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# A NOVEL REACTION FOR SYNTHESIS OF NITROGEN HETEROCYCLIC COMPOUNDS.

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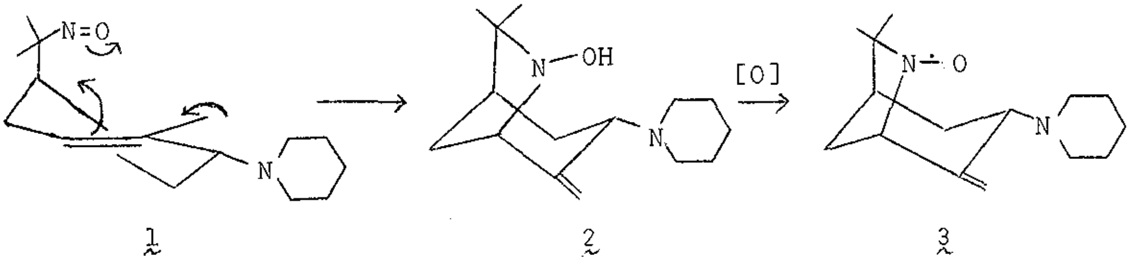
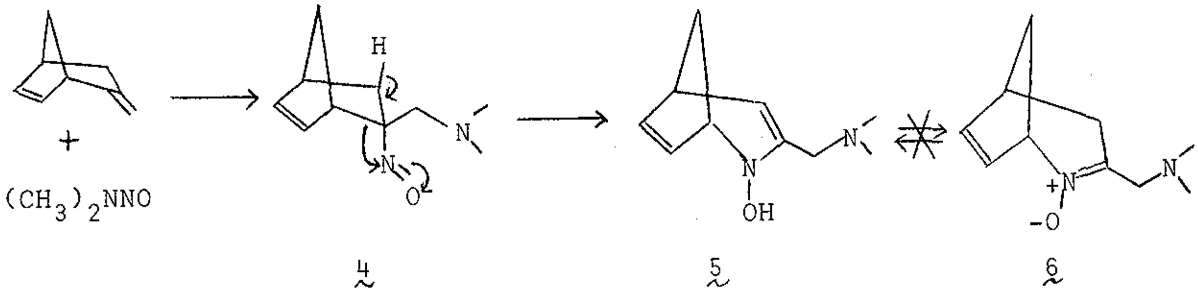
Where stereoelectronic requirements are satisfactorily met for an intramolecular nucleophilic attack of an electron rich center at a C-nitroso group, the C-nitroso compounds rearrange to form the cyclic hydroxylamines.

Some time ago we observed a skeletal rearrangement obviously involving a nucleophilic attack at the nitrogen center of the *tert*-alkylnitroso group (see **1**) obtained during photoaddition of N-nitrosopiperidine to α-pinene.[1] Such nucleophilic reactions at a nitroso group is hitherto unknown and when occurs intramolecularily with a participation of labile π or σ electrons, they are a novel reaction for azapolycyclic synthesis.



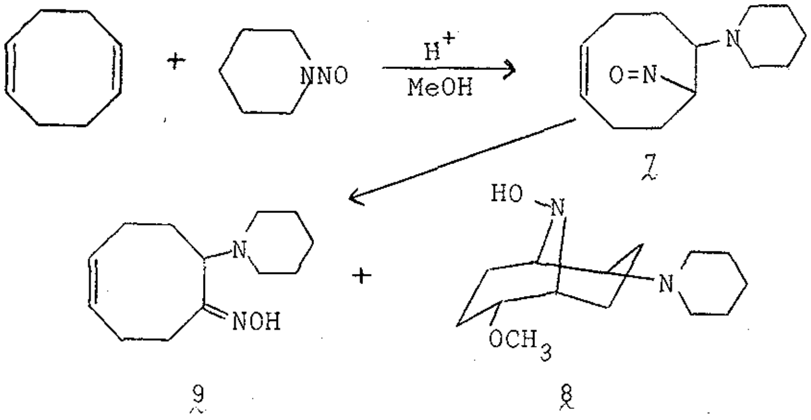
Furthermore, the bicyclic hydroxylamines, such as 2, obtained from the rearrangement are readily oxidized to relatively stable nitroxides,[2] e.g. 3. Unfortunately C-nitroso compounds generally survive only a transient existence in solution owing to their rapid transformation by other pathways.[3] We wish to report cases of the novel azabicyclic syntheses by this rearrangement route which occurs when a transient C-nitroso compound has substantial lifetime.

The tert-C-nitrosoalkene 4 was obviously formed in equilibrium with the corresponding dimer in the photoaddition of N-nitrosodimethylamine to 5-methylenenorbornene as witnessed by the u.v. absorption at 292 nm as well as the blue color of the isolated oil. Nitrosoalkene 4, isolated in 23% yield, rearranged on sublimation at room temperature to hydroxylamine 5. The presence of ene-hydroxylamine group as in 5 was indicated by the proton and $^{13}$C N.M.R. signals at τ 5.15



(m, $H_4$), 169.8 ppm ($C_3$) and 83.7 ($C_4$) from TMS and the u.v. absorption at 243 nm (ε, 1620 in methanol) among other pertinent data. This information also discredited the tautomeric nitrone 6 as the possible structure. Prolonged exposure to the air converted 4 to the corresponding nitroxide radical showing[2] an E.S.R. signal of an equal triplet ($g = 2.0067$, $a_N = 14.25$ G) and, further, to a tar.

Photoaddition of N-nitrosopiperidine to 1,5-cyclooctadiene in an acidified methanol solution gave C-nitroso compound 7 as shown by the corresponding dimeric u.v. absorption at 290 nm for the photolysate. The addition was worked up to give oxime 9 [m.p. 137-138°; 37%; i.r. 3170, 3020, 1640, 1570, 1095, 955, 948, 895 $cm^{-1}$; n.m.r. τ 4.39 (m, 2H), 6.92 (m, 2H), 7.50 (m, 4H), 7.75 (m, 4H), 8.50 (m, 6H)] and the rearranged product 8 [38%, m.p. for the perchlorate 202-203° (decomposition); i.r. 3200, 1110, 1050 and 620 $cm^{-1}$; n.m.r. τ 6.60 (m, 6H), 6.73 (s, 3H)]. Hydroxylamine 8 was oxidized by hydrogen peroxide to give the corresponding nitroxide isolated as a brown solid which showed a triplet ESR signal



($g = 2.0067$, $a_N = 17.25$ G with the line width of 5.5 G). This E.S.R. pattern supports the assigned bicyclic [3.3.1] skeleton rather than the alternative bicyclic [4.2.1] skeleton, since the nitroxides of the latter skeleton generally exhibit distinctive hyperfine splittings with α-hydrogens.

No doubt the rearrangements are facilitated by favorable stereoelectronic factors generated by the disposition of the interacting group in the C-nitroso compounds. It also indicates that a nitroso group can provide a significant electron deficient nitrogen center to accept nucleophilic attacks.

## References

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