The effect of central bond torsional mobility on the Rydberg state ring opening of alkylcyclobutenes

Bruce H.O. Cook and William J. Leigh

Abstract: The stereochemistry of the π,R(3*s*) excited state ring opening of a series of bicyclic alkylcyclobutenes has been studied in hydrocarbon solution with 228 nm excitation. In these compounds, the C=C bond is shared between the cyclobutene ring and a five-, six-, or seven-membered ancillary ring, which has the effect of restricting the torsional mobility about the central C—C bond in the isomeric diene products. It has previously been shown that monocyclic alkylcyclobutenes undergo stereospecific *conrotatory* ring opening upon excitation at the long wavelength edge of the π,R(3*s*) absorption band (228 nm), and nonstereospecific ring opening upon irradiation at shorter wavelengths (within the π,π* absorption band). Different behaviour is observed for the bicyclic systems studied in the present work. The bicyclo[3.2.0]hept-1-ene, bicyclo[4.2.0]oct-1-ene, and one of the bicyclo[5.2.0]non-1-ene derivatives yield nearly the same mixtures of *E*,*E*- and *E*,*Z*-diene isomers upon irradiation at 214 and 228 nm, with the product mixtures being heavily weighted in favor of the isomer(s) corresponding to disrotatory ring opening. The results may indicate that the stereochemical characteristics of the Rydberg-derived ring opening of alkylcyclobutenes depends on the ability of the molecule to twist about the "central" bond (i.e., the C=C bond in the cyclobutene) as ring opening proceeds. It is proposed that restricting the torsional mobility about the central bond activates internal conversion from the π,R(3*s*) to the π,π* potential energy surface, from which predominant disrotatory ring opening ensues.

Key words: cyclobutene, Rydberg, ring opening, photopericyclic, electrocyclic.

Résumé : Opérant en solution dans des hydrocarbures et avec une excitation à 228 nm, on a étudié la stéréochimie de l'ouverture de cycle dans l'état excité π,R(3*s*) d'une série d'alkylcyclobutènes bicycliques. Dans ces composés, la liaison C=C est partagée entre le cycle du cyclobutène et un cycle ancillaire à cinq-, six- ou sept-chaînons qui a pour effet de restreindre la mobilité torsionnelle autour de la liaison C—C centrale des produits diéniques isomères. Il a été démontré antérieurement que les alkylcyclobutènes monocycliques subissent une ouverture de cycle *conrotatoire* stéréospécifique lors de leur excitation dans la portion de grande longueur d'onde de la bande d'absorption π,R(3*s*) (228 nm) et une ouverture de cycle non stéréospécifique par irradiation à des longueurs d'onde plus faibles (dans la bande d'absorption π,π*). Dans le présent travail, on observe un comportement différent pour les systèmes bicycliques. Lors de leur irradiation à 214 ou à 228 nm, le bicyclo[3.2.0]hept-1-ène, le bicyclo[4.2.0]oct-1-ène et un des dérivés du bicyclo[5.2.0]non-1-ène conduisent pratiquement tous aux même mélanges *E*,*E*- et *E*,*Z*- de diènes isomères; les mélanges contiennent principalement les isomères résultant d'une ouverture disrotatoire du cycle. Les résultats suggèrent que les caractéristiques stéréochimiques de l'ouverture de cycle d'alkylcyclobutènes se produisant dans la région de Rydberg dépend de la facilité de la molécule à se retourner autour de la liaison centrale (c'est-à-dire la liaison C=C du cyclobutène) lorsque l'ouverture de cycle se produit. On suggère qu'une restriction de la mobilité torsionnelle autour de la liaison centrale active la conversion interne de π,R(3*s*) à la surface d'énergie potentielle π,π* à partir de laquelle il résulte une ouverture de cycle disrotatoire.

Mots clés : cyclobutène, Rydberg, ouverture de cycle, photopéricyclique, électrocyclique.

[Traduit par la Rédaction]

Introduction

The direct irradiation of simple alkylcyclobutenes in the gas phase or solution results in electrocyclic ring opening and stereospecific [2 + 2]-cycloreversion to yield the corresponding alkyne and alkene (1–4). It has been known for several years that contrary to early indications (5), the ring opening reaction proceeds *non*stereospecifically (6, 7), in apparent violation of simple orbital symmetry selection rules for photoelectrocyclic reactions (8) as well as the results of

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Dedicated to Professor Don Arnold for his contributions to chemistry.

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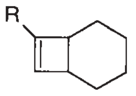
high level ab initio calculations (9, 10), all of which predict that the process should proceed with preferred *disrotatory* stereochemistry when initiated by population of the lowest π,π^* excited singlet state of the molecule. Assuming that orbital symmetry selection rules are, in fact, obeyed in the π,π^* reaction, there are at least three possible explanations for this behaviour (6): (*i*) ring opening proceeds *adiabatically*, yielding the photochemically allowed (disrotatory) diene isomer(s) in the lowest π,π^* excited singlet state, from which the forbidden (thermally allowed, conrotatory) isomer(s) are formed via *E*,*Z*-isomerization; (*ii*) the conrotatory isomers are formed via reaction from upper vibrational levels of the ground state of the cyclobutene, populated by internal conversion in competition with disrotatory π,π^* state ring opening; and (*iii*) the conrotatory isomers are formed via competing reaction of the radical-cation-like $\pi,\mathrm{R}(3s)$ Rydberg excited singlet state, which is known to be of similar energy to the π,π^* (valence) singlet state in alkylcyclobutenes (4, 11, 12), just as it is in other aliphatic alkenes (13–15).[2]

Much of our work in this area over the past 15 years has been directed at attempting to distinguish between these possibilities, through studies of the effects of substituents, excitation wavelength, and various structural constraints on the stereochemistry of the reaction (4, 6, 12, 16–23). By the mid-1990s, we had concluded: (*i*) that the $\pi,\mathrm{R}(3s)$ state is responsible for the [2 + 2]-cycloreversion reaction but is not involved in ring opening (12, 24); and (*ii*) that the adiabatic, π,π^* state ring opening mechanism most adequately accounts for the nonstereospecificity of the reaction (19, 21, 22).

