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PHOTOINDUCED [2+2] CYCLOADDITION BETWEEN ARYL VINYL ETHER AND ALKYL VINYL ETHER VIA ELECTRON TRANSFER[1)]

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The [2+2] photocycloaddition between aryl vinyl ethers and alkyl vinyl ethers occurs upon irradiation of acetonitrile solutions in the presence of an electron acceptor such as 1,4-dicyanobenzene, giving predominantly cis head-to-head cycloadducts. The mechanistic features of this photoreaction are described.

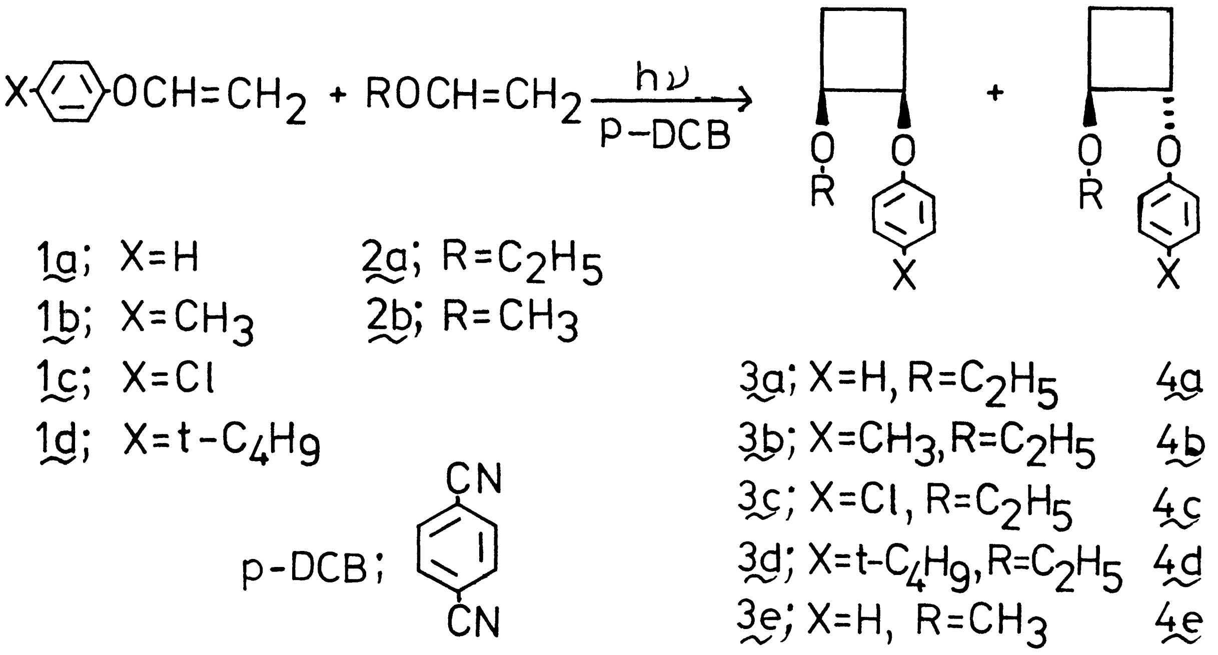
Electron-rich aromatic olefins such as N-vinylcarbazole, indenes, and styrenes undergo the cyclodimerization via their dimer cation radicals upon irradiation in the presence of an electron acceptor.2) Major products in these photoreactions have been shown to be the trans head-to-head cycloadducts. Similar photoreaction occurs with phenyl vinyl ether(1a),3) but no such a reaction has been reported with alkyl vinyl ethers. Recently, we have also demonstrated that the photoinduced cross addition between two different electron-rich unsaturated compounds occur via heterodimer cation radicals.4) We now report the photoinduced [2+2] cycloaddition between aryl and alkyl vinyl ethers, which predominantly affords the cis head-to-head cycloadducts.

Irradiation of an acetonitrile solution containing 1a(17 mmol), ethyl vinyl ether (2a, 170 mmol), and 1,4-dicyanobenzene(p-DCB, 8 mmol) through Pyrex with a 300 W high-pressure mercury arc gave cis- and trans-1-ethoxy-2-phenoxycyclobutanes(3a and 4a) as major products with 80% recovery of p-DCB. A small amount of a mixture of the dimers of 1a was also detected, but the dimers of 2a was not detected by GLC of the reaction mixture. The cross adducts were isolated by column chromatography on silica gel. Their structures were assigned from their analytical and spectral data.5)

Similar photoreactions of other pairs, 1a-d and 2a-b, in the presence of p-DCB gave the corresponding [2+2] cycloadducts, 3b-e and 4b-e. The results are summarized in Table 1. A striking feature of these reactions is that the cis isomers, 3a-e, are obtained as major products, in contrast with the other photocyclodimerizations previously reported.2,3)

In the 1a - 2a - p-DCB system, the product ratios of the cross adducts to the homodimers of 1a, [Cross]/[Homo], linearly increased with an increase in the concentration ratio of 2a to 1a, [2a]/[1a], (Fig. 1), although the relative quantum yield for the formation of the cross adducts decreased(Fig. 2).

