Fluorination of Haloaromatic Compounds^{1,2}

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The reactions of BrF_3 , ClF_3 , and IF_5 with C_6Cl_6 , C_6Br_6 , $C_6Cl_5-CF_3$, and other haloaro-ic compounds are described. These reactions are not readily controlled, and explosions matic compounds are described. frequently occurred, particularly when BrF₃ and ClF₃ were used. Dehalogenation of the reaction products led to certain aromatic fluorocarbons, for example, C_6ClF_5 and C_6ClF_4 -CF₃. Completely fluorinated aromatic compounds were not easily obtained, and therefore the process is not recommended for the production of these species.

Introduction 1.

Until the recent disclosure of new methods for preparing hexafluorobenzene [1-3]³ the only published syntheses [4,5] of aromatic fluorocarbons were the conversions of hexachlorobenzene to hexafluorobenzene and of pentachloro- α, α, α -trifluorotoluene to octafluorotoluene by an indirect procedure involving addition of bromine trifluoride, exchange fluorination with antimony pentafluoride, and dehalogenation with zinc.

Attempts were made to modify the method so as to prepare reactive mono- and bi-functional derivatives, as well as the parent fluorocarbons. For ex ample, it was hoped that the final product in the following scheme would be obtained:

$$C_6Br_6 \xrightarrow{BrF_3} C_6F_4Br_8 \xrightarrow{Zn} C_6F_4Br_2$$

Previously, a synthesis of a compound of this type and its conversion to a polyphenyl of low molecular weight was reported [6] from this laboratory. How ever, the synthesis was extremely laborious. The present work was undertaken to find a shorter path to the desired compound, which it is anticipated would lead to the synthesis of thermally stable polymers. The compound prepared earlier was tetrafluoro 1,4-diiodobenzene [6], and in the present work it was expected and hoped that the *meta* and *ortho* isomers would also be obtained.

Results and Discussion 2.

In trying to repeat this previously described preparation, difficulties were experienced in the later, high-temperature stages of the bromine trifluoride reaction. The conditions of temperature and concentration prescribed in the literature led to explosions very frequently, and less severe reaction conditions were insufficient for producing the desired degree of fluorination. It was concluded that the operations described in the original paper are very close to the margin of safety. Milder fluorinations were conducted with apparent safety, leading ultimately to very poor yields of the fluorocarbons but to satisfactory yields of their monochloro derivatives. The stages of these syntheses are identified in the following summary, in which most formulas represent merely typical or rough average composition:



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The fluorination of hexabromobenzene proceeded smoothly, but subsequent reactions produced none of the desired perfluoroaromatic derivatives, although several new compounds were isolated. The scheme of synthesis requires that bromine trifluoride react

only by addition, converting the original $-\dot{C}Br$

groups to saturated CFBr groups. From the be-

havior of the fluorination products, it appears that the bulk and lability of bromine hinder addition and

favor replacement, leading to unreactive CF₂ groups.

The following scheme accounts for some of the products:



The hypothetical primary product XXIX contains "allylic" bromine atoms, easily replaced.

A number of other polyhalogen derivatives of benzene were treated with halogen fluorides as well. The products from tetrahalobenzenes resembled those from the related hexahalobenzenes, but the fluorination was less easily managed. It was noticed that, during the zinc dehalogenation stage, some hydrogen is introduced into the ring when ethanol is the solvent; this occurs to a much greater extent with acetamide as solvent. The dehalogenation in acetamide of one lot of intermediate, approximately $C_6Br_2F_6$ (XXI), resulted in a large yield of a trifluorobenzene, boiling point 83 ° C, identified by its ultraviolet and mass spectra. The precursor of the trifluorobenzene is not clear. Its formation probably involves the replacement of "aromatic" or "unsaturated" bromine by hydrogen. This replacement is known to be effected by zinc plus mild acid [7]

and occasionally by the action of bases on "aromatic" bromine [8]. In aliphatic fluorocarbons, the replacement of halogen by hydrogen has also been reported by Miller [9].