The first conclusion was based on an analysis of the photochemistry of a series of 7-substituted bicyclo[4.2.0]oct-7-ene derivatives (**1**), in which the energy of the $\pi,\mathrm{R}(3s)$ state varies systematically as a function of the nonconjugating substituent attached to the cyclobutenyl C=C bond (12). The quantum yield of ring opening products is highest in the case of the 7-trifluoromethyl derivative **1c**, in which the $\pi,\mathrm{R}(3s)$ state is significantly higher in energy than the π,π^* singlet state, and the yields of ring opening relative to cycloreversion products increase with increasing excitation wavelength between 193 and 214 nm (the opposite is true for **1a**, **1b**). Furthermore, the degree of nonstereoselectivity associated with ring opening is roughly constant throughout the series of compounds, and does not vary with excitation wavelength. It was thus concluded that the π,π^* state alone is responsible for ring opening, and hence, that the nonstereospecificity of the reaction somehow originates in the specific manner in which ring opening proceeds on the potential energy surface of this electronic state. However, it is difficult to rule out the possibility that the trifluoromethyl substituent in **1c** might also affect excited state dynamics in addition to altering the relative energies of the $\pi,\mathrm{R}(3s)$ and π,π^* states, and perhaps cause a fundamental change in the reactivity of the π,π^* state compared to that in the parent compound. Indeed, recent ultrafast time-resolved experiments (25, 26), as well as detailed theoretical calculations (27–29), strongly suggest that such possibilities *cannot* be ignored in other cycloalkenes such as cyclohexene and norbornene. Thus, there may be other viable explanations for the observed trends in the photoreactivity of **1a**–**1c** that go well beyond simple arguments based on the effects of the substituents on the relative energies of the $\pi,\mathrm{R}(3s)$ and π,π^* excited states in these molecules. One possibility is that in **1a** and **1b**, ring opening proceeds from both the $\pi,\mathrm{R}(3s)$ and π,π^* states, each with a high degree of stereoselectivity (conrotatory from the Rydberg state and disrotatory from the π,π^* state); in **1c**, ring opening proceeds only from the π,π^* state, but with a lower degree of disrotatory stereoselectivity owing to a fundamental change in excited-state dynamics caused by the strongly polarizing trifluoromethyl substituent. Such alternatives are difficult to rule out solely on the basis of simple product studies.



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a. R = H
b. R = Me
c. R = CF$_3$

The second conclusion was based on an examination of the photochemistry of the series of constrained cyclobutenes **2** and **4**, comparing the relative yields of isomeric dienes obtained upon 214-nm photolysis of these compounds to values predicted from the quantum yields for direct *E*,*Z*-photoisomerization of the corresponding isomeric dienes (19, 21, 22). For example, 214 nm irradiation of *cis*-2,2,6,7-tetramethylbicyclo[3.2.0]hept-1-ene (*cis*-**2**) in hydrocarbon solution yields a mixture of three diene isomers, *E*,*E*-, *E*,*Z*-, and *Z*,*E*-**3** (eq. [1]); the two *E*,*Z*-isomers are formed in a ratio that is *identical* (within experimental error) to that obtained from direct (254 nm) irradiation of the photochemically allowed (*E*,*E*) diene isomer (21). Reasonable (but not perfect) agreement was also observed between the isomeric diene ratios obtained from 214-nm photolysis of the symmetrically substituted bicyclic cyclobutenes **4**, and values calculated from the quantum yields for *E*,*Z*-photoisomerization of their isomeric dienes **5** (19, 22). This series of compounds bears the important feature that the dienes **3** and **5a**–**5d** are constrained to exist in the *s*-cis conformation, similar to that which would (presumably) be formed directly in the electrocyclic ring opening reaction. This allows one to independently determine the excited state torsional decay characteristics of the product in the conformation in which it is initially formed from ring opening of the corresponding cyclobutene derivative. Acyclic dienes generally prefer the *s*-trans conformation, so such analyses are more problematic with monocyclic cyclobutenes.

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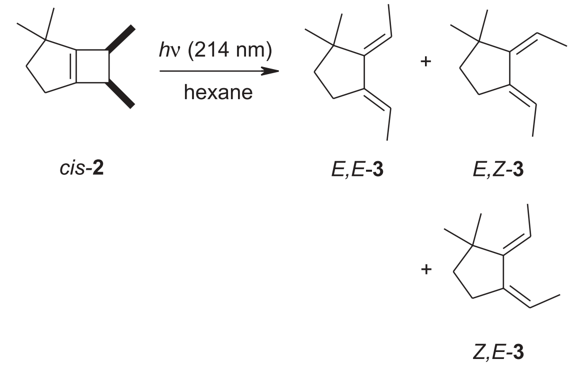
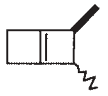
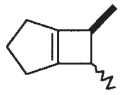
[2] There is a long-standing debate, which to our knowledge has never been resolved, as to the identity of the excited state responsible for the weak long-wavelength absorptions in the condensed phase UV absorption spectra of tetraalkyl-substituted alkenes — whether they are the Rydberg absorptions, substantially reduced in intensity and blue-shifted relative to their character in the gas phase spectrum, or those corresponding to a very weak transition to a low-lying valence state such as the π,σ^* state (13). We favour the Rydberg state assignment because of the similarities between the photochemistry of alkenes in hydroxylic solvents and the chemistry of the corresponding radical cations under similar conditions (14, 15). The photochemistry of 1,2-dimethylcyclobutene in methanol exhibits similar features as that of other alkenes in hydroxylic media (4).

