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# The Reaction of Diazonium Ion Generated from α-Azohydroperoxide with Phenols. The Isolation and Reaction of Diazoether Intermediate

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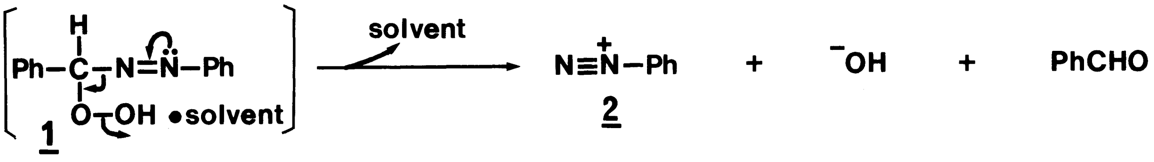
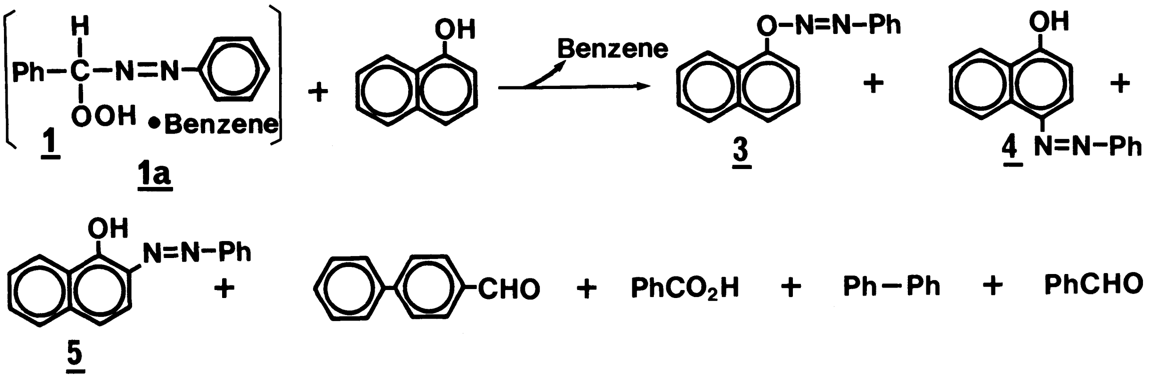
The reaction of benzenediazonium ion generated from α-azohydroperoxide with 1-naphthol gave a diazoether which rearranged to 2- and 4-phenylazo-1-naphthols.

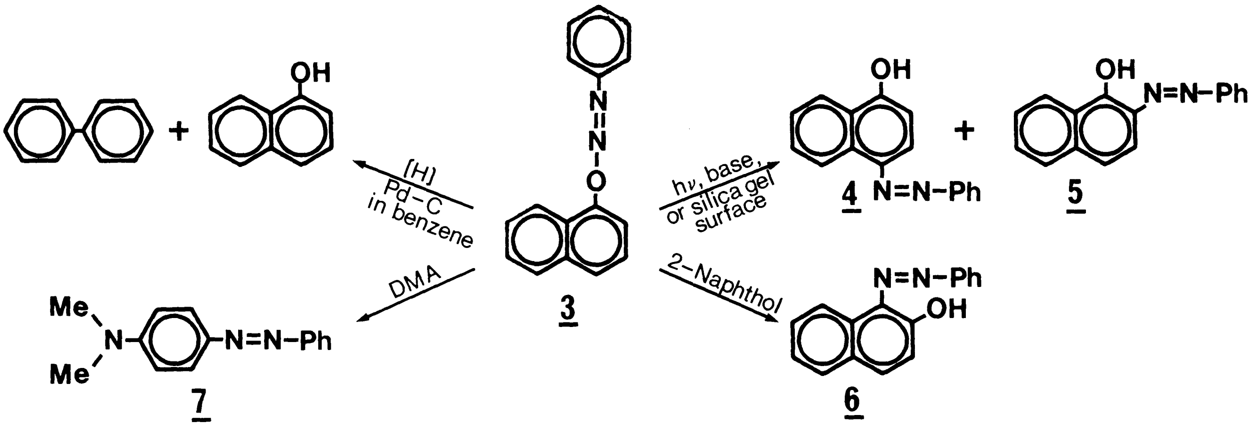
Recently we have reported that a 1:5 molecular complex of α-azohydroperoxide (1) with solvent generates benzenediazonium ion (2) when the solvent molecules are eliminated from the complex completely.[1)] In the present study we have investigated the coupling reaction of benzenediazonium ion 2 generated from 1, with 1-naphthol and phenol in a solid state. Now we report for the first time the isolation of a diazoether intermediate (3) in the reaction of diazonium ion 2 with 1-naphthol, and the rearrangement of 3 to azonaphthols 4 and 5.



