Chemistry of *syn-o,o′*-Dibenzene

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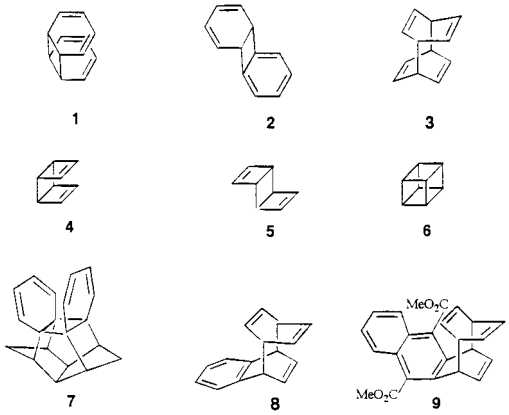
Abstract: A new and improved synthesis *cis,syn-o,o′*-dibenzene **1** was developed to obtain **1** in larger amounts with improved purity. *syn*-Dibenzene **1** undergoes thermolysis to two molecules of benzene at a rate slower than that of the thermodynamically more stable *anti*-dibenzene **2**. Kinetic analysis revealed that the higher thermal stability of **1** is due to the higher heat of activation in thermolysis. Photoelectron spectroscopy of **1** showed that the through-bond interaction between the two cyclohexadiene units in *o,o′*-dibenzenes is more important than their through-space interaction. A comparative study on the thermolyses of related *syn-o,o′*-arene:benzene dimers suggests that thermolyses of *syn-o,o′*-arene:benzene dimers proceed via their *anti*-isomers as an intermediate. *syn*-Dibenzene **1** also undergoes adiabatic photolysis to one molecule of excited benzene and one molecule of ground-state benzene in good efficiency. The mechanisms of these reactions are discussed.

Introduction

Due to the high internal energy of benzene cyclodimers, these compounds are expected to possess unusual chemical and physical properties of both experimental and theoretical significance. The two *o,o′*-dimers, *syn-o,o′*-dibenzene **1** and *anti-o,o′*-dibenzene **2**, differ from each other only in their topology and are of particular interest. Both compounds have now been synthesized: *anti-o,o′*-dibenzene **2** by several different groups since the 1960s[1] and *syn-o,o′*-dibenzene **1** in our laboratory in 1987.[2] Although **2** is now available in gram quantities,[1a] our original synthesis of **1** only yielded the target compound in minute quantities and of doubtful purity,[2] which limited the scope of our investigations. In this work, we wish to report an improved synthesis of **1**. The availability of both **1** and **2** enables a parallel study of their highly exoergic thermolyses, formally symmetry-forbidden 4n-retro-cycloadditions to two molecules of benzene as governed by the Woodward−Hoffmann Rules.[3] Because of their unique topology, dibenzenes **1** and **2** may be an ideal system for the comparative study of the relative importance of intramolecular through-space (π: π) and through-bond (σ: π) interaction between two 1,3-cyclohexadiene systems. Such a study may delineate these two types of interactions on a quantitative basis. The synthesis of the *p,p′*-dibenzene **3** remains elusive at this moment.[4] Recently, there is a renewed interest in these systems, particularly on the effect of electron transfers.[5]



Although the analogous *syn*- and *anti*-[$2\pi + 2\pi$] cyclobutadiene dimer systems, tricyclo[4.2.0.0]octa-2,6-diene **4** and **5**, have been prepared by the thermal dimerization of their monomers,[6] the same type of reaction cannot be applied to give the dimers of benzene. Both the chemistry and the spectroscopy of dienes **4** and **5** have been studied extensively. By analyzing their photoelectron (PE) spectra, one of us (R.G.) has shown that their through-bond interactions are much stronger than their through-space interactions. As a result, the symmetric π-orbital lies at higher energy than the antisymmetric π-orbital.[7] This interaction accounts for the observation that *syn*-octamethyltricyclo[4.2.0.0^{2,5}]octa-3,7-diene and related systems yield only to a very minor extent to the corresponding cubanes.[8] The importance of through-bond interaction has also been observed in *anti*-dibenzene **2**. The energy difference between the symmetric and antisymmetric π-orbitals amounts to 0.67 eV.[9,10] While both the chemistry and the PE spectrum of a rigid cage-

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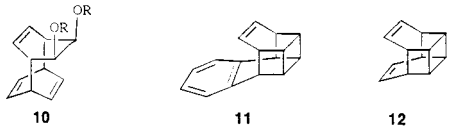
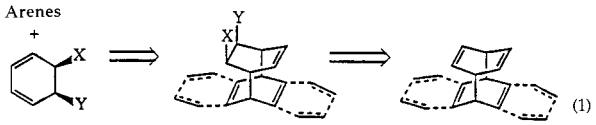
like derivative of dibenzene **1**, an intramolecular dimer **7** related to pagodane, have been investigated and have led to many interesting results,[11] only a paltry amount of experimental data is available due to the limited availability of **1**. Furthermore, molecular modeling of **1** reveals that the cyclobutyl ring in **1** is flexible in contrast to the rigid skeletal framework of **7**. It will be interesting to compare the through-bond interaction of two π-systems in dibenzenes **1**, **2**, and related systems with those in **4** and **5** as well as to compare the through-bond interaction of two $\pi-$systems in **1** with those in **7**.



10 **11** **12**

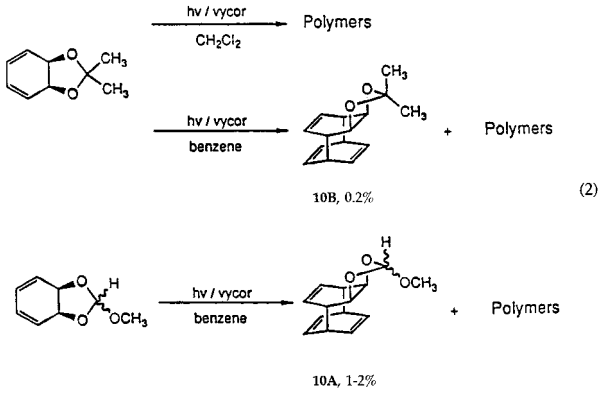
Results and Discussion

Synthesis of 1. We were also interested in the preparation of the other cyclodimer of benzene, *p,p′*-dibenzene **3**, and have synthesized the mixed cyclodimers related to **3**,[4] the naphthalene:benzene dimer **8**[12] and the anthracene:benzene dimer **9**.[13] The key step in the syntheses of these compounds is the photocycloaddition of a 1,2-disubstituted cyclohexadiene, a masked benzene, to the arene, followed by the low-temperature elimination of the 1- and 2-substituents (eq 1). In contrast to the



(1)

syntheses of **8** and **9** and due to the overlap in the ultraviolet absorption spectra of benzene and cyclohexadienes, the photocycloaddition of 1,3-cyclohexadiene derivatives to benzene led to a complex mixture of products. These included polymeric material insoluble in benzene, which precipitates out of the solution and coats the light source, and often effectively disrupts the photocycloaddition. These polymeric products may be derived from both the excited singlet and from triplet cyclohexadienes which result from the energy transfers from the excited benzene. The yield of the $4\pi + 4\pi$ adduct **10** is usually very poor, ranging from 0.2 to 2% (eq 2). All efforts to eliminate



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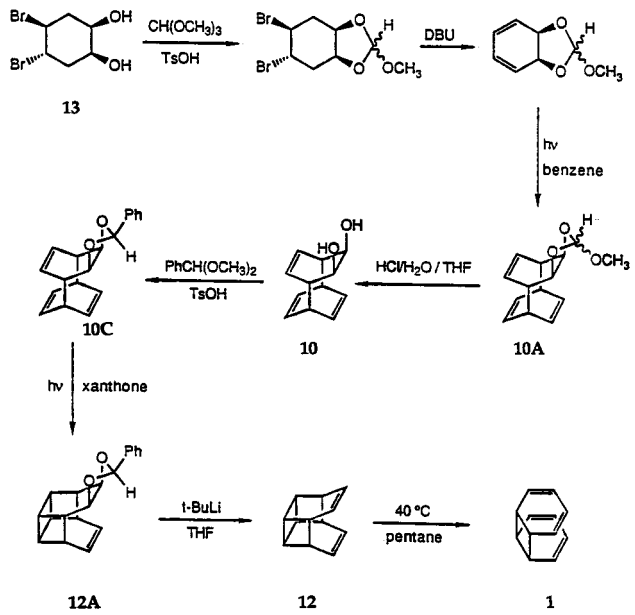
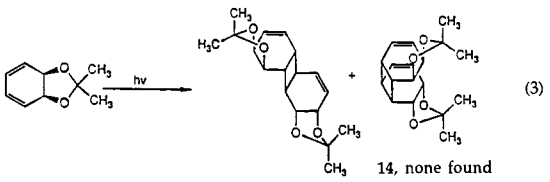
the substituents from adduct **10** to form *p,p′*-dibenzene **3** failed.[4] Since dimer **8** was synthesized from a pentacyclic intermediate

Scheme 1



11,[12] this work led to the synthesis of a pentacyclic dimer **12** of benzene from **10** as a potential intermediate in the synthesis of other interesting products.[14] In an effort to purify **12** by sublimation at 50−55 °C at 12 Torr, we were surprised to find that the sublimate was contaminated with **1**, that is, a symmetry-forbidden intramolecular retrocycloaddition had occurred under such a mild condition. Since both **1** and **12** are thermally unstable and volatile hydrocarbons exhibiting similar chromatographic properties, we were unable to separate these two hydrocarbons by common chromatographic techniques. A reasonably pure sample of **1** was prepared by refluxing a pentane solution of **12** (bath temperature 40 °C) for 9.7 days until most of **12** was decomposed. The only other detectable product was benzene. Subsequent work indicated that **1** prepared by this method was contaminated with **12**, and we were unable to reproduce the reported isolated yield of 16% of **1** in acceptable purity from the thermolysis of **12**.[2] In contrast to **2**, which may be prepared in gram quantities in a matter of several days,[1a] the preparation of **1** requires the intensive effort of a skilled laboratory worker over a period of many weeks in order to yield a few milligrams of the impure product. The overall yield of **1** from the dibromodiol **13** is about 0.01% (Scheme 1). Since we were unable to synthesize the *cis,syn*-$[2\pi + 2\pi]$ dimers of derivatives of *cis*-3,5-cyclohexadien-1,2-diol, for example **14**, in detectable yield by either direct or sensitized irradiation of their monomers (eq 3), the photocycloaddition of cyclohexa-



(3)

dienes to benzene remains the only viable alternative in

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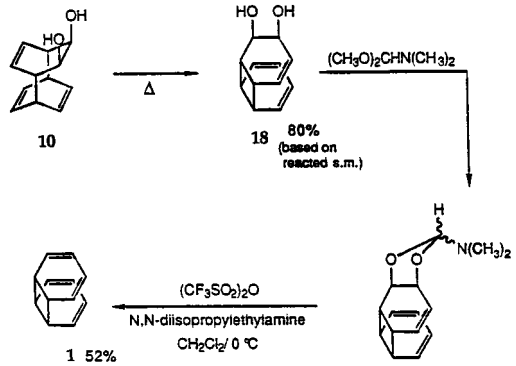
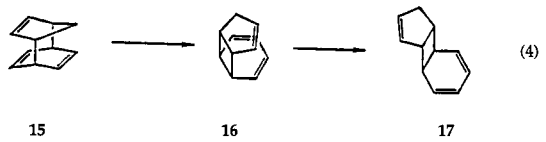
Scheme 2



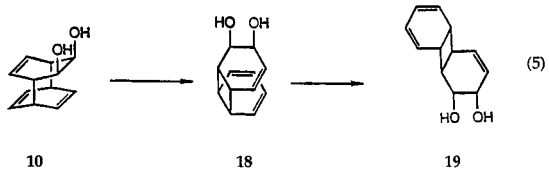
constructing the basic skeleton of **1** and **3**. Although products prepared from several runs had to be pooled to carry out the next step of the synthesis, it was apparent that an improved synthesis of **1** from the pentacyclic adduct **12** is needed to achieve our study on the chemistry and spectroscopy of **1**.

