

1165. Preparation of Polyfluoroaromatic Compounds by the Reaction of Perhalogeno-aromatic Compounds with Potassium Fluoride in Sulpholan*

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Perchloro- and perbromo-aromatic compounds react with potassium fluoride in sulpholan to give polyfluoroaromatic compounds. Hexachlorobenzene gave a mixture (% molar yields) of C_6F_6 (0.4%), C_6ClF_5 (25%), $C_6Cl_2F_4$ (24%), and 1,3,5- $C_6Cl_3F_3$ (30%). Hexabromobenzene reacted similarly. Pentachlorobenzotrifluoride gave octafluorotoluene (2%), 3-chloroheptafluorotoluene (41%), and 3,5-dichlorohexafluorotoluene (4%). Octachloronaphthalene gave octafluoronaphthalene (52%). In these halogen-exchange reactions potassium fluoride was much more active in sulpholan than in other aprotic media.

FINGER and his co-workers¹ prepared 1,3,5-trichlorotrifluorobenzene by treating hexachlorobenzene with potassium fluoride in dimethylformamide and in dimethyl sulphoxide. Maynard² used *N*-methylpyrrolidone as solvent and obtained 1,3,5-trichlorotrifluorobenzene (23%), dichlorotetrafluorobenzene (34%), and a small quantity of chloropentafluorobenzene. Vorozhtsov *et al.*³ found that, in the absence of a solvent, hexachlorobenzene reacted with potassium fluoride at 450–500° in an autoclave to give hexafluorobenzene (21%), chloropentafluorobenzene (20%), dichlorotetrafluorobenzene (14%), and trichlorotrifluorobenzene (12%).

As an extension of preliminary work in this laboratory,⁴ we now report that tetrahydrothiophen 1,1-dioxide (sulpholan) is a particularly effective reaction medium for this type of halogen exchange. When hexachlorobenzene was treated with potassium fluoride in sulpholan at 230–240° for 18 hr., the following molar yields of products were obtained: C_6F_6 , 0.4%; C_6ClF_5 , 25%; $C_6Cl_2F_4$, 24%; 1,3,5- $C_6Cl_3F_3$, 30%. Neither hexachlorobenzene nor chloropentafluorobenzene gave a significant yield of hexafluorobenzene with this reagent. However, when chloropentafluorobenzene was treated with the more powerful fluorinating agent caesium fluoride in sulpholan at 160–190° for 18 hr., hexafluorobenzene was obtained in 42% yield together with starting material.

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¹ G. C. Finger, C. W. Kruse, R. H. Shiley, R. H. White, and H. A. Whaley, Abstracts, Organic Chemistry Division, XVIth International Congress of Pure and Applied Chemistry, Paris, July 1957, p. 303.

² J. T. Maynard, *J. Org. Chem.*, 1963, **28**, 112.

³ N. N. Vorozhtsov, V. E. Platonov, and G. G. Yakobson, *Izvest. Akad. Nauk. S.S.S.R., Ser. khim.*, 1963, 1524.

⁴ F.P. 1,360,917/1964.

Each of the chlorofluorobenzenes was characterised by reduction.⁵ Chloropentafluorobenzene gave pentafluorobenzene in 82% yield. Partial reduction of dichlorotetrafluorobenzene gave a mixture of 1,2,3,5-tetrafluorobenzene (39%), 1,2,3,4-tetrafluorobenzene (2%), and 4-chloro-1,2,3,5-tetrafluorobenzene (35%), a result which showed that mainly 1,3-dichlorotetrafluorobenzene was initially present. Reduction of trichlorotrifluorobenzene gave 1,3,5-trifluorobenzene in 72% yield, indicating that the trichlorotrifluorobenzene was largely the symmetrical isomer.

