3h-D: ^{1}H NMR[‡] ($CDCl_3$) δ 7.39 (d, $J_{5,6}$ = 10 Hz, 1 H, H_5), 7.32 and 7.29 (overlapping m, 6 H, meta and para), 7.23 (m, 4 H, ortho), 6.45 (d, $J_{5,6}$ = 10 Hz, 1 H, H_6), 6.35 (br s, 1 H, OH)—the assignments of the hydroxyl peak was confirmed by double-resonance irradiation of the water peak at 1.6 ppm. Only trace amounts of a doublet ($J_{3,5}$ = 3 Hz, H_3 of **3h**) could be detected. ^{13}C NMR[‡] ($CDCl_3$) δ 181.48 (C_1), 156.52 (C_5), 145.48 (C_2), 142.39 (ipso), 128.86 (meta), 127.78 (ortho), 127.61 (para), 124.45 (C_6), 54.74 (C_4)—absorptions at ca. 123.04 (C_3) were not detected; assignments of the vinyl carbons were confirmed by correlating the residual CH coupling in two off-resonance decoupled spectra to the known proton absorptions; MS (55 eV), *m/e* 263 (M^+, 16.04%), 246 (M − OH, 5.01%), 235 (M − CO, 7.11%), 216 (M − CO − OHD, 6.28%), 158 (5.44%), 129 (11.31%), 105 (PhCO, 100%).

2-Hydroxyspiro[4.5]dec-1-en-3-one (21). The enol was prepared according to the general procedure of Naoshima et al.[19] 1,1-Cyclohexanediacetic acid (**22**, 10 g, 0.5 mol, Aldrich) was dissolved in 35 mL of methanol containing 3.5 mL of concentrated H_2SO_4 and refluxed for 3 h to give a nearly quantitative yield (11.2 g, 0.5 mol) of diester **23**. The latter was reacted with freshly distilled trimethylsilyl chloride (25.4 mL, 0.2 mol) and sodium as described[19] to yield 2,3-bis(trimethylsiloxy)spiro[4.5]dec-2-ene (**24**). Crude **24** was hydrolyzed[19] to acyloin **25**, a small portion of which was purified by preparative TLC. The bulk of crude **25** was refluxed overnight with copper acetate in methanol until a red copper precipitate was formed. After workup, the product mixture was distilled (80 °C/2 Torr) to yield 1 g (12% overall yield) of the desired α-keto enol **21**. The latter was further purified by GLC (3 ft × $^1/_4$ in. copper column packed with 10% SE-30 on Chromosorb P; oven, 140 °C; flow, 100 cm^3/min; retention time, 8 min).

21: R_f (25% acetone in hexane) 0.30; ^{1}H NMR ($CDCl_3$) δ 6.50 (s, 1 H, vinyl), 5.43 (br s, 1 H, OH), 2.27 (s, 2 H), 1.47 (br s, 10 H); IR (neat) 3340 (br, s, OH), 1690 (s, C=O), 1640 and 1620 (m, C=C) cm^{-1}; MS (70 eV), *m/e* 166 (M^+), 138 (M − CO), 123 (M − CH_2COH), 95 (M − CH_2COCOH).

23: ^{1}H NMR ($CDCl_3$) δ 3.63 (s, 6 H, CH_3O), 2.50 (s, 4 H, CH_2CO), 1.46 (br s, 10 H, ring); IR (neat) 1730 (s, C=O) cm^{-1}; MS (70 eV), *m/e* 228 (M^+), 197 (M − OCH_3), 155 (M − $CH_3O_2CCH_2$), 123 (M − $CH_3O_2CCH_2$ − OCH_3), 95 (M − $CH_3O_2CCH_2$ − CH_3OCO).

24: ^{1}H NMR ($CDCl_3$) δ 2.40 (s, 2 H), 2.13 (s, 2 H), 1.47 (br s, 10 H), 0.23 (s, 18 H).

25: R_f (25% acetone in hexane) 0.27; ^{1}H NMR ($CDCl_3$) δ 4.26 (t, J = 10 Hz, 1 H), 2.23–2.13 (m, 4 H), 1.47 (br s, 10 H).

Reaction of 21 with $O_2^{\bullet-}$. Enol **21**, KO_2, and 18-crown-6 in an equimolar ratio were added to toluene and allowed to react for 8 h according to the general oxidation procedure.[7a] Acidic products in a 90% yield were isolated and diazotized.[11] The resulting methyl esters were separated by GLC (7 ft × $^1/_4$ in. copper column packed with 7% SE-52 on Chromosorb P; oven, 115 °C; flow, 100 cm^3/min) to give three peaks in a ratio of 1:1:2 with retention times of 12, 18, and 33 min. On the basis of their spectral data, these products were identified as aldehydo ester **29** and diesters **27** and **23**, respectively.

27: ^{1}H NMR ($CDCl_3$) δ 3.73 (s, 3 H, CH_3O), 3.66 (s, 3 H, CH_3O), 2.63 (s, 2 H, CH_2CO), 1.53 (br s, 10 H, ring); IR (neat) 1735 (s, C=O) cm^{-1}; MS (70 eV), *m/e* 214 (M^+), 183 (M − OCH_3), 155 (M − CO_2CH_3), 95 (M − CO_2CH_3 − HCO_2CH_3).

29: ^{1}H NMR ($CDCl_3$) δ 9.69 (s, 1 H, aldehydic), 3.67 (s, 3 H, CH_3O), 2.56 (s, 2 H, CH_2CO), 1.50 (br s, 10 H, ring); IR (neat) 1735 and 1700 (s, C=O) cm^{-1}; MS (70 eV), *m/e* 183 (M − H), 155 (M − CHO), 123 (M − CO_2CH_3).

Photosensitized Cis/Trans Isomerization of 1-(1-Propenyl)cycloalkenes[1]

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The photosensitized cis/trans isomerization of a series of 1-(1-propenyl)cycloalkenes is reported. A plot of the photostationary state trans/cis ratio vs the sensitizer triplet energy for 1-(1-propenyl)cyclopentene shows a constant trans/cis ratio of ~1.0 with high-energy sensitizers (E_T > 61 kcal/mol). The plot shows one maxima at E_T ~ 55 kcal/mol with low-energy sensitizers (E_T < 61 kcal/mol). This type of plot is very similar to those obtained with acyclic dienes such as piperylene. The 1-(1-propenyl)cyclohexene system shows a similar plot with high-energy sensitizers, but with low-energy sensitizers this system shows two maxima occurring at 56 and 47 kcal/mol, respectively. This double-maxima plot is rationalized by an unusually low trans/cis decay ratio for the s-cis relaxed triplet state of the 1-(1-propenyl)cyclohexene system. This double maxima is not observed in other diene systems due to a high trans/cis decay ratio for their s-cis relaxed triplet states. The photosensitized cis/trans isomerization of 2-ethylidene-10-methyl-1(9)-octalin was also studied as a model for a conformationally locked s-trans system. The 1-(1-propenyl)cycloheptene system undergoes photosensitized cis/trans isomerization, but photostationary cis/trans isomerization data could not be obtained due to a very efficient photosensitized dimerization of this diene system.

Introduction

The triplet sensitized cis/trans isomerization of conjugated dienes has been extensively studied over the past 25 years, resulting in a fairly clear mechanistic picture.[2] The generally accepted mechanism, shown in Scheme I, involves excitation of the ground-state sensitizer (sens^0) to the first excited singlet state (sens^1) followed by intersystem crossing to the triplet state (sens^3). Collisional deactivation of the sensitizer triplet state by the ground-state diene results in formation of the vertical diene triplets. Havinga first demonstrated the importance of ground-state conformations on the photochemistry of polyenes.[3] The s-trans and s-cis conformational isomers are included for each cis and trans configurational isomer as their importance has been demonstrated by Saltiel.[4]

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[1] (a) The initial phase of this work was presented at the 178th National Meeting of the American Chemical Society, Washington, D.C., Sept 1979, Abstract ORGN 171. (b) Taken, in part, from the undergraduate honors thesis of W. D. Inman. (c) Taken, in part, from the M.S. Thesis of M. A. Chaidez.

[2] (a) Saltiel, J.; D'Agostino, J.; Megarity, E. D.; Metts, L.; Neuberger, K. P.; Wrighton, M.; Zafiriou, D. C. In *Organic Photochemistry*; Chapman, O. L., Ed.; Marcel Dekker: New York, 1973; pp 1–177. (b) Saltiel, J.; Charlton, J. L. In *Rearrangements in Ground and Excited States*; de Mayo, P., Ed.; Academic Press: New York, 1980; Vol. 3, pp 25–89.

[3] Gielen, J. W. J.; Jacobs, H. J. C.; Havinga, E. *Tetrahedron Lett.* **1976**, *41*, 3751–3754, and references therein.

[4] Saltiel, J.; Metts, L.; Sykes, A.; Wrighton, M. *J. Am. Chem. Soc.* **1971**, *93*, 5302–5303.

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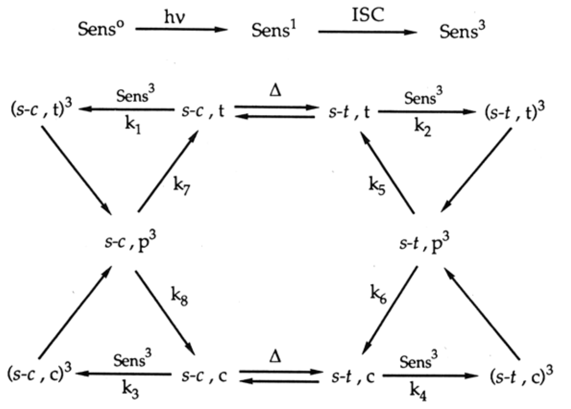
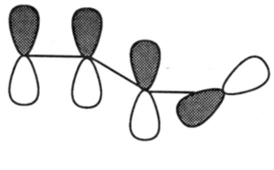
Scheme I



Equilibrium rapidly occurs in the ground state between s-cis and s-trans isomers, but the s-cis and s-trans vertical triplet states do not readily equilibrate. The s-cis vertical triplets are rapidly transformed into a common s-cis geometrically relaxed triplet state (s-c, p^3) from which ground-state dienes are again produced by internal conversion. A similar process occurs for the s-trans vertical triplets. The temperature dependence of the photoisomerization of stilbene has ruled out the original hypothesis of nonvertical energy transfer from the ground state directly to the p^3 state.[5] Saltiel prefers the so-called "hot-band" mechanism in which excitation is never nonvertical but can occur from a ground-state molecule that is already twisted.

