72162-99-3; **8**, 59523-07-8; **9**, 72163-08-7; **10**, 72163-09-8; **11**, 72163-00-9; **12**, 72163-02-1; **13a**, 72163-01-0; **13b**, 72163-01-0; **14a**, 74855-11-1; **14b**, 65961-30-0; **15**, 930-30-3; **16a**, 36269-80-4; **16b**, 74855-12-2; **17a**, 74855-13-3; **17b**, 74855-14-4; **18a**, 72163-04-3; **18b**, 74892-16-3; **18c**, 74855-15-5; **19a**, 74892-17-4; **20a**, 74957-64-5; **20b**, 74892-18-5; **20c**, 74892-19-6; **21a**, 74892-13-0; **21b**, 74892-14-1; **21c**, 74855-01-9; **22a**, 74855-02-0; **22b**, 74877-67-1; **23a**, 74855-03-1; **24a**, 74855-04-2; **24b**, 74855-05-3; **25a**, 59137-83-6; **25b**, 74855-06-4; *exo*-**27**, 74855-07-5; *endo*-**27**, 74892-15-2; **28**, 74855-08-6; 2-bromo-2-cyclohexenone ethylene ketal, 70156-98-8; 2-cyclohexenone, 930-68-7; 2-bromo-2-cyclopentenone ethylene ketal, 68241-78-1; 2-cyclopentenone, 930-30-3; isobutylene, 115-11-7; methylenecyclohexane, 1192-37-6; ethylene, 74-85-1; isopropenyl acetate, 108-22-5; 1-pentene, 592-41-6; propene, 115-07-1; propyne, 74-99-7; (*E*)-octa-2,7-dien-4-ol, 74855-09-7; (*Z*)-octa-2,7-dien-4-ol, 74855-10-0; 1-bromopropene, 590-14-7; 4-pentenal, 2100-17-6.

Photochemistry of Cycloalkenes. 9. Photodimerization of Cyclohexene[1]

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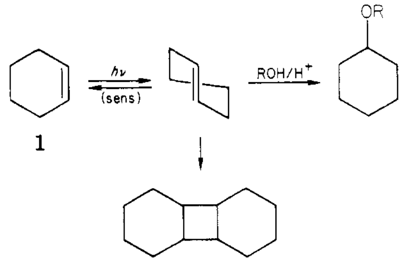
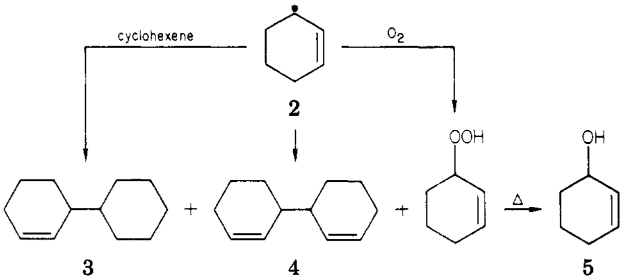
The photodimerization of cyclohexene has been restudied. Either direct or triplet-sensitized irradiation produced a stereoisomeric mixture of [2 + 2] dimers **6**–**8**, respectively, as primary products with the cis,trans isomer **7** predominating. The direct-irradiation process was complicated by the accompanying formation of the radical-derived products **3**–**5**. Dimerization is interpreted in terms of initial light-induced cis → trans isomerization of cyclohexene, followed by a nonstereospecific ground-state $[2_s + 2_a]$ addition of *trans*-cyclohexene to the cis isomer. By contrast, cycloheptene showed little tendency to undergo photodimerization; attempted *p*-xylene-sensitized dimerization afforded instead principally the sensitizer–olefin adduts **10** and **11**. Comparison is made with the copper(I) triflate catalyzed photodimerization of cyclohexene and cycloheptene.

