17. *Reactions of Aryl Radicals with Aliphatic Compounds. Part II.* The Reactions of Phenyl Radicals with Some Esters.*

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Reactions have been carried out of benzoyl peroxide, phenylazotriphenylmethane, nitrosoacetanilide, and benzene diazohydroxide with ethyl acetate, methyl acetate, ethyl chloroacetate, methyl chloroacetate, ethyl trichloroacetate, ethyl bromoacetate, and ethyl phenylacetate. The main products have been determined quantitatively. The reactions with ethyl chloroacetate gave benzene but no chlorobenzene, but whereas benzoyl peroxide with ethyl bromoacetate gave bromobenzene but no benzene, a similar reaction with phenylazotriphenylmethane gave some benzene in addition to bromobenzene. Diethyl dichlorosuccinate was obtained from the reaction between benzoyl peroxide and ethyl chloroacetate, but not from the corresponding reactions with phenylazotriphenylmethane or nitrosoacetanilide. Succinic esters were not obtained from reactions with ethyl bromoacetate, but diethyl diphenylsuccinate was obtained in all of the reactions with ethyl phenylacetate.

In Part I the results were reported of a quantitative investigation of the products formed in the reactions between phenyl radicals and carbon tetrachloride, chloroform, and bromoform. The aryl radicals were derived from (*a*) benzoyl peroxide, (*b*) phenylazotriphenylmethane, (*c*) nitrosoacetanilide, and (*d*) benzene diazo-hydroxide and -acetate. The present communication describes the results obtained in a similar investigation into the reactions between phenyl radicals and ethyl acetate, methyl acetate, ethyl chloroacetate, methyl chloroacetate, ethyl trichloroacetate, ethyl bromoacetate, and ethyl phenylacetate. Reactions of this type do not appear to have been previously reported apart from the qualitative observation that the reaction between nitrosoacetanilide and ethyl acetate gives benzene, acetaldehyde, and acetic acid.[1, 2]

The extension of this investigation to include reactions with aliphatic esters necessitated the development of a general method of analysis for the estimation of benzene, chlorobenzene, and bromobenzene in admixture with a large excess of the solvent ester. Ultraviolet absorption spectrophotometry was used (see below). The reliability of the method was tested with mixtures of known composition. In addition, it was possible to separate benzene from mixtures with ethyl chloro-, bromo-, and phenyl-acetate by co-distillation with a large excess of carbon tetrachloride. Mixtures of bromobenzene and ethyl bromoacetate were also analysed by hydrolysis and subsequent dinitration (cf. Part I).

The results now reported on the reactions of benzoyl peroxide, phenylazotriphenylmethane, and nitrosoacetanilide with ethyl acetate, ethyl chloroacetate, and ethyl bromoacetate are summarised in Table 1. The most significant observations in these results

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* Part I, preceding paper.

[1] Grieve and Hey, *J.*, 1934, 1805.

[2] Waters, *J.*, 1937, 113 (see also Makin and Waters, *J.*, 1938, 843, and Hanby and Waters, *J.*, 1939, 1792).

are (*a*) the absence of chlorobenzene from the products of the reaction between nitrosoacetanilide and ethyl chloroacetate and (*b*) the absence of benzene from the products of the reaction between benzoyl peroxide and ethyl bromoacetate. On these two points the reactions in question depart from the behaviour shown in the corresponding reactions with chloroform and bromoform reported in Part I.

TABLE 1. *Average yields of products obtained in reactions with ethyl acetate, ethyl chloroacetate, and ethyl bromoacetate expressed as moles per mole of radical source.*

	With ethyl acetate	With ethyl chloroacetate		With ethyl bromoacetate	
Radical source	PhH	PhH	PhCl	PhH	PhBr
Benzoyl peroxide	0·90	1·29	0	0	0·70
Phenylazotriphenylmethane	0·43	0·93	0	0·08	0·33
Nitrosoacetanilide	0·40	0·28	0	—	—

It has been reported by Kharasch and Gladstone [3] that the main products formed in the reactions between acetyl peroxide and acetic and chloroacetic acids are methane and carbon dioxide. Methyl chloride was not found in the products of the reaction with chloroacetic acid, or in corresponding reactions with methyl chloroacetate and with methyl dichloroacetate.[4,5] These results are in general agreement with those now reported for the reactions with benzoyl peroxide, phenylazotriphenylmethane, and nitrosoacetanilide. It may be noted that even in the reaction with trichloroacetyl chloride and acetyl peroxide methane was found in the products (0·35 mole per mole of peroxide) and very little methyl chloride (0·05 mole per mole of peroxide),[5] whereas the reaction now reported between benzoyl peroxide and ethyl trichloroacetate gave mainly chlorobenzene and some benzene. The reaction between acetyl peroxide and ethyl bromoacetate does not appear to have been reported but the free-radical catalysed addition of methyl bromoacetate to an olefin has been shown to give rise to a γ-bromo-ester, which implies removal of the bromine atom in preference to the hydrogen atom.[6] In similar addition reactions with methyl chloroacetate and methyl dichloroacetate [7] it is the hydrogen atom and not the chlorine atom which is removed in the reactions of these esters with the free radical.

