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Photochemistry of Alkenes. 6. Direct Irradiation of 1,5-Hexadienes: [1,2] and [1,3] Sigmatropic Allyl Shifts[1a,b]

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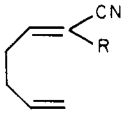
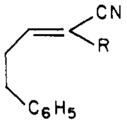
Abstract: The photochemical behavior of a series of alkyl-substituted 1,5-hexadienes has been studied. Competing allylcyclopropane formation and rearrangement to an isomeric 1,5-hexadiene via competing [1,2] and [1,3] sigmatropic allyl shifts, respectively, were observed. In one case a [3,2] product (**30** from **27**) and in another a [3,3] product (**35** from **31**) was obtained, but only in low yield. Extensive cis ⇄ trans isomerization competed with the allyl shifts, and, in addition, other products were obtained which are characteristic of the photochemical behavior of isolated double bonds. At low conversion diene **10t** underwent stereoselective rearrangement to **8t** and **11t**, whereas the cis isomer **10c** afforded mixtures of the cis and trans isomers of **8** and **11**. Attempts to induce the allyl migrations by sensitization with *p*-xylene or by irradiation at 254 nm afforded only cis ⇄ trans isomerization. It is concluded that the allyl migrations occur via an excited state involving interaction between the double bonds and requiring a conformation in which the central C_3–C_4 bond is in a plane orthogonal to both double bonds, as proposed previously. In contrast with the acyclic dienes, 1,5-cyclooctadiene (**50**) afforded products **51**–**53** from competing [3,2], [1,3], and [3,3] allyl shifts, respectively. The divergent behavior in this case apparently arises because appropriate interaction between the two double bonds can occur only in the boat conformation.

The 1,5-hexadiene system is of importance as it is the basic chromophore of a number of unsaturated polymers including 1,4-polybutadiene, 1,4-polyisoprene, and rubber. Studies of the effect of ultraviolet light on these elastomers have revealed a number of structural changes including cis ⇄ trans isomerization, appearance of vinyl and vinylidene double bonds, and formation of cyclopropyl groups.[2] The difficulties inherent in working with polymeric systems precluded detailed study of the photoreactions involved, although several mechanistic possibilities have been proposed.[2b,c]

Photochemical studies have been conducted on just two nonpolymeric systems, both rather specialized, and have led to conflicting results. Irradiation of caryophyllene and isocaryophyllene afforded competing cis ⇄ trans isomerization, fragmentation, allylcyclopropane formation, and rearrangement via either a [1,3] or [3,3] sigmatropic shift.[3] 1,5,9-Cyclododecatriene underwent competing cis ⇄ trans isomerization and isomerization via consecutive [1,3] and [3,3] sigmatropic rearrangements; no allylcyclopropane formation is reported.[4] Divergent behavior has also been reported for the various 1,5-diene analogues which have been studied. Acrylonitrile derivatives of types A and B (R = H, CN, and CO_2R) are reported to undergo only [1,3] rearrangement,[5]



A



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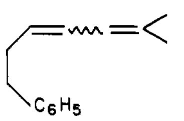
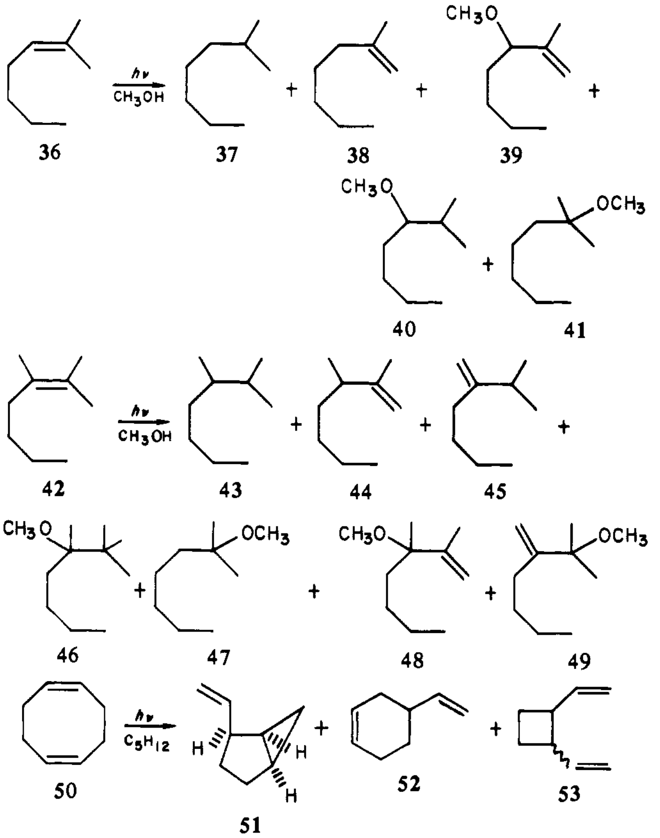


C

whereas dienes of type C afforded both [1,3] rearrangement and allylcyclopropane formation.[6] We report here the insights gained from a systematic study of the photochemical properties of a model series of 1,5-hexadienes. Emphasis is placed on the use of alkyl substituents to follow the course taken by the various modes of rearrangement.

Scheme I



Results

The results from irradiation of a series of variously substituted 1,5-hexadienes in pentane solution are summarized in Tables I and II. The dienes underwent facile rearrangement on irradiation through quartz, even if the double bonds were only mono- or disubstituted.[7] In each case, one or more allylcyclopropanes were

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[1] (a) Presented in part at the 10th IUPAC Symposium on Natural Products, Dunedin, Aug 1976. (b) For part 5 see P. J. Kropp, H. G. Fravel, Jr., and T. R. Fields, *J. Am. Chem. Soc.*, **98**, 840 (1976). (c) On leave from the Department of Scientific and Industrial Research, Wellington, New Zealand. (d) Alfred P. Sloan Research Fellow, 1972–1976.

[2] (a) L. Bateman, *J. Polym. Sci.*, **2**, 1 (1947); (b) M. A. Golub and C. L. Stephens, *J. Polym. Sci., Part C*, 765 (1967); *J. Polym. Sci., Polym. Chem. Ed.*, **6**, 763 (1968); (c) P. Carstensen, *Makromol. Chem.*, **135**, 219 (1970); **142**, 131 (1971).

[3] R. B. Bates, G. D. Forsythe, G. A. Wolfe, G. Ohloff, and K. H. Schulte-Elte, *J. Org. Chem.*, **34**, 1059 (1969); K. H. Schulte-Elte and G. Ohloff, *Helv. Chim. Acta*, **54**, 370 (1971).

[4] C. J. Attridge and S. J. Baker, *Tetrahedron Lett.*, 387 (1970).

[5] (a) R. C. Cookson, V. N. Gogte, J. Hudec, and N. A. Mirza, *Tetrahedron Lett.*, 3955 (1965); (b) R. C. Cookson, *Q. Rev. Chem. Soc.*, 423 (1968); (c) R. F. C. Brown, R. C. Cookson, and J. Hudec, *Tetrahedron*, **24**, 3955 (1968); (d) R. C. Cookson and J. E. Kemp, *J. Chem. Soc. D*, 385 (1971); (e) M. Sharma, *J. Am. Chem. Soc.*, **97**, 1153 (1975).

