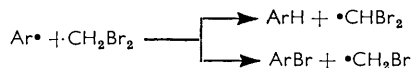


732. Reactions of Aryl Radicals with Aliphatic Compounds.
*Part V.*¹ *Reactions with Methylene Dibromide and Bromoform*

By J. I. G. CADOGAN, D. H. HEY, and P. G. HIBBERT

The reactions of a series of aryl radicals, derived from the corresponding peroxides or arylazotriphenylmethanes, with methylene dibromide and bromoform have been studied. It has been shown that with all aryl radicals studied bromine is abstracted about four times more readily than hydrogen from methylene dibromide, whereas almost exclusive abstraction of bromine occurs from bromoform. No identifiable products of bromomethyl or dibromomethyl radicals concomitantly produced were detected, although it was shown that bromomethyl radicals produced by the decomposition of bis-bromoacetyl peroxide, and of bromoacetyl *p*-chlorobenzoyl peroxide, and by photolysis of bromomethylmercuric bromide, in methylene dibromide could be detected. It has also been shown that the radical-induced addition of methylene dibromide to hept-1-ene gives 1,3-dibromo-octane as a major product.

In Part IV,¹ reactions of aryl radicals derived from diaryl peroxides and arylazotriphenylmethanes with chloroform, carbon tetrachloride, and bromotrichloromethane were described. We now extend this work to reactions with methylene dibromide and bromoform. As in Part IV the investigation involves the determination of the course of the reaction of the radical Ar• with the polyhalogenomethane, *e.g.*, for methylene dibromide the determination of the molar ratio of products ArH and ArBr:



It was also of interest to compare the behaviour of aryl radicals in these reactions with that of alkyl radicals exemplified by hexyl and octyl, and to determine the fate of the various bromomethyl radicals produced in the abstraction reactions.

EXPERIMENTAL

Reagents.—Diacyl peroxides were those used in Part IV. In addition dinonyl peroxide, n_D^{25} 1.4410 (lit.,² n_D^{30} 1.4388) was prepared as described by DeTar and Wells³ (99% pure by titration). Methylene dibromide was purified by fractional distillation, collected at 97° (n_D^{25} 1.5377) and stored over anhydrous magnesium sulphate. Bromoform was shaken successively with concentrated sulphuric acid, saturated aqueous sodium hydrogen carbonate, and water. It was then dried (CaCl₂) and fractionated in the dark. The product was collected at 148°.

The chromatographic equipment used was that described in Part IV.

Bisbromoacetyl Peroxide.—Bromoacetyl bromide (2.3 g., 0.011 mole) was added to a stirred aqueous solution (10 ml.) of sodium peroxide (0.50 g., 0.064 mole) at -5° during 10 min. The mixture was stirred for a further 10 min. and the product, m. p. 47.5°, filtered off (0.46 g., 30%). The peroxide gave an iodine titre of 99%, contained bromine, and its structure was further confirmed by examination of the infrared spectrum, when the presence of C=O (1818 and 1786 cm.⁻¹) and -O-O- (877 and 862 cm.⁻¹) groups was established.

Bromoacetyl p-Chlorobenzoyl Peroxide.—Bromoacetic acid (100 g., 0.72 mole) was boiled under reflux with acetic anhydride (330 g., 3.2 mole) for 5 hr. The excess of acetic anhydride was removed by distillation, and other distillates which had b. p. <120°/8 mm. were discarded. Further distillation gave $\alpha\alpha'$ -dibromoacetic anhydride (34 g., 36%), b. p. 122°/8 mm., n_D^{23} 1.5160 (Found: Br, 62.5. Calc. for C₄H₄Br₂O₃: Br, 61.5%) (lit.,⁴ b. p. 153—155°/25 mm.). *p*-Chloroperbenzoic acid (4.4 g. 0.025 mole) in methylene dichloride (150 ml.) was extracted

¹ Part IV, J. I. G. Cadogan, D. H. Hey, and P. G. Hibbert, preceding Paper.

² L. S. Silbert and D. Swern, *J. Amer. Chem. Soc.*, 1959, **81**, 2364.

³ D. F. DeTar and D. V. Wells, *J. Amer. Chem. Soc.*, 1960, **82**, 5839.

⁴ E. E. Smisson, *J. Amer. Chem. Soc.*, 1954, **76**, 5805.

with aqueous sodium hydroxide (100 ml., 4% w/w). This solution was then shaken with a solution of $\alpha\alpha'$ -dibromoacetic anhydride (6.7 g., 0.025 mole) in methylene chloride (75 ml.). The organic layer was dried (MgSO_4), and removal of the solvent at room temperature under reduced pressure gave bromoacetyl p-chlorobenzoyl peroxide (2.73 g., 29%) m. p. 36°. The product gave an iodine titre of 97%, contained chlorine and bromine, and the presence of C=O (1792 and 1767 cm^{-1}) and -O-O- (855 and 848 cm^{-1}) groups was confirmed by examination of the infrared spectrum.

