A thesis

CONCERNING COPPER AND ALKYLSALICYLALDOXIMES.

Presented by

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The thesis is submitted to the University of Kent at Canterbury for the degree of Ph.D. in the Faculty of Natural Science.

Since graduating with honours in Chemistry at the University of Manchester, the author has been engaged in full time research under the joint supervision of Professor J.A. Connor and Dr. R. Price.

No portion of the work referred to in this thesis has been submitted in support of an application for another degree or qualification of this or any other University or other Institution of Learning.

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His mother for the typing of the thesis.

Abbreviations.

Me	=	**Methyl**
Et	=	**Ethyl**
Pr	=	**Propyl**
Bu	=	**Butyl**
Ar	=	**Aryl**
R	=	**Alkyl**
L	=	**Ligand**
n	=	**normal**
i	=	**iso**
t	=	**tert**
s	=	singlet
d	=	doublet
t	=	triplet (**when in N.M.R. data**)
q	=	quartet
J	=	coupling constant
Hz	=	Hertz
I.R.	=	Infrared
U.V.	=	Ultraviolet
M.S.	=	Mass Spectrum
N.M.R.	=	Nuclear Magnetic Resonance
G.L.C.	=	Gas Liquid Chromatography
T.L.C.	=	Thin Layer Chromatography
A.A.	=	Atomic Absorption
T.M.S.	=	Tetramethylsilane
P.V.C.	=	Poly Vinyl Chloride
b.pt	=	Boiling point
m.pt	=	Melting point

EQUIPMENT.

A.A. UNICAM SP90A series 2.

using a copper lamp at wavelength 324.8nm and slit width 1.5mm. Air flow of 5 l min.$^{-1}$, acetylene flow 1 l min.$^{-1}$.

U.V. UNICAM SP800.

1 cm path length cells.

I.R. PERKIN ELMER 683.

liquids as liquid film on NaCl plates.

solids as KBr discs.

G.L.C. PYE series 104 Dual Flame Ionisation Detector.

SP1000 W.C.O.T. capillary column with split injection, nitrogen as carrier gas and hydrogen/air flame.

M.S. V.G. Analytical modified MS-9.

N.M.R. JEOL JNM-PS-100.

100 MHz for Proton and 24.1 MHz for ^{13}C spectra.

T.M.S. used as standard and $CDCl_3$ as solvent.

ABSTRACT.

Copper, a metal known for centuries due to ease of production of the pure metal, is now mined from poorer and poorer quality ores. A review of the methods used to produce copper metal from its ores and of the organic compounds which are used or which have been proposed for use as ligands in the hydrometallurgical production of copper is presented in Chapter 1. The ligands of choice for industrial use are 5-t-alkyl-2-hydroxybenzaldoximes or 5-t-alkyl-2-hydroxybenzoketoximes. Both of these are derived from 4-nonylphenol which is itself a complex mixture of isomeric alkylphenols of unknown composition.

The thesis describes the preparation of thirteen isomerically pure 5-alkyl-2-hydroxybenzaldoximes of known structure and a study of the effects caused by the variation of this chain structure. The benzaldoximes are prepared in the following way - a Reimer-Tiemann reaction on a 4-alkylphenol to produce the 5-alkyl-2-hydroxybenzaldehyde which was then reacted with hydroxylamine hydrochloride to yield the desired oxime. Of the 4-alkylphenols used, one was purchased, two were prepared by a Fries rearrangement of a phenyl ester followed by Clemmensen reduction of the ketone and the remaining ten prepared by a Friedel-Crafts alkylation of phenol with an alkene mixture which would yield one isomerically pure 4-alkylphenol. The alkyl chains have elemental formulae of C_5H_{11}, C_7H_{15}, C_8H_{17} or C_9H_{19}. Many of these oximes are novel in that they have only been previously reported as mixtures with other isomeric contaminants. Also many of the precursors are novel and for the majority of compounds described in Chapters 3, 4 and 5, proton and ^{13}C N.M.R. and mass spectra have not been reported previously.

Capilliary column G.L.C. has been used to try and identify components of the commercially available oxime ligands. The hydroxybenzaldoximes have been converted to their copper(II) complexes which have been characterised by their infrared spectrum and their melting point.

A review of methods used in studying kinetics of copper complexation with oxime ligands is presented in the final chapter together with the reasons for the preferred use of a quiescent interface cell (Lewis cell) method. Significant differences in the rate of copper complex formation (extraction) were observed in low polarity solvents with variation in the alkane chain structure.

The structure of the alkyl chain causes little variation in the rate of decomposition (strip) of the copper complex upon treatment with aqueous sulphuric acid. Using the following notation Ar-CRR'R" the structure of the alkyl chain will be presented as RR'R". The observed order of K_{ext} in hexane is: Et n-Pr n-Pr; Me Me Et; Me Me i-Bu; Me Et $n\text{-}C_5H_{11}$; various (the industrial extractant Acorga P50); Me Me $n\text{-}C_6H_{13}$; Me Et n-Pr; Me Me n-Bu; Me n-Pr n-Bu; Et Et n-Bu; Me Me CH_2CMe_3. The observed order for K_{ext} in toluene is: Me Me CH_2CMe_3; H H $n\text{-}C_6H_{13}$; H H $n\text{-}C_8H_{17}$; Et Et Et; various (Acorga P50). The observed differences are due to steric effects and attempts to rationalise the observed ordering and chain structure are presented.

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CHAPTER 1. INTRODUCTION.

Copper is a word that, to the organic chemist, conjures up alkyl- and aryl-cuprolithium reagents (1,2,3). However its organic chemistry stretches to include, for example, aromatic nucleophilic substitution (4,5,6). But does one think beyond that? What of cables, electrical equipment, and alloys such as brass and bronze? These industries use vast amounts of copper and the quantity needed will not decrease significantly in the future. In fact, it is estimated (7) that every U.S. citizen requires 25 lbs of copper a year.

The working of copper began centuries ago. In 3000B.C. the Egyptians used copper (8). The atomic symbol for copper is Cu. This is short for Cuprum, a corrupt form of Cyprum which was the name given to copper by the Romans, as it came from the island of Cyprus. Copper can be found as the metal, called native copper, and it is this that would first have been used. It is likely that the effect of roasting the green rocks found with native copper would have been observed to yield the metal (9,10).

The ores of copper can be divided roughly into two classes, sulphide ores and oxidised ores. It is estimated that 90% of copper occuring in the earth's surface is in the form of sulphide ores (9). Representative sulphide ores are Chalcopyrite (34.5), Bornite (63.3), Chalcocite (79.8) and Covellite (66.4), (the number in brackets is the copper content by weight percent) (11). Representative oxidised ores are Azurite (55.3), Malachite (57.4), Chrysocolla (36.1) (11,12). In general, the oxidised ores have been formed by the weathering and aerial oxidation of sulphide ores (9). In opencast mines the surface layers are usually oxidised copper ores. Some ore deposits such as the mines at Lake Superior (12) have quantities of native copper. However, all the ores mentioned so far have other rock mixed in with them and the true copper content may be 0.5 to 2% copper. It is becoming economical to

work ores with a copper content as low as 0.4% (13,14). The waste dumps of previously mined ore may have a higher copper content than ores currently being worked. However, the mining, crushing and grinding costs have already been paid on these waste dumps. Another potential source of copper is from deep sea nodules (15).

The production of pure copper from its ore can be accomplished by two routes, pyrometallurgy and hydrometallurgy. A brief outline of pyrometallurgy will now be presented, followed by an outline of hydrometallurgy. At present about 80% of copper is produced by pyrometallurgical methods (9).

PYROMETALLURGY.

Pyrometallurgy, as the name implies, uses heat as part of the purification process. However, as the copper content of the ore is low, it is necessary to concentrate the copper first. The concentration process is called flotation. The mined ore is first ground to fine particles, the final grinding being in the presence of water to produce a slurry. This slurry is added to a flotation tank where air is blown in from the bottom and chemicals are added. These chemicals are usually xanthate salts (16,17), such as potassium n-amyl xanthate ($KS_2CO(CH_2)_4CH_3$), sodium ethyl xanthate and other saturated alkyl chain xanthates. These xanthates selectively attach to the copper sulphide particles which are carried to the surface where they are removed by skimming. The other minerals present sink to the bottom of the tank and are discarded to waste dumps.

The material floated comprises the copper-containing sulphide ores and may contain 20-30% copper by weight (12,17). However, any oxidised copper ores and native copper are rejected as waste. Subsequent purification of the floated material is effected by roasting (870-970K) and smelting (1470K) (9,12). Air is blown through the molten metal ores to remove the sulphur as sulphur dioxide, and the liquid copper is separated. At this stage the copper is about 98.5% pure and is called

blister copper (9). To purify it further electrochemical cells are often used(13);this process is called electrowinning. A significant source of copper is from scrap copper-containing materials such as old cables and alloys (13). This is reworked as blister copper if it is sufficiently pure, or else it is smelted.

HYDROMETALLURGY.

This is based on liquid-liquid extraction technology. The important step is the concentration of a weak, impure, copper-containing solution to a much stronger solution of copper ions containing no other metal ions.

A) Leaching.

The first stage is solubilising the copper ores. Leaching of the copper-containing ores is accomplished in a variety of ways with a variety of reagents. One method is heap (or dump) leaching in which a dilute sulphuric acid solution is passed through a mound of broken ore, collected and then treated by methods which will be described shortly. In one recent example, a plant capable of processing 6 million tons per year of copper oxide and copper sulphide ores by heap leaching, has been constructed (18). A version of this is in situ leaching where the ore body is broken up underground by explosives and then leached. In Ohio, U.S.A. a large deposit of very lean copper ore has been profitably worked with in situ leaching (9). The use of a nuclear device has been suggested for in situ leaching (19). The major drawback with in situ leaching is collection of the leach liquor. These three types of leaching may continue for years before the dump is exhausted of copper; a much more rapid method is vat leaching (9). In this process the ore is ground to fine particles and leached in a large vessel or vat with a sulphuric acid solution which is more concentrated than that used in dump leaching. The residence time can be a matter of hours and the leached liquor often contains sufficient copper to be electrowon. At Chuquicamata in Chile a plant to recover 150,000 tons per year of copper uses a vat leach/electrowinning process (20).

The leaching system used is not limited to sulphuric acid which is not suitable for some ores. One alternative system uses a strong solution of ferric chloride (21). A 99% recovery of copper can be achieved after two hours at 378K (22). One advantage that chloride leaching processes have over sulphate leaching processes is that the leaching is much more rapid at atmospheric pressure in the chloride leach than in the sulphate leach (23). One process which involves a ferric chloride leach is the CYMET process (23) in which chalcopyrite is treated with ferric chloride in electrolytic cells. The copper is extracted as copper(I) chloride and elemental sulphur is precipitated. The CYPRUS process which has superceded the CYMET process, leaches copper as both copper(I) and copper(II) chlorides with ferric chloride. The copper(I) chloride precipitates from solution at high copper(I) concentrations. The copper(I) is isolated, melted and then reduced with hydrogen to give copper metal. A recent development (24) treats the chalcopyrite ore with sulphur at 590-670K for 4 hours in an atmosphere of nitrogen. This transforms the chalcopyrite to covellite and pyrite. If these are then contacted with the ferric chloride solution at 340K, 95% of the copper is leached and none of the iron is leached. The rate of leaching is increased relative to the leaching of chalcopyrite. This contrasts with the leach at 375K which leaches iron as well as copper from the ore. The CLEAR process that is in industrial use (25) uses a leach similar to that described in the CYPRUS process. Investigations of the small scale use of ferrous chloride and oxygen pressure for the leaching of mixed sulphide ores of iron, nickel and copper (26) have been reported. The ore is treated with a ferrous chloride solution in dilute hydrochloric acid at pH2. The mixture is heated to 380K for 8 hours at an oxygen pressure of 0.377 MPa. This leaching produces elemental sulphur as a byproduct and the iron that is leached from the ore is precipitated as a mixture of hydrated iron oxides. The Minimet Recherche process uses an acidic (pH 1) copper(II) chloride solution as the leaching agent. Sodium chloride is present in

a concentration of 250g l^{-1} to prevent precipitation of copper(I)chloride and the leach takes place almost at the boiling point of the solution. The copper(I) chloride solution is treated with LIX65N (a liquid-liquid extractant described later) and air is blown through the solution to oxidise the copper(I) to copper(II) and extract it simultaneously (23,27). One leaching system, the Arbiter process, goes to the other end of the pH scale and uses ammonia and pressure to leach the ores (28) after concentration by flotation. It has been found (29) that the addition of ammonium salts to the leach liquor improves the yield of copper leached. This is believed to be due to a buffering effect neutralising the hydroxide ions produced in the leach. These hydroxide ions can react with the ore to produce an insoluble coating of hydrated iron oxide. Certain bacteria such as Thiobacillus Ferrooxidans will oxidise copper sulphide ores. Use of cultures of these bacteria can reduce both consumption of leach acid and leaching time (30). The waste products of some Fungi such as Aspergillus Niger (31) can also leach copper.

After the copper ore has been leached, the copper is in a solution from which it must be recovered. One specific case (using LIX65N) has already been mentioned above. Another method, the cementation of copper upon scrap iron, has been in use from the seventeenth century (32,33). The copper-containing solution is mixed with scrap iron and this results in copper being deposited on the surface of the iron and iron going into solution as a result of a redox reaction such as $Cu^{2+} + Fe^{0} \rightleftharpoons Cu^{0} + Fe^{2+}$. This process is wasteful of acidic leaching agent as 1.5 moles of leach acid may be neutralised by the scrap iron in the time required for one mole of copper to cement out onto the iron (32). A more recently developed method is to contact the copper-containing solution with sulphur dioxide to reduce it to a mixed (copper(I), copper(II)) sulphate which precipitates from the solution and is isolated by filtration. Two treatments of this salt have been proposed: one is pyrolysis to copper metal, and the other is dissolution in an aqueous acetonitrile solution.

Removal of the acetonitrile by distillation causes disproportionation to copper metal and copper(II) (34,35). Another intriguing method involves the clever use of redox potentials in that copper is leached as copper(I) by contact with acidic copper(II) systems. The copper(I) is stabilised by acetonitrile by the formation of species such as $CuA(MeCN)_3$ where A is an anion such as chloride. Salting out of the acetonitrile and copper complex and separation gives a copper(I) solution of high copper content. The acetonitrile is removed by distillation whereupon disproportionation to copper metal and copper(II) takes place, the copper(II) being reworked as the leaching agent (36). Another method which works on the laboratory scale is reduction of the liquor by hydrogen (37) to produce copper metal.

B) Extraction.

A method first used commercially at the Bluebird mine, Miami, U.S.A. (38) in 1968 is growing in importance. This is liquid-liquid extraction and in 1978 more than 200,000 tons of copper metal were produced by liquid-liquid extraction techniques (39). Liquid-liquid extraction consists in mixing the leach liquor, which is often aqueous acid, with an extractant in an organic solvent such as kerosene. The metal is transported into the organic phase from which it is later removed, for example by the process mentioned above using acetonitrile as a complexing agent.

The extraction process can be accomplished by two general types of reagent following the pathways outlined below:-

1) $2\overline{L} + Cu^{2+} \rightleftharpoons \overline{CuL_2}^{2+}$

2) $2\overline{LH} + Cu^{2+} \rightleftharpoons \overline{CuL_2} + 2H^+$

The forward reaction will henceforth be referred to as extraction and the reverse reaction as strip. The bar denotes a species in the organic phase. The second pathway releases hydrogen ions and hence the equilibrium constant is sensitive to the pH of the solution. Careful design of the ligand is necessary as the following properties are desired

in the industrial reagents:-

1) Speed:- rapid approach to equilibrium on extraction and strip,

2) Selectivity:- preferential complexation with the desired metal,

3) Solubility:- both the ligand and its complex must be readily soluble in the desired solvent system,

4) Separation:- rapid phase disengagement after mixing the organic and aqueous phases,

5) Stability:- the ligand and metal complex must be stable to the desired operating conditions.

As has already been mentioned, the feed solution is usually acidic although it can be ammoniacal. Most of the ligands in industrial use extract copper by the general pathway indicated in 2 above. Ligands which extract copper by the pathway indicated in 1 above will be discussed first. One ligand based upon a hydrazine-sulphinate-thiocarbamate structure A (Figure 1), is said to be an effective ligand for copper extraction from an aqueous solution (40). Another ligand developed by the General Mills Company is LIX34 (41), which has the structure B (Figure 1). A similar compound C (Figure 1) can only be used in water-miscible solvents (42). Possible extractants for an acidic chloride leach liquor are aliphatic amines such as tri-isooctylamine (43). These extract the metal as the tetrachlorometallate ion, $[CuCl_4]^{2-}$, however the ligands are not very selective.

Thiophosphate esters such as bis(2-ethylhexyl)dithiophosphate, $PS_2(OR)_2^-$, have been proposed (44,45) for the extraction of copper from an ammoniacal feed solution. In heptane, if the concentration of ammonia is greater than six molar, then the copper is extracted as a copper amine complex which would cause problems if an acid stripping stage was used. Diisobutyrylmethane D (Figure 1) can accomplish a 95% recovery of copper from a copper-containing sludge that has been subjected to an ammonia leach (46).

Acid is released as copper is extracted by the other general class of extractants, see equation 2 above. Substituted carboxylic

acids, called versatic acids, have been suggested as possible extractants. These are typically tertiary monocarboxylic acids (47,48,49,50) $R_2MeCCOOH$, (R is C_3H_7 or C_4H_9), and are used as mixtures. A solution containing copper (30.20g l^{-1}) and nickel (6.35g l^{-1}) had been obtained from an ammonical leach of copper and nickel ores. This solution was treated with a 2 molar solution of versatic acid in kerosene to produce an organic phase containing copper (28.39g l^{-1}) and nickel (6.10g l^{-1}) (51). This result shows that the versatic acid has poor selectivity for the separation of copper from nickel. It might appear obvious to use an acidic leach liquor as the feed for the versatic acid extractants, to prevent coextraction of ammonia, and considerable research into selectivity at various pH's has been done (43,45). Figure 4 shows extraction at various pH values for various metals with versatic acids. Another oxygen donor system is a β-diketone which can exist as the enol tautomer. A ligand developed for commercial use is Hostarex DK-16 (52). The general structure is believed to be $RCOCH_2COR'$ ($R=C_{12}H_{25}$; $R'=CH_nCl_mF_l$; $l+n+m=3$) (53). This has rapid extraction kinetics from ammoniacal solutions but suffers from poor selectivity. Figure 5 shows the extraction of various metals with Hostarex DK-16 as a function of pH.

A great deal of copper complex chemistry has been done with Schiff bases and these have been investigated as possible extractants, for example compounds E and F (Figure 1) (54,55,56). These compounds typify the inherent problem of Schiff bases which is hydrolysis. Under acidic conditions in the stripping process the Schiff base easily hydrolyses back to the free amine and aldehyde. It is also known (57) that in a chloride medium the extracted complex can have the structure G rather than the expected structure H (Figure 1). The azo group is isoelectronic with the azomethine group of Schiff bases and azo compounds such as I (Figure 2) have been patented for copper extraction (58). With a feed solution of copper (0.2gl^{-1}) and iron (0.8gl^{-1}) at pH 2.3 the extraction of copper is 94% after 20 minutes and no iron was extracted

with this ligand, I. Another system similar to a Schiff base is an oxime and it is this that most ligands in commercial use are based upon. Figure 6 shows the commercial oxime-based extractants. These ligands have a high selectivity for copper at low pH values. For the reagent ACORGA P5000 under simulated plant conditions, the extraction of copper is 95% in 15 seconds and 98% in 30 seconds (65). The structure of the group R' is very important as the following shows:- under otherwise identical conditions the rate of copper extraction decreases in the order H>Me > CH_2Ph>Ph (66,67,68). The structure of the alkyl chain is very important as shown by the observation that, when R=C_7H_{15}, the rate of copper extraction and strip is greater than when R=C_9H_{19} (69).

Another demonstration of a small change in structure causing large changes in the rate of extraction is provided by compounds J, K, L (Figure 2). Under identical conditions the rate of copper extraction of J is twice that of K and twenty times that of L (70).

The ligand M (Figure 2) (71), which has been evaluated for the extraction of copper, shows that the search for ligands with the arrangement O-C-C-C=N has been thorough. The other major contender for commercial use is the ligand N (Figure 2) known as KELEX 100, which had by 1975 reached pilot plant testing (72). The ligand is reported to have excellent stripping characteristics (73,74,75,76,77), and to be suitable for industrial use.

A ligand for the separation of copper from zinc has been proposed, P (Figure 2), but this needs a large excess of ligand for quantative extraction of copper (78). There are two pathways that copper extraction technology may take in the future, these are the use of semi-permeable membranes and polymer-supported extractants. Two reagents, Q and R (Figures 2 and 3) have been described (79) for copper transport across a polymer-supported membrane. Both of these reagents were capable of transporting almost 90% of copper from the feed to the solution for electrowinning but R was more selective for copper than Q. A polymer based upon S (Figure 3) has been proposed for copper extraction (80).

S was found to extract copper as CuL where L represents the O,N donor system of the polymer chain, this was believed to be due to steric effects imposed by the polymer chain. A polyurethane foam impregnated with LIX64N has also been studied (81). A sugar nucleus has been combined with long alkyl chains, see Figure 7, and this can act in a membrane by transporting a metal ion along the chain using the heteroatoms to chelate the metal.

LIX64N has been studied in different diluents and it was found that a tenfold decrease in the rate of copper extraction occurs on changing from an aliphatic petroleum solvent to an aromatic petroleum solvent (67,83). The effects are believed to be due to hydrogen bonding between hydroxyl protons and aromatic nuclei in the solvent. However, it is not certain whether the hydrogen bonding is more important before or after complex formation. Synergism, the addition of a small quantity of substance to enhance desirable properties in the mixture, is demonstrated in LIX64N. LIX64N is a mixture of LIX65 and LIX63, T (Figure 3), in approximately 99:1 ratio and the kinetics of extraction and strip are far superior to pure LIX65 (84). Another example is provided by the experience with K and U (Figure 3). Under experimental conditions K extracted 49% copper from a feed solution in 5 minutes whereas a mixture of K (90%) and U (10%) extracted 94% copper in the same length of time (85).

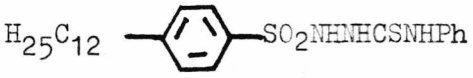
The ligand ACORGA P5000 has an extremely rapid extraction rate for copper but a rather poor stripping rate. It was found that a mixture of ACORGA P5000 and nonylphenol improved the stripping rate and phase separation properties significantly (83). Problems have been experienced with handling this mixture and these can be overcome by substituting tridecanol, $C_{13}H_{27}OH$, for nonylphenol.

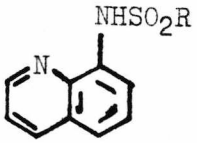
The cost of pyrometallurgy will increase as the grade of ore becomes poorer and the problems of sulphur dioxide emission have to be cured. Hydrometallurgy is not affected as much by the grade of ore to be used and the physical size of plant can be much less. This will result in an increase in the use of hydrometallurgy (86).

The industrial ligand ACORGA P5000 is based upon nonylphenol which is manufactured by a Friedel-Crafts alkylation of phenol with propylene trimer. This results in the extractant being a mixture of compounds which differ in the structure of the alkyl chain and the exact composition can vary from batch to batch. Some examples presented above show that slight changes in alkyl chain structure can affect the kinetics of extraction and strip significantly. Hence the purpose of the author's research is to synthesise single isomer extractants containing alkyl chains of precisely defined structure and compare the extraction and strip rates of these ligands.

Figure 1. Ligands proposed for copper extraction.

A.





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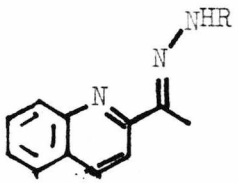

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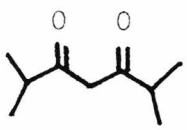

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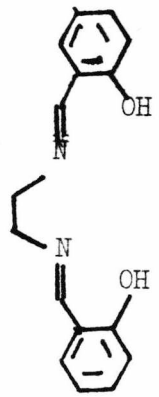

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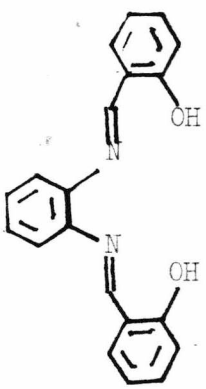

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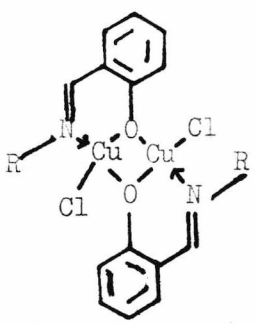

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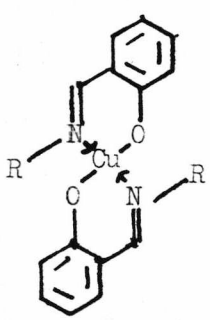
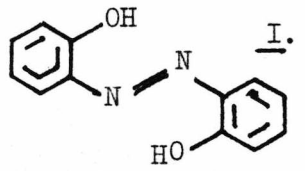
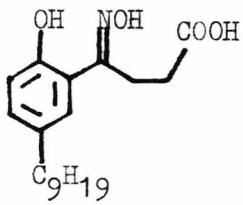


H.

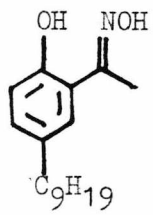
Figure 2. Ligands proposed for copper extraction.



I.



J.



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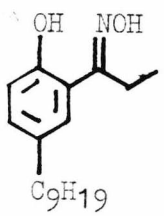

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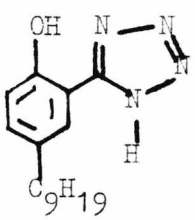

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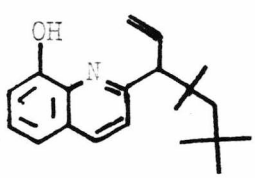

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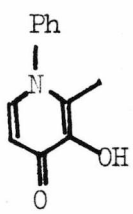

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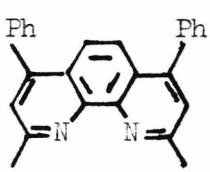
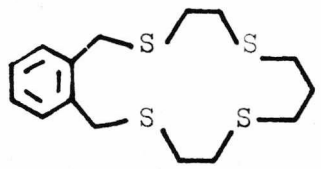


Q.

Figure 3. Ligands proposed for copper extraction.



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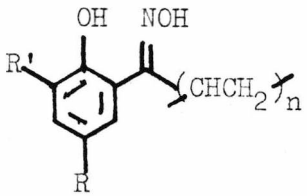
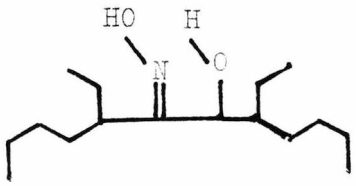
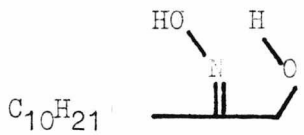


R Me Cl
R' NO_2 H

S.

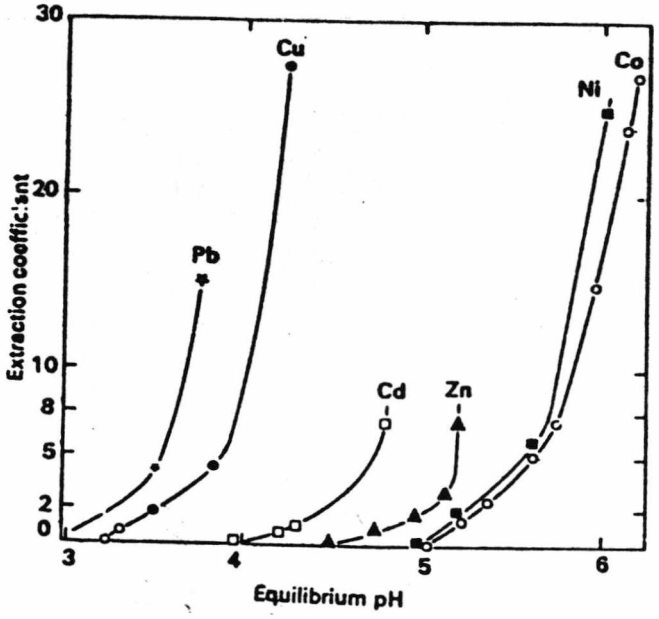


T.



U.

FIGURE 4. Extraction of metals with versatic acids.



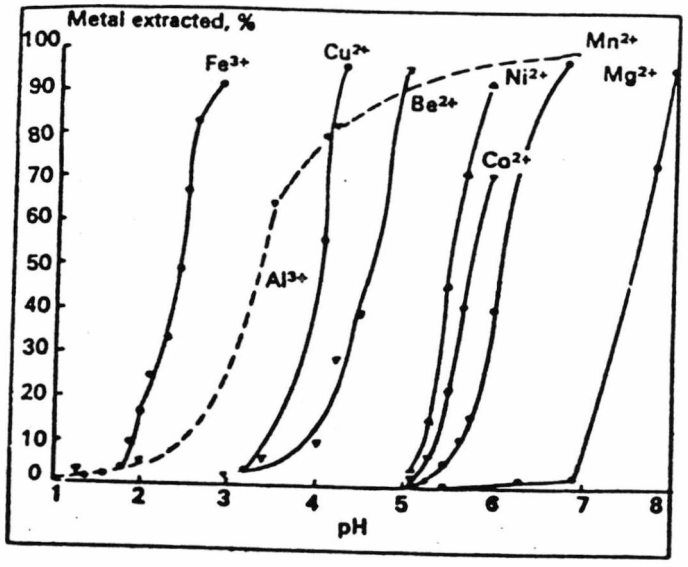
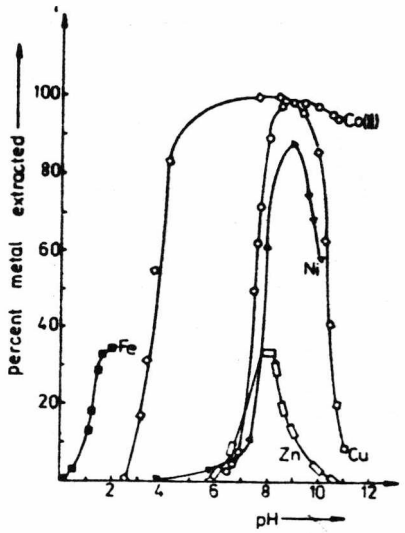
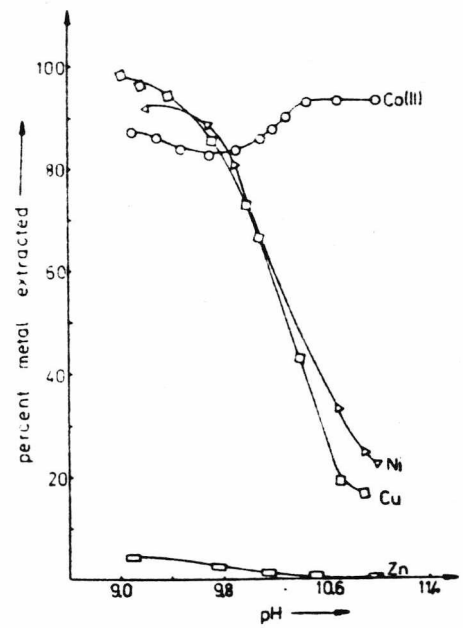


FIGURE 5. Extraction of metals with hostarex DK-16.

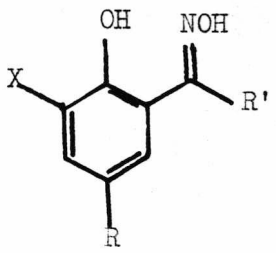


. Effect of pH on the extraction of metals by a 2.5% v/v solution of Hostarex DK-16 in kerosene. Aqueous phases: 0.01 *M* solutions of metal salts in 0.25 *M* ammonium sulphate.



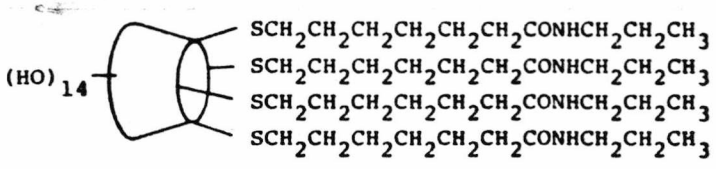
Effect of pH on the extraction of metals by a 2.5% solution of Hostarex DK-16 in kerosene. Aqueous phases: 0.01 *M* solutions of metal salts in 0.3 *M* ammonium carbonate.

Figure 6. Commercial aromatic hydroxyoxime ligands.



