450. *Union of Aryl Nuclei. Part VII. Reactions with Acyl Peroxides.*

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Reactions have been carried out between a number of acyl peroxides and (*a*) benzene and (*b*) pyridine. In the benzene series these reactions frequently provide good preparative methods for diaryl derivatives, but in the pyridine series the reaction is not one of general applicability, probably owing to the formation of pyridine oxide. Reactions are also described between benzoyl peroxide and (*a*) quinoline and (*b*) 2 : 2 : 4-trimethylpentane, between phthalic acid peroxide and nitrobenzene, and between *m*-nitrobenzoyl peroxide and molten benzoic acid. It is shown that when 1-methyl hydrogen 4-nitrophthalate is converted into a peroxide, by formation of the acid chloride and treatment with hydrogen peroxide, a mixture of two isomerides is obtained. The reactions of the peroxides conform to the free-radical mechanism put forward in an earlier communication (*J.*, 1934, 1966).

Lippmann (*Monatsh.*, 1886, **7**, 521) obtained diphenyl by heating benzoyl peroxide in benzene at 140°, but since he also obtained the same hydrocarbon by thermal decomposition of the peroxide admixed with sand there was no evidence that the benzene had participated in the reaction. The formation of diphenyl by prolonged boiling of benzoyl peroxide in benzene was also observed by Orndorff and White (*Amer. Chem. J.*, 1893, **15**, 347). The first clear indication of the course followed in these reactions came from the work of Gelissen and Hermans (*Ber.*, 1925, **58**, 285), who showed that *p*-chlorobenzoyl and *m*-nitrobenzoyl peroxide react with benzene to give only 4-chlorodiphenyl and 3-nitrodiphenyl respectively, and that 4 : 4′-dichlorodiphenyl and 3 : 3′-dinitrodiphenyl were not formed. In subsequent papers these authors were able to substantiate this view beyond all doubt (*Ber.*, 1925, **58**, 476, 479, 764, 984, 2396; 1926, **59**, 662; etc.). From the reaction between benzoyl peroxide and benzene these workers isolated not only benzoic acid, diphenyl, and phenyl benzoate, but also smaller quantities of *p*-terphenyl, quaterphenyl, esters of higher phenols, and resinous products. Further, when benzoyl peroxide was used with toluene or diphenyl, the resulting products were 2- and 4-methyldiphenyl or *p*-terphenyl respectively. These authors interpreted these reactions as follows :

$$(\mathrm{R{\cdot}CO_2})_2 + \mathrm{R'H} \xrightarrow{\text{main reaction}} \mathrm{RR'} + \mathrm{R{\cdot}CO_2H} + \mathrm{CO_2} \quad . \quad . \quad . \quad . \quad . \quad (\mathrm{A})$$

$$(\mathrm{R{\cdot}CO_2})_2 + \mathrm{R'H} \xrightarrow[\text{side reaction}]{} \mathrm{RH} + \mathrm{R{\cdot}CO_2R'} + \mathrm{CO_2} \quad . \quad . \quad . \quad . \quad . \quad (\mathrm{B})$$

Products such as terphenyl and quaterphenyl resulted from the further action of the peroxide on the hydrocarbons initially formed. Overhoff and Tilman (*Rec. Trav. chim.*, 1929, **48**, 993) investigated the reaction of benzoyl peroxide with pyridine and recorded the isolation of 2- and 4-phenylpyridine. The first attempt to apply the reaction to suitable aromatic compounds with the object of investigating the directive influence of substituent groups or atoms in this reaction was made by Hey (*J.*, 1934, 1966), and the results obtained clearly showed that the reaction was not governed by the normal laws for cationoid or anionoid substitution reactions.

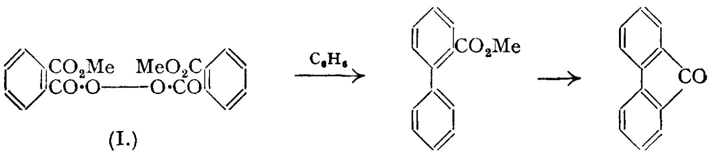
The mechanism of the reaction between acyl peroxides and various organic liquids attracted the attention of Boeseken, Gelissen, and Hermans, but these authors rejected the possibility of the intervention of free radicals (*Annalen*, 1935, **519**, 133; *Rec. Trav. chim.*, 1935, **54**, 760), although they had recognised the marked similarity between certain reactions of the diazo-compounds and the reactions of acyl peroxides (*Ber.*, 1925, **58**, 984). Wieland and Razubaiev (*Annalen*, 1930, **480**, 157) and Wieland, Schapiro, and Metzger (*Annalen*, 1934, **513**, 93) also refused to accept a free radical mechanism mainly on the grounds that in the thermal decomposition of a mixed peroxide, R·CO·O·O·COR′, the product contained only the compound RR′, and RR and R′R′ were absent. These workers maintained that if free radicals were involved all three products would be formed. On the other hand, in the thermal decomposition of the peroxide the two dissimilar radicals R and R′ would probably be produced in close proximity, and being radicals of short life would tend to react together at once according to the Frank–Rabinowitch principle. The view that these reactions involve the participation of free radicals was first put forward by Hey (*loc. cit.*) and later elaborated by Hey and Waters (*Chem. Reviews*, 1937, **21**, 169). The general scheme for the reaction with a compound R′H may be represented as follows :

1. $(\mathrm{R{\cdot}CO_2})_2 \longrightarrow \mathrm{R{\cdot}} + \mathrm{R{\cdot}CO_2{\cdot}} + \mathrm{CO_2}$
2. $\mathrm{R{\cdot}} + \mathrm{R'H} \longrightarrow \mathrm{RR'} + \mathrm{H{\cdot}}$
3. $\mathrm{R{\cdot}} + \mathrm{R'H} \longrightarrow \mathrm{RH} + \mathrm{R'{\cdot}}$
4. $\mathrm{R{\cdot}CO_2{\cdot}} + \mathrm{R'H} \longrightarrow \mathrm{R{\cdot}CO_2R'} + \mathrm{H{\cdot}}$
5. $\mathrm{R{\cdot}CO_2{\cdot}} + \mathrm{R'H} \longrightarrow \mathrm{R{\cdot}CO_2H} + \mathrm{R'{\cdot}}$
6. $\mathrm{R{\cdot}CO_2{\cdot}} + \mathrm{H{\cdot}} \longrightarrow \mathrm{R{\cdot}CO_2H}$
7. $\mathrm{R{\cdot}CO_2{\cdot}} + \mathrm{R'{\cdot}} \longrightarrow \mathrm{R{\cdot}CO_2R'}$
8. $\mathrm{R{\cdot}} + \mathrm{H{\cdot}} \longrightarrow \mathrm{RH}$
9. $\mathrm{R{\cdot}} + \mathrm{R'{\cdot}} \longrightarrow \mathrm{RR'}$

These reactions are accompanied by further reactions between the free radicals and atoms with the products formed in the primary reactions.