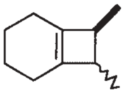
[1] 



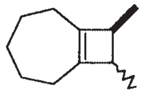
*cis-/trans-***4a**



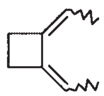
*cis-/trans-***4b**



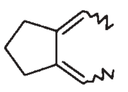
*cis-/trans-***4c**



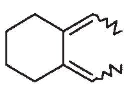
*cis-/trans-***4d**



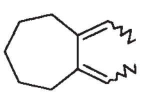
5a



5b



5c

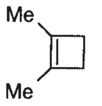


5d

Thus, the mechanism that emerged from these studies is one in which the π,π* excited singlet state of the cyclobutene undergoes purely disrotatory ring opening, but with internal conversion to the ground state potential energy surface occurring *after* the diene is fully formed rather than at a geometry intermediate between reactant and product (19, 21, 22); a mixture of diene isomers is formed not because the reaction itself is nonstereospecific, but because the product is formed in an excited singlet state whose main avenue for relaxation to the ground state is cis,trans-isomerization.

This mechanism is fully compatible with orbital symmetry selection rules, as well as with high level theoretical studies that indicate that within the first ~50 fs after excitation to the π,π* (1^1B_2) state, ring opening is initiated with the disrotatory stereochemistry that is predicted by orbital symmetry (9, 10). Mathies and co-workers (30, 31) had previously reached the same conclusion on the basis of an analysis of the resonance Raman spectrum of cyclobutene. However, the vibrational assignments on which their analysis was based have been refuted (32), and it appears that a different experimental approach will be required to define the stereochemistry of the process on this timescale (10, 32). To date, however, neither theory nor ultrafast spectroscopic methods have been able to address the question of why, if π,π* state ring opening proceeds with a high degree of stereochemical integrity in its very early stages, mixtures of both dis- and conrotatory dienes are *ultimately* formed upon irradiation of stereo-labelled cyclobutene derivatives in solution.

More recent results from our laboratory strongly suggest that the adiabatic ring opening mechanism, with only the π,π* state being involved in the reaction, may be incorrect, or at least not general (4). If the π,R(3*s*) excited state of cyclobutene is really not involved in ring opening, as was concluded on the basis of the photochemistry of **1a**–**1c** (12), then it would be predicted that photolysis of cyclobutene derivatives with especially low Rydberg state energies, under conditions where the Rydberg state is selectively and exclusively excited, should lead *only* to cycloreversion. This premise was tested with the monocyclic, 1,2-disubstituted cyclobutene derivatives **6** and **7**, whose gas phase UV absorption spectra indicate to have spectroscopic π,R(3*s*) excited singlet states of substantially lower energies than the valence (π,π*) state (4). Indeed, photolysis of the three compounds at the long-wavelength edge of their Rydberg absorptions (228 nm) leads mainly to [2 + 2]-cycloreversion in both the gas phase and solution, consistent with the previous assignment of this reaction mode to the π,R(3*s*) Rydberg state. Surprisingly however, all three derivatives also undergo ring opening upon excitation under these conditions, and furthermore, the stereochemically labelled derivatives *cis-* and *trans-***7** appear to do so with clean, *conrotatory* stereochemistry — the stereochemistry associated with the *ground state* ring opening reaction. In a subsequent paper, we showed that high yields of ring opening products are obtained upon 228 nm photolysis of other 1,2-dialkylcyclobutenes (**8** and **9**) as well, and by comparing the quantum yields for product formation to values calculated on the basis of RRKM theory, demonstrated that the process is most likely a discrete reaction of the Rydberg excited state, rather than being the result of internal conversion to upper vibrational levels of the ground state of the cyclobutene, from which thermal ring opening would ensue (23).



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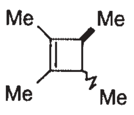

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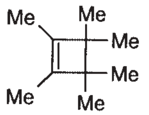

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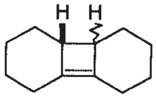

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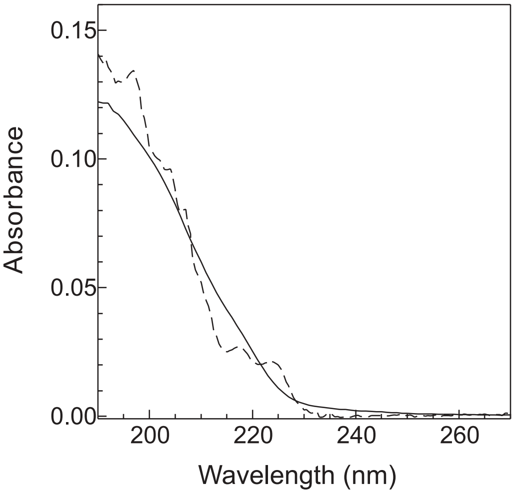
These latest discoveries require that we reconsider the possibility that the overall nonstereospecificity observed with shorter wavelength excitation, where the valence and Rydberg absorptions overlap, is in fact due to competing *stereospecific* reactions from the π,π* and π,R(3*s*) excited states. As a first step in this reanalysis, we have chosen to have a closer look at the possible role of the Rydberg state in the ring opening of some of the compounds that led us in the first place to conclude that the π,π* state reacts adiabatically (22). We thus report the results of a study of the photolysis of the cis- and trans-isomers of the bicyclic cyclobutene derivatives **4b**–**4d** at 228 nm, where the π,R(3*s*) Rydberg absorptions are well-isolated from the higher energy π,π* absorption band and can be excited selectively.

Results

The UV absorption spectra of *cis*-7,8-dimethylbicyclo[4.2.0]oct-1-ene (*cis*-**4c**) in the gas phase (1 atm = 101.325 kPa, SF_6 buffer) and in hexane solution are shown in Fig. 1. The spectra and the differences between them are very similar to those reported earlier for *cis*-1,2,3,4-tetramethylcyclobutene (*cis*-**7**) (4); they clearly show both that the π,R(3*s*) excited state is significantly lower in energy than the valence (π,π*) state in this compound, and that it should be populated selectively upon photolysis with

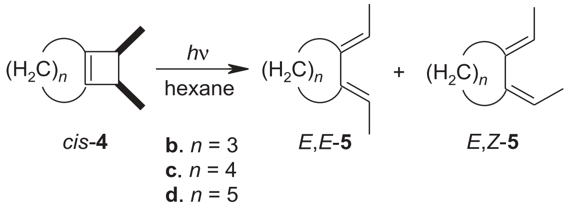
Fig. 1. UV absorption spectra of *cis*-**4c** in the gas phase (– – –) and in hexane solution (——).



monochromatic 228-nm light, at the long-wavelength edge of the absorption spectrum. As expected, the fine structure associated with the gas phase Rydberg absorptions in *cis*-**4c** is washed out in the solution phase spectrum, leaving behind a weak, featureless absorption that tails out to >230 nm. Similar features are observed in the spectra of *trans*-**4c** and the cis- and trans-isomers of **4b** and **4d** in hexane solution under similar conditions (22).

