343. *The Preparation and Examination of Organic Fluorine Compounds. Part XXIV.* The Halogenation of Fluorobenzene.*

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The directing effect of fluorine in fluorobenzene has been examined for (i) iron-catalysed chlorination and bromination, (ii) chlorination by iodine chloride and bromination by iodine bromide, and (iii) high-temperature radical halogenation. The isomer ratios in the radical high-temperature substitutions are not wholly accounted for by statistical distribution, influenced by the steric *ortho*-effect.

Previous authors have examined the halogenation of fluorobenzene by electrophilic reagents [1] and also its vapour-phase bromination. In the latter case the investigation was only qualitative and the isomer ratio could not be determined: Holleman thermogravimetric analysis was impossible because of the similarity of the physical constants of the products, and it was proved only that the amount of *meta*-isomer was substantially increased and that of the *para*-isomer decreased, whence complete analogy with the halogenation of chloro- and bromo-benzene was assumed.[3] Our investigations have concerned both the above types of halogenation of fluorobenzene.

Chlorination in presence of an iron catalyst gave 84% of *p*- and 16% of *o*-chlorofluorobenzene, the ratio being determined by means of ultraviolet-absorption vapour spectra.

In chlorination of fluorobenzene by electrophilic reagents, as in its nitration,[4] the *para*-orienting effect predominates. The following explanation can be offered: The negative

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* Part XXIII, *J. Org. Chem.*, in the press.

[1] Schiemann and Pillarsky, *Ber.*, 1931, **64**, 1340; Varma, Venkataraman, and Nilkintiah, *J. Indian Chem. Soc.*, 1944, **21**, 112; Ferguson, Garner, and Mack, *J. Amer. Chem. Soc.*, 1954, **76**, 1251.

inductive ($-I$) and the positive conjugative ($+K$) effect counteract each other, though the former is quantitatively the more powerful.[5] At the *ortho*-positions the two opposing effects are approximately equal; but in propagation through the ring the inductive effect weakens whilst the conjugative effect remains almost unchanged so that at the *para*-position the latter predominates and substitution occurs there.

Thus the fluorine substituent causes electronic deactivation at the *ortho*-positions. But this effect must not be confused with the steric *ortho*-effect which is lowest for fluorine, with its smallest van der Waals radius, of all the halogens. The steric effect, though smallest with fluorine, does however operate, as expected on theoretical grounds, for the amount of *ortho*-isomer formed decreases as the space-demand of an electrophilic substituent increases; for instance, we have found the following amounts of *ortho*-substitution of fluorobenzene: chlorination, 16%; nitration, 8%;[6] bromination, 1·8%; chlorosulphonation, *ca.* 1%.[7]

The electronic deactivating *ortho*-effect is clearly observed when second and third chlorine atoms are introduced on chlorination of fluorobenzene, for very little substitution occurs at the positions *ortho* to fluorine.[8]

Iron-catalysed bromination of fluorobenzene proceeds essentially similarly: monobromination gave 98·2% of *para*- and 1·8% of *ortho*-isomer, in line with the greater space-demand of the bromine cation. In a similar reaction, catalysed by aluminium bromide at 54—57° Ferguson, Garner, and Mack [1] found *ortho* 10·5%, *meta* 0·2%, and *para* 89·3%.

Hitherto iodine chloride has been known in preparative organic chemistry principally as an iodinating agent,[9] being generally used in glacial acetic acid. Lambourne and Robertson,[10] however, found that in a polar solvent one-fifth of the reaction was chlorination. We find that in a non-polar solvent, *e.g.*, carbon tetrachloride, or in absence of a solvent chlorination is the principal reaction, just as bromination is known to be with iodine bromide.[11] From fluorobenzene under these conditions there are formed 80% of chlorofluorobenzenes and less than 20% of fluoroiodobenzenes: at room temperature there is practically no iodination, and at 60° not more than 20%. Reaction in a polar solvent such as methanol or acetic acid gives mainly *p*-fluoroiodobenzene and no chlorofluorobenzene can be isolated.

Similarly, iodine bromide in carbon tetrachloride gives mainly bromofluorobenzenes and there is less than 5% of iodination.