R	R'	X	Name.	Reference.
C_9H_{19}	H	H	Acorga P5000	59
C_9H_{19}	Me	H	SME 529	60
C_9H_{19}	Ph	H	LIX 65	61
C_9H_{19}	Ph	Cl	LIX 70	62
C_9H_{19}	CH_2Ph	H	Acorga P17	63
C_7H_{15}	H	H		64

FIGURE 7. An artificial membrane for metal transport based upon a sugar nucleus.



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CHAPTER 2. SYNTHESIS OF ALKYLPHENOL PRECURSORS.

The synthetic route for making oximes required as extractants is by formylation of an alkylphenol followed by oximation. Of the thirteen extractants synthesised, two have n-alkyl chains and the remaining eleven contain t-alkyl chains. One of the desired alkylphenols, 4-(1,1-dimethylpropyl) phenol was available commercially (Aldrich Chemical Co.), and the remaining ten were synthesised by an acid catalysed Friedel-Crafts reaction of an alkene mixture and phenol (Chapter 3). The mixture of alkenes was such that only one alkylphenol would be synthesised from that particular mixture of alkenes. As 2,4,4-trimethylpent-1-ene was available commercially (Aldrich Chemical Co.), this was used to make one of the desired alkylphenols, 4-(1,1,3,3-tetramethylbutyl) phenol. The other nine mixtures of alkenes were synthesised by the route shown in Figure 1 which exemplifies the synthesis of the alkene mixture used to synthesise 4-(1-ethyl-1-methylbutyl) phenol. The Grignard reagent from 1-bromoethane (1,2) was reacted with pentan-2-one and after hydrolysis of the magnesium alkoxide the desired alcohol, 3-methylhexan-3-ol was isolated. The 3-chloro-3-methylhexane was made by contacting the 3-methylhexan-3-ol with concentrated hydrochloric acid at room temperature (3). The desired mixture of alkenes was synthesised by the dehydrohalogenation of 3-chloro-3-methylhexane by potassium ethoxide in ethanol (4).

The route to the 4-n-alkylphenols is shown in Figure 2 which exemplifies the synthesis of 1-(4-hydroxyphenyl)heptan-1-one. Heptanoic acid was transformed to the acid chloride by thionyl chloride (5,6) and reacted with phenol to give the desired phenyl heptanoate. Using aluminium chloride the phenyl heptanoate was subjected to a Fries rearrangement (5,6) to yield 1-(2-hydroxyphenyl)heptan-1-one and 1-(4-hydroxyphenyl)heptan-1-one. By extraction of the reaction mixture with aqueous sodium hydroxide solution and acidification to pH 3 the 1-(4-hydroxyphenyl)heptan-1-one precipitates and can be filtered off.

The chapter will be split into two sections, the first being the

characterisation of the compounds synthesised and the second being the experimental details.

A) Characterisation of alkylphenol precursors.

1) Characterisation of 4-n-alkylphenol precursors.

a) Phenyl heptanoate.

The infrared spectrum showed a strong carbonyl stretch at 1740cm^{-1} attributed to the ester carbonyl (7). The absence of ν(O-H) was noted.

In discussing the proton and ^{13}C N.M.R. spectra the carbons will be referred to as a (carbon bearing oxygen) and b,c,d (ortho, meta and para carbons respectively). The aliphatic carbons are referred to as 1(carbonyl) and up to 7(methyl).

Proton N.M.R. δ 6.9-7.4,m,5H (aromatic ring protons); 2.43,t,J=7Hz, 2H(carbon 2); 1.66,bt,J=6Hz(carbon 3); 1.1-1.5,bm,6H(carbons 4-6); 0.87,t,J=6Hz,3H(carbon 7). p.p.m. ($CDCl_3$, T.M.S.).

^{13}C N.M.R: δ 171.94,s(carbon 1); 150.94,s(carbon a); 129.35,d(carbon c); 125.58,d(carbon 6); 121.58,d(carbon d); 34.46,t(carbon 2); 31.54,t (carbon 5); 28.87,t(carbon 4); 24.99,t(carbon 3); 22.56,t(carbon 6); 14.07,q(carbon 7). p.p.m. ($CDCl_3$, T.M.S.)

b) 1-(4-hydroxyphenyl)heptan-1-one.

The infrared spectrum showed a broad absorption at 3350 cm^{-1} assigned to the hydroxyl group and an absorption at 1685 cm^{-1}, assigned to the conjugated carbonyl group. A band at 825 cm^{-1} was assigned to two adjacent hydrogens on a benzene ring (7). The proton N.M.R. was as follows : δ 7.90,d,J=9Hz,2H(carbon c); 6.96,d,J=9Hz,2H(carbon b); 2.98,t,J=7Hz,2H(carbon 2); 1.76,bt,J=7Hz,2H(carbon 3); 1.35,bs,6H(carbons 4-6); 0.88,bt,J=7Hz,3H(carbon 7). p.p.m. ($CDCl_3$, T.M.S.).

c) Discussion of the spectra of phenyl heptanoate and 1-(4-hydroxyphenyl)heptan-1-one.

The infrared spectra of phenyl heptanoate showed that neither phenol nor heptanoic acid was present in the phenyl heptanoate as there was no ν(O-H). The infrared spectrum of 1-(4-hydroxyphenyl)heptan-1-one gave a

good indication of the desired para-isomer because ν (C=O) is observed at 1685cm^{-1} rather than at 1655-1635 which would be expected (7) in the intramolecularly H-bonded ortho-isomer, and because of the single, strong absorption at 825cm^{-1} ν (C_{aryl}-H).

The proton N.M.R. of phenyl heptanoate was as expected and the deshielding effect of the ester group upon the protons attached to carbons 2 and 3 (δ 2.43, 1.66 p.p.m.) was noted. The assignments of the aromatic carbon resonances was by comparison with the published ^{13}C N.M.R. spectrum of phenol (8). The aliphatic carbon resonances were assigned by comparison of the proton decoupled spectrum with the partially proton coupled spectrum and by calculation of theoretical values of the chemical shifts (9,10,11).

The proton N.M.R. spectrum of 1-(4-hydroxyphenyl)heptan-1-one clearly confirms the para substitution of the aromatic nucleus. The effect of conjugating the carbonyl group to the aromatic nucleus shows in the deshielding of the protons attached to carbon-2 (δ 2.98 p.p.m.) when compared with the expected value of δ ca2.4 p.p.m. (7,9) for an aliphatic ketone.

2) Characterisation of t-alcohols and t-alkylhalides.

The carbons will be numbered as follows for the discussion and assignment of the N.M.R. spectra (see Figure 3 for 3-methylhexan-3-ol as as example). The carbon bearing the hydroxyl (or chloride) group is numbered 1. The longest chain is counted up from carbon-1 as 2,3 etc., in the example shown this is the propyl chain numbered 2,3 and 4. Then the next longest chain, in this example the ethyl is numbered 5 and 6, and finally the shortest chain, in this example the methyl group is carbon-7.

a) Infrared spectra.

The infrared spectra of all the t-alcohols showed a strong, broad absorption around 3400cm^{-1} due to the O-H stretch and a band at 1165cm^{-1} assigned to the tertiary C-O stretch (12,13). The band at lowest wavenumber in the region 800-710cm^{-1} is supposed to be characteristic of a carbon-alkyl chain stretch (12,13). The bands in this region are

collected in table 1.

b) 2-methylhexan-2-ol.

Proton N.M.R: δ 1.58,bs,1H,labile; 1.2-1.5,m,6H; 1.18,s,6H; 0.89,bt,J=7Hz,3H. p.p.m. ($CDCl_3$, T.M.S.)

^{13}C N.M.R: δ 70.90,s(carbon 1); 43.87,t(carbon 2); 29.12,q(carbon 6); 26.79,t(carbon 3); 23.45,t(carbon 4); 14.13,q(carbon 5). p.p.m. ($CDCl_3$, T.M.S.)

c) 3-methylhexan-3-ol.

Proton N.M.R: δ 1.1-1.6,m,6H; 1.15,s,3H; 0.92,t,J=6Hz,3H; 0.89,t,J=6Hz,3H. p.p.m. ($CDCl_3$, T.M.S.)

^{13}C N.M.R: δ 72.76,s(carbon 1); 43.87,t(carbon 2); 34.32,t(carbon 5); 26.32,q(carbon 7); 17.24,t(carbon 3); 14.75,q(carbon 4); 8.23,q(carbon 6). p.p.m. ($CDCl_3$, T.M.S.)

d) 2,4-dimethylpentan-2-ol.

Proton N.M.R: δ 1.5-1.9,m,1H; 1.38,d,J=6Hz,2H; 1.21,s,6H; 0.95,d,J=6Hz,6H. p.p.m. ($CDCl_3$, T.M.S.)

^{13}C N.M.R: δ 71.44,s(carbon 1); 52.57,t(carbon 2); 29.89,q(carbon 5); and two resonances at 24.85 and 24.61 p.p.m. assignable to carbons 4 and 3 respectively.

e) 3-ethylpentan-3-ol.

Proton N.M.R: δ 2.16,bs,1H,labile; 1.44,q,J=7Hz,6H; 0.85,t,J=8Hz, 9H. p.p.m. ($CDCl_3$, T.M.S.)

^{13}C N.M.R: δ 74.7,s(carbon 1); 30.67,t(carbon 2); 7.84,q(carbon 3). p.p.m. ($CDCl_3$, T.M.S.)

f) 2-methyloctan-2-ol.

Proton N.M.R: δ 1.74,bs,1H,labile; 1.17,bs,10H; 1.08,s,6H; 0.84,t,J=6Hz,3H. p.p.m. ($CDCl_3$, T.M.S.)

^{13}C N.M.R: δ 70.98,s(carbon 1); 44.11,t(carbon 2); 31.91,t(carbon 5); 29.89,t(carbon 4); 29.19,q(carbon 8); 24.38,t(carbon 3); 22.67,t (carbon 6); 14.05,q(carbon 7). p.p.m. ($CDCl_3$, T.M.S.)

g) 3-methyloctan-3-ol.

Proton N.M.R: δ 1.86,s,1H,labile; 1.1-1.5,m,ca.10H; 1.14,s,ca.3H;

0.88,bt,J=6Hz,6H. p.p.m. ($CDCl_3$, T.M.S.)

^{13}C N.M.R: δ 72.76,s(carbon 1); 41.54,t(carbon 2); 34,32,t(carbon 7); 32.77,t(carbon 4); 26.40,q(carbon 9); 23.76,t(carbon 3); 22.90,t (carbon 5); 14.13,q(carbon 6); 8.30,q(carbon 8). p.p.m. ($CDCl_3$, T.M.S.)

h) 3-ethylheptan-3-ol.

Proton N.M.R: δ 1.70-1.10,m,10H; 0.82,bt,J=7Hz,9H. p.p.m. ($CDCl_3$, T.M.S.)

^{13}C N.M.R: δ 71.12,s(carbon 1); 38.72.t(carbon 2); 31.91,t(carbon 6); 26.96,t(carbon 3); 22.90,t(carbon 4); 13.86,q(carbon 5); 8.36,q (carbon 7). p.p.m. ($CDCl_3$, T.M.S.)

i) 4-methyloctan-4-ol.

Proton N.M.R: δ 1.97,s,1H,labile; 1.15-1.6,m,10H; 1.09,s,3H; 0.96,bt,J=6Hz,6H. p.p.m. ($CDCl_3$, T.M.S.)

^{13}C N.M.R: δ 72.61,s(carbon 1); 44.57,t(carbon 6); 41.93,t(carbon 2); 27.02,q(carbon 9); 26.48,t(carbon 3); 23.6,t(carbon 4); 17.39,t (carbon 7); 14.83,q(carbon 8); 13.9,q(carbon 5). p.p.m. ($CDCl_3$, T.M.S.)

j) 4-ethylheptan-4-ol.

Proton N.M.R: δ 1.95,bs,1H,labile; 1.1-1.6,m,10H; 0.92,t,J=7Hz,6H; 0.76,t,J=7Hz,3H. p.p.m. ($CDCl_3$, T.M.S.)

^{13}C N.M.R: δ 75.19,s(carbon 1); 41.66,t(carbon 2); 32.16,t(carbon 5); 17.21,t(carbon 3); 14.35,q(carbon 4); 8.36,q(carbon 6). p.p.m. ($CDCl_3$, T.M.S.)

k) 2-chloro-2-methylhexane.

Proton N.M.R: δ 1.1-1.8,m,6H; 1.55,s,6H; 0.91,t,J=6Hz,3H. p.p.m. ($CDCl_3$, T.M.S.)

^{13}C N.M.R: δ 70.51,s(carbon 1); 46.05,t(carbon 2); 32.53,q(carbon 6); 27.49,t(carbon 3); 23.06,t(carbon 4); 14.13,q(carbon 5). p.p.m. ($CDCl_3$, T.M.S.)

l) 3-chloro-3-methylhexane.

Proton N.M.R: δ 1.05-1.9,m,ca.6H; 1.44,s,ca.3H; 0.96,t,J=7Hz,3H; 0.88,t,J=8Hz,3H. p.p.m. ($CDCl_3$, T.M.S.)

^{13}C N.M.R: δ 74.78,s(carbon 1); 46.20,t(carbon 2); 36.88,t(carbon 5); 29.35,q(carbon 7); 18.09,t(carbon 3); 14.28,q(carbon 4); 9.16,q (carbon 6). p.p.m. ($CDCl_3$, T.M.S.)

m) 3-chloro-3-ethylpentane.

Proton N.M.R: δ 1.75,q,J=6Hz,6H; 0.95,t,J=6Hz,9H. p.p.m. ($CDCl_3$, T.M.S.)

^{13}C N.M.R: δ 79.67,s(carbon 1); 33.0,t(carbon 2); 8.77,q(carbon 3). p.p.m. ($CDCl_3$, T.M.S.)

n) 2-chloro-2,4-dimethylpentane.

Proton N.M.R: δ 1.7-2.0,m,1H; 1.68,d,J=5Hz,2H; 1.58,s,6H; 0.99,d, J=6Hz,6H. p.p.m. ($CDCl_3$, T.M.S.)

^{13}C N.M.R: δ 70.51,s(carbon 1); 54.51,t(carbon 2); 33.08,q(carbon 5); 25.39,q(carbon 4); 24.77,d(carbon 3). p.p.m. ($CDCl_3$, T.M.S.)

o) 2-chloro-2-methyloctane.

Proton N.M.R: δ 1.7-1.4,m,ca.2H; 1.47,s,ca.6H; 1.27,bs,8H; 0.84,t, J=5Hz,3H. p.p.m. ($CDCl_3$, T.M.S.)

^{13}C N.M.R: δ 70.12,s(carbon 1); 46.28,t(carbon 2); 32.46,t(carbon 5); 31.91,q(carbon 8); 29.58,t(carbon 4); 25.16,t(carbon 3); 22.75,t (carbon 6); 14.13,q(carbon 7). p.p.m. ($CDCl_3$, T.M.S.)

p) 3-chloro-3-methyloctane.

Proton N.M.R: δ 1.78,t+q,J=ca.6Hz,4H; 1.5,s,3H; 1.1-1.4,m,6H; 1.0,t,J=8Hz,3H; 0.9,t,J=6Hz,3H. p.p.m. ($CDCl_3$, T.M.S.)

^{13}C N.M.R: δ 74.39,s(carbon 1); 43.95,t(carbon 2); 36.96,t(carbon 7); 32.30,t(carbon 4); 29.35,q(carbon 9); 24.53,t(carbon 3); 22.83,t (carbon 5); 14.13,q(carbon 6); 9.16,q(carbon 8). p.p.m. ($CDCl_3$, T.M.S.)

q) 3-chloro-3-ethylheptane.

Proton N.M.R: δ 1.73,t+q,J=ca.7Hz,6H; 1.1-1.5,m,4H; 0.92,bt,J= 7Hz,9H. p.p.m. ($CDCl_3$, T.M.S.)

^{13}C N.M.R: δ 78.50,s(carbon 1); 40.28,t(carbon 2); 33.61,t(carbon 6); 26.69,t(carbon 3); 23.29,t(carbon 4); 14.07,q(carbon 5); 8.73,q(carbon 7). p.p.m. ($CDCl_3$, T.M.S.)

r) 4-chloro-4-methyloctane.

Proton N.M.R: δ 1.1-1.9,m,ca. 10H; 1.53,s,ca.3H; 0.94,bt,J=7Hz,6H. ($CDCl_3$, T.M.S.)

^{13}C N.M.R: δ 72.24,s(carbon 1); 46.59,t(carbon 6); 44.11,t(carbon 2); 29.97,q(carbon 9); 27.02,t(carbon 3); 23.14,t(carbon 4); 18.16,t (carbon 7); 14.36,q(carbon 8); 14.13,q(carbon 5). ($CDCl_3$, T.M.S.)

s) Discussion of N.M.R. spectra of t-alcohols and t-alkyl halide

The proton N.M.R. spectra show the deshielding effect of the hydroxyl group upon protons attached to the α-carbons and the shielding effect upon protons attached to the β-carbons. Of interest is the greater deshielding effect of chlorine compared with hydroxyl which is readily seen in the comparison of 3-chloro-3-methylhexane with 3-methylhexan-3-ol for example. In these, the singlet attributed to the methyl group is at δ 1.44 p.p.m. in the chloride and at δ 1.15 p.p.m. in the alcohol. The ^{13}C N.M.R. chemical shifts of the same alkylhalide and alcohol are listed in table 2. The point of interest is the resonance of the chlorine-bearing carbon. Calculation of the chemical shift from literature sources (9,10,11) gives a value of the shift of this carbon in the alkylhalide of approximately 17 p.p.m. less than in the alcohol, whereas it is ca. 2 p.p.m. greater. This discrepancy is noted in all the t-alcohols and t-alkylhalides. The chlorine atom deshields the α and β-carbons relative to the t-alcohol. Standard methods for the calculation of ^{13}C N.M.R. shifts of alcohols (10) give values which are generally within 2 p.p.m. of the observed chemical shifts in the compounds reported here.

3) Characterisation of alkene mixture.

As the syntheses of the desired alkenes produced complex mixtures of isomeric alkenes, the proton N.M.R. spectra are correspondingly complex. The olefinic protons resonated in the range δ 4.5-5.2 p.p.m. and the chemical shifts of the aliphatic protons was in the range δ 0.7-2.0 p.p.m. However, the ratio of the integration of the signals of

the olefinic and aliphatic protons was consistent with the expected mixture of alkenes. The principal features of the infrared spectra of the alkene mixtures are collected in table 3. For the components in each mixture of alkenes, see the experimental section.

B) Experimental.

The syntheses of phenyl nonanoate and 1-(4-hydroxyphenyl)nonan-1-one are described elsewhere (14). Also described in reference (14) are the syntheses of 2-methyloctan-2-ol, 3-ethylheptan-3-ol, 2-chloro-2-methyl octane, 3-chloro-3-ethylheptane and the alkene mixtures derived from each of these alkyl halides. The elemental analyses are collected in Table 4. The alkyl halides were used without further purification and b.pt and elemental analyses were not obtained upon these compounds.

1) Phenyl heptanoate.

A 3-necked, 500ml, round bottomed flask was fitted with a pressure equalising dropping funnel and a drying tube. Heptanoic acid (Aldrich Chemical Co.) (182.3g, 1.4moles) was placed in the flask and stirred (magnetically) and heated to 308K. Freshly distilled thionyl chloride (183.3g, 1.54moles) was slowly added, maintaining the temperature at 308-313K. After addition was complete, the mixture was heated at this temperature for a further 2 hours and then excess thionyl chloride was removed in vacuo. The heptanoyl chloride was then added to stirred, molten phenol over 30 minutes and the mixture formed was heated at 363K for a further 3 hours. Distillation yielded the desired product, phenyl heptanoate b.pt. 387K, 2.0mm Hg (393K, 2.0mm Hg 15) as a colourless, mobile oil. Yield 267.4g, 1.3moles, 96%.

2) 1-(4-hydroxyphenyl)heptan-1-one.

The desired product was synthesised by a Fries rearrangement (5,6,15) of phenyl heptanoate (section 1). To a slurry of aluminium trichloride (187g, 1.25moles) in petroleum ether (120-160 fraction, 625 cm^3) at 283K was rapidly added phenyl heptanoate (243.6g, 1.18moles) and the mixture brought rapidly to reflux. The mixture was refluxed for 3 hours, then

poured onto ice (1Kg) and concentrated hydrochloric acid (200 cm^3) and stirred until hydrolysis was complete. The phases were separated and the organic phase was washed with water (500 cm^3) and sodium hydrogen carbonate solution (5%, 500 cm^3). The organic phase was then extracted with sodium hydroxide solution (5%, 3x500 cm^3). The aqueous phase was acidified to pH 3 (universal indicator paper, temperature less than 293K). A brown solid precipitated from the acidified solution which was then filtered. The precipitated solid was washed with water twice and then dried in vacuo. Recrystallisation (ethanol) yielded the desired product 1-(4-hydroxyphenyl)heptan-1-one as a light brown solid, m.pt, 351.5-3K (354-4.5K, 5). Yield 114.5g, 0.56moles, 47%.

3) 2-methylhexan-2-ol.

A 500ml, 4-necked round bottomed flask was fitted with a dry nitrogen inlet, reflux condenser with drying tube and pressure-equalising dropping funnel. In the round bottomed flask were placed magnesium turnings (28.4g, 1.17mol), dry diethyl ether (50 cm^3) and a crystal of iodine. Stirring (mechanical) was started and dry 1-bromobutane (160g, 1.17mol) in dry diethyl ether (125 cm^3) was placed in the dropping funnel. Approximately 15 cm^3 of this alkyl halide solution was added to the reaction vessel. When the reaction commenced, indicated by a loss of colour and rise in temperature, the solution of alkyl halide was added at a rate sufficient to maintain a gentle reflux. After the addition was complete, the mixture was refluxed for 30 minutes and then 1-bromobutane (1g) in diethyl ether (1 cm^3) was added and reflux continued for 30 minutes to remove the last traces of magnesium turnings. When no magnesium turnings were left the reaction mixture was cooled to 278K. A mixture of dry acetone (67.9g, 1.17mol) in dry diethyl ether (75 cm^3) was slowly added whilst maintaining the temperature at 278-83K. After addition of the acetone-ether mixture was complete, the mixture was refluxed for 30 minutes and then poured onto ice (500g). The mixture was stirred whilst cold, and cold 30% sulphuric acid was slowly added until

the mixture was acidic to universal indicator paper. The phases were then separated and the organic phase washed with 5% potassium carbonate solution (100 cm^3), water (100 cm^3) and then dried (anhydrous sodium sulphate). The solvent was removed by distillation under reduced pressure to give the desired product 2-methylhexan-2-ol (116.9g, 1.0mol, 86%), b.pt 415K (413K, 735mm Hg, 2).

4) 3-methylhexan-3-ol.

This was synthesised by the method described in section 3 using the following reagents:- bromoethane (127.5g, 1.17mol), magnesium turnings (28.4g, 1.17mol) and pentan-2-one (100.6g, 1.17mol) to yield the desired product, 3-methylhexan-3-ol (129.1g, 1.11mol, 95%), b.pt 410K (409-411K, 1).

5) 3-ethylpentan-3-ol.

This was synthesised by the method described in section 3 using the following reagents:- bromoethane (127.5g, 1.17mol), magnesium turnings (28.4g, 1.17mol) and pentan-3-one (100.6g, 1.17mol) to yield the desired product, 3-ethylpentan-3-ol (100.6g, 0.87mol, 74%), b.pt 413K (413-5K, 1).

6) 2,4-dimethylpentan-2-ol.

This was synthesised by the method described in section 3 using the following reagents:- iodomethane (144g, 1mol), magnesium turnings (24.3g, 1mol) and 4-methylpentan-2-one (90g. 0.9mol) to yield the desired product, 2,4-dimethylpentan-2-ol (87.66g, 0.76mol, 84%), b.pt 405K (406K, 16).

7) 3-methyloctan-3-ol.

This was synthesised by the method described in section 3 using the following reagents:- 1-bromopentane (151g, 1mol), magnesium turnings (24.3g, 1mol) and butan-2-one (72g, 1mol) to yield the desired product, 3-methyloctan-3-ol (120.7g, 0.84mol, 84%), b.pt 455K (374K, 30mm Hg 17).

8) 4-methyloctan-4-ol.

This was synthesised by the method described in section 3 using the following reagents:- 1-bromobutane (137g, 1mol), magnesium turnings

(24.3g, 1mol) and pentan-2-one (86g. 1mol) to yield the desired product, 4-methyloctan-4-ol (122.8g, 0.85mol, 85%), b.pt 453K (452K, 2).

9) 4-ethylheptan-4-ol.

This was synthesised by the method described in section 3 using the following reagents:- bromoethane (100.3g, 0.92mol), magnesium turnings (22.4g, 0.92mol), heptan-4-one (100g, 0.88mol) to yield the desired product, 4-ethylheptan-4-ol (108.9g, 0.76mol, 86%), b.pt 453K (451-2K, 18).

10) 2-chloro-2-methylhexane.

A mixture of crude 2-methylhexan-2-ol (112.7g, 0.97mol) (section 3) and concentrated hydrochloric acid (500 cm^3) was stirred for 30 minutes and then the phases were separated. The organic phase was washed with potassium carbonate solution (1%, 100 cm^3) and water and then dried (anhydrous sodium sulphate) to give 2-chloro-2-methyl hexane (123.33g, 0.92mol, 95%).

11) 3-chloro-3-methylhexane.

This was synthesised by the method described in section 10 using the following reagents:- 3-methylhexan-3-ol (126g, 1.09mol) (section 4) and concentrated hydrochloric acid (650 cm^3) to yield 3-chloro-3-methylhexane (123g, 0.91mol, 84%).

12) 3-chloro-3-ethylpentane.

This was synthesised by the method described in section 10 using the following reagents:- 3-ethylheptan-3-ol (98g, 0.85mol) (section 5) and concentrated hydrochloric acid (500 cm^3) to yield 3-chloro-3-ethylpentane (82.08g, 0.61mol, 72%).

13) 2-chloro-2,4-dimethylpentane.

This was synthesised by the method described in section 10 using the following reagents:- 2,4-dimethylpentan-2-ol (50g, 0.43mol) (section 6) and concentrated hydrochloric acid (250 cm^3) to give 2-chloro-2,4-dimethyl pentane (37.1g, 0.28mol, 64%).

14) 3-chloro-3-methyloctane.

This was synthesised by the method described in section 10 using the following reagents:- 3-methyloctan-3-ol (110.8g, 0.82mol) (section 7) and concentrated hydrochloric acid (500 cm^3) to give 3-chloro-3-methyloctane (104.1g, 0.64mol, 78%).

15) 4-chloro-4-methyloctane.

This was synthesised by the method described in section 10 using the following reagents:- 4-methyloctan-4-ol (120.8g, 0.83mol) (section 8) and concentrated hydrochloric acid (500 cm^3) to give 4-chloro-4-methyloctane (109.8g, 0.68mol, 80.5%).

16) Alkene mixture A.

A mixture of alkenes is produced by an E2 elimination of hydrogen chloride with base (4) from a t-alkyl halide. The alkenes in mixture A, obtained from 2-chloro-2-methylhexane are 2-methylhex-1-ene and 2-methylhex-2-ene.

2-chloro-2-methylhexane (120.3g, 0.89mol) (section 10) was added, during 20 minutes, to a refluxing solution of potassium hydroxide (95g) in ethanol (530 cm^3). The mixture was refluxed for a further 90 minutes and then poured onto water (1l). The phases were separated and the organic phase washed with water (2x100 cm^3) and then steam distilled with cohabation, that is to say that the organic compound was refluxed with water, the vapours condensed and the phases separated. The aqueous phase returned to the distillation vessel and the organic phase was collected.

The organic phase was dried (anhydrous sodium sulphate) and distilled, boiling range 365-9K (366-9K, 1) to yield the desired mixture of alkenes, A (79.6g, 0.81mol, 91%).

17) Alkene mixture B.

The alkene mixture, B, consists of five components, the E and Z-isomers of 3-methylhex-2-ene and 3-methylhex-3-ene, and 2-ethylpent-1-ene. This mixture, B, was synthesised by the method described in section 16 using the following reagents:- 3-chloro-3-methylhexane (120.0g, 0.89mol)

(section 11), potassium hydroxide (90g) and ethanol (500 cm^3) to yield the desired mixture of alkenes, B (61.31g, 0.63mol, 70%), b. range 364-9K (366-9K, 1).

18) Alkene C.

The alkene, C, 3-ethylpent-2-ene, was synthesised by the method described in section 16 using the following reagents:- 3-chloro-3-ethyl pentane (80.0g, 0.59mol) (section 12), potassium hydroxide (80g) and ethanol (400 cm^3) to yield 3-ethylpent-2-ene (51.1g, 0.52mol, 88%), b.pt 367-9K (368-70K, 1).

19) Alkene mixture D.

The alkene mixture, D, was composed of 2,4-dimethylpent-1-ene and 2,4-dimethylpent-2-ene. The alkene mixture, D, was synthesised by the method described in section 15 using the following reagents:- 2-chloro-2,4-dimethylpentane (35.1g, 0.26mol) (section 13), potassium hydroxide (4 5g) and ethanol (250 cm^3) to give the desired alkene mixture, D (19.1g, 0.19mol, 75%), b. range 362-7K.

20) Alkene mixture E.

The alkene mixture, E, was composed of 3-methyloct-2-ene, 3-methyloct-3-ene and 2-ethylhept-1-ene. The alkene mixture, E, was synthesised by the method described in section 16 using the following reagents:- 3-chloro-3-methyloctane (100g, 0.62mol) (section 14), potassium hydroxide (85g) and ethanol (500 cm^3) to give the desired alkene mixture, E (71.8g, 0.56mol, 92%), b. range 405-12K.

21) Alkene mixture F.

The alkene mixture, F, was composed of 4-methyloct-3-ene, 4-methyloct-4-ene and 2-propylhex-1-ene. The alkene mixture, F, was synthesised by the method described in section 16 using the following reagents:- 4-chloro-4-methyloctane (104.8g, 0.65mol) (section 15), potassium hydroxide (84g) and ethanol (500 cm^3) to give the desired alkene mixture, F (65.8g, 0.52mol, 81%), b. range 405-12K.

22) Alkene mixture G.

The alkene mixture, G, was composed of 4-ethylhept-3-ene and 3-propylhex-2-ene. The alkene mixture was synthesised by an acid catalysed dehydration of the tertiary alcohol, 4-ethylheptan-4-ol as follows. To stirred concentrated ortho-phosphoric acid (500 cm^3) at 418K was slowly added 4-ethylheptan-4-ol (108g, 0.75mol) (section 9) over ca.2 hours. The desired alkene mixture distills from the reaction mixture and was washed with potassium carbonate solution (1%, 50 cm^3) and water (50 cm^3) and then dried (anhydrous sodium sulphate). The yield of the desired alkene mixture, G, was 90.5g, 0.67mol, 89% , b. range 403-10K.

FIGURE 1. Synthesis of alkene mixture used to synthesise 4-(1-ethyl-1-methylbutyl)phenol.

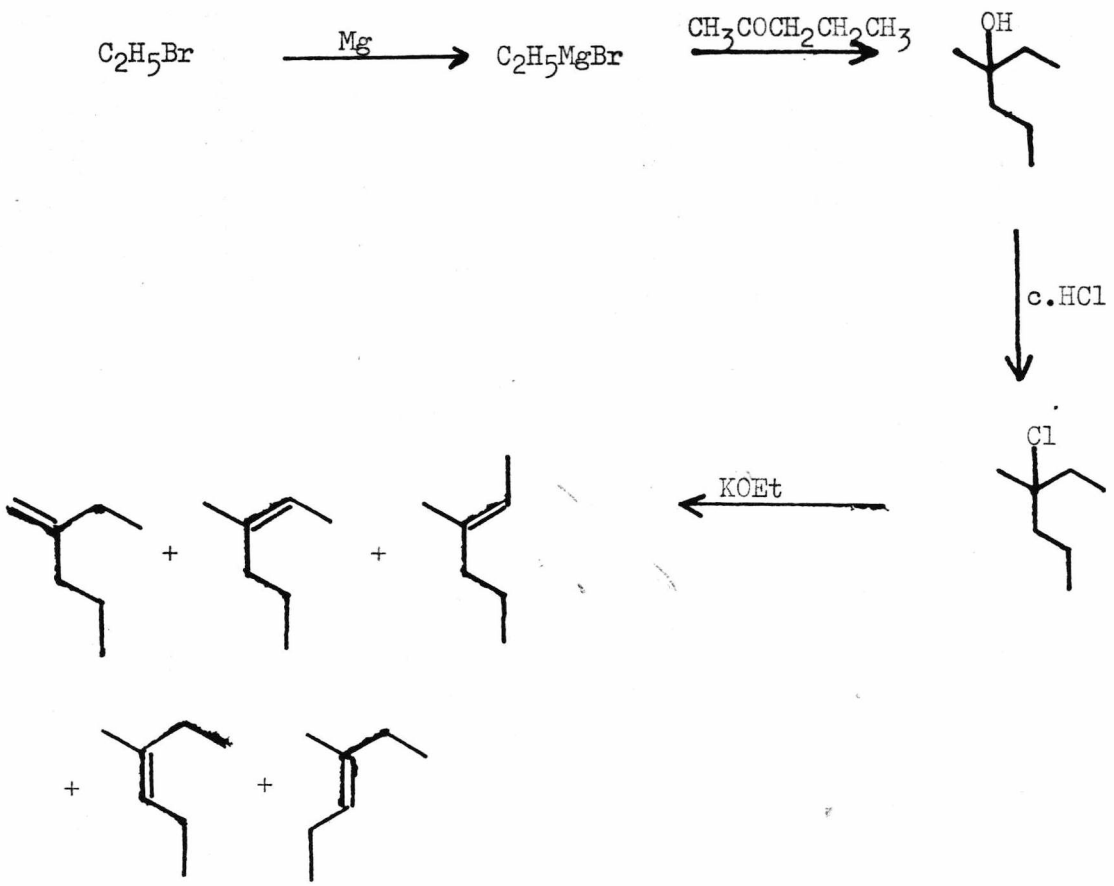

FIGURE 2. Synthesis of 4-(n-heptan-1-one)phenol.