[6] E. C. Sanford and G. S. Hammond, *J. Am. Chem. Soc.*, **92**, 3497 (1970). One the other hand, the parent 4-phenyl-1-butene is reported to be photoinert in solution: see K. Salisbury, *J. Chem. Soc. B.*, 931 (1971).

[7] By contrast, mono- and disubstituted monoenes require exteneded irradiation under these conditions (unpublished data from these laboratories).

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Table I. Irradiation of 1,5-Hexadienes[a]

			product (yield, %)[b]			
diene	solvent	time, h	diene	[1,2]	[1,3]	other
1	CH_3OH	6	1 (49)	2 (17)		
	C_5H_{12}	6	(72)	(10)		
3	CH_3OH	8	3 (45)	4 (9), 5 (4)		6 (1)
	C_5H_{12}	4	(84)	(3) (2)		(1)
7	CH_3OH	6	7 (31)	8c (4), 8t (7), 9 (5)	10c (2), 10t (2)	11c (1), 11t (1), 12 (1)
	C_5H_{12}	4	(63)	(3) (6) (4)	(3) (3)	(1) (1) (1)
10t	CH_3OH	4	10c (27), 10t (25)	8c (2), 8t (6), 11c (3), 11t (2)	7 (6)	9 (1), 12 (4)
	C_5H_{12}[c]	12	(35) (65)			
10c	CH_3OH	3	(35) (16)	8c (3), 8t (2), 11c (2), 11t (1)	(3)	(1) (2)
13	CH_3OH	4	13 (25)	14 (10), 15 (4)	16 (4)	17 (12)
	C_5H_{12}	6	(32)	(8) (4)	(3)	(12)
	CH_3OH[d]	120	(99)			
18	CH_3OH	6	18 (61)	19 (12)		
	C_5H_{12}	8	(55)	(14)		
20	CH_3OH[e]	1.5	20 (10)	21 (6), 22 (1)	23 (3)	24 (1), 26 (1)
	C_5H_{12}	4	(7)	(16) (5)	(5)	(4), 25 (1), 26 (2)
27c	CH_3OH[c]	8	27c (50), 27t (50)			
	CH_3OH[d]	120	(65) (35)			
	C_5H_{12}	3	(22) (20)	28c (17)	29 (9)	30 (1)
31c	C_5H_{12}[f]	2	31c (12), 31t (10)	32c (2), 32t (2), 33c (7), 33t (2)	34 (7)	35 (1)
31t	C_5H_{12}[f]	2	(11) (20)	(1) (2) (4) (4)	(5)	(1)

[a] Irradiations were conducted on 110-mL solutions containing 0.02 mol of the olefin by using a quartz immersion well and a 450-W, medium-pressure mercury arc. [b] Figures in parentheses indicate yields of photoproducts or recovered starting material as determined by gas chromatographic analysis relative to an internal hydrocarbon standard. [c] *p*-Xylene sensitized; Corex filter employed. [d] Irradiated at 254 nm. [e] A complex mixture of methyl ethers was obtained in 30% yield. [f] A number of early eluting peaks were obtained in approximately 11% total yield. In addition, a mixture believed to be the cis and trans isomers of 1-methoxy-3,5,5-trimethyl-2,6-heptadiene (57) was obtained in 1% yield.

obtained. Accompanying allylcyclopropane formation in most cases was the generation of an isomeric 1,5-hexadiene. In several cases additional products were obtained, as discussed below. Material balances were limited by the competing formation of polymeric products. The conversion of diene **1** to the cyclopropane **2** was found to occur with a quantum yield of 0.2 at 185 nm. Products **6**, **10**, and **12** were identified by comparison with commercial specimens, while products **2**, **4**, **16**, **17**, and **29** were identified by comparison of their spectral data with those previously reported. The remaining structural assignments were made on the basis of spectral data as outlined in the Experimental Section.

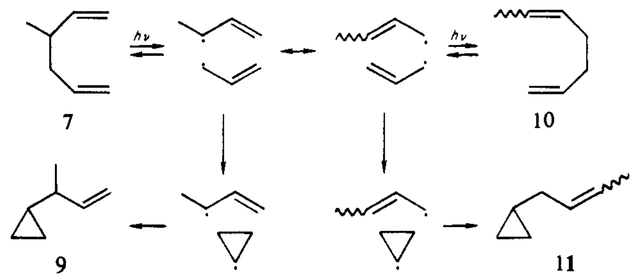
The same products were also obtained from irradiation of the dienes in methanol solution (Table I). In the case of diene **20** there was the accompanying formation of a complex mixture of methyl ethers which was not further investigated. The monoolefinic analogues **36** and **42** similarly afforded methyl ethers, along with products from reduction and double bond migration, on irradiation in methanol (Scheme I).

The cyclic analogue 1,5-cyclooctadiene (**50**) afforded the rearranged dienes **52** and **53**, along with the allylcyclopropane **51**. A study of the stereoisomers **10c** and **10t** at low conversion showed that the trans isomer **10t** underwent stereoselective rearrangement to **8t** and **11t** whereas the cis isomer **10c** afforded mixtures of the cis and trans isomers of **8** and **11** (Table III). In a control run irradiation of allylcyclopropane **8t** afforded no observable products. Attempts to induce the [1,2] and [1,3] allyl shifts by either *p*-xylene-sensitized irradiation of dienes **10t** and **27t** or by direct irradiation of diene **27c** at 254 nm led to cis ⇄ trans isomerization as the only detectable photoreaction. Finally, a comparison of the ultraviolet absorption spectra of diene **1** and the monoolefinic analogue 1-hexene revealed an enhanced absorption by the diene which was more than double that of 1-hexene at wavelengths above 230 nm (Table IV).

Discussion

Allylcyclopropane Formation. Any one of four structural changes might account for allylcyclopropane formation from 1,5-dienes: [1,2] or [3,2] allyl migration, [1,2] hydrogen migration, or [1,4] vinyl migration. Of these, only the first is in total accord with the observed behavior. For example, a [1,2] hydrogen shift would have led to cyclopropane **8** from diene **3** and a [1,4] vinyl shift to cyclopropane **9** from diene **10**, contrary to observation.[8] A [3,2] allyl shift would have led to the allylic isomer **11**, instead of **9**, from diene **7** and vice versa from diene **10**,[8b] as well as to the allylic isomers of cyclopropanes **15**, **21–22**, and **28** from dienes **13**, **20**, and **27**, respectively. Only in one case was any [3,2] product observed: allylcyclopropane **30** was obtained in low yield from diene **27**, along with the [1,2] product **28** as the major product. (The reason for competing formation of the [3,2] product in this case is discussed below.) Thus, although in some cases the structure of the diene does not permit a distinction between two or more pathways, only a mechanism involving a [1,2] allyl shift would consistently predict the observed principal product(s).

