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# CHEMISTRY OF SINGLET OXYGEN. VIII.

## AN UNUSUAL ALLENIC OXYGENATION PRODUCT (1).

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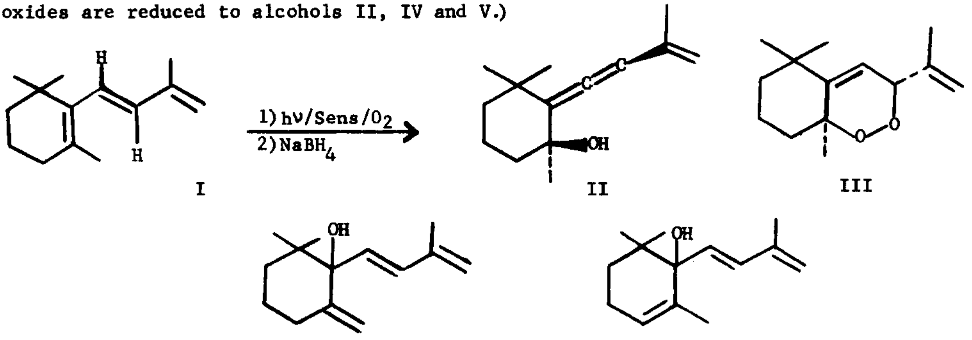
IN connection with studies of the protective action of carotenoids in photodynamic systems, (1,3) we are investigating the dye-sensitized photooxygenation of certain model compounds. The photooxygenation of 3-methyl-1-(2,6,6-trimethylcyclohexen-1-yl)-1,3-butadiene (I) (4), followed by reduction, leads to a novel allenic product (II), in addition to products resulting from more conventional Diels-Alder type addition of oxygen (III) and ene-type addition (IV and V). (Endoperoxide III is inert to the conditions under which the initial hydroperoxides are reduced to alcohols II, IV and V.)



Photooxygenation of I sensitized by rose bengal was carried out in methanol in the apparatus previously described (5). Oxygen uptake was rapid; 2.84 mmoles of I absorbed 2.84 mmoles of $O_2$ in 11 min, at which time the uptake became very slow. The reaction mixture was reduced overnight at 4° with excess $NaBH_4$, and worked up by ether extraction followed by filtration through Celite. Gas chromatography of the residue on a 10 ft. column of 5% FS-1265 gave three major peaks, relative retention times 54, 72 and 100, corresponding to II + V, IV, and III, respectively. Alcohols II and V could be separated on a 6 ft. column of 10% FFAP, but endoperoxide III cannot be isolated from the latter column. All four products (which are liquids) could also be separated by careful column chromatography on silica gel and elution with methylene chloride.

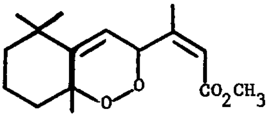
Compound II was assigned the allenic alcohol structure on the basis of key i.r. bands ($CCl_4$) at 3665 (OH), 1945 (allene), and 890cm$^{-1}$ ($C=CH_2$); u. v. absorption ($C_2H_5OH$) at $\lambda_{max}$ 222 nm ($\epsilon$=25,800) and significant n.m.r. bands ($CCl_4$) at 8.98, 8.74, 8.69 (all s, 3 H, sat. $C-CH_3$), 8.36 (s, 1 H, OH), 8.22 (broad s, 3 H, allylic $CH_3$), 5.11 (m, 2 H, $C=CH_2$), and 3.95 τ (s, 1 H, allenic vinyl) (6).

Endoperoxide III had key i.r. bands ($CCl_4$) at 1650 (C=C) and 900 cm$^{-1}$ ($C=CH_2$), and no OH absorption. The n.m.r. spectrum ($CDCl_3$) had resolved bands at 8.89, 8.86, 8.42 (all s, 3 H, sat. $CH_3$), 8.17 (broad s, 3 H, allylic $CH_3$), 5.47 (d, j=4 Hz, 1 H, H-C-O), 5.09 (m, 2H, $C=CH_2$), and 4.43τ (d, J=4 Hz, 1H, isolated olefinic H). The data are very similar to those reported by Mousseron for the similar endoperoxide VI (7).

