The use of chlorine trifluoride as a halogenating agent

Ellis, John F.

Ellis, John F. (1952) *The use of chlorine trifluoride as a halogenating agent*, Durham theses, Durham University. Available at Durham E-Theses Online: http://etheses.dur.ac.uk/9164/

DURHAM COLLEGES IN THE UNIVERSITY OF DURHAM.

A THESIS

SUBMITTED By JOHN F. ELLIS
ST. CUTHBERT'S SOCIETY.

A CANDIDATE FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY
1952.

THE USE OF CHLORINE TRIFLUORIDE AS A HALOGENATING AGENT

ACKNOWLEDGMENTS.

I desire to express my indebtedness to Dr. W.K.R.Musgrave, under whose supervision this work was carried out, and also to the Durham Colleges in the University of Durham and the Durham County Education Committee for maintenance awards during the period of this research.

CONTENTS.

CONTENTS.

(continued)

SUMMARY.

When chlorine trifluoride, diluted by nitrogen, reacts with carbon tetrachloride it gives rise to fluorotrichloromethane and difluorodichloromethane. The extent of reaction is increased by rise of temperature and addition of catalyst (cobaltous fluoride) but the amount of reaction at $0^{o}C$ is very small. From consideration of this, it is thought justifiable to assume that carbon tetrachloride acts as an inert solvent in reactions of chlorine trifluoride with aromatic compounds at $0^{o}C$.

The reaction of chlorine trifluoride, diluted by nitrogen, with benzene, its homologues and its substituted derivatives in carbon tetrachloride solution at $0^{o}C$ has been studied. In the case of benzene a number of catalysts were used, and the results compared with those obtained under uncatalysed conditions. At all other times, cobaltous fluoride was employed as catalyst. In all cases, except that of fluorobenzene, it was seen that substitution of fluorine and chlorine occurred in the nucleus, and a small amount of side chain fluorination also occurred in the case of toluene.

The relative amounts of fluoro- and chloro-derivative formed, however, depended on the test compound and catalyst concerned, and no difluoro-derivative was isolated from the products of the fluorobenzene experiment. Substitution was in every case the predominant reaction, but addition also occurred in all cases giving rise to products of varying stability, which, from their properties and analyses, appear to be cyclohexane, cyclohexene and cyclohexadiene derivatives. In the case of benzene only, under certain conditions, small quantities of compounds analysing as halogenated diphenyls were also obtained, and in the case of benzotrichloride there was a certain amount of replacement to give benzodichlorofluoride.

PART I.

INTRODUCTION, HISTORICAL AND THEORETICAL.

Part I : Introduction, Historical and Theoretical.

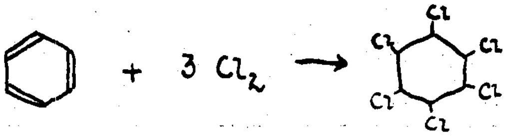
Although the introduction of halogens into organic compounds has been the subject of considerable study for many years, no detailed investigation of the reaction of chlorine trifluoride with any organic compound of the aromatic series had been reported in the literature previous to 1950. In the aliphatic series the only work carried out which gave a characterised product was due to Hückel (Nachr. Akad. Wiss. Math. Physik. Klasse (Göttingen), 1946, 36) who used chlorine trifluoride to bring about replacement of bromine in bromodifluoronitromethane by fluorine to give rise to a small yield of trifluoronitromethane.

The lack of attention paid to chlorine trifluoride since its discovery in 1930 may be principally attributed to two causes - (i) the exceptional reactivity of the reagent (Ruff and Krug, Z. anorg. allgem. Chem., 1930, 190, 270; Booth and Pinkston, Chem. Rev., 1947, 41, 421; Domange and Neudorffer, Compt. rend., 1948, 226, 920) and (ii) difficulties in the preparation of fluorine which is required for its synthesis. The second of these factors has now been overcome (Leech, Quart. Reviews, 1949, 3, 22; Rudge, J. Soc. Chem. Ind., 1949, 69, 247) and as a result of the subsequent availability of chlorine trifluoride on a commercial scale

(Leech, loc. cit.; Porter, Chem. Eng., 1948, 55 (4), 102) it has become possible to make a more detailed study of the reaction of chlorine trifluoride with various organic compounds.

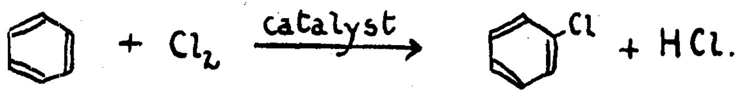
In so far as the introduction of chlorine into aromatic compounds is concerned the methods which have been employed in the literature fall into two main categories - (i) those involving direct chlorination and (ii) those which employ the diazonium reaction.

The reaction of chlorine with benzene and its homologues is determined by the conditions of temperature and the presence or absence of catalysts and light. Boiling benzene or benzene exposed to sunlight reacts with chlorine in the absence of catalysts to give rise to the additive compound hexachlorocyclohexane.



Although it is not unlikely that similar addition compounds may tend to be formed from alkyl benzenes, their reaction is complicated by the fact that two points of attack, namely the nucleus and the side chain are presented to the halogen. Investigation of the behaviour of toluene has shown that in sunlight in the absence of catalysts, toluene is chlorinated in the methyl group almost exclusively giving successively benzyl chloride, benzalchloride and finally benzotrichloride. Similar reaction ensues if chlorine is passed through boiling toluene. The combined conditions of refluxing hydrocarbon and the presence of sunlight is apparently the most successful way of introducing chlorine into the side chain without any nuclear substitution. This is a general rule, holding not only for toluene, but for all alkyl benzenes (Holleman and van Laan, Proc. K. Akad. Wetensch. Amsterdam, 1905, 8, 512 ; Cohen, Dawson, Blockey and Woodmansey, J. Chem. Soc., 1910, 97, 1623).

On the other hand, several catalysts, for example iodine and ferric chloride cause substitution to occur only in the nucleus, even when other conditions favour side chain halogenation. It is thus possible to arrange conditions in such a way as to obtain products halogenated exclusively in the nucleus or in the side chain in the case of alkyl benzenes: in the case of benzene itself the action of chlorine in the presence of such catalysts gives rise to the monosubstituted chlorobenzene without formation of addition products.



The first investigator to employ such catalysts to promote nuclear substitution was H. Müller (J. Chem. Soc., 1862, 15, 41) who employed iodine and antimony pentachloride, and showed that they effectively catalysed the formation of chlorobenzenes from hydrocarbons by the action of chlorine. Numerous other halogen carriers have been employed by later investigators, notably aluminium chloride, mercuric chloride, molybdenum pentachloride and the aluminium-mercury couple.

In order to effect side chain halogenation it is essential that such compounds which may promote nuclear halogenation must be absent; according to Haüssermann and Beck (Ber., 1892, 25, 2445) this side chain substitution is promoted by sulphur or phosphorus trichloride, though halogenation occurs quite smoothly in their absence. The use of phosphorus pentachloride as catalyst in a side chain halogenation has also been reported (Schiemann and Baumgarten, Ber., 1937, 70, 1418) though Booth, Elsey and Burchfield (J. Amer. Chem. Soc., 1934, 57, 2066) state that phosphorus pentachloride causes extensive formation of tar during chlorinations, so diminishing the yield of required product.

The chlorination of benzene homologues and benzene derivatives having substituents other than alkyl groups, in the presence of carrier catalysts, has been shown to give rise to further substitution in the nucleus via a mechanism involving attack at anionoid centres in the ring by the positively charged chlorine ion Cl^+. This theory is too well known to need further mention here.

The alternative method for the production of aromatic chloro-compounds is from the corresponding primary amine through the appropriate diazonium salt. Two modifications are in general use - (i) Sandmeyer's method (Ber., 1884, <u>17</u>, 1633 and 2650) in which the diazonium chloride is treated with cuprous chloride in hydrochloric acid and the mixture subsequently warmed. If R represents an aryl radical we thus have

$$R - NH_2 \xrightarrow[0^{o}c]{NaNO_2 \ \& \ H\,Cl \text{ at}} R - N_2Cl \xrightarrow[\text{H Cl then heat}]{Cu_2Cl_2 \text{ in}} R - Cl + N_2$$

- and (ii) the method due to Gattermann (ibid, 1890, <u>23</u>, 1218) which consists in treatment of the diazonium chloride solution with copper bronze or copper powder.

With the exception of certain reactions which are specific in character, and have only limited applicability, the methods available for the introduction of fluorine into organic compounds (other than by reaction with chlorine trifluoride) fall into six major groups as follows:-

(1) Preparation of aromatic fluoro-compounds from amines via diazonium compounds -

Schmitt and von Gehren (J. prakt. Chem. 1870, (2) <u>1</u>, 394) were the first workers to make an aromatic fluoro-compound by diazotisation of p-amino-benzoic acid in 40% aqueous hydrofluoric acid: subsequent decomposition of the diazonium fluoride gave p-fluorobenzoic acid. Later, Wallach and Heusler (Ann., 1888, 243, 219) isolated certain diazonium piperidides and obtained fluoro compounds from them by decomposition in aqueous hydrofluoric acid: the intermediate compounds were however, unstable, and the yields low. Swarts (Bull. acad. roy. Belg., 1913, 241) reported that very good yields of a number of fluoro compounds were obtained by diazotisation of the corresponding amines in concentrated aqueous hydrofluoric acid followed by decomposition of the diazonium fluoride by heating.

Balz and Schiemann (Ber., 1927, 60, 1186) devised a two stage process for preparing aromatic fluorides, in which the diazonium fluoborate was first isolated from the amine: this salt was then dried and decomposed by heating in the dry state.

$$R.NH_2 \xrightarrow[0^{o}c]{NaNO_2 \text{ and } H\,Cl \text{ at}} R.N_2Cl \xrightarrow{HBF_4} R.N_2BF_4 \xrightarrow{\text{heat}} R.F + N_2 + BF_3.$$

This type of reaction was extensively developed in subsequent years by Schiemann and other workers and a considerable number of experimental modifications are known.

More recently Ferm and van der Werf (J. Amer. Chem. Soc., 1950, 72, 4809) have reported that excellent yields of aromatic fluoro-compounds can be obtained by diazotisation of corresponding amines dissolved in anhydrous hydrogen fluoride, followed by reflux to decompose the diazonium fluoride.

(2) The replacement of other halogens by fluorine by the use of inorganic fluorides -

The principle of this method consists in causing a double exchange to occur between an organic halide and an inorganic fluoride. Where the organic halogen to be substituted is chemically very active, substitution is usually simple; thus for example acyl halides may be converted to acyl fluorides by use of antimony trifluoride (Meslans et al., Compt. rend., 1890, 110, 717) or hydrogen fluoride (Fredenhagen and Cadenbach, Z. physik. Chem., 1933, A164, 201). Alkyl monohalides are converted to the fluorides by the use of silver, mercurous or mercuric fluorides, a fluoride of mercury being generally most convenient (Henne, J. Amer. Chem. Soc., 1938, 60, 1569 and other papers of this series).

Polyhalides with several halogen atoms linked to the same carbon atom are best fluorinated with antimony trifluoride in the presence of pentavalent antimony in small quantities (Swarts, Bull. acad. roy. Belg., 1893, (3), 24 and subsequent publications). Hydrogen fluoride can act as the source of fluorine for organic di- or tri-halides, the halogen atoms of which are all linked to a single carbon atom; e.g. the conversion of $C_6H_5.C\,Cl_3$ to $C_6H_5.CF_3$ (Osswald, Müller and Steinhaüser, Ger. Pat., 1933, 575593) and of $C\,Cl_3C\,Cl = C\,Cl_2$ to $CF_3\,C\,Cl = C\,Cl_2$ (Henne, Whaley and Stevenson, J. Amer. Chem. Soc., 1941, 63, 3478).

The use of the halogen fluorides in the substitution of fluorine for other halogens could justifiably be included in this section, but as a detailed consideration of their reactions with organic compounds is to be made later, it is sufficient here to note the method for the sake of completeness.

(3) Addition of hydrogen fluoride to olefinic or acetylenic linkages. -

By this process olefines and hydrogen fluoride have been successfully combined giving fluorides (von Grosse and Lind J. Org. Chem., 1938, 3, 26; von Grosse, Wacker and Lind, J. Phys. Chem., 1940, 44, 275) and higher alkynes give 2 - 2 difluoro-alkanes exclusively (von Grosse and Lind, Amer. Chem. Soc. Baltimore Meeting, 1939) Acetylene itself reacts with difficulty at room temperature to give a mixture of vinyl fluoride and ethylidene difluoride.

(4) The use of metallic fluorides of higher valency states which are capable of replacing hydrogen in organic compounds by fluorine.

This method has been devised by Fowler and his collaborators (Ind. Eng. Chem., 1947, 39, 292) and it involves the indirect use of fluorine. The fluorides of the higher valency states of certain metals (e.g. cobalt tri-fluoride and silver difluoride) are sufficiently active as fluorinating agents to replace hydrogen by fluorine and also to saturate double bonds with fluorine when the hydro-carbon vapour is passed over them at 300-350°c. Manganese trifluoride and cerium tetrafluoride have also been employed in vapour phase fluorinations.

The reaction is typified by the equation -

$$R.H + 2\,CoF_3 \xrightarrow{300-350^{\circ}c.} R.F + 2\,CoF_2 + HF$$

- and the heat produced is considerably less than that of direct fluorination, and hence causes less fusion of carbon - carbon bonds.

The use of cobaltic and argentic fluorides is also applicable to the liquid phase fluorination of compounds already containing appreciable amounts of fluorine but this type of reaction is too vigorous for any less stable compounds.

(5) Fluorination by electrochemical method -

Simons (J. Electrochem. Soc., 1949, 47) has shown that, when certain organic compounds are dissolved in anhydrous hydrogen fluoride and electrolysed under conditions such that no free fluorine is produced in the experiment, it is possible to obtain fluorocarbons and fluoro-carbon derivatives from the reaction products. When the method was applied to carboxylic acids, ketones alcohols and ethers the principal products of the electrolysis were fluoro-carbons with the same number of carbon atoms as the hydro-carbon radical of the organic compound although the occurrence of further fragmentation and of polymerisation was noted.

(6) The direct action of fluorine upon organic compounds.

The introduction of fluorine into organic compounds has been in many cases accomplished by the direct action of fluorine upon them, as opposed to the indirect methods which have been discussed (vide supra). The first successful fluorination of a hydro-carbon was reported by Bockemüller (Ann., 1933, 506, 20): gaseous fluorine was passed into a dilute solution of cyclohexane in dichlorodifluoromethane in glass apparatus at - 80°C and a yield of approximately 33% of monofluorocyclohexane $C_6H_{11}F$ was reported. Later workers investigating the fluorination of ethane (Calfee and Bigelow, J. Amer. Chem.

Soc., 1937, 59, 2072; Young, Fukuhara and Bigelow, ibid, 1940, 62, 1171) carried out work in the vapour phase over copper wire screens and obtained a number of substitution products together with carbon tetrafluoride.

A detailed study of the fluorination of benzene was carried out by Fukuhara and Bigelow (ibid, 1941, 63, 2792) in the vapour phase with copper gauze packing. The ultimate products isolated were CF_4, C_2F_6, C_3F_8, C_4F_{10}, C_5F_{10}, C_6F_{12}, C_6HF_{11} and $C_{12}F_{22}$: no aromatic fluorides were obtained. These results indicate that addition followed by substitution, and also fragmentation and polymerisation all occur during direct fluorination.

Such phenomena have all been explained by Bigelow (Chem. Rev., 1947, 40, 89ff.) on the basis of the theory of atomic chain reactions. The fluorine molecule is first split into atoms by thermal or catalytic action (or both) :-

$$F_2 \rightleftharpoons 2F^{\bullet}$$

- after which the following processes may occur.

(1) Addition

$$R_2C = CR_2 + F^{\bullet} \longrightarrow R_2CF - \underset{\bullet}{C}R_2$$

$$R_2CF - \underset{\bullet}{C}R_2 + F_2 \longrightarrow R_2CF - CFR_2 + F^{\bullet}$$

(2) Substitution

$$RH + F^{\bullet} \longrightarrow HF + R^{\bullet}$$

$$R^{\bullet} + F_2 \longrightarrow RF + F^{\bullet}$$

(3) Fragmentation

$$RCF_2 - CF_2R + F^{\bullet} \rightarrow RCF_3 + {}^{\bullet}CF_2R$$

$${}^{\bullet}CF_2R + F_2 \rightarrow RCF_3 + F^{\bullet}$$

(4) Dimerisation

$$R^{\bullet} + R^{\bullet} \rightarrow R - R \text{ (chain breaker)}$$

(5) Polymerisation

$$R_2CF - \underset{\bullet}{C}R_2 + R_2C = CR_2 \rightarrow R_2CF - CR_2 - CR_2 - \underset{\bullet}{C}R_2$$

until formation of end product by

$$R_2CF\ (CR_2)_n - \underset{\bullet}{C}R_2 + F_2 \rightarrow R_2CF\ (CR_2)_n - CFR_2 + F^{\bullet}$$

Elementary fluorine has also been employed in the replacement of other halogens. Thus carbon tetrachloride was converted into a mixture of chlorofluoromethanes and carbon tetrafluoride by fluorine diluted with nitrogen in the presence of cobaltic fluoride as a "fluorine-carrier" catalyst (Ruff and Keim, Z. anorg. allgem. Chem., 1931, 201, 245). In the presence of arsenic and bromine the reaction was moderated in such a way that the product was almost pure fluorotrichloromethane (Simons, Bond and Mc. Arthur, J. Amer. Chem. Soc., 1940, 62, 3477). These last authors found also that when a mixture of fluorine and difluorodichloromethane was passed over a mercury catalyst at high temperatures a good yield of triflurochloromethane resulted.

The method of direct fluorination has been the subject of considerable study in the past few years and numerous modifications in experimental technique and catalytic conditions have been reported in the literature (e.g. Miller, J. Amer. Chem. Soc., 1940, 62, 341; Cady et al., Ind. Eng. Chem., 1947, 39, 290; Musgrave and Smith, J. Chem. Soc., 1949, 3021). It is difficult to draw a firm line between this method and the method using metallic halides. When copper is used as catalyst it shows little change, but other metals are certainly converted to fluorides which may 'carry' the fluorine.

Beyond these six main reaction groups, one other method, of limited scope, may be noted: this is the reaction of aryl iodo-difluorides with certain aromatic and polynuclear compounds (Bockemuller, Ber., 1931, 64, 522; Garvey, Halley and Allen, J. Amer. Chem. Soc., 1937, 59, 1827). Such a process may bring about either substitution or polymerisation, or both: thus diethylaniline gives p-fluorodiethylaniline together with tetraethylbenzidine, and anthracene gives 9-fluoro-anthracene.

Chlorine trifluoride as a Halogenating Agent.

Having reviewed the general methods by which chlorine and fluorine may be introduced into organic molecules, it is now possible to consider the chemistry of the halogen fluorides, particularly chlorine trifluoride, and to examine their possibilities as reagents in organic chemistry.

All seven of the known halogen fluorides have been prepared either by direct union of the two halogen constituents under various conditions, or, in the cases of some higher fluorides, by the direct fluorination of the lower fluoride. Iodine pentafluoride was first definitely characterised by Moissan (Compt. rend., 1902, 135, 563), bromine trifluoride was discovered independently by Lebeau (ibid, 1905, 141, 1015) and Prideaux (J. Chem. Soc., 1906, 89, 316), whilst all the rest were first prepared by Ruff and his co-workers between 1925 and 1933.

Chlorine monofluoride was first made from the elements (Ruff and Ascher, Z. anorg. allgem. Chem., 1928, 176, 258) as also was chlorine trifluoride (Ruff and Krug, ibid, 1930, 190, 270). On the technical scale chlorine trifluoride is obtained by heating the elements in nickel apparatus, first forming the monofluoride (200°C) then the trifluoride at 280°C (Leech, Quart. Reviews, 1949, 3, 22; see also Porter, Chem. Eng., 1948, 55, (4), 102). Bromine monofluoride was made from the elements at 10°C (Ruff and Braida, Z. anorg. allgem. Chem., 1933, 214, 81) and was found to be thermally unstable, disproportionating at relatively low temperatures -

$$3\,BrF \longrightarrow BrF_3 + Br_2.$$

Bromine pentafluoride and iodine heptafluoride were obtained by fluorination of bromine trifluoride at 200°C. (Ruff and Menzel, ibid, 1931, <u>202</u>, 49) and iodine pentafluoride at 280°C (Ruff and Keim, ibid, 1930, <u>193</u>, 176) respectively.

The halogen fluorides, like fluorine itself, are exceptionally reactive; their outstanding chemical property is their powerful oxidising action upon almost every type of chemical element or compound. The approximate order of their reactivity may be written as the series -

$$ClF_3 > BrF_5 > IF_7 > ClF > BrF_3 > IF_5 > BrF$$

but it should be noted that little is known about the chemical properties of bromine monofluoride owing to its thermal instability. Observations show that the halogen fluorides apparently react, at least to some extent, with all metals (Booth and Pinkston, Chem. Rev., 1947, <u>41</u>, 421) though in certain cases fluoride filming occurs, preventing further reaction, especially at lower temperatures. If no protective film is formed a vigorous reaction ensues; the fluorination of several metals with chlorine trifluoride at various temperatures is reported by Hückel (Nachr. Akad. Wiss. Math. Physik. Klasse (Göttingen), 1946, 36).

In so far as the non-metallic elements are concerned, the only cases where no reaction with halogen fluorides has been reported are those of nitrogen, oxygen and the rare gases. Generally speaking, the only differences in the reaction of non metals towards the halogen fluorides from that of metals is that fluoride filming does not occur and the reactions generally proceed at, or relatively near, room temperature. By reaction with a halogen fluoride either at, or slightly above, room temperature, boron, silicon, phosphorus, arsenic, antimony, sulphur, selenium and tellurium all give rise to the corresponding fluorides: the reactions which occur in these cases are generally of a violent nature. Hydrogen burns in the halogen fluorides though considerable heating is sometimes required for its ignition.

Reactions between the halogen fluorides and chlorine, bromine and iodine often occur readily and various equilibria are set up: the available data is however only of a qualitative nature (Booth and Pinkston, loc. cit.) except for the reaction between chlorine and chlorine trifluoride which is stated to proceed to completion with formation of chlorine monofluoride thus :-

$$Cl_2 + ClF_3 \longrightarrow 3\,Cl\,F$$

(Schmitz and

Schumacher, Z. Naturforsch., 1947, 2a, 362).

The halogen fluorides have found practical application as fluorinating agents in inorganic chemistry. Thus thionyl chlorofluoride $SOClF$ is obtained by the reaction of bromine trifluoride or iodine pentafluoride upon thionyl chloride (Soll, F.I.A.T. Rev. German Science (1939-46), Inorg. Chem. Pt. I, 1948, 192). Sulphuryl bromofluoride SO_2BrF is obtained by the interaction of sulphur dioxide, bromine trifluoride and bromine in an autoclave at room temperature (Kwasnik, ibid, 193). The same author (ibid, 243) has also reported the preparations of carbonyl chlorofluoride $COClF$ (from carbon monoxide and chlorine monofluoride), carbonyl bromofluoride $CO\,Br\,F$ (from carbon monoxide and bromine trifluoride) and carbonyl iodofluoride $CO^{I}F$ (from carbon monoxide and iodine pentafluoride). The reaction of liquid bromine trifluoride on a number of metallic chlorides, bromides and iodides has been investigated by Sharpe and Emeleus (see Sharpe, Quart. Reviews, 1950, 4, 121) and, with the exception of silver, the products were generally the highest known fluorides of the metals concerned, though films of reagent-insoluble fluorides often prevented complete reaction. For example, plumbous, thallous and cobaltous halides yielded mixtures of lower and higher fluorides. Where the product was volatile (e.g. uranium hexafluoride) or reagent-soluble (e.g. alkali metal fluorides) conversion to the fluoride was quantitative. The fluorides of sodium, potassium, monovalent silver, barium, rubidium and caesium dissolved in excess of the reagent giving bromotetrafluorides, of which those of the last two metals were relatively unstable.

More generally, where a metal has more than one valence state, the amount of any particular fluoride formed by reaction of the halide of such a metal with a halogen fluoride depends upon the oxidising power of the latter. This variation in oxidising power has been illustrated by a study of the reactions of halogen fluorides with tricobalt tetroxide and cobaltous chloride (Gall, Miller, Verdelli and Loomis, Amer. Chem. Soc. New York Meeting, Sept. 1947). In reactions with the oxide, chlorine trifluoride gave more than 95% cobaltic fluoride whilst chlorine monofluoride and bromine pentafluoride gave 98% and 90% cobaltous fluoride respectively and iodine pentafluoride did not react. Cobaltous chloride was completely converted to cobaltic fluoride by chlorine trifluoride, while mixtures of 55% CoF_3 and 45% CoF_2, 45% CoF_3 and 55% CoF_2 were obtained by use of bromine penta- and tri-fluorides respectively. Iodine pentafluoride gave only cobaltous fluoride, which amounted to 72% of the total solid product.

The data regarding reaction of the halogen fluorides with organic compounds is scanty and often only qualitative in nature. Previous to 1949, the only records giving details of the employment of a halogen fluoride to obtain a desired product concerned bromine trifluoride and iodine pentafluoride (vide infra), together with one single mention of chlorine trifluoride (Hückel, Nachr. Akad. Wiss. Math. Physik Klasse (Göttingen), 1946, 36) which has already been noted (see page 1).

