

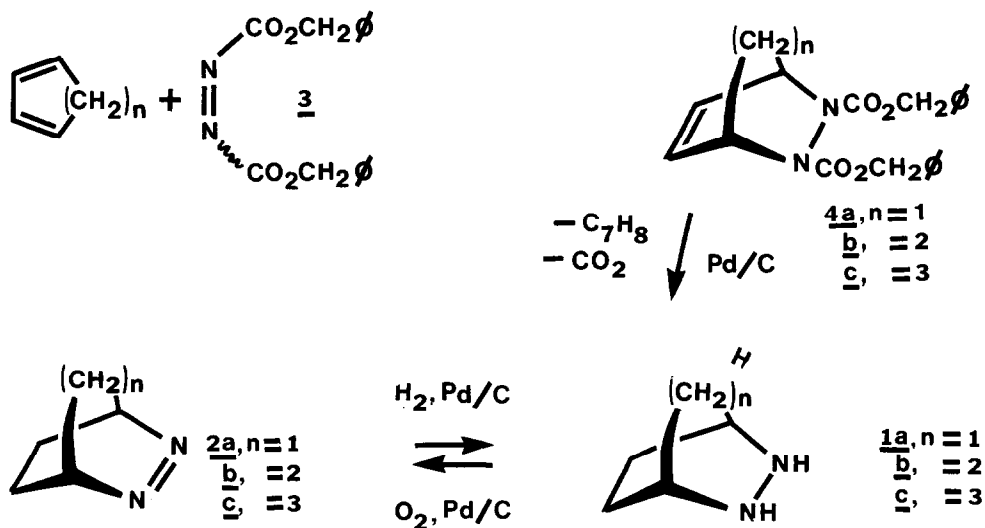
## AN EFFICIENT SYNTHESIS OF BICYCLIC HYDRAZINES AND AZO ALKANES

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Aliphatic bicyclic hydrazines 1 are a class of oxidation-labile compounds (2) usually generated under hydrolytic conditions. Of key importance is their intermediacy in the preparation of cis-azo alkanes 2, substances which serve as thermal (3) and photochemical (4) mechanistic probes, lone-pair interaction models (5), entrants to the excited state (6) and synthetic precursors to a diversity of materials (7). In connection with previous work (8) we should like to report a highly efficient, two-step preparation of bicyclic hydrazines under neutral non-aqueous conditions and their controlled oxidation to the corresponding azo alkane. Furthermore the latter reverts cleanly to hydrazine upon catalytic hydrogenation.



Cyclopentadiene reacts with dibenzylazodicarboxylate (3) (acetone or ether, 10°, 3 hr) to yield adduct 4a (9) (quant., mp 69-70°). Treatment of 4a with hydrogen over catalyst (5% Pd/C, CH<sub>3</sub>OH, 40 lb) proceeds smoothly to provide 2,3-diazabicycloheptane (10) (1a) in quantitative yield (white, low melting solid, nmr (CDCl<sub>3</sub>/TMS  $\tau$ 6.48 (2H, s), 7.2 (2H,s,NH), 8.2-8.8 (6H,m)). In contrast to other reduction systems (11), no secondary N-N bond cleavage of the hydrazine is observed under these conditions.

As is customary for combination of diene rings containing more than five carbons and acyclic azodicarbonyl derivatives cycloaddition is best effected under photochemical conditions which cis-isomerize azodicarboxylate 3 (12). Thus 1,3-cyclohexadiene (hv, pyrex, ether (13), 48 hr) and 1,3-cycloheptadiene (72 hr) combine with azo-ester 3 to give bicycloadducts 4b (90-95%, colorless oil) and 4c (75-85%, mp 108-109°). Hydrogenolysis as described furnishes hydrazines 1b (95%, mp 67-69° (ether-hexane), lit (11) 67-70°; nmr (CDCl<sub>3</sub>/TMS  $\tau$ 6.40 (2H, s, NH), 7.15 (2H, m), 7.8-8.7 (8H, m); dibenzoate, mp 170-171°, lit (12) 171.5-172.5°) and 1c (14) (quant., nmr (CDCl<sub>3</sub>/TMS)  $\tau$ 6.05 (2H, s, NH), 6.60-6.82 (2H, broad s), 7.7-8.5 (10H, m). The present procedure is particularly useful for hydrazines and precursors which may be sensitive to acid, base or temperatures above ambient (15).

Compounds 1a-c are readily oxidized to azo alkanes 2a-c by treatment with a variety of oxidants including air (8). A convenient, and rapid new procedure entails bubbling an oxygen stream into a solution of the hydrazine and a catalytic suspension of 5% Pd/C (CH<sub>3</sub>OH, 10 min). Filtration, solvent removal and sublimation yields azo alkanes 2a-c in 80-95% yields from adducts 4. (2c, 2,3-diazabicyclo(3.2.2)-nonene-2, mp 150-151°; nmr (CDCl<sub>3</sub>/TMS)  $\tau$ 4.75-5.05 (2H, broad s), 7.9-8.6 (10H, m)) (9).

In accord with the absence of N-N bond rupture during the reduction of compound 4, azo derivatives 2 may be hydrogenated over 5% Pd/C (CH<sub>3</sub>OH, 40 lb) to provide hydrazines 1 quantitatively.

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13. Photocycloaddition takes place cleanly in ether avoiding solvent addition processes encountered in THF (12).
14. Unless oxygen is rigorously excluded from the work-up of hydrazines 1a-c, small amounts of azo compounds 2a-c will arise; 2c characterized as the mono-phenyl thiourea (9) (mp 133-134<sup>o</sup>).
15. For example 2,3-diazabicyclo(2.2.1)-7-exo-methylene derivatives (16) are conveniently prepared in this manner; N. Dahlberg (Copenhagen), unpublished work.
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