731. *Reactions of Aryl Radicals with Aliphatic Compounds. Part IV.*[1] *A Quantitative Study of Abstraction from Chloroform, Carbon Tetrachloride, and Bromotrichloromethane*

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A quantitative study of the reactions of aryl and hexyl radicals, derived from the corresponding diacyl peroxides and arylazotriphenylmethanes, with chloroform, carbon tetrachloride, and bromotrichloromethane under nitrogen has revealed that (i) the reactivity of an aryl radical is independent of the nature of the substituent, (ii) hydrogen and bromine are abstracted almost exclusively from chloroform and bromotrichloromethane respectively, and (iii) hydrogen is abstracted by an aryl radical more readily from chloroform than is chlorine from carbon tetrachloride, whereas for the hexyl radical the ratio of reactivities is reversed. Products derived from trichloromethyl radicals liberated in these reactions have also been isolated. Under oxygen in bromotrichloromethane, di-*p*-chlorobenzoyl peroxide gave *p*-dichlorobenzene but little *p*-bromochlorobenzene, while phosgene, bromine, and chlorine were also formed. The significance of these results is discussed.

QUANTITATIVE measurements have been reported recently for a number of free-radical reactions involving abstraction of atoms. DeTar and Wells[2] studied the relative reactivities of various substrates in donating a hydrogen atom to the 1-hexyl radical produced by the decomposition of heptanoyl peroxide, while Bridger and Russell[3] have made a similar but more comprehensive study of abstraction by the phenyl radical produced from phenylazotriphenylmethane.

Qualitative observations on the abstraction reactions of aryl radicals with polyhalogenomethanes have been reported by several workers. Böeseken and Gelissen[4a,b] isolated benzene and chlorobenzene, respectively, from the reactions between dibenzoyl peroxide and chloroform and carbon tetrachloride, together with hexachloroethane and *p*-trichloromethylbenzoic acid. The behaviour of these solvents with *N*-nitrosoacetanilide, benzenediazohydroxide and phenylazotriphenylmethane was also investigated by Waters,[5] Grieve and Hey,[6] and Wieland and Heymann,[7] who showed that benzenediazohydroxide gave benzene only on reaction with chloroform, and chlorobenzene with carbon tetrachloride; phenylazotriphenylmethane gave chlorobenzene on reaction with carbon tetrachloride, and chlorobenzene was formed from the reaction of *N*-nitrosoacetanilide with chloroform. Waters[5] also isolated bromobenzene from the rection of bromoform with *N*-nitrosoacetanilide.

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[1] Part III, D. H. Hey and Rasmy Tewfik, *J.*, 1965, 2402.

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

[3] R. F. Bridger and G. A. Russell, *J. Amer. Chem. Soc.*, 1963, **85**, 3754.

[4] (*a*) J. Böeseken and H. Gelissen, *Rec. Trav. chim.*, 1924, **43**, 869; (*b*) H. Gelissen, *Chem. Zentr.*, 1925, *i*, 47.

[5] W. A. Waters, *J.*, 1937, 113.

[6] W. S. M. Grieve and D. H. Hey, *J.*, 1934, 1797.

[7] H. Wieland and K. Heymann, *Annalen*, 1934, **514**, 154.

The first semi-quantitative information concerning the reactions between aromatic radicals and aliphatic solvents was provided by Hey and Peters,[8] who reinvestigated the reactions between the four sources of the phenyl radical mentioned above and chloroform and carbon tetrachloride, and also studied the reactions with bromoform. The corresponding reactions with bromotrichloromethane were studied by Hey and Tewfik.[1] The results are summarised in Table 1.

TABLE 1

Reaction between phenyl radicals and chloroform, carbon tetrachloride, bromoform and bromotrichloromethane

	Products in moles/mole source					
	With CCl_4	With $CHCl_3$		With $CHBr_3$		With $CBrCl_3$
Radical source	PhCl	PhH	PhCl	PhH	PhBr	PhBr
$(PhCOO)_2$	1·28	1·37	0	0·17	0·76	1·05
$Ph\cdot N{:}N\cdot CPh_3$	0·27	0·90	0	0·31	0·40	0·85
$PhN(NO)COCH_3$	0·32	0·20	0·15	—	—	0·17
$Ph\cdot N_2Cl$ (method *A*) *	0·28	0·47	0	—	—	0·24
,, (method *B*) *	0·35	0·49	0	0·01	0·04	0·45
,, (method *C*) *	0·06	0	0·11	0·04	0·20	0·06

* For description of methods (A)—(C) see ref. 8.

The results obtained with chloroform and carbon tetrachloride agreed with previous observations, but the isolation of benzene *and* chlorobenzene from the reaction of nitrosoacetanilide with chloroform and of both benzene *and* bromobenzene from all the reactions with bromoform were unexpected. Hey and Peters interpreted the common abstraction pattern shown by dibenzoyl peroxide and phenylazotriphenylmethane as an indication that the mode of formation of a phenyl radical in these cases did not affect the nature the primary abstraction products. The anomalies revealed in the reactions of *N*-nitrosoacetanilide were not explained. The work summarised so far, however, was carried out before the advent of the technique of gas–liquid chromatography. The quantitative investigation using this technique, of the interaction of aryl radicals derived from diacyl peroxides, arylazotriphenylmethanes, and *N*-nitrosoacetarylamides with chloroform, carbon tetrachloride, and bromotrichloromethane has now been undertaken. Further, in view of the variation in reactivity of aryl radicals towards aromatic compounds which results from variation of the substituent in the radical,[9] it was of interest to see whether similar variations in reactivity were apparent in the abstraction reactions of aryl radicals with polyhalogenomethanes. Corresponding abstraction reactions involving the hexyl radical derived from heptanoyl peroxide have also been investigated in order to provide a wider comparison of reactivities.

