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STEREOSELECTIVITY IN THE PHOTOCYCLODIMERIZATION OF PHENYL VINYL ETHER VIA ELECTRON-TRANSFER

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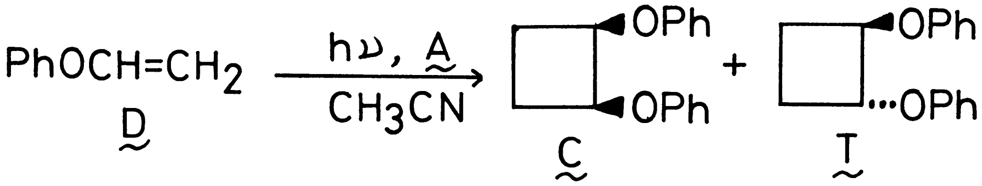
The stereoselectivity in the photocyclodimerization of phenyl vinyl ether(**D**) via electron-transfer depends strongly upon the concentration of **D** and the reaction temperature.

The photocyclodimerization of electron-rich aromatic olefins via a photoinduced electron-transfer has been widely investigated from mechanistic and synthetic viewpoints.[1,2] In this photoreaction, the dimer cation radicals of olefins have been postulated as reactive intermediates. However, no information is available to date about the relationship between the stereochemistry of the cyclodimers and the structures of reactive intermediates. We now report that the stereochemistry of the cyclodimers produced in the photocyclodimerization of phenyl vinyl ether(**D**) via electron-transfer is strongly influenced by the concentration of substrate and the reaction temperature.

It is known that **D** undergoes the photocyclodimerization upon irradiation in polar solvents in the presence of electron acceptor(**A**) to give cis- and trans-1,2-diphenoxycyclobutanes, **C** and **T**, as major products.[2,3] We determined the quantum yield(ϕ_p) for the formation of **C** and **T** and the product ratio, [**C**]/([**C**]+[**T**]) and [**T**]/([**C**]+[**T**]), in a wide range of concentrations of **D**([**D**] = 0.002-2.0 mol/dm^3), employing 9,10-dicyanoanthracene(DCA) as **A** and acetonitrile as solvent.[4] These results are shown in Table 1 and Figure 1.



The product ratios, [**C**]/([**C**]+[**T**]) and [**T**]/([**C**]+[**T**]), were independent of the reaction time, the structure of the electron acceptors, and their concentration. The ratio [**C**]/([**C**]+[**T**]) markedly increased with decreasing the concentration of **D** in the low concentration range([**D**] = 0.002-0.1 mol/dm^3). On the other hand, a constant product ratio, [**C**]/([**C**]+[**T**]) : [**T**]/([**C**]+[**T**]) = 40 : 60, was obtained in the high concentration range([**D**] = 0.1-2.0 mol/dm^3); this value was in agreement with that previously reported.[2] These results indicate that (1) the cis-dimer(**C**) is formed with a high stereoselectivity at the low concentration of **D** and (2) the product ratios

Table 1. Effect of the Concentration of the Substrate on the Product Distribution and the Quantum Yields in the Photocyclodimerization of Phenyl Vinyl Ether(D)[a,b]

[D]/mol/dm^3	[C] : [T]	ϕ_p	[D]/mol/dm^3	[C] : [T]	ϕ_p
0.002	96 : 4	0.04	0.05	44 : 56	0.64
0.0033	90 : 10	0.08	0.1[c]	42 : 58	0.68(0.71)
0.004	84 : 16	0.11	0.125	41 : 59	0.73(0.80)
0.005	73 : 27	0.16	0.167	41 : 59	0.74(0.92)
0.008	70 : 30	0.27	0.25	40 : 60	0.69(1.09)
0.01	61 : 39	0.29	0.5	40 : 60	0.66(1.32)
0.0125	55 : 45	0.33	0.75	40 : 60	0.57
0.02	50 : 50	0.46	1.0	40 : 60	0.58
0.025	49 : 51	0.50	1.5	40 : 60	0.47
0.04	46 : 54	0.62	2.0	40 : 60	

[a] Dry acetonitrile solution under argon atmosphere; [DCA] = 1.0×10^{-4} mol/dm^3. Irradiation time; 3 min. Irradiation temperature; 298 ± 0.2 K. [b] Values in parentheses were obtained from ref. 2b. [c] More than 90% of the DCA fluorescence was quenched by D at this concentration.

[C]/([C]+[T]) and [T]/([C]+[T]) become independent of the concentration of D at the high concentration([D] $\geq$ 0.1 mol/dm^3).

