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SENSITIZED PHOTOLYSIS OF BENZOYL AZIDE. A NITRENE SINGLET-TRIPLET EQUILIBRIUM

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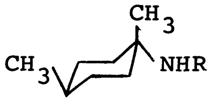
The acetophenone-sensitized photolyses of benzoyl azide in cis- and trans-1,4-dimethylcyclohexanes gave the N-substituted benzamides stereospecifically. The photolyses in 2,3-dimethylbutane showed the same insertion regioselectivity ratio toward the C-H bonds as that of singlet benzoylnitrene in the direct photolysis. These facts indicate the existence of the singlet nitrene despite the triplet photosensitization and provide a chemical evidence for the establishment of a singlet-triplet equilibrium for benzoylnitrene.

Photolyses of acyl azides evolve nitrogen to give the isocyanates and some products derived from the carbonylnitrene intermediates,1) though their thermolyses afford almost quantitatively the isocyanates by the well-known Curtius rearrangement.2) In these photolyses by earlier investigators, the light which can directly excite the azide used has been mainly employed.3) At the present time, a report for the sensitized photodecomposition is lacking. In the acetophenone-photosensitized decomposition of benzoyl azide, we have obtained the results which suggest the existence of the singlet nitrene derived from the triplet. This is the first observation for the spin conversion in the electronic multiplicities of the nitrene.

A dichloromethane (1 mol) solution of benzoyl azide (1, 10 mmol) and a hydrocarbon (1 mol) in the presence of acetophenone (20 mmol) was irradiated, with stirring at 20 °C, by light from a high pressure mercury lamp under an atmosphere of nitrogen. For the purpose of cutting shorter wave length than 320 nm, a $CuSO_4$-NH_3 aqueous solution (120 g of $CuSO_4 \cdot 5H_2O$ in 1 l of 3M-NH_3 aqueous) was circulated as a filter. On the irradiation in the absence of acetophenone, no nitrogen-evolution was observed and no azide-decomposition was indicated by liquid chromatography. Thus, the presence of the filter completely inhibited the direct excitation of 1. The irradiation was continued until the evolution of nitrogen was no longer observed. Separation of the products and determination of the yields were done vapor phase chromatographically, the respective products being identified by comparing their retention times and IR and NMR spectra with those of the authentic samples.4)

The results from the photolyses of 1 in cis- and trans-1,4-dimethylcyclohexanes (DMCH) are listed in Table 1, compared with those from the direct photolyses (mainly by 254 nm).5) Each of the reactions gave N-substituted benzamide (2) and benzamide, while the sensitized photolyses gave no rearrangement product, phenyl isocyanate, in contrast with the direct photolyses. The photolytic Curtius rearrangement proceeds via the photoexcited singlet azide,5,6) but not via the triplet.

Table 1. Photolyses of Benzoyl Azide in cis- and trans-1,4-Dimethylcyclohexanes.

Product (%)a,b)	cis-1,4-DMCH		trans-1,4-DMCH	
	Sensitized	Direct	Sensitized	Direct
	10	9	0	0
	0	0	9	8
RNH_2	22	13	21	12
C_6H_5NCOc)	0	49	0	50

a) Calculated on the basis of the azide used.

b) R ; C_6H_5CO-

c) The isocyanate was separated as its carbamate.5)

Furthermore, the point to be emphasized among the results is that the sensitized photolysis of 1 with either cis- or trans-1,4-DMCH gives only one tertiary benzamide.7) The sensitized photolysis was completely stereospecific in the formation of 2 like the direct photolysis. The direct photolysis produces singlet benzoylnitrene as a primary species, some of which decays to the triplet.3) It has been verified that benzoylnitrene is inserted toward the C-H bonds of hydrocarbons in the singlet state, but that not in the triplet.5) Consequently, the present photodecomposition suggests the existence of singlet benzoylnitrene in spite of the triplet photosensitization. We considered this finding quite surprising and wanted further supporting evidence for the intervention of the singlet nitrene.

The sensitized photolysis of 1 was carried out in a dichloromethane solution of 2,3-dimethylbutane. From the yields of the N-substituted benzamides (2), the regioselectivity ratio was estimated for the primary and the tertiary C-H bonds in 2,3-dimethylbutane, compared with that resulted from the direct photolysis (Table 2). Table 2 shows that the regioselectivity resulted from the sensitized photolysis is essentially the same as that from the direct one. Hence, 2 on the sensitized photolysis must be formed by the insertion of benzoylnitrene having the same electronic multiplicity as in the case of the direct photolysis.

Table 2. Photolyses of Benzoyl Azide in 2,3-Dimethylbutane.

Photolysis	Product (%)a)		Regioselectivity	
	$(CH_3)_2CHCH(CH_3)CH_2$ $\vert$ C_6H_5CONH	$(CH_3)_2CHC(CH_3)_2$ $\vert$ C_6H_5CONH	Primary	Tertiary
Sensitizedb)	1.2	11.4	1	57
Direct5)	1.7	17.0	1	60

a) Calculated on the basis of the azide used.

b) In addition, benzamide was obtained in the yield of 21 %.

Thus, the acetophenone-sensitized reaction of benzoyl azide gives the singlet-derived products. This fact suggests that benzoylnitrene reacts by way of the singlet state in spite of the initially generated triplet, and is a chemical evidence for the establishment of a rapid equilibrium between the lowest singlet and triplet electronic states of benzoylnitrene.

Then the energy splitting between both states should be so small as to allow the thermally reversible mechanism. This energy difference was estimated in value of 7.4 kJ/mol from the total energies of both the lowest states by means of the Electron-Hole-Potential method.8) Such a rapid equilibrium between singlet and triplet electronic states has been indicated also for some arylcarbenes.9,10) The kinetic study gave a singlet-triplet energy splitting of ca. 12 kJ/mol for diphenylcarbene.11)

References

1) W. Lwowski, "Carbonylnitrenes," in "Nitrenes," ed. by W. Lwowski, Interscience Publishers, New York (1970). p. 185, and references quoted therein.

2) S. Patai, ed., "The chemistry of the azide group," in "The Chemistry of Functional Groups," Interscience Publishers, New York (1973).

3) Y. Hayashi and D. Swern, J. Am. Chem. Soc., 95, 5205 (1973); E. Eibler and J. Sauer, Tetrahedron Lett., 1974, 2565; E. Eibler, J. Skura, and J. Sauer, ibid., 1976, 4325; G. R. Felt and W. Lwowski, J. Org. Chem., 41, 96 (1976).

4) The N-substituted benzamides were obtained by condensation of benzoyl chloride with two amino-2,3-dimethylbutanes and two 1,4-dimethylcyclohexylamines, the carbamate was synthesized by reaction of phenyl isocyanate and methanol.

5) M. Inagaki, T. Shingaki, and T. Nagai, Chem. Lett., 1981, 1419.

6) cf. S. Linke, G. T. Tisue, and W. Lwowski, J. Am. Chem. Soc., 89, 6308 (1967).

7) Although the secondary benzamides were detected vapor phase chromatographically, their yields were not determined.

8) S. Yamabe and T. Shingaki, manuscript in preparation.

9) G. L. Closs and B. E. Rabinow, J. Am. Chem. Soc., 98, 8190 (1976).

10) X. Creary, J. Am. Chem. Soc., 102, 1611 (1980); P. P. Gaspar, B. L. Whitsel, M. Jones, Jr., and J. B. Lambelt, ibid., 102, 6108 (1980).

11) Calculated from the energy splitting $\leq$ 3 kcal/mol in Ref. 9.

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