2.1. Fluorinations with Halogen Fluorides

The procedures for hexachlorobenzene and pentachloro- α, α, α -trifluorotoluene were much alike throughout and are therefore described together. The hexachlorobenzene was a commercial product; the pentachloro- α, α, α -trifluorotoluene was a semiliquid slush or wet crystalline mass obtained by exhaustive chlorination of α, α, α -trifluorotoluene [10]. The bromine trifluoride was a commercial product, from several sources, used without purification.

The originally described procedure involved the slow addition of halocarbon to excess bromine trifluoride, in the cold in several portions, with intermittent heating to 100° C after addition of each portion. Two attempts to repeat the procedure led to destructive explosions in the later heating stages. Some of the associated patent specifications suggest other operating conditions [5]. A limited proportion of bromine trifluoride could be reacted smoothly with the halocarbon feed by adding the bromine trifluoride slowly to a stirred slurry of the halocarbon in liquid bromine.

Two forms of apparatus were used for different batch sizes. For batches of up to 500 g of halocarbon, the feed slurry was contained in a 500-ml nickel beaker in an ice bath, and stirred with a ¹/₈-hp stirrer. Bromine trifluoride was dripped in from a copper separatory funnel with a brass needle valve, in which the packing was replaced by Teflon and located on the downstream side, while the delivery tube was long and offset, to allow safe manipulation of the valve. Addition of bromine trifluoride usually required about 4 to 6 hr per batch. Operation was usually conducted outside the building when weather permitted, although in the laboratory a hood with good draft was sometimes used. Warm, humid weather was undesirable, as the condensation of water in the mixture led to waste of bromine trifluoride, excess heat, and accelerated corrosion. In equipment of this size, reaction began energetically and proceeded relatively smoothly until the addition of 1.6 to 1.8 moles of bromine trifluoride per mole of hexachlorobenzene or pentachloro- α, α, α -trifluorotoluene had been completed. After this point, reaction became very slow or ceased. A slight excess of bromine trifluoride appeared to remain unreacted after warming to 20° to 30° C and standing covered overnight.

Large batches (6 kg) of pentachloro- α, α, α -trifluorotoluene were fluorinated in a larger apparatus consisting of a welded Monel can of about 4-liter capacity with widened top to retain foam, a 15-gal ice bath, a 1-liter Monel separatory funnel, and a $\frac{3}{4}$ -hp stirrer. This reaction vessel was monitored by a thermocouple and automatic recorder. The operator was shielded and remained at a distance, except for short trips to change valve settings or to add ice to the bath. The course of reaction in this equipment was not quite consistent with observations in the smaller system. The temperature record on the chart was zigzagged, fluctuating between $+10^{\circ}$ and $+80^{\circ}$ C. An accumulation of bromine trifluoride in the cold alternated with a relatively rapid reaction (and temperature rise) which temporarily exhausted the bromine trifluoride and thus allowed the mixture to cool. Usually, the bromine trifluoride valve was turned off as soon as a sharp temperature rise began. When the flow was resumed before excessive cooling had ensued, accumulation of bromine trifluoride was lessened; and, with the best management, preparation of a large batch was completed in only 3 hr. Because of the great fluctuations observed, it is uncertain whether any of the large batches reached the same end point as the small batches.

There is a possibility that halogen replacement and chain-scission reactions could continue indefinitely, leading to CF_4 as the end product. However, carbon balances showed that loss of carbon in volatile form amounted, at most, to a very small percentage in the fluorination of pentachloro- $\alpha, \alpha, \alpha,$ -trifluorotoluene, although it may have reached 8 percent with hexabromobenzene. It seems obvious that a large batch should not be started too cold, and that it would be quite hazardous to add very much bromine trifluoride until after the occurrence of some temperature rise that indicates the initiation of normal reaction.

