

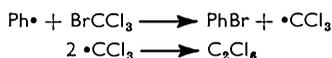
**441. Reactions of Aryl Radicals with Aliphatic Compounds. Part III.<sup>1</sup>  
The Reactions of Phenyl Radicals with Bromotrichloromethane**

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Results are reported on the reactions of phenyl radicals derived from four different sources with bromotrichloromethane.

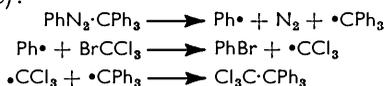
In a previous Communication<sup>2</sup> the results were reported of a semiquantitative study of the reactions between phenyl radicals derived from four different sources and carbon tetrachloride, chloroform, and bromoform. Results are now reported on similar reactions carried out with bromotrichloromethane.

The decomposition of benzoyl peroxide in an excess of bromotrichloromethane at 85° for three days gave bromobenzene and hexachloroethane as the main products of the reaction. This result is to be expected on account of the weakness of the carbon-bromine bond and is in agreement with the known behaviour of bromotrichloromethane in free-radical addition reactions with ethylenic double bonds.<sup>3,4</sup> The main reaction can be represented thus:



In addition acidic compounds are formed, which include *p*-trichloromethylbenzoic acid and smaller quantities of benzoic, phthalic, and terephthalic acids, the latter being derived from hydrolysis of some of the *p*-trichloromethylbenzoic acid during the working-up procedure. The formation of *p*-trichloromethylbenzoic acid in this reaction is in close agreement with the known results of similar reactions carried out with carbon tetrachloride and chloroform.<sup>2,5</sup>

A similar reaction with phenylazotriphenylmethane gave bromobenzene and 1,1,1-trichloro-2,2,2-triphenylethane as the main products of the reaction. No hexachloroethane was detected. Minor products were triphenylmethanol, triphenylmethane, and tetraphenylmethane. The main reactions can be represented as follows (without implying any mechanistic significance):



<sup>1</sup> Part II, D. H. Hey and J. Peters, *J.*, 1960, 89.

<sup>2</sup> D. H. Hey and J. Peters, *J.*, 1960, 79.

<sup>3</sup> M. S. Kharasch, O. Reinmuth, and W. H. Urry, *J. Amer. Chem. Soc.*, 1947, **69**, 1105.

<sup>4</sup> J. I. G. Cadogan, Enid G. Duell, and P. W. Inward, *J.*, 1962, 4164.

<sup>5</sup> J. Böseken and H. Gelissen, *Rec. Trav. chim.*, 1924, **43**, 869.

This reaction thus follows closely the corresponding reactions with carbon tetrachloride<sup>2,6</sup> and with chloroform.<sup>2</sup>

The decomposition of nitrosoacetanilide in bromotrichloromethane gave a product from which only bromobenzene, acetic acid, and a little phenol were isolated. It thus follows closely the corresponding reaction with carbon tetrachloride.<sup>2</sup> The reactions with benzenediazonium chloride were carried out by the three procedures (A), (B), and (C) previously reported.<sup>2</sup> Bromobenzene was formed in all three cases. Hexachloroethane was isolated only in method (B). Method (C) also gave phenol and small quantities of 4-hydroxy- and 2-hydroxy-azobenzene.

The qualitative and semiquantitative correspondence shown between the reactions with carbon tetrachloride and with bromotrichloromethane is summarised in the Table.

Yields of bromobenzene from bromotrichloromethane and of chlorobenzene from carbon tetrachloride by reaction with phenyl radicals from different sources (expressed as moles per mole of radical source)

Radical source	With BrCCl <sub>3</sub> †	With CCl <sub>4</sub> †
	PhBr	PhCl
Benzoyl peroxide .....	1.05	1.28
Phenylazotriphenylmethane .....	0.85	0.27
Nitrosoacetanilide .....	0.17	0.32
Benzenediazonium chloride (A) * .....	0.24	0.28
Benzenediazonium chloride (B) * .....	0.45	0.35
Benzenediazonium chloride (C) * .....	0.06	0.06

\* For description of methods (A), (B), and (C), see Experimental section. † Ref. 2. ‡ This work.

#### EXPERIMENTAL

The reactions, reagents, and analytical methods were similar to those described in Part I.<sup>2</sup> Bromotrichloromethane was purified by repeated fractionation; the pure product had b. p. 105°,  $n_D^{26}$  1.5025.