Bromomethylmercuric Bromide.—Bromomercuriethanol (m. p. 153°, lit.,⁵ m. p. 158°), prepared by Hofmann and Sand's method,⁵ was treated with diazomethane followed by hydrogen bromide as described by Freidlina⁶ to give bromomethylmercuric bromide, m. p. 125–126° (lit.,⁶ m. p. 123–125°).

Bromomethyl Benzoate.—A suspension of paraformaldehyde (2.0 g.) in benzoyl bromide (12.5 g.) was maintained at 105° for 7 days. The resulting brown solution was fractionally distilled to give a fraction, b. p. 132°/16 mm., n_D^{25} 1.5585 (lit.,⁷ b. p. 135–137°/18 mm.) (Found: C, 45.6; H, 3.5. Calc. for $\text{C}_8\text{H}_7\text{BrO}_2$: C, 44.7; H, 3.3%). The distillation was complicated by sublimation of unchanged paraformaldehyde. The ester was not immediately affected by water, but was hydrolysed after 3 hr. on being heated on a water-bath with hydrochloric acid (d 1.18). Benzoic acid (38%, m. p. and mixed m. p. 121°) was precipitated from the solution and the filtrate was shown to contain formaldehyde (29%), (2,4-dinitrophenyl)hydrazone, m. p. and mixed m. p. 166°. Treatment of the ester with dry hydrogen bromide in carbon tetrachloride at room temperature and at the b. p. gave no methylene dibromide.

Addition of Methylene Dibromide to Hept-1-ene.—A mixture of hept-1-ene (8.10 g., 1 mol.), methylene dibromide (42.1 g., 3 mol.) and dibenzoyl peroxide (1.9 g., 0.1 mol.) was added dropwise during 15 hr. to methylene dibromide (100 g., 7 mol.) maintained at 105°. After completion of the addition, the solution was kept at 105° for 18 hr. The mixture was washed with saturated sodium hydrogen carbonate solution, and dried (MgSO_4). The methylene dibromide was removed (b. p. 98°) and the residue was distilled to give one fraction (8.93 g.), b. p. 60–140°/0.05 mm. (bulk 74°). This fraction was separated by preparative g.l.c., previous experiments having shown that no satisfactory separation could be effected by fractional distillation. The two products which were revealed in this way (100 \times 2 cm. A column, 160°, nitrogen gas flow 80 ml. min^{-1} , sample size 2 ml.) had relative retention times of 1 and 2 hr., respectively. The lower-boiling product was distilled at 74°/0.05 mm. and its purity established by qualitative g.l.c. (Pye-Argon Chromatograph, APM column, 150°, argon gas flow 60 ml. min^{-1}). It was identified as 1,3-dibromo-octane by comparison of its refractive index, g.l.c. retention times, and infrared spectra, with those of the compound prepared as described below (Found: C, 36.3; H, 5.8; Br, 57.4. $\text{C}_8\text{H}_{16}\text{Br}_2$ requires C, 35.3; H, 5.9; Br, 58.8%). The higher boiling product (g.l.c. estimated b. p. >300°) had the following analysis: Found: C, 31.7; H, 4.9; Br, 61.7% [$\text{C}_8\text{H}_{15}\text{Br}_3$ requires C, 27.3; H, 4.3; Br, 68.5%. $\text{C}_{15}\text{H}_{30}\text{Br}_2$ (2:1 adduct) requires C, 48.5; H, 8.1; Br, 43.4%]. The yields of 1,3-dibromo-octane and suspected 1,1,3-tribromo-octane were 29 and 10% respectively based on olefin: n.m.r. data are given below.

Photo-induced Decomposition of Bromomethylmercuric Bromide in Methylene Dibromide.—A mixture of bromomethylmercuric bromide (1.50 g., 1 mol.) and methylene dibromide (13.6 g., 19.5 mol.) was irradiated in a silica tube by a Hanovia U.V.S. 500 medium-pressure mercury arc (2537 Å) in a stream of nitrogen for 2 hr. The black mixture was analysed by g.l.c. (two columns) when 1,2-dibromoethane (0.15 g., 40%) was identified. A control experiment showed that methylene dibromide was stable under the conditions of the experiment.

