

Chemistry of *anti-o,o'*-Dibenzene

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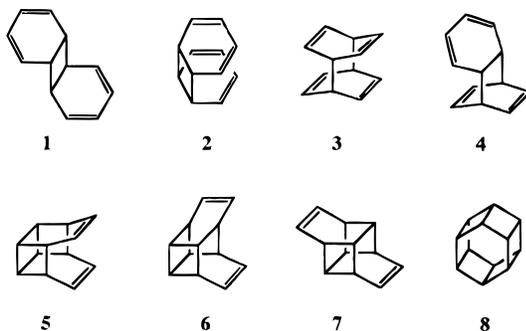
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Abstract: A new and efficient preparation of *anti-o,o'*-dibenzene **1** has been achieved in three steps from *cis*-3,5-cyclohexadiene-1,2-diol **25**. Utilizing a method for deoxygenation of 1,2-diols developed in our laboratory, *anti*-tetraol **23** was converted to **1** in 65% yield on a 0.5 g scale. This has allowed us to explore the chemistry of *anti*-dibenzene extensively. The kinetics for thermal reversion of **1** to benzene have been studied in three different solvents. The direct photolysis of **1** to benzene has been found to form excited benzene in unit efficiency. This high efficiency of adiabatic photon up-conversion in the singlet manifold is unprecedented. No light was detected in the thermal dissociation of **1** in solution using various sensitizers. The chemiluminescence spectrum from the thermolysis of **1** in the presence of perylene has been recorded and found to correspond to the emission of perylene excimer. Although the efficiency of the chemiluminescent process was very low, it has proven to be one of a very few examples of chemiluminescent reactions from pure hydrocarbons. The possible mechanisms were discussed. Benzene 1,4-endoperoxide **36** was formed during the photolysis of monoperoxide **34** at low temperature. Peroxide **36** underwent a quantitative concerted retrocycloaddition to benzene and singlet oxygen. The half-life of **36** was determined to be 29 min at $-30\text{ }^{\circ}\text{C}$.

Introduction

Cyclodimers of benzene, a subset of the $(\text{CH})_{12}$ series,¹ are expected to have interesting physical and chemical properties because of their unique topology and high internal energy. Among the eight possible cyclodimers, five cyclodimers, **1**,^{2–4} **2**,⁵ **4**,⁶ **5**,⁷ and **6**,⁸ and derivatives of **3**⁹ and **7**,¹⁰ have been realized in the last 30 years. However, studies of their chemistry have been rather limited due to poor synthetic yields, instability or purification problems. The thermolytic behavior of most of these cyclodimers has been studied, and photoelectron spectra of some have been taken and explained by through-bond interactions.



Of the aforementioned, *anti-o,o'*-dibenzene **1** and *syn-o,o'*-dibenzene **2** are of special theoretical and experimental interest.

Compound **1** has been synthesized by three different groups, Schroder² in 1969, Berson³ in 1972, and Grimme⁴ in 1981. Compound **2** was synthesized more recently in our own laboratory.⁵ The half-life for the thermal decomposition of **1** to two molecules of benzene was found to be 5.75 h at $40\text{ }^{\circ}\text{C}$ in carbon tetrachloride, and the free energy of activation was estimated to be 24.7 kcal/mol at $30\text{ }^{\circ}\text{C}$ in THF-*d*₈.² The activation parameters of thermolysis for **2** were also determined.⁵

Photoelectron spectroscopic investigations and model calculations have shown that the four-membered ring interacts strongly with the double-bond system. The photoelectron spectra of **1** and **2** have been taken by Gleiter.^{11,12} While the first ionization potentials of the two compounds are quite similar, the second ionization potential of **1** is 0.18 eV higher than that of **2**. These results were analyzed in terms of the intramolecular π,π - and σ,π -interactions.^{13,14} It was suggested that both butadiene units in **1** interact strongly via a through-bond mechanism, while those of **2** interact via both through-bond and through-space mechanisms. The results also suggest that the through-bond interaction between the two butadienes is stronger than the through-space interaction.

Even though it was reported that thermolysis and photolysis of **1** yielded benzene as the product,² detailed mechanistic analysis was not performed. Compound **1** may exhibit adiabatic photodissociation¹⁵ and chemiluminescence¹⁶ phenomena because of its high internal energy and/or higher energy HOMO state. In order to pursue more detailed studies of the properties

[⊗] Abstract published in *Advance ACS Abstracts*, July 15, 1997.

(1) Scott, L. T.; Jones, M., Jr. *Chem. Rev.* **1972**, *72*, 181–202.
 (2) (a) Schroder, G.; Martin, W.; Rottele, H. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 69–70. (b) Rottele, H.; Martin, W.; Oth, J. F. M.; Schroder, G. *Chem. Ber.* **1969**, *102*, 3985–3995. (c) Oth, J. F. M.; Rottele, H.; Schroder, G. *Tetrahedron Lett.* **1970**, 61–66.
 (3) Berson, J. A.; Davis, R. F. *J. Am. Chem. Soc.* **1972**, *94*, 3658–3659.
 (4) Bielig, D.; Grimme, W.; Heinze, U. Unpublished results.
 (5) Yang, N. C.; Hrnjez, B. J.; Horner, M. G. *J. Am. Chem. Soc.* **1987**, *109*, 3158–3159.
 (6) Braun, R.; Kummer, M.; Martin, H.-D.; Rubin, M. B. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 1059–1060.
 (7) Yang, N. C.; Horner, M. G. *Tetrahedron Lett.* **1986**, *27*, 543–546.
 (8) (a) Martin, H.-D.; Pfohler, P. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 847–848. (b) Martin, H.-D.; Pfohler, P.; Urbanek, T.; Walsh, R. *Chem. Ber.* **1983**, *116*, 1415–1421.

(9) Gan, H.; King, J. L.; Yang, N. C. *Tetrahedron Lett.* **1989**, *30*, 1205–1208.

(10) Kostermans, G. B. M.; Dansik, P.; Wolf, W. H.; Bickelhaupt, F. J. *Am. Chem. Soc.* **1987**, *109*, 7887–7888.

(11) Gleiter, R.; Gubernator, K.; Grimme, W. *J. Org. Chem.* **1981**, *46*, 1247–1250.

(12) Gleiter, R.; Yang, N. C.; Gan, H. Unpublished results.

(13) Gleiter, R.; Schafer, W. *Acc. Chem. Res.* **1990**, *23*, 369–375.

(14) (a) Hoffmann, R. *Acc. Chem. Res.* **1971**, *4*, 1–9. (b) Paddon-Row, M. N. *Acc. Chem. Res.* **1982**, *15*, 245–251. (c) Prinzbach, H.; Sedelmeier, G.; Kruger, C.; Goddard, R.; Martin, H.-D.; Gleiter, R. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 271–272.

(15) Turro, N. J.; McVey, J.; Ramamurthy, V.; Lechtken, P. *Angew. Chem. Int. Ed. Engl.* **1979**, *18*, 572–586.

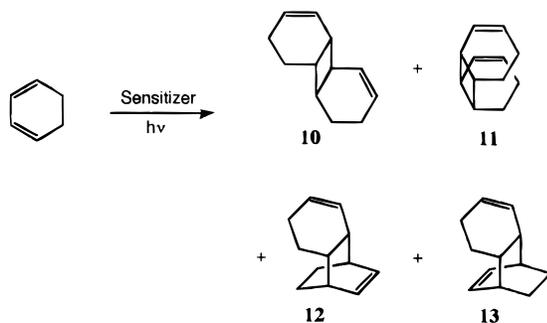
(16) Gundermann, K.-D.; McCapra, F. *Chemiluminescence in Organic Chemistry*; Heidelberg: Springer-Verlag, 1987.

of **1**, a new and efficient synthesis was definitely needed. In this paper, we report our efforts to develop a new and efficient way to synthesize *cis,anti,cis*-tricyclo[6.4.0.0^{2,7}]dodeca-3,5,9,11-tetraene (*anti-o,o'*-dibenzene **1**) and its derivatives. We also report our study of their properties such as adiabatic photodissociation and chemiluminescence and our synthesis of benzene *endo*-peroxide from **1**.

Results and Discussion

Synthesis of anti-*o,o'*-Dibenzene 1. Since benzene itself does not add thermally or photochemically to arenes, the synthesis of arene-benzene cyclodimers has been achieved only through indirect routes involving several steps. Low temperature photodissociation of cyclobutene¹⁷ or cyclobutane-1,2-dione⁶ to olefin, ring opening of bicyclohexene to cyclohexadiene,¹⁸ and decomposition of an unstable azo compound to cyclohexadiene³ and deacetalization to olefin^{7,19,20} have been employed in the final stages of the synthesis to achieve these compounds. Of the several synthetic strategies utilized toward the synthesis of arene-benzene cyclodimers, the method of "masked 1,3,5-cyclohexatriene" has been the most general in application.²¹ The general masked 1,3,5-cyclohexatriene methodology involves photocycloaddition of aromatic hydrocarbons with dicarboxy- or dihydroxy-substituted 1,3-cyclohexadienes, the structure of which is properly modified. The substituents of the photoadducts obtained from cyclohexadienes are then further transformed to a double bond.

The success of this strategy in the synthesis of **1** relies primarily on efficiencies of photocycloaddition and transformation of the substituent functionality to an olefinic bond. It was reported by Hammond²² that the irradiation of 1,3-cyclohexadiene with various sensitizers resulted in 90% conversion to three dimers, **10**, **11**, and **12**, in a 3:1:1 ratio. The photosensitized dimerizations of *cis*-3,5-cyclohexadiene-1,2-diol derivatives have also been observed in the synthesis of naphthalene-benzene and anthracene-benzene cyclodimers.^{23,24} Therefore, the most important concerns are the ease and mildness of reaction conditions in the deoxygenation to an olefinic bond since **1** undergoes a facile thermal dissociation to benzene.



Among the notable methods, the base-induced elimination of 2-phenyl-1,3-dioxolanes, developed by Whitham,²⁵ and the

(17) Grimme, W.; Honer, P.; Kammerling, H. T.; Waldraff, R.; Wirz, J. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1353-1355.

(18) Grimme, W.; Koser, H. G. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 307-308.

(19) (a) Yang, N. C.; Chen, M.-J.; Chen, P. *J. Am. Chem. Soc.* **1984**, *106*, 7310-7315. (b) Yang, N. C.; Chen, M.-J.; Chen, P.; Mak, K. T. *J. Am. Chem. Soc.* **1982**, *104*, 853-855.

(20) Mak, K. T.; Srinivasachar, K.; Yang, N. C. *Chem. Comm.* **1979**, 1038-1040.

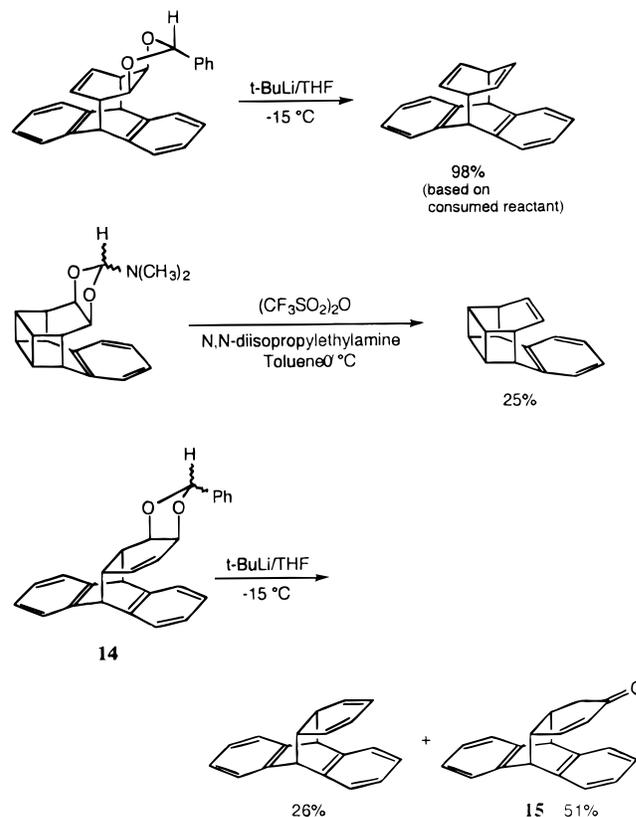
(21) McCullough, J. J. *Chem. Rev.* **1987**, *87*, 811-860.

(22) Valentine, D.; Turro, N. J.; Hammond, G. S. *J. Am. Chem. Soc.* **1964**, *86*, 5202-5208.

(23) Mak, K. T. Ph.D. Thesis, The University of Chicago, 1980.

(24) Chen, M.-J., Ph.D. Thesis, The University of Chicago, 1982.

Scheme 1



decomposition of 2-dimethylamino-1,3-dioxolanes in the presence of trifluoromethanesulfonic anhydride and diisopropylethylamine, which was developed in our laboratory,²⁶ are both suitable at room temperature or below. The Whitham method has been successfully applied to the synthesis of the [4 + 4] dimers of benzene and anthracene and of benzene and naphthalene (Scheme 1).^{9,19} The latter method was successfully carried out to convert to the cage cyclodimer of benzene and naphthalene.²⁶ However, when the Whitham method is used to make 1,3-cyclohexadiene units, it could present some problems, since both the allylic proton and the benzylic proton are acidic. In fact, treatment of **14** with *tert*-butyllithium was found to yield **15** as the major product in the preparation of the [4 + 2] dimer of benzene and anthracene.¹⁹ Therefore, it is desirable to apply the second method to the synthesis of **1**.

