

A Stable Nitroxide Radical Derived from α -Pinene

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Summary Photoaddition of *N*-nitrosopiperidine to α -pinene gave 6,6-dimethyl-2-methylene-3-piperidino-7-azabicyclo[3,2,1]octan-7-ol which was oxidized by air to the corresponding nitroxide radical.

THE piperidinium radical-initiated photoaddition of *N*-nitrosopiperidine¹ to α -pinene gave the oxime (3), *via*² compounds (1) and (2), in 89% yield[†] at -40°C or lower. However, at 0°C or higher, a mixture of rearranged products

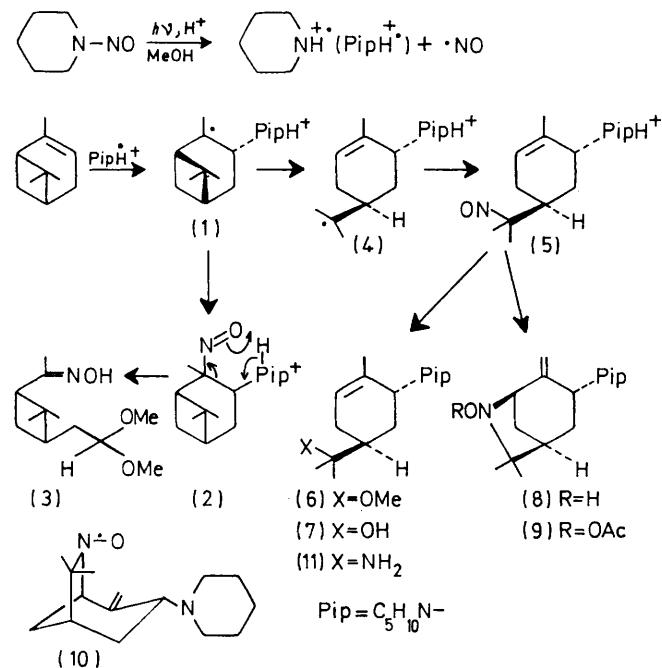
(6), (7), and (8) and other minor compounds[‡] were obtained in addition to a much lower yield of the oxime (3). The scission of the cyclobutane ring, (1) \rightarrow (4), is much more sensitive to temperature changes, in agreement with the characteristics of a stepwise radical reaction.³

The crystalline hydroxylamine (8), m.p. $134\text{--}135^\circ$, (*ca.* 20%) was readily oxidized by air, particularly under basic conditions, to give yellow needles of the nitroxide (10) (e.s.r. spectrum, d of t, $a_{\text{N}} = 14$, $a_{\text{H}} = 8$ G in CCl_4) and it

[†] The isolated products were characterized by their i.r., n.m.r., o.r.d., and mass spectral data.

[‡] Irradiation with a 200 W Hanovia lamp and a Norex filter. The minor compounds included various acid-catalysed rearrangement products of α -pinene. Control experiments showed that (6), (7), and (8) were not derived from these rearrangement products.

was therefore acetylated under nitrogen to (9) which showed a clean n.m.r. spectrum with the expected signals. Brief hydrogenation of the nitroxide (10) over Pt regenerated (8) which showed n.m.r. signals similar to those of (9). The i.r. spectra of (8)–(10) showed the



expected characteristic bands, e.g. for the exocyclic double bond at *ca.* 3090, 1650, and 900 cm^{-1} and for the *gem*-dimethyl group at 1385 and 1365 cm^{-1} . Their mass spectra have, in addition to their respective parent-ion peaks, the common prominent peaks at 233, 176, 174 (piperidinotropylium ion), 150 and 91 (tropylium ion).

Catalytic hydrogenation of (8) or (10) over Pt-black gave dihydro-(8) which was readily oxidized by air to the dihydro-derivative of the nitroxide (10) (e.s.r. spectrum, *d of t*, $a_N = 15$, $a_H = 8$ G in CCl_4). More drastic hydrogenation of (10) yielded (11) and dihydro-(11). The close similarity of the n.m.r. patterns and the intense mass spectral peak at 178 for (6), (7), and (11) support the structural assignments.

Besides undergoing nucleophilic substitution⁴ to give compounds (6) and (7), the *C*-nitroso-compound (5) may also undergo prototropic intramolecular addition of the nitroso-group to the olefin to give (8); both reactions are apparently acid-catalysed. The ring closure in (5) is no doubt facilitated by the ready axial orientation of the nitroso-isopropyl group in so far as the bulky *trans*-piperidino-group tends to assume the equatorial conformation. Nitroxides are excellent spin labels;^{5,6} in particular bicyclic nitroxides have special applicability in labelling crystals owing to the molecular shape.⁷ Furthermore, the presence of the piperidino-group makes nitroxide (10) a potentially valuable pH-dependent spin label.

Financial support and a Bursary award (to H.H.Q.) from the National Research Council of Canada is gratefully acknowledged.

(Received, 11th February 1974; Com. 180.)

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