Direct Liquid Phase Fluorination of Halogenated Aromatic Compounds[1]

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Direct liquid phase fluorination of chlorinated aromatic compounds proceeded by addition and polymerization, yielding the corresponding 1,2,3,4,5,6-hexafluorocyclohexane derivatives, decafluorobicyclohexyls, and low molecular weight polytetrafluorocyclohexenes. The following substrates followed this general reaction sequence: *o*-dichlorobenzene, *p*-dichlorobenzene, 1,2,4-trichlorobenzene, 1,3,5-trichlorobenzene, 1,2,4,5-tetrachlorobenzene, tetrachlorobiphenyl, and hexachlorobiphenyl. The fluorination of tetrachlorophthatic anhydride yielded 1,2,3,4,5,6-hexafluorotetrachlorocyclohexane-1,2-dicarboxylic acid anhydride. Perfluorobicyclohexyl and low molecular weight polydecafluorocyclohexenes were obtained in the fluorination of hexafluorobenzene; the fluorination of chloropentafluorobenzene proceeded in an analgous manner. The chlorofluorocyclohexanes obtained by the fluorination of *o*-dichlorobenzene, 1,2,4-trichlorobenzene, and 1,3,5-trichlorobenzene were dehydrohalogenated to give aromatic fluoro and chlorofluoro compounds. Decafluorobiphenyl was obtained in the dehydrohalogenation of decafluorohexachlorobicyclohexyl. Substitution was observed in the fluorination of *o*-dichlorobenzene.

The direct liquid phase fluorination of organic compounds, under investigation in this laboratory since 1958, was utilized in the synthesis of fluoramino[2] and aliphatic fluoronitro compounds.[3] The investigation of the scope and limitation of this fluorination technique with regard to the nature of organic substrates led to the examination of direct liquid phase fluorination of halogenated aromatic compounds reported in this paper.

Early attempts to directly fluorinate aromatic hydrocarbons, and organic compounds in general, resulted in explosions and "burning" of substrates to hydrogen fluoride and carbon tetrafluoride.[4] The differences between direct fluorination and other halogenation reactions were emphasized by Moissan, who predicted that the probability of accomplishing a controllable substitution utilizing elementary fluorine was remote.[5] The attempts to "tame" the reactions of elementary fluorine with organic compounds, however, continued. Bancroft and Jones[6] in 1929 reported explosions in vapor or liquid phase fluorination of benzene and toluene. Several years later, Bancroft and Whearty[7] again investigated the fluorination of benzene, but this time used fluorine diluted with nitrogen. Although explosions were avoided, only tarry, noncharacterizable products were obtained.

Bockemuller[8] investigated the fluorination of several aromatic compounds, but in all cases obtained only nondistillable, high fluorine content tars, and concluded that in direct liquid phase fluorination reactions, aromatic compounds behave as cyclohexatrienes and undergo addition and polymerization rather than substitution reactions.

The fluorination of hexachlorobenzene and 1,3,5-trichlorobenzene was reported[7,9] to give chlorofluorobenzenes by the displacement of one or more chloro groups of the substrates by fluorine. Recently, Brooke, *et al.*,[10] reported excellent yields of hexachlorohexafluorocyclohexane in the liquid phase fluorination of hexachlorobenzene. Bigelow and Pearson[11] also studied the liquid phase fluorination of hexachlorobenzene and obtained small amounts of tetrafluorohexachlorocyclohexene and hexachlorohexafluorocyclohexane.

The differing results obtained by these three groups of investigators under apparently very similar reaction conditions led to a brief reinvestigation of direct liquid phase fluorination of hexachlorobenzene. We confirmed the findings of Brooke, *et al.* Hexachlorobenzene underwent smooth fluorination in either carbon tetrachloride or 1,1,2-trichloro-1,2,2-trifluoroethane solution and consumed approximately 3 mol of fluorine to give a product analyzing for $C_6Cl_6F_6$, practically quantitatively.

The addition of fluorine to hexachlorobenzene suggested that other halogenated aromatic compounds might react similarly, and, consequently, a number of such compounds were examined under direct liquid phase fluorination conditions. 1,2,4-Trichlorobenzene and 1,3,5-trichlorobenzene underwent fluorination in 1,1,2-trichloro-1,2,3-trifluoroethane solution at 0 ± 5°, consuming approximately 3 mol of fluorine rapidly and without burning or explosions. In both cases, the yield of reaction products amounted to the sum of weights of fluorine and the trichlorobenzene employed, indicating that fluorination proceeded by addition rather than by substitution.