With regard to the fate of the radicals formed by abstraction of hydrogen or halogen from the ester, the results obtained with acetyl peroxide have shown that methyl chloroacetate gives dimethyl dichlorosuccinate and methyl dichloroacetate gives dimethyl tetrachlorosuccinate in practically quantitative yield based on the methane liberated.[4,5] Also, in similar reactions with acetic and chloroacetic acids high yields of succinic and dichlorosuccinic acids were obtained.[3,4] In contrast, the reactions between benzoyl peroxide and acetic acid gave benzene in high yield but no succinic acid.[8] The only products identified from the solvent radical were some homophthalic and homoterephthalic acids, which may be formed in a manner analogous to the formation of the ωωω-trichlorotoluic acids from benzoyl peroxide and carbon tetrachloride (see Part I). Good yields of the dimer, dimethyl diphenylsuccinate, were reported from reactions between acetyl peroxide and methyl phenylacetate.[5]

In the reactions now reported with benzoyl peroxide, phenylazotriphenylmethane, and nitrosoacetanilide no dimethyl or diethyl succinate was isolated from methyl or ethyl acetate, but diethyl dichlorosuccinate was obtained, in a yield of 65% based on the quantity of benzene isolated, from the reaction between benzoyl peroxide and ethyl chloroacetate. Diethyl dichlorosuccinate was, however, not obtained from reactions with phenylazotriphenylmethane or nitrosoacetanilide. The absence of the dimer from the

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[3] Kharasch and Gladstone, *J. Amer. Chem. Soc.*, 1943, **65**, 15.
[4] Kharasch, Jensen, and Urry, *J. Org. Chem.*, 1945, **10**, 386.
[5] Kharasch, McBay, and Urry, *J. Org. Chem.*, 1945, **10**, 394.
[6] Kharasch, Skell, and Fisher, *J. Amer. Chem. Soc.*, 1948, **70**, 1055.
[7] Kharasch, Urry, and Jensen, *J. Amer. Chem. Soc.*, 1945, **67**, 1626.
[8] Gladstone, *J. Amer. Chem. Soc.*, 1954, **76**, 1581.

reaction with phenylazotriphenylmethane may be due to the preferential reaction of the radical $\cdot CHCl\cdot CO_2Me$ with triphenylmethyl to give an ester of βββ-triphenyl-α-chloropropionic acid (see Experimental section) in much the same way as 1,1,1-triphenyl-2,2,2-trichloroethane is formed in the corresponding reactions with carbon tetrachloride and chloroform (see Part I). It may also be noted that with cumene, 2,3-dimethyl-2,3-diphenylbutane is formed from reactions with benzoyl peroxide and acetyl peroxide but none was isolated from the reaction with phenylazotriphenylmethane.[9,10] In the reactions now reported with ethyl bromoacetate no diethyl succinate or dibromosuccinate was isolated. In contrast to the above results the solvent dimer, diethyl diphenylsuccinate, was obtained in all the reactions of ethyl phenylacetate, although in some cases the yield was small. These results are summarised in Table 2, which also shows that there is little correlation between the yield of dimer and that of the benzene formed in the same reaction.

TABLE 2. *Yields of dimer and of benzene formed in reactions with ethyl phenylacetate.*

	Yield of dimer	
Reagent	Moles per mole of reagent	Moles per mole of benzene isolated
Benzoyl peroxide	0·27	0·61
Phenylazotriphenylmethane	0·05	0·15
Nitrosoacetanilide	0·01	0·05
Benzene diazohydroxide	0·04	0·18

EXPERIMENTAL

General Procedure.—Experimental conditions were as in Part I.

Quantitative Analytical Methods.—(*a*) For the estimation of small quantities of PhX, where X is H, Cl, or Br, in the presence of a large excess of ethyl acetate, ethyl chloroacetate, or ethyl bromoacetate, the ultraviolet absorption spectra of the mixtures at 240—280 mμ in purified n-heptane were measured on a Unicam SP. 500 spectrophotometer. The solvent was purified by allowing it (3000 ml.) to stand over oleum (6 × 300 ml.) for six weeks with occasional shaking. It was then separated, washed successively with water, aqueous sodium hydroxide (many times), and water, and dried for 7 days over potassium hydroxide pellets. The product was collected at 95—100°. Tables 3, 4, and 5 show the wavelengths used and the relevant extinction coefficients.

TABLE 3. *Extinction coefficients.*

Wavelength (mμ)	247·0	248·9	252·6	254·8	259·0	261·0
Benzene	0·642	2·156	0·660	2·739	0·472	1·859
Ethyl acetate (× 10^2)	1·44	0·667	0·315	0·215	0·151	0·129
Ethyl chloroacetate	0·143	0·114	0·072	0·050	0·025	0·018

TABLE 4. *Extinction coefficients.*

Wavelength (mμ)	253·1	257·9	259·8	264·7	270·0	271·8
Chlorobenzene	1·837	3·389	2·472	4·455	1·746	3·358
Ethyl chloroacetate	0·067	0·032	0·023	0·009	0·004	0·003

TABLE 5. *Extinction coefficients.*

Wavelength (mμ)	261·9	263·2	265·2	270·5	272·2
Bromobenzene	1·183	1·124	1·311	0·676	0·891
Ethyl bromoacetate	0·287	0·250	0·195	0·100	0·080

This method of analysis was tested with synthetic mixtures and the average negative errors found on a range of three or four mixtures in each case were as follows: benzene in ethyl acetate, 4·7%; benzene in ethyl chloroacetate, 3·0%; chlorobenzene in ethyl chloroacetate, 3·0%; bromobenzene in ethyl bromoacetate, 0·1%.