Usually the only consequence of sensitized irradiation of alkenes in various media, either protic or aprotic, is cis ⇄ trans isomerization about the double bond. A notable exception is the behavior of cyclohexenes and cycloheptenes, which undergo protonation on sensitized irradiation in protic media—a phenomenon not shared by either acyclic, exocyclic, or larger ring cyclic olefins, on one hand, or smaller ring cyclic olefins, on the other hand.[3,4] It has been proposed that photoprotonation involves an initial light-induced cis → trans isomerization of the olefin, followed by ground-state protonation of the resulting highly strained *trans*-cycloalkene intermediate (Scheme I), rather than protonation of an excited state of the olefin.[3] This proposal has recently been supported by studies with cycloheptene and 1-phenylcyclohexene and -heptene, which show the involvement of an intermediate in the photoprotonation process having a lifetime much longer than would be expected for an excited state.[5]

Scheme I



Scheme II



On sensitized irradiation in aprotic media cyclohexenes undergo instead [2 + 2] cyclodimerization.[3,6,7] Two reports on the photodimerization of cyclohexene have appeared; in both cases methyl acetoacetate was employed as photosensitizer.[6,7] A mixture of three [2 + 2] dimers (**6**–**8**) was obtained in low yield, along with a number of other products from which they could be separated only with difficulty—including 3-cyclohexylcyclohexene (**3**), 3,3′-bicyclohexenyl (**4**), and several olefin–sensitizer adducts. It was thus concluded that the triplet-sensitized photodimerization of cyclohexene is of limited preparative value.[7] Products **3** and **4** presumably originate, as shown in Scheme II, ,via the cyclohexenyl radical **2**, formed by abstraction of an allylic hydrogen atom from cyclohexene by methyl acetoacetate. The formation of three [2 + 2] dimers suggests that the dimerization process is not stereospecific. However, it was noted that since methyl acetoacetate is capable of abstracting hydrogen atoms, the actual stereospecificity of the reaction may be greater than that observed due to secondary epimerization. Indeed,

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[1] Part 8: P. J. Kropp, *J. Am. Chem. Soc.*, **95**, 4611 (1973).

[2] Alfred P. Sloan Research Fellow, 1972–1976.

[3] (a) P. J. Kropp and and H. J. Krauss, *J. Am. Chem. Soc.*, **89**, 5199 (1967); (b) P. J. Kropp, *ibid.*, **91**, 5783 (1969).

[4] For reviews see (a) J. A. Marshall, *Science*, **170**, 137 (1970); (b) P. J. Kropp, *Org. Photochem.*, **4**, 1 (1979).

[5] (a) R. Bonneau, J. Joussot-Dubien, L. Salem, and A. J. Yarwood, *J. Am. Chem. Soc.*, **98**, 4329 (1976); (b) R. Bonneau, J. Joussot-Dubien, J. Yarwood, and J. Pereyre, *Tetrahedron Lett.*, 235 (1977); (c) Y. Inoue, S. Takamuku, and H. Sakurai, *J. Chem. Soc., Perkin Trans. 2*, 1635 (1977); (d) W. G. Dauben, H. C. H. A. van Riel, J. D. Robbins, and G. J. Wagner, *J. Am. Chem. Soc.*, **101**, 6333 (1979).

[6] M. Tada, T. Kokubo, and T. Sato, *Bull. Chem. Soc. Jpn.*, **43**, 2162 (1970).

[7] R. G. Salomon, K. Folting, W. E. Streib, and J. K. Kochi, *J. Am. Chem. Soc.*, **96**, 1145 (1974).

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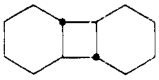
Table I. Sensitized Dimerization of Cyclohexene (1)[a]

solvent	sensitizer	time, h	yield, %[b] 1	6	7	8
ether	benzene	18	73	8	14	5
	p-xylene	8	11	26	46	17
ether[c]	*p*-xylene	24	60	12	16	6
pentane	*p*-xylene	8	11	24	42	23
ethanol	*p*-xylene	8	11	16	24	11[d]
(none)[e]	*p*-xylene	16		31	51	18

[a] Irradiations were conducted as described in the experimental section, using 100-mL solutions containing 20 mmol of olefin and 20 mmol of sensitizer. [b] Determined by gas chromatographic analysis of aliquots removed from the irradiation mixture. [c] Contained 40 mmol of *cis*-2-octene. [d] Cyclohexyl ethyl ether also obtained (30% yield). [e] Conducted by using a 150-mL *p*-xylene solution containing 50 g of cyclohexene. Yields in this case are relative.