It is known that the $[4\pi + 4\pi]$-cycloadduct of benzene and cyclopentadiene **15** undergoes a facile Cope rearrangement at 65 °C to the *syn*-$[2\pi + 2\pi]$-cycloadduct **16** ($t_{1/2} = 2$ h), which in turn undergoes a sequential rearrangement to the *anti*-isomer **17** at a much slower rate at the same temperature ($t_{1/2} = 24$ h).[13] The thermolysis of **17** to benzene and cyclopentadiene requires an even more vigorous condition ($t_{1/2} = 35$ h at 80 °C, eq 4).[15] On the basis of this knowledge, our experience in the



(4)

synthesis of **8** and **9**, and the facile bis-dehydroxylation of 1,2-diols to the corresponding olefins via the Mak−Yang reaction,[16] an alternate synthesis of **1** was designed to circumvent the thermolysis of **12** as a key step in the synthesis of **1** (Scheme 2). When the thermal Cope rearrangement of **10** was attempted, we discovered that the rate of conversion of **10** to **18** and the rate of subsequent rearrangement of **18** to **19** were much closer to each other than those reported for related compounds in the **15** series (eq 5). Nevertheless, diol **18**, contaminated with small



(5)

amounts of **10** and **19**, was obtained in good yield by careful manipulations and may be converted directly to dibenzene **1** containing biphenyl as the only detectable byproduct. Pure dibenzene **1** was obtained from this mixture by HPLC, mp 54.0−54.5 °C, λ_{max}(cyclohexane) 260 nm ($\epsilon = 4500$). We wish to point out that these values differ from those originally reported from our laboratory, mp 45−46 °C, λ_{max}(cyclohexane) 240 nm ($\epsilon = 4900$).[2] The formation of biphenyl in the synthesis of **1** and in the synthesis of **2** via the Mak−Yang reaction suggests that biphenyl was not derived from the dibenzenes under the experimental conditions, but from a side-reaction in the Mak−Yang reaction. A plausible pathway was proposed previously.[1a]

Photoelectron, UV Absorption, and PMR Spectroscopy. Photoelectron Spectra. The He(I) photoelectron (PE) spectrum of **1** is shown in Figure 1, and the recorded first vertical ionization energies are listed in Table 1. The PE spectrum of **1** shows four transitions (band 1−4) below 10 eV. The calculated values were obtained using a 6-31G* basis.[17] This comparison is based on the assumption that Koopmans' theorem[18] is valid, that is, the calculated orbital energies, ϵ_j, can be correlated with the recorded vertical ionization energies.

To understand the differences between **1** and **2** we consider the correlation diagrams in Figure 2 a and b. On the left side of each figure the two linear combinations (a_u, b_g, and a_2, b_1, respectively) are shown which result from the highest occupied π MOs of two butadiene fragments. In the case of **1**, the corresponding orbital energies are split due to a through-space interaction. This is not the case for **2** due to the large separation of both π-units. At the right side of each figure are shown the highest occupied σ-orbitals (b_u, a_u, and b_2, b_1, respectively), the so-called Walsh orbitals of the central four-membered ring system.[19] For the reason of symmetry only one linear combination (**1**:b_1, **2**:a_u) interacts with the corresponding Walsh orbital, which yields a destablization of the π-combination as shown in Figure 2.[19]

The smaller splitting for **2** (0.67 eV) is due to the through-space interaction of the π-system in **1** which is not present in **2**. The qualitative interaction diagram of Figure 2 is confirmed by the MO calculation as shown in Table 1. These calculations confirm the assignment given.

UV Absorption Spectra. Previously, we were puzzled by a marked blue-shift (240 nm vs 266 nm)[2] of the UV absorption of **1** versus **2**. The large difference in the observed electronic transitions may be the result of an impurity, most probably **12**, in the original sample of **1**. However, the pure sample of **1** obtained by HPLC exhibits a UV maximum at 260 nm which is still blue-shifted from that of **2** despite the lower HOMO of **1**. A closer examination of the orbital interactions in the antibonding levels reveals that both through-bond and through-space interactions similar to those in the bonding levels may take place. The symmetric π^* levels of cyclohexadienyl systems in **1**, π^*_+, which are lowered by favorable through-space interaction, cannot undergo a favorable through-bond interaction with the antibonding σ^* orbital. The LUMO of *cis*-dibenzene **1** is thus π^*_-, the anti-symmetric π^*-level. Since the through-bond interaction in the bonding level is known to be appreciably stronger than the through-space interaction, the LUMO of **2** will be lower than that of **1**. The electronic transitions of closely related compounds may be correlated to the gaps between their HOMOs and LUMOs. The orbital interactions that raise both the HOMO and LUMO levels of **1** relative to those of **2** may

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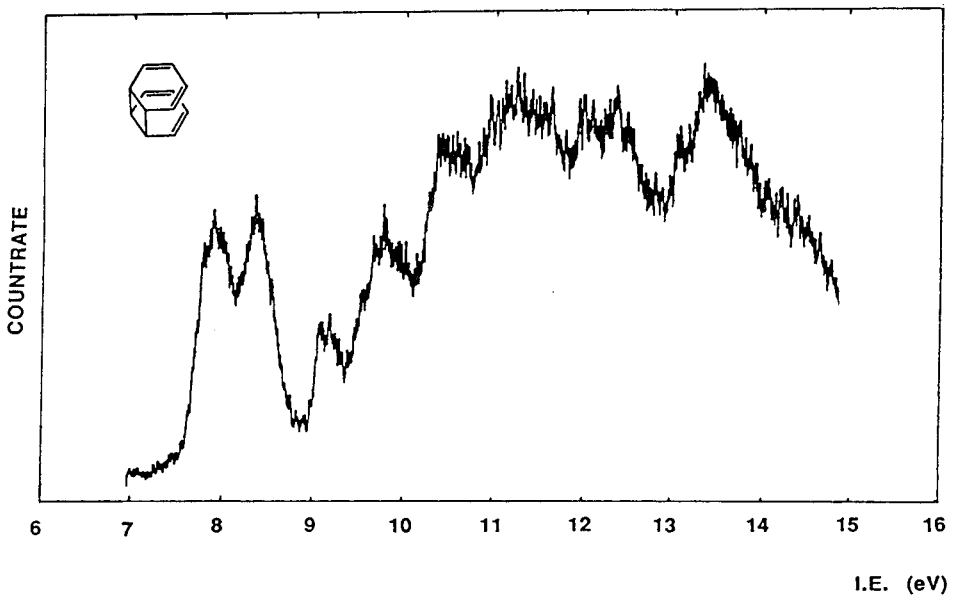


Figure 1. PE spectrum of *syn*-dibenzene **1**.

Table 1. PE Spectra of *o,o′*-Dibenzenes, Values in eV, and Assignments Are Given in Brackets[9,10]

band	**1** exptl	calcd	**2**	**7**
1	7.88[$b_1(\pi^+ - \sigma)$]^a	7.85^b	7.85[$a_u(\pi^+ - \sigma)$]^8	7.6[$b_1(\pi^+ - \sigma)$]^9
2	8.34[$a_2(\pi^-)$]^a	8.17^b	8.52[$b_g(\pi^-)$]^8	8.1[$a_2(\pi^-)$]^9
3	9.1[$b_2(\sigma)$]^a	11.02^b	10.15[$b_u(\sigma^-)$]^8	9.1[$b_2(\sigma)$]^9
4	9.75[$a_1(\sigma)$]^a	11.18^b	10.4[$a_u(\sigma)$]^8	9.65[$a_1(\sigma)$]^9

^{a} Experimental values. ^{b} Values calculated from HF/6−31*G orbital energies.

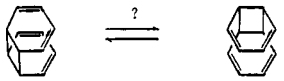
result in similar UV absorptions in two *o,o′*-dibenzenes. Accordingly, we also carried out SCF-CI calculations on the UV absorptions of dibenzenes **1** and **2** using the Gaussian program and a 6-31G set,[17] assuming that **1** and **2** exist in a distorted C2 geometry. We obtained similar values for both isomers using both Hartree−Fock (HF), 232 nm, and density functional approaches (DFT), 244 nm.[20] These results and the qualitative estimate of HOMO−LUMO gaps of **1** and **2** give no basis for the large difference in the UV maxima reported originally by one of us using an impure sample.[2]

Proton Magnetic Resonance Spectrum. A $C_{10}H_{10}$ hydrocarbon structurally related to dibenzene **1**, hypostrophene **20**, is known to undergo degenerate Cope rearrangement (eq 6).[21]

(6)

20

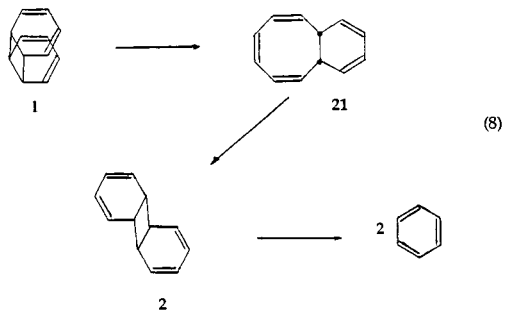
Hypostrophene displays only two PMR signals at δ 3.2 ppm (6H) and 6.1 ppm (4H) under common laboratory conditions. Ab initio molecular orbital calculations suggest that a similar symmetry-allowed 5,5′-suprafacial-sigmatropic shift may occur in dibenzene **1** in the *syn*-configuration and cannot occur in dibenzene **2** in the *anti*-configuration. It will be interesting to examine the PMR spectrum of dibenzene **1** for this possible degenerate symmetry-allowed shift (eq 7). Theoretically, such



(7)

a degenerative rearrangement might lead to the equivalency of all C−H's in dibenzene **1**.

Both *syn*-dibenzene **1** and *anti*-dibenzene **2** exhibit three sets of proton resonance under common laboratory conditions (Figure 3). The noticeable differences are that the cyclobutyl proton resonance in dibenzene **1** is downfield-shifted from that in **2** (from 3.26 to 3.60 ppm) and that the outer olefinic protons are upfield-shifted (from 5.64 to 5.40 ppm). The inner olefinic proton resonance remains at approximately the same position, 5.76 ppm for **1** and 5.70 ppm for **2**. Due to the thermal instability of dibenzene **1** with respect to its possible rearrangement to *cis*-bicyclo[6.4.0]-2,4,6,9,11-pentaene **21** (eq 8), we found no



(8)

experimental evidence to demonstrate the 5,5′-sigmatropic shift in dibenzene **1**. In the meantime, the synthetic complexity and our limited resources prevented us from investigating the possible existence of this rearrangement in an appropriate isotopic-labeled dibenzene **1**, as in the case of hypostrophene.[21] The resonances of olefinic protons in dibenzene **1** resemble closely those in caged dibenzene **7** (δ 5.30 and 5.73 ppm). The shifts are presumably due to the through-space interaction between two cyclohexadienyl rings. Similar shifts in PMR signals were also observed in related $2\pi_s + 2\pi_s$ *syn*- and *anti*-naphthalene: benzene cyclodimers **22** and **23**. Although we failed to isolate the metastable *anti*-dimer **23** in pure form, the experimental results indicated that the cyclobutyl protons in *syn*-dimer **22** are downfield-shifted from those in *anti*-dimer **23**, while the

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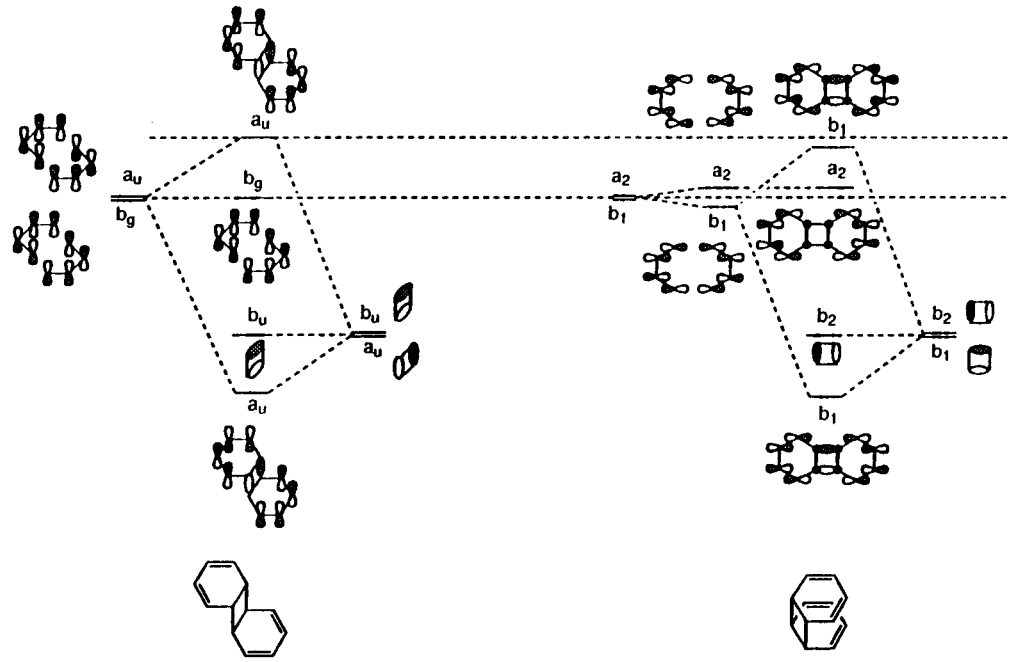


Figure 2. Schematic representation of orbital interaction in dibenzenes **1** and **2**.