The reaction product obtained in the fluorination of 1,2,4-trichlorobenzene was separated into several fractions. The low-boiling fraction amounting to approximately 50% of the total product and analyzing for $C_6H_3Cl_3F_6$, was identified as 1,2,3,4,5,6-hexafluoro-1,2,4-trichlorocyclohexane on the basis of elemental analysis, infrared spectrum, and physical properties. The higher boiling material, amounting to *ca.* 30% of the total product, analyzed for $C_{12}H_6Cl_6F_{10}$. Its molecular weight was determined as 610 ± 60. On the basis of elemental analysis, physical properties, infrared spectrum, and molecular weight, this material was characterized as hexachlorodecafluorobicyclohexyl,

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(1) Presented in part at the Fourth International Symposium on Fluorine Chemistry, Estes Park, Colo., July 1967.

(2) V. Grakauskas, Abstracts, 140th National Meeting of the American Chemical Society, Chicago, Ill., September 1961, p 23 M; Third International Symposium on Fluorine Chemistry, Munich, Germany, September 1965.

(3) V. Grakauskas and K. Baum, *J. Org. Chem.*, **33**, 3080 (1968).

(4) H. Moissan, *Ann. Chim. Phys.*, **19**, 272 (1891).

(5) H. Moissan, "Das Fluor und Seine Verbinderugen," Verlag M. Krayn, Berlin, 1900, pp 236 ff.

(6) W. D. Bancroft and N. C. Jones, *Trans. Amer. Electrochem. Soc.*, **55**, 183 (1929).

(7) W. D. Bancroft and S. F. Whearty, *Proc. Nat. Acad. Sci. U. S.*, **17**, 183 (1931).

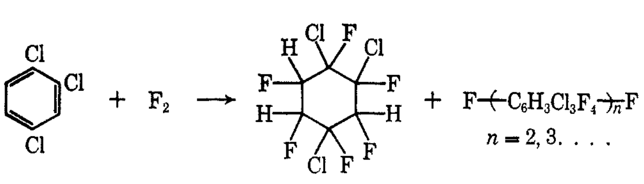
(8) W. Bockemuller, *Ann.*, **506**, 20 (1933).

(9) S. F. Whearty, *J. Phys. Chem.*, **35**, 3121 (1931).

(10) G. M. Brooke, R. D. Chambers, J. Heyes, and W. K. R. Musgrave, *J. Chem. Soc.*, 729 (1964).

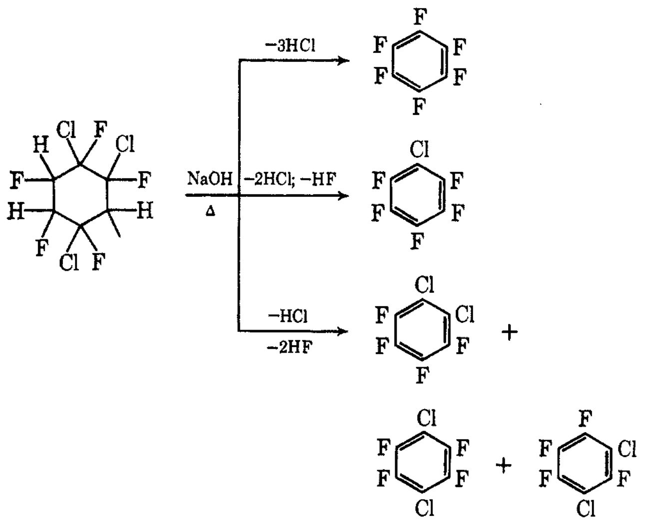
(11) L. A. Bigelow and J. H. Pearson, *J. Amer. Chem. Soc.*, **56**, 2773 (1934).

probably a mixture of several isomers. The remainder of the product, a white solid comprising the distillation residue, analyzed for $C_6H_3Cl_3F_4$. On the basis of elemental analysis and physical properties, this material was characterized as a mixture of polytichlorotetrafluorocyclohexenes, $(C_6H_3Cl_3F_4)_n$.



The fluorination product of 1,3,5-trichlorobenzene was treated in an analogous manner as that above, and the reaction products were identified as 1,2,3,4,5,6-hexafluoro-1,3,5-trichlorocyclohexane, decafluorohexachlorobicyclohexyl, and polytrichlorotetrafluorocyclohexenes.

Additional confirmation of the structures of the above reaction products was obtained in their dehydrohalogenation to aromatic fluorocarbons. 1,2,3,4,5,6-Hexafluoro-1,2,4-trichlorocyclohexane underwent a facile dehydrohalogenation on treatment with sodium hydroxide to give a mixture of hexafluorobenzene, chloropentafluorobenzene, and the three isomers of dichlorotetrafluorobenzene. The individual compounds in the mixture were identified by fluorine nmr spectra (see Experimental Section for details).

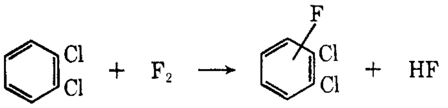


1,2,3,4,5,6-Hexafluoro-1,3,5-trichlorocyclohexane, the monomeric fluorination product of 1,3,5-trichlorobenzene, underwent dehydrohalogenation under similar conditions, and gave a mixture of aromatic compounds similar in composition to that obtained from the 1,2,4-trichloro isomer. *m*-Dichlorotetrafluorobenzene was the only dichlorotetrafluorobenzene isomer in this dehydrohalogenation.

