

Aroyl Peroxides. Part VI.¹ Reactions of Aroyl Peroxides with Nitrogen Dioxide

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The products of the decomposition of benzoyl peroxide in carbon tetrachloride in the presence of nitrogen dioxide have been investigated quantitatively, and the mechanism previously suggested has been confirmed. The reaction of benzoyl peroxide with nitrogen dioxide in the absence of solvent has been found to be similar, but less complex. The formation of benzoyl nitrate was indicated by the isolation of a nitration product from reactions in the presence of *p*-xylene. The decomposition of a series of aroyl peroxides in the presence of nitrogen dioxide gave the corresponding nitro-compounds.

THE formation of nitrobenzene by the decomposition of benzoyl peroxide in carbon tetrachloride in the presence of nitrogen dioxide has been reported.² As well as nitrobenzene, which is formed by combination of phenyl radicals with nitrogen dioxide, and products of reactions of phenyl radicals with carbon tetrachloride,^{3,4} benzoic acid was formed in high yield (*ca.* 1.3 mol per mol of peroxide). It was suggested that this was formed by hydrolysis, during work-up, of benzoyl nitrate, which arose by combination of benzoyloxy radicals with nitrogen dioxide. In order to confirm these suggestions we now report a more comprehensive study of this reaction.

The results of a quantitative study of the reaction in carbon tetrachloride are given in Table 1. The possibility that benzoic acid is formed by reaction of benzoyloxy radicals with adventitious water was eliminated by

TABLE 1

Yields (mol per mol peroxide) of products of the reaction of benzoyl peroxide (0.050 mol) with nitrogen dioxide (0.577 mol) in carbon tetrachloride (120 ml) at 80°

Benzoic acid	1.283
<i>p</i> -Trichloromethylbenzoic acid	0.048
<i>o</i> -Trichloromethylbenzoic acid	0.002
Hexachloroethane	0.003
Chlorobenzene	0.204
Nitrobenzene	0.158
Biphenyl	0.002
Benzylidene chloride	0.003
Benzoic anhydride	0.037
4-Chlorobiphenyl	0.001
Nitrobiphenyls	Trace
Nitrophenols	Trace
Phosgene	Trace
Nitrate ion	≤ 0.7
Residue (g per g peroxide)	0.006

conducting the reaction in the presence of added water or an efficient solid drying agent, neither of which had any effect on the product yields. Since benzoic acid is formed only in the presence of nitrogen dioxide, it is likely that it is formed by subsequent hydrolysis of benzoyl nitrate as previously suggested. An analogous explanation (hydrolysis of benzoyl hypiodite) has been suggested for the formation of large quantities of benzoic acid when benzoyl peroxide decomposes in carbon tetrachloride in the presence of iodine.⁵

The reactions (1)–(11) may occur during the decom-

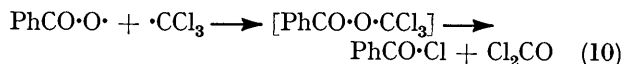
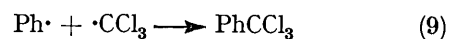
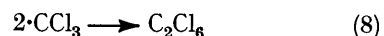
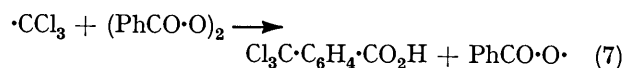
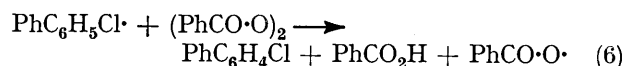
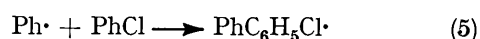
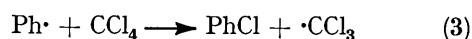
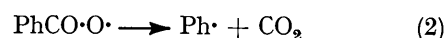
¹ Part V, P. Lewis and G. H. Williams, *J. Chem. Soc. (B)*, 1969, 120.

