



A novel *cis*–*trans* photoisomerization of vinylidenecyclopropanes via an electron-transfer chain process

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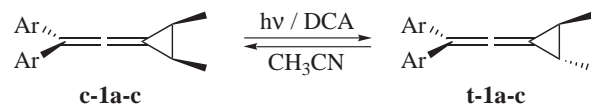
Abstract—The *cis*–*trans* photoisomerization of 1-bis(4-methoxyphenyl)vinylidene-2,3-dimethylcyclopropanes in aerated acetonitrile was sensitized by 9,10-dicyanoanthracene and chloranil in the presence of an additive via an electron-transfer chain process, in which the cation radicals generated from the vinylidenecyclopropanes were involved as chain carriers. © 2001 Elsevier Science Ltd. All rights reserved.

Photoinduced electron-transfer reactions of small ring compounds have been the subject of considerable interest from mechanistic and synthetic viewpoints in recent years.^{1–6} The substrates so far examined include cyclopropanes, methylenecyclopropanes, oxiranes, aziridines, cyclobutanes, methylenecyclobutanes, and so on. However, little is known about the photoinduced electron-transfer reactions of vinylidenecyclopropanes, although it is expected that a variety of such reactions is feasible.^{7–10} We now report a novel *cis*–*trans* photoisomerization of *cis*- and *trans*-1-bis(4-methoxyphenyl)-vinylidene-2,3-dimethylcyclopropanes (**c-1a** and **t-1a**) in the presence of an electron acceptor, which involves an electron-transfer chain mechanism. A key step of this photoreaction is the generation of the free radical cation from **1a** as a chain carrier.

Irradiation of an aerated acetonitrile solution containing **c-1a** and 9,10-dicyanoanthracene (DCA) through an aqueous CuSO₄–NH₃ filter solution (>350 nm light) caused the *cis*–*trans* isomerization to give **t-1a** (Scheme 1).¹¹ Prolonged irradiation afforded a photostationary state (PSS) mixture of **c-1a** and **t-1a** in a 1:3 ratio. Similar irradiation of **t-1a** afforded the same PSS. This photoisomerization was also sensitized by chloranil (CHL), which is a typical triplet electron-transfer sensitizer. Efficiencies for the photoisomerization of **c-1a**

and **t-1a** depended on the concentration of dissolved oxygen, the polarity of solvents, and the additives, although the PSS ratios were not changed. The photoisomerization in the presence of air proceeded much faster than that in the absence of air. The photoisomerization in acetonitrile occurred much faster than that in less polar solvents such as dichloromethane and benzene. The addition of aromatic hydrocarbons such as phenanthrene (Phen) and biphenyl (BP) and metal salts such as Mg(ClO₄)₂ accelerated the photoisomerization, where the values of $\Phi_{c \rightarrow t}$ exceed unity. Similar irradiation of **c-1b–c** in the presence of DCA or CHL caused the *cis*–*trans* photoisomerization, but the efficiencies for the isomerization decreased with decreasing the electron-donating ability of substituents on the phenyl rings of **1**. These results are summarized in Fig. 1 and Tables 1 and 2.

The fluorescence of DCA in acetonitrile was efficiently quenched by **c-1a–c** at nearly diffusion-controlled rates. The free energy changes (ΔG) for a single electron-transfer from **c-1a–c** to the excited singlet DCA (¹DCA*) were estimated to be negative (Table 3).¹²



a; Ar = *p*-MeOC₆H₄ **b**; Ar = *p*-MeC₆H₄ **c**; Ar = Ph

Scheme 1.

Keywords: photoisomerization; vinylidenecyclopropane; photoinduced electron-transfer; cation radical; chain process.