Photolyses of *cis*- and *trans*-**4b**–**4d** were carried out using the light from 16 W Zn (214 nm) and Cd (228 nm) resonance lamps, on argon-saturated solutions containing 0.06 M substrate and 0.001 M of *n*-octane as an internal GC standard. The solutions were analyzed by capillary gas chromatography between ca. 0.2 and 2–5% conversion of substrate (except in the case of *trans*-**4b** with 214 nm light, which was analyzed between 3.5 and 9% conversion). The photolyses produced mixtures of *E*,*E*- and *E*,*Z*-**5b**–**5d** as the only detectable products under the analytical conditions employed in this work (eqs. [2] and [3]), except in the case of *trans*-**4d**, which also afforded small amounts of *Z*,*Z*-**5d**. Relative product yields were determined from the intercepts of plots of relative product concentrations (e.g., [*E*,*E*]/[*E*,*Z*]-**5** in the case of the cis-isomers, and the inverse for the trans-isomers) vs. % conversion of starting material, which are shown in Figs. 2–4 for the 214 and 228 nm photolyses of *cis*- and *trans*-**4b**–**4d**. Plotting the data in this way magnifies the effects of secondary photolysis on the primary isomeric diene yields (as well as the errors associated with the measurement of relatively small GC peak areas); the plots for all six of the compounds studied in this work generally had nonzero slopes, indicative of significant secondary photolysis effects throughout the course of the experiments in each case. Thus, the intercepts represent the best estimates of the true primary isomeric diene yields in the photolyses. Table 1 summarizes the results of these experiments, where the isomeric diene ratios are expressed as the relative yields of disrotatory:conrotatory isomers as defined above. It should be noted that while error bars were not specifically calcu-

[2]



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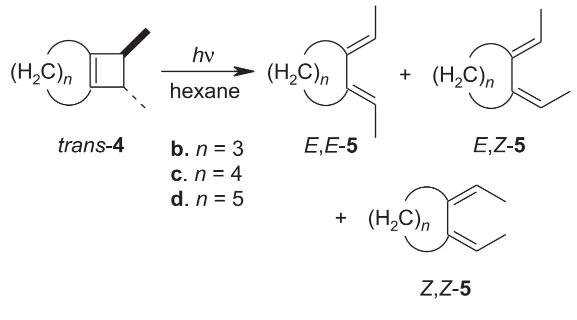


Fig. 2. Plots of DIS:CON diene isomer ratios vs. % conversion of **4**, for the photolysis of (*a*) *cis*- and (*b*) *trans*-6,7-dimethylbicyclo[3.2.0]hept-1(5)-ene (*cis*- and *trans*-**4b**) in deoxygenated hexane solution at 214 nm (●, ——) and 228 nm (○, – – –).

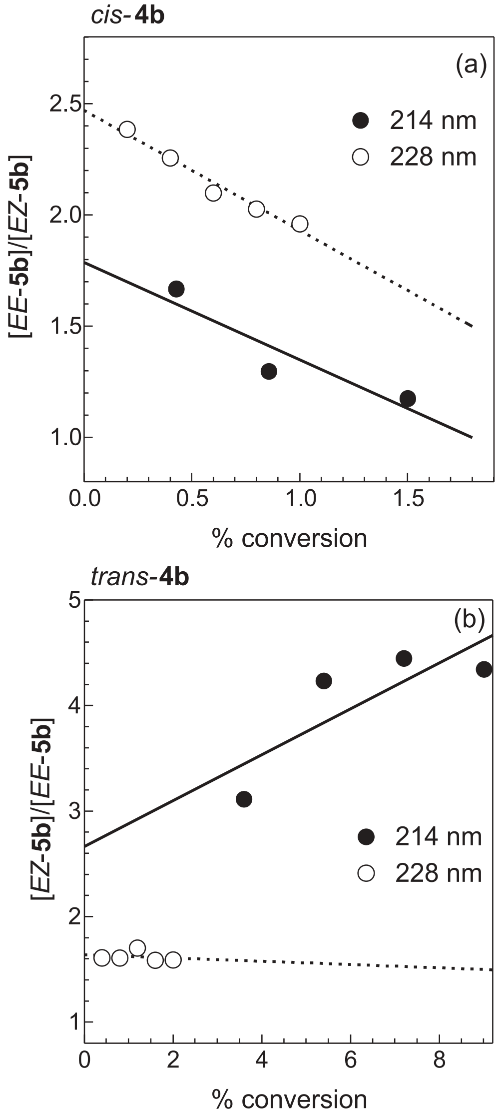


Fig. 3. Plots of DIS:CON diene isomer ratios vs. % conversion of **4**, for the photolysis of (*a*) *cis*- and (*b*) *trans*-7,8-dimethylbicyclo[4.2.0]oct-1(6)-ene (*cis*- and *trans*-**4c**) in deoxygenated hexane solution at 214 nm (●, ——) and 228 nm (○, – – –).