The mechanism of action of these interhalogen compounds was studied by investigating the isomer ratios. Spectroscopic analysis of the chlorofluorobenzenes formed by iodine chloride in carbon tetrachloride gave the ratios: *ortho*, 6·1%; *meta*, 2·7%; *para*, 91·2%. The fluoroiodobenzene formed in methanol was the almost pure *para*-compound. Bromination with iodine bromide gave the ratios: *ortho*, 2·1%; *meta*, 1·8%; *para*, 96·1%. Comparison of these ratios with those obtained in the purely electrophilic iron-catalysed halogenations shows that here too substitution is purely electrophilic: nucleophilic substitution would have given mainly the *meta*-isomer.

Since iodine separates on chlorination with iodine chlorine whilst the issuing gases contain hydrogen chloride and no detectable amounts of hydrogen iodide, we propose the following reaction sequences:

$$\begin{aligned}
&(a)\ 2\mathrm{ICl} \rightleftharpoons \mathrm{I_2} + \mathrm{Cl_2}\\
&(b)\ \mathrm{ICl} + \mathrm{Cl_2} \rightleftharpoons \mathrm{Cl^+} + \mathrm{ICl_2^-}\\
&(c)\ \mathrm{ICl} \rightleftharpoons \mathrm{I^+} + \mathrm{Cl^-}\\
&(d)\ \mathrm{I^+} + \mathrm{Cl_2} \rightleftharpoons \mathrm{ICl} + \mathrm{Cl^+}
\end{aligned}$$

The I^+ formed in reaction (*c*) accounts for the small amount of iodination, but most of this ion is used in the faster reaction (*d*) which, leading to Cl^+, accounts for the predominant chlorination. The separation of iodine is mainly due to a secondary reaction:

$$\mathrm{F{\cdot}C_6H_4{\cdot}H} + \mathrm{ICl} \longrightarrow p\text{-}\mathrm{F{\cdot}C_6H_4{\cdot}Cl} + \mathrm{HI}$$
$$\mathrm{HI} + \mathrm{ICl} \longrightarrow \mathrm{I_2} + \mathrm{HCl}$$

A similar mechanism can be postulated for iodine bromide.

For free-radical halogenation of fluorobenzene we have used the high-temperature technique of Wibaut and his school.[2,3b] It is known that under these conditions, in the presence of first-order substituents, the proportion of *meta*-isomer is considerably greater. For instance, on bromination of bromobenzene Wibaut[2] found the *m*-dibromobenzene content of the product to be 25% at 380° rising to 60% at 630° while the *para*-content fell from 52% to 21%, the *ortho*-content remaining about constant (19—26%); he found similar results with chlorobenzene; and he assumed similar isomer distribution with fluorobenzene although in this case all he could determine was a decreased *para*-content at higher temperatures.

We have chlorinated and brominated fluorobenzene in the vapour phase in a smooth silica tube at 260—680° without a catalyst or carrier, with results shown in Table 1.

TABLE 1. *Halogenation of fluorobenzene in the vapour phase.*

C_6H_4BrF				C_6H_4ClF			
Temp.	*o*- (%)	*m*- (%)	*p*- (%)	Temp	*o*- (%)	*m*- (%)	*p*- (%)
260°	1·8	6·4	91·8	260°	1·7	32·0	66·3
345	1·9	5·6	92·5	345	2·7	47·2	50·1
420	3·7	8·0	88·3	450	9·5	57·5	33·0
500	5·2	31·0	63·8	520	9·0	58·0	33·0
600	11·5	60·5	28·0	600	11·5	56·5	32·0
680	13·8	60·2	26·0	680	10·0	58·0	32·0

For radical-halogenation Wibaut suggests that at the high temperatures concerned the reactants have such high energy contents that differences in activation energy of the individual carbon atoms of the benzene ring do not influence the reaction velocities at these positions; he believes the isomer ratio to be determined statistically. Since in a monosubstituted benzene there are two *ortho*-, two *meta*-, and one *para*-position the isomer distribution should thus be *ortho* 40%, *meta* 40%, and *para* 20%. That there is less *ortho*- and more *meta*-isomer in practice is attributed by Wibaut to steric hindrance at the *ortho*-position. Now the fluorine in fluorobenzene has a relatively small atomic volume, so on Wibaut's hypothesis fluorobenzene should give more *ortho*-isomer than bromobenzene; but, as shown above, the reverse is found experimentally for chlorination and bromination. Similar contradictions of the hypothesis are found in other reactions of halogenobenzenes, as shown in Table 2. The decrease in the amount of *ortho*-substitution must therefore be attributed mainly to energetic causes and in no case solely to steric

TABLE 2. *Amounts* (%) *of* ortho-*substitution of halogenobenzenes.*

	PhF	PhCl	PhBr	PhI
Chlorination : electrophilic	16·0	39·0	45·1	—
radical	11·5	15·0	—	—
Nitration : electrophilic	8·0	30·1	37·6	43·3
radical	38·0	—	—	—
Bromination : electrophilic	1·8	11·2	13·1	18·2
radical	11·5	18·0	20·0	—

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[2] Wibaut, *Experientia*, 1949, **5**, 340.

