Photoreversion of Naphthalene-Benzene Cyclodimers and Naphthalenes-Furan Cyclodimers

Taehee Noh*, Daekyun Kim, and Shinho Jang

Department of Chemistry Education, Seoul National University, Seoul 151-742, Korea
*Received December 7, 1996*

An adiabatic photoreaction is a chemical process that occurs entirely on a single excited electronic energy surface.[1] Even though many photoreactions involving small structural changes occur adiabatically, few examples exist for which photochemical carbon-carbon bond breaking and making occur adiabatically. The photochemical electrocyclic ring opening of Dewar-structured aromatic compounds and the photochemical rearrangement of benzvalenes have been found to be adiabatic.[2] The efficient generation of electronically excited products has been observed in some photochemical electrocyclic dissociations of 1,2-dioxetanes,[2] dibenzenes,[3] naphthalene-benzene dimers,[4,5] anthracene-benzene dimers,[6] anthracene-naphthalene dimers,[7] and anthracene-furan dimers.[8] Although several cyclodimers with the unit of naphthalenes have been synthesized, their photoreactions, except for the [4+4] and cage dimers (**1** and **2**) of naphthalene and 1,4-difluorobenzene,[4,5] have rarely been studied. In this study, we investigated the photoreversion reactions of the cage dimer (**3**) of naphthalene and benzene, the cage dimer (**4**) of 1-naphthalenecarbonitrile and furan, the cage dimer (**5**) of 2-naphthalenecarbonitrile and furan, the *syn*- [2+2] dimer (**6**) of naphthalene and benzene, and the *syn*- [2+2] dimer (**7**) of 1-naphthalenecarbonitrile and furan (Scheme 1).

The syntheses of **3** and **6** using electrolytic bisdecarboxylation of diacids were reported in 1979.[9] Later, the synthesis of **3** using a dehydroxylation method from 2-dimethylamino-1,3-dioxolane derivative and the preparation of 6 through the Cope rearrangement of the [4+4] dimer have been also accomplished.[10] The cyclodimers **3** and **6** were synthesized from the methyl orthoformate of *cis*- 3,5-cyclohexadiene-1,2-diol by a modified method (Scheme 2). A benzene solution of naphthalene (1.989 g, 1.55 x 10^{-2} mole) and the methyl orthoformate (6.069 g, 4.40 x 10^{-2} mole), which was prepared from 1,4-cyclohexadiene in 4 steps,[6] was irradiated through a Pyrex filter with a 450 watt Hanovia medium pressure mercury lamp for 16 hours under a nitrogen atmosphere. After the reaction mixture in tetrahydrofuran was

treated with aqueous HCl solution, the [4+4] diol (**8**) was isolated in 47.9% yield by extraction with dichloromethane and silica gel chromatography eluting with *n*- hexane-diethyl ether mixtures of increasing polarity.[11] Heating **8** (0.199 g, 8.29 x 10^{-4} mole) in ethanol at 73 °C for 5 hours under a nitrogen atmosphere yielded the *syn*- [2+2] diol (**9**), which was isolated in 81.2% yield based on the consumed **8**.[12] The half-life of the Cope rearrangement of **8** at the temperature was 3.8 hours. The diol **9** (67.1 mg, 2.80 x 10^{-4} mole) was then converted to its dimethylformamide acetal with excess *N,N*- dimethylformamide dimethyl acetal under anhydrous conditions.[13] The crude dimethylformamide acetal in dichloromethane was treated with trifluoromethanesulfonic anhydride (0.1 mL) and *N,N*- diisopropylethylamine (0.05 mL) for 30 minutes to give **6** in 27.6% isolated yield. The compound **3** was prepared from triplet sensitized intramolecular cyclization of **8** followed by dehydroxylation of the corresponding cage diol (**10**) in 58.5% yield.[13] Structural identification for all known compounds was achieved by comparison with the ^{1}H NMR data in literature.

