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The synthesis of fluorine-containing organic compounds

John Savory

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A THESIS

entitled

THE SYNTHESIS OF FLUORINE-CONTAINING ORGANIC COMPOUNDS.

submitted by

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A candidate for the degree of Doctor of Philosophy

1961.

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CONTENTS

SUMMARY.

Mixtures of iodine pentafluoride and iodine, and bromine
trifluoride and bromine have been shown to behave as iodine mono-
fluoride and bromine monofluoride respectively in their reactions with
fluoro-olefins. Several fluoro-olefins have been used and excellent
yields of the corresponding iodo- or bromofluoroalkanes obtained. A
similar reaction, using a mixture of bromine and chlorine as a source
of bromine chloride, has also been investigated. Reactions of iodine
monochloride and iodine monobromide with chlorotrifluoroethylene
previously described in the literature, were reinvestigated and
disclosed a discrepancy with the previous report.

The pyrolysis of pentafluoroiodoethane has been studied, and
optimum conditions found for its conversion by this means to perfluoro-
butane.

The product from this reaction between "iodine monofluoride"
and hexafluoropropene was shown to be the new compound heptafluoro-
2-iodopropane. Several reactions of this compound were investigated:
reaction with sulphur; hydrolysis; coupling reaction; formation of
2-heptafluoropropyl zinc iodide and subsequent hydrolysis; formation
of the Grignard reagent and subsequent reaction with water, acetone
and propionaldehyde; and formation of the lithium reagent and
subsequent decomposition, attempted hydrolysis, reaction with acetone
and propionaldehyde. These reactions were similar to the corresponding
reactions of heptafluoro-1-iodopropane.

The use of lithium-halogen exchange as a source of olefins from
polyhaloalkanes has been studied; the procedure being to replace
chlorine or iodine by lithium using n-butyl lithium, and then eliminate
halide using a halogen on an adjacent carbon atom, thus forming a

double bond. Pentafluoroiodoethane, 1,2-diiodotetrafluoroethylene and 1-chloro-2-iodotetrafluoroethane all produced tetrafluoroethylene; heptafluoro-2-iodopropane gave hexafluoropropene; 1,1,2-trichloro-trifluoroethane gave chlorotrifluoroethylene; 1,4-dichlorododecafluoro-2, 3-dimethylbutane gave 4-chloroundecafluoro-2, 3-dimethybut-1-ene; and dichlorodecafluorocyclohexane gave a mixture of perfluorocyclo-hexadienes and perfluoro- and monochloroperfluorocyclohexenes.

An analytical procedure for determining fluorine in volatile organic compounds has been devised; this involves weighing the sample as a gas after measuring it into a bulb froma vacuum system, and then converting the organically bound fluorine to fluoride ion using the biphenyl-sodium-dimethoxyethane complex.

CHAPTER 1.

INTRODUCTION.

INTRODUCTION.

Preparation of Fluoroalkyl Iodides and Bromides.

Probably the most important method of preparing fluoroalkyl iodides and bromides described up to the present time, is that involving the decarboxylation of the silver salt of a fluorocarboxylic acid in the presence of free halogen. It is essential that the reactants are extremely dry, and under these conditions it is claimed that the yields are almost quantitative. The temperature required to allow the reaction to proceed at a reasonable rate varies depending on the nature of the two reactants. Silver monofluoroacetate and bromine react at 180° to 260° to produce bromofluoromethane [1a]

$$CH_2FCOOAg + Br_2 \longrightarrow CH_2FBr + CO_2 + AgBr$$
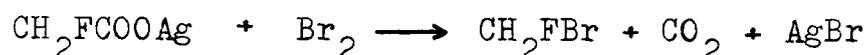
whereas silver trifluoroacetate and bromine react similarly at 50° to produce bromotrifluoromethane in 88% yield.[26] Hauptschein[2] has decarboxylated the silver salts of trifluoroacetic, pentafluoropropionic, heptafluoro-n-butyric and hexafluoroglutaric acids in the presence of iodine at 100° for six hours, and obtained the corresponding fluorocarbon iodides, and in the last case, diiodide. The same worker [3] reacted the first three of the silver carboxylates mentioned, with bromine and chlorine, and obtained the corresponding fluorocarbon bromides and chlorides.

A more detailed study of this type of reaction has been made by Crawford and Simons[4], who treated several silver perfluorocarboxylates with iodine and bromine at room temperature in fluorocarbon solvents and obtained high yields of the corresponding perfluoroalkyl halides. They also isolated the intermediate complexes of general formula $(Rf\ CO_2)_2\ AgX$, Rf represents a fluoroalkyl group.

A few reactions have been described[5],[6] where either a fluorocarboxylic acid, acyl halide or anhydride has been heated in the presence of a free halogen, producing the corresponding fluoro-alkyl halide. The temperature necessary to promote reaction in these cases was usually higher than in those reactions involving the silver fluorocarboxylates. The yields, however, were again usually quite high.

A second extremely useful method for preparing fluoroiodides and bromides of formula $RfCH_2X$ (X = I,Br) involves decomposing tosylates or other esters of fluoroalcohols in the presence of either sodium bromide or iodide. Tiers[7] first reported this reaction when he prepared the tosyl esters of several fluoroalcohols, and reacted them with sodium chloride, bromide and iodide in ethylene glycol at 150° to 220°.

Another reaction using fluoroalcohols is that involving halogenation of the hydroxyl group using either phosphorous tribromide[8],[9],[10], iodine and red phosphorous[11],[12], or potassium iodide and phosphoric acid[13]. The same type of fluoroalkyl iodide is obtained from the treatment of diazo compounds of formula $RfCH_2N_2$ with iodine or hydrogen iodide[14],[15].

The treatment of polyhaloalkanes under controlled conditions with bromine trifluoride or iodine pentafluoride, has afforded in some cases excellent yields of fluoroalkyl iodides and bromides[16]. Banks et al.[17] has reacted liquid bromine trifluoride with carbon tetrachloride or tetrabromide forming mixtures of chlorofluoromethanes or bromofluoromethanes, the proportion of which depends on the reaction conditions.

With carbon tetraiodide, bromofluoromethanes and carbon tetrafluoride
are formed. Iodine pentafluoride converts carbon tetrabromide into
a mixture of bromofluoromethanes, while with carbon tetraiodide,
trifluoroiodomethane is formed in good yield. Tetraiodoethylene and
iodine pentafluoride give pentafluoroiodoethane.

Haszeldine[18] has also fluorinated tetrafluoro-1, 2-diiodoethane
with iodine pentafluoride to give an excellent yield of pentafluoro-
iodoethane. Krespan[19] claims to have prepared trifluoroiodomethane
by the reaction of trifluoroacetyl chloride with dry potassium iodide
in an autoclave at an elevated temperature. Other methods of pre-
paring fluoroiodoalkanes and fluorobromoalkanes involve the use of the
fluoro-olefins.

(a). Addition of interhalogen compounds to fluoro-olefins.

(b). Addition of fluoroiodoalkanes to fluoro-olefins.

(c). Reactions of fluoro-olefins with iodide and bromide ions.

These methods will be described in detail in the discussion on the
reactions of the fluoro-olefins which follows.

Reactions of fluoro-olefins.

Electrophilic addition reactions.

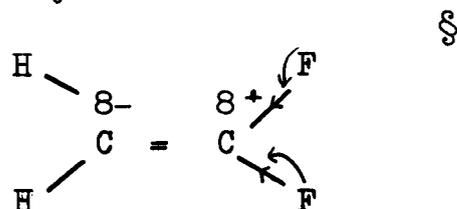In these reactions the polarisation of the double bond and hence
the direction of attack of the electrophilic ion, depends on various
electronic effects which are possible in the olefin. The most important
effects are the strong positive inductive effect caused by the presence
of fluorine in the molecule, the hyperconjugative effect $\left(\underline{} \overset{F}{\underset{F}{C}}^+ \ F^- \right)$

of the trifluoromethyl group, and the mesomeric effect of a halogen

which is bonded with an unsaturated carbon atom $\rightleftharpoons$ C$\begin{smallmatrix}F\\ \ddot{F}\end{smallmatrix}$

Generally, therefore, any olefin containing a difluoromethylene group

has a positive centre on the carbon atom of this group, as in

1, 1 – difluoroethylene

§

$$\begin{smallmatrix}H\\ \\ H\end{smallmatrix}\!\!\!>\overset{8-}{C} = \overset{8+}{C}\!\!\!<\begin{smallmatrix}F\\ \\ F\end{smallmatrix}$$

A difluoromethylene group exerts a stronger mesomeric effect than

a fluorochloromethylene or dichloromethylene group, and therefore in

chlorotrifluoroethylene or 1, 1 – dichlorodifluoroethylene the positive

centre is also on the difluoromethylene carbon atom

$$\begin{smallmatrix}F\\ \\ F\end{smallmatrix}\!\!\!>\overset{8+}{C} = \overset{8}{C}\!\!\!<\begin{smallmatrix}F\\ \\ Cl\end{smallmatrix} \qquad \begin{smallmatrix}F\\ \\ F\end{smallmatrix}\!\!\!>\overset{8+}{C} - \overset{8-}{C}\!\!\!<\begin{smallmatrix}Cl\\ \\ Cl\end{smallmatrix}$$

Also any olefin containing a trifluoromethyl group has a negative

centre on the carbon atom adjacent to this group, as in 1,1,1 – tri-

fluoropropene

$$CF_3 \longleftarrow \overset{8-}{CH} = \overset{8+}{CH_2}$$
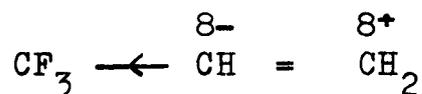
These mesomeric and hyperconjugative effects can work together as in

hexafluoropropene

$$CF_3 \longleftarrow \overset{8-}{CF} - \overset{8+}{C}\!\!\!<\begin{smallmatrix}F\\ \\ F\end{smallmatrix}$$
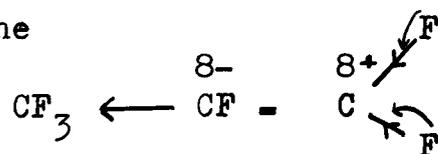
Haszledine[20] has added hydrogen bromide and hydrogen iodide to

vinylidene fluoride and 1-chloro-2, 2-difluoroethylene, when in both

§ Note The usual notation δ is in this thesis denoted by 8.

cases the halogen atom becomes attached to the positive centre.

$$HX + \overset{8+}{CF_2} = \overset{8-}{CH_2} \longrightarrow CF_2X - CH_3 \quad (X = Br, I)$$

$$HX + \overset{8+}{CF_2} - \overset{8-}{CHCl} \longrightarrow CF_2X - CH_2Cl$$
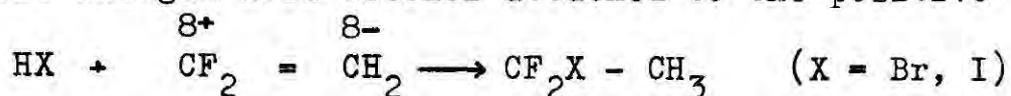
The same worker has reacted hydrogen bromide with 3,3,3-trifluoro-propene[21] and hexafluoropropene[22] under conditions favouring electrophilic addition

$$HBr + CF_3 - \overset{8-}{CH} = \overset{8+}{CH_2} \longrightarrow CF_3 - CH_2 - CH_2Br$$

$$HBr + CF_3 - \overset{8-}{CF} = \overset{8+}{CF_2} \longrightarrow CF_3 - CFH - CF_2Br$$
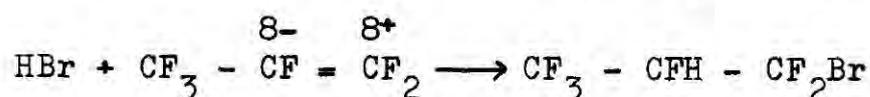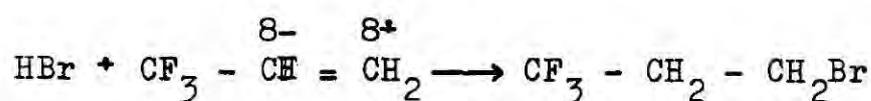
It has also been shown[22] that the rate of addition by an electrophilic mechanism decreases with increase in the number of fluorine atoms in the compound:

$$CH_3 \cdot CH ; CH_2 > CF_3 \cdot CH \cdot CH_2 > CF_3 \cdot CF : CF_2$$

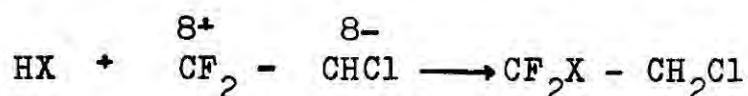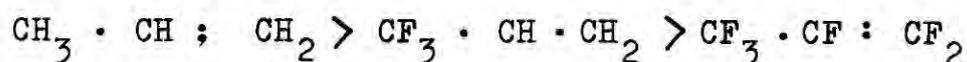In certain cases there are opposed electronic effects and the direction of addition has had to be settled by experiment

$$CF_3 \cdot CH : CH \cdot CO_2C_2H_5 + HBr \longrightarrow CF_3 \cdot CHBr \cdot CH_2 \cdot CO_2C_2H_5 \quad (23)$$

$$CH_3 \cdot CH : CF_2 + HF \longrightarrow CH_3 \cdot CH_2CF_3 \quad (24)$$
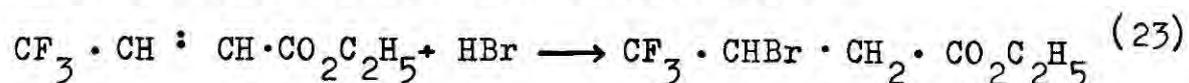
A few reactions between hydrogen bromide and fluoro-olefins involving the use of a catalyst such as calcium sulphate or activated carbon and an elevated temperature have been reported. One cannot be sure, however, that such reactions proceed solely by an electrophilic mechanism.

$$HBr + CF_2 : CFCl \longrightarrow CF_2Br \cdot CHClF \quad (25)$$

$$HBr + CF_3CH:CH_2 \longrightarrow CF_3 \cdot CH_2 \cdot CH_2Br \quad (26)$$

$$HBr + CF_2 : CCl_2 \longrightarrow CF_2Br \cdot CHCl_2 \quad (25)$$
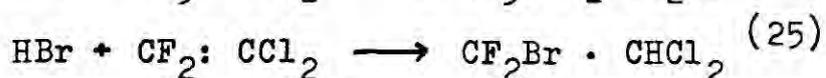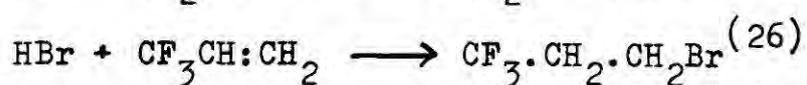
The electrophilic addition of iodine monochloride to a fluoro-olefin was first reported by Barr[27] who bubbled chlorotrifluoroethylene into a solution of iodine monochloride in an inert solvent at 0°. The product was stated to consist of only one isomer, $CF_2CI-CFClI$, which is in agreement with the product expected from the polarisation of the olefin $\overset{8+}{CF_2} : \overset{8-}{CFCl}$. Haszledine[28] accomplished the same addition without a solvent, by performing the reaction in an autoclave at 50°; he obtained the same product as before. All other additions of this type have resulted in an addition which could have been forecasted from considering the polarisation of the olefin.

$$IBr + CF_2 : CFCl \longrightarrow CF_2Br . CFClI \quad [28]$$

$$ICl + CF_2 : CFH \longrightarrow CF_2Cl . CFHI \quad [29,][30]$$

$$ICl + CF_2 : CH_2 \longrightarrow CF_2Cl . CH_2I \quad [20]$$

$$ICl + CF_2 : CF_2 \longrightarrow CF_2I . CF_2Cl \quad [31]$$

$$IBr + CF_2 : CF_2 \longrightarrow CF_2I . CF_2Br \quad [31]$$

$$IBr + CF_2 : CH_2 \longrightarrow CF_2Br . CH_2I \quad [32]$$

$$ICl + \overline{CF_2 . CF : CF . CF_2} \rightarrow \overline{CF_2 . CFCl . CFI . CF_2} \quad [20]$$

$$ICl + CF_3 . CF : CF_2 \longrightarrow CF_3 . CFI . CF_2Cl \quad [33]$$
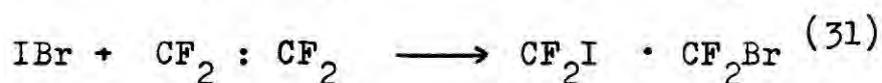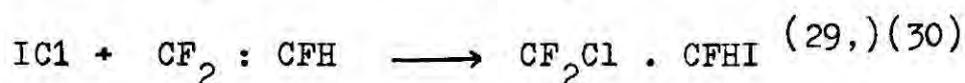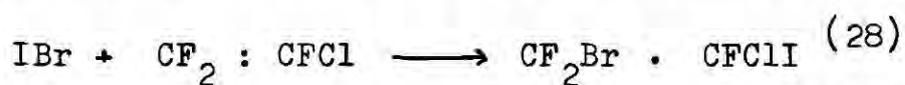
The reaction of iodine monochloride with decafluorocyclohexene[20], however, resulted only in the formation of 1,2-dichlorodecafluorocyclohexane.

Simons and Brice[34] have added the elements of iodine and fluorine to tetrafluoroethylene, hexafluoropropene, perfluorobutene, perfluorocyclobutene, decafluorocyclohexene, perfluoro(methylcyclohexene) and

perfluoro(vinylcyclohexane) using a vapour phase reaction at 170° between the olefin and iodine pentafluoride. Schmeisser and Scharf[35] have made iodine monofluoride by a low temperature reaction between iodine and fluorine, although Durie[36] earlier observed iodine monofluoride spectroscopically; it is possible, therefore, that the previous reaction proceeds through an iodine monofluoride intermediate.

The elements of bromine and chlorine have so far not been added to fluoro-olefins, but have, however, been added to hydrocarbon-olefins by means of a mixture of bromine and chlorine[37].

Bromine monofluoride has never been isolated but the conductometric measurements made by Quarterman et al [38] provide evidence for its formation when bromine is dissolved in bromine trifluoride.

Self ionisation of interhalogen compounds is discussed by Clark.[39]

Nucleophilic additions to fluoro-olefins.

Nucleophilic additions to fluoro-olefins occur easily in those containing a difluoromethylene group, when the reaction occurs more readily than electrophilic addition. These reactions usually proceed readily at room temperature in the presence of alkaline catalysts such as sodium alkoxides, caustic alkali, potassium cyanide, benzyl trimethyl ammonium hydroxide, borax, and a sodium dispersion in dimethyl formamide. In every case reported to date in which olefins of the type $CF_2:CX'X^2$ ($X = H, Br, Cl, CF_3$ and/or F,) have been treated under basic conditions with amines,[40-45] alcohols[40][42][44][56], thiols[42][57], phenols[52][48] bisulphites[40][43], Grignard reagents[58], and lithium compounds[59], saturated addition products have been reported except in certain cases (52,)[57][59], when the saturated product was unstable with respect to an

olefin and either hydrogen fluoride or lithium fluoride. Furthermore, the addition products invariably had the structure $CF_2R \cdot CX'X^2H$ in which the anionic fragment R became attached to the carbon atom bearing the two fluorine atoms. In all these compounds, especially those formed by the addition of amines, the fluorine atoms on the α–carbon atom with respect to the nucleophilic group are quite labile and hydrolyse easily[41][49][52]. The mechanism for these base catalysed addition reactions has been postulated by Miller[49][53] as being:

$$CH_3O^- + F \overset{\curvearrowright}{} \overset{}{\underset{}{C}} = \overset{}{C} \quad \xrightarrow[\text{controlling}]{\text{rate}} \quad CH_3O- \overset{F}{\underset{}{C}} - \bar{C}$$

$$CH_3O- \overset{F}{\underset{}{C}} - \bar{C} + CH_3OH \quad \xrightarrow{\text{fast}} \quad CH_3O- \overset{F}{\underset{}{C}} - \overset{H}{C} - + CH_3\bar{O}$$
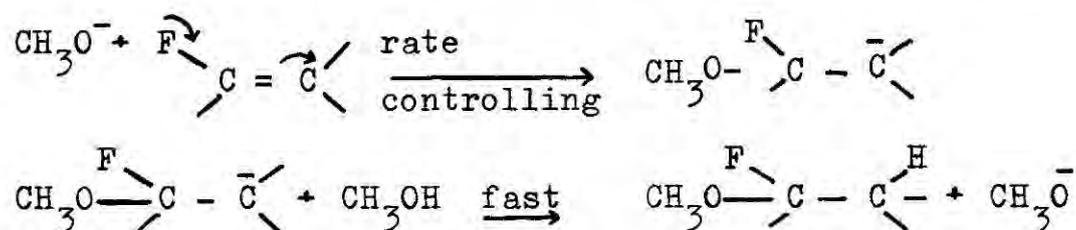
In sharp contrast to the behaviour of fluoro-olefins containing CF_2– group described above, those containing CClF –or CCl_2– such as CClF– $CClF^{(53)}$, $CCl_2 = CClF^{(53)}$, and $CCl_2 – CClCF_3^{(60)}$ are relatively unreactive and do not appear to undergo base catalysed additions leading to saturated products. When they do react they give vinyl ethers.

Miller[61-64] has found the same structural requirements to be necessary for the attack on fluoro-olefins by halide ions i.e. attack only takes place on the carbon atom bearing the two fluorine atoms. This worker has investigated attack by all four halide ions and found the rate of reaction to be $\bar{F} > Cl^- > I^-$; the reaction proceeds with an SN2– mechanism as illustrated by the following example

$$I^- + CF_2 – CF – CF_2Cl \quad \rightleftharpoons \quad \left[I \cdots CF_2 \cdots CF \cdots CF_2Cl \right]^-$$

$$\left[I \cdots CF_2 \cdots CF \cdots CF_2Cl \right]^- \quad \rightleftharpoons \quad ICF_2 – CF = CF_2 + Cl^-$$
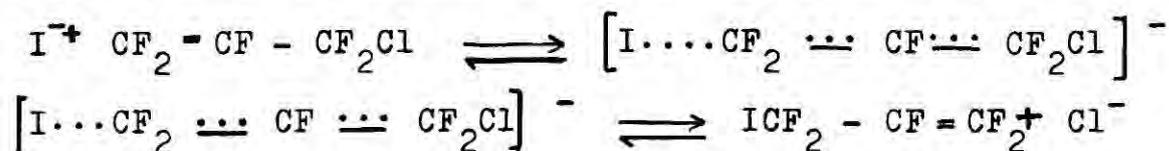
This reaction proceeds smoothly using sodium iodide in acetone as the source of halide ion, the equilibrium is disturbed owing to the greater insolubility of sodium chloride in acetone over that of sodium iodide. Other sources of halide ions used were sodium chloride, lithium chloride, lithium bromide all in acetone, potassium fluoride in dimethyl formamide, and tetraethylammonium fluoride in chloroform or methylene chloride.

Addittion of free radicals to fluoro-olefins.

The addition of free radicals to fluoro-olefins generally proceeds quite smoothly and easily, the mechanism being as follows:-

$$RX \xrightarrow{hv} R\cdot + X\cdot \quad \text{Initiation.}$$

$$R\cdot + \underset{b}{\overset{a}{C}} = \underset{d}{\overset{c}{C}} \longrightarrow R - \underset{b}{\overset{a}{C}} - \underset{d}{\overset{c}{C}}\cdot \quad \text{Propogation.}$$

$$R - \underset{b}{\overset{a}{C}} - \underset{d}{\overset{c}{C}}\cdot + RX \rightarrow R - \underset{b}{\overset{a}{C}} - \underset{d}{\overset{c}{C}} - X + R\cdot \quad \text{Termination.}$$

$$R - \underset{b}{\overset{a}{C}} - \underset{d}{\overset{c}{C}}\cdot + \underset{b}{\overset{a}{C}} - \underset{d}{\overset{c}{C}} \longrightarrow R\left[\underset{b}{\overset{a}{C}} - \underset{d}{\overset{c}{C}}\right]_n\cdot \quad \text{Telomerisation.}$$

$$R\left[\underset{b}{\overset{a}{C}} - \underset{d}{\overset{c}{C}}\right]_n\cdot + RX \longrightarrow R\left[\underset{b}{\overset{a}{C}} - \underset{d}{\overset{c}{C}}\right]_n - X + R\cdot \quad \text{Telomer Termination.}$$
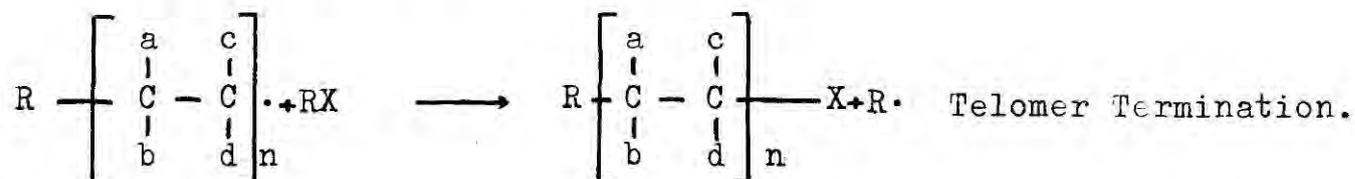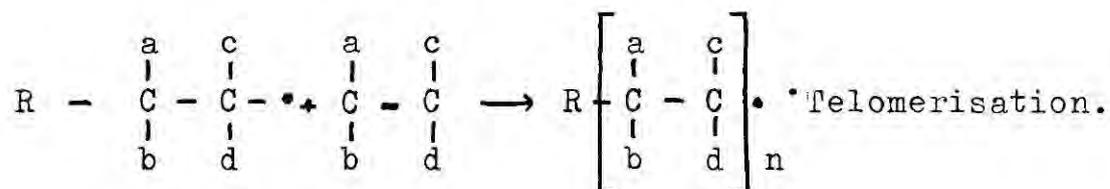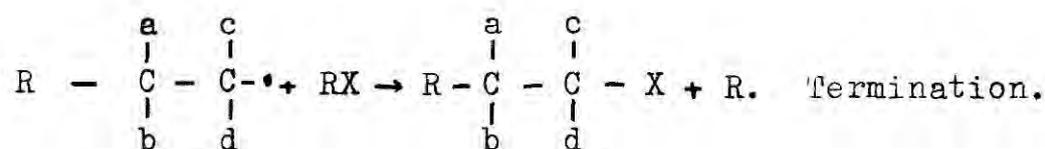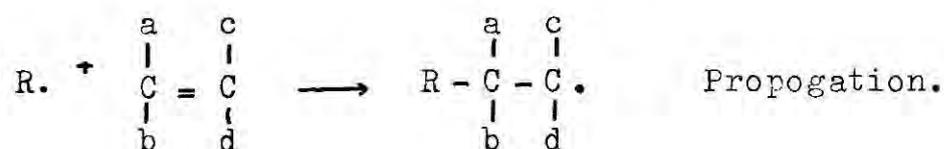
The structure of the addition product can be predicted in most cases by using an empirical rule involving the Pauling electronegativity

and the atomic refraction of a, b, c and d.[65] Most of the results

so far obtained have been by the addition of halogens, hydrogen

bromide and polyfluoroalkyl iodides [22][28][46][66-76][111], where

initation is by halogen atoms or fluoroalkyl radicals, formed by heat

or light. The addition of hydrogen bromide does not readily result

in telomerisation and forms an addition product which in some cases

is the same as from electrophilic addition, and in others the addition

is the opposite way round.

$$HBr + CH_2 : CF_2 \longrightarrow CH_2Br \cdot CF_2H \quad [32]$$

$$HBr + CF_2 : CFCl \longrightarrow CF_2Br \cdot CFClH \quad [77]$$

$$HBr + CF_3 \cdot CH : CH_2 \longrightarrow CF_3CH_2CH_2 \cdot Br \quad [21]$$

$$HBr + CF_3 \cdot CF : CF_2 \longrightarrow CF_3 \cdot CFH \cdot CF_2Br \quad [22]$$
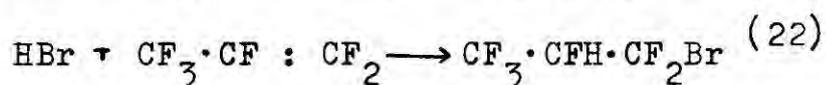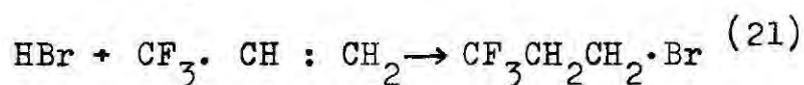
In the case of polyfluoroalkyliodide additions to fluoro-olefins

telomerisation occurs readily; the value of n can be controlled by

varying the proportion of iodide to olefin. The direction of attack

by the polyfluoroalkylradical is the same as that of the bromine atom.

The ease of free radical attack to fluoro-olefins has been shown to be

the following[20]

$$CF_2:CH_2 > CF_2 : CF_2 > CF_2 : CHCl > CF_2 : CFCl > CF_3 \cdot CF : CF_2$$

$$> CF_3 \cdot CF : CF \cdot CF_3 > \overline{CF_2 \cdot CF : CF \cdot CF_2} > \overline{CF_2 \cdot CF_2 \cdot CF : CF \cdot CF_2 \cdot CF_2}$$
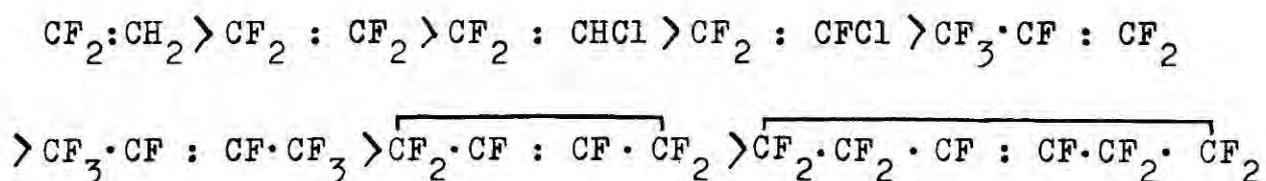
The formation of more than one isomer from this type of addition

has only been reported in two cases, both involving the olefin tri-

fluoroethylene. Haszledine[30] first reported this from the free radical

addition of hydrogen bromide and trifluoroiodomethane.

$$HBr + CF_2 : CFH \longrightarrow CF_2H- CHFBr \quad 58\%$$
$$CF_2Br - CH_2F \quad 42\%$$

$$CF_3I + CF_2:CFH \longrightarrow CF_3 \cdot CHF \cdot CF_2I \quad 80\%$$
$$CF_3 \cdot CF_2 \cdot CHFI \quad 20\%$$
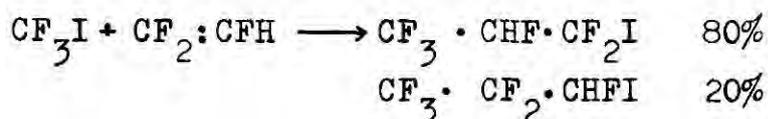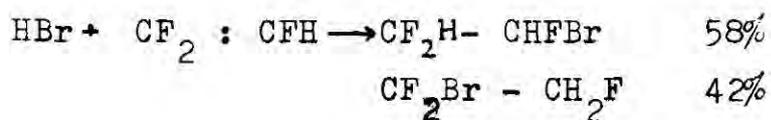
Miller[63] has obtained similar results using dichlorofluoro-iodomethane, the addition again going both ways. Hauptschein[78][79], and his co-workers have performed reactions between hexafluoropropene and various iodides by thermal means whereas initiation by ultraviolet light had proved unsuccessful. The mechanism proposed for these reactions was a novel one in that it was thought that a stepwise addition of intermediate iodides occurred

$$C_3F_7I + CF_3 \cdot CF : CF_2 \longrightarrow CF_3 \cdot CFI \cdot CF_2 \cdot C_3F_7$$

$$CF_3 \cdot CFI \cdot CF_2 \cdot C_3F_7 + CF_3 \cdot CF:CF_2 \longrightarrow CF_3 \cdot CFI \cdot CF_2 CF \cdot \overset{\overset{CF_3}{|}}{C_4F_9}$$

$$CF_3 \cdot CFI \cdot CF_2 \overset{\overset{\cdot CF_3}{}}{CF} \cdot C_4F_9 + CF_3 \cdot CF:CF_2 \longrightarrow CF_3 \cdot CFI \cdot CF_2 \cdot \overset{\overset{CF_3}{}}{CF} \cdot CF_2 \cdot \overset{\overset{CF_3}{|}}{CF} \cdot C_4F_9$$
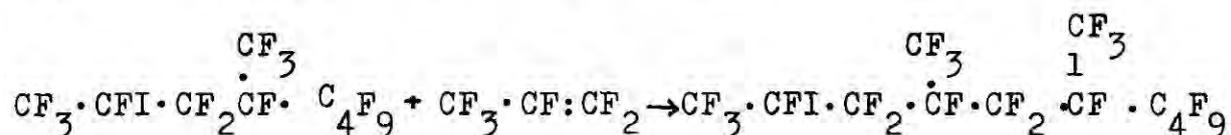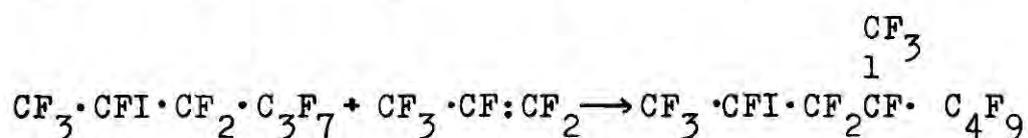
Reactions of perfluoroalkyl iodides.

Perfluoroalkyl iodides are the most reactive of the three perfluoroalkyl halides, as shown by the activation energies (1.7, 2.3, and 7.4 kcal./mole. respectively) required to convert trifluoromethyl iodide, bromide and chloride into free radicals[80]. The powerful electron attraction of the perfluoroalkyl group results in the absence of any simple nucleophilic reactions of these iodides, but does promote reactions caused by heterolytic fission to the negative perfluoroalkyl and positive iodine ions. The existence of these ions

has been shown from exchange of radioactive iodine in sodium iodine with iodine in trifluoroiodomethane in alcoholic solution[81].

$$CF_3I \rightleftharpoons CF_3^- + I^+$$

$$I^+ + {}^*I^- \rightleftharpoons I_2 \rightleftharpoons {}^*I^+ + I^-$$

$$CF_3^- + {}^*I^+ \rightleftharpoons CF_3{}^*I$$
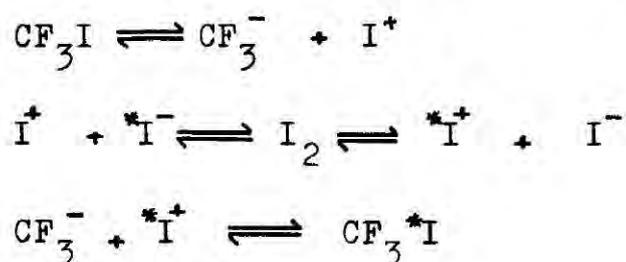
Reactions involving this type of ionisation include the replacement of iodine in CF_3I by hydrogen[81] using potassium hydroxide in acetone. Haszledine[82] reacted heptafluoroiodopropane with alcoholic potassium hydroxide at 100° and obtained lH-heptafluoropropane 70% yield, and also[83] obtained the following lH-fluorocarbons from the corresponding iodo compounds by the same procedure

$$C_4F_9H \ (47\%), \ C_5F_{11}H \ (41\%), \ C_6F_{13}H \ (32\%),$$

$$C_7F_{15}H \ (36\%) \ \text{and} \ C_8F_{17}H \ (27\%).$$
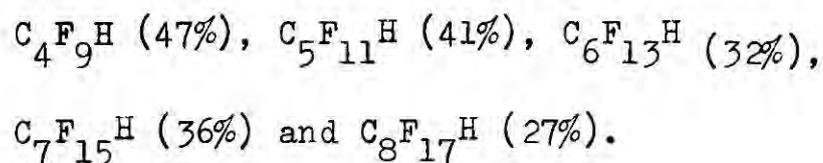
Reaction with sulphur.

Hauptschein and Grosse[84] were the first to perform this reaction, when they heated heptafluoro-1-iodopropane(A) and sulphur at 250° for fourteen hours in a sealed glass vessel. They obtained a mixture of the corresponding mono, di and trisulphides, the disulphide being the main product

$$2C_3F_7I + nS \longleftarrow C_3F_7 \fbox{S}_n C_3F_7 + I_2 (n = 1,2,3.)$$
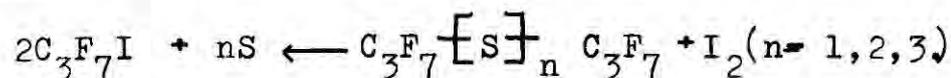
More drastic conditions i.e. higher temperatures and longer periods, resulted in the formation of higher sulphides to the exclusion of the monosulphide. Tridecafluoro-2-iodohexane (B) and 1,2-dichlorotrifluoro-1-iodoethane[85] both reacted in a similar manner at 180° forming a similar mixture (n = 2-5). Brandt, Emeleus and Haszeldine[86] reacted

CF_3I and sulphur and at 205° there was 70% conversion to $(CF_3)_2S_2$; this was converted to $(CF_3)_2S$ by ultraviolet irradiation for thirteen days. Haszeldine and Kidd[87] repeated the former reaction at 310° and obtained a 75% yield of the disulphide.

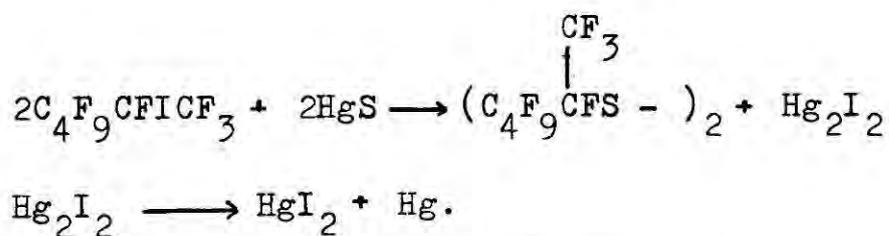Haszeldine and Kidd[88] have also reacted trifluoroiodomethane and (A) with sulphur in an autoclave, employing the following conditions; 265° for 24 hours, 310° for 36 hours or 410° for 14 hours, the latter temperature only gave any appreciable yield when the disulphide (36%) only was characterised.

The reaction of A and B with mercuric sulphide under ultraviolet irradiation has been shown by Hauptschein[89] to produce a mixture of the disulphide and high polysulphides, thus facilitating the isolation of a pure sample of the former.

$$2C_4F_9CFICF_3 + 2HgS \longrightarrow (C_4F_9\overset{\overset{\displaystyle CF_3}{|}}{C}FS-)_2 + Hg_2I_2$$

$$Hg_2I_2 \longrightarrow HgI_2 + Hg.$$

Under thermal conditions (235°) the reaction of B with mercuric sulphide gave what was thought to be a heterocyclic fluorocarbon sulphur compound $C_{12}F_{24}S_2$ in good yield, together with a small amount of perfluoro-2-hexyl di- and polysulphides[89]. The mechanism suggested for this reaction is as follows:-

$$2C_4F_9CFICF_3 + 2HgS \longrightarrow (C_4F_9\overset{\overset{\displaystyle CF_3}{|}}{C}FS-)_2 + Hg_2I_2$$

$$Hg_2I_2 \longrightarrow Hg + HgI_2$$

$$(C_4F_9\overset{\overset{\displaystyle CF_3}{|}}{C}FS \; — \;)_2 + HgS \longrightarrow C_4F_9\overset{\overset{\displaystyle CF_3}{|}}{\underset{\underset{\displaystyle CF_3}{|}}{\underset{S \; - \; C \; - \; C_4F_9}{|}}{C}} \; - \; S \qquad + HgF_2 + S$$

$$Hg + S \longrightarrow HgS$$
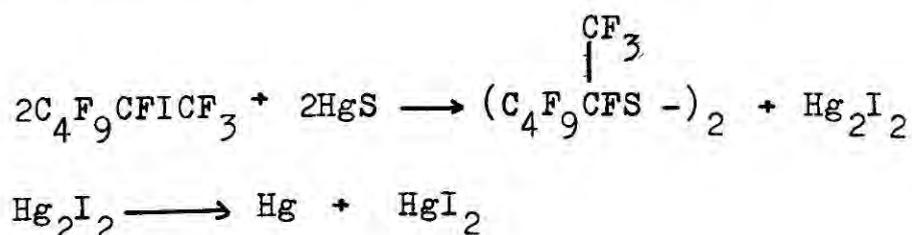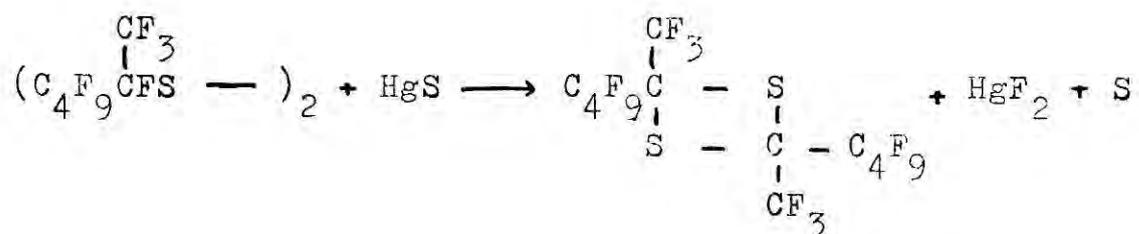
A disulphide of suspected formula X or Y

$$\begin{array}{ccc} CF_3 - CF & - & CF_2 \\ | & & | \\ S & & S \\ | & & | \\ CF_2 - CF & - & CF_3 \end{array} \qquad\qquad \begin{array}{ccc} CF_3 - CF & - & CF_2 \\ | & & | \\ S & & S \\ | & & | \\ CF_3 - CF & - & CF_2 \end{array}$$
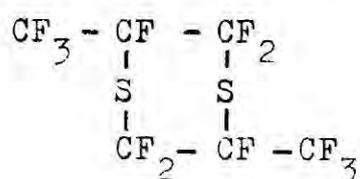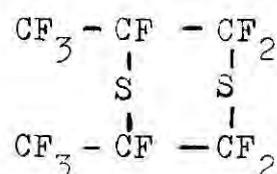
(X)   (Y)

has been made by the pyrolysis of C_3F_7COONa with sulphur at $300^{o(90)}$ and also in improved yields by the reaction between hexafluoropropene and sulphur at $300^{o(91)}$.

Wurtz - type condensation.

The neatest way of performing this type of reaction is to expose the iodide to ultraviolet light in the presence of mercury;

$$2RfI \xrightarrow[u.v.]{Hg} \quad Rf - Rf + Hg \; I_2$$

The following fluoroalkyl iodides have been coupled easily by this method giving almost quantitative yields;

A   B

$CF_2Cl-CFClI, CF_2BrCFClI^{(28)}, \quad CF_3CF_2CF_2I$

$Rf \left[CF_2CF(CF_3) \right]_n I^{(78)} \quad (n = 1-4)$

$Rf(CH_2 \cdot CF_2)_n \; I^{(79)} \; (n = 1-6) \; (Rf = CF_3, \; CF_3CF_2CF_2, CF_2ClCFCl,$

$CF_3CF(CF_2Cl), \; CF_3CF_2CF(CF_3) \; and \; C_4F_9CF(CF_3)$
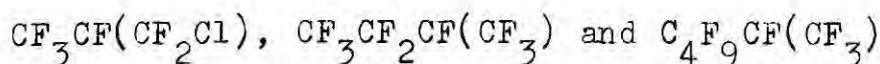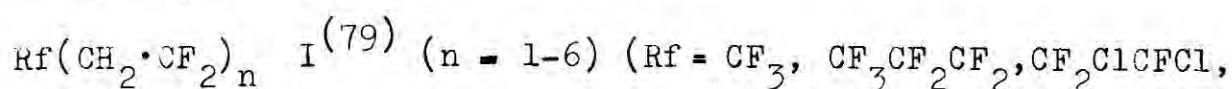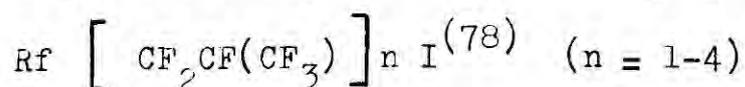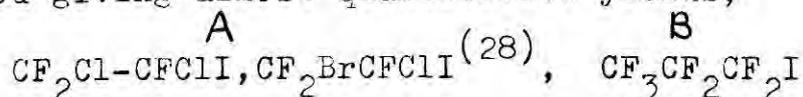
but in contrast trifluoroiodomethane and pentafluoroiodoethane fail to form coupling products. A more conventional way of accomplishing

this type of reaction has been shown by Henne[93],[94], who has coupled A and B using zinc and an acetic anhydride-methylene chloride solvent pair, and by Hauptschein[85] who coupled 1,3,4,trichloro-hexafluoro-1 iodobutane using the same reagent. Haszeldine[73] has similarly reacted 1 chlorohexafluoro-1 iodopropane with zinc in dioxane at 110° to produce 3,4-dichlorododecafluorohexane.

Hauptschein[85] has also attempted the coupling of $C_3F_7\left[CF_2CF(CF_3)\right]nI$ series (n -1-4) by reacting them under the following conditions; mercury and heat, concentrated sulphuric acid and heat, heat alone, heat in the presence of excess hexafluoropropene. The yields of coupling products were poor to moderate.

Certain fluoroalkyl bromides undergo similar reaction; Harmon[95] observed internal coupling when he treated 1,3-dibromohexafluoropropane with zinc dust to obtain perfluorocyclopropane. Tarrant[96] and co-workers used zinc and n-propanol in the presence of zinc chloride for the following reaction.

$$(CH_3)_2\ CBr\ CH_2CF_2Br \longrightarrow \overline{CF_2CH_2C}\ (CH_3)_2$$
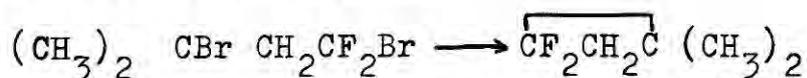
Formation of Lithium derivatives.

Lithium is the only element in Group 1 of the periodic table which has been shown to form relatively stable and reactive perfluoro-alkyl derivatives. Although perfluoroalkyl iodides do not react directly with lithium[92], perfluoroalkyl lithium compounds can be prepared by a halogen-metal interchange with an alkyl-lithium.

$$RLi + C_3F_7I \longrightarrow C_3F_7Li + RI$$

Trifluoromethyliodide, however, does not undergo this conversion[97],

trifluoromethyl-lithium has been reported but without experimental details.[98][99].

Reactions of Lithium derivatives.

Mcbee and his co-workers[97][100], have been responsible for investigating most of these reactions.

Syntheses involving perfluoroalkyl-lithium compounds are best conducted by adding the alkyl-lithium and the other reactant simultaneously in an ether solution of the perfluoroalkyl iodide at -40° to -50°. Perfluoroalkyl lithium reagents are unstable with respect to hexafluoropropene and lithium fluoride, and undergo displacement and addition reactions common to lithium alkyls but usually in poorer yields; in some instances the perfluoroalkyl lithium reagent causes reduction of ketones to occur[100].

A summary of reactions of heptafluoropropyllithium investigated by Mcbee[97][100], is given in the following table.

Reactant.	Product(s) (% Yield.)	% Conversion.
$3N\ H_2SO_4$	$CF_3CF_2CF_2H$ (99.4)	63.8
C_2H_5CHO	$C_3F_7CHOHC_2H_5$ (94)	50
$(CH_3)_2CO$	$C_3F_7COH(CH_3)_2$ (29)	
	$CH_3COCH = C(CH_3)_2$ (33)	
	C_3F_6 (3)	
	C_3F_7H (7)	
C_6H_5CHO	$C_3F_7CHOHC_6H_5$ (54.4)	
CH_3COCl	$C_3F_7COH(CH_3)CH_2COC_3F_7$ (6.2)	52
	C_3F_6 (10)	
$C_6H_5COOC_2H_5$	$C_3F_7COC_6H_5$ (4.8)	60
	C_3F_6 (47)	

Reactant.	Product(s) (% yield)	% Conversion.
$C_6H_5COC_6H_5$	C_3F_6 (56)	47
C_3F_7CHO	perfluorobutraldehyde polymer	
$C_3F_7COOC_2H_5$	$(C_3F_7)_2$ CHOH (42)	
	C_3F_6 (25)	
$(C_2H_5)_2$ SiCl$_2$	$(C_3F_7)_2$ Si$(C_2H_5)_2$ (32)	
	C_3F_6 (24)	

Under certain conditions propionaldehyde, acetone and benzaldehyde were converted to aldol type products and hexafluoropropene, as well as the alcohol. No similar case for normal alkyl lithiums has been reported.

Heptafluoropropane was only formed in reactions where there was enolizable or strongly acidic hydrogen atoms. It is unlikely, therefore, that homolytic fission of the heptafluoropropyllithium occured in any of these reactions, or heptafluoropropane would result from free radical attack on the solvent.

A series reactions involving lithium exchange at low temperatures between n-butyl-lithium and trichlorobromomethane, carbon tetrachloride, trichloroiodomethane, and carbon tetrachloride all resulted in the formation of the corresponding trihalo lithium reagent, which on warming was shown to be unstable with respect to dihalocarbene and lithium fluoride. The dihalocarbenes were then reacted with cyclohexene to form various norcarane derivatives. It was shown that n-butyl lithium exchanged more efficiently than methyl lithium[101].
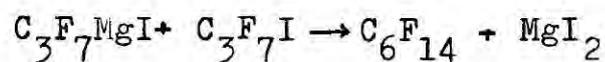
Perfluoroalkyl Grignard reagents.

These can be prepared from perfluoroalkyl iodides and magnesium in basic solvents in the usual manner. Although heptafluoro-n-propylmagnesium iodide ha s been the most widely investigated because of its stability[102-107], there are indications that the less stable trifluoromethyl magnesium iodide can be prepared by using special precautions[108-110]. The nature of the solvent, the reac tion temperature, the dilution of the perfluoroalkyl iodide, and the purity of the magnesium used in the reaction have all been investigated in the preparation of perfluoroalkyl Grignard reagents. Tetrahydropyran, tetrahydrofuran, tertiary amines, ethyl ether and n-butyl ether have all been used as solvents, but the aliphatic ethers are less effective for the stabilisation of the Grignard reagent than of the other compounds. The stability of perfluoroalkyl Grignard reagents increases but the rate of their formation and the ease of initiation of the reaction decreases with decreasing temperature. As a practical compromise between these temperature effects the reaction is initiated at room temperature or above, and then the reaction temperature is lowered. Grignard reagent formation and reaction has been observed down to -80°; the optimum temperature appears to be about -20° [102]. The purity of the magnesium employed in the reaction has been cited as a critical factor in the formation of perfluoroalkyl Grignard reagents[102], but there appears to be no general agreement on this point. Although heptafluoro-n-propyl magnesium iodide reacts with aldehydes, acid chlorides and esters to form the expected secondary alcohols, ketones and tertiary alcohols[104][105], there are no

recorded attempts to extend these reactions to the preparation of
other perfluoroalkyl metallic compounds. Trifluoromethyl magnesium
iodide undergoes similar reactions, but the conditions for its
formation are difficult to reproduce precisely[109]. Better overall
yields are obtained in reactions employing perfluoroalkyl Grignard
reagents if the Grignard is formed in the presence of the substance
with which it is to react. These remarks on the stability of
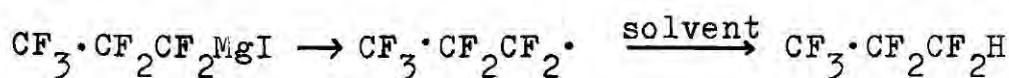perfluoroalkyl Grignard reagents do not apply to the aromatic series;
the reagent formed from bromopentafluorobenzene and magnesium in
ether[112] is stable at the boiling point of ether, because elimination
of magnesium fluoride is obviously quite difficult in an aromatic
system. Conventional Grignard reactions have been performed with
this compound: hydrolysis gave pentafluorobenzene, acetaldehyde gave
1-(pentafluorophenyl) ethanol, and reac tion with carbon dioxide gave
perfluorobenzoic acid in low yield.

An exchange reaction between perfluoroalkyl iodides and phenyl
magnesium bromide occurs at normal a nd low temperatures in ether
solution and should be more useful from a manipulative standpoint[113-115].

Reactions of Perfluoroalkyl Grignard Reagents.