The quantum yield for the formation of C and T decreased with decreasing the concentration of D in the low concentration range([D] $\leq$ 0.1 mol/dm^3), but the quantum yield approached a constant value($\phi_p = 0.70 \pm 0.05$) at the high concentration([D] = 0.1 - 0.5 mol/dm^3)(Table 1). These results clearly suggest that the photoreaction at high concentrations proceeds through the mechanism different from that at low concentrations.

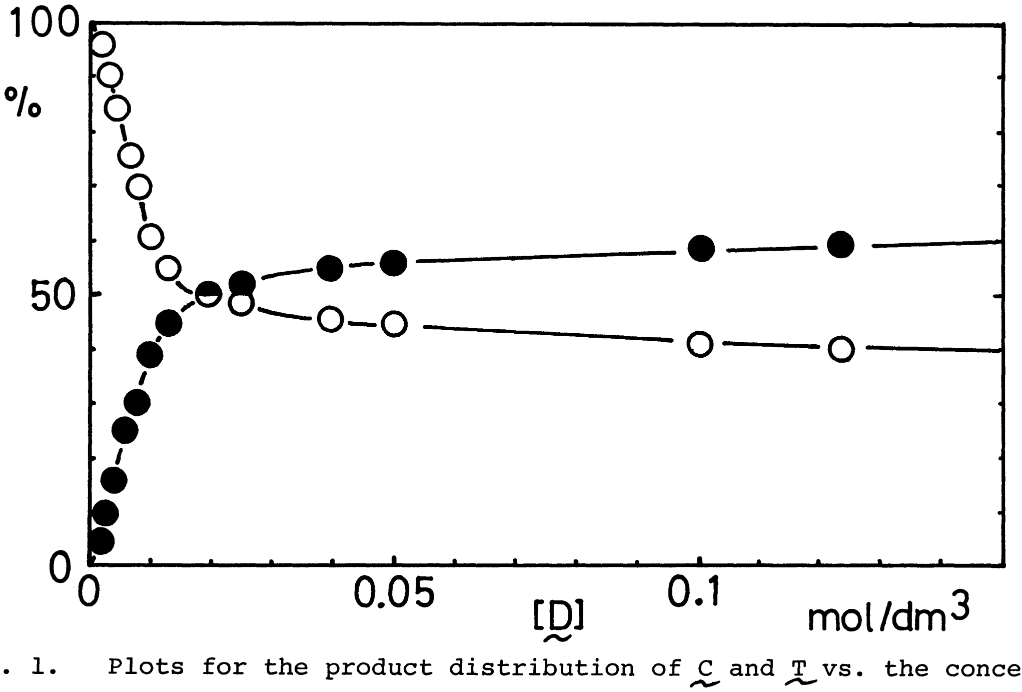


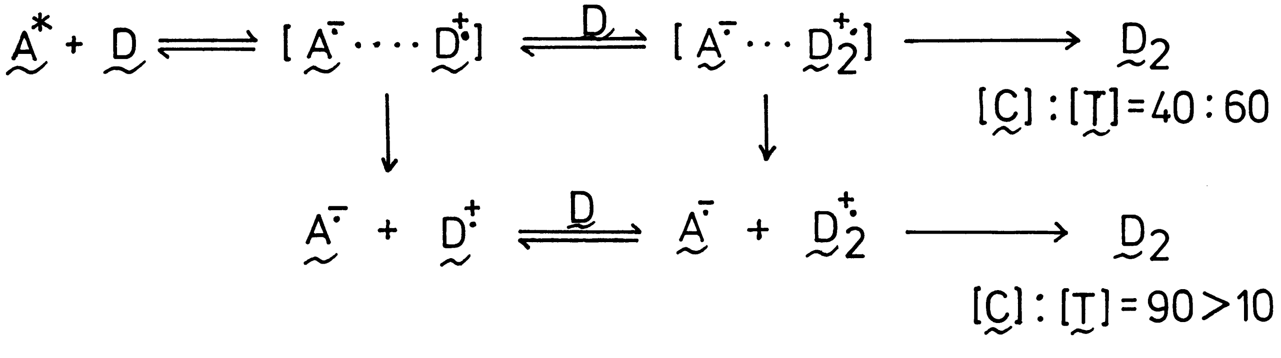
Fig. 1. Plots for the product distribution of C and T vs. the concentration of D([D]) in dry acetonitrile solution under argon atmosphere using DCA as A: [DCA] = 1.0×10^{-4} mol/dm^3, C; -○- , T; -●-.

