CHEMISTRY LETTERS, pp. 1621-1624, 1985. © 1985 The Chemical Society of Japan

GENERATION OF ARENEDIAZONIUM ION FROM MOLECULAR COMPLEX OF α-AZOHYDROPEROXIDE WITH SOLVENTS. A NEW ROUTE FOR DIAZONIUM ION

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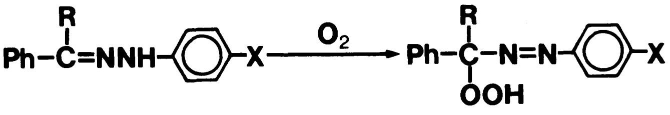
Arenediazonium ions are generated from molecular complexes of α-azohydroperoxides with solvents (crystals or oils) under anhydrous conditions, when the solvated molecules are removed from these complexes.

α-(p-Bromophenyl)azobenzyl hydroperoxide (2a) is obtained as a stable crystal (dec. 114 °C) free from solvents.1,2) However, we found in the present study that α-azohydroperoxides 2b-d are isolated as solvated molecular complexes. When all the solvated molecules are removed from these complexes, 2b-d decompose to give diazonium ions.



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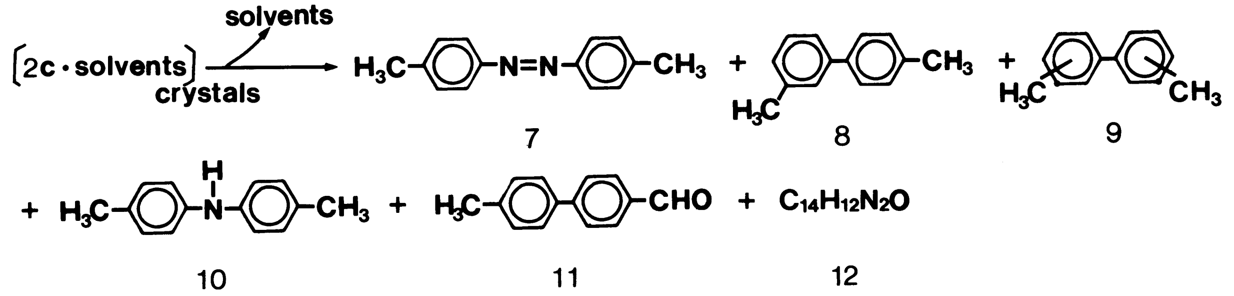
a : R = H ; X = Br
b : R = H ; X = H
c : R = H ; X = CH_3
d : R = CH_3 ; X = H

When oxygen gas was bubbled through a benzene solution of benzaldehyde phenylhydrazone (1b) (1.1×10^{-1} M) for 3 hours at room temperature, crystals were formed. Recrystallization of the crude crystals from benzene gave yellow needles (dec. 58 °C), NMR spectrum of which indicated that this is a molecular complex of 2b and benzene (1:5).3,4) Recrystallization of this crystal from isopropyl alcohol gave a molecular complex of 2b and isopropyl alcohol (1:5) (dec. 54 °C) (see Fig. 1), while that from petroleum ether yielded a complex of 2b and petroleum ether (dec. 64 °C).3) Similarly, oxygenation of 1c in benzene provided a molecular complex of 2c and benzene (1:5) (dec. 38 °C). Recrystallization of this complex from isopropyl alcohol gave a complex of 2c and isopropyl alcohol (1:5) (dec. 43 °C). Oxygenation of 1d in benzene gave solvated oils which are complexes of 2d and benzene (1:5).

Attempts to obtain solvent free α-azohydroperoxides 2b-d were failed. But, when all the solvated molecules were removed from these complexes by standing under ordinary atmosphere at room temperature or by vacuum at low temperature, 2b-d decomposed rapidly to give several compounds.