² G. B. Gill and G. H. Williams, *J. Chem. Soc.*, 1965, 5756.

³ D. H. Hey and J. Peters, *J. Chem. Soc.*, 1960, 79.

⁴ J. I. G. Cadogan, D. H. Hey, and P. G. Hibbert, *J. Chem. Soc.*, 1965, 3939.

position of benzoyl peroxide in carbon tetrachloride.^{3,4} Reactions involving collisions of radicals, both of whose stationary concentrations must be very low, and those



representing benzoyloxylation of chlorobenzene, are not included, since their contribution is negligible. 4-Chlorobiphenyl is probably formed by reactions (5), (6), and (11). Dehydrogenation of the σ -complexes $\text{PhC}_6\text{H}_5\text{Cl}$ by reaction with benzoyloxy radicals is known not to take place.⁶ The small yield of biphenyl probably arises as a result of attack of phenyl radicals on the 1-position of chlorobenzene in reaction (5). Although disproportionation of the resulting σ -complexes to give biphenyl and dichlorodihydrobiphenyls, which would be expected readily to undergo dehydrohalogenation, has been suggested as a minor contributor in the reactions of benzoyl peroxide with chlorobenzene⁷ and fluorobenzene,¹ this is not a likely route to biphenyl in the present reactions, because chloride ions were not detected. Biphenyl may be formed by dechlorination of these σ -complexes, possibly by trichloromethyl radicals to give carbon tetrachloride, or, less probably, by dimerisation of phenyl radicals.

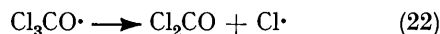
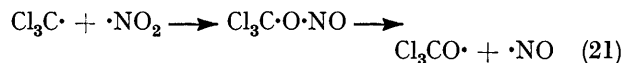
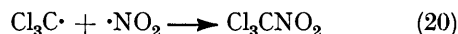
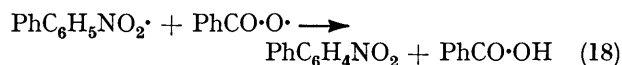
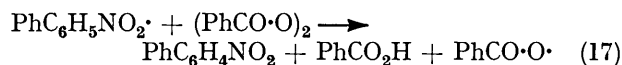
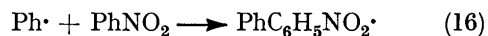
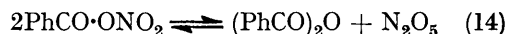
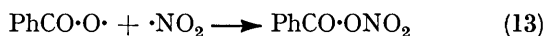
In the presence of nitrogen dioxide, the additional reactions (12)–(22) may occur. Reactions (16)–(19)

⁵ G. S. Hammond and L. M. Soffer, *J. Amer. Chem. Soc.*, 1950, **72**, 4711.

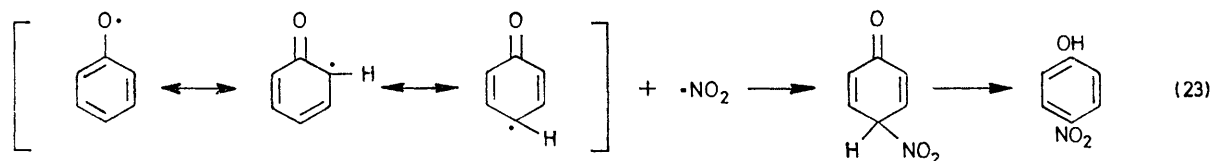
⁶ G. B. Gill and G. H. Williams, *J. Chem. Soc.*, 1965, 7127.

