Cyclobutene Photochemistry.[1] The Photochemistry of *cis*- and *trans*-Bicyclo[5.2.0]non-8-ene

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Direct photolysis of *cis*- and *trans*-bicyclo[5.2.0]non-8-ene in hydrocarbon solution with monochromatic far-UV (185–214 nm) light sources affords *cis,cis*- and *cis,trans*-1,3-cyclononadiene via formal electrocyclic ring opening, cycloheptene (and acetylene) via formal ($\sigma 2s + \sigma 2s$) cycloreversion, and minor amounts of molecular rearrangement products. Product quantum yields have been determined for the 185-nm photolyses. The two isomers lead to similar distributions of the isomeric 1,3-cyclononadienes, with similar quantum yields at 185 nm; the diene mixtures are in both cases weighted in favor of the less thermodynamically stable cis,trans isomer. The product distributions vary only slightly with excitation wavelength over the 185–214-nm range. Quantum yields for direct photoisomerization of *cis,cis*- and *cis,trans*-1,3-cyclononadiene have also been determined. Two mechanisms are considered to explain the nonstereospecificity associated with the ring-opening process: a nonconcerted pathway involving initial cyclobutene bond homolysis and subsequent relaxation of common biradical intermediates, and a pericyclic pathway involving adiabatic, disrotatory ring opening to yield dienes in the first excited singlet state. While the results do not allow a definitive distinction between the two mechanisms, the nonconcerted pathway is suggested to be the more reasonable on the basis of the photobehavior of other cyclobutene derivatives that have been studied. The quantum yield of cycloreversion product is ca. 4 times higher from the cis isomer compared to that from the trans isomer, due to the stereochemical requirements of the process.

Introduction

It has recently been shown that the photochemical ring opening of alkylcyclobutene derivatives in solution proceeds nonstereospecifically.[3-6] Recent studies of the stereochemistry of this reaction have included a series of stereoisomeric monocyclic cyclobutenes (1–3[3,4]), as well as

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a variety of bicyclic derivatives (4–7).[3,5,6] In general, the results for all these compounds appear to conflict with the widely accepted view[7] that the photochemical ring opening of cyclobutene is governed by orbital symmetry selection rules,[8] which predict that the reaction should proceed stereospecifically and in concerted, disrotatory fashion. In fact, there is only a single example in the literature which supports this view.[9]

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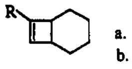

a. R = H
b. R = CH_3
c. R = CF_3

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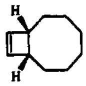

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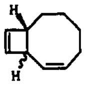

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In principle, there are at least four mechanistic possibilities that could account for the overall nonstereospecificity of the reaction:[3-5] (i) adiabatic, disrotatory π,π^*-state ring opening to yield diene(s) in the first excited singlet state; (ii) competitive ring opening from two (or more) excited states (e.g., the π,π^* and π,R(3s) states); (iii) competitive electrocyclic ring opening from both excited and vibrationally excited ground-state surfaces; and (iv) excited state ring opening by a "nonconcerted" pathway.

The far-UV photolyses of *cis*- and *trans*-1[3] both result in the formation of mixtures of the (three) isomeric 2,4-hexadienes weighted in favor of the formally symmetry-forbidden isomer(s). It has been shown that the preferred formation of formally forbidden diene isomers from *both* cyclobutene stereoisomers is incompatible with the adiabatic electrocyclic ring-opening mechanism. The behavior of 2 and 3 do not allow conclusions as firm as those from 1 to be made since in each case, diene mixtures weighted in favor of the formally allowed isomers are formed upon photolysis in solution.[4]

A potentially better test of the adiabatic electrocyclic ring-opening mechanism can be carried out by comparing the isomeric diene distribution obtained from cyclobutene ring opening with the distribution expected based on independent characterization of the excited-state behavior of the dienes.[3] The analysis can be quite complex, however, depending on the number of diene geometric isomers involved and the similarity between the stable conformers of the dienes and the planar s-cis conformers that would be initially obtained upon concerted cyclobutene ring opening. Compared to monocyclic systems, the analysis is potentially more straightforward for bicyclic cyclobutenes such as 5 since there are only two stable 1,3-diene geometric isomers that are accessible by excited state ring opening.

The distribution of *cis,cis*- and *cis,trans*-1,3-cyclooctadiene obtained from 185-nm photolysis of 5 (R = H) is exactly that which would be predicted if ring opening proceeds by the adiabatic, purely disrotatory mechanism, according to an analysis of the type outlined above.[3] The extraordinary fit of the isomeric diene distribution from 185-nm photolysis of 5 with the adiabatic mechanism may be coincidental, however, since photolysis of the same compound at slightly longer wavelengths (193 nm) leads to a different distribution of isomeric dienes.[5] Furthermore, the stable ground-state conformers of *c,c*- and *c,t*-cyclooctadiene are in fact quite different from the (hypo-

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[1] Part 4 of the series. For Part 3, see ref 4.

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[3] Clark, K. B.; Leigh, W. J. *J. Am. Chem. Soc.* **1987**, *109*, 6086.

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[8] Woodward, R. B.; Hoffmann, R. *The Conservation of Orbital Symmetry*; Verlag Chemie: Weinheim, 1970.

[9] (a) Saltiel, J.; Ng Lim, L.-S. *J. Am. Chem. Soc.* **1969**, *91*, 5404. (b) In fact, we have recently observed rather different results for these compounds, which are more in line with the behavior of 1–6: Leigh, W. J.; Zheng, K. *J. Am. Chem. Soc.*, in press.