For example, when isopropyl alcohol was removed from the complex of 2b and isopropyl alcohol (1:5) by standing at room temperature, 2b decomposed to give oils which contain azobenzene (3) (7%), diphenyl (4) (7%), p-phenylbenzaldehyde (5) (13%),5) benzaldehyde (58%), and compound (6), mp 33 °C, $C_{13}H_{10}N_2O$ (7%).6) Similarly, when the solvent was removed from the complex of 2c and isopropyl alcohol (1:5), 2c decomposed to give p,p'-dimethylazobenzene (7) (18%), ditolyls (8, mp 12 °C and 9, oils) (7% each),7-9) di(p-tolyl)amine (10) (9%),10) p-tolylbenzaldehyde (11) (38%



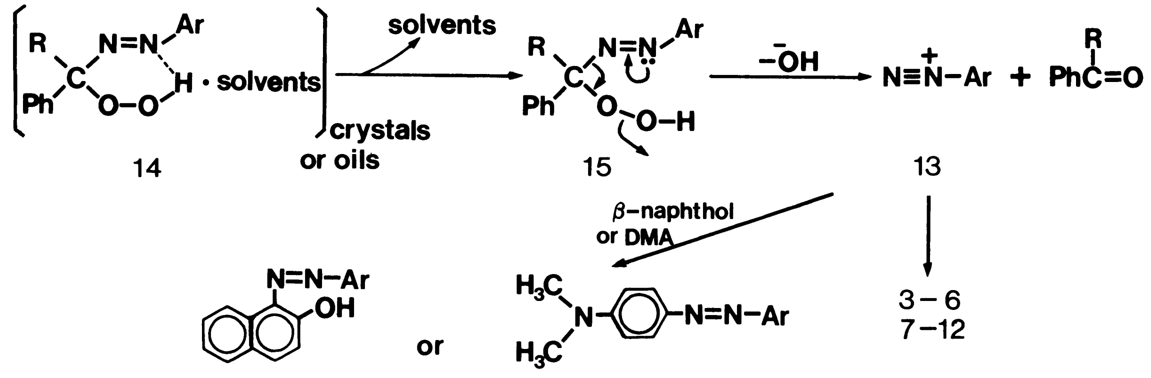
Scheme 1.

),11) benzaldehyde (trace), and compound (12), mp 63 °C, $C_{14}H_{12}N_2O$ (18%)6) (Scheme 1). In the similar manner, the complex of 2d and benzene (oils) gave azobenzene (3), diphenyl (4), and acetophenone.

These product studies suggest that an arenediazonium ion is generated from 2, and this is a key intermediate of the reaction. The formation of aryl radicals and cations from arenediazonium ions, and the formation of azoarenes by the coupling of aryl radicals and arenediazonium ions are known.12)

In fact, we could trap the diazonium ion intermediate by β-naphthol. The complex of 2b and isopropyl alcohol (1:5) was mixed with β-naphthol (excess), and the mixture (solids) was allowed to stand at room temperature. When the solvent was evaporated from the mixture, the decomposition of 2b occurred to give an azo coupling product, α-phenylazo-β-naphthol, in 59% yield. Similarly, when a mixture of the complex of 2d with benzene (oils) and β-naphthol was allowed to stand at room temperature, α-phenylazo-β-naphthol was formed in 44% yield. A mixture of the complex of 2d with benzene (1:5) and N,N-dimethylaniline gave N,N-dimethyl-4-phenylazoaniline in 21% yield (Scheme 2).

In order to obtain further insight into mechanism of this novel reaction, the following studies were undertaken. The molecular complex of 2b and isopropyl alcohol (1:5) (dec. 54 °C) was allowed to stand at room temperature, and the changes of both weight and NMR spectrum of the complex were measured at several intervals of time (Fig. 1). When approximately three molecules of isopropyl alcohol were evaporated from the complex (ca. 50 min), the crystalline solid slightly deformed (B). When all the solvated molecule was evaporated out (ca. 100 min), 2b decomposed suddenly to give oily substances (D), which contain the compounds 3 - 6 and benz-



Scheme 2.

aldehyde. Photo pictures which show the change of appearance of the crystals, are attached in Fig. 1.

All our observations can be explained by assuming the following mechanism. In a complex, the solvent molecules are located so as to fasten the intramolecular hydrogen bonding between peroxy hydrogen and β-nitrogen of α-azohydroperoxide as indicated in 14.[13-15] This hydrogen bond greatly diminishes the electron donating power of the lone pair electrons of the β-nitrogen atom, which plays a role for the destruction of α-azohydroperoxide in the manner indicated by 15, and so this stabilizes α-azohydroperoxide. When the surrounding solvent molecules are removed from the complex, the hydrogen bond weakens, and hence the electron donating effect of the lone pair electrons of the β-nitrogen atom is activated. This induces the extrusion of diazonium ion (13) from α-azohydroperoxide in the manner indicated by the arrows in 15 (Scheme 2). The diazonium ion (13) generated so far reacts further to give 3 - 6 and/or 7 - 12. Note that the formation of 8 and 9 poses an interesting problem. We consider that these compounds are formed by the coupling of cation radical (17), a resonance form of aryl cation (16),[16] which is generated by the decomposition of 13. Details of this mechanism, however, must be studied further.