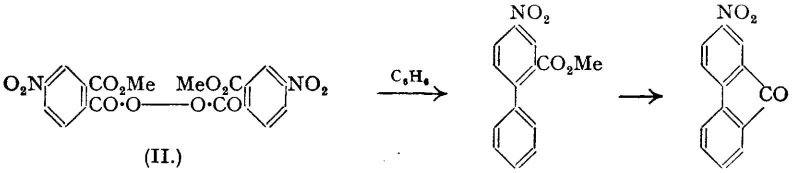
The present communication, which is based on work completed in 1941, the records of which were partly destroyed by enemy action, is mainly directed to the reactions of a number of acyl peroxides with benzene and with pyridine, which were found to follow in general the reaction scheme outlined above. The peroxides used were *o-nitrobenzoyl*, *m*-nitrobenzoyl, *p*-nitrobenzoyl, *p*-chlorobenzoyl, *p*-methoxybenzoyl, 1-naphthoyl, 2-naphthoyl, cinnamoyl, phenylacetyl, 2 : 2′-dicarboxybenzoyl, *2 : 2′-dicarbomethoxybenzoyl*, *5-nitro-2 : 2′-dicarbomethoxybenzoyl*, and phthaloyl. The peroxides were prepared from the acid chlorides and hydrogen peroxide; *m*-nitrobenzoyl peroxide was also prepared by the nitration of benzoyl peroxide.

In reactions with boiling benzene the three nitrobenzoyl peroxides gave 2-nitrodiphenyl, 3-nitrodiphenyl, and 4-nitrodiphenyl in yields of 60, 80, and 53% respectively, and *p*-methoxybenzoyl peroxide gave 4-methoxydiphenyl in 23% yield. 2-Naphthoyl peroxide gave 2-phenylnaphthalene in 19% yield. The 2 : 2′-dicarbomethoxybenzoyl peroxide (I) reacted readily with boiling benzene to give in 55% yield methyl diphenyl-2-carboxylate, which was identified by hydrolysis and ring closure to give fluorenone:



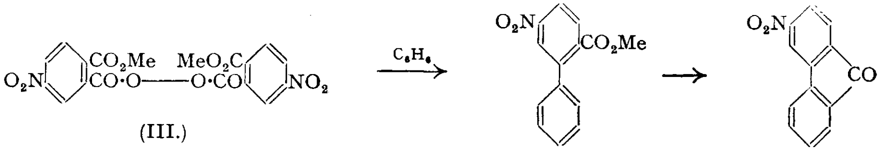
(I.)

The corresponding reaction with the 5-nitro-2 : 2′-dicarbomethoxybenzoyl peroxide was less straightforward. The peroxide obtained in the normal manner from 1-methyl hydrogen 4-nitrophthalate, prepared as described by Wegscheider and Lipschitz (*Monatsh.*, 1900, **21**, 802), proved to be a mixture of two isomerides. The less soluble peroxide of higher melting point underwent reaction with boiling benzene to give 2-methyl hydrogen 4-nitrophthalate and the hitherto unknown *methyl 4-nitrodiphenyl-2-carboxylate*, identified by hydrolysis and ring closure to give 2-nitrofluorenone. The peroxide of higher melting point must therefore have the constitution (II):



(II.)

The more soluble peroxide of lower melting point could not be obtained entirely free from the isomeric peroxide, and the reaction with benzene gave a mixture of nitrodiphenylcarboxylic esters, which on hydrolysis and ring closure gave a mixture of 2- and 3-nitrofluorenone. The more soluble peroxide must therefore be regarded as having the constitution (III):



(III.)

At the time when this work was completed it was not clear how the peroxide (II) could be formed from 1-methyl hydrogen 4-nitrophthalate, and if the starting material was homogeneous, as claimed by Wegscheider and Lipschitz (*loc. cit.*), it had to be assumed that some rearrangement must have taken place either in the formation of the acid chloride or in the subsequent reactions. In a recent communication (*J. Amer. Chem. Soc.*, 1947, **69**, 1548) Cason has shown that in the conversion of each of the two isomeric half esters of an unsymmetrically substituted dibasic acid into the ester acid chlorides by treatment with thionyl chloride a mixture of the two isomeric acid chlorides is obtained. Ställberg-Stenhagen (*J. Amer. Chem. Soc.*, 1947, **69**, 2568) has studied the conditions under which this type of rearrangement takes place, and considers it likely that it may be due to the intermediate formation of the anhydrides. In the light of these observations the formation of the two isomeric peroxides from 1-methyl hydrogen 4-nitrophthalate is not unexpected, since the action of thionyl chloride would probably result in the formation of the two isomeric acid chlorides.

No pure products were isolated from the reaction of 1-naphthoyl peroxide or of phthaloyl peroxide with benzene. On the other hand, 2 : 2′-dicarboxybenzoyl peroxide proved to be remarkably stable, and after being boiled with benzene for 120 hours most of it was recovered unchanged. In view of this stability nitrobenzene was chosen as a reactant of higher boiling point. With this solvent reaction took place readily at 140°, and a mixture of 2- and 4-nitrodiphenyl-2′-carboxylic acid was isolated in good yield. The very reactive phenylacetyl peroxide decomposed in benzene solution at 30°, and only dibenzyl, formed by dimerisation of the benzyl radicals, was isolated from the product. This result is in full agreement with that recorded by Kharasch, Kane, and Brown (*J. Amer. Chem. Soc.*, 1942, **64**, 1621), who isolated only dibenzyl and phenylacetic acid from the decomposition of phenylacetyl peroxide in carbon tetrachloride solution. From the reaction between cinnamoyl peroxide and benzene, stilbene was obtained in small yield together with much polymerised material.

