

**712.** *Halogenation in the Liquid Phase by Means of Chlorine Trifluoride.*

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When benzene (1 mol.) in carbon tetrachloride solution, and in the presence of a variety of catalysts, is treated with chlorine trifluoride (0.5 mol.) the main reaction is one of substitution, and the products are chlorobenzene and fluorobenzene. Some halogenated addition compounds are also produced in smaller quantities, and, in certain cases, products suspected to be halogenated diphenyls are formed.

ALTHOUGH some of the interhalogen compounds have been used in organic chemistry for several years (Sharpe, *Quart. Reviews*, 1950, **4**, 127) very little attention has been paid to chlorine trifluoride. This has been due mainly to two factors : (a) the great reactivity of the reagent

(Ruff and Krug, *Z. anorg. Chem.*, 1930, **190**, 270; Booth and Pinkston, *Chem. Reviews*, 1947, **41**, 421), and (b) difficulties in the preparation of fluorine, which is needed for its synthesis. Now that the second of these factors has been overcome (Leech, *Quart. Reviews*, 1949, **3**, 22; Rudge, *J. Soc. Chem. Ind.*, 1949, **69**, 247) and chlorine trifluoride can be prepared on a large scale (Leech, *loc. cit.*; Porter, *Chem. Eng.*, 1948, **55**, No. 4, 102), it has become possible to make a more detailed study of its possibilities as a reagent in organic chemistry.

No detailed reports on the reaction between chlorine trifluoride and organic compounds have hitherto been made, although Burnett and Banks (*Chem. Soc. Symp. on Fluorine Chemistry*, Nov., 1949) and Porter (*loc. cit.*) have stated that such reactions can result in the introduction of both chlorine and fluorine into the organic compound, while Haszeldine (private communication to Sharpe, *loc. cit.*) states that, in the vapour phase, benzene and toluene react with chlorine trifluoride to give substitution and addition compounds.

We now record our observations on the controlled reaction between benzene and chlorine trifluoride in carbon tetrachloride solution and in the presence of several different catalysts. The catalysts, as can be seen from Table I, were chosen because they were either well-known halogen carriers or were salts of transitional metals which have been used 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.*, 1949, 3021, 3026). It can be seen (Tables I and II) that the main reaction in all cases, including the non-catalysed experiment, is one of substitution, the chief products being chlorobenzene and fluorobenzene. Some addition products which, by their reactions and analyses, appear to be chlorofluoro-*cyclohexanes*, -*cyclohexenes*, and -*cyclohexadienes* are also produced; but only in Expt. 7 are they formed in reasonably large quantity. Occasionally, it was possible to isolate from the higher-boiling fractions, before they decomposed, small quantities of what appeared to be chlorofluorodiphenyls because of their analytical composition and their stability to aqueous permanganate and bromine water.

TABLE I.

Expt.	Catalyst.	Wt. of ClF <sub>3</sub> used (g.) and rate of flow (g./hr.).	Tar, g.	C <sub>6</sub> H <sub>5</sub> F, g.	C <sub>6</sub> H <sub>5</sub> Cl, g.	Addition cpds., g.	Diphenyls, g.	Residue in flask, g.
1	None	55; 10	16.34	7.5	10.38	2.62	2.54	0.62
2	I <sub>2</sub>	55; 10	9.86	4.57	10.59	2.62	—	1.36
3	HgCl <sub>2</sub>	60; 10	20.6	8.3	15.6	2.67	—	0.28
4	CoCl <sub>2</sub>	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 <sub>2</sub>	60; 10	14.82	11.94	28.45	2.79	—	8.4
7	CoF <sub>2</sub>	45; 4	12.12	8.7 (11.6)	22.67 (30.27)	6.29 (8.39)	—	3.41
8	CoF <sub>2</sub>	45; 5	13	6 (8)	14.6 (19.5)	—	—	0.95

All experiments were carried out at 0° except Expt. 8 which was at 77°.