0022-3263/91/1956-1574$02.50/0

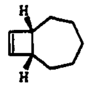
Table I. Product Yields from 185,[a] 193,[b] and 214[c] nm Photolysis of Deoxygenated Pentane Solutions of *cis*- and *trans*-Bicyclo[5.2.0]non-8-ene (8) at 23 °C[d]

compound	wavelength, nm	*c,c*-9	*c,t*-9	10	11	other[e]
	185	12	33	45	4	5
cis-8	193	12	33	43	7	5
	214	15	33	42	≈3	6
	185	15	46	15	18	6
trans-8	193	12	48	22	12	5
	214	14	50	24	7	5

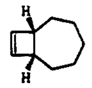
[a] Low-pressure mercury lamp, in conjunction with LiF filter to remove 254-nm component. [b] ArF excimer laser. [c] Zn resonance lamp. [d] Product yields determined from slopes of concentration vs time plots (see Figure 1), for runs monitored between 0.3 and ca. 4% conversion of starting material. The VPC detector was not calibrated. Errors are ca. ±10%. [e] Not identified.

thetical) planar conformers that would be expected if ring opening follows the pericyclic pathway. Thus their photoisomerization behavior may not accurately reflect the torsional decay characteristics of the diene conformers that would be formed via concerted cyclobutene ring opening.

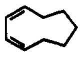
In an effort to provide further insight into the mechanistic details of the photochemical ring opening of alkylcyclobutenes, we have studied the photochemistry of *cis*- and *trans*-bicyclo[5.2.0]non-8-ene (8) in hydrocarbon solution with 185–214-nm light. Because ring opening of 8 can be expected to yield only two isomeric dienes—*cis,cis*- and *cis,trans*-1,3-cyclononadiene (*c,c*- and *c,t*-9, respectively)—mechanistic analysis of the isomeric diene distributions from photolysis of 8 might be more straightforward than is the case with monocyclic derivatives. To this end, quantum yields for the direct cis–trans photoisomerization of *c,c*- and *c,t*-9 have also been determined. The results of this study are reported below.



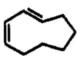
cis-8



trans-8



c,c-9



c,t-9

Results

Cyclobutenes *cis*- and *trans*-8 were synthesized as a 4:1 mixture by a three-step procedure involving triplet-sensitized cycloaddition of maleic anhydride to cycloheptene,[10] acid-catalyzed hydrolysis of the tricyclic anhydrides, and bisdecarboxylation of the resulting bicyclic cyclobutanedicarboxylic acids with lead tetraacetate.[3,4] They were isolated and purified by semipreparative gas chromatography to >99.9% purity. The two isomers were identified on the basis of their ^{1}H and ^{13}C NMR, IR, UV, and mass spectra. In particular, the chemical shifts of the bridgehead protons in the ^{1}H NMR spectra of *cis*- and *trans*-8 are diagnostic of their respective stereochemistries (δ = 2.89 and δ = 2.53 ppm for *cis*- and *trans*-8, respectively).[4]

The ultraviolet absorption spectra of *cis*- and *trans*-8 in deoxygenated cyclohexane solution (not shown) are very similar to those reported previously for *cis*- and *trans*-1, respectively.[4] They each consist of single absorption bands with apparent maxima at 187 nm (ϵ = 4900–5500). In the spectrum of *trans*-8, this absorption band is slightly broader and extends to slightly longer wavelengths than that in the spectrum of the cis isomer. This is a common feature in the spectra of isomeric alkylcyclobutenes.[4] The gas-phase spectra show only edge absorption above 185 nm, which extends (i.e., $\epsilon \leq 50$ M^{-1} cm^{-1}) to ca. 210 nm.

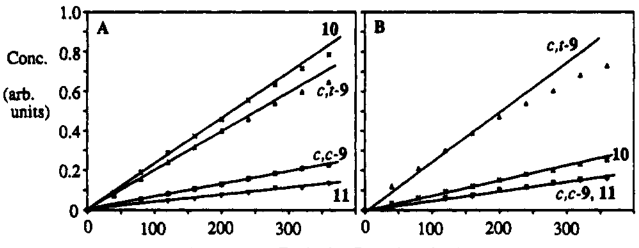
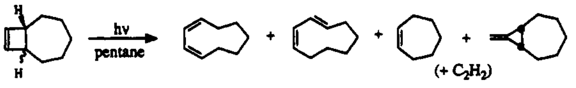


Figure 1. Plots of product concentration (relative to internal standard; uncalibrated detector) versus excitation dose for 193-nm photolysis of deoxygenated 0.02 M pentane solutions of *cis*-8 (a) and *trans*-8 (b). The maximum conversion in these photolyses was ca. 3%.

Photolysis of deoxygenated 0.02 M pentane solutions of *cis*- and *trans*-8 with a filtered[3,11] low-pressure mercury lamp (185 nm) afforded mixtures of the products shown in eq 1. The products, except for acetylene, were identified by co-injection of authentic samples on at least two VPC columns in each case. In both cases, the photolysates also contained two additional minor unidentified products, which were formed in yields less than 3%. Compound *trans*-8 could not be detected as a product from the photolysis of *cis*-8, and vice versa, in yields greater than ca. 1% (the limits of detection of our VPC method). Acetylene was not specifically identified in the photolysis mixtures, but can be assumed to be formed along with 10 in these cases.[3–6,9] Similar experiments were carried out using an argon fluoride excimer laser (193 nm; ca. 20–30-mJ pulses) and a Zn resonance lamp (214 nm) as excitation sources. Solution concentrations were 0.02 M for the 193-nm photolyses and 0.04–0.06 M for the 214-nm photolyses.



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Product yields were determined from the initial slopes of concentration vs time plots, determined by monitoring the course of the photolyses between 0.3 and ca. 4% conversion by VPC. Examples of such plots are shown in Figure 1 for the 193-nm photolyses. Product yields for photolysis of *cis*- and *trans*-8 with the three excitation sources to low (≤4%) conversion are collected in Table I. The 214-nm photolyses were also carried out with 0.08–0.1 M pentane solutions of *cis*- and *trans*-8, yielding results identical with those obtained with the lower concentration solutions.

The latter experiments verify that the diene distributions reported in Table I represent the true primary yields from photolysis of 8 at 214 nm. In the photolyses at 185 and 193 nm, the experimental conditions (i.e., substrate concentration and conversion range monitored) have been chosen to be well within those required to avoid secondary photolysis of the dienes.[3–5] Thus, the distributions reported are believed to represent the true primary product yields in each case.

