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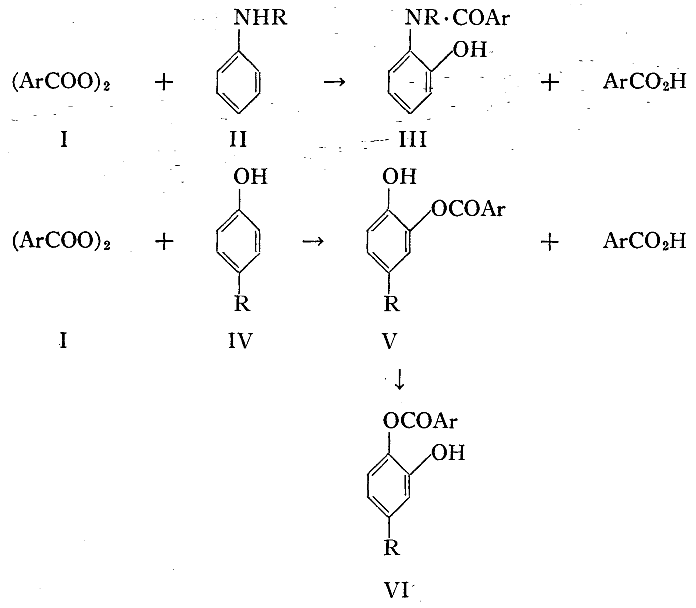
ORGANIC PEROXIDES
VI. REACTION OF PHENOLS AND SECONDARY AROMATIC AMINES WITH *p*-NITROBENZOYL AND *p,p′*-DINITROBENZOYL PEROXIDES

J. T. Edward and S. A. Samad[1]

Benzoyl peroxide (I; Ar = Ph) reacts with secondary aromatic amines (II) to give substituted *o*-benzamidophenols (III; Ar = Ph) (1, 2), and with phenols (IV) to give *o*-benzoyloxyphenols (V or VI; Ar = Ph) (3). Yields in these reactions are at best only fair, and the availability of *p,p′*-dinitrobenzoyl peroxide (I; Ar = $C_6H_4 \cdot NO_2$-*p*), prepared



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[1] *Holder of Colombo Plan Fellowship, 1957–1960.*

for another investigation (4), prompted us to study its reactions with a few amines and phenols. These are listed in Table I, in which are also shown the yields of phenolic products. These yields are about the same as those obtained earlier with benzoyl peroxide, but with α- and β-naphthol crystalline phenolic products could be obtained by oxidation with *p,p'*-dinitrobenzoyl peroxide but not with benzoyl peroxide.

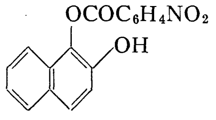
TABLE I

Yields from reactions of amines or phenols with *p,p'*-dinitrobenzoyl peroxide

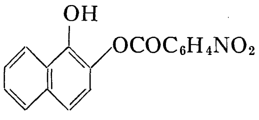
	Phenolic product		*p*-Nitrobenzoic acid
Amine or phenol	Formula*	Yield (%)	Yield (%)
N-Methylaniline	III; R = Me	38	55
N-Ethylaniline	III; R = Et	45	59
N-Butylaniline	III; R = Bu	42	65
Diphenylamine	III; R = Ph	52	55
Phenol	—	—	90
p-Methoxyphenol	—	—	91
p-Cresol	VI; R = Me	44	61
p-Bromophenol	V; R = Br	16	80
α-Naphthol	VIII	40	62
β-Naphthol	VIII	80	59

*In all cases Ar = $C_6H_4 \cdot NO_2$-*p*.

