

## Reactions of Trifluoromethyl Radicals. Part I. The Photochemical Reactions of Trifluoroiodomethane with Benzene and Some Halogenobenzenes

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The photochemical reaction of trifluoroiodomethane with benzene in the presence of mercury gives good yields of benzotrifluoride, and similar reactions occur with fluoro-, chloro-, and bromo-benzene to give mixtures of the corresponding halogenobenzotrifluorides. Detailed analysis of the gaseous and liquid products of these reactions is described and the thermal reaction of trifluoroiodomethane with bromobenzene has been re-examined.

THE reactions of arenes with trifluoromethyl radicals from the photolysis of hexafluoroacetone fail to give significant yields of trifluoromethylarenes,<sup>1-4</sup> and no attempt has apparently been made to isolate or identify possible aromatic products from the related reactions with hexafluoroazomethane.<sup>5-7</sup> The thermal reactions of chloro-, bromo-, and iodo-benzene with trifluoroiodomethane at 198 °C do give reasonable yields of the corresponding halogenobenzotrifluorides, and isomer ratios from these reactions have been given,<sup>8</sup> but the

formed by the reactions of trifluoromethyl radicals from the photolysis of trifluoroiodomethane in benzene or in fluoro-, chloro-, or bromo-benzene are now reported.

*Reactions with Benzene.*—Irradiation of a 1 : 1 mixture of trifluoroiodomethane and benzene with u.v. light leads to only a very slow reaction, even in a silica vessel (Table I, experiment 1), but the trifluoromethyl radicals produced are accounted for almost quantitatively as fluoroform (39%) and benzotrifluoride (58%) [equation

TABLE I

Reactions of trifluoroiodomethane with benzene <sup>a</sup>

Expt. no.	t/h	Reactants			Products <sup>b</sup>					
		CF <sub>3</sub> I	C <sub>6</sub> H <sub>6</sub>	Hg	CF <sub>3</sub> I	C <sub>6</sub> H <sub>6</sub>	CF <sub>3</sub> H <sup>c</sup>	PhCF <sub>3</sub>	C <sub>6</sub> H <sub>4</sub> (CF <sub>3</sub> ) <sub>2</sub>	Unident. <sup>d</sup>
1 <sup>e,f</sup>	425	57.8	58.1		50.0	52.2	3.1	4.5		
2	250	44.0	35.3	67	3.0	11.0	5.1	15.0	2.4	20
3	160	58.6	83.9	92	15.3	49.0	11.2	21.6		14
4 <sup>g</sup>	100	58.6	285	89 <sup>h</sup>		230	3.3	38.0	2.9	5

<sup>a</sup> Quantities in mmol (except unidentified products). <sup>b</sup> For g.l.c. conditions, see Experimental section. <sup>c</sup> Contained traces of hexafluoroethane (<0.1 mmol) in each case. <sup>d</sup> Involatile ether-soluble material; given as % by weight of the consumed reactants; shown by g.l.c. and mass spec. in experiment 4 to contain bistrifluoromethyl-biphenyls and -terphenyls and their reduction products. <sup>e</sup> Ambient temperature (ca. 50 °C produced by the lamp); remainder at 80 ± 2 °C. <sup>f</sup> Hydrogen (0.7 mmol) also produced. <sup>g</sup> Also gave cyclohexane (0.12 mmol), cyclohexene (0.31 mmol), and cyclohexa-1,3-diene (0.12 mmol). <sup>h</sup> Increase in weight during reaction corresponded to 62 mmol iodine atoms, but probably contaminated with small amounts of ether-insoluble tar formed according to equation (13). This, and losses during work-up presumably account for the missing benzene and trifluoromethyl radicals. No trifluoromethylmercury(II) iodide (H. J. Emeléus and R. N. Haszeldine, *J. Chem. Soc.*, 1949, 2948) could be detected with certainty.

