4.40 and 5.18 to be replaced by signals at δ 5.99 and 5.36. The new signals were assigned to the ring proton of the *meso-* and (+/−)-borolanes by comparison with authentic samples.

(+/−)-2,4,5-Triphenyl-1,3,2-borolane: ¹H NMR (CD₃CN) δ 5.36 (s, 2 H), 7.36-7.92 (m, 15 H); ¹¹B NMR (CD₃CN) δ 28; MS (GC/MS, EI) m/e 300 (M⁺, base), 222, 193, 90.

meso-2,4,5-Triphenyl-1,3,2-borolane: ¹H NMR (CD₃CN) δ 5.99 (s, 2 H), 7.01-7.98 (m, 15 H); ¹¹B NMR (CD₃CN) δ 32; MS (GC/MS, EI) m/e 300 (M⁺, base), 222, 193, 90.

Photolysis of Tetramethylammonium (2-Phenylcyclopropyl)triphenylborate in the Presence of CH₃OH. The borate (64.2 mg, 0.15 mmol) in a N₂-purged solution (10 mL of acetonitrile and 1.0 mL of CH₃OH) was irradiated at 300 nm in a Rayonet reactor. Analysis of the solution by GC after the borate has been consumed shows the formation of biphenyl, dihydrobiphenyl, and 1,3-diphenylpropane in a ratio of ca. 1:1:1.

Photolysis of Cesium (2-Phenylcyclopropyl)dimethylphenylborate in the Presence of MeOH. A N₂-purged solution of borate **3** (30.6 mg, 0.08 mmol) and 50 μL of methanol was prepared in 3 mL of THF. The irradiation at 254 nm was monitored by ¹¹B NMR spectroscopy and by gas chromatography. The yield of 1,3-diphenylpropane from this reaction was 25%. The other products formed in this reaction were identified by comparison with authentic samples: toluene (2%); styrene (1%); allyl-

benzene (8%); *cis*-β-methylstyrene (6%); and *trans*-β-methylstyrene (30%).

This reaction was repeated with MeOD (dried over molecular sieves). After the borate was consumed, the solution was quenched with CH₃C-O₂D. Analysis by GC/MS showed the presence of dideuteriated 1,3-diphenylpropane (80% D₂, see the following text). Collection of this product by preparative GC gave pure 1,3-diphenylpropane-*1,3-d₂*: MS (EI, GC/MS) m/e 198 (M⁺), 106, 93 (base); ¹H NMR (CDCl₃) δ 1.95 (m, 2 H), 2.63 (t, 2 H), 7.18-7.31 (m, 10 H). For deuterium-incorporation analysis, the region around the parent ions was scanned and averaged over entire peak: natural abundance m/e 196 (100), 197 (17), 198 (1); deuteriated m/e 198 (100), 197 (27), 196 (2).

Cyclobutene Photochemistry.[1] Reinvestigation of the Photochemistry of *cis*- and *trans*-Tricyclo[6.4.0.0²,⁷]dodec-1-ene
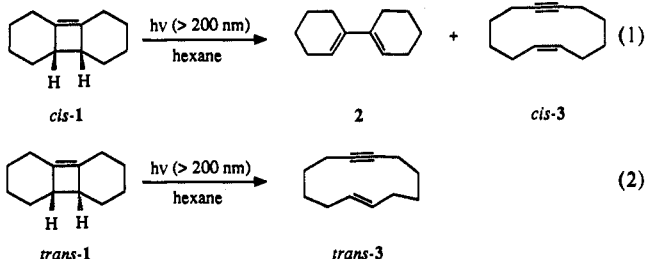
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Contribution from the Department of Chemistry, McMaster University, Hamilton, Ontario, Canada L8S 4M1. Received August 13, 1990

Abstract: The direct photolyses of *cis*- and *trans*-tricyclo[6.4.0.0²,⁷]dodec-1-ene in hydrocarbon solution have been reinvestigated with 193-nm, 214-nm, and broad-band UV (>200 nm) light sources. The two compounds undergo competitive stereospecific fragmentation (yielding *cis*- or *trans*-cyclododec-7-en-1-yne, respectively) and ring opening (yielding 1,1'-bicyclohexenyl). The observation of 1,1'-bicyclohexenyl formation from *both* cyclobutene isomers differs from the results of a previous study of the photochemistry of these compounds, which concluded that only the cis isomer undergoes ring opening upon photolysis in solution, presumably via a disrotatory electrocyclic pathway. The present results verify the conclusions of several recent studies that the photochemical ring opening of alkylcyclobutenes in general proceeds nonstereospecifically.