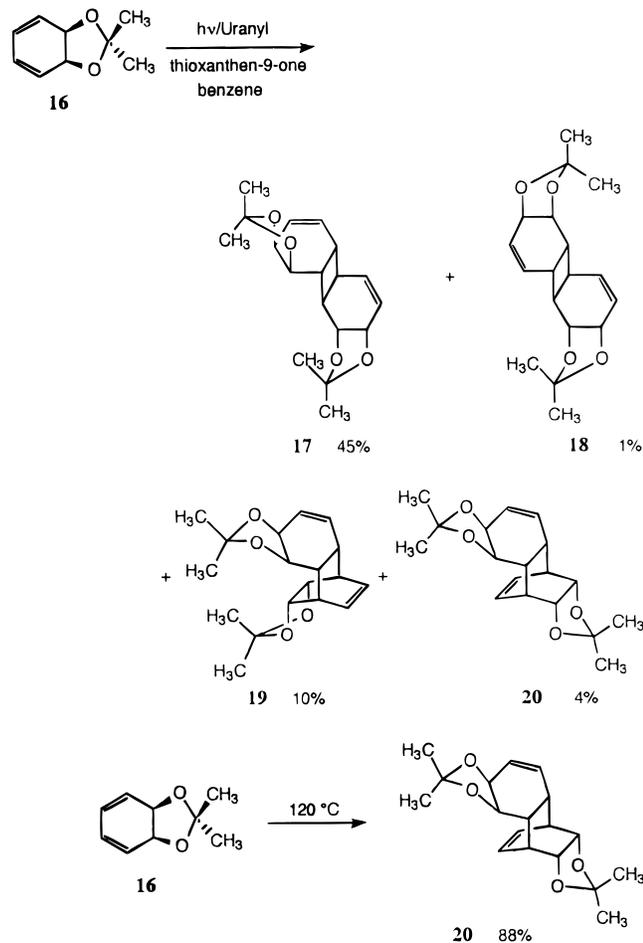
The sensitized dimerization of diene **16**, previously used in the synthesis of anthracene-benzene dimers,^{19,23} in the presence of xanthone with a medium pressure mercury lamp through a Uranyl glass filter, proved to be too slow. The irradiation through a Pyrex filter under the same conditions gave polymers and several dimers, one of which was the desired compound **17** of anti structure. The isolated yield of **17** was 40%. The irradiation of **16** in the presence of thioxanthone²⁷ through a Uranyl glass filter gave the same dimer mixture but with less polymeric material. The isolated products from the photo-reaction mixture contained two [2 + 2] dimers, **17** and **18**, with 45% and 1% yields, and two [4 + 2] dimers, **19** and **20**, with 10% and 4% yields (Scheme 2). The two [4 + 2] dimers were identified from the chemical shifts of the olefinic peaks in their proton NMR spectra (Table 1). The minor [4 + 2] isomer **20**

(25) Hines, J. N.; Peagram, M. J.; Thomas, E. J.; Whitham, G. H. *J. Chem. Soc., Perkin Trans. I* **1973**, 2332-2337.

(26) King, J. L.; Posner, B. A.; Mak, K. T.; Yang, N. C. *Tetrahedron Lett.* **1987**, *28*, 3919-3922.

(27) DeBoer, C. D.; Schlessinger, R. H. *J. Am. Chem. Soc.* **1972**, *94*, 655-656.

Scheme 2



displayed upfield chemical shifts for the olefinic protons because of an anisotropic effect. This analysis was further confirmed from the study of the thermal dimerization of **16**. Heating **16** at 120 °C under a nitrogen atmosphere for 12 h gave 88% of **20**. No other dimers were observed in a ¹H-NMR spectrum.

If the steric hindrance of the two ketal groups is the major factor in determining the stability of the diradicals, the ketal groups should be facing opposite directions. In this case, the possible intermediates would be **A**, **B**, **C**, and **D** as shown in Scheme 3. The major [2 + 2] dimer could be dimer **17** because the diradical intermediate **A** is the most stable. The minor [2 + 2] dimer could be dimer **21** because the allylic diradical **B** is more stable than diradical **C**. However, it was found that the minor [2 + 2] isomer had an anti structure.²⁸ Following the subsequent reactions from the major [2 + 2] dimer **17** to **1**, described later, **1** was obtained from the minor [2 + 2] isomer. Therefore, the minor [2 + 2] isomer should be **18** which resulted from the energetically less favorable diradical intermediate **C**. Only the *exo*-[4 + 2] dimer **19** was formed from the diradical intermediates **B** and **D**.

The product distributions in the photosensitized dimerizations of 1,3-cyclohexadiene²² and **16** were a little different. The *anti*-[2 + 2] dimers **10** and **17** were the major products in both photoreactions. No *syn*-[2 + 2] dimer **21** or **22** was observed in the reaction of **16**, while the *syn*-[2 + 2] dimer **11** was isolated in as great a yield as the *exo*-[4 + 2] dimer **12** in the reaction of 1,3-cyclohexadiene. It is interesting to note that the minor [2 + 2] dimer of **16** was formed from the less stable diradical **C**. These are to some extent related to the steric hindrance of the ketal groups.

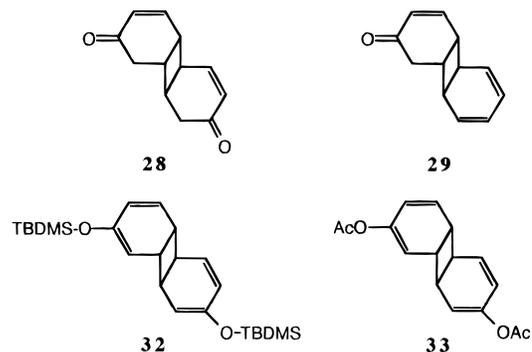
(28) Yang, N. C.; Gan, H.; Balog, A. Unpublished results.

The *anti*-[2 + 2] dimer **17** was hydrolyzed to **23** in an acidic medium in 88% yield (Scheme 4). Tetraol **23** was then converted to its dimethylformamide acetal **24** by heating **23** in the presence of excess *N,N*-dimethylformamide (DMF) dimethyl acetal under anhydrous conditions. The crude **24** was treated with trifluoromethanesulfonic anhydride and diisopropylethylamine at 0 °C to give **1** in 65% yield. It is noteworthy that the overall yield of the last two steps is 65% and that the side product, biphenyl, can be easily separated by silica gel column chromatography with pentane, which is an advantageous solvent due to its low boiling point.²⁹ Hence, the relatively unstable and volatile compound **1** can be obtained and easily purified on a 0.5 g scale.

cis-3,5-Cyclohexadiene-1,2-diol (**25**) has lately become readily available by microbial oxidation with the bacteria *Pseudomonas putida*.³⁰ Aldrich has used this technique to make the compound available commercially (Aldrich 30,152-3). The irradiation of **25** in the presence of thioxanthen-9-one in methanol through a Uranyl glass filter gave **23** in 42% yield. *anti*-*o,o'*-Dibenzene **1** could be prepared in 27% overall yield as shown in Scheme 4. In large scale reactions, however, the irradiation step was troublesome, because the mixture of diol dimers precipitated and blocked the light. The isolation of tetraol **23** was also difficult. Diene **16** can also be easily obtained from **25** in high yield.

Synthesis of Substituted Benzene Dimers. Yang and Chen have reported that treatment of the isomeric 2-phenyl-1,3-dioxolane **14** with *tert*-butyllithium gave the [4 + 2] anthracene-benzene dimer and enone **15** in yields of 26% and 51%, respectively.¹⁹ In this reaction, the lithium enolate is the logical intermediate in the formation of enone **15**. Substituted benzene dimers may thus be synthesized from the enolate via its interaction with an appropriate alkylating or acylating agent.

To make triene diol **26**, 2.4 equiv of diisopropylethylamine and 1.2 equiv of trifluoromethanesulfonic anhydride were added to the acetal **24** at room temperature (Scheme 5). The reaction mixture was further hydrolyzed with a hydrochloric acid solution to give triene diol **26**. Diol **26** was then converted to ketal **27** with 2,2-dimethoxypropane in the presence of catalytic *p*-toluenesulfonic acid. Treatment of ketals **17** and **27** with *n*-butyllithium and LTMP^{31,32} gave enones **28** and **29** in 49% and 40% yields, respectively.



In order to make substituted benzene dimers, we attempted to trap metal enolates with several electrophiles. After LTMP

(29) Yang, N. C.; Noh, T.; Gan, H.; Halfon, S.; Hrmjez, B. *J. Am. Chem. Soc.* **1988**, *110*, 5919–5920.

(30) (a) Taylor, S. C. In *Enzymes In Organic Synthesis*; CIBA Foundation Symposium III, Pitman: London, 1985. (b) Ley, S. V.; Sternfeld, F.; Taylor, S. *Tetrahedron Lett.* **1987**, *28*, 225–226.

(31) (a) Krizan, T. D.; Martin, J. C. *J. Am. Chem. Soc.* **1983**, *105*, 6155–6157. (b) Taylor, S. L.; Lee, D. Y.; Martin, J. C. *J. Org. Chem.* **1983**, *48*, 4158–4159.

(32) (a) Olofson, R. A.; Dougherty, C. M. *J. Am. Chem. Soc.* **1973**, *95*, 581–582. (b) Olofson, R. A.; Dougherty, C. M. *J. Am. Chem. Soc.* **1973**, *95*, 582–584.

Scheme 3

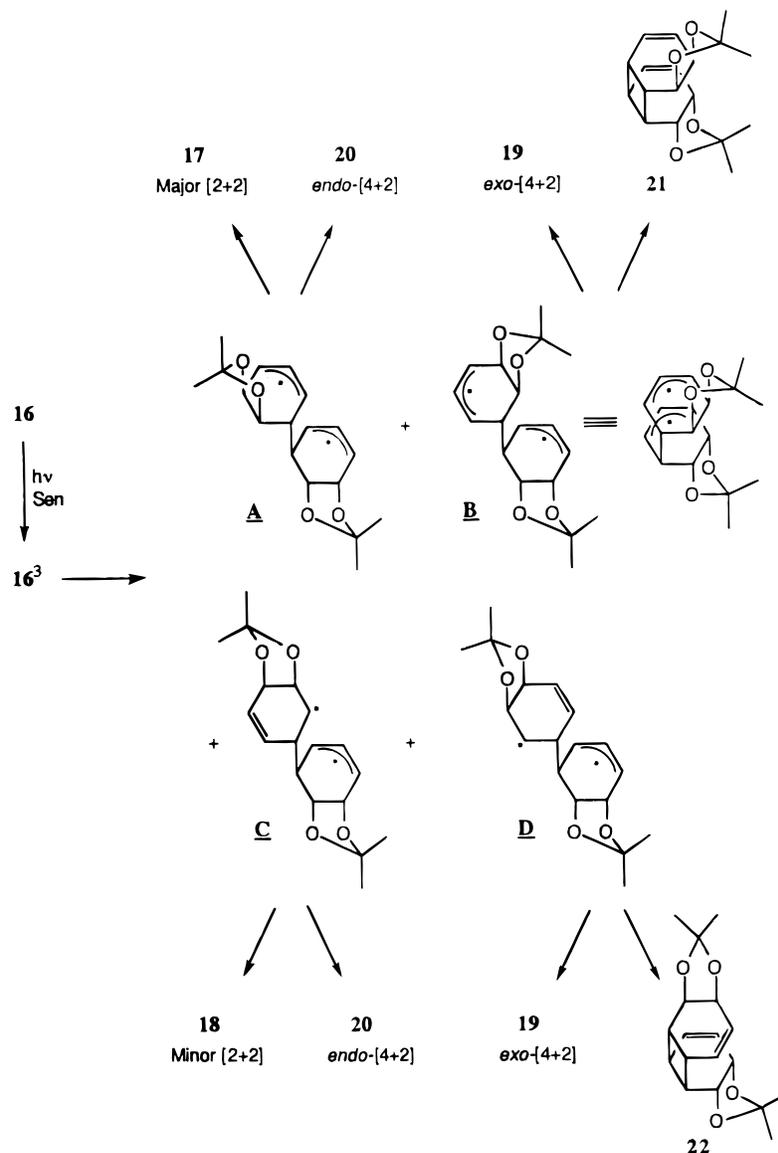


Table 1. Chemical Shifts of Olefinic Protons in the [4 + 2] Dimers **12**, **13**, **19**, and **20**

compd	solvent	chemical shift (ppm)
12 (exo)	CCl ₄	6.28 (2H, quintet)
		6.28–5.35 (2H, br)
13 (endo)	CCl ₄	5.96 (2H, quintet)
		5.42 (2H, br)
19 (exo)	CDCl ₃	5.98 (2H, s)
		5.82 (1H, dd)
20 (endo)	CDCl ₃	5.67 (1H, d)
		5.97 (2H, s)
		5.57 (1H, ddd)
		5.49 (1H, dd)

treatment of **27** in dry THF, *tert*-butyldimethylsilyl chloride (TBDMS-Cl) and 0.4–1.0 equiv of triethylamine³³ were added. After workup, only signals of enone **29** were present in a ¹H NMR spectrum. Adding LTMP to TBDMS-Cl and **27** in THF at –78 °C and warming the solution up to 0 °C³⁴ provided the same result. On the other hand, addition of TBDMS-Cl in hexamethylphosphoramide (HMPA) gave silyl ether **30** (Scheme

