

ELECTRON-TRANSFER PHOTOXYGENATION. 8.
DICYANOANTHRACENE-SENSITIZED
PHOTOXYDATION OF ORTHO-DIMETHOXYBENZENE¹

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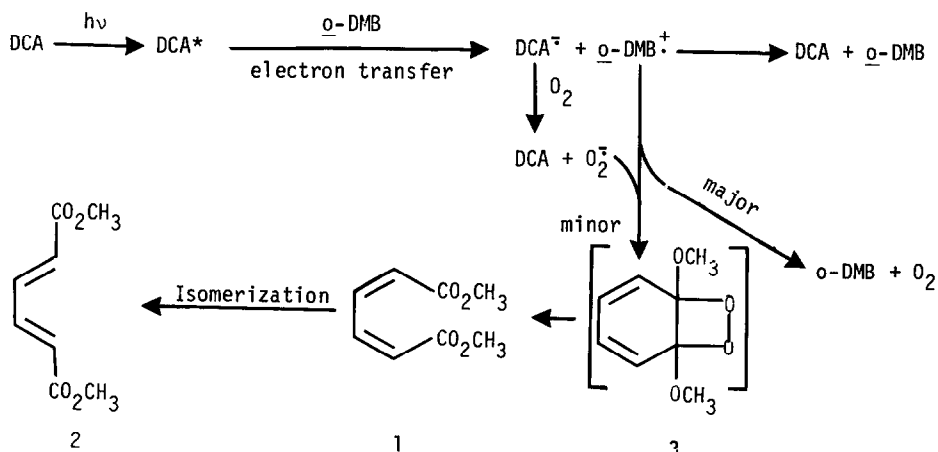
Summary: Two cleavage products, cis,cis-dimethylmuconate (1) and trans,trans-dimethylmuconate (2), are inefficiently produced in the 9,10-dicyanoanthracene (DCA) sensitized photooxidation of ortho-dimethoxybenzene (o-DMB) in polar solvents. An electron transfer mechanism is proposed in which superoxide ion (O_2^-) combines with ortho-dimethoxybenzene to form a dioxetane (3), which cleaves to form (1). The initial product is 1, which is rapidly converted to 2 and other products under the conditions; no cis-trans isomer is formed.

Studies of oxidative cleavage of ring-oxygenated aromatic compounds are of interest as possible mimics for dioxygenase-mediated cleavages of phenols and catechols to muconic acid derivatives.² Although more highly substituted compounds react with singlet oxygen, it has been reported³ that dimethoxylated benzenes (in particular, 3,5-di-*t*-butyl-1,2-dimethoxybenzene) are unreactive to photosensitized oxygenation under the usual conditions. In contrast, similarly substituted phenols are comparatively easy to photooxygenate. Our recent interest⁴ in the 9,10-dicyanoanthracene (DCA) sensitized photooxygenation of organic compounds led us to study the photooxidation of ortho-dimethoxybenzene (o-DMB). These compounds were reported to be essentially unreactive in the cyanoaromatic sensitized oxygenation.^{3,4C} We now report that, although the reaction of dimethoxybenzenes is extremely inefficient, some cleavage of the ring to muconic esters is observed.

Photolysis⁵ of oxygenated acetonitrile and methanol solutions of o-DMB (~0.1M) and DCA (~10⁻⁴M) at room temperature slowly destroys the starting material. No reaction was observed in benzene. A complex mixture of products is formed, from which cis,cis-dimethylmuconate (1) and trans,trans-dimethylmuconate (2) were isolated by gas chromatography⁶ and identified by comparison of their spectra with those of known compounds.⁹ The yields of products 1 and 2 as a function of irradiation time are shown in Table I. In addition, a large amount of poorly characterized polar products is also present. The time course of the reaction shows

that the product 1 does not build up, but is destroyed more rapidly than it is created. Product 2 is destroyed more slowly. The inability of Rose Bengal, a known singlet oxygen sensitizer,⁸ to photooxygenate o-DMB under the same conditions leads us to propose a mechanism analogous to that proposed for cyanoaromatic sensitized oxygenation of aromatic olefins (Scheme I). Radical ion recombination to yield the dioxetane (3) and subsequent ring cleavage leads to the observed products. The absence of reaction in benzene can be attributed to the failure of ion pairs to separate in nonpolar solvents, and is comparable to the solvent effects observed with aryl olefins.^{4a} The inefficiency of the reaction, even in acetonitrile (which also makes methoxybenzenes excellent quenchers for the cyanoaromatic-sensitized oxidation of other compounds^{4b}) implies that back electron transfer predominates over reaction. The factors which control reaction vs. back electron transfer from the ions have not yet been elucidated.

