c. **Tail-to-Tail Dimer.**—Activated manganese dioxide (8.70 g) was added to a solution of III (2.40 g) in 50 ml of acetone. The mixture was refluxed for 2 hr in a nitrogen atmosphere. After cooling and filtration, the acetone solution was stripped to a red residue; weight 0.075 g. A chloroform washing (500 ml) of the insoluble oxide was stripped to a red residue (2.314 g). The infrared spectra of both residues were superimposable upon that of authentic IV. No III was recovered.

2,6-Di-*t*-butylphenol.—Activated manganese dioxide (8.7 g) was added to a solution of 2,6-di-*t*-butylphenol (6.8 g) in 50 ml of benzene. The mixture was refluxed for 2 hr. The material soluble in benzene was red, weighed 6.72 g (98%), and was identified by infrared spectrum as 3,3′5,5′-tetra-*t*-butyldiphenoquinone. The molecular weight by mass spectral analyses of a sample crystallized from methanol was 408 (calcd, 408). The crystallized yield was 4.12 g. (60%).

Reaction of Oligomer with Oxides.—Oligomeric 2,6-xylenol polymer was dissolved in ether. The ether solution was extracted three times with a 5% NaOH solution, two times with a 10% KOH solution, and once with water. The solution was dried and stripped. The last base wash was acidified and extracted with ether to detect residual 2,6-xylenol. None was detected.

The low molecular weight oligomer (0.460 g) was dissolved in 50 ml of ethyl ether. Lead dioxide (2.00 g) was added. The mixture was stirred for 15 min at room temperature. After filtration, the ether solution was washed with 20 ml of 10% KOH solution. The base was acidified and extracted with ether. The ether was dried and stripped to afford 12 mg of 2,6-xylenol, identified by infrared spectrum and mass spectrum.

The oligomer (1.957 g) was treated similarly with silver oxide (0.429 g). 2,6-Xylenol (9 mg) was isolated.

The oligomer (1.957) was allowed to react with activated manganese dioxide (0.970 g) to give 70 mg of a base-soluble mixture which was composed of 2,6-xylenol (52 mg) and 2,2′,6,6′-tetramethyl-*p*,*p*′-biphenol. The limited solubility of the latter in petroleum ether (bp 30–60°) was used to separate the components. A washing of the MnO_2 with chloroform gave a 74-mg mixture of polymer and 3,3′,5,5′-tetramethyldiphenoquinone. The quinone (53 mg) was isolated by means of its limited solubility in ethyl ether.

Reaction of 2,6-Xylenol Dimer with Manganese Dioxide.—The dimer II ($n = 0$) was prepared by the method of Lindgren.[9] After several crystallizations from petroleum ether (bp 50–110°), the melting point of the dimer was 107–108°. It was treated with base as in the above section. The dimer (0.939 g) was dissolved in 25 ml of acetone and treated with activated manganese (0.261 g) under nitrogen for 30 min. The base-soluble reaction products were shown to be a mixture of 2,6-xylenol (54 mg) and dimer III (13 mg) by infrared spectra and mass spectra.

Reaction of 2,6-Xylenol Dimer and Oligomer with Copper-Pyridine. a.—The head-to-tail dimer (0.895 g), treated as above with base to remove traces of 2,6-xylenol, was dissolved in 5 ml of pyridine and poured into 15 ml of pyridine containing cuprous chloride (35 mg). The latter solution had been stirring in air for 30 min during which time the copper salt had dissolved and a deep green color had formed. The reaction mixture was stirred rapidly for 30 sec and then poured into a 25% HCl solution. The acid solution was extracted with ether, which in turn was washed with 10% KOH. The base was acidified with hydrochloric acid and extracted with ether. The ether layer was washed with water, dried, and stripped to give 18 mg of 2,6-xylenol, identified by infrared spectrum and undepressed melting point upon admixture with authentic material, and 20 mg of III, identified by infrared spectrum.

b.—Oligomer II (0.575 g) was allowed to react in the same fashion as the dimer II ($n = 0$) with the copper system. The base-soluble material weighed 7 mg and displayed an infrared spectrum identical with that of III. It was derivatized by conversion with activated manganese dioxide to IV (5 mg) identified by infrared spectrum and undepressed melting point with authentic material.

Reaction of 2,6-Xylenol Oligomer with Potassium Ferricyanide.—Oligomer II (1.69 g) was dissolved in ethyl ether (50 ml) and shaken for 30 sec with 5% sodium hydroxide solution (25 ml) containing $K_3Fe(CN)_6$ (0.329 g). The layers were separated. The ether layer contained oligomer (1.50 g). The base-soluble reaction products were I (4.7 mg) and dimer III (18.6 mg).