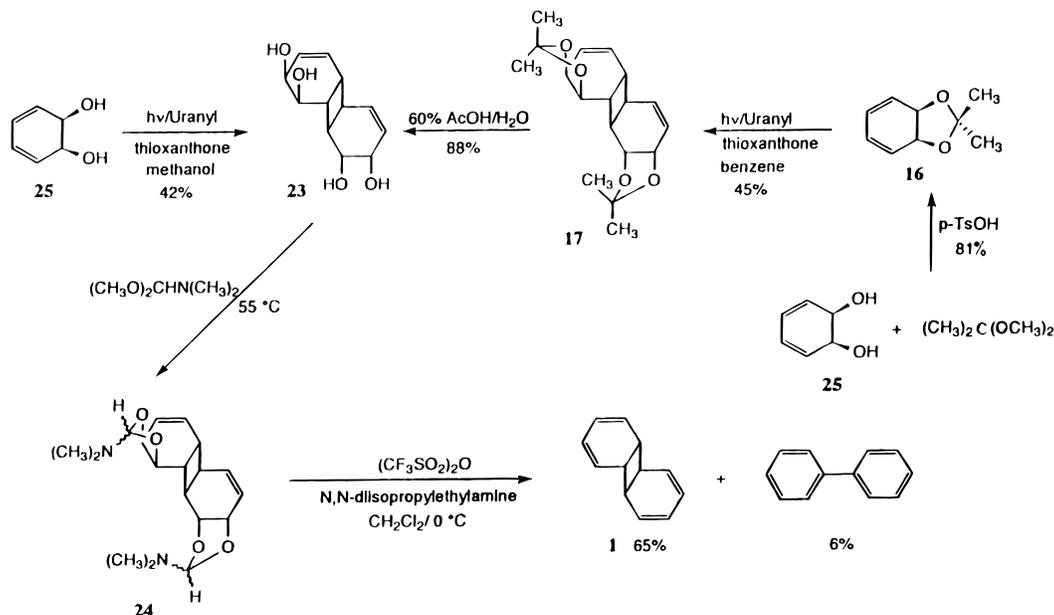
6). This phenomenon was probably caused by the strong dissociation of the lithium enolate in HMPA.³⁵ The separation of **30** was, however, troublesome. Compound **30** was so thermally unstable that it decomposed at distillation conditions, and the silicon–oxygen bond slowly fragmented on a silica gel column, a reverse phase column, and an alumina column. Consecutive silica gel chromatographies followed by sublimation gave crude **30**, which was about 85% pure by integrating the proton peaks in a ¹H NMR spectrum. The ¹H NMR peaks of impurities were mostly in the 0–1 ppm region. However, reaction with acetic anhydride in HMPA to form enol acetate **31** was successful. A pentane extraction followed with two silica gel column chromatographies of the crude brown oily mixture afforded a mixture of **31** and phenyl acetate in a ratio of 2.15:1. The yield of **31** was 15%. The mixture was further purified by sublimation and silica gel chromatography. Compounds **32** and **33** have also been synthesized from **17** by this method. However, **32** decomposed to **28** completely on a silica gel column, and the separation of **33** from the reaction mixture was also troublesome. Hence, a reasonably pure sample was never obtained.

(33) (a) Rasmussen, J. K. *Synthesis* **1977**, 91–110. (b) Stork, G.; Hudrlík, P. F. *J. Am. Chem. Soc.* **1968**, *90*, 4462–4464. (c) Stork, G.; Hudrlík, P. F. *J. Am. Chem. Soc.* **1968**, *90*, 4464–4465.

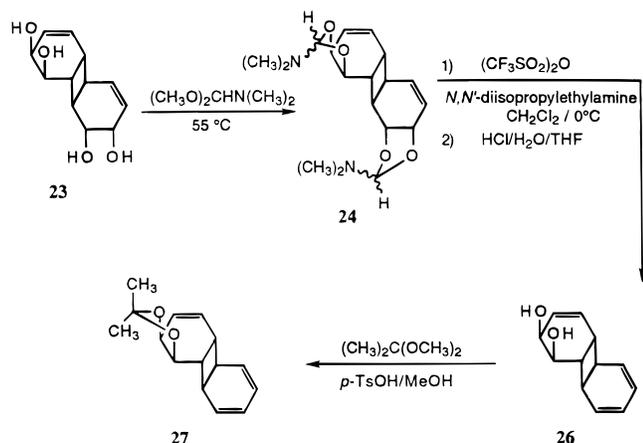
(34) Corey, E. J.; Gross, A. W. *Tetrahedron Lett.* **1984**, *25*, 495–498.

(35) Fraser, R. R.; Mansour, T. S. *Tetrahedron Lett.* **1986**, *27*, 331–334.

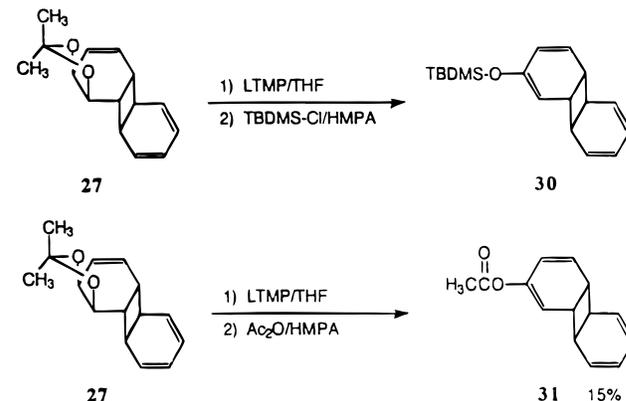
Scheme 4



Scheme 5



Scheme 6



Control experiments with ketal **27** were performed to study the nucleophilic effect of the metal enolate on trapping with electrophiles. The reaction with KDA in the presence of 18-crown-6 as a base using acetic anhydride in HMPA as the electrophile gave mainly phenyl acetate. Small amounts of phenol and **29** were also observed in the ^1H NMR spectrum. However, the reaction using LTMP produced mainly **31**. It is well-known that the rate of *O*-alkylation is a function of the strength of the interaction between the cation and anion.³⁶ The degree of dissociation is parallel to the size of the cation into free ions. Moreover, a metal enolate chelated by a crown ether exists mostly as a monomeric contact ion pair. Therefore, a potassium enolate used with 18-crown-6 should be more reactive than a lithium enolate by itself. However, our results showed the opposite effect. This could be explained by an alternative pathway of the enolates. Two control experiments were performed to study this hypothesis. After treatment of ketal **27** with LTMP, HMPA or THF was added; the same workup procedure as before was used, and the reaction mixture was analyzed by ^1H NMR. In the case of HMPA, peaks due to phenol and other unidentified aromatic compounds were found, and no olefinic peak was observed. In the case of THF, only peaks due to **29** were observed in a ^1H NMR spectrum. It is very difficult to perform a quantitative study of this reaction,

because phenol could easily be lost in the aqueous extraction ($\text{p}K_{\text{a}} = 10$) and in the evaporation process. However, these two control experiments clearly showed that the free enolate decomposed mainly into phenol and presumably benzene. The decomposition of metal enolate is facile when a cation with 18-crown-6, a big cation, or HMPA is used. This facile decomposition of enolates compared to **1** is consistent with the observation that deprotonation of a dioxetane bearing a phenolic substituent generates an unstable phenoxide-substituted dioxetane which decomposes 4.4×10^6 times faster than the protonated form.³⁷ This facile decomposition is probably responsible for the low yield (40%) conversion of **27** to enone **29**. It was found later that acetic anhydride as an electrophile worked in THF as well as in HMPA and that HMPA as a solvent was needed for TBDMS-Cl to react with the lithium enolate.

Enol acetate **31** is a colorless oil which becomes a white solid at low temperature. Its structure was confirmed by spectral analysis. The IR spectrum showed a strong absorbance at 1745 cm^{-1} due to the vinyl acetate substituent. The ^{13}C NMR spectrum was also supportive of the enol acetate structure. Fourteen peaks were observed: 8 representing olefinic carbons,

(36) Jackman, L. M.; Lange, B. C. *Tetrahedron* **1977**, *33*, 2737–2769.

(37) (a) Schaap, A. P.; Gagnon, S. D. *J. Am. Chem. Soc.* **1982**, *104*, 3504–3506. (b) Schaap, A. P.; Handley, R. S.; Giri, B. P. *Tetrahedron Lett.* **1987**, *28*, 935–938. (c) Schaap, A. P.; Chen, T.-S.; Handley, R. S.; DeSilva, R.; Giri, B. P. *Tetrahedron Lett.* **1987**, *28*, 1155–1158. (d) Schaap, A. P.; Sandison, M. D.; Handley, R. S. *Tetrahedron Lett.* **1987**, *28*, 1159–1162.

Table 2. Activation Parameters for the Thermal Decomposition of **1** to Two Molecules of Benzene in Three Solvents^a

activation parameter	cyclohexane- <i>d</i> ₁₂	acetone- <i>d</i> ₆	acetonitrile- <i>d</i> ₃
E_a , kcal/mol	24.69 ± 0.95	24.20 ± 0.33	24.72 ± 0.62
ΔH^\ddagger , kcal/mol	24.10 ± 0.95	23.61 ± 0.33	24.13 ± 0.62
ΔS^\ddagger , eu	-2.23 ± 2.29	-3.42 ± 1.00	-2.11 ± 1.89
ΔG^\ddagger , kcal/mol ^b	24.76 ± 1.63	24.63 ± 0.61	24.76 ± 1.18

^a Parameters were obtained by the proton NMR method. ^b Activation parameters at 298.15 K.

Table 3. Activation Parameters for the Thermolysis of Enol Acetate **31** and anti-*o,o'*-Dibenzene **1** in Cyclohexane-*d*₁₂^a

activation parameter	enol acetate 31	anti- <i>o,o'</i> -dibenzene 1
E_a , kcal/mol	24.88 ± 0.35	24.69 ± 0.95
ΔH^\ddagger , kcal/mol	24.29 ± 0.35	24.10 ± 0.95
ΔS^\ddagger , eu	-2.72 ± 1.07	-2.23 ± 2.29
ΔG^\ddagger , kcal/mol ^b	25.03 ± 0.64	24.76 ± 1.63

^a Parameters were obtained by the proton NMR method. ^b Activation parameters at 298.15 K.

4 representing cyclobutane carbons, and 2 representing acetate carbons. Under electron impact ionization, a strong M - 2 ion was observed while the molecular ion did not appear. This EI pattern was consistent with **1**.

Thermolysis of 1 and 31. Kinetic analyses of the thermolysis of **1** in the temperature range of 39.2–70.9 °C in cyclohexane-*d*₁₂, acetone-*d*₆, and acetonitrile-*d*₃ were performed by NMR spectroscopy. The activation parameters, obtained from transition state theory, are shown in Table 2. We have found that the activation enthalpy is about 24 kcal/mol, and that the thermolysis of anti-*o,o'*-dibenzene **1** proceeds with little or no activation entropy, as is usually found in a highly exoergic process. We have not observed any solvent effect in this thermolysis. Activation parameters of the thermolysis of **2** in cyclohexane-*d*₁₂ were measured by Gan,³⁸ in our laboratory, to be $E_a = 27.4 \pm 0.6$ kcal/mol, $\Delta H^\ddagger = 26.8 \pm 0.6$ kcal/mol, $\Delta S^\ddagger = -0.9 \pm 1.6$ eu, and $\Delta G^\ddagger = 27.1 \pm 1.1$ kcal/mol. It is interesting to note that **1** is kinetically less stable than **2**, although **1** is thermodynamically more stable than **2** due to the steric interaction between the two cyclohexadiene units. The possible mechanisms were discussed elsewhere.^{5,38}

The thermolysis of **31** gave phenyl acetate and benzene. The kinetics of this thermolysis was examined in the temperature range of 40.5–61.4 °C in cyclohexane-*d*₁₂ using ¹H NMR. The activation parameters obtained from transition state theory are shown in Table 3. The rate of decomposition of **31** was slower than that of **1**. For example, the half-life of **31** at 60 °C is 56 min, while that of **1** is 33 min at the same temperature.

Photolysis of 1 and 31. It has been reported that the photolysis of **1** yielded two molecules of benzene as product. Simple orbital symmetry analysis^{39,40} of the photodissociation of **1** indicates that the excited **1** is correlated to one excited state and one ground state of benzene and that this electrocyclic conversion is photochemically allowed. The high exothermicity in the conversion of **1** to benzene may distort the normal energy surfaces to tilt the excited state surface and thus to allow the production of the excited state benzene.^{19,41}

An adiabatic photoreaction is a chemical process that occurs entirely on a single excited electronic energy surface.⁴¹ Even though many photoreactions involving small structural changes and minor covalent bonding changes occur adiabatically, a few examples exist for which photochemical carbon-carbon bond breaking and making occur adiabatically.¹⁵ These include photochemical electrocyclic reaction and photochemical cyclo-dissociation. The photochemical electrocyclic ring openings of Dewar benzene, Dewar naphthalene, and Dewar anthracene to the corresponding aromatic hydrocarbons have been found to be adiabatic.⁴² The benzvalene structure of aromatic compounds has also been found to be involved in adiabatic photoreactions.⁴³ The generation of electronically excited products has been observed in the photochemical electrocyclic dissociations of the [2 + 2] dimers of carbonyl compounds (1,2-dioxetanes),⁴⁴ the [4 + 4] and [4 + 2] dimers of benzene and anthracene,^{19,45} and the cage dimer of 1,4-difluorobenzene and naphthalene.⁴⁶ Upon photoexcitation of **1** at 335 nm, the only emission observed was attributed to benzene fluorescence.²⁹ This was confirmed by the absence of emission from a benzene sample irradiated at the same wavelength and by the excitation spectrum of **1** which possesses a peak shape similar to the UV spectrum of **1**. The efficiency of photolysis of **1** was determined with the aid of a potassium ferrioxalate actinometer,⁴⁷ and the efficiency of the formation of excited benzene from **1** was determined by comparing the integrated emission spectrum with that of benzene.⁴⁸

Since the energy of the first excited singlet state of benzene is 110 kcal/mol while that of the exciting light at 335 nm is only 85.3 kcal/mol,⁴⁷ the results demonstrate that part of the chemical energy liberated from the photochemical dissociation of **1** is available for the excitation of benzene during the adiabatic conversion. Adiabatic photochemical reactions generally occur with light that is more energetic than is necessary for the excitation of the product. An earlier contribution from Turro and co-workers has demonstrated the "red light-to-blue light uphill conversion" in the generation of n, π^* excited states of acetone from the direct or sensitized photolysis of tetramethyldioxetane,⁴⁹ but such uphill conversions generally occur in the triplet manifold. Therefore, this photon uphill conversion in the singlet manifold with such high efficiency is unprecedented.