Introduction

Several years ago, it was reported that direct photolysis of *cis*-tricyclo[6.4.0.0²,⁷]dodec-1-ene (*cis*-**1**) in hydrocarbon solution affords 1,1'-bicyclohexenyl (**2**) and *cis*-cyclododec-7-enyne (*cis*-**3**) as the major products (see eq 1).[3] Photolysis of the trans isomer

(*trans*-**1**) under similar conditions, on the other hand, was reported to afford only *trans*-cyclododec-7-enyne (*trans*-**3**; see eq 2). For many years, the results of this study have provided the prototypical examples illustrating the stereochemistry associated with two fundamental photochemical pericyclic reactions:[4] the electrocyclic ring opening of cyclobutene and the $(\sigma_{2s} + \sigma_{2s})$ cycloreversion reaction of four-membered cyclic hydrocarbons. Until recently,[5-9] this study has provided the only example that illustrates the stereochemistry of the former reaction.

Simple orbital symmetry selection rules,[4] as well as more sophisticated ab initio theoretical calculations,[10] predict that the

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(1) Part 5 of the series. Part 4: see ref 8.
(2) (a) Natural Sciences and Engineering Research Council of Canada University Research Fellow, 1983-1993. To whom correspondence should be addressed. (b) Permanent address: Department of Chemistry, Zhongshan University, Guangzhou, People's Republic of China.
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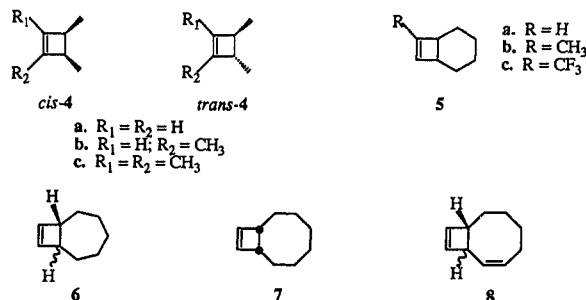(7) Leigh, W. J.; Zheng, K.; Clark, K. B. *Can. J. Chem.*, in press.
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photochemical interconversion of cyclobutene and 1,3-butadiene should proceed stereospecifically via the disrotatory pathway. The reported behavior of *cis-* and *trans-1* verifies this prediction. Formation of **2** directly by concerted pericyclic pathways requires disrotatory opening of *cis-1* and conrotatory opening of *trans-1*. Photochemical ring opening of the latter compound by the symmetry-allowed (disrotatory) pathway should result in the initial formation of the highly strained cis,trans isomer of **2**, which is now known to undergo rapid thermal isomerization to *cis,cis-2* and (in smaller amounts) thermally allowed conrotatory ring closure to yield *cis-1*.[11] Neither **2** nor *cis-1* was observed as a product from photolysis of *trans-1*,[3] indicating that both the disrotatory and conrotatory concerted ring-opening pathways are relatively high energy processes in the excited state of this compound. Presumably, the barrier to excited-state conrotatory opening of *trans-1* would be symmetry-imposed, while the barrier to disrotatory opening would be the result of the large strain energy which must be introduced in the formation of *cis,trans-2*.

Several recent studies[5–9] have provided results that conflict with those previously reported for *cis-* and *trans-1*. These more recent studies have provided several examples which indicate that, in general, the photochemical ring opening of alkylcyclobutene derivatives proceeds nonstereospecifically to yield a distribution of all possible, stable isomers of the corresponding conjugated dienes. This general feature is characteristic of the photochemical ring opening of several monocyclic **4**[5,7] and bicyclic alkylcyclobutene derivatives **5–8**[5,6,8]. Before reconciliation of the apparent fun-

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

cis-4 *trans-4* **5**

a. R$_1$ = R$_2$ = H
b. R$_1$ = H; R$_2$ = CH$_3$
c. R$_1$ = R$_2$ = CH$_3$

6 **7** **8**

damental differences between the photobehavior of **1** and simpler alkylcyclobutenes was attempted, it seemed prudent to reinvestigate the direct photolysis of the former compounds in solution, with use of both monochromatic and broad-band UV sources as well as modern analytical techniques, which afford higher sensitivity than the methods available 20 years ago. The results of this study are reported below.

