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-alkynitroso 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 intramolecularly with a participation of labile π or σ electrons, they are a novel reaction for azapolycyclic synthesis.
Furthermore, the bicyclic hydroxylamines, such as \( \mathcal{Z} \), obtained from the rearrangement are readily oxidized to relatively stable nitroxides, \( \text{e.g.} \ \mathcal{Y} \). Unfortunately, C-nitroso compounds generally survive only a transient existence in solution owing to their rapid transformation by other pathways.

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 \( \mathcal{Y} \) 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 \( \mathcal{Y} \), isolated in 23% yield, rearranged on sublimation at room temperature to hydroxylamine \( \mathcal{Z} \). The presence of ene-hydroxylamine group as in \( \mathcal{Z} \) was indicated by the proton and \( ^{13} \mathrm{C} \) N.M.R. signals at \( \tau \) 5.15.
(m, H₄), 169.8 ppm (C₃) and 83.7 (C₄) 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 an E.S.R. signal of an equal triplet (g = 2.0067, aN = 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

Received, 22nd July, 1976