The UV absorption spectrum of **31** was quite similar to that of **1**. The maximum absorption wavelength of **31** was 265 nm in cyclohexane. The irradiation of **31** through a Vycor filter

(41) (a) Forster, T. *Pure Appl. Chem.* **1970**, *24*, 443–449. (b) Forster, T. *Pure Appl. Chem.* **1973**, *34*, 225–234. (c) Michl, J. *Pure Appl. Chem.* **1975**, *41*, 507–534.

(42) (a) Turro, N. J.; Ramamurthy, V.; Katz, T. J. *Nouv. J. Chim.* **1977**, *1*, 363–365. (b) Carr, R. V.; Kim, B.; McVey, J. K.; Yang, N. C.; Gerhartz, W.; Michl, J. *Chem. Phys. Lett.* **1976**, *39*, 57–60. (c) Yang, N. C.; Carr, R. V.; Li, E.; McVey, J. K.; Rice, S. A. *J. Am. Chem. Soc.* **1974**, *96*, 2297–2298.

(43) (a) Renner, C. A.; Katz, T. J.; Pouliquen, J.; Turro, N. J.; Waddell, W. H. *J. Am. Chem. Soc.* **1975**, *97*, 2568–2570. (b) Turro, N. J.; Lechtken, P.; Lyons, A.; Hautala, R. R.; Carnahan, E.; Katz, T. J. *J. Am. Chem. Soc.* **1973**, *95*, 2035–2037.

(44) Turro, N. J.; Devaquet, A. *J. Am. Chem. Soc.* **1975**, *97*, 3859–3862.

(45) 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*, 3908–3911.

(46) Kimura, M.; Kura, H.; Nukada, K.; Okamoto, H.; Satake, K.; Morosawa, S. *J. Chem. Soc., Perkin Trans. I* **1988**, 3307–3310.

(47) Murov, S. L. *Handbook of Photochemistry*; Marcel Dekker Inc.: New York, 1973.

(48) Parker, C. A. *Photoluminescence of Solutions*; Elsevier Publishing Co.: New York, 1968.

(49) (a) Turro, N. J.; Lechtken, P. *Tetrahedron Lett.* **1973**, 565–568. (b) Turro, N. J.; Brewer, D.; Farneth, W.; Ramamurthy, V. *Nouv. J. chim.* **1978**, *2*, 85–89.

(38) Gan, H. Ph.D. Thesis, The University of Chicago, 1990.

(39) Woodward, R. B.; Hoffmann, R. *The Conservation of Orbital Symmetry*; Academic Press: New York, 1970.

(40) (a) Bryce-Smith, D. *Chem. Commun.* **1969**, 806–808. (b) van der Lugt, W. Th. A. M.; Oosterhoff, L. J. *J. Am. Chem. Soc.* **1969**, *91*, 6042–6049. (c) Grimbert, D.; Segal, G.; Devaquet, A. *J. Am. Chem. Soc.* **1975**, *97*, 6629–6632. (d) Hoffmann, R.; Davidson, R. B. *J. Am. Chem. Soc.* **1971**, *93*, 5699–5705.

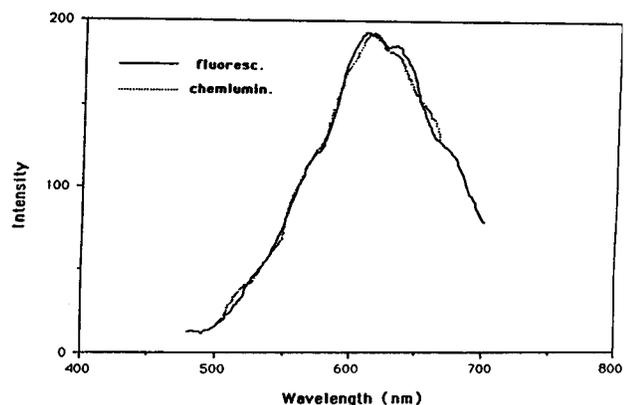


Figure 1. Chemiluminescence spectrum of **1** in the presence of perylene at 190 °C and fluorescence spectrum of solid perylene at 180 °C. Intensities are normalized to compare the two spectra.

Table 4. Calculated Internal Energies of **1**^a

method	energy	ref
group additivity	53.8	53
MNDO	15	54
ab initio (STO-3G)	14	54
MINDO/3	43.2	11
	46.1	55
3-21G	56.0	56
6-21G*	57.5	56

^a Energies are given in kcal/mol relative to two molecules of benzene.

gave phenyl acetate and benzene as decomposition products. In the irradiation of **31** in cyclohexane at 310 nm, only a small peak resembling the benzene emission was observed. However, a quantitative analysis was not conducted because the signal-to-noise ratio was too small in the experiment. Since phenyl acetate does not emit fluorescence, adiabatic conversion from the excited enol acetate to the excited phenyl acetate cannot be observed directly.

Chemiluminescence. Thus far, thermal conversion of Dewar benzene to benzene,⁵⁰ thermal conversion of Dewar benzene to benzo[*c*]-1,3,5-cyclooctatriene,⁵¹ and solid state thermal decomposition of the [4+4] dimer of benzene and anthracene⁵² have been reported to be chemiluminescent in pure hydrocarbon chemistry. In the case of Dewar benzene and benzo[*c*]-1,3,5-cyclooctatriene, excited triplet products were produced. The phosphorescence of these aromatic products in fluid solutions was very weak, and indirect methods were required for observation. 9,10-Dibromoanthracene (DBA), which has an intense emission, was found to be a useful sensitizer for detecting the triplet products by energy transfer.⁵⁰

The internal energies of **1** have been calculated by several methods^{11,53–57} which are summarized in Table 4. The calculated energy change of **1** to two molecules of benzene is in the

(50) Lechtken, P.; Breslow, R.; Schmidt, A. H.; Turro, N. J. *J. Am. Chem. Soc.* **1973**, *95*, 3025–3027.

(51) (a) Case, R. S.; Dewar, M. J. S.; Kirschner, S.; Pettit, R.; Slegeir, W. *J. Am. Chem. Soc.* **1974**, *96*, 7581–7582. (b) Frey, H. M.; Martin, H.-D. *Chem. Commun.* **1975**, 204–205.

(52) Yang, N. C.; Yang, X. *J. Am. Chem. Soc.* **1987**, *109*, 3804–3805.

(53) Benson, S. W. *Thermodynamical Kinetics*; Wiley: New York, 1976; Chapter 2.

(54) (a) Engelke, R.; Hay, P. J.; Kleier, D. A.; Wadt, W. R. *J. Am. Chem. Soc.* **1984**, *106*, 5439–5446. (b) Engelke, R. *J. Am. Chem. Soc.* **1986**, *108*, 5799–5803. (c) Dougherty, D. A.; Schlegel, H. B.; Mislow, K. *Tetrahedron* **1978**, *34*, 1441–1447.

(55) Doering, W. E.; Roth, W. R.; Breuckmann, R.; Figge, L.; Lennartz, H.-W.; Fessner, W.-D.; Prinzbarch, H. *Chem. Ber.* **1988**, *121*, 1–9.

(56) Schriver, G. W.; Gerson, D. J. *J. Am. Chem. Soc.* **1990**, *112*, 4723–4728.

(57) Lissi, E. *J. Am. Chem. Soc.* **1976**, *98*, 3386–3387.

Table 5. Spectroscopic and Ionic Properties of Some Aromatic Compounds^{a,b}

compd	$E_{0,0}(S)$ (kcal/mol)	$E_{0,0}(T)$ (kcal/mol)	IP (eV)	$E_{ox}(CH_3CN)^c$ (eV)	$-E_{red}$ (eV)
DMA	71.8(398)			0.87	1.976(75% DO) ^e
DBA	70.5(406) ^d	40.2(711) ^d	7.58		
CAN	71.0(403) ^d				1.58(CH ₃ CN) ^f
DCAN	67.8(422) ^f				0.98(CH ₃ CN) ^f
TCAN	66.9(428) ^f				0.45(CH ₃ CN) ^f
perylene	65.8(435)	35.1(814)	7.07	0.85	1.67(DMF)
rubrene	55.1(519) ^g		6.42 ^h	0.88 ^g	1.47 ^g
benzene	110(261)	84.3(339)	9.245	2.30	3.31 ⁱ

^a Reference 47. ^b Reference 59. ^c Reference 60. ^d Reference 61. ^e 75% Dioxane-water, 0.1 M tetra-*n*-butylammonium iodide. ^f References 62 and 63. ^g Reference 64. ^h Reference 65. ⁱ Reference 66.

range of 14–57.5 kcal/mol, depending on the method of calculation. The abnormally low values of 14–15 kcal/mol may be neglected for practical reasons. Generally, high level calculations result in high internal energies. Even though the accuracy of these calculations is not clear, the exothermic enthalpy change for thermolysis of **1** is estimated to be about 55–60 kcal/mol. Since the thermal rearrangement of Dewar benzene to benzene, which has similar enthalpy values ($\Delta H_f = \sim -60$ kcal/mol, $\Delta H^\ddagger = 23-25$ kcal/mol) showed chemiluminescence,⁵⁰ there is a reasonable possibility that the thermal decomposition of **1** is chemiluminescent under certain conditions.

In addition to the high strain energy, the ionization potential of **1** (7.85 eV) is lower than that of 1,3-cyclohexadiene due to the σ,π -interaction between the cyclobutane and cyclohexadiene moieties.¹¹ One may also expect that electron affinities of **1** is increased by this interaction. Therefore, both electron-rich and electron-poor sensitizers (Table 5) were used to test the sensitized chemiluminescence from the thermal decomposition of **1**.

In order to ascertain that the luminescence was not derived from a peroxide contaminant from either **1** or the sensitizer, all experiments were carried out under rigorously degassed conditions using freshly prepared **1** (checked by NMR to be free of peroxide contaminant). In general, we found that decompositions of **1** in the presence of electron-poor sensitizers, 9-cyanoanthracene (CNA), 9,10-dicyanoanthracene (DCNA), and 2,6,9,10-tetracyanoanthracene (TCNA), yield no detectable light emission. Furthermore, the decomposition of **1** in the presence of 9,10-dibromoanthracene (DBA) which is known to detect triplet benzene efficiently⁵⁰ yields also no detectable light emission. However, consistent light emissions were observed when electron-rich sensitizers, 9,10-dimethylanthracene, perylene, and rubrene, were used in the thermal decomposition of **1**. The results obtained from this series of observations are thus consistent with the CIEEL mechanism proposed by Schuster with **1** functioning as the acceptor (Scheme 7).⁸⁸

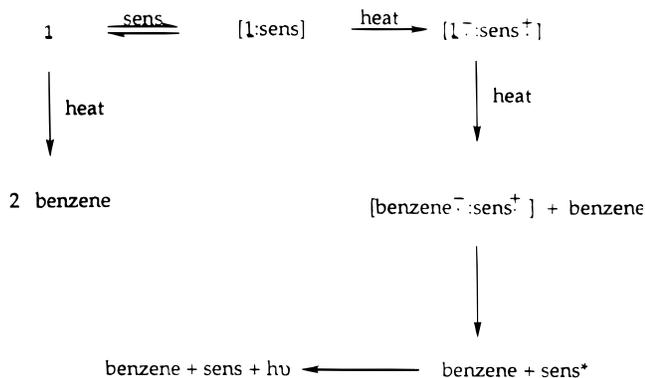
Subsequently, we have succeeded in the synthesis of a mono-endo-peroxide of **1**, **34**. Although **34** is not formed under ordinary experimental condition from **1**, we failed to record the chemiluminescence of perylene in the thermal decomposition of 9 mg of **34** in the presence of perylene. The result indicated that the formation of a small amount of **34** as a contaminant in **1** is not the source of the observed chemiluminescence.

We succeeded in obtaining a chemiluminescence spectrum in the thermal decomposition of **1** in the presence of perylene which is identical with the fluorescence spectrum of solid perylene.^{67,68} We also succeeded in determining the quantum

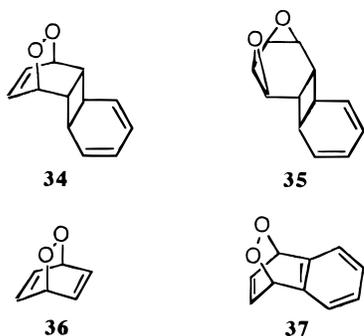
(58) Schuster, G. B. *Acc. Chem. Res.* **1979**, *12*, 366–373.

(59) Scaiano, J. C. *Handbook of Organic Photochemistry*; CRC Press, Inc.: Vol. 1, 1989.

Scheme 7

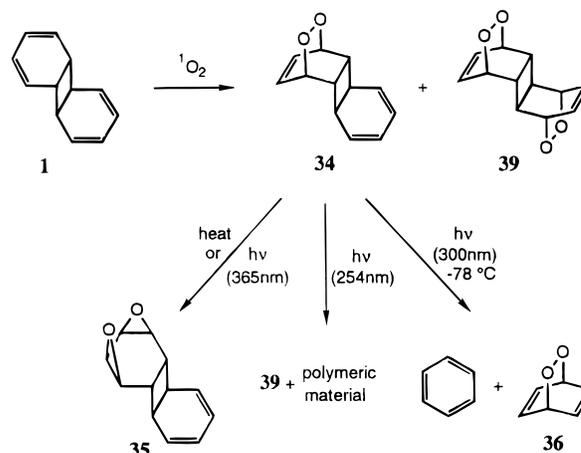


yield of chemiluminescence using adamantylidoadamantane-1,2-dioxetane as a secondary standard;⁶⁹ Φ_{cl} was about 1×10^{-8} . Our observation is also consistent with the view that the triplet of the sensitizer is formed in the energizing step and that the chemiluminescence results from the triplet:triplet annihilation of the sensitizer. This explanation would account for the failure of this process in the thermal decomposition of **1** in solutions containing the sensitizers. The low quantum yield of this process prevents us from carrying out a detailed mechanistic study of this chemiluminescence.



