intensity), 78 (M^+, 100.0)], **2b** [0.3905 g, 0.0036 mol, 66.7 mol %; MS, m/e (relative intensity), 112 (M + 2, 6.8), 111 (M + 1, 11.5), 110 (M^+, 100.0)], and **2c** [0.0561 g, 0.0003 mol, 5.6 mol %; MS, m/e (relative intensity), 220 (M + 2, 4.7), 219 (M + 1, 12.0), 218 (M^+, 57.2), 109 (100.0)].

Reduction of di-1-naphthyl sulfide (**3**; 1.1010 g, 0.0038 mol) yielded a THF solution of reduction products, which was analyzed by GC/MS with tetradecane (0.3080 g, 0.0016 mol) and was found to contain **3a** [0.0512 g, 0.0004 mol, 10.4 mol %; MS, m/e (relative intensity), 128 (M^+, 100.0)], one regioisomeric **3b** [0.1280 g, 0.0005 mol, 13.0 mol %; MS, m/e (relative intensity), 256 (M^+, 69.1), 128 (100.0)], one regioisomeric **3c** [0.01000 g, 0.000039 mol, 1.0 mol %; MS, m/e (relative intensity), 254 (M^+, 100.0)], one isomer of **3d** [0.1450 g, 0.0005 mol, 13.0 mol %; MS, m/e (relative intensity), 292 (M + 2, 2.9), 291 (M + 1, 8.4) 290 (M^+, 35.5), 129 (83.9), 128 (100.0)], one isomer of **3e** [0.0576 g, 0.0002 mol, 5.1 mol %; MS, m/e (relative intensity) 290 (M + 2, 7.4), 289 (M + 1, 12.8), 288 (M^+, 100)], and unreacted **3** [0.6320 g, 0.0022 mol, 57.4 mol %; MS, m/e (relative intensity), 288 (M + 2, 8.6), 287 (M + 1, 26.2), 286 (M^+, 100.0), 115 (80.0)].

Reduction of 1-naphthalenethiol (**4**; 0.5904 g, 0.0037 mol) yielded a THF solution of reduction products, which was analyzed by GS/MS with tetradecane (0.3180 g, 0.0015 mol) and was found to contain **4a** [0.0061 g, 0.000047 mol, 1.3 mol %; MS, m/e (relative intensity), 130 (M^+, 100.0), 129 (96.1)], one isomer of **4b** [0.2989 g, 0.0018 mol, 50.0 mol %; MS, m/e (relative intensity), 164 (M + 2, 4.0), 163 (M + 1, 8.3), 162 (M^+, 49.2), 129 (100.0), 128 (90.3)], one isomer of **4c** [0.0829 g, 00003 mol, 8.3 mol %; MS, m/e (relative intensity), 322 (M^+, 5.6), 290 (25.6), 162 (50.2), 160 (53.6), 128 (100.0)], and **4d** [0.1157 g, 0.007 mol, 11.1 mol %; MS, m/e (relative intensity), 318 (M^+, 10.6), 160 (100.0), 128 (78.8)].

Reduction of di-4-quinolinyl sulfide (**5**; 0.5004 g, 0.0017 mol) yielded a THF solution of the reduction products, which was analyzed by GC/MS with tetradecane (0.3000 g, 0.0015 mol) and was found to contain unreacted **5** [0.0864, 0.0003 mol, 18 mol%; MS, m/e (relative intensity), 290 (M + 2, 7.2), 289 (M + 1, 23.8), 288 (M^+, 100.2)] and only one regioisomer **5a** [0.3456 g, 0.0014 mol, 79 mol %; MS, m/e (relative intensity), 258 (M + 2, 2.0), 257 (M + 1, 16.7), 256 (M^+, 100), 255 (97.8)].

Acknowledgment. Enthusiasm and support for this research by Drs. R. E. Overfield and A. Kaldor are appreciated, and special thanks go to Dr. L. Ebert for informative discussions and to Hudson Luce for help with calculations.

The 193-nm Photochemistry of Some Fused-Ring Cyclobutenes: Absence of Orbital Symmetry Control

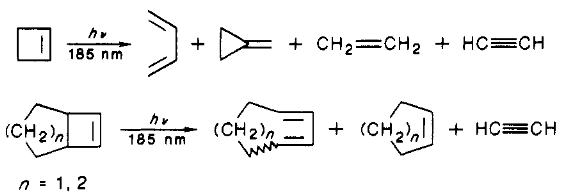
William G. Dauben* and Jeanne E. Haubrich

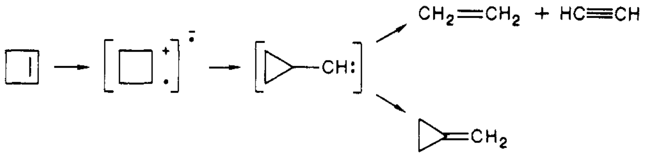
Department of Chemistry, University of California, Berkeley, California 94720

Received August 3, 1987

The photochemistry of *cis*-bicyclo[6.2.0]dec-9-ene (**1**), *cis*-bicyclo[6.2.0]deca-2,9-diene (**4**), and *trans*-bicyclo[6.2.0]deca-2,9-diene (**8**) has been examined at 193 nm in pentane solution. The photochemistry of **1** was complicated by the apparent formation of the thermally labile diene **15**, which prevented direct determination of the primary photoproducts of **1**. Dienes **4** and **8** were found to eliminate acetylene stereoselectively to give mainly the syn-elimination products **17** and **18**, respectively. Ring opening of **4** and **8** gave, as primary products, trienes **5**, **6**, and **16**, indicating that the stereospecificity suggested by the Woodward–Hoffmann rules of orbital symmetry was not followed.

The irradiation of cyclobutenes at 185 nm recently has been studied. The photoreaction of an *n*-heptane solution of cyclobutene at 185 nm yields 1,3-butadiene, methylenecyclopropane, ethylene, and acetylene.[1] Irradiation of fused-ring cyclobutenes gives rise to conjugated cyclic 1,3-dienes, cycloalkenes, and acetylene, but no methylenecyclopropane products were detected.[2] The ring opening to butadiene is thought to be a π,π^* electrocyclic process,[1,2] and fragmentation products and the methylenecyclopropane have been suggested to come from carbenes formed via the Rydberg excited states of the cyclobutenes.[1-3]





The stereochemistry of the ring opening of cyclobutene and of the cleavage of cyclobutene to ethylene and acetylene cannot be determined for cyclobutene itself, and it was not determined for the ring-fused cyclobutenes.[4] However, the stereochemistry of cyclobutene photoreaction has been observed for the tetrasubstituted cyclobutenes *cis*- and *trans*-tricyclo[6.4.0.0^{2,7}]dodec-1-ene upon irradiation at $\lambda > 200$ nm in pentane.[5] The fragmentation reaction of these cyclobutenes occurred stereospecifically to give *Z* olefin from the cis-fused cyclobutene and *E* olefin from the trans-fused cyclobutene. This result was explained in terms of a retro [2 + 2] cycloaddition reaction, which would be expected to give the observed stereospecificity.[5] The specificity can also be explained by a

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[1] (a) Adam, W.; Oppenländer, T.; Zang, G. *J. Am. Chem. Soc.* **1985**, *107*, 3921. (b) For a review of 185-nm photochemistry, see: Adam, W.; Oppenländer, T. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 661. Steinmetz, M. G. *Org. Photochem.* **1987**, *8*, 67.

