216. *Halogenation in the Liquid Phase by Chlorine Trifluoride. The Reaction with Benzene Derivatives and with Carbon Tetrachloride.*

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When chlorine trifluoride reacts with substituted benzene and benzene homologues both substitution and addition of chlorine and fluorine occur, substitution predominating as with benzene (Ellis and Musgrave, *J.*, 1950, 3608). In all cases chlorine substitution is in excess of fluorine substitution but this excess can not be explained by reaction between the chlorine trifluoride and the solvent (carbon tetrachloride) giving the chlorinating agent chlorine monofluoride.

In an earlier paper (*J.*, 1950, 3608) we discussed the reaction between chlorine trifluoride and benzene in carbon tetrachloride and in the presence of several catalysts. Extension of this work to benzene homologues and derivatives under the same conditions and with cobalt fluoride as catalyst has shown that the percentage substitution in benzene homologues is about the same as for benzene but that, with increase in size of the side chain, the percentage of fluoro-derivative decreases and the amount of unchanged test compound increases. In all cases, about twice as much addition compound was obtained as from benzene. Results for halogenated derivatives of benzene and its homologues showed no correlation. Fluorobenzene alone reacted completely but it gave no trace of difluorobenzene even when precautions were taken to avoid possible causes of decomposition. *p*-Difluorobenzene (Schiemann and Pillarsky, *Ber.*, 1929, **62**, 3041; Dunker and Starkey, *J. Amer. Chem. Soc.*, 1939, **61**, 3005) was quite stable to the other reagents present, but in the presence of chlorine trifluoride and cobaltous fluoride it decomposed almost completely. Thus it probably decomposes as it is formed. This would also account for the somewhat lower yield of other products.

All of the addition compounds except those from benzotrichloride and benzotrifluoride were less stable than those from benzene, and decomposed readily on distillation. Analysis after a single distillation generally showed the addition of one chlorine and one fluorine atom per molecule.

The substitution compounds were all examined in a 38-plate concentric-tube fractionating column (Naragon and Lewis, *Analyt. Chem.*, 1946, **18**, 449) but it was not possible to separate any of the fluoro-derivatives except that from chlorobenzene, since they were generally obtained in small amounts, had boiling points near to those of the test compounds, and distilled with the unchanged test compound or as intermediate fractions. Some chlorofluorobenzene was isolated from chlorobenzene, which, from its refractive index can only have been the *para*-isomer. The greater amounts of chloro-derivatives enabled pure samples of some isomers to be separated and examination of graphs of refractive index of distillate against volume distilled often showed that other isomers could not be present. Wherever possible, confirmation of structure was obtained by conversion of the pure samples into the corresponding benzoic acids, either by oxidation or hydrolysis. In general the results are similar to those of chlorination (Reese, *Chem. Reviews*, 1934, **14**, 55; Wertyporoch, *Annalen*, 1932, **493**, 153; Varma *et al.*, *J. Indian Chem. Soc.*, 1944, **21**, 112).

All of the compounds examined except benzotrichloride gave, as did benzene, a considerably greater proportion of chloro- than fluoro-substitution product. We suggested (*loc. cit.*) that this was probably due to reaction between chlorine trifluoride and the solvent giving the chlorinating agent chlorine monofluoride, although Ruff and Krug (*Z. anorg. Chem.*, 1930, **190**, 270) claim that reaction between the two, even in the liquid state, occurs only on warming. Results have shown (Table, Expts. 1—6) that some reaction occurs even at 0° and increases considerably with rise in temperature but that, when benzene is present (Expts. 7 and 8), the chlorine trifluoride reacts preferentially with it and not at all with the solvent and, even if this were not so, the heat of reaction does not raise the temperature sufficiently for the production of enough chlorine monofluoride. Since in experiments 1—3 the volume of reaction mixture plus products agreed very closely with the initial volume of carbon tetrachloride, there can have been no errors due to incomplete condensation.

Expt.	ClF_3, g.; flow rate, g./hr.	Temp., °c.	CCl_2F_2, ml.	Intermediate fraction, ml.	CCl_3F, ml.	CCl_4 carried over, ml.
1	40; 6	25	0·5	1·0	12·5	16·0
2	42; 5	25	2·1	1·6	16·9	16·5
3	41; 6	0	—	0·5	2·8	6·5
4	43; 6	20	4·2	1·0	13·3	16·0
5	40; 6	25	3·1	—	20·5	22·0
6	42; 6	0	—	0·7	3·9	6·0
7	30; 6	6	—	—	—	6·0
8	65; 10	9	—	—	—	5·9

In all cases the chlorine trifluoride was diluted with nitrogen (5 l./hr.).