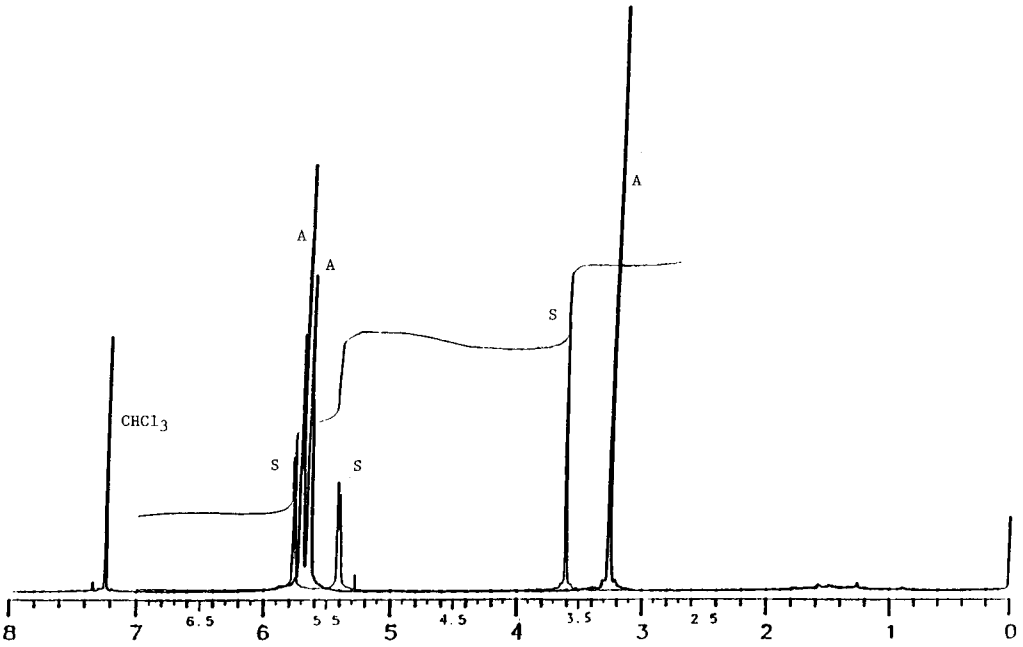


Figure 3. Comparative PMR spectra of dibenzenes **1** (peaks **S**) and **2** (peaks **A**), the signal at 7.24 ppm is due to chloroform.

corresponding outer olefinic protons are upfield-shifted (vide infra). Since the degenerate rearrangement is unlikely in dimer **7** due to the steric restrain of its caged structure, and in dimer **22** due to the barrier imposed by the benzene resonance in the naphthalene moiety of the system, we conclude that such a rearrangement cannot be demonstrated at present.

Thermolyses of 1 and Related *syn-o,o′*-Arene:Benzene Dimers 22 and 25. Although it has been reported that the thermolysis of dibenzene **1** yields two molecules of benzene,[2] the mechanistic aspects of this reaction have not been carefully investigated due to the limited supply of this compound. We were intrigued by our previous observation that *syn*-dibenzene **1** was more stable thermally than *anti*-dibenzene **2**, and the higher stability of **1** was the result of a large entropy of activation in the thermolysis ($\Delta H^{\ddagger} = 22.5 \pm 1.3$ kcal/mol, $\Delta S^{\ddagger} = -14.0 \pm 2.2$ eu).[2] On the basis of this observation, we proposed that thermolysis of *syn*-dibenzene **1** may proceed via *anti*-dibenzene **2** as an intermediate: the rearrangement of **1** via a disrotatory ring opening to pentaene **21** followed by its known rearrangement to *anti*-dibenzene **2** (eq 8).[2] This conclusion, although made on the basis of faulty data likely derived from an impure sample, will be discussed in a later section. Since we were also interested in the chemistry of *p,p′*-dibenzene **3**, we had already synthesized the *p,p′*-dimer of naphthalene:benzene **8**[12] and a *p,p′*-dimer of anthracene:benzene **9**.[13] These dimers underwent a smooth Cope rearrangement to the respective *syn-o,o′*-arene:benzene dimer **22** and **25** at a lower temperature than their thermolyses, and these *syn*-dimers were isolated and characterized.[12,13] Since all *syn-o,o′*-arene:benzene dimers may undergo thermolysis via a similar mechanism, we initiated a dual probe on the mechanism of the thermolysis of dibenzene **1**, that is, parallel to the development of a more

Table 2. Activation Parameters for the Thermolysis of *syn-o,o′*-Dibenzene **1**

experiment	E_a (kcal/mol)	$\Delta H^{\ddagger}$ (kcal/mol)	$\Delta S^{\ddagger}$ (eu)	$\Delta G^{\ddagger}$ (kcal/mol)
1	27.8 ± 0.6	27.2 ± 0.6	0.2 ± 1.6	27.2 ± 1.1
2	27.0 ± 0.5	26.4 ± 0.5	−2.0 ± 1.4	27.0 ± 0.9
average	27.4 ± 0.6	26.8 ± 0.6	−0.9 ± 1.6	27.1 ± 1.1

Table 3. Activation Parameters for the Thermolyses of 4nπ-Arene:Benzene Dimers

dimer	E_a (kcal/mol)	$\Delta H^{\ddagger}$ (kcal/mol)	$\Delta S^{\ddagger}$ (eu)	$\Delta G^{\ddagger}$ (kcal/mol)	ref
22	28.4	27.8	−1.8	28.3	4
25	28.2	27.5	−2.0	28.2	4
1	27.4	26.8	−0.9	27.1	−
2	24.7	24.1	−2.2	24.8	1a
7	38.2	37.8	2.9	−	8
29	33.8	33.1	16.3	27.4	4
30	23.0	22.4	1.7	21.9	4

efficient synthesis of **1** of high purity in order to reexamine its kinetics of thermolysis. We also made a comparative thermolysis study of the analogous *syn-o,o′*-arene:benzene dimers **22** and **25**.

After we had achieved an improved synthesis of pure *syn*-dibenzene **1**, we reinvestigated its thermolysis in duplicate runs in cyclohexane-d_{12}, both at six different temperatures ranging from 60 to 100 °C; progress of the reaction was monitored by PMR spectroscopy. In both runs first-order kinetic behavior was observed. We found that dimer **1** was kinetically more stable than dimer **2**, but the stability was the result of a higher activation enthalpy in the thermolysis. The activation parameters, obtained from transition state theory, are shown in Table 2. The activation enthalpy of this thermolysis is 26.8 ± 0.6 kcal/mol, and the reaction proceeds with little or no activation entropy ($\Delta S^{\ddagger} = 0.9 \pm 0.9$ eu) as is usually observed in highly exoergic processes. Our results clearly indicate that *syn-o,o′*-dibenzene **1** is kinetically more stable than its *anti*-isomer **2** ($\Delta H^{\ddagger} = 24.7 \pm 1.0$ kcal/mol, $\Delta S^{\ddagger} = -2.23 \pm 2.29$ eu), despite the possibility that dimer **1** may be thermodynamically less stable than dimer **2** because of unfavorable overlapping interactions of the cyclohexadiene rings.

It was suggested that the stability of **1** may be related to its lower HOMO level.[7] However, this cannot explain why **7** is more stable than **2** even though its HOMO level lies much higher in energy than that of **2** ($\Delta E = 0.25$ eV). Therefore, other factors must be more important in this consideration.

The activation parameters of the thermolyses of $2\pi_s + 2\pi_s$ and other 4nπ arene- benzene dimers **1**, **2**, **7**, **22**, **25**, **29**, and **30** are listed in Table 3. The results indicate that, within experimental error, the thermolyses of all three *syn-o,o′*-arene:benzene dimers, **1**, **22**, and **25**, proceed with similar activation parameters. Dimer **1** is thermally more stable than dimer **2**, while dimer **7** is much more stable than both dimer **1** and **2**. It has been suggested that dimer **7** undergoes thermolysis via a stepwise mechanism and a biradical intermediate.[10] The formation of the biradical intermediate involves the cleavage of an allylic bond with the release of the strain energy of a cyclobutane ring of approximately 26.2 kcal/mol.[22] The high value of the heat of activation (37.8 kcal/mol) is in agreement with this suggestion. Alternatively, Doering and his collaborators postulated a forbidden-concerted-[$2\pi_s + 2\pi_a$] cycloreversion mechanism for the thermolysis of cyclobutanes, including **7**, on the basis of transition-state resonance energies higher than the calculated heats of formation of biradical intermediates in the thermolysis of a series of cyclobutanes.[23] If the thermolyses of **1**, **2**, and **7** all proceed via the same mechanistic pathway, we must account for the large difference in the heat of activation between **1** and **7**. Alternatively, the thermolysis of **1** may proceed via a pathway different from those of both **2** and **7**, in which case we must account for the anomaly on the thermolytic pathway of **1**.

Birney and Berson found that there is a relationship between kinetic and thermodynamic stabilities in cycloreversion reactions.[24] Grimme and co-workers noticed a linear dependence on the heat of activation with the resonance energy gained in the thermolysis of $4\pi_s + 2\pi_s$ arene:benzene dimers, for example, **26**−**28**.[25] A plot of the heat of activation of thermolysis of arene:benzene adducts **26**−**28** versus the resonance energy gained in the process yields a slope of −0.43. We have noticed a similar structural dependence on the heat of activation of the thermolyses of $4\pi_s + 4\pi_s$ arene:benzene dimers, **29**−**30** (Table 3),[4] namely that the heat of activation decreases as the heat of reaction becomes more favorable. Although the $4\pi_s + 2\pi_s$ adducts tabulated by Grimme may undergo a symmetry-allowed cycloreversion to their components, the thermolyses of 4n-adducts are expected to proceed via a stepwise dissociation. It is reasonable to assume that the thermolyses of a related series of $2\pi_s + 2\pi_s$ arene:benzene dimers may bear a similar type of relationship between heats of activation and the resonance energies of arene products, anthracene, naphthalene, or benzene, gained in the thermolyses.

Since the resonance energy gained in the arene moiety in the thermolyses of [$2\pi_s + 2\pi_s$] arene:benzene dimers **1**, **22**, and **25** are 36, 26, and 22 kcal/mol respectively, the lack of appreciable change in their heats of activation clearly indicates that their thermolyses proceed via a different mechanistic pathway from other arene:benzene dimers. Two possible mechanisms are proposed for the thermolysis of dimer **1**.

