Part I: oxidations using peroxytrifluoracetic acid: part II: the telomerisation of fluorinated olefins

Chambers, R. D.

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DURHAM COLLEGES IN THE UNIVERSITY OF DURHAM

A THESIS

entitled

PART I: OXIDATIONS USING PEROXYTRIFLUOROACETIC ACID.

PART II: THE TELOMERISATION OF FLUORINATED OLEFINS.

Submitted by R. D. CHAMBERS, B.Sc.
(University College)

A candidate for the degree of Doctor of Philosophy
1959.

ACKNOWLEDGEMENTS

The work recorded in this thesis was carried out under the direction of Dr. W.K.R. Musgrave, and I wish to express my thanks to him for his continual help and encouragement. I would also like to record my indebtedness to: Dr. R.E. Dodd of King's College (University of Durham) for the determination of infra-red spectra, and Mr. P. Goggin for practical assistance in the first part of this work; the Department of Scientific and Industrial Research and the Ministry of Supply for maintenance grants; and to the Imperial Smelting Corporation for supplying monomers used in the second part of this work.

MEMORANDUM

The work reported here was carried out by the author at the University Science Laboratories, Durham, between September 1956 and July 1959. It is original except where acknowledged by reference, and has not been presented for any other degree.

The work described in PART I has provided subject material for a lecture delivered by Dr. W.K.R. Musgrave at the symposium: 'Recent Advances in Fluorine Chemistry', (Manchester, April 1958), summarised in 'Chemical Age', Vol.79, No.2026, p.878, and the publication: 'The Oxidation of Aromatic Hydrocarbons and Phenols by Trifluoroperoxyacetic Acid', J.C.S., 1959, 1804 (May).

PART II was carried out as a contract from the Ministry of Supply. The work is part of a programme with the aim of synthesising new oils and greases with high thermal stability, and possible resistance to radiation.

R.D. CHAMBERS.

SUMMARY

PART I

Oxidation of Benzene Homologues

Benzene homologues other than toluene (i.e. meta-xylene, pseudo-cumene, and mesitylene) have been shown to undergo electrophilic hydroxylation on treatment with peroxytrifluoroacetic acid. An alkyl group in the position para- with respect to the hydroxyl group introduced, migrates so that the para quinone can be formed; a mechanism for the rearrangement has been postulated.

Oxidation of Phenols

By starting with the phenols, good yields of some quinones have been obtained. Meta-2 xylenol gave para-xyloquinone; and pseudo-cumenol (2,3,5 tri-methyl phenol) gave pseudo-cumoquinone. Other phenols, e.g. cresols, and ortho-xylenols, gave tars; an explanation of this sequence has been put forward based on the stability of the quinones.

2,4,5 Tri-methyl phenol (i.e. containing a methyl group in the position para- to the hydroxyl group) gave 2,4,5 tri-methyl quinole in good yield. Other methods described in the literature for the preparation of this compound are unreliable.

High Temperature Vapour-Phase Chromatography

The analysis of complex mixtures of high boiling materials required the development of a reliable system for working temperatures about 200°C. This was achieved after much

investigation, by constructing a thermistor detector, and using a column incorporating 'Apiezon L' high vacuum grease as stationary phase.

PART II

Polymers

Octafluorocyclohexa-1,3- and -1,4- dienes became available via the controlled fluorination of benzene. Attempts to form homopolymers by gamma-irradiation of these compounds were unsuccessful. A series of co-polymers with hydrocarbon olefins and the 1,3-diene have been prepared, i.e. with butadiene, styrene, methyl-methacrylate. No co-polymers with halogenated olefins (i.e. C_2F_4 and CF_2CFCl) could be obtained.

Telomers

A 'reactive' olefin-tetrafluoroethylene (easily forms a homopolymer), when irradiated with CF_3I, and C_2F_5Cl gave solid products of the formula $CF_3(C_2F_4)_nI$, with average 'n'-values between 5 and 10.

An 'unreactive' olefin-hexafluoropropene, has been irradiated with various telogens, and an order of relative telogen reactivity has been established, i.e. methyl alcohol = methyl mercaptan $>$ CF_2Br_2 $>$ CCl_4 = C_2F_5I. Products consisted mainly of the 'n' = 1 telomers.

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PART I

OXIDATIONS USING PEROXYTRIFLUOROACETIC ACID

CHAPTER I

HISTORICAL SURVEY AND INTRODUCTION

HISTORICAL SURVEY

The literature on the subject of oxidation reactions and their mechanisms is vast, embracing the fields of organic and physical chemistry. This survey is intended to cover, and in some way connect the material which is relevant to the present investigation and some of the problems involved in it.

Peroxytrifluoroacetic Acid

Peroxytrifluoroacetic acid is produced by the addition of High Test hydrogen peroxide to trifluoroacetic anhydride, or merely to trifluoroacetic acid.[1] The formation can be represented:-

$$(CF_3CO)_2O + H_2O_2 \longrightarrow CF_3COOOH + CF_3COOH.$$

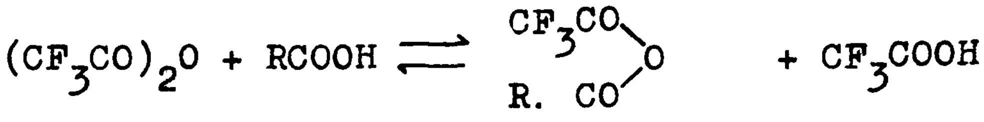
$$\text{or} \quad CF_3COOH + H_2O_2 \longrightarrow CF_3COOOH + H_2O.$$

It is said that the peroxy acid can then ionise in the following manner.

$$CF_3COOOH \rightleftharpoons CF_3COO^- + OH^+$$

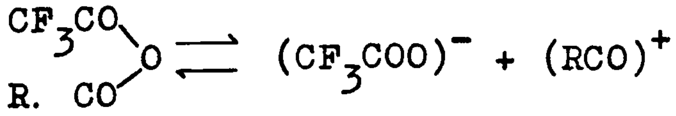
There is strong evidence in favour of this ionisation in the work done on mixed anhydrides at Birmingham where esterification of hydroxy compounds has been brought about by mixing the reagents with trifluoroacetic anhydride.[2]

The reactions are said to take place via the formation of a mixed anhydride (I) which then ionises to give an acyliumcation $(RCO)^+$ because of the extreme electronegativity of the $-CF_3$ group.

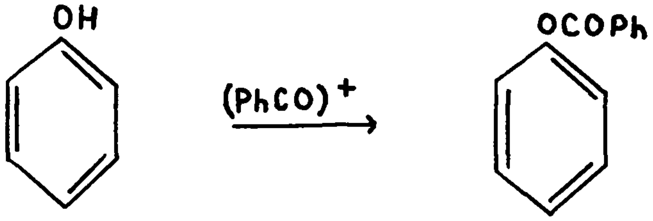


$$(CF_3CO)_2O + RCOOH \rightleftharpoons \begin{matrix} CF_3CO \\ R.\ CO \end{matrix}\!\!>O + CF_3COOH$$

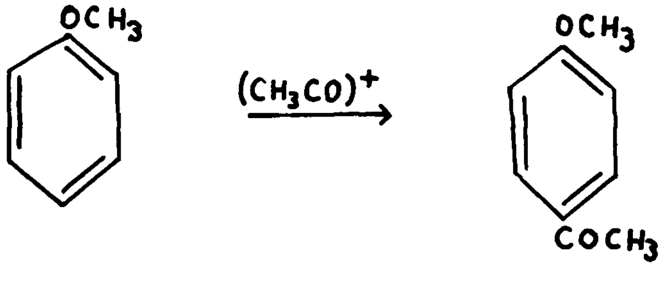
(I)



$$\begin{matrix} CF_3CO \\ R.\ CO \end{matrix}\!\!>O \rightleftharpoons (CF_3COO)^- + (RCO)^+$$



Similarly, activated hydrocarbons have been made to react with carboxylic or sulphonic acids to give ketones and sulphones respectively.



W. D. Emmons appears to have been the first to use peroxytrifluoroacetic acid, and following are some of the reactions to which he applied the reagent:-

1. The oxidation of nitrosamines to nitramines.[1,3.]

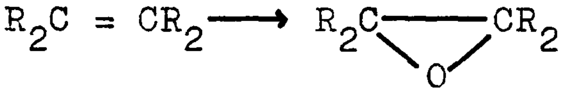
$$R_2N.NO \longrightarrow R_2N.NO_2$$

2. The oxidation of aromatic amines to nitro compounds;[4] a reaction previously carried out using Caro's acid and peracetic acid but in poor yields.

$$Ar.NH_2 \longrightarrow Ar.NO_2$$

3. The oxidation of olefins;[5] most peroxy acids have been used for this purpose, performic being one of the most effective. Peroxytrifluoroacetic acid has the advantage of increased reactivity, and leads to considerable practical advantages in the preparation of alpha-glycols.

4. The epoxidation of olefins,[6] especially those with substituents which increase the electron density at the double-bond. This reaction is dependent on the presence of a buffer in the reaction medium e.g. di-basic sodium phosphate or sodium carbonate or bicarbonate.



$$R_2C = CR_2 \longrightarrow R_2C\overset{}{\underset{O}{-}}CR_2$$

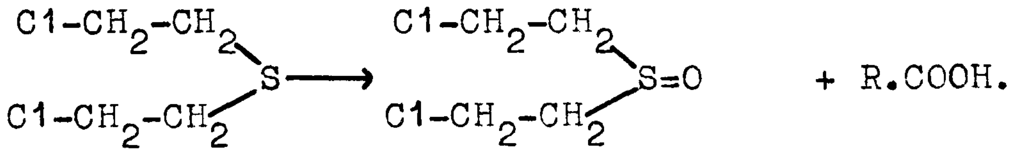
5. The oxidation of ketones to esters,[7] and cyclic ketones to lactones,[8] rapidly and in good yields.

$$RR'C{=}O \longrightarrow R.COOR'$$

The per-Acids[34]

These reagents can be represented by the general formula, R.COOOH. They are mainly used for adding oxygen to atoms which possess unshared electrons and the epoxidation of olefins

e.g.



$$(Cl{-}CH_2{-}CH_2)_2S \longrightarrow (Cl{-}CH_2{-}CH_2)_2S{=}O \quad + R.COOH.$$

The common per-acids have been prepared as following[9]:-

Perbenzoic: Benzoyl peroxide plus sodium methoxide, or 'in situ' by bubbling oxygen into benzaldehyde.

Monoperphthalic: Acetic anhydride plus 30% hydrogen peroxide.

Peracetic: Acetic anhydride plus 30% hydrogen peroxide.

Performic: Formic acid plus 30% hydrogen peroxide; this is a hazardous reagent to handle.

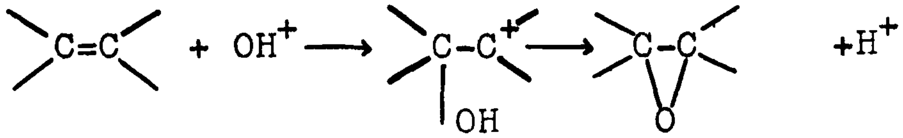
Now that High Test (80-90%) hydrogen peroxide is commercially available, it will probably be used in these preparations to better effect than 30% hydrogen peroxide.

In this class of reagents we can include Caro's acid (H_2SO_5),[10] and hydrogen peroxide in anhydrous hydrogen fluoride.[10,11]

The per-acids have been used extensively for the epoxidation of olefins and the mechanism of this process has received much attention. It is now accepted that for this reaction, the per-acids are electrophilic reagents since -E, or -I substituents will accelerate, and +E, or +I substituents retard the reaction (i.e. a -I and -E substituent will increase the -ve charge on the C- atom when replacing H in C-H).

e.g. -C(Alk) = CH- Accelerated.

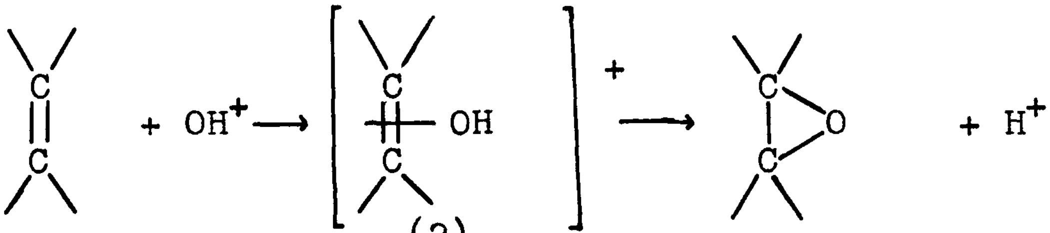
It has been suggested that the peracids act by the provision of free hydroxyl cations[12]:-



(1)

This mechanism has been refuted on the basis that the expoxidation is always cis addition; if the stage involving a carbonium cation actually existed (1), we should expect free rotation about the single bond produced and both cis and trans forms of the epoxide would be formed.

It has been pointed out that cis addition would automatically follow if the initial attack (either by OH^+ or the highly polarised peracid) gave rise to a structure analagous to a DEWAR π-complex (2).[13,14]



(2)

The opening of an epoxide ring always results in inversion, producing specifically trans glycols[13] cf. halogenation.

Kinetics have shown that the reactivity of perbenzoic acid follows the double bond orders of the olefinic links in the series styrene > trans-stilbene > triphenylethylene > tetraphenylethylene, and hence the alternative view has been put forward that perbenzoic acid acts as a 'double-bond' reagent i.e. attacking the double bond rather than one of the constituting atoms.[15]

Oxidation of Aromatic Systems

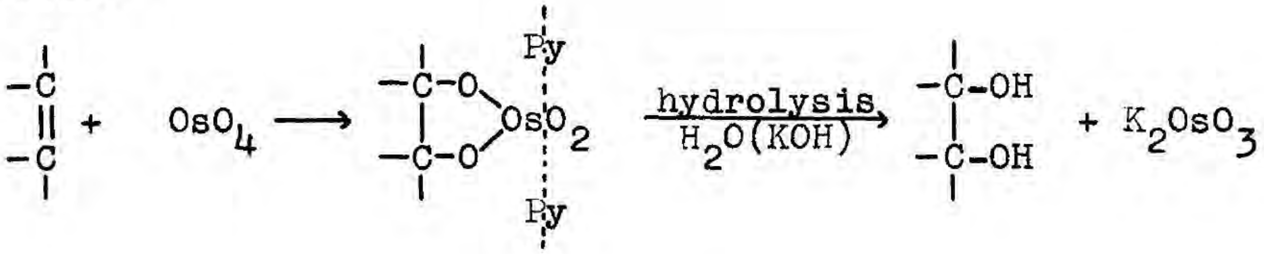
Aromatic rings can be oxidised in various ways, depending on the process taking place. There are four modes of reaction which can occur.[16]

1. Hydrogen abstraction: This is characteristic of a free radical process, resulting in an aromatic free radical which can then dimerise or interact with the initiator. Thus, attack by free hydroxyl radicals can lead to dimerisation or substitution of a hydroxyl group into the aromatic system.[17,18]

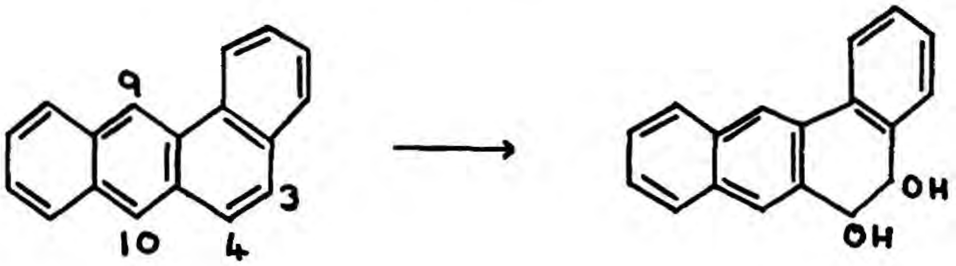
2. Substitution: Possible via a free radical[17,18] or an ionic process.

3. Addition: The 'double-bond' reagents[19] are known as such because they will react with the bond in an aromatic hydrocarbon which possesses the highest double-bond order, rather than the points of highest free-valency (the 'meso' positions). Examples are osmium tetroxide, ozone and diazoacetic ester; they form addition complexes across two adjacent carbon atoms.

In the case of osmium tetroxide, if applied in equimolecular proportions (osmium tetroxide is often used in only catalytic amounts) under anhydrous conditions, and in the presence of pyridine, highly coloured complexes can be isolated.[20]



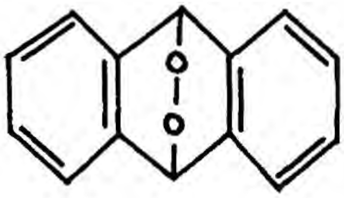
e.g. with 1:2 benanthracene and its derivatives it adds exclusively to the 3,4 bond, although the 9,10 (meso) positions are those normally attacked by other reagents.[21]



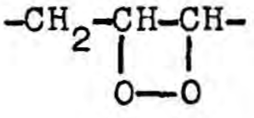
The addition complexes can also lead to rupture of the aromatic ring, especially with ozone, giving di-aldehydes, aldehydo-acids[16] etc.

4. Peroxide Formation: With certain steroid hydrocarbons and with anthracene, it is possible to obtain the trans-annular addition of oxygen.[22,50]

i.e.

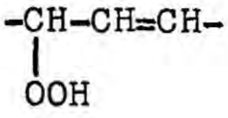


It is also possible to form a hydroperoxide on the side chain. Groups like $-CH_2-CH{=}CH-$ can be oxidised to give peroxides which were once thought to have the cyclic structure (3) but are now known to exist as (4) i.e. a hydroperoxide.[23]



$$\begin{array}{l}-\mathrm{CH_2}-\mathrm{CH}-\mathrm{CH}-\\ \qquad\;\;|\qquad|\\ \qquad\;\;\mathrm{O}-\mathrm{O}\end{array}$$

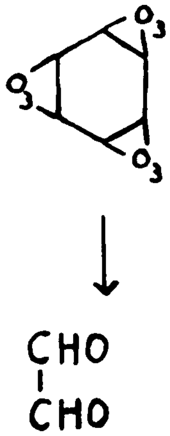
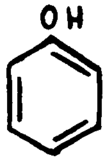
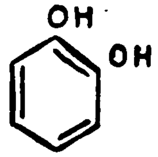
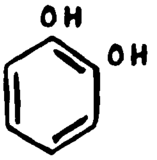
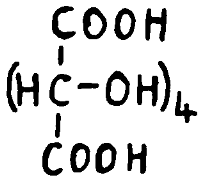
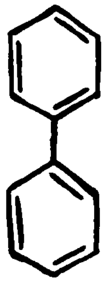
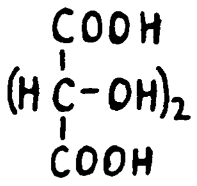
(3)



$$\begin{array}{l}-\mathrm{CH}-\mathrm{CH}{=}\mathrm{CH}-\\ \;\;|\\ \mathrm{OOH}\end{array}$$

(4)

TABLE.I. PRODUCTS OF OXIDATION OF BENZENE BY DIFFERENT REAGENTS.

O_3	·OH (X- or GAMMA-RAYS; $(C_6H_5COO)_2$)	·OH ($H_2O_2 + FeSO_4$)	H_2O_2 (PLUS OsO_4)
 $\mathrm{CHO{-}CHO}$ 1	 2,3		 6,7
	 3		 $\mathrm{COOH{-}(HC{-}OH)_4{-}COOH}$
	 2,3,4	 5	 $\mathrm{COOH{-}(HC{-}OH)_2{-}COOH}$ $(COOH)_2$ 7

1. HARRIES and WEISS (1904)[24]
2. PERRET and PERROT (1945)[17]
3. STEIN and WEISS (1948, 1949)[18]
4. GELISSEN and HERMANS (1925)[25]
5. CROSS et. al. (1900)[26]
6. COOK and SCHOENTAL (1950)[27]
7. MILAS (1946)[28]

This type of compound (4) has been formed on aromatic side-chains.

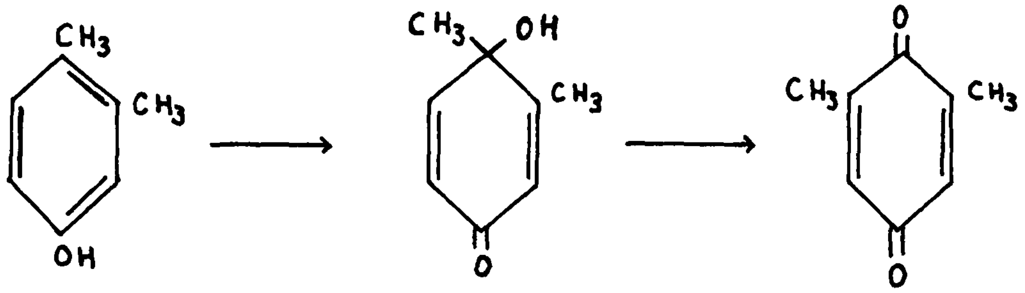
The literature is not very well defined on the oxidation of aromatic systems compared with other oxidation reactions.

Table 1 shows the products which have been obtained in the oxidation of benzene. Comparison is made between: ozonolysis; the attack of free hydroxyl radicals produced in aqueous solution via X-, or gamma-rays, benzoyl peroxide, or from a mixture of hydrogen peroxide and ferrous sulphate; and reaction with hydrogen peroxide containing catalytic amounts of osmium tetroxide.

This series illustrates how varied the products of an oxidation reaction can be, depending on the reagent and the REACTION CONDITIONS employed.

Kirmagoi and Wolfenstein[29] oxidised toluene with alkaline potassium persulphate to dibenzyl, and para cresol to dihydroxy dibenzyl; acid persulphate oxidised para cresol to 4-methyl catechol and 3-methyl hydroquinone.

An emulsion of ortho xylene in dilute sulphuric acid was electrolysed,[30] by Fichter and Renderspacher, giving 3,4 di-methyl phenol (5), which was then further oxidised through the quinole (6), to 2,6 benzoquinone (7).

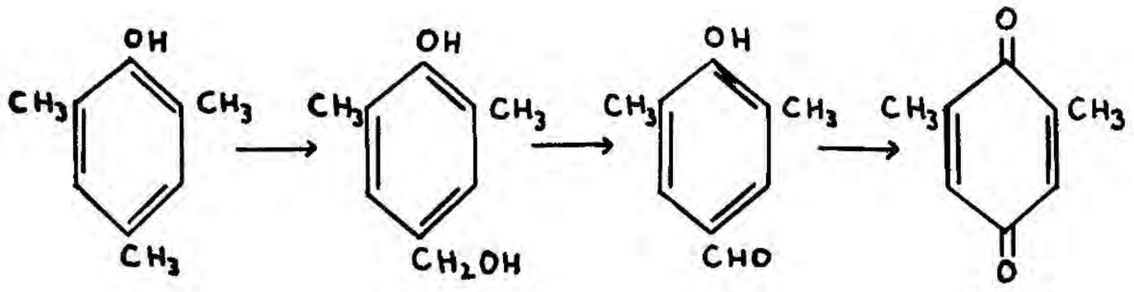


(5) (6) (7)

At the same time, some di-xylenol and ortho-tolyl aldehyde was isolated. The electrolytic oxidation of ethyl benzene gave a variety of products but mainly ethyl benzoquinone.

Waters has oxidised phenols[31] with benzoyl peroxide and with free hydroxyl radicals. Hydrogen abstraction occurred, giving rise to mesomeric free phenolic radicals. Dihydric phenols and various products arising from coupling of the free phenolic radicals were isolated. Phenol and cresols appear to have resulted mainly in dihydroxy derivatives, but mesitol gave many dimers corresponding to the ways in which the phenolic radicals coupled.

Booth and Saunders[32] oxidised mesitol and guaiacol with peroxidase plus hydrogen peroxide.. They isolated products formed by side-chain attack on the methyl group in a position para to the original hydroxyl group i.e. an alcohol (8), aldehyde (9), and meta-xyloquinone (10), together with other products.

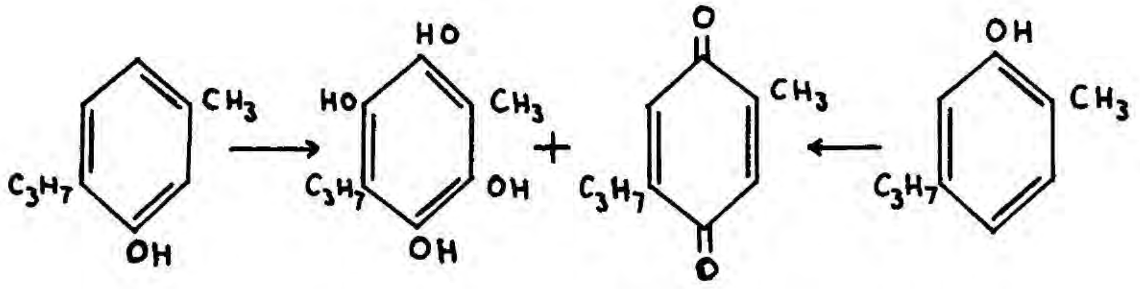


(8) (9) (10)

Teuber and Rau used Fremy's salt, No.$(SO_3K)_2$,[33] and other metal salts of nitrosodisulphonic acid, to oxidise phenols. Para and ortho quinones were prepared i.e. ortho quinones were obtained in cases where the position para to the hydroxyl group was blocked by a substituent, and the ortho position vacant. (Average yield 70%).

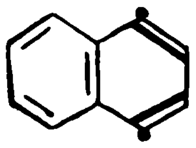
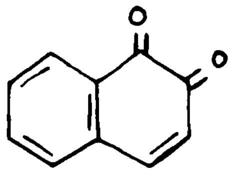
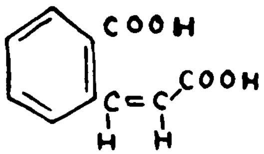
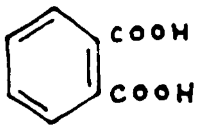
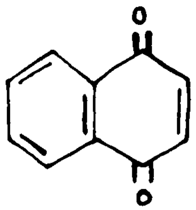
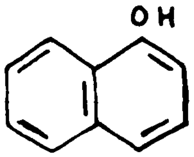
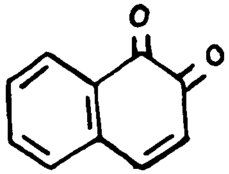
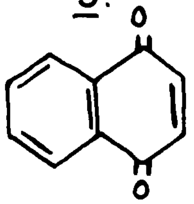
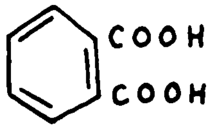
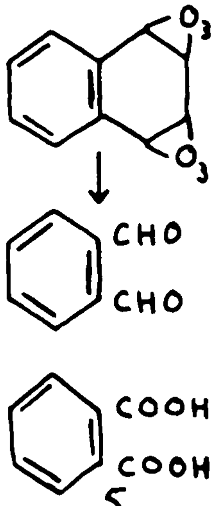
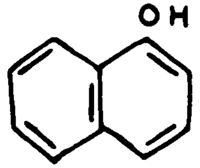
Reactions of the Peracids with Aromatic Systems.[34]

Peracetic acid appears to be the only peracid used to any extent with aromatic systems. Henderson and Boyd[35] oxidised carvacrol (11) and thymol (12) (2, and 3, para cymenol), with peracetic acid to thymoquinone (13) and tetrahydroxy para cymene (14) in both cases; para-tert.-butyl phenol gave di-hydric phenols.



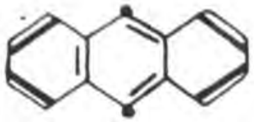
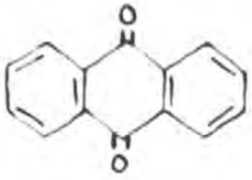
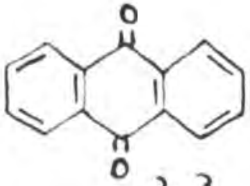
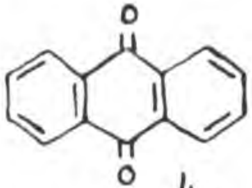
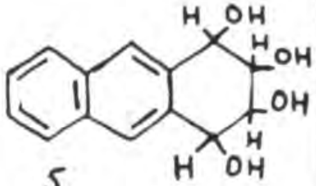
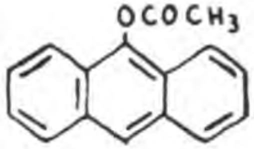
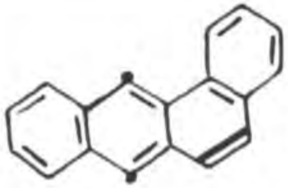
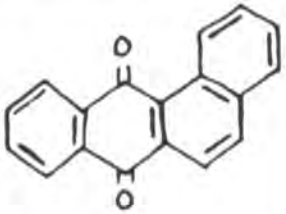
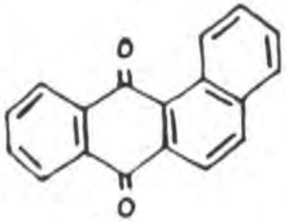
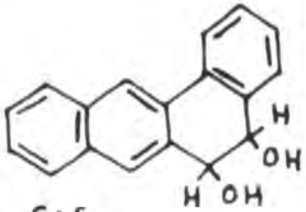
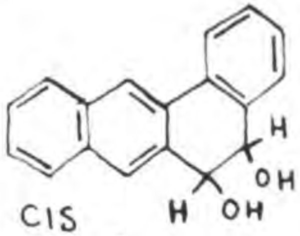
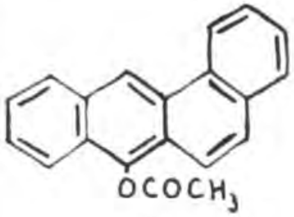
(12) (14) (13) (11)

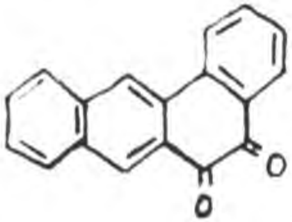
TABLE.2.

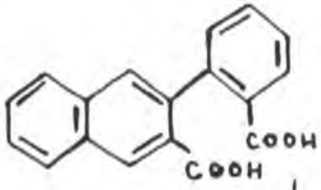
HYDROCARBON	CH_3COOOH	H_2O_2 in ACETIC ACID	H_2O_2 PLUS OsO_4	OZONE	BENZOYL-PEROXIDE.
 NAPHTHALENE	   1.	 2.	 3.  3.  3.  3, 4.	 5.	 6.

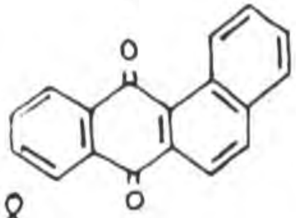
1. BÖESEKEN and SLOOFF (1930)[3]
2. ARNOLD and LARSON (1940)[39]
3. MILAS (1946)[28]
4. COOK and SCHOENTAL (1950)[27]
5. HARRIES and WEISS (1905)[40]
6. PERRET and PERROT (1945)[17]

TABLE.3.

HYDROCARBON	CH_3COOOH and C_6H_5COOOH	H_2O_2 or CrO_3 in ACETIC ACID	H_2O_2 PLUS OsO_4	OsO_4 in PYRIDINE.	$Pb(OCOCH_3)_4$
 ANTHRACENE.	 1.	 2, 3.	 4.	 5.	 6.
 1,2-BENZANTHRA-CENE.			 CIS	 CIS 8	 9



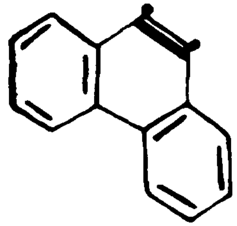
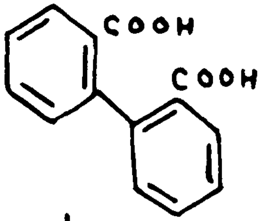
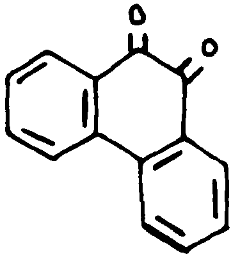
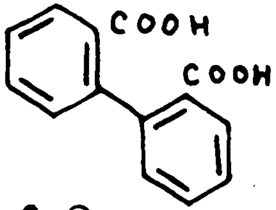
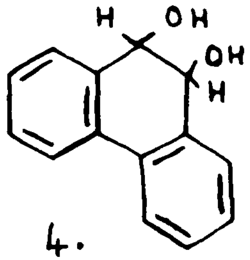
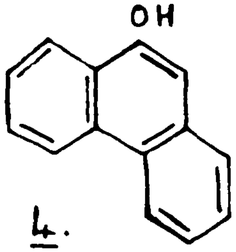
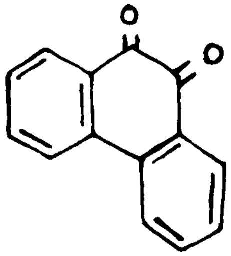
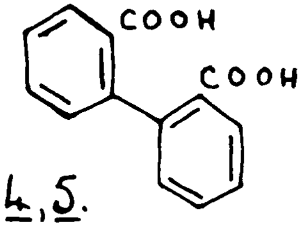
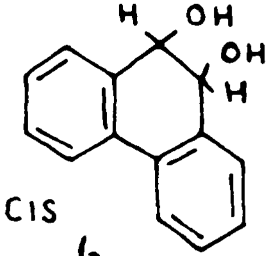




4, 8

1. ROITT and WATERS(1949)[41]
2. CHARRIER and MOGGI(1927)[42]
3. HENDERSON and BOYD(1910)[35]
4. COOK and SCHOENTAL(1950)[27]
5. BERENBLUM and SCHOENTAL(1949)[43]
6. MEYER (1911)[44]
7. ARNOLD and LARSON[39]
8. COOK and SCHOENTAL(1948)[21]
9. FIESER and HERSHBERG(1938)[45]

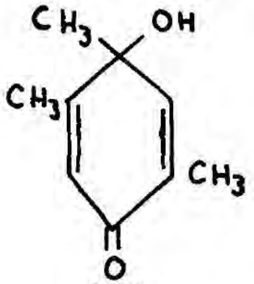
TABLE. 4.

HYDROCARBON	CH_3COOOH	H_2O_2 in ACETIC ACID	H_2O_2 PLUS OsO_4	OsO_4 in PYRIDINE	O_3
 PHENANTHRENE.	 1.	  2, 3.	 4.  4.   4, 5.	 CIS 6.	DI-OZONIDE (STRUCTURE DOUBTFUL) 7.

1. BOESEKEN and SLOOFF (1930)[38]
2. HENDERSON and BOYD (1910)[35]
3. CHARRIER and MOGGI (1927)[42]
4. COOK and SCHOENTAL (1950)[27]
5. MILAS (1946)[28]
6. CRIEGEE et. al. (1942)[20]
7. HARRIES and WEISS (1905)[40]

Fugita etal.,[36] oxidised para cymene to thymohydroquinone and thymoquinone; they found that excess peracetic acid would break down the quinones formed, to dicarboxylic acids.

Bamburger and Rising,[37] using neutralised Caro's acid (permonosulphuric acid) oxidised toluene to para cresol and the corresponding quinole; pseudocumenol to 3,4,6 tri-methyl quinole (15) and di-pseudocumenol; and mesitol to mesityl (16) quinole, and 3,5 di-methyl 4-hydroxy benzyl alcohol (17).



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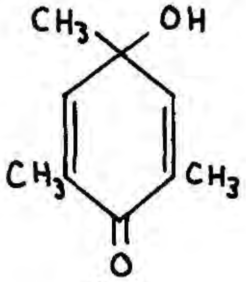
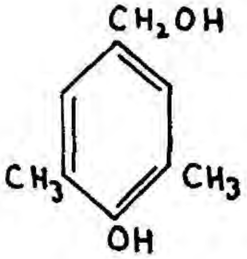


(16)



(17)

These products were accompanied by unidentified material. Tables 2, 3, and 4 show the products which have been obtained in the oxidation of naphthalene, anthracene, 1,2 benzanthracene, and phenanthrene with: perbenzoic acid; peracetic acid; and a mixture of hydrogen peroxide and acetic acid. For comparison, the tables also show products which have been obtained by the action of other reagents.

Carbon atoms which are the points of highest free valency (meso positions), and bonds possessing the greatest double-bond order are shown in heavier print in the molecular structure of the hydrocarbons.

Reactions with 1,2 benzanthracene are the most interesting to note because, in this case, products arising from meso attack can be clearly differentiated from those arising from attack of the reactive bond (between carbon-atoms 3,4).

There has been a great deal of discussion in the literature about the mode of reaction of some oxidising agents, and with a number of them, the mechanisms are by no means agreed upon. Permanganate oxidations of aromatic hydrocarbons can be taken as an example; the products are complex mixtures containing phenols, quinones, hydroquinones and other products. Since the reactions tend to go past the phenol stage, Shoental has interpreted this as characteristic of an ionic reaction,[16] but Waters[46] holds the opinion that permanganate and related reagents react by abstracting atomic hydrogen from the hydrocarbons, and then the addition of neutral hydroxyl radicals occurs.

A complication in some reactions may be that under certain conditions, a particular process (free radical or ionic) is energetically most favourable but a slight change in conditions e.g. an increase in temperature, is sufficient to make another process energetically possible, and hence more than one process may occur at the same time.

Some of the apparent divergences of opinion in the literature over the ease of certain reactions e.g. peracetic acid on aromatic hydrocarbons, may arise from differing experimental conditions. Arnold and Larson[39] have shown that peracetic acid prepared from excess acetic anhydride and perhydrol (30% hydrogen peroxide) is unreactive to benzene and toluene whereas a mixture of glacial acetic acid and perhydrol reacts. It is not possible to decide to what extent peracetic acid is being formed and hence responsible for these reactions.

Approach to the Present Investigation

Most of the oxidising agents which have been used appear to involve free radical intermediates, but there are cases in the literature, where oxidation appears to involve electrophilic attack by the oxidising agent. The most apparent examples are those supplied by the organic peracids; these may or may not involve the existence of free hydroxyl cations. It has been proved conclusively that reactions of organic peracids with ketones (Baeyer Villiger reaction), and with olefins, involve electrophilic attack. However, it does not necessarily follow, that a particular peracid will be a simple electrophilic reagent toward aromatic systems, even if it is the case for reactions with olefinic compounds.

Derbyshire and Waters[47] have demonstrated the existence of the OH^+ entity. They calculated that this should exist to a considerable extent in a solution of hydrogen peroxide in 10-Normal acid. Acetic acid plus hydrogen peroxide was unreactive to mesitylene and other aromatic hydrocarbons but addition of sulphuric acid to the mixture caused reaction to occur; mesitylene gave a good yield of mesitol.

There appears to be no justification for neglecting the formation of peracetic acid on the addition of mineral acid; it is known that mineral acids catalyse this formation. The peroxide bond in peracetic acid should be more highly polarised than the peroxide bond in the more symmetrical hydrogen peroxide molecule. Hence, peracetic acid, if formed to any extent, should have a greater tendancy than hydrogen peroxide, to produce OH^+.