Decomposition of Bisbromoacetyl Peroxide in Methylene Dibromide.—Bisbromoacetyl peroxide (1.71 g., 1 mol.) in methylene dibromide (17.06 g., 16 mol.) was kept in nitrogen at 80° for 72 hr. An experiment in which the rate of gas evolution was measured indicated that the half-life of the peroxide at this temperature was ca. 40 min. The brown mixture was analysed by g.l.c.; the following products were identified: bromoform (0.11 mole/mole peroxide), 1,1,2-tribromoethane (0.13 mole/mole peroxide), and 1,2-dibromoethane (0.10 mole/mole peroxide). There was an undistillable residue (0.29 g., b. p. >300°).

Decomposition of a Mixture of Bisbromoacetyl Peroxide and Di-p-chlorobenzoyl Peroxide in Methylene Dibromide.—Bisbromoacetyl peroxide (1.80 g., 2 mol.), di-p-chlorobenzoyl peroxide

⁵ K. A. Hofmann and J. Sand, *Ber.*, 1900, **33**, 1340.

⁶ R. C. Freidlina, A. N. Nesmejanow, and F. A. Tokarewa, *Ber.*, 1936, **69**, 2019.

⁷ L. H. Ulich and R. Adams, *J. Amer. Chem. Soc.*, 1921, **43**, 660.

(1.02 g., 1 mol.), and methylene dibromide (17.03 g., 30 mol.) were kept in nitrogen at 80° for 72 hr. The mixture was then analysed by g.l.c.; the following were identified: chlorobenzene (0.16 m/m chlorobenzoyl peroxide), 1-bromo-4-chlorobenzene (0.59 m/m), bromoform (0.10 m/m bromoacetyl peroxide), 1,1,2-tribromoethane (0.14 m/m) and 1,2-dibromoethane (0.10 m/m). *p*-Chlorobenzoic acid, m. p. and mixed m. p. 232—233° (0.32 g., 0.63 m/m peroxide), was filtered off from the reaction mixture. A control experiment showed that 20 g. methylene dibromide retained 0.02 g. *p*-chlorobenzoic acid in solution at room temperature.

Decomposition of Bromoacetyl p-Chlorobenzoyl Peroxide in Methylene Dibromide.—The peroxide (0.01 g., 1 mol.) was allowed to decompose in methylene dibromide (33.20 g., 55 mol.) in nitrogen at 80° for 72 hr. G.l.c. gave chlorobenzene (0.075 m/m peroxide), 1-bromo-4-chlorobenzene (0.29 m/m), and bromoform (0.22 m/m). A soda-lime trap in the system increased in weight by 0.13 g. (0.86 mole CO₂/mole peroxide), and *p*-chlorobenzoic acid (0.18 g., 0.36 m/m peroxide), m. p. 225—230°, mixed m. p. 235—237°, was filtered off from the reaction mixture.

Preparation of 1,3-Dibromo-octane.—*N*-Bromosuccinimide (45 g., 0.25 mol.), oct-1-ene (84 g., 0.75 mol.) and carbon tetrachloride (190 ml.) were boiled under reflux for 2 hr. Succinimide (22 g., 88%), m. p. 120—121°, was filtered off and the filtrate was fractionally distilled through a 40 × 1 cm. vacuum-jacketed column. The fraction of b. p. 89°/20 mm. (21 g., 50%) was collected and redistilled at 24°/0.05 mm. (Found: C, 50.4; H, 8.0%. Calc. for C₈H₁₅Br: C, 50.3; H, 7.9%). The product was a mixture of 1-bromo-oct-2-ene (80%) and 3-bromo-oct-1-ene (20%).⁸ Hydrogen bromide (37 g., 0.46 mol.) was passed for 6 hr. through the mixture of the bromo-octenes (10.5 g., 0.055 mol.) containing dibenzoyl peroxide (1 g., 0.004 mol.). The temperature of the mixture rose to 50° and the peroxide dissolved. The black, liquid product was chromatographed on a basic alumina column (20 × 2 cm.) and the colourless liquid (11.10 g.), which was eluted with light petroleum (b. p. 60—80°) (200 ml.) was collected and distilled. Five fractions, b. p. 40—44°/0.05 mm., were collected and examined by g.l.c. Each fraction contained a small amount of the starting bromo-olefins with varying amounts of 1,2-dibromo-octane, 2,3-dibromo-octane, and a major unknown product X (estimated total yield of dibromides 55%). The proportional yields of reaction products were 2,3-dibromo-octane (2%), 1,2-dibromo-octane (21%), unknown X (60%), and a second unknown Y (17%). The relative peak height of X was increased on two g.l.c. columns by the addition of a sample of the 1:1-adduct of hept-1-ene with methylene dibromide. The identity of X as 1,3-dibromo-octane was confirmed by separation of the compound from the other products by preparative g.l.c., whereupon the product (b. p. 78°/0.2 mm.) had an infrared spectrum and refractive index (n_D^{26} 1.4920) identical with those of the 1:1-adduct of methylene dibromide with hept-1-ene. The n.m.r. spectrum (tetramethylsilane as internal standard) of 1,3-dibromo-octane in carbon tetrachloride showed absorptions at τ (a) 5.94 (multiplet), (b) 6.47 (triplet), (c) 7.75 (quartet), (d) 8.23 (unresolved), (e) 8.65 (unresolved), (f) 9.08 (partially resolved triplet) with integrals in the ratio a : b : c : (d + e) : f of 1 : 2 : 2 : 8 : 3, as did the adduct of hept-1-ene and methylene dibromide.