In all experiments except 7 and 8 the benzene (100 g.) was mixed with carbon tetrachloride (500 ml.).

In Expts. 7 and 8 only 75 g. of benzene were used and were mixed with 750 ml. of carbon tetrachloride. The figures in parentheses are the corresponding yields from 100 g. of benzene.

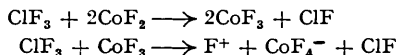
TABLE II.

Expt.	Frac-tion.	Yield, g.	B. p./8 mm.	Action on KMnO <sub>4</sub> & Br <sub>2</sub> , aq.	Possible formula.	Analysis.			
						Found, % Cl.	% F.	Calc., % Cl.	% F.
1	a	1.10	29—30°	decol.	C <sub>6</sub> H <sub>5</sub> Cl <sub>2</sub> F <sub>2</sub>	37.6	20.1	38.0	20.3
	b	0.32	69—70	nil	C <sub>6</sub> H <sub>5</sub> Cl <sub>2</sub> F <sub>4</sub>	31.6	33.5	31.6	33.8
	c	1.20	87—88	rapidly decol.	C <sub>6</sub> H <sub>5</sub> ClF	27.1	14.7	26.8	14.3
2	d	2.54	130—132	nil	C <sub>12</sub> H <sub>9</sub> ClF	19.6	7.8	17.2	9.2
	a	2.62	40—44	decol.	C <sub>6</sub> H <sub>5</sub> Cl <sub>2</sub> F <sub>2</sub>	38.0	19.9	38.0	20.3
3	a	1.40	31—32	decol.	C <sub>6</sub> H <sub>5</sub> Cl <sub>2</sub> F	42.8	11.5	42.5	11.4
	b	0.77	70—72	decol.	C <sub>6</sub> H <sub>5</sub> Cl <sub>3</sub> F <sub>2</sub>	46.0	16.4	48.1	17.2
4	c*	0.5	m. p. 242 (d)	nil	C <sub>6</sub> H <sub>3</sub> Cl <sub>3</sub>	81.0	—	81.0	—
	a	0.72	26—27	decol.	C <sub>6</sub> H <sub>5</sub> Cl <sub>2</sub> F <sub>3</sub> or C <sub>6</sub> H <sub>5</sub> Cl <sub>2</sub> F <sub>3</sub>	34.8	27.6	34.6	27.8
5	b	0.45	76	nil	C <sub>12</sub> H <sub>7</sub> ClF <sub>2</sub>	15.9	16.9	15.8	16.5
	a	1.42	72—75	decol.		34.4	27.6		
6	a	0.46	25—26	decol.		34.9	27.8		
	b	2.33	58—60	decol.		34.8	27.4		
7	a	2.01	56—58	decol.	as in Expt. 4a	34.2	27.6		as in Expt. 4a
	b	4.28	76—78	decol.		31.8	24.4		

\* Crystallised from reaction mixture after removal of carbon tetrachloride.

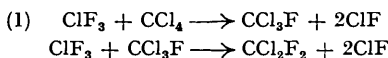
Of the catalysts used, cobaltous fluoride gave rise to the greatest total yield. Increase in the amount of catalyst and solvent coupled with decrease in the flow rate of the chlorine trifluoride (Expt. 7) appeared to have little effect on the production of substitution products but increased, by a factor of three, the formation of addition products. When this experiment was carried out at the boiling point of carbon tetrachloride, the yields were reduced. Silver fluoride and iodine had little or no catalytic effect, although the former has a pronounced effect in direct fluorination. Iodine may have formed the milder fluorinating agent, iodine pentafluoride, as an intermediate (Ruff and Krug, *loc. cit.*), but since it has been found that this reagent does not replace the hydrogen of organic compounds by fluorine (Sharpe, *loc. cit.*), it is not surprising that it did not act as a catalyst.

