297. *Homolytic Aromatic Substitution.   Part XII.* * *Reactions with Phenyl Iodosobenzoate.*

By D. H. Hey, C. J. M. Stirling, and Gareth H. Williams.

The decomposition of phenyl iodosobenzoate in nitrobenzene at 125° has been shown to result in the formation of a mixture of isomeric nitrodiphenyls. The proportion in which these isomers occur in the mixture has been shown to be the same as that arising from the decomposition of benzoyl peroxide in the same solvent at the same temperature. This fact, coupled with the occurrence of by-products of the type usually associated with reactions of homolytic arylation, leads to the conclusion that benzoyloxy-radicals are produced by the homolytic decomposition of phenyl iodosobenzoate, and that phenyl radicals result from the benzoyloxy-radicals by loss of carbon dioxide. The anomalously high yield of benzoic acid which accompanies the reaction of phenyl iodosobenzoate with nitrobenzene has been shown most probably to arise from the hydrolysis of phenyl iodosobenzoate by the small amount of water present in the solvent.   Phenyl iodosobenzoate has also been shown to be capable of effecting the carbon–carbon fission of the vicinal glycol, benzpinacol, by means of a non-homolytic mechanism.

CRIEGEE and BEUKER [1] have found that compounds of the type $RI(O \cdot CO \cdot R')_2$ (where R = aryl, R' = alkyl) resemble lead tetra-acetate in their general reactions.   In particular, they react with olefins to form glycol diacetates, and effect the fission of vicinal glycols. Sandin and McCormack [2] subsequently reported that *sym.*-trinitrotoluene was converted into *sym.*-trinitro-*m*-xylene in 20% yield by phenyl iodosoacetate in hot acetic acid.   These authors recognised the analogy with the methylation of aromatic compounds with lead tetra-acetate,[3] and suggested that phenyl iodosoacetate might undergo homolytic decomposition to give methyl radicals in a manner analogous to that of lead tetra-acetate.   Recently, in Parts VI [4] and X,[5] the reactions of lead tetrabenzoate have been investigated, and it was shown that homolytic decomposition takes place in inert aromatic solvents at temperatures above 100° with the production of free phenyl radicals.   In addition, the reaction of lead tetrabenzoate with vicinal glycols at 15° was shown to result in fission, and so to be quite distinct from the high-temperature decomposition and not to involve free radicals. No work appears to have been carried out on phenyl iodosobenzoate as a potential phenylating agent.   In the present communication the reactions of phenyl iodosobenzoate have been investigated with reference to the known reactions of benzoyl peroxide and lead tetrabenzoate.

* Part XI, preceding paper.
[1] Criegee and Beuker, *Annalen*, 1939, **541**, 218.
[2] Sandin and McCormack, *J. Amer. Chem. Soc.*, 1945, **67**, 2051.
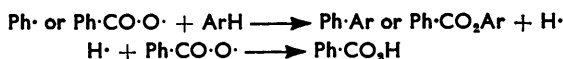[3] Fieser, Clapp, and Daudt, *ibid.*, 1942, **64**, 2052.
[4] Hey, Stirling, and Williams, *J.*, 1954, 2747.
[5] *Idem, J.*, 1955, 3963.

Phenyl iodosobenzoate was first prepared by Arbuzov.[6] In 1949, Richards [7] described the use of phenyl iodosobenzoate and other phenyl iodosoacylates as catalysts in addition polymerisation. It is now shown that the decomposition of phenyl iodosobenzoate in nitrobenzene gives rise to nuclear phenylation, a mixture of the three isomeric nitrodiphenyls being obtained. The composition of the mixture has been determined by ultraviolet spectroscopy and the results are in very close agreement with those obtained in similar reactions with benzoyl peroxide and lead tetrabenzoate.[4] The phenylation of pyridine with phenyl iodosobenzoate has been reported in Part X.[5] Thus it is clear that the phenylating action of phenyl iodosobenzoate is closely analogous to that of benzoyl peroxide, lead tetrabenzoate, and the various diazo-derivatives discussed in Part I by Hey, Nechvatal, and Robinson.[8] At temperatures above 100°, phenyl iodosobenzoate undergoes homolytic decomposition to liberate benzoyloxy-radicals which, by subsequent decarboxylation, provide phenyl radicals.