There is no record of any reaction between bromine monofluoride and organic compounds; presumably this is due to its thermal instability and subsequent difficulties in purification and handling. Some qualitative work on iodine heptafluoride was reported by Ruff and Keim (Z. anorg. allgem. Chem., 1930, 193, 176). Reactions were usually violent generally with the apparent production of complex mixtures of degraded organic fluorides and iodine. The direct reaction between, for instance, iodine heptafluoride and benzene and other hydrocarbons is reported to proceed with spontaneous ignition. Similarly, bromine pentafluoride is stated to react in a violent manner with organic compounds under direct conditions often with incandescence or even explosion (Ruff and Menzel, ibid, 1931, 202, 49). In the case of chlorine monofluoride no observation of a controlled reaction was made; a wide range of organic compounds tested were all seen to catch fire in an atmosphere of chlorine monofluoride (Ruff and Ascher, ibid, 1928, 176, 258). Similarly chlorine trifluoride was stated by its discoverers (Ruff and Krug, ibid, 1930, 190, 270) to undergo violent and often explosive reactions with benzene, ether, paraffin oil, acetic acid and other organic compounds.

It seems apparent that in the cases of chlorine mono- and tri- fluorides, bromine pentafluoride and iodine heptafluoride, the results of direct interaction with organic compounds not already containing halogens, in non-moderated conditions, give rise to complex mixtures of organic degradation products. This state of affairs is however, most probably only due to the fact that the reaction conditions used were not conducive to the formation of stable products. According to the reports, there seems to have been little or no attempt to control the violence of the reactions which were merely effected by direct contact.

The first case of a halogen fluoride substituting the hydrogen of an aromatic nucleus to give an aromatic fluoride was reported by Ruff and Keim (ibid, 1931, 201, 245). These investigators caused benzene to react with iodine pentafluoride at temperatures below 50°C, and although the principal products of the reaction were carbonized matter and iodobenzene and other iodinated derivatives, a small quantity of fluorobenzene was also formed. As the latter interdistilled with unchanged benzene it was only qualitatively characterised; the mixture was nitrated and a mixture of nitro-compounds containing fluorine but no iodine was obtained.

When, however, the halogen fluorides were used to replace other halogens in stable highly halogenated organic molecules, much more satisfactory results were obtained. Thus Ruff and Keim (loc cit.) were able to prepare trichlorofluoromethane in reasonable yield by maintaining iodine pentafluoride in contact with carbon tetrachloride at 30-35°C for an extended period; a small quantity of difluoro-derivative was also formed. By the reaction of iodine pentafluoride on iodoform, Simons, Bond and Mc.Arthur (J. Amer. Chem. Soc., 1940, 62, 3477) obtained fluoroform together with a small quantity of difluorodi-iodomethane. When carbon tetraiodide was reacted with iodine pentafluoride in glass apparatus the product was found to be trifluoroiodomethane (Banks, Emeleus, Haszeldine and Kerrigan, J. Chem. Soc., 1948, 2188). Emeleus et al. have also shown that iodine pentafluoride reacts with carbon tetrabromide giving bromofluoromethanes, and with tetraiodoethylene to give iodopentafluoroethane.

Lebeau (Compt. rend., 1905, 141, 1018) and also Ruff and Braida (Z. anorg. allgem. Chem., 1932, 206, 63) observed that bromine trifluoride reacted violently with organic compounds but the first investigators to carry out a controlled reaction were Nutting and Petrie (U.S. Pat., 1934, 1961622) who showed that mixed chlorofluoromethanes could be obtained by reaction with carbon tetrachloride. This reaction was subjected to further study by Emeleus et al. (J. Chem. Soc., 1948, 2188) who showed that in copper apparatus using nitrogen as diluent the chief product was fluorotrichloromethane with a smaller quantity of difluorodichloromethane. These last authors also showed that bromine trifluoride reacts with carbon tetraiodide to give carbon tetrafluoride together with mixed bromofluoromethanes.

Mc.Bee, Lindgren and Ligett (Ind. Eng. Chem., 1947, <u>39</u>, 378) used bromine trifluoride in the course of syntheses of hexafluorobenzene and octafluorotoluene. Hexachlorobenzene and trifluoromethylpentachlorobenzene reacted smoothly with bromine trifluoride at moderate temperatures, fluorine was added to double bonds, chlorine was replaced by fluorine and bromine was introduced in limited amounts. The approximate constitutions of products obtained from C_6Cl_6 and $C_6Cl_5.CF_3$ were $C_6Br_2Cl_4F_6$ and $C_6Br_2Cl_3F_6.CF_3$ respectively. Subsequent treatment of these intermediates with antimony pentafluoride, then zinc dust in alcohol gave rise to the required fluoro compounds C_6F_6 and $C_6F_5.CF_3$.

Bromine trifluoride has also been found to be effective for the partial substitution of fluorine and bromine into certain Kerosene fractions without appreciable side reactions (Shenk, private comm. to Booth and Pinkston, Fluorine Chemistry (ed. Simons) I, 199). The hydro-carbon mixture was maintained below 40°C in dilute solution in methylene chloride.

Apart from the work of Hückel which has already been cited, the only reports on the controlled reaction of chlorine trifluoride with organic compounds previous to 1950 gave no details. Porter (Chem. Eng., 1948, 55, (4), 102) and also Burnett and Banks (Chem. Soc. Symp. on Fluorine Chemistry, Nov. 1949) have stated that the reaction of chlorine trifluoride with organic compounds results in the introduction of both fluorine and chlorine, whilst Haszeldine (private comm. to Sharpe, Quart. Reviews, 1950, 4, 128) has reported that evidence has been obtained of the production of chlorofluoro-addition and also substitution compounds, in the vapour phase reaction of chlorine trifluoride with benzene and toluene.

From the preceding review it can be seen that the possibility of employing chlorine trifluoride as a halogenating agent either to substitute hydrogen by halogen, or to replace other halogen by fluorine, or to prepare halogeno-additive compounds had been largely neglected and the mechanism of the reaction between chlorine trifluoride and organic compounds remained unknown. In order to attempt to throw some light on these features, it was therefore decided to investigate the reaction of chlorine trifluoride with (a) carbon tetrachloride (b) benzene and (c) benzene derivatives, all in the liquid phase and in the presence and absence of various catalysts. The examination of the reaction of carbon tetrachloride with chlorine trifluoride was of primary interest to ascertain whether the carbon tetrachloride would prove relatively inert to the action of the latter reagent, thus enabling it to be used as a solvent. In addition it was essential to know the extent of any reaction with the solvent so that it could be taken into account in formulating possible reaction mechanisms.

The data which has been obtained by the present investigators will be set out in five main sections :-

(i) Reaction with carbon tetrachloride
(ii) Reaction with benzene
(iii) Reaction with benzene homologues
(iv) Reaction with halobenzenes
(v) Reaction with perhalomethylbenzenes.

(i) The reaction between Chlorine Trifluoride and Carbon Tetrachloride.

The fluorination of carbon tetrachloride has been described by various investigators over a considerable number of years. Fluorotrichloromethane was first prepared by Swarts (Bull. acad. roy. Belg., 1893 (3), 24) by the reaction of antimony trifluoride on carbon tetrachloride in the presence of small quantities of pentavalent antimony salts required as "fluorine carrier."

The reaction of fluorine with carbon tetrachloride was first carried out by Ruff and Keim (Z. anorg. allgem. Chem., 1931, 201, 245) under controlled conditions. Several moderators or 'fluorine carriers' were employed, the most satisfactory being cobaltic fluoride. It was found that fluorotrichloromethane, difluorodichloromethane, trifluorochloromethane and carbon tetrafluoride were all formed in proportions which were dependent upon experimental conditions. The reaction of carbon tetrachloride with fluorine has been reported by Bigelow, Pearson, Cook and Miller (J. Amer. Chem. Soc., 1933, 55, 4614) as giving rise to a residual solution with a very strong chlorinating action which would be compatible with formation of considerable quantities of chlorine monofluoride, as this latter compound is postulated as having a strong chlorinating action (Bigelow et al., ibid, 1940, 62, 267; Ind. Eng. Chem., 1947, 39, 360). It is therefore likely that the course of the reaction could be represented by the equations :-

$$C\,Cl_4 + F_2 \longrightarrow C\,Cl_3F + ClF$$

$$C\,Cl_3F + F_2 \longrightarrow C\,Cl_2F_2 + ClF$$

$$C\,Cl_2F_2 + F_2 \longrightarrow C\,ClF_3 + ClF$$

$$C\,ClF_3 + F_2 \longrightarrow CF_4 + ClF$$

Reaction of iodine pentafluoride with carbon tetrachloride in a quartz vessel at temperatures below 50°C gave rise to fluorotrichloromethane as main product and a small quantity of difluorodichloromethane (Ruff and Keim, loc. cit.). As no lower fluorides of iodine are known the initial reaction would probably be covered by the equation :-

$$3\,C\,Cl_4 + IF_5 \longrightarrow 3\,C\,Cl_3F + 2\,Cl\,F + I\,Cl.$$

followed by

$$3\,C\,Cl_3F + IF_5 \longrightarrow 3\,C\,Cl_2F_2 + 2\,Cl\,F + I\,Cl.$$

occurring to a much smaller extent. Interaction between the halogen fluorides in side-reactions would be very likely.

According to Banks, Emeleus, Haszledine and Kerrigan (J. Chem. Soc., 1948, 2188) the reaction between bromine trifluoride and carbon tetrachloride at atmospheric pressure in copper apparatus readily gives rise to the volatile products fluorotrichloromethane and difluorodichloromethane, but to obtain reasonably good yields of trifluorochloromethane it is necessary to carry out the reaction in an autoclave. This is in agreement with the observation (Smith, Ann. Rep. Chem. Soc., 1947, 44, 98) that in reactions with inorganic fluorides the replacement of the first two chlorine atoms in a group - $C\,Cl_3$ is relatively easy, but replacement of the third requires more vigorous action.

The mechanism of the reaction between bromine trifluoride and carbon tetrachloride is postulated by Emeleus et al. (loc. cit., above) as being a simple stepwise substitution of fluorine for chlorine with the bromine trifluoride being transformed in stages into unstable lower fluoride forms which enter into reaction. Thus :-

$$C\,Cl_4 + Br\,F_3 \longrightarrow C\,Cl_3F + BrF_2$$

$$C\,Cl_3F + Br\,F_2 \longrightarrow C\,Cl_2F_2 + BrF$$

It is to be presumed that any bromine monofluoride formed would subsequently disproportionate into bromine and bromine trifluoride (Ruff and Braida, Z. anorg. allgem. Chem., 1933, 214, 91), -

$$3\,BrF \longrightarrow Br_2 + BrF_3$$

- and the

trifluoride would enter into further reaction. The fact that no compounds containing more than one carbon atom per molecule were observed as reaction products is quoted by Emeleus and his co-workers as evidence tending to indicate that organic free radicals play no significant part in the reaction mechanism.

In the present reactions, the controlled reaction between chlorine trifluoride and carbon tetrachloride, using nitrogen as diluent was observed to give rise to fluorotrichloromethane, and in certain cases a smaller amount of difluorodichloromethane as well. Experiments were carried out in steel apparatus under uncatalysed conditions and also in the presence of anhydrous cobaltous fluoride. This compound was employed as it had consistently given the best overall yield in the series of reactions with benzene (see section (ii)) and had been employed as catalyst in the reactions with benzene derivatives (see sections (iii), (iv), and (v)). In the series of experiments carried out the effect of changes in temperature between 0°C and 25°C was also noted.

The results of the experimental work are summarised in Table I: in all the cases mentioned 0·5 litre of dry carbon tetrachloride was treated with chlorine trifluoride (5-7 grs./hour) in a nitrogen stream (5 l./hour). The reaction

TABLE I

Expt No.	Cata-lyst	ClF_3(g) passed	Time (hrs)	Temp. (°C)	Products							Carried over C Cl4 (mls)	Residue (mls) u-c.exp. only.
					CCl_2F_2 (mls)	Distn. temp.°	Inter. medt. (mls)	Distn. temp.°	CCl_3F (mls)	Distn. temp.°	CCl_3F n_D^{20}		
1.	None	40	6.5	25	0.5	-28	1.0	+6 to +9	12.5	+23 to +24	1.3830	16.0	462
2.	None	42	8.0	25	2.1	-28 to -26	1.6	-14 to 0	16.9	+23 to +24	1.3842	16.5	455
3.	None	41	6.75	0	-	-	0.5	+6 to +9	2.8	+23 to +24	1.3831	6.5	484
4.	CoF_2 (10g)	43	7.0	20	4.2	-28 to -26	1.0	-6 to 0	13.3	+23 to +25	1.3830	16.0	-
5.	CoF_2 (10g)	40	6.5	25	3.1	-28 to -26	-	-	20.5	+23 to +25	1.3834	22.0	-
6.	CoF_2 (10g)	42	6.75	0	-	-	0.7	0 to +3	3.9	+23 to +25	1.3830	6.0	-

under such conditions is mild in nature and at a temperature of 0°C is extremely slow: observations made, show however that the extent of the reaction is considerably increased by raising the temperature to about 25°C. This is in agreement with the qualitative submission of Ruff and Krug (ibid, 1930, 190, 270), in which it is stated that the reaction of liquid chlorine trifluoride on carbon tetrachloride is slight except on heating, when it becomes violent.

Furthermore, the yields of fluorochloromethanes under the conditions of the experiments are improved by lengthening the period of contact between the chlorine trifluoride and carbon tetrachloride: i.e. the chlorine trifluoride utilisation is greater when the flow rate is slower compared with the fixed flow rate of nitrogen. The influence of the cobaltous fluoride upon the reaction was to increase to some extent the yields of fluorochloromethanes relative to the amounts isolated from uncatalysed experiments carried out under analogous conditions.

Chlorine trifluoride appears to behave in a similar way towards carbon tetrachloride as bromine trifluoride and iodine pentafluoride. It is, however, much more reactive then the latter reagent, the action of which is stated (Ruff and Keim, loc. cit.) to be very slow even at 30-35°C in the absence of diluents. The mild nature of the fluorinating action of iodine pentafluoride is further accentuated by the fact that only a few per cent of fluorotrichloromethane was changed to difluorodichloromethane when the former was passed through boiling iodine pentafluoride and the resulting gas mixture heated to 225°C. Comparison of the reactions of chlorine and bromine trifluorides with carbon tetrachloride is rather more difficult owing to differences in experimental conditions. In the work carried out by Emeleus et al, (loc. cit.), bromine trifluoride was distilled in a slow nitrogen stream into carbon tetrachloride contained in a water-cooled copper trap thus giving less mild reaction conditions than in the series of experiments with chlorine trifluoride, since the bromine trifluoride (b.p. 127°C) was in prolonged and continuous contact with the carbon tetrachloride. Even under such conditions no trifluorochloromethane was obtained from experiments with carbon tetrachloride and bromine trifluoride at atmospheric pressure so that it is unlikely that bromine trifluoride would be more reactive than chlorine trifluoride were analogous conditions of reaction to be employed.

In an attempt to explain solvent effects in the reaction between benzene and chlorine trifluoride in carbon tetrachloride solution previous to the experiments summarised in Table I, it was postulated (Ellis and Musgrave, J. Chem. Soc., 1950, 3609) that there were two possible ways of attack of chlorine trifluoride on carbon tetrachloride.

(1) <u>i</u> $ClF_3 + C\,Cl_4 \rightarrow C\,Cl_3F + 2ClF.$

followed by

<u>ii</u> $C\,Cl_3F + ClF_3 \rightarrow C\,Cl_2F_2 + 2ClF.$

or

(2) <u>i</u> $C\,Cl_4 + ClF_3 \rightarrow C\,Cl_2F_2 + ClF + Cl_2$

followed by

<u>ii</u> $Cl_2 + ClF_3 \rightarrow 3ClF$

Schmitz and Schumacher (Z. Naturforsch., 1947, <u>2a</u>, 362) report reaction (2) <u>ii</u> as proceeding to completion in the gas phase.

Even without the results which have been quoted in Table I, the alternative (2) seems rather unlikely as under the mild conditions of the experiments it is doubtful whether two chlorine atoms would simultaneously be replaced by two fluorine atoms.

The results obtained confirm reaction series (1), the chief reaction product being fluorotrichloromethane with an amount of difluorodichloromethane as secondary product compatible with the reaction (1) ii occurring subsequent to, and competitive with the reaction (1) i. The absence of trifluorochloromethane from the reaction products is as expected from the small amounts of difluoro-derivative isolated and the fact that chlorine in compounds $R.C\,ClF_2$ is much more difficult to replace by fluorine than that in monofluoro-derivatives of the type $R.C\,Cl_2F$ (Smith, loc. cit.).

Were the reaction series (2) to be operative absolutely, no fluorotrichloromethane would be formed, which is untrue, and were it to occur simultaneously with the series (1) to an appreciable extent one might expect a much greater proportion of difluorodichloromethane in the reaction product than is actually observed. It seems, therefore, that the subsequent reactions (1) i and (1) ii are the only acceptable view of the overall reaction between chlorine trifluoride and carbon tetrachloride under the conditions noted.

From an examination of the results obtained at 0°C it seems unlikely that there will be any appreciable reaction of chlorine trifluoride with carbon tetrachloride in the presence of the much more reactive compounds which have aromatic nuclei. Since the experiments concluded were carried out under similar conditions it would thus appear legitimate to assume that carbon tetrachloride is to all intents and purposes, an inert solvent for the series of reactions carried out on benzene and its derivatives.

Although the nature of the reaction between carbon tetrachloride and chlorine trifluoride has been decided upon (vide supra) the mechanism of the substitution of fluorine for chlorine in the organic molecule remains to be discussed.

Of the four mechanisms which appear to be feasible, two are of the free radical type, and the third and fourth involve anionoid and cationoid replacements respectively. In either free radical mechanism we must first assume the dissociation

$$\mathrm{Cl\,F_3} \rightleftharpoons \mathrm{Cl\,F} + \mathrm{F}^{\bullet} + \mathrm{F}^{\bullet} \; \ldots\ldots\ldots\ldots\ldots \; (1)$$

followed by one of the two processes.-

a) $\mathrm{C\,Cl_4} + \mathrm{F}^{\bullet} \longrightarrow {}^{\bullet}\mathrm{C\,Cl_3} + \mathrm{Cl\,F}$

$${}^{\bullet}\mathrm{C\,Cl_3} + \mathrm{Cl\,F_3} \longrightarrow \mathrm{C\,Cl_3F} + \mathrm{ClF} + \mathrm{F}^{\bullet}$$

and subsequently

$$\mathrm{C\,Cl_3F} + \mathrm{F}^{\bullet} \longrightarrow {}^{\bullet}\mathrm{C\,Cl_2F} + \mathrm{ClF}$$

$${}^{\bullet}\mathrm{C\,Cl_2F} + \mathrm{ClF_3} \longrightarrow \mathrm{C\,Cl_2F_2} + \mathrm{ClF} + \mathrm{F}^{\bullet}$$

or b) $C\,Cl_4 + F^{\cdot} \longrightarrow C\,Cl_3F + Cl^{\cdot}$

$Cl^{\cdot} + Cl\,F_3 \longrightarrow 2\,Cl\,F + F^{\cdot}$

and subsequently

$C\,Cl_3F + F^{\cdot} \longrightarrow C\,Cl_2F_2 + Cl^{\cdot}$

$Cl^{\cdot} + Cl\,F_3 \longrightarrow 2\,Cl\,F + F^{\cdot}$

In either replacement mechanism the initiating reaction would be the dissociation

$Cl\,F_3 \rightleftharpoons Cl\,F + F^+ + F^-$ .... (2)

followed by either

a) Anionoid replacement :-

$C\,Cl_4 + F^- \longrightarrow C\,Cl_3F + Cl^-$

$Cl^- + F^+ \longrightarrow Cl\,F$

and subsequently

$C\,Cl_3F + F^- \longrightarrow C\,Cl_2F_2 + Cl^-$

$Cl^- + F^+ \longrightarrow Cl\,F$

or b) Cationoid replacement :-

$C\,Cl_4 + F^+ \longrightarrow C\,Cl_3F + Cl^+$

$Cl^+ + F^- \longrightarrow Cl\,F$

and subsequently

$$C\,Cl_3F + F^+ \longrightarrow C\,Cl_2F_2 + Cl^+$$

$$Cl^+ + F^- \longrightarrow Cl\,F.$$

Of these, mechanism (1) b) is unlikely as the analogous reaction of $Cl^\bullet$ with $H\text{-}CR_3$ has been proved (from study of optical isomers of products when a compound $H\text{-}CR'R''R'''$ was used) to occur via the radical $^\bullet CR_3$ thus:-

$$Cl^\bullet + H\text{-}CR_3 \longrightarrow H\,Cl + {}^\bullet CR_3$$

$$^\bullet CR_3 + Cl_2 \longrightarrow Cl\text{-}CR_3 + Cl^\bullet$$

and not

$$Cl^\bullet + H\text{-}CR_3 \longrightarrow Cl\text{-}CR_3 + H^\bullet$$

$$H^\bullet + Cl_2 \longrightarrow Cl^\bullet + H\,Cl$$

(Brown, Kharasch and Chao, J. Amer. Chem. Soc., 1940, 62, 3435).

Thus if a free radical mechanism were to be adopted it would most likely be identified with (1) a). Generally speaking, however, most of the organic reactions known to occur via a free radical mechanism are rapid and vigorous in nature, and the reaction under consideration is slow and of a mild character. Furthermore no polymerisation has been observed in this or the analogous reaction of carbon tetrachloride with bromine trifluoride (Banks, Emeleus, Haszeldine and Kerrigan, loc cit.) and this would be expected if a free radical mechanism were operating.

$$\text{e.g.}\quad {}^{\bullet}C\,Cl_3 + {}^{\bullet}C\,Cl_3 \longrightarrow C_2Cl_6 \text{ etc.}$$

An anionotropic replacement is also unlikely: one of the requirements for the reaction $A^- + B\text{-}C \longrightarrow A\text{-}B + C^-$ is that the electrol affinity of C should be as high and that of A as low as possible (since electrons move from A to C in the transition state). In this case the electron affinity of fluorine is 4·13 e.v. and of chlorine 3·72 e.v. (from data collected by Glockler, Fluorine Chemistry, (ed. Simons) I, 321) which would infer that the reaction $F^- + Cl - C\,Cl_3 \longrightarrow F - C\,Cl_3 + Cl^-$ is most unlikely.

The relative electron affinities tend to support the possibility of cationoid change $F^+ + Cl - C\,Cl_3 \longrightarrow F - C\,Cl_3 + Cl^+$. This possibility is further supported by the fact that chlorine trifluoride can give rise to the substitution of fluorine in aromatic compounds (which is generally accepted as a cationoid reaction), and also the reaction is catalysed by cobaltous fluoride and this process may be best expressed as follows.

$$ClF_3 + 2\,CoF_2 \longrightarrow 2\,CoF_3 + ClF$$

$$CoF_3 + ClF_3 \longrightarrow ClF + F^+ + CoF_4^-$$

$$F^+ + CCl_4 \longrightarrow CCl_3F + Cl^+$$

$$Cl^+ + CoF_4^- \longrightarrow CoF_3 + ClF$$

Subsequently, difluorodichloromethane may be formed by parallel reactions.

(ii) The reaction of Benzene with Chlorine Trifluoride using Carbon Tetrachloride as solvent.

Apart from references which give no details (see introduction), and the qualitative treatment of Ruff and Krug (Z. anorg. allgem. Chem., 1930, 190, 270) in which benzene is stated to 'react violently' with liquid chlorine trifluoride, the interaction of these two reagents is not dealt with in the literature and does not seem to have been studied.

A series of experiments was therefore carried out on the controlled reaction of chlorine trifluoride with benzene. It was decided that all such experiments would be carried out in the liquid phase using carbon tetrachloride as solvent for the benzene and nitrogen as diluent for the chlorine trifluoride gas-stream. A number of different compounds were employed as catalysts (see Table II) : these were either well known halogen carriers or salts of transitional metals which had been employed as catalysts in the direct fluorination of organic compounds (Cady et al., Ind. Eng. Chem., 1947, 39, 290 ; Fowler et al., ibid, p. 292 ; Musgrave and Smith, J. Chem. Soc., 1949, 3021).

Inspection of Tables II and III shows that the principal reaction in all cases, including the non-catalysed experiment, is one of substitution, the chief products being chlorobenzene and fluorobenzene. Certain addition products, appearing, on the grounds of their reactions and analyses, to be chlorofluorocyclohexadienes, -cyclohexenes and -cyclohexanes were also obtained from the reaction products, but only in experiments 7 and 9 were they obtained in reasonable quantity. The attempted redistillation of these compounds, even under reduced pressure, generally caused decomposition with evolution of hydrogen halide, and formation of tar. Occasionally it was possible to isolate from the higher boiling fractions before the onset of decomposition, small quantities of what were apparently chlorofluorodiphenyls : these were stable towards bromine water and aqueous potassium permanganate at room temperature, and their analysis tended also to support the view that there had been some dimerisation.

