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# ELECTRON-TRANSFER PHOTOOXYGENATION. 8. TRAPPING OF INTERNAL NUCLEOPHILES

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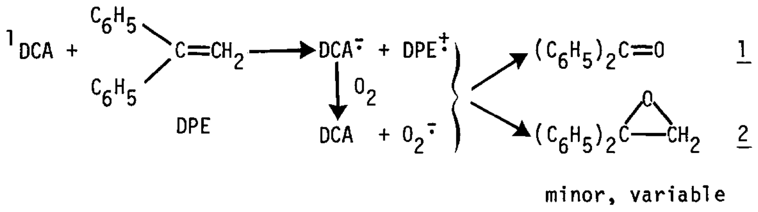
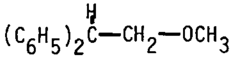
Abstract: Irradiation of 5,5-diphenylpent-4-en-1-ol, sensitized by 9,10-dicyanoanthracene under $N_2$, leads to 2-(diphenylmethyl)-tetrahydrofuran (7). Under $O_2$, a related oxidation product, 2-(diphenylhydroxymethyl)-tetrahydrofuran is produced.

Previous work from this group [1-3] has demonstrated that the primary step in the photooxygenation of 1,1-diphenylethylene (DPE) and other cyanoaromatic olefins in $CH_3CN$, sensitized by cyanaoaromatic sensitizers such as 9,10-dicyanoanthracene (DCA), is electron transfer from the olefin to the singlet excited sensitizer. The reduced sensitizer then reacts with oxygen to produce superoxide ion, $O_2^-$, which in turn reacts with the intermediate radical cation ($DPE^+$) to give the major oxidation product, benzophenone (1), along with varying amounts of epoxide (2). In MeOH, besides 1 and 2, the photooxygenation produces two methanol adducts, 3 and 4, as shown in Scheme 1.

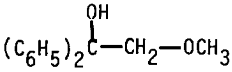
Scheme 1:



In $CH_3OH$:

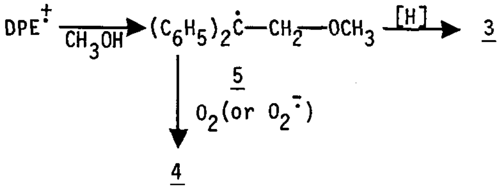


$(C_6H_5)_2CH-CH_2-OCH_3$ 3

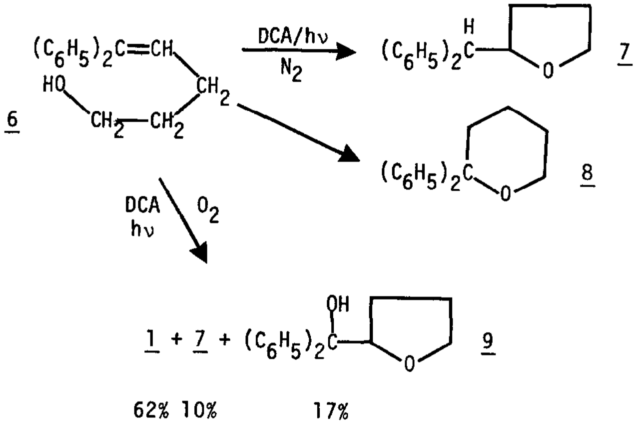


$(C_6H_5)_2C(OH)-CH_2-OCH_3$ 4

Adducts 3 and 4 were suggested to be formed in competion with this process by the trapping of DPE$^{+}$ by MeOH to give radical 5. Reduction of 5 to give 3 was previously described in anaerobic solution by Arnold and co-workers[4,5]; 4 was suggested to come from oxidation (direct or following reduction) of radical 5.[1]



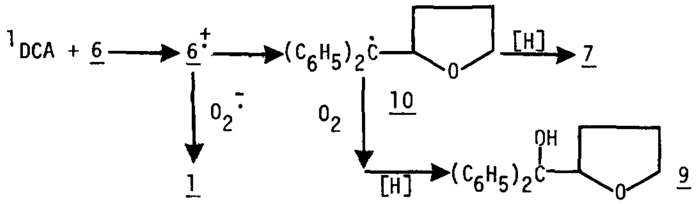
We thought that an internal nucleophile should compete particularly effectively with the reaction of the radical cation wth $O_2^{-}$. 5,5-Diphenyl-pent-4-en-1-ol (6)[6] was selected as a substrate to test this hypothesis. In fact, irradiation of 6 sensitized by DCA in $N_2$-saturated MeCN led to cyclization to give the anti-Markovnikov adduct, 2-(diphenylmethyl)-tetrahydrofuran 7[7], as the major volatile product. In contrast, acid treatment of 6 led to rapid Markovnikov cyclization to form the six-membered ring cyclic ether, 2,2-diphenyltetrahydropyran 8[8].



