The Role of Central Bond Torsional Motions in the Direct *cis* ⇌ *trans*-Photoisomerization of Conjugated Dienes

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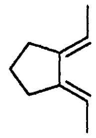
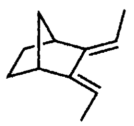
The photochemistry of the *E,E*- and *E,Z*-geometric isomers of 1,2-bis(ethylidene)-cyclopentane and -cyclobutane, and 2,3-bis(ethylidene)norbornane has been studied in hydrocarbon solution at room temperature; the results are inconsistent with the classical theoretical models for diene *cis* ⇌ *trans* photoisomerization and ring closure, which assume that both processes involve only simple torsional motions about (one or both of) the termini of buta-1,3-diene.

The direct *cis*⇌*trans*-photoisomerization of conjugated dienes is one of the best known and most fundamentally important reactions in organic photochemistry,[1,2] as evidenced by the large number of experimental[3–10] and theoretical[11–13] studies which have been directed at defining the mechanism of the process. The most commonly accepted mechanism of the the reaction describes it as occurring by torsional relaxation about one of the double bonds (while the four-carbon framework maintains or assumes a planar structure) to an allylmethylene geometry, which corresponds to that at an avoided crossing between the ground and excited singlet state surfaces.[1,2,5–11] The classical mechanism for cyclobutene formation is similar in that planarity of the four-carbon framework is maintained while torsion about both double bonds takes place.[14,15] Decay to the cyclobutene ground state surface at the avoided crossing is thought to be preferred for the disrotatory ring-closure mode because the energy gap between the ground and excited state surfaces is smaller for this stereochemical pathway than for the ground-state-allowed conrotatory one.[14] These models are predicated on the assumption that the C(2)–C(3) bond (buta-1,3-diene numbering) has enhanced double bond character in the lowest π,π^* singlet state. Most known aspects of diene photochemistry are consistent with the classical models, except for the fact that the dominant mode of excited state relaxation in acyclic dienes is s-*cis*–s-*trans*-conformer interconversion.[9,16]

As part of our continuing studies of the mechanism of the photochemical ring opening of cyclobutene,[17,18] we have initiated a study of the photochemistry of a series of torsionally constrained 1,3-dienes and their isomeric cyclobutene derivatives. We report the preliminary results of a study of the photochemistry of the constrained dienes **1–3**, since they bear directly on recent theoretical work which questions the validity of the classical mechanisms for diene photoisomerization processes.[12,13]

Direct irradiation (254 nm) of deoxygenated 0.02 mol dm^{-3} pentane solutions of the *E,E*-isomers of 1,2-bis(ethylidene)-cyclopentane **1** and -cyclobutane **3**, and 2,3-bis(ethylidene)-norbornane **2**† results in the formation of the corresponding *E,Z*-isomers and *cis*-cyclobutenes **4–6**.‡ The corresponding


E,E-**1**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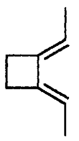
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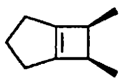
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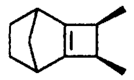
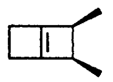

cis-**5**


cis-**6**

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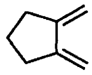
† The *E,E*-isomers of **1** and **3** were prepared from nona-2,7-diyne and octa-2,6-diyne, respectively, by the method of Nugent and co-workers.[19] Compound *E,E*-**2** was prepared by a three-step sequence starting from norcamphor. All three compounds were identified on the basis of their symmetrical ^1H and ^{13}C spectra, which were similar to those reported previously for these compounds.[20,21]

‡ The ^1H and ^{13}C NMR, IR and mass spectra of *E,Z*- and *Z,Z*-**3** are similar to the published data.[20] The *E,Z*- and *Z,Z*-isomers of **1** and **2** were identified on the basis of their ^1H NMR, ^{13}C NMR and mass spectra. The *cis*- and *trans*-isomers of **4** and **6** were identified from their ^1H and ^{13}C NMR, UV absorption and mass spectra. The *cis*- and *trans*-isomers of **5** were tentatively identified on the basis of their GC retention times, mass and UV absorption spectra. See: W. J. Leigh, K. Zheng and K. B. Clark, *Can. J. Chem.*, 1990, **68**, 1988. Complete spectral characterization for all compounds will be reported in a full paper.