Haszeldine[102] has prepared 1-heptafluoropropylmagnesium bromide
from heptafluoro-1-iodopropane and magnesium at -50° (60% yield).
During the preparation and on allowing it to decompose, he obtained
heptafluoropropane (76%), hexafluoropropene (6%) and tetradecafluoro-
hexane (2%). He suggests that the following reactions are responsible
for these products:-

$$CF_3 \cdot CF_2CF_2MgI \longrightarrow CF_3 \cdot CF_2CF_2 \cdot \xrightarrow{\text{solvent}} CF_3 \cdot CF_2CF_2H$$

$$CF_3 \cdot CF_2CF_2MgI \longrightarrow CF_3CF_2\bar{C}F_2 \cdot \overset{+}{M}gI$$

$$CF_3 - \underset{\underset{F}{\overset{|}{\downarrow}}}{CF} - \overset{\frown}{\bar{C}}F_2 \longrightarrow CF_3 - CF = CF_2 \overset{+}{} F^-$$

$$C_3F_7MgI + C_3F_7I \longrightarrow C_6F_{14} + MgI_2$$
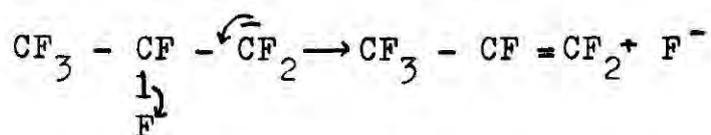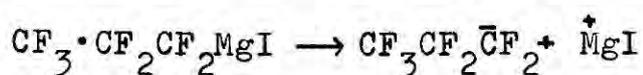
In a later paper[104] he describes the following reactions of heptafluoro-npropyl magnesium iodide.

Reactant.	Products (% yield)	
CH_3CHO	$C_3F_7 \cdot CHOHCH_3$ (41)	
C_2H_5CHO	$C_3F_7CHOHC_2H_5$ (45)	
C_3H_7CHO	$C_3F_7CHOHC_2H_7$ (40)	
CF_3CHO	$C_3F_7CHOHCF_3$ (29)	
C_2F_5CHO	$C_3F_7CHOHC_2F_5$ (30)	
C_3F_7CHO	$C_3F_7CHOHC_3F_7$ (27)	
CH_3COCl	$C_3F_7COCH_3$ (15)	$C_3F_7CClOHCH_3$ (22)
C_2H_5COCl	$C_3F_7COC_2H_5$ (18)	$C_3F_7CClOHC_2H_5$ (27)
C_3H_7COCl	$C_3F_7COC_3H_7$ (21)	$C_3F_7CClOHC_3H_7$ (23)
CF_3COCl	$C_3F_7COCF_3$ (36)	$C_3F_7CClOHCF_3$ (11)
C_2F_5COCl	$C_3F_7COC_2F_5$ (41)	$C_3F_7CClOHC_2F_5$ (13)
C_3F_7COCl	$C_3F_7COC_3F_7$ (31)	$C_3F_7CClOHC_3F_7$ (16)
$CH_3CO_2C_2H_5$	$CH_3COC_3F_7$	
$C_2H_5CO_2C_2H_5$	$C_2H_5COC_3F_7$	

Reactant.   Products (% yields)

$C_3H_7CO_2C_2H_5$ $C_3H_7COC_3F_7$

$CF_3CO_2C_2H_5$ $CF_3COC_3F_7$

$C_2F_5CO_2C_2H_5$ $C_2F_5COC_3F_7$

In the last series of reactions small amounts of C_3F_7CHROH and

$(C_3F_7)_2CROH$ were formed.

Henne and Francis[105] made heptafluoropropylmagnesium bromide

by a similar method, but in much lower yield and performed the

following series of reaction:-

Reactant.   Products. (% yields)

$(CH_3)_2CO$ $C_3F_7C(OH)(CH_3)_2$ (10)

                $CH_3COCH = C \cdot CH(CH_3)$

C_3H_7CHO $C_3H_7CH(OH)C_3F_7$ (16)
                Small amounts of aldol
                type compounds.

C_3F_7CHO $C_3F_7CH(OH)C_3F_7$ (Very low)

$HCOOC_2H_5$ C_3F_7CHO (24)

$C_3F_7COOC_2H_5$ $C_3F_7COC_3F_7$ (20)

C_3F_7COCl $C_3F_7COC_3F_7$ (4)

C_3F_7CHO

CO_2 C_3F_7COOH (41)

As mentioned previously, exchange between phenyl magnesium

bromide and heptafluoro-1-iodopropane and pentafluoroiodoethane

occurs readily at low tempe ratures.[113][115] Mixing of these

reactants in the presence of acetone produced on hydrolysis the corresponding tertiary alcohols, yields being 65% at 0° [113] and 38% at -78°[115] respectively. This exchange reaction was used also to investigate the reaction between 1-heptafluoropropyl magnesium bromide and a variety of aldehydes and ketones. For these reactions heptafluoro-1-iodopropane was placed in a flask and treated simultaneously with phenyl magnesium bromide and the carbonyl compounds; the temperature of reaction was about $-40, -50^o$. The following yields of alcohols were obtained from reactions with the carbonyl compounds indicated.

$$CH_3CHO \qquad C_3F_7 \cdot CHOH \cdot CH_3 \quad (30\%)$$

$$C_3H_7CHO \qquad C_3F_7 \cdot CHOH \cdot C_2H_7 \quad (45.5\%)$$

$$C_6H_5 \cdot CO \cdot CH_3 \qquad C_6H_5 \cdot COHCH_3 \cdot C_3F_7 \quad (77.4\%)$$

$$C_6H_5COC_6H_5 \qquad C_6H_5 \cdot COHC_6H_5 \cdot C_3F_7 \quad (62\%)$$

$$C_6H_{10}O \qquad C_6H_{10}OHC_3F_7 \quad (90\%)$$
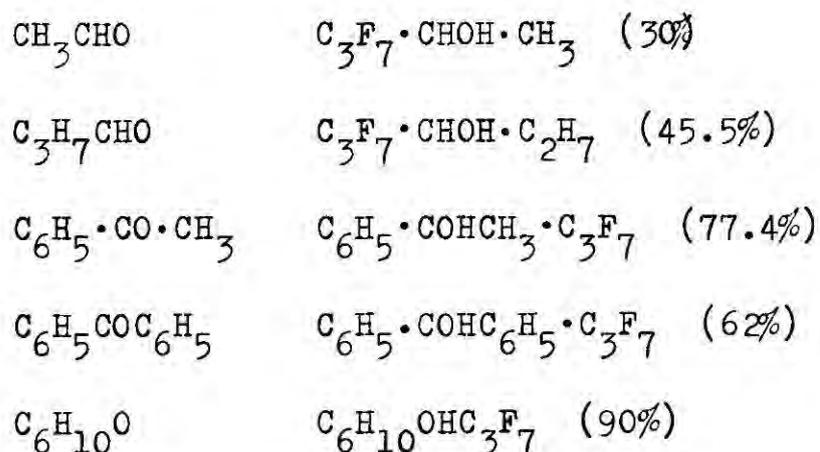
Perfluoroalkylzinc derivatives.

Trifluoromethylzinc derivatives have not been reported, but, however, some higher perfluoroalkylzinc halides are known[116]. 1-Heptafluoropropylzinc iodide and bisheptafluoro-n-propylzinc have been prepared in dioxane or 1,2-dimethoxyethane solution and have been isolated as stable solvates[116][117]; the removal of solvent molecules by high vacuum sublimation has been reported[118], but not confirmed[117]. The ether solvate molecules are readily displaced by stronger bases, and the 1:1 pyridine addition compounds of 1-heptafluoropropyl zinc iodide and bisheptafluoro-n-propylzinc are

formed from the 1,2-dimethoxyethane solvates of these substances in this manner. The attempted preparation of l-heptafluoropropyl zinc iodide from heptafluoro-l-iodopropane in diethyl ether solution leads only to the formation of heptafluoropropane[116]; this observation is accounted for by an organic peroxide-zinc induced free radical chain reaction between the iodide and ether. Reaction of heptafluoro-l-iodopropane with zinc in commercial grade dioxane yields 42% 1H-heptafluoropropane[97] which is also explained by the presence of per-oxides in the solvent[116].

The chemical reactivity of l-heptafluoropropyl zinc iodide appears to lie between that of the very reactive perfluoroalkyl magnesium halides and the relatively unreactive perfluoroalkyl mercury compounds. Neither l-heptafluoropropyl zinc iodide in dioxan solution nor the pure dioxan adduct reacts with carbonyl compounds or acid chlorides, with the exception of the reaction of the pure dioxan adduct with perfluoroacid chlorides which yield small amounts of the expected ketone. Reaction with aldehydes, ketones, acid anhydrides and acid chlorides containing enolizable hydrogen, yielded hepta-fluoropropane and condensation and solvent cleavage products on long refluxing. Reaction with paraformaldehyde at 130° for five days gave 1H-heptafluoropropane (46%); similar reactions with aceticanhydride and acetyl chloride formed the same product (56% and 78% respectively).

1-Heptafluoropropyl zinc iodide reacted quite readily with chlorine and bromine but heat was required to initiate reaction with iodine. Hydrolysis using aqueous acid or base occurred readily; oxygen had no effect even over long periods.[116][117]

CHAPTER 2.

DISCUSSION OF THE EXPERIMENTAL WORK.

DISCUSSION OF EXPERIMENTAL WORK.

The Addition of Halogen Monohalides to Fluoro-Olefins.

Halogen Monofluorides.

Bromine trifluoride and iodine pentafluoride are extremely

reactive compounds, and they have been used alone for the preparation

of chloro- , bromo- , and idofluoroalkanes by their reactions with

polyhaloalkanes and alkenes. Banks et al.[17] prepar ed trifluoro-

iodomethane and pentafluoroiodoethane by the reaction of iodine

pentafluoride with carbon tetraiodide and tetraiodoethylene. Emeleus

and Haszeldine[92] obtained pentafluoroiodoethane from the reaction

between iodine pentafluoride and 1,2-diiodotetrafluoroethane. The

reactions of bromine trifluoride and iodine pentafluoride with

fluoro-olefins, however, have not been investigated extensively

whereas reactions between other, much less reactive interhalogen

compounds and fluoro-olefins are quite well known and will be

discussed later. Simons and Brice[34] investigated some reactions

of iodine pentafluoride and higher iodine fluorides with fluoro-

olefins at temperatures of 175 - 250°, in the gas phase, for the

purpose of preparing fluorocarbon iodides. The yields, although not

quoted, are necessarily limited by the fact that only one of the

fluorine atoms in any particular molecule of iodine pentafluoride

can react to yield fluorocarbon iodide; two remaining molecules of

fluorine per molecule of iodine pentafluoride are then available

for reaction with the fluorocarbon iodide, thus reducing the yield.

$$RfI + 3F_2 \longrightarrow RfF + IF_5$$

The present worker has found that yields of fluorocarbon

bromides and iodides obtained by the reaction of fluoro-olefins with

bromine trifluoride and iodine pentafluoride, in the liquid phase, under autogenous pressure, may be substantially increased by the addition of a quantity of bromine or iodine, as the situation requires sufficient to make the mixtures equivalent to the halogen monofluoride. These mixtures will in future often be referred to as "bromine fluoride and "iodine fluoride".

Iodine Fluoride.

These reactions were all performed in a stainless steel autoclave which was rotated in order that the contents might be thoroughly mixed.

The stoichometric proportions of fluoro-olefin, iodine penta-fluoride and iodine used were those required by the equation

$$5 \; >C = C< + 2I_2 + IF_5 \longrightarrow 5 \quad \underset{F}{>C} - \underset{I}{C<}$$
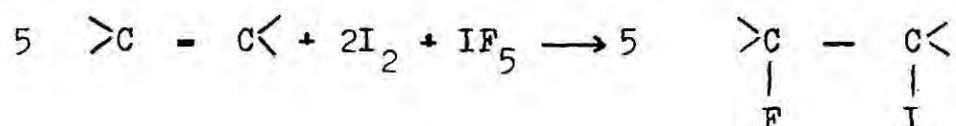
Some of the reactions proceeded readily at room temperature, whereas others required heat. Table 1 gives a summary of reactions performed; yields are based on the amount of olefin used up.

TABLE 1.

Olefin.	Duration of Reaction.	Temperature.	Product(s)	Yield.	Conversion.
$CF_2:CF_2$	10 hrs.	Ambient	C_2F_5I	86%	71.5%
$CF_2:CH_2$	15 "	103°	$CF_3 \cdot CH_2I$	86%	100%
$CF_3CF:CF_2$	24 "	150°	$CF_3 \cdot CFI \cdot CF_3$	99%	100%
$CF_2:CFCl$	4 "	Ambient	$CF_2I \cdot CF_2Cl$	45%	100%
			$CF_3 \cdot CFClI$	37%	
$CF_2:CCl_2$	6 "	170°	$CF_3 \cdot CFCl_2$	25%	85%
			$CF_2I.CFCl_2$	31%	

TABLE 1. (continued.) 28.

Olefin.	Duration of Reaction.	Temperature.	Product(s)	Yield.	Conversion.
			$CF_3 \cdot CCl_2I$	23%	
$CCl_2 \cdot CCl_2$	4 hrs.	190°	$CCl_2F \cdot CCl_2F$	51%	40%

Only very recently has iodine monofluoride been prepared[35] from elemental fluorine and iodine at -78° using trichlorofluoromethane as solvent, although Durie[36] earlier observed iodine monofluoride spectroscopically. It is therefore possible that the mixtures of iodine pentafluoride and iodine which have acted as excellent sources of iodine monofluoride in the reactions shown in Table 1, have in fact been a source of the compound iodine monofluoride. If this is so, then the following equilibrium must lie appreciably to the right

$$IF_5 + 2I_2 \rightleftharpoons 5IF$$
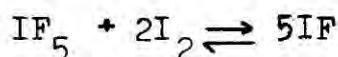
Presumably therefore, iodine fluoride reacts with fluoro-olefins much more readily than does either iodine pentafluoride or iodine, and the equilibrium is continually disturbed by removal of "iodine fluoride", thus driving the reaction to completion. Many other complicated reaction schemes involving the self-ionisation of the iodine pentafluoride may be devised to account for the reactions between iodine pentafluoride plus iodine, with fluoro-olefins, but the mode of addition is most easily explained in terms of this iodine monofluoride

$$\overset{\delta +}{I} - \overset{\delta -}{F} + \overset{\delta +}{CF_2} : \overset{\delta -}{CF} \cdot CF_3 \longrightarrow CF_3 \cdot CFI \cdot CF_3$$
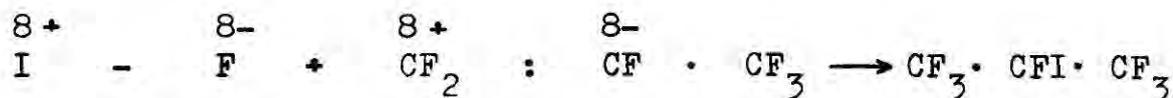
Many workers have shown that nucleophilic addition to fluoro-olefins occurs very easily and that olefins containing a terminal difluoromethylene group are the most reactive (see introduction); the

nucleophile invariably becomes attached to the difluoromethylene group. The same direction of attack occurs in electrophilic addition reactions to fluoro-olefins i.e. the electrophile avoids attack on the difluoromethylene group (see introduction). This situation can be rationalised by considering the ability of fluorine atoms in a difluoromethylene group to "back-donate" non-bonding p-electrons to the olefinic double bond. Chlorine will also "back-donate" electrons but does so less readily than fluorine, as will be shown later in this discussion.

Addition to Tetrafluoroethylene.

This reaction proceeded readily at room temperature resulting in the formation of pentafluoriodoethane.

$$I - F + CF_2 : CF_2 \longrightarrow CF_3 \cdot CF_2 I$$
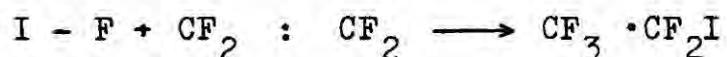
Formation of a small amount of 1,2-diiodotetrafluoroethane was probably caused by the exothermic nature of the main reaction providing sufficient energy for the addition of iodine to tetrafluoroethylene.

This method of preparing pentafluoroiodoethane in good yield from easily obtainable materials appears to be an improvement on previous methods of preparing this useful compound.

Addition to 1,1-Difluoroethylene.

This addition occurred in only one direction, which was that postulated from electronic considerations; the conversion was quantitative.

The possibility that the reaction had in fact produced two inseparable isomers was ruled out by the preparation of 1, 1, 1 - trifluoro - 2 - iodoethane by a different route. This first of all

involved preparing trifluoroethanol from trifluoroacetic acid by the method of Henne[119].

$$CF_3COOH + C_6H_5COCl \longrightarrow CF_3COCl + C_6H_5COOH$$

$$CF_3COCl + LiAlH_4 \longrightarrow CF_3CH_2OH + LiCl + Al(Cl)_3$$
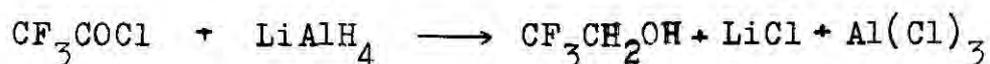
The trifluoroethanol was isolated pure by distillation.

The next stage was the preparation of the tosyl ester of this alcohol and its reaction with sodium iodide at a fairly high temperature, as described by Tiers, Brown and Reid[120]. A high boiling solvent, tetraethyleneglycol dimethyl ether was used in this reaction; 1,1,1-trifluoro-2-iodoethane was evolved and was shown to have an infrared spectrum identical to the product from the "iodine fluoride"-1, 1-difluoroethylene reaction, thus excluding the formation of 1,1,2-trifluoro - 1 - iodoethane from the latter.

$$CF_3CH_2OH + pCH_3 - C_6H_4 - SO_2Cl \longrightarrow CF_3CH_2-O-SO_2-C_6H_4- CH_3$$

$$CF_3CH_2-O-SO_2- C_6H_4 - CH_3 + NaI \longrightarrow CF_3CH_2I + CH_3-C_6H_4-SO_2-ONa$$
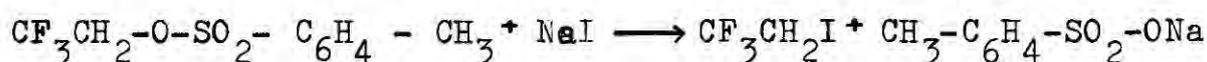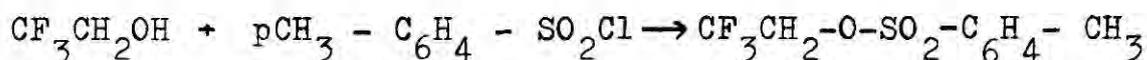
Analysis for fluorine on 1,1,1-trifluoro-2-iodoethane prepared by either method, repeatedly gave a value which was one fluorine atom low. This may be attributed to the removal of one atom of fluorine as some type of complex with the diphenylsodium-dimethoxyethane reagent which was used to decompose the compound. It is however, significant that no analysis figures for fluorine have been quoted in the literature for 1,1,1-trifluoro-2-iodoethane which has been prepared by four different methods.[32][120][124][125]

Addition to Hexafluoropropene.

Quantitative conversion to a single isomer heptafluoro-2-iodopropane was obtained, the structure of which was determined by:

F^{19} magnetic resonance spectrum which consisted of a low field doublet and a high field septet and the intensity distribution was consistent with the compound having this structure; non-identical infrared spectrum with heptafluoro-1-iodopropane; and reaction with potassium hydroxide in acetone to give only 2H-heptafluoropropane. These two spectra and the reaction also ruled out the possibility of the product being a mixture of the two isomers of heptafluoroiodopropane. This complete conversion to heptafluoro-2-iodopropane at the expense of any heptafluoro-1-iodopropane must have been helped considerably by the relatively strong electronic effects working in the hexafluoro-propene. The "back-donation" of electrons from the difluoromethylene group have a complimentary action to the strong inductive effect of the trifluoromethyl group

$$\overset{\delta+}{I} - \overset{\delta-}{F} + \overset{\delta+}{CF_2} : \overset{\delta-}{CF}. CF_3 \longrightarrow CF_3 \cdot CFI \cdot CF_3$$
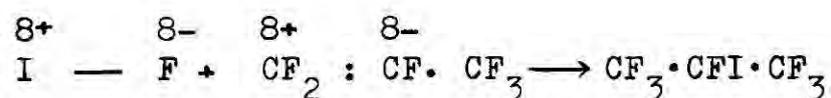
Hexafluoropropene has been shown to be less reactive than tetra-fluoroethylene, chlorotrifluoroethylene and 1,1-difluoroethylene in its free radical addition reactions with iodofluoroalkanes[22] and its ability to homopolymerise[78]. It is in keeping therefore with this reactivity that the addition of "iodine fluoride" to hexafluoro-propene requires more vigorous conditions than the addition of "iodine fluoride" to the other olefins mentioned above.

Chlorotrifluoroethylene.

A substantial amount of both possible isomers were obtained from this reaction, which proceeded readily at room temperature. Separation of these isomers was very difficult and could only be accomplished on a small scale using an analytical size V.P.C. column by trapping out

the two components as they emerged from the detector. The two

components gave equivalent analyses but different infrared spectra,

and were characterised by preparing an authentic sample of one of

them by a known route. This was via the addition of iodine mono-

chloride to tetrafluoroethylene in an autoclave heated to 50°, and

produced 1-chloro-2-iodotetrafluoroethane[11]; this had an identical

infrared spectrum to the first isomer to emerge from the V.P.C.

column. The ratio of the isomers present was found by measuring the

two peak areas on the V.P.C. chromatograms; this necessitated

assuming equal thermal conductivities for the two isomers in the

vapour phase.

The direction of addition is effected partly by electronic effects

which cause the following reaction:-

$$\overset{\delta+}{I} - \overset{\delta-}{F} + \quad \overset{\ddot{F}}{\underset{\ddot{F}}{\overset{\delta+}{C}}} = \overset{\ddot{F}}{\underset{Cl}{\overset{\delta-}{C}}} \longrightarrow CF_3 \cdot CFClI \quad 45\%$$
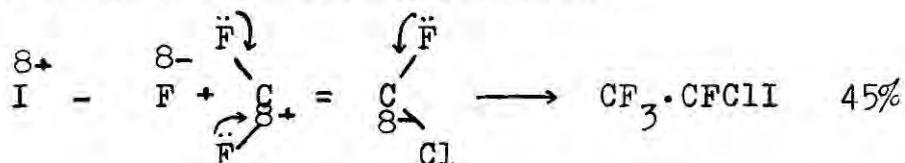
and partly by what is probably a steric factor operating, which

discourages the attachment of the large iodine atom to the carbon atom

already containing a chlorine atom.

Therefore the following reaction occurs to the extent stated.

$$I - F + CF_2 : CFCl \longrightarrow CF_2I \cdot CF_2Cl \quad 55\%$$
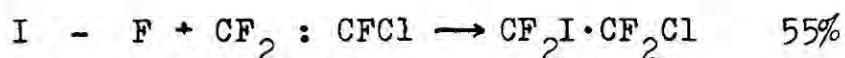
The formation of two isomers from this reaction was not in

accordance with the addition of iodine monochloride and iodine mono-

bromide to chlorotrifluoroethylene[27][28], where the addition was

stated to obey entirely electronic considerations forming only one

isomer.

$$\overset{\delta+}{I} - \overset{\delta-}{X} + \overset{\delta+}{CF_2} : \overset{\delta-}{CFCl} \longrightarrow CF_2X - CFClI \quad (X = Cl \text{ or } Br)$$
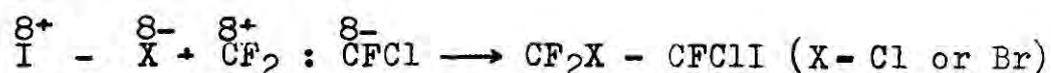
These two reactions were therefore reinvestigated and will be discussed later.

Addition to 1,1-Dichlorodifluoroethylene.

Both possible isomers, $CF_2I \cdot CFCl_2$ and $CF_3 \cdot CCl_2I$, were formed in this reaction together with some 1,1-dichlorotetrafluoroethane formed by direct addition of fluorine to the double bond. This last addition probably took place because of the relatively high temperature (170°) used for the reaction; simple addition of fluorine from iodine pentafluoride, to olefinic double bonds does take place at high temperatures as is shown in the next reaction to be discussed.

The three products were separated by large scale V.P.C; and the two isomers were characterised by their equivalent analyses, different infrared spectra and the fact that one of them had an infrared spectrum identical to one of the products from the addition of iodine monochloride to chlorotrifluoroethylene. This was $CF_2I - CCl_2F$ as is explained by the following equations.

$$2I-F + 2CF_2:CCl_2 \longrightarrow CF_2I - CCl_2F + CF_3 \cdot CCl_2I$$

$$2I - Cl + 2CF_2:CFCl \rightarrow CF_2I - CCl_2F + CF_2Cl - CFClI$$
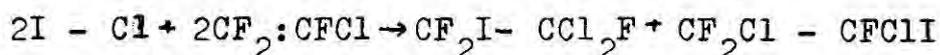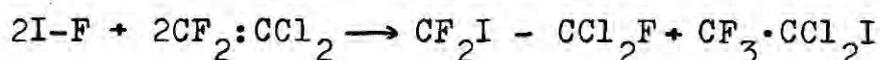
The formation of two isomers is again explained by the electronic effect and polar effect working against each other. With 1,1-dichloro-difluoroethylene the polarisation is greater than in chlorotrifluoroe-thylene because of the smaller back donation of electrons from $:CCl_2$ in comparison to $:CFCl$. The steric effect, however, of $:CCl_2$ is greater than $:CFCl$ and this appears to compensate almost exactly the increased polar effect, thus forming the same proportion of isomers as in the addition of iodine fluoride to chlorotrifluoroethylene.

$$\overset{8+}{2I} - \overset{8-}{F} + \overset{8+}{2CF_2} : \overset{8-}{CCl_2} \longrightarrow CF_3 \cdot CCl_2I + CF_2I \cdot CFCl_2$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\quad 43\% \qquad\qquad 57\%$$
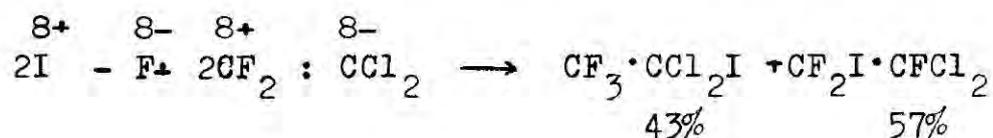
This proportion of each isomer was again determined from peak areas.

Addition to Tetrachloroethylene.

No simple addition product of iodine fluoride and tetrachloroe-thylene was isolated from this reaction; the only product isolated was 1,2-difluorotetrachloroethane which was easily separated from the starting material by distillation through a fractionating column. A fairly high temperature was necessary to promote this simple addition of fluorine to tetrachloroethylene. Probably the crowding of the four large chlorine atoms around the two carbon atoms sterically discourage the introduction of an even larger iodine atom.

This simple method of preparing 1,2-difluorotetrachloroethane was investigated further by a reaction between tetrachloroethylene and iodine pentafluoride alone at 220° for four hours; a yield of 62% and a conversion of 85% was obtained. This 1,2-difluorotetrachloroethane produced was dechlorinated by a conventional method using zinc dust in ethanol, yielding 1,2-dichlorodifluoroethylene (76%).

It should be noted that these reactions between "iodine fluoride" and fluoro-olefins and for that matter later reactions between other halogen monohalides, were not investigated under widely varying conditions. It is possible therefore that in some cases less drastic conditions might produce similar results to those described.

Bromine Fluoride.

These reactions were also performed in a stainless steel autoclave ; most of them were so vigorous at room temperature that an inert diluent, 1,1,2-trichloro-trifluoroethane was added to moderate the reaction.

The yields obtained were in most cases lowered because of decomposition resulting from failure to moderate the reaction sufficiently.

The stoichometric proportions of fluoro-olefins, bromine trifluoride and bromine used in the reactions were those required by the equation

$$3 \,>\!C = C\!<\; +\; Br_2 + BrF_3 \longrightarrow 3 \,>\!\underset{\underset{F}{l}}{C} - \underset{\underset{Br}{l}}{C}\!<$$
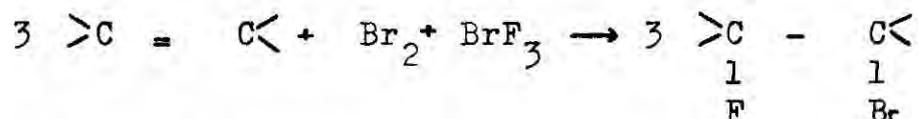
Table 2 gives a summary of reactions.

TABLE 2.

Olefin.	Duration of Reaction.	Temperature.	Product(s)	Yield.	Conversion.
$CF_2{:}CF_2$	2 hrs.	Ambient	CF_3CF_2Br	67.5%	88%
$CF_3{:}CF{:}CF_2$	2 "	Ambient	$CF_3 \cdot CFBrCF_3$	45.5%	85%
$CF_2{:}CFCl$	2 "	Ambient	$CF_2Cl \cdot CF_2Br$	73%	86.5%
			$CF_3 \cdot CFClBr$	13%	
cC_6F_{10}	26 "	265°	$cC_6F_{11}Br$	78%	100%

"Bromine fluoride" has never been isolated but conductometric measurements made by Quarterman et al.[38] provide for its formation when bromine is dissolved in bromine trifluoride. Possibly the addition of the "bromine fluoride" to these olefins occurs via a definite compound "bromine fluoride" as formed by the following equilibrium.

$$BrF_3 + Br_2 \rightleftharpoons 3BrF$$
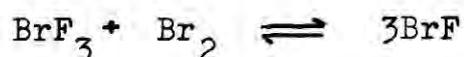
If this is the case then "bromine fluoride" reacts with fluoro-olefins more readily than bromine trifluoride or bromine, thus displacing the equilibrium to the right eventually driving the

reaction to completion. Again, however, as with the "iodine fluoride" additions, the actual mechanism of addition may only be postulated.

Addition to Tetrafluoroethylene.

This action was extremely vigorous and could only be performed on a relatively small scale in the presence of an inert diluent, otherwise almost complete decomposition to carbon tetrafluoride and carbon occurred. The choice of 1,1,2-trichlorotrifluoroethane as diluent was rather unfortunate since separation of the product, pentafluorobromoethane, from this compound could not be performed by simple distillation. Separation by large scale V.P.C. was, however, quite straightforward. Only a small amount was separated by this method and the total yield of pentafluorobromoethane was calculated from this separation.

Addition to Hexafluoropropene.

This reaction was performed without a diluent; some decomposition occurred which accounted for the low yield of 2-bromoheptafluoro-propane. The latter was the only volatile product obtained and its structure was determined by : F^{19} magnetic resonance spectrum which consisted of a low field doublet and a high field septet and the intensity distribution was consistent with the compound having this structure; and non-identical infrared spectrum with 1-bromoheptafluoro-propane. These two spectra also ruled out the possibility of the product being a mixture of the two isomers of bromoheptafluoropropane.

The same electronic considerations as with the addition of "iodine fluoride" to hexafluoropropene, account for the formation of 2-bromo-heptafluoropropane from this reaction:-

i.e. $\overset{\delta+}{Br} - \overset{\delta-}{F} + \overset{\delta+}{CF_2} : \overset{\delta-}{CFCF_3} \longrightarrow CF_3 \cdot CFBr \cdot CF_3$
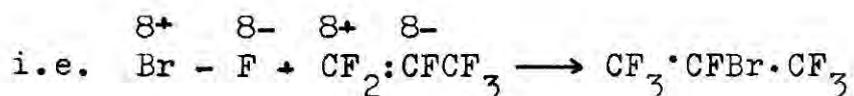
Addition to Chlorotrifluoroethylene.

1,1,2-Trichlorotrifluoroethane was used as a diluent for this reaction and moderated it sufficiently for no decomposition to occur. Only one product was formed, a lot of which was isolated pure by distillation; this gave a single peak on analytical V.P.C. and analysed as bromochlorotetrafluoroethane (1). A sample of one of the isomers of this compound, 1-bromo-2-chlorotetrafluoroethane (2) was prepared by the addition of "bromine chloride" to tetrafluoroethylene (see later); the infrared spectrum of (1) contained all the peaks of (2) together with a few extra ones. This was almost conclusive evidence that (1) contained a mixture of two isomers, (2) and 1-bromo-1-chlorotetrafluoroethane. The proportion of these two isomers was determined using infrared spectroscopy.

As with the addition of "iodine fluoride" to chlorotrifluoroethylene electronic and steric effects are postulated to account for the addition occurring in two directions

$\overset{\delta+}{2Br} - \overset{\delta-}{F} + \overset{\delta+}{2CF_2} : \overset{\delta-}{CFCl} \longrightarrow \underset{15\%}{CF_3 \cdot CFClBr} + \underset{85\%}{CF_2Br \cdot CF_2Cl}$
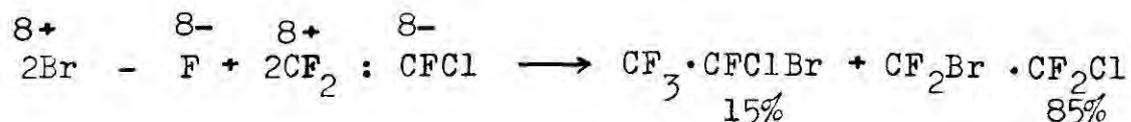
Addition to Decafluorocyclohexene.

Decafluorocyclohexene was found to be extremely unreactive to any form of attack by the bromine trifluoride - bromine mixture and required extremely vigorous conditions in order to produce bromo-undecafluorocyclohexane; this was, however, eventually formed in excellent yield. This lack of reactivity of decafluorocyclohexene

is in keeping with Haszeldine's[20] finding that iodine monochloride

does not add to this olefin whereas it adds quite readily to

perfluorocyclobutene. Probably there is a steric effect operating

in the six membered ring, which is removed in the four membered ring

by the strain present.

"Bromine Chloride."

Addition to Tetrafluoroethylene.

In order to prepare 1-bromo-2-chlorotetrafluoroethane for the

purpose of investigating the product from the reaction between "bromine

fluoride" and chlorotrifluoroethylene, it was decided to attempt the

addition of "bromine chloride" to tetrafluoroethylene. It is well

known that a mixture of bromine and chlorine is in equilibrium with

bromine chloride

$$Br_2 + Cl_2 \rightleftharpoons 2BrCl$$
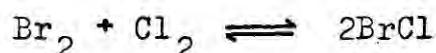
and therefore the reaction between tetrafluoroethylene and a mixture

of bromine and chlorine was attempted. This reaction appeared to

proceed quite readily at room temperature and resulted in the formation

of three products in roughly equal amounts. These were separated easily

by large scale V.P.C. but only one was characterised which was 1-bromo-

2-chlorotetrafluoroethane. The other two products were probably 1,2-

dichlorotetrafluoroethane and 1,2-dibromotetrafluoroethane.

Since this reaction was carried out, Buckles et al.[37] have

used mixtures of bromine and chlorine as an effective source of bromine

chloride for addition reactions to olefins; they did not attempt any

reactions with fluoro-olefins.

Iodine Monochloride and Iodine Monobromide.

Addition to Chlorotrifluoroethylene.

Barr et al.[27] claimed that $CF_2Cl \cdot CFClI$ was the only product from the reaction between iodide monochloride and chlorotrifluoroethylene performed in a solvent at 0°. Haszeldine[28] repeated the reaction in an autoclave at 45° without a solvent and supported Barr's claim of only one product, since on replacing the iodine in his product by fluorine followed by dehalogenation, Haszeldine obtained only tetrafluoroethylene

$$CF_2Cl \cdot CFClI \longrightarrow CF_2Cl \cdot CF_2Cl \longrightarrow CF_2 {:} CF_2$$
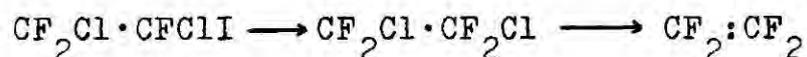
Haszeldine also claimed that the reaction between iodine monobromide and chlorotrifluoroethylene in an autoclave at 100° yielded $CF_2Br \cdot CFClI$ but no $CF_2I \cdot CFClBr$. Since the addition of "bromine fluoride" and "iodine fluoride" to chlorotrifluoroethylene was not specific, this was an apparent contradiction to the view that reactions of these mixtures with fluoro-olefins involve the monofluorides.

However, the reactions of chlorotrifluoroethylene with iodine monobromide and iodine monochloride have been reinvestigated, and it has been found that a substantial amount of both possible isomers was obtained in each case. (See Table 3).

$$\overset{\delta+}{2CF_2} {:} \overset{\delta-}{CFCl} + \overset{\delta+}{2I} {-} \overset{\delta-}{X} \longrightarrow CF_2X \cdot CFClI + CF_2I \cdot CFClX \quad (X = Br, Cl)$$
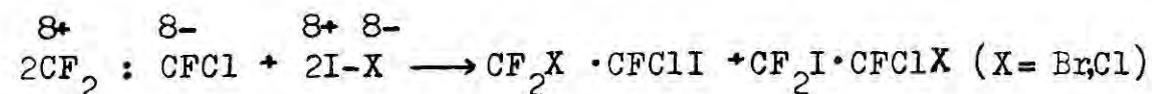
TABLE 3.

	Duration of Reaction.	Temperature.	Products.	Yield.
Iodine Monochloride.	3 hrs.	45°	$CFCl_2 \cdot CF_2I$	29%
			$CF_2Cl \cdot CFClI$	57%
Iodine Monobromide.	2 hrs.	100°	$CF_2Br \cdot CFClBr$	22%
			$CF_2I \cdot CFClBr$	14%
			$CF_2Br \cdot CFClI$	44%

The reactions were carried out in an autoclave under similar conditions to those used by Haszeldine; $CF_2Cl \cdot CFClI$ and $CF_2I \cdot CFCl_2$ were separable by V.P.C. and $CF_2I \cdot CFCl_2$ (together with $CF_3 \cdot CCl_2I$) wa s obtained independently from the reaction between "iodine fluoride" and 1,1-dichlorodifluoroethylene. When a mixture of $CF_2Cl \cdot CFClI$ and $CF_2I \cdot CFCl_2$ was irradiated with ultraviolet light in the presence of mercury, $CF_2Cl \cdot CFClI$ quickly reacted to give coupled products, whereas $CF_2I \cdot CFCl_2$ was relatively unchanged.

Only partial separation of the peaks could be obtained when $CF_2Br \cdot CFClI$ and $CF_2I \cdot CFClBr$ were examined by V.P.C. but by collecting early and late "cuts" as the components emerged from the detector, two fractions with equivalent analysis but different infrared spectra were obtained. These spectra, although different, were very similar; this can be attributed to the extreme similarity of the two compounds; the only difference in their structure is that two large atoms are interchanged. The isomers were distinguished by irradiating with ultraviolet light in the presence of mercury, when $CF_2Br \cdot CFClI$ coupled

rapidly leaving $CF_2I \cdot CFClBr$ relatively unchanged; the carbon-iodine
bond in a group $-CFClI$ is much weaker than the corresponding bond in
$-CF_2I$.

Addition of Iodine Monochloride to Hexafluoropropene.

This reaction has been mentioned in the literature[33] but no
experimental details were given; it was, however, stated that the
reaction produced 1-chloro-2-iodohexafluoropropane; no other product
was mentioned.

A fairly high temperature (200°) was used for the reaction in
view of that needed for the addition of "iodine fluoride" to hexa-
fluoropropene; the reaction was carried out in an autoclave and
produced two products which were easily separable by distillation viz.
1,2-dichlorohexafluoropropane (11%) and 1-chloro-2-iodohexafluoro-
propane (58%). The latter gave a single peak on V.P.C. and it was
therefore assumed that the other isomer, 2-chloro-1-iodohexafluoro-
propane, had not been formed. The aforementioned statement in the
literature coupled with analogy with the addition of "iodine fluoride"
to hexafluoropropene which gave only 2-iodoheptafluoropropane, was
reasonable evidence for characterising the product as 1-chloro-2-
iodohexafluoropropane.

$$\overset{\delta+}{I} - \overset{\delta-}{Cl} + CF_3 \longleftarrow \overset{\delta-}{CF} : \overset{\delta+}{C} \longrightarrow CF_3 \cdot CFI \cdot CF_2Cl$$
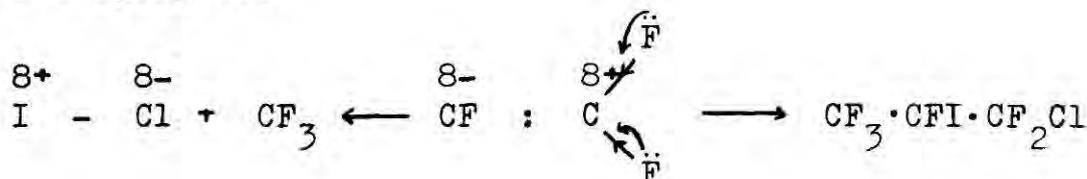
Summary of Factors Affecting Direction of Addition of Halogen.
Monohalides to Fluoro-Olefins.

The halogen monohalides react with fluoro-olefins which contain no
other halogen, to give products which can be predicted by a consideration

of the polarisation resulting from a difference in electronegativity between the halogens in the halogen halide, and of the point at which the nucleophile usually becomes attached to the fluoro-olefin. However, this situation does not apply when other halogens are present in the olefin; a steric factor appears to operate which modifies the aforementioned considerations. Crowding will exist in a group $-CF\ X\ Y$ $(X = Cl;\ Y = Br\ or\ I)$ and there will be a subsequent tendency to resist its formation. Thus, this steric factor encourages the formation of $CF_2I \cdot CFClY$ $(Y = Br,\ Cl\ or\ F)$ from chlorotrifluoroethylene when other considerations predict only $CF_2Y \cdot CFClI$; 1, 1-dichlorodifluoroethylene yielded $CF_2I \cdot CFCl_2$ and $CF_3 \cdot CCl_2I$ with "iodine fluoride" when only $CF_3 \cdot CFClI$ might have been predicted. Probably this steric factor accounts for the fact that $CFCl_2 \cdot CFCl_2$ and not $CFCl_2 \cdot CCl_2I$ was isolated from the reaction between "iodine fluoride" and tetrachloroethylene.

The effect of this steric factor and of the various polarisations of the halogen monohalides is clarified by a study of the addition of four halogen monohalides to chlorotrifluoroethylene.(see Table 5).

In order to simplify this conception of the steric effect and polarisation, the atomic radii and electronegativity of the halogens need to be considered (see Table 4).

TABLE 4.

	Atomic Radius according to Pauling.[121]	Electronegativity according to Pauling.[122]
Fluorine.	$0.64 A^{\circ}$	4.0
Chlorine.	$0.99 A^{\circ}$	3.0
Bromine.	$1.14 A^{\circ}$	2.8
Iodine.	$1.33 A^{\circ}$	2.4

TABLE 5.

Halogen Monohalide.		ΔE	Product from polarisation effects. $\overset{\delta+}{CF_2}:\overset{\delta-}{CFCl}$ P		Product from steric effects. S	
$\delta+$	$\delta-$					
I 1.33*	F 0.67*	1.6	$CF_3 \cdot CFClI$	45%	$CF_2I \cdot CF_2Cl$	55%
I 1.33	Cl 0.99	0.6	$CF_2Cl \cdot CFClI$	67%	$CF_2I \cdot CFCl_2$	33%
I 1.33	Br 1.14	0.4	$CF_2Br \cdot CFClI$	76%	$CF_2I \cdot CFClBr$	24%
Br 1.14	F 0.64	1.2	$CF_3 \cdot CFClBr$	15%	$CF_2Br \cdot CF_2Cl$	85%

ΔE = difference in electronegativity between the two halogens in the halogen monohalide.

* Atomic Radius.

1. "Iodine Fluoride"

This compound has the largest ΔE value and contains the largest and smallest atoms of all the halogen monohalides.

The large ΔE value is therefore helping the formation of $P(CF_3 \cdot CFClI)$, but against this is the relative ease of attaching the large iodine atom to this same group. This latter effect is therefore helping the formation of $S(CF_2Cl \cdot CF_2I)$.

2. Iodine Monochloride.

The smaller ΔE value in this case should mean that less of $P(CF_2Cl - CFClI)$ is formed than in 1. The replacement of fluorine by the larger chlorine, however, means that the formation of $S(CF_2I \cdot CFCl_2)$ is more difficult than in 1. This latter effect appears to over-rule the smaller ΔE value, resulting in the formation of more of P and less of S than in 1.

3. Iodine Monobromide.

The same effect, only to a larger extent, as in 2 is occurring. The smaller ΔE value is again over-ruled by the even larger bromine atom and results in even more of P $(CF_2Br\cdot CFClI)$ and less of S $(CF_2I\cdot CFClBr)$ than in 2.

4. "Bromine Fluoride."

A direct comparison with 1 is taken to explain the results from this reaction. The lower ΔE value than in 1 should decrease the amount of P, but the replacement of I in 1 by Br should facilitate the formation of P $(CF_3\cdot CFClBr)$ since the steric effect must be less. It appears, however, that this decrease in ΔE is the most important fact governing this addition, and causes more of S $(CF_2Br\cdot CF_2Cl)$ and less of P than in 1, to be formed.

Future Work.

There is no reason why the additions of "iodine fluoride" and "bromine fluoride", especially the former, could not be extended to a variety of other fluoro-olefins, polyhalo-olefins and even simple hydrocarbon olefins provided that the reaction was controlled sufficiently.

Workers[123] in this laboratory have already met with success in the formation of heptafluoroiodocyclobutane from hexafluorocyclobutene and "iodine fluoride."

Pyrolysis of Pentafluoroiodoethane.

An extremely efficient method of coupling fluorocarbon iodides has been developed by irradiation with ultraviolet light in the presence of mercury[78]; in the case of pentafluoroethyl and trifluoromethyl iodide, however, this procedure results in the formation of the mercurial RfHgI.[92] It was thought, therefore, that the development of a method of coupling these two iodides might be useful, especially as a means of preparing pure perfluoroethane and perfluorobutane. The usual method of preparation involves direct fluorination of the respective hydrocarbons, followed by a rather difficult separation of the products.

In view of the failure of ultraviolet irradiation in inducing coupling of these two iodides, the obvious method to turn to was the breaking up of the alkyl iodide into free radicals by the application of heat.

$$Rf\ I \rightleftharpoons Rf\cdot + I\cdot \quad (Rf = CF_3, C_2F_5)$$

$$2Rf\cdot \longrightarrow Rf\cdot Rf$$

$$2I\cdot \longrightarrow I_2$$
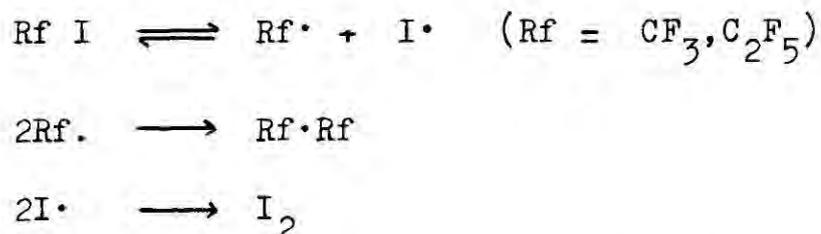
This led to the carrying out of a series of experiments involving the passing of pentafluoroiodoethane through a hot silica tube under a variety of conditions.

The following products were formed in varying ratios from these reactions: perfluoroethane I, tetrafluoroethylene ll and perfluoro-butane lll. l and ll were formed together, ll usually being in slight excess, the formation being aided by very high temperature and low pressure. Similarly, the formation of lll was enhanced by higher

pressures (300 mm. to 760 mm.) and medium temperatures (500°-650°).
These reactions always involved the liberation of free iodine and
etching of the silica tube seemed to indicate the formation of some
fluorine.

The results of these pyrolyses are summarised in the following
table:

Reaction.	Pressure Range mm.	Temperature.	$\%C_2F_6$	$\%C_2F_4$	$\%C_4F_{10}$	%Conversion.
1. Circulation	760 - 400	550 - 600°	–	–	100	68.5
2. Circulation	760 - 400	800°	18	26	56	90
3. Circulation with nitrogen.	760	800°	5.5	14.5	80	90
4. Vacuum transfer	–	800°	16	15	69	93
5. Vacuum transfer	–	330°	–	–	–	1
6. Vacuum transfer through glass helices	–	400°	5	7	8	20
7. Vacuum transfer with heat source directly before cold trap.	–	1400°	48	52	–	100
8. Atmospheric evaporation in a nitrogen stream	760	800°	32	24	44	34

The following reaction scheme accounts for all the products formed.

a. $C_2F_5I \longrightarrow C_2F_5\cdot + I\cdot$

b. $C_2F_5\cdot + C_2F_5\cdot \longrightarrow C_4F_{10}$

c. $C_2F_5\cdot \longrightarrow C_2F_4 + F\cdot$

d. $C_2F_5\cdot + F\cdot \longrightarrow C_2F_6$

e. $F\cdot + F\cdot \longrightarrow F_2$

f. $C_2F_5 \cdot + F_2 \longrightarrow C_2F_6 + F \cdot$

g. $C_2F_4 + F_2 \longrightarrow C_2F_6$

h. $C_2F_5I + F \cdot \longrightarrow C_2F_6 + I \cdot$

i. $I \cdot + I \cdot \longrightarrow I_2$
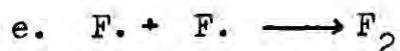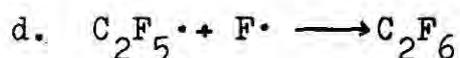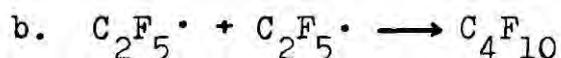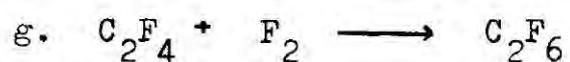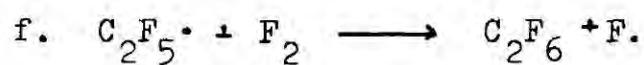
Reaction (1) proceeded at a reasonable rate until the
perfluorobutane formed diluted the pentafluoroiodoethane to such an
extent that a negligible amount of heat was available for pyrolysis
of the latter. The mechanism for the reaction is obviously a, b and i.

Reaction 2 involved such a high temperature that dilution by
stable products did not hinder the reaction. The reason for this is
that the products themselves could get hot enough to break pentafluoro-
iodoethane into free radicals by collision. The higher temperature,
however, gave the pentafluoroethyl radicals enough energy to dis-
proportionate (c), thus causing the formation of tetrafluoroethylene
and perfluoroethane (c-h). The reason for slight excess of the former
can be explained by loss of fluorine by reaction with the silica tube;
etching of the latter bears this out.

Reaction 3 has an improved yield of perfluorobutane over Reaction
2 mainly because the pressure is maintained at atmospheric pressure
by the introduction of nitrogen, thus ensuring an ample supply of third
bodies necessary for radical-radical recombination as in (b).

Reaction 4 needs to be compared directly with Reaction 2. The
low pressure used in Reaction 4 should enable the C_2F_5 radical to have
a longer life, thus giving it more time to disproportionate to
tetrafluoroethylene and perfluoroethane at the expense of perfluorobutane
formation.

This reasoning, however, does not agree with the results, and it would appear that the fast flow through the hot tube using vacuum transfer means that the C_2F_5 radicals acquire less energy than in the longer contact time using the circulation method. The extra energy gained in the latter enhances disproportionation.

In all four vacuum transfer reactions, tetrafluoroethylene and perfluoroethane were formed in roughly equal amounts, in contrast to the circulation reactions when tetrafluoroethylene was formed in excess. This can be explained again by the very fast flowrate in the vacuum transfer reactions which makes removal of fluorine by collision with the walls of the apparatus less favourable.

Reaction 5. The temperature used in this reaction coupled with the rapid flowrate was obviously not favourable for the production of free radicals from the pentafluoroiodoethane.

Reaction 6. The large surface area available from the glass helices appears to aid the disproportionation reaction. Possibly this is because collision of a C_2F_5 radical with a solid body helps the reaction to proceed via (c).

Reaction 7. The principle behind this reaction was to get the gas hot enough to ensure complete conversion to C_2F_5 and I radicals, and then to cool quickly in order to remove energy before disproportionation could occur. This failed, but the reaction provided more evidence f or disproportionation occurring more easily at high temperatures.