epimerization of the highly strained isomer **6** to a mixture of **6–8**, presumably via reversile abstraction of the tertiary hydrogen atoms, was demonstrated by irradiating **6** in acetone solution.[7,8]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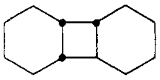
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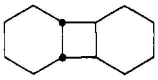
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An obvious means of eliminating the undesirable formation of **3**, **4**, and the olefin-sensitizer adducts while simultaneously circumventing any possible epimerization of dimers **6–8** would be to use a nonabstracting sensitizer, such as benzene. However, it is reported that benzene does not sensitize the dimerization of cyclohexene.[7] This is highly surprising in view of the fact that benzene and its simple alkyl derivatives are commonly used to sensitize the protoprotonation of cycloalkenes.[3,4] In view of these many unanswered questions, the dimerization of cyclohexene has now been subjected to closer scrutiny. During the course of this study comparison has been made with cycloheptene.

Results

Cyclohexene. As shown in Table I, *p*-xylene-sensitized irradiation of cyclohexene in ether, pentane, or ethanol solution afforded a mixture of dimers **6–8** in high yield with no significant amounts of accompanying products. In ethanol there was some competing formation of cyclohexyl ethyl ether. In all cases the cis,trans isomer **7** was formed predominantly and the cis–anti–cis isomer **8** was formed in lowest yield, but the exact ratios varied slightly with solvent. In all cases the ratios were similar to those previously observed with methyl acetoacetate as sensitizer,[7] but the yields were substantially higher. Even in neat *p*-xylene the same three isomers were obtained in a comparable ratio. Similar results were obtained with benzene as the sensitizer; however, in this case the irradiation mixture became yellow and the rate of conversion of cyclohexene was substantially slower. Irradiation in the presence of 2-octene reduced the rate of disappearance of cyclohexene, presumably because of competition by the added olefin for triplet energy from the sensitizer, but afforded dimers **6–8** in a similar ratio. As shown in Table II, irradiation at -40 °C afforded dimers **6–8** in similar relative yields except for a slight decrease in the amount of dimer **8**.

Table II. Effect of Temperature on the Sensitized Dimerization of Cyclohexene (1)[a]

temp, °C	time, h	yields, %[b] 1	6	7	8
37	16	10	27	44	19
-40	16	6	30	46	12

[a] Irradiations were conducted as described in the experimental section, using 12.5-mL solutions containing 2.5 mmol of olefin and 2.5 mmol of *p*-xylene. [b] Determined by gas chromatographic analysis of aliquots removed from the irradiation mixture.

Table III. Dimerization of Cyclohexene (1) by Direct Irradiation[a]

% 1	time, h	yields, %[b] 1	3	4	5	6[c]	7[c]	8[c]
2	96	28	*d*	*d*	*d*	2.0	2.6	1.0[e]
50	96	90	*d*	*d*	*d*	2.0	2.5	1.0

[a] Irradiations were conducted on 110-mL pentane solutions as described in the experimental section. [b] Determined by gas chromatographic analysis following purification to remove **3–5** by chromatography through a silver nitrate–alumina column. [c] Relative yields. [d] Product present but yield not determined. [e] Absolute yield 3%.

Table IV. Quantum Yields for Formation of Dimers 6–8[a]

light intensity[b]	Φ[c] 6	7	8
21.70	0.025 ± 0.002	0.037 ± 0.004	0.020 ± 0.002
17.22	0.023 ± 0.001	0.038 ± 0.002	0.014 ± 0.003
14.70	0.034 ± 0.002	0.045 ± 0.005	0.020 ± 0.005
8.47	0.022 ± 0.004	0.029 ± 0.008	0.013 ± 0.004
6.80	0.018 ± 0.002	0.026 ± 0.003	0.012 ± 0.002
2.98	0.019 ± 0.003	0.027 ± 0.005	0.009 ± 0.002

[a] Irradiations were conducted at 254 nm as described in the experimental section, using ether solutions which were 0.2 M each in cyclohexene and *p*-xylene. [b] Einsteins/min, 10^{-7}; obtained by using the benzene-sensitized isomerization of *trans*-2-octene for actinometry as described in the experimental section. [c] Absolute quantum yields for dimer formation with standard deviations.

