

## 1992 Merck–Frosst Award Lecture Orbital symmetry and the photochemistry of cyclobutene<sup>1</sup>

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Direct photolysis of alkyl-substituted cyclobutene derivatives in solution with monochromatic far-UV light sources results in competing ring opening to the corresponding substituted 1,3-butadiene derivatives and fragmentation to the corresponding alkene and alkyne via formal [2+2] cycloreversion. The excited states leading to the two types of products have been identified. Cycloreversion occurs stereospecifically and arises as a result of excitation of the  $\pi, R(3s)$  Rydberg state, which is of comparable energy to the  $\pi, \pi^*$  state in alkylcyclobutenes. In spite of its stereospecificity, the reaction is nonconcerted; evidence is presented to suggest that it occurs by a mechanism involving [1,2] migration (ring contraction) to yield a cyclopropylcarbene intermediate, which then fragments to yield the alkyne and alkene. The stereochemistry at C3 and C4 in the starting cyclobutene is retained in the alkene produced in the reaction. Ring opening proceeds nonstereoselectively (from the  $\pi, \pi^*$  singlet state) in well over a dozen systems that have been investigated, and possible mechanisms to account for this are discussed. It is proposed that orbital symmetry plays a role in the reaction, but only in the early stages of ring opening. Bicyclic cyclobutene derivatives in which the cyclobutene double bond is located across the [0] bridge undergo ring opening with a high degree of disrotatory stereoselectivity. Possible reasons for this unusual behavior are discussed in light of recent *ab initio* theoretical results.

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La photolyse directe de dérivés du cyclobutène substitués par des groupes alkyles, réalisée en solution, à l'aide de sources de lumière UV-lointain monochromatique, conduit à une compétition entre l'ouverture de cycle conduisant aux dérivés buta-1,3-diènes substitués correspondants et une fragmentation conduisant à l'alcène et à l'alcyne correspondants par le biais d'une cycloréversion [2+2] formelle. Les états excités conduisant à ces deux types de produits ont été identifiés. La cycloréversion se produit stéréospécifiquement et elle est le résultat de l'excitation de l'état Rydberg  $\pi, R(3s)$  dont l'énergie est comparable à celle de l'état  $\pi, \pi^*$  des alkylcyclobutènes. Malgré sa stéréospécificité, la réaction n'est pas concertée; on présente des données suggérant qu'elle se produit par un mécanisme impliquant une migration [1,2] (contraction de cycle) qui conduit à un intermédiaire cyclopropène qui se fragmente ensuite pour donner l'alcène et l'alcyne. La stéréochimie en C3 et en C4 du cyclobutène de départ est conservée dans l'alcène qui se forme au cours de la réaction. L'ouverture du cycle se produit d'une façon qui n'est pas stéréospécifique (à partir d'un état singulet  $\pi, \pi^*$ ) dans plus d'une douzaine de systèmes que nous avons examinés; on discute des divers mécanismes possibles pour expliquer les résultats. On propose que la symétrie des orbitales joue un rôle dans la réaction, mais seulement au début de la réaction d'ouverture de cycle. Les cyclobutènes bicycliques dans lesquels la double liaison du cyclobutène se trouve sur le pont [0] subissent la réaction d'ouverture de cycle avec un degré élevé de sélectivité disrotatoire. On discute des raisons possibles de ce comportement inhabituel à la lumière de résultats théoriques *ab initio* récents.

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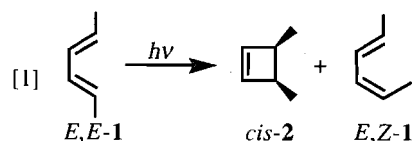
### Introduction

The thermal and photochemical interconversions of cyclobutene and 1,3-butadiene play a central role in any textbook treatment of orbital symmetry selection rules and pericyclic reactions (1–3). Figure 1 illustrates the classical orbital and state correlation diagrams for the conrotatory ( $C_2$  symmetry) and disrotatory ( $C_s$  symmetry) interconversion pathways (1). The ground states of cyclobutene and 1,3-butadiene correlate in  $C_2$  symmetry, so that conrotatory interconversion proceeds with no symmetry-imposed barrier. In  $C_s$  symmetry, on the other hand, the ground state of the diene correlates with a doubly excited state of cyclobutene (and vice versa); the result is a substantial barrier to ground state disrotatory interconversion owing to orbital symmetry considerations. The barrier results from the avoided crossing of the two surfaces in the intermediate stages of the reaction (see Fig. 1b). Since the lowest ( $\pi, \pi^*$ ) excited singlet state of 1,3-butadiene correlates with the  $\pi, \pi^*$  singlet state of cy-

clobutene in  $C_s$  symmetry, the direct photochemical interconversions are predicted to proceed in disrotatory fashion.

As indicated above, the thermal interconversions are predicted by orbital symmetry to proceed in conrotatory fashion, and there are hundreds of examples in the literature that demonstrate that this is indeed the case (for reviews, see ref. 4). The degree of conrotatory stereospecificity in the thermal interconversions often exceeds 99%. Similarly, there are numerous examples that illustrate the preferred disrotatory stereochemistry of the photochemical ring closure of 1,3-butadiene derivatives to the corresponding cyclobutene (5; also ref. 3a, pp. 495–499, and refs. cited). For example, *E,E*-2,4-hexadiene (*E,E*-1) has been reported to yield *cis*-3,4-dimethylcyclobutene (*cis*-2) stereospecifically, albeit in low quantum yield owing to competing *cis,trans* isomerization, upon direct photolysis in solution (eq. [1]) (5c).

