Cyclobutene photochemistry. Adiabatic photochemical ring opening of alkylcyclobutenes

William J. Leigh, J. Alberto Postigo, and K.C. Zheng

Abstract: The photochemistry of the *cis* and *trans* isomers of a series of dimethylbicyclo[n.2.0]alk-(n+2)-enes (n = 2–5) (bicyclic cyclobutene derivatives in which the C═C bond is shared by the two rings) in pentane solution is described. Irradiation of these compounds using monochromatic 193- or 214-nm light sources results in ring opening to yield the corresponding 1,2-bis(1-ethylidene)cycloalkanes (C_4–C_7) in high chemical and quantum yields. In all cases, the reaction proceeds with a high (70–90%) degree of disrotatory stereoselectivity. Quantum yields for direct *cis,trans* photoisomerization of the isomeric *E,E*- and *E,Z*-1,2-bis(1-ethylidene)cycloalkanes have also been determined. The product distributions from irradiation of the cyclobutenes are wavelength dependent, but for 214-nm excitation the isomeric diene distributions obtained from cyclobutene ring opening agree fairly closely with those calculated from the quantum yields for *cis,trans* photoisomerization of the isomeric dienes on the assumption that the process involves purely disrotatory ring opening to yield a single diene isomer in the lowest excited singlet state. The results are consistent with an orbital-symmetry-controlled, adiabatic mechanism for ring opening.

Key words: photochemistry, cyclobutene, electrocyclic, adiabatic, conical intersection, orbital symmetry.

Résumé : On décrit la photochimie des isomères *cis* et *trans* d'une série de diméthylbicyclo[n.2.0]alc-(n+2)-ènes (n = 2–5) (dérivés cyclobutènes bicycliques dans lesquels la liaison C═C est partagée entre deux cycles) en solution dans le pentane. L'irradiation de ces composés utilisant des sources de lumière monochromatique (193 ou 214 nm) provoque une ouverture de cycle qui conduit aux 1,2-bis(1-éthylidène)cycloalcanes (C_4–C_7) correspondants avec des rendements chimiques et quantiques élevés. Dans tous les cas, la réaction se produit avec un degré élevé (70–90%) de stéréosélectivité disrotatoire. On a déterminé les rendements quantiques pour la photoisomérisation *cis/trans* des *E,E*- and *E,Z*-1,2-bis(1-éthylidène)cycloalcanes. Les distributions des produits dérivant de l'irradiation des cyclobutènes dépendent de la longueur d'onde, mais, pour l'excitation à 214 nm, les distributions des diènes isomères obtenues pour l'ouverture de cycle du cyclobutène sont en assez bon accord avec ceux calculés à partir des rendements quantiques pour la photoisomérisation *cis/trans* des diènes isomères en supposant que le processus implique une ouverture de cycle strictement disrotatoire pour conduire à un seul diène isomère dans l'état singulet excité le plus bas. Les résultats sont en accord avec un mécanisme, pour l'ouverture de cycle, qui serait adiabatique et sous contrôle d'une symétrie des orbitales.

Mots clés : photochimie, cyclobutène, électrocyclique, adiabatique, intersection conique, symétrie d'orbitales.

[Traduit par la rédaction]

Introduction

The photochemical ring opening of simple alkylcyclobutenes in solution is known to proceed nonstereoselectively (1–5). While this appears to be quite general, there is increasing evidence to suggest that orbital symmetry factors (which predict that ring opening should proceed with disrotatory stereospecificity (6)) *do* play a role in the reaction. Firstly, isolated examples for which a high degree of disrotatory stereoselectivity is observed have been reported (7–9). Secondly, the UV resonance Raman spectrum of cyclobutene has been proposed to be consistent with initial *disrotatory* rotation of the C_1—C_4 and C_2—C_3 bonds immediately after excitation to the lowest excited singlet state (10) (this interpretation has recently been questioned, however (11)). Finally, we have recently reported a study of (C_3/C_4) substituent effects on the quantum yield for ring opening of 1,2-dimethylcyclobutene (12). This study indicates that *syn*-dimethyl substitution at C_3/C_4 reduces the absolute and relative (to cycloreversion) quantum yields for ring opening in a manner that is consistent with the process involving *initial* excited state disrotation about the C_1—C_4 and C_2—C_3 bonds of the cyclobutene ring. Each of these suggest that the photochemical ring opening of cyclobutene at least begins on the (disrotatory) pathway predicted by orbital symmetry selection rules.

Photopericyclic reactions are conventionally explained in terms of the avoided crossing model of Van der Lugt and Oosterhoff, in which stereospecific product formation results from internal conversion to the ground state surface at an

Received September 19, 1995.

This paper is dedicated to Professor Richard F.W. Bader on the occasion of his 65th birthday.

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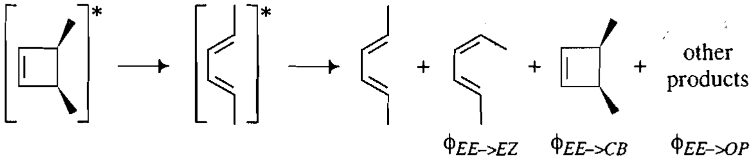
Scheme 1.



$$[1]\quad (EE/EZ)_{\text{from CB}} = (1 - \phi_{EE\text{->}EZ} - \phi_{EE\text{->}CB} - \phi_{EE\text{->OP}})/\phi_{EE\text{->}EZ}$$

avoided crossing (the pericyclic minimum) between the ground and excited state surfaces for the photochemically allowed (thermally forbidden) pathway (13, 14). This is the mechanistic model that is traditionally employed to explain, for example, why conjugated dienes undergo photochemical ring closure with a high degree of disrotatory stereospecificity (15). If it is valid — and recent theoretical work suggests it is not (16–19) — then the ultimate formation of formally-forbidden diene isomers must be due to some intervening process that competes with internal conversion at the avoided crossing for disrotatory interconversion. The possibilities that have been considered include (1, 9): (*i*) internal conversion to upper vibrational levels of the ground state (before the pericyclic minimum is reached), from which conrotatory ring opening ensues (1, 12); (*ii*) internal conversion to biradicaloid geometries on the diene ground state surface, from which torsional relaxation yields a mixture of isomeric dienes (20); and (*iii*) complete disrotatory ring opening on the excited state surface to yield fully open diene(s) in the first excited singlet state (i.e., adiabatically), followed by decay to the ground state by *cis,trans* isomerization (1, 9, 20). Another, recently suggested possibility is that excited-to-ground state internal conversion occurs via one or more *conical intersections* (geometries where the excited and ground state surfaces are degenerate) (21–23), after which the loss in disrotatory stereochemistry occurs on the ground state surface (17). According to calculations, the approach of the excited molecule to the conical intersection geometry involves rupture of the C_3—C_4 bond (cyclobutene numbering) and substantial twisting about *all three* of the remaining C—C bonds in the cyclobutene/1,3-butadiene framework (17).

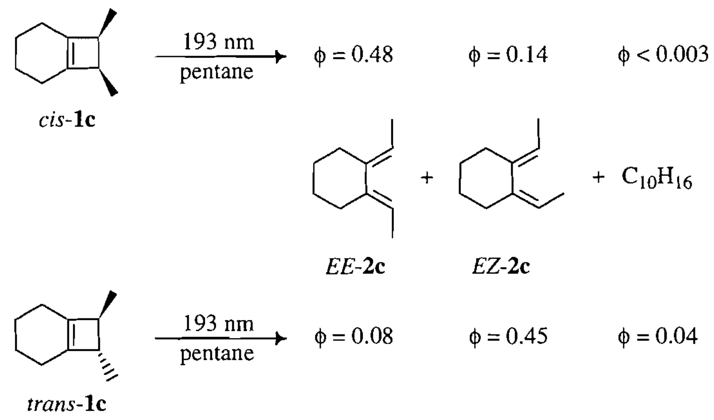
Of these, the adiabatic ring-opening mechanism is potentially the easiest to test experimentally. According to this mechanism, a given cyclobutene, appropriately labelled with substituents at C_3 and C_4 in order to track the stereochemistry of the process, will open in purely disrotatory fashion to yield a single (vide infra) diene isomer in the lowest excited singlet state (see Scheme 1). The excited product would then decay to the ground state, yielding *its* characteristic mixture of products. In principle, this characteristic mixture should be the same as that obtained when the diene itself is irradiated directly in solution. Thus, the experimental study of this mechanism would involve comparing isomeric diene distributions obtained from cyclobutene ring opening to distributions calculated from the quantum yields for direct photoisomerization of the corresponding orbital-symmetry-allowed diene isomer. The relevant expression is given by eq. [1], which relates the observed *EE/EZ* diene ratio from ring opening of an appropriate *cis*-disubstituted cyclobutene ($(EE/EZ)_{\text{from CB}}$) to the quantum yields for formation of the *EZ*-diene ($\phi_{EE\rightarrow EZ}$), cyclobutene ($\phi_{EE\rightarrow \text{CB}}$), and other products ($\phi_{EE\rightarrow \text{OP}}$) from direct irradiation of the *EE*-diene.

The main difficulty with applying this analysis to most of the cyclobutenes that have been studied results from the fact that the photochemistry of aliphatic dienes is conformation-dependent (24–27). Clearly, cyclobutene ring opening would be expected to yield the excited diene in an *s-cis* conformation, so it is the excited state behaviour of the *s-cis* diene conformer that must be known for a reliable analysis of the product distributions obtained from cyclobutene ring opening. Since most acyclic dienes exist preferentially in the *s-trans* conformation in solution at room temperature, they are poor models for the excited state behaviour of dienes under the conditions in which they are (presumably) formed by cyclobutene ring opening; thus, an analysis of this type is meaningless for monocyclic cyclobutenes and their corresponding dienes. A second potential difficulty is that in the case of *cis*-3,4-disubstituted cyclobutenes, there are two stereochemically distinct disrotatory ring-opening modes available, one leading to *E,E*-diene and the other leading to the *Z,Z* isomer. Should ring opening occur by both modes competitively, then an analysis of the type represented in Scheme 1 would clearly not be expected to model the observed diene distribution accurately. Fortunately, however, *Z,Z*-dienes are formed in extremely low yields from irradiation of every *cis*-3,4-disubstituted cyclobutene that has been reported (3, 5), so that this potential difficulty can be safely neglected. Presumably, the preferred formation of the *E,E*- over the *Z,Z*-diene isomer can be attributed to the different steric requirements of the two possible disrotatory ring opening modes (12).