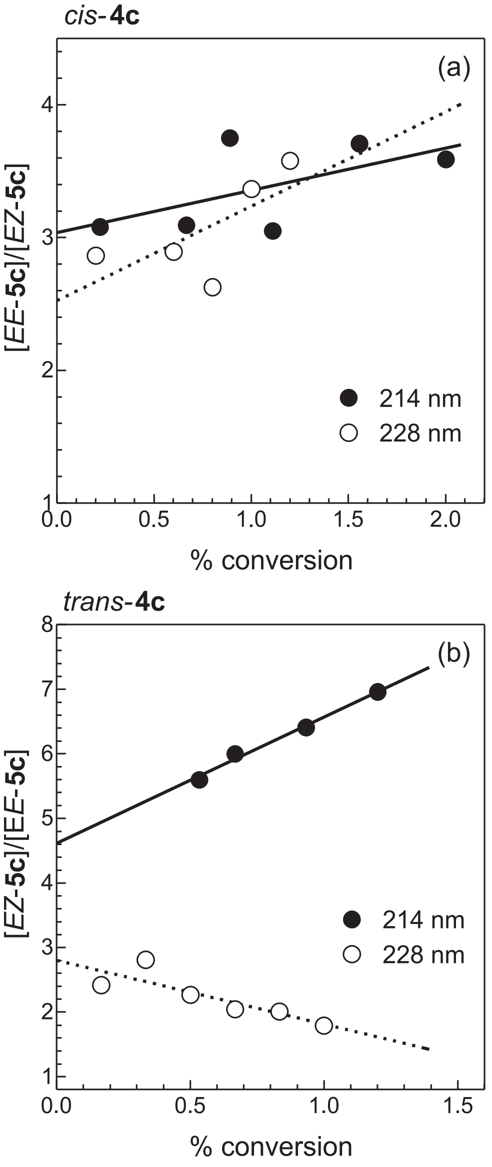
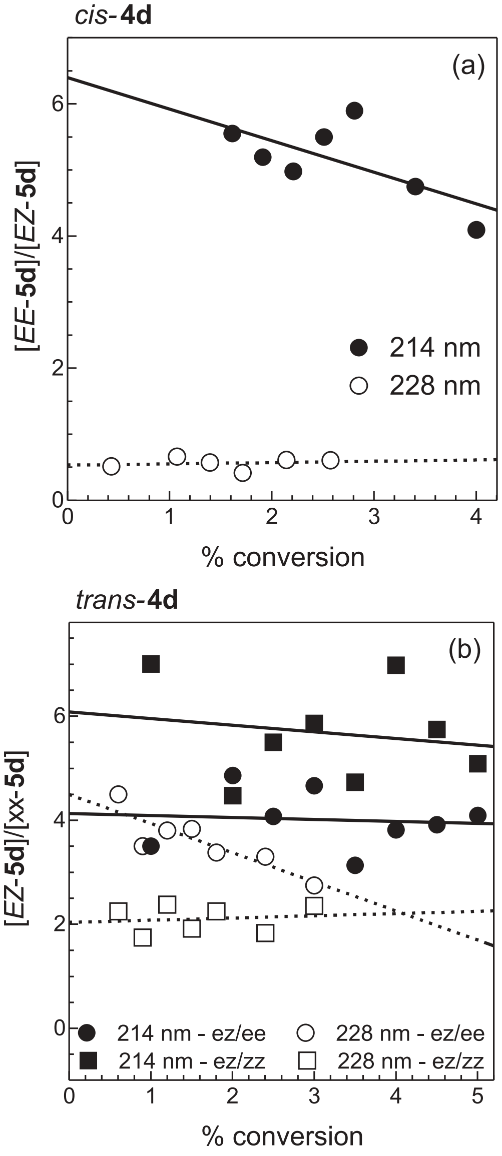


Fig. 4. Plots of DIS:CON diene isomer ratios vs. % conversion of **4**, for the photolysis of (*a*) *cis*- and (*b*) *trans*-8,9-dimethylbicyclo[5.2.0]non-1(7)-ene (*cis*- and *trans*-**4d**) in deoxygenated hexane solution at 214 nm (filled symbols, ——) and 228 nm (open symbols, – – –).



lated for each of the data points shown in the plots of Figs. 2–4, they will naturally be largest at low conversions and decrease in size with increasing conversion. This is of particular concern for the results of photolysis of *trans*-**4b** at 214 nm, which was carried out with a more dilute sample (and to higher conversion of starting material) than the other experiments. Thus, the *E*,*Z*/*E*,*E*-ratio reported for this experiment in Table 1 should be considered a lower limit, with the true value of *E*,*Z*-**5b**/*E*,*E*-**5b** being a maximum of about 4.0 (as previously reported (22)). Also included in the table are the analogous product ratios obtained with 193 nm excitation, from previous work (22). The 214 nm product ratios obtained in the present work are in satisfactory agreement with those reported previously (22).

Table 1 also contains the photostationary state (pss) compositions for direct irradiation of **5b**–**5d** with 228 nm light, which were determined under the same conditions as those employed above for photolysis of the cyclobutenes. These ratios were determined by exhaustive photolysis of samples of *E*,*E*- and *E*,*Z*-**5**, which led to the formation of complex mixtures of *cis*- and *trans*-**4** and other isomeric products, but common mixtures of *E*,*E*-, *E*,*Z*-, and *Z*,*Z*-**5**. Comparison of the diene photostationary state ratios to the isomeric diene ratios from photolysis of the cyclobutenes verifies that the latter more or less accurately represent the true primary product ratios from photolysis of *cis*- and *trans*-**4b** and **4c**. The situation is less clear for *cis*- and *trans*-**4d**, in particular that of the cis-isomer, where the relative yields of *E*,*E*-, *E*,*Z*-, and *Z*,*Z*-**5d** are very similar to the diene pss ratio at 228 nm. The extinction coefficient at 228 nm is significantly lower for this compound than for the others studied in this work

Table 1. Isomeric diene ratios from direct irradiation of bicyclic cyclobutenes *cis*- and *trans*-**4b-d** as deoxygenated solutions in hexane at 25°C, expressed as the ratios of disrotatory:conrotatory isomers.