Of the compounds which were tried as catalysts, two, namely iodine and silver monofluoride, had only a negligible catalytic effect. In the case of iodine it is possible that inter-action with chlorine trifluoride gave rise to iodine pentafluoride (Ruff and Krug, loc. cit.) which is a much milder fluorinating agent than chlorine trifluoride. As iodine pentafluoride is stated only to produce trace quantities of fluorobenzene from benzene by direct action

(Ruff and Keim, Z. anorg. allgem. Chem. 1931, 201, 245) it is therefore not surprising that under the mild conditions of the experiment carried out (Table II, experiment 2) iodine did not act as a catalyst. The behaviour of silver monofluoride appears to be rather more difficult to explain as it has a pronounced effect upon direct fluorination (Cady et al., loc. cit.). One possible explanation of its behaviour is that chlorine trifluoride under the experimental conditions was an insufficiently strong fluorinating agent of fluorination when silver monofluoride is employed as a catalyst in conjunction with elementary fluorine. (c.f. Sharpe, Quart. Reviews, 1950, 4, 121 states that silver difluoride is not obtained by the reaction of bromine trifluoride upon silver halides).

Mercuric chloride (Table II, experiment 3) also does not appear to have any very marked effect - this is presumably due to lack of reaction with chlorine trifluoride (c.f. Ruff and Krug, loc. cit.) - though some increase in chlorination over the uncatalysed experiment is observed. Antimony trifluoride appears to facilitate a considerable amount of addition as well as catalyse appreciable chlorination, and of the cobalt salts, cobaltous fluoride tends to encourage most chlorination whilst cobaltous chloride seems to give rise to more fluorination but less addition than any other catalyst.

TABLE II

Expt.	Catalyst	Wt. of ClF_3 (g.) and flow rate (g/h).	Tar (g.)	Fluoro-benzene (g.)	Chloro-benzene (g.)	Ttl. Addn. Cpds. (g.).	Di-phenyls (g.).	Sec. Dec. (g.)
1.	None.	55 : 10	16·34	7·5	10·38	2·62	2·54	0·62
2.	I_2.	55 : 10	9·86	4·57	10·59	2·62	-	1·36
3.	$HgCl_2$.	60 : 10	20·60	8·3	15·6	2·67	-	0·28
4.	$CoCl_2$.	60 : 10	11·42	13·1	15·75	0·72	0·45	4·84
5.	AgF.	59 : 10	8·40	8·11	11·17	1·42	-	8·02
6.	CoF_2.	60 : 10	14·82	11·94	28·45	2·79	-	8·40
7.	CoF_2.	45 : 4	12·12	8·7 (11·6)	22·67 (30·27)	6·29 (8·39)	-	3·41
8.	CoF_2.	45 : 5	13·00	6·0 (8·0)	14·6 (19·5)	-	-	0·95
9.	SbF_3.	61 : 10	13·30	8.15	21·57	24·40	-	3·14

All experiments were carried out at 0°C except experiment 8 (77°C). In all except expts. 7 and 8 benzene (100 g.) was dissolved in carbon tetrachloride (500 ml.): in expts. 7 and 8 benzene (75 g) was dissolved in 750 mls CCl_4. Figures in parentheses gave corresponding yields per 100 g. benzene.

TABLE III. Addition products and diphenyls from benzene experiments. Part 1.

Expt.	Frac.	Yield (g.)	B.P. ^{0}C/8 mm.	n_D^{20}	Action of Br_2aq. and $KMnO_4$ aq.	Possible Formula.	Analysis			
							Found %. Cl	F	Calcd. % Cl.	F.
1.	a.	1·10	29 - 30	1·4827	decol.	$C_6H_6Cl_2F_2$.	37·6	20·1	38·0	20·3
	b.	0·32	69 - 70	1·4595	nil.	$C_6H_6Cl_2F_4$.	31·6	33·5	31·6	33·8
	c.	1·20	87 - 88	1·5442	rapid decol.	C_6H_6Cl F.	27·1	14·7	26·8	14·3
	d.	2·54	130 - 132	1·5950	nil.	$C_{12}H_8Cl$ F.	19·6	7·8	17·2	9·2
2.	a.	2·62	40 - 44	1·4883	decol.	$C_6H_6Cl_2F_2$.	38·0	19·9	38·0	20·3
3.	a.	1·40	31 - 32	1·5200	decol.	$C_6H_5Cl_2F$.	42·8	11·5	42·5	11·4
	b.	0·77	70 - 72	1·4992	decol.	$C_6H_5Cl_3F_2$.	46·0	16·4	48·1	17·2
	c.	0·50	*m.p.242 (d.).	-	nil.	$C_6H_3Cl_9$.	81·0	-	81·0	-

---

*-This substance crystallised from reaction mixture after removal of carbon tetrachloride, and was recrystallised from hot alcohol.

(continued overleaf)

TABLE III. Part 2.

Expt.	Frac.	Yield (g.)	B.P. °C/8 mm.	n_D^{20}	Action of Br_2 aq. and $KMnO_4$ aq.	Possible Formula	Analysis Found %		Analysis Calcd %	
							Cl	F	Cl	F
4.	a.	0·72	26-27	1·4700	decol.	$C_6H_5Cl_3F_2$.	34·8	27.6	34·6	27·8
	b.	0·45	76	-	nil.	$C_{12}H_7Cl\ F_2$	15·9	16·9	15·8	16·5
5.	a.	1·42	72-75	1·4761	decol.	as 4a.	34·4	27·6	as 4a.	
6.	a.	0·46	25-26	1·4861	decol.		34·9	27·8		
	b.	2·33	58-60	1·4830	decol.		34·8	27·4		
7.	a.	2·01	56-58	1·4826	decol.		34·2	27·6		
	b.	4·28	76-80	1·4858	decol.		31·8	24·4		
9.	a.	3·28	50 (14 mm.)	1·5035	decol.	$C_6H_6Cl\ F$	33·2	14·5	26·8	14·3
	b.	21·12	55-105	-	decol.	as 9a.	27·45	11·4	as 9a.	

No addition compounds or diphenyls were obtained from expt. 8.

Of all the catalysts employed, cobaltous fluoride and antimony trifluoride gave rise to the greatest total yield, though when the latter was used, a considerable amount of the isolated products was in the form of partly decomposed and non-redistillable addition compounds. When cobaltous fluoride was used, increase in the amounts of catalyst and solvent (in experiments 7 and 8, 100 grams catalyst were employed as compared with 10 grams in all other cases) coupled with decrease in the flow rate of chlorine trifluoride, did not appear to influence greatly the formation of substitution products, but increased the formation of addition products approximately threefold (see expt. 7). The overall yield was considerably reduced when the experimental temperature was increased to the boiling point of carbon tetrachloride (see expt. 8) and this is presumably due to the occurrence of more total decomposition under these conditions. It is also noteworthy that no stable addition compounds were obtained under the conditions of experiment 8.

Before considering in detail what may happen when chlorine trifluoride is allowed to attack a benzene nucleus, it is advantageous to discuss the simpler case of the possibilities of attack by a halogen molecule X_2. (c.f.

Bigelow, Tompson and Tarrant, Ind. Eng. Chem., 1947, 39, 360).

Such a molecule may be caused to dissociate in two ways:-

(1) To form ions, usually promoted by a carrier catalyst e.g. a metallic halide MX_3.

$$X_2 + MX_3 \rightleftharpoons X^+ + MX_4^-$$

(2) Into atoms, this often being promoted by the action of heat and /or light.

$$X_2 \rightleftharpoons 2X\cdot$$

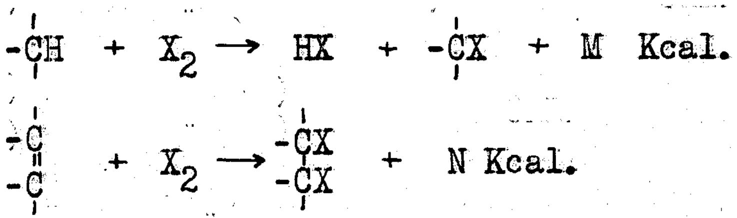
It may thus attack the benzene nucleus by either of two mechanisms,

(1) ionic, involving cationoid substitution via the ion X^+, or

(2) atomic, in which the active atomic halogen brings about reaction.

In the case of fluorine, which is the most electronegative of all elements, the nuclear charge is high and positive; it would therefore be expected that it should react as an atom rather than as an ion since the removal of an electron from it to form a positive ion F^+ would be most difficult. Thus the chain mechanisms which actually occur in organic fluorination are not unexpected.

One of the fundamental causes of the violence of these reactions has been attributed by Bockemüller (Ann., 1933, 506, 20) to the very high heat of formation of hydrogen fluoride and C-F bonds. Thus:-



$$-\overset{|}{\underset{|}{C}}H + X_2 \rightarrow HX + -\overset{|}{\underset{|}{C}}X + M \text{ Kcal.}$$

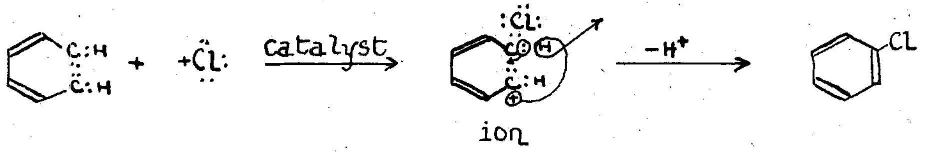
$$\begin{matrix}-\overset{|}{C}\\ \| \\ -\underset{|}{C}\end{matrix} + X_2 \rightarrow \begin{matrix}-\overset{|}{C}X\\ | \\ -\underset{|}{C}X\end{matrix} + N \text{ Kcal.}$$

When X = Cl, M = 23 and N = 33; when X = F, M = 103 and N = 107. The heat of dissociation of a C-C bond is approximately 71 Kcal.

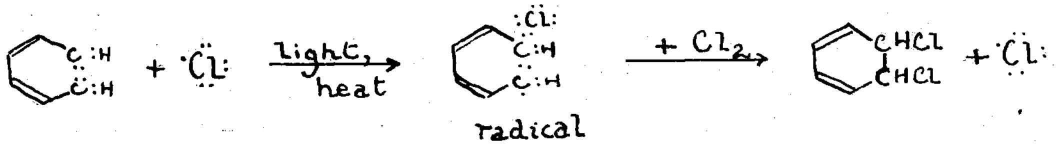
Since in the case of fluorine the heats of formation exceed the heat of dissociation of a C-C bond even without the heat of activation, the likelihood of complete breakdown is considerably greater in the case of halogenation by fluorine than by chlorine : this is found to be true in practice.

It has been observed (see pp 3-4) that in the case of benzene, by regulation of the experimental conditions chlorine may give rise to either orthodox substitution by the ionic mechanism, or addition. In the latter case an atomic mechanism is inferred. We can thus have

(a) Substitution



(b) Addition



Results obtained from the direct fluorination of benzene (Bigelow and Fukuhara, J. Amer. Chem. Soc., 1941, 63, 2792) showed that addition followed by substitution, fragmentation and dimerisation all occurred; hence free radical processes might be assumed (see pp. 10-11). The initial reaction of stepwise addition to an aromatic nucleus was demonstrated by Bigelow, Tompson and Tarrant (loc. cit.), the compound $C_6H_3Cl\ (CF_3)_2$, having a highly deactivated nucleus, being employed. This gave rise to $C_6H_3F_2Cl\ (CF_3)_2$, $C_6H_3F_4Cl\ (CF_3)_2$ then $C_6H_3F_6Cl\ (CF_3)_2$. Further progressive fluorination substituted the chlorine, and then the hydrogen; finally fragmentation and polymerisation occurred.

The reaction of chlorine trifluoride with benzene is more complex than that of either chlorine or fluorine for it appears to give rise to both substitution and addition products, together with a little polymerisation in some cases. In other words, it can be said that it is most probable that both ionic and radical processes are occurring parallel to one another. Making a rough general comparison it would appear that the halogenating action of chlorine trifluoride is intermediate between that of chlorine and that of fluorine. It is much more vigorous in action than chlorine, but appears to give rise to less fragmentation and decomposition than fluorine. The amounts of halogen introduced by these reagents vary considerably; thus, no aromatic derivatives were obtained by reaction of fluorine with benzene, indicating that addition of six fluorine atoms occurs before any subsequent action. On the other hand, with chlorine trifluoride, substitution products appear to the greatest extent, with polyhalo-addition products being formed in smaller quantity, whilst chlorine in the presence of carrier catalysts gives rise to substitution exclusively, as a stepwise process.

To account for the formation of fluorobenzene in the chlorine trifluoride experiments with benzene, the ionic mechanism of cationoid substitution generally accepted for halogenation (c.f. Dewar, Electronic Theory of Organic Chemistry, p.160 ff.) is inferred. It is then possible to postulate the initial dissociation.

$$ClF_3 \longrightarrow ClF + F^+ + F^-$$

in the case of the uncatalysed reaction whilst in catalysed reactions the initiating process is probably analogous to the type (1) described on page 46. When cobaltous fluoride is employed as catalyst the first reaction is to give the trifluoride :-

$$ClF_3 + 2\,CoF_2 \longrightarrow 2\,CoF_3 + ClF$$

We then may have

$$ClF_3 + CoF_3 \longrightarrow ClF + F^+ + CoF_4^-$$

The subsequent reactions are then

$$C_6H_6 + F^+ \longrightarrow C_6H_5F + H^+$$

$$H^+ + F^- \longrightarrow HF$$

in the uncatalysed case, and

$$C_6H_6 + F^+ \longrightarrow C_6H_5F + H^+$$

$$H^+ + CoF_4^- \longrightarrow CoF_3 + HF$$

in the catalysed experiment. This theory assumes, as is indicated by experimental results, that it is easier to produce the positive fluoride ion F^+ from chlorine trifluoride than from fluorine itself. The difficulty of formation of F^+ from F_2 and the reasons for assuming an atomic chain mechanism for direct fluorination have been already discussed (vide supra).

The formation of chlorobenzene in the series of experiments carried out is attributed to the chlorinating action of chlorine mono-fluoride (Bigelow et al., J. Amer. Chem. Soc., 1940, 62, 267; Ind. Eng. Chem., 1947, 39, 360). If we assume that such chlorination occurs by the ionic mechanism, then the processes involved consist in

$$\text{(a)} \quad ClF \rightarrow Cl^{+} + F^{-}$$

$$C_6H_6 + Cl^{+} \rightarrow C_6H_5Cl + H^{+}$$

$$H^{+} + F^{-} \rightarrow HF.$$

in the uncatalysed experiment and

$$\text{(b)} \quad ClF + CoF_3 \rightarrow Cl^{+} + CoF_4^{-}$$

$$C_6H_6 + Cl^{+} \rightarrow C_6H_5Cl + H^{+}$$

$$H^{+} + CoF_4^{-} \rightarrow HF + CoF_3$$

where cobaltic fluoride acts as catalyst. Such mechanisms for chlorination and fluorination would explain why the effluent gases of each experiment (except expt.4) contained hydrogen fluoride but no halogens or hydrogen chloride. The detection of hydrogen chloride in experiment 4 could best be explained on the basis of the reactions

$$Co\,Cl_2 + Cl\,F_3 \rightarrow Co\,F_2 + Cl_2 + Cl\,F.$$

followed by $Cl_2 + C_6H_6 \rightarrow C_6H_5Cl + H\,Cl.$

Such reactions would not be valid in the case of mercuric chloride, since no hydrogen chloride was evolved during experiment 3, but from observations made (Ruff and Krug, loc. cit., see also p.38) it seems unlikely that either fluoride of mercury is formed under the prevailing experimental conditions and therefore the objection cannot be sustained.

In no case was any attempt made to obtain any evidence from the state of the catalyst at the conclusion of the experiments, as it was so intimately mixed with tarry decomposition product as to render this impossible.

It has already been inferred (see section (i)) that the secondary reaction of the chlorine trifluoride with the carbon tetrachloride solvent under the conditions of the series of experiments under consideration is negligible (excepting in experiment 8 for which no corresponding figures are available). This is borne out by the fact that there is only a very small difference in the yield of chlorobenzene in experiments 6 and 7 even though the amount of solvent per gram of benzene has been doubled in the latter. Were appreciable fluorination of the solvent to occur, considerably larger quantities of chlorine monofluoride would probably be produced in the latter case, and it would be expected that this would lead to a greater increase in chlorination than is actually observed. The loss of carbon tetrachloride per experiment is of the order of 50 mls., but most of this can be accounted for by the normal losses incurred in working up the product. Blank experiments showed that losses due to the passage of the nitrogen stream through the carbon tetrachloride at 0°C for the normal period of an experiment were of the order of 2% (i.e. about 10 mls.) whilst using the modified apparatus at 77°C they were rather higher (approximately 0·5% per hour).

Fluorobenzene could not be isolated as such from the reaction mixture since it apparently formed an azeotrope with carbon tetrachloride and small quantities of unchanged benzene, containing about 10% by weight of fluorobenzene. It was therefore characterised by conversion into 44 difluorodiphenyl-sulphone (Huntress and Carten, J. Amer. Chem. Soc., 1940, 62, 512) and p-chlorofluorobenzene (Varma, Venkat Raman and Nikantiah, J. Indian Chem. Soc., 1944, 21, 112). The amount of fluorobenzene produced per experiment was estimated by analysis of the azeotrope for fluorine, and confirmed by the conversions outlined. Trial experiments showed that, with a solution of fluorobenzene in carbon tetrachloride containing a small quantity of benzene, the best yields of sulphone and chloro-compound obtainable were

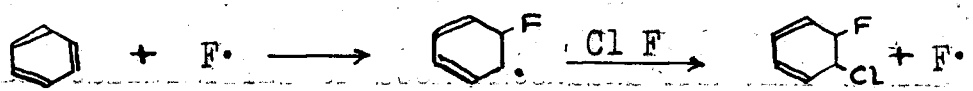
25% and 51·5% respectively, the isolation of the sulphone being made rather more difficult by the presence of the benzene. Experiments carried out on the azeotrope gave results correlating to the analytical figures.

The addition compounds and diphenyl derivatives were not produced in sufficient quantity for absolute characterisation, except in experiment 9 where attempted redistillation of the addition products brought about decomposition. The formation of such compounds is probably due to the operation of a free radical mechanism (vide supra). Such a process would depend in the first place upon the dissociation

$$ClF_3 \longrightarrow ClF + 2F\cdot$$

followed by $ClF \longrightarrow Cl\cdot + F\cdot$

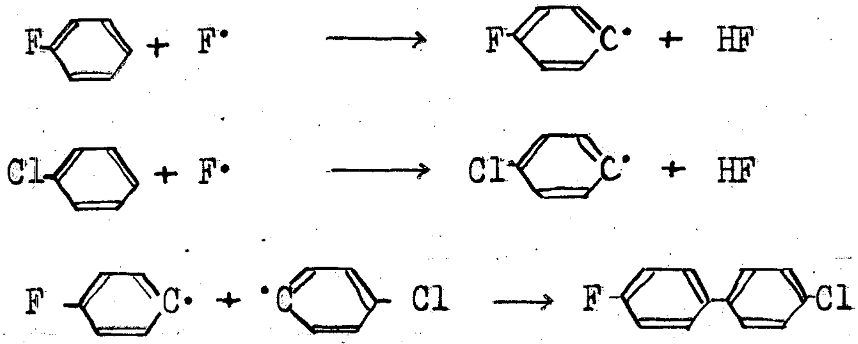
It would then be possible to have, for example



The possibilities of such processes are very varied and a large range of such compounds could be formed.

The production of halogenated diphenyls could be explained on the basis of the following possible mechanism; it involves the assumption that they are secondary products given by reaction of radicals with substitution products, forming free halophenyls which then interact to give a binuclear compound.

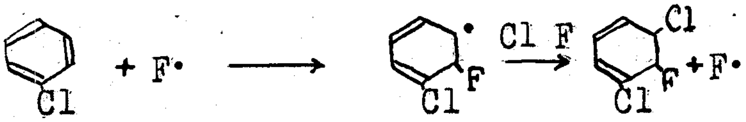
e.g.



It should be noted that Col. 6 of Table III which gives details of the possible formulae of addition compounds and diphenyl derivatives is included merely as a suggestion of some of the possibilities, which are many and varied, based on analytical data and stability or otherwise to reagents usually employed as tests for olefinic double bonds. Variations in the boiling points of substances giving similar analytical figures may be due to the fact that they are isomers.

In certain cases addition compounds were formed, apparently having odd numbers of halogen atoms per benzene nucleus. The most reasonable explanation for the formation of such compounds is that they are the products of secondary action of free radicals in substitution compounds formed by the ionic mechanism.

e.g.



This view is supported by the evidence obtained by reaction of chlorine trifluoride with halobenzenes (see section (iv)), when similar compounds were produced.

In any event, the reaction of chlorine trifluoride with benzene is most complex; to account for the various phenomena which appear to occur, it seems necessary to postulate the simultaneous occurrence of both ionic and free radical processes. It would thus appear that the extent of chlorine and fluorine substitution, and the amounts of addition compounds and dimers formed in the reaction, are bound up, (a) in considerations of the dissociations of chlorine tri- and mono-fluorides which give rise to reaction intermediates subsequently forming the products concerned, and (b), in the effects of catalysts upon such processes.

(iii) The reaction of Alkylbenzenes with Chlorine Trifluoride using Carbon Tetrachloride as solvent.

When the series of chlorine trifluoride experiments was extended to cover the alkylbenzenes it was decided to employ cobaltous fluoride as catalyst in all cases as it had proved to be one of the most successful compounds for this purpose in the experiments with benzene itself. It was observed that when toluene, ethyl-benzene or cumene (1 mol.) was caused to react with chlorine trifluoride (0·5 mol.) diluted by nitrogen, in carbon tetrachloride solution and in the presence of the catalyst, both substitution and addition occurred as in the case of benzene. Of the substitution products, those containing chlorine predominated, and the amounts of fluorine containing substitution product decreased as the size of the side chain increased. In all the experiments a certain amount of the hydrocarbon under test was recovered unchanged at the end of the experiment in question. This amount was found to increase with increasing size of the side chain.

A summary of the experiments carried out is given in Table IV : these were all carried out under analogous conditions and the results are therefore directly comparable. The corresponding experiment with benzene is included for purposes of comparison.

TABLE IV Reaction of ClF_3 with benzene and alkyl benzenes using CoF_2 catalyst.

Compound under test (100g.)	Wt. of ClF_3 (g.) and flow rate (g./h.)	Recovered Hydro-Carbon (g.)	Tar (g.)	Fluoro-derivative		Chloro-derivative (g.)	Addition product (g.)	Secondary Decomp. (g.)
				Nuclear (g.)	Side-Chain (g.)			
Benzene	60 : 10	-	14·8	11·9	-	28·4	2·8	8·4
Toluene	52 : 9	19·0	12·9	8·2	1·8	22·1	20·1	3·7
Ethyl-benzene	45 : 8·5	27·6	14·8	3·7	-	19·8	12·7	1·3
Cumene	40 : 8	39·0	11·5	2·2	-	22·2	10·6	1·8

In so far as substitution as a whole is concerned, this is almost entirely restricted to entry into the nucleus, the only exception being a small amount of side chain fluorination in the case of toluene, giving rise to benzyl fluoride. As far as can be seen from reference to the chlorinated derivatives, the ionic mechanism of substitution is confirmed, with substitution occurring into the ortho- and para- positions, excepting in the case of cumene where only p-chlorocumene was isolated. The absence of irregularities in the distillation curves plotting refractive index values against % distilled when the mixtures of isomeric chloro-compounds were fractionated through a concentric tube column (38 theoretical plates), coupled with the fact that amounts of pure ortho and para derivative were obtainable, indicated the absence of any meta-chloro derivative in the cases of toluene and ethyl benzene. In the case of cumene, chlorination was found to occur exclusively in the para position; this is presumably attributable to steric hindrance. The absence of o-chlorocumene in the products of the reaction of chlorine with cumene has been reported in the literature (Genvresse, Bull. Soc. Chim. Fr., 1893 (3), 9, 223), it being stated that only the p-derivative and higher chlorinated compounds were isolated. The steric effect in the formation of cumene derivatives has also been observed in nitration where the amount of para derivative isolated exceeds the amount of ortho to a large extent (c.f. Constam and Goldschmidt, Ber., 1888, <u>21</u>, 1157 ; Vavon and Callier, Bull. Soc. Chim, Fr., 1927 (4), <u>41</u>, 357).

The ortho and para substitution in the cases of toluene and ethyl benzene was as expected from the well known directing effect of alkyl groups. These results concur with observations made by other workers in this field (e.g. Hubner and Mujert, Ber., 1873, <u>6</u>, 790 ; Seelig, Ann., <u>237</u>, 130 and 151 ; Schramm, Ber., 1885, <u>18</u>, 1273 ; Cline and Reid, J. Amer. Chem. Soc., 1927, <u>49</u>, 3153. Compare also Reese, Chem. Rev., 1934, <u>14</u>, 55).

In the cases of the fluorinated derivatives, no definite information could be obtained regarding the configuration and relative amounts of isomeric substitution products, owing to the low yields and difficulties in isolation of specimens in a pure state. Using a concentric tube column (38 theoretical plates), it was possible to obtain from the products of the toluene experiment a small quantity of mixed fluorotoluenes which on oxidation gave a mixed fluorobenzoic acid (m.p. 158°C). This compares with ortho - $F.C_6H_4.CO_2H$, m.p. 122°, meta - m.p. 123° and para -, m.p. 182°C. In the other cases no pure fluoro-compound could be obtained.

In all three cases the estimation of the total amount of fluoro-compound was carried out by analysis of the fluorine content of the mixture of unchanged hydrocarbon and fluorinated derivative after as much as possible of the former had been removed in a pure state by fractionation processes.

TABLE V. Total Substitution, Addition, Etc. in Benzene and Homologues.