Thus, although the existence and reaction of OH^+ has been conclusively proved, the origin of this ion remains in some doubt.

It seemed that if the other peracids could be regarded as electrophilic reagents, then peroxytrifluoroacetic acid was likely to be an excellent source of free hydroxyl cations. Examples of the superior oxidising power of peroxytrifluoroacetic acid has already been demonstrated by Emmons[1,3-7] and his co-workers, and the ease of formation of the ion, CF_3COO^-, is clearly demonstrated in the work of

Stacey, Tatlow and their co-workers.[2] They showed that mixed anhydrides derived partly from trifluoroacetic acid, are slightly ionised into negative trifluoroacetate, and positive acylium ions. By analogy, peroxytrifluoroacetic acid should ionise, producing the negative trifluoracetate ion, and OH^+ with comparable ease.

$$CH_3COOOH \rightleftharpoons CF_3COO^- \quad + \quad OH^+$$

With this background, it was decided to investigate reactions with peroxytrifluoroacetic acid, and the series benzene, toluene, meta-xylene, pseudo-cumene (1,3,4 trimethyl benzene), and mesitylene. The reactivity was expected to increase in the series. By using one equivalent of oxidant, under mild conditions, it was hoped to be able to identify reaction intermediates which would enable some definite conclusions about the mechanism of the reaction to be drawn.

In view of the fairly high yield of quinones in the cases where their formation was possible, it seemed worthwhile to investigate the oxidation of phenols by peroxytrifluoroacetic acid to see whether it offered any improvement on existing methods.[48,49] The reactions are not to be compared with the hydrocarbon reactions however, since the conditions were different.

Lynch and Pausacker[15] found that the reactivity of perbenzoic acid to olefins depended on the double bond order of the olefinic links and suggested that the reagent behaves as a double-bond reagent. Waters[41] disagreed with this inference on the basis of being able to isolate products arising from only 'meso'-attack, in reactions with polycyclic hydrocarbons.

It was decided that the reaction of peroxytrifluoroacetic acid and polycyclic (carcinogenic) hydrocarbons was worthy of careful investigation; reactions with naphthalene, anthracene, 1:2 benzanthracene and pyrene were envisaged. It was thought that the reagent may behave in a manner analagous to halogenation and only attack the 'meso' positions.

The opinion was held, that the work of Waters did not go into sufficient detail, in order to identify reaction products other than those arising from meso-attack. It was the aim in this investigation to be able to decide absolutely whether only meso attack occurs, or whether this is accompanied by attack on the reactive bonds, Unfortunately, events have only allowed time to begin this part of the investigation.

CHAPTER II

DISCUSSION OF RESULTS

DISCUSSION OF RESULTS

THE OXIDATION OF BENZENE HOMOLOGUES

Since the equilibrium in which peroxytrifluoroacetic acid is formed is set up instantaneously,

$$(CF_3CO)_2O + H_2O_2 \rightleftharpoons CF_3COOOH + CF_3COOH$$

it was not necessary to preform it before mixing with the hydrocarbon solution. In later experiments, it was found that trifluoroacetic acid could be used instead of the anhydride. The yields were lower by one-third, but the same products were obtained, and its use cut out the losses incurred in preparing the anhydride.

It was found that a 30-40% conversion of alkyl benzenes into a mixture of phenols and quinone could be effected.

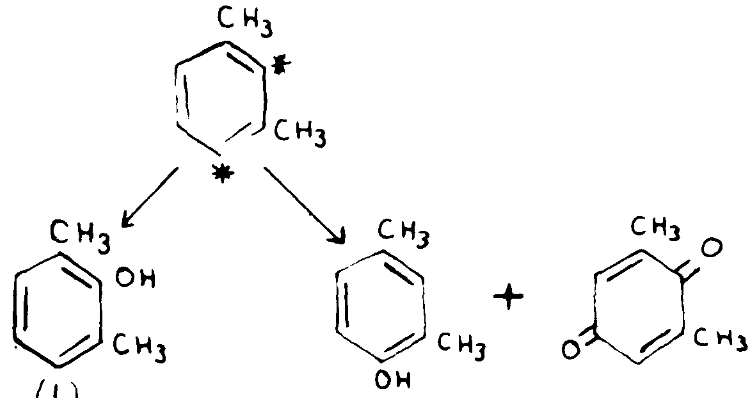
The aqueous layers yielded only trifluoracetic acid, and traces of a gum; no appreciable breakdown of the aromatic ring appeared to have occurred, otherwise, unsaturated acids would have been isolated.

Proof of the electrophilic oxidation came from the reactions with meta-xylene and pseudo-cumene (see FIGURE 1). In the former case, the products were meta-2 and meta-4 xylenols, (1 and 2 respectively), and meta-xyloquinone (3), in yields of 15%, 35% and 20% respectively, based on the amount of hydrocarbon used up.

Oxidation of pseudo-cumene gave 2,3,6 tri-methyl phenol (5), 2,4,5 tri-methyl phenol (6), and pseudocumoquinone (7).

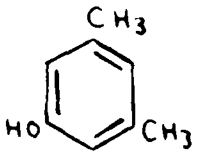
FIGURE 1.

meta-XYLENE



(1) (2) (3)

NO



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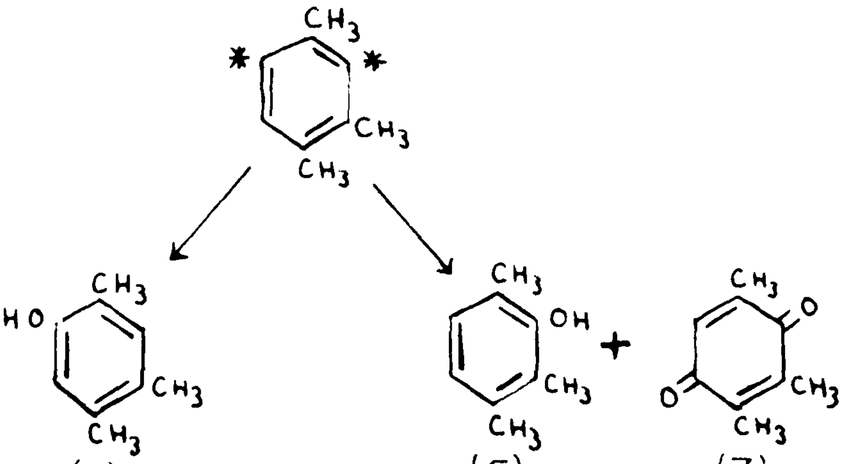
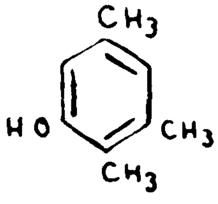
(4)

PSEUDO-CUMENE



(6) (5) (7)

NO



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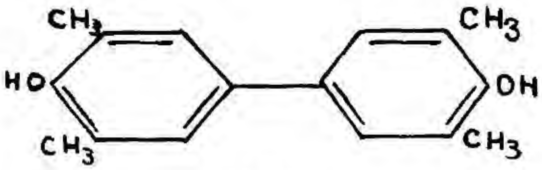
(8)

In FIGURE 1, the positions in the meta-xylene, and pseudo-cumene nuclei which are activated by <u>two</u> methyl groups, are indicated. It can easily be seen that the reaction products obtained, are those which arise from attack of these positions (indicated by stars). The absence of meta-5 xylenol (4), and 3,5,6 tri-methyl phenol (8) in the reaction products from meta-xylene and pseudo-cumene respectively, confirms that no free-radical process took place. In addition, if a free-radical process had been operating, we would have expected to isolate dimers, and compounds arising from side-chain attack, e.g. Cosgrove and Waters[31] isolated (9) and (10) from the reaction of meta-2 xylenol with benzoyl peroxide.



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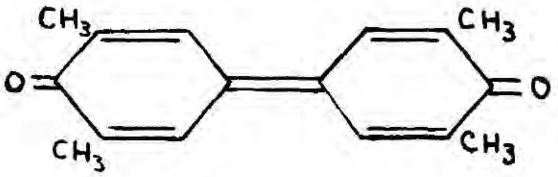
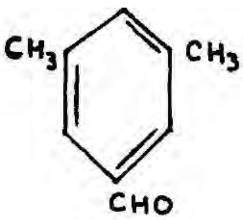
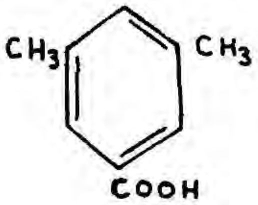


(10)

Booth and Saunders[32] isolated (11) and (12) from the oxidation of mesitylene with peroxidase plus hydrogen peroxide.



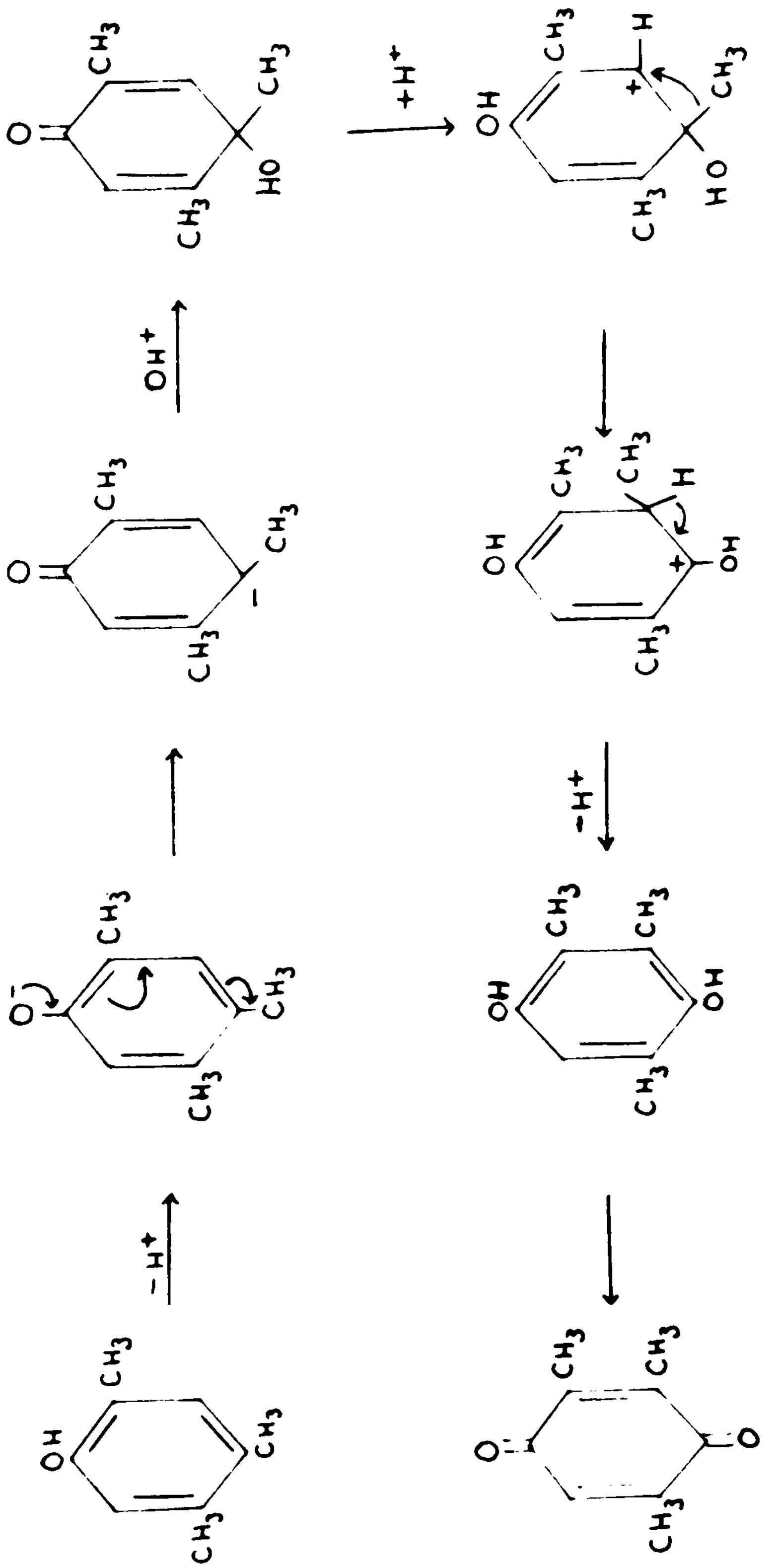
(11)



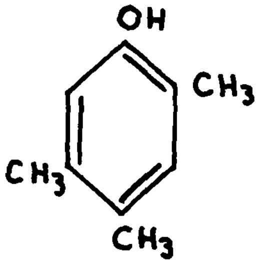
(12)

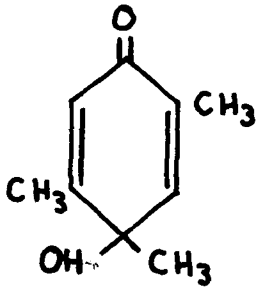
The reaction of peroxytrifluoroacetic acid with mesitylene gave mesitol in good yield, together with a small

FIGURE 2.



amount of pseudocumoquinone. The latter probably resulted from the formation and rearrangement of mesityl quinole. This compound itself was not isolated from the reaction mixture, but by treating 2,4,5 tri-methyl phenol (13) with peroxytrifluoroacetic acid, the ocrresponding 2,4,5 tri-methyl quinole (14) was isolated in about 10% yield. The mechanism for the complete reaction is probably as shown in FIGURE 2.

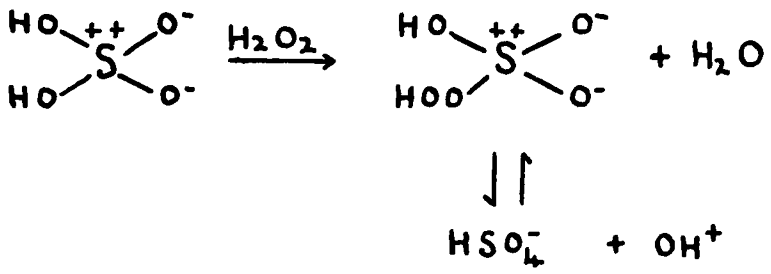

(13)


(14)

Derbyshire and Waters[47] effected electrophilic hydroxylation of mesitylene and other aromatic hydrocarbons by adding concentrated sulphuric acid to a mixture of the hydrocarbon and hydrogen peroxide, in acetic acid solution. They attributed this oxidation to an ionisation of the hydrogen peroxide under the strongly acid conditions, producing free hydroxyl cations i.e. rather than the production and ionisation of peracetic acid.

$$HO\text{-}OH \rightleftharpoons HO^{-} + OH^{+}$$

Cosgrove and Waters did not consider what appears to be an alternative explanation, the production and ionisation of Caro's acid.

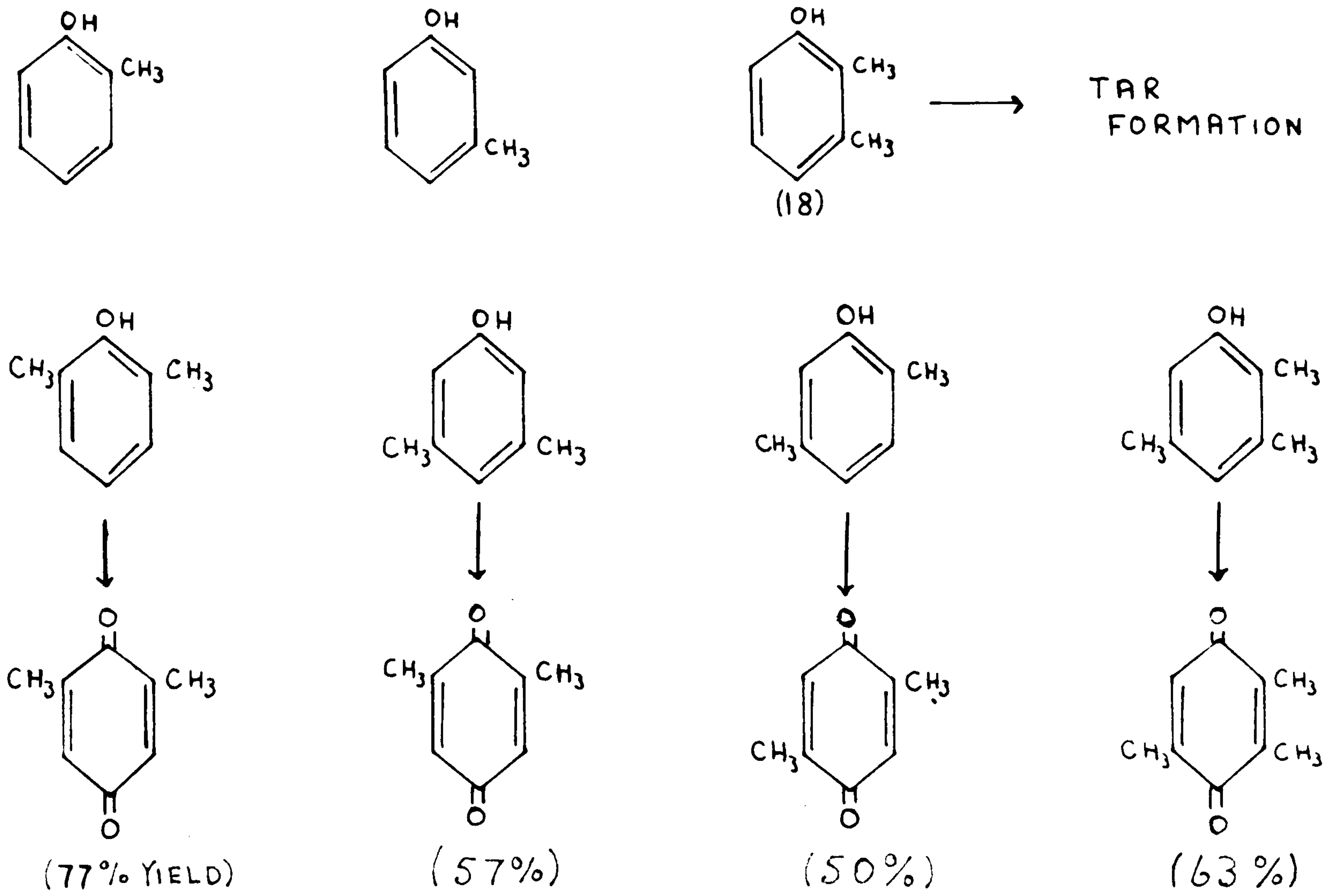


In the present series of reactions, the fact that the reaction products were the same, using either trifluoroacetic acid, or trifluoroacetic anhydride, and 'high-test peroxide' shows that the reaction process was the same in each case. Trifluoroacetic anhydride gave a greater yield of products than did trifluoroacetic acid, and it is obvious that in the reactions using the anhydride, peroxytrifluoroacetic acid had been formed, and ionised producing OH^+. If reaction had occurred via ionisation of hydrogen peroxide under the acid conditions, then trifluoroacetic acid would have given a greater yield of products than the anhydride.

OXIDATION OF PHENOLS

Bamberger[37] claims to have isolated very small amounts of tri-methyl quinole (14), and other quinoles by the oxidation of methyl phenols with Caro's acid. He was able to rearrange them in the presence of either acid or alkali but gives no experimental details; this has not been confirmed because other workers have not been able to repeat the preparation of the quinoles[31].

FIGURE 3.



In the present work, the phenols oxidised could be divided into three types.

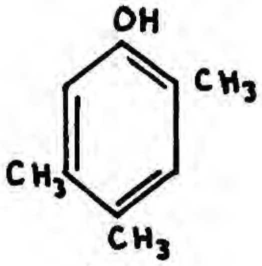
(a) Those giving a quinole.

(b) Those giving a quinone directly.

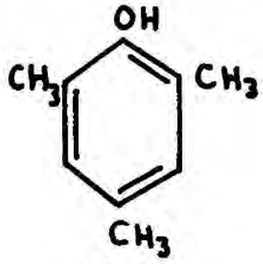
(c) Those giving tars.

(a) Oxidation of mesitol with peroxytrifluoroacetic acid did not yield any quinole; this reaction was complicated by the fact that mesitol is not strongly absorbed on alumina, and separation of pseudocumoquinone and tri-methyl phenol, from any quinole formed, was not very well defined. A red paste of unknown composition was obtained.

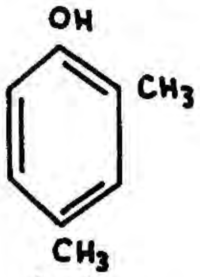
Since 2,4,5 tri-methyl phenol (13) easily yielded a quinole, but mesitol, and 2,4 di-methyl phenol (15 and 16 respectively) did not, the oxidation of 4,5 di-methyl phenol (17) should indicate which element of the structure of 2,4,5 tri-methyl phenol aids the production of a quinole.



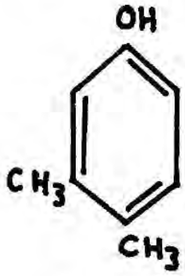
(13)



(15)



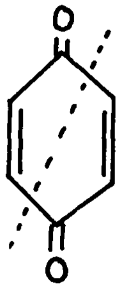
(16)



(17)

(b) and (c) FIGURE 3 shows the phenols which have been oxidised, and the quinones which were obtained from them. The cresols, and 2,3 di-methyl phenol (18) gave tars, while others gave excellent yields of quinones. It has not been possible to explain this on the basis of the stability of the quinone which is formed. Erdtman[55] investigated the stability of methoxy, and methyl substituted quinones, by their reaction with acetic anhydride plus concentrated sulphuric acid; and by treating with acid and alkali.

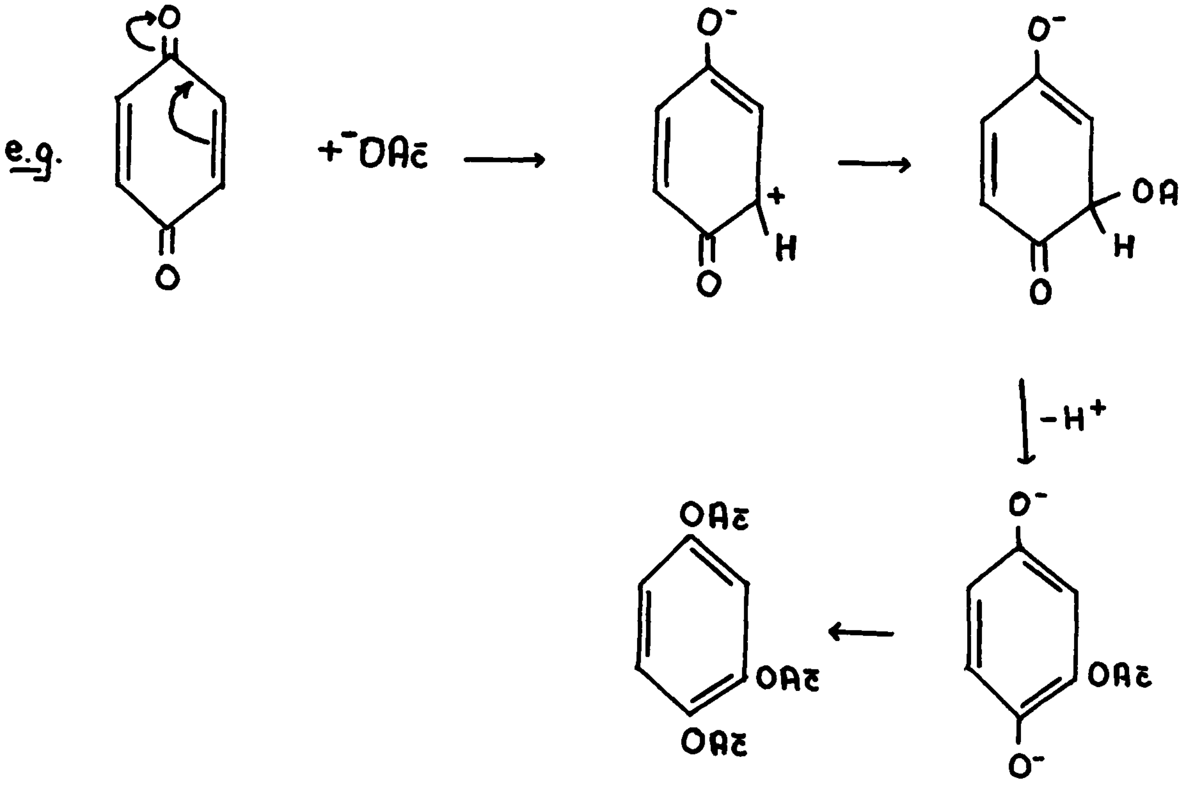
Erdtman[55] has described a quinone as two keto-enoid systems, of the type (19), and the effect of substituents on



(19)

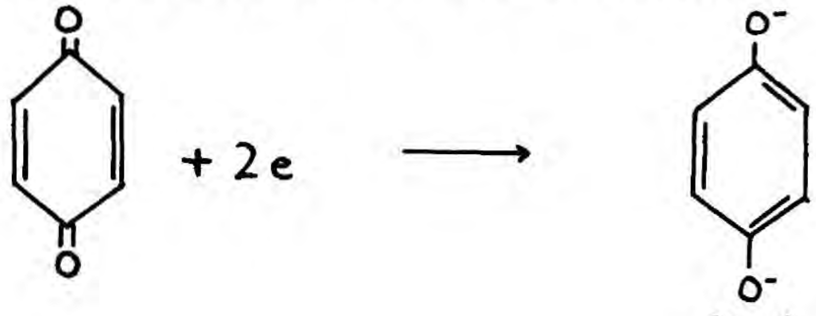
the reactivity of the quinone nucleus depends on the polarisation of the two attached conjugated systems.

The reaction of acetic anhydride (plus sulphuric acid) carried out by Erdtman on quinones, was simple addition of acetic anhydride.



Reduction takes place during this process, since the transformation of a quinone to the di-anion of a hydroquinone (20), requires the addition of two electrons.

<u>i.e.</u>



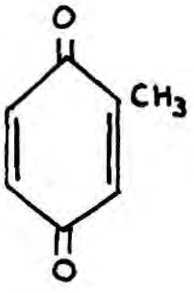
(20)

The redox potential of a quinone is a measure of its oxidising power, and the tendency for this process to occur, since it is related to the free energy released.

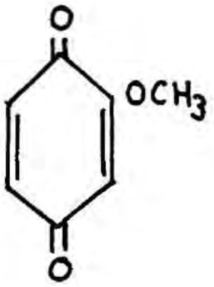
Since quinones are cationoid systems i.e. have a tendency to attract electrons, they are stabilised by electropositive substituents (capable of releasing electrons), whereas the hydroquinone di-anion is stabilised by electronegative substituents (electron attractors). Hence, methyl quinones tend to be more stable as the number of substituents increases.

Although this generalisation holds, the arrangement of the substituents is obviously very important, because on this rests their effectiveness.

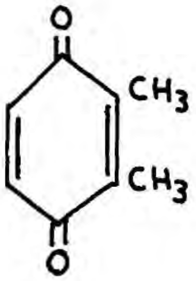
Erdtman found that toluqinone (21), and methoxy quinone (22) polymerised very easily with acid and alkali, and reacted immediately with acetylating mixture, to give a tri-acetate; 2,3 di-methyl quinone (23) was again sensitive to these reagents but the 2,5 and 2,6 isomers (24 and 25 respectively) were remarkably stable, particularly the 2,6 isomer (meta-xyloquinone).



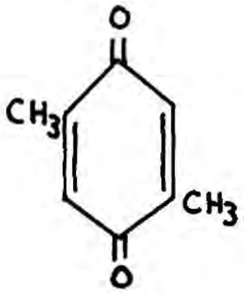
(21)



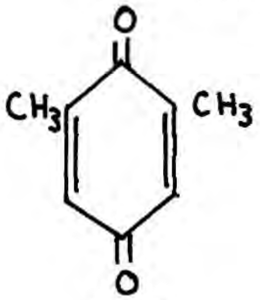
(22)



(23)

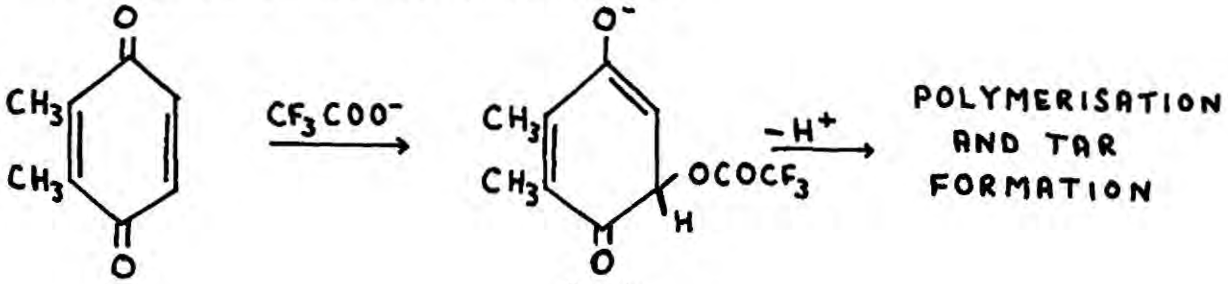


(24)



(25)

The instability of toluquinone, and 2,3 di-methyl quinone can be explained on the basis of being unsymmetrical and the attack could be envisaged:-



(26)

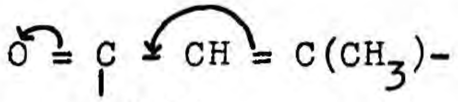
To predict any mechanism for the polymerisation occurring after the stage (26), to product tars, would be merely conjecture. The important point is that the factor determining whether tars are formed or not appears to be whether a system

$$O = \underset{|}{C} - CH = C\underline{H}-$$

(27)

is available for the final expulsion of the hydrogen atom underlined, as a proton.

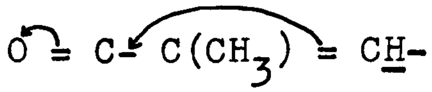
The system



$$O = \underset{|}{C} - CH = C(CH_3)-$$

(28)

obviously leads to stability, as shown in the case of 2,5 di-methyl quinone (24). At first sight, there appears to be no reason for the stability of 2,6 di-methyl quinone (25) (meta-xyloquinone) because although one of the systems is stabilised by this means, there is at the same time, another system



$$O = C - C(CH_3) = C\underline{H}-$$

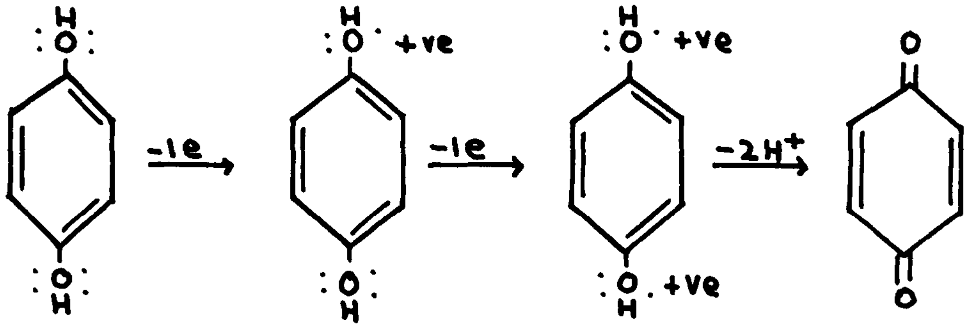
(29)

which might be capable of conjugation as shown, and the final expulsion of a proton.

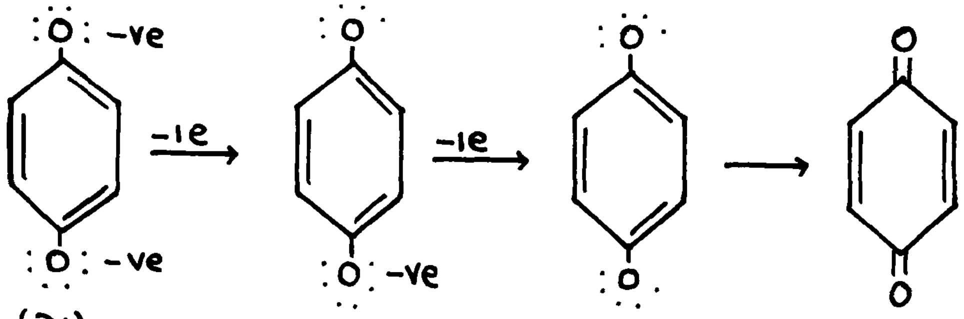
Erdtman gave no explanation for the stability of 2,6 di-methyl quinone. The fact which was not appreciated at that time, is that a methyl substituent in a keto-anoid system (27) can conjugate with the carbonyl group, whether attached to the alpha, or beta carbon atom (with respect to the carbonyl group). Thus, in (29), the alpha methyl group would prevent the polarisation indicated (which would result in the elimination of a proton).

Colour Formation

In the oxidation of a hydroquinone to a quinone, whether the oxidation occurs from the unionised hydroquinone (30), or the di-anion (31), the intermediates are free-radical in nature.



(30)



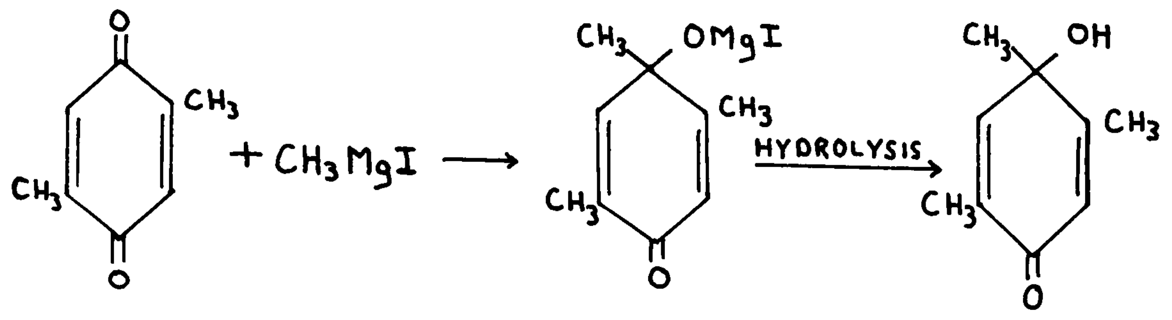
(31)

These intermediates (semiquinones) are analogous to the highly coloured Wurster salts, and account for the intense colour changes produced during the oxidation of phenols with peroxytrifluoroacetic acid.

The phenols with methyl groups para to the hydroxyl group did not exhibit the full colour sequence. This was obviously because oxidation progressed through quinoles, and these rearranged very slowly to the hydroquinone, whose subsequent oxidation produces intense colour.

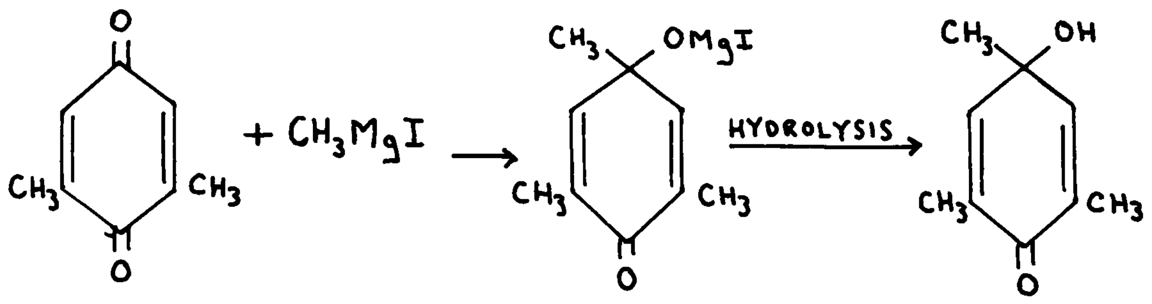
Reaction of Grignard Reagents and Quinones

Bamburger and Blangey[54] obtained a small amount of 1,2,5 tri-methyl quinole by the reaction of methyl magnesium iodide, and para xyloquinone.



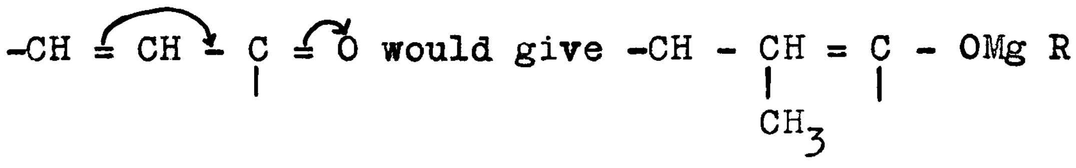
This reaction has been repeated in connection with the present investigation. The products were eluted over alumina, and some quinole was isolated; in addition to the quinole, a quantity of white needles (m.p. 214°C) was obtained. Thus, it seems obvious that dimerisation had occurred, but the constitution of the material is still unknown.

The reaction of methyl magnesium iodide, and meta-xyloquinone gave a very small amount of 1,3,5 tri-methyl quinole,



and some high melting material.

Perhaps similar considerations apply in these reactions as apply in the oxidation of phenols. Any fully conjugated system of the type



$$-CH = CH - \underset{|}{C} = O \text{ would give } -CH - \underset{\substack{|\\ CH_3}}{CH} = \underset{|}{C} - OMg\ R$$

with a grignard reagent, but if the conjugation were reduced by the introduction of an electron donor into either the alpha or beta position (with respect to the carbonyl group) then the carbonyl group should polarise simply to give $>\overset{+}{C}-O^{-}$, and this would yield the quinole.

Suggestions for Further Work

1. The reaction of quinones with grignard reagents appears to involve an abnormal reaction to give some dimeric products, this field is worth pursuing.

2. Peroxytrifluoroacetic acid oxidised benzotrichloride quantitatively to benzoic acid but benzotrifluoride was not effected. It would be interesting to attempt to oxidise amino- and hydroxy-benzotrifluoride in order to determine whether any trifluoroacetic acid is produced by the reaction.

Oxidation of Polycyclic Systems

Insufficient investigation has been carried out in this section to enable definite conclusions to be drawn. The oxidation of phenanthrene, and phenanthraquinone to diphenic acid is in agreement with the manner in which we would expect an electrophilic reagent to react with these systems.

Future Work

1. It is evident that a careful investigation of the oxidation of 1,2 benzanthracene would be very valuable.

CHAPTER III

EXPERIMENTAL

EXPERIMENTAL

SECTION 1:- THE OXIDATION OF BENZENE HOMOLOGUES

Previous workers have carried out reactions by dropping the reactant into pre-formed peroxytrifluoroacetic acid. Some initial experiments in this investigation were carried out on anisole, in an attempt to effect hydroxylation. At first, the pre-formed peracid was dropped slowly into a mixture of anisole and chloroform; these conditions proved to be too drastic, because the product was a dark, viscous tar.

The procedure was adopted, of preparing the peracid 'in situ'; 'high-test peroxide' (85% hydrogen peroxide) was added slowly to a mixture of trifluoroacetic anhydride, anisole, and chloroform. Under these conditions, guaiacol (ortno-methoxy phenol) was identified amongst the reaction products. Similarly, mesitylene yielded some mesitol.