The decomposition of phenyl iodosobenzoate has been shown to afford an anomalously high yield of benzoic acid (1·43 mol./mol.) in nitrobenzene. Free benzoic acid can arise in the decomposition in only two ways : (1) By combination of a benzoyloxy-radical with a free hydrogen atom which has been liberated from the nitrobenzene nucleus during substitution by a benzoyloxy or phenyl radical :

$$\text{Ph· or Ph·CO·O· + ArH} \longrightarrow \text{Ph·Ar or Ph·CO}_2\text{Ar + H·}$$
$$\text{H· + Ph·CO·O·} \longrightarrow \text{Ph·CO}_2\text{H}$$

(2) By the attack of a free hydrogen atom on phenyl iodosobenzoate :

$$\text{PhI(O·CO·Ph)}_2 + \text{H·} \longrightarrow \text{PhI + Ph·CO·O· + Ph·CO}_2\text{H}$$

Mechanisms involving the abstraction by benzoyloxy-radicals of nuclear hydrogen atoms from the aromatic solvent are not tenable, since in the case of nitrobenzene, for example, the process must yield an amount of dinitrodiphenyl equivalent to the benzoic acid formed by this mechanism :

$$\text{Ph·CO·O· + Ar·H} \longrightarrow \text{Ph·CO}_2\text{H + Ar·}$$
$$\text{Ar· + Ar·H} \longrightarrow \text{Ar·Ar + H·}$$
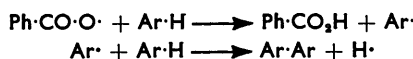
No products corresponding to Ar·Ar were formed in any of the reactions studied.

As the free benzoic acid can therefore arise only by mechanisms (1) and (2), its molar yield should ideally be equal to the sum of the molar yields of diaryl and " ester " benzoic acid, which is obtained by hydrolysis of the products of substitution by benzoyloxy-radicals and, in any case, should not be greater than unity. In the decomposition of phenyl iodosobenzoate, however, the molar yield of free benzoic acid is 1·43, while the sum of the molar yields of nitrodiphenyl and " ester " acid is 0·50. The following possible sources of benzoic acid in the decomposition and subsequent working-up have therefore been checked and a probable explanation of the anomaly has been found.

(a) Incomplete decomposition of the reagent with subsequent hydrolysis of undecomposed starting material : The fact that decomposition was complete was readily established by testing for phenyl iodosobenzoate with starch–iodide. Negative results were obtained in every case and, moreover, an increase in the period of heating did not affect the yield of free benzoic acid.

(b) Formation of benzoic anhydride : Lippmann [9] has implied that benzoic anhydride is formed in the decomposition of benzoyl peroxide in " amylene." In order to account on an analogous basis for the yield of benzoic acid formed in the present reactions, any benzoic anhydride produced in the decomposition of phenyl iodosobenzoate must be hydrolysed during the extraction of the free acid. It has, however, been shown that benzoic

[6] Arbuzov, *J. prakt. Chem.*, 1931, **131**, 357.
[7] Richards, U.S.P. 2,467,231.
[8] Hey, Nechvatal, and Robinson, *J.*, 1951, 2892.
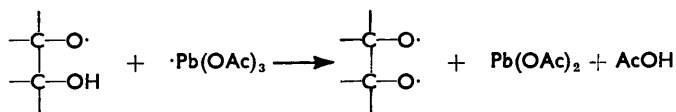[9] Lippmann, *Monatsh.*, 1884, **5**, 559.

anhydride is not appreciably hydrolysed by saturated aqueous sodium hydrogen carbonate under the conditions used in the working up.

(c) Hydrolysis of esters : It was shown that no benzoic acid was formed when a mixture of phenyl benzoate with the three isomeric nitrophenyl benzoates was treated with aqueous sodium hydrogen carbonate under the conditions used for the extraction of the free acid.

(d) Presence of water in the solvent : Determination of the concentration of water in the nitrobenzene showed that the amount present is just sufficient to account for the amount of benzoic acid obtained. Addition of excess of water to the reaction mixture has been shown (Table 1) to result in a substantial increase in the yield of benzoic acid, with a corresponding decrease in the yields of the products of nuclear phenylation and benzoyl-oxylation, although even in the presence of a considerable excess of water the hydrolysis is not quite quantitative. Thus the rate of the homolysis must be sufficiently large compared with the rate of hydrolysis, so that the former reaction still takes place to a minor extent. It would appear, therefore, that hydrolysis of phenyl iodosobenzoate by the small amount of water present in the solvent provides the most likely explanation of the high yield of benzoic acid, although this does not necessarily exclude the possibility that other factors may contribute.

