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Organic Photochemical Reactions. XXXII.[1] Photochemical Ring-Cleavage Reactions of 2,2-Diaryloxetanes in the Presence of Electron Donor

Kenichi Nakabayashi,† Shin Fujimura, Masahide Yasuda, and Kensuke Shima*
Department of Industrial Chemistry, Faculty of Engineering, Miyazaki University, Gakuen-Kibanadai, Miyazaki 889-21

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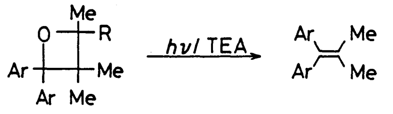
Synopsis. Photochemical ring-cleavage reactions of 2,2-diaryloxetanes in the presence of triethylamine gave 1,1-diarylethenes selectively.

The cleavage of the oxetane ring has been studied in reactions with Brønsted acid or metal ion as well as in pyrolysis[2] or infrared multiphoton induced photolysis.[3] In these studies, the regiochemical control of ring cleavage has been an interesting subject. We previously reported that regioselective ring-cleavage reactions of 2,2-diaryloxetanes (**1**) into substituted benzophenone and alkene pairs are achieved by a photochemical electron transfer from **1** to a typical electron acceptor, such as aromatic nitriles.[1] Thus, the photochemical electron transfer has proved to be a useful method for the ring cleavage of oxetanes. Therefore, our attention was focused on the photochemical reaction of **1** in the presence of electron donors (Scheme 1).



	Ar	R		Ar
1a	C_6H_5	H	2a	C_6H_5
1b	C_6H_5	Me	2b	p-MeC_6H_4
1c	p-MeC_6H_4	H	2c	p-ClC_6H_4
1d	p-MeC_6H_4	Me		
1e	p-ClC_6H_4	H		
1f	p-ClC_6H_4	Me		
1g	p-$MeOC_6H_4$	H		
1h	p-$MeOC_6H_4$	Me		

Scheme 1.

Results and Discussion

Reaction Products. Photoreactions of **1** were carried out by irradiation in the presence of an electron donor at 254 nm. In attempts to find the optimum reaction conditions, the photoreaction of **1b** was carried out under various conditions. Hexane, cyclohexane, dibutyl ether, and tetrahydrofuran (THF) were found to be better solvents, since the photoreaction was relatively efficient, while methanol and acetonitrile were poor solvents (Table 1). As an electron donor, triethylamine (TEA) was better than the other amines tested (e.g. aliphatic or aromatic amines). Therefore, photochemical ring-cleavage reactions were performed with TEA in hexane throughout the present investigation.

Photochemical ring-cleavage reactions of **1a—d** in the presence of TEA gave the corresponding 1,1-diarylethene (**2**), while acetaldehyde or acetone was not detected by careful GLC analysis, though these compounds were expected as other products of the ring cleavage of **1**. The reaction products were unambiguously identified by direct comparisons with authentic samples which were prepared by acid-catalyzed fragmentation of the corresponding oxe-

Table 1. Chemical and Quantum Yields in the Photochemical Ring Cleavage of **1b** in the Presence of TEA

Solvent	Yield of **2a**[a)] %	Conv. of **1b** %	ϕ[b)]
Hexane	48	70	0.046
Cyclohexane	50	68	—[c)]
Dibutyl ether	64	67	0.020
THF	73	51	0.027
MeOH	24	66	—[c)]
MeCN	28	57	0.013

a) GLC yields based on consumed **1**. b) Quantum yields at [TEA]=0.07 mol dm^{-3}. c) Not determined.

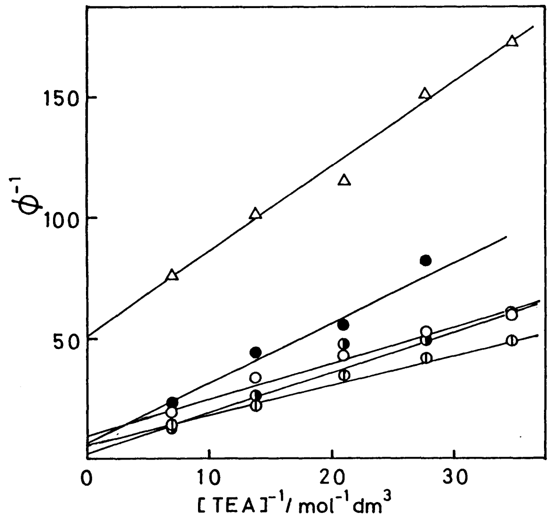


Fig. 1. Double-reciprocal plots of quantum yields vs. concentration of TEA for the photochemical ring-cleavage of **1a** (○), **1b** (⦶), **1c** (◑), **1d** (●), and **1f** (△) in hexane.

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† Present address: Department of Chemistry, Faculty of Education, Miyazaki University, Gakuen-Kibanadai, Miyazaki 889-21.