Although the mechanism shown in Scheme I is readily accepted, there has been some question as to the structure of the relaxed triplet p^3 states. Several structures have been postulated that include the allyl-methylene species **1** and the 1,4-biradical species **2**. Theoretical studies have



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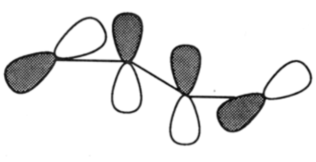
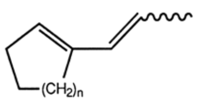


2

predicted that structure **1** should be the lowest energy form of triplet-state butadiene[6] while experimental studies have provided evidence for both structures **1**[7] and **2**.[8] Our approach to this question involves construction of a model system in which the degree of rotation about one of the double bonds is geometrically restricted while rotation about the other double bond is not restricted. We thus chose to study a series of 1-(1-propenyl)cycloalkenes **3** (n = 1, 2, or 3) in which decreasing the cycloalkene ring size



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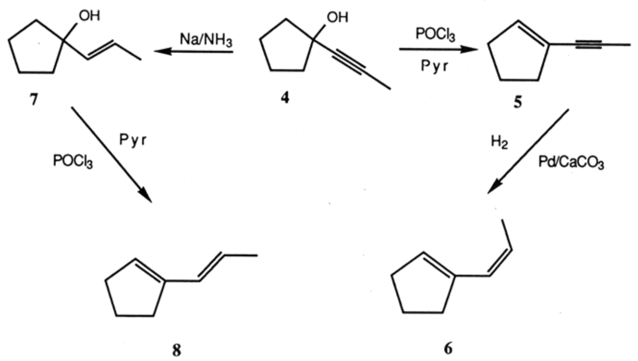
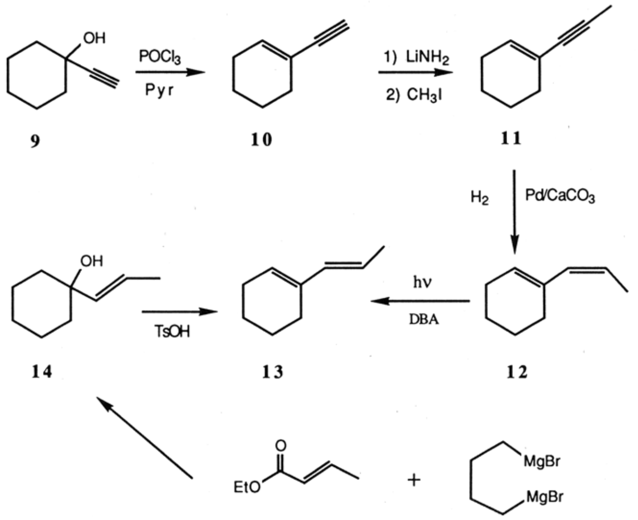
would progressively restrict rotation about one of the double bonds while leaving the other one relatively unchanged. In this paper we report our detailed study of the triplet sensitized photochemistry of these conjugated dienes.

Scheme II



Scheme III



Results

1-(1-Propenyl)cycloalkene Synthesis. The synthesis of the cyclopentyl system (delineated in Scheme II) begins with 1-(1-propynyl)cyclopentanol (**4**). Dehydration of **4** with $POCl_3$/pyridine provides the enyne **5** in 74% yield. Controlled hydrogenation of **5** over $Pd/CaCO_3$ in piperidine gives the desired *cis*-1-(1-propenyl)cyclopentene (**6**) in 40% yield. The trans isomer is obtained by sodium/liquid ammonia reduction of **4** to produce the trans-alkenol **7** (35%) followed by dehydration of **7** with $POCl_3$/pyridine to generate *trans*-1-(1-propenyl)cyclopentene (**8**) in 91% yield.

The synthesis of the cyclohexyl system is outlined in Scheme III. 1-Ethynylcyclohexanol (**9**) is readily dehydrated (86%) to enyne (**10**) followed by alkylation (49%) of the terminal alkyne by treatment with $LiNH_2$ and then CH_3I to give 1-(1-propynyl)cyclohexene (**11**). Hydrogenation of **11** over $Pd/CaCO_3$ in piperidine gives *cis*-1-(1-propenyl)cyclohexene (**12**) in 84% yield. *trans*-1-(1-Propenyl)cyclohexene (**13**) can be prepared by two different methods. In method A the 9,10-dibromoanthracene-photosensitized isomerization of **12** readily gives **13** in 95% yield. In method B the trans isomer **13** is prepared by using a novel reaction based on the method of Nenitzescu.[9] The di-Grignard of 1,5-dibromopentane is reacted with ethyl crotonate to generate *trans*-1-(1-

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[5] Saltiel, J.; Marchand, G. R.; Kirkor-Kaminska, E.; Smothers, W. K.; Mueller, W. B.; Charlton, J. L. *J. Am. Chem. Soc.* **1984**, *106*, 3144–3151.

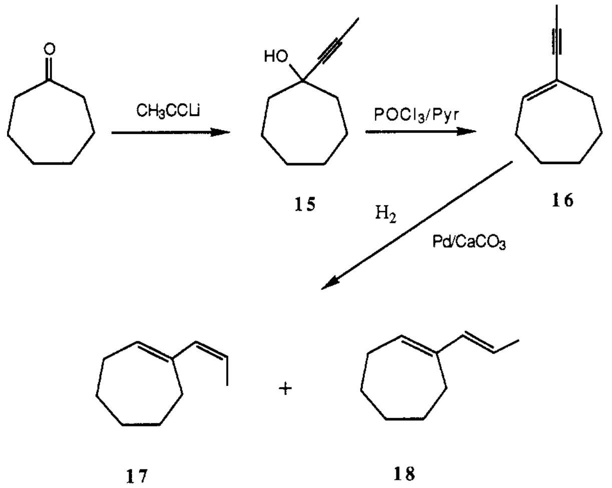
[6] (a) Hoffman, R. *Tetrahedron* **1966**, *22*, 521–545. (b) Evleth, E. M. *Chem. Phys. Lett.* **1966**, *3*, 122–124. (c) Evleth, E. M.; Poirer, R. A. *J. Photochem.* **1985**, *30*, 423–435.

[7] Saltiel, J.; Rousseau, A. D.; Sykes, A. *J. Am. Chem. Soc.* **1972**, *94*, 5903–5905.

[8] Saltiel, J.; Metts, L., Wrighton, M. *J. Am. Chem. Soc.* **1969**, *91*, 5684–5685.

[9] Nenitzescu, C. C., Necsoiu, I. *J. Am. Chem. Soc.* **1950**, *72*, 3483–3486.

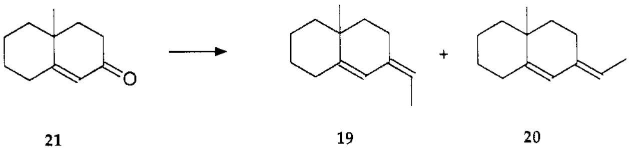
Scheme IV



propenyl)cyclohexanol (**14**) in 30% yield. Dehydration of **14** provides **13** in 32% yield. Clearly method A is preferable, although we have not carried out any large-scale preparations of **13** using method A.

Our route to the cycloheptyl system is given in Scheme IV. Addition of the lithium salt of propyne to cycloheptanone yields 1-(1-propynyl)cyclopentanol (**15**) in 30% yield. Dehydration of **15** using $POCl_3$/pyridine provides enyne **16** (71%), while reduction of **16** over $Pd/CaCO_3$ in piperidine provides a 6.4:1 ratio (42% yield) of *cis*- and *trans*-1-(1-propenyl)cycloheptene, **17** and **18**, respectively. We were unable to completely separate **17** and **18**, although samples about 90% cis/10% trans and 90% trans/10% cis can be obtained by preparative gas chromatography (GC).

(*Z*)- and (*E*)-2-ethylidene-10-methyl-1(9)-octalin,[10] **19** and **20**, respectively, were prepared from 10-methyl-1-(9)-octalone-2 (**21**)[11] employing the Corey modification of



the Wittig reaction.[12] The reaction gave a mixture of 17% **19** and 83% **20**. Although the *E* and *Z* isomers could not be separated by preparative GC, the relative ratio can be easily determined by ^1H NMR. The proton at C-1 resonates at a significantly lower field in **19** (δ 5.9) than in **20** (δ 5.4) due to steric deshielding by the adjacent methyl group.[13]

Photochemistry of the 1-(1-Propenyl)cycloalkenes. Trans/cis photostationary state [$(t/c)_{PSS}$] values were measured for 1-(1-propenyl)cyclopentene and 1-(1-propenyl)cyclohexene employing 0.03 M *cis*- or *trans*-1-(1-propenyl)cycloalkene and 0.01–0.05 M sensitizer in degassed benzene. The samples were irradiated in Pyrex vessels by using a Rayonett photochemical reactor employing either 300-nm (for high-energy sensitizers) or 350-nm (for low-energy sensitizers) lamps. In the absence of sensitizer the 1-(1-propenyl)cycloalkenes undergo very slow cis/trans photoisomerization after extremely long irradiation times. In the presence of sensitizers the $(t/c)_{PSS}$ is reached well before direct irradiation would have produced any noticeable isomerization. To keep the photolysis time to a minimum, two basic procedures were used depending upon the energetics of the energy transfer from triplet sensitizer to ground-state diene. Solutions of predominantly cis or trans diene were employed with high-energy sensitizers (triplet energy (E_T) > than 60 kcal/mol), while with low-energy sensitizers (E_T < 60 kcal/mol) an isomer ratio close to the final $(t/c)_{PSS}$ was used. In all cases the $(t/c)_{PSS}$ was approached from solutions rich in trans isomer as well as solutions rich in cis isomer.