[3] (*a*). Wibaut, van de Lande, and Wallagh, *Rec. Trav. chim.*, 1933, **52**, 794; 1937, **56**, 65; (*b*) van Loon and Wibaut, *ibid.*, 1937, **56**, 815.

[4] Holleman, *ibid.*, 1903, **23**, 261; Swartz, *ibid.*, 1913, **33**, 263.

[5] Bird and Ingold, *J.*, 1938, 918.

[6] Oláh and Pavláth, *Acta Chim. Acad. Sci. Hung.*, 1954, **4**, 111.

[7] Oláh, Pavláth, Kuhn, and Varsányi, *ibid.*, 1955, **7**, 431, and unpublished results.

[8] *Idem, Tagungsber. Chem. Ges. D.D.R*, 1955, in the press; Oláh and Pavláth, " Vegyipari Kutató Intézetek Közleményei," Vol. IV, p. 48.

[9] Sandin, Drake, and Leger, *Org. Synth.*, Coll. Vol. II, p. 196; Woollett and Johnson, *ibid.*, p. 343; Wallingford and Krueger, *ibid.*, p. 349.

[10] Lambourne and Robertson, *J.*, 1947, 1167.

[11] Militzer, *J. Amer. Chem. Soc.*, 1938, **60**, 256.

causes. Although Wibaut's hypothesis is thus not fully adequate it remains true that the relatively high heat-energy of the molecules in high-temperature reactions must play a substantial part in determining orientation.

Recently the orientation in radical reactions has been explained in terms of the free-valency theory introduced by molecular-orbital considerations.[12] The free valency gives information about the electron distribution of the conjugated systems, and its value is in some measure characteristic of the binding power of the individual carbon atoms. In radical reactions the radical has for disposal one uncompensated electron which "attempts" to be incorporated into a bond with compensation of spin; and the greater the free valency of a carbon atom the greater is its disposition for reaction with the uncompensated electron. However, Hey and Williams,[13] using bond orders given by Sandorfy,[14] calculated the free valencies for halogenobenzenes, which indicate the order $o > p > m$, so that the observed isomer ratios cannot be explained by free valency alone.

Previous authors have paid no attention to Coulomb forces on the grounds that neutral radicals were under consideration. But some neutral radicals possess dipole moments, and in these cases their interaction with the free charges appearing on the atoms of the ring will increase or decrease the activation energy. Moreover, even radicals, such as those from halogen atoms, which have no dipole moment when alone, will become polarized under the influence of the charges on the ring atoms. Thus neutral radicals will in fact be subject to Coulomb forces, which will vary from one position in the ring to another, being greatest where the free charge is greatest. For the halogenobenzenes the largest free charges are at the *meta*-positions, usually about $0{\cdot}10$—$0{\cdot}14 \times 10^{-10}$ unit, the values at the *para*- and the *ortho*-positions being about one-third of these. *E.g.*, Ri and Eyring [15] have calculated the charge distribution as follows:

	PhF	PhCl	PhBr	PhI
ortho	0·0363	0·0473	0·0446	0·0194
meta	0·0933	0·115	0·116	0·0909
para	0·00351	0·0271	0·0305	0·00651

We conclude that the orientation in high-temperature halogenations is due to three factors: (1) The high energy content of the radical favours statistical distribution. (2) Owing to interaction with the uncompensated electrons of the radicals the free valencies at the ring carbon atoms contribute to changes in the activation energy, higher free valency lowering the activation energy and thus increasing the proportion of substitution at that position. (3) Neutral radicals, whether they have normally a dipole moment or whether polarisation is induced by the free charge appearing at ring carbon atoms, will be influenced by that free charge; the greater the free charge, the greater is the amount of substitution at that position.