Table 1 Quantum yields for *cis*⇌*trans*-photoisomerization and cyclobutene formation from 254 nm irradiation of 1,2-bis(ethylidene)-cycloalkanes **1–3** in deoxygenated pentane solution at 23 °C[a]

Compound	$\phi_{EE\text{-}EZ}$	$\phi_{EZ\text{-}EE}$	$\phi_{EZ\text{-}ZZ}$	ϕ_{CB}	ϕ_{other}	Angle for $\Delta H_f = 3^b$
1	0.24 ± 0.02	0.39 ± 0.04	0.09 ± 0.01	0.10 ± 0.02 (*E,E*) 0.13 ± 0.01 (*E,Z*)	<0.002 (*E,E*) ≈ 0.01 (*E,Z*)	37°
2	0.30 ± 0.03	0.28 ± 0.03	0.06 ± 0.01	0.03 ± 0.01 (*E,E*) 0.03 ± 0.01 (*E,Z*)	≈ 0.003 (*E,E*) <0.005 (*E,Z*)	31°
3	0.12 ± 0.02	0.11 ± 0.03	0.011 ± 0.005	<0.005 (*E,E*) <0.005 (*E,Z*)	≈ 0.01 (*E,E*) ≈ 0.01 (*E,Z*)	27°

[a] Determined using the formation of *E,Z*-**1** from irradiation of *E,E*-**1** as a secondary actinometer. Relative quantum yields were calculated from the slopes of product concentration *vs.* time plots, which monitored product formation by GC between 0.2 and *ca.* 5% conversion. The secondary actinometer was calibrated by potassium ferrioxalate actinometry. The data were corrected for differences in GC response factors. [b] The central bond dihedral angle at which the calculated (MMX) heat of formation of the corresponding bis(methylene)cycloalkane (**7–9**) is 3.0 kcal mol^{-1} (1 cal = 4.184 J) higher than that of its stable ground-state geometry.



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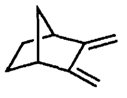

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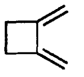

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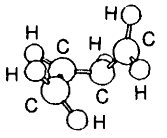

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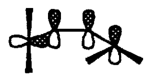

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E,Z-diene isomers were isolated by gas chromatography (GC) from preparative scale photolyses of the *E,E*-isomers (along with the cyclobutenes), and identified on the basis of their ^{1}H and ^{13}C NMR and UV absorption spectra.‡ Direct irradiation of *E,Z*-**1–3** yields the corresponding *E,E*- and *Z,Z*-diene isomers, the corresponding *trans*-cyclobutene derivatives, and small amounts of isomeric compounds which have not yet been identified.§ Quantum yields for *cis* ⇌ *trans*-photoisomerization and for formation of cyclobutenes and other minor products were determined for all compounds in the series relative to the *cis* ⇌ *trans*-photoisomerization of *E,E*-**1**, which was determined to be $\phi_{EE \rightarrow EZ} = 0.24 \pm 0.02$ by ferrioxalate actinometry, and are collected in Table 1.

The dienes studied in this work all have planar s-*cis*-structures with 'central bond' dihedral angles close to 0°, but with varying abilities to twist about the dihedral. This is demonstrated clearly by molecular mechanics (MMX) calculations. The results of MMX dihedral driver calculations for the corresponding bis-(methylene)cycloalkanes **7–9**[22] are listed along with the quantum yield data for **1–3** in Table 1. The data listed are the central bond angles to which the dihedrals must be driven (from *ca.* 0°) to cause a 3.0 kcal mol^{-1} increase in the heats of formation of the ground state molecules.

The quantum yields for *cis*⇌*trans*-photoisomerization of **1** and **2** are of similar magnitude to those reported for the hexa-2,4-dienes,[3,7] and can thus be considered typical of conjugated dienes in general.[1] In contrast, those for *E,E*- and *E,Z*-**3** are significantly lower, and we find no evidence for the formation of other products (or fluorescence) which might account for the decrease in the efficiency of the process in these cases.