As shown in Table III, qualitatively similar results were obtained when cyclohexene was irradiated directly except that the dimers **6–8** were accompanied by the radical products **3–5** and by a large number of minor products which were not characterized. Long irradiation times were necessary because of the weak absorption by cyclohexene above 200 nm. Similar results were obtained at two different concentrations.

Monitoring of both the indirect and sensitized irradiations revealed no change in the ratios of stereoisomers **6–8** as a function of time. Contrary to triplet carbonyl-sensitized photodimerization studied previously,[6,7] interconversion of stereoisomers **6–8** by photoepimerization would not be expected with the nonabstracting sensitizers employed here. This was confirmed by a control experiment in which it was found that **6**, the most highly strained isomer, was unchanged on irradiation in the presence of *p*-xylene under conditions identical with those under which cyclohexene underwent substantial conversion to a mixture of isomers **6–8**. *Thus all three stereoisomers are clearly primary photoproducts of both singlet and triplet-sensitized dimerization of cyclohexene.*

The quantum yields for formation of dimers **6–8** in ether solution were determined at several light intensities, as shown in Table IV. The quantum yields increased slightly with increasing light intensity while maintaining a constant

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(8) No reason is given for changing from methyl acetoacetate to acetone as sensitizer for the control study.

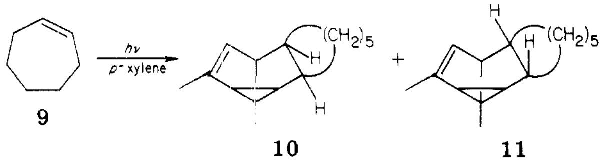
Table V. Comparison between Cyclohexene (1) and Cycloheptene (9) on Sensitized Irradiation[a]

olefin	solvent	time, h	recovery, %[b] olefin	recovery, %[b] sens	products[c]
1	pentane	4	28	96	6 (16), 7 (28), 8 (15)
9	pentane	4	64	67	10 (23), 11 (9)
	ether	18	14	18	10 (58), 11 (22)

[a] Conducted as described in the experimental section, using 100-mL solutions containing 20 mmol of olefin and 20 mmol of *p*-xylene. [b] Determined by gas chromatographic analysis of aliquots removed from the irradiation mixture. [c] Yields given in parentheses.

ratio of approximately 1.6:2.3:1.0, respectively.

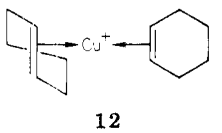
Cycloheptene. Quite surprisingly, cycloheptene (**9**) underwent somewhat slower disappearance than cyclohexene on *p*-xylene-sensitized irradiation and failed to exhibit any significant formation of dimer. *p*-Xylene disappeared at almost the same rate as cycloheptene (Table V), and the only significant products were two crossed adducts which are assigned structures **10** and **11** by comparison of the spectral data with that reported for other olefin–sensitizer adducts.[9] By contrast, cyclohexene afforded no detectable adducts with either benzene or *p*-xylene, and there was no significant loss of sensitizer during the irradiations.



Discussion

From the preceding results it is clear, contrary to previous reports,[6,7] that (1) cyclohexene undergoes cyclodimerization on irradiation in the presence of triplet sensitizers such as benzene or *p*-xylene; (2) under these conditions dimers **6**–**8** are formed in high yield without the accompanying formation of side products; and (3) the dimerization process is nonstereospecific, giving all three dimers as primary products. All three dimers are also obtained in a similar ratio as primary photoproducts on direct irradiation.

These results differ significantly from those observed previously for copper(I)-sensitized photodimerization of cyclohexene, which afforded mainly **6** (49%), some **7** (8%), and no **8**.[7] It has been proposed that the metal-catalyzed photodimerization involves light-induced cis → trans isomerization of cyclohexene followed by ground-state cycloaddition of the resulting highly strained *trans*-cyclohexene to a molecule of the cis isomer,[7] perphaps within the cis,trans complex **12**.[4b] The dimer **6** formed predominantly in this case has the stereochemistry that would be expected for $[2_s + 2_a]$ cycloaddition as required by orbital symmetry,[10] assuming that it is the trans isomer which reacts suprafacially.[11] The formation of a small amount of the less strained cis,trans dimer **7** may indicate some nonstereospecificity in the cycloaddition process.