Previously, it has been suggested that **1** may rearrange thermally to **2** via a concerted disrotary ring-opening to *cis*-bicyclo[6.4.0]dodeca-2,4,6,9,11-pentaene **21** on the basis of a highly negative activation entropy in the thermolysis of **1** (eq 8).[2] However, our efforts to repeat this kinetic measurement were not successful. In the meantime, King and Durnell in our laboratory have detected a transient minor product in the thermolyses of related *syn-o,o′*-arene:benzene dimers **22** and **25**.[9,10] The result is illustrated by PMR spectroscopic analyses of the thermolysis of dimer **22** in Figures 4 and 5. A minor product **23** was detected which exhibits peaks in the PMR attributable to the corresponding *anti*-isomer. Figure 4 is the PMR of pure dimer **22**, and Figure 5 is the PMR of dimer **22** after being heated at 40 °C for 21 days in cyclohexane-d_{12}. Several new peaks appeared, particularly those at the higher field. These peaks disappeared either by heating at a higher temperature or for a longer period of time. By comparing the PMR spectrum of *syn*-dibenzene **1** to that of *anti*-dibenzene **2** in Figure 2, vide supra, we note that the cyclobutyl protons in the *anti*-isomer **2** at 3.26 ppm are upfield-shifted from those in **1** at 3.60 ppm by approximately 0.3 ppm. In addition, the olefinic protons are spaced further apart in **1** at 5.40 and 5.78 ppm than in **2** at 5.64 and 5.70 ppm. The minor transient product

(22) Benson, S. W. *Thermochemical Kinetics*, 2nd ed.; Wiley-Interscience: New York, 1976; pp 28 and 63.

(23) Doering, W. v. E.; Roth, W. R.; Breuckmann, R.; Figge, L.; Lenmartz, H.-W.; Fessner, W.-D.; Prinzbach, H. *Chem. Ber.* **1988**, *121*, 1−9.

(24) Birney, D. M.; Berson, J. A. *Tetrahedron* **1985**, *42*, 1561−1570.

(25) Bertsch, A.; Grimme, W.; Reinhardt, G. *Angew. Chem., Int. Ed. Engl.* **1986**, 377−378.

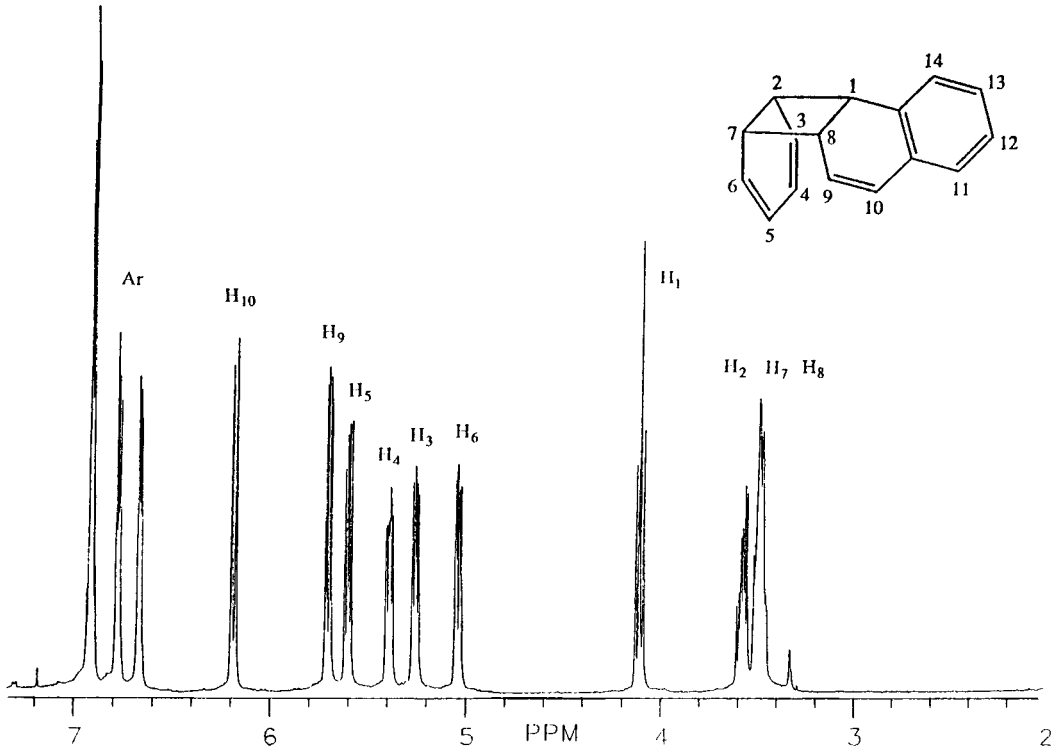
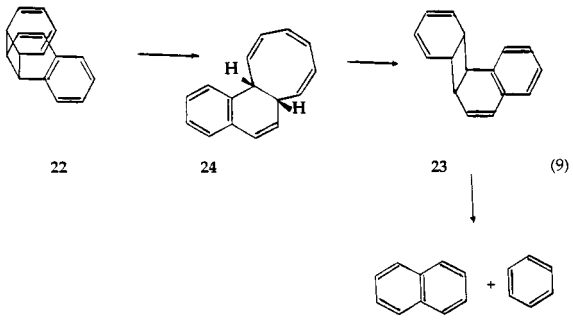
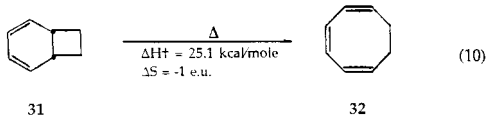


Figure 4. PMR spectrum of *syn-o,o′*-naphthalene:benzene dimer **22**.

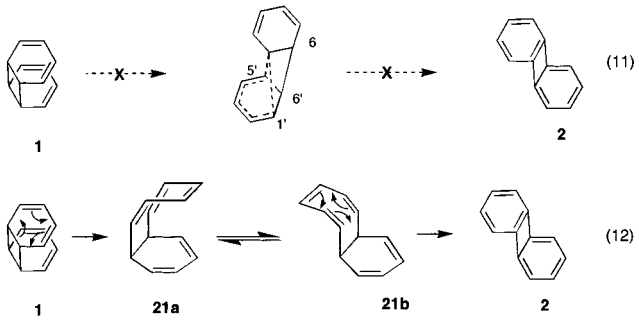
formed in this reaction displays the cyclobutyl signals at higher fields, approximately 0.3 ppm higher than those in dimer **22**, no olefinic signals in the higher-field region from 5 to 5.5 ppm, and the olefinic signals are closer together in the 5.6−5.8 ppm region. These changes are closely analogous to the changes from *syn*-dibenzene **1** to *anti*-dibenzene **2**. We thus assigned the structure of this minor transient product to *anti-o,o′*-naphthalene:benzene dimer **23** (eq 9). However, we were unable to increase



the yield of **23** formed in the thermolysis (the data given represents the optimized effort), and the amount of **23** formed (8%) in the thermolysis was too small for its isolation and additional characterization. Since such a rearrangement is not possible in dimer **7** due to its cage-like structure, this observation provides a rational basis for the difference between the thermolytic behavior of the rigid cage-like dimer **7** and those of the "more flexible" dimers **1**, **22**, and **25**. In addition, this explanation is also in agreement with the kinetics of the thermal rearrangement of bicyclo[4.2.0]octa-2,4-diene **31** to cycloocta-1,3,5-triene **32** via an analogous disrotatory ring opening, which was investigated by Huisgen, Winstein, and their co-workers (eq 10).[26,27] They found the enthalpy of activation of this



rearrangement to be 25.5 and 25.1 kcal/mol, with a small entropy of activation of −2 and −1 eu, respectively. These values are quite close to the activation parameters of the thermolyses of *syn-o,o′*-arene:benzene dimers given in Table 3. It is possible that the similarity of the activation parameters between the thermolysis of *syn-o,o′*-dimers (**1**, **22**, and **25**) and the rearrangement of the bicyclooctadiene to cyclooctatriene may be coincidental. However, this observation, coupled with the detection of a transient intermediate in the thermolyses of **22** and **25** and the marked stability of **7** (which cannot undergo disrotatory ring opening because of its cagelike structure), strongly suggests this reaction pathway for the thermolysis of dibenzene **1**. The thermolysis of dibenzene **1**, therefore, may proceed through dibenzene **2** prior to its dissociation to two benzenes, as is shown in eq 8, above. In this mechanism, the disrotatory opening of the cyclobutane ring to *cis*-pentaene **21a** is the rate-determining step (eq 12). Pentaene **21a** undergoes a



conformational change to pentaene **21b** which is known to undergo a disrotary ring closure with an activation energy of

(26) Huisgen, R.; Boche, G.; Dahmen, A.; Fechtl. W. *Tetrahedron Lett.* **1968**, 5215−5219.

(27) Glass, D. S.; Watthey, J. W. H.; Winstein, S. *Tetrahedron Lett.* **1965**, 377.

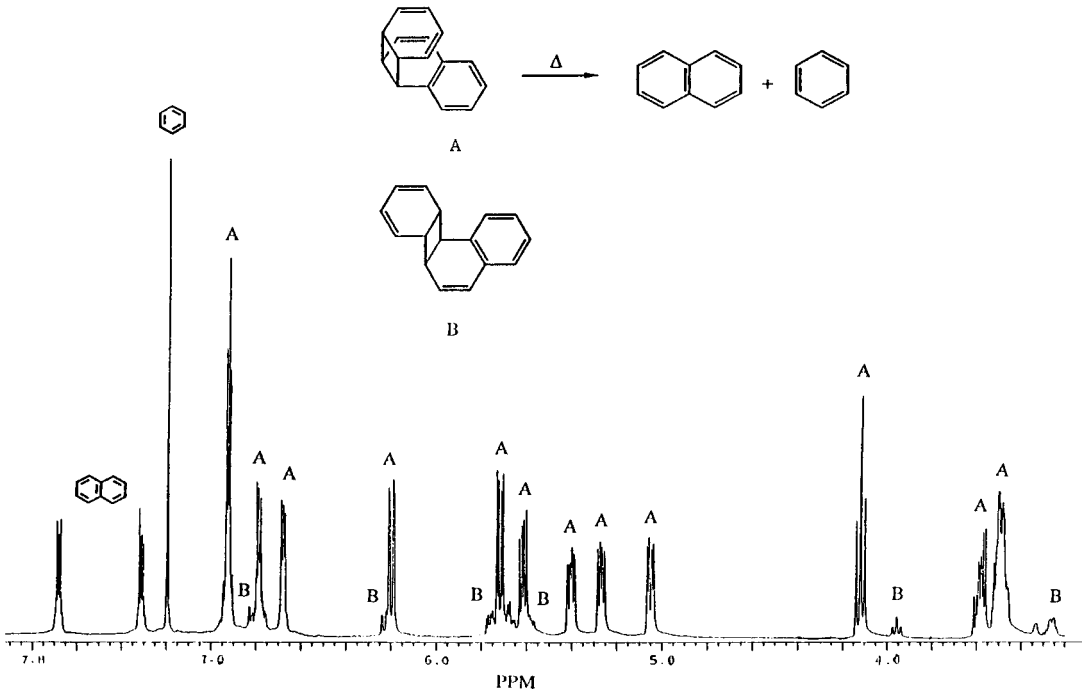
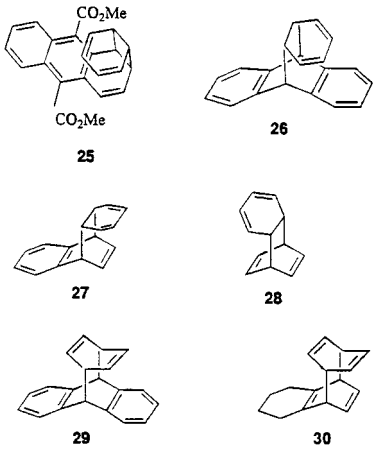


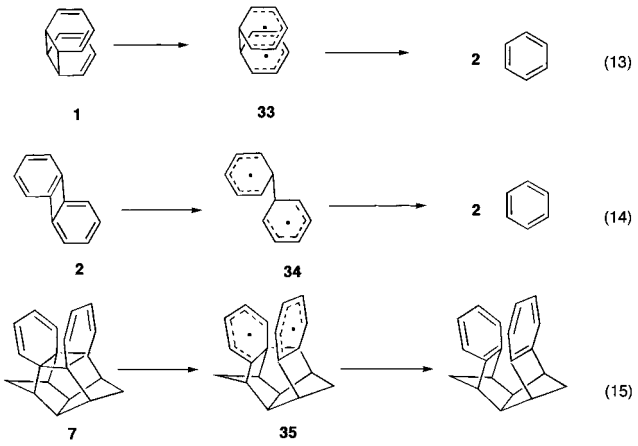
Figure 5. PMR spectrum of dimer **22** after being heated at 40 °C for 21 days, peaks marked with B are attributed to dimer **23**.