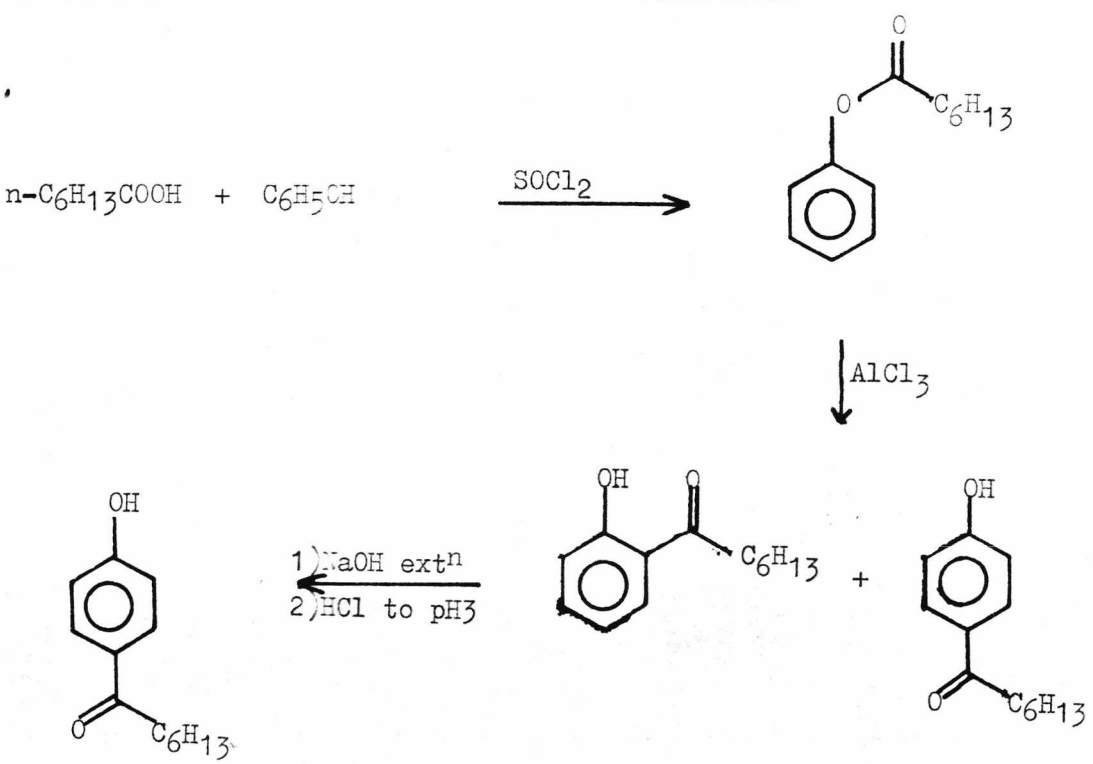

FIGURE 3. Numbering of alkyl chains for assignment and discussion of N.M.R. spectra.

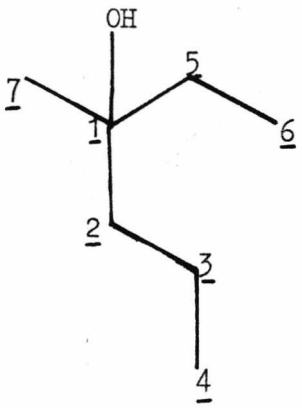

TABLE 1. Infrared spectra (800-710 cm^{-1}) of t-alcohol and t-alkyl halides.

R R'R"C-X

R,R'R".	X = OH.	X = Cl.
Me_2(n-Bu)	725	728
Me_2(i-Bu)	758	780
Me_2(n-C_6H_{13})	720	720
MeEt(n-Pr)	738	740
MeEt(n-C_5H_{11})	721	722
Me(n-Pr)(n-Bu)	723	725
Et_3	760	731
Et_2(n-Bu)	725	725
Et(n-$Pr)_2$	735	

TABLE 2. ^{13}C N.M.R. of 3-chloro-3-methylhexane and 3-methylhexan-3-ol.

	CHEMICAL SHIFT.	
Carbon.	t-alcohol.	t-alkyl halide.
1	72.76 (74.49)	74.78 (68.59)
2	43.87 (47.10)	46.20 (50.10)
3	17.24 (18.61)	18.09 (15.96)
4	14.75 (14.84)	14.28 (14.35)
5	34.32 (35.27)	36.88 (40.60)
6	8.73 (7.93)	9.16 (6.87)
7	26.32 (27.51)	29.35 (30.14)

The numbers in brackets are the calculated chemical shift (4).

TABLE 3. Infrared spectra of alkene mixtures.

Alkene mixture.	Infrared absorption/cm^{-1}.			
	a	b	c	d
A	3080,w	1650,m	893,s	830,m
B	3085,w	1670,w, 1645,m	890,m	840,m,795,m
C		1665,w		825,s
D	3090,m	1650,m	888,s	835,m
E	3085,m	1655,m	885,s	812,w
F	3085,m	1664,w, 1640,m	887,s	840,m
G		1665,m		805,m,795,m

a ν (CH) of $R_2C=CH_2$

b ν (C=C)

c δ (CH) out of plane, $R_2C=CH_2$

c δ (CH) out of plane, $R_2C=CHR$

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CHAPTER 3. SYNTHESIS OF ALKYLPHENOLS.

To aid discussion of these alkyl-substituted compounds the alkyl chains will be numbered as shown in Figure 1 and the compounds will be referred to by this number. For example, 4-n-nonylphenol will be referred to as phenol -(2).

Of the thirteen alkylphenols to be described in this chapter, one, 4-(1,1-dimethylpropyl)phenol, phenol-(3), was purchased (Aldrich Chemical Co.). Two, phenols (1) and (2), were synthesised by the Clemmensen reduction (1, 2,) of the corresponding ketone described in Chapter 2. The remaining ten, phenols (4) to (13), were synthesised by a Friedel-Crafts alkylation of phenol with an alkene using a phosphoric acid/Fullers Earth catalyst (3, 4).

The remainder of the chapter is to be split into three parts: A) The spectroscopic data on the alkylphenols, B) the capillary G.L.C. of the synthesised alkylphenols and the industrially available heptyl and nonylphenols, and finally C) the synthetic details.

A) Spectroscopic characterisation of alkylphenols.

The infrared, proton and ^{13}C N.M.R. and mass spectra of the alkylphenols will be described.

1) Infrared spectra of alkylphenols.

The infrared spectra of all solid alkylphenols were recorded as a KBr disc, the liquid alkylphenols were recorded as liquid films between NaCl plates. All the alkylphenols showed O-H stretch as a broad band centered on 3400 cm^{-1}(5) and a band at 820cm^{-1} characteristic of a p-disubstituted benzene. As the alkylphenols differ in the structure of the alkyl chain it was hoped that the 800-710cm^{-1} region of the spectrum could be used for characterisation (6, 7). The position of the absorption band at lowest wavenumber in this region is characteristic of the carbon bearing substituent-to-(longest alkyl chain) stretch (6, 7). The relationship between the length of the longest alkyl chain and the wavenumber of the absorption appears to be roughly inverse, (graph

below Table 1). This limits the usefulness of the technique in, say, differentiating between a butyl and a pentyl chain, but observing an ethyl chain, as in phenol -(3) and -(6), is easy.

2) Mass spectra of alkylphenols.

The principal features from the mass spectra of the alkylphenols are collected in Table 2. There are two parts to the table, one for the molecular ions and the second for the fragment ions. The numbers in the table are the relative intensities.

All the alkylphenols show a molecular ion and the major fragmentation pathway is by loss of an alkyl radical. The structure of the alkylphenol can be represented as $HO\text{-}C_6H_4\text{-}CRR'R''$. The major fragmentation is by loss of R"; the larger the radical R" is, the more readily it is lost, with one exception. In phenol-(13), in which R = Et, R'=R"=Pr, the loss of ethyl radical appears to be favoured. In the fragmentation of base peak ions to the ion of m/e 107 (when m/e 107 is not the base peak) a cyclopropyl···benzene ring ion/radical pair may be involved (8) which eliminates an alkene fragment to give an ion $C_7H_7O^+$. Hence mass spectrometry is a useful technique for indicating the size of the groups R,R' and R" but it does not define their structure (n-,isc-, etc).

3) Proton N.M.R. and ^{13}C N.M.R.

The proton and ^{13}C N.M.R. of all the alkylphenols will be presented and selected portions will be presented as Table 3. The proton N.M.R. will be presented as a chemical shift (relative to T.M.S. = 0 p.p.m.), multiplicity, coupling constant and integration. The ^{13}C N.M.R. were analysed by comparison with the partially proton-decoupled spectra. The chemical shift of the proton-decoupled spectrum is given along with the multiplicity of the partially proton-decoupled spectrum. For some assignments the chemical shift of the carbon atom was calculated (9, 10).

The numbering system used for the assignments is as follows. For the aryl ring carbons the one bearing the hydroxyl group is labelled a, then the ortho, meta and para carbons are b, c, and d respectively.

The alkyl chain numbering starts with the carbon bonded to the aryl ring as 1. Then working down the longest chain n + 1, n + 2....until the terminal methyl. The next longest chain is then worked from carbon 1 and finally the shortest chain. See Figure 2 for an example.

a) 4-n-heptylphenol, phenol-(1).

Proton N.M.R:- δ 6.4-7.2,1H labile; 6.92,d,J=8Hz,2H(carbon c); 6.66,d, J=8Hz,2H(carbon b); 2.45,t,J=7Hz,2H(carbon 1); 1.50,bm,2H(carbon 2); 1.24,bs,8H(carbon 3-6); 0.86,t,J=5Hz,3H(carbon 7). p.p.m. ($CDCl_3$, T.M.S.)

^{13}C N.M.R:- δ 153.20,s(carbon a); 135.22,s(carbon d); 129.43,d(carbon c); 115.23,d(carbon b); 35.10,t(carbon 1); 31.81,m(carbons 2 and 5); 29.31,m(carbons 3 and 4); 22.73,t(carbon 6); 14.14,q(carbon 7). p.p.m. ($CDCl_3$, T.M.S.)

b) 4-n-nonylphenol, phenol-(2).

Proton N.M.R:- δ 7.04,d,J=8Hz,2H; 6.76,d,J=8Hz,2H; 5.70,bs,1H,labile; 2.52,t,J=7Hz,2H; 1.5-1.7,bm,2H; 1.27,bs,12H; 0.87,t,J=6Hz,3H. p.p.m. ($CDCl_3$, T.M.S.)

^{13}C N.M.R:- δ 153.37,s; 135.29,s; 129.47,d; 115.15,d; 35.18,s(carbon 1); 22.81,t(carbon 8); 14.19,q(carbon 9). Also 31.79(carbon 7?); 30.82(carbon 2?); 29.60, 29.36, 28.63, 28.27. p.p.m. ($CDCl_3$ T.M.S.)

c) 4-(1,1-dimethylpropyl)phenol, phenol-(3).

Proton N.M.R:- δ 7.21,d,J=8Hz,2H; 6.81,d,J=8Hz, 2H; 5.09,bs,1H,labile; 1.59,q,J=8Hz,2H; 1.23,s,6H; 0.66,t,J=8Hz,3H. p.p.m. ($CDCl_3$, T.M.S.)

^{13}C N.M.R:- δ 152.76,s; 141.84,s; 127.04,d; 114.78,d; 37.25,s (carbon 1); 36.88,t(carbon 2); 28.51,q(carbon 4); 9.10,q(carbon 3). p.p.m. ($CDCl_3$, T.M.S.)

d) 4-(1,1-dimethylpentyl)phenol, phenol-(4).

Proton N.M.R:- δ 7.11,d,J=9Hz,2H; 6.71,d,J=9Hz,2H; 6.03,bs,1H,labile; 1.51,bt,J=9Hz,2H(carbon 2); 1.21,s,6H; 0.95-1.3,bm,4H; 0.79,t,J=7Hz,3H. p.p.m. ($CDCl_3$, T.M.S.)

^{13}C N.M.R:- δ 152.52,s; 142.21,s; 126.92,d; 115.15,d; 44.53,t(carbon 2); 37.00,s(carbon 1); 29.12,q(carbon 6); 26.93,t(carbon 3); 23.41,t (carbon 4); 14.07,q(carbon 5). p.p.m. ($CDCl_3$, T.M.S.)

e) 4-(1-ethyl-1-methylbutyl)phenol, phenol-(5).

Proton N.M.R:- δ 7.07,d,J=9Hz,2H; 6.69,d,J=9Hz,2H; 5.28,s,1H,labile; 1.3-1.8,m,4H(carbons 2 and 5); 1.18,s,3H; 0.9-1.2,m,2H; 0.64,bt,J=9Hz, 6H(carbons 4 and 6). p.p.m. ($CDCl_3$, T.M.S.)

^{13}C N.M.R:- δ 152.79,s; 140.46,s; 127.64,d; 114.85,d; 45.60,t, (carbon 2); 40.51,s(carbon 1); 35.61,t(carbon 5); 23.66,q(carbon 7); 17.50,t(carbon 3); 14.85,q(carbon 4); 8.61,q(carbon 6). p.p.m. ($CDCl_3$, T.M.S.)

f) 4-(1,1-diethylpropyl)phenol, phenol-(6).

Proton N.M.R:- δ 7.09,d,J=9Hz,2H; 6.71,d,J=9Hz,2H; 4.98,s,1H,labile; 1.59,q,J=7Hz,6H; 0.62,t,J=7Hz,9H. p.p.m. ($CDCl_3$, T.M.S.)

^{13}C N.M.R:- δ 152.73,s; 139.60,s; 128.02,d; 114.70,d; 43.09,s (carbon 1); 28.77,t(carbon 2); 7.95,q(carbon 3). p.p.m. ($CDCl_3$, T.M.S.)

g) 4-(1,1,3-trimethylbutyl)phenol, phenol-(7).

Proton N.M.R:- δ 7.13,d,J=9Hz,2H; 6.75,d,J=9Hz,2H; 4.84,s,1H,labile; 1.23,s,6H; 1.2-1.6,m,3H; 0.68,d,J=8Hz,6H. p.p.m. ($CDCl_3$, T.M.S.)

^{13}C N.M.R:- δ 153.07,s; 142.31,s; 127.14,d; 114.19,d; 53.64,t(carbon 2); 37.47,s(carbon 1); 29.83,q(carbon 5); 25.00,d(carbon 3); 24.91,q (carbon 4). p.p.m. ($CDCl_3$, T.M.S.)

h) 4-(1,1,3,3-tetramethylbutyl)phenol, phenol-(8).

Proton N.M.R:- δ 7.24,d,J=9Hz,2H; 6.74,d,J=9Hz,2H; 4.58,s,1H,labile; 1.66,s,2H; 1.31,s,6H; 0.70,s,9H. p.p.m. ($CDCl_3$, T.M.S.)

^{13}C N.M.R:- δ 153.01,s; 142.45,s; 127.28,d; 114.54,d; 57.03,t(carbon 2); 37.98,s(carbon 1); 31.79,q(carbon 4); 31.36,s(carbon 3); 30.82,q (carbon 5). p.p.m. ($CDCl_3$, T.M.S.)

i) 4-(1,1-dimethylheptyl)phenol, phenol-(9).

Proton N.M.R:- δ 7.03,d,J=8Hz,2H; 6.67,d,J=8Hz,2H; 5.01,s,1H,labile; 1.46,bt,J=6Hz,2H; 1.17,bs,14H; 0.79,t,J=7Hz,3H. p.p.m. ($CDCl_3$, T.M.S.)

^{13}C N.M.R:- δ 152.65,s; 142,23,s; 126.93,d; 114.87,d; 44.73,t (carbon 2); 37.05,s(carbon 1); 31.81,t(carbon 5); 30.04,t(carbon 4); 29.13,q(carbon 8); 24.68,t(carbon 3); 22.67,t(carbon 6); 14.08,q(carbon 7). p.p.m. ($CDCl_3$, T.M.S.)

j) 4-(1-ethyl-1-methylhexyl)phenol, phenol-(10).

Proton N.M.R:- δ 7.10,d,J=8Hz,2H; 6.74,d,J=8Hz,2H; 6.20,bs,1H,labile; 1.4-1.8,m,4H(carbons 2 and 7); 1.22,s,3H; 0.9-1.3,m,6H(carbons 3,4 and 5); 0.83,t,J=5Hz,3H(carbon 6); 0.66,t,J=8Hz,3H(carbon 8). p.p.m. ($CDCl_3$,T.M.S.)

^{13}C N.M.R:- δ 152.64,s; 140.27,s; 127.53,d; 114.78,d; 42.95,t (carbon 2); 40.28,s(carbon 1); 35.67,t(carbon 7); 32.64,t(carbon 4); 23.78,t(carbon 3); 23.54,q(carbon 9); 22.56,t(carbon 5); 14.07,q(carbon 6); 8.61,q(carbon 8). p.p.m. ($CDCl_3$, T.M.S.)

k) 4-(1,1-diethylpentyl)phenol, phenol-(11).

Proton N.M.R:- δ 7.01,d,J=9Hz,2H; 6.62,d,J=9Hz,2H; 5.52,s,1H,labile; 1.56,m.6H(carbons 2 and 6); 1.4-0.8,m,4H(carbons 3 and 4); 0.58,t,J=6Hz, 9H. p.p.m. ($CDCl_3$, T.M.S.)

^{13}C N.M.R. δ 152.53,s; 139.91,s; 127.90,d; 114.73,d; 42.80,s(carbon 1); 36.33,t(carbon 2); 29.26,t(carbon 6); 25.66,t(carbon 3); 23.47,t (carbon 4); 14.08,q(carbon 5); 7.92,q(carbon 7). p.p.m. ($CDCl_3$, T.M.S.)

l) 4-(1-methyl-1-propylpentyl)phenol, phenol-(12).

Proton N.M.R:- δ 7.08,d,J=8Hz,2H; 6.72,d,J=8Hz,2H; 5.08,s,1H,labile; 1.4-1.8,m,4H(carbons 2 and 6); 0.9-1.4,m,6H(carbons 3, 4 and 7); 1.24,s, 3H; 0.83,bt,J=6Hz,6H. p.p.m. ($CDCl_3$, T.M.S.)

^{13}C N.M.R:- δ 152.75,s; 140.87,s; 127.52,d; 114.86,d; 46.01,t (carbon 6); 43.17,t(carbon 2); 40.25,s(carbon 1); 26.46,t(carbon 3); 24.29,q(carbon 9); 23.48,t(carbon 4); 17.47,t(carbon 7); 14.84,q(carbon 8); 14.04,q(carbon 5). p.p.m. ($CDCl_3$, T.M.S.)

m) 4-(1-ethyl-1-propylbutyl)phenol, phenol-(13).

Proton N.M.R:- δ 7.13,d,J=9Hz,2H; 6.75,d,J=9Hz,2H; 5.7,s,1H,labile; 1.4-1.8,m,6H(carbons 2 and 5); 0.8-1.3,m,4H(carbon 3); 0.85,t,J=9Hz,3H (carbon 6); 0.66,t,J=9Hz,6H(carbon 4). p.p.m. ($CDCl_3$, T.M.S.)

^{13}C N.M.R:- δ 152.53,s; 140.33,s; 127.83,d; 115.03,d; 42.92,s (carbon 1); 39.87,t(carbon 2); 29.99,t(carbon 5); 16.83,t(carbon 3); 14.94,q(carbon 4); 8.05,q(carbon 6). p.p.m. ($CDCl_3$, T.M.S.)

4) Discussion of proton and ^{13}C N.M.R. spectra.

The proton N.M.R. spectra of the aromatic protons clearly show the

para-substitution pattern. The quaternary carbon - methyl δ1.2 p.p.m. is readily distinguishable from methyl groups on a chain (Et,n-Pr.....) δ ca 0.6-1.0 p.p.m. The ^{13}C N.M.R. spectra have several interesting features. The resonances of carbon d can be split into three groups. The first group, phenols (1) and (2), has resonances of δ ca.135 p.p.m., the second group, phenols (5), (6) and (10) to (13) has resonances δ ca.140 p.p.m. and the third group, phenols (3), (4) and (7) to (9), has resonances δ ca.142 p.p.m. The difference lies in the groups attached to carbon 1. The first group has two hydrogens and an alkyl chain, the second group has two methyls and an alkyl chain whilst the third group has either one methyl or no methyl group attached to this carbon. The resonance attributed to carbon 1 also follows the same rough grouping. The resonances of terminal methyls (as opposed to methyl groups attached to carbon 1) are of interest. As one would expect, the terminal methyl groups of the i-Bu (7) and t-amyl (8) compounds resonate at quite different frequencies from the terminal methyl of an n-alkane chain. The resonances of the terminal methyl groups can be split into two groups. The first having a resonance at δ ca.8 p.p.m. belong to ethyl groups whereas the terminal methyl of a propyl or longer chain resonate at δ ca.14 p.p.m.

B) Capillary G.L.C.

Figure 3 and Figure 4 show capillary G.L.C. traces of commercial nonylphenol and commercial heptylphenol. These chromatograms were obtained at 463K using a hexane solution of the alkylphenol. To identify components of the commercial nonylphenol, a sample of commercial nonyl phenol doped with an alkylphenol of known structure was run on G.L.C. and the trace compared with the trace of commercial nonylphenol. Thus one could see the difference in traces and thus identify that component. The same procedure was followed for heptylphenol. As it is known (11) that in commercial nonylphenol carbon 1 is quaternary, then one can say that the major components of commercial nonylphenol have at least one more branch in the alkyl chain than the nonylphenols described in this work.

C) Synthesis of alkylphenols.

1). 4-n-heptylphenol, phenol-(1)

1-(4-hydroxyphenyl)heptan-1-one (110g, 0.53 moles) was dissolved in chloroform (928ml) and water (155ml). Freshly prepared zinc amalgam (290g) was added and hydrogen chloride was bubbled through the reaction mixture. The temperature rose to reflux and was then allowed to cool spontaneously. After 4 hours the reaction mixture was brought to reflux and refluxed for 19 hours whilst purging with hydrogen chloride. The reaction mixture was then cooled, filtered and separated. Chloroform was removed by distillation under reduced pressure and the product was dissolved in water (200ml) and chloroform (200ml). The organic phase was washed with water (4x200ml) and dried (anhydrous sodium sulphate). The solvent was removed by distillation under reduced pressure and the product was then distilled (b.pt 395-405K, 1.5mm Hg) to yield a white crystalline solid, 4-n-heptylphenol, m.pt 310K (m.pt 309K, 12), 41.82g (0.218 moles, 41%).

2). 4-n-nonylphenol, phenol-(2).

The synthesis is described in reference 13.

3). 4-(1,1-dimethylpentyl)phenol, phenol-(4).

The mixture of isomeric alkenes from 2-methylhexan-2-ol (Chapter 2) (95g, 0.97 moles) was added over 3 hours to a mixture of phenol (100g,1.07 moles), fulcat 22A (1.0g) (a fullers earth) and orthophosphoric acid (0.1ml) at 363-8K. The mixture was stirred at this temperature for a further hour and then anhydrous sodium carbonate (3g) was added. The mixture was stirred for 10 minutes and then filtered through celite whilst hot. Distillation (from anhydrous sodium carbonate (1g)) gave the desired product, phenol-(4), as a viscous colourless oil, (b.pt 425-9K 6mm Hg), 124.2g (0.65 moles, 67%).

4). 4-(1-ethyl-1-methylbutyl)phenol, phenol-(5).

This was synthesised by the method described in 3 (above) using the following reagents:- the alkene from 3-methylhexan-3-ol (56.31g, 0.57 moles), phenol (58.28g, 0.62 moles), fulcat 22A (1g) and orthophosphoric acid (0.1ml). Distillation yielded the desired product, phenol-(5),

(b.pt 397K 1.0mm Hg), 53.05g (0.28 moles, 48%).

5). 4-(1,1-diethylpropyl)phenol, phenol-(6).

This was synthesised by the method described in 3 (above) using the following reagents:- the alkene from 3-ethylpentan-3-ol (44.18g, 0.45 moles), phenol (42.38g, 0.45 moles), fulcat 22A (1g) and orthophosphoric acid (0.1ml). Distillation yielded the desired product, phenol-(6), (b.pt 399-403K, 1.7mm Hg), m.pt 345-7K (Lit 348.5-9.5K, 14), 52.5g (0.27 moles, 61%).

6). 4-(1,1,3-trimethylbutyl)phenol, phenol-(7).

This was synthesised by the method described in 3 (above) using the following reagents:- the alkene from 2,4-dimethylpentan-2-ol (54.18g, 0.55 moles), phenol (57.34g, 0.61 moles), fulcat 22A (1g) and orthophosphoric acid (0.31ml). Distillation yielded the desired product, phenol-(7), (b.pt 395-7K, 1.5mm Hg), m.pt 300-2K (Lit. 304-5K, 14), 67.29g (0.35 moles, 64%).

7). 4-(1,1,3,3-tetramethylbutyl)phenol, phenol-(8).

This was synthesised by the method described in 3 (above) using the following reagents:- 2,4,4-trimethylpent-1-ene (Aldrich Chemical Co.) (90g, 0.80 moles), phenol (84.48g, 0.88 moles) fulcat 22A (1g) and orthophosphoric acid (0.1ml). Distillation yielded the desired product, phenol-(8), (b.pt 353-7K, 0.7mm Hg), m.pt 356-7K (Lit 359K, 15), 117.4g (0.57 moles, 71%).

8). 4-(1,1-dimethylheptyl)phenol, phenol-(9).

The synthesis is described in reference 13.

9). 4-(1-ethyl-1-methylhexyl)phenol, phenol-(10).

This was synthesised by the method described in 3 (above) using the following reagents:- the alkene from 3-methyloctan-3-ol (68.3g, 0.54 moles), phenol (54.6g, 0.6 moles), fulcat 22A (1g) and orthophosphoric acid (0.1ml). Distillation yielded the desired product, phenol-(10), (b.pt 409-11K, 1.5mm Hg) as a viscous, colourless oil. Yield 55.1g, (0.25 moles, 46%).

10). 4-(1,1-diethylpentyl)phenol, phenol-(11).

The synthesis is described in reference 13.

11). 4-(1-methyl-1-propylbutyl)phenol, phenol-(12).

This was synthesised by the method described in 3 (above) using the following reagents:- the alkene from 4-methyloctan-4-ol (64.0g, 0.47 moles), phenol (49.32g, 0.52 moles), fulcat 22A (1g) and orthophosphoric acid (0.1ml). Distillation yielded the desired product, phenol-(12), as a viscous, colourless oil, (b.pt 425K, 2.5mm Hg). Yield 70.1g, (0.32 moles, 68%).

12). 4-(1-ethyl-1-propylbutyl)phenol, phenol-(13).

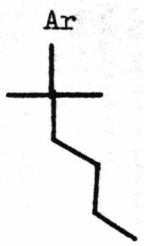
This was synthesised by the method described in 3 (above) using the following reagents:- the alkene from 4-ethylheptan-4-ol (85.0g, 0.63 moles), phenol (64.63g, 0.69 moles), fulcat 22A (1g) and orthophosphoric acid (0.1ml). Distillation yielded the desired product, phenol-(13), as a viscous colourless oil, (b.pt 441K, 6.0mm Hg). Yield 57.28g, (0.26 moles, 42%).

Figure 1. Alkyl chain structures.

4-n-heptylphenol (1)

4-n-nonylphenol (2)

4-(1,1-dimethylpropyl)-phenol (3)



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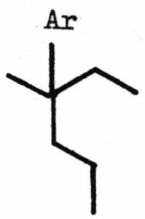

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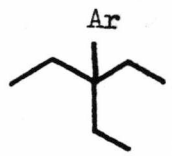

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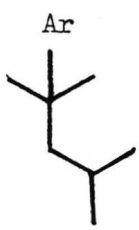

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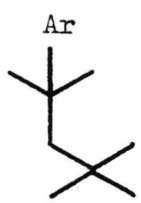

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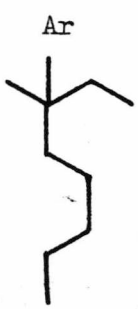

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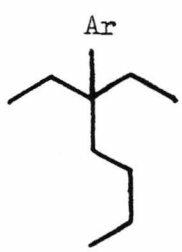

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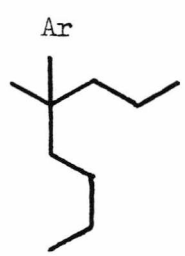

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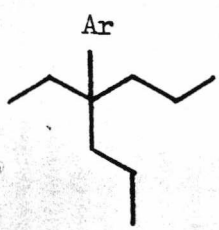


(13)

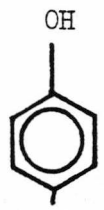
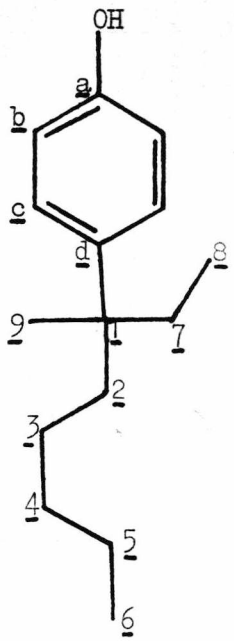
Ar = 

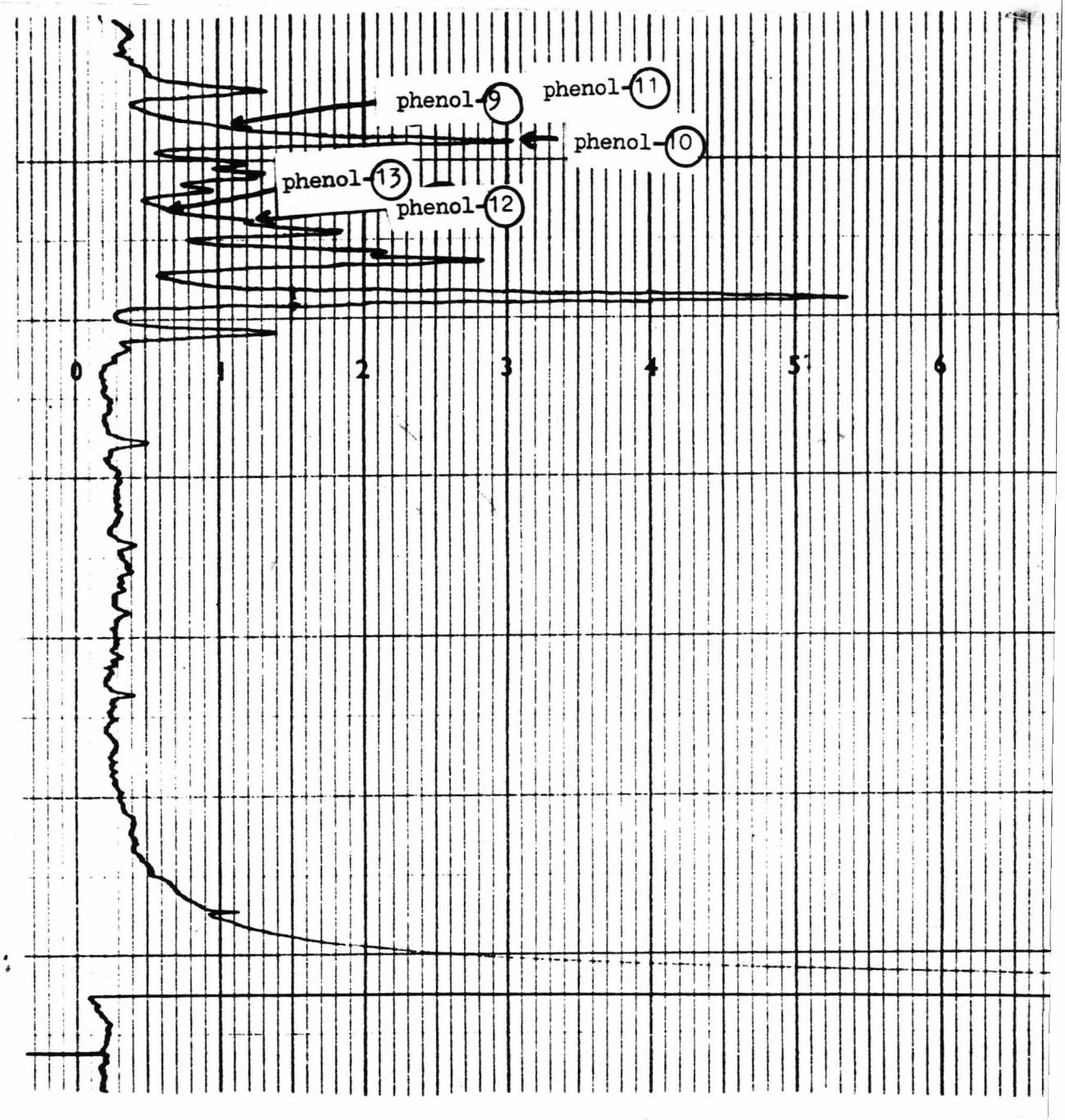
FIGURE 2. Example of the numbering system to be employed for discussing N.M.R. data.