Methylene chloride was next used as a solvent, and milder conditions were obtained by maintaining the reaction flask immersed in an ice-bath contained in a dewar-flask. It was found that trifluoroacetic acid could be used instead of trifluoroacetic anhydride, a lower yield of products being obtained.

Under these mild conditions, mesitylene yielded crude mesitol, but reaction with pseudo-cumene, and meta-xylene produced dark red oils. These oils had very high boiling points. By distilling under vacuum, using a multiple receiver-adaptor, several fractions were obtained; these varied in shades of red, and in some cases, partially crystallised. An extensive black residue was left in the distillation flask in each case.

Phenols and quinones are known to interact, forming pheno—quinones. It was believed that the red oils constituted such a mixture. Smith and his co-workers[49] reported the formation of red oils (pheno-quinones) in the preparation of quinones from phenols (via the amino-phenol), and were unable to separate them; distillation was particularly ineffective. The infra-red absorption spectra of the oils produced from pseudo-cumene and meta-xylene, confirmed the presence of carbonyl and hydroxyl groups (either free or hydrogen bonded).

It was confirmed that the red oils were not simply quinhydrones (mixtures of quinones and hydroquinones) since attempts to oxidise them completely to quinones were unsuccessful. Oxides of nitrogen, chromic acid, and manganese dioxide were used as oxidising agents for this purpose.

Thus, the problem resolved itself into the development of a method for separating phenol-quinones mixtures. Authentic mixtures were made up, and a resolution was sought by means of liquid elution chromatography; paper

Paper Chromatogram

(One-way)

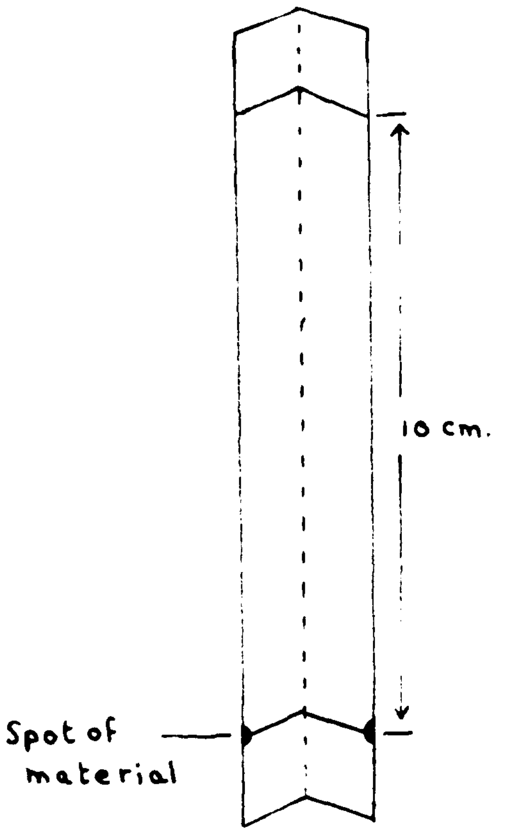
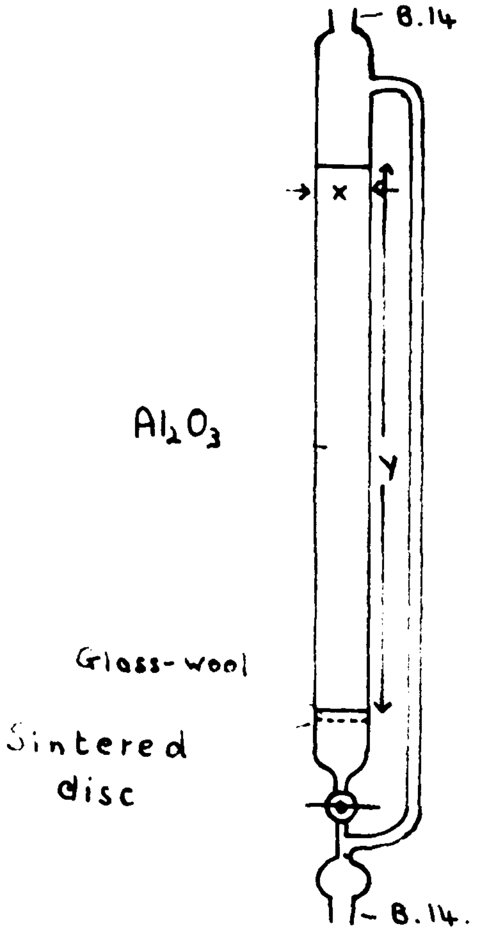


FIG. 2.

Liquid Elution.



Column 'A'

X = 2 cm. Y = 44 cm.

Column 'B'

X = 1·3 cm. Y = 24 cm.

FIG. 1.

chromatography being used as a quick means of comparing different eluting solvents on the mixtures. Using an alumina column, it was possible to separate quinones and phenols from quinone-phenol mixtures, using light petroleum ether (b.p. 40-60^{o}C), benzene, or methylene chloride as eluent; apart from mesitol, the phenols investigated could not be removed quantitatively from the column. Deactivating the alumina rendered separations impossible.

It was decided to analyse the mixtures with the aid of high temperature Vapour-phase Chromatography. The reaction products did not lend themselves easily to Vapour-phase Chromatography and, in addition, it has been shown that quinones and phenols interact enough to prevent separation by this means. The problem was overcome by methylating the mixture; the methyl ethers so formed were ideal for analysis and separation by Vapour-phase Chromatography.

It was not possible to confirm the mechanism of reaction by hydroxylation of toluene because, under conditions necessary to cause reaction to occur, the toluene reacted vigorously, with much breakdown, to give a complex reaction product which was not easy to separate. Benzene behaved similarly.

Liquid Elution Chromatography

The columns were constructed as shown in FIGURE 1. When the apparatus was clean and dry, a plug of glass wool was placed above the sintered disc, and a slurry of alumina in the eluting solvent, was added. The column was tapped with a piece of rubber tube after each small addition, this prevented air-bubbles being formed (air-bubbles, and breaks in the column give rise to chanelling, and hence non-uniform bands).

The inclusion of a tap in the construction, enabled a column of alumina which had been made up from a slurry, to be kept for a short while before use, without running dry. When the first fractions had been eluted from the column, the apparatus could be fitted up as a soxhlet extractor in order to remove strongly absorbed components. Even continuous extraction in this manner with methyl alcohol was not sufficient for quantitative recovery of the phenols investigated.

Paper Chromatography

Method 1. The Rf value (the distance moved by the component divided by the distance moved by the solvent during elution) of a component for a particular eluent can be determined quickly and simply: a strip of chromatography paper is folded, taking care not to touch the paper with the fingers (FIGURE 2); a line is drawn across the paper a short distance from one end, and another line is drawn parallel to it, 10 cms. away. A spot of material is placed at each edge of the paper, just sufficient to show on the other side, and the paper is then placed in a measuring cylinder containing the eluent, the level not being sufficient to reach the spots. The cylinder is closed by a rubber bung and the paper developed until the solvent front has reached the second line. At this stage, the paper is removed, dried, and the distance from the starting line represents the Rf value of any components.

Method 2. In the 'two-way' method a square of paper is cut and a spot of material is placed at a suitable distance (the origin) diagonally from one corner. The paper is then laid with one edge immersed in a trough of solvent contained in a glass tank; the lid is replaced, and downward elution commenced. After the solvent front has reached a convenient distance from the origin, the paper is removed, dried, and re-eluted in the same manner, but using a different eluent, and developing in a direction at right-angles to the original direction. This technique has been applied to a remarkable extent in the elucidation and separation of complex mixtures of amino-acids.

Both the methods described were used with a variety of eluting agents, in an attempt to separate the components of the red oils. Diazotised sulphanilic acid, and ammoniacal silver nitrate were used as spot-tests to detect phenolic components.

Little, or no success was achieved in effecting an actual separation, the original spot moved as one in all cases. The one exception to this was an elution with benzene in an atmosphere of ammonia. Here, a purple spot was left behind; this probably arose from some hydroquinone.

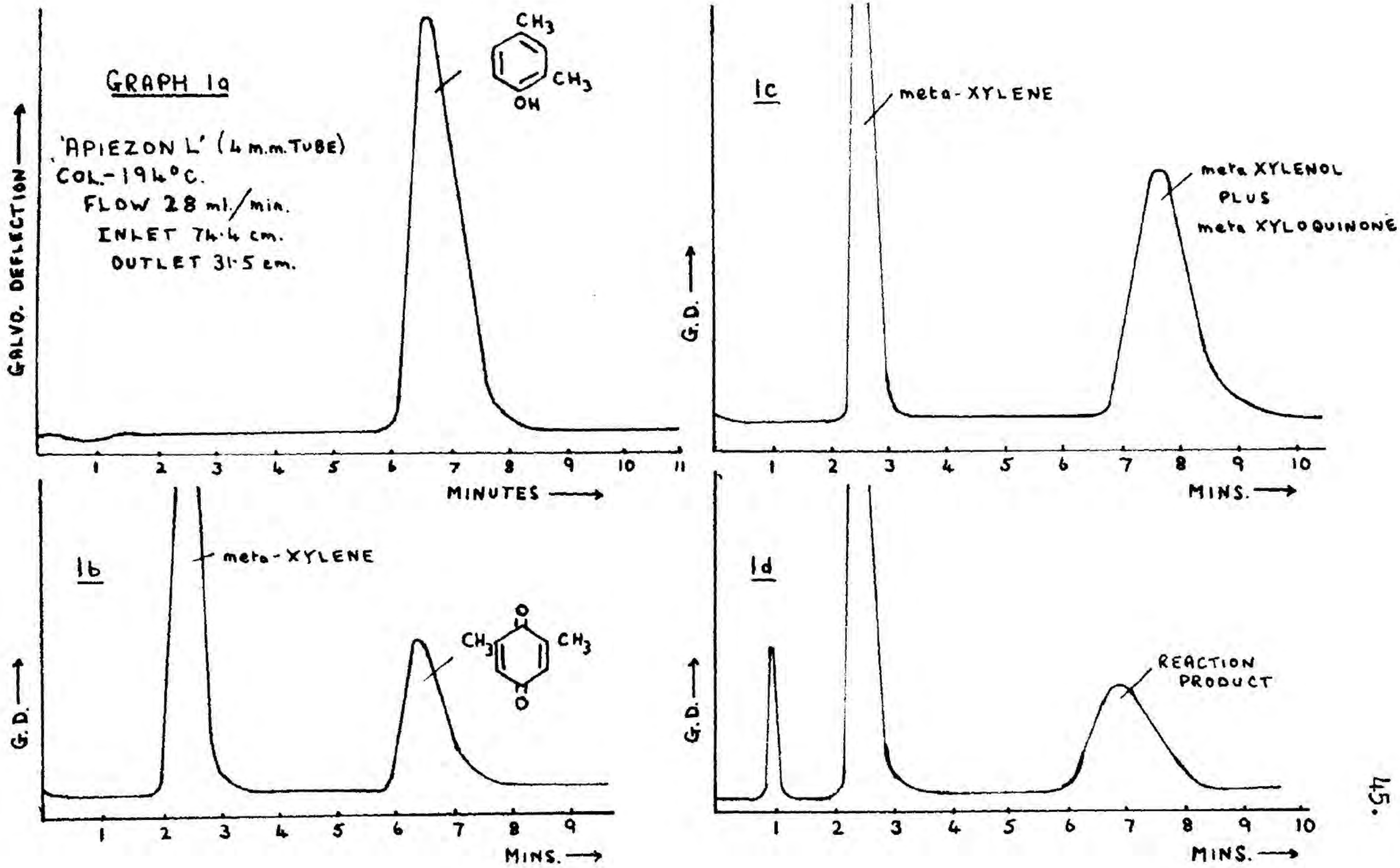
Elution Chromatography of Authentic Components.

Samples of 2,4,5 tri-methyl phenol, tri-methyl quinone, and tri-methyl hydroquinone were eluted separately over alumina (Column A), using methylene chloride, and benzene as eluting agents. Only the tri-methyl quinone could be recovered quantitatively from the column.

2,4,5 tri-methyl phenol could be removed in small amounts by using the column as a continuous extractor, and refluxing for several hours; the sample could not be recovered quantitatively.

When tri-methyl hydroquinone (0.2gm.) was eluted, the eluent gradually became yellow. Elution was continued until the eluent had become pale yellow again (430 ml. of eluent had emerged from the column). Continuous extraction was not employed, in order to simplify the process; thus eliminating any effects (oxidation) caused as a result of heating. On evaporating the solvent, a yellow oil (0.15 gm.) remained, which did not give a silver mirror with ammoniacal silver nitrate, showing that no tri-methyl hydroquinone was present (a positive test was obtained with the starting material).

Thus, the hydroquinone must have been oxidised to


GRAPH 1a
'APIEZON L' (4 m.m. TUBE)
COL.-194°C.
FLOW 28 ml./min.
INLET 74·4 cm.
OUTLET 31·5 cm.
GALVO. DEFLECTION
CH3
CH3
OH
MINUTES
1
2
3
4
5
6
7
8
9
10
11
1b
meta-XYLENE
CH3
CH3
O
O
G.D.
MINS.
1c
meta-XYLENE
meta XYLENOL
PLUS
meta XYLOQUINONE
G.D.
MINS.
1d
REACTION
PRODUCT
G.D.
MINS.

quinone on the column during elution.

Elution of an authentic mixture of tri-methyl quinone and 2,4,5, tri-methyl phenol did not yield a quantitative recovery of quinone; approximately half the quinone was recovered.

Vapour-phase Chromatography of Phenol-Quinone Mixtures

Compound formation between phenols, and quinone is a well known phenomenon; pheno-quinones are produced, which can be liquids, or solids corresponding to definite compounds.

When meta-xyloquinone (yellow solid, m.p. 73°C), is added in equimolecular proportions to meta-4 xylenol (white solid, m.p. 65°C), the mixture produced, is a viscous, dark red oil.

During Vapour-phase Chromatography, the interaction between components in a mixture is often observed. Their mutual solubilities have an effect which causes the individual peaks to be unsymmetrical, as compared with the peaks produced by injecting pure samples.

Cases have been reported where individual retention times have been altered slightly by incorporating components into a mixture; but no example of a phenomenon akin to azeotrope formation in distillation, has been reported.

GRAPHS 1a, and 1b are the chromatograms of pure meta-4 xylenol, and meta-xyloquinone respectively;

GRAPH 1c was obtained from an authentic mixture of meta-xyloquinone (0.5 gm.), meta-4 xylenol (0.7gm.), and meta-xylene (0.7 gm); GRAPH 1d is a chromatogram of the reaction products obtained from the methylene chloride layer in an oxidation of meta-xylene.

It can be seen that only one peak is obtained in the chromatograms of these mixtures, and at a retention time much later than those of the individual components.

That considerable interaction occurs, is clearly shown from a chromatogram of the meta-xylene reaction products: the products contain meta-2 and meta-4 xylenols, whose individual peak maxima would be clearly defined in a chromatogram obtained from a simple mixture of the two phenols; and the two peaks would cover a considerably greater area than that covered by the third peak in GRAPH 1d

meta-XYLENE.

A. Using Trifluoroacetic Acid Plus Hydrogen Peroxide as Oxidant:-

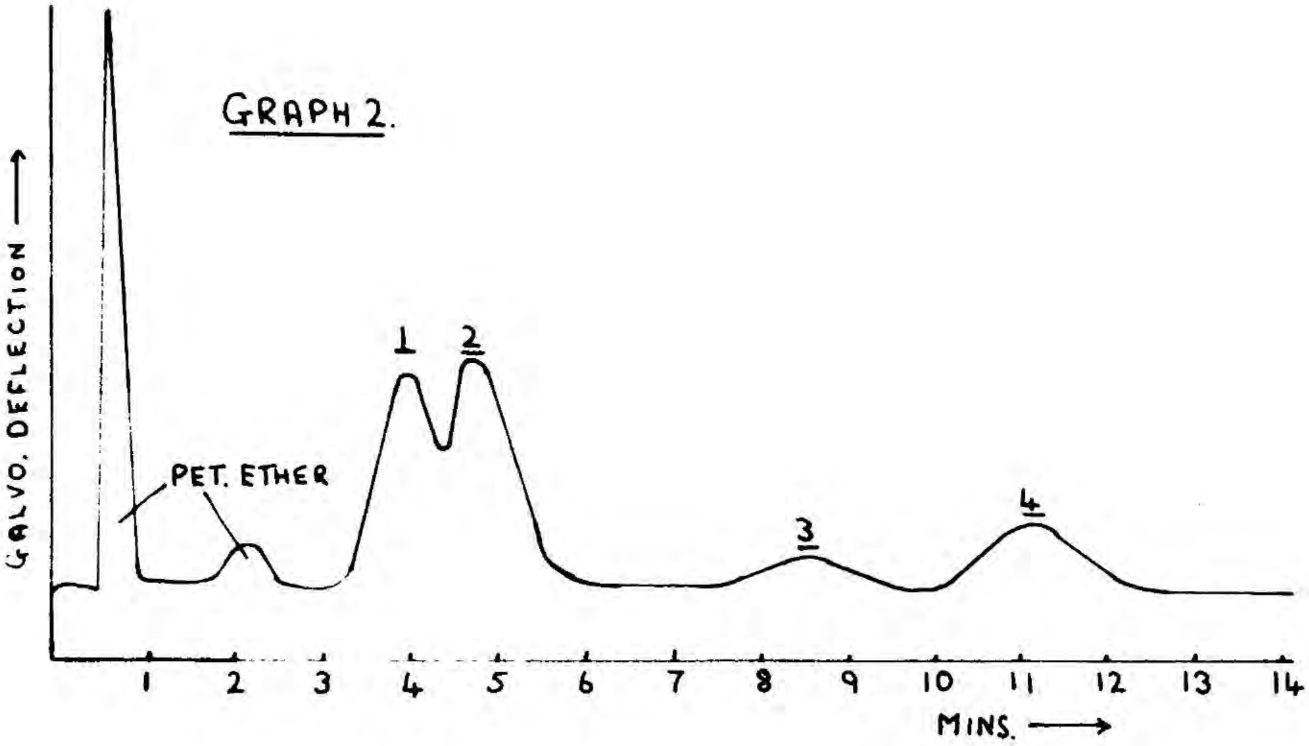
A mixture of meta-xylene (12.9 gm. - 0.12 mole), and trifluoroacetic acid (20.2 gm. - 0.18 mole.) in methylene chloride (50 mls) was maintained well stirred, and cooled by crushed ice contained in a dewar flask; 'high test peroxide' (5.3 mls.) was added, dropwise, over a period of half an hour (5.3 mls. weighs 6.3 gm., and being 85% hydrogen peroxide, this corresponds to 0.19 mole.). After 24 hours, the mixture was neutralised by the addition of solid sodium hydrogen carbonate; a small amount of water was added to the mixture to aid the process.

When neutralised, the layers were separated, and the aqueous layer was extracted several times with methylene chloride, the extracts being added to the initial methylene chloride layer.

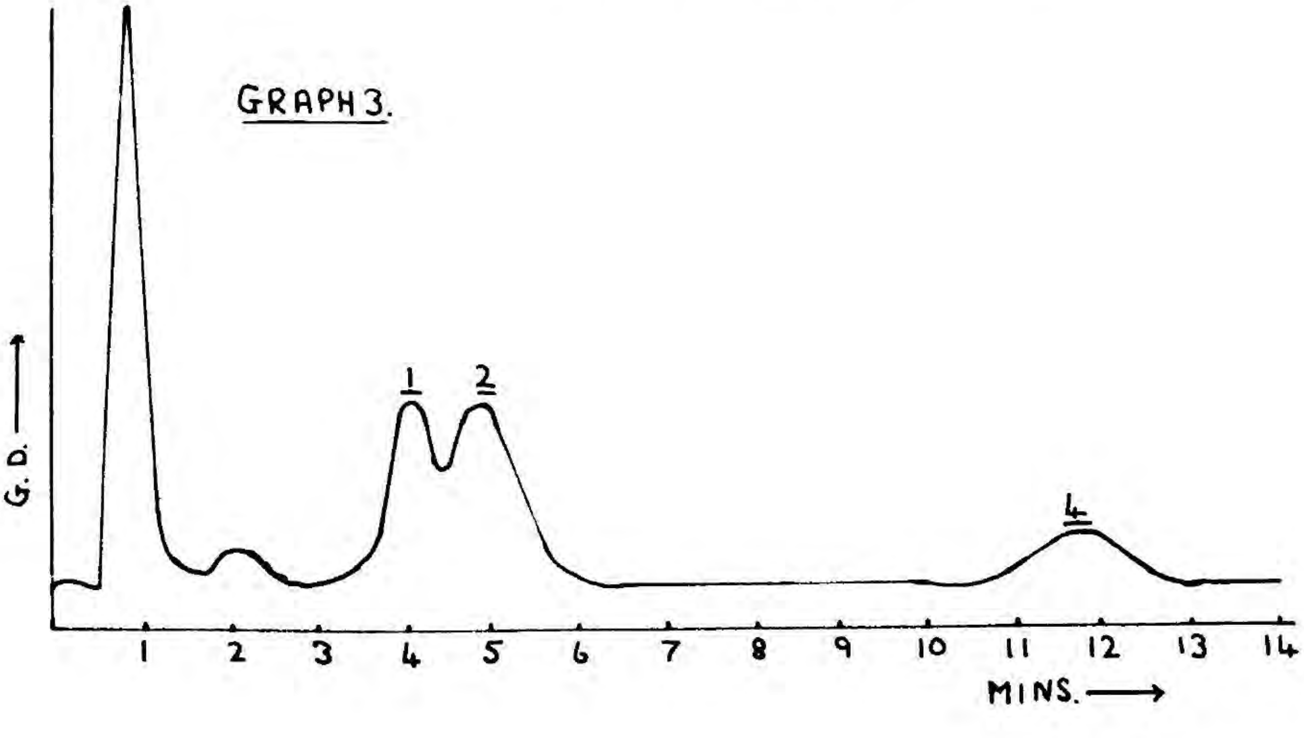
Aqueous Layer: After re-acidifying with dilute sulphuric acid, the layer was continuously extracted with methylene chloride. The methylene chloride was removed by distillation, leaving a dark residue containing trifluoroacetic acid, which had been extracted by the process; the trifluoroacetic acid,was removed by warming under high vacuum, and only a minute amount of a gum remained. Thus, there were no di-carboxylic acids formed by breakdown of the aromatic system.

Methylene Chloride Layer: Methylene chloride was removed by distillation, and then the meta-xylene was removed, as far as possible, under reduced pressure, using an oxygen-free nitrogen 'air leak'. 6.3 gm. of meta-xylene was recovered, and 3.3 gm. of a red oil remained.

There is a tendency for meta-xylene to form an azeotrope with methylene chloride, and it is thus not possible to account for all of the meta-xylene. In a further experiment, meta-xylene in the methylene chloride distillate was estimated by Vapour-phase Chromatography.


GRAPH 2.

GRAPHS 2 and 3 :- 'APIEZON L' (4 m.m. TUBE)
COL.-196°C. FLOW - 30 ml./min.
PRESS. DROP OVER COLUMN - 42cm.


GRAPH 3.

By this procedure, it was possible to account for all of the starting quantity of meta-xylene.

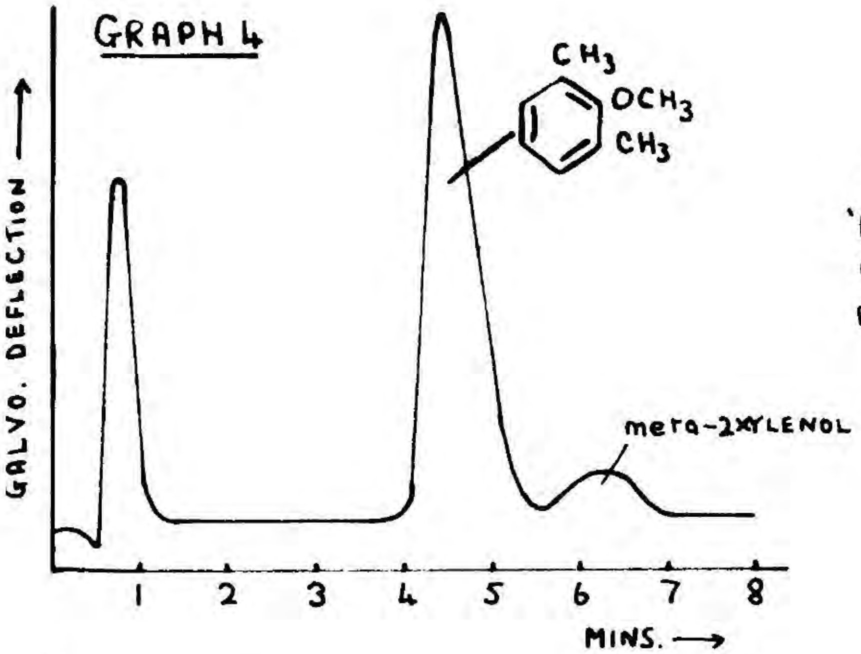
Methylation: The red oil (3.3 gm.) was dissolved in methyl alcohol (6 ml.), and dimethyl sulphate (3 gm.) was added. Whilst being well stirred, the mixture was cooled to -5°C and a 2:1, water-sodium hydroxide solution was added (7 gm.). A vigorous reaction occurred, which quickly subsided.

After removing the freezing mixture, the reaction vessel was gradually warmed; and finally, the mixture was refluxed over a small bunsen flame for one hour. On cooling, water was added, and the mixture was extracted several times with ether, the extract being very dark. Removal of the ether left 2.5 gm. of a dark liquid.

Vapour-Phase Chromatography of the Methylation Products: A chromatogram of the products (GRAPH 2) showed, apart from the peak corresponding to methylene chloride, the main peaks of equal area, 1 and 2; and two subsidiary peaks 3 and 4, in order of increasing retention time.

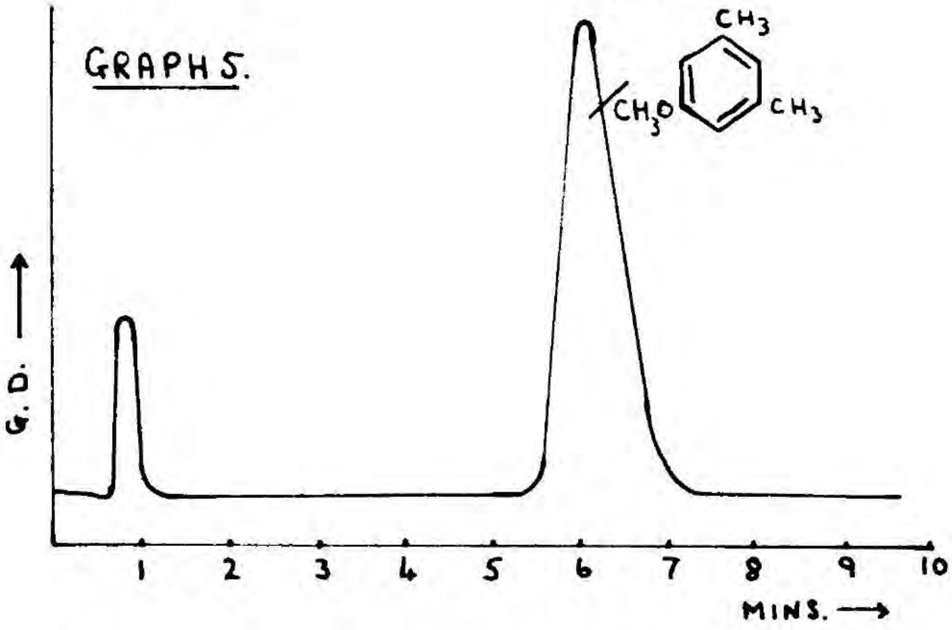
Elution over Alumina: 2.1 gm. of the methylation products remained, and this was eluted (Column A), with light petroleum ether; eluent was collected until coloured material began to emerge. Removal of the solvent left a colourless liquid (1.8 gm.) whose vapour phase chromatogram

GRAPH 4

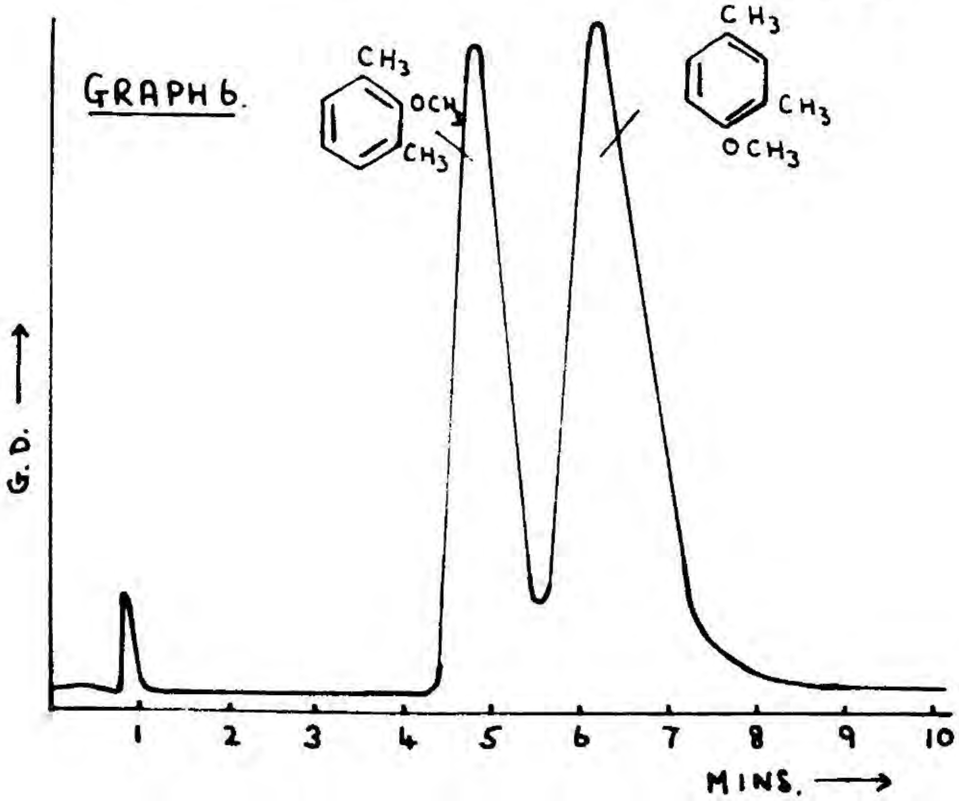


GRAPHS 4, 5, 6:-
'APIEZON L' (4 m.m. TUBE)
COL.-194°C. FLOW-24 ml/m.
PRESS. DROP. - 44·6 cm.

GRAPH 5.



GRAPH 6.



(GRAPH 3) showed peaks corresponding to <u>1</u> and <u>2</u> and <u>4</u>, but <u>3</u> was absent.

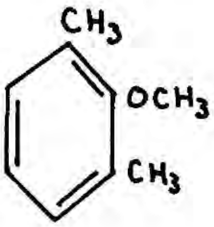
Identification and Isolation of meta-Xylyl Ethers.

Authentic 1 gm. samples of the three isometic meta-xylenols were dissolved in methyl alcohol, and methylated as described above. An average yield of 0.85 gm. of meta-xylyl methyl ethers were obtained after extracting the reaction mixture with ether, and then removing the ether by distillation.

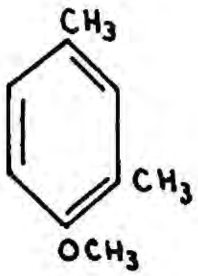
The products when distilled, still contained some unchanged meta-xylenols (GRAPH 4). It was necessary to elute over alumina in light petroleum ether, in order to remove this impurity since the retention times of the two components are too close for a convenient separation by vapour-phase chromatography.

After elution, a sample of each ether was further purified by Vapour Phase Chromatography, using the trapping system which has been described. Their infra-red spectra were characterised.

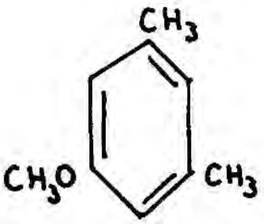
GRAPHS 5 and 6 show that the retention time of the methyl ether of meta-2 xylenol(1), differs from the retention times of meta-4, and meta-5 xylyl methyl ethers (2 and 3 respectively) which were approximately equivalent.



(1)



(2)



(3)

By a comparison of the retention times of the peaks in GRAPHS 2 and 3, with those of the authentic methyl ethers (GRAPHS 5 and 6), it was possible to identify peak 1 as meta-2 xylyl methyl ether. The retention times of both the meta-4 and meta-5 xylyl methyl ethers, coincided exactly with peak 2, and it was thus impossible to distinguish between them by this means.

The components corresponding to peaks 1 and 2 were condensed out from the rest of the mixtures, and a sample was submitted for carbon-hydrogen, and infra-red analysis.

Analysis;

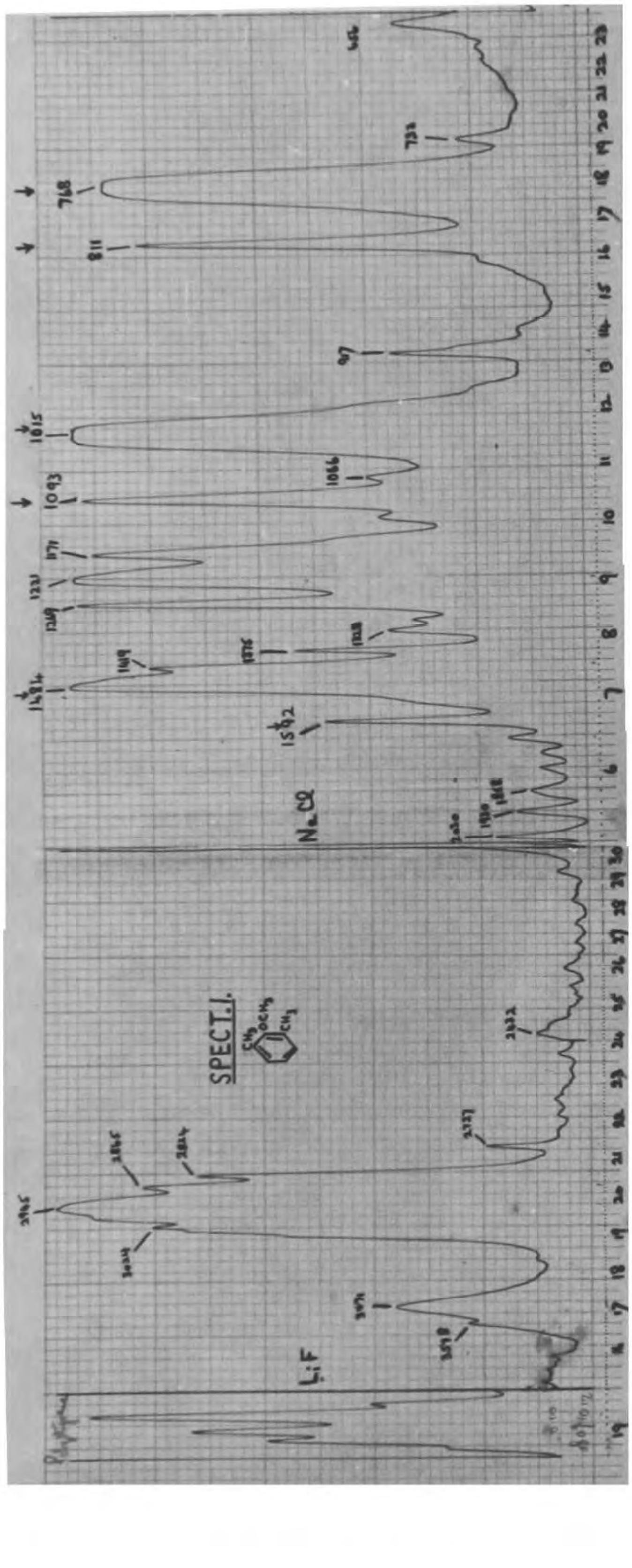
Calculated for $C_9H_{12}O_2$: C, 79.4%; H, 8.8%.

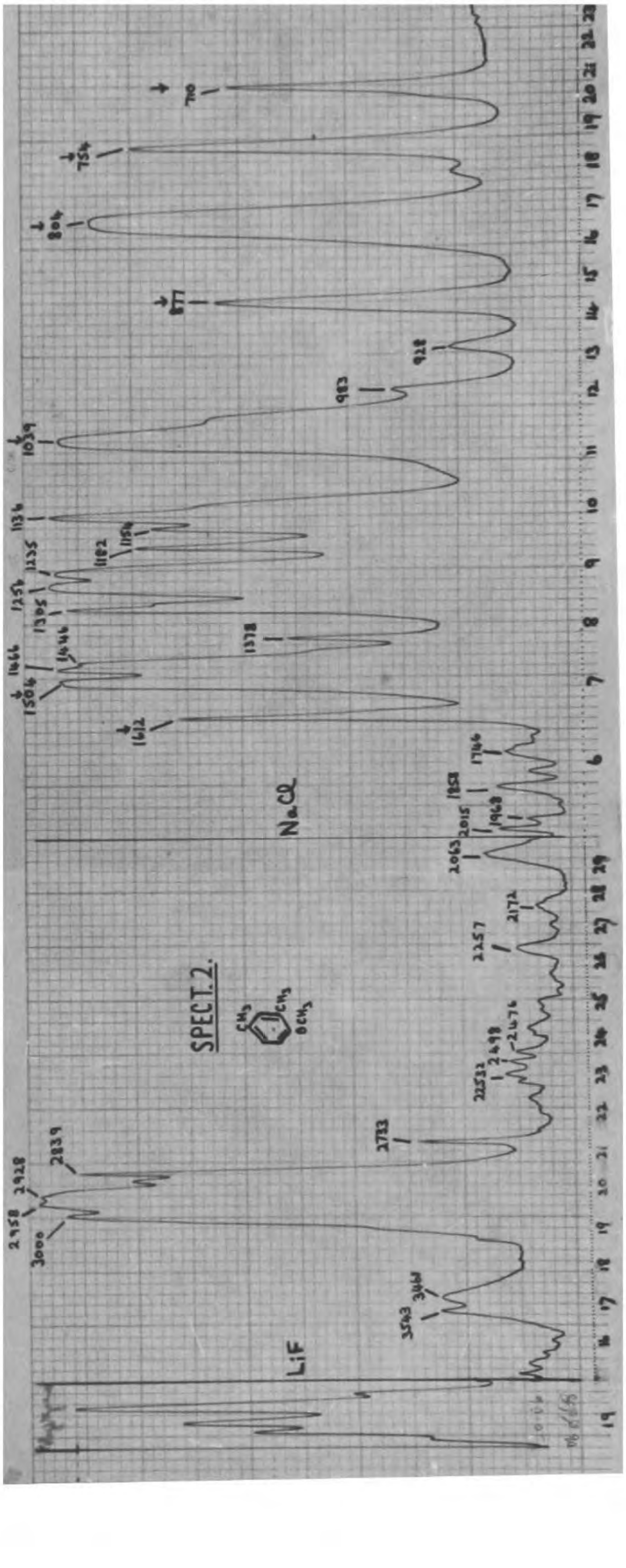
Found: C, 79.0%; H, 8.9%.