For the estimation of benzene, co-distillation with carbon tetrachloride followed by dinitration was also used, while for the estimation of bromobenzene in ethyl bromoacetate use was

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[9] Hey, Pengilly, and Williams, *J.*, 1956, 1463.

[10] Kharasch, McBay, and Urry, *J. Org. Chem.*, 1945, **10**, 401.

also made of the procedure described for the estimation of bromobenzene in bromoform (cf. Part I).

(*b*) For the estimation of benzoic acid the procedure described in Part I was followed.

Preparation and Purification of Reagents.—Methyl and ethyl acetate (" AnalaR ") were shaken thrice with saturated aqueous sodium carbonate, thrice with 50% aqueous calcium chloride, and twice with brine. The methyl ester was dried (K_2CO_3) and collected at 55—57°. The ethyl ester was dried ($CaCl_2$) and collected at 76·5—76·7°. Methyl and ethyl chloroacetates (B.D.H.) were washed, as described above, and, after being dried (Na_2SO_4) were collected at 129—130°/757 mm. and 143—143·2°/760 mm. respectively. Ethyl trichloroacetate, ethyl bromoacetate, and ethyl phenylacetate were similarly treated and after being dried ($CaCl_2$) were collected at 100—100·5°/*ca.* 30 mm., 158—158·5°/758 mm., and 99—99·3°/14 mm. respectively. Benzoyl peroxide, phenylazotriphenylmethane, and nitrosoacetanilide were prepared as described in Part I.

Reactions with Benzoyl Peroxide.—(i) *With ethyl acetate.* Benzoyl peroxide (24·2 g.) in ethyl acetate (300 ml.) was allowed to decompose under the conditions outlined in Part I. The solution, which became pale yellow and deposited no solid on cooling, was extracted with aqueous sodium carbonate and the extract was saturated with sodium chloride. Acidification with hydrochloric acid to pH 6 gave an acid (0·24 g.), m. p. 210—211°, which on recrystallisation from aqueous ethanol gave biphenyl-4-carboxylic acid, m. p. and mixed m. p. 224° (Found: C, 78·9; H, 5·5. Calc. for $C_{13}H_{10}O_2$: C, 78·8; H, 5·4%). Further acidification to pH 5 gave a second crop (0·10 g.) of less pure acid, m. p. 185—186° (Found: C, 77·5; H, 5·0%). Addition of excess of hydrochloric acid deposited a clear, yellow, viscous oil (9·66 g.), which on distillation at 0·5 mm. gave a sublimate of benzoic acid (0·68 g.) and two fractions, (*a*) b. p. 141°/0·5 mm. (6·32 g.) and (*b*) b. p. 141—170°/0·05 mm. (1·30 g.). The main fraction (*a*), which was redistilled at constant temperature, was obtained as a very viscous, colourless liquid which set to a glass when cooled in solid carbon dioxide (Found: C, 67·5; H, 5·8%). On very long standing it partially solidified to a white paste. It was soluble in aqueous alkali and had equiv. 217, but crystalline derivatives could not be obtained. Tests for unsaturation and for ketonic, aldehydic, or phenolic properties were negative. Oxidation of a portion (0·23 g.) with alkaline potassium permanganate gave terephthalic acid (0·08 g.), identified as its methyl ester, m. p. and mixed m. p. 139°, The infrared spectrum of fraction (*a*) indicated the presence of benzoic acid and biphenyl-4-carboxylic acid. The dried ($CaCl_2$) ethyl acetate solution was slowly fractionated in the 45 cm. column and the distillate collected at 75—80° (292·4 g.). The concentration of benzene in this distillate was determined by measurement of the optical densities at six wavelengths of two solutions of the distillate in n-heptane, as described above. The results are shown in Table 6.

TABLE 6.

Benzene–ethyl acetate distillate

	8·9305 g./l.		8·8776 g./l.	
Wavelength (mμ)	*D*	c_{PhH}	*D*	c_{PhH}
247·0	0·258	0·205	0·260	0·210
248·9	0·493	0·201	0·506	0·208
252·6	0·160	0·201	0·151	0·187
254·8	0·580	0·205	0·600	0·212
259·0	0·106	0·198	0·113	0·213
261·0	0·391	0·205	0·403	0·211
Average c_{PhH} (g./l.)	0·205			
Yield of benzene (g.) ...	6·71			

TABLE 7.