Van der Lugt and Oosterhoff proposed that disrotatory ring closure starts in the diene  $S_1$  state, crosses onto the  $S_2$



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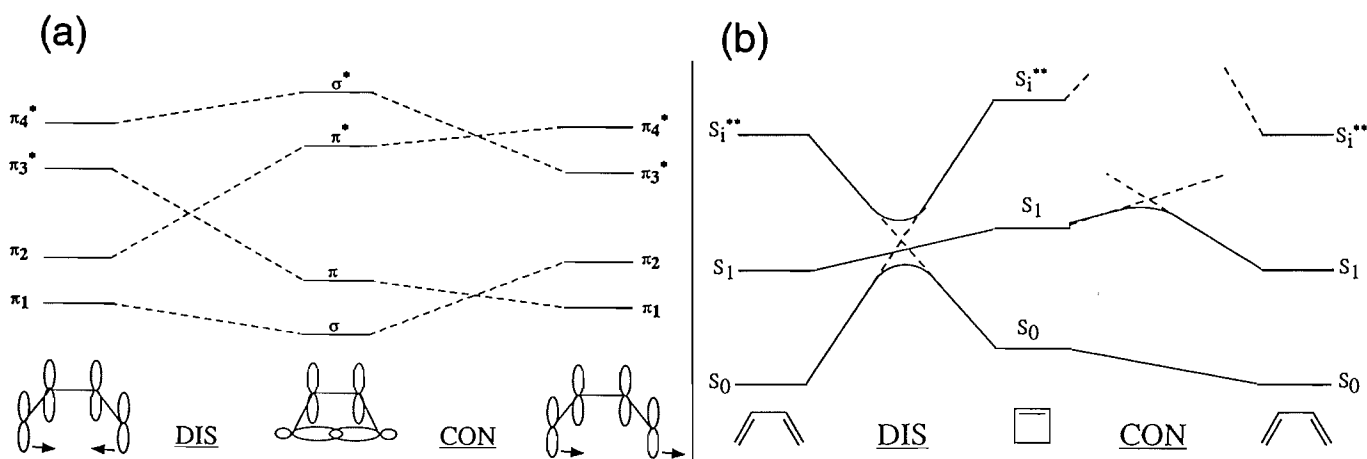


FIG. 1. Orbital (a) and state (b) correlation diagrams for the con- and disrotatory interconversions of cyclobutene and 1,3-butadiene (1).

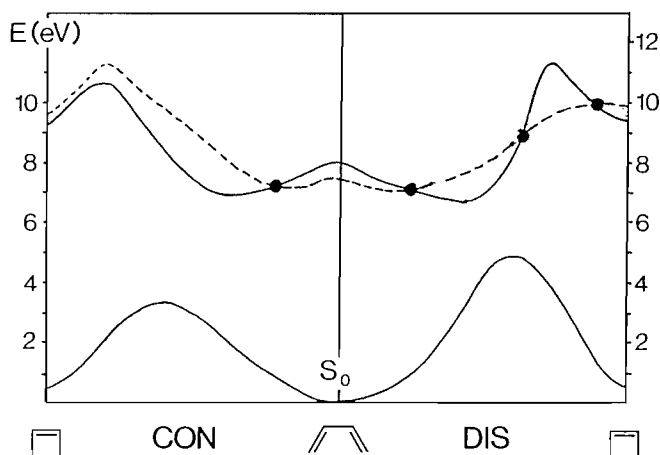


FIG. 2. Calculated (*ab initio*) state correlation diagrams for the con- and disrotatory interconversions of cyclobutene and 1,3-butadiene (9b).

potential energy surface and proceeds to a well (the avoided crossing) from which internal conversion to the ground state surface occurs (see Fig. 2) (6). The process cannot occur entirely on the  $S_1$  surface (even though the  $S_1$  state of butadiene correlates directly with the  $S_1$  ( $\pi, \pi^*$ ) state of cyclobutene in  $C_s$  symmetry) because the cyclobutene excited singlet state is at least 50 kcal/mol higher in energy than that of the diene (6, 8). The geometry of the reacting molecule at the  $S_2$  energy minimum is similar to that at the transition state for the thermal disrotatory process, so once the excited molecule has entered the ground state surface, it can proceed to cyclobutene or revert to diene. The *ab initio* calculations of Grimbert *et al.* suggested that these general features are common to the ground and excited state energy surfaces for both the conrotatory and disrotatory ring closure reactions (7). However, in the latter case the energy gap between the  $S_2$  and  $S_0$  surfaces is substantially smaller so that the rate of  $S_2 \rightarrow S_0$  internal conversion at the avoided crossing is greater for the disrotatory reaction pathway (7). Morihashi *et al.* showed that the probability of the  $S_2 \rightarrow S_0$  transition is  $10^{12}$  times greater for the disrotatory pathway than

for the conrotatory one (9). The state correlation diagrams for the conrotatory and disrotatory interconversions of cyclobutene and 1,3-butadiene, from the *ab initio* calculations of Morihashi and Kikuchi (9b), are summarized in Fig. 2.

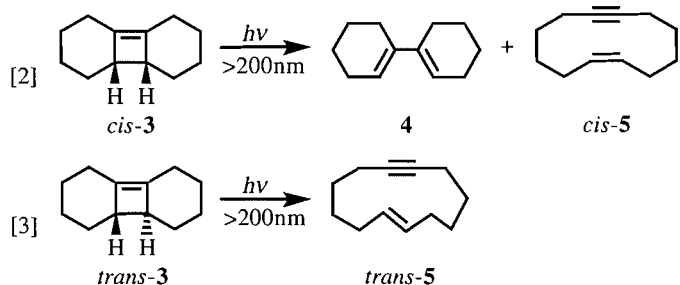
Each of the studies described above makes the classical assumption that orbital symmetry is conserved throughout the transformation; i.e., that  $C_s$  and  $C_2$  symmetry are maintained in the disrotatory and conrotatory interconversions, respectively. More recent calculations have specified less stringent symmetry requirements for the excited state reaction and explored the possibility that it proceeds asymmetrically. On the basis of semi-empirical (MINDO/3) calculations, Pichko *et al.*, proposed that the photochemical ring closure of 1,3-butadiene occurs by disrotatory closure of the *relaxed* butadiene singlet (10). Thus, following Franck-Condon excitation, butadiene initially relaxes to the allylmethylene biradical geometry, and then undergoes disrotatory terminal-group rotation (over an activation barrier of 8.4 kJ/mol) to reach the geometry at which internal conversion to the ground state surface occurs.