Reaction 8 should have given a similar result to Reaction 3. The discrepancy is probably due to the much greater amount of nitrogen in the former. This involves a much lower concentration of C_2F_5 radicals

than in Reaction 3, and hence less likelihood of (b) occurring, thus allowing the reaction to proceed via (c) to a considerable extent.

A modification to the scheme of reactions was considered as an alternative explanation for the formation of tetrafluoroethylene and perfluoroethane in these reactions.

$$C_2F_5I \longrightarrow C_2F_5 \cdot + I \cdot \quad (1)$$

$$C_2F_5 \cdot + C_2F_5 \cdot \longrightarrow C_2F_5 \cdots C_2F_5 \longrightarrow C_2F_4 + C_2F_6 \quad (11)$$
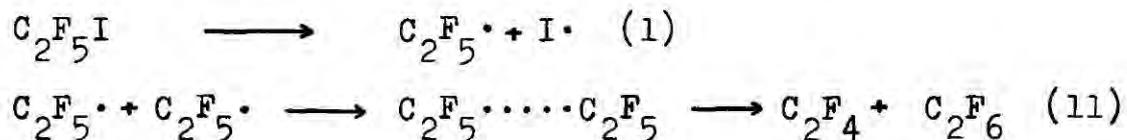
It was thought that (11) might occur because of the high energy which was available in most of these reactions. The only drawback to this scheme lies in the fact that equal amounts of tetrafluoroethylene and perfluoroethane would be formed; this was not found in Reactions 1, 2 and 3. An explanation could have been found in the pyrolysis of the perfluoroethane to give tetrafluoroethylene and fluorine. This was tested with authentic perfluoroethane which was found to be stable when heated for four hours by a Bunsen flame (800°) in a similar apparatus to that used for the circulating experiments.

The original purpose of the series of reactions, however, was to prepare perfluorobutane and Reactions 1 and 3 provided the best conditions for this preparation.

Reaction 1 provided the better yield, but at the expense of a lower conversion. The mixture formed, however, was very easily separated into its two components by preprative scale V.P.C. Reaction 2 had a better conversion, but involved a more difficult separation of the products since the retention times of tetrafluoroethylene, perfluoroethane and perfluorobutane are close enough to hinder

separation on a very large scale. Possibly low temperature

distillation could be developed to make this separation easier.

Reactions of Heptafluoro-2-iodopropane.

Summary.

Heptafluoro-2-iodopropane has been found to undergo very similar reactions to heptafluoro-1-iodopropane. The lithium and Grignard reagents formed from these two compounds, however, have been found to differ in their readiness to eliminate lithium or magnesium fluoride forming hexafluoropropene; the n-propyl compound was much more stable than the iso-propyl in this respect.

Reaction with Potassium Hydroxide in Acetone.

Banus et al.[81] carried out such a reaction in a sealed glass tube using trifluoroiodomethane; they found that the reaction was exothermic and that it had gone to completion after about thirty minutes, resulting in the formation of fluoroform (70% yield). Haszeldine[82] has reacted heptafluoro-1-iodopropane with alcoholic potassium hydroxide in a sealed tube at 100° over a period of ten hours; this resulted in the formation of 1H-heptafluoropropane (70% yield).

The method used for the former workers appeared to be the simplest and, therefore, the present worker carried out the reaction between heptafluoro-2-iodopropane and potassium hydroxide in acetone in a sealed glass tube at room temperature. This reaction was exothermic and was complete after thirty minutes. The only volatile product, 2H-heptafluoropropane, was isolated in good yield (75%) by large scale V.P.C.

This reaction is almost certainly ionic, the initial ionisation of the heptafluoro-2-iodopropane being as follows

$$CF_3 \cdot CFI \cdot CF_3 \rightleftharpoons CF_3\bar{C}FCF_3 + I^+$$
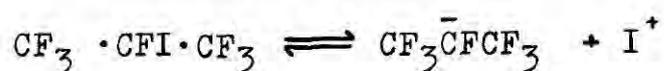
Coupling Reaction.

Hauptschein and his co-workers[78a],[79] have developed the method of coupling iodofluoroalkanes with ultraviolet light in the presence of mercury, so that primary or secondary iodides of the type Rf I or $RfCH_2CF_2I$ (Rf   perfluoroalkyl group) can be coupled quantitatively

$$Hg + 2RfI \longrightarrow Rf - Rf + HgI_2$$
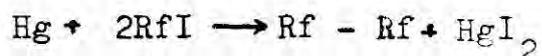
Heptafluoro-2-iodopropane was reacted under similar conditions and after three days irradiation an almost quantitative yield of tetradecafluoro-2, 3-dimethylbutane was obtained.

$$2 \ CF_3 \cdot CFI \cdot CF_3 + Hg \longrightarrow \begin{array}{c} CF_3 \diagdown \quad \diagup CF_3 \\ CF - CF \\ CF_3 \diagup \quad \diagdown CF_3 \end{array} + HgI_2$$
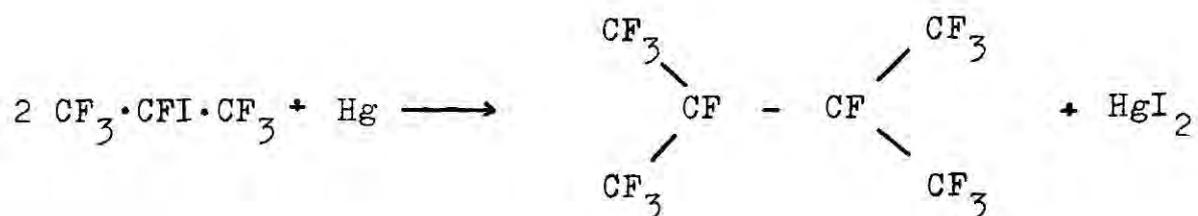
Reaction with Sulphur.

This followed essentially the procedure adopted by Hauptschein and Grosse[84] who reacted heptafluoro-1-iodopropane with sulphur in a sealed glass vessel heated to 250° for fourteen hours. The products obtained were iodine (96%), heptafluoro-n-propyl disulphide

$(CF_3 \cdot CF_2 \cdot CF_2 \cdot S \cdot S \cdot CF_2 \cdot CF_2 \cdot CF_3)$ (47%) b.p. 122.2° ,
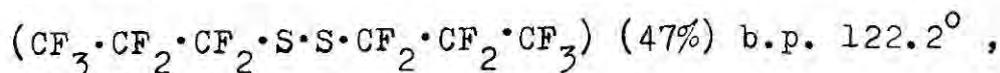
heptafluoro-n-propyl trisulphide$(CF_3 \cdot CF_2 \cdot CF_2 \cdot S \cdot S \cdot S \cdot CF_2 \cdot CF_2 \cdot CF_3)$(18.7%)

b.p. 153°, and some suspected heptafluoro n propyl monosulphide which was not characterised but was thought to boil in the region of 90°. The infrared spectra of the di-and trisulphides were almost identical.

The reaction between heptafluoro-2-iodopropane and sulphur in a sealed tube heated to 243° for thirteen hours yielded heptafluoroisopropyl

monosulphide (1) (11%) b.p. 116°, heptafluoroisopropyldisulphide(2) (36%) b.p. 119°, and heptafluoroisopropyl trisulphide (3)(18.5%) b.p. 150°.

$$CF_3 \diagdown \atop CF_3 \diagup CF - S - CF \diagup CF_3 \atop \diagdown CF_3 \qquad ; \qquad CF_3 \diagdown \atop CF_3 \diagup CF - S - S - CF \diagup CF_3 \atop \diagdown CF_3 \qquad ;$$

(1)   (2)

$$CF_3 \diagdown \atop CF_3 \diagup CF - S - S - S - CF \diagup CF_3 \atop \diagdown CF_3$$

(3)
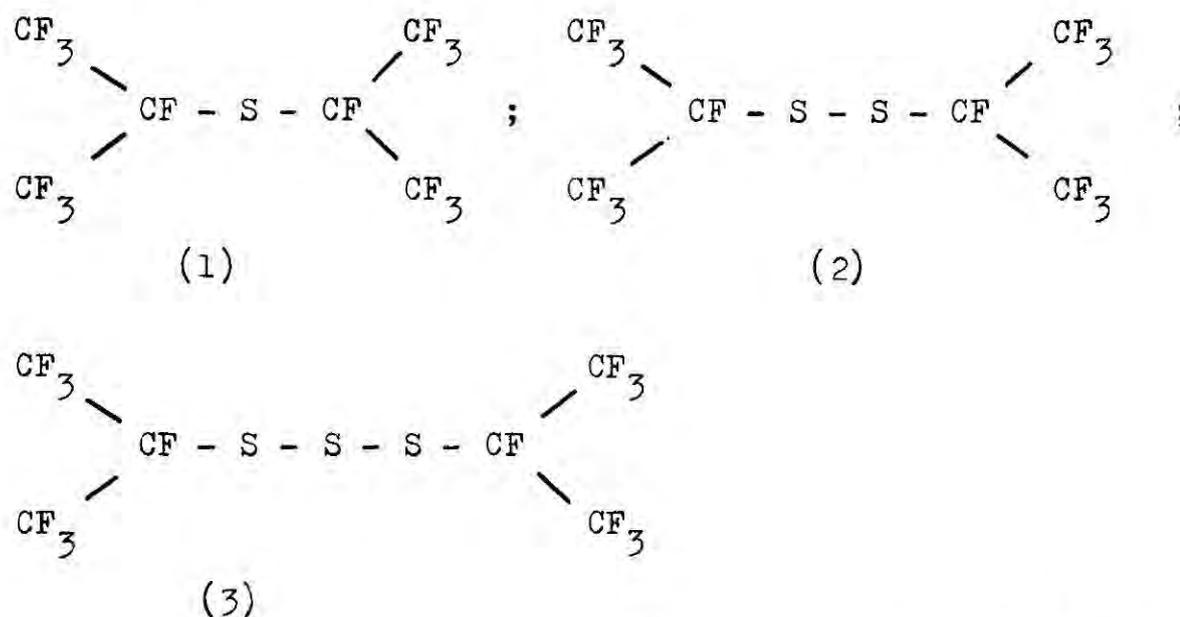
These products were separated by preprative scale V.P.C. as was some unreacted heptafluoro-2-iodopropane which showed that a conversion of 92.5% had been achieved. The infrared spectra of the di and trisulphides were very similar.

The relatively low yield of products isolated (65.5%) was mainly due to mechanical losses in the working up procedure, and probably partly due to the formation of involatile polysulphides; similar losses were experienced by Hauptschein and Grosse.

Hauptschein, Braid and Lawlar[85] found that the secondary iodide tridecafluoro-2-iodohexane and also 1,2-dichloro-1-iodotrifluoroethane both reacted with sulphur in a similar manner to heptafluoro-1-iodopropane but at a lower temperature (180°).

No reaction occurred, however, between heptafluoro-2-iodopropane and sulphur when they were heated together at 185° for fifteen hours. It appears, therefore, that the ease of reaction of heptafluoro-2-

iodopropane with sulphur is very similar to that of heptafluoro-1-
iodopropane.

Reaction with Zinc; Preparation and Hydrolysis of 2-Heptafluoropropylzinc
iodide.

The method of Miller, Bergman and Fainberg[116] who prepared
1-heptafluoropropylzinc iodide from heptafluoro-1-iodopropane and
zinc dust in dioxane, was adopted. The solvent was purified rigorously
since the presence of peroxides have been found to inhibit the reactions[97]

The reaction between heptafluoro-2-iodopropane and zinc dust in
dioxane proceeded in a similar manner to the reaction described by
Miller et al.[116] Small amounts of hexafluoropropene and 2H-heptafluoro-
propane were formed in the initial preparation of the 2-heptafluoro-
propylzinc iodide, whereas Miller and his co-workers, in their reaction,
obtained only 1H-heptafluoropropane which they attributed to radical
abstractions of a hydrogen atom from the solvent by perfluoro-n-propyl
radicals. Chambers[126] has repeated this reaction carried out by
Miller et al. and observed the formation of a similar amount of hexa-
fluoropropene (together with some 1H-heptafluoropropane) to that
obtained by the present worker using heptafluoro-2-iodopropane. The
formation of this olefin is obviously via elimination of zinc fluoride.

Hydrolysis of the 2-heptafluoropropylzinc iodide using sodium
hydroxide gave 2H-heptafluoropropane (46.5%); Chambers obtained
1H-heptafluoropropane (53%). Miller et al. obtained 1H-heptafluoro-
propane (77%) by a similar hydrolysis, but these latter workers carried
out the reaction on a much larger scale than Chambers and the present
worker.

No reactions of 2-heptafluoropropylzinc iodide were attempted, due

to Miller et al. finding that 1-heptafluoropropylzinc iodide was relatively unreactive.

Preparation and Reactions of 2-Heptafluoropropylmagnesium Bromide.

The usual method of preparing perfluoroalkyl Grignard reagents has been to react the corresponding iodide directly with magnesium (see Introduction). The drawbacks to this method are the necessity of using absolutely pure reactants, and the relatively high temperature (approximately -20°) required to allow the reaction to proceed. It was thought that the 2-heptafluoropropyl Grignard reagent would be less stable with respect to decomposition to magnesium fluoride and hexafluoropropene, than the 1-heptafluoropropyl Grignard reagent; this might therefore cause spontaneous decomposition at -20°. This assumption of the instability of the 2-heptafluoropropyl Grignard reagent was based on the well known fact that isopropyllithium eliminates lithium hydride more readily than n-propyllithium.

The method of McBee and his co-workers[115] was therefore adopted whereby the perfluoroalkyl Grignard reagent was formed by an exchange at low temperature between the perfluoroalkyl iodide and phenylmagnesium bromide. The simplicity of this method and its accomplishment at low temperatures where the product perfluoroalkyl Grignard reagent is quite stable, are obvious advantages over the other method involving the perfluoroalkyliodide and magnesium.

The reaction was carried out at either -40° or -78° by slowly mixing heptafluoro-2-iodopropane and phenylmagnesium bromide at one of these temperatures, using diethyl ether as solvent. Reactions of

propyl
2-heptafluoro mangesium bromide, however, were usually carried out by

mixing the three reagents; heptafluoro-2-iodopropane,phenylmagnesium
bromide and the other reactant, simultaneously; the exchange reaction
between the first two appeared to occur in preference to direct reaction
between phenylmagnesium bromide and the other reactant (acetone or
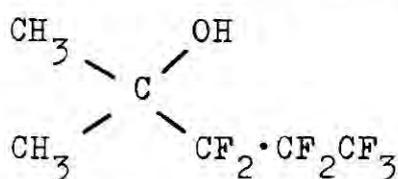propionaldehyde) thus making this procedure of reaction possible.

Reaction with Ethanol.

There is no mention in the literature of the hydrolysis or
ethanolysis of any perfluoroalkyl Grignard reagent.

The reaction of 2-heptafluoropropylmagnesium bromide with ethanol
was accomplished by firstly forming the Grignard reagent at -78° and
than adding ethanol at this temperature; hexafluoropropene (76%) and
2H-heptafluoropropane (9%) were formed and were separated by preprative
scale V.P.C. This ethanolysis reaction was preferred to hydrolysis
because of the low temperature at which the reaction was carried out
when water would quickly freeze. Also it was thought that the mild
reaction with ethanol might not lead to the formation of "hot spots"
in the reaction mixture which would then lead to decomposition of the
Grignard reagent. It appears, however, that ethanol has very little
reaction, if any, with the 2-heptafluoropropyl Grignard reagent; the
latter appears to decompose to hexafluoropropene in preference to
reacting with ethanol. Possibly the 2H-heptafluoropropane was formed
by radical abstraction of a hydrogen atom from the solvent by a
perfluoroisopropyl radical as stated by Haszeldine[102] (see introduction),
and not by reaction of 2-heptafluoropropyl magnesium bromide with
ethanol.

Reaction with Acetone.

Pierce, Meiner and McBee[113] reacted 1-heptafluoropropylmagnesium bromide with acetone by mixing heptafluoro-1-iodopropane, phenyl-megnesium bromide and acetone in ether solution at 0°; 3,3,4,4,5,5,5-heptafluoro-2-methylpentan-2-ol (I) (65% yield) b.p. 107 - 108° was obtained by distillation after hydrolysis of the reaction mixture.

$$
\begin{array}{cc}
\underset{\underset{CH_3}{\overset{CH_3}{\diagdown}}\underset{\diagup}{C}\underset{\diagup}{\overset{\diagdown}{CF_2 \cdot CF_2 CF_3}}}{\overset{OH}{\diagup}} & \underset{\underset{CH_3}{\overset{CH_3}{\diagdown}}\underset{\diagup}{C}\underset{\diagup}{\overset{\diagdown}{CF(CF_3)_2}}}{\overset{OH}{\diagup}} \\
(1) & (2)
\end{array}
$$
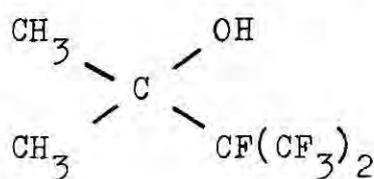
A similar reaction with pentafluoroiodoethane carried out at -78° resulted in a 38% yield of the corresponding alcohol, 3,3,4,4,4-pentafluoro-2-methylbutan-2-ol.[115]

Heyes and Musgrave[127] working in this laboratory used this procedure at 0° with heptafluoro-2-iodopropane, and obtained the corresponding alcohol in approximately 35% yield. The present worker carried out this reaction at -78° in an attempt to improve the yield and completely characterise the product; again a 35% yield of 3,4,4,4-tetrafluoro-2-methyl-3-trifluoromethylbutan-2-ol (2) was obtained, which had infrared absorptions at 3635(M) and 3472(S) cms^{-1} characteristic of OH stretching frequencies, and at 3021(M) 2950(W) and 2899(W) cms^{-1} characteristic of CH stretching frequencies[130]. This compound was isolated by preprative scale V.P.C. as was iodobenzene; the amount of the latter obtained accounted for 69.5% of the heptafluoro-2-iodopropane.

Reaction with Propionaldehyde.

The low yield obtained in the reaction with acetone led to a compromise of temperature being tried for this reaction. Using the same procedure as with the acetone reaction at a "mixing" temperature of -40° to -50°, a 17.5% yield of 1,1,1,2-tetrafluoro-2-trifluoro-methylpentan-3-ol(A) was obtained which had infrared absoptions at: 3704(W), 3623(M), 3448(S) cms^{-1}; and 2994(MS), 2959(M), 2890(W) cms^{-1} which confirmed the presence of OH and CH[130].

$$CH_3 \cdot CH_2 \cdot CH \overset{\displaystyle OH}{\underset{\displaystyle CF(CF_3)_2}{\Big\langle}}$$
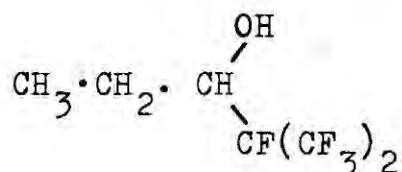
A.

Haszeldine[104] obtained the corresponding secondary alcohol from 1-heptafluoropropylmagnesium iodide in 45% yield using the direct method of formation of the Grignard reagent from heptafluoro-,1-iodopropane and magnesium.

McBee and his co-workers[113-115] did not carry out any reactions with propionaldehyde but obtained only moderate yields of the corresponding alcohols from reaction between 1-heptafluoropropyl-magnesium bromide and acetaldehyde and butraldehyde,(30%) and (40%) respectively.

Preparation and Reactions of 2-Heptafluoropropyl Lithium.

The preparation of this lithium reagent was carried out after the method of Pierce, McBee and Judd[97]. These workers used an exchange reaction at low temperatures (-40° to -78°) between methyl lithium and heptafluoro-1-iodopropane as in the preparation of the

Grignard reagent. Also, as in this Grignard reagent preparation,
reactions of 1-heptafluoropropyl lithium were carried out by mixing
all the reactants: heptafluoro-1-iodopropane, methyl lithium and other
reactant, simultaneously in ether solution at a low temperature. Again
the alkyl lithium underwent the exchange reaction in preference to
direct reaction with the other reactant (acetone or propionaldehyde),
thus making this procedure possible.

Miller and Kim[101] carried out similar reactions using various
polyhaloalkanes and found that n-butyl lithium exchanged lithium for
halogen much more efficiently than methyl lithium. The present worker,
therefore, used n-butyl lithium for the following reactions, except
in one case when the 1-iodobutane produced by the exchange interfered
with the purification of the main product from the reaction.

Preparation and Decomposition.

2-Heptafluoropropyl lithium was prepared in pentane solution by
mixing n-butyl lithium and heptafluoro-2-iodopropane at -78°. On
warming to room temperature this decomposed quantitatively to
hexafluoropropene with the elimination of lithium fluoride.

This emulated the finding of Pierce et al.[97] who similarly had
obtained a quantitative yield of hexafluoropropene from the decomposition
of 1-heptafluoropropyl lithium.

Hydrolysis and Ethanolysis.

Pierce et al.[97] on allowing 1-heptafluoropropyl lithium to
warm to 0° and then hydrolysing with 3N sulphuric acid, obtained a 99%
yield of 1H-heptafluoropropane.

This procedure was repeated with 2-heptafluoropropyl lithium at

-10°, using either pentane or ether as solvent, but in either case only hexafluoropropene (66% yield) was obtained.

Treatment of the cold reaction mixture (kept at -78°) with ethanol produced again only hexafluoropropene (67%). A modification of this, using ether as solvent and treating the cold reaction mixture with a cold mixture of ether and ethanol, again produced only hexafluoropropene (66%).

It was thought that the use of ethanol which formed a homogenous mixture with the other reactants might undergo a controlled reaction with 2-heptafluoropropyl lithium thus eliminating decomposition of the latter by what might have been a too vigorous reaction with water. It now seems probable, however, that 2-heptafluoropropyl lithium decomposes to hexafluoropropene and lithium fluoride before it reaches a temperature at which any appreciable reaction with ethanol occurs. It also appears that 2-heptafluoropropyl lithium eliminates lithium fluoride at a lower temperature than 1-heptafluoropropyl lithium since only hexafluoropropene was obtained from treatment with 3N sulphuric acid at -10°; this decomposition most probably occurs below -10°. This is compatable with normal and isopropyl lithium where lithium hydride is eliminated from the latter much more readily than from the former.

Reaction with Propionaldehyde.

Pierce et al.[97] reacted 1-heptafluoropropyl lithium with propionaldehyde at -40° by the procedure already discussed and obtained 4,4,5,5,6,6,6-heptafluorohexan-3-ol (1) in 77% yield; this was the best yield from any reaction of 1-heptafluoropropyl lithium attempted by these workers.

$$CH_3CH_2CH \underset{CF_2-CF_2CF_3}{\overset{OH}{<}}$$

(1)

$$CH_3CH_2CH \underset{CF(CF_3)_2}{\overset{OH}{<}}$$
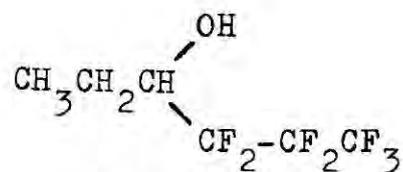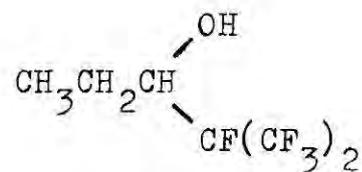
(2)

The present worker followed this procedure using heptafluoro-2-iodopropane as a source of 2-heptafluoropropyl lithium; a temperature of -78° was used in order to try to prevent any decomposition of the lithium reagent to hexafluoropropene. After hydrolysis of the reaction mixture with 3N sulphuric acid followed by fractional distillation, impure 1,1,1,2-tetrafluoro-2-trifluoromethylpentan-3-ol (2) (approximately 53% yield) was obtained and was characterised by its almost identical infrared spectrum to that of (2) obtained from the reaction between propionaldehyde and 2-heptafluoropropylmagnesium bromide. The slight difference between the two infrared spectra is undoubtedly due to the difference in film thickness used to record them. The impurity in (2) could not be removed by V.P.C. since they both had almost the same retention time (a peak with an inflection was obtained). This impurity was probably some non-fluorine containing compound since it lowered the fluorine analysis without showing any extra bands in the infrared spectrum; fluorine containing compounds usually have very strong absorption bonds in the infrared spectrum at relatively low concentrations. A conversion of 71% of the heptafluoro-2-iodopropane was obtained, which was a higher value than that obtained by Pierce et al. (50%). Formation of hexafluoropropene and aldol condensation type products must have accounted for the lithium reagent not converted to (2).

Reaction with Acetone.

Pierce et al.[97] carried out this reaction with 1-heptafluoro-propyl lithium at -74°, and obtained on hydrolysis and distillation 3,3,4,4,5,5,5-heptafluoro-2-methylpentan-2-ol (29%) and mesityl oxide (33%).

An exact repetition of this reaction using heptafluoro-2-iodopropane as a source of 2-heptafluoropropyl lithium gave 3,4,4,4-tetrafluoro-2-methyl-3-trifluoromethylbutan-2-ol (13%) and mesityl oxide (19.5%); these two products were isolated by preprative scale V.P.C.

The formation of mesityl oxide or any similar product, by an aldol condensation type of reaction induced by a lithium reagent is so far isolated to 1 and 2-heptafluoropropyl lithium reagents.

Summary.

The yields of alcohols from the reactions of acetone and propion-aldehyde with 2-heptafluoropropyl lithium and Grignard reagents are lower than those described in the literature for the corresponding reactions of 1-heptafluoropropyl lithium and Grignard reagents. This is probably due partly to the increased instability of the isopropyl reagent over the n-propyl one, and partly because the present worker carried out the reactions on a much smaller scale than those performed by Mcbee and his co-workers.

Future Work.

Several other reactions of these 2-heptafluoropropyl lithium and Grignard reagents need to be investigated e.g. reactions with acetaldehyde, butraldehyde, acetyl chloride, acetophenone, benzophenone, carbon dioxide diethyldichlorosilane and trimethylchlorosilane etc.

The decomposition of the Grignard reagent and its reaction with

oxygen also requires investigation. The latter should provide a
route to hexafluoroacetone.

$$CF_3 \\ \diagdown CFMgBr + \tfrac{1}{2}O_2 \longrightarrow CF_3 \diagup CF\text{-}O\text{-}MgBr$$

$$CF_3 \\ \diagdown CF\text{-}O\text{-}MgBr + H_2O \longrightarrow \left[CF_3 \diagdown CFOH \right] + MgBr(OH)$$

$$\downarrow$$

$$CF_3 \\ \diagdown C = O + HF$$
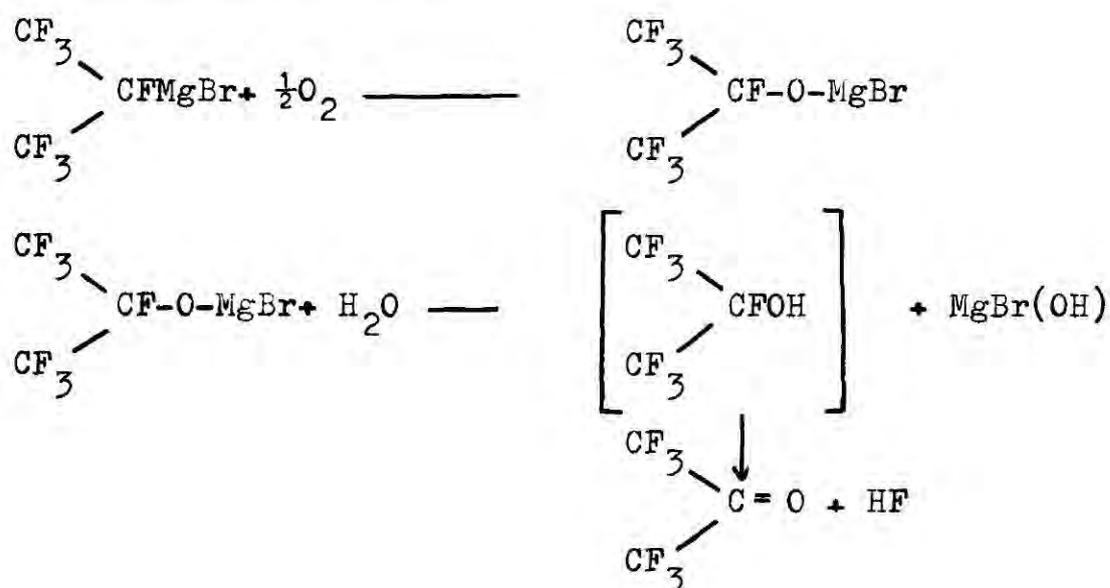
REACTIONS OF FLUOROCARBON IODIDES AND CHLORIDES WITH n-BUTYL LITHIUM

Remarkably few reactions between fluorocarbon halides and alkyl
lithiums have been recorded, but in those investigated it has been
consistently shown that chlorine, bromine and iodine are readily
replaced by lithium at low temperatures. The fluorocarbon lithium
so formed has then decomposed at a higher temperature with the
formation of lithium fluoride and the corresponding fluoro-olefin.
Mcbee and co-workers[97] studied the reaction of methyl lithium with
heptafluoro-1-iodopropane and trifluoroiodomethane at -78°; the
former on warming to room temperature gave, as expected, lithium
fluoride and hexafluoropropene. Trifluoroiodomethane, however,
appeared to exchange iodine for lithium and then eliminate fluoride
to form difluorocarbene. Some evidence for this elimination was
provided in the formation of some tetrafluoroethylene from the coupling
of two difluorocarbene radicals, but the majority of the latter must
have reacted with the solvent and other compounds present to form

several unidentified products.

Miller and Kim[101] performed similar reactions between n-butyl lithium and bromotrichloromethane, carbon tetrachloride, trichloro-iodomethane and carbon tetrabromide at low temperatures. The decomposition of the product then produced dihalocarbenes and lithium halide; the former being reacted directly with cyclohexene giving excellent yields of norcarane derivatives. These workers also showed that n-butyl lithium exchanged more efficiently than methyl lithium. Dixon[59] investigated several reactions on the addition of alkyl and lithiums to fluorinated olefins at low temperatures, which on warming decomposed with respect to lithium fluoride and an olefin.

$$RLi + CF_2{:}CF_2 \longrightarrow CF_2R{\cdot}CF_2Li \longrightarrow RCF{:}CF_2 + LiF$$
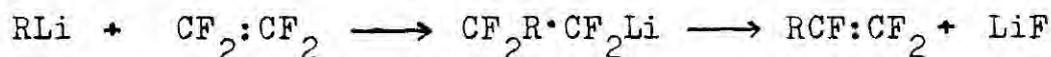
It was decided therefore to extend these types of reactions for the special purpose of producing fluoro-olefins from fluorocarbon halides, the results are summarised in the following table, all reactions being performed at -78°.

Fluorocarbon halide. (1 mol.)	No. of Mols.of n BuLi	Product(s) (% Yield)
C_2F_5I	1	C_2F_4 (88)
CF_3CFICF_2	1	C_3F_6 (73.5)
$CF_2I{\cdot}CF_2I$	2	C_2F_4 (87)
$CF_2I{\cdot}CF_2Cl$	2	C_2F_4 (78)
		C_2F_3Cl (trace)
$CF_2Cl{\cdot}CFCl_2$	2	C_2F_3Cl (78.5)
$CF_3(CF_2Cl)CF{\cdot}CF(CF_2Cl)CF_3$	2	$CF_3(CF_2Cl)CF{\cdot}C{:}CF_2(CF_3)$ (22)

Fluorocarbon halide (1 mol.)	No. of Mols. of n BuLi	Product(s) (% Yield)
Cyclic-$C_6Cl_2F_{10}$	2	cC_6F_{10} (trace)
		$1:3C_6F_8$ (trace)
		$1:4C_6F_8$ (trace)
		C_6F_9Cl (15.5)

Two conclusions may be drawn from this summary:

a.) Generally only one halogen is replaced by lithium despite there being two replaceable halogens and two equivalents of n-butyl lithium present.

b.) Lithium halide is eliminated in preference to lithium fluoride.

Pentafluoroiodoethane.

Formation of pentafluoroethyllithium appeared to take place at low temperatures; this then decomposed readily at a higher temperature liberating lithium fluoride and an almost theoretical amount of tetrafluoroethylene. Evidence for the initial formation of pentafluoro-ethyl lithium was provided by the formation of n-butyl iodide, which can only have come from a lithium-iodine exchange. Attempted hydrolysis of the lithium derivative at -78° resulted only in the formation of a very small quantity of pentafluoroethane with again an almost theoretical amount of tetrafluoroethylene. This hydrolysis was carried out in the presence of ethanol so as to make the reaction mixture homogeneous, but it appears that a similar reaction occurred to that when 1-heptafluoropropyllithium was treated with ethanol at -78° forming hexafluoropropene in quantitative yield. It appears, therefore, that pentafluoroethyl lithium is more susceptible to decomposition than

reacting with water or ethanol.

Heptafluoro-2-iodopropane.

Preparation of 2-heptafluoropropyl lithium, and its decomposition and various other reactions are discussed elswhere.

Tetrafluoro-1, 2-diiodoethane.

A series of reactions between tetrafluoro-1, 2-diiodoethane and n-butyl lithium were performed in an attempt to replace both the iodine atoms by lithium; it was thought that this might then eliminate two molecules of lithium fluoride, resulting in the formation of the hitherto unknown difluoroacetylene.
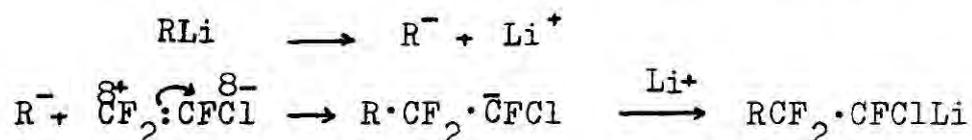
The first two reactions, performed in pentane at -78° resulted in the immediate decomposition of the tetrafluoro-2-iodoethyl lithium compound originally formed, into tetrafluoroethylene and lithium iodide. A similar reaction at -90° gave the same results, showing that the decrease in temperature had not stabilised the monolithium derivative sufficiently to introduce a second lithium atom. An effort was made to carry out this latter effect by using two strong donor solvents: tetrahydrofuran at -78° and -90° and ethyleneglycoldimethylether at -78°. In both of these reactions very little tetrafluoroethylene was actually evolved, but analytical V.P.C. showed that a considerable amount, roughly the theoretical yield, remained in solution. The white precipitate formed during the reaction was completely dissolved by the addition of water, thus showing that no lithium fluoride had been eliminated, and, therefore, no dilithium compound formed since this would undoubtedly eliminate lithium fluoride.
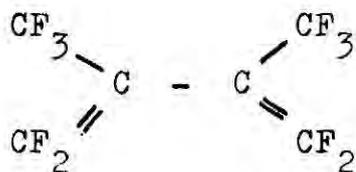
1-Chlorotetrafluoro-2-iodoethane.

This reaction was carried out at -90° in pentane solution, when it was hoped that lithium-iodine exchange would initially take place, and the compound formed would be more stable to lithium chloride elimination than the corresponding one in the previous reaction was to lithium iodide elimination. This supposition was unrealised when tetrafluoroethylene was obtained in good yield, and only lithium chloride was eliminated.

1,1,2-trichlorotrifluoroethane.

Treatment of this compound with two mols. of n-butyl lithium solution in pentane, resulted in the replacement of one chlorine by lithium, followed by lithium chloride elimination and formation of chlorotrifluoroethylene in 78% yield. This reaction involved the disappearance of rather more than half of the n-butyl lithium but this could be explained by the addition of some of the latter to the chlorotrifluoroethylene, followed by lithium fluoride elimination. Dixon[59] actually performed such a reaction by mixing the reactants at a low temperature, and then warming to allow the adduct to decompose to 1-chloro-1, 2-difluorohex-1-ene in 60% yield. It seems, therefore, surprising that so little chlorotrifluoroethylene did react in this manner in this reaction between n-butyl lithium and 1-chlorotetrafluoro-2-iodoethane in pentane solution. Dixon, however, used ether as a solvent, the donor properties of which probably aids the addition of alkyl lithiums to fluoro-olefins via a nucleophilic mechanism.

$$RLi \longrightarrow R^- + Li^+$$

$$R^- + \overset{\delta+}{C}F_2 \colon \overset{\delta-}{C}FCl \longrightarrow R \cdot CF_2 \cdot \bar{C}FCl \overset{Li^+}{\longrightarrow} RCF_2 \cdot CFClLi$$

Summary.

It has been shown from the investigation of the reactions of
n-butyl lithium with tetrafluoro-1, 2-diiodoethane, 1-chlorotetrafluoro-
2-iodoethane and 1,1,2-trichlorotrifluoroethane, that after initial
formation of a monolithium compound, elimination of lithium chloride
or iodide occurs immediately even at -90°.

Since it was impossible to replace two halogens on adjacent
carbon atoms, the formation of dilithium derivatives from the following
two compounds was investigated.

(a) <u>1,4-dichlorododecafluoro-2, 3-dimethylbutane.</u>

This was prepared by coupling 1-chloro-2-iodohexafluoropropane
prepared from iodine monochloride and hexafluoropropene, by irradiating
with ultraviolet light in the presence of mercury. This reaction
produced 1,4-dichlorododecafluoro-2, 3-dimethylbutane(I) in excellent
yield (85%).

$$
\begin{array}{cc}
\underset{CF_2Cl}{\overset{CF_3}{\diagdown}}CF - CF\underset{CF_2Cl}{\overset{CF_3}{\diagup}} & \underset{CF_2Cl}{\overset{CF_3}{\diagdown}}CF - C\underset{CF_2}{\overset{CF_3}{\diagup}} \\
I & II
\end{array}
$$

Treatment of this compound with n-butyl lithium at -78° resulted
only in the replacement of one chlorine atom by lithium; the product
then decomposed to give 4-chloroundecafluoro-2, 3-dimethylbut-1-ene (11)
in quite a low yield. A trace of a more volatile product was detected
by analytical V.P.C., but this was not in sufficient quantity to be
characterised. It is possible, however, that this compound was the
diene III formed by the replacement of both chlorine atoms by lithium.

$$CF_3\diagdown_{C} \diagup^{CF_3}$$

(structure of diene III, with two CF_3 groups, two central carbons $C-C$, and two CF_2 groups double-bonded)

III.

The infrared spectrum of II had two absorptions in the double bond region at 1748(s) and 1802(MW) cms^{-1}; the former is obviously the C $=CF_2$ stretching frequency in II and the latter possibly due to the presence of a trace of III. This impurity was not in sufficient quantity to influence the analysis, but perhaps the fact that the infrared spectrum wa s recorded on a gaseous sample meant that this sample was enriched with III; III would obviously be more volatile than II.

It is significant that all the n-butyl lithium reacted, thus indicating that quite a lot of II was probably lost by a "Dixon" type addition[59] of the alkyl lithium.

The main purpose of this reaction was to make the diene III and, therefore, the obvious repetition of the reaction with equimolar proportions of I and n-butyl lithium was not attempted. A reaction with these proportions should increase the yield of II, since there should be no excess n-butyl lithium to add to the olefin formed.

(b) Dichlorodecafluorocyclohexane.

This reaction was performed in two different solvents, heptane and pentane. The former facilitated the isolation of volatile products and the latter of the involatile ones. The identification from the reaction in heptane of decafluorocyclohexene and octafluorocyclohexa -1:3 and 1:4 - dienes, which were isolated by preprative scale V.P.C. is evidence for the replacement of both chlorine atoms by lithium.

The dichlorodecafluorocyclohexane had previously been shown[128] to consist of a mixture of 1,2; 1,3; and 1,4 dichlorodecafluorocyclohexanes in the proportions shown in the following reaction scheme, which explains the formation of the products obtained.

34%   1.

48%   2.

18%   3.
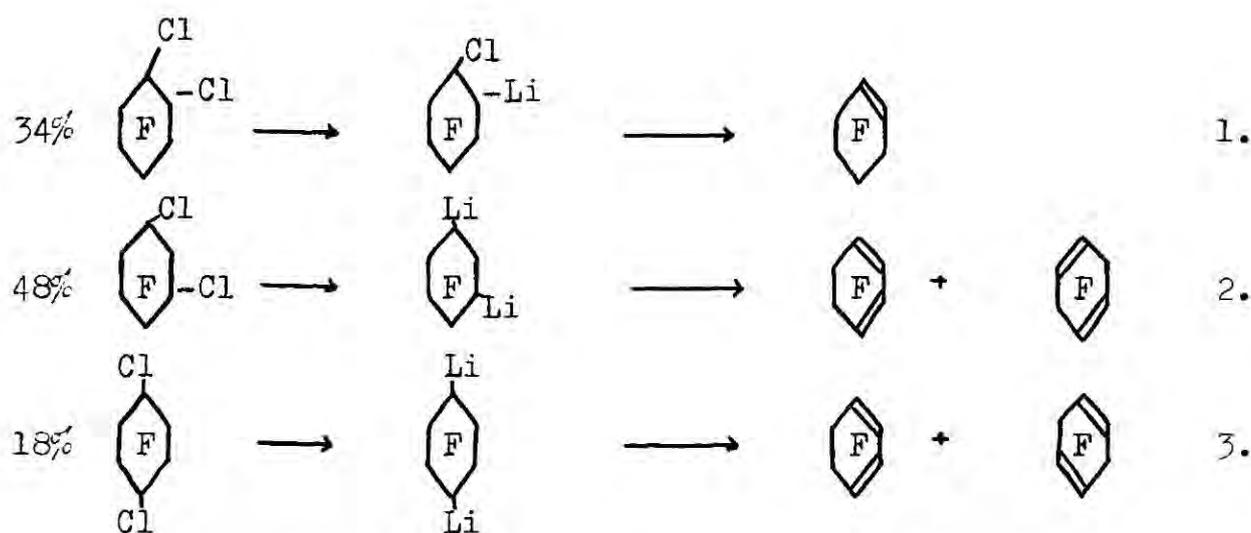
The main volatile product, however, was chlorononafluorocyclohexene which was obviously formed by the replacement of only one chlorine in these three isomers followed by elimination of lithium fluoride.

34%   4.

48%   5.

18%   6.
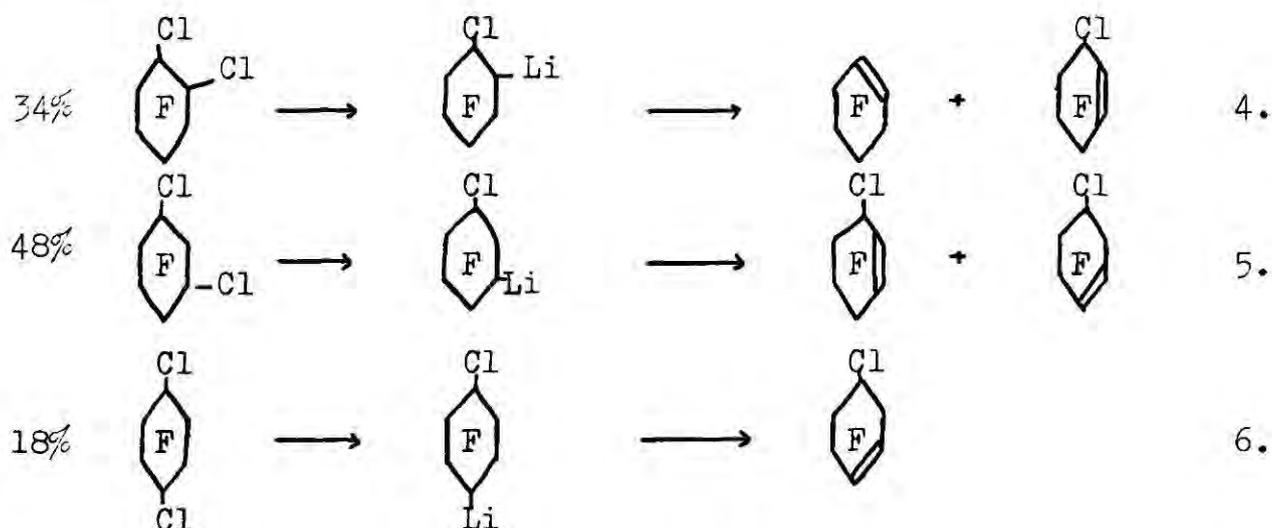
The infrared spectrum of this chlorononafluorocyclohexene (I.R.Spectrum No.28) showed two absorptions at 1761(MS) and 1701(W) cms^{-1} in the region characteristic of a double bond influenced by
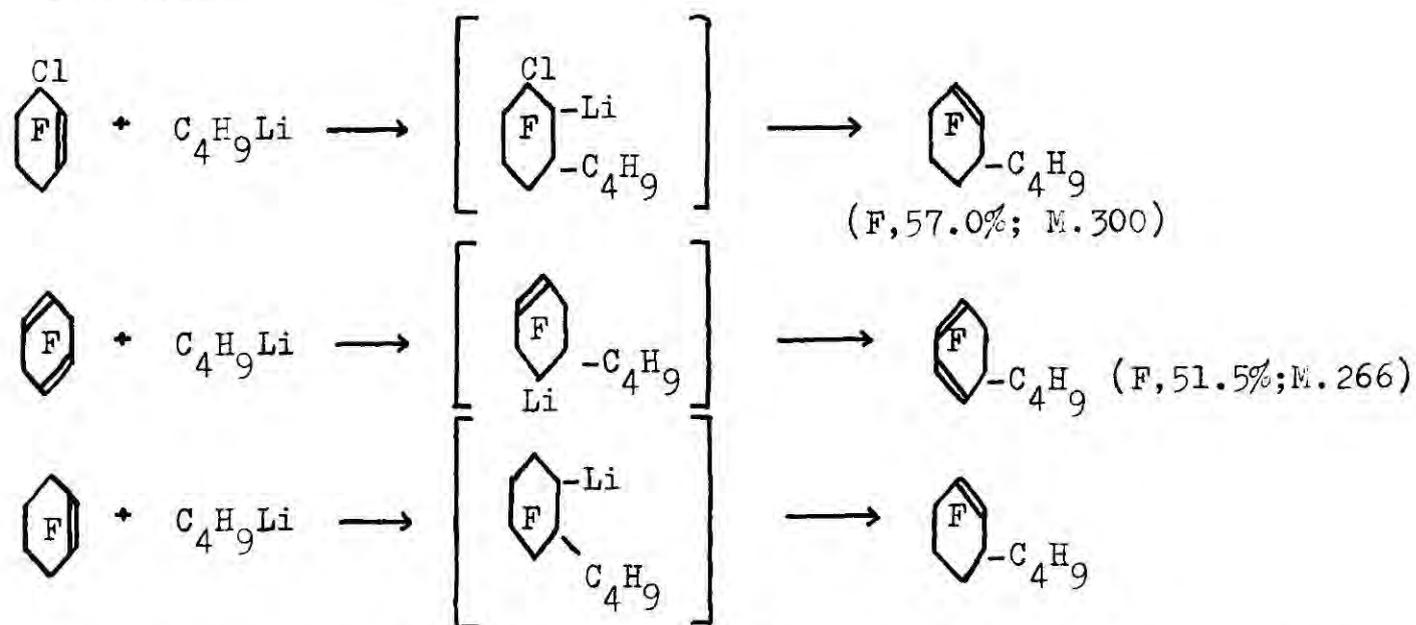
fluorine substitution. It can therefore be suggested that the

absorption at 1761 cms^{-1} is due to 3-chlorononafluorocyclohexene and

the one at 1701 cms^{-1} due to 4-chlorononafluorocyclohexene, since

the 3-chloro isomer is present in the greater amount, as is obvious

from the above equations.

The low yield of decafluorocyclohexene in comparison to

chlorononafluorocyclohexene indicates the occurrence of elimination

of lithium fluoride as suggested in 4 as well as elimination of lithium

chloride, since there would not be sufficient chlorononafluorocyclohexene

formed from 5 and 6 to make up the proportions of decafluorocyclohexene

and chlorononafluorocyclohexene obtained from the reaction, should
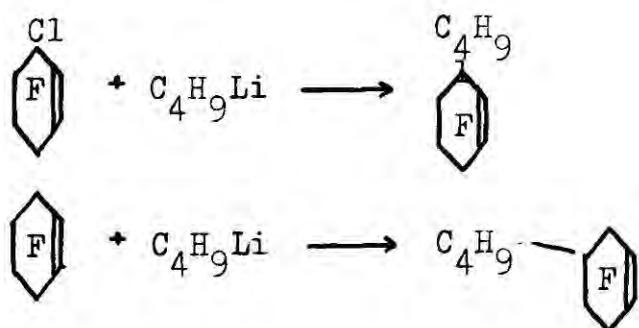
4 go entirely to decafluorocyclohexene.

It would seem, however, from previous reactions discussed that

elimination of lithium chloride would occur at a lower temperature

than elimination of lithium fluoride. This suggests that 4 should

give entirely decafluorocyclohexene. Insufficient evidence is available

however, to state exactly what has occurred in this reaction.

The reaction is pentane solution enabled less volatile products

to be isolated from this reaction, only one of these, however, contained

fluorine. This latter was isolated by preprative scale V.P.C. and

was found to contain no chlorine; it was also shown to be unsaturated

by its reduction of potassium permanganate, and by the presence of a

strong absorption in the infrared spectrum at 1739 cms^{-1} which is only

slightly lower than the absorption region (1745 - 1755 cms^{-1}) given by

Burdon and Whiffen[129] for the -CF =CF- stretching frequency in

fluorocyclohexenes. The presence of a n-butyl group in this material

is strongly indicated by the presence of absorptions at 2874 and 2941 cms^{-1} which are characteristic of CH stretching frequencies to be found in such a group.[130] The fluorine analysis (F,47.2%) and molecular weight (299) unfortunately do not coincide with any particular compound and therefore this material is probably a mixture of compound. It is probable that this material contains the following type of compound (see equations) prepared by the addition of n-butyl lithium to a double bond in the various volatile unsaturated products from this reaction, mentioned previously, followed by elimination of lithium halide.

$$\text{(ring, Cl, F)} + C_4H_9Li \longrightarrow \left[\text{(ring, Cl, F, -Li, -C_4H_9)} \right] \longrightarrow \text{(ring, F, -C_4H_9)}$$
$$(F,57.0\%;\ M.300)$$

$$\text{(ring, F)} + C_4H_9Li \longrightarrow \left[\text{(ring, F, -C_4H_9, Li)} \right] \longrightarrow \text{(ring, F, -C_4H_9)}\ (F,51.5\%;M.266)$$

$$\text{(ring, F)} + C_4H_9Li \longrightarrow \left[\text{(ring, F, -Li, C_4H_9)} \right] \longrightarrow \text{(ring, F, -C_4H_9)}$$

Also products from the direct elimination of lithium chloride or lithium fluoride are possible.

$$\text{(ring, Cl, F)} + C_4H_9Li \longrightarrow \text{(ring, C_4H_9, F)}$$

$$\text{(ring, F)} + C_4H_9Li \longrightarrow C_4H_9\text{—(ring, F)}$$

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CHAPTER 3.

EXPERIMENTAL WORK.

Infra-red Spectroscopy.

Considerable use was made of infra-red spectroscopy for identification of products, the infra-red spectra of all new compounds have been recorded. A Grubb-Parsons Type G.S.2A double beam grating infra-red spectrometer was used to obtain these spectra.

The sample was either in the form of a thin film between potassium bromide discs, or as a gas in a cylindrical cell (5" long x $1\frac{1}{2}$" diameter) with potassium bromide or sodium chloride end windows.

Pressure Reactions.

Unless otherwise stated, pressure reactions were performed using a stainless steel autoclave (527 mls.) which was rotated at an angle (see diagram 1.) in order to ensure thorough mixing of the contents. The charging of this autoclave with a gas, was accomplished by using a simple vacuum system (see diagram 2.) The gas was condensed and weighed as a solid in a cold florentine flask which was then attached to the vacuum system. The autoclave, which was already charged with any liquid or solid reagents, was also attached to the vacuum system and cooled by immersing the base in liquid air. The olefin was then condensed into the autoclave by vacuum transfer.

Gases were handled using standard high vacuum techniques.

Molecular weights.

These were determined by Regnault's method. For this method a glass bulb (126.4 mls.) fitted with a high vacuum tap and B 10 cone was required; the volume of the bulb was found by weighing the amount of water it contained at a known temperature. The bulb was then

evacuated using a vacuum system with a mercury diffusion pump, weighed, filled with the unknown vapour to an accurately measured pressure again using a vacuum system, and then re-weighed. The weight of vapour occupying the bulb at a known pressure afforded the molecular weight.

Fractionation 'in vacuo! see diagram 3.