The structures of the phenols obtained from the substituted anilines are without doubt represented by III (Ar = $C_6H_4 \cdot NO_2$-*p*), since they show no basic properties. The oxidation product of *p*-cresol (IV; R = Me) slowly gave a green color on treatment with *p*-aminodimethylaniline and sodium hypochlorite. This color reaction is considered diagnostic of a free para position in a phenol (3), so that the oxidation product probably has the structure VI (R= Me, Ar = $C_6H_4 \cdot NO_2$-*p*), similar to that found for the product from *p*-cresol and benzoyl peroxide (3); in each case the compound V (R = Me, Ar = Ph or $C_6H_4 \cdot NO_2$-*p*) is probably formed first, but rearranges by acyl migration. On the other hand, the phenol from the reaction of *p*-bromophenol (IV; R = Br) appears from the color reaction to have no free para position, and so is probably represented by V (R = Br; Ar = $C_6H_4 \cdot NO_2$-*p*). Both α- and β-naphthol reacted with *p,p'*-dinitrobenzoyl peroxide to give the same product, which accordingly must be VII or VIII. The latter was shown to be correct, since methylation of the product with diazomethane followed by alkaline hydrolysis gave 1-methoxy-2-naphthol. Evidently the compound (VII) first formed by reaction of β-naphthol rearranges to VIII.

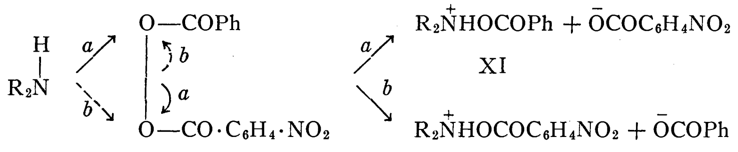


VII



VIII

The mechanisms of the reactions of benzoyl peroxide with amines (5) and phenols (6) have been investigated recently and shown to involve nucleophilic attack of the amino or hydroxyl group on a peroxide oxygen with displacement of a benzoate ion. With the unsymmetrical peroxide, *p*-nitrobenzoyl peroxide (X), this attack may take place on the oxygen (α) adjacent to the benzoyl group, with expulsion of a *p*-nitrobenzoate ion (route *a*) or on the oxygen (β) adjacent to the *p*-nitrobenzoyl group, with expulsion of a benzoate ion (route *b*). Dibenzylamine (IX; R = CH_2Ph) attacks by route *a* in boiling


IX X XI

chloroform (7). Diphenylamine (IX; R = Ph) might accordingly be expected to react by this route to give *o*-(*N*-phenylbenzamido)phenol (III; R = Ar = Ph) (via the intermediate XI (R = Ph) (5)) and *p*-nitrobenzoic acid. In fact, evidence could be obtained only for its reaction by route *b*. A mixture of phenolic products was obtained, from which only the nitro derivative (III; R = Ph, Ar = $C_5H_4 \cdot NO_2$-*p*) could be obtained crystalline (17% yield). Infrared and combustion analysis indicated that the uncrystallizable phenolic fraction remaining was *not* a simple mixture of the two phenols (III; R = Ph; Ar = Ph and $C_6H_4 \cdot NO_2$-*p*).

The reaction of phenols with the unsymmetrical peroxide (X) also follows a complex course. *p*-Cresol gave a mixture of benzoic and *p*-nitrobenzoic acids, and a gummy phenolic fraction from which the *p*-nitrobenzoyloxy derivative (VI; R = Me, Ar = $C_6H_4 \cdot NO_2$-*p*) could be crystallized in 13% yield, but from which the benzoyloxy derivative (VI; R = Me, Ar = Ph) was absent, since nothing could be distilled from the phenolic fraction at temperatures up to 270° at 0.1 mm pressure (cf. ref. 3). β-Naphthol also gave a complex phenolic mixture, from which only the *p*-nitrobenzoyloxy derivative (VIII) could be obtained crystalline.

It is evident that, like tributylphosphine (8) and unlike dibenzylamine (7), phenols and secondary aromatic amines attack the β oxygen of *p*-nitrobenzoyl peroxide (X), although yields are low because of competing reactions giving complex phenolic products.