Benzene–ethyl chloroacetate distillate (*a*)

	0·2675 g./l.			
Wavelength (mμ)	*D*	c_{PhH}	*D*	c_{PhH}
247·0	0·161	0·246	0·157	0·239
248·9	0·515	0·237	0·507	0·234
252·6	0·163	0·245	0·157	0·235
254·8	0·637	0·232	0·630	0·229
259·0	0·122	0·257	0·117	0·246
261·0	0·434	0·233	0·429	0·230
Average c_{PhH} (g./l.)	0·239			
Yield of benzene (g.) ...	9·65			

The residue from the above distillation was distilled with a 10 cm. Vigreux column to give two fractions, (*c*) b. p. 40—80°/0·2 mm. (1·39 g.), and (*d*) b. p. 100—120°/0·05 mm. (0·50 g.). Fraction (*c*) was redistilled at atmospheric pressure and collected at 218—220°, from which was isolated only biphenyl (0·38 g.) and, after hydrolysis, phenol (0·02 g.) and benzoic acid (0·30 g.). In a subsequent experiment on half-scale, the yield of benzene was 3·69 g. In a further experiment, 29·9 ml. (at N.T.P.) of carbon dioxide were collected in a gas burette from benzoyl peroxide (0·2300 g.) in ethyl acetate (20 ml.), *i.e.*, 1·4 mole per mole of peroxide.

(ii) *With methyl acetate.* Benzoyl peroxide (24·2 g.) in methyl acetate (148 g.) was boiled under reflux for 8 days, after which no more carbon dioxide was evolved. Distillation with a 45 cm. column gave a distillate (142·2 g.), b. p. 55—56°, which by the ultraviolet spectrophotometric method was shown to contain about 0·5 g. of benzene. The residue from this distillate was dissolved in carbon tetrachloride (100 ml.), and the solution was extracted with aqueous sodium carbonate. The aqueous extract was washed with carbon tetrachloride and the main solution and washings were combined and dried ($CaCl_2$). The solution was then distilled and the quantity of benzene in the distillate, determined by the nitration method, was found to be 5·90 g. (*m*-dinitrobenzene, 12·72 g.). The residue from the removal of the carbon tetrachloride was distilled twice, first at atmospheric pressure and then at 0·2 mm., but yielded no products which could be identified. The sodium carbonate washings gave biphenyl-4-carboxylic acid (0·50 g.), m. p. 219°, and benzoic acid (1·50 g.), m. p. 120° after recrystallisation from water, together with resinous acidic material.

(iii) *With ethyl chloroacetate.* Benzoyl peroxide (24·2 g.) in ethyl chloroacetate (245 g.) was allowed to decompose under the general conditions outlined above. The cold solution was extracted with aqueous sodium carbonate and dried (Na_2SO_4). Acidification of the alkaline extract to pH 7 gave biphenyl-4-carboxylic acid (0·34 g.), m. p. 205—210°, which was raised to 219° on recrystallisation from aqueous ethanol. Further acidification to pH 5 and saturation with sodium chloride gave benzoic acid (2·52 g.), m. p. 117—118° which was raised to 121° on recrystallisation from water. Further acidification gave a yellow oil (*ca.* 0·5 g.) which did not solidify. The dried ethyl chloroacetate solution was distilled with a 45 cm. column and the following fractions were collected: (*a*) b. p. 78—80°/760 mm. (10·8 g.); (*b*) b. p. 139—142°/760 mm. (22·2 g.); (*c*) b. p. 142—143°/760 mm. (155 g.); (*d*) b. p. 65°/*ca.* 25 mm. (44 g.); and (*e*) residue (*ca.* 20 g.). The benzene in fraction (*a*) and the benzene and chlorobenzene in fractions (*b*) and (*c*) were determined by the ultraviolet spectrophotometric method (Tables 7 and 8). Fraction (*d*) was redistilled at atmospheric pressure and gave ethyl chloroacetate b. p. 142—144°. The residue (*e*) was distilled at 25 mm. to remove a little ethyl chloroacetate after which the following fractions were collected: (*f*) b. p. up to 126°/12—15 mm. (0·64 g.); (*g*) b. p. 126—128°/12—15 mm. (7·06 g.); (*h*) b. p. 128—133°/12—15 mm. (3·19 g.); (*i*) b. p. 100—120°/0·5 mm. (0·45 g.); (*j*) residue (*ca.* 4 g.). Fraction (*f*) consisted mainly of ethyl chloroacetate, identified by reaction with ammonia to give chloroacetamide, m. p. 117°. Fractions (*g*) and (*h*) partially solidified and gave ethyl *meso*-dichlorosuccinate (4·38 g.), m. p. 58—59° which on recrystallisation from aqueous ethanol was raised to 62°, both alone and on admixture with an authentic specimen (Found: Cl, 29·0. Calc. for $C_8H_{12}O_4Cl_2$: Cl, 29·2%). The liquid portion of these fractions (5·68 g.) is regarded as consisting mainly of ethyl (±)-dichlorosuccinate (Found: Cl 28·9%) for which b. p. 129·5°/12·5 mm. has been reported.[11] Hydrolysis of fractions (*i*) and (*j*) followed by extraction with chloroform and acidification showed them to contain biphenyl (0·52 g.) and phenyl benzoate (0·30 g.).