EXPERIMENTAL

Materials.—Solvents. Chloroform (1000 ml.) was shaken with sulphuric acid (*d* 1·84; 3 × 100 ml.), saturated sodium hydrogen carbonate solution (2 × 100 ml.), and water (2 × 500 ml.). It was dried over anhydrous magnesium sulphate and fractionally distilled in nitrogen. The pure solvent had b. p. 60·5° and contained no trace of impurity when examined by gas–liquid chromatography (g.l.c.). Carbon tetrachloride, b. p. 75°, was purified as for chloroform and stored over potassium hydroxide pellets. It contained no trace of impurity when examined by g.l.c. Bromotrichloromethane was fractionally distilled through a 120 × 3 cm. helix-packed column fitted with a take-off head of the total reflux, partial take-off type. The apparatus was protected from the light by silver foil, and the distillation followed by g.l.c. until a sample free from both carbon tetrachloride and an unknown higher-boiling impurity was obtained. The pure product had b. p. 106°, n_D^{26} 1·5025 and was stored in a dark bottle in an atmosphere of nitrogen over anhydrous magnesium sulphate.

Diacyl peroxides. Dibenzoyl peroxide, purified by precipitation from chloroform solution by methanol, had m. p. 105° (decomp.). Di-*p*-tolyl-, di-*p*-nitro-, and di-*p*-chlorobenzoyl

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[8] D. H. Hey and J. Peters, *J.*, 1960, 79.

[9] J. I. G. Cadogan, D. H. Hey, and G. H. Williams, *J.*, 1955, 1425, and subsequent Papers.

peroxides, prepared in the normal manner, had m. p.s 137° (decomp.), 158° (decomp.), and 141° (decomp.), respectively. Each peroxide was pure (100 ± 1% by titration). Diheptanoyl peroxide, prepared as described by DeTar and Wells,[2] had n_D^{25} 1·4340 and was 96% pure by titration.

p-Chlorophenylhydrazotriphenylmethane, prepared by Gomberg's method,[10] was oxidised to *p*-chlorophenylazotriphenylmethane, m. p. 108·5° (lit.,[11] m. p. 108°), by the method of Wieland, Hove, and Borner.[12] Phenylazotriphenylmethane, similarly prepared, had m. p. 106°. *cis*-1-Bromo-2-chlorocyclohexane (b. p. 46°/0·05 mm.; n_D^{23} 1·5245) was prepared as described by Goering and Sims,[13] who reported n_D^{25} 1·5238, from 1-chlorocyclohexane (b. p. 80°/90 mm.; $n_D^{25\cdot5}$ 1·4774), prepared as described by Braude and Coles,[14] who reported n_D^{25} 1·4772. *trans*-1-Bromo-2-chlorocyclohexane (b. p. 105°/15 mm.; $n_D^{25\cdot5}$ 1·5180, after purification by alumina) was prepared as described by Goering and Sims,[13] who reported n_D^{25} 1·5173. *trans*-1,2-Dibromocyclohexane had b. p. 72°/1·5 mm. (lit.,[15] b. p. 99—103°/16 mm.), and *trans*-1,2-dichlorocyclohexane b. p. 36°/0·05 mm. (lit.,[16] b. p. 71°/15 mm.).

General and Analytical Procedures.—Two gas–liquid chromatographs were used. In general, products from the abstraction reactions were analysed with a Perkin-Elmer " Fraktometer " model 116, fitted with a high-sensitivity dual control thermal conductivity detector. All injections from 5—20 µl. were made with a " Samplejector " syringe, which enables injections to be reproduced to within 0·05 µl. Three columns were used; a 1·7 metre Q column (Apiezon L on Celite) at 140—150° with a hydrogen gas flow of *ca.* 50 ml. min.$^{-1}$ for nitrobenzene and substituted nitrobenzenes, a 2 metre U column (squalane on brick dust) at 60—130° with a hydrogen gas flow of *ca.* 50 ml. min.$^{-1}$ for the majority of analyses (chloroform, chlorobenzene, 1-bromo-4-chlorobenzene, etc.) and a 2 metre A column (didecyl phthalate on Celite) was used to confirm the identity of compounds revealed by the other two columns. The quantitative measurements of products were carried out using an internal standard (marker) technique. The chromatogram of the reaction mixture to be analysed was first examined and a marker of suitable retention time chosen. A known weight of marker was then added to a portion of the reaction mixture in approximately the same concentration as the reaction products. Similarly, mixtures of authentic samples of reaction products and solvents containing this weight of marker were then examined and calibration graphs constructed; the ratio of marker to product peak height was plotted against the ratio of marker to product weight. With hydrogen as carrier gas the plots were always linear. From the calibration graphs the weight of each product in the reaction mixture was calculated.

The second chromatograph, a Pye-Argon instrument with a β-ray detector, was used mainly for qualitative examination of high-boiling products. Three columns were used; an APM column (4 ft. × 4 mm. i.d., 10% Apiezon M on Celite) with an argon gas flow of 60 mls. min.$^{-1}$ at temperatures up to 150°, an APL column (4 ft. × 4 mm. i.d., 10% Apiezon L on Celite) with an argon gas flow of 30 ml. min.$^{-1}$ at 150—200°. A PEGA column (4 ft. × 4 mm. i.d., 10% polyethyleneglycol adipate on Celite) with an argon gas flow of 30 ml. min.$^{-1}$ at 100—200° was used to confirm the identity of the compounds revealed by the first two columns.

Except where otherwise stated the experiments with the polyhalogenomethanes were carried out in a closed apparatus under a slight positive pressure of air, oxygen, or nitrogen. The gases were not passed through the body of the reaction mixture.

Abstraction Reactions of Polyhalogenomethanes with Peroxides and Arylazotriphenylmethanes.—(i) *Chloroform and diaroyl peroxides.* The peroxide, usually 0·20 to 2·00 g. (1 mol.), in chloroform (50 mol.) was boiled under reflux for four weeks and the reaction mixture analysed by g.l.c. without any prior work-up. The acid formed in the reaction mixture was then extracted with saturated sodium hydrogen carbonate solution (4 × 50 ml.), the alkaline extracts being acidified with hydrochloric acid (2N) and extracted with ether (2 × 50 ml.). The ethereal solution was dried ($MgSO_4$) and allowed to evaporate at room temperature. The results are in Table 2.

[10] M. Gomberg, *Ber.*, 1897, **30**, 2043.

