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THE REARRANGEMENT OF AN α-SUBSTITUTED BICYCLIC NITROSO COMPOUND WITH LITHIUM ALUMINUM HYDRIDE

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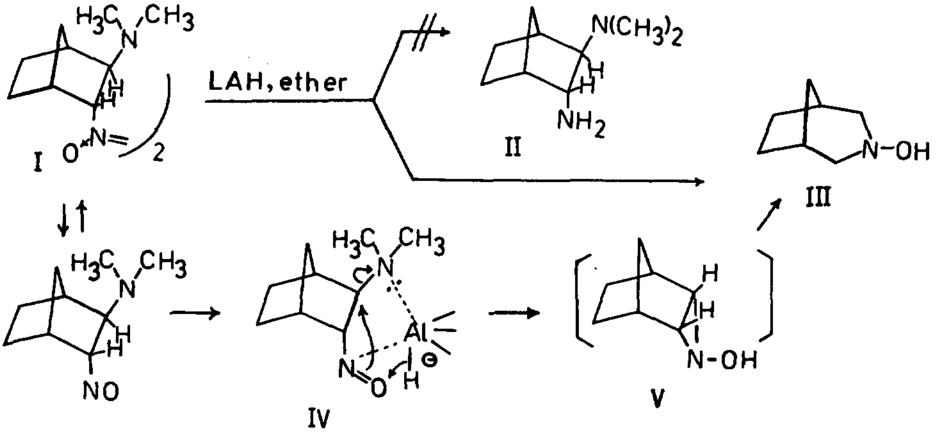
We wish to communicate our work on the novel reduction of *trans*-2-*endo*-3-*exo*-dimethylaminonorbornane dimer (I) with lithium aluminum hydride (LAH). Nitroso dimer I was prepared by one-step light-induced addition of N-nitrosodimethylamine to norbornene (1).

Although LAH has been used successfully for reducing α-substituted nitroso compounds in refluxing tetrahydrofuran to primary amines (1,2), reduction of I under various conditions gave a complex mixture, from which no II could be obtained. However, by adding I to LAH suspension in ether with reflux (1 hr.), the reaction mixture gave, upon chromatography, a skeletally rearranged product N-hydroxyl-3-azabicyclo[3,2,1]octane (III), m.p. 86-87° (40% yield).



Elementary analysis and mass-spectrometric analyses clearly established the molecular formula of III as $C_7H_{13}NO$ (m/e 127). Compound III showed strong ir absorption bands at 3180

(O-H stretching), 1450 (O-H bending), and 1212 cm^{-1} (C-N bending). In the nmr spectrum (Fig. 1), the D_2O exchangeable hydroxyl proton appeared at τ2.4. The pair of doublets at τ6.82 (J=10 Hz, 4 Hz, 2H) and the doublet at τ7.45 (J=10 Hz, 2H) were assigned to exo-protons and endo-protons adjacent to the nitrogen atom, respectively. The two-proton multiplet at τ7.75 was assigned to the bridgehead protons.

Barber and Lunt (3) have demonstrated that tertiary nitroalkanes were reduced to hydroxylamines prior to the rearrangement and subsequent reduction to amines.

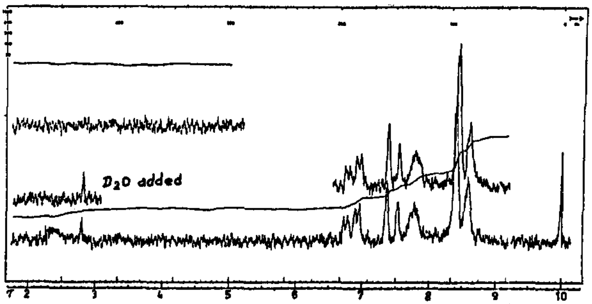


Fig. 1. NMR Spectrum (in $CDCl_3$, 60 Hz) of N-hydroxyl-3-azabicyclo[3,2,1] octane.

Reductive rearrangement of I resembles in part that of 3-nitroisocamphane (4). The unique reductive deamination of I suggests that coordinated complex IV is a possible intermediate in the hydride induced rearrangement of I. The coordination of dimethylamino-nitrogen should facilitate the intramolecular nucleophilic displacement reaction as shown to produce a new C-N bond, and subsequent LAH opening of strained fused aziridine intermediate V (5) leads to the bicyclic hydroxylamine III.

The synthesis of hydroxylamine III and additional work on reduction of α-substituted nitroso compounds is in progress.

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References

(1) Shi-chow Chen, Ph.D. Dissertation, Simon Fraser University, 1970; Y.L. Chow, C. Colón, and S.C. Chen, J. Org. Chem., 32, 2109 (1967).

(2) R. Biela, I. Hahnemann, H. Panovsky, and W. Pritzkow, J. Prakt. Chem., 33, 282 (1966).

(3) H.J. Barber and E. Lunt, J. Chem. Soc., 1187 (1960).

(4) G.E. Lee, W.R. Wragg, S.J. Corne, N.D. Edge, and H.W. Reading, Nature, 181, 1717 (1958).

(5) F.D. Marsh, Fr. Patent 1,383,044 and also Chem. Abstr., 63, 11499h (1965).