TABLE 8.

	Fraction (*b*) 0·9942 g./l.			Fraction (*c*) 0·9130 g./l.		
Wavelength (mμ)	*D*	c_{PhH}	c_{PhCl}	*D*	c_{PhH}	c_{PhCl}
252·6	0·082	0·017		0·076	0·017	
254·8	0·083	0·012		0·075	0·009	
259·0	0·040	0·033		0·030	0·011	
259·8	0·036		0·00	0·032		0·00
261·0	0·042	0·013		0·020	0·002	
264·7	0·016		0·00	0·016		0·00
270·0	0·008		0·00	0·008		0·00
271·8	0·007		0·00	0·007		0·00
Average c_{PhH} (g./l.)		0·019			0·010	
Yield of benzene (g.) ...		0·42			1·7	

(iv) *With ethyl trichloroacetate.* A solution of benzoyl peroxide (24·2 g.) in ethyl trichloroacetate (257 g.) was allowed to decompose under the general procedure described above. The cooled solution was extracted with aqueous sodium hydroxide and dried ($CaCl_2$). The alkaline extract was washed with carbon tetrachloride and boiled to remove organic solvent, and from it was obtained biphenyl-4-carboxylic acid (0·13 g.), m. p. 224°, and benzoic acid (4·22 g.), m. p.

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[11] Kuhn and Wagner-Jauregg, *Ber.*, 1928, **61**, 504.

119·5° after recrystallisation from water. Carbon tetrachloride (40 ml.) was added to the ethyl trichloroacetate solution, the whole was distilled, and a fraction collected at 70—100°. Nitration of this fraction, as described in Part I, gave *m*-dinitrobenzene (2·76 g. ≡ 1·28 g. of benzene), m. p. 82—84°. Further distillation at 70—80°/30 mm. gave a fraction (227 g.), a portion (28·9 g.) of which was hydrolysed and nitrated. This gave 1-chloro-2,4-dinitrobenzene (1·75 g.), m. p. 43—45°. This corresponds to a total quantity of 13·8 g. of 1-chloro-2,4-dinitrobenzene ≡ 7·63 g. of chlorobenzene. No products were identified in the residue.

(v) *With ethyl bromoacetate.* Benzoyl peroxide (24·2 g.) in ethyl bromoacetate (300 g.) was allowed to decompose under the standard conditions, after which the cooled solution was extracted with aqueous sodium carbonate and dried (Na_2SO_4). Acidification of the aqueous extract, first to pH 7 and then to pH 3, gave only benzoic acid (1·05 g. and 7·28 g.), m. p. 118—119° after recrystallisation from water (charcoal). Biphenyl-4-carboxylic acid was not found. The ethyl bromoacetate solution was distilled at 30 mm. and a fraction, b. p. 70—80° (280 g.), was collected. The bromobenzene content of this fraction [to which was added fraction (*a*) below] was estimated by the spectrophotometric method and the results are given in Table 9. These results were confirmed by hydrolysis of a portion (29·20 g.) of the distillate and subsequent nitration, as described in Part I. This procedure gave 1-bromo-2,4-dinitrobenzene, m. p. 69—70° (1·89 g. ≡ 1·20 g. of bromobenzene) which corresponds to a total quantity of 11·5 g. of bromobenzene in the whole distillate. Distillation of the residue after removal of solvent gave two fractions: (*a*) b. p. 76—80°/30 mm. (11·84 g.) and (*b*) b. p. 100°/1 mm. (3·28 g.). Fraction (*a*) gave mainly ethyl bromoacetate (10·5 g.) on redistillation at 157—160°/760 mm. and this was added to the main distillate (above) before hydrolysis and nitration. Fraction (*b*) gave only benzoic acid (0·25 g.). In a repetition of this experiment the main products were benzoic acid (9·07 g.) and bromobenzene (10·0 g.). Carbon tetrachloride (50 ml.) was added to the reaction mixture before the excess of solvent was removed and it was then distilled off. Nitration of this distillate gave no *m*-dinitrobenzene. Ethyl succinate was not found.

TABLE 9.

	Bromobenzene–ethyl bromoacetate distillate 2·0594 g./l.	
Wavelength (mμ)	*D*	c_{PhBr}
261·9	0·662	0·079
263·2	0·592	0·092
265·2	0·508	0·095
270·5	0·255	0·085
272·2	0·238	0·090
Average c_{PhBr} (g./l.)	0·088	
Yield of bromobenzene (g.) ...	12·0	