[11] D. H. Hey and G. S. Misra, *J.*, 1949, 1809.

[12] H. Wieland, H. Hove, and K. Borner, *Annalen*, 1936, **446**, 31.

[13] H. L. Goering and L. L. Sims, *J. Amer. Chem. Soc.*, 1955, **77**, 3465.

[14] E. A. Braude and J. A. Coles, *J.*, 1950, 2014.

[15] H. R. Snyder and L. A. Brooks, *Org. Synth.*, Coll. Vol. II, p. 171, J. Wiley and Sons, Inc., New York.

[16] B. Carrol, D. G. Kubler, H. W. Davies, and A. M. Whaley, *J. Amer. Chem. Soc.*, 1951, **73**, 5382.

TABLE 2

Reaction of radicals with chloroform

	Products (mole/mole source)				
R in $(RCO_2)_2$	RH	RCl	$R{\cdot}CO_2H$	C_2Cl_6	R accounted for (%)
p-$CH_3{\cdot}C_6H_4$ [1]	1·46	0·01	0·12	0·40	74
Ph [2]	1·72	0·01	—	0·57	95
p-$Cl{\cdot}C_6H_4$	1·68	0·01	0·01	0·86	84
p-$Cl{\cdot}C_6H_4$ [3]	0·89	0·0	—	—	89
p-$NO_2{\cdot}C_6H_4$	1·10	0·01	0·0	0·0	55
Hexyl	0·89	0·02	—	—	91

[1] $Ph{\cdot}CH_2Cl$ (0·01) was also formed. [2] p-$CCl_3{\cdot}C_6H_4{\cdot}CO_2H$ (0·17 mole/mole) was also formed. $PhCCl_3$ was absent. [3] With p-chlorophenylazotriphenylmethane.

In view of the absence of hexachloroethane and the low accountance of peroxide in the reaction with di-p-nitrobenzoyl peroxide, the decomposition was repeated with 10 g. of peroxide. After extraction of the acid, the main chloroform solution was dried ($MgSO_4$) and the chloroform. removed by fractional distillation. The liquid residue (10·75 g.) was distilled to give the following fractions: (*a*) 5·79 g., b. p. 102°/12 mm., (*b*) 0·73 g., bath 180°/0·05 mm., (*c*) 0·10 g., bath 180°/1 μ, and a residue (2·53 g.). Fraction (*a*) was a mixture of nitrobenzene, p-chloronitrobenzene, and an unknown higher-boiling liquid in a ratio of 70 : 1 : 9. The unknown product, a yellow liquid which was not benzotrichloride, was separated from the known compounds by preparative g.l.c. (Found: C, 41·4; H, 2·4; Cl, 55·8. $C_7H_5Cl_3$ requires C, 42·9; H, 2·6; Cl, 54·5%). Fractions (*b*) and (*c*), a mixture of yellow gum and liquid, appeared to decompose as the temperature of the bath was increased and were discarded. The residue, a dark brown gum, was washed with anhydrous ether (2 × 15 ml.) and the resulting insoluble solid (0·97 g.) had m. p. 185—200° decomp. This could not be recrystallised, decomposed when chromatographed on basic alumina, and no identifiable products were obtained from chromatography on silica.

(ii) *Chloroform and* p-*chlorophenylazotriphenylmethane.* The azo-compound (0·62 g., 1 mol.) was dissolved in chloroform (9·01 g., 27·5 mol.) and allowed to decompose at 60° in nitrogen for 17 hr. The mixture was analysed by g.l.c. without any work-up and chlorobenzene was identified. 1,4-Dichlorobenzene and hexachloroethane were not detected (see Table 2).

(iii) *Chloroform and heptanoyl peroxide.* The peroxide (0·107 g., 1 mol.) and chloroform (2·29 g., 46 mol.) were heated in a sealed tube at 80° for 40 hr. The mixture was analysed by G.L.C.; hexane and 1-chlorohexane were identified (see Table 2).

(iv) *An equimolar mixture of chloroform and carbon tetrachloride with diacyl peroxides.* The peroxide (10 g.) was boiled under reflux in an equimolar mixture of the two solvents (25 mol. of each) for 14 days. The mixture was analysed by g.l.c.; results are in Table 3. Further details of experimental procedures are described below under the peroxide concerned.

TABLE 3

Decomposition of diacyl peroxides in an equimolar mixture of chloroform and carbon tetrachloride

	Products (mole/mole peroxide)					
R in $(RCO_2)_2$	RH	RCl	RH/RCl	RCO_2H	C_2Cl_6	R accounted for (%)
p-$CH_3{\cdot}C_6H_4$	1·06	0·32	3·4	0·06	0·49	72
p-$Cl{\cdot}C_6H_4$	1·37	0·39	3·5	0·02	0·72	89
p-$NO_2{\cdot}C_6H_4$	0·86	0·30	2·9	0·02	0·03	60
Hexyl *	0·22	0·40	0·55	—	—	—

* In a sealed tube at 80°.

(iv*a*) *Di-*p-*tolyl peroxide.* The results obtained by g.l.c. were qualitatively confirmed by standard experimental procedures. In addition a neutral fraction (0·51 g.) was obtained, which gave a positive chlorine test and was shown by g.l.c. to be a mixture of eight compounds.

(iv*b*) *Di-*p-*nitrobenzoyl peroxide.* The clear brown reaction mixture, after analysis by g.l.c., was extracted with saturated sodium hydrogen carbonate solution (4 × 50 ml.). The alkaline extracts were acidified (HCl, 2N) and the acidic solution extracted with ether (2 × 50 ml.). Evaporation of the ether at room temperature gave *p*-nitrobenzoic acid (0·07 g.), m. p. 228—229°, mixed m. p. 230—232°. The main solution was dried ($MgSO_4$) and the chloroform and carbon tetrachloride distilled off. Distillation of the residue (5·72 g.) gave the following fractions: (i) 4·84 g., 84—100°/11 mm.; (ii) 0·79 g., 60°/0·05 mm.; and a residue (2·62 g.). Fractions (i) and (ii) were combined and shown by g.l.c. to be a mixture of nitrobenzene, *p*-chloronitrobenzene, and an unknown, higher-boiling compound in a ratio of 7 : 3 : 1. The unknown compound was separated from the nitrobenzenes by preparative g.l.c. and was shown (infrared) to be identical with the unknown liquid which was isolated from the reaction between di-*p*-nitrobenzoyl peroxide and chloroform. From the residue an unidentified brown solid (1·37 g.), m. p. 55—60° decomp., was obtained, which was washed with ether (2 × 15 ml.) to leave a stable unidentified light brown solid (0·80 g.), m. p. 150—170° (Found: C, 48·0; H, 2·9; Cl, 24·3; N, 6·5%).

