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ELECTRON TRANSFER PHOTOOXYGENATION OF 3,5-CYCLOHEPTADIENONES AND RELATED COMPOUNDS[1]

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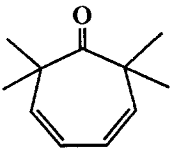
3,5-Cycloheptadienones undergo electron transfer to photoexcited DCA in oxygen-free CH_3CN solution to give triplet products which arise via back electron transfer form initially formed radical ion pairs. Photooxygenation of 2,2,7,7-tetramethyl-3,5-cycloheptadienone (1) and the derived methyl ether (4) under electron-transfer conditions results in unusual hydroperoxide-derived products. The related alcohol (3) gives a product strongly suggestive of intramolecular capture by an OH group of a diene radical cation.

Photoinduced electron-transfer reactions of organic compounds in general, and electron-transfer photooxygenations in particular, have been the subject of extensive study in recent years.[2] We have recently reported[3] that 3,5-cycloheptadienones 1 and 2 efficiently quench the fluorescence of 9,10-dicyanoanthracene (DCA) and 9,10-dimethoxyanthracene (DMA) by an electron transfer mechanism, demonstrating that these cycloheptadienones can function as either electron donors or acceptors. Not unexpectedly, the carbonyl compounds are poorer electron donors toward DCA ($k\frac{1}{q} = 2.2 \times 10^9$ L mol^{-1} s^{-1}) than the corresponding alcohol 3 (1.2×10^{10}) and methyl ether 4 (1.1×10^{10}), consistent with the established homoconjugative interaction between the diene and ketone moieties in 3,5-cycloheptadienones.[4]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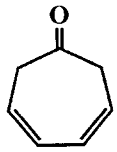
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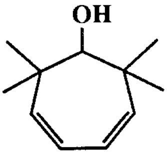
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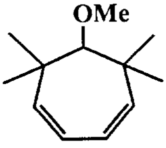
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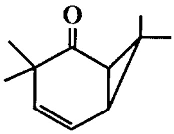
We have previously reported the photochemistry of ketones 1 and 2 on direct and "classical" triplet sensitized excitation.[5] It was of obvious interest to us to examine the behavior of these compounds induced by electron-transfer sensitization mechanisms, in which radical ions would be logical reaction intermediates. Accordingly, we investigated the reactions of 1 and 2 sensitized by DCA in the presence and absence of oxygen. When a solution of 1 in acetonitrile (AN) containing DCA was irradiated at 405 nm[6] in the absence of O_2, only a single product was formed, identified as 5. Similar DCA-sensitized excitation of 2 gave 6. These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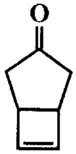
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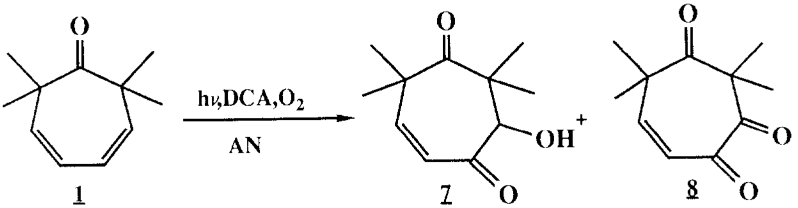
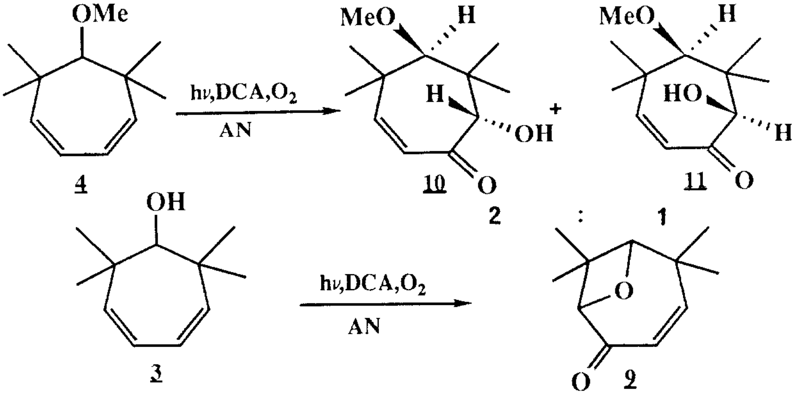
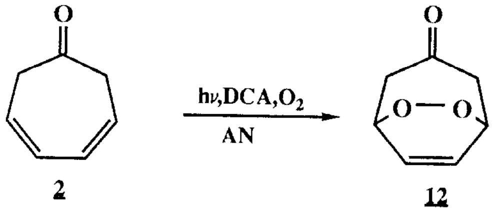
products are known[5] to arise from ketone triplet states, which under the present conditions are presumably formed by back electron-transfer between DCA radical anions and dienone radical cations, since triplet energy transfer from ^{3}DCA* to 1 should be unfavorable by ca. 12 kcal/mol. Formation of triplet states from radical ion pairs is a well-known process in energetically favorable situations.[7]