Compound under test.	Recovd. startg. matl.	Substitution			Addition Product.	Tar.
		Fluoro	Chloro	Total		
Benzene	-	11·9	28·4	40·3	11·2	14·8
Toluene	19·0	12·3	27·3	39·6	29·4	15·9
Ethyl benzene	27·6	5·1	27·4	32·5	19·4	20·4
Cumene	39·0	3·6	36·4	40·0	20·4	18·9

Table V gives details of the total amounts of various types of product isolated from reaction mixtures. The figures refer to grams of product per 100 grams of hydrocarbon actually reacted (except Col. 2 which gives amount of unchanged starting material per 100 grams. submitted to reaction). Since secondary decomposition (Table IV, Col. 9) was the result of decomposition of lower boiling addition compounds during fractionation processes in the cases of alkyl benzenes, and the decomposition of non-redistillable addition compounds in the case of benzene the figure in Col. 6 of the above table is a composite, based on the sum of Cols. 8 and 9 (Table IV) and referred to 100 grs. of reacted hydrocarbon. The data for benzene are again included for comparative purposes, and it is broadly seen that whilst substitution is again the main reaction in the cases of the alkyl benzenes, addition appears to occur to a greater extent.

In the cases of benzene and toluene the ratio of the amount of chlorination to fluorination in regard to the substitution products is around 2 : 1, and this ratio then increases with increase in the size of the side chain through ethyl-benzene (5 : 1) to cumene, where it is approximately 10 : 1 and the yield of fluoro-compound is very small.

The addition compounds produced by reaction with alkyl-benzenes are considerably less stable than those obtained from benzene and consequently much more difficult to isolate. Attempts were made in all cases to obtain these compounds in a reasonably pure state by carrying out the initial distillation under reduced pressure to remove solvent and substitution compounds. After this process had been carried out, however, the liquid, originally orange coloured, turned black. Continuance of the reduced pressure distillation gave rise in all cases to a viscous oil which turned brown during distillation, and very soon blackened and evolved hydrogen halides. A specimen of distillate was taken for immediate analysis by the sodium fusion method, and the distillate was also observed to decolourise aqueous potassium permanganate solution and bromine water. The residue in the flask at the end of this distillation was weighed and noted as reaction tar (Table IV, Col. 4; Table V, Col. 7.). From inspection of the reaction products of the alkylbenzene experiments, it seemed most unlikely that the transparent orange coloured carbon tetrachlorideextracts contained much tar, as opposed to the dark brown, opaque extracts obtained from benzene experiments, and it therefore appears most probably that this tar consists, ar least in part, of the decomposition products of higher boiling addition compounds.

Attempted redistillation of the viscous oil containing the bulk of the addition compounds under reduced pressure resulted only in the formation of more tar and the evolution of hydrogen chloride and hydrogen fluoride. Usually a small quantity of lower boiling addition compound distilled with the substitution products: this decomposed during subsequent fractionation, being left as still-pot residue (Table IV, Col. 9.).

From analytical data available, the addition compounds obtained from alkyl-benzenes seem in the main to have been formed by addition of one chlorine and one fluorine atom per aromatic nucleus. Details of analyses carried out on these compounds will be found in the corresponding experimental section.

The mechanism of the reaction between chlorine trifluoride and benzene homologues would appear to be essentially similar to the reaction with benzene itself, involving the assumption of simultaneous ionic and free radical processes giving rise to substitution and addition compounds respectively. The total amount of substitution appears to be fairly constant throughout the series, but in the cases of the alkyl benzenes, about twice as much, or more, addition occurred than in the corresponding benzene experiment (c.f. with toluene, the extent of addition was rather more than 2·5 times that observed with benzene). The amount of complete degradation occurring in the cases of the alkyl-benzenes appears to be less than in the case of benzene, the nett total recovery of organic product being correspondingly higher. A complicating feature in explaining the reaction of chlorine trifluoride with alkyl benzenes is the isolation of unchanged starting material, especially since no halogen (and actually only hydrogen fluoride) was detected in the waste gases arising from each experiment. The amount of unchanged hydrocarbon increased with increase in the number of carbon atoms in the side chain (and thus also with increasing activation of the nucleus). The most feasible explanation of this appears to be that once some addition compound has formed, it is easier for further addition to take place, so building up a polyhalogen additive product; this involves the assumption that the less stable higher boiling addition compounds were polyhalogen in character, and contained much more halogen than the addition compounds actually analysed. If this were true it would mean that the halogen utilisation could be balanced in such a way as to leave some hydrocarbon unreacted.

Experimental testing-out of this hypothesis could not, unfortunately, be effected, as the higher boiling addition compounds were so unstable that decomposition occurred with evolution of hydrogen halides before they could be isolated and analysed.

(iv) Reaction of Chlorine Trifluoride with Halobenzenes in Carbon Tetrachloride solution.

The treatment of chlorobenzene and fluorobenzene with 0·5 mol. of chlorine trifluoride using nitrogen as diluent and carbon tetrachloride as solvent in the presence of cobaltous fluoride catalyst was seen to give rise to both addition and substitution as in the case of benzene itself. In the case of chlorobenzene substitution predominated over addition to a much larger extent than with fluorobenzene. The latter compound appeared to behave exceptionally, as no nuclear-substituted fluoro-derivative could be traced in the reaction products obtained from it.

A summary of the results obtained from experiments carried out with these halobenzenes is given in Table VI, the corresponding experiment with benzene being included for the sake of comparison. All experiments were performed under similar conditions and the results may therefore be directly compared.

Generally speaking, the results obtained are in agreement with the theory that substitution is occurring by the ionic mechanism outlined in section (ii), as the entry of the second substituent is restricted to positions expected from the

TABLE VI. Reaction of $Cl\ F_3$ with Halobenzenes compared with Benzene.

Test Cpd. (100 g. in 500 mls CCl_4)	$Cl\ F_3$ (g.) and flow rate (g./h.)	Recov. Test Cpd. (g.)	Tar (g.)	Fluoro Deriv. (g.)	Chloro Deriv. (g.)	Ttl. Substn. per 100 g. reacted (g.)	Addn. Cpds. (g.)	Sec. Dec. (g.)	Ttl. Addn. per 100 g. reacted (g.)
Benzene	60 : 10	-	14·8	11·9	28·4	40·3	2·8	8·4	11·2
Chloro-benzene	43 : 8	14·9	9·1 (10·7)	17·8* (20·7)	40·8‡ (48·0)	68·7	2·5 (2·9)	2·2 (2·6)	5·5
Fluoro-benzene	49 : 8	-	7·6	-	27·0*	27·0	12·1	2·6	14·7

‡ Dichlorobenzene isolated consisted of 38·7 g. para- and 2·1 g. ortho-isomer.
* Only p-chlorofluorobenzene was obtained in these cases.
Figures in parentheses refer to amounts per 100 g. test compound reacted.
In all experiments 10 g. CoF_2 was used as catalyst.

accepted directing influence of the first, i.e. principally to the ortho and para positions in these cases. (c.f. Reese, Chem. Rev., 1934, 14, 55). There appears, however, to be a very marked bias in favour of substitution in the para position and only in the substitution of chlorine into chlorobenzene was any ortho derivative isolated, but even in this case the para derivative was formed in large excess (see Table VI footnote). Observations noted in the literature of the liquid phase chlorination of chlorobenzene using chlorine under various catalytic conditions (Cohen and Hartley, J.Chem. Soc. 1905, 87, 1362; Van der Linden, Rec. Trav. Chim., 1911, 30, 328) state that in all cases studied the predominant product is p-dichlorobenzene. The extent of this predominance in these cases is, however considerably less than in the experiment with chlorine trifluoride. The chlorination of fluorobenzene at room temperature in the presence of iron filings has been observed to give rise exclusively to p-chlorofluorobenzene (Varma et al., J. Indian Chem. Soc., 1944, 21, 112).

The recovery of unchanged starting material was again observed in the case of chlorobenzene, though to a less extent than in the experiments with alkyl benzenes (section (iii))

The total amount of substitution products obtained from chlorobenzene exceeds by about 70% the corresponding amount in the benzene experiment, which in turn exceeds the nett substitution product from fluorobenzene by about 50%. The ratio of substituted chloro- to substituted fluoro-compound in the benzene and chlorobenzene experiments is about the same, but in the case of fluoro-benzene, no difluoro-derivative could be isolated. Analysis of the solvent removed from the reaction products in the fluorobenzene experiment proved the absence of any unchanged starting material or fluorinated derivatives which might have interdistilled with it. (c.f. Found Cl 91·9%, Calc. for CCl_4, 92·2%).

Regarding the absence of difluorobenzenes from the reaction products of the fluorobenzene experiment, the presence of meta- and ortho-derivatives would not be expected in any case from considerations of the halogenation of fluorobenzene which has been shown (Varma et al., loc. cit.) to give rise exclusively to para-derivatives. Furthermore it is reported (Beilstein, Org. Chem., Series EII, 5, 147) that o-difluorobenzene decomposes on standing in the air so that its non-isolation in the present experiment is not surprising. Investigations made on the stability of p-difluorobenzene showed that its solution in carbon tetrachloride was stable at room temperature to 0·1 N sodium hydroxide solution, saturated aqueous sodium bicarbonate, anhydrous hydrogen chloride and anhydrous hydrogen fluoride. When, however, a solution of p-difluorobenzene (14 g.) in carbon tetrachloride (250 ml.) was treated in the presence of cobaltous fluoride (2 g.) with 0·5 mol. of chlorine trifluoride at 0°C using nitrogen as diluent, copious evolution of hydrogen fluoride occurred. After freeing from inorganic impurities, and drying, the only product left after removal of solvent (pure $C\,Cl_4$ n_D^{20} 1·4612, found Cl 92·1% calc. Cl 92·2%) was 0·42 g. of undistillable, brown, partially-decomposed viscous liquid; a sample of this decolourised aqueous potassium permanganate, and a specimen on immediate analysis gave Cl 26·3%, F 11·4%. Subsequently, this decomposed completely, giving a black tar.

On the basis of these results it can therefore be postulated that any p-difluorobenzene which might be formed in the first place by the reaction of chlorine trifluoride with fluorobenzene, would be subsequently decomposed by secondary reaction with chlorine trifluoride into products not isolated. This would explain the absence of any p-difluorobenzene in the reaction product, and also the fact that the recovery of organic material from the fluorobenzene experiment is lower than in any other case where cobaltous fluoride was employed as catalyst.

In assessing the total amount of addition in each case (Table VI, Col. 10), the amount lost during subsequent fractionating processes (Table VI, Col. 9) was taken into consideration as in the cases of the alkyl benzenes. It is seen that this amount is smallest in the case of chlorobenzene, where it is about one half the corresponding amount for benzene itself, and rather more than one third of the amount observed in the case of fluorobenzene. According to analytical data, the addition products isolated, which all decolourise aqueous potassium permanganate and bromine water, appear to contain at least one additional chlorine and one additional fluorine atom per molecule. Analyses of these products are given in the experimental section.

(v) Reaction of Chlorine Trifluoride with Perhalomethylbenzenes in Carbon Tetrachloride solution.

When benzotrifluoride and benzotrichloride were caused to react with chlorine trifluoride (0·5 mol.) in carbon tetrachloride solution in the presence of cobaltous fluoride catalyst under similar conditions to those employed in other investigations, both substitution and addition were observed to occur as in the case of benzene. Substitution was in both cases the major reaction, and it occurred to about twice the extent of addition. Replacement of fluorine for chlorine in the side-chain occurred to a small extent in the case of benzotrichloride, resulting in the formation of a small quantity of benzodichlorofluoride.

A summary of results obtained from the experiments is given in Table VII, together with comparable data for the corresponding benzene experiment. Owing to the close proximities of the boiling points of the isomers concerned it was not possible to obtain a great amount of detailed information regarding the orientation of the substituted derivatives; also, the fluorinated derivatives were inseparable from unchanged starting material. The nett amounts of fluoro-compound and unchanged starting material were estimated in each case by halogen analysis. In the case of

TABLE VII. Reaction of ClF_3 with Perhalomethylbenzenes compared with Benzene.

Test Cpd. (100 g. in 500 mls CCl_4)	ClF_3(g.) and flow rate (g./h.)	Recv. Test Cpd. (g.)	Tar (g.)	Side Chain Repl. (g.)	Fluoro-deriv. (g.)	Chloro-deriv. (g.)	Ttl. Nucl. Sbstn. per 100 g. reacted (g.)	Addn. Cpds. (g.)	Sec. Dec. (g.)	Ttl. Addn. per 100 g. reacted
Benzene	60 : 10	-	14·8	-	11·9	28·4	40·3	2·8	8·4	11·2
Benzo-trifluoride	33 : 6	13·2	9·3 (10·7)	-	8·2 (9·5)	26·2 x (30·2)	39·7	10·6 (12·2)	5·1 (5·9)	18·1
Benzo-trichloride	25 : 5	37·6	3·4 (5·5)	1·2 (1·9)	15·4 (24·7)	17·0 (27·3)	52·0	11·2 (18·0)	6·7 (10·7)	28·7

Figures in parentheses refer to amounts per 100 g. test compound reacted.
In all experiments 10 g. CoF_2 was used as catalyst.

x. Chloro-derivative in this case was all m-chlorobenzotrifluoride.

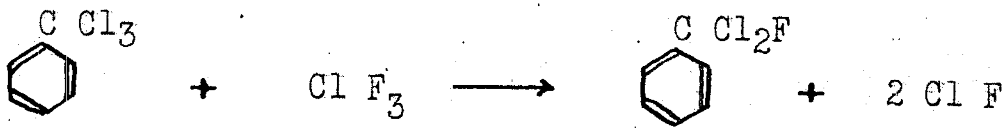
benzotrifluoride chlorination occurs exclusively in the meta position, a fact which reasonably concurs with the known data regarding the halogenation of benzotrifluoride (c.f. Wertyporoch, Ann., 1932, 493, 153; Simons and Ramler, J. Amer. Chem. Soc., 1943, 65, 389), and supports the theory of substitution by the ionic mechanism.

From examination of the boiling points of the fluorinated derivatives of benzotrifluoride it seems unlikely that any ortho isomer was formed, but the mixture of benzotrifluoride and fluorobenzotrifluoride may contain some para isomer in addition to meta. Hydrolysis with 80% sulphuric acid gave only a mixture of benzoic and fluorobenzoic acids from which no definite information was obtainable. Similar indefinite results were obtained from the mixture of benzotrichloride and fluorobenzotrichloride (s) and from the mixture of chlorobenzotrichlorides which were hydrolysed by a boiling aqueous suspension of calcium carbonate. It has been stated (Wertyporoch, loc. cit.) that the chlorination of benzotrichloride using chlorine with antimony pentachloride as catalyst yields principally the meta-derivative.

Generally speaking, as far as substitution is concerned it is seen that in both cases, as in benzene, chlorination exceeds fluorination, though the extent of fluorination is greater in the case of benzotrichloride than in either that of benzotrifluoride or benzene. Indeed, the ratio of fluorination to chlorination is greater in the case of benzotrichloride is more nearly 1 : 1 than in the case of any other aromatic compound studied. The recovery of unchanged starting material is also observed in experiments with perhalomethylbenzenes and this is most marked in the case of benzotrichloride.

Addition compound isolated from the benzotrifluoride experiment appeared to have been formed by addition of one fluorine and one chlorine atom per benzotrifluoride molecule, and that in the case of benzotrichloride apparently contained rather more "additional" halogen per molecule. Details of analyses and other properties of these compounds are given in the experimental section.

The side reaction in the case of benzotrichloride involving the replacement of fluorine for chlorine in the side chain with the resulting formation of benzodichlorofluoride may be attributed to a replacement reaction of the same type observed when chlorine trifluoride reacts with carbon tetrachloride viz:-



(c.f. $C\,Cl_4 + Cl\,F_3 \longrightarrow C\,Cl_3F + 2\,Cl\,F$.)

A discussion of this type of reaction has already been made (vide p. 32 et. seq.).

PART II : Experimental.

(i) Reaction of Chlorine Trifluoride with Carbon Tetrachloride.

Apparatus:

In order to measure the input rate of chlorine trifluoride the flowmeter described previously (Ellis and Musgrave, J. Chem. Soc., 1950, 3608) was at first used. This was later replaced by a much more efficient type shown in Diagram I. The chief advantages of this latter are that (1) it can be given far greater sensitivity without impairing efficiency, and (2) it is easier to clean and maintain, there being no possibility of purely local blockage.

The reaction vessel used for experiments carried out without catalysts is shown in Diagram II : when a catalyst (anhydrous cobaltous fluoride) was employed, the modified reaction vessel (Diagram III) was used in order that the mixture could be stirred. The reaction vessel 'A' for uncatalysed work was of approximately 1.2 litre capacity and was constructed of mild steel, having a steel head carrying input and output lines of 5/16" copper tubing. The head was fixed to the cylindrical vessel by means of six bolts with a steel to lead knife-edge seal.

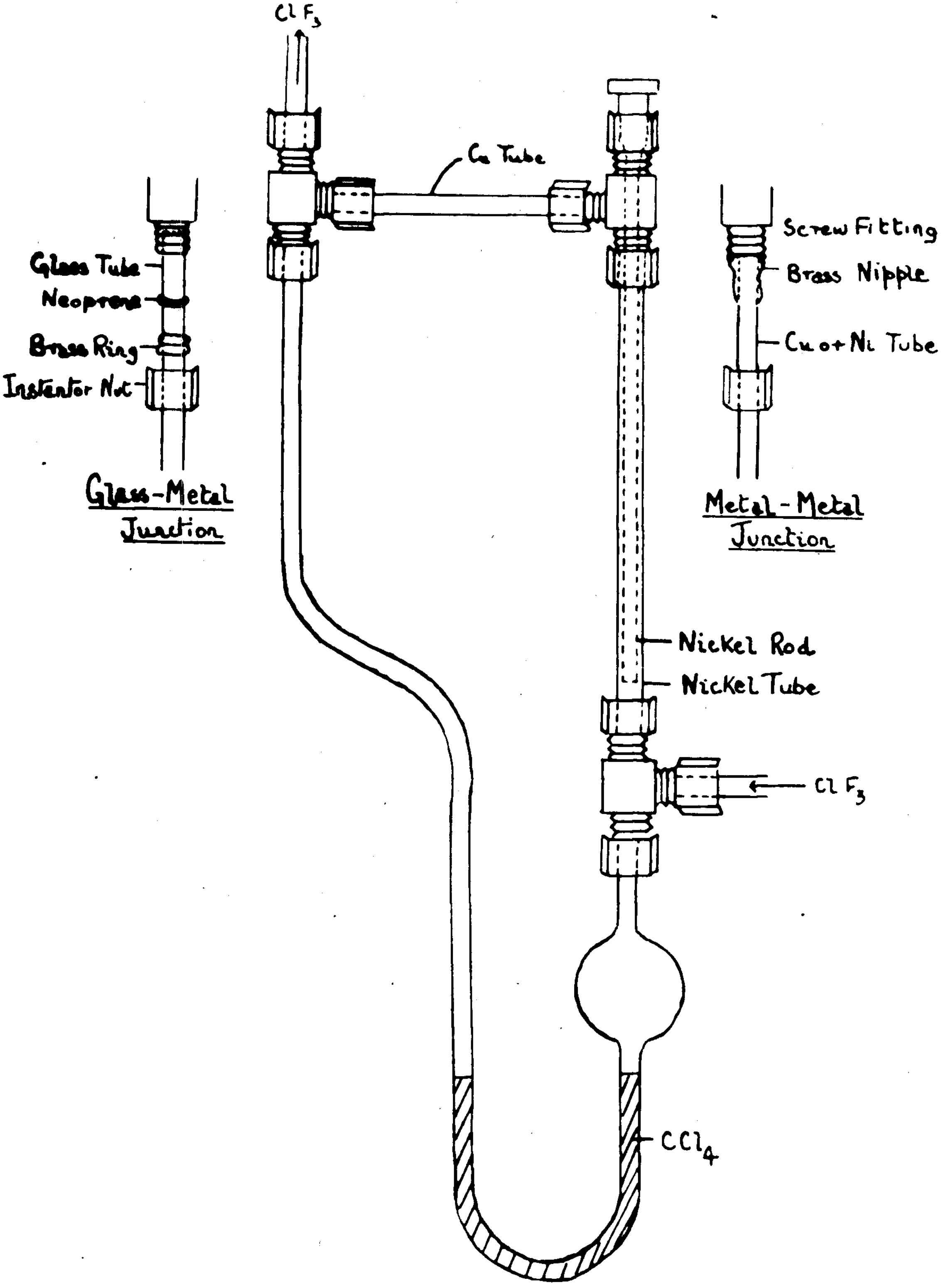
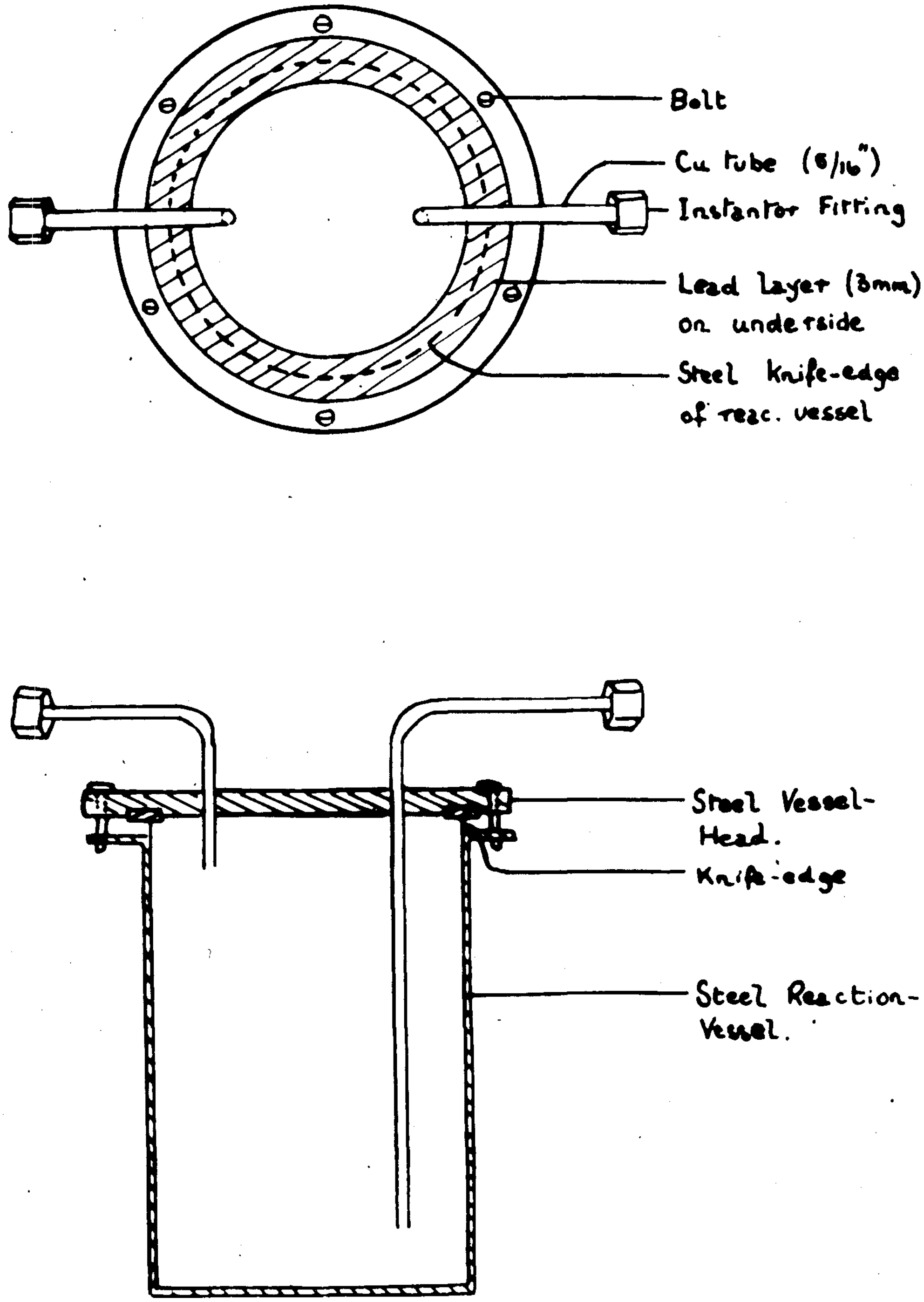


DIAGRAM I Cl F_3 Flowmeter



<u>DIAGRAM II.</u> - <u>Plan and Elevation of Vessel A.</u>

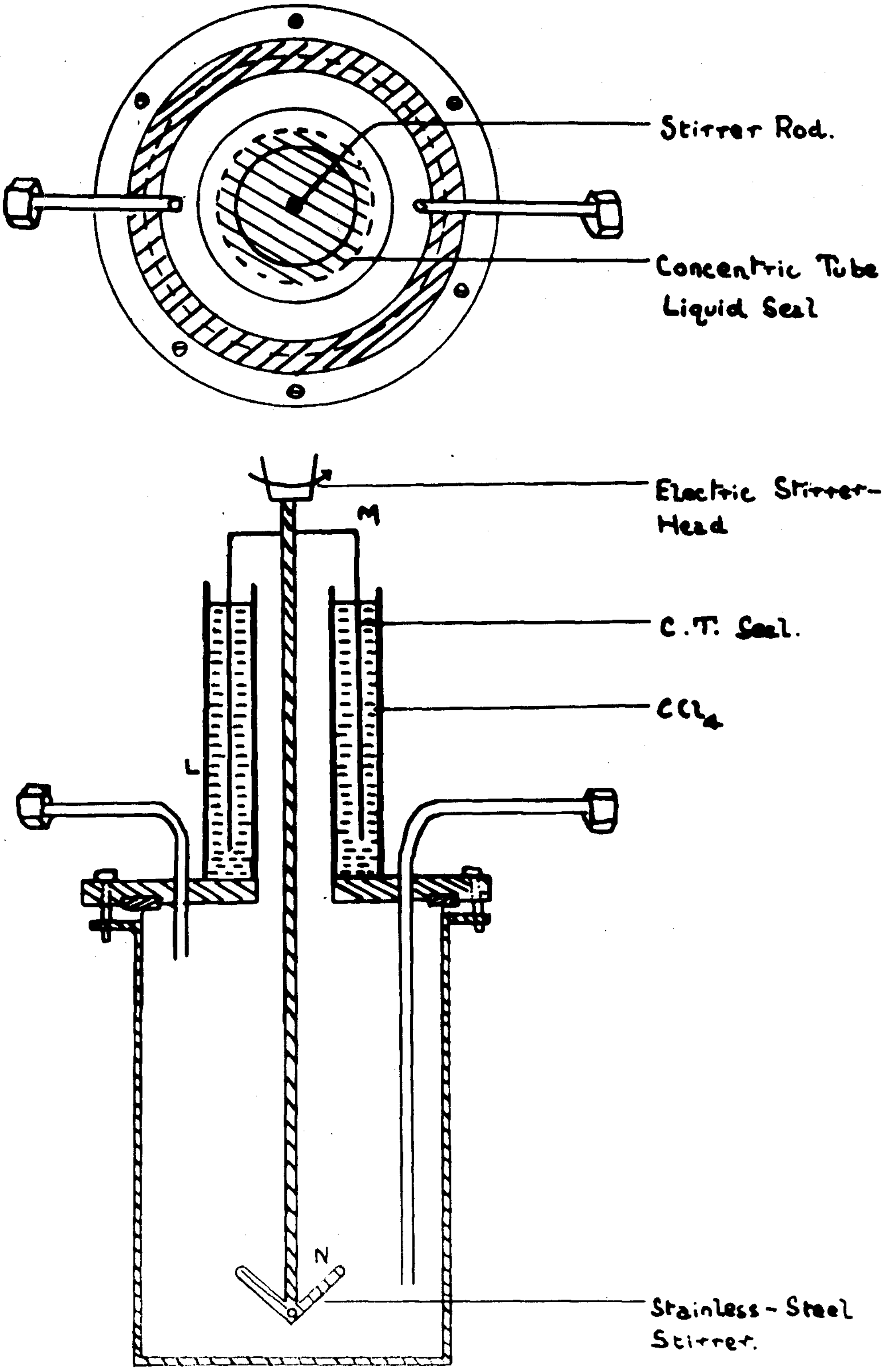


DIAGRAM III. Plan and Elevation of Vessel AA.

