Photochemical Synthesis of 1-Azetines

By NIEN-CHU C. YANG,* BONGSUB KIM, WEILONG CHIANG, and TATSUO HAMADA
(*Department of Chemistry, University of Chicago, Chicago, Illinois* 60637)

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 analogus 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 N_2 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, C*Me*), 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—58 °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, C*Me*), 1·38 (s, 6H, C*Me*), 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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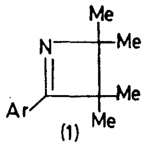
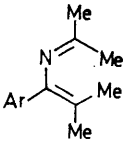

(1)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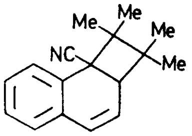
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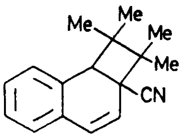
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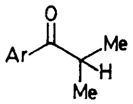
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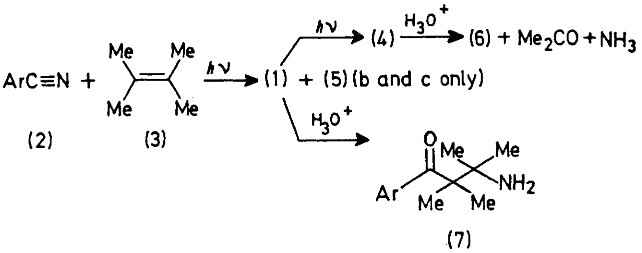

(2) (3) (7)

a; Ar = Ph
b; Ar = 1-naphthyl
c; Ar = 2-naphthyl

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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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