We have recently described our preliminary efforts to test the adiabatic mechanism for photochemical cyclobutene ring opening (9, 28). These studies employed cyclobutene derivatives whose isomeric dienes are *structurally constrained* to exist in the *s-cis* conformation, in order to minimize difficulties associated with the conformational factors noted above. The first study involved a comparison of the diene distributions obtained from ring opening of the isomeric bicyclic cyclobutenes *cis*- and *trans*-**1c** (eq. [2]) with values calculated from the quantum yields for direct photoisomerization of the corresponding isomeric *s-cis* dienes *E,E*- and *E,Z*-**2c** (9). Comparison of the observed diene distributions from irradiation of **1c** with the so-calculated values (see Scheme 1) indicate that the adiabatic mechanism satisfactorily describes the isomeric diene distribution from photochemical ring opening of *cis*-**1c**, but it does not in the case of the *trans* isomer (9).

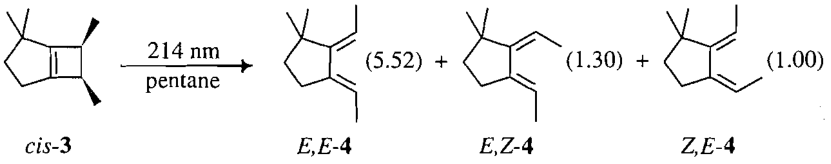
A second, potentially more precise type of comparison employs an asymmetrically substituted *cis*-cyclobutene, whose corresponding (*s-cis*) *E,E*-diene photoisomerizes to yield two *E,Z* isomers in a characteristic ratio (28). This sys-

[2]

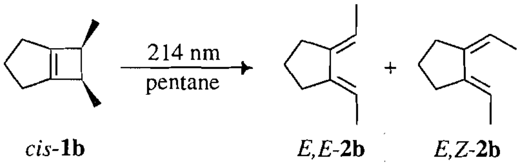


tem has the advantage that quantum yield determinations are unnecessary; the validity of the adiabatic mechanism can be tested by simply comparing product ratios from irradiation of the cyclobutene with those from irradiation of the corresponding allowed diene isomer. The system reported is *cis*-2,2,6,7-tetramethylbicyclo-[3.2.0]hept-1^5-ene (**3**), whose irradiation (214 nm) in pentane solution yields a mixture of *E,E*-, *E,Z*-, and *Z,E*-1,2-bis(ethylidene)-3,3-dimethylcyclopentane (**4**; see eq. [3]). As predicted by the adiabatic mechanism, the relative yields of *E,Z*- and *Z,E*-**4** obtained from irradiation of **3** (*EZ*/*ZE* = 1.30 ± 0.12) are identical to those obtained in the direct irradiation (254 nm) of *E,E*-**4** (*EZ*/*ZE* = 1.25 ± 0.11) within experimental error. The distribution of allowed and forbidden dienes ([*EE*-**4**]/[*EZ*-**4** + *ZE*-**4**] = 2.4 ± 0.3) is similar to that obtained from irradiation of *cis*-6,7-dimethylbicyclo-[3.2.0]-hept-1^5-ene (*cis*-**1b**) at the same wavelength ([*EE*-**2b**]/[*EZ*-**2b**] = 2.0 ± 0.3; see eq. [4]), which in turn agrees with the ratio predicted from quantum yields for photoisomerization of *EE*-**2b** (see eq. [1]) within experimental error. This is the best evidence for the validity of the adiabatic ring-opening mechanism that has been obtained to date.

[3]

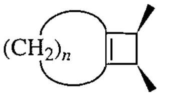


[4]

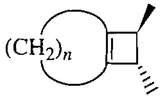


In addition to proceeding cleanly and yielding a predictable mixture of isomeric dienes, the ring opening of these compounds shows the additional unusual feature of proceeding in remarkably high quantum efficiency compared to those of other compounds that have been studied (3, 4, 12). Clearly, some aspect of the unique structures of these molecules is responsible for reducing the rate of nonproductive excited state decay relative to that of ring opening. Three basic differences between the structures of these compounds and simple monocyclic cyclobutenes can be noted: increased ring strain, decreased rotational flexibility of the substituents on the cyclobutene double bond, and decreased central-bond torsional flexibility in the isomeric 1,3-diene products (9). The latter possibility is related to the ability of the system to allow C_1–C_2 torsion during ring opening, which is required according to the conical intersection model for the process (17). Experimental evidence for the importance of such torsional modes in the photochemical ring opening of cyclobutene has been reported by Mathies and co-workers (10).

In the present work, we report the results of a more comprehensive study of the photochemical ring opening of specially constrained cyclobutene derivatives. Primarily, we wished to attempt to identify the factors that are responsible for the anomalous photobehavior of **1b,c** with respect to ring opening, and to test the adiabatic mechanism for this process in a more detailed and systematic way. We thus report the photochemistry of the series of compounds **1a–d** in hydrocarbon solution with monochromatic 193- and 214-nm light sources. We also report complete details of a study of the photochemistry of the series of isomeric *E,E*- and *E,Z*-1,2-bis(ethylidene)cycloalkanes **2a–d**. Preliminary results for three members of this series of dienes have been reported previously (9, 29).

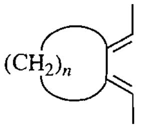


cis-**1**

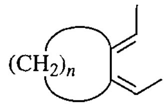


trans-**1**

a. $n = 2$
b. $n = 3$
c. $n = 4$
d. $n = 5$



EE-**2**

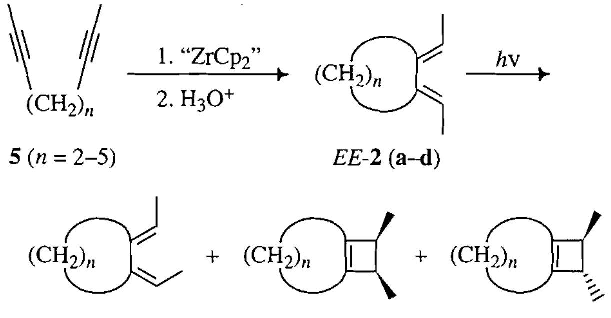


EZ-**2**

Results

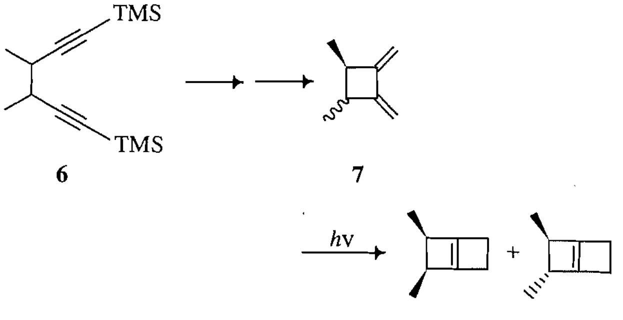
The dienes *E,E*-**2** were prepared by zirconocene-mediated intramolecular coupling of the corresponding dialkynes **5** (n = 2–5; eq. [5]) (30, 31). Exhaustive irradiation of the *E,E*-diene (254 nm) was then carried out to afford isomeric mixtures consisting largely of the *E,E*- and *E,Z*-dienes and the *cis* and *trans*-substituted cyclobutenes, which were separated and purified by semi-preparative gas chromatography. The irradiation mixtures usually also contained several other minor products; these were all determined to be isomers of **1** and **2** by GC/MS, but were isolated and rigorously identified in only certain cases (see experimental section). The *Z,Z* isomers of **2b–d** were tentatively identified by GC/MS, on the basis of comparisons of retention times and mass spectra (relative to the other components of the mixtures) to *Z,Z*-**2a**, which is a known compound and was isolated and rigorously identified from the exhaustive irradiation of *E,E*-**2a**. Because these compounds were minor components of extremely complex reaction mixtures, however, they were not isolated and rigorously identified.

[5]



While the first step in this procedure was successful for the synthesis of all four *E,E*-dienes in the series, the subsequent photoisomerization as a means of generating the desired cyclobutene derivatives was useful only for **2b–d**. In the case of *E,E*-**2a**, direct irradiation led to *cis,trans* photoisomerization and the formation of several minor products whose yields were similar to those of the desired cyclobutene derivatives. Thus, *cis*- and *trans*-**1a** were synthesized by photocyclization of 3,4-dimethyl-1,2-bis-(methylidene)cyclobutane (**7**), which was prepared as a mixture of isomers by zirconocene-mediated cyclization of the dialkyne **6** (eq. [6]) followed by bis-desilylation. This procedure led to excellent chemical yields of the desired cyclobutenes **1a**, which in spite of their rather substantial lability toward polymerization could be separated and purified by semi-preparative GC, and stored under liquid nitrogen until required.

[6]



The structures of **1a–d** and **2a–d** were assigned on the basis of their mass, infrared, and high-resolution ^1H and (except for **1a**) ^{13}C NMR spectra (see experimental section). The *cis* and *trans* isomers of **1a–d** are readily distinguishable on the basis of ^1H and ^{13}C NMR spectroscopy; the present series of compounds exhibit the same spectral regularities with C_3/C_4 stereochemistry as has been reported previously for other systems (20, 32). Ultraviolet absorption spectra of *cis*- and *trans*-**1a–d**, and *E,E*- and *E,Z*-**2a–d**, were recorded in deoxygenated pentane solution at 23°C, and are shown in Figs. 1 and 2, respectively.

Direct irradiation of deoxygenated, ca. 0.02 M pentane solutions of **1b–d** with the pulses from an Ar/F_2 excimer laser (193 nm; 15 ns; 20 mJ; 0.5 Hz repetition rate) resulted in the clean formation of *E,E*- and *E,Z*-**2b–d** as the major products. In the irradiations of the *trans* isomers, minor amounts of the compounds identified (tentatively; vide supra) as *Z,Z*-**2b–d** were also formed, as indicated by comparison of the GC and GC/MS characteristics of the photolysates to those of the crude mixtures from direct irradiation of the *E,Z*-dienes. No other products were observed in yields greater than ca. 3% in any case. Quantum yields for formation of the three products from **1b–d** were determined from the slopes of concentration vs. laser dose plots, using the ring opening of bicyclo[4.2.0]oct-6-ene (1) as actinometer for 193-nm irradiations. Representative plots of this type are shown for *cis*- and *trans*-**1d** in Fig. 3.

Irradiation of deoxygenated, ca. 0.02 M pentane solutions of **1a–d** with 214-nm light was carried out using a Zn resonance lamp as the light source. The photolyses of **1b–d** were carried out with vigorous stirring of the solutions, and were monitored over a 0.1–4% conversion range. Relative product yields were calculated from the initial slopes of concentration vs. time plots, examples of which are shown in Fig. 4 for *cis*- and *trans*-**1d**. Quantum yields for ring opening of *cis*- and *trans*-**1a** were determined on unstirred solutions with 214-nm excitation, using the initial slopes of product concentration vs. time plots to determine product yields, and uranyl oxalate actinometry to determine light intensities (12).

Table 1 lists the quantum yield data from irradiation of **1a–d** at 214 nm and **1b–d** at 193 nm. The table also lists *EE*/*EZ* diene ratios from *cis*- and *trans*-**1a–d** and *EE*/*ZZ* diene ratios from *trans*-**1a–c** (the yield of the *Z,Z*-diene from *trans*-**1d** was too low to be determined); these were calculated from the slopes of concentration vs. time plots as described above.

