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DICYANOANTHRACENE-SENSITIZED PHOTOOXYGENATION OF THUJOPSENE

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9,10-Dicyanoanthracene-sensitized photooxygenation of thujopsene proceeded by singlet oxygen, but the reaction with added biphenyl caused an electron transfer and produced a novel product which has no longer possessed the cyclopropane ring. The ring cleavage is best explained in terms of intermediary formation of a radical cation.

Recently, much attention has been attracted to electron transfer photooxygenation, which proceeds *via* radical cations of organic substrates, produced by electron transfer to the excited state of a sensitizer. However, the reactions, studied ever since, are almost limited to aromatic compounds; arenes,[1,2] arylalkenes,[3,4] arylalkynes,[5] arylcyclopropanes,[6,7] aryloxiranes,[8,9] and arylaziridines,[10] and only a few examples of aliphatic compounds are known.[11,12] In some cases, singlet oxygen ($^1O_2$) was suggested to be an active species in 9,10-dicyanoanthracene (DCA)-sensitized reaction. This has been recently verified indeed.[13]

From the view point of quenching of DCA fluorescence and oxidation potential, some aliphatic olefins seem to be susceptible of the electron-transfer photooxygenation. Particularly, vinylcyclopropanes, *e.g.*, thujopsene (**1**),[14] which is a dioxetane-forming alicyclic compounds, are worthwhile to be examined; **1** showed the oxidation potential as low as 1.30 V *vs.* SCE in MeCN and quenched DCA fluorescence.

Irradiations of **1** in an MeCN solution with DCA (0.1 mM) by means of a 400-W high-pressure mercury lamp, through an aqueous 0.9 M-$NaNO_2$ layer (thickness: 0.6 cm) to cut off light shorter than 400 nm in wavelength, yielded allylhydroperoxides (**2** and **3**) and a ketoaldehyde (**4**), a cleavage product of a dioxetane (**5**), all characterized as $^1O_2$-oxidation products,[14] as displayed in Table 1. For the first time, **2** [δ=0.61(3H, s), 1.06(3H, s), 1.15(3H, s), 4.55(1H, tt, J=9, 2 Hz), 5.17(2H, d, J=2 Hz), 8.33(1H, br. s, OOH)] and **3** [δ=0.64(3H, s), 1.06 (3H, s), 1.16(3H, s), 1.43(3H, s), 5.12(1H, d, J=10.5 Hz), 5.31(1H, dd, J=10.5, 1.5 Hz), and 7.2–8.7(1H, br., OOH)] were isolated as colorless oils, and were reduced to known allyl alcohols, **6** and **7**, respectively.

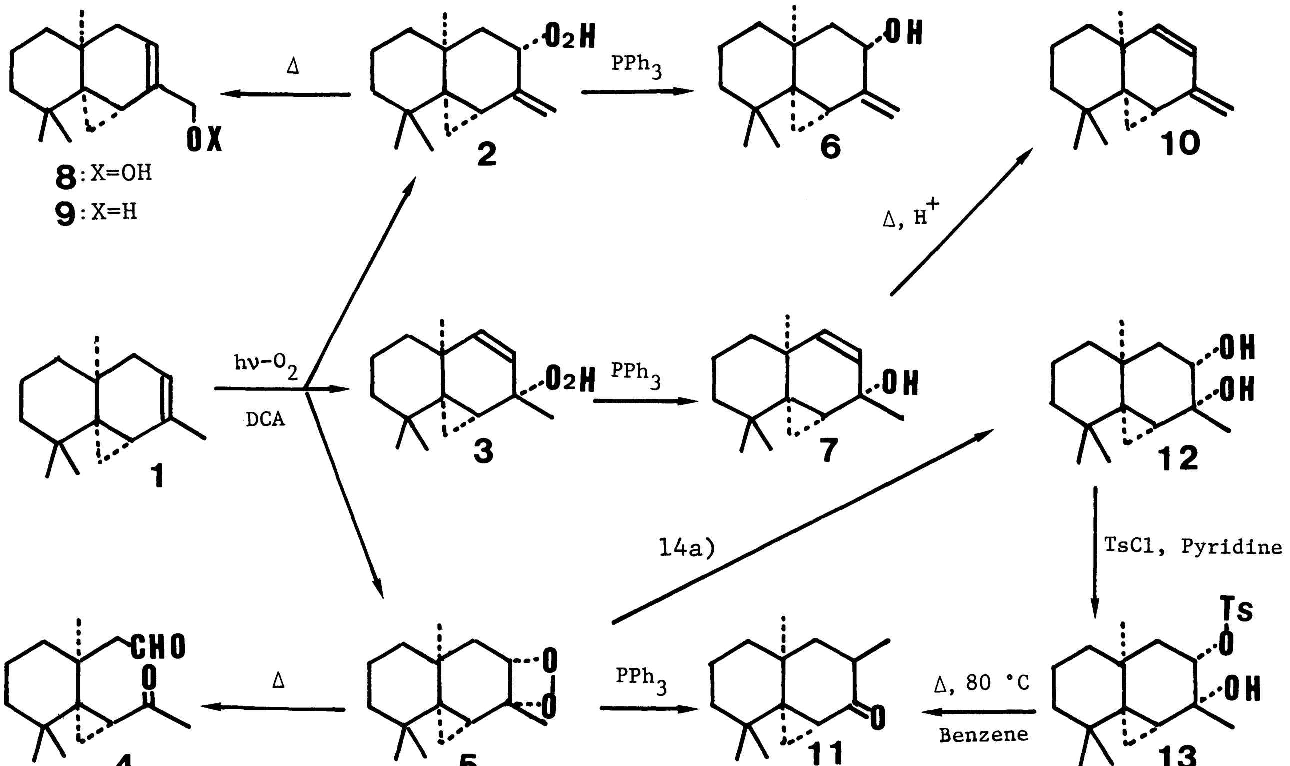
Formation of several secondary products were inevitable, but combined yields of such secondary products in the same solvent were constant within experimental error. Particularly, i) when the reaction mixture was heated, a primary allylhydroperoxide (**8**) [δ=0.61(3H, s), 1.10(3H, s), 1.13(3H, s), 4.47(2H, br. s), 5.46(1H, br. d, J=6 Hz), and 7.93(1H, br., OOH)] has isolated instead of **2**, and **8** could be reduced by sodium sulfite to thujopsenol (**9**), ii) the tertiary allyl alcohol, **7**, was readily dehydrated to thujopsadiene (**10**) during the work up, and iii) PPh_3-

