16. *Reactions of Aryl Radicals with Aliphatic Compounds. Part I. The Reactions of Phenyl Radicals with Carbon Tetrachloride, Chloroform, and Bromoform.*

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The main products formed in the reactions of benzoyl peroxide, phenylazotriphenylmethane, nitrosoacetanilide, and benzene diazo-hydroxide and -acetate, with carbon tetrachloride, chloroform, and bromoform have been determined quantitatively. Some earlier qualitative results on these reactions require modification. Only the reaction between nitrosoacetanilide and chloroform gives both benzene and chlorobenzene but all the reactions with bromoform give both benzene and bromobenzene. The formation of the ωωω-trichlorotoluic acids in the reactions of benzoyl peroxide with carbon tetrachloride and with chloroform is discussed.

IN recent years considerable attention has been devoted to the quantitative investigation of the reactions between aryl radicals from various sources and aromatic compounds. No similar systematic work has been undertaken on the reactions between aryl radicals and saturated aliphatic compounds. The two problems are essentially different in that in the aromatic series the overall reaction is one of substitution, probably proceeding by addition followed by elimination, whereas in the aliphatic series the primary reaction is abstraction of hydrogen (or halogen), which may be followed by a chain-reaction. The present communication describes the results of investigations designed to provide both qualitative and quantitative information on the reactions between aryl radicals from different sources and some saturated aliphatic halogenated hydrocarbons.

Reactions with four sources of phenyl radicals have been chosen for investigation, namely (*a*) benzoyl peroxide, (*b*) phenylazotriphenylmethane, (*c*) nitrosoacetanilide, and (*d*) benzene diazo-hydroxide and -acetate. Earlier work on some of these reactions is qualitative. Boeseken and Gelissen [1] reported the reactions between benzoyl peroxide and both carbon tetrachloride and chloroform and they isolated, as the main products, chlorobenzene and benzene, respectively, together with hexachloroethane and ωωω-trichloro-*p*-toluic acid. The reaction with carbon tetrachloride was re-investigated by Ikeda and Wakita [2] with substantially the same results. The reactions of nitrosoacetanilide and benzene diazohydroxide with both carbon tetrachloride and chloroform were reported by Grieve and Hey [3] and by Waters [4]. The former reagent gave chlorobenzene with both carbon tetrachloride and chloroform, whereas the latter reagent gave chlorobenzene with carbon tetrachloride and benzene with chloroform. The reaction between phenylazo-triphenylmethane and carbon tetrachloride gave chlorobenzene and 1,1,1-trichloro-triphenylethane [5]. Bromoform has been used only in reaction with nitrosoacetanilide, which led to the formation of bromobenzene [4].

Quantitative study of the reactions between phenyl radicals and carbon tetrachloride, chloroform, and bromoform requires an accurate method for the estimation of benzene, chlorobenzene, and bromobenzene in the presence of a large excess of the halogenated solvent. For this purpose a method based on dinitration was developed and tested with experimental mixtures of known composition. Both benzene and chlorobenzene could be converted under standardised conditions into the dinitro-derivatives in more than 95% yield and bromobenzene could be dinitrated in at least 97% yield after the removal of the excess of bromoform by alkaline hydrolysis. The methods employed for the isolation of

[1] Boeseken and Gelissen, *Rec. Trav. chim.*, 1924, **43**, 869.
[2] Ikeda and Wakita, *Bull. Liberal Arts College, Wakayama Univ.*, 1955, **5**, 12.
[3] Grieve and Hey, *J.*, 1934, 1797.
[4] Waters, *J.*, 1937, 113.
[5] Wieland and Heyman, *Annalen*, 1934, **514**, 145.

the other products from the reactions varied with the nature of the source of phenyl radicals used and are described in the Experimental section.

In the reactions between phenyl radicals and carbon tetrachloride, chloroform, and bromoform it must be assumed that the primary reaction is abstraction of hydrogen or halogen from the solvent molecule to give benzene or a halogenobenzene. The subsequent behaviour of the halogenated alkyl radical thus formed will lead to the formation of further products. The yields of benzene and halogenobenzene obtained in the reactions with benzoyl peroxide, phenylazotriphenylmethane, nitrosoacetanilide, and benzene diazo-hydroxide and -acetate are summarised in the Table. The results obtained with carbon tetrachloride are in agreement with expectation. The yield of chlorobenzene is highest when benzoyl peroxide is used. The lower yields with the other reagents are a reflection of the tarry nature of the reaction mixtures. The very low yield obtained with benzene-diazonium chloride by method (C) is accompanied by a relatively high yield of phenol, which implies that a faster heterolytic reaction becomes predominant under these conditions.

The reactions with chloroform show the expected formation of benzene in good yield with both benzoyl peroxide and phenylazotriphenylmethane and in moderate yield from benzenediazonium chloride by methods (A) and (B). The concomitant formation of benzene and chlorobenzene in almost equivalent yield from the reaction with nitroso-acetanilide is unexpected. Earlier qualitative work had recorded the formation of only chlorobenzene in this reaction. A similar abnormal result is found in the reaction with benzenediazonium chloride by method (C). Here again much phenol is formed. The formation of chlorobenzene is in keeping with the fact that the benzene diazoacetate formed in this reaction is tautomeric with nitrosoacetanilide, but the absence of benzene is un-expected. The reactions with bromoform are unusual in that they all give mixtures of benzene and bromobenzene. With phenylazotriphenylmethane the yields of benzene and bromobenzene are almost equivalent, but with the other reagents the yields of benzene and bromobenzene are in the approximate ratio of one to four. The foregoing results indicate that some of the earlier qualitative work has given misleading results.