Decomposition of Diacyl Peroxides and Arylazotriphenylmethanes in Bromoform.—The general experimental and analytical procedures have been described in Part IV.¹ The radical source (1 mol.) was allowed to decompose in bromoform (20 ml.) in nitrogen or air at 80° for 72 hr. (peroxide) or 18 hr. (azo-compound). The resulting mixtures were analysed by g.l.c., and the results are given in Table 1.

Reactions with Methylene Dibromide.—The general experimental and analytical procedures are described in Part IV.¹ Decompositions were carried out at 80° in nitrogen for 72 hr., with 0.5—10 g. of peroxide in a 5—60 molar excess of solvent. The yields of primary abstraction products are listed in Table 2. After being diluted to 60 molar excess, the products resulting from reactions carried out in 5, 15, and 30 molar excess of solvent were analysed without any further work-up. Absolute yields of acids and other products were obtained from reactions on a larger scale and two typical experiments are described in more detail below.

(a) *With dibenzoyl peroxide.* The peroxide (6.00 g.) was allowed to decompose at 80° for 72 hr. in methylene dibromide (63.3 g., 14 mol.). After removal of the excess of solvent the residue (10.03 g.) was distilled to give: (i) b. p. 20—60°/50 mm. (6.10 g.), (ii) a semi-solid (1.81 g.), which sublimed from a bath at 150°/0.05 mm., and (iii) a residue (1.72 g.).

Hydrogen bromide (0.11 mole/mole peroxide) was evolved during the reaction. Fraction

⁸ M. S. Kharasch, R. Malec, and N. C. Yang, *J. Org. Chem.*, 1957, **22**, 1443.

(i) contained benzene, bromobenzene, and bromoform and no extraneous products. Fraction (ii) was dissolved in benzene and extracted with aqueous sodium hydroxide to give benzoic acid (1.37 g.), m. p. 118—119°, mixed m. p. 119—120°. Distillation of the benzene solution gave an unidentified lachrymatory liquid (0.38 g.), b. p. 74°/0.05 mm., which did not contain benzyl bromide (infrared). The residue (iii) was not identified but it decomposed on treatment with alkali to give an acid (0.06 g.), m. p. 100—200° (decomp.), and an acidic gum (1.11 g.).

TABLE 1
Reaction of aryl radicals with bromoform at 80°

Ar: from (ArCO ₂) ₂	Atmosphere	Products mole/mole source					Ar accounted for (%)
		ArBr	ArH	CH ₂ Br ₂	CBr ₄	Ar·CO ₂ H	
<i>p</i> -Cl·C ₆ H ₄ ·	N ₂	1.00	0.04	—	1.0	0.61	82
<i>p</i> -Cl·C ₆ H ₄ ·	N ₂	1.08	0.04	—	0.3	0.59	85
<i>p</i> -NO ₂ ·C ₆ H ₄ ·	N ₂	0.27	0.01	—	0.8	1.05	67
<i>p</i> -Cl·C ₆ H ₄ ·*	Air	0.83	0.05	0.14	0.24	—	88
Ph·	Air	0.94	0.02	—	0.54	—	—
<i>p</i> -Cl·C ₆ H ₄ ·	Air	0.85	0.03	—	1.2	0.80	84
<i>p</i> -Cl·C ₆ H ₄ ·	Air	0.75	0.02	0.18	2.7	0.85	81
<i>p</i> -NO ₂ ·C ₆ H ₄ ·	Air	0.21	0.01	—	2.3	1.60	90
Ph·*	Air	0.85	0.06	0.21	0.05	—	91

* Arylazotriphenylmethane was used.