(v) *Bromotrichloromethane and diaroyl peroxides.* The reactions with di-*p*-tolyl, di-*p*-chlorobenzoyl and dibenzoyl peroxides, usually 0·20 g. to 2·00 g., were carried out in a 20 molar excess of solvent at 80° in an atmosphere of nitrogen for 72 hr. When this procedure was applied to di-*p*-nitrobenzoyl peroxide the peroxide was recovered unchanged from the solvent. The result quoted in the Table was obtained from a reaction which was boiled under reflux (106°) in a 20 molar excess of solvent in an atmosphere of nitrogen for 24 hr. In all cases the reaction mixture was analysed by g.l.c. and then worked up for acid content in the usual way. The results are given in Table 4.

(vi) *Bromotrichloromethane and arylazotriphenylmethanes.* The radical source (1 mol.) in bromotrichloromethane (19—22 mol.) was allowed to decompose at 80° for 17—18 hr. The reaction mixtures were analysed by g.l.c. The results are in Table 4.

TABLE 4

Reactions of aryl radicals with bromotrichloromethane

			Products (mole/mole source)					
Ar•	Source [1]	Atmosphere	ArBr	ArCl	C_2Cl_6	CCl_4	$ArCO_2H$	Ar• accounted for (%)
p-CH_3•C_6H_4•[3]...	P	N_2	0·92	0·02	0·57	0·10	0·22	78
Ph• [2]	P	N_2	1·45	0·02	0·57	—	trace	83
p-Cl•C_6H_4•	P	N_2	1·54	0·07	0·77	0·10	0·20	85
p-Cl•C_6H_4•	P	Air	1·26	0·55	0·48	—	0·14	98
p-Cl•C_6H_4•	P	O_2	0·03	0·98	0·01	0·79	0·21	61
p-NO_2•C_6H_4• ...	P	N_2	1·50	0·07	0·01	0·13	trace	79
p-Cl•C_6H_4•	A	N_2	1·00	0·0	0·0	0·0	—	100
Ph•	A	Air	0·99	0·01	0·0	0·0	—	100

[1] P = diaroyl peroxide: A = arylazotriphenylmethane. [2] *p*-CCl_3•C_6H_4•CO_2H (0·20) was also formed. [3] $CHCl_3$ (0·62) and *p*-Br•C_6H_4•CH_2Br (0·50) (m. p. and mixed m. p. 50—51°) were also formed.

*The Reaction between Di-*p*-chlorobenzoyl Peroxide and Bromotrichloromethane in the Presence of Oxygen.*—Reactions were carried out in the presence of air and oxygen at 80° for 72 hr. g.l.c. and other analyses of the reaction mixtures are in Table 4.

Preliminary experiments indicated that phosgene and bromine were products of the reaction. The halogens produced in the reaction were originally trapped by a mixture of oct-1-ene and carbon tetrachloride, and the phosgene in aqueous aniline as diphenylurea. Although phosgene appeared to be trapped satisfactorily, the halogen trap presented certain difficulties as the formation of the 1 : 1-adduct of oct-1-ene and bromotrichloromethane prevented quantitative distillation of the halogen derivatives. However, g.l.c. of the contents of the olefin trap revealed the presence of two products which were separated by preparative g.l.c. (100 × 2 cm. column, 150°, nitrogen gas flow 70 ml. $min.^{-1}$). These were (*a*) a product, retention time 30 min., b. p. 120°/21 mm., with an infrared spectrum very similar to that of the dibromo-octanes (Found: C, 42·7; H, 7·0%. $C_8H_{16}BrCl$ requires C, 42·1; H, 7·0%), and (*b*) 1,2-dibromo-octane, infrared spectrum identical with that of an authentic sample, n_D^{24} 1·4925 (cf. authentic sample n_D^{24} 1·4940) (Found: C, 35·6; H, 5·8; Br, 58·8%. Calc. for $C_8H_{16}Br_2$; C, 35·3; H, 5·9; Br, 58·6%). The evidence strongly suggested that the lower-boiling product is 1-bromo-2-chloro-octane. In order to confirm this result, oct-1-ene was replaced by cyclohexene. The experiment was conducted in a stream of oxygen and the halogens were trapped in a blackened cyclohexene–benzene trap at 5°. A control experiment showed that the 1 : 1-adduct of cyclohexene and bromotrichloromethane was not formed under these conditions, and by analysis of the products in the trap, without any work-up, quantitative measurements were obtained. Comparison with authentic specimens by g.l.c. on two columns confirmed the indentity of the products as *trans*-1,2-dichlorocyclohexane, *trans*-1-bromo-2-chlorocyclohexane and *trans*-1,2-dibromocyclohexane. The results obtained are given in Table 5.

TABLE 5

Volatile products from the reaction between di-*p*-chlorobenzoyl peroxide and bromotrichloromethane in the presence of oxygen

	Products (mole/mole peroxide)					Products (mole/mole peroxide)			
Molar excess of solvent	$COCl_2$	Br_2	Cl_2	Gas flow (ml. min.$^{-1}$)	Molar excess of solvent	$COCl_2$	Br_2	Cl_2	Gas flow (ml. min.$^{-1}$)
20	4·0	—	—	7·5	80	3·6	—	—	7
20	4·0	1·87	0·94	7	80	4·2	1·73	1·00	8
40	4·0	—	—	8					

DISCUSSION

Reactions of Diaroyl Peroxides and p-*Chlorophenylazotriphenylmethane with Chloroform and Carbon Tetrachloride.*—From previous work it was known that benzene was a main product of the reaction of phenyl radicals, produced by the decomposition of dibenzoyl peroxide, with chloroform (Table 1). The results in Table 2 confirm this observation and further show that the presence of substituents (Cl, Me, NO_2) in the *para*-position of the phenyl radical, derived from the corresponding diaroyl peroxide, does not alter significantly the reactivity of the radical towards chloroform. *p*-Chlorophenyl radicals derived from *p*-chlorophenylazotriphenylmethane behaved similarly to give chlorobenzene but no *p*-dichlorobenzene, as did hexyl radicals derived from heptanoyl peroxide, which gave hexane with only a trace of hexyl chloride.