Table I. Quantum Yield and Photostationary State Data for Benzophenone Photosensitized Cis–Trans Isomerization

diene	$\Phi_{c\to t}$	$\Phi_{t\to c}$	$\sum\Phi$	$\Phi_{c\to t}/\Phi_{t\to c}$	$(t/c)_{PSS}$
1-(1-propenyl)cyclohexene	0.45	0.57	1.02	0.79	0.78
1-(1-propenyl)cyclopentene	0.53	0.48	1.01	1.10	1.00

Table II. $(t/c)_{PSS}$ for 1-(1-Propenyl)cyclopentene

sensitizer	sensitizer E_T,[a] kcal/mol	$(t/c)_{PSS}$[b]
acetone (I)	~80	1.04
acetophenone (II)	73.7	1.03
benzophenone (III)	68.6	1.00
thioxanth-9-one (IV)	65.5	1.04
flavone (V)	62.0	1.04
Michler's ketone (VI)	61.0	1.00
2-acetonaphthone (VII)	59.3	1.63
1-benzoylnaphthalene (VIII)	57.5	2.13
1-naphthaldehyde (IX)	55.7	2.70
fluoranthene (X)	54.2	2.68
1,2,3,4-dibenzanthracene (XI)	50.8	2.00
1,2-dibenzanthracene (XII)	47.2	1.62
9,10-dimethyl-1,2-dibenzanthracene (XIII)	44.3	1.48

[a] Taken from: Sandros, K. *Acta Chem. Scand.* **1964**, *18*, 2355. Ramamurthy, V.; Liu, R. S. H. *J. Am. Chem. Soc.* **1976**, *98*, 2935. [b] Obtained by extrapolating a plot of experimental $(t/c)_{PSS}$ values vs sensitizer concentration to infinite dilution.

If the triplet energy of the sensitizer is more than 3 kcal/mol above the triplet energy of both the s-t,t and s-t,c isomers, the left-hand side of Scheme I can be ignored since the s-trans isomers account for more than 95% of the conformational s-trans/s-cis equilibrium.[14] If $k_2 = k_4$ and if $\Phi_{isc} = 1.0$, the following relationships hold, where $\Phi_{c/t}$ is the quantum yield for cis to trans photoisomerization and $\Phi_{t/c}$ is the quantum yield for trans to cis photoisomerization:[15]

$$(t/c)_{PSS} = k_5/k_6 = (\Phi_{c/t})/(\Phi_{t/c})$$

$$\Phi_{c/t} + \Phi_{t/c} = 1.0$$

The experimental data for benzophenone sensitization of **8** and **13** are in good agreement with this prediction as shown in Table I. Thus it can be concluded that, with benzophenone as photosensitizer, dienes **8** and **13** are normal dienes behaving photochemically in a manner very similar to acyclic dienes such as 1,3-pentadiene. All of the high-energy sensitizers produce identical $(t/c)_{PSS}$ as predicted by Scheme I.

When the triplet energy of the sensitizer falls below about 61 kcal/mol, the $(t/c)_{PSS}$ does not remain constant but is now a function of both the sensitizer triplet energy and the sensitizer concentration. A plot of sensitizer

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(10) McMurry, J. E.; Coppolino, A. P. *J. Org. Chem.* **1973**, *38*, 2821–2827.

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Table III. $(t/c)_{PSS}$ for 1-(1-Propenyl)cyclohexene

sensitizer	sensitizer E_T,[a] kcal/mol	$(t/c)_{PSS}$[b]
acetone (I)	~80	0.78
acetophenone (II)	73.7	0.78
benzophenone (III)	68.6	0.78
biphenyl (XIV)	65.7	0.78
naphthalene (XV)	60.8	0.78
1-chloronaphthalene (XVI)	59.5	1.02
2-acetonaphthone (VII)	59.3	1.20
2-naphthaldehyde (XVII)	59.5	1.31
1-benzoylnaphthalene (VIII)	57.5	1.50
1-acetonaphthone (XVIII)	56.3	1.95
1-naphthaldehyde (IX)	55.7	2.30
fluoranthene (X)	54.2	1.00
9-fluorenone (XIX)	53.3	1.16
1,2,3,4-dibenzanthracene (XI)	50.8	1.80
1,2-dibenzanthracene (XII)	47.2	2.20
benzanthrone (XX)	47.0	1.75

[a] Taken from: Sandros, K. *Acta Chem. Scand.* **1964**, *18*, 2355. Ramamurthy, V.; Liu, R. S. H. *J. Am. Chem. Soc.* **1976**, *98*, 2935. [b] Obtained by extrapolating a plot of experimental $(t/c)_{PSS}$ values vs sensitizer concentration to infinite dilution.

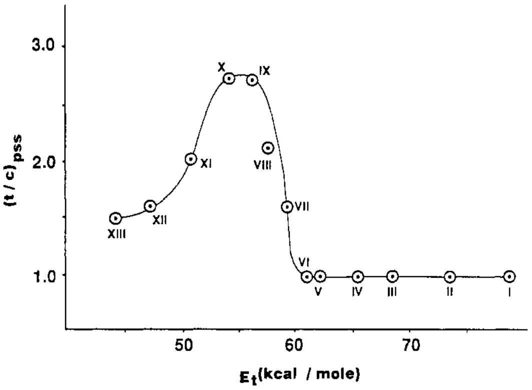


Figure 1. Plot of $(t/c)_{PSS}$ values vs sensitizer triplet energy for the 1-(1-propenyl)cyclopentene system. Each $(t/c)_{PSS}$ value was obtained by extrapolation, to infinite dilution, of a plot of the $(t/c)_{PSS}$ vs sensitizer concentration. See Table II for the identity of each sensitizer.

concentration vs $(t/c)_{PSS}$ gives a linear plot for all low-energy sensitizers using both the 1-(1-propenyl)cyclopentene and the 1-(1-propenyl)cyclohexene systems. The $(t/c)_{PSS}$ values extrapolated to infinite dilution for the 1-(1-propenyl)cyclopentene system and each sensitizer are shown in Table II, while Table III shows the $(t/c)_{PSS}$ values extrapolated to infinite dilution for the 1-(1-propenyl)-cyclohexene system and each sensitizer. In each case the chemical yield of the cis–trans photosensitized isomerization was greater than 95% as determined by GC analysis. These sensitizer concentration effects are believed to be caused by reverse energy transfer from the vertical triplet-state diene to the ground-state sensitizer.[16] This reverse energy transfer from triplet-state diene to ground-state sensitizer

$$\text{sens}^3 + \text{diene}^0 \rightleftharpoons \text{sens}^0 + \text{diene}^3$$

would be important only when the forward step is not significantly exothermic. Thus, no sensitizer concentration effects are observed for the high-energy sensitizers.

Figures 1 and 2 show plots of $(t/c)_{PSS}$ values versus triplet sensitizer energies for 1-(1-propenyl)cyclopentene and 1-(1-propenyl)cyclohexene, respectively. Each $(t/c)_{PSS}$ value was obtained by extrapolation using the method described above. Figure 1 resembles similar plots obtained for simple acyclic dienes.[8] Figure 2, however, is strikingly different from Figure 1 in possessing two maxima at E_T values of 56 and 47 kcal/mol.

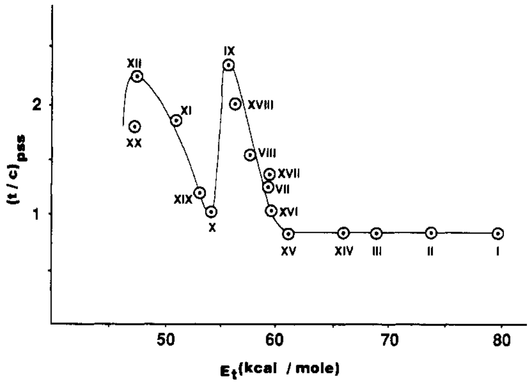
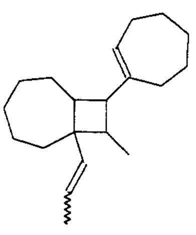


Figure 2. Plot of $(t/c)_{PSS}$ values vs sensitizer triplet energy for the 1-(1-propenyl)cyclohexene system. Each $(t/c)_{PSS}$ value was obtained by extrapolation, to infinite dilution, of a plot of the $(t/c)_{PSS}$ vs sensitizer concentration. See Table III for the identity of each sensitizer.

The sensitized photochemistry of 1-(1-propenyl)cycloheptene is considerably more complicated than the cyclopentyl and cyclohexyl systems. Photosensitization of the cycloheptyl system produces both cis–trans isomerization and dimerization. The dimerization proceeds very rapidly, and thus $(t/c)_{PSS}$ values could not be measured. Two dimeric products were isolated by preparative GC. These dimers appear, from their ^{1}H NMR spectra, to be geometrical isomer mixtures of the general structures **22** and **23**, although other similar structures could be drawn.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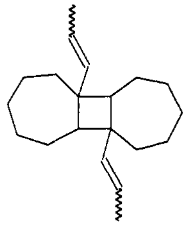
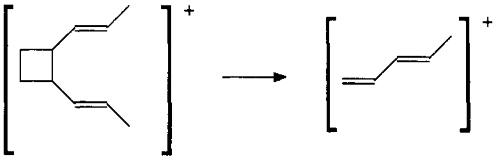

23

GC MS data provided parent ions for each at *m/e* 272 in support of the proposed structures. The base peak for each occurs at *m/e* 136, indicating possible cleavage to the molecular ion of the monomer. This is consistent with a divinyl-substituted cyclobutane. For example, **24**, the molecular ion from a cyclobutane photodimer of 1,3-pentadiene,[17] gives ion **25** as the base peak. Similar base peaks are found in the mass spectra of other divinylcyclobutanes formed by photodimerization of 1,3-pentadiene as well as isoprene.[18]


24 **25**

Photochemistry of 2-Ethylidene-10-methyl-1(9)-octalin. The $(t/c)_{PSS}$ values for each sensitizer (listed in Table IV) were measured for 2-ethylidene-1-methyl-1-(9)-octalin employing the same techniques used with the

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(16) Sandros, K. *Acta Chem. Scand.* **1964**, *18*, 2355.

