144. *Direct Preparation and Some Reactions of Chlorofluorobenzenes.*[1]

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Direct fluorination of hexachlorobenzene gives chlorofluorocyclohexanes of average composition [$C_6Cl_6F_6$]. Dehalogenation of this mixture with iron filings packed in a cobalt fluoride reactor gives high yields of hexafluorobenzene and chlorofluorobenzenes. Chloropentafluorobenzene forms a Grignard reagent with magnesium in diethyl ether when activated with 1,2-dibromoethane but forms material of high molecular weight when tetrahydrofuran is used as solvent.

A number of spectacular advances have been made recently in aromatic fluorine chemistry but the basic synthetic intermediates, hexafluorobenzene and bromopentafluorobenzene, have still remained relatively inaccessible. Hexafluorobenzene has been prepared by a number of methods [2] but, so far, the only route suitable for application on a reasonably large scale has required initial fluorination of benzene with cobalt trifluoride, then dehydrofluorination of the complex product to give polyfluorocyclohexadienes. These dienes have been defluorinated by passage over heated iron gauze, giving hexafluorobenzene and polyfluorobenzenes.[3] Routes to bromo- and iodo-pentafluorobenzene require the halogenation of pentafluorobenzene, but pentafluoroiodobenzene has also been prepared by the reaction of pentafluorophenylhydrazine (which can be obtained from hexafluorobenzene) with silver oxide in methyl iodide.[4]

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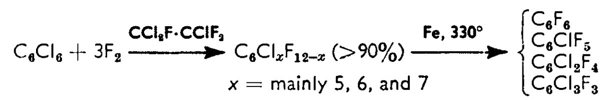
[1] Preliminary communication, *Proc. Chem. Soc.*, **1963**, 94.

[2] (*a*) Johncock, Mobbs, and Musgrave, *Ind. Eng. Chem., Process Design and Development*, 1962, **1**, 267; (*b*) Banks, Birchall, Haszeldine, Simm, Sutcliffe, and Umfreville, *Proc. Chem. Soc.*, 1962, 281; and references cited.

[3] Gething, Patrick, Tatlow, Banks, Barbour, and Tipping, *Nature*, 1959, **183**, 586; Gething, Patrick, Stacey, and Tatlow, *ibid.*, p. 588; Coe, Patrick, and Tatlow, *Tetrahedron*, 1960, **9**, 240.

[4] Birchall, Haszeldine, and Parkinson, *J.*, 1962, 4966.

We report the first simple preparation of synthetically important perchlorofluorobenzenes, as well as hexafluorobenzene, by a method which can be used on a large scale. A mixture of perchlorofluorocyclohexanes can be prepared in high yield by the direct fluorination of hexachlorobenzene at room temperature or above, and dehalogenation of this mixture gives hexafluorobenzene and perchlorofluorobenzenes in high overall yield.



$$C_6Cl_6 + 3F_2 \xrightarrow{CCl_2F\cdot CClF_2} \underset{x\ =\ \text{mainly 5, 6, and 7}}{C_6Cl_xF_{12-x}\ (>90\%)} \xrightarrow{Fe,\ 330^\circ} \left\{\begin{array}{l} C_6F_6\\ C_6ClF_5\\ C_6Cl_2F_4\\ C_6Cl_3F_3\end{array}\right.$$

We have been unable to obtain resolution of the isomeric dichlorotetrafluorobenzenes on any of the stationary phases which we use in our vapour-phase chromatography apparatus. However, the nuclear magnetic resonance spectrum of the mixture indicates that the ratio of isomers is $o : m : p = 22 : 48 : 30$.

