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CHEMISTRY OF SINGLET OXYGEN. XXII.
PHOTOOXIDATION OF NITRONES[1]

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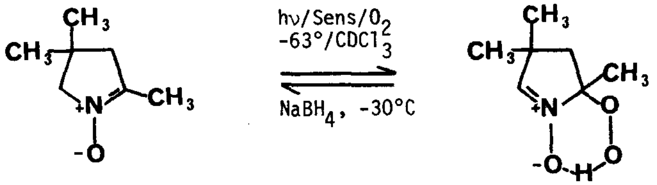
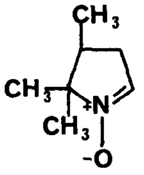
Singlet oxygen is known to undergo a 1,4-cycloaddition reaction with dienes analogous to the Diels-Alder reaction[2]. A recent communication[3] reported that it can also undergo a 1,3-dipolar addition reaction with diazomethane, an extremely reactive species. We wish to report our results on the photooxygenation of some stable 1,3-dipolar reagents, aldo- and ketonitrones[4].

2,4-4-Trimethyl-Δ^1-pyrroline-N-oxide[5] (I) was photolyzed in $CDCl_3$ solution containing 2×10^{-5} M methylene blue as sensitizer at -63°C ($CHCl_3$/Dry Ice bath, 650 W DWY Tungsten-Halogen lamp with 3% $K_2Cr_2O_7$ filter, cutoff 550 nm). The conversion of I to II was quantitative, with uptake of one mole of oxygen.



I   II



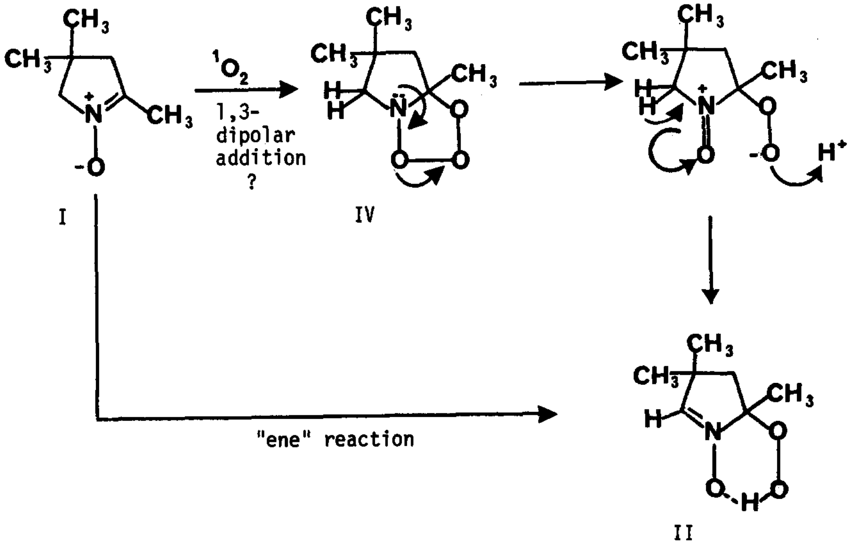
III

The structure of II was assigned by the nmr of the solution at -55° (Varian HA-100): δ 1.27 (3H, s), 1.33 (3H, s), 1.61 (3H, s), 2.37 (center of AB quartet, 2H, δ = 65 Hz, J = 14 Hz); 7.08 (1H, s), 13.60 (1H, s). After solvent removal, the product (II), obtained as a white solid, was stable at 0°C for *ca* ~5 min, but decomposed violently with gas evolution on warming to room temperature or upon contact with silica gel. The decomposition products have not been characterized but vary with decomposition temperature.

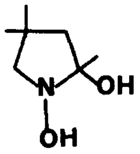
Reduction of II by $NaBH_4$ at -30°C gave back I quantitatively; nmr (Varian T-60); δ 1.11 (6H, s), 2.00 (3H, quintet, J = 1.6 Hz), 2.50 (2H, quartet, J = 1.6 Hz), 3.72 (2H, quartet, J = 1.6 Hz); mass spectrum, parent ion at m/e = 127. Warming II in the presence of tetramethylethylene did not give any detectable oxidation product of the olefin.

After photooxidation under comparable conditions, 4,5,5-trimethyl-Δ^1-pyrroline-N-oxide[5] (III) in which two methyl groups replace the reactive methylene hydrogens at the C5 position in I, was recovered unchanged, and no O_2 uptake was observed.

