

Boiling Range of Starting Material, ° C.	% in Desired Boiling Range		
	XCT	Diol 45	Mirando J
< 160 (atm. pressure)	14	23	29
160 (atm.)-147 (10 mm.)	45	24	22
147-208 (10 mm.)	37	46	35
> 208 (10 mm.)	4	7	14

The fractions were increasingly viscous, the low boiling ones being thin oils and those boiling above 300° C. at atmospheric pressure, brittle resins. Fractions of the three crudes having identical boiling ranges varied considerably in appearance and physical properties, but the fractions were so broad that the differences may have resulted largely from differing distributions of material within a fraction. Thus the cut from the XCT crude boiling between 147-208° C. at 10 mm. was markedly less viscous than the corresponding cuts from the Diol 45 and Mirando J crudes; but in the XCT crude most of this fraction came over between 147-175° C. at 10 mm., whereas with Diol 45 and Mirando J much of the material boiled near the upper end of the cut.

#### ACKNOWLEDGMENT

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the work described in this paper, is acknowledged. That author expresses appreciation to H. A. B. Dunning, whose interest and financial support made that early work possible.

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PRESENTED before the Symposium on Fluorine Chemistry as paper 51, Division of Industrial and Engineering Chemistry, 110th Meeting of the AMERICAN CHEMICAL SOCIETY, Chicago, Ill. The work described in this paper is covered also in a comprehensive report of work with fluorine and fluorinated compounds undertaken in connection with the Manhattan Project. This report is soon to be published as Volume I of Division VII of the Manhattan Project Technical Series.

# PREPARATION OF BIS(TRIFLUOROMETHYL)BENZENES

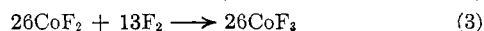
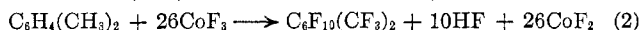
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COMMERCIALY available xylene fractions, pure *m*-xylene, and pure *p*-xylene were converted to bis(trichloromethyl)benzenes by liquid-phase chlorination. The mixtures obtained therefrom were fluorinated with hydrogen fluoride alone and in the presence of antimony halides. Highest yields of bis(trifluoromethyl)benzenes were obtained by fluorination of 1,4-bis(trichloromethyl)benzenes. The conversion of xylene to bis(trifluoromethyl)benzenes in a commercial mixture was about 44%.

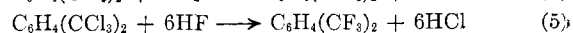
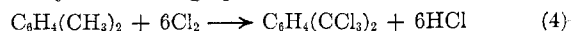
AFTER it was demonstrated that fluorocarbons would be useful in the separation of uranium isotopes by gaseous diffusion, it became evident that the properties of perfluorodimethylcyclohexane, C<sub>8</sub>F<sub>16</sub>, made it suitable for use in this process. The isomeric perfluorodimethylcyclohexanes can be prepared by the reaction of xylenes with either fluorine or certain metal fluorides, of which cobalt trifluoride (CoF<sub>3</sub>) is representative. As illustrated

by Equations 1, 2, and 3, relatively large quantities of fluorine are required for these processes.



A process requiring less elemental fluorine for the production of perfluorodimethylcyclohexane was desired, since large scale production of fluorine appeared to be both difficult and expensive. Such a process would include the introduction of fluorine into the xylene molecule by a fluorinating agent which could be prepared without the use of fluorine.

The chlorination of aromatic compounds containing methyl groups and subsequent fluorination of resulting trichloromethyl compounds is described in the patent literature (1, 4, 5, 7). Hence, it was believed that, in the production of perfluorodimethylcyclohexane, it would be advantageous to convert xylene to bis(trifluoromethyl)benzene, which could then be fluorinated with CoF<sub>3</sub> at a considerable saving in fluorine. This sequence is illustrated by the following equations:

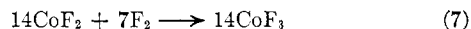
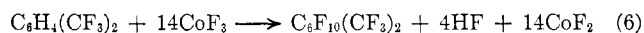


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In practice, the economy in fluorine is even greater than shown by Equations 1, 2, 3, 6, and 7 because the yield of perfluorodimethylcyclohexane from bis(trifluoromethyl)benzene is substantially greater than the yield from xylene.