Bernardi and Robb and their co-workers have reported MCSCF *ab initio* calculations (11) that suggest that internal conversion to the ground state surface during ring closure occurs via a conical intersection (12), or a point where ground and excited state surfaces are degenerate. The calculated geometry of the molecule at the conical intersection for ring closure is described as a tetraradicaloid structure in which all  $\pi$ -bonds in the molecule are broken. This more complex mechanism for the reaction will be discussed in more detail later in this account.

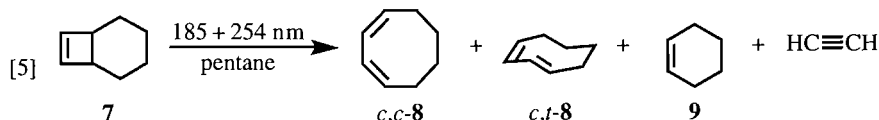
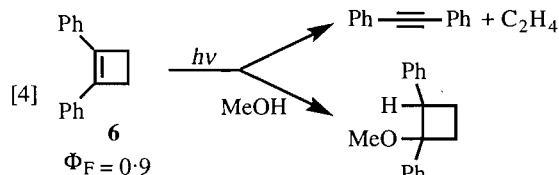
Until recently, the *only* example that demonstrates the stereochemistry of photochemical cyclobutene ring opening was that of Saltiel and Ng-Lim, who reported the results of direct photolysis of the tricyclic, isomeric cyclobutene derivatives *cis*- and *trans*-3 (eqs. [2] and [3]) (13). Diene 4 is the product of (photochemically allowed) disrotatory ring-opening of *cis*-3. The apparent failure of *trans*-3 to yield this product is an indication that ring opening does *not* proceed by the formally forbidden, conrotatory pathway; in this case, the disrotatory pathway is effectively blocked since it must yield the highly strained *cis,trans* isomer of 4.

The apparent neglect of this prototypical excited state

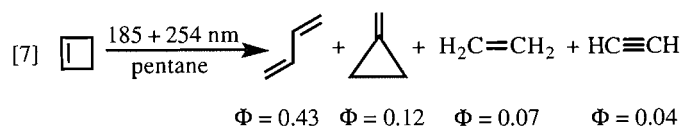
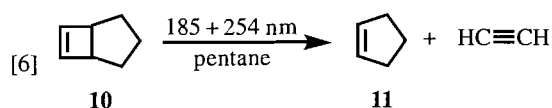
pericyclic reaction by photochemists is presumably due to the fact that, in general, phenylated cyclobutenes do not



undergo ring opening upon photolysis in solution (14–16).<sup>3</sup> For example, 1,2-diphenylcyclobutene yields only the products of formal [2+2] cycloreversion upon direct photolysis in hydrocarbon solution (14, 16), undergoes solvent addition upon photolysis in methanol solution (15), and fluoresces with high efficiency (16) (see eq. [4]). Evidently,



tolysis (185 + 254 nm) of cyclobutene itself in pentane solution results in the formation of 1,3-butadiene, methylenecyclopropane, acetylene, and ethylene in the quantum yields shown in eq. [7] (21).



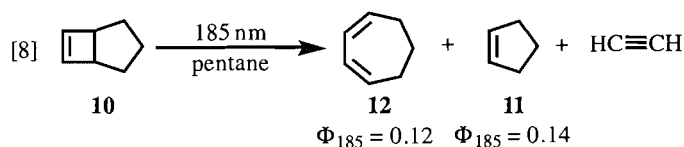
Our interest in this area was initiated by the report of Inoue *et al.* of the photochemistry of 7 and 10. We originally set about to show simply that photolysis of these molecules with *monochromatic* far-UV radiation, under conditions where the primary diene products *are not* subject to secondary photolysis with the 254 nm component of the low-pressure mercury lamp, would afford results that are both internally consistent and compatible with the earlier report by Saliel and Ng Lim on the photochemistry of *cis*- and *trans*-3. Indeed, photolysis of 10 in pentane with a low-pressure mercury lamp in conjunction with a  $\gamma$ -irradiated LiF crystal filter to remove the 254 nm component of the light source ( $OD^{185}$

conjugated cyclobutenes undergo ring opening upon photolysis only if the reaction is accompanied by the relief of ring strain, as for example with the cases of benzocyclobutenes (17) and Dewar aromatics (18). Interestingly, the former have been reported to open nonstereospecifically, while Dewar aromatics yield the corresponding fully aromatic isomer adiabatically from both the singlet and triplet excited states. With unstrained systems, photochemical ring opening evidently occurs only with cyclobutenes bearing nonconjugating substituents, necessitating the use of far-UV photochemical techniques for the study of the reaction.