Similar work has since been reported in the Patent literature⁶ on the reaction of hexachlorobenzene with potassium fluoride in sulpholan. Nuclear magnetic resonance (n.m.r.) spectroscopy showed that the dichlorotetrafluorobenzene product consisted of a mixture of 1,3-dichloro- (81%), 1,2-dichloro- (18%), and 1,4-dichloro-tetrafluorobenzene (1.5%), and that the trichlorotrifluorobenzene was a mixture of 1,3,5-trichloro- (95%) and 1,2,3-trichloro-trifluorobenzene (5%).

The reaction of hexabromobenzene with potassium fluoride in sulpholan at 200° for 16 hr. gave the following molar yields of products: C₆BrF₅, 1%; C₆Br₂F₄, 19%; C₆Br₃F₃, 62%. The dibromotetrafluorobenzene appeared to be mainly the 1,3-dibromo-isomer since its infrared spectrum was the same as that of a sample prepared⁴ by the bromination of 1,2,3,5-tetrafluorobenzene. However, small quantities of 1,2- and 1,4-dibromotetrafluorobenzene may have been present. Tribromotrifluorobenzene was probably the symmetrical isomer, because its melting point was similar to that of the compound prepared⁷ by the bromination of 1,3,5-trifluorobenzene.

Pentachlorobenzotrifluoride,^{8,9} with potassium fluoride in sulpholan at 195–250° during 18 hr., gave: octafluorotoluene, 2%; 3-chloroheptafluorotoluene, 41%; 3,5-dichlorohexafluorotoluene, 4%.

The structure of 3-chloroheptafluorotoluene was allocated on the basis of its physical properties, elemental analysis, and n.m.r. spectrum. 3,5-Dichlorohexafluorotoluene was obtained in 97% purity by gas chromatography; the allocation of structure was again supported by n.m.r. spectroscopy.

Octachloronaphthalene was completely fluorinated by potassium fluoride in sulpholan at 230–240°, giving octafluoronaphthalene in 50–60% yield. Since octachloronaphthalene is commercially available, this method provides a satisfactory one-stage route to octafluoronaphthalene.

The effectiveness of sulpholan as a reaction medium for the preparation of highly fluorinated aromatic compounds can be attributed to its high boiling point and good thermal stability, its chemical stability and the absence of side-reactions which could form nucleophilic impurities, and the high cation solvation and low anion solvation of the alkali-metal fluoride in this medium. These points are illustrated in the Table, which compares

The reaction of hexachlorobenzene (0.1 mole) with potassium fluoride (1.0 mole)

Aprotic medium	Temp.	Time (hr.)	Product (% molar yield)
Benzonitrile	175	18	C ₆ Cl ₆ recovered
Nitrobenzene	193	20	C ₆ Cl ₆ recovered
Dimethylformamide *	153	36	C ₆ Cl ₃ F ₃ , 51; C ₆ Cl ₄ F ₂ , 24
Dimethyl sulphoxide * ...	180—190	5	C ₆ ClF ₅ , 0.4; C ₆ Cl ₂ F ₄ , 3; C ₆ Cl ₃ F ₃ , 3
N-Methylpyrrolidone † ...	—	—	C ₆ ClF ₅ , small; C ₆ Cl ₂ F ₄ , 34; C ₆ Cl ₃ F ₃ , 23
Sulpholan	230—240	18	C ₆ F ₆ , 0.4; C ₆ ClF ₅ , 25; C ₆ Cl ₂ F ₄ , 24; C ₆ Cl ₃ F ₃ , 30

* Finger *et al.*¹ reported C₆Cl₃F₃ as the only product, in unspecified yield. † Product obtained by Maynard² after re-treating all fluid fractions from initial fluorination of hexachlorobenzene.

⁵ R. E. Florin, W. J. Pummer, and L. A. Wall, *J. Res. Nat. Bur. Stand.*, 1959, **62**, 119; U.S.P. 2,967,894/1961.

⁶ F. Nyman, B.P. 970,746/1964.

⁷ G. C. Finger, F. H. Reed, and J. L. Finnerty, *J. Amer. Chem. Soc.*, 1951, **73**, 153.