Wavelength (nm)	*cis*-**4b** (*EE*/*EZ*)	*trans*-**4b** (*EZ*/*EE*)	*cis*-**4c** (*EE*/*EZ*)	*trans*-**4c** (*EZ*/*EE*)	*cis*-**4d** (*EE*/*EZ*)	*trans*-**4d** (*EZ*/*EE*+*ZZ*) [*EE*:*EZ*:*ZZ*]
193[a]	2.5 ± 0.4	9.1 ± 1.2	3.4 ± 0.4	5.6 ± 0.7	9.1 ± 0.9	3.6 ± 0.4
214	1.8 ± 0.6	2.7 ± 1.4[b]	3.0 ± 0.5	4.6 ± 0.3	6.9 ± 1.0	1.8 ± 0.4 [1.0:3.7:1.0]
228	2.47 ± 0.07	1.64 ± 0.11	2.5 ± 0.8	2.8 ± 0.4	0.54 ± 0.12	1.4 ± 0.2 [1.0:4.5:2.3]
pss[c]	5.0:4.1:1.0		2.3:2.0:1.0		2.1:4.1:1.0	

Note: The ratios reported correspond to *E*,*E*/*E*,*Z*-**5** ratios from the *cis*-isomers and *E*,*Z*/*E*,*E*-**5** ratios from the *trans*-isomers. The *Z*,*Z*-isomers were not detected at conversions less than ~2% in any of the photolyses except that of *trans*-**4d**, which contained small amounts of all three diene isomers at *t* = 0. The DIS:CON ratios for the latter compound are thus expressed as *E*,*Z*/(*E*,*E* + *Z*,*Z*). The values listed for the 214 and 228 nm photolyses, which were carried out on 0.06 M solutions in all cases but one, are the intercepts from the plots of product ratio vs. %conversion shown in Figs. 2–4. Those for 193 nm photolyses are reproduced from ref. 22, and were determined using 0.02 M solutions of **4**.

[a] From ref. 22.

[b] From photolysis of a 0.02 M solution of *trans*-**4b**.

[c] Photostationary state compositions from photolysis of the corresponding dienes (**5**) at 228 nm, expressed as *EE*:*EZ*:*ZZ*.

(22), and thus, we cannot rule out the possibility that secondary photolysis effects distort the true product ratios in this case.

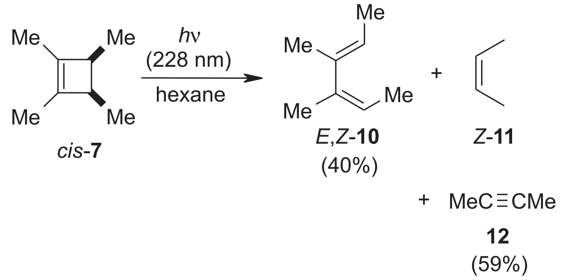
Discussion

The solution phase absorption spectra of monocyclic 1,2-dialkylcyclobutenes such as *cis*- and *trans*-**7** consist of a dominant π,π* absorption band with maximum below 195 nm, and a weak tail absorption that extends out to ~230 nm (4, 16). In the corresponding gas phase spectra, the latter is intensified considerably and takes on distinctive fine structure, characteristic of olefinic π,R(3*s*) absorptions (13). The gas and solution phase spectra of *cis*-**4c** show similar characteristics to those of **7** in this regard (22). Interestingly, the solution phase UV spectra of *cis*- and *trans*-**4b** show enhanced (though weak) absorption in the 220–240 nm range compared with the other compounds in the series, and are virtually identical to one another. The solution phase spectra of *cis*- and *trans*-**4c** and **4d**, on the other hand, show the similarities and differences characteristic of monocyclic 1,2-dialkylcyclobutenes of corresponding stereochemistry at C-3 and C-4 (4, 16, 22). It can thus be concluded that the relative energies of the (spectroscopic) valence and Rydberg excited states are unaffected by the structural constraints imposed by the ancillary cycloalkyl ring in these compounds.

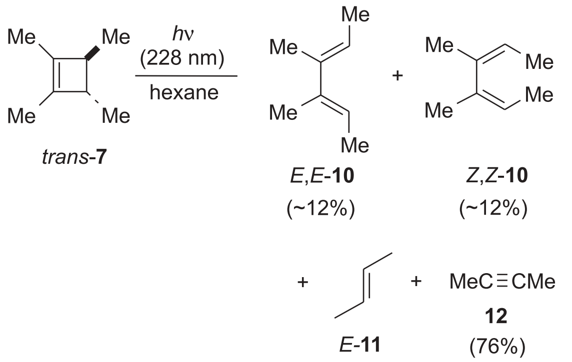
Direct irradiation of *cis*-**7** with 228 nm light in hydrocarbon solution or in the gas phase at 1 atm (1 atm = 101.325 kPa) results in stereospecific conrotatory ring opening, affording the isomeric diene *E*,*Z*-**10** in ca. 40% overall yield, along with *Z*-2-butene (*Z*-**11**) and 2-butyne (**12**) in ca. 60% yield (eq. [4]) (4). Direct irradiation of the trans-isomer under the same conditions, on the other hand, yielded a mixture of all three diene isomers (25% total), *E*-**11**, and **12** (ca. 75%), with the yield of *E*,*Z*-**10** relative to those of the *E*,*E*- and *Z*,*Z*-isomers increasing continuously over the 0.15–0.4% conversion range. However, control experiments showed the relative isomeric diene yields to be distorted by secondary photolysis effects, and demonstrated that the yields of *E*,*Z*-**10** observed under these conditions are consistent with the *actual* formation of a ca. 1:1 mixture of *E*,*E*- and *Z*,*Z*-**10**. We thus concluded that ring opening of *trans*-**7** at 228 nm very likely exhibits similar conrotatory selectivity to that of the cis-isomer, producing a nearly equal mixture of the *E*,*E*- and *Z*,*Z*-dienes.