Benzene endo-Peroxide. In contrast to anthracene and higher members of the arene series, benzene and naphthalene do not react with singlet oxygen to form endoperoxides **36** (2,3-dioxo-5,7-bicyclo[2.2.2]octadiene) and **37**.^{70,71} It is estimated from the kinetic data and calculated delocalization energies that reactivity indices for the addition of singlet oxygen to benzene and naphthalene are respectively 10^{12} – 10^{13} and 10^7 – 10^8 times lower than that of anthracene.⁷¹ Compound **37** was indirectly synthesized by Vogel.⁷² In contrast to anthracene 9,10-endoperoxide (**38**), which underwent homolysis of the O–O

Scheme 8



bond upon heating,⁷³ **37** thermally dissociated to naphthalene and singlet oxygen quantitatively. The half-life of this process was 303 min at 20 °C.

In contrast to benzene and naphthalene, cyclic 1,3-dienes react readily with singlet oxygen. The mixture of monoperoxide **34** and diperoxide **39** was expected. The final step to make **36** should be attempted at very low temperature since **36** is expected to be much more unstable than **37** due to its higher gain of the delocalization energy. Low temperature photolysis has proven to be a useful method to detect intermediates which are short-lived at room temperature. Compound **36** should be stable under these experimental conditions.

As expected, Methylene Blue-sensitized photooxygenation of **1** in CH_2Cl_2 at room temperature with a 360 W sun lamp afforded two cycloadducts **34** and **39** (Scheme 8). After 80 min, the ratio of **34** and **39** was about 2:1 by proton NMR. Since the reactivity of the monoadduct was comparable to that of **1**, the photoreaction was stopped to prevent exclusive formation of **39**. Diperoxide **39** slowly precipitated out of the solution, and monoperoxide **34** was slowly decomposed on a silica gel column. The isolated yield of **34** was 36% based on the starting **1** and 44% based on the consumed **1**.

Compound **34** is a white solid with a melting point of 114–116 °C (dec). The structure of **34** is in agreement with its ^1H NMR, ^{13}C NMR, and IR spectra. The high resolution electron impact ionization mass spectrum shows its molecular ion peak at m/e 188.0852, in agreement with the composition $\text{C}_{12}\text{H}_{12}\text{O}_2$. It has an absorption maximum at 275 nm with an extinction coefficient of 3000 and a long tail which reaches beyond 380 nm in the UV spectrum.

Monoperoxide **34** thermally rearranged to bisepoxide **35**.⁷⁴ A solution of **34** in chloroform was refluxed for 19 h. The NMR spectrum of the reaction mixture showed mainly **35** with small amounts of byproducts. The HPLC analysis of the reaction mixture indicated that the quantity of side products containing cyclohexadiene units was about 5%. The isolated yield of **35** was 55%. Several products were observed when **34** was heated at 80 °C. No attempt was made to isolate these compounds.

Kearns⁷⁵ has studied the photochemical decomposition of bicyclic endoperoxides theoretically. He concluded that the first

(72) Schafer-Ridder, M.; Brocker, U.; Vogel, E. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 228–229.

(73) (a) Rigaudy, J.; Baranne-Lafont, J.; Defoin, A.; Cuong, N. K. *C. R. Acad. Sci. Ser. C* **1975**, *280*, 527. (b) Rigaudy, J.; Defoin, A.; Baranne-Lafont, J. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 413–415.

(74) (a) Foster, C. H.; Berchtold, G. A. *J. Org. Chem.* **1975**, *40*, 3743–3746. (b) Maheshwari, K. K.; De Mayo, P.; Wiegand, D. *Can. J. Chem.* **1970**, *48*, 3265–3268.

(60) Pysh, E. S.; Yang, N. C. *J. Am. Chem. Soc.* **1963**, *85*, 2124–2130.
 (61) Yang, X. Ph.D. Thesis, The University of Chicago, 1988.
 (62) Mattes, S. L.; Farid, S. *Chem. Commun.* **1980**, 126–128.
 (63) Albin, A.; Sprei, S. *Gazz. Chim. Ita.* **1985**, *115*, 227–232.
 (64) Hercules, D. M. *Acc. Chem. Res.* **1969**, *2*, 301–307.
 (65) Takahashi, T.; Harada, Y.; Sato, N.; Seki, K.; Inokuchi, H.; Fujisawa, S. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 380–382.
 (66) Gerson, F.; Ohya-Nishiguchi, H.; Wydler, C. *Angew. Chem.* **1976**, *88*, 617–618.
 (67) Nelson, K. A.; Dlott, D. D.; Fayer, M. D. *Chem. Phys. Lett.* **1979**, *64*, 88–93.
 (68) Auweter, H.; Ramer, D.; Kunze, B.; Wolf, H. C. *Chem. Phys. Lett.* **1982**, *85*, 325–329.
 (69) (a) Schuster, G. B.; Turro, N. J.; Steinmetzer, H.-C.; Schaap, A. P.; Falser, G.; Adam, W.; Liu, J. C. *J. Am. Chem. Soc.* **1975**, *97*, 7110–7118. (b) Lechtken, P. *Chem. Ber.* **1976**, *109*, 2862–2870. (c) Lechtken, P.; Reissenweber, G.; Grubmüller, P. *Tetrahedron Lett.* **1977**, 2881–2884.
 (70) Stevens, B.; Perez, S. R.; Ors, J. A. *J. Am. Chem. Soc.* **1974**, *96*, 6846–6850.
 (71) (a) Biermann, D.; Schmidt, W. *J. Am. Chem. Soc.* **1980**, *102*, 3163–3173. (b) Biermann, D.; Schmidt, W. *J. Am. Chem. Soc.* **1980**, *102*, 3173–3181.

excited singlet and triplet states have the electronic configurations of $\pi^2_{CC} n^1_{OO} \sigma^*_{CO}$. Kern's analysis predicts that excitation of an endoperoxide to the first excited state (long-wavelength photolysis) should lead to the cleavage of oxygen–oxygen bond because an electron is promoted to the O–O antibonding orbital. The excitation to the second excited state (short-wavelength photolysis) would lead to the cleavage of carbon–oxygen bond because this transition from n_{OO} to σ^*_{CO} should strengthen the O–O bond while weakening the C–O bond.^{75–77} Since this was actually observed in the process of photodissociation of **34**, **36** was difficult to obtain in high purity. The irradiation of **34** in chloroform-*d* at -50°C with a low pressure mercury lamp gave a very complex mixture which included **39** as the major compound. Two small proton peaks at about 6.8 and 5.2 ppm, presumably belonging to **36**, disappeared, while the amount of **39** increased after warming the reaction mixture to room temperature for 3 min. Under these irradiation conditions, the decomposition of endoperoxides to hydrocarbons and oxygen proceeded as well as their polymerization via radical intermediates. The irradiation of **34** in chloroform-*d* at room temperature through a 313 nm interference filter with a medium pressure mercury lamp gave bisepoxide products. During the initial stage of the irradiation, diperoxide **39** and bisepoxide **35** were the major compounds. For example, 17% of **39**, 11% of **35**, and 34% of **34** were observed in the NMR spectrum after 30 min of irradiation; however, tetraepoxide **40** was the only identifiable product at the final stage. The irradiation of **34** at 365 nm under the same conditions gave mainly bisepoxide **35** by homolysis of the O–O bond (Scheme 8).

Since the endoperoxide structure of **34** was transformed so readily to the epoxide, it would be desirable to excite the diene moiety exclusively to convert **34** to **36**. It was reported that the irradiation of cyclohepta-1,3,5-triene endoperoxide at 294 nm resulted in recovery of the starting material even after 14 h.⁷⁸ This is because the more intense π,π^* transition of the 1,3-diene protects the endoperoxide from photodecomposition in the region of the diene absorption. Therefore, **34** in THF-*d*₈ cooled to -78°C was irradiated through a 300 nm interference filter with a medium pressure mercury lamp. The ¹H NMR⁷⁹ at -45°C showed mainly two peaks at 6.72 (olefinic protons) and 5.17 ppm (bridgehead protons) in a 2:1 ratio. The major byproduct was **39**, most of which precipitated from the solution at that temperature. These two peaks of **36** disappeared completely at room temperature.

There are at least two different decomposition modes to consider in the thermochemical reaction of endoperoxides: loss of molecular oxygen and cleavage of the O–O bond. In the thermal decomposition of **36**, no NMR peaks other than those belonging to **39** were observed; this excluded the possibility of **36** decomposing to *syn*-benzene dioxide.⁸⁰ Monoperoxide **34** could be used as a dienophile to confirm the existence of singlet oxygen which might come from the decomposition of **36**. After **34** was irradiated under the same conditions for a short time, about 44% of **34** was consumed, and some of **39** precipitated

Table 6. Results and Activation Parameters for the Thermal Decompositions of Arene Endoperoxides

compd	ΔH^\ddagger (kcal/mol)	ΔS^\ddagger (eu)	¹ O ₂ yield (%)
43 ^a	31.8 ± 0.3	7.4 ± 0.8	50
42 ^a	29.8 ± 0.3	-1.8 ± 0.8	95
37 ^b	23.2 ± 0.9	0.2 ± 1.1	~100
36 ^c	17.8 ± 0.5	-0.4 ± 1.9	90 ± 3

^a Reference 83. ^b Reference 71. ^c Parameters were obtained in THF-*d*₈ by proton NMR spectroscopy.

out. The proton NMR of the solution showed the presence of **34** (56%), **36** (23%), and a small amount of **39**. After 10 min at room temperature, **36** had completely decomposed to benzene and presumably singlet oxygen. The decreased amount of **34** which formed **39** was 93% compared to the decomposed **36**. Therefore, it was reasonable to conclude that the pathway to the formation of benzene and singlet oxygen was almost quantitative in the decomposition of **36**.

The presence of singlet oxygen in the thermal decomposition of **36** was also confirmed by a trapping experiment with 9,10-dimethylanthracene (DMA). After **34** was almost completely decomposed to **36**, 11.1 equiv of DMA was added to the photoreaction mixture in a dry ice–ether bath, and the solution was slowly warmed to room temperature. After 15 min, the methyl peak of 9,10-dimethylanthracene 9,10-endoperoxide (**41**) at 2.06 ppm was compared with the internal standard. An authentic sample of **41** was prepared independently⁸¹ and compared with the mixture of the trapping experiment. The yield of **41** was 87%. A trapping experiment with 1,3-diphenylisobenzofuran⁸² showed similar results. However, no quantitative analysis was performed because of insufficient resolution at the proton NMR peaks of 1,3-diphenylisobenzofuran and 1,2-dibenzoylbenzene.

The thermolysis of arene endoperoxides has been extensively studied,⁸³ and some of the results are summarized in Table 6. Wasserman and Scheffer reported the first instance of singlet oxygen formation from meso-substituted anthracene and rubrene peroxides.⁸² Turro and co-workers showed that the yield of singlet oxygen is higher from 9,10-diphenyl-1,4-dimethylanthracene 1,4-endoperoxide (**42**) than from 9,10-diphenyl-1,4-dimethylanthracene 9,10-endoperoxide (**43**) and that singlet oxygen formation from arene endoperoxide, which has a low activation entropy, is a concerted retrocycloaddition.⁸⁴ A similar observation was noted in the thermal dissociation of **36**.⁷²

A kinetic analysis of the thermolysis of **36** in the temperature range of -47.0 to -30.0°C in THF-*d*₈ was performed by NMR spectroscopy. The activation parameters are calculated to be $E_a = 18.40 \pm 0.45$ kcal/mol, $\Delta H^\ddagger = 17.81 \pm 0.45$ kcal/mol, $\Delta S^\ddagger = -0.40 \pm 1.90$ eu, and $\Delta G^\ddagger = 17.93 \pm 1.02$ kcal/mol. The half-life of **36** at -30°C was 29 min, and the activation energy was about 5 kcal/mol lower than that of **37** (23.7 ± 0.7 kcal/mol). A nearly zero value of ΔS^\ddagger again indicated a concerted cleavage of **36** to benzene and singlet oxygen. Therefore, our results are in agreement with a concerted cleavage of **36** to benzene and singlet oxygen, and the rate of arene endoperoxide thermolysis to the corresponding arene and singlet oxygen is related to delocalization energy of the arene product.

(81) Schmidt, R.; Schaffner, K.; Trost, W.; Brauer, H.-D. *J. Phys. Chem.* **1984**, *88*, 956–958.

(82) (a) Wasserman, H. H.; Scheffer, J. R. *J. Am. Chem. Soc.* **1967**, *89*, 3073–3075. (b) Wasserman, H. H.; Scheffer, J. R.; Cooper, J. L. *J. Am. Chem. Soc.* **1972**, *94*, 4991–4996.

(83) Turro, N. J.; Ramamurphy, V. In *Rearrangements in Ground and Excited States*; Mayo, P., Ed.; Academic Press: New York, 1980; Vol. 3, pp 1–24.

(84) (a) Turro, N. J.; Chow, M.-F.; Rigaudy, J. *J. Am. Chem. Soc.* **1979**, *101*, 1300–1302. (b) Turro, N. J.; Chow, M.-F.; Rigaudy, J. *J. Am. Chem. Soc.* **1981**, *103*, 7218–7224.