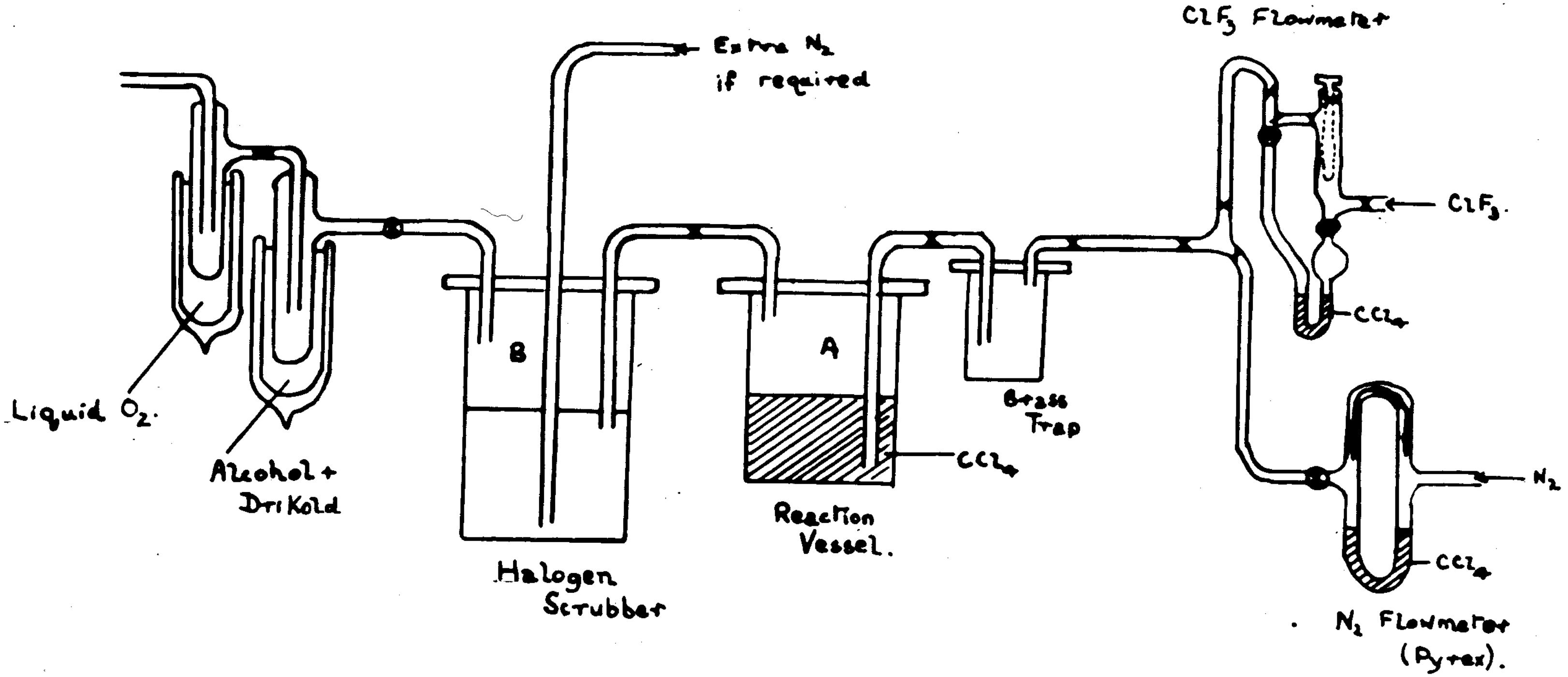
The modified reaction vessel 'AA' employed in catalysed experiments was substantially similar to A, but had concentric tubes fitted to the lid so that a sealed stirrer could be used. Carbon tetrachloride was employed as the sealing liquid. A third vessel, used to contain halogen absorbent, was also much the same as A, differing only in that it was somewhat larger (circa 1·5 litre) and was fitted with an extra inlet tube through which nitrogen could be blown to flush the system or to bring about further dilution of the chlorine trifluoride.

Experimental.

The experimental set up is shown in Diagram IV. The chlorine trifluoride and nitrogen were metered into the circuit by separate lines linked up by a T-piece, and the gas mixture conducted into the reaction vessel A via a brass safety trap. The output line of A led to the halogen scrubber B which in turn was connected to the pyrex-glass product receivers C and D.

For the uncatalysed experiments dry carbon tetrachloride (500 mls.) was placed in vessel A and the circuit connected up as in Diagram IV. The receiver C was immersed in alcohol-drikold contained in a Dewar flask, and D in liquid

DIAGRAM IV. Experimental Set-up (Solvent Expts.).



X = Compression Union (brass washer).

⊗ = Compression Union (neoprene washer).

oxygen contained in a second Dewar. The vessel B was charged with a solution of 252 grs. of sodium sulphite heptahydrate and 80 grs. sodium hydroxide in water (1 litre) and this solution acted as halogen absorbent. (Elementary antimony and rock sulphur were first tested as halogen absorbents but were found to be of no value, as they exhibited negligible action with chlorine trifluoride diluted by nitrogen even at 170°C).

The passage of chlorine trifluoride (5-7 gr./hr.) diluted by nitrogen (5 l./hr.) was then commenced. At the half-way stage in each experiment B was emptied and recharged with the same amount of fresh solution. At the conclusion of each experiment the receiver C was immersed in liquid oxygen and the contents of D distilled into it. After sealing up by means of tightly fitting rubber caps, C and its contents were maintained overnight in a Dewar of liquid oxygen, fractionation of the products being effected the following day.

For the catalysed experiments the procedure was slightly modified. Dry carbon tetrachloride (500 mls.) was placed together with 10 grs. of anhydrous cobaltous fluoride in the vessel AA (Diagram III) which replaced the vessel A in the experimental circuit (as shown in Diagram IV).

The sealing device L-M was filled up with carbon tetrachloride so that the head of liquid in L above the base of the seal was approximately twice the height of the carbon tetrachloride within the reaction vessel. The stainless steel vane-stirrer N was driven electrically. In order to restrict the possibility of back-pressures the amount of liquid in the scrubber (B) was reduced so that the end of the input tube protruded only 0·5" below the surface of the solution. This necessitated changing the contents of B four times per experiment, each time using 750 mls. of alkaline sodium sulphite solution, made up as previously directed. Otherwise the catalysed experiments were carried out in the same way as those in which no catalyst was employed. The collection of products was carried out in an identical manner and they were bulked for overnight storage in liquid oxygen previous to fractionation, as before.

In all cases, details of chlorine trifluoride passed are to be found in Table I (p.29). For experiments at 0°C the reaction vessel was maintained in a bath of ice and water: all other experiments were carried out at room temperature on the day of working (c.f. Table I).

Fractionation of the products.

In order to separate the reaction products a low temperature column constructed on similar lines to that of Ramler and Simons (Ind. Eng. Chem. Anal., 1938, 10, 648) was employed. Instead of using a thermocouple, however, as described by those authors, temperatures were read off directly with the aid of a pentane thermometer placed in a thermowell filled with alcohol. A diagram of the fractionating apparatus employed is shown overleaf (DiagramV). The heating nipple was covered with asbestos paper and wound with oxynichrome tape (6 ohms). It was placed in series with a 17 ohm rheostat and controlled from a 20 volt source, currents of 0·9 -1·1 amp being used.

Operation of the apparatus was carried out as described by Ramler and Simons (loc. cit.), the whole system being placed inside a large silvered Dewar flask. During introduction of the sample through the input line of tap B (Diagram V) the condenser was charged with liquid nitrogen and the reservoir bulb was similarly cooled; tap A was open to the atmosphere via a calcium chloride tube. To operate, only a small quantity of liquid nitrogen was left in the large outer Dewar, and the upper part of the apparatus was insulated against heat changes by means of cotton-wool

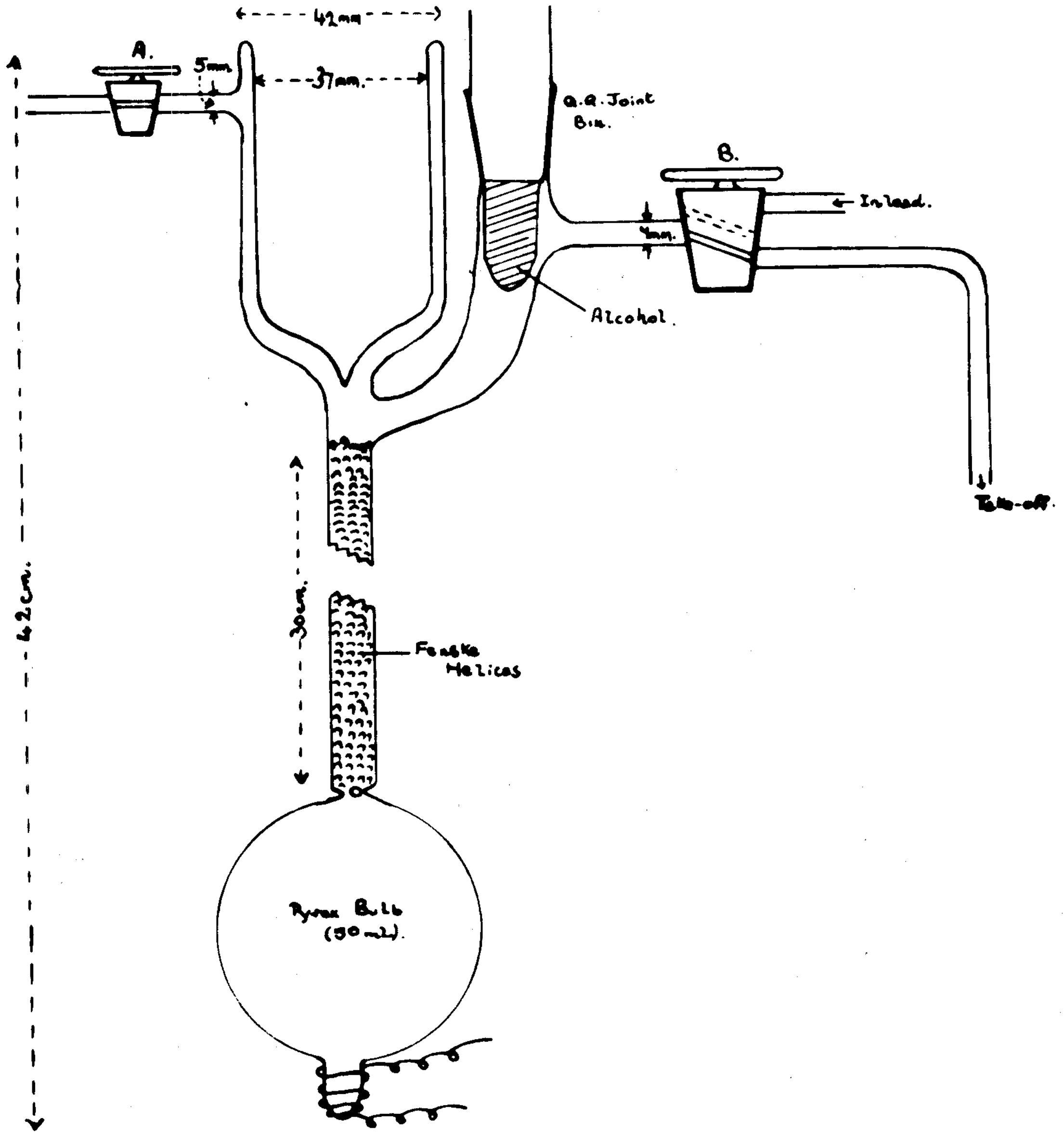


DIAGRAM V.

Column for low-temperature fractionation.

wadding. Cooling of the condenser was altered to alcohol-drikold mixture and heat was then applied through the heating nipple until the commencement of a reflux. After 30 minutes refluxing to establish equilibrium tap A was closed and tap B opened to the take-off line leading to a graduated receiver cooled in alcohol-drikold mixture. These fractions were generally collected; dichlorodifluoromethane (b.p. -28 to -26°C), intermediate, and trichlorofluoromethane (b.p. 23 to 25°C); a residue of carbon tetrachloride was left. Details of the reaction products collected in each experiment are given in Table I.

Characterisation of Reaction Products.

(1) Dichlorodifluoromethane :-

A 3 mls. sample was taken and distilled onto anhydrous magnesium sulphate; after redistillation through the column described it had b.p. -28°C. A sample (approximately 100mgr.) was sealed up and analysed by the sodium fusion method of Musgrave, Smith and Tatlow (J. Chem. Soc., 1949, 3026). It gave Cl 58·9%, F 31·2%. (Calculated for $C\,Cl_2F_2$, Cl 58·68%, F 31·41%).

(2) Trichlorofluoromethane :-

A 15 mls. sample was taken, dried over anhydrous magnesium sulphate and re-fractionated through the column. The centre fraction had b.p. 24°C and n_D^{20} 1·3846. On analysis it gave Cl 77·7%, F 13·6%. (Calculated for C Cl_3F, Cl 77·45%, F 13·82%).

(ii) Reaction of Chlorine Trifluoride with Benzene in Carbon Tetrachloride solution.

Apparatus

To carry out reactions in the liquid phase a similar experimental set-up to that used in the experiments with carbon tetrachloride alone (see Diagram IV) was employed, though the halogen scrubber and receivers for the collection of volatile products were dispensed with, and a different reaction vessel was used. This reaction vessel was constructed of mild steel and had a screw-on head, carrying inlet and outlet tubes and having provision for a mercury seal to work in conjunction with a stirrer (c.f. Diagram III). A lead washer was fitted on the inside of the head. Owing to the evolution of corrosive gases it was not possible to employ an electrically driven stirrer-head, and a water turbine type was used; the stirrer itself was again made from stainless steel. For the experiment carried out at 77^0 C the stirrer was fitted with a mercury seal (since no halogens were observed to be evolved during reactions at 0^0C) and two metal condensers, one carrying a water line, and the other containing ice and water were fitted by brass unions to the outlet tube of the reaction vessel. Otherwise, chlorine trifluoride and nitrogen were metered in as for the experiments in the previous section, and the gas-mixture was conducted to the reaction vessel via a brass safety trap. The glass flowmeter parts were protected by perspex shields as a further safety precaution.

Experimental

A summary of experiments carried out and products resulting is given in Tables II and III (pp. 42-44). In all experiments except Nos. 1, 7 and 8, benzene (100 grs.) was dissolved in carbon tetrachloride (500 mls.) to which the anhydrous catalyst (10 grs.) had been added, the reaction vessel was maintained at 0°C by means of a bath of ice and water, and chlorine trifluoride was led in at 10 grs./hr. diluted by nitrogen (12 L./hr.). Vigorous stirring was carried on until approximately 60 grams of chlorine trifluoride had been passed. In Experiment 1, no catalyst was used though other conditions were the same, but in Experiment 7 benzene (75 grs.) in carbon tetrachloride (750 mls.) was treated with 45 grams of chlorine trifluoride in the presence of 100 grams of anhydrous cobaltous fluoride catalyst. The flow rate of chlorine trifluoride was reduced to 4 grs./hr though that of the diluent nitrogen stream was the same: experimental temperature was also identical with that of the other experiments. The conditions in Experiment

8 were the same as those of Experiment 7 except that the chlorine trifluoride flow rate was rather higher (5 grs./hr.) and the temperature of the reaction vessel during the experiment was raised to 77°C.

It is seen therefore, that in all cases one molecule of benzene was treated with approximately 0·5 molecule of chlorine trifluoride. During the progress of each experiment qualitative tests on the exit gases from the reaction vessel were carried out at regular intervals for (a) free halogens (starch-iodide paper), (b) hydrogen chloride (silver nitrate solution on glass rod) and (c) hydrogen fluoride (etching test on moistened glass rod). Copious evolution of hydrogen fluoride was observed in all experiments but only in Experiment 4 were positive tests for hydrogen chloride given during the passage of chlorine trifluoride. In no case was free halogen ever detected.

When the required amount of chlorine trifluoride had been added, nitrogen alone was allowed to stream though the apparatus for a period of 10-15 minutes. The chlorine trifluoride cylinder was then disconnected and the apparatus dismantled. The contents of the reaction vessel were poured into saturated sodium hydrogen carbonate solution (approximately 0·5 litre) and the mixture was stirred well.

The reaction vessel was washed out with a further 50 mls. carbon tetrachloride, then with water. It was found that there was a tendency for the insoluble inorganic matter, which was intimately mixed with quantities of insoluble resinous and tarry by-products to collect at the interface between the organic and aqueous layers. To ensure as little loss of organic product as possible, the procedure adopted in working up was to pour the whole of the mixture into a large separating funnel and separate the bulk of the heavy organic layer. The bulk of the aqueous layer was then removed from the residue by decantation, and rejected. The residue, containing any insoluble matter was then filtered with suction through a Whatman No. 40 filter paper, and the organic layer of the filtrate was separated and combined with the bulk of the carbon tetrachloride solution removed previously.

The reaction product, now free from insoluble matter, was washed twice more with saturated sodium hydrogen carbonate solution to bring about complete removal of free acid, and then with water until it was neutral. Finally, it was dried over anhydrous magnesium sulphate. The products obtained were at this stage generally dark brown, or almost black, opaque liquids.

In all experiments except Experiment 9 the following procedure was employed to establish the nature of the reaction products. The dried reaction mixture was filtered to eliminate magnesium sulphate and then distilled through a fractionating system until measurements of boiling point and refractive index showed that the distillate was no longer pure carbon tetrachloride (b.p 76·75°C, n_D^{20} 1·4615).

The fractionating system for this work consisted of a hard-glass column (27 mm. internal bore) packed with finely clipped nickel turnings, and with an effective packing distance of 75 cm. It was fitted at top and bottom with drip measures, and had a heated jacket to counteract heat losses. The glass column tube was first wound with fine asbestos rope, over which was fitted a layer of thin copper foil. This, in turn, was covered with a layer of asbestos paper, inside which a control thermometer was fixed at the top of the column, and again wound with asbestos rope. Counter-wound on this asbestos rope was the heating coil consisting of 10 yards of oxynichrome resistance tape (23 ohms/yard). This was protected by a further binding with asbestos rope and lagged on the outside with thick pliable asbestos. The heater was controlled from a rectified 215 volt A./C. source with the aid of rheostats.

In work involving the removal of relatively large amounts of solvent a 500 ml. still pot fitted with a thermowell was heated by means of an electrically controlled oil bath. The still head was constructed in such a way as to allow partial take-off through a tap, of the liquid refluxing in the condenser. The distillation temperature was measured by the insertion of a corrected thermometer into a still-head thermowell having a mercury contact. All thd necessary connections were made with ground-glass joints, and, to avoid losses during lengthy fractionations, a carbohydrate grease (insoluble in hydrocarbons and carbon tetrachloride) was employed in conjunction with them.

The column was tested by the distillation through it of a standard mixture of normal-heptane and methyl-cyclohexane. Comparison of the results obtained with the curve of Lecky and Ewell (Ind. Eng. Chem. Anal., 1940, 12, 544) gave an efficiency value of 27 theoretical plates. The hold-up of this column amounted to 14 mls.

For the removal of carbon tetrachloride from the reaction product a boil-up rate of approximately 90 drops per minute was employed and a take-off ratio of 1 : 30. After the removal of pure carbon tetrachloride as described the residual liquid was transferred to a simple distillation apparatus, and rapidly distilled, first at atmospheric pressure (until the distillation temperature reached 140°C) then under reduced pressure (about 10 mm.) in order to remove tarry material (Table II, Col. 5). The distillates were combined, the total volume being 80-120 mls. The product at this stage from Experiment 2 contained some free iodine; this was removed by washing with aqueous sodium thio-sulphate, then water and drying over anhydrous magnesium sulphate. The recombined tar-free fractions were then distilled using a second fractionating system.

The column employed in this second system was constructed from a pyrex glass tube (15 mm. internal bore) and again fitted with drip measures. It was packed over a distance of 80 cm. with 4 mm. single turn Fenske helices, and was fitted with a compensating jacket similar to that used with the solvent column already described; a still-head of the same pattern as before was used. For use with this system two necked still-pots (in various sizes) were employed, one neck carrying a thermowell and the other fitted directly to the column. All connections were again made with ground-glass joints treated with carbohydrate grease. At first, still-pot heating was carried out using an electrically controlled oil bath, but it was later found to be much more satisfactory and convenient to employ direct external heating, the still pot being mantled by magnesia lagging, wound with oxy-nichrome resistance tape (approximately 150 ohms) and insulated by a further ¾" layer of magnesia lagging outside the element. The supply of heat was controlled from a rectified A./C. source (215 volts) with the aid of fixed resistances and rheostats. The efficiency of this column was computed from results obtained by distillation of the standard mixture described (vide supra.). A value of 22 theoretical plates was obtained; the hold up of the column was also determined and found to be 4 mls.

When the tar-free product obtained from the simple distillation was subjected to fractionation through the system under similar operating conditions to those described for the removal of solvent, the first fraction to be collected boiled over the range 77·2-77·7°C. This, from its analytical composition, was apparently a ternary azeotrope comprising carbon tetrachloride, fluorobenzene and a small quantity of benzene, and containing approximately 10% by weight of fluorobenzene.

The residue in the still pot was then fractionally distilled under reduced (8 mm.) pressure through a third column. This was 35 cm. in length, 11 mm. bore and packed with 4 mm. Fenske helices: it had a heat-compensating jacket as described for the other two columns and was equipped with a built-in still head giving total take-off. For lower boiling fractions the receiver of this system was cooled in alcohol-drikold mixture.

Using this column, chlorobenzene was first removed (b.p 22/8 mm), followed by the addition compounds as given in Table III. The chlorobenzene was redistilled through the same column at atmospheric pressure and had b.p. 132·5°C/752 mm. n_D^{20} 1·5246. On analysis this gave Cl 31·4% (Calculated for C_6H_5Cl, Cl 31·55%).

The halogenated addition compounds and halogenated diphenyls which follow chlorobenzene in the final fractionation were tested for unsaturation by shaking with

(a) cold dilute aqueous potassium permanganate and

(b) dilute bromine water. Their refractive indices were noted, and analyses for chlorine and fluorine were carried out using the sodium fusion method of Musgrave, Smith and Tatlow (loc. cit.). The latter process was adopted for the analysis of all reaction products, with slight modifications in certain cases which will be noted in due course. The collected data relating to these compounds is summarized in Table III. Only in Experiments 7 and 9 were they obtained in quantities sufficient to attempt further work with them, but it was found, however, that they underwent decomposition upon subsequent attempted redistillation, even under reduced pressure, with the evolution of hydrogen fluoride and hydrogen chloride.

Experiment 9 was worked up rather differently from Experiments 1-8 in order to see if removal of tars and most addition compounds at an early stage would improve the useful yield by cutting down decomposition. The dried reaction product, after the completion of the preliminary processes, was all submitted to distillation under reduced pressure in a simple apparatus having two receivers in series. The first of these was cooled in alcohol-drikold and the second by means of liquid nitrogen. By using this apparatus all the solvent and lower fractions were first removed (up to 30°C/40 mm.) After transferring to a smaller distilling vessel, chlorobenzene and a small quantity of lower boiling addition compound were collected (up to 40°C/10 mm). The bulk of the addition products were then distilled over (55-105°C/8 mm.) and subjected to block analysis. A residual reaction tar was left behind in the distilling flask.