To account for the production of fluorobenzene by the usual ionic process, we can postulate that the initial process in the non-catalysed reaction is  $\text{ClF}_3 \longrightarrow \text{ClF} + \text{F}^+ + \text{F}^-$ , while, in the case of the catalysed reactions, and taking cobalt fluoride as an example, we can have (cf. Bigelow *et al.*, *Ind. Eng. Chem.*, 1947, **39**, 360)

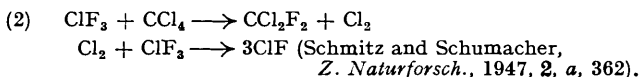


This theory assumes, as the experimental results indicate, that it is easier to produce the positive fluoride ion from chlorine trifluoride than from fluorine itself. The work of Bigelow *et al.* (*J. Amer. Chem. Soc.*, 1950, **72**, 2411; and earlier papers of this series) has shown that fluorine itself attacks the aromatic nucleus by an atomic chain mechanism and proceeds first, by addition, to the saturated hexafluoride and then by substitution of the hydrogen atoms in this compound. The inability of elementary fluorine to give rise to substitution products is due to the difficulty in removing an electron completely in order to produce the positive ion.

The formation of chlorobenzene in the present series of experiments is explained by the chlorinating action of the chlorine fluoride (Bigelow *et al.*, *ibid.*, 1940, **62**, 267; *Ind. Eng. Chem.*, 1947, **39**, 360), and since some of this is also formed in converting the catalyst into the higher valency state, we have a partial explanation of the formation of this product in higher molecular proportion than fluorobenzene. The rest of the chlorobenzene is probably produced as a secondary process owing initially to reaction between the chlorine trifluoride and the solvent, resulting in the formation of more chlorine fluoride:



or



Of these (1) is considered the more likely (see Emeléus *et al.*, *J.*, 1948, 2188, for the reaction between carbon tetrachloride and bromine fluoride) since if (2) occurred to any extent, there would be some interaction between the chlorine and the benzene, with evolution of hydrogen chloride. Since it was possible to detect this gas only in one case (Expt. 4) the mechanism (2) does not seem possible. In this one case it can be explained by reaction between the catalyst and the chlorine trifluoride to produce the necessary chlorine:  $\text{CoCl}_2 + \text{ClF}_3 \longrightarrow \text{CoF}_2 + \text{ClF} + \text{Cl}_2$  (Schmitz and Schumacher, *loc. cit.*; Sharpe and Emeléus, *J.*, 1948, 2186), but the same process cannot occur in Expt. 3, since in this case no hydrogen chloride was detected. The absence of hydrogen chloride in the effluent gases is taken as confirmation of the mechanism suggested above, since this would result, in all cases except when a metallic chloride is used as catalyst, in the evolution of hydrogen fluoride only. Further support comes from the fact that a slightly increased yield of chlorobenzene resulted in Expt. 7 when a greater volume of solvent was used. No attempt was made to obtain any evidence from the state of the catalyst at the end of each reaction, since it was so intimately mixed with tarry material as to make this impossible. It is noteworthy (Expts. 4, 6, and 7) that use of cobaltous chloride as catalyst increased the amount of fluorobenzene produced, while cobaltous fluoride increased considerably the relative amount of chlorobenzene. The extent to which attack by chlorine trifluoride occurs on the solvent is difficult to estimate, since it depends on the relative rates of reaction of the benzene and the carbon tetrachloride with the reagent, and their concentrations. It may not be great, since, as has already been stated, doubling the volume of solvent per g. of benzene (Expt. 7) results in only a slight increase in the yield of chlorobenzene. The loss of carbon tetrachloride in any experiment varies between 50 and 100 ml., but this can be accounted