EXPERIMENTAL

Reactions of Secondary Aromatic Amines with p,p′-Dinitrobenzoyl Peroxide

The peroxide (0.01 mole) was added gradually to a stirred solution of the amine (0.01 mole) in benzene (50 ml) at 20–25°. After standing overnight, the solution was worked up in the usual way (2) for acid and phenol fractions (cf. Table I). *N*-Methylaniline gave *o*-(*N*-methyl-*p*′-nitrobenzamido)phenol (III; R = Me, Ar = $C_6H_4 \cdot NO_2$-*p*), colorless needles from ethanol, m.p. 197–198°. Calc. for $C_{14}H_{12}O_4N_2$: C, 61.76; H, 4.41; N, 10.29%. Found: C, 61.92; H, 4.26; N, 10.14%. *N*-Butylaniline gave *o*-(*N*-butyl-*p*′-nitrobenzamido)-phenol (III; R = Bu, Ar = $C_6H_4 \cdot NO_2$-*p*), colorless plates from benzene, m.p. 167°. Calc. for $C_{17}H_{18}O_4N_2$: C, 64.97; H, 5.73; N, 8.91%. Found: C, 64.86; H, 5.55; N, 8.69%. Diphenylamine gave *o*-(*N*-phenyl-*p*′-nitrobenzamido)phenol (III; R = Ph, Ar = $C_6H_4 \cdot NO_2$-*p*), yellow plates from ethanol, m.p. 240°. Calc. for $C_{19}H_{14}O_4N_2$: C, 68.26; H, 4.19; N, 8.38%. Found: C, 68.08; H, 4.16; N, 8.56%.

N-Ethylaniline gave *o*-(*N*-ethyl-*p*′-nitrobenzamido)phenol (III; R = Et, Ar = $C_6H_4 \cdot NO_2$-*p*), colorless plates from 50% aqueous ethanol, m.p. 152°. Calc. for $C_{15}H_{14}O_4N_2$: C, 62.93; H, 4.89; N, 9.78%. Found: C, 62.83; H, 4.93; N, 9.63%. This phenol crystallized from other solvents with a certain amount of firmly held solvent, probably entrapped by clathrate formation, which is known to be particularly easy for phenolic compounds (9). Thus it crystallized from benzene in plates which, after being dried at 80° at 3 mm for 24 hours, melted at 90–92°, solidified, and remelted at 118°. Calc. for $C_{15}H_{14}O_4N_2 + 1/6\ C_6H_6$: C, 64.21; H, 5.01%. Found: C, 63.82; H, 4.97%. The phenol crystallized from toluene in prisms, m.p. 120°. Calc. for $C_{15}H_{14}O_4N_2 + 1/12\ C_7H_8$: C, 63.68; H, 4.99; N, 9.53%. Found: C, 63.26; H, 5.18; N, 9.60%. It crystallized from bromobenzene in prisms, m.p. 130°. Calc. for $C_{15}H_{14}O_4N_2 + 1/3\ C_6H_5Br$: C, 60.29; H, 4.63; N, 8.28%. Found: C, 60.18; H, 4.93; N, 8.18%.

Reaction of Diphenylamine with p-Nitrobenzoyl Peroxide

Diphenylamine (3.32 g) in benzene (70 ml) was treated as above with *p*-nitrobenzoyl peroxide (5.74 g). The acid fraction (3.1 g) was composed of benzoic and *p*-nitrobenzoic acids, as shown by its melting point of 193–200°. It was dissolved in alkali, filtered, and reprecipitated with mineral acid. The dried precipitate was analyzed for nitrogen, and contained 5.31%, corresponding to 37% benzoic + 63% *p*-nitrobenzoic acid.

Removal of the acid fraction from the benzene solution left a precipitate of phenolic material (0.75 g), m.p. 206–208° (decomp.). Found: C, 65.72; H, 4.41; N, 6.80%. A further 0.8 g, m.p. 202–206° (decomp.), was removed from the benzene solution from aqueous alkali. Crystallization from acetic acid yielded *o*-(*N*-phenyl-*p*′-nitrobenzamido)phenol (III; R = Ph, Ar = $C_6H_4 \cdot NO_2$-*p*) (1.05 g, 17%), m.p. and mixed m.p. 239°. No other pure compound could be obtained from the phenolic fraction.