(17) Paisley, H. M.; Brittain, E. F. H.; Wells, C. H. J. *J. Chem. Soc. B* **1969**, 185–187.

(18) Brittain, E. F. H.; Wells, C. H. J.; Paisley, H. M. *J. Chem. Soc. B* **1968**, 304–307.

Table IV. $(t/c)_{PSS}$ for 2-Ethylidene-10-methyl-1(9)-octalin

sensitizer	sensitizer E_T,[a] kcal/mol	$(t/c)_{PSS}$[b]
acetone (I)	~80	1.01
acetophenone (II)	73.7	1.00
benzophenone (III)	68.6	1.02
naphthalene (XV)	60.8	1.02
1-chloronaphthalene (XVI)	59.5	1.11
2-acetonaphthone (VII)	59.3	1.06
1-acetonaphthone (XVIII)	56.3	1.12
1-naphthaldehyde (IX)	55.7	1.17
fluoranthene (X)	54.2	1.81
1,2,5,6-dibenzanthracene (XXI)	52.3	1.98
1,2,3,4-dibenzanthracene (XI)	50.8	1.69
pyrene (XXII)	48.3	1.63
1,2-dibenzanthracene (XII)	47.2	1.46

[a] Taken from: Sandros, K. *Acta Chem. Scand.* **1964**, *18*, 2355. Ramamurthy, V.; Liu, R. S. H. *J. Am. Chem. Soc.* **1976**, *98*, 2935. [b] Obtained by extrapolating a plot of experimental $(t/c)_{PSS}$ values vs sensitizer concentration to infinite dilution.

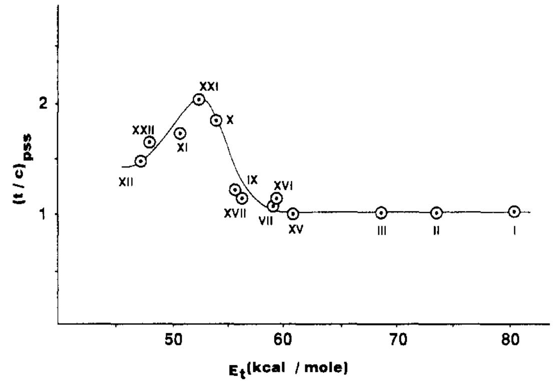


Figure 3. Plot of $(t/c)_{PSS}$ values vs sensitizer triplet energy for the 2-ethylidene-10-methyl-1(9)-octalin system. Each $(t/c)_{PSS}$ value was obtained by extrapolation, to infinite dilution, of a plot of the $(t/c)_{PSS}$ vs sensitizer concentration. See Table IV for the identity of each sensitizer.

1-(1-propenyl)cycloalkenes. The $(t/c)_{PSS}$ values for each sensitizer were obtained by extrapolation of the sensitizer concentration to infinite dilution. In the octalin system the high-energy sensitizers again did not show any concentration effects; however, in marked contrast to the 1-(1-propenyl)cycloalkenes, the low-energy sensitizers showed only small concentration effects. Figure 3 shows a plot of $(t/c)_{PSS}$ versus sensitizer triplet energy for 2-ethylidene-1-methyl-1(9)-octalin. This plot is similar to plots obtained with acyclic dienes.

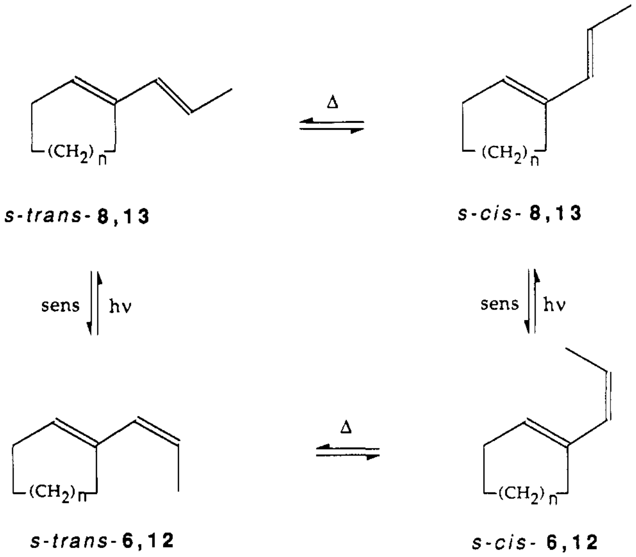
Diels–Alder Reactions with 1-Alkenylcycloalkenes. The second-order rate constant for the reaction of maleic anhydride with 1-vinylcyclohexene in chloroform was measured at 30, 40, and 48 °C, which provides an activation energy for the reaction of 12.5 kcal/mol. This is similar to the activation energies obtained for the Diels–Alder reactions of maleic anhydride and butadiene (13.2 kcal/mol)[19] and also for maleic anhydride and 1,3-cyclohexadiene (11.4 kcal/mol).[20] The second-order rate constants for the Diels–Alder reaction of maleic anhydride with both geometrical isomers of 1-(1-propenyl)cyclopentene as well as both geometrical isomers of 1-(1-propenyl)cyclohexene were also measured in chloroform. The cis isomers reacted significantly slower than the trans isomers, and thus the cis isomer kinetics were carried out at 40 °C while the trans isomer kinetics were carried out at 26 °C. The kinetic results are shown in Table V. The Diels-Alder reactions of both **8** and **13** with maleic anhydride have been described,[9] although only the melting point of the product was reported. ^1H NMR supports the general structure **26** for these compounds. Proton H_a appears at δ 5.5–5.7 when $n = 0$ and at δ 5.2–5.3 when $n = 1$, while protons H_b and H_c occur at δ 3.2–3.4 in each adduct.

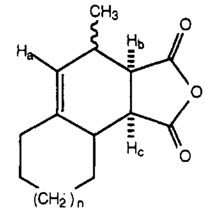
Table V. Second-Order Rate Constants for the Diels–Alder Reaction of 1-(1-Propenyl)cycloalkenes with Maleic Anhydride[a]

compound	10^5 k, L mol^{-1} s^{-1}	T, °C	k_{trans}/k_{cis}
cis-1-(1-propenyl)cyclopentene (**6**)	6.6	40	20
trans-1-(1-propenyl)cyclopentene (**8**)	130	26	
cis-1-(1-propenyl)cyclohexene (**12**)	2.8	40	20
trans-1-(1-propenyl)cyclohexene (**13**)	56	26	

[a] Measured by following the decrease in the maleic anhydride ^1H NMR signal in $CHCl_3$.

Scheme V





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Discussion

Sensitizer triplet energy vs $(t/c)_{PSS}$ value plots have been used to approximate the vertical triplet energies of cis and trans dienes.[15a] Our plots can be interpreted by reference to Scheme V. When the triplet energy of the sensitizer lies more than 3 kcal/mol above the acceptor's triplet energy, the energy-transfer rate is nearly diffusion-controlled. When this difference between the senzitizer and acceptor triplet energies is below 3 kcal/mol, the triplet transfer requires vibrational activation of the sensitizer and/or acceptor.[21]

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[19] Gehlawat, J. K. *Ind. Chem. Eng. B* **1972**, *14*, 22–25.

[20] Eckert, C. A.; Grieger, R. A. *J. Am. Chem. Soc.* **1970**, *92*, 7149–7153.

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Sandros has developed the following equation, which expresses the ratio of the rate constant of triplet energy transfer (k) to the diffusion-controlled rate constant (k_d) as a function of the triplet energy difference (ΔE_T) between sensitizer and acceptor:[16]

$$k/k_d = [1 + \exp(-\Delta E_T/RT)]^{-1}$$

When ΔE_T is at least 3 kcal/mol for every s-cis and s-trans isomer of a particular diene, triplet energy is transferred to all isomers at the diffusion-controlled rate constant, i.e., $k_1 = k_2 = k_3 = k_4 = k_d$. Thus, the $(t/c)_{PSS}$ is a function only of the decay ratios for the relaxed p^3 states. Since the s-trans isomers make up more than 95% of the ground-state diene,[14] the $(t/c)_{PSS}$ values will equal the decay ratio (k_5/k_6) for the s-t-p^3 state. When the ΔE_T of the sensitizer falls below 3 kcal/mol for the s-t,t isomer, k_4 becomes less than k_d, and the concentration of the trans isomer increases in the photostationary mixture. We assign the triplet energy of the s-trans,trans isomer as 3 kcal/mol below the first inflection point in Figures 1 and 2. Therefore, the E_T of *s-trans*-**8** is assigned as 58 kcal/mol (61 − 3 kcal/mol), and the E_T of *s-trans*-**13** is also assigned as 58 kcal/mol (61 − 3 kcal/mol). The rising slope again reaches an inflection point when triplet energy transfer to the s-trans,cis isomer no longer occurs at the diffusion-controlled rate. The concentration of the s-cis,trans isomer is much greater than the concentration of the s-cis,cis isomer due to the inherent steric problems in the s-cis,cis isomer.[22] Thus, we see an increase in the concentration of the cis isomer below the second inflection point. Therefore, we assign the E_T of *s-trans*-**6** as 52 kcal/mol (55 − 3 kcal/mol) and the E_T of *s-trans*-**12** is assigned as 53 kcal/mol (56 − 3 kcal/mol).