⁸ E. T. McBee, J. S. Newcomer, W. E. Burt, and Z. D. Welch, in "Preparation, Properties, and Technology of Fluorine and Organic Fluoro Compounds," ed. Slessor and Schram, McGraw-Hill, New York, 1951, p. 784.

⁹ W. B. Ligett, U.S.P. 2,654,789/1953.

the effect of a number of aprotic media on the reaction of hexachlorobenzene with potassium fluoride. According to Parker,¹⁰ cation solvation by electron-donor solvents decreases in the series $\text{Me}_2\text{SO} > \text{Me}_2\text{N}\cdot\text{CHO} > \text{sulpholan} > \text{PhCN}, \text{PhNO}_2$. Referring to the Table, dimethyl sulphoxide was an unsatisfactory solvent, as a low yield of impure product was obtained. Others¹¹ have noted the formation of sulphur-containing impurities when dimethyl sulphoxide is used in the preparation of aryl fluorides. The greater degree of fluorination in sulpholan at 230–240° than in either dimethylformamide at 153° or in *N*-methylpyrrolidone at 190° must be due, in part, to a temperature effect. Neither benzonitrile nor nitrobenzene was an effective medium for the fluorination of hexachlorobenzene.

The much greater base strength of phenyltrimethylammonium hydroxide in sulpholan than in water has been attributed¹² to the low anion solvation of the hydroxide ion in the former medium. Presumably, the lack of solvation of the closely related fluoride ion in sulpholan must be responsible to some extent for the high-reactivity of potassium fluoride in this medium.

EXPERIMENTAL

Infrared spectra were measured with a Perkin-Elmer Infracord 137. Sulpholan (Whiffen and Sons Ltd.) was redistilled before use, b. p. 121°/4 mm., and was a solid at ambient temperature. Hexachlorobenzene and potassium fluoride were B.D.H. reagents. Hexabromobenzene was prepared¹³ by bromination of 1,4-dibromobenzene. Pentachlorobenzotrifluoride, b. p. 278–281°, m. p. 83–86° (lit.,⁹ 78–82°), was prepared as described before.^{8,9} Halowax-1051, a product of the Koppers Company, Pittsburgh, was found to be essentially pure octachloronaphthalene; it was used without further purification. Cæsium fluoride (American Potash and Chemical Corporation) was dried at 130°/0.1 mm., for 8 hr. before use.

Reaction of Hexachlorobenzene with Potassium Fluoride.—A stirred slurry of potassium fluoride (1160 g., 20 moles) in sulpholan (2560 g.) was dried by azeotropic distillation with benzene (150 c.c.) in a 5-l. flask fitted with a 1-ft. vacuum-jacketed column packed with glass helices. The benzene was distilled off, hexachlorobenzene (570 g., 2.0 moles) added, and the mixture stirred at 230–240° (internal temperature) for 18 hr. The liquid (b. p. 120–130°) collected from the column during this period was combined with a liquid fraction (b. p. 66–82°/24 mm.) obtained at the end of the reaction (287 g. in all). Further distillation gave a solid (89.6 g.), b. p. 130°/24 mm., followed by recovered sulpholan (2234 g.), b. p. 129°/5 mm.

The fluorinated liquid product (287 g.) was washed with water, dried (CaSO_4), and fractionally distilled through a 2-ft. column packed with Dixon gauzes (1/16 × 1/16 in.), to give (i) a mixture (9.8 g.), b. p. 100–116°, containing hexafluorobenzene (13%) and chloropentafluorobenzene (81%); the former was separated by gas chromatography and had the same infrared spectrum as that of an authentic sample,¹⁴ (ii) chloropentafluorobenzene (100.9 g.), b. p. 116.5°/756 mm., n_D^{20} 1.4244 (Found: C, 35.1; Cl, 17.0; F, 46.9. Calc. for C_6ClF_5 : C, 35.6; Cl, 17.5; F, 46.9%), (iii) a mixture (10.2 g.), b. p. 118–156°, (iv) 1,3-dichlorotetrafluorobenzene (103.1 g.), b. p. 156–157°/759 mm., n_D^{20} 1.4678 (Found: C, 32.2; Cl, 31.9; F, 34.8. Calc. for $\text{C}_6\text{Cl}_2\text{F}_4$: C, 32.9; Cl, 32.4; F, 34.7%), and (v) a residue (50.6 g.).