Other aromatic nitriles such as 1,2-dicyanobenzene, 1,4-dicyanonaphthalene, and 9,10-dicyanoanthracene were also effective as the electron acceptor. The fluorescence of the aromatic nitriles in acetonitrile was quenched by either 1 or 2 nearly at a



diffusion controlled rate. From the Rehm-Weller equation,6) the free energy changes (ΔG) for the photoinduced electron transfer process are estimated to be -28.4 kcal/mol for 1a and -28.9 kcal/mol for 2a when p-DCB was used as the electron acceptor.7,8) The photocycloaddition of 1 to 2 was inefficient either in the absence of the electron acceptor or in nonpolar solvents.

These results can be explained in terms of the electron transfer mechanism shown in Scheme 1. One-electron transfer occurs from 1 and 2 to the excited singlet state of the electron acceptor A to give the cation radicals($1^{+\cdot}$ and $2^{+\cdot}$) and the anion radical ($A^{-\cdot}$). The competitive addition of $1^{+\cdot}$ to 1 and 2 produces the dimer cation radicals 5 and the heterodimer cation radicals 6, which lead to the "Homo" and "Cross" cyclodimers. The ratio of [Cross]/[Homo] would depend on the concentration ratio of [2]/[1] (see Fig. 1), since both 1 and 2 have similar oxidation potentials7) and also similar nucleophilicity. If the reactivity of $2^{+\cdot}$ is similar to that of $1^{+\cdot}$, then the homodimers of 2 should be produced in appreciable amounts along with the cross adducts

Table 1. Photocycloaddition of 1 and 2 in the presence of p-DCB

1	2	Products	Total Yield(%)a)	Ratio of cis/transb)
1a	2a	3a, 4a	14	3a/4a = 73/27
1b	2a	3b, 4b	38	3b/4b = 94/6
1c	2a	3c, 4c	16	3c/4c = 86/14
1d	2a	3d, 4d	50	3d/4d = 98/2
1a	2b	3e, 4e	23	3e/4e = 92/8

a) Isolated yields based on 1 used. b) Determined by GLC.

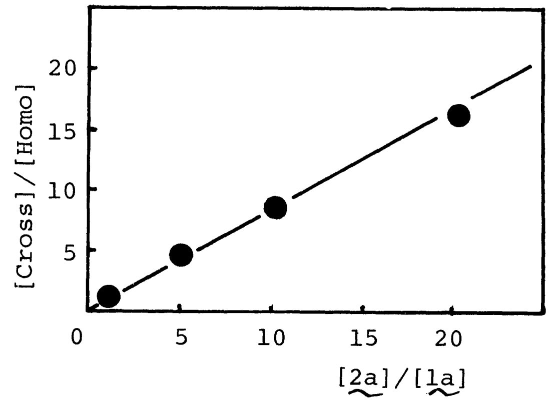


Fig. 1. Plot of [Cross]/[Homo] vs. molar ratio [**2a**]/[**1a**] in degassed acetonitrile solutions; [**1a**]=0.3 M, [**2a**]=0.3, 1.5, 3.0, 6.0 M, [p-DCB]=0.15 M.