Partial fluorinations were conducted upon some 30 small batches and 4 large batches involving, in all, 27 kg of pentachloro- α, α, α -trifluorotoluene, 4 kg of hexachlorobenzene, and 5 kg of hexabromobenzene. No explosions occurred in this stage, although the sharp rises in temperature observed with the large batches suggest that this might be possible with poor management. The character of products from this stage is shown in table 1. The analyses indicate that the present chlorofluoro intermediates, as obtained from this work, are less highly fluorinated and less saturated than those in the literature. It appeared desirable to saturate the materials to the highest possible extent, as any double bonds would lack fluorine atoms needed later, and would probably fail to take up fluorine in the exchange-fluorination step. Accordingly, the clear liquid products of the first step were mixed with more bromine trifluoride and heated to above 100° C, but with disappointing results.

Mixtures containing less than 10 to 15 percent by weight of bromine trifluoride, heated to 110° to 115° C for 6 hr, appeared to lose the fluorinating agent by evaporation, and the analysis and properties were unchanged. Mixtures containing 20 percent by weight of bromine trifluoride, heated to 120° to 130° C, appeared inert until a sudden explosive reaction occurred, vaporizing and spattering the product. In one instance, an explosion of material derived from hexachlorobenzene allowed about a 20 percent recovery of a clean, waxy, crystalline product, XII, probably similar to that mentioned in the literature [4]. Further high-temperature reactions were abandoned.

Other expedients found ineffective were the incorporation of small proportions of cobalt, lead, or manganese as possible catalysts, and, also, long exposure to fluorine gas at 25° C. When selected, high-boiling low-fluorine material derived from pentachloro- α, α, α -trifluorotoluene (II, V) was mixed with bromine trifluoride to form a clear solution, exposure to bright sunlight caused slow formation of bromine and evolution of heat. A low-boiling, highfluorine fraction (III) did not react under the same conditions, although its analysis indicated some unsaturation. Chlorine trifluoride was able to react with these first-stage products (II). Bromine was evolved at first, and the mixture later became clear. The change in properties was, however, minor and the yield of fluoroaromatic products from a trial batch was not notably improved. An attempt to introduce chlorine trifluoride into cold, previously fluorinated material resulted in accumulation without reaction until an explosion destroyed the mixture. The method was not pursued further, despite its possible merits.

2.2. Hexafluorobenzene, Octafluorotoluene, and Some Chloro Derivatives

From the composition of intermediates quoted in the literature, it was hoped that the fluorinated materials could be dehalogenated without the intervention of an antimony pentafluoride reaction. When this step was omitted, however, the yield of product boiling under 145° C was nil; therefore antimony pentafluoride was used as prescribed. The reaction product was sometimes distilled to yield the rough fractions shown in tables 2 and 3, and was sometimes steam-distilled. A steam distillation residue, 40 percent by weight, yielded no useful low-boiling products upon subsequent dehalogenation.

TABLE 1. Fluorination stages for pentachloro- α, α, α -trifluorotoluene

Reaction	Fluorinating agent	Halocarbon	Product formula ª	Weight	d_4^{24}	$n_{_{\mathbf{D}}}^{^{24}}$
a	BrF_3 , cold, 4,800 g BrF_2 hot 200 g	C ₆ Cl ₅ -CF ₃ , 5,600 g	$C_7Br_{0.8}Cl_{3.7}F_{7.8}$ IIa	7, 600	2.00	1.4536
C	SbF ₅ , 1,300 g	11a,° 3,234 g	$C_7Br_{0.5}Cl_{3.5}F_{9.0}$	2,890	1. 87	1. 4186

^a Average composition.

^b Product from reaction (a).

° Product from reaction (b).