This paper reports a study of the chlorination of xylenes and the subsequent conversion of bis(trichloromethyl)benzenes to bis(trifluoromethyl)benzenes.

#### CHLORINATION OF XYLENE

It is difficult and expensive to separate the pure isomers of xylene from commercially available mixtures of *o*-, *m*-, and *p*-xylene. Therefore, it was necessary to evaluate the process using mixtures of xylenes which could be obtained at reasonable cost. Since *o*-xylene cannot be converted to 1,2-bis(trichloromethyl)benzene, it was desirable to use a xylene fraction relatively free of *o*-xylene ( $\beta$ ). Accordingly, most of the work was conducted with readily available commercial xylene fractions as starting materials. Three different commercial fractions were used, designated as xylenes A, B, and C. Xylene B was a coal-tar distillate boiling at 137.9–139.4° C., and xylene C was a distillate boiling at 138.4–139.4° C. These fractions were believed to contain substantially no *o*-xylene. The percentage of *p*-xylene was greater in xylene C than in xylene B. Xylene A, which had a wider boiling range, was known to contain a small percentage of *o*-xylene as well as other impurities such as ethylbenzene. In certain instances pure xylenes, obtained from the Eastman Kodak Company, were used.

Xylene was chlorinated photochemically in the apparatus shown diagrammatically in Figure 1. A chlorination tube, *D*, was prepared by sealing 24-mm. Pyrex tubing to one end of a 30-mm. sintered Gooch crucible, *E*. A chlorine inlet tube was provided by sealing 8-mm. tubing to the other end of the crucible. The over-all height of the tube was about 120 cm. This was mounted between two 40-watt fluorescent lamps, *F*.

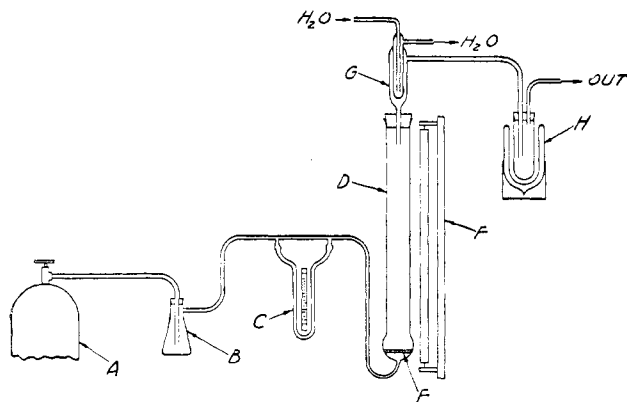


Figure 1. Apparatus for Chlorination of Xylenes

Chlorine was introduced from cylinder *A* through safety trap *B* and flowmeter *C*. Gases from the reaction passed through reflux condenser *G* into a receiver immersed in a dry ice-trichloroethylene bath, *H*. After a short induction period the reaction proceeded very rapidly. The desired reaction temperature was maintained during initial stages of chlorination by cooling the bottom part of the chlorination tube in an ice bath. Later, when the rate of reaction became sluggish, the desired reaction temperature of about 100° C. was maintained by heating the lower portion of the tube electrically. The turbulence of the liquid produced by introduction of chlorine was adequate to maintain a uniform temperature throughout.

Generally, samples of the chlorination mixture were withdrawn at intervals, freed of chlorine and hydrogen chloride by aeration, and analyzed for chlorine (3). In a few cases the course of reac-

tion was followed by observing the weight increase. After purging with air to remove dissolved chlorine and hydrogen chloride, the final product was used for subsequent fluorination experiments without further purification.

While the patent literature describes the chlorination of xylene at 150° C. (5), it was found advantageous to control the temperature of the reaction mixture during chlorination so that the maximum temperature did not exceed 110° C. When the reaction was carried out at this lower temperature, chlorinolysis was less extensive, and less difficulty with burning was encountered during early stages of chlorination.

To determine the degree to which mixtures of *m*- and *p*-xylenes should be chlorinated for production of the maximum possible amount of bis(trichloromethyl)benzenes, a comparison of the rates of chlorination of *m*- and *p*-xylenes was desired. *m*- and *p*-Xylenes were chlorinated under similar conditions, samples being withdrawn at regular intervals to determine the degree of chlorination.