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Table II. Quantum Yields for Product Formation from 185-nm Photolysis of *cis*- and *trans*-Bicyclo[5.2.0]non-8-ene in Pentane Solution at 23 °C[a]

compound	*c,c*-9	*c,t*-9	10	11
cis-8	0.06 ± 0.02	0.16 ± 0.04	0.26 ± 0.07	*b*
trans-8	0.04 ± 0.01	0.13 ± 0.03	0.05 ± 0.01	0.05 ± 0.02

[a] By cyclooctene actinometry, with 0.02 M solutions irradiated between 0.3 and ca. 5% conversion with a filtered low-pressure mercury lamp. The VPC detector was calibrated for differences in response to products. [b] Not determined.

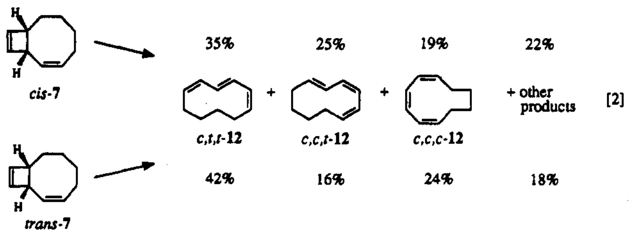
Quantum yields for product formation from 185-nm photolysis of *cis*- and *trans*-8 were determined by cyclooctene actinometry,[12] using 0.02 M solutions and the filtered low-pressure mercury lamp as excitation source. In these experiments, the VPC detector was calibrated for differences in response toward the various products. The results are collected in Table II.

Quantum yields for the direct cis–trans photoisomerization of *c,c*- and *c,t*-9 were determined with 254-nm excitation, using the photoisomerization of *cis,cis*-1,3-cyclooctadiene as the actinometer ($\Phi_{c,c \to c,t} = 0.28$[13]). The results obtained for the photoisomerization of 9 from these experiments were $\Phi_{c,c \to c,t} = 0.26 \pm 0.04$ and $\Phi_{c,t \to c,c} = 0.45 \pm 0.06$. Electrocyclic ring closure is a very minor competing reaction in the direct photolysis of these dienes;[14] the quantum yields for closure of *c,c*-9 to *cis*-8 and *c,t*-9 to *trans*-8 are both estimated to be less than ca. 0.002.

Brief photolysis (360 nm) of 0.005 M pentane solutions of *c,t*-9 in the presence of a trace of iodine lead to essentially complete (>99%) conversion of *c,c*-9. Continued photolysis afforded no further change in the composition of the solution.

Discussion

The most striking aspect of the results of photolysis of *cis*- and *trans*-8 (Table I) is the similarity in the distribution of isomeric dienes obtained from photochemical ring opening of the two compounds. In both cases, the distribution is weighted in favor of the thermodynamically less stable cis,trans isomer. While the nonstereospecificity associated with this reaction appears to be quite general[3-6,9] and was thus expected, the observation of a common (or nearly so) distribution of ring-opening products from photolysis of isomeric cyclobutene derivatives is unusual. In fact, while this work was in progress it was reported that photolysis of *cis*- and *trans*-7 yields similar distributions of stereoisomeric 1,3,5-cyclodecatrienes (**12**; see eq 2).[6] The mechanistic implications of this particular aspect of the photochemistry of 7 were not discussed in detail, however.



[2]

As with simple alkenes,[15] at least two singlet excited states are accessible in alkylcyclobutenes in the 185–214-nm region.[4,15,16] In fact, gas-phase UV absorption spectroscopy indicates that three singlet excited states are accessible above 185 nm in mono- and disubstituted alkylcyclobutenes such as **2** and **3**, and the observation of slight wavelength dependence in the isomeric diene distributions from their direct photolysis suggests that at least two of these may be responsible for ring opening.[4] The three lowest energy transitions in the gas-phase UV spectra of **2** and **3** have been assigned to the π,π^* valence, π,R(3s) Rydberg, and π,R(3p) Rydberg transitions.[4] In the solution-phase spectra, the π,π^* transition is the prominent one, and the Rydberg transitions are reduced in intensity and blue-shifted compared to the gas-phase spectra. The Rydberg transitions may be mixed substantially with valence transitions (e.g. σ,π^*).[4,15d]

In *cis*- and *trans*-8, the π,π^* valence and the π,R(3s) Rydberg states will be of comparable energies[4] and both may contribute to the photochemistry that is observed for these compounds. As might be expected considering the similar π,π^* and π,R(3s) state energies in these compounds, there are only minor variations in the product distributions from direct photolyses of the two isomers in the 185–214-nm range (Table I). Through the study of a series of substituted bicyclo[4.2.0]oct-7-ene derivatives (**5**),[5] it has been verified[16] that the Rydberg state is primarily responsible for fragmentation (formal $\sigma_{2s} + \sigma_{2s}$ cycloreversion, which affords acetylene and **10** in the present cases) and the minor amounts of rearrangement products (i.e. **11**) that are also formed. The π,π^* state is apparently mainly responsible for ring opening to the isomeric conjugated dienes. The lack of stereospecificity in this latter process can thus be explained in terms of either an adiabatic electrocyclic mechanism (i.e., concerted disrotatory opening to yield diene in the first excited singlet state), a nonconcerted pathway, or a more complex mechanism involving partial internal conversion to vibrationally excited levels of the cyclobutene ground state.[3-6]

An attractive mechanism to account for the similar distributions of isomeric dienes obtained from photolysis of *cis*- and *trans*-8 is a nonconcerted pathway which involves either a set of intermediates that is common to both bicyclononene isomers or different intermediates which decay to yield a common distribution of isomeric dienes. Either possibility could result if excited-state ring opening proceeds by a biradical mechanism, initiated by homolysis of the C_1–C_7 bond. Homolysis of this bond in *cis*- and *trans*-8 would initially yield stereoisomeric (90,90)-biradical intermediates (in which the p orbitals of the biradical termini are orthogonal to the C=C bond), which could then relax to *cis,cis*- or *cis,trans*-dienes either by synchronous rotation of the biradical termini or by stepwise pathways involving the intermediacy of allylmethylene biradical geometries. The latter is commonly considered to be the lowest energy geometry on the singlet excited state surfaces of conjugated dienes.[17] The observed diene distributions from photolysis of *cis*- and *trans*-8 dictate that the favored torsional decay pathways of the two (90,90)-biradicals must in both cases proceed toward geometries which ultimately lead predominantly to the

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(12) (a) Srinivasan, R.; Brown, K. H. *J. Am. Chem. Soc.* **1978**, *100*, 2589. (b) Schuchmann, H.-P.; von Sonntag, C.; Srinivasan, R. *J. Photochem.* **1981**, *15*, 159.