The synthesis of **7** was recently accomplished in our laboratories through the photocycloaddition of furan to 1-naphthalenecarbonitrile at a low temperature followed by a facile Cope rearrangement at room temperature.[14] The compound **4** was prepared from the photocycloaddition of furan to 1-naphthalenecarbonitrile at a low temperature followed by a triplet-sensitized intramolecular cyclization in 14.3% yield based on the consumed 1-naphthalenecarbonitrile.[14,15] The compound **5** was prepared by the photoreaction of 2-naphthalenecarbonitrile and furan as previously reported.[16]
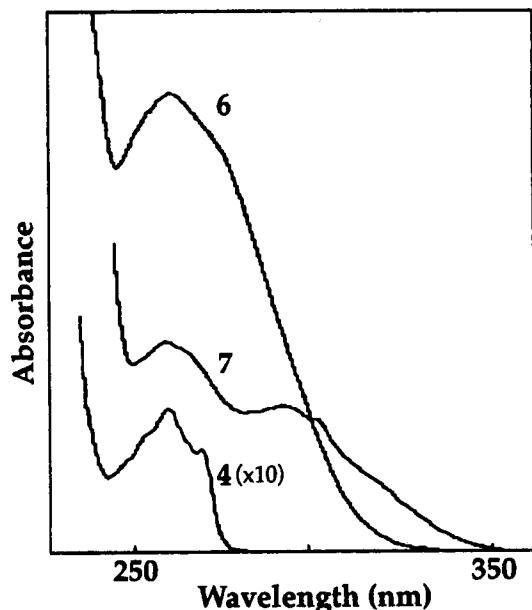
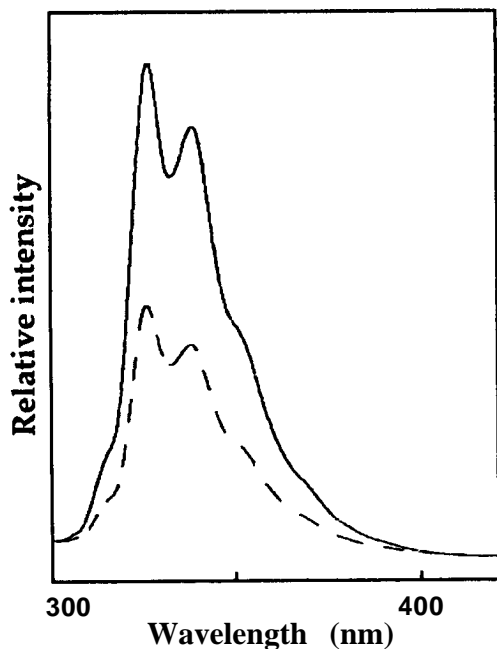The electronic absorption spectra of the cyclodimers **3**-**7**
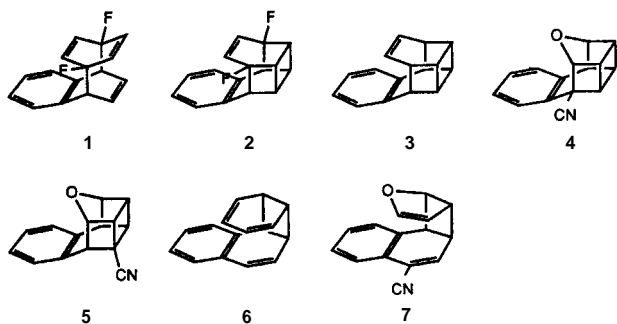
Scheme 2.
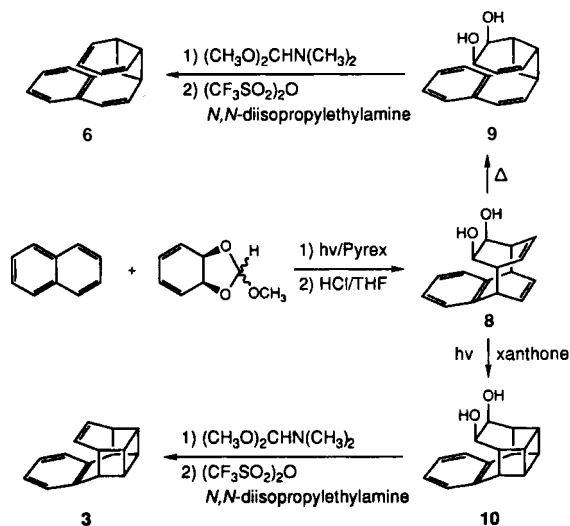
Scheme 1.