Table 2. Effect of Temperature on the Product Distribution in the Photocyclodimerization of Phenyl Vinyl Ether(**D**)[a]

temp/K	[**D**]=0.2 mol/dm^3 [b]	[**D**]=0.1 mol/dm^3	[**D**]=0.005 mol/dm^3
	[**C**] : [**T**]	[**C**] : [**T**]	[**C**] : [**T**]
231 ± 1	37 : 63 [c]		
248 ± 1		38 : 62	49 : 51
273 ± 0.2	40 : 60 [c]	39 : 61	57 : 43
298 ± 0.2	41 : 59	42 : 58	73 : 27
338 ± 0.2		48 : 52	89 : 11
355 ± 0.2	52 : 48		
381 ± 0.5		55 : 45	95 : 5
416 ± 0.5		63 : 37	97 : 3
430 ± 1	73 : 27		

[a] Degassed dry acetonitrile solution; [DCA] = 1.0 x 10^{-4} mol/dm^3. [b] 1,4-Dicyanobenzene(0.1 mol/dm^3) was used as **A**. [c] 1,2-Dicyanobenzene(0.1 mol/dm^3) was used.

The one-electron transfer from **D** to an excited electron acceptor(**A***) is an exothermic process from the following facts: (1) When DCA is used as **A**, the negative free energy change(ΔG = -43.0 kJ/mol) is estimated from the Rehm-Weller equation for this electron-transfer process.[2c,5] (2) A near diffusion controlled rate(k_q = 8.4 x 10^9 mol^{-1} dm^3 s^{-1}) was obtained in the fluorescence quenching experiment of DCA by **D** in acetonitrile.[2c] For this photoreaction, we propose an electron-transfer mechanism involving the contact radical ion pair $[\mathbf{A}^{\cdot -}\cdots\mathbf{D}^{\cdot +}]$ and the solvent separated cation radical $\mathbf{D}^{\cdot +}$ as reactive intermediates(Scheme 1).[6] At high concentration of **D**, the termolecular complex $[\mathbf{A}^{\cdot -}\cdots\mathbf{D}_2^{\cdot +}]$ is formed by the association of the contact ion pair $[\mathbf{A}^{\cdot -}\cdots\mathbf{D}^{\cdot +}]$ with other **D** prior to the dissociation of $[\mathbf{A}^{\cdot -}\cdots\mathbf{D}^{\cdot +}]$ to $\mathbf{A}^{\cdot -}$ + $\mathbf{D}^{\cdot +}$. The cyclodimers $\mathbf{D}_2$ (**C** and **T**) are produced in a constant ratio through a back electron-transfer; $[\mathbf{A}^{\cdot -}\cdots\mathbf{D}_2^{\cdot +}] \longrightarrow \mathbf{A} + \mathbf{D}_2$. At the high concentration of **D**([**D**] ≥ 0.5 mol/dm^3), the quantum yield decreases with increasing the concentration of **D**, although the product ratio remains constant. This observation can be explained by the assumption that a bulk dielectric constant may decrease at high substrate concentrations.



Scheme 1.

On the other hand, at low concentrations, the dimer cation radical $\mathbf{D}_2^{+\cdot}$ is formed by a nucleophilic attack of other **D** on the solvent separated cation radical $\mathbf{D}^{+\cdot}$. The $\mathbf{D}_2^{+\cdot}$ thus formed has a sandwich-type configuration and leads to the formation of the cis-dimer **C**.[7] This hypothesis was supported by temperature effect on the photocyclodimerization of **D** in the presence of **A** such as DCA and dicyanobenzenes(Table 2). The product ratio [**C**]/([**C**]+[**T**]) increased with a rise in the reaction temperature even at high concentrations. It seems likely that $[\mathbf{A}^{-\cdot}\cdots\mathbf{D}_2^{+\cdot}]$ and $[\mathbf{A}^{-\cdot}\cdots\mathbf{D}^{+\cdot}]$ dissociate into the solvent separate $\mathbf{D}_2^{+\cdot}$ and $\mathbf{D}^{+\cdot}$ at high temperature. Thus, the formation of **C** predominates under these conditions.

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3) Small amounts of phenol and 1-methyl-3-phenoxypyridine were produced as by-products. The photocyclodimers **C** and **T** are stable under the reaction conditions. No cycloreversion of **C** and **T** to **D** was observed. The isomerization of **T**→**C** and **C**→**T** was also negligible(< 1%) in the DCA-sensitized photoreaction. See ref. 2c.

4) The quantum yield measurements were performed by irradiation with an Eiko-sha "merry-go-round" actinometer apparatus, using an Eiko-sha 300 W high-pressure mercury lamp with an aqueous $CuSO_4$-NH_3 filter solution for 405 nm irradiation. The quantum yields for the formation of **C** and **T** depended upon the irradiation temperature and also the concentration of electron acceptors. The details will be reported in a full paper.

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