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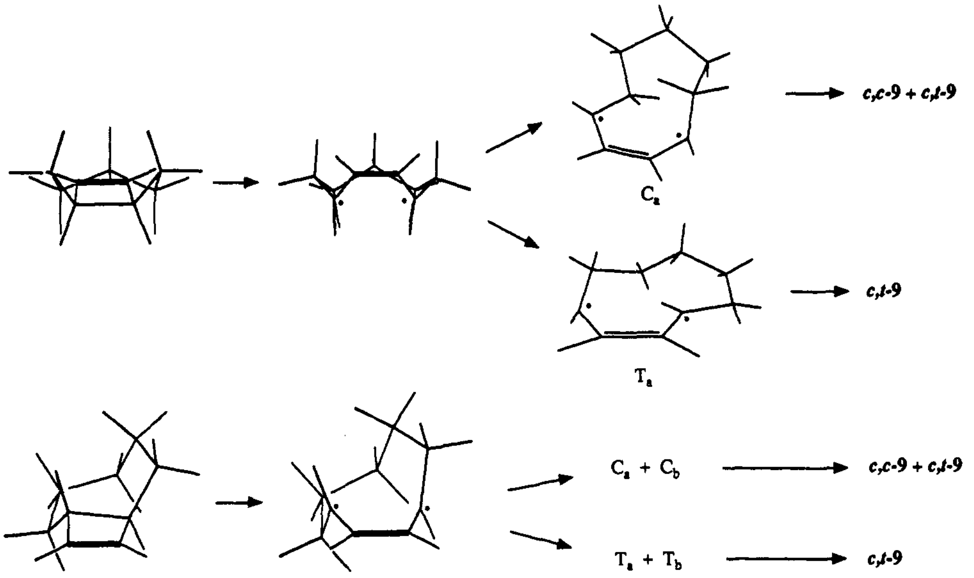
Scheme I. Nonconcerted Mechanism for Photochemical Ring Opening of *cis*- and *trans*-8



cis,trans-diene. For the synchronous relaxation pathways, Dreiding models suggest that the most facile rotations available to the (90,90)-biradicals derived from C_1–C_7 homolysis in *cis*- and *trans*-8 are indeed those that lead to *c,t*-9 in both cases.

Scheme I depicts the stepwise biradical mechanism for excited-state ring opening of *cis*- and *trans*-8, starting from the lowest energy ground-state conformations of the isomeric bicyclononenes according to AM1 semiempirical calculations (ΔH_f = 22.4 and 28.4 kcal/mol, respectively). The scheme also shows representations of the (90,90)-biradicals obtained by stretching the C_1–C_7 bond in each of the two compounds, and (from Dreiding models) the conformations of the (0,90)-biradicals that would be obtained from rotation of a single terminus in the (90,90)-cis-biradical.

Because of symmetry, *cis*-8 leads to just two possible (0,90)-allylmethylene biradicals, one in which the allyl moiety is "locked" in an s-cis geometry (C_a) and one in which it is locked in an s-trans geometry (T_a). Similar relaxation of the (90,90)-biradical from *trans*-8 can also lead to either C_a or T_a, as well as two additional geometries due to the asymmetry associated with the molecule. If relaxation to ground-state diene occurs by rotation of the methylene fragments in these biradicals, then the s-cis geometries can yield both *c,c*- and *c,t*-9 while the s-trans geometries can yield only *c,t*-9. For both *cis*- and *trans*-8, the least sterically demanding pathways for conversion of the (90,90)-biradicals to (0,90) geometries appear to be those that lead to the s-trans biradical conformers, according to molecular models.

The foregoing analysis indicates that a stepwise ring-opening pathway involving biradical intermediates can provide a reasonable explanation for the near-common diene distribution obtained from photolysis of *cis*- and *trans*-8 specifically, and for the general result that this reaction proceeds nonstereospecifically in a number of alkylcyclobutene derivatives. Since stereoisomeric cyclobutenes will generally lead to *different* biradical conformers (whose further torsional decay may differ, in general), the fact that different diene distributions are generally obtained from *cis*- and *trans*-cyclobutene stereoisomers (e.g., those from photolysis of 1–3) is not incompatible with this mechanism. There are, however, several aspects which render the analysis quite hypothetical. Firstly, there are a number of different conformations possible for the (0,90)-biradical species. These derive from the two (90,90) species with differing degrees of accompanying atomic motions elsewhere in the ring, many of which involve transannular steric interactions of fairly subtle differences in severity. Secondly, if torsional decay to ground-state dienes occurs entirely within the singlet manifold, then it likely occurs over a timescale that is too fast to allow large-scale conformational changes elsewhere in the ring.[18] It is thus difficult to assess the most likely mode of torsional decay of the (90,90)- and (0,90)-biradicals on the basis of molecular models. Of course, if intersystem crossing to the triplet state occurs after entry into the biradical manifold, then conformational equilibration of the biradicals would presumably be possible during their lifetime.[17,18] However, given the relatively high reactivity of singlet biradicals in general,[18] it seems unlikely that intersystem crossing to the triplet state could compete with torsional relaxation to the ground state.