It is not clear why almost exclusive hydrogen abstraction from chloroform occurs. The factors influencing the course of the reaction are the energetics of the bond-breaking and bond-making processes, the relative resonance energies of the possible radicals $\cdot CHCl_2$ and $\cdot CCl_3$, and the relative magnitudes of the non-bonded interactions involving entering and leaving radicals and molecules of the solvent and product. If bond breaking alone controlled the direction of attack of the incoming aryl radical, the strength of the C–H bond (90 kcal. mole^{-1}, cf. C–Cl 70—75 kcal. mole^{-1}) would suppress the abstraction of hydrogen. On the other hand the greater strength of the Ar–H bond relative to the Ar–Cl bond favours hydrogen abstraction. Combination of these factors suggests that abstraction of chlorine would be favoured to the extent of only one kcal. mole^{-1}. The greater resonance energy of the trichloromethyl radical has been invoked [17] to explain the greater ease of abstraction of hydrogen, but this is unlikely to be the only explanation as is discussed below. It may be that this is an important factor but its contribution cannot be accurately assessed in the absence of any data concerning the nature of non-bonded interactions in the system.

The present work has shown that aryl or hexyl radicals can also abstract a chlorine atom from chloroform but only to a negligible extent. With this knowledge it became possible to assess the ease of abstraction of hydrogen from chloroform relative to the ease of abstraction of chlorine from carbon tetrachloride [cf. reactions (i) and (ii)]. Thus the peroxide

$$R\cdot + CHCl_3 \xrightarrow{k_H} RH + \cdot CCl_3 \qquad \text{(i)}$$

$$R\cdot + CCl_4 \xrightarrow{k_{Cl}} RCl + \cdot CCl_3 \qquad \text{(ii)}$$

was allowed to decompose in a large excess of an equimolar mixture of chloroform and carbon tetrachloride and the relative molar yield of products derived from abstraction of hydrogen or chlorine determined by gas–liquid chromatography. Provided the excess of

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[17] C. Walling, " Free Radicals in Solution," J. Wiley and Sons Inc., New York, 1957, p. 47.

solvents is large enough the molar ratio of products is to a first approximation equal to the ratio k_H/k_{Cl}.

Similar competition methods have been used in other quantitative studies of radical reactions.[2,3,18] The possibility of formation of RCl by an indirect route involving acyloxy radicals, reaction (iii), has been discounted by earlier workers [2] when R is alkyl:

$$RCO_2\cdot + CCl_4 \longrightarrow RCO_2Cl \longrightarrow RCl + CO_2 \qquad \text{(iii)}$$

That this also obtains for aryl radicals follows from comparison of the results of the competition experiments using chloroform, carbon tetrachloride, and diaroyl peroxides (Table 3) and those obtained by Bridger and Russell [3] using phenylazotriphenylmethane. Both sources give free aryl radicals but the latter does not give aroyloxy-radicals, hence, if formation of ArCl by a route such as (iii) occurs, then the values of k_H/k_{Cl} now reported and those obtained by Bridger and Russell, should differ. In fact, the value of k_H/k_{Cl} obtained in each case are in agreement. Modes of formation of RH, other than route (i), can also be ignored on the basis of the known properties of aryl radicals. The results of the competition experiments, obtained with a series of aryl radicals (Table 3) show that, as with chloroform alone, directive effects based solely on the relative strengths of the bonds involved in the abstraction processes, are not manifest, *i.e.*, hydrogen abstraction from chloroform occurs approximately three times more readily on a molar basis than abstraction of chlorine from carbon tetrachloride, regardless of the nature of the substituent in the radical. In this case, however, the preferred abstraction of hydrogen cannot be attributed solely to the resonance energy of the trichloromethyl radical, since in the reaction with carbon tetrachloride, not only is the C–Cl bond weaker than the C–H bond in chloroform, but a trichloromethyl radical is also formed. If the resonance energy of the latter were in fact a dominant factor then carbon tetrachloride might be expected to be more, rather than less, reactive towards aryl radicals than chloroform. The observed relative reactivities may be a function of polar factors, but in the absence of a quantitative measure of non-bonded forces between the species [$Ar\cdot$ $H{-}CCl_3$], [$Ar\cdot$ $Cl{-}CCl_3$], [$Ar{-}H$ $\cdot CCl_3$], and [$ArCl$ $\cdot CCl_3$], nothing further can be said at this time.

That the nature of the attacking radical can be important in certain circumstances in determining the mode of reaction with chloroform and carbon tetrachloride follows from the results of the experiments carried out with the hexyl radical (Table 3). In this case the reactivities of carbon tetrachloride and chloroform are reversed since chlorine is more easily abstracted from carbon tetrachloride than is hydrogen from chloroform, the molar ratio of hexane to chlorohexane being almost identical with that obtained by DeTar and Wells [2] in a similar experiment. The preferred reaction of the hexyl radical with carbon tetrachloride rather than chloroform can be correlated with the relative reactivities of these compounds in their addition reactions with oct-1-ene, carbon tetrachloride reacting more readily than chloroform.[19]

Reactions of Diaroyl Peroxides and p-*Chlorophenylazotriphenylmethane with Bromotrichloromethane*.—The ease of homolysis of the C–Br bond in bromotrichloromethane makes this reagent perhaps the best known addendum in free radical addition reactions of olefins.[20] The almost exclusive abstraction of bromine, rather than chlorine, by phenyl and substituted phenyl radicals (cf. Table 4) derived from peroxides and *p*-chlorophenylazotriphenylmethane might therefore be expected. The results are, however, in agreement with this expectation only when the reactions are carried out under nitrogen, and in addition there is no significant change with variation in the substituent. Reaction with di-*p*-chlorobenzoyl peroxide in the presence of air at 80° leads, however, to a much increased proportion of *p*-dichlorobenzene, while reaction in the presence of oxygen gives

[18] D. R. Augood, D. H. Hey, and G. H. Williams, *J.*, 1952, 2094; J. I. G. Cadogan and P. W. Inward, *J.*, 1962, 4170.