TABLE 2
Decomposition of diacyl peroxides (1 mol.) in methylene dibromide at 80°

R in (RCO ₂) ₂	CH ₂ Br ₂ (mol.)	Products (mole/mole peroxide)					R accounted for (%)
		RH	RBr	RBr/RH	CHBr ₃	RCO ₂ H	
Ph	5	0.16	0.65	4.0	0.01	—	—
	15	0.20	0.79	4.0	0.04	0.46	72
	30	0.20	0.79	4.0	0.10	—	—
	60	0.20	0.82	4.1	0.16	—	—
<i>p</i> -Cl·C ₆ H ₄	15	0.22	0.84	3.8	0.08	0.50	78
	30	0.23	0.83	3.6	0.13	0.50	78
	60	0.26	1.16	4.4	0.25	0.50	95
	70*	0.21	0.67	3.2	0	—	88
	102	0.25	0.87	3.5	0.45	—	—
	206	0.27	0.83	3.1	0.75	—	—
<i>p</i> -NO ₂ ·C ₆ H ₄	15	0.16	0.64	4.0	0.10	0.70	79
	30	0.17	0.70	4.1	0.16	—	—
	60	0.18	0.70	3.9	0.27	—	—
<i>p</i> -CH ₃ ·C ₆ H ₄ †	15	0.08	0.57	7.0	0.01	0.38	57
	30	0.09	0.55	6.0	0.04	—	—
	60	0.07	0.48	7.0	0.08	—	—
Hexyl	52	0.32	0.43	1.3	—	0.08	44
Octyl	25	0.26	0.84	3.3	0	—	—

* With *p*-chlorophenylazotriphenylmethane. † Inefficient G.L.C. separation of PhCH₃ and CH₂Br₂ led to an accuracy of only (±20%) in the estimation of PhCH₃.

A unique aspect of the decomposition of dibenzoyl peroxide in methylene dibromide is the precipitation of an unstable, yellow, halogen-containing solid (0.21 g. from 2.0 g. peroxide) on treatment of the reaction mixture with light petroleum. The solid was assumed to be a product of attack on the *para*-position of the benzene ring as comparable solids were not produced in reactions of *p*-substituted peroxide.

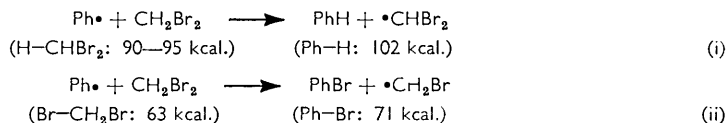
(b) *With di-p-chlorobenzoyl peroxide.* In an experiment with di-*p*-chlorobenzoyl peroxide (9.89 g., 1 mol.) and methylene dibromide (78.79 g., 14.2 mol.), the carbon dioxide evolved (1.2 moles/mole peroxide) was measured by absorption in soda lime. A net loss in weight of 0.75 g. was found to have occurred during the reaction. A control experiment with methylene dibromide (81.27 g.) lost 0.08 g. under the same conditions. *p*-Chlorobenzoic acid (m. p. and mixed m. p. 231—233°) was precipitated during the reaction. Excess of solvent was removed

and the residue was distilled to give the following fractions: (i) b. p. 99° (8.08 g.); (ii) b. p. 70—95°/30 mm. (2.68 g.); (iii) b. p. 20°/0.05 mm. (0.21 g.); (iv) a sublimate at 0.05 mm. from a bath at 80° (4.46 g.); (v) a residue (5.90 g.). Hydrogen bromide was evolved at bath temperatures >150°. Fractions (i)—(iii) contained methylene dibromide, bromoform, chlorobenzene, and no extraneous products (g.l.c.). Fraction (iv) was *p*-bromochlorobenzene (m. p. and mixed m. p. 59—60°). A portion of the residue (2.45 g.) dissolved in chloroform was extracted with saturated sodium hydrogen carbonate solution and the organic layer dried over magnesium sulphate. The tarry residue (1.59 g.) remaining after removal of the solvent was chromatographed on basic alumina and on silica but no solid products were obtained. Acidification of the alkaline extract gave *p*-chlorobenzoic acid (1.08 g.), m. p. and mixed m. p. 239—240°.

Addition of Bromoform to Hept-1-ene.—Hept-1-ene (2.11 g.; 1 mol.), bromoform (86.6 g.; 16 mol.) and di-*t*-butyl peroxide (0.31 g.; 1 mol.) were kept at 105° for 72 hr. After removal of bromoform g.l.c. analysis of the residue showed that two major products were present: one was identical with the high boiling product of the addition of methylene dibromide to hept-1-ene.