The readiness with which peroxides react with aromatic compounds, including nitrobenzene, suggested that in some reactions, especially those carried out at higher temperatures, a secondary reaction might ensue between the peroxide and the aromatic acid formed as a normal product of the main reaction (A). In order to test the extent of this possibility a reaction was carried out between *m*-nitrobenzoyl peroxide and molten benzoic acid at 125°. The acidic products were fractionally precipitated with alkali, and from the least soluble fractions a mixture of nitrodiphenylcarboxylic acids was obtained. From this mixture the hitherto unknown 3-*nitrodiphenyl*-3′- and -4′-*carboxylic acids* were isolated. Since neither product could be ring-closed to yield a nitrofluorenone, the only alternative constitution, namely that of 3-nitrodiphenyl-2′-carboxylic acid, is eliminated. In the absence of evidence to the contrary the acid of higher melting point is regarded as having the carboxyl group in the 4′-position. Substitution at the *meta* and *para* positions with respect to the carboxyl group is in agreement with results previously obtained in similar reactions with ethyl benzoate (Hey, *J.*, 1934, 1968). A small quantity of nitrobenzene was also isolated (reaction B), together with some 3 : 3′-dinitrodiphenyl. The latter product is possibly due to the localised explosive decompositions in the body of the liquid, which were a characteristic feature of this reaction.

The reaction between benzoyl peroxide and pyridine was investigated by Overhoff and Tilman (*loc. cit.*), who reported the formation of 2- and 4-phenylpyridine only. In view of the close correspondence between the reactions of benzoyl peroxide and those of nitrosoacetanilide and benzene diazohydroxide, which have already been shown to give rise to substitution at all three positions in the pyridine nucleus, it was considered highly probable that in the case of benzoyl peroxide also all three isomerides were formed. A repetition of this reaction gave a mixture of phenylpyridines in 35% yield from which the picrates of 2-, 3-, and 4-phenylpyridine were isolated. The comparatively low yield of phenylpyridines in this reaction is accompanied by a yield of benzoic acid corresponding to 1·2 mols. per mol. of peroxide used. This indicates the occurrence of a secondary reaction of a type which does not arise in the reactions with benzene, and may be due to the formation of pyridine oxide (cf. Meisenheimer, *Ber.*, 1926, **59**, 1848). This tendency was much more marked in later experiments with substituted benzoyl peroxides. For example, when *o*-nitrobenzoyl peroxide was boiled with pyridine, the acidic fraction consisting of *o*-nitrobenzoic acid accounted for 87% of the peroxide used, and no nitrophenylpyridines were isolated. Similar results were obtained when *m*- and *p*-nitrobenzoyl peroxides were used. On the other hand, both *p*-chlorobenzoyl peroxide and *p*-methoxybenzoyl peroxide reacted readily with pyridine at 95°, and gave mixtures of *p*-chlorophenylpyridines and *p*-methoxyphenylpyridines respectively, both in 27% yield. From these mixtures 2- and 4-*p*-chlorophenylpyridine and 2- and 4-*p*-methoxyphenylpyridine were isolated by fractional crystallisation of the picrates. The reactions of 1-naphthoyl peroxide and of 2-naphthoyl peroxide with pyridine gave mixtures of 1-naphthylpyridines and 2-naphthylpyridines in small yield. In the former case only one 1-naphthylpyridine was isolated in pure form as the picrate: in the latter case fractionation of the picrates of the 2-naphthylpyridines gave the three isomeric 2-naphthylpyridine picrates, identical with the three products previously obtained by Elks and Hey (*J.*, 1943, 444) from the reaction between 1-2′-naphthyl-3 : 3-dimethyltriazen and pyridine. The major isomeride in the mixture was also prepared from the reactions between diazotised β-naphthylamine and pyridine, and between nitrosoaceto-β-naphthalide and pyridine. In both reactions with the naphthoyl peroxides a small quantity of naphthalene was also isolated (reaction B). Reactions with pyridine were also carried out with 2 : 2′-dicarbomethoxybenzoyl peroxide and with cinnamoyl peroxide. In the former case the methyl esters of a mixture of pyridylbenzoic acids were obtained from which two picrates were formed; in the latter case a small quantity of α-stilbazole was isolated from the product.

A reaction between benzoyl peroxide and quinoline at 105° gave a mixture of phenylquinolines, which was treated with picric acid and the resulting complex mixture of picrates submitted to fractional crystallisation. 4-Phenylquinoline picrate and 5-phenylquinoline picrate were isolated and identified, and indications were obtained of the presence of three other isomerides, but none of these was obtained in a form sufficiently pure for unambiguous identification. For reference purposes the seven isomeric phenylquinolines were synthesised. Of these 5- and 7-phenylquinoline, which had not been reported at that time, were prepared from 3-aminodiphenyl by the Skraup reaction. The mixture of 5- and 7-phenylquinolines thus obtained was separated by fractional crystallisation of the picrates. The more soluble isomeride was identified as the picrate of 5-phenylquinoline by mixed melting point with an authentic specimen prepared at about the same time from 1-5′-quinolyl-3 : 3-dimethyltriazen and benzene (Elks and Hey, *loc. cit.*). The second and less soluble *picrate* must therefore be that of the hitherto unknown 7-phenylquinoline.

Some preliminary experiments were also carried out on reactions between acyl peroxides and saturated aliphatic compounds of various types. It was not possible to pursue this work further in 1941, but reference may be made to the reaction of benzoyl peroxide with 2 : 2 : 4-trimethylpentane. This differed from all the preceding reactions with aromatic and heterocyclic compounds in that the product contained a relatively small yield of benzoic acid and a proportionately high yield of benzene, *i.e.*, predominance of reaction B. Some diphenyl and diphenyl-4-carboxylic acid were also isolated, these being formed presumably as the result of secondary reactions. The difference thus revealed in the reactions of benzoyl peroxide with aromatic and aliphatic compounds is in complete accord with the established properties of the phenyl radical (Hey and Waters, *loc. cit.*).

EXPERIMENTAL.