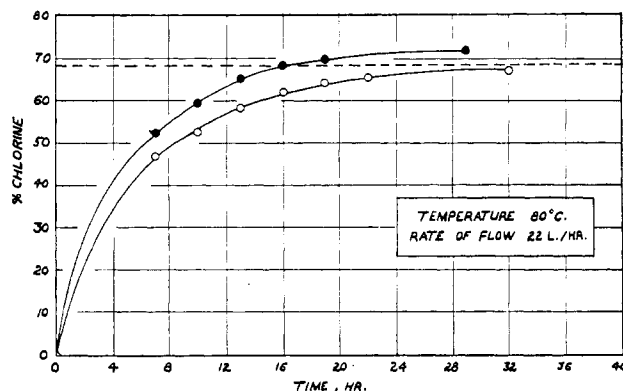


Figure 2. Relative Rates of Chlorination of *m*-Xylene (●) and *p*-Xylene (○)

The data obtained are plotted in Figure 2 and show clearly that *m*-xylene is chlorinated more rapidly than *p*-xylene. They also show that *m*-xylene is converted rapidly to a product containing more chlorine than is required for bis(trichloromethyl)benzene, the additional chlorine being a result of substitutive and/or additive chlorination of the benzene ring. Undoubtedly these reactions occur simultaneously with side-chain chlorination. As a consequence, maximum conversion of *m*-xylene to 1,3-bis(trichloromethyl)benzene is not achieved until more than the theoretical amount of chlorine has been introduced. It was predicted, and later verified, that mixtures of *m*- and *p*-xylenes should be overchlorinated in order to obtain maximum conversion to bis(trichloromethyl)benzenes.

#### FLUORINATION OF BIS(TRICHLOROMETHYL)BENZENES

Fluorinations were conducted in an electrically heated nickel-lined autoclave having a capacity of about 600 ml. The head of the autoclave was attached by compression fittings to a nickel block fitted with a gage, a safety disk, and a valve. Agitation was provided by mounting the autoclave and heater on a rocking device. Temperatures were determined by a thermocouple placed between the heater and the autoclave.

About 0.75 mole of bis(trichloromethyl)benzenes was placed in the autoclave. After the autoclave was secured in position, hydrogen fluoride was added from a small weighed cylinder, the transfer of hydrogen fluoride being facilitated by heating the cylinder. When the transfer was completed and the valves closed, the autoclave was heated to the desired temperature.

The reaction mixture was agitated until the pressure became constant at the particular temperature employed. Then the autoclave was cooled to room temperature and the gases were discharged into a dilute solution of sodium hydroxide. The liquid product was poured from the autoclave, steam-distilled,

TABLE I. FLUORINATION OF BIS(TRICHLOROMETHYL)BENZENES

Expt. No.	Effect of Agitation			Effect of Catalysts						Effect of Time		
	13	22	33	74	71	56	68	72	52	77	42	65
C <sub>6</sub> H <sub>4</sub> Cl <sub>2</sub> , mole	1.0	1.0	0.50	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.44	0.75
HF, moles	14	13.8	6.0	9.0	9.0	9.0	9.0	9.0	9.0	9.0	8.0	9.0
Catalyst	None	SbCl <sub>2</sub> F <sub>3</sub>	None	None	SbCl <sub>5</sub>	SbF <sub>3</sub>	None	SbCl <sub>5</sub>	SbF <sub>3</sub>	None	None	None
Max. temp., ° C.	150	117	148	105	101	104	152	152	158	152	150	152
Total time, hr.	24	14	16	7	7	7	7	7	7	2.5	3.0	7.0
Max. pressure, lb./sq. in.	5000	2000	5000	900	1200	900	1400	1500	2050	1300	1100	1400
Type of autoclave	Stationary	Stationary	Rocking			Rocking					Rocking	
C <sub>2</sub> H <sub>4</sub> F <sub>6</sub> , moles	0.01	...	0.20	0.27	0.32	0.36	0.33	0.35	0.34	0.22	0.20	0.33
Yield, %	1.0	0.0	40	36	47	48	44	47	45	29	45	44