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

[20] J. I. G. Cadogan, *Roy. Inst. Chem. Lecture Ser.*, 1961, No. 6.

apparently almost exclusive abstraction of chlorine by the *p*-chlorophenyl radical. Further, in the presence of oxygen phosgene, bromine, and chlorine are major products of the reaction (Table 5). It is also significant that in the reactions of di-*p*-chlorobenzoyl peroxide the yield of hexachloroethane formed by dimerisation of trichloromethyl radicals, falls from a high value of 77% in nitrogen to 1% in oxygen. It is clear that different mechanisms operate in the two extreme cases (in nitrogen and in oxygen), the reaction carried out in air representing an intermediate behaviour.

In nitrogen the *p*-chlorophenyl radical abstracts a bromine atom to give *p*-bromochlorobenzene and a trichloromethyl radical which appears eventually as hexachloroethane, thus:

$$\mathrm{Ar\bullet + BrCCl_3 \longrightarrow ArBr + \bullet CCl_3} \tag{iv}$$

$$\mathrm{2\bullet CCl_3 \longrightarrow C_2Cl_6} \tag{v}$$

In oxygen, where *p*-dichlorobenzene is the major product, the aryl radical must react with a species which must be a chlorine donor and which is more reactive than bromotrichloromethane. The following rationalisation is in accord with the experimental results: a trichloromethyl radical, formed as in reaction (iv), and which normally dimerises in nitrogen, is captured by oxygen to give a new peroxy-radical (I), which in turn abstracts halogen from bromotrichloromethane to give the peroxide (II) and a trichloromethyl radical, thus giving rise to a chain reaction. The peroxy-radicals (I) have been previously postulated as intermediates in the oxidation of chloroform and carbon tetrachloride.[21-23] The peroxide (II) is now assumed to react with a *p*-chlorophenyl radical to give 1,4-dichlorobenzene and an intermediate (III) which, on decomposition, gives phosgene, bromine, chlorine, and oxygen. Direct decomposition of the peroxide (II) can also give the same products, while phosgene and chlorine can also arise by decomposition of (I). The detailed mechanism of the breakdown of the peroxide (II) and of the peroxy-intermediate (III) is unknown. That replacement of nitrogen by air does not lead to a similar change in behaviour of the aryl radical derived from arylazotriphenylmethanes may be attributed (*a*) to the fact that decomposition of such reagents leads to evolution of nitrogen which displaces air in the reaction vessels and (*b*) to competitive removal of trichloromethyl radicals by combination with free triphenylmethyl radicals present: it has been shown that 1,1,1-trichloro-2,2,2-triphenylethane is a product of such reactions.[1] The possibility that 1,4-dichlorobenzene arises from reaction of *p*-chlorophenyl radicals with phosgene cannot be eliminated but is considered to be unlikely in view of the low reactivity of the C–Cl bond in acyl chlorides towards free radicals.[24]

$$\begin{aligned}
\mathrm{CCl_3\bullet + O_2} &\longrightarrow \mathrm{CCl_3{\cdot}O_2\bullet\ (I)}\\
\mathrm{2\,(I)} &\longrightarrow \mathrm{2COCl_2 + Cl_2}\\
\mathrm{(I) + BrCCl_3} &\longrightarrow \mathrm{CCl_3{\cdot}O{\cdot}O{\cdot}Br\ (II) + \bullet CCl_3}\\
\mathrm{\bullet Ar + (II)} &\longrightarrow \mathrm{ArCl + \bullet CCl_2O{\cdot}OBr\ (III)}\\
\mathrm{(III)} &\longrightarrow \mathrm{COCl_2 + \tfrac{1}{2}Br_2 + \tfrac{1}{2}O_2}\\
\mathrm{2\,(II)} &\longrightarrow \mathrm{2COCl_2 + Br_2 + Cl_2 + O_2}
\end{aligned}$$

The high yield of carbon tetrachloride formed in experiments under oxygen indicates that trichloromethyl radicals behave as do aryl radicals in abstracting a chlorine atom from the intermediate (II). The above explanation rests on the assumption that the intermediate trichloromethyl radicals are trapped by oxygen, in which case it might be expected that anomalous abstractions might also occur when diacyl peroxides are decomposed in chloroform in the presence of air or oxygen. In practice the decomposition pattern in chloroform was found to be identical in air and nitrogen, a result which is attributed to the

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[21] A. T. Chapman, *J. Amer. Chem. Soc.*, 1935, **57**, 416.

[22] J. Bednar and J. Teply, *Coll. Czech. Chem. Comm.*, 1960, **25**, 842 (*Chem. Abs.*, 1960, **54**, 20,445).

[23] D. F. DeTar and C. Weis, *J. Amer. Chem. Soc.*, 1956, **78**, 4296.

[24] J. C. Allen, J. I. G. Cadogan, and D. H. Hey, *J.*, 1965, 1918.

fact that the reactions were carried out at the boiling point, *i.e.*, in an inert atmosphere. The reactions in bromotrichloromethane which gave anomalous results were carried out at 80°, *i.e.*, below the boiling point. Reactions carried out *at the boiling point* in air gave results identical with those carried out in nitrogen, thus supporting the above rationalisation.