Phenol - (10), 4-(1-ethyl-1-methylhexyl)phenol.



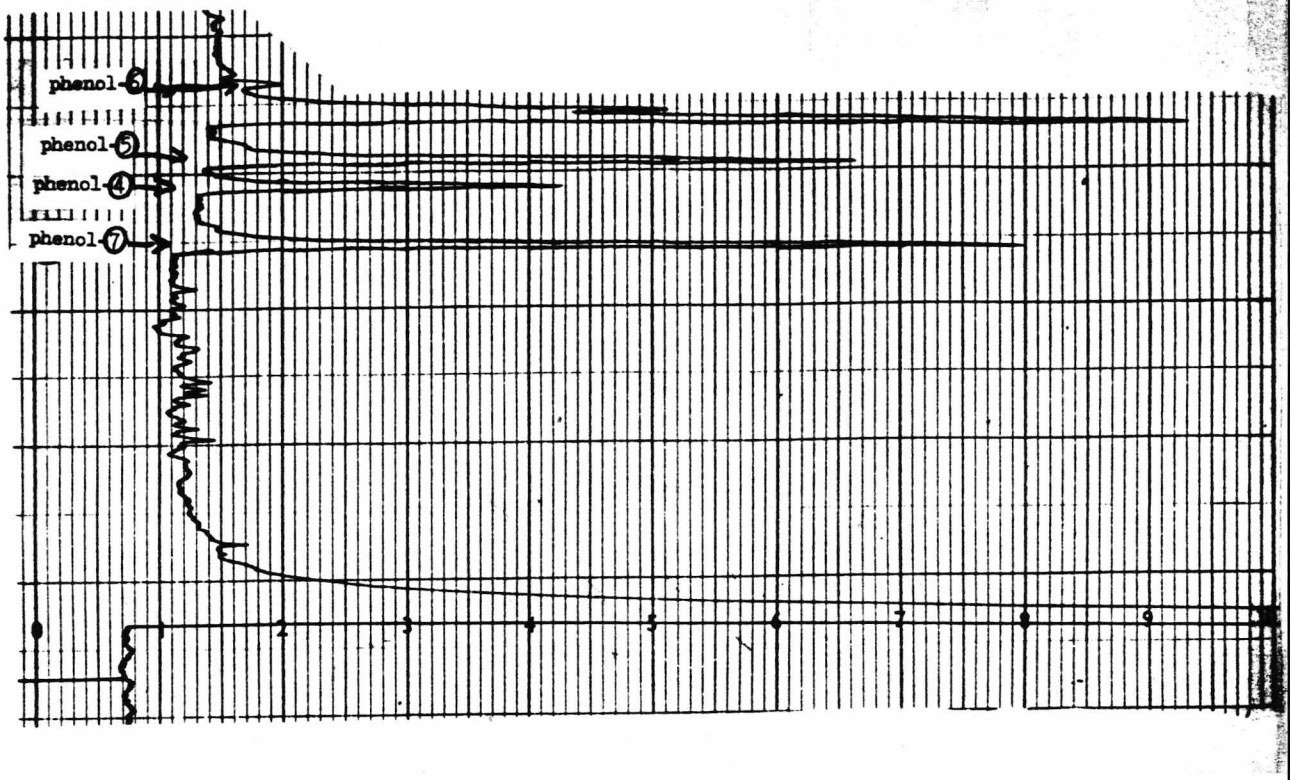
For Table 3) a terminal methyl group is defined as a methyl group not attached to carbon - 1 . Thus in phenol - (10), carbons -6 and 8 are terminal methyl groups but carbon - 9 is not.

FIGURE 3. G.L.C. of Nonylphenol.



Phenol.	Retention time (minutes).
(9)	23.4
(11)	23.4
(10)	22.9
(13)	21.3
(12)	21.0

FIGURE 4. G.L.C. of Heptylphenol.



Phenol.	Retention time (minutes).
(6)	17.5
(5)	15.2
(4)	14.5
(7)	12.9

TABLE 1). Infrared absorption frequencies of the alkylphenols in the 800-710 cm^{-1} region.

Phenol	Longest alkylchain (carbonatoms).	Absorption frequency (cm^{-1}).
(3)	2	768 m
(6)	2	760 m
(5)	3	727 w
(7)	3	728 w
(8)	3	none
(13)	3	740 m
(4)	4	730 w
(11)	4	730 w
(12)	4	730 w
(10)	5	725 w
(9)	6	730 w
(1)	7	715 w
(2)	9	710 m

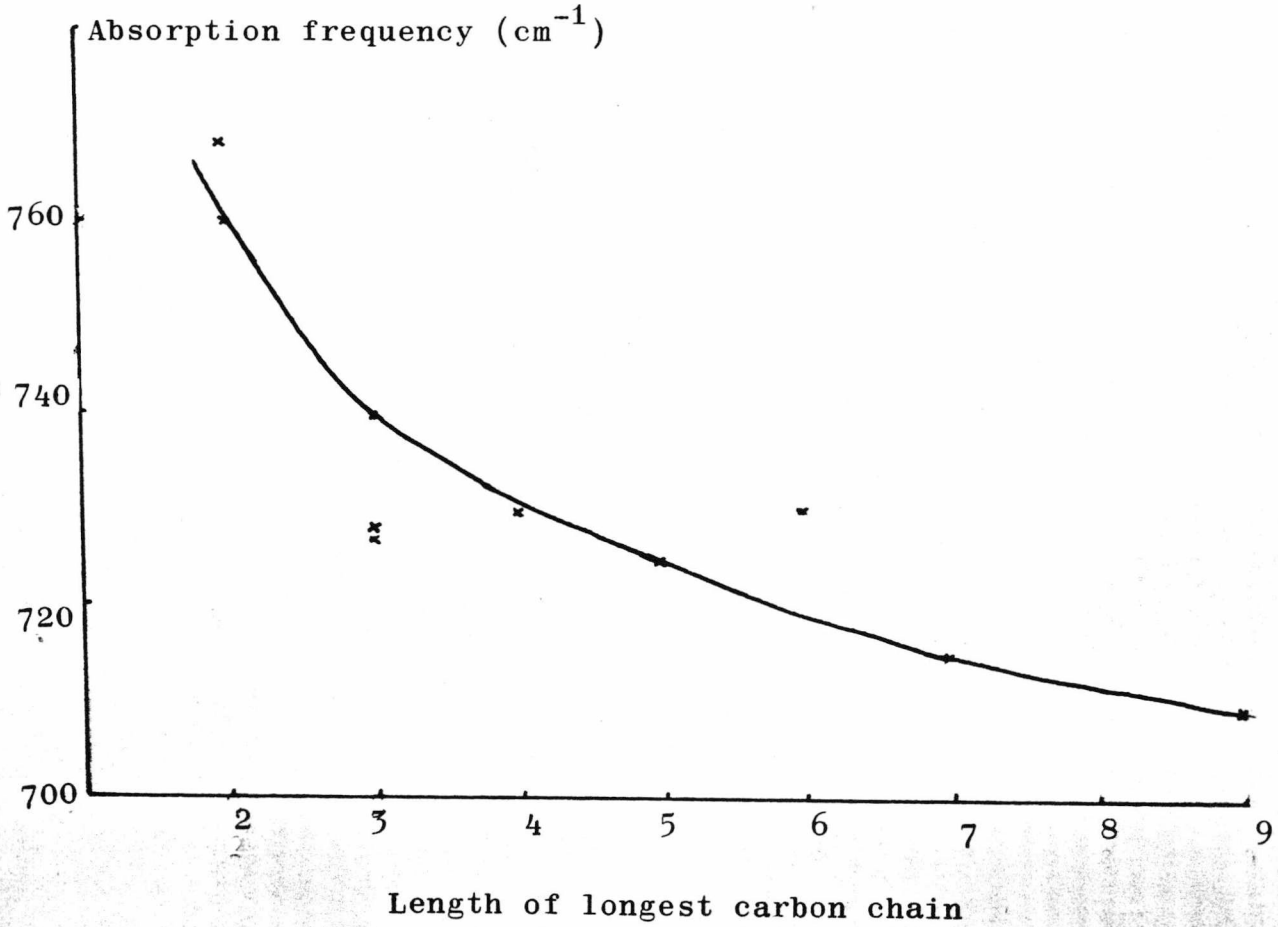


Table 2. Mass spectra of alkylphenols

Phenol-(X)	$M^{+\cdot}$ (m/e)				Fragment (m/e)						
(X)	164	192	206	220	191	177	163	149	135	121	107
(3)	14							8	<u>100</u>		24
(1)		19									<u>100</u>
(4)		10							<u>100</u>		14
(5)		18					63	<u>100</u>		46	89
(6)		12					84			42	<u>100</u>
(7)		6							<u>100</u>	7	8
(8)			6						<u>100</u>		10
(2)				25							<u>100</u>
(9)				7					<u>100</u>		22
(10)				13	43			<u>100</u>		47	61
(11)				6	20		16			26	52
(12)				19		77	96			81	<u>100</u>
(13)				8	70	29					<u>100</u>

Table 3. Proton and ^{13}C N.M.R. chemical shifts, δ/p.p.m.

	Proton.		^{13}C N.M.R.		
	b.	c.	d.	1	terminal-CH_3
(1)	6.66	6.92	135.22	35.10	14.14.
(2)	6.76	7.04	135.29	35.18	14.19.
(3)	6.81	7.21	141.84	37.25	9.10.
(4)	6.71	7.11	142.21	37.00	14.07.
(5)	6.69	7.07	140.46	40.51	14.85, 8.61
(6)	6.71	7.09	139.60	43.09	7.95
(7)	6.75	7.13	142.31	37.47	24.91
(8)	6.74	7.24	142.45	37.98	31.79
(9)	6.67	7.03	142.23	37.05	14.08
(10)	6.74	7.10	140.27	40.28	14.07, 8.61
(11)	6.62	7.01	139.91	42.80	14.08, 7.92
(12)	6.72	7.08	140.87	40.25	14.84, 14.04
(13)	6.75	7.13	140.33	42.92	15.94, 8.05

Table 4. Elemental analyses of alkylphenols.

Phenol.	Carbon. obs.	Carbon. calc.	Hydrogen. obs.	Hydrogen. calc.
(1)	80.90	(81.20)	11.03	(10.48)
(4)	81.45	(81.20)	10.51	(10.48)
(5)	81.07	(81.20)	10.13	(10.48)
(6)	80.75	(81.20)	10.75	(10.48)
(7)	81.41	(81.20)	10.26	(10.48)
(8)	81.26	(81.50)	10.91	(10.75)
(10)	81.98	(81.76)	11.16	(10.98)
(12)	81.53	(81.76)	11.18	(10.98)
(13)	81.71	(81.76)	11.24	(10.98)

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CHAPTER 4. SYNTHESIS OF ALKYLSALICYLALDEHYDES.

The next stage in the synthesis of the desired alkylsalicylaldoximes is the formylation of the alkylphenols described in Chapter 3. Two methods of formylation were used - the Reimer-Tiemann reaction (1, 2) and a route I.C.I. (3) developed for the industrial synthesis of the ligand that prompted this research. The 'I.C.I.' formylation procedure is outlined in Figure 1. In practice, the Reimer-Tiemann reaction was found to be the preferred formylation procedure. This was because, while both procedures produced comparable yield of the desired alkylsalicylaldehyde, the Reimer-Tiemann reaction is a relatively quick, one-pot reaction compared to the 'I.C.I' method which involves tedious separations after iron(III) oxidation to the intermediate Schiff base.

The Reimer-Tiemann reaction leaves a large quantity (ca.50%) of unchanged alkylphenol with the desired alkylsalicylaldehyde product (based upon ratios of integration from a proton N.M.R. spectrum of the crude mixture) as well as undesired products from side reactions. Fractional distillation under reduced pressure yielded the desired alkylsalicylaldehyde product and the unreacted alkylphenol. Column chromatography (4) was successful in effecting the separation though the method is tedious given the scale on which it was necessary to work. A successful method of separating the desired alkylsalicylaldehyde product from the crude reaction mixture was to react the mixture with formaldehyde under acidic conditions (5). See Figure 2. This results in the unreacted alkylphenol reacting with the formaldehyde and the desired alkylsalicylaldehyde could be readily distilled from the reaction mixture.

The remainder of the chapter will be split into two sections; in the first the spectroscopic data of the alkylsalicylaldehydes will be described followed, in the second section, by the experimental details.

A). Characterisation of alkylsalicylaldehydes.

1) Infrared spectra.

The infrared spectra of all the alkylsalicylaldehydes described in this chapter showed the following features:- ν O-H stretch (3150 cm^{-1}), νAr C(O)-H (2730cm^{-1}), νconjugated carbonyl (1660cm^{-1}) and an absorption characteristic for two adjacent hydrogens on an aromatic nucleus (835cm^{-1}) (6). In contrast with the infrared spectra of the alkylphenols in the range 720-800cm^{-1} all of the alkylsalicylaldehydes exhibit three absorptions in this range at 775cm^{-1}, 743cm^{-1} and 720cm^{-1}. All are of medium intensity and approximately in the intensity ratio 2:3:2 respectively. Only the alkylsalicylaldehyde -(6), 5-(1,1-diethylpropyl)-2-hydroxybenzaldehyde, exhibited a fourth absorption at 767cm^{-1} which is assigned to the C-Ethyl group of the alkyl chain.

2) Mass spectra.

The principal features of the mass spectra are collected in Table 1. The table is split into two sections, the first is the molecular ion and the second section is the fragmentation pattern. The structure of the alkyl chain is that of Figure 1 in Chapter 3 where Ar is 2-hydroxybenzaldehyde and the alkyl chain is attached to position 5 of the aromatic nucleus.

3) Proton and ^{13}C N.M.R. spectra.

The method for numbering the carbons in the alkyl chains is described in Chapter 3, however the numbering of the carbons in the aromatic nucleus will be as follows:- the carbon bearing the aldehyde group is carbon-a, the one bearing the hydroxyl group is carbon-b and so on continuing around the ring.

a) 5-n-heptyl-2-hydroxybenzaldehyde, aldehyde-(1).

Proton N.M.R:- δ10.74,bs,1H; 9.68,s,1H; 7.24,s, ca.1H; 7.26,d,J=9Hz,ca.1H; 6.84,d,J=9Hz,1H; 2.56,t,J=7Hz,2H; 1.45-1.75,m,2H; 1.30,bs, 8H; 0.89,t,J=6Hz,3H; p.p.m. ($CDCl_3$, T.M.S.)

^{13}C N.M.R:- δ196.46,d(aldehyde carbon); 159.71,s(carbon b); 137.29,d(carbon d); 134.24,s(carbon e); 132.72,d(carbon f); 120.35,s (carbon a); 117.37,d(carbon c); 34.73,t(carbon 1); 31.87,t(carbon 2 or 5);

31.44,t(carbon 2 or 5); 29.19,t(carbons 3 and 4); 22.73,t(carbon 6); 14.08,q(carbon 7). p.p.m. ($CDCl_3$, T.M.S.)

b) 2-hydroxy-5-n-nonylbenzaldehyde, aldehyde-(2).

Proton N.M.R:- δ 10.60,bs,1H; 9.73,s,1H; 7.28,s,ca.1H; 7.30,d,J=9Hz, ca.1H; 6.88,d,J=9Hz,1H; 2.61,t,J=7Hz,2H; 1.45-1.8,m,2H; 1.31,bs,12H; 0.91,t,J=6Hz,3H. p.p.m. ($CDCl_3$, T.M.S.)

c) 5-(1,1-dimethylpropyl)-2-hydroxybenzaldehyde, aldehyde-(3).

Proton N.M.R:- δ 10.80,s,1H; 9.85,s,1H; 7.42,s,ca.1H; 7.46,d,J=9Hz, ca.1H; 6.88,d,J=9Hz,1H; 1.63,q,J=7Hz,2H; 1.28,s,6H; 0.69,t,J=8Hz,3H. p.p.m. ($CDCl_3$, T.M.S.)

^{13}C N.M.R:- δ 196.81,d; 159.43,s; 140.99,s(carbon e); 135.16,d(carbon d); 130.55,d; 120.12,s; 117.20,d; 37.36,s(carbon 1); 36.76,t(carbon 2); 28.38,q(carbon 4); 7.09,q(carbon 3). p.p.m. ($CDCl_3$, T.M.S.)

d) 5-(1,1-dimethylpentyl)-2-hydroxybenzaldehyde, aldehyde-(4).

Proton N.M.R:- δ 10.67,s,1H; 9.77,s,1H; 7.42,s,ca.1H; 7.47,d,J=9Hz,ca. 1H; 6.90,d,J=9Hz,1H; 1.5-1.7,m,2H; 1.31,s,ca.6H; 0.95-1.4,m,ca.4H; 0.83,t, J=7Hz,3H. p.p.m. ($CDCl_3$, T.M.S.)

^{13}C N.M.R:- δ 196.79,d; 159.41,s; 141.31,s; 135.03,d; 130.40,d; 120.01,s; 117.23,d; 44.20,t(carbon 2); 37.06,s(carbon 1); 28.90,q(carbon 6); 26.94,t(carbon 3); 23.29,t(carbon 4); 14.02,q(carbon 5). p.p.m. ($CDCl_3$, T.M.S.)

e) 5-(1-ethyl-1-methylbutyl)-2-hydroxybenzaldehyde, aldehyde-(5).

Proton N.M.R:- δ 10.80,s,1H; 9.77,s,1H; 7.37,s,ca.1H; 7.40,d,J=9Hz, ca.1H; 6.88,d,J=9Hz,1H; 1.4-1.9,m,4H; 1.26,s,ca.3H; 1.0-1.4,m,ca.2H; 0.67,t,J=7Hz,6H. p.p.m. ($CDCl_3$, T.M.S.)

^{13}C N.M.R:- δ 196.79,d; 159.35,s; 139.48,s; 135.39,d; 131.25,d; 120.10,s; 117.17,d; 45.29,t(carbon 2); 40.54,s(carbon 1); 35.56,t(carbon 5); 23.29,q(carbon 7); 17.44,t(carbon 3); 14.75,q(carbon 4); 8.53,q(carbon 6). p.p.m. ($CDCl_3$, T.M.S.)

f) 5-(1,1-diethylpropyl)-2-hydroxybenzaldehyde, aldehyde-(6).

Proton N.M.R:- δ 10.84,bs,1H; 9.78,s,1H; 7.40,s,ca.1H; 7.43,d,J=9Hz, ca.1H; 6.90,d,J=9Hz,1H; 1.70,q,J=7Hz,6H; 0.67,t,J=7Hz,9H. p.p.m. ($CDCl_3$,T.M.S)

^{13}C N.M.R:- δ 196.82,d; 159,29,s; 138.82,s; 135.71,d; 131.81,d; 119.98,s; 117.06,d; 43.14,s(carbon 1); 28.60,t(carbon 2); 7.86,q(carbon 3). p.p.m. ($CDCl_3$, T.M.S.)

g) 2-hydroxy-5-(1,1,3-trimethylbutyl)benzaldehyde, aldehyde-(7).

Proton N.M.R:-δ10.89,s,1H; 9.89,s,1H; 7.48,s,ca.1H; 7.49,d,J=9Hz,ca. 1H; 6.93,d,J=9Hz,1H; 1.2-1.7,m,ca.3H; 1.32,s,ca.6H; 0.70,d,J=8Hz,6H. p.p.m. ($CDCl_3$, T.M.S.)

^{13}C N.M.R:- δ 196.79,d; 159.41,s; 141.49,s; 135.23,d; 130.46,d; 119.99,s; 117.08,d; 53.12,t(carbon 2); 37.39,s(carbon 1); 29.54,q(carbon 5); 24.92,d(carbon 3); 24.84,q(carbon 4). p.p.m. ($CDCl_3$, T.M.S.)

h) 2-hydroxy-5-(1,1,3,3-tetramethylbutyl)benzaldehyde, aldehyde-(8).

Proton N.M.R:- δ 10.72,s,1H; 9.76,s,1H; 7.44,s,ca.1H; 7.46,d,J=9Hz, ca.1H; 6.85,d,J=9Hz,1H; 1.75,s,2H; 1.38,s,6H; 0.74,s,9H. p.p.m. ($CDCl_3$, T.M.S.)

^{13}C N.M.R:- δ 196.64,d; 159.35,s; 141.62,s; 135.28,d; 130.41,d; 119.92,s; 116.88,d; 56.61,t(carbon 2); 37.90,s(carbon 1); 32.30,s(carbon 3); 31.81,q(carbon 4); 31.44,q(carbon 5). p.p.m. ($CDCl_3$, T.M.S.)

i) 5-(1,1-dimethylheptyl)-2-hydroxybenzaldehyde, aldehyde-(9).

Proton N.M.R:- δ 10.75,bs,1H; 9.71,s,1H; 7.40,s,ca.1H; 7.43,d,J=9Hz, ca.1H; 6.86,d,J=9Hz,1H; 1.5-1.7,m,2H; 1.30,s,ca.6H; 1.0-1.4,m,ca.8H; 0.84,bt,J=6Hz,3H. p.p.m. ($CDCl_3$, T.M.S.)

^{13}C N.M.R:- δ 196.64,d; 159.35,s; 141.25,s, 134.92,d; 130.34,d; 119.98,s; 117.12,d; 44.42,t(carbon 2); 37.05,s(carbon 1); 31.75,t(carbon 5); 29.97,t(carbon 4); 28.82,q(carbon 8); 24.62,t(carbon 3); 22.62,t (carbon 6); 14.02,q(carbon 7). p.p.m. ($CDCl_3$, T.M.S.)

j) 5-(1-ethyl-1-methylhexyl)-2-hydroxybenzaldehyde, aldehyde-(10).

Proton N.M.R:-δ10.81,s,1H; 9.81,s,1H; 7.40,s,ca.1H; 7.42,d,J=9Hz, ca.1H; 6.91,d,J=9Hz,2H; 1.4-1.9,m,4H; 1.28,s,ca.3H; 1.0-1.4,m,ca.6H; 0.83,t,J=7Hz,3H; 0.68,t,J=7Hz,3H. p.p.m. ($CDCl_3$, T.M.S.)

^{13}C N.M.R:- δ 196.82,d; 159.35,s; 139.55,s; 135.46,d; 131.23,d; 120.05,d; 117.18,d; 42.78,t(carbon 2); 40.52,s(carbon 1); 35.40,t(carbon 7); 32.60,t(carbon 4); 23.88,t(carbon 3); 23.34,q(carbon 9); 22.61,t(carbon 5);

14.08,q(carbon 6); 8.59,q(carbon 8). p.p.m. ($CDCl_3$, T.M.S.)

k) 5-(1,1-diethylpentyl)-2-hydroxybenzaldehyde, aldehyde-(11).

Proton N.M.R:-δ10.78,bs,1H; 9.78,s,1H; 7.39,s,ca.1H; 7.41,d,J=9Hz, ca.1H; 6.89,d,J=9Hz,1H; 1.5-1.9,m,6H; 0.9-1.5,m,4H; 0.85,t,J=6Hz,3H; 0.66,t,J=7Hz,6H. p.p.m. ($CDCl_3$, T.M.S.)

^{13}C N.M.R:- δ 196.81,d; 159.35,s; 139.54,s; 135.47,d; 131.41,d; 119.99,s; 117.18,d; 42,73,s(carbon 1); 36.40,t(carbon 2); 29.24,t(carbon 6); 25.71,t(carbon 3); 23.47,t(carbon 4); 14.12,q(carbon 5); 7.91,q (carbon 7); p.p.m. ($CDCl_3$, T.M.S.)

l) 2-hydroxy-5-(1-methyl-1-propylpentyl)benzaldehyde, aldehyde-(12).

Proton N.M.R:- δ 10.75,bs,1H; 9.73,s,1H; 7.36,s,ca.1H; 7.40,d,J=9Hz, ca.1H; 6.88,d,J=9Hz,1H; 1.4-1.8,m,4H; 1.28,s,ca.3H; 0.95-1.4,m, ca.6H; 0.83,t,J=6Hz,6H. p.p.m. ($CDCl_3$, T.M.S.)

^{13}C N.M.R:- δ 196.77,d; 159.29,s; 139.85,s; 135.28,d; 131.01,d; 120.14,s; 117.18,d; 45.64,t(carbon 6); 42.90,t(carbon 2); 40.22,s(carbon 1); 26.39,t(carbon 3); 24.19,q(carbon 9); 23.40,t(carbon 4); 17.43,t(carbon 7); 14.81,q(carbon 8); 14.08,q(carbon 5); p.p.m. ($CDCl_3$, T.M.S.)

m) 5-(1-ethyl-1-propylbutyl)-2-hydroxybenzaldehyde,aldehyde-(13).

Proton N.M.R:- δ 10.84,s,1H; 9.78,s,1H; 7.45,s,ca.1H; 7.44,d,J=9Hz, ca.1H; 6.90,d,J=9Hz,1H; 1.5-1.8,m,6H; 0.8-1.4,m,ca.4H; 0.87,t,J=6Hz,ca.6H; 0.67,t,J=6Hz,3H. p.p.m. ($CDCl_3$, T.M.S.)

^{13}C N.M.R:- δ 196.82,d; 159.35,s; 139.43,s; 135.46,d; 131.50,d; 120.05,s; 117.12,d; 42.96,s(carbon 1); 39.43,t(carbon 2); 29.74,t(carbon 5); 16.78,t(carbon 3); 14.87,q(carbon 4); 7.98,q(carbon 6). p.p.m. ($CDCl_3$,T.M.S.)

4). Discussion of spectra.

The infrared spectra of the alkylsalicylaldehydes shows that the phenolic hydrogen is hydrogen bonded as the O-H stretch is lowered to $3150cm^{-1}$ when compared to the O-H stretch in the parent alkylphenols which appear at $3400cm^{-1}$. This hydrogen bonding will be intramolecular with the oxygen of the carbonyl group ortho to the phenolic hydroxyl group. The carbonyl stretching frequency of $1660cm^{-1}$ shows that the carbonyl group is

conjugated to an unsaturated system (the aromatic nucleus in this case) as a non-conjugated aldehyde carbonyl stretch would be about 1710cm^{-1}(6). A C-H stretch is observed at 2730cm^{-1}, which is not observed in the parent alkylphenols, and is assigned to the C-H stretch of the aldehyde group.

As one can see in the mass spectra (Table 1) the primary fragmentation is by loss of an alkyl radical from the alkyl chain to give benzylic radical cation. As was noted in Chapter 3, the loss of an ethyl or larger radical is preferred to loss of a methyl radical. Loss of CO is observed as secondary fragmentation, eg m/e 135 ⟶ 107 in aldehydes -(1) and(2) and m/e 163 ⟶ 135 in aldehyde -(3). If one describes these alkylsalicyl-aldehydes as Ar-CR,R'R" then for R,R'R" ≠ Me the m/e of the base peak is 135. This could be thought of as Ar-CH_2^+ and is likely to have been formed by sequential loss of alkene fragments from the initially formed Ar-CRR'$^+$ If R=Me and R',R"≠Me then the base peak is formed by loss of the larger alkyl radical R' or R". If R=R'=Me then the base peak has m/e 163 from loss of the alkyl radical R". Thus one can see that the fragmentation pattern of an alkylsalicylaldehyde is very similar to that observed for the parent alkylphenol and is readily accounted for.

i) The proton and ^{13}C- N.M.R. spectra of the alkyl chains, of these aldehydes, were almost identical to the proton and ^{13}C- N.M.R. spectra of the alkylphenol the aldehyde was synthesised from. Given the N.M.R. data of just the alkyl chain it is impossible to tell if it is from an alkylphenol or from an aldehyde. The ^{13}C N.M.R. resonances of aldehydes -(3) to (13) and alkylphenols -(3) to (13) were compared. The carbon atoms were split into four groups. Group 1 being the quaternary carbon - carbon 1, group 2 is the methylene group(s) adjacent to carbon 1, group 3 is the methyl group(s) adjacent to carbon 1 and group 4 consists of the remaining carbons in the alkyl chain. The difference in δ(p.p.m.) of the resonance of the carbon atom in the alkyl chain of the aldehyde, when compared to the equivalent carbon atom in the alkyl chain of the alkylphenol the aldehyde was derived from, was noted. For group 1 the

average deviation was +0.02 p.p.m. with deviations ranging from -0.08 to +0.24 p.p.m. being observed. Group 2 showed average deviation of -0.24 p.p.m. with deviations ranging from +0.07 to -0.54 p.p.m., group 3 had an average deviation of -0.14 p.p.m. with a range of -0.39 to +0.62 p.p.m. In group 4, with the exception of aldehyde -(8), all the deviations were in the range -0.10 to +0.10 p.p.m., aldehyde -(8), showing deviations of +0.9 to +1.0 p.p.m.

ii) The proton and ^{13}C N.M.R. spectra of the aromatic ring (see Table 2 for an example). The chemical shift of the phenolic proton was expected to alter drastically on going to the aldehyde from the phenol as intramolecular hydrogen bonding could take place. The introduction of the carbonyl group has deshielded the hydrogens and the carbons in the aromatic nucleus with the exception of carbon -e which has been shielded by almost 1 p.p.m. The carbon para to the aldehyde group suffers the greatest deshielding in both the proton and ^{13}C N.M.R. spectra. This implies that the mesomeric effect of adding the carbonyl greatly outweighs the inductive effect and that the mesomeric effect has a deshielding action whereas the inductive effect has a shielding action. Carbons -c and e in the ^{13}C N.M.R. spectra suffer the least deshielding which again points to a large mesomeric influence of the carbonyl group.

B). Experimental.

The elemental analyses of the aldehydes are collected in Table 3. Aldehydes -(1) to (7) and (9) to (13) were obtained as yellow oils and aldehyde -(8) was obtained as a yellow solid. The 2,4-dinitrophenylhydrazine (2,4-DNP) derivatives were prepared (7) and recrystallised from ethanol and dried in vacuo. The melting points and elemental analyses of the 2,4-DNP derivatives are collected in Table 4.

1). 5-n-heptyl-2-hydroxybenzaldehyde, aldehyde-(1).

A solution of sodium hydroxide (105.3g) in water (105.3cm^3) was added to a solution of 4-n-heptylphenol (51.05g, 0.27 moles) (Chapter 3) in ethanol (52.7 cm^3). The mixture was stirred (mechanically) and heated

to 338K. Trichloromethane (35.1g) was slowly added, maintaining the temperature at 338-343K. After the addition was complete the mixture was heated at this temperature for a further hour and then left to cool to ambient temperature. A solution of concentrated sulphuric acid (55.5 cm^3) in water (454 cm^3) was added to the reaction and the mixture was stirred for 10 minutes before the phases were separated. The solvent was removed from the organic phase by distillation under reduced pressure and the crude product, aldehyde-(1), was dissolved in petroleum ether (300 cm^3, 100-120 fraction). The resulting mixture was added to a solution of concentrated sulphuric acid (104.6g) in water (137.6 cm^3). Formaldehyde liquor (21.03g, 40% solution in water) was added to the acidic solution and the mixture stirred mechanically and heated to 363-368K for 24 hours. The mixture was then cooled, separated and the organic phase washed with water until it was acid free (universal indicator paper). The organic phase was dried (anhydrous sodium sulphate) and the solvent was removed by distillation under reduced pressure. The crude product was distilled under reduced pressure (425K, 4mm Hg) to yield the desired product, aldehyde-(1) (14.76g, 67mmole, 24.8%).

2). 2-hydroxy-5-n-nonylbenzaldehyde, aldehyde-(2).