Fig. 1. Ultraviolet absorption spectra of *cis* (——) and *trans* (– · – · –) **1a–d** in deoxygenated pentane solution at 23 °C.

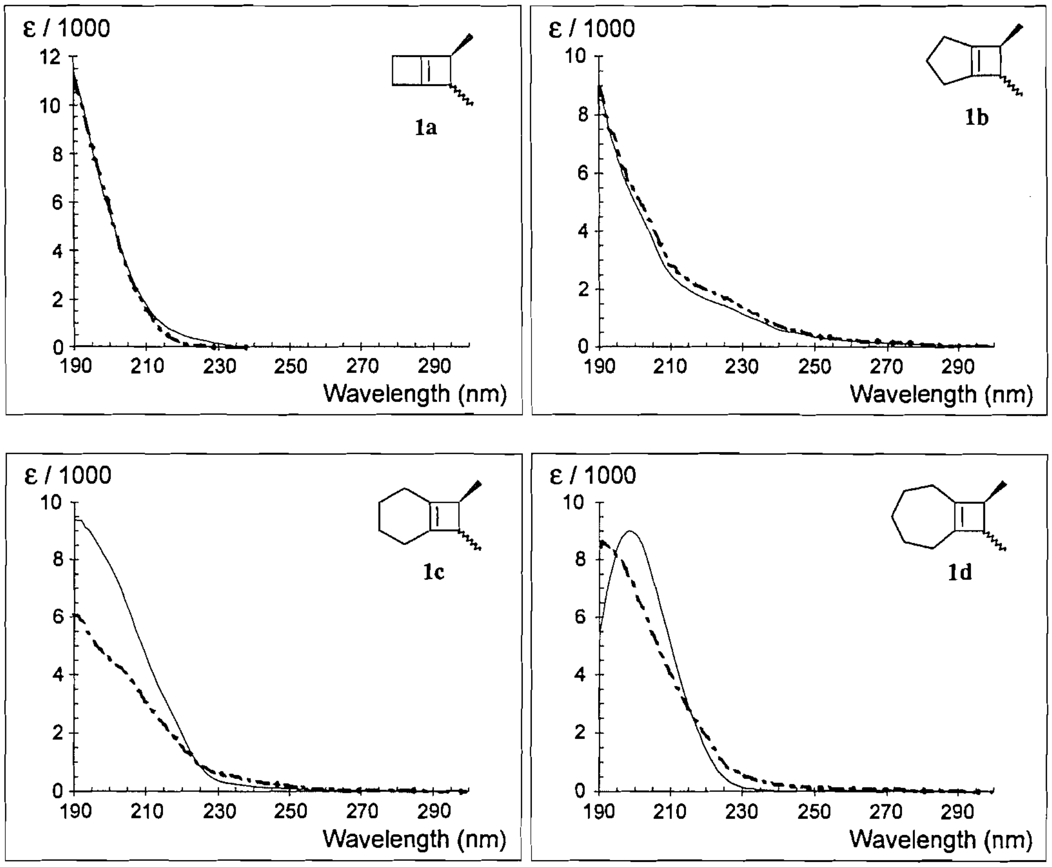


Table 1. Quantum yields for diene formation[a] and isomeric diene ratios[b] from 193- or 214-nm irradiation of deoxygenated 0.02 M pentane solutions of *cis*- and *trans*-**1a–d**.

Compound	$\phi_{EE\text{-}2}$	$\phi_{EZ\text{-}2}$	ϕ_{total}	$(EE\text{-}2/EZ\text{-}2)^{193}$	$(EE\text{-}2/ZZ\text{-}2)^{193}$	$(EE\text{-}2/EZ\text{-}2)^{214}$	$(EE\text{-}2/ZZ\text{-}2)^{214}$
cis-**1a**	0.55 ± 0.04	0.32 ± 0.06	0.87	*n.d.*	*n.d.*	1.7	[c]
cis-**1b**	0.42 ± 0.05	0.17 ± 0.03	0.59	2.5	[c]	2.0	[c]
cis-**1c**	0.48 ± 0.06	0.14 ± 0.02	0.62	3.4	[c]	4.1	[c]
cis-**1d**	0.68 ± 0.05	0.075 ± 0.008	0.75	9.1	[c]	5.6	[c]
trans-**1a**	0.066 ± 0.009	0.61 ± 0.04	0.68	*n.d.*	*n.d.*	0.11	10.0 ± 1.0
trans-**1b**	0.065 ± 0.008	0.59 ± 0.07	0.66	0.11	3.0 ± 0.6	0.45	4.3 ± 0.4
trans-**1c**	0.08 ± 0.02	0.45 ± 0.06	0.57	0.18	7.3 ± 1.4	0.29	8.6 ± 0.8
trans-**1d**	0.19 ± 0.03	0.67 ± 0.05	0.86	0.28	[c]	0.21	[c]

[a] Quantum yields for product formation from *cis*- and *trans*-**1a** were determined using filtered 214-nm excitation and uranyl oxalate actinometry. Those for product formation from **1b–d** were determined using 193-nm excitation and bicyclo[4.2.0]oct-7-ene actinometry.

[b] Calculated from the initial slopes of product concentration versus irradiation dose plots; errors were calculated from the standard deviations of the slopes; *n.d.* = not determined.

[c] *Z*,*Z*-**2** was not formed in sufficient yield to enable determination of the yield.

A control experiment was performed, in which a deoxygenated pentane solution containing 0.015 M *cis*-**1c** and 0.0011 M 1,3-cyclooctadiene (**8**) was irradiated (193 nm) to ca. 4.5% conversion of the cyclobutene. At these low conversions, isomerization of **8** to *cis,trans*-1,3-cyclooctadiene (the major product of irradiation of **8** (33)) could not be detected in the photolysate within our detection limits (ca. 10^{-6} M). Analogous results were obtained in the irradiation (214 nm) of *cis*- and *trans*-**1d**, employing low concentrations of *E*,*E*-**2b** as the standard.

As mentioned above, direct irradiation of *E*,*E*- and *E*,*Z*-**2a–d** in deoxygenated pentane solution led predominantly to

Fig. 2. Ultraviolet absorption spectra of *E,E* (——) and *E,Z* (········) **2a–d** in deoxygenated pentane solution at 23°C.

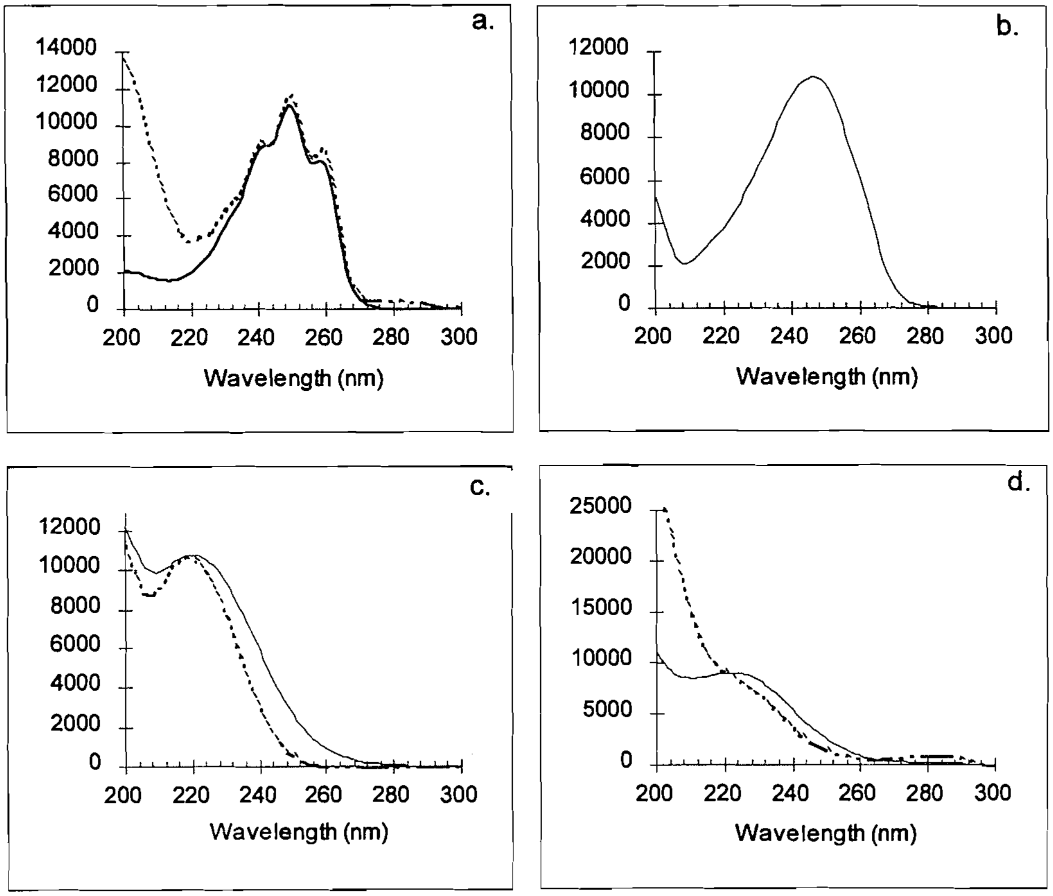


Table 2. Quantum yields for direct *cis,trans* photoisomerization and the formation of cyclobutene (**1**) and "other products" from 254-nm irradiation of deoxygenated 0.02 M pentane solutions of *E,E*- and *E,Z*-**2a–d**.[a]

Compound	$\phi_{EE\text{-}EZ}$	$\phi_{EZ\text{-}EE}$	$\phi_{\mathrm{EE\text{-}1}}$[b]	$\phi_{\mathrm{EZ\text{-}1}}$[c]	$\Sigma\phi_{\mathrm{OP}}(EE)$[d]	$\Sigma\phi_{\mathrm{OP}}(EZ)$[d]
2a	0.12 ± 0.02	0.11 ± 0.03	< 0.005	< 0.005	< 0.005	0.011 ± 0.005[e]
2b	0.24 ± 0.02	0.39 ± 0.04	0.10 ± 0.02	0.13 ± 0.01	0.06 ± 0.01	0.17 ± 0.03
2c	0.20 ± 0.03	0.27 ± 0.03	0.05 ± 0.01	0.019 ± 0.004	0.06 ± 0.02	0.06 ± 0.01
2d	0.21 ± 0.03	0.14 ± 0.06	0.15 ± 0.02	0.12 ± 0.06	0.05 ± 0.01	0.06 ± 0.01

[a] Determined by potassium ferrioxalate actinometry. The *ZZ*-dienes were rigorously identified only for *Z,Z*-**2a**.

[b] Quantum yield for formation of *cis*-**1** from *E,E*-**2**.