(vi) *With ethyl phenylacetate.* Benzoyl peroxide (24·2 g.) in ethyl phenylacetate (246 g.) was allowed to decompose according to the general procedure. The cooled solution was extracted with aqueous sodium hydroxide and dried (Na_2SO_4). Acidification of the aqueous extract in stages gave only benzoic acid (2·44 g., 0·82 g., and 0·31 g.). No diphenyl-4-carboxylic acid was isolated, although the initial low melting points for the benzoic acid indicated that a second acid was probably present. Carbon tetrachloride (75 ml.) was added to the ethyl phenylacetate solution and by use of the 45 cm. column the distillate was collected at 76—80°. This operation was repeated with a further quantity (50 ml.) of carbon tetrachloride. The total distillate on nitration gave *m*-dinitrobenzene (14·82 g. ≡ 6·88 g. of benzene), m. p. 80—81°. Further fractionation was continued under reduced pressure, and the distillate (211 g.) was collected at 97°/12 mm. The residue (*ca.* 30 g.) set to a semi-solid mass, which was triturated with ethanol and cooled in ice. This gave ethyl *meso*-diphenylsuccinate (2·75 g.), m. p. 135—136° raised to 141° on recrystallisation from ethanol * (Found: C, 73·8; H, 7·0. Calc. for $C_{20}H_{22}O_4$: C, 73·6; H, 6·8%). The ethanolic mother-liquors were distilled and, after removal of ethanol at atmospheric pressure and ethyl phenylacetate (*ca.* 15 g.) at 80—84°/10 mm., three fractions were collected as follows: (*a*) b. p. 110—120°/0·02 mm. (2·15 g.); (*b*) b. p. 120—125°/0·02 mm. (1·79 g.); and (*c*) b. p. 125—140°/0·02 mm. (2·03 g.). All three

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* The melting point of this compound was not depressed on admixture with an authentic specimen prepared by Dr. C. W. Rees by the catalytic (PtO_2) hydrogenation of a sample of ethyl diphenylmaleate kindly supplied by Dr. C. J. Timmons.

fractions gave more ethyl *meso*-diphenylsuccinate (0·09 g., 0·40 g., and 1·48 g.) and the combined liquid components were hydrolysed with aqueous sodium hydroxide. The resulting acid had m. p. 172—175° after three recrystallisations from water (Found: C, 69·3; H, 5·4. Calc. for $C_{16}H_{14}O_4$: C, 71·1; H, 5·2%). (±)- and *meso*-Diphenylsuccinic acid have m. p. 183° and 252° respectively. It is thus probable that the liquid component of the fractions (*a*), (*b*), and (*c*) is mainly ethyl (±)-diphenylsuccinate, which, when pure, is reported to melt at 84—85°.[12] There was no evidence of the presence of products which might arise from nuclear phenylation.

Reactions with Phenylazotriphenylmethane.—(i) *With ethyl acetate*. A solution of phenylazotriphenylmethane (11·0 g.) in ethyl acetate (200 ml.) was kept at 55° for 15 hr. and at the b. p. for a further 24 hr. The resulting yellow solution was fractionated with the 45 cm. helix-packed column and the distillate collected at (*a*) 75—77° (76·1 g.) and (*b*) 77° (85·4 g.). The residue (*ca.* 40 ml.) was cooled, and tetraphenylmethane (0·32 g.), m. p. 265—270° raised to 280·5° after three recrystallisations from benzene, separated (Found: C, 93·8; H, 6·4. Calc. for $C_{25}H_{20}$: C, 93·7; H, 6·3%). Distillation of the residue with a 10 cm. Vigreux column gave ethyl acetate (14·6 g.), b. p. 77—78°, which was added to distillate (*b*) above. No further distillate could be obtained down to a pressure of 0·005 mm. with a bath temperature of 180°. The concentration of benzene in fractions (*a*) and (*b*) was determined by measurement of the optical density of a solution of each in n-heptane (Table 10).

The non-volatile red oil (9·1 g.) was dissolved in benzene–light petroleum (b. p. 40—60°) (1 : 3; 80 ml.) and the solution was well cooled. Triphenylmethane (0·25 g.) separated (m. p. 72—74°). After addition of more light petroleum (50 ml.) the solution was chromatographed on alumina and eluted successively with light petroleum, benzene–light petroleum, and benzene–ether (see Part I). The only products isolated were (i) triphenylmethane (2·47 g.), (ii) a colourless semi-solid product (0·5 g.), which showed a strong blue fluorescence in ultraviolet light, and (iii) an orange oil. A non-fluorescent solid, m. p. 146—148° from ethanol, was subsequently obtained from (ii).

TABLE 10.

	Benzene–ethyl acetate distillates			
	Fraction (*a*) 9·0234 g./l.		Fraction (*b*) 9·0192 g./l.	
Wavelength (mμ)	*D*	c_{PhH}	*D*	c_{PhH}
247·0	0·164	0·054	0·169	0·062
248·9	0·165	0·049	0·168	0·050
252·6			0·064	0·055
254·8	0·156	0·050	0·165	0·053
259·0	0·039	0·053	0·041	0·060
261·0	0·100	0·052	0·106	0·051
Average c_{PhH} (g./l.)		0·052		0·055
Yield of benzene (g.) ...		0·44		0·61

Total yield of benzene 1·05 g.

