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The Non-sensitized Photoreaction of Azoxybenzene

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Since Knipscheer[1] reported the photochemical rearrangement of azoxybenzene to 2-hydroxyazobenzene, its rearrangement has been postulated to be intramolecular[2] and, by means of tracer methods, this postulation has been confirmed.[3-5] Through a recent study of the photoreduction of azoxybenzene, Tanikaga concluded that the irradiation of azoxybenzene without benzophenone as a sensitizer never affords azobenzene in an ethanol solution and, thus, that azobenzene is formed from an excited triplet state of azoxybenzene,[6] while the rearrangement product of azoxybenzene and its isomerization product are formed through an excited singlet state of *trans*-azoxybenzene.[7] This paper will describe some different results from Tanikaga's photoreduction product of azoxybenzene and the overlooked irradiation product.

trans-Azoxybenzene was irradiated with a high-pressure mercury lamp in a chloroform (fairly concentrated) solution at room temperature for 113 hr. After the removal of the solvent under mild conditions, the irradiated mixture was chromatographed on silica gel by elution with benzene. In the column, the mixture showed at least eight colored adsorption bands. These components were designated as A, B, C, D, E, F, G, and H in their order of separation. After the removal of the solvent under reduced pressure, petroleum ether was added to each fraction, if possible, in order to crystallize it. Of these eight components, A, B, and G were obtained in a crystalline form. Then high-resolution mass spectroscopic measurements were made of all of these components. The mass spectra of both the products A and F showed a parent peak at 182 *m/e*, a base peak at 77 *m/e*, and similar fragmentational patterns between these peaks in each fragment. Exact mass measurements showed that both A and F had the molecular formula of $C_{12}H_{10}N_2$. On the basis of these results, and also their IR spectra and melting points, the products A and F were deduced to be *trans*- and *cis*-azobenzene respectively, as a similar phenomenon appeared when the mixture of *trans*- and *cis*-azoxybenzene was chromatographed; the former was eluted faster than the latter by benzene. Product B, the main product, was shown to be 2-hydroxyazobenzene from its mass spectral fragmentational pattern, its exact mass measurement (molecular formula, $C_{12}H_{10}N_2O$), its IR spectrum, and its melting point. Product G was postulated to be 4-hydroxyazobenzene on the basis of its melting point and its fragmentational pattern in the mass spectrum, which was extremely analogous to that of the product B. From these two spectra, the relatively intensive fragment, 121*m/e*, could be used to distinguish hydroxyazobenzene from azoxy-[8] and azobenzene. Fraction C was the starting material. For the other products, D, E, and H, the structural analyses attempted using by the method of mass spectroscopic analysis and exact mass measurements were unsuccessful because of impurities present in each case.

In our experimental results, it is interesting that we detected the reductive formation of azobenzene from azoxybenzene and the production of 4-hydroxyazobenzene which results from the unusual photochemical rearrangement of azoxybenzene. First, the formation of azobenzene without a sensitizer leads us to suggest that this may be due to the solvent effect or to the yield of azobenzene being detectable only in a large-scale experiment. Recent studies have progressively clarified the solvent effects on the photochemical pathway;[9] however, more information is required before we can decide that the difference in results between Tanikaga's and ours are due only to the solvent effect. Now, it seems better to consider that the formation of azobenzene had been overlooked because of its low yield. This may also be true for the formation of 4-hydroxyazobenzene. This compound is a well-known Wallach rearrangement

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[3] M. M. Shemyakin, V. J. Maimind and B. K. Vachichunaite, *Chem. & Ind.*, **1958**, 755.

[4] M. M. Shemyakin, T. E. Agadzhanyan, V. J. Maimind, R. V. Kudryavtsev, and D. N. Kursanov, *Dokl. Akad. Nauk. SSSR.*, **135**, 346 (1960).

[5] S. Oae, T. Fukumoto and M. Yamagami, This Bulletin, **34**, 1873 (1961), and *ibid.*, **36**, 601 (1963).

[6] R. Tanikaga, *ibid.*, **41**, 1664 (1968).

[7] R. Tanikaga, *ibid.*, **41**, 2151 (1968).

[8] J. H. Bowie, R. G. Cooks and G. E. Lewis, *Aust. J. Chem.*, **20**, 1601 (1967).

[9] About this see the most recent review; T. Matsuura, *Kagaku no Ryoiki*, **23**, (7) 653 (1969).

product of azoxybenzene[10] upon heating with concentrated sulfuric acid. The photochemical mechanism of its formation suggests that it might be accompanied by an intermolecular reaction or a solvated oxygen atom, one which comes from the reduction of azoxybenzene, with its photoreaction to the extent that azobenzene is produced.

Experimental

As the light source, a UVL-100p (Rikoh Kagaku Co., Ltd.) high-pressure mercury lamp was used; mass spectra and exact mass measurements were performed and measured by means of a JMS-OlSG (Japan Electron Optics Lab.) double-beam focused high-resolution mass spectrometer with an ionizing voltage of 75 eV. The mp's are uncorrected.

Irradiation of Azoxybenzene. The azoxybenzene (Tokyo Kasei, once chromatographed on silica gel before use) (2 g) was dissolved in 25 m*l* of chloroform, sealed in an Erlenmeyer flask, and then irradiated with the lamp for 113 hr at room temperature. After the removal of the solvent under reduced pressure, the mixture was chromatographed on silical gel (Kieselgel, 7734, Merck); upon elution with about 3 *l* of benzene, the eight components described above were separated in aliphabetical order. The yields (in weight) were 6 mg for A, 79.8 mg for B, 1.8 g for C, 3.0 mg for D, 2.08 mg for E, 2.18 mg for F, and 2.68 mg for G (H was not weighed, but it appeared to be almost the same amount as E.).

Product A showed IR absorption bands at 690, 770, 920, 1018, 1065, 1150, 1220, 1300, 1456, 1480, 1580, 1700—2000, and 3030 cm^{-1} (KBr) and fragments in the mass spectrum (relative abundance) at 182 (96.2), 154 (2.9), 105(20.8), and 77(100)*m/e*, and it melted at 67.0—67.5°C (rhombic). These data and exact mass measurements supported the idea that this was azobenzene.

Product B showed IR absorption bands at 670, 750, 760, 805, 910, 930, 990, 1010, 1020, 1060, 1100, 1140, 1180, 1210, 1240, 1280, 1305, 1310, 1360, 1410, 1455, 1485, 1530, 1550, 1595, 1700—2000, and 3030 cm^{-1} (KBr) and fragments in mass spectrum (relative abundance) at 198(100), 121(13.3), 105(4.7), 93(21.7), and 77(37.4)*m/e*, and it melted at 83.5—84.0°C (needles). These data and exact mass measurement supported the idea that this was 2-hydroxyazobenzene.

Product F showed almost the same IR spectrum as A, and its mass spectral fragmentational pattern was quite coincident with that of A. Thus, it was deduced to be a isomer of A, that is, *cis*-azobenzene. Product G melted at 131.8—132.1°C (orange prisms), and its mass spectrum had almost the same characteristic fragments for hydroxyazobenzene as B. Therefore, this may be deduced to be a isomer of B, that is, 4-hydroxyazobenzene. Component C was the starting material; for the other products, D, E, and H, the structural analyses were unsuccessful for the reason presented above.

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[10] O. Wallach and L. Belli, *Ber.*, **13**, 525 (1880).