The 1:5 molecular complex of 1 with benzene (1a) was prepared using the method reported by us previously.[1)] A solid mixture of the complex 1a and 1-naphthol (excess) was stirred under open air at room temperature in the dark for several hours.



Scheme 1.

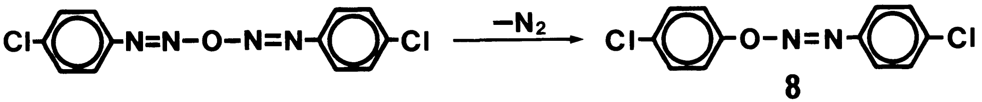


Scheme 2.

During this period, the solvent molecule had evaporated away from the mixture, and 1 decomposed, giving rise to a reddish solid. The seperation by silica gel TLC gave several compounds: diazoether 3 (17%), 4-phenylazo-1-naphthol (4) (42%),[2] 2-phenylazo-1-naphthol (5) (4%),[2] 4-phenylbenzaldehyde (32%),[3] benzoic acid (23%), diphenyl (trace), and benzaldehyde (trace) (Scheme 1).[4]

These compounds were separated by TLC using benzene-ethyl acetate (9:1) as an eluent. However, the diazoether 3 was sensitive to light, acid, base, etc., and so special care was needed to obtain it in a pure form and high yield. We could obtain 3 in 60% yield by carrying out the separation as follows. The reaction mixture obtained above was dissolved into a small amount of benzene and spotted on the short silica gel TLC plate (ca. 10 cm wide) rapidly. The spot was developed by benzene in the dark. The band appearing at the middle part was collected rapidly before drying out completely. The collected part was extracted with benzene in the dark. The evaporation of the solvent at 40 °C in vacuo in the dark gave 3 as an oil. The compound 3 was stable in benzene in the dark, but decomposed to give 4 and 5 together with tarry materials when it was left to stand for a while at room temperature.

The structure of the diazoether 3, $C_{16}H_{12}N_2O$, was assigned by chemical and spectroscopic data as follows (Scheme 2). The catalytic hydrogenation of 3 over Pd-C in benzene gave 1-naphthol and diphenyl in 45% and 39% yields respectively. When a benzene solution of 3 was exposed to light (fluorescent lamp), it decomposed to give 4 and 5 in 45% and 4% yields respectively. When standing on a silica gel TLC plate, 3 rearranged to 4 and 5. Diazoether 3 gave 4 and 5 immediately when an alcoholic solution of 3 was treated with aqueous sodium hydroxide or hydrochloric acid. When a benzene solution of 3 and 2-naphthol was stirred at room temperature, 1-phenylazo-2-naphthol (6)[2] was formed in 26% yield accompanied with 4 and 5. The reaction of 3 with dimethylaniline gave N,N-dimethyl-4-phenylazoaniline (7) in 10% yield. The $^1$H-NMR spectrum of 3 in benzene-$d_6$ at 100 MHz showed several absorption peaks due to aromatic protons at $\delta$ 6.46 (1H, d, J=8 Hz), 7.10 (7H, m), 7.58 (3H, m), 8.40 (1H, t, J=5 Hz). The coupling pattern of the protons is of close similarity to that of 1-methoxynaphthalene.[5]



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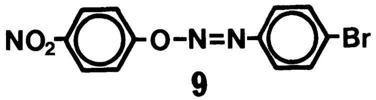

