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DIFFERENT PHOTOLYTIC BEHAVIOR OF 1,3-BIS(α-DIAZOBENZYL)BENZENE IN SOLUTIONS VS. IN CRYSTALS AND MATRICES

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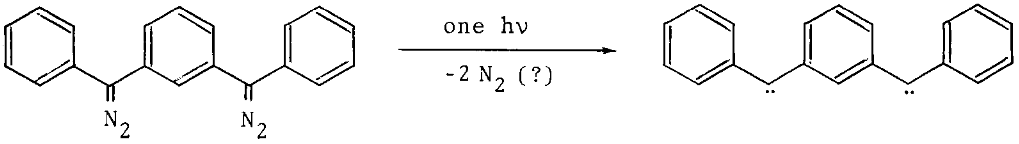
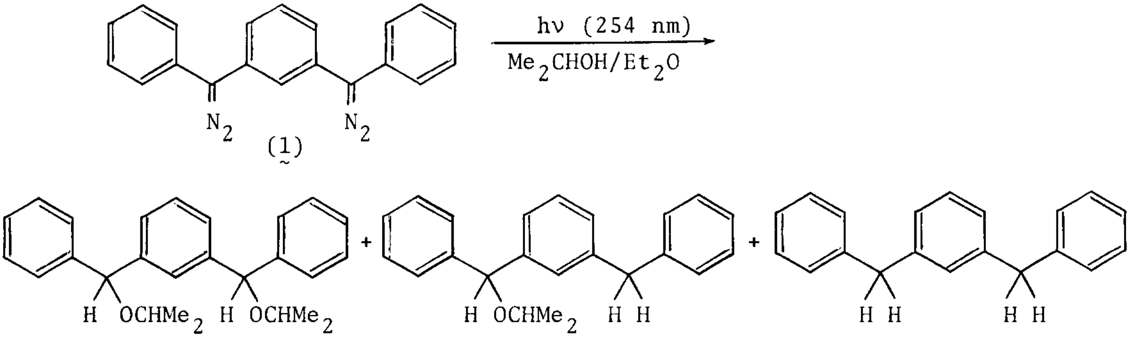
Partial photolysis (25 % conversion) of 1,3-bis(α-diazobenzyl)-benzene (1) in 2-propanol/ether (8:1, v/v) at ambient temperature gave a series of products due to monodiazomonocarbene in addition to unreacted 1, excluding the possibility of the one-photon cleavage of two nitrogen molecules from 1 under these conditions.

Photochemical decomposition of 1,3-bis(α-diazobenzyl)benzene (1) oriented in a single crystal of benzophenone leads to the formation of m-phenylenebis(phenylmethylene) (2) in the ground quintet state.[1] Recently, Itoh and coworkers examined the kinetic behavior of these processes in benzophenone crystals and in rigid glasses at 4.2 and 77 K, and found that the quintet ESR signals were observable as soon as the uv irradiation was started.[2] The rate of formation of the quintet species showed a linear dependence on the light intensity. An isosbestic point was observed when photolysis of 1 in rigid glasses was monitored by uv absorption spectroscopy.[3] It is concluded from these findings that quintet 2 is formed directly from 1 by the one-photon process. Since diazodiphenylmethane is known not to undergo induced decomposition in solution unless decomposed in high concentration to give a large amount of benzophenone azine,[4] the above conclusion raises the question whether the two diazo groups in 1 are cleaved by one photon even in fluid solution. We would like to furnish a negative answer obtained by the product analyses of the photolytic reactions in solution.[5]



(1) (2)

Photolysis of **1** in 2-propanol/ether (8:1, v/v) at room temperature with a low pressure mercury lamp gave the bis(isopropoxy), monoisopropoxymonomethylene and bis(methylene) derivatives (**3**, **4** and **5**, respectively) in a molar ratio of 32 : 9 : 1.[6]