### The photochemistry of alkylcyclobutenes

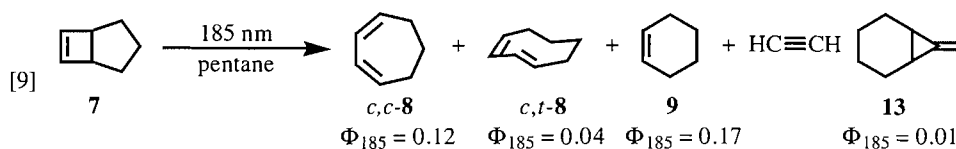
Inoue *et al.* reported in 1983 that photolysis of bicyclo[4.2.0]oct-7-ene (7) in pentane solution with an unfiltered low-pressure mercury lamp (185 + 254 nm) gives rise to *cis,cis*- and *cis,trans*-1,3-cyclooctadiene (8), cyclohexene (9), and ethylene (eq. [5]) (19). The apparent nonstereospecificity of ring opening was explained by noting that 8 absorbs strongly at 254 nm (the major component of the low-pressure mercury lamp) and undergoes facile *cis,trans* photoisomerization upon photolysis at this wavelength (20). Photolysis of bicyclo[3.2.0]hept-6-ene (10) under similar conditions was found to afford only cyclopentene (11) and acetylene (eq. [6]) (19). Adam *et al.* later reported that pho-

~ 0.2;  $OD^{254} > 5$ ), or with an ArF excimer laser (193 nm), resulted in the formation of 1,3-cycloheptadiene (12) and cyclopentene (11) in comparable yields (eq. [8]) (22). As expected, the absence of 12 as a product of photolysis of 10 with the unfiltered light source is simply due to its substantial photolability at 254 nm; this diene undergoes photochemical ring closure to yield 10 with a quantum yield of ca. 0.35 (*Sd,e*).



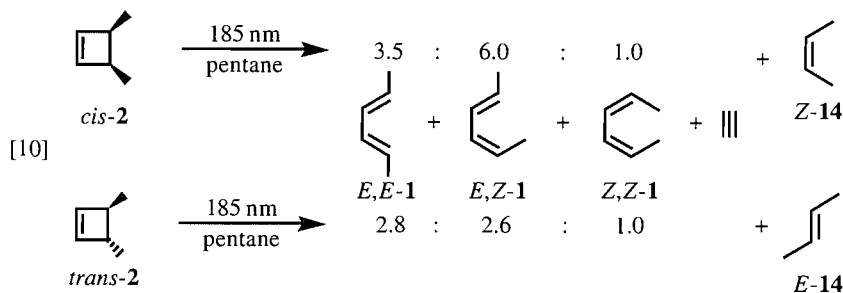
To our considerable surprise, however, photolysis of 7 under similar conditions gave rise to *mixtures* of *cis,cis*- and *cis,trans*-8, in addition to cyclohexene (9) and small amounts of the methylenecyclopropane derivative 13 (eq. [9]). To demonstrate that the apparent nonstereospecificity of diene formation was not due to secondary photolysis effects, 10 was photolyzed in the presence of small amounts of *c,c*-8 under the above conditions, and the photolysate was monitored for the formation of the *cis,trans* isomer between 0.3 and 3% conversion. None could be detected within the limits of sensitivity of our analytical method, verifying that secondary diene photolysis does not contribute to the observed product distributions under conditions of monochromatic photolysis to low conversions.

<sup>3</sup>Also, W. J. Leigh and A. Postigo, unpublished results.



Even more interesting results were obtained from monochromatic far-UV photolysis of the monocyclic derivatives *cis*- and *trans*-3,4-dimethylcyclobutene (**2**); these afforded mixtures of the three isomeric 2,4-hexadienes weighted in favour of the *formally forbidden* diene isomer(s) in each case (eq. [10]). Similar investigations of the photochemistry of a

wide variety of mono-, bi-, and tricyclic alkylcyclobutene derivatives have been reported since our initial study (23–29), and indicate that the nonstereospecificity of the photochemical ring opening reaction is quite general. The results of these studies will be discussed in detail throughout this account.

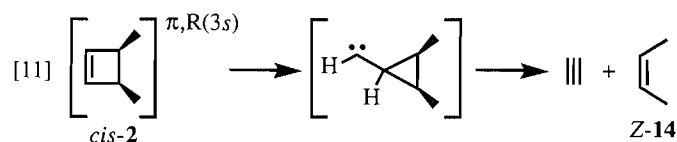


#### Identification of the excited state(s) responsible for ring opening and cycloreversion

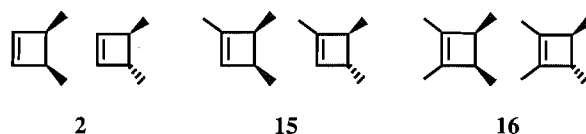
It has long been known that population of the triplet state of alkylcyclobutenes through triplet sensitization results in (2+2) dimerization, and does *not* lead to unimolecular isomerization or fragmentation (30; see, however, ref. 18). Thus, it is clear that both ring opening and cycloreversion arise from the excited singlet state manifold. As numerous workers have pointed out (19, 21, 22), there are two excited singlet states of similar energies in simple alkylcyclobutenes, the  $\pi,\pi^*$  (valence) state and the  $\pi,\text{R}(3s)$  (Rydberg) state (31). In principle, both could give rise to ring opening and cycloreversion products, though by very different mechanisms.

Since population of the  $\pi,\text{R}(3s)$  state in simple alkenes involves promotion of a  $\pi$ -electron to a spatially diffuse  $3s$  orbital, the classical picture of the electronic structure of this state is that of a semi-ionized species that possesses radical cation character at the  $\text{C}=\text{C}$  bond (32). Since cyclobutene radical cations are known to undergo (thermal) ring opening in the gas phase (33) (the stereochemistry is evidently unknown), it is possible that Rydberg state involvement could account for the nonstereospecificity associated with this aspect of cyclobutene photochemistry, if Rydberg-derived ring opening occurs nonstereospecifically or in conrotatory fashion competitive with  $\pi,\pi^*$  state-derived disrotatory ring opening. The possibility that the cycloreversion process is derived from Rydberg state excitation is a more concrete one. It is well known that direct photolysis of simple alkenes in solution results in the predominant formation of products derived from carbene intermediates formed via [1,2]-hydrogen or alkyl migrations (32). In simple di-, tri-, and tetra-substituted alkenes, the  $\pi,\text{R}(3s)$  state is lower in energy than the  $\pi,\pi^*$  state in the gas phase as well as in solution (31), and has been conclusively identified as the one responsible for the formation of these types of products (32, 34). With

cycloalkenes, ring contraction is often the predominant mode of Rydberg-derived [1,2]-alkyl migration. In the case of cyclobutene, ring contraction would yield cyclopropylcarbene, which is known to fragment to acetylene and ethylene (35). In substituted systems, the alkene that is produced in this process is formed stereospecifically, with the stereochemistry defined by the substitution in the carbene (35). The possible stereospecific formation of *Z*-2-butene from photolysis of *cis*-**2** by this mechanism is illustrated in eq. [11].