Average yields of products obtained in reactions of phenyl radicals with carbon tetrachloride, chloroform, and bromoform expressed as moles per mole of radical source (reaction temperatures are given in parentheses).

Radical source	With CCl_4 PhCl		With $CHCl_3$ PhH	PhCl		With $CHBr_3$ PhH	PhBr
Benzoyl peroxide	1·28	(76°)	1·37	0	(62°)	0·17	0·76 (80°)
Phenylazotriphenylmethane	0·27	(55°)	0·90	0	(55°)	0·31	0·40 (55°)
Nitrosoacetanilide	0·32	(20°)	0·20	0·15	(20°)	—	—
Benzene diazonium chloride (A) * ...	0·28	(0—20°)	0·47	0	(0—20°)	—	—
,, ,, (B) * ...	0·35	(0—20°)	0·49	0	(0—20°)	0·01	0·04 (0—20°)
,, ,, (C) * ...	0·06	(0—20°)	0	0·11	(0—20°)	0·04	0·20 (0—20°)

* For description of methods (A), (B), and (C), see Experimental Section.

In the products from the reactions with phenylazotriphenylmethane, it is significant that no halogenotriphenylmethane was found, and that appreciable quantities of triphenyl-methane were isolated. The formation of the latter, even from the reaction with carbon tetrachloride, suggests that the phenylazotriphenylmethane used may not have been entirely free from benzene and ethanol. A similar problem was encountered by Kharasch, McBay, and Urry [5a] in the reaction between acetyl peroxide and trichloroacetyl chloride, which gave significant quantities of methane and much less methyl chloride.

Kharasch and Buchi [6] have shown that methyl radicals derived from acetyl peroxide react with n-butyl, s-butyl and t-pentyl chlorides with abstraction of both hydrogen and chlorine, although hydrogen was abstracted more readily than chlorine. Edwards and Mayo [7] obtained methyl chloride from the reaction between acetyl peroxide and carbon

[5a] Kharasch, McBay, and Urry, *J. Org. Chem.*, 1945, **10**, 394.
[6] Kharasch and Buchi, *J. Amer. Chem. Soc.*, 1951, **73**, 632.
[7] Edwards and Mayo, *J. Amer. Chem. Soc.*, 1950, **72**, 1265.

tetrachloride, and methane but not methyl chloride in a similar reaction with chloroform. Further, many investigations have been reported on the peroxide- or light-induced addition of carbon tetrachloride, chloroform, and bromoform to olefinic double bonds. Kharasch, Urry, and Jensen [8] showed that carbon tetrachloride, chloroform, and bromoform add to the olefin $RCH:CH_2$ to give $RCHCl \cdot CH_2 \cdot CCl_3$, $RCH_2 \cdot CH_2 \cdot CCl_3$, and $R \cdot CHBr \cdot CH_2 \cdot CHBr_2$, respectively. The formation of these products was regarded as indicating that chloroform loses a hydrogen atom in preference to a chlorine atom but that bromoform loses a bromine atom in preference to a hydrogen atom. The results now reported for the reactions with phenyl radicals are in agreement with these earlier observations with two important exceptions, namely (a) the reaction of nitrosoacetanilide with chloroform, which has been shown to involve both hydrogen and chlorine abstraction, and (b) the reactions with bromoform, which indicate that hydrogen and bromine abstraction is a general feature. It would appear that the factors which influence the severance of the C–H and C–Br bonds in bromoform are more delicately balanced than was previously suspected.

The anomaly revealed in the reaction between nitrosoacetanilide and chloroform is not entirely unexpected because this reagent has also shown an abnormal behaviour in other investigations. For example, the very low yields of carbon dioxide obtained in its decomposition have been freely commented upon and again in its reaction with pyridine the relative yields of the three isomeric phenylpyridines are significantly different from those obtained with other sources of the phenyl radical.[9] It has in fact been suggested by Huisgen and Horeld [10] that in the decomposition of nitrosoacetanilide no truly *free* radicals are involved, but that a complex is formed between this compound and the solvent within which the homolytic reaction takes place. Within such a complex the chances of the formation of both chlorobenzene and acetic acid would be enhanced and the absence of hexachloroethane, another notable anomaly in this reaction, would not be unexpected. It is also possible that the decomposition reactions of nitrosoacetanilide involve the simultaneous occurrence of a homolytic and a heterolytic reaction.

The manner in which the $\omega\omega\omega$-trichlorotoluic acids are formed in the reactions of benzoyl peroxide with carbon tetrachloride and chloroform is obscure, but it has now been established that the *meta*-isomer is absent and that the *para*-isomer is accompanied by a small proportion (2—3%) of the *ortho*-isomer. These results suggest the existence of a mesomeric benzoate radical as represented below:
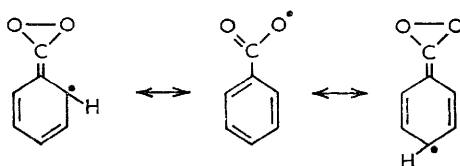
This suggestion receives some support from the observation that the yield of $\omega\omega\omega$-trichlorotoluic acids is not increased when benzoic acid is added to the reaction between benzoyl peroxide and carbon tetrachloride, thus indicating the improbability of a direct attack by the trichloromethyl radical on a benzoic acid molecule.

