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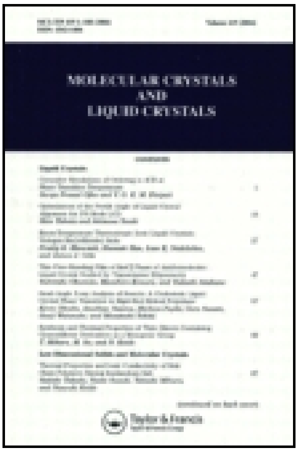

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Chemical Reactivity of p-(Acetyl-N-Methyl)-Aminophenylnitrene in the Crystalline Environment

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CHEMICAL REACTIVITY OF *p*-(ACETYL-N-METHYL)-AMINOPHENYLNITRENE IN THE CRYSTALLINE ENVIRONMENT

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Abstract While some arylnitrenes generated photochemically in crystals of the corresponding azides afforded azo compounds selectively, *p*-(acetyl-N-methyl)aminophenylnitrene **1** yielded an azo compound **AZ** and an insertion product **CH** competitively in the crystalline environment. The selectivity was found to be controlled by the time and the temperature of irradiation. The azo compound **AZ** was produced predominantly (**CH**/**AZ** = 0.64) when UV irradiation was performed at cryogenic temperatures (77 K) for a long time (6 hours). On the other hand, the insertion product **CH** was produced exclusively (**CH**/**AZ** = 9.3), when **2** was irradiated at higher temperatures (around 270 K) for a short time (8 minutes).

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INTRODUCTION

The solid state has recently become the promising organic reaction environment in respect to high selectivity reflecting the three-dimensional regulation of molecular arrangement.[1] We found that some arylnitrenes generated photochemically in crystals of corresponding azides, such as by *p*-carboxy, *p*-acetylamino or *p*-nitrophenyl azide, yielded the corresponding azo compounds exclusively after warming up the photolyzed crystals.[2] The topochemical reactivity was rationalized in terms of the crystal structures of aryl azides. In azide crystals, azido groups are arranged facing to each other in an anti-parallel manner based on the dipolar interaction. This packing pattern is considered to be a common feature for crystal structures of aryl azides, and rationalizes the formation of azo compounds in terms of coupling of facing triplet nitrenes.

In the case of *p*-(acetyl-N-methyl)aminophenylnitrene (**1**) generated photochemically in the host crystal of the corresponding azide (**2**), not only an azo compound (**AZ**) but also an insertion product (**CH**) was produced competitively (Figure 1), through a hydrogen abstraction by nitrene **1** and recombination of the generated radical pair. Here we report how the product ratio was controlled by the time and the temperature of UV photolysis in the crystalline environment.

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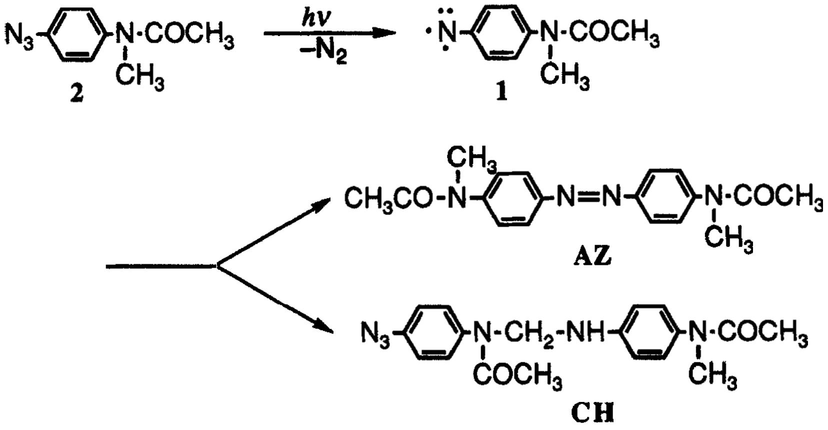

FIGURE 1 Reactivity of *p*-(acetyl-N-methyl)aminophenylnitrene in crystals.

EXPERIMENTAL

Data collections for X-ray crystal structure analysis were performed at room temperature on a Rigaku AFC-5 four-circle diffractometer by using graphite monochromated Mo Kα radiation. The structure of *p*-(acetyl-N-methyl)aminophenyl azide **2** was solved by direct methods and refined by a block diagonal least-square refinement.[3]

Finely ground polycrystals of azide **2** were irradiated by an ultrahigh pressure mercury-lamp in a quartz sample tube for ESR measurement. The temperature was controlled by a temperature controller (JEOL ES-DVT2). After annealing the photolyzed sample at room temperature for an hour, the products were separated by gel permeation chromatography (JAI LC-908), and the structures of products were determined by NMR, IR and mass spectroscopy. The conversion of the reaction was estimated by measuring the recovered azide **2**, and the product ratio was determined by absorption coefficients at 300 nm of each product (**AZ** or **CH**) recorded on a UV-VIS spectrometer (JASCO V-570).