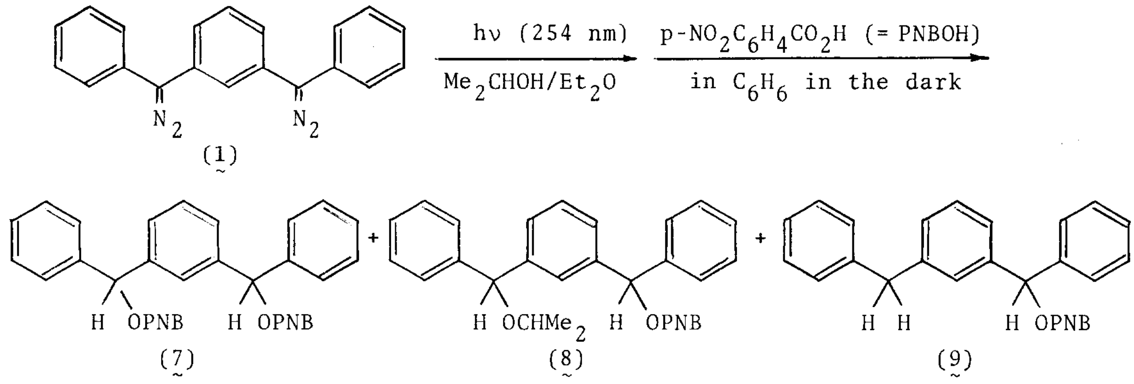


(**1**)

(**3**) (**4**) (**5**)

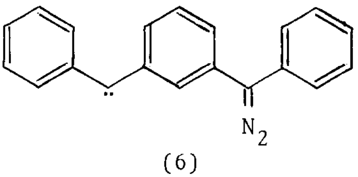
It is well established that photolysis of diazodiphenylmethane in 2-propanol gives diphenylmethyl isopropyl ether and diphenylmethane through the reaction of diphenylcarbene in the singlet and triplet states, respectively, with the solvent molecule.[7] Thus products **3**, **4** and **5** could be formed by either one of the following two mechanisms. One is the formation of singlet carbene **2** by the one-photon process as observed in crystals and matrices, followed by the reaction with 2-propanol in competition with intersystem crossing of **2** to the triplet and quintet states.[5] Alternatively, the products can be obtained by a successive removal of nitrogen molecules with the intermediacy of monodiazomonocarbene (**6**) in the two-photon process. In the latter case, the two sites are considered to react independently. Products **3**, **4** and **5** are ascribed to the doubly singlet (S,S), singlet, triplet (S,T), and doubly triplet (T,T) reactions. If we assume the singlet vs. triplet reactivity ratio[8] at each carbenic center to be 5.5 : 1, the product ratio of **3** : **4** : **5**, namely, (S,S) : (S,T) : (T,T) should be expressed by $(5.5 : 1)^2 = 30 : 11 : 1$, which turns out to be close to the observed ratio.

In order to distinguish between the two mechanisms, a partial photolysis of **1** in solution was carried out. A conversion of the reaction in 2-propanol/ether (8:1, v/v) was monitored by a decrease in absorbance at 520 nm and the irradiation was stopped at 25 % conversion. The unreacted diazo group was allowed to react with p-nitrobenzoic acid in refluxing benzene after evaporation of the original solvent in vacuo in the dark.[9] Gel permeation chromatography[10] of the reaction mixture gave three p-nitrobenzoates **7**, **8** and **9**. Ethers **3** and **4** were not found.[9] Diester **7** (52 %) is undoubtedly due to unphotolyzed **1**.



Monoesters 8 and 9 (in a 6 : 1 molar ratio) are derived from 6 which in turn is obtained by the cleavage of only one nitrogen molecule from 1. The product ratio stands for the singlet vs. triplet reactivity of monocarbene 6 and fits reasonably well with the previously assumed value of 5.5 : 1. Thus the photolysis of 1 in fluid solution is concluded to proceed through 6 and require a second photon for the subsequent reaction to give 2.

How can we rationalize the different photolytic behavior of 1 in fluid solution vs. in crystal and matrix ? When the molecule of 1 absorbs a photon (λ = 254 nm), the photoexcited state is attained which is more than 100 kcal mol^{-1} higher in energy than the ground state. Since removal of a nitrogen molecule is estimated to use the energy not higher than 30 kcal mol^{-1},[11] initially generated 6 will still be in the excited state. In the course of the internal conversion, there could be a chance of the excess energy being transferred to the vibrational mode of the second diazo group to eliminate the remaining N$_2$. In fluid solution, the excess energy in 6 can be dissipated by translational and overall rotational modes. Collision with solvent molecules allows 6 to react to give the monodiazomonosubstituted products (the precursors to 8 and 9). Thus the chance of the nitrogen molecule to leave from 6 would be low in solution. The lifetime of 6 is now estimated to be longer than the reciprocal of its reaction rate with 2-propanol (a few ns at ambient temperature)[12] and shorter than the detection limit of the CW ESR method (a few ms at cryogenic temperature).