23.3 kcal/mol to **2**,[2d] and **2** is known to dissociate to two molecules of benzene much faster than **1** under the same experimental conditions. Since the thermal dissociation of *anti*-dimer **23** is expected to be slower than that of dimer **2**, the failure to observe intermediates **2** and **21** in the thermolysis of dimer **1** is not unexpected.



Alternatively, *syn*-dibenzene **1** may also rearrange directly to *anti*-dimer **2** via a symmetry-allowed 1,5-sigmatropic shift. For other *syn-o,o′*-dimers **22** and **25**, their rearrangements to the corresponding *anti*-isomers may be achieved by a similar 1,5-sigmatropic shift of the cyclohexadienyl ring. However, this direct pathway is judged to be not preferred on the theoretical ground, vide infra.

A Theoretical Treatment of the Chemistry of Dibenzenes. If the rigid dimer **7** dissociates into its monomeric form via a stepwise mechanism and a biradical intermediate **33**, and the thermolyses of dimer **1** and **2** proceed via different reaction pathways from that of dimer **7**, an important experimental observation will have to be accounted for, that is, the substantial difference between kinetic parameters in the thermolysis of **7** from its flexible analogues **1** and **2** (eqs 13, 14, and 15).



There is considerable interest in the thermolysis of cyclobutanes to two molecules of ethylene, a subject explored by Doering and his collaborators[23] and recently reviewed by Berson.[24,28] The discussion concerns whether the biradical formed in the stepwise cleavage of cyclobutanes represents the transition state or an intermediate on the potential surface in the thermolysis (Figure 6). Zewail and co-workers detected a transient by using femto-second laser spectroscopy coupled with mass spectrometry in a molecular beam.[29] Their observations provide experimental evidence for the existence of tetramethylene biradical and its tetramethyl derivative as intermediates in chemical reactions. Therefore, a biradical in thermolysis of a cyclobutane is in an energy well following the transition state.

To contribute to the discussion on the mechanism of the thermolyses of **1** and **2** to benzene we carried out quantum mechanical calculations using the Gaussian 94 and 98 programs.[17] The ranges of variation of energy values using different sets in calculations have been noted previously by Shriver and Gerson.[30] Geometry optimizations were carried out using density

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(29) Pederson, S.; Herek, J. L.; Zewail, A. H. *Science* **1994**, *266*, 1359−1364.

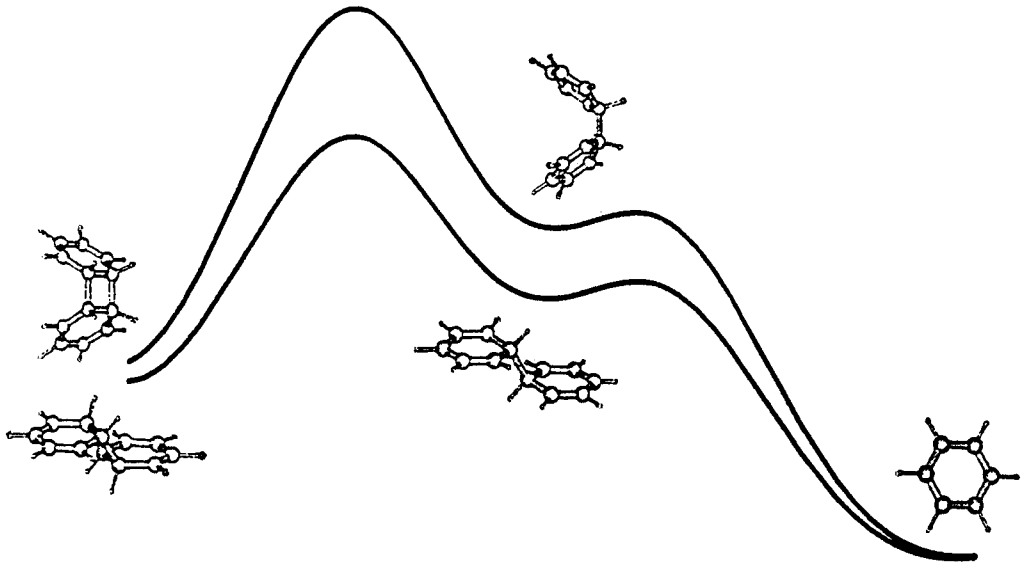

Figure 6. Schematic representation of thermolyses of dibenzenes **1** and **2** via biradical intermediates.

Table 4. Calculated Enthalpies of Formation of *o*,*o*′-Dibenzenes and Related Molecules Relative to Two Molecules of Benzene (in kcal/mol)

method	**1**	**33**	**2**	**34**	**28**	reference
Gaussian 86 or 88 with RHF 3-21G set	60.3	−	56.0	−	46.0	29
Gaussian 86 or 88 with RHF 6-31G* set	61.0	−	57.5	−	54.3	29
Gaussian 94 or 98 with UB3LYP/6-31G* set	60.8	78.9	57.4	72.8	54.9	this work

function theory (DFT)[20] with the (U)B3LYP/6-31G* functional[31] for both dibenzenes and the biradical intermediates **34** and **35**. At this level of theory, the energies of **1** and **2** are 60.8 and 57.4 kcal/mol, respectively higher than two molecules of benzene, in good agreement with energy values in the literature.[30] These values are listed in Table 4. We note that the values for dibenzenes from different laboratories are in general agreement with each other. The energy difference between **1** and biradical **34** is 18.1 kcal/mol, which is higher than that between **2** and biradical **35**, 15.4 kcal/mol. If the stability of biradicals were involved in determining the rate of thermolyses of flexible dibenzenes, this could offer a qualitative explanation of the higher $\Delta H^{\ddagger}$ for thermolysis of **1** than that of **2**.

Accordingly, we also performed ab initio calculations on the activation energies for the formation of biradicals **34** and **35** from dibenzenes **1** and **2** (Figure 6) as well as the pericyclic rearrangement of **1** to **2** via the pentaene intermediates **21a** and **21b** (eq 12, vide supra). We explore the activation energies of these pathways using Gaussian 94[17] with the (U)B3LYP/6-31G* level of DFT.[20] The values were 39.3 kcal/mol for the formation of **34** from 1 and 41.3 kcal/mol for the formation of **35** from **2**. These values far exceed the experimental values of 27.4 kcal/mol and 24.7 kcal/mol for the thermolyses of dimers **1** and **2**, and indicate clearly that biradicals do not represent the transition states in the thermolyses of flexible dimers **1** and **2**. However, the value for the *syn*-biradical **34** formation from **1** of 39.3 kcal/mol is in reasonable agreement with the experimental value for the thermolysis of rigid dimer **7**. Note that dimer **7** cannot undergo disrotatory ring opening to form an octatriene as **1** and **2** and must dissociate by a stepwise mechanism and a biradical intermediate **33**, 38.2 kcal/mol. Dibenzene **1** may also rearrange directly to dibenzene **2** via a suprafacial 1,5-sigmatropic shift in which the 1,1′-σ-bond migrates to the 5′-position by a 60° rotation of the 6,6′-bond (eq 11). The distance between the migrating 1-carbon to both 1′-C origin and the 5′-C terminus is estimated to be over 2.9 Å at the transition state, which is too far for an appreciable stablization of a 1,5-sigmatropic shift.[32] No meaningful results were obtained in our calculations via this pathway, and this direct pathway is thus not preferred.

Since the thermolysis of *syn*-2π + 2π naphthalene:benzene dimer **22** may proceed via the tricyclic-**24** and *anti*-isomer **23** as the intermediate (eq 9), a similar process may occur in the thermolysis of dibenzenes **1** and **2** via a pentaene intermediate **21**. The cyclooctatriene moiety of **21** may exist in either the *cis*- or the *trans*-conformations, **21a** and **21b**, and we propose that dibenzene **1** may open to pentaene **21a** (equation 12, first step). We thus carried out ab initio calculations on the thermal rearrangments of dibenzene **1** to pentaene **21a**, the relative stabilities between **21a** and **21b**, and the energy barrier of conformational changes between **21a** and **21b**. The results (Figure 7) indicate that **21a** is destablized by 2.23 kcal/mol from **21b** and the activation energy barrier for conformational change of **21a** to **21b** is 5.13 kcal/mol. The calculations also show that the barrier of cyclization of pentaene **21b** to **2** is 22.09 kcal/mol which is in good agreement with the experimental value of 23.3 kcal/mol, vide supra.[2] The experimental value for the thermolysis of dibenzene **1** is 27.2 kcal/mol. The theoretical calculation, $\Delta H = 27.95$ kcal/mol, thus supports that dibenzene **1** may rearrange via pentaene **21** to dibenzene **2**, which dissociates to two molecules of benzene under experimental conditions.

At this time, we conclude that the mechanism of thermolysis of **2** plays a key role in the understanding of the chemistry of 4n-dimers of benzene. We are now exploring the possibility that dibenzene **2** may thermolyze to two benzenes via a concerted-[2π_s + 2π_a] cycloreversion[23] as well as via other reaction pathways. These symmetry-allowed pathways might have an activation energy barrier in better agreement with our experimental results.

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(32) Wiest, O.; Houk, K. N. *Top. Curr. Chem.* **1996**, *183*, 1−22; Kless, A.; Nendel, M.; Wilsey, S.; Houk, K. N. *J. Am. Chem. Soc.* **1999**, *121*, 4523−4524.

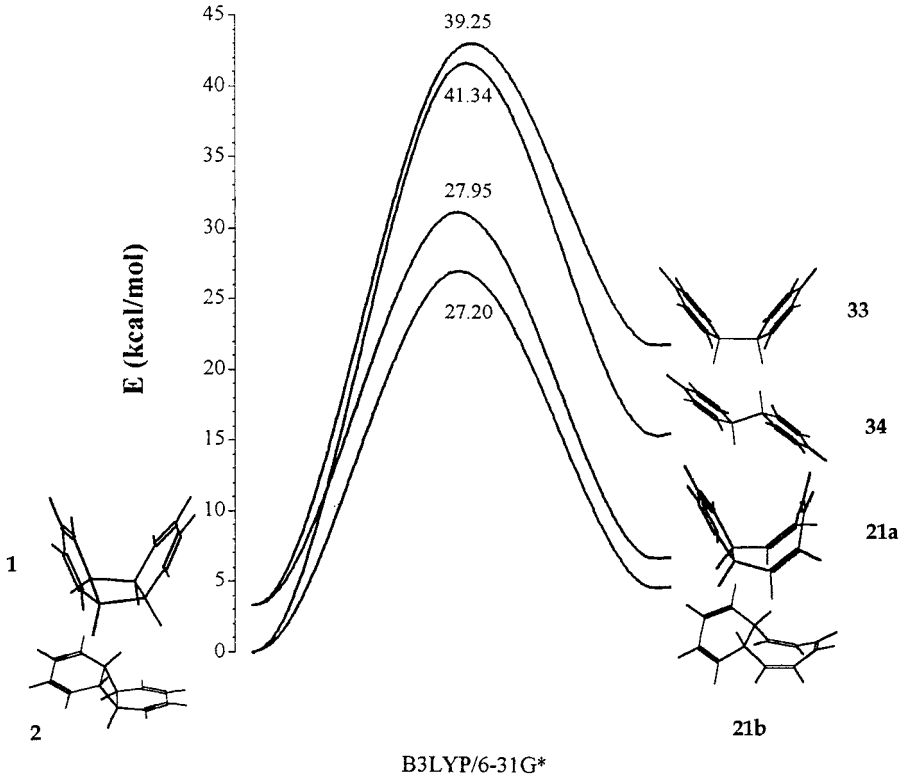

Figure 7. Various reaction pathways calculated at the (U)B3LYP/6-31G* level.