Excitation at 405 nm of an oxygen-saturated solution of 1 and DCA in AN (no reaction occurred in benzene) resulted in efficient consumption of 1 (ϕ_{-1} = 0.11) and formation of two new products, 7 and 8 (ratio 30/1) in 60% yield, the balance being unidentified resinous material. Compound 7 was identified spectroscopically[8], and by oxidation using Cu^{II} acetate[9] to the unsymmetrical triketone 8.[10] Under similar conditions, alcohol 3 was cleanly converted to 9[11] (ϕ_{-3} 0.16) and 4 was converted to 10[12] and 11.[13] Under conditions which generate singlet oxygen (sensitization using Rose Bengal, Methylene Blue or tetraphenylporphine),[14] no reactions of 1, 3 and 4 were observed, and the substrates could be quantitatively recovered. Consistent with the uninvolvement of $^1O_2$ in these reactions was the lack of observation of a solvent isotope effect in AN.[15] Dienone 2 has been reported by Adam[16] to react with $^1O_2$ to give the 1,4-adduct 12 and the same product was seen under DCA sensitization, indicating that the four methyl groups in 1, 3 and 4 effectively block the approach of $^1O_2$ to the 1,3-diene

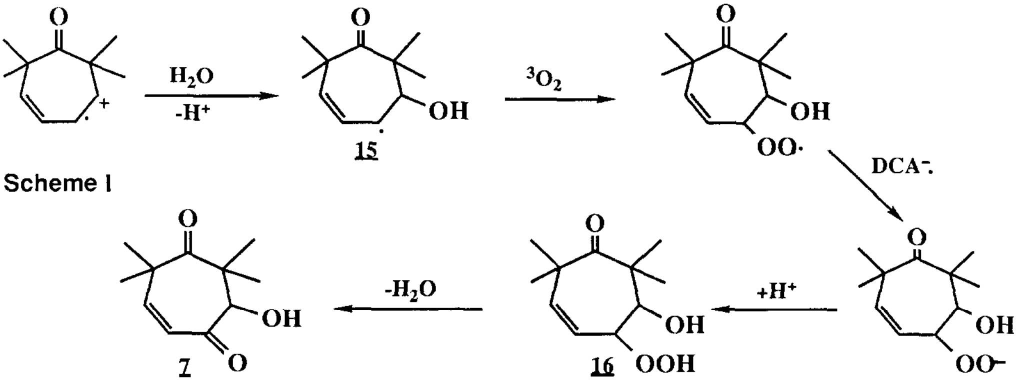






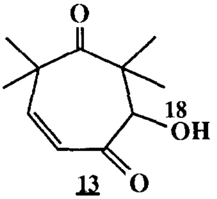
moiety in these systems.

To account for the novel course of DCA-sensitized photooxygeneration of 1, 3 and 4, mechanisms are proposed involving diene radical cations (RC). In the case of 1, a dioxetane was initially believed to be the intermediate leading to the oxygenated products 7 and 8. Although some dioxetane participation cannot be rigorously excluded at this time,[17] further experiments suggest that traces of water (<0.005%) present in AN intercept the RC of 1 to form an α-hydroxyallylic radical (15), which in turn is intercepted by $^3O_2$ to give α-hydroxyhydroperoxide (16). Compound 16 readily dehydrates even at -78°C to give 7 (Scheme I).



Scheme I

Addition of a small amount of H_2O^{18} to dried AN solvent containing DCA/O_2 and irradiation leads to formation of 13 as determined by MS. Methanol acts in a very similar manner, yielding 14.