*Reaction with Benzoyl Peroxide.*—Benzoyl peroxide (24.2 g.) in bromotrichloromethane (397 g.) was allowed to decompose at 85° for 3 days in the dark. After 5 days in the refrigerator *p*-trichloromethylbenzoic acid (3.27 g.) separated (m. p. 196—197° after crystallisation from carbon tetrachloride). The bromotrichloromethane solution was washed with aqueous sodium carbonate and dried (Na<sub>2</sub>SO<sub>4</sub>). The aqueous extract was boiled, and subsequent acidification with hydrochloric acid gave a mixture of acids from which benzoic acid (0.24 g.), m. p. 119°, phthalic acid (0.07 g.), m. p. 190°, and terephthalic acid (1.525 g.), m. p. >300° were isolated by the method previously described.<sup>2</sup> The main bromotrichloromethane solution was fractionated and the distillate was collected at 104—105°. Refractionation gave bromotrichloromethane and left a residue (10.45 g.), which on dinitration (as previously described) gave 1-bromo-2,4-dinitrobenzene (1.125 g. ≡ 0.715 g. of bromobenzene). The residue from the main distillation deposited hexachloroethane (5.45 g.), m. p. 185°, which was filtered off. Distillation of the filtrate gave a liquid, b. p. 104—155°/760 mm. (12.37 g.), and left a residue (17.78 g.). The liquid distillate contained a little bromotrichloromethane but consisted largely of bromobenzene, which on dinitration gave 1-bromo-2,4-dinitrobenzene (11.75 g. ≡ 7.47 g. of bromobenzene). The residue deposited more hexachloroethane (2.97 g.), which was filtered off. Fractionation of the filtrate gave (i) bromobenzene (8.30 g.), b. p. 40°/2 mm., estimated as 1-bromo-2,4-dinitrobenzene (13.06 g.); (ii) hexachloroethane (2.0 g.), b. p. 60°/2 mm., and (iii) a product, b. p. 100—105°/2 mm. (0.3 g.), which on hydrolysis gave some terephthalic acid (methyl ester, m. p. and mixed m. p. 140°). The total weights of bromobenzene and hexachloroethane from this experiment are therefore 16.48 and 10.42 g., respectively.

*Reaction with Phenylazotriphenylmethane.*—A solution of phenylazotriphenylmethane (17.4 g.) in bromotrichloromethane (298 g.) was maintained at 55° for 8 hr. The temperature was then raised to 75° for 20 hr. No solid product separated at 0°. The excess of solvent was removed by distillation and the distillate was refractionated. The residues for both processes were washed with carbon tetrachloride and the combined solutions were distilled with steam. The organic layer in the distillate boiled below 155° and dinitration gave 1-bromo-2,4-dinitrobenzene (10.32 g. ≡ 6.56 g. of bromobenzene), m. p. 69°. The residue from the steam-distillation solidified (19.8 g.) and trituration with ether gave 1,1,1-trichloro-2,2,2-triphenylethane

<sup>6</sup> H. Wieland and K. Heymann, *Annalen*, 1934, 514, 154.

(5.15 g.), m. p. 237° after crystallisation from benzene. Subsequent trituration with benzene-light petroleum (b. p. 40—60°) gave triphenylmethanol (1.10 g.), m. p. and mixed m. p. 160—164° after crystallisation from ethanol. Chromatographic treatment of the benzene-light petroleum mother-liquor and successive elution with light petroleum, benzene-light petroleum, and benzene-ether gave tetraphenylmethane (0.02 g.), m. p. and mixed m. p. 284°, and triphenylmethanol (0.91 g.) m. p. 154—157°. Final distillation of the high-boiling residue at 0.3 mm. gave some triphenylmethane (0.30 g.), m. p. 85°, triphenylmethanol (0.08 g.), m. p. 150—153°, and 1,1,1-trichloro-2,2,2-triphenylethane (0.06 g.), m. p. 235—236°. No hexachloroethane was detected.

*Reaction with Nitrosoacetanilide.*—A solution of nitrosoacetanilide (8.2 g.) in bromotrichloromethane (298 g.) was maintained at 25° and after 4 days it was heated at 75° for 1 hr. The reaction mixture was extracted successively with aqueous sodium hydroxide, and dilute hydrochloric acid, and dried ( $\text{Na}_2\text{SO}_4$ ). The alkaline washings gave phenol (0.31 g.) and acetic acid but no product was obtained from the acid washings. The bromotrichloromethane solution was fractionated and the distillate collected at 104—105°. The distillate was refractionated and the residues from both distillations were combined and again distilled. Dinitration gave 1-bromo-2,4-dinitrobenzene (2.04 g.  $\equiv$  1.30 g. of bromobenzene), m. p. 67—69° after crystallisation from ethanol. No other products were isolated.

*Reactions with Benzenediazonium Chloride.*—Reactions with bromotrichloromethane (298 g.) were carried out with diazotised aniline (from 18.6 g. of base) as follows: (A) by dropwise addition of the diazonium solution to a vigorously stirred cold mixture of the organic liquid and aqueous sodium hydroxide, (B) by addition of aqueous sodium hydroxide to the cold mixture of organic liquid and diazonium solution, and (C) by addition of aqueous sodium acetate to the cold mixture of the organic liquid and the diazonium solution, as previously described.<sup>2</sup> The products from these reactions were distilled with steam. The organic distillates were separated and dried ( $\text{Na}_2\text{SO}_4$ ). Excess of bromotrichloromethane was collected at 104—105° and the distillate was refractionated. The combined residues were distilled up to 155° and dinitration of the distillates gave from (A) 1-bromo-2,4-dinitrobenzene (11.925 g.  $\equiv$  7.58 g. of bromobenzene), m. p. 69°, from (B) 1-bromo-2,4-dinitrobenzene (22.12 g.  $\equiv$  14.06 g. of bromobenzene), m. p. 65—69°, and from (C) 1-bromo-2,4-dinitrobenzene (2.97 g.  $\equiv$  1.89 g. of bromobenzene), m. p. 66—68°. Hexachloroethane was isolated only from reaction (B). Reaction (C) also gave phenol (1.15 g.) and small quantities of 4-hydroxy- and 2-hydroxy-azobenzene, m. p.s and mixed m. p.s 152 and 80°, respectively.