DISCUSSION

Abstraction Reactions with Methylene Dibromide.—Consideration of bond dissociation energies alone in the two possible abstraction reactions of a phenyl radical with methylene dibromide suggests that a fine balance would exist between abstraction of bromine and hydrogen:

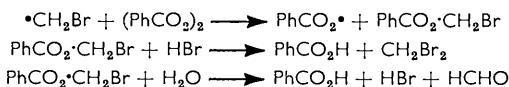


The experimental results (Table 2) are in accord with this and indicate that abstraction of bromine occurs approximately four times as readily as abstraction of hydrogen. Further, as is the case in abstraction from chloroform and bromotrichloromethane¹ and from bromoform, the introduction of substituents in the *p*-position of an aryl radical does not markedly affect its reactivity. It is also noteworthy that whereas the abstraction behaviour of the octyl radical is similar to that of the aryl radicals studied, the hexyl radical is much less selective and abstracts hydrogen and bromine from methylene dibromide to approximately the same extent. It is of interest that Fox, Evans, and Szwarc⁹ have predicted a value of $k_{\text{H}}/k_{\text{Br}} = ca. 2$ for the reaction of methyl radicals with methylene dibromide at 65°.

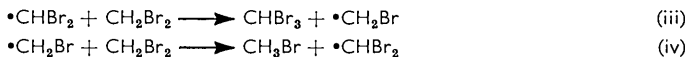
Since interaction of aryl and alkyl radicals with methylene dibromide leads to abstraction of both bromine and hydrogen, it follows that bromomethyl and dibromomethyl radicals should also be formed [reactions (i) and (ii)]. However, although a careful search was made, bromoform and methyl bromide were the only identifiable products of either of these radicals found (*vide infra*). Dimerisation and radical-coupling, the obvious chain termination processes, do not appear to occur, because none of 1,2-dibromoethane, 1,1,2-tribromoethane, or 1,1,2,2-tetrabromoethane were found as products. Moreover, since it has been shown that the radicals formed in the thermal reaction of bisbromoacetyl peroxide and the photolytic reaction of bromomethylmercuric bromide in methylene dibromide do in fact dimerise or couple, then those formed in the corresponding reactions of diaryl peroxides must react in other ways before they have an opportunity of coupling. The alternative possibility, that bromomethyl or dibromomethyl radicals are not formed in the reactions with diaryl peroxides at all is unlikely, since it was shown that bromomethyl radicals derived from the peroxide-initiated reaction of methylene dibromide with hept-1-ene give 1,3-dibromo-octane in good yield. Neither do chain termination reactions with radicals derived from the peroxide occur. Benzyl bromides from the reaction $\text{Ar}\cdot + \cdot\text{CH}_2\text{Br} \longrightarrow \text{ArCH}_2\text{Br}$ were not found in the reactions, neither were bromomethyl esters from the reaction $\text{ArCO}_2\cdot + \cdot\text{CH}_2\text{Br} \longrightarrow \text{ArCO}_2\cdot\text{CH}_2\text{Br}$. The possibility that such

⁹ R. J. Fox, F. W. Evans, and M. Szwarc, *Trans. Faraday Soc.*, 1961, **57**, 1915.

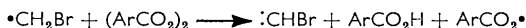
esters, formed either as indicated above or by induced decomposition of the peroxide, might undergo decomposition by water or hydrogen bromide as shown below can also be discounted because methylene dibromide was not formed in the reaction between hydrogen bromide and bromomethyl benzoate:



Indeed 4*N*-hydrochloric acid was required to hydrolyse the ester. Further, formaldehyde was not formed during the decomposition of dibenzoyl peroxide in methylene dibromide. It is possible that the bromo- and dibromo-methyl radicals might be accounted for by the observed formation of bromoform produced by reactions (i) and (ii) followed by (iii) and (iv):



Support for this sequence is provided by the detection (g.l.c.) of methyl bromide among the products of the reaction involving dibenzoyl peroxide. That this sequence will not necessarily account for the missing bromomethyl radicals follows from the fact that it is a chain sequence and in theory only *one* bromomethyl radical can lead to a high yield of bromoform. This is supported by the results of decompositions (*e.g.*, di-*p*-chlorobenzoyl peroxide) carried out in increasing dilution (Table 2), wherein the chances of removal of bromomethyl radicals by other, albeit unknown, reactions is decreased and hence the probability of formation of bromoform is increased. Thus the yield increases from 8 to 75% as the dilution increases from 15 to 206 molar. The mechanism of formation of the acids produced in the reaction is also uncertain, but it is possible that they arise mainly by abstraction of hydrogen from the solvent: $\text{ArCO}_2\bullet + \text{CH}_2\text{Br}_2 \longrightarrow \text{ArCO}_2\text{H} + \bullet\text{CHBr}_2$. An alternative route to the acids involves induced decomposition of the peroxide by bromomethyl radicals as follows:



Such a route would lead to the production of carbenes but products corresponding to dimerisation, coupling, or insertion of bromocarbene or dibromocarbene were not detected in the reaction products. On the other hand some support for a mechanism involving interaction of *p*-chlorobenzoyloxy-groups with bromomethyl radicals follows from the observation that the yield of *p*-chlorobenzoic acid is increased at the expense of primary abstraction products when bromomethyl radicals, produced by the decomposition of the less stable bisbromoacetyl peroxide, were allowed to react together with the more stable di-*p*-chlorobenzoyl peroxide in methylene dibromide (Table 3). A more positive

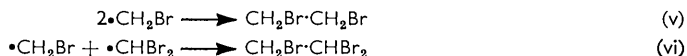
TABLE 3
Reaction of *p*-chlorobenzoyl and bromoacetyl peroxide with methylene dibromide

Source	Products [(mole/mole (ArCO ₂) ₂)]			ArBr ArH	ArCO ₂ H ArBr + ArH
	ArBr	ArH	Ar-CO ₂ H		
(ArCO ₂) ₂	0.85	0.23	0.50	3.7	0.46
(ArCO ₂) ₂ + (CH ₂ BrCO ₂) ₂	0.59	0.16	0.63	3.7	0.84
ArCO ₂ O ₂ C·CH ₂ Br	0.29	0.08	0.36	3.6	1.0

demonstration of the participation of bromomethyl (or bromoacetyloxy-) radicals in the formation of *p*-chlorobenzoic acid is given by the decomposition of bromoacetyl *p*-chlorobenzoyl peroxide in methylene dibromide wherein bromoacetyloxy-radicals, which very rapidly decompose to give bromomethyl radicals,¹⁰ and *p*-chlorobenzoyloxy-radicals are produced at the same rate. In this case the relative yield of *p*-chlorobenzoic acid is even further increased.

¹⁰ C. Walling, "Free Radicals in Solution," J. Wiley and Sons, Inc., New York, 1957, p. 491.

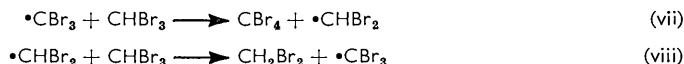
The decomposition of bisbromoacetyl peroxide alone in methylene dibromide and in the presence of di-*p*-chlorobenzoyl peroxide in methylene dibromide leads to the formation of 1,1,2-tribromoethane, 1,2-dibromoethane, and bromoform, thus confirming that bromomethyl radicals are formed by reactions (iii) and (iv) followed by (v) and (vi):



It is more significant however that the decomposition of bromoacetyl *p*-chlorobenzoyl peroxide does not lead to the formation of 1,1,2-tribromoethane and 1,2-dibromoethane but only to bromoform, suggesting that the sole mode of formation of the latter is by reaction (iii) and that $\cdot\text{CH}_2\text{Br}$ radicals are specifically consumed by *p*-chlorobenzoyloxy-radicals or their precursor to give *p*-chlorobenzoic acid as one of the products. The results obtained from the experiment involving both bisbromoacetyl and di-*p*-chlorobenzoyl peroxides can then be rationalised on the basis of the shorter half-life of the aliphatic peroxide, *i.e.*, the bromomethyl radicals would have reacted before a significant concentration of *p*-chlorobenzoyloxy-radicals would have been built up, whereas the decomposition of the mixed peroxide would lead to the almost simultaneous formation of these radicals. That bromomethyl radicals combine on a large scale with aromatic fragments from the diaroyl peroxides can be discounted because the accountance of the peroxides is very high. It appears from the reaction of di-*p*-chlorobenzoyl peroxide with methylene dibromide (60 mol.), when 95% of the peroxide can be accounted for, that the residue is derived largely from bromomethyl radicals alone. The weight of the residue corresponded to only 47% of the bromomethyl radicals, but the relatively high carbon content of the residue (Found: C, 39.9; H, 2.5; Br, 36.2. CH_2Br requires C, 12.8; H, 2.1; Br, 85.1%) indicates that the deficiency in weight might be made up by the observed loss of hydrogen bromide during work-up.

Reactions of Aryl Radicals with Bromoform.—The results of experiments carried out with diaroyl peroxides and with arylazotriphenylmethanes and bromoform, summarised in Table I, indicate that almost exclusive abstraction of bromine by aryl radicals occur. These results differ from those of Hey and Peters¹¹ who reported ratios of bromine abstraction to hydrogen abstraction in the region of 1 : 3—4.5. The latter results must be considered to be less accurate since they were obtained without the aid of gas chromatography.