(75) Kearns, D. R. *J. Am. Chem. Soc.* **1969**, *91*, 6554–6563.

(76) Balci, M. *Chem. Rev.* **1981**, *81*, 91–108.

(77) (a) Hou, S.-Y.; Dupuy, C. G.; McAuliffe, M. J.; Hrovat, D. A.; Eisenthal, K. B. *J. Am. Chem. Soc.* **1981**, *103*, 6982–6983. (b) Schmidt, R.; Brauer, H.-D. *J. Photochem.* **1986**, *34*, 1–12. (c) Blumenstock, Th.; Jesse, K.; Comes, F. J.; Schmidt, R.; Brauer, H.-D. *Chem. Phys.* **1989**, *130*, 289–298.

(78) Adam, W.; Balci, M. *J. Am. Chem. Soc.* **1979**, *101*, 7542–7547.

(79) Noh, T.; Yang, N. C. *J. Am. Chem. Soc.* **1991**, *113*, 9412–9414.

(80) (a) Vogel, E.; Altenbach, H.-J.; Cremer, D. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 935–937. (b) Altenbach, H.-J.; Vogel, E. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 937–939. (c) Vogel, E.; Altenbach, H.-J.; Sommerfeld, C.-D. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 939–940.

Experimental Section

General Information. Chemicals obtained commercially were used without further purification unless otherwise noted. CAN, DBA, DCA, DPA, perylene, rubrene, thioxanthen-9-one, and xanthone were recrystallized before use. DMA was purified by following a procedure in the literature.⁸⁵ 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) and DMF dimethyl acetal (94%) were distilled at reduced pressures prior to use. *N,N*-Diisopropylethylamine, pyridine, 2,2,6,6-tetramethylpiperidine, and triethyl amine were dried by refluxing over and then distilling from drying agents. Potassium *tert*-butoxide (95%) was purified by sublimation. Solvents used for photocycloadditions and other anhydrous reactions were purified by procedures in the literature.⁸⁵

Melting points are reported uncorrected. ¹H NMR spectra were obtained at 500 MHz on a Chicago DS-1000 spectrometer. The proton NMR peaks of some compounds were assigned on the basis of double irradiation experiments. ¹³C NMR was obtained either at 100 MHz on a Varian XL-400 FT-NMR spectrometer or at 75 MHz on a General Electric NMR QE-300 spectrometer. Chemical shifts (δ) are reported as parts per million (ppm) downfield from TMS. Infrared (IR) spectra were recorded on a Nicolet Instrument Corporation 20 SXB FT-IR spectrometer. Ultraviolet and visible spectra were recorded on a Varian Cary 219 UV/vis spectrophotometer or a Perkin-Elmer Lambda 5 UV/vis spectrophotometer. Fluorescence spectra were recorded on a Perkin-Elmer MPF-66 fluorescence spectrophotometer. Mass spectra (MS) were obtained on a VG 70-250 double focusing magnetic sector mass spectrometer. Chemical ionization (CI) mass spectra were obtained with isobutane as the reagent gas. Elemental analyses were performed by Micro-Tech Laboratories, Inc., Skokie, IL or by Midwest Microlab, Indianapolis, IN.

General Preparative Irradiation Procedure. Most preparative irradiations were performed with a 450 W Hanovia medium pressure mercury lamp irradiating through a cylindrical Vycor, Pyrex, or Uranyl filter which was placed between the light source and a quartz immersion well cooled with water. The immersion well was inserted in a Pyrex jacket equipped with a condenser and an argon gas dispersion inlet tube. The reaction solutions were placed into the outer jacket and purged with argon for more than 20 min before irradiation. During the irradiation a gentle stream of argon was maintained. The reactions were followed with either TLC or proton NMR spectrum analysis.

Photosensitized Dimerization of 16. Diene **16** (3.22 g, 2.12×10^{-2} mol) and thioxanthen-9-one (0.120 g, 5.65×10^{-4} mol) were dissolved in 100 mL of dry benzene. After deaeration by bubbling with argon gas, the solution was cooled in an ice-water bath and irradiated for 40 min through a Uranyl glass filter. Silica gel chromatography of the mixture eluting with hexane-EtOAc, followed by recrystallization from hexane gave four products: **17** (1.462 g, 45%), **19** (0.32 g, 10%), **20** (0.122 g, 4%), and **18** (35 mg, 1%). **17**: mp 158–159 °C; ¹H NMR (CDCl₃) δ 5.82 (2H, dd, $J = 10.4, 3.4$ Hz, olefinic H), 5.66 (2H, dd, $J = 10.4, 1.1$ Hz, olefinic H), 4.54 (2H, m, -CH(OR)-), 4.32 (2H, d, $J = 5.7$ Hz, -CH(OR)-), 2.65 (2H, d, $J = 5.6$ Hz, cyclobutyl H), 2.39 (2H, br s, cyclobutyl H), 1.36 (6H, s, -CH₃), 1.34 (6H, s, -CH₃); ¹³C NMR (CDCl₃) δ 128.65, 125.54, 109.32, 72.37, 70.41, 35.01, 32.52, 28.13, 26.69; IR (CCl₄) 3026, 2986, 2936, 2915, 2866, 1379, 1369, 1236, 1166, 1155, 1067, 1053, 1020, 869 cm⁻¹; MS (CI⁺, isobutane) *m/e* 305 (M + 1), 247, 189 (100), 171, 143. Anal. Calcd for C₁₈H₂₄O₄; C, 71.03; H, 7.95. Found: C, 70.90; H, 7.99. **19**: mp 141–143 °C; ¹H NMR (CDCl₃) δ 5.98 (2H, s, olefinic H), 5.82 (1H, dd, $J = 10.3, 3.8$ Hz, olefinic H), 5.67 (1H, d, $J = 10.2$ Hz, olefinic H), 4.56 (1H, dd, $J = 6.8, 2.7$ Hz, -CH(OR)-), 4.51 (1H, d, $J = 4.2$ Hz, -CH(OR)-), 4.42 (1H, dd, $J = 5.8, 2.2$ Hz, -CH(OR)-), 4.17 (1H, dd, $J = 6.8, 5.8$ Hz, -CH(OR)-), 3.03 (1H, m, HCC₃), 2.50–2.43 (2H, m, HCC₃) 2.28 (1H, m, HCC₃), 1.51 (3H, s, -CH₃), 1.41 (3H, s, -CH₃), 1.35 (3H, s, -CH₃), 1.32 (3H, s, -CH₃); ¹³C NMR (CDCl₃) δ 132.85, 128.75, 126.30, 122.35, 108.95, 108.00, 73.51, 71.75, 70.40, 69.64, 38.50, 34.53, 33.19, 32.73, 28.12, 26.54,

26.02, 24.74; IR (KBr) 2983, 2926, 2908, 1372, 1257, 1223, 1206, 1159, 1068, 1042, 1006, 931, 886, 870 cm⁻¹; MS (CI⁺, isobutane) *m/e* 305 (M + 1), 289, 247, 189, 171 (100), 143. Anal. Calcd for C₁₈H₂₄O₄; C, 71.03; H, 7.95. Found: C, 70.99; H, 7.81. **20**: mp 147–149 °C; ¹H NMR (CDCl₃) δ 5.97 (2H, m, olefinic H), 5.57 (1H, ddd, $J = 10.4, 4.0, 1.2$ Hz, olefinic H), 5.49 (1H, dd, $J = 10.2, 1.3$ Hz, olefinic H), 4.30 (1H, dd, $J = 7.3, 3.1$ Hz, -CH(OR)-), 4.26 (1H, dd, $J = 7.2, 3.0$ Hz, -CH(OR)-), 4.18 (1H, d, $J = 1.6$ Hz, -CH(OR)-), 4.17 (1H, d, $J = 1.4$ Hz, -CH(OR)-), 2.86 (2H, m, HCC₃), 2.34 (1H, m, HCC₃) 2.22 (1H, d, $J = 9.1$ Hz, HCC₃), 1.35 (3H, s, -CH₃), 1.33 (3H, s, -CH₃), 1.31 (3H, s, -CH₃), 1.28 (3H, s, -CH₃); ¹³C NMR (CDCl₃) δ 132.36, 129.30, 128.79, 126.65, 108.57, 107.61, 78.58, 78.34, 77.60, 70.86, 40.97, 40.70, 34.30, 33.13, 28.30, 26.81, 25.38, 24.97; IR (KBr) 2988, 2932, 1377, 1365, 1237, 1229, 1061, 1046, 887 cm⁻¹; MS (CI⁺, isobutane) *m/e* 305 (M + 1), 247 (100), 189, 171, 129, 95. Anal. Calcd for C₁₈H₂₄O₄; C, 71.03; H, 7.95. Found: C, 71.13; H, 8.04. **18**: mp (hexane) 211–212 °C; ¹H NMR (CDCl₃) δ 5.81 (2H, dd, $J = 10.2, 1.8$ Hz, olefinic H), 5.62 (2H, d, $J = 10.4$ Hz, olefinic H), 4.42 (2H, m, -CH(OR)-), 4.41 (2H, m, -CH(OR)-), 2.83 (2H, m, $J = 6.0$ Hz, cyclobutyl H), 2.64 (2H, d, $J = 6.3$ Hz, cyclobutyl H), 1.45 (6H, s, -CH₃), 1.37 (6H, s, -CH₃); ¹³C NMR (CDCl₃) δ 129.48, 125.82, 108.22, 72.73, 71.23, 37.33, 30.83, 28.18, 26.56; IR (KBr) 3029, 2983, 2941, 2870, 1375, 1371, 1230, 1160, 1098, 1069, 1033, 1024, 925, 873 cm⁻¹; MS (CI⁺, isobutane) *m/e* 305 (M + 1), 247, 189 (100), 171, 143, 95. Anal. Calcd for C₁₈H₂₄O₄; C, 71.03; H, 7.95. Found: C, 71.12; H, 8.04.

Thermal dimerization of 16. Diene **16** (2.51 g, 1.65×10^{-2} mol) in a 10-mL round bottom flask under nitrogen was immersed into a 120 °C oil bath. After 12 h, the reaction mixture was cooled to room temperature to form a yellow powder. The proton NMR spectrum of this reaction mixture showed mainly **20**. No peaks representing **17**, **18**, or **19** were observed. Silica gel column chromatography eluting with CH₂Cl₂-EtOAc yielded 2.22 g of **20** (88%).

Hydrolysis of 17 (Preparation of 23). In a 1-L round bottom flask, **17** (2.00 g, 6.57×10^{-3} mol) was dissolved in 600 mL of 60% acetic acid in water. After standing overnight, the acetic acid and water were removed under vacuum to give a yellowish solid. After washing with chloroform, the crude tetraol **17** was recrystallized from 90% ethanol in water to afford white crystals (1.30 g, 88%): mp 275–277 °C; ¹H NMR (DMSO-*d*₆) δ 5.76 (2H, dd, $J = 9.9, 1.6$ Hz, olefinic H), 5.60 (2H, dd, $J = 10.0, 2.2$ Hz, olefinic H), 4.51 (2H, d, HCO), 4.06 (2H, s, -OH), 4.05 (2H, s, -OH), 3.67 (2H, br d, $J = 3.7$ Hz, HCO), 2.38 (2H, br d, cyclobutyl H), 2.21 (2H, br s, cyclobutyl H); ¹³C NMR (DMSO-*d*₆) δ 138.00, 128.98, 68.10, 65.02, 38.34, 36.13; IR (KBr) 3370–3270 (strong, br), 3026, 2913, 2884, 1390, 1346, 1342, 1229, 1148, 1099, 1055, 1025, 846 cm⁻¹. Anal. Calcd for C₁₂H₁₆O₄; C, 64.27; H, 7.19. Found: C, 64.21; H, 6.97.

Synthesis of 1. Tetraol **23** (1.00 g, 4.46×10^{-3} mol) was added to 5 mL of DMF dimethyl acetal (3.76×10^{-2} mol). This mixture was stirred at 55 °C under nitrogen for 15 h or until a clear solution was obtained. The excess DMF acetal was removed under vacuum to yield acetal **24** as a yellow viscous liquid. To the crude cyclic DMF acetal **24** in 200 mL of dry CH₂Cl₂ was added *N,N*-diisopropylethylamine (3.5 mL, 2.01×10^{-2} mol, 4.51 equiv) under nitrogen, and the solution was cooled with an ice-water bath. A solution of trifluoromethanesulfonic anhydride (1.7 mL, 1.01×10^{-2} mol, 2.26 equiv) in 100 mL of dry CH₂Cl₂ was added dropwise over 40 min. After 30 min of additional stirring, 3 mL of DBU was added to the reaction mixture. The volume of the reaction mixture was reduced to approximately 100 mL under reduced pressure and then passed through a silica gel column with CH₂Cl₂. Evaporation of the eluent yielded a yellowish oil which was further chromatographed over a silica gel column with pentane as eluent to yield 0.45 g (65%) of **1** and 38 mg of biphenyl (6%). Sublimation of **1** gave white crystals: mp 27–29 °C; ¹H NMR (CDCl₃) δ 5.70 (4H, dd, $J = 8.0, 2.6$ Hz, olefinic H), 5.64 (4H, d, $J = 8.3$ Hz, olefinic H), 3.26 (4H, br s, cyclobutyl H); ¹³C NMR (CDCl₃) δ 127.50, 121.72, 43.75; IR (CHCl₃) 3057, 3032, 3012, 2931, 2879, 1734, 1579, 1377, 1038 cm⁻¹; UV (cyclohexane) λ_{\max} nm (ϵ): 266 (6000); MS (CI⁺, isobutane) *m/e* 157 (M + 1 - 2H, very weak), 155 (100), 128, 115; MS (EI⁺) *m/e* 156 (M - 2H, very weak), 154 (100), 152, 141, 128, 115.