Decafluorohexachlorobicyclohexyls, the dimeric fluorination products of 1,2,4-trichlorobenzene and 1,3,5-trichlorobenzene, were dehydrohalogenated with aqueous sodium hydroxide at 80–100°. Decafluorobiphenyl was identified by its fluorine nmr spectrum as one of the components in the dehydrohalogenation mixture.

The fluorination of *o*-dichlorobenzene and *p*-dichlorobenzene was examined next. *o*-Dichlorobenzene underwent fluorination in 1,1,2-trichloro-1,2,2,-trifluoroethane solution and consumed approximately three moles of fluorine. The distillable portion of the fluorination product analyzed for $C_6H_4Cl_2F_6$, and on the basis of elemental analysis and physical properties, the material was characterized as 1,2-dichloro-1,2,3,4,5,6-hexafluorocyclohexane. The distillation residue analyzing for $C_{12}H_8Cl_4F_{10}$, molecular weight 575 ± 60, was characterized as decafluorotetrachlorobicyclohexyl, containing some higher molecular weight condensation products.

Unexpected results were obtained in the dehydrohalogenation of 1,2-dichloro-1,2,3,4,5,6-hexafluorocyclohexane with sodium hydroxide. In addition to pentafluorobenzene, the dehydrohalogenation product mixture also contained hexafluorobenzene and chloropentafluorobenzene. The latter two compounds could be produced only in the dehydrohalogenation of dichloroheptafluorocyclohexane. The formation of dichloroheptafluorocyclohexane in the fluorination of *o*-dichlorobenzene could have taken place by the displacement of hydrogen either before or after the addition. If the latter was the case, *o*-dichlorofluorobenzene must have been produced as a side reaction product from *o*-dichlorobenzene *via* substitution–fluorination.



The possibility that *o*-dichlorobenzene underwent aromatic substitution prior to the addition was investigated using a low fluorine to substrate ratio. Neat *o*-dichlorobenzene was used and the fluorination was carried out at somewhat slower rate than that using a diluent. No difficulties were encountered with the control of the exotherm, although occasional blue flashes of light at the tip of the fluorine inlet tube were noticed when attempts were made to increase the rate of fluorination. The fluorine nmr spectrum of this fluorination mixture exhibited two signals at ϕ 108.5 and 110.5. The signal at ϕ 110.5, an eight-line multiplet, was assigned to 1,2-dichloro-4-fluorobenzene by comparing it with the fluorine nmr spectrum of an authentic sample (see Experimental Section for details). The signal at ϕ 108.5 might be due to 1,2-dichloro-3-fluorobenzene, the only other possible dichlorofluorobenzene isomer, but no assignment has been made.

The results of the above experiment not only confirmed the preceding considerations regarding the dehydrohalogenation reactions, but also provided the first example of substitution in an aromatic nucleus under direct liquid phase fluorination conditions.[12]

The fluorination of *o*-dichlorobenzene and the de-

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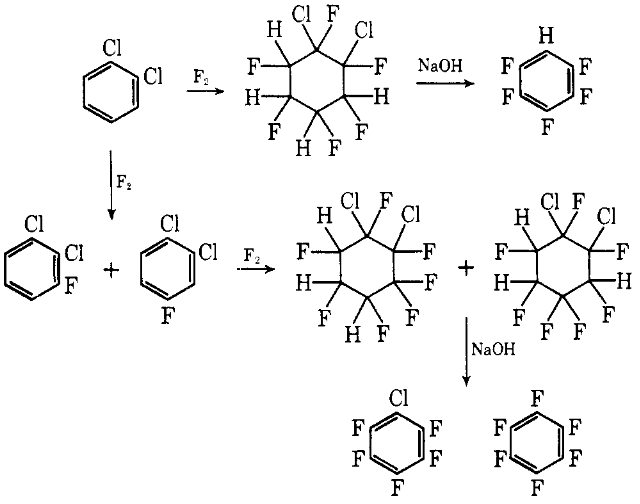
[12] Subsequent to the preliminary report of this work at the Fourth International Symposium on Fluorine Chemistry, Estes Park, Colo., July 1967, C. L. Coon, M. E. Hill, and D. L. Ross, *J. Org. Chem.*, **33**, 1387 (1968), reported three examples of aromatic fluorine substitution.

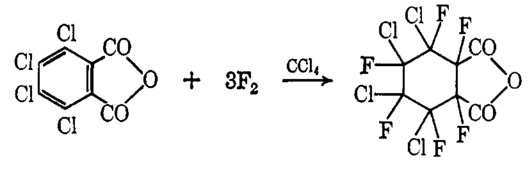
hydrohalogenation of monomeric products is represented by the following equations.