Significant features of the reactions in bromoform, as in methylene dibromide, are the absence of identifiable products of the dibromomethyl radicals produced as a result of the primary abstraction process $\text{Ar}\cdot + \text{CHBr}_3 \longrightarrow \text{ArBr} + \cdot\text{CHBr}_2$ and also the high yield of the corresponding benzoic acid. Another similarity between the reactions in bromoform and methylene dibromide involves the formation of carbon tetrabromide in the former case and bromoform in the latter. Carbon tetrabromide can arise by the following chain sequence:

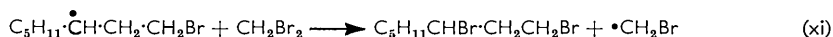
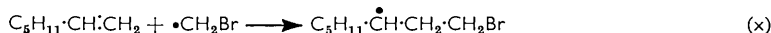
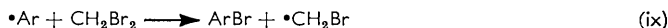


whence it can be seen that in theory a high yield of carbon tetrabromide can arise from a disproportionately small quantity of tribromomethyl radicals. This interpretation is supported by the fact that methylene dibromide was detected among the products of the reactions of phenylazotriphenylmethane (0.21 m/m), *p*-chlorophenylazotriphenylmethane (0.14 m/m), and di-*p*-chlorobenzoyl peroxide (0.18 m/m) with bromoform. Experimentally it was found that the yield of carbon tetrabromide varied widely in apparently identical experiments suggesting that the chain length was markedly dependent on the presence of impurities.

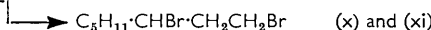
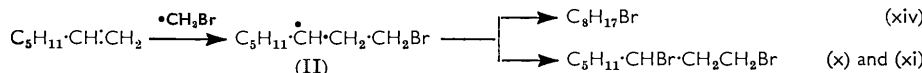
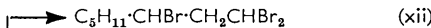
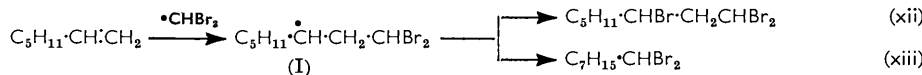
¹¹ D. H. Hey and J. Peters, *J.*, 1960, 79.

The reactions between diaroyl peroxides and bromoform are affected by oxygen (see Table 1). Reactions carried out in air (protected by a drying tube) gave higher yields of acid and lower yields of bromobenzenes than reactions carried out in nitrogen, but the relative rate ratios were not affected.

Addition of Methylene Dibromide and Bromoform to Hept-1-ene.—Although the addition of bromoform to alk-1-enes has been reported,¹² that of methylene dibromide has not been described. The major product of the reaction with hept-1-ene, namely 1,3-dibromo-octane, is presumably formed by the orthodox chain reaction:



However, alternative reactions can theoretically occur with corresponding differences in products. Since it has been shown that aryl and octyl radicals abstract bromine from methylene dibromide three to four times as readily as hydrogen (Table 2), a mixture of four products can be formed:



The absence of 1-bromo-octane and 1,1-dibromo-octane in the reaction products indicates that both intermediate radicals (I) and (II) preferred to abstract bromine. However, in view of the tendency of the octyl radical to abstract hydrogen from methylene dibromide to a certain extent, it is surprising that products of hydrogen abstraction were not detected in the addition reaction.

As it is probable that 1,1-dibromo-3-octyl radicals (I) are formed together with 1-bromo-3-octyl radicals (II), and as products of hydrogen abstraction of these radicals are not found, 1,1,3-tribromo-octane should be a product of the reaction. A high-boiling compound was isolated from the reaction mixture in 33% yield relative to the yield of 1,3-dibromo-octane; this ratio agrees well with the theoretical ratio of bromomethyl and dibromomethyl radicals in the system. The compound was unstable and the analysis indicated that some dehydrobromination may have occurred. In an attempt to confirm the identity of 1,1,3-tribromo-octane the radical induced addition of bromoform to hept-1-ene was carried out, Kharach, Jensen, and Urry¹² having reported that the major product of this reaction was the required tribromo-octane. In our hands the addition gave two major products one of which had a G.L.C. retention time identical with that of the high boiling product from the addition of methylene dibromide to hept-1-ene.

Thanks are accorded to the D.S.I.R. for the award of a Research Studentship to P. G. H. Acknowledgment is also made to Mr. B. W. Harris who carried out exploratory experiments on the addition of methylene dibromide to alk-1-enes.

KING'S COLLEGE, STRAND, LONDON W.C.2.

[Present address (J.I.G.C.): ST. SALVATOR'S COLLEGE, UNIVERSITY OF ST. ANDREWS, ST. ANDREWS, FIFE.] [Received, November 12th, 1964.]

¹² M. S. Kharasch, E. V. Jensen, and W. H. Urry, *J. Amer. Chem. Soc.*, 1947, **69**, 1100.