This was synthesised by the method described in section 1) using the following reagents:- 4-n-nonylphenol (17.47g, 79mmol, Chapter 3)), trichloromethane (10.3 cm^3) and formaldehyde liquor (4.7 cm^3) to yield the desired product, aldehyde-(2) (b.pt. 420K, 3.5mmHg) (9.07g, 37mmol, 46%).

3). 5-(1,1-dimethylpropyl)-2-hydroxybenzaldehyde, aldehyde-(3).

This was synthesised by the method described in section 1) using the following reagents:- 4-(1,1-dimethylpropyl)phenol (50.0g, 305mmol, Aldrich Chemical Co.), trichloromethane (39.0 cm^3) and formaldehyde liquor (18 cm^3) to yield the desired product, aldehyde-(3) (b.pt 381K, 0.5mmHg), (25.07g, 131mmol, 43%).

4). 5-(1,1-dimethylpentyl)-2-hydroxybenzaldehyde, aldehyde-(4).

This was synthesised by the method described in section 1) using the following reagents:- 4-(1,1-dimethylpentyl)phenol (60.0g, 313mmol, Chapter 3)) trichloromethane (40.5 cm^3) and formaldehyde liquor (34.9 cm^3) to yield the desired product, aldehyde-(4) (b.pt 449K, 4.5mm Hg) (21.1g, 96mmol, 31%).

5). 5-(1-ethyl-1-methylbutyl)-2-hydroxybenzaldehyde, aldehyde-(5).

This was synthesised by the method described in section 1) using the following reagents:- 4-(1-ethyl-1-methylbutyl)phenol (45.73g, 238mmol, Chapter 3)) trichloromethane (30.6 cm^3) and formaldehyde liquor (22.1 cm^3) to yield the desired product, aldehyde-(5) (b.pt. 403K, 0.7mm Hg) (24.01g, 109mmol, 46%).

6). 5-(1,1-diethylpropyl)-2-hydroxybenzaldehyde, aldehyde-(6).

This was synthesised by the method described in section 1) using the following reagents:- 4-(1,1-diethylpropyl)phenol (34.0g, 177mmol, Chapter 3)) trichloromethane (23.0 cm^3) and formaldehyde liquor (11.1 cm^3) to yield the desired product, aldehyde-(6) (b.pt 426K, 5mmHg) (12.84g, 58mmol, 33%).

7). 2-hydroxy-5-(1,1,3-trimethylbutyl)benzaldehyde, aldehyde-(7).

This was synthesised by the method described in section 1) using the following reagents:- 4-(1,1,3-trimethylbutyl)phenol (19.2g, 100mmol, Chapter 3)) trichloromethane (13.0 cm^3) and formaldehyde liquor (7.6 cm^3) to yield the desired product, aldehyde-(7) (b.pt 389K, 0.5mmHg) (10.06g, 46mmol, 46%).

8). 2-hydroxy-5-(1,1,3,3-tetramethylbutyl)benzaldehyde, aldehyde-(8).

This aldehyde was synthesised by the route outlined in Figure 1). Water (78 cm^3) was placed in a 1000 cm^3, 3-necked round bottom flask fitted with a reflux condenser, thermometer and mechanical stirrer. Then, in this order, were added sodium carbonate (8.48g, 80mmol), 4-(1,1,3,3-tetra methylbutyl)phenol (164g, 800mmol, Chapter 3), 4-toluidine (171.2g, 1.6 mol) and paraformaldehyde (48g, 1.60mmol) and the mixture heated and stirred at 333K until a homogeneous solution was obtained. The mixture

was kept at this temperature for a further 8 hours when xylene (244 cm^3) was added and the mixture was left to cool to ambient temperature. The phases were separated and the organic phase was washed with water (120 cm^3). The solution was placed in a 2 litre round bottomed flask and a solution of iron (III) sulphate (396.5g) and concentrated sulphuric acid (81.7g) in water (550 cm^3) was added. The mixture was stirred (mechanically) and heated to 368K for 21 hours. Water (500 cm^3) was added and the phases were separated. The organic phase was washed with water (300 cm^3), and on cooling, with the addition of water, was found to be extremely viscous. The organic phase was added to a solution of sulphuric acid (165.1g) in water (396.5 cm^3) and the mixture heated to 369K and stirred (mechanically) for 6 hours. The mixture was allowed to cool to 343K and then separated. The organic phase was washed with water (8x150 cm^3) at 343K, dried (anhydrous sodium sulphate) and the solvent removed by distillation under reduced pressure. The crude product was distilled under reduced pressure to yield the desired product, aldehyde-(8) (b.pt 408K, 2mmHg) (41.18g, 176mmol, 22%), as a yellow solid (m.pt 319-321K, (323K, 8)).

9). 5-(1,1-dimethylheptyl)-2-hydroxybenzaldehyde, aldehyde-(9).

This was synthesised by the method described in section 8) using the following reagents:- 4-(1,1-dimethylheptyl)phenol (45.0g, 200mmol, Chapter 3)), paraformaldehyde (11.25g, 310mmol) and 4-toluidine (32.83g, 310mmol) to yield the desired product, aldehyde-(9) (b.pt 394K, 0.1mmHg) (12.15g, 49mmol, 25%).

10). 5-(1-ethyl-1-methylhexyl)-2-hydroxybenzaldehyde, aldehyde-(10).

This aldehyde, aldehyde-(10) was synthesised by the Reimer-Tiemann reaction as described in section 1) using 4-(1-ethyl-1-methylhexyl)phenol (48.81g, 0.22 moles, Chapter 3)) and trichloromethane (27.9 ml). The crude product was distilled and the mixture of phenol-(10) and aldehyde-(10) purified by column chromatography on silica using dichloromethane as eluant. Fractions were monitored by T.L.C. (CH_2Cl_2, silica plates) and solvent was removed by distillation under reduced pressure. This yielded

the desired product, aldehyde-(10) (13.95g, 56mmol, 25%).

11). 5-(1,1-diethylpentyl)-2-hydroxybenzaldehyde, aldehyde-(11).

This was synthesised by the method described in section 1) using the following reagents:- 4-(1,1-diethylpentyl)phenol (52.57g, 239mmol, Chapter 3)) trichloromethane (30.9 cm^3) and formaldehyde liquor (26.6 cm^3) to yield the desired product, aldehyde-(11) (b.pt 441K, 5.0mmHg) (16.44g, 66mmol.28%).

12). 2-hydroxy-5-(1-methyl-1-propylpentyl)benzaldehyde, aldehyde-(12).

This was synthesised by the method described in section 1) using the following reagents:- 4-(1-methyl-1-propylpentyl)phenol (33.34g, 152mmol.) trichloromethane (19.5ml) and formaldehyde liquor(17.8cm^3) to yield the desired product, aldehyde-(12) (b.pt 407K, 2.5mmHg) (15.67g, 71mmol, 47%).

13). 5-(1-ethyl-1-propylbutyl)-2-hydroxybenzaldehyde, aldehyde-(13).

This was synthesised by the method described in section 1) using the following reagents:- 4-(1-ethyl-1-propylbutyl)phenol (44.59g, 200mmol, Chapter 3)) trichloromethane (25.9 cm^3) and formaldehyde liquor (22.3 cm^3) to yield the desired product, aldehyde-(13) (b.pt 435K, 3.5mmHg) (11.55g, 47mmol, 24%).

FIGURE 1. I.C.I. formylation of alkylphenols.

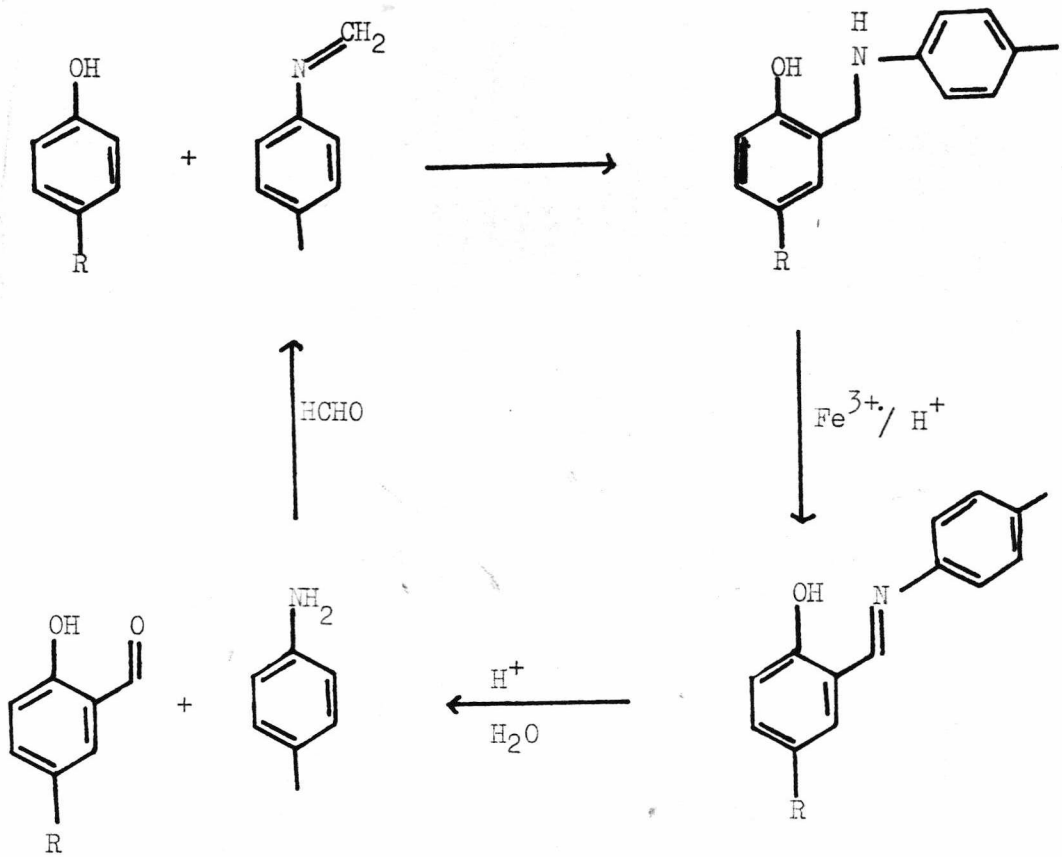


FIGURE 2. Purification of desired alkylsalicylaldehydes.

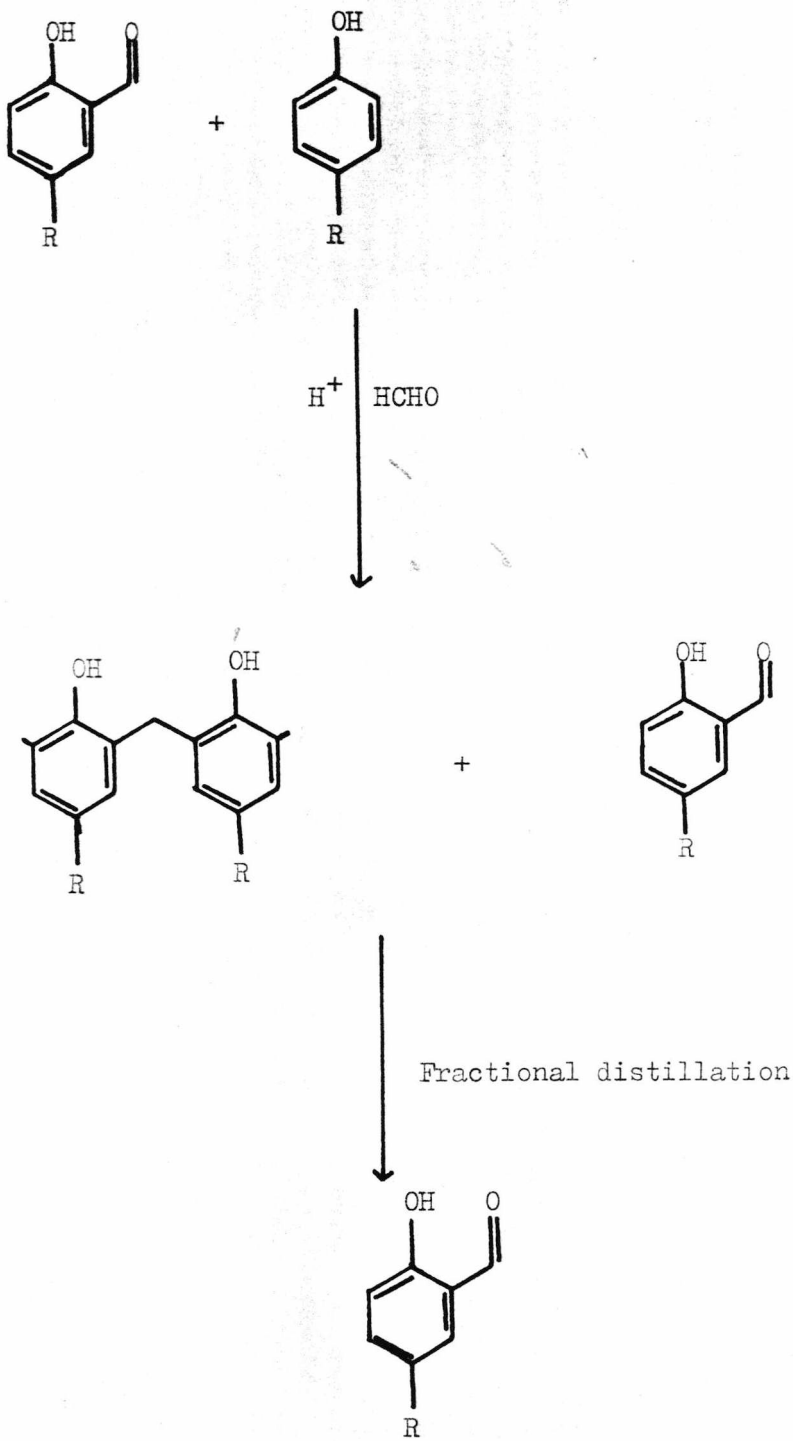
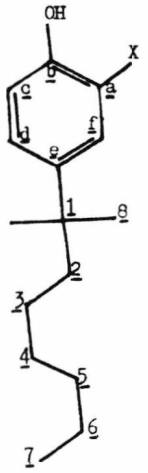


Table 1 Mass Spectra of Alkylsalicyladehyde

Salicyladehyde - (X)	$M^{+\cdot}$ (m/e)				Fragment (m/e)								
X	192	220	234	248	219	205	191	177	163	149	135	121	107
(1.) n - C_7H_{15}		28									100		32
(2.) n - C_9H_{19}				43		2			8	2	100	2	13
(3.) Me_2 Et	6								100		33		22
(4.) Me_2 n-Bu		9							100		14		16
(5.) Me Et n-Pr		25				33	94	100	34	76	89	23	52
(6.) Et_3		9					78		13	48	100		27
(7.) Me_2 i-Bu		5					30		100		28		
(8.) Me Et(CH_2CMe_3)			3						100		7		
(9.) Me_2 n-C_6H_{13}				10					100	4	8		5
(10) Me Et n-C_5H_{11}				7	34			100		49	65		21
(11) Et_2 n-Bu				21	86	8	75	12	58	37	100	8	19
(12) Me n-Pr n-Bu				20	11	84	100	26	37	67	68	25	28
(13) Et n-Pr_2				22	51	97		12	50	28	100	5	14

Table 2. Comparison of Proton and ^{13}C N.M.R. data of phenol - (9) and aldehyde - (9)



Phenol - (9) X = H

Aldehyde - (9) X = CHO 5

	PHENOL - (9)	ALDEHYDE - (9)	SHIFT IN δ (p.p.m.)
^1H ASSIGNMENT	δ, p.p.m.	δ, p.p.m.	
Phenolic proton	5.01	10.75	-5.74
H g	-	9.71	-
H c	6.67	6.86	-0.19
H d	)	7.43	-0.40
H f	) 7.03	7.40	-0.37
H 8	1.17	1.30	-0.13
H 2	1.46	1.5 - 1.7	-0.15
H 3,4,5,6	1.17	1.0 - 1.4	0
H 7	0.79	0.84	-0.05
^{13}C ASSIGNMENT			
a	114.87	119.98	-5.11
b	152.65	159.35	-6.70
c	114.87	117.12	-2.25
d	126.93	134.92	-7.99
e	142.23	141.25	0.98
f	126.93	130.34	-3.41
g	-	196.64	-
1	37.05	37.05	0
2	44.73	44.42	0.31
3	24.68	24.62	0.06
4	30.04	29.97	0.07
5	31.81	31.75	0.06
6	22.67	22.62	0.05
7	14.08	14.02	0.06
8	29.13	28.82	0.31

TABLE 3. Elemental analysis of alkylsalicylaldehydes.

Alkylsalicylaldehyde.		Found (Calculated).	
		Carbon.	Hydrogen.
(1)	$C_{14}H_{20}O_2$	76.00 (76.32)	9.67 (9.15)
(2)	$C_{16}H_{24}O_2$	77.73 (77.38)	9.91 (9.74)
(3)	$C_{12}H_{16}O_2$	77.13 (74.97)	9.11 (8.39)
(4)	$C_{14}H_{20}O_2$	76.66 (76.32)	9.51 (9.15)
(5)	$C_{14}H_{20}O_2$	76.46 (76.32)	9.52 (9.15)
(6)	$C_{14}H_{20}O_2$	76.20 (76.32)	9.14 (9.15)
(7)	$C_{14}H_{20}O_2$	77.06 (76.32)	9.57 (9.15)
(8)	$C_{15}H_{22}O_2$	77.46 (76.88)	10.27 (9.46)
(9)	$C_{16}H_{24}O_2$	77.00 (77.38)	10.34 (9.74)
(10)	$C_{16}H_{24}O_2$	77.58 (77.38)	10.25 (9.74)
(11)	$C_{16}H_{24}O_2$	77.28 (77.38)	10.09 (9.74)
(12)	$C_{16}H_{24}O_2$	78.08 (77.38)	9.51 (9.74)
(13)	$C_{16}H_{24}O_2$	78.42 (77.38)	10.34 (9.74)

Table 4. M.pt. and elemental analysis of 2,4-DNP derivatives of Alkylsalicyaldehydes

Alkylsalicyaldehyde (2,4 - DNP DERIVATIVE)	M.pt.(°C)	Analysis found (calculated) Carbon	Hydrogen	Nitrogen
(1)	148 - 9	59.34(59.99)	6.02(6.04)	14.19(13.99)
(2)	172 - 3	61.47(61.67)	6.59(6.59)	13.10(13.08)
(3)	216 - 7.5	57.50(58.06)	5.34(5.41)	14.83(15.05)
(4)	184 - 4.5	59.59(59.99)	6.03(6.04)	13.72(13.99)
(5)	174	59.50(59.99)	6.09(6.04)	14.03(13.99)
(6)	177 - 78	59.75(59.99)	5.94(6.04)	13.92(13.99)
(7)	180 - 1	59.62(59.99)	6.14(6.04)	13.89(13.99)
(8)	190 - 1	60.44(60.86)	6.46(6.32)	13.42(13.52)
(9)	166 - 6.5	61.27(61.67)	6.59(6.59)	13.05(13.08)
(10)	144 - 5	61.85(61.67)	6.66(6.59)	13.05(13.08)
(11)	154	61.34(61.67)	6.64(6.59)	13.10(13.08)
(12)	145	61.27(61.67)	6.65(6.59)	13.01(13.08)
(13)	152 - 3	61.33(61.67)	6.66(6.59)	13.13(13.08)

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CHAPTER 5. ALKYLSALICYLALDOXIMES AND COPPER COMPLEXES.

This chapter is concerned with the synthesis of the desired alkylsalicylaldoximes. These were synthesised from the alkylsalicylaldehydes, described in Chapter 4, by reaction of the aldehyde group with hydroxylamine (1).

Purification of each alkylsalicylaldoxime was effected by conversion to the copper complex (2) which was then recrystallised. To obtain the pure alkylsalicylaldoxime, a solution of the copper complex of the alkylsalicylaldoxime was contacted with an aqueous sulphuric acid solution which, after separation of the organic phase, drying and solvent removal, yielded the desired alkylsalicylaldoxime (2). The characterisation of each alkylsalicylaldoxime was performed upon samples purified by this route whilst the individual copper complexes were characterised by their melting point, elemental analysis and infrared spectrum. An attempt to obtain a conventional proton N.M.R. spectrum of a copper complex was not successful. As copper (II) has a d^9 electronic structure and is therefore paramagnetic, this failure to obtain a conventional N.M.R. spectrum was not unexpected. Using the technique of Fast Atom Bombardment (FAB) mass spectroscopy (3) it was hoped that mass spectra of the copper complexes would be obtained. Unfortunately technical difficulties in the preparation of samples suitable for FAB mass spectroscopy resulted in poor quality, non-reproducible spectra.

This chapter will be split into two sections, the first being the characterisation of the alkylsalicylaldoximes and their copper complexes, the second section is the experimental details.

A). Characterisation of alkylsalicylaldoximes and their copper complexes.

The numbering of compounds follows that described in Figure 1 in Chapter 3. The numbering of carbon atoms for the N.M.R. spectra is the same as that described in Chapter 4 where the aldoxime group replaces the aldehyde group.

1) Infrared spectra of the alkylsalicylaldoximes.

All the infrared spectra showed a broad absorption at 3400 cm^{-1} with a shoulder around 3200 cm^{-1} (free O-H (oxime hydroxyl) and chelated O-H (phenolic hydroxyl) respectively). At 1625 cm^{-1} an absorption appeared which can be attributed to the C=N stretch (C=O stretch in the aldehyde appears at 1660 cm^{-1}) (4). In the 800-715 cm^{-1} region all the alkylsalicylaldoximes exhibited absorptions at 715 cm^{-1}, 743 cm^{-1} and 790 cm^{-1}. This is to be compared with the alkylsalicylaldehydes which all exhibited absorptions at 720 cm^{-1}, 743 cm^{-1} and 775 cm^{-1}.

2) Infrared spectra of the copper complexes.

The infrared spectra of the copper complexes all showed an absorption about 3200 cm^{-1} (O-H stretch) and an absorption about 1645 cm^{-1} (C=N stretch) (4). The absorptions in the region 715-800 cm^{-1} are collected in Table 1.

3) Mass spectra of the alkylsalicylaldoximes.

Information obtained from mass spectra are collected in Table 2. The table is split into two sections. The first section shows the relative intensity of the molecular ion, the second section shows the relative intensities of fragment ions.

4) Proton and ^{13}C N.M.R. spectra of the alkylsalicylaldoximes.

a) 5-n-heptyl-2-hydroxybenzaldoxime, oxime-(1).

Proton N.M.R:- δ 10.0,bs,1H(phenolic O-H); 8.5,bs,1H(oxime O-H); 8.17,s,1H; 7.10,dd,^{3}J=9Hz,^{4}J=2Hz,1H; 6.96,d,^{4}J=2Hz,ca.1H; 6.92,d,^{3}J=9Hz, ca.1H; 2.57,t,J=8Hz,2H; 1.5-1.8,m,ca.2H; 1.34,bs,ca.8H; 0.94,t,J=6Hz,3H. p.p.m. ($CDCl_3$, T.M.S.)

^{13}C N.M.R:- δ 154.84,s(carbon b); 152.5,d(aldoxime carbon); 134.24,s (carbon e); 131.32,d(carbon d); 130.22,d(carbon f); 116.39,d(carbon c); 116.13,s(carbon a); 34.86,t(carbon 1); 31.81,t(carbon 2 or 5); 31.57,t (carbon 2 or 5); 29.19,t(carbons 3 and 4); 22.67,t(carbon 6); 14.08,q (carbon 7). p.p.m. ($CDCl_3$, T.M.S.)

b) 2-hydroxy-5-n-nonylbenzaldoxime, oxime-(2).

Proton N.M.R:- δ 8.80,bs,2H(phenolic and oxime O-H); 8.16,s,1H; 7.09,dd,^{3}J=9Hz,^{4}J=2Hz,1H; 6.94,d,^{4}J=2Hz,ca.1H; 6.90,d,^{3}J=9Hz,ca.1H; 2.56,t,J=8Hz,2H; 1.45-1.75,m,ca.2H; 1.27,bs,ca.12H; 0.89,t,J=7Hz,3H. p.p.m. ($CDCl_3$, T.M.S.)

c) 5-(1,1-dimethylpropyl)-2-hydroxybenzaldoxime, oxime-(3).

Proton N.M.R:- δ 9.90,bs,1H(phenolic O-H); 8.30,bs,1H(oxime O-H); 8.13,s,1H; 7.17,dd,^{3}J=8Hz,^{4}J=2Hz,1H; 7.01,d,^{4}J=2Hz,1H; 6.85,d,^{3}J=9Hz,1H; 1.59,q,J=7Hz,2H; 1.32,s,6H; 0.64,t,J=7Hz,3H. p.p.m. ($CDCl_3$, T.M.S.)

^{13}C N.M.R:- δ 154.60,s(carbon b); 153.38,d(aldoxime carbon); 140.88,s(carbon e); 129.12,d(carbon d); 128.08,d(carbon f); 116.19,d(carbon c); 115.76,s(carbon a); 37.25,s(carbon 1); 36.82,t(carbon 2); 28.53,q(carbon 4); 9.08,q(carbon 3). p.p.m. ($CDCl_3$, T.M.S.)

d) 5-(1,1-dimethylpentyl)-2-hydroxybenzaldoxime, oxime-(4).

Proton N.M.R:- δ 10.0,bs,1H(phenolic O-H); 8.70,bs,1H(oxime O-H); 8.16,s,1H; 7.21,dd,^{3}J=9Hz,^{4}J=2Hz,1H; 7.05,d,^{4}J=2Hz,1H; 6.87,t,^{3}J=9Hz,1H; 1.4-1.6,m,2H; 1.22,s,ca.6H; 0.9-1.3,m,ca.4H; 0.82,t,J=7Hz,3H. p.p.m. ($CDCl_3$, T.M.S.)

^{13}C N.M.R:- δ 154.47,s(carbon b); 153.26,d(aldoxime carbon); 141.19,s(carbon e); 128.94,d(carbon d); 127.85,d(carbon f); 116.15,d(carbon c); 115.72,s(carbon a); 44.36,t(carbon 2); 36.93,s(carbon 1); 29.01,q(carbon 6); 26.93,t(carbon 3); 23.34,t(carbon 4); 14.08,q(carbon 5). p.p.m. ($CDCl_3$, T.M.S.)

e) 5-(1-ethyl-1-methylbutyl)-2-hydroxybenzaldoxime, oxime-(5).

Proton N.M.R:- δ 9.80,bs,1H(phenolic O-H); 8.17,s,1H(aldoxime O-H);

7.17,dd,^{3}J=9Hz,^{4}J=2Hz,1H; 7.00,d,^{4}J=2Hz,1H; 6.88,d,^{3}J=9Hz,1H; 1.5-1.8,m, 4H; 1.26,s,ca.3H; 0.9-1.5,m,ca.2H; 0.94,t,J=7Hz,3H; 0.65,t,J=6Hz,3H. p.p.m. ($CDCl_3$, T.M.S.)

^{13}C N.M.R:- δ 154.60,s(carbon b); 153.44,d(aldoxime carbon); 139.24, s(carbon e); 129.49,d(carbon d); 128.58,d(carbon f); 116.08,d(carbon c); 115.60,s(carbon a); 45.40,t(carbon 2); 40.40,s(carbon 1); 35.46,t(carbon 5); 23.40,q(carbon 7); 17.43,t(carbon 3); 14.81,q(carbon 4); 8,53,q(carbon 6). p.p.m. ($CDCl_3$, T.M.S.)

f) 5-(1,1-diethylpropyl)-2-hydroxybenzaldoxime, oxime-(6).

Proton N.M.R:- δ 9.70,bs,1H(phenolic O-H); 8.22,s,1H; 7.80,bs,1H (aldoxime O-H); 7.24,dd,^{3}J=8Hz,^{4}J=2Hz,1H; 7.06,d,^{4}J=2Hz,1H; 6.95,d,^{3}J=9Hz, 1H; 1.68,q,J=7Hz,6H; 0.65,t,J=6Hz,9H. p.p.m. ($CDCl_3$, T.M.S.)

^{13}C N.M.R:- δ 154.66,s(carbon b); 153.68,d(aldoxime carbon); 138.45,s (carbon e); 129.92,d(carbon d); 129.07,d(carbon f); 116.08,d(carbon c); 115.42,s(carbon a); 42.96,s(carbon 1); 28.64,t(carbon 2); 7.86,q(carbon 3); p.p.m. ($CDCl_3$, T.M.S.)

g) 2-hydroxy-5-(1,1,3-trimethylbutyl)benzaldoxime, oxime-(7).

Proton N.M.R:- δ 10.00,bs,1H(phenolic O-H); 8.50,bs,1H(aldoxime O-H); 8.20,s,1H; 7.24,dd,^{3}J=9Hz,^{4}J=2Hz,1H; 7.10,d,^{4}J=2Hz,1H; 6.92,d,^{3}J=9Hz,1H; 1.2-1.7,m,ca.3H; 1.30,s,ca.6H; 0.72,d,J=6Hz,6H. p.p.m. ($CDCl_3$, T.M.S.)

^{13}C N.M.R:- δ 154.34,s(carbon b); 153.32,d(aldoxime carbon); 141.31,s (carbon e); 129.19,d(carbon d); 127.97,d(carbon f); 116.08,d(carbon c); 115.60,s(carbon a); 53.32,t(carbon 2); 37.35,s(carbon 1); 29.68,q(carbon 5); 24.86,q+d(carbons 3 and 4). p.p.m. ($CDCl_3$, T.M.S.)

h) 2-hydroxy-5-(1,1,3,3-tetramethylbutyl)benzaldoxime, oxime-(8).

Proton N.M.R:- δ 8.15,s,1H; 7.24,dd,^{3}J=9Hz,^{4}J=2Hz,1H; 7.08,d,^{4}J=2Hz,1H; 6.87,d,^{3}J=9Hz,1H; 1.72,s,2H; 1.35,s,6H; 0.73,s,9H. p.p.m. ($CDCl_3$, T.M.S.)

^{13}C N.M.R:- δ 154.85,s(carbon b); 153.62,d(aldoxime carbon); 141.39,s (carbon e); 129.47,d(carbon d); 128.14,d(carbon f); 116.03,d(carbon c); 115.40,s(carbon a); 56.86,t(carbon 2); 37.87,s(carbon 1); 32.33,s(carbon 3); 31.80,q(carbon 4); 31.57,q(carbon 5). p.p.m. ($CDCl_3$, T.M.S.)

i) 5-(1,1-dimethylheptyl)-2-hydroxybenzaldoxime, oxime-(9).

Proton N.M.R:-δ 9.70,bs,1H(phenolic O-H); 8.20,s,1H; 7.46,bs,1H (aldoxime O-H); 7.22,dd,^{3}J=9Hz,^{4}J=2Hz,1H; 7.03,d,^{4}J=2Hz,1H; 6.87,d,^{3}J=9Hz,1H; 1.4-1.7,m,2H; 1.23,s,ca.6H; 1.16,bs,ca.8H; 0.82,t,J=6Hz,3H. p.p.m. ($CDCl_3$, T.M.S.)

^{13}C N.M.R:-δ 154.68,s(carbon b); 153.45,d(aldoxime carbon); 141.30,s (carbon e); 129.03,d(carbon d); 127.96,d(carbon f); 116.24,d(carbon c); 115.75,s(carbon a); 44.65,t(carbon 2); 37.04,s(carbon 1); 31.79,t(carbon 5); 30.01,t(carbon 4); 29.02,q(carbon 8); 24.70,t(carbon 3); 22.65,t(carbon 6); 14.03,q(carbon 7). p.p.m. ($CDCl_3$, T.M.S.)

j) 5-(1-ethyl-1-methylhexyl)-2-hydroxybenzaldoxime, oxime-(10).

Proton N.M.R:-δ 10.00,bs,1H(phenolic O-H); 8.50,bs,1H(oxime O-H); 8.22,s,1H; 7.23,dd,^{3}J=9Hz,^{4}J=2Hz,1H; 7.06,d,^{4}J=2Hz,1H; 6.96,d,^{3}J=9Hz,1H; 1.50-1.95,m,4H; 1.00-1.50,bs,9H, 0.88,t,J=7Hz,3H; 0.68,t,J=7Hz,3H. p.p.m. ($CDCl_3$, T.M.S.)