This method of assigning triplet energies gives results similar to those determined spectroscopically for the 1,3-pentadienes. The vertical triplet energies of *s-trans,trans*- and *s-trans,cis*-1,3-pentadiene are 59 and 57 kcal/mol, respectively, as determined by the oxygen perturbation method.[15a] The inflection points in the $(t/c)_{PSS}$ plot for 1,3-pentadiene occur at 62 and 60 kcal/mol triplet energy, which corresponds to triplet energies of 59 and 57 kcal/mol for *s-trans,trans*-1,3-pentadiene and *s-trans,cis*-1,3-pentadiene, respectively.

Figure 2 shows a very curious double maxima in the $(t/c)_{PSS}$ plot. A third inflection point is observed at 54 kcal/mol. Below this energy the rate of transfer to *s-cis*-**13** is no longer diffusion-controlled, and only transfer to *s-cis*-**12** is diffusion-controlled, causing preferential excitation of *s-cis*-**12**, and thus the percentage of **13** again increases in the photostationary state. We assign the triplet energy of *s-cis*-**13** as 51 kcal/mol (54 − 3 kcal/mol). A final inflection point occurs at 47 kcal/mol where now energy transfer to *s-cis*-**12** is no longer diffusion-controlled. Thus, we assign the triplet energy of *s-cis*-**12** as 43 kcal/mol (47 − 3 kcal/mol). We are not able to assign the triplet energies of *s-cis*-**8** and *s-cis*-**6** from Figure 1 because a second maxima is not observed with the 1-(1-propenyl)cyclopentene system.

Figure 2 also allows us to estimate the decay ratio (k_7/k_8) for the *s-cis*-p^3 state. Below 56 kcal/mol the energy transfer is occurring at the diffusion-controlled rate for both *s-cis*-**12** and *s-cis*-**13**, and thus the $(t/c)_{PSS}$ value below 56 kcal/mol should equal the cis-p^3 decay ratio. Unfortunately, since the triplet energies of *s-trans*-**12** and *s-cis*-**13** are relatively close (53 and 51 kcal/mol, respectively), we can assign only a rough estimate of 1.0 for this decay ratio. This is the lowest observed value for the $(t/c)_{PSS}$ below the inflection point at 56 kcal/mol. Of course, the decay ratio could be significantly lower than our estimated value.

It is quite interesting that we observe the double maxima curve with the 1-(1-propenyl)cyclohexene system and not with the 1-(1-propenyl)cyclopentene system. Furthermore, no other diene system, to our knowledge, gives such a double-maxima curve. The initial results from photosensitized cis/trans isomerization of stilbene gave double-maxima curves.[15a] However, these were soon shown to be artifacts.[23] Points for donors that were found to form complexes with stilbene or that underwent some photodecomposition were discarded. The new plots showed only one maximum.[24] We have discarded points for the same sensitizers eliminated by Hammond. Furthermore, all of our cis/trans isomerizations gave chemical yields of at least 95%. Thus, we believe that our results are not due to such extraneous factors.

We first considered that the double maxima in Figure 2 might be caused by the presence of an unusualy high concentration of the s-cis,cis isomer in the 1-(1-propenyl)cyclohexene system as compared to the 1-(1-propenyl)cyclopentene system. Dreiding models indicate that the equilibrium between *s-trans*-**12** and *s-cis*-**12** might have a larger percentage of the s-cis isomer than the equilibrium between *s-trans*-**6** and *s-cis*-**6** (see Scheme V). We chose to probe this question using the second-order rate constant for Diels–Alder reaction of these dienes with maleic anhydride. We first studied the reaction of maleic anhydride with 1-vinylcyclohexene as a model system for the 1-(1-propenyl)cycloalkenes. We obtained an activation energy (12.5 kcal/mol) for 1-vinylcyclohexene that is similar to that found for other Diels–Alder additions of 1,3-dienes to maleic anhydride.[19,20] The Diels–Alder reaction can occur only from the s-cis conformation, and thus the rate of this reaction will be a function of the amount of each isomer present in the s-cis conformation. Since many other factors are involved as well, we employed the Diels–Alder rate ratios of **8**/**6** and **13**/**12**. This should eliminate rate differences arising from the different ring sizes. If there is a significantly different amount of s-cis isomer present in the cyclohexyl system as compared to the cyclopentyl system, then these two rate ratios should be significantly different. The cis isomers, as expected, reacted considerably slower than the trans isomers, and thus the cis isomer kinetics were run at a higher temperature. The results, shown in Table V, reveal that these two systems give identical rate ratios. The cyclopentyl isomers react about 3 times more slowly than the cyclohexyl isomers, although it is not clear from models why this should be the case. However, since both systems give an identical rate ratio, this rules out different amounts of s-cis,cis isomers in the cyclopentyl and cyclohexyl systems being responsible for the double maxima in Figure 2.

A second possible explanation for the double maxima in Figure 2 involves a consideration of the decay ratios for the s-cis-p^3 states (k_7/k_8) and the s-trans-p^3 states (k_5/k_6). The decay ratio for the s-trans-p^3 states is actually the $(t/c)_{PSS}$ value for the high-energy sensitizers and thus is easily determined as the constant value of the $(t/c)_{PSS}$ above the first inflection point. For most systems that have been measured, the s-trans-p^3 decay ratio is near unity. We propose that for most systems, including the 1-(1-propenyl)cyclopentene system, the s-cis-p^3 decay ratio

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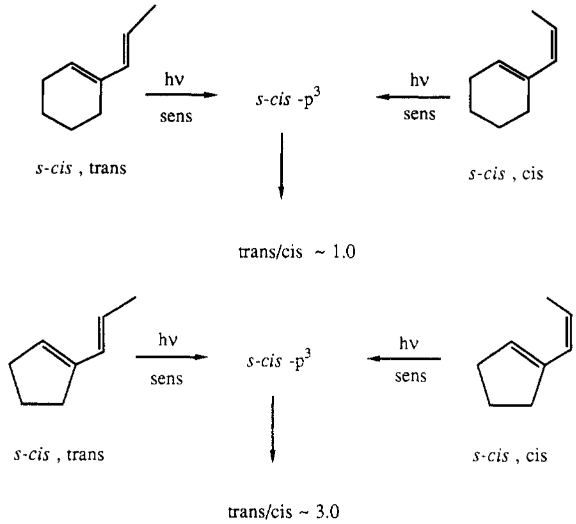
[22] Lowry, T. H.; Richardson, K. S. *Mechanism and Theory in Organic Chemistry*, 3rd ed.; Harper and Row: New York, 1987; p 920.

[23] Valentine, D.Ph.D. Thesis, California Institute of Technology, Pasadena, CA, 1965.

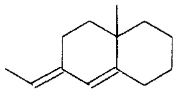
[24] Herkestroeter, W. G.; Hammond, G. S. *J. Am. Chem. Soc.* **1966**, *88*, 4769–4777.

Scheme VI



is considerably larger than 1.0, so that when energy transfer is occurring efficiently to only the s-cis isomers, there is no drop in the $(t/c)_{PSS}$ ratio due to the high value of the s-cis-p^3 decay ratio. However, if the s-cis-p^3 decay ratio was about unity, one would see the decrease observed in Figure 2. Our proposal is illustrated in Scheme VI.

If this proposal is valid, then a 1-(1-propenyl)cyclohexene system configurationaly locked into the s-trans conformation would give a high-energy sensitizer decay ratio near unity, while a similar molecule conformationally locked in the s-cis conformation would also give a high-energy sensitizer decay ratio near unity. We selected the two molecules **20** and **27** as models of the s-trans and s-cis locked systems. Figure 3 shows only a single maximum and a high-energy decay ratio of about unity as predicted for the s-trans locked system, 2-ethylidene-10-methyl-1-(9)-octalin (**19** and **20**). This finding is consistent with our proposal, but unfortunately we have not yet been successful in the synthesis of **27**. We are currently pursuing the synthesis of **27** and other s-cis and s-trans locked cyclohexyl systems.



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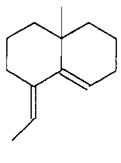
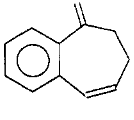


27

Other explanations are possible for the double maxima in Figure 2. An obvious explanation would involve the formation of exiplexes with the low-energy sensitizers. Yang has provided evidence that singlet exiplexes formed between anthracene and 1,3-dienes can regenerate the 1,3-dienes.[25] This provides another mechanism for cis/trans isomerization. Finally, one should also consider the Schenck mechanism[26] for cis/trans isomerization of dienes in which a low-energy triplet sensitizer adds to the diene to form an allylic radical that can revert to diene or form addition products.[27] We tentatively rule out both exiplexes and radical intermediates as explanations for the double maxima in Figure 2 primarily since these two mechanisms would also generate considerable amounts of addition products. In all cases the chemical yield of cis/trans isomerization was greater than 95%, which provides strong evidence against these other mechanisms.

The triplet sensitized photolysis of the 1-(1-propenyl)cycloheptene system (**17** and **18**) proceeds with both cis/trans isomerization of the propenyl group and dimerization. Unfortunately, both reactions proceed competitively so that we could not measure accurate $(t/c)_{PSS}$ values. A reasonable mechanism for the dimerization involves cis/trans isomerization of the endocyclic double bond and then cycloaddition of this *trans*-cycloheptene moiety to either of the double bonds in dienes **17** and **18**. This provides for a total of 16 possible cyclobutane dimers. GC analysis indicates that at least five dimers were formed, but they could not be successfully separated, although we did obtain two sets of product mixtures that are reasonably assigned as cis/trans isomers of dimers **22** and **23**. Hart has observed the triplet-state dimerization of the conjugated cycloheptene **28**, which was shown to proceed via addition of the *trans*-cycloheptene moiety to the ground-state cycloheptene.[28] However, *trans*-cycloheptene gives less than 1% of cyclodimers formed via [2a+2s] cycloaddition of the trans isomer to the cis isomer.[29] The major thermal reaction (>90%) of *trans*-cycloheptene is isomerization to the cis isomer, while *trans*-1-phenylcycloheptene generates small amounts of thermal dimerization products.[30] Kropp has shown that *trans*-cyclohexene gives cyclodimers as the major products, while *trans*-cycloheptene will only give dimers in the presence of Cu^I salts.[31] He has proposed that ring strain is the key to *trans*-cycloalkene dimerization. However, other factors must also be relatively important since the trans endocyclic isomers of **17** and **18** cannot be significantly more strained than *trans*-cycloheptene itself. Perhaps conjugation is the key since **28** readily dimerizes and 2-cycloheptenone also gives significant amounts of dimer formed via cycloaddition of the trans isomer to the cis isomer.[30] We are continuing to investigate the factors responsible for dimerization in *trans*-cycloheptene systems.