The solvent fractions and chlorobenzene and low-boiling addition compound were recombined and fractionated in the manner described before, except that the simple distillation following the removal of pure carbon tetrachloride was eliminated. It was found that after the distillation of chlorobenzene the addition compound remaining commenced to decompose in the still-pot. It was therefore distilled out without using a column and analysed as a mixture.

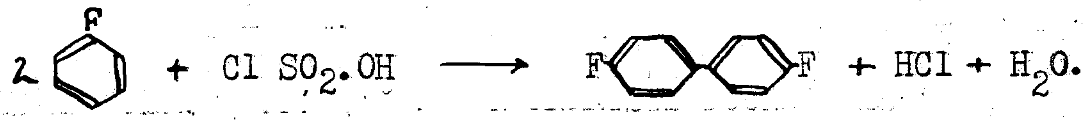
Despite numerous efforts made it was not possible to obtain any pure fluorobenzene from the ternary azeotrope in which it distilled. It was observed that no separation could be effected by distillation with the columns described; the introduction of other components merely set up further complications. Attempted separation by freezing was also unsuccessful, as were efforts to remove carbon tetrachloride as the solid product $C\,Cl_4.2H_2S.23H_2O$. obtained by passing hydrogen sulphide through the carbon tetrachloride solution at -5°C in the presence of the theoretical quantity of water (De Forcrand, J. Chem. Soc., 1883, 44 (Abs.), 961). Trial experiments indicated that the precipitation of this compound in the presence of fluorobenzene brought about incorporation of the latter into the crystal mass.

Fluorobenzene in the azeotrope was therefore characterised in two ways, (a) conversion to 4-4′- difluorodiphenyl-sulphone (Huntress and Carten, J. Amer. Chem. Soc., 1940, 62, 512) and

(b) conversion into p-chlorofluorobenzene (Varma et al., J. Indian Chem. Soc., 1944, 21, 112). Isolation of the former compound is somewhat complicated by the presence of benzene in the azeotrope.

(a) Preparation of 4-4′-Difluoro-diphenyl-sulphone.

The azeotrope (5 mls., containing 0·75 gr. of fluorobenzene by analysis) was treated with excess redistilled chloro-sulphonic acid (3 mls.) and maintained at 40°C for 1 hour in a flask fitted with a reflux condenser. The mixture was then poured onto crushed ice, carbon tetrachloride (5 mls) was added, and the organic layer was separated. This was then washed twice with water and dried over anhydrous magnesium sulphate. Carbon tetrachloride was then removed from the solution by distillation under reduced pressure. The oily residue was dissolved in absolute alcohol (20 mls.) to which a drop of phenolphthalein indicator solution had been added. Any benzenesulphonyl-chloride (originating from reaction of chlorosulphonic acid on any benzene in the azeotrope) was then destroyed by treating this solution at 50°C with dilute alcoholic sodium hydroxide solution until it was faintly alkaline. The mixture was then brought to neutrality by the dropwise addition of very dilute hydrochloric acid and any precipitated sodium chloride was filtered off. The filtrate was then evaporated to dryness under reduced pressure. The product was then washed with water to remove sodium salts and recrystallised from aqueous alcohol.



Yield 150 mgr. M.p. 98°C. On analysis found F 14·8% (Calculated for $C_{12}H_8O_2SF_2$, F 15·0%).

(b) Preparation of p-chlorofluorobenzene.

To the azeotrope (26 mls., containing 4 grs. fluorobenzene by analysis) was added iron filings (0·4 gr.) and the mixture was placed in a flask fitted with a reflux condenser. A stream of chlorine was then maintained through this mixture until the gain in weight was 1·75 grs. This allowed for the conversion of the small amount of benzene present into dichlorobenzene. The product was filtered and washed with dilute(2N.) sodium hydroxide to remove chlorine and acid impurities. After washing with water until neutral it was dried (anhydrous calcium chloride) and distilled through a small column. The fraction b.p 129·5 - 130·5°C was collected.

Yield 2·52 grs. On analysis found F 14·5% Cl 27·4%. (Calculated for $C_6H_4Cl\ F$, F 14·56%, Cl 27·20%).

(iii) Reaction of Chlorine Trifluoride with Alkyl-benzenes in Carbon Tetrachloride solution.

The apparatus used for these experiments was identical to that employed in carrying out the reaction of chlorine trifluoride with benzene using carbon tetrachloride as solvent. In all experiments the dry alkyl benzene (100 gr.) was dissolved in dry carbon tetrachloride (500 ml.) to which had been added anhydrous cobaltous fluoride (10 gr.) as catalyst. The reaction vessel was kept at $0^{o}C$ whilst chlorine trifluoride (8-9 grs./hr.), diluted by nitrogen (12 l./hr.), was passed in with stirring until the addition of 0·5 mol. per mol. of hydrocarbon had been accomplished.

At intervals during the reaction, qualitative tests for halogens, hydrogen fluoride and hydrogen chloride were carried out on the effluent gases as in the benzene experiments. In all cases hydrogen fluoride was detected but other tests proved to be negative. After the required amount of chlorine trifluoride had been added, nitrogen alone was allowed to flow for 10-15 minutes to clear the apparatus of halogens. The reaction product was then poured into saturated aqueous sodium hydrogen carbonate solution and freed from inorganic impurities in a similar manner to the products obtained from benzene experiments. After drying over anhydrous magnesium sulphate the reaction product was in all cases a clear orange coloured liquid. Details of the working-up of these reaction products are submitted below in sectional form.

Toluene Experiment.

After a trial experiment had indicated that the products of the reaction included unchanged toluene and its monofluoro- and monochloro- substituted derivatives, it was decided that, in order to obtain any absolute information regarding such products which have their boiling points so close together, it would be necessary, at least in the final stages, to employ a more accurate apparatus for fractional distillation than any already described. Furthermore, it would be essential, having regard to the quantities of material available, for any such apparatus to have as low a hold up as possible, thus rendering packed columns impracticable.

A concentric tube fractional distillation apparatus of the type described by Naragon and Lewis (Anal. Chem., 1946, 18, 449) was therefore constructed. The specifications of this column were:-

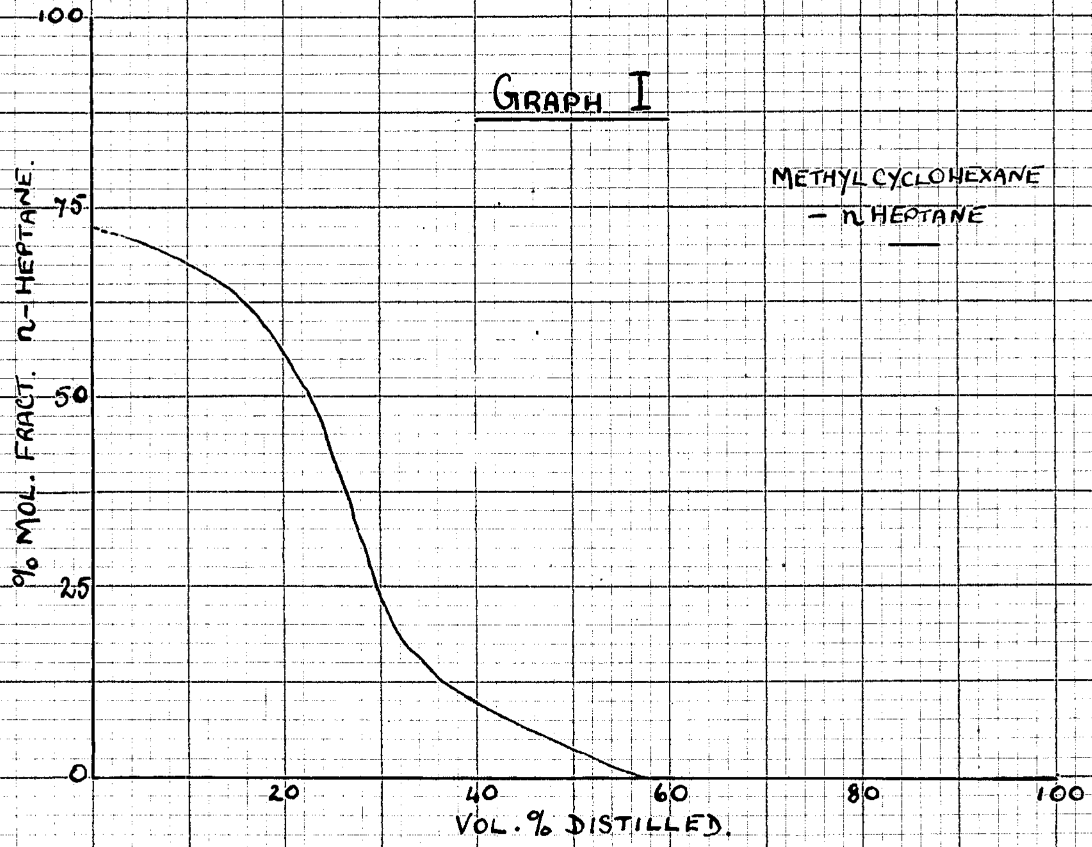
Length of column = 30 cm.
Internal diameter of outer tube (Trubore) = 8±0·01 mm.
External diameter of innter tube (Pyrex) = 5±0·1 mm.

This column was tested by the distillation through it of a standard mixture of methyl-cyclohexane and normal heptane. The mixture used had a value for n_D^{20} of 1·4165 and the mol. fraction of n-heptane was 0·1638 (c.f. Bromiley and Quiggle, Ind. Eng. Chem., 1933, 25, 1136).

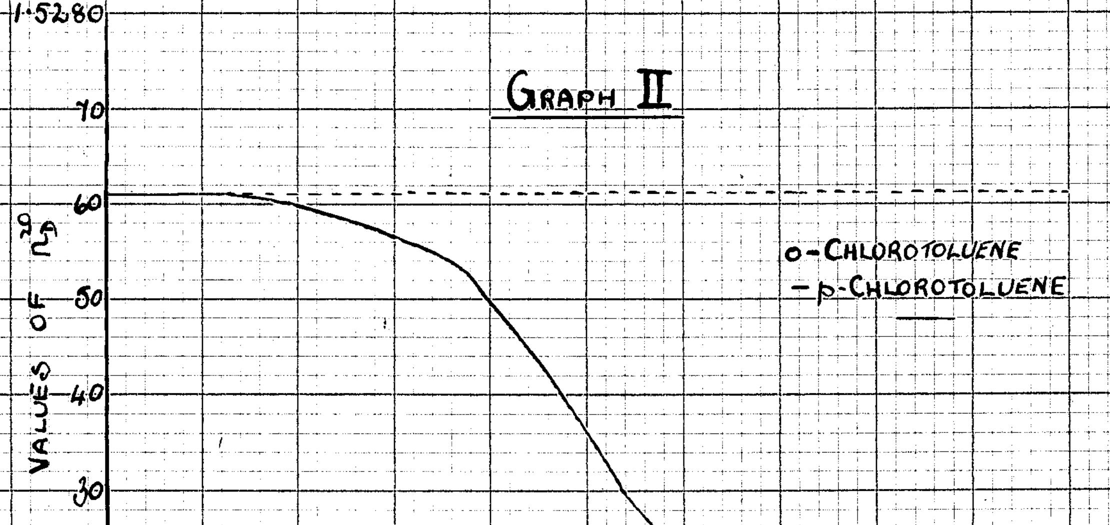
The column was used in conjunction with a mantled still pot as described in section (ii), the heating of which was controlled from a rectified 215 volt A.C. mains source with the aid of a "Variac" transformer. A charge of 25 mls. was employed and the system put into equilibrium (1 hour) using a boil-up rate of 75 drops per minute return to the still pot. Distillation was carried out using a take-off of 1 ml./hr. and values of n_D^{20} were taken at intervals of 1 ml. A curve plotting volume % distilled against mol. fraction % of normal heptane was drawn with the aid of the refractive index data of Bromiley and Quiggle (loc. cit.) and a value for the efficiency of the column was obtained by comparison with the curve of Lecky and Ewell (Anal. Chem. 1940, 12, 547). The distillation curve is shown in Graph I, and the efficiency value was computed as 38 theoretical plates. The operational hold-up of the system was found to be approximately 1·5 mls.

The column was then employed to investigate the possibility of separating ortho and para- chloro toluenes by fractional distillation. Specimens of pure ortho and para chloro toluene were obtained by distillation of stock reagents through the 22-plate Fenske-helix-packed column under atmospheric pressure using a boilup rate of 90 drops per minute and a take-off rate of approximately 1 : 24. By taking centre-cuts, O-chlorotoluene b.p 158·9°C, n_D^{20} 1·5261 and p-chlorotoluene b.p. 162°C n_D^{20} 1·5211, were obtained. A still pot charge of 25 mls of a 50% by volume mixture of these two compounds was employed, and submitted to distillation through the column under the same conditions as the standard platage-determining experiment; results obtained gave rise to Graph II in which values of n_D^{20} are plotted against % by volume distilled over.

It was observed that, though pure ortho and para chloro toluenes were obtainable at the beginning and end of the distillation, the intermediate fraction exceeded 50% by volume of the total distillate. In order to see whether reduction in the take off rate would improve the separation the distillation was repeated with a 16 ml. still pot charge and a take off rate of 0·5 ml./hr. The results obtained were plotted in Graph III and it was seen that though the



GRAPH I

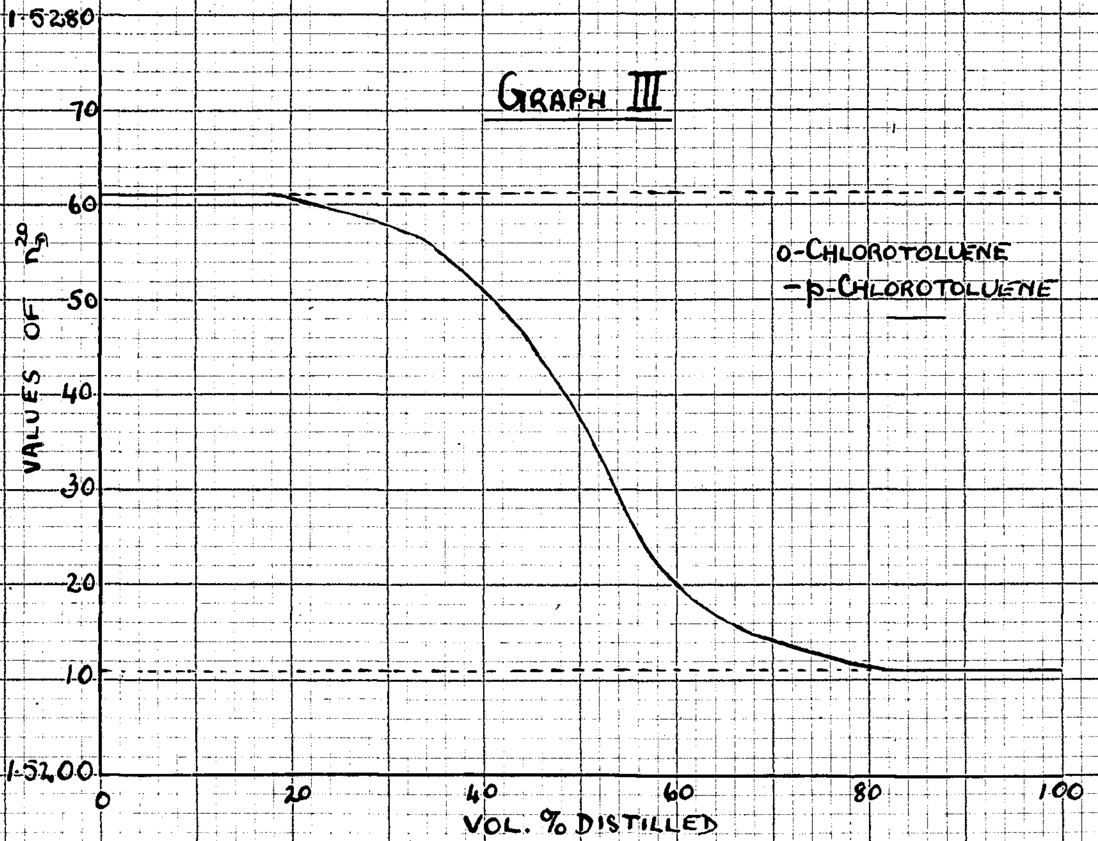


GRAPH II

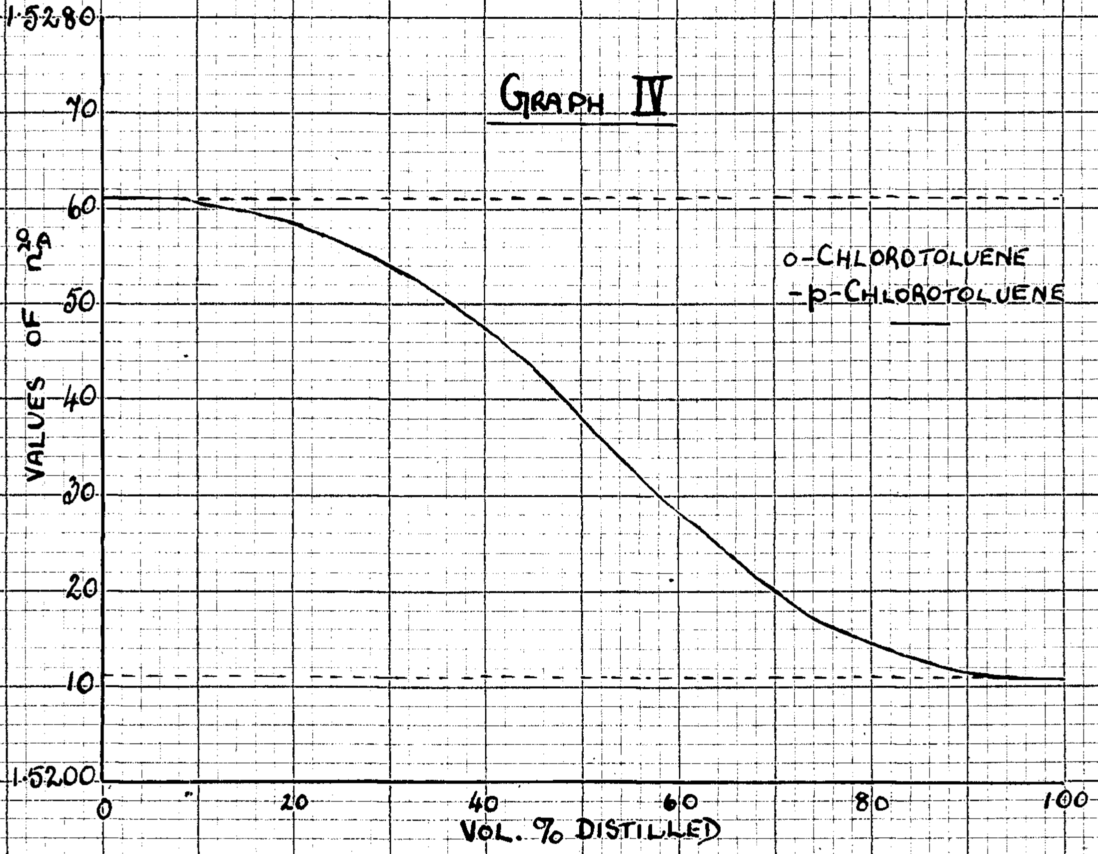
separation was slightly sharper the intermediate fraction was still about 50% of the total.

It was therefore decided that absolute separation of the isomers from the reaction product could not be achieved by this means, but that characterisation of extreme fractions should be possible. As certain distillations in subsequent work were to be carried out under reduced pressure one further experiment was completed with the standard mixture (50% by volume of each) of O- and p-chlorotoluenes. This involved the attempted fractionation at 14 mm. pressure, the column system being slightly modified to include (a) a three-necked mantled still pot carrying a fine capillary air-bleed in addition to a thermowell and column connection, and (b) a device of the 'Perkin triangle' type to permit change of distillate receiver without alteration of the equilibrium conditions through the column.

Using a boilup rate of 40 drops per minute and a take-off rate of 1 ml./hr., figures were obtained from which Graph IV was plotted. The boiling point ranged from 54°C/14 mm. (ortho-) to 57·5°C/14 mm. (para-). The separation was rather less effective than the atmospheric pressure distillation, approximately 65% of the distillate being



Graph III



Graph IV

collected as intermediate fraction.

The reaction product from the toluene experiment with chlorine trifluoride was first submitted to distillation under reduced pressure in a simple apparatus having two receivers in series, one cooled in alcohol-drikold mixture and the second in liquid nitrogen. A first fraction consisting mainly of solvent was distilled at temperatures up to 30°C/40 mm. The residual liquid was transferred to a smaller distilling flask and the second fraction consisting mainly of toluene and substitution products, together with a little lower-boiling addition compound was distilled up to 75°C/10 mm: these two fractions were then recombined.

There then distilled unstable addition compound as a viscous oil b.p. 100-160°C/10mm. (see Table IV, Col. 8), leaving a black tarry residue (see Table IV, Col. 4). Immediate analysis of a specimen of the addition compound gave Cl 23·5%, F 12·8%. (c.f. calculated for $C_7H_8Cl\,F$, Cl 24·2%, F 13·0%).

The recombined first fractions were freed from most of the carbon tetrachloride by distillation through the solvent column under similar conditions to those described for benzene experiments. The remaining liquid was distilled under the same operating conditions through the 22 plate column packed with Fenske helices and gave rise first of all to carbon tetrachloride b.p. 76·8°C, n_D^{20} 1·4614. Continuation of the distillation gave a fraction b.p. 110-117° containing toluene and fluorotoluenes.

After these fractions had been collected, the residual liquid was distilled through the same column under reduced (12 mm.) pressure with total take-off and an operational throughput of approximately 3 mls/hr. This distillation gave first of all a small fraction b.p. 38°C/12 mm, n_D^{20} 1·4916, which analysed as C_7H_7F (Found F 17·1%, Calculated F 17·28%). It had b.p. 139°C/760 mm. and was therefore concluded to be benzyl fluoride. Subsequently a mixture of chlorotoluenes b.p. 52-57°C/12 mm. was obtained. A residue left in the still pot at this stage (see Table IV, Col. 9) was assumed to have arisen from lower-boiling addition compounds which did not survive these distillation processes.

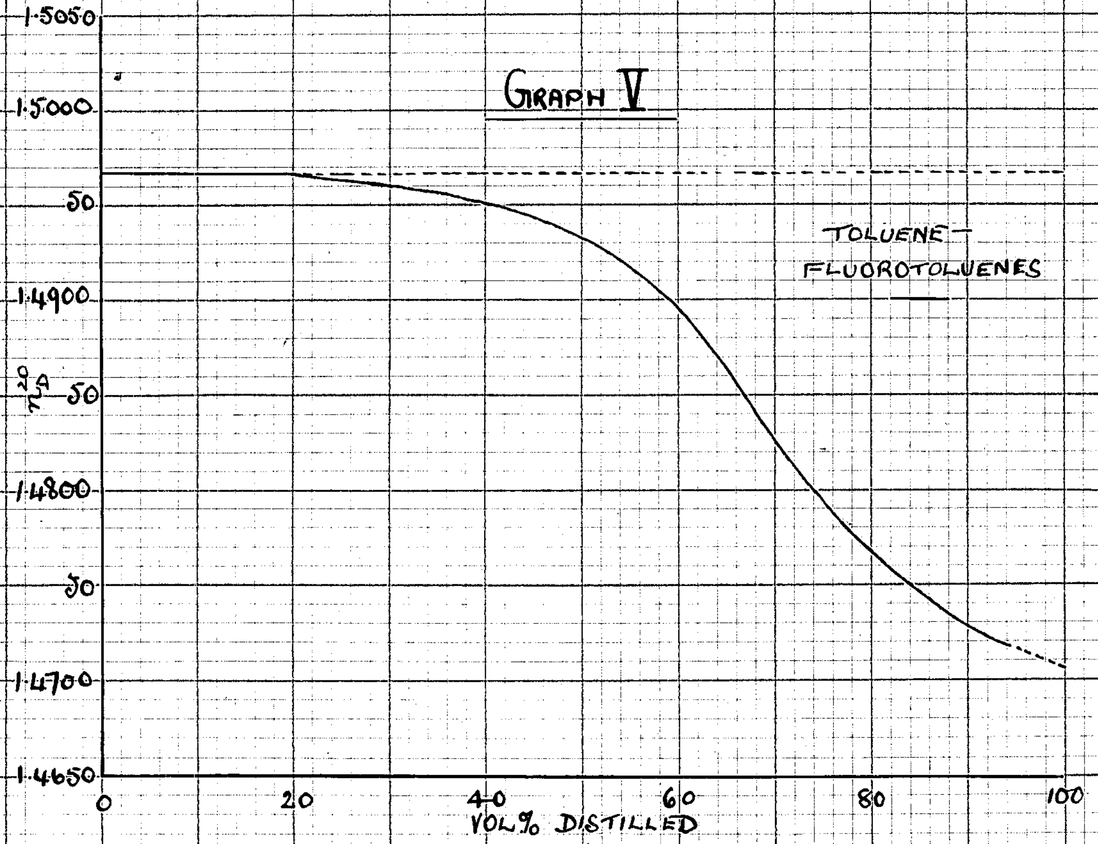
The mixture of toluene and fluorotoluenes (27·2 gr.) was submitted to distillation through the concentric tube column, with a boil-up rate of 75 drops per minute, and a take-off rate of 1 ml./hr. From results obtained a graph was plotted connecting n_D^{20} with the volume % distilled over (Graph V)

An estimate of the total amount of fluorotoluene in the mixture had already been obtained by fluorine analysis (see Table IV, Col. 5.).