Previous reports of the direct fluorination of hexachlorobenzene [5,6] do not include the separation and characterisation of the products, except that Bigelow and Pearson [5] isolated small amounts of material, $C_6Cl_6F_6$ and $C_6Cl_6F_4$. The experimental conditions employed by these workers were different from those reported here. We have found that the passage of a three-molar proportion of fluorine diluted with nitrogen through a stirred slurry of hexachlorobenzene in 1,1,2-trichlorotrifluoroethane at room temperature gave a mixture of perchlorofluorocyclohexanes of average composition (by halogen analysis of the mixture) of $C_6Cl_xF_{12-x}$ where x = mainly 5—7. The infrared spectrum of the mixture showed that it did not contain unsaturated material, and the perchlorofluorocyclohexanes were identified by g.l.c., authentic samples being used for comparison which had been prepared previously in this laboratory by other methods.[7] When a mixture of perchlorofluorocyclohexanes, obtained as described above, was further fluorinated first at room temperature and then at 200°, the composition of the product was $C_6Cl_xF_{12-x}$, where x is mainly 4—6. However, the use of fluorine to raise the fluorine content of the perchlorofluorocyclohexane mixture in this way is not an efficient reaction because yields of only 50% have been recorded for this stage, as compared with >90% for the initial fluorination of hexachlorobenzene.

The easier removal of chlorine than fluorine from perchlorofluorocyclohexanes has been demonstrated previously [2a,7] and we have found that dehalogenation of $[C_6Cl_6F_6]$av. over iron gauze at 330—340 gives good yields of aromatic compounds. However, the composition of the products varied with the size of the sample dehalogenated and regeneration of the iron gauze was found to be inconvenient. Much more consistent and easily reproducible results were obtained by using a cobalt fluoride reactor [8] in which the cobalt fluoride had been replaced by iron filings (see Table 1). The composition of the product was independent of the sample size and only the proportion of chlorine containing material changed slowly with increasing life of the iron filings (see Table 2). Fine iron filings gave higher overall yields of aromatic material probably because it was possible to pack a greater quantity of the fine filings into the reactor.

We have begun to investigate the functional properties of chlorine in chlorofluorobenzenes, beginning with chloropentafluorobenzene. Bromopentafluorobenzene and pentafluoroiodobenzene form the corresponding Grignard reagents very easily in diethyl ether [9] but no reactions of chloropentafluorobenzene have been reported. We found that chloropentafluorobenzene formed a Grignard reagent in diethyl ether after the magnesium

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[5] Bigelow and Pearson, *J. Amer. Chem. Soc.*, 1934, **56**, 2773.

[6] Bancroft and Whearty, *J. Phys. Chem.*, 1931, **35**, 3121; Fukuhara and Bigelow, *J. Amer. Chem. Soc.*, 1938, **60**, 427.

[7] Chambers, Heyes, and Musgrave, *Tetrahedron*, 1963, **19**, 891.

[8] Barbour, Barlow, and Tatlow, *J. Appl. Chem.*, 1952, **2**, 127.

[9] Nield, Stephens, and Tatlow, *J.*, 1959, 166; Pummer and Wall, *J. Res. Nat. Bur. Stand.*, 1959, **63***A*, 167.

TABLE 1.

Dehalogenation of perchlorofluorocyclohexanes: composition of the products (yield in parentheses).

Sample (g.)	C_6F_6 (%)	C_6ClF_5 (%)	$C_6Cl_2F_4$ (%)	$C_6Cl_3F_3$ (%)	$C_6Cl_4F_2$ (%)	C_6Cl_5F (%)	Impurities (%)	Total yield of aromatic material (%)
Iron-gauze method (*a*)								
5	20(14)	45(28)	25(14)	10(5)	—	—		61
20	20(19)	25(21)	20(16)	15(11)	8(5)	2(1)	10	73
Modified fluorinator (3 *kg. coarse iron filings*) (*a*)								
5	25(14)	35(18)	20(9·5)	5(2)	—	—	15	43·5
10	25(15)	35(20)	20(10)	5(2)	—	—	15	47
20	25(16)	35(21)	20(11)	5(2·5)	—	—	15	50·5
Containing fine iron filings (5 *kg.*) (*b*)								
20	30(22)	40(27)	20(12·5)	5(3)	—	—	5	64·5

(*a*) At 330°, nitrogen flow, 60 ml. per min. (*b*) At 340°, nitrogen flow, 60 ml. per min.