The fluorination of *p*-dichlorobenzene in 1,1,2-trichloro-1,2,2-trifluoroethane proceeded similarly to that of the *ortho* isomer, yielding a mixture of 1,4-dichloro-1,2,3,4,5,6-hexafluorocyclohexane, decafluorotetrachlorobicyclohexyl, and polydichlorotetrafluorocyclohexenes, characterized on the basis of their elemental analyses and their physical properties.

1,2,4,5-Tetrachlorobenzene was fluorinated in carbon tetrachloride to give 1,2,3,4,5,6-hexafluoro-1,2,4,5-tetrachlorocyclohexane, identified by its elemental analysis. The nondistillable fraction of the product, analyzing for $C_6H_2Cl_4F_4$, appeared to be a mixture of polytetrafluorotetrachlorocyclohexenes.

In order to determine if functional groups might interfere in the fluorination of chlorinated aromatic compounds, the fluorination of tetrachlorophthalic anhydride was examined. The fluorination in carbon tetrachloride was relatively sluggish; a considerable amount of unreacted fluorine escaped from the reactor during the course of fluorination and some unreacted starting material was recovered. The fluorination product was characterized as hexafluoro-3,4,5,6-tetrachlorocyclohexane-1,2-dicarboxylic acid anhydride on the basis of its elemental analysis, infrared spectrum, and physical properties. No polymeric material was produced in the fluorination of tetrachlorophthalic anhydride.



The fluorination of halogenated biphenyls was investigated next. Tetrachlorobiphenyl[13] underwent rapid fluorination in 1,1,2-trichloro-1,2,2-trifluoroethane and gave a product analyzing for $C_{12}H_6Cl_4F_{10}$, molecular weight 750 ±75, which was separated into two fractions on distillation. The distillate analyzed for $C_{12}H_6Cl_4F_{12}$, and, on the basis of elemental analysis and physical properties, the material was characterized as dodecafluorotetrachlorobicyclohexyl. Its infrared spectrum was very similar to that of the dimeric fluorination products of dichlorobenzenes. The distillation residue was characterized as a mixture of fluorinated dimers and higher molecular weight condensation products of the general empirical structure $(C_{12}H_6Cl_4F_{10})_n$.

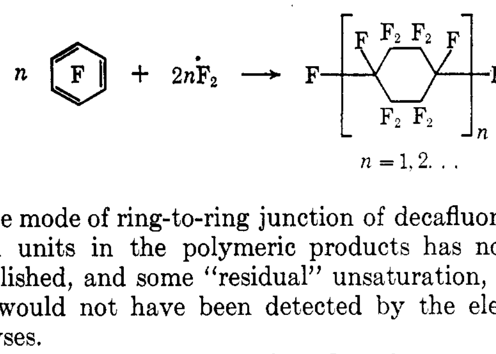
$$C_6H_3Cl_2 - C_6H_3Cl_2 + F_2 \longrightarrow F\left[C_6H_3F_5Cl_2 - C_6H_3F_5Cl_2\right]_nF$$

The fluorination of hexachlorobiphenyl[13] gave a viscous liquid, elemental analysis of which indicated a mixture of the dodecafluoro adduct and higher molecular weight polydecafluorohexachlorobicyclohexenes.

$$C_6H_2Cl_3{-}C_6H_2Cl_3 + F_2 \longrightarrow F\left[C_6H_2Cl_3F_5{-}C_6H_2Cl_3F_5\right]_nF$$
$$n = 1, 2, 3\ldots\ldots$$

The facile fluorination of chlorinated aromatic compounds suggested that fluorinated benzenes might also undergo fluorination in an analogous manner, and, consequently, the fluorination of hexafluorobenzene and chloropentafluorobenzene was investigated.

The fluorination of hexafluorobenzene in 1,1,2-trichlo-1,2,2-trifluoroethane at 20° with 3 mol of fluorine gave a viscous oil, which on distillation yielded perfluorobicyclohexyl and several fractions of higher molecular weight products identified on the basis of their elemental analyses as polydecafluorocyclohexenes. The yield of polyperfluorocyclohexenes in this fluorination amounted to only 55%, and, since all hexafluorobenzene was consumed, it was assumed that perfluorocyclohexane comprised the remainder of the product, but the material codistilled with the solvent and was not characterized.



The mode of ring-to-ring junction of decafluorocyclohexyl units in the polymeric products has not been established, and some "residual" unsaturation, if present, would not have been detected by the elemental analyses.

The direct fluorination of hexafluorobenzene differed significantly from that of hexachlorobenzene. Whereas in the latter case, the monomeric hexafluoro adduct was the sole reaction product, the fluorination of hexafluorobenzene yielded predominantly polymeric products. The polymerization in this case was more pronounced in the fluorination of trichlorobenzenes or dichlorobenzenes.

The fluorination of chloropentafluorobenzene in 1,1,2-trichloro-1,2,2-trifluoroethane proceeded similarly to that of hexafluorobenzene. The distillable portion of the fluorination product was identified as $C_{12}Cl_2F_{20}$ on the basis of its elemental analysis and its physical properties. The nondistillable fraction, analyzing for C_6ClF_9, apparently contained a mixture of polychlorononafluorocyclohexenes.