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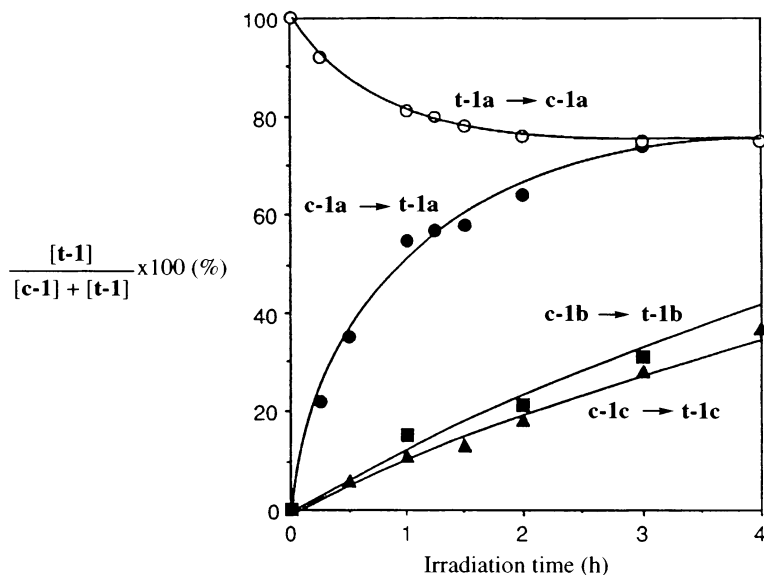


Figure 1. Plots of **c-1** and **t-1** % versus irradiation time. $[DCA]=5 \times 10^{-4} \text{ mol dm}^{-3}$, $[c-1]=[t-1]=8.4 \times 10^{-2} \text{ mol dm}^{-3}$ in CD_3CN .

Table 1. Effects of oxygen, solvents, and substituents on the photoisomerization of **c-1** to **t-1** in the presence of DCA

Entry	Substrate	Solvent	ϵ^a	Atmosphere	ϕ^b
1	c-1a	CH_3CN	37.5	Degassed	0.17
2	c-1a	CH_3CN	37.5	Aerated	0.67 (1.0) ^c
3	c-1a	CH_3CN	37.5	Argon	0.23
4	c-1a	CH_2Cl_2	8.9	Aerated	0.25
5	c-1a	C_6H_6	2.3	Aerated	0.017
6	c-1b	CH_3CN	37.5	Aerated	0.01
7	c-1c	CH_3CN	37.5	Aerated	0.009

^a ϵ =dielectric constant of solvent.

^b Values at >400 nm irradiation, $[DCA]=5 \times 10^{-4} \text{ mol dm}^{-3}$, $[c-1]=1 \times 10^{-2} \text{ mol dm}^{-3}$.

^c The value in parentheses is a limiting quantum yield.

Table 2. Effects of sensitizers and additives on the photoisomerization of **c-1a** to **t-1a** in aerated acetonitrile solution

Entry	Sensitizer	Additive ^a	ϕ^b
1	DCA	–	0.67
2	DCA	$LiClO_4 (5 \times 10^{-3})$	2.57
3	DCA	$Mg(ClO_4)_2 (2.5 \times 10^{-3})$	4.65
4	DCA	$Mg(ClO_4)_2 (5 \times 10^{-3})$	13.7
5	DCA	$BP (1.5 \times 10^{-3})$	1.32
6	DCA	$BP (1 \times 10^{-2})$	1.87
7	DCA	$Phen (1 \times 10^{-2})$	3.33
8	CHL	–	0.80
9	CHL	$Mg(ClO_4)_2 (2.5 \times 10^{-3})$	2.14

^a Concentrations of additives (mol dm^{-3}) are designated in parentheses.

^b Values at >400 nm irradiation, $[DCA]=5 \times 10^{-4} \text{ mol dm}^{-3}$, $[CHL]=5 \times 10^{-4} \text{ mol dm}^{-3}$, $[c-1a]=1 \times 10^{-2} \text{ mol dm}^{-3}$.