 TABLE 2.
 Fractions of fluorinated hexachlorobenzene after treatment with antimony pentafluoride

Boiling point	Weight	d ²⁰ 4	n_{D}^{24}	Gross composition				
				С	Br	Cl	F	
° C/mm 50 to 90/7 90 to 105/7	$g \\ 1, 427 \\ 1, 209$	1.87	1.4427 1.4740	6	0.3	4.0	6.2	
	Boiling point ° C/mm 50 to 90/7 90 to 105/7	Boiling point Weight ° C/mm 50 to 90/7 g 1,427 90 to 105/7	Boiling point Weight d ²⁰ 4 ° C/mm 50 to 90/7 1,427 1,427 1.87 202 90 to 105/7 1.202 2.00	Boiling point Weight d_4^{20} n_D^{24} ° C/mm 50 to 90/7 g 1, 427 1.87 1.4427 90 to 105/7 1.202 2.00 1.4749	Boiling point Weight d_4^{20} n_D^{24}	$\begin{array}{c c} \text{Boiling} \\ \text{point} \\ \end{array} \\ \hline \begin{array}{c} \text{Weight} \\ \text{point} \\ \end{array} \\ \hline \begin{array}{c} d^{20} \\ d^{20} \\ d^{20} \\ \end{array} \\ \hline \begin{array}{c} n_{D}^{24} \\ \hline \\ C \\ \end{array} \\ \hline \begin{array}{c} \text{Br} \\ \hline \\ C \\ \end{array} \\ \hline \begin{array}{c} \text{Br} \\ \hline \\ 0 \\ 1 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ \end{array} \\ \hline \begin{array}{c} 0 \\ 0 \\ 0 \\ 0 \\ \end{array} \\ \hline \begin{array}{c} 0 \\ 0 \\ 0 \\ 0 \\ \end{array} \\ \hline \begin{array}{c} 0 \\ 0 \\ 0 \\ 0 \\ \end{array} \\ \hline \begin{array}{c} 0 \\ 0 \\ 0 \\ \end{array} \\ \hline \end{array} \\ \hline \begin{array}{c} 0 \\ 0 \\ 0 \\ \end{array} \\ \hline \end{array} \\ \hline \begin{array}{c} 0 \\ 0 \\ 0 \\ \end{array} \\ \hline \begin{array}{c} 0 \\ 0 \\ 0 \\ \end{array} \\ \hline \end{array} \\ \hline \begin{array}{c} 0 \\ 0 \\ 0 \\ \end{array} \\ \hline \end{array} \\ \hline \begin{array}{c} 0 \\ 0 \\ 0 \\ \end{array} \\ \hline \end{array} \\ \hline \end{array} \\ \hline \begin{array}{c} 0 \\ 0 \\ 0 \\ \end{array} \\ \hline \end{array} \\ \hline \end{array} \\ \hline \begin{array}{c} 0 \\ 0 \\ 0 \\ \end{array} \\ \hline \end{array} \\ \hline \end{array} \\ \hline \end{array} \\ \hline \begin{array}{c} 0 \\ 0 \\ 0 \\ \end{array} \\ \hline \end{array} \\ \end{array} \\$	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	

TABLE 3. Fractions of fluorinated pentachloro- α, α, α -tri-
fluorotoluene after treatment with antimony pentafluoride

Num- ber	Boiling point	Weight	d ²⁴	n_{D}^{24}	Gross composition			
					C	Br	Cl	F
III	$^{\circ}$ C/mm 25 to 70/10	$g \\ 2,460 \\ 420$	1.836	1.4016	7	0.1	3.3	9.1
V	60 to 115/2	1,430 1,347	$1.882 \\ 1.998$	1.4239 1.4470	7	.48	3.7 3.9	8. 5 7. 8

Dehalogenation in ethanol was conducted as described in the literature [4]. Higher-boiling residues from this step were then dehalogenated in acetamide. The dehalogenation in ethanol furnished relatively pure perhaloaromatic compounds (VI, VII, XVII), but corresponding fractions from the acetamide operation were heavily contaminated with hydrogen compounds (VIII, IX), as indicated by mass spectra, higher refractive index, and lower density. Products of the two operations are compared in table 4. All of the octafluorotoluene was highly contaminated with heptafluorotoluene. The combined product apparently contained about 48 percent C₆F₅CF₃ and 50 percent C₆F₄HCF₃. Iodination of the mixture in fuming sulfuric acid converted the latter component into nearly pure 2-iodoheptafluorotoluene. The perfluorotoluene, which did not react, was subsequently hydrolyzed, yielding pentafluorobenzene.