[2] Inoue, Y.; Sakae, M.; Hakushi, T. *Chem. Lett.* **1983**, 1495.

[3] Kropp, P. J.; Fields, T. R. *J. Am. Chem. Soc.* **1974**, *96*, 7559.

[4] While this work was in progress, it has been found that bicyclo[4.2.0]oct-7-ene and *cis*- and *trans*-3,4-dimethylcyclobutene ring open upon irradiation at 185 and 193 nm in pentane to give all possible diene products: Leigh, W. J., private communication.

[5] Saltiel, J.; Lim, N. *J. Am. Chem. Soc.* **1969**, *91*, 5404.

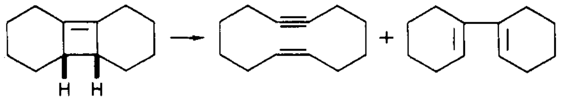
0022-3263/88/1953-0600$01.50/0 © 1988 American Chemical Society

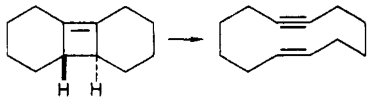
Table I. Amounts of Photoproducts in the Irradiation of 1–3 at 193 nm[a]

		% yield of photoproduct[b]									
reactant	% conversion	1	2	3	9	10	11	12	13	14	other[c]
1	5		30	12	38	14	2.4	0.1	1.6	0.9	1.0
1	28		27	10	36	17	1.7	1.7	2.0	1.4	3.2
1	40		29	11	31	18	1.5	1.6	1.8	1.7	4.4
2	2	4.6		58	0	0	37	0	0	0	0
2	15	4.9		60	2	0	18	0	0	0	15
3	5	0	100		0	0	0	0	0	0	0
3	58	1.1	91		0	0	4.3	0	0	0	3.6

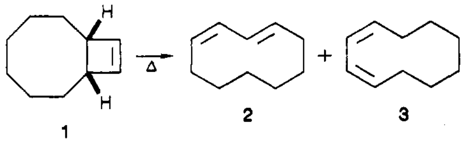
[a] Solutions of alkenes in pentane (7.4 mM) were irradiated at room temperatures. [b] Yields are reported as percentages of total photoproducts at the given percent conversion, as determined by capillary GC. [c] Total yield of all unidentified minor products, excluding 12–14.

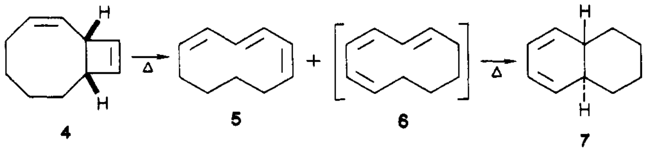
singlet carbene fragmentation reaction of the cyclobutene.[2] The stereochemistry of the electrocyclic ring opening of these tricyclic cyclobutenes appears to follow the Woodward–Hoffmann rules of orbital symmetry,[6] in that the disrotatory product, the *Z,Z* diene, is obtained from the cis-fused cyclobutene, and no diene is obtained from the trans-fused cyclobutene due to the fact that the allowed product would have to form a highly strained (*E*)-cyclohexene olefin.[5]





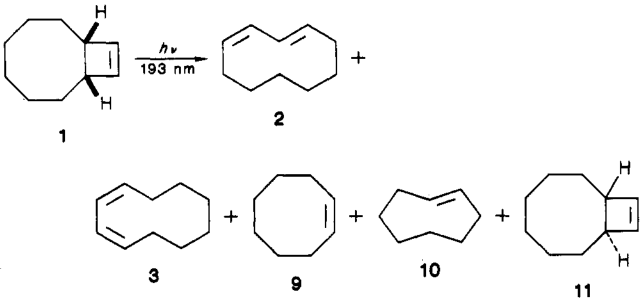
The stereochemistry of the primary product of the photochemical ring opening of cyclobutenes is of interest for two reasons. First, comparison of photochemical and thermal ring openings permits an evaluation of mechanistic details of the two processes; i.e., is each photoproduct a primary product, or is it a product formed in the vibrationally excited ground state? Second, does photochemical ring opening follow the Woodward–Hoffmann rules of orbital symmetry[6] as does the thermal process? For example, *cis*-bicyclo[6.2.0]dec-9-ene (1) reacts thermally at 170 °C to yield, nearly specifically, (*E,Z*)-cyclodeca-1,3-diene (2) and the *Z,Z* isomer 3 in a ratio of 38:1.[6b,7,8] Similarly, *cis*-bicyclo[6.2.0]deca-2,9-diene (4) undergoes thermally induced ring opening at 140–150 °C in both the clockwise and counterclockwise conrotatory manners in a ratio of 3:2 to yield the thermally stable (*Z,E,Z*)-cyclodeca-1,3,5-triene (5) and the thermally unstable *E,Z,Z* isomer 6, isolated as *trans*-1,3-hexalin (7).[7a,9]





The photochemically initiated ring openings of *cis*-bicyclo[6.2.0]dec-9-ene (1) and of *cis*- and *trans*-bicyclo[6.2.0]deca-2,9-diene (4 and 8, respectively) have now been studied in order to compare the results of photochemical and thermal ring opening of these compounds. The stereochemistry of the photochemical ring openings was examined in order to see if these reactions follow the rules of orbital symmetry, and the stereochemistry of the products formed by loss of acetylene in the photochemical reaction was established in order to see if the results were consistent with the proposed carbene and/or the retro [2 + 2] cycloaddition mechanism.