Preparation of Peroxides.—Unless otherwise stated the peroxides were prepared from a solution of the acid chloride (2 mols.) in chloroform by shaking below 4° with aqueous 25% sodium hydroxide (2 mols.) and 20-vol. hydrogen peroxide (1 mol.) according to a modification of the procedure used for the preparation of *p*-chlorobenzoyl peroxide by Gelissen and Hermans (*Ber.*, 1925, **58**, 292). The peroxides were precipitated from the chloroform solution by the addition of methyl alcohol, and many had to be purified by a repetition of this process since the peroxides do not always lend themselves to crystallisation from hot or warm solvents owing to their instability. Because of the explosive nature of the peroxides, analyses for carbon and hydrogen by combustion were generally discarded in favour of the iodometric method used by Boeseken and Gaster (*Rec. Trav. chim.*, 1930, **49**, 102). Similar difficulties with combustion analyses have been previously recorded by Milas and Panagiotakos (*J. Amer. Chem. Soc.*, 1940, **62**, 1878). The general method of preparation is illustrated by the preparation of *o*-nitrobenzoyl peroxide.

o-*Nitrobenzoyl Peroxide.*—A solution of *o*-nitrobenzoyl chloride (100 g.) in chloroform (100 c.c.) was shaken at 2° with 20-vol. hydrogen peroxide (200 c.c.) and 25% aqueous sodium hydroxide (65 c.c.). The crystalline peroxide which separated was filtered off and addition of methyl alcohol to the chloroform filtrate precipitated a further quantity. The total product (61 g.) was washed well with methyl alcohol and dried over sulphuric acid. Crystallisation from chloroform gave o-*nitrobenzoyl peroxide* in colourless plates, m. p. 147° (explosive decomp.) (Found: C, 51·4; H, 2·3. $C_{14}H_8O_8N_2$ requires C, 50·6; H, 2·4%).

The following peroxides were similarly prepared: *m*-nitrobenzoyl (m. p. 134°), *p*-nitrobenzoyl (m. p. 157°), *p*-chlorobenzoyl (m. p. 138°), *p*-methoxybenzoyl (m. p. 127° from alcohol; purity 97·8% by titration), 1-naphthoyl * (m. p. 98°), 2-naphthoyl * (m. p. 140° from chloroform) (Found: C, 77·1; H, 4·1. Calc. for $C_{22}H_{14}O_4$: C, 77·2; H, 4·1%), 2 : 2′-*dicarbomethoxybenzoyl* (Found: C, 60·4; H, 4·1. $C_{18}H_{14}O_8$ requires C, 60·3; H, 3·9%. Purity 99·8% by titration), cinnamoyl peroxide (m. p. 130°), and phenylacetyl. *m*-Nitrobenzoyl peroxide was also prepared by the nitration of benzoyl peroxide as described by Gelissen and Hermans (*Ber.*, 1925, **58**, 293).

2 : 2′-Dicarboxybenzoyl peroxide was prepared from phthalic anhydride by the method of Baeyer and Villiger (*Ber.*, 1901, **34**, 764). Phthaloyl peroxide was prepared from *s*-*o*-phthaloyl chloride (5 g.), prepared by the method of Ott (*Org. Synth.*, 1931, **11**, 88), which was added with vigorous stirring to a solution of sodium phosphate (10 g.) in 20-vol. hydrogen peroxide (40 c.c.). After ½ hour, 10% aqueous sodium hydroxide (10 c.c.) was added and stirring was continued for 2½ hours. The white precipitate was collected, washed with water, and dried (1 g.; yield 24%). The product decomposed without melting at about 125°. In another preparation a solution of phthaloyl chloride (15 g.) in chloroform (15 c.c.) was shaken with a mixture of 20 vol. hydrogen peroxide (48 c.c.) and 25% aqueous sodium hydroxide (24 c.c.). The precipitated peroxide was collected at the pump, washed with water, and

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* Since this work was completed both 1-naphthoyl peroxide and 2-naphthoyl peroxide have been described by Kharasch and Dannley (*J. Org. Chem.*, 1945, **10**, 406), who reported m. p.s of 98·2° and 138° respectively.

dried (4·3 g.; yield 33%). The product decomposed at 125° (cf. von Pechmann and Vanino, *Ber.*, 1894, **27**, 1512).

Phenylacetyl peroxide was prepared by shaking a solution of phenylacetyl chloride (5 g.) in light petroleum (30 c.c.) with a cold mixture of 20-vol. hydrogen peroxide (10 c.c.) and 25% sodium hydroxide (5 c.c.). The peroxide separated in colourless flakes, which were filtered off and washed successively with ice-cold water, methyl alcohol (10 c.c.), and light petroleum (30 c.c.). The dry crystalline peroxide (1 g.) exploded on contact with a spatula. Vanino and Thiele (*Ber.*, 1896, **29**, 1727) recorded m. p. 41° (decomp.) for phenylacetyl peroxide.

Reactions with Benzene.—(i) *o*-Nitrobenzoyl peroxide (5 g.) was added to benzene (45 c.c.) and the mixture boiled under reflux for 18 hours. After removal of excess of benzene by distillation, the residue was heated with 25% aqueous sodium hydroxide (40 c.c.) for 4 hours at 100°. The mixture was extracted with benzene, and on distillation 2-nitrodiphenyl (1·8 g.) was obtained, m. p. and mixed m. p. with an authentic specimen, after crystallisation from dilute alcohol, 37°.

(ii) *m*-Nitrobenzoyl peroxide (25 g.) was refluxed with benzene (100 c.c.) for 24 hours and the product was worked up as described above for the *ortho* compound. After removal of excess of benzene from the extract, a residue of straw-coloured crystals (12 g.) was obtained, which after recrystallisation from alcohol melted, both alone and in admixture with 3-nitrodiphenyl, at 61°.

(iii) *p*-Nitrobenzoyl peroxide (5 g.) was refluxed with benzene (35 c.c.) for 48 hours and the product worked up as for the *ortho* compound. After treatment with alkali the crude 4-nitrodiphenyl was filtered off from the diluted mixture. Crystallisation from alcohol with charcoal gave 4-nitrodiphenyl (1·6 g.), m. p. and mixed m. p. with an authentic specimen, 112°.

(iv) *p*-Methoxybenzoyl peroxide (10 g.) was boiled under reflux with benzene (100 c.c.) for 16 hours. After removal of excess of benzene, the residue was boiled with 10% aqueous-alcoholic sodium hydroxide for 2 hours. The alcohol was removed by distillation and the residue diluted and filtered. The residual solid was distilled in a vacuum and the product (1·4 g.), after crystallisation from alcohol, gave 4-methoxydiphenyl, m. p. 89°.