Adiabatic Photodecomposition of Dibenzenes.[33] Dewar benzenes and $2\pi_s + 2\pi_s$ dimers of benzene are among the most energetic derivatives of benzene. Both types of compounds will yield over 80 kcal/mol of energy in the form of enthalpy and enthalpy of activation.[34] In a previous communication, we demonstrated that thermolysis of dibenzene **2**, under optimal sensitized conditions, yields an excited polynuclear aromatic sensitizer in extremely low yield.[1a] Since energetic arene precursors, in the form of either dimers or Dewar isomers, will undergo adiabatic photochemical reactions,[35] the photochemistry of dibenzenes **1** and **2** was thus investigated. It has been reported that the photolysis of dibenzene **2** yields two molecules of benzene, but the nature of their excited state is not known.[2a] Using light at 345 nm at the red-edge of dibenzene's absorption (equivalent to 85 kcal/einstein) where benzene has no detectable absorption, there is 148 kcal/mol of enthalpy of reaction available for the photochemical dissociation of dibenzene **1**. Since the energy of the first excited state of benzene is 110 kcal/mol and the adiabatic photochemical reaction of **1** to one molecule each of excited- and ground-state benzene is a symmetry-allowed process, we expected this reaction to occur efficiently for both dibenzenes **1** and **2**. We found that the only emission observed in the irradiation of dibenzenes at 300−345 nm is benzene fluorescence (Figure 1S).[33] This was confirmed by the absence of emission from a benzene sample of the same concentration and at the same wavelength, as well as by the excitation spectrum of benzene fluorescence from the irradiation of **1**, which possesses a peak shape identical to the UV absorption of **1** (Figure 2S). The quantum efficiency of photolysis of **1** and **2** ($\phi_{[-cpd]}$) was determined with the aid of a potassium ferrioxalate actinometer.[36] The quantum efficiency of the formation of excited benzene from **1** and **2** ($\phi_{[benz^*]}$), 0.41 and 0.32, respectively, was determined by comparing the integrated emission spectrum with that of benzene (Table 5). Adiabatic photochemical reactions generally occur with light more energetic than that needed for the excitation of the product.[34] Contributions by Turro and co-workers demonstrated the "red-light to blue-light uphill conversions" in the generation of n,π^* excited states of acetone from the direct or sensitized photolysis of tetramethyl-dioxetane,[37] but such upconversions have a propensity to occur in the triplet mani-fold. Our finding in the detection of benzene fluorescence, the formation of excited benzene in its singlet excited state in the photolysis of *o,o′*-dibenzenes, demonstrates that such upconversions can also occur efficiently in the singlet manifold.

Table 5. A Summary on Photochemical Decompositions of *o,o′*-Dibenzenes

	anti-o,o′-dibenzene	*syn-o,o′*-dibenzene
$\phi_{[-cpd]}$	1.04 ± 0.09	1.01 ± 0.14
$\phi_{[benz^*]}$	0.32 ± 0.03	0.41 ± 0.03

Experimental Methods.

General Preparative Irradiation Procedure. All preparative irradiations were performed with a Hanovia medium-pressure mercury lamp (450 W) irradiated through a Vycor, Pyrex, or Uranyl glass filter which was placed in a quartz immersion well cooled with chilled water. The immersion well was inserted in a Pyrex jacket equipped with a water-cooled condenser and an inert gas (nitrogen or argon) dispersion inlet tube. The reaction solution was placed in the outer jacket and deaerated for at least 20 min before the lamp was activated. During the irradiation, a gentle stream of inert gas was passed through the

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solution to provide sufficient agitation. The reactions were followed by PMR until the maximum amount of desired products was accumulated.

Synthesis of Diol 10 from Dibromodiol 13 (Scheme 1). In a 50-mL round-bottom flask a solution of dibromodiol **13** (16.0 g, 5.84×10^{-2} mol) and a catalytic amount of *p*-toluenesulfonic acid monohydrate (16.9 mg) in trimethylorthoformate (20 mL) was stirred at room temperature for 4 h. The solvent was then removed under reduced pressure, and the oily residue was dissolved in 100 mL of diethyl ether and transferred to a 250-mL separatory funnel. The ether solution was washed with saturated aqueous sodium carbonate solution (2×100 mL), water (100 mL), and brine (100 mL). The aqueous layers were further extracted twice with diethyl ether (2×100 mL). The combined organic layers were dried over anhydrous magnesium sulfate, the solution filtered, and the solvent evaporated under reduced pressure. The resulting colorless crystals were dried overnight under vacuum (0.05 mmHg) to yield 18.3 g (99%) of orthoformate of **13**. PMR indicated that the reaction affords two stereoisomers, **a** and **b**. The ratio between these two isomers had been shown by further investigation to be dependent on the reaction time:

time (hours)	4	6	14
ratio (**a:b**)	3.3:1.0	2.0:1.0	1.3:1.0

The major isomer exhibits PMR ($CDCl_3$) δ 5.77 (s, 1H), 4.45 (q, 1H), 4.38 (m, 1H), 4.36 (q, 1H), 4.19 (q, 1H), 3.34 (s, 3H), 2.79 (dt, 1H), 2.71 (m, 1H), 2.37 (dt, 1H), 2.25 (m, 1H). The characteristic signals of the minor isomer in PMR ($CDCl_3$) are δ 5.68 (s, 1H) and 3.42 (s, 3H). Separation of the two isomers was not attempted. The product was used in the next reaction without further purification.

The dibromocyclohexanediol orthoformate was then converted to the cyclohexadiendiol by dehydrobromination. A solution of 60.6 g (0.192 mol) of the orthoformate of **13** in 400 mL of benzene was stirred in a 1000-mL round-bottom flask. DBU (61.0 g, 0.401 mol) was added to this in one portion. The solution was then stirred and refluxed under nitrogen for 6 h. During the reaction a white solid (DBU hydrobromide) precipitated from the solution. Upon completion of the reaction, 300 mL of 5% potassium hydroxide was added to dissolve the precipitate, and the reaction solution was cooled to room temperature and transferred to a 1000-mL separatory funnel. After discarding the aqueous phase, the organic phase was washed once again with 300 mL of 5% potassium hydroxide, once with 400 mL of water, and once with 400 mL of brine. The water phases were back-extracted with benzene (2×100 mL). The combined organic phases were then dried over anhydrous magnesium sulfate, filtered, and evaporated under reduced pressure to afford a yellow liquid which was distilled under reduced pressure, bp 61−62 °C (0.45 mmHg) to yield diene orthoformate as a colorless liquid (14.7 g, 49%).

Diene orthoformate (6.43 g, 4.17×10^{-2} mol, in 750 mL of dry benzene) obtained in the previous experiment was added to the photoreaction apparatus. The solution was deaerated with argon for 30 min and cooled in a constant-temperature bath to 3−5 °C. The solution was then irradiated with a 450-W medium-pressure mercury lamp through a Vycor filter for 20 h. The reaction progress was monitored by PMR. When more than 80% of the diene had been consumed, the solvent was evaporated under reduced pressure to give a brown liquid. Isolation of the [4 + 4] adduct from the reaction mixture was not attempted. Instead, the crude product was used in the conversion of diol **10**.

In a 250-mL round-bottom flask, the crude reaction mixture obtained above was dissolved in 50 mL of tetrahydrofuran; to this was added 50 mL of 0.2 N hydrochloric acid. The solution was stirred at room temperature for 3 h, and then a concentrated solution of potassium hydroxide was added dropwise until all of the acid had been neutralized. The solution was transferred into a 1000-mL separatory funnel, and 250 mL of 0.2 N potassium hydroxide was added. This was then extracted with ethyl acetate (3×150 mL), and the aqueous phases were discarded. The combined organic phases were washed once with 0.2 N potassium hydroxide (250 mL), once with water (500 mL), and once with brine (250 mL). After drying over anhydrous sodium carbonate, the solution was filtered and the solvent removed under reduced pressure to give a deep red liquid (2.1 g) which was chromatographed on silica gel (70−230 mesh, active III), eluting with dichloromethane−ethyl acetate solvent mixture. The enriched [4 + 4]-diol **10** was collected by elution with 10% ethyl acetate, and it was further purified via recrystallization from dichloromethane−hexane. Colorless crystals (**10**) were obtained (0.082 g, 1.0% based on the diene orthoformate): mp 124−125 °C. PMR ($CDCl_3$) δ 6.41 (dd, 2H, −CH═CH−, $J_{AA'} = 4.74$, $J_{AX} = 3.57$), 6.27 (dd, 2H, −CH═CH−, $J_{AA'} = 4.81$, $J_{AX} = 3.38$), 5.98 (dd, 2H, −CH═CH−, $J_{AA'} = 5.19$, $J_{AX} = 3.31$), 4.56 [br d, 2H, −CH(OR)−CH(OR)−, $J = 4.84$], 3.21 (m, 2H, −C═C−CH−C═C−), 3.06 [m, 2H, −C═C−CH−C(OR)−], 2.27 (br d, 2H, −OH, $J = 5.73$); PMR (CD_3OD) δ 6.37 (dd, 2H, −CH═CH−, $J_{AA'} = 4.77$, $J_{AX} = 3.58$), 6.20 (dd, 2H, −CH═CH−, $J_{AA'} = 4.84$, $J_{AX} = 3.38$), 5.86 (dd, 2H, −CH═CH−, $J_{AA'} = 5.31$, $J_{AX} = 3.23$), 4.52 [s, 2H, −CH(OR)−CH(OR)−], 3.16 (m, 2H, −C═C−CH−C═C−), 2.98 [m, 2H, −C═C−CH−C(OR)−]; CMR ($CDCl_3$) δ 138.3, 136.1, 133.9, 69.5, 51.6, 39.3.

Instead of chromatography, a simplified procedure was developed later to purify [4 + 4]-diol **10**. This procedure involved the following steps. After the reaction solution was neutralized, the solvent was concentrated under reduced pressure to remove most of the tetrahydrofuran. The residue was then transferred to a 1000-mL separatory funnel and extracted with chloroform (2×100 mL). The organic phases were combined and extracted with 20% silver nitrate twice (2×50 mL). To the combined aqueous solution was added 400 mL of concentrated ammonium hydroxide (29.4%). The resulting dark solution was extracted with chloroform (2×150 mL). The organic phase was then washed with water (200 mL), dried over anhydrous magnesium sulfate, and filtered, and the solvent was evaporated. A yellow solid resulted which was recrystallized from dichloromethane-hexane to afford colorless crystals (**10**). With this procedure 89 mg of diol **10** (0.63% based on diene used) was obtained starting from 11.4 g diene orthoformate used in the photoaddition.

Synthesis of Phenylacetal of Diol 10 and 10PA. Diol **10** (30 mg, 0.158 mmol) was dissolved in 0.5 mL (3.33 mmol) of benzaldehyde dimethyl acetal and 0.5 mL of $CHCl_3$. To this solution 3 mg of *p*-toluensulfonic acid was added. The mixture was stirred at room temperature for 3 h, after which the reaction mixture was transferred in 50 mL of ether to a separatory funnel. The organic layer was washed twice with 0.1 M KOH, once with distilled water, and once with brine. The aqueous layers were back-washed with 50 mL of ether, and the organic layers were combined, dried over sodium sulfate, filtered, and concentrated under reduced pressure. The crude product, containing cyclic acetal **10PA**, benzaldehyde, and benzaldehyde dimethyl acetal, was chromatographed with centrifugal assistance on silica gel, on a Chromatotron with hexanes−ethyl acetate gradient elution. The cyclic phenyl acetal **10PA** eluted with 19:1 hexane/ethyl acetate, with a yield of 35 mg (80%). The producet was recrystallized from dichloromethane/hexane to give white needles, mp. 143−143.5 °C.

