

Photochemical Synthesis of 1-Azetines

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Summary Aromatic nitriles react with 2,3-dimethylbut-2-ene photochemically to give stable 1-azetines.

1-AZETINES are a group of uncommon heterocyclic compounds.¹ A simple member of the group, 2-phenyl-1-azetine, was reported to undergo ready decomposition.² 2-Phenyl-3,3,4,4-tetramethyl-1-azetine (**1a**) was suggested as the intermediate in the photochemical addition of benzonitrile (**2a**) to 2,3-dimethylbut-2-ene (**3**) to give the enamine (**4a**).³ However, naphthonitriles were reported not to undergo the analogous reaction, but to give a tricyclic adduct (**5**) instead.^{3,4} Since naphthonitriles form well characterized exciplexes with olefins and dienes,⁵ in connection with our interest on the chemistry of exciplexes,⁶ we re-examined the photochemistry of 1-naphthonitrile (**2b**) with (**3**) and found that the azetine (**1b**) is formed as the major product. Consequently we also re-examined the photochemical reactions of (**2a**) and (**3**) and isolated the azetine (**1a**) as the primary product. These azetines are

crystalline solids which may be sublimed *in vacuo* without thermal decomposition and are stable upon treatment with dilute oxalic acid (0.1%) in ethanol at room temperature (21 °C). Polymethylation of the 1-azetine ring apparently stabilizes the heterocyclic system with respect to decomposition.

A solution of (**2b**) (0.51 g) and (**3**) (7.1 g) in n-hexane (110 ml) was irradiated under N₂ with a Hanovia Hg-arc through a Corex filter. Progress of the reaction was followed by gas chromatography on an SE-30 column. Most of (**2b**) (89%) was consumed after 8.75 h. The composition of reaction mixture at that time consisted of (**1b**), (**2b**), (**4b**), (**5b**),⁴ and (**6b**) in a relative ratio of 35:10:9:28:1 respectively. In contrast to (**1a**), (**1b**) appears to be photostable under the experimental conditions, while (**5b**) is not. Prolonged irradiation yielded a mixture of (**1b**) and (**4b**) in a ratio of 1.3 to 1. The azetine (**1b**) was isolated from the reaction mixture in 30–40% yield by chromatography on neutral alumina, m.p. 96–98 °C

(sublimed); u.v. (cyclohexane) λ_{\max} 243 (ϵ 19,000), 293 (7000), 305 (8200), 318 (5800), and 323 nm (5200); i.r. (KBr) 1680 cm^{-1} (C=N); n.m.r. (CDCl_3) δ 1.46 (s, 6H, CMe), 1.47 (s, 6H, Me), and 7.43–7.94 (m, 7H, ArH); m.s. (70 eV) m/e 237.1510.† The structure of (1b) was confirmed by its hydrolytic cleavage to (7b) which was characterized as its acetyl derivative, m.p. 137°C (benzene–ligroin). Owing to its susceptibility to hydrolysis, samples of (4b) isolated were always contaminated with (6b). However, samples of $> 90\%$ purity were obtained which were characterized by spectroscopic methods, but did not yield satisfactory elemental analysis.

We subsequently examined the photochemistry of (2a) (3.4 g) and (3) (7.4 g) in n-hexane (110 ml). At low conversion (3.5 h), the reaction mixture consisted of (1a), (2a), and (4a) in a ratio of 7:84:9 respectively. The yield of (1a) began to diminish somewhat and the yield of (4a) increased as the irradiation proceeded. After 20 h, the composition of the reaction mixture was (1a):(2a):(4a) = 5:5:54.5:40. The reaction was therefore interrupted after 3.5 h. The evaporated reaction mixture was treated with 0.1% oxalic acid in ethanol at 21°C , in which (1a) was stable while (4a) was completely hydrolysed to (6a). The azetine (1a) was isolated from the hydrolysate by chromatography on neutral alumina: yield 0.29 g [29% based on (2a) consumed]; m.p. $57\text{--}58^\circ\text{C}$ (CH_2Cl_2 –ligroin); u.v. (MeOH) λ_{\max} 245 (15,800) and 287 nm (shoulder, 7400); i.r. (KBr) 1670 cm^{-1} (C=N); n.m.r. (CDCl_3) δ 1.36 (s, 6H, CMe), 1.38 (s, 6H, CMe), 7.43 (m, 3H, ArH), and 7.73 (m, 2H, ArH).

Preliminary investigation on the photochemistry of 2-naphthonitrile (2c) and (3) in n-hexane indicated that both (1c) and (5c) are formed in a ratio of 1.5:1.

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† Unless otherwise stated, satisfactory elemental analyses have been obtained for all new compounds reported in this communication.

¹ For a recent synthesis of 1-azetines, see A. Hassner and A. B. Levy, *J. Amer. Chem. Soc.*, 1971, **93**, 2051.

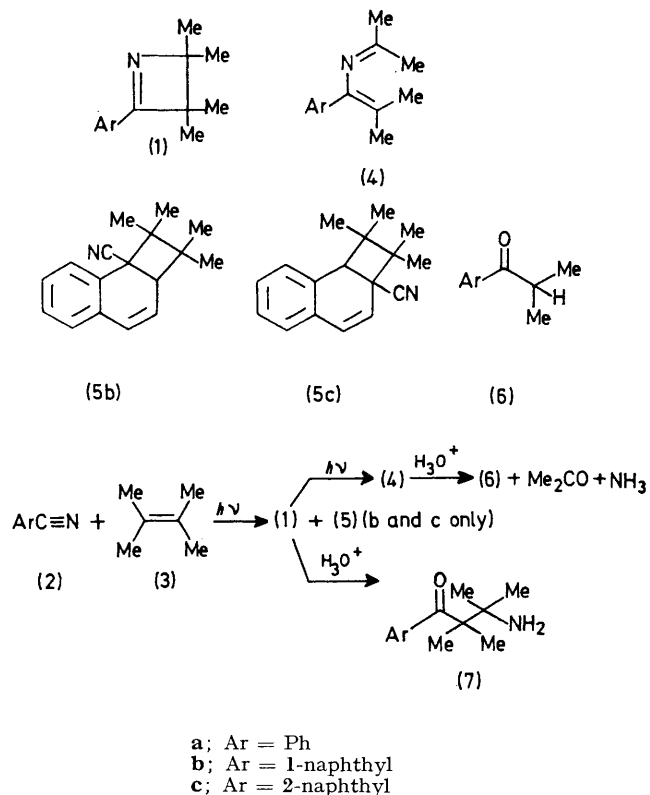
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³ T. S. Cantrell, *J. Amer. Chem. Soc.*, 1972, **94**, 5929.

⁴ J. J. McCullough, R. C. Miller, D. Fung, and W.-S. Wu, *J. Amer. Chem. Soc.*, 1975, **97**, 5942.

⁵ G. N. Taylor, *Chem. Phys. Letters*, 1971, **10**, 355.

⁶ N. C. Yang, D. M. Shold, and J. K. McVey, *J. Amer. Chem. Soc.*, 1975, **97**, 5004; N. C. Yang, K. Srinivasachar, B. Kim, and J. Libman, *ibid.*, p. 5006.



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