Electron Spin Resonance Spectrum.—The esr spectrum was observed by the use of a Varian V 4500 spectrometer with a 6-in. magnet and 100-kc/sec field modulation. A 10% solution of 2,6-xylenol in benzene was added to a tube (2 mm) containing activated manganese dioxide.[3] The tube was shaken until the color of the liquid above the solids was yellow, and was then placed in the spectrometer in such a way that the solid–liquid interface was in the cavity of the spectrometer.

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Fluorination of Perhalobenzenes with Potassium Fluoride in Polar Solvents

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In an effort to prepare highly fluorinated aromatic species an extensive study has been made of the reactions of hexachloro- and hexabromobenzene, pentachlorobenzotrifluoride, and 1,4-bis(trifluoromethyl)tetrachlorobenzene with potassium fluoride in polar solvents. The most desirable solvents were found to be N-methylpyrrolidone or tetramethylene sulfone. The reaction was found to be straightforward until three fluorine atoms had been introduced. Continued reaction gave not only further fluorination but also significant amounts of hydrogen-containing species. This was especially evident with hexabromobenzene and was also noted, although to a lesser degree, with hexachlorobenzene and pentachlorobenzotrifluoride. Completely fluorinated products were obtained only from 1,4-bis(trifluoromethyl)tetrachlorobenzene.

The fluorination of chlorinated aliphatic compounds with potassium fluoride in a polar solvent is a convenient method for the preparation of many highly fluorinated materials.[1,2] The reaction has been shown[3] to proceed by nucleophilic displacement of chlorine by fluoride ion, and with certain substrates perfluoro- or monohydroperfluoro olefins are obtained in high yield.[2,4,5] In contrast, hexachlorobenzene has been

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[1] A. L. Henne, *Org. Reactions*, **2**, 49 (1944).

[2] J. T. Maynard, *J. Org. Chem.*, **28**, 112 (1963).

[3] W. T. Miller, J. H. Friedland, and H. Goldwhite, *J. Am. Chem. Soc.*, **82**, 3091 (1960).

[4] (a) A. L. Henne and J. Sedlak, 138th National Meeting of the American Chemical Society, New York, N. Y., Sept 1960; (b) A. L. Henne, U. S. Patent 3,024,290 (March 6, 1962).

[5] G. W. Holbrook and O. R. Pierce, U. S. Patent 3,197,513 (July 27, 1965) (to Dow Corning Corp.).

reported to give only trichlorotrifluorobenzene as the major product.[2,6] Although dichlorotetrafluorobenzene was obtained by refluorination of all fluid fractions from the initial fluorination, it was not possible to force the reaction to produce hexafluorobenzene.

In an effort to prepare more highly fluorinated aromatic species an extensive study has been made of the fluorination with potassium fluoride of hexachloro- and hexabromobenzene, pentachlorobenzotrifluoride, and 1,4-bis(trifluoromethyl)tetrachlorobenzene.

Discussion

Solvent and Reaction Conditions.—The most desirable reaction solvents were found to be N-methylpyrrolidone, as previously reported,[2] and tetramethylene sulfone. The yields were slightly higher using tetramethylene sulfone, and a somewhat less complex product was obtained. Solvents such as 2-pyrrolidone with a labile hydrogen were unsuitable, giving highly reduced products and little or no fluorination.

The best results were obtained with moderate temperatures and reaction times. Temperatures higher than 200° and reaction times longer than 12 hr gave a higher degree of fluorination, but at the expense of overall yield and an increase in degradation products. With hexachlorobenzene in N-methylpyrrolidone intractable tars were obtained. The tars were soluble in acetone and did not contain any starting material or partially fluorinated aromatic products. However, in addition to carbon, hydrogen, and nitrogen, large amounts of chlorine and fluorine were present, indicating substantial solvent–substrate interaction. The degradation products from tetramethylene sulfone were primarily gaseous. Infrared analysis showed the major constituents to be SO_2 and butadiene, together with propylene and other alkenes or alkanes.

Perhalobenzenes. Hexachlorobenzene.—The course of the reaction of hexachlorobenzene in N-methylpyrrolidone at 200° is illustrated in Table I. With the exception of fraction 1, it was possible to separate the products by fractional distillation into fractions containing successively fewer chlorine atoms. The fluorination was found to be straightforward until three chlorine atoms had been replaced, after which hydrogen substitution occurred.

