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INTRAMOLECULAR [2 + 2] PHOTOCYCLOADDITION. 2.[1)]
MECHANISM OF INTRAMOLECULAR PHOTOCYCLIZATION OF α,ω-BIS(p-VINYLPHENYL)ALKANES

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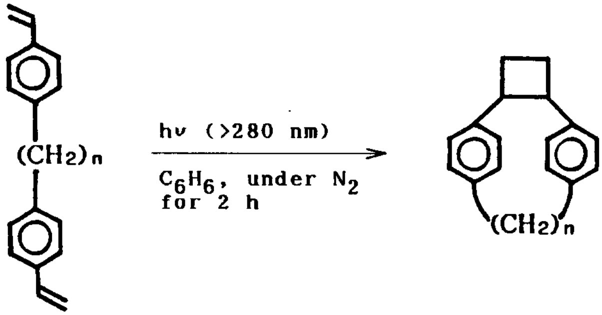
Abstract: From the photophysical measurements of the title reaction, the formation of cyclophanes is concluded to be facilitated by high microscopic concentration of styrene moieties and depressed by strain loaded at the transition state.

Photocyclodimerization of styrene was found two decades ago and studied extensively,2) but there were few reports on the physicochemical investigation which could reveal the deep insight of the reaction, since styrene itself polymerizes very readily under the photoirradiation at a high concentration. The condition is absolutely necessary for its cyclodimerization, because of the short lifetime of the excited species. Overcoming this difficult concentration problem, we recently found a facile intramolecular photocycloaddition of the title compounds 1,1) which have almost the same reactivities as styrene itself, and revealed several interesting features, so that we were prompted to study the mechanism of the reaction in relation to the styrene cyclodimerization.2) Here in this communication, we would like to report the kinetic work on the intramolecular photocycloaddition.

Olefins 1 were prepared by the sequence of the following reactions;3,4)



(1)

1a n=3
b n=4
c n=5
d n=6

2a n=3
b n=4
c n=5
d n=6

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Grignard coupling, Friedel-Crafts acylation, $LiAlH_4$-reduction, and DMSO-$KHSO_4$-dehydration. They were purified by recrystallization from MeOH. Measurements of fluorescence spectra, fluorescence decay curves, and quantum yields were carried out as reported.[5] Nonpolar isooctane (ε=1.94, η=0.504 cp at 20 °C) was used as the solvent. The fluorescence decay curves of olefins 1a - 1d are well fitted to a single exponential function and moreover any excimer fluorescence emission were not detected, so that olefins 1 do not form any emitting intramolecular excimers.[6]

Table I Kinetic Parameters of the Photocycloaddition.

Olefin	n	Φ_f	τ_f, ns$^{a)}$	Φ_d	k_f, 10^9 s^{-1}	k_n^{intra}, 10^9 s^{-1} $^{b)}$	k_d, 10^9 s^{-1}	ΔE_{st}, kcal/mol$^{c)}$
1a	3	0.048	2.30	0.031	0.021	0.34	0.014	52.6
1b	4	0.047	2.46	0.38	0.019	0.19	0.15	43.5
1c	5	0.040	2.15	0.39	0.019	0.21	0.18	37.4
1d	6	0.085	4.39	0.25	0.019	0.095	0.057	34.9
-$^{d)}$	∞	0.20	13.37	-	0.015	-	-	28.7$^{e)}$

a) Excitation at 294 nm; emission at 310 nm.
b) The rate constant of non-radiative process k_n is assumed to be equal to the rate constant for p-methylstyrene: $k_n = 0.060 \times 10^9\ s^{-1}$.
c) Strain energies calculated by MM2 for cis-(1,2)ethano[2.n]paracyclophanes 2.
d) p-Methylstyrene as a model of the olefin possessing the infinitively long linkage.
e) For cis-diphenylcyclobutane. The calculated strain energy for trans isomer is 27.6 kcal/mol.

The kinetic scheme of reaction (1) is made clear by the analyses of fluorescence decay curves and the products. The scheme and the notation of rate parameters are written as follows;

$$M + h\nu \rightarrow M^* \tag{2}$$

$$M^* \rightarrow M + h\nu_1 \qquad k_f \tag{3}$$

$$M^* \rightarrow M \qquad k_n^{intra} + k_n \tag{4}$$

$$M^* \rightarrow C \qquad k_d \tag{5}$$

$$p\text{-}MSt^* \rightarrow p\text{-}MSt + h\nu_2 \qquad k_f \tag{6}$$

$$p\text{-}MSt^* \rightarrow p\text{-}MSt \qquad k_n \tag{7}$$

where M and C are olefin 1 and cyclophane 2, respectively, and k_f, k_d, k_n^{intra}, and k_n are rate constants of fluorescence decay, cyclization, intramolecular inter chromophore-quenching, and other nonradiative quenching, respectively. Under the steady state approximation on the concentration of M^*, the following equations are led;