28

Experimental Section

General Methods. Nuclear magnetic resonance spectra (NMR) were recorded on a Varian EM-390 spectrometer with CCl_4 or $CDCl_3$ as solvent and tetramethylsilane as internal standard. Analytical gas chromatography (GC) was carried out on a Perkin-Elmer Model 881 gas chromatograph with a 20 ft × $^1/_8$ in. column packed with 15% Carbowax 20M on 60/80 Chromosorb W (column a), a 10 ft × $^1/_8$ in. column packed with 15% DC-200 on 60/80 Chromosorb W (Column b), or a 10 ft × $^1/_8$ in. column packed with 0.1% SP-1000 on Carbopack (column c). Preparative GC was carried out on a Varian 90-P gas chromatograph using

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[25] (a) Yang, N.-C. C.; Shold, D. M. *J. Chem. Soc., Chem. Commun.* **1978**, 978. (b) Yang, N.-C. C.; Srinivasachar, K.; Kim, B.; Libman, J. *J. Am. Chem. Soc.* **1975**, *97*, 5006–5008.

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[30] Joussot-Dubien, J.; Bonneau, R.; Fornier de Violet, P. In *Excited States in Organic Chemistry and Biochemistry*; Pullman, B., Goldblum, N., Eds.; Reidel Publishing Co.: Dordrecht, Holland, 1977; p 271.

[31] Kropp, P. J.; Snyder, J. J.; Rawlings, P. C.; Favel, H. G. *J. Org. Chem.* **1980**, *45*, 4471–4474.

a 10 ft × 1/4 in. column packed with 15% Carbowax 20 M on 60/80 Chromosorb Q (column d), a 10 ft × 1/4 in. column packed with 3% OV-17 on 60/80 Chromosorb W (column e), and a 10 ft × 1/4 in. column packed with 15% FFAP on 60/80 Chromosorb G (column f). Infrared (IR) spectra were recorded on a Perkin-Elmer 137 Infracord as either neat samples on NaCl salt plates or as KBr pellets prepared by using a Wilkins Mini Press. Ultraviolet (UV) spectra were recorded on a Perkin-Elmer Model 552 spectrometer. GC mass spectra were determined on an AEI-MS-9 electron impact spectrometer (70 eV) with column c. Melting points were recorded by using either Electrothermal or Thomas-Hoover capillary melting point apparatuses and are uncorrected. Combustion analyses were done by Chemalytics, Inc., Tempe, AZ. Anhydrous magnesium sulfate was used for all drying operations.

Chemicals and Reagents. Naphthalene, benzophenone, benzhydrol, acetophenone, and 1-acetonaphthone were Matheson, Coleman, and Bell (MCB) reagent grade chemicals. Naphthalene and benzophenone were recrystallized from absolute ethanol; benzhydrol was recrystallized from 30–60 petroleum ether; acetophenone and 1-acenaphthone were distilled prior to use. Acetone and acetonitrile were MCB spectrograde chemicals and were used without further purification. 9-Fluorenone (98%), thioxanth-9-one, Michler's ketone {4,4′-bis(dimethylamino)-benzophenone}, 1,2,3,4-dibenzanthracene (97%), 2-acenaphthone (99%), flavone, and 2-naphthaldehyde (98%) were supplied by Aldrich Chemical Co. and sublimed prior to use. 1-Chloronaphthalene (99%) and 1-naphthaldehyde were obtained from Aldrich and distilled prior to use. 1,2,5,6-Bibenzanthracene (97%) was obtained from Aldrich and recrystallized from 1:1 benzene/ethanol prior to use. Fluoranthene and 1,2-benzanthracene were obtained from CalBiochem. Fluoranthene was recrystallized from absolute ethanol, and 1,2-benzanthracene was sublimed prior to use. 9,10-Dimethyl-1,2-benzanthracene and 1-benzoylnaphthalene were ICN Pharmaceuticals, Inc., reagent grade chemicals and sublimed prior to use. Reagent grade pyrene was obtained from K&K laboratories and sublimed before use. Benzene (MCB spectrograde) was washed with concentrated H_2SO_4 until the acid phase no longer turned dark, then washed with saturated NaCl and water, dried, and then distilled from CaH_2 prior to use. Fisher Chemical Co. reagent grade dimethyl sulfoxide (DMSO) was distilled from CaH_2 prior to use. Raney nickel was obtained from Davidson Specialty Chemical Co. 1-(1-Propynyl)cyclopentanol was purchased from Farchan Division, Story Chemical Co., and 1-(1-ethynyl)cyclohexanol was purchased from MCB. Maleic anhydride was sublimed before use.

1-(1-Propynyl)cyclopentene (5). A solution of 50 mL of $POCl_3$ in dry pyridine (50 mL) was added dropwise to a stirred solution of 1-(1-propynyl)cyclopentanol (**4**, 90 g, 0.726 mol) in 50 mL of dry pyridine at such a rate as to maintain a gentle reflux. After the addition was complete, the mixture was heated at 90 °C for 45 min, and then 600 mL of H_2O was added to dissolve the pyridinium salts. The resulting mixture was extracted with 3 × 150 mL of 30–60 °C petroleum ether. The combined organic extracts were washed with 3 × 100 mL of 5% HCl and 2 × 100 mL of saturated $NaHCO_3$ and dried. The mixture was fractionally distilled to give 57.0 g (74%) of **5**: bp 72–74 °C (39 Torr); ^1H NMR (CCl_4) δ 1.88 (s, 3 H), 1.5–2.0 (m, 2 H), 2.1–2.5 (m, 4 H), 5.67 (s, 1 H); IR (neat) 2900, 1440, 1040, 950, 810 cm^{-1}. Anal. Calcd for C_8H_{18}: C, 90.51; H, 9.49. Found: C, 90.21; H, 9.28.

***cis*-1-(1-Propenyl)cyclopentene (6).** A solution of **5** (1.0 g, 9.4 mmol) in 50 mL of piperidine was hydrogenated over 50 mg of 5% Pd on $CaCO_3$ in a 500-mL Paar hydrogenation flask. The initial hydrogen pressure was 35 lb/in.^{2}, and the reaction was stopped after a drop in pressure of 7.8 lb/in.^{2} (9.4 mmol). H_2O (500 mL) was added to the reaction vessel, and the resulting mixture was extracted with 3 × 50 mL of 30–60 °C petroleum ether. The combined organic extracts were washed with 2 × 50 mL of 5% HCl and 2 × 50 mL of saturated $NaHCO_3$ and dried, and the petroleum ether was removed by rotary evaporation. GC analysis on column c showed five components with 40% **6** and 9% **8**. Preparative GC on column f gave pure samples of the cis diene **6**: ^1H NMR (CCl_4) δ 1.78 (d, 3 H, J = 6.1 Hz), 2.1–2.2 (m, 2 H), 2.1–2.7 (m, 4 H), 5.0–5.5 (m, 2 H), 5.81 (d, 1 H, J = 11.7 Hz); IR (neat) 3020, 1640, 1450, 965, 820 cm^{-1}; UV (EtOH) λ_{max} 237 nm (ϵ = 17 500); MS (low resolution) m/e 108.1 (54%), 92.8 (100%); calculated parent 108.2. Anal. Calcd for C_8H_{12}: C, 88.82; H, 11.18. Found: C, 88.49; H, 10.87.

***trans*-1-(1-Propenyl)cyclopentanol (7).** Ammonia (500 mL) was condensed into a 1-L flask equipped with a dry-ice condensor and drying tube, mechanical stirrer, and nitrogen inlet. Sodium (11.7 g, 0.509 mol) was slowly added to the stirred ammonia over a period of 1 h. Alcohol **4** (30.0 g, 0.242 mol) was added slowly, and the resulting mixture was refluxed for 2 h. A few crystals of NH_4Cl were then added to destroy the remaining sodium followed by cautious addition of H_2O (300 mL). The resulting mixture was extracted with 3 × 100 mL of diethyl ether, and the combined ethereal extracts were washed with 2 × 150 mL of 5% HCl and 2 × 150 mL of saturated $NaHCO_3$ and dried, and the ether was removed by rotary evaporation. The crude product was distilled through a 16-in. spinning band column to give 10.6 g (35%) of **7**: bp 65–67 °C (11 Torr); ^1H NMR (CCl_4) δ 1.65 (d, 3 H, J = 6.6 Hz), 1.3–2.0 (m, 9 H), 5.25–5.75 (m, 2 H); IR (neat) 3300, 2900, 1450, 1380, 1000, 975 cm^{-1}. Anal. Calcd for $C_8H_{14}O$: C, 76.14; H, 11.18. Found: C, 75.90; H, 11.08.

***trans*-1-(1-Propenyl)cyclopentene (8).** With use of the procedure outlined for the preparation of **5**, 9.0 g (0.071 mol) of alcohol **7** was converted to 7.01 g (91%) of **8**. Preparative GC on column f provided pure samples of the trans diene **8**: ^1H NMR (CCl_4) δ 1.72 (d, 3 H, J = 6 Hz), 1.90 (t, 2 H, J = 6.6 Hz), 2.32 (t, 4 H, J = 6.6 Hz), 5.40 (br s, 1 H), 5.36 (overlapping pair of doublets confirmed by decoupling experiments, 1 H, J_1 = 6.0 Hz, J_2 = 15.3 Hz), 6.09 (d, 1 H, J = 15.3 Hz); IR (neat) 3010, 2900, 1440, 960, 770 cm^{-1}; UV (EtOH) λ_{max} 235 nm (ϵ = 24 600). Anal. Calcd for C_8H_{12}: C, 88.82; H, 11.18. Found: C, 88.59; H, 10.92.