[c] Quantum yield for formation of *trans*-**1** from *E,Z*-**2**.

[d] Estimated total quantum yield for formation of unknown products from *E,E*- ($\Sigma\phi_{\mathrm{OP}}(EE)$) and *E,Z*- ($\Sigma\phi_{\mathrm{OP}}(EZ)$) **2**.

[e] Quantum yield for formation of *Z,Z*-**2a** from the *E,Z* isomer. No other products are formed, within the limits of our detection method.

cis,trans photoisomerization and the stereospecific formation of *cis*- and *trans*-**1a–d** (from *E,E*- and *E,Z*-**2a–d**, respectively). Other products were also formed in yields of ≤10% in some cases, but these were not rigorously identified. In the cases of *E,Z*-**2b** and **2c**, the most prominent of the minor photoproducts were those tentatively identified as the corresponding *Z,Z*-diene isomers, on the basis of GC/MS and GC retention time comparisons to *Z,Z*-**2a**, which was isolated and rigorously identified (vide supra). Irradiation of *E,Z*-**2d** yielded *E,E*-**2d** and *trans*-**1d** quite cleanly, and a minor product tentatively identifiable as *Z,Z*-**2d** could be detected only after extensive irradiation of the solution. Quantum yields for *cis,trans* photoisomerization and formation of **1a–d** and other minor products were determined in deoxygenated pentane solution (ca. 0.02 M) using potassium ferrioxalate actinometry. Quantum yields for the formation of minor products (*Z,Z*-**2** and all other unidentified products) were estimated in each case by GC (assuming equal response factors to the averages of those of the identified products) at ca. 5% conversion of starting material. Table 2 lists the results of these experiments.

Fig. 3. Product concentration versus laser dose plots for the formation of *E,E* (■) and *E,Z* (◆) **2d** from the photolysis (193 nm) of *cis* (A) and *trans* (B) 8,9-dimethylbicyclo[5.2.0]non-1^7-ene (**1d**) in deoxygenated pentane solution at 23°C. The laser intensity was not the same in the two experiments.

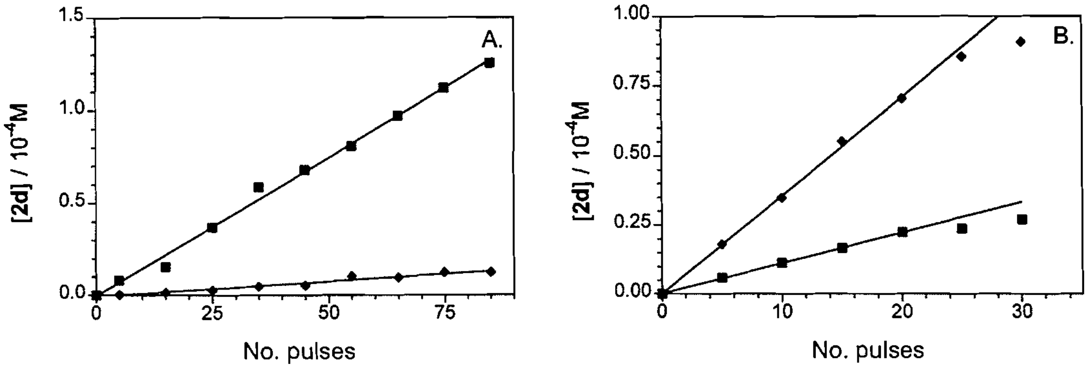
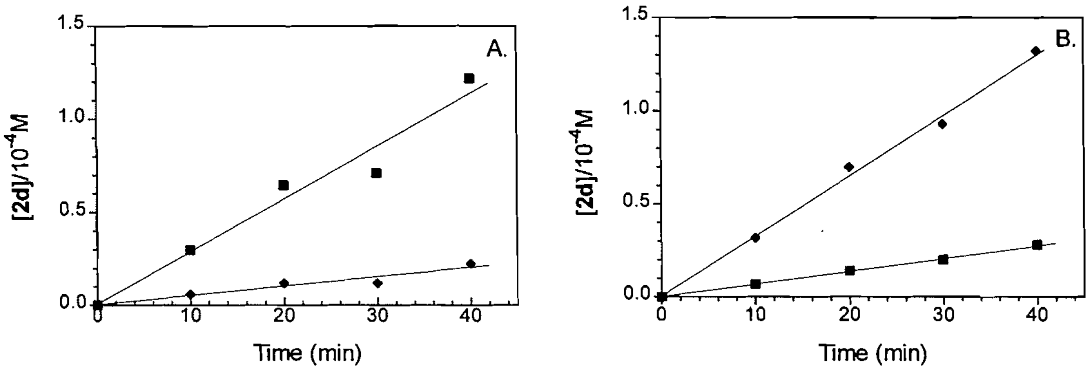


Fig. 4. Product concentration versus irradiation time for the formation of *E,E* (■) and *E,Z* (◆) **2d** from the photolysis (214 nm) of *cis* (A) and *trans* (B) 8,9-dimethylbicyclo[5.2.0]non-1^7-ene (**1d**) in deoxygenated pentane solution at 23°C.



Discussion

The solution-phase UV absorption spectra of the series of bicyclic cyclobutene derivatives **1a–d** (Fig. 1) exhibit interesting trends. We previously reported spectra of several monocyclic alkylcyclobutene derivatives with *cis*- and *trans*-dimethyl substitution at C3/C4, and noted that those of the *cis* isomers are red-shifted with respect to those of the *trans* isomers (32). This was attributed to a stereochemical effect on the relative extinction coefficients of the π,π^* and Rydberg(π,R(3*s*))-like absorption bands. This is particularly noticeable in the gas phase UV spectra of these compounds, where the latter are considerably more intense than in the solution phase spectra. In solution, these absorption bands are sufficiently reduced in intensity that the result is an apparent broadening and red shift in the position of the prominent band in the spectra of the *cis* isomers compared to that in the spectra of the *trans* isomers. Similar differences are observed in the solution phase spectra of *cis*- / *trans*-**1d** and *cis*- / *trans*-**1c**, while the effect is absent altogether in the spectra of *cis*- and *trans*-**1a,b**. We do not understand the origins of the stereochemical effect on the spectra of monocyclic and relatively unstrained bicyclic alkylcyclobutenes such as **1c,d**, but it is interesting to note that the effect is truncated in the more highly strained members of the present series of compounds. It is clear that incorporation of the cyclobutenyl double bond into a second cycloalkyl ring has a significant effect on the UV absorption spectrum of the cyclobutenyl chromophore, to an extent that depends on the size of the ancillary ring.

The UV spectra of the isomeric dienes (Fig. 2) are consistent with an increasing amount of torsional flexibility about the central bond with increasing ancillary ring size throughout the series. For both **2a** and **2b** the long-wavelength bands in the spectra of the *E,E* and *E,Z* isomers are almost perfectly superimposable and exhibit maxima at ~250 nm, consistent with the molecules having planar, *s-cis* conformations that are roughly the same for the *E,E* and *E,Z* isomers. The spectra of the higher members of the series show maxima at shorter wavelengths, consistent with their preferred conformations having twisted *s-cis* geometries. The spectra of *E,E*-**2b** and **2c** are slightly red-shifted, but otherwise similar to those of the parent 1,2-dimethylenecycloalkanes (34).

Direct irradiation of *cis*- and *trans*-**1a–d** leads to ring opening to the isomeric dienes (**2a–d**) with a high degree of disrotatory stereoselectivity in each case (Table 1). None of these compounds undergo formal [2+2]-cycloreversion to any detectable extent, presumably because this process would lead to the formation of the corresponding, highly strained C_4–C_7

Table 3. Observed[a] and calculated[b] diene ratios from irradiation of *cis*-**1** in pentane solution at 23°C.

cis-**1**	$^{193}(EE\text{-}\mathbf{2}/EZ\text{-}\mathbf{2})_{\mathrm{obs}}$	$^{214}(EE\text{-}\mathbf{2}/EZ\text{-}\mathbf{2})_{\mathrm{obs}}$	$(EE\text{-}\mathbf{2}/EZ\text{-}\mathbf{2})_{c,\mathrm{calc}}$
1a	*n.d.*	1.7 ± 0.2	8 ± 1
1b	2.5 ± 0.4	2.0 ± 0.4	2.2 ± 0.4
1c	3.4 ± 0.4	4.1 ± 0.3	3.7 ± 0.4
1d	9.1 ± 0.9	5.6 ± 0.9	3.7 ± 0.8

[a] Observed diene distributions from irradiation (193 and 214 nm) of *cis*-**1** (see Table 1); calculated from the slopes of concentration vs. time plots for the formation of *EE*- and *EZ*-**2**; *n.d.* = not determined.

[b] Expected diene ratios calculated using the quantum yield data in Table 2 and eq. [1].

Table 4. Observed[a] and calculated[b] diene ratios from irradiation of *trans*-**1** in pentane solution at 23°C.

trans-**1**	$^{193}(EZ\text{-}\mathbf{2}/EE\text{-}\mathbf{2})_{\mathrm{obs}}$	$^{214}(EZ\text{-}\mathbf{2}/EE\text{-}\mathbf{2})_{\mathrm{obs}}$	$(EZ\text{-}\mathbf{2}/EE\text{-}\mathbf{2})_{t\text{-}2,\mathrm{calc}}$	$^{193}(EE\text{-}\mathbf{2}/ZZ\text{-}\mathbf{2})_{\mathrm{obs}}$	$^{214}(EE\text{-}\mathbf{2}/ZZ\text{-}\mathbf{2})_{\mathrm{obs}}$	$(EE\text{-}\mathbf{2}/ZZ\text{-}\mathbf{2})_{t\text{-}2}$
a	—	9.1 ± 1.1	8.0 ± 0.9	*n.d.*	10.0 ± 1.0	9.1 ± 1.5
b	9.1 ± 1.2	2.2 ± 0.3	1.4 ± 0.2	3.0 ± 0.6	4.3 ± 0.4	3.7 ± 0.7
c	5.6 ± 0.7	3.5 ± 0.4	2.6 ± 0.4	7.3 ± 1.4	8.6 ± 0.8	9.2 ± 1.8
d	3.6 ± 0.4	4.8 ± 0.8	5.6 ± 1.1	[c]	[c]	[c]

[a] Observed diene distributions from irradiation (193 and 214 nm) of *trans*-**1** (see Table 1); calculated from the slopes of concentration vs. time plots for the formation of *EE*-, *EZ*-, and *ZZ*-**2**; *n.d.* = not determined.

[b] Expected *EZ*/*EE*-diene ratios calculated using the quantum yield data in Table 2 and eq. [1] ($(EZ\text{-}\mathbf{2}/EE\text{-}\mathbf{2})_{t\text{-}2,\mathrm{calc}}$), and *EE*/*ZZ* diene ratios obtained from direct irradiation of *E*,*Z*-**2** ($(EE\text{-}\mathbf{2}/ZZ\text{-}\mathbf{2})_{t\text{-}2}$).