Scheme II



In prevous studies on the photobehavior of 1,5-hexadienes either the mechanism of allylcyclopropane formation was unresolved[3] or a mechanism was proposed involving initial homolytic cleavage of the diene to a radical pair, followed by cyclization and recombination,[2c] as shown in Scheme II for dienes **7** and **10**. However, the lack of any observable formation of allylcyclopropane **11** from diene **7** or of allylcyclopropane **9** from diene **10** argues against such a mechanism,[8b] as does the general absence of [3,2] products. Moreover, the stereochemistry of the migrating group is retained. Thus, although irradiation of either *cis*- or *trans*-1,5-heptadiene (**10**) was complicated by accompanying cis ⇄ isomerization, at low conversion **10t** afforded only **11t**, and **10c**

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[8] (a) There was no detectable formation of **8c** and no more than a trace, if any, of **8t** from diene **3**. (b) Cyclopropane **9** was formed in a minor amount (1%) on extended irradiation of diene **10**, apparently as a secondary product from the rearranged diene **7**. Similarly, diene **7** afforded cyclopropane **11** in minor amount (1%) as a secondary product.

Table II

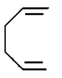
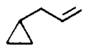
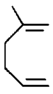
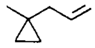
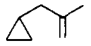
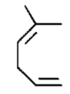
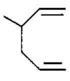
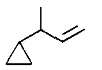
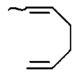
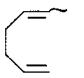
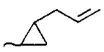
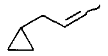
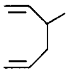
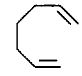
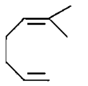
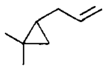
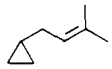
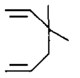
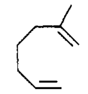
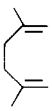
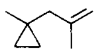
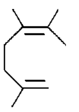
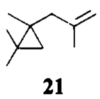
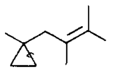
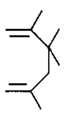
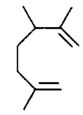
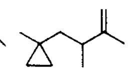
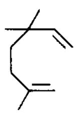
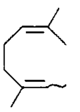
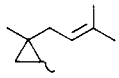
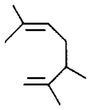
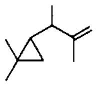
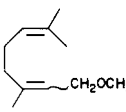
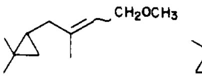
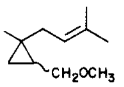
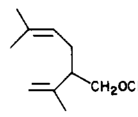
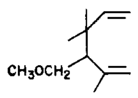
diene	[1,2]	[1,3]	other
 **1**	 **2**		
 **3**	 **4**  **5**		 **6**
 **7**	 **8**  **9**	 **10**	
 **10**	 **8**  **11**	 **7**	 **12**
 **13**	 **14**  **15**	 **16**	 **17**
 **18**	 **19**		
 **20**	 **21**  **22**	 **23**	 **24**  **25**  **26**
 **27**	 **28**	 **29**	 **30**
 **31**	 **32**  **33**	 **34**	 **35**

Table III. Low-Conversion Irradiation of Dienes 10c and 10t[a]

diene	time, h	yield, %[b]					
		10c	10t	8c	8t	11c	11t
10c	0.5	87	8	0.4	0.3	0.5	0.1
10t	0.5	11	81	c	1.0	d	0.6

[a] Irradiations were conducted on 1% methanolic solutions in a quartz tube with a 450-W mercury arc as described in the Experimental Section. [b] Determined by gas chromatographic analysis. [c] Trace. [d] None detected.

Table IV. Ultraviolet Absorption Data for Diene 1 and 1-Hexene[a]

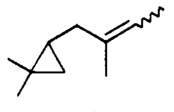
λ, nm	ε	
	1	1-hexene
220	6.3	3.1
230	4.1	2.0
240	2.4	0.60
250	1.8	0.20
260	1.3	0.15
270	1.1	0.10
280	0.8	0.03

[a] Methanol solution.

gave predominantly **11c** (Table III). On the other hand, the degree of stereospecificity for cyclopropane formation varied with the structure of the diene. Thus at low conversion **10t** afforded **8t** specifically, whereas **10c** gave both **8c** and **8t** in approximately equal quantities (Table IV). It would thus appear that although discrete allyl radicals are not involved, rearrangement is not totally concerted. The mechanism is discussed in more detail below.

It is noteworthy that although dienes **3**, **7**, **10**, **13**, and **20** all afforded both of the two possible [1,2] sigmatropic allyl migration products, in each case the predominant product was that in which the more highly substituted allyl moiety was transformed into a cyclopropane ring. For dienes **27** and **31**, in which both allyl groups are disubstituted, the predominant product was that involving the 2,3-disubstituted lower moiety. Indeed, in the case of **27** this was the only product; the allylcyclopropane **54** was not detected.

Isomeric 1,5-Diene Formation. Both [1,5] and [3,3] allyl migrations have been considered for this process in the case of caryophyllene,[3] and [3,3] rearrangement was observed with 1,5,9-cyclododecatriene.[4] The two modes of rearrangement would either lead to the same product (dienes **7**, **10**, **13**, and **20**) or be degenerate (dienes **1**, **3**, and **18**) for each of the dienes studied except **27** and **31**. Irradiation of **27** afforded only the [1,3] product **29**; the [3,3] product **55** could not be detected. Neryl and geranyl methyl ethers (**31c** and **31t**) afforded principally the [1,3] product **34** accompanied by small amounts of the isomeric [3,3] diene **35**. Since irradiation of dienes **31ct** is complicated by a rapid formation



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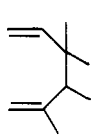

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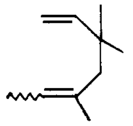

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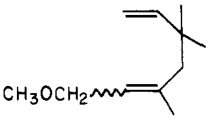

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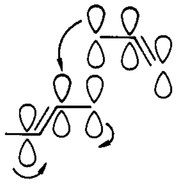
of the [1,3] product **34** and the formation of isomer **35** in only small amounts, it is not clear whether **35** arises via a small amount of competing [3,3] rearrangment or via secondary [1,3] rearrangement of diene **34**. In either event, [1,3] rearrangement is the predominant, if not exclusive, behavior.

Of the various dienes studied, only **27** and **31** are structurally capable of affording two different [1,3] rearrangement products, depending on how each end of the diene system is involved. As with allylcyclopropane formation, the predominant products (**29** and **34**) were those in which the 2,3-disubstituted allyl moiety underwent rearrangement. None of the isomeric diene **56** was detected from **27** and only trace amounts of diene **57** were detected from **31**. It is interesting to note the contrast with diene **13**, which underwent substantial rearrangement of the 3,3-dimethallyl portion to afford **16**.

Other Photoproducts. In addition to the allylcyclopropanes and rearranged dienes, several photoproducts were obtained which are typical of monoenic systems. As noted above, there was extensive competing cis ⇄ trans isommerication. There were also a number of products (**6**, **12**, **17**, **24**, and **25**) which resulted from 1,2 double bond migration in the starting diene or one of the primary photoproducts. This photoprocess is common for alkenes,[1b] as evidenced by the conversion of **36** to **38** and of **42** to **44** and **45**. In addition, diene **20** afforded the isomeric diene **26**, which probably arose via rearrangement of the π,R(3s) Rydberg excited state **58** to the carbene intermediate **59**. The formation of a mixture of methyl ethers on irradiation of diene **20** in methanol probably involves nucleophilic trapping of the Rydberg intermediate **58** (Scheme III). Both modes of photobehavior are common for alkenes, particularly those which are highly substituted.[9] The monoenes **36** and **42** similarly afforded mixtures of methyl ethers on irradiation in methanol.