$$I_0 - (k_f + k_n + k_n^{intra} + k_d)[M^*] = 0 \tag{8}$$

$$\Phi_f = k_f[M^*]/I_0 = k_f/(k_f + k_n + k_n^{intra} + k_d) \tag{9}$$

$$1/\tau_f = k_f + k_n + k_n^{intra} + k_d \tag{10}$$

$$\Phi_d = k_d/(k_f + k_n + k_n^{intra} + k_d) \tag{11}$$

For p-methylstyrene at the sufficiently high dilution, equations (9) and (10) are simplified as follows;

$$\Phi_f = k_f/(k_f + k_n) \tag{12}$$

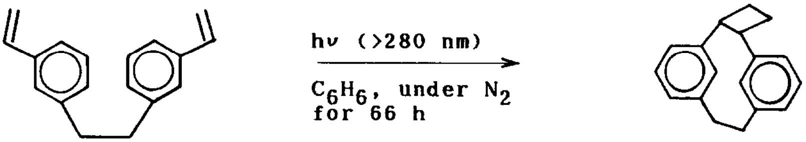
$$1/\tau_f = k_f + k_n \tag{13}$$

Rate constants k_f, k_n, k_n^{intra}, and k_d were evaluated from Φ_f, Φ_d, and τ_f by using the above equations. The calculated rate constants as well as experimental values for k_f, τ_f, and Φ are listed in Table I.

According to the total rate constants of intramolecular paths $k_n^{intra} + k_d$, olefins 1a - 1c have the same order of advantage for intramolecular interchromophor interaction, while this interaction of olefin 1d becomes substantially unfavorable in the competition with other processes, because of mainly the long chain and additionally the difficulty of taking the eclipsed chain conformation$^{7)}$ for the chromophore interaction. The advantage of olefins 1a - 1c can be called an entropic one, since the interaction is governed by one of the entropic factors, namely the microscopic concentration of styrene moieties.

The single exponential fluorescence decay curves, no detectable excimer emission, and the same order of the intramolecular chromophore interaction ($k_d + k_n^{intra}$) for n=3, 4, and 5 clearly suggest that the typical excimer, whose formation is most favorable at n=3 for benzene derivatives,$^{7)}$ does not participate in this reaction. There are several mechanistic works reported so far which suggested the importance of the excimer in the styrene cycloaddition because of the formation of the cis-cyclodimer, although Caldwell reported that the excimer formation generally impedes cycloaddition in an energy sense, and chief advantage of excited state complex formation will be entropic.$^{8)}$ The above experimental results support strongly this Caldwell's suggestion.

If the cyclization takes place through a late transition state or product like transition state, the strain possessed in the product considerably depresses the rate. Therefore, strain energies of products cis-(1,2)ethano[2.n]paracyclophanes 2 (n=3 - 6) were estimated by MM2 calculation,$^{9)}$ and listed in Table I. The energy increases monotonously from n=6 to 3, so that one can easily assume the maximum of the cyclization rate at n=5 because olefins 1a, b, and c (n=3 - 5) have almost the same entropic advantage as mentioned above. This is indeed the case: A maximum value for k_d is observed at n=5, but not at n=3 or 4, as shown in Table I.



5

6 Yield 60.9%

(14)

The calculated strain energies of cis-(1,2)ethano[2.2]paracyclophane 3 and trans-(1,2)ethano[2.6]paracyclophane 4 are 77.9 kcal/mol and 50.0 kcal/mol, which are extremely high compared with those of anti,cis-(1,2)ethano[2.2]metacyclophane 6 (ΔE_{st} = 61.6 kcal/mol)$^{10)}$ and cis-(1,2)ethano[2.6]paracyclophane 2d (ΔE_{st} = 34.9

kcal/mol). These relatively high calculated strain energies of 3 and 4 are consistent with the fact that 1,2-bis(*p*-vinylphenyl)ethane and 1,6-bis(*p*-vinylphenyl)hexane 1d did not give cyclophanes 3 and 4 under photoirradiation.1)

Consequently we can comment on the cyclodimerization of styrene under the direct photoirradiation; i.e., the reaction does occur efficiently (Φ = ca. 0.4), if two styrene moieties are arranged at least in the vicinity of each other, although the reaction of styrene itself recorded only meager yields in literatures so far.2a,b)

References and Notes

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(9) We are indebted to Prof. Eiji Ōsawa, Hokkaido University for providing the MM2 program.

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