Recent theoretical calculations have led to the proposal of a fundamentally different mechanism for the photoisomerization processes of conjugated dienes compared to the classical models.[12,13] These studies are based on the tenet that excited-to-ground state internal conversion processes occur at *conical intersections*—geometries where the two surfaces actually touch[12,13,23]—rather than at avoided surface crossings. According to *ab initio* (MCSCF) calculations, the structures of buta-1,3-diene at the three conical intersections (CIs) found for the excited singlet state surface are tetraradicaloid with all three C–C bonds twisted, as a result of substantial pyramidalization at one of the two central carbons.[13] In the s-*cis*-like CI **10** which is proposed to be involved in the photochemistry of s-*cis*-dienes, the two terminal bonds are twisted by *ca.* 20° and 80°, while the central bond is twisted by *ca.* 50°. This should be compared to the allylmethylene species **11** whose involvement is implicit in the avoided-crossing model for the *cis*⇌*trans*-photoisomerization of conjugated dienes.

The particularly intriguing implication of the conical intersection mechanism for conjugated diene photochemistry is that *cis* ⇌ *trans*-isomerization about one or the other double bond involves simultaneous torsional motions about the central C–C single bond. This has been suggested previously in the photoisomerization of opsin-bound retinal,[24] but to our knowledge, there are no examples in the literature which might address this implication. The anomalously low quantum yields for *cis* ⇌ *trans*-photoisomerization of *E,E*- and *E,Z*-**3** are consistent with the theory's prediction that inhibiting the torsional mobility of the central (single) bond of a conjugated diene should result in a reduction in the efficiency of the process. At the very least, our results for these compounds are incompatible with the classical theoretical view of the process, which requires planarization of the four-bond framework and rotation about only one of the (double) bonds as the system relaxes to the allylmethylene geometry. The fact that the quantum yields observed for **1** and **2** are similar to those commonly observed for acyclic systems[3,6,7] indicates that it is unnecessary for the excited diene to twist to the full 52° dihedral angle predicted by calculation[13] in order for efficient photochemistry to occur.

The quantum yields for cyclobutene formation from **1–3** are similar to those reported by Aue and Reynolds for the bis(methylene) analogues **7–9**.[25] For both sets of compounds, the quantum yields for cyclobutene formation follow the same trend with decreasing central bond torsional flexibility as those for *cis*⇌*trans*-photoisomerization in **1–3**, and are thus also consistent with the ramifications of the conical intersection mechanism. However, it does not seem likely that this is the only factor that is important in this aspect of diene photoreactivity. It would be expected that the efficiency of

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§ Minor products were identified as isomers of **1–3** on the basis of GC–MS analyses. Their chemical yields (relative to the identified products) totalled <2% for **1**,**2** and <10% for **3**. Photolysis of a 0.005 mol dm^{-3} mixture of (*E,E*)- and (*E,Z*)-**3** in *n*-hexadecane to *ca.* 5% conversion to (*Z,Z*)-**3** verified that no lower molecular mass products are formed (ϕ < 0.001).

cyclobutene formation should also be affected by the distance between the termini of the diene system; this distance increases systematically throughout the series with decreasing ring size, according to our MMX calculations. It should be noted that this explanation is analogous to the product-ring strain argument originally advanced by Aue and Reynolds.[25]

A good deal of caution must yet be exercised in accepting the ramifications of our results for **1–3**. However, it is interesting that the ring-opening reaction of the isomeric cyclobutenes **3–6** and larger-ring analogues also exhibits unusual features compared to the behaviour of non-constrained cyclobutene derivatives;[17,26] this may well be ascribable to the reduced flexibility in the reaction centre which results from their special structures. Further work in this area is in progress.

We thank the NSERC (Canada) for financial support, and Dr M. A. Robb of King's College, London, for a preprint of ref. 13.

Received, 17th August 1993; Com. 3/05003C

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