^{13}C N.M.R:-δ 154.47,s(carbon b); 153.44,d(aldoxime carbon); 139.43,s (carbon e); 129.55,d(carbon d); 128.64,d(carbon f); 116.15,d(carbon c); 115.72,s(carbon a); 42.69,t(carbon 2); 40.40,s(carbon 1); 35.65,t(carbon 7); 32.66,t(carbon 4); 23.89,t(carbon 3); 23.46,q(carbon 9); 22.61,t(carbon 5); 14.08,q(carbon 6); 8.65,q(carbon 8). p.p.m. ($CDCl_3$, T.M.S.)

k) 5-(1,1-diethylpentyl)-2-hydroxybenzaldoxime, oxime-(11)

Proton N.M.R:-δ 10.00,bs,1H(phenolic O-H); 8.65,bs,1H(aldoxime O-H); 8.18,s,1H; 7.20,dd,^{3}J=9Hz,^{4}J=2Hz,1H; 7.06,d,^{4}J=2Hz,1H; 6.93,d,^{3}J=9Hz,1H; 1.5-1.9,m,6H; 1.0-1.4,m,4H; 0.86,t,J=6Hz,3H; 0.66,t,J=7Hz,6H. p.p.m. ($CDCl_3$, T.M.S.)

^{13}C N.M.R:-δ 154.41,s(carbon b); 153.44,d(aldoxime carbon); 139.12,s (carbon e); 129.79,d(carbon d); 129.00,d(carbon f); 116.13,d(carbon c); 115.83,s(carbon a); 42.80,s(carbon 1); 36.33,t(carbon 2); 29.20,t(carbon 6); 25.73,t(carbon 3); 23.47,t(carbon 4); 14.14,q(carbon 5); 7.99,q (carbon 7). p.p.m. ($CDCl_3$, T.M.S.)

l) 2-hydroxy-5-(1-methyl-1-propylpentyl)benzaldoxime, oxime-(12).

Proton N.M.R:-δ10.00,bs,1H(phenolic O-H); 8.50,bs,1H(oxime O-H); 8.18,s,1H; 7.20,dd,^{3}J=9Hz,^{4}J=2Hz,1H; 7.02,d,^{4}J=2Hz,1H; 6.96,d,^{3}J=9Hz,2H; 1.5-1.8,m,4H; 1.30,s,ca.3H; 1.0-1.4,m,ca.6H; 0.83,bt,J=7Hz,6H. p.p.m. ($CDCl_3$, T.M.S.)

^{13}C N.M.R:- δ154.54,s(carbon b); 153.08,d(aldoxime carbon); 139.55,s (carbon e); 129.19,d(carbon d); 128.33,d(carbon f); 116.03,d(carbon c); 115.78,s(carbon a); 45.89,t(carbon 6); 43.08,t(carbon 2); 40.10,s(carbon 1); 26.39,t(carbon 3); 24.01,q(carbon 9); 23.40,t(carbon 4); 17.37,t(carbon 7); 14.81,q(carbon 8); 14.02,q(carbon 5). p.p.m. ($CDCl_3$, T.M.S.)

m) 5-(1-ethyl-1-propylbutyl)-2-hydroxybenzaldoxime, oxime-(13).

Proton N.M.R:-δ9.98,bs,1H(phenolic O-H); 8.55,bs,1H(oxime O-H); 8.18, s,1H; 7.20,dd,^{3}J=9Hz,^{4}J=2Hz,1H; 7.04,d,^{4}J=2Hz,1H; 6.92,d,^{3}J=9Hz,1H; 1.4-1.9 m,6H; 0.6-1.34,m,ca.4H; 0.95,t,J=6Hz,ca.6H; 0.65,t,J=7Hz,ca.3H. p.p.m. ($CDCl_3$, T.M.S.)

^{13}C N.M.R:- δ154.41,s(carbon b); 153.50,d(aldoxime carbon); 139.36,s (carbon e); 129.66,d(carbon d); 128.87,d(carbon f); 116.13,d(carbon c); 115.76,s(carbon a); 42.86,s(carbon 1); 39.63,t(carbon 2); 29.81,t(carbon 5); 16.74,t(carbon 3); 14.87,q(carbon 4); 7.99,q(carbon 6). p.p.m. ($CDCl_3$, T.M.S.)

5) Discussion of Spectra.

The infrared spectra of the copper complexes when compared with those of the oximes show some interesting differences. The higher frequency of ν(C=N) in the complexes (1645 cm^{-1}) compared with that in the ligands (1625 cm^{-1}) suggests that there is greater double bond character in the former. This result is surprising in view of the most plausible structure of the copper complex (Figure 1). A strong interaction between the copper atom and nitrogen is expected to reduce the double bond character in the azomethine bond. The structure shown in Figure 1 is supported by the ν(O-H) of the oxime hydroxyl group which is lowered from 3400 cm^{-1}, in the alkylsalicylaldoxime, to 3200 cm^{-1} in the copper complex. This

shows that in the copper complex the oxime hydroxyl hydrogen is exhibiting intramolecular hydrogen bonding that does not occur in the alkylsalicylaldoxime.

The phenolic hydrogen in the alkylsalicylaldoximes is assigned to the ν(O-H) at 3200 cm^{-1} by comparison with the I.R. spectra of the alkylsalicylaldehydes which exhibit ν(O-H) at 3150 cm^{-1}. Comparison of the 800-715 cm^{-1} region of the I.R. spectra in the alkylsalicylaldoximes with the corresponding region of the I.R. spectra of the alkylsalicylaldehydes shows that they are almost identical. However, this region of the I.R. spectra of the copper complexes does show distinct absorption. Table 1) gives the absorption at lowest wavenumber, in the range 800-715 cm^{-1}, for each copper complex, the corresponding absorption observed in the I.R. spectrum of the great-grandparent alkylphenol and the longest alkyl chain in that compound. For complexes -(1), (2) and (3) the absorption, at lowest wavenumber in the region 800-715 cm^{-1}, is ca.10 cm^{-1} greater than for the corresponding phenol -(1), (2) or (3). The complex -(6) has an absorption at 765 cm^{-1}, 5 cm^{-1} higher than for phenol -(6), whereas complex -(8) shows an absorption at 715 cm^{-1} that phenol -(8) does not have a corresponding absorption. For all the remaining complexes, they exhibit absorptions at lower wavenumbers. There does not appear to be a discernable trend to the variation of this absorption in the complex and corresponding phenol.

The mass spectra, Table 2, all show an ion of m/e attributed to the molecular ion though for oximes -(8),(9) and (13) these ions are of low relative intensity (<10%). As with the alkylphenols and alkylsalicylaldehydes, the major fragmentation pathway is by loss of an alkyl radical to give a benzylic cation. Only oxime -(1) (n-heptyl chain) showed an ion of m/e (217) attributed to loss of H_2O from the molecular ion. The loss of H_2O, from the initially formed fragment ion, is facile, for example oxime -(1), base peak m/e 150 and an ion m/e 132 (80%). The comments about the fragmentation observed for the alkyl phenols (Chapter 3)

and alkylsalicylaldehydes (Chapter 4) also apply for these alkylsalicylaldoximes. The preferential loss of an ethyl radical, from the molecular ion, to a larger alkyl radical observed in oximes - (10), (11) and (13) is an unexplained anomaly.

In Table 3 is a list of ^{1}H and ^{13}C N.M.R. of aldehyde -(9) and oxime -(9) for comparison. The change in function of an aldehyde to an oxime shows up clearly in both the proton and ^{13}C N.M.R. spectra of the aromatic ring but produces little difference in the chemical shifts of the alkyl chain protons and carbons. For the proton N.M.R. the change in hydrogen bonding of the phenolic proton clearly shows with a change in chemical shift of 1.05 p.p.m. As the oxime is in the anti configuration the hydroxyl in the oxime group can shield the hydrogen attached to carbon-g which is clearly observed

As the chemical shift of Hc is virtually unaltered, then the inductive effect of changing an aldehyde to an oxime may not be very great. The shielding of hydrogens Hf and Hd is probably due to mesomeric effects as structures, shown in Figure 2, can be assigned as high energy canonical forms available to the oxime but unavailable to the aldehyde.

These canonical structures can be proposed to account for the variation in chemical shifts of the ^{13}C N.M.R. spectra, as carbons - a, b, d and f are the most affected (change in δ 2.38 p.p.m. to 5.89 p.p.m.) whereas carbons - c and e, which do not bear a partial negative charge, have less than 1 p.p.m. change in chemical shift. The most dramatic change in chemical shift is with carbon -g, the aldehyde (aldoxime) carbon. This is shielded by 43 p.p.m. on changing the aldehyde to the aldoxime and whilst some is attributable to the mesomeric effect, a large part must be attributed to the inductive effect.

B . EXPERIMENTAL.

The elemental analyses and melting points of the oximes are collected in Table 4. Table 5 is the collection of melting points and elemental analyses of the copper complexes. The copper complexes of oximes -(1) and

(2) were dark green plates, whereas the complexes (3) to (13) were brown, fine hairlike crystals. The oximes were white crystals or pale yellow oils.

a) 5-n-heptyl-2-hydroxybenzaldoxime and copper complex.

A mixture of 5-n-heptyl-2-hydroxybenzaldehyde, (14.0g, 65mmol, Chapter 4), toluene (13.2 cm^3), propan-2-ol (1.7 cm^3), water (5.7 cm^3) and hydroxylamine hydrochloride (4.79g, 69mmol) was stirred at room temperature. Anhydrous sodium carbonate (3.62g, 34mmol) was slowly added to minimise frothing. The mixture was stirred for 24 hours, after which time water (20 cm^3, 323K) was added and the mixture separated. The organic phase was washed with sulphuric acid (20 cm^3, 6% wt/vol) and then washed with warm water until it was acid free (6x20 cm^3, 323K). Toluene (100 cm^3) was added and the toluene solution shaken with a solution of copper(II) sulphate (5.0g) and sodium acetate (1g) in water (100 cm^3). The phases were separated and the organic phase shaken again with a solution of copper sulphate (5.0g) and sodium acetate (1.0g) in water (100ml). The phases were separated and the organic phase washed with water (50 cm^3) and dried (anhydrous sodium sulphate). The solvent was removed by distillation under reduced pressure and the crude product was recrystallised from ethanol and then dried in vacuo. This yielded the copper complex of 5-n-heptyl-2-hydroxybenzaldoxime (8.32g, 16mmol, 46%).

The oxime was regenerated by dissolving the copper complex in diethylether (2% wt/vol) and shaking the diethylether solution with an equal volume of sulphuric acid (1.5M). The phases were separated and the organic phase washed with water (2xequal volume) and dried (anhydrous sodium sulphate). The solvent was then removed by distillation under reduced pressure to yield the desired oxime.

b) 2-hydroxy-5-n-nonylbenzaldoxime and copper complex.

These were synthesised by the method described in section a) using the following reagents:- 2-hydroxy-5-n-nonylbenzaldehyde (7.0g, 28mmol, Chapter 4), hydroxylamine hydrochloride (2.14g, 31mmol) and anhydrous

sodium carbonate (1.62g, 15mmol) to yield the desired oxime and copper complex (4.75g, 8mmol. 58%).

c) 5-(1,1-dimethylpropyl)-2-hydroxybenzaldoxime and copper complex.

These were synthesised by the method described in section a) using the following reagents:- 5-(1,1-dimethylpropyl)-2-hydroxybenzaldehyde (9.2g, 42mmol, Chapter 4), hydroxylamine hydrochloride (3.2g, 46mmol) and anhydrous sodium carbonate (2.46g, 23mmol) to yield the desired oxime and copper complex (4.51g, 9mmol, 45%).

d) 5-(1,1-dimethylpentyl)-2-hydroxybenzaldoxime and copper complex.

These were synthesised by the method described in section a) using the following reagents:- 5-(1,1-dimethylpentyl)-2-hydroxybenzaldehyde (19.10g, 87mmol, Chapter 4), hydroxylamine hydrochloride (6.53g, 94mmol) and anhydrous sodium carbonate (4.94g, 47mmol) to yield the desired oxime and copper complex (10.14g, 19mmol, 43%).

e) 5-(1-ethyl-1-methylbutyl)-2-hydroxybenzaldoxime and copper complex.

These were synthesised by the method described in section a) using the following reagents:- 5-(1-ethyl-1-methylbutyl)-2-hydroxybenzaldehyde (19.3g, 88mmol, Chapter 4), hydroxylamine hydrochloride (9.31g, 134mmol) and anhydrous sodium carbonate (5.1g, 48mmol) to yield the desired oxime and copper complex (12.7g, 24mmol, 54%).

f) 5-(1,1-diethylpropyl)-2-hydroxybenzaldoxime and copper complex.

These were synthesised by the method described in section a) using the following reagents:- 5-(1,1-diethylpropyl)-2-hydroxybenzaldehyde (12.11g, 51mmol, Chapter 4), hydroxylamine hydrochloride (3.80g, 55mmol) and anhydrous sodium carbonate (2.87g, 27mmol) to yield the desired oxime and copper complex (6.2g, 12mmol, 42%).

g) 2-hydroxy-5-(1,1,3-trimethylbutyl)benzaldoxime and copper complex.

These were synthesised by the method described in section a) using the following reagents:- 2-hydroxy-5-(1,1,3-trimethylbutyl)benzaldehyde (38.86g, 177mmol, Chapter 4), hydroxylamine hydrochloride (13.48g, 194mmol) and anhydrous sodium carbonate (10.19g, 97mmol) to yield the desired oxime

and copper complex (22.74g, 43mmol, 48%).

h) 2-hydroxy-5-(1,1,3,3-tetramethylbutyl)benzaldoxime and copper complex.

These were synthesised by the method described in section a) using the following reagents:- 2-hydroxy-5-(1,1,3,3-tetramethylbutyl)benzaldehyde (8.56g, 37mmol, Chapter 4), hydroxylamine hydrochloride (2.91g, 42mmol) and anhydrous sodium carbonate (2.22g, 21mmol) to yield the desired oxime and copper complex (3.83g, 7mmol, 37%).

i) 5-(1,1-dimethylheptyl)-2-hydroxybenzaldoxime and copper complex.

These were synthesised by the method described in section a) using the following reagents:- 5-(1,1-dimethylheptyl)-2-hydroxybenzaldehyde (18.0g, 73mmol, Chapter 4), hydroxylamine hydrochloride (5.49g, 79mmol) and anhydrous sodium carbonate (1.1g, 20mmol) to yield the desired oxime and copper complex (11.25g, 19mmol, 48%).

j) 5-(1-ethyl-1-methylhexyl)-2-hydroxybenzaldoxime and copper complex.

These were synthesised by the method described in section a) using the following reagents:- 5-(1-ethyl-1-methylhexyl)-2-hydroxybenzaldehyde (1.47g, 6mmol, Chapter 4), hydroxylamine hydrochloride (0.49g, 7mmol) and anhydrous sodium carbonate (0.37g, 4mmol) to yield the desired oxime and copper complex (0.87g, 1mmol, 49%).

k) 5-(1,1-diethylpentyl)-2-hydroxybenzaldoxime and copper complex.

These were synthesised by the method described in section a) using the following reagents:- 5-(1,1-diethylpentyl)-2-hydroxybenzaldehyde (14.6g, 58mmol, Chapter 4), hydroxylamine hydrochloride (4.46g, 64mmol) and anhydrous sodium carbonate (3.37g, 32mmol) to yield the desired oxime and copper complex (9.87g, 17mmol, 58%).

l) 2-hydroxy-5-(1-methyl-1-propylpentyl)benzaldoxime and copper complex.

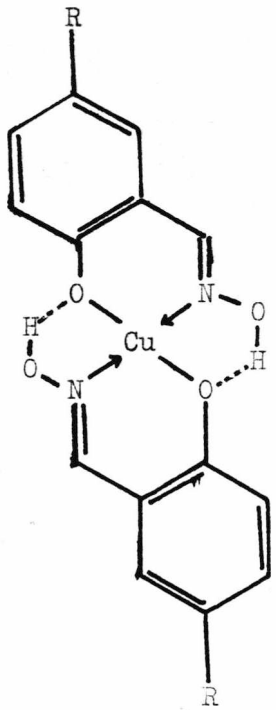
These were synthesised by the method described in section a) using the following reagents:- 2-hydroxy-5-(1-methyl-1-propylpentyl)benzaldehyde (17.52g, 70mmol, Chapter 4), hydroxylamine hydrochloride (5.35g, 77mmol) and anhydrous sodium carbonate (4.04g, 38mmol) to yield the desired oxime

and copper complex (11.20g, 19mmol, 50%).

m) 5-(1-ethyl-1-propylbutyl)-2-hydroxybenzaldoxime and copper complex.

These were synthesised by the method described in section a) using the following reagents:- 5-(1-ethyl-1-propylbutyl)-2-hydroxybenzaldehyde (12.0g, 48mmol, Chapter 4), hydroxylamine hydrochloride (3.67g, 53mmol) and anhydrous sodium carbonate (2.77g, 26mmol) to yield the desired oxime and copper complex (6.8g, 12mmol, 48%).

FIGURE 1. The structure of a copper complex with a substituted salicylaldoxime.



$R=C_nH_{2n+1}$, n=5,7,8,9.

FIGURE 2. Canonical forms available to oxime that are unavailable to aldehyde.

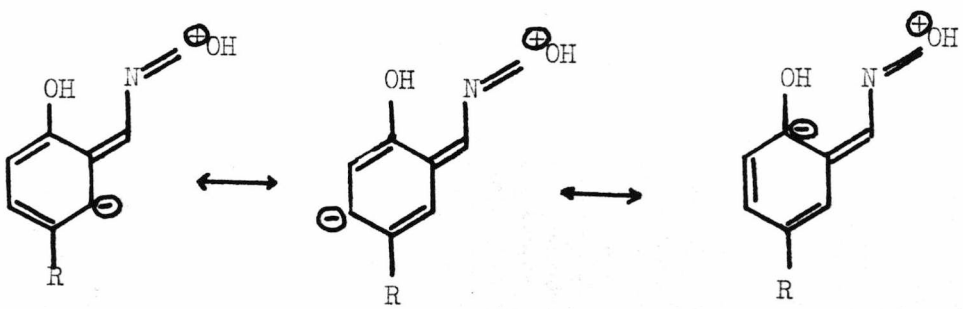


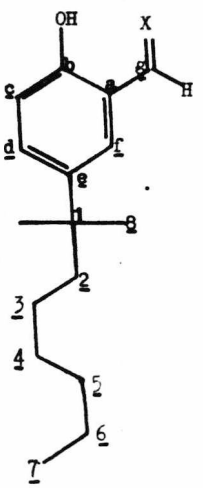
TABLE 1. Infrared absorption frequencies in the 800-715cm^{-1} region for the copper complexes and precursor alkylphenols.

Complex	length of longest alkyl chain (carbon atoms)	absorption frequency complex (cm^{-1})	corresponding absorption frequency alkylphenol (cm^{-1})
(3)	2	780	768
(6)	2	765	760
(5)	3	718	727
(7)	3	724	728
(8)	3	715	none
(13)	3	724	740
(4)	4	723	730
(11)	4	725	730
(12)	4	723	730
(10)	5	718	725
(9)	6	724	730
(1)	7	724	715
(2)	9	720	710

Table 2. Mass Spectrum of Alkylsalicyladoximes

M+	Alkylsalicyladoximes												
	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)	(13)
263		69							7	22	12	26	5
249								4					
235	35			29	29	21	22						
207			15										
FRAGMENT													
234										57	78	2	63
220		1		5	4					8		82	44
217	12												
216											11		12
206				3	76	100				3	58	100	
202													28
192		3			100					100		2	
178			100	100		4	100	65	100		33	5	32
174													17
160			35	8			63	100	11		18		39
150	100	100			33	42				28	100	43	70
132	80	28	20	8	8	6	17	15	6		48	6	100

Table 3 Comparison of proton and ^{13}C N.M.R. data of aldehyde - (9) and oxime - (9)



Aldehyde - (9) X = O

Oxime - (9) X = NCH

	ALDEHYDE - (9)	OXIME - (9)	SHIFT IN δ, p.p.m
^1H ASSIGNMENT	δ,p.p.m.	δ,p.p.m.	
Phenolic proton	10.75	9.70	1.05
H g	9.71	8.20	1.51
H c	6.86	6.87	-0.01
H d	7.43	7.22	0.19
H f	7.40	7.03	0.37
H 8	1.30	1.23	0.07
H 2	1.5 - 1.7	1.4 - 1.7	0
H 3,4,5,6	1.0 - 1.4	1.16	0
H 7	0.84	0.82	1 - 0.02
^{13}C ASSIGNMENT			
a	119.98	115.75	4.23
b	159.35	154.68	4.67
c	117.12	116.24	0.88
d	134.92	129.03	5.89
e	141.25	141.30	-0.05
f	130.34	127.96	2.38
g	196.64	153.45	43.19
1	37.05	37.04	0.01
2	44.42	44.65	-0.23
3	24.62	24.70	-0.08
4	29.97	30.01	-0.04
5	31.75	31.79	-0.04
6	22.62	22.65	-0.03
7	14.02	14.03	-0.01
8	28.82	29.02	-0.02

Table 4. M.pt. and elemental analysis of the oximes

OXIME	M.pt.(°C)	ANALYSIS FOUND (CALCULATED) CARBON	HYDROGEN	NITROGEN
(1) $C_{14}H_{21}NO_2$	49 - 50	71.57(71.49)	9.30(8.94)	6.11(5.96)
(2) $C_{16}H_{25}NO_2$	48 - 50	72.64(73.00)	9.94(9.51)	5.34(5.32)
(3) $C_{12}H_{17}NO_2$	58 - 59	69.73(69.56)	8.54(8.21)	6.74(6.76)
(4) $C_{14}H_{21}NO_2$	51 - 52	72.96(71.49)	9.46(8.94)	5.78(5.96)
(5) $C_{14}H_{21}NO_2$	OIL	71.31(71.49)	9.26(8.94)	5.76(5.96)
(6) $C_{14}H_{21}NO_2$	62 - 63	71.23(71.49)	9.27(8.94)	5.93(5.96)
(7) $C_{14}H_{21}NO_2$	59 - 60	71.44(71.49)	9.19(8.94)	6.05(5.96)
(8) $C_{15}H_{23}NO_2$	109 - 111 (120-1,5)	72.33(72.29)	9.47(9.24)	5.77(5.62)
(9) $C_{16}H_{25}NO_2$	40 - 42	73.07(73.00)	9.83(9.51)	5.11(5.32)
(10) $C_{16}H_{25}NO_2$	OIL	73.91(73.00)	9.98(9.51)	4.86(5.32)
(11) $C_{16}H_{25}NO_2$	OIL	72.56(73.00)	9.71(9.51)	5.08(5.32)
(12) $C_{16}H_{25}NO_2$	OIL	73.01(73.00)	10.29(9.51)	5.06(5.32)
(13) $C_{16}H_{25}NO_2$	87 - 88	72.92(73.00)	9.81(9.51)	5.24(5.32)

Table 5. M.pt. and elemental analysis of copper complexes

COMPLEX	M.pt.(°C)	ANALYSIS FOUND (CALCULATED) CARBON	HYDROGEN	NITROGEN	COPPER
(1) $C_{28}H_{40}CuN_2O_4$	180 - 181	61.43(63.22)	7.53(7.53)	5.14(5.27)	11.86(11.95)
(2) $C_{32}H_{48}CuN_2O_4$	179 - 180	63.85(65.36)	8.04(8.17)	5.08(4.77)	10.98(10.81)
(3) $C_{24}H_{32}CuN_2O_4$	212 - 213	60.51(60.57)	6.92(6.73)	6.01(5.89)	13.36(13.35)
(4) $C_{28}H_{40}CuN_2O_4$	88 - 89	64.64(63.22)	7.92(7.53)	5.11(5.27)	9.40(11.95)
(5) $C_{28}H_{40}CuN_2O_4$	142 - 142.5	62.93(63.22)	7.85(7.53)	5.38(5.27)	10.98(11.95)
(6) $C_{28}H_{40}CuN_2O_4$	222 - 224	62.97(63.22)	7.73(7.53)	5.27(5.27)	14.46(11.95)
(7) $C_{28}H_{40}CuN_2O_4$	133.5 - 134	62.04(63.22)	7.61(7.53)	5.46(5.27)	
(8) $C_{30}H_{44}CuN_2O_4$	161 (205-6,5)	71.21(64.34)	9.52(7.86)	5.56(5.00)	11.34(11.35)
(9) $C_{32}H_{48}CuN_2O_4$	132 - 134	65.34(65.36)	8.46(8.17)	5.09(4.77)	10.70(10.81)
(10) $C_{32}H_{48}CuN_2O_4$	109 - 110	65.19(65.36)	8.48(8.17)	4.75(4.77)	9.56(10.81)
(11) $C_{32}H_{48}CuN_2O_4$	85 - 86	65.30(65.36)	8.53(8.17)	4.54(4.77)	9.40(10.81)
(12) $C_{32}H_{48}CuN_2O_4$	122	65.20(65.36)	8.48(8.17)	4.71(4.77)	9.58(10.81)
(13) $C_{32}H_{48}CuN_2O_4$	144 - 145	65.59(65.36)	8.48(8.17)	4.92(4.77)	9.40(10.81)

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CHAPTER 6. COMPARISON OF RATES OF EXTRACTION AND STRIP OF OXIMES AND COPPER COMPLEXES.

Many methods have been reported which enable the rates of extraction of copper with the oximes -(1) to -(13) (Chapter 5) (and the rates of stripping of the copper complexes -(1) to -(13), Chapter 5) to be compared. These range from stopped flow spectrophotometry (1) in a homogeneous solution to a method known as A.K.U.F.V.E. which is a Swedish abbreviation for "apparatus for continuous measurement of distribution factors in solvent extraction." (2,3,4,5,6,7,8,9). The latter uses an aqueous phase and an immiscible organic phase which are rapidly stirred to obtain a homogeneous emulsion. Methods such as rising drop (10,11,12) and Lewis cell (13,14,15) allow the rate, at a quiescent interface, to be calculated.

The reaction between an ortho-hydroxy oxime (such as oximes -(1) to -(13)) and an aqueous copper solution is believed to take place at the interface between the aqueous and organic phases (4,5,11,16,17,18,19,20) despite reports to the contrary (21,22). Hence the rate of the reaction will be highly dependent upon the structure of the interface which will in turn be dependent upon the organic solvent. At an aqueous-organic interface, the extractants will tend to line up to hydrogen bond with the aqueous phase (22,23,24,25), see Figure 1, whereas in the bulk organic phase the molecules will tend to dimerise (22,23,24,25) by hydrogen bonding. Thus the more the organic solvent is able to hydrogen bond to the oxime the less will be the dimer/monomer ratio and large variations in the rate will be observed (10,18,26,27,28,29). As the commercially used extractants are in kerosene solution to obtain an interfacial structuring similar to plant operating conditions, an aliphatic solvent should be used. Also the reaction is interfacial, so knowledge of the interfacial area should be available.

The A.K.U.F.V.E. method consists of a reaction vessel which is

usually double walled, to permit flow of a heating (or cooling) liquid to maintain a constant temperature, with a stopcock at the base with little 'dead' volume to allow samples to be removed. A Quickfit lid with inlet for the rapid addition of liquid is necessary. The interior of the vessel is equipped with baffles and an efficient stirrer to obtain a homogeneous emulsion of aqueous and organic solvent. This apparatus is identical to the apparatus used by Nchanga Consolidated Copper Mines (N.C.C.M.) (30) for studying extractants under simulated plant operating conditions.

The variation between the two methods is the method of studying reaction rates. The A.K.U.F.V.E. method is generally used as a relaxation technique. The system is brought to equilibrium, stirring is stopped and the emulsion allowed to settle. One phase is removed and the equilibrium conditions disturbed by, say, the addition of radioactive copper to the aqueous phase. The two solutions are rapidly mixed together and stirring commenced to obtain the emulsion. Samples are removed via the stopcock into an ultracentrifuge and the phases separated and analysed. Thus the return to equilibrium of the system is measured and information about the extraction and stripping reaction is obtained. With the N.C.C.M. method the system is studied from the start of the extraction (or stripping) reaction, with samples being removed and separated by gravity before analysis for extraction (or strip). Both of these methods have the advantage of being operated under conditions similar to the operation of commercial solvent extraction plants if an aliphatic solvent (such as hexane) is used. However, little information on the interfacial area is known as the droplet size in the emulsion will be very dependent upon the rate of stirring and design of baffles in the reaction vessel.

The N.C.C.M. method has a further drawback in that gravity separation of the organic and aqueous phases is used. For the commercial extractant, Acorga P50, which is 2-hydroxy-5-nonylbenzaldoxime, the extraction of copper reaches 95% of the theoretical maximum in 15 seconds under simulated plant conditions (31).

Unless an organic solvent such as chloroform or other polar solvent

was used a significant proportion of reaction would occur during phase separation.

As information about the interfacial area is desirable, two methods of studying reactions at a quiescent interface were studied. The rising (or falling) drop method (10,11,12) is one of these methods and the other being the Lewis Cell (13,14,15).

The rising drop method (see Figure 2) has been applied to studying the kinetics of an interfacial reaction, such as liquid-liquid extraction. In this, the column is filled with the copper-containing aqueous phase and the extractant in an organic solvent is forced in through the needle at the base. The drops rise up the column and are collected at the top. The take off head allows the level of the interface to be maintained. For calibration of drop volume the number of drops needed to fill the space between marks A and B is counted. As this section of tubing is of known constant diameter the total volume of the counted drops is known and hence the average volume of each drop. Assuming each drop to be a perfect sphere then the surface area of each drop is calculated. The time of contact of the aqueous and organic phases is readily measured and can be varied by varying the length, l, of the column. For a falling drop the collection device is shown and again the average drop volume and surface area can be calculated.

The drawbacks with this method are 1) assuming all drops to be the same size, 2) all drops to be perfect spheres, and 3) unknown effects of drop formation and dissolution. Also the contact time is limited by the practical size of the column and so only initial rates can be reliably measured.

The Lewis cell method (13,14,15) allows measurement of the interfacial area (see Figure 3). In this, the two phases are placed within the vessel with the baffle at the interface - hence the interfacial area is known. The vessel is maintained at constant temperature and each phase is stirred. The design of the stirrer is such

that each phase is stirred at the same rate (both stirrers driven by the same motor) but the direction of rotation of the stirrer is different in the aqueous phase to the organic phase. The baffle is to prevent vortexing at the interface. Samples can be removed from either phase, if so desired, and the contact time can be varied at will. Like the N.C.C.M. and the rising drop methods, the extraction (or strip) reaction is monitored from the start. The major drawback is that the dynamics of transport of molecules from the bulk phase to the interfacial zone is unknown.

A variation of the Lewis call method places the interface in a rotating disc as the hydrodynamics of a rotating disc are known (19,20). The apparatus consists of a vessel, such as that in Figure 4, with an internal compartment which can be rotated. The internal compartment has a millipore filter in the base which acts as the site of the interface. The interface is first characterised by electrochemical methods, to determine the effective area, and then used as a normal Lewis cell apparatus. As the hydrodynamics of a rotating disc are known, the transport of molecules from the bulk phase to the interface can be calculated.

A choice of method for studying the kinetics had to be made and as it was desired to work in aliphatic solvents such as hexane, the stopped flow spectrophotometry and N.C.C.M. methods were ruled out. The assumptions in the rising drop technique and the limitations of contact time were considered too great for the anticipated subtle differences in reaction rates for oximes -(1) to -(13) and so this method was not attempted. This left a choice between A.K.U.F.V.E., the Lewis cell method and its rotating disc variation. As the study was to be a comparative study between a range of compounds it was felt that knowledge of hydrodynamics was not important as long as the same experimental conditions were maintained and so the rotating disc method was rejected.

The choice of the Lewis cell rather than the A.K.U.F.V.E. method was made on the basis that the interfacial area in the Lewis cell is known but in the A.K.U.F.V.E.method the interfacial area is unknown.

This Chapter will be split into three sections - the experimental details, the results and the discussion.

1) EXPERIMENTAL.

a) Equipment and reagents.

The stirrer (Figure 3) was loaned by I.C.I. Organics (Blackley) and the vessel used for the extraction and stripping rates is shown in Figure 3.

The reaction studied is

$$2\ LH + Cu^{2+} \rightleftharpoons L_2Cu + 2H^+$$

where LH is the extractant under study. Thus acid is released as the reaction proceeds and a pH meter and electrode was used to monitor the pH of the aqueous phase. The pH meter was a PTI-6 universal digital pH meter (accurate to $\pm$ 0.002 pH units, supplied by Roach Associates), and the pH electrode was a combination pH electrode made by Electronic Instruments Ltd. A servoscribe (made by Rikadenki Limited) was connected to the pH meter to record change in pH with respect to time. For atomic absorption spectroscopy a Unicam SP90A series 2 atomic absorption spectrometer was used. This was operated with a lamp wavelength of 324.8nm and a slit width of 1.5mm. The air flow to the flame was 5 l min^{-1} and acetylene flow was 1 l min^{-1}.

The aqueous and organic solutions and reaction vessel were maintained at 298 $\pm$ 0.1K by a thermostat bath. The aqueous solutions were made from Analytical Reagent (A.R.) grade copper(II) sulphate with distilled water. The organic solvents were either A.R. toluene or hexane and the extractants used were prepared as described in Chapters 2 - 5 . For comparison purposes and characterisation of the apparatus, Acorga P50 (henceforth called P50, gift from I.C.I. Organics (Blackley)) was used without further purification.

b) Preparation of solutions and calibration of pH meter.