TABLE II. FLUORINATION OF 1,3-BIS(TRICHLOROMETHYL)BENZENE

Expt. No.	X-m-205	X-m-212 <sup>a</sup>	X-m-213 <sup>a</sup>	X-m-206	X-m-207	X-m-210
C <sub>6</sub> H <sub>4</sub> Cl <sub>2</sub> , moles	0.81	0.82	0.82	0.76	0.81	0.69
% Cl	68.9	70.3	70.3	72.6	72.6	71.5
HF, moles	10.0	10.8	10.0	12.25	14.4	9.5
Max. temp., ° C.	155	130	155	160	115	143
Total time, hr.	8.5	7	12.5	9.5	8	8
C <sub>2</sub> H <sub>4</sub> F <sub>6</sub> , moles	0.27	0.35	0.29	0.24	0.29	0.25
C <sub>6</sub> H <sub>4</sub> ClF <sub>3</sub> , moles	...	...	...	0.09	0.11	0.10
C <sub>6</sub> H <sub>2</sub> Cl <sub>2</sub> F <sub>4</sub> , moles	...	...	...	0.06	0.04	...
Yield of C <sub>2</sub> H <sub>4</sub> F <sub>6</sub> , %	33	43	40	32	36	36
Total yield of fluorinated product, %	...	...	...	58	55	52

<sup>a</sup> Polychloroxylenes boiling at 135–145° C. at 3 mm. were used; undistilled chlorination mixtures were used in the other experiments.

and rectified to determine the yield of bis(trifluoromethyl)benzenes.

**EFFECT OF AGITATION.** The reaction between bis(trichloromethyl)benzenes and hydrogen fluoride is essentially one between two mutually insoluble materials. Consequently, unless the mixture is agitated, the only contact between the reactants is at the interface. Experiments showed that little or no conversion to bis(trifluoromethyl)benzenes occurred when bis(trichloromethyl)benzenes were treated with hydrogen fluoride without agitation during the reaction period. As Table I shows, the yield of bis(trifluoromethyl)benzenes was increased from about 1% to about 40% by agitation of the reaction mixture.

**EFFECT OF CATALYSTS.** Antimony halides have been shown to be effective catalysts for trifluorinations with hydrogen fluoride (8). It was assumed that the use of antimony halides might increase the conversion of bis(trichloromethyl)benzenes to bis(trifluoromethyl)benzenes, and the effect of these catalysts was investigated.

When the fluorination was carried out at 100° C. in the absence of a catalyst (Table I), the yield of bis(trifluoromethyl)benzenes was 36%. The use of an antimony trifluoride (SbF<sub>3</sub>) or antimony pentachloride (SbCl<sub>5</sub>) catalyst under similar conditions of time and temperature resulted in an increase in the yield of bis(trifluoromethyl)benzenes to about 48%. However, if the fluorinations were carried out at 150° C. for the same time, yields of bis(trifluoromethyl)benzenes were substantially the same in the presence or absence of antimony halides. Thus, at temperatures of about 100° C. the use of antimony halides definitely improved yields of bis(trifluoromethyl)benzenes, but at about 150° C. there was no appreciable effect.

**VARIATIONS IN TIME.** Studies were made to determine the minimum time required to give maximum yields of bis(trifluoromethyl)benzenes at 150° C. in the absence of catalyst (Table I). Since the yields of bis(trifluoromethyl)benzenes were essentially the same after 3 and after 7 hours and substantially lower after 2.5 hours, it may be concluded that the minimum time necessary for complete reaction under the conditions employed is about 3 hours.

**FLUORINATION OF CHLORINATED *m*-XYLENE.** In an attempt to find commercially applicable methods for improving yields of bis(trifluoromethyl)benzenes, relatively pure isomeric bis(trichloromethyl)benzenes, prepared from *m*-xylene and from *p*-xylene, were fluorinated. Table II presents data for the fluorination of chlorinated *m*-xylene.

When *m*-xylene was chlorinated to a 68.9% chlorine content, and the polychloroxylenes were subsequently fluorinated with hydrogen fluoride, the resultant yield of 1,3-bis(trifluoromethyl)benzene was 33%. Fluorination of chlorinated *m*-xylenes containing 70.3% chlorine gave, on an average, 42% yields of bis(trifluoromethyl)benzenes. Substantial amounts of mono- and dichlorobis(trifluoromethyl)benzenes were obtained in addition to the desired bis(trifluoromethyl)benzenes, and the total yield of fluorinated product approached 60%. Since yields of bis(trifluoromethyl)benzenes were actually increased when the material fluorinated was obtained by over chlorination of *m*-xylene, it is assumed that the increase in chlorine content upon overchlorination is not entirely due to ring chlorination of bis(trichloromethyl)benzene already present in the mixture.