All the above-discussed fluorinations proceeded smoothly even at fast fluorination rates except those of hexafluorobenzene, which in two cases resulted in explosions occurring in the middle of fluorination runs. The causes of these explosions are unknown; it is possible that they were initiated by a sudden polymerization of octafluorocyclohexadiene intermediate.

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(13) Tetrachlorobiphenyl and hexachlorobiphenyl were obtained from Monsanto Chemical Co. under the trade name Aroclor. Both compounds were mixtures of isomers, as determined by their nmr spectra.

Experimental Section

Apparatus.—Fluorinations were carried out in glass standard taper three-necked flasks equipped with a mechanical stirrer, a glass inlet tube extending below the liquid level, and a standard taper thermometer well with an opening for gas exit. Standard fluorine handling hardware[14] was used, and fluorine was diluted with nitrogen (1:3 to 1:5 ratio).

1,2,3,4,5,6-Hexachlorohexafluorocyclohexane.—A solution–suspension of 57 g (0.2 mol) of hexachlorobenzene in 350 ml of carbon tetrachloride was fluorinated at 0 ± 5° with 0.6 mol of fluorine (4.5 hr). The reaction mixture was concentrated and degassed at 45° (0.1 mm) to give 75 g of a pale yellow oil.

Anal. Calcd for $C_6Cl_6F_6$: C, 18.5; Cl, 53.9; F, 28.5. Found: C, 18.1; Cl, 53.6; F, 28.5.

Fluorination of 1,3,5-Trichlorobenzene.—A solution of 36.3 g (0.2 mol) of 1,3,5-trichlorobenzene in 350 ml of 1,1,2-trichloro-1,2,2-trifluoroethane was fluorinated at 0 ± 5° with 0.6 mol of fluorine (2.0 hr) and the fluorination mixture was distilled to give (1) 18.5 g of colorless liquid, bp 38–41° (0.1 mm); and (2) 38 g of distillation residue which solidified at room temperature.

Anal. Calcd for $C_6H_3Cl_3F_6$: C, 24.4; H, 1.0; F, 38.6. Found (1): C, 23.9; H, 0.9; F, 36.9. Calcd for $C_{12}H_6Cl_6F_{10}$: C, 26.0; H, 1.1; F, 34.4. Found (2): C, 26.6; H, 0.9; F, 33.7.

Fluorination of 1,2,4-Trichlorobenzene.—A solution of 54.5 g (0.3 mol) of 1,2,4-trichlorobenzene in 400 ml of 1,1,2-trichloro-1,2,2-trifluoroethane was fluorinated at −5 ± 5° with 0.9 mol of fluorine (1.5 hr) and the fluorination mixture was distilled to give (1) 40 g of a colorless liquid, bp 72–76° (25 mm); (2) 21.5 g of colorless viscous oil, bp 130–135° (0.1 mm); and (3) 19 g of distillation residue (white solid).

Anal. Calcd for $C_6H_3Cl_3F_6$: C, 24.4; H, 1.0; F, 38.6. Found (1): C, 23.8; H, 1.1; F, 37.4. Calcd for $C_{12}H_6Cl_6F_{10}$: C, 26.0; H, 1.1; F, 34.4; mol wt, 553. Found (2): C, 26.6; H, 0.9; F, 34.8; mol wt, 610 ± 60. Calcd for $(C_6H_3Cl_3F_4)_n$: C, 28.0; H, 1.2; F, 29.5. Found (3): C, 27.8; H, 0.9; F, 31.2.

Dehydrohalogenation of 1,2,3,4,5,6-Hexafluoro-1,2,4-trichlorocyclohexane and 1,2,3,4,5,6-Hexafluoro-1,3,5-trichlorocyclohexane.—A solution of 20 g of sodium hydroxide in 25 ml of water and 21 g of 1,2,3,4,5,6-hexafluoro-1,2,4-trichlorocyclohexane was placed into a 100-ml round-bottoned flask equipped with a stirrer and a reflux condenser and heated at 95–100° for 3 hr. A colorless liquid began to reflux when the reaction temperature was reached. The reaction mixture was cooled to 50° and distilled at 25 mm. The distillate was separated from a small amount of water and distilled to give (1) 6.2 g of a colorless liquid, bp 80–100°; (2) 3.8 g of a colorless liquid, bp 110–125°; and (3) 2.6 g of a colorless liquid, bp 135–140°. All fractions were analyzed by nmr.

The fluorine nmr spectra were obtained using undiluted samples. Fraction 1 exhibited four signals. A singlet at ϕ 163.1 was assigned to hexafluorobenzene on the basis of the reported[15] fluorine nmr spectrum for the compound, and also by comparing the spectrum with that of an authentic sample of hexafluorobenzene. The other three signals, multiplets at ϕ 141.3 and 162.2 and a triplet at ϕ 157.0, were assigned to *ortho*, *meta*, and *para* fluorines, respectively, of chloropentafluorobenzene. The reported[16] ϕ values for the compound was 140.8, 161.5, and 156.3, respectively. The approximate ratio of hexafluorobenzene to chloropentafluorobenzene was 1.3:1.