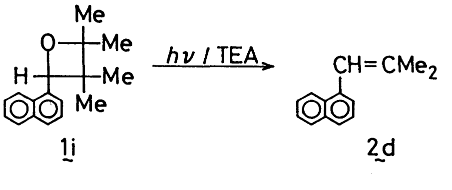
Table 2. Limiting Quantum Yields (ϕ^∞) in Photochemical Ring Cleavage of **1a—d, f** with TEA in Hexane

Oxetane	ϕ^∞
1a	0.09
1b	0.22
1c	0.31
1d	0.20
1f	0.02

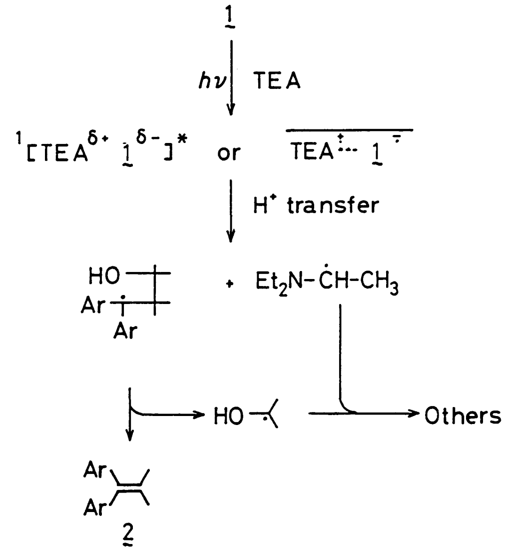
tanes with *p*-toluenesulfonic acid. Substituted benzophenones and alkenes were not produced in the photoreaction. At low conversions (<5%), material balances were better than 90%, though other unreclaimed reactions increasingly occurred at higher conversions.

Quantum Yields. The formation of **2** increased linearly with the irradiation time up to 3% conversion. The formation of **2** increased with an increase in the concentration of TEA, but remarkably decreased at concentrations of TEA higher than 0.1 $\mathrm{mol\,dm^{-3}}$. Since TEA has absorption at 254 nm in the UV spectrum, the absorption of incident light by TEA occurred to some extent. From the above-mentioned results, the photoexcitation of TEA would not bring about the ring-cleavage reactions of **1**. Therefore, the quantum yield (ϕ) for the formation of **2** at a given concentration of TEA was calculated on the basis of the light intensities absorbed by **1**. Thus, the quantum yields (ϕ) in various solvents were determined for the photochemical ring-cleavage reactions of **1b** (Table 1). Moreover, the limiting quantum yields (ϕ^∞) were determined by the usual double-reciprocal plots of ϕ vs. the concentration of TEA, for the photochemical ring-cleavage reactions of **1** in hexane (Fig. 1). The photochemical ring cleavage of **1a—d** proceeded in moderately high quantum yields, while those of **1f** occurred inefficiently. In the case of **1e**, **g**, **h**, no photochemical ring-cleavage occurred. The results are listed in Table 2.

Mechanism. No reaction occurred at all upon direct irradiation of **1** in the absence of TEA. The photochemical ring-cleavage of **1** occurred efficiently in nonpolar solvents, but proceeded inefficiently in polar solvents. Therefore, the exciplex formation between **1** and TEA can be assumed as being an initiation process, though no exciplex emission was observed in the cases of **1**-TEA pairs. An analogous 2,2,3,3-tetramethyl-4-(1-naphthyl)oxetane (**1i**) forms an emissive exciplex ($\lambda_{\max}$ 420 nm) with TEA in hexane; the photoreactions of **1i** with TEA gave 1-(1-naphthyl)-2-methylpropene (**2d**) (Scheme 2). Therefore, we assume a possible mechanism involving the exciplex formation followed by proton transfer from TEA to **1** in the exciplex or the ion pairs, as shown in Scheme 3. Similar mechanisms have been postulated for the photoreaction of aromatic hydrocarbons with TEA.[4] In a manner similar to that for acid-catalyzed fragmentation of oxetane ring, the protonated oxetane gives products (**2**) accompanying the formation of hydroxyalkyl radical which gives untractable materials. In polar solvents, the ion pair would dissociate into free ion radicals, and the inefficient photochemical ring-cleavage reactions would be attributed to the occurrence of unreclaimed reaction from free ion radicals.



Scheme 2.



Scheme 3.

In conclusion, it was found that photochemical ring-cleavage reactions of **1** in the presence of electron donors give the corresponding 1,1-diarylethenes selectively, in contrast with the photoreaction in the presence of electron acceptors[1] which affords substituted benzophenones and alkenes.

Experimental

Gas chromatography was performed on a Shimadzu GC-8A gas chromatograph using a 50 cm column of 2% OV-1 or 2% OV-17 on Chromosorb W. UV spectra and fluorescence spectra were obtained on a Hitachi 150-20 spectrometer or a Hitachi MPF-4 spectrometer, respectively.

Materials. Solvents were purified by usual methods.[5] Triethylamine was distilled before use. Preparation of oxetanes (**1**) were carried out by irradiation of benzene solution containing the substituted benzophenone or 1-naphthaldehyde and the alkene by high-pressure Hg lamp according to the procedure described in the previous paper.[1]

Photoreactions and Determination of Quantum Yields. Concentration of **1** were set in 0.01 $\mathrm{mol\,dm^{-3}}$ and concentration of TEA was variable between 0.03 and 0.144 $\mathrm{mol\,dm^{-3}}$. Aliquot portions (4 $\mathrm{cm^3}$) of reactant solutions and actinometer solutions were introduced into quartz tubes (8 mm, i.d.) and degassed by four freeze-pump-thaw cycles under high vacuum. Irradiation was carried out with an Eikosha EL-A 10 low-pressure Hg lamp using a "merry-go-round" turntable. Incident light intensity (I^0) was determined by the use of photocleavage reaction of 1,2,3,4-tetraphenylcyclobutane to stilbene as an actinometer.[6] Quantum yields were calculated using light intensities (I) corrected by Eq. 1:

$$I = I^0 \varepsilon^1[\mathbf{1}]/(\varepsilon^1[\mathbf{1}] + \varepsilon^{\mathrm{TEA}}[\mathrm{TEA}]) \qquad (1)$$

where ε^1 and $\varepsilon^{\mathrm{TEA}}$ represent molar extinction coefficient of **1** and TEA at 254 nm, respectively.

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