EXPERIMENTAL

Determination of the Isomer Ratios in Chloro- and Bromo-fluorobenzene.—Ultraviolet absorption spectra have often been used for analysis of aromatic compounds,[16] but the differences in extinction are not great for solutions so that errors tend to be large. We have determined the isomer ratio for chloro- and bromo-fluorobenzene by means of the ultraviolet absorption spectra of the vapour in equilibrium with the liquid. The composition of the vapour mixture then yields that of the liquid by application of Raoult's and Henry's laws. Alternatively the composition of the liquid phase can be determined directly if, in place of

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[12] Coulson, *J. Chim. phys.*, 1948, **45**, 243; Daudel and his co-workers, *Bull. Soc. chim. France*, 1950, **17**, 66; Longuet-Higgins and his co-workers, *Trans. Faraday Soc.*, 1951, **47**, 553.

[13] Hey and Williams, *Discuss. Faraday Soc.*, 1953, **14**, 216.

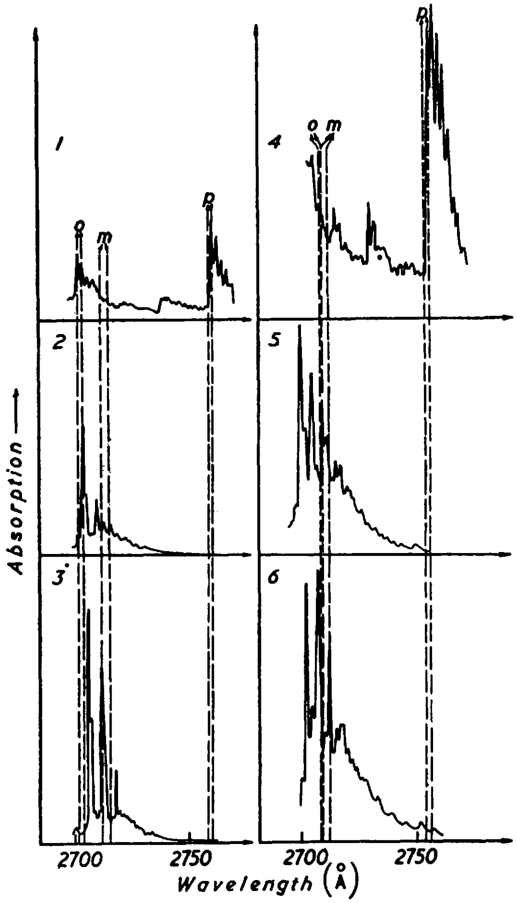
[14] Sandorfy, *Bull. Soc. chim. France*, 1949, **16**, 615.

[15] Ri and Eyring, *J. Chem. Phys.*, 1940, **8**, 433.

[16] *E.g.*, Fry, Nusbaum, and Randall, *J. Appl. Chem.*, 1946, **17**, 150; Nielsen and Smith, *Ind. Eng. Chem. Anal.*, 1943, **15**, 609; Robertson, Ginsburg, and Matsen, *ibid.*, 1946, **18**, 746.

molar extinction coefficients, the absorption coefficients of the saturated vapours of the pure components at the appropriate temperature are used :[17] $\beta = (\log I_0/I)/d$, where d is the layer thickness (in mm.).

Having the vapour spectra of the pure components we did not measure actual extinctions but only differences in the extinction at neighbouring points of the spectra, choosing as " analytical pair " a sharp maximum for the particular isomer and its adjacent minimum.



Wavelengths of " analytical pairs " used in analysis of isomeric mixtures of chloro- and bromo-fluorobenzene (cf. Table 3).

C_6H_4BrF : 1, *p*-; 2, *o*-; 3, *m*-.
C_6H_4ClF : 4, *p*-; 5, *o*-; 6, *m*-.

We then change the above formula to $\Delta\beta = (\log I_1/I_2)/d$, where I_1 and I_2 are the intensities for the analytical pair.[18]

The Figure shows the vapour spectra of the isomeric chloro- and bromo-fluorobenzenes and the analytical pairs where the difference in optical density provides the values of I_1/I_2. The quantitative data for these pairs are in Table 3.