Reaction with Phenols with p,p′-Dinitrobenzoyl Peroxide

Solutions of the phenol (0.01 mole) and peroxide (0.01 mole) in chloroform (50 ml) were refluxed for 4–6 hours. Carboxylic acids were removed by extraction with aqueous sodium bicarbonate, and the chloroform solution dried over sodium sulphate and evaporated. The residue was dissolved in the minimum quantity of hot benzene. The solution on cooling deposited crystals of phenolic compound. In this way, *p*-cresol gave pale yellow plates of 4-*p*-nitrobenzoyloxy-*m*-cresol (VI; R = Me, Ar = $C_6H_4 \cdot NO_2$-*p*), m.p. 164°. Calc. for $C_{14}H_{11}O_5N$: C, 61.54; H, 4.03; N, 5.13%. Found: C, 61.73; H, 4.12; N, 5.20%. *p*-Bromophenol gave colorless needles of 2-*p*-nitrobenzoyloxy-4-bromophenol (V; R = Br, Ar = $C_6H_4 \cdot NO_2$-*p*), m.p. 187–188°. Calc. for $C_{13}H_8O_5NBr$: C, 46.15; H, 2.36; N, 4.14%. Found: C, 46.19; H, 2.30; N, 4.15%. α-Naphthol and β-naphthol gave yellow needles of 2-*p*-nitrobenzoyloxy-1-naphthol (VIII), m.p. 182°. Calc. for $C_{17}H_{11}O_5N$: C, 66.02; H, 3.56; N, 4.53%. Found: C, 66.14; H, 3.57; N, 4.59%.

1-Methoxy-2-p-nitrobenzoyloxynaphthalene

A solution of diazomethane in dry ether was added to a solution of 2-*p*-nitrobenzoyloxy-1-naphthol (3.11 g) in ether until a yellow color persisted. After 20 minures, excess diazomethane was destroyed with dilute hydrochloric acid. The ether solution was washed with dilute aqueous potassium hydroxide and then water, dried, and concentrated. The residue crystallized from ethanol in yellow needles, m.p. 140°, of 1-methoxy-2-*p*-nitrobenzoyloxynaphthalene (1.65 g; 51%). Calc. for $C_{18}H_{12}O_5N$: OMe, 9.59%. Found: OMe, 9.49%.

1-Methoxy-2-naphthol

A solution of 1-methoxy-2-*p*-nitrobenzoyloxynaphthalene (1 g) and potassium hydroxide (5 g) in methanol–water (9:1 v/v; 100 ml) was refluxed for 3 hours. After removal of most of the methanol by distillation, the solution was acidified. The precipitate was removed by filtration and washed with aqueous sodium bicarbonate. The residue (0.32 g) crystallized from ligroin as colorless plates of 1-methoxy-2-naphthol, m.p. 90° (reported m.p. 90.5° (10); 2-methoxy-1-naphthol has been prepared recently, and has m.p. 53.5–54.5 (11)). Calc. for $C_{11}H_{10}O_2$: C, 75.86; H, 5.75%. Found: C, 75.51; H, 5.52%. The benzoate, prepared in the usual way with benzoyl chloride in pyridine, crystallized from methanol as colorless rods, m.p. 107°. Calc. for $C_{18}H_{14}O_3$: C, 77.40; H, 5.04%. Found: C, 77.59; H, 5.17%.

Reaction of p-Cresol with p-Nitrobenzoyl Peroxide

The reaction of the peroxide (2.87 g) with *p*-cresol (1.08 g) in chloroform (50 ml) gave a mixture of benzoic and *p*-nitrobenzoic acids (1.72 g), m.p. 198–210°. This melting point corresponds to that of a mixture of 75% of *p*-nitrobenzoic acid and 25% benzoic acid. The phenolic fraction afforded 4-*p*-nitrobenzoyloxy-*m*-cresol (0.35 g; 13%), m.p. and mixed m.p. 164°, and an uncrystallizable gum (1.63 g). This was separated by chromatography on alumina into several fractions showing strong infrared bands at 3350 cm^{-1} (bonded OH) and 1745 cm^{-1} (ester CO), but none of these could be induced to crystallize.

Reaction of β-Naphthol with p-Nitrobenzoyl Peroxide

Reaction of the peroxide (5.74 g) with β-naphthol (2.88 g) in chloroform (90 ml) gave an acidic mixture (2.78 g) indicated by its melting point (188–199°) to be made up of about 65% of *p*-nitrobenzoic and 35% of benzoic acid. The phenolic fraction gave 2-*p*-nitrobenzoyloxy-1-naphthol (0.678; 11%), m.p. and mixed m.p. 182°, and a gum (3.95 g) which by chromatography on alumina gave several gummy fractions.

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