EXPERIMENTAL

General Procedure.—The solution of benzoyl peroxide, phenylazotriphenylmethane, or nitrosoacetanilide in a ten- to twenty-fold molar excess of the solvent, was contained in a flask fitted with a side-arm for the insertion of a thermometer and with a double-surface reflux condenser, the top of which was closed by a mercury seal. Air was flushed from the system by passage of nitrogen. The solution was brought rapidly to the desired temperature. The

[8] Kharasch, Urry, and Jensen, *J. Amer. Chem. Soc.*, 1947, **69**, 1100.
[9] Hey, Stirling, and Williams, *J.*, 1955, 3963.
[10] Huisgen and Horeld, *Annalen*, 1949, **562**, 137.

reactions with benzoyl peroxide were carried out at 80° during 3 days, those with phenylazo-triphenylmethane at 55° for 30 hr., and those with nitrosoacetanilide at room temperature (*ca.* 20°) for 2—3 days. When the solvent had a boiling point below 80°, the reaction with benzoyl peroxide was carried out at the boiling point for a suitably longer time. The reactions in the two-phase system with aqueous benzene diazohydroxide or diazoacetate were carried out at 0° for 3 hr. and then at room temperature for a further period up to 3 days. In experiments designed to measure the carbon dioxide evolved, this was done in small-scale reactions by means of a gas burette containing liquid paraffin, or by passage of the gases (carbon dioxide and nitrogen) through a tube containing paraffin wax chips and absorption of the carbon dioxide in a weighed tube containing either soda-lime or Carbosorb (B.D.H.). Most of the reactions were carried out at least in duplicate.

Quantitative Analytical Methods.—(*a*) *Estimation of small quantities of* PhX, *where* X *is* H, Cl, *or* Br, *in the presence of a large excess of carbon tetrachloride, chloroform, or bromoform.* It was established that under the standard conditions employed benzene could be converted into *m*-dinitrobenzene, chlorobenzene into 1-chloro-2,4-dinitrobenzene, and bromobenzene into 1-bromo-2,4-dinitrobenzene, in yields greater than 95% from mixtures of these compounds with chloroform, carbon tetrachloride, or bromoform. The detailed procedures are illustrated by the following examples:

(i) Estimation of benzene in chloroform or carbon tetrachloride. To a mixture of benzene (4·03 g.) and chloroform (or carbon tetrachloride) (25 ml.) vigorously stirred at 0—5° was added dropwise a cooled mixture of nitric acid (*d* 1·51; 6 ml.) and sulphuric acid (*d* 1·84; 6 ml.). The temperature was kept below 5° throughout the addition. Subsequently the mixture was warmed until the chloroform (or carbon tetrachloride) boiled under reflux and a further 12 ml. of the mixed acids were added slowly. The mixture was boiled under reflux for a further hour, after which the organic solvent was removed by distillation. When cold the reaction mixture was poured slowly into ice–water and the precipitate was collected in a weighed funnel and washed well with ice–water until the washings were colourless. The filter and precipitate were dried to constant weight over sulphuric acid *in vacuo*. *m*-Dinitrobenzene (8·40 g., 97%), m. p. 80—82°, was obtained.

(ii) Estimation of chlorobenzene in carbon tetrachloride. To a solution of chlorobenzene (2·00 g.) in carbon tetrachloride (25 ml.) was added sulphuric acid (*d* 1·84; 4 ml.), and the mixture was cooled to 5—10°. To this vigorously stirred mixture was added dropwise a mixture of nitric acid (*d* 1·51; 8 ml.) and sulphuric acid (*d* 1·84; 4 ml.), the temperature being kept below 10°. After 30 min., the mixture was boiled under reflux for a further 30 min. and the solvent was then removed by distillation. The residue was poured slowly into ice–water and the product collected, washed, and dried as in (i) above. 1-Chloro-2,4-dinitrobenzene (3·53 g., 98%) m. p. 44—48°, was obtained.

(iii) Estimation of bromobenzene in bromoform. A mixture of bromobenzene (1·39 g.) and bromoform (20 g.) was boiled under reflux for 8 hr. with aqueous sodium hydroxide (25 g. in 150 ml.). The cooled mixture was extracted with chloroform (3 × 35 ml.), and the extract dried (CaCl$_2$). This solution was then nitrated as described under (ii) above. 1-Bromo-2,4-dinitrobenzene (2·19 g., 100%), m. p. 68—70°, was obtained.

(*b*) *Estimation of benzoic acid.* Because benzoic acid co-distils from the reaction mixtures during the removal of solvent by distillation, it was removed before distillation: it was extracted by washing the mixture several times with dilute aqueous sodium hydroxide or with saturated aqueous sodium carbonate. The aqueous extract was subsequently washed once with the solvent used in the reaction and this was added to the main bulk of the reaction mixture. The aqueous solution was then washed once with ether and warmed to 70—80° with stirring. When cold, the solution was acidified and the precipitated benzoic acid was extracted with several portions of methylene chloride. After being dried (MgSO$_4$) the solvent was allowed to evaporate at room temperature, leaving dry crystalline benzoic acid. When other acids, in addition to benzoic acid, were present the method outlined above was suitably modified, as described later.

Preparation and Purification of Reagents.—Carbon tetrachloride (B.D.H.; " AnalaR ") was shaken several times with sulphuric acid (*d* 1·84) and then successively with water, aqueous sodium hydroxide, and water. It was dried (KOH), fractionated, and collected at 77·8—78·0°. Chloroform (M. and B. Analytical Grade containing 1% of ethanol), shaken with sulphuric acid and washed as for carbon tetrachloride, was dried over calcium chloride for 7 days and then

over phosphoric oxide.   It was fractionated in a stream of nitrogen and collected at 60·8°.   It was stored in darkness under nitrogen.   Bromoform (B.D.H.) was purified by a modification of the method of Smyth and Rogers.[11]   It was shaken with sulphuric acid (*d* 1·84) until this no longer became coloured and was then shaken rapidly with two portions of aqueous sodium hydrogen carbonate and then with water.   It was dried (CaCl$_2$) for 3 days and fractionally frozen until approximately 95% had solidified.   The liquid was then drained off.   This operation was repeated six times to give a product, m. p. 7·8—8·0°, which was stored under nitrogen. It was redistilled immediately before use and collected at 148·8—149°.