TABLE4.Fluoroaromatic compounds from ethanol and
acetamide dehalogenations

Boiling range	Nominal formula	From	ethanol	From a	cetamide	Identification	
		d_{4}^{26}	n_{D}^{26}	d_{4}^{26}	n_{D}^{26}		
° C 80 to 83	C_6F_6	1.628	1.3640	1.52	1.3704	XVI, XVIa	
119 to 124 102 to 111 138 to 130	C_6CIF_5 C_7F_8 C_7CIF_7	1.672 1.61 1.67		1.576		X VII, X VIIa VI, VIII VII IX	

An examination of the chloroheptafluorotoluene by nuclear magnetic resonance, for which the authors are indebted to H. S. Gutowsky of the University of Illinois, indicated predominantly 2-chloroheptafluorotoluene with about 15 percent of another isomer, probably 4-chloroheptafluorotoluene.

The structure of the chloroheptafluorotoluene was further established as having the chlorine atom *ortho* [11] to the trifluoromethyl group by conversion

to 1,2,3,4-tetrafluorobenzene. The *ortho* structure shows that fluorine atoms usually failed to add *ortho* to the trifluoromethyl group of the starting material, probably because of steric hindrance.

3. Experimental Procedure

3.1. Hexachlorobenzene and Bromine Trifluoride

A mixture of 100 g of hexachlorobenzene and 200 g of bromine was stirred in a 500-ml nickel beaker, surrounded by an ice bath. A supply of 264 g (1.92 moles) of bromine trifluoride was placed in a copper separatory funnel and about 50 g of this supply was dripped in slowly, with stirring, until the slurry had become nearly liquid. Further increments of hexachlorobenzene were added, followed by minor additions of bromine trifluoride. until a total of 285 g (1.00 mole) of hexafluorobenzene and about 150 g of bromine trifluoride had been added. The remaining bromine trifluoride was then slowly added. The total addition occupied 3 hr; stirring was continued overnight. Bromine and excess bromine trifluoride volatilized, leaving $340 \text{ g of a clear liquid, } d_4^{25} 1.993.$

Analysis: Found: C, 17.2; Br, 15.9; Cl, 40.6; F, 25.0.

3.2. Pentachloro- α, α, α -trifluorotoluene and Bromine Trifluoride (large batch)

In a Monel reactor having a 3.5—liter well and fitted with a ³/₄-hp stirrer was placed 5.72 kg (18.0 moles) of crude pentachloro- α, α, α -trifluorotoluene. From a large Monel separatory funnel, 4.3 kg (31.4 moles) of bromine trifluoride was added to the stirred halocarbon over a period of 6 hr. The reactor was surrounded by crushed ice in a 15-gal can. A distant thermocouple recorder showed temperature fluctuations between $+10^{\circ}$ and $+50^{\circ}$ C. The liquid product weighed 8.48 kg.

In the large-scale work with pentachloro- α, α, α trifluorotoluene a total of 21.60 kg (67.7 moles) of pentachloro- α, α, α -trifluorotoluene and 15.54 kg (113 moles) of bromine trifluoride were reacted to yield 30.42 kg of fluorination product (II). Of this quantity, 28.5 kg was treated with 12.3 kg (57 moles) of antimony pentafluoride, giving a recovery of 20.2 kg of product (III–V). The product was dehalogenated with 16.1 kg of zinc in ethanol, the recovery being 12.38 kg of dehalogenated material, which yielded upon distillation 656 g (about 2.7 moles) of mixed polyflurotoluenes (VI), 4,895 kg (18.7 moles) of 2-chloro- $\alpha, \alpha, \alpha, 3, 4, 5, 6$ -heptafluorotoluene (VII), and 5.5 kg of residue. The smaller operations with 4 kg of hexachlorobenzene yielded about 25 g (about 1%) of crude hexafluorobenzene (XVI) and 307 g (about 12%) of chloropentafluorobenzene (XVII).