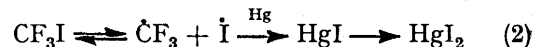
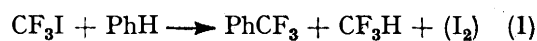
methods of analysis used lacked sensitivity and, in our view (see later), do not yield reliable results. Furthermore, the addition of trifluoromethyl radicals to the benzene ring becomes reversible at ca. 130 °C,<sup>3,5</sup> and above this temperature it is by no means certain that the position of initial attack by a trifluoromethyl radical will be accurately reflected by the isomer distribution finally obtained. Detailed studies of the products

<sup>1</sup> S. W. Charles and E. Whittle, *Trans. Faraday Soc.*, 1960, **56**, 794; S. W. Charles, J. T. Pearson, and E. Whittle, *ibid.*, 1961, **57**, 1356.

<sup>2</sup> J. L. Holmes and K. O. Kutsche, *Trans. Faraday Soc.*, 1962, **58**, 333.

<sup>3</sup> G. A. Chamberlain and E. Whittle, *Trans. Faraday Soc.*, 1971, **67**, 2077.

(1)]. The low availability of trifluoromethyl radicals in this system is not surprising, and presumably arises



because of preferred recombination following fission

<sup>4</sup> S. W. Charles, J. T. Pearson, and E. Whittle, *Trans. Faraday Soc.*, 1963, **59**, 1156.

<sup>5</sup> G. E. Owen, J. M. Pearson, and M. Szwarc, *J. Amer. Chem. Soc.*, 1965, **61**, 1722.

<sup>6</sup> A. P. Stefani and M. Szwarc, *J. Amer. Chem. Soc.*, 1962, **84**, 3661.

<sup>7</sup> I. M. Whittimore, A. P. Stefani, and M. Szwarc, *J. Amer. Chem. Soc.*, 1962, **84**, 3799.

<sup>8</sup> E. S. Huyser and E. Bedard, *J. Org. Chem.*, 1964, **29**, 1588.

of the carbon-iodine bond. Accordingly, all subsequent reactions described here were carried out in the presence of mercury, which effectively removes the iodine atoms and leads to a much more convenient rate of generation of 'free' trifluoromethyl radicals [equation (2)].<sup>9</sup> However, in the presence of mercury and

even after complete decomposition of the iodo-compound, yields of *ca.* 65% of benzotrifluoride are obtained together with small amounts of fluoroform, hexafluoroethane, and involatile material and, perhaps surprisingly, *ca.* 10% of a mixture of bistrifluoromethylbenzenes [*o*- and *p*-C<sub>6</sub>H<sub>4</sub>(CF<sub>3</sub>)<sub>2</sub>] (see later). These

TABLE 2  
Photochemical reactions with PhX at 80 °C<sup>a</sup>

Expt. no. Vessel <sup>b</sup> t/h Reactants	X = F				X = Cl			
	5 SiO <sub>2</sub> 100	6 SiO <sub>2</sub> 100	7 P 34	8 P 34	9 SiO <sub>2</sub> 100	10 SiO <sub>2</sub> 100	11 P 75	12 P 75
CF <sub>3</sub> I	59.0	58.6	38.5	38.6	58.8	58.3	38.3	38.8
PhX	281	293	197	199	258	272	196	196
Hg	86	84	44	51	57	55	47	51
Products <sup>c</sup>								
CF <sub>3</sub> I	12.0	15.6	31.9	30.8	15.6	14.6	16.0	14.1
PhX	250	264	191	193	228	238	176	177
CF <sub>3</sub> H	3.59	3.83	0.13	0.19	5.05	5.68	0.84	0.90
C <sub>2</sub> F <sub>6</sub>	0.22	0.22	0.003	0.006	0.03	0.04	0.03	0.01
CF <sub>2</sub> X					0.67	0.87		
HX	Trace <sup>d</sup>	Trace <sup>d</sup>			3.12	3.74	0.17	0.18
PhH					1.70	2.05	0.37	0.76
PhI					3.00	2.90	0.25	0.42
PhCF <sub>3</sub>					0.75	0.83	0.07	0.09
C <sub>6</sub> H <sub>4</sub> X·CF <sub>3</sub> <sup>e</sup>	27.7	25.5	4.24	5.06	23.1	25.0	15.7	16.1
C <sub>6</sub> H <sub>4</sub> I·CF <sub>3</sub> <sup>f</sup>					0.52	0.58		
Residue <sup>g</sup>	4	4	15	15	3	5	5	4