[c] *ZZ* isomer was not formed in sufficient yield to enable yield determination.

cycloalkyne (35, 36). Another noteworthy feature of the present results is that *cis*- and *trans*-**1a** undergo ring-opening regiospecifically to yield the various geometric isomers of **2a**. In principle, **1a** has two ring opening modes available: one involving cleavage of the (unsubstituted) C5—C6 bond to yield **7**, and one involving cleavage of the (substituted) C2—C3 bond to yield **2a**. The fact that only the latter occurs in detectable yield is consistent with previous results that indicate that the efficiency of photochemical cyclobutene ring opening depends to some extent on the strength of the cyclobutenyl C3—C4 bond (12, 20).

The possibility that the overall nonstereoselectivity of photochemical ring opening might be explained by a mechanism in which purely disrotatory ring opening occurs adiabatically is suggested by the experimental results of Michl, Yang, and co-workers (37, 38), which demonstrated that direct irradiation of Dewar naphthalene (38) and Dewar anthracene (37) affords the corresponding aromatic hydrocarbons in the lowest excited singlet states. This was evidenced by the observation of the characteristic fluorescence of the aromatic hydrocarbons upon excitation of the corresponding Dewar isomers in solution.

If ring opening of alkylcyclobutenes proceeds in stereospecific, disrotatory fashion to yield a single diene isomer in the lowest excited singlet state, the final distributions of *E*,*E*- and *E*,*Z*-diene isomers obtained by irradiation of *cis*- and *trans*-**1a**–**d** should be determined by the excited state decay characteristics of the initially formed (allowed) diene isomer. These characteristics are given in quantitative form as the ratio of the quantum yields for productive vs. nonproductive decay of the diene (9, 28). Thus, the relevant equation for calculation of the expected distribution of *EE*- and *EZ*-dienes from irradiation of the *cis* cyclobutenes ($(EE/EZ)_{c,\mathrm{calc}}$) is given in Scheme 1 (eq. [1]), which assumes that ring opening yields the *E*,*E*-diene to the exclusion of the other formally allowed product, the *Z*,*Z* isomer. That this assumption is reasonable follows from the fact that extremely low yields of *Z*,*Z*-dienes are observed in the photolyses of every *cis*-dimethyl substituted alkylcyclobutene that has yet been reported (3–5). The results of these calculations are listed in Table 3 along with the observed *EE*/*EZ* diene ratios from irradiation of *cis*-**1a**–**d** with the 193- and 214-nm light sources.

A similar equation can be employed to calculate the expected *EZ*/*EE* diene ratios from irradiation of the *trans* cyclobutenes ($(EZ/EE)_{t,\mathrm{calc}}$). In these cases, the *E*,*Z*-diene is the only formally allowed ring-opening product, so no assumptions regarding the initial excited state product distribution are necessary in order to simplify the calculation. These compounds actually provide additional mechanistic information over that obtainable from the *cis* isomers, in that *two* detectable products are formed upon excited state decay of the *E*,*Z*-dienes: the *E*,*E*- and *Z*,*Z*-diene isomers. The adiabatic ring-opening mechanism would predict that, in these cases, the *EE*/*ZZ* diene distribution from ring opening of a *trans*-3,4-disubstituted cyclobutene should be identical to the *EE*/*ZZ* distribution from direct irradiation of the corresponding *E*,*Z*-diene (28). Table 4 summarizes the observed *EZ*/*EE* and *EE*/*ZZ* diene ratios from direct irradiation of *trans*-**1a**–**d**, along with the expected *EZ*/*EE* ratios (according to eq. [7]) and the *EE*/*ZZ* diene ratios obtained in the direct irradiation of *E,Z*-**2a**–**d**.

As can be seen from inspection of Tables 3 and 4, the degree of agreement between the observed and calculated isomeric diene ratios varies for the two excitation wavelengths. For 214 nm excitation, the calculated and observed *EE*/*EZ* diene ratios agree within experimental error in seven cases out of eight (i.e., in all cases but *cis*-**1a**). In the cases of the *trans* isomers (**1a**–**c**), the similarity in the diene distributions from direct irradiation of cyclobutene and *E,Z*-diene extends as well to the *EE*/*ZZ* diene ratios, although the errors in these ratios are somewhat large due to the fact that the *Z,Z*-dienes are formed in relatively low yields in each case. The *EE*/*ZZ* ratio could not be determined reliably for *trans*-**1d**, as the yield of the *ZZ*-diene is extremely low in this case; irradiation of *E,Z*-**2d** also yields *Z,Z*-**2d** in unusually low yield, however.

For the most part, the present data support a mechanism in which ring opening occurs in purely disrotatory fashion to *first* yield the allowed diene isomer in the same electronic excited state that is populated upon direct excitation of the particular diene isomer and that is responsible for *cis,trans* isomerization; once formed, the excited diene then relaxes to form its characteristic mixture of products. In fact, this conclusion can be stated in more general terms. *The data support a mechanism in which ring opening occurs on the excited state surface in disrotatory fashion, but decay to the ground state surface(s) for product formation does not occur at the classical avoided crossing for cyclobutene–butadiene interconversion. Rather, it occurs at the same place(s), yielding a similar product distribution, as is(are) involved when the allowed diene isomer is itself excited directly.*

The behaviour of one compound in the series (*cis*-**1a**) is very clearly different from the others, in that its isomeric diene distribution is not modelled accurately by the excited state decay characteristics of the corresponding disrotatory diene (*E,E*-**2a**). We do not believe that the anomalously low disrotatory stereoselectivity observed in this case is due to an experimental artifact resulting from secondary irradiation of the *E,E*-diene. While ruling this out is admittedly more difficult to do in this case because of the shorter wavelength cutoff in the UV absorption spectrum of *cis*-**1a** compared to those in the spectra of **1b**–**d**, we note that irradiation of *trans*-**1a** (which should be subject to similar problems) leads to very high yields of *E,Z*-**2a** (there is, furthermore, no significant difference in the quantum yields for *cis,trans* photoisomerization of *E,E*- and *E,Z*-**2a** (29)). One possible explanation is that ring opening by the pathway leading to the *Z,Z*-diene isomer is much more important in *cis*-**1a** than in *cis*-**1b**–**d**; this would lead to a lower *EE*/*EZ* diene ratio than that predicted from consideration of the quantum yields for photoisomerization of the *E,E*-diene alone, due to isomerization of the *Z,Z*-diene to the *E,Z* isomer. Such behaviour could result from the considerably higher degree of ring strain afforded by the ancillary cyclobutyl ring (compared to that afforded by the ancillary rings in *cis*-**1b**–**d**), which might outweigh the normally dominant steric effects between the C_3–C_4 methyl groups and reduce the discrimination between the two possible disrotatory ring-opening modes. This explanation seems unlikely, however, given the sheer magnitude of the difference between the calculated and observed *EE*/*EZ* ratios for this compound (a simple calculation reveals that the yield of *E,Z*-**2a** formed by the *Z,Z*-diene route would have to be four times greater than that formed by the *E,E*-diene route, in order to account for the difference between the observed and calculated *EE*/*EZ* diene ratios). Besides, one would also expect that the observable yield of the *Z,Z*-diene should be significant if this were true, and such is not the case.

There is an intriguing wavelength dependence observed in the diene distributions throughout the two series of compounds **1b**–**d**, as is clear from inspection of Tables 3 and 4. With 214-nm excitation, the observed *EE*/*EZ* diene distributions very closely match those expected on the basis of the adiabatic ring-opening mechanism, as discussed above. On the other hand, the observed ratios for 193-nm excitation clearly deviate from the expected values in some cases, and the data reveal different trends in the variations in the degree of deviation throughout the two series of compounds. For the *cis* compounds, the deviation from expected behaviour increases with ancillary ring size (being largest for **1d**), while it decreases accordingly for the *trans* compounds. In both cases, the deviation occurs in the direction of a *higher* degree of overall disrotatory stereospecificity than the adiabatic mechanism can account for.

Comparison with theoretical models

In terms of the avoided crossing model for excited state pericyclic reactions, the data suggest that in the ring-opening reaction, conversion to the ground state at the avoided crossing does not occur; the excited molecule proceeds instead to the fully open geometry corresponding to the lowest excited singlet state of the symmetry-allowed diene isomer. The excellent agreement between observed and expected diene distributions further suggests that ring opening by the symmetry-forbidden conrotatory pathway does not occur to a significant extent.

This is consistent with the theoretical calculations of Devaquet and co-workers (14) and Morihashi and Kikuchi (39), which suggest that there may be a relatively small barrier between the pericyclic (2^1A_g) minimum for excited singlet state disrotatory ring opening/closure and the lowest Franck–Condon excited singlet (^1B_u) state of *s-cis* 1,3-butadiene (39). The barrier arises as a result of an allowed crossing of the ^1B_u and 2^1A_g states at intermediate geometries for ring closure of the diene. The pericyclic minimum (at which the cyclobutenyl C3—C4 is *partially* broken) occurs on the doubly excited 2^1A_g surface, access to which must involve internal conversion from the initially populated excited state of either cyclobutene (in ring opening) or 1,3-butadiene (in ring closure). Morihashi and Kikuchi determined that the probability of internal conversion from the pericyclic minimum to the ground state, while substantially higher than that on the conrotatory side, is quite low ($\sim 10^{-4}$) (39). Thus, these calculations suggest that full formation of electronically excited *s-cis* diene by disrotatory ring opening could occur competitively with internal conversion to the ground state surface at the pericyclic minimum, providing that such a barrier is small enough.

This model for photopericyclic reactions contains the implicit assumption that product selection in a photochemical reaction occurs *on the excited state surface* after initial relaxation to the favored equilibrium geometry; i.e., that the formation of different products in a photochemical reaction involves motion along different reaction coordinates on the excited state surface (18). Thus, the formation of *E,Z*-diene by *disrotatory* ring opening of a *cis*-3,4-disubstituted cyclobutene can only result if electronically excited *E,E*-diene is fully formed *prior* to decay to the ground state by *cis,trans* isomerization. The ramifications of these statements are actually easier to understand from the point of view of diene photochemistry: the mixture of products that is normally formed from irradiation of an *s-cis* diene (geometric isomers, cyclobutene, and the *s-trans* conformer in acyclic systems) results from partitioning amongst different *excited state* reaction coordinates, according to the avoided crossing model.