RESULTS AND DISCUSSION

UV photolysis of powdered crystals of *p*-(acetyl-N-methyl)aminophenyl azide **2** afforded nitrenes **1** at a cryogenic temperature. While arylnitrenes in solution undergo a valence-isomerization to afford 3H-azepines predominantly,[4] nitrenes **1** in crystals were found to

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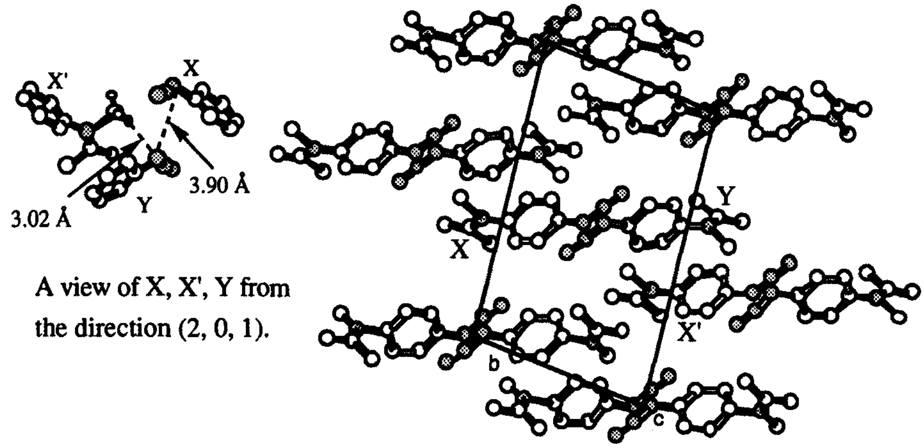
afford not only an azo compound **AZ** but also an insertion product **CH** competitively.



A view of X, X', Y from the direction (2, 0, 1).

FIGURE 2 The crystal structure of *p*-(acetyl-N-methyl)aminophenyl azide **2**.

The difference in reactivity between in solution and in crystals may be rationalized when the crystal structure of aryl azide **2** is taken into account (Figure 2). First, the crystal structure of aryl azide **2** is characterized by the arrangement of azido groups facing to each other to form a head-to-head dimer (X,Y). Incidentally this crystal feature is commonly observed in crystals of aryl azides. Therefore the generated nitrenes **1** in crystals are surrounded by azido or nitreno groups of adjacent molecules, the intermolecular distance between nitrogen atoms alpha to the phenyl ring ($N\alpha$) being considerably short (3.90 Å). Second, the azido group of the molecule Y is located close to an N-methyl group of the molecule X' in the adjacent dimeric pair (X',Y). The intermolecular distance between the nitrogen atom ($N\alpha$) and the N-methyl group of X' is only 3.02 Å, which is much shorter than that between nitrogen atoms ($N\alpha$) of the facing azido groups. As a chemical consequence of nitrene **1** in such a crystalline environment, the generated nitrene **1** may react either with the facing nitrene to afford the azo compound **AZ** through a translational diffusion (path a in Figure 3), or with an N-methyl group of the adjacent molecule to afford the insertion product **CH** through a rotational diffusion (path b in Figure 3) as a result of abstraction and recombination processes.[5]

The relative ratio of the insertion product **CH** *vs.* the azo compound **AZ** was determined to be *ca.* 3:2, when the reaction was terminated at room temperature after photolyzing powdered crystals of azide **2** at 77 K for 1 hour. Since the activation energy for formation of azo compound in a fluid medium is estimated to be *ca.* 0 kcal/mol[6] and that of hydrogen abstraction by arylnitrene is to be *ca.* 10 kcal/mol,[7] the difference in activation energies for both processes in the fluid media can hardly explain the obtained product ratio. In order to discuss factors determining the product distribution in the crystalline environment, the UV photolysis was performed under two different conditions.

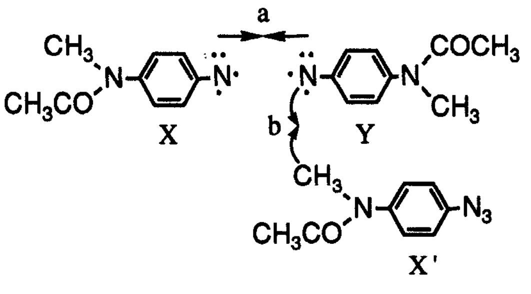


FIGURE 3 Competitive diffusional processes in crystals.

First, the dependence of the irradiation time on the product distribution is examined by changing the length of irradiation time from 20 minutes to 4 hours, keeping the temperature of irradiation at 123 K. After the photolysis, the reaction was quenched at room temperature. The obtained product ratio of **CH** *vs.* **AZ** was found to decrease with increasing the irradiation time (Figure 4a). This peculiar phenomenon may be rationalized when the inhomogeneity of the reaction sites is taken into account. In short irradiation time, the generated nitrene is surrounded by unreacted azides (site A). While after prolonged irradiation, the generated nitrene faces to the nitreno group of the adjacent molecule which is already photo-decomposed (site B). The observed tendency suggests that the insertion product **CH** is formed from site A, and that the azo compound **AZ** is produced only from the site B.