<sup>a</sup> Quantities in mmol (except residue); liquid and gaseous phases irradiated. <sup>b</sup> SiO<sub>2</sub> = silica; P = Pyrex. <sup>c</sup> For g.l.c. conditions, see Experimental section. <sup>d</sup> SiF<sub>4</sub> and CO<sub>2</sub> also produced. <sup>e</sup> For isomer proportions, see Table 4. <sup>f</sup> Isomer ratio, *o* : *m* : *p* ~ 2.3 : 1.4 : 1.0. <sup>g</sup> Ether-soluble material; given as % by weight of the consumed reactants.

TABLE 3  
Reactions with bromobenzene<sup>a</sup>

Expt. no.	13	14	15	16	17	18	19	20	21	22 <sup>b</sup>
Activation	U.v.	U.v.	U.v.	U.v.	U.v.	U.v.	U.v.	Heat	Heat	Heat
Vessel <sup>c</sup>	SiO <sub>2</sub>	SiO <sub>2</sub>	P	P	P	P	P	P	P	P
T/°C	80	80	80	80	80	80	80	200	200	198
t/h	100	25	100	96	96	43	43	72	71	72
Phase <sup>d</sup>	m	m	m	l <sup>e</sup>	l <sup>e</sup>	v <sup>f</sup>	v <sup>f</sup>	m	m	m
Reactants										
CF <sub>3</sub> I	58.0	62.3	38.8	38.8	38.8	3.86	3.86	11.4	10.7	10.7
PhBr	287	280	194	194	196	20.7	20.4	89.0	94.4	94.4
Hg	82	85	54	49	53	12	10			
Products <sup>g</sup>										
CF <sub>3</sub> I	0.89	45.1	8.36	25.8	30.8	2.15	1.27	7.23	7.10	<i>h</i>
PhBr	233	256	176	185	189	19.4	18.5	84.5	91.2	<i>h</i>
CF <sub>3</sub> H	16.7	4.70	2.81	0.70	0.21	0.75	1.17	1.95	1.75	<i>h</i>
C <sub>2</sub> F <sub>6</sub>		0.04		0.003	0.002	0.02	0.02			
CF <sub>3</sub> Br	3.06	0.17	0.42					0.01	0.01	<i>i</i>
PhH	11.7	1.30	0.22	0.06	0.05	0.01	0.02	0.09	0.06	<i>i</i>
PhI	12.7	10.1	0.22	0.07	0.006	0.009	0.014	0.98	0.97	<i>i</i>
PhCF <sub>3</sub>	3.82	0.20	0.04	0.01	0.007	0.005	0.008	0.042	0.035	<i>j</i>
C <sub>6</sub> H <sub>4</sub> Br·CF <sub>3</sub> <sup>k</sup>	24.1	8.84	16.6	6.25	3.89	0.821	1.27	2.09	1.73	2.76
C <sub>6</sub> H <sub>4</sub> I·CF <sub>3</sub> <sup>l</sup>	1.26 <sup>l</sup>	0.30 <sup>l</sup>						0.01 <sup>m</sup>	0.009 <sup>m</sup>	<i>i</i>
Residue <sup>n</sup>	3 <sup>o</sup>	3	4	7	10	2	2			

