The Photo-oxidation of an Enolate Anion: Evidence for Singlet Oxygen as the Intermediate

By ROBERT H. YOUNG and HAROLD HART*

(*Department of Chemistry, Michigan State University, East Lansing, Michigan* 48823)

EVIDENCE is accumulating[1] that the sensitized photo-oxidation of enes, dienes, and various aromatic and heterocyclic substrates proceeds *via* singlet oxygen. Whilst studying substituent effects on the photochemistry of dienones,[2] we irradiated diacetylfilicinic acid (I).[3] Instead of the usual dienone type of rearrangement,[4] we observed a new photo-oxidation, which we consider proceeds *via* singlet oxygen.

Despite its $\lambda_{\max}$ 300 mμ (ϵ 13,800), (I) in the un-ionized form was inert to prolonged (2 days) irradiation with a Hanovia L 450 w lamp, through Pyrex, in ether, in methanol (N_2 or O_2 atmosphere) and in 0·1N-NaOMe in methanol (N_2 atmosphere). However under the latter conditions, but in the presence of air or O_2, (Ia)† photolyzed smoothly to (II; R = CO_2Me), m.p. 77·5—79°.‡ § The reaction was followed by the appearance of new bands at 271 and 250 mμ in place of the band at 340 mμ [due to (Ia)]. The structure of (II; R = CO_2Me) rests on its spectral properties and on its conversion into the known[5] (II; R = H), m.p. 104—105°, in 79% yield with 2N-NaOH at 100°.

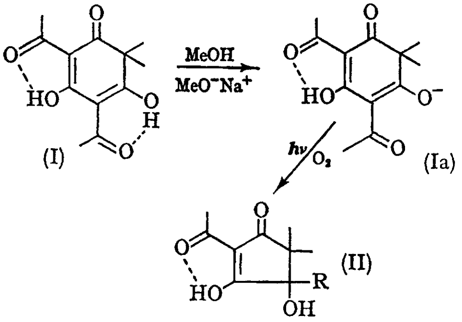
We suggest that (Ia) functions both as sensitizer and as acceptor for singlet oxygen, according to the scheme. The initial product of step (3) may have structure (III) or (IV) which, on further reaction with solvent and base by conventional steps (including a benzilic-acid type rearrangement[6]) can furnish the observed product.

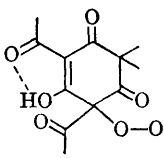
$$\text{(Ia)} \xrightarrow{h\nu} {}^1\text{(Ia)} \rightsquigarrow {}^3\text{(Ia)} \qquad (1)$$

$$^3\text{(Ia)} + {}^3O_2 \rightarrow \text{(Ia)} + {}^1O_2 \qquad (2)$$

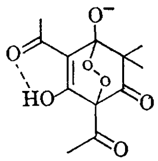
$$\text{(Ia)} + {}^1O_2 \rightarrow \text{product} \qquad (3)$$

Evidence for the intermediacy of singlet oxygen comes from two experiments. Irradiation of (Ia) (0·2% solution containing excess of methoxide) as above but with a 200 w tungsten lamp gave about 4% reaction in 2 hr., but the addition of 0·007% Rose Bengal, under the same conditions, gave a 98% yield (as measured by u.v.; over 70% isolated) of (II; R = CO_2Me) in 35 min. Thus the





(III)



(IV)

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† Evidence that (I) is the tautomer shown, and that the proton lost furnishes (Ia), will be presented in the full paper. Also in the dark, (Ia) was inert to oxygen.

‡ All new compounds gave satisfactory analyses and spectra consistent with the assigned structures.

§ With ethanol and sodium ethoxide, (II; R = CO_2Et) was obtained, m.p. 80—81°.

function of (Ia) as a sensitizer can be replaced by dyes known to produce singlet oxygen.[1]

Second, reflux of an 0·15% solution of (Ia) containing excess of methoxide in the dark for one hour with a 5-molar excess of 9,10-diphenylanthracene peroxide[7] in methanol containing sufficient ether to dissolve the peroxide, afforded (II; R = CO_2Me) in 50% isolated yield. Thus chemically produced singlet oxygen brings about the same reaction.

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