TABLE 3. *log* I_1/I_2 *for the isomers.*

	C_6H_4ClF; d = 22 mm.; 10°				C_6H_4BrF; d = 53 mm.; 10°			
	λ (Å)	*o*	*m*	*p*	λ (Å)	*o*	*m*	*p*
ortho-Pair	2708·5—2707·9	0·286	−0·020	−0·003	2703·4—2701·2	1·129	0·070	−0·135
meta-Pair	2711·5—2708·5	−0·081	0·435	−0·061	2711·0—2714·7	0·061	1·000	0·035
para-Pair	2755·6—2754·0	0·001	−0·007	1·022	2760·0—2758·4	0·005	−0·005	0·992

For the chlorofluorobenzenes the analytical pair for the *para*-isomer corresponds to the 0-0 transition, and for the *ortho*- and *meta*-isomer to the 2–2 transition of the lower-frequency

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[17] Oláh, Pavláth, Kuhn, and Varsányi, *Acta Chim. Acad. Sci. Hung.*, 1955, **7**, 431.
[18] Vaughn and Stearn, *Analyt. Chem.*, 1949, **21**, 1361.

normal vibration concomitant to the 0–0 transition. For the bromofluorobenzenes the analytical pairs for the *ortho*- and the *para*-isomer correspond to the 0–0 transition, and for the *meta*-isomer to the 1–1 transition of a lower-frequency vibration; however, in place of the 0–0 transition for the *ortho*-isomer there is a maximum of an intense band due to the *para*-isomer and corresponding to a 0–1 transition of a C–X vibration.

The experimental error in recording and reading each point of an analytical pair was 0·003, in conformity with previous experience. Since there are two points, the maximum error for a pair was 0·006, which on the basis of Table 3 gives the following maximum errors: C_6H_4ClF, *o*- 2·1%, *m*- 1·4%, *p*- 0·6%; C_6H_4BrF, *o*- 0·5%, *m*- 0·6%, *p*- 0·6%. The error due to presence of other components is of a lower order of magnitude: *e.g.*, for determination of *o*-chlorofluorobenzene, errors in determination of the *meta*-isomer cause an error of (0·006/0·435) × 100% (cf. Table 3), which, multiplied by 0·020, causes an error of ∼0·0003 in log I_0/I. The accuracy of the analysis is illustrated in Table 4 which gives results for four known mixtures.

TABLE 4. *Analysis of mixtures of known composition.*

Isomer	Compn. (%)	Found (%)	Compn. (%)	Found (%)
o-C_6H_4ClF	62·43	62	28·92	29·5
m- ,,	25·55	25	56·40	56
p- ,,	12·02	13	14·68	14·5
o-C_6H_4BrF	61·59	62	24·09	23·5
m- ,,	30·11	30·5	51·82	51·5
p- ,,	8·30	7·5	24·09	25·0

Our spectroscopic method determines the relative amounts of the isomers. In obtaining the sample for analysis we removed unchanged fluorobenzene and then isolated the mixed isomeric substitution products in one fraction (the b. p.s of the isomers are too similar to permit separation by distillation). Thus, in our method, if there is any loss in the isolation of the products it does not affect the isomer ratio.

The spectral bands are well separated, and the final error in the determination never exceeds 2% and is in general less than 1%.

Chlorination of Fluorobenzene with an Iron Catalyst.—Chlorine was passed into fluorobenzene (48 g., 0·5 mole) containing iron powder, with stirring and ice-cooling, until the increase in weight was 14 g. (0·4 mole). Then the mixture was steam-distilled, and the volatile organic layer was separated and washed with 5% aqueous sodium hydroxide and then with water, dried, and distilled through a 40 cm. Widmer column. After removal of unchanged fluorobenzene (6 g.) the residue was shown spectroscopically to contain 16% of *o*- and 84% of *p*-chlorofluorobenzene. Distillation of the residue gave a fraction (42 g.), b. p. 129—131°, shown spectroscopically to be almost pure *para*-isomer (Found: Cl, 28·0. Calc. for C_6H_4ClF: Cl, 27·2%).

Bromination of Fluorobenzene with an Iron Catalyst.—Bromine (64 g., 0·4 mole) was added to stirred, cooled fluorobenzene (48 g., 0·5 mole) containing iron powder (1 g.). The mixture was heated on the water-bath until evolution of hydrogen bromide ceased (∼1 hr.), then distilled in steam and worked up as before, giving unchanged fluorobenzene (4 g.) and a residue shown spectroscopically to contain 98·2% of *p*- and 1·8% of *o*-bromofluorobenzene. Distillation gave almost pure *para*-isomer (62 g.), b. p. 151—153° (Found: Br, 45·3. Calc. for C_6H_4BrF: Br, 45·8%).

In this and the preceding experiment the amount of *meta*-isomer was less than the experimental error (1%).