**FLUORINATION OF 1,4-BIS(TRICHLOROMETHYL)BENZENE.** 1,4-Bis(trichloromethyl)benzene was prepared by chlorinating *p*-xylene; the crude bis(trichloromethyl)benzene was purified by recrystallization. Table III gives data for the fluorination of 1,4-bis(trichloromethyl)benzene. When pure 1,4-bis(trichloromethyl)benzene (melting point 110° C.) was fluorinated, yields of bis(trifluoromethyl)benzene ranged from 75 to 81%. These yields are considerably higher than those obtained from mixtures of 1,3- and 1,4-bis(trichloromethyl)benzenes. Although the use of overchlorinated *m*-xylene resulted, upon fluorination, in higher yields of bis(trifluoromethyl)benzene, overchlorinated *p*-xylene gave yields of only 14 to 32%.

**FLUORINATION OF BIS(TRIFLUOROMETHYL)BENZENES FROM TECHNICAL XYLENES.** Initial experiments were conducted by chlorinating commercial xylenes (xylene A) to a chlorine content of approximately 68%, and fluorinating the chlorinated product with hydrogen fluoride at 150° C. The average yields of bis(trifluoromethyl)benzenes were about 39% (Table IV). Since this xylene fraction was known to contain substantial quantities of *o*-xylene and since *o*-xylene is not converted to 1,2-bis(trifluoromethyl)benzene by this process, the low yield was attributed, in part, to the presence of *o*-xylene in the mixture.

A xylene mixture substantially free of *o*-xylene was available (xylene B). Chlorination of this mixture to about 68% chlorine content and subsequent fluorination of the mixture of polychloroxylenes under similar conditions showed a marked increase in yields of bis(trifluoromethyl)benzenes. Average yields of bis(trifluoromethyl)benzenes, obtained by fluorinating chlorinated xylene B, were about 44%. This value is in close agreement with results obtained in commercial operation (8).

TABLE III. FLUORINATION OF 1,4-BIS(TRICHLOROMETHYL)BENZENE

Expt. No.	X-p-216	32	79	80
C <sub>6</sub> H <sub>4</sub> Cl <sub>2</sub> , mole	0.70	0.50	0.75	0.75
HF, moles	10.0	9.0	9.0	9.0
Max. temp., ° C.	210	150	150	150
Total time, hr.	12	16	7	7
C <sub>2</sub> H <sub>4</sub> F <sub>6</sub> , mole	0.57	0.39	0.56	0.56
Yield, %	81	78	75	75

TABLE IV. EFFECT OF VARIATION IN TECHNICAL XYLENE ON FLUORINATION OF BIS(TRICHLOROMETHYL)BENZENES

Expt. No.	33	59	60	42	68	69
$C_6H_4Cl_2$						
Type	A	A	A	B	B	B
Mole	0.50	0.75	0.75	0.44	0.75	0.75
HF, moles	6.0	9.0	9.0	8.0	9.0	9.0
Max. temp., ° C.	148	152	154	150	152	154
Total time, hr.	16	7	7	3	7	7
Max. pressure, lb./sq. in.	..	1500	1500	1100	1400	1300
$C_6H_2F_6$ , mole	0.20	0.30	0.28	0.20	0.33	0.33
Yield, %	40	40	38	44	44	44

TABLE V. DEGREE OF CHLORINATION OF XYLENE C IN THE FLUORINATION OF TECHNICAL BIS(TRICHLOROMETHYL)BENZENES

Expt. No.	X-H-218	X-H-219	X-H-220	X-H-221 <sup>a</sup>	X-H-224	X-H-226	X-H-227	X-H-223	X-H-222
$C_6H_4Cl_2$ , grams	235	245	220	250	255	220	215	200	205
% Cl	68.3	68.3	68.3	68.3	68.8	69.8	69.7	70.5	70.5
HF, moles	16.0	12.5	13.0	13.0	13.5	10.0	10.0	12.5	12.5
Max. temp., ° C.	150	185	225	140	126	205	180	165	200
Total time, hr.	4.5	14.0	7.0	9	9.5	6	13.5	9	12.5
$C_6H_2(CF_3)_2$ , grams	35.4	39.4	31.3	36.7	36.7	51.7	47.7	57.8	59.8
Yield, %	23	23	23	22	21	36	32	42	43

<sup>a</sup> Twenty grams of  $SbCl_5$  were used.

