

STABLE FREE RADICALS XI. PHOTOCHEMISTRY OF A NITRONYL NITROXIDE

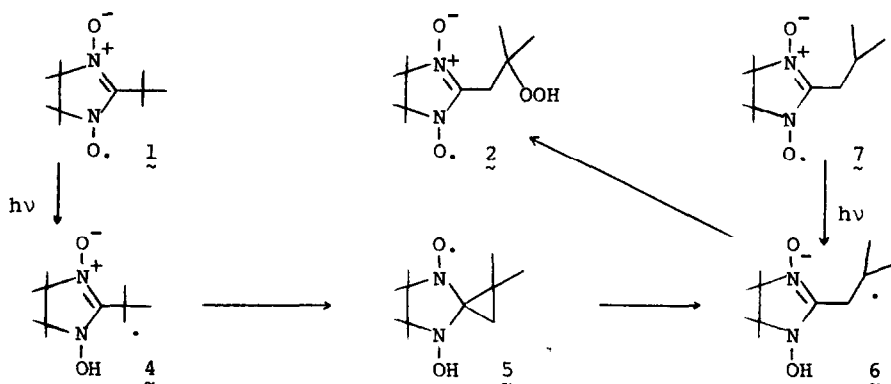
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The photochemistry of organic radicals has received little attention. Notable exceptions are the classical studies on triphenylmethyl radical<sup>2</sup> and recent studies on diphenylpicrylhydrazyl<sup>3</sup> and di-alkylnitroxides.<sup>4</sup> The latter work illustrates an analogy between the photo-elimination of carbon monoxide from 3-cyclopentenone and the photo-elimination of nitric oxide from a 3-pyrroline-N-oxyl, and demonstrates that excitation of both ketones and nitroxides can lead to hydrogen abstraction from solvent. Since both functional groups have lowest energy  $n, \pi^*$  states, nitroxides thus appear to serve as doublet models for ketone photochemistry in which the distinction between singlet and triplet states is lost.

During studies on nitronyl nitroxides<sup>5</sup> we examined the photochemistry of the tert-butyl derivative 1. Splitting of the non-bonding orbitals of 1 results in two  $n, \pi^*$  transitions,  $\lambda_{\max}^{\text{H}_2\text{O}}$  544 nm ( $\epsilon=2330$ ), and 520 (2120). Additional  $\pi, \pi^*$  bands appear at 313 nm ( $\epsilon=18,900$ ) and 304 (13,700). Irradiation of 1 in water (>410 nm light) caused a gradual change of the initial 5-line esr spectrum,  $\underline{a}^{\text{N}(1)} = \underline{a}^{\text{N}(2)} = 8.15\text{G}$ , to a similar spectrum in which each of the five lines were split into a 1:2:1 triplet. The reaction proceeded well in air in the presence of sodium bicarbonate which served to stabilize the products. Preparative photolysis of 100 mg of 1 in 1.5 l of 0.06M aqueous bicarbonate yielded, after tlc separation, 13 mg of recovered 1 and two new radicals, 2<sup>6</sup> (57 mg, mp 94-96°) and 3<sup>6</sup> (8 mg, mp 65-67°). The similar esr spectra of the two compounds [(water) 2,  $\underline{a}^{\text{N}} = 8.17\text{G}$ ,  $\underline{a}_{\text{CH}_2}^{\text{H}} = 1.81\text{G}$ ; 3,  $\underline{a}^{\text{N}} = 8.13\text{G}$ ,  $\underline{a}_{\text{CH}_2}^{\text{H}} = 1.86\text{G}$ ] suggested that they were closely related nitronyl nitroxides bearing methylene groups at the 2-positions. The identical coupling of both methylene hydrogens indicated that the methylenes are probably bonded to symmetrical centers.<sup>5,7</sup> Further support for these

structures was obtained by the quantitative conversion of 2 to 3 with triphenylphosphine, by similar ultraviolet and visible spectra of 1, 2 and 3, and by X-ray analysis of 2.<sup>8</sup>