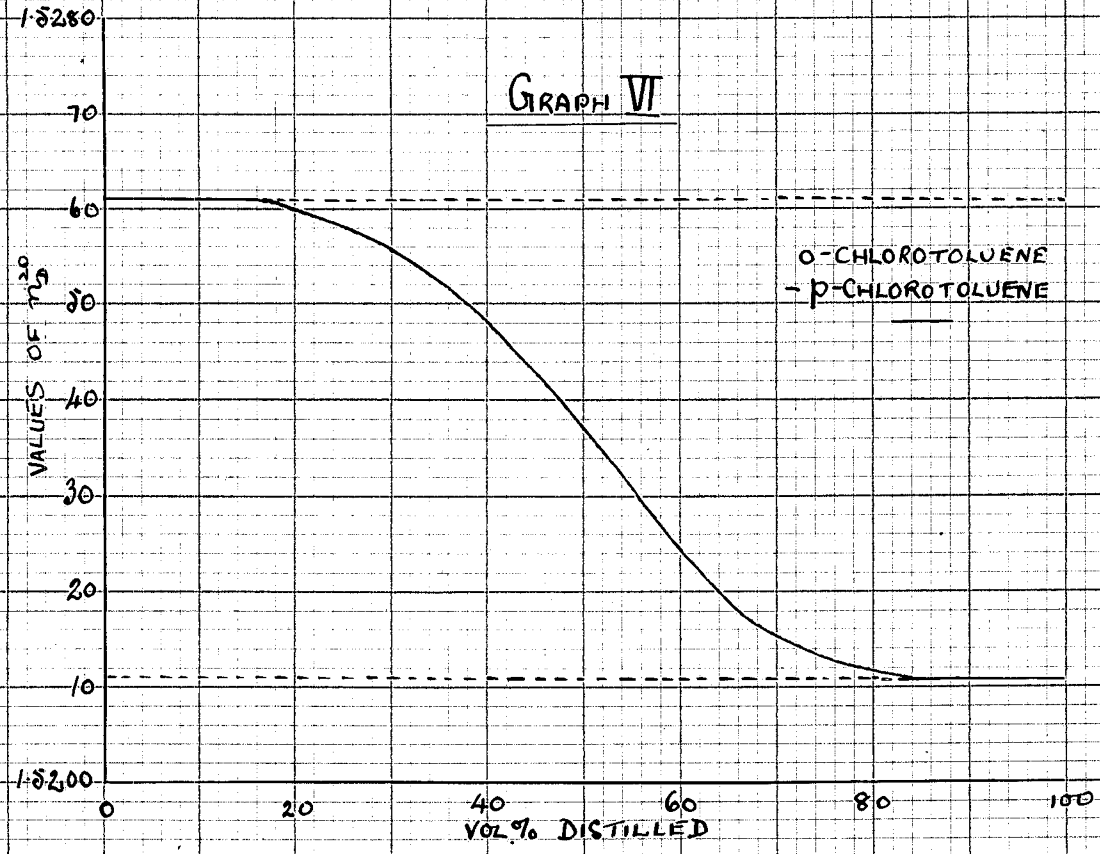
By this means toluene (b.p. 110°C) of purity given by n_D^{20} 1·4966 to 1·4955 (11 mls.) was first distilled over and collected. The fractionation then gave rise to an intermediate n_D^{20} 1·4949 to 1·4755 (14 mls.) and a third fraction (fluorotoluene mixture) having n_D^{20} 1·4743 to 1·4715 (3 5 mls.). A specimen of the latter having n_D^{20} 1·4715 was analysed and gave **F** 17·1% (Calc. for C_7H_7F, F 17·28%). Oxidation of this third fraction with aqueous potassium permanganate gave rise to a mixed fluorobenzoic acid m.p. 158°C (c.f. ortho- $F.C_6H_4CO_2H$ m.p. 122°, meta- m.p. 123° and para- m.p. 182°C).

Distillation of the chlorotoluene mixture (22·1 gr.) was also effected through the concentric tube column under the same operating conditions as for the toluene-fluorotoluene mixture. The course of the distillation was followed as before and the results gave rise to Graph VI. From this fractionation three main fractions were obtained, viz:-

(a) O-chlorotoluene, b.p. 159°C n_D^{20} 1·5261 to 1·5260 ... 4 mls.
(b) Intermediate, n_D^{20} 1·5258 to 1·5213 ...11 mls.
(c) p-chlorotoluene, b.p. 162°C n_D^{20} 1·5212 to 1·5211 ..4·5 mls.



GRAPH V



GRAPH VI

Identification of the fractions (a) and (c) was completed by analysis and oxidation.

(a) gave Cl 27·9% (Calc. for C_7H_7Cl, Cl 28·06%) and on oxidation with aqueous potassium permanganate gave an acid m.p. 141°, mixed m.p. with O-chlorobdnzoic acid 141°C.

(b) gave Cl 28·0% (Calc. for C_7H_7Cl, Cl 28·06%) and by permanganate oxidation gave an acid m.p. 241°, mixed m.p. with p-chlorobenzoic acid 241°C.

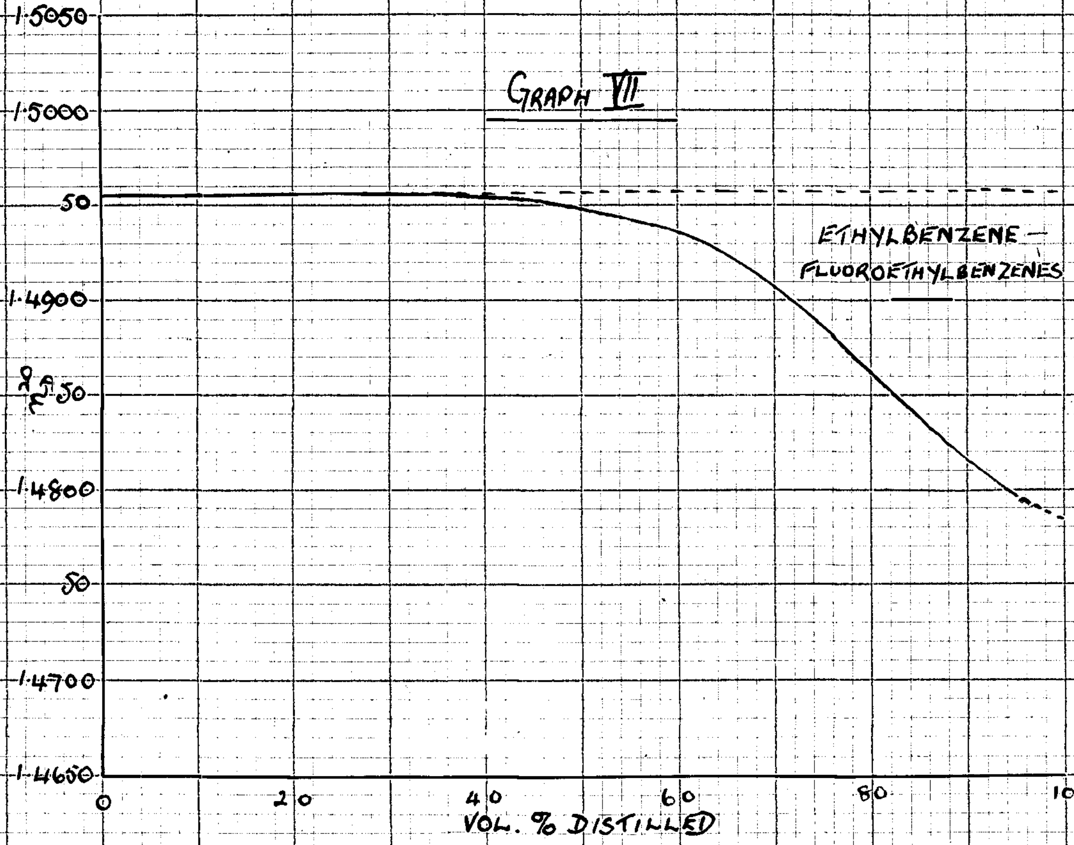
The absence of any m-chlorotoluene (b.p. 161·8°C, $n_D^{18\cdot7}$ 1·5225) is confirmed by the absence of irregularities in the distillation curve (see Graph VI) and the fact that it was possible to isolate pure head and tail fractions from the distillate.

Ethylbenzene Experiment

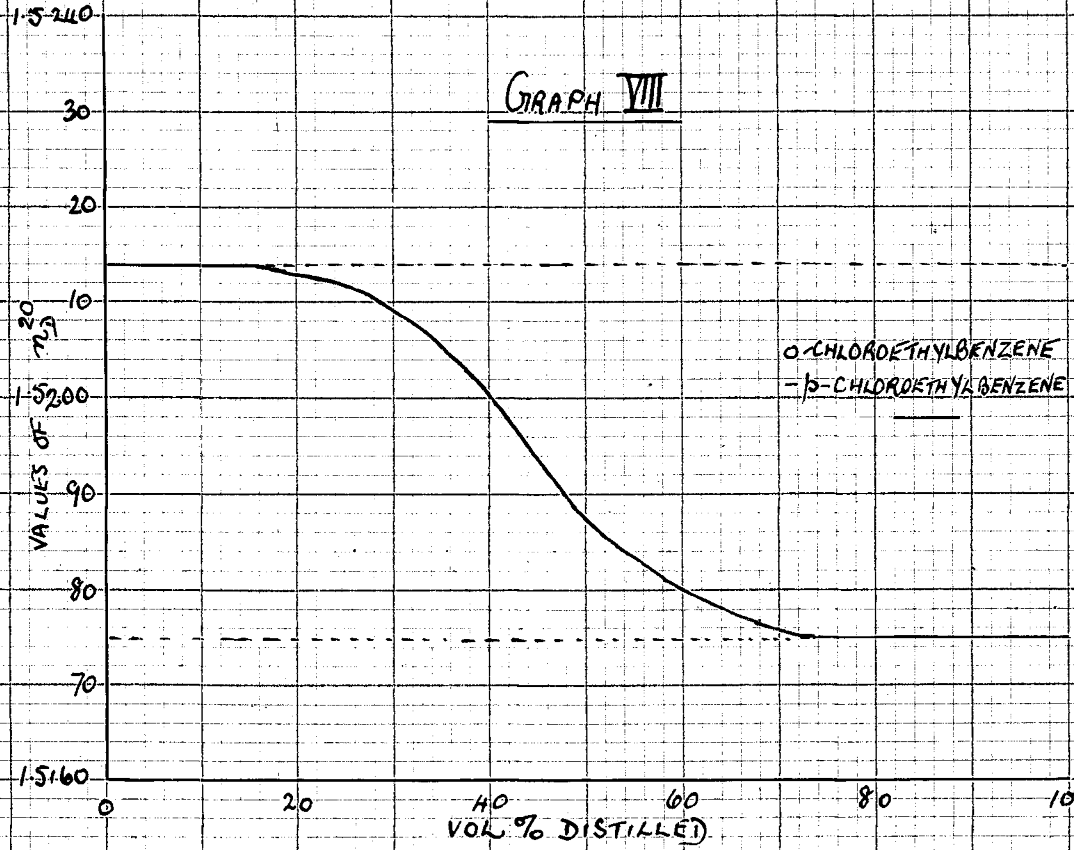
The method used in working up the products of this experiment was identical with that used in the analogous case of toluene. Unstable addition compounds (see Table IV, Col. 8) were removed (b.p. 85-125°C/10 mm.) in the primary distillation as was reaction tar (see Table IV, Col. 4). Immediate analysis of a sample of the addition product gave Cl 24·0%, F 11·2% (c.f. Calculated for $C_8H_{10}Cl\,F$, Cl 22·1%, F 11·8%). The rest of the reaction product was freed from carbon tetrachloride by fractional distillation as in the case of toluene and subsequent fractionation through the 22 plate column gave, using a boilup of 90 drops/min. and take off ratio of approximately 1 : 30, a fraction (31·3 gr.) b.p. 136-140°C containing ethyl benzene and fluoroethyl-benzenes. Continued fractionation through the same column under reduced pressure, using total take-off, as in the toluene experiment, gave a mixture of chloroethyl-benzenes (19·8 gr.) b.p. 66-70°C/10 mm. and left a still pot residue (see Table IV, Col.9.).

The mixture of ethylbenzene and fluoroethyl-benzenes was submitted to fractionation through the concentric tube column under the conditions used in the corresponding distillation of the toluene-fluorotoluene mixture. After the removal of ethyl benzene (b.p. 136°C) of purity given by n_D^{20} 1·4958 to 1·4943 (19 mls.) the residual liquid was analysed and an estimate of the total fluoro-compound present was made (see Table IV, Col. 5). The fractionation was continued and from the results Graph VII was constructed. It was not, however, possible to isolate any fluoroethylbenzene in a pure state.

GRAPH VII



GRAPH VIII



The concentric tube column was again employed under the same operating conditions to fractionate the mixture of chloroethyl-benzenes. This fractionation gave rise to :-

(a) O-chloroethylbenzene b.p. 179·5°C, n_D^{20} 1·5214 to 1·5213
.... 4 mls.

(b) Intermediate n_D^{20} 1·5211 to 1·5180 .... 6 mls.

(c) p-chloroethylbenzene b.p. 184·5°C, n_D^{20} 1·5176 to 1·5175
.... 6 mls.

The distillation curve for this fractionation is given by Graph VIII.

The identities of fractions (a) and (c) were confirmed by analysis and oxidation as before.

(a) gave Cl 25·2%, Calc. for C_8H_9Cl, Cl 25·26%; on permanganate oxidation it gave an acid m.p. 141°, mixed m.p. with O-chlorobenzoic acid 141°C.

(c) gave Cl 25·2%, Calc. for C_8H_9Cl, Cl 25·26%; on oxidation ($KMnO_4$) it gave rise to an acid m.p. 241°, mixed m.p. with p-chlorobenzoic acid 241°C.

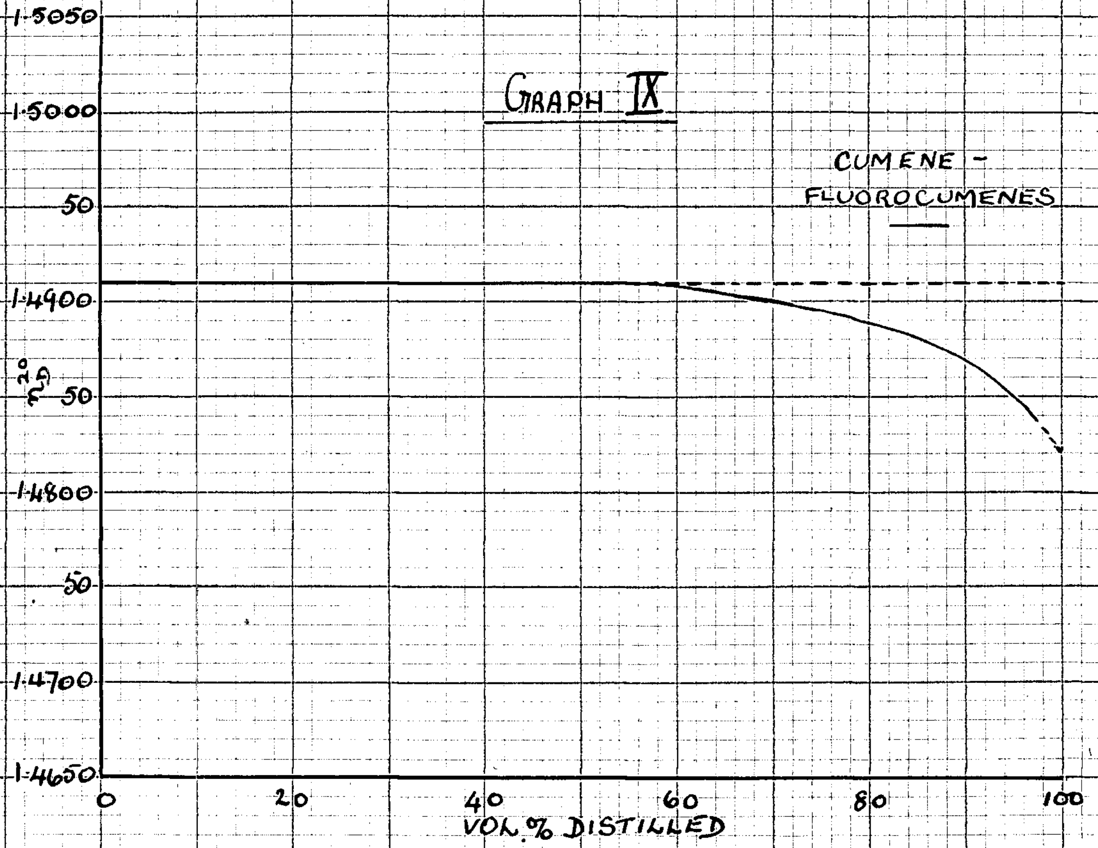
Inspection of the distillation curve evidences the absence of any m-chloro derivative (c.f. toluene experiment).

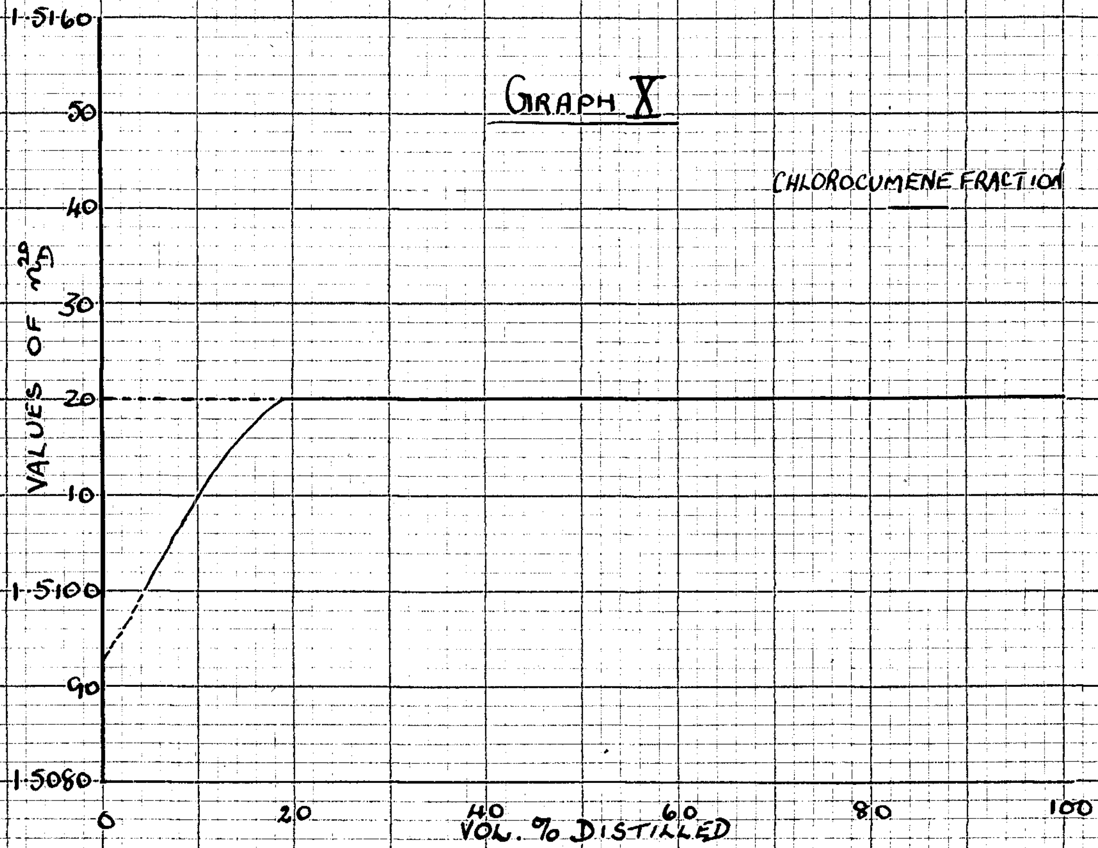
Cumene Experiment.

The reaction product was worked up by an analogous process to those already cited for ethyl benzene and toluene. Unstable addition product (b.p. 88-110°C/8 mm.) and reaction tar were removed at the outset (see Table IV, Cols. 8 and 4 respectively). Immediate analysis of a specimen of the addition compound gave Cl 22·6%, F 10·1% (c.f. calculated for $C_9H_{12}Cl\ F$, Cl 20·3%, F 10·9%).

After removal of the solvent, fractionation was carried out through the 22 plate column under reduced pressure using total take off, with a throughput rate of about 3 mls/hr. as in previous preliminary fractionations at reduced pressure. This gave rise to a fraction b.p. 43-49°C/10 mm. (41·2 gr.) consisting of cumene and fluorocumene (s), and also a chlorocumene fraction b.p. 75-78°C/10 mm. (22·2 gr.), leaving a small residue (see Table IV, Col. 9).

The mixture of cumene and fluorocumene(s) was fractionally distilled through the concentric tube column at atmospheric pressure under the normal operating conditions as previously described. Cumene (b.p. 152°C) of purity given by n_D^{20} 1·4910 to 1·4896 was removed (35 mls.), and a sample of the residual liquid was analysed in order to give an estimate of the total fluorocompound present. The distillation was continued and


GRAPH IX
CUMENE – FLUOROCUMENES
1·5050
1·5000
50
1·4900
n20D
50
1·4800
50
1·4700
1·4650
0
20
40
60
80
100
VOL.% DISTILLED


GRAPH X
CHLOROCUMENE FRACTION
1·5160
50
40
VALUES OF n20D
30
20
10
1·5100
90
1·5080
0
20
40
60
80
100
VOL.% DISTILLED

the results were plotted (see Graph IX). It was not, however, possible to isolate any fluorocumene free from cumene.

The chlorocumene fraction was submitted to distillation through the concentric tube column under reduced pressure (15 mm.) with a boilup rate of 48 drops per minute and a take off rate of 1 ml./hr. The distillation curve from this fractionation is shown in Graph X. The process gave rise to 2 mls. of liquid b.p. 80°C/15 mm, n_D^{20} 1·5102 to 1·5111 ; followed by p-chlorocumene b.p. 81°C/15 mm., n_D^{20} 1·5118 to 1·5120. This latter was characterised by analysis (Found Cl 23·1%, Calcd. for $C_9H_{11}Cl$, Cl 23·0%) and oxidation to an acid m.p. 241°C which had an unchanged m.p. when mixed with p-chlorobenzoic acid. The first fraction on oxidation gave an acid m.p. 236° which after 2 recrystallisations rose to 241° and gave a mixed m.p. of 241°C with p-chlorobenzoic acid. It seems to be highly probable that this fraction was also p-chlorocumene, but that it contained traces of some impurity which depressed the value of the refractive index.

(iv) Reaction of Chlorine Trifluoride with Halo-benzenes in Carbon Tetrachloride solution.

Fluorobenzene was prepared from aniline as described by Flood (Org. Synth. (Coll.) II, 295). Experiments using chlorine trifluoride were carried out in the same way as those involving alkyl benzenes (see previous section). Qualitative tests on the effluent gases during the progress of the reactions gave positive results for hydrogen chloride. More copious evolution of hydrogen fluoride was observed in the case of fluorobenzene than with any other compound studied. Preliminary working up of the reaction mixtures was carried out as in the alkylbenzene experiments, and the products, after drying, were transparent orange coloured liquids.

Chlorobenzene Experiment.

Distillation to remove reaction tar and addition compounds (Table VI, Cols. 4 & 8 respectively) was carried out in a simple apparatus as for the experiments in the preceding section. The addition product was rather more stable than the corresponding products obtained from alkyl benzenes, and it distilled at 88-92°C/8 mm. without decomposition. It had n_D^{20} 1·5172 and on analysis gave Cl 46·3%, F 13·2%. Small quantities were found to decolourise aqueous potassium permanganate and bromine water, and from analytical figures it seems possible that it was a mixture of $C_6H_5Cl_2F$ (Calc. Cl 42·6%, F 11·4%) and $C_6H_5Cl_3F_2$ (Calc. Cl 48·2%, F 17·2%).

Carbon tetrachloride was removed from the reaction product by fractionation first through the solvent column, and subsequently through the 22 plate helices-packed column as in previous experiments. Continuation of the distillation through the latter column gave a fraction (32·7 g.; b.p. 130-133°C) containing chlorobenzene and chlorofluorobenzene. The product which remained was then distilled under reduced pressure through a hard glass column 85 cm. in length, 14 mm. internal bore, packed with 4 mm. single turn Fenske helices and having a compensatory heating jacket as described for the other packed columns. This column had a built in still-head giving total take-off, and was used in conjunction with a mantled still-pot. Using a throughput of 2 mls./hr. fractionation gave rise to :-

(a) 38·7 gr. p-dichlorobenzene b.p. 62°C/10 mm, m.p. 53°C (solidifies in receiver). On analysis this gave Cl 48·3%

(Calc. for $C_6H_4Cl_2$, Cl 48·3%). A mixed m.p. with a specimen of pure p-dichlorobenzene was also 53°C.