A portion of the solid, b. p. 130°/24 mm., was twice recrystallised from ethanol, to give 1,3,5-trichlorotrifluorobenzene, m. p. 61–62° (lit.,¹⁵ 62–63°) (Found: F, 24.4. Calc. for $\text{C}_6\text{Cl}_3\text{F}_3$: F, 24.2%).

Reaction of Chloropentafluorobenzene with Cæsium Fluoride.—A suspension of cæsium fluoride (76 g., 0.5 mole) in chloropentafluorobenzene (45.5 g., 0.22 mole) and sulpholan (200 c.c.) was stirred under reflux at 160–170° for 10½ hr., then at 170–190° for 7 hr. The reaction mixture was steam-distilled, to give a liquid (39.2 g.) consisting of hexafluorobenzene (17.5 g.) and chloropentafluorobenzene (21.2 g.).

¹⁰ A. J. Parker, *Quart. Rev.*, 1962, **16**, 163.

¹¹ G. C. Finger, L. D. Starr, D. R. Dickerson, H. S. Gutowsky, and J. Hamer, *J. Org. Chem.*, 1963, **28**, 1666.

¹² C. H. Langford and R. L. Burwell, *J. Amer. Chem. Soc.*, 1960, **82**, 1503.

¹³ A. Eckert and B. Steiner, *Monatsh.*, 1915, **36**, 269.

¹⁴ B. Gething, C. R. Patrick, J. C. Tatlow, R. E. Banks, A. K. Barbour, and A. E. Tipping, *Nature*, 1959, **183**, 586.

¹⁵ G. C. Finger, F. H. Reed, E. W. Maynert, and A. M. Weiner, *J. Amer. Chem. Soc.*, 1951, **73**, 149.

Reaction of Hexabromobenzene with Potassium Fluoride.—A mixture of potassium fluoride (16.0 g., 0.27 mole) and hexabromobenzene (14.4 g., 0.026 moles) in sulpholan (40 c.c.) was stirred at 200° for 16 hr. The mixture was steam-distilled, to give a product (9.5 g.) consisting of (% molar yield): $C_6Br_5F_5$, 1%; 1,3- $C_6Br_2F_4$, 19% (each was separated by gas chromatography and had the expected infrared spectrum); 1,3,5- $C_6Br_3F_3$, 62%, m. p. 94.5–96° (from ethanol) (lit.,⁷ 98–98.5°) (Found: C, 19.5; Br, 65.3; F, 15.9. Calc. for $C_6Br_3F_3$: C, 19.5; Br, 65.0; F, 15.5%).

Reaction of Pentachlorobenzotrifluoride with Potassium Fluoride.—A suspension of potassium fluoride (2500 g., 43 moles) in sulpholan (6000 g.) was dried by azeotropic distillation with benzene. After benzene was removed, pentachlorobenzotrifluoride (1302 g., 4.1 moles; 85% purity) was added and the mixture stirred under reflux at 195° for 7 hr., 213° for 7 hr., and finally at 213° rising to 250° during 4 hr. A liquid (612 g.), b. p. 80–138°, was collected during this period from the 1-ft. column attached to the apparatus. Further distillation gave a liquid (177.5 g.), b. p. 90–96°/15 mm.