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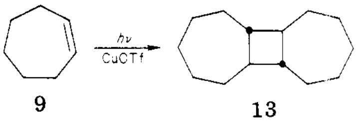
By contrast, cyclodimerization induced by either direct or triplet-sensitized irradiation affords relatively more of the cis,trans dimer **7** and some of the even less highly strained cis–anti–cis dimer **8**. Reaction once again apparently involves an initial cis → trans photoisomerization followed by ground-state cycloaddition of *trans*-cyclohexene to a molecule of the cis isomer.[12] However, the cycloaddition process is significantly less concerted in this case, affording substantial amounts of the less strained dimers **7** and **8**. The higher degree of stereospecificity in the metal-catalyzed photodimerization may be due to the intramolecularity of the cycloaddition process resulting from both alkenes being coordinated to the copper(I) cation, which exerts a sort of template effect.

A similar facilitating influence by the copper(I) ion is seen in the case of cycloheptene, which undergoes metal-catalyzed photodimerization to afford the trans–anti–trans dimer **13**,[7] the product expected from $[2_s + 2_a]$ cycloaddition of *trans*-cycloheptene to the cis isomer.[10] In this less highly strained case the metal-catalyzed cycloaddition is stereospecific. By contrast, cycloheptene was found in the present study not to undergo dimerization on *p*-xylene-sensitized irradiation, presumably because the trans isomer is not sufficiently strained to undergo intermolecular [2 + 2] cycloaddition. Instead a slower addition to *p*-xylene occurred, via a process that is generally believed to involve trapping of a singlet excited state of the sensitizer by the alkene.[9]



Alternatively it might be proposed that formation of the cis,trans dimer **7** on either direct or sensitized irradiation involves concerted ground-state cycloaddition of two molecules of *trans*-cyclohexene. However, there was no increase in the relative amount of **7** formed with increasing light intensity or decreasing temperature as might be expected in such a case. Hence the formation of dimers **6**–**8** apparently involves a nonstereospecific cycloaddition of *cis*- and *trans*-cyclohexene. The nonstereospecificity presumably arises from a nonconcertedness caused by the high degree of strain involved in the formation of the normally preferred trans–anti–trans dimer **6**.

Simple alkenes do not normally undergo thermal [2 + 2] cycloaddition. Reaction in this case is apparently attributable to the high degree of strain released by *trans*-cyclohexene. By contrast *trans*-cycloheptene is insufficiently strained to undergo cycloaddition in the absence of the copper(I) ion. It is curious that *trans*-cyclohexene will react with its cis isomer but not *cis*-2-octene. Likewise the reluctance of cyclohexene to undergo addition to *p*-xylene is puzzling.[13] Our studies on the photochemical

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(9) J. Cornelisse, V. Y. Merritt, and R. Srinivasan, *J. Am. Chem. Soc.*, **95**, 6197 (1973), and references cited therein.

(10) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry", Academic Press, New York, 1969.

(11) Since one face of the *trans*-cyclohexene double bond is sterically shielded by the polymethylene bridge, the trans isomer is better suited for suprafacial than antarafacial addition; see ref 7.

(12) The similarity in results obtained on both direct and sensitized irradiation suggests that the sensitizer is not directly involved in the cycloaddition process.

(13) R. Srinivasan and J. A. Ors, *Chem. Phys. Lett.*, **42**, 506 (1976), have observed a similar difference in reactivity between cyclohexene and cycloheptene for undergoing 1,3-addition to anisole and have suggested that such factors as differences in steric effects and ionization potentials of the olefins play a role. It would appear that this question merits further consideration.

properties of cycloalkenes continue.