In expts. 1—3 there was no catalyst; cobalt fluoride (10 g.) was used in expts. 4—6. In expts. 7 and 8 the carbon tetrachloride contained cobalt fluoride + benzene (100 g.).

EXPERIMENTAL

Halogenation of Benzene Derivatives.—The apparatus and technique were as previously described (Ellis and Musgrave, *loc. cit.*), the test compound (100 g.) in carbon tetrachloride (500 ml.) being stirred with cobalt fluoride (10 g.) and treated at 0° with chlorine trifluoride (0·5 mol.), diluted with nitrogen (12 l./hr.). As before, no free halogen or hydrogen chloride could be detected in the exit gases. The method of working up differed only in that improved filtration and washing of the residues with carbon tetrachloride cut down the overall loss of solvent to 30—40 ml. (previously 50—100 ml.). Each reaction mixture was distilled rapidly under reduced pressure, solid carbon dioxide–ethanol traps being used, to separate solvent and substitution products (*A*) from addition products and tar (*B*) with the minimum decomposition of the latter. The product *A* was then fractionated through a 22-plate column and each fraction refractionated through a 38-plate concentric-tube column [length of concentric tube portion, 32 cm.; outside diameter of inner tube, 6·8 mm.; inside diameter of outer tube, 8·0 mm.; a boil-up rate of 75 drops/min. and a take-off rate of 1 ml./hr. being used]. The efficiency of the column was determined by distilling *n*-heptane–methyl*cyclo*hexane (Lecky and Ewell, *Analyt. Chem.*, 1940, **12**, 547; Bromiley and Quiggle, *Ind. Eng. Chem.*, 1933, **25**, 1136). By using it, pure samples of *o*- and *p*-chlorotoluenes were obtained from 16 ml. of a mixture of equal parts of the two at reduced (14 mm.) as well as atmospheric pressure. It was not as efficient under reduced pressure as at atmospheric pressure but no estimate of the efficiency under reduced pressure was made.

Toluene. Distillation of the washed and dried reaction mixture gave (*A*), b. p. <100°/10 mm., fractionation of which gave: (*a*) Carbon tetrachloride. (*b*) A mixture (27·2 g.) of toluene and fluorotoluene, b. p. 110—117° (19·0 g. of toluene and 8·2 g. of fluorotoluene, by fluorine analysis), separated into toluene (11 ml.), n_D^{20} 1·4966—1·4955, intermediate fraction (14 ml.), n_D^{20} 1·4948—1·4755, and fluorotoluenes (3·5 ml.), n_D^{20} 1·4743—1·4715 (Found, in specimen from last ml.; F, 17·1. Calc. for C_7H_7F: F, 17·3%) [oxidation with permanganate gave a mixture of fluorobenzoic acids (40%), m. p. 158°]. (*c*) Benzyl fluoride (1·8 g.), b. p. 38—39°/12 mm., which after redistillation (1 g.) had b. p. 139°, n_D^{20} 1·4916 (Found: F, 17·1%) [oxidation with permanganate gave benzoic acid (75%), m. p. and mixed m. p. 122°]. (*d*) Chlorotoluenes (22·1 g.), b. p. 52—57°/12 mm., separated into (i) *o*-chlorotoluene (4 ml.), b. p. 159°, n_D^{20} 1·5261 (Found: Cl, 27·9. Calc. for C_7H_7Cl: Cl, 28·1%) [oxidation gave *o*-chlorobenzoic acid (68%), m. p. and mixed m. p. 141°]; (ii) intermediate fraction (11 ml.), n_D^{20} 1·5258—1·5213; and (iii) *p*-chlorotoluene (4·5 ml.), b. p. 162°, n_D^{20} 1·5211 (Found: Cl, 28·0%) [oxidation gave *p*-chlorobenzoic acid (75%), m. p. and mixed m. p. 241°]. *m*-Chlorotoluene must be absent since it would distil with the *para*-isomer and affect its physical constants. (*e*) Residue (addition compounds) (3·7 g.).