Since highest yields of bis(trifluoromethyl)benzenes were obtained from 1,4-bis(trichloromethyl)benzene, it was believed that conversion to bis(trifluoromethyl)benzenes could be increased by employing as starting material a fraction of technical xylenes richer in *p*-xylene than those previously used. Therefore, xylene C was obtained and investigated for utility as starting material for the commercial process. However, when chlorinated xylene C (68.3% chlorine) was fluorinated under conditions similar to those employed with other chlorinated fractions, the resulting yields of bis(trifluoromethyl)benzene averaged only about 22% (Table V). It was evident that the bis(trichloromethyl)benzenes had changed in quality upon the change in ratio of *m*-xylene to *p*-xylene in the starting coal tar fraction. This change in quality of chlorinated xylenes may be attributed to the differences in relative chlorination rates of the meta and para isomers. Since *m*-xylene chlorinates more readily than *p*-xylene and is more readily overchlorinated, a mixture of chlorinated *m*- and *p*-xylenes containing 68% chlorine would have substantial quantities of xylene derivatives containing dichloromethyl groups, even though the chlorine percentage appeared sufficient. When, xylene C was chlorinated to a higher chlorine content than necessary for xylene B (70.5%) and the chlorination products were treated with hydrogen fluoride, resultant yields of bis(trifluoromethyl)benzenes were about 43% (Table V). The comparative figures show that xylene C required a higher degree of chlorination than did xylene B for production of maximum yields of bis(trifluoromethyl)benzenes upon fluorination of the intermediate chlorinated fraction.

#### ACKNOWLEDGMENT

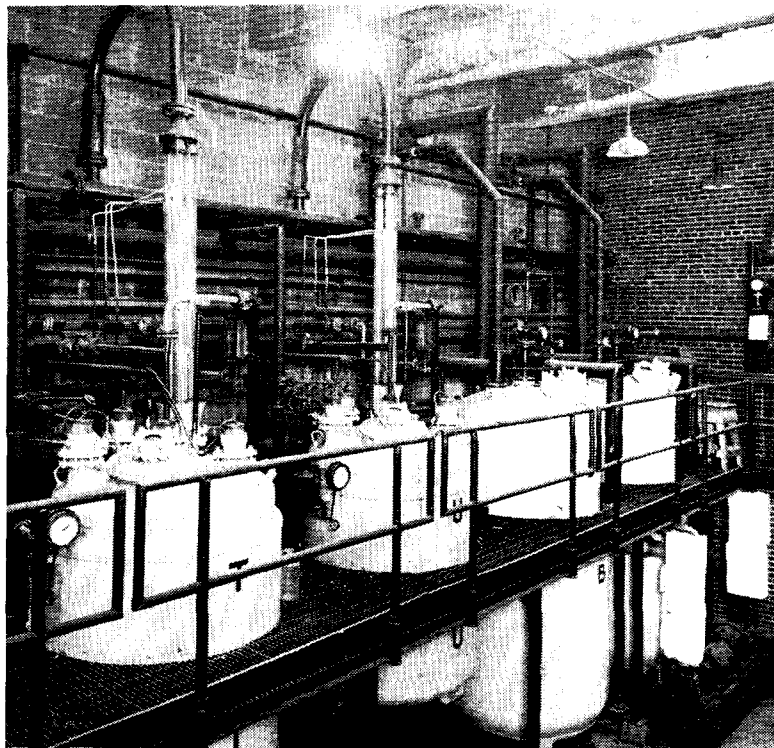
The authors wish to acknowledge cooperation of the Hooker Electrochemical Company in supplying bis(trichloromethyl)benzenes and xylene samples for the investigation reported here. They also wish to acknowledge the assistance of J. F. Miller, A. M. Ribley, M. D. Kinzie, and M. H. Danzig in performing the analytical work. This research

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PRESENTED before the Symposium on Fluorine Chemistry as paper 67, Division of Industrial and Engineering Chemistry, 110th Meeting of AMERICAN CHEMICAL SOCIETY, Chicago, Ill. This paper contains material abstracted from doctoral theses of P. E. Weimer and G. M. Rothrock, submitted to the faculty of Purdue University. The work described in this paper is covered also in a comprehensive report of work with fluorine and fluorinated compounds undertaken in connection with the Manhattan Project. This report is soon to be published as Volume I of Division VII of the Manhattan Project Technical Series.



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