TABLE I

FLUORINATION OF HEXACHLOROBENZENE WITH KF IN N-METHYL-2-PYRROLIDONE[a]

Fraction	Bp, °C (mm)	Mole %	No. of chlorines
1	75–159 (732)	0.6	0–1
2	159–161 (732)	14.8	2
3	108 (42)	68.4	3
4	130 (30)	16.2	4
		100.0	

Composition of fractions			
Fraction	Structure	Mole %	Yield, %
1	C_6F_5H	5	<0.5
	1-H-2-Cl-C_6F_4	25	
	C_6F_5Cl	70	
2	1,3-Cl_2-C_6F_4	75	8
	1,2-Cl_2-C_6F_4	13	1.4
	1,4-Cl_2-C_6F_4	1	0.1
	1-H-3,5-Cl_2-C_6F_3	11	1.2
3	1,3,5-Cl_3-C_6F_3	100	49.2
4	1,2,3,5-Cl_4-C_6F_2	67	7
	1,2,3,4-Cl_4-C_6F_2	33	35

[a] Temperature, 200°; time, 4 hr; yield, 70%.

The directive effect of a single fluorine is shown by the fact that the difluorotetrachlorobenzene fraction was composed primarily of the *meta* isomer, lesser amounts of the *ortho* isomer, and none of the *para* isomer. This may be attributed to activation by a general inductive withdrawal of electrons from all positions and particularly from the *meta* position, coupled with a back-conjugation of electrons to the *para* position as described by Tatlow.[7]

Further fluorination of these isomers would be expected to give all three isomeric trichlorotrifluorobenzenes in approximately equal yield. However, it was found that 1,3,5-trichlorotrifluorobenzene accounted for all but a small part of this fraction. It is believed that the 1,2,3 and 1,2,4 isomers are formed, but are rapidly fluorinated to yield the various isomeric dichlorotetrafluorobenzenes.

It was established that *sym*-trichlorotrifluorobenzene is quite unreactive in this system. Fluorination of a purified sample for 4 hr at 200° gave a 5.6% conversion to 2,4-dichloro-1,3,5-trifluorobenzene and a 4.2% conversion to 1,3-dichlorotetrafluorobenzene. The remainder of the starting material was recovered. The failure to obtain a higher yield from this fluorination is thought to be due to several factors. In the first place all fluorine atoms are *meta* to each other, leading to a mutual deactivation toward further nucleophilic attack on the remaining positions. Reaction with potassium hydroxide in ethanol gave complete conversion to 1,3,5-triethoxytrichlorobenzene. There was no evidence of displacement of chloride ion, thus giving further support to the concept of deactivation of all positions *para* to fluorine.

A second factor is the apparent change in the character of the reaction, leading to significant amounts of the hydrogen-containing products. The reaction path leading to the hydrogen-containing species is unknown. It is interesting, however, to note that in all cases the hydrogen is *para* to fluorine, indicating that directive effects are operative in reduction as well as fluorination.

Hexabromobenzene.—Hexabromobenzene was found to give a pattern similar to that of hexachlorobenzene. However, the degree of fluorination was greater and the amount of reduction was greatly increased. As shown in Table II only a 23% yield of *sym*-$C_6F_3Br_3$ was obtained as compared to a 50% yield of the corresponding *sym*-$C_6F_3Cl_3$. Fractions containing one to two bromines accounted for 67% of the products from C_6Br_6. The most striking difference was in the amount of reduction. The total yield of reduced products was 46%. In contrast C_6Cl_6 gave a 1–2% yield of hydrogen-containing products. Symmetrical $C_6F_3Br_3$ was found to be resistant to further fluorination but, unlike $C_6Cl_3F_3$, gave almost complete conversion to the reduced species.

Trifluoromethyl-Substituted Perhalobenzenes.—Since fluorination of perhalobenzenes did not give a high degree of fluorination, attention was turned to

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[6] G. C. Finger and C. W. Kruse, *J. Am. Chem. Soc.*, **78**, 6034 (1956).

[7] J. C. Tatlow, Second International Symposium on Fluorine Chemistry, Estes Park, Colo., July 1962.

TABLE II

REACTION OF HEXABROMOBENZENE WITH KF IN TETRAMETHYLENE SULFONE[a]

Fraction	Bp, °C (mm)	Mole %	No. of bromines
1	61–63 (42)	28.9	1
2	111 (42)	37.7	2
3	145--146 (24)	33.4	3
		100.0	

Composition of fractions

Fraction	Structure	Mole %	Yield, %
1	1-H-3-Br-C_6F_4	31	7
	1,3-H_2-5-Br-C_6F_3	69	15
2	1,2-Br_2-C_6F_4	3	0.8
	1,3-Br_2-C_6F_4	12	3.4
	1,4-Br_2-C_6F_4	1	0.3
	1-H-3,5-Br_2-C_6F_3	68	19
	1-H-2,6-Br_2-C_6F_3	5	1.4
	1-H-2,3-Br_2-C_6F_3	12	3.4
3	1,3,5-Br_3-C_6F_3	100	23.3

[a] Temperature, 200°; time, 4 hr; yield, 74%.

trifluoromethyl-substituted perhalobenzenes. It was hoped that the strongly electronegative trifluoromethyl group would activate all positions and give completely fluorinated products. This was not achieved with pentachlorobenzotrifluoride. The principal product was obtained in 60% yield and was only partially fluorinated (Table III).