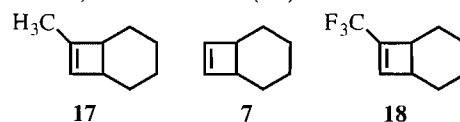


To define the individual contributions of the  $\pi,\pi^*$  and  $\pi,\text{R}(3s)$  states to the formation of the various products of cyclobutene photolysis, it is necessary to systematically vary the relative energies of the two states. The obvious ways of doing this involve either preferentially lowering the energy of the  $\pi,\text{R}(3s)$  state with alkyl substituents at the  $\text{C}=\text{C}$  bond or preferentially lowering the  $\pi,\pi^*$  state with conjugating substituents at the  $\text{C}=\text{C}$  bond. The first approach was exploited in a study of the photochemistry of the series of monocyclic compounds **2**, **15**, and **16**; unfortunately, there are no regular variations in photoproduct distributions throughout the series that might allow a correlation to be made (27). Since phenylated cyclobutenes do not ring-open upon photolysis, the second approach similarly does not allow identification of the role of the Rydberg state in contributing to the ring opening reaction.



The approach we employed for the solution of this problem involved systematically *raising* the energy of the  $\pi, R(3s)$  state relative to that of the  $\pi, \pi^*$  state by trifluoromethyl substitution (28). The strong electron-withdrawing character of this substituent was expected to destabilize the radical-cation-like alkene Rydberg without substantially altering the energy of the  $\pi, \pi^*$  state (since it is nonconjugative). The gas- and solution-phase UV absorption spectra and  $\pi$ -ionization potentials (measured by photoelectron spectroscopy) of the series of bicyclo[4.2.0]oct-7-ene derivatives **7**, **17**, and **18** verify that trifluoromethyl substitution does indeed have the anticipated effect on the singlet excited state manifold of cyclobutene derivatives, just as it does in simple alkenes such as norbornene (34). Thus, the  $\pi, R(3s)$  state is substantially

lower in energy than the  $\pi, \pi^*$  state in **17**, but higher in energy than the  $\pi, \pi^*$  state in **18** (28).



Photolysis of the three compounds in pentane solution with 193 nm light results in competitive ring opening and cycloreversion as shown in eq. [12]. Table 1 lists the quantum yields for formation of dienes and cyclohexene from photolysis of the three compounds, the isomeric diene distributions obtained from each, and the positions of the  $\pi, R(3s)$  and  $\pi, \pi^*$  band maxima from the gas-phase UV-absorption spectra (28).

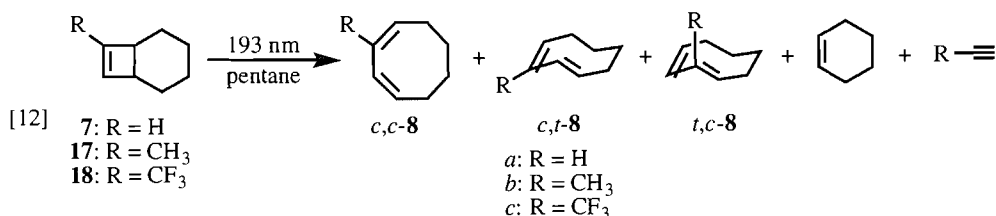


TABLE 1. Gas-phase spectroscopic properties and product quantum yields from photolysis (193 nm) of substituted bicyclo[4.2.0]oct-7-enes **7**, **17**, and **18**<sup>a</sup>

	<b>17</b> (R = CH <sub>3</sub> )	<b>7</b> (R = H)	<b>18</b> (R = CF <sub>3</sub> )
$\pi$ -IP <sup>b</sup>	8.5 ± 0.1	9.0 ± 0.1	9.7 ± 0.2
$E_{\pi, R(3s)}$ (eV) <sup>c</sup>	5.91	6.37	≥6.7
$E_{\pi, \pi^*}$ (eV) <sup>c</sup>	6.40	≥6.70	≥6.62
$\Phi_{\text{dienes}}$ <sup>d</sup>	0.087	0.175	0.292
$\Phi_{\text{cyclohexene}}$	0.13	0.14	0.030
$c, c / (c, t + t, c)$ <sup>e</sup>	1.3	1.3	1.8

<sup>a</sup>Photolysis in deoxygenated pentane solution at 22°C. Relative errors in quantum yields are ca. 5%. Data from ref. 28.

<sup>b</sup>Lowest vertical ionization potential from gas-phase photoelectron spectrum.

<sup>c</sup>Position of absorption band maximum in gas-phase UV absorption spectrum.

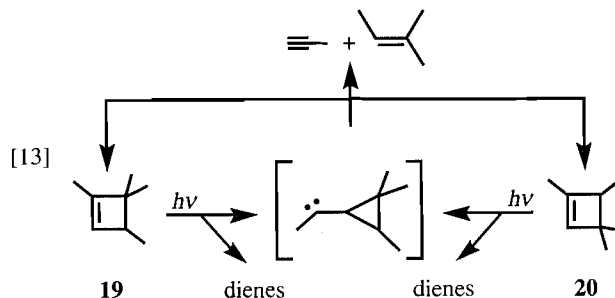
<sup>d</sup>Total quantum yield for diene formation.