(ii) *With ethyl chloroacetate*. A solution of phenylazotriphenylmethane (11·0 g.) in ethyl chloroacetate (184 g.) was kept at 55° for 30 hr. The orange-red solution deposited bistriphenylmethyl peroxide (0·06 g.), m. p. 178° raised to 182° on recrystallisation from chloroform and undepressed on admixture with an authentic specimen. Two portions of carbon tetrachloride (each of 40 ml.) were added to the solution and the mixture was fractionated until the carbon tetrachloride was removed. Nitration of the distillate gave *m*-dinitrobenzene (4·93 g. ≡ 2·29 g. of benzene), m. p. 82—83°. Fractionation was continued at *ca.* 250 mm. until only 10 ml. remained. The first 20 ml. of distillate was collected separately and the spectrophotometric method showed the absence of chlorobenzene. Further distillation was continued at *ca.* 150 mm. with a 10 cm. Vigreux column until all the ethyl chloroacetate had been removed. No further distillate could be obtained up to a bath temperature of 140° and a pressure of 0·1 mm. (absence of ethyl dichlorosuccinate). The non-volatile residue was dissolved in benzene and cooled in ice, whereupon triphenylmethane (2·62 g.) separated, having m. p. 84—85°. The residue in

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[12] Reimer, *Ber.*, 1881, **14**, 1804.

benzene–light petroleum was chromatographed on alumina as before and gave only triphenylmethane (1·0 g.), m. p. 88—90°, and an orange oil.

(iii) *With methyl chloroacetate.* A solution of phenylazotriphenylmethane (11·0 g.) in methyl chloroacetate (163 g.) was used and the procedure outlined above for the corresponding reaction with ethyl chloroacetate was followed except as mentioned below. The products obtained were bistriphenylmethyl peroxide (0·13 g.), m. p. 178°, *m*-dinitrobenzene (4·69 g. ≡ 2·18 g. of benzene), triphenylmethane (3·48 g.), m. p. 87—88°, and a colourless solid (0·08 g.), m. p. 121·5° after recrystallisation from aqueous ethanol (Found: C, 75·0; H, 5·7; Cl, 10·5. Calc. for $C_{22}H_{19}O_2Cl$: C, 75·3; H, 5·5; Cl, 10·1%). The analytical figures are in agreement with those required for the methyl ester of α-chloro-βββ-triphenylpropionic acid. No chlorobenzene or methyl dichlorosuccinate was detected.

(iv) *With ethyl bromoacetate.* A solution of phenylazotriphenylmethane (11·0 g.) in ethyl bromoacetate (300 g.) was treated as described above for the corresponding reaction with ethyl chloroacetate. The solution became very dark and did not deposit a solid on cooling. Distillation with carbon tetrachloride (four portions of 40 ml.) and subsequent nitration of the distillate gave *m*-dinitrobenzene (0·44 g. ≡ 0·20 g. of benzene), m. p. 82—83°. Most of the ethyl bromoacetate (275·0 g.) was removed at 70—80°/30 mm. The residue was distilled at 30 mm. with a 10 cm. Vigreux column and further ester (12·5 g.) was removed. After redistillation at atmospheric pressure (at which pressure it was all collected below 160°), it was added to the main fraction. Hydrolysis and nitration of a portion (32·75 g.) of the total distillate gave 1-bromo-2,4-dinitrobenzene (0·30 g.), which is equivalent to a total of 1·65 g. of bromobenzene. The residue from which the solvent had been removed gave no further distillate up to a bath temperature of 140°/0·1 mm. (absence of ethyl succinate). The non-volatile residue, treated as described before, gave triphenylmethane (2·86 g.) and a dark, viscous oil (8 g.).

(v) *With ethyl phenylacetate.* A solution of phenylazotriphenylmethane (11·51 g.) in ethyl phenylacetate (246 g.) was kept at 55° for 42 hr. Carbon tetrachloride (120 ml.) was used to remove benzene and nitration of the distillate by the standard procedure gave *m*-dinitrobenzene (3·8 g. ≡ 1·76 g. of benzene). The excess of the ester was removed at 120°/*ca.* 20 mm. and the residue was distilled with a 10 cm. Vigreux column, the pressure being gradually reduced to 0·02 mm. The total distillate was redistilled at 87—90°/6 mm. The non-volatile residue from the first distillation was dissolved in benzene (20 ml.) and cooled in ice. Triphenylmethane (2·50 g.), m. p. 80—82°, was filtered off and the filtrate was diluted with light petroleum and chromatographed on alumina. Elution as in the previous reactions gave (*a*) tetraphenylmethane (0·02 g.), m. p. 270°, (*b*) a yellow glass, and (*c*) an orange oil. Fraction (*b*), triturated with ice-cold ethanol, gave ethyl *meso*-diphenylsuccinate (0·57 g.), m. p. 130° raised to 137° on recrystallisation from ethanol and undepressed on admixture with an authentic specimen. The ethanol mother-liquors yielded a gum, which was rechromatographed in light petroleum and gave triphenylmethane (0·35 g.), m. p. 80—83°.