Nature of the Excited State. The failure of either *p*-xylene-sensitized irradiation or direct irradiation at 254 nm to induce any photoreaction other than cis ⇄ trans isomerization indicates that neither the usual singlet nor triplet π,π^* excited state is involved in the allyl migrations, contrary to prior assumption.[3] It thus appears that there is an interaction between the double bonds which gives rise to a new state to which the diene may also be excited. It has been suggested that such an interaction occurs when the 1,5-diene attains a conformation in which the central C_3–C_4 bond is in a plane orthogonal to both double bonds.[10] In such a conformation the two π systems will be coupled by orbital overlap with the central C_3–C_4 bond (cf. **60**). However, the resulting σ-coupled transition apparently does not account for the enhanced absorption of 1,5-dienes at wavelengths above 230 nm as shown in Table IV, since irradiation at 254 nm effected cis ⇄ trans isomerization but no detectable [1,2] or [1,3] rearrangement. The competing formation of products typical of the π,π^* and π,R(3s) states of isolated alkenes may involve other conformations of the diene in which there is less σ–π interaction. Consistent with this is the modest quantum yield for the [1,2] rearrangement of diene **1**.



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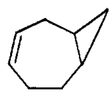

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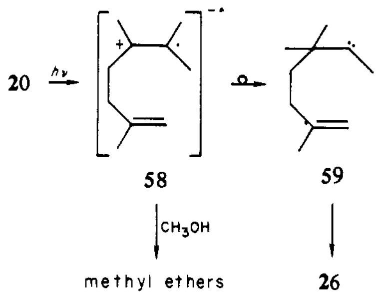
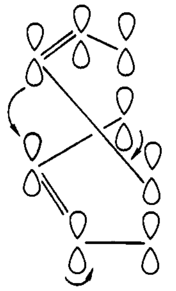
Scheme III



Further details of the migration process require knowledge of the stereochemistry at C_3 and C_4. Photoinduced [1,3] sigmatropic rearrangements occur suprafacially with retention of configuration in the migrating carbon, whereas [1,2] migrations should involve inversion of configuration.[11] This latter process should be accompanied by a disrotatory ring closure at C_1 and C_3, thereby correctly predicting, for example, the observed stereospecific formation of **8t** from **10t** (cf. **60**). The observed preference for rearrangement to be centered in the more highly substituted of the two allyl moieties probably reflects enhanced stabilization of the transition state by the additional substituents.

1,5-Cyclooctadiene (50) and 4-Ethenylcyclohexene (52). Although the conformation proposed for maximum overlap, in which the C_3–C_4 bond is in a plane orthogonal to that of the two double bonds, is available to acyclic systems, it is not necessarily possible in cyclic analogues. 4-Ethenylcyclohexene (**52**), in which such a conformation is not possible, affords only carbene-derived products analogous with those formed from the monoenic analogue cyclohexene.[12] In the case of 1,5-cyclooctadiene (**50**) this conformation is not possible in the chair form but can be attained in the boat form, in which case interaction can be through space as well as through bond.[13] Diene **50** underwent photorearrangement somewhat more slowly than might be expected for a system in which the double bonds are disubstituted. Moreover, it failed to afford the expected [1,2] product **61** but gave instead the allylcyclopropane **51**, the apparent product of a [3,2] sigmatropic shift, for which the boat conformation is best suited. The syn isomer is that expected from a concerted rearrangement of the boat form (cf. **62**), although the possibility that rearrangement



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[9] T. R. Fields and P. J. Kropp, *J. Am. Chem. Soc.*, **96**, 7559 (1974); (b) P. J. Kropp, E. J. Reardon, Jr., Z. L. F. Gaibel, K. F. Williard, and J. H. Hattaway, Jr., *ibid.*, **95**, 7058 (1973).

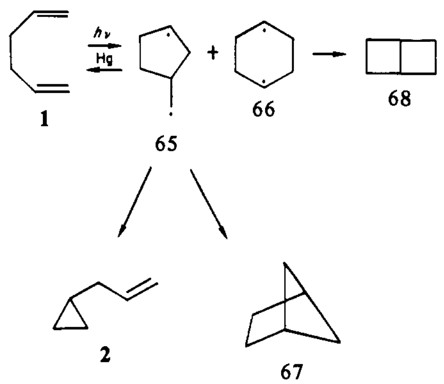
[10] R. C. Cookson, J. Henstock, and J. Hudec, *J. Am. Chem. Soc.*, **88**, 1060 (1966).

[11] For a discussion of orbital symmetry considerations in sigmatropic rearrarrangements of 1,5-dienes, see J. M. Coxon and B. Halton in "Organic Photochemistry", Cambridge University Press, London, 1974, pp 47–57 and references cited therein.

[12] R. Srinivasan and K. H. Brown, *Tetrahedron Lett.*, 3645 (1978).

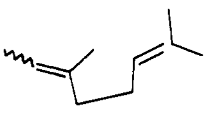
[13] R. Hoffmann, E. Helibronner, and R. Gleiter, *J. Am. Chem. Soc.*, **92**, 706 (1970).

Scheme IV



is nonconcerted or occurs from the cis,trans isomer of **50** cannot be excluded. Diene **50** also afforded both the [1,3] product **52** and the [3,3] product **53** as a mixture of the cis and trans isomers. Since a concerted, photochemical, [3,3] sigmatropic rearrangement would be forced by orbital symmetry to occur antarafacially, the formation of both **53c** and **53t** may reflect a nonconcerted rearrangement in this case, although the possible involvement of the cis,trans isomer of **50** once again cannot be excluded.

The only other example of a [3,2] product seen in this study is allylcyclopropane **30**, which was formed in low yield from diene **27**.[14] It is possible in this case that the presence of a methyl substituent at the β position of one of the double bonds destabilizes the extended conformation **63** sufficiently that the usually less



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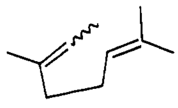

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preferred boatlike conformation **64** is populated to a moderate extent. It is this latter conformation which is best suited for [3,2] or [3,3] rearrangement. Dienes **18** and **20**, which similarly bear a β substituent, may also undergo rearrangement via a [3,2] allyl shift, but such a process would be structurally indistinguishable from a [1,2] shift.

Comparison with Mercury-Sensitized Isomerization. 1,5-Hexadiene (**1**) also affords allylcyclopropane (**2**) on gas-phase, mercury-sensitized irradiation.[15] However, the reaction pathway is quite different from that observed here for direct, solution-phase irradiation of 1,5-dienes. Bicyclo[2.1.1]- and bicyclo[2.2.0]hexanes (**67** and **68**) are formed as accompanying photoproducts in the former, but not latter, case[15] (Scheme IV). Moreover, a recent study of substituted analogues has shown that allylcyclopropane formation involves a formal [1,4] vinyl rather than a [1,2] allyl shift.[16] It thus appears that the mercury-sensitized products arise via the diradical intermediates **65** and **66**.[15e,16]

Summary. From the present results it is seen that acyclic 1,5-dienes principally undergo competing [1,2] and [1,3] sigmatropic allyl migrations on direct irradiation, presumably via an excited state which arises when the diene has a conformation in which there is orbital interaction between the two double bonds and the central C_3–C_4 bond. There are competing photoreactions typical of isolated double bonds, which may arise from conformations having reduced oribtal overlap. Cyclic olefins which cannot adopt a similar conformation exhibit divergent behavior. 1,5-Cyclooctadiene (**50**), which can achieve interaction only via a boat conformation, undergoes competing [3,2], [1,3], and [3,3] sigmatropic rearrangements.