In addition to the investigation of the homolytic decomposition of phenyl iodoso-benzoate it has now been shown that this reagent is capable of effecting carbon–carbon fission in a vicinal glycol by a non-homolytic process. Phenyl iodosobenzoate reacts rapidly with benzpinacol in benzene solution at 80° to give a quantitative yield of benzo-phenone, with the consumption of an equivalent amount of phenyl iodosobenzoate. No products corresponding to a free-radical reaction could be found.[10] The correspondence between the reactions of lead tetrabenzoate and those of phenyl iodosobenzoate is thus established.

A comparison of the reactions of lead tetra-acetate and of acetyl peroxide has been reported by Kharasch, Friedlander, and Urry.[11] Whereas the reaction of a vicinal glycol with lead tetra-acetate results in cleavage of a carbon–carbon bond, that with acetyl peroxide results in oxidation to a hydroxy-ketone and finally a diketone. The reaction which results in the fission of vicinal glycols does not possess any of the characteristics of a homolytic process. This same contrast has been shown between the reactions of a vicinal glycol with lead tetrabenzoate on the one hand and benzoyl peroxide on the other (cf. Part VI [4]). The reactions of phenyl iodosobenzoate clearly follow very closely the pattern shown by lead tetrabenzoate, and both reagents effect the fission of vicinal glycols at temperatures well below those at which homolytic decomposition occurs. The conclusions thus reached are at variance with those put forward by Cordner and Pausacker [12] for the oxidation of vicinal glycols with lead tetra-acetate and phenyl iodoso-acetate. These authors postulate the intermediate formation of a triacetoxylead radical, which reacts *specifically* upon the hydrogen atom of the adjacent hydroxyl group, thus :

$$-\overset{|}{\underset{|}{C}}-O\cdot \quad + \quad \cdot Pb(OAc)_3 \longrightarrow -\overset{|}{\underset{|}{C}}-O\cdot \quad + \quad Pb(OAc)_2 + AcOH$$
$$-\overset{|}{\underset{|}{C}}-OH \qquad\qquad\qquad\qquad -\overset{|}{\underset{|}{C}}-O\cdot$$

Free radicals are, in general, notably non-selective in their reactions and it seems unlikely that a triacetoxylead radical would take part in such a highly specific reaction to the extent required for the almost quantitative character of the reaction. Such triacetoxy-lead radicals have been postulated by Kharasch and his co-workers [11] in the high-temperature decomposition of lead tetra-acetate and are considered to break down further into lead acetate and acetoxyl radicals. Moreover, the present demonstration that lead tetrabenzoate and phenyl iodosobenzoate react with vicinal gycols by a non-homolytic mechanism renders unlikely the intervention of free radicals in the analogous reactions with lead tetra-acetate and phenyl iodosoacetate.

[10] Cf. ref. 4.
[11] Kharasch, Friedlander, and Urry, *J. Org. Chem.*, 1949, **14**, 91; 1951, **16**, 533.
[12] Cordner and Pausacker, *J.*, 1953, 102; Pausacker, *ibid.*, p. 107.

EXPERIMENTAL

Reagents.—Nitrobenzene (" AnalaR ") was purified as previously described.[4] The water content of nitrobenzene purified in this way, as determined by the Karl Fischer method, was 0·1% w/v. Chloroform was dried and freed from ethanol with calcium chloride. Benzoic anhydride (Hopkin and Williams) was crystallised to constant m. p. 41°. Benzpinacol was prepared by the reduction of benzophenone with zinc and acetic acid.[13] It crystallised from benzene–light petroleum (b. p. 40—60°) in white needles, m. p. 186—187°.

Phenyl iodosobenzoate was prepared by a modification of Arbuzov's method.[6] Iodoso-benzene [14] (37 g.) was added to a solution of benzoic acid (41 g.) in chloroform (500 ml.). The mixture was shaken gently until the iodosobenzene had dissolved, and the solution was then filtered. Chloroform was distilled off from the filtrate, and the solid residue was thoroughly washed with boiling light petroleum (b. p. 40—60°) (2 × 100 ml.). The crude material was recrystallised from chloroform–light petroleum, to yield phenyl iodosobenzoate, m. p. 159—160° (62 g.) (Found : C, 53·8; H, 3·3%; equiv., 223. Calc. for $C_{20}H_{15}O_4I$: C, 53·8; H, 3·4%; equiv., 223). The equivalent was determined iodometrically by the method used for lead tetra-benzoate.[4]