(85) Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. *Purification of Laboratory Chemicals*; Pergamon Press: Oxford, 1980.

(86) Hatchard, C. G.; Parker, C. A. *Proc. Roy. Soc.* **1956**, A235, 518–536.

(87) Schaap, A. P.; Thayer, A. L.; Blosssey, E. C.; Neckers, D. C. *J. Am. Chem. Soc.* **1975**, 97, 3741–3745.

Photodimerization of 25. Diol **25** (2.00 g, 1.78×10^{-2} mol, 97% purity) and thioxanthen-9-one (75 mg, 3.53×10^{-4} mol) in 140 mL of dry methanol were irradiated through a Uranyl glass filter for 60 min. The solvent was evaporated to yield a brownish solid. Unreacted **25** and the sensitizer were washed with two 20 mL portions of CH_2Cl_2 . The resulting brownish powder (1.43 g) was recrystallized from 110 mL 60% ethanol in water yielding 0.741 g of **23**. The filtrate was further recrystallized from 50 mL of 90% ethanol in water to yield 89 mg. The total amount of **25** was 0.83 g (42%).

Preparation of 27. Tetraol **23** (1.0 g, 4.459×10^{-3} mol) was converted to the corresponding DMF acetal **24** as described earlier. To this in 70 mL of dry CH_2Cl_2 was added *N,N*-diisopropylethylamine (1.9 mL, 1.09×10^{-2} mol, 2.45 equiv) under nitrogen. Trifluoromethanesulfonic anhydride (0.9 mL, 5.35×10^{-3} mol, 1.20 equiv) in 70 mL of dry CH_2Cl_2 was then added dropwise over 15 min, and the mixture was stirred for an additional 30 min. After removal of the solvent, the resulting brown oil was dissolved in EtOAc and washed with water. The aqueous layer was extracted with EtOAc. After removal of the solvent from the combined EtOAc extracts, the resulting oil was dissolved in 50 mL of THF and 50 mL of 1 N aqueous HCl solution and stirred for 7 h. After neutralizing with NaOH solution, THF was evaporated, and the aqueous solution was extracted with EtOAc three times. The combined organic layers were washed with water and brine and dried over anhydrous magnesium sulfate. After filtration, EtOAc was evaporated to afford a yellow oil. To the crude triene diol **26** in 10 mL of methanol were added 2,2-dimethoxypropane (30 mL) and 15 mg of *p*-toluenesulfonic acid monohydrate and the mixture was stirred for 3 h. Triethylamine was added to neutralize the organic acid, and most of 2,2-dimethoxypropane and methanol were evaporated under vacuum. The resulting oil was dissolved in ethyl ether and washed with saturated aqueous sodium bicarbonate solution twice and brine. The organic layer was dried over anhydrous magnesium sulfate and concentrated under reduced pressure. The resulting oil was purified by silica gel column chromatography with hexane- CH_2Cl_2 to produce white crystals (0.265 g, 26%). **27**: mp (hexane) 79–80 °C; ^1H NMR (CDCl₃) δ 5.84 (1H, dd, $J = 10.3, 4.0$ Hz, olefinic H), 5.79 (1H, m, olefinic H), 5.73 (1H, m, olefinic H), 5.68–5.61 (3H, m, olefinic H), 4.53 (1H, m, -CH(OR)-), 4.29 (1H, dd, $J = 5.3, 2.0$ Hz, -CH(OR)-), 3.32 (1H, m, cyclobutyl H), 2.87 (1H, m, cyclobutyl H), 2.70 (1H, m, cyclobutyl H), 2.61 (1H, m, cyclobutyl H), 1.37 (3H, s, -CH₃), 1.34 (3H, s, -CH₃); ^{13}C NMR (CDCl₃) δ 129.85, 127.38, 125.23, 125.12, 122.49, 122.40, 108.92, 72.26, 70.42, 41.87, 41.66, 38.27, 32.43, 28.12, 26.65; IR (CHCl₃) 3031, 3012, 2913, 1381, 1371, 1239, 1057, 865 cm⁻¹; UV (cyclohexane) λ_{maxnm} (ϵ): 275 (3000), 204 (4400); MS (CI⁺, isobutane) m/e 231 (M + 1, weak), 171, 155 (100), 137, 123, 107; HRMS (CI⁺, isobutane) calcd for C₁₅H₁₉O₂ (M + 1) 231.1385, observed 231.1403.

Preparation of 28 (Deketalization of 17). Diketal **17** (0.10 g, 3.28×10^{-4} mol), in a 10-mL flame-dried round bottom flask, was dissolved in 5 mL of dry THF. In a dry ice:2-propanol bath was added 1.6 M *n*-butyl lithium in hexane (1.25 mL, 2.0×10^{-3} mol) to the solution under nitrogen. This solution was stirred in the dry ice:2-propanol bath for 15 min and then in an ice-water bath for 15 min. Cold water (2 mL) was added, and the mixture was stirred for 5 min. The reaction mixture was then poured into 30 mL of water, and the aqueous solution was extracted with 30 mL CH_2Cl_2 three times. The combined organic solution was washed with saturated aqueous sodium bicarbonate solution and brine and was then dried over anhydrous sodium sulfate. After filtration, the solvent was evaporated to give 91 mg of a yellow oil. The oil was purified by a silica gel chromatotron plate, eluting with hexane-EtOAc to yield 30 mg of a white solid (49%). **28**: mp (CH_2Cl_2 -hexane) 157–158 °C; ^1H NMR (CDCl₃) δ 6.92 (2H, dd, $J = 10.2, 3.6$ Hz, olefinic H), 6.18 (2H, d, $J = 10.3$ Hz, olefinic H), 2.88 (2H, br s, cyclobutyl H), 2.82 (2H, br s, cyclobutyl H), 2.42 (4H, m, -CH₂CO-); ^{13}C NMR (CDCl₃) δ 197.25, 144.81, 129.86, 37.44, 36.89, 33.28; IR (CDCl₃) 3031, 2936, 2923, 2919, 2896, 1672, 1392, 1253, 1162 cm⁻¹; UV (CH₃OH) λ_{maxnm} (ϵ): 324 (110), 233 (12 800); MS (CI⁺, isobutane) m/e 189 (M + 1, 100), 146, 128, 117, 106. Anal. Calcd for C₁₂H₁₂O₂; C, 76.57; H, 6.43. Found: C, 76.60; H, 6.51.

Preparation of enone 29 (Deketalization of 27). To tetramethylpiperidine (457 mg, 3.24×10^{-3} mol) in a flame-dried 10-mL round bottom flask in an ice-water bath was added 1.6 M *n*-butyllithium (2

mL, 3.20×10^{-3} mol) in hexane under nitrogen. After 30 additional min, the mixture was stirred at room temperature for 30 min. Dry THF (3 mL) was added to this white slurry. Dimethyl ketal **27** (50 mg, 2.17×10^{-4} mol) in a 10-mL round bottom flask was dissolved in 2 mL of dry THF and put into a dry ice:2-propanol bath under nitrogen. Two-thirds of the LTMP solution (9.82 equiv) was added to the ketal solution, and the mixture was stirred in a dry ice:2-propanol bath for 5 min and then in an ice-water bath for 25 min. The reaction mixture was poured into 20 mL water and extracted three times with 30 mL CH_2Cl_2 . The combined organic extracts were washed with brine and dried over anhydrous sodium sulfate. After filtration, the solvent was evaporated to give 93 mg of a yellow oil. The oil was purified by preparative TLC using CH_2Cl_2 as the eluting solvent to give 15 mg of an oily solid (40%). **29**: ^1H NMR (CDCl₃) δ 6.91 (1H, dd, $J = 10.4, 4.0$ Hz, =CHCO-), 6.07 (1H, dd, $J = 10.3, 1.3$ Hz, -CH=CCO-), 5.85 (1H, m, olefinic H), 5.74 (1H, m, olefinic H), 5.68 (1H, br d, $J = 9.6$ Hz, olefinic H), 5.64 (1H, dd, $J = 9.6, 3.8$ Hz, olefinic H), 3.35 (1H, m, cyclobutyl H), 3.13 (1H, m, cyclobutyl H), 2.84 (2H, m, cyclobutyl H), 2.44 (2H, m, -CH₂CO-); ^{13}C NMR (CDCl₃) δ 197.95, 150.08, 128.16, 126.09, 125.25, 123.09, 122.14, 44.27, 40.39, 37.94, 37.76, 34.45; IR (CHCl₃) δ 3029, 3013, 1668, 1615, 1392, 1238, 1217, 866, 776 cm⁻¹; MS (CI⁺, isobutane) m/e 173 (M + 1), 123, 95 (100), 79; HRMS (CI⁺, isobutane) calcd for C₁₂H₁₃O (M + 1) 173.0966, observed 173.0923.

Preparation of Silyl Enol Ether 30. Ketal **27** (0.25 g, 1.09×10^{-3} mol) in 10 mL dry of THF was treated with an LTMP solution (5.52×10^{-3} mol) as previously described. The solution was then cooled in an ice-water bath, and *tert*-butyldimethylsilyl chloride (1.636 g, 1.09×10^{-2} mol) in 5 mL of dry HMPA was added. After the solution had been stirred for 30 min, cold water was added. This was extracted with 40 mL of pentane four times. The combined organic extracts were washed with cold saturated aqueous sodium bicarbonate solution three times and cold brine and dried over anhydrous sodium sulfate. After filtration, the solvent was evaporated under reduced pressure to give a yellow oil. Silica gel chromatography with pentane- CH_2Cl_2 , reverse phase chromatography (Whatman, LKC 18G, Linear-K) with methanol, silver nitrate extraction, sublimation, and recrystallization in pentane all failed to purify the desired silyl ether. Consecutive silica gel chromatographies with pentane- CH_2Cl_2 and sublimation followed by a silica gel chromatography with pentane- CH_2Cl_2 gave 139 mg of crude product. ^1H NMR (CDCl₃, internal standard CHCl₃; 7.24 ppm): δ 5.75–5.69 (3H, m, olefinic H), 5.66–5.62 (2H, m, olefinic H), 5.53 (1H, d, $J = 10.1$ Hz, olefinic H), 4.81 (1H, d, $J = 4.9$ Hz, olefinic H), 3.30 (1H, m, cyclobutyl H), 3.24–3.17 (3H, m, cyclobutyl H), 0.94 (9H, s, (CH₃)₃C-), 0.16 (3H, s, CH₃Si-), 0.15 (3H, s, CH₃Si-).

Preparation of 31. Ketal **27** (0.30 g, 1.30×10^{-3} mol) in 5 mL of dry THF was treated with an LTMP solution (7.0 equiv) as previously described. After the solution had been stirred for 30 min, 2 mL of acetic anhydride in 7 mL of dry HMPA was added under nitrogen. This reaction solution was stirred for 30 min in an ice-water bath. To the reaction mixture was added 20 mL water, and the mixture was extracted with 30 mL pentane five times. The combined organic layers were washed with cold 5% aqueous sodium bicarbonate solution three times and cold brine. The solution was dried over anhydrous sodium sulfate, filtered, and evaporated under reduced pressure to give a yellow oil. This oil was dissolved in CH_2Cl_2 and passed through a short silica gel column (10 g). The elutant was purified by silica gel chromatotron using pentane- CH_2Cl_2 as eluent. One of the fractions was a mixture of enol acetate **31** and phenyl acetate in a ratio of 2.15:1. The yield of **31** was 15%. The mixture was further purified by sublimation and silica gel chromatography for studying the property of **31**: ^1H NMR (CDCl₃) δ 5.77 (1H, dd, $J = 9.9, 4.0$ Hz, olefinic H), 5.73–5.71 (2H, m, olefinic H), 5.64–5.62 (2H, m, olefinic H), 5.52 (1H, d, $J = 9.9$ Hz, olefinic H), 5.28 (1H, d, $J = 5.5$ Hz, CH=C(OR)-), 3.41–3.37 (1H, m, cyclobutyl H), 3.30 (3H, m, cyclobutyl H), 2.14 (3H, s, CH₃CO-); ^{13}C NMR (CDCl₃) δ 169.35, 144.88, 130.53, 127.06, 127.02, 122.07, 122.02, 121.33, 112.50, 43.83, 43.71, 43.51, 43.38, 20.98; IR (CHCl₃) 3032, 2884, 1745, 1662, 1371, 1231, 1136, 918 cm⁻¹; MS (CI⁺, isobutane) m/e 213 (M + 1 - 2H), 171, 137, 123, 95 (100), 79; MS (EI⁺) m/e 212 (M - 2H), 170, 136, 94 (100), 78; UV (cyclohexane) λ_{maxnm} : 265.

Kinetics for the Thermolysis of 1 and 31. Each sample solution (0.079–0.081 M of **1** in acetone-*d*₆, cyclohexane-*d*₁₂, or in acetonitrile-*d*₃, and 0.021 M enol acetate **31** in cyclohexane-*d*₁₂) was divided into five or six NMR tubes with 0.5 mL of volume each. Each NMR tube was degassed with argon and a dry ice:2-propanol bath using a Firestone valve (six freeze–pump–thaw cycles at 0.01 mmHg) and was then sealed under argon. Kinetic experiments were performed in a proton NMR probe thermostated at desired temperatures. The 500 MHz Chicago DS-1000 spectrometer with KINET program was used to collect several NMR spectra separated by delays appropriate for a kinetic study. The probe was allowed to equilibrate for at least 1.5 prior to any thermolysis experiment to ensure the stability of temperature. The overall fluctuation of the probe during each thermolysis was ± 0.3 °C. To minimize error, at least five kinetic measurements were performed and at least one and a half half-lives were monitored before terminating the experiment. The decrease of the olefinic peaks was monitored and integrated for each kinetic run. These data were analyzed by the first order reaction rate law.

