-1-ol.

A solution of the acid (0•01 mole) in butan-1-ol (100 mls) was refluxed for 20 hours. G.l.c. analysis showed that n-butyl pentanoate (10 %) was the product.

4.16. Refluxing pentanoic acid in butan-1-ol with nitric acid.

A solution of pentanoic acid (0•01 mole) in butan-1-ol (100 mls) with 3 drops of conc. nitric acid was refluxed for 20 hours. G.l.c. analysis showed that n-butyl pentanoate (80 %) was the product. The solvent was removed under reduced pressure to give a brown oil. Use of preparative scale t.l.c. (dichloromethane as developing solvent) led to the recovery of the dibutyl acetal of butanal (0•0001 mole) and n-butylpentanoate.

4.17. Refluxing butan-1-ol and nitric acid.

Butan-1-ol (100 mls) with conc. nitric acid (3 drops) was refluxed for 20 hours. The solvent was removed under reduced pressure to give the dibutyl acetal of butanal (0•05 mole), after distillation (70°C at 1•0 mm Hg).

4.18. Refluxing butanal and nitric acid in butan-1-ol.

Butanal (0•1 mole) in butan-1-ol (100 mls) with conc. nitric acid (3 drops) was refluxed for 20 hours. The solvent was removed under reduced pressure to give the dibutyl acetal of butanal (80 %) after distillation (172-174°C at 5 mm Hg).

4.19. n-Butyl nitrite.

The nitrite was prepared from nitrous acid and butan-1-ol[478] and was obtained as a colourless liquid (75 %) bp 76-77°C (lit.[478] 77°C).

4.20. Refluxing n-butyl nitrite in butan-1-ol.

A solution of the nitrite (0•01 mole) in butan-1-ol (100 mls) was refluxed for 20 hours. The solvent was removed under reduced pressure to give, after distillation, the dibutyl acetal of butanal (0·003 mole)

4.21. n-Butyl nitrate.

The nitrate was prepared from butan-1-ol and nitric and sulphuric acids and was obtained as a colourless liquid (67 %) bp 133-134°C (lit[479] 133-134°C).

4.22. Refluxing n-butyl nitrate in butan-1-ol.

A solution of the nitrate (0·01 mole) in butan-1-ol (100 mls) was refluxed for 20 hours. The solvent was removed under reduced pressure to give, after distillation, the dibutyl acetal of butanal (0·002 mole).

4.23. Refluxing 3-hydroxyiminobutan-2-one in butan-1-ol.

A solution of the oximinoketone (0·02 mole) in butan-1-ol (100 mls) was refluxed for 20 hours. After this time, no reaction had occurred.

4.24. Refluxing 3-hydroxyiminobutan-2-one and nitric acid in butan-1-ol.

A solution of the oximinoketone (0·02 mole) in butan-1-ol (100 mls) with conc. nitric acid (3 drops) was refluxed for 20 hours. G.l.c. analysis showed that 20 % of the oximinoketone had reacted and acetic acid (12 %) was formed.

4.25. Refluxing 3-nitrobutan-2-one and nitric acid in toluene.

A solution of the nitroketone (0·01 mole) in toluene (100 mls) with nitric acid (3 drops) was refluxed for 20 hours. G.l.c. analysis showed that 23 % of the nitroketone had reacted and acetic acid (6 %) was formed.

4.26. Reaction of toluene with dinitrogen tetroxide.

Dinitrogen dioxide (0·008 mole) was added to toluene (50 mls) and was refluxed for 6 hours. The solvent was removed under reduced pressure to give a brown oil. Use of preparative scale t.l.c. (dichloromethane as the developing solvent) led to the isolation of phenyl nitromethane (50 %), benzaldehyde (5 %), benzylalcohol (4 %) and benzoic acid (3%).

4.27. Refluxing 2-nitrocyclohexanone in butan-1-ol.

A solution of the nitroketone (0·05 mole) in butan-1-ol (50 mls) was refluxed for 20 hours. The solvent was removed under reduced pressure to give a brown oil ν max. 2960, 2935, 1740, 1558, 1180 and 1160 cm^{-1}. This oil was examined by t.l.c. . Only one spot was obtained when the plates were developed in benzene, benzene: 60/80 petrol (1:1) and 60/80 petrol.