Experimental Section

General Methods. Infrared spectra were obtained on carbon tetrachloride solutions with a Perkin-Elmer 421 grating spectrophotometer. Gas chromatographic analyses were performed on an Aerograph 90-P instrument using 10 ft × 0.25 in. columns packed with (A) 20% Carbowax 20M or (B) 20% SF-96 on 60–80-mesh Chromosorb W or a 20 ft × 0.25 in. column packed with (C) 20% β,β'-oxydipropionitrile on 60–80-mesh Chromosorb P. Unless otherwise indicated, ^{1}H NMR spectra were determined in chloroform-*d* solution 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 (given in hertz), and assignment. Mass spectra were obtained by using an AEI MS-902 spectrometer; the m/e values reported include the parent ion peak, if detectable, and all other peaks above m/e 39 which are greater than 5% of the base peak.

Irradiations. Unless otherwise indicated, irradiations were conducted using a Hanovia 450-W, medium-pressure mercury arc and a water-cooled quartz immersion well. The solution was purged with nitrogen for 30 min before irradiation. Vigorous stirring during irradiation was effected by a magnetic stirring bar. Products from samples irradiated in pentane were obtained after removal of the solvent by distillation. Product isolation from irradiations conducted in methanol was effected by addition of the irradiation solution to water semisaturated with sodium chloride and continuous extraction with pentane followed by removal of the pentane by distillation. The yields quoted are relative to a suitable hydrocarbon standard which was added prior to irradiation. The progress of photochemical reactions was monitored by gas chromatographic analysis of aliquots removed periodically. Irradiations at 254 nm were conducted by using an RPR-100 Rayonet photochemical reactor equipped with a circular array of 16 G8T5 lamps. Unless otherwise indicated, the starting olefins were obtained commercially.

Irradiation of 1,5-Hexadiene (1). A. In Methanol. A 110-mL methanolic solution containing 1.64 g of olefin was irradiated as described above for 6 h. Gas chromatographic analysis (column C, 25 °C) afforded only two peaks, whose constituents were collected and rechromatographed on column B (35 °C). Diene **1** was recovered from the first peak.

2′-Propenylcyclopropane (**2**) was obtained from the second peak as a colorless liquid: ν_{max} 3080, 3007, 2980, 2900, 2838, 1641, 1437, 1425, 1013, 992, 908 cm^{-1}; ^{1}H NMR τ 4.08 (m, 1, CH-2′), 4.95 (m, 2, CH_2-3′), 8.03 (t with further fine splitting, 2, J = 6.2 Hz, CH_2-1′), 9.24 (m, 1, CH-1α), 9.56 (m, 2, CH-2α and -3β), 9.94 (m, 2, CH-2β and -3β) [lit.[17] ν_{max} 3012, 1639, 1013, 990, 910 cm^{-1}; ^{1}H NMR (CCl_4) τ 4.17 (m, 1), 4.98 (t, 2), 8.05 (t, 2), 8.67–10.00 (m, 5)].

B. In Pentane. A 110-mL solution of olefin (1.64 g) in pentane was irradiated as described above for 6 h. Gas chromatographic analysis (column C, 25 °C) revealed little change over the last 2 h of irradiation as a result of polymer buildup on the probe. Gas chromatographic analysis showed the presence of 1 and **2**.

Irradiation of 2-Methyl-1,5-hexadiene (3). A. In Methanol. A 110-mL methanolic solution containing 1.92 g of olefin was irradiated as described above for 8 h. Gas chromatographic analysis (column C, 50 °C) afforded four major peaks, whose constituents were rechromatographed on column B (35 °C).

1-Methyl-1-(2-propenyl)cyclopropane (**4**) was obtained from peak A as a colorless liquid: ν_{max} 3072, 2998, 2955, 2899, 2867, 1638, 1449, 1425, 1383, 1007, 991, 911 cm^{-1}; ^{1}H NMR τ 4.16 (m, 1, CH-2′), 4.98 (m, 2, CH_2-3′), 8.02 (dt, 2, J = 7.0, 1.0 Hz, CH_2-1′), 8.98 (s, 3, CH_3-1), 9.74 (m, 4, CH_2-2 and -3) [lit.[18] ^{1}H NMR ($CHCl_3$) τ 3.81–4.58 (m, 1), 4.78–5.25 (m, 2), 8.03 (d, J = 7 Hz, 2), 8.98 (s, 3), 9.74 (m, 4)]. Diene **3** was recovered from peak B.

5-Methyl-1,4-hexadiene (**6**) was obtained as the major component of peak C as a colorless liquid whose infrared spectrum and gas chromatographic retention time were identical with those of a commercial sample.

(2-Methyl-2-propenyl)cyclopropane (**5**) was isolated from peak D as a colorless liquid: ν_{max} 3076, 3001, 2968, 2913, 2875, 1648, 1454, 1373, 1014, 888 cm^{-1}; ^{1}H NMR τ 5.19 and 5.27 (2 br s, 2, CH_2-3′), 8.09 (d, 2, J = 7 Hz, CH_2-1′), 8.22 (s with fine splitting, 3, CH_3-2′), 9.19 (m, 1, CH-1α), 9.54 (m, 2, CH-2α and -3α), 9.95 (m, 2, CH-2β and -3β); mass spectrum, m/e (relative intensity) 96.0938 (calcd for C_7H_{12},

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(14) It is not clear why no [3,2] product was observed from the closely related diene **31**, although one formed in low yield may have escaped detection as an impurity in another product.

(15) (a) R. Srinivasan, *J. Phys. Chem.*, **67**, 1367 (1963); (b) R. Srinivasan and F. I. Sonntag, *J. Am. Chem. Soc.*, **89**, 407 (1967); (c) R. Srinivasan and K. H. Carlough, *ibid.*, **89**, 4932 (1967); (d) J. E. Baldwin and J. E. Gano, *J. Org. Chem.*, **32**, 3506 (1967); (e) J. E. Baldwin and J. E. Gano, *ibid.*, **34**, 612 (1969).

(16) T. D. R. Manning and P. J. Kropp, in preparation.

(17) R. Srinivasan, *J. Am. Chem. Soc.*, **83**, 4923 (1961).

(18) Y. N. Bubnov, O. A. Nesmeyanova, T. Y. Rudashevskaya, B. M. Mikhailov, and B. A. Kazansky, *Tetrahedron Lett.*, 2153 (1971).

96.0939), 96 (9), 95 (5), 81 (100), 79 (26), 70 (7), 68 (68), 67 (87), 65 (9), 56 (10), 55 (92), 54 (38), 53 (64), 51 (14), 50 (9), 44 (10), 43 (14), 42 (15), 41 (82), 39 (99).

B. In Pentane. A 110-mL pentane solution containing 1.92 g of olefin was irradiated as described above for 4 h. The irradiation was stopped at this stage as a white polymer had formed on the probe. Gas chromatographic analysis as outlined above revealed the presence of **3**–**6**.