The residue (*B*; 33 g.) left after removal of (*A*) gave: (i) a viscous oil (20·1 g.), b. p. 100—160°/10 mm., which decolorised aqueous permanganate and bromine water and decomposed when kept (Found: Cl, 23·5; F, 12·8. Calc. for C_7H_8ClF: Cl, 24·2; F, 13·0%), and (ii) a tarry residue (12·9 g.).

Ethylbenzene. Fractionation of (*A*), b. p. <85°/10 mm. gave: (*a*) carbon tetrachloride. (*b*) Ethylbenzene (19 ml.), b. p. 136°, n_D^{20} 1·4957—1·4945. (*c*) A mixture (14 ml.) of ethylbenzene and ethylfluorobenzenes (3·7 g. by analysis), b. p. 137—140°, n_D^{20} 1·4943—1·4792. (*d*) *o*-Chloroethylbenzene (4 ml.), b. p. 179·5°, n_D^{20} 1·5214 (Found: Cl, 25·2. Calc. for C_8H_9Cl: 25·3%) [oxidation gave *o*-chlorobenzoic acid (55%), m. p. and mixed m. p. 141°]. (*e*) *o*- and *p*- (and possibly some *m*-)chloroethylbenzenes (6 ml.), n_D^{20} 1·5211—1·5180. (*f*) *p*-Chloroethylbenzene (6 ml.), b. p. 184·5, n_D^{20} 1·5175 (Found: Cl, 25·2%) [oxidation gave *p*-chlorobenzoic acid (65%), m. p. and mixed m. p. 241°].

The residue (*B*; 28 g.) after distillation of (*A*) gave: (i) unstable addition compounds (12·7 g.), b. p. 85—125°/10 mm., which decolorised aqueous permanganate and bromine water (Found: Cl, 24·0; F, 11·2. Calc. for $C_8H_{10}ClF$: Cl, 22·1; F, 11·8%), and (ii) tar (14·8 g.).

Cumene. Fractionation of (*A*), b. p. <88°/8 mm. gave: (*a*) Carbon tetrachloride. (*b*) Cumene (35 ml.), b. p. 152°, n_D^{20} 1·4910—1·4895. (*c*) A mixture (12 ml.) of cumene and fluorocumenes, b. p. 153—156°, n_D^{20} 1·4893—1·4828 [containing fluorocumenes (2·8 g.)]. (*d*) *p*-Chlorocumene (18·5 ml.), b. p. 82°/15 mm., n_D^{20} 1·5120 (Found: Cl, 23·1. Calc. for $C_9H_{11}Cl$: Cl, 23·0%) [oxidation (difficult) gave *p*-chlorobenzoic acid (25%), m. p. and mixed m. p. 241°].

The residue (*B*; 22·1 g.) gave: (i) unstable addition compounds (10·6 g.), b. p. 88—110°/8 mm., which decolorised aqueous permanganate and bromine water (Found: Cl, 22·6; F, 10·1. Calc. for $C_9H_{12}ClF$: Cl, 20·3; F, 10·9%), and (ii) tar (11·5 g.).

Chlorobenzene. Fraction (*A*), b. p. <88°/8 mm. gave: (*a*) Carbon tetrachloride. (*b*) *p*-Chlorofluorobenzene (1·5 ml.), b. p. 129·8/754 mm., n_D^{20} 1·4967—1·4973 (Found: Cl, 27·4; F, 14·4. Calc. for C_6H_4ClF: Cl, 27·2; F, 14·55%). (*c*) A mixture (14 ml.) of chlorobenzene and *p*-chlorofluorobenzene, n_D^{20} 1·4973—1·5237. (*d*) Chlorobenzene (1 ml.), b. p. 132°, n_D^{20} 1·5243 (Found: Cl, 31·4. Calc. for C_6H_5Cl: Cl, 31·55%).

Separation of fractions (*b*), (*c*), and (*d*) required three distillations through the concentric-tube column, *o*-dichlorobenzene (4 ml.) being used as chaser for the chlorobenzene. The boiling point and refractive index indicated that *o*- and *m*-chlorofluorobenzene could only be present in minute amounts, if at all. The bulked fractions before distillation contained 17·8 g. of chlorofluorobenzene and 14·9 g. of chlorobenzene (Found: Cl, 29·2; F, 7·95%), and were quite stable to aqueous permanganate and bromine water.

(*e*) *p*-Dichlorobenzene (38·7 g.), b. p. 62°/10 mm., m. p. and mixed m. p. 53° (Found: Cl, 48·3. Calc. for $C_6H_4Cl_2$: Cl, 48·3%). (*f*) *o*-Dichlorobenzene (2·1 g.), b. p. 69°/10 mm., 180°/755 mm., n_D^{20} 1·5511, f. p. −15·5°, mixed f. p. −16° (Found: Cl, 48·2%).