(v) 2-Naphthoyl peroxide (10 g.) was boiled under reflux with benzene (100 c.c.) for 24 hours. Excess of benzene was removed, and the product was boiled with 10% aqueous-alcoholic sodium hydroxide for 3 hours. The alcohol was distilled off and the residue diluted and filtered. The precipitated solid was collected, washed with hot water, and dried (3·5 g.). The product, purified by distillation with steam followed by crystallisation from alcohol, was 2-phenylnaphthalene, m. p. and mixed m. p. with an authentic specimen, 101°.

(vi) 2 : 2′-Dicarboxybenzoyl peroxide (17 g.) was boiled under reflux with benzene (100 c.c.) for 120 hours; at the end of this time much undissolved material remained which was filtered off (12 g.) and found to consist of substantially pure unreacted peroxide. Concentration of the filtrate deposited a crystalline solid (2 g.), which was recrystallised from benzene. On sublimation, phthalic anhydride was obtained. No other product was isolated. In view of its stability at the temperature of boiling benzene the peroxide (18 g.) was added to nitrobenzene (80 c.c.) stirred at 140°. Carbon dioxide was evolved, and the reaction was completed by heating at 160° for ½ hour. After removal of excess of nitrobenzene under reduced pressure, the residue was dissolved in benzene and extracted with aqueous sodium hydroxide (5%). Acidification followed by extraction with ether gave a mixture of acids (17·5 g.) which was refluxed with chloroform (150 c.c.), and the insoluble phthalic acid (7·6 g.) filtered off. Concentration of the chloroform solution to 30 c.c. resulted in the separation of 4-nitrodiphenyl-2′-carboxylic acid (2·3 g.), m. p. and mixed m. p. 224—226° (cf. Grieve and Hey, *J.*, 1932, 1891, footnote). Evaporation of the filtrate left a viscous solid, from which 2-nitrodiphenyl-2′-carboxylic acid (1·7 g.), m. p. and mixed m. p. 165—166°, was isolated by crystallisation from benzene (cf. Bell, *J.*, 1934, 838).

(vii) 2 : 2′-Dicarbomethoxybenzoyl peroxide (15 g.) was boiled under reflux with benzene (100 c.c.) for 24 hours. No unchanged peroxide could be detected at the end of this period. The solution was extracted with 10% aqueous sodium carbonate (3 × 50 c.c.), and the benzene was then evaporated and the residue distilled. Methyl diphenyl-2-carboxylate (4·4 g.) was collected at 300—310°. A portion of this product (2 g.) was hydrolysed with 10% alcoholic potassium hydroxide (25 c.c.) to give diphenyl-2-carboxylic acid, m. p. and mixed m. p. 112° after crystallisation from dilute alcohol. A portion of the acid (0·5 g.), dissolved in concentrated sulphuric acid (5 c.c.), gave a deep red coloration and, on dilution and addition of alkali, fluorenone (0·4 g.) was precipitated, m. p. and mixed m. p. 83° after crystallisation from alcohol.

(viii) The peroxide derived from 1-methyl hydrogen 4-nitrophthalate was obtained as follows: finely powdered 4-nitrophthalic anhydride was boiled under reflux for ½ hour with methyl alcohol (cf. Wegscheider and Lipschitz, *loc. cit.*), and after removal of the excess of methyl alcohol the residual syrup crystallised. The resulting 1-methyl ester of 4-nitrophthalic acid was converted into the acid chloride by reaction with thionyl chloride at 60°. The crude acid chloride (55 g.) in the form of a viscous syrup was dissolved in chloroform (50 c.c.) and shaken with a mixture of 20-vol. hydrogen peroxide (80 c.c.) and 25% aqueous sodium hydroxide (40 c.c.). The solid which separated together with the chloroform layer was treated with methyl alcohol, and the oil which separated solidified overnight at 0° (25·4 g.; yield 50%). The product was dissolved in hot acetone (200 c.c.), and addition of cold methyl alcohol (350 c.c.) precipitated a pale yellow solid (A) (10 g.), m. p. 143°. Water was added to the filtrate until it became opalescent, and on standing colourless prisms separated (B) (12·5 g.), m. p. 110°. These two products were treated separately as follows.

Peroxide (A). The *peroxide* was further purified by reprecipitation several times from acetone by addition of methyl alcohol. The final product had m. p. 153° (Found: C, 48·4; H, 2·85. $C_{18}H_{12}O_{12}N_2$ requires C, 48·2; H, 2·7%. Purity by titration 100·1%). The peroxide (7·5 g.) was boiled under reflux with benzene (100 c.c.) for 48 hours, at the end of which time no unreacted peroxide could be detected. On cooling, straw-coloured needles separated (2 g.), m. p. 139°, which after recrystallisation from benzene was raised to 143°, which agrees with the recorded m. p. for 2-methyl hydrogen 4-nitrophthalate (cf. Wegscheider and Kuŝy von Dúbrav, *Monatsh.*, 1903, **24**, 825). The filtrate was extracted with 10% aqueous sodium carbonate, and the aqueous layer acidified and extracted with ether.

Evaporation of the ether gave a further quantity of crude 2-methyl hydrogen 4-nitrophthalate (1·8 g.), m. p. 137°. The benzene solution was evaporated and the residue distilled in high vacuum. A fraction (2·7 g.) collected at 70—80°/0·00001 mm. solidified on cooling. *Methyl* 4-*nitrodiphenyl*-2-*carboxylate* separated in needles m. p. 70° after crystallisation from dilute alcohol (Found: C, 65·6; H, 4·5. $C_{14}H_{11}O_4N$ requires C, 65·4; H, 4·3%). A portion of this ester (0·6 g.) was hydrolysed by heating with 10% alcoholic potassium hydroxide (10 c.c.). The solution was diluted to 100 c.c. with water and acidified. The precipitated 4-nitrodiphenyl-2-carboxylic acid (0·5 g., m. p. 170°) separated from dilute alcohol in needles, m. p. 172° (cf. Heilbron, Hey, and Wilkinson, *J.*, 1938, 115). A portion of the purified acid (0·4 g.) was dissolved in concentrated sulphuric acid (5 c.c.) and the solution poured into cold water (20 c.c.) and made slightly alkaline. The precipitated 2-nitrofluorenone crystallised from alcohol in golden needles, m. p. and mixed m. p. 218°.