Experimental Section

General. Infrared spectra were obtained in carbon tetrachloride solution, using a Perkin-Elmer 421 grating spectrophotometer, and ultraviolet spectra were obtained by using a Cary 14 spectrophotometer. Gas chromatographic analyses were performed on a Varian Aerograph 90-P or a Hewlett-Packard 5750 instrument, using 10 ft × 0.25 in. stainless steel columns containing 20% Carbowax 20M on 60–80-mesh Chromosorb W. Melting points were determined with a Thomas-Hoover capillary apparatus and are uncorrected and uncalibrated. Proton magnetic resonance spectra were determined in chloroform-*d* solutions with a Varian XL-100 spectrometer, using 0.3% tetramethylsilane as an internal standard; data are reported in the following manner: multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = unresolved multiplet, and br = broadened); integration; coupling constant; and assignment. Mass spectra were obtained by using an AEI MS-902 spectrometer; *m/e* values reported include the parent ion peak and other significantly large peaks appearing above *m/e* 55.

Irradiations. Unless otherwise indicated, irradiations were conducted by using a Hanovia 450-W medium-pressure mercury arc and a water-cooled quartz immersion well. Sensitized irradiations were conducted with a Vycor sleeve about the lamp. The solution was purged with nitrogen prior to irradiation and stirred magnetically throughout the irradiation. The relative rate experiment was conducted in an RPR-100 Rayonet photochemical reactor equipped with a circular array of 16 G8T5 lamps. Starting materials were obtained commercially and purified by distillation. Pentane was purified by passage through an alumina column impregnated with silver nitrate[14] (cutoff ≤200 nm). The progress of photochemical reactions was monitored by gas chromatographic analysis of aliquots removed periodically, determined relative to an internal hydrocarbon standard.

Irradiation of Cyclohexene. A. Sensitized. The results from sensitized irradiation of cyclohexene in a variety of solvents are summarized in Table I. Removal of solvent by distillation followed by isolation of the first component by preparative gas chromatographic techniques afforded ***trans–anti–trans*-dodecahydrobiphenylene (6)** as a colorless solid, mp 41–42 °C (lit.[7] mp 41–42 °C), which was identical in all respects with a specimen prepared independently by copper triflate sensitized dimerization of cyclohexene.[7]

Isolation of the major component afforded ***cis,trans*-dodecahydrobiphenylene (7)** as a colorless liquid which was identical in every respect with a specimen prepared independently by copper triflate sensitized dimerization of cyclohexene.[7]

Isolation of the third component afforded ***cis–anti–cis*-dodecahydrobiphenylene (8)** as a colorless liquid which had spectral properties and a relative gas chromatographic retention time similar to those reported.[7]

B. Direct. The results from direct irradiation of cyclohexene are summarized in Table III. Isolation of three of the products afforded specimens of dimers **6**–**8** which were identical with those described above. Isolation of a fourth product afforded **3-cyclohexylcyclohexene (3)** as a colorless liquid: IR ν_{max} 3023, 2926, 2856, 1445, 1370, 1349, 1312, 1133, 1044, 988, 950, 886, 869, 719, 698 cm^{-1}; ^{1}H NMR τ 4.38 (s, 2, CH-1 and -2) (lit.[7] NMR δ 5.63); mass spectrum, *m/e* 164 (73), 135 (10), 122 (10), 121 (12), 109 (7), 108 (10), 107 (6), 97 (11), 96 (13), 95 (7), 94 (7), 93 (8), 91 (8), 83 (58), 82 (100), 81 (77), 80 (43), 79 (32), 77 (12), 67 (56), 55 (52).

Isolation of a fifth component afforded **3,3′-bicyclohexenyl (4)** as a colorless liquid which was identical in every respect with a specimen prepared independently by acetophenone-sensitized irradiation of cyclohexene:[15] IR ν_{max} 3021, 2930, 2862, 2839, 1645, 1447, 1432, 1339, 1310, 1140, 1130, 1055, 969, 897, 874, 865, 803, 720 cm^{-1}; NMR τ 4.34 (m); mass spectrum, *m/e* 162 (1), 81 (100), 80 (68), 79 (39).

Isolation of the final component afforded **2-cyclohexen-1-ol (5)**, which was identical in every respect with a commercial specimen.