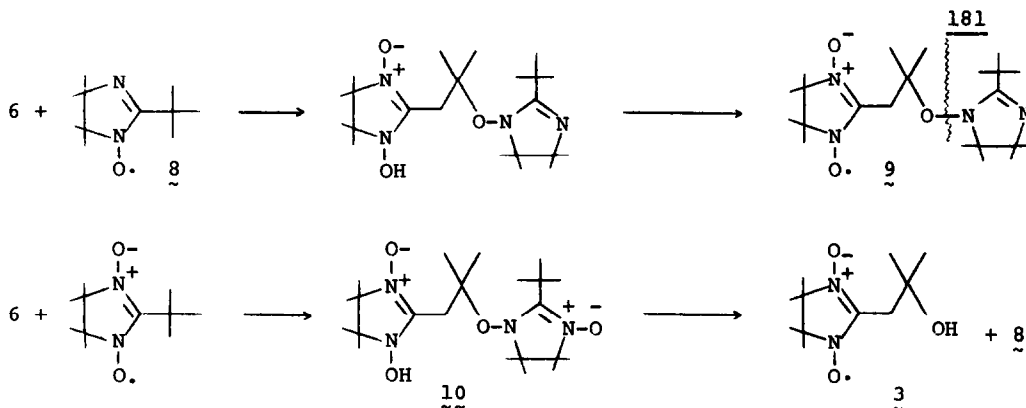


The formation of the peroxide 2 is satisfactorily explained by conversion of 1 to the cyclopropyl nitroxide 5 by light-induced hydrogen abstraction from the tert-butyl group. Tert-butyl benzoquinone undergoes an analogous reaction to give a spiro[2,5]octane intermediate,<sup>9</sup> and intramolecular radical trapping by the nitronyl group in 4 has ample bimolecular precedents.<sup>10</sup> The cyclopropane 5 presumably undergoes spontaneous ring opening to give carbon radical 6 which reacts with oxygen to form the hydroperoxide 2.

The intermediacy of 6 was consistent with the observation that irradiation of the isobutyl nitronyl nitroxide 7<sup>11</sup> under identical conditions yielded about the same ratio of 2 to 3 (75% total yield). Furthermore the carbon radical 6 could be trapped by irradiation of 1 in deoxygenated water in the presence of  $7 \times 10^{-4}$  M imino nitroxide 8.<sup>11</sup> The trapping product was isolated in its oxidized form 9<sup>6</sup> in 15% yield, mp. 132-134°, esr (water)  $a_{N(1)} = a_{N(2)} = 8.05\text{G}$ ,  $a_{CH_2}^H = 1.82\text{G}$ . The appearance of C=N absorption at  $\nu_{\text{max}}^{CCl_4} 1615 \text{ cm}^{-1}$  (present in imino nitroxides<sup>11</sup> but not in nitronyl nitroxides<sup>5</sup>) and the appearance of important mass spectral fragments at 181.1686 ( $C_{11}H_{22}N_2$ ) and 182.1763 ( $C_{11}H_{23}N_2$ ) provide good support for 9.

Further evidence for the intermediacy of 6 was obtained by carrying out the irradiation of 1 either in degassed solutions or at higher concentrations. Similar product composition was obtained in both cases. In degassed water 100 mg

of 1 yielded 18 mg of the alcohol 3, 9 mg of 8, 5 mg of adduct 9, 4 mg of 1, CH<sub>3</sub> in place of C(CH<sub>3</sub>)<sub>3</sub>, and 17 mg of recovered 1. The appearance of significant amounts of the alcohol 3 and imino nitroxide 8 suggests that 3 is formed by trapping of the carbon radical 6 by starting nitronyl nitroxide 1, and that the resulting adduct 10 undergoes spontaneous fragmentation. The possibility



that in the presence of air 3 is formed by a dark or photo-reaction of the peroxide 2 could be discounted since 2 gave no 3 under the photochemical reaction conditions.

It is interesting that the isobutyl nitronyl nitroxide 7 was not formed on irradiation of 1, nor was 1 formed on irradiation of the isobutyl derivative. Moreover irradiation in deuterium oxide failed to give mass spectroscopically detectible deuterium incorporation into the starting materials. The failure of the carbon radical intermediates 4 and 6 to revert to their nitronyl nitroxide precursors may be attributable to hydrogen bonding stabilization of the hydroxyl hydrogen by water. Similar hydrogen bonding stabilization of 1,4-diradicals formed in the type II photochemistry of ketones has been invoked to explain the marked solvent effects on these reactions.<sup>12</sup> The observation that the above reactions are largely suppressed in non-hydroxylic solvents<sup>13</sup> supports this view and suggests that 4 and 6, when formed in non-hydroxylic solvents, undergo intramolecular hydrogen atom transfer more rapidly than they undergo intramolecular radical addition to the nitrone grouping.

## REFERENCES

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