The mixture to be separated was contained in a vessel which was attached to the vacuum system at A. This vessel was immersed in liquid air and the whole apparatus pumped to a 'sticking' vacuum with all the taps open. T1 and all Ts were closed and the mixture was transferred to B, T2 then being closed. C was then cooled to a temperature at which one of the components of the mixture had zero vapour pressure, and the mixture then transferred several times between B and D, when the less volatile component was condensed into C. The two separate materials were then removed from the apparatus by vacuum transfer back to A.

This method of Fractionation was very useful for separating gaseous products from large quantities of solvent.

CLAMP TO FIXED FRAMEWORK
HOLDING AUTOCLAVE AT DESIRED ANGLE

STAINLESS
STEEL VALVE

PULLEY

OUTLET TUBE

ASBESTOS TUBE WOUND WITH HEATER
AND COVERED WITH MAGNESIA CEMENT

BALL RACE

SCREWS BEARING
ONTO PRESSURE PLATE

THERMOCOUPLE HARD SOLDERED
TO AUTOCLAVE

STAINLESS STEEL
PRESSURE PLATE

LEAD WASHER
AS SEAL.

BRASS CYLINDER
FITTING INTO
LARGE BALL RACE.

SUPPORT FOR
BALL RACE

DIAGRAM I

OIL PUMP

DIAGRAM 2

To McLeod gauge, A
Mercury diffusion pump,
Oil pump

T2   T   T

T   T

B   C   D

DIAGRAM 3

Reactions of a mixture of Iodine Pentafluoride and Iodine with Fluoro-Olefins.

The molecular proportions used in these reactions were those required by the equation.-

$$5 \; \text{>C} : \text{C<} + IF_5 + 2I_2 \longrightarrow 5 \; \text{>CF.CI<}$$
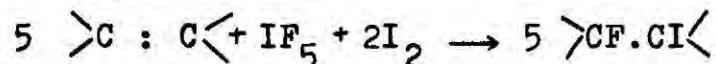
Yields are based on the amount of olefin which reacted.

(1)

Tetrafluoroethylene: prepared by the pyrolysis of teflon.

A steel tube (3 ft. long x 1 inch internal diameter), blocked at one end and connected at the other to a system of two cooled traps (-183°), a manometer, a manostat and an oil pump, was charged with teflon shavings (100g.) which were held in the centre of the tube (1 ft.) by a packing of steel wool at either end. This central part of the tube was then heated in an electric furnace at 550-600° for one hour, the pressure being reduced to, and controlled at 5mm mercury. Tetrafluoroethylene (95% yield) was condensed into the cooled traps, and was shown by analytical V.P.C. using silicone trimer as stationary phase at 0° to contain a trace of hexafluoropropene. Low temperature distillation through a packed column afforded pure tetrafluoroethylene.

The autoclave charged with iodine pentafluoride (44.4g., 0.20 mole.), iodine (102g. 0.4 mole.) and tetrafluoroethylene (100g. 1.00 mole.) was rotated for 10 hours without heating. It was then vented through two cooled traps (-78° and -183°) to condense volatile material, leaving unreacted iodine and residual liquid. The colder trap (-183°) contained unreacted tetrafluoroethylene (7.5g.) as shown by infra-red spectrum and analytical V.P.C. retention time on silicone trimer stationary phase at 0° C.

The content (190g.) of the other cooled trap (-78°) was separated into its two components in 20g. batches on preprative scale V.P.C. using dinonylphthalate as stationary phase at room temperature, nitrogen flow-rate, 100 mls./min. This gave further unreacted tetrafluoroethylene (21g.) and pentafluoroiodoethane (152g.86%) (Found: F,38.2; I, 51.8; M, 243.3. Calc. for C_2F_5I: F,38.6, I,51.6%; M,245.9,) (I.R.Spectrum No.1.)

A small amount of tetrafluoro - 1, 2 - diiodoethane was obtained as residue and was identified by its coincident retention time with that of an authentic sample, using analytical V.P.C., tricresyl phosphate stationary phase at 120°.

The authentic sample of tetrafluoro - 1, 2 - diiodoethane was prepared by heating equimolar proportions of tetrafluoro - ethylene and iodine in the autoclave at 160° for 24 hours. [2]

Reaction at 85°

The same amounts of tetrafluoroethylene, iodine penta-fluoride and iodine were reacted at 85° for 10 hours. The extent of reaction, and yield of pentafluoroiodoethane was very similar to the previous reaction.

1. 1-Difluoroethylene.

The autoclave, charged with iodine pentafluoride(18g; 0.080 mole), iodine (40g, 0.157 mole), and 1,1-difluoroethylene (25g, 0.390 mole) was rotated for fifteen hours at 103°. No gaseous material was vented from the autoclave; the remaining liquid was washed with alkaline sodium thiosulphate to remove iodine, dried

over magnesium sulphate, and distilled giving 1,1,1-trifluoro-2-iodoethane (70g. 86%) (Found: I, 61.3; M.209; Calc. for $C_2H_2F_3I$: I, 61.4%; M.210) b.p. 54.8°, n_D^{25} 1.3980 (lit. 55°, 1.3981 [3] (I.R. Spectrum No.2). Analytical V.P.C. using tricresyl phosphate as stationary phase at 50° showed that this material consisted of a single component, having a retention time coincident with that of an authentic sample of 1,1,1-trifluoro-2-iodoethane. The infrared spectrum of this authentic sample was identical with that of the reaction product, thus confirming that the latter was not a mixture containing 1,1,2-trifluoro-1-iodoethane.

Preparation of Authentic 1,1,1-trifluoro-2-iodoethane.

The **first stage** of this synthesis was the preparation of trifluoroethanol; the method used was that described by Henne[4] involving the following two reactions.

$$CF_3COOH + C_6H_5COCl \longrightarrow CF_3COCl + C_6H_5COOH$$

$$CF_3COCl + LiAlH_4 \longrightarrow CF_3CH_2OH + LiCl + Al(Cl)_3$$
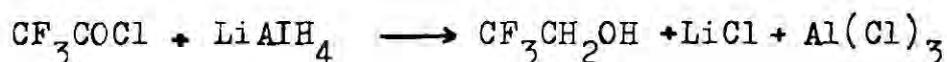
Benzoyl chloride and trifluoroacetic acid were slowly mixed at room temperature and then heated to 150° for twelve hours, thus driving off trifluoroacetyl chloride. This was then bubbled into a suspension of lithium aluminium hydride in ether, refluxed, and the trifluoroethanol then isolated by distillation through a packed column.

The **second stage** of the synthesis involved the following two reactions as described by Tiers, Brown and Reid. [5]

$$CF_3CH_2OH + pCH_3C_6H_4SO_2Cl \longrightarrow CF_3CH_2O \cdot SO_2 \cdot C_6H_4 \cdot CH_3$$

$$CF_3CH_2 \cdot O \cdot SO_2 \cdot C_6H_4 \cdot CH_3 + NaI \longrightarrow CF_3CH_2I + pCH_3 \cdot C_6H_4 \cdot SO_2ONa$$
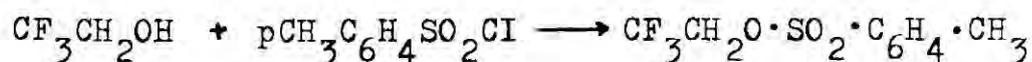
In the first reaction the trifluoroethanol and para toluenesulphonyl chloride were heated at 50° in an aqueous medium, and sodium hydroxide solution added. The tosyl ester was then extracted with petroleum ether, isolated by distilling off the solvent, and purified by washing with concentrated ammonia solution to remove unreacted para-toluenesulphonyl chloride. The final stage in the synthesis was the reaction of this tosyl ester with sodium iodide at 240° using tetra-ethyleneglycol dimethylether as solvent. 1,1,1-difluoro-2-iodoethane distilled from the reaction mixture and was purified by preprative scale V.P.C. using tricresyl phosphate as stationary phase at 65°, nitrogen flowrate, 120 mls./minute.

Analysis of this compound prepared by either method repeatedly gave a low value for fluorine (F,18.2; 18.5; 18.0. Calc. for $C_2H_2F_3I$:F, 27.1%). This strongly indicates that one of the fluorine atoms was taken up in some type of complex with the biphenyl-sodium dimethoxyethane reagent ($C_2H_2F_2I$ requires F, 18.1%.) No other example of low result using this reagent has ever been observed.

Hexafluoropropene.

The autoclave, charged with iodine pentafluoride (29.5g., 0.132 mole.) and iodine (67g., 0.264 mole.) and hexafluoropropene (100g., 0.660 mole.) was rotated for twenty-four hours at 150°. No gaseous material was vented from the autoclave; the residue was washed with

alkaline sodium thiosulphate to remove iodine, dried over magnesium

sulphate, and distilled yielding heptafluoro - 2 - iodopropane

(196g., 99%) (Found: F, 44.6; I, 42.9. $C_3 F_7$ I requires F, 44.9 ;

I, 42.8%), b.p. 39° / 744 mm., n_D^{20} , 1.32631, (I. R. Spectrum No.3).

Analytical V.P.C. using tricresyl phosphate as stationary phase at

50° indicated that this material consisted of a single component.

Proof of the structure of heptafluoro - 2 - iodopropane.

The infra-red spectrum differed from that of heptafluoro - 1 -

iodopropane whose infra-red spectrum has been described [6] and

which is given for comparison (I.R. Spectrum No.4).

Hydrolysis with potassium hydroxide in acetone (see page 113) gave

2H - heptafluoropropane, which was characterised by its identical

infra-red spectrum to that of authentic 2H - heptafluoropropane

described in the literature [7]. Hydrolysis of heptafluoro - 1 -

iodopropane under identical conditions has been shown to give

1 H - heptafluoropropane [8].

Coupling reaction using ultraviolet irradiation in the presence

of mercury gave tetradecafluoro - 2, 3 - dimethylbutane (see page 113)

whereas a similar reaction with heptafluoro - 1 - iodopropane has

been described [9] and results in the formation of perfluorohexane.

^{19}F resonance spectrum.

The spectra of liquid heptafluoro - 2 - iodopropane was

determined using a Varian 4300 N.M.R. spectrometer operating at 40

Mc./ sec. This spectrum was found to consist of a low field doublet

and a high field septet. The intensity distribution between the multiplets is consistent with the compound being heptafluoro - 2 - iodopropane. Further evidence for its identity is provided by the observed chemical shifts; these were measured from trifluoroacetic acid (used as an external reference) to the centres of the multiplets

Doublet. $CF_3.\ CF_3\ .\ CF.group$	Septet. (.CF. group)	Coupling Constants
- 82 C/sec.	2790 C/sec.	12.9 C/sec.

Chlorotrifluoroethylene.

This was prepared by the dechlorination of 1,1, 2 - trichloro-trifluoroethylene using zinc dust in ethanol, as described by Buxton et al. [10]. 1,1, 2 - trichlorotrifluoroethane was slowly added to a refluxing suspension of zinc dust in ethanol, and the chloro-trifluoroethylene evolved was purified by low temperature distillation through a packed column. The latter consisted of a column ($2\frac{1}{2}$ ft long x 1 inch diameter) packed with glass helices and cooled by an outer jacket containing carbon tetrachloride and solid carbon dioxide.

The autoclave, charged with iodine pentafluoride (35g., 0.1518 mole.), iodine (80.5g., 0.317 mole.), and chlorotrifluoroethylene (92.5g., 0.794 mole.) was rotated for four hours without heating. On venting the apparatus, 20 mls. of gas was obtained, thus showing that the reaction was almost quantitative. The remaining liquid was washed with $\frac{N}{10}$ alkaline sodium thiosulphate to remove iodine, dried over magnesium sulphate, and distilled yielding a fraction b.p. 53 - 57° corresponding to chlorotetrafluoroiodoethane (171g. 81%). (Found : F, 29.4; Calc. for $C_2\ ClF_4$ I: F, 29.0%).

Analytical V.P.C. using tricresyl phosphate as stationary phase at 42° showed that this material consisted of a mixture of two components, whose relative amounts were 55% and 45% as deduced from peak areas. This deduction involved assuming equal thermal conductivities for the two components; this is justified since they are isomers wi th very similar physical properties.

Separation by V.P.C.

This could not be accomplised on a large scale due to almost complete tailing of the first peak over the second; the following stationary phases, temperature ranges, and nitrogen flowrates were tried:

Dinonyl phthalate, 50° - 120°, 70 - 150 mls./min.

Brickdust-dinonyl phthalate, 50° - 65°, 50 - 100 mls./min.

Tricresyl phosphate, 40° - 100°, 100 - 120 mls./min.

Silicone high vacuum grease, 120°, 110° mls./min.

A complete separation and isolation of both isomers was accomplised, using an analytical column with tricresyl phosphate as stationary phase at 42°, nitrogen flowrate 17 mls./min. Injection of 0.3g. of material was the critical amount separable and gave as first component (55% of the mixture) (94g., 45%), 1-chlorotetrafluoro-2-iodoethane. (Found: F, 29.5; Calc. for C_2ClF_4I. F, 29.0%) b.p. 57.6^o, $n_D^{18.5}$ 1.395 (lit.[11], $56,5^o$, 1.393). (I.R. Spectrum No.5) This sample had an identical infrared spectrum and analytical V.P.C. retention time on tricresyl phosphate as stationary phase at 42°, to an authentic sample of 1-chlorotetrafluoro-2-iodoethane. (see page for details of preparation.)

The second component (45% of the mixture) (77g. 37%), was,
therefore, 1 - chlorotetrafluoro - 1 - iodoethane. (Found: F,28.7;
$C_2 CIF_4$ I requires F, 29.0%), b.p. 57.7^o, n_D^{25} 1.3900. (I.R.
spectrum No.6). This material liberated iodine on exposure to light,
much more readily than 1 - chlorotetrafluoro - 2 - iodoethane.

1,1 - Dichlorodifluoroethylene.

The autoclave was charged with iodine pentafluoride (7.3g.,
0.033 mole.), iodine (16.8g. 0.066 mole.), and 1,1 - dichloro-
difluoroethylene (22.0g., 0.165 mole.), and rotated for six hours
at 170°. The contents were then distilled from the autoclave under
reduced pressure, and fractionated in vacuo through a cooled trap
(-78°), giving one gaseous and one liquid fraction. The former was
separated into two components by preprative scale V.P.C. using
tricresyl phosphate as stationary phase at room temperature, nitrogen
flowrate 110 mls./min., yielding 1,1 - dichlorotetrafluoroethane
(5.9g., 25%) (Found: F, 44.4; CI, 41.3; M. 171 Calc. for
$C_2 CI_2 F_4$: F, 44.5; CI, 41.5%; M. 171) and recovered 1,1 -
dichlorodifluoroethylene (3.4g), which was identified by its infra-
red spectrum. The less volatile fraction (21g.) was shown by
analytical V.P.C. using tricresyl phosphate as stationary phase at
100°, to contain two components in the ratio 57% to 43% as determined
by peak areas.

A separation of this mixture, using 0.5g. batches, was acc-
omplished by preprative scale V.P.C. using tricresyl phosphate as

Stationary phase at 100°, nitrogen flowrate 210 mls. /min. The first component (57% of the mixture) was identified as 1,1 - dichloro - trifluoro - 2 - iodoethane (12g., 31%). Found: F, 20.7; $C_2CI_2F_3I$ requires F, 20.4%). b.p. $98^{\circ}/763$ mm; n_D^{20} 1.44450. (I.R.spectrum No.7). This infra-red spectrum was identical to that of one of the addition products of iodine monochloride to chlorotrifluoroethylene (see page 99); this proves the structure of this compound, since only one product from either reaction can be identical to one from the other reaction.

$$CF_2 : CCI_2 + IF \longrightarrow CF_2I - CCI_2F + CF_3 - CCI_2I$$
$$CF_2 : CFCI + ICI \longrightarrow CF_2I \cdot CCI_2F + CF_2CI - CFCI\ I$$
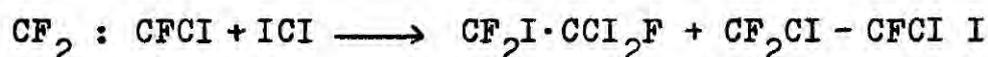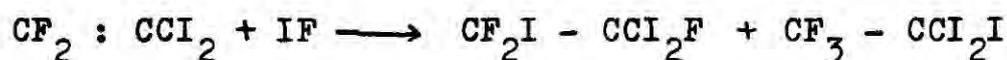
The second component (43% of the mixture) must therefore be 1,1 - dichlorotrifluoro - 1 - iodoethane (9g., 23%). Found: F,20.6; $C_2CI_2F_3I$ requires F,20.4%). (I.R. spectrum No.8a). On exposure to light and especially when heated, this compound liberated iodine rapidly, so much so as to make determination of boiling point and refractive index impracticable.

Tetrachloroethylene.

The autoclave, charged with iodine pentafluoride (44.4g.,0.20 mole.), iodine (100.6g., 0.40 mole.), and tetrachloroethylene (165.9g., 1,00 mole.), was rotated for twelve hours at 110°. When the autoclave was opened, an aliquot of the liquid inside was shown by analytical V.P.C. using tricresyl phosphate as stationary phase at 140°, to consist only of unreacted tetrachloroethylene. The autoclave was resealed and rotated at 190° for a further four hours. After removal

of free iodine by filtration and washing with alkaline sodium

thiosulphate, the products were distilled through a concentric tube

column (22 theoretical plates) and a fraction b.p. 92 - 93° (41.5g.

51%) was collected corresponding to tetrachloro - 1, 2 - difluoroethane

(Found: F,18.8; CI, 69.1. Calc. for $C_2CI_4F_2$: F, 18.6; CI,69.6%).

b.p. 93° n_D^{20} 1.41449 (lit.[12] 93° n_D 1.41247, 1.4264, 1.4115).

The residue (100g.) consisted of unchanged tetrachloroethylene.

Reaction with iodine Pentafluoride at 220°.

The autoclave was charged with iodine pentafluoride (22g., 1,00

mole.) tetrachloroethylene (322g., 2,00 mole.) and rotated at 220° for

four hours. On working up as before there was obtained tetrachloro - 1,

2 - difluoroethane (215g., 62%) and recovered tetrachloroethylene (48g.)

Dechlorination of Tetrachloro - 1, 2 - difluoroethane.

A stirred mixture of methylated spirits (50mls.) and zinc dust (7g.,

0.107g. atom) contained in a 3N flask fitted with a dropping funnel,

mechanical stirrer, and Friedrich condenser, was heated to reflux and

was kept refluxing by the dropwise addition of a solution of tetra-

chloro - 1, 2 - difluoroethane (11.2g., 0.055 mole.) in methylated

spirits (10 mls.). After the addition, heat was again applied in order

to continue the refluxing for three and a half hours. A mixture of

methylated spirits and some volatile material were collected in a

cooled trap (-78°), and were separated by fractionation in vacuo, the

methylated spirits being condensed in a trap cooled to - 78°. This

separation yielded 1, 2 - dichlorodifluoroethylene (5.3g., 72.5%).

(Found: F, 28.1; CI, 53.4; M.132. Calc. for $C_2CI_2F_2$: F, 28.6;

CI, 53.3%; M.133). (I.R. Spectrum No.8b).

Reactions of Fluoro-Olefins with a mixture of Bromine Trifluoride and Bromine.

The molecular proportions used in these reactions were those

required by the equation

$$3 \ >C : C< \quad + \quad BrF_3 + Br_2 \longrightarrow 3 \ >CF \cdot CBr$$
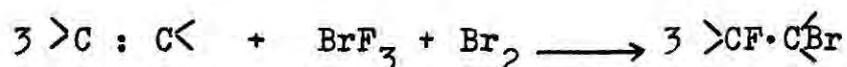
Tetrafluoroethylene.

The autoclave was charged with tetrafluoroethylene (16.9g., 0.169

mole.), bromine trifluoride (7.7g., 0.0562 mole.), bromine (9g.,

0.0563 mole.) and 1,1,2 - trichlorotrifluoroethane (230g.), as diluent,

and rotated without heating for two hours. Gaseous material, vented

from the autoclave and produced by refluxing the solvent, consisted of

tetrafluoroethylene (2g.) and pentafluorobromoethane (2g.), Found:

F.47.7; Br.39.5; M.201. Calc. for C_2BrF_5 : F,47.7; Br,40.2%; M.199),

and giving the correct infra-red spectrum [13] (I.R.Spectrum No.9.).

No further amount of pentafluorobromoethane could be obtained from the

residual solvent by refluxing the solvent, but separation of an aliquot

by preprative scale V.P.C. using tricresyl phosphate as stationary

phase at 20°, nitrogen flowrate 100 mls./min., showed that a con-

siderable quantity of pentafluorobromoethane (18g., 67.5%) remained in

 solution.

Reaction without Diluent.

The above quantities of tetrafluoroethylene, bromine trifluoride,

and bromine were reacted under the same conditions in the absence of

the diluent. The reaction was very vigorous and caused decomposition and formation of carbon tetrafluoride. The latter was characterised by its coincident retention time with an authentic sample using analytical V.P.C. with silicone trimer as stationary phase at 0°.

Hexafluoropropene.

The autoclave, charged with bromine trifluoride (7.5g., 0.055 mole) bromine (9g., 0.056 mole.), and hexafluoropropene (25g., 0.167 mole.) was rotated for two hours without heating. The gaseous products were distilled at atmospheric pressure yielding 2-bromoheptafluoropropane (16g., 45.5%), contaminated with a small amount of hexafluoropropene; this was shown by analytical V.P.C. using silicone trimer as stationary phase at 0°.

A pure sample of 2-bromoheptafluoropropane was obtained by preprative scale V.P.C. with tricresyl phosphate as stationary phase at room temperature, nitrogen flowrate 130 mls./min. (Found F,53.7; Br., 31.2; M.248. C_3BrF_7 requires F, 53.4; Br., 32.1%; M. 248.9) (I.R.Spectrum No.10). Some pure hexafluoropropene (3.8g.) was obtained from the distillation and was characterised by its infrared spectrum and retention time as analytical V.P.C. using the same conditions as above. A considerable amount of free carbon was formed in the reaction.

Proof of the structure of 2-Bromoheptafluoropropane.

Only one isomer was indicated by analytical V.P.C. using silicone trimer as stationary phase at 0°, since the pure sample gave a single peak.

The infrared spectrum of this compound differed from that of

1-bromoheptafluoropropane which has been described[14] and which
has the following bands.

1350(s) 1290(ms) 1240(s) 1180(m) 1140(s) 910(s) 841(s) 760(s)(shoulder)
742(s) 680(m) cm5^{-1}

^{19}F Resonance Spectrum.

This spectrum was determined under identical conditions to that
of heptafluoro-2-iodoethane (see page 88) and again the spectrum
was found to consist of a low field doublet and a high field septet.
The intensity distribution between the multiplets was consistent with
the compound being 2-bromoheptafluoropropane. Further evidence was
provided by the observed chemical shifts; these were measured from
trifluoroacetic acid (used as an external reference) to the centres
of the multiplets.

Doublet.	Septet.	Coupling Constants.
32c/sec.	2600c/sec	8.9c/sec.

Chlorotrifluoroethylene.

An autoclave, charged with bromine trifluoride (20g., 0.150 mole.),
bromine (24g., 0.150 mole.), chlorotrifluoroethylene (52.5g.,0.450 mole.)
and 1,1,2-trichlorotrifluoroethane (154g.) was rotated for two hours
without heating. Unreacted chlorotrifluoroethylene (7g.) was vented
from the autoclave and was characterised by its infrared spectrum. The
residual liquid (232g.) was washed with alkaline sodium thiosulphate
to remove bromine and was distilled through a packed column(2ft.x $\frac{3}{8}$ in.
diameter) giving a fraction, boiling range 21-23° which analysed as
bromochlorotetrafluoroethane (44g.).(Found: F,34·19; M.216.7 Calc. for

C_2BrClF_4 : F, 35.3%. M.215.4) b.p. 22.2°. The residual liquid from

this distillation was shown by analytical V.P.C. using dinonylphthalate

as stationary phase at 50°, to consist of 1,1,2 - trichlorotrifluoroe-

thane together with a considerable amount of undistilled bromochloro-

tetrafluoroethane. The total amount of the latter was estimated by

preprative scale V.P.C. using dinonylphthalate as stationary phase

at 50°, nitrogen flowrate 110mls./min., by weighing the amount trapped

out from a known weight of the mixture injected. This showed that 28g.

of bromochlorotetrafluoroethane was present in the mixture, and thus

the total amount formed in the reaction could be found (72g. 86%).

Constitution of the Bromochlorotetrafluoroethane.

Two isomers of this compound, 1 -bromo - 2 - chlorotetrafluoroe-

thane and 1 - bromo 1 - chlorotetrafluoroethane, were expected from

this reaction by analogy with the reaction of chlorotrifluoroethylene

with iodine pentafluoride and iodine. Analytical V.P.C. using tricresyl

phosphate as stationary phase at room temperature, gave a single peak as

did the following stationary phases: dinonyl phthalate at room temperature,

silicone elastomer at room temperature, and silicone trimer at 0°. The

infrared spectrum (I.R. spectrum No.11), however, was different from

that of authentic 1-bromo-2-chlorotetrafluoroethane (I.R.Spectrum No.12)

(preparation see page 98   ). The difference was that the bromochloro-

tetrafluoroethane contained all the bands of 1-bromo-2-chlorotetra-

fluoroethane together with a few extra ones. It was, therefore, deduced

from this evidence that a mixture of the isomers 1 - bromo-2-

chlorotetrafluoroethane and 1-bromo-1-chlorotetrafluoroethane had been

formed in the reaction.

Estimation of the Isomeric Ratio by Infrared Spectroscopy.

It can be seen from the two spectra Nos. 11 and 12, that there are two strong bands at 1042 cms^{-1} and 901 cm^{-1} which are common to both spectra. Spectrum No.11 was repeated at 4.7 m.m. mercury pressure and spectrum No.12 taken at pressures varying from 2 m.m. to 5 m.m. mercury. The heights of the two peaks at 1042 and 901 cms^{-1} were then measured.

Compound.	1042 cms^{-1}		901 cm^{-1}	
	Pressure.	Height	Pressure	Height.
Bromochlorotetrafluoroethane.	4.7mm Hg.	88mm.	4.7mm Hg.	68.5mm.
Authentic 1-bromo-2-chloro tetrafluoroethane.	2,0mm.Hg.	62.5mm.	2.0mm. Hg.	43.5mm.
"	3.2 mm Hg.	78.5 mm.	3.2 mm Hg.	58.5mm.
"	3.9 mm.Hg.	86 mm.	3.9 mm Hg.	65.5mm.
"	4.0 mm HG.	89.5 mm.	4.0 mm.Hg.	70 mm.
"	5.0 mm.Hg.	96 mm.	5.0 mm.Hg.	81 mm.

This meant that 4.7 mm. of the mixture of the isomers contained 4.0 mm. of 1-bromo-2-chlorotetrafluoroethane and, therefore, 0.7mm. of 1-bromo-1- chlorotetrafluoroethane the ratio thus being 85% to 15% respectively.

Synthesis of 1-Bromo-2-chlorotetrafluoroethane.

The autoclave, charged with bromine (65g., 0.813 mole.), chlorine (29g., 0.817 mole.), and tetrafluoroethylene (81.7g., 0.817 mole.), was rotated without heating for forty-five minutes. The contents of the autoclave were vented through a cooled trap (-183°), and reaction products (74g.) were separated from unreacted tetrafluoroethylene (71g.) by fractionation in vacuo. Analytical V.P.C. using tricresyl phosphate as stationary phase at 42° showed that the product contained three

components in roughly equal amounts. These were then separated by preprative scale V.P.C. using tricresyl phosphate as stationary phase at 36°, nitrogen flowrate 100 mls./min. the middle component only was isolated and was found to be 1-bromo - 2 - chlorotetrafluoroethane (Found: F,34.7; M.216.8. C_2BrClF_4 requires F,35.3%; M.215.4.) b.p. 22.2^o. (I.R.Spectrum No.12). The method of preparation meant that only this isomer of bromochlorotetrafluoroethane could be formed.

Decafluorocyclohexane.

An autoclave (10 ml. capacity) was charged with decafluoro-clohexane (6.5g., 24.8 m moles.), bromine trifluoride (1.13g., 8.25m. moles) and bromine (1.32g., 8.26 m.moles), and shaken for twenty-six hours at 265°. A colourless liquid (7g.) was obtained which gave a single peak on analytical V.P.C. using tricresyl phosphate as stationary phase at 100°; this was shown to be bromoundecafluoro-cyclohexane (78%) (Found: F,57.6; Br. 23.2. Calc. for C_6BrF_{11}: F.57.9; Br.22.2%). b.p. 92°/735 mm. (lit. $90 - 92^o$ [15]) n_D^{20} 1.32206.

(I.R.Spectrum No.12b)

Addition of Iodine Monochloride to Chlorotrifluoroethylene.

The autoclave, charged with iodine monochloride (28g. 0.172 mole.) and chlorotrifluoroethylene (20g., 0.172 mole.) was rotated for three hours at 45°. No gaseous products were vented from the autoclave, and the liquid content was washed several times with $\frac{N}{20}$ sodium thio-sulphate to remove iodine, dried over magnesium sulphate in the dark in a nitrogen atmosphere, and distilled in the same inert atmosphere. The bulk of the material (41g.) distilled in the boiling range 97 - 101°.

Analytical V.P C. using tricresyl phosphate as stationary phase at 80°, showed that the distillate consisted of a small amount of 1,1,2 - trichlorotrifluoroethane together with two major components whose retention times did not differ sufficiently to allow their complete separation. (See diagram 4). The ratio of the peak areas of these two components was 33% to 67%; this was the approximate composition of the mixture since these two components were later shown to be isomers. Pure samples of each component were obtained by collecting early and late "cuts" corresponding to the chromatogram, using the above mentioned analytical column injecting 0.15 ml. aliquots. That complete separation had been achieved could be observed from the infrared spectra which differed completely; the first component (13.5g., 29%) (Found: F,19.6. Calc. for $C_2CI_2F_3I$: F,20.4%) b.p. 98°, n_D^{20} 1.44450. (I.R.Spectrum No.13.) had an identical infrared spectrum with that of 1, 1 - dichlorotrifluoro - 2 - iodoethane, being one of the isomers obtained from the addition of iodine pentafluoride and iodine to 1, 1 - dichlorodifluoroethylene (see page 91). The second component was, therefore, 1, 2 - dichlorotrifluoro - 1 - iodoethane (27.5g. 57%.) (Found: F,19.8. $C_2CI_2F_3I$ requires F,20.4%) b.p. 98.1^o. (I.R.Spectrum No.14.). This second component liberated iodine rapidly at room temperature which prevented determination of its refractive index.

The structure of these two isomers was confirmed by irradiating the mixture (6.0g.) with ultraviolet light in the presence of mercury (3og.) for four hours. The isomers to which the formula $CF_2CI.CFCI$ I has been assigned, coupled very rapidly leaving $CFCI_2$. CF_2I relatively unchanged. This was observed by analytical V.P.C. using tricresyl

phosphate as stationary phase at 80°. It has been established [16]

that compounds containing a - CFCII group couple much more easily

under these conditions, than compounds containing a $-CF_2I$ group.

Addition of Iodine Monobromide to Chlorotrifluoroethylene.

The autoclave was charged with iodine monobromide (142g. 0.686 mole.

and chlorotrifluoroethylene (81g.) (0.695 mole.) and rotated for two

hours at 100°. No gaseous material remained and the liquid products

were washed three times with $\frac{N}{20}$ sodium thiosulphate and dried over

magnesium sulphate, air and light were excluded as far as was possible

from these operations. Distillation of these liquids under reduced

pressure gave an iodine - coloured distillate (168g.,) which rapidly

liberated iodine on exposure to oxygen and light. Analytical V.P.C.

using tricresyl phosphate as stationary phase at 110° , showed that

the distillate contained three components, the last two having very

similar retention times (see diagram 5.) The proportion of the first

peak in the mixture was found by injecting a weighed aliquot onto a

preprative V.P.C. column using tricresyl phosphate as stationary phase

at 110°, and weighing the amount of the first peak isolated: this was

identified as 1,2- dibromo - 1 - chlorotrifluoroethane (38g., 22%).

Found: F,20.2. Calc. for $C_2Br_2ClF_2$: F, 20.6%).

The other two components could not be separated completely, but

a pure sample of the last one was collected by a late cut using an

analytical V.P C. column with tricresyl phosphate as stationary phase

at 110°, nitrogen flowrate 19 mls./min. with a 0.1 ml. injection.

This was 1 - bromo - 2 - chloro - 2 - iodotrifluoroethane,

$CF_2Br. CFClI$ (Found: F,17.3, C_2BrClF_3I requires F,17.6%).

(I.R. Spectrum No.15) : rapid liberation of iodine at elevated temperature obscured the boiling point.

The other component, 1 - bromo - 1 - chloro - 2- iodotrifluoro - ethane CF_2I - CFClBr, was obtained by irradiating a portion of the mixture with ultraviolet light in the presence of mercury for thirty minutes : $CF_2Br.CFClI$ reacted very quickly leaving unchanged $CF_2I \cdot CFCl$ Br which was isolated by preprative scale V.P.C. using tricresyl phosphate as stationary phase at 130°, nitrogen flowrate 110 mls./min. (Found: F, 18.0; C_2Br ClF_3I requires F, 17.6%) b.p. $120.1^{\circ}/768$ mm. (I.R. Spectrum No.16).

The assignment of each structure to these two isomers $CF_2I \cdot CFCl$ Br and $CF_2Br \cdot CFClI$ was made on the following evidence.-

1. The compound containing the -CFClI group would liberate iodine more readily and couple with ultraviolet light in the presence of mercury more rapidly.

2. Analogy with the reaction of iodine monochloride with chlorotrifluoroethylene where the isomer in excess contained the -CFClI group and had the longest retention time on analytical V.P.C. using tricresyl phosphate as stationary phase.

Estimation of the ratio of the two isomers present was made by extrapolating the two merged peaks in diagram 5 in order to find the peak areas. This gave the ratios as 24% to 76% which corresponded to 1 - bromo - 1 - chloro - 2 - iodotrifluoroethane (31g., 14%) and 1 - bromo - 2 - chloro - 2 - iodotrifluoroethane (99g., 44%).

DIAGRAM 4
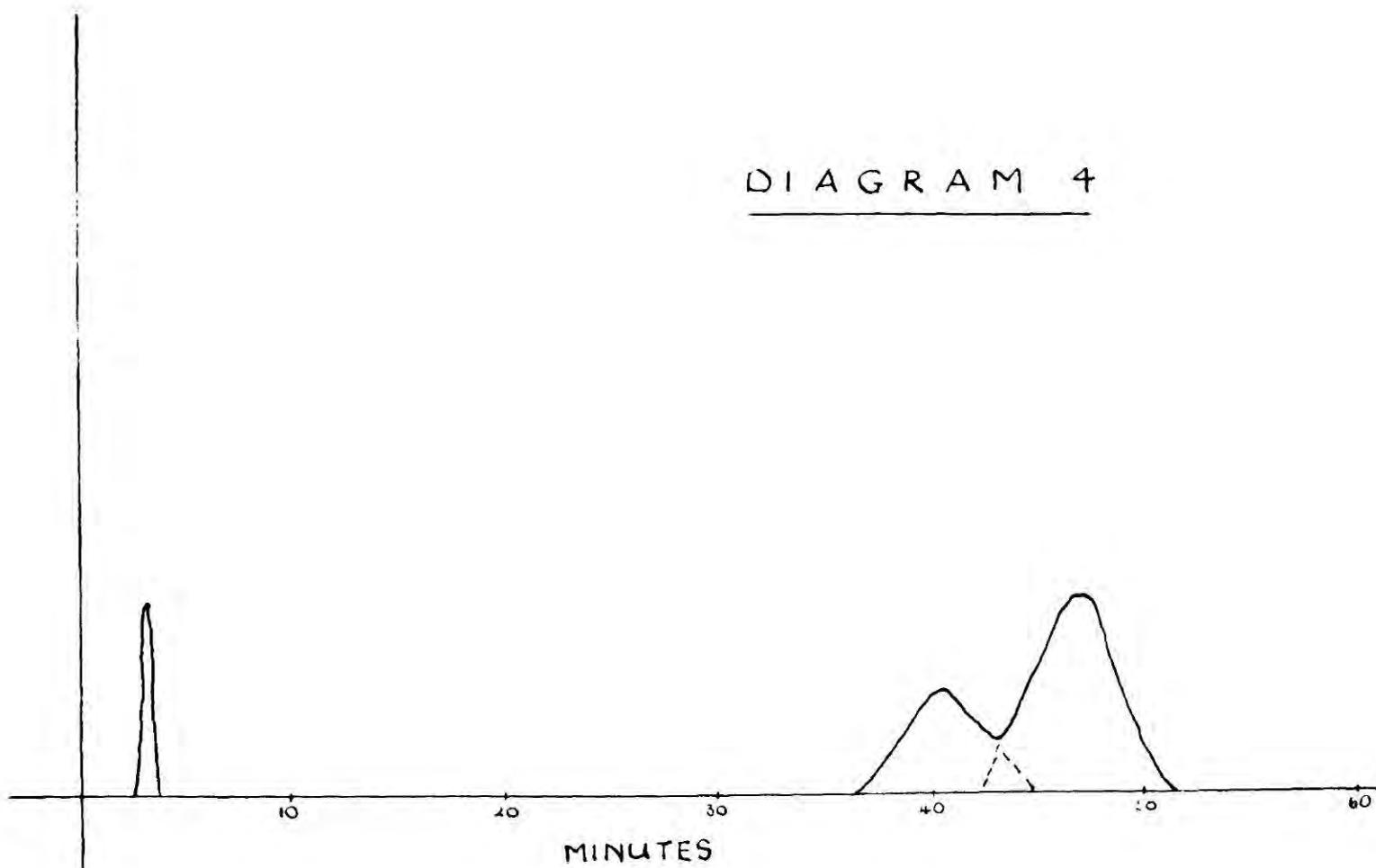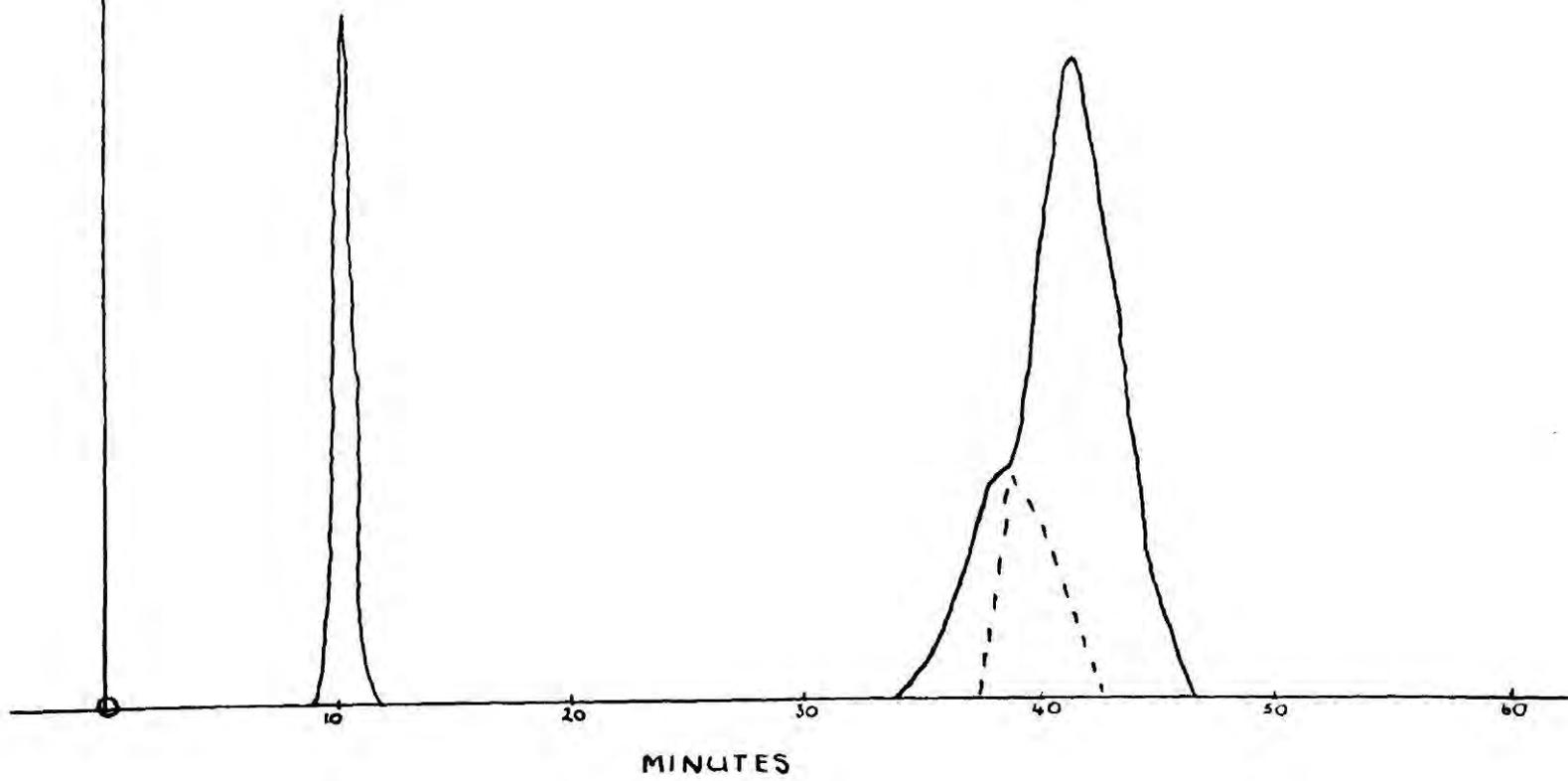
MINUTES

DIAGRAM 5

MINUTES

Addition of Iodine Monochloride to Hexafluoropropene.

The autoclave was charged with iodine monochloride (72g., 0.444 mole.) and hexafluoropropene (66.5g., 0.444 mole.), and rotated for sixteen hours at 200°. The autoclave was vented through a cooled trap (-78°), and the volatile material collected was shown to be unreacted hexafluoropropene (12g.) by its infrared spectrum and its coincident retention time with an authentic sample on analytical V.P C. using tricresyl phosphate as stationary phase at room temperature. The remaining liquid was washed with alkaline sodium thiosulphate to remove iodine, dried over magnesium sulphate, and distilled through a Vigreux column. (1.ft. x $\frac{3}{8}$ in. diameter) giving two fractions. The first fraction was assumed to be 1,2 - dichlorohexafluoropropane (9g., 11%) b.p. 35 - 37° (lit 34.7)[16], and the second one distilled in the boiling range 80 - 80.5° corresponding to 1 - chlorohexafluoro - 2 - iodopropane (66g., 58%) (Found: F,36.2; Calc. for C_3ClF_6I :F,36.5%) b.p. 80.0°/756 mm. n_D^{20} 1.37636. (I.R. Spectrum No.17).

This second fraction gave a single peak on analytical V.P.C. using tricresyl phosphate as stationary phase at 85°, and it was therefore assumed that a single isomer had been formed. Anology with the addition of 'iodine monofluoride' to hexafluoropropene gave the following formula for the product: $CF_3.CFI.CF_2Cl$. It has been mentioned in the literature[17], that the addition of iodine mono-chloride to hexafluoropropene did in fact give this compound but no details were given.

DIAGRAM 6
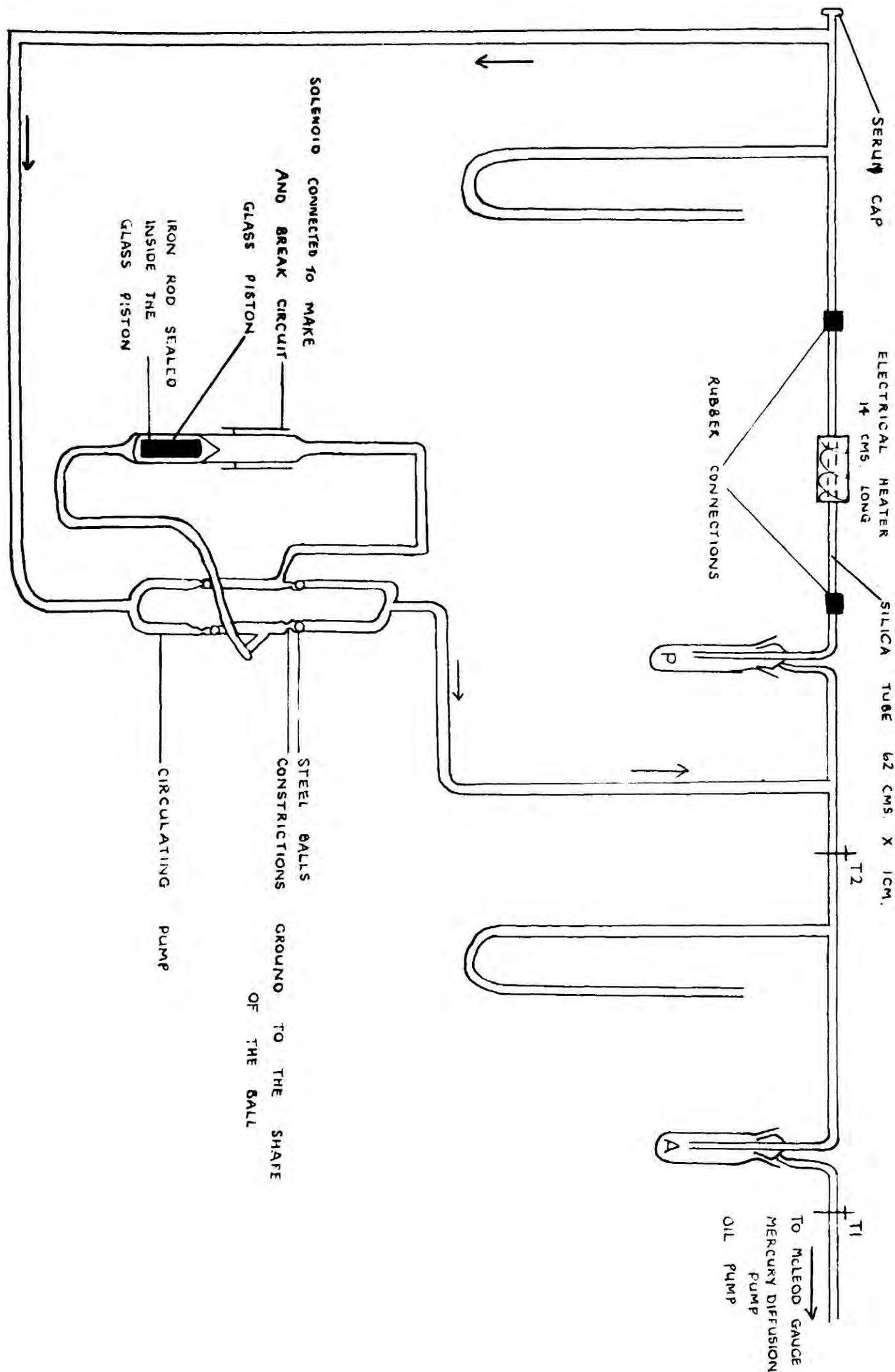
Reactions of Fluorocarbon Iodides and Chlorides.

Pyrolysis of Pentafluoroiodethane.

A vacuum system was devised (see diagram 6) whereby a gas could be circulated continuously through a hot silica tube of internal diameter 10mm. Provision was made in the form of a serum cap attached to the system for the removal from time to time of samples of the gas for analysis by V.P.C. The usual stationary phase was silicone trimer in P.V.C. tubing at 0°.

Pyrolysis at 550 - 600°.

Trap A was charged with pentafluoroiodethane (14.5g., 0.059 mole.) which was then frozen and the whole apparatus evacuated through T1 and T2. T1 was closed and the contents of A allowed to expand to fill the whole system to about one atmosphere. T2 was then closed and the system between T1 and T2 kept at about one atmosphere by means of judicial cooling with an ice bath. The pentafluoroiodoethane in the other part of the apparatus was then circulated at 30 mls./min. whilst the heater was quickly brought to 600°. Traces of free iodine were formed at 500°; this formation became considerable at 550 - 600°. As the iodine was liberated, the pressure in the system decreased and was carefully brought back to atmospheric pressure by the introduction of more pentafluoroiodoethane through T2. The time taken for the total contents of trap A to be introduced into the circulating system was two hours. After a further thirty minutes the formation of iodine and decrease of pressure had ceased, the latter remaining at 250mm. mercury.

Investigation of a sample of the gas by analytical V.P C. using silicone trimer as stationary phase at 0° showed that two components were present. This volatile material (8.2g.) was then condensed into P and separated into its two components by preprative scale V.P.C. using dinonyl phthalate as stationary phase at room temperature, nitrogen flowrate 100 mls./min. yielding perfluorobutane (4.8g. 86% yield 68.5% conversion) (Found: M.236. Calc. for C_4F_{10} : M.238)(I.R. Spectrum No.18.); this infrared spectrum was identical to that of authentic perfluorobutane described in the literature[18]. The other component was unreacted pentafluoroiodoethane (2.9g.) characterised by its infrared spectrum and coincident retention time on analytical V.P.C. using silicone trimer as stationary phase at 0°, with an authentic sample.

Pyrolysis at 800°.

Reaction 1.

The circulating system was filled to one atmosphere with pentafluoroiodoethane (8.0g., 32.5m. mole.), which was then circulated for twenty minutes through the silica tube heated by a small gas flame. Initially a flame 2 cms. long appeared inside the tube, iodine was rapidly liberated and the pressure fell. The product gas was shown by analytical V.P C. using silicone trimer as stationary phase at 0° to consist of three components whose peak areas were measured. Equal thermal conductivities of the product were assumed so that these peak areas could be related directly to molar proportions. This assumption seems reasonable in view of the similarity of the three products. In all the future experiments describing the pyrolysis of pentafluoro-
iodoethane,

this assumption is made and the peak areas ratio i.e. molar ratio then transferred to the percentage ratio by weight of each component. These three components were identified by their coincident retention times with authentic samples as being perfluoroethane (18%), tetrafluoro-ethylene (26%) and perfluorobutane (56%); preprative scale low temperature V.P C. was not developed sufficiently to isolate these three components separately and so carry out further methods of identification. Other possible products from the reaction, which, however, had retention times different from the above compounds were tetrafluoromethane, hexafluoropropene, octafluoropropane and trifluoroiodomethane. The volatile material was condensed into P and separated by preprative scale V.P.C. using dinonyl phthalate as stationary phase at 23°, nitrogen flowrate 100 mls./min. into unreacted pentafluoroiodoethane (0.8g.) , and a mixture of perfluoroethane, tetrafluoroethylene and perfluorobutane. (2.7g. 90% conversion).

Reaction 11.

Reaction 1 was repeated with the introduction of nitrogen into the system through T2 to keep the pressure at one atmosphere. After twenty minutes, when the pyrolysis appeared to be complete, the volatile material (3.0g.) was investigated as before and shown to consist of perfluoroethane (5.5%), tetrafluoroethylene (14.5%) and perfluorobutane (80.0%), with again a 90% conversion of the starting material.

Note: All the pyrolysis reactions described in this section were investigated by analytical V.P.C. as described in Reaction 1.

Pyrolysis of Pentafluoroiodoethane by Vacuum Transfer through a hot
tube.

For the first series of these reactions the vacuum system shown

in diagram 7 was used.

Reaction 1.

Pentafluoroiodoethane (5.0g., 20.3m mole.) was charged into one

of the traps A, which was then cooled and the apparatus evacuated.

The silica tube (internal diameter 10mm.) was then heated to about

800° over a length of 2 cms. by means of a Bunsen flame, and the

pentafluoroiodoethane was passed through this tube four times by means

of simple vacuum transfer between the two traps A. A considerable

amount of iodine was liberated and the volatile product (21g.) was

shown to consist of perfluoroethane (16%), tetrafluoroethylene(15%),

and perfluorobutane (69%) using the same analytical V.P C. conditions

as before. A small amount of C_2F_5I, approximately 7% of the initial

amount was also detected.

Reaction 2.

Reaction 1 was repeated using an electrical heater to heat the

silica tube to 300°. This heater was identical to the one shown in

diagram 6. The conversion of starting material was approximately 1%

and, therefore, no attempt was made to identify the products.

Reaction 3.

Reaction 1 was repeated using a reaction tube (60 cms. x 0.8 cms

diameter) packed with glass helices and heated in a long electric

furnace to 400°. The volatile product (4.0g.) was shown to consist of

perfluoroethane (5%),tetrafluoroethylene (7%), perfluorobutane (8%),

and unreacted pentafluoroiodoethane (80%). Only a little free iodine was liberated.