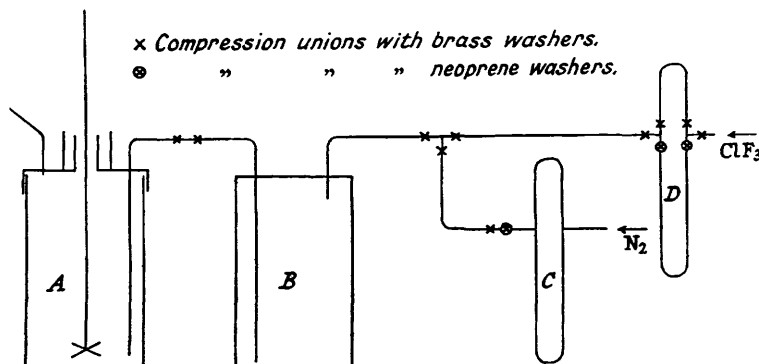
for to some extent by normal losses in working up the products. Blank experiments showed that losses due to bubbling nitrogen through the carbon tetrachloride at 0° for the period of the experiments were only about 2%, while at 77°, with the modified apparatus, they were slightly higher (0.5%/hour).

Fluorobenzene itself could not be isolated from the reaction mixture since it appears to form an azeotrope with carbon tetrachloride and benzene, containing about 10% by weight of fluorobenzene. The amount produced was therefore determined by fluorine analysis, and confirmed by conversion into 4:4'-difluorodiphenyl sulphone (Huntress and Carten, *J. Amer. Chem. Soc.*, 1940, **62**, 512) and *p*-chlorofluorobenzene (Varma *et al.*, *J. Indian Chem. Soc.*, 1944, **21**, 112). Model experiments showed that, with a solution of fluorobenzene in carbon tetrachloride containing a little benzene, the best yields of these two compounds obtainable were 25% and 51.5%, respectively. The presence of benzene complicated slightly the isolation of the sulphone. Experiments carried out on the azeotrope gave results which agreed with those obtained by analysis.

The addition compounds and diphenyl derivatives (Table II) were not produced in sufficient quantity for characterisation. Variation in the boiling points of substances which give the same analytical figures may be due to the fact that they are isomers. In any case, the formulæ are suggested only to give some idea of the possibilities, of which there are, in most cases, several. Attempts will be made to synthesise them by other methods.

#### EXPERIMENTAL.

The reaction vessel *A* (see figure) was of mild steel and had a screw-on lid carrying inlet and outlet tubes, and having provision for a mercury seal. It was connected by copper tubing to a safety trap *B*



and thence, through flow-meters *C* and *D* to nitrogen and chlorine trifluoride cylinders. The flow-meter *C* and the lower part of *D* were made from hard glass. The upper part of *D* consisted of a copper tube joining two pieces of copper rod, through each of which was drilled a very fine hole. The liquid in the manometers was carbon tetrachloride. Joints were made with compression unions, neoprene being used instead of brass rings for the metal-to-glass joints. In experiments carried out at 77°, the stirrer was fitted with a mercury seal (no halogens escape from the reaction mixture), and two condensers, one water and the other ice and water, were connected, by means of brass unions, to the outlet tube.

In all experiments, except Nos. 1, 7, and 8, benzene (100 g.) was dissolved in carbon tetrachloride (500 ml.), to which had been added 10 g. of anhydrous catalyst, and the reaction mixture was kept at 0° and treated with chlorine trifluoride (approx. 60 g.) at the rate of 10 g./hour. The chlorine trifluoride was diluted with nitrogen at the rate of 12 l./hour. In Expt. 1 no catalyst was used, but in Expt. 7, benzene (75 g.) in carbon tetrachloride (750 ml.) and in the presence of 100 g. of catalyst was treated with chlorine trifluoride (45 g.) at the rate of 4 g./hour. Again the reaction mixture was cooled to 0° by ice and water, and the chlorine trifluoride was diluted with nitrogen at 12 l. hour. Conditions in Expt. 8 were the same as in Expt. 7, except that the flow rate of the chlorine trifluoride was slightly greater (5 g./hour) and the experiment was carried out at 77°.