<sup>e</sup>Ratio of yields of isomeric dienes (error is ca. 10%).

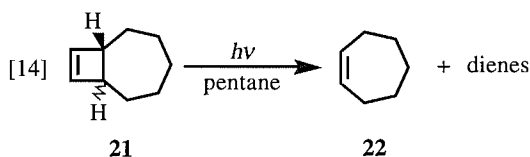
As the data in Table 1 show, the quantum yield for cycloreversion, while substantial in the cases of **7** and **17**, is very small for the trifluoromethyl-substituted compound **18**. This trend indicates that cycloreversion arises nearly exclusively from the Rydberg state. On the other hand, the quantum yields for ring opening *increase* in opposite fashion, indicating that this aspect of cyclobutene photoreactivity is due to  $\pi, \pi^*$  state excitation. The effect of varying the photolysis wavelength on the observed product distributions from the three compounds is also consistent with these conclusions. Significantly, since ring opening of all three derivatives is nonstereospecific (and yields similar distributions of isomeric dienes), the apparent violation of orbital symmetry selection rules cannot be due to the intervention of more than one singlet excited state.

#### Scope and mechanism of the cycloreversion reaction

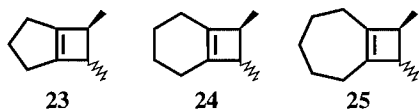
The suggestion that Rydberg-derived cycloreversion proceeds by a mechanism involving initial [1,2]-alkyl migration (ring contraction) to yield a cyclopropylcarbene intermediate, which then fragments to yield the corresponding alkyne and alkene (eq. [11]), has been investigated directly (24). Cyclopropylcarbenes are known to undergo *ring contraction* to yield cyclobutenes in addition to fragmenting to an alkene and acetylene. With this in mind, we studied the photochemistry of the isomeric, unsymmetrically substituted cyclobutenes **19** and **20**. The two compounds were found to interconvert in low yield upon photolysis in solution; the most reasonable mechanism for this process is via common cyclopropylcarbene intermediate(s), one of which is shown in eq. [13].



The cycloreversion reaction is suppressed when it must produce a relatively unstable alkene or alkyne product. Thus, photolysis of *cis*- and *trans*-bicyclo[5.2.0]non-8-ene (**21**) yields cycloheptene (**22**) in both cases (eq. [14]), but the quantum yield for formation of this product (185 nm) is ca. five times lower for the *trans* isomer ( $\Phi = 0.26$  from *cis*-**21** vs.  $\Phi = 0.05$  from *trans*-**21**) (25). The difference is presumably due to the fact that in the latter case, stereospecific "cycloreversion" must produce *trans*-cycloheptene. Even

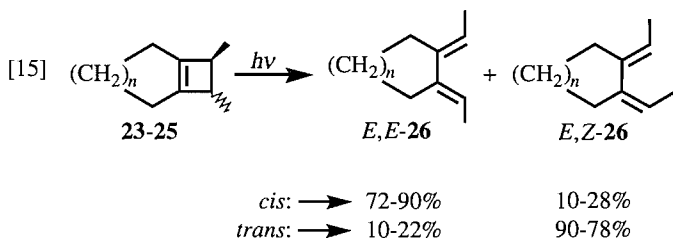


more remarkably, the fragmentation reaction is completely suppressed in the photolyses of compounds **23–25** (30, 29);<sup>4</sup> in these cases, fragmentation would produce highly strained C5–C7 cycloalkynes.



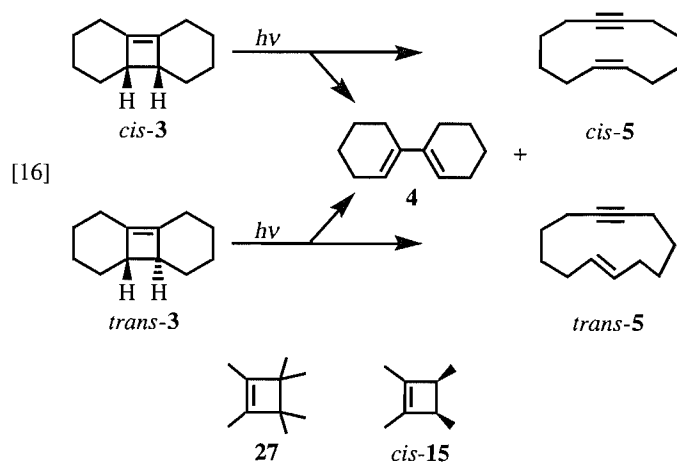
#### Scope and mechanism of the ring opening reaction

It is clear from the various examples already discussed that, in general, the photochemical ring opening of cyclobutenes does not follow orbital symmetry selection rules. Nevertheless, certain observations suggest very strongly that orbital symmetry does (or at least, *can* in certain instances) play a role in the reaction. The most compelling of these is the fact that compounds **23–25** consistently open with a high (though not complete) degree of disrotatory stereospecificity (eq. [15]) (ref. 29 and footnote 4). There are a number of structural features present in these compounds that set them apart from the monocyclic and other bicyclic systems that have been studied; the role that these features play in altering the general behavior of cyclobutenes with respect to ring opening will be discussed in more detail later.