The organic solution of oxime extractant was prepared by dissolving

the required weight of oxime (to produce 0.010M) in the solvent and making the solution up to the desired volume in a volumetric flask. Solutions of lower concentrations would be prepared by dilution of aliquots from this solution. A solution of higher concentration would be prepared by this method. No check upon the concentration was made. For the preparation of a copper complex solution, for stripping reaction kinetics, a solution would be prepared using the required weight of copper complex to produce a solution 0.005M in copper. For use in the stripping reaction aliquots would be diluted to 0.0005M

The aqueous mixture for the stripping reaction was prepared by mixing 98% A.R. sulphuric acid (150g) with water (800 cm^3) and after allowing it to cool the solution was made up to 1000cm^3. The aqueous copper(II) sulphate solution for the extraction reaction was prepared by dissolving the weight of A.R. copper(II) sulphate in distilled water required to produce a 0.020M solution (based on the stoichiometry $CuSO_4.5H_2O$). Solutions of lower copper concentration were prepared by the dilution of aliquots of this solution. As the hydration of the copper(II) sulphate may vary the solution was always checked for copper content by the following method: An aliquot (25.0cm^3) of the copper-containing solution (0.020M) was diluted to 100cm^3 with distilled water. Anhydrous sodium carbonate was added in small portions with swirling, until a persistant pale blue precipitate could be seen. Acetic acid (25% v/v in distilled water) was added to just dissolve the precipitate and potassium iodide (2g) was added. The iodine released was titrated with standard sodium thiosulphate solution (0.10M). As the endpoint was approached (disappearance of colour due to iodine) aqueous starch solution was added as an indicator and titration was continued until the blue colour disappeared. The reactions occuring are :

$$2\ Cu^{2+} + 4I^- \longrightarrow 2\ CuI + I_2$$

$$2\ S_2O_3^{2-} + I_2 \longrightarrow S_4O_6^{2-} + 2I^-$$

so the copper concentration can be readily calculated. The titration

procedure would be repeated with a fresh 25 cm^3 aliquot of copper (II) solution. If the results from the two titrations varied by more than 2% a further repeat analysis would be performed.

Before use in any experiments the solutions used would be warmed to 298 ± 0.1K. The pH meter was calibrated in buffer solutions of pH 7.00 and pH 4.00 at 293 ± 0.1K, the pH meter was equipped with a temperature compensation probe to eliminate temperature induced changes in reading of pH. The calibration of the pH meter was checked at intervals.

c) Dependance upon rate with stirrer speed.

A solution of copper(II) sulphate (0.020M, 250cm^3) was placed in the reaction vessel (Figure 3) with the stirrer operating at a known, constant rate. The pH probe was placed in the aqueous phase and the baffle on the stirrer adjusted to the height of the aqueous phase. The organic phase (a solution of P50, 0.010M in hexane, 250cm^3) was poured rapidly, and carefully, on to the baffle. This was to obtain a rapid establishment of initial conditions with little disturbance of the interface. The pH was noted at 5 minute intervals over a 1 hour period.

By the attachment of a small piece of paper on to the stirrer shaft the number of revolutions over a set time could be counted and so the number of revolutions per minute were calculated. At each stirrer speed the experiment was repeated, and no variation between observed pH values at a specific time, for a specific stirrer speed, was observed.

As shown earlier (section 1a) the rate of acid release is directly proportional to the extraction of copper, so that a comparison of pH after a specific time with stirrer speed will show the variation in rate of copper extraction with stirrer speed. The experiment was performed with stirrer speeds of 60,90 and 128 r.p.m. The observed pH after a specific time was lower when the system was stirred at 90 r.p.m. than when the system was stirred at 60 r.p.m. However, the observed pH values were identical at stirring speeds of 90 and 128 r.p.m. Thus the assumption made is that at a stirrer speed of 128 r.p.m. (the speed used in all future experiments -

checked at intervals) the observed rate of copper extraction will be independant of mass transfer from bulk phase to interfacial region.

d) Dependence of rate of extraction on pH.

The dependence of the rate of extraction with change in pH was determined. The apparatus was used as described in section c) with the same concentration of copper and P50 as mentioned there. However, a constant pH had to be maintained. This was accomplished by attaching a piece of capillary P.V.C. tubing to a burette and introducing one end into the aqueous phase. This enabled a solution of sodium hydroxide (0.010M) to be introduced into the aqueous phase and the amount of base added with respect to time was noted. The amount of copper extracted could be calculated at five minute intervals. To a first approximation the rate of copper extraction at time t (minutes) is given by the difference between the amount of copper extracted at time $(t + n)$ and time $(t - n)$ divided by $2n$. This 'rate' is calculated at time, t, = 7.5, 12.5 and 17.5 minutes and the result expressed graphically in Figure 5. This shows that the change in pH, over measured range, does not affect the rate significantly. As the rate of copper extraction is independant of pH, over the measured range, then the pH can be allowed to vary during an experimental run to determine extraction rates. A direct measurement of change in pH with respect to time will allow one to observe changes in the rate of copper extraction and relate these wholly to other changes in the experimental conditions.

e) Dependence of rate of extraction upon copper and ligand concentrations.

Extraction runs were performed whilst varying the copper concentration and the P50 concentration. It was assumed that oximes -(1) to -(13) would behave similarly to P50 at the same concentrations as all are 5-alkyl-2-hydroxybenzaldoximes. With a copper concentration of 0.020M the P50 concentration (in hexane) was varied from 0.051M to 0.0004M. The rate of copper extraction was calculated at 10 minutes and these rates are expressed graphically in Figure 6. Over the range of P50 concentrations

0.0004 - 0.003M the plot is linear so the rate of extraction is directly proportional to the concentration of extractant. The non-linearity of the plot at extractant concentrations higher than 0.003M could be due to saturation of the interfacial region resulting in steric hindrance to the formation of the copper complex.

Figure 7 shows the variation of rate of extraction with respect to copper concentration after 10 minutes. The extractant concentration was kept constant (at 0.020M or 0.051M) and the copper concentration varied from 0.0004M to 0.020M. The data does not appear to fit a linear plot and so the order of reaction was calculated by plotting the log of rate against the log of copper concentration, shown in Figure 8. This gives the order of the reaction to be 0.5 for the P50 concentration, 0.020M, and an order of 0.67 for the P50 concentration 0.051M.

The proposed scheme for the extraction reaction is shown in Figure 9 (24) and making the assumption that the rate determining step is loss of a proton (III → IV) or simultaneous loss of two protons (V→VI). The calculated rate equation for the simultaneous loss of two protons (V→VI) is $\text{Rate} = k'[(LH)_2][Cu^{2+}] - k''[L_2Cu][H^+]^2$ - A

For the sequential loss of two protons (III→IV→VI) the calculated rate equation is

$$\text{Rate} = \frac{k_1k_2[(LH)_2][Cu^{2+}] - k_{-1}k_{-2}[L_2Cu][H^+]^2}{k_2 + k_{-1}[H^+]} \quad \text{- B}$$

As the pH lies in the range of 4.5 → 3.0 the maximum value for $[H^+]$ is 1×10^{-3}M so the maximum value for $[H^+]^2$ is 1×10^{-6}. As the extraction reaction, after 10 minutes, is less than 5% towards equilibrium, then $[(LH)_2][Cu^{2+}] \gg [L_2Cu][H^+]^2$ so the equations can be simplified to

$$\text{Rate} = k'[(LH)_2][Cu^{2+}] \quad \text{- A}$$

$$\text{Rate} = \frac{k_1k_2[(LH)_2][Cu^{2+}]}{k_2 + k_{-1}[H^+]} \quad \text{- B}$$

for equation B making the assumption that $k_2 > k_{-1}[H^+]$ this can be further simplified to

$$\text{Rate} = k_1[(LH)_2][Cu^{2+}] \quad \text{- B}$$

Thus it is possible to accommodate the observed independence of rate and pH, and the unity order of the extraction reaction with respect to extractant concentration. However, both mechanisms would require that the order of the extraction reaction with respect to copper concentration should be unity which is not found to be the case from the experimental results. This could be due to: i) a different extraction mechanism operating, ii) mass transfer effects or, a combination of both of these. So for the kinetic studies with oximes -(1) to -(13) it was decided to use a large excess of copper so as to minimise the change in copper concentration as the extraction proceeds. The concentration of extractant was chosen to be 0.001M as this should give rates directly proportional to extractant concentration (non linearity is observed in the rate: extractant concentration dependence at concentrations > 0.003M).

f) The stripping reaction.

The extraction reaction can be followed by a change in pH in the aqueous phase but this method can not be used for the stripping reaction because 3M sulphuric acid is used and changes in acid concentration could not be measured. Use of a copper(II) ion-selective electrode was postulated but rejected as it was unlikely to function correctly at the pH of the stripping solution. Following the loss of copper complex by U.V. spectroscopy was considered but it was decided, after experimentation, that atomic absorption spectroscopy would be more accurate. A stripping reaction was performed as follows:- sulphuric acid (section b, 250 cm^3) was placed in the kinetic vessel and the baffle adjusted to the height of the aqueous phase. A hollow glass tube of 1 cm diameter was fastened with the mouth of the tube 0.5 cm below the surface of the aqueous phase. The solution of copper complex (section b, 250 cm^3) was added and the phases were stirred in a contrarotatory manner at 128 r.p.m. Samples (1.0 cm^3) were removed from the aqueous phase at 10 minute intervals by a pipette placed down the tube into the aqueous phase. This enabled samples to be taken from the bulk aqueous phase without contact with the organic phase.

The sample removed was diluted to 5 cm^3 with distilled water and atomic absorption spectroscopy performed to determine the copper concentration.

2. RESULTS.

a) Extraction.

It was initially planned to use hexane as a solvent for all the kinetic experiments but solubility problems with the copper complexes of the 5-n-nonyl-, 5-n-heptyl-, and 5-(1,1-diethylpropyl) - salicylaldoximes necessitated toluene being used as a solvent for the study of these compounds. P50 and 5-(1,1,3,3-tetramethylbutyl)salicylaldoxime were also studied in toluene solution so that comparisons could be made with the oximes studied in hexane solution. For each oxime, a number of extraction runs were performed and the amount of copper extracted at various times was calculated. The average of these values at certain times are collected in Table 1 (hexane solution) and Table 2 (toluene solution). The standard deviation was usually within 10% of the average value. The greatest deviation was obtained with oxime - (13), for which the deviation rose to 16% of the average value. The extraction curves in hexane solution are collected in Figure 10 and in Figure 11 are collected the extraction curves in toluene. Table 3 gives a calculated rate constant for the extraction reaction. Two points are readily apparent from the graphs and Tables:-

I. There are great variations in the rate of copper extraction with changes in the alkyl chain structure.

II. In hexane solution, P50 will extract copper at a greater rate than oxime - (8) but in toluene the reverse situation occurs.

As was stated above, the deviation of experimental results is generally within 10% of the average value and the measured difference in rates of copper extraction, of different oximes, are often greater than 10%.

b) Stripping.

Figure 12 shows the stripping curves for copper complexes - (4), (5),

(7) and (9)-(13) in hexane solution. A comparison with Figures 10 and 11 shows that the stripping reaction occurs at a greater rate than the extraction reaction. After 30 minutes the calculated rate of stripping of copper from complexes (4) and (5) respectively are 43.3×10^{-6} and 44.6×10^{-6} mmol min^{-1} cm^{-2}. The difference between these two calculated rates is less than the experimental error associated with each and so the rates of stripping for each copper complex can be said to be identical within experimental error.

3. DISCUSSION,

a) Stripping.

The rates of stripping of the copper complexes studied are all identical within experimental error and much greater than those observed for the extraction reaction in hexane solution. No explanation is offered and further work upon the stripping reaction with different conditions and/or a different method of measuring the kinetics is necessary.

b) Other work on extraction.

It has been reported (29) that, in 5-alkyl-2-hydroxybenzaldoximes where the alkyl chain is n-C_mH_{2m+1} (m=2,4,6,8,10,12), $C(CH_3)_3$ or $C(CH_3)_2CH_2C(CH_3)_3$ (oxime -(8)), the length or structure of the alkyl chain does not significantly influence the position of the equilibrium in the extraction of copper from dilute acidic sulphate solution. However no data upon the rate of approach of equilibrium has been presented. No other work on the direct comparison of alkyl chain structures with respect to the rate of copper extraction has been published and comparisons between reported kinetic studies (1,2,5,6,10,13,18,19,29,32, 33,34) are hindered due to the wide variation in methods of study employed.

c) Observed kinetic rate law.

The data presented in Tables 1 and 2 can be fitted to an experimental rate equation

$$\text{Rate} = \frac{k[(\text{oxime})_2]}{[H^+]}$$

Integration gives the equation

$$kt = (2E+H)\ln\left(\frac{E}{E-n}\right)$$

where H is the initial concentration of hydrogen ions.

E is the initial concentration of $(oxime)_2$

n is the concentration of extracted copper at time t

The value of the rate constant is calculated graphically and the results collected in Table 3, the pH of the aqueous phase initially being 4.50. However, earlier (section 1d) it was found that in the pH range 4.50-3.00, with a copper concentration of 0.02 moles l^{-1} and an oxime concentration of 0.010moles l^{-1}, the rate was independent of the hydrogen ion concentration.

As shown in section 1e, at high oxime concentrations ($>$ 3mmoles l^{-1}) the rate does not have an integral order with respect to oxime concentration and this could be the result of diffusion effects. As the hydrogen ion is more mobile than either oxime, copper complex or copper(II) ion then the rate may apparently be independent of hydrogen ion concentration (at an oxime concentration of 0.010M), whereas it is actually inversely dependent upon the hydrogen ion concentration.

Figure 13 shows the alkyl chain structures of the oximes/copper complexes and it must be stressed that P50, the oxime used industrially, is a complex mixture which contains some more highly branched alkyl chains than most of the oximes studied here.

Table 3 is a collection of the observed rate constants for the oximes studied in hexane and in toluene solution. A direct comparison of oximes against one another will be made with reference to this table.

d) Hexane solution - Extraction.

The observed ordering of oximes with respect to greatest rate of extraction is as follows :-

oxime -(n)	Ar - CRR'R"	Relative rate of extraction.
(n)	RR'R"	
13	Et n-Pr n-Pr	2.41
3	Me Me Et	2.25
7	Me Me i-Bu	2.18
10	Me Et $n\text{-}C_5H_{11}$	2.18
P50	various	2.02
9	Me Me $n\text{-}C_6H_{13}$	1.74
5	Me Et n-Pr	1.43
4	Me Me n-Bu	1.39
12	Me n-Pr n-Bu	1.26
11	Et Et n-Bu	1.20
8	Me Me CH_2CMe_3	1.00

Of the four slowest extractants, three, oximes -(4), (11) and (12), contain an n-butyl chain. Also, of the oximes -(1) to (13) these are the only ones with an n-butyl chain. A dramatic example is seen with oximes -(3), (4) and (9). Oxime -(3) has an ethyl group, (4) has an n-butyl group and (9) has an n-hexyl group, and the observed rate constants are 1.37×10^{-3}, 0.85×10^{-3} and 1.06×10^{-3}.

Comparing oximes -(3), (5) and (7) changing a methyl to a n-propyl chain shows the extractant but increasing it further to an n-pentyl chain increases the rate constant. Consider oximes -(3), (4), (7) and (8), (see Figure 13), specifically picture oximes -(7) and (8) as oxime -(3) with hydrogens replaced by methyl groups and oxime -(4) as a hydrogen replaced by an ethyl group. Replacement of one hydrogen ((4)) results in a drop in the rate constant. Replacement of two hydrogens ((7)) maintains a similar value for the rate constant but replacement of all three hydrogens ((8)) results in a dramatic drop in the rate constant. This suggests that the presence of a quaternary carbon in the chain and not adjacent to the ring is highly undesirable.

The industrially-used extractant, P50, is a mixture of various isomeric oximes. A sample of P50 that showed faster extraction kinetics

than usual has been prepared (35) and upon study of the ^{13}C N.M.R. spectrum of this sample it was observed that the ratio of integrals of resonances at ca.142 p.p.m. to those at ca.140 p.p.m. was greater than in samples with slower rates of extraction. However, no correlation between the ^{13}C N.M.R. spectra of an isomerically pure oxime and its rate of extraction of copper could be found in the present work. From this it can be stated that there is no evidence for electronic effects caused by variation in alkyl chain structure observed so that the variation in the rates of copper extraction are due purely to steric effects.

e) Toluene solution - Extraction.

The observed ordering of oximes with respect to the rate of extraction is as follows :-

oxime -(n),	Ar - CRR'R",	relative rate of extraction.
(8)	Me Me CH_2CMe_3	1.95
(1)	H H n-C_6H_{13}	1.74
(2)	H H n-C_8H_{17}	1.59
(6)	Et Et Et	1.32
P50	various	1.00

The most striking observation is that upon changing from hexane to toluene solvent, oxime -(8) becomes a more rapid extractant than P50. In fact, the observed rate constant for P50 is twice that of the observed rate constant for oxime -(8) in hexane solution, however in toluene the observed rate constant for P50 is half that of the observed rate constant for oxime -(8).

Also a general decrease in the rate constant on changing from hexane to toluene is observed.

Comparison of oximes -(1) and (2) implies that, beyond a certain length of alkyl chain, increasing the chain length has little effect upon the rate of copper extraction.

f) Suggestions for possible further work.

As little difference in the rates of stripping of the copper

complexes studied was observed, much more work needs to be done on this process to find if similar effects in stripping as with extraction are observed with variation in alkyl chain structure. The conditions of study and/or analyses of copper stripping need to be studied more closely with a view to enhancing observed differences in rates beyond the limits of experimental error. Slowing the rate of stripping may be desirable and greater accuracy of analysis of the dilute copper-containing solutions would be of great assistance.

For the extraction reaction, a study of all the oximes described here in one solvent system would be desirable as would further study of the pH dependence of extraction rate with respect to oxime concentrations. The variable, non-integral order of the extraction reaction with respect to oxime concentration needs to be studied if any work is considered under conditions that are not almost constant in copper concentration as the extraction proceeds. The synthesis of oximes, Ar-CRR'R", with

R	R'	R"
Me	Me	n-C_3H_7, n-C_5H_{11}, n-C_7H_{15}, n-C_8H_{17}.
Me	Et	Et, n-C_4H_9, n-C_4H_9, n-C_6H_{13}

should be considered for studying the effects of introducing -C_2H_4- units into a chain. Also, the introduction of chain branching has only been touched upon (oximes -(7) and (8)) and others need to be studied. However, new techniques for synthesising the oximes with chain branching may well have to be developed as the essential step of introducing the alkyl chain in a Friedel-Crafts alkylation (Chapter 3) could well introduce rearrangement reactions and mixtures of two or more isomeric alkylphenols would be produced.

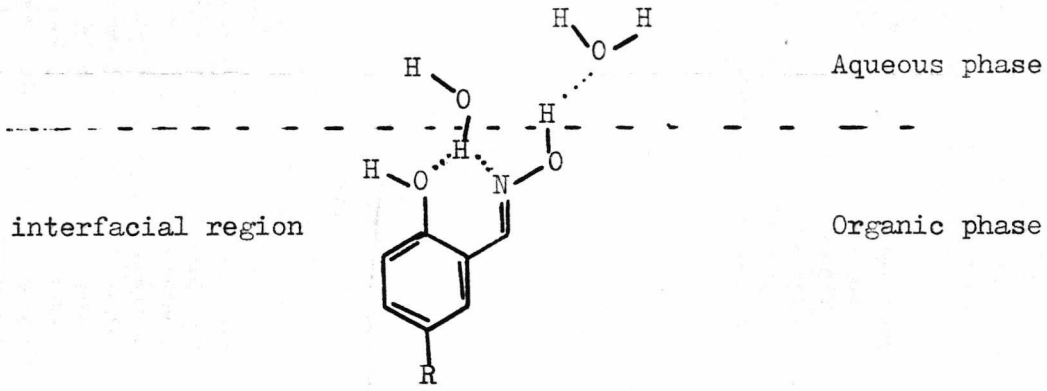
Surface tension studies upon isomerically pure oximes may produce useful correlations with the observed variation in rates. Computer modelling of the steric constraints with respect to the interfacial area could be of great potential use in explaining why an apparently small change in structure (for example oximes -(7) and (8)) can produce dramatic differences in observed rates of copper extraction. This could

also be expanded to consider the structuring of the aqueous and organic solvents at the interfacial region when compared to the bulk phases.

g) Conclusions.

The work has shown that changes in an alkyl chain structure between ISOMERIC 5-alkylsalicylaldoximes, where the alkyl chain is far away from the site of co-ordination, produces readily detectable changes in the rate of complex formation. It also shows that this area of chemistry is large and poorly understood and potentially of great importance.

FIGURE 1. Aqueous-organic interface.



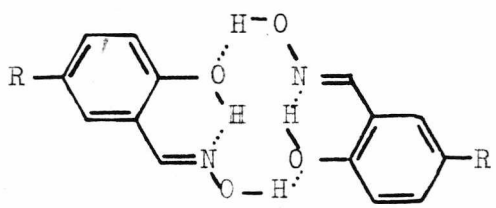


FIGURE 2. Rising drop apparatus.

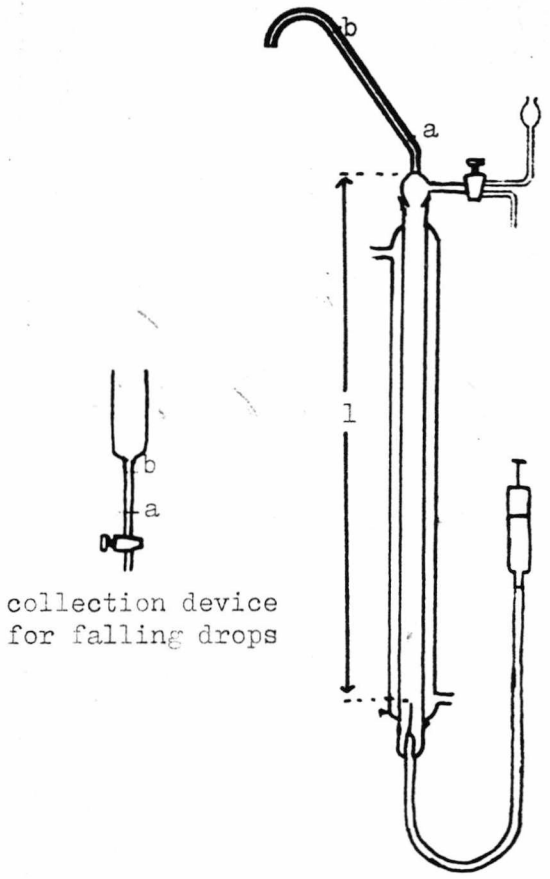
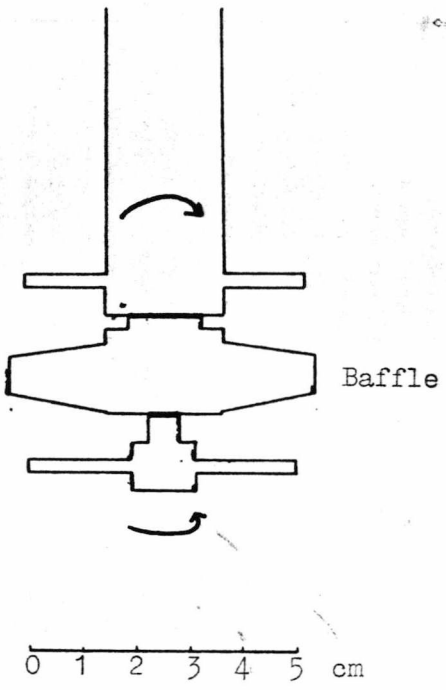
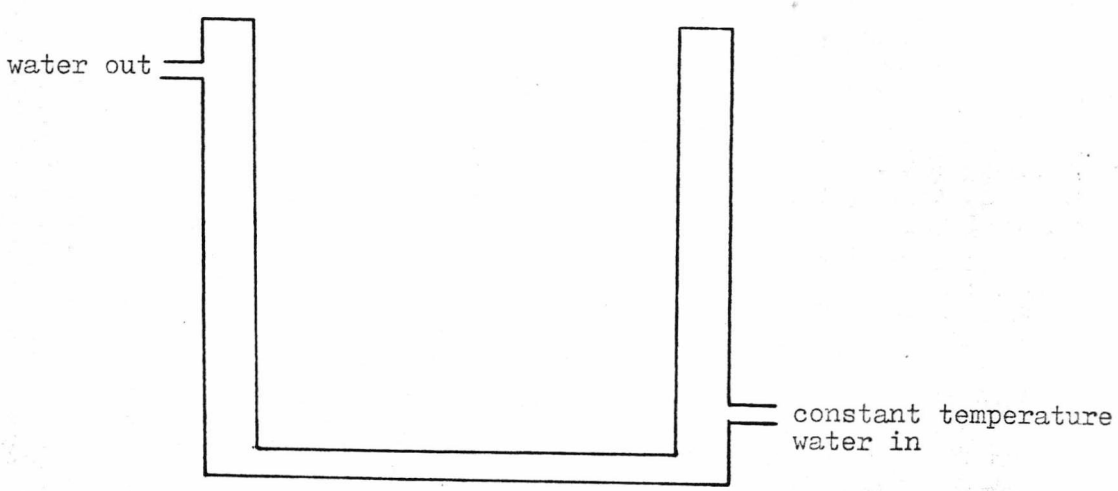


FIGURE 3. Contra rotarory stirrer & kinetic vessel, drawn to scale.





Interfacial area = 88.7 cm^2.

FIGURE 4. Rotating disc apparatus.

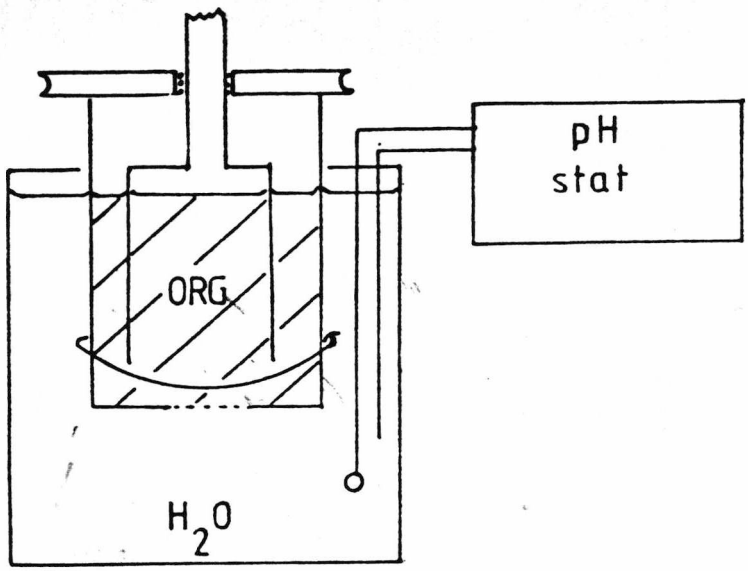
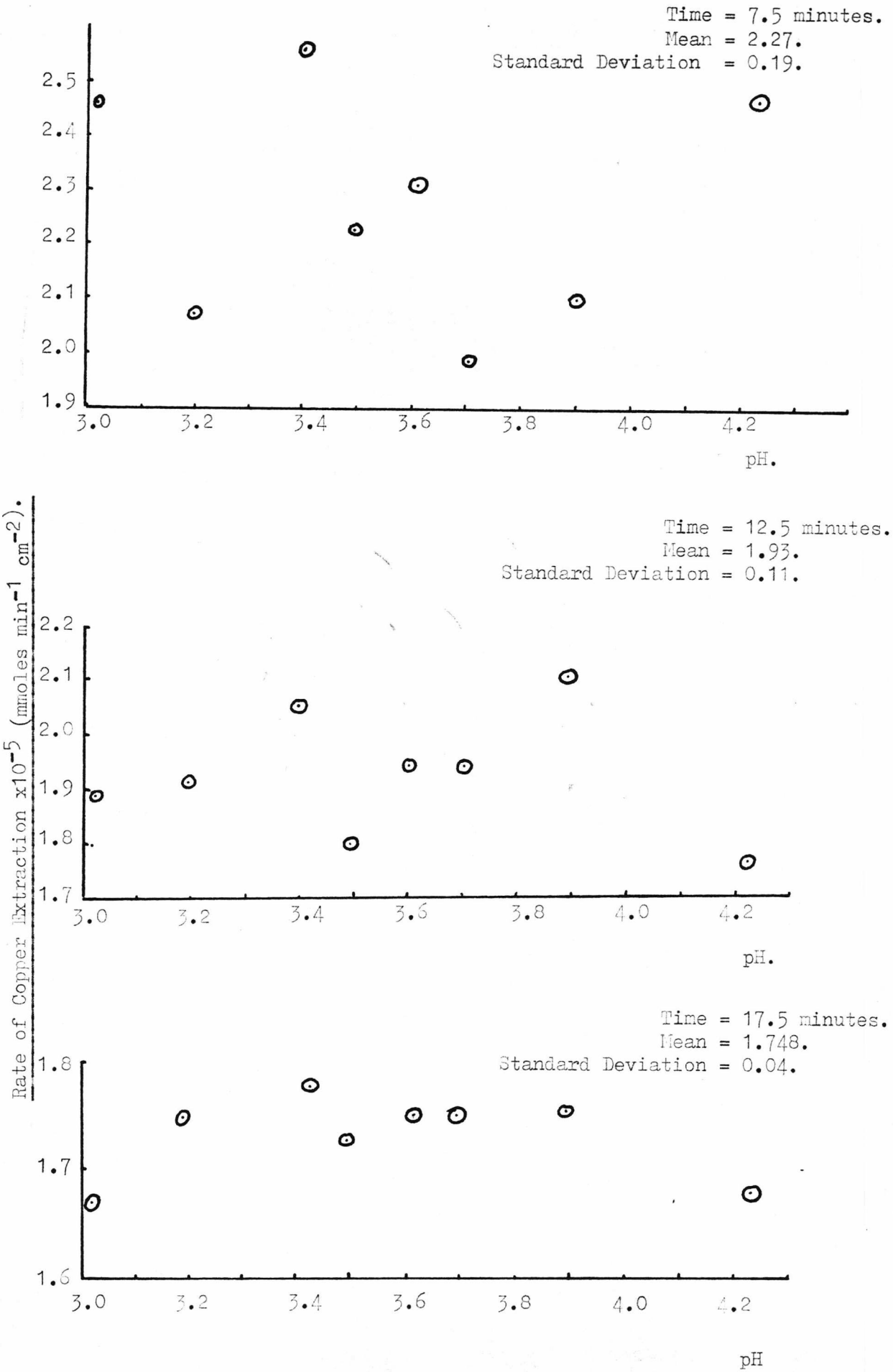


FIGURE 5. Rate of copper extraction with respect to pH.



