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# CHEMISTRY OF SINGLET OXYGEN. VI.

## PHOTOOXYGENATION OF ENAMINES: EVIDENCE FOR AN INTERMEDIATE (1).

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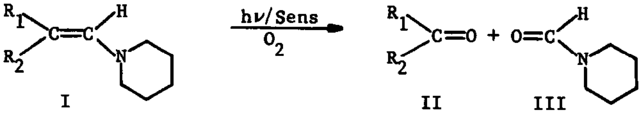
Photooxidation of heterocyclic bases is of interest because of the relationship to the mechanism of "Photodynamic Action", the toxic effect on organisms of certain photosensitizers, light, and oxygen (4). Since the only isolable photooxidation products of many heterocyclic compounds are extensively degraded (4,5), we are studying enamines as models for more complex systems, in the hope of elucidating the chemistry of the primary photooxidation steps. Enamines (I) prove to be excellent substrates for dye-sensitized photooxygenation; the C-C double bond is cleaved to give a ketone or aldehyde (II) and an amide (III) (6,7a).



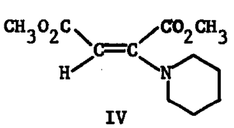
(a) $R_1 = R_2 = CH_3$

(b) $R_1 = R_2 = C_6H_5$

(c) $R_1 = C_6H_5$, $R_2 = H$

Thus Ia produced acetone and N-formylpiperidine (III) in 96 and 100% yield respectively, Ib gave benzophenone and III (90 and 90%), and Ic gave benzaldehyde and III (48 and 49%); unidentified non-volatile compounds are also produced in the latter case. Photooxygenations were carried out in benzene using zinc tetraphenylporphine as sensitizer; the apparatus has been described (8). Oxygen uptake was rapid and ceased abruptly after one mole $O_2$ per mole of enamine had been taken up. Absolute yields quoted are based on enamine and were determined by g.l.c. using an internal standard; products were characterized by spectroscopic and gas-chromatographic comparison with authentic materials. Addition of 0.1 M 2,6-di-*t*-butylphenol, a good free-radical inhibitor, produced no effect either on $O_2$ uptake rate or on product yield in photooxidations of Ia or Ic.

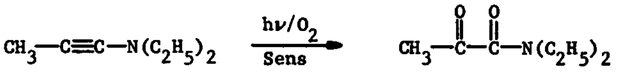
Under the same conditions, enamine (IV)(7b), and β-methoxystyrene (V) (7c), both of which have double bonds which are less electron-rich than those of enamines Ia-c, failed to produce cleavage. However, N,N-diethyl-1-propynylamine (VI) (7d) smoothly took up one mole of oxygen to give N,N-diethylpyruvamide (VII) in a reaction analogous to the cleavage of Ia-c.



IV

$C_6H_5CH{=}CHOCH_3$

V



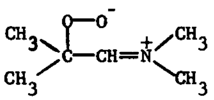
$$CH_3{-}C{\equiv}C{-}N(C_2H_5)_2 \xrightarrow[\text{Sens}]{h\nu/O_2} CH_3{-}\overset{O}{\overset{\|}{C}}{-}\overset{O}{\overset{\|}{C}}{-}N(C_2H_5)_2$$

VI VII

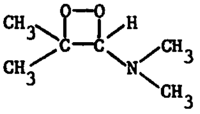
Photooxygenation of β-piperidinostyrene (Ic) was carried out at -60° in $CH_3OH$-$CH_2Cl_2$; $NaBH_4$ was added to the cold solution, and the resulting suspension allowed to warm to room temperature. From this solution, a 72% yield (after sublimation and recrystallization) of 2-N-piperidino-1-phenylethanol (VIII), m.p. 69.5-70° (reported (9) 67-69°) was isolated. If the photooxygenation was carried out at room temperature and the resulting solution reduced with sodium borohydride, no appreciable amount of VIII could be detected.

Photooxygenation of N,N-dimethyl isobutenylamine (IX) was carried out at about -60° in $CDCl_3$ until reaction was complete. The nmr spectra of the resulting solution showed no gross change between -60° and -21°, except that broad resonances split into sharp multiplets. At -21°, the nmr spectrum showed, along with resonances (2.22 δ, 2.98 δ, 8.12 δ) caused by a calculated 6.5% conversion to the final products acetone and dimethylformamide, new resonances at 4.5-5.0 δ (1H) 2.4-2.6 δ (6H), and 1.1-1.7 δ (6H). On warming the solution to room temperature, this spectrum was replaced within twenty minutes by a spectrum which showed only resonances attributable to acetone and dimethylformamide (~90% yield by peak areas), along with minor resonances attributable to 10% of a byproduct. Similar behavior was observed with photooxidized solutions of enamines Ia and Ic, but the spectra were more complex.

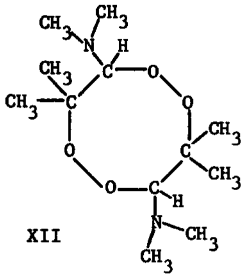
These experiments demonstrate that an intermediate is formed which retains the C-C bond and is oxygenated at least on the position $\beta$ to the nitrogen. This intermediate is stable at low temperatures and breaks down to the observed products near room temperature. The nmr spectrum of the intermediate from IX is not consistent with either of the two most likely structures X and XI. The resonances near 5 and 2.5$\delta$ are at too high field for the aldimmonium C-H and $\overset{+}{N}CH_3$ in X, while the complexity of each of the resonances is inconsistent with the sole presence of compound XI, in which all resonances should be sharp singlets near the observed positions, except that the two $C\text{-}CH_3$ groups would be magnetically nonequivalent. Possibly dimeric or polymeric species are present, perhaps formed from X or XI; a possible structure for a dimer would be XII, which has several configurational and conformational isomers, and could account for the complexity of the spectra and their temperature dependance (10). Further experiments will obviously be required.



X



XI



XII

A zwitterionic intermediate analogous to X has been suggested by Matsuura to account for unusual cleavage products in the photooxygenation of purine derivatives (11); either XI or XII should cleave in the same way; such cleavage has ample analogy (12). Formal 1,2 cycloaddition of this sort contrasts with the normal mode of photooxidative addition of oxygen to olefins which produces allylic hydroperoxides, apparently by a cyclic, non-polar transition state similar to that of the "ene" reaction (13). However, enamines are known to react with many dienophiles to give net 1,2 cycloaddition (14).

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