Second, the dependence of the quenching temperature on the product ratio of **CH/AZ** was examined by changing the quenching temperature from 243 K to 293 K, keeping the irradiation time for one hour and the irradiation temperature at 123 K. If the irradiation temperature and time are kept constant, the ratio of site A *vs.* site B should be the same. The product ratio of **CH/AZ**, however, changes depending on the quenching temperature. This suggests that the competitive formation of **CH** and **AZ** may occur at site B depending on the difference in the activation energies of the rotational or translational diffusion processes of nitrene **1**. Judged from the dependence on the product ratio of **CH/AZ**, the activation energy of the rotational diffusion may be larger than that of the translational one. This means the rotational diffusion occur more easily in crystals of **2** at higher temperatures to yield the insertion product **CH**.

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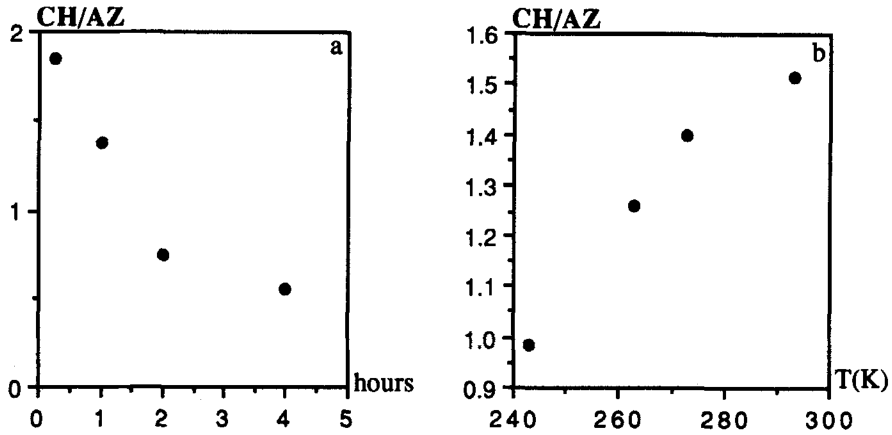

FIGURE 4 a) Dependence of the irradiation time on the product ratio of **CH/AZ**. (irradiation temperature: 123 K, quenching temperature: r.t.)
b) Dependence of the quenching temperature on the product ratio of **CH/AZ**. (irradiation temperature: 123 K, irradiation time: 1 hour)

The dependence of the irradiation time and the quenching temperature on the product ratio may be utilized as a methodology of controlling the product distribution **CH/AZ** in solid state photolysis of crystals of **2**. When UV photolysis is performed at very low temperatures (*e.g.* 77 K) for a long time (*e.g.* 6 hours) and the reaction is terminated at low temperatures (*e.g.* 243 K), azo compound **AZ** is formed predominantly, the obtained product ratio of **CH** *vs.* **AZ** being 0.64. On the contrary, when UV irradiation

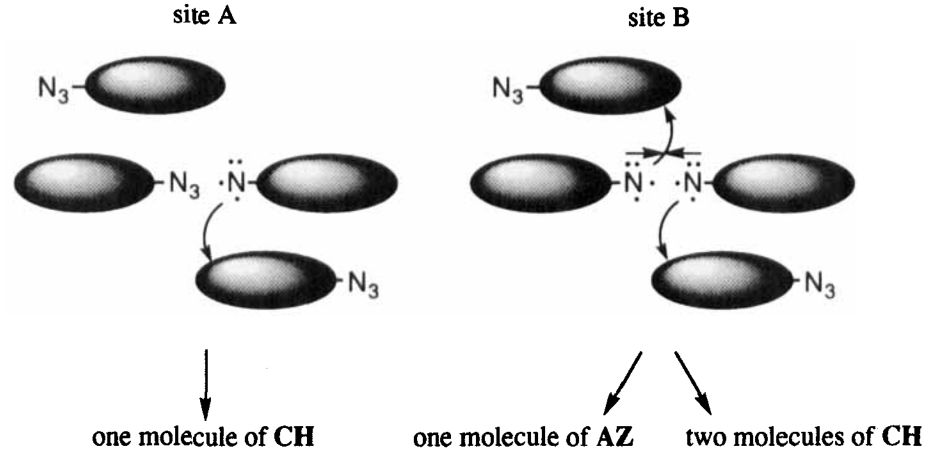

FIGURE 5 Product formation derived from the different sites around the nitrene.

is performed at higher temperatures (*e.g.* 253 **K**) for short period (*e.g.* 8 minutes) and the reaction is completed at room temperature, the obtained product ratio is heavily inclined to the insertion product (**CH/AZ** = 9.3). The control of the product distribution in such a manner is considered to be characteristic of the solid state reaction.

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CONCLUSION

By UV irradiation of the polycrystals of *p*-(acetyl-N-methyl)aminophenyl azide, the azo compound **AZ** and the insertion product **CH** were yielded competitively. We could produce each of two product selectively, by controlling the time of UV irradiation and the temperature of the irradiation of the azide and the quenching temperature of the photolyzed sample. The difference in the environment around the generated nitrenes, in particular, contributes much to the product distribution. The above results strongly suggest that the local reactive environment and the diffusional processes in crystals are the vital factors for determining the reaction path in the solid state.

ACKNOWLEDGMENT

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