

Diazo-compounds in Heterocyclic Synthesis. Aziridine Ring Expansion in a Retro-Diels-Alder Reaction

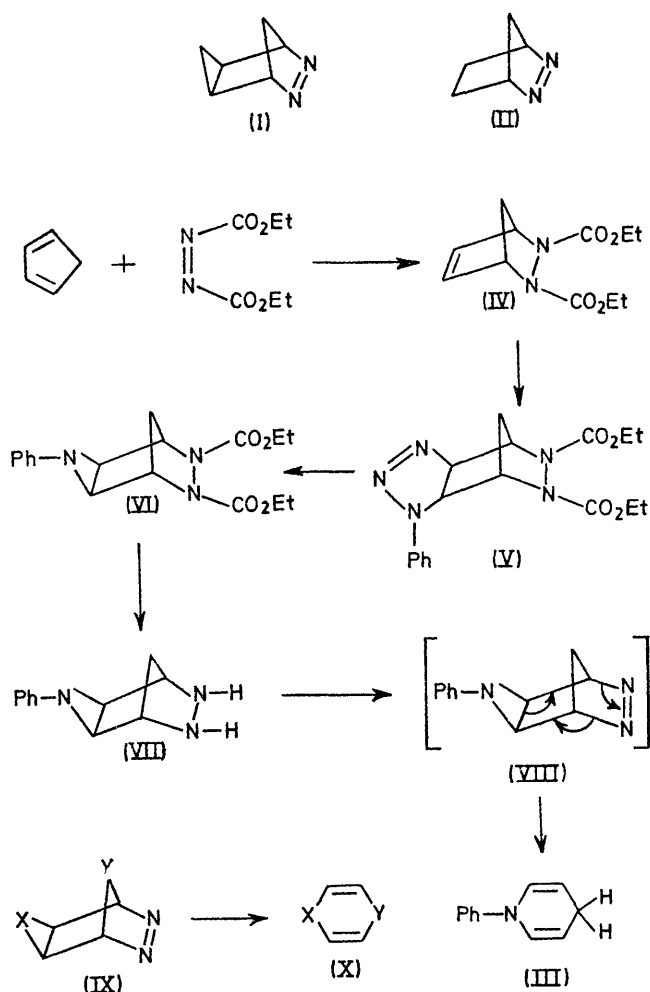
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Summary Hydrolysis and decarboxylation of *exo*-diethyl 3-phenyl-3,6,7-triazatricyclo[3,2,1,0^{3,4}]octane-6,7-dicarboxylate followed by mild oxidation gives *N*-phenyl-1,4-dihydropyridine (50—70%), thus affording a simple route for the conversion of cyclopentadiene into 1,4-dihydropyridines.

THE remarkable rate enhancement of 10^{11} for loss of molecular nitrogen from diazo-compound (I) compared with (II) has been attributed largely to relief of strain and steric interactions on opening the *exo*-cyclopropane ring and the near ideal geometry of the transition state for this ready retro-Diels-Alder reaction.¹ Synchronous loss of nitrogen and double-bond formation from (I) gave 1,4-cyclohexadiene quantitatively. The synthetic potential of this reaction has been developed in a synthesis of semi-bullvalene.²

We now report the conversion of cyclopentadiene into the dihydropyridine (III) (44—61% overall) *via* the analogous aziridine ring expansion. Bicyclic precursor (IV) was prepared from cyclopentadiene and diethyl azodicarboxylate (95%).³ Subsequent 1,3-dipolar addition of phenyl azide to (IV) gave exclusively the *exo*-adduct (V), m.p. 124—125°⁴ (92.5%). Photolysis of this triazoline in acetone (sun lamp; Pyrex filter)⁵ gave exclusively the *exo*-dicarboxylate (VI) (99%), m.p. 124—124.5°; M^+ 331; ν_{\max} (Nujol) 1740 and 1720 cm^{-1} ; δ (CDCl_3) 1.12—1.45 (7H, t, J 7 Hz), 2.00—2.28 (1H, d, J 10 Hz), 2.81 (2H, s), 4.01—4.41 (4H, q, J 7 Hz), 4.85 (2H, s), and 6.72—7.36 (5H, m) p.p.m. Hydrolysis and decarboxylation of (VI) (hot KOH) gave the hydrazine (VII) as an unstable brown oil ν_{\max} (neat) 3240 and 1600 cm^{-1} ; δ (CCl_4) 1.05—1.32 (1H, m), 1.91—2.19 (1H, d, J 10 Hz, further split), 2.33—2.42 (2H, s), 3.26 br (2H, s, disappears on addition of D_2O), 3.69 (2H, s), and 6.58—7.33 (5H, m) p.p.m., which was readily oxidized by oxygen in CH_2Cl_2 or better by yellow mercuric oxide to the dihydropyridine (III) [50—70% from (VI)], presumably by spontaneous decomposition of the diazo-compound (VIII). The product was identical in all respects with that published.⁶



The successful synthesis of (III) suggests that the conversion of (IX) into (X) may have general application to the synthesis of novel heterocyclic systems.

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⁵ Cf. (a) S. McLean and D. M. Findlay, *Tetrahedron Letters.*, 1969, **27**, 2219; (b) P. Scheiner, *J. Org. Chem.*, 1965, **30**, 7.

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