The oil was distilled (120-125°C at 0·5 mm Hg) to give a clear oil with the same I.R. spectrum as above and δ ($CDCl_3$) 4·3 (2H, triplet), 3·95 (2H, triplet), 1·1-2·4 (12H, complex) and 0·92 (3H, triplet). This was identified as the n-butyl ester of 6-nitrohexanoic acid (83 %) by comparison with an authentic sample.

4.28. Refluxing 2-nitrocyclohexanone in propan-1-ol.

A solution of the nitroketone (0·005 mole) in propan-1-ol (50 mls) was refluxed for 20 hours. The solvent was removed under reduced pressure to give a brown oil ν max. 2980, 1740 1555, 1460, 1380, 1180 and 1160 cm^{-1}. This oil was distilled under reduced pressure (135-140°C at 0·8 mm Hg) to give a clear oil with the same I.R. spectrum as above and δ ($CDCl_3$) 4·34 (2H, triplet), 3·91 (2H, triplet), 1·2-2·4 (10H, complex) and 0·92 (3H, triplet). This was identified as the n-propyl ester of 6-nitrohexanoic acid (79 %) by comparison with an authentic sample.

4.29. 6-Nitrohexanoic acid.

The acid was prepared by reacting 2-nitrocyclohexanone with sodium bicarbonate[332] and was obtained as a clear oil bp 140-145°C at 0·35 mm Hg (lit.[332] 136°C at 0·3 mm Hg).

4.30. n-Butyl ester of 6-nitrohexanoic acid.

6-Nitrohexanoic acid (0·005 mole) and butan-1-ol (15 mls) with conc. sulphuric acid (3 drops) was refluxed for 20 hours. The reaction mixture was poured into water (150 mls), extracted with ether (3x100 mls), washed with water (2x100 mls) and dried over sodium sulphate. The ether and excess butan-1-ol were removed under reduced pressure to give a brown oil which was distilled (140-142°C at 0·6 mm Hg) to give a clear oil(83 %) ν max. 2960, 2935, 1740, 1558, 1180 and 1160 cm^{-1} and δ ($CDCl_3$) 4·3 (2H, triplet), 3·95 (2H, triplet), 1·1-2·4 (12H, complex) and 0·92 (3H, triplet). Found C, 55·0; H, 8·8; N, 6·15. Required for $C_{10}H_{19}NO_4$ C, 55·28; H, 8·81; N, 6·45.

4.31. n-Propyl ester of 6-nitrohexanoic acid.

6-Nitrohexanoic acid (0·005 mole) and propan-1-ol (15 mls) with conc. sulphuric acid (3 drops) was refluxed for 20 hours. The reaction mixture was poured into water (150 mls), extracted with ether (3x100 mls), washed with water (2x100 mls) and dried over sodium sulphate. The ether and excess propan-1-ol were removed under reduced pressure to give a brown oil which was distilled (120-122°C at 0·5 mm Hg) to give a clear oil ν max. 2980, 1740, 1555, 1460, 1380, 1180 and 1160 cm^{-1} and δ ($CDCl_3$) 4·34 (2H, triplet), 3·91 (2H, triplet), 1·2-2·4 (10H, complex) and 0·92 (3H, triplet). Found, C, 53·35; H, 8·65; N, 6·58. Required for $C_9H_{17}NO_4$ C, 53·19; H, 8·43; N, 6·89.

Results of quantitative measurements of the formation of 3-hydroxyimino-butan-2-one from 3-nitrobutan-2-one in various solvents (3b.11)

Solvent.	Degassing procedure	Reaction Time (hours)	/ Yield of Oximinoketone.
Methanol	N_2 flush	16	10•3
		20	14
		24	15•8
		28	18
		32	19•8
		36	23•5
Ethanol	N_2 flush	16	19•4
		20	24•3
		24	27•7
		28	30•7
		32	34•7
Propan-2-ol	N_2 flush	12	26•6
		16	33•7
		20	37•1
		24	40•5
Methanol	N_2 atmosphere	12	9•9
		16	11•9
		20	14•9
		24	19•3
Ethanol	N_2 atmosphere	8	11•3
		12	15•8
		16	21•3
		20	25•7

Solvent.	Degassing procedure	Reaction Time (hours)	% Yield of Oximinoketone.
Benzene	N_2 atmosphere	18	11·9
		21	13·4
		24	13·8
		28	15·3
		36	17·3
Toluene	N_2 atmosphere	16	19
		20	20
		24	22·9
		28	23·6
		36	23·2

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