Reaction of Fluorobenzene with Iodine Chloride.—(*a*) Iodine chloride (40·5 g., 0·25 mole) in carbon tetrachloride (200 ml.) was added to stirred, cooled fluorobenzene (24 g., 0·25 mole), then the whole was refluxed for 10 hr. Iodine was filtered off, and the filtrate washed with 10% aqueous sodium carbonate until neutral and then with aqueous sodium thiosulphate until free from residual iodine, dried ($CaCl_2$), and distilled. After removal of carbon tetrachloride and fluorobenzene, a fraction (5·5 g.), b. p. 125—135° (Found: Cl, 27·6%), was obtained and shown spectroscopically to contain *p*- 91·2%, *o*- 6·1%, and *m*-chlorofluorobenzene 2·7%. No dichloro-derivative could be isolated. The distillation residue contained 0·5 g. of fluoroiodobenzene.

(*b*) Similar amounts of reactants in dry methanol (150 ml.) were refluxed for 5 hr., then after removal of most of the solvent by distillation were worked up as in (*a*). No chlorofluorobenzene was obtained but, instead, *p*-fluoroiodobenzene, b. p. 180—185° (Found : I, 56·45. Calc. for C_6H_4IF : I, 57·15%).

Reaction of Fluorobenzene with Iodine Bromide.—Iodine bromide (52 g., 0·25 mole) in carbon tetrachloride (250 ml.) was added with stirring and cooling to fluorobenzene (24 g., 0·25 mole) in carbon tetrachloride (50 ml.). After being kept at 50° for 5 hr. the mixture was worked up as in the experiments with iodine chloride to give fractions, (i) b. p. 148—152° (6·2 g.), shown spectroscopically to contain 96·1% of *p*-, 2·1% of *o*-, and 1·8% of *m*-bromofluorobenzene (Found : Br, 45·2%), and (ii) *p*-fluoroiodobenzene, b. p. 182—185° (Found : I, 56·7%).

Chlorination of Fluorobenzene in the Vapour Phase.—Reaction was carried out in a smooth, transparent silica tube (1 m. long, 25 mm. in diameter) heated in a vertical electric furnace for 75 cm. of its length. The temperature variation of the furnace was 6—8° at 600° and 2—3° at 400°. Fluorobenzene was dropped into an evaporator at 120° and mixed at that temperature with a chlorine stream passing at a rate of 20 l./hr. for reaction up to 345° or 4 l./hr. for reaction at >450°. The gases issuing from the reaction tube were condensed in acetone–carbon dioxide, distilled in steam, washed with aqueous alkali and water, dried ($CaCl_2$), and distilled through a 40 cm. Widmer column.

Isomer ratios for the products are given in Table 1. Other details are in Table 5 and refer to 0·5 mole of fluorobenzene. There was no reaction at room temperature.

TABLE 5. *Chlorinations.*

Temp.	Time of reaction (min.)	Product g.	Product b. p.	Residue after steam-distn. (g.)
260°	48	1·5	125—132°	—
345	43	1·6	125—131	—
450	35	3·1	122—128	0·5
520	33	3·3	,,	0·4
600	30	4·1	123—129 *	2·1
680	36	3·8	124—130 †	2·5

* Also a fraction (1·9 g.), b. p. 155—163°, probably dichlorofluorobenzenes (Found : Cl, 42·6. Calc. for $C_6H_3Cl_2F$: Cl, 43·0%).

† Also a fraction (2·5 g.), b. p. 158—164°, probably dichlorofluorobenzenes (Found : Cl, 42·7%).

Bromination of Fluorobenzene in the Vapour Phase.—The apparatus was that used for chlorination. Bromine vapour was mixed at 80° with the fluorobenzene by means of a stream of nitrogen at 30 l./hr. Unchanged bromine was removed from the products by washing them with aqueous sodium thiosulphate; otherwise working up was as for chlorination.

Isomer ratios for the products are given in Table 1. Other details are in Table 6 and refer to 0·5 mole of fluorobenzene.

TABLE 6. *Brominations.*

Temp.	Br (g.)	Time (min.)	Product g.	Product b. p.	Residue after steam-distn.
260°	40	48	2·1	150—152°	—
345	44	<46	2·7	149—152	—
420	64	42	3·2	150—153	—
500	36	32	14·2	148—152	3·5 g., tar
600	36	50	16·3	149—153	5·2 g.
680	32	50	14·9	148—152	9·5 g., tar

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