TABLE 2.

Variation in composition of the products with the life of the fine iron filings.

Total amount added (g.)	C_6F_6 (%)	C_6ClF_5 (%)	$C_6Cl_3F_4$ (%)	$C_6Cl_2F_3$ (%)	$C_6Cl_4F_4$ (%)	C_6Cl_5F (%)	Impurities (%)	Total yield of aromatic material (%)
0—10			Non-aromatic material					0
10—900 (*a*)	30(22)	40(27)	20(12·5)	5(3)	—	—	5	64·5
900—1000 (*b*)	25(18)	40(26·5)	25(15)	5(3)	trace	—	5	62·5

(*a*) 330°, nitrogen flow 60 ml. per min. (*b*) 340°, nitrogen flow 60 ml. per min.

had been activated by 1,2-dibromoethane, and this gave pentafluorobenzene in 67% yield on hydrolysis. Reaction of the Grignard reagent with methylmercury(II) iodide gave 50% of methylpentafluorophenylmercury. It has been reported that carbonation of pentafluorophenylmagnesium bromide or iodide in diethyl ether gives a low yield of pentafluorobenzoic acid[9] and also, that a high yield is obtained from pentafluorophenylmagnesium bromide when tetrahydrofuran is used as solvent.[10] Carbonation of pentafluorophenylmagnesium chloride gave 41% of pentafluorophenylbenzoic acid after preforming of the reagent in diethyl ether and then changing of the solvent to tetrahydrofuran before passage of carbon dioxide. The latter procedure was necessary because when formation of the Grignard reagent in tetrahydrofuran was attempted, material of high molecular weight, m. p. >360°, was produced in high yield.

Attempts to prepare bi- and ter-phenyl derivatives from the Grignard reagent were unsuccessful. There was no reaction between pentafluorophenylmagnesium chloride in tetrahydrofuran and chloropentafluorobenzene, hexafluorobenzene, or decafluorobiphenyl but the diethyl ether remaining after the change of solvent may have reduced the reactivity of the Grignard reagent. However, generation of pentafluorophenylmagnesium chloride in tetrahydrofuran in the presence of excess of hexafluorobenzene gave only a polymer and the reaction of pre-formed pentafluorophenylmagnesium bromide in tetrahydrofuran again gave only a polymer.

The production of material of high molecular weight in these reactions most probably occurs by nucleophilic displacement of halogen by the Grignard reagent on a fluoroaromatic ring. However, since the polymers usually contained a small amount (~5%) of halogen other than fluorine, more complicated reaction schemes cannot yet be excluded. The

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[10] Harper and Tamborski, *Chem. and Ind.*, 1962, 1824.

infrared spectra of the polymers obtained from reactions described above were very similar and relatively simple, each having three major bands near 1475, 970, and 710 cm.$^{-1}$. Absorption near 1500 cm.$^{-1}$ is consistent with a polyfluorophenylene structure since the spectra of all penta- and tetra-fluorophenyl compounds show absorption in this region.

Chloropentafluorobenzene underwent the Ullman reaction with copper powder at 230°, giving decafluorobiphenyl.

EXPERIMENTAL

The cobalt fluoride reactor was of the design described by Barbour, Barlow, and Tatlow[8] and the 10-amp. fluorine generator was on loan from Imperial Chemical Industries Ltd.