This analysis confirmed that the sample was a mixture of isomeric meta-xylyl methyl ethers.

By lowering the column temperature, it was possible to re-chromatograph the mixture (V.P.C.), and condense out a sample enriched in the component corresponding to peak 2.

A comparison of the infra-red spectra of the two samples condensed out, with the spectra of authentic methyl ethers,


SPECT.1.
LiF
NaCl
2945
3034
2865
2834
3571
3598
2727
2432
2020
1930
1868
1592
1484
1449
1376
1328
1249
1231
1171
1093
1066
1015
917
811
768
732
696


SPECT.2.
LiF
NaCl
3000
2958
2928
2839
3503
3448
2733
2522
2498
2476
2257
2172
2063
2015
1968
1851
1744
1612
1504
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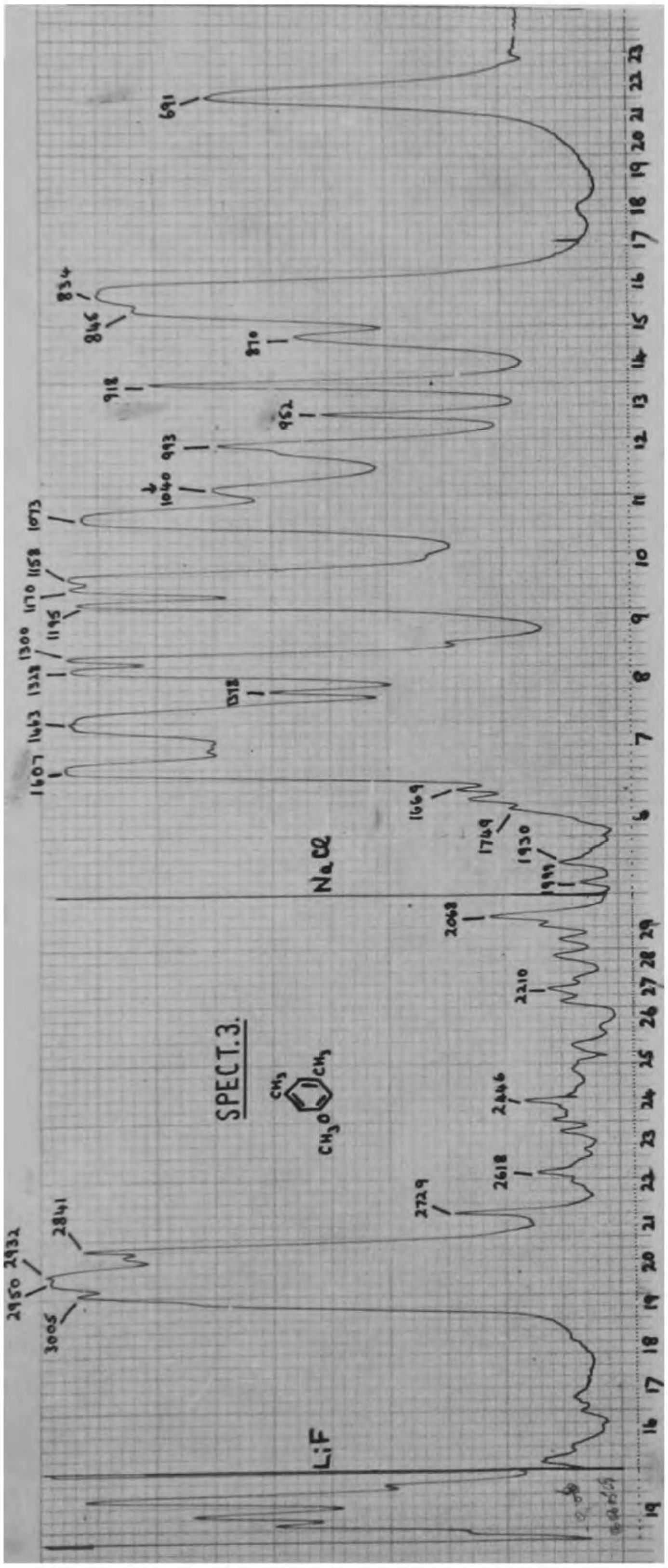
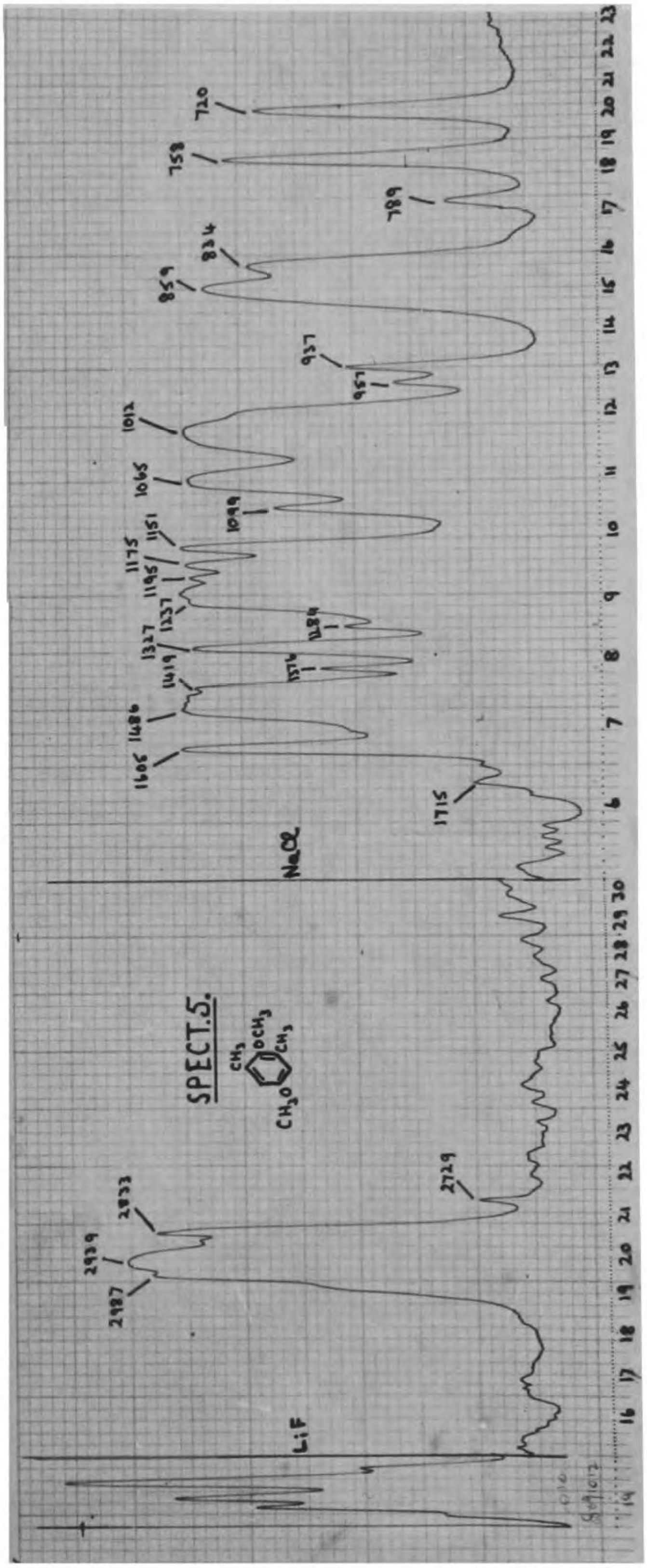
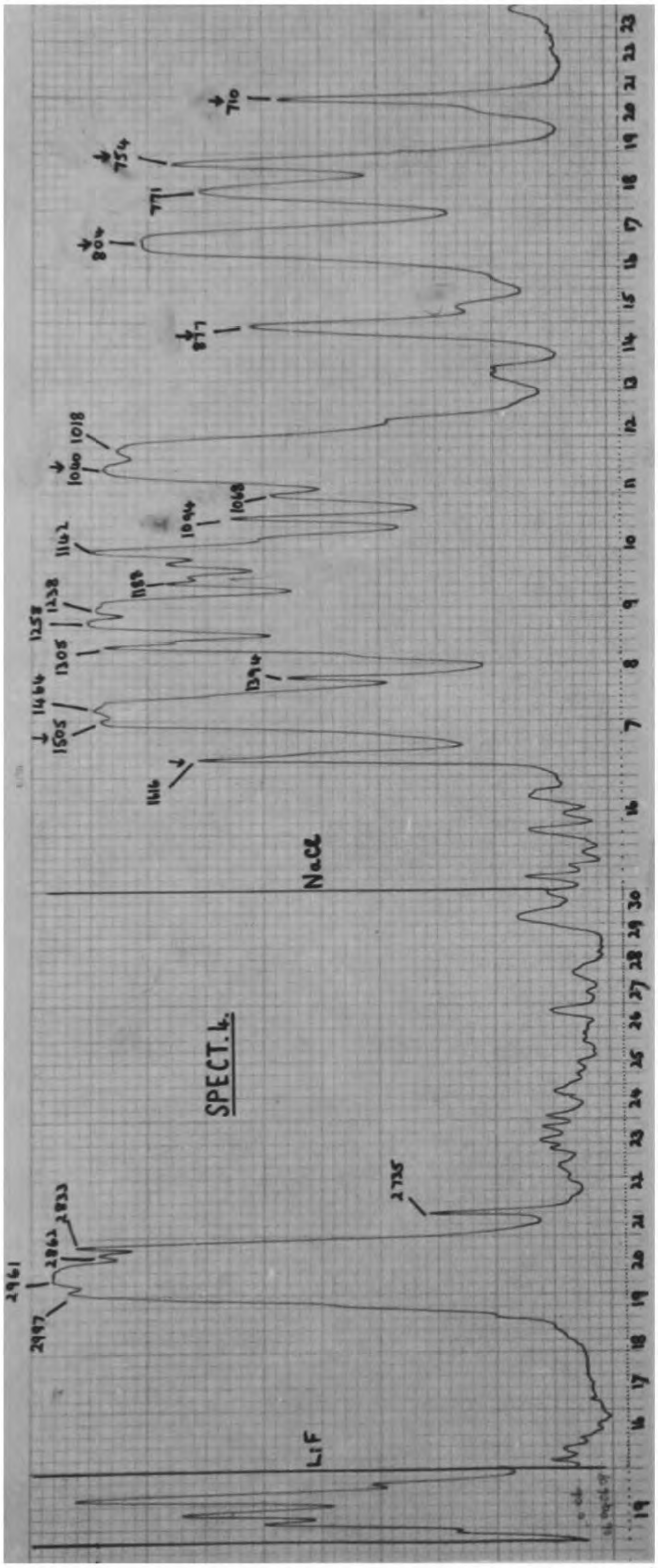
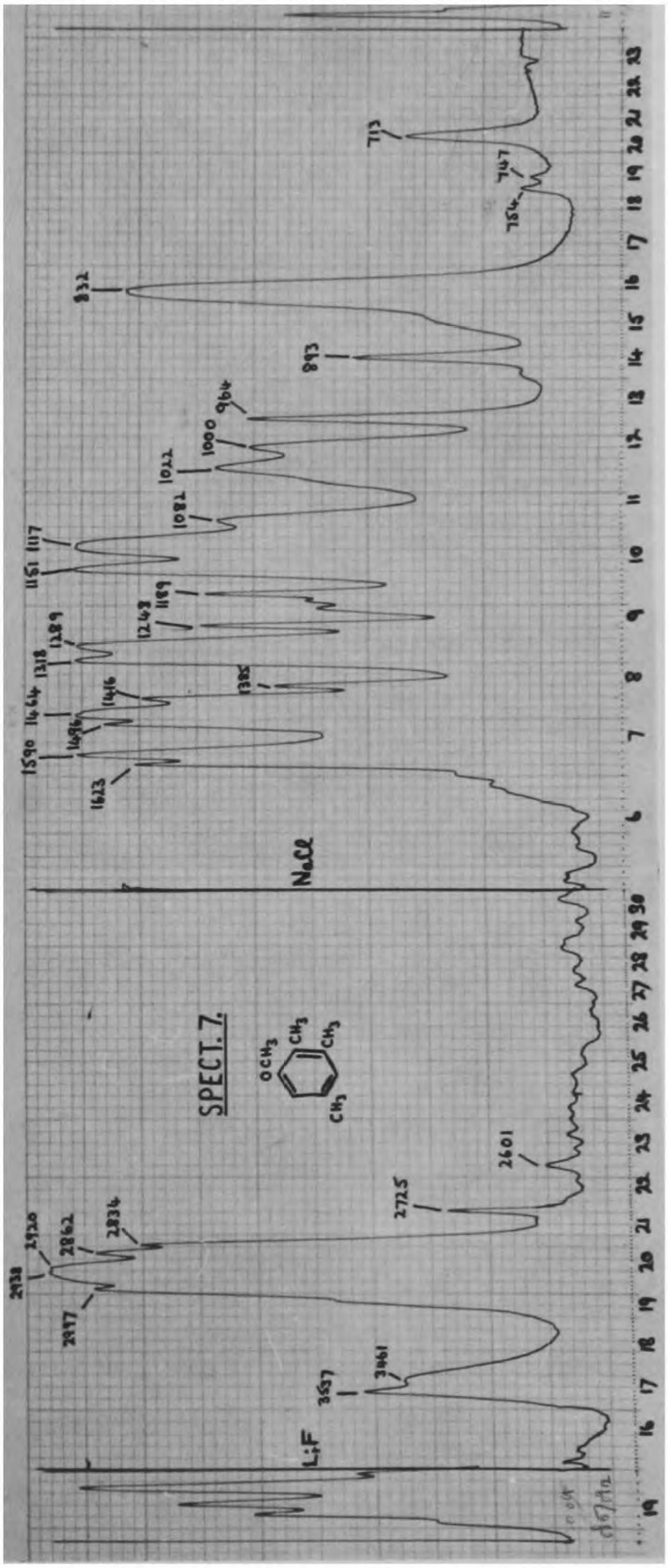
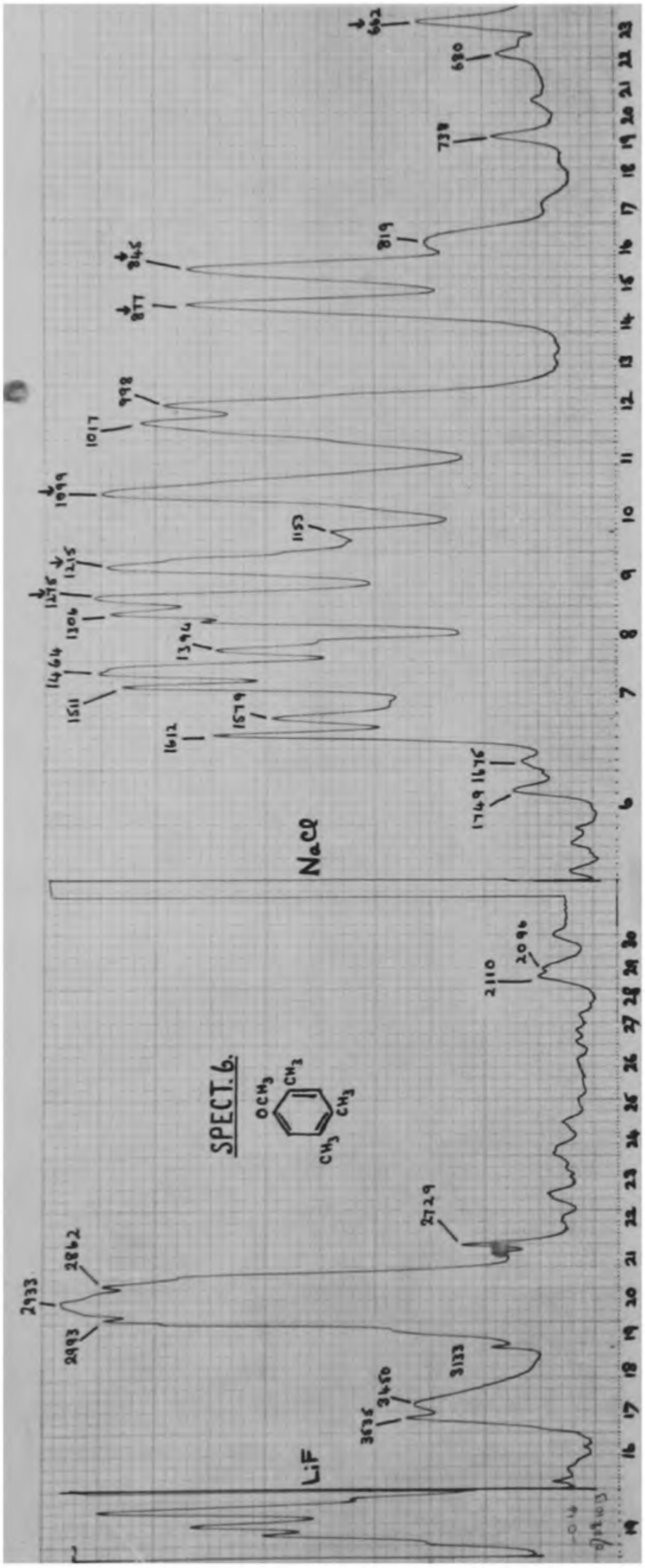
1235
1182
1156
1136
1039
1378
983
928
877
804
754
710

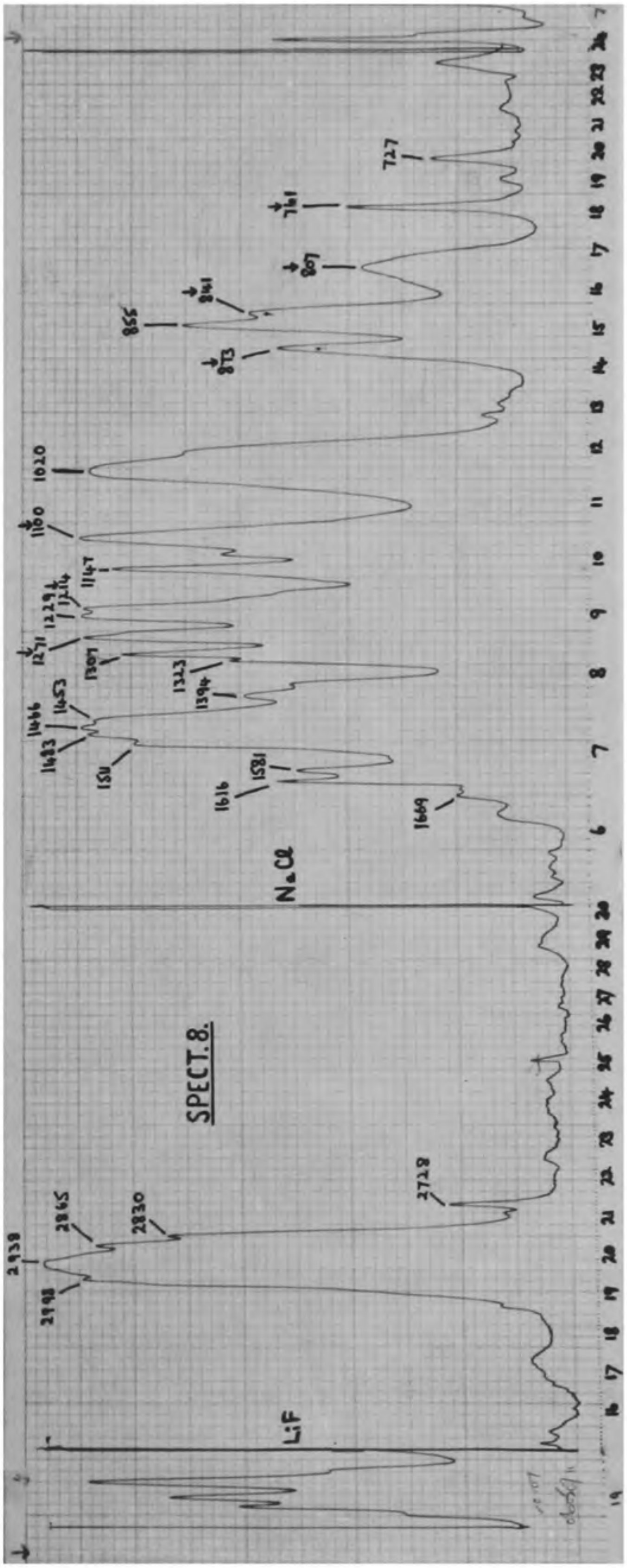

SPECT.3.

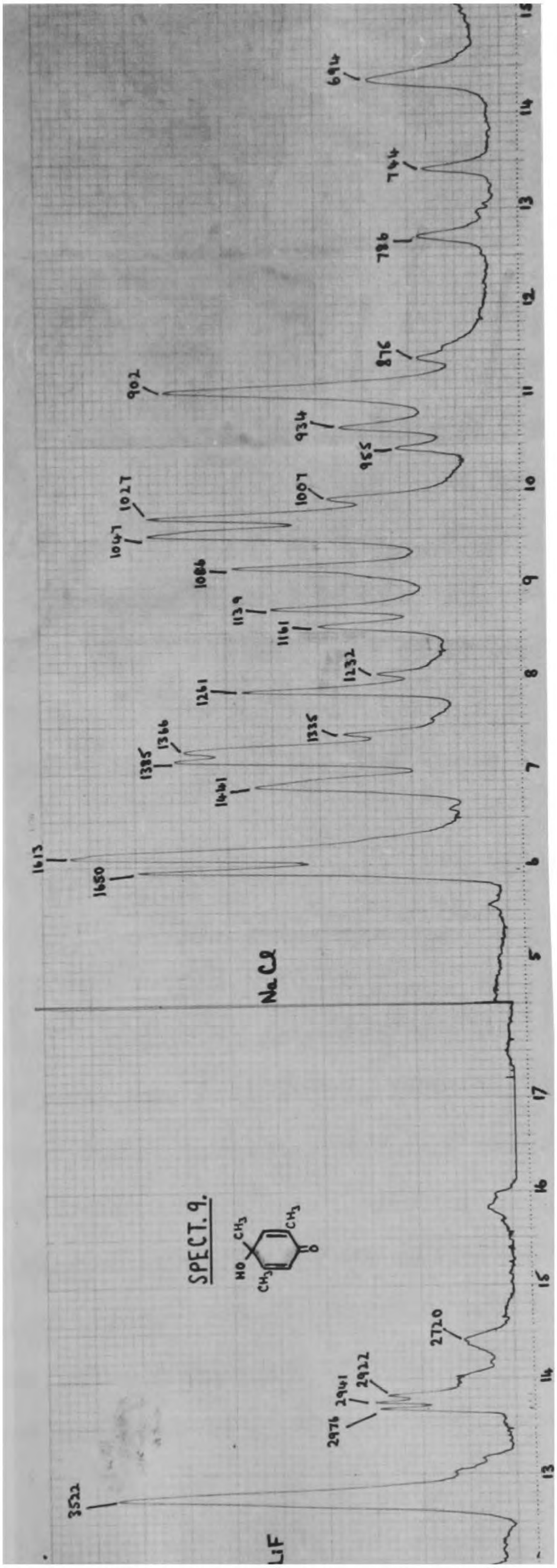

SPECT.5.


SPECT. 6.
LiF
NaCl
2987
2961
2862
2833
2725
1616
1505
1464
1394
1305
1258
1238
1188
1142
1094
1068
1080
1018
877
804
771
754
710


SPECT. 7.
OCH3
CH3
CH3
CH3
LiF
NaCl
3537
3461
2987
2958
2920
2862
2834
2725
2601
1623
1590
1496
1464
1416
1385
1318
1289
1248
1199
1151
1117
1082
1022
1000
964
893
832
754
747
713


SPECT. 6.


SPECT. 8.


SPECT. 9.
HO
CH3
CH3
CH3
O
LiF
NaCl
3522
2976
2941
2922
2720
1650
1613
1461
1385
1366
1335
1261
1232
1161
1139
1086
1047
1027
1007
955
934
902
876
786
744
694
13
14
15
16
17
5
6
7
8
9
10
11
12
13
14
15

confirmed the presence of meta-2 xylyl methyl ether (peak 1), and showed that the other component was meta-4 xylyl methyl ether (peak 2); no meta-5 isomer was present.

Examination of Infra-Red Spectra.

The spectra of the authentic meta-2(SPECT.1), meta-4 (SPECT.2), and meta-5 xylyl methyl ethers (SPECT.3), show similarity in the 3,000-2,800 cm^{-1} region (Carbon-hydrogen stretching vibrations of substituents in an aromatic ring).

Obvious differences occur in the 1620-1480 $cm.^{-1}$ (carbon-carbon stretching vibrations in the aromatic ring). and in the 900-650 $cm.^{-1}$ regions (out of plane carbon-hydrogen bending vibrations).

Relevant absorption bands for the three isomers occur at (v-max.):-

meta-2: (1592,1484), 1093,1066,1015, (811,768) $cm.^{-1}$.
meta-4: (1612,1504), 1039, (877,804,754,710) $cm.^{-1}$.
meta-5: (1607), 1039, (952,691) $cm.^{-1}$.

The 768 $cm.^{-1}$ (SPECT.1, meta-2), 804 $cm.^{-1}$ (SPECT.2, meta-4), and 845-834 $cm.^{-1}$ (SPECT.3, meta-5) bands can be associated with 1,2,3; 1,2,4; and 1,3,5 tri-substituted benzenes respectively.

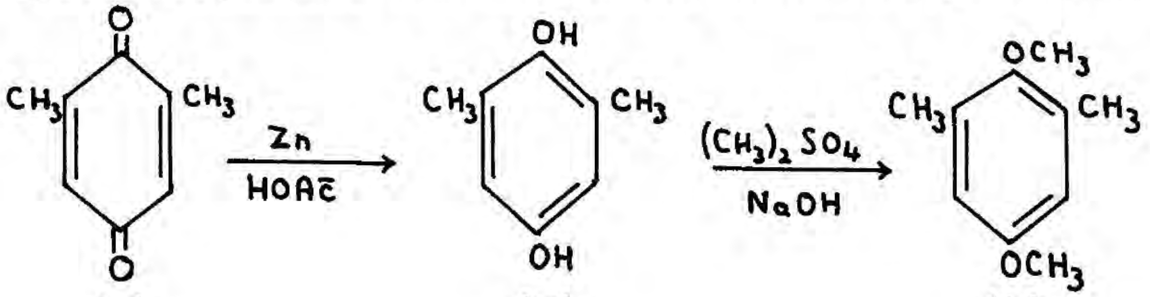
The samples analysed (a mixture corresponding to the peaks 1 and 2, obtained from Reaction A, and a sample enriched in the later component 2; N.B.SPECT.4 was obtained from the sample enriched in 2) gave almost identical spectra

having strong absorption bands at (v-max.):-
(1616,1505), 1094,1068,1040,1018, (877,804,771,754,710)cm.$^{-1}$.

Bands characteristic of the meta-2, and meta-4 isomers are easily recognised, but the absence of absorption maxima at 952, and 691 cm.$^{-1}$, rules out the presence of the meta-5 isomer in the mixture.

Identification of Peak 4 as meta-Xylohydroquinone Di-Methyl Ether.

Authentic meta-xyloquinone was reduced with zinc turnings, and 60% acetic acid at 110°C. The hydroquinone did not separate on adding water to the mixture; therefore, after neutralising, the mixture was extracted with ether; these operations being carried out under an atmosphere of nitrogen. After evaporating off the ether, the meta-xylohydroquinone was methylated in the adopted manner.



(4) (5) (6)

A low yield of product was obtained, which consisted of two components (V.P.C.). Elution over alumina (Column A) in light petroleum ether removed the component which had the greater retention time. The retention time of the remaining component coincided exactly with peak 4, and a sample was condensed out.

Analysis:

Calculated for $C_{10}H_{14}O_2$: C,72.3%; H,8.4%

Found: C,71.7%; H,7.9%.

Infra-Red Analysis.

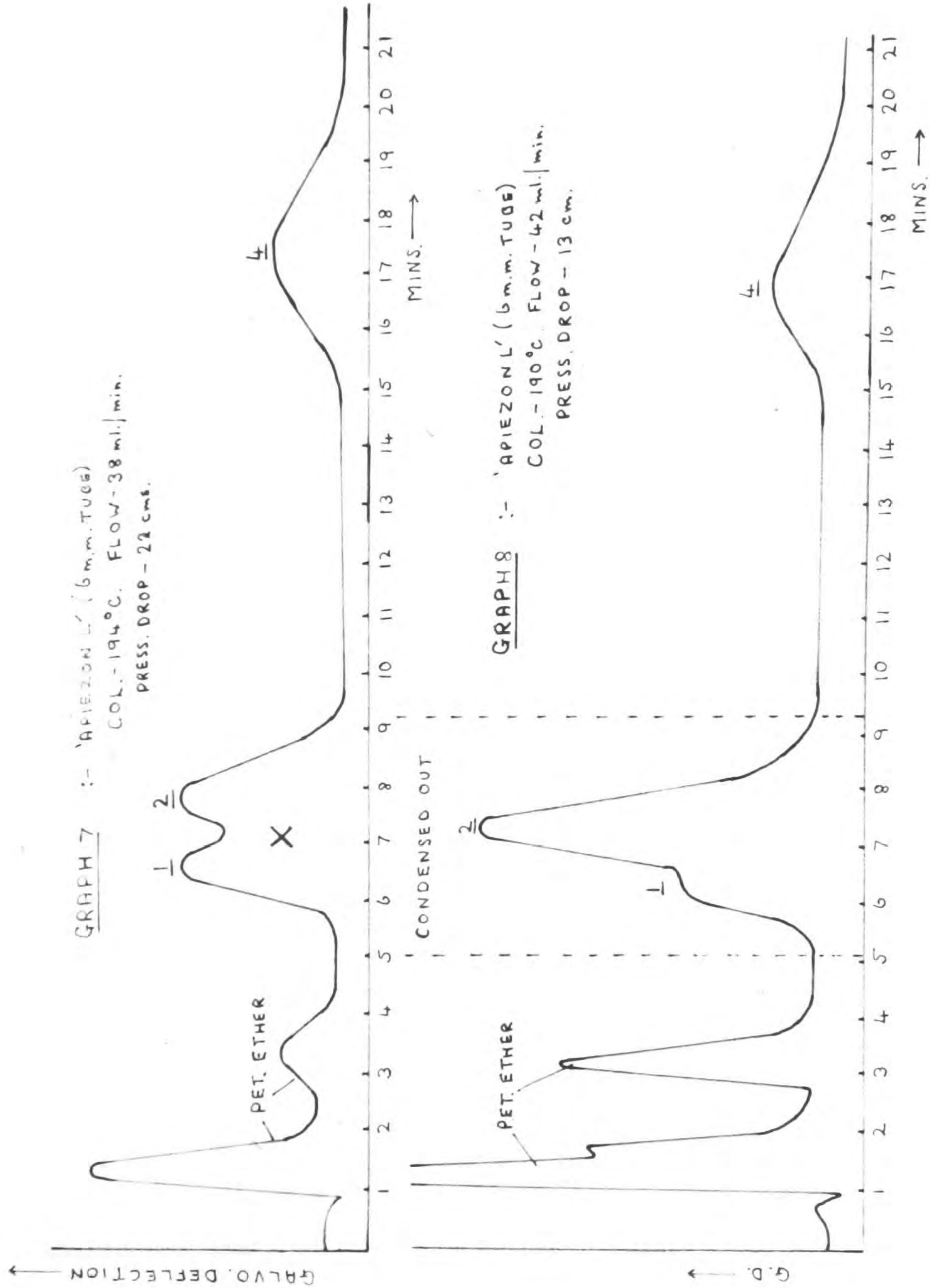
Relevant absorption bands in the spectrum (SPECT.5), were obtained at (v-max.):-

2987-2833, 1605, 859-834 cm.$^{-1}$

Absorption in the regions: immediately below 3000 cm.$^{-1}$ (carbon-hydrogen stretching vibrations of substituents in an aromatic ring); 1620-1480 cm.$^{-1}$ (carbon-carbon stretching vibrations in a mono-nuclear aromatic ring); and 850-840 cm.$^{-1}$ (carbon-hydrogen, out of plane vibrations for a 1,2,3,5 tetra-substituted benzene), is in agreement with the compound being meta-xylohydroquinone di-methyl ether(6).

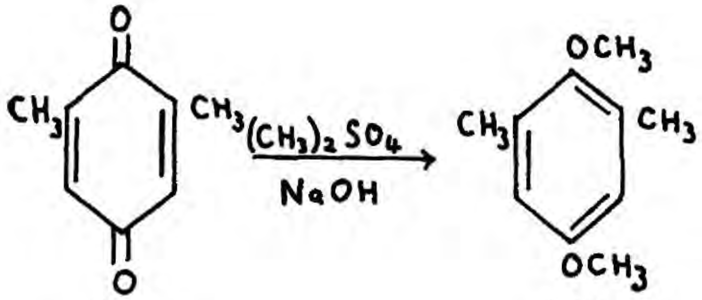
Methylation of meta-Xyloquinone.

It was originally thought that all of the meta-xylohydroquinone di-methyl ether (peak 4) resulted from methylation of meta-xylohydroquinone(5) present in the reaction mixture. However, methylation of authentic meta-xyloquinone(4) gave a 30% yield of meta-xylohydroquinone di-methyl ether, the infra-red spectrum of which, was identical to SPECT.5.



GRAPH 7 :- 'APIEZON L' (6 m.m. TUBE)
COL. - 194°C. FLOW - 38 ml./min.
PRESS. DROP - 22 cms.

GRAPH 8 :- 'APIEZON L' (6 m.m. TUBE)
COL. - 190°C. FLOW - 42 ml./min.
PRESS. DROP - 13 cm.



(4) (6)

Quantitative Estimations

The quantitative estimation of a particular compound in a mixture, by Vapour-Phase Chromatography, requires a previous calibration of the column, by injecting a known weight of the compound, and determining the area of the peak produced. Peak height is often used for this purpose, but this is not accurate; interaction of a compound with other components in a mixture often occurs, and this causes the corresponding peak to be more diffuse than a peak produced by the pure compound. A calibration for each component to be estimated is necessary, since different compounds give different responses.

The methylation products, after elution on alimina, were analysed by vapour-phase chromatography, using a 4 mm (internal diameter) column (GRAPH 3) and a 6 mm column (GRAPH 7); the 6 mm column gave more symmetrical peaks, and was preferred for this reason.

In calculating the amount of phenols originally present in the reaction mixture, from estimations of the methyl ethers produced, the 15% loss during methylation (observed for the authentic phenols), was allowed for.

Thus, from the area of X, in GRAPH 7, and a calibration of pure meta-xylyl methyl ethers, it was calculated that the original 3.3 gm. of reaction products contained 1.1 gm. of meta-xylenols. It was estimated that the meta-xylohydroquinone di-methyl ether peak, corresponded to 0.7 gm. of meta-xylohydroquinone.

An elution without previous methylation, of the same quantity of reaction products, obtained under identical conditions, yielded 0.8 gm. of meta-xyloquinone, (m.p.65°C; m.p. of an authentic specimen 69°C; mixed m.p. 66°C).

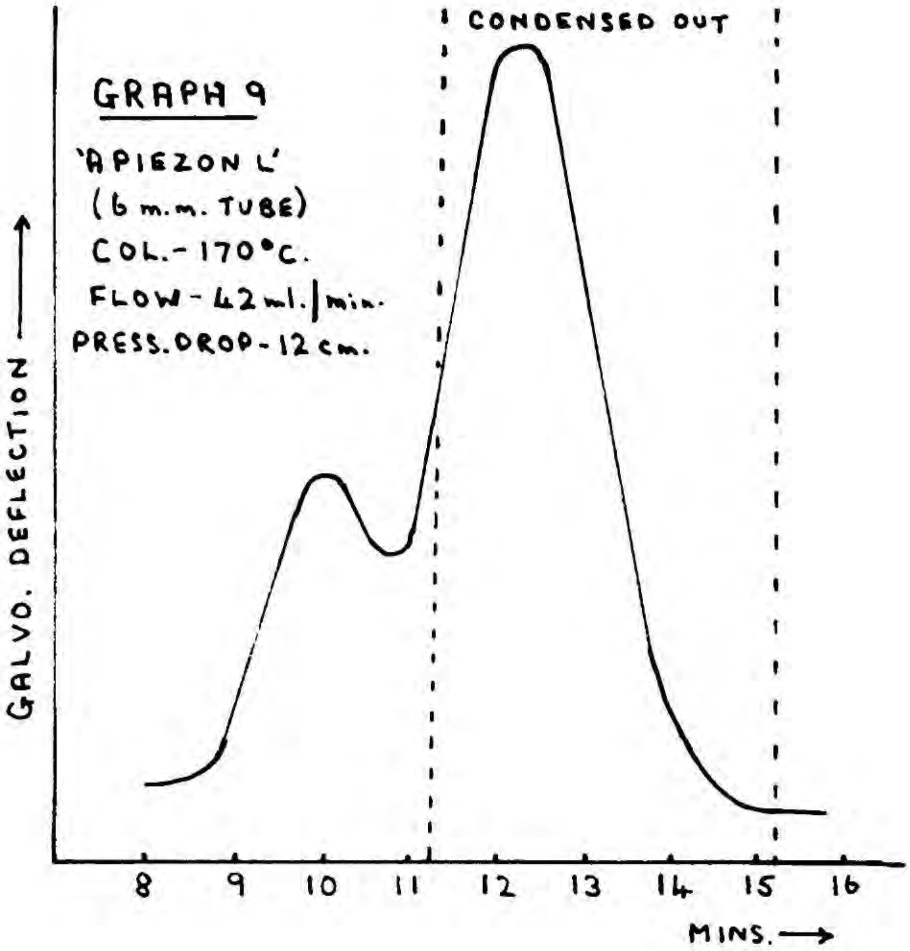
Of the 0.7 gm. of meta-xylohydroquinone indicated by GRAPH 7, 0.3 gm. should have been produced (as its di-methyl ether) by methylation of the quinone (30% yield). This leaves approximately 0.4 gm. of meta-xylohydroquinone which must have been present in the original reaction mixture.

Thus, of the 3.3 gm. of reaction products, at least 2.3 gm. consisted of meta-xylenols, meta-xylohydroquinone, and meta-xyloquinone.

meta-XYLENE.