IR (CCl_4) 3044, 2948, 2919, 2830 (w), 1457, 1401, 1310, 1216, 1088, 1059 (s), 1026, 1018; mass spectrum (CI, isobutane) 279, 200, 173, 155, 154, 107, 95, 94, 91, 79, 78, 67. HRMS: calcd for $C_{19}H_{19}O_2$: 279.1385. Found: 279.1306. PMR ($CDCl_3$) 7.43 (m, 2H, ArH), 7.29 (m, 3H, ArH), 6.52 (br s, 2H, −CH═CH−), 6.32 (br s, 2H,−CH═CH−), 6.00 (br s, 2H, −CH═CH−), 5.64 (s, 1H, acetal H), 4.99 (br s, SH, −CH(OR)−CH(OR)−), 3.16 (br s, 4H, bridgehead H); CMR (CD_2Cl_2) 139.3, 137.6, 134.4, 133.7, 129.9, 128.6, 128.0, 104.6, 79.8, 48.9, 39.7; UV (hexanes) 266 (66), 262 (110), 256 (130), 250 (120), 207 (4900). Analysis: calcd for $C_{19}H_{18}O_2$: C, 81.98; H, 6.52. Found: C, 81.52; H, 6.60.

Photocyclization of Acetal 10PA. Phenylacetal **PA** (35 mg, 0.126 mmol) and xanthone (13.3 mg, 0.075 mmol) were dissolved in 2 mL of CH_2Cl_2 in a 10-mm NMR tube and deaerated for 10 min with argon. The solution was immersed in a constant-temperature bath at −17 °C and irradiated through a Pyrex filter with a 450-W Hanovia medium-pressure Hg lamp for 2 h. During this time the temperature of the bath rose to −12 °C. The reaction mixture was concentrated under reduced pressure and chromatographed on silica with gradient elution with hexanes−ethyl acetate solvent mixture. Unreacted triene **10PA** (5 mg) eluted with 2% ethyl acetate, followed by cage acetal **12PA** (25 mg, 71%) and xanthone (13 mg) which eluted with 5% ethyl acetate. The

product acetal was recrystallized from CH_2Cl_2/hexane, to give white needles, mp 173−174 °C.

IR (CCl_4) 3028, 2964, 2892, 1458, 1401, 1306, 1216, 1088, 1063, 1027, 1007, 983; mass spectrum (Cl, isobutane) 279 (2.75), 277 (2.98), 201 (3.48), 200 (4.51), 172 (15.4), 171 (10.8), 155 (28.6), 154 (46.4), 143 (11.3),128 (10.9), 107 (48.8), 105 (32.4), 96 (11.1), 95 (100), 94 (50.8), 91 (18.1), 79 (20.2), 78 (51.8). HRMS (CI, isobutane) calcd for $C_{19}H_{19}O_2$: 279.1385. Found: 279.1348. PMR ($CDCl_3$) 7.32−7.35 (m, 5H, ArH), 6.30 (m, 2H, $J_{AA'} = 9.6$, $J_{AX} = 7.2$, $J_{AX'} = 0.3$, −CH═CH−), 5.60 (s, 1H, acetal H) 4.33 (br s, 2H, −CH(OR)−CH(OR)−), 3.49 (m, 4H, bridgehead H), 3.07 (m, 2H, cyclobutyl H), 2.85 (m, 2H, cyclobutyl H); CMR ($CDCl_3$) 137.8, 132.3 130.1, 129.0, 127.6, 102.3, 73.0, 44.0, 33.1, 32.1, 31.6; UV (hexane) 266 (92), 262 (260), 256 (310), 250 (280), 207 (3770). Analysis: calcd for $C_{19}H_{18}O_2$: C, 81.98; H, 6.52. Found: C, 81.57; H, 6.59.

Synthesis of Caged Diene 12. Phenylacetal **12PA** (24.9 mg, mmol) was dissolved in 0.5 mL of dry THF under N_2 and stirred and cooled in an ice bath. To the solution, 150 μL of *tert*-butyl lithium solution (1.6 M in pentane) was added dropwise over about 1 min. The solution immediately turned deep brown. The solution was allowed to warm slowly to 20 °C, and after 1 h the solution was light brown. Another 120 μL of *tert*-butyl lithium solution was added, and the reaction was continued for an additional 1.5 h. After this time, 200 μL of H_2O was added, and the reaction mixture was transferred in ether to a separatory funnel. The organic layer was washed once with 0.1 M KOH, once with distilled H_2O, and once with brine. The aqueous layers were all back-washed with fresh ether, and the organic layers were combined and dried over Na_2SO_4. The solution was filtered and concentrated under reduced pressure to yield 13.1 mg of diene **12** (94%). An analytical sample could be prepared by dissolving the crude product in several drops of methanol at room temperature and by precipitation of the diene by rapid cooling to −25 °C. Alternatively, the sample could be sublimed at 35−40 °C at 10 Torr to give white plates, mp 73−76°.

IR (KBr) 3024, 2954, 2931, 2852, 1436, 872, 804; mass spectrum (CI, isobutane) 157, 156, 155, 91, 79, 78. HRMS (CI, isobutane) calcd for $C_{12}H_{11}$: 155.0861. Found: 155. PMR ($CDCl_3$) 6.17 (m, 4H, $J_{AA'} = 9.7$, $J_{AX} = 7.4$, $J_{AX'} = 0.0$, −CH═CH−), 3.38 (br m, 4H, C−CH−C═), 2.90 (m, 4H, −CH−C−C═); CMR ($CDCl_3$) 130.88 (d, $J_{CH} = 157.5$), 41.07 (d, $J_{CH} = 138.0$), 32.90 (d, $J_{CH} = 148.9$).

When sublimation of diene **12** was attempted at 55−60 °C at 12 Torr, dibenzene **1** appeared as an oil which was more volatile than diene **12**. PMR ($CHCl_3$) 5.79 (dd, 4H, $J = 8.5$, $J' = 2.3$, ═CH−CH═), 5.43 (br d, 4H, $J = 8.5$, ═CH−C−), 3.62 (s, 4H, cyclobutyl H).

This oil was treated with phenylurazole and lead tetraacetate at 0 °C for 1 h and worked up by transferring the reaction mixture in CH_2Cl_2 to a separatory funnel and washing the organic layer once with 0.1 M HCl, once with 0.1 M KOH, and once with brine. The organic layers were all back-washed with fresh CH_2Cl_2, and the combined organic layers were dried over $MgSO_4$. The solution was filtered and concentrated under reduced pressure to yield a small amount of product whose NMR spectrum indicated the presence of unreacted phenylurazole. PMR ($CHCl_3$) δ 6.30 (m), 4.42 (m), 3.05 (m), 2.76 (m), 2.41 (m), 2.30 (m) ppm.

Synthesis of Dibenzene 1 via the Thermolysis of Diene 12. Since we were unable to separate **1** and **12** by common chromatographic techniques and the photorearrangement of **12** to **1** is faster than the thermolysis of **1** to two molecules of benzene, we were able to heat **12** in refluxing pentane (34−5 °C) to affect the its rearrangement to **1** prior to its complete thermolysis.

Preparation of 2-Dimethylamino-1,3-Dioxolane Derivative of Diol 10. In a 10-mL round-bottom flask, 21.8 mg (0.11 mmol) of diol **10** was dissolved in 1.0 mL of dichloromethane. An excess of neat *N,N*-dimethylformamide dimethyl acetal (DMF acetal) (2.0 mL) was added, and the reaction solution was stirred at room temperature for 1 h. The solvent and the excess DMF acetal were then evaporated, leaving 28.8 mg of the white solid **10A**. PMR ($CDCl_3$) indicated only one stereoisomer had been formed: δ 6.44 (dd, 2H, −CH═CH−), 6.28 (dd, 2H, −CH═CH−), 5.87 (dd, 2H, −CH═CH−), 5.27 [s, 1H, $CH(OR)_2(NR_2)$], 4.79 [s, 2H, −CH(OR)−CH(OR)−], 3.13 (m, 2H, −C═C−CH−C═C−), 3.05 [m, 2H, −C═C−CH−C(OR)−], 2.30 [s, 6H, $-N(CH_3)_2$].

If the compound was kept in chloroform-*d* for 3 h, it isomerized to the stereoisomer **10B**. PMR ($CDCl_3$) δ 6.48 (m, 2H, −CH═CH−), 6.30 (m, 2H, −CH═CH−), 5.94 (m, 2H, −CH═CH−), 5.29 [s, 1H, $CH(OR)_2(NR_2)$], 5.01 [s, 2H, −CH(OR)−CH(OR)−], 3.15 [m, 4H, −C═C−CH−C═C− and −C═C−CH−C(OR)−], 2.23 (s, 6H, $-NCH_3$). The ratio between the stereoisomers **10A:10B** was 1:1.24. Separation of the two was not attempted. CMR ($CDCl_3$) of the mixture was obtained: δ 138.51 (138.48), 136.85 (136.68), 133.76 (132.98), 114.66 (112.49), 79.61 (76.34), 48.84 (48.21), 39.05 (38.83), 37.52 (37.42). The mixture was used in subsequent reactions without further purification.

Attempted Elimination of 2-Dimethylamino-1,3-Dioxolane Derivative of 10. In a 5-mL round-bottom flask, 25.7 mg (0.105 mmol) of 2-(dimethylamino)-1,3-dioxolane derivative (mixture of stereoisomers) was dissolved in 2.5 mL of dry dichloromethane. To this was added 33 μL (0.19 mmol) of *N,N*-diisopropylethylamine. The solution was stirred under nitrogen while the temperature was maintained at 0 °C with an ice−water bath. A solution of trifluoromethanesulfonic anhydride (16 μL, 0.095 mmol) in dichloromethane (1.0 mL) was then added dropwise via syringe over a period of 3 min. The solution was allowed to react at 0 °C under nitrogen for 2 min before adding 0.016 mL (0.11 mmol) of DBU to quench the remaining acid. The reaction mixture was then partitioned between dichloromethane (25 mL) and saturated sodium carbonate solution (25 mL). The aqueous layer was back-extracted with 25 mL of dichloromethane. The organic layers were then washed once more with saturated aqueous sodium carbonate solution, dried over anhydrous sodium carbonate, and filtered, and the solvent was evaporated under reduced pressure, leaving a yellow oil. PMR and TLC showed that there was none of the desired *p,p′*-dibenzene **3** or its Cope rearrangement product, *syn-o,o′*-dibenzene **1** produced.

The reaction mixture was purified via preparative TLC with dichloromethane as eluent. A pure white solid was obtained which was determined to be the carbonate of diol **10** (5.3 mg): mp 147.5−148.5 °C; PMR ($CDCl_3$) δ 6.45 (br s, 2H, −CH═CH−), 6.30 (br d, 2H, −CH═CH−, $J = 0.82$), 5.95 (br d, 2H, −CH═CH−, $J = 1.98$), 5.24 [s, 2H, −CH(OCOO)CH−], 3.27 [br d, 4H, −C═C−CH−C═C− and −C═C−CH−C(OR)−, $J = 2.19$]; CMR ($CDCl_3$) δ 154.79, 138.18, 136.18, 132.86, 78.41, 47.46, 38.33. IR (CCl_4) 1837, 1819, 1808, 1356, 1167, 1056 cm^{-1}.