Results and Discussion

The tricyclic hydrocarbons *cis-* and *trans-1* were synthesized according to the published procedures[12] and purified by semi-preparative gas chromatography (vpc) to >99.5% purity.

Direct photolysis of deoxygenated 0.02 M pentane solutions of *cis-* and *trans-1* with an unfiltered Zn resonance lamp (214 nm) produced mixtures of two major products in each case. These were shown to be *cis-* and *trans-3* (from *cis-* and *trans-1*, respectively) and 1,1'-bicyclohexenyl (**2**), as shown in eqs 3 and 4.
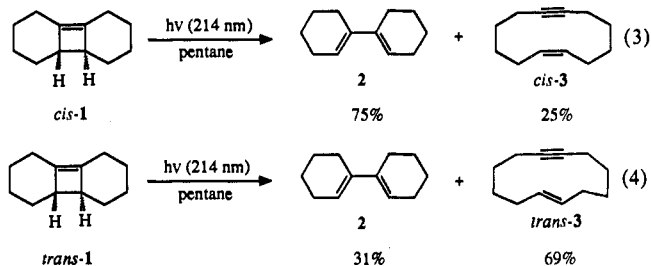
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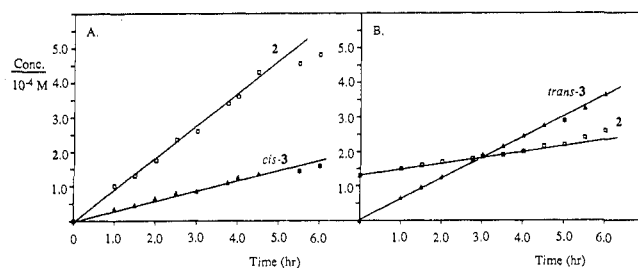

Figure 1. Concentration vs time plots for the 214-nm photolyses of 0.02 M *cis-1* (A) and *trans-1* (B) in deoxygenated *n*-pentane solution at 22 °C.

Table I. Relative Rates of Product Formation from Photolysis (214 nm) of *cis-* and *trans-1* in Deoxygenated Pentane Solution at 22 °C[a]

cyclobutene	**2**	*cis-3*	*trans-3*
cis-1	3.25	1.0	
trans-1	0.63		2.14

[a] From the slopes of concentration vs time plots (see Figure 1) with use of optically matched solutions of identical concentrations of **1** and internal vpc standard, irradiating concurrently. Errors are ca. ±10%.

Product **2** was identified by vpc coinjection with an authentic sample and by GC/MS analysis of the photolysates. The cycloalkenynes *cis-* and *trans-3* were identified after isolation from larger scale photolyses of *cis-* and *trans-1*, respectively, the former in the presence of 10^{-5} M triphenylene as reported previously.[3] The photoproducts were identified on the basis of their ^{1}H and ^{13}C NMR, IR, and mass spectra, which in all cases agreed satisfactorily with those previously reported. Photolyses of solutions of similar concentration were also carried out with the unfocused pulses (193 nm, ca. 25 mJ, 0.5-Hz repetition rate) from an Ar/F$_2$ excimer laser and with a medium-pressure mercury (>200-nm) resonance lamp. The latter experiments were carried out in an attempt to reproduce the reported conditions for photolysis of these compounds as closely as possible. Product yields were determined from the slopes of concentration vs time plots, constructed in each case for runs monitored between 0.3 and 5% conversion of starting material. Examples of such plots are shown in Figure 1 for 214-nm photolyses of *cis-* and *trans-1*, carried out under equivalent conditions with optically dense solutions of identical concentrations of **1** and internal standard. For these particular experiments, the relative slopes of the concentration vs time plots are proportional to the relative quantum yields for product formation from *cis-* and *trans-1*. The (normalized) slopes of these plots are presented in Table I. The relative product yields from photolysis of *cis-1* are wavelength-independent, within experimental error. In the case of *trans-1*, the relative yield of **2** is slightly higher at shorter excitation wavelengths.

