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

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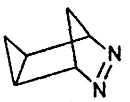
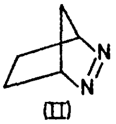
Summary Hydrolysis and decarboxylation of *exo*-diethyl 3-phenyl-3,6,7-triazatricyclo[3,2,1,$0^{2,4}$]octane-6,7-dicarboxylate followed by mild oxidation gives *N*-phenyl-1,4-dihydropyridine (50—70%), thus affording a simple route for the conversion of cyclopentadiene into 1,4-dihydropyridines.

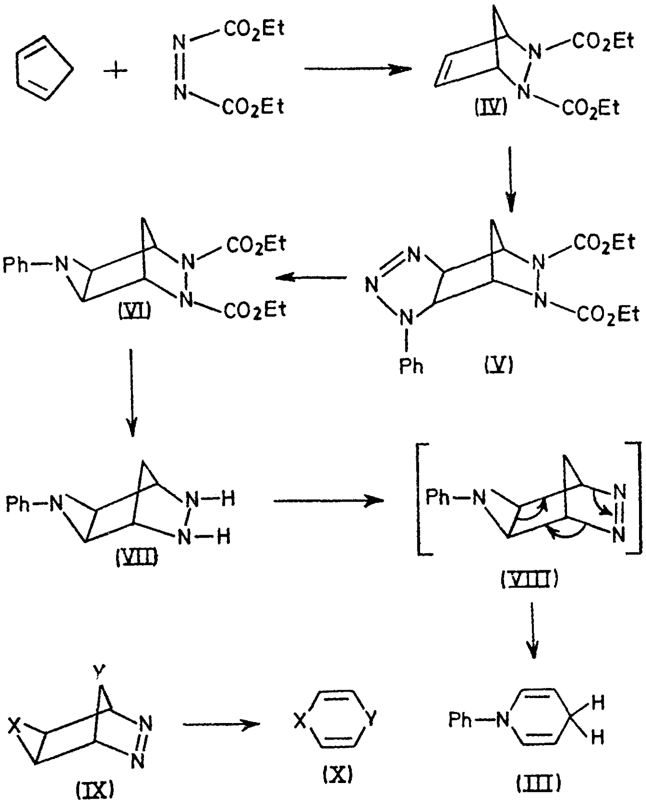
The remarkable rate enhancement of 10^{11} for loss of molecular nitrogen from diazo-compound (I) compared with (II) has been attributed largely to relief of strain and steric interactions on opening the *exo*-cyclopropane ring and the near ideal geometry of the transition state for this ready retro-Diels–Alder 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 semibullvalene.[2]



(I)



(II)



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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