1-Ethynylcyclohexene (10). With use of the procedure outlined for the preparation of **5**, 100 g (0.806 mol) of 1-(1-ethynyl)cyclohexanol (**9**) was converted to 73.5 g (86%) of **10**: bp 62–63 °C (44 Torr) (lit.[32] bp 52–53 °C (30 Torr)); ^1H NMR (CCl_4) δ 1.6 (m, 4 H), 2.1 (m, 4 H), 2.75 (s, 1 H), 6.2 (m, 1 H); IR (neat) 3325, 1627 cm^{-1}.

1-(1-Propynyl)cyclohexene (11). A small amount of $FeCl_3$ (0.05 g) and a 0.5-g portion of lithium were added with stirring to 1 L of liquid ammonia. The solution immediately turned a deep blue color, and after stirring for 30 min, it turned an opaque grey color indicative of $LiNH_2$ formation. The remainder of the lithium (4.86 g, 0.70 mol total) was added over a period of 1 h and then stirred for an additional 2 h. To this stirred mixture was added dropwise 73.5 g (0.693 mol) of terminal alkyne **10** followed by dropwise addition of CH_3I (117 g, 0.82 mol). The mixture was stirred for 12 h while the ammonia was allowed to evaporate. The residue was extracted with 2 × 100 mL of 30–60 °C petroleum ether. The combined organic extracts were washed with 2 × 100 mL of 5% HCl, 2 × 100 mL of saturated $NaHCO_3$, and 100 mL of H_2O and dried. The petroleum ether was removed by rotary evaporation, and the crude product was distilled through a 16-in. spinning band column to give 40.8 g (49%) of **11**: bp 60–64 °C (10 Torr) (lit. bp[33] 54–55 °C (4.5 Torr)); ^1H NMR (CLc_4) δ 1.6 (br s, 4 H), 1.88 (s, 3 H), 2.0 (br multiplet, 4 H), 5.88 (br s, 1 H).

***cis*-1-(1-Propenyl)cyclohexene (12).** With use of the procedure outlined for the preparation of **6**, 2.0 g (0.167 mol) of **11** in 75 mL of piperidine was hydrogenated over 5% Pd on $CaCO_3$ (100 mg). GC analysis (column a) indicated four components including 84% **12** and 7% **13**. Preparative GC (column f) gave pure samples of **12**: ^1H NMR (CCl_4) δ 1.6 (m, 4 H), 1.75 (d, 3 H, J = 6.1 Hz), 2.1 (m, 4 H), 5.1–5.9 (m, 3 H); IR (neat) 3020, 2950, 1640, 1450, 920, 850, 810, 720 cm^{-1}; UV (EtOH) λ_{max} 230 nm (ϵ = 12 800) [lit.[33] λ_{max} 229 nm (ϵ = 12 600)].

***trans*-1-(1-Propenyl)cyclohexene (13). Method A.** A 1.0-g (0.0082 mol) sample of cis diene **12** in 100 mL of 60–90 °C petroleum ether (degassed by bubbling nitrogen through the solution for 10 min) saturated with 9,10-dibromoanthracene was irradiated in a Pyrex vessel with a 450-W medium-pressure Hanovia mercury lamp for 200 min with continual nitrogen purging. GC analysis (column b) indicated the sample to be 95% **13** and 5% **12**. The petroleum ether was partially evaporated, and the 9,10-dibromoanthracene removed by filtration. The remainder of the petroleum ether was removed by rotary evaporation, and prep-

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arative GC (column f) of the residue gave pure samples of **13**: ^{1}H NMR δ 1.6 (m, 4 H), 1.72 (d, 3 H, J = 6 Hz), 2.05 (br s, 4 H), 5.1–5.75 (m, 2 H), 5.98 (d, 1 H, J = 15.5 Hz); IR (neat) 3020, 2900, 1620, 1450, 965, 910, 760 cm^{-1}; UV (EtOH) λ_{max} 232 nm (ϵ = 20400) [lit.[33] λ_{max} 230 nm (ϵ = 26800)].

Method B. The following is a modification of the method of Nenitzescu and Necsoiu.[9] To 8.03 g (0.33 mol) of Mg in 50 mL of dry ether under N_2 was added dropwise 25 g (0.11 mol) of 1,5-dibromopentane in 250 mL of dry ether. The mixture was then refluxed for 1 h and cooled to room temperature (RT), and 25.1 g (0.22 mol) of ethyl crotonate in 50 mL of dry ether was added dropwise with stirring. The resulting mixture was stirred at RT for an additional 12 h, 100 mL of 5% HOAc was added, and the ether layer was removed. The organic layer was washed with 2 × 100 mL of saturated $NaHCO_3$ and dried. The ether was removed by rotary evaporation, and the excess ethyl crotonate destroyed by refluxing the crude mixture for 4 h in 70 mL of 40% alcoholic KOH. The EtOH was removed by rotary evaporation, and 100 mL of H_2O was added to the residue, which was then extracted with 2 × 50 mL of ether. The combined ether extracts were dried, and the ether removed by rotary evaporation to give 4.6 g (30%) of crude *trans*-1-(1-propenyl)cyclohexanol (**14**): ^{1}H NMR (CCl_4) δ 1.15 (s, 1 H), 1.3–1.6 (br s, 10 H), 1.6–1.8 (m, 3 H), 5.5–5.7 (m, 2 H). Crude **14** (4.0 g, 28 mmol) was refluxed for 1 h in 25 mL of ether containing 25 mg of *p*-toluenesulfonic acid. The resulting solution was washed with 2 × 25 mL of saturated $NaHCO_3$ and dried, and the ether removed by rotary evaporation. The crude product was distilled to give 1.1 g (32%) of **13**: bp 50–53 °C (3 Torr) (lit.[9] bp 56 °C (3 Torr)).

1-(1-Propynyl)cycloheptanol (15). Propyne (18 g, 0.45 mol) was bubbled into a solution of 260 mL of 1.6 M *n*-butyllithium in hexane contained in a 500-mL flask equipped with a dry-ice condensor. To this lime-green slush was slowly added dry cycloheptanone (46.6 g, 0.416 mol) in 100 mL of dry hexane, and the resulting mixture was stirred for 12 h. Then 250 mL of H_2O was added, and the resulting mixture extracted with 3 × 100 mL of diethyl ether. The combined ether extracts were washed with 2 × 200 mL of H_2O and dried, and the ether was removed by rotary evaporation. The crude product was fractionally distilled to give 19.2 g (30%) of **15**: bp 108–11 °C (9 Torr); ^{1}H NMR (CCl_4) δ 1.55 (br m, 8 H), 1.75 (br m, 4 H), 1.79 (s, 3 H), 2.22 (s, 1 H); IR (neat) 3600, 3400, 2950, 1460, 1030, 780 cm^{-1}. Anal. Calcd for $C_{10}H_{16}O$: C, 78.90; H, 10.59. Found: C, 79.08; H, 10.43.

1-(1-Propynyl)cycloheptene (16). Using the procedure outlined for the preparation of **5**, 17 g (0.112 mol) of 1-(1-propynyl)cycloheptanol (**15**) was converted to 10.6 g (71%) of **16**: bp 64–69 °C (3.5 Torr); ^{1}H NMR (CCl_4) δ 1.55 (br m, 6 H), 1.83 (s, 3 H), 2.15 (br m, 4 H), 5.88 (t, 1 H, J = 6.2 Hz); IR (neat) 2910, 2850, 1445, 960, 850 cm^{-1}. Anal. Calcd for $C_{10}H_{14}$: C, 89.49; H, 10.51. Found: C, 89.29; H, 10.38.

***cis*- and *trans*-1-(1-Propenyl)cycloheptene (17 and 18, Respectively).** Using the procedure outlined for the preparation of **6**, 1.0 g (7.5 mmol) of **16** in 40 mL of piperidine was hydrogenated over 5% Pd on $CaCO_3$ (50 mg). GC analysis (column a) indicated the crude product to be 45% **17** and 7% **18**. Preparative GC (column e) gave pure samples of both dienes. **17**: ^{1}H NMR (CCl_4) δ 1.6 (br m, 6 H), 1.70 (d, 3 H, J = 6.0 Hz), 2.25 (br m, 4 H), 5.0–5.75 (m, 3 H); IR (neat) 2920, 1640, 1445, 1360, 1060, 860 cm^{-1}; UV (EtOH) λ_{max} 236 nm (ϵ = 9920). Anal. Calcd for $C_{10}H_{16}$: C, 88.16; H, 11.84. Found: C, 87.92; H, 11.79. **18**: IR (neat) 2910, 1450, 965, 850, 775 cm^{-1}; UV (EtOH) λ_{max} 239 nm (ϵ = 20000).

1-Vinylcyclohexene. With use of the procedure outlined for the preparation of **5**, 2.0 g (0.019 mol) of 1-ethynylcyclohexene (**10**) in 75 mL of piperidine was converted to 1.50 g (72%) of 1-vinylcyclohexene: ^{1}H NMR ($CDCl_3$) δ 1.5–1.8 (m, 4 H), 2.0–2.3 (m, 4 H), an ABX pattern with lines at 4.85, 5.00, and 5.18 (AB portion, 2 H) and lines at 6.22, 6.32, 6.41, and 6.52 (X portion, 1 H), 5.78 (m, 1 H).