Reaction 4.

The vacuum transfer apparatus was modified (see diagram 8) in order to study the effect of sudden cooling on the hot reaction mixture. Pentafluoroiodoethane (2.5g., 10.0m. moles.) was transferred from B to A through a silica tube of internal diameter 10mm. heated by a gas-oxygen flame. The volatile product consisted of perfluoroethane (48%), and tetrafluoroethylene (52%); complete conversion of the starting material was achieved and a considerable amount of free iodine was liberated.

Pyrolysis of Pentafluoroiodoethane at atmospheric pressure.

An apparatus (see diagram 9) involving the passage through a hot silica tube (internal diameter 10mm) of pentafluoroiodoethane in a stream of nitrogen, was devised for this reaction. Trap A was charged with pentafluoroiodoethane (10.0g., 0.046 mole.), and the latter was then slowly evaporated in a stream of nitrogen (flowrate 30 mls./min.) through the silica tube (internal diameter 10mm.) heated by a gas 'bat-winged' burner over a length of 12 cms. The volatile product (3.5g.) was shown to consist of perfluoroethane (11%), tetrafluoroethylene (8%), perfluorobutane (15%), and unreacted pentafluoroiodoethane (66%). Quite a lot of free iodine was liberated.

SILICA TUBE (60cms x 1·0cms.)

A

RUBBER CONNECTIONS

A

McLEOD GAUGE

OIL PUMP

DIAGRAM 7

RUBBER CONNECTION

SILICA TUBE

(60cms x 1·0cms)

OXYGEN – GAS
FLAME

P.V.C CONNECTION

LIQUID AIR

B14

A

B

McLEOD GAUGE

OIL PUMP

DIAGRAM 8

NITROGEN

RUBBER CONNECTIONS

SILICA TUBE (60 cms X 10 cms)

A

BATWINGED BUNSEN BURNERS

DIAGRAM 9

B 34

B19

3"

250 MLS.

INDENTATIONS APPROXIMATELY
1" LONG AND ¼" DEEP

WIDE - BORE TAP

DIAGRAM 10
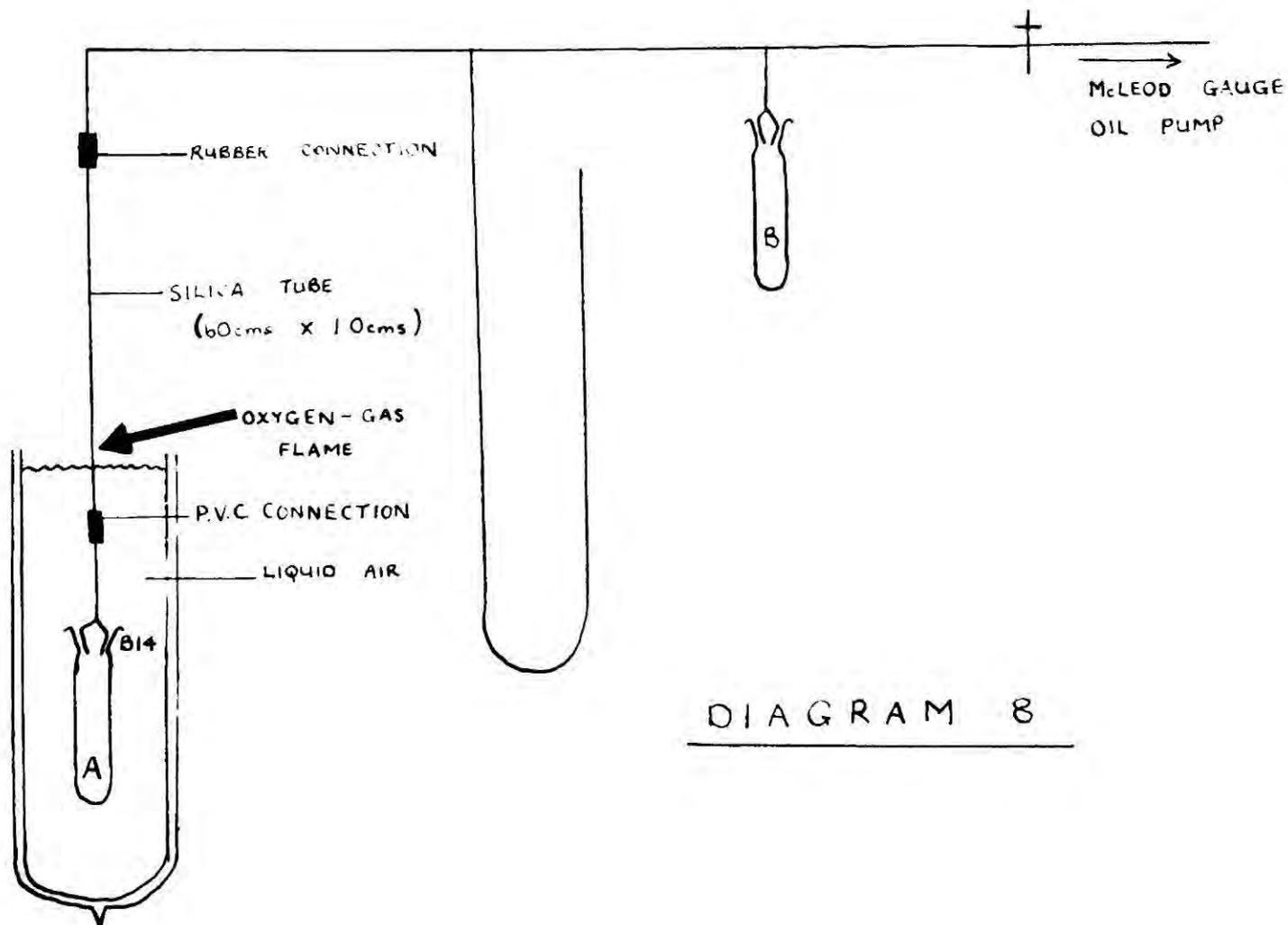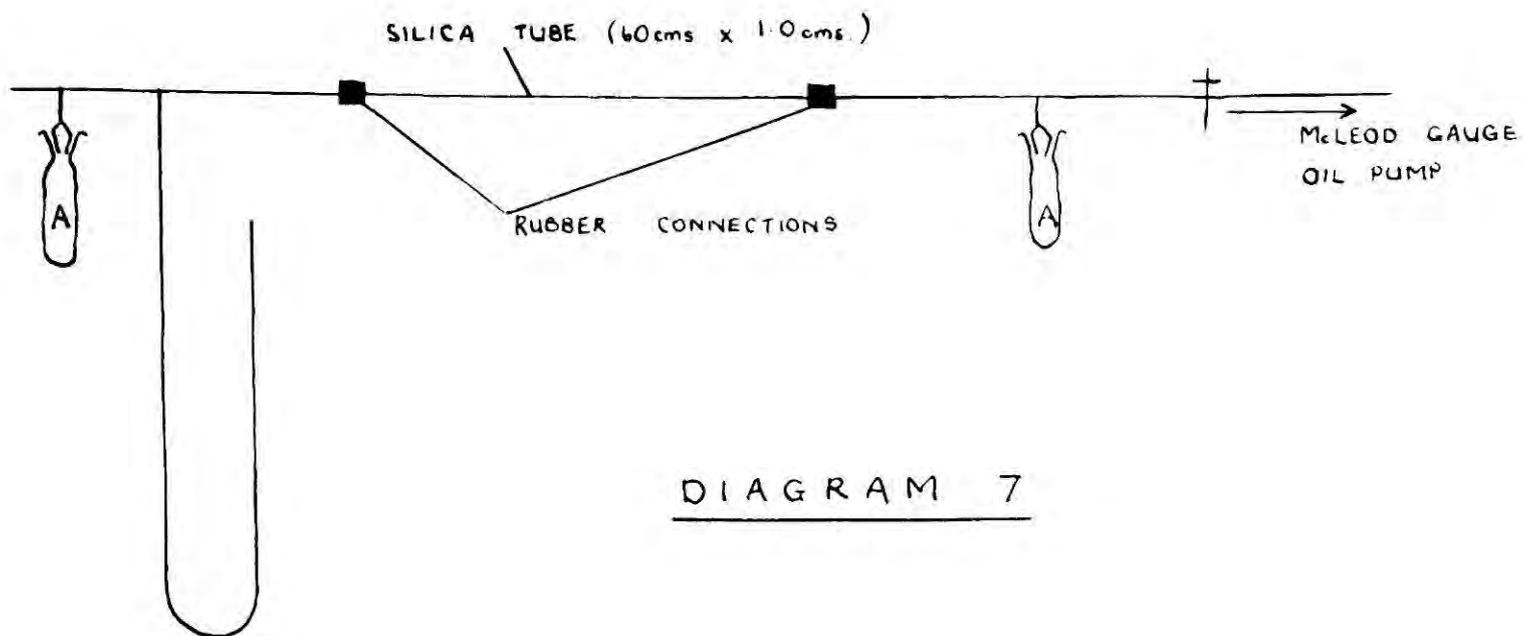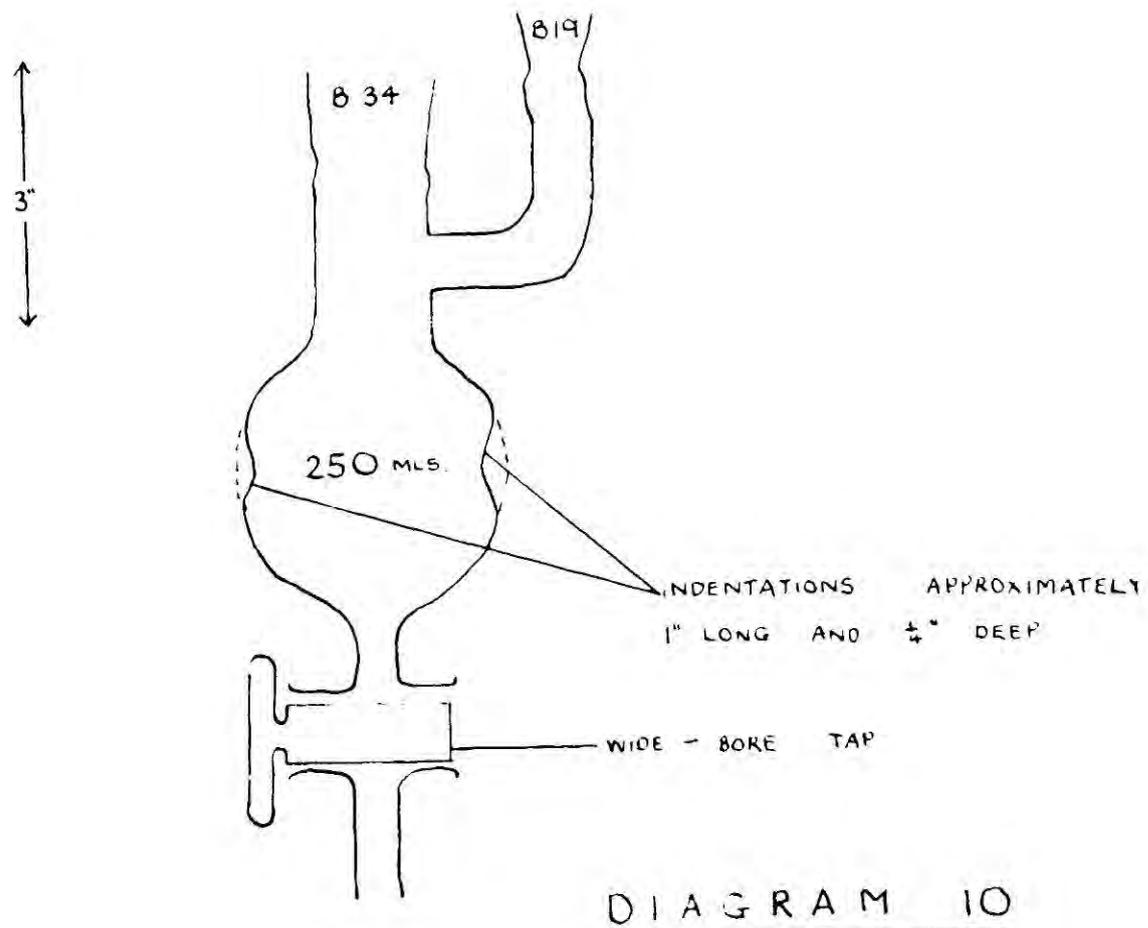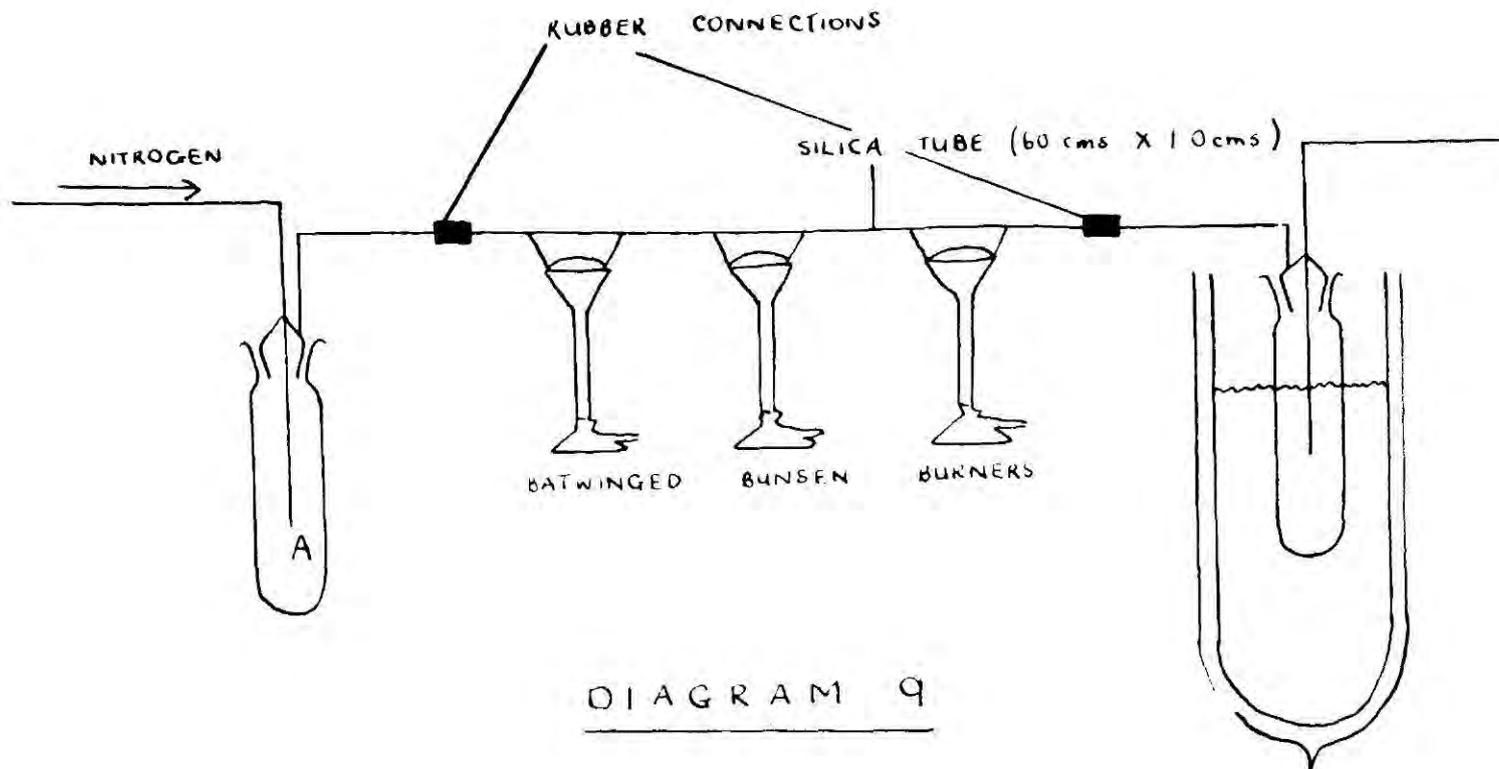
REACTIONS OF HEPTAFLUORO - 2 - IODOPROPANE.

Hydrolysis.

Heptafluoro - 2 - iodopropane (4.5g., 15.2m. mole.), potassium hydroxide (3.5g., 62.2m. mole.), and acetone (10 mls.) contained in a Pyrex tube which was sealed under vacuum, were shaken at room temperature. The reaction mixture turned dark brown after a few minutes and the tube became quite warm; this evolution of heat, however, ceased after thirty minutes, thus indicating that the reaction was complete. The volatile material was removed from the reaction tube by attaching the latter to a vacuum system by means of rubber tubing. The whole of this reaction mixture was introduced onto a preprative scale V.P.C. column using tricresyl phosphate as stationary phase at 35°, nitrogen flowrate 110 mls./min. which yielded 2H - heptafluoropropane (1.95g., 75%) (Found: M.172: Calc. for C_3F_7H : M.171). (I.R. Spectrum No.19); this infrared spectrum was identical to that of authentic 2H - heptafluoropropane described in the literature[19]. This preprative scale V.P C. run also yielded a trace of unreacted heptafluoro - 2 - iodopropane and a considerable amount of acetone; both of these were identified by their retention times on the same V.P C. apparatus.

Coupling Reaction, Preparation of Tetradecafluoro-2, 3-dimethylbutane.

A Carius tube was charged with heptafluoro - 2 - iodopropane (10g., 0.0338 mole.) and just enough clean, dry mercury so as to form a continuous length along the tube when the latter was placed horizontally. This tube was sealed under vacuum and irradiated with

ultraviolet light for three days whilst being shaken in a horizontal position. The source of the ultraviolet light was a Hannovia Model 11 lamp, tube type 501/1, which using the reflecter gives an intensity of 510 microwatts/cm^2 at a distance of 36 in.

The volatile products were removed from the tube under vacuum and separated by preprative scale V.P.C. using tricresyl phosphate as stationary phase at 80°, nitrogen flowrate 120 mls./min., into recovered heptafluoro - 2 - iodopropane (0.3g.,) and tetradecafluoro - 2, 3 - dimethylbutane (5.5g., 96.5%). (Found: F,78.4; M.337.5. C_6F_{14} requires: F,78.7%; M.338). b.p. 60.0°/756 mm. n_D^{20} 1.31483. (I.R.Spectrum No.20).

Reaction with Sulphur.

Heptafluoro - 2 - iodopropane (20g., 0.0677 mole.) and flowers of sulphur (28g.) were sealed under vacuum in a large Carius tube (approx. 100 mls.) and heated in a horizontal position at 243° for thirteen hours, which liberated a considerable amount of free iodine. The volatile material (11g) was removed under vacuum and shown to consist of a mixture of four components by analytical V.P.C. using tricresyl phosphate as stationary phase at 120°. Each of these four components was isolated by preprative scale V.P.C. using tricresyl phosphate as stationary phase at 80°, nitrogen flowrate 125 mls./min. with 0.8g. aliquot injections. This yielded the following materials in order of their retention times: unreacted heptafluoro - 2- iodopropane (1.5g.), characterised by its infrared spectrum and retention time on analytical V.P.C. using tricresyl phosphate as stationary phase at 45°; perfluoroisopropyl disulphide $(CF_3CFCF_3)_2S_2$ (4.5g., 36%) (Found: F,65.7.

$C_6F_{14}S_2$ requires F, 66.1%) b.p. $119^°/773$ mm., n_D^{20} 1.32614 (I.R.

Spectrum No.21); <u>perfluoroisopropyl monosulphide,</u> $(CF_3CFCF_3)_2S$,(1.3g.,

11%) (Found: F, 71.2. $C_6F_{14}S$ requires F, 71.7%) b.p. $116.9^°/762$ mm.

(I.R.Spectrum No.22); <u>perfluoroisopropyl trisulphide</u> $(CF_3CFCF_3)_2S_3$

(2.5g., 18.5%) (Found: F,61.4. $C_6F_{14}S_3$ requires F, 61.3%) b.p. $150.0^°/$

764 mm., n_D^{20}, 1.36092. (I.R.Spectrum No.23).

<u>Reaction with Zinc, Preparation and Hydrolysis of Heptafluoroisopropyl-</u>
<div align="right"><u>zinc iodide.</u></div>

<u>Purification of Reagents.</u>

<u>Zinc Dust.</u> Commercial zinc dust (200g.) was treated with 10%

sulphuric acid (500 mls.) and allowed to stand for thirty minutes when

the supernatant solution was poured off. The zinc was washed several

times with distilled water until the supernatant solution gave no

precipitate with barium chloride. After washing three times with

acetone, the zinc dust was dried under vacuum at $100^°$.

<u>Dioxane.</u> Commercial dioxane usually contains a certain amount of

glycol acetal and some water. On storage the acetal tends to undergo

hydrolysis and the liberated acetaldehyde gives rise to rapid peroxide

formation. The following purification processes were carried out. A

mixture of commercial dioxane (2 litres) conc. hydrochloric acid (27 ml.)

and some water (200 mls.) were refluxed for twelve hours; during which

time a slow stream of nitrogen was bubbled through the solution to

entrain acetaldehyde. The solution was cooled, and potassium hydroxide

pellets added slowly with shaking until they no longer dissolved and

a second layer had separated. The dioxane was decanted, treated with

fresh potassium Hydroxide pellets to remove adhering aqueous liquor,

decanted into a clean flask, and refluxed with sodium for 12 hours.

The solvent was then distilled and stored under nitrogen.

Preparation of Heptafluoroisopropylzinc iodide.

Zinc dust (6.6g., 0.101g.atom.), dioxane (20 mls.), and 8 mls. of a mixture of heptafluoro - 2 - iodopropane (15g., 0.0506 mole.) in dioxane (11 mls.) contained in a 3N flask fitted with a mechanical stirrer, dropping funnel and Friedrich condenser, were heated until the solution was just refluxing. The remainder of the mixture of hepta-fluoro - 2 - iodopropane and dioxane was then added at such a rate as to maintain this refluxing with slightly less heating than before. After the addition, the reaction mixture was refluxed with stirring for a further two hours during which time a gas (2.9.) was evolved. Analytical V.P.C. using tricresyl phosphate as stationary phase at room temperature, showed that this gas consisted of a mixture of hexafluoropropene (1.9g.) and 2H-heptafluoropropane (1.0g.,) by means of coincident retention times with authentic samples; the ratio of the amounts of these two components was determined by their peak areas. Also the infrared spectrum of the mixture showed only bands characteristic of these two gases.

Hydrolysis. The above reaction mixture was cooled to room temperature and treated with 2N sodium hydroxide (15mls.), the addition taking ten minutes. The mixture was then refluxed for one and a half hours, when 2H - heptafluoropropane was evolved (4.0g., 46.5%) (Found: M.171.Calc. for C_3F_7H:M.170); the infrared spectrum was identical to No.19 which in turn was identical to that of authentic 2H-heptafluoropropane described in the literature.[19]

Preparation of Heptafluoroisopropyl magnesium bromide and Reaction
                                                    with Ethand.

A three necked flask (250 mls.) fitted with a mercury sealed stirrer,
Friedrich condenser and dropping funnel, was swept with nitrogen and
charged with heptafluoro-2-iodopropane (15.0g., 0.0506 mole.) and ether
(30 mls.); this solution was stirred, cooled (-78°) in an acetone-solid
carbon dioxide bath, and phenyl magnesium bromide (0.0506 mole.) in
ether (45 mls.) was added over a period of twenty-five minutes. This
was followed by the addition of cooled (-50°) ethanol (5g. 0.189 mole.)
in ether (30 mls.) over the same length of time. The reaction mixture
was allowed to warm to room temperature at the rate of 30° per hour,
and was finally refluxed for three hours. Gaseous products were
collected in a cooled trap (-78°) in which some ether also condensed.
Separation of these materials by preprative scale V.P.C. using tricresyl
phosphate as stationary phase at room temperature, nitrogen flowrate
120 mls./min., gave hexafluoropropene (6.0g., 76%), and 2H-heptafluoro-
propane (1.0g., 9%) (Found: M.172. Calc. for C_3F_7H: M.171); both of
these materials were characterised by their infrared spectra and coin-
cident retention times with authentic samples using analytical V.P C.
with tricresyl phosphate as stationary phase at room temperature.

Preparation of Heptafluoroisopropylmagnesium bromide and Reaction with
                                                    Acetone.

Heptafluoro-2-iodopropane (15g., 0.0506 mole.) in ether (30 mls.)
was cooled (-78°) and a solution of phenylmagnesium bromide (0.0506 mole.)
in ether (44.5 mls.) was added slowly over a period of thirty minutes
simultaneously with a mixture of acetone (9.0g., 0.155 mole.) and ether
(10 mls.).

The reaction mixture was slowly warmed to room temperature when

hexafluoropropene (1.0g.) was evolved and identified by its infrared

spectrum and retention time on analytical V.P.C. using tricresyl

phosphate as stationary phase at room temperature; it was also shown

by the same analytical V.P.C. that a considerable amount more remained

dissolved in the ether. Ice cold 2N sulphuric acid (20 mls.) was

slowly added to the reaction mixture, resulting in the disappearance

of the solid. The ether layer was separated, dried over magnesium

sulphate and most of the solvent removed by distillation through a

packed column. The residue was distilled under vacuum at 100° and

the distillate was separated by preprative scale V.P.C. using tricresyl

phosphate as stationary phase at 150°, nitrogen flowrate 210 mls./min.

giving 3,4,4,4-tetrafluoro-2-methyl-3-trifluoromethylbutan-2-ol

(4,0g., 35%) (Found: F,57.8; $C_6F_7H_7O$ requires F,58.3%) b.p. $109^{\circ}/756$ mm.

n_D^{20} , 1.33421, (I.R. Spectrum No.24) and iodobenzene (8.5g., 69.5%)

The latter was characterised by its coincident retention time with an

authentic sample on analytical V.P.C. using silicone elastomer as

stationary phase at 150°.

A black oily liquid (4.0g.) remained from the vacuum distillation.

Preparation of Heptafluoroisopropylmagnesium bromide and Reaction with Propionaldehyde.

Heptafluoro-2-iodopropane (15g. 0.0506 mole.) in ether (25 mls.)

solution was cooled to -40° and treated with phenylmagnesium bromide

(0.0506 mole.) in ether (24 mls.) and propionaldehyde (5.9g.,0.102 mole.)

in ether (20 mls.) simultaneously over a period of forty minutes. This

reaction mixture was warmed to room temperature at the rate of 30° per

hour when a small amount of hexafluoropropene was evolved and was

characterised by its coincident retention time with an authentic sample using analytical V.P.C. with tricresyl phosphate as stationary phase at room temperature. The mixture was then cooled by an ice bath and treated with ice cold 2N sulphuric acid (20 mls.). The two layers were separated and the aqueous one extracted twice with ether; the combined ether extracts were dried over magnesium sulphate, and most of the ether removed by distillation through a 1 ft. column packed with glass helices. The residue was distilled under reduced pressure (15mm. Hg.) from a boiling water bath and was introduced onto a preprative scale V.P C. column using tricresyl phosphate as stationary phase at 150°, nitrogen flowrate 210 mls./min. This gave 1,1,1,2-tetrafluoro- 2 - trifluoro - methylpentan - 3 - ol (2g., 17.5%) (Found: F, 58.1 ; M. 227.1 by Victor Meyer's method. $C_6F_7H_7O$ requires: F, 58.3%; M.228) b.p. 109° n_D^{20} , 1.32875. (I.R. Spectrum No.25).

A black oily residue (3g.,) was also obtained from the reduced pressure distillation.

<u>Preparation and reactions of Heptafluoroisopropyllithium.</u>

<u>Preparation of n ButylLithium.</u>

<u>Lithium Shot.</u> The diagram shown in diagram 10 was filled with a mechanical stirrer, air condenser, and ring burner; petroleum oil (b.p. 220 - 240°) and small pieces of lithium metal were then introduced into the apparatus. After purging the apparatus with nitrogen the oil was heated to boiling and the lithium dispersed by vigorous stirring. The stirring was discontinued after about five minutes and the apparatus was allowed to cool to room temperature. The oil was run off, and the lithium shot washed three or four times with pentane and eventually

washed directly into the reaction vessel.

n Butyl Lithium was prepared as described by Gilman et al.[20]

n Butyl bromide (68.5g., 0.5 mole.) in dry pentane (100 mls.) was

gradually added to lithium shot (6.9g., 1,0 mole.) in pentane (400

mls.) contained in a three-necked flask fitted with a dropping funnel,

mechanical stirrer, and Friedrich condenser. The solution soon

turned dark blue and the addition was controlled so as to maintain

steady refluxing. When all the n butyl bromide had been added, the

solid lithium bromide was allowed to settle and the supernatant liquid

was transferred to a graduated dropping funnel via P.V.C. tubing.

The strength of the solution was determined by hydrolysis of an aliquot

(1 ml.) and titrated with acid (0.1N) using bromocresol green as

indicator (91% yield).

n-Butyl lithium in pentane solution is stable for several months;

for reactions requiring ethers as solvents, the pentane was usually

removed by evaporation and replaced by the ether.

Methyl Lithium was prepared by a similar proceedure using methyl

iodide in place of n butyl bromide.

Preparation and Decomposition of Heptafluoroisopropyl Lithium.

Heptafluoro-2-iodopropane (15.0g., 0.0506 mole.) in dry pentane

(50 mls.), and a 0.73N solution of n-butyl lithium in pentane (69.5 mls.

0.0506 mole.) were added simultaneously to pentane (20 mls.) con-

tained in a 3N flask fitted with a mechanical stirrer and two dropping

funnels, and cooled to -78° in an acetone-solid carbon dioxide bath.

the time taken for the above addition was about thirty minutes, after

which the reaction mixture was slowly warmed to room temperature and

refluxed for one hour. Hexafluoropropene (5.6g., 73.5%) (Found:
M.151 Calc. for C_3F_6 : M.150) was evolved, purified by fractionation
in vacuo, and further characterised by its infrared spectrum and
coincident retention time with an authentic sample on analytical V.P.C.
using tricresyl phosphate as staionary phase at room temperature. The
remaining pentane solution was investigated by analytical V.P.C. using
tricresyl phosphate as staionary phase at 140°, and shown to contain
a peak with a retention time coincident with authentic n-butyl iodide.
A test solution of n-butyl iodide in pentane was made, and by comparison
of peak areas from this and the reaction product, it was shown that
approximately 7.5g. of n-butyl iodide had been formed in the reaction
(80% yield).

Preparation and attempted Hydrolysis of Heptafluoroisopropyl lithium.

Heptafluoroisopropyl lithium was pepared on the same scale using
the same procedure as above, and four attempts to hydrolyse it were
made.

Reaction 1. Ethanol (50 mls.) was added to the reaction mixture
immediately after the mixing of the heptafluoro-2-iodopropene and
n-butyl lithium, and the mixture warmed to refluxing as before.
Hexafluoropropene (5.1g., 67%) was evolved and characterised as before
by its infrared spectrum and retention time.

Reaction 2. The reaction mixture from the preparation of the hepta-
fluoroisopropyl lithium was warmed to -10° and treated with 2N sulphuric
acid (40 mls.). Hexafluoropropene (5.0g., 66%) was again the only
gaseous product.

Reaction 3. Reaction 2 was repeated with diethylether as solvent

instead of pentane; this again resulted in the formation of hexafluoro-
propene (5.0g., 66%) which was partially isolated from the ether by
fractionation in vacuo and then obtained pure by preprative scale V.P.C.
using tricresyl phosphate as stationary phase at room temperature,
nitrogen flowrate 100 mls./min.

Reaction 4. Ether was again used as solvent. The cold (-78°) reaction
mixture was treated with a mixture of ethanol (10 mls.) and ether (50
mls.) cooled to -60°; this again gave hexafluoropropene (5.0g., 66%).

Preparation of Heptafluoroisopropyl Lithium and Reactions with
Propionaldehyde.

A solution of heptafluoro-2-iodopropane (30g.,0.1012 mole.) in
ether (60 mls.) contained in a 3N flask fitted with mechanical stirrer
and two dropping funnels, was cooled to -78° and treated simultaneously
with methyl lithium in ether solution (74.4 mls.), 1.36N, 0.1012 mole.)
and freshly distilled propionaldehyde (11.8g., 0.204 mole.) in ether
(60 mls.). The addition was carried out over a period of thirty
minutes and the reaction mixture was then warmed to room temperature
at the rate of 30° per hour; this resulted in the evolution of hexa-
fluoropropene (1.5g.). Ice cold 2N sulphuric acid (60 mls.) was added
to the reaction mixture, the two layers were separated, the aqueous
one extracted with ether, and the ether portions combined and dried
over magnesium sulphate. Ether, propionaldehyde and heptafluoro-2-
iodopropane were removed by distillation through a packed column; this
distillate was analysed for fluorine and shown from this analysis to
contain 9.5g. of unreacted heptafluoro-2-iodopropane. The residual
liquid was then distilled through a 1 ft. Vigreux column yielding a

distillate (9.0g. 53% yield, 70% conversion) of boiling range 109° - 112°, which gave a peak always with a slight inflection, when investigated by analytical V.P.C. using tricresyl phosphate or silicone elastomer as stationary phase at temperatures ranging from 80° to $12o^o$. No separation of the two components could therefore be hoped for by peprative scale V.P.C.

The infrared spectrum of this product (I.R.Spectrum No.26) was almost identical to 1,1,1,2-tetrafluoro-2-trifluoromethylpentan - 3 - ol prepared from heptafluoroisopropyl magnesium bromide and propionaldehyde (I.R.Spectrum No.25), but the analysis and moleacular weight were both very low (Found: 51.8; M.174.1.$C_6F_7H_7O$ requires F,58.3%; M.228). This suggests the presence of some non-fluorine containing impurity whose infrared spectrum did not appear, due to the low concentration and thin film.

A black oily residue (7.0g.) was obtained from the distillation.

A preliminary reaction identical to the above one was carried out using n-butyl lithium instead of methyl lithium. It was found, however, that the n-butyl iodide formed in this reaction could not be separated from the product by distillation whereas methyl iodide was easily separated.

Preparation of Heptafluoroisopropyl Lithium and Reaction with Acetone.

Heptafluoro - 2- iodopropane (20g., 0.0676 mole.) and ether (20 mls.) contained in a 3N flask, were cooled to -78° and treated with methyl lithium (0.0676 mole.) in ether (80 mls.) and pure dry acetone (12g., 0.207 mole.) in ether (20 mls.) over a period of twenty-five minutes. This mixture was slowly brought to room temperature and hexafluoropropene (1.5g.) was evolved. Treatment with 2N sulphuric acid (40 mls.)

followed by separation of the layers and distillation of the ether, was carried out as previously described. The residue from the ether distillation was distilled under reduced pressure and this distillate separated by preprative scale V.P.C. using tricresyl phosphate as stationary phase at 150°, nitrogen flowrate 170 mls./min, into 3,4,4,4-tetrafluoro - 2 - methyl - 3 - trifluoromethyl - 2 - ol (2.5g., 13%) (Found: F,57.5; $C_6F_7H_7O$ requires F, 58.3%), b.p. 109°, infrared spectrum identical to the same product prepared from heptafluoroisopropyl magnesium bromide and acetone (I.R.Spectrum No.24.), and mesityl oxide (2.0g. 19.5%). The latter had a coincident retention time with an authentic sample when investigated by analytical V.P.C. with tricresyl phosphate as stationary phase at 115°.

A black oil (4.7g.) remained from the final distillation.

REACTIONS OF FLUOROCARBON IODIDES AND CHLORIDES WITH n-BUTYL LITHIUM.

Pentafluoroiodoethane: Preparation and decomposition of pentafluoroethyl lithium.

A 3N flask fitted with a mechanical stirrer, Friedrich condenser and dropping funnel and containing pentane (15 mls.) was cooled to -78° and charged with pentafluoroiodoethane (5.0g., 0.0203 mole.) by its evaporation from a small flask in a slow stream of nitrogen, into the reaction vessel. n-Butyl lithium (0.0203 mole.) in pentane (27.6 mls.) was slowly added over a period of thirty minutes and the reaction mixture was allowed to warm to room temperature during two hours; the reaction was continued under pentane reflux for a further hour and a half.

Tetrafluoroethylene (2.04g., 88%), was evolved, and collected in a liquid air trap, together with quite a lot of pentane; these were separated by fractionation in vacuo. The tetrafluoroethylene was characterised by its identical infrared spectrum to that of pure authentic tetrafluoroethylene, and by its coincident retention time with the latter using analytical V.P.C. with silicone trimer as stationary phase at 0°.

Preparation and Hydrolysis of Pentafluoroethyl Lithium.

The initial reaction mixture at -78° in the above reaction was treated with a mixture of 2N sulphuric acid (7 mls.) and ethanol (7 mls.); on warming to reflux tetrafluoroethylene (2.0g., 87%) was evolved and identified as before. Analytical V.P.C. using silicone trimer as stationary phase at 0° gave a small peak besides the large one of tetrafluoroethylene; this could be attributed to a trace of pentafluoroethane.

<u>Tetrafluoro-1, 2-diiodoethane.</u>

<u>Reaction 1.</u>

Tetrafluoro-1, 2-diidoethane (10.0g., 0.0283 mole.) in pentane
(10 mls.) contained in a 3N flask, was cooled to -50° and treated with
n-butyl lithium (0.0566 mole.) in pentane (74 mls.) A white precipitate
was formed immediately and tetrafluoroethylene (2.7g., 95%) was evolved.
The reaction mixture was warmed to room temperature and an aliquot
(1 ml.) was hydrolysed and titrated with standard acid. The titration
showed that approximately half of the n-butyl lithium had reacted.
The white precipitate was shown to consist entirely of lithium iodide
by its inorganic nature and complete solubility in water.

<u>Reaction 2.</u>

This reaction was carried out similarly to Reaction 1 except that
the tetrafluoro-1, 2-diiodoethane was added to the n-butyl lithium
solution cooled to -78°. The same products as in Reaction 1 were
obtained.

<u>Reaction 3.</u>

Reaction 2 was repeated with the reaction flask cooled to -90°
using a methylene chloride-liquid air "slush" bath. Lithium iodide was
again precipitated immediately, tetrafluoroethylene (2.6g., 92%) was
evolved on warming above about -60°.

<u>Reaction 4.</u>

Reaction 2 was repeated using ethyleneglycoldimethylether as
solvent; this is readily cleaved by n-butyl lithium, and therefore the
two had to be mixed at -50° after evaporating off most of the pentane
in a rapid stream of nitrogen. Lithium iodide was again precipitated

at -78°, but tetrafluoroethylene could not be isolated from the solvent by distillation. The presence of tetrafluoroethylene in the solvent was shown by analytical V.P.C. using silicone trimer as stationary phase at 0°. No lithium fluoride was formed, since all the precipitate dissolved in water.

Reaction 5.

The same result as Reaction 4 was obtained when tetrahydrofuran was used as solvent instead of ethyleneglycoldimethylether, at either -78° or -90°.

1-Chlorotetrafluoro - 2 - iodoethane:

This was prepared by the reaction between iodine monochloride and tetrafluoroethylene in the rotating autoclave at 45°.[21] The reaction, when performed on a molar scale gave a yield of 81% of 1 - chlorotetrafluoro - 2 - iodoethane.

1 - Chlorotetrafluoro - 2 - iodoethane (15g., 0.057 mole.) and pentane contained in a 3N flask which was cooled to -90°, were slowly treated with n-butyl lithium (0.114 mole.) in pentane (125 mls.) resulting in the formation of a small amount of white precipitate. More precipitate was formed during the warming up period, and tetrafluoroethylene (4.45g., 78%) was evolved. The latter contained a trace of chlorotrifluoroethylene as was shown by analytical V.P.C. with silicone trimer as stationary phase at 0°, using authentic samples of both tetrafluoroethylene and chlorotrifluoroethylene to compare retention times.

Most of the precipitate dissolved on the addition of water, but a small amount remained undissolved; this was consistent with the

precipitate being mainly lithium chloride with a trace of lithium
fluoride.

1,1,2 - Trichlorotrifluoroethane.

Pentane (20 mls.) contained in a flask cooled to -78°, was treated
simultaneously with 1,1,2 - trichlorotrifluoroethane (19.3g.,0.103 mole.
in pentane (25 mls.) and n-butyl lithium (0.206 mole.) in pentane
(174 mls.). Chlorotrifluoroethylene (9.5g., 78.5%) was evolved on
warming to reflux and was characterised by its infrared spectrum and
coincident retention time with an authentic sample using analytical
V.P.C. with tricresyl phosphate as stationary phase at room temperature
also, lithium chloride was precipitated and characterised later by its
solubility in water. The unreacted n-butyl lithium was hydrolysed with
water forming two clear layers. The pentane portion was shown to
contain n-butyl chloride (10.8g., 80%); this amount was determined by
making up test mixtures of authentic n-butyl chloride in pentane and
comparing peak areas on analytical V.P.C. using tricresyl phosphate
as stationary phase at 160°. The pentane from the organic layer was
then removed by distillation through a concentric tube column (22
theoretical plates), and the residue (3.0g.) was shown by analytical
V.P.C. under identical conditions to the above, to contain six
components: pentane, octane, n-butyl chloride, n-butyl bromide all
characterised by coincident retention times with authentic samples,
and two other components. These latter were isolated by preprative
scale V.P.C. using tricresyl phosphate as stationary phase at 148°,
nitrogen flowrate 120 mls./min., but were found to contain neither
chlorine nor fluorine.

Dichlorodecafluorocyclohexane.

This was isolated from the reaction between cobalt trifluoride and hexachlorobenzene and consisted of a mixture of the 1,2; 1,3; and 1,4 - dichlorodecafluorocyclohexanes.[22]

Pure dry heptane (15 mls.) contained in a 3N flask was cooled to -78° and a solution of dichlorodecafluorocyclohexane (15.7g.,0.045 mole.) in heptane (25 mls.) was added dropwise simultaneously with a solution of n-butyl lithium (0.090 mole.) in heptane (164 mls.). The reaction was slowly warmed as before and at -20° an aliquot (1 ml.),was removed and hydrolysed. Titration of this sample showed that all the n-butyl lithium had reacted. Volatile material (6 g.) was separated from the solvent by refluxing,using a Friedrich condenser and cooled trap (-78°). Preprative scale V.P.C. using tricresyl phosphate as stationary phase at room temperature, nitrogen flowrate 110 mls./min., separated this volatile material into the following three components:

Decafluorocyclohexene: this was only formed in very small amounts (approx. 0.1g.) and was identified by its coincident retention time with an authentic sample on analytical V.P.C. using tricresyl phosphate as stationary phase at room temperature, and also by its identical infrared spectrum with this authentic sample (I.R. Spectrum No.26b)

Octafluorocyclohexa-1: 4-diene: this was formed in roughly the same amount as the decafluorocyclohexene and was identified by an identical procedure. (I.R. Spectrum No.27).

Chlorononafluorocyclohexene (2.0g., 14.8%) (Found: F,58.1; CI,13.8; M.279. C_6F_9CI requires: F,61.4; CI,12.8%; M.278.5).(I.R.Spectrum No.28). This compound was easily oxidised by potassium permanganate in acetone

solution which strongly indicated unsaturation. This unsaturation was confirmed by two peaks at $1761(m), 1698(w)$ cms^{-1} in infrared spectrum which is the region where characteristic frequencies of the carbon-carbon double band are observed.

Octafluorocyclohexa-1: 3-diene: roughly the same amount was formed as decafluorocyclohexene, and the identification procedure was identical (I.R.Spectrum No.29).

No sign of any unreacted dichlorodecafluorocyclohexene was observed among the products.

Reaction with Dichlorodecafluorocyclohexane in Pentane Solution.

The previous reaction was repeated in pentane solution, but separation of any volatile products from the solvent was found to be impracticable. Lithium fluoride and chloride (2.7g.) were filtered from the reaction mixture, and pentane was distilled through a packed column. The residue from this distillation was shown to contain five components using analytical V.P C. with tricresyl phosphate as stationary phase at 150°. Three of these components were in large excess, two of which were characterised by their retention times on the above mentioned analytical V.P.C. using authentic samples; these were pentane and n-butyl chloride. The other component (1.4g.) was isolated using preprative scale V.P.C. with tricresyl phosphate as stationary phase at 150°, nitrogen flowrate 200 mls./min. (Found: F,47.2; CI,nil; M.299 b.p.152-5°/735 mm. n_D^{20} 1.38063 (I.R.Spectrum No.30). This compound gave a single peak on the analytical V.P.C. under the conditions described above, and was also shown to be unsaturated by its reduction of a 1% solution of potassium permanganate in acetone.

Reaction with 1,4-Dichlorododecafluoro-2, 3-dimethylbutane 1.

$$CF_3 \diagdown CF_3$$

$$CF - CF$$

$$CF_2Cl \diagup CF_2Cl.$$
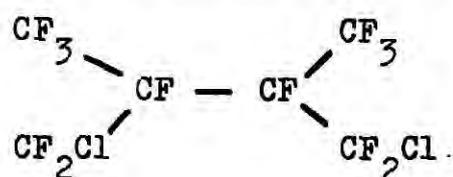
1.

Preparation of 1.

A carius tube was charged with 1-chloro-2-iodohexafluoropropane (40.6g., 0.13 mole.) and mercury (60g.) and was sealed under vacuum. The tube was then shaken whilst in a horizontal position and was irradiated for eight days with ultraviolet light using a Hannovia ultraviolet lamp; the colour changes of the mercury were red, yellow and finally dark yellowish-grey. Volatile material (20.5g.) was removed under vacuum and was found by analytical V.P.C. using silicone elastomer as stationary phase at 100° to consist of a single component; 1,4-dichlorododecafluoro-2, 3-dimethylbutane (20.5g., 85%) (Found: F.61.0; Cl, 19.5; $C_6Cl_2F_{12}$ requires F, 61.45; Cl. 19.15%) b.p. $117.3^{\circ}/$ 765 mm., n_D^{20} 1.32128 (I.R.Spectrum No.31.)

Reaction with n-Butyl Lithium.

A solution of n-butyl lithium (0.0432 mole.) in heptane (68.5 mls.) contained in a 3N flask fitted with a mechanical stirrer, dropping funnel and Friedrich condenser, was cooled to -78° and a solution of 1,4-dich-lorododecafluoro-2, 3-dimethylbutane (8g., 0.0216 mole.) in heptane (10 mls.) was added dropwise over a period of thirty minutes. The reaction was continued by warming the reactants to room temperature over a period of two hours. An aliquot (1 ml.) of this reaction mixture was hydrolysed and a neutral solution was obtained; this showed that all

the n-butyl lithium had reacted. Volatile products were collected
in a cooled trap (-78°) by distillation through a Vigreux column
collecting a fraction boiling range $20 - 98^{\circ}$; a considerable amount
of heptane and n-butyl chloride also distilled. Preprative scale
V.P.C. using tricresyl phosphate as stationary phase at 70°, nitrogen
flowrate 120 mls./min. enabled four cuts of this distillate to be
isolated; each one corresponding to a single peak.

CUT I.

This was obtained in only a small amount and could not be
identified, but its volatility and retention time indicated that it
might be decafluoro-2, 3-dimethylbutadiene $\overline{\overline{\text{ll}}}$.

CUT 11.
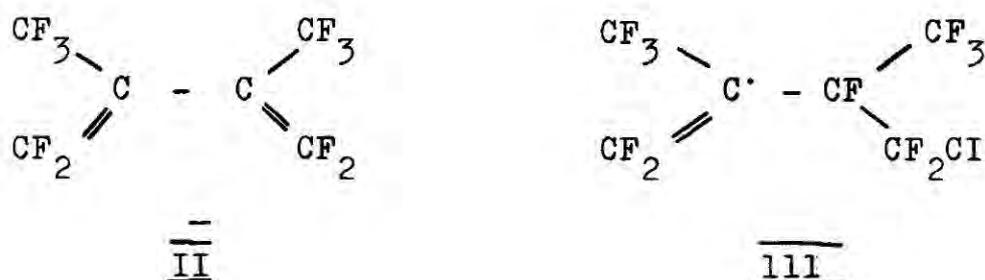
This was characterised as 4 - chloroundecafluoro-2, 3-dimethylbut-
1 - ene $\overline{\text{lll}}$ (1.3g., 22%) (Found: F, 65.6; CI.10.6; M.318. C_6CIF_{10}
requires : F, 66.0; CI.11.2%; M. 316.5) b.p. $86.6^{\circ}/764$ mm. n_D^{20} 1.30611.
(I.R.Spectrum No.32). Reduction of potassium permanganate in acetone
confirmed unsaturation already indicated by the band at 1748 cms.$^{-1}$
in the infrared spectrum.

CUT 111. - Heptane.

CUT 1V. - n-Butyl chloride which was identified by its retention time
on analytical V.P.C., silicone elastomer as stationary phase at 100°

This last component was combined with the residue from the distillation and the total amount of n-butyl chloride (0.82g.,) present was determined by using the analytical V.P.C. described above, comparing peak areas with a test mixture of authentic n-butyl chloride in heptane.

