

Ring-Splitting Reaction of 2,2-Diarylthietane by Electron-Transfer Photosensitization of 9,10-Dicyanoanthracene

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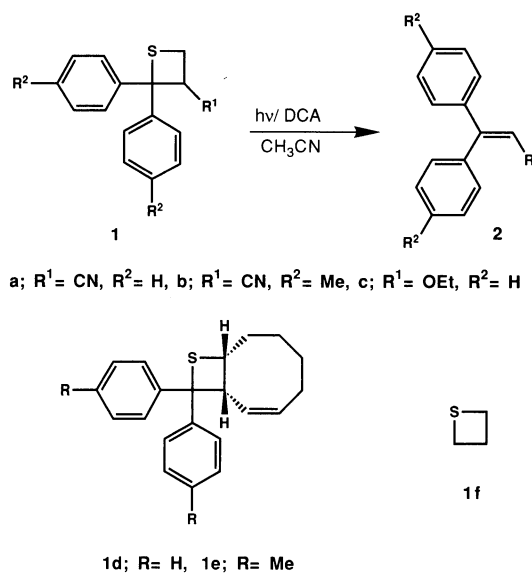
Synopsis. A 9,10-dicyanoanthracene (DCA)-photosensitized reaction of 3-cyano- or 3-ethoxy-2,2-diarylthietane in acetonitrile gave selectively 2-cyano- or 2-ethoxy-1,1-diarylethene. The ring-splitting reaction proceeds via a one-electron oxidation of the sulfur atom of thietane ring by a photochemical electron transfer to the excited singlet state of DCA.

The photochemical electron transfer has provided an efficient method for a ring-splitting reaction of a small-membered ring.¹⁾ In relation to the development of a photochemical metathesis reaction between a ketone and alkene, we have extensively studied the retro Paterno-Büchi reaction of 2,2-diaryloxetanes.^{2,3)} The efficient photochemical ring-splitting of 2,2-diaryloxetanes in the presence of an electron acceptor occurred, but gave a substituted benzophenone and alkene pair, starting materials for the preparation of oxetanes.²⁾ The photochemical ring splitting of 2,2-diaryloxetanes in the presence of an electron donor resulted in a different direction from the case in the presence of an electron acceptor to give 2,2-diarylethenes, though the yield is still low.³⁾ In order to develop an efficient photochemical metathesis reaction, our interest is, therefore, directed toward ring-splitting the analogous 2,2-diarylthietane. We report here on a 9,10-dicyanoanthracene (DCA)-photosensitized ring-splitting reaction of 3-substituted 2,2-diarylthietane (**1**).

Results and Discussion

Photoreaction. A DCA-photosensitized reaction of 3-cyano-2,2-diphenylthietane (**1a**) was performed in acetonitrile at 366nm-irradiation to give 2-cyano-1,1-diphenylethene (**2a**). Similarly, a DCA-photosensitized reaction of 3-cyano-2,2-di-*p*-tolylthietane (**1b**) and 2,2-

diaryl-3-ethoxythietane (**1c**) gave 2-cyano-1,1-di-*p*-tolylethene (**2b**) and 2-ethoxy-1,1-diphenylethene (**2c**), respectively (Scheme 1). The results are shown in Table 1. Though insoluble materials which were probably derived from sulfur were formed at higher conversion, other products, such as substituted thiobenzophenone and alkene, were not formed at all. However, no photoreaction of the bicyclic thietane compound (**1d, e**) occurred to recover the starting materials. Direct irradiation of **1a** at 313nm light resulted in a ring-splitting reaction, though no ring splitting of 2,2-diaryloxetanes occurred due to direct irradiation.



Scheme 1.

Table 1. DCA-Photosensitized Ring-Splitting Reaction of 2,2-Diarylthietane (**1**)

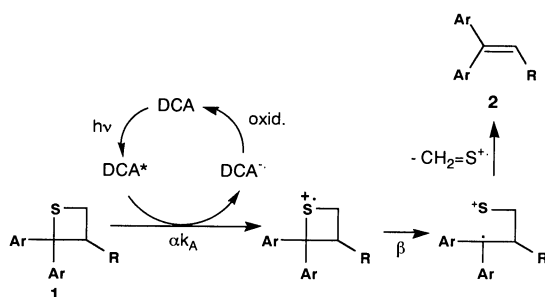
Run No.	1 ($E_{1/2}^{ox}/V$) ^{a)}	Product (Yields/%) ^{b,c)}	Conv. of 1	$K_{SV}^{d)}$	$I/S^{e)}$	$\Phi^f)$
1	1a (1.61)	2a (41)	50	23.7	17.2	0.21
2	1b (1.53)	2a (13)	15	115	119	0.52
3	1c (1.67)	2c (17)	25	167	153	0.10
4	1d (1.46)	— ^{g)}		180		
5	1e (1.48)	— ^{g)}		173		
6 ^{h)}	1a	2a (25)	31			0.04

a) Oxidation potentials vs. Ag/AgNO₃. b) An acetonitrile solution containing **1** (0.05 mol dm⁻³) and DCA (2×10⁻⁵ mol dm⁻³) was irradiated at 366 nm. c) GLC yields based on **1** used. d) Stern–Volmer constants for the fluorescence quenching of DCA by **1**. e) The intercept-to-slope ratio for a double reciprocal plots of ϕ vs. [**1**]. f) Limiting quantum yields for the formation of **2**. g) No reaction. h) Direct irradiation at 313 nm.

