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THE ROLE OF OXYGEN AS AN ELECTRON ACCEPTOR IN DIMERIZATION OF SOME STYRENE DERIVATIVES

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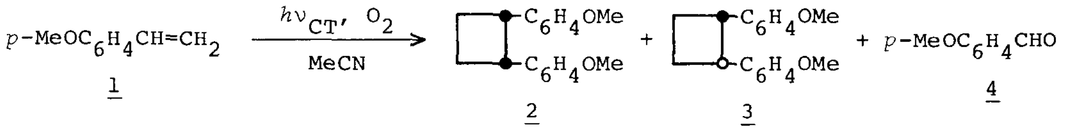
Abstract: Irradiation of the CT bands of *p*-methoxy- and *p*-methylstyrene with oxygen induced the dimerization of the olefins through their cation radicals generated by electron transfer on CT excitation.

Much current interest has been focused on photoreactions induced by exciplexes and excited electron-donor-acceptor complexes.1) Electron-rich olefins are photochemically dimerized *via* their cation radicals in polar solvents in the presence of various electron acceptors such as nitriles, anhydrides, pyrylium salts, and ferric ions.2) In a previous work in our laboratory,3) oxygen was shown to serve as an electron acceptor in photooxidation of hexamethylbenzene. This communication describes the role of oxygen as the electron acceptor in the photodimerization of some styrene derivatives in a polar solvent.

Irradiation of a solution (3 ml) of *p*-methoxystyrene (1, 0.59 mol/dm^3) in acetonitrile under oxygen atmosphere in a uranium glass tube with a 400-W high pressure mercury lamp (effective at 366 nm) for 16 hours at room temperature (conversion: 43%) afforded *cis*- and *trans*-1,2-diarylcyclobutane (the head-to-head cycloadducts, 2 and 3, respectively; yield: 31%, 2/3 = 5/95) together with the oxidative cleavage product, *p*-methoxybenzaldehyde (4, 30%).



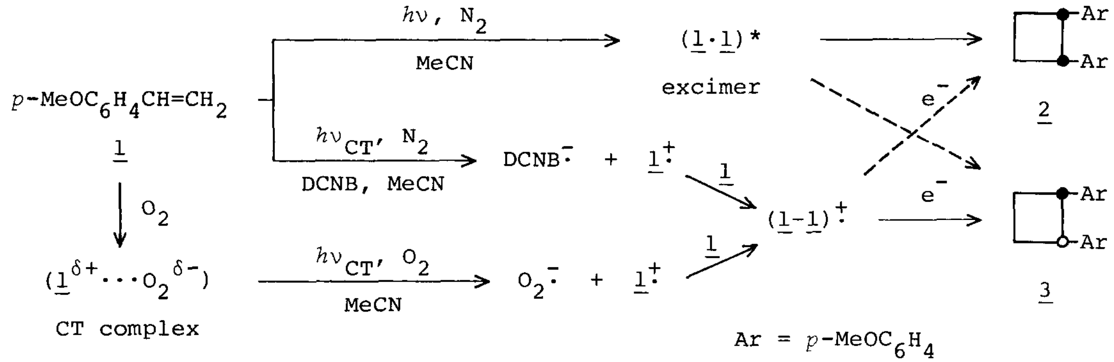
On the basis of the following observations, this dimerization is shown to proceed through the cation radicals of the olefin resulting from electron transfer from the olefin to oxygen on excitation of the charge-transfer (CT) complex formed between them.

First, the longest wavelength end of the absorption band of 1 lies at 325 nm in acetonitrile. However, on saturation of the solvent with oxygen a new absorption band due to the CT complex between the olefin and oxygen4,5) appeared in the range of 320-370 nm; this band disappeared reversibly on introduction of argon to exclude oxygen. The use of 366-nm light, therefore, excites only the CT complex. Actually, no reaction products were essentially detected on irradiation under nitrogen in acetonitrile. Although the CT band was observed in benzene in a similar region to that in acetonitrile, irradiation of 1 under oxygen in this solvent with 366-nm light gave no dimers, probably due to inefficient generation of the cation radicals and $O_2^{\overline{\cdot}}$ in the nonpolar solvent.

