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Solid State Bimolecular Photoreaction in a Simple Polycrystalline Mixture of Acridine and Carbazole

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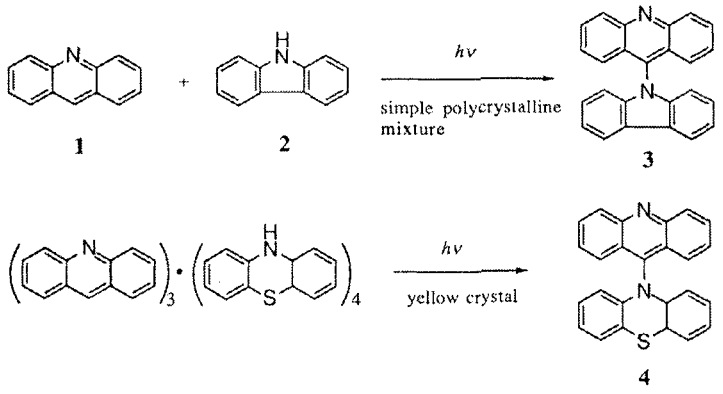
Irradiation of a simple polycrystalline mixture of acridine and carbazole gave a condensation product as a sole product.

Keywords: Solid state bimolecular photoreaction; simple polycrystalline mixture; photoaddition reaction; acridine; carbazole

INTRODUCTION

Development of new solid state bimolecular photoreactions between two different molecules is inevitable for extending the scope of solid state photochemistry. Reactions in two-component molecular crystals [1] occur within the lattice to afford higher specificitity and selectivity than those in simple polycrystalline mixtures [2] at the interface of microcrystals. However, photoreactions in simple crystalline mixtures such as hydrogen abstraction [3], addition [4] and condensation [5] are also valuable from a synthetic aspect. Previously we reported that irradiation of yellow crystal of acridine and phenothiazine caused electron transfer to give a condensation product **4** as a sole product [6]. Herein, occurrence of similar condensation reaction was found in a simple polycrystalline mixture of acridine and carbazole.



1 2 3 4

The crystalline mixture was prepared by dissolving acridine (**1**) and carbazole (**2**) in acetonitrile followed by evaporation to dryness. Measurement of IR and powder X-ray diffraction gave same spectral patterns as the sum of those of both components, confirming to be a simple polycrystalline mixture of **1** and **2**. Despite that crystallization was examined from various solvents such as ethyl acetate and methanol, two-component molecular crystal of **1** and **2** was not formed.

The pulverized mixture (20 mg) was placed between two Pyrex plates and irradiated with a 400 W high-pressure mercury lamp under argon at 15 ℃ for 24 h. The reaction mixture was submitted to HPLC determination to give a condensation product (**3**) [7] as a sole product in 39% yield at 28% and 39% conversion of **1** and **2**, respectively. The molecular structure of **3** was confirmed by X-ray crystallographic analysis (Figure 1) [8].

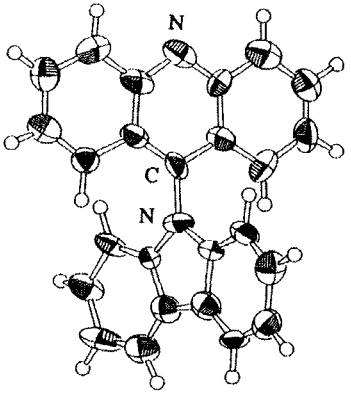


Figure 1. Molecular structure of 3 by X-ray crystallographic analysis.

Photolysis in solution phase was carried out as follows. A solution (100 ml) of **1** (5 mmol) and **2** (5 mmol) in acetonitrile was internally irradiated with a 100 W high-pressure mercury lamp under argon bubbling for 24 h at room temperature. Filtration of the irradiated solution afford biacridane in 20% yield as a solid. After evaporation of the filtrate, the residue was dissolved in THF followed by filtration to give the condensation product **3** in 17% yield. The filtrate was further submitted to preparative silica gel TLC to give **3** in 2% yield.

In the case of the yellow crystal of **1** and phenothiazine, the reaction mechanism could be explained from photoinduced electron transfer and protron transfer process followed by the radical coupling and then dehydrogenation [6]. We obtained the evidence for electron transfer by the successful measurement of the transient absorption spectra of the microcrystals by femtosecond diffuse reflectance spectroscopy and assignment to be acridine anion radical and phenothiazine cation radical [6]. However, clear transient absorption spectra of the microcrystals of **1** and **2** could not be obtained due to the very small amount of anthracene which was contained as an impurity in carbazole reagent. Nevertheless, similar reaction mechanism via electron transfer may be applicable to the simple polycrystalline mixture of **1** and **2**.

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[7] Selected data for **3**: mp 257–259 °C (MeCN); IR (KBr) no NH band; ^{1}H NMR (THF-d_8) δ 8.17–8.42 (m, 4H), 7.62–7.90 (m, 2H), 7.06–7.40 (m, 8H), 6.70–6.83 (m, 2H); UV λ_{max} (5% THF in MeCN) 361 (log ε 4.04), 289 (4.18), 249 nm (5.07). Anal. calcd for $C_{25}H_{16}N_2$: C, 87.18; H, 4.68; N, 8.13. Found: C, 87.58; H, 4.81; N, 8.17.

[8] Crystal data of **3:** yellow prism crystal (MeCN); $M = 344.42$; $0.10 \times 0.10 \times 0.30$ mm; monoclinic; space group $P2_1$; $a = 11.366(1)$, $b = 11.8813(9)$, $c = 12.7956(8)$ Å, $\beta = 93.172(6)°$; $V = 93.172(6)$ Å^3; $Z = 4$; $D_c = 1.326$ g cm^{-3}; GOF 2.47. The structure was solved by direct method (SHELX86) and refined by the full-matrix least-squares procedure to $R = 0.050$ and $R_w = 0.090$ for 2392 independent observed reflectons [$F_0 > 3\sigma(F_0)$] of total 2877 reflections with $2\theta < 120.1°$ using Cu K_α radiation.