The residue (*B*; 11·6 g.) gave: (i) addition compounds (2·5 g.), b. p. 88—92°/8 mm., n_D^{20} 1·5172, which decolorised aqueous permanganate and bromine water (Found: Cl, 46·3; F, 13·2. Calc. for $C_6H_5Cl_2F$: Cl, 42·6; F, 11·4%), and (ii) tar (9·1 g.).

Fluorobenzene. Fractionation of (*A*), b. p. <63°/10 mm., gave: (*a*) Carbon tetrachloride (no fluorine could be detected in any of several samples analysed). (*b*) *p*-Chlorofluorobenzene (27 g.), b. p. 130°, n_D^{20} 1·4965 (Found: Cl, 27·0; F, 14·7. Calc. for C_6H_4ClF: Cl, 27·2; F, 14·55%). (*c*) Residue (2·6 g.).

The residue (*B*; 19·7 g.) gave : (i) addition products (2·4 g.), b. p. 63—67°/19 mm., n_{D}^{20} 1·4652 (Found : Cl, 27·1; F, 23·0%), which decolorised aqueous permanganate and bromine water; (ii) addition products (9·7 g.), b. p. 90—135°/10 mm., n_{D}^{20} 1·5153 (Found : Cl, 21·2; F, 26·4. Calc. for $C_6H_5ClF_2$: Cl, 17·7; F, 38·0%); and (iii) tar (7·6 g.).

A similar experiment, on half-scale, in which the mixture was neutralised with potassium fluoride (solid) and was never allowed to come into contact with aqueous reagents gave : (*a*) Carbon tetrachloride (approx. 200 ml.), containing less than 1% of fluorine; (*b*) *p*-chlorofluorobenzene (11·2 g.), b. p. 130° ; (*c*) residue (2·8 g.) ; (*d*) addition compounds (4·8 g.), b. p. 60—140°/8 mm.; and (*e*) tar (4·5 g.).

Benzotrifluoride. (*A*), b. p. <63°/14 mm., gave : (*a*) Carbon tetrachloride. (*b*) A mixture (21·4 g.) of benzotrifluoride and *αααx*-tetrafluorotoluene (13·2 g. and 8·2 g., respectively, by fluorine analysis), b. p. 102·5°, n_{D}^{20} 1·4076, which distilled unchanged through the concentric-tube column. (*c*) *m*-Chlorobenzotrifluoride (26·2 g.), b. p. 138·5°, n_{D}^{20} 1·4467 (Found : Cl, 19·5; F, 31·7. Calc. for $C_7H_4ClF_3$: Cl, 19·7; F, 31·6%) [hydrolysis with 80% sulphuric acid gave *m*-chlorobenzoic acid (51%), m. p. and mixed m. p. 156°].

The residue (*B*; 19·9 g.) gave : (i) addition products (10·6 g.), b. p. 63—88°/14 mm., n_{D}^{20} 1·4352 (Found : Cl, 18·1; F, 37·6. Calc. for $C_7H_5ClF_4$: Cl, 17·7; F, 37·95%), which decolorised aqueous permanganate and bromine water; and (ii) tar (9·3 g.).

Benzotrichloride. (*A*), b. p. <145°/10 mm., gave : (*a*) Carbon tetrachloride. (*b*) αα-Dichloro-α-fluorotoluene (1·2 g.), b. p. 65°/8 mm., 178°, n_{D}^{20} 1·5170 (Found : Cl, 39·6; F, 10·7. Calc. for $C_7H_5Cl_2F$: Cl, 39·7; F, 10·6%) [hydrolysis with concentrated sulphuric acid at 70° for 30 minutes gave benzoic acid (69%), m. p. and mixed m. p. 122°]. (*c*) A mixture (53 g.) of benzotrichloride and fluorobenzotrichloride, b. p. 100·5/15 mm., n_{D}^{20} 1·5507, which did not separate during distillation. Analysis (Found : Cl, 52·4; F, 2·6%) showed the mixture to contain fluorobenzotrichloride (15·4 g.) and benzotrichloride (37·6 g.). (*d*) Chlorobenzotrichlorides (17 g.), b. p. 125°/15 mm., n_{D}^{20} 1·5717, which did not separate during distillation (Found : Cl, 61·6. Calc. for $C_7H_4Cl_4$: Cl, 61·7%) [Hydrolysis with water and calcium carbonate (Schiemann and Baumgarten, *Ber.*, 1937, **70**, 1419) gave a mixture of chlorobenzoic acids (60%), m. p. 146° (Found : Cl, 22·6. Calc. for $C_7H_5O_2Cl$: Cl, 22·7%)].