Thus in all cases, one molecule of benzene was treated with approximately 0.5 molecule of chlorine trifluoride. During the process, qualitative tests for halogens (starch-iodide), hydrogen chloride (silver nitrate solution on glass rod), and hydrogen fluoride (etching test) in the exit gases were made at regular intervals. Copious amounts of hydrogen fluoride were found to be present, but free halogens were never detected. Only in Expt. 4 was there ever a positive test for hydrogen chloride. When the correct weight of chlorine trifluoride had been added, and then nitrogen alone had been allowed to flow for about 15 minutes, the reaction mixture was poured into a saturated solution of sodium hydrogen carbonate. It was then filtered, shaken with sodium hydrogen carbonate, and then with water until neutral. After being dried ( $\text{MgSO}_4$ ), the carbon tetrachloride was distilled through a column of

approximately 30 theoretical plates, and a take-off ratio of about 1 : 30. The column was packed with nickel turnings. The purity of the distillate was checked by refractive-index measurements, and when these showed that the distillate was no longer pure carbon tetrachloride, the residue in the flask was transferred to a simple distillation apparatus and distilled rapidly, first at atmospheric pressure, and then under reduced pressure, in order to remove tars (see col. 5, Table I). The fractions obtained (100—150 ml.) were recombined and distilled through another 30-plate column packed with Fenske helices and having a much smaller volume than the first in order to keep distillation hold-up losses to a minimum. By this means the mixture of carbon tetrachloride, fluorobenzene, and benzene was collected over the range 77.2—77.7°. Attempts to isolate the fluorobenzene by distillation, freezing, or removal of carbon tetrachloride *via* the solid  $\text{CCl}_4 \cdot 2\text{H}_2\text{S} \cdot 23\text{H}_2\text{O}$  [De Forcrand, *J.*, 1883, **44** (Abs.), 961] have so far failed. The residue in the still-pot was fractionated under reduced pressure and gave chlorobenzene (b. p. 22—24°/8 mm., 132.5°/752 mm.,  $n_D^{20}$  1.5246) (Found: Cl, 31.3. Calc.: Cl, 31.4%), halogenated addition compounds, and halogenated diphenyls. Details of these are given in the tables.

*Preparation of 4 : 4'-Difluorodiphenyl Sulphone.*—The azeotrope (5 ml., containing 0.75 g. of fluorobenzene by analysis) was treated with redistilled chlorosulphonic acid (3 ml.) and heated under reflux at 40° for one hour. It was then poured on crushed ice, carbon tetrachloride (5 ml.) was added, and the organic layer was separated. It was washed twice with water and dried ( $\text{MgSO}_4$ ), and the carbon tetrachloride distilled off under reduced pressure. The oily residue was dissolved in absolute alcohol to which a drop of phenolphthalein had been added, and benzenesulphonyl chloride was destroyed by treating this solution at 50° with dilute alcoholic sodium hydroxide until it was faintly alkaline. After being made exactly neutral, the filtrate was evaporated to dryness under reduced pressure. The product was washed with water to remove sodium salts, and then recrystallised from aqueous alcohol; yield 150 mg., m. p. 98° (Found: F, 14.8. Calc. for  $\text{C}_{12}\text{H}_8\text{O}_2\text{SF}_2$ : F, 15%).

*Preparation of p-Chlorofluorobenzene.*—To the azeotrope (26 ml., containing 4 g. of fluorobenzene by analysis), in a flask fitted with a reflux condenser, were added iron filings (0.4 g.), and chlorine was passed in with occasional shaking until the gain in weight was 1.75 g. This allowed for the conversion of the small amount of benzene present into dichlorobenzene. The product was filtered, washed with 2N-sodium hydroxide and then with water until neutral, and dried ( $\text{CaCl}_2$ ). On distillation through a short column the fraction, b. p. 129.5—130.5°, was collected; yield 2.52 g. (Found: Cl, 27.4; F, 14.5. Calc. for  $\text{C}_6\text{H}_4\text{ClF}$ : Cl, 27.2; F, 14.6%).

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