The fluorine nmr spectrum of fraction 2 consisted of the same four signals as fraction 1, but chloropentafluorobenzene was by far the predominant component in the mixture. The ratio of chloropentafluorobenzene to hexafluorobenzene, 40:1, was obtained by triangulation.

The fluorine nmr spectrum of fraction 3 consisted of a doublet of doublets at ϕ 135.1, a multiplet at ϕ 160.3, and a pair of triplets at ϕ 118.2, assigned to the fluorines of *m*-dichlorotetrafluorobenzene (reported[16] ϕ 134.5, 160.6, and 118.4, respectively); A_2X_2 patterns at ϕ 136.7 and 156.2 assigned to the fluorines of *o*-dichlorotetrafluorobenzene (reported[16] ϕ 136.1 and 155.6), and a sharp singlet at ϕ 140.2 assigned to the fluorines of *p*-dichlorotetrafluorobenzene (reported[16] ϕ 140.0). The approximate ratio of *meta/ortho/para* isomers in the mixture was 1:2:1.

The dehydrohalogenation of 1,2,3,4,5,6-hexafluoro-1,3,5-trichlorocyclohexane was carried out under identical reaction conditions with those of the 1,2,4-trichloro isomer. The reaction products, characterized by nmr, were identical with those above, with the exception that *m*-dichlorotetrafluorobenzene was the only dichlorotetrafluorobenzene isomer.

Dehydrohalogenation of Decafluorohexachlorobicyclohexyl.—Decafluorohexachlorobicyclohexyl, 17 g, obtained in the fluorination of 1,3,5-trichlorobenzene, was dehydrohalogenated with aqueous sodium hydroxide, following the reaction conditions described above. The reaction product was extracted with methylene chloride and distilled to give 4.0 g of pale yellow liquid, bp 60–85° (0.1 mm). The distillation residue, amounting to 5.0 g, was not characterized.

The fluorine nmr spectrum in carbon tetrachloride consisted of multiplets at ϕ 138.2, 150.8, and 161.6, of a 2:1:2 area ratio attributed to the *ortho*, *para*, and *meta* fluorines, respectively, of decafluorobiphenyl, in good agreement with those reported[17] for the compound: ϕ 138.1, 150.2, and 160.6. The concentration of decafluorobiphenyl in the mixture was estimated at 30–50%.

Fluorination of 1,2,4,5-Tetrachlorobenzene.—A solution–suspension of 86.5 g (0.4 mol) of 1,2,4,5-tetrachlorobenzene in 650 ml of carbon tetrachloride was fluorinated at 10 ± 5° with 1.3 mol of fluorine and the fluorination mixture was distilled to give (1) 70 g of colorless liquid, bp 52–55° (0.1 mm); and (2) 58 g of distillation residue.

Anal. Calcd for $C_6H_2Cl_4F_6$: C, 21.8; H, 0.6; Cl, 43.0; F, 34.5. Found (1): C, 22.4; H, 0.5; Cl, 46.4; F, 30.7. Calcd for $(C_6H_2Cl_4F_4)_n$: C, 24.7; H, 0.7; Cl, 48.7; F, 25.9. Found (2): C, 25.3; H, 0.6; Cl, 47.5; F, 26.2.

1,2,3,4,5,6-Hexafluorotetrachlorocyclohexane-1,2-dicarboxylic Acid Anhydride.—A suspension of 67 g (0.2 mol) of tetrachlorophthalic anhydride in 600 ml of carbon tetrachloride was fluorinated at 25° with 1 mol of fluorine. The fluorination was sluggish, and a considerable amount of unreacted fluorine escaped from the reactor. The reaction mixture was filtered and the filter cake was washed with 50 ml of carbon tetrachloride. The solid, amounting to 32 g, was identified as the starting material by its melting point. The combined tetrachloride filtrate and washings were distilled to give 45 g of a colorless liquid: bp 63–66° (0.1 mm); ir, characteristic anhydride absorption peak at 5.54 μ.

Anal. Calcd for $C_8Cl_4F_6O_3$: C, 24.0; Cl, 35.5; F, 28.5. Found: C, 23.8; Cl, 36.0; F, 30.0.

Fluorination of Tetrachlorobiphenyl.[13]—A solution of 40 g (0.137 mol) of tetrachlorobiphenyl in 650 ml of 1,1,2-trichloro-1,2,2-trifluoroethane was fluorinated at −5° with 0.76 mol of fluorine (3.0 hr), and the fluorination mixture was concentrated to give 67 g of a white solid, mp 64–68°, molecular weight 755 ± 70. A portion of the material, 40 g, was distilled to give (1) 9.8 g of a colorless viscous oil, bp 122–125° (0.2 mm); and (2) 28.5 g of distillation residue which solidified at room temperature.