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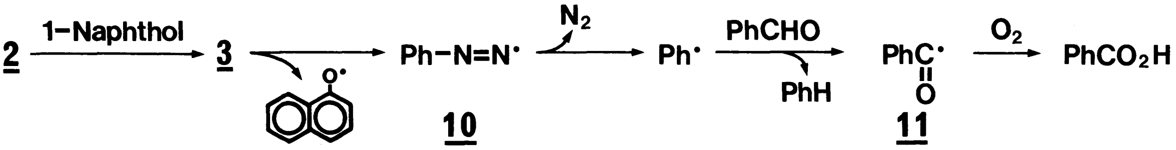
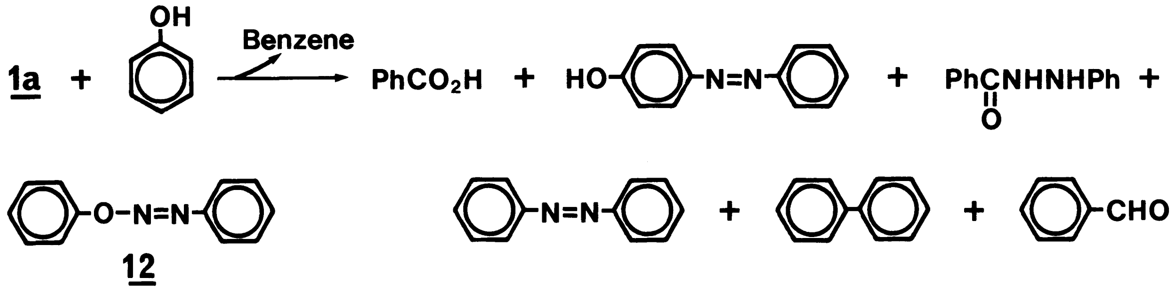
The diazoether of the type 8 was already known. In 1960, Kauffmann et al. reported the formation of the diazoether 8 by the elimination of nitrogen from an explosive diazoanhydride which was formed in the reaction of 4-chlorobenzenediazonium ion at pH 6.5 - 7.5.[6] The chemical reactivity of 3 found in this study is very much similar to that of 8 reported by those authors, suporting the structure of 3. In 1908, Dimroth and Hartmann reported the formation of diazoether (9) in the reaction of 4-bromobenzenediazonium ion with 4-nitrophenol. The diazoether 9 rearranged to 2-(4-bromophenylazo)-4-nitrophenol upon heating.[7]



Scheme 3.

The formation of a fairly good amount of benzoic acid in the reaction of 1a with 1-naphthol is explained as follows (Scheme 3). Benzenediazonium ion 2 generated from 1 reacts with 1-naphthol to give 3, which then produces naphthoxy and phenyldiimide (10) radicals by the homolytic cleavage of the O-N bond. The radical 10 generates phenyl radical which abstracts a hydrogen from benzaldehyde formed from 1 together with 2, to give benzoyl radical (11). The radical 11 reacts with oxygen giving rise to formation of benzoic acid. The formation of benzoic acid via the radical-chain autoxidation involving 11 is known.[8] And the formation of phenyl radical from 10 is also known.[9] In fact, we found that 4-chlorobenzoic acid was formed in good yield when a mixture of the diazoether 3 and 4-chlorobenzaldehyde was kept standing open to air at room temperature.



Scheme 4.

In addition, the reaction of the complex 1a with phenol under open air at room temperature produced benzoic acid in 36% yield together with 4-phenylazophenol

(13%),$^{2)}$ N-benzoyl-N'-phenylhydrazine (12%), azobenzene (6%), diphenyl (trace), and benzaldehyde (trace) (Scheme 4). The diazoether (12) could not be isolated in this case, but it is reasonable to assume that 12 formed at initial stage, decomposes to generate phenyl radical which initiates the autoxidation of benzaldehyde into benzoic acid in a manner similar to that described above. It is interesting to note that the formation of substituted phenoxy and phenyl radicals was reported in the reaction of benzenediazonium ion with substituted phenolate ions.$^{10)}$

The isolation of diazoether 3 in the reaction of benzenediazonium ion 2 with 1-naphthol, and the rearrangement of 3 to azonaphthols 4 and 5 have no precedent. The rearrangement of the diazoether 3 to azonaphthols is particularly interesting in connection with the mechanism of the well known diazo coupling reaction.$^{11,12)}$

In the previous study, the molecular complex of α-azohydroperoxide 1 with isopropyl alcohol was used as a source of benzenediazonium ion 2.$^{1)}$ In the present study, however, we found that the molecular complex of 1 with benzene is the most suitable diazonium ion source for obtaining the diazoether intermediate. We are currently investigating the isolation of more stable diazoethers and the mechanism of the new rearrangement of the diazoether 3 to azonaphthols 4 and 5.

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