The combined product (789 g.) was washed with water, dried ($CaSO_4$), and distilled through a 2-ft. vacuum-jacketed column packed with Dixon gauzes (1/16 × 1/16 in.), to give (i) benzene (44 g.), b. p. 80–82°, (ii) a mixture (22 g.), b. p. 82–104°, (iii) octafluorotoluene (23 g.), b. p. 104°, n_D^{20} 1.3687 (lit.,¹⁶ b. p. 102–103°, n_D^{19} 1.3680) (Found: C, 35.4; F, 64.0. Calc. for C_7F_8 : C, 35.6; F, 64.4%), with the same infrared spectrum as an authentic sample,¹⁶ (iv) a mixture (63.5 g.), b. p. 104–136°, (v) 3-chloroheptafluorotoluene (416 g.), b. p. 136°/758 mm., n_D^{21} 1.4071 (Found: C, 33.0; Cl, 14.2; F, 52.2. C_7ClF_7 requires C, 33.3; Cl, 14.0; F, 52.7%), ν_{max} 1507, and 1479 cm^{-1} (fluorinated aromatic ring), (vi) 3-chloroheptafluorotoluene (45 g.), b. p. 136–137° (96% purity), (vii) a mixture (57 g.), b. p. 137–169°, (viii) 3,5-dichlorohexafluorotoluene (50 g.), b. p. 169–170°, n_D^{20} 1.4450 (97% purity) (Found: C, 30.2; Cl, 26.2; F, 41.5. $C_7Cl_2F_6$ requires C, 31.2; Cl, 26.4; F, 42.4%), ν_{max} 1458 cm^{-1} (fluorinated aromatic ring), and (ix) a residue (35 g.).

Reaction of Octachloronaphthalene with Potassium Fluoride.—A stirred slurry of potassium fluoride (2500 g., 43 moles) in sulpholan (6000 g.) was dried by azeotropic distillation with benzene. Octachloronaphthalene (1470 g., 3.6 moles) was added, and the mixture was stirred at 235° for 14 hr., then distilled to give (i) crude octafluoronaphthalene (573 g.), b. p. 130°/15 mm., and (ii) sulpholan (3000 g.), b. p. 180°/80 mm. Fraction (i) was washed with water, dried, and redistilled, to give octafluoronaphthalene (510 g.), m. p. 83.5–85.5° (from ethanol), b. p. 92–93°/10 mm. (97% pure by gas chromatography). An analytical sample of octafluoronaphthalene, m. p. 86–87° (lit.,¹³ 86–87°) (Found: C, 43.8; F, 55.3. Calc. for $C_{10}F_8$: C, 44.1; F, 55.85%), was prepared by further fractional distillation of the product under reduced pressure.

Fluorine-19 Nuclear Magnetic Resonance Spectra.—3,5-Dichlorohexafluorotoluene. The spectrum contained three chemically shifted peaks in the intensity ratio 3 : 1 : 2, indicating a symmetrical structure. The values of the chemical shifts confirm this assignment. The shifts are $F_{(2)}$ 52.24 p.p.m., $F_{(4)}$ 59.50 p.p.m., CF_3 106.48 p.p.m., to low field of hexafluorobenzene as internal reference. These values can be compared with values calculated from the shifts in 3,5-dichlorotetrafluorobenzene¹⁷ and octafluorotoluene.¹⁸ The effect of Cl and of CF_3 groups on ^{19}F shifts are (p.p.m. to low field of C_6F_6): Cl *ortho* 21.69, *meta* 1.03, *para* 6.22; CF_3 *ortho* 22.9, *meta* 2.3, *para* 15.0. These give calculated shifts for the above compound of $F_{(2)}$ 21.69 + 22.9 + 6.22 = 50.81 p.p.m., and $F_{(4)}$ 21.69 + 21.69 + 15.0 = 58.38 p.p.m.

3-Chloroheptafluorotoluene. The spectrum contained five chemically shifted peaks of equal intensity at positions to low field of hexafluorobenzene as internal reference. The shifts are CF_3 108.52, $F_{(2)}$ 46.92, $F_{(4)}$ 38.82, $F_{(5)}$ 2.43, $F_{(6)}$ 28.90 p.p.m. The calculated values are $F_{(2)}$ 46.19, $F_{(4)}$ 37.31, $F_{(5)}$ 3.33, $F_{(6)}$ 30.72 p.p.m.

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