B. Using Trifluoroacetic Anhydride plus Hydrogen Peroxide Oxidant:-

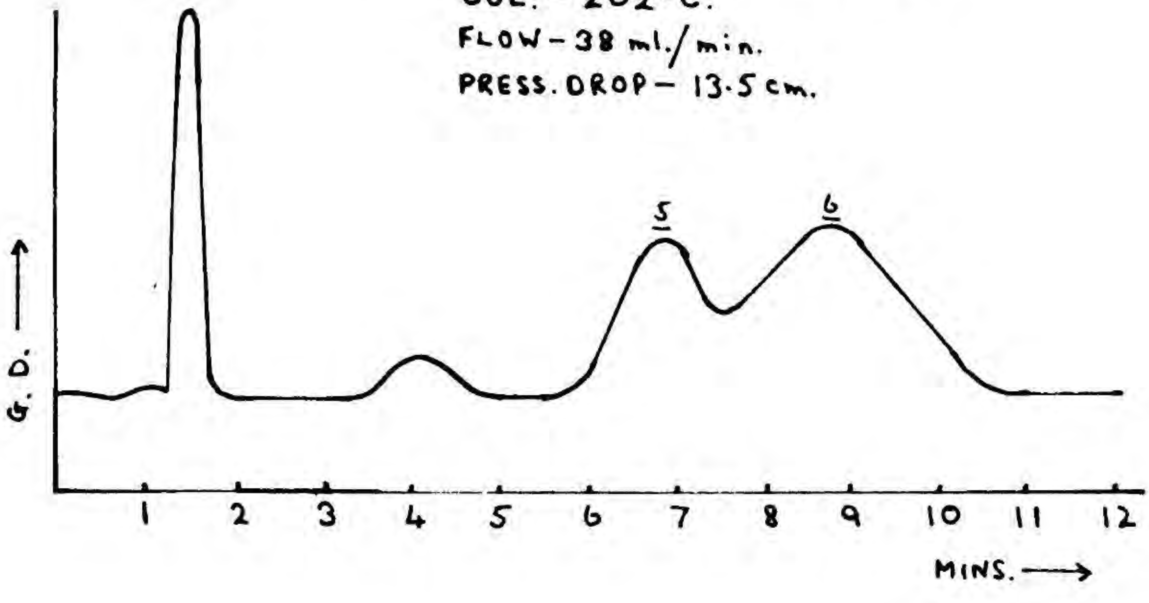
A mixture of meta-xylene (16 gm.-0.15 mole) and trifluoroacetic anhydride (30 gm.-0.14 mole), was treated with 'high-test peroxide' (16 ml-0.21 mole), under the same



GRAPH 9

'APIEZON L'
(6 m.m. TUBE)
COL. - 170°C.
FLOW - 42 ml./min.
PRESS. DROP - 12 cm.

GRAPH 10 :- 'APIEZON L' (6 m.m. TUBE)
COL. - 202°C.
FLOW - 38 ml./min.
PRESS. DROP - 13.5 cm.



conditions as in A, and the reaction mixture was worked up in the same manner.

Aqueous Layer: A minute amount of a gum was obtained.

Methylene Chloride Layer: 5.6 gm. of a red oil was obtained, and 10 gm. of unused meta-xylene was accounted for.

Methylation: The red oil yielded 4.5 gm. of products on methylation, and the vapour-phases chromatogram showed peaks with retention times identical to 1,2,3, and 4, obtained in Reaction A(GRAPH 2), but in this case, 2 was present in a much greater proportion than in A(Compare GRAPHS 7 and 8).

Elution: The component corresponding to peak 3 was removed by eluting over alumina (Column A) in light petroleum ether.

As in Reaction A, components corresponding to peaks 1 and 2 (GRAPH 8) were condensed out. After lowering the column temperature, it was possible to condense out a sample enriched in the component 2 (GRAPH 9).

Examination of Infra-Red Spectra.

Strong absorption bands can be observed (SPECT. 5, as in Reaction A, was obtained from the sample enriched in 2) at (v-max.):-

(1614,1505), 1092,1035,1018, (877,804,771,752,710) cm.$^{-1}$.

Again, the absence of maxima at 952 and 691 cm.$^{-1}$ rules out the meta-5 isomer, but the presence of the meta-2, and meta-4 isomers has been confirmed.

Quantitative Estimates: It was estimated that the peak areas of the methyl ethers in GRAPH 8 correspond to 2.4 gm. of meta-xylenols, and approximately 1 gm. of meta-xylohydroquinone. The elution of an equal amount of products from an identical reaction, without previous methylation, yielded 1.3 gm. of meta-xyloquinone.

Of the 1 gm. of meta-xylohydroquinone indicated by GRAPH 8, 0.5 gm. should have been produced (as its di-methyl ether) by methylation of the quinone. This leaves 0.5 gm. of meta-xylohydroquinone which must have been present in the reaction mixture.

Thus, of the 5.6 gm. of reaction products (red oil), at least 4.2 gm. consisted of meta-xylenols, meta-xylohydroquinone, and meta-xyloquinone.

Experiment Involving the Elution of Reaction Products Before Methylation. (Oxidation of meta-Xylene)

The red oil (5.4 gm.), obtained by the oxidation of meta-xylene with a mixture of 'high-test peroxide', and trifluoroacetic anhydride, was eluted over an alumina column (43x1.1 cm.), using methylene chloride as eluent.

The eluent, which was yellow as the first band emerged quickly darkened; when it was no longer coloured, methyl alcohol was added to the top of the column, and a second fraction was obtained in this way.

Column 1. 5.4 gm. eluted.

Fraction 1. (methylene chloride):- Removal of the solvent left a dark paste (4.23 gm.).

Fraction 2. (methyl alcohol):- A black solid (0.82 gm.) was obtained. This solid was methylated, giving a dark, viscous material (0.48 gm.), but V.P.C. did not reveal the presence of methyl ethers of either meta-xylenol, or meta-xylohydroquinone.

The paste obtained from Fraction 1 was eluted over a second column of the same dimensions as the first. An initial methylene chloride fraction was collected whilst the eluent remained yellow. Fraction 2 was collected when the emergent methylene chloride became dark.

Column 2. 4.2 gm. eluted.

Fraction 1. (methylene chloride):- meta-xyloquinone (0.9 gm.).

Fraction 2. (methylene chloride):- A dark paste (2.7 gm.).

Fraction 3. (methyl alcohol):- A viscous oil (0.93 gm.). This was methylated, and the product (0.48 gm.) was shown to be largely meta-2 xylyl methyl ether (probably containing some meta-4 isomer).

Fraction 2 was re-eluted over Column 3.

Column 3. 2.7 gm. eluted.

Fraction 1. (methylene chloride):- meta-xyloquinone (0.44 gm.).

Fraction 2. (methyl alcohol):- A viscous red oil (1.6 gm.). This was methylated, and the product (0.49 gm.) on analysis (V.P.C.) was shown to contain meta-2 and meta-4 xylyl methyl ethers. The chromatogram contained later peaks, one of which corresponded to meta-xylohydroquinone of di-methyl ether.

PSEUDO-CUMENE. (1,3,4 Tri-Methyl Benzene)

A. Trifluoroacetic Anhydride plus Hydrogen Peroxide used as Oxidant:-

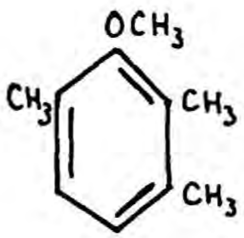
A mixture of pseudo-cumene (19 gm. - 0.16 mole), and trifluoroacetic anhydride (32.6 gm. - 0.15 mole) in methylene chloride (50 ml.), was treated with 'high test peroxide' (6.5 ml. - 0.19 mole), and the reaction mixture was worked up in the manner described for the Reactions A and B, with meta-xylene.

Aqueous Layer: Only a minute amount of a gum was obtained.

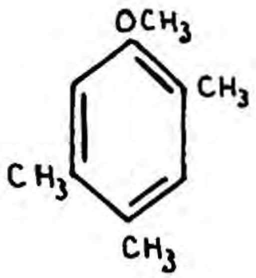
Methylene Chloride Layer: A red oil (6.2 gm.) was isolated and 12 gm. of unused pseudo-cumene was accounted for, by recovery, and by V.P.C. of the methylene chloride distillates.

Methylation: After methylation of the red oil, and elution of the products over alumina (Column A), in light petroleum ether, a clear liquid was obtained (2.5 gm.). The vapour-phase chromatogram showed two peaks, 5 and 6 (GRAPH 10).

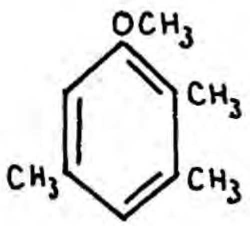
Authentic samples of the isomeric pseudo-cumenols were methylated, a 90% yield of methyl ethers being obtained. Retention times of these authentic ethers were determined, and it was found that the 2,3,6 tri-methyl, 1-methoxy isomer (7) coincided exactly with 5, but the 2,4,5 tri-methyl, and 2,3,5 tri-methyl isomers (8 and 9 respectively) had equivalent retention times, coinciding exactly with 6. Hence, a sample of a mixture of the components corresponding to 5 and 6, was condensed out, and samples of authentic pseudo-cumenyl methyl ethers were purified by V.P.C. These samples were submitted for infra-red analysis.



(7)



(8)



(9)

Elution without previous methylation, of an equal amount of reaction product from an identical reaction, yielded 1.7 gm. of pseudo-cumoquinone.

Pseudo-Cumoquinone, Mono-Semicarberzone:

M.p. and mixed m.p. with an authentic sample, 252°C (decomp.); m.p. of authentic compound, 252°C (decomp.).

Analysis:

Calculated for $C_{10}H_{13}N_3O_2$: C,58.0%; H,6.3%

Found: C,58.0%; H,6.3%.

Examination of Infra-Red Spectra.

Authentic samples of the methyl ethers of 2,4,5 and 2,3,5 tri-methyl phenol (SPECT.6 and 7 respectively), had absorption bands at (v-max.):-

2,4,5;- 1275,1215,1099,877, 845 cm.$^{-1}$

2,3,5:- 1189,1151,1117,964, 832 cm.$^{-1}$

These values are in reasonable agreement with the accepted ranges, characteristic of 1,2,4,5 (870-855 cm.$^{-1}$) and 1,2,3,5 (850-840 cm.$^{-1}$) tetra substituted benzenes (carbon-hydrogen, out of plane vibrations).

The sample of methylated reaction products, condensed out via vapour-phase chromatography, had absorption bands (SPECT.8) at (v-max.):-

1271,1214,1100,873,841,807 cm.$^{-1}$.

The absence of strong absorption at 832 cm.$^{-1}$ and other characteristic bands, rules out the 2,3,5 isomer (9); 2,4,5 tri-methyl phenyl methyl ether (8) was obviously present, and the band at 807 cm.$^{-1}$ (absorption characteristic of 1,2,3,4 tetra-substitution, between 810-800 cm.$^{-1}$ is additional confirmation of the presence of 2,3,6 tri-methyl phenyl methyl ether (7).

B. Trifluoroacetic Acid plus Hydrogen Peroxide as Oxidant:-

Reactions were carried out in the same manner as in Reaction A: the products were of the same constitution as in A, but in lower yield.

MESITYLENE. (1,3,5 Tri-Methyl Benzene)

Trifluoroacetic Acid plus Hydrogen Peroxide as Oxidant:-

A mixture of mesitylene (18.7 gm. - 0.15 mole), trifluoroacetic acid (18.6 gm. - 0.16 mole), and methylene chloride (50 ml.) was treated with 'high-test peroxide' (6 ml. - 0.21 mole); the reaction was worked up in the same manner adopted for previous reactions.

Aqueous Layer: A minute amount of a gum was obtained.

Methylene Chloride Layer: 14 gm. of mesitylene was recovered, leaving a red viscous oil (4.5 gm.), from which no more mesitylene could be removed.

Elution: The red oil (1.6 gm.) was eluted over alumina (Column A), using methylene chloride as eluent. After 30 ml. of eluent had emerged clear (Fraction 1), a yellow band appeared, and 10 ml. was collected. (Fraction 1). After the yellow band itself had emerged, the eluent remained yellow, hence a further 20 ml. was collected (Fraction 3); elution was allowed to proceed for a further 80 ml. (Fraction 4).

Fraction 1:- No residue remained on removing the solvent.

Fraction 2:- A yellow oil (0.25 gm.).

Fraction 3:- A reddish crystalline solid (0.5 gm.).

Fraction 2:- The yellow oil was dissolved in alcohol (4 ml.), water was added until slightly turbid, and this turbidity was removed again with a few drops of alcohol. Semicarbazide hydrochloride (0.25 gm.) and crystalline sodium acetate (0.4 gm.) was added, and the mixture heated for two hours on a hot water bath. A deep red colour developed, and on cooling, yellow crystals were deposited from solution, m.p. 227°C; twice recrystallised from alcohol, m.p. 252°C (decomp.). The melting point was not depressed when a sample was mixed with an authentic specimen of pseudo-cumoquinone mono-semicarbazone, m.p. 252°C (decomp.).

Analysis:

Calculated for $C_{10}H_{13}N_3O_2$: C,58.0%; H,6.3%.

Found: C,57.0%; H,6.4%.

Fractions 3 and 4: From these solids, pure mesitol was sublimed, m.p. 70°C. The melting point was not depressed when samples were mixed with authentic specimens of mesitol, m.p. 70°C.

Thus, the original 4,5 gm. of red oil consisted of approximately 3.5 gm. mesitol, and 0.8 gm. pseudocumoquinone.

Preparation of Trifluoroacetic Anhydride.

The preparation was carried out according to Stacey et al,[51] who used a slightly lower proportion of phosphorus pentoxide than the original method by Swarts[51].

Phosphorus pentoxide was weighed out into a round-bottomed flask, the quantity being approximately 0.87 gm. per gram of trifluoroacetic acid available for conversion to the anhydride. The flask was fitted with a reflux condenser and a dropping funnel, and was cooled in an ice-salt bath; the ingress of moisture was prevented by fitting calcium chloride tubes to the condenser and dropping funnel.

Trifluoroacetic acid was dropped slowly into the phosphorus pentoxide, and heat was evolved in the process. After allowing the mixture to stand for sufficient time for the acid to percolate through the phosphorus pentoxide, the mixture was distilled, using a receiver cooled in a solid carbon-dioxide - acetone freezing mixture. In order to remove all of the anhydride (b.pt.39°C) from the phosphorus pentoxide residue, it was necessary to have the oil-bath temperature at about 110°C for a considerable time. For a final purification, the anhydride was re-distilled.

Using this method, yields between 70-80% have been obtained.

SECTION 2:- THE OXIDATION OF PHENOLS TO QUINONES.

These reactions, as already stated in the introduction, were an application of the reactions involving oxidation of hydrocarbons, rather than an extension to the problem.

In each case, the phenols were treated with four equivalents of oxident (a much greater excess has been shown to lead to considerable breakdown of the quinones formed) at room temperature, in methylene chloride solution.

The temperature was allowed to rise, and invariably, within half an hour after the addition of hydrogen peroxide, the heat of reaction was sufficient to cause the methylene chloride to reflux. Colour changes took place, through red to almost black, and then to orange-yellow, over a period of eight hours. The last stage often needed the aid of a warm water bath for completion. There were exceptions to this sequence; ortho-3 xylenol (2,3 di-methyl phenol), and ortho and meta cresol all gave reaction mixtures which remained black. Phenols which contained a methyl group in the position para to the initial hydroxyl group i.e. mesitol and 2,4,5 tri-methyl phenol did not exhibit the red, and black stages.

Oxidation of ortho-Cresol, meta-Cresol, and ortho-3 Xylenol (2,3 Di-Methyl Phenol)

The reaction mixtures quickly went black on addition of hydrogen peroxide, and on neutralisation, yielded black tars.

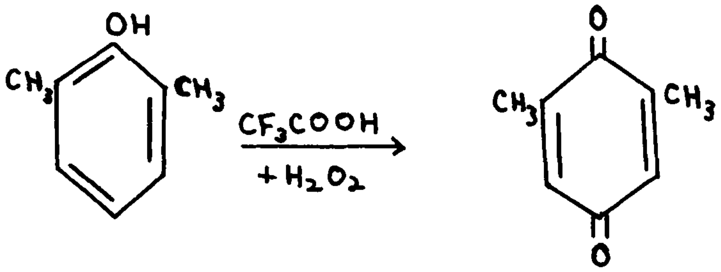
meta-XYLOQUINONE.

From meta-2 Xylenol (2,6 di-methyl phenol): A mixture of meta-2 xylenol (10 gm. - 0.08 mole), and trifluoroacetic acid (10 gm. - 0.09 mole), in methylene chloride (50 ml.) was treated with 'high-test peroxide' (10 ml. - 0.36 mole) at room temperature.

During the first hour, the mixture turned dark, and became quite warm. After 7½ hours, the mixture was warmed for half an hour in a water-bath at 50°C; the colour changed from dark-red, to yellow. The mixture, on cooling, was neutralised with sodium hydrogen carbonate, and extracted with methylene chloride; the extracts were dried over anhydrous magnesium sulphate, and distilled.

Crude meta-xyloquinone (8.6 gm. - 77% yield) was obtained, which melted at 69°C. After being recrystallised twice from alcohol or ether, m.p. 71°C (Literature 73°C);

mixed m.p. with an authentic specimen of meta-xyloquinone, 72°C; authentic specimen, m.p. 74.5°C.



<u>From meta-5 Xylenol (3,5 di-methyl phenol)</u>: A mixture of meta-5 xylenol (8.2 gm. - 0.07 mole), trifluoroacetic acid (8 gm. - 0.07 mole), dissolved in methylene chloride (50 ml.) was treated with 'high-test peroxide' (7.5 ml. - 0.27 mole), and the reaction was carried out, in the same manner, as for meta-2 xylenol.

Crude meta-xyloquinone was obtained (5.3 gm. - 57% yield); and this was purified by eluting over alumina (Column B), using methylene chloride as eluent (m.p. and mixed m.p. with an authentic specimen, 73°C; authentic specimen m.p. 74.5°C).

Oxidation of meta-2 xylenol Using Trifluoroacetic Anhydride plus Hydrogen Peroxide as Oxidant.

A mixture of meta-2 xylenol (20 gm. - 0.16 mole), trifluoroacetic anhydride (32 -5 gm. - 0.5 mole), and methylene chloride (50 ml.) was cooled in an ice-bath, and 'high-test peroxide' (10 ml. - 0.36 mole) was added. After half an hour, the mixture was allowed to come to room temperature, and stirring was continued for a further eight hours.

After neutralising, the methylene chloride layer yielded a reddish solid (17 gm.).

Elution: The red solid (2.6 gm.) was eluted in methylene chloride, over alumina (Column B). Fraction 1 was collected as a yellow band emerged; the Column was then continuously extracted with ether for two hours (Fraction 2).

Fraction 1:- meta-xyloquinone (1.8 gm.) was obtained on removal of the solvent (m.p. and mixed m.p. with an authentic specimen, 73°C).

Fraction 2:- A brown-white solid (0.5 gm.), m.p. 158°C; treatment with light petroleum ether left a white solid, m.p. 170-172°C.

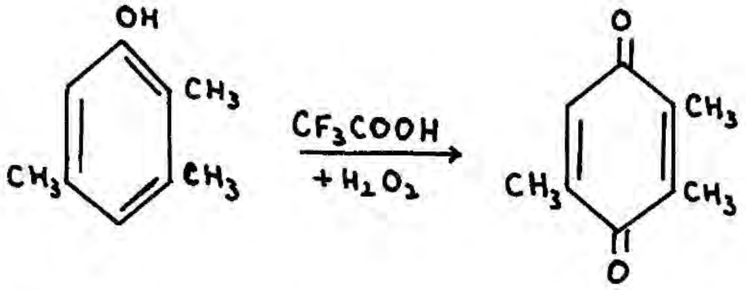
An attempt to acylate the compound, using acetic anhydride and one drop of concentrated sulphuric acid, resulted in the formation of a dark tar. Shortage of time prevented further investigation of this compound.

PSEUDO-CUMOQUINONE (2,3,5 tri-methyl benzoquinone).

From Pseudo-Cumenol (2,3,5 tri-methyl phenol): A mixture of 0.09 pseudo-cumenol (10 gm. - 0.07 mole), trifluoroacetic acid (10 gm. - 0.09 mole) and methylene chloride (50 ml.), was treated with 'high-test peroxide' (9 ml. - 0.27 mole) at room temperature.

The mixture turned very dark, and heat of reaction caused the methylene chloride to reflux slightly. After $7\frac{1}{2}$ hours, the mixture was warmed for half an hour, until the colour had changed from red to yellow.

Pseudo-cumoquinone (7 gm.) was obtained as a yellow oil (63% yield); it is usually obtained as an oil when slightly impure, since its melting point is so low (Lit. 23°C). The mono-semicarbazone was prepared, m.p. 252°C (decomop.), and the melting point was not depressed when mixed with an authentic specimen of pseudo-cumoquinone mono-semicarbazone.



Oxidation of Mesitol.

Mesitol (5 gm. - 0.04 mole), dissolved in methylene chloride (50 ml.) was oxidised, using trifluoroacetic acid (5 gm. - 0.04 mole) and 'high-test peroxide' (4.4 ml. - 0.16 mole) in the manner described for pseudo-cumenol.

After the addition of hydrogen peroxide, the solution became slightly warm, and a yellow colour developed during the first hour; the dark colour, produced in the reactions with meta-xylenol and pseudo-cumenol, were not observed.

A red, viscous oil was produced (3.6 gm.), and by eluting this over alumina in methylene chloride, a small amount of pseudo-cumoquinone was isolated from the first fraction. The remaining fractions were red pastes, which appeared to contain some unreacted mesitol.

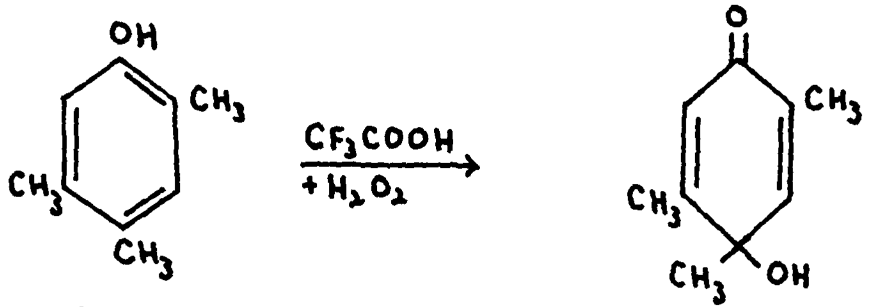
Oxidation of 2,4,5 Tri-Methyl Phenol.

Reaction 1: 'High-test peroxide' (4.5 ml. - 0.16 mole) was added to a mixture of 2,4,5 tri-methyl phenol (10) (5.1 gm. - 0.04 mole), and trifluoroacetic acid (9 gm. - 0.08 mole) in methylene chloride (50 ml.). The only colour-change observed was that the solution gradually became yellow. After eight hours, the mixture was refluxed for half an hour and then neutralised.

A viscous, dark oil (3.0 gm.) was obtained from the methylene chloride layer, and this was eluted over alumina (Column B), using methylene chloride as eluent.

The first fraction was collected as a yellow band began to emerge from the column. This fraction yielded a brownish yellow paste (1.2 gm.). The paste was taken up in about 10 ml. of ether, and the ether was allowed to evaporate slowly in a desiccator, causing fractional crystallisation to occur.

When the volume of ether had been reduced to about 2 ml. the mixture was filtered, and white crystals (0.1 gm.) were obtained, which melted at 113-114°C. These were re-crystallised twice from water, sublimed, and allowed to stand in a desiccator over phosphorus pentoxide for two days; the melting point was then constant at 116°C. This corresponds to the melting point of the tri-methyl quinole (11), prepared by Bamberger.[37]



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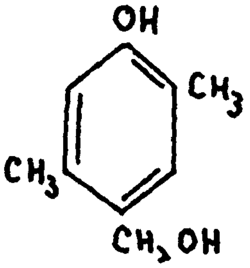
Analysis:

Calculated for $C_9H_{12}O_2$; C,71.0%; H,7.9%.

Found; C,71.1%; H,8.4%.

It is worth noting that a carbon-hydrogen analysis cannot differentiate between a tri-methyl quinole, and a benzyl alcohol derivative, (e.g. 12), which have the same molecular formula. However, the three possible isomers of this type of compound have melting points much higher than 116°C.



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Reaction 2: An attempt was made to prepare tri-methyl quinole in greater yield than in Reaction 1. 'High-test peroxide' (8.2 ml. - 0.3 mole) was added to a mixture of 2,4,5 tri-methyl phenol (9.7 gm. - 0.07 mole), trifluoroacetic acid (10 gm. - 0.08 mole), and methylene chloride (50 ml.).

A red oil (6.7 gm.) was obtained, and this was eluted over alumina (Column B). Fraction 1 was obtained by continuously extracting the column with methylene chloride until a pale yellow band had emerged, and the eluent was no longer coloured. Fraction 2 and Fraction 3 were obtained by continuously eluting with ether, and methyl alcohol respectively.

Fraction 1:- Removal of the solvent left a viscous yellow brown oil (2.7).

Fraction 2:- A yellow oil (1.1 gm.).

Fraction 3:- A dark red oil (2.0 gm.).

Fraction 1: By fractional crystallisation from ether, as described in Reaction 1, white crystals (1.1 gm.) were obtained as the first crop. After recrystallising from water, these did not depress the melting point when mixed with a sample of the quinole obtained from Reaction 1.

Benzoate: A portion of the quinole was shaken with benzoyl chloride, and sodium hydroxide in the normal way, until a derivative was obtained.

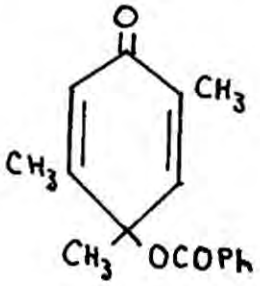
The product was recrystallised twice from aqueous alcohol m.p. 82-83°C. After four further recrystallisations from the same solvent, the melting point was constant at 93°C.

Analysis:

Calculated for $C_{16}H_{16}O_3$ (13); C,75.0%; H,6.3%.

Found: C,75.2%; H,6.5%.

i.e.



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Examination of Infra-Red Spectrum.

The spectrum was obtained from a sample of tri-methyl quinole which had been purified for analysis by recrystallising several times from water, and then subliming (SPECT. 9).

Revelant absorption bands were observed at (v-max.):- 3522,1650,1613 cm.$^{-1}$.

The band at 3522 cm.$^{-1}$ is characteristic of a hydroxyl group, although this isslightly below the normal frequency (3636-3610 cm.$^{-1}$). This may be due to a concentration effect or to hydrogen bonding.

Bands at 1650, and 1613 cm.$^{-1}$ arise from the carbonyl and ethylenic parts of the molecule respectively. Being due to a conjugated system (an unsaturated ketone), these bands are said to occur at a frequency, some 30 cm.$^{-1}$ below the normal frequencies arising from individual carbonyl and ethylenic groups.

Proof that the molecule is not aromatic lies in the absence of strong absorption between 1500 and 1480 $cm.^{-1}$; this is the conventional means of differentiating between the spectra due to ethylenic, and aromatic systems, since an aromatic compound would produce strong absorption in that region.

Fraction 2: It was assumed that the oil produced was a quinone, but the compound could not be reduced. Sulphur dioxide, and zinc dust at 110°C were used for this purpose. A semicarbazone could not be obtained.

Fraction 3: The red oil gave a silver mirror with ammoniacal silver nitrate, and reduced Fehling's solution, but had no effect on Schiffs reagent; the original phenol produced a silver mirror but had no effect on Fehling's solution. No derivative was obtained with 2,4 di-nitrophenyl hydrazine hydrochloride in boiling absolute alcohol.

Attempts were made to acetylate the oil, using acetic anhydride and fused sodium acetate, and using acetic anhydride plus one drop of concentrated sulphuric acid; no derivative was isolated from either reaction.

No further investigation of Fractions 2 or 3 was carried out.

Reaction 3: A greatly improved yield of tri-methyl quinole was obtained, when 'high-test peroxide' (9.3 ml. - 0.3 mole) was added to a mixture of 2,4,5 tri-methyl phenol (10 gm. - 0.07 mole), and trifluoroacetic acid (10 gm. - 0.08 mole), in the methylene chloride (50 ml.). The reaction was continued for 24 hours at room temperature, and the mixture was not refluxed.

A red oil was obtained (8.5 gm.), which was eluted over alumina, as in Reaction 2.

Fraction 1:- A dark red solid (5.5 gm.) was obtained after removal of the solvent. This was crude, tri-methyl quinole.

Fraction 2:- A red oil (0.32 gm.).

Fraction 3:- A dark gum (1.9 gm.).

An alternative method to fractional crystallisation from ether, for isolation of the quinole from impurities (e.g. quinole), is to dissolve the mixture in a little ether, and then add a slight excess of petroleum ether (b.p. 40-60°C). The quinole is precipitated very pure, and an almost complete precipitation can be obtained by cooling the mixture in an acetone-solid carbon dioxide bath.

THE PREPARATION OF AUTHENTIC QUINONES.

Pseudo-cumoquinone (2,5,6 tri-methyl quinone).

The preparation was carried out according to the method of Smith et al,[49] using one fifth of the stated amounts as far as possible, but with slight modification e.g. some of the solutions required more solvent for the preparation.

Sulphanilic acid (21 gm.) was dissolved by warming, in a solution of sodium carbonate (5.3 gm.) in water (110 ml.).

The solution was cooled to 15°C, and a solution of sodium nitrate (7.4 gm.) in water (25 ml.) was added, and the mixture was then immediately poured into a mixture of ice (120 gm.) and concentrated hydrochloric acid (22 mls.), and allowed to stand for thirty minutes.

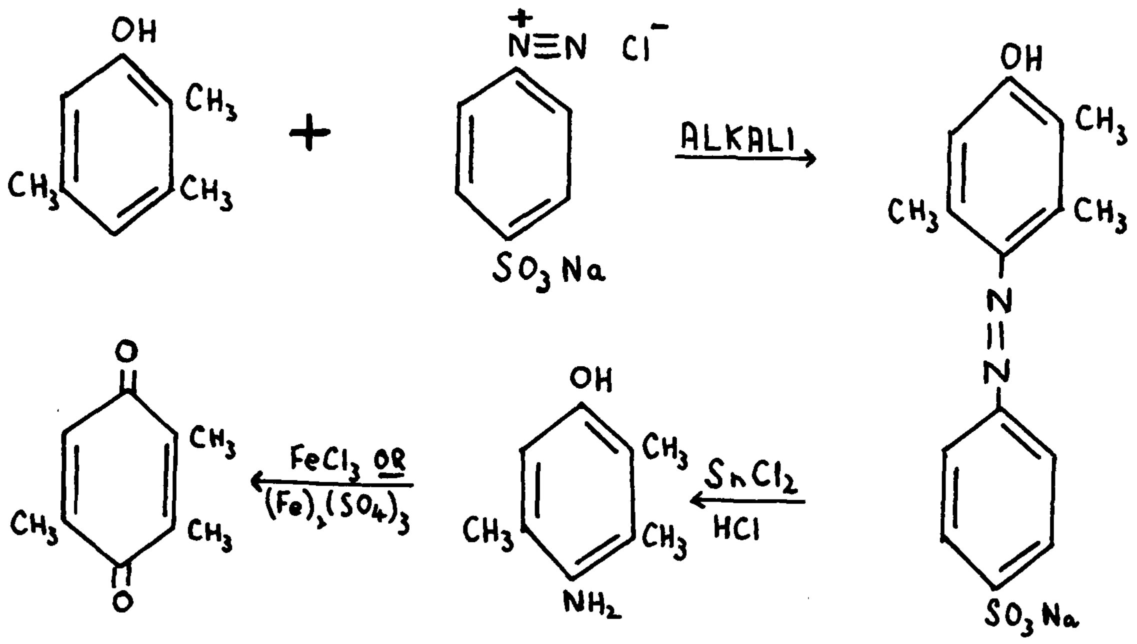
The diazonium solution was poured into a well-stirred solution of 2,3,5 tri-methyl phenol (12.6 gm.) in water (60 ml.) containing sodium hydroxide (15 gm.); excess alkali at this point was important.

The mixture was allowed to stand overnight and wan then made strongly acid with concentrated hdrochloric acid (50 ml.).

Without removing the red azo compound, stannous chloride (33 gm.) in concentrated hydrochloric acid (40 ml.) was added, and the solution heated to almost boiling, until it cleared, and became dark brown. Care was taken at this stage, not to <u>boil</u> the solution, otherwise tri-methyl amino-phenol could have been lost in the steam.

The mixture was transferred to a large flask, excess ferric chloride (160 gm.) was added, and the mixture <u>at once</u> steam-distilled. It was necessary to use a very large flask (five litres) for the distillation, otherwise, the extensive foaming can spread into the condenser.

The distillate was extracted several times with portions of ether; on removing the ether, pseudo-cumoquinone (8 gm.) was observed as a yellow oil (58% yield).



If the steam-distillation had not been carried out immediately following the addition of ferric chloride, extensive amounts of chloroquinones may have been formed.

In this case, elution over alumina produced a reasonably pure product, but in other cases, even this process gave an unsatisfactory product.

In later experiments, ferric sulphate was used in place of ferric chloride as oxidising agent, giving products of satisfactory purity, and in yields of the same order as those obtained using ferric chloride.

Mono-Semicarbazone: Pseudo-cumoquinone (1 gm.) was dissolved in alcohol (5 ml.); water was added until slightly turbid, and this turbidity was removed with a few drops of alcohol. Semicarbazide hydrochloride (0.5 gm.) and crystalline sodium acetate (0.75 gm.) was added.

The mixture was heated on a hot-water bath for half an hour, during which time it turned a deep red colour. On cooling, the derivative crystallised and was filtered off, m.p. 233°C (decomp.); recrystallised three times from alcohol, m.p. 252°C (decomp.).

Analysis:

Calculated for $C_{10}H_{13}N_3O_2$: C,58.0%; H,6.3%.
Found: C,57.5%; H,6.5%.

Hydroquinone: Pseudo-cumoquinone (1 gm.) was dissolved in 60% acetic acetic acid, and zinc turnings were added, the mixture turned dark red, and on heating to 110°C became clear. The hot acetic acid was decanted into water, where the hydroquinone separated out; it was recrystallised from aqueous alcohol treated with sulphur dioxide (to prevent re-oxidation of the hydroquinone); m.p. 167°C (Literature 169°C).

This compound was included into authentic mixtures, for the investigation of methods of separation.

Tri-Methyl Hydroquinone Di-Acetate: Tri-methyl hydroquinone (1 gm.) was dissolved in acetic anhydride (10 ml.), and two drops of concentrated sulphuric acid was added; the mixture was refluxed for twenty minutes. On cooling, the mixture was poured onto ice, and made alkaline with ammonia. The derivative was filtered off, and recrystallised from aqueous alcohol; m.p. 110°C.

Analysis:

Calculated for $C_{13}H_{16}O_4$: C,66.1%; H,6.7%.

Found: C,66.1%; H,6.7%.

Meta-Xyloquinone.

The preparation was carried out as for pseudo-cumoquinone, using two-thirds the quantities used by Smith et al.[49]

Thus, from 31.6 gm. of 2,6 di-methyl phenol, 15.5 gm. of meta-xyloquinone was obtained (45% yield). The melting point of the crude product was very low, and could not be raised to within 10°C of the literature value (73-74°C), even after several recrystallisations from alcohol and ether, and elution over alumina.

The same preparation was carried out using ferric sulphate as oxidising agent; 19.5 gm. of meta-xyloquinone was obtained, which was easily recrystallised pure from alcohol, m.p. 74°C - (55% yield).

Several attempts to prepare a semicarbazone of this quinone were unsuccessful; it is not obvious why this should be so.

Para-Xyloquinone.

Using ferric sulphate as oxidising agent, in the method of Smith et al, 10 gm. of para-xylenol yielded 5 gm. of crude para-xyloquinone, (45% yield).

After recrystallising twice from alcohol, m.p. 124°C (Literature 123°C).

Toluquinone.

The method of Smith et al. was attempted, but no toluquinone was obtained (no claim is made by Smith for this particular preparation).

The preparation was achieved by the method of Clarke,[52] by oxidising ortho-toluidine with manganese dioxide. 'Bench' manganese dioxide yielded no quinone, but when precipitated manganese dioxide was used, the method was successful:-

Ortho-toluidine (40 gm.) was dissolved in dilute sulphuric acid (160 gm. concentrated sulphuric acid, 480 gm. water), precipitated manganese dioxide (140 gm.) was added, and steam passed into the mixture (slowly at first, then sufficient for steam distillation), contained in a five litre flask (to offset foaming).

The distillate was cooled, and crystals of toluquinone separated out; these were filtered off, and the filtrate was extracted several times with portions of ether. Toluquinone (10 gm.) was isolated (22% yield), m.p. 67°C (Literature 68°C).

According to Noelting and Baumann[53], ortho- and meta-toluidine can be oxidised by chromic acid to toluquinone.

Both of these preparations were attempted but scarcely any quinone was obtained in either case.

SECTION 3:- THE OXIDATION OF POLYCYCLIC SYSTEMS.

PHENANTHRENE

A mixture of phenanthrene (20 gm. - 0.1 mole), and trifluoroacetic acid (24 gm. 0.2 mole), in methylene chloride (70 ml.) was treated with 'high-test peroxide' (8.2 ml. - 0.29 mole) at 0°C, and the mixture was stirred for eighteen hours.

The reaction mixture was worked up in the usual way.

Aqueous Layer: A precipitate was obtained on acidifying, this was filtered off, and the filtrate concentrated until more solid was precipitated. A total of 6.8 gm. of a brownish solid was obtained.

The solid was dissolved in sodium carbonate solution; this was boiled for fifteen minutes with decolourising charcoal and then filtered. After re-acidifying, a white precipitate was formed; the solid was filtered off, m.p. 226°C. This was recrystallised from aqueous alcohol, m.p. 228°C. (m.p. for diphenic acid, 228°C).

Methylene Chloride Layer: After drying, the solvent was removed by distilling in an atmosphere of nitrogen, and a crystalline residue remained (13.0 gm.).

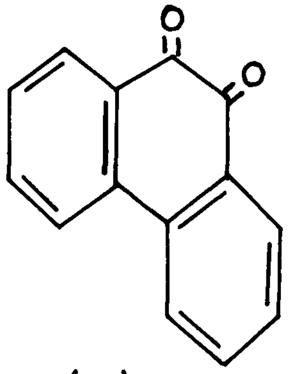
Elution: The residue (13 gm.) was eluted in methylene chloride over alumina (Column 50x2.5 cms). Progress of the band of unused phenanthrene down the column was followed by means of the violet phosphorescence produced by ultra-violet light.

Two fractions were obtained, the first (6.4 gm.) consisted of a mixture of pure phenanthrene, and the second (6.3 gm.) consisted of a mixture of phenanthrene and phenanthraquinone.

A green band, and a dark-brown band remained on the column after elution.

A small amount (2 gm.) of the second fraction was eluted over a second column of alumina (100x2.5 cms.) in benzene. When the yellow band reached the foot of the column, the eluent was collected in 80 ml. batches. Each of the batches gave a slight phosphorescence under ultra-violet light, but that did not necessarily indicate that more than a trace of phenanthrene was present.