The Fate of Trichloromethyl Radicals Produced in the Reactions of Diaroyl Peroxides with Chloroform, Carbon Tetrachloride, and Bromotrichloromethane.—The fate of the trichloromethyl radicals produced in reaction of di-*p*-chlorobenzoyl peroxide with bromotrichloromethane in the presence of oxygen has been discussed above. In reactions carried out under nitrogen the final products of reaction of the trichloromethyl radicals produced in the abstraction processes vary according to the peroxide employed and are mainly independent of the nature of the polyhalogenomethane. In the case of di-*p*-chlorobenzoyl peroxide, in all three solvents, the trichloromethyl radicals produced in the primary abstraction process: $Ar\cdot + CXCl_3 \longrightarrow ArX + \cdot CCl_3$, appear as the dimer, hexachloroethane, the yields of ArX and hexachloroethane being almost equivalent. When the decomposition is carried out in bromotrichloromethane, replacement of the chlorine atom in the peroxide by a methyl group leads to the production of less than an equivalent of hexachloroethane, and to the formation of *p*-bromobenzyl bromide (0·50 mole/mole peroxide), chloroform (0·62 mole/mole peroxide), and carbon tetrachloride (0·10 mole/mole peroxide). The formation of carbon tetrachloride can be accounted for on the basis of abstraction of chlorine from bromotrichloromethane thus: $\cdot CCl_3 + BrCCl_3 \longrightarrow CCl_4 + \cdot CBrCl_2$. The identity reaction $\cdot CCl_3 + BrCCl_3 \longrightarrow CCl_3Br + \cdot CCl_3$, although much more favoured, is not detectable. The presence of chloroform and *p*-bromobenzyl bromide, formed in almost approximately equivalent amounts, indicates that interaction with the alkyl side chain occurs. The possible reaction paths are shown in Schemes 1 and 2.

It is probable that both reactions occur since small concentrations of the peroxide and *p*-bromotoluene are present in the reaction mixture, and it is significant that addition of *p*-bromotoluene (0·8 mol.) to the reaction between the peroxide (1 mol.) and bromotrichloromethane (20 mol.) increased the yield of *p*-bromobenzyl bromide from 50% to 72%. The isolation of small amounts of benzyl chloride from the reaction of di-*p*-methylbenzoyl peroxide with chloroform can be explained in a similar way, the difference in yields being a function of the greater reactivity of bromotrichloromethane in this type of reaction.

$$\begin{array}{rcl}
\cdot CCl_3 + (CH_3\cdot C_6H_4\cdot CO_2)_2 & \longrightarrow & CHCl_3 + \cdot CH_2\cdot C_6H_4\cdot CO_2\cdot O_2C\cdot C_6H_4\cdot CH_3 \\
 & & \Big\downarrow {\scriptstyle BrCCl_3} \\
 & & BrCH_2\cdot C_6H_4\cdot CO_2\cdot O_2C\cdot C_6H_4CH_3 + \cdot CCl_3 \\
 & & \Big\downarrow \\
 & & BrCH_2\cdot C_6H_4\cdot + 2CO_2 + CH_3\cdot C_6H_4\cdot \\
Br\cdot CH_2\cdot C_6H_4\cdot + BrCCl_3 & \longrightarrow & BrCH_2\cdot C_6H_4Br + \cdot CCl_3
\end{array}$$

Scheme 1

$$\begin{array}{rcl}
(CH_3\cdot C_6H_4\cdot CO_2)_2 & \longrightarrow & 2CH_3\cdot C_6H_4\cdot CO_2\cdot \\
CH_3\cdot C_6H_4\cdot CO_2\cdot & \longrightarrow & CH_3\cdot C_6H_4\cdot + CO_2 \\
CH_3\cdot C_6H_4\cdot + BrCCl_3 & \longrightarrow & CH_3\cdot C_6H_4\cdot Br + \cdot CCl_3 \\
\cdot CCl_3 + Br\cdot C_6H_4\cdot CH_3 & \longrightarrow & CHCl_3 + Br\cdot C_6H_4\cdot CH_2\cdot \text{ etc.} \ldots
\end{array}$$

Scheme 2

Decomposition of dibenzoyl peroxide in all three solvents also leads to a reduction in yield of hexachloroethane, but in these cases *p*-trichloromethylbenzoic acid is formed. The formation of this product from similar reactions was first reported by Boeseken and

Gelissen [4a] and later by Hey and Peters,[8] who noted that it was not derived from the reaction of trichloromethyl radicals with benzoic acid, another product present. The genesis of this compound has not been satisfactorily explained although it is likely that the reactions follow from the addition of the trichloromethyl radical to the *p*-position of the aromatic ring in the peroxide. DeTar and Weis [23] suggest that in chloroform the resulting intermediate stabilised hexadienyl radical (IV) undergoes concerted breakdown to give benzoic acid and a *p*-trichloromethylbenzoyloxy-radical, which in turn abstracts hydrogen from the solvent to give the observed acid [reaction (vi)]. This suggestion is not in accord with the experimental observations now recorded in that (*a*) benzoic acid is not formed to any significant extent in bromotrichloromethane, (*b*) an intermediate *p*-trichloromethylbenzoyloxy-radical would be expected to decompose to give a *p*-trichloromethylphenyl radical, end products of which were not detected, and (*c*) no abstractable hydrogen is available in bromotrichloromethane. It is more likely that the intermediate radical (IV) undergoes homolysis of the peroxy-bond with concerted hydrogen abstraction to give *p*-trichloromethylbenzoic acid in one stage as shown in reaction (viii) (a similar reaction can also occur in the *o*-canonical form). This rationalisation is in accord with experimental facts and is preferred to the suggestion of Walling and Savas [25] that a further intermediate, the α-lactone (V), is involved [reaction (vii)]. These workers did not formulate a concerted decomposition such as is now postulated and discounted it on the basis of an absence of a deuterium isotope effect in the induced decomposition of ring deuterated benzoyl peroxide in cyclohexane. It would appear that this is a mistaken conclusion since by analogy with known substitution reactions in benzene, which proceed by an initial addition step followed by loss of hydrogen, the rate-determining step in reaction (viii) is the formation of the trichloromethylcyclohexadienyl peroxide radical (IV), subsequent intramolecular abstraction of hydrogen being kinetically insignificant. This sequence would give rise to no isotope effect, as was observed, in fact, by Walling and Savas.[25] The acidic hydrogen atom in the isolated *p*-trichloromethylbenzoic acid cannot come from the solvent (carbon tetrachloride or bromotrichloromethane) or from an aromatic structure by *direct* abstraction from the nucleus, and hence, ruling out working-up procedure and adventitious moisture, it must arise from a *hydroaromatic* structure such as (IV). The conclusion that the hydrogen atom of *p*-trichloromethylbenzoic acid originates in the *p*-position of the peroxide [reaction (viii)] is in accord with the observation that *p*-substituted peroxides do not undergo this type of reaction.