<sup>a</sup> Quantities in mmol (except residue). <sup>b</sup> Results from ref. 8. <sup>c</sup> SiO<sub>2</sub> = silica; P = Pyrex. <sup>d</sup> m = mixed, l = liquid, v = vapour. <sup>e</sup> Tubes contained both phases but were fixed vertically, the vapour phase being shielded from the light. <sup>f</sup> Liquid phase shielded; the better recovery of trifluoromethyl radicals in the vapour-phase experiments is attributed to the lower proportion of involatile products formed under these conditions. <sup>g</sup> For g.l.c. conditions, see Experimental section. <sup>h</sup> Detected but not measured. <sup>i</sup> Not mentioned. <sup>j</sup> Not detected. <sup>k</sup> For isomer proportions, see Table 4. <sup>l</sup> Isomer ratio, *o* : *m* : *p* ~ 2.3 : 1.4 : 1.0. <sup>m</sup> Quantity too small for meaningful measurement of isomer ratio. <sup>n</sup> Ether-soluble; % by weight of the consumed reactants. <sup>o</sup> Distilled at 80 °C and 25 mmHg and shown by g.l.c. (Pye 104, 2 m Apiezon L, 180 °C) to contain at least 25 components.

with a reactant ratio close to 1 : 1, a lower yield of benzotrifluoride (35—50%) is obtained and a significant proportion (14—20%) of high boiling material is formed (experiments 2 and 3). Conditions more suited to a quantitative study of this and related reactions involve the use of a five-fold excess of benzene (experiment 4);

conditions were chosen for the initial investigations with the halogenobenzenes.

*Reactions with the Halogenobenzenes.*—Reactions with these substrates in silica vessels under the optimum conditions developed for benzene lead to complications.

<sup>9</sup> R. N. Haszeldine, *J. Chem. Soc.*, 1949, 2856.

With fluorobenzene (Table 2, experiments 5 and 6), some degradation leading to attack on the wall of the reaction vessel is evident, and with the chloro- and bromo-compounds, replacement of the aryl halogen atom by hydrogen, iodine, and trifluoromethyl occurs. Chlorobenzene gives chlorotrifluoromethane, hydrogen chloride, benzene, iodobenzene, benzotrifluoride, and the iodobenzotrifluorides (*o*-, *m*-, and *p*-IC<sub>6</sub>H<sub>4</sub>CF<sub>3</sub>) in addition to the 50–60% yield of chlorobenzotrifluorides (*o*-, *m*-, and *p*-ClC<sub>6</sub>H<sub>4</sub>CF<sub>3</sub>) (Table 2, experiments 9 and 10). With bromobenzene, which apparently does not yield substitution products in the absence of mercury,<sup>8</sup>

work (Table 4) were determined by g.l.c. of the liquid products (see Experimental section), and their reproducibility is indicated by the data from duplicate runs shown in the Tables. Concern regarding the validity of these ratios as a reflection of the initial point of attack on the arene centred around the possibility of preferential photochemical breakdown or isomerisation of some of the products,<sup>10</sup> and on the effect of phase on the reactions, most of which involved irradiation of both liquid and vapour phases.

The former point was investigated by irradiation in both silica and Pyrex in the presence of mercury and

TABLE 4  
Isomer distributions from the halogenobenzenes<sup>a</sup>

Expt. no. <sup>b</sup>	Substrate	XC <sub>6</sub> H <sub>4</sub> CF <sub>3</sub> (%)			Expt. no. <sup>b</sup>	Substrate	XC <sub>6</sub> H <sub>4</sub> CF <sub>3</sub> (%)		
		<i>o</i>	<i>m</i>	<i>p</i>			<i>o</i>	<i>m</i>	<i>p</i>
5	PhF	44.8	28.8	26.4	13	PhBr	44.0	31.0	25.0
6	PhF	43.2	29.0	27.8	14	PhBr	50.1	27.0	22.9
7	PhF	48.3	26.4	25.3	15	PhBr	50.0	28.0	22.0
8	PhF	48.2	26.6	25.2	16	PhBr	47.5	29.6	22.9
9	PhCl	48.6	26.9	24.5	17	PhBr	47.0	30.4	22.6
10	PhCl	48.8	26.6	24.6	18	PhBr	48.7	28.7	22.6
11	PhCl	51.4	25.2	23.4	19	PhBr	49.0	28.6	22.4
12	PhCl	51.7	25.1	23.2	20	PhBr	48.9	31.2	19.9
					21	PhBr	48.7	31.6	19.7
					22 <sup>c</sup>	PhBr	47.5	22.8	29.7

<sup>a</sup> For g.l.c. conditions, see Experimental section. <sup>b</sup> See Tables 2 and 3. <sup>c</sup> Results from ref. 8.