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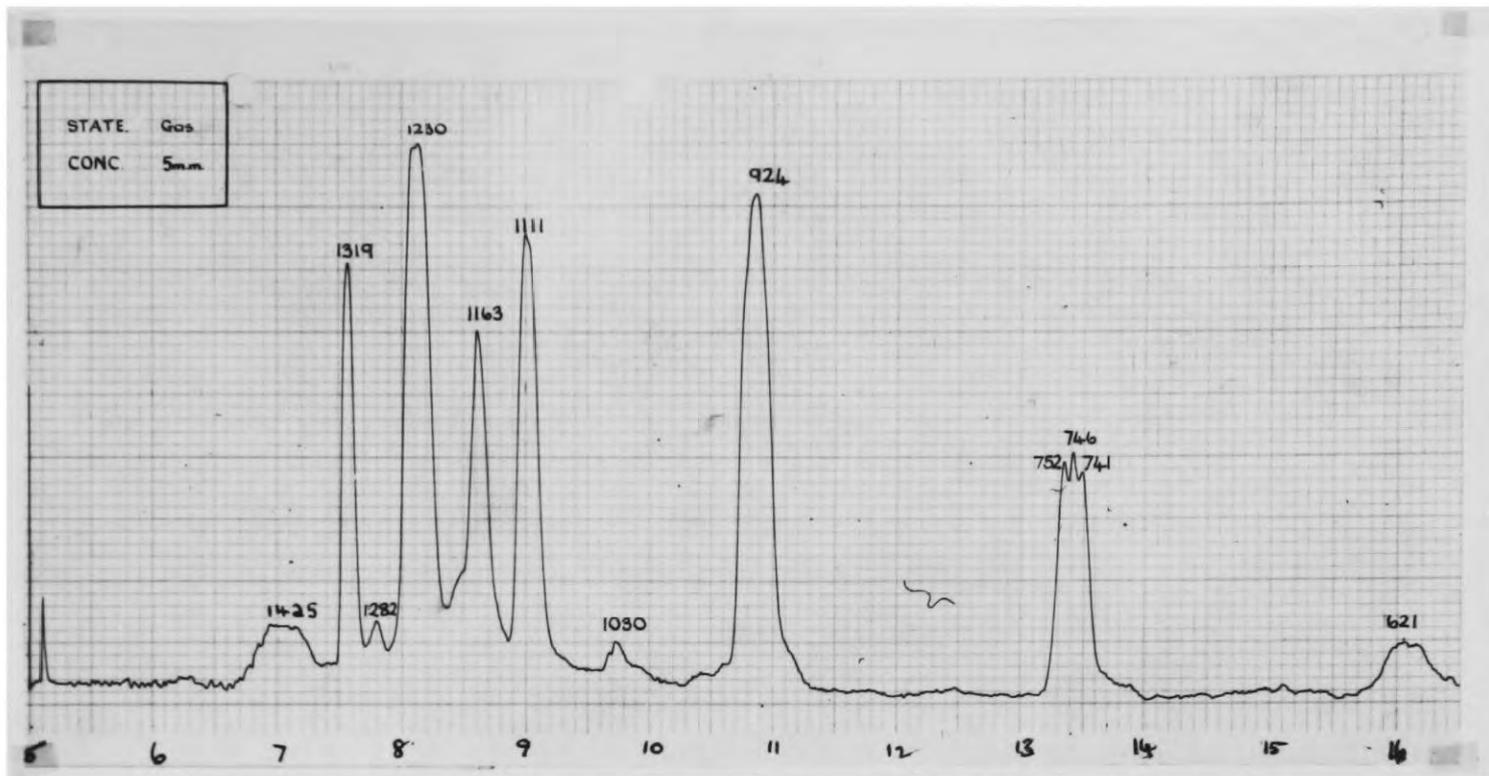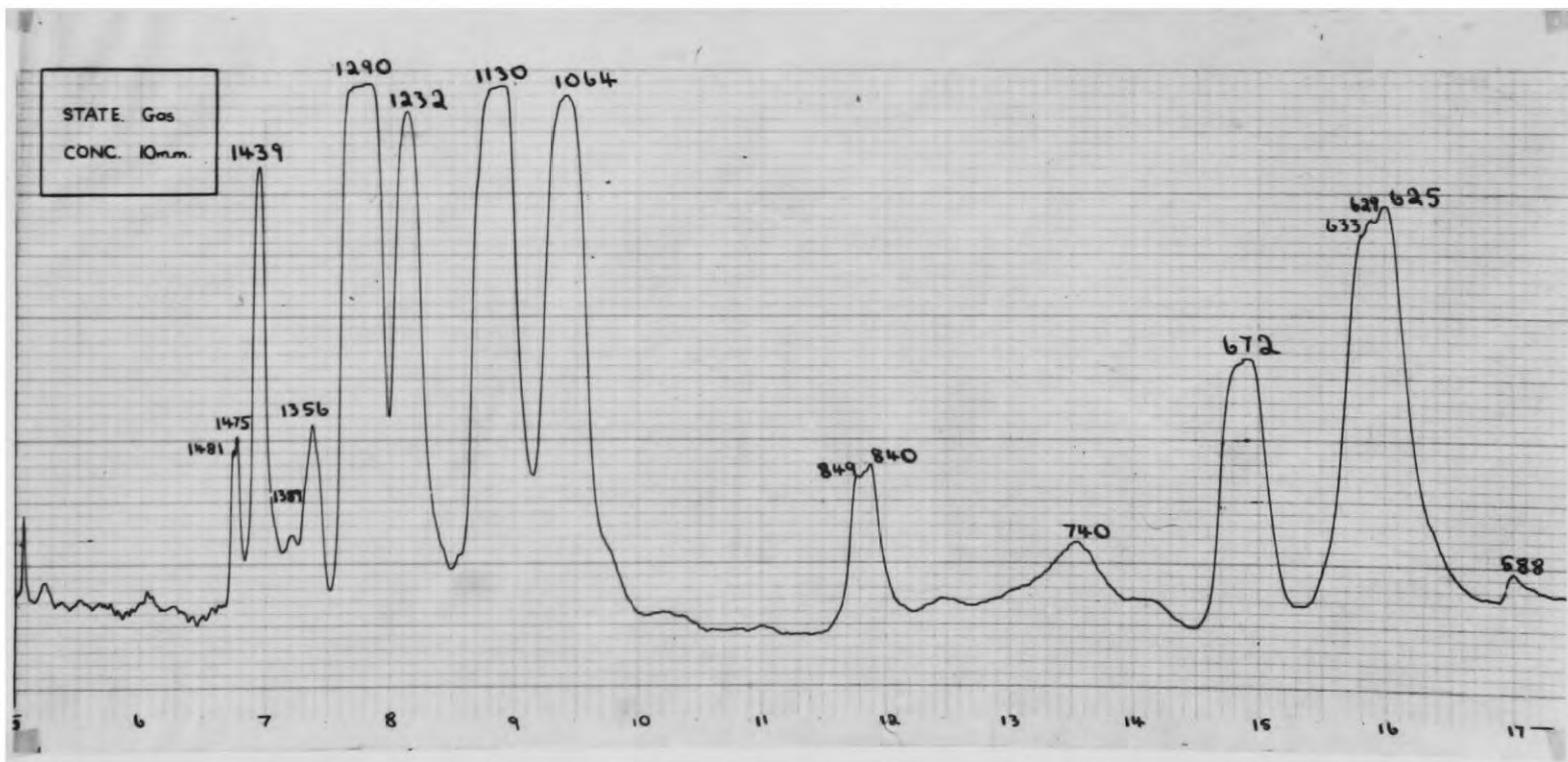
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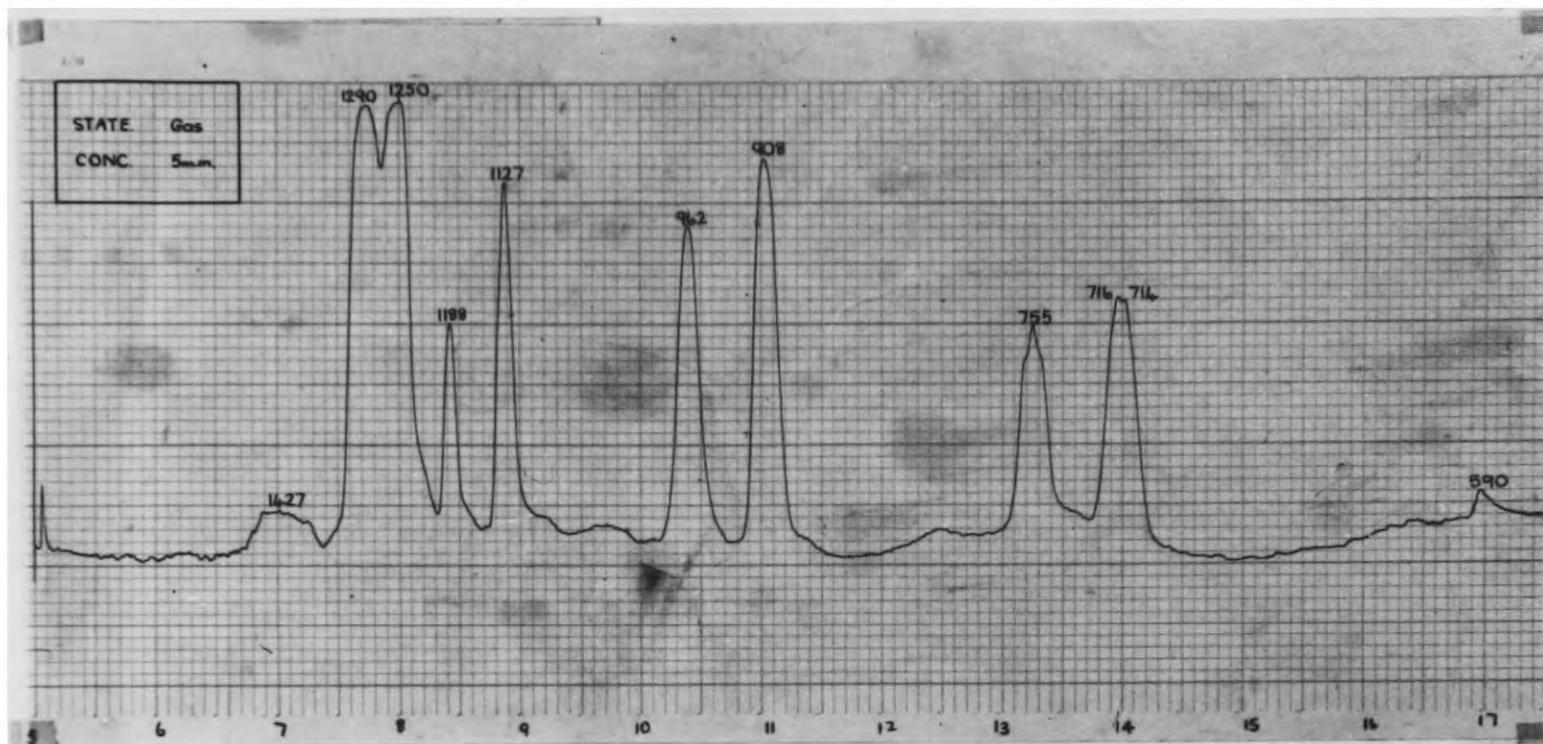
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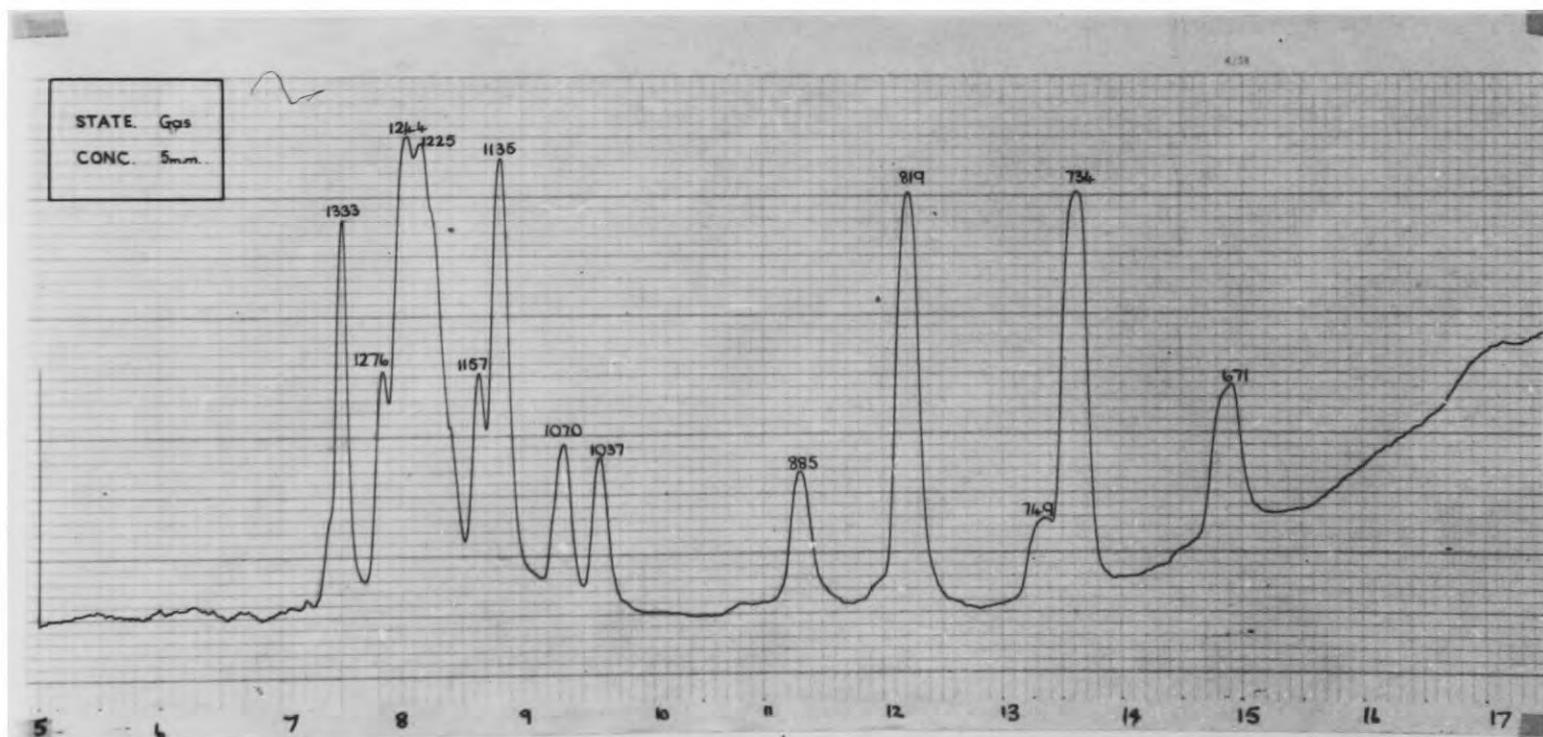
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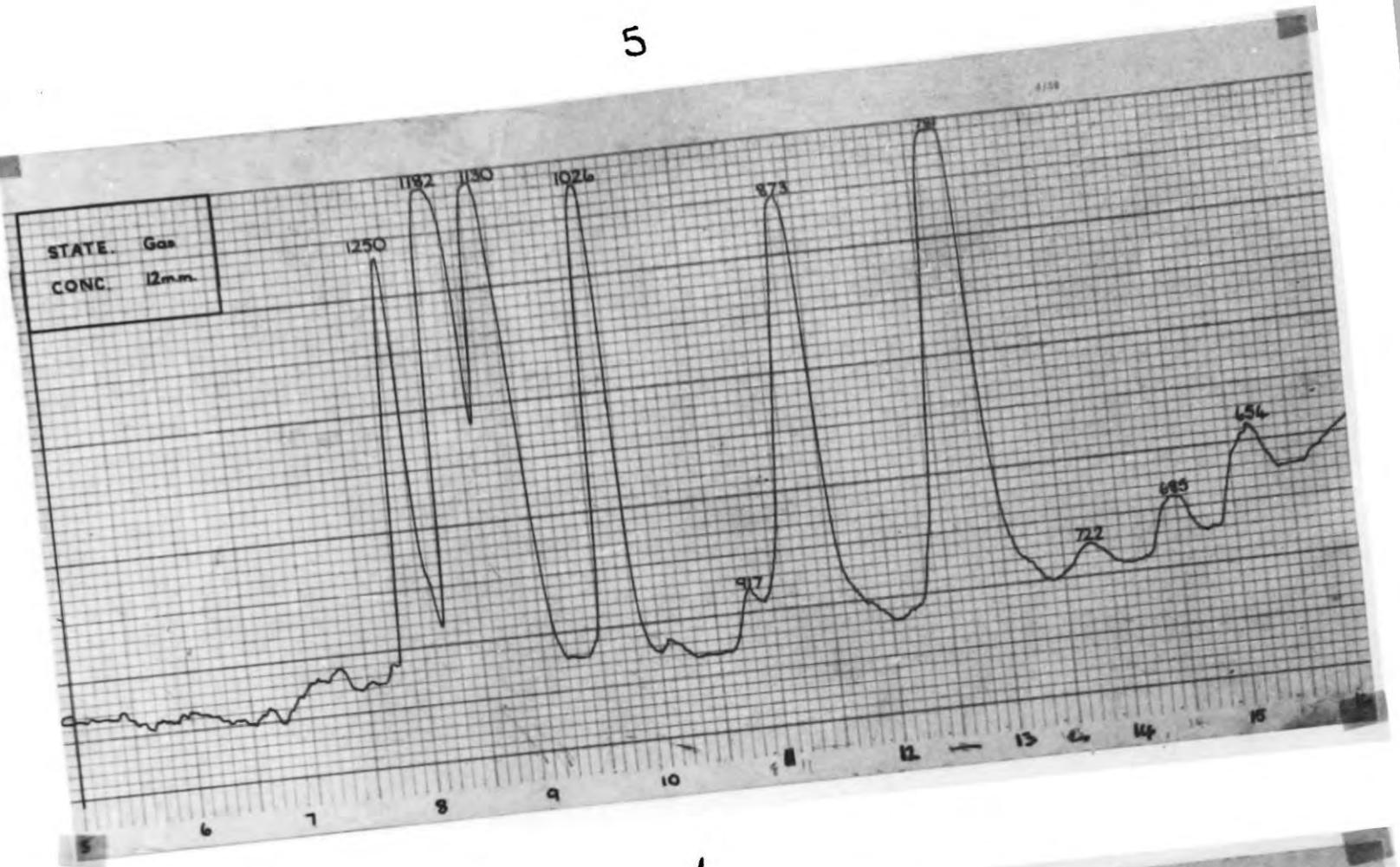
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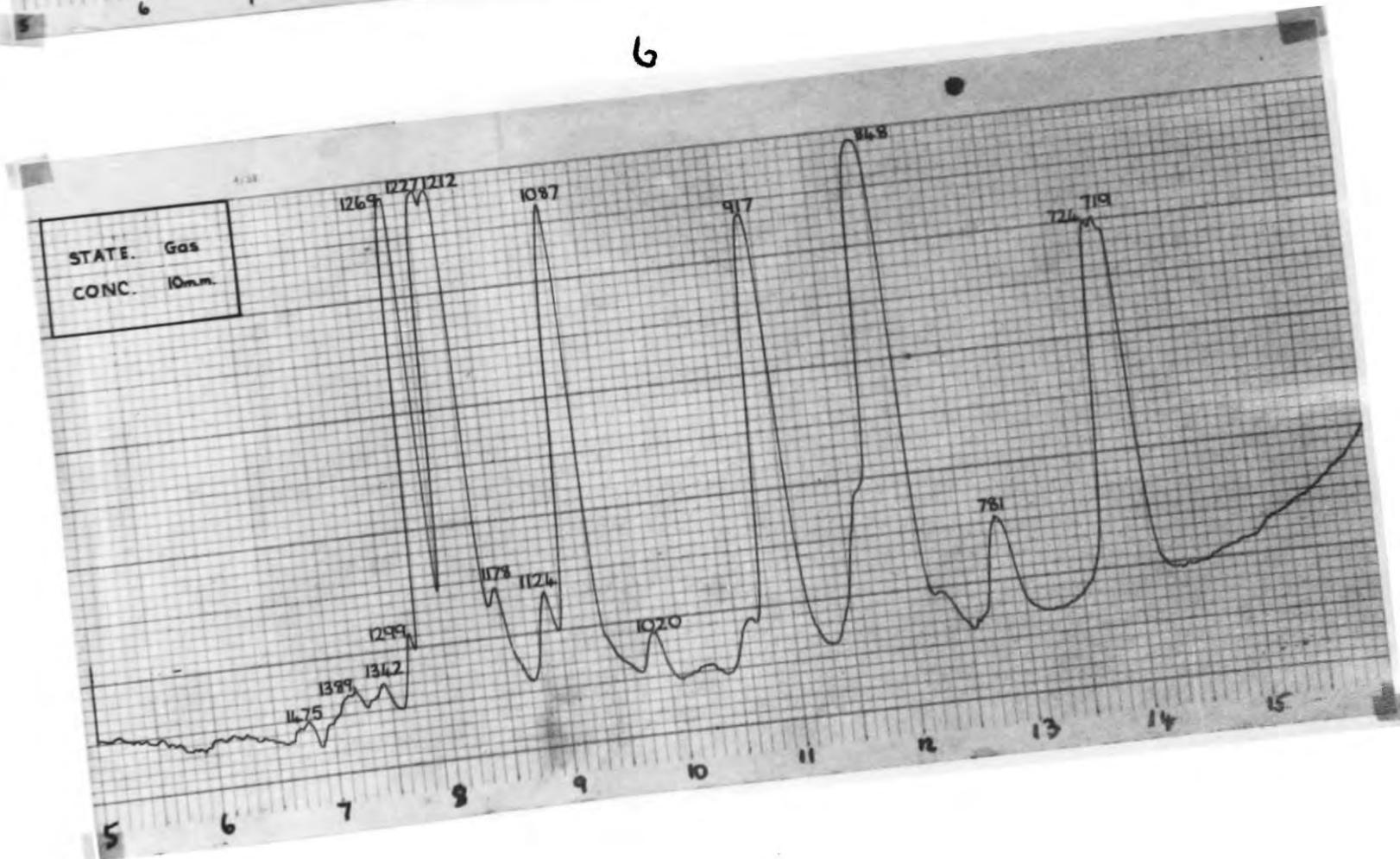
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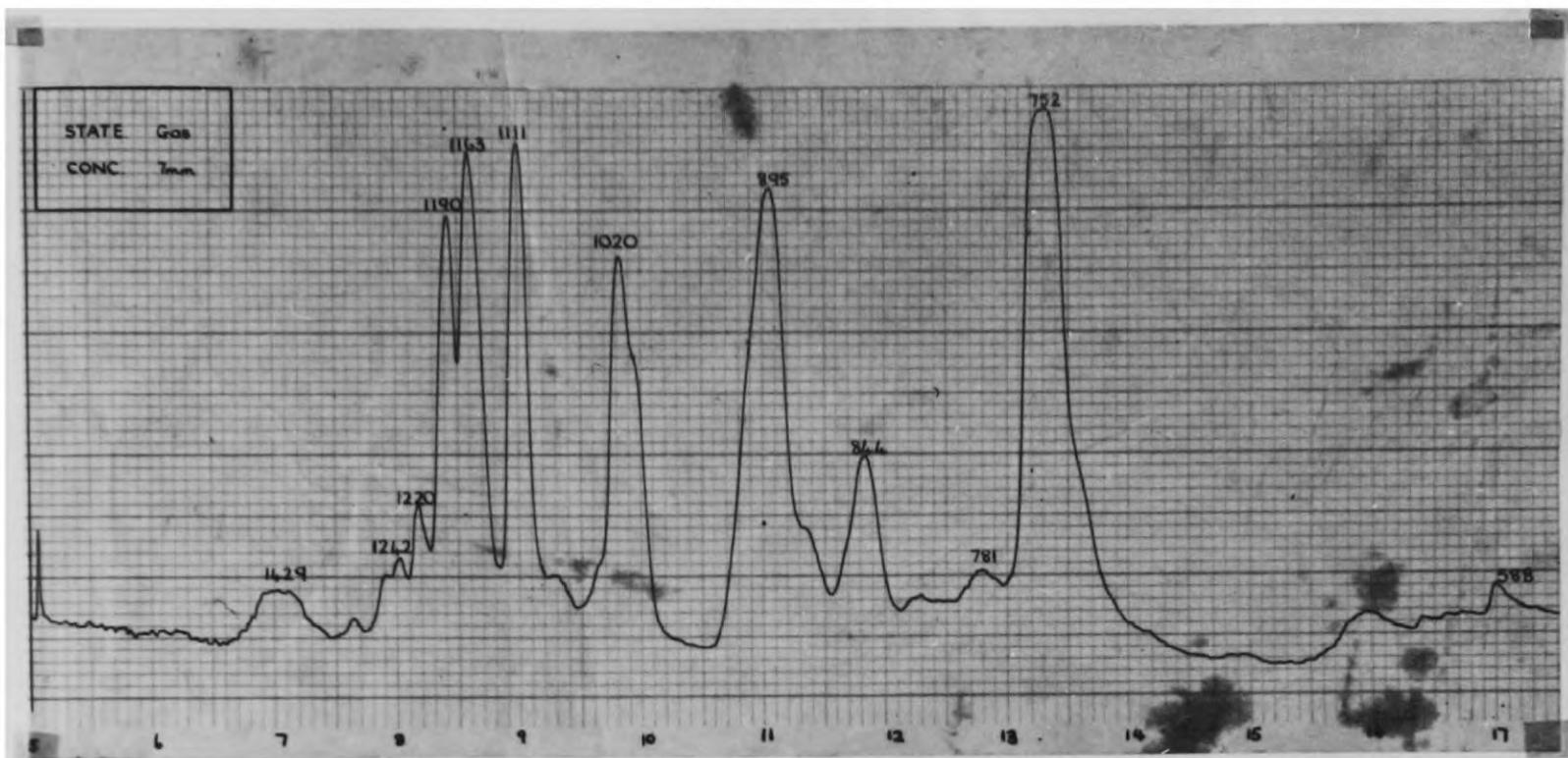
8a.
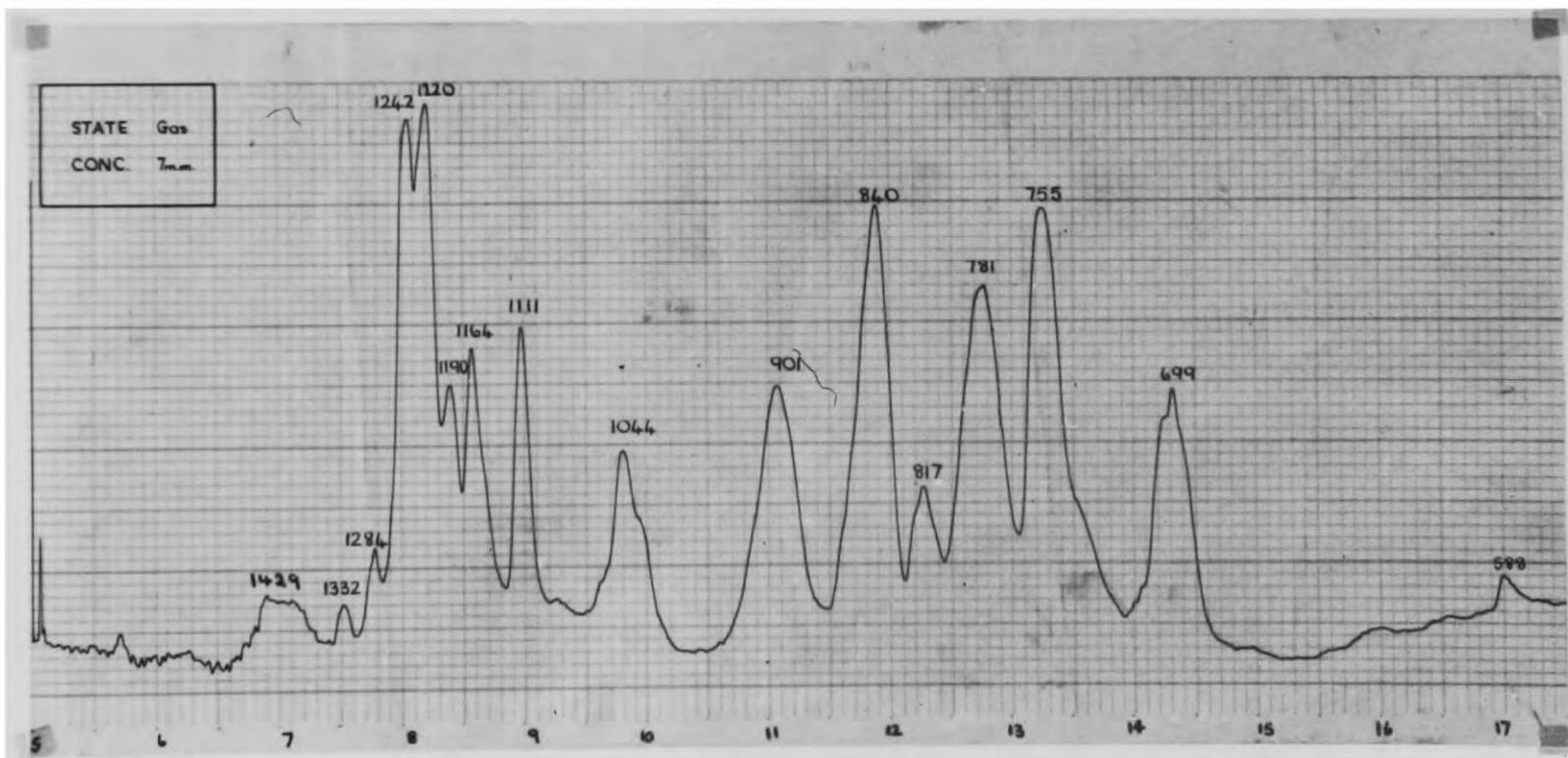
8b.

9

12b.

12

13

14

15

16

144.

19

20

21

22

147.

STATE. Gas
CONC. 8 m.m.

23

STATE. Liquid
CONC. Contact Film

24

STATE. Liquid
CONC. 0·01 m.m.

25

STATE. Liquid
CONC. Contact Film.

26

27

26b

150.

151.