The photochemistry of 6 and 7, recently reported by Dauben and Haubrich,[6] provides additional support for the nonconcerted ring-opening mechanism, although it does not rule out other mechanistic possibilities. As shown in eq 2, *cis*- and *trans*-7 also afford nearly common distributions of stereoisomeric ring-opening products, in addition to 1,3-cyclooctadienes via competing fragmentation. Of special pertinence is the observation that the relative ring-opening/fragmentation product yields from photolysis of both *cis*- and *trans*-7 are ca. 6 times higher than that from photolysis of 6.[6] The C_1–C_8 bond in 7 is presumably much weaker than it is in 6, and thus would be expected to lead to increased yields of ring opening compared to fragmentation products if the former is initiated by C_1–C_8 bond homolysis. Unfortunately, product quantum yields were not determined for these compounds. It should be noted however, that *cis*-7 is also substantially more reactive than *cis*-6 toward thermal ring opening, which clearly proceeds by an electrocyclic mechanism.[19] If excited-state pericyclic processes follow similar structure–reactivity relationships as ground-state ones, then the relative reactivity of these two compounds toward photochemical ring opening is also compatible with an electrocyclic mechanism such as that described below.

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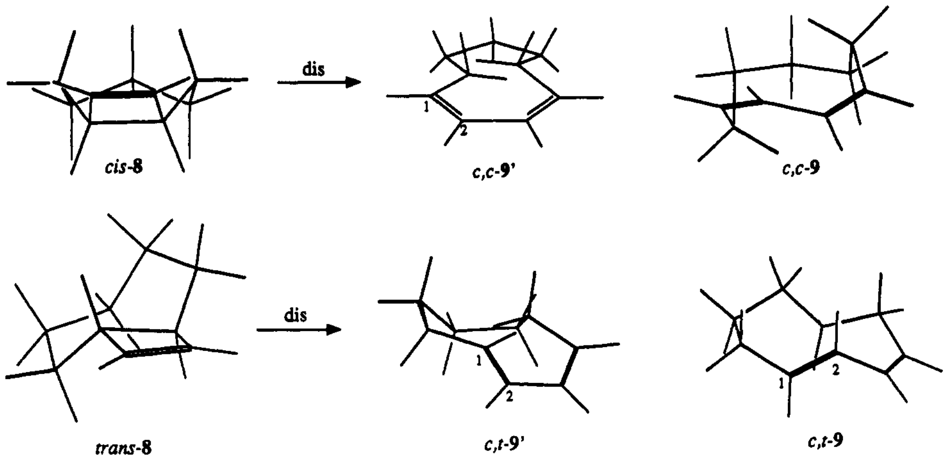
Scheme II. Calculated Ground-State Structures of *cis*- and *trans*-8 and *c,c*- and *c,t*-9 (AM1), and Hypothetical Diene Conformers Obtained from Disrotatory Cyclobutene Ring Opening



A second mechanistic possibility that needs to be considered is the adiabatic pericyclic pathway. This ring-opening pathway would afford the dienes (initially stereospecifically) in the excited singlet state, decay from which would produce a mixture of isomeric dienes.[17] In order to analyze the results for 8 within the framework of this mechanism, it is necessary to know the excited-state torsional decay characteristics of the specific diene conformers afforded in the primary step.[3] If these conformers are similar to or identical with the stable ground-state diene conformers, then this information is available from the quantum yields for direct cis–trans photoisomerization of the isomeric dienes.[17] If *cis*-8 opens to yield exclusively *c,c*-9 in the lowest excited singlet state, then a mixture of *c,c*- and *c,t*-9 in the ratio *c,t*-9/*c,c*-9 ≈ 0.3 should be produced, based on the value $\Phi_{c,c\rightarrow c,t} = 0.26$ obtained from the direct photoisomerization of this diene isomer. Similarly, if *trans*-8 opens to yield singlet excited *c,t*-9, a mixture of *c,c*- and *c,t*-9 in the ratio *c,t*-9/*c,c*-9 ≈ 1.3 is expected (from $\Phi_{c,t\rightarrow c,c} = 0.45$). These "expected" diene ratios, calculated on the basis of the adiabatic ring-opening mechanism, are clearly very different from the distributions of isomeric dienes that are actually obtained from photolysis of 8. Thus to a first approximation, this analysis argues against the pericyclic mechanism for the process.

It is however, necessary to consider the similarities between the stable ground-state conformations of the dienes (whose excited-state torsional decay characteristics are reflected in the quantum yields for direct cis–trans photoisomerization) and the conformers that would be initially obtained upon concerted cyclobutene ring opening, because the torsional decay characteristics of excited diene singlets are likely to be conformation-dependent.[17] The lowest energy ground-state conformations of *cis*- and *trans*-8 and *c,c*- and *c,t*-9 (according to AM1 semiempirical calculations) are shown in Scheme II, along with representations of the corresponding planar (or nearly planar) s-cis diene conformers (*c,c*-9′ and *c,t*-9′) that would be expected if ring opening follows the concerted pericyclic pathway. As can be seen from the scheme, disrotatory ring opening of *cis*- and *trans*-8 should yield *c,c*- and *c,t*-9 in relatively high energy, planar s-cis conformations which are clearly different from the stable ground-state conformers. It seems most reasonable to assume that the excited-state torsional decay characteristics of these conformers might differ considerably from those of the stable ground-state conformers.[17] Thus, the conclusion that the near common diene distributions obtained from photolysis of *cis*- and *trans*-8 are incompatible with the adiabatic electrocyclic excited-state ring-opening mechanism cannot be considered to be reliable, based on this evidence.

Considering the substantially lower thermodynamic stability that should be associated with *trans*-8 compared to the cis isomer (due primarily to ring strain), the trends in the quantum yields for ring opening and fragmentation of the two isomers deserve brief comment. The data in Table II show that the overall photoreactivity of the cis-isomer is substantially higher than that of the trans isomer. Since the quantum yields for ring opening are similar for the two compounds, the difference in their behavior is due primarily to a dramatic difference in the efficiency of the fragmentation reaction; the fragmentation quantum yield is about a factor of 5 more efficient in *cis*-8 than in *trans*-8. In fact, the reason for this difference is straightforward. It is known that cyclobutene photofragmentation proceeds stereospecifically[4,6,9a] and largely through population of the π,R(3s) state, probably by a route involving initial [1,2]-alkyl migration (ring contraction) yielding a cyclopropylmethylene species which fragments to acetylene and the alkene.[5,16] In the case of *trans*-8, fragmentation by the analogous pathway would produce *trans*-cycloheptene. Thus, it is reasonable that fragmentation of *trans*-8 is much less efficient than the corresponding reaction of *cis*-8 (which will yield *cis*-cycloheptene). It should be noted that photolysis of *cis*-7 yields *cis,cis*-1,3-cyclooctadiene as the major fragmentation product while *trans*-7 yields the cis,trans isomer. These results are consistent with those for *cis*- and *trans*-8 discussed above.