Anal. Calcd for $(C_{23}H_6Cl_4F_{10})_n$: C, 29.9; H, 1.2; F, 39.4. Found: C, 29.5; H, 1.2; F, 39.8.

Anal. Calcd for $C_{12}H_6Cl_4F_{12}$: C, 27.7; H, 1.2; F, 43.8. Found (1): C, 28.4; H, 0.9; F, 45.5. Calcd for $C_{12}H_6Cl_4F_{10}$: C, 29.9; H, 1.2; F, 39.4. Found (2): C, 30.4; H, 1.0; F, 41.0.

Fluorination of Hexachlorobiphenyl.[13]—A solution of 12 g (0.034 mol) of hexachlorobiphenyl in 350 ml of 1,1,2-trichloro-1,2,2-trifluoroethane was fluorinated at −5° with 0.25 mol of fluorine and the fluorination mixture was concentrated to give 19 g of viscous oil.

Anal. Calcd for $C_{12}H_4Cl_6F_{12}$: C, 24.4; H, 0.6; F, 38.7. Calcd for $C_{12}H_4Cl_6F_{10}$: C, 26.1; H, 0.71; F, 34.5. Found: C, 25.8; H, 0.4; F, 34.8.

Fluorination of *o*-Dichlorobenzene.—A solution of 44.1 g (0.3 mol) of *o*-dichlorobenzene in 650 ml of 1,1,2-trichloro-1,2,2-trifluoroethane was fluorinated at −20 ± 5° with 0.93 mol of fluorine (3.5 hr) and the product was distilled to give (1) 31 g of a colorless liquid, bp 35–45° (0.1 mm); and (2) 39.5 g of viscous distillation residue which solidified at room temperature.

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[14] Allied Chemical Corp., Data Sheet PD-TA,85413A.

[15] I. J. Lawrenson, *J. Chem. Soc.*, 1117 (1965).

[16] P. Bladon, D. W. A. Sharp, and J. M. Winfield, *Spectrochim. Acta*, **20**, 1033 (1964).

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Anal. Calcd for $C_6H_4Cl_2F_6$: C, 27.5; H, 1.5; F, 43.7. Found (1): C, 27.2; H, 1.2; F, 41.8. Calcd for $C_{12}H_8Cl_4F_{10}$: C, 29.7; H, 1.6; F, 39.2; mol wt, 484. Found (2): C, 30.3; H, 1.3; F, 40.6; mol wt, 575 ±60.

In another experiment, 50 g (0.34 mol) of undiluted *o*-dichlorobenzene was fluorinated at −10 to −15° with 0.15 mol of fluorine (2.5 hr). The fluorination mixture was washed with three 50-ml portions of water and distilled to give 48 g of a colorless liquid, bp 31–33° (0.1 mm). The fluorine nmr spectrum exhibited two signals at ϕ 108.5 and 110.5. The signal at ϕ 110.5, an eight-line symmetrical multiplet, was assigned to 1,2-dichloro-4-fluorobenzene. The fluorine nmr spectrum of an authentic sample of 1,2-dichloro-4-fluorobenzene consisted of an identical signal at ϕ 110.5; $J_{H\text{-}o\text{-}F} = 8.3$ cps, $J_{H\text{-}p\text{-}F} = 7.6$ cps and $J_{H\text{-}m\text{-}F} = 5.4$ cps.

Fluorination of *p*-Dichlorobenzene.—A solution of 73.5 g (0.5 mol) of *p*-dichlorobenzene in 650 ml of 1,1,2-trichloro-1,2,2-trifluoroethane was fluorinated at −20 ± 5° with 1.5 mol of fluorine and the fluorination mixture was distilled to give (1) 35 g of a colorless liquid, bp 33–38° (0.1 mm); (2) 21 g of a colorless liquid, bp 123–128° (0.1 mm); and (3) 52 g of distillation residue which solidified to a white solid.

Anal. Calcd for $C_6H_4Cl_2F_6$: C, 27.5; H, 1.5; F, 43.7. Found (1): C, 28.7; H, 1.5; F, 40.4. Calcd for $C_{12}H_8Cl_4F_{10}$: C, 29.7; H, 1.6; F, 29.2. Found (2): C, 30.4; H, 1.3; F, 41.2. Calcd for $(C_6H_4Cl_2F_4)_n$: C, 32.3; H, 1.8; F, 34.1. Found (3): C, 31.8; H, 1.2; F, 36.3.

Dehydrohalogenation of 1,2-Dichloro-1,2,3,4,5,6-hexafluorocyclohexane.—A mixture of 9.5 g of sodium hydroxide and 9.0 g of 1,2-dichloro-1,2,3,4,5,6-hexafluorocyclohexane was heated at 90–95° in a distillation apparatus for 2.0 hr. The reaction mixture turned pale yellow and sodium hydroxide pellets gradually disintegrated. The reaction mixture was distilled at 40–70° (25 mm), and the distillate was separated from a small amount of water and distilled to give 4.5 g of liquid, bp 75–100°, and 1.5 g of liquid, bp 50–70° (25 mm).