The formation of diazonium ions from α-azohydroperoxides in the autoxidation of hydrazones[17] and in photooxidation of arylazonaphthols[18] has been reported. However, the generation of diazonium ions from the solvated complex of α-azohydroperoxide in the manner reported in this paper has no precedent. The present study provides a new route for generating diazonium ions under anhydrous conditions.

This study was supported partially by a Grant-in-Aid for Scientific Research (No. 59340032) from the Ministry of Education, Science and Culture.

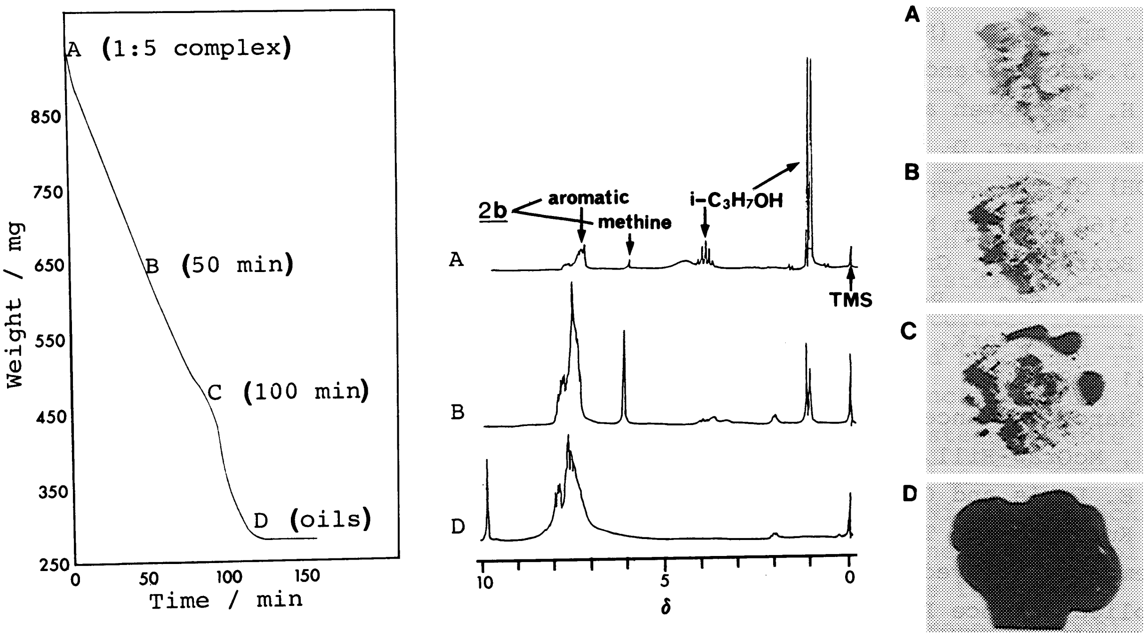
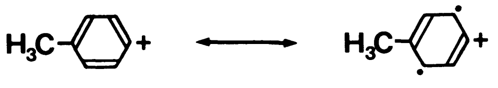


Fig. 1. Changes of weight, NMR spectrum (acetone-D_6), and photo picture of the complex of 2b·i-C_3H_7OH.



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3) When oxygenation of 1 was conducted by the method reported originally by Bush and Dietz (Ref. 1), the solvated molecular complexes of α-azohydroperoxide (2b) were also obtained.
4) The solvated molecular complex of 1:5 described in the text was obtained as follows. Crystals of the molecular complexes of 2b or 2c obtained by recrystallization were taken out first by decanting the solution, and then by transferring the crystals onto a filter paper and air dried for several minutes. The ratio of the solvent in the complex depends on the degree of dryness. The solvated 1:2 and 1:1 complexes were also obtained. They all showed the same decomposition point.
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(Received July 24, 1985)