TABLE 5  
Effect of irradiation on the isomer mixtures

Vessel <sup>c</sup>	<i>t</i> /h	X	Reactants <sup>a</sup>				Products <sup>b</sup>			
			PhX	Hg	XC <sub>6</sub> H <sub>4</sub> CF <sub>3</sub>			XC <sub>6</sub> H <sub>4</sub> CF <sub>3</sub>		
					<i>o</i>	<i>m</i>	<i>p</i>	<i>o</i>	<i>m</i>	<i>p</i>
SiO <sub>2</sub>	120	Cl	258	77	10.6 (49.5)	5.76 (26.6)	5.46 (23.9)	46.3	28.4	25.3
P	120	Cl	155	71	6.37 (49.5)	3.47 (26.5)	3.28 (23.9)	49.2	27.4	23.4
SiO <sub>2</sub>	40	Br	115	43	4.06 (43.1)	2.99 (31.1)	2.41 (25.8)	42.0	32.1	25.9
P	40	Br	52.9	39	1.87 (43.1)	1.38 (31.1)	1.11 (25.8)	42.8	30.2	27.0

<sup>a</sup> In mmol, isomer proportions (%) (figures from g.l.c.) in parentheses. <sup>b</sup> Isomer proportions (%); absolute quantities not determined. <sup>c</sup> SiO<sub>2</sub> = silica; P = Pyrex.

loss of bromine is substantial and an appreciable proportion of iodobenzene is formed (Table 3, experiments 13 and 14), particularly at low conversions of trifluoriodomethane (experiment 14).

These difficulties are caused mainly by photochemical breakdown of the aromatic carbon-halogen bond, and their significance is greatly reduced when the same reactions are carried out in Pyrex vessels (which also eliminate the possibility that photochemical activation of the aromatic ring occurs before attack by the trifluoromethyl radical) (Table 2, experiments 7, 8, 11, and 12; Table 3, experiments 15–19). Separate experiments show that the photochemical decomposition of chloro- or bromo-benzene in the presence of mercury gives some benzene but mainly involatile material and, as expected, is much slower in Pyrex than in silica.

*Determination of Isomer Ratios.*—The isomer ratios from the halogenobenzotrifluorides obtained in this

the parent halogenobenzene of mixtures of the isomeric chloro- or bromo-benzotrifluorides, made up in approximately the proportions produced during the reactions with trifluoriodomethane. The only significant effect on the isomer ratios was a 3% reduction in the proportion of *o*-chlorobenzotrifluoride which occurred during irradiation for 120 h in silica (Table 5). However, the results shown in Tables 2–4 reveal that prolonged irradiation in silica results in a reduced proportion of *o*-halogenobenzotrifluoride in all cases, again indicating that the results from the Pyrex vessels are the more trustworthy.

The effect of phase was investigated by means of reactions with bromobenzene in which only the liquid or the vapour phase was irradiated; closely similar isomer ratios and percentage yields of aromatic products were obtained (Tables 3 and 4, experiments

<sup>10</sup> Cf. K. E. Al-Ani, *J. Chem. Phys.*, 1973, **58**, 5073.

16—19), but the vapour-phase reactions led to a marked increase in the yield of fluoroform (see later).

**Thermal Reactions.**—The isomer distributions produced during the photochemical reactions of chloro- and bromo-benzene at 80 °C differ significantly from those reported by Huyser and Bedard for the corresponding reactions induced thermally at 198—200 °C (e.g. Table 4, experiment 22).<sup>8</sup> Furthermore, the difference lies in the opposite direction from the expected move towards a less selective reaction at the higher temperature, perhaps suggesting that the photochemical reactions may involve excited states which do not participate in the thermal reactions.