Benzoyl peroxide (Hopkin and Williams) was dissolved in the minimum quantity of chloroform, the solution filtered, and the upper layer removed.   The peroxide was precipitated from the chloroform solution by the slow addition of cold anhydrous methanol at 0° with stirring. This operation was repeated twice and the residual chloroform was removed under a vacuum. The peroxide (m. p. 105°) was stored in a desiccator in darkness.   Phenylhydrazotriphenyl-methane was prepared by Gomberg's method[12] and it was oxidised to phenylazotriphenyl-methane as described by Wieland, vom Hove, and Börner.[13]   The azo-compound, purified by repeated precipitation from benzene solution with ethanol at 0°, had m. p. 108°.   Nitrosoacet-anilide, m. p. 52—53°, was prepared by the method of France, Heilbron, and Hey,[14] using nitrosyl chloride prepared as described by Girard and Pabst.[15]

Reactions with Benzoyl Peroxide.—(i) *With carbon tetrachloride.*   Benzoyl peroxide (24·2 g.) in carbon tetrachloride (200 ml.) was kept at the boiling point (76°) as described above under the general procedure.   The mixture was then kept for 5 days in a refrigerator; crystalline material slowly separated (3·91 g.; m. p. 183—186°), and was recrystallised twice from carbon tetra-chloride.   ωωω-Trichloro-*p*-toluic acid (3·59 g.) separated in plates, m. p. 196·5° (Found: C, 40·3; H, 2·3; Cl, 43·9.   Calc. for C$_8$H$_5$O$_2$Cl$_3$: C, 40·1; H, 2·1; Cl, 44·4%).   Davies and Perkin[16] reported m. p. 196—197°.   The carbon tetrachloride mother-liquid contained hexa-chloroethane (0·32 g.; m. p. 184° with sublimation).   The main carbon tetrachloride solution was extracted with aqueous sodium carbonate and dried (CaCl$_2$).   The aqueous alkaline extract was boiled in order to hydrolyse the ωωω-trichlorotoluic acids to the corresponding phthalic acids.   Subsequent acidification with concentrated hydrochloric acid gave a bulky, gelatinous precipitate.   This suspension of acids was saturated with sodium chloride and shaken with toluene (30 ml.) to remove benzoic acid, and the toluene layer, the aqueous layer, and the solid in suspension were separated by centrifugation.   The toluene solution was extracted with aqueous sodium carbonate, the alkaline extract was acidified, and the benzoic acid was extracted with methylene chloride.   This dried extract on evaporation at room temperature gave benzoic acid, m. p. 118—119° (0·13 g.) after recrystallisation from water.   The m. p. of a mixture with an authentic specimen was 120°.   The aqueous layer from the centrifugation was extracted with acetone–methylene chloride (1 : 1 by vol), the extract was dried (Na$_2$SO$_4$), and the solvent allowed to evaporate.   The residue (0·06 g.), m. p. 190—191°, was phthalic acid (strong fluorescein test and mixed m. p.).   The insoluble residue from the centrifugation was washed successively with boiling water (100 ml.), glacial acetic acid (5 ml.), and ether (10 ml.), and then dried (H$_2$SO$_4$).   The residue (2·50 g.), m. p. >300°, contained terephthalic acid.   The water and acetic acid washings were combined and yielded more phthalic acid (0·04 g.; m. p. 180—190°).   The ether washing gave terephthalic acid (0·03 g.; m. p. >300°).   The combined samples of the acids melting above 300° were examined for the presence of isophthalic acid by application of the method of separation by means of the thallous salts.[17]   Isophthalic acid was not found but the identity of the terephthalic acid was confirmed by preparation of the methyl ester, m. p. 137—139° (mixed m. p. 139°), by Bryce-Smith and Turner's method.[18]

The main carbon tetrachloride solution, from which the acids had been extracted, was fractionated and the distillate collected at 76—80°.   This was carefully refractionated and collected at 76—80°, the small residue being added to the combined fractions (*a*) and (*b*) below before nitration.   The distillate (b. p. 76—80°) was treated with nitrating acids as described

[11] Smyth and Rogers, *J. Amer. Chem. Soc.*, 1930, **52**, 2227.
[12] Gomberg, *Ber.*, 1897, **30**, 2043.
[13] Wieland, vom Hove, and Börner, *Annalen*, 1926, **446**, 31.
[14] France, Heilbron, and Hey, *J.*, 1940, 369.
[15] Girard and Pabst, *Bull. Soc. chim. France*, 1878, **30**, 531.
[16] Davies and Perkin, *J.*, 1922, **121**, 2202.
[17] Bryce-Smith, *Chem. and Ind.*, 1953, 244.
[18] Bryce-Smith and Turner, *J.*, 1953, 864.

