

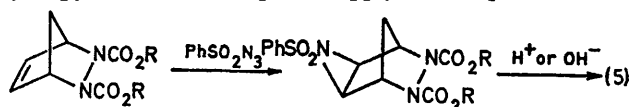
Nuclear Synthesis of 1,4-Dihydropyridines by Rearrangement of Aziridinobicyclo[2,2,1]pyridazine Carboxylates

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Summary The adducts of cyclopentadiene and azodicarboxylate esters were treated with benzenesulphonyl azide producing the fused aziridine derivatives, (4) and (5); hydrolysis of the ethyl ester (4) gave the diazatriacyclene (7) whereas hydrolysis of the t-butyl ester led to the dihydropyridine (9).

process should be amenable toward the synthesis of dihydropyridines. Attempts to apply this sequence to the



(1) R = Et

(2) R = Bu^t

(3) R = Et

(4) R = Bu^t

THE recent report¹ describing the synthesis of divinyl amine derivatives from aziridinosulpholens suggested that this

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latter were fruitless owing mainly to the failure of cyclopentadiene to form a cyclic adduct with sulphur dioxide. The readily available² cycloaddition product (1) from cyclopentadiene and diethyl azodicarboxylate was therefore chosen as a suitable precursor. When a benzene solution

pentane 1:5:1), the aziridine derivative (3) was obtained in excellent yield (97%, m.p. 123–124°; i.r. 1325, 1170, 760 cm⁻¹; m/e 395).[‡]

Treatment of (3) with methanolic KOH (2 h, 65°) produced only the diazatricyclene (6) (93%) [m.p. 180–181°; i.r. 3235, 2850–2600 cm⁻¹; m/e 250 (*M*⁺ – 1)]. The 1,3-elimination process is kinetically too favourable to be intercepted under these conditions. The rapid transformation of (3) into (6) is in marked contrast to the host of products resulting from the alkaline hydrolysis of (1)³ and represents a striking example of the 1,3-*trans*-orientation required for 1,3-elimination reactions.⁴

The *t*-butyl ester (2) (m.p. 99–100°; i.r. 2980, 1740, 1692 cm⁻¹) was synthesised (92%) from cyclopentadiene and di-*t*-butyl azodicarboxylate. Addition of benzenesulphonyl azide to (2) in benzene (20 h, 80°) gave (4) (m.p. 145–147°; i.r. 3048, 1700, 1582) (90%). Removal of the ester function in (4) under acidic conditions, minimised 1,3-elimination owing to protonation of the hydrazine (5). Thus, addition of dry hydrogen chloride to an ethanolic solution of the *t*-butyl derivative (4) containing excess of mercuric oxide afforded the dihydropyridine (8) (m.p. 86–89°; i.r. 3060, 1680, 1630, 1610, 1350, 1185 cm⁻¹) (63%).

This study was supported by the National Institute of Health.

(Received, 21st July 1972; Com. 1268.)

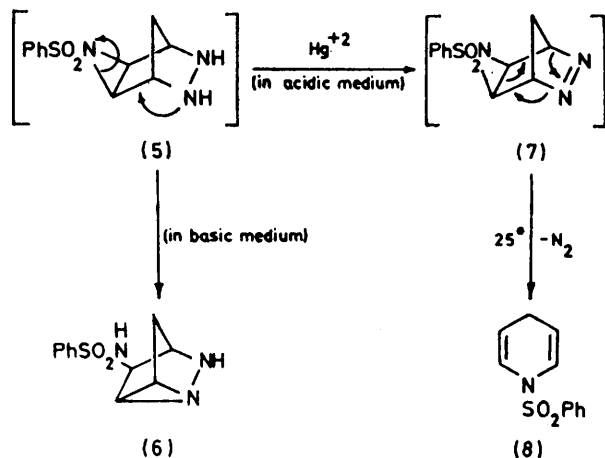
[‡] All new compounds gave satisfactory combustion and n.m.r. spectral analyses.

¹ A. I. Meyers and T. Takaya, *Tetrahedron Letters*, 1971, 2609.

² P. G. Gassman and K. T. Mansfield, *Org. Synth.*, 1969, **49**, 1.

³ S. G. Cohen, R. Zand, and C. Steel, *J. Amer. Chem. Soc.*, 1961, **83**, 2895; In the absence of the bridged methylene group in (2), hydrolysis proceeds normally to the cyclic azo-compounds, J. A. Berson and S. S. Olin, *J. Amer. Chem. Soc.*, 1969, **91**, 778.

⁴ S. Cristol and B. B. Jarvis, *J. Amer. Chem. Soc.*, 1967, **89**, 401.



of (1) and benzenesulphonyl azide was heated (80°, 6 h) and the concentrate chromatographed on silica gel (ether-