⁷ E. L. Eliel, S. Meyerson, Z. Welvart, and S. H. Wilen, *J. Amer. Chem. Soc.*, 1960, **82**, 2936.

represent the phenylation of nitrobenzene,⁸ but those



representing the analogous benzoyloxylation are not included since their contribution is negligible. The trace of nitrophenols detected may be formed as a result of reaction (15). The hypothetical phenyl nitrite would be expected to dissociate into phenoxy radicals and nitric oxide, the latter accounting for the observed bright blue colour of the frozen reaction mixtures by its combination with nitrogen dioxide to give dinitrogen trioxide. Nitrophenols may then be formed by reaction of phenoxy radicals with nitrogen dioxide (23) or by nitration of



phenyl nitrite by benzoyl nitrate and subsequent dissociation of the products by reactions analogous to (15). A process analogous to (23) involving tri-*t*-butylphenoxy radicals and nitrogen dioxide has been reported.⁹

Surprisingly, reaction (20) does not appear to occur, since no chloropicrin was formed. Phosgene, however, must have been formed *via* reactions (21) (which represents the combination of trichloromethyl radicals with nitrogen dioxide *via* an oxygen atom) and (22). This process has previously been suggested by Gray¹⁰ to account for the formation of phosgene in the pyrolysis of chloropicrin.

Although benzoic acid is a product of several reactions, the contribution of these is grossly insufficient to account for the observed yield of this product. The main source of benzoic acid must therefore be the benzoyl nitrate formed in reaction (13). This is supported by the detec-

⁸ G. B. Gill and G. H. Williams, *J. Chem. Soc. (B)*, 1966, 880.

⁹ C. D. Cook and R. C. Woodworth, *J. Amer. Chem. Soc.*, 1953, **75**, 6242.

¹⁰ P. Gray, *Trans. Faraday Soc.*, 1955, **51**, 1367.

¹¹ F. Francis, *Ber.*, 1906, **39**, 3798.

tion of nitrate ions in the products. Although the reversible reaction (14) has long been known to occur,¹¹ since benzoic anhydride was not hydrolysed under the conditions used, benzoic acid must have been formed directly from benzoyl nitrate during work-up, by reaction (24).

This was confirmed by the results of the decomposition of benzoyl peroxide in nitrogen dioxide alone (Table 2), in

TABLE 2

Yields (mol per mol peroxide) of products of reaction of benzoyl peroxide (0.010 mol) with nitrogen dioxide (0.350 mol) at 80°

Acid ^a	1.443
Nitrobenzene	0.368
<i>m</i> -Dinitrobenzene	0.066
4-Nitrobiphenyl	0.028
Residue (g per g peroxide)	0.018

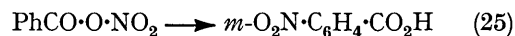
^a Calculated as *m*-nitrobenzoic acid. Since benzoic and 3,5-dinitrobenzoic acids were also present in almost equivalent amounts (*ca.* 10%), this approximation entails little error.

which the nitrobenzene yield was approximately doubled because phenyl radicals were not lost by attack on the solvent. The most striking feature of the results, however, was that the products were strongly indicative of the occurrence of heterolytic nitration by either benzoyl nitrate or dinitrogen pentoxide, although the absence of benzoic anhydride from the products of this reaction points to the former. Benzoyl nitrate is known to undergo rearrangement, particularly in nitrobenzene solution, to *m*-nitrobenzoic acid.¹¹ Since this was the major acidic component of the products of this reaction

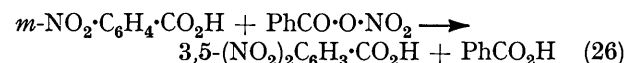
it is not unreasonable to assume that it was formed thus (25). Nitration of *m*-nitrobenzoic acid by benzoyl



nitrate gives 3,5-dinitrobenzoic and benzoic acids (26), which were also formed in approximately equivalent amounts, and nitration of nitrobenzene gives *m*-dinitrobenzene. The reduced prevalence of nitration and



consequently higher yield of benzoic acid resulting from hydrolysis of benzoyl nitrate in the reaction in carbon tetrachloride may be due to dilution and to the less polar nature of the solvent.