The formation of methylenecyclopropane in the far-uv photolysis of cyclobutene has been proposed to arise from cyclobutylidene, formed as a result of [1,2]-hydrogen migration in the π,R(3s) state.[16b] While methylenecyclopropane is apparently a major product of the photolysis of cyclobutene itself, we have found no evidence for the formation of analogous compounds in the photolyses of 1–3.[3,4] Minor amounts of methylenecyclopropanes are formed in the photolyses of 5[3] and 8, however. It is interesting that both *cis*- and *trans*-8 afford the cis-fused methylenecyclopropane derivative 11, since [1,2]-H migration should proceed with retention of stereochemistry at the ring junctions in *cis*- and *trans*-8 (leading to cis- and trans-fused cyclobutylidene intermediates, respectively; see eq 3). While the stereochemistry of the ring expansion of cyclobutylidenes is evidently not known,[20] it is possible

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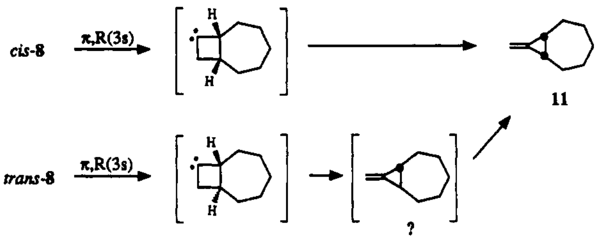
(20) Baron, W. J.; DeCamp, M. R.; Hendrick, M. E.; Jones, M., Jr.; Levin, R. H.; Sohn, M. B. In *Carbenes, Vol. 1*; Jones, M., Jr., Moss, R. A., Eds.; John Wiley & Sons: New York, 1973; p 1.

that the trans-fused isomer of **11**, if initially formed from *trans*-**8**, is thermally converted to the observed cis isomer under our experimental conditions.



[3]

Conclusions

Direct photolysis of *cis*- and *trans*-bicyclo[5.2.0]non-8-ene (**8**) in hydrocarbon solution with far-UV light leads to products resulting from (nonstereospecific) ring opening, fragmentation, and molecular rearrangement. The two isomers afford a nearly common distribution of *cis,cis*- and *cis,trans*-1,3-cyclononadiene, weighted in favor of the thermodynamically less stable cis,trans isomer. Based on crude molecular modeling studies and other evidence, it has been concluded that a biradical mechanism, involving a set of common intermediates from the two cyclobutene isomers, best accounts for the observed results. A pericyclic mechanism, in which ring opening proceeds adiabatically to the symmetry-allowed (disrotatory) pathway to yield the dienes in the first excited singlet state, cannot be rigorously ruled out however.

The fragmentation reaction, which is thought to afford cycloheptene and acetylene predominantly by a stepwise pathway involving the π,R(3s) state, proceeds with 5-fold higher efficiency from *cis*-**8** compared to the trans isomer. This is due to the high degree of stereospecificity associated with the reaction, which necessitates that the latter isomer fragment to yield *trans*-cycloheptene.

Further studies, aimed at better distinguishing between concerted and nonconcerted pathways for excited-state cyclobutene ring opening, are in progress.

Experimental Section

^{1}H NMR spectra were recorded on Varian EM390 (90 MHz) or Bruker AM500 (500 MHz) spectrometers in carbon tetrachloride (or deuteriochloroform were noted) and ^{13}C NMR spectra were recorded at 125.6 MHz on the Bruker AM500; all are reported in parts per million downfield from tetramethylsilane. Mass spectra were recorded on a VG7070 mass spectrometer interfaced with a Varian 3700 gas chromatograph, equipped with a 30 m × 0.25 mm DB-1 (Chromatographic Specialties, Inc.) fused silica capillary column. Exact masses were determined on a VGH ZABE mass spectrometer, and employed a mass of 12.000000 for carbon. Ultraviolet absorption spectra were recorded in pentane solution using a Perkin-Elmer Lambda 9 spectrometer equipped with a Model 3600 data station. The spectrometer sample compartment was continuously flushed with nitrogen, and sample and reference solutions were deoxygenated with argon prior to recording the spectrum. Infrared spectra were recorded on a Perkin-Elmer 283 spectrometer in carbon tetrachloride solution or as the neat liquids (where noted); spectra are reported in wavenumbers, calibrated using the 1601.9-cm^{-1} polystyrene absorption.

Analytical VPC separations were carried out using a Hewlett-Packard 5890 gas chromatograph (injector temperature = 120 °C) equipped with a flame ionization detector, a Hewlett-Packard HP-3396 recording integrator, and one of the following columns: (a) 1.0 μm SPB-1 wide-bore capillary column (30 m × 0.75 mm i.d. borosilicate; Supelco, Inc.); (b) 2.0 μm HP-17 megabore capillary column (10 m × 0.53 mm i.d. fused silica; Hewlett-Packard, Inc.).

Semipreparative VPC separations employed a Hewlett-Packard 5750B gas chromatograph equipped with a thermal conductivity detector (detector temperature = 120 °C) and one of the following stainless steel columns: (c) 3.8% UC W982 on 80/100 Supelcoport (24 ft × $^1/_4$ in.); (d) 20% oxybis(dipropionitrile) (ODPN) on Chromosorb 80/100 PNAW (20 ft × $^1/_4$ in.); (e) 20% 1,2,3-tris-(2-cyanoethoxy)propane (TCEP) on Chromosorb 80/100 PNAW (10 ft × 1.4 in.).

n-Pentane, 2,2,4-trimethylpentane (isooctane), and cyclohexane were Baker Photrex grade and used as received from the supplier. Pyridine (Fisher Reagent) was dried over potassium hydroxide and distilled from barium oxide. Dimethyl sulfoxide (Fisher Reagent) was distilled from calcium hydride. Cycloheptene, bromoform, maleic anhydride, acetophenone, lead tetraacetate, 1,1-dichloroethane, and potassium *tert*-butoxide were all used as received from Aldrich Chemical Co. Cyclooctene (Aldrich) was distilled at atmospheric pressure.