Irradiation of 3-Methyl-1,5-hexadiene (7). A. In Methanol. A 110-mL methanolic solution containing 1.92 g of olefin was irradiated as described above for 6 h. Gas chromatographic analysis (column C, 25 °C) afforded nine major peaks whose constituents were collected and rechromatographed on column B (35 °C). Diene **7** was recovered from peak A.

***trans*-1-Methyl-2-(2-propenyl)cyclopropane (8t)** was obtained from peak B as a colorless liquid: ν_{max} 3075 (sh), 3063, 3000, 2953, 2928, 2899, 2870, 1639, 1450, 1378, 1020, 993, 911 cm^{-1}; ^{1}H NMR τ 4.09 (m, 1, CH-2′), 4.95 (m, 2, CH$_2$-3′), 8.02 (m, 2, CH$_2$-1′), 8.96 (d, 3, J = 5.2 Hz, CH$_3$-1), 9.54 (m, 2, CH-2α and -3α), 9.81 (m, 2, CH-1β and -3β); mass spectrum, m/e (relative intensity) 96.0936 (calcd for C_7H_{12}, 96.0939), 96 (5), 95 (3), 82 (5), 81 (77), 79 (15), 77 (6), 68 (15), 67 (43), 66 (5), 65 (8), 56 (6), 55 (94), 54 (100), 53 (28), 51 (9), 50 (5), 42 (7), 41 (45), and 39 (65).

(1-Methyl-2-propenyl)cyclopropane (9) was obtained from peak C as a colorless liquid: ν_{max} 3079, 3001, 2965, 2928, 2875, 1636, 1452, 1367, 1014, 993, 911 cm^{-1}; ^{1}H NMR τ 4.12 (m, 1, CH-2′), 5.00 (m, 2, CH$_2$-3′), 8.60 (m, 1, CH-1′), 8.91 (d, 3, J = 6.6 Hz, CH$_3$-1′), 9.5 (br m, 3, CH-1α, -2α, and -3α), 9.90 (m, 2, CH-2β and -3β); mass spectrum, m/e (relative intensity) 96.0935 (calcd for C_7H_{12}, 96.0939), 96 (2), 95 (3), 82 (6), 81 (81), 79 (22), 77 (7), 69 (8), 68 (89), 67 (100), 66 (9), 65 (9), 55 (75), 54 (29), 53 (42), 51 (9), 50 (5), 42 (9), 41 (47), 39 (52).

1,6-Heptadiene (12) was obtained from peak D as a colorless liquid whose spectral data and gas chromatographic retention time were identical with those of a commercial sample.

***trans*-1,5-Heptadiene (10t)** was obtained from peak E as a colorless liquid: ν_{max} 3079, 2964, 2919, 2856, 1637, 1450, 1438, 1375, 990, 965, 911 cm^{-1}; ^{1}H NMR τ 4.18 (m, 1, CH-2), 4.54 (m, 2, CH-5 and -6), 4.99 (m, 2, CH$_2$-1), 7.90 (br s, 2, CH$_2$-3 and -4), 8.35 (m, 3, CH$_3$-6). These data are identical with those obtained from the major component of a commerical sample of *trans*- and *cis*-1,5-heptadiene.

***cis*-1-Methyl-2-(2-propenyl)cyclopropane (8c)**, the major component of peak F, was obtained as a colorless liquid: ν_{max} 3078 (sh), 3074, 3000, 2952, 2930, 2910, 2875, 1639, 1450, 1389, 1014, 992, 911 cm^{-1}; ^{1}H NMR τ 4.04 (m, 1, CH-2′), 4.94 (m, 2, CH$_2$-3′), 7.94 (m, 2, CH$_2$-1′), 8.96 (d, with further fine splitting, 3, J = 5.0 Hz, CH$_3$-1), 9.23 (m, 3, CH-1α, -2α, and -3α), 10.30 (m, 1, CH-3β); mass spectrum, m/e (relative intensity) 96.0938 (calcd for C_7H_{12}, 96.0939), 96 (3), 95 (3), 82 (5), 81 (64), 79 (12), 77 (5), 66 (14), 67 (38), 66 (5), 65 (7), 56 (5), 55 (84), 54 (100), 41 (38), 39 (60).

***cis*-1,5-Heptadiene (10c)** was obtained from peak G as a colorless liquid: ν_{max} 3076, 3015, 2980, 2920, 2858, 1639, 1440, 1368, 990, 912 cm^{-1}; ^{1}H NMR τ 4.14 (m, 1, CH-2), 4.54 (m, 2, CH-5 and -6), 4.95 (m, 2, CH$_2$-1), 7.86 (m, 4, CH$_2$-3 and -4), 8.38 (d with further fine splitting, 3, J = 5.3 Hz, CH$_3$-6). These data are identical with those obtained from the minor component of a commercial sample of *trans*- and *cis*-1,5-heptadiene.

***trans*-(2-Butenyl)cyclopropane (11t)** was obtained from peak H as a colorless liquid: ν_{max} 3075, 3005, 2965, 2917, 1375, 1014, 965 cm^{-1}; ^{1}H NMR τ 4.51 (m, 2, CH-2′ and -3′), 8.11 (br m, 2, CH$_2$-1′), 8.34 (m, 3, CH$_3$-3′), 9.24 (br m, 1, CH-1α), 9.60 (m, 2, CH-2α and -3α), 9.95 (m, 2, CH-2β and -3β); mass spectrum, m/e (relative intensity) 96.0942 (calcd for C_7H_{12}, 96.0939), 96 (10), 95 (6), 82 (5), 81 (71), 79 (18), 77 (7), 69 (7), 68 (42), 67 (55), 66 (6), 65 (7), 56 (7), 55 (100), 54 (32), 53 (37), 51 (8), 41 (48), 39 (58).

***cis*-(2-Butenyl)cyclopropane (11c)** was obtained from peak I as a colorless liquid: ν_{max} 3079, 3010, 2965, 2920, 2865, 1383, 1014 cm^{-1}; ^{1}H NMR τ 4.52 (m, 2, CH-2′ and -3′), 8.02 (m, 2, CH$_2$-1′), 8.41 (d with further fine splitting, 3, J = 5.8 Hz, CH$_3$-3′), 9.22 (br m, 1, CH-1α), 9.59 (m, 2, CH-2α and -3α), 9.94 (m, 2, CH-2β and -3β); mass spectrum, m/e (relative intensity) 96.0942 (calcd for C_7H_{12}, 96.0939), 96 (9), 95 (6), 82 (6), 81 (67), 79 (18), 77 (6), 69 (6), 68 (47), 67 (61), 66 (5), 65 (7), 57 (6), 56 (9), 55 (100), 54 (33), 53 (35), 51 (8), 41 (44), 39 (58).

B. In Pentane. A 110-mL solution of olefin (1.92 g) in pentane was irradiated as described above for 4 h. Preparative gas chromatography as outlined above yielded **7**–**12**.

Irradiation of *trans*-1-Methyl-2-(2-propenyl)cyclopropane (8t). A quartz tube (1-cm diameter) containing 5 mg of olefin, 1 mL of methanol, and 2 mg of heptane (internal standard) was irradiated under an atmosphere of nitrogen in front of a 450-W, medium-pressure light backed by a reflector. Aliquouts were withdrawn at 0.5-h intervals and analyzed as previously described. Gas chromatographic analysis (column C, 25 °C) of the aliquouts revealed a steady decline in starting material and no production of any other monomeric products. All starting material had disappeared after 1.5 h.