The mechanism of the reaction is probably a "conventional" singlet oxygen ene reaction, rather than a 1,3-dipolar cycloaddition, although such ene reactions on double bonds containing heteroatoms are rare. A 1,3-dipolar mechanism would give a five membered ozonide-like intermediate (IV) which could then undergo further reaction to give the observed product. Failure to observe any such product in the case of III, where rearrangement would be blocked, casts doubt on this explanation, but does not rule it out completely.



The reduction, although somewhat surprising at first glance, presumably involves reduction of the immonium and hydroperoxide functions in II, followed by loss of water from the intermediate carbinolhydroxylamine (V).



V

The rates of chemical reaction (k_r) and physical quenching (k_q) of singlet oxygen with I and III were determined by the competitive inhibition of the first-order photooxygenation of diphenylisobenzofuran, (DPBF) followed by DPBF fluorescence, a technique developed by Young et al[6] and described in detail earlier.[7,8] Studies were carried out in $CHCl_3$ over a concentration range of I and III of 0.4 - 4 x $10^{-3}\underline{M}$ and an initial DPBF concentration of 2 x $10^{-6}\underline{M}$, sensitized by methylene blue (2.5 x $10^{-6}\underline{M}$). The kinetic plots are shown in Fig. 1. For I, $k_r + k_q$ = 2.1 x $10^7\underline{M}^{-1}s^{-1}$ and for III, k_q = 5 x $10^7\underline{M}^{-1}s^{-1}$.[9] Thus III quenches $^1O_2$ efficiently even though it fails to react at all. The mechanism of this quenching is probably a charge transfer interaction analogous to that proposed with electron-rich compounds such as amines[10] and phenols[7], although formation of an unstable adduct analogous to IV followed by its breakdown to starting materials is not ruled out.

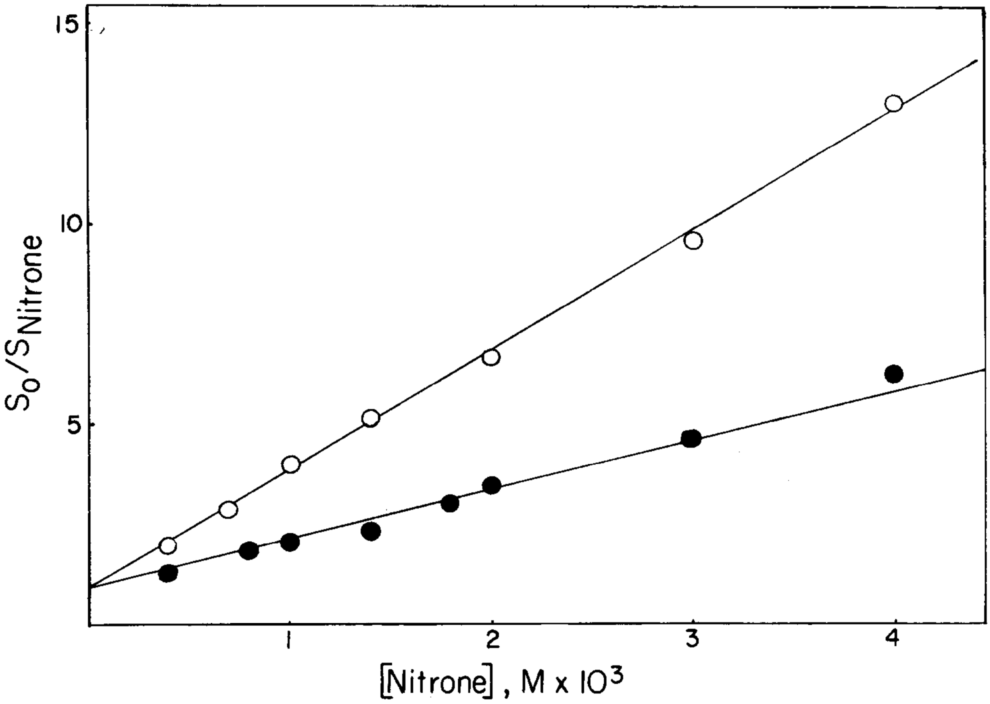


Fig. 1. Slope of first order plot of disappearance of diphenylisobenzofuran (DPBF) in absence of nitrones (S_0) divided by slope in their presence (S_N) as a function of nitrone concentration [●, compound (I); ○, compound (II)].

The reaction is shown to be a singlet oxygen reaction by the fact that oxygen was not consumed when either the light or the sensitizer was absent and that an excellent first order inhibition of the photooxidation of diphenylisobenzofuran[7,8,11] by I and III was observed. The present results neither confirm nor refute the earlier report[3] which proposed a 1,3-dipolar adduct as the intermediate for the reaction of singlet oxygen with diazomethane. Further studies are under way.

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