In order further to establish the presence of a heterolytic nitrating agent, a separate aromatic substrate capable of nitration (*p*-xylene) was added. The results are given in Table 3. The formation of 1,4-dimethyl-5-nitrobenzene in this reaction constituted unequivocal

TABLE 3

Yields (mol per mol peroxide) of products of the reaction of benzoyl peroxide (0.010 mol) with nitrogen dioxide (0.081 mol) and *p*-xylene (0.010 mol)

Acid ^a	1.709
Benzene	0.042
Nitrobenzene	0.088
<i>p</i> -Tolynitromethane	0.043
1,4-Dimethyl-5-nitrobenzene	0.065
Biphenyl	0.019
2,5-Dimethylbiphenyl	0.035
Residue (g per g peroxide)	0.067

^a As *m*-nitrobenzoic acid.

confirmation of this postulate, since this compound could not be formed by any homolytic process, and was not formed in appreciable yield from *p*-xylene and nitrogen dioxide in the absence of benzoyl peroxide.* The *p*-tolynitromethane formed concomitantly must have arisen by combination of nitrogen dioxide with *p*-methylbenzyl radicals, formed from *p*-xylene by α -hydrogen abstraction by benzoyloxyl and/or phenyl radicals. 2,5-Dimethylbiphenyl is the product of phenylation of *p*-xylene.

The efficiency of nitrogen dioxide as a scavenger of benzoyloxyl radicals is indicated by the extents to which these radicals undergo decarboxylation. In reactions

the aryl radicals and nitrogen dioxide, and this therefore constitutes a useful route to such nitro-compounds on a reasonable scale. The chloro-compounds (ArCl), the normal products of aryl radical attack on carbon tetrachloride,³ were formed in much lower yield than in the absence of nitrogen dioxide. The high yields of carboxylic acids (ArCO₂H) presumably result from the hydrolysis of the corresponding acyl nitrates.

Abstraction of hydrogen atoms from the aliphatic side-chain accounts for the rather low yield of *m*-nitrotoluene and high yield of complex acids obtained from the reaction with *m*-toluoyl peroxide. The stationary concentration of aryl radicals available for combination with nitrogen dioxide is thereby reduced. This also applies to the reaction with *o*-methoxycarbonylbenzoyl peroxide where methyl *o*-nitrobenzoate was formed in low yield and a large amount of a non-volatile residue was obtained.

The reactivity of the naphthalene nucleus to homolytic attack is well known. It is susceptible to hydrogen abstraction and is readily aroyloxylated.¹² Consequently, very low yields of 2-chloro- and 2-nitro-naphthalene were obtained from the reaction with 2-naphthoyl peroxide, large amounts of 2-naphthoic and substituted acids were formed, and much high-boiling residue was obtained.

TABLE 4

Yields (mol per mol peroxide) of products of reactions of aroyl peroxides (0.005 mol) with nitrogen dioxide in carbon tetrachloride (20 ml) at 80°

Peroxide (ArCO-O) ₂	Nitrogen dioxide (mol)	ArCO ₂ H	ArCl	ArNO ₂	Residue (g per g peroxide)
Benzoyl	0.046	1.438	0.230	0.181	0.0052
<i>m</i> -Chlorobenzoyl	0.041	1.290	0.194	0.248	0.0096
<i>m</i> -Bromobenzoyl	0.042	1.183	0.207	0.214	0.0116
<i>o</i> -Nitrobenzoyl	0.054	1.314	0.183	0.233	0.0087
<i>p</i> -Nitrobenzoyl	0.079	1.218	0.176	0.339	0.0052
<i>m</i> -Toluoyl	0.042	1.825 ^b	0.007	0.163	0.0064
<i>m</i> -Methoxybenzoyl	0.031	1.423	0.165	0.217	0.0090
Monomeric phthaloyl ^a	0.068	1.020 ^c	0.000	0.240 ^c	0.0117
<i>o</i> -Methoxycarbonylbenzoyl	0.081	0.817	0.003	0.138	0.0329
Di-2-naphthoyl	0.050	1.864 ^d	0.004	0.039	0.0233

^a In carbon tetrachloride (50 ml) at 100°. ^b Includes 1.091 mol per mol peroxide of high-melting acids, expressed as *m*-toluic acid.