above but no *m*-dinitrobenzene was found. The residue after the removal of the carbon tetra-chloride deposited large crystals of hexachloroethane (2·95 g.), m. p. and mixed m. p. 186°, which were collected by filtration. The filtrate was distilled and the following fractions were collected: (*a*) b. p. 70—100°/760 mm.; (*b*) b. p. 100—135°/760 mm. (*a* + *b* = *ca*. 25 g.); (*c*) sublimate/1 mm., m. p. 186° (8·27 g.); (*d*) b. p. 80—90°/1 mm. (0·14 g.); (*e*) b. p. 90—100°/1 mm. (0·18 g.); (*f*) b. p. 105—115°/ 1 mm. (0·18 g.). The residue weighed 1·8 g. Fractions (*a*) and (*b*) contained some carbon tetrachloride in addition to chlorobenzene, and nitration as described above gave 1-chloro-2,4-dinitrobenzene, m. p. 48° (27·33 g. ≡ 15·2 g. of chlorobenzene) (Found: Cl, 17·8. Calc. for $C_6H_3O_4N_2Cl$: Cl, 17·5%). Fraction (*c*) consisted of pure hexachloroethane. Hydrolysis of fraction (*f*) gave phenol and terephthalic acid (methyl ester, m. p. 138°), which suggests that this fraction contains phenyl ωωω-trichloro-*p*-toluate (Found: C, 54·6; H, 3·3; Cl, 28·5. Calc. for $C_{14}H_9O_2Cl_3$: C, 53·3; H, 2·9; Cl, 33·7%). An authentic sample of this ester had b. p. 126—129°/2 mm. and behaved similarly on hydrolysis. The non-volatile residue had an odour of 4-chlorodiphenyl. It was boiled with aqueous sodium hydroxide; subsequent extraction with chloroform gave 4-chlorodiphenyl (0·03 g.), m. p. 73° and mixed m. p. 75°. The alkaline solution gave a trace of phenol and some benzoic acid (0·22 g.).

In a second experiment with benzoyl peroxide (12·10 g.) and carbon tetrachloride (150 ml.), the carbon dioxide evolved (2·83 g.) was collected in a weighed soda-lime tube. The chloro-benzene, estimated by nitration, as in the first experiment, gave 1-chloro-2,4-dinitrobenzene, m. p. 47—48° (12·38 g. ≡ 6·87 g. of chlorobenzene). In three other experiments benzoyl peroxide (12·1 g.) and carbon tetrachloride (30 ml.) gave terephthalic acid (2·36 g. ≡ 3·41 g. of ωωω-trichloro-*p*-toluic acid) but no benzoic acid; benzoyl peroxide (6·05 g.) and carbon tetra-chloride (200 ml.) gave terephthalic acid (1·71 g. ≡ 2·47 g. of ωωω-trichloro-*p*-toluic acid); and benzoyl peroxide (12·1 g.) and carbon tetrachloride (100 ml.) containing benzoic acid (6·1 g.) gave terephthalic acid (2·13 g. ≡ 3·08 g. of ωωω-trichloro-*p*-toluic acid).

(ii) *With chloroform.* Benzoyl peroxide (24·2 g.) in chloroform (200 ml.) was allowed to decompose at the boiling point of the solution for 3 weeks. The odour of carbonyl chloride was perceptible if the reflux condenser was left open to the atmosphere. The solution, after being kept in the refrigerator for 5 days, deposited ωωω-trichloro-*p*-toluic acid (6·45 g.), m. p. and mixed m. p. 196·5° (Found: C, 39·5; H, 2·1; Cl, 43·9. Calc. for $C_8H_5O_2Cl_3$: C, 40·1; H, 2·1; Cl, 44·4%). The chloroform solution was extracted with aqueous sodium carbonate and dried (CaCl₂). The aqueous extract was boiled and acidified, and the resulting suspension of acids was treated as described under (i) above to give benzoic acid (0·44 g.), phthalic acid (0·21 g.), and terephthalic acid (1·34 g.). Isophthalic acid was not found. The dried chloroform solution was fractionated and a distillate (195 ml.) was collected at 60—80°. The total distillate [with fraction (*a*) below] was nitrated as described above and gave *m*-dinitrobenzene (22·2 g. ≡ 10·32 g. of benzene), m. p. 82—83°. The residue from the distillation was cooled to 0° and gave hexa-chloroethane (8·13 g.), m. p. and mixed m. p. 186° with sublimation, together with a liquid, which was distilled to give the following fractions: (*a*) b. p. 60—75°/760 mm. (14·0 g.); (*b*) b. p. 75—140°/760 mm. (2·59 g.); (*c*) sublimate/1 mm. (4·87 g.); (*d*) residue (2·0 g.). Fraction (*a*) was nitrated with the main chloroform distillate. Fraction (*b*) was further fractionated with a 3-cm. column to give (*b, i*), b. p. 75—80°/760 mm. (0·84 g.); (*b, ii*), b. p. 80—100°/760 mm. (0·61 g.); and (*b, iii*), b. p. 100—140°/760 mm. (0·51 g.). On treatment with the nitrating acids, these fractions gave respectively *m*-dinitrobenzene (0·63 g.), m. p. 74—76° raised to 84—86° after one recrystallisation from aqueous ethanol, *m*-dinitrobenzene (0·07 g.), m. p. 76—80°, and hexachloroethane. Chlorobenzene was not found in these fractions. Fraction (*c*) consisted of hexachloroethane, m. p. 185° with sublimation. The residue, fraction (*d*), was boiled for 4 hr. with aqueous sodium hydroxide, and the cooled solution was extracted with benzene. Evapor-ation of the benzene gave impure diphenyl (0·42 g.), m. p. 60—62°, which after recrystallisation had m. p. and mixed m. p. 69°. Saturation of the alkaline solution with carbon dioxide gave a strong odour of phenol and further acidification gave benzoic acid (0·30 g.), m. p. 120° after recrystallisation from water.

In a second identical experiment the following quantities of main products were obtained: *m*-dinitrobenzene (23·4 g. ≡ 10·89 g. of benzene), ωωω-trichloro-*p*-toluic acid (8·32 g.), and hexachloroethane (10·54 g.).