However, in our hands, the thermal reaction of bromobenzene with trifluoroiodomethane at 200 °C, followed by analysis by g.l.c. gives an isomer ratio (Table 4, experiments 20 and 21) which is much more consistent with that obtained from the photochemical reactions; products which were not detected by Huyser and Bedard, notably an appreciable yield of iodobenzene, are also formed (Table 3, experiments 20 and 21). We find accurate analysis of the isomeric bromobenzotrifluorides in the presence of a large excess of bromobenzene to be impossible by i.r. spectroscopy (the method used by Huyser and Bedard); however, the i.r. spectrum of the mixture of isomers produced in our thermal reactions resembles that of a standard mixture made up in the proportions indicated by the chromatographic analysis rather than that of a mixture with the proportions given by Huyser and Bedard.

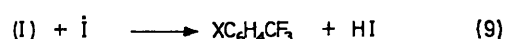
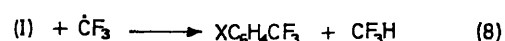
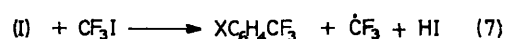
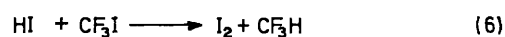
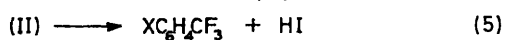
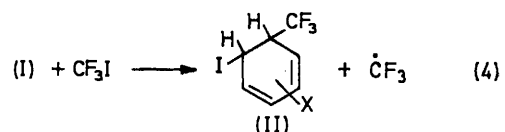
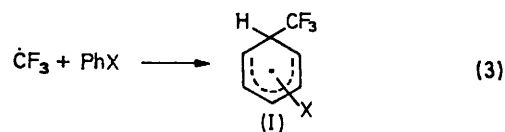
No explanation for this anomaly is apparent to us, but there now seems no reason to believe that the photochemical experiments involve a different reaction pathway from those initiated thermally.

#### DISCUSSION

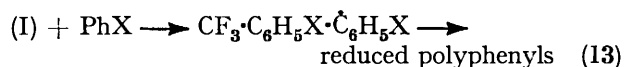
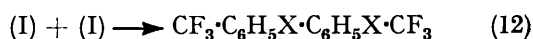
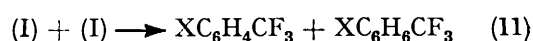
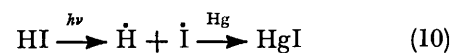
The probability that the reaction of polyfluoroalkyl radicals with benzene and/or substituted benzenes proceeds *via* the formation of a  $\sigma$ -complex (I) [equation (3)], analogous to that produced during the attack of aryl radicals on arenes,<sup>11</sup> has been discussed by others and is generally accepted.<sup>1-8,12</sup> The route from intermediates of type (I) to the trifluoromethylarenes, which form by far the major products of the present reactions, is much less clear. Huyser and Bedard favour the chain-mechanism propagated by equations (4)—(6) for their thermal reactions,<sup>8</sup> but induced decomposition of trifluoroiodomethane by the intermediate (I) [equation (7)] is a clear alternative to equations (4) and (5).

It has been argued that equation (8) is unlikely to occur in the liquid phase or at other than low pressures in the gas phase,<sup>7</sup> and equation (6) therefore seems the most likely source of fluoroform.<sup>8</sup> However, during the present work, appreciable yields of fluoroform were produced only in the reaction with benzene in the absence of mercury, in the vapour-phase photochemical

reaction with bromobenzene, and in the thermal reactions with bromobenzene, and it seems likely that it is only in these reactions that the concentration of



hydrogen iodide becomes appreciable. In all other cases, the hydrogen atom lost from the  $\sigma$ -complex (I) appears for the most part in the high-boiling residues, shown by mass spectrometry to contain biphenyls and terphenyls carrying a variable number of additional hydrogen atoms. Traces of cyclohexadienes, cyclohexene, and cyclohexane are also formed in the reaction with benzene. It is probable, therefore, that equations (5), (7), and/or (9) are responsible for the high yields of trifluoromethylarenes formed in most of the reactions, that they are followed by equation (10), and that the hydrogen atom produced in equation (10) is absorbed by the by-products produced in equations (11)—(13).