^c These values have been doubled to give a more valid comparison with product yields from other peroxide decompositions, since each molecule of monomeric phthaloyl peroxide can give rise to only one (bifunctional) radical. ^d Includes 1.205 mol per mol peroxide of high-melting acids, expressed as 2-naphthoic acid.

with benzoyl peroxide in carbon tetrachloride alone, about 80% of the benzoyloxyl radicals formed are decarboxylated whereas, in the presence of nitrogen dioxide, only about 20% escape trapping as benzoyl nitrate.

The results of experiments in which other aroyl peroxides reacted with an excess of nitrogen dioxide in carbon tetrachloride at 80° are given in Table 4. In each case, the only mononuclear nitro-compounds (ArNO₂) formed were those in which the nitro-group occupied the position in the aromatic nucleus formerly occupied by the unpaired electron in the aryl radical Ar•. Since these nitro-compounds were those which would not normally be obtained in quantity by heterolytic nitration, they must have been formed by direct combination between

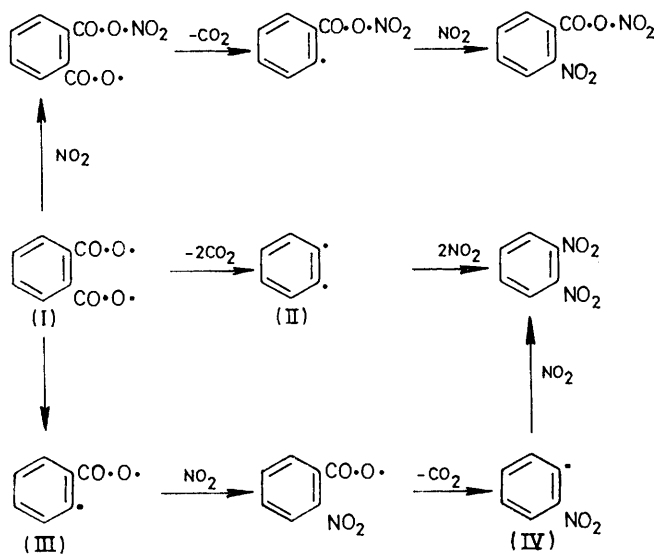
From the reaction of monomeric phthaloyl peroxide with nitrogen dioxide in carbon tetrachloride, only *o*-dinitrobenzene and *o*-nitrobenzoic acid were obtained. Phthalic acid, *o*-dichlorobenzene, and *o*-chloronitrobenzene, which might be expected as products of this reaction, were not detected.

o-Nitrobenzoyl nitrate, hydrolysis of which gives *o*-nitrobenzoic acid can be formed by the route shown (Scheme) from the diradical (I) resulting from primary fission of the O-O bond. *o*-Dinitrobenzene may be formed *via* the diradical (II) ('triplet benzyne'), but if so it must be assumed that (II) is insufficiently reactive to abstract chlorine from carbon tetrachloride. If, alternatively, (I) is decarboxylated in a stepwise manner, attack of (III) and/or (IV) on carbon tetrachloride must

* We thank Mr. W. K. A. Moss for this result.

¹² D. I. Davies, D. H. Hey, and G. H. Williams, *J. Chem. Soc.*, 1961, 3117.

be inhibited by the presence of *ortho*-substituents. The results do not permit a distinction between these alternatives.