Decomposition of Phenyl Iodosobenzoate in Nitrobenzene.—Reactions were carried out in duplicate in a thermostat maintained at 125° ± 0·1° by the method previously used by Augood, Hey, and Williams in Part II.[15] Reaction flasks containing nitrobenzene (190 ml.) were placed in the thermostat 1 hr. before addition of the reagent. Phenyl iodosobenzoate (11·15 g.) was slowly added to the nitrobenzene with shaking, and a further 10 ml. of solvent were added drop-wise. The mixtures were removed from the thermostat after 72 hr., reactions then being complete. The cold mixtures were extracted with saturated sodium hydrogen carbonate solution (3 × 75 ml.), and washed with water. Nitrobenzene was removed by distillation at 20 mm. through a 25 cm. helix-packed column. Esters in the residue were hydrolysed by boiling with 150 ml. of 2N-sodium hydroxide for 15 hr. The unsaponifiable material was thoroughly extracted with benzene (3 × 50 ml.), and the benzene extracts, after being dried (CaCl₂), together with benzene washings of the calcium chloride, were reduced in volume by distillation to 70 ml. The residue from the distillation was chromatographed on an alumina column (25 × 2 cm.) and eluted successively with benzene (100 ml.) and with ether (100 ml.). Ether and benzene were removed from the combined eluates by distillation through a 25 cm. helix-packed column, and subsequent distillation of the residue by the method described by Augood, Hey, and Williams [15] gave a mixture of nitrodiphenyls as a pale yellow semi-solid b. p. 118—138°/0·5 mm. The products obtained from these reactions are listed in Table 1. Expt. 3 was carried out under the

TABLE 1. *Products obtained in reactions with nitrobenzene at 125° (mol./mol. of reagent).*

Reagent	Free Ph·CO₂H	Ph·CO₂H from ester	Ph·C₆H₄·NO₂	Higher phenylated products *
PhI(O·CO·Ph)₂				
1 & 2 (mean)	1·43	0·27	0·23	0·01
3	1·84	0·02	0·10	0·01
4	1·43	—	—	—
(Ph·CO₂)₂				
5	0·74	0·11	0·65	0·03
6	0·75	—	—	—

* Calc. as Ph·C₆H₄·C₆H₄·NO₂.

same conditions, except that water (1·80 g., 0·05 mol./mol. of nitrobenzene) was added to the nitrobenzene. Expt. 4 was carried out under the same conditions as expts. 1 and 2, except that the reagent was dissolved in cold nitrobenzene. The apparatus was closed with a phosphoric oxide tube in addition to the calcium chloride tube, and then placed in the thermostat. The period of heating was extended to 96 hr. in this experiment. The results of expt. 5 are quoted in Part VI,[4] and expt. 6 was carried out under the same conditions as expt. 5 with the addition of water (0·9 g.). Analyses for nitrogen on the mixtures of isomeric nitrodiphenyls were as follows : (1) 7·25; (2) 6·85; (3) 6·95 (Calc. for $C_{12}H_9O_2N$: N, 7·0%). The phenyl iodoso-benzoate accounted for as products derived from benzoyloxy-radicals in expts. 1 and 2 amounts to 95%.

[13] Sagumenny, *Bull. Soc. chim. France,* 1880, **34**, 329.
[14] Lucas, Kennedy and Formo, *Org. Synth.,* 1942, **22**, 70.
[15] Augood, Hey, and Williams, *J.,* 1952, 2094.

Free benzoic acid formed in these reactions was isolated as follows : the sodium hydrogen carbonate extracts of the reaction mixture were washed with methylene chloride, acidified with concentrated hydrochloric acid, and then saturated with sodium chloride. The precipitated benzoic acid was thoroughly extracted with methylene chloride (4 × 30 ml.). The aqueous layer was rejected and the combined extracts, after being dried (Na_2SO_4), were allowed to evaporate at room temperature. The residual benzoic acid had m. p. and mixed m. p. 117—119°. Benzoic acid which resulted from the hydrolysis of esters was isolated in the same manner as the benzoic acid formed in the phenylation of pyridine.[5]

Extent of Hydrolysis of Benzoic Anhydride.—Benzoic anhydride (3·0 g.) was dissolved in benzene (75 ml.). The solution was treated in the same manner as for the isolation of free benzoic acid. Benzoic acid (0·05 g.), m. p. and mixed m. p. 120°, was obtained.