treatment of the mixture caused a reduction of remaining **5** to a methyl-migrated saturated ketone (**11**) [δ=0.63(3H, s), 1.11(3H, s), 1.14(3H, d, J=7 Hz), 1.15(3H, s), and 2.58(1H, sext, J=7 Hz). δ(C)=6.3(t), 17.0(q), 19.1(t), 23.1(d), 26.8(q), 28.1(q), 29.3(q), 32.6, 33.6, 37.7, 38.4(t), 40.0(d), 40.2(t), 52.3(t), and 214.5], colorless needles, mp 39.5–41 °C, which was identical with a sample prepared in 55% yield from a cis-glycol (**12**)14a) *via* a monotosylate (**13**).

Table 1. Photooxidation of Thujopsene Sensitized by DCA and RB

Runs	Sensitizer	Solvents	Yields/%							Ratio I:II:III
			Mode I		Mode II		Mode III			
			2	**8**	**3**	**10**	**4**	**11**	**12**	
1	DCA(0.1 mM)	MeCN	22	0	23	0	55	0	0	0.4:0.4:1.0
2	DCA(0.1 mM)	MeCN	5	13	14	0	43	0	0	0.4:0.3:1.0
3	DCA(0.1 mM)	MeCN	21a)	0	16a)	5	30	14	0	0.5:0.5:1.0
4	DCA(0.1 mM)	MeCN:MeOH (4:1)	1	6	34	0	47	0	0	0.1:0.7:1.0
5	DCA(0.1 mM)	MeOH	30a)	0	0	13	10	0	0	3.0:0.1:1.0
6	RB(2 mM)	MeCN	21	0	23	8	30	0	8	0.5:0.8:1.0
7	RB(0.5 mM)	MeCN	25a)	0	0	14	37	13	1	0.5:0.3:1.0

a) The reaction mixture was reduced by triphenyl phosphine after the irradiation and the hydroperoxides were isolated as the corresponding allyl alcohols.

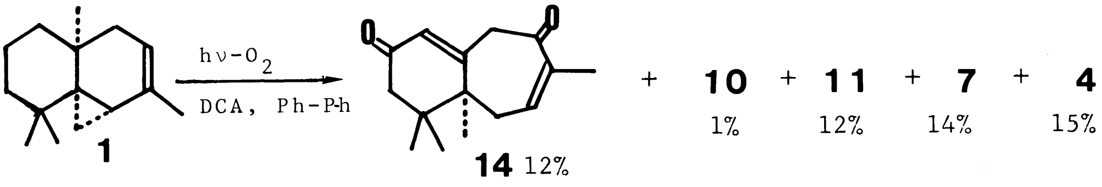


Scheme 1.