in cyclohexane were compared. The UV spectra of **3, 4,** and **5** are characterized by the onset of absorption around 290 nm and by a maximum around 260 nm because these compounds have the *o*- xylene system as a common characteristic chromophore. However, the absorption band at the longer wavelength side for **6** and **7** is shifted to longer wavelength than that of **4** (Figure 1). The cyclodimer **6** has an absorption maximum at 262 nm and a long tail which reaches beyond 340 nm. The cyclodimer **7** exhibited a low-intensity band tailing until *ca.* 350 nm. Compared to the

UV spectrum of 1,2-dihydronaphthalene, the tail reaches to the longer wavelength, which may be explained by through-bond interactions of double bonds and cyclobutyl ring.[17]

Thermal stability of the cyclodimers is sufficient to allow the study of the photocycloreversion at room temperature. Irradiation of the cyclodimers (~10^{-2} M) through a Vycor filter resulted in the corresponding naphthalenes quantitatively. When **3** or **6** in cyclohexane was irradiated at 260 nm, very

Figure 1. The electronic absorption spectra of **4, 6** and **7** in cyclohexane.
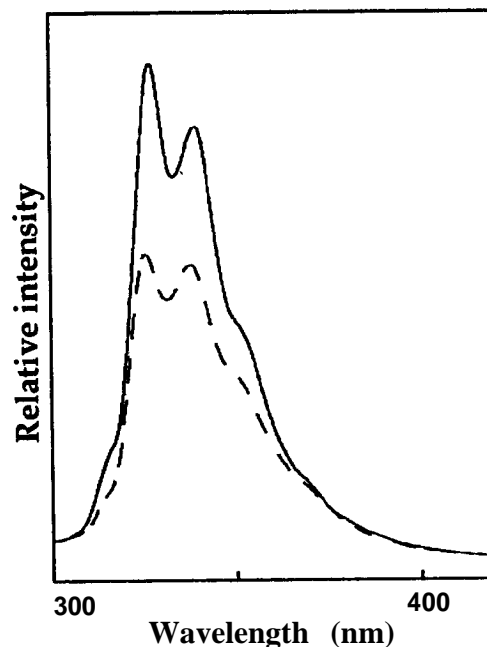

Figure 3. Emission spectra of **6** (dotted line) and naphthalene (solid line) in cyclohexane. These emission spectra are observed by the irradiation of UV light at 260 nm with the same absorbance at that wavelength.

Figure 2. Emission spectra of **3** (dotted line) and naphthalene (solid line) in cyclohexane. These emission spectra are observed by the irradiation of UV light at 260 nm with the same absorbance at that wavelength.
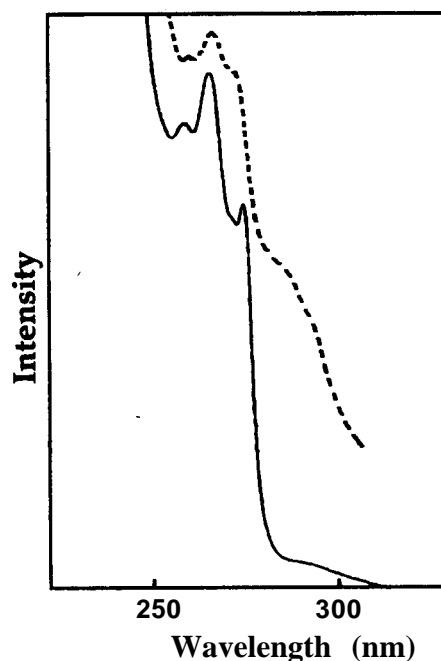
Figure 4. UV spectrum (solid line) and excitation spectrum (dotted line, λ_{em}= 330 nm) of **3** in cyclohexane.
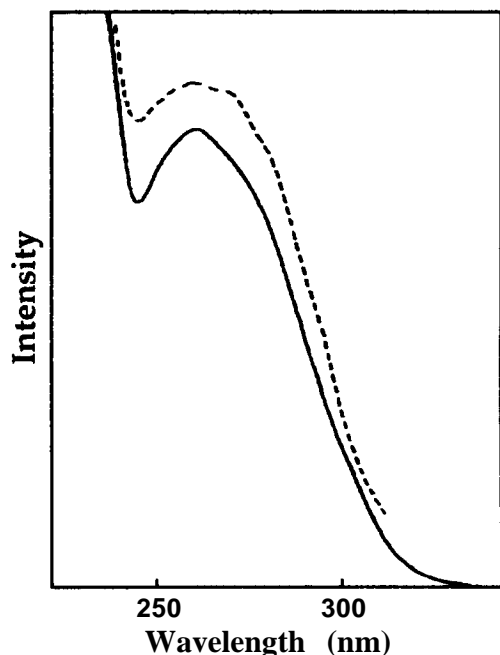
Figure 5. UV spectrum (solid line) excitation spectrum (dotted line, λ_{em}=330 nm) of **6** in cyclohexane.