Recent theoretical calculations by Bernardi, Robb, Olivucci and their co-workers suggest a fundamentally different mechanism for such reactions, in which product formation results from evolution along a *single* (preferred) excited state reaction coordinate (21, 23). Decay to the ground state surface then occurs at a single *conical intersection* of the ground and excited state potential energy surfaces to yield a mixture of products that is dictated by the structure of the molecule at the conical intersection, the atomic trajectories that are activated as the excited molecule approaches it, and various barriers that the molecule encounters on the ground state surface as it cascades to stable products. Thus, the formation of *all* the products of direct irradiation of an *s-cis* diene is proposed to be due to funnelling through a single conical intersection of the doubly excited (2^1A_g) and ground (1^1A_g) state potential energy surfaces. At the $2^1A_g/1^1A_g$ conical intersection calculated for *s-cis* butadiene, the molecule is twisted about all three carbon–carbon bonds; the termini (the C1—C2 and C3—C4 bonds in 1,3-butadiene) are twisted in disrotatory fashion, while the central (C2—C3) bond is effectively twisted by ca. 52° as a result of pyramidalization at C2 or C3 (16, 18, 19). One particularly intriguing aspect of this mechanism is the suggestion that torsion about the terminal double bonds of a diene is *accompanied by* torsional motions about the *central* (single) bond. This contrasts expectations based on the avoided crossing model, in which *cis,trans* photoisomerization and disrotatory ring closure are both assumed to involve planarization of the four-carbon framework. We have recently published preliminary experimental evidence that provides tentative support for the importance of central bond torsional motions, and hence for the conical intersection mechanism, in the *cis,trans* photoisomerization of constrained *s-cis* dienes (29).

It seems reasonable to expect that ring opening of cyclobutene should proceed by a pathway that involves internal conversion to the ground state surface at the same conical intersection as is proposed to be involved in the photochemistry of *s-cis* 1,3-butadiene: that which is characterized by disrotatory twisting of the incipient diene double bonds *and* twisting of the central bond. In terms of reaction products, one would expect a distribution that bears a strong resemblance to that obtained from direct excitation of the corresponding diene. In general, an exact match would not be expected if the product distribution depends on the direction of approach to the conical intersection, since this would most reasonably be expected to be different for the cyclobutene and the diene.

The striking similarities in the isomeric diene distributions obtained from cyclobutene ring opening (with 214-nm excitation) and direct diene irradiation, which are observed in all but one of the present series of compounds, may indicate that, in fact, the direction of approach to the conical intersection is *approximately the same* for a given cyclobutene and its corresponding disrotatory diene. This would be the case if ring opening occurs in disrotatory fashion on the ^1B_u surface, after which rapid crossing to the 2^1A_g surface and procession to the $2^1A_g/1^1A_g$ conical intersection occurs by an identical route to that followed when the diene is excited directly.

While there is agreement that the UV resonance Raman spectrum of cyclobutene indicates there to be activation of central (C=C) bond torsional modes within a few tens of femtoseconds after excitation of the molecule (10, 11), our results suggest that large-scale motions of this type are not required for efficient ring opening. If they were, one might expect there to be *some* observable difference in the photobehaviour of **1a–d** as the incipient flexibility of the system changes throughout the series as a function of ancillary ring size. Except for *cis*-**1a**, this does not appear to be the case. There is no variation throughout the series in the degree of agreement between observed and "expected" product distributions (for 214-nm excitation), nor is there any variation in the overall quantum yields for ring opening. Furthermore, the quantum yields for ring opening of **1a–d** are unusually high, compared to monocyclic systems. These considerations suggest that (large-scale) central bond torsion can only be important *after* the ring-opening stage of the reaction (on the excited state surface) is complete.

The conical intersection model is better able to account for the observation of higher disrotatory stereoselectivity with higher excitation energy than is the avoided crossing model; higher energy excitation could provide access to a different pathway for approach of the excited molecule to the conical intersection, one that results in a higher degree of disrotatory stereoselectivity in product formation. An alternate explanation is that the higher excitation energy populates an upper electronic excited state, whose involvement somehow results in a higher degree of disrotatory stereoselectivity. We can provide no reasonable explanation (using either theoretical model) for the difference in the trends in the wavelength dependence of the *cis* and *trans* isomers of this series of compounds.

Summary and conclusions

The isomeric *s-cis* diene distributions obtained from irradiation of alkylcyclobutenes that are structurally constrained at the cyclobutenyl C=C (central) bond are, for the most part, dictated by the excited state decay characteristics of a *single* diene isomer — that which forms by adiabatic ring opening by the disrotatory pathway predicted by orbital symmetry selection rules. Thus, the overall nonstereoselectivity of the reaction is most likely the result of *stereospecific* ring opening to yield an *electronically excited* product. Both the avoided crossing and conical intersection models for photopericyclic reactions can account for the qualitative aspects of the present data, but the latter appears to do so more completely than the former.

Other aspects of the photochemistry of aliphatic dienes are potentially exploitable for further verification of the adiabatic mechanism for excited state cyclobutene ring opening, and to further address the validity of theoretical models for the process. These include photochemical *s-cis* → *s-trans* conformer interconversion (in acyclic systems) and cyclobutene formation. The former should be detectable using matrix isolation techniques, while the latter could be probed by monitoring photoracemization of an optically active cyclobutene or the interconversion of isomeric cyclobutenes, which are both linked to a single diene isomer via disrotatory ring closure. Experiments of these types are in progress.

Experimental

^{1}H NMR spectra were recorded on Bruker AM300 or AM500 spectrometers, while ^{13}C NMR spectra were recorded at 125.6 MHz on the Bruker AM500; all were recorded in deuteriochloroform (or where noted, carbon tetrachloride) solution and are reported in parts per million downfield from tetramethylsilane. Condensed phase infrared spectra were recorded on a BioRad FTS40 infrared spectrometer as neat samples or in carbon tetrachloride solution (where noted). GC/FTIR analyses were carried out using the same spectrometer, interfaced to a Hewlett–Packard 5890 gas chromatograph via a BioRad GC/C 32 interface and equipped with a DB-17 megabore capillary column (30 m × 0.53 mm; Chromatographic Specialties). Gas chromatographic analyses were carried out using a Hewlett–Packard 5890 gas chromatograph equipped with a flame ionization detector, a Hewlett–Packard 3790 recording integrator, and both conventional heated and cold on-column injectors. A DB-1 microbore capillary column (15 m × 0.2 mm; Chromatographic Specialties, Inc.) was employed in conjunction with the latter, while a DB-1 megabore capillary column (30 m × 0.53 mm; Chromatographic Specialties, Inc.) or a HP-17 megabore capillary column (15 m × 0.53 mm, Hewlett–Packard, Inc.) were used with the conventional injector. GC/MS analyses were performed using a Hewlett–Packard 5890 gas chromatograph equipped with a HP-5971A mass selective detector and a DB-1 microbore capillary column (12 m × 0.2 mm; Chromatographic Specialties, Inc.). Exact masses were determined using a VGH ZABE mass spectrometer, and employed a mass of 12.000 000 for carbon.

Semi-preparative gas chromatographic separations employed a Varian 3300 gas chromatograph equipped with a thermal conductivity detector, a Hewlett–Packard 3390A recording integrator, and one of the following stainless steel columns: (*a*) 20% TCEP on 80/100 Chromosorb PNAW (20 ft × 1/4 in., Chromatographic Specialties, Inc.); (*b*) 20% TCEP on 80/100 Chromosorb PNAW (6 ft × 1/4 in., Chromatographic Specialties); or (*c*) 3.8% UC-W982 on 80/100 Supelcoport (24 ft × 1/4 in., Supelco, Inc.).

Ultraviolet absorption spectra were recorded using a Perkin–Elmer Lambda 9 spectrometer which is interfaced with an IBM PS2 model 30-286 and controlled by software supplied by the manufacturer. The spectrometer sample compartment was continuously flushed with dry nitrogen, and the sample and reference were deoxygenated with a stream of argon prior to recording the spectrum.

Pentane (Baker Photrex), hexanes (Fisher Reagent), *n*-nonane (Matheson, Coleman & Bell), and uranyl sulfate trihydrate (Alfa Ventron) were used as received from the suppliers. Tetrahydrofuran (Caledon Reagent) was dried over calcium hydride and distilled from sodium/benzophenone. Hexamethylphosphoramide, *n*-butyllithium (2.5 M in hexane), zirconocene dichloride, iodomethane, *n*-decane, *cis,cis*-1,3-cyclooctadiene, and 1,8-nonadiyne were used as received from Aldrich Chemical Co. Cerium(IV) sulfate tetrahydrate (Aldrich) was recrystallized three times from distilled water. 1,7-Octadiyne, 1,6-heptadiyne (Wiley Organics), and 1,5-hexadiyne (Lancaster) were purified by alumina column chromatography using hexanes as the eluant. 2,6-Octadiyne, 2,7-nonadiyne, 2,8-decadiyne, and 2,9-undecadiyne were prepared according to the procedure of Negishi et al. (30), and purified by alumina column chromatography (hexanes eluant). Oxalic acid (BDH Reagent) was recrystallized three times from water. Uranyl oxalate was prepared according to the published procedure and recrystallized three times from water (40).

Synthetic photolyses employed a Rayonet photochemical reactor fitted with 12 253.7-nm lamps and a merry-go-round apparatus. Deoxygenated solutions were irradiated in a 30-mL capacity quartz cell.

The (*E,E*)-1,2-bis(ethylidene)cycloalkanes (*E,E*-**2a–d**) were prepared according to the published procedures (30, 31). The *E,Z*- and *Z,Z*- diene isomers and the bicyclic cyclobutenes *cis*- and *trans*-**1b–d** were prepared by 253.7-nm irradiation of deoxygenated 2 M pentane solutions (10.0 mL) of the corresponding *E,E* isomer. For isolation of the dienes, the irradiations were stopped after the photostationary state had been reached; more extensive irradiation times were employed for the synthesis of the cyclobutenes **1b–d**. Following irradiation, the solvent was removed by distillation and the mixtures were passed through an alumina column, eluting with hexane. Following concentration of the solutions by careful distillation, isolation and further purification were achieved by preparative gas chromatography using column (*b*). Analytical and spectroscopic data for these compounds are similar to published data for all three isomers of **2a** (vide infra) (31, 41), *E,E*- and *E,Z*-**2b** (31, 42), *E,E*- and *E,Z*-**2c** (9, 31), and *E,E*-**2d** (31). The following lists complete spectroscopic data for all new or tentatively identified compounds (*Z,Z*-**2b**, *Z,Z*-**2c**, *E,Z*-**2d**, and *Z,Z*-**2d**), as well as previously unpublished data for the others.

*(*E,E*)-1,2-Bis(ethylidene)cyclobutane (*E,E-**2a***)* (31, 41): IR (gas): 2961 (m), 2929 (m), 2855 (m), 1578 (m), 1561 (s), 1416 (w), 1314 (w), 1068 (s), 1011 (s); ^{1}H NMR, δ: 1.51 (d, J = 6.9 Hz, 6H), 2.49 (br s, 4H), 5.43 (q, J = 6.5 Hz, 2H); ^{13}C NMR, δ: 13.21, 24.99, 111.47, 141.60; MS, *m/z* (*I*): 108 (45), 93 (86), 91 (96), 79 (100), 77 (83), 66 (16), 65 (17), 53 (12), 51 (39), 39 (51), 27 (41).