(iii) *With bromoform.* A solution of benzoyl peroxide (24·2 g.) in bromoform (379 g.) was allowed to decompose at 80° under the conditions outlined above. Evolution of carbon dioxide was more rapid than in the reactions with carbon tetrachloride and chloroform. The solution

became deep red-brown and deposited a pale yellow solid (1·88 g.; m. p. *ca.* 375°), which was insoluble in most organic solvents but soluble in warm aqueous alkali, from which it was recovered on acidification. Crystallisation from dimethylformamide containing a little ethanol gave a powder, m. p. 390° (Found: C, 45·9; H, 2·5; Br, 37·0%). The bromoform solution was extracted with aqueous sodium carbonate and dried (CaCl₂). The aqueous extract was boiled and acidified. The resulting suspension of acids gave (as above) benzoic acid (4·51 g.), but no phthalic, isophthalic, or terephthalic acid. The dried bromoform solution was fractionated at atmospheric pressure and two fractions were collected: (*a*) b. p. 80—140° (20 g.) and (*b*) b. p. 140—150° (329 g.). Hydrolysis and nitration of fraction (*a*), as described above, gave *m*-dinitrobenzene (2·88 g. ≡ 1·34 g. of benzene), m. p. 79—80° raised to 87° on recrystallisation from aqueous ethanol. Hydrolysis and nitration of a portion of fraction (*b*) gave 1-bromo-2,4-dinitrobenzene, m. p. and mixed m. p. 68—69°, in quantity equivalent to a total of 11·9 g. of bromobenzene in the whole fraction. The dark viscous residue from the distillation gave a solid tar which was separated and extracted with boiling ethanol to give a yellow solid (1·47 g.), m. p. *ca.* 170° with decomposition, and four recrystallisations from ethanol gave a colourless solid which decomposed at 200—210° (Found: C, 25·1; H, 2·0; Br, 56·1%). The liquid residue gave the following fractions: (*a*) b. p. 60—80°/12—15 mm. (16·70 g.); (*b*) b. p. 80°/12—15 mm. (4·77 g.); (*c*) b. p. 80—100°/12—15 mm. (1·44 g.); and (*d*) residue (8·0 g.). Fraction (*a*) was redistilled at atmospheric pressure, collected at 140—150°, and added to the bromoform distillate before nitration. Fraction (*b*) distilled at 150—200° with some decomposition and liberation of bromine and hydrogen bromide. Fraction (*c*) solidified; recrystallisation from aqueous ethanol gave carbon tetrabromide, m. p. and mixed m. p. 92°.

Reactions with Phenylazotriphenylmethane.—(i) *With carbon tetrachloride.* A solution of phenylazotriphenylmethane (17·4 g.) in carbon tetrachloride (150 ml.) was heated to 55°; nitrogen was then evolved and the solution became deep red. After 8 hr. at 55° the solution was boiled under reflux for 24 hr. The solution was cooled to 0° but solid did not separate. The excess of carbon tetrachloride was distillated off, and treatment of the distillate with nitrating acids (as described above) did not give *m*-dinitrobenzene. The residue was distilled with steam until no more organic distillate was obtained. The aqueous distillate was washed with carbon tetrachloride (4 × 25 ml.), and the washings were combined with the organic distillate. The dried (MgSO₄) solution distilled completely below 135°, and nitration of the whole gave 1-chloro-2,4-dinitrobenzene (2·50 g. ≡ 1·39 g. of chlorobenzene), m. p. 48°. The residue from the steam-distillation was obtained as a yellow solid, which was dried over sulphuric acid. Subsequent trituration with ether (20 ml.) gave 1,1,1-trichloro-2,2,2-triphenylethane (2·01 g.), m. p. 214—220° raised to 236·5° on recrystallisation from benzene (Found: C, 66·4; H, 4·2; Cl, 29·4. Calc. for C₂₀H₁₅Cl₃: C, 66·4; H, 4·2; Cl, 29·4%). Wieland and Heyman [5] have reported m. p. 237°. When the ethereal solution was allowed to evaporate tetraphenylmethane (0·15 g.), m. p. 272°, separated. Recrystallisation from benzene raised the m. p. to 280°, which was undepressed on admixture with an authentic specimen. Complete removal of the residual ether left a yellow oil, which slowly deposited more 1,1,1-trichloro-2,2,2-triphenylethane (2·44 g.), m. p. 216—220°. The residual yellow liquid (10·64 g.) was triturated with cold benzene–light petroleum (b. p. 40—60°) (1 : 3; 20 ml.). On strong cooling triphenylmethane (2·20 g.), m. p. 78—85°, separated. After two recrystallisations from aqueous ethanol the m. p. (and mixed m. p.) was 92° (Found: C, 93·4; H, 6·5. Calc. for H₁₉H₁₆: C, 93·4; H, 6·6%). The benzene–light petroleum solution was chromatographed on alumina and the column eluted successively with light petroleum, benzene–light petroleum, and benzene–ether with a gradually increasing ether concentration. The only products isolated were triphenylmethane (1·10 g.), m. p. 89—90°, and 1,1,1-trichloro-2,2,2-triphenylethane (0·40 g.), m. p. 232—233°. The residue was recovered as a yellow oil (7·0 g.), which probably contained more of these products. Hexachloroethane was not detected nor was any triphenylmethanol isolated, which would have been formed during the working up if triphenylchloromethane had been a reaction product. In a second experiment with phenylazotriphenylmethane (11·51 g.) in carbon tetrachloride (150 ml.) and in which the steam-distillation was omitted, the following products were obtained: 1-chloro-2,4-dinitrobenzene (1·99 g. ≡ 1·11 g. of chlorobenzene), 1,1,1-trichloro-2,2,2-triphenylethane (3·63 g.), tetraphenylmethane (0·15 g.), and triphenylmethane (2·40 g.). There was no evidence of hexachloroethane or triphenylchloromethane.