(6)

References and Notes

1) (a) K. Itoh, Chem. Phys. Lett., 235 (1967). (b) E. Wasserman, R. W. Murray, W. A. Yager, A. M. Trozzolo, and G. Smolinsky, J. Am. Chem. Soc., **89**, 5076 (1967).

2) K. Itoh, T. Takui, and Y. Teki, Abstract of the 46th Annual Meeting of the

Chemical Society of Japan, October, Niigata, Japan, p. 17 (1982).

3) K. Itoh, H. Konishi, and N. Mataga, *J. Chem. Phys*., **48**, 4789 (1968).

4) T. Onescu, D. Bogdan, M. Contineanu, and G. Balaceanu, *Ber. Bunsenges. Phys. Chem*., **72**, 274 (1968).

5) The decomposition of **1** in the presence of olefins is reported to show non-stereospecific additions (S. Murahashi, Y. Yoshimura, Y. Yamamoto, and I. Moritani, *Tetrahedron*, **28**, 1485 (1972).).

6) The isolated products gave satisfactory analytical and spectral data. Compound **3**: ^{1}H NMR($CDCl_3$) δ 1.16, 1.23 (d, 12H, Me_2C), 3.65 (sept, 2H, $\underset{\sim}{C}HMe_2$), 5.47 (s, 2H, $\underset{\sim}{H}CO^iPr$), 7.2 ~ 7.4 (m, 14H, aromatic). Compound **4**: ^{1}H NMR($CDCl_3$) δ 1.17, 1.18, 1.21, 1.23 (dd, 6H, Me_2C), 3.65 (sept, 1H, $C\underset{\sim}{H}Me_2$), 3.97 (s, 2H, CH_2), 5.45 (s, 1H, $\underset{\sim}{H}CO^iPr$), 7.2 ~ 7.4 (m, 14H, aromatic). Compound **5**: prepared independently from m-dibenzoylbenzene by Wolff-Kishner reduction. ^{1}H NMR($CDCl_3$) δ 3.81 (s, 4H, CH_2), 6.8 ~ 7.2 (m, 14H, aromatic).

7) D. Bethell, G. Stevens, and P. Tickle, *J. Chem. Soc., Chem. Commun*., 792 (1970).

8) The reactivity ratio is given by the ratio of the equilibrium concentrations times the bimolecular rate constants for both species.

9) This procedure was employed to avoid possible decomposition of the remaining diazo group during workup, chromatography and other analytical procedures. Compounds **3** and **4** were warranted by independent experiments to be stable in refluxing benzene in the presence of p-nitrobenzoic acid.

10) Performed on a Japan Analytical Industry Co. Ltd. model LC-09 instrument using JAIGEL 1H and 2H columns with chloroform elution. The isolated products gave satisfactory analytical and spectral data. Diester **7**: ^{1}H NMR ($CDCl_3$) δ 7.03 (s, 2H, $\underset{\sim}{H}COPNB$), 7.2 (m, 14H, aromatic), 8.08 (bs, 8H, PNB). Monoester **8**: ^{1}H NMR($CDCl_3$) δ 1.10, 1.16 (d, 6H, Me_2C), 3.59 (sept, 1H, $CHMe_2$), 5.38 (s, 1H, $\underset{\sim}{H}CO^iPr$), 7.02 (s, 1H, $\underset{\sim}{H}COPNB$), 7.0 ~ 7.4 (m, 14H, aromatic), 8.17 (s, 4H, PNB). Monoester **9**: ^{1}H NMR($CDCl_3$) δ 4.30 (s, 2H, CH_2), 7.02 (s, 1H, $\underset{\sim}{H}COPNB$), 6.8 ~ 7.4 (m, 14H, aromatic), 8.15 (s, 4H, PNB).

11) D. Bethell, D. Whittaker, J. D. Callister, *J. Chem. Soc*. 2466 (1965).

12) Recent studies placed the bimolecular rate constants for the OH insertion of arylcarbenes at ~$10^8\ M^{-1}s^{-1}$. For 9H-fluoren-9-ylidene, chlorophenylmethylene and 10-silaanthracen-9(10H)-ylidene, see respectively: J. J. Zupancic and G. B. Schuster, *J. Am. Chem. Soc*., **102**, 5958 (1980). D. Griller, M. T. H. Liu, and J. C. Scaiano, *ibid*., **104**, 5549 (1982). T. Sugawara, H. Iwamura, H. Hayashi, A. Sekiguchi, W. Ando, and M. T. H. Liu, Abstract of the Symposium on Photochemistry, October, Kanazawa, Japan, p. 375 (1982).

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