The residue (*B*; 14·6 g.) gave : (i) addition products (11·2 g.), b. p. 145—155°/10 mm., n_{D}^{20} 1·5352 (Found : Cl, 54·2; F, 13·0. Calc. for $C_7H_5Cl_4F$: Cl, 56·8; F, 7·6); and (ii) tar 3·4 g.).

The Stability of p-*Difluorobenzene.*—*p*-Difluorobenzene (2·3 g.), b. p. 89°, n_{D}^{20} 1·4420 (Schiemann and Pillarsky, *Ber.*, 1929, **62**, 3041; Dunker and Starkey, *J. Amer. Chem. Soc.*, 1939, **61**, 3005), was dissolved in carbon tetrachloride (80 g.) and shaken for several hours with (*a*) saturated aqueous sodium hydrogen carbonate (25 ml.) or (*b*) 0·1N-sodium hydroxide (25 ml.); no fluoride ion appeared in the aqueous layer. The organic layer, after being washed with water until neutral and dried ($MgSO_4$), distilled constantly at 77·4°, and analysis in each case (Found : Cl, 89·5%) confirmed that no reaction had occurred.

Similarly, when the azeotrope (5 ml.) was saturated with either anhydrous hydrogen chloride or anhydrous hydrogen fluoride and shaken at 20° for 1 hour, analysis (Found : Cl, 89·4%, in each case) showed that no reaction had occurred.

Reaction with Chlorine Trifluoride.—Chlorine trifluoride (6 g., 0·5 mol.), diluted with nitrogen (12 l./hr.), was passed during 1¼ hours into an ice–water-cooled solution of *p*-difluorobenzene (14 g.) in carbon tetrachloride (150 ml.), containing cobalt fluoride (2 g.). Hydrogen fluoride was evolved but no hydrogen chloride or chlorine. The mixture was washed with saturated aqueous sodium hydrogen carbonate and then with water until neutral, and then dried ($MgSO_4$). Fractionation gave : (i) carbon tetrachloride (fluorine test negative) and (ii) a residue (0·42 g.), which decolorised aqueous permanganate (Found : Cl, 26·35; F, 11·35%). Thus almost complete decomposition of the difluorobenzene had occurred.

Reaction between Chlorine Trifluoride and Carbon Tetrachloride.—In the uncatalysed experiments (Table, 1—3) dry carbon tetrachloride (500 ml.) was treated with chlorine trifluoride, the products were passed through alkaline sodium sulphite solution [$Na_2SO_3,7H_2O$ (252 g.), NaOH (80 g.), in 1 l. water] to remove halogens (Emeléus *et al.*, *J.*, 1948, 2188), and then through two glass traps, one cooled in carbon dioxide–ethanol and the other in liquid oxygen. The contents of these traps were distilled into a low-temperature fractionating column (Ramler and Simons, *Ind. Eng. Chem. Anal.*, 1930, **10**, 648), which was capable of separating methyl chloride and methyl bromide.

In the catalysed experiments a stirrer was introduced through a carbon tetrachloride seal and, to restrict flow resistance, the volume of alkaline sulphite solution was reduced but it was renewed four times in each experiment. The use of benzene in experiments 7 and 8 made it possible to use a stirrer with a mercury seal and, in order to make the reaction conditions identical with those of experiments 1—6, the exit gases were also bubbled through alkaline sulphite solution. In all cases the products were distilled from the low-temperature still and three fractions were collected : (i) Dichlorodifluoromethane, b. p. −28° to −26°, which was redried ($MgSO_4$) and redistilled (Found : Cl, 58·9; F, 31·2. Calc. for CCl_2F_2 : Cl, 58·7; F, 31·4%) ; (ii) intermediate fraction, b. p. −26° to 23° ; and (iii) trichlorofluoromethane, b. p. 23—25°. This also was redried ($MgSO_4$) and redistilled (Found : Cl, 77·7; F, 13·6. Calc. for CCl_3F : Cl, 77·45; F, 13·8%).

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