30

31

32

DIAGRAM II

VAPOUR   PHASE   CHROMATOGRAPHY
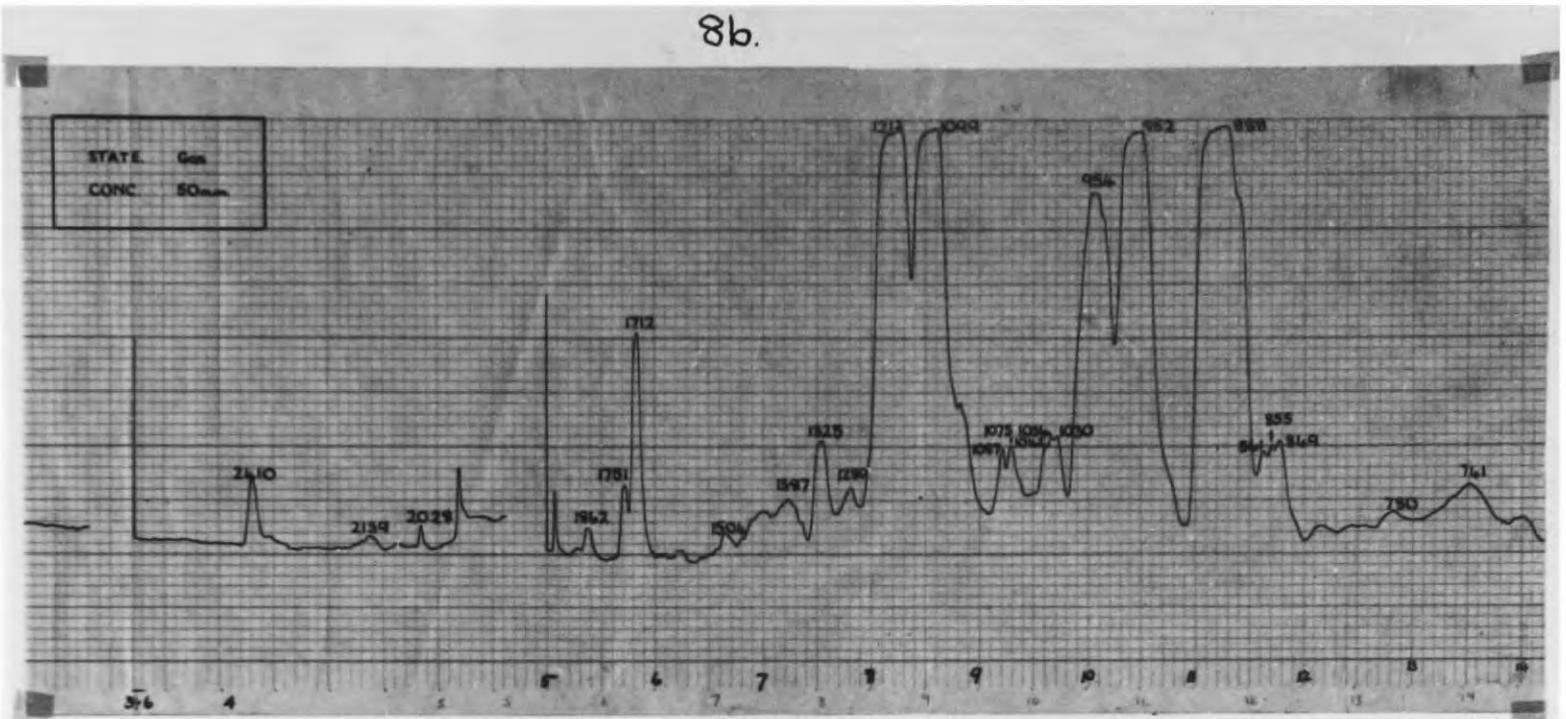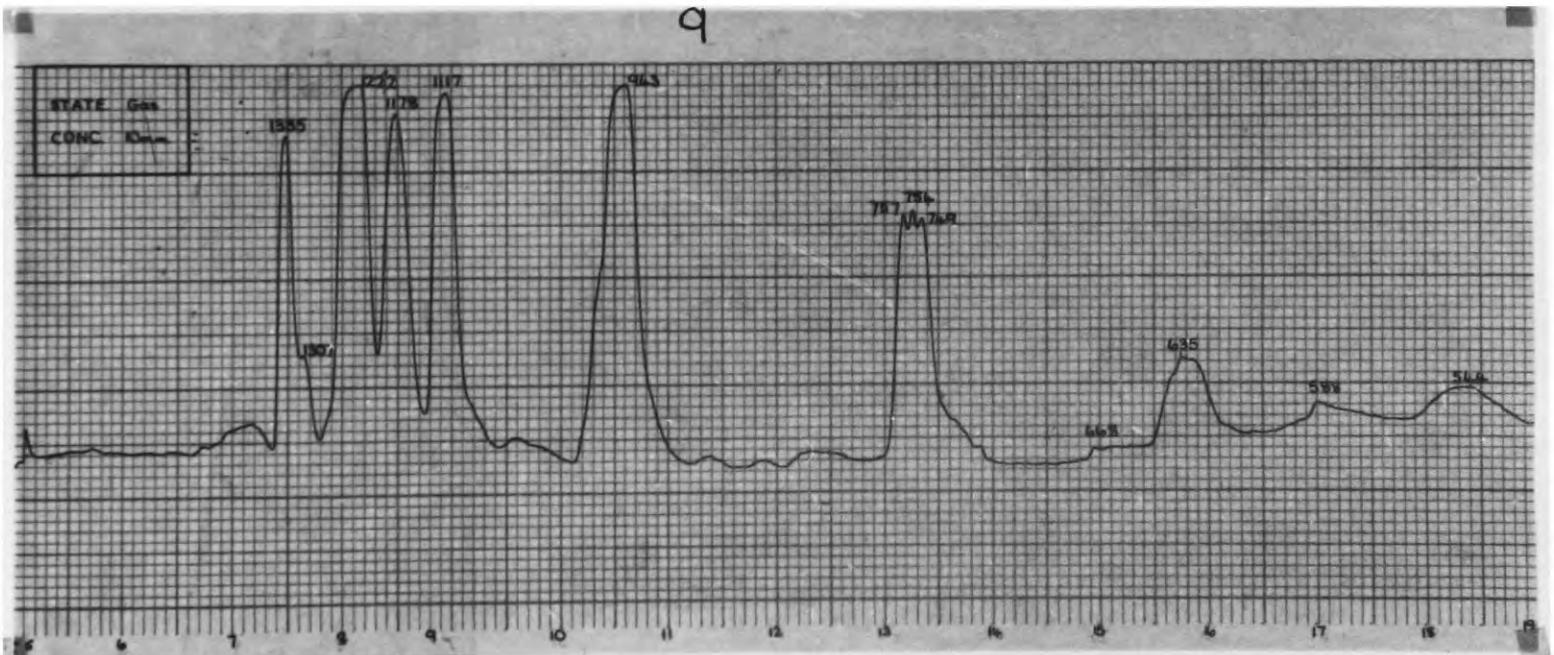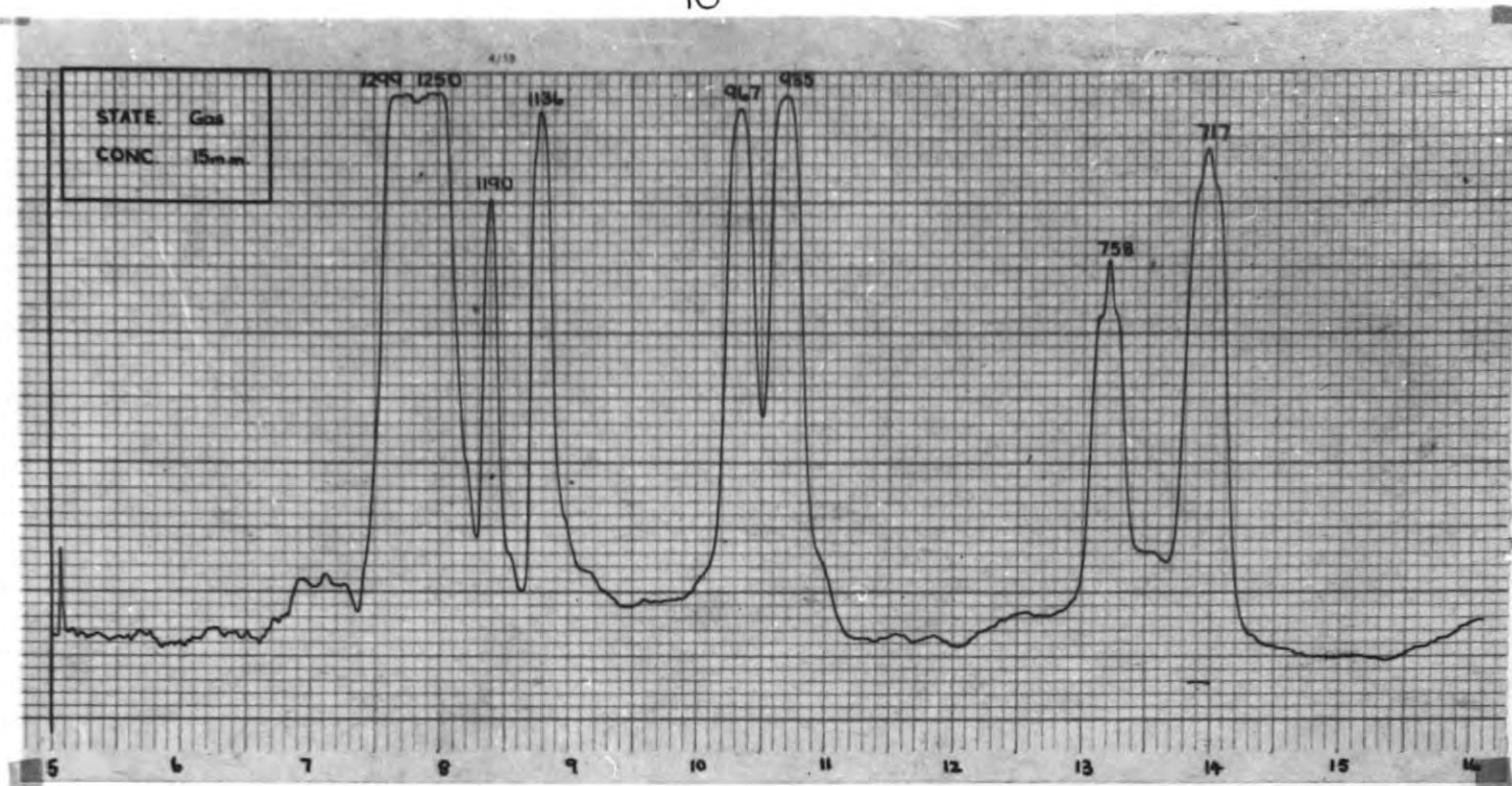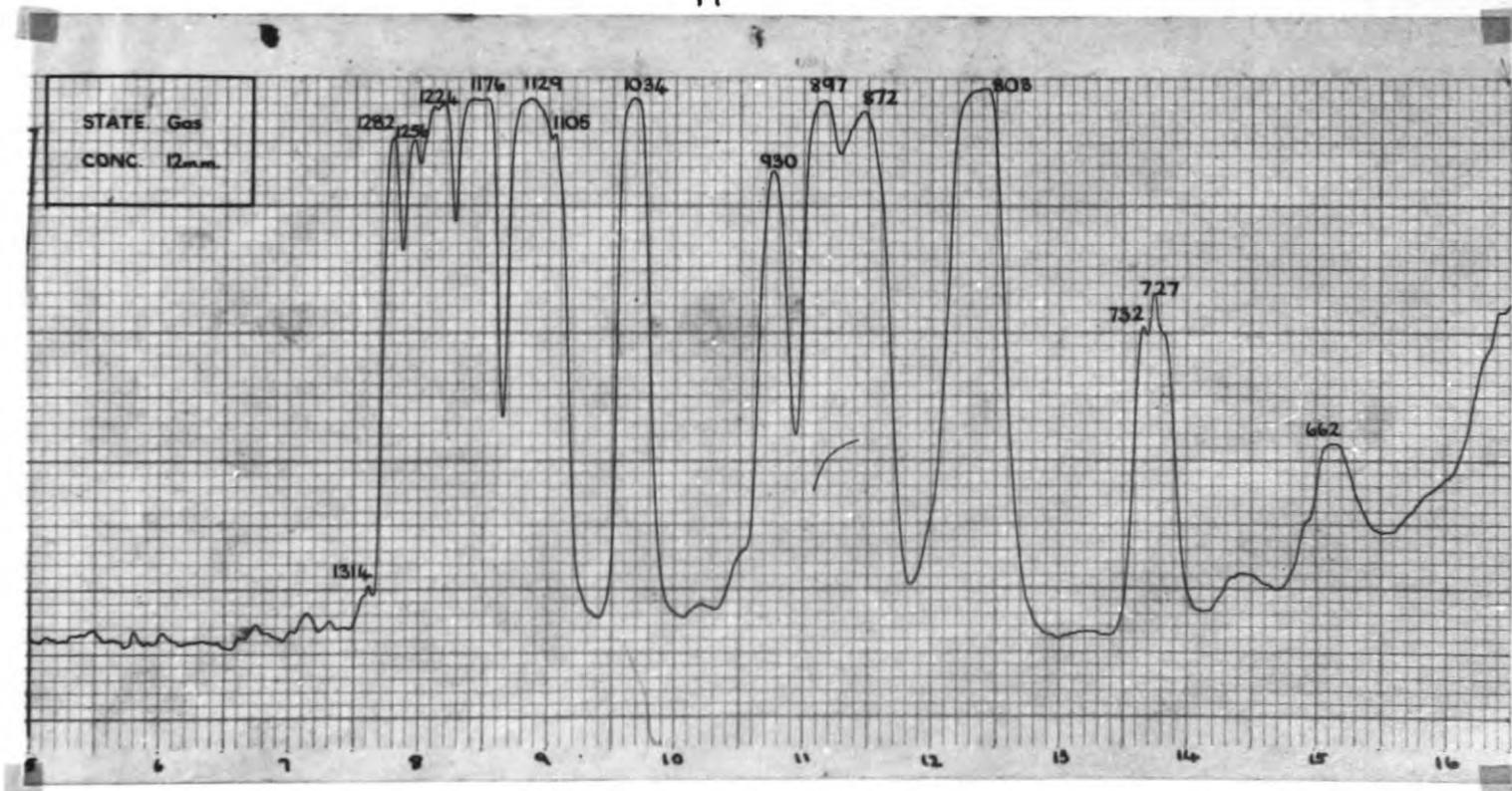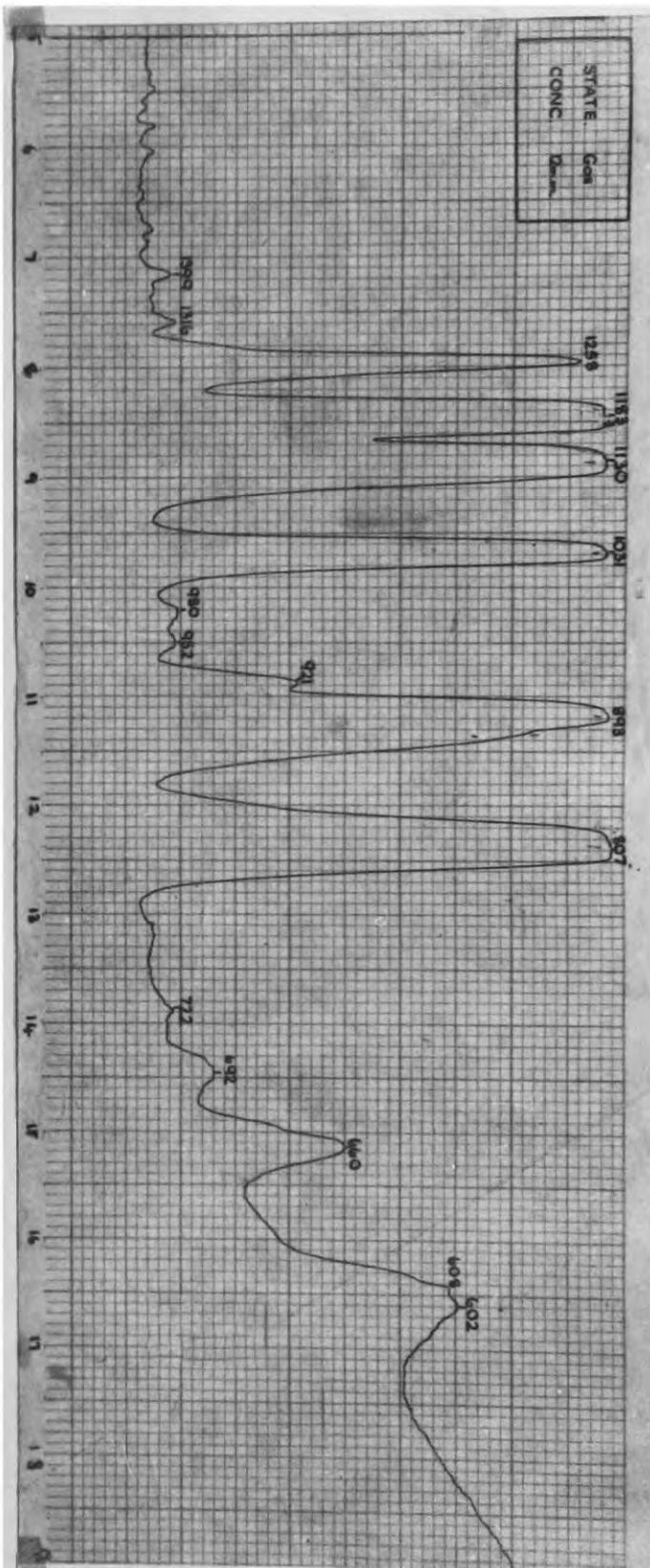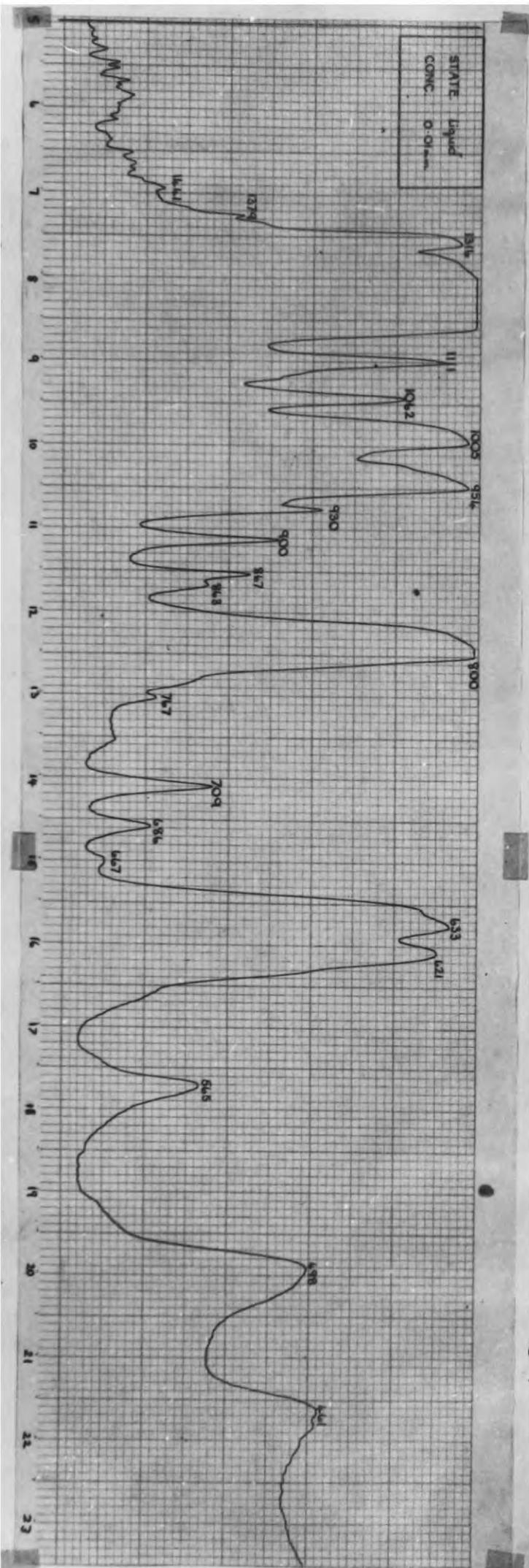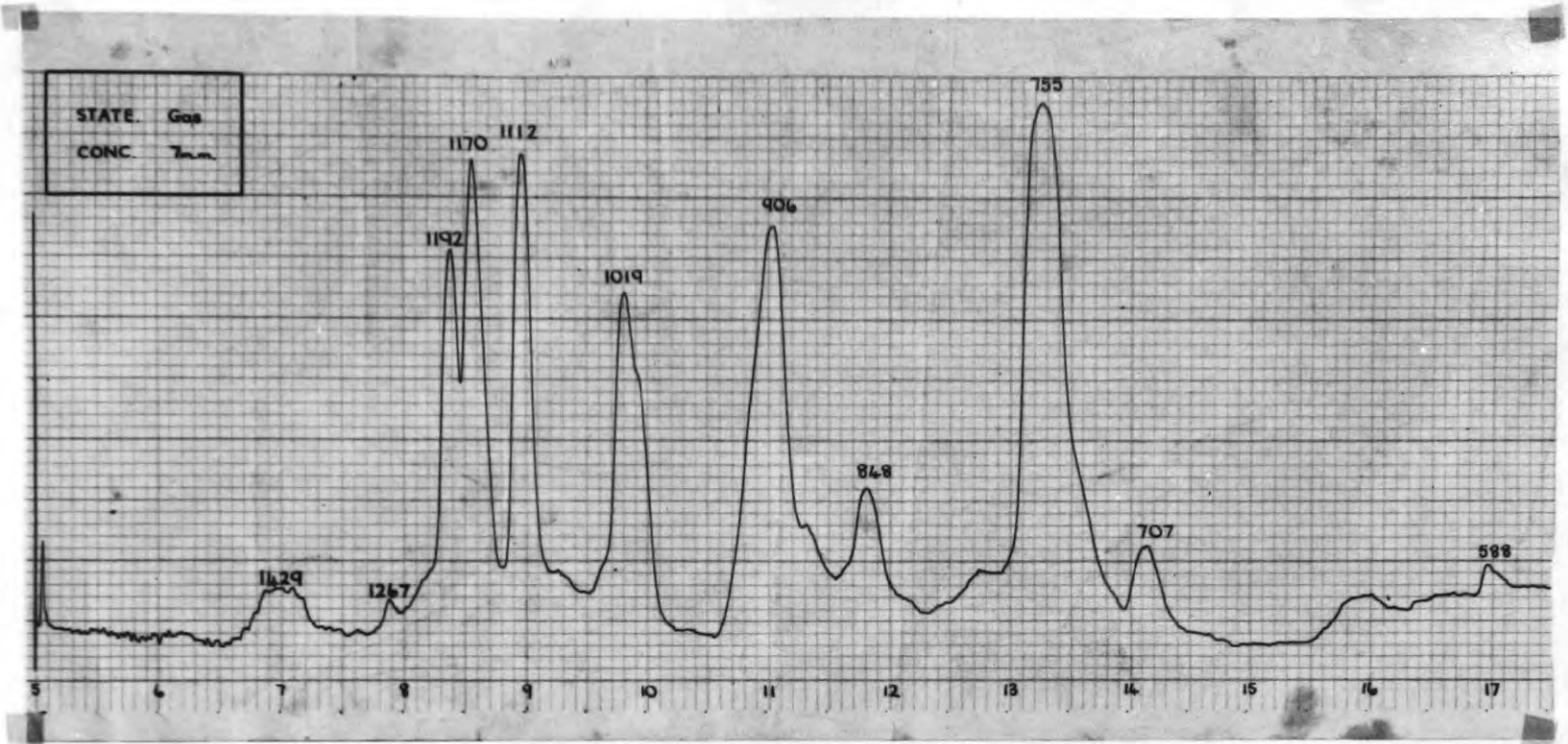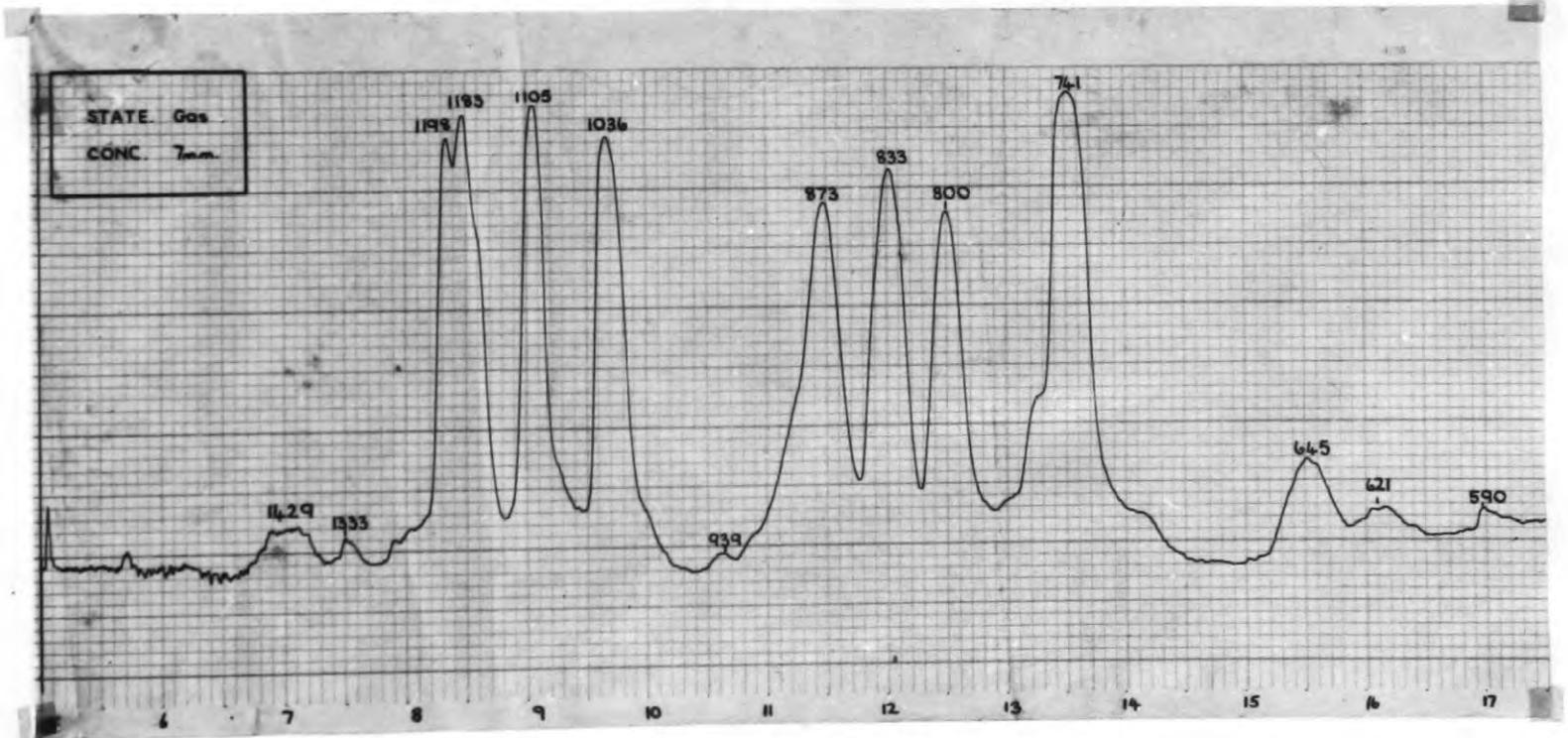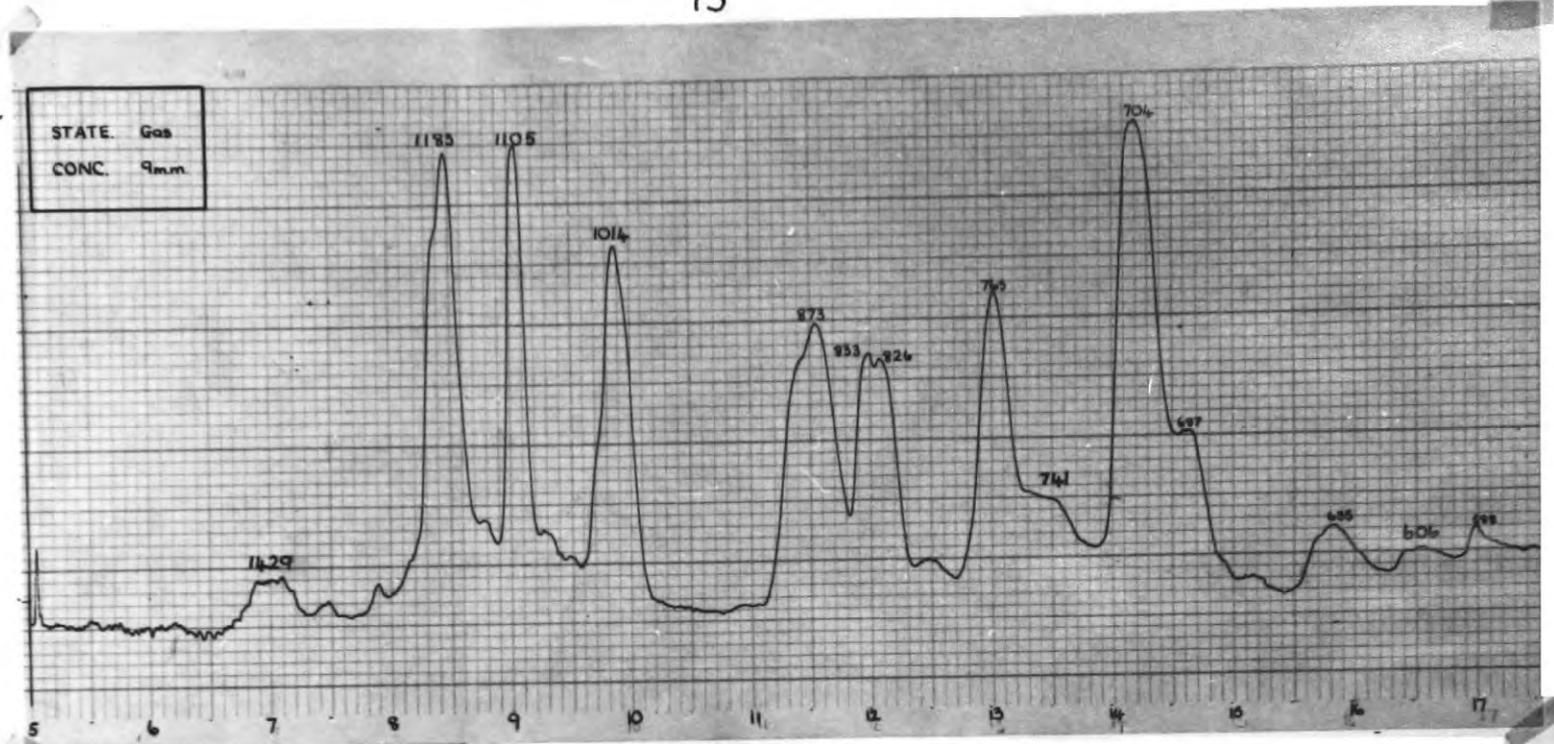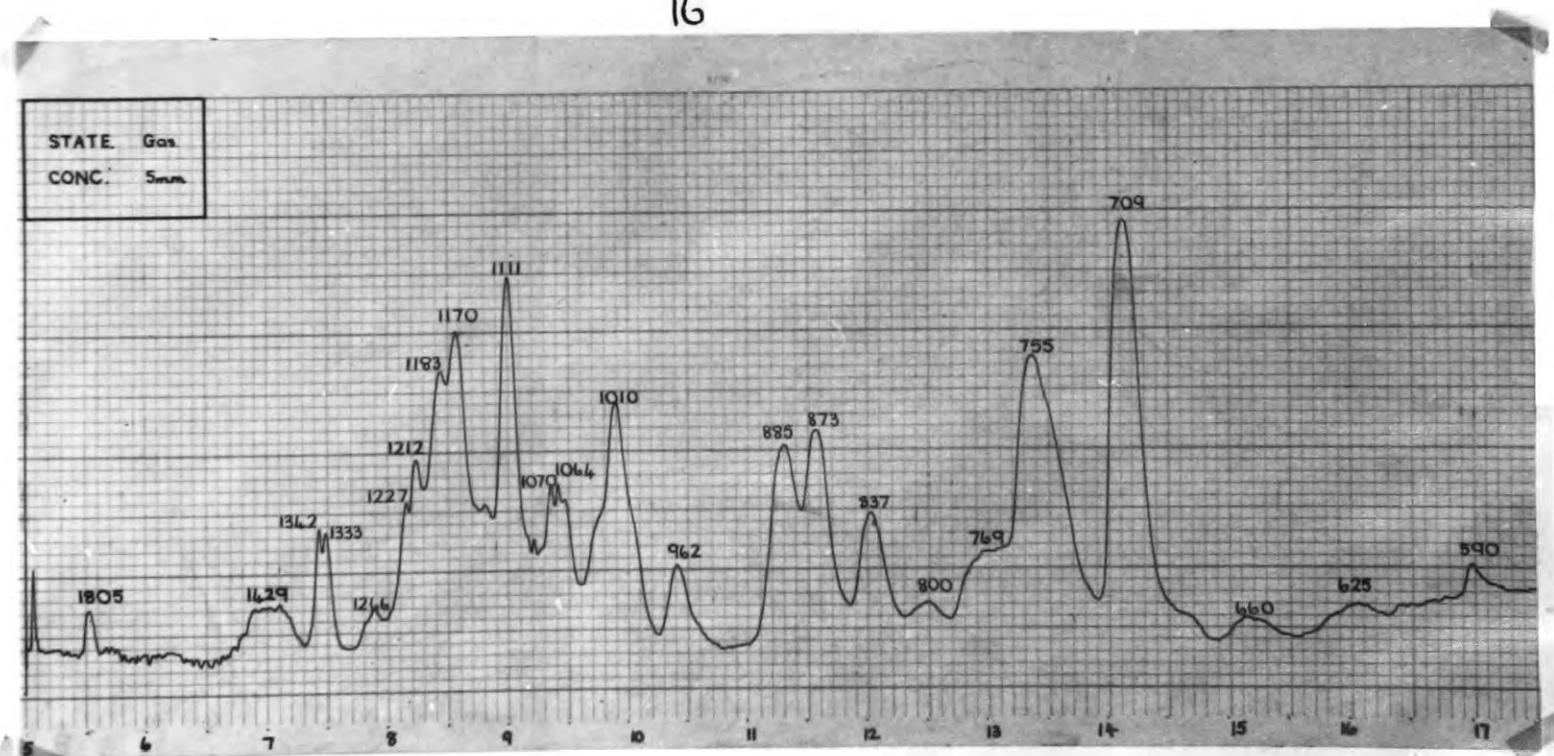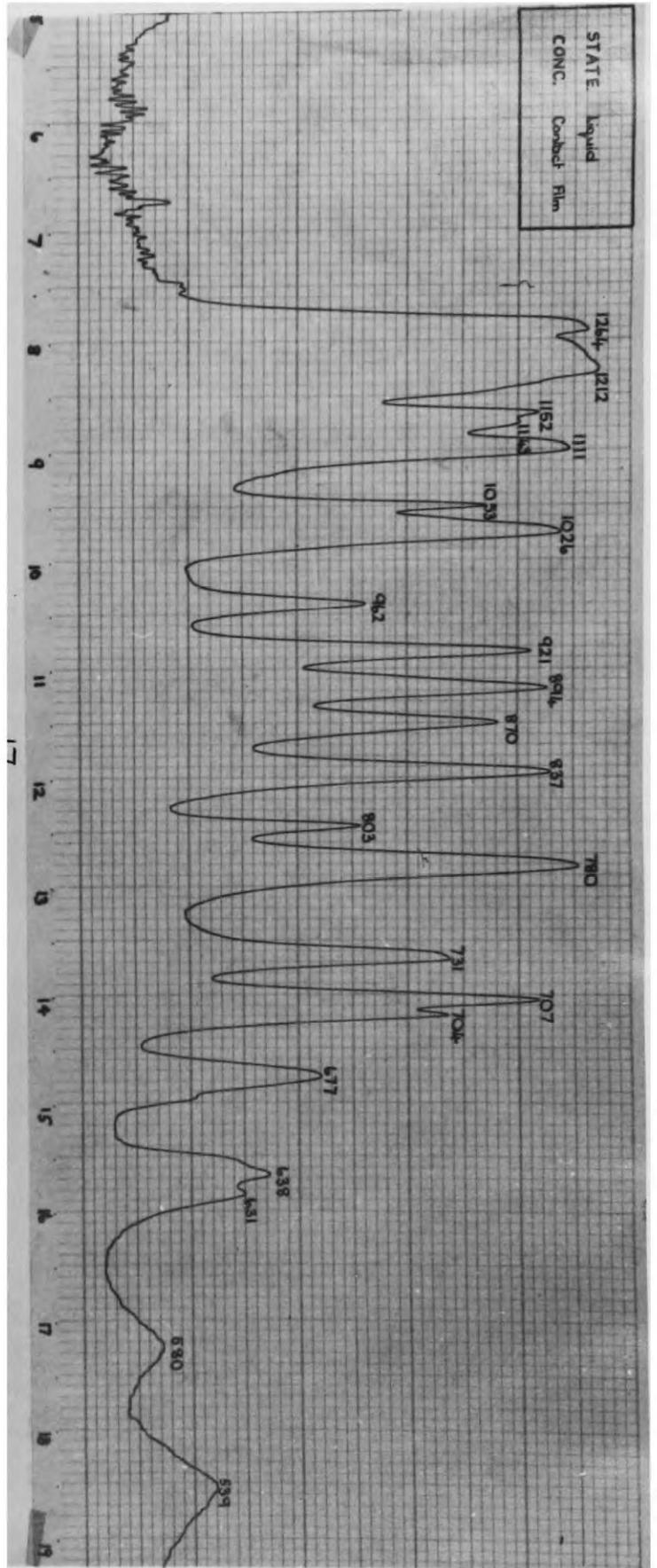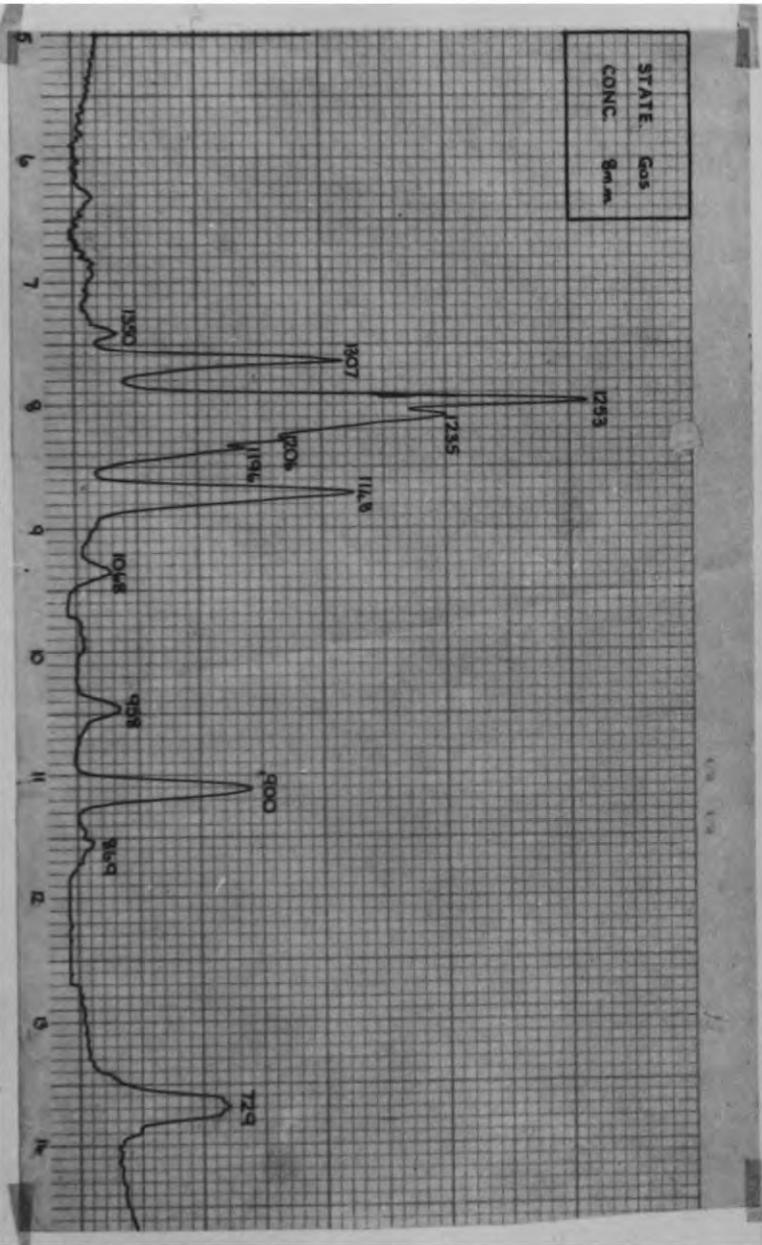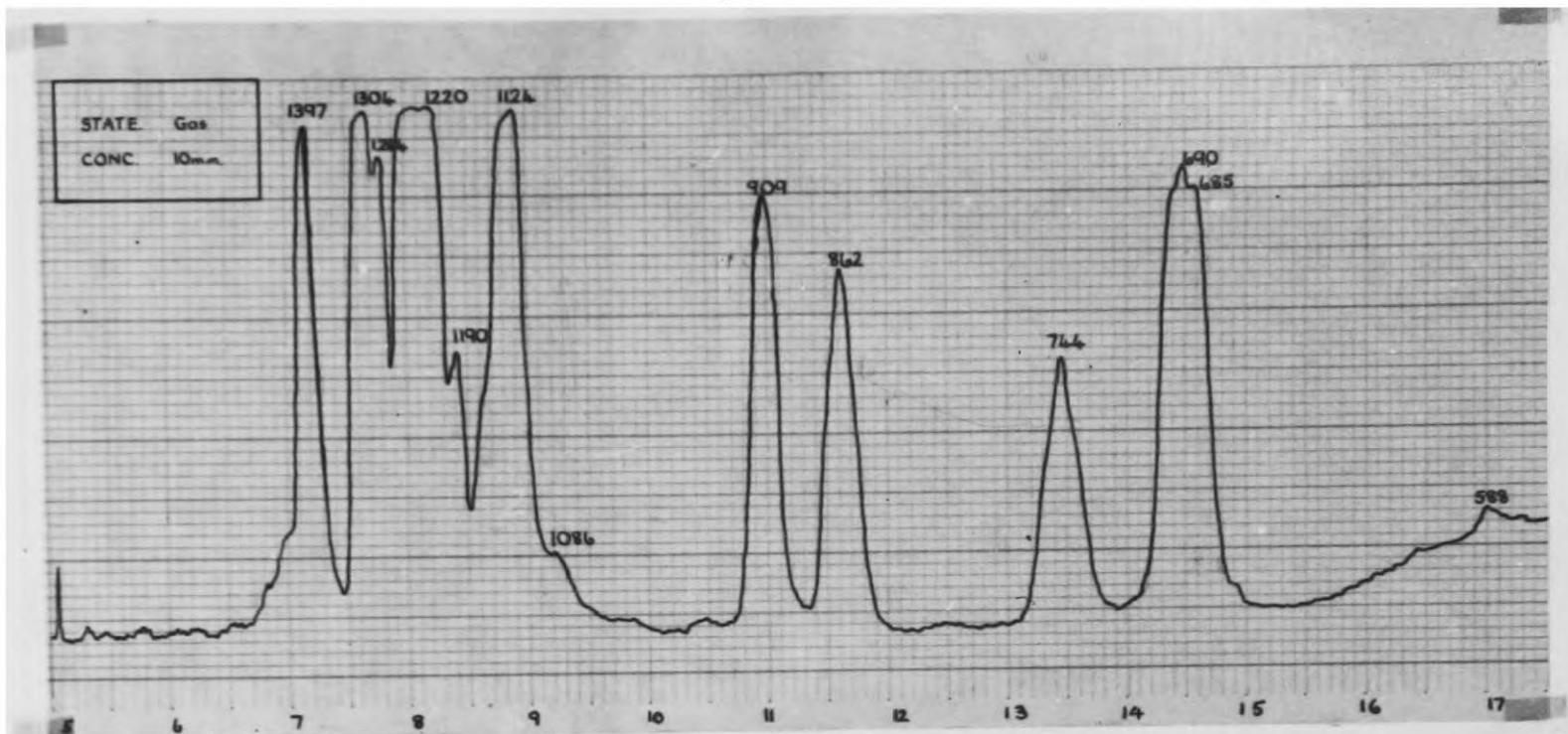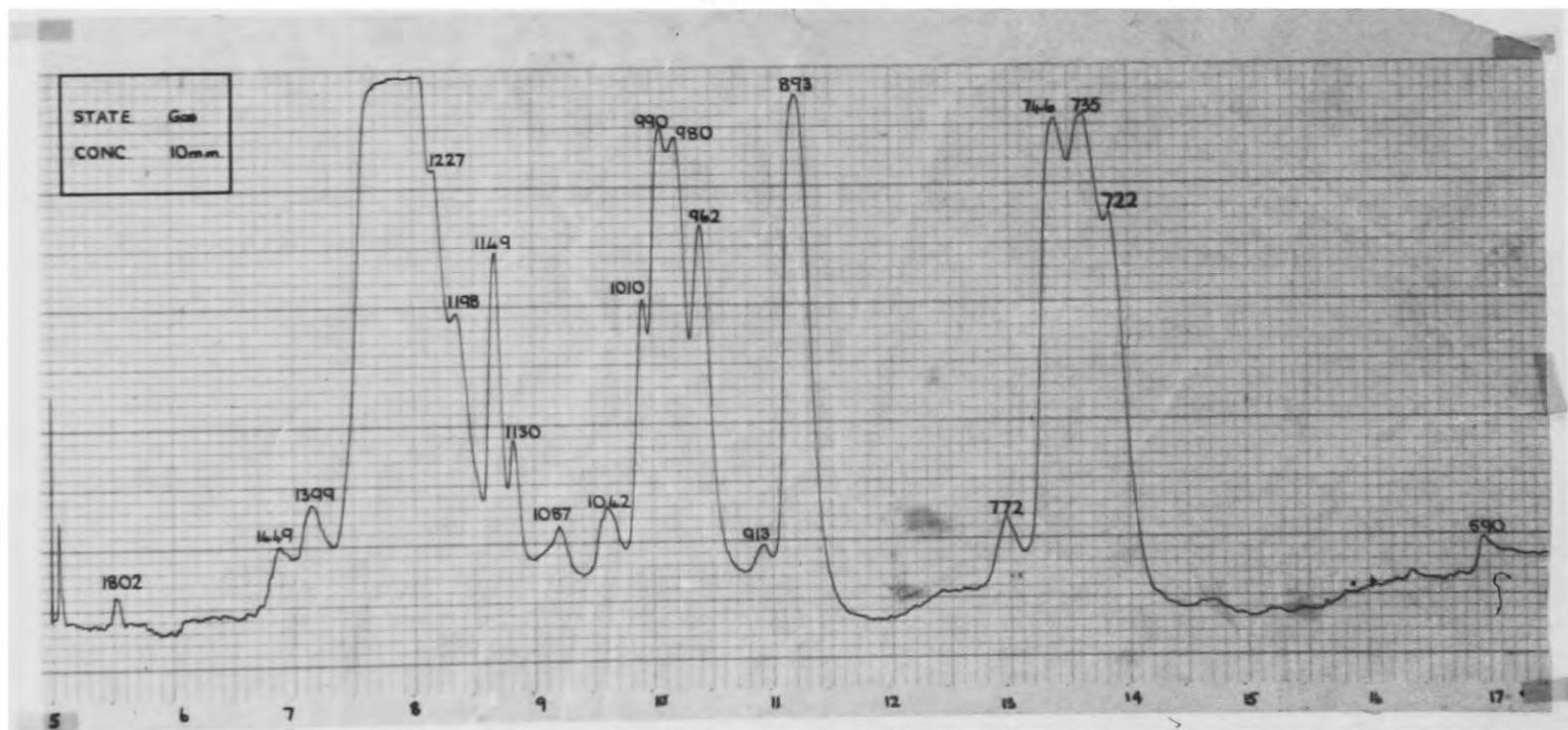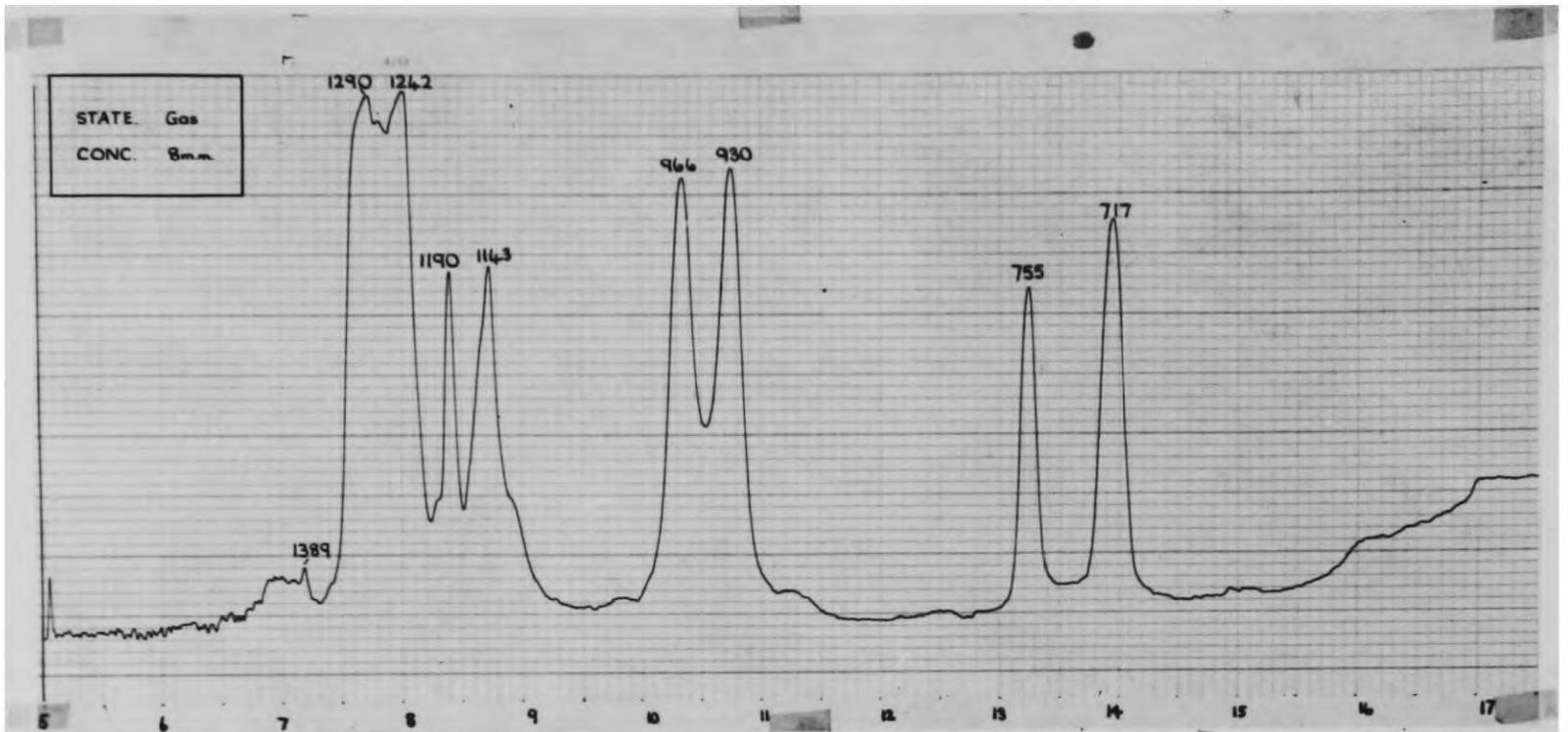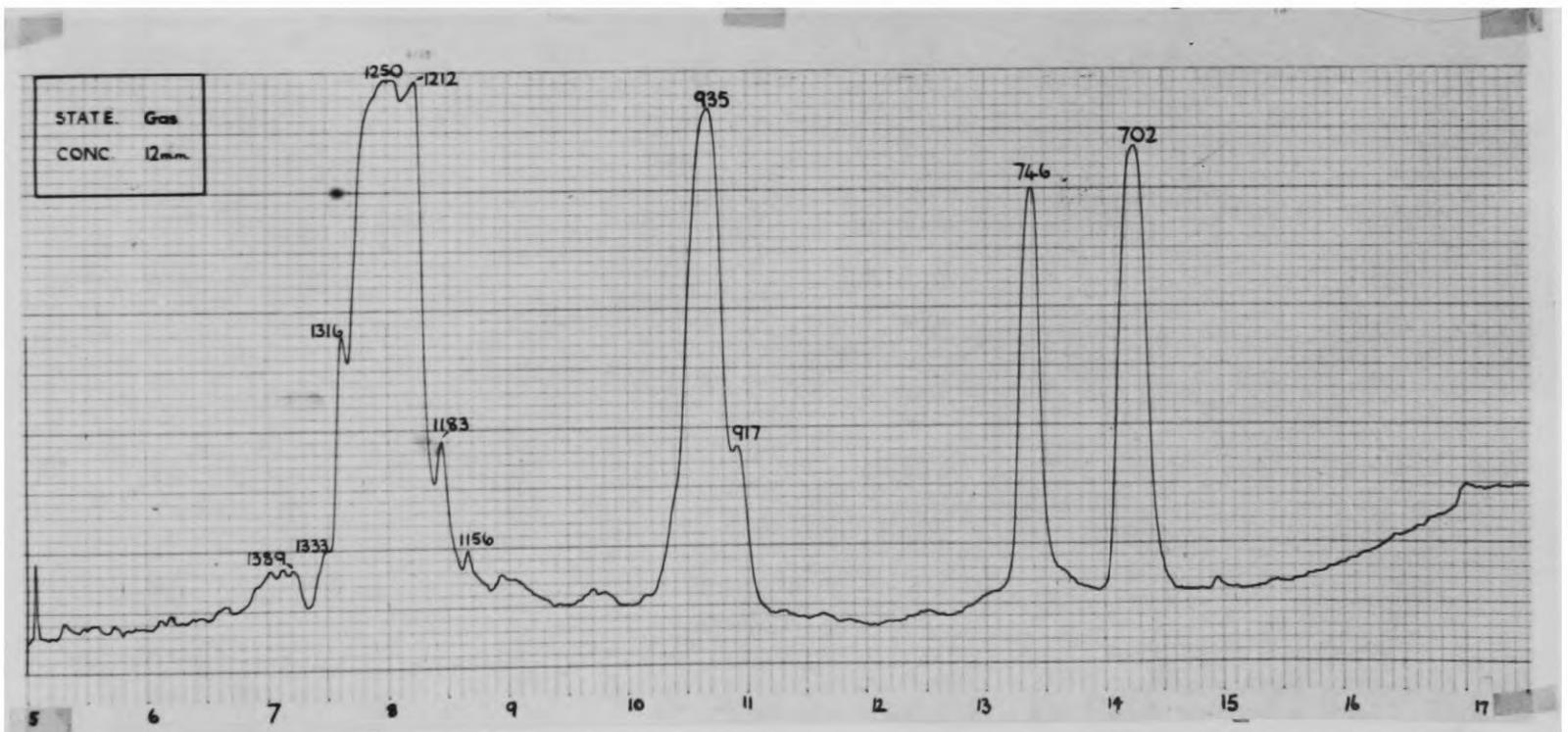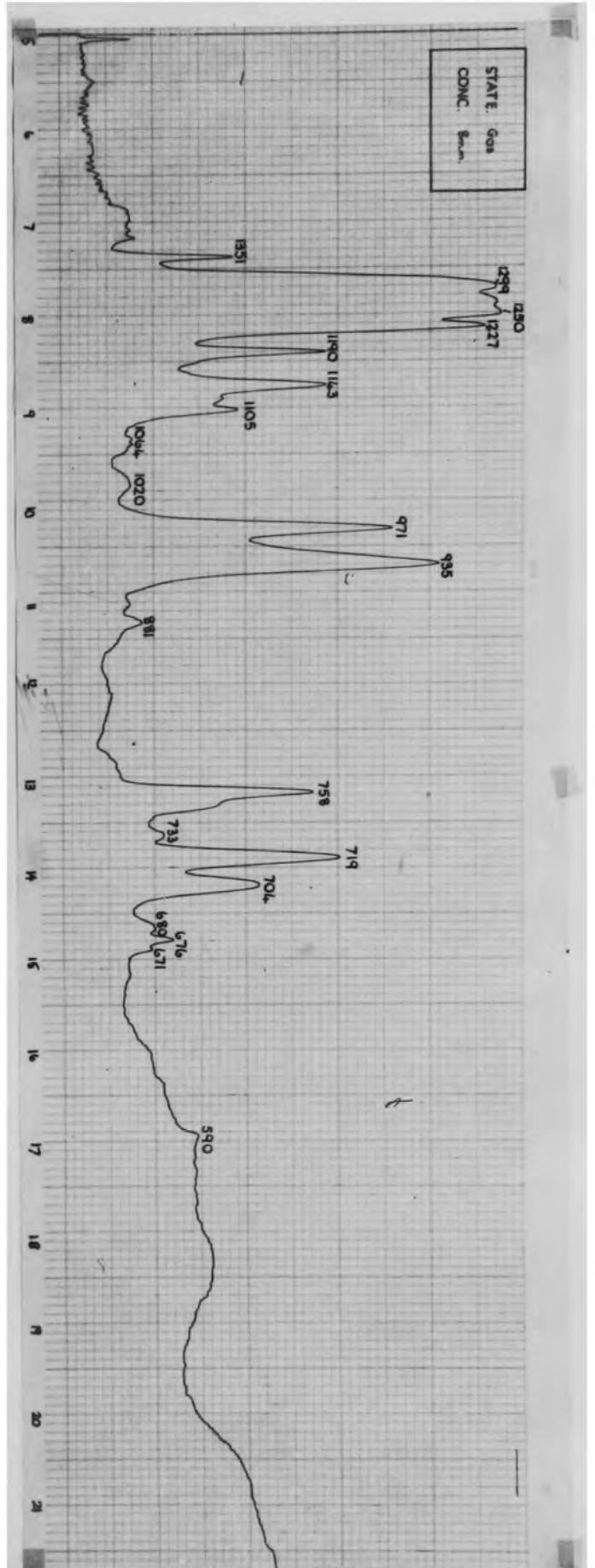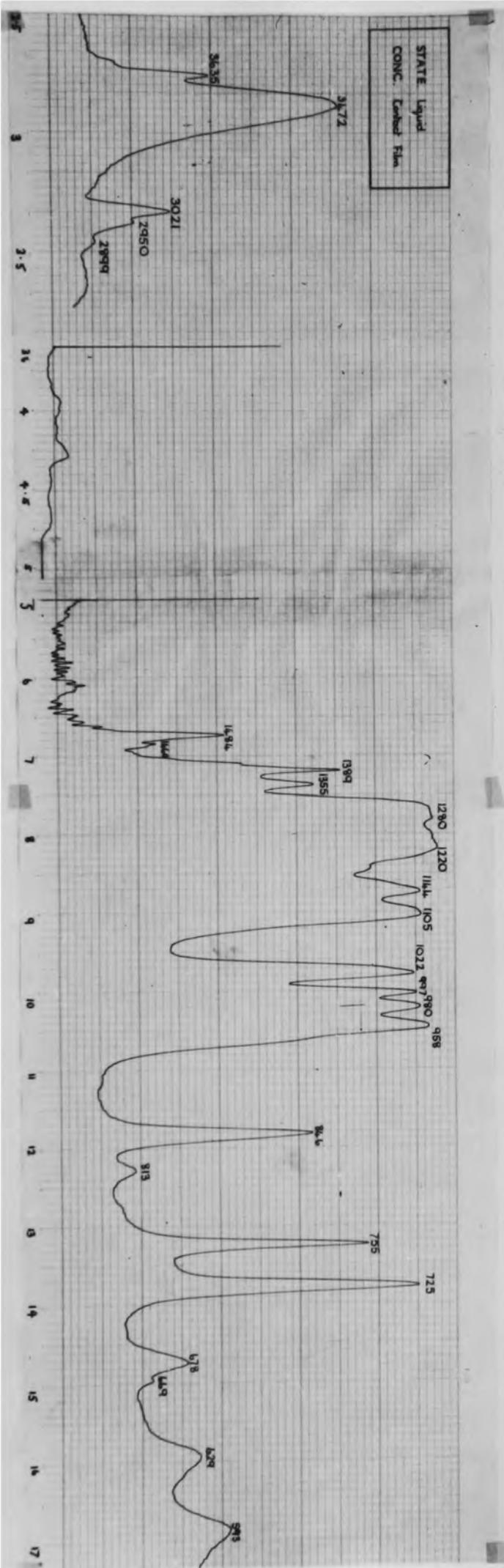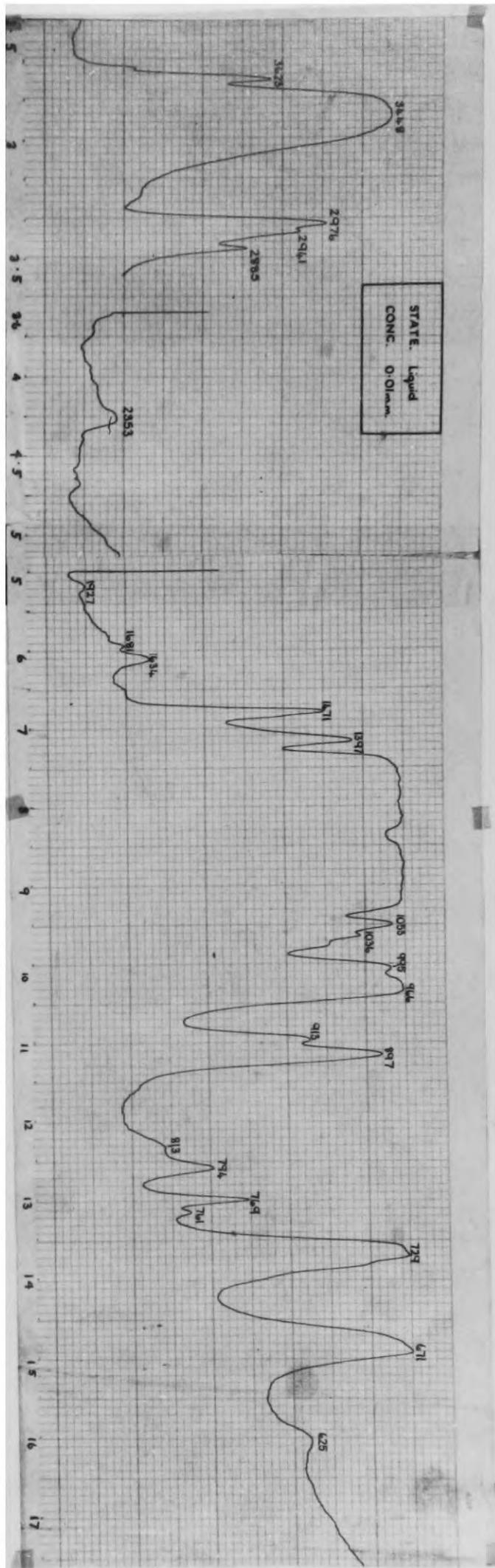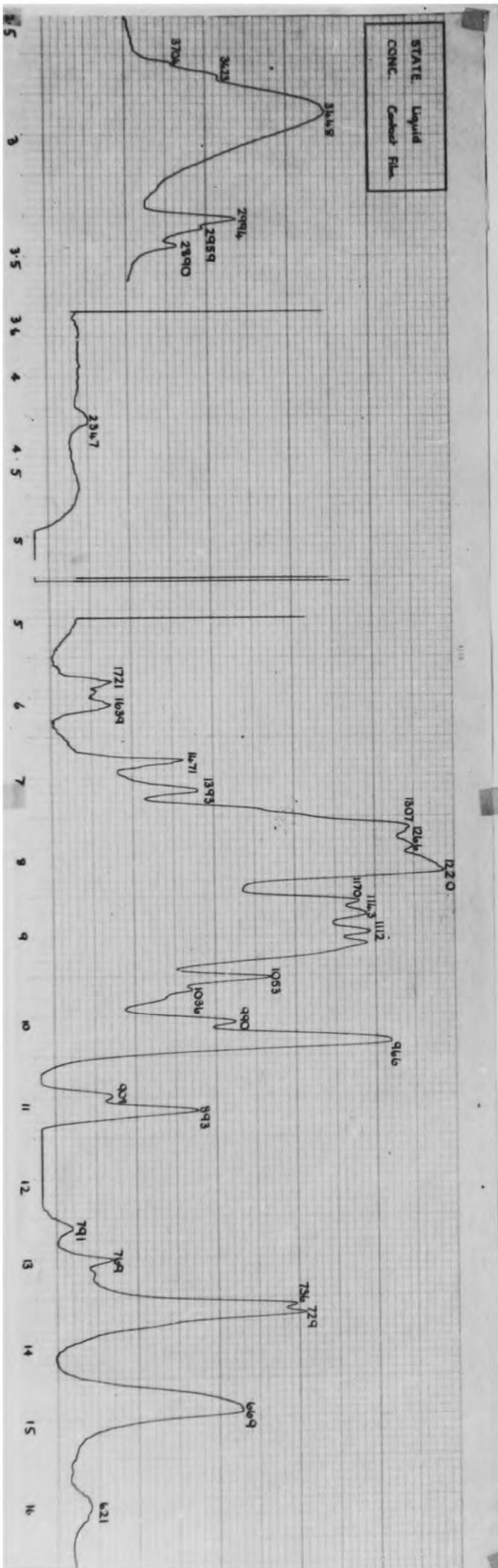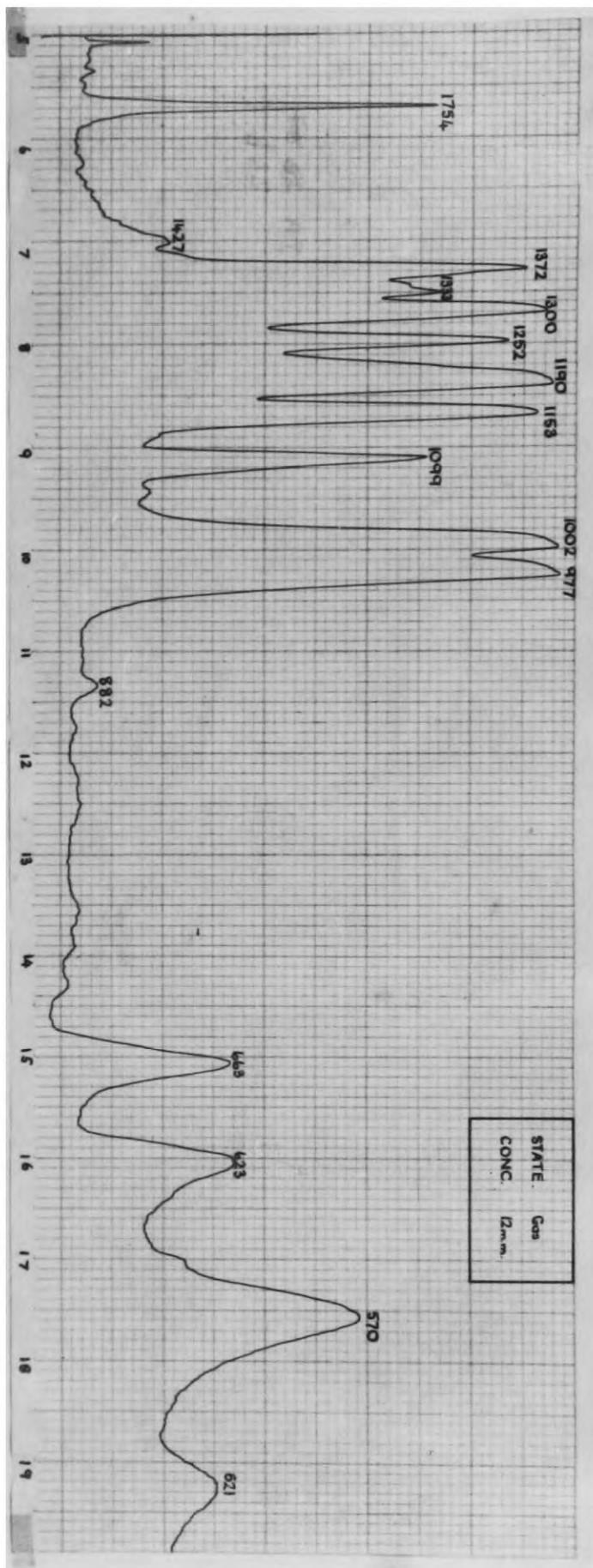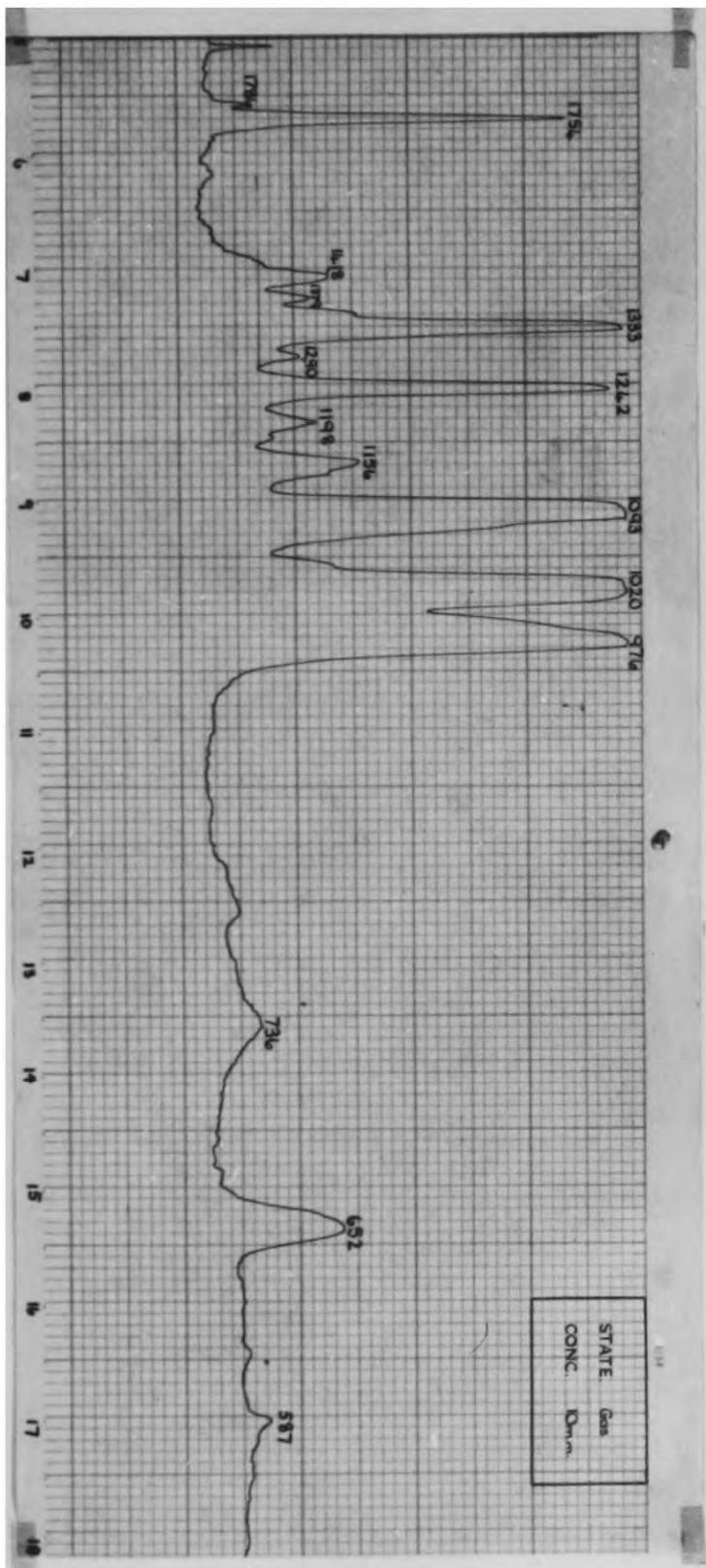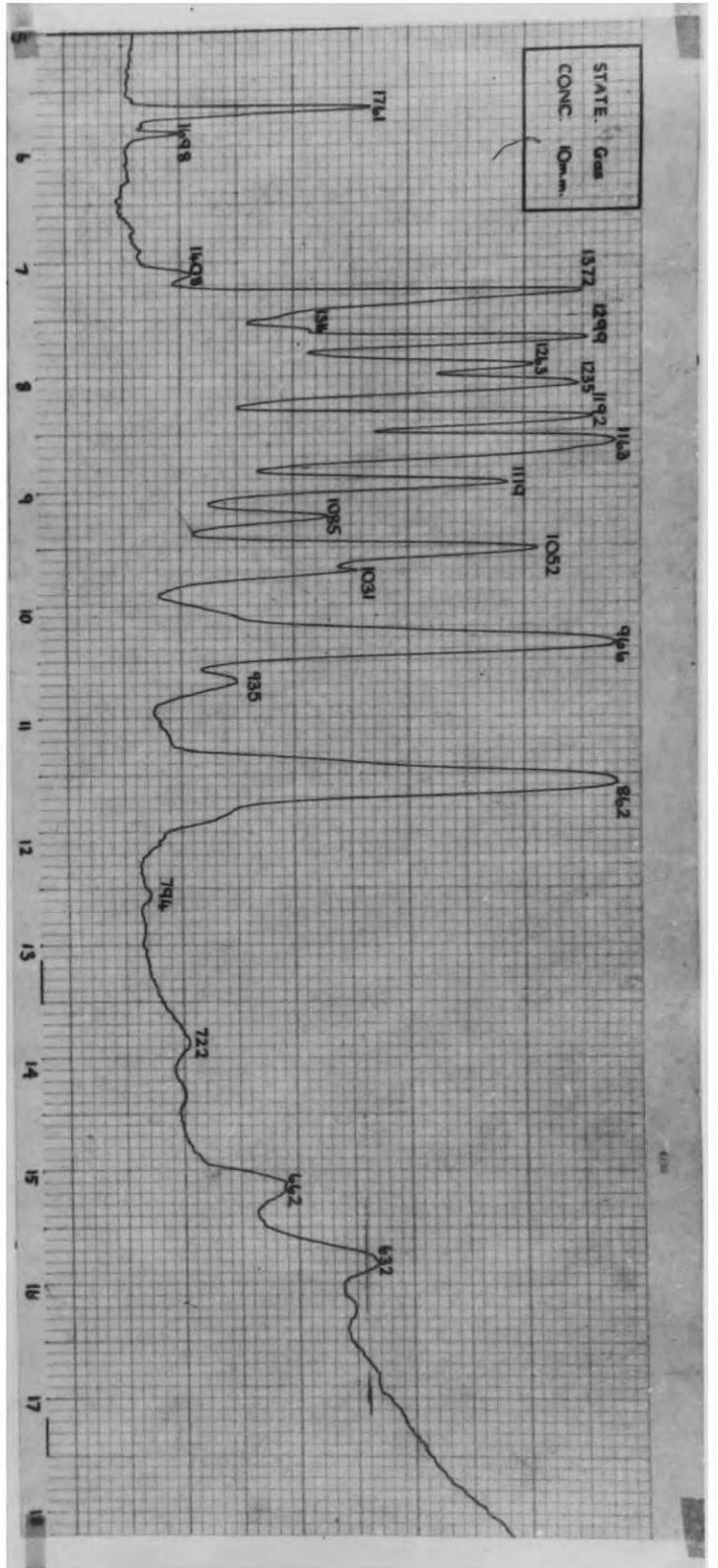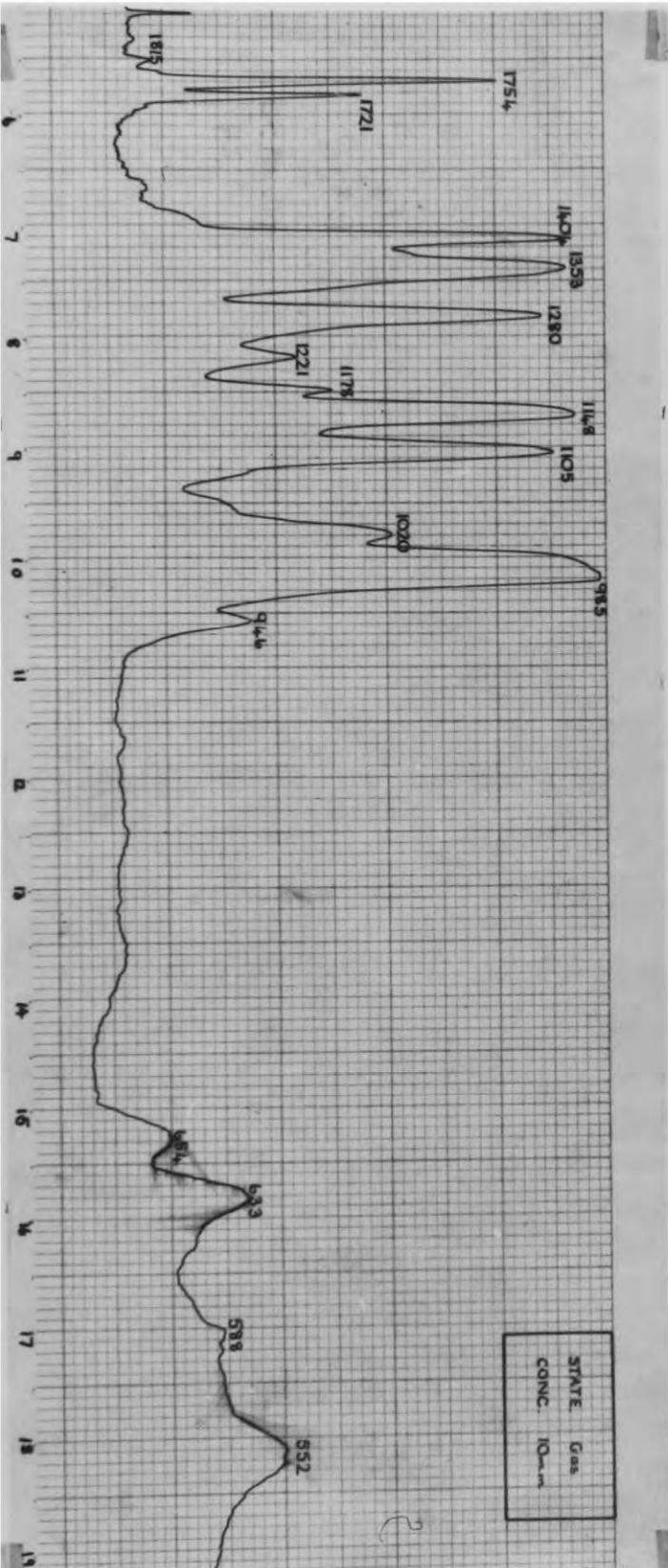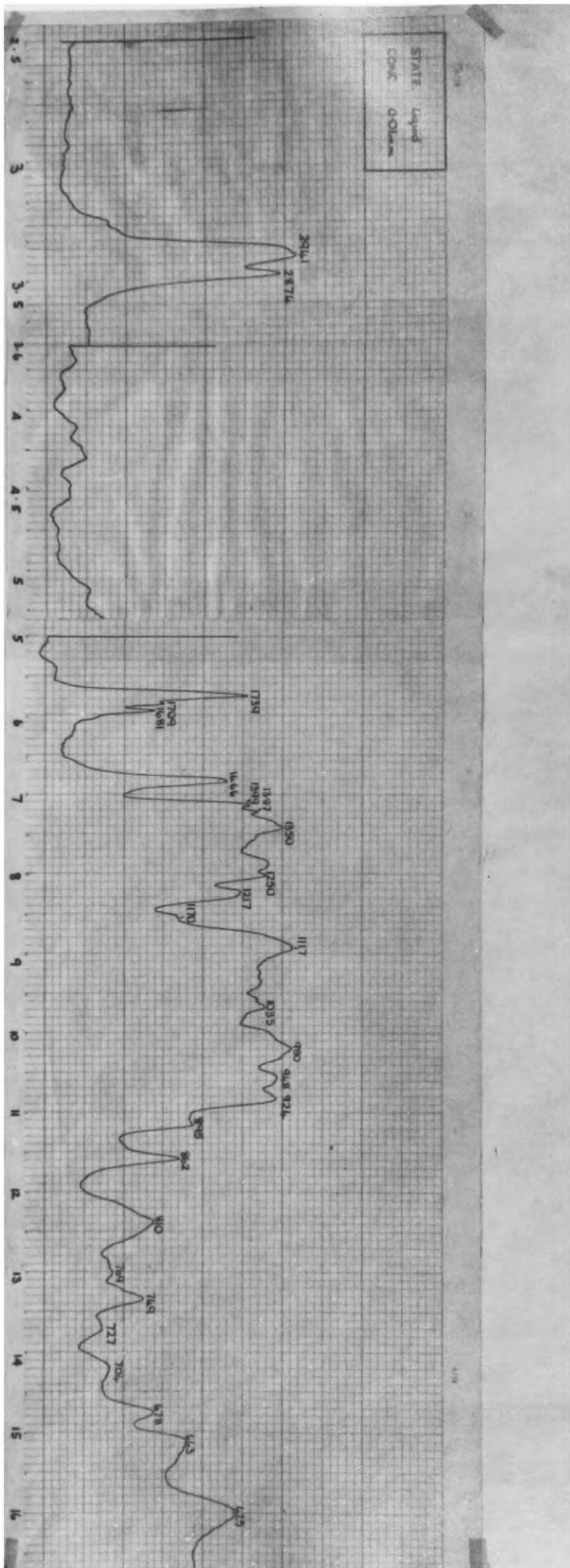
Analytical.