The product distributions obtained upon irradiation at this wavelength, where the π,R(3*s*) states of the cyclobutenes are selectively populated, are much different than those obtained with shorter wavelength (193–214 nm) excitation, where both conrotatory and disrotatory diene isomers are formed in similar amounts. Since both excited states are populated in the 193–214 nm wavelength range, it was concluded that the π,π* state must be responsible for ring opening to yield the disrotatory diene isomer(s), and that reaction competes effectively with internal conversion to the lower energy Rydberg state. At short excitation wavelengths, the conrotatory isomers may arise because the π,π* process occurs adiabatically, as we previously concluded (22), or because the π,R(3*s*) excited state is also populated (by direct excitation and (or) by internal conversion from the π,π* state), or both.

[4]



[5]



The present work shows that in contrast, the mixtures of diene isomers formed upon ring opening of the fused bicyclic cyclobutenes *cis*- and *trans*-**4b** and **4c** at 228 nm are only modestly different from those obtained with shorter wavelength excitation, where in each case there is a very distinct preference for the formation of the disrotatory diene isomers. In all cases but *cis*-**4b**, there appears to be a consistent wavelength dependence in the product ratios, with the yield of conrotatory product(s) increasing modestly as the excitation wavelength increases. As we found previously in our studies of the photochemistry of **7** at this wavelength (and as the data of Figs. 2–4 clearly show), secondary photolysis effects are generally very difficult to control, and thus, the product ratios reported cannot be considered to be quantitatively accurate. Nevertheless, the trends are clear; the corresponding disrotatory diene isomers are the major products of irradiation of both isomers of **4b** and **4c** at 228 nm, just as they are at shorter irradiation wavelengths.

Assuming that the Rydberg state is indeed *exclusively* excited in these compounds upon absorption of a 228 nm photon, the fact that similar distributions of diene isomers are observed for **4b** and **4c** as with shorter excitation wavelengths (where the π,π* state is also directly populated) suggests either that ring opening within the Rydberg state exhibits similar characteristics to π,π* state ring opening in these compounds or that (conrotatory) Rydberg state ring opening is less efficient than in monocyclic derivatives, allowing internal conversion to the π,π* state (at a non-Franck–Condon geometry), from which ring opening occurs with predominant disrotatory stereochemistry, to compete more effectively.

One interpretation of the results for **4b** and **4c** is that Rydberg state ring opening, in addition to proceeding with preferred conrotatory stereochemistry, also involves twisting about the “central” C=C bond as ring opening proceeds; accordingly, incorporating the cyclobutenyl C=C bond in a second ancillary ring would be expected to result in a structurally induced barrier to Rydberg state ring opening. Scheme 1 shows a hypothetical reaction coordinate diagram for dis- and conrotatory ring opening on the π,π* and π,R(3*s*) excited state surfaces, which incorporates these ideas and illustrates their possible ramifications on the stereochemical characteristics of the reaction. Disrotatory (π,π* state) ring opening is assumed to proceed, at least initially, with little deviation of the 4-carbon system from planarity, since short wavelength (≤214 nm) irradiation of **4a**–**4d** proceeds with high efficiency, with no real variation in quantum yield throughout the series (22); the π,π* surface falls in energy along this reaction coordinate, as predicted both by simple orbital symmetry considerations (8) and recent ab initio calculations (9, 10). If the π,R(3s) surface rises in energy along the disrotatory reaction coordinate, the result will be a thermally activated crossing of the two surfaces at some intermediate geometry (A). The conrotatory reaction coordinate is represented as projecting perpendicularly to the disrotatory one, as it involves both conrotatory twisting about C1—C4 and C2—C3 and torsion about the central C1—C2 bond, leading eventually to *s-trans*-diene. In monocyclic cyclobutenes, the π,R(3*s*) surface is proposed to fall in energy along this reaction coordinate, while the π,π* surface increases in energy owing to orbital symmetry effects, thus resulting in preferred conrotatory ring opening upon selective population of the Rydberg state. In **4b**–**4d** on the other hand, motions along the conrotatory (+ central bond torsion) reaction coordinate in the π,R(3*s*) state encounter the structurally induced barrier, possibly allowing the excited molecule to traverse the (presumably somewhat smaller) barrier to the π,π* surface along the disrotatory reaction coordinate, from which ring opening proceeds with the characteristics of that excited state. It might further be expected that the structurally induced barrier to Rydberg state conrotatory ring opening should decrease as the size and flexibility of the ancillary ring increases, and thus, allow reaction via this pathway to be more competitive with internal conversion to the π,π* state, where ring opening proceeds with preferred disrotatory stereochemistry. Unfortunately, the data for *cis*- and *trans*-**4d** are not sufficiently reliable to address this possibility in a conclusive way; certainly, there is no evidence for it in the wavelength dependence associated with the ring openings of *cis*- and *trans*-**4b** and **4c**.

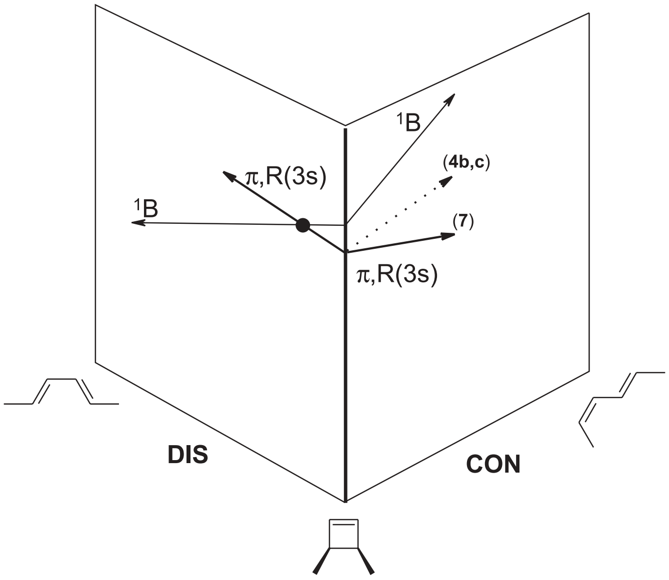
It is relevant to point out the analogy between cyclobutene Rydberg state ring opening and the ring opening of cyclobutene radical cations ($CB^{\cdot+}$), to the extent that the latter species constitutes a reasonable model for the “semi-ionized” olefinic π,R(3*s*) Rydberg state (14, 15). The reaction has been extensively studied in recent years (33–42), and is known to proceed with the preferred conrotatory stereochemistry (36) that theory predicts (39, 43–47). Calculations indicate that the reaction proceeds via two competing conrotatory pathways: a nonsynchronous concerted pathway leading to *s-cis*-1,3-butadiene (*s-cis*-$BD^{\cdot+}$) radical cation, and one involving rotation about the ionized double bond leading to *s-trans*-$BD^{\cdot+}$ via a transition state exhibiting structural characteristics of the cyclopropylcarbinyl radical cation (43, 45–47). Interestingly, photolysis of $CB^{\cdot+}$ in a low-temperature matrix has been reported to yield *s-trans*-$BD^{\cdot+}$ exclusively (39).