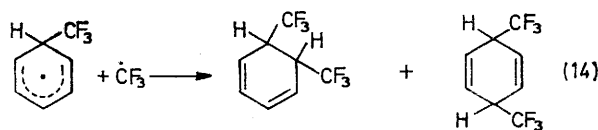


Calculations based on reported<sup>4,7</sup> figures for the relative reactivities of benzene and benzotrifluoride towards trifluoromethyl radicals reveal that the yield of bistrifluoromethylbenzenes (*ca.* 10%) formed in the reaction of trifluoroiodomethane with benzene cannot be accounted for by further attack on the benzotrifluoride formed during the reaction. Since only the *ortho*- and *para*-isomers are detected, it is likely that they are formed by combination of trifluoromethyl radicals with the  $\sigma$ -complex [equation (14)], followed by oxidation of the cyclohexadienes by any of the radicals

<sup>11</sup> G. H. Williams, 'Homolytic Aromatic Substitution,' Pergamon, Oxford, 1960, pp. 49 *et seq.*

<sup>12</sup> M. Ya. Turkina, I. P. Gragerov, and S. L. Dobyichin, *Zhur. Org. Khim.*, 1971, 7, 1541.

present in the system.<sup>13</sup> Bistrifluoromethylarenes are detected only in trace amounts in the other reactions studied.



Because of the high yields of trifluoromethylarenes produced in the reactions described here, we believe that the photochemical reactions provide a sound basis for the study of reactivity and orientation in the attack of trifluoromethyl radicals on aromatic compounds. Discussion of the isomer distributions produced during the reactions with the halogenobenzenes will be incorporated in a later paper in this series.

#### EXPERIMENTAL

**Materials.**—Trifluoroiodomethane,<sup>14</sup> benzene, fluorobenzene, chlorobenzene, and bromobenzene were purified by fractional distillation, and their purity was confirmed by g.l.c. and i.r. spectroscopy. All reference compounds except *p*-bromobenzotrifluoride<sup>15</sup> and 1,2-bistrifluoromethylbenzene<sup>16</sup> were commercial samples, the purities of which were confirmed by g.l.c. and by i.r. spectroscopy (where reference spectra were available) or elemental analysis.

**Apparatus.**—Except where otherwise stated, reaction tubes were of ca. 300 ml capacity (cylindrical, ca. 30 × 3.5 cm i.d.) and, for reactions above ambient temperature, were heated in a rectangular furnace, one side of which was cut away to permit irradiation. The apparatus was agitated during irradiation, which in every case was provided by a Hanovia S500 lamp placed 15 cm from the reaction vessel. Temperature control during reactions at 80 °C was to ±2 °C, and thermal reactions were conducted in a completely enclosed electric furnace at 200 ± 2 °C. G.l.c. was achieved with a Perkin-Elmer 451 fractometer (thermistor detector), a Griffin and George D6 (gas-density balance), and a Pye Series 104 chromatograph (model 24) (flame ionisation). I.r. spectra were measured with a Perkin-Elmer No. 21 instrument and mass spectra with an A.E.I. MS/2H instrument.

**Procedure.**—Reaction tubes were loaded *in vacuo* with degassed reagents and sealed *in vacuo*. Non-condensable products were adsorbed on charcoal and condensable gaseous products were separated by fractional condensation *in vacuo* to give trifluoroiodomethane (condensing at -130 °C) and a -196 °C fraction, which was analysed by gas-solid chromatography on the PE 451 instrument with a 4 m column of alumina at room temperature. Less volatile products were dissolved in ether, and the solution was filtered, washed with aqueous potassium iodide, and dried. The solution was concentrated by distillation through a packed fractionating column, the distillate being shown by g.l.c. to contain no reaction products. The concentrated