The *ortho,para*-directing effect[8] of a trifluoromethyl group and the *meta*-directing effect of nuclear fluorine combine to lead to a relatively simple reaction path. Reduction was minimized but not eliminated. It is possible that the reduced species arose from impurities in the starting material.

Fluorination[9] of 1,4-bis(trifluoromethyl)tetrachlorobenzene gave high (80%) yields of perfluoro-*p*-xylene. Reaction was rapid and complete, giving no reduced or partially fluorinated products. In contrast to hexachloro- and hexabromobenzene the reaction proceeded readily in dimethylformamide at 150°, thus emphasizing the powerful activating effect of a trifluoromethyl group toward nucleophilic ring substitution by fluoride ion (Table III).

TABLE III

Structure of Product	Yield, %
Fluorination of $CF_3C_6Cl_5$ with KF[a]	
1-CF_3-3-Cl-C_6F_4	9
1-CF_3-3-Cl-4-H-C_6F_3	1.3
1-CF_3-3,5-Cl_2-C_6F_3	60
1-CF_3-3,5-Cl_2-4-H-C_6F_2	12
Fluorination of 1,4-$(CF_3)_2C_6Cl_4$ with KF[b]	
1,4-$(CF_3)_2C_6F_4$	80

[a] Time, 4 hr; temperature, 200°; tetramethylene sulfone. [b] Time, 24 hr; temperature, 150°; dimethylformamide.

Experimental Section

General Fluorination Procedure.—A standard procedure was used for all experiments. A slurry was made of the starting material (0.17 mole), potassium fluoride (1.1 moles), and solvent (500 ml). In the initial experiments the potassium fluoride was rigorously dried and pulverized. Later results indicated that nothing was gained by this procedure, and the reagent was used as received. The slurry was heated with vigorous stirring during the reaction period. On completion the reaction mixture was diluted with an equal volume of water and steam distilled to remove the products. The residue produced during the reaction was separated by filtering, while hot, after steam distillation. The fluorinated products were separated by fractional distillation and identified by elemental analysis, infrared, nmr (F^{19} and H^1 spectra), and gas chromatography. Compounds which were isolated in a pure state are shown in Table IV.

TABLE IV

Compd	Found	Literature
sym-$C_6Cl_3F_3$	Mp 60.0°	60–62[c]
sym-$C_6Br_3F_3$	Mp 97.0–97.5°	98.0–98.5[c]
$C_6Cl_4F_2$	Mp 71.5–72.0°[a]	54[d]
	Mp 66.5–68.0°[b]	
1,4-$(CF_3)_2C_6F_4$	Bp 121.5–123°	122[e]
	$n^{25}D$ 1.3588	$n^{19}D$ 1.3610[e]

[a] Recrystallized from ethanol. Isomer content not known. [b] Crude; mixture of *meta* (67%) and *ortho* (33%) isomers. [c] G. C. Finger, F. H. Reed, and R. E. Oesterling, *J. Am. Chem. Soc.*, **73,** 145 (1951). [d] N. N. Vorozhlzov, Jr., G. G. Yakobson, and N. I. Krizhechkovskaya, *Zh. Obshch. Khim.*, **31,** 1222 (1961). [e] B. Gething and J. C. Tatlow, *J. Chem. Soc.*, 1574 (1961).

Reaction of *sym*-Trichlorotrifluorobenzene with Alcoholic KOH.—Potassium hydroxide (5.61 g, 0.1 mole), *sym*-trichlorotrifluorobenzene (4.64 g, 0.0197 mole), and absolute ethanol (100 ml) were sealed in a heavy-walled glass tube. The tube was shaken until solution was complete, then heated for 70 hr on a steam bath. The vessel was opened and the contents were poured into water. The flocculent precipitate which formed was removed by filtration and washed with a large volume of water. Recrystallization from acetone gave 1,3,5-triethoxytrichlorobenzene, mp 108.5–109.5° (5.7 g, 0.018 mole), in 91.9% yield.

Anal. Calcd for $C_{12}H_{15}Cl_3O_3$: H, 4.77. Found: H, 4.24; F, 0.00.

Acknowledgment.—The authors wish to express their appreciation to J. J. Burke of the Mellon Institute for conducting the nmr studies.

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[8] J. F. Bunnett and R. E. Zahler, *Chem. Rev.*, **49**, 315 (1951).

[9] W. X. Bajzer, Dow Corning Corp., private communication.