The present results for *cis-1* agree satisfactorily with the earlier report that photolysis of this compound in pentane solution with broad-band UV light (>200 nm) affords **2** and *cis-3* in a ratio of about 3:1.[3] We also find that *trans-3* is indeed the major product of photolysis of *trans-1* under similar conditions, but the observation that **2** is also formed from the photolysis of this compound (in 20–30% yield) was unexpected. The source of the discrepancy between the previously reported and present results for *trans-1* is not clear. In our hands, **2** is formed in easily detectable amounts from photolysis of both isomers of **1** with monochromatic or broad-band UV light. Whatever the explanation, it is now clear that both *cis-* and *trans-1* undergo photochemical ring opening upon direct photolysis in solution. The present results are consistent with the photobehavior of **4–8**[5–9] and verify that photochemical ring opening of simple alkylcyclobutene derivatives is nonstereospecific, in general.

Careful attempts were made to determine whether *cis-1* is formed in the photolysis of *trans-1* in trace amounts, with use of vpc conditions that were established to be capable of resolving the two isomers to base line. In the photolysate from a 214-nm run (pentane solution) carried to ca. 5% conversion, a very minor component with the correct vpc retention time for *cis-1* was found

Photochemistry of Tricyclo[6.4.0.0²,⁷]dodec-1-ene

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to be present. The product was tentatively identified as *cis*-1 on the basis of vpc striking experiments with an authentic sample; however, it is formed in yields that are too low to enable isolation or additional verification by GC/MS. From the relative peak areas, the amount of this component present in the mixture is roughly 0.5% of the amount of 2 present. This determination is very crude, since the product is formed in amounts that are just slightly above the lower limit of detection under our vpc conditions. Control vpc injections of pentane solutions containing *trans*-1 (0.02 M), 2 (4×10^{-4} M), and *cis*-1 (($4-8$) $\times 10^{-6}$ M) verified that the absolute yield of *cis*-1 formed in the photolysis of *trans*-1 is less than 1% of the yield of 2.

The tentative detection of *cis*-1 in the mixture obtained from photolysis of *trans*-1 is potentially significant, and our inability to quantify its yield more accurately is disappointing. Its detection in the photolysate would provide evidence that ring opening of *trans*-1 proceeds at least partially to yield the highly strained cis,trans isomer of 2, formally by the symmetry-allowed disrotatory ring-opening pathway. Saltiel and co-workers have reported that, in cyclohexane solution at room temperature, *cis,trans*-2 (generated by triplet sensitization) undergoes unimolecular isomerization ($k \approx 1.5 \times 10^6$ s^{-1}) to yield *cis,cis*-2 (96.8%) and *cis*-1 (3.2%).[11] Thus, under steady-state photolysis conditions, ca. 97% of the *cis,trans*-2 that is initially formed from excited-state ring opening of *trans*-1 would ultimately be detected as *cis,cis*-2. Using Saltiel's data[11] and our rough determination of the yield of *cis*-1 from photolysis of *trans*-1, we estimate that ring opening of *trans*-1 initially yields *cis,trans*- and *cis,cis*-2 in a ratio of ca. 1:5 or less. This ratio should be considered to represent an upper limit of the relative yield of the *cis,trans*-diene from photolysis of *trans*-1, owing to the tentative nature of our identification of *cis*-1 as a photoproduct and the possibility that it is formed as a result of secondary photolysis of 2. Unfortunately, it is not possible to carry out a similar determination of the yield of *cis,trans*-2 from photolysis of *cis*-1 via this procedure.

Photolysis (214 nm) of *cis*- and *trans*-1 (0.02 M) in deoxygenated methanol solution afforded product mixtures similar to those observed with pentane as solvent. In both cases, the relative yield of 2 is somewhat higher in methanol (2:3 = 3.5:1 and 1:1.8 from *cis*- and *trans*-1, respectively) compared to that in pentane under similar conditions (2:3 = 2.9:1 and 1:3.0 from *cis*- and *trans*-1, respectively). In particular, no new products ascribable to trapping of *cis,trans*-2 by methanol were formed in detectable yield. This was shown by comparing the photolysates to that from acetophenone-sensitized photolysis of 2 in neutral methanol. The latter photolysis afforded two products, tentatively identified as 9 and 10 on the basis of GC/MS analysis, along with smaller amounts of 2. Compounds 9 and 10 have been reported to be the main products of nucleophilic trapping of *cis,trans*-2 in neutral and acidic methanol solution.[11] Neither of these products was

9   10

formed in detectable amounts in the direct irradiation of *cis*- and *trans*-1 in methanol solution. However, since methanol does not significantly quench the formation of *cis*-1 in the triplet-sensitized photolysis of 2,[11b] the yields of 9 and 10 from direct irradiation of *trans*-1 (given our estimate above of the upper limiting yield of *cis,trans*-2 in this case) might be small enough to escape detection under our vpc conditions. We conclude that *cis,trans*-2 is, at most, a very minor product in the direct photolyses of *cis*- and *trans*-1.