Irradiation of *trans*-1,5-Heptadiene (10t). A. In Methanol. A 110-mL methanolic solution containing 1.92 g of olefin (commercial sample contaminated with 12% of cis isomer) was irradiated as described above for 4 h. Gas chromatographic analysis (column C, 25 °C) afforded nine major peaks, which were shown by their spectral properties to correspond to the same compounds observed for the irradiation of diene **7**.

B. Sensitized. A 110-mL pentane solution containing 1.92 g of olefin and 2.0 g of *p*-xylene was irradiated as described above for 12 h with the use of a Corex filter. Gas chromatographic analysis (column C, 25 °C) afforded two peaks which were shown to consist of *trans*- and *cis*-1,5-heptadiene (65% and 35%, respectively). Samples of each of these compounds were collected by preparative gas chromatographic methods and used in the irradiations described below.

C. Low Conversion. A quartz tube 1 cm in diameter containing 95 mg of **10t** (99%) and 10 mL of methanol was irradiated for 0.5 h under an atmosphere of nitrogen while positioned in front of a 450-W, medium-pressure lamp backed by a reflector. The results are summarized in Table III.

Irradiation of *cis*-1,5-Heptadiene (10c). A solution of 70 mg of *cis*-1,5-heptadiene (99%) in 7 mL of methanol was irradiated as described in the preceding section. The results are summarized in Tables I and III.

Irradiation of 6-Methyl-1,5-heptadiene (13). A. In Methanol. A 110-mL methanolic solution containing 2.2 g of olefin was irradiated as described above for 4 h. Gas chromatographic analysis (column B, 55 °C) afforded five major peaks, whose constituents were collected and rechromatographed on column C (35 °C).

3,3-Dimethyl-1,5-hexadiene (16) was obtained from peak A as a colorless liquid: ν_{max} 3079, 3025, 2963, 2927, 2910, 2870, 1640, 1378, 1362, 993, 910 cm^{-1}; ^{1}H NMR τ 4.18 (m, 2, CH-2 and -5), 5.03 (m, 4, CH$_2$-1 and -6), 7.96 (dt, 2, J = 7.2, 1.0 Hz, CH$_2$-4), 9.00 (s, 6, (CH$_3$)$_2$C-3) [lit.[19] ν_{max} (neat) 1640, 1378, 1363, 910 cm^{-1}; ^{1}H NMR (neat) τ 3.85–4.58 (m, 2), 4.83–5.30 (m, 4), 7.97 (d with further fine splitting, 2), 9.00 (s, 6)].

1,1-Dimethyl-2-(3-propenyl)cyclopropane (14)[20] was obtained from peak B as a colorless liquid: ν_{max} 3078, 3057, 2988, 2973, 2941, 2920, 2890, 2867, 1641, 1450, 1376, 1020, 990, 907 cm^{-1}; ^{1}H NMR τ 4.06 (m, 1, CH-2′), 4.96 (m, 2, CH$_2$-3′), 7.94 (m, 2, CH$_2$-1′), 8.95 (s, 6, (CH$_3$)$_2$C-1), 9.50 (m, 2, CH-2α, and -3α), 10.06 (m, 1, CH-3β); mass spectrum, m/e (relative intensity) 110.1092 (calcd for C_8H_{14}, 110.1095), 110 (2.2), 95 (19), 81 (9), 69 (77), 68 (9), 67 (35), 66 (10), 56 (17), 55 (16), 54 (17), 53 (15), 43 (11), 41 (100), 39 (100).

2-Methyl-1,6-heptadiene (17) was obtained from peak C as a colorless liquid: ν_{max} 3077, 2974, 2937, 2860, 1641, 1446, 1375, 990, 911, 887 cm^{-1}; ^{1}H NMR τ 4.15 (m, 1, CH-6), 4.98 (m, 2, CH$_2$-7), 5.29 (br s, 2, CH$_2$-1), 7.97 (t, 4, J = 7.2 Hz, CH$_2$-3 and -5), 8.27 (s with further fine splitting, 3, CH$_3$-2), 8.46 (m, 2, CH$_2$-4) [lit.[21] ν_{max} (film) 1640, 1465, 1380, 995, 915 cm^{-1}; ^{1}H NMR τ 4.4–5.1 (m, 3), 5.37 (s, 2), 8.04 (m, 4), 8.30 (s, 3), 8.70 (m, 2)].

Diene **13** was recovered from peak D.

(3-Methyl-2-butenyl)cyclopropane (15) was obtained from peak E as a colorless liquid: ν_{max} 3079, 3005, 2975, 2925, 2913, 2882, 2857, 1443, 1375, 1012 cm^{-1}; ^{1}H NMR τ 4.76 (t with further fine splitting, 1, J = 7 Hz, CH-2′), 8.09 (m, 2, CH$_2$-1′), 8.29 (br s with fine splitting, 3, trans CH$_3$-3′), 8.39 (br s, 3, cis CH$_3$-3′), 9.27 (m, 1, CH-1α), 9.62 (m, 2, CH-2α and -3α), 9.97 (m, 2, CH-2β and -3β); mass spectrum, m/e (relative intensity) 110.1092 (calcd for C_8H_{14}, 110.1095), 110 (14), 95 (50), 93 (6), 82 (16), 81 (20), 79 (10), 78 (8), 69 (53), 68 (15), 67 (100), 66 (10), 65 (9), 56 (9), 55 (22), 54 (13), 53 (23), 51 (9), 41 (94), 39 (50).

B. In Pentane. A 110-mL solution of olefin (2.2 g) in pentane was irradiated as described above for 6 h. Preparative gas chromatography as outlined above gave **13**–**17**.

C. Sensitized. A 110-mL methanolic solution containing 2.2 g of olefin and 2.2 g of *p*-xylene was irradiated as described above for 8 h with the use of a Corex filter. The only observed result was a steady decrease in both starting olefin and sensitizer.

D. At 254 nm. A quartz tube (1-cm diameter) containing 110 mg of olefin and 5 mL of methanol was irradiated at 254 nm under an atmosphere of nitrogen for 120 h. No reaction was observed.

Irradiation of 2,5-Dimethyl-1,5-hexadiene (18). A. In Methanol. A 110-mL methanolic solution containing 2.2 g of olefin was irradiated as described above for 6 h. Gas chromatographic analysis (column C, 70

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°C) afforded two major peaks, whose constituents were collected and rechromatographed on column B (50 °C).

1-Methyl-1-(2-methyl-2-propenyl)cyclopropane (19) was obtained from peak A as a colorless liquid: ν_{max} 3075, 2998, 2963, 2949, 2913, 1647, 1450, 1385, 1374, 1012, 891 cm^{-1}; ^{1}H NMR τ 5.25 (br s, 2, CH$_2$-3′), 8.05 (s, 2, CH$_2$-1′), 8.25 (br s, 3, CH$_3$-2′), 9.02 (s, 3, CH$_3$-1), 9.70 (s, 4, CH$_2$-2 and -3); mass spectrum, *m/e* (relative intensity) 110.1092 (calcd for C$_8$H$_{14}$, 110.1095), 110 (1), 109 (1), 96 (5), 95 (63), 82 (12), 81 (38), 79 (7), 77 (5), 69 (5), 68 (18), 67 (48), 56 (13), 55 (100), 54 (10), 53 (17), 41 (35), 39 (37).