The last of the yellow batches gave a small amount of a yellow solid; this melted over a range, 194-197°C; when mixed with a sample of pure phenanthraquinone (14) (m.p. 203°C), m.p. 196-199°C.



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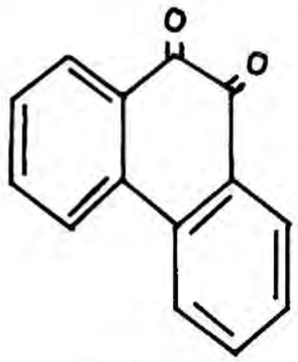
Removal of the benzene which had emerged from the column before the yellow band appeared, yielded pure phenanthrene (1.2 gm.). Thus, less than 2.5 gm. of phenanthraquinone was produced in the total reaction product.

<u>Oxidation of Phenanthraquinone</u>.

'High-test peroxide' (3 ml. - 0.17 mole), was added to a mixture of phenanthraquinone (16 gm. - 0.07 mole) and trifluoroacetic acid (6 gm. - 0.05 mole) in methylene chloride (50 ml.).

The reaction was worked up in the usual way. From the aqueous layer, diphenic acid (15) (13.6 gm.) was isolated, m.p. 230°C (Literature 229°C).



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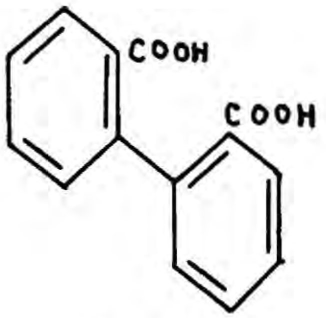

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Analysis:

Calculated for $C_{14}H_{10}O_4$(15); C,69.6%; H,4.1%.

Found: C,69.2%; H,4.1%.

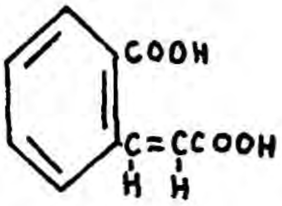
Unreacted phenanthraquinone (3.5 gm.) was recovered from the methylene chloride layer.

NAPHTHALENE.

This reaction could not be carried out homogeneously because, using the normal proportions of reagents, the naphthalene would not dissolve to a sufficient extent. The reaction was continued with undissolved naphthalene present. After 24 hours, the mixture was filtered and then worked up in the usual way.

An unsaturated acid was obtained from the aqueous layer which was probably ortho carboxy—cinnamic acid. (16).

The methylene chloride layer was extracted with sodium hydroxide solution, and on acidification of the extracts, alpha-naphthol (17) was obtained.



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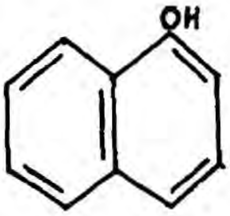

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Oxidation of Alpha Naphthol.

Alpha naphthol (10 gm. - 0.07 mole) was dissolved in a mixture of trifluoroacetic acid (10 gm. - 0.09 mole), and methylene chloride (50 ml.), and 'high-test peroxide' (5.8 ml. - 0.21 mole) was added. The mixture was stirred for 24 hours and then worked up in the usual way.

The products were:-

(i) A large quantity of dark brown material which was insoluble in aqueous sodium bicarbonate, and in methylene chloride. On drying, it yielded a brown powder, soluble in sodium hydroxide.

(ii) A brown tar was obtained from the methylene chloride layer, from which a yellow quinone was sublimed (m.p. 125°C). This corresponds to 1,4 naphthaquinone (m.p. 125°C) which is also yellow; 1,2 naphthaquinone is red (m.p. 115°C).

The residual tarry mass left after sublimation, dissolved in sodium hydroxide, and could not be re-precipitated by hydrochloric acid. This probably consists of a mixture of unreacted alpha-naphthol, and naphthaquinone.

(iii) Acidification of the aqueous layer gave a pale yellow precipitate.

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CHAPTER IV

HIGH TEMPERATURE VAPOUR-PHASE CHROMATOGRAPHY

High Temperature Vapour-Phase Partition Chromatography

Introduction

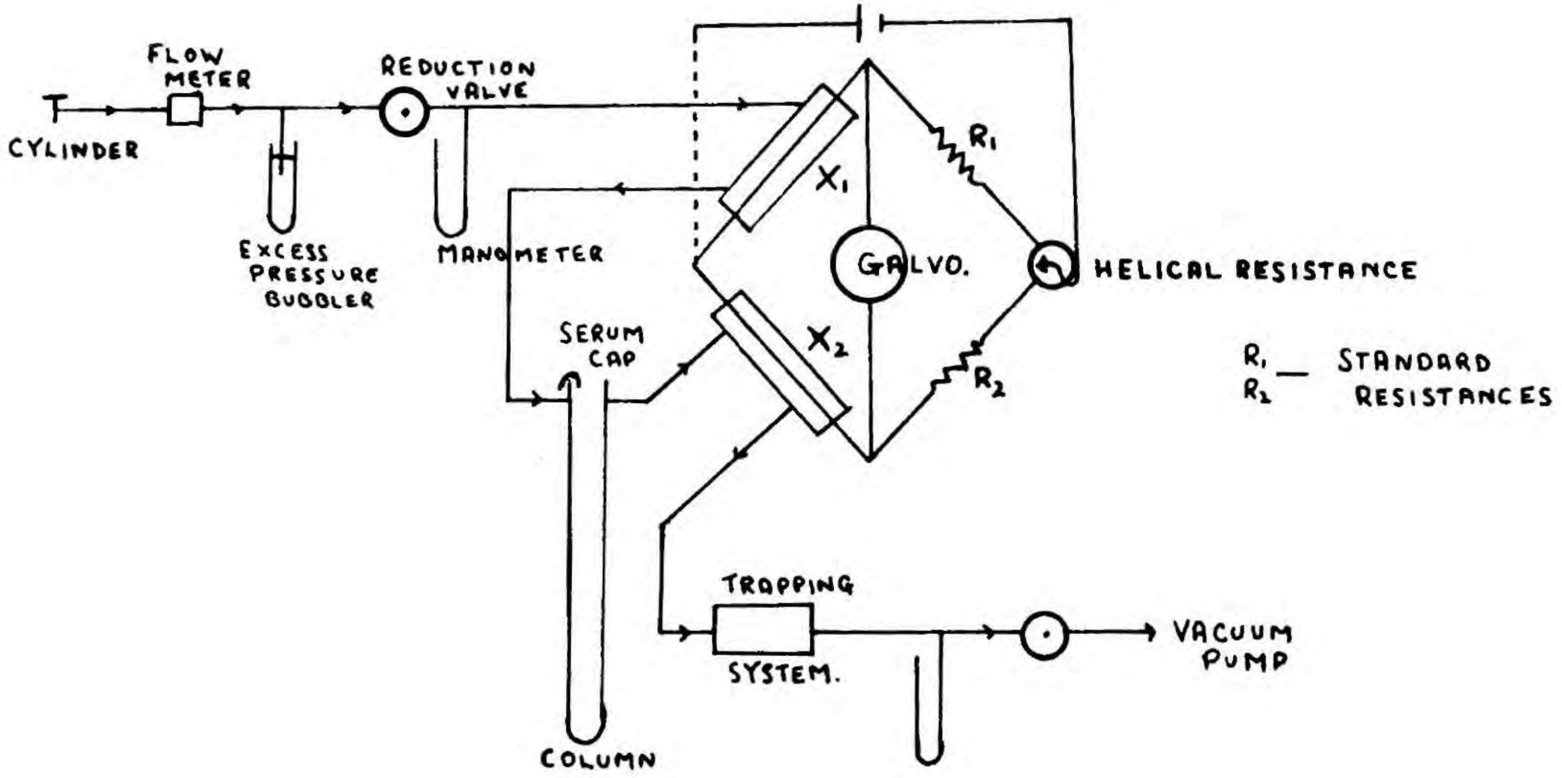
Vapour-phase chromatography[1] can be defined as the separation of gases or vapours by eluting in an inert carrier-gas, over a stationery liquid phase (e.g. dinonylphthalate) which is supported on some inert porous material (kieselguhr). Hence the terms CARRIER-GAS, STATIONARY PHASE, AND INERT PHASE.

Stationary Phases.[2]

A stationary phase must possess some solvent power for the components of mixtures which are to be separated. In theory, it should also be stable, inert, and non-volatile over the temperature range at which it is being used. Obviously there are no 'perfect' stationary phases but up to 120°C there is a host of liquids, or low melting solids which will meet almost any requirement; at higher temperatures, the choice is considerably restricted.

When a range considerably higher than 120°C is required, the choice becomes extremely limited. The difficulty lies, in finding compounds with a sufficiently low vapour pressure. Most of the high temperature stationary-phases 'bleed' in the initial period of running but this quickly reduces to an acceptable amount; silicone oil, and Silicone and 'Apiezon' high vacuum greases have been used extensively. The use of esters of di-nitro diphenic acid

FIGURE 1. VAPOUR-PHASE CHROMATOGRAPHY SYSTEM.



has been quoted. More recently, plasticizers have been applied to this purpose;[3] e.g. a useful Stationary-phase can be obtained by heating succinic acid and di-ethylene glycol, together with a little para-toluene sulphonic acid and di-glycerol (to produce cross-linking).

Detectors

Various methods have been used to record continuously the constitution of a carrier-gas as it emerges from the column. Some of these methods appear to have served more to demonstrate the remarkable practical skill of the inventors, who were able to make them work rather than provide an easily reproducable and reliable method of detection.

Glass and metal thermal conductivity cells are the most common forms of detection in use. The hydrogen-flame method depends on using hydrogen as carrier-gas and, on emerging from the column, burning it below a thermocouple junction. A beta-ray detector has been described which involves passing the emergent gas between a radioactive strontium source and a recording instrument.

One of the accepted systems for a vapour-phase chromatography apparatus is as shown in FIGURE 1. X_1 and X_2 can represent the suspended wires (spirals have been used with excellent results) in a nickel or platinum wire catharometer, or the corresponding components of other detectors. R_1 and R_2 are standard resistances with a low temperature co-efficient. X_1 and X_2, and similarly R_1, R_2 are made almost equal. The bridge can be balanced by adjusting the variable resistance.

Samples are injected into the carrier-gas through a serum cap by means of a hyperdermic syringe. On emerging from the column the sample gives rise to a deflection on the galvanometer (or automatic recorder); its presence alters the thermal conductivity of the carrier-gas and subsequently, the resistance in the conductivity cell (X_2). The way in which the thermal conductivity of a carrier-gas is altered by the addition of a sample is said to depend on temperature. By altering the temperature peak reversal can sometimes be obtained.

Carrier-Gases

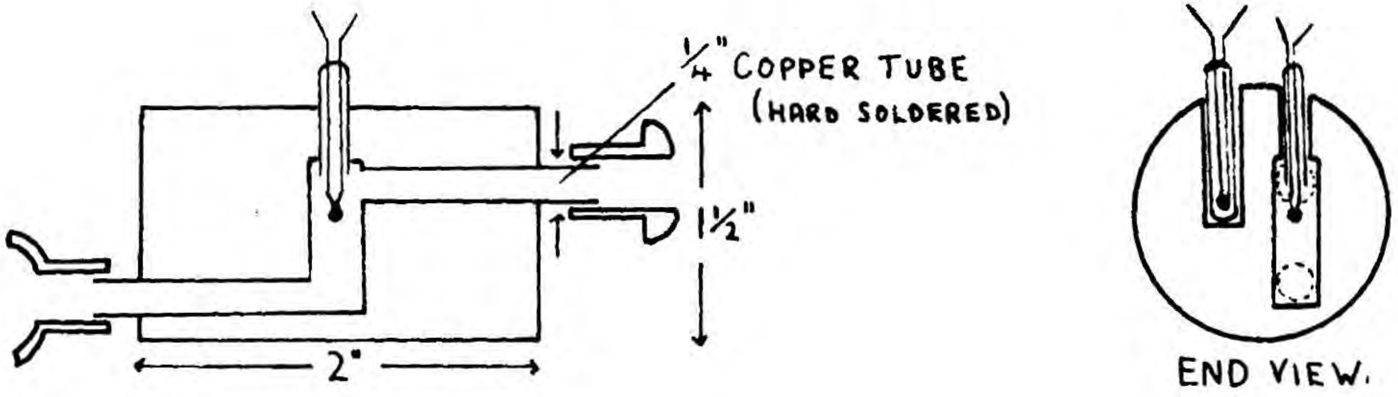
Nitrogen is the most common carrier gas in use but this is because of its cheapness. Hydrogen and helium are considerably more efficient in that, to a rough approximation, the peak area for a component is directly proportional to the mass, regardless of the component. Thus, for a quantitative analysis only an initial calibration would be required.

The Development of a High Temperature Apparatus in the Laboratory.

When it became desirable to identify and preferably separate small quantities of high boiling phenols (boiling points of the order of 200°C), the apparatus which was being used in the laboratory, very effectively at temperatures up to 100°C, was totally inadequate for the purpose. Until this time only quite volatile compounds had been subjected to V.P.C., and no need for a heated detector had arisen. It had not been necessary either to make the connection between column and detector as short as possible or to heat it (i.e. to avoid condensation).

Thus, an initial apparatus was constructed; the short lead from column to detector was wound with a heater. The detector itself consisted of four nickel wires, suspended in four glass tubes. Nitrogen passed through two of these tubes, through the column, and then through the remaining tubes. The detector was first heated by immersing the tubes in an oil-bath. This method produced great instability in the detector and was replaced by surrounding the tubes with copper turnings, which were contained in an electrically heated beaker. With this system, it was possible to examine synthetic mixtures containing the required phenols, but the detector was far from satisfactory. The sensitivity diminished quickly with temperature and this was accompanied by a deterioration in stability. It is the author's opinion that instability is inherent in a detector constructed from glass, and that at elevated temperatures, detectors constructed from metal blocks should be used.

FIGURE 2. THE THERMISTOR DETECTOR.



The Thermistor Detector.

Thermistors have been incorporated in a commercial H.T.V.P.C. apparatus[4] but their use is not very well described in the literature.[5] A satisfactory design was developed as shown in FIGURE 2. Ball-joints and thermistors were sealed to the copper and brass respectively by means of a cold-curing silicone rubber.[6]

Thermistors of the STANTEL 'A' type were used;[7] the bead which was in the direct stream of gases had the glass sheath removed, hence increasing its sensitivity. The other thermistor, which formed the standardising arm of the Wheatstone Bridge circuit, was left sheathed and was simply maintained at the same temperature as the unsheathed one. It was not introduced into a stream of the carrier gas, since the opinion is held that this leads to instabilities in the system, rather than to correct for the variations (e.g. of flow-rate) which this procedure is reputed to do. The third and fourth arms of the bridge were wire-wound resistors, approximately 50 ohms each.

In this particular apparatus, 1,000 ohms thermistors (i.e. room temperature resistance) were used but since then, pairs with values 2,000 and 500,000 ohms each have been used in the laboratory, with equal stability but somewhat less sensitivity.

DIAGRAMMATIC REPRESENTATION OF THE SYSTEM (NOT TO SCALE)

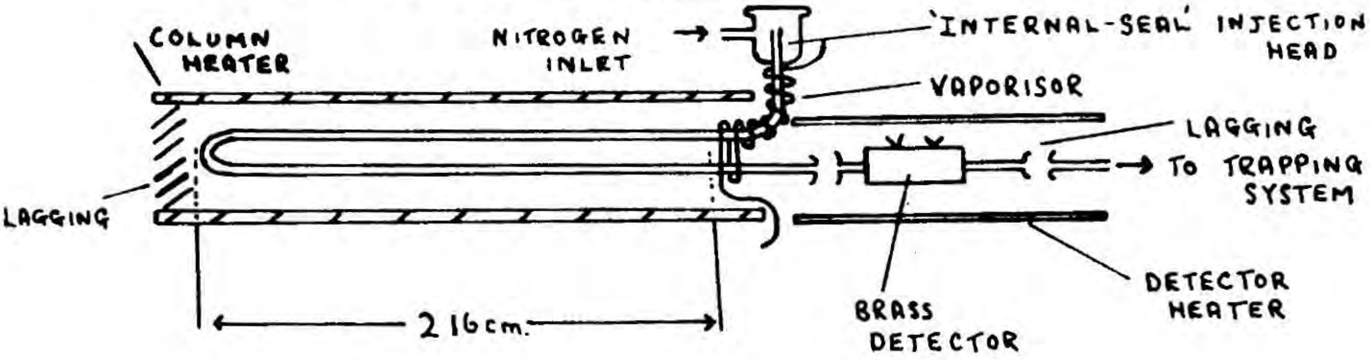


FIGURE 3.

TRAPPING SYSTEM.

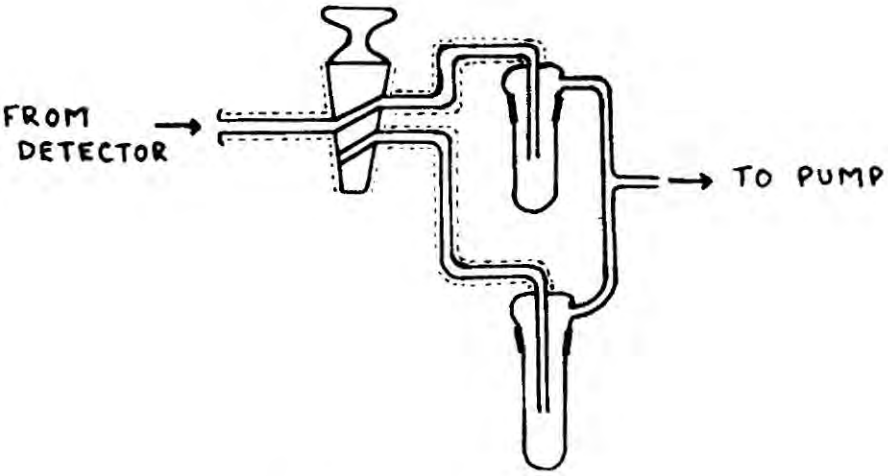


FIGURE 4.

Heating.

Initially, the brass-block was heated by immersing in copper turnings contained in a glass vessel which was electrically heated. The idea was that an equilibrium would be set up, giving rise to a steady temperature gradient throughout the copper turnings. Although this gave a system more stable than that which the nickel-wire catharometer provided, it was not satisfactory. It appears that in such a system, any slight changes are quickly transmitted to the brass-block.

The most satisfactory method of heating was by means of a cylindrical heater, packed with woolly asbestos, which extended from the column heater to the trapping system (see FIGURE 3).

Column Design.

The columns were used vertically at first but with the advent of longer columns, it was decided to arrange them horizontally. This arrangement leads to a more uniformly heated column, since convection currents will not run along the length of the column heater in this case; but the main advantage is the ease of aligning the system and the effective use of a simple heater for the detector and the connecting tubes (FIGURE 3).

A vaporising heater was wound round the inlet of the column and a few turns of the same heater were employed to prevent condensation in the column outlet to the detector.

The vaporisor was normally maintained at approximately 50°C. higher than the column temperature, this aided the production of well defined peaks on the chromatograms.

Columns have been made from 4 mm. and 6 mm. internal diameter 'pyrex' tube. The 4 mm. column was the more efficient as far as peak definition is concerned and because of the small diameter, a greater pressure drop (e.g. 40 cms.) across the column was needed to maintain a reasonable flow rate (e.g. 30 mls/min). Although the small pressure drop is the more ideal condition, it was found in practice that the reducing valve would not maintain this gradient (e.g. 13 cms.) as consistent as the large pressure drop. Hence, it was not as easy to maintain reproduceable conditions with the 6 mm. column as with the 4 mm. column (essential for analysis on a calibrated column).

The advantages of the 6 mm. column were that it was possible to do actual preparative separations quicker, since larger amounts could be injected at once, and that the peaks were rather more symmetrical with the 6 mm. column.

The 'internal seal' type injection head safeguards against any material being blown-back down the nitrogen inlet on vaporising.

A pre-heater for the nitrogen entering the column has been used but it was found not to be essential, and since it can be a source of instability, it was eliminated.

Trapping System.

The simple system shown in FIGURE 4 was used; this suffered the disadvantage that the pump needed to be disconnected before a trap could be removed. This simple form was however, adequate for the immediate purpose, and had the advantage that there was little effect on the galvanometer by changing the tap to the alternative trap.

It is obvious how the system could be elaborated to include more traps, and a system of taps so that each trap could be isolated without needing to stop running the apparatus.

As shown, a heater was wound around the connections and the tap. The tap-grease used was Silicone High Vacuum grease, and it performed extremely well at 140°C (the running temperature of the trapping system).

Column Packings.

Various stationary-phases have been examined but only Silicone and Apiezon'L' high vacuum greases were satisfactory; they were used in the proportion - 4 parts, with 10 parts Kieselguhr.

Both of these greases functioned well, without excessive 'bleeding' at temperatures up to and over 210°C.

In each case about 4-5% of the grease was collected in the waste-trap after the first 5-6 hours running at 200°C. After this, the amount collected was small enough to be insignificant (i.e. good analyses indicated that uncontaminated substances were being condensed out). Apiezon grease was found to discolour quite quickly but this did not appear to impair its efficiency.

No resolution between any of the isomeric meta-xylenols could be obtained with silicone grease. Apiezon'L' resolved meta-2 from meta-4 and meta-5 xylenols, but not the meta-4 and meta-5 isomers from each other, even on extending the length of the column.

A variety of compounds including hydrocarbons, phenols, and quinones, with boiling points up to 210°C have been analysed. It appears that even higher boiling compounds could be analysed if stable at the necessary column temperature.

Running Temperatures.

For Apiezon'L' on Kieselguhr, the column temperature normally used was 195°C. but it is quite efficient over a wide range of temperatures. The detector heater was always maintained at 140°C; any higher temperature would probably have melted some of the soft-solder wire connections to the thermisters. This can of course be overcome by using hard-solder.

Electrical Circuit.

The circuit diagram (FIGURE 5) was found to be satisfactory at a detector temperature of 140°C. Since the system was potentially too sensitive (unsteady base-line), a shunt resistance of 48 ohms was placed in parallel with the galvanometer and a resistance of 98 ohms in series with the accumulator (this was later replaced by a potentiometer across the accumulator). These optimum values were found by trial. Under these conditions, an extremely steady base-line was maintained and a full-scale deflection (50 cms, one metre from the galvanometer) resulted by injecting two drops of cumene (b.pt.152°C)with the column temperature at 160°C.

A cell-current of approximately 17 m.a. was produced. It was found that over a period of three months, the 98 ohm resistance in series with the accumulator had to be gradually replaced by progressively smaller resistances, in order to maintain a constant cell-current. Since the accumulator was maintained fully charged, this fall in current must be due to pieces of the thermistor beads breaking off and lowering their resistance.

When the detector temperature is changed, it is usually necessary to change the position of the variable resistances before a balance can be obtained. This is one advantage of maintaining a constant detector temperature, regardless of the column temperature. Some workers advocate <u>not</u>

having column and detector at the same temperature but there appears to be no practical basis for this opinion.

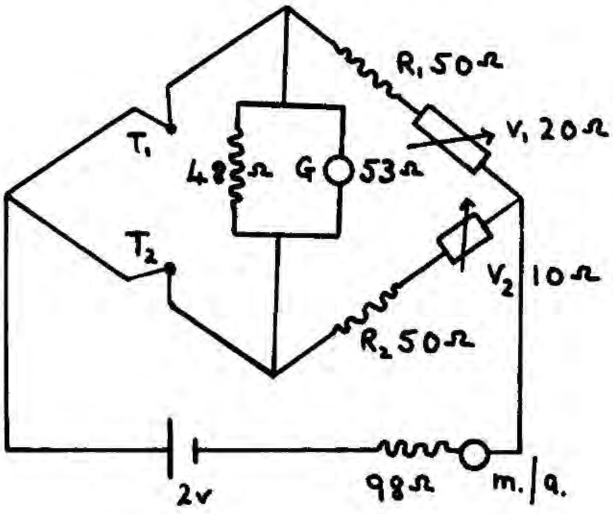


FIGURE 5.

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PART II

TELOMERISATION OF FLUORINATED OLEFINS

CHAPTER V

RADIATION CHEMISTRY

THE EFFECT OF RADIATION ON ORGANIC MOLECULES.[1]

Absorbtion of Energy.

The absorbtion of light waves (infra-red, visible, and ultra-violet) depends in general, on the molecular structure of the absorbing material, and not on its atomic composition. The energy of gamma-rays is almost entirely absorbed by ejecting electrons from the atoms through which they pass, and this process is almost independent of molecular structure.. Thus, the absorbtion of gamma-rays is less selective than that of light.

When a quantum of light is absorbed, the energy is stored in the molecule, which becomes excited; it can then undergo one of many possible reactions, or lose its energy as heat or light (fluorescence). When a quantum of gamma-rays is absorbed by an atom, it loses an electron. The energy of the quantum absorbed is always much greater than that required to eject an electron from the atom, and this excess is stored as kinetic energy of the ejected electron. This electron is then sufficiently energetic to produce ionisation in the atoms through which it passes. Almost all of the ionisations are produced by the ejected electrons and the effect of the initial absorbtion can usually be neglected. Thus, the ions produced are not distributed, uniformly throughout the solution, but are concentrated along the track of the ejected electron. These effects illustrate some difference between Photochemistry and Radiation chemistry.

The energy required to produce an ion pair(w) is approximately 32.5 ev. (gases) for gamma-rays, whereas the ionisation potential of most gases is considerably less than this value. The extra energy is dissipated in 'excitation', a term used to denote that an electron in the molecule has been raised to a higher energy level. This process is quite different from the excitation of a molecule by heating, when the energy is used up initially to increase the strain in a bond, causing it to increase its vibrations and oscillations.

Free radicals, and excited molecules both have a very short life in condensed phases (10^{-9} to 10^{-6} sec.) but for different reasons. Free radicals are extremely reactive entities, and their life is so short because they react readily; they do <u>not</u> decompose, or change spontaneously. In contrast, excited molecules are inherently unstable, and must lose their energy even if no collision with other molecules occurs.

Transference of Energy.

In complex molecules, energy of excitation can be transferred both intra- and inter-molecularly. Energy can be transmitted from one molecule to another, even when they are not in direct physical contact; this is achieved by 'radiationless transitions', -processes which can only be described in quantum mechanical terms. Energy transfer within the same molecule is called 'internal conversion'. Here, the excited molecule returns to the ground state, and the excess energy is converted into vibrational and oscillational energy. The molecule then behaves as it would if heated to a much higher temperature, and the irradiated substance can undergo changes similar to those which occur on pyrolysis.

The influence of excitation is difficult to assess on any quantitative basis.

Reactions of Ions.

Ions which are formed on irradiation are really free-radical ions, since they contain an uneven number of electrons; this distinguishes them from the stable ions produced by the dissociation of salts.

Negative Ion Formation.

The electron which is originally ejected from an atom ('thermal electron') can be captured by a neutral molecule ('ion-pair' formation), this process is not accompanied by a large change in energy; or the electron can recombine with a radical, a process accompanied by a large change in energy.

In ion-pair formation, relative electron affinities determines with which atom the electron will combine. Oxygen and halogens have a high affinity; molecules such as straight-chain paraffins have low affinities; hydrogen and nitrogen cannot combine with 'thermal' electrons.

When an electron is captured by a neutral molecule, the product may dissociate, or the negative molecule may be stable.

Eg.. $AB + e \rightarrow AB^-$ (or A^-B)

or $AB + e \rightarrow A\cdot + B^-$

Charge Neutralisation.

If the positive ion recaptured an electron, then the most probable products would be two radicals, one of which would be excited.

ie. $A^+ + e \rightarrow C\cdot + D^*$

For the recombination of two ion radicals, the presence of a third body is necessary, to remove the excess energy.

ie. $A^- + B^+ \xrightarrow{(M)} A\cdot + B\cdot + M^* \rightarrow AB$

M^* is usually less reactive than the free radicals produced.

Dissociation Of Ions.

If the free radical ion is unstable, it can probably dissociate in a number of ways. A great deal of useful data has been obtained for gaseous hydrocarbons, from the mass spectrograph.[2]

eg. $C_4H_{10}^+ \rightarrow C_4H_{10} + e$

and $C_4H_{10} \rightarrow CH_3\cdot + C_3H_7^+$

or $C_4H_{10} \rightarrow CH_4 + C_3H_6^+$

There is no way of proving that similar changes occur in the liquid phase.

In the main, the reactions produced by gamma-rays are ascribed to free radicals, formed by the processes described. Reaction of an ion with a neutral molecule is a rare event.

Reaction in Gases.

The chemical changes produced in gases on irradiation, are ideal for study with the use of a mass spectrometer. Definite information concerning the type of radicals formed, and their stabilities can be obtained.

Consideration of the data produced has lead to the conclusion that the reactions in gases can best be interpreted in terms of free-radical ions and excited molecules. Lind[3] originally neglected the effect of excited molecules, but explained the products formed from methane, on the formation of clusters round a positive ion.

ie. $CH_4 \rightsquigarrow CH_4^+ + e$

$$CH_4^+ + CH_4 \longrightarrow (CH_4)_2^+$$

$$(CH_4)_2^+ + e \longrightarrow (CH_4)_2^* \quad \text{(highly activated)}$$

$$(CH_4)_2^* \longrightarrow H_2 + C_2H_6$$

The cluster theory was disproved by Smith and Essex[4], who showed that the presence of a charged plate (which would quickly attract and neutralise positive ions) had very little effect on the radiochemical decomposition of nitrous acid and ammonia, showing that most of the dissociation arose from excited molecules.

Lind and Bardwell[5] found that the presence of inert gases catalysed some reactions eg. the alpha-particle induced polymerisation of acetylene.

Reactions in Liquids.

Only indirect methods are available for identifying different ions formed, and any quantitative experiments must be based on assumptions.

Liquid phase reactions differ from those in the gas phase for the following reasons:-

(i) More frequent collisions occur between molecules and hence deactivation of excited states occurs readily.

(ii) 'Third-bodies' are more generally available for radical recombination reactions.

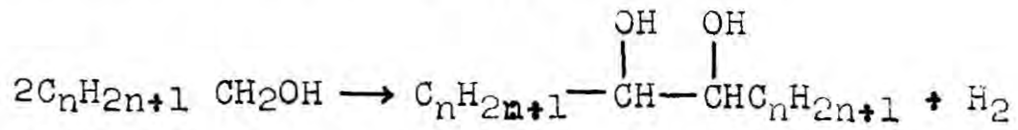
(iii) The surrounding molecules, besides removing energy, as in (i) and (ii) also prevent fragments of a decomposing molecule from escaping from each other. Surrounding molecules cause the fragments to rebound and recombine, as described by the Franck-Rabinowitch[6] 'cage-effect'.. The larger the fragment, the lower the probability of escape. Hydrogen atoms, and methyl groups can 'escape' with relative ease (hence the formation of cross-links in some polymers).

McDonnell[7] investigated the irradiation of straight chain alcohols with alpha-particles and came to the conclusion that 90% of the overall reaction processes were covered by the reactions:-

(a) $CnH2n+1\ CH_2OH \rightarrow CnH2n+2 + HCHO$

(b) $C_nH_{2n+1}\,CH_2OH \longrightarrow C_nH_{2n+1}-CHO + H_2$

(c)



$$2C_nH_{2n+1}\,CH_2OH \longrightarrow C_nH_{2n+1}-\overset{OH}{\overset{|}{C}}H-\overset{OH}{\overset{|}{C}}HC_nH_{2n+1} + H_2$$

Thus, all the reaction was confined to the carbon atom attached to the hydroxyl group.

It is worth noting that it is not necessarily the weakest bond which breaks eg. the energy to break the C-C bond is 15 k.cal. per mole less than that required to break a C-H bond, yet hydrogen is often produced in largest yield on irradiation of organic material. This must be due to an initial localisation of energy in the C-H bond.

Irradiation of Solids.

The only class of solids which have received careful investigation have been macro molecules (i.e. polymers). Reactions which can occur on irradiation of a large molecule are limited. The 'cage-effect' would prevent dissociation into large radicals, since immediate recombination would occur. Reactions which could occur are:-

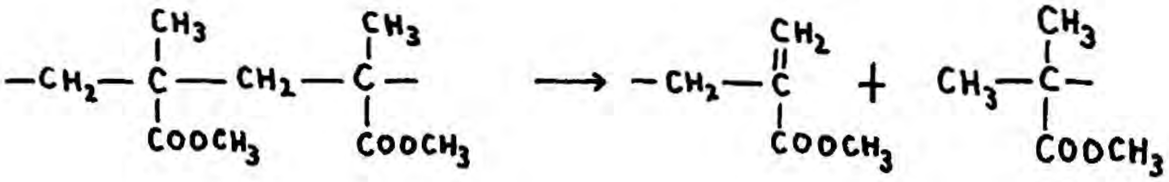
(i) Loss of a hydrogen atom or methyl group, to give a radical macro molecule (and hence cross-linking).

eg. $-CH_2-CH_2- \longrightarrow H + -CH_2-\dot{C}H- \longrightarrow$ cross link.

The extent of cross-linking can be determined from the degree of swelling produced with solvents in which it was soluble before irradiation. The energy needed to produce a cross-link varies considerably from polymer to polymer.

(ii) The dissociation into two stable molecules which cannot combine.

e.g.



$$-CH_2-\underset{COOCH_3}{\overset{CH_3}{C}}-CH_2-\underset{COOCH_3}{\overset{CH_3}{C}}- \longrightarrow -CH_2-\underset{COOCH_3}{\overset{CH_2}{\overset{\|}{C}}} + CH_3-\underset{COOCH_3}{\overset{CH_3}{C}}-$$

Degradation is often accompanied by the production of colour, due to the production of large unsaturated (conjugated) systems.

DOSIMETRY.

Units of Dose.

One roentgen(r) is defined as that quantity of X- or gamma-rays, such that the associated corpuscular emission (electrons) produced per ml. of air at N.T.P. (0.001293 gm), produce in air, 1.e.s.u. of electricity of either charge.

Thus, exposure to air of 1 roentgen results in an energy absorbtion of 83 ergs per gm., or 93 ergs per gm. in water. (These values are obtained from the measured value of the energy required to form an ion-pair i.e. $W = 0.109$ ergs/ml. of air- this value can be assumed to be the same for water- and the fact that 1e.s.u.$\equiv 2.1 \times 10^9$ ion pairs).

This definition of a roentgen for aqueous system is not satisfactory because, although for calculation they can be assumed to be the same, the number of ion pairs formed by one r in air will differ from the number formed in solution. This follows from the difference in mass, and hence difference in stopping powers.

To overcome this difficulty another unit was defined, the roentgen equivalent physical (rep).

One rep is defined as the quantity of X or gamma-rays which releases the equivalent amount of energy in water, as one roentgen releases in air.

For convenience, the rad (R) was defined: one rad corresponds to an energy absorbtion of 100 ergs per gm. in water.

Radiation-Chemical Yield:

The accepted convention for expressing the amount of chemical reaction per unit radiation dose, is by means of the 'G' value. The 'G' value for a reaction is the number of molecules which have been changed for 100 ev of energy absorbed.

CALIBRATION OF THE SOURCE.

The most convenient method for dose-rates of medium intensity, is via a ferrous sulphate dosimeter, which makes use of the overall reaction.

$$2H_2O + O_2 + 4Fe^{++} \rightsquigarrow 4Fe^{+++} + 4OH^-$$

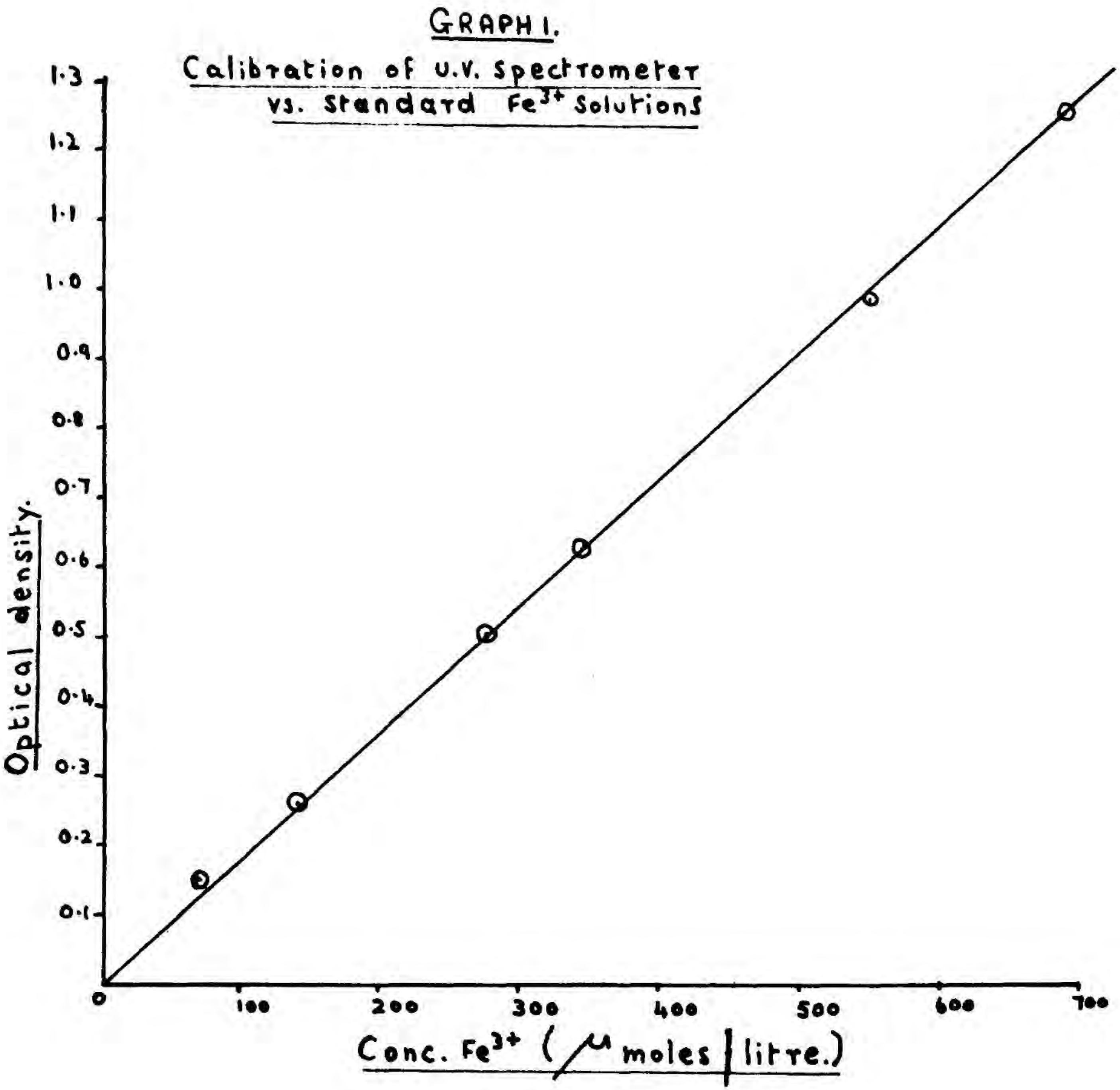
'G' values have been quoted for this reaction ranging from 15 to 20. It is therefore of fundemental importance to state the 'G' value used when quoting dose rates.