Mechanism. The fluorescence of DCA was quenched by **1a—e** at a diffusion-controlled limit. The free-energy change for the electron transfer from **1a—e** to the excited singlet state of DCA ($^1\text{DCA}^*$) was calculated to be negative by the Rehm-Weller equation⁴⁾ using the reduction potential of $^1\text{DCA}^*$ (1.76V)¹⁾ and the oxidation potential of **1** shown in Table 1. For the usual kinetic treatment, we assume Scheme 2 involving a photochemical electron transfer as the key pathway. A steady-state analysis of Scheme 2 gives

$$\phi^{-1} = (\alpha\beta)^{-1}\{1 + (k_A\tau[\mathbf{1}])^{-1}\} = (\alpha\beta)^{-1}\{1 + (K_{SV}[\mathbf{1}])^{-1}\}, \quad (1)$$

where α and β denote the fractions for the formation of $\mathbf{1}^+$ and for the formation of **2** from $\mathbf{1}^+$, respectively; k_A and τ represent the rate constant for the quenching of $^1\text{DCA}^*$ by **1** and the lifetime of $^1\text{DCA}^*$ ($\tau = 15.3$ ns in acetonitrile²⁾), respectively. According to Eq. 1, the intercept-to-slope ratio (I/S) for the usual double reciprocal plots of ϕ vs. the concentration of **1** equals the Stern-Volmer constants (K_{SV}) for the fluorescence quenching of DCA by **1**. Indeed, the double reciprocal plots of ϕ_2 vs. $[\mathbf{1}]$ gave a linear relationship and the I/S values show a satisfactory agreement with the K_{SV} values, as shown in Table 1. These results show that the ring-splitting reaction of **1** certainly proceeds via an electron transfer from **1** to $^1\text{DCA}^*$, followed by a cleavage reaction of the cation radicals.



Scheme 2.

Therefore, it is reasonable that the splitting of the thietane ring proceeds via an initial cleavage of the S-C2 bond, resulting in an opened cation radical stabilized by the aryl group and sulfur atom. This result is in contrast to the photosensitized reaction of 2,2-diaryloxetanes, which proceeds via bond cleavage between the C2—C3 bond to give substituted benzophenone and alkene. The oxidation potentials of **1a—e** were observed to be in the 1.46 to 1.67 V range and were much lower than that for 2,2-diaryloxetanes.²⁾ The oxidation potentials of **1a—e** are rather close to that of unsubstituted thietane (**1f**; $E_{1/2}^{\text{ox}} = 1.30$ V). It is deduced for an electron release to occur from the sulfur atom of thietanes in an anodic oxidation and photochemical electron transfer, that a positive charge of $\mathbf{1}^+$ might develop over the sulfur atom. Thus, the different direction for ring splitting between 2,2-diarylthietane and 2,2-diaryloxetane can be attributed to the distribution of positive charge of the cation radicals, i.e., positive charge might develop over the sulfur atom for 2,2-diarylthietane and the aryl group for 2,2-diaryloxetane.

Experimental

^1H and ^{13}C NMR spectra were taken on a Bruker AC-250P spectrometer for a chloroform- d_1 solution using tetramethylsilane as the internal standard. Mass spectra were taken on a JEOL JMS-D300S spectrometer. A GLC analysis was performed using a Shimadzu GC 14A with a capillary column (CBP1-M-25-025). The oxidation potentials were measured in acetonitrile at a 500 mV s^{-1} of sweep rate on a Hokuto Denko HA-501G and an HB-105 using Ag/AgNO₃ as a reference electrode.

Preparation of 2,2-Diarylthietanes (1a—c). Thiobenzophenone and *p,p'*-dimethylthiobenzophenone were prepared by the reaction of benzophenone and *p,p'*-dimethylbenzophenone with hydrogen sulfide in the presence of hydrogen chloride, respectively.⁵⁾ Since these thiobenzophenones were readily oxidized, accompanied by a disappearance of the blue color, they were used for the preparation of thietanes without purification. The preparation of **1a** was performed from a photoaddition of thiobenzophenone (0.05 mol) with acrylonitrile (1.06 mol) in cyclohexane (100 ml). Similarly, **1b—e** were prepared from a photoreaction of substituted thiobenzophenone with acrylonitrile, ethyl vinyl ether, or 1,3-cyclooctadiene according to the literature.⁶⁾ Commercially available **1f** was used.

2,2-Diphenyl-3-cyanothietane (1a). Yield 24%. Mp 84.5—85.0°C (lit.⁷⁾ 84°C). ^{13}C NMR $\delta = 24.3, 39.4, 60.9, 117.6, 125.2, 127.4, 128.2, 128.5, 128.7, 132.4, 140.3, 146.1$.