The data for **1** in acetone-*d*₆, cyclohexane-*d*₁₂, and acetonitrile-*d*₃ were fitted to the eqs 1–3:

$$\ln k = 28.738(\pm 0.504) - 12180(\pm 165)/T \quad (1)$$

$$\ln k = 29.336(\pm 1.453) - 12423(\pm 478)/T \quad (2)$$

$$\ln k = 29.397(\pm 0.951) - 12442(\pm 313)/T \quad (3)$$

The data for **31** in cyclohexane-*d*₁₂ were fitted to the following equation:

$$\ln k = 29.090(\pm 0.540) - 12514(\pm 176)/T \quad (4)$$

The activation parameters for these cases are tabulated in Tables 2 and 3.

Determination of Quantum Yields for the Formation of Excited Benzene and the Photodecomposition upon Direct Irradiation of 1. The quantum yield of excited benzene upon direct irradiation of **1** was determined by comparing the emission spectra of benzene and **1** with similar optical density at the excitation wavelength.⁴⁸ The optical density of **1** in these experiments was less than 0.11, while samples of benzene were adjusted to similar optical density. Samples were degassed at 0.01 mmHg using six freeze–pump–thaw cycles. To measure the emission spectrum of **1**, the excitation wavelength was set at 300 nm to ensure that the light was absorbed only by **1**. The emission spectrum of benzene was taken under the same conditions with 254.3 nm as the excitation wavelength.

The total quantum yield for the photodecomposition of anti-*o,o'*-dibenzene **1** was determined with the aid of a potassium ferrioxalate actinometer.^{47,86} The actinometry solution was prepared according to the procedure of Murov.⁴⁷ The measurements were performed on a Perkin-Elmer MPF-66 fluorescence spectrophotometer. To avoid uneven stirring effects, a narrow quartz cell with 1 mL volume capacity and 1 cm path length was used.

Visual Detection of Chemiluminescence from the Thermolysis of Oily Samples of Benzene Dimers in the Presence of Sensitizers.

The general procedure for observing the chemiluminescence of a sample of **1** and sensitizer is as follows: A mixture of **1** and a sensitizer (10–25 mg) in a 5 mm NMR tube were partially dissolved with a small amount of CH₂Cl₂. By careful removal of the solvent under reduced pressure, most of the oily **1** and solid sensitizer were coated on the wall of the tube. The sample was degassed by six freeze–pump–thaw cycles (at 0.01 mmHg) and was sealed under argon. These samples were successively dropped into an oil bath preheated to 190 °C, and the luminescence was observed by the dark-adapted eyes of a number of individuals in a dark room. The sensitizers used were DBA, DMA, rubrene, perylene, CAN, DCA, TCAN, and BPEA. Usually 13–20 mg of **1** and 10–25 mg of sensitizer were used in these experiments. In the case of TCAN, 32 mg of **1** and about 11 mg of TCAN were used. Control experiments showed that BPEA without **1** gave light when heated under the same conditions. Samples of **5** and **31** with rubrene or perylene were also studied. In these experiments, 10.5 mg of **5** and 13–15 mg of sensitizers and 12 mg of **31** and 13–14 mg of sensitizers were used.

Recording of Chemiluminescence Spectra. Samples were decomposed with an oil bath (usually ~ 190 °C) which was constructed with a Pyrex Modified Thiele-Dennis melting tube filled with silicone oil. The chemiluminescence emission from the decomposing sample was collected by a lens assembly and focused onto the slit of a UFS-200 Flat Field Spectrograph (spectral range 200–800 nm) which resolved the incident light and reflected it to a DIDA-512G Reticon Detector Head for signal recording.⁶² The Detector Head was controlled by an OMSA ST-120 Detector Controller (Princeton Instruments, Inc.) operated through an IBM PC system 200 with the aid of ST-120 software. The detection system was calibrated at room temperature with the emission lines at 365.0, 404.7, 435.8, 546.1, and 579.1 nm from an Oriol mercury-argon lamp (Model 6035, operated at 17 mA). The system was thus determined to cover a wavelength range of 330–670 nm with an estimated resolution of 5 nm. It was further tested by using the known chemiluminescence of adamantylideneadamantane 1,2-dioxetane.⁶⁹

The fluorescence measurement of solid perylene in an oil bath preheated to 180 ± 2 °C was performed on a Perkin-Elmer MPF-66 fluorescence spectrophotometer.

The chemiluminescence spectrum of the oily **1** in the presence of perylene was recorded at 190 °C using the 300-micron slit. The exposure time in this case was set to 5 s (300 scans) to cover the burst of light emission from the sample which usually occurred about 1–2 s after immersion in the oil bath. Ten spectra from the decomposition of a mixture of about 15 mg of oily **1** and 18 mg of perylene were added together. The total amount of **1** used for the measurements was 149 mg (9.537×10^{-4} mol). The data were smoothed three times. The resulting spectrum is magnified and shown in Figure 1 (broken line). In order to estimate the quantum efficiency of the chemiluminescence from the thermolysis of oily anti-*o,o'*-dibenzene **1** in the presence of perylene, decalin solutions of adamantylideneadamantane 1,2-dioxetane was used as a reference.

Diels–Alder Reaction of 1 with Singlet Oxygen. A solution of **1** (79 mg, 5.06×10^{-4} mol) and Methylene Blue (10 mg) in 15 mL of dry CH₂Cl₂ was placed in a 25-mL round bottom flask and purged with oxygen for 5 min. The mixture was irradiated through a UV cutter filter with a 360 W sun lamp at room temperature while maintaining a gentle stream of oxygen through the solution for 80 min. The reaction mixture was separated by a silica gel column chromatography, eluting with pentane and CH₂Cl₂ to afford 15 mg of unreacted **1** and 34 mg of monooxide **34**. The later fractions of the column showed decomposed products. The isolated yield of **34** was 36% based on the starting **1** and 44% based on the consumed **1**. **34**: mp (CH₂Cl₂–hexane) 114–116 °C (dec); ¹H NMR (CDCl₃) δ 6.79 (2H, m, *J* = 3.9 Hz, C=CHCO), 5.71 (2H, dd, *J* = 7.8, 2.7 Hz, olefinic H), 5.47 (2H, m, *J* = 2.1 Hz, olefinic H), 4.68 (2H, m, =CCHO), 3.11 (2H, br s, *J* = 2.0 Hz, cyclobutyl H), 2.56 (2H, br s, cyclobutyl H); ¹³C NMR (CDCl₃) δ 131.27, 125.63, 121.34, 72.20, 44.70, 32.67; IR (CHCl₃) 3033, 2956, 1618, 1604, 1587, 1377, 1230, 1037 cm⁻¹; UV (cyclohexane) λ nm (ϵ): 275 (3000); MS (EI⁺) *m/e* 188 (M), 115, 103, 91, 81, 78 (100); HRMS (EI⁺) calcd for C₁₂H₁₂O₂ 188.0837, observed 188.0852.

Compound **39** was prepared for analytical purposes by using polymer-bound Rose Bengal.⁸⁷ The white powder decomposed slowly to a pale brown solid starting at 147 °C, and the brown solid did not melt up to 285 °C. **39**: ¹H NMR (CDCl₃) δ 6.87 (4H, m, *J* = 3.9 Hz, olefinic H), 4.63 (4H, m, *J* = 2.9 Hz, =CCHO), 2.53 (4H, br s, cyclobutyl H); IR (KBr) 3065, 2970, 2944, 1374, 1242, 1040, 942, 899 cm⁻¹; MS (EI⁺) *m/e* 220 (M), 188 (M – O₂), 104, 91, 81 (100), 78.

Thermal Rearrangement of 34. A solution of **34** (31 mg, 1.65×10^{-4} mol) in 40 mL of chloroform was refluxed for 16 h under nitrogen. The solvent was then evaporated under vacuum to give a yellow powder. The NMR of the reaction mixture showed mainly **35** with very small amounts of byproducts. The HPLC analysis of the reaction mixture indicated that the side products containing cyclohexadiene moieties were present in less than 5%. The reaction mixture was separated by a silica gel column chromatography eluting with CH₂Cl₂–EtOAc to give bisepoxide **35** (17 mg, 55%) as a white powder: mp (CH₂Cl₂–hexane) 136–138 °C (dec); ¹H NMR (CDCl₃) δ 5.78 (2H, dd, *J* = 7.7, 2.7 Hz, olefinic H), 5.62 (2H, m, olefinic H), 3.49 (2H, d, *J* = 2.6 Hz, epoxy H), 2.95–2.93 (4H, m, 2 epoxy H and 2 cyclobutyl

H), 2.81 (2H, d, $J = 2.2$ Hz, cyclobutyl H); ^{13}C NMR (CDCl_3) δ 125.78, 122.35, 50.36, 48.01, 40.05, 32.85; IR (CHCl_3) 3025, 3018, 2938, 1603 (weak), 1584, 1418, 1372, 1268, 1058, 944, 875 cm^{-1} ; UV (cyclohexane) $\lambda_{\text{nm}}(\epsilon)$: 274 (3200); MS (EI^+) m/e 188 (M), 128, 115, 110, 91, 81 (100), 78; HRMS (EI^+) calcd for $\text{C}_{12}\text{H}_{12}\text{O}_2$ 188.0837, observed 188.0837.

Photolysis of 34 at 313 nm. A solution of **34** in chloroform- d (1.99×10^{-2} M), containing dodecane as an internal standard, was placed in a quartz NMR tube with a septum. This solution was deaerated by bubbling argon in a dry ice:2-propanol bath for 20 min. The solution was then irradiated at room temperature through a 313 nm interference filter with a medium pressure mercury lamp. The photoreaction was followed by proton NMR. After 30 min, 17% of **39**, 11% of **35**, and 34% of **34** were observed. After 4 h and 50 min, tetraepoxide **40** was the only identifiable product.

An analytical sample of **40** was prepared by the thermal rearrangement of **39**. The white powder did not melt up to 285 °C but decomposed slowly to a pale brown solid. **40**: ^1H NMR (CDCl_3) δ 3.55 (4H, d, $J = 2.3$ Hz, OCCHOCO), 2.95 (4H, d, $J = 2.2$ Hz, HCCHOCO), 2.52 (4H, s, cyclobutyl H); IR (KBr) 3038, 2931, 2916, 1424, 1369, 1276, 1203, 1038, 938, 874 cm^{-1} ; MS (EI^+) m/e 220 (M), 191, 173, 145, 133, 117, 105, 103, 94, 91, 81 (100), 77; HRMS (EI^+) calcd for $\text{C}_{12}\text{H}_{12}\text{O}_4$ 220.0736, observed 219.9892.

Irradiation of 34 at 300 nm. A solution of **34** in THF- d_8 (1.99×10^{-2} M) was placed in a quartz NMR tube with a septum. After 20 min of argon bubbling in a dry ice:2-propanol bath, ^1H -NMR spectra were recorded at -45 °C. ^1H NMR (THF- d_8 , -45 °C) δ 6.74 (2H, m, $J = 3.6$ Hz, C=CHCO), 5.65 (2H, dd, $J = 7.3$, 3.0 Hz, olefinic H), 5.46 (2H, m, olefinic H), 4.61 (2H, m, =CCHO), 2.93 (2H, br s, cyclobutyl H), 2.50 (2H, br s, cyclobutyl H). The solution was placed in a Dewar flask containing a quartz window. The Dewar was filled with dry ice-ethyl ether, and the temperature of that bath was kept at about -78 °C. The sample was irradiated through a 300 nm (± 5 nm) interference filter with a 450 W medium pressure mercury lamp for 5 h. The proton NMR at -45 °C showed mainly two peaks in a 2:1 ratio, at 6.72 ppm (olefinic protons) and 5.17 ppm (bridgehead protons), respectively.⁷⁹ A small amount of **39** was also observed. When the reaction mixture was warmed to room temperature over 3 min, these two peaks disappeared. When a 4.55×10^{-2} M solution of **34** was irradiated for 4.5 h, about 44% of **34** was consumed and some of **39**

precipitated out. The NMR of the solution showed the presence of **34** (56%), **36** (23%), and a small amount of **39**. The yield of **36** based on the consumed **34** was 52%. After 10 min at room temperature, **36** completely decomposed, and the amount of **34** decreased while **39** increased. The yield of trapping singlet oxygen generated from **36** was 93%.

Trapping Singlet Oxygen from the Thermal Decomposition of 36 with DMA. A solution of **34** in THF- d_8 (1.43×10^{-5} mol, 4.10×10^{-2} M) containing dodecane as an internal standard was prepared and irradiated as described before. The amount of **36** upon completion of irradiation was 6.67×10^{-6} mol (46%) as measured by ^1H -NMR. To this in a dry ice:2-propanol bath was added a solution of DMA in THF- d_8 (7.42×10^{-5} mol, 11.1 equiv). The solution was then slowly warmed to room temperature. After 15 min, proton NMR spectra of the mixture and an authentic sample of 9,10-dimethylanthracene 9,10-endoperoxide⁸¹ (**41**) were taken. **41**: ^1H NMR (THF- d_8 , -45 °C) δ 7.40 (4H, dd, aromatic H), 7.23 (4H, dd, aromatic H), 2.06 (6H, s, CH_3O -). The methyl peak of **41** at 2.06 ppm from the mixture was compared with the internal standard. The formation of **41** from DMA and singlet oxygen, based on the amount of **36**, was 87%.

Kinetics for the Thermolysis of 36. A solution of 0.046–0.053 M of **36** in THF- d_8 (3.0–3.5 mg in 0.35 mL) was irradiated for 5–11 h as described before. The overall temperature fluctuation at the probe during each thermolysis was ± 0.5 °C. The data were fitted to the following equation

$$\ln k = 30.259(\pm 0.955) - 9258(\pm 225)/T \quad (5)$$

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