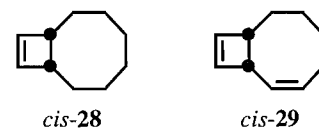


We believe that orbital symmetry *does* play a role in the photochemical ring opening of alkylcyclobutenes, but only in the initial stages of the reaction on the excited state potential energy surface. One piece of supporting evidence for this idea can be obtained from the behavior of *cis*- and *trans*-**3**, whose photochemistry was reinvestigated in light of our results for the numerous other cyclobutenes we have studied (26). It was found that, in fact, both isomers yield ring opening products upon photolysis (214 nm) in solution (eq. [16]). However, *trans*-**3** yields diene with ca. 5 times lower efficiency than does the *cis* isomer. This would be the expected result if disrotatory motions are involved in the initial stages of ring opening; such motions are impeded in *trans*-**3** because the disrotatory pathway leads to the highly strained *cis,trans* isomer of 1,1'-bicyclohexenyl (**4**). Similarly, the permethylated cyclobutene **27** undergoes ring opening with less than half the efficiency of *cis*-**15** (footnote 3); in this case, disrotatory motions are presumably impeded because of the necessity of buttressing two of the methyl groups at C3 and C4 as the rotation occurs.

<sup>4</sup>Also W. J. Leigh, K. Zheng, and A. Postigo, unpublished results.

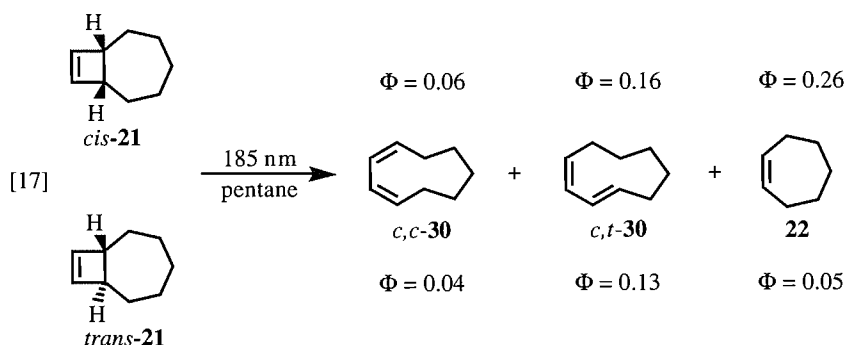


It may also be pertinent to note that the efficiency of photochemical ring opening appears to depend on the bond strength of the C3–C4 bond (25), just as is the case in ground state electrocyclic ring opening reactions (4d). This is demonstrated by a comparison of the diene/alkene ratios obtained from photolysis of compounds *cis*-**28** (ca. 1.0) and *cis*-**29** (3.6) (23). Molecular models show that the  $\pi$ -system of the cyclooctenyl C=C bond in *cis*-**29** is almost perfectly coplanar with the fragmenting cyclobutenyl C–C bond. The weakening of the latter in *cis*-**29** compared to the corresponding bond in *cis*-**28** is also manifested in the relative rates of thermal ring opening of the two compounds (23, 36).



If the above assessment of the initial stages of ring opening is correct, the ultimate loss of stereochemistry must then be due to intervening processes that occur after ring opening is initiated, and which compete with the normal internal conversion processes that are thought to characterize photopericyclic reactions (i.e., internal conversion to the ground state surface at the avoided crossing (6–9)). Several possibilities have been suggested (22, 25): (i) internal conversion to upper vibrational levels of ground state cyclobutene, from which conrotatory ring opening occurs; (ii) internal conversion to ground state biradical(oid) species; and (iii) adiabatic, disrotatory ring opening to yield diene in the first excited singlet state, from which *cis,trans* isomerization ensues. While the first possibility has not yet been investigated experimentally, the results of photolysis of compounds **21** (25) and **29** (23) are consistent with the second, biradical mechanism for ring opening; in both cases, the *cis* and *trans* isomers yield very similar distributions of *cis,cis* and *cis,trans* dienes (eq. [17]), suggesting the involvement of a common set of intermediates, or at least that reaction of the two isomers proceeds through a common point on the excited state surface prior to product formation (25). It is interesting to note that the major diene isomer formed from photolysis of the two isomers of **21** is the less thermodynamically stable *cis,trans* isomer.

The adiabatic ring opening mechanism has been studied in greatest detail, since in this case it is a somewhat more straightforward task to design experiments with which to test

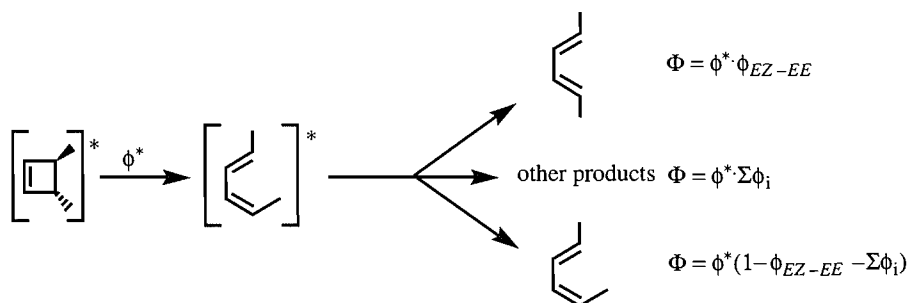


the mechanism. If ring opening occurs exclusively to yield fully open, excited dienes by the disrotatory pathway, then the observed diene distribution from cyclobutene ring opening would be expected to be dictated by the decay characteristics of the excited dienes, and thus predictable provided that the quantum yields for *cis,trans* isomerization and other photochemical processes of the dienes are known (Scheme 1) (22). While analyses of this type have been carried out for most of the cyclobutene derivatives discussed above, predicted diene distributions very rarely match those actually observed from photolysis of the cyclobutene derivative. In all of these cases, however, the stable ground state conformation of the diene is very different from the planar *s-cis* conformation in which the excited diene would be formed by disrotatory ring opening, so that independent characterization of the excited state behavior of the dienes themselves may not provide a realistic indication of their behaviour when formed by cyclobutene ring opening (22, 25) (the photochemistry of dienes is known to be conformation dependent (37)).