Table 1. The Efficiency of Adiabatic Photoreversion of the Cyclodimers

	1[a]	2[b]	3[c]	4[c]	6[c]
Φ_{Np^*}	0.55	0.22[c]	0.50±0.02	0	0.63±0.01

[a]Taken from ref 5, in hexane. [b]Taken from ref 4, in ethanol. [c]The average of at least two separate determinations in cyclohexane.

efficient fluorescent emission from naphthalene was observed (Figures 2 and 3). The excitation spectra also showed that the emission from naphthalene as impurity is negligible (Figures 4 and 5). However, no monomer emission was observed for the photolysis of **4, 5,** or **7,** as revealed by the excitation spectrum. The efficiency of the formation of excited naphthalene from **3** and **6** was determined by comparing the emission spectrum with that of naphthalene with a JASCO spectrofluorometer (Table 1).[4]

The resonance energy of furan is less than that of benzene by about 20 kcal/mole.[18] Therefore, the decomposition of naphthalene-benzene dimers is expected to be much more exothermic than that of naphthalene-furan dimers. Higher exothermicity in the conversion of **3** and **6** than **4, 5,** and **7** to their unit components distorts the normal energy surfaces more and thus allows greater production of the excited state naphthalene.[2] The lower quantum yield of adiabaticity in the photoreversion of **2** (0.22) than that of **3** (0.50) may be explained by the stabilization of bridge C-C bonds with fluorine atoms on the bridgehead as estimated with substituted benzene dimers.[6c] The lower quantum yield of adiabaticity in the photoreversion of **3** (0.50) than that of **6** (0.63) was observed, although the cage dibenzene is estimated to have more internal energy than the *syn*-[2+2] dibenzene by about 20 kcal/mole.[19] The lower efficiency of adiabaticity of **2** (0.22) than that of **1** (0.55) has also been

observed previously.[4,5] Since the photo-initiated dissociation of the cage structure should involve more steps than that of the [2+2] and [4+4] structures, the lower efficiency of adiabatic photodissociation may be due to more deactivation pathways available. A detailed theoretical analysis on the energetic of the photoreactions is under investigation in our laboratories.

