Reaction of Singlet Oxygen with Pseudopelletierine and Tropinone

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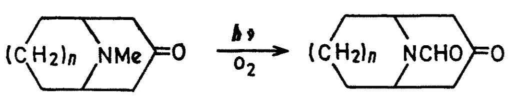
Summary The oxidation of *N*-methyl groups in pseudopelletierine and tropinone to *N*-formyl groups by a photochemical reaction involving singlet oxygen is described.

THE chemistry of singlet oxygen generated either chemically or by energy transfer has recently been reviewed.[1,2] The most commonly observed process is (2 + 4)cycloaddition to diene systems resulting in the formation of *endo*-peroxides. Also known are allylic oxidation with concomitant double bond shift,[1,2] and cleavage of double bonds, possibly *via* a dioxetan intermediate.[3] We report an oxidation reaction of the natural products pseudopelletierine (**1**) and tropinone (**2**) in which singlet oxygen functions in a different, previously undescribed way.



(**1**) $n = 1$ (**3**) $n = 1$
(**2**) $n = 0$ (**4**) $n = 0$

Photolysis of pseudopelletierine (**1**) in benzene solution saturated with oxygen followed by chromatography over silica gel (methylene chloride) yields a single product, m.p. 169—170°, in overall yields of 55—60%. This substance is assigned the *N*-formyl structure, (**3**) on the basis of: i.r ($CHCl_3$) ν_{max} 1660 and 1710 cm^{-1}; n.m.r. ($CDCl_3$ with Me_4Si) δ 8·21 (C*H*O), 4·21 and 4·99 (bridgehead protons differentially deshielded by the carbonyl); the mass spectrum which is analogous to that of pseudopelletierine[4] (*m/e* 167, M^+), 139 (M — CO or M — C_2H_4), 124 (M — CH_3CO), 110 (*N*-formyldihydropyridinium), and the elemental analysis which was correct for $C_9H_{13}NO_2$. Photolysis of tropinone (**2**) under the same conditions yields the homologous *N*-formyl compound (**4**) (yield 40—50%) which in this case proved to be extremely hygroscopic. Data relevant to the structure assignment are: i.r. ($CHCl_3$) ν_{max} 1680 and 1710 cm^{-1}); n.m.r. ($CDCl_3$ with Me_4Si) δ 8·26 (s, 1H); 4·88 and 4·40 (1H each, broad); mass spectrum (*m/e*

153, M^+), 125, 96, 82, *etc.*,[5] and elemental analysis which was correct for $C_8H_{11}NO_2$.

The reaction does not occur in the absence of light, nor in the absence of oxygen. That photochemically generated singlet oxygen is indeed involved is suggested by the fact that both reactions may be effected when light is absorbed by sensitizers (Rose Bengal, naphthalene, or triphenylene). In addition it is possible to quench the reaction by addition of 1,4-diazabicyclo-octane, a known scavenger of singlet oxygen.[6]

The mechanism whereby these transformations are accomplished is not entirely clear. We find that neither singlet oxygen alone (generated from hydrogen peroxide/sodium hypochlorite)[7] nor ground-state oxygen in the presence of a radical initiator (benzoyl peroxide at 80°) converts the *N*-methyl group into *N*-formyl, although starting material is consumed in both instances. On the other hand, we find that CrO_3/pyridine under non-photchemical conditions[8] does effect these transformations in yields similar to those obtained from the photochemical processes.

A simple rationalization of these results is that the carbonyl moiety acts as the sensitizer in direct photolysis, and its (presumably triplet) excited state is quenched by dissolved oxygen. In this way singlet oxygen is generated adjacent to the *N*-methyl group. There is precedent for the formation of α-hydroperoxides under these conditions,[9] a species which might lose the elements of water to yield the observed products. Such an overall reaction differs from that observed in the usual reaction of singlet oxygen with tertiary amines where the ultimate products are aldehydes and simpler amines.[9]

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