The irradiation of the cyclobutene 4[10] in pentane using a low-pressure mercury resonance lamp (185 + 254 nm, without an Acton 185-nm bandpass filter) resulted in extensive polyermization due to the relatively rapid reaction of the photoproducts upon irradition by the 254-nm light. Therefore, all irradiations were performed at 193 nm by using a Lambda-Physik EMG101 excimer laser with a fluorine/argon/helium gas mixture. Under these conditions, most of the photoproducts did not undergo extensive polymerization or secondary reaction at low conversion of starting material to products. The primary products slowly formed secondary products.



The preparative photoinduced reaction of 1[10] in pentane solution using 193-nm light and analysis of the reaction mixture by gas chromatography indicated the formation of five compounds, 2, 3, and 9–11, in isolable amounts and three other compounds, 12–14, in amounts too small to allow isolation and identification. These materials represent either primary and secondary photoproducts or thermal products formed upon capillary gas chromatographic analysis of the photoproducts. The amounts of these products at different percent conversions are listed in Table I.

Products 2,[7a] 3,[7a] 9, and 10[11] were identified by comparison of ^{1}H NMR spectra and by capillary GC coinjec-

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[6] (a) Woodward, R. B.; Hoffmann, R. *The Conservation of Orbital Symmetry*; Verlag Chemie: Weinheim, Germany, 1970. (b) Marvell, E. N. *Electrocyclic Reactions*; Academic: New York, 1980.

[7] (a) Radlick, P.; Fenical, W. *Tetrahedron Lett.* **1967**, 4901. (b) Bloomfield, J. J.; McConaghy, J. S., Jr.; Hartmann, A. G. *Tetrahedron Lett.* **1969**, 3723.

[8] The ratio of 38:1 was taken from our results when making 2 thermally from 1 at 170 °C. The minor isomer 3 may have been a secondary product arising from a 1,5 hydrogen shift on 2 (see ref 6b).

[9] Dauben, W. G.; Michno, D. M. *J. Am. Chem. Soc.* **1981**, *103*, 2284.

[10] The dienes 1 and 4 were prepared by a modification of a published procedure[7a,9] using [(triisopropylphenyl)sulfonyl]hydrazine in place of (tolylsulfonyl)hydrazine. The lower temperature used for the decomposition of the [(triisopropylphenyl)sulfonyl]hydrazone reduced the amount of thermally rearranged products, making isolation of pure 1 and pure 4 easier; see Experimental Section.

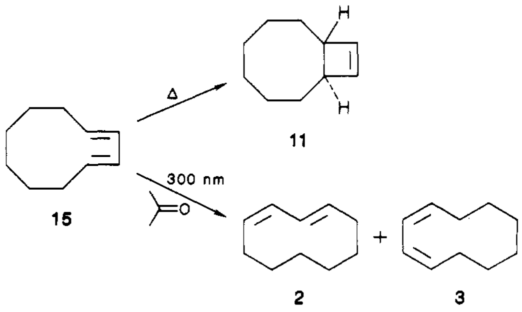
[11] Inoue, Y.; Takamuku, S.; Sakurai, H. *Synthesis* **1977**, 111.

tion with authentic samples. Product **11**[12] was present in amounts too small to allow isolation and was identified by capillary GC coinjection with an authentic sample on two different columns. Three of the products detectable by GC, **12**–**14**, were also formed in amounts too small to allow isolation and were not identified.

The amount of product **11**, but not of any other product, varied slightly with the GC injector and column temperatures. Higher temperature gave larger amounts of **11**, indicating that **11** may be formed thermally after the irradiation. Prepared samples of **1**–**3**, **9**, and **10** were stable to the capillary GC conditions, so these were not the source of **11**.

It seemed that the precursor of **11** was too unstable to be detected by GC. In an effort to isolate the thermally unstable product, photoproducts of **1** in pentane were extracted with 20% aqueous silver nitrate solution. The aqueous solution was added to concentrated ammonium hydroxide solution and extracted with pentane. The materials extracted by silver nitrate included (*E*)-cyclooctene (**10**), product **11**, and some residual **1** in a ratio of 32:42:25, respectively, as determined by capillary GC. When the mixture was irradiated for 5 min in pentane at 300 nm with acetone as a sensitizer, decadienes **2** (14%) and **3** (12%) were produced. Irradiation of alkene **1** or **11** alone under similar conditions gave less than 1% of dienes **2** and **3** after 40 min.

Thus, there is a product that is extracted by silver nitrate, that decomposes thermally to give **11**, and that forms dienes **2** and **3** upon acetone-sensitized irradiation. The initial formation of (*E,E*)-cyclodeca-1,3-diene (**15**) would explain these results since it can be expected to thermally cyclize to **11** and to convert to **2** and **3** upon sensitized irradiation.



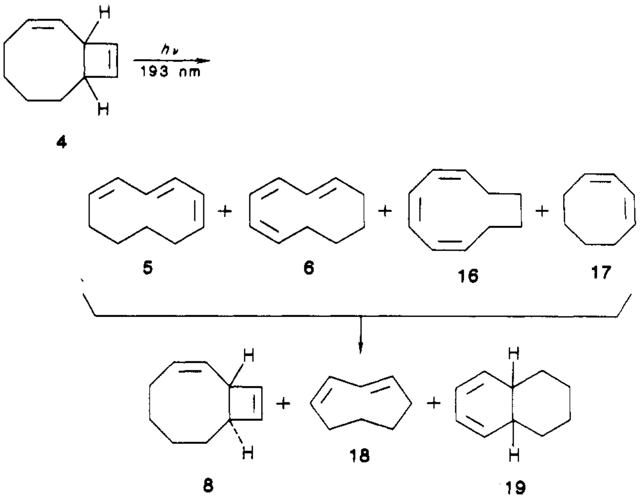
Impure diene **15** could also be isolated from products made by irradiating **2** at 193 nm. A sample of **15** that also contained **2** and **11** was observed to have a λ_{max} of 241 nm. Since λ_{max} of **2** is 221 nm and λ_{max} of **11** is probably below 200 nm, the observed absorption at 241 nm attributed to **15**. This is further evidence that this photoproduct is really (*E,E*)-cyclodeca-1,3-diene, since there are no other products one would expect to get from photoisomerization of **1** or **2** that would absorb at such a long wavelength. Attempts to isolate **15** in pure form were unsuccessful due to the small amount present and to the instabiility of the material to silica gel or GC conditions.

Pentane solutions of pure dienes **2** and **3** were each irradiated at 193 nm in order to judge if ring closure to cyclobutene is rapid. As shown in Table I, *Z,Z* diene **3** produced only **2** at low percent conversion. The *E,Z* diene **2** rapidly produced **3**, **11**, and **1**, but **1** represented only about 5% of the products of **2** at up to 15% conversion. Therefore, ring closure back to **1** is not an important side reaction at low conversions of **1**.