Fluorination of Hexachlorobenzene.—Fluorine (6·4 g./hr.) diluted with nitrogen (3 l./hr.) was bubbled into a stirred slurry of hexachlorobenzene in 1,1,2-trichlorotrifluoroethane (760 g; 4 moles) contained in a three-necked 1-l. flask. The whole apparatus was situated in a fume-cupboard and protected by a blast screen. Originally a reflux condenser was attached to the flask but under these conditions explosions occurred within the flask. When the condenser was omitted, the vapour in the vessel kept to a minimum, and the outlet left open to the fume extraction system, reaction proceeded smoothly and no explosions occurred during many subsequent fluorinations. The trichlorotrifluoroethane acted as a diluent and heat-transfer agent and was conveniently fluorinated during the process to dichlorotetrafluoroethane (b. p. 3°) which boiled from the mixture. The amount of fluorine used was calculated to be sufficient to saturate fully the hexachlorobenzene present (170 g.; 4·5 moles) and to fluorinate the trichlorotrifluoroethane (80 g.; 2 moles), this required a reaction time of 39 hr. A paste remained (516 g.) of approximate average composition $C_6Cl_6F_6$ (Found: Cl, 54·9; F, 27·6. Calc. for $C_6Cl_6F_6$: Cl, 52·1; F, 27·9%). The infrared spectrum showed no absorption in the region 1800—1500 cm.$^{-1}$, indicating the absence of unsaturated material. Analytical-scale g.l.c. with silicone elastomer as stationary phase showed that the mixture of perchlorofluorocyclohexanes consisted of $C_6Cl_xF_{12-x}$ where $x = 4$ (5% yield), 5 (25%), 6 (37%), and 7 (23%) together with a small amount of recovered hexachlorobenzene (3%). The apparatus was calibrated by using authentic samples of chlorofluorocyclohexanes, prepared previously by another method.[7]

Further Fluorination of $[C_6Cl_6F_6]$av.—A mixture of perchlorofluorocyclohexanes (128 g.) was obtained by the procedure described above, starting with hexachlorobenzene (100 g.), and the mixture was further fluorinated by passage of fluorine; first (20 g., 0·5 mole) at room temperature, then (20 g., 0·5 mole) at 100°, and finally at 200° (20 g., 0·5 mole), until a total of 60 g. of fluorine had been used. A colourless liquid (84 g.) remained which was shown, by g.l.c., to contain a mixture of perchlorofluorocyclohexanes $C_6Cl_xF_{12-x}$ where $x = 3$ (4%), 4 (18%), 5 (23%), 6 (11%), and 7 (3%).

Dehalogenation of Chlorofluorocyclohexanes.—Dehalogenations were carried out by using the iron-gauze technique[3] and also using a cobalt fluoride reactor[8] containing (*a*) coarse iron filings (3 kg.) and (*b*) fine iron filings (5 kg.). Best yields of highly fluorinated material were obtained by using fine iron filings (see Table 1). Hexafluorobenzene and chloropentafluorobenzene were identified by comparison of the infrared spectra and retention times with those of authentic specimens previously prepared.[7] Dichlorotetrafluoro- and trichlorotrifluorobenzenes were identified by comparison of the retention times with other samples of isomeric dichlorotetrafluoro- and trichlorotrifluoro-benzenes prepared by another route.[7] Samples of $C_6Cl_2F_4$ and $C_6Cl_3F_3$ were analysed (Found: Cl, 33·1; F, 34·5. Calc. for $C_6Cl_2F_4$: Cl, 32·1; F, 34·7 and Found: Cl, 44·7; F, 23·7. Calc. for $C_6Cl_3F_3$: Cl, 45·2; F, 24·2%).

Ratio of Isomers of Dichlorotetrafluorobenzene.—The relevant n.m.r. data on these and other perchlorofluorobenzenes have been reported elsewhere.[7] Present spectra were recorded on an A.E.I. R.S.2 spectrometer operating at a frequency of 60 Mc./sec. Percentage composition of the isomers was determined by comparing the areas under the peaks arising from the separate isomers; the areas were estimated graphically and by weighing the cut-out spectra.