Taking into account the product distributions similar to those of Rose Bengal (RB)-sensitized oxygenation, the DCA-sensitized oxygenation of **1** is reasonably suggested to proceed not by electron-transfer but by the $^1O_2$-oxygenation mechanism. Indeed, this has been confirmed by the fact that the rate of the oxygenation in MeCN-d_3 enhanced as k_D/k_H=2.63,15) as well as 75%-quenching by addition of β-

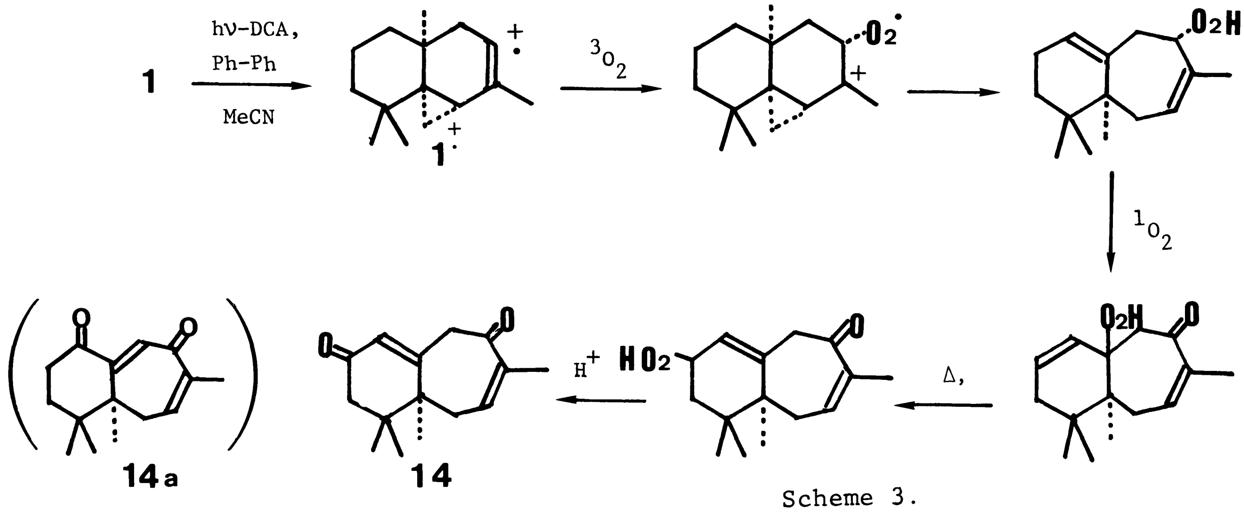
carotene (0.1 mol equivalent to **1**).[16)]

When the oxygenation was performed by co-sensitization with DCA and biphenyl,[6,9,10)] a change of the product distribution, i.e., an absence of **2** and a formation of the new product (**14**), was observed after PPh_3-treatment (Scheme 2), indicating a contribution of the other process, and this must be the electron-transfer oxygenation.



Scheme 2.

The new product, **14**, a colorless oil, showed the ^1H and ^{13}C NMR spectra [δ=0.87 (3H, s), 1.06(3H, s), 1.20(3H, s), 1.79(3H, s), 2.04(1H, d, J=16 Hz), 2.50(2H, m), 2.58(1H, d, J=16 Hz), 3.45(2H, s), 5.89(1H, s), and 6.58(1H, dd, J=8.5, 6 Hz). δ(C)=18.4(q), 23.2(q), 24.6(q), 26.5(q), 33.2(t), 39.5, 47.0, 49.0 (t), 50.0(t), 127.7(d), 138.1, 142.8(d), 160.5, 194.5, and 198.1], from which the absence of the cyclopropane ring is evident, and the structure depicted in the scheme is fully consistent to the observations. An alternative structure, **14a**, was ruled out by the appearance of a strongly deshielded methylene signal at 3.45 which should be assigned to a methylene linked to two sp^2-carbons. Furthermore, **14a** should have the signals of mutually spin-coupled methylenes, but this was not the case. The cleavage of the cyclopropane ring suggests the involvement of a radical cation as shown in Scheme 3.[17)]



Scheme 3.

Consequently, it might be concluded that aliphatic olefins having considerable reactivity towards $^1O_2$ are likely to be oxidized not by electron transfer process but by $^1O_2$. Even in such a case, electron transfer can be realized by indirect means as described above, where the oxygenation process was competitive with the $^1O_2$-oxygenation. Although complicated product distribution and low yields for characterized products of this DCA-biphenyl-sensitized photooxygenation should reserve a detailed discussion, the electron-transfer oxygenation may well be responsible for other products. Interestingly, the carbon framework of **14** was same to the major product formed in the oxalic acid-induced rearrangement of **1**.18)

Studies on other aliphatic substrates will be reported elsewhere.

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17) For formation of **14**, the first oxygenation step to $\mathbf{1}^{+\cdot}$ is explained by neutral oxygen species. An attack of $O_2^{-\cdot}$, that is very plausible, however, must result in the formation of uncharged intermediate like a dioxetane, **5**. In fact, we do not eliminate such a possibility for a simultaneous formation ,of **4** and **10**.

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