Neither **2** nor **3** produced **12**, **13**, or **14** when irradiated at 193 nm. Products **12**–**14** must be primary photoproducts of **1**. Product **11**, on the other hand, appears to be a secondary product made by thermal reaction of **15**.

Both cyclooctenes **9** and **10** are present as products at low percent conversion of **1**, which would indicate that both are primary products. However, since *E,Z* isomerization of cyclooctene upon direct irradiation is a relatively efficient process,[13] it is possible that a small amount of *E* isomer is produced from the *Z* isomer. Thus, the photochemistry of **1** at 193 nm is complicated both by the facile *E,Z* isomerization of cyclooctene and by the apparent presence of the thermally unstable compound **15**. As shown in Table I, all of the products **2**, **3**, and **9**–**14** are present at low conversions, and therefore, it is not clear what are the primary photoproducts of **1**. This fact is particularly evident in the case of the formation of *E,Z* diene **2**, a photochemically orbital symmetry nonallowed product.

The dienes **4** and **8** exhibit photochemistry similar to that of **1**, but in these cases, the primary products were more easily distinguished from secondary products. The preparative photo-induced reaction of a 98%-pure sample of **4** in pentane solution using 193-nm light and analysis of the reaction by capillary gas chromatography indicated the formation of seven compounds, **5**,[7a] **6**,[14] **8**,[14b] **16**,[15] **17**,[16] **18**,[17] and **19**.[14b] These seven compounds were identified by capillary GC coinjection and comparison of ^{1}H NMR spectra with those of authentic samples. In the analysis, small amounts of several minor products were detected but could not be isolated in sufficient amount to permit identification.



As shown in Table II, at low conversions of **4** to products under analytical irradiation conditions (see Experimental Section), only compounds **5**, **6**, and **16**–**18** were formed. However, **18** is at least partially a secondary product of **17**, since the ratio of **18** to **17** changes from 0.03 to 0.28 by the time **4** is 57% converted to products. Although it is not possible to tell if **18** is exclusively a secondary product from these data, it can be said that the elimination of acetylene

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(12) Radlick, P.; Klem, R.; Spurlock, S.; Sims, J. J.; van Tamelen, E. E.; Whitesides, T. *Tetrahedron Lett.* **1968**, 5117.

(13) Srinivasan, R.; Schuchmann, H. -P.; von Sonntag, C. *J. Photochem.* **1981**, *15*, 159.

(14) (a) Gottlieb, A. J. Ph.D. Thesis, University of California, Berkeley, 1983. (b) Dauben, W. G.; Kellogg, M. S. *J. Am. Chem. Soc.* **1980**, *102*, 4456.

(15) A ^{1}H NMR spectrum was available from previous studies in this group. Dauben, W. G.; Michno, D. M. *Tetrahedron* **1981**, *37*, 3263.

(16) Commercially available from Aldrich.

(17) Liu, R. S. H. *J. Am. Chem. Soc.* **1967**, *89*, 112.

Table II. Yields of Products in the Irradiation of 4, 5, and 8 at 193 nm[a]

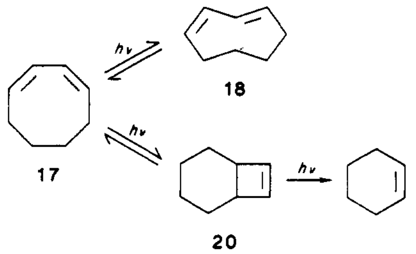
		% yield of product							
reactant	% conversion	5	6	8	16	17	18	19	other
4	1	35	25	0	19	21	0.7	[b]	0
4	3	31	23	0	21	17	0.9	[b]	7.2
4	5	24	19	0	16	13	1.1	16	11
4	10	24	18	0	16	13	1.0	15	13
4	57	18	16	10	13	10	2.9	19	11
5	5		0	0	100	0	0	0	0
5	29		13	3.7	53	0	0	9.0	21
5	62		15	5.2	35	0.7	0.5	17	27
5	82		17	6.1	19	2.1	0.9	30	25
8	2	42	16		24	3.1	9.8	2.5	2.5
8	6	45	13		26	2.3	5.0	7.0	1.7
8	62	36	12		24	3.4	4.5	11	10

[a] Reactions were done in pentane (4.7 mM) at room temperature. Yields are reported as percentages of total products at the given percent conversion, as determined by capillary GC. [b] This material eluted between the reactant and impurity in the reactant and could not be detected in small amounts.

is highly stereoselective, since the initial ratio of **18** to **17** is 3:97. The yields shown at 57% conversion under the same analytical irradiation conditions are very similar to those obtained in the preparative irradiations.

As seen in Table II, compound **8** is clearly a secondary product of **4**. Compound **19**, on the other hand, eluted so close to the starting material that small amounts could not be detected, and it could not be determined whether **19** is a primary product of **4**. Later studies of compound **8** indicated that **19** could be a secondary photoproduct.

In order to determine the precursors of the secondary photoproducts of **4**, some of the primary products were irradiated at 193 nm. Irradiation of **17** gave mostly *E*,*Z* isomerization to **18**. At a relatively slow rate there was an inefficient formation of the cyclobutene **20**, which, upon extended irradiation, produced cyclohexene. No **20** was found in the mixture of the photoproducts of **4**, indicating that the octadiene products **17** and **18** were not being lost via this cyclization and that the total amount of **17** and **18** reflects the true amount of octadiene produced from **4**.



A sample of triene **5**[9] that was greater than 99% pure was irradiated in pentane with 193-nm light (see Table II). The initial reaction product was the *Z*,*Z*,*Z* triene **16**, and then gradually all the photoproducts observed in the irradiation of diene **4** were produced. The extremely minor unidentified products formed from **4** were present in greater amounts when **5** was irradiated, confirming that these are photoproducts of the triene (secondary products from diene **4**). Even at high percent conversions of **5**, a state of photoequilibrium between trienes **5**, **6**, and **16** was not observed because the efficiency of cyclized photoproduct formation was different for the three trienes; the ratios of these trienes changed continuously.

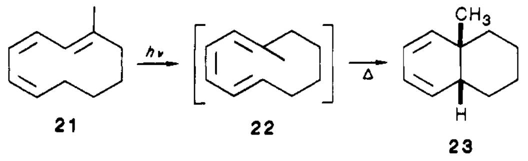
Hence, in the irradiation of **4**, the consistency of the ratios of trienes **5**, **6**, and **16** at less than 10% conversion, as shown in Table III, suggests that none of these trienes could be produced solely as a secondary product via *E*,*Z* isomerization from a different triene; all are primary products. In addition, it is unlikely that these trienes interconvert so rapidly, compared to the reaction of **4**, that a triene photoequilibrium was established before the first photoproduct observation was made. If this were the case, the ratios of the trienes should be the same whether they are produced from the cis starting material **4** or its trans isomer **8**. This was not observed, as can be seen in Table III.