The calibration was carried out according to the method of Weiss (Nucleonics, July 1952,p.28).

Experimental.

Preparation of Standard Fe^{3+} Solutions.

Iron alum (1.2 gm) ie. $Fe_2(SO4)_3.(NH_4)_2SO_4. 24H_2O$ was dissolved in approximately 100 mls. of 0.8N Sulphuric acid. This solution was passed twice through a Jones Reductor (to make certain that no iron remained in the Fe^{3+} state). Thus, a stock solution of Fe^{2+} was obtained; this was



GRAPH I.

Calibration of U.V. Spectrometer vs. Standard Fe^{3+} Solutions titrated against $^N/10$ potassium permanganate (standardised against As_2O_3), and found to be 0.011N.

$$\underset{(2 \times 55.85)}{2FeSO_4} + H_2SO_4 + \underset{(16)}{O} \rightarrow Fe_2(SO_4)_3 + H_2O$$

Hence N for Fe^{2+} in this reaction is 55.85 ie. M.

125 ml. of this standard Fe^{2+} solution was placed in a 250 ml. graduated flask together with 2 ml. of 20 vol. hydrogen peroxide. The mixture was shaken, and then allowed to stand for half an hour before making up to 250 ml with 0.8N Sulphuric acid. Thus, a solution containing 0.0055 moles Fe^{3+} per litre had been obtained, ie. 5,500 μ-moles per litre (micro $\equiv \mu = 10^{-6}$).

Standard solutions of increasing dilution were then made up, and their optical densities were determined on a 'Unicam' ultra-violet spectrometer at 20°C, using demineralised (resin column) distilled water as a standard. The results were plotted on GRAPH 1.

Slope (extinction coefficient) $e = 1.2 \times 10^{-3}$

Preparation of Dosimeter Solution.

The following constituents were made up to one litre with distilled water:-

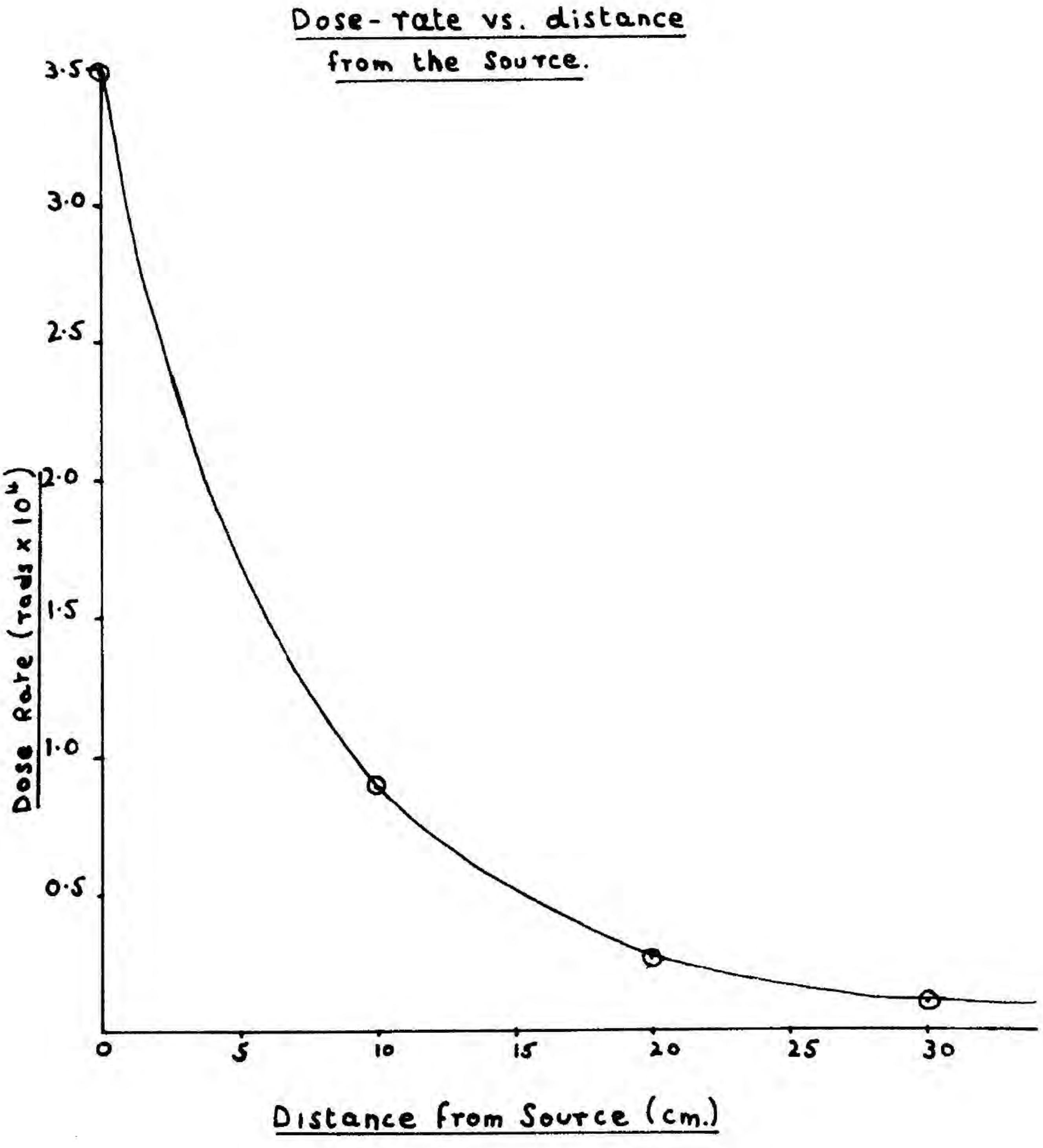
0.4 gm. Ferrous ammonium sulphate.

0.6 gm. KCl

22 ml. concentrated sulphuric acid.

The addition of potassium chloride rules out the necessity for using 'conductivity water', the salt somehow

GRAPH 2.



Dose-rate vs. distance from the Source.

nullifies the effect of slight impurities which may be present in distilled water.

Small polythene capsules were carefully washed, rinsed with dosimeter solution, and then filled with the solution. They were placed at various distances from the source tube, on a board which had been situated at a level approximately co-inciding with the centre of the source capsule. (This was determined by fixing a piece of glass to the tube, and irradiating for a few hours; the darkening was proportional to the distance from the source capsule). The samples of dosimeter solution were irradiated for fifteen hours, after which their optical densities were determined.

The 'G' value which was accepted in this calibration was

<u>'G'=15.5 moles / litre / kilo rep</u>.

Thus, the dose could be calculated from the formula

$$\text{Dose}, = \frac{\text{Optical D.}}{e} \times \frac{10^3}{15.5} \times 0.97 \text{ rads}$$

GRAPH 2 is a plot of dose rate against distance from the source, and it can be observed that this falls off exponentially, to a steady value.

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CHAPTER VI

INTRODUCTION

TELOMERISATION.

Telomerisation has been defined by Hanford and Joyce as: "the process of reacting together under polymerisation conditions, a molecule YZ which is called a telogen with more than one unit of a polymerisable compound having ethylenic unsaturation, called a taxogen, to form products called telomers, having the formula $Y(A)_n Z$, where $(A)_n$ is a divalent radical formed by chemical union, with the formation of new carbon bonds, n being any integer greater than one, and Y and Z being fragments of the telogen attached to the terminal taxogens"

The first example was found by Hanford et al.[2], who attempted to polymerise ethylene in a medium of water and carbon tetrachloride; the product was low molecular weight material containing chlorine.

i.e. $nH_2C{=}CH_2 + CCl_4 \rightarrow Cl_3C(CH_2CH_2)_nCl$

The product consisted mainly of compounds corresponding to n=1-4, but has shown to vary with varying proportions of reactions. This was explained as a chain-transfer process, (telogens are often called chain-transfer agents).

$$R\cdot + CCl_4 \rightarrow RCl + \cdot CCl_3$$

$$\cdot CCl_3 + H_2C{=}CH_2 \rightarrow Cl_3C\ CH_2CH_2\cdot$$

$$Cl_3C\ CH_2CH_2\cdot + nH_2C{=}CH_2 \rightarrow Cl_3C(CH_2CH_2)\cdot_{n+1}$$

$$Cl_3C(CH_2CH_2)\cdot_{n+1} + CCl_4 \rightarrow Cl_3C(CH_2CH_2)_{n+1}Cl + \cdot CCl_3$$

TABLE 1.

Haloalkanes.

CH_3Cl

CH_3Br

CH_3I

CH_2Cl_2

CH_2Br_2

CH_2I_2

CH_2ClI

CCl_3F

C_2H_5Br

C_2H_5I

CH_3CCl_3

Cl_3CCCl_3

$CH_3CCl_2CH_3$

Haloalkenes

$Cl_2C{=}CCl_2$

Haloaldehydes

Cl_3CCHO

$ClCH_2CH_2CHO$

Haloacids, Esters, and Anhydrides.

$ClCH_2COOH$

$ClCH_2COOCH_3$

$Cl_2CHCOOH$

$Cl_2CHCOOC_2H_5$

Cl_3CCOOH

$Cl_3CCOOC_2H_5$

$Cl_3CCOOC_3H_7$

$CH_3CHBrCOOH$

$BrCH_2CH_2COOH$

$(ClCH_2CO)_2O$

$(Cl_2CHCO)_2O$

$(Cl_3CCO)_2O$

$(CH_3CHBrCO)_2O$

Haloalcohols

$BrCH_2CH_2OH$

Cl_3CCH_2OH

$ClCH_2CHOHCH_2OH$

$HOCH_2CHClCH_2OH$

Haloethers.

$ClCH_2OCH_3$

$ClCH_2OCH_2Cl$

$ClCH_2CH_2OCH_2CH_2Cl$

Haloaromatics

$PhCCl_2CCl_3$

C_6Cl_6

Acyl Halides

CH_3COCl

CH_3COBr

$ClCH_2COCl$

$CH_3CH_2CH_2COCl$

$ClCOCOCl$

$COCl_2$

Sulfonyl Halides

$C_6H_5SO_2Cl$

Cl_3CSO_2Cl

CH_3SO_2Cl

$2\cdot CCl_3 \rightarrow Cl_3CCCl_3$

The difference between telomerisation and co-polymerisation is obvious from the fact that telomers contain several polymerised molecules of a polymerisable substance, and the fragments of only <u>one</u> other molecule. Co-polymers contain a number of each of two or more monomer units in their structures, but not fragmented.

TABLE 1[3], is a list of organic compounds containing reactive halogens, which have been used, or suggested as telogens.

Hanford et al[3] found that in halo-alkanes, the order of reactivity is $I > Br > Cl$; and that reactivity deminishes with the number of halogens i.e. $CCl_4 > CHCl_3 > CH_2Cl_2 > CH_3Cl$.

Inorganic compounds such as HCl, $SOCl_2$, SCl_2, S_2Cl_2, and $SiCl_4$[4], have been used as telogens.

Hydrogen can be considered as the simplest telogen,

$$nCH_2{=}CH_2 + H_2 \rightarrow H(CH_2CH_2)_nH.$$

and, in theory, all compounds which contain a carbon-hydrogen bond, are capable of acting as telogens. The affectiveness of a hydrogen atom in telomerisation reactions will depend on its position in the molecule, and the effect of surrounding groups. In aliphatic compounds, secondary and tertiary hydrogen atoms are more reactive than primary, but steric hinderance, or suitable activating groups can change this order. "Aromatic hydrogens" are inert unless activated by ring substituents. The hydroxyl hydrogen eg. as in tertiary butyl alcohol (all the other hydrogens are primary in this alcohol) and water, are inert. Numerous hydrogen containing compounds have been listed as telogens[5], amongst them, sodium bisulphite.[6]

eg. $nCH_2{=}CH_2 + NaHSO_3 \rightarrow H(CH_2CH_2)_nSO_3Na$

The materials produced from this reaction are surface active.

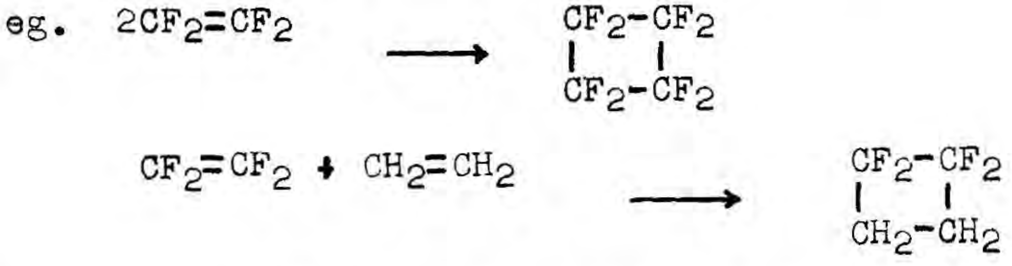
Ethylene appears to be the only hydrocarbon olefin from which telomers have been prepared easily.

Fluoro-olefins[7]

Fluorinated olefins show the same reactions as hydrocarbon olefins i.e. electrophilic, nucleophilic, and free-radical addition; and polymerisation. The major differences from the hydrocarbon series are: the increased tendancy for nucleophilic addition to occur;

eg. $CF_2{=}CFCl + CH_3OH \xrightarrow{KOH} CH_3OCF_2{-}CHFCl$

the tendancy to form cyclic dimers under pressure;



$$\text{eg. } 2CF_2{=}CF_2 \longrightarrow \begin{array}{c} CF_2{-}CF_2 \\ | \quad\; | \\ CF_2{-}CF_2 \end{array}$$

$$CF_2{=}CF_2 + CH_2{=}CH_2 \longrightarrow \begin{array}{c} CF_2{-}CF_2 \\ | \quad\; | \\ CH_2{-}CH_2 \end{array}$$

and the ease with which they undergo telomerisation reactions.

The reactions of fluoro-olefins with polyhalogenoalkyl radicals have been investigated in great detail[8]

Haszeldine carried out reactions with trifluoroiodimethane as telogen, and irradiated mixtures of this compound, and fluoro-olefins with ultra-violet light.

eg. $CF_3I + nC_2F_4 \rightarrow CF_3(C_2F_4)_nI$

$CF_3I + nCF_2CFCl \rightarrow CF_3(CF_2CFCl)_nI$

It was found that the value of n could be controlled by varying the proportion of trifluoroiodomethane in the reaction mixture. Thus, a molar ration of trifluoroiodomethane to tetrafluoroethylene of 10:1 resulted in 94% of heptafluoroiodopropane. Equimolecular amounts gave products with n=1,2,3, and $>$ 3, in 16,10,5 and 63% yields respectively.

The importance of such investigations lies in the fact that telomerisation reactions of this sort are a means of synthesis of fluorocarbon compounds which do not involve fluorination of the corresponding hydrocarbon derivative (a process which is usually not applicable to compounds containing a functional group). The scope of the method is illustrated in the use by Haszeldine[9], of a telogen derived as the adduct from chlorotrifluoroethylene, and iodine chloride.

$ICl + CF_2{=}CFCl \rightarrow CF_2ClCFClI\ (+\ CF_2ICF_2Cl)$

Haszeldine quoted this addition to be specific in giving only the adduct $CF_2ClCFClI$. It has since been shown by several workers, that both modes of addition occur.

By irradiating the ethane $CF_2ClCFClI$, and chlorotrifluoroethylene, an interesting series can be obtained.

ie. $CF_2ClCFClI + nCF_2{=}CFCl \longrightarrow Cl(CF_2CFCl)_nI$

A 13:1 molar ratio $CF_2ClCFClI:CF_2CFCl$ gave a 75% yield of the butane (n=2), whereas equimolar quantities gave n=2, 18%; n=3, 14%; n=4, 17%; n=4, 39%.

Replacement of iodine in these telomers is achieved by the direct action of chlorine; terminal $CF_2Cl{-}CFCl{-}$ groups can then be converted to $CF_2{=}CF{-}$ by zinc and ethanol. The olefin is then available for all of the addition reactions.

The telomer mixtures obtained from these reactions are oils and waxes; they remain liquid to a higher value of n than the corresponding telomers of $CF_3(C_2F_4)_nI$.

From the results of his extensive survey, Haszeldine[9] was able to draw several general conclusions about the factors which influence the telomerisation of olefins by poly halogenoalkyl radicals, which are outlined here.

Factors Influencing Telomerisation by Polyhalogenoalkyl Radicals.

The studies were carried out using telogens of the form R-CFXY.

(a) Initiation Step: Initiation was achieved via the radical RCFX· (eg. $CF_3\cdot$, $C_2F_5\cdot$, $CF_2ClCFCl\cdot$), formed from R-CFXY. The rate of generation of the initiating radical RCFX· (eg. R=polyhalogenoalkyl, or F ; X=halogen or hydrogen; Y=a halogen of higher molecular weight than X) depends on the following factors:-

(i) The strength of the C-Y bond i.e. the weaker C-Y, the greater the ease of generation of RCFX· (and the greater the stability of this radical). The nature of both Y and X determines the C-Y bond strength which decreases in the series Y=F > Cl > Br > I for a given X, and which has been predicted to decrease in the series RCF_2-Y(Y=F) > RCF_2-Y (R=Cl) > RCHF-Y(Y=Cl) > RCFCl-Y(Y=Cl) > RCF_2-Y(Y=Br) > RCHF-Y (Y=Br) > RCFCl-Y(Y=Br) > RCFBr-Y(Y=Br) > RCF_2-Y(Y=I) > RCHF-Y(Y=I) > RCFCl-Y(Y=I) > RCFBr-Y(Y=I) > RCFI-Y(Y=I). The effect of X on the C-Y bond energy has been investigated[10], and the reason for the effect has been attributed to the stability of the RCFX· radical produced, and the increase in steric strain which occurs as X becomes larger.

(ii) The conditions used for supplying the energy required to break the C-Y bond eg. dose-rate, intensity of ultra-violet light, temperature, concentration of peroxide etc., depending on the initiation used.

After generation of RCFX·, attack on the olefin depends mainly on the reactivity of the olefin, and to a lesser extent on the reactivity of the attacking radical RCFX·. In general, halogen bonded to the doubly-bonded carbon atoms, or to carbon atoms adjacent to them, in an olefin containing more than three carbon atoms, decreases the ease of free-radical attack, relative to the unsubstituted olefin[11]. Halogeno-ethylenes are special cases, since the polyfluoro- and chloropolyfluoro-ethylenes polymerise readily. In general the greater the atomic weight of the halogen in a halogeno- ethylene, and the more symmetrical the halogen is distributed (cf. $CF_2=CCl_2$ and $CFCl=CFCl$), the less readily does the olefin polymerise, and the less readily is it attacked by a free radical.

The reactivity of RCFX· is seldom of sufficient importance to be decisive in telomerisation reactions since the more reactive olefins readily combine with even the least reactive radicals. It is only with olefins heavily, or symmetrically substituted by halogen such as chlorine or bromine, or in which inhibition of radical attack occurs, that the less reactive radicals fail to add, and more reactive radicals must be used (eg. X in R-CFX·=H,F,Cl; as opposed to Br and I)

(B) Propagation: The efficiency of the propagation step which is **always** competing with the chain transfer step

$$RCFX\ (olefin)\cdot + RCFXY \longrightarrow RCFX\ (olefin)\ Y + RCFX\cdot$$

depends upon (i) the ease of polymerisation of the olefin, (ii) the reactivity of the intermediate free radical RCFX (olefin)· towards the olefin and towards RCFXY, (iii) the stability of the product $RCFX(olefin)_nY$, and (iv) the relative ease of the chain-transfer step.

(i) An olefin which reacts readily with fragments of a decomposing peroxide to give a polymer of high molecular weight, will in general, tend to giva a longer-chain polymer with RCFXY than one which does not. This is illustrated by comparison of tetrafluoro ethylene, chlorotrifluoro ethylene or trifluoro ethylene, with say trichloroethylene or hexafluoropropene. The ease of polymerisation is related to the ease of radical attack.

(ii) Why a radical such as $RCFX\cdot CH_2CH_2\cdot$ should attack RCFXY rather than another molecule of ethylene, whereas a radical such as $RCFX\cdot CF_2CF_2\cdot$ should attack another molecule of tetrafluoro ethylene rather than RCFXY, is related to the difference between the C-Y and C-C bond energies in $RCFX\cdot CH_2CH_2Y$ and $RCFX\cdot CH_2CH_2CH_2CH_2\cdot$, or in $RCFX\cdot CF_2CF_2Y$ and $RCFX\cdot CF_2CF_2CF_2CF_2\cdot$. This is an aspect which has not yet been elecidated.

The choice of telogen in some cases is governed by the olefin to be telomerised. If trifluoroiodmethene is used in the telomerisation of chlorotrifluoroethylene, then the initiating radical $CF_3\cdot$, is more reactive than the intermediate $CF_3CF_2CFCl\cdot$ and the chain-transfer process is not efficient, short chains being produced when equimolecular proportions of reactants are used. Such cases do not occur often.

(C) Chain Transfer.

(i) The C-Y bond in both telogen and telomer is important. If the bond is weak in the telogen compared with the bond in the telomer, eg. the C-I bond in trifluoroiodomethane compared with the bond in $CF_3(CH_2CH_2)_nI$, then chain-transfer easily occurs, and the products are mainly the n=1 and n=2 compounds. However, if the C-Y bond is strongest in the telogen, then the propagation reaction is favoured, giving longer chains; coupling reactions can even occur.

i.e. 2 RCFX $(\text{olefin})_n \longrightarrow$ RCFX$(\text{olefin})_n(\text{olefin})_n$CFXR

Formation of shorter chains is not necessarily achieved by having a large excess of telogen present.

(ii) Cases arise where the C-Y bond strengths in the telogen RCFXY and telomer RCFX$(\text{olefin})_n$Y are imilar and thus have an equal possibility of breaking.

eg. $CF_2ClCFClI + CF_2\ CFCl \longrightarrow CF_2ClCFClCF_2CFClI$ etc.,

Thus, the terminal iodine atom is attached to the telogen and telomers via the -CFClI group. To prevent formation of long chains, a large excess of telogen must be used.

(iii) When a reactive olefin (i.e. one which easily homopolymerises) is used with an efficient telogen (i.e. one which easily forms radicals) eg. trifluoroiodomethane, the initiating radical $CF_3\cdot$ is not very reactive, but sufficiently so, to react with the olefin. The chain-transfer process is favoured, but short chains can be obtained by having a large excess of telogen present.

(iv) When a telogen which is efficient is used with an unreactive olefin, then the product tends to be RCFX$(\text{olefin})_n$Y where mainly n=1, and it is difficult to encourage the formation of longer chains by increasing the proportion of olefin. Examples of unreactive olefins are :-

C_2H_4, C_2H_2, $CH_2{=}CHCF_3$, $CH_2{=}C{=}CH_2$, $CH_3CH{=}CH_2$, $CF_3CF{=}CF_2$, and $CFCl{=}CFCl$.

Olefins of intermediate reactivity are:-

CH_2CF_2, CH_2CHF, CH_2CHCl and $CH_2{=}CHCOOCH_3$

Attempts have been made to cause olefins like ethylene and hexafluoropropene to give a telomer $RCFX(\text{olefin})_nY$ with n=4, or 5, by reducing the proportion of chain-transfer agent RCFXY. This resulted in the intermediate radical undergoing reactions other than addition to another molecule of olefin, i.e. disproportionation, dimerisation, or expulsion of halogen to give an olefin.

Thermal Telomerisation.

Hauptschain, Braid and Lawlor[12] extended telomerisation reactions to unreactive olefins. Previous investigations had dealt mainly with photochemical, or peroxide induced telomerisations of fluoro-olefins which are easily polymerised by free-radical initiators, i.e. reactive olefins. Hauptschein et al., investigated thermally induced telomerisations of unreactive olefins.

The conclusion was reached that such reactions do not involve a significant contribution of a chain mechanism; instead, they postulated that thermal telomerisation of unreactive olefins proceeds via successive addition steps. It was indicated that addition across the double bond occurs simultaneously at both carbon atoms, without dissociation of the telogens (i.e. iodo-compounds).

Reactions were carried out with hexafluoropropene and:- CF_3I, C_3F_7I, $C_4F_9CFICF_3$, $C_4F_9CF(CF_3)CF_2CF(CF_3)I$ and $CF_2ClCFClI$, as telogens.

Telomers $R[CF_2CF(CF_3)]_n I$ were obtained, where :- $R=CF_3$, C_3F_7, $C_4F_9CF(CF_3)$, $C_4F_9CF(CF_3)\ CF_2CF(CF_3)$; and $CF_2ClCFCl$; and values of $n=1$ to > 10.

This is an excellent example of how a telomer series can be ascended, using the previous telomer as the next telogen. In thermal synthesis, the telomer must contain the $-CF_2I$ group before it can act as telogen, otherwise, the temperature required to overcome the higher activation energy is often excessive.

Iodine in the telomers was replaced by fluorine, by passing the telomer over cobalt trifluoride.

Work Carried out by The Imperial Smelting Corporation.

Telomerisation.

In connection with the present contract of work, issued by the Ministry of Supply; I.S.C. Ltd., investigated the commercial application of telomers of fluoro-olefins, as synthetic oils or greases.

Thermal telomerisations using $CF_2ClCFClI$ as telogen, were carried out with chlorotrifluoroethylene and vinylidine fluoride.

i.e. $CF_2ClCFClI + nCF_2CFCl \rightarrow Cl(CF_2CFCl)nI.$

$$CF_2ClCFClI + nCF_2CH_2 \rightarrow CF_2ClCFCl(CF_2CH_2)_nI$$

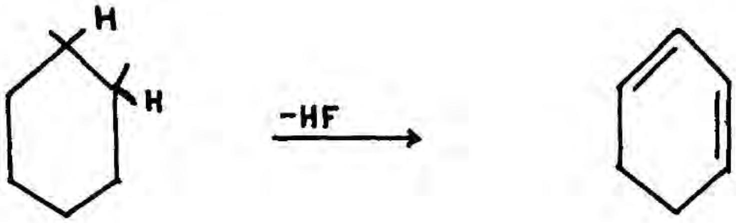
Difficultry was experienced in the replacement of iodine by chlorine, or fluorine in these telomers. The conclusion was reached that some substitution of iodine had occurred during telomerisation, which produced compounds with iodine in positions other than terminal; this would explain the difficultry experienced in replacing the iodine.

Coupling reactions of the telomers were investigated; mercury and zinc were found to act slowly, zinc plus acetic anhydride was more satisfactory.

One of the most productive experiments carried out, was the peroxide initiated telomerisation of vinylidine fluoride, using $SOCl_2$ as telogen. Oils containing sulphur were obtained below 100°C, but above this temperature, no sulphur was detected in the product.

Polymerisation of Octa fluoro cyclohexa-1,3- and-1,4- dienes.

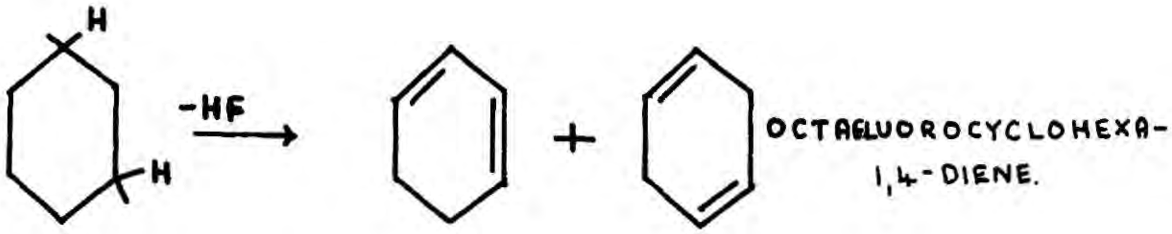
The controlled fluorination of benzene (cobalt trifluoride) has given a route to polyfluoro cyclohexanes. By choosing the appropriate conditions, a maximum yield of decafluorocyclohexanes can be obtained. These, by elimination of hydrogen cluoride, yield the octafluoro cyclohexa-dienes.



OCTAFLUOROCYCLOHEXA--1,3-DIENE.

TABLE 2.

Comonomer	Relative Rate of Reaction	Molecular Weight	Fluorocarbon Content
Ethylene	Much Faster	High	up to 50 mole %
Butadiene	" "	"	"
Vinyl Chloride	Slower	"	High
Styrene	Much slower	Low	High
Methyl methacrylate)	" "	"	"
Acrylonitrile) Ethyl acrylate)	Slower	Fairly high	Low
Vinylidene Fluoride)	"	" "	"
Chlorotrifluoroethylene)	Much slower	Low	Very low?



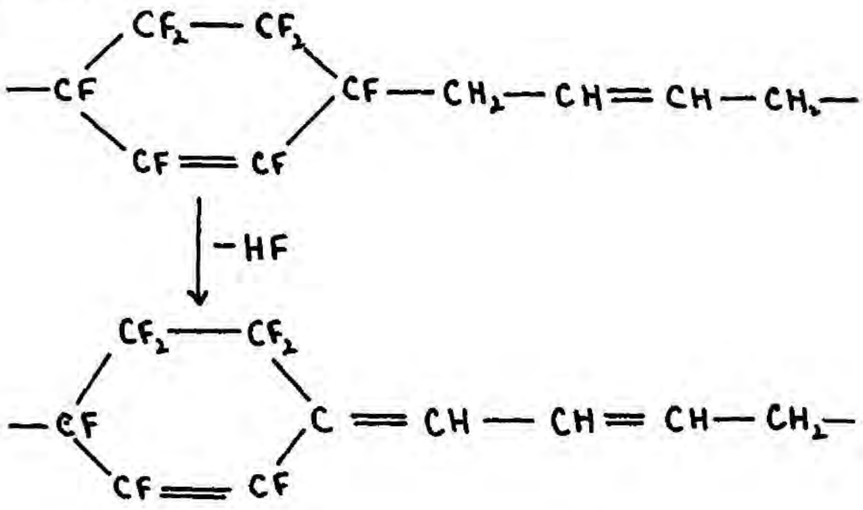
The dienes were found to be air-sensitive, especially the -1,3-isomer.

Such compounds immediately suggested themselves for polymerisation, and use in co-polymerisation reactions with other monomers.

It was found that the dienes did not form homopolymers, and this was attributed to extremely stable radicals produced from the dienes, which show no tendancy to combine with each other, or to attack other molecules to initiate a chain mechanism.

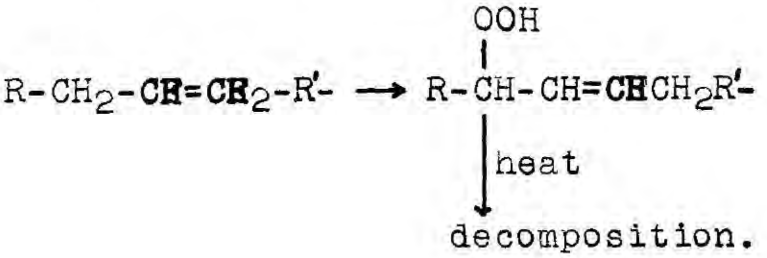
Co-polymers with many monomers were produced, and TABLE 2 shows the initial co-polymers which were prepared. The dienes have since been co-polymerised with an extensive range of other monomers. All of these polymerisations were carried out by an emulsion process, a technique which involves complex recipes; the products are, as a consequence considerably contaminated, and a rigid purification process is called for.

The co-polymer with butadiene was the most helpful as a rubber. It was tested for heat stability by measuring the rate of weight loss in vacuo, and in air. The co-polymers was found to decompose in vacuo via the elimination of hydrogen fluoride,



and by scission of polymer chains, with the evolution of constituent monomers.

It was expected that in air, the decomposition process was the normal oxidation of poly-dienes i.e. attack on the allylic hydrogen atoms.



$$\begin{array}{ccl} \mathrm{R\text{-}CH_2\text{-}CH{=}CH_2\text{-}R'\text{-}} & \longrightarrow & \mathrm{R\text{-}\overset{\overset{OOH}{|}}{C}H\text{-}CH{=}CHCH_2R'\text{-}} \\ & & \quad\Big\downarrow \text{heat} \\ & & \quad \text{decomposition.} \end{array}$$

CHAPTER VII

DISCUSSION OF RESULTS

DISCUSSION.

POLYMERS.

Attempts to polymerise octafluorocyclohexa-1,3-, and -1,4- dienes, each in its pure state, and also as an equimolecular mixture of both compounds, by means of gamma-irradiation were unsuccessful. The 1,3- diene left a very small amount of a viscous oil when distilled after irradiation.

The 1,3- diene was found to form co-polymers easily, and in excellent yields (70-100%) with various monomers; the results are shown in the table.

Samples of all of the polymers are being investigated by Dr. Wright, of the Royal Aircraft Establishment, Farnborough, for heat stability. At the time of writing, details were available only on the butadiene-C_6F_8 rubber. It was found that this rubber, prepared by means of gamma-irradiation, lost considerably less weight in the 500-700°C range, than similar samples provided by the Imperial Smelting Corp. Ltd., (prepared by emulsion polymerisation). Both of the samples however, were considerably more stable to heat than 'Viton A' (a co-polymer of CH_2CF_2 and CF_3CFCF_2) see Straus and Wall (Report No. 6177, Nat. Bureau of Standards, Oct. 6th 1958), according to whom, 'Viton A' is 90% volatilised at 450°C. It also appears that the

CO-POLYMERS OF 1,3.-C_6F_8

MONOMER	APPEARANCE OF POYMER	SOLUBILITY IN BENZENE AND ACETONE	MOLES MONOMER: C_6F_8		% FLUORINE
			STARTING RATIO	CONSTITUTION OF POYMER	
STYRENE	White, glassy	Soluble	5:1	5.4:1	19.4
STYRENE	White, glassy	Soluble	1:1	2.2:1	33.1
METHYL-METHACRYLATE	Solid, glass, (perspex)	Soluble	5:1	5:1	19.0
" "	White powder	Soluble	1:4	6:1	18.1
BUTADIENE	Brown rubber	Swells	4:1	1.5:1	41.8

butadiene- C_6F_8 rubber retains its rubber properties to low temperatures (approx. -80°C).

The styrene, and methyl methacrylate co-polymers prepared by gamma-irradiation, have infra-red spectra which are almost identical with those of similar co-polymers with approximately the same fluorine content, prepared by the emulsion method (I.S.C.) Ltd..,). The butadiene co-polymer prepared by gamma-irradiation differs in having a strong peak at (v-max)1397 cm.$^{-1}$. This has been attributed to some 1,4 addition of cyclic diene molecules to butadiene (1,2 addition to butadiene is most common), which probably does not occur by the emulsion method.

The increased thermal stability of the rubber prepared via gamma-irradiation could arise from the fact that this material does not contain any of the fragments of impurities which the rubber prepared via an emulsion method must contain (ie. as introduced in the recipe). In addition, a slight degree of cross-linking may exist in the gamma-initiated product.

The butadiene rubber has been shown to decompose thermally, with the elimination of hydrogen fluoride. This probably comes from the points where the butadiene residues are joined to the fluorinated rings, where a carbon atom carrying hydrogen atoms is attached to a carbon atom carrying a tertiary fluorine atom. In view of this, attempts have been made to prepare co-polymers of the 1,3-cyclic diene, and fully halogenated simple olefins, such as:- $CF_2=CF_2$, $CF_2=CFCl$, $CF_2=CCl_2$, and $CF_3CF=CF_2$. With the first two of these, the polymers obtained appeared, by analysis, and their infra-red spectra, to be homopolymers of the simple olefin. Very little, if any, of the cyclic diene had been incorporated into the polymers.

In the other two cases, oily residues were left after distilling the unchanged starting materials from the irradiated mixture. One of the products corresponded to $-[-(CF_2-CCl_2)_{2-3}-(C_6F_8)-]_n-$. Analysis of the products from the 1,3-diene, and CF_2 CCl_2 (ie. containing only fluorine as halogen) could cast little light on to their constitution. It seems possible that they arose from ill-defined fragmentation reactions. Yields of these oils were very low, and their constitution requires further investigation, particularly molecular weight.

Future Work.

The following lines require investigation:-

(i) Preparation of long chain co-polymers from octafluorocyclohexa 1,4-diene with simple hydrogen and oxygen containing monomers.

(ii) Reaction of the 1,4-diene, and $CF_2=CCl_2$ and $CF_3CF=CF_2$

(iii) Co-polymerisations in the presence of telogens, so that the incorporation of their fragments in the chain can be used to modify the properties of the polymers.

TELOMERS.

The present investigation is being carried out with two objects in mind, (i) comparison of gamma-initiated telomerisation with other methods (ultra-violet and thermally induced), and (ii) the prospect of being able to promote reactions which cannot easily be achieved by other means.

The work described here must be regarded as an initial survey of the method, and of particular telogens, with more detailed work to follow.

Using a 'reactive' olefin, tetrafluoroethylene, and either ethyl chloride or trifluoromethyl iodide as telogen, it was found that solids $CF_3(CF_2CF_2)nI$ with relatively high values of 'n' were obtained. The value of 'n' was influenced to some extent by increasing the molecular proportion of telogen in the mixture, but this effect was not comparable to the influence of the proportion of telogen on 'n' value, which is observed in ultra-violet, or thermally induced telomerisations.

Increasing the molecular proportion of tetrafluoroethylene from $1C_2F_4$: 16 C_2H_5Cl, to $1C_2F_4$: $8C_2H_5Cl$ had little effect, the average 'n' value being approximately five in each case.

Using C_2F_4, and CF_3I in the molar ratios 1:3, 1:4, and 1:13 gave solids with average 'n' values of 10,7 and 6 respectively.

An 'unreactive' olefin hexafluoropropene, was investigated with a series of five telogens; methyl alcohol, methyl mercaptan, carbon tetrachloride, difluorodibromomethane, and pentafluoroethyl iodide.

Using a 5:1 molar excess of telogen: methyl alcohol, methyl mercaptan, and CF_2Br_2gave excellent yields of the simple addition compounds, such as $CH_2OH\left[CF(CF_3)-CF_2\right]_nH$, where n=1. In the case of CF_2Br_2 however, there was some product which, by analysis, contained the telomer corresponding to n=2. Carbon tetrachloride, and pentafluoroethyl iodide gave low yields of the n=1; and n=1, plus n=2 telomers respectively.

One point which has shown up in the reactions with methyl alcohol, and CF_2Br_2, is that the product appears to be a <u>mixture</u> of isomers. According to the literature telomerisations by other methods appear to be more specific, in giving only one addition product. Since the reaction mixture from methyl alcohol is less complex, it is being investigated further, in order to characterise the actual isomers produced.

The effect of time of irradiation is under investigation. It will obviously depend on the olefin employed, and stability of the telomers initially produced. If the olefin is unreactive, and the chain-transfer process is not efficient, then the time of irradiation will only effect the overall yield, and not the constitution of the product.