A Griffin and George Mark 11B model with two U-shaped columns (3 ft x $\frac{1}{4}$ in.) was used for most analytical work. The packings consisted of kieselguhr as inert support with 40% of stationary phase, the latter usually being dinonyl phthalate (D.N.P.), tricresyl phosphate (T.C.P.) or silicone elastomer. A low temperature apparatus involving a thermistor detector[*] was constructed where the column packing was silicone trimer on kiesulguhr. The column was constr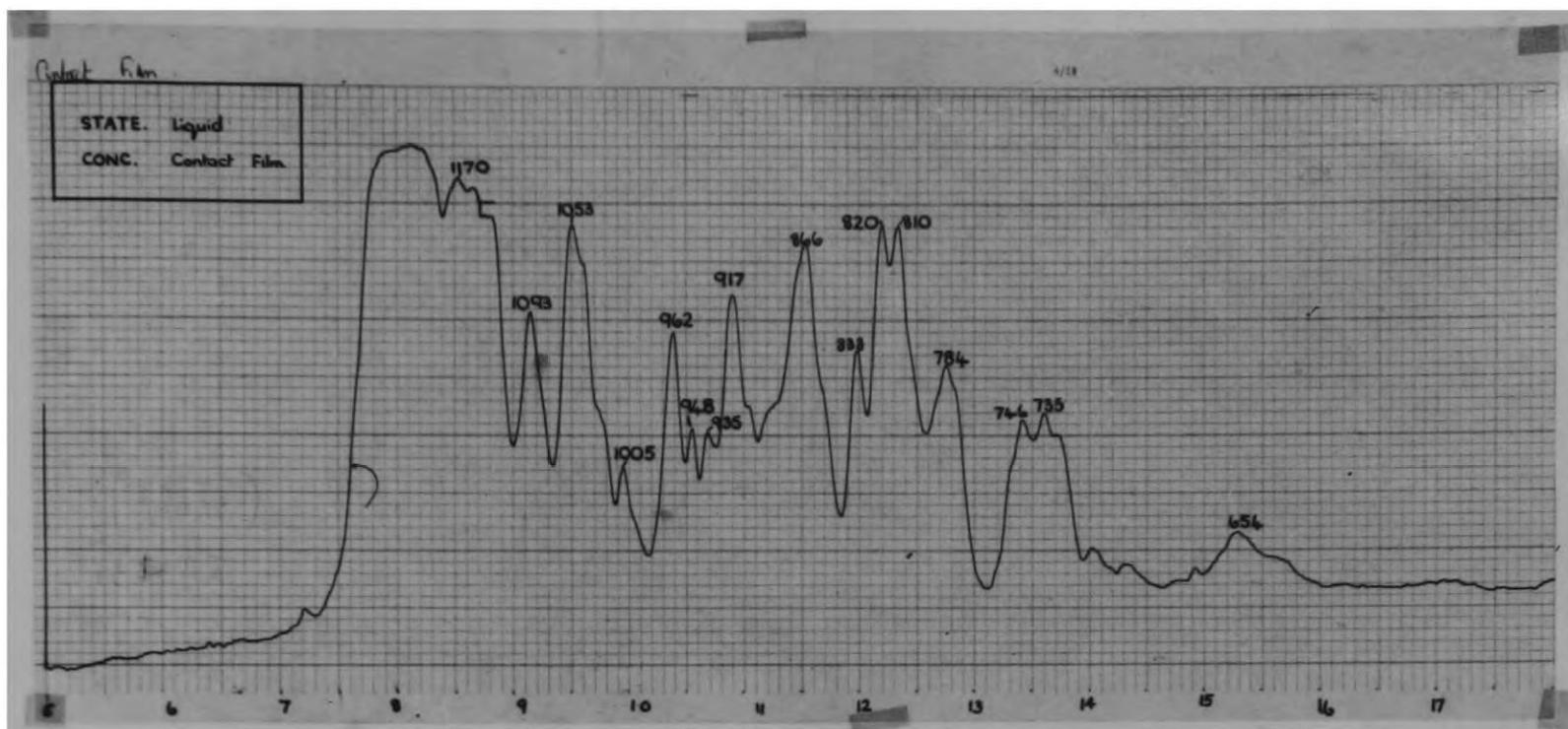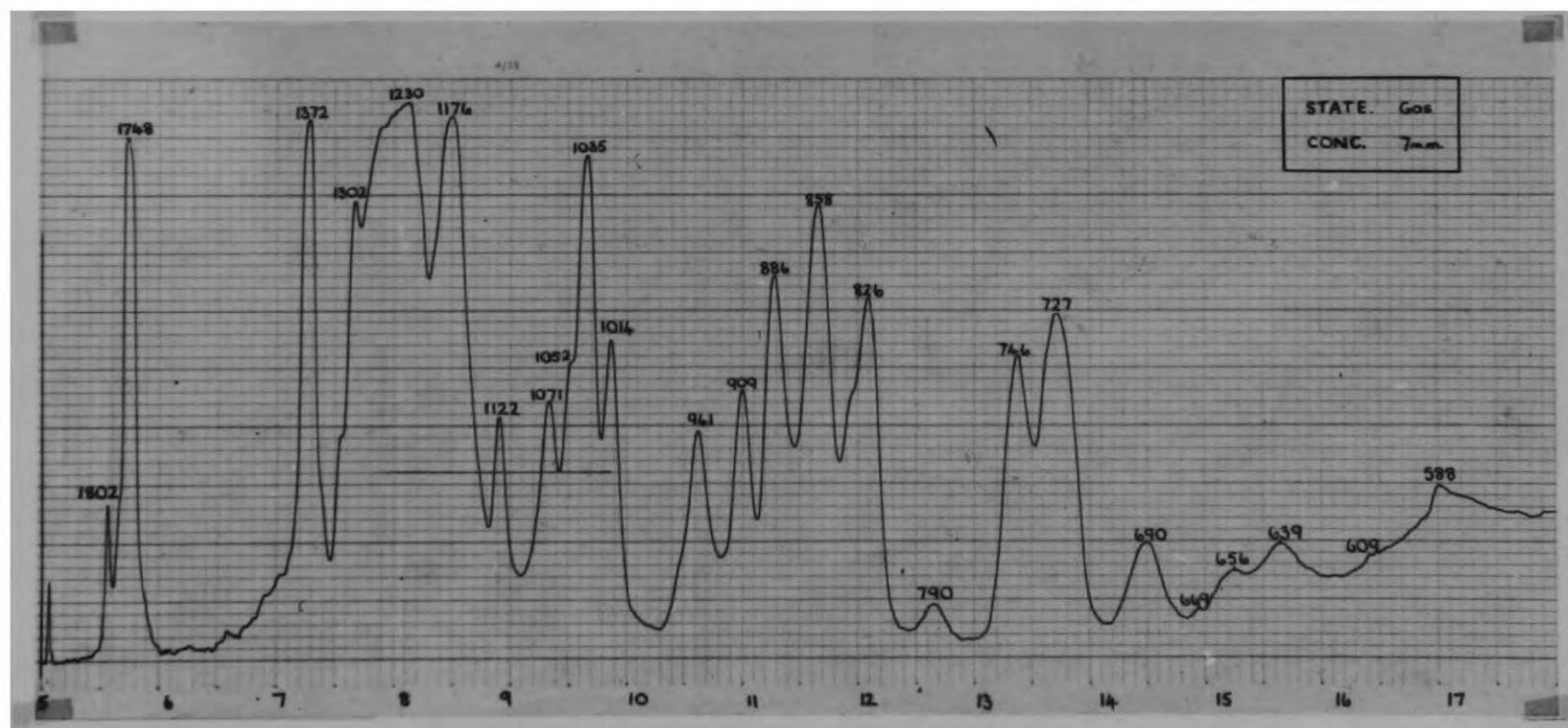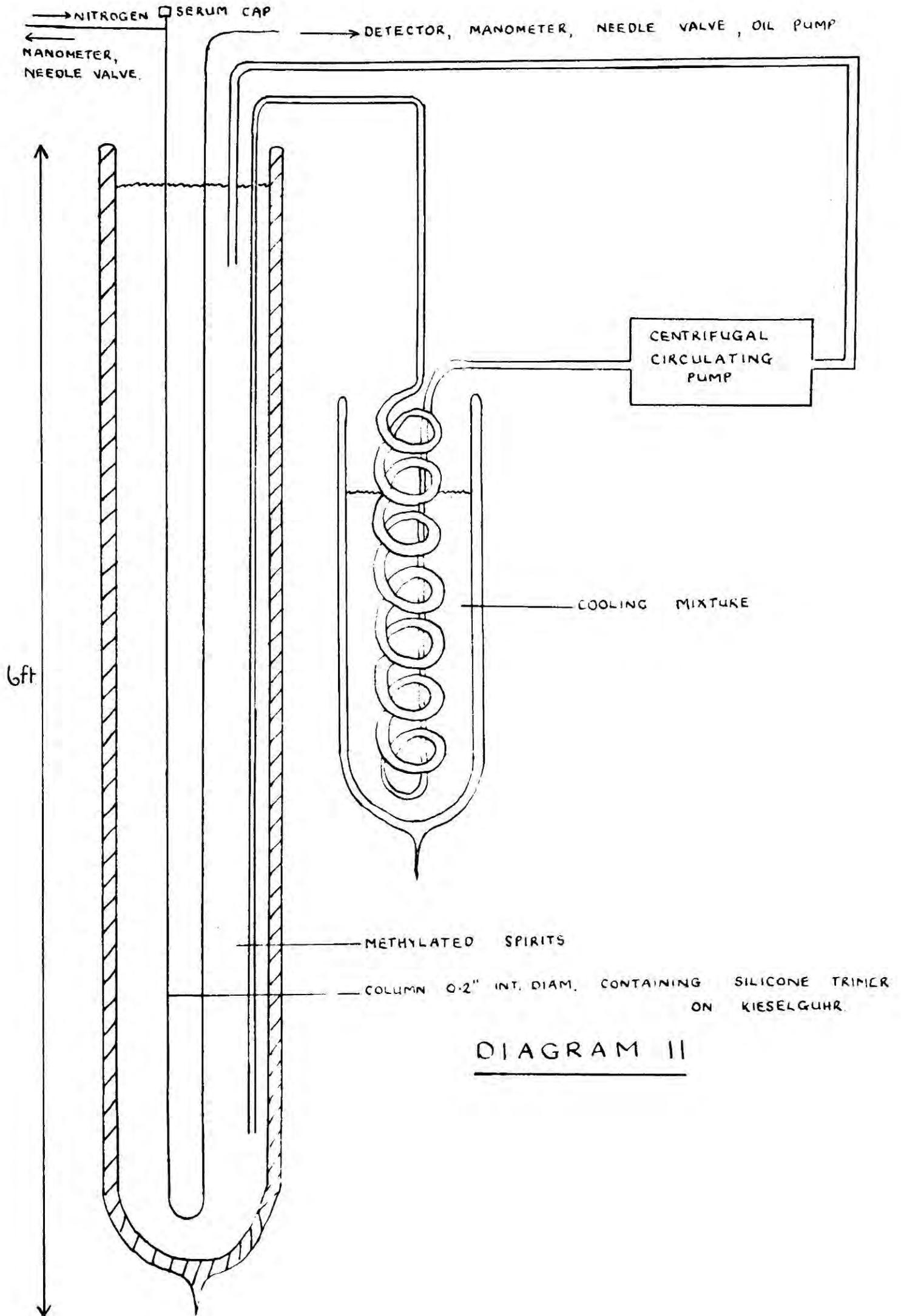ucted in two ways. The first one consisted of sixteen feet of P.V.C.tube (0.3 in. internal diameter) which after packing was coiled into a Dewar flask; the latter could then be filled with ice or other cooling mixtures. Results on this column were reproducable provided that the column was not disturbed at all. The second column containing this packing was a twelve ft. x 0.2 in. internal diameter glass U-tube which was cooled by immersion in a long (6 ft.) Dewar flask containing cold methylated spirits. The latter was cooled by circulation through a copper spiral in a cooling bath using a centrifugal circulating pump. The temperature of the methylated spirits was adjusted by varying the length of copper spiral, the cooling bath, and/or the rate of circulation (see Diagram 11.).

Preprative Scale.

This apparatus consisted of a horizontal column leading to a separately heated detector and then to a trapping system; the carrier gas, nitrogen was sucked through the apparatus.

[*] MUSGRAVE, Chem. and Ind. 1959, 46.

Columns. (see diagram 12.)

These consisted of two U-tubes (8 ft. x $\frac{7}{8}$ in. each containing ca. 375g. packing) connected by narrow bore silicone rubber tubing and packed with the same proportions of materials as described for analytical scale. The heating system consisted of a rectangular aluminium box (6 ft. x 9 ins.) lagged with fibre glass, containing a detachable lid, and heated by a strip heater positioned beneath a false bottom. Rapid change of temperature was acquired by means of a "blower" which circulated the air inside the box past the heater. The nitrogen, prior to coming in contact with the sample was heated inside the box by passage through twenty-five feet of copper tube (spiral). The sample was either injected into the nitrogen stream through a serum cap, or evaporated directly in the nitrogen stream by diverting the latter through a trap containing the sample. The injected sample was quickly vapourised by means of a preheater, which consisted of a glass tube (2 ft. x $\frac{3}{4}$ in. diameter) packed with glass wool and heated by means of a heating tape to about 100° above the temperature of the box.

Detector.

This was of the thermister type sealed into an aluminium block and incorporating a bypass of the nitrogen stream through this block; the diameters of the glass tubes leading past the thermistor bead and through the bypass were arranged so that 80% of the nitrogen went through the latter. The detector was positioned inside a small aluminium box which was packed with asbestos wool; this box also contained a small electrical heater which was controlled by a variac.

<u>Trapping System.</u> (see diagram 13.)

This was of the straight manifold variety with fitments for U-shaped traps. A heating tape was wound round the manifold (A) to prevent premature condensation.

DIAGRAM 12

DIAGRAM 13

158.
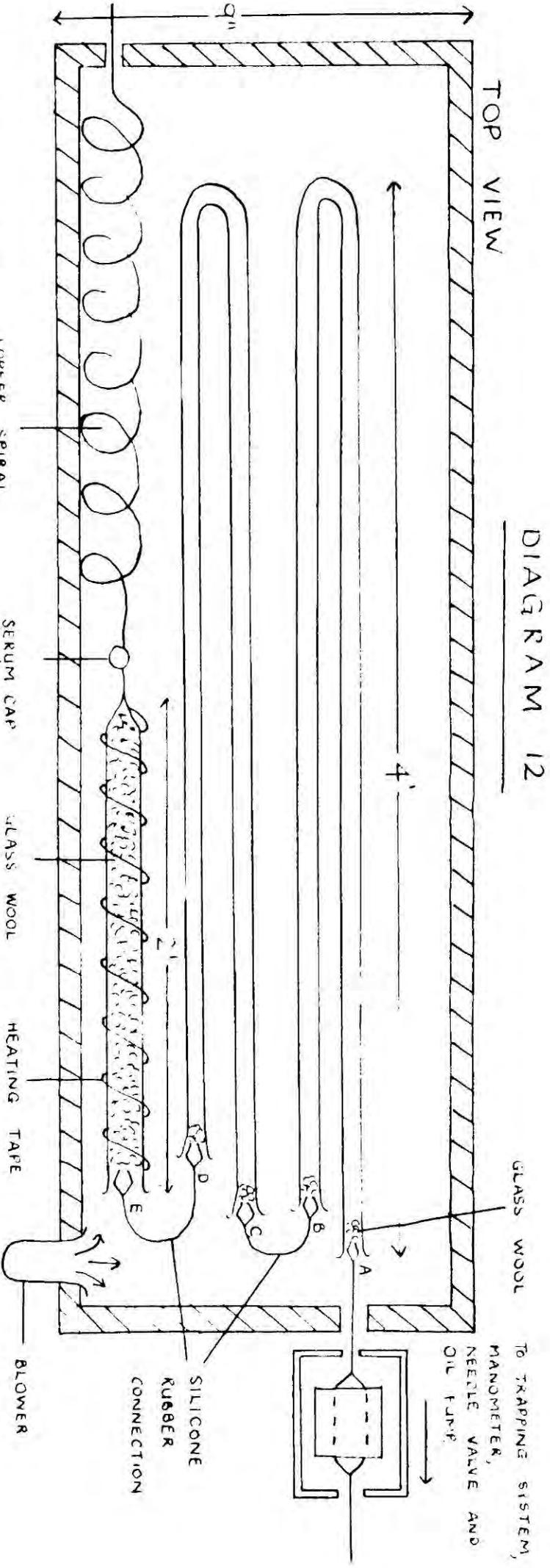
CHAPTER 4.

ANALYTICAL SECTION.

THE DETERMINATION OF FLUORINE IN
VOLATILE ORGANIC COMPOUNDS.

INTRODUCTION.

Microdetermination of organic fluorine compounds usually involves three steps: decomposition of the organic substance, separation of the resulting inorganic fluorine compound and determination of fluorine by a direct or indirect method.
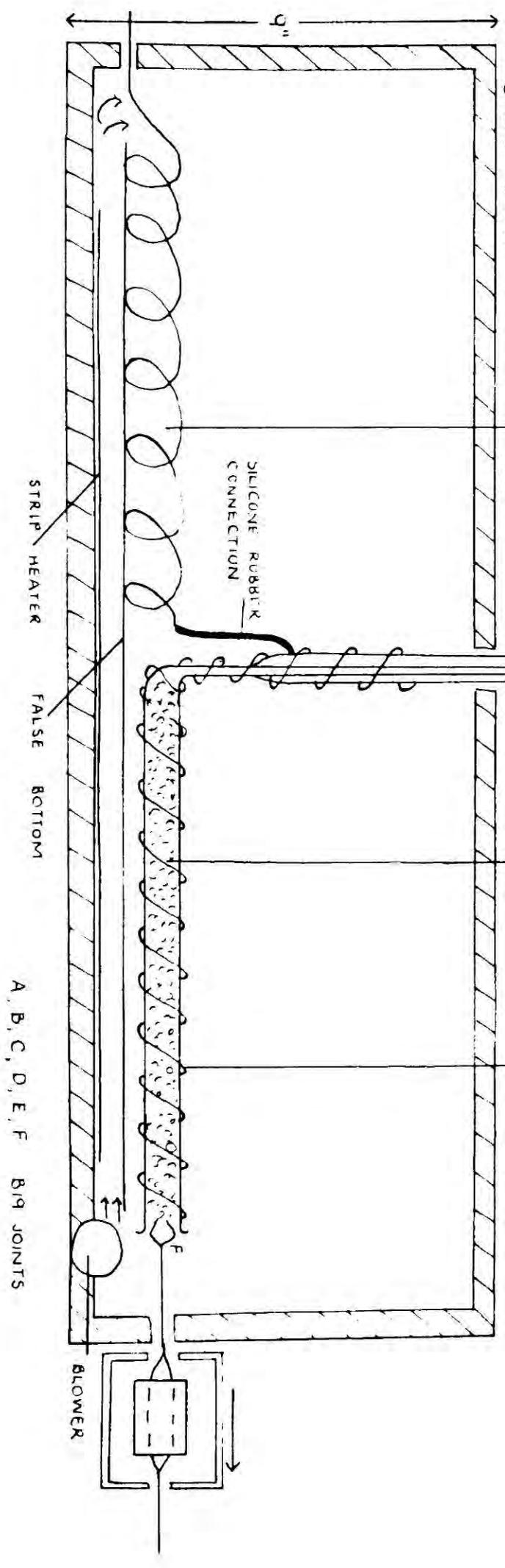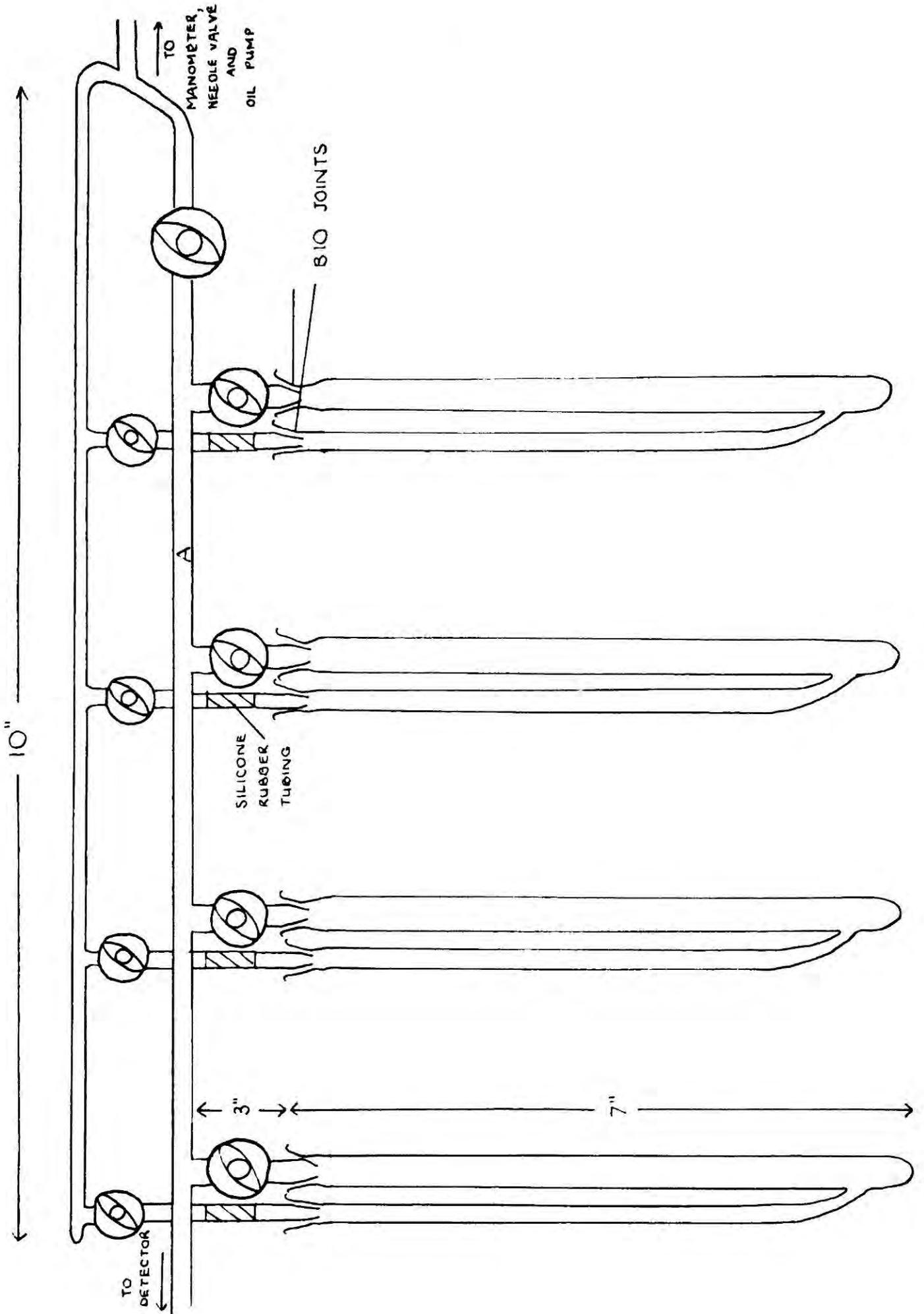
Decomposition.

The cleavage of the organically bound fluorine can be effected by oxidation, reduction, alkaline fusion or hydrolysis.

In a review of the microdetermination of fluorine in organic compounds, Ma[1] lists the numerous variations of bombs, reagents and temperatures recommended for the decomposition of organic fluorine compounds.

Decomposition by catalytic oxidation at high temperatures has been frequently used; this was first reported by Clark[2] who found this method effective for the decomposition of mono and difluoro compounds using a quartz microcombustion tube containing platinum foil heated to 900°. Clark and Rees[3] later reported that some polyfluoro compounds required a temperature of 1150°, and Freier et al.[4] found it necessary to use this temperature for all highly fluorinated substances. Belcher[5] employed a platinum micro combustion tube which could withstand high temperatures, but which had the disadvantage of being opaque and pliable.

Hubbard and Henne[6] applied this type of decomposition to the analysis of fluorine in gaseous samples. The latter was measured in a mercury gas burette and was passed over silica heated to 900°; the silicon tetrafluoride so formed was collected in water and the

fluoride ion then titrated with cerous nitrate. This method was also applied to compounds containing chlorine as well as fluorine; the chloride was titrated by the Volhard method.

Analysis for fluorine in gaseous samples has also been accomplished by Keslans[7] by a type of "oxygen flask" method. The apparatus consisted of a 500 ml. bulb fitted with a stopper containing two platinum electrodes which led to a fine mesh of platinum spirals. The bulb was charged with standard alkli, evacuated, and about 400 mls. of oxygen were introduced so that a partial vacuum remained. The platinum mesh was brought to redness and the gaseous sample, an alkyl fluoride, was measured into the bulb, when it ignited on the platinum mesh. The hydrofluoric acid thus formed was taken up in the alkali and estimated either gravimetrically or by titration of the excess alkali.

Belcher, Leonard and West[8] have recently used the "oxygen flask" method for the decomposition of involatile samples containing fluorine. The sample (ca.100 mg.) is wrapped in filter paper and clamped in a platinum wire attached to the stopper of a 250 ml. conical flask. Water is placed in the flask to absorb acid gases and the flask is filled with oxygen. The paper is lighted and the stopper immediately replaced; combustion is complete in a few seconds. When absorption of acid gases is complete the fluoride ion is determined spectrophotometrically as the blue complex of cerium (lll) alizarin complexone. This method could be applied to very involatile liquids by allowing them to soak onto the filter paper, but for most fluorine containing liquids the method is impracticable.

Oxidation with a sodium peroxide-sucrose mixture has been reported by Rush, Cruikshank and Rhodes[9]. Ma in his review states that sodium peroxide fusion is the most difficlut microdecomposition procedure since the proportion of sample and reagents has to be very carefully controlled; otherwise incomplete oxidation or explosion results.

Belcher et al.[10] decomposed organic fluorine compounds with sodium or potassium in a nickel bomb at 600° for one hour, Savchenko[11] recommended a temperature of 900°. A steel bomb was used by Korshun, Klimorva and Chumachenko[12] who suggested heating at 800° for ten minutes. Ma and Gwirtsman[13] decomposed samples in a Parr micro bomb using a copper washer in place of the usual rubber or lead one; sodium was used for mono, and potassium for poly-fluoro compounds. The fusion reaction was carried out by heating the bomb with a Bunsen burner for fifteen minutes. Alkaline fusion methods using calcium carbonate, calcium oxide or calcium hydroxide have not always given quantitative yields of the corresponding inorganic fluorides[14]. Hydrolytic methods have only limited application, being useful for compounds such as tertiary fluorides which liberate hydrogen fluoride on heating in acid solution.

These methods described all have serious drawbacks. Fusion with sodium or potassium appears to be the best method but suffers from the fact that very high temperatures are required especially for stable fluorine compounds; this of course tests the construction of the bomb considerably and frequent cases of the latter "blowing" are experienced. Catalytic oxidation methods also require very high

temperatures which limit their use. The "oxygen flask" method is much simpler but can not be used for volatile compounds; it would therefore appear that decomposition by reduction in solution would be the most convenient procedure. Vaughan and Niewland[15] suggested the use of a solution of sodium in liquid ammonia as the reducing agent but this was limited because of the sparing solubility of many organic compounds in liquid ammonia.

Scott, Walker and Hansley[16] showed that concentrated solutions of the addition compounds of sodium with biphenyl, naphthalene and other aromatic hydrocarbons could be prepared in suitable solvents. For concentrated solutions of the order of 1 to 2 g.atoms of sodium per litre of sodium biphenyl or naphthene complexes, only dimethyl ether or dimethoxyethane could be used. These complexes contained 1 g. atom of sodium dissolved per mole of hydrocarbon and further uptake of sodium was difficult. These solutions contain hydrocarbon anions which are potentially a powerful source of electrons and therefore excellent reducing agents.

Benton and Hamill[17] were the first to realise the possibility of using these complexes as electron transfer reagents in the reduction of organic halogen other than fluorine, to halide; they used a 0.5 M solution of the sodium naphthalene-dimethoxyethane complex. The organic compound containing bromine or chlorine was sealed in a thin walled glass vessel which was broken in the presence of excess of the complex causing a vigorous reaction to occur. The excess reagent was decomposed and the halide extracted with water; this extract was acidified and titrated potentiometrically with silver nitrate. Solids

were analysed by dissolving them in a small amount of toluene. A
number of mono and polychloro or polybromo compounds gave good results,
but compounds containing a reactive hydrogen atom such asp-chloro-
aniline formed insoluble unreactive salts and gave low results.
Hexabromobenzene and 2,2-difluoroheptane did not react at all, and
compounds containing nitro groups also proved difficult.

Pecherer, Gambrill and Wilcox[18] carried out some experiments
with the sodium complexes of naphthalene and anthracene and the ketyl
from benzophenone in dimethoxethane but they then concentrated on the
sodium biphenyl complex for the estimation of ethylene halides in
petroleum. They then extended this method to the analysis of a number
of bromine and chlorine containing aliphatic and aromatic compounds;
the restriction to organic compounds with only non-reactive groups did
not apply. Ligett[19] expanded this work of Pecherer et al. into a
simple analytical procedure and also developed a convenient method of
preparing the reagent and for storing it over considerable periods.
Ligett advocated a number of solvents: toluene, benzene, ether or othe1
water immiscible solvents dissolving the sample before decomposition
with excess 1.3 M sodium biphenyl-dimethoxyethane complex. After
extraction with water and nitric acid the halide was determined by the
Volhard technique. Provided samples were completely soluble the
reaction was instantaneous; no fluorine-containing compounds were
analysed.

Ma[1] in his review mentions that Bennett and Debrecht[31]
reported that reduction by sodium diphenyl-dimethoxyethane complex
is generally applicable to fluoro compounds, the decomposition being

complete in a few minutes. No detailed procedure was published.

Johncock, Musgrave and Wiper[20] developed this method of decomposition for all fluorine containing organic compounds which were soluble in di-isopropyl ether. The latter was used as a solvent since toluene, benzene or petroleum ether as advocated by Ligett formed emulsions during the aqueous extraction. Samples were weighed in a gelatin capsule and the top removed before introduction into the di-isopropyl ether. 10 mls. of the reagent were added; the reaction was usually complete within two minutes and the halides were extracted with water and made up to a known volume. The procedure for the determination of fluoride was by alkalimetry after passing an aliquot of the aqueous extract through a cation exchange column.[21]

Determination.

Fluoride may be determined either volumetrically, gravimetrically or spectrophotometrically. The first can involve either titration of the fusion solution with thorium nitrate using sodium alizarin sulphonate as indicator, a reaction which is non-stoichiometric and requires a comparative colour technique[10], or by the application of a cation exchange resin which then allows the total halogen to be determined by alkalimetry this latter method will be described later. The gravimetric method[22] involves a lengthy procedure in which lead chloro-fluoride is precipitated. Belcher, Leonard and West[8] in a recent paper have determined fluoride ion by a spectrophotometric procedure involving the formation of the blue complex of fluoride ion with the red chelate of cerium (111) and alizarin complexone (1,2-dihydroxanthraquison-3-ylmethylamine-N N diacetic acid). All these

methods give good results in the hands of experienced analysts; the latter probably is the quickest and easiest. Chloride or other halogen cannot, however, be determined by direct titration of the fusion solution with silver nitrate because of the large nitrate ion concentration and therefore the longer indirect methods of Brown and Musgrave[23] or Belcher, MacDonald and Nutten[24] must be used.

Banks, Cuthbertson and Musgrave[21] were the first to realise the advantages offered by the application of a cation exchange resin in allowing the total halogen in an organic compound to be determined by alkalimetry. Earlier, however, Samuelson[25] had indicated the use of an anion exchange resin for the separation of fluoride, chloride and iodide ions, and Osborn[26] had mentioned the conversion of inorganic fluoride by a cation exchange resin to hydrofluoric acid which could be titrated directly.

The method of Banks, Cuthbertson and Musgrave[21] involved the decomposition of the organic compound, ca.10 mg., with sodium in a nickel bomb, such as described by Belcher and Tatlow[27], at 600 - 700°. The inorganic halides so formed were taken up in 100 mls. of solution; the salts were converted to their corresponding acids by passage through a column containing the cation exchange resin, amberlite I.R. 120(H). This resin was chosen because of its good exchange rate, high exchange capacity and no great tendency to change its volume on conversion from one form to another. The total halide content of a 10 ml. aliquot was determined by titration with alkali using methyl red screened with methlene blue as indicator. The chloride was directly estimated by neutralisation of a second aliquot

with the exact amount of alkali followed by evaporation of the solution
to an optimum chloride concentration of about 2 mg. per 10 mls. and
titration with silver nitrate using dichloro-R-fluorescein as indicator.
The only condition under which this indicator functions is when it is
operating in a solution of pure halides, which is the case in this
titration. The fluoride is found by difference. Nitrogen could be
determined as cyanide in the fusion solution by the method of Deniges[28]
provided the organic compound did not contain oxygen. In the chloride
determination, cyanide was removed by treating the fusion solution
with aqueous formaldehyde solution[23]. Cyanate was converted by the
cation exchange resin to cyanic acid which decomposed to ammonia and
carbon dioxide; the former was retained on the column and did not
interfere, and the latter could be removed by boiling the solution.

Eger and Yarden[29] in a paper published at the same time as
Banks, Cuthbertson and Musgrave, and also in a later paper[30],
described the determination of fluorine in organic compounds; they
carried out the decomposition using sodium peroxide in a modified
Parr bomb, and used a cation exchange resin, amberlite I.R-120(H)
to remove excess sodium ions. They then titrated with thorium nitrate
using sodium alizarin sulphonate as indicator. These workers said
that the method could be applied to other halogen besides fluorine
and that chloride and bromide could be determined in the same solution
but no details were given.

Johncock, Musgrave and Wiper[20] used the same method as Banks,
Cuthbertson and Musgrave[21] for the determination of fluoride and
chloride in the decomposition solution.

A quicker method of determining fluoride and other halide has been described by Belcher, Macdonald and Nutten[24] and involves firstly titration of the total halogen using standard sodium hydroxide solution. Other halogen can then determined by a colour comparison procedure involving the use of mercury oxycyanide.

DISCUSSION.

The semi-micro determination of fluorine and other halogen in organic compounds is carried out in this department using the decomposition method of Johncock, Musgrave and Wiper[20] and until recently the method of Banks, Cuthbertson and Musgrave[21] for the actual determination of fluoride and other halides. Recently, however, the determination of other halides has been carried out by the mercury oxycyanide method of Belcher, Macdonald and Nutten[24].

This combined procedure has the advantage over all other methods yet described in that it is quick, requires no expensive apparatus and can be carried out successfully by a person with little analytical experience. Also samples of considerable volatility can be analysed provided sufficient care is taken during the weighing of the sample. Disadvantages to this method of decomposition are the limitation to only those compounds which are soluble in diisopropyl ether, and the fact that some compounds on reaction with the sodium biphenyl dimethoxyethane complex might result in the formation of anions which might then upset the alkalimetric procedure. No one has, however, yet encountered the latter. The other easily carried out procedure, the "oxygen-flask" method of decomposition, overcomes the disadvantages of the sodium biphenyl dimethoxy-ethane method, but has the disadvantage in its limitation to non-volatile materials. It is convenient that compounds which are insoluble in di-isopropyl ether are most likely to be either solids or high boiling oils and, therefore, useful for the "oxygen-flask" method. A combination of the two would

seem to deal with all possibilities except perhaps for stable high

boiling fluorocarbons or fluorocarbon polymers for which the

conditions of the "oxygen-flask" method might not be drastic enough;

in these cases alkaline fusion in a bomb would have to be used.

Of the methods of determining fluoride the spectrophotometric

one and the alkalimetric one involving the anion exchange resin are

the simplest; determination of other halides is then carried out by

the mercury oxycyanide method.

There have been, up to the present, no really convenient and

simple methods for determining fluorine and other halogens in very

volatile organic compounds; the only ones described being the

"oxygen-flask" method of Meslans[7] and the combustion tube-silica

method of Henne and Hubbard[6].

It was decided, therefore, to modify the sodiumbiphenyl

dimethoxyethane method of decomposition to the decomposition of

gaseous and volatile organic fluorine containing compounds. The

boiling range of samples investigated was -60° to 81° but there is

no reason why this could not be extended especially on the gaseous

side. Any condensable gas could be analysed. This method would be

especially useful for relatively high boiling highly fluorinated

organic compounds which have very high vapour pressures; of these

only perfluorobenzene (b.p. 81°) was investigated.

Since the gases had to be weighed in a glass bulb of about 100 mls.

capacity it was necessary to use an ordinary analytical balance reading

to four decimal places. Consequently, rather larger samples (40 -

60 mg.) than in the method of Johncock, Musgrave and Wiper[20], needed

to be taken in order that the error in the weighing should not give too big an error in the estimation.

Di-isopropyl ether was used as solvent for the decomposition because of its use in the decomposition of samples by the method of Johncock, Musgrave and Wiper[20]; this meant that the blank determination used for the latter could be applied to the "gas" analyses. The reagent was stored in bottles each containing about 110 mls. Since 10 mls. of reagent were usually used for each decomposition, each bottle sufficed for ten analyses and one blank determination. It was found impracticable to use some of the reagent and store the remainder for a few days, since when this remainder was used, more then 10 mls. per decomposition were required and usually inconsistent results were obtained. The decomposition reaction was usually complete within five minutes; it appeared to take a slightly longer period than the decomposition of liquids or solids of similar structure since these give homogeneous reaction mixtures whereas the former is a heterogeneous reaction.

The sodium halides formed in this reaction were extracted with water and made up to a known volume.

As in the case of Johncock, Musgrave and Wiper fresh resin was necessary for each ion exchange procedure; this was because of the presence of some organic material in the aqueous extract. Banks, Cuthbertson and Musgrave[21] were able to regenerate the resin used in their ion exchange columns. Quantitative results were obtained using five grams of resin.

Experimental.

Preparation of the sodium biphenyl-dimethoxyethane complex.

Purification of Reagents.

Biphenyl - was recrystallised once from meths. and dried under vacuum. M.Pt. 70 - 71°.

Dimethoxyethane - was distilled three times from potassium, the last time in the presence of the ketyl of benzophenone which has a deep blue colour and is only stable in the absence of water and peroxides (b.p. 66 - 68°)

Toluene - sulphur free toluene was distilled over sodium.

Sodium Dispersion.

Clean sodium (60 g., 2.61 g. atoms) and toluene (60g.) were placed in a 2N 250 ml. flask with indented sides to prevent swirling. A nitrogen inlet was arranged, the outlet being through a vertical air condenser down the centre of which was the freely suspended rod of the dispersator. The toluene was gently refluxed and the dispersator run at maximum speed for fifteen minutes. The heating and dispersator were turned off and the dispersion was allowed to cool to room temperature.

Preparation of the Complex.

This was carried out essentially as described by Ligett[19] and Sezerat.[32]

The sodium dispersion was transferred to a nitrogen swept 2 litre 3N flask fitted with a dropping funnel, mechanical stirrer and reflux condenser. The total volume of toluene was made up to 300 mls. and dimethoxyethane (750 mls.) were added. Biphenyl (400 g., 2.6 moles.)

T3

TO McLEOD GAUGE
MERCURY DIFFUSION
PUMP
OIL PUMP

T2

T4

B10

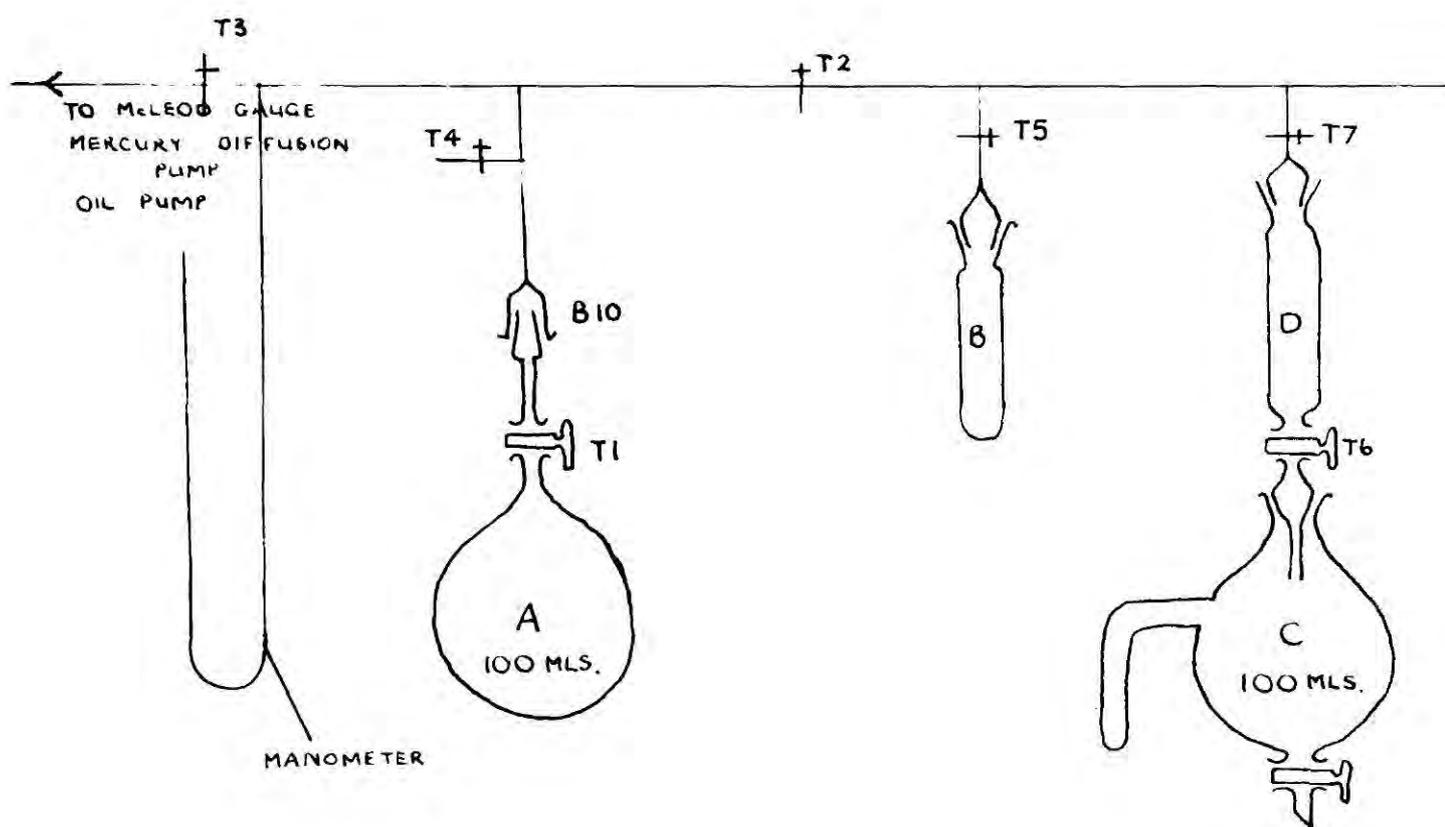T5

T7

T1

B

D

T6

A
100 MLS.

C
100 MLS.

MANOMETER

DIAGRAM 14

in dimethoxyethane (500 mls.) were then added with stirring over a period of two hours. The reaction started after a few minutes and the solution first turned green and finally black; the reaction was exothermic and the temperature was kept below 30° by cooling in an ice-water bath. Stirring was continued for a further hour and the reaction mixture was allowed to stand overnight. The reagent was then thoroughly stirred and transferred to 110 ml. bottles which were stored at 0°. All the sodium appeared to have reacted.

Analytical Procedure.

The tap and cone of flask A were carefully greased, avoiding excess grease (Apiezon L), and the flask then evacuated to a sticking vacuum on the apparatus shown in diagram 14. The taps T_1 T_2 and T_3 were closed, T_4 opened and the bulb was removed from the vacuum line. The grease from the cone was carefully cleaned using a cloth moistened in ether, the bulb, tap and neck were polished with a chamois leather and weighed to the nearest tenth of a milligramme after leaving in the balance case for fifteen minutes. A was re-attached to the vacuum line and with B, which contained the sample to be analysed, cooled in liquid air and T_1, T_2, T_3 and T_5 open, the apparatus was again pumped down to a sticking vacuum. T_3 was closed and B was allowed to warm slowly until the pressure in the system was such as to introduce a 40 - 60 mg. sample into A. T_1 was closed and the weight of the sample found by removing, cleaning and weighing A as before. A was returned to the vacuum line which was evacuated with T_2, T_3, T_6 and T_7 open, and the sample was transferred to C by closing T_3, opening T_1 and

cooling the side-arm of C in liquid air. T_6 was closed and the unit comprising of C and D removed after releasing the vacuum at T_4. The sample was allowed to warm to room temperature and expand into C, the biphenyl sodium dimethoxyethane complex (10 mls.) was added via D followed by di-isopropyl ether (25 mls.) taking care to leave the bore of T_6 full of liquid to maintain a partial vacuum in C. C was carefully shaken for five minutes when the reagent should form a permanent green colour; if the mixture turned brown then a further 5 or 10 mls. of reagent had to be added and the appropriate blank correction much later. The sodium halides were extracted with water and the extract was made up to 100 mls.

A 10 mls. aliquot was passed through the cation exchange resin column containing 5g. of amberlite I.R.- 120(H) resin and eluted with 60 mls. of water added in 15 ml. quantities. The eluate was heated to boiling and immediately cooled.

Analysis of only one Halogen was present.

The solution was simply titrated with standard 0.02N sodium hydroxide solution using methyl red-methylene blue (3 and 2 drops respectively) as indicator.

Analysis if Fluorine and other Halogens were present.

Mercury oxycyanide solution was prepared by shaking mercury oxycyanide (20g.) with one litre of distilled water; the solution was neutralised with approximately 0.1N sulphuric acid using methyl red -methylene blue as indicator, and filtered into a brown glass bottle.

The total halogen was determined by titration with sodium hydroxide solution as described above, and the other halogen found by

the mercury oxycyanide method as describedby Belcher et al.[24]
This involved placing the neutralised solution in a light box alongside
the same volume of water containing the indicator methyl red-methylene
blue; the colours should be identical. Mercury oxycyanide (10 mls.)
was added to the portion containing the halogen, which turned bright
green; the colour was then brought back to its original by addition
of standard 0.01N sulphuric acid solution. This known volume of the
latter was then added to the distilled water portion as was mercury
oxycyanide solution (10 mls.). The colour of this portion was then
brought back to its original by means of standard 0.01N sodium
chloride solution. This last titration afforded "other halogen" and
therefore fluorine could then be found from the first titration.

Blank Determination.

This was carried out by shaking di-isopropyl ether (25 mls.)
with the biphenyl sodium dimethoxyethane reagent in a stoppered
separating funnel. Any sodium halide was extracted with water followed
by the procedure as for determination of only one halogen i.e. titration
with standard sodium hydroxide.

RESULTS.

Compound (b.p. °C)	Weight taken gm.	Amount of Fluorine Calc. %	Found %	Amount of Chlorine Calc. %	Found %	Amount of Bromine Calc. %	Found %	Amount of Iodine Calc. %	Found %	Molecular Weight Calc.	Found.
CFCl=CFCl (22)	0.0570	28.6	28.1	53.3	53.4					132.9	132
(CF₃)₂CF·CF(CF₃)₂ (60)	0.0456	78.7	78.4							338.1	337.5
CCl₂F·CF₃ (-2)	0.0625	44.5	44.4	41.5	41.3					171	171
CF₂Cl·CF₂I (56)	0.0480	29.0	29.5								
CF₂Cl·CF₂Br (22)	0.0562	35.3	34.9							215.4	216
C₂F₅I (13)	0.0546	38.6	38.2					51.6	51.8	245.9	245.3
C₂F₅Br (-20)	0.0600	47.8	47.4			40.2	39.5				
(CF₃)₂CFI (39)	0.0579	44.9	44.6					42.9	42.8		
(CF₃)₂CFBr (12)	0.0584	53.4	53.7			32.1	32.2			248.9	248
CF₃Br (-60)	0.0529	38.3	37.9			53.7	53.9				
CF₂:CFCl (-27)	0.0620	48.9	48.6	30.4	30.9						
C₆F₆ (81)	0.0572	61.2	61.0								

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