EXPERIMENTAL

Carbon tetrachloride, *p*-xylene, and aroyl peroxides were prepared and purified by standard methods. Dinitrogen tetroxide, prepared by the pyrolysis of lead nitrate in a steel tube, was condensed in liquid air after passage through phosphoric oxide, redistilled in oxygen through phosphoric oxide, condensed, and sealed in ampoules. The solid product was white, indicating the absence of dinitrogen trioxide, and therefore of water.

2,5-Dimethylbiphenyl was prepared by treatment of 2,5-dimethylaniline with pentyl nitrite in benzene at 80°. ^{13,14} After chromatography on alumina followed by fractional distillation, it was obtained as a pale yellow oil, b.p. 126–127° at 11 mmHg, *n*_D²⁵ 1.5769 (lit., ¹⁵ b.p. 283° at 760 mmHg, *n*_D²⁵ 1.5733; lit., ¹⁶ b.p. 106–108° at 4 mmHg, *n*_D²⁵ 1.5775).

p-Tolynitromethane, prepared from *p*-methylbenzyl bromide and silver nitrate, ¹⁷ was obtained as a pale yellow liquid, b.p. 88° at 1 mmHg, *n*_D²⁰ 1.5309 (lit., ¹⁷ b.p. 99° at 3 mmHg; lit., ¹⁸ *n*_D²⁰ 1.5311).

Other reference compounds were either available commercially or were prepared and purified by standard methods.

Unless otherwise stated, g.l.c. analyses were carried out by use of a column packed with Apiezon 'L' grease on Celite 545, and a high-sensitivity β-ionisation detector with argon as the carrier gas.

Extraction of Benzoic Anhydride and Benzoic Acid.—Extraction of solutions of benzoic anhydride, benzoic acid, and mixtures of benzoic anhydride with benzoic acid, with saturated aqueous sodium hydrogen carbonate under the conditions described below for the work-up of product mixtures showed that less than 0.7% of the anhydride was hydrolysed, and that more than 99.3% of the acid was unchanged.

Decomposition of Benzoyl Peroxide in Carbon Tetrachloride in the Presence of Nitrogen Dioxide.—Benzoyl peroxide, carbon tetrachloride, and an ampoule containing a

known weight of dinitrogen tetroxide were sealed in a Carius tube under nitrogen. The ampoule was broken *in situ* by sharply inverting the tube, which was then maintained at 80° for 72 h in a thermostat. After being cooled in liquid air, the tube, which contained a blue solid, was opened, and the excess of nitrogen oxides was allowed to evaporate in a stream of nitrogen. Acids were obtained by quantitative extraction of the solution with aqueous sodium hydrogen carbonate and acidification of the extracts. Any trichloromethylbenzoic acids were hydrolysed by boiling the weighed combined acids under reflux with aqueous 10% sodium hydroxide for 24 h and the products were analysed by Volhard chloride assay.

Exhaustive extraction of the acidified (HCl) solution with ether gave all organic acids except terephthalic, which is insoluble in ether. The solid isolated gave no anisole derivatives (g.l.c.) on treatment with diazomethane, nor did it contain nitrogen or chlorine. The product of methylation was almost entirely methyl benzoate.

The deep yellow or red colour produced by alkali during the hydrolysis indicated the presence of nitrophenols.

After most of the solvent (which contained >0.05% benzene or chloropicrin) was removed, crystalline hexachloroethane was deposited. The solvent contained only small amounts of co-distilled chlorobenzene as impurity.

Hydrolysis of the organic residue, under the conditions used for the trichloromethylbenzoic acids, allowed benzylidene chloride to be estimated as chloride ion. The alkaline layers on acidification and extraction with ether gave benzoic acid only; no anisole was detected in the methyl benzoate resulting from methylation of this acid component. The inert organic layer contained chlorobenzene, hexachloroethane, nitrobenzene, biphenyls, and 4-chlorobiphenyl (g.l.c.); a very small amount of mixed nitrobiphenyls was also obtained.