References

1. (a) Forster, T. *Pure & Appl. Chem.* **1970,** *24,* 443. (b) Forster, T. *Pure& Appl. Chem.* **1973,** *34,* 225.
2. Turro, N. J.; McVey, J.; Ramamurthy, V.; Lechtken, P. *Angew. Chem. Int. Ed. Engl.* **1979,** *18,* 572, and references therein.
3. Yang, N. C.; Noh, T.; Gan, H.; Halfon, S.; Hrnjez, B. J. *J. Am. Chem. Soc.* **1988,** *110,* 5919.
4. Kimura, M.; Kura, H.; Nukada, K.; Okamoto, H.; Satake, K.; Morosawa, S. *J. Chem. Soc., Perkin Trans. 1* **1988,** 3307.
5. Okamoto, H.; Kimura, M.; Satake, K.; Morosawa, S. *Bull. Chem. Soc. Jpn.* **1993,** *66,* 2436.
6. (a) Yang, N. C.; Chen, M.-J.; Chen, P.; Mak, K. T. *J. Am. Chem. Soc.* **1982,** *104,* 853. (b) Yang, N. C.; Chen, M.-J.; Chen, P. *J. Am. Chem. Soc.* **1984,** *106,* 7310. (c) Kimura, M.; Okamoto, H.; Kura, H.; Okazaki, A.; Nagayasu, E.; Satake, K.; Morosawa, S.; Fukazawa, M.; Abdel-Halim, H.; Cowan, D. O. *J. Org. Chem.* **1988,** *53,* 3908.
7. (a) Albini, A.; Fasani, E.; Faiardi, D. *J. Org. Chem.* **1987,** *52,* 155. (b) Albini, A.; Fasani, E. *J. Am. Chem. Soc.* **1988,** *110,* 7760.
8. Noh, T.; Lim, H.; Kim, D. *Bull. Korean Chem. Soc.* **1997,** *18,* 247.
9. Mak, K. T.; Srinivasachar, K.; Yang, N. C. *J. Chem. Soc., Chem. Comm.* **1979,** 1038.
10. King, J. L. Ph.D. Thesis, The University of Chicago, 1988.
11. **8:** mp 119.5-120.0 ℃; ^{1}H NMR (CDCl$_3$, 80 MHz), 7.10 (4H, m), 6.38 (2H, dd, J =5.0, 3.2 Hz), 6.08 (2H, dd, J = 5.4, 3.1 Hz), 3.69 (4H, m), 3.12 (2H, m), 2.25 (2H, dd, J =4.4, 1.7 Hz); IR (CHCl$_3$) 3700-3120, 3050, 3015, 2950, 1630, 1020 cm^{-1}; UV (Ethanol) λ_{nm}(ε); 277.4 (640), 269.6 (660); MS (CI$^+$, methane) m/e 241 (M+1), 223, 205, 129, 128 (100), 95, 83, 66.
12. **9:** mp 140.0-141.8 ℃ (dichloromethane-hexane); ^{1}H NMR (CDCl$_3$, 200 MHz) 7.12 (2H, m), 6.96 (2H, m), 6.29 (1H, dd, J =9.8, 1.5 Hz), 6.02 (1H, ddd, J =9.8, 5.7, 1.6 Hz), 5.85 (1H, dd, J =9.8, 3.4 Hz), 5.64 (1H, dd, J = 10.0, 3.4 Hz), 4.04 (3H, m), 3.64 (2H, m), 2.88 (1H, m), 2.23 (1 H, br s), 1.47 (1 H, br s); ^{13}C NMR (CDCl$_3$, 50 MHz) 133.09, 131.74, 130.93, 128.64, 128.41, 128.07, 128.00, 127.89, 127.45, 127.31, 69.37, 65.60, 42.78, 41.97, 38.37, 35.16; IR (CHCl$_3$) 3600-3200, 3025, 2980, 2925, 1605, 1235 cm^{-1}; UV (Ethanol) λ_{nm}(ε); 273.8 (6280); MS (CI$^+$, methane) m/e 241 (M+1, very weak), 240, 222, 205, 129, 128 (100), 95; Elemental analysis;

360 *Bull. Korean Chem. Soc.* **1997,** Vol. 18, No. 4

Communications to the Editor

Cald. for $C_{16}H_{16}O_2$; C, 80.00%, H, 6.67%. Found; C, 79.13%, H, 6.57%.

13. King, J. L.; Posner, B. A.; Mak, K. T.; Yang, N. C. *Tetrahedron Lett.* **1987,** *28,* 3919.
14. Noh, T.; Kim, D. *Tetrahedron Lett.* **1996,** *37,* 9329.
15. Elemental analysis of **4:** Cald. for $C_{15}H_{11}NO$; C, 81.45%, H, 4.98%, N, 6.33%. Found; C, 81.48%, H, 5.09%, N, 6.22%.
16. Sugioka, T.; Pat, C.; Sakurai, H. *Chem. Lett.* **1972,** 791.
17. Gleiter, R.; Schafer, W. *Acc. Chem. Res.* **1990,** *23,* 369.
18. Wheland, G. W. *Resonance in organic chemistry;* Wiley: New York, 1955; p 85.
19. Schriver, G. W.; Gerson, D. J. *J. Am. Chem. Soc.* **1990,** *112,* 4723.