Further elution gave the monoformate ester of diol **10** as a colorless liquid (16 mg). PMR ($CDCl_3$) δ 8.01 (s, 1H, HCO−), 6.48 (m, 2H, −CH═CH−), 6.27 (m, 2H, −CH═CH−), 6.02 (m, 2H, −CH═CH−), 5.73 [d, 1H, −C−CH−C(OCOR)−, $J = 7.21$], 4.67 [br t, 1H, −C−CH−C(OR)−, $J = 7.72$], 3.23 (m, 2H), 3.09 [m, 1H, −CH−C(OCOR)−], 3.00 [m, 1H, −CH−C(OR)−], 1.71 (d, 1H, −OH, $J = 9.69$); IR (CCl_4) 3576, 3045, 2952, 2931, 1732, 1371, 1162 cm^{-1}. Repeating the reaction at the refluxing temperature gave the same results.

Cope Rearrangement of Diol 10 to Diol 18. In a 250-mL round-bottom flask equipped with a condenser, a solution of 22 mg (1.16 mmol) of diol **10** in 100 mL of absolute ethanol was stirred while heating to reflux for 3 h. After the reaction was completed, the solvent was removed under reduced pressure. The residue was dissolved in 20 mL of dichloromethane and 5 mL of *n*-hexane. The solvent was then evaporated slowly on a Rotavap until only 5−7 mL of solution remained, at which point a white crystalline precipitate diol **10** formed on the wall of the flask (7.1 mg). The remaining solution was decanted from the precipitate, and the solvent was evaporated to give a mixture of diol **10**, *syn*-[2 + 2]-diol **18** and a trace of *anti*-[2 + 2]-diol **19**. This mixture was separated via preparative TLC on silica gel, eluting with ethyl acetate/*n*-hexane (1/1) and developing the plate three times. Two strong bands ($R_f = 0.65/3$ and $R_f = 0.50/3$) were observed by UV light (254 nm). Upon recovery of these two bands from the TLC plate, the faster moving one was identified as **10** (72.5 mg recovered), while the slower moving band was diol **18** as a waxy solid (75.7 mg, 34%). PMR ($CDCl_3$) δ 6.05 (m, 1H), 5.79 (m, 2H), 5.69 (m, 1H), 5.48 (dd, 1H, $J = 9.55$, $J' = 5.47$), 5.36 (dd, 1H, $J = 9.80$, $J' = 3.66$), 4.42 (dd, 1H, $J = 9.19$, $J' = 3.37$), 4.32 (dd, 1H, $J = 5.53$, $J' = 3.61$), 3.68 (m, 1H), 3.51 (br t, 1H), 3.42 (m, 1H), 2.64 (ddd, 1H, $J = 17.68$, $J' = 8.81$, $J'' = 1.77$), 2.43 (br s, 1H), 2.22 (br s, 1H); CMR ($CDCl_3$) δ 131.29, 128.43, 127.83, 124.07, 123.88, 123.39, 69.26, 65.93, 44.34,

43.08, 37.25, 32.44; IR (CCl_4) 3640, 3569, 3033, 2926, 1586, 1379, 1073, 1047, 1023 cm^{-1}; UV (CH_3OH) λ_{max} (ϵ) = 278.3 nm (2054); MS (Cl^+) *m*/*e* 155 (M + 1 − H_2O), 112 (M − 78). A trace of *anti*-[2 + 2]-diol **19** was also detected in the PMR spectrum of the reaction mixture. If the reaction solution was allowed to reflux for 8 h or longer, substantial amounts of **19** could be isolated via a Chromatotron, eluting with 5% diethyl ether in dichloromethane. PMR ($CDCl_3$) δ 5.96 (m, 1H), 5.76 (m, 3H), 5.65 (m, 2H), 4.26 (br s, 1H), 3.91 (br t, 1H), 3.12 (m, 1H), 2.89 (m. 1H), 2.74 (br s, 2H), 2.30 (br s, 1H), 2.05 (br s, 1H).

Preparation of 2-Dimethylamino-1,3-Dioxolane Derivatives of *syn*-[2 + 2]-Diol 18. *syn*-[2 + 2]-Diol **18** (0.139 g, 7.32×10^{-4} mol) obtained from Cope rearrangement of **10** was dissolved in excess *N*,*N*-dimethylformamide dimethyl acetal (2.5 mL) and stirred at room temperature for 2 h. The solution was then evaporated to dryness, affording a brown oily residue which was further dried under vacuum at room temperature for 2 h. This crude product was shown by PMR to be a mixture of two stereoisomers and was used for the subsequent elimination step without further purification. The reaction is quantitative.

Preparation of *syn-o,o′*-Dibenzene 1. The above 2-(dimethylamino)-1,3-dioxolane derivative of *syn*-[2 + 2]-diol **18** and 0.24 mL of *N*,*N*-diisopropylamine (1.38×10^{-3} mol) were dissolved in 12 mL of dry dichloromethane. The solution was stirred at 0 °C (ice−water bath), and 0.11 mL of trifluoromethanesulfonic anhydride (6.54×10^{-4} mol) was added dropwise over a period of 3 min via syringe. The reaction solution was stirred for another 7 min and then filtered through a short-column of silica gel (3 cm × 3 cm) with the aid of dichloromethane (100 mL). The filtrate was concentrated under reduced pressure, affording a pale yellow residue which was dissolved in pentane (5 mL) and filtered through a short column of silica gel (3 cm × 3 cm) with pentane as eluent (150 mL). The solvent was removed under reduced pressure to give 0.0654 g of a colorless crystalline material. PMR spectra indicated the material was a mixture of *syn-o,o′*-dibenzene **1** (51.8% from **18**) and biphenyl (10.3% from **18**).

Purification of *syn-o,o′*-Dibenzene 1 by High-Pressure Liquid Chromatography (HPLC). An analytical sample of *syn-o,o′*-dibenzene **1** was separated from biphenyl by high-pressure liquid chromatography using a Water Associates HPLC system, vide supra. Semipreparative scale HPLC was performed with a Dupont Instruments 9.4 mm × 25 cm Zorbax silica gel column, using hexane as eluent at a flow rate of 2.0 mL of per min. The retention time for *syn-o,o′*-dibenzene **1** and biphenyl were 9.29 and 10.65 min, respectively. A solution of 20.5 mg of the above mixture in 3 mL of hexane was prepared and injected repeatedly in 0.015 mL aliquots. The collected *syn-o,o′*-dibenzene **1** solution was concentrated and transferred into a small sublimator (20 mL). The solvent was removed under reduced pressure to give a colorless crystalline residue which was sublimed at 0 °C under pressure of 10 mmHg. Colorless needles of **1** condensed on the coldfinger was collected: mp 54.3−54.6 °C. PMR ($CDCl_3$) δ 5.76 (dd, 4H, J = 7.9, J' = 2.6 Hz), 5.40 (br d, 4H, J = 8.5 Hz), and 3.60 ppm (s, 4H); UV (cyclohexane) λ_{max} (ϵ) = 260 nm (4500).

Synthesis of *syn,o,o′*-Naphthalene:Benzene Dimer 22. The dimer **22** was synthesized from the thermal Cope rearrangement of a 0.1 M solution of the *p*,*p′*-dimer **8** in chloroform or cyclohexane at 40−50 °C. The rearrangement was complete after 4 h. The product was purified by semipreparative HPLC on a 0.94 cm × 25 cm Zorbax silica gel column using hexane as the eluent. The retention time of dimer **22** was 25.61 min. *syn-o,o′*-Dimer **22** displays: mp 60−61 °C; PMR-(cyclohexane-d_{12}) (Figure 3) δ 6.92 (m, 2H, ArH), 6.78 (m, 1H, ArH), 6.67 (m, 1H, ArH), 6.19 (dd, 1H, $J_{10,9}$ = 10.0, $J_{10,8}$ = 1.4, H_{10}), 5.71 (dd, 1H $J_{9,10}$ = 9.9, $J_{9,8}$ = 3.9, H_9), 5.61 (dd, 1H, $J_{5,6}$ = 9.7, $J_{5,4}$ = 5.5, H_5), 5.39 (dd, 1H, $J_{4,3}$ = 9.8, $J_{4,5}$ = 5.5, H_4), 5.26 (dd, 1H, $J_{4,3}$ = 9.7, $J_{3,2}$ = 5.3, H_3), 5.04 (dd, 1H, $J_{6,5}$ = 9.9, $J_{6,7}$ = 4.0, H_6= 4.11 (t, 1H, J = 9.5, H_1), 3.46−3.60 (m, 3H, H_2, H_7, and H_8); CMR (cyclohexane-d_{12}) δ 133.8, 132.4, 129.0, 128.6, 128.4, 127.7, 127.7, 127.7, 127.3, 124.8, 124.4, 45.2, 44.2, 42.7, 40.7; IR (CS_2) 3056, 3029, 3016, 2918, 2880, 1489, 1451, 811, 788, 755, 738, 700 cm^{-1}.

Attempts to Detect Metastable Intermediates in the Thermolysis of Dimer 22. In our attempts to detect a metastable intermediate, the *anti*-dimer **23**, in the thermolysis of dimer **22**, we found that the reaction was too slow at temperatures below 40 °C. Although the reaction was faster at 55 °C, the relative amount of **23** formed was not improved. The temperature 40 °C was then chosen for our investigation, and the result is displayed in Figure 4.

Activation Parameters for Thermal Decompositions of Dibenzene 1 and Dimer 22, and for the Thermal Rearrangement of Dimer 8 to Dimer 22. The activation parameters of these processes were obtained from their rates of decomposition in cyclohexane-d_{12} by PMR spectroscopy. The thermal decomposition of **1** was determined in duplicate runs, that of **22** in both cyclohexane-d_{12} and chloroform-*d*. The experimental details are given in the Supporting Information.

Activation Parameters (298 K) for Decompositions of Dimers **1**, **22**, and **8**

dimer	E_a, (kcal/mol)	$\Delta H^‡$ (kcal/mol)	$\Delta S^‡$ (eu)	$\Delta G^‡$ (kcal/mol)
1	27.4 ± 0.8	26.8 ± 0.8	−0.9 ± 1.6	27.1 ± 1.1
22	28.4 ± 0.2	27.5 ± 0.2	−1.7 ± 0.6	28.2 ± 0.2
22 (CDC_{l3})[a]	−	28.8 ± 1.1	7.6 ± 2.9	−
8	23.2 ± 0.4	22.8 ± 0.4	1.4 ± 1.3	23.2 ± 0.8

[a] A trial run.

Conclusions

A pure sample of *syn-o,o′*-dibenzene **1** was obtained for the first time. The chemistry and spectroscopy of **1** were studied in comparison to those of the *anti*-isomer **2**, particularly with respect to the influence of through-bond and through-space interactions between the two 1,3-cyclohexadienyl systems. Photoelectron spectroscopy of **1** and **2** reveals that the through-bond interaction between the two cyclohexadienyl systems is more important than the through-space interaction. *syn*-Dibenzene **1** undergoes thermolysis to two molecules of benzene at a slower rate than thermodynamically more stable *anti*-dibenzene **2**. Kinetic analysis reveals that the higher thermal stability of **1** is due to the higher heat of activation in thermolysis. Molecular orbital calculations of dibenzenes, the corresponding bis-cyclohexadienyl diradicals, and the transition states of thermolyses of dibenzenes **1** and **2** suggest that diradicals are not intermediates in the thermolyses. A comparative study on the thermolyses of *syn-o,o′*-arene:benzene dimers suggests that the thermolyses of *syn-o,o′*-arene:benzene dimers proceed via their *anti*-isomers as intermediates. *syn*-Dibenzene **1** also undergoes adiabatic photolysis to one molecule of excited benzene and one molecule of ground-state benzene in good efficiciency. Since the adiabatic photochemical formation of excited benzene from dibenzene **1** may be achieved with light longer than 320 nm in wavelength, the process represents an upconversion of a less energetic photon to one of higher energy. The mechanisms of these reactions were discussed.

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Supporting Information Available: The chemiluminescent and its excitation spectra of dibenzene **1**, the general information concerning sources of chemicals and instrumentation used, an improved synthesis of 4,5-dibromo-1,2-cyclohexanediol **13**, methodology used in determining the kinetic parameters of the thermolyses of dibenzenes, and results obtained (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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