With this in mind, we have studied the photochemistry of the bicyclic cyclobutenes *cis*- and *trans*-24 (29), whose isomeric dienes are constrained to be *s-cis* (AM1 calculations predict a twist angle of ca. 36° in the parent diene, 1,2-bis-methylidencyclohexane). The work has recently been extended to include the analogous bicyclo[4.2.0]hept-1<sup>5</sup>-ene (23) and bicyclo[5.2.0]non-1<sup>7</sup>-ene (25) systems (eq. [15]) (footnote 4). Table 2 lists the observed *EE/EZ* diene ratios from photolysis of these compounds, along with the corresponding ratios calculated from the independently determined quantum yields for *cis,trans* isomerization of the dienes according to the equation given in Scheme 1.

Several interesting trends emerge from these data. First of all, the high degree of disrotatory stereospecificity observed for the ring opening of *cis*- and *trans*-24 is quite general within this special class of constrained systems. Secondly, these compounds undergo ring opening with considerably higher efficiency than other compounds with dialkyl substitution at the cyclobutene double bond (e.g., 15). This can be explained conveniently enough by noting that the ancillary ring induces additional strain in the cyclobutenyl ring, as evidenced by the substantially lower activation energies for thermal ring opening of these compounds compared to those of monocyclics (38). Thirdly, the *EE/EZ* diene ratios observed in the photolyses of these compounds are reproduced by the values calculated on the basis of the adiabatic mechanism defined in Scheme 1 in only two cases (*cis*-23 and *cis*-24). We conclude that the adiabatic ring opening pathway cannot account for the nonstereospecificity of the reaction.

Thus, it might be concluded that the general nonstereospecificity of the reaction is due to intervening internal conversion processes that occur before the system reaches the avoided surface crossing for disrotatory ring opening. If this is the case, then the unusually high degree of stereospecificity that is observed for 23–25 might be attributed to structurally induced suppression of these processes. Keeping in mind that the rates of internal conversion processes are affected by rovibrational factors, it is worth noting that the “alkyl substituents” on the C=C bond are more or less locked in 23–25; furthermore, the isomeric dienes are highly constrained with respect to rotation about the central C—C bond. In principle, either or both of these factors could af-



$$\text{Predicted: } (EE/EZ) = \phi_{EZ-EE} / (1 - \phi_{EZ-EE} - \Sigma \phi_i)$$

SCHEME 1. The adiabatic mechanism for cyclobutene ring opening.

TABLE 2. Comparison of observed diene distributions from photolysis (193 nm) of **23–25** with values calculated according to the adiabatic ring opening mechanism<sup>a</sup>

Isomer	Compound	( <i>EE/EZ</i> ) <sub>obs</sub>	( <i>EE/EZ</i> ) <sub>calc</sub> <sup>b</sup>
<i>cis</i>	<b>23</b>	2.5 ± 0.4	2.2 ± 0.4
<i>cis</i>	<b>24</b>	3.4 ± 0.6	3.7 ± 0.4
<i>cis</i>	<b>25</b>	9.1 ± 1.3	2.9 ± 0.4
<i>trans</i>	<b>23</b>	0.11 ± 0.02	0.71 ± 0.09
<i>trans</i>	<b>24</b>	0.18 ± 0.03	0.38 ± 0.05
<i>trans</i>	<b>25</b>	0.29 ± 0.04	0.19 ± 0.03

<sup>a</sup>Photolysis at 193 nm in pentane solution; 22°C.

<sup>b</sup>Calculated from the quantum yields for photoreaction of the corresponding *E,E*- and *E,Z*-dienes (see eq. [15]), according to the equation in Scheme 1.

fect the rates of internal conversion processes at partially open geometries. Because the rigidity of these compounds varies regularly throughout the series, accompanying variations in the degree of stereospecificity would be expected. However, it is difficult to understand why the variation observed within the series of *cis*-dimethyl compounds (increasing stereospecificity with increasing ancillary ring size) is *opposite* to that observed within the series of *trans*-dimethyl compounds (decreasing stereospecificity with increasing ancillary ring size).

Bernardi and Robb and their co-workers recently reported MCSCF calculations on the photochemical ring opening of 7-methylbicyclo[4.2.0]oct-7-ene (**17**) (39), experimental results for which were discussed earlier. This report follows an earlier study of the photochemical ring closure of 1,3-butadiene, in which was reported the existence of real surface crossings ("conical intersections") between the excited and ground state surfaces for disrotatory conversion of butadiene to cyclobutene (*vide supra*) (11). It was proposed that during the ring closure reaction of 1,3-butadiene, funneling to the ground state surface occurs at the conical intersection rather than at the avoided surface crossing. The geometry of the reacting species at this stage is one in which all the  $\pi$ -bonds in the molecule are broken, a tetraradicaloid species with the C2—C3 bond twisted by 78°. Excited state ring opening of **17** was proposed to proceed through three such surface crossings; the three conical intersection structures have the common feature of having the (former) cyclobutene double bond twisted by an angle close to 90°. The formation of three isomeric dienes in the reaction is explained as being due to the fact that three different surface crossings exist and, at each one, the reacting species can further relax to give all three of the diene isomers after entering the ground state surface (39).

This theoretical model can adequately explain why ring opening leads to a distribution of isomeric dienes in most of the cyclobutene systems that have been studied experimentally. It might also explain why nearly common distributions of products are formed in systems such as *cis*- and *trans*-**21**, if there is a single conical intersection geometry that is accessible from both isomers of the cyclobutene. Compounds **23–25** are special in that they are prevented from achieving the 80–90° twist angle that characterizes the geometry of the system at the conical intersection. It is possible that in such cases, the system is forced to open largely via the avoided crossing, or perhaps adiabatically, or per-

haps via other surface crossings<sup>5</sup> in a pathway that leads predominantly to the disrotatory product(s). It is clear that further study is required in order to develop a complete understanding of the remarkable complexities of this "prototypical" photoelectrocyclic reaction.

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