Hydrolysis of Esters.—A mixture of equal quantities of phenyl benzoate with each of the isomeric nitrophenyl benzoates (2 g.) was dissolved in benzene (75 ml.), and the solution was treated in the same manner as in the experiment described above with benzoic anhydride. No benzoic acid was obtained.

Hydrolysis of Phenyl Iodosobenzoate by Water Present in the Solvent.—A Karl Fischer determination of the water present in the nitrobenzene showed the concentration to be $5·5 \times 10^{-3}$ mol./mol. The concentration of the reagent used was $12·5 \times 10^{-3}$ mol./mol. If each mole of water caused the hydrolysis of one mole of phenyl iodosobenzoate with the production of two moles of benzoic acid, and if hydrolysis were quantitative, the yield of free benzoic acid could be accounted for. Thus, in expts. 1 and 2 (Table 1), the excess of free benzoic acid over the sum of the yields of diaryls and " ester " benzoic acid is 0·93 mole/mole of reagent. This is the amount of benzoic acid which must be accounted for by hydrolysis of the reagent, if it is assumed that the extraction of nitrodiphenyls and " ester " benzoic acid is quantitative. The amount of water present in the nitrodiphenene used (200 ml.) amounts to 0·20 g. on the basis of the Karl Fischer determinations. This is capable of producing 0·022 mole of benzoic acid by the hydrolysis of phenyl iodosobenzoate, and since 11·15 g. of phenyl iodosobenzoate were used, this represents a yield of 0·89 mole of benzoic acid per mole of phenyl iodosobenzoate. Thus the discrepancy in the yield of benzoic acid is reduced to 0·04 mole/mole of reagent, and since the extraction of nitrodiphenyl and " ester " benzoic acid is certainly not quantitative. and a 5% error in the Karl Fischer estimation perfectly conceivable, the result is probably well within the limits of accuracy of the experiment.

Determination of the Composition of the Mixture of Nitrodiphenyls.—The determination of the ratio of isomers present in the mixture of isomeric nitrodiphenyls formed in the decomposition of phenyl iodosobenzoate in nitrobenzene was carried out by ultraviolet spectrophotometry with the aid of a Unicam " S.P. 500 " quartz spectrophotometer, the method of calculation described by Cadogan, Hey, and Williams[16] being used. The calibration curves for the pure isomers had been obtained previously.[4] The compositions of the mixtures obtained by this means are given in Table 2. The overall error of each determination was ±2%. The results obtained in similar reactions with benzoyl peroxide, which are quoted from Part VI,[4] are included for comparison.

TABLE 2. *Mean isomer ratios in reactions with nitrobenzene at 125°.*

	Isomers (%)		
Reagent	*o-*	*m-*	*p-*
Phenyl iodosobenzoate	57·5	14	28·5
Benzoyl peroxide	56	16	28

Reaction of Phenyl Iodosobenzoate with Benzpinacol.—A mixture of benzpinacol (3·2280 g.) and phenyl iodosobenzoate (4·4809 g.) was dissolved in sodium-dried " AnalaR " benzene (100 ml.). The solution was boiled under reflux for 60 min. and then cooled rapidly to room temperature. 10% Sulphuric acid (50 ml.) and excess of potassium iodide were added, and the liberated iodine was titrated with 0·05N-sodium thiosulphate. The aqueous layer was made alkaline with sodium hydrogen carbonate and thoroughly extracted with benzene (2 × 35 ml.). Benzoic acid (m. p. and mixed m. p. 119°) was isolated from the aqueous solution in the manner described above. The benzene extracts, after being dried (Na_2SO_4), were reduced to a small volume by distillation through a 25 cm. helix-packed column. Distillation of the residue yielded first iodobenzene, b. p. 110°/50 mm. (converted to 1-iodo-4-nitrobenzene, m. p. and mixed m. p.

[16] Cadogan, Hey, and Williams, *J.*, 1954, 794.

171°), and subsequently benzophenone, b. p. 90°/0·2 mm., m. p. and mixed m. p. 46—47°. The results of experiments carried out in duplicate are shown in Table 3.

TABLE 3. *Results obtained in the oxidation of benzpinacol with phenyl iodosobenzoate.*

	Mol./mol. of benzpinacol	
	(1)	(2)
Yield of benzophenone	1·97	1·91
Phenyl iodosobenzoate consumed	1·00	1·00

KING'S COLLEGE (UNIVERSITY OF LONDON),
    STRAND, LONDON, W.C.2.