Secondly, higher *cis*-dimer compositions were observed on irradiation with shorter wavelength light which could excite uncomplexed monomers rather than the CT complex; irradiation in a Pyrex tube with the high pressure mercury lamp (effective at 313 nm) resulted in the *cis/trans* ratio of 16/84 (47% yield) and irradiation in a quartz tube with a low pressure mercury lamp (effective at 254 nm) resulted in the ratio of 63/37 (56% yield). Furthermore, irradiation under nitrogen in acetonitrile with 313-nm light gave the dimers (63%) in a ratio of *cis/trans* = 87/13. In this case the dimerization is assumed to proceed through an excimer.[6)]

Thirdly, irradiation of a solution (3 ml) of 1 (0.59 mol/dm^3) in the presence of *p*-dicyanobenzene (DCNB, 0.12 mol/dm^3) in acetonitrile in a Pyrex tube with the high pressure mercury lamp gave the *cis*- and *trans*-dimers (42% yield) in a ratio of 2/98[7)] as reported by Yamamoto *et al.*[2b)] This dimerization is reported to arise from olefin cation radicals,[2b)] and the isomer ratio in this reaction is very similar to that in the dimerization in the presence of oxygen.

Scheme 1

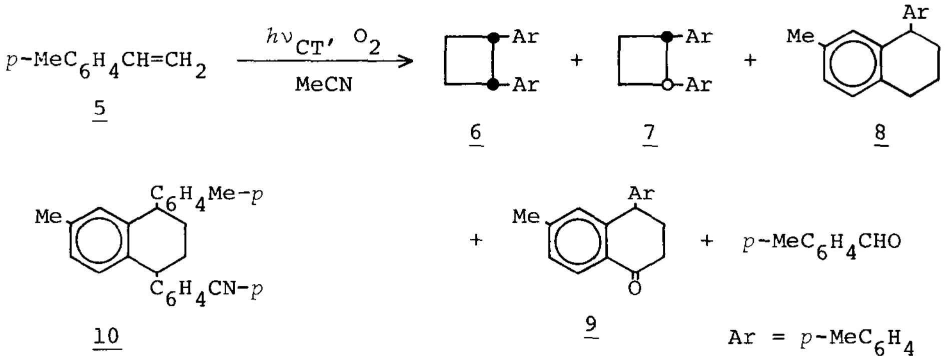


Lastly, a triplet mechanism through the excited CT complex or triplet sensitization by aldehyde 4 formed during irradiation can be ruled out because triplet sensitization using benzophenone under nitrogen in acetonitrile gave the dimers (50% yield) in a different isomer ratio (2/3 = 13/87) from that in the dimerization under oxygen mentioned above, and because 4 could hardly sensitize the dimerization on irradiation in a uranium glass tube. On 4-sensitized irradiation of 1 in a Pyrex tube (313 nm) under nitrogen in acetonitrile, the dimers were produced in a ratio of 2/3 = 22/78 (75% yield).

Therefore, the dimerization processes of 1 in the absence and presence of electron acceptors could be summarized as shown in Scheme 1.

p-Methylstyrene (5) also exhibited an absorption band due to the CT complex with oxygen at the region of 310-370 nm in acetonitrile. Excitation of this complex by irradiating a solution of 5 (0.61 mol/dm^3) in acetonitrile under oxygen atmosphere in a Pyrex tube with the 400-W high pressure mercury lamp (313 nm) led to the formation of three cyclodimers (20%) and a dimeric ketone of the olefin (20%) together with *p*-methylbenzaldehyde (8%). The cyclodimers were *cis*- and *trans*-1,2-diarylcyclobutane (the head-to-head adducts, 6 and 7, respectively) and the tetralin derivative, 7-methyl-1-(*p*-methylphenyl)-1,2,3,4-tetrahydronaphthalene (8) (isomer ratio: 6:7:8 = 1:2:1). The ketone was identified as 6-methyl-4-(*p*-methylphenyl)-1,2,3,4-tetrahydronaphthalen-1-one (9).8)

Irradiation of 5 (0.69 mol/dm^3) in the presence of DCNB (0.13 mol/dm^3) instead of oxygen under nitrogen afforded 1-(*p*-cyanophenyl)-6-methyl-4-(*p*-methylphenyl)-1,2,3,4-tetrahydronaphthalene (10)[9] as a main product (30%), which corresponds to a substitution product of the electron acceptor with 8, together with the olefin dimers (5%, 6:7:8 = 12:16:72).