*(*E,Z*)-1,2-Bis(ethylidene)cyclobutane (*E,Z-**2a***)* (41): IR (gas): 2962 (m), 2929 (m), 2855 (m), 1470 (s), 1382 (s), 1261 (s), 1097 (s), 1015 (s); ^{1}H NMR, δ: 1.61 (d, 3H, J = 7.0 Hz), 1.72 (d, J = 7.0 Hz, 3H), 2.48 (br s, 4H), 5.11 (cplx q, J = 7.0 Hz, 1H), 5.57 (cplx q, J = 7.0 Hz, 1H); ^{13}C NMR, δ: 13.94, 14.60, 24.98, 26.42, 116.07, 117.29, 140.22, 142.47; MS, *m/z* (*I*): 108 (33), 93 (81), 91 (89), 79 (100), 77 (97), 53 (31), 51 (49), 39 (76), 27 (51).

*(*Z,Z*)-1,2-Bis(ethylidene)cyclobutane (*Z,Z-**2a***)* (41): IR (gas): 2963 (m), 2928 (m), 2866 (m), 1602 (m), 1448 (w), 1412 (w), 1261 (s), 1097 (s), 1015 (s); ^{1}H NMR, δ: 1.77 (d, J = 7.1 Hz, 6H), 2.41 (br s, 4H), 5.06 (q, J = 7.1 Hz, 2H); MS, *m/z* (*I*): 108 (44), 93 (79), 91 (84),79 (100), 77 (95), 65 (41), 53 (27), 51 (42), 39 (67), 27 (46).

*(*E,E*)-1,2-Bis(ethylidene)cyclopentane (*E,E-***2b***)* (31, 42): IR (gas): 2961 (m), 2928 (s), 2855 (m), 1678 (m), 1561 (s), 1261 (s), 1101 (m), 1068 (s), 1011 (s); ^{1}H NMR, δ: 1.51 (quintet, 2H), 1.60 (d, J = 7.0 Hz, 6H), 2.23 (t, 4H), 5.21 (m, 2H); ^{13}C NMR, δ (CCl_4): 14.8, 23.8, 30.4, 111.1, 141.1; MS, m/z (I): 122 (75), 107 (45), 105 (25), 94 (35), 93 (75), 79 (50), 77 (80), 67 (35), 65 (30), 55 (25), 41 (40).

*(*E,Z*)-1,2-Bis(ethylidene)cyclopentane (*E,Z-***2b***)* (42): IR (gas): 2941 (s), 2872 (m), 1641 (w), 1450 (m), 909 (m); UV (pentane), λ_{max} (ε): 249 nm (9900 M^{-1} cm^{-1}); ^{1}H NMR, δ: 1.61 (quintet, 2H), 1.74 (d, 3H), 1.79 (d, 3H), 2.35 (cplx, 4H), 5.48 (m, 1H), 5,77 (m, 1H); ^{13}C NMR, δ: 15.10, 15.41, 23.78, 31.09, 36.42, 116.06, 120.32, 141.10.

*(*Z,Z*)-1,2-Bis(ethylidene)cyclopentane (*Z,Z-***2b***;* identification tentative): MS, m/z (I): 122 (21), 107 (39), 105 (20), 95 (13), 94 (45), 93 (83), 79 (50), 77 (55), 67 (47), 65 (30), 55 (40), 41 (30).

cis-*6,7-Dimethylbicyclo[3.2.0]hept-1(5)-ene (*cis-***1b***)* (43): IR (gas): 2965 (s), 2900 (s), 2868 (m), 1459 (w), 1380 (w), 1337 (w), 795 (m); ^{13}C NMR, δ: 14.11, 26.32, 29.81, 38.67, 153.34; MS, m/z (I): 122 (17), 107 (21), 93 (55), 91 (38), 79 (45), 77 (35), 65 (31), 51 (34), 39 (51).

trans-*6,7-Dimethylbicyclo[3.2.0]hept-1(5)-ene (*trans-***1b***)* (43): IR (gas): 2966 (s), 2901 (s), 2865 (m), 1460 (w), 1383 (w), 1331 (w), 790 (m); ^{13}C NMR, δ: 17.50, 26.20, 29.75, 44.62, 152.60; MS, m/z (I): 122 (25), 107 (20), 93 (61), 91 (43), 79 (44), 77 (37), 65 (33), 51 (41), 39 (45).

*(*E,E*)-1,2-Bis(ethylidene)cyclohexane (*E,E-***2c***)* (9, 30, 31): IR (gas): 2959 (m), 2939 (s), 2857 (s), 1443 (m), 1375 (w), 1235 (w), 1001 (w), 905 (w), 843 (w), 808 (w); ^{1}H NMR, δ: 1.58 (d, 6H), 1.59 (m, 4H), 2.16 (br s, 4H), 5.26 (q, 2H); ^{13}C NMR, δ: 12.90, 26.29, 27.95, 115.71, 142.03; MS, m/z (I): 136 (45), 121 (10), 107 (45), 93 (50), 91 (65), 79 (100), 77 (50), 67 (20), 65 (20), 53 (20), 51 (19), 39 (40).

*(*E,Z*)-1,2-Bis(ethylidene)cyclohexane (*E,Z-***2c***)* (9): IR (neat): 3035 (w), 2935 (s), 2860 (s), 1442 (m), 1375 (w), 1238 (w), 993 (m), 907 (m), 837 (s), 807 (m); ^{1}H NMR, δ: 1.60 (d, 3H), 1.60 (m, 4H), 1.67 (d, 3H), 2.10 (m, 2H), 2.74 (m, 2H), 5.12 (cplx, 2H); ^{13}C NMR, δ (CCl_4): 12.69, 14.11, 27.19, 27.94, 28.66, 37.89, 116.48, 118,85, 137.39, 142.16; MS, m/z (I): 136 (30), 121 (15), 107 (45), 93 (50), 91 (75), 79 (100), 77 (50), 67 (25), 65 (27), 53 (16), 51 (16), 41 (21), 39 (43).

*(*Z,Z*)-1,2-Bis(ethylidene)cyclohexane (*Z,Z-***2c***;* identification tentative*)*: MS, m/z (I): 136 (33), 121 (8), 107 (85), 105 (39), 93 (40), 91 (39), 79 (100), 77 (65), 67 (30), 65 (32), 39 (15).

cis-*7,8-Dimethylbicyclo[4.2.0]oct-1(6)-ene (*cis-***1c***)* (9): IR (neat): 2905 (br, s), 1465 (m), 1438 (s), 1375 (m), 1363 (m), 1315 (m), 1233 (m), 1125 (m), 1017 (w), 968 (w), 928 (w), 885 (w), 815 (w), 805 (w); ^{1}H NMR, δ: 0.94 (d, 6H), 1.62 (m, 4H), 1.75 (d, 2H), 1.86 (d, 2H), 2.78 (cplx q, 2H); ^{13}C NMR, δ (CCl_4): 13.19, 22.34, 22.92, 40.48, 144.74; MS, m/z (I): 136 (22), 121 (17), 107 (40), 105 (13), 93 (51), 91 (59), 79 (100), 77 (46), 67 (21), 65 (18), 53 (20), 51 (19). 41 (25), 39 (43).

trans-*7,8-Dimethylbicyclo[4.2.0]oct-1(6)-ene (*trans-***1c***)* (9): IR (neat): 2917 (br, s), 2840 (s), 1443 (s), 1438 (m), 1327 (m), 1291 (m), 1260 (m), 1223 (m), 1123 (w), 1043 (w), 967 (m); ^{1}H NMR, δ: 1.08 (d, 6H), 1.60 (m, 2H), 1.66 (m, 2H), 1.77 (d, 2H), 1.85 (d, 2H), 2.19 (cplx q, 2H); ^{13}C NMR, δ (CCl_4): 16.94, 22.44, 23.04, 46.42, 143.69; MS, m/z (I): 136 (23), 121 (19), 107 (48), 105 (17), 93 (57), 91 (46), 79 (100), 77 (48), 67 (24), 65 (18), 53 (25), 51 (20), 41 (31), 39 (50).

*(*E,E*)-1,2-Bis(ethylidene)cycloheptane (*E,E-***2d***)* (30, 31): IR (gas): 3034 (w), 2392 (s), 2868 (m), 1870 (w), 1647 (w), 1452 (m), 1384 (w), 1346 (w), 1315 (w), 1035 (w), 977 (w), 840 (w), 806 (w); ^{1}H NMR, δ: 1.45–1.55 (m, 6H), 1.56 (d, 6H), 2.21 (m, 4H), 5.37 (q, 2H); ^{13}C NMR, δ: 13.03, 27.78, 29.38, 31.80, 117.40, 146.06; MS, m/z (I): 150 (52), 135 (16), 121 (41), 107 (37), 105 (21), 93 (96), 91 (75), 79 (100), 77 (62), 67 (38), 55 (18), 53 (28), 39 (50). 27 (31).

*(*E,Z*)-1,2-Bis(ethylidene)cycloheptane (*E,Z-***2d***)*: IR (gas): 2968 (m), 2931 (s), 2864 (m), 2681 (w), 1457 (m), 1384 (w), 1350 (w), 957 (w), 822 (w), 798 (w); ^{1}H NMR, δ: 1.51 (br s, 6H), 1.59 (d, 3H), 1.63 (d, 3H), 2.16–2.22 (m, 4H), 5.22 (sextet, 2H); ^{13}C NMR, δ: 14.04, 14.95, 27.42, 29.46, 29.52, 29.68, 38.00, 117.38, 121.33, 140.27, 145.31; MS, m/z (I): 150 (56), 135 (18), 121 (43), 107 (39), 105 (21), 93 (97), 91 (69), 81 (28), 79 (100), 77 (60), 69 (3), 67 (41), 55 (17), 53 (29), 39 (54), 27 (30). Exact Mass, calcd. for $C_{11}H_{18}$: 150.1409; found: 150.1418.