From these results, we propose a photoinduced electron-transfer mechanism as shown in Scheme 2 for the photoisomerization of **c-1** to **t-1**. The first stage is one electron-transfer from **c-1** to the excited singlet of DCA or the excited triplet state of CHL to give a radical ion pair $[DCA^{\bullet-} \cdots c-1^{+\bullet}]$ or $[CHL^{\bullet-} \cdots c-1^{+\bullet}]$, respectively. The

Table 3. Thermodynamic and kinetic parameters for photo-induced electron-transfer from **c-1** to $^1DCA^*$

Cyclopropane	$k_q^a (\text{mol}^{-1} \text{ dm}^3 \text{ s}^{-1})$	$E_{p/2}^{ox,b} (\text{V})$	$\Delta G^c (\text{kJ mol}^{-1})$
c-1a	8.3×10^9	0.60	–98.3
c-1b	9.0×10^9	0.65	–93.5
c-1c	8.6×10^9	0.85	–74.2

^a Rate constant for the fluorescence quenching of DCA in aerated acetonitrile. $\tau(DCA, CH_3CN)=15.4 \text{ ns}$.

^b Oxidation potential (V versus $Ag/AgClO_4$).

^c Calculated free energy change for the one electron-transfer process from **c-1** to $^1DCA^*$ by Rehm–Weller equation. See reference 12.

radical ion pair produces the free radical ions $DCA^{\bullet-}$ (or $CHL^{\bullet-}$) and $c-1^{+\bullet}$, or decays by back electron-transfer to the ground states of DCA (or CHL) and **c-1**. Dissociation of the radical ion pair to the free radical ions occurs more efficiently in acetonitrile than other less polar solvents, and is accelerated by adding metal salts^{1a,4b,4d,13} or aromatic hydrocarbons,^{4a,4d,4e,14} or dissolved molecular dioxygen.¹⁵ In the presence of additives, *cis*–*trans* isomerization occurs via the ring cleavage of $c-1^{+\bullet}$ at the C1–C2 bond to give $2^{+\bullet}$.¹⁶ The

- Y. *J. Synth. Org. Chem. Jpn.* **1989**, *47*, 916–930; (c) Loupy, A.; Tchoubar, B.; Astruc, D. *Chem. Rev.* **1992**, *92*, 1141–1165.
14. A possible explanation for the effect of aromatic hydrocarbons (ArH) is as follows: (i) Hole transfer from $\text{ArH}^{\bullet+}$ to **c-1** facilitates the generation of $\text{c-1}^{\bullet+}$ since the oxidation potential of **c-1** is lower than that of ArH. (ii) π -Complexation between $\text{c-1}^{\bullet+}$ and ArH accelerates the dissociation of $[\text{DCA}^{\bullet-} \cdots \text{c-1}^{\bullet+}]$ or $[\text{CHL}^{\bullet-} \cdots \text{c-1}^{\bullet+}]$. See: (a) Majima, T.; Pac, C.; Sakurai, H. *J. Am. Chem. Soc.* **1980**, *102*, 5265–5273; (b) Majima, T.; Pac, C.; Nakasone, A.; Sakurai, H. *J. Am. Chem. Soc.* **1981**, *103*, 4499–4508.
15. The role of molecular dioxygen can be interpreted as a rapid electron-transfer from $\text{DCA}^{\bullet-}$ to O_2 which suppresses the back electron-transfer from $\text{DCA}^{\bullet-}$ to $\text{c-1}^{\bullet+}$. See: (a) Eriksen, J.; Foote, C. S.; Parker, T. L. *J. Am. Chem. Soc.* **1977**, *99*, 6455–6456; (b) Spada, L. T.; Foote, C. S. *J. Am. Chem. Soc.* **1980**, *102*, 391–393; (c) Eriksen, J.; Foote, C. S. *J. Am. Chem. Soc.* **1980**, *102*, 6083–6088. (d) Lewis, F. D.; Petisce, J. R.; Oxman, J. D.; Nepras, M. J. *J. Am. Chem. Soc.* **1985**, *107*, 203–207.
16. Trapping of $\text{2}^{\bullet+}$ with nitriles, molecular dioxygen, and methanol was unsuccessful. The C1–C2 bond cleavage is supported by the (3+2) photocycloaddition of 1-bis(4-methoxyphenyl)vinylidene-2,2,3,3-tetramethylcyclopropane with nitriles via photoinduced electron-transfer.⁷ However, an alternative process via C2–C3 bond cleavage may not be ruled out.