The material of the first fraction, examined by nmr, contained pentafluorobenzene, hexafluorobenzene, and chloropentafluorobenzene in a 5:1:05 ratio, estimated by the triangulation of the signals. Hexafluorobenzene and pentafluorobenzene were isolated from the mixture by gas chromatography. The proton nmr spectrum of pentafluorobenzene in carbon tetrachloride exhibited a symmetrical doublet, $J = 3.1$ cps; a doublet of triplets, $J = 6.5$ cps; and a doublet of triplets, $J = 10.1$ cps; at δ 6.90. The fluorine nmr spectrum exhibited a doublet of triplets at ϕ 138.9 for *ortho* fluorines, a triplet at ϕ 153.5 for the *para* fluorine, and a symmetrical multiplet at ϕ 162.1 for the *meta* fluorine. The reported[15] ϕ values are 139.1, 154.0, and 162.6, respectively. The fluorine nmr spectrum of hexafluorobenzene exhibited a singlet at ϕ 163.1; reported[15] ϕ 162.9. The two remaining multiplet signals at ϕ 141.3 and 157.1 of the spectrum of the mixture were assigned to chloropentafluorobenzene on the basis of the reported[16] values for the *ortho* and *meta* fluorines of the compound, ϕ 141.3 and 157.0. The signal of the *para* fluorine at ϕ 162.2 was obscured by the hexafluorobenzene singlet.

The second fraction of dehydrohalogenation product, also examined by nmr, contained chloropentafluorobenzene and pentafluorobenzene in a 3:1 ratio.

Fluorination of Hexafluorobenzene.—A solution of 55.8 g (0.3 mol) of hexafluorobenzene in 750 ml of 1,1,2-trichloro-1,2,2-trifluoro-ethane was fluorinated at 20° with 0.9 mol of fluorine (1.5 hr) and the fluorination mixture was fractionated to give: (1) 15.8 g of colorless liquid, bp 30–35° (0.1 mm) (solidified to a white solid, mp 70–75°); (2) 12.5 g of colorless oil, bp 90–95° (0.1 mm); (3) 10.0 g of a viscous oil, bp 130–135° (0.1 mm); and (4) 8.5 g of distillation residue which solidified to a white solid at room temperature.

The material of fraction 1 was identified as perfluorobicyclohexyl, reported[18] mp 74–75°.

Anal. Calcd for $C_{12}F_{22}$: C, 25.6; F, 74.4. Found: C, 26.0; F, 75.5.

The elemental analyses of fractions were practically identical.

Anal. Calcd for $(C_6F_{10})_n$: C, 27.5; F, 72.5. Found (2–4): C, 27.6; F, 23.6.

1,1,2-Trichloro-1,2,2-trifluoroethane, removed in the concentration of the fluorination mixture, was examined by nmr and and did not contain hexafluorobenzene.

Fluorination of Chloropentafluorobenzene.—A solution of 40.5 g (0.2 mol) of chloropentafluorobenzene in 650 ml of 1,1,2-trichloro-1,2,2-trifluoroethane was fluorinated with 0.7 mol of fluorine at 25° (1.5 hr) and the fluorination mixture was distilled to give 21.5 g of colorless liquid, bp 60–80° (0.05 mm), and 10.5 g of distillation residue, a viscous oil. The elemental analyses of both fractions were identical.

Anal. Calcd for C_6ClF_9: C, 25.8; F, 61.4. Calcd for C_6ClF_{10}: C, 24.2; F, 63.9. Found: C, 26.5; F, 59.6.

Registry No.—1,2,3,4,5,6-Hexachlorohexafluorocyclohexane, 308-11-2; 1,2,3,4,5,6-hexafluoro-1,3,5-trichlorocyclohexane, 20643-01-0; 1,2,3,4,5,6-hexafluoro-1,2,4-trichlorocyclohexane, 20643-02-1; hexafluorobenzene, 392-56-3; chloropentafluorobenzene, 344-07-0; *o*-dichlorotetrafluorobenzene, 1198-59-0; *m*-dichlorotetrafluorobenzene, 1198-61-4; *p*-dichlorotetrafluorobenzene, 1198-62-5; 1,2,3,4,5,6-hexafluoro-1,2,4,5-tetrachlorocyclohexene, 20643-03-2; 1,2,3,4,5,6-hexafluorotetrachlorocyclohexane-1,2-dicarboxylic acid anhydride, 20643-05-4; 1,2,3,4,5,6-hexafluoro-1,2-dichlorocyclohexane, 20643-04-3; 1,2,3,4,5,6-hexafluoro-1,4-dichlorocyclohexane, 20643-06-5.

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