Preparation of Pentafluorophenylmagnesium Chloride.—Ethylene dibromide (0·5 ml.) was added to magnesium turnings (1·50 g.) in dry ether (15 ml.). The reaction started on being heated under reflux and more ethylene dibromide (0·5 ml.) was added after 15 min. Chloropentafluorobenzene (1·01 g.) was added after a further 10 min. Ethylene dibromide (0·5 ml.)

was added after intervals of 20 and 50 min., respectively, followed by more dibromide (0·25 ml.), after an interval of 80 min., and the reaction was completed by 30 minutes' refluxing.

Reactions of Pentafluorophenylmagnesium Chloride.—(*a*) *Hydrolysis.* Water (3 ml.) was added to the Grignard reagent, followed by dilute sulphuric acid (3 ml.). The ethereal layer was distilled *in vacuo*, and redistilled *in vacuo* from phosphorus pentoxide. Analytical g.l.c. showed the presence of pentafluorobenzene alone in this ethereal solution, and this was separated from the ether by preparative-scale g.l.c. The pentafluorobenzene (0·56 g., 67%) had an infrared spectrum identical with that of an authentic specimen.

(*b*) *Carbonation to pentafluorobenzoic acid.* ' Pentafluorophenylmagnesium chloride was prepared as described above from chloropentafluorobenzene (1·01 g.) in ether (15 ml.). The Grignard solution was then distilled with dry tetrahydrofuran (100 ml.) until the total column of the solution was 30 ml. Dry carbon dioxide was bubbled rapidly through the solution at room temperature for 1·5 hr., dilute sulphuric acid was added, and the mixture extracted continuously with ether for 15 hr. The extract was dried ($MgSO_4$) and the solvent distilled to leave a solid, which was sublimed (120°/0·05 mm.), recrystallised from n-hexane, and re-sublimed. The pentafluorobenzoic acid (0·43 g., 41%), m. p. 102·5—103·5° (lit., 103—104°) [10] had an infrared spectrum identical with that of an authentic sample prepared from pentafluorophenylmagnesium bromide by the method of Harper and Tamborski.[10]

(*c*) *Reaction with methylmercury*(II) *iodide.* Methylmercury(II) iodide (1·83 g.) was added as a suspension in ether (10 ml.) to pentafluorophenylmagnesium chloride prepared by the above method from chloropentafluorobenzene (1·00 g.) in ether (15 ml.), and the mixture was heated under reflux for 3 hr. Water (25 ml.) was added, the ether layer was separated and dried ($MgSO_4$), and then the ether was removed by vacuum transfer. Sublimation of the residue in a vacuum at room temperature gave methylpentafluorophenylmercury (0·95 g., 50%), which had an infrared spectrum identical with that of the compound prepared previously.[11]

Reaction of Chloropentafluorobenzene with Magnesium in Tetrahydrofuran.—Chloropentafluorobenzene (2·03 g.) was added to magnesium turnings (1·00 g.) in dry tetrahydrofuran (10 ml.), and a small crystal of iodine added. The reaction started when slightly warmed, and a vigorous exothermic reaction occurred. The mixture was heated under reflux for 2·5 hr., during which time a precipitate was formed, and dilute sulphuric acid (10 ml.) was added to the dark solution. The mixture was filtered and the pale buff precipitate (1·45 g.) dried *in vacuo* (P_2O_5). This product did not melt or show signs of decomposition at 360°.

Decafluorobiphenyl.—Chloropentafluorobenzene (5·0 g., 0·025 mole) was treated with copper powder (5·0 g., 0·08 mole) in a sealed tube at 230° for 280 hr. The product was extracted with ether and the ether evaporated to give decafluorobiphenyl (2·85 g.). Recrystallisation from benzene gave white crystals, m. p. 69° (Found: F, 56·5. Calc. for $C_{12}F_{10}$: F, 56·9%), and the infrared spectrum was identical with that of a sample of decafluorobiphenyl which was prepared by another method.[12]

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[11] Chambers, Coates, Livingstone, and Musgrave, *J.*, 1962, 4367.

[12] Nield, Stephens, and Tatlow, *J.*, 1959, 166.