Peroxide (*B*). The *peroxide* (8·1 g.), after purification by precipitation (Found: C, 49·1; H, 2·8. $C_{18}H_{12}O_{12}N_2$ requires C, 48·2; H, 2·7%), was boiled under reflux with benzene (100 c.c.) and the product worked up as described above for peroxide (A). The acid (4·5 g.) liberated on acidification of the carbonate extracts proved to be 4-nitrophthalic acid, m. p. and mixed m. p. 163°. The viscous residue obtained on evaporation of the benzene was hydrolysed with alcoholic potassium hydroxide, and after dilution and acidification a crude acid (2 g.) was obtained which was distilled at 200—220°/0·00001 mm. The resulting orange-coloured crystalline product (0·3 g.), m. p. 160—172° after crystallisation from dilute acetic acid, was treated with concentrated sulphuric acid to effect ring closure. The product was poured into water, and the mixture made slightly alkaline and filtered. Crystallisation from alcohol gave yellow-brown plates and golden needles (m. p. *ca.* 190°). Recrystallisation from glacial acetic acid gave a small quantity of 2-nitrofluorenone m. p. 214°. A second product, m. p. 220—225°, regarded as 3-nitrofluorenone from melting point, colour, and crystalline form, could not be obtained pure.

(ix) Phenylacetyl peroxide was prepared in benzene solution by shaking a solution of phenylacetyl chloride (10 g.) in benzene (50 c.c.) with 20-vol. hydrogen peroxide (20 c.c.) and aqueous 25% sodium hydroxide (10 c.c.) at 10° for 20 minutes. The benzene layer was separated, dried over sodium sulphate at 10°, and after decantation allowed to warm up to 30°. When evolution of gas had ceased, excess of benzene was removed by distillation and the residue was boiled under reflux with 10% aqueous alcoholic sodium hydroxide (30 c.c.). The alcohol was distilled off, and the solution diluted to 100 c.c. and extracted with ether. Distillation of the extract gave a fraction, b. p. 150—180°/20 mm., which partially solidified on cooling. Crystallisation of the solid from dilute alcohol gave dibenzyl (1·2 g.), m. p. and mixed m. p. 51°.

(x) Cinnamoyl peroxide (20 g.) was boiled under reflux with benzene (500 c.c.) for 24 hours. After removal of most of the excess of benzene the residue was boiled under reflux with 25% aqueous alcoholic sodium hydroxide for 16 hours. The mixture was extracted with benzene; removal of the solvent from the dried extract left a residue which was distilled under reduced pressure. A small quantity of stilbene (0·6 g.) was collected at 160°/20 mm. which solidified on cooling, and had m. p. 124° after crystallisation from alcohol.

Reactions with Pyridine.—(i) Benzoyl peroxide (60 g.) was added in small quantities to pyridine (200 c.c.) stirred at 100°. Considerable evolution of gas ensued, and the rate of addition was adjusted so that no increase in temperature was caused. When the addition was complete, excess of pyridine was removed by distillation and the residue was boiled under reflux for 5 hours with a mixture (250 c.c.) of equal parts by volume of concentrated hydrochloric acid and water. The mixture was subsequently made alkaline with 30% aqueous sodium hydroxide and extracted thrice with benzene (500 c.c.). After removal of benzene the residue was distilled under reduced pressure, and two fractions were collected, b. p. 156—186° (13·5 g.), and b. p. 200—210° (0·6 g.). The two fractions were combined, dissolved in hot alcohol, and added to a hot solution of picric acid (30 g.) in alcohol (390 c.c.). The mixture was boiled under reflux for ½ hour and filtered hot (filtrate, A). The residue (12 g.) was fractionally crystallised from alcohol, and yielded bright golden needles of 4-phenylpyridine picrate (3·8 g.), m. p. and mixed m. p. 196°. The alcoholic filtrate (A) was cooled, and the crystalline mass which separated (47 g.) was fractionally crystallised from alcohol. Repeated crystallisation gave specimens of pure 3-phenylpyridine picrate in fibrous yellow needles, m. p. and mixed m. p. 163°, and 2-phenylpyridine picrate in orange-yellow prisms, m. p. and mixed m. p. 176°. The main bulk of the product from the filtrate consisted of impure 2-phenylpyridine picrate. In another experiment the peroxide (60 g.) was added to pyridine (200 c.c.) as above, and after removal of excess of pyridine at 100° under reduced pressure, the residue was dissolved in benzene (750 c.c.) and extracted first with 5% aqueous sodium hydroxide and subsequently with 15% hydrochloric acid. Acidification of the alkaline extract deposited benzoic acid (36 g.). Basification of the acid extract, followed by extraction with benzene and evaporation, gave a mixture of crude phenylpyridines (19 g.), from which the three isomerides were isolated in the form of their picrates. The original benzene extract left a tarry residue (5·4 g.) on evaporation.

(ii) *o*-Nitrobenzoyl peroxide (20 g.) was added to pyridine (100 c.c.) stirred at 110°. A vigorous reaction ensued. After removal of excess of pyridine by distillation the residue was dissolved in benzene and extracted successively with 5% aqueous sodium hydroxide and with 15% hydrochloric acid. The alkaline washings gave *o*-nitrobenzoic acid (17·3 g.), m. p. and mixed m. p. 146°. The basic fraction consisted of a small tarry residue (1·7 g.), whereas the neutral fraction gave a small quantity (0·5 g.) of an oil with the odour of nitrobenzene. In similar reactions with *m*-nitrobenzoyl peroxide (20 g.) and with *p*-nitrobenzoyl peroxide (20 g.), the main products were *m*-nitrobenzoic acid (18 g.) and *p*-nitrobenzoic acid (11 g.) respectively.

(iii) *p*-Chlorobenzoyl peroxide (20 g.) was added to pyridine (80 c.c.) stirred at 95°. When evolution of gas had ceased the mixture was boiled under reflux for 2 hours and excess of pyridine was removed under reduced pressure. The residue was boiled with 25% aqueous sodium hydroxide (100 c.c.) and extracted with benzene. After removal of solvent, the residue (6 g.) was distilled under reduced pressure and the main fraction (3·4 g.), collected at 170—175°/20 mm., was dissolved in hot alcohol and treated with a hot solution of picric acid (8 g.) in alcohol (50 c.c.). Fractionation of the resulting picrates from acetone gave 4-*p*-chlorophenylpyridine picrate, m. p. and mixed m. p. 228—229°, and 2-*p*-chlorophenylpyridine picrate, m. p. and mixed m. p. 167—168° (cf. Butterworth. Heilbron, and Hey, *J.*, 1940, 356).