Synthetic photolyses employed a Hanovia 450-W medium-pressure mercury lamp with quartz or Pyrex immersion wells (Ace Glass, Inc.), or a Rayonet photochemical reactor fitted with two to twelve 253.7-nm lamps and a merry-go-round apparatus.

Preparation of Compounds. *cis*- and *trans*-Bicyclo[5.2.0]non-8-ene (8). Cycloheptene (10 g, 0.104 mol), maleic anhydride (11.4 g, 0.116 mol), and acetophenone (5.0 g, 0.042 mol) were dissolved in ethyl acetate (Caledon; 350 mL) in a Pyrex immersion well equipped with a magnetic stirrer. The solution was deoxygenated by bubbling dry nitrogen through the solution for ca. 20 min., with stirring and cooling in an ice–water bath. The solution was then irradiated with a 450-W medium-pressure mercury lamp, agitating constantly with the magnetic stirrer as well as with a slow stream of dry nitrogen. After 15-h irradiation, ^{1}H NMR analysis of the crude photolysate revealed the disappearance of maleic anhydride to be >95% complete. Evaporation of the solvent on a rotary evaporator afforded an orange-yellow oil which was further distilled under vacuum (ca. 0.5 mmHg) to remove acetophenone and unreacted anhydride.

The orange, viscous oil that remained (20 g, 0.103 mol) was added to 8% aqueous hydrochloric acid (50 mL) and tetrahydrofuran (10 mL) and stirred for ca. 12 h at room temperature, affording a solid precipitate. The liquid was separated by decanting and extracted with ether (3 × 50 mL). The ether extracts were combined with the solid precipitate, benzene (25 mL) was added, and the solvent was evaporated on the rotary evaporator. The solid that remained was dissolved in ether (50 mL), dried over anhydrous sodium sulfate, and filtered. Evaporation of the solvent afforded a light brown solid (21.0 g).

A portion of the solid from above (4.9 g) was dissolved in dry pyridine (60 mL), and the resulting solution was placed in a 100-mL two-neck round-bottom flask equipped with a condenser connected to three sequential dry ice/acetone traps. The mixture was saturated with oxygen, lead tetraacetate (15 g, 0.034 mol) was added, and a slight positive pressure of nitrogen was applied. The mixture was then placed in a 70 °C oil bath, where vigorous evolution of carbon dioxide occurred with 2–3 min. The mixture was left for a further 1 h at 70 °C and then cooled to room temperature. The pyridine was then removed by careful vacuum distillation (ca. 1 mmHg). After the mixture had been distilled to dryness, the distillate collected in the traps was combined and ether (25 mL) was added. The solution was washed with 5% aqueous hydrochloric acid (5 × 50 mL), water (5 × 10 mL) until neutral to litmus, and saturated brine (10 mL), dried over anhydrous sodium sulfate, filtered, and concentrated by careful distillation. Gas chromatographic analysis of the colorless liquid that remained (1.6 g) indicated it to consist of two major components (ca. 4:1). The two components were initially separated as a mixture from remaining solvent and low molecular weight byproducts by semipreparative VPC (column c) and were then isolated in >99.5% purity by several passes through column d or e and one final pass through column c. They were identified as *cis*-**8** (major component) and *trans*-**8** on the basis of their ^{1}H NMR, IR, and mass spectra. The ^{1}H NMR spectra agreed satisfactorily with those recently reported by Stierman and Johnson.[21]

***cis*-Bicyclo[5.2.0]non-8-ene (*cis*-8):** ^{1}H NMR (500 MHz) δ 1.17 (m, 2 H), 1.37 (m, 2 H), 1.75 (m, 6 H), 2.89 (d, J = 12.6 Hz, 2 H), 6.06 (s, 2 H); IR (neat) 3126 (w), 3041 (w), 2923 (s), 2852 (s), 1566 (w), 1463 (m), 1454 (m), 1441 (m), 1289 (m), 1146 (w),

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[21] Stierman, T. J.; Johnson, R. P. *J. Am. Chem. Soc.* **1985**, *107*, 3971.

1048 (w), 924 (m), 848 (m), 773 (m), 753 (s), 688 (m); MS *m/e* (*I*) 122 (4), 121 (5), 107 (19), 94 (32), 93 (64), 91 (16), 81 (59), 80 (85), 79 (100), 77 (33), 68 (21), 67 (36), 66 (18), 65 (14), 55 (15), 54 (19), 51 (12), 41 (29); UV (cyclohexane) λ_{max} = 187 nm (ϵ = 4900).

***trans*-Bicyclo[5.2.0]non-8-ene (*trans*-8)**: ^{1}H NMR (500 MHz) δ 1.33 (m, 2 H), 1.56 (m, 4 H), 1.73 (m, 4 H), 2.53 (dd, *J* = 12.2, 3.1 Hz, 2 H), 6.14 (s, 2 H); IR (neat) 3102 (w), 3039 (m), 2924 (s), 2856 (s), 1551 (w), 1447 (m), 1284 (w), 1253 (w), 1223 (w), 1215 (w), 805 (m), 763 (m), 729 (m), 683 (s); MS *m/e* (*I*) 122 (1), 121 (2), 107 (14), 94 (20), 93 (34), 91 (19), 81 (37), 80 (40), 79 (100), 77 (34), 68 (16), 67 (32), 66 (16), 65 (16), 55 (13), 54 (14), 53 (27), 51 (16), 41 (36); UV (cyclohexane) λ_{max} = 187 nm (ϵ = 5600).