On the basis of the similar distributions of isomeric dienes, which are obtained in the photolysis of the cis and trans isomers of 6[8] and in those of 8,[6] we have proposed that cyclobutene ring opening may proceed largely via a nonconcerted pathway involving biradical intermediates.[8] Because of geometric constraints imposed by the cyclic structures of 6 and 8, ring opening of the two isomers of these compounds in each case yields common biradical intermediates or at least a set of biradicals that decay to common

distributions of products. The analogous biradicals formed from ring opening of monocyclic systems are not subject to the same constraints as those from 6 and 8. Thus, isomeric monocyclic cyclobutenes would not be expected to afford common distributions of dienes and, indeed, they do not.[5,7] The analogous biradicals from *cis*- and *trans*-1 are subject to even greater geometric constraints than those from 6 and 8, and we would expect that both compounds should yield (initially) the cis,cis isomer of 2 predominantly. The extremely low estimated yield of *cis,trans*-2 from photolysis of *trans*-1 is consistent with this expectation.

If the nonconcerted ring-opening mechanism is indeed general, then it would further be predicted that the quantum yield of ring-opening products from photolysis of *trans*-1 should be at least as large as that from *cis*-1, all else being equal. Examination of the relative quantum yields listed in Table I shows that this is not the case; 2 is formed with a quantum yield ca. 5 times higher from *cis*-1 than from *trans*-1. It is possible that the higher ring-opening quantum yield from *cis*-1 might be ascribable to this isomer possessing a higher degree of strain compared to the trans isomer. We have not verified this experimentally, but note that AM1 calculations[13] predict heats of formation of 9.82 and 8.59 kcal/mol for *cis*- and *trans*-1, respectively. Presumably, this difference in (calculated) thermodynamic stability is the result of buttressing of the endo hydrogens at C_6 and C_9 in the stablest ground-state geometry of *cis*-1 (the calculated interatomic distance is 2.05 Å). If this is the case, then the result should be a weakened C_6–C_9 bond in the cis isomer compared to that in the trans isomer. We have previously noted that there appears to be a dependence of ring-opening quantum yields on C_3–C_4 bond strength in simple cyclobutene derivatives.[8] The alternative possibility—that the higher quantum yield of 2 from *cis*-1 is due to partial control of ring opening by orbital symmetry factors—cannot be ruled out, however.

Summary and Conclusions

Direct photolysis of the cis and trans isomers of the tricyclic cyclobutene derivative 1 results in competing ring opening to 1,1'-bicyclohexenyl (2) and stereospecific fragmentation in both cases. The tentative detection of *cis*-1 from photolysis of the trans isomer and an estimate of its relative yield indicate that the highly strained cis,trans isomer of 2 may be formed directly, along with the cis,cis isomer, in the case of *trans*-1 at least. The results are consistent with the photochemical behavior of a number of other, simpler alkylcyclobutene derivatives.[5-9] They verify that, in general, the main pathway for excited-state ring opening of simple cyclobutenes does not follow orbital symmetry selection rules.

Experimental Section

^{1}H NMR spectra were recorded on Varian EM390 (90-MHz) or Bruker AM500 (500-MHz) spectrometers in carbon tetrachloride (or deuteriochloroform where noted), and ^{13}C NMR spectra were recorded at 125.6 MHz on the Bruker AM500; all are reported in parts per million downfield from tetramethylsilane. Mass spectra were recorded on GC/MS systems consisting of either (a) a VG7070 mass spectrometer interfaced with a Varian 3700 gas chromatograph equipped with a 30 m × 0.25 mm DB-1 (Chromatographic Specialties, Inc.) fused-silica capillary column or (b) a Hewlett-Packard Model 5971A mass-selective detector interfaced with a Hewlett-Packard HP5890 gas chromatograph equipped with a 12 m × 0.2 mm HP-1 fused-silica capillary column. Ultraviolet absorption spectra were recorded in pentane solution with a Perkin-Elmer Lambda 9 spectrometer equipped with a Model 3600 data station. The spectrometer sample compartment was continuously flushed with nitrogen, and sample and reference solutions were deoxygenated with argon prior to recording the spectrum. Infrared spectra were recorded on a Perkin-Elmer 283 spectrometer in carbon tetrachloride solution or as the neat liquids and were calibrated with use of the 1601.9-cm^{-1} polystyrene absorption.