3.3. Hexabromobenzene and Bromine Trifluoride

In a 500-ml nickel beaker cooled in an ice bath were placed 138 g (0.25 mole) of hexabromobenzene and 100 ml of bromine. During 3 hr, a mixture of 53 g (0.38 mole) of bromine trifluoride and an equal volume of bromine was added from a copper separatory funnel with stirring. The product (XIX) which formed during the addition weighed 62.5 g and consisted of clear, oily liquid and crystals. It distilled with decomposition at 200° to 250° C under atmospheric pressure, evolving large amounts of bromine. Partial distillation with less decomposition occurred at 1 to 2 mm.

Analysis: Calculated for $C_6Br_4F_6$: C, 14.2; Br, 63.2; F, 22.5. Found: Liquid—C, 14.1; Br, 63.6; F, 19.7. Crystals—C, 14.0; Br, 66.0; F, 17.7.

Another experiment used 552 g (1 mole) of hexabromobenzene and 274 g (2 moles) of bromine trifluoride. Half of the hexabromobenzene was put in the beaker, stirred with 300 g bromine, and onequarter of the bromine trifluoride was added gradually, causing the mixture to become almost completely liquid. The remaining hexabromobenzene was then added, followed gradually by the remaining bromine trifluoride. The operation required 6 hr. After evaporation of volatile substances, the yield was 445 g of clear liquid, d_4^{25} 2.65. Table 5 gives a resume of these fluorination products (XIXa to d, XXVIII).

TABLE 5. Fluorination of hexabromobenzene

Agent	$\begin{array}{c} {\rm Mole} \\ {\rm ratio:} \\ {\rm Br} \ {\rm F}_{3/} \\ {\rm C}_6 {\rm Br}_6 \end{array}$	Yield	d_{4}^{24}	$n_{ m D}^{24}$	Gross composition			Identifi-
0					С	Br	F	cation
${\operatorname{Br}}{\operatorname{F}}_3$ {Br}{\operatorname{F}}_3	$3 \\ 1.5$	$wt \ \% \ 56 \ 45$	2. 58	$1.4248 \\ 1.4682$	$ \begin{array}{c} 6\\ 6 \end{array} $	$4.0 \\ 4.0$	5. 9 5. 3	XIXa XIXb
${\mathop{\rm Br} olimits {\rm F}_3} \atop {\mathop{\rm IF} olimits {\rm IF}_5} $	$\begin{array}{c}2\\1.7\\a&5\end{array}$	\sim^{82}_{50}	2.65 2.68 2.4	$1.5342 \\ 1.4913$	$\frac{6}{-6}$	4.0 3.3	3.5 $\bar{6}.1$	XIXc XIXd XXVIII

^a Fluorinating agent to hexabromobenzene.

3.4. Hexabromobenzene and Iodine Pentafluoride

In a Monel bomb of about 40-ml capacity, a mixture of 30 g (0.05 mole) of hexabromobenzene and 54 g (0.24 mole) of iodine pentafluoride was heated for 80 hr at 170° C. The product, after removal of iodine by thiosulfate, consisted of 18 g of mobile liquid (XXVIII), d_2^{45} 2.4, n_D^{20} 1.4913.

Analysis: Calculated for $C_6Br_4F_6$: C, 14.20; Br, 63.2; F, 22.5. Found: C, 15.4; Br, 56.4; F, 24.9. A larger batch consisting of 0.5 mole of C_6Br_6 and 0.5 mole of IF₅, heated under the same conditions, suddenly evolved bromine, causing the bomb to open and leaving a nearly stoichiometric residue of carbon. No reaction occurred at 96°.