It seems obvious, and it has been proved with many radiation induced **reactions**, that dose-rate only effects the overall yield.

The octafluorocyclohexa-1,3- and-1,4- dienes are compounds which fit the description of monomers which are difficult to polymerise (ie. impossible), and it is intended to subject them to a series of telomerisation reactions.

Only one of these has so far been carried out, and that is the reaction of undecafluorocyclohexane with octafluorocyclohexa-1,3-diene. A high boiling liquid containing 69.1% fluorine; and a residual solid containing 67.6% fluorine, were obtained. Since the fluorine content of the individual reactants are both very close to these figures it is impossible to draw any definite conclusion about the constitution of the product at this stage.

Telogens.

From the survey which has been made, the order of telogen reactivity can be assessed as:-

$CH_3SH=CH_3OH > CF_2Br_2 > CCl_4=C_2F_5I$.

This order is of course, with respect to an 'unreactive' olefin. To obtain more insight into relative telogen reactivity and efficiency, and what factors influence these, it will be necessary to irradiate some of these telogens with a series of olefins of gradually increasing 'reactivity'.

Future Work.

1. The first stage of more detailed work, will involve irradiation experiments on a much larger scale than those described here.
2. Investigation of other halogen containing compounds as telogens eg. ICl, $SiCl_4$, $SOCl_2$, and possibly Cl_2 (the reaction between Cl_2 and C_2F_4 is reputed to be explosive.)
3. A survey of the use of hydrogen containing compounds as telogens. Since methyl alcohol is such an efficient telogen, other compounds (possibly some aromatic) should contain hydrogen with telogen activity. This reaction could lead to new compounds which would be difficult to synthesise by other methods.

CHAPTER VIII

EXPERIMENTAL

EXPERIMENTAL

VACUUM APPARATUS

The apparatus was designed, using conventional devices to suit the problem in hand, and the laboratory space. A diagram of the apparatus is shown in FIGURE 1.

Construction

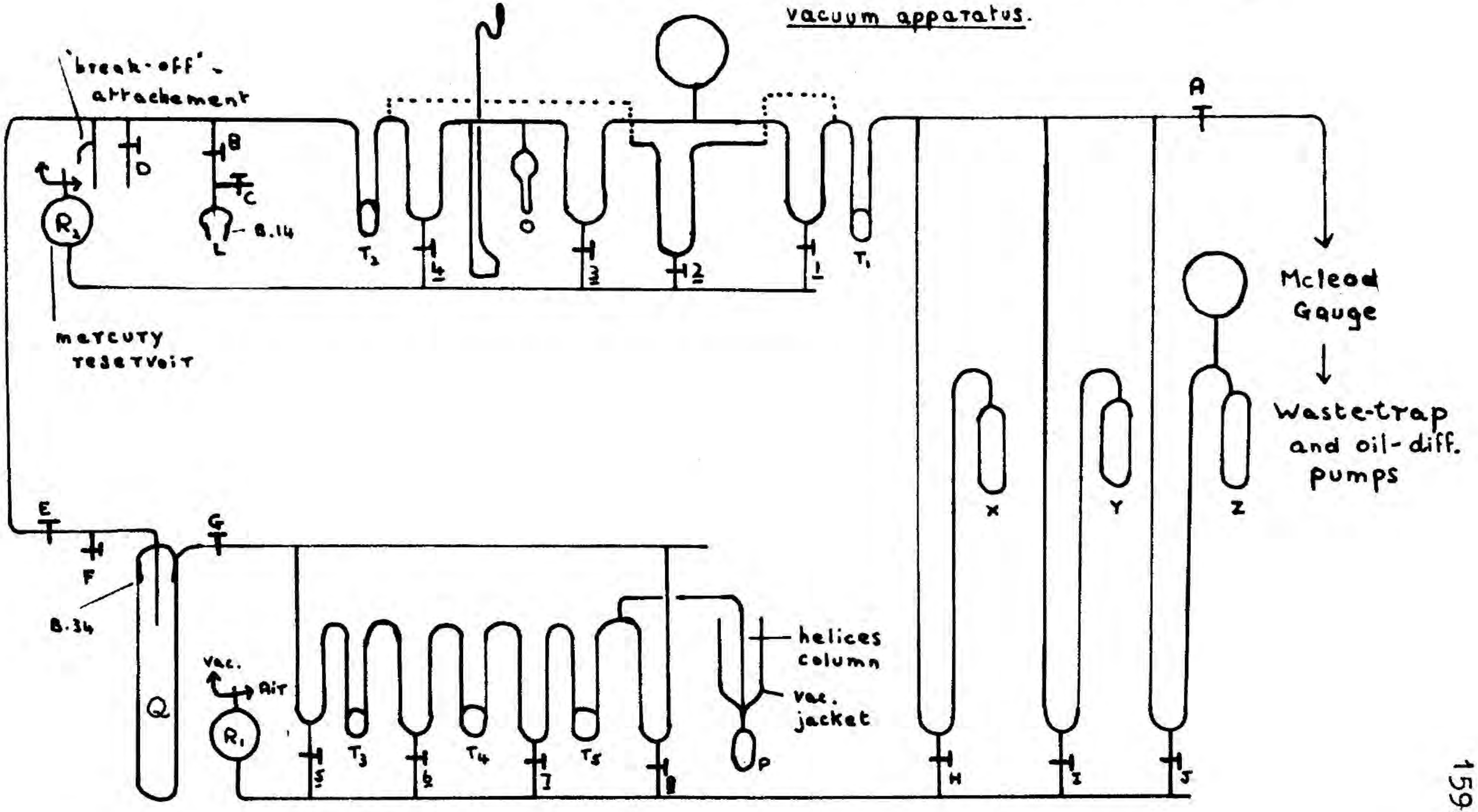
The mercury float-valves were constructed from 8 mm. (inside diameter) and 11 mm. (outside diameter) (float) bore glass tube. The tube from which the float was to be constructed was sealed at one end; the 8 mm. tube was then heated, and allowed to collapse until a suitable seating for the float was obtained. A good seal was produced by grinding the float into the seating, using a smear of fine grinding paste.

A core of soft-iron was placed into the float, held firm with a little picene, and then sealed off. Picene serves to prevent movement of the iron inside the valve; this can sometimes cause the valve to crack. A soft-iron core serves the dual purpose of giving weight to the valve, to aid opening; and allowing a magnet to be applied if the valve sticks.

The line was constructed from 11 mm. diameter tube, and large bore taps were used when placed directly in the line; the vessel O was made from a 250 ml. flask.

Connections from the mercury reservoirs, to the float-valves and storage system, were of thick-walled capilliary

FIG. 1. Diagrammatic representation of the vacuum apparatus.



tube. The mercury reservoirs each incorporated a three-way, hollow-barrel tap. Storage vessels X, Y, and Z were connected to the line via U-tubes with arms longer than 80 cm. In this way, mercury could be introduced through taps H, I, J, enabling the vessels to be sealed from the line by a pressure difference up to one atmosphere if necessary, in either arm.

Working

The apparatus was connected to a 'Metrovic' rotary oil pump, in series with two mercury diffusion pumps which were operated by bunsen burners. The oil pump was capable of evacuating the system to 0.05 mm., and the diffusion pumps further evacuated to a 'sticking-vacuum' (i.e. as registered by a 'vacustat'), which is generally regarded as a rough measure of a pressure below 10^{-4}mm.

A break-off attachment was incorporated (the side-arm contained a ball-bearing) to enable materials to be transferred to the system without coming into contact with the atmosphere.

Calibration

The volumes enclosed between the float-valves 1 and 4, and 3 and 4, required to be calibrated; for this purpose, an extra U-tube manometer was attached at D.

Solid carbon dioxide was placed in the large trap Q, and surrounded by a liquid-air trap. After evacuating

(10^{-4} mm.), the carbon dioxide was transferred to trap T_3 in the fractionating train, and any uncondensed material was pumped off. The distillation process was repeated, and in this way, carbon dioxide free from air was obtained.

A bulb with tap, and B.14 cone connected, was attached to the line at L; the volume of the bulb and bore of the tap had previously been determined by weighing, and reweighing full of water at 20°C. After evacuating, valves 2 and 4 were closed, and the carbon dioxide was allowed to evaporate, filling the line and the calibrated bulb to a pressure which could be read from the extra manometer which had been attached.

When the calibrated bulb had been filled to about 25 cm. pressure, the tap was closed, and carbon dioxide in the line was condensed again; tap E was closed, valves 1-4 opened, and the system evacuated. Valves 2 and 3 were closed, and carbon dioxide in the bulb was transferred to O by surrounding O with liquid air. Valve 4 was closed, the carbon dioxide allowed to expand, and its pressure was noted, i.e. in V_1; valve 1 was closed, the carbon dioxide condensed again in O by surrounding with liquid air, valve 3 opened; and the carbon dioxide was allowed to expand, i.e. into V_2. The pressure was again measured. Thus, from the simple relationship $PxVx = PyVy$, the volumes of V_1 and V_2 were calculated.

By adding further amounts of carbon dioxide in the manner described, readings over a range of pressures were obtained.

Before constructing the manometer, the volume per unit length of the arms was determined: a known weight of mercury was added to the tube, and the length which it occupied in the tube was measured.

Volume per unit length = 0.86 ml./cm.

The volumes of V_1 and V_2 calculated at certain pressures were corrected to zero pressure by subtracting the volume of the manometer arm exposed at that particular pressure, which would otherwise contain mercury at zero pressure (i.e. $\frac{1}{2}$ pressure x 0.86 ml.).

The volumes at zero pressure were found to be:

V_1:- 477 ml.
V_2:- 3,090 ml.

SECTION 1:- POLYMERISATION OF OCTAFLUOROCYCLOHEXADIENES

Octafluorocyclohexa-1,3-diene was transferred via a break-off attachment, to the storage vessel X; gaseous olefins were stored in Z after purification. The starting materials were freed from air by allowing to warm up in the storage system, re-condensing in liquid air and then evacuating to 10^{-4} cm. This procedure was repeated several times to remove all traces of air.

Reaction mixtures were sealed in Carius tubes for irradiation; these were initially attached to B.14 cones for connection to the vacuum line. The tubes incorporated a thickened portion, which facilitated sealing-off under vacuum; this thickening was achieved by rotating the tube in an oxygen-coal gas torch, and with judicious pulling or pushing, the glass was allowed to collapse to the required degree.

In all experiments, before final sealing of the tubes, any trace of air was removed by the procedure just described. Unless otherwise stated, the Carius tube experiments described in this investigation were subject to a dose-rate of 3×10^4 rads per hour during irradiation.

Homopolymerisation of Octafluorocyclohexadienes

Tubes containing octafluorocyclohexa-1,3-diene (2 gm.); -1,4-diene (2 gm.); and a tube containing a mixture of the -1,3- (1 gm.) and the-1,4- (1 gm.) dienes, were sealed in the absence of oxygen, and irradiated for approximately twelve weeks.

The tubes were opened, and the products distilled in an atmosphere of nitrogen; a trace of a viscous oil was left as residue from the tube which had contained the -1,3-diene alone. There was not enough material for investigation. No other products were obtained.

Attempted Co-Polymerisation of Octafluorocyclohexa-1,3-diene and Per-Halo Olefins

1. Kel-F Monomer (1,1,2-trifluoro 2-chloro ethylene; $CF_2 = CFCl$)

A Carius tube was charged with $CF_2 = CFCl$ (4.4 gm.), and octafluorocyclohexa-1,3-diene (2.4 gm.), i.e. molar ratio 3.4 CF_2CFCl : $1C_6F_8$.

Irradiation time:- 15 days.

The tube was cooled in liquid air before opening, after which it was quickly transferred to the large trap Q; Q was then immersed in liquid air. The purpose of taps E and G was to enable the trap Q to be isolated for the inclusion of tubes.

When cold, Q was evacuated and then the liquid-air bath was removed; this allowed the volatile material to be pumped off and collected in a cold trap at T_2.

Residue:- A white powder (0.93 gm.).

Analysis:

Found: F,48.2%; Cl, 27.7% (sodium fusion).

Calculated for $(CF_2CFCl)n$: F,49.0%; Cl, 30.4%.

Thus, there appears to have been only slight inclusion of octafluorocyclohexa-1,3-diene into a homo-polymer of 1,1,2-trifluoro 2-chloro ethylene. This was borne out by the infra-red spectrum of a sample; this showed strong absorbtion bands at 1199, and 1125 $cm.^{-1}$, which is in agreement with a spectrum quoted by Weiblen ('Fluorine

Chemistry', Vol.2, ed. by Simons, p.497), of a homo-polymer corresponding to $(CF_2\text{-}CFCl)n$.

The volatile material was transferred to trap T5 for fractionation: with valve 8 closed, T3 was immersed in liquid air, and T4 and T5 in baths made by mixing methylene chloride and liquid air until a slurry was obtained (-96°C). Fractionation was allowed to continue for $\frac{3}{4}$ hour, and the less volatile fraction corresponded to 2.6 gm. as C_6F_8.

Thus, all of the octafluorocyclohexa-1,3-diene had been recovered, together with a little entrained $CF_2,CFCl$.

2. <u>Tetrafluoroethylene ($CF_2 = CF_2$)</u>

Tubes were charged in the ratios shown in the table. Time of irradiation:- 45 days.

	Starting Mole Ratio	Wts. (gm.) C_6F_8	C_2F_4	Recovd. Wts. C_6F_8	C_2F_4	Wt. of Polymer
A	1 C_6F_8 : 1 C_2F_4	5	2.5	5.5*	1.9	0.5 g.
B	2 C_6F_8 : 1 C_2F_4	9.5	2.1	9.3	1.7	0.3 g.
C	1 C_6F_8 : 2 C_2F_4	2.7	2.2	2.7	1.8	0.4 g.

*incomplete fractionation

Analyses:

Theoretical for $(CF_2CF_2)n$; F, 76.0%

Found:- (sodium fusion)

A. F, 71.1%

B. F, 68.1%

C. F, 72.5%.

This shows that there is no possibility of being able to include a significant amount of octafluorocyclohexa-1,3-diene into a co-polymer with tetra fluoroethylene.

3. **1,1-Difluoro 2,2-Dichloroethylene ($CF_2 = CCl_2$)**

A tube was charged with $CF_2.CCl_2$(3.1 gm.), and 1,3-C_6F_8 (1.8 gm.) i.e. mole ratio 2.9 $CF_2.CCl_2$: 1 C_6F_8.

Time of irradiation:- 46 days.

Little effect was observed, except a few oily drops developed after a few weeks' irradiation.

The tube was opened, and after unused $CF_2.CCl_2$ had been removed, the remaining liquid was distilled into the following fractions:-

Fraction 1. B.p. 35-50°C. (0.5 gm.)

Analysis: (Biphenyl sodium)

F, 53.5%; Cl, 18.2%.

A polymer with 1 mole C_6F_8 to 2 mols. $C_2F_2Cl_2$ requires F,53.3%; Cl, 19.9%.

Fraction 2. B.p. 55-70°C. (0.6 gm.). This was recovered octafluorocyclohexa-1,3-diene.

Oily residue B.p. 80°C. (0.8 gm.).

Analysis: (Biphenyl sodium). F = 40.6%, Cl = 31.1%.

A polymer with 1 mol C_6F_8 to 2 mols $C_2F_2Cl_2$ requires F = 46.5%, Cl = 29.0%, and a formula $-\!\![C_6F_8-(C_2F_2Cl_2)2-3]\!\!-_n$ is therefore indicated.

4. Hexafluoropropene ($CF_3 - CF = CF_2$)

Tubes were charged with:-

A. Hexafluoropropene (2.2 gm.) plus 1,3-C_6F_8 (3.4 gm.); mole ratio 1 C_3F_6 : 1 C_6F_8.

B. Hexafluoropropene (1.8 gm.) plus 1,3-C_6F_8 (5.6 gm.); mole ratio 1 C_3F_6 : 2 C_6F_8.

Time of irradiation:- 45 days.

The tubes were opened, and the unused starting materials were recovered by distillation at atmospheric pressure. In each case, after removal of the unused octafluorocyclohexa-1,3-diene, an oily residue (B.p. 80°C.) remained.

Residue from A. 0.4 gm.

Analysis: (Biphenyl sodium) F, 64.2%.

Residue from B. 0.6 gm.

Analysis: (Biphenyl sodium) F, 67.4%.

Since C_3F_6 has 76.0%F., and C_6F_8 has 67.9%F., these results are peculiar and need further investigation. The experiment will be repeated on a larger scale.

Butadiene ($CH_2 = CH - CH = CH_2$) plus Octafluorocyclohexa-1,3-diene.

Butadiene was introduced into the vacuum line; a trap connected to a tube containing sodium hydroxide pellets was attached at L and evacuated. The butadiene was passed over the sodium hydroxide by condensing in the trap, and then allowing it to distil back into the vacuum line. In this way, stabiliser (e.g. hydroquinone) was removed.

A tube was charged with butadiene (2.5 gm.) and 1,3 C_6F_8 (2.6 gm.), i.e. mole ratio 3.9 butadiene : 1 C_6F_8.

Time of irradiation:- 5 days 12 hours.

The tube was opened, transferred to the vacuum line, and volatile material removed.

Wt. of polymer:- 2.9 gm.

The volatile material was fractionated for 30 minutes, from a solid carbon dioxide-acetone bath (-76°C), until the vapour-pressure at this temperature dropped from 6 mm. to approximately zero.

Fraction 1: Recovered butadiene (1.6 gm.). The molecular weight of this material was determined: a bulb was attached to the vacuum line, and its weight determined when evacuated. A known volume of Fraction 1 was condensed into the bulb, and its weight determined.

Molecular weight, 50. (Butadiene, 54; C_6F_8, 224).

Thus, an efficient fractionation had taken place.

Fraction 2: Recovered octafluorocyclohexa-1,3-diene (0.5 gm.).

Constitution of the Polymer

From the amounts of starting materials used up (0.9 gm. butadiene; 2.1 gm. 1.3-C_6F_8), the molar constitution of the product was determined as, 3.1 butadiene: 2 C_6F_8. A 3:2 ratio would require the analysis, F, 49.4%.

Analysis: (After the polymer had been warmed to 50°C. at 10^{-4} cm., to remove all traces of the monomers).

Found: F, 48.1% (sodium fusion).

Considering that the polymer is probably not homogenous, this is quite remarkable agreement.

When first removed from the tube, the polymer was a translucent rubber; it turned slightly brown on standing, but prolonged contact with air did not increase this discolouration.

Effect of Heat on the Rubber

A portion of the rubber (0.84 gm.) was heated in the vacuum line at 150°C. for six hours; the volatile material was collected and weighed (0.10 gm.).

The rubber discoloured considerably during the process, and a 12% loss in weight (0.11 gm.) coincided with the weight of the volatile material collected (proving the efficiency of the system).

Analysis: F, 48.4% (sodium fusion).

Thus, the rubber must have decomposed uniformly, giving off the constituent materials in the proportion in which they had originally combined. This evidence indicates a very regular structure.

A portion of the rubber (0.114 gm.) which had been heated in vacuo at 150°C., was heated in air for twelve hours at 150°C. The material, which was discoloured already, appeared to partly resinify, and a slight gain in weight was noted (final weight 0.116 gm.).

Analysis: F, 47.9%.

The constancy of these fluorine analyses is a good indication that the sodium fusion method gives reliable results for the analysis of these polymers.

Methyl Methacrylate ($CH_2 = C(CH_3)COOMe$)plus Octafluorocyclohexa 1,3-diene

Starting Ratio 5:1:- Stabilised methyl methacrylate was shaken several times with portions of dilute sodium hydroxide solution, until the sodium hydroxide layer was no longer coloured. The methyl methacrylate was then washed several times with water, and dried by standing over freshly ignited magnesium sulphate.

Methyl methacrylate (3.0 gm.) was weighed directly into a Carius tube which was then attached to the vacuum line and cooled in liquid air before evacuating. This process, rather than distilling the material into the Carius tube, was adopted, because methyl methacrylate (and also styrene) has a tendency to polymerise in the vacuum line on distillation.

The tube was charged with octafluorocyclohexa-1,3-diene (1.3 gm.); thus the starting molar ratio was 5.1 methyl methacrylate: 1 C_6F_8.

Time of irradiation:- 3 days, 6 hours.

A very hard, transparent glass (4.2 gm.) was obtained, which had set into a mould of the Carius tube.

Analysis: F, 19.0% (sodium fusion).

A 5 methyl methacrylate: 1 C_6F_8 molar ratio would require an analysis; F, 20.9%.

The analysis is not in such good agreement with the known constitution (i.e. a 100% conversion of starting materials was effected), but this probably indicates that the polymer is not quite homogeneous in this case.

Starting Ratio 1:4 :- A tube was charged with methyl methacrylate (1.2 gm.) and octafluorocyclohexa-1,3-diene(10.3g.) in the manner already described; thus the starting molar ratio was 1 methyl methacrylate: 3.9 C_6F_8.

Time of irradiation:- 4 days, 17 hours.

Removal of the volatile material left a white powder (1.6 gm.).

Analysis: F, 18.1% (sodium fusion).

This analysis corresponds to a molar constitution of 6 methyl methacrylate: 1 C_6F_8 (i.e. this ratio would give; F, 18.5%).

Styrene (Ph-CH = CH_2) plus octafluorocyclohexa-1,3-diene.

Starting Ratio 5:1 :- Styrene was de-stabilised by washing with dilute sodium hydroxide solution and water; and then drying over freshly ignited magnesium sulphate.

Styrene (2.9 gm.) was weighed into a Carius tube which was then charged with octafluorocyclohexa 1.3-diene (1.3 gm.) on the vacuum line; thus, the starting molar ratio was 4.8 styrene: 1 C_6F_8.

Time of irradiation:- 7 days, 3 hours.

After removing the volatile material, a white crystalline solid remained. A very small amount of material was removed from the upper portion of the irradiation tube, similar in appearance (and texture) to cellophane paper, but slightly opaque. (Total weight of polymer, 3.6 gm.).

The volatile material was fractionated for half an hour from trap T5 at -40°C., with T4 at -50°C (acetone-carbon dioxide), and T3 in liquid air. Valve 8 was closed during the process.

Fraction 1:- 1,3-C_6F_8 (0.3 gm.).

Fraction 2:- Styrene (0.4 gm.).

Thus, the molar ratio of starting materials used up was 5.4 styrene: 1 C_6F_8, and corresponds to:- F,19.7%.

<u>Starting Ratio 1:1</u>

A tube was charged with styrene (1.5 gm.) and octafluorocyclohexa-1,3-diene (5.1 gm.) in the manner described above; i.e. molar ratio 1 styrene: 1.2 C_6F_8.

Time of irradiation:- 15 days, 16 hours.

The volatile material was removed, leaving a white crystalline polymer (4.0 gm.).

Analysis: F, 33.1%.

N.B. A molar ratio of 2.2 styrene: 1 C_6F_8 corresponds to F, 33.3%.

SECTION 2. TELOMERISATION OF FLUORINATED OLEFINS

TETRAFLUOROETHYLENE

1. Tetrafluoroethylene plus Ethyl Chloride.

(i) Molar Ratio 1:16 :- Two Carius tubes were each filled with tetrafluoroethylene (1 gm.), and ethyl chloride (10 gm.), i.e. molar ratio 1 tetrafluoroethylene: 15.8 ethyl chloride. The reagents were dry, and the tubes were evacuated before sealing. They were introduced into a steel pressure vessel, and pressurised to twenty atmospheres.

Time of irradiation:- 7 days. (in pressure-vessel).

Dose-rate inside the pressure-vessel:- 0.46 x 10^4 rads. per hour.

After opening one of the tubes, volatile material was removed and was shown to be unused starting materials. A white solid (1.9 gm.) was left.

Analysis: (sodium fusion).

F, 67.5%; Cl, 2.5%.

The fluorine analysis corresponds to a compound $C_2H_4Cl(C_2F_4)_5H$ (i.e. this requires: F, 67.4%; Cl, 6.3%).

The contents of the remaining tube gave corresponding results.

<u>(ii) Molar Ratio 1:8</u> :- Three tubes were filled with tetrafluoroethylene (1 gm.) and ethyl chloride (5 gm.) i.e. molar ratio, 1 tetrafluoroethylene : 7.9 ethyl chloride; they were pressurised as in (i) but one tube was retained as a control experiment while the others were irradiated.

Time of irradiation:- 5 days. (in pressure-vessel).

On opening the control tube, the starting materials were recovered. The irradiated tubes gave results identical with those obtained for the earlier experiments (i) using a 1:16 molar ratio of reactants.

The solids were treated with a variety of solvents (CCl_4, $CHCl_3$, C_6H_6, $C_2H_5OC_2H_5$, CH_3COCH_3, C_2H_5I, C_2H_5Br., and a mixture of $CCl_2F.CCl_2F$. and $CCl_3.CClF_2$). The solids appeared to be insoluble in all of these, but to make quite sure, 1.5 gm. was refluxed with about 50 gm. of $C_2Cl_4F_2$, filtered hot, and the filtrate evaporated. The residue was heated to 100°C. under vacuum, to ensure removal of solvent, and was found to weigh about 15 mg.

Analysis: (sodium fusion).

F, 60.9%; Cl, 6.1%.

This analysis corresponds to an average formula $C_2H_4Cl(C_2F_4)_{2.5}H$ (i.e. this would require: F, 60.5%; Cl, 11.6%).

Values for the chlorine analysis involve large experimental error since they are derived from very small titration values.

The material extracted by $C_2Cl_4F_2$ must have been the portion with the lowest molecular weight. From the two analyses (before extraction, and extracted material), it seems that the solid product was a mixture of $C_2H_4Cl(C_2F_4)n$ H, with values of n ranging between two and eight.

2. <u>Tetrafluoroethylene plus Trifluoromethyl Iodide.</u>

<u>(i) Molar Ratio 1:3</u> :- A tube was charged with tetrafluoroethylene (1.1 gm.) and trifluoromethyl iodide (3.6 gm.), i.e. molar ratio $1C_2F_4$: 2.8 C_2F_5I. The tube was placed in a pressure-vessel, and pressurised to 500 lbs./sq.in. and then irradiated.

Time of irradiation:- 1 day, 22 hours. (in pressure-vessel).

On opening the tube, the volatile material was shown to be starting materials; a white powder (1.0 gm.) remained. This was heated to 100°C. in vacuo, but no volatile material was collected.

Analysis: (sodium fusion)

F, 66.8%; I, 10.1%.

This indicates an average formula approximating to $CF_3(C_2F_4)_{10}I$ (i.e. this requires: F, 68.4%; I, 10.6%).

<u>(ii) Molar Ratio 1:4</u> :- A tube was charged with tetrafluoroethylene (2.3 gm.), and trifluoromethyl iodide (4.6 gm.), i.e. molar ratio $1C_2F_4$: 4 C_2F_5I.

Time of irradiation:- 2 days (in pressure-vessel).

A white solid (0.2 gm.) was obtained as the only product.

Analysis: (sodium fusion)

F, 62.9%; I, 15.0%.

The iodine analysis indicates an average formula approximating to $CF_3(C_2F_4)_6I$ (i.e. this requires: F, 64.3%; I, 15.9%).

HEXAFLUOROPROPENE

1. Hexafluoropropene plus pentafluoroethyl iodide

Hexafluoropropene (1.6 gm.) and pentafluoroethyl iodide (13.1 gm.) was sealed in a Carius tube, i.e. molar ratio, 1 C_3F_6 : 5 C_2F_5I.

Time of irradiation:- 28 days.

After irradiation, the tube was placed in the vacuum line, and volatile products and starting materials were removed. A greasy, off-white solid (0.11 gm.) remained.

Analysis: F, 60.5%; I, 13.5% (sodium fusion).

This probably consisted largely of the compound $C_2F_5(C_3F_6)_2I$ (i.e. this requires F, 59.1%; I, 23.3%).

The volatile material was removed from the vacuum line, and allowed to warm to room temperature, at atmospheric pressure. A liquid (1 gm.) remained, and this was distilled into two fractions:-

(i) B.P. 45°C.

Analysis: F, 42.2%; I, 40.0% (sodium fusion).

Theoretical for:

(a) C_2F_5I; F, 38.6%; I, 51.6%.

(b) $C_2F_5(C_3F_6)I$; F, 52.7%; I, 32.1%.

(c) $C_2F_5(C_3F_6)_2I$; F, 59.1%; I, 23.3%.

Thus, (i) appears to have been a mixture of C_2F_5I and the telomer corresponding to 'n' = 1. (Probably an azeotrope).

(ii) Residue (B.p. 110°C.)

Analysis: F, 50.7%; I, 40.0%.

According to the fluorine analysis, (ii) appears to have consisted largely of the telomer corresponding to 'n' = 1.

2. Hexafluoropropene plus carbon tetrachloride

Carbon tetrachloride (12.0 gm.) was weighed directly into a Carius tube which was then attached to the vacuum line and charged with hexafluoropropene (2.2 gm.); i.e. a molar ratio, 1 hexafluoropropene : 5.3 carbon tetrachloride.

Time of irradiation:- 28 days.

The tube was cooled in liquid air before opening, and then allowed to come to room temperature, causing the unchanged hexafluoropropene to distil off. The remaining liquid was distilled, and split up into the following fractions:-

(i) B.p. 70°C. (5.2 gm.)

(ii) B.p. 70-76°C. (4.8 gm.)

(iii) B.p. 76-90°C. (0.4 gm.)

(iv) Residue (0.9 gm.). Crystals (0.3 gm.) were deposited from the residue liquid on standing; these were filtered from the mother-liquor for analysis.

Analysis: (Biphenyl-sodium)

Liquid: F, 36.5%; Cl, 43.3%.

Theoretical for:

(a) $CCl_3(C_3F_6)Cl$; F, 37.5%; Cl, 46.8%.

(b) $CCl_3(C_3F_6)_2Cl$; F, 50.2%; Cl, 31.4%.

Thus, the residue liquid appears to have consisted mainly of the telomer corresponding to 'n' = 1.

Analysis: (Biphenyl sodium)

Residue solid: F, 5.7%; Cl, 78.6%.

This analysis cannot be explained as a telomer; the only possibility lies in the formation of CCl_3-CCl_3, by the coupling of $.CCl_3$ radicals.

C_2Cl_6 would require; Cl, 89.8%.

On this basis, it appears that the residue solid consisted of hexachlorethane, contaminated with the 'n' = 1 telomer. There was insufficient material to purify, or even for further analysis.

Fractions (i), (ii) and (iii) were analysed by vapour-phase chromatography and were shown to be carbon tetrachloride; (i) contained some dissolved hexafluoropropene.

Two drops of the residue liquid were injected onto a column (Apiezon 'L') at 158°C. No peak was recorded for this sample, indicating that the material had a very high boiling point; it probably gave rise to a long, low plateau which was not detectable.

3. Hexafluoropropene plus methyl mercaptan

A tube was charged with hexafluoropropene (2.4 gm.) and methyl mercaptan (3.8 gm.); i.e. a molar ratio, 1 hexafluoropropene: 5 methyl mercaptan.

Time of irradiation:- 28 days.

The tube was cooled before opening, the temperature was gradually allowed to rise to -10°C., and the gas evolved (Hexafluoropropene) was collected. By allowing the tube to warm to room teperature, more gas was evolved (methyl mercaptan) and collected in a separate trap. In this way, a negligible amount of hexafluoropropene was recovered, but the second fraction corresponded to 2.2 gm. of methyl mercaptan.

Since this indicates starting materials used up in the molar ratio, 1 hexafluoropropene : 2.2 methyl mercaptan, obviously the method of separating the recovered gases was not very efficient, and the recovered methyl mercaptan must have contained some hexafluoropropene.

The remaining liquid was distilled and 90% boiled at 82-84°C.(i); the residue (ii) was liquid, but contained particles of sulphur.

A sample of (i) was analysed by vapour-phase chromatography (Apiezon 'L'; 130°C.; flow 40 ml. per minute). Peaks were obtained at 2 minutes and 7$\frac{3}{4}$ minutes (ratio of peak heights, 19.5 : 1 respectively).

Using the trapping system which has been described, a sample of the major peak (2 minutes) was condensed out over several runs.

Analysis: (Biphenyl sodium)

F, 56.8%.

Theoretical for:

(a) $H(C_3F_6)CH_2SH$; F, 57.5%.

(b) $H(C_3F_6)_2CH_2SH$; F, 65.6%.

Thus, the sample condensed out, which was the major reaction product (approx. 90% yield), was the telomer corresponding to 'n' = 1. The minor component contained in (i) was probably the 'n' = 2 telomer.

Analysis of the residue liquid (ii) by vapour-phase chromatography, gave peaks with retention times corresponding to those obtained from (i) (ratio of peak heights 13 : 1 respectively).

4. Hexafluoropropene plus methyl alcohol

Methyl alcohol (2.2 gm.) was weighed directly into a Carius tube which was then attached to the vacuum line and charged with hexafluoropropene (2.3 gm.); i.e. molar ratio 1 hexafluoropropene : 4.6 methyl alcohol.

Time of irradiation:- 28 days.

No hexafluoropropene was recovered from the tube; the contents were distilled and split up into the following fractions:-

(i) B.p. 80°C. (0.5 gm.)
(ii) B.p. 80-110°C. (1.3 gm.)
(iii) B.p. approximately 117°C., (1.7 gm.).
(iv) Residue, b.p. 118-160°C. (0.1 gm.)

These fractions were analysed, using vapour-phase chromatography (Apiezon 'L'; 150°C.; flow 30 ml. per min.):-

(i) A single peak corresponding to methyl alcohol.

(ii) Peaks were obtained with retention times of $2\frac{3}{4}$ (corresponding to methyl alcohol), 4, and $4\frac{1}{2}$ minutes; the third peak was an inflexion of the second, without a clear separation (ratio of peak heights, 8:3.3:1 respectively).

(iii) Peaks with retention times corresponding exactly to those obtained from (ii) were observed (ratio of peak heights 1:11.6:3.8 respectively). By lowering the column temperature (110°C; flow 28 ml. per min.) it was possible to condense out a sample constituted of the two major components.

Analysis: (Biphenyl sodium)

F, 62.0%.

Theoretical for:

(a) $H(C_3F_6)CH_2OH$; F, 62.7%

(b) $H(C_3F_6)_2CH_2OH$; F, 68.7%.

Thus, the major reaction product (yield 90%) was the telomer corresponding to n = 1 (two isomers).

(iv) Two peaks, with retention times corresponding exactly to the two later components in (iii), were obtained.

5. Hexafluoropropene plus difluoro-dibromo methane (CF_2Br_2)

A Carius tube was charged with hexafluoropropene (2.6 gm.) plus difluoro-dibromo methane (16.0 gm.); i.e. molar ratio 1:4.4 respectively.

Time of irradiation:- 28 days.

The tube was opened and hexafluoropropene (0.5 gm.) was recovered, by maintaining the temperature at -10°C. Unreacted CF_2Br_2 was removed, and the remaining liquid separated by distillation into the following fractions:-

(i) B.p. 80°C. (0.9 gm.)

(ii) B.p. 80-110°C. (1.0 gm.)

(iii) B.p. 110-140°C. (1.3 gm.)

The fractions were analysed by vapour-phase chromatography.

(i) A single peak was obtained; the retention time corresponded to CF_2Br_2.

(ii) One major peak, and two minor peaks (Apiezon 'L'; 150°C.; flow 30 ml. per min.) were obtained, at retention times 4, 10, and 18 mins; (ratio of peak heights, 18:1:1 respectively).

Analysis of fraction (ii) (Biphenyl sodium)

F, 41.0%; Br, 42.3%.

Theoretical for:

(a) $CF_2Br(C_3F_6)Br$; F, 42.3%; Br, 44.5%.

(b) $CF_2Br(C_3F_6)_2Br$; F, 52.2%; Br, 31.4%.

Thus, the major component in (ii) must have been the telomer corresponding to n = 1.

(iii) Peaks were obtained, with retention times identical to those obtained in (ii); (ratio of peak heights 8:8:1).

Analysis: (Biphenyl sodium)

F, 49.2%; Br, 33.2%.

Thus, the major component in (iii), was the telomer corresponding to 'n' = 2, i.e. contaminated with telomers corresponding to 'n' = 1, and probably 'n' = 3.

By lowering the column temperature, or altering the flow rate to obtain greater separation efficiency, some of these major peaks could be slightly resolved into a greater complexity. This indicates that a number of isomers were present.

OCTAFLUOROCYCLOHEXA-1,3-DIENE

Reaction of Undecafluorocyclohexane ($C_6F_{11}H$) and Octafluorocyclohexa-1,3-diene

Undecafluorocyclohexane (6.0 gm.) was weighed into a Carius tube which was then attached to the vacuum line, and charged with octafluorocyclohexa-1,3-diene (2.7 gm.); a molar ratio 1.8 $C_6F_{11}H$: 1 C_6F_8.

Time of irradiation:- 45 days.

The tube was opened and distilled at atmospheric pressure. The unreacted starting materials were recovered (B.p. $<$ 80°C.), and a residue (1.0 gm.) remained (B.p. $>$ 100°C.).

The distillation was continued at reduced pressure (1 m.m.). A fraction distilled between 100-120°C. (0.6 gm.):-

Analysis:- (sodium fusion), - F, 69.1%.

The residue was in the form of a clear viscous gel. This was treated with carbon tetrachloride and part of the material was dissolved, leaving a small amount of yellowish crystals:-

Analysis:- (sodium fusion), - F, 67.6%.

Since C_6F_8 has 67.9% F., and $C_6F_{11}H$ has 70.6% F., it is most difficult to make deductions from analysis in this case. More of these compounds are to be made and tested for stability.

Preparation of Pentafluoroethyl Iodide

This material was kindly prepared and purified by Mr. J. Savory, using a modified reaction of iodine pentafluoride on tetrafluoroethylene (unpublished work by Musgrave and Savory).

Preparation of Trifluoromethyl Iodide

The preparation was carried out according to the method of Haszeldine (J.C.S.,1951,584). Apparatus consisted of a 250 ml. two-necked flask; one of the necks was fitted with a vertical air-condenser, below a water-condenser (to retain iodine). Dry nitrogen entered the other neck, and on emerging from the top of the water condenser, was led through a series of traps cooled in acetone-solid carbon dioxide baths, and then bubbled through sulphuric acid, to prevent the ingress of moisture.

Dry silver trifluoroacetate (60 gm.), and re-sublimed iodine (180 gm.) were ground together thoroughly, and placed in the flask (which had been carefully dried). The flask was heated, using a bunsen flame, by starting at the edge, and working towards the material at the bottom of the flask.

Trifluoromethyl iodide was condensed in the traps, while most of the iodine was retained by the condensers. For further purification, the trifluoromethyl iodide was bubbled through 10% sodium hydroxide solution (to remove iodine), before storing in aspirators.

Various yields of trifluoromethyl iodide have been obtained from this preparation, ranging from 14, to 60%.

Crucial factors determining the yield are: the dryness of the apparatus and reactants; grinding together of the reactants; and the final heating procedure.

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