C. Quantum Yields. Benzene (Fisher Certified, thiophene free) was repeatedly washed with concentrated sulfuric acid (6 mL of acid for every 50 mL of benzene) until the acid layer no longer turned yellow. The benzene was then washed consecutively once with water, twice with a saturated sodium bicarbonate solution, twice with water, and twice with a saturated sodium chloride solution and then stored over anhydrous magnesium sulfate. Finally, the benzene was filtered and fractionally distilled from phosphorus pentoxide, the middle fraction being taken.[16] *trans*-2-Octene (Chemical Samples) was fractionally distilled three times. *n*-Octane (Matheson, Coleman, and Bell) and *n*-decane (Chemical Samples) were passed through a silver nitrate–alumina column.[14] Cyclohexene (Eastman) was purified by spinning-band distillation. *p*-Xylene (Eastman) and ether (Mallinckrodt, anhydrous) were used as received.

An ether solution 0.2 M in cyclohexene, 0.2 M in *p*-xylene, and 0.002 M in *n*-decane was prepared; 3.0-mL portions of this solution were placed in each of four 11 × 87 mm Vycor tubes, which were then attached to a high-vacuum line, outgassed with a series of four freeze–pump–thaw cycles, and sealed. The amount of light absorbed in each experiment was determined by the benzene-sensitized isomerization of *trans*-2-octene.[17] A benzene solution 0.1 M in *trans*-2-octene and 0.014 M in *n*-octane as an internal standard was prepared. A 3.0-mL portion of this solution was placed into each of three Vycor tubes which were then attached to a high-vacuum line, outgassed with a series of four freeze–pump–thaw cycles, and sealed. The isomerization was usually kept to under 5%, and the observed values obtained for *cis*-2-octene were corrected for a small amount of back isomerization.[18]

The irradiations were carried out at 254 nm by using a Rayonet RPR-100 photochemical reactor initially equipped with a circular array of 16 G8T5 lamps. The light intensity was changed by varying the number of lamps in the reactor. The cyclohexene sample tubes and the actinometry tubes were irradiated in parallel on a merry-go-round apparatus suspended in the center of the reactor. The lamps were ignited 1 h in advance to ensure stability. Irradiations were conducted to less than 5% conversion, at which level the rate of conversion was linear with time.

D. Temperature Studies. The irradiations outlined in Table II were conducted at 254 nm, using the apparatus previously described.[19]

Sensitized Irradiation of Cycloheptene. The results from sensitized irradiation of cycloheptene are summarized in Table V. Removal of solvent by distillation followed by isolation of the major product by preparative gas chromatographic techniques afforded ***endo*-1,12-dimethyltetracyclo[8.3.0.0^{2,13}.0^{3,9}]tridec-11-ene (10)** as a colorless liquid: IR ν_{max} 3042, 3006, 2915, 2851, 1640, 1451, 1442, 1376, 1356, 1340, 956, 880 cm^{-1}; ^{1}H NMR τ 4.94 (s, 1, CH-11), 8.24 (s, 3, CH$_3$-12), 8.68 (s, 3, CH$_3$-1); mass spectrum, *m/e* 202.1718 (calcd for $C_{15}H_{22}$ 202.1721), 202 (14), 187 (13), 107 (15), 106 (100), 105 (14), 90 (42), 68 (16).

***exo*-1,12-Dimethyltetracyclo[8.3.0.0^{2,13}.0^{3,9}]tridec-11-ene (11)** was obtained as a colorless liquid: IR ν_{max} 3031, 3000, 2918, 2852, 1639, 1454, 1446, 1377, 1077, 980, 886, 869, 838 cm^{-1}; ^{1}H NMR τ 4.95 (s, 1, CH-11), 8.34 (s, 3, CH$_3$-12), 8.86 (s, 3, CH$_3$-1); mass spectrum, *m/e* 202.1718 (calcd for $C_{15}H_{22}$ 202.1721), 202 (66), 187 (54), 159 (21), 146 (12), 145 (34), 131 (24), 120 (14), 119 (15), 117 (13), 107 (27), 106 (100), 105 (29), 94 (28), 93 (14), 92 (14), 91 (60), 81 (16), 79 (22), 77 (17), 67 (30).

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