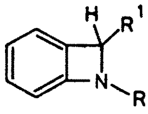
Preparation and Some Reactions of Benzazetidines

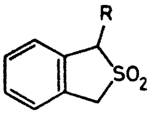
By MICHAEL LANCASTER and DAVID J. H. SMITH*
(*Chemistry Department, University of Leicester, Leicester* LE1 7RH)

Summary Photolysis of sultams (**3**) lead to benzazetidines (**1**) *via* quinonemethane imine intermediates which can be trapped by dienophiles.

BENZOCYCLOBUTANES have been used extensively in the synthesis of natural products, since they readily form *o*-quinodimethane intermediates which can be trapped by intramolecular Diels-Alder reactions.[1] However, the corres-

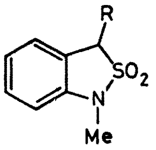


(1)



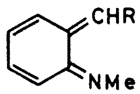
(2)

a; R^1 = H R^2 = Ph
b; R^1 = H R^2 = Me
c; R^1 = Me, R^2 = Me



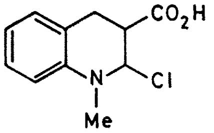
(3)

a; R = H
b; R = Me

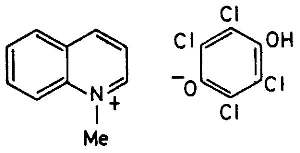


(4)

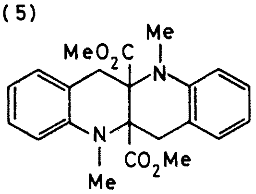
a; R = H
b; R = Me



(5)



(6)



(7)

ponding nitrogen analogues, the benzazetidines (**1**), are little known; only the *N*-phenyl derivative (**1a**) is well described.[2]

One of the more convenient methods of forming benzocyclobutanes involves the thermal extrusion of sulphur dioxide from the sulphones (**2**).[3] We have found that photolysis (300 nm; CH_2Cl_2) of the sultam (**3a**)[4] gave (**1b**) (62%) as a white crystalline material† (m.p. 118—119 °C from EtOH), $\delta(CDCl_3)$: 6·97 (4H, m), 4·73 (2H, s), and 2·23 (3H, s).

That a quinonemethane imine intermediate (**4a**) is involved can be demonstrated by photolysis in the presence of *trans*-chloroacrylic acid. The initial product (**5**) was decomposed by treatment with sodium hydrogen carbonate,[5] the resulting dihydroquinoline being trapped with chloranil as the known salt (**6**).[6] Photolysis of (**3a**) in the presence of dimethyl acetylenedicarboxylate gave a compound $C_{22}H_{24}N_2O_4$ (88%), tentatively formed as (**7**)† (m.p. 124—126 °C from EtOH), *via* further reaction of (**4a**) with the initially formed Diels–Alder adduct. The ^1H n.m.r. data [$\delta(CDCl_3)$: 6·92 (8H, m), 4·82 (2H, s), 4·18 (2H, s), 3·68 (3H, s), 3·53 (3H, s), 2·28 (3H, s), and 2·23 (3H, s)] are best accommodated by assuming that one *N*-methyl is pseudoaxial and the other pseudoequatorial.

Treatment of (**3a**) with potassium t-butoxide followed by methyl iodide afforded (**3b**)[7] (55%) (b.p. 138—140 °C at 0·1 mmHg). Photolysis of (**3b**) gave a mixture of compounds from which *N*-methyl-*o*-aminostyrene was isolated (52%) (b.p. 108 °C at 14 mmHg) which is presumably formed by a [1,5] hydride shift from (**4b**).‡ Flash-vacuum thermolysis (650 °C) of (**3b**), however, produced (**1c**) (61%) (b.p. 86—88 °C at 0·04 mmHg), $\delta(CDCl_3)$: 7·03 (4H, m), 4·87 (1H, q, *J* 6 Hz), 2·30 (3H, s), and 0·89 (3H, d, *J* 6 Hz).

(*Received*, 11*th February* 1980; *Com.* 142.)

---

† All new compounds have correct elemental analysis and mass spectra.

‡ We have observed similar [1,5] hydride shifts on photolysis of compounds (**2**; R = CH_2Ph and $CH_2CH{=}CH_2$), and the results will be published elsewhere.

[1] (a) W. Oppolzer, *Synthesis*, 1978, 793; (b) K. C. Nicolaou and W. E. Barnette, *J. Chem. Soc., Chem. Commun.*, 1979, 1119. (c) T. Kametani, H. Matsumoto, H. Nemoto, and K. Fukumoto, *J. Am. Chem. Soc.*, 1978, **100**, 6218.

[2] E. M. Burgess and L. McCullagh, *J. Am. Chem. Soc.*, 1966, **88**, 1580.

[3] For a review of thermal extrusions of SO_2 see F. Vogtle and L. Rossa, *Angew. Chem., Int. Ed. Engl.*, 1979, **18**, 515.

[4] J. F. Bunnett, T. Kato, R. R. Flynn, and J. A. Skorcz, *J. Org. Chem.*, 1963, **28**, 1.

[5] W. P. Norris, *J. Org. Chem.*, 1968, **33**, 4540.

[6] E. A. Braude, J. Hannah, and R. Linstead, *J. Chem. Soc.*, 1960, 3249.

[7] J. A. Skorcz and J. T. Suh, *J. Heterocycl. Chem.*, 1972, **9**, 219.