(b) 2·1 gr. o-dichlorobenzene b.p. 69°C/10 mm, n_D^{20} 1·5511. Analysis:- found Cl 48·2%, Calc. for $C_6H_4Cl_2$, Cl 48·3%. The b.p. was determined as 180°C/755 mm, and f.p. -15·5°C. With a sample of o-dichlorobenzene f.p. -16·5°C a mixed f.p. of -16°C was observed.

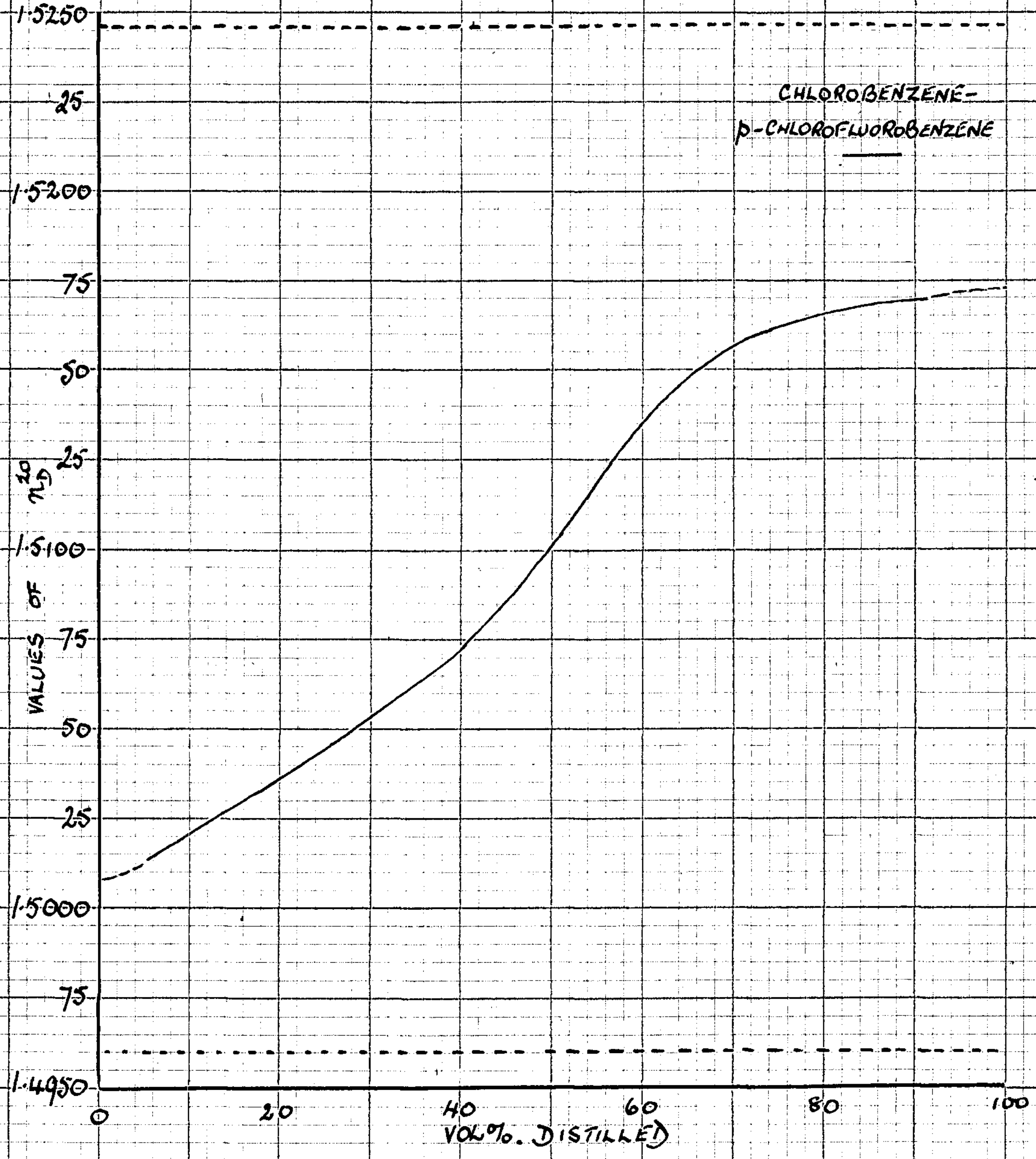
(c) An undistillable residue remained in the still-pot (Table VI, Col.9).

The mixture of chlorobenzene and chlorofluorobenzene was submitted to distillation through the concentric tube column after analytical determination (Cl 29·2%, F 7·95%) to arrive at the amounts of fluoro-compound and unchanged starting material present in the mixture (see Table VI). Using a boil-up rate of 75 drops per minute and a take-off rate of 1 ml./hr. results were obtained from which Graph XI was plotted. The distillation gave rise to three fractions:-

(i) 9 mls., n_D^{20} 1·5010 - 1·5055, enriched in chlorofluoro-compound.

(ii) 9 mls., n_D^{20} 1·5065 - 1·5148, intermediate fraction.

GRAPH XI



CHLOROBENZENE-
p-CHLOROFLUOROBENZENE
1·5250
25
1·5200
75
50
25
1·5100
75
50
25
1·5000
75
1·4950
VALUES OF n_D^{20}
0
20
40
60
80
100
VOL%. DISTILLED

(iii) 8 mls., n_D^{20} 1·5155 - 1·5173, enriched in chlorobenzene

The fraction (i) was recycled through the concentric tube column under the same conditions as before, the results being plotted on Graph XIIa. This distillation gave two fractions:-

(iv) 1·5 mls., n_D^{20} 1·4967 - 1·4972, p-chlorofluorobenzene, b.p. 129·8°C/754 mm.

(v) 6·0 mls., n_D^{20} 1·4978 - 1·5083, mixture of p-chlorofluorobenzene and chlorobenzene.

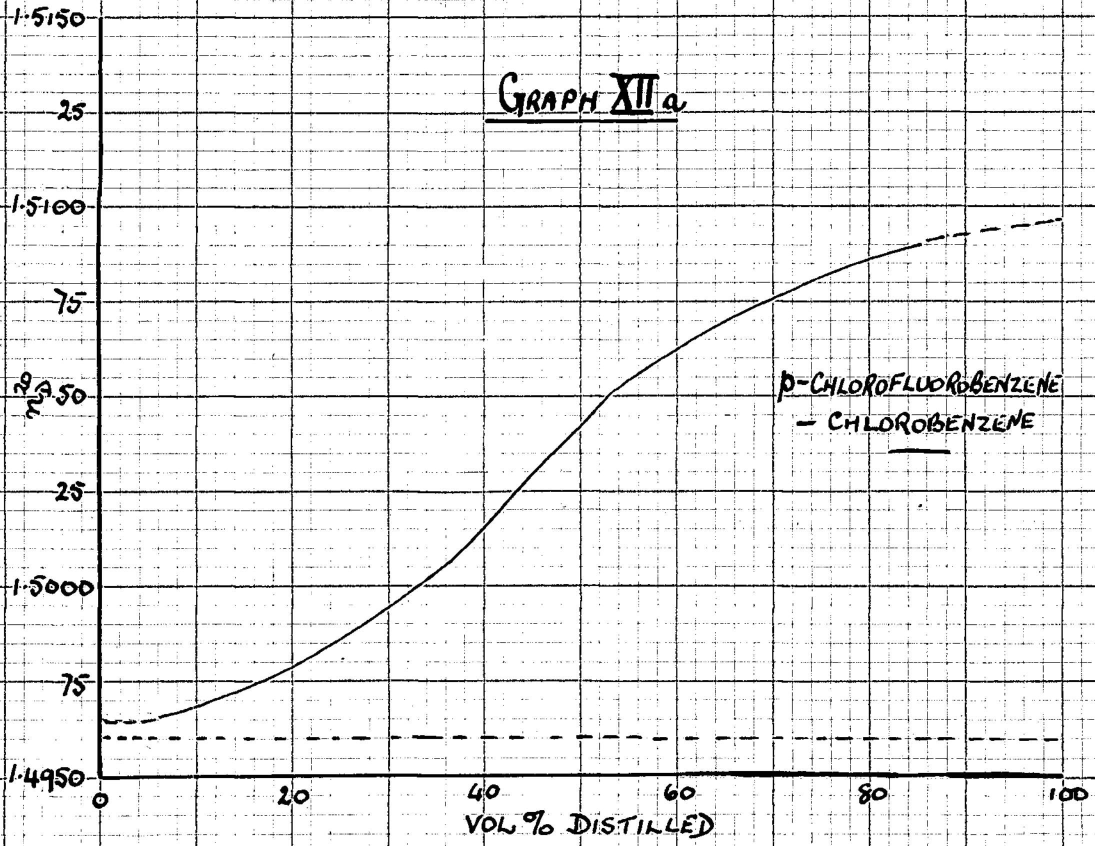
On analysis fraction (iv) gave Cl 27·4% F 14·4%, calc. for $C_6H_4Cl\ F$, Cl 27·2%, F 14·55%

To fraction (iii) was added 4 mls. pure o-dichlorobenzene (b.p. 180°C) to act as distillate chaser and this mixture was submitted to distillation through the concentric tube column as before. The results of this fractionation are plotted in Graph XIIb, two fractions being collected :-

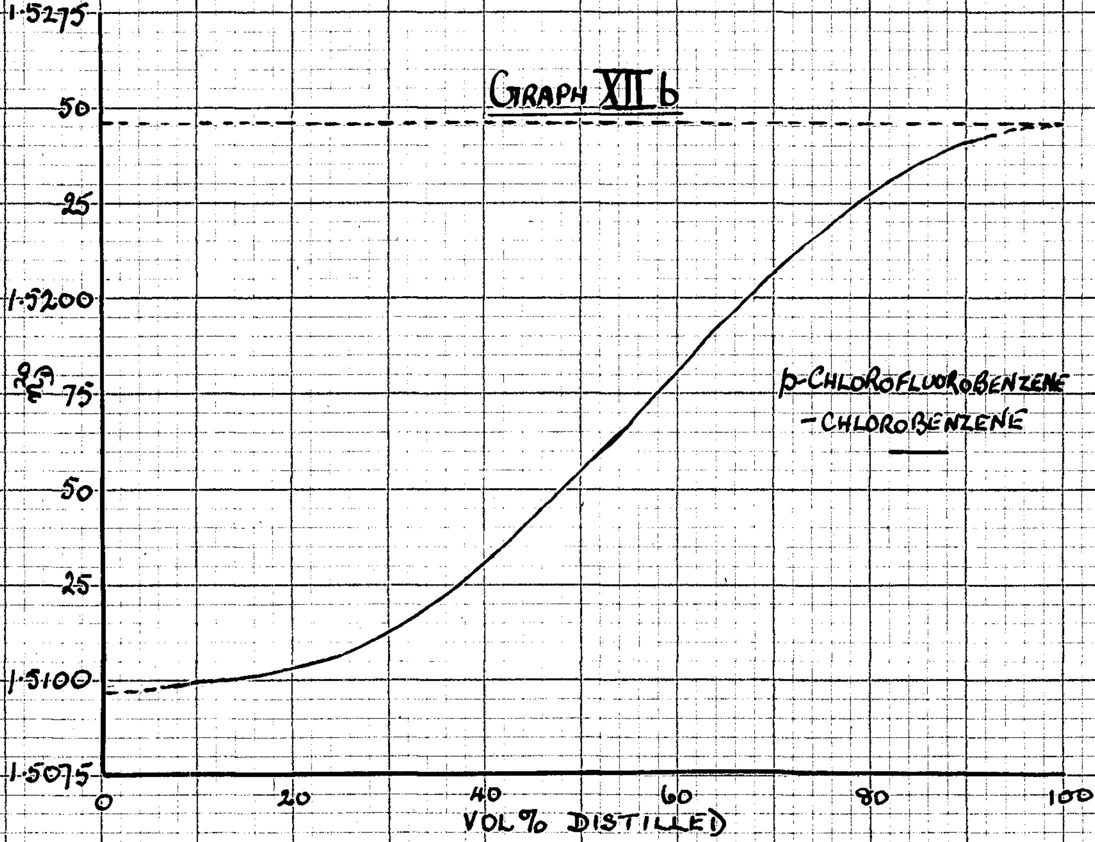
(vi) 6·0 mls. n_D^{20} 1·5098 - 1·5223, mixture of chlorobenzene and p-chlorofluorobenzene

(vii) 1·0 ml. n_D^{20} 1·5237 - 1·5243, chlorobenzene, b.p. 132·2°C/762 mm.

On analysis fraction (vii) gave Cl 31·4%, calc. for C_6H_5Cl, Cl 31·55%



GRAPH XII a



GRAPH XII b

The absence of ortho- and meta-chlorofluorobenzenes (b.p.'s 137·6° and 127·6°C respectively) from the reaction mixture is confirmed by the absence of irregularities in the distillation curves and the boiling points and refractive indices of pure extreme fractions. (b.p.'s 129·8° and 132·2°C).

Fluorobenzene Experiment.

The reaction product was dealt with in an identical manner to that from the chlorobenzene experiment, reaction tar and addition products being removed in preliminary distillations. (See Table VI). Addition product was collected in two fractions from the simple distillation, the lower-boiling fraction being the more stable. These were :-

(a) 2·4 gr; b.p. 63-67°C/10 mm.; n_D^{20} 1 4652.
Analysis gave Cl 27·1%, F 23·0%

(b) 9·7 gr; b.p. 90-135°C/10 mm.; n_D^{20} 1·5153
Analysis gave Cl 21·2%, F 26·4%. This fraction decomposed after standing for 1-2 days.

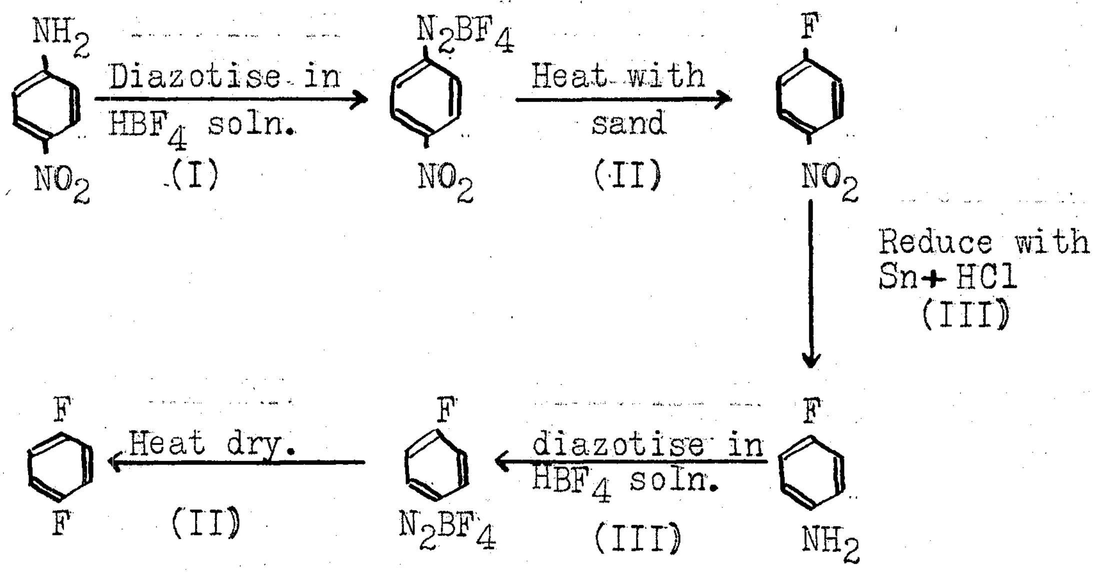
Specimens of fractions (a) and (b) were shown to decolourise aqueous potassium permanganate and bromine water and analyses show a halogen content comparable with that of the cyclohexadiene derivative $C_6H_5F_2Cl$ (Calc. Cl 23·6%, F 25·3%).

Solvent, which was removed in the same way as for the chlorobenzene experiment was carbon tetrachloride of purity given by n_D^{20} 1·4615 and analysis gave Cl 91·9% (Calc. for $C\,Cl_4$, Cl 92·2%). Neither unchanged fluorobenzene nor difluorobenzene were traceable in this solvent fraction. Subsequent fractionation through the 22 plate column gave only chlorofluorobenzene b.p. 130°C, leaving a still-pot residue (Table VI, Col. 9).

As a check, the chlorofluorobenzene fraction was distilled through the concentric tube column with a boil-up of 75 drops/min. and take-off of 1 ml./hr. It distilled uniformly at 130°C and had values of n_D^{20} from 1·4960 to 1·4964. Analysis gave Cl 27·0%, F 14·7% (Calcd. for $C_6H_4Cl\,F$, Cl 27·2%, F 14·55%). On the basis of the physical properties the fraction was concluded to be pure p-chlorofluorobenzene.

Investigations on the stability of p-difluorobenzene.

p-Difluorobenzene was synthesised from p-nitraniline by the series of reactions outlined below :-



References :- (I) Starkey, Org. Synth (Coll.) II, 225.

(II) Schiemann, Ber., 1929, 62, 3041.

(III) Dunker and Starkey, J.Amer.Chem.Soc., 1939, 61, 3005.

By use of these processes 350 gr. p-nitraniline yielded 17 gr. redistilled p-difluorobenzene b.p. 89°C, n_D^{20} 1·4420.

Stability of p-$C_6H_4F_2$ in $C\,Cl_4$ to aqueous bicarbonate.

p-Difluorobenzene (2·32 g.) was dissolved in carbon tetrachloride (78·64 g.). The mixture was shaken with aqueous sodium bicarbonate solution, then with water until neutral, and dried (anhydrous $MgSO_4$). It was then distilled through the 22 plate column using a boil-up of 90 drops/min. and take off approximately 1 : 30. Distillation occurred uniformly at 77·4°C, leaving no residue. Analysis of the distillate gave Cl 89·5%, F 1·0% (Calc. for original mixture Cl 89·6%, F 0·97%). It is thus seen than p-difluorobenzene dissolved in carbon tetrachloride is stable to hydrolysis by aqueous bicarbonate, and that it interdistils azeotropically with carbon tetrachloride.[*]

Stability of p-$C_6H_4F_2$ in $C\,Cl_4$ to cold dilute alkali.

p-Difluorobenzene (0·4 g.) was dissolved in carbon tetrachloride (25 ml.) and to the solution was added 0·1 N - NaOH (50 ml.). The mixture was continuously shaken at 20°C and 5 ml. aliquots of the aqueous layer were titrated with standard acid at half-hourly intervals. After 3 hours the titre per aliquot had fallen by only 0·03 ml. of 0·1048 N hydrochloric acid showing that hydrolysis was negligible under the conditions described.

Stability of p-$C_6H_4F_2$ in C Cl_4 to anhydrous acid gases.

Azeotrope from * above (5 mls.) was saturated at 0°C with anhydrous hydrogen chloride. The mixture was stoppered, allowed to attain 20°C and shaken for one hour. It was then washed with aqueous sodium bicarbonate, then water until neutral and dried (anhydrous Mg SO_4). After redistillation analysis gave Cl 89·4%, F 1·0%, the mixture of organic products apparently being unchanged.

Azeotrope (5 mls.) was saturated with anhydrous hydrogen fluoride at 20°C, and the above experiment repeated. Unchanged azeotrope (found Cl 89·4%, F 1·0%) was again recovered.

Reaction of chlorine trifluoride with p-$C_6H_4F_2$ in C Cl_4 solution

p-Difluorobenzene (14 g.) was dissolved in carbon tetrachloride (250 mls.) and anhydrous cobaltous fluoride (2 g.) was added. Chlorine trifluoride (6 gr.= 0·5 mol.) was passed in nitrogen (12 l./hr.) at 0°C over a period of 1¼ hours. Copious evolution of hydrogen fluoride was observed during the process, but tests for hydrogen chloride and halogens in the effluent gases proved negative. The resulting product was washed with aqueous sodium bicarbonate, then with water until neutral, and dried (anhydrous $MgSO_4$). The product was a deep-yellow coloured liquid. Most of the carbon tetrachloride was removed by distillation through the solvent column under the normal operating conditions. The last 20 mls. was fractionated through the 22 - plate helices-packed column under the same conditions as for the $C_6H_4F_2$ - $C Cl_4$ azeotrope. When all carbon tetrachloride had been removed the residue amounted to only 0·42 gr. of undistillable matter. This decolourised aqueous potassium permanganate and a specimen on immediate analysis gave Cl 26·3%, F 11·35%. The carbon tetrachloride distillate had n_D^{20} 1·4612 and on analysis gave Cl 92·1% (Calc. for $C Cl_4$, Cl 92·2%), proving that no fluoro-compound was contained in it.

(v) Reaction of Chlorine Trifluoride with Perhalomethylbenzenes in Carbon Tetrachloride solution.

The chlorine trifluoride experiments were carried out in the same way as for investigations with other substituted benzenes (see sections (iii), (iv)). The exit gases contained as before hydrogen fluoride but no hydrogen chloride or halogens. Reaction products were freed from inorganic impurities by the general method (described in section (ii)) and, after drying, were transparent, yellow liquids.

Benzotrifluoride Experiment.

Removal of reaction tar and addition compound (see Table VII) from the product was brought about by simple distillation under reduced pressure as described for previous experiments. The addition product distilled at 63-88 °C/14 mm. and was similar in nature to that obtained from chlorobenzene. It decolourised aqueous potassium permanganate and bromine water and had n_D^{20} 1·4352 ; on analysis it gave Cl 18·1%, F 37·6%. This compares with Cl 17·7%, F 37·95% calculated for the cyclohexadiene derivative $C_7H_5Cl\ F_4$.

Slight modification was necessary for the halogen analysis of benzotrifluoride and benzotrichloride derivatives by the sodium fusion method. To ensure complete conversion to sodium halide it was essential to fuse for 2½ hours at 750-800°C.

After the removal of solvent from the reaction product as in previous experiments, fractionation through the 22 plate helices-packed column gave rise to :-

(i) Fraction distilling 100-104°C (21·4 g.) which was a mixture of fluorobenzotrifluoride with unchanged benzotrifluoride. Analysis gave F 41·8% whence it was estimated that the mixture contained 13·2 g. benzotrifluoride and 8·2 g. of fluoro-derivative.

(ii) Fraction distilling 136-138°C (26·2 g.), containing chlorobenzotrifluoride.

Fraction (i) distilled unchanged through the concentric tube column at 102·5°C, having n_D^{20} 1·4076. Hydrolysis of a sample by refluxing 6 hours at 130°c with 80% sulphuric acid led only to the formation of a mixture of carboxylic acids, m.p. 108°C (probably mixed benzoic and fluorobenzoic acids).

Fraction (ii) distilled unchanged through the concentric tube column at 138·5°C, having n_D^{20} 1·4464-1·4467. On analysis it gave Cl 19·5%, F 31·7% (Calc. for $C_7H_4Cl\,F_3$, Cl 19·66%, F 31·58%). On hydrolysis by the method described above a sample of it gave an acid m.p. 156°C, mixed melting point with m-chlorobenzoic acid m.p. 156°C. Fraction (ii) was therefore concluded to be m-chlorobenzotrifluoride.

Benzotrichloride Experiment.

As in the previous experiment, reaction tar and addition compounds (see Table VII) were removed by preliminary reduced pressure distillation. The addition compound boiled in the range 145-155°C/10 mm, had n_D^{20} 1·5352, and on analysis gave Cl 54·2%, F 13·0%. It is seen from analytical figures that this had an average composition of about three "additional" halogen atoms per molecule of benzotrichloride. (c.f. $C_7H_5Cl_4F$, Calc. Cl 56·8%, F 7·6%; $C_7H_5Cl_4F_3$, Calc. Cl 49·3%, F 14·2%; $C_7H_4Cl_4F_2$, Calc. Cl 53·0%, F 14·2%; $C_7H_5Cl_5F_2$, Calc. Cl 58·2%, F 12·5%). Further separation of the mixture of addition compounds did not prove possible.

After removal of solvent by methods previously described, fractionation of the product remaining was carried out through the helices-packed reduced pressure column described in connection with the chlorobenzene experiment (section(iv)). Under similar conditions to those described there, fractionation gave rise to :-

(i) Fraction (1·2 g.) b.p. 65°C/8 mm., n_D^{20} 1·5170. This had b.p. 178°C/760 mm., and gave on analysis Cl 39·6%, F 10·7% (Calc. for $C_7H_5Cl_3F$, Cl 39·66%, F 10·61%. Hydrolysis of a sample with sulphuric acid (dens. 1·85) by heating at 70° for ½ hour, led to formation of an acid m.p. 122°, mixed melting point with benzoic acid 122°C. The fraction was therefore concluded to be benzodichlorofluoride.

(ii) Fraction (53·0 g.) b.p. 91-96°C/10 mm., which was a mixture of benzotrichloride and fluoro-derivative. Analysis gave Cl 52·4% F 2·6%, whence the amount of fluoro-compound was assessed at 15·4 g. and unchanged benzotrichloride 37·6 g. This fraction distilled unchanged through the concentric tube column, b.p. 100·5°C/15 mm., n_D^{20} 1·5507. Hydrolysis of a sample by refluxing with an aqueous suspension of calcium carbonate as described by Schiemann and Baumgarten (Ber., 1937, <u>70</u>, 1419) gave rise to a mixture of carboxylic acids m.p. 102°C, probably containing benzoic and fluorobenzoic acids.

(iii) Fraction (17·0 g.), b.p. 120°C/10 mm, which was a mixture of chlorobenzotrichlorides. On distillation through the concentric tube column it was recovered unchanged, b.p. 125°C/15 mm, n_D^{20} 1·5717. Hydrolysis of a sample by the method described above gave a mixture of chlorobenzoic acids m.p. 146°C.

INDEX.

INDEX