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THE ACTION OF BENZOYL PEROXIDE ON 2-NAPHTHOL.
A NOVEL SYNTHESIS OF A QUINOL DIBENZOATE.

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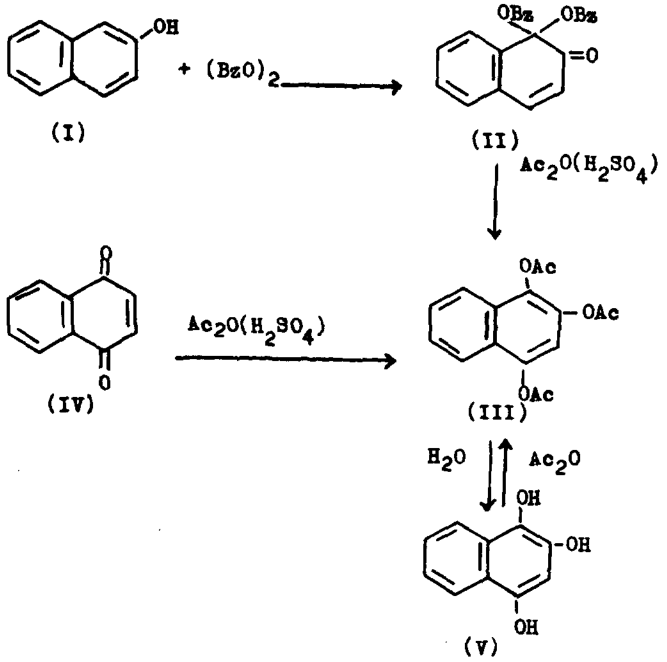
Cosgrove and Waters[1] carried out the oxidation of certain phenols with benzoyl peroxide in chloroform solution and found that they undergo benzoyloxylation usually ortho to the phenolic group. In a few cases[2] para benzoyloxylation, and the formation of diphenoquinones have also been noted. In an effort to study the oxidation of certain bicyclic heterocyclic systems, we did a model oxidation first of 2-Napthol with benzoyl peroxide. Our results were unique in that the reaction product contained substantial amount (35-40 per cent) of the quinol dibenzoate II. In a typical experiment, 2-Naphthol (0.33 mole) was refluxed in chloroform (40 ml) solution with benzoyl peroxide (0.34 mole) for 6 hours. After removal from the chloroform solution of the benzoic acid formed (3.8 g) with aqueous sodium bicarbonate, and the alkali soluble matter (4 g), the chloroform residue on trituration with methyl alcohol yielded a colourless neutral product (1.2 g). It was crystallised from acetone, giving crystals, m.p. 186-87° (Found: C, 74.9; H, 4.5%; $C_{24}H_{16}O_5$ requires C, 75.0; H, 4.2%).



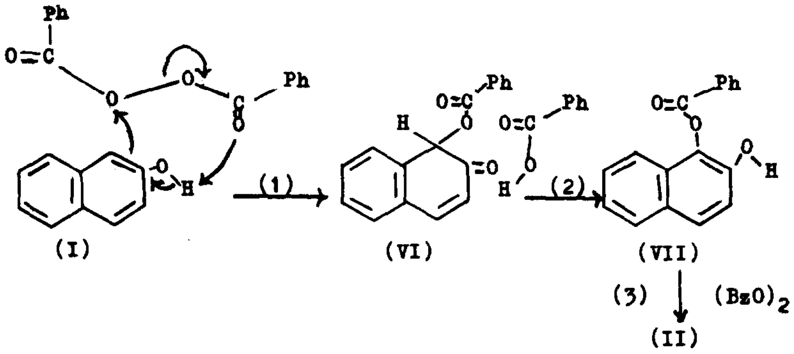
The reactions which supported the formulation of the neutral product m.p.186-87° as II were as follows: When warmed at 50° for 2 hours with an Ac_2O-H_2SO_4 mixture (10 ml; Ac_2O containing 3 per cent H_2SO_4), it gave 1,2,4-triacetoxy naphthalene (III) m.p.135° (Found: C, 62.8; H, 5.0%; Calc. for $C_{16}H_{14}O_6$, C, 63.6; H, 4.6%). Its (III) ultra violet spectrum (alcohol) had λ_{max} 222.5, 281 (log ϵ 5.7, 3.6). This triacetate was identical with that obtained from α-naphthaquinone (IV) by similar Ac_2O-H_2SO_4 treatment (Thiele's Acetylation Reaction) in m.p. 135° and ultra violet spectrum

λ_{max} 222.8, 281 (log ϵ 5.7, 3.65). The triacetoxy compound (III) could be hydrolysed with 10 per cent sulphuric acid to 1,2,4-trihydroxy naphthalene (V) m.p.153° (lit.[3] m.p.154°) which again could be reacetylated to (III) with Ac_2O. Finally, the neutral product when refluxed with 80 per cent sulphuric acid, after steam distillation, yielded 2 moles of benzoic acid in the steam distillate.

It is remarkable that the Ac_2O-H_2SO_4 reagent with II yielded the triacetate (III) rather than the expected 1-Benzoyloxy 2,4-diacetoxy naphthalene (III with 1-OBz instead of 1-OAc). This could be due to a process of acetolysis occurring in II prior to its conversion into the triacetate (III).

In the experiment with benzoyl peroxide, the alkali soluble matter contained some unchanged 2-Naphthol. There were, however, indications for the presence also of small amount of 1-benzoyloxy 2-naphthol (VII) as well as of other products which are being looked into.

Benzoyloxylation with benzoyl peroxide (cf. the reaction with naphthalene itself[4,5]) usually occurs by a homolytic process. Such a mechanism was in fact first advanced by Cosgrove and Waters[1,2] for the benzoyloxylation of phenols, but now it is believed[6] that this change is the result of an electrophilic substitution of the phenol by benzoyl peroxide. On this basis, the substitution in the 2-Naphthol may be represented as in steps (1) and (2).



The formation of the dibenzoate (II) can then be explained in the same manner as those of the quinol diacetates in the reaction of phenols with lead tetra acetate[7,8]. This is shown in step (3), the change involving a repetition of substitution by benzoyl peroxide occurring with the initially formed monobenzoyloxy compound (VII). Such a substitution step giving (II) finds an analogy in the reported formation[9] of 1,1-dibromo 2-keto compound (II, two Br in place of the two OBz) by further bromination of 1-bromo 2-naphthol. It may, however, be mentioned that the formation of quinol dibenzoates in the reaction of benzoyl peroxide with phenols has not yet been described in literature and the present study provides the first instance of the possibility of their formation in this reaction. The fairly high yield in which II can be obtained is indicative of the high reactivity of the naphthalene nucleus (cf. ref.9, also 4 and 5) enabling the additional substitution step (3) to occur.

We are currently engaged in ascertaining the conditions leading to monobenzoyloxylation and dibenzoyloxylations in various phenolic compounds as well as in exploring their synthetic utility.

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