Analytical vpc separations were carried out with a Hewlett-Packard 5890 gas chromatograph equipped with a flame ionization detector, a Hewlett-Packard HP-3396 recording integrator, and (a) a 1.0-μm SPB-1

(13) AM1 calculations were carried out with Version 2.1 of the general purpose molecular orbital computational package AMPAC: Austin Method 1 Package, 1.0 QCPE 506. Dewar Research Group and Stewart, J. P. *QCPE Bull.* **1986**, *6*, 24a,b.

wide-bore capillary column (30 m × 0.75 mm (i.d.) borosilicate; Supelco, Inc.; injector temperature 120 °C) or (b) a 0.2-μm DB-1701 capillary column (12 m × 0.2 mm (i.d.) fused silica; Chromatographic Specialities, Inc.; cold on-column injection). The detector was not calibrated for possible (presumably minor) differences in response toward starting materials and photoproducts.

Semipreparative vpc separations employed a Hewlett-Packard 5750B gas chromatograph equipped with a thermal conductivity detector (detector temperature 120 °C; injector temperature 120 °C) and a 15% Carbowax 20M on 60/80 Chromosorb W (5 ft × ¹/₄ in.) stainless steel column.

n-Pentane and 2,2,4-trimethylpentane (isooctane) were Baker Photrex grade and were used as received from the supplier. Methanol (HPLC) was used as received from Caledon Laboratories. *n*-Dodecane was Aldrich Gold Label.

1,1'-Bicyclohexenyl (**2**) was prepared by the reported method[14] and was identical with an authentic sample obtained from K&K Laboratories. *cis*-Tricyclo[6.4.0.0^{2,7}]dodec-1-ene (*cis*-**1**) was prepared by acetophenone-sensitized photolysis of **2** as reported.[15] *trans*-Tricyclo[6.4.0.0^{2,7}]dodec-1-ene (*trans*-**1**) was prepared by the procedure of Moore and Moser.[12] The latter compounds exhibited the following spectral features, which agree satisfactorily with the less complete data reported previously for these compounds.[12,15]

cis-Tricyclo[6.4.0.0^{2,7}]dodec-1-ene (cis-1), ¹H NMR (CCl₄): δ 1.17 (m, 6 H), 1.70 (br t, 4 H), 1.75 (br s, 4 H), 2.20 (dd, 2 H), 2.38 (br s, 2 H). ¹³C NMR (CCl₄): δ 25.36, 27.61, 28.16, 42.78, 138.01. IR (neat): 2924 (s), 2854 (s), 1700 (w), 1455 (m), 1442 (s), 1301 (m), 1222 (w), 1166 (m), 1038 (w), 969 (w), 921 (w), 888 (w), 818 (w), 600 (w). MS: *m/e* (*I*) 162 (28), 147 (10), 133 (25), 119 (42), 105 (45), 91 (100), 79 (88), 65 (44), 53 (44), 41 (90). UV (pentane): λ_{max} 206 nm (ϵ 9000).

trans-Tricyclo[6.4.0.0^{2,7}]dodec-1-ene (trans-1). ¹H NMR (CCl₄): δ 1.06 (m, 2 H), 1.21 (m, 4 H), 1.71 (br s, 2 H), 1.79 (br s, 4 H), 1.83 (m, 2 H), 1.93 (m, 2 H), 2.20 (d, 2 H). ¹³C NMR (CCl₄): δ 25.81, 25.98, 27.49, 32.32, 46.90, 136.94. IR (neat): 2930 (s), 2854 (s), 1442 (s), 1432 (m), 1333 (w), 1300 (m), 1229 (w), 1169 (m), 1150 (w), 1110 (w), 1026 (w), 975 (m), 812 (m), 613 (w); MS: *m/e* (*I*) 162 (100), 147 (15), 133 (36), 119 (38), 105 (41), 94 (67), 91 (92), 79 (85), 67 (27). UV (pentane): λ_{max} 214 nm (ϵ 8900).