***cis,cis*-1,3-Cyclononadiene (*c,c*-9)** was prepared by base-catalyzed isomerization of 1,2-cyclononadiene[22] with potassium *tert*-butoxide in dimethyl sulfoxide at 72 °C.[23] Workup afforded a colorless liquid from which *c,c*-**9** was isolated by semipreparative VPC (column c). It had the following spectral characteristics: IR (neat) 3054 (s), 3003 (s), 2920 (s), 2856 (s), 1636 (m), 1478 (m), 1458 (s), 1443 (s), 1089 (m), 1051 (m), 978 (m), 878 (m), 843 (m), 815 (m), 768 (s), 733 (s), 707 (m), 661 (s); MS *m/e* (*I*) 122 (28), 107 (17), 93 (51), 81 (71), 80 (68), 79 (100), 67 (47), 53 (27), 41 (39), 39 (50). The 500-MHz ^{1}H NMR spectrum agreed satisfactorily with the published high-resolution spectrum.[21,24]

***cis,trans*-1,3-Cyclononadiene (*c,t*-9)** was prepared by gas-phase pyrolysis of *cis*-8. A sample of *cis*-8 (0.2 g, 0.0016 mol) was placed in a Pyrex tube, degassed using three freeze/pump/thaw cycles, seated under vacuum (ca. 30 mTorr), and heated in an oil bath at 198 °C for 1 h. After cooling, the tube was opened and analyzed by VPC, which indicated the presence of a single product (ca. 33%) in addition to unreacted *cis*-8. The product was isolated by semipreparative VPC (column e; injector/column/detector temperature = 120/90/150 °C) and identified as *c,t*-**9** on the basis of the following spectral characteristics: IR 3012 (m), 2932 (s), 2855 (s), 1653 (w), 1455 (s), 970 (m), 954 (w), 906 (w), 870 (w), 686 (w); MS *m/e* (*I*) 122 (14), 107 (13), 94 (18), 93 (42), 91 (16), 81 (54), 80 (60), 79 (100), 77 (30), 67 (49), 53 (20), 41 (29), 39 (35). The 500-MHz ^{1}H NMR spectrum agreed satisfactorily with the published high-resolution spectrum.[21,24]

Brief photolysis of a 0.005 M pentane solution of *c,t*-**9** containing a trace of iodine resulted in rapid, essentially complete conversion to *c,c*-**9**.

***cis*-8-Methylenebicyclo[5.1.0]octane (11)** was prepared by the method of Arora and Binger[25] and purified by semipreparative VPC (column c). Its ^{1}H NMR (90 MHz) spectrum agreed satisfactorily with that previously reported:[26] 1.2–1.7 (cplx m, 10 H), 1.90 (m, 1 H), 2.04 (m, 1 H), 5.22 (s, 2 H); IR (CCl_4) 3072 (m), 2980 (s), 2925 (s), 2855 (s), 1752 (m), 1460 (s), 1451 (s), 1350 (w), 1162 (w), 905 (w), 884 (s); MS *m/e* (*I*) 122 (4), 107 (34), 93 (63), 79 (100), 67 (44), 53 (30), 41 (39).

Photolysis of *cis*- and *trans*-8. Quantitative cyclobutene photolyses employed a 10-W Osram low-pressure mercury lamp, the pulses (193 nm, ca. 10 ns, 20–30 mJ, 1-Hz repetition rate) from a Lumonics TE-861M excimer laser filled with an argon/fluorine/helium mixture, or a 16-W Philips 93106E zinc resonance lamp (214 nm). Irradiations with the low-pressure mercury lamp were carried out with a lithium fluoride filter,[11] fabricated by the method described previously.[3] Photolyses with the mercury or zinc resonance lamps were carried out using a cylindrical metal casing which surrounds the lamp and which incorporates a 1-in. port to contain the sample cell and filter. The lamps were given a 20-min warmup period before each experiment and cooled with a stream of dry nitrogen.

The photolyses were carried out at ambient temperature (ca. 23 °C) in 10 × 25 mm cylindrical Suprasil UV cells (Hellma). Solutions of *cis*- or *trans*-8 in pentane (0.02 M for the 185- and 193-nm photolyses; 0.04–0.10 M for the 214-nm photolyses), with 0.001 M isooctane or *n*-octane as internal standard, were deoxygenated with a stream of dry nitrogen in an ice bath for ca. 10 min prior to photolysis. The photolyses were monitored between 0.3 and 5–10% conversion by withdrawing aliquots at suitable time intervals for VPC analysis. Products were identified by coinjection of photolysates taken to ca. 10% conversion with authentic samples on columns a and b. Relative product yields were determined from the slopes of concentration versus time plots constructed for all components of the mixture relative to the internal standard. The concentration vs time plots were linear up to at least 3% conversion in each case. Figure 1 shows examples of such plots for the photolyses of *cis*- and *trans*-8 with the 193-nm light source.

Quantum yields for product formation were determined for the 185-nm photolyses by cyclooctene actinometry, using 0.02 M pentane solutions of *cis*-8, *trans*-8, and *cis*-cyclooctene, each containing 0.001 M isooctane as internal standard. The solutions were alternately photolyzed with the filtered 185-nm source and analyzed by VPC (FID response factors were determined from standard solutions of the products) between 0.2 and 3.0% conversion. Quantum yields were derived from concentration vs time plots and employed a value of 0.32 for the quantum yield of cis–trans photoisomerization of the actinometer.[12b]

Quantum yields for the direct cis–trans photoisomerization of *c,c*- and *c,t*-**9** were determined by photolyzing deoxygenated 0.02 M pentane solutions of the dienes in a Rayonet reactor fitted with a merry-go-round and two 254-nm lamps. The photoisomerization of *cis,cis*-1,3-cyclooctadiene ($\Phi_{c,c\rightarrow c,t}$ = 0.28[13]) was employed as the actinometer. The progress of the photoisomerizations were monitored by VPC analysis (column a) between 0.5 and 5.0% conversions, and quantum yields were determined from the slopes of concentration vs time plots as described above. The VPC detector was calibrated for differences in response toward the C_8 and C_9 dienes.

Computational studies were carried out using AM1, Version 2.1, of the general purpose molecular orbital computational package AMPAC.[27]

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[24] We thank Professor R. P. Johnson for sending us ^{1}H NMR spectra of *c,c*-**9**, *c,t*-**9**, and other C_9H_{14} isomers.

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