3.5. Iodide Dehalogenations

To a solution of 515 g (3.4 moles) of sodium iodide in 1 liter of acetone in an Erlenmeyer flask was added 400 g of crude fluorination product (XIX) of density 2.65. The mixture was stoppered and left overnight with occasional shaking. After pouring onto ice and removing iodine with bisulfite and thiosulfate, the product was dried and distilled, yielding (XX) 13.5 g, bp $100^{\circ}/35$ mm, $d_4^{25} 2.09$, $n_2^{24} 1.4426$; molecular weight (in benzene), 380; (XXI) 185 g, bp 111° to 113° C/35 mm, $d_4^{25} 2.39$, $n_2^{24} 1.4964$, mp -15° to -17° C, molecular weight (in benzene), 420; (XXII) 59g, bp 95° to $100^{\circ}/5$ mm, $d_4^{25} 2.56$. Fraction (XXII) deposited crystals in the receiver. The analysis of (XXI) suggested that it might be impure C₆Br₂F₆. As a byproduct, a 660-g sample of fluorination product liberated 1 mole of iodine and no fluoride ions.

3.6. Acetamide Dehalogenation

To a three-necked flask containing 95 g of zinc dust and 20 g of sodium iodide in 300 g of acetamide at 100° C, 200 g of fraction XXI (preceding paragraph) was slowly added. The product, bp 83°, amounted to 50 g, had d_4^{25} 1.28 to 1.32, and showed the mass spectrometer peaks and ultraviolet absorption characteristics of impure 1,3,4-trifluorobenzene (XXVII).

3.7. Ethanol Dehalogenation

Absolute alcohol (700 ml) and 81.07 g of zinc dust were stirred in a large three-necked flask, and 310 g of fraction XXI was gradually added. The crude untreated products (XIX), from the reaction of a total of 4.5 kg (8.15 moles) of hexabromobenzene with bromine trifluoride, were processed likewise. The total product was fractionally distilled in a jacketed column. The principal fractions were (XXIII) 121.6 g (0.48 mole), C₆H₂BrF₅, bp 121° to 123° C, d²⁵₄ 1.78, n^{25}_{25} 1.4080; (XXIV) 11.5 g (0.05 mole) impure C₆H₂BrF₃, bp 144° to 146°; (XXV) 225 g (about 0.70 mole) of a fraction mainly consisting of C₆H₂Br₂F₄ and C₆Br₂F₆, bp 164° to 169°/750 mm, 60° to 64°/10 mm, d²⁵₄ 2.09, n^{25}_{25} 1.4565, mp -7.5°; and (XXVI) 20 g of higher-boiling material, bp 80° to 82°/10 mm, d²⁵₄ 2.21. Fraction XXIV was identified by mass spectrometer.

Analysis: Found for XXIII: C, 28.5; H, 0.8; Br, 32.3; F, 38.3. Calculated for $C_6H_2BrF_5$: C, 28.9; H, 0.8; Br, 32.3; F, 38.2. Found for XXV: C, 21.0; H, 0.6; Br, 48.5; F, 28.6. Calculated for $C_6HBr_2F_5$: C, 22.0; H, 0.3; Br, 48.9; F, 29.0. Found for XXVI: C, 22.3; H, 0.4; Br, 55.6; F, 21.5.

3.8. Bromine Trifluoride and Chloranil

Chloranil, 123 g (0.5 mole), was stirred in a nickel beaker with 200 ml of bromine while being cooled in an ice bath. Bromine trifluoride, 100 g (0.75 mole), prediluted with 100 ml of bromine, was gradually dropped in over a period of 4 hr. The product, 130 g, was filtered to yield crystals and an oil. The crystals, after washing with ligroin and recrystallizing from methanol, melted at 64° to 65.5°. The oil distilled at 50° to 98° under 1 mm pressure, and had d_{25}^{25} 2.04. A small sample of the crystals, treated with zinc in ethanol and then oxidized with nitric acid, vielded trichloroquinone.

Analysis: Found for crystals: C, 21.0; Br, 23.7; Cl, 40.7; F, 5.9. Calculated for $C_6BrCl_4FO_2$: C, 20.8; Br, 23.2; Cl, 41.2; F, 5.5. Found for oil: C, 18.2; Br, 26.7; Cl, 32.5; F, 13.0. Calculated for $C_6BrCl_4F_3O_2$: C, 18.8; Br, 20.9; Cl, 37.0; F, 14.9.

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