(iv) *p*-Methoxybenzoyl peroxide (20 g.) was added to pyridine (80 c.c.) stirred at 100—110°, and the product was worked up as described above for the reaction with *p*-chlorobenzoyl peroxide. The basic product (3·4 g.), b. p. 170—195°/14 mm., which solidified when cold, was treated with alcoholic picric acid; fractionation of the resulting picrates from acetone gave 2-*p*-methoxyphenylpyridine picrate, m. p. and mixed m. p. 190°, and 4-*p*-methoxyphenylpyridine picrate, m. p. and mixed m. p. 205° (cf. Haworth, Heilbron, and Hey, *J.*, 1940, 360).

(v) 1-Naphthoyl peroxide (15 g.) was stirred with pyridine (80 c.c.) at 100°. When reaction had ceased excess of pyridine was removed in a vacuum, and the residue was dissolved in benzene (300 c.c.), which was extracted successively with 5% aqueous sodium hydroxide and 15% hydrochloric acid. Evaporation of the benzene left a small tarry residue (1·4 g.), from which a small quantity of naphthalene sublimed on heating (0·05 g.; m. p. and mixed m. p. 79°). The acid extract was basified and extracted with benzene, evaporation of which left a dark liquid residue (1·9 g.), which was treated with alcoholic picric acid. Crystallisation of the resulting picrate from acetone (with charcoal) gave a 1-*naphthylpyridine picrate* in pale yellow needles, m. p. 196° (Found: C, 58·1; H, 3·3; N, 12·8. $C_{15}H_{11}N,C_6H_3O_7N_3$ requires C, 58·1; H, 3·2; N, 12·9%). No isomerides were isolated.

(vi) 2-Naphthoyl peroxide (20 g.) was added to pyridine (80 c.c.), stirred at 105°, and the reaction product was worked up as described in (v). A small quantity of naphthalene, m. p. and mixed m. p. 79°, was isolated from the neutral fraction by sublimation. The basic residue (2·6 g.) was treated with a solution of picric acid (3 g.) in boiling alcohol, and fractional crystallisation of the resulting picrates from acetone (with charcoal) gave three isomeric 2-naphthylpyridine picrates, (*a*) yellow needles, m. p. 200° (Found: C, 58·0; H, 3·2. Calc. for $C_{15}H_{11}N,C_6H_3O_7N_3$: C, 58·1; H, 3·2%); (*b*) yellow needles, m. p. 179° (Found: N, 12·8. Calc. for $C_{15}H_{11}N,C_6H_3O_7N_3$: N, 12·9%); (*c*) yellow prisms, m. p. 216°, in very small yield. The compounds (*a*), (*b*), and (*c*) showed no depression in melting point on admixture with the corresponding compounds prepared from 1-2′-naphthyl-3 : 3-dimethyltriazen and pyridine (Elks and Hey, *J.*, 1943, 444).

(vii) 2 : 2′-Dicarbomethoxybenzoyl peroxide (40 g.) was added to pyridine (150 c.c.) stirred at 100°. When reaction was complete, excess of pyridine was removed under reduced pressure and the residue dissolved in benzene (500 c.c.) and extracted with a saturated aqueous solution of sodium hydrogen carbonate. After removal of the benzene the residue was distilled under reduced pressure, and two fractions were collected: (*a*) b. p. 60°/0·1 mm. (2·3 g.); (*b*) b. p. 110—150°/0·1 mm. (4·2 g.), Fraction (*a*) was identified as methyl benzoate by hydrolysis. Fraction (*b*) was treated with a hot solution of picric acid (6 g.) in alcohol (40 c.c.). Fractional crystallisation of the resulting picrates from acetone gave two isomeric *methyl* o-*pyridylbenzoate picrates*: (*a*) orange-yellow prisms, m. p. 243° (0·5 g.) (Found: C, 51·2; H, 3·0. $C_{13}H_{11}O_2N,C_6H_3O_7N_3$ requires C, 51·6; H, 3·2%); (*b*) fine yellow matted fibres, m. p. 196° (1·3 g.) (Found: C, 51·9; H, 3·2%).

(viii) Cinnamoyl peroxide (30 g.) was added in small quantities to pyridine (200 c.c.) stirred at 110°. When evolution of gas ceased, excess of pyridine was removed under reduced pressure. The residue was dissolved in benzene (500 c.c.) and extracted first with 10% aqueous sodium hydroxide and then with 10% hydrochloric acid. The acid extract was made alkaline, extracted with benzene, and the benzene removed. The residue (0·7 g.) was treated with a solution of picric acid (1 g.) in boiling alcohol. The resulting picrates were crystallised from alcohol, and α-stilbazole picrate was obtained in golden needles, m. p. and mixed m. p. with an authentic specimen 204°. A portion of the picrate was warmed with 5% aqueous sodium hydroxide and the liberated α-stilbazole was extracted with ether. After the ethereal extract had been washed free from picric acid, the dried solution was evaporated and the residual α-stilbazole isolated, m. p. and mixed m. p. 91°. The authentic specimen was made from α-stilbazole prepared from benzaldehyde and 2-methylpyridine as described by Lénárt (*Annalen*, 1915, **410**, 95).

Miscellaneous Reactions.—m-*Nitrobenzoyl peroxide and benzoic acid.* The peroxide (20 g.) was added to molten benzoic acid (75 g.) at 125°, and when addition was complete the temperature was raised to 150° for 1 hour. The product was dissolved in 10% aqueous sodium hydroxide (500 c.c.) and extracted with ether. The aqueous layer was warmed to remove ether, and concentrated hydrochloric acid was added to the hot solution until precipitation began. Further acidification was then effected with 5% hydrochloric acid (30 c.c.) to give precipitate (A), with a further 20 c.c. to give precipitate (B), and with a further 20 c.c. to give precipitate (C). Precipitate (A) was sublimed in high vacuum (150°/0·00001 mm.), and the sublimate (1·2 g.) crystallised from glacial acetic acid. 3-*Nitrodiphenyl*-4′-*carboxylic acid* separated in yellow plates, m. p. 301° (Found: C, 64·4; H, 3·3. $C_{13}H_9O_4N$ requires C, 64·2; H, 3·7%). In similar manner the sublimate from precipitate (B) (0·9 g.; 120°/0·00001 mm.) was crystallised from glacial acetic acid, and 3-*nitrodiphenyl*-3′-*carboxylic acid* separated in flat needles, m. p. 262° (Found: C, 63·9; H, 4·0%). Precipitate (C) consisted almost exclusively of benzoic acid. Evaporation of the ethereal extract from the alkaline washing left a brown syrup (0·7 g.), from which a small quantity of 3 : 3′-dinitrodiphenyl separated, m. p. 200° after crystallisation from dilute alcohol (cf. Ullmann and Bielecki, *Ber.*, 1901, **34**, 2177).