Tetralin-type dimer 8 is reported to be produced only through the olefin cation radicals.2d) Therefore, ketone 9 and diaryltetralin 10 are assumed to be quenching products of tetralin-type dimer cation radicals by oxygen species ($O_2^{\overset{-}{\cdot}}$ or O_2) and DCNB (anion radical or neutral molecule), respectively.

In conclusion, the CT complexes of some styrene derivatives with oxygen give, under illumination in a polar solvent, the olefin dimers through the dimer cation radicals, and these could be quenched with acceptor molecules such as oxygen and DCNB leading to definite products.10)

Investigation concerning the detailed mechanism for the formation of the quenching products is now in progress.

References and Notes

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5) Copolymerization of styrene and α-methylstyrene with oxygen was reported to be initiated by irradiation of the CT bands between the olefins and oxygen: T. Kodaira, K. Hashimoto, Y. Sakanaka, S. Tanihata, and K. Ikeda, Bull. Chem. Soc. Jpn., 51, 1487 (1978).

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7) An absorption band due to the CT complex between 1 and DCNB was observed at the region of 320-390 nm in acetonitrile. Irradiation of this band (366 nm) gave the dimers in a similar isomer ratio.

8) Compound 9 was isolated by column chromatography on silica gel; oil; MS: m/e 250 (M^+, 100%), 235, 222, 208; IR(KBr): 1670 cm^{-1}, $\nu_{C=O}$; ^1H nmr($CDCl_3$): δ 2.24 (s, 3H, CH_3), 2.30 (s, 3H, CH_3), 2.3-2.65 (m, 4H, CH_2CH_2), 4.0-4.25 (m, 1H, CH), 6.7-8.0 (m, 7H, aromatic H); ^{13}C nmr($CDCl_3$): δ 197.7, 146.4, 144.3, 140.7, 136.2, 130.6, 129.8, 129.2, 128.4, 127.9, 127.2, 44.8, 36.5, 31.9, 21.7, 21.0. The phenylhydrazone of 9, mp 131-133°C (dec); Anal. Found: C, 84.73; H, 7.10; N, 8.26%. Calcd for $C_{24}H_{24}N_2$: C, 84.66; H, 7.10; N, 8.22%.

9) Compound 10 was isolated by column chromatography on silica gel and found to be a 1:1 mixture of *cis*- and *trans*-isomers; mp 111-112°C; MS: m/e 337 (M^+), 245 (100%), 234, 219, 208; IR(KBr): 2210 cm^{-1}, $\nu_{C=N}$; ^1H nmr($CDCl_3$): δ 1.6-2.1 (m, 4H, CH_2CH_2), 2.16 and 2.18 (s, 3H, CH_3), 2.30 (s, 3H, CH_3), 3.95-4.35 (m, 2H, 2xCH), 6.6-7.55 (m, 11H, aromatic H); ^{13}C nmr($CDCl_3$): δ 153.3, 153.2, 144.0, 143.9, 140.0, 139.6, 136.3, 136.1, 135.7, 135.3, 135.2, 132.1, 131.0, 130.7, 129.9, 129.6, 129.0, 128.6, 127.5, 127.3, 119.0, 109.9, 45.7, 45.6, 45.3, 44.8, 30.9, 30.1, 29.7, 21.0. Anal. Found: C, 89.03; H, 6.87; N, 4.16%. Calcd for $C_{25}H_{23}N$: C, 88.97, H. 6.87, N. 4.15%.

0) Recently, Arnold *et al.* reported the trapping of intermediate trienes with acrylonitrile and methyl acrylate in the [2 + 4] dimerization and the related cross-addition of 1,1-diphenylethylene: D. R. Arnold, R. M. Borg, and A. Albini, J. Chem. Soc., Chem. Commun., 1981, 138.

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