solution was either analysed directly by g.l.c. or fractionally distilled with the addition of decalin as a 'chaser' to facilitate separation of all the benzene derivatives from high-boiling material before analysis by g.l.c. Rigorous checks were carried out to ensure that quantitative analysis was achieved by these methods. The conditions used for the chromatographic analysis of each product mixture were as follows: benzene, experiment 1, PE 451, 2 m trixylenyl phosphate (TXP), 90 °C, experiment 2, D6, 3 m TXP, 100 °C, experiment 3, PE 451, 2 m Silicone MS550, experiment 4, main fraction (b.p. 80–103 °C), Pye 104, 6 m Bentone, 72 °C and 8 m TXP, 74 °C, high-boiling material (b.p. 29–44 °C at 4 mmHg), D6, 2 m Silicone MS550, 150 °C; chlorobenzene, PE 451, 2 m TXP, 155 °C; fluorobenzene, D6, 3 m TXP, 73 °C (for *o*:*p* ratio) and 8 m Silicone MS550, 96 °C (for *m*:*p* ratio); bromobenzene, Pye 104, 2 m Bentone, 145 °C (ca. 30% w/w of the stationary phase on Celite in each case; carrier gas, N<sub>2</sub>). Complete quantitative calibration with standard mixtures of pure components was conducted for all chromatographic analyses.<sup>17</sup> The results are shown in Tables 1–4.

**Irradiation of Chlorobenzene.**—Chlorobenzene (32.2 g, 286 mmol) and mercury (12.15 g, 60.5 mmol) were irradiated at 80 °C in a 300 ml silica tube for 96 h and gave hydrogen chloride (0.069 g, 1.9 mmol). The walls of the reaction tube were coated with a film of dark brown solid, and filtration and distillation of the liquid products gave chlorobenzene (32.1 g, 285 mmol), shown by g.l.c. (Pye 104, 6 m Bentone, 170 °C) to contain benzene (0.016 g, 0.21 mmol). Similar irradiation in Pyrex led to quantitative recovery of the chlorobenzene, shown to be pure by g.l.c.

**Irradiation of Bromobenzene.**—Bromobenzene (44.4 g, 283 mmol) and mercury (13.45 g, 66.9 mmol) were irradiated at 80 °C in a 300 ml silica tube for 100 h and gave a trace of hydrogen bromide (0.0081 g, 0.1 mmol). The liquid products were filtered, distilled, analysed by g.l.c. (Pye 104, 6 m Bentone, 170 °C), and shown to contain bromobenzene (42.5 g, 271 mmol) and benzene (0.15 g, 1.9 mmol). An organic tar (0.45 g) and an inorganic solid (1.55 g) were also formed. Irradiation of bromobenzene (30.8 g, 196 mmol) and mercury (15.45 g, 76.9 mmol) in Pyrex for 100 h at 80 °C gave hydrogen bromide (0.004 g), benzene (0.006 g), and bromobenzene (30.7 g).

**Irradiation of the Isomer Mixtures.**—Chloro- or bromobenzene and mixtures of the corresponding halogenbenzotrifluorides were irradiated at 80 °C in the presence of mercury under the conditions shown in Table 5. In each case, traces of hydrogen halide, benzene, and benzotrifluoride were formed, and the isomer distributions after the irradiation, determined in the usual way, are shown in Table 5.

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<sup>13</sup> Cf. G. E. Corbett and G. H. Williams, *J. Chem. Soc.*, 1964, 3437.

<sup>14</sup> R. N. Haszeldine, *J. Chem. Soc.*, 1951, 584.

<sup>15</sup> M. Markarian, *J. Amer. Chem. Soc.*, 1952, **74**, 1858.

<sup>16</sup> W. R. Hasek, W. C. Smith, and V. A. Engelhardt, *J. Amer. Chem. Soc.*, 1960, **82**, 543.

<sup>17</sup> G. P. Irvin, Ph.D. Thesis, Manchester, 1970.