Reactions with Nitrosoacetanilide.—(i) *With ethyl acetate.* A solution of nitrosoacetanilide (14·0 g.) in ethyl acetate (250 ml.) was maintained at 20° for 2 days and then boiled under reflux for 5 hr. The evolved gases were passed through a solution of 2,4-dinitrophenylhydrazine in aqueous hydrochloric acid before reaching the cold traps and the Carbosorb absorption tube. A little acetaldehyde 2,4-dinitrophenylhydrazone (0·2 g.) was collected (m. p. and mixed m. p. 161°). Some carbon dioxide (0·1 g.) was retained but no products were collected in the cold traps. The reaction mixture was washed with aqueous sodium hydroxide, which removed acetic acid (4·0 g.). The dried (Na_2SO_4) ethyl acetate solution was distilled with a 45 cm. helix-packed jacketed column and two fractions were collected: (*a*) b. p. 70—76° (16·4 g.) and (*b*) b. p. 76° (163·0 g.). The residue was then distilled with a 10 cm. Vigreux column to give a fraction (*c*) of b. p. 76—79° (27·7 g.) and a non-volatile tar (8·0 g.). No products were obtained from the residue. Fractions (*b*) and (*c*) were combined and the benzene content of fraction (*a*) and of the combined fractions (*b*) and (*c*) was estimated by the ultraviolet spectrophotometric method. The results are reported in Table 11.

(ii) *With ethyl chloroacetate.* A solution of nitrosoacetanilide (14·3 g.) in ethyl chloroacetate (245 g.) was maintained at 20° for 3 days and then at 80° for 8 hr. Carbon dioxide (0·03 g.) and acetic acid (4·9 g.) were estimated as in the previous reactions. Four portions of carbon tetrachloride (50 ml. each) were added to the ethyl chloroacetate solution and the whole of the carbon tetrachloride was recovered by distillation. Nitration of the distillate gave *m*-dinitrobenzene (4·10 g. ≡ 1·91 g. of benzene). Fractionation was continued at *ca.* 25 mm. until

50 ml. of distillate had been collected. This fraction was shown by the ultraviolet spectrophotometric method to contain no chlorobenzene. After removal of more ethyl chloroacetate (150 g.), a residue (5·5 g.) was obtained from which further products could not be isolated.

TABLE 11.

	Benzene–ethyl acetate distillates					
	Fraction (*a*) 9·0641 g./l.		Fractions (*b* & *c*) 7·4292 g./l.		Fractions (*b* & *c*) 8·7960 g./l.	
Wavelength (mμ)	*D*	c_{PhH}	*D*	c_{PhH}	*D*	c_{PhH}
247·0	0·216	0·137	0·171	0·102	0·202	0·119
248·9	0·308	0·115	0·241	0·090	0·285	0·105
252·6	0·120	0·138	0·087	0·097	0·105	0·117
254·8	0·320	0·110	0·259	0·089	0·307	0·105
259·0	0·080	0·140	0·065	0·110	0·076	0·130
261·0	0·215	0·110	0·134	0·086	0·205	0·104
Average c_{PhH} (g./l.)		0·125		0·096		0·113
Yield of benzene (g.) ...		0·23		2·47		2·45

Total yield of benzene 2·69 g.

(iii) *With ethyl phenylacetate.* A solution of nitrosoacetanilide (14·3 g.) in ethyl phenylacetate (246 g.) was kept at 20° for 3 days and then at 70° for 8 hr. No carbon dioxide or acetaldehyde was obtained but acetic acid (4·7 g.) was isolated in the normal manner. Three portions of carbon tetrachloride (50 ml. each) were added to the solution and were recovered by distillation. Nitration gave *m*-dinitrobenzene (6·04 g. ≡ 2·80 g. of benzene), m. p. 82—84°. The excess of ester was then collected at 100°/*ca.* 14 mm. until approximately 30 ml. remained, which were distilled through a 10 cm. Vigreux column. The following fractions were collected: (*a*) b. p. 80—84°/3—4 mm. (20·7 g.); (*b*) b. p. 65°/2 mm. (5·07 g.); (*c*) b. p. 60°/0·5 mm. (5·77 g.); (*d*) non-volatile residue (*ca.* 4·0 g.). Fractions (*a*), (*b*), and (*c*) on redistillation gave mainly ethyl phenylacetate but a small residue was added to (*d*), which was then dissolved in benzene–light petroleum (b. p. 40—60°) (1 : 4) and chromatographed on alumina. Elution with the same solvent gave ethyl *meso*-diphenylsuccinate (0·30 g.), m. p. 135°, which had m. p. and mixed m. p. 141° on recrystallisation from ethanol.

Reaction with Benzenediazonium Chloride.—With ethyl phenylacetate. One reaction was carried out by method *B* (see Part I) with aniline (18·6 g.) and ethyl phenylacetate (246 g.). The organic layer was separated and the aqueous layer washed with carbon tetrachloride. The combined ester and carbon tetrachloride solution was washed with aqueous acid and alkali. The carbon tetrachloride was distilled off and nitration gave *m*-dinitrobenzene (15·08 g. ≡ 7·00 g. of benzene), m. p. 79—80°. The ethyl phenylacetate was collected at 120°/15 mm. and the black residue (23·0 g.) was dissolved in benzene–light petroleum (b. p. 40—60°) (1 : 2) and chromatographed on alumina. Successive elution with benzene–light petroleum, benzene, benzene–ether, and ether gave biphenyl (0·05 g.), ethyl *meso*-diphenylsuccinate (2·40 g.), m. p. and mixed m. p. 139—140°, and much viscous tar.

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