(ii) *With chloroform.* A solution of phenylazotriphenylmethane (11·0 g.) in chloroform (200 ml.) was treated as described above for the reaction with carbon tetrachloride. The

colour changed from yellow to red and then to orange. After removal of excess of chloroform (150 ml.), carbon tetrachloride (3 × 50 ml.) was added, and the fractionation was continued until approximately 50 ml. remained. This was well-cooled and deposited 1,1,1-trichloro-2,2,2-triphenylethane (1·90 g.), m. p. 230—233°, m. p. and mixed m. p. 235° after recrystallisation from benzene. The remainder of the solvent was removed under slightly reduced pressure; nitration of the total combined distillates as described above gave *m*-dinitrobenzene (4·80 g. ≡ 2·23 g. of benzene), m. p. 75—76°. Trituration of the red gum with ether (50 ml.) gave 1,1,1-trichloro-2,2,2-triphenylethane (0·70 g.), m. p. 225—228°. The ether was then removed and the residue was dissolved in benzene–light petroleum (b. p. 40—60°). On cooling triphenyl-methane (1·0 g.), m. p. 78—82°, separated and subsequent chromatographic treatment gave triphenylmethane (1·49 g.), 1,1,1-trichloro-2,2,2-triphenylethane (0·20 g.), and an orange-coloured oil (5 g.). No hexachloroethane or triphenylchloromethane was isolated or detected.

(iii) *With bromoform.* A solution of phenylazotriphenylmethane (8·81 g.) in bromoform (189 g.) was kept at 55° until evolution of nitrogen had practically ceased, after which the solution was maintained for a further 28 hr. at 55—60°. The almost black solution did not deposit solid. Carbon tetrachloride (4 × 40 ml.) was added and removed by fractionation. Nitration of the total distillate gave *m*-dinitrobenzene (1·32 g. ≡ 0·61 g. of benzene). Most of the bromoform was removed at 100°/*ca.* 25 mm., and distillation of the residue at atmospheric pressure removed the remainder. Hydrolysis and nitration (as described above) of a portion (30·64 g.) of the total distillate (168·0 g.) gave 1-bromo-2,4-dinitrobenzene (0·46 g. ≡ 0·29 g. of bromobenzene), which corresponds to a total of 1·60 g. of bromobenzene from the total distillate. Benzene (30 ml.) was added to the residue; after 24 hr. at 0° triphenylmethane (0·40 g.) separated (m. p. and mixed m. p. 92°). The benzene was removed at 40 mm. and the residue was dissolved in benzene–light petroleum (1 : 1) and chromatographed on alumina. Elution with benzene–light petroleum, benzene, benzene–ether, and ether gave only tar and buff-coloured solid (0·50 g.), m. p. 152—154°, which contained bromine. Further purification by crystallisation from ethanol and by further chromatography failed to raise the melting point.

Reactions with Nitroacetanilide.—(i) *With carbon tetrachloride.* A solution of nitrosoacetanilide (16·4 g.) in carbon tetrachloride (300 ml.) was maintained at 20° for 4 days after which it was heated at 75° for 1 hr. The evolved gases were passed through a trap cooled in solid carbon dioxide–acetone, a weighed absorption tube containing " Carbosorb," and a trap cooled in liquid air. No condensate was collected in the cold traps but a small quantity of carbon dioxide (0·32 g.) was retained. The reaction mixture was filtered from tar (*ca.* 0·5 g.) and extracted several times with aqueous sodium hydroxide and twice with dilute hydrochloric acid, and dried (Na_2SO_4). The acid extract did not give a product on basification. The alkaline extract was washed with ether, saturated with carbon dioxide, and again extracted with ether. The latter extract yielded phenol (0·32 g.) on evaporation. The aqueous alkaline solution was shown to contain acetic acid (4·60 g.). The carbon tetrachloride was fractionated and the distillate collected at 75—78° until the residue was approximately 50 ml. Nitration of the distillate did not give either *m*-dinitrobenzene or 1-chloro-2,4-dinitrobenzene. The residue was fractionated first at atmospheric pressure and then at 30 mm. The total distillate was redistilled at atmospheric pressure and the whole was collected at 78—135°. Nitration gave 1-chloro-2,4-dinitrobenzene (6·88 g. ≡ 3·82 g. of chlorobenzene), m. p. 48°. The non-volatile residue (*ca.* 4·0 g.) did not yield more material below 150°/0·5 mm. Further experiments were carried out and the products were worked up with the aid of chromatographic columns but the results obtained were substantially as described above.

(ii) *With chloroform.* A solution of nitrosoacetanilide (16·4 g.) in chloroform (244 ml.) was kept at 20° for 4 days and then boiled under reflux for 8 hr. The apparatus, conditions, and method of working up were the same as those used in the reaction with carbon tetrachloride. No condensate collected in the cold traps but carbon dioxide (0·38 g.) was absorbed. No phenol was found but acetic acid (4·1 g.) was present in the aqueous washings. Chloroform (200 ml.) was removed and carbon tetrachloride (2 × 50 ml.) was added to the residue. Distillation was continued until 120 ml. had been collected. Nitration of the combined distillates gave *m*-dinitrobenzene (2·86 g. ≡ 1·33 g. of benzene), m. p. 80—82°. The residue was dissolved in carbon tetrachloride and passed through alumina; the column was washed with sufficient carbon tetrachloride to displace all the reaction products. The total carbon tetrachloride solution was distilled, first at atmospheric pressure, then at 14 mm. and finally at 0·5 mm., and the total distillate thus obtained was redistilled. The fraction collected at

78—140° was nitrated and gave 1-chloro-2,4-dinitrobenzene (3·16 g. ≡ 1·75 g. of chloro-benzene), m. p. 46—48°. A small fraction (0·70 g.) collected above 140° was shown to be phenyl acetate (b. p. 190—195°). Hexachloroethane was not detected and no other products could be isolated from the residue. A second experiment, with nitrosoacetanilide (16·4 g.) in chloroform (163 ml.) and omission of extraction of the acetic acid, gave *m*-dinitrobenzene (3·67 g. ≡ 1·70 g. of benzene) and 1-chloro-2,4-dinitrobenzene (3·44 g. ≡ 1·82 g. of chloro-benzene).