2,2-Di-*p*-tolyl-3-cyanothietane (1b). Yield 16%. Mp 93.5—94.0°C. ^1H NMR $\delta = 2.35$ (6H, s), 3.29 (1H, t, $J = 8, 7$ Hz), 3.54 (1H, t, $J = 9.1$ Hz), 4.96 (1H, t, $J = 9.0$ Hz), 7.05—7.57 (8H, m). ^{13}C NMR $\delta = 21.1, 24.2, 39.5, 60.7, 117.8, 125.0, 128.0, 129.1, 129.3, 137.2, 137.7, 137.9, 143.4$. MS m/z 279 (M^+), 233 ($M - \text{SCH}_2$), 226 ($M - \text{CH}_2\text{CHCN}$). Found: C, 77.35; H, 6.20; N, 5.04%. Calcd for $\text{C}_{18}\text{H}_{17}\text{SN}$: C, 77.42; H, 6.09; N, 5.02%.

3-Ethoxy-2,2-diphenylthietane (1c). Yield 31%. Mp 69.5—70.5°C (lit.⁶⁾ 71—72°C). ^{13}C NMR $\delta = 15.2, 32.7, 64.3, 70.0, 79.8, 126.0, 126.6, 126.8, 127.6, 128.2, 129.7, 140.6, 147.7$.

10,10-Diphenyl-*cis*-9-thiabicyclo[6.2.0]-2-decene (1d). Yield 26%. Mp 108—109°C (lit.⁷⁾ 110.5°C). ^{13}C NMR $\delta = 24.5, 25.8, 28.0, 34.4, 47.2, 55.9, 60.5, 125.8, 126.4, 126.8, 128.1, 128.4, 128.7, 129.4, 131.4, 141.6, 148.6$.

10,10-Di-*p*-tolyl-*cis*-9-thiabicyclo[6.2.0]-2-decene (1e). Yield 12%. Mp 150—151°C. ^1H NMR $\delta = 1.56—2.33$ (8H, m), 2.31 (3H, s), 2.33 (3H, s), 3.41 (1H, td, $J = 11.0, 3.1$ Hz), 4.64 (1H, dd, $J = 10.7, 4.8$ Hz), 5.42 (2H, m), 6.89—7.54 (10H, m). ^{13}C NMR $\delta = 20.9, 21.1, 24.5, 25.8, 28.0, 34.3, 47.1, 55.9, 60.1, 125.6, 128.5, 128.8, 129.0, 129.3, 131.6, 135.9, 136.3, 138.9, 146.9$. MS m/z 334 (M^+). Found: C, 82.68; H, 7.90%. Calcd for $\text{C}_{23}\text{H}_{26}\text{S}$: C, 82.63; H, 7.78%.

Photochemical Ring-Cleavage Reaction. A DCA-photosensitized ring-splitting reaction was performed for an acetonitrile solution containing a given concentration of **1** ($0.02—0.1$ mol dm^{-3}) and DCA (2×10^{-5} mol dm^{-3}) by irradiating at 366 nm, whereas the direct irradiation of **1a** (0.05 mol dm^{-3}) in acetonitrile was performed at 313 nm. Aliquot portions (4 ml) of the reactant solutions and actinometer were introduced into Pyrex tubes (8 mm, i.d.) and degassed by four freeze-pump-thaw cycles under high vacuum. Irradiation was carried out with a high-pressure mercury lamp (Eikosha PIH-300) under cooling with water by the use of appropriate light filters and a merry-go-round turntable. Details concerning the filter and actinometer have been described in the literature.⁸⁾

2-Cyano-1,1-diphenylethene (2a). ^1H NMR $\delta = 5.74$ (1H, s), 7.25—7.48 (10H, m). ^{13}C NMR $\delta = 94.9, 117.9, 128.5, 128.6, 128.7, 129.6, 130.1, 130.4, 137.0, 138.9, 163.2$. MS m/z 205

(M⁺). IR 2220 cm⁻¹ (ν_{CN}).

2-Cyano-1,1-di-*p*-tolylethene (2b). ¹H NMR δ =2.39 (3H, s), 2.41 (3H, s), 5.65 (1H, s), 7.19–7.34 (8H, m). ¹³C NMR δ =21.3, 21.4, 93.4, 113.3, 128.5, 129.2, 129.3, 129.6, 134.4, 136.4, 140.2, 140.8, 163.2. MS m/z 233 (M⁺).

2-Ethoxy-1,1-diphenylethene (2c). ¹H NMR δ =1.33 (3H, t, J =7.0 Hz), 3.97 (2H, q, J =7.1 Hz), 6.49 (1H, s), 7.17–7.43 (10H, m). ¹³C NMR δ =15.4, 68.9, 120.2, 126.3, 126.4, 127.9, 128.2, 128.4, 129.8, 137.8, 140.7, 145.1. MS m/z 224 (M⁺), 196 (M–Et), 166 (M–CHOEt).

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