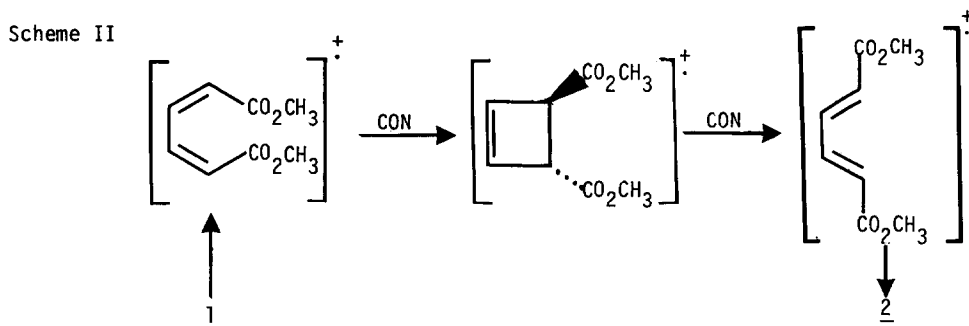
Scheme I



As the formation of the trans,trans isomer was unexpected, photoisomerization of cis,cis-dimethylmuconate (1) and trans,trans-dimethylmuconate (2) was examined under the same photooxygenation conditions. After two hours irradiation of cis,cis-dimethylmuconate, 90% of starting material had disappeared and trans,trans-dimethylmuconate (34%) was observed (see Table II). No cis,cis isomer was found after 4 hours irradiation of the trans,trans isomer. Cis,cis-dimethylmuconate is, therefore, assumed to be the primary photooxygenation product and is subsequently isomerized to the trans,trans isomer (2) at a rate which is fast compared to photooxidation of dimethoxybenzene. Both isomers are rapidly destroyed in side reactions, suggesting that the yield of the initial cleavage reaction may be quite high.

The isomerization of 1 and 2 sensitized by DCA is interesting and was examined carefully at intermediate stages by NMR. No cis,trans-dimethylmuconate⁹ was found at any stage of the reaction, although a few percent would have been detected. No isomerization occurred in the absence of DCA. Although isomerization of two double bonds following absorption of a single quantum is well known in triplet-sensitized reactions,¹⁰ it is always accompanied by isomeri-

zation of one double bond. To explain the puzzling stereospecificity, we suggest as a tentative working hypothesis that the isomerization proceeds on the radical cation surface via two consecutive thermal conrotatory reactions as shown in Scheme II. Further work will be required to substantiate this hypothesis.



Addition of *trans*-stilbene to the photooxygenation mixture results in a slight increase in the rate of *o*-DMB disappearance; work is being done to examine this phenomenon.

Table I. DCA Sensitized Photooxygenation of *o*-DMB

Irradiation Time (hrs)	Conversion of <i>o</i> -DMB (%)		Yield of 1 (%)*		Yield of 2 (%)*	
	CH ₃ CN	CH ₃ OH	CH ₃ CN	CH ₃ OH	CH ₃ CN	CH ₃ OH
0	0	0	0	0	0	0
2	0.37	----	0	0	0	----
5	4.25	----	0	----	2.72	----
7	----	0.77	----	16.60	----	5.13
8	9.21	----	0	----	3.84	----
10	15.24	4.51	0	4.97	6.80	15.04
12	19.84	4.01	0.88	7.28	7.38	28.46
14	25.84	6.45	0.75	5.28	7.14	22.99
17	32.89	10.71	0.74	4.00	7.52	20.31
20	46.07	----	0.64	----	7.12	----

*Based on reacted *o*-DMB.

Table II. DCA Sensitized Isomerization of *Cis,Cis*-¹ and *Trans,Trans*-² dimethylmuconate

Irradiation Time (hrs)	Conversion of 1 (%)	Yield of 2 (%)
0	0	0
2	90	34
4	97	34.8

References:

1. Paper no 7: L.E. Manring, M.K. Kramer and C.S. Foote, J. Phys. Chem., *in press*. J.J-Liang thanks the government of the Republic of China for fellowship support. Supported by NSF Grants CHE77-21560 and CHE80-20141.
2. a) O. Hayaishi, "Oxygenases", New York: Academic Press, 1962;
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b) J. Eriksen and C.S. Foote, J. Phys. Chem., **82**, 2659 (1978);
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d) D.S. Steichen and C.S. Foote, J. Am. Chem. Soc., **103**, 1855 (1981).
5. All of these photolyses were carried out at room temperature with a 1200 W mercury lamp with a CuSO_4 filter solution and oxygen bubbling at various times (see Table I). The reaction of 1,1-diphenylethylene under comparable conditions is complete in 30 minutes (see ref. 4c).
6. UCW-98 column.
7. Cis,cis-dimethylmuconate was obtained by treating cis,cis-muconic acid, (prepared by oxidation of phenol with peracetic acid [C.A. 26, 2970 (1932)], with diazomethane in ether. Trans,trans-muconic acid is commercially available and was also methylated with diazomethane.
8. R.W. Denny and A. Nickon, Organic Reactions, **20**, 133 (1973); N.J. Turro, "Modern Molecular Photochemistry", Menlo Park, CA: Benjamin/Cummings, 1978; p.587.
9. Compared with the NMR spectra of cis,trans-dimethylmuconate. Cis,trans-muconic acid was prepared as described by J.A. Elvidge, et. al., J. Chem Soc., 2235 (1950).
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