Reactions with Benzenediazonium Chloride.—These reactions were carried out in three ways as follows: (*A*) An ice-cold aqueous solution of benzenediazonium chloride was added dropwise to a vigorously stirred mixture of the organic liquid and aqueous sodium hydroxide containing a two-fold excess of base over that necessary to neutralise all the acid present. The temperature was maintained at 0—5° during the addition and for a further 3 hr. It was then allowed to reach room temperature and the mixture was stirred for a further 24 hr. (*B*) The ice-cold aqueous diazonium chloride solution was mixed with the organic liquid and stirred vigorously at 0—5° during the addition of the aqueous sodium hydroxide. The conditions of temperature and time were the same as those of method (*A*). (*C*) The ice-cold aqueous diazonium chloride and the organic liquid were stirred together at 0—5° while an aqueous solution containing a slight excess of sodium acetate was added dropwise. The conditions of time and temperature were as in methods (*A*) and (*B*) except that it was necessary to continue stirring at room temperature up to 72 hr.

(i) *With carbon tetrachloride.* The reactions were carried out with " AnalaR " aniline (18·6 g.) and carbon tetrachloride (150 ml.). The reaction mixture from method (*A*) contained much insoluble tar and there was an odour of phenyl isocyanide. It was distilled with steam, and the carbon tetrachloride distillate was dried (MgSO₄) and fractionated. Approximately half of the liquid was removed and when this was nitrated *m*-dinitrobenzene was not obtained. The majority of the residual carbon tetrachloride was then removed and the orange residue was then distilled up to 140°. The small residue (*ca.* 1 g.) contained hexachloroethane. The distillate was combined with the second half of the main carbon tetrachloride fraction; nitration of the whole gave 1-chloro-2,4-dinitrobenzene (11·14 g. ≡ 6·18 g. of chlorobenzene), m. p. 47—48°. Products were not obtainable from the tarry residue (13·2 g.) of the steam-distillation. The reaction mixture from method (*B*) similarly gave 1-chloro-2,4-dinitrobenzene (13·60 g. ≡ 7·55 g. of chlorobenzene), m. p. 47—49°. *m*-Dinitrobenzene was not obtained. In addition hexachloroethane (1·1 g.), m. p. 185° after recrystallisation from ethanol, was obtained. The reaction mixture from method (*C*) contained less tar and had an odour of phenol. It gave 1-chloro-2,4-dinitrobenzene (2·62 g. ≡ 1·45 g. of chlorobenzene), m. p. 50°, but no *m*-dinitro-benzene. Hexachloroethane was not detected. The alkaline washings of the carbon tetra-chloride steam-distillate gave phenol (6·30 g.).

(ii) *With chloroform.* These reactions were carried out with aniline (23·25 g.) and chloroform (163 ml.) as described above for reactions with carbon tetrachloride, but the steam-distillation was omitted. Method (*A*) gave a dark tar with an odour of phenyl isocyanide. The organic and aqueous layers were separated. Phenol was not obtained. Carbon tetrachloride (4 × 50 ml.) was used during the fractionation to assist the removal of benzene and nitration of the combined chloroform–carbon tetrachloride distillates gave *m*-dinitrobenzene (19·59 g. ≡ 9·09 g. of benzene). 1-Chloro-2,4-dinitrobenzene was not obtained when a higher fraction (2·0 g.), b. p. 80—170°, was nitrated but hexachloroethane (4·17 g.) was isolated. The black residue weighed 10 g. In similar manner method (*B*) gave *m*-dinitrobenzene (20·44 g. ≡ 9·49 g. of benzene) and hexachloroethane (4·84 g.). Chlorobenzene and phenol were not obtained. Method (*C*) gave phenol (7·96 g.) and 1-chloro-2,4-dinitrobenzene (5·60 g. ≡ 3·11 g. of chloro-benzene), m. p. 47—48°. *m*-Dinitrobenzene and hexachloroethane were not obtained.

(iii) *With bromoform.* Reactions were carried out by methods (*B*) and (*C*) only, aniline (18·6 g.) and bromoform (379 g.) being used. Distillation with steam was omitted. The dark orange layer from method (*B*) was separated from the aqueous layer and the latter was washed with carbon tetrachloride. The combined carbon tetrachoride–bromoform solution was washed successively with dilute aqueous sodium hydroxide, dilute sulphuric acid, and water, and dried (CaCl₂). The carbon tetrachloride was removed by fractionation, and nitration gave *m*-dinitrobenzene (0·32 g. ≡ 0·15 g. of benzene), m. p. 74—75°. Most of the bromoform was distilled off at 10 mm.; hydrolysis and nitration of the product gave 1-bromo-2,4-dinitro-benzene (2·01 g. ≡ 1·28 g. of bromobenzene), m. p. 68—70°. No other products were isolated.

The reaction product from method (*C*) gave in similar manner *m*-dinitrobenzene (1·22 g. ≡ 0·57 g. of benzene), m. p. 77—78°, and 1-bromo-2,4-dinitrobenzene (10·01 g. ≡ 6·36 g. of bromobenzene), m. p. 68—69°.   In addition, phenol (2·8 g.) was isolated from the alkaline extract.