The First Example of Cation Radical Induced Decarboxylation from Carbonates

Young Sook Park and Wang Keun Lee*

Department of Chemistry Education, Chonnam National University, Kwang-Ju 500-757, Korea
Received January 13, 1997

In the course of our investigation of cation radical induced oxidation of carbonates, we have discovered that thianthrene cation radical perchlorate $(\mathbf{1}, Th^{+} \cdot ClO_4^-)$ readily oxidizes *tert*- butyl phenyl carbonate (**2**) in acetonitrile at room temperature. This is a novel reaction of carbonates, and offers the first example of cation radical induced decarboxylation. Carbonates, diester of carbonic acid, are known as stable organic compounds and as useful intermediates for a variety of industrial and synthetic applications. Alkyl aryl carbonates undergo the loss of carbon dioxide or are converted to diaryl carbonates at reasonable rates only if heated in the region 180-200 °C.[1] In contrast, the reaction (Scheme 1) of this very stable carbonate **2** with **1** at room temperature leads to rapid oxidative decarboxylation. Quantitative data are listed in Table 1. Product balances account for 88% of the *tert*- butyl groups which appear as cations, 91% of the phenoxy groups, and 95.1% of the cation radicals.
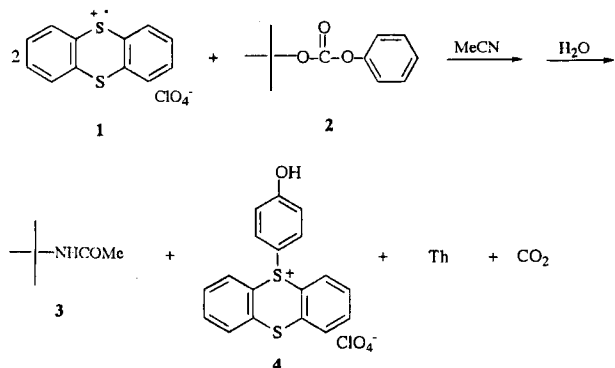
The major products are *N-tert*- Butylacetamide (**3**)[2] from *tert*- butyl cations, 5-(4-hydroxyphenyl)thianthreniumyl perchlorate (**4**)[3] from phenoxy radicals, thianthrene (Th) and carbon dioxide. Thus, the intermediates which are trapped in the course of oxidative decomposition were *tert*- butyl cations and phenoxy radicals. *tert*- Butyl cations reacted with

the solvent acetonitrile to give a Ritter-type intermediate ($Me_3CN=^+CMe$), which reacted with water during work-up, to give **3**. The simplest representation of the reaction of **1** with **2** and the formation of **3** and **4** is given in eq 1-5.

Table 1. Products of Reaction of Thianthrene Cation Radical Perchlorate with *tert*- Butyl Phenyl Carbonate in MeCN at Room Temperature[a]

Reactants, mmol x 10^2		Products (%),[b] mmol x 10^2			
1	2	3	4[c]	Th[d]	PhOH
100	50	44	45	49	0.5
		(88)	(45)	(49)	(1)

[a]Reaction was carried out by adding acetonitrile by syringe to a stirred, septum-capped round-bottomed flask containing 1.00 mmol of **1** and 0.50 mmol of **2** under argon atmosphere. The color of **1** was discharged within 10 minutes, but stirring was continued overnight. Water (5 mL) was added. The solution was neutralized with $NaHCO_3$ and extracted repeatedly with CH_2Cl_2 (4 x 20 mL). [b]Products were identified and quantified by GC, using the method of "standard addition" of authentic samples,[16] and by ^{1}H NMR and GC/MS. GC analyses were made with a 2 m x 1/8 in. stainless steel column packed with 10% OV-101 on Chrom W. Reaction was run four times, and the averaged yields of products are given. [c]Isolated yield. 100 x (mmol of product)/ initial mmol of $Th^+ \cdot ClO_4^-$. This represents 90% of the phenoxy groups in the carbonate **2**. [d]A small amount (1.1%) of thianthrene 5-oxide (ThO) was also obtained.[17]

Scheme 1.

$$Th^+ + Me_3CO\overset{O}{\overset{\|}{C}}OPh \rightleftharpoons Th + \left[Me_3CO\overset{O}{\overset{\|}{C}}OPh\right]^{+\cdot} \quad (1)$$

$$\left[Me_3CO\overset{O}{\overset{\|}{C}}OPh\right]^{+\cdot} \longrightarrow Me_3C^+ + CO_2 + OPh \quad (2)$$

$$Me_3C^+ + MeCN \longrightarrow Me_3CN=^+CMe \quad (3)$$

$$Me_3CN=^+CMe + H_2O \longrightarrow Me_3CNHCOMe + H^+ \quad (4)$$

$$Th^+ + OPh \longrightarrow 4 \quad (5)$$