[P50] = 0.010M
[Cu^{2+}] = 0.020M

FIGURE 6. Rate of copper extraction with respect to [P50]

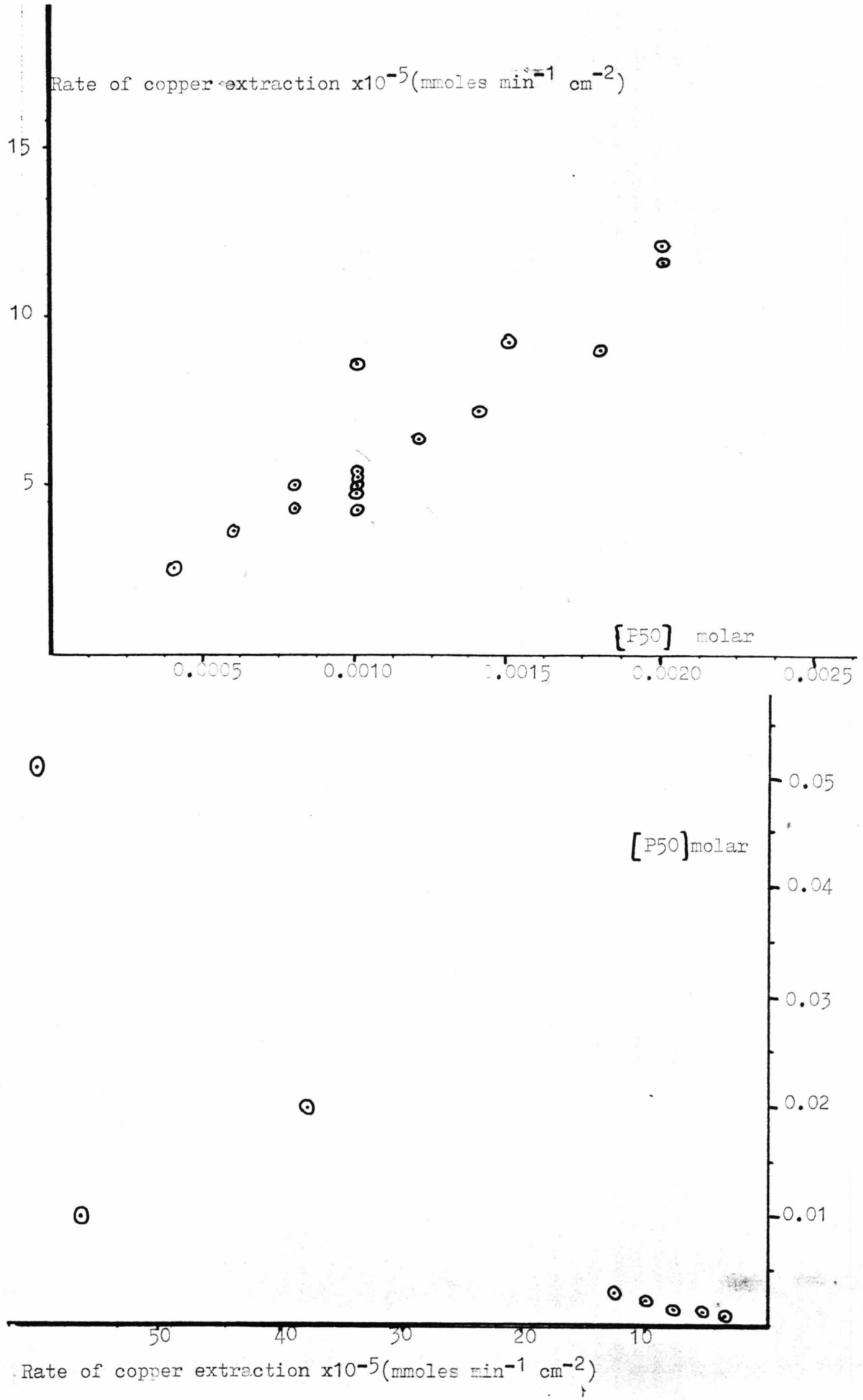
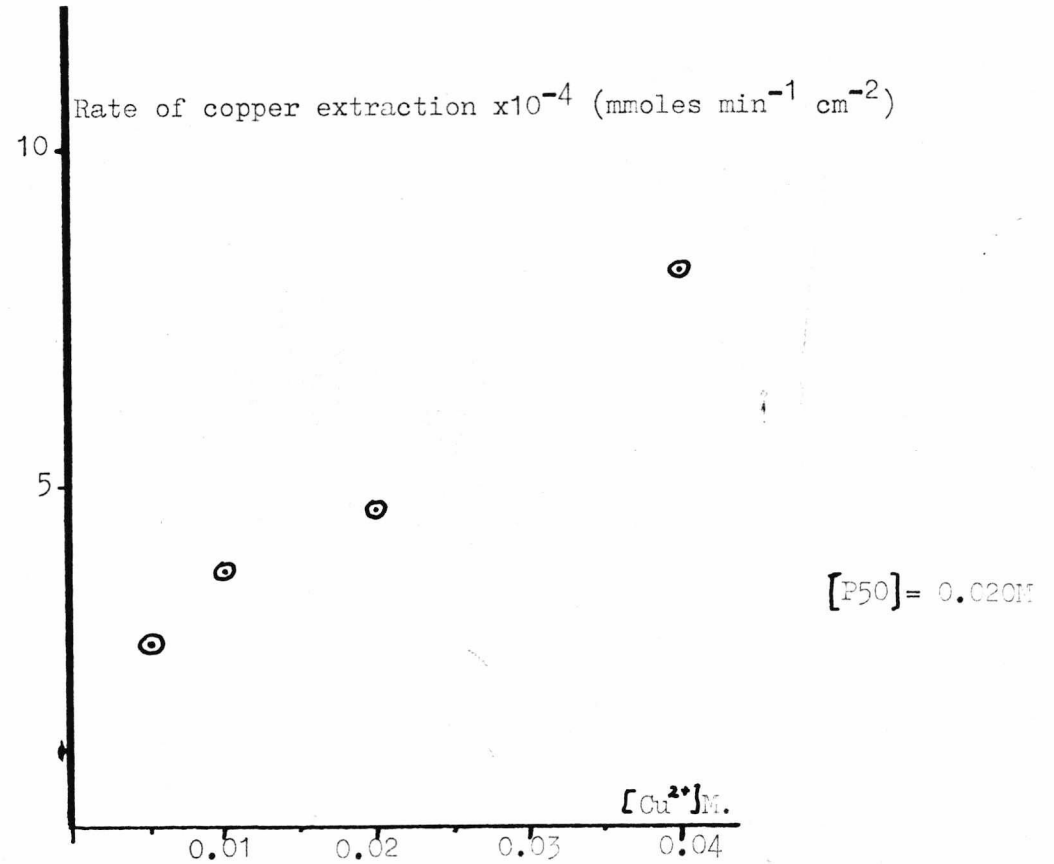


FIGURE 7. Variation of rate of copper extraction with respect to $[Cu^{2+}]$



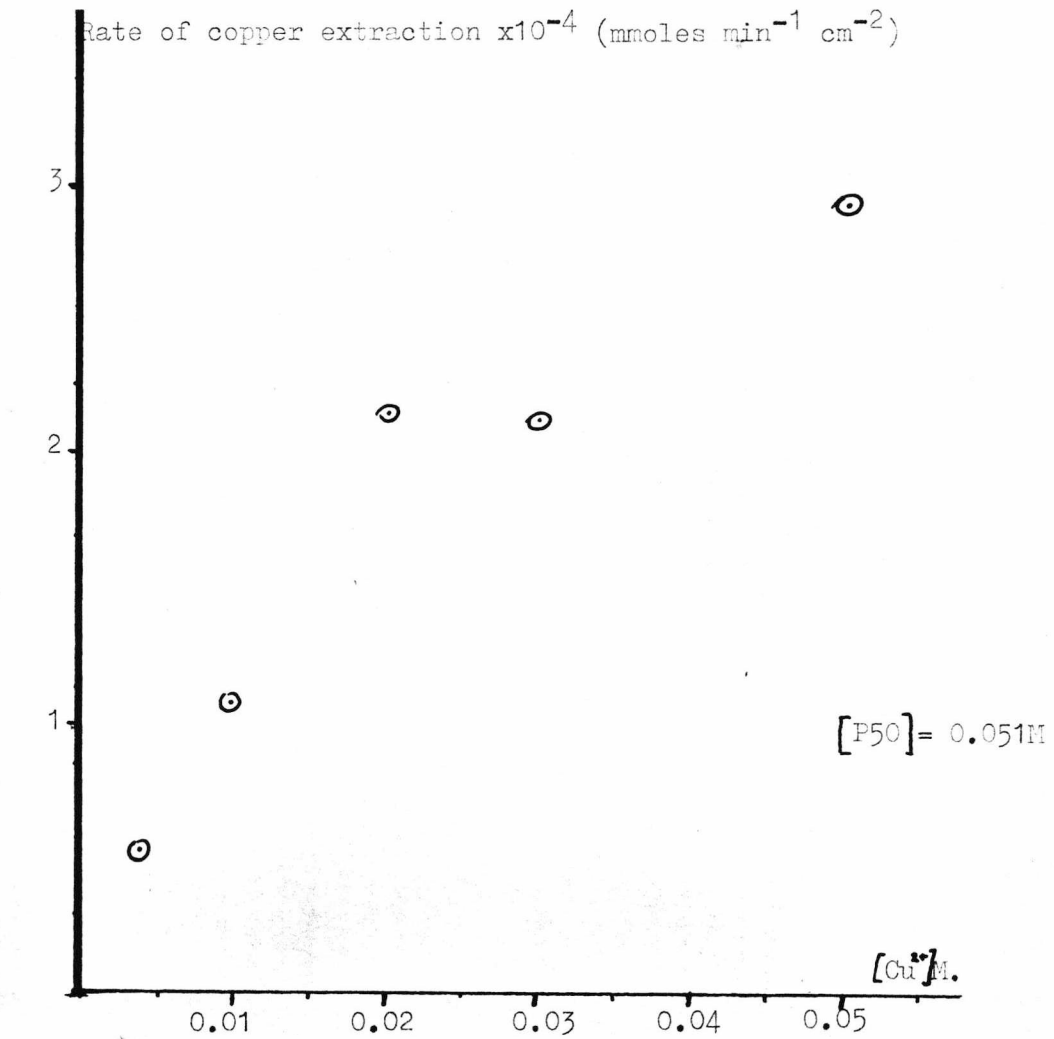


FIGURE 8. Log[Cu^{2+}] with respect to Log (rate).

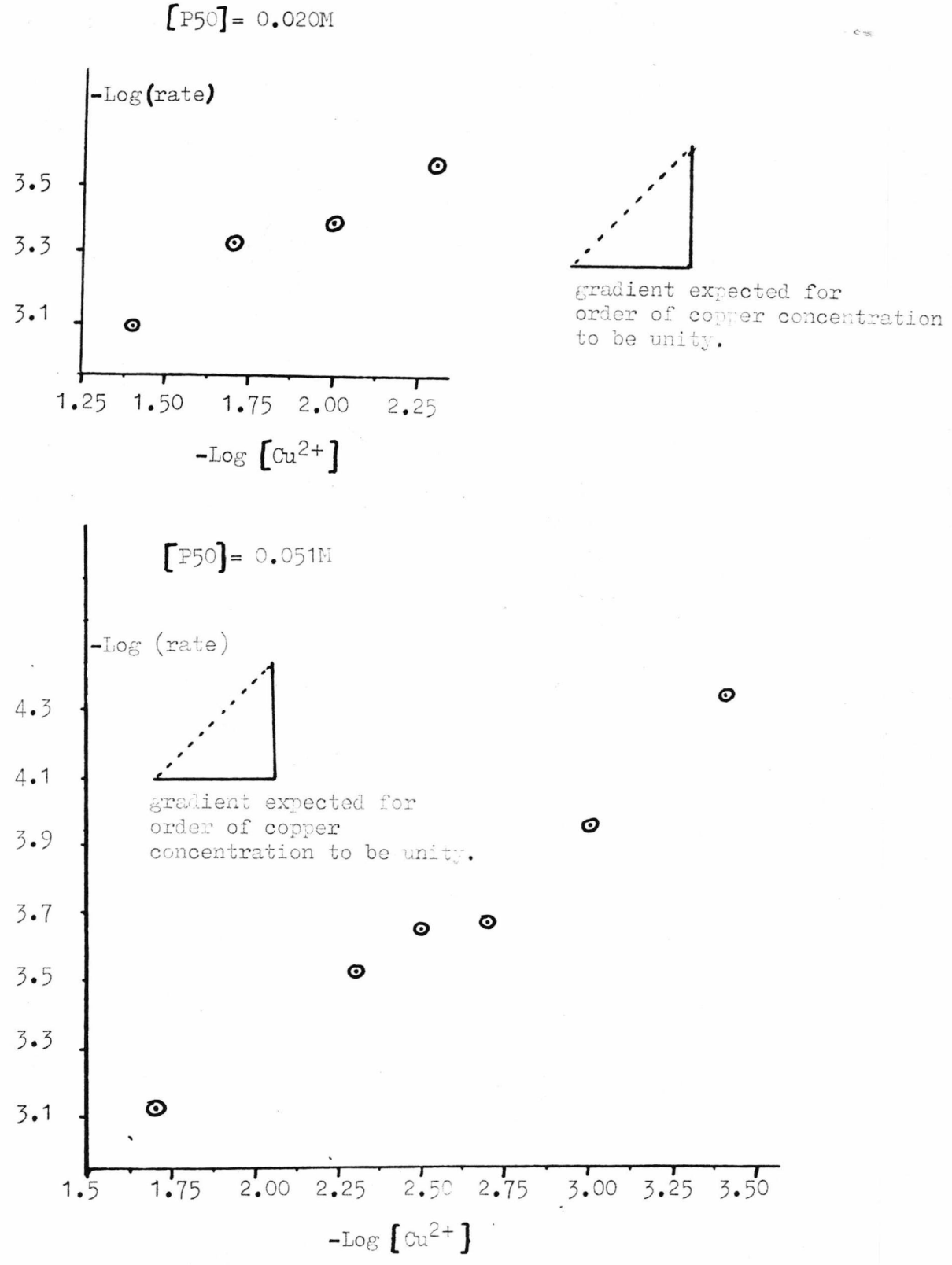
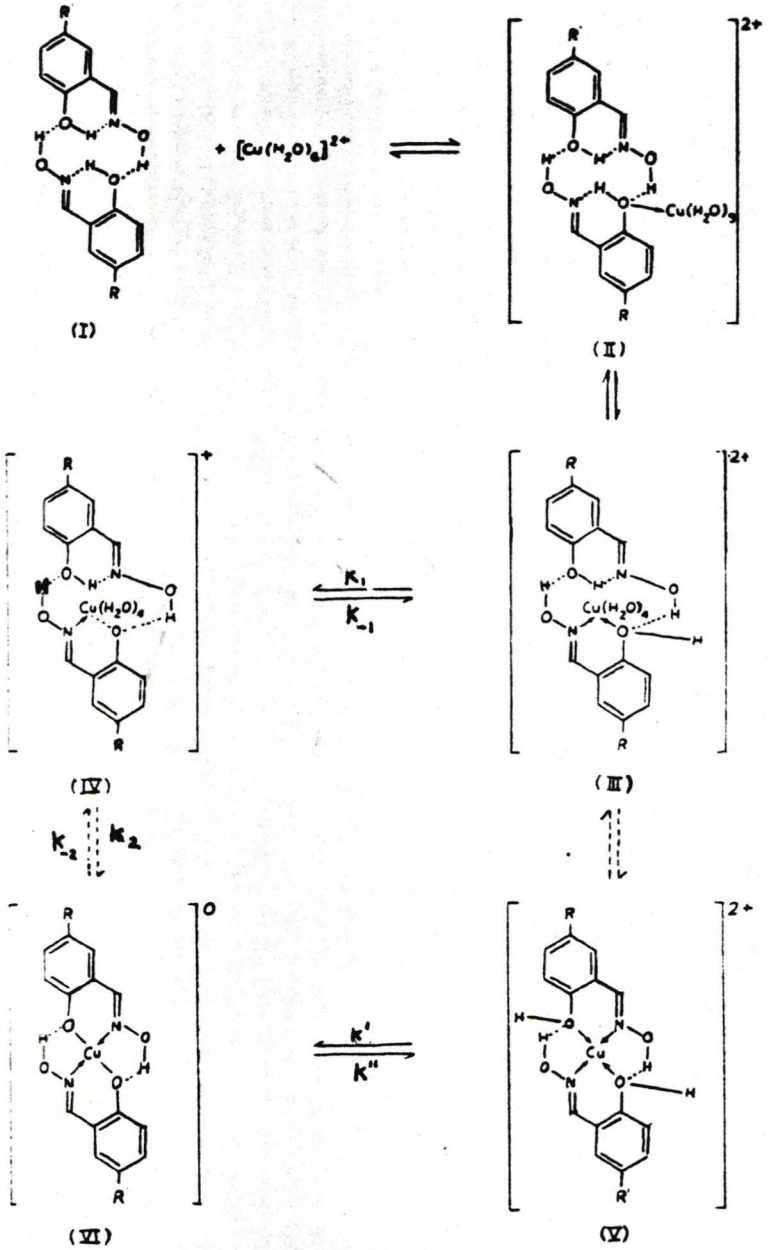


FIGURE 9. Proposed reaction scheme for the extraction of copper by a salicylaldoxime ligand.



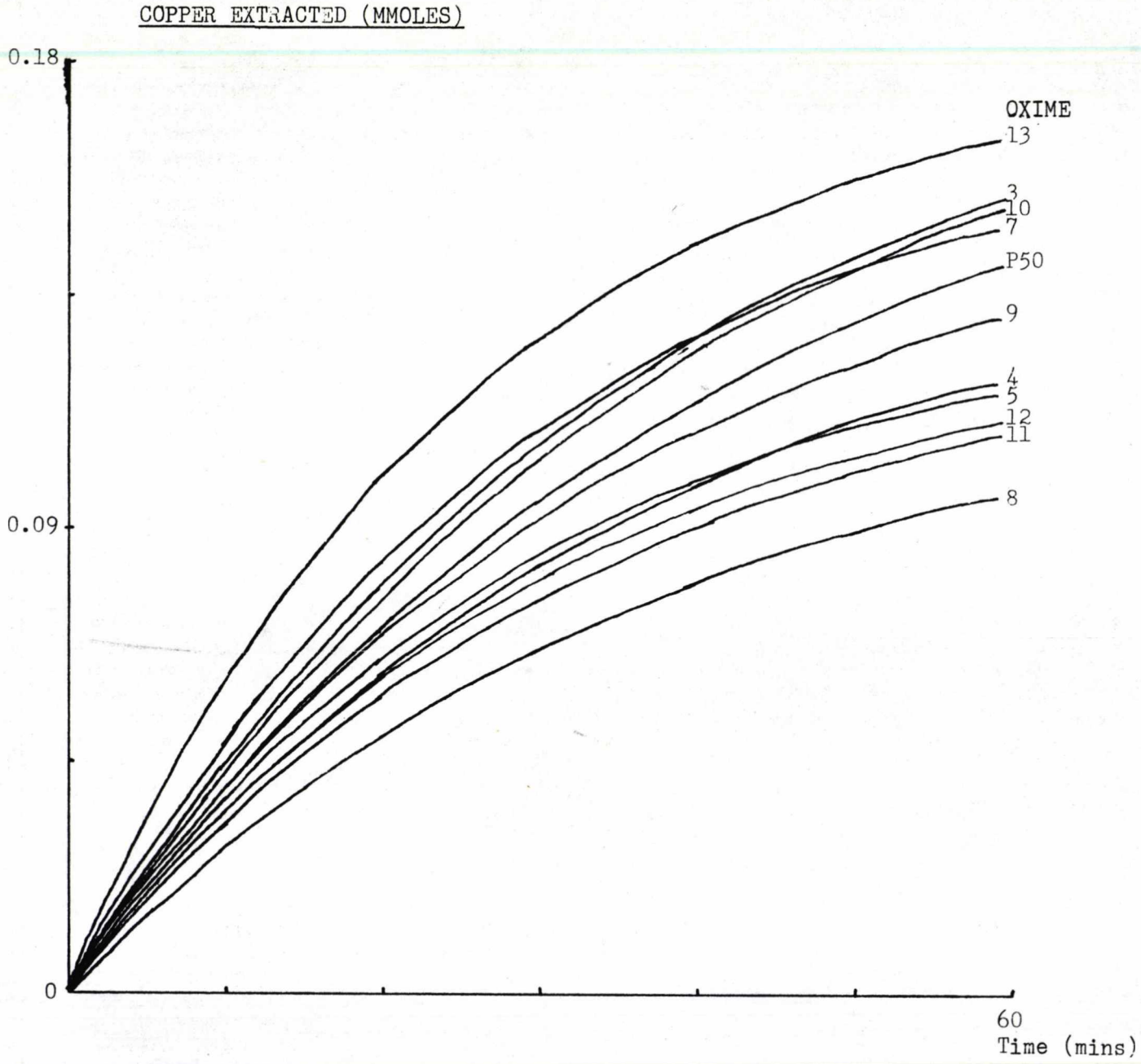
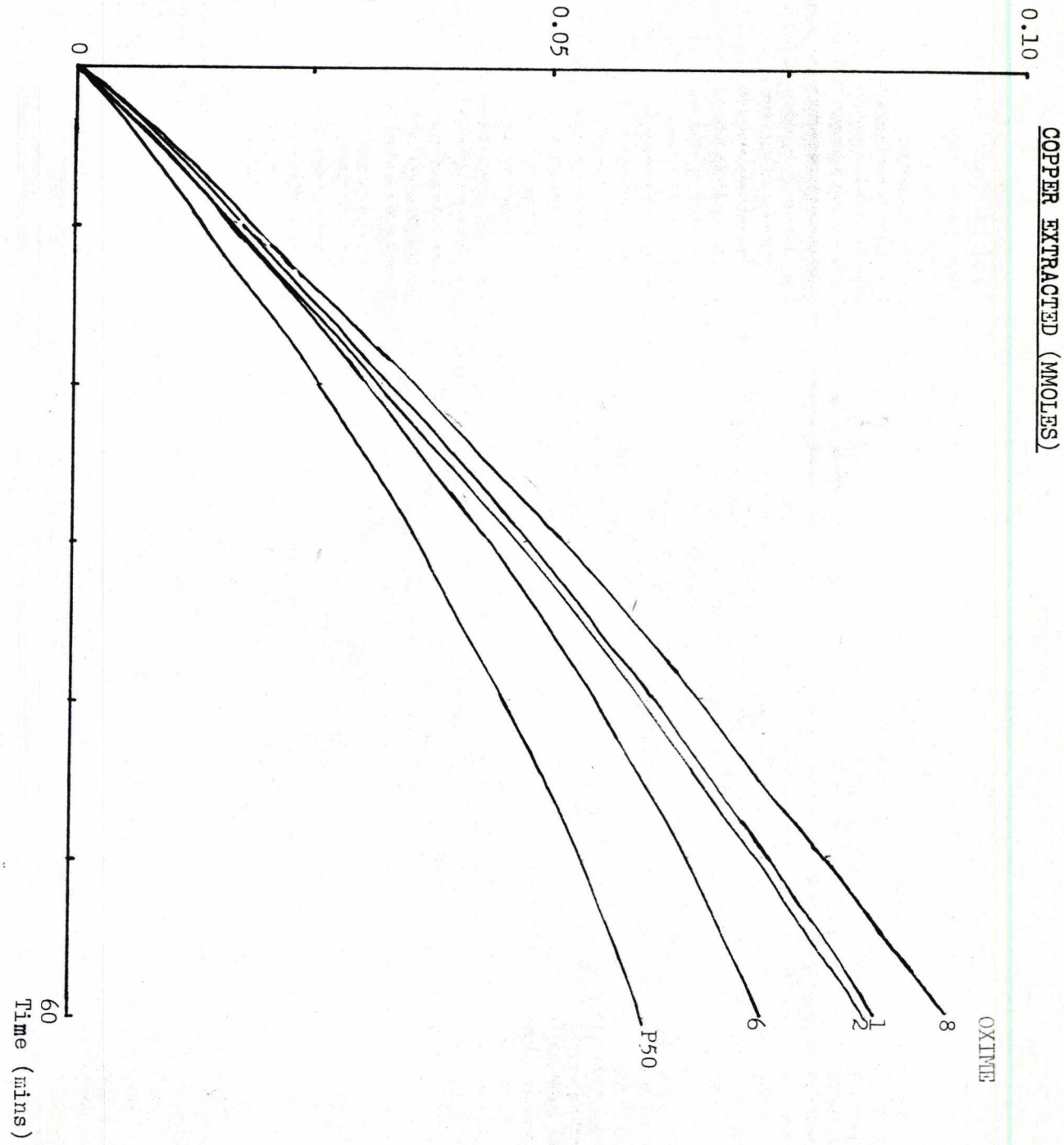


FIGURE 10. Copper extraction in hexane solution

FIGURE 11. Copper extraction in toluene solution



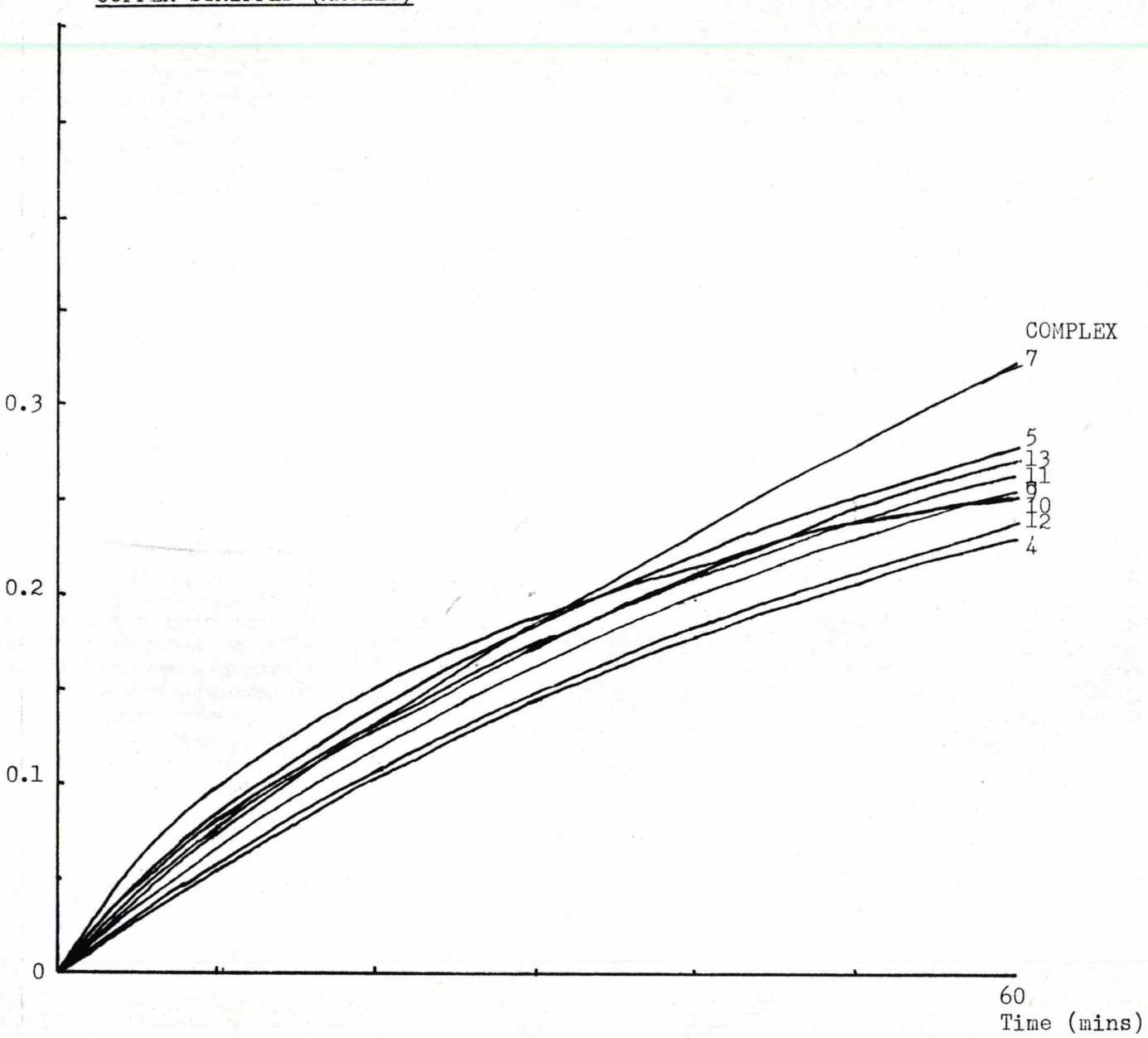


FIGURE 12. Stripping of copper complex in hexane solution.

FIGURE 13. Alkyl chain structures.

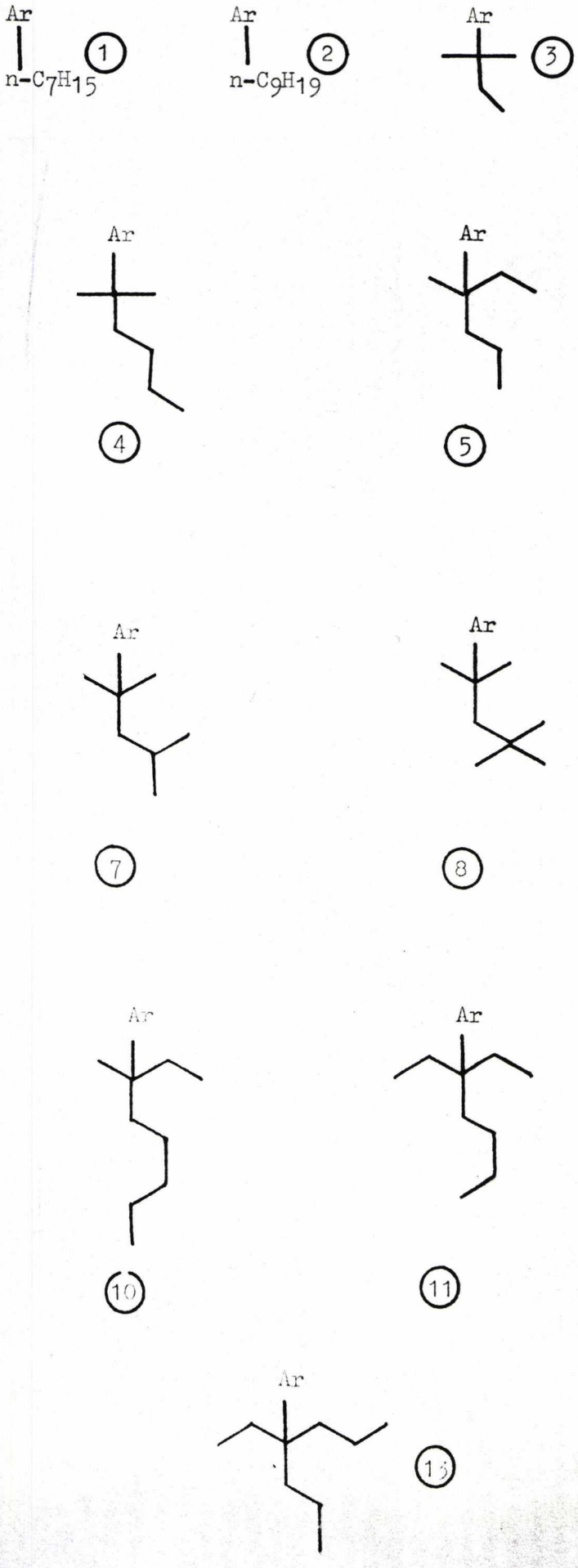


TABLE 1. Extraction of copper with respect to time for oximes (3) - (5), (7) - (13) and P50 in hexane solution.

The figures in the Table are the number of millimoles of copper extracted at that time.

	Time (mins.).					
Oxime.	10.	20.	30.	40.	50.	60.
P50	0.046	0.082	0.110	0.131	0.147	0.158
(3)	0.045	0.085	0.117	0.138	0.155	0.168
(4)	0.037	0.068	0.091	0.108	0.122	0.131
(5)	0.041	0.072	0.094	0.110	0.122	0.130
(7)	0.046	0.089	0.120	0.141	0.152	0.159
(8)	0.037	0.059	0.074	0.088	0.101	0.113
(9)	0.044	0.077	0.102	0.120	0.136	0.146
(10)	0.040	0.079	0.108	0.132	0.150	0.165
(11)	0.035	0.063	0.084	0.100	0.111	0.120
(12)	0.037	0.067	0.088	0.104	0.115	0.122
(13)	0.052	0.096	0.122	0.144	0.159	0.171

TABLE 2. Extraction of copper with respect to time for oximes (1), (2), (6), (8) and P50 in Toluene.

The figures in the Table are the number of millimoles of copper extracted at that time.

	Time (mins.).					
Oxime.	10.	20.	30.	40.	50.	60.
P50	0.013	0.026	0.036	0.046	0.054	0.060
(1)	0.019	0.036	0.053	0.064	0.077	0.085
(2)	0.016	0.032	0.047	0.061	0.073	0.084
(6)	0.016	0.031	0.044	0.055	0.065	0.073
(8)	0.017	0.035	0.052	0.067	0.080	0.093

TABLE 3. Values of pseudo rate constants for extraction reaction.

Hexane solution.

oxime.	pseudo rate constant $x10^3$.
P50	1.23
(3)	1.37
(4)	0.85
(5)	0.87
(7)	1.33
(8)	0.61
(9)	1.06
(10)	1.33
(11)	0.73
(12)	0.77
(13)	1.47

Toluene solution.

oxime.	pseudo rate constant $x10^3$.
P50	0.19
(1)	0.33
(2)	0.30
(6)	0.25
(8)	0.37

TABLE 4. Stripping of copper complexes with respect to time in hexane solution.

The figures in the Table refer to the number of millimoles of copper stripped into aqueous phase.

	Time (mins.).					
Oxime.	10.	20.	30.	40.	50.	60.
(4)	0.052	0.102	0.146	0.175	0.207	0.231
(5)	0.078	0.132	0.175	0.197	0.250	0.302
(7)	0.074	0.132	0.190	0.231	0.278	0.323
(9)	0.067	0.116	0.161	0.197	0.231	0.261
(10)	0.098	0.150	0.186	0.214	0.238	0.257
(11)	0.079	0.129	0.172	0.206	0.242	0.264
(12)	0.058	0.105	0.141	0.183	0.209	0.239
(13)	0.089	0.138	0.184	0.211	0.246	0.283

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