Diene 18 was obtained from peak B.

B. In Pentane. A 110-mL solution of olefin (2.2 g) in pentane was irradiated as described above for 8 h. Preparative gas chromatography as outlined above gave **18** and **19**.

2,5,6-Trimethyl-1,5-heptadiene (20). A. Synthesis. Pyrolysis of the ester formed by treatment of 2,3-dimethyl-3-buten-2-ol with diketene according to the method previously outlined[22] yielded 5,6-dimethyl-5-hepten-2-one (48% overall isolated yield) as a colorless liquid: bp 49 °C (4 mm); ν_{max} 2990, 2921, 1720, 1359, 1160 cm^{-1}; lit.[22] bp 72–74 °C (10 mm).

The anion of dimethyl sulfoxide was prepared in the usual manner from sodium hydride (0.10 mol, 4.8 g of 50% mineral oil suspension) and 50 mL of dimethyl sulfoxide. The anion was cooled in ice and treated dropwise with a solution of 37.5 g (0.100 mol) of triphenylphosphonium bromide in 110 mL of dimethyl sulfoxide over a 20-min period. The mixture was stirred at room temperature for 10 min, and then 14.0 g (0.100 mol) of ketone was added dropwise over a 20-min period with cooling. After 30 min the mixture was treated with a little water, the semicrystalline salt filtered, and the solution worked up in the usual manner by extraction with pentane. The pale yellow crude oil (13.8 g) was distilled under vacuum to give 9.8 g (71% yield) of diene **20** as a colorless liquid: bp 67 °C (25 mm); ν_{max} 3071, 2964, 2917, 2858, 1644, 1447, 1371, 1150, 883 cm^{-1}; ^{1}H NMR τ 5.30 (br s, 2, CH$_2$-1), 7.92 (m, 4, CH$_2$-3 and -4), 8.26 (br s, 3, CH$_3$-2), 8.36 (s, 9, CH$_3$-5, -6, and -6); mass spectrum, *m/e* (relative intensity) 138.1410 (calcd for C$_{10}$H$_{18}$, 138.1408), 138, (15), 123 (12), 95 (7), 83 (100), 82 (37), 81 (11), 67 (12), 55 (88), 53 (6), 43 (11), 41 (38), 39 (15).

B. Irradiation in Pentane. A 110-mL pentane solution containing 2.76 g of olefin was irradiated as described above for 4 h. Gas chromatographic analysis (column C, 55 °C) afforded five major peaks along with many minor peaks. The constituents of the major peaks were collected and rechromatographed on column B (55 °C).

1-(2-Methyl-2-propenyl)-1,2,2-trimethylcyclopropane (21) was obtained from peak A as a colorless liquid: ν_{max} 3073, 3047, 2963, 2894, 2871, 1649, 1450, 1389, 1379, 1373, 1117, 1021, 887 cm^{-1}; ^{1}H NMR τ 5.27 (m, 2, CH$_2$-3′), 7.94 (s, 2, CH$_2$-1′), 8.31 (s, 3, CH$_3$-2′), 8.91 (s, 6, (CH$_3$)$_2$C-2), 9.00 (s, 3, CH$_3$-1), 9.81 (d, 1, J = 5 Hz, CH-3), 9.87 (d, 1, J = 5 Hz, CH-3); mass spectrum, *m/e* (relative intensity) 138.1410 (calcd for C$_{10}$H$_{18}$, 138.1408), 138 (0.6), 123 (25), 95 (25), 83 (100), 82 (24), 81 (25), 67 (31), 55 (78), 43 (6), 41 (42), 39 (8).

2,5,5-Trimethyl-1,6-heptadiene (26), the first component of peak B, was obtained as a colorless liquid: ν_{max} 3080, 2962, 2866, 1642, 1450, 1378, 1373, 1362, 999, 910, 884 cm^{-1}; ^{1}H NMR τ 4.22 (dd, 1, J = 18.0, 10.0 Hz, CH-6), 5.07 (dd, 1, J = 10.0, 1.7 Hz, trans CH-7) 5.09 (dd, 1, J = 18.0, 1.7 Hz, cis CH-7), 5.34 (m, 2, CH$_2$-1), 8.08 (m, 2, CH$_2$-3), 8.29 (br s, 3, CH$_3$-2), 8.65 (m, 2, CH$_2$-4), 9.00 (s, 6, (CH$_3$)$_2$C-5); mass spectrum, *m/e* (relative intensity) 138.1404 (calcd for C$_{10}$H$_{18}$, 138.1408), 138 (0.6), 123 (12), 110 (6), 109 (5), 96 (8), 95 (44), 83 (14), 82 (26), 81 (29), 79 (8), 70 (30), 69 (87), 68 (19), 67 (58), 57 (6), 56 (6), 55 (71), 53 (18), 44 (17), 41 (100), 39 (31).

1-(2,3-Dimethyl-3-butenyl)-1-methylcyclopropane (25), the second component of peak B, was obtained as a colorless liquid: ν_{max} 3070, 2958, 2913, 2868, 1640, 1450, 1381, 1370, 1004, 884 cm^{-1}; ^{1}H NMR τ 5.29 (m, 2, CH$_2$-4′), 7.61 (q with further fine splitting, 1, J = 6.5 Hz, CH-2′), 8.82 (m, 3, CH$_3$-3′), 8.96 (d, 3, J = 6.5 Hz, CH$_3$-2′), 8.97 (s, 3, CH$_3$-1), 9.78 (m, 4, CH$_2$-2 and -3); mass spectrum, *m/e* (relative intensity) 138.1410 (calcd for C$_{10}$H$_{18}$, 138.1408), 138 (9), 123 (46), 110 (12), 109 (32), 96 (19), 95 (61), 83 (29), 82 (61), 81 (39), 79 (9), 70 (92), 69 (100), 68 (24), 67 (62), 55 (70), 53 (16), 41 (100), 39 (27).

2,3,3,5-Tetramethyl-1,5-hexadiene (23), the first component of peak C, was obtained as a colorless liquid: ν_{max} 3087, 3072, 2963, 2916, 2872, 1635, 1443, 1372, 887 cm^{-1}; ^{1}H NMR τ 5.23 and 5.37 (2 m, 2, CH$_2$-1), 5.26 (s with further fine splitting, 2, CH$_2$-6), 7.89 (s, 2, CH$_2$-4), 8.22 and 8.29 (2 s with further fine splitting, 6, CH$_3$-2 and -5), 8.94 (s, 6, (CH$_3$)$_2$C-3); mass spectrum, *m/e* (relative intensity) 138.1406 (calcd for C$_{10}$H$_{18}$, 138.1408), 138 (2), 123 (10), 95 (5), 84 (5), 83 (68), 82 (26), 81 (10), 67 (24), 56 (6), 55 (100), 53 (7), 44 (13), 42 (38), 41 (51).

2,3,6-Trimethyl-1,6-heptadiene (24), the second component of peak C, was obtained as a colorless liquid: ν_{max} 3077, 2964, 2932, 2871, 1643, 1446, 1372, 885 cm^{-1}; ^{1}H NMR τ 5