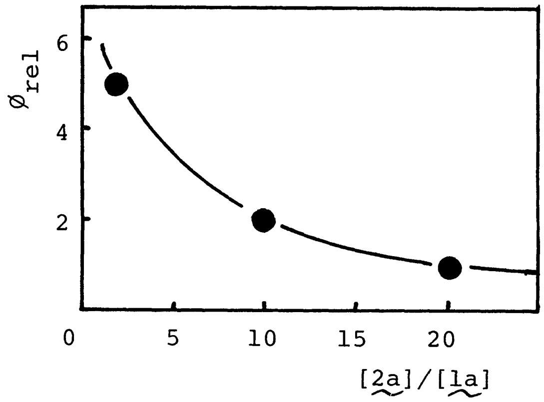
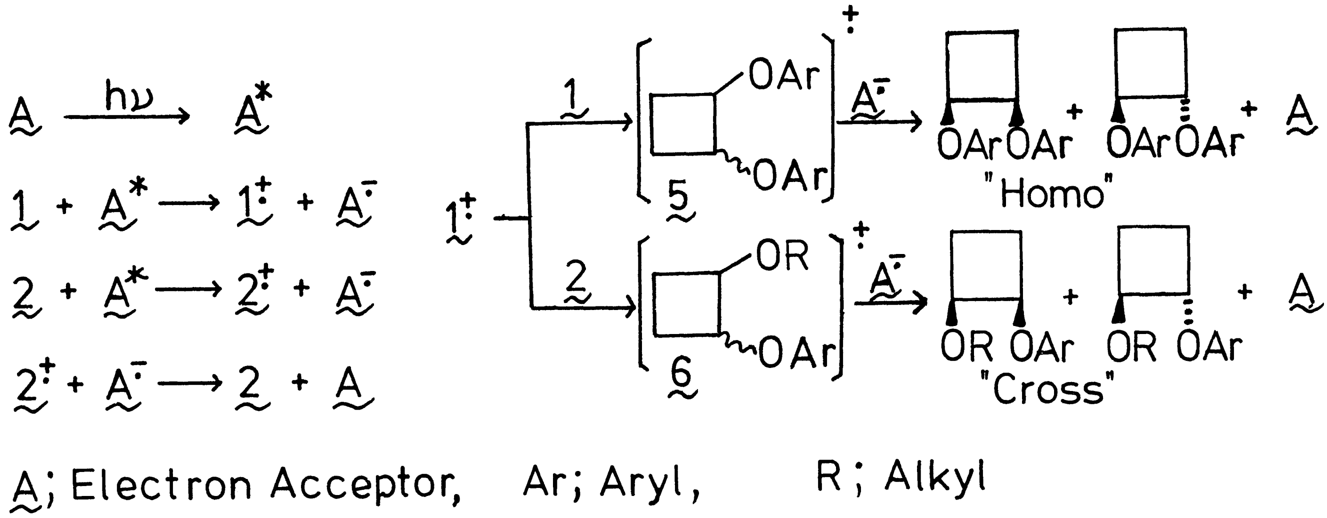


Fig. 2. Plot of Ø_{rel} vs. molar ratio [**2a**]/[**1a**] in degassed acetonitrile solutions; [**1a**]=0.3 M, [**2a**]=0.6, 3.0, 6.0 M, [p-DCB]=0.15 M.

through the dimer cation radicals of **2** and **6**. However, the relative quantum yield for the formation of the cross adducts decreased when a large excess of **2** was used (Fig. 2). In addition, no homodimers of **2** were detected in the reaction mixtures of the photoreactions. Thus, the only fate of $\mathbf{2}^{+\cdot}$ is supposed to be quenching by a back electron transfer from $\mathbf{A}^{-\cdot}$ to $\mathbf{2}^{+\cdot}$.[9]

Our findings provide an example of the selective cis cyclobutane formation via the cation radical intermediate. Unfortunately, no reasonable explanation can be given for this selectivity at present.



A; Electron Acceptor, Ar; Aryl, R; Alkyl

Scheme 1

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1) The present work was partially supported by a Grant-in-Aid for Scientific Research from the Ministry of Education of Japan.

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5) **3a**; ^{1}H NMR δ(CCl_4) 1.15(3H, t, J=7 Hz), 1.30-1.70(2H, m), 1.90-2.30(2H, m), 3.43(2H, q, J=7 Hz), 3.72-3.97(1H, m), 4.20-4.44(1H, m), 6.70-6.90(3H, m), 7.00-7.25(2H, m): **4a**; ^{1}H NMR δ(CCl_4) 1.12(3H, t, J=7 Hz), 1.98-2.25(4H, m), 3.25-3.60(2H, m), 4.00-4.20(1H, m), 4.50-4.70(1H, m), 6.70-6.90(3h, m), 7.08-7.28(2H, m).

6) $\Delta G(\mathrm{kcal/mol}) = 23.06[E(D/D^{+})_V - E(A^{-}/A)_V - e^{2}/\varepsilon a] - E_{0-0}(\mathrm{kcal/mol})$; D. Rehm and A. Weller, Israel J. Chem., 8, 259(1970).

7) The oxidation potentials of **1a**($E_{p/2}$=1.28 V) and **2a**($E_{p/2}$=1.26 V) and the reduction potential of p-DCB($E_{1/2}$=-1.82 V) were obtained by cyclic voltammetry: Pt electrode, tetraethylammonium perchlorate(0.1 M) in acetonitrile solutions, vs. Ag/0.01 M Ag^{+}: cf. D. R. Arnold and A. J. Maroulis, J. Am. Chem. Soc., 98, 5931(1976).

8) These values were calculated by using the energy of an excited singlet state of p-DCB(E_S=98.6 kcal/mol); S. L. Murov, in "Handbook of Photochemistry", Marcel Decker, New York, N.Y., 1970.

9) The hole transfer from **2**$^{+\cdot}$ to **1** is unlikely since the relative quantum yield for formation of the cross adducts decreased with an increase in the relative concentration of **2a**(see Fig. 2).

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