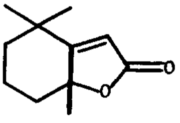
Allylic alcohol IV had diagnostic i.r. bands ($CCl_4$) at 3600 (OH), 1650, 1610 (C=C), 970 (trans H-C=C-H), and 885 cm$^{-1}$ ($C=CH_2$). The u.v. spectrum ($C_2H_5OH$) was $\lambda_{max}$ 230nm ($\epsilon$=25,000). The n.m.r. spectrum ($CCl_4$) had resolved bands at 9.12, 9.10 (both s, 3 H, sat. $C-CH_3$), 8.46 (m, 4 H, ring $CH_2$), 8.30 (s, 1 H, disappears on exchange with $D_2O$, OH), 8.17 (broad s, 3 H, allylic $CH_3$), 5.09 (m; 4 H, $C=CH_2$), and 3.29τ (AB quartet, J=16 Hz, 2 H, trans H-C=C-H).

Alcohol V gave a characteristic retro-Diels-Alder fragment at m/e 150 as the base peak (loss of isobutylene) ; this cleavage was not observed for the exocyclic isomer IV. The compound had key i.r. bands ($CCl_4$) at 3680 (OH), 1605 (C=C), 970 (trans H-C=C-H) and 885 cm$^{-1}$ ($C=CH_2$). Insufficient material was available for a satisfactory n.m.r. spectrum, but on the very weak spectrum obtained, indication of $C=CH_2$ and allylic $CH_3$ bands was found.

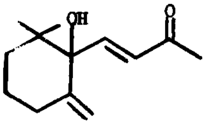
In addition to compounds II-V, traces of compounds VII and VIII were found, and were identified by comparison with authentic materials produced in the photooxygenation of β - ionone (7b).



VI



VII



VIII

Triene 1 was also oxidized with $NaOCl/H_2O_2$ (5) in diglyme (8); in this case, as in all previous cases (9), the product distribution was essentially identical to that of the photooxygenation; the distributions are summarized in the Table. Since a small amount of III decomposes on the column, the distributions are not completely reproducible.

Compound II is the product of an ene reaction involving transfer of an $sp^2$-type hydrogen, at least formally. This is the first case in which such a product has been isolated in a photooxygenation (10); furthermore, we have found no analogous transfer of an $sp^2$-H with carbon or nitrogen enophiles. The stereochemistry of compound II (OH and isopropenyl groups <u>cis</u>) is tentatively assigned on the assumption that the stereochemical course of the reaction is the same as that in the normal photooxygenation, in which the entering oxygen is cis to the transferred hydrogen (11).

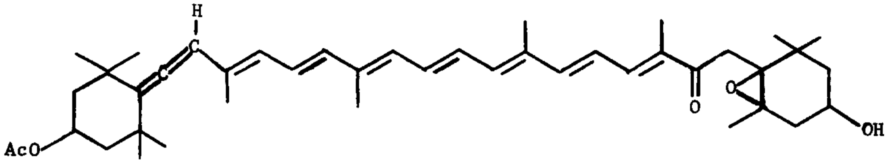
TABLE

Products of Oxygenation of Triene I.

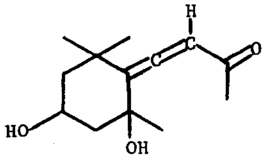
| | Amounts of Product Formed (%)[a] | | | |
|---|---|---|---|---|
| Conditions | II | III | IV | V |
| $h\nu/O_2$<br>Rose Bengal,<br>Methanol | 8 | 61 | 27 | 4 |
| $NaOCl/H_2O_2$<br>(Diglyme) | 10 | 51 | 33 | 5 |

a. Reduced with $NaBH_4$ before analysis. Amounts determined by gas chromatography, internal standard. Volatiles accounted for 85% of the total residue in each case; minor products and any unreacted I omitted.

A further interesting feature of this reaction is that product II has a structure analogous to that of fucoxanthin (IX) and similar carotenoids (12) and of a compound (X) isolated from a grasshopper defensive secretion (13). The close similarity between the products of photooxygenation and of biosynthetic oxygenation in other cases has been remarked upon by several authors (7a, 9, 14). Photooxygenation may prove to be a synthetically useful route to structures containing this allenic alcohol moiety, in spite of the fact that II is a minor component of the oxygenation mixture and the fact that we have so far been unable to observe a similar reaction in other polyene systems (15).



IX



X

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