This explanation is obviously highly speculative, and undoubtedly not the only one possible. Nevertheless, it contains a number of features that might be tested experimentally. For example, the idea that ring opening on the π,R(3*s*) potential energy surface can be impeded by the introduction of a structurally induced barrier might be tested through studies of the temperature dependence of the reaction stereochemistry in these and monocyclic cyclobutenes as a function of excitation wavelength. Ultrafast time-resolved studies, along the lines of those recently reported for other aliphatic alkenes (25, 26), would also offer potentially invaluable information on the mechanism. Finally, it still remains to be established to what extent the π,R(3*s*) state contributes to the ring opening of alkylcyclobutenes at shorter excitation wavelengths (185–214 nm), where the π,π* excited singlet state is also populated. Further work in this area is clearly necessary.

Summary and conclusions

Alkylcyclobutenes have two low-lying excited singlet states of similar energy, the π,π* (valence) and π,R(3*s*) (Rydberg) state, and both lead to electrocyclic ring opening to the isomeric 1,3-dienes. The Rydberg state is markedly lower in energy than the π,π* state in 1,2-dialkylcyclobutenes, a characteristic that allows the photochemistry associated with this excited state to be studied under conditions of selective excitation.

Scheme 1.



In such compounds, excitation at the short wavelengths necessary for population of the π,π^* state results in non-stereospecific ring opening, and the yields of formally allowed (disrotatory) diene isomers relative to the formally forbidden (conrotatory) ones vary with excitation wavelength and the stereochemistry and other structural characteristics of the substrate. On the other hand, selective excitation at the long-wavelength edge of the absorption band, where the π,R(3*s*) Rydberg state absorptions appear in the gas phase spectrum, results in reaction characteristics that vary much more dramatically with substrate structure; monocyclic derivatives open with clean conrotatory stereospecificity, while bicyclic derivatives, in which the cyclobutenyl C=C bond is shared with a second ancillary ring, appear to exhibit predominant disrotatory stereoselectivities, similar to what is observed upon shorter wavelength (π,π^*) excitation. These results are interpreted as suggesting that the Rydberg state process involves both conrotatory motions about the cyclobutenyl C1—C4 and C2—C3 bonds *and* twisting about the C=C bond as the reaction is initiated on the excited-state surface. Impeding the latter motions through appropriate structural constraints has the effect of directing the molecule over a barrier and onto the π,π^* state surface, in which ring opening with predominant disrotatory stereochemistry ensues. The wavelength dependent stereoselectivities that have been observed with most of the compounds that have now been studied suggest that internal conversion from the π,π^* state to the lower-lying Rydberg state is slow relative to ring opening, or at best competitive with it.

The true degree of disrotatory stereoselectivity that is associated with the π,π^* state reaction unfortunately remains poorly defined, though it is clear that in some cases at least, it is very high. At least two viable mechanisms remain which could explain the non-stereospecificity observed upon excitation of alkylcyclobutenes in the region of the π,π^* absorption: adiabatic ring opening within the π,π^* state, and the competing involvement of the Rydberg state, populated either by direct absorption or (incomplete) internal conversion from the π,π^* state. Further study of the reaction will be necessary to conclusively distinguish between these possibilities.

Experimental

The cyclobutenes studied in this work were prepared and purified as previously reported (22), while photoproducts were identified by GC coinjection with authentic samples or after isolation from semipreparative scale photolyses of the corresponding cyclobutene derivative. The cyclobutenes were purified to >99% purity by semipreparative gas chromatography (20% TCEP on 80/100 Chromosorb PNAW, 0.25″ × 6″, stainless steel, Chromatographic Specialties, Inc.), followed where necessary by passage through a 1:5 (silver nitrate:silica gel) microcolumn using pentane as the eluant. Only the sample of *trans*-**4d** remained contaminated with isomeric dienes after this treatment, but the amounts were small (ca. 1% in total by GC), and were accounted for in the analyses of the 214 and 228 nm photolyses of this compound. Hexanes (BDH Omnisolv) and *n*-octane (Aldrich) were used as received from the suppliers. UV absorption spectra were recorded using a Cary 50 UV–vis spectrophotometer in 1 cm Suprasil cells. Analytical gas chromatographic separations were carried out using a Hewlett-Packard 5890 gas chromatograph equipped with a flame ionization detector and a 0.22 mm × 15 m DB-1 fused silica microbore capillary column (Chromatographic Specialties, Inc.). FID response factors were determined for all compounds by construction of standard working curves from mixtures of stock solutions of the pure compounds.

Samples for photolysis contained the cyclobutene (ca. 0.06 M) and *n*-octane (0.001 M) in hexane solution. Aliquots (ca. 0.3 mL) were placed in 5 mm quartz tubes containing a micro stirring bar, sealed with rubber septa, and deoxygenated with a stream of dry argon. Photolyses were carried out using 16 W Philips 93106E zinc or 16 W Philips 93107E cadmium resonance lamps for irradiation at 214 or 228 nm, respectively, with constant agitation of the solutions with a magnetic stirrer. Aliquots were removed from the cells by microlitre syringe at suitable photolysis intervals and analysed by GC. Product formation was monitored as a function of photolysis time in all cases.

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