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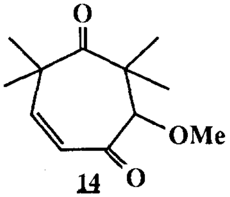

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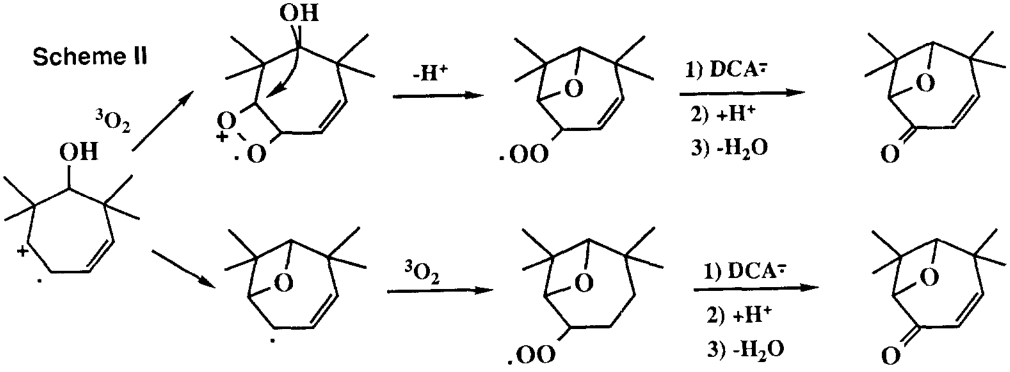
The formation of 9 from 3 (Scheme II) is proposed to involve intramolecular attack of the hydroxyl group on the RC of the dioxetane or more likely on the original RC.



Scheme II

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6. A 10^{-4} M DCA solution in AN containing 10^{-2} M substrate and 5×10^{-3} MH_2O was irradiated with a 450 W medium pressure Hanovia Hg Lamp through 1 cm of $CuSO_4$ filter solution (27 g $CuSO_4 \times 5H_2O$; 30 g $NaNO_2$, 50 ml NH_4OH diluted to 1000 ml with H_2O).

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8. ^{13}C NMR ($CDCl_3$): 211.586, 198.953, 152.361, 126.566, 77.484, 51.671, 50.475, 29.140, 25.801, 25.801, 25.973, 19.536;
   ^{1}H NMR ($CDCl_3$): 1.027, 1.403, 1.423, 1.580 (s, 3H each); 3.930 (d, 1H, J = 4.0 Hz), 4.920 (d, 1H, J = 4.1 Hz); 6.33 (AB dd, 2H, J = 12.66 Hz).

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10. ^{13}C NMR ($CDCl_3$): 206.228, 204.469, 191.590, 154.789, 128.505, 56.894, 52.007, 27.302, 23.075;
    ^{1}H NMR ($CDCl_3$): 1.442 (s, 6H); 1.437 (s, 6H); 6.505 (AB dd, 2H, J = 12.30 Hz).

11. ^{1}H NMR ($CDCl_3$): 0.951, 1.269, 1.310, 1.321 (s, 3H each); 2.922 (s, 1H); 3.591 (s, 3H); 3.699 (d, 1H, J = 4.5 hZ); 4.566 (d, 1H, J = 4.53 Hz); 6.145 (AB dd, 2H, J = 12.68 Hz).

12. ^{1}H NMR ($CDCl_3$): 0.933, 1.291, 1.332, 1.350 (s, 3H each); 2.992 (s, 1H); 3.523 (s, 3H); 4.236 (d, 1H, J = 4.9 Hz); 3.857 (d, 1H, J = 5.0 Hz); 6.106 (AB dd, 2H, J = 12.56 Hz).

13. ^{13}C NMR ($CDCl_3$): 204.139, 151.594, 125.296, 96.210, 92.385, 44.193, 40.479, 29.946, 28.199, 21.606, 19.694;
    ^{1}H NMR ($CDCl_3$): 1.039, 1.092, 1.182, 1.654 (s, 3H each); 3.948 (t, 1H, fine splitting 1.6 Hz); 4.202 (t, 1H, fine splitting 1.6 Hz); 6.059 (AB dd, 2H, J = 12.06 Hz each signal split by fine splitting into a doublet, J_1 = 1.8 Hz; J_2 = 1.89 Hz). Decoupling experiments showed that long-range W-type couplings are responsible for the fine splittings.

14. Solutions containing O_2 of sensitizers (10^{-4} - 10^{-5} M) in dry AN containing 10^{-2} - 10^{-3} M substrate were irradiated using a 450 W medium pressure Hanovia Hg Lamp through 1 cm of 500 nm cutoff filter (1.2 g $K_2Cr_2O_7$ in 1 L H_2O). Control experiments showed efficient formation of $^{1}O_2$ under these conditions.

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