*(*Z,Z*)-1,2-Bis(ethylidene)cycloheptane (*Z,Z-***2d***;* identification tentative*)*: MS, m/z (I): 150 (6), 135 (33), 121 (71), 107 (83), 93 (100), 91 (87), 79 (100), 77 (83), 67 (41), 65 (32), 53 (25), 41 (27), 39 (49), 29 (20), 27 (28).

cis-*8,9-Dimethylbicyclo[5.2.0]non-1(7)-ene (*cis-***1d***)*: IR (gas): 3087 (w), 2971 (w), 2932 (s), 2866 (m), 1641 (w), 1452 (m), 993 (w), 913 (m); ^{1}H NMR, δ: 0.90 (d, J = 7 Hz, 6H), 1.49 (cplx m, 4H), 1.65 (cplx m, 2H), 1.88 (cplx m, 2H), 2.02 (cplx. m, 2H), 2.57 (br q, 2H); ^{13}C NMR, δ: 13.11, 28.31, 29.04, 29.67, 38.35, 145.12; MS, m/z (I): 150 (27), 135 (16), 121 (34), 107 (35), 105 (18), 93 (90), 91 (69), 81 (51), 79 (100), 77 (61), 67 (51), 63 (9), 55 (23), 53 (32), 39 (63), 27 (36). Exact Mass, calcd. for $C_{11}H_{18}$: 150.1409; found: 150.1418.

trans-*8,9-Dimethylbicyclo[5.2.0]non-1(7)-ene (*trans-***1d***)*: IR (gas): 2966 (m), 2920 (s), 2866 (m), 1459 (m), 1378 (w), 977 (w), 831 (w), 815 (w); ^{1}H NMR, δ: 1.02 (d, J = 7 Hz, 6H), 1.51 (br s, 4H), 1.58 (cplx m, 4H), 1.95 (cplx m, 4H); ^{13}C NMR, δ: 16.96, 28.53, 29.07, 29.69, 44.11, 146.22; MS, m/z (I): 150 (33), 135 (17), 121 (39), 107 (42), 105 (22), 93 (99), 91 (77), 81 (25), 79 (100), 77 (61), 67 (39), 65 (25), 55 (16), 53 (25), 39 (52), 27 (29). Exact Mass, calcd. for $C_{11}H_{18}$: 150.1409; found: 150.1409.

The irradiation of *E,Z*-**2b,c** also yielded minor amounts of hydrogen migration products, which were identified as 1-ethyl-2-vinylcyclopentene from *E,Z*-**2b**, and 2-ethyl-3-ethylidenecyclohexene from *E,Z*-**2c**:

1-Ethyl-2-vinylcyclopentene: ^{1}H NMR, δ: 0.98 (t, 3H, J = 7 Hz), 1.80 (t, 2 H), 2.22 (cplx q, 2 H), 2.44 (cplx, 2H), 4.97 (cplx t, 1 H), 5.02 (cplx m, 1 H), 6.65 (dd, 1 H); ^{13}C NMR, δ:

12.87, 21.41, 32.43, 36.26, 112.37, 131.04, 133.31, 144.51; MS, *m/z* (*I*): 122 (20); 107 (23); 93 (60); 91 (64); 79 (100); 77 (53); 65 (17); 51 (15); 39 (27); 27 (17).

2-Ethyl-3-ethylidenecyclohexene: ^{1}H NMR, δ: 1.02 (t, 3H, *J* = 7.2 Hz), 1.63 (br t, 2H), 1.67 (d, 3H, *J* = 6.8 Hz), 2.09 (br m, 2H), 2.14 (cplx q, 2H), 2.26 (br t, 2H), 5.43 (q, 1H); 5.49 (br t, 1 H); ^{13}C NMR, δ: 13.01, 13.41, 22.59, 25.44, 25.52, 25.72, 115.78, 123.04, 135.09, 138.57. MS, *m/z* (*I*): 136 (25); 121 (7); 107 (100); 93 (31); 91 (97); 79 (99); 77 (55); 65 (21); 51 (17); 41 (18); 39 (30).

Preparation of cis- *and* trans-*2,3-dimethylbicyclo[2.2.0]hex-1(4)-ene* (cis- *and* trans-***1a***)

In a flame-dried, 150-mL two-necked flask, fitted with an addition funnel, magnetic stirrer, reflux condenser, and nitrogen inlet, were placed (±)-2,3-butanediol di-*p*-tosylate (19.90 g, 0.05 mol) and tetrahydrofuran (50.0 mL). The system was purged with dry nitrogen and then cooled with an external isopropanol – Dry Ice bath to −78°C, after which a solution of lithium trimethylsilylacetylide (generated from trimethylsilylacetylene (9.82 g, 0.1 mol) and *n*-butyllithium) in tetrahydrofuran (25 mL) was added dropwise over a period of 1 h with vigorous stirring. The resulting solution was stirred for an additional hour at −78°C, allowed to warm to room temperature, and then quenched with ice (20 g) and extracted with pentane (3 × 10 mL). The combined extracts were dried with sodium sulfate, filtered, and the solvent was evaporated to yield a colourless oil that was tentatively identified as 3,4-dimethyl-1,6-bis(trimethylsilyl)-1,5-hexadiyne (4.75 g, 0.019 mol, 38%) on the basis of its ^{1}H NMR and mass spectra: ^{1}H NMR, δ (CDCl$_3$): 0.11 (s, 9H), 1.71 (d, 3H), 5.01 (q, 1H); MS, *m/z* (*I*): 235 (13), 207 (3), 162 (75), 161 (43), 156 (2), 147 (22), 138 (13), 110 (14), 96 (14), 83 (12), 81 (11), 73 (100), 59 (12), 43 (11). The material was used without further purification in the following step.

In a flame-dried, 50-mL two-necked flask fitted with magnetic stirrer, addition funnel, reflux condenser, and gas inlet were placed zirconocene dichloride (2.92 g, 0.01 mol) and tetrahydrofuran (15 mL). The system was purged with dry nitrogen and cooled to −78°C with an external Dry Ice bath. A solution of *n*-butyllithium (0.02 mol) in tetrahydrofuran (5 mL) was added dropwise with stirring over a period of 1 h. After stirring at −78°C for an additional hour, a deoxygenated solution of 3,4-dimethyl-1,6-bis(trimethylsilyl)-1,5-hexadiyne (2.50 g, 0.01 mol) in tetrahydrofuran (5 mL) was added to the reaction mixture by means of a double-headed needle. The resulting solution was stirred at −78°C for an additional 3 h, warmed to room temperature, quenched with ice (20 g), and extracted with pentane (3 × 10 mL). The extracts were combined, the solvent was evaporated, and the residue (1.74 g) was dissolved in dichloromethane (10 mL) and placed in a 25-mL roundbottom flask. Trifluoroacetic acid (3.0 mL) was added and the mixture was stirred for 12 h at room temperature. The resulting brown reaction mixture was quenched with water (10.0 mL) and extracted with pentane (3 × 5 mL). The extracts were combined, dried over sodium sulfate, filtered, carefully distilled to remove the solvent, and finally bulb-to-bulb distilled under vacuum to yield a colourless liquid (0.73 g, 66%) that contained two major isomeric products according to GC/MS analysis. Small (ca. 10 mg) quantities of the two components were isolated by semi-preparative GC (column *c*), and identified as *cis*- and *trans*-3,4-dimethyl-1,2-(bis)-methylenecyclobutane (*cis*- and *trans*-**7**) on the basis of comparison of their ^{1}H NMR spectra to the published data (41).

The remaining portion of the mixture from above was dissolved in pentane (5 mL), placed in a quartz irradiation tube, and sealed with a rubber septum. The solution was deoxygenated with a stream of N$_2$, and photolysed (253.7 nm) to ca. 70% conversion. GC and GC/MS analysis indicated the formation of two major products, which were isolated and purified by semi-preparative GC (column *a*), and identified as *cis*- and *trans*-**1a** on the basis of their GC retention times, ^{1}H NMR, UV, and mass spectra (see below). As is also known to be the case for the parent compound, bicyclo[2.2.0]hex-1(4)-ene, *cis*- and *trans*-**1a** are relatively unstable compounds, with half-lives of ca. 15 h in pentane solution (1 × 10^{-2} M) at 25°C. The samples were stored under liquid nitrogen prior to their use in photolysis experiments.

cis-*2,3-Dimethylbicyclo[2.2.0]-hex-1(4)-ene* (cis-***1a***): IR (gas): 2962 (s), 2929 (s), 2872 (m), 2855 (m), 1450 (w), 1381 (w), 1353 (w), 1261 (m), 1101 (m); ^{1}H NMR, δ: 1.60 (d, *J* = 6.5 Hz, 6H), 1.76 (cplx m, 4H), 2.21 (q, *J* = 7.2 Hz, 2H); MS, *m/z* (*I*): 108 (39), 93 (78), 91 (83), 79 (100), 77 (94), 66 (24), 65 (29), 53 (29), 51 (41), 39 (63), 27 (41).

trans-*2,3-Dimethylbicyclo[2.2.0]-hex-1(4)-ene* (trans-***1a***): IR (gas): 2962 (s), 2929 (s), 2872 (w), 2856 (w), 1451 (w), 1261 (m); ^{1}H NMR, δ: 1.60 (d, *J* = 6.5 Hz, 6H), 1.76 (cplx m, 4H), 2.14 (cplx m, 2H); MS, *m/z* (*I*): 108 (40), 93 (96), 91 (96), 79 (95), 77 (100), 66 (23), 65 (27), 53 (33), 51 (44), 39 (64), 27 (42).

Quantitative photolyses employed a Rayonet photochemical reactor fitted with a merry-go-round and two 253.7 nm lamps, a 16-W Phillips 93106E Zn resonance lamp (214 nm) either alone or in conjunction with a 214 nm interference filter (Acton Research Corp. 214-B-ID), or the unfocussed pulses from a Lumonics 510 excimer laser containing Ar/F$_2$/He mixtures (193 nm, ca. 15 ns, 20 mJ, 0.5 Hz repetition rate). Solutions were contained in 5-mm quartz tubes sealed with rubber septa for 214 nm or 253.7 nm photolyses, or 1 × 2.5-cm round Suprasil UV cells (sealed with rubber septa) for 193 nm photolyses, and were deoxygenated with a stream of dry nitrogen or argon prior to irradiation. *n*-Decane was employed as an internal GC standard in all cases; the VPC detector responses were calibrated using solutions of known concentrations of substrate and standard. The solutions were vigorously stirred with a magnetic stirrer during the photolyses.

Quantum yields for product formation from 253.7 nm irradiation of dienes **2a–d** were carried out by ferrioxalate actinometry (44, 45), using 0.02 M solutions in pentane, and are the averages of triplicate single point determinations taken at conversions of 10% or less.

Quantum yields for product formation from 214-nm irradiation of *cis*- and *trans*-**1a** were carried out on unstirred solutions, using the initial slopes of product concentration vs. time plots to determine product yields, and uranyl oxalate actinometry (40, 44, 46) to determine light intensities.

Quantum yields for product formation from 193-nm irradiation of cyclobutenes **1b–d** were determined using the irradiation of bicyclo[4.2.0]oct-7-ene as the actinometer (1).

Irradiation of substrate and actinometer were followed as a function of light dose between 0.5 and 5% conversion, and quantum yields were determined from the slopes of concentration vs. time plots after correction of the raw data with the corresponding GC response factors.

Acknowledgments

We gratefully acknowledge the assistance of the McMaster University Regional Centre for Mass Spectrometry for Exact Mass determinations, the Natural Sciences and Engineering Research Council of Canada for equipment and operating grants, and M. Olivucci for helpful discussions.

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