Table III. Ratios of Trienes 5, 6, and 16 in the Irradiations of 4 and 8

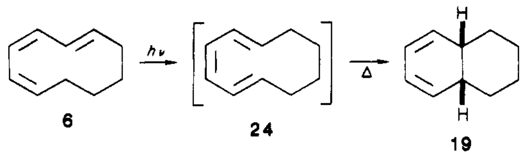
		relative amounts of trienes		
reactant	% conversion	5	6	16
4	1.2	44	32	24
4	3.3	41	33	25
4	5.1	41	32	27
4	10.0	41	31	27
8	1.8	51	19	29
8	3.4	52	16	32
8	5.8	53	15	31
8	14.0	53	17	29

Diene **8** was obtained from the photoreaction of **19** at 254 nm.[14b] A sample of diene **8** that was greater than 99% pure was obtained by preparative gas chromatography followed by liquid chromatography over silver nitrate impregnated alumina. Diene **8** was irradiated in pentane with 193-nm light. The initial products were **5**, **6**, and **16**–**18** (Table II). A plot of product formation versus percent conversion is given in Figure 1 and shows that **19** is a secondary photoproduct of **8**. Product **17** was also formed from isomerization of **18**, as indicated by the increasing ratio of **17** to **18** as the reaction progressed. The initial ratio of **17** to **18** of 1:3, however, is large enought that it appears that diene **17** is also a primary product.

Summarizing the results of the study of primary and secondary photoproduct formation from dienes **4** and **8**, i.e., **5**, **6**, **16**, **17** and **5**, **6**, **16**, **17**, **18**, respectively, it was found that they arise either from acetylene extrusion from the cyclobutene portion of the molecule, or from ring opening of the vinylcyclobutene portion of the molecule to form a triene. Compound **19** was found to be a secondary photoproduct of **8** and is therefore likely to be a secondary photoproduct of **4** also. Diene **19** may be formed by photochemical ring closure of **6** and/or **16**. On the other hand, it is known that (*E*,*Z*,*Z*)-1-methylcyclodeca-1,3,5-triene (**21**) upon irradiation at −80 °C with light of 254- or 300-nm wavelength gives rise to the *E*,*Z*,*E* isomer **22**, which in turn, when warmed to 20 °C; is transformed into *cis*-10-methyl-1,3-hexalin (**23**).[14a] The unsubstituted (*E*,*Z*,*E*)-cyclodeca-1,3,5-triene (**24**) is known to have a half-life of about 0.5 s at 20 °C and to ring close, thermally,



21 22 23



6 24 19

to **19**,[18] thus suggesting an alternate two-step route for the formation of **19** from **6**. The diene **8** is known to be formed when triene **6** is irradiated.[14,19] Thus, the formation of these secondary photoproducts follows known pathways.

The elimination of acetylene gave almost exclusively (*Z*,*Z*)-cyclooctadiene (**17**) as a primary product from cis-fused **4** and gave (*E*,*Z*)-cyclooctadiene (**18**) as the major primary product from the trans-fused **8**.

Discussion

The photochemical ring opening of the cyclobutene ring in both **4** and **8** gives rise to three trienes **5**, **6**, and **16** as primary products. However, the photochemical orbital symmetry allowed disrotatory concerted cyclobutene opening of **4** should yield only the *Z*,*Z*,*Z* triene **16** and the highly strained (and not found) (*E*,*E*,*Z*)-cyclodeca-1,3,5-triene (**25**), while **8** should give only the *Z*,*E*,*Z* triene **5** and the *E*,*Z*,*Z* triene **6**.

First considering the formation of **5** and **6** from **4**, a possible explanation could be that they are thermal rearrangement products which form from a highly unstable primary photoproduct, such as the allowed *E*,*E*,*Z* triene **25**, which was not detected (and is unknown). If the thermal rearrangments were on a time scale faster than our analytical measurements, the products would appear as primary products. Attempts were made to prepare and detect **25** at low temperature but to no avail. It is to be appreciated that other strains cyclic *E* olefins, such as phenylcyclohexene[20] and cycloheptene,[21] are known to rapidly isomerize to *Z* olefins at room temperature.

This postulate of a thermal rrearrangement of an unstable product does not appear reasonable when the results with cyclobutene **8** are considered. The photochemical orbital symmetry allowed process with **8** would predict only trienes **5** and **6**, not **16**. Authentic samples of trienes **5**[7a] and **6**[14] were both found to be stable to the gas chromatographic analysis used, and therefore, these trienes cannot be thermal precursors of **16**. Thus, direct formation of **16** and **8** does not follow the photochemical orbital symmetry rules. Such direct evidence is not available in the reaction of **4**.

A second possibility is that the ring-opening reaction occurs from a vibrationally excited ground state. The question of whether alkenes may react via a vibrationally excited ground state generated by internal conversion from direct irradiation has been investigated in the gas phase for the case of tetramethylethylene (**26**).[22] Both thermal reaction at 430 °C and 185-nm irradiation of **26** gave the two products 2,3-dimethyl-1-butene (**27**) and 3,3-dimethyl-1-butene (**28**). However, irradiation also yielded

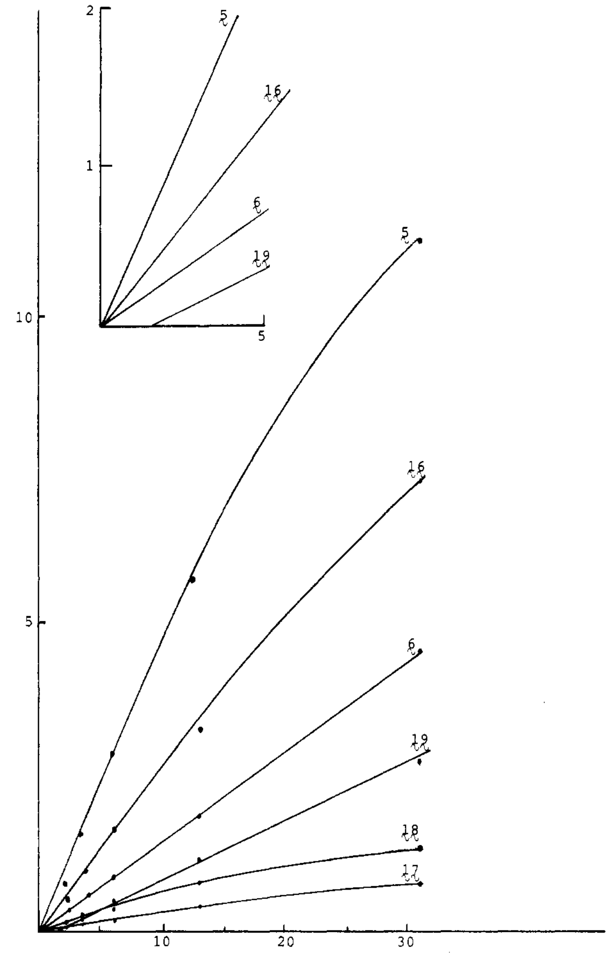
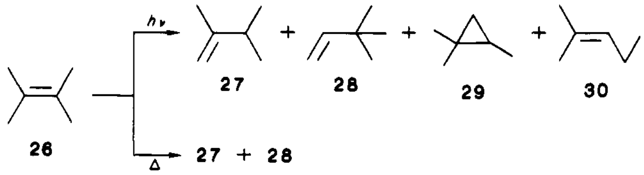