Benzoyl peroxide and quinoline. Benzoyl peroxide (60 g.) was added to quinoline (200 g.) stirred at 100—105°. When reaction was complete, the temperature was raised to 160° for ½ hour, and excess of quinoline was removed under reduced pressure. The residue was dissolved in benzene (300 c.c.) and extracted with aqueous sodium hydrogen carbonate. The distilled quinoline was also extracted with 5% aqueous sodium hydroxide, and acidification of the combined extracts gave benzoic acid (37 g.). After evaporation of the benzene the residue was distilled and two fractions were collected: (*a*) b. p. 140—200°/0·5 mm. (17·5 g.); (*b*) b. p. 200—250°/0·5 mm. (4·5 g.). Fraction (*a*) was treated with a hot alcoholic solution of picric acid; fractional crystallisation of the resulting picrates from acetone gave 4-phenylquinoline picrate (2·5 g.), m. p. and mixed m. p. 224°, 5-phenylquinoline picrate, m. p. and mixed m. p. 208—210°, and the following picrates which gave mutual melting point depressions both with each other and with authentic specimens of phenylquinoline picrates: (*a*) yellow sphaerolites, m. p. 204° (Found: N, 12·1. $C_{15}H_{11}N,C_6H_3O_7N_3$ requires N, 12·9%); and in very small quantity (*b*) yellow fibrous needles, m. p. 213°, and (*c*) yellow needles, m. p. 192°.

Authentic specimens of the picrates of the seven isomeric phenylquinolines were prepared. 2-Phenylquinoline and 3-phenylquinoline were prepared by the method of Friedländer and Gohring (*Ber.*, 1883, **16**, 1833). The picrates were prepared in the normal manner : that of the former melted at 191° and of the latter at 205° (cf. Knorr, *Annalen*, 1888, **245**, 380; Hübner, *Ber.*, 1908, **41**, 483). 4-Phenylquinoline was prepared by the method of Kenner and Statham (*J.*, 1935, 301) and converted into the picrate, m. p. 225°. 6- and 8-Phenylquinoline were prepared from 4-aminodiphenyl and 2-aminodiphenyl respectively by a modification of the method of La Coste and Sorger (*Annalen*, 1885, **230**, 8). Concentrated sulphuric acid (3·5 c.c.) was added slowly with cooling to a mixture of 4-aminodiphenyl (3·5 g.), anhydrous glycerol (4·5 c.c.), and sodium *m*-nitrobenzenesulphonate (4 g.). The mixture was heated in an oil-bath at 130° under reflux and finally at 150° with frequent shaking. As soon as the reaction started the flask was removed from the oil-bath, and after the vigorous reaction had subsided heating was continued at 160° for 7 hours. The cold reaction mixture was diluted to 300 c.c. and made strongly alkaline with ammonia. The precipitated solid was extracted with boiling benzene; evaporation of the benzene left a residue of 6-phenylquinoline (2·3 g.), m. p. 109° after crystallisation from alcohol. The *picrate* separated from acetone in flat yellow needles, m. p. 205° (Found : N, 12·7. $C_{15}H_{11}N,C_6H_3O_7N_3$ requires N, 12·9%). By using 2-aminodiphenyl in place of 4-aminodiphenyl, 8-phenylquinoline was prepared in 44% yield as an oil, b. p. 210°/20 mm. The *picrate* separated from acetone in yellow needles, m. p. 200° (Found: N, 12·6. $C_{15}H_{11}N,C_6H_3O_7N_3$ requires N, 12·9%). Möhlau and Berger (*Ber.*, 1893, **26**, 2004) have recorded m. p. *ca.* 210° for this picrate, which was prepared from a base derived from the action of solid benzenediazonium chloride on quinoline. A mixture of 5- and 7-phenylquinoline was prepared from the reaction between 3-aminodiphenyl (6 g.), glycerol (8 c.c.), sodium *m*-nitrobenzenesulphonate (6 g.), and concentrated sulphuric acid (6 c.c.), carried out as described above for the reaction with 4-aminodiphenyl. The product (3·7 g.) was treated with alcoholic picric acid, and the picrates were boiled under reflux with alcohol (450 c.c.) and filtered off. Recrystallisation of the insoluble residue from acetone gave 7-*phenylquinoline picrate* in stout golden needles, m. p. 210°, which depressed the melting point of 5-phenylquinoline picrate (Found : N, 12·3. $C_{15}H_{11}N,C_6H_3O_7N_3$ requires N, 12·9%). A further quantity of 7-phenylquinoline picrate separated from the mother liquor, and finally a small quantity of 5-phenylquinoline picrate separated, m. p. 210° both alone and on admixture with an authentic specimen prepared by the action of 1-5′-quinolyl-3 : 3-dimethyltriazen on benzene (Elks and Hey, *loc. cit.*).

Benzoyl peroxide and 2 : 2 : 4-*trimethylpentane*. The peroxide (54 g.) was added to 2 : 2 : 4-trimethylpentane (200 c.c.) stirred at 100°. When reaction had ceased, excess of trimethylpentane was removed by distillation, and the residue was dissolved in ether (200 c.c.) and extracted with aqueous sodium hydrogen carbonate. Acidification of the aqueous extracts deposited benzoic acid (14 g.). Fractional distillation of the recovered trimethylpentane gave a fraction (10 c.c.), boiling below 84°, which was identified as benzene by conversion into *m*-dinitrobenzene. After removal of the ether, the residue was distilled under reduced pressure and the following fractions were collected : (*a*) b. p. 113—126°/12 mm. (6·5 g.); (*b*) b. p. 142—160°/12 mm. (2·8 g.); (*c*) b. p. 150—220°/0·2 mm. (5·2 g.); (*d*) b. p. 150—250°/0·00001 mm. (3·0 g.). Fraction (*a*) deposited crystals of diphenyl, m. p. and mixed m. p. 70°. Fraction (*b*) gave a further quantity of benzoic acid, and fraction (*c*) gave diphenyl-4-carboxylic acid, m. p. and mixed m. p. 220—222°. Fraction (*d*) was a resin.

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