DCA was consumed rapidly during the irradiation (10min.) of DCA ($1.69\times10^{-4}$M) and 6 ($1.96\times10^{-3}$M) in $N_2$-saturated MeCN, as shown by UV analysis. It was previously pointed out[1,9] that DCA can form and be regenerated from olefin adducts, as demonstrated by the disappearance of DCA absorption on photolysis with olefins and its reappearance on standing. This reaction of DCA limits the conversion at low sensitizer concentrations. However, a 60% conversion of 6 can be reached by adding additional DCA to the solution during photolysis.

Photolysis of 6 ($1.05\times10^{-2}$M) in $O_2$-saturated solution, sensitized by DCA ($2.5\times10^{-4}$M), gave three major products, 1, 7, and a new product, 2-(diphenylhydroxymethyl)-tetrahydrofuran (9)[10]. These compounds were separated by preparative GC (20% DC-200/500, 180° C), and identified by infrared, mass, and NMR spectra[7,8,10].

The internal trapping products 7 and 9 are easily explicable by the previously suggested electron-transfer mechanism[1]. Electron transfer occurs between $^1$DCA and 6 to form DCA$^{-}$ and $6^{+}$. The radical cation intermediate is rapidly trapped by the internal hydroxyl group to give radical 10, which is reduced to 7 under $N_2$ or reacts with $O_2$ to give 9 (following reduction by one of the reducing species in solution). The cyclization competes with reaction of 6 with $O_2^{-}$ to give 1. In the case of DCA-sensitized oxidation of DPE in MeOH[1], a much larger fraction of reaction with $O_2^{-}$ occurs than in the present case, where the trapping is with an internal nucleophile. For 6, the ratio (7+9)/1 is 0.43, whereas for DPE, the ratio (3+4)/1 is only 0.12. These results confirm that there is a competition between $O_2^{-}$ and internal nucleophile for addition to the radical cation. Cleavage is no longer the major reaction when the nucleophile is internal.



We also examined the rose bengal-sensitized oxidation of 6 in $O_2$-saturated MeCN.[11] No benzophenone (1) was found, indicating that $^1O_2$ is not involved in the reaction sensitized by DCA.

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4. A.J.Maroulis, Y.Shigemitsu and D.R.Arnold, *J.Am.Chem.Soc.*, 100, 535 (1978).
5. P. J. Kropp, in "Organic Photochemistry", A. Padwa, ed., Marcel Dekker Inc. New York, Vol. 4, p. 124 (1979).
6. The olefinic alcohol 6 was prepared from the corresponding diol according to J.B.Billman *et al.*, *Tetrahedron*, 32, 1061(1976).
7. Spectral data for 7: MS m/e 238 ($M^+$), 167 ($Ph_2CH^+$), 71 ($C_4H_7O^+$), 42 ($C_3H_3^+$). NMR($\delta$, $CDCl_3$, TMS), 1.54-2.00(4H), 3.77-3.85(2H), 3.91(d, J=8.7 Hz, 1H), 4.55-4.63(1H), 7.12-7.38(10H).
8. Spectral data for 8: MS m/e 238 ($M^+$), 161 ($M^+$-77), 105 ($PhCO^+$), 77 ($Ph^+$). NMR($\delta$, $CDCl_3$, TMS), 1.52-1.78(4H), 2.32(t,J=5.3 Hz, 2H), 3.71(t, J=5.87 Hz, 2H), 7.13-7.42(10H).
9. K. A. Brown-Wensley, S. L. Mattes, and S. Farid, *J. Am. Chem. Soc.* 100, 4162 (1978).
10. Spectral data for 9: MS m/e 254 ($M^+$), 236 ($M^+$-18), 183 ($Ph_2COH^+$), 105 ($PhCO^+$), 77 ($Ph^+$), 71 ($C_4H_7O^+$). IR ($CHCl_3$) 3570 (OH). NMR($\delta$, $CDCl_3$, TMS) 1.39-2.04(4H), 3.61-3.94(2H), 4.58-4.9(1H), 7.12-7.60(10H). The NMR spectrum is consistent with the data of G.Descotes, J.C.Martin and G.Labrit, *Bull. Soc. Chim. (France)*, 4151(1969).
11. The products of this reaction are under study and will be reported in a future paper.

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