Figure 1. Percent products formed versus percent conversion of 8 from the irradiation of 8 at 193 nm. The insert shows an expanded plot at low percent conversion for some of the photoproducts.



26 27 28 29 30

27 + 28

1,1,2-trimethylcyclopropane (**29**) and 2-methyl-2-pentene (**30**). Since more products were obtained in the irradiation of **26** than in the thermal reaction, it was concluded that, in the 185-nm irradiation, reaction probably did not occur from a ground state populated with low vibrational energies, such as those generated in the thermal reaction of **26**. However, it was noted that irradiation could possibly produce a more highly vibrationally excited ground state from which **26** might yield products other than those obtained thermall.[22,23]

Similarly, the irradiation of **4** in pentane at 193 nm yielded several more products than were formed by thermal reaction of **4** at 150 °C, the latter reaction yielding only **5** and **6**. Thus, it is unlikely that vibrationally excited

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Table IV. Ratios of Ring-Opened Photoproducts to Other Photoproducts for Various Cyclobutenes[a]

compound	products compared	ratio
1	**2** + **3** + **11**[b]:**9** + **10**	0.8
4	**5** + **6** + **16**:**17** + **18**	4.5
8	**5** + **6** + **16**:**17** + **18**	6.2
cyclobutene	butadiene:ethylene + methylenecyclopropane	2.3[c]

[a] Initial ratios at less than 5% conversion are reported for **1**, **4**, and **8**. The ratios increase as the reactions progress. [b] Product **11** is thought to come from **15**, a ring-opened product. [c] Determined from quantum yields (ref 1).

ground states similar to those generated by heating at 150 °C are being produced from the photoexcited state during the irradiation of **4**. As with **26**, it is not possible to rule out reaction from a more highly vibrationally excited ground state of **4**. For that matter, further reaction could form from a highly vibrationally excited ground state of a photochemically symmetry allowed product. These same concepts are also true of cyclobutene **1**, which gives several more products from irradiation at 193 nm than from the thermal reaction.

Irradiation of **4** at -78 °C gave the same product mixture as at 25 °C, showing that thermal reaction due to heating of the reaction vessel or solution by the laser beam was also not a source of products in these experiments. In addition, to insure that two-photon excitation was not a source of the disallowed products, control experiments were done in which the intensity of light was reduced by factor of 10. No change in product ratios was observed, indicating that two-photon excitation is not a significant process in these reactions.

It has been suggested that photochemically excited cyclobutenes may ring open adiabatically to the first excited singlet state of the corresponding diene and decay via *E*,*Z* isomerization from the excited state of the diene.[24] Isomerization from the diene excited state would be expected to give all possible diene isomers, and hence this model could also explain the failure of these cyclobutene ring openings to be stereospecific.

Addition of an alkene bond allylic to the cyclobutene ring to give **4** and **8** increases the amount of ring opening relative to elimination in these compounds when compared to **1** and to cyclobutene (Table IV). Otherwise, the alkene in such a position has little effect on the photochemistry of the cyclobutene, i.e., no di-π-methane products or other new products were isolated. Previous studies have shown that otherwise unconjugated 1,4-dienes do not yield di-π-methane products upon direct irradiation.[25] No products from rearrangement of the alkene in the larger ring were formed. The extra strain in the cyclobutene olefinic bond must make it more reactive than the other olefins in **4** and **8**.

The photochemistry of cyclobutenes **1**, **4**, and **8** demonstrates that ring opening of cyclobutenes is not necessarily a disrotatory electrocyclic process, as predicted by the Woodwarrd-Hoffmann rules. It may be that, for cyclobutene, the energy of direct irradiation is high enough that energetically disfavored "forbidden" or radical pathways are possible, hence the Woodward-Hoffmann rules do not predict the products. Other mechanisms, such as reaction from vibrationally excited thermal states, production of and reaction from the excited state of the corresponding diene,[24] or even reaction from an excited state of cyclobutene other than a π,π* state, could also account for the lack of sterospecificity in these ring openings.

Turning now to the acetylene elimination reaction, the highly stereoselective syn elimination from **4** is similar to the results obtained from the earlier mentioned irradiation of *cis*-tricyclo[6.4.0.0^{2,7}]dodec-1-ene,[5] and thus, **4** probably fragments through either a retro [2 + 2] cycloaddition or a singlet carbene fragmentation.[26] The selectivity found in the fragmentation of **4** disfavors a radical reaction pathway which should give both dienes **17** and **18** as products. The syn elimination from **8** is also favored, but is less selective. The extra strain due to the *E* olefin in **18** could make its formation less favorable as compared to that of **17**, resulting in less specificity. Thus, in this latter case the mechanism or mechanisms involved in the fragmentation are less clear.

Experimental Section

General Methods. Reagents were obtained from commercial suppliers and used without purification unless otherwise noted. Tetrahydrofuran (THF) was distilled from sodium/benzophenone immediately prior to use. Methanol was distilled from magnesium methoxide. Pentane for irradiations was prepared by stirring commercial grade pentane over 96% sulfuric acid several times, then over aqueous 10% potassium hydroxide solution, and then over water. The pentane was filtered through neutral alumina (activity 1) and distilled.

Irradiations at 193 nm were done by using a Lambda-Physik EMG101 excimer laser with an argon/fluorine/helium gas mixture (10 Hz, 60 mW). Irradiations at 185 nm were done by using a 10-W Osram HNS 10-W/U OZ low-pressure mercury resonance lamp (185 + 254 nm).