In a separate experiment, the sodium hydrogen carbonate extract of the reaction mixture was analysed for nitrate ion by the Kjeldahl method, giving a minimum estimate.

Effect of Added Water.—A series of experiments was carried out in which known amounts of water, and in some cases a drying agent (Hi-Drite; minus 10 mesh) were added to reactions in which benzoyl peroxide was allowed to decompose in carbon tetrachloride, in the presence and absence of nitrogen dioxide. The yields of benzoic acid, trichloromethylbenzoic acids, and nitrobenzene were determined by the methods described above.

Decomposition of Benzoyl Peroxide in Nitrogen Dioxide.—(i) *In the absence of added substances.* Benzoyl peroxide was allowed to decompose in nitrogen dioxide alone for 72 h at 80°. After the reaction, nitrogen oxides were removed from the blue mixtures by carefully warming the opened Carius tubes until no more brown fumes were evolved. Anhydrous ether was added, and the contents of the tubes were washed out and the solvent was distilled off under reduced pressure. Pure nitrobenzene distilled out at 110° and 14 mmHg followed by *m*-dinitrobenzene (b.p. 165° at 14 mmHg, m.p. and mixed m.p. 90°). A less volatile fraction sublimed at 90° and 0.5 mmHg, and the sublimate, on crystallisation from water gave *m*-nitrobenzoic acid (m.p. and mixed m.p. 140°). The residue from the sublimation, on crystallisation from

¹⁵ C. G. Overberger and A. J. Rosenthal, *J. Amer. Chem. Soc.*, 1960, **82**, 117.

¹⁶ J. Colonge and P. Brison, *Compt. rend.*, 1960, **251**, 2723.

¹⁷ N. Kornblum, R. A. Smiley, R. K. Blackwood, and D. C. Iffland, *J. Amer. Chem. Soc.*, 1955, **77**, 6269.

¹⁸ M. Konowaloff, *Chem. Zentr.*, 1899, **70**, I, 1238.

¹³ Hwang Shu, *Acta Chim. Sinica*, 1959, **25**, 171.

¹⁴ J. I. G. Cadogan, *J. Chem. Soc.*, 1962, 4257.

ethanol, gave 4-nitrobiphenyl (m.p. and mixed m.p. 114°). The i.r. spectrum of the total residue indicated that 2- and 3-nitrobiphenyls were also present.

The i.r. spectrum of the acid fraction was very similar to that of *m*-nitrobenzoic acid, but with a few extra peaks, which were due to benzoic and 3,5-dinitrobenzoic acids. By comparison with i.r. spectra of various synthetic mixtures, it was estimated that about 10% of the mixture was benzoic acid and about 10% was 3,5-dinitrobenzoic acid.

(ii) *In the presence of p-xylene.* Benzoyl peroxide was allowed to decompose in nitrogen dioxide in the presence of a small amount of *p*-xylene for 72 h at 80°. After the reaction, nitrogen oxides were removed and the residue was dissolved in *p*-xylene. This solution was then extracted for acids as previously described. The i.r. spectrum of the solid isolated was very similar to that of the acidic mixture obtained in the absence of *p*-xylene.

Solvents were distilled from the organic solution and the distillate was redistilled and analysed for benzene by g.l.c.

at 120°. The organic liquors were distilled under reduced pressure and the products were shown by chromatography at 150 and 200° to be nitrobenzene, *p*-tolyl nitromethane, 2,5-dimethylnitrobenzene, and biphenyl. 4,4'-Dimethylbibenzyl was not detected.

(iii) *Decomposition of aroyl peroxides in carbon tetrachloride in the presence of nitrogen dioxide.* The reactions were conducted in sealed tubes and worked up as described above. Acidic products, after crystallisation from water, were characterised by m.p. and mixed m.p. with authentic specimens. Solid organic products were characterised by comparison of their i.r. spectra and refractive indices with those of authentic specimens. Organic products were distilled and estimated by g.l.c.

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