Relevant to this discussion of the nature of products of induced decomposition of dibenzoyl peroxide is the isolation by Davies, Hey, and Williams [26] of the lactone (VIII) of 2′-hydroxybiphenyl-2-carboxylic acid from the decomposition of dibenzoyl peroxide in chlorobenzene and biphenyl. These workers suggested that the lactone arose by combination of phenyl and benzoyloxy-radicals to give an intermediate (VI), dehydrogenation of which would give the lactone (VIII). In view of the foregoing discussion it seems more likely that the intermediate radical (VI), and hence the lactone (VIII), also arises by induced decomposition of dibenzoyl peroxide as shown in reaction (ix).* A reaction path involving an α-lactone (VII) would involve nucleophilic attack on an aromatic ring and is therefore unlikely.

Yet another mode of behaviour on decomposition in chloroform, carbon tetrachloride or bromotrichloromethane is shown by di-*p*-nitrobenzoyl peroxide, when little or no hexachloroethane is formed, the reactions being accompanied by a lower accountance of the peroxide as identified products and by a large unidentified residue. By analogy with reactions of other free radicals [27] it is possible that interaction of trichloromethyl radicals

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* We acknowledge helpful discussion on this point with Dr. M. J. Perkins.

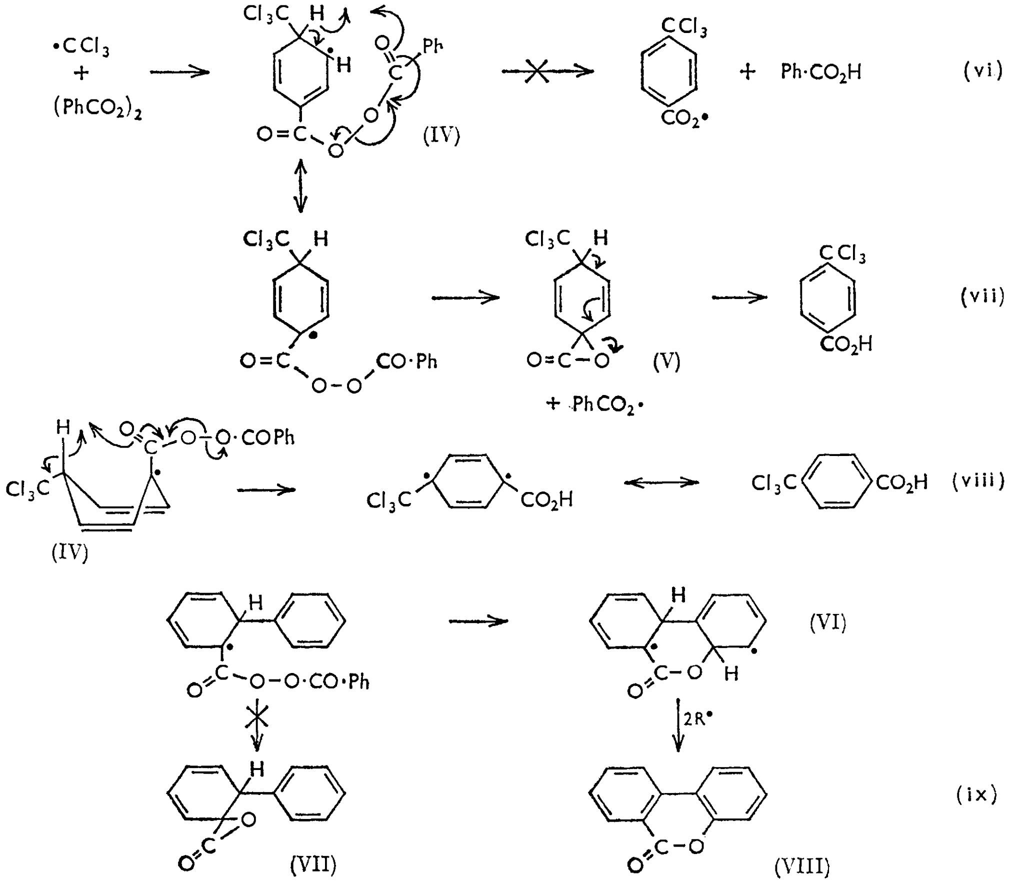
[25] C. Walling and E. S. Savas, *J. Amer. Chem. Soc.*, 1960, **82**, 1738.

[26] D. I. Davies, D. H. Hey, and G. H. Williams, *J.*, 1961, 562.

[27] J. I. G. Cadogan, D. H. Hey, and W. A. Sanderson, *J.*, 1961, 3879; R. A. Jackson and W. A. Waters, *J.*, 1960, 1653.

with the nitro-group occurs or with the carbonyl group in a manner similar to that suggested by Cooper,[28] who also noted anomalous effects during the decomposition of nitrobenzoyl peroxides.

Finally, it is necessary to comment on the formation of substituted benzoic acids in the reactions involving substituted peroxides. The small amounts which are formed in the presence of chloroform (Tables 2 and 3) can be attributed to direct interaction of aroyloxy-radicals with the solvent. The amount is enhanced in the case of di-*p*-methylbenzoyl peroxide by interaction with the side chain as discussed above, and decreased in the case of the nitrobenzoyl peroxide and benzoyl peroxide also for reasons previously discussed. In the case of bromotrichloromethane, however, despite the absence of hydrogen in the solvent the yields of acids, except in the case of the nitro- and unsubstituted compounds, are increased significantly. Since hydrolysis of intermediates can be discounted on experimental grounds, the mode of formation of the carboxylic acids in these cases is not yet understood.



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St. Andrews, Fife.] [*Received, November* 12*th*, 1964.]

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[28] W. Cooper, *J.*, 1952, 2408.