^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ on a UCB 250 (250 MHz, FT) and UCB 200 (50.78 MHz, FT) spectrometer, respectively. Chemical shifts are reported in units of δ from internal tetramethylsilane. Data are tabulated in order: multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet), number of protons, coupling constant in hertz. IR spectra were recorded on a Perkin-Elmer Model 281 spectrometer.

All analytical gas chromatography data were obtained by using a Hewlett-Packard 5790A (flame-ionization detector) gas chromatograph equipped with an HP 5880 integrating recorder. Helium was used as carrier gas. A 30 m × 0.25 mm DB-1 column (J and W Scientific) was used. Preparative gas chromatography was done at 90 °C by using a Varian Aerograph Series 1400 GC instrument with a 7 ft × 0.25 in. column packed with 1% SF96-50 plus 0.1% IGPAL on Chromosorb G, 70-80 mesh. All preparative GC separations were done with an injector temperature of 130 °C, a detector temperature of 130-140 °C, and a column temperature of 90 °C.

***cis*-Bicyclo[6.2.0]dec-9-ene (1).** *cis*-Bicyclo[6.1.0]nonane-9-carboxaldehyde[7a] (3.20 g, 21.4 mmol) in freshly distilled methanol (5 mL) was added over a period of 10 min to a slurry of [(triisopropylphenyl)sulfonyl]hydrazine[27] (6.39 g, 21.4 mmol) in methanol (30 mL) at -10 °C. The mixture was stirred for 30 min at -10 °C, and the solids were collected by filtration. The material was dried by using a rotary evaporator and left overnight in a vacuum desiccator over P_2O_5 in a refrigerator at 5 °C. The product was 5.91 g (64%) of a white solid: mp 113-116 °C; IR (CCl_4) 3200 (br), 2975, 2940, 2880, 1700, 1600, 1465, 1170, 1160, 890 cm^{-1}; ^1H NMR (250 MHz) δ 1.0 (m, 5), 1.3 (m, 22), 1.6 (m, 4), 2.0 (m, 2), 2.9 (m, 1), 4.2 (m, 2), 6.13 (d, 0.33, *J* = 8.1 Hz), 6.89 (d, 0.67, *J* = 6.8 Hz), 7.18 (s, 2), 7.45 (m, 0.5).

The semipurified hydrazone (7.00 g, 16.2 mmol) was added, carefully, to oil-free NaH (445 mg, 18.5 mmol) in THF (24 mL) at 0 °C. The mixture was allowed to stand until the hydrogen evolution had ceased, and the reaction mixture was heated at 60 °C for 16 h. The mixture was cooled to room temperature and

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[24] For a detailed discussion of this mechanism, see: Clark, K. B.; Leigh, W. J. *J. Am. Chem. Soc.* **1987**, *109*, 6086.

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was quenched with water. The mixture was extracted with pentane, and pentane extracts were washed with aqueous 1% sulfuric acid solution, aqueous saturated sodium bicarbonate solution, and water. The organic solution was dried ($MgSO_4$), solvents were removed by using a rotary evaporator, and the residual material was filtered through 3 g of silica gel with pentane as eluent. The solvent was removed by using a rotary evaporator to yield 1.63 g of a colorless liquid which was 79% of **1** and 21% of cyclooctene **9** (crude yield: 58%). The material was purified by preparative GC to give 70% (by weight of the injected material) of pure **1**; hence the yield from the hydrazone was 40%. Although **1** is a known compound, no spectral data are given in the literature:[7a] IR (thin film) 3140, 3020, 2940, 2860, 1465, 1440, 1300, 1030, 850, 765, 690 cm^{-1}; ^1H NMR (250 MHz) δ 1.5 (m, 12), 2.73 (d, 2, J = 10.6 Hz), 5.96 (s, 2); ^{13}C NMR δ 26.20, 27.34, 30.53, 48.04, 139.30.

***cis*-Bicyclo[6.1.0]non-2-ene-9-carboxaldehyde [(Triisopropylphenyl)sulfonyl]hydrazone (31).** *cis*-Bicyclo[6.1.0]non-2-ene-9-carboxaldehyde[7a,9] (3.60 g, 24.0 mmol) was allowed to react with [(triisopropylphenyl)sulfonyl]hydrazine[27] (6.83 g, 22.9 mmol) as above. Workup as above yielded 5.95 g of a white solid (60%). A sample was recrystallized from ethyl acetate/pentane for analysis: mp 124–127 °C; IR ($CDCl_3$) 3100 (br), 2970, 2940, 2880, 1605, 1470, 1430, 1170, 1160, 890 cm^{-1}; ^1H NMR (250 MHz) δ 1.3 (m, 19), 1.4 (m, 7), 1.9 (m, 3), 2.9 (m, 1), 4.2 (m, 2), 5.34 (d, 1, J = 11.4 Hz), 5.7 (m, 1), 6.21 (d, 0.4, J = 8.6 Hz), 7.18 (d, 0.6, J = 5.4 Hz), 7.25 (s, 2). Anal. Calcd for $C_{25}H_{38}N_2SO_2$: C, 69.72; H, 8.89; N, 6.51. Found: C, 69.67; H, 9.07; N, 6.46.

***cis*-Bicyclo[6.2.0]deca-2,9-diene (4).** Hydrazone **31** (389 mg, 0.905 mmol) was converted to diene **4** and purified in the same manner as for diene **1** to yield 32.3 mg (27%) of **4** as a colorless liquid. Spectral data agree with the literature:[9] IR (thin film) 3140, 3050, 3020, 2930, 2860, 1650, 1570, 1455, 1445, 1300, 800, 720, 690 cm^{-1}; ^1H NMR δ 1.5 (m, 6), 2.1 (m, 2), 3.0 (m, 1), 3.68 (m, 1), 5.38 (dt, 1, J = 11.0 Hz, 1.6 Hz), 5.6 (m, 1), 6.01 (d, 1, J = 2.7 Hz), 6.08 (d, 1, J = 2.7 Hz); ^{13}C NMR δ 26.00, 27.79, 29.17, 32.29, 45.59, 52.83, 126.73, 131.88, 137.56, 140.11.

Large-Scale Irradiations. For preparative purposes, a 180–250-mL sample of alkene or diene (7.5×10^{-3} M) in pentane was put in a cylinder (1-ft long, 1.5-in. diameter) which had a Suprasil window on each end and had two 14/20 openings on one side. A stir bar was put in the cylinder, and the two openings were covered with rubber septa. The solution was deoxygenated by bubbling nitrogen through it for 30 min. The tube was then placed in the 193-nm laser beam such that the beam entered through one of the Suprasil windows at a level above the stir bar. The solution was irradiated with stirring and with a slow flow of nitrogen through the cylinder. Reaction was monitored by capillary GC.