Under our analytical conditions, the latter compound undergoes thermal rearrangement to **2** in the vpc injector at injector temperatures higher than 150 °C. All analyses were thus carried out with an injector temperature of 120 °C or less and an oven temperature programmed from 100 to 150 °C. This was shown to lead to accurate analyses of mixtures of *trans*-**1** and **2** by comparing results obtained under conventional vpc injection conditions (column a) with those obtained with column b, cold on-column injection techniques, and lower oven temperatures.

The isomeric cyclododecenynes *cis*- and *trans*-**3** were isolated from large-scale photolyses of *cis*- and *trans*-**1**, respectively, as reported by Saltiel and Ng Lim.[3] They exhibited spectral features similar to those published.[3]

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cis-Cyclododec-7-enyne (cis-3). ¹H NMR (CCl₄): δ 1.73 (m, 4 H), 1.79 (m, 4 H), 2.40 (m, 8 H), 5.56 (t, 2 H). ¹³C NMR (CCl₄): δ 17.96, 24.81, 25.28, 29.18, 80.62, 130.19. IR (CCl₄): 3080 (m), 2934 (s), 2860 (s), 1447 (m), 1434 (m), 1332 (m), 1050 (w), 963 (w), 910 (w), 706 (m), 655 (m). MS: *m/e* (*I*) 162 (5), 147 (10), 133 (21), 119 (31), 105 (38), 91 (100), 79 (90), 67 (35), 53 (32), 39 (60).

trans-Cyclododec-7-enyne (trans-3). ¹H NMR (CCl₄): δ 1.56 (m, 4 H), 1.61 (m, 4 H), 1.95 (m, 4 H), 2.03 (m, 4 H), 5.64 (m, 2 H). ¹³C NMR (CCl₄): δ 18.99, 26.33, 28.11, 29.96, 81.03, 130.30. IR (neat): 2934 (s), 2860 (s), 1452 (s), 1443 (m), 1325 (m), 1035 (w), 963 (s), 740 (w). MS: *m/e* (*I*) 162 (5), 147 (12), 133 (22), 119 (32), 105 (44), 91 (100), 79 (95), 67 (41), 53 (30), 41 (71), 39 (65).

Quantitative photolyses employed a 16-W Philips 93106E zinc resonance lamp (214 nm), the pulses (193 nm, ca. 10 ns, 20–30 mJ, 1-Hz repetition rate) from a Lumonics TE-861M excimer laser filled with an argon/fluorine/helium mixture, or a 450-W Hanovia medium-pressure mercury lamp. Photolyses with the zinc resonance lamp were carried out with a cylindrical metal casing, which surrounds the lamp and incorporates a 1-in. port to contain the sample cell. The lamp was given a 20-min warm-up period before each experiment and cooled with a stream of dry nitrogen. Laser and Zn-lamp photolyses were carried out in 10 × 25 mm cylindrical Suprasil UV cells (Hellma).

Quantitative photolyses were all carried out at ambient temperature (ca. 23 °C). Solutions of *cis*- and *trans*-**1** in pentane or methanol (0.02–0.06 M), with 0.0005 M *n*-dodecane as internal standard, were deoxygenated with a stream of dry nitrogen in an ice bath for ca. 10 min prior to photolysis. The photolyses were monitored between 0.5 and 5–10% conversion by withdrawing aliquots at suitable time intervals for vpc analysis. Major products were identified by GC/MS (system b) and by coinjection of photolysates taken to ca. 10% conversion with authentic samples. Relative product yields were determined from the slopes of concentration versus time plots constructed for all components of the mixture relative to the internal standard. The concentration vs time plots were linear up to at least 3% conversion in each case. Figure 1 shows examples of such plots for the photolyses of *cis*- and *trans*-**1** in pentane with the 214-nm light source, carried out simultaneously with solutions of identical concentrations of substrate (optical densities >5) and internal standard. Table I lists the slopes of product concentration vs time plots constructed for these runs.

Photolysis of a deoxygenated methanol solution containing **2** (0.02 M) and acetophenone (0.01 M) in a Rayonet reactor fitted with 12 300-nm lamps resulted in the formation of three main products after ca. 20% conversion. These were identified as *cis*-**1** (25%), **9** (47%), and **10** (18%) on the basis of GC/MS analysis. The mass spectra of **9** and **10** were similar to those reported for these compounds.[11b]