Photostationary State Determinations. A 0.03 M solution of *cis*- and/or *trans*-1-(1-propenyl)cycloalkene and various concentrations of sensitizer were prepared in benzene. At least four different sensitizer concentrations between 0.01 and 0.05 M were employed. Nonane was added as an internal standard to determine the chemical yield of the isomerization by GC. The samples were contained in a 10 × 1 cm Pyrex tube equipped with a stopcock and a side arm sealed with a septum for sampling the mixture by syringe. The samples were freeze–thaw degassed through three cycles at 10^{-4} Torr. Dry nitrogen (1 atm) was then added, and the samples were irradiated in a Rayonet photochemical reactor equipped with 16 300-nm bulbs or 16 350-nm bulbs. The samples were rotated by a turntable within the reactor and analyzed by GC using column c for the cyclopentene system and column b for the cyclohexene system. The trans/cis ratios were measured from the GC peak areas of each isomer at the photostationary state. The mass-to-area response factors (Rf) were calculated by the internal standardization method where Rf = (mass of diene/area of diene) × (area of standard/mass of standard). The same Rf values were obtained for the *cis*- and *trans*-1-(1-propenyl)cyclopentenes and also for the *cis*- and *trans*-1-(1-propenyl)cyclohexenes. Therefore, the trans/cis GC area ratios are equivalent to the trans/cis mass ratios for these 1-(1-propenyl)cycloalkenes. The $(t/c)_{PSS}$ values reported in Tables II–IV were obtained by extrapolating a plot of the experimental $(t/c)_{PSS}$ vs sensitizer concentration to infinite dilution. Least-squares analysis of these plots gave R values of at least 0.99 in every case.

Quantum Yields. (a) Actinometry. The benzophenone/benzhydrol actinometer system was employed.[34] A series of five benzophenone/benzhydrol mixtures in benzene (2 mL) were prepared with each sample 0.10 M in benzophenone and varying concentrations of benzhydrol (0.30, 0.10, 0.07, 0.05, and 0.04 M). The samples were degassed (10^{-4} Torr) through three freeze-thaw cycles in identical 1 × 10 cm Pyrex tubes equipped with stopcocks and side arms sealed with a septum. The 0.10 M benzophenone/0.10 M benzhydrol sample was selected as the actinometer solution. The five solutions were rotated on a turntable equidistant from the 16 350-nm bulbs housed in the Rayonet reactor. The photolysis time was 5.0 min at 20 °C. The change in benzophenone concentration in each tube was calculated by the n–π^* absorption band of the benzophenone. The intercept of a plot of the ratio of the concentration of benzophenone photoreduced in the 0.1 M benzhydrol solution to the concentration of benzophenone photoreduced in the other solutions gives a value of 0.79 for the quantum yield of benzophenone photoreduction in the 0.1 M benzhydrol/0.1 M benzophenone solution.

(b) Cis/Trans Photoisomerization Quantum Yields. A 2-mL benzene solution 0.1 M in both benzhydrol and benzophenone contained in a 1 × 10 cm Pyrex photolysis tube and a 2-mL benzene solution 0.06 M in 1-(1-propenyl)cycloalkene, 0.05 M in benzophenone, and 0.05 M in nonane contained in an identical 1 × 10 cm Pyrex photolysis tube were degassed (10^{-4} Torr) through thre freeze-thaw cycles. Both samples were photolyzed for 3 min at 20 °C on a turntable (equidistant from the 16 350-nm bulbs) housed in the Rayonet reactor. The quantum yield for cis/trans photoisomerization was calculated from the decrease in absorption of the benzophenone in the actinometer tube and the reduced area of the original isomer in the isomerization tube.

Photosensitization of 17 and 18. A mixture of **17** (86%) and **18** (14%) (0.66 g, 4.8 mmol) and benzophenone (1.14 g, 6.2 mmol) in acetonitrile (125 mL) was placed in a Pyrex photolysis tube, degassed by bubbling N_2 for 10 min, and then irradiated for 18 min with a medium-pressure Hanovia mercury lamp under continuous N_2 purging. The acetonitrile was removed by rotary evaporation, and the benzophenone removed by column chromatography over neutral alumina in hexane. Removal of the hexane yielded 0.6 g of crude product. GC analysis on column a revealed four products with **22** and **23** each about 40% of the mixture. Preparative GC on column d provided samples of **22** and **23**. **22**: ^{1}H NMR ($CDCl_3$) δ 0.87 (three overlapping doublets, 3 H, J = 6.6 Hz), 1.0–2.0 (br m, 20 H), 1.71 (d, 3 H, J = 6 Hz), 1.8–2.3 (br m, 3 H), 4.8–5.1 (m, 2 H), 5.45 (m, 1 H); MS (low resolution) *m/e* 272, 136 (100%), calcd parent 272. **23**: ^{1}H NMR ($CDCl_3$) δ 0.7–1.8 (br m, 20 H), 1.77 (d, 6 H, J = 6.0 Hz), 2.0–2.6 (br m, 2 H), 5.0–6.2 (m, 4 H); MS (low resolution) *m/e* 272, 136 (100%), calcd parent 272.

10-Methyl-1(9)-octalone-2 (21). With use of the procedure of Marshall and Fanta[11] 2 g (1 mol) of 2-methylcyclohexanone

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was converted to 48 g (30%) of **21**: bp 96–98 °C (2 Torr) (lit.[5] bp 82–83 °C (0.7 Torr)); ^{1}H NMR (CCl_4) δ 1.4–2.6 (m, 12 H), 1.3 (s, 3 H), 5.5 (s, 1 H); IR (neat) 1670, 1595, 1450, 1325, 1255, 1205, 1190, 860 cm^{-1}.

2-Ethylidene-10-methyl-1(9)-octalin (19 and 20).[10] Dry dimethyl sulfoxide (DMSO, 10 mL) was added to 1.2 g (0.030 mol) of pentane-washed sodium hydride under nitrogen, and the mixture was stirred at 70 °C until hydrogen evolution ceased (45 min). The resulting slurry was cooled to RT, and 12.5 g (0.035 mol) of ethyltriphenyl phosphonium iodide (prepared in 73% yield from triphenylphosphine and ethyl iodide in toluene) was added followed by 25 mL of dry DMSO. The bright orange-colored mixture was stirred for 20 min at RT followed by dropwise addition of ketone **21** (4.10 g, 0.025 mol) in 25 mL of dry DMSO over a period of 15 min. The resulting mixture was stirred at 60 °C for 36 h and cooled to RT, and 50 mL of pentane followed by 50 mL of H_2O was added to the mixture. The triphenylphosphine oxide was removed by filtration, and the filtrate was extracted with 4 × 100 mL of pentane. The combined pentane extracts were washed with 3 × 100 mL of 1:1 H_2O/DMSO and dried, and the pentane was removed by rotary evaporation. Distillation afforded 2.65 g (60.2%) of *cis*- and *trans*-2-ethylidene-10-methyl-1(9)-octalin (**19** and **20**, respectively): bp 90–92 °C (2 Torr).

Kinetics of the Diels–Alder Addition of Maleic Anhydride to the 1-(1-Propenyl)cycloalkenes. An NMR tube containing maleic anhydride (11.3 mg, 15.3 mmol), 4 mL of $CDCl_3$, and 10 μL of $CHCl_3$ was equilibrated in the variable-temperature probe of the EM-390 spectrometer at the desired temperature (calibrated by using the ethylene glycol peak shift method). To this tube was added 15.3 mmol of the desired diene. The decrease in the maleic anhydride peak height, with the $CHCl_3$ peak height as a standard, was followed. The second-order rate constants for these reactions, employing equal concentrations of diene and maleic anhydride, were determined by using the following equation:

$$1/(d - x) - 1/d = kt$$

where d is the initial concentration of maleic anhydride and x is the amount of maleic anhydride reacted at time t. The slope of a plot of $1/(d - x)$ vs t provides the second-order rate constant.[35] The adducts were not isolated, but they showed characteristic ^{1}H NMR peaks for the alkene proton at δ 5.6–5.7 in the adducts from **6** and **8** and at δ 5.2–5.3 in the adducts from **12** and **13**. All of the adducts showed the protons α to the carbonyl groups at δ 3.2–3.4. Finally, the saturated methyls appeared as doublets at δ 1.12 in the adducts from **6** and **12** while they appeared at δ 1.24 and δ 1.42 in the adducts from **13** and **8**, respectively.

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Pressure-Induced Diastereoselectivity in Photoinduced Diels–Alder Reactions[†]

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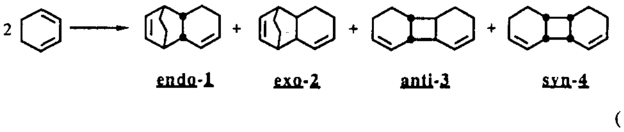
The product distributions for the photochemical electron transfer and triplet–triplet energy-transfer-induced dimerization of 1,3-cyclohexadiene (CHD) were determined as a function of pressure and solvent in the range of 0.1–203 MPa. In the case of the photochemically (dicyanonaphthalene sensitized) induced electron-transfer dimerization, differences in activation volumes for the formation of *endo*-**1** and *exo*-**2** adduct are small and positive in acetonitrile (ca. +1 to +2 cm^3/mol) but are negative and unusually large (ca. −9 to −12 cm^3/mol) in benzene. The results are consistent with the involvement of different types of solvated ion pairs in the two solvents. Although the product distribution does not change for any of the sensitizers and pressures used in the triplet-sensitized reaction, the efficiency of dimerization was surprisingly both pressure and solvent dependent. The activation volumes for efficiency of dimerization of CHD by triplet–triplet energy transfer fall in the range −22 to +2.1 cm^3/mol and depend on both the triplet energy of the sensitizer and the solvent used.

Introduction

The dimerization of 1,3-cyclohexadiene (CHD) has been investigated (eq 1 and Table I) under a variety of conditions.[1-3] The thermal dimerization requires long reaction times and produces a mixture of the *endo*-**1** and *exo*-**2** Diels–Alder adducts (eq 1) in poor yield. In contrast, the dimerization of CHD induced by means of radical cation catalysis produces good yields of the Diels–Alder adducts.[2,3] In the latter case, both thermal electron acceptors and



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