Analytical Irradiations. A solution of alkene or diene in pentene (1 mg/mL) and a stir bar were purt in a 1-cm-diameter Suprasil tube, and the tube was sealed with a rubber septum. The solution was deoxygenated by bubbling nitrogen through it for 10 min. The tube was placed in the beam of a 193-nm laser such that the stir bar was below the area at which the beam entered the tube. The tube was irradiated, with stirring, for short intervals of time. In some cases, one or two $^1/_8$-in.-thick quartz windows were placed in the beam between the source and the tube in order to reduce the intensity of the light. Cooled runs were made by placing the sample tube in a bath of ice water or dry ice/methanol which was in a 2-cm-diameter Suprasil tube. Ice in the bath was changed frequently to insure that the bath did not warm above 0 °C. Reaction progress was monitored by capillary GC using a column temperature of 70 °C.

Identification of Photoproducts of *cis*-Bicyclo[6.2.0]dec-9-ene (1). Products were identified by comparison of ^1H NMR spectra and capillary GC coinjection with authentic samples of **2**,[7a] **3**,[7a] **9**, **10**,[11] and **11**.[12]

Extraction of *cis*-Bicyclo[6.2.0]dec-9-ene (1) Photoproducts with $AgNO_3$. Evidence of (*E*,*E*)-Cyclodeca-1,3-diene (15). A pentane solution of photoproducts from the 193-nm preparative irradiation of **1** at room temperature was extracted with 25% aqueous $AgNO_3$ solution. The phases were separated, and the aqueous phase was washed once with pentane and poured into ice cold 27% aqueous ammonium hydroxide solution. The resulting solution was extracted twice with pentane, and pentane extracts were washed with water three times and dried ($MgSO_4$). Capillary GC analysis showed the resulting pentane solution to contain residual **1** (25%), **10** (32%), and **11** (42%). Compound **15** was not detectable by this analysis, as explained in the results section.

In order to isomerize **15** into the detectable **2** and **3**, a 4-mL sample of the above pentane solution was mixed with a drop of spectroscopic-grade acetone in a 9-mm-wide quartz tube. The solution was deoxygenated by bubbling N_2 through it for 10 min. The solution was irradiated at 300 nm in a Rayonet reactor at room temperature for 5 min. Analysis by GC showed the mixture to contain **1** (21%), **2** (14%), **3** (12%), **10** (25%), and **11** (26%), as well as some low-boiling materials thought to be actone dimers. The solution was irradiated for an additional 10 min, and the mixture contained (excluding acetone dimers) **1** (21%), **2** (8%), **3** (19%), **10** (17%), and **11** (29%).

When a sample of **1** or of **11** alone was irradiated for 40 min under similar conditions, only traces of dienes **2** and **3** were formed. Hence, **2** and **3** were not produced by **1** or **11**, but appear to be produced by isomerization of **15**.

Product **15** could also be isolated from the 193-nm photoproducts of **2** in pentane at 0 °C by extraction with silver nitrate solution as above. This sample of **15** isolated from the photoproducts of **2** also contained residual **2** and **11**. The sample was extracted with silver nitrate solution a second time, and the materials extracted by silver nitrate were reisolated, in order to reduce the amounts of **2** and **11** relative to **15**. The sample, in pentane, was filtered through 1 g of silica gel with pentane as eluent. A UV spectrum of this material had a λ_{max} of 241 nm.

Silver Nitrate Impregnated Alumina. Silver nitrate (10 g) was dissolved in acetonitrile (150 mL) in a round-bottomed flask. Alumina (neutral, activity 1, 100 g) was added to the solution. The acetonitrile was removed, first by using a rotary evaporator and then by using a vacuum pump. The solid was dried at 60 °C in the dark in a vacuum oven for 5 h.

Identification of Photoproducts of *cis*- and *trans*-Bicyclo[6.2.0]deca-2,9-diene (4 and 8). Photoproducts of diene **4** were separated by a combination of preparative GC and chromatography over silver nitrate impregnated alumina. All photoproducts except **16** were identified by comparison of ^1H NMR spectra and by capillary GC coinjection with authentic samples. An authentic sample of **17** was obtained commercially (Aldrich). Compounds **5**,[9] **6**,[14] **8**,[14b] **18**,[17] and **19**[14b] were prepared according to literature procedures.

A sample of (*Z*,*Z*,*Z*)-cyclodeca-1,3,5-triene was not available for coinjection, so a sample of photoproduct **16** was hydrogenated by using 10% Pd/C catalyst in pentane at room temperature and pressure. The fully reduced material was identified as cyclodecane by GC coinjection with an authentic sample and by its characteristic ^1H NMR spectrum (one signal at δ 1.52).

Irradiation of (*Z*,*Z*)-Cycloocta-1,3-diene (17) at 193 nm. Commercially obtained **17** was purified by preparative GC and irradiated at 193 nm under the above analytical conditions. The major products, (*Z*,*E*)-cycloocta-1,3-diene (**18**)[17] and *cis*-bicyclo[4.2.0]oct-7-ene (**20**),[17] were identified by coinjection with authentic samples on a capillary GC. After extended irradiation, cyclohexene and other unidentified secondary products were also observed.

Acknowledgment. This investigation was supported by NIH Grant DK00709, National Institute of Diabetes and Digestive and Kidney Diseases. The laser was partially supported by the San Francisco Laser Center, a regional facility supported by the National Science Foundation and the National Institutes of Health.

Registry No. **1**, 17385-24-9; **2**, 76745-42-1; **3**, 14833-88-6; **4**, 19043-20-0; **5**, 75993-26-9; **6**, 112137-53-8; **8**, 40815-16-5; **9**, 931-88-4; **10**, 931-89-5; **11**, 21196-42-9; **15**, 56325-57-6; **16**, 75993-36-1; **17**, 3806-59-5; **18**, 3806-60-8; **19**, 13304-05-7; **20**, 3806-82-4; **31**, 112070-25-4; 2,4,6-(i-Pr)$_3C_6H_2SO_2NHNH_2$, 39085-59-1; *cis*-bicyclo[9.1.0]nonane-9-carboxaldehyde, 28860-73-3; bicyclo[6.1.0]nonane-9-carboxaldehyde [(2,4,6-triisopropylphenyl)sulfonyl]hydrazone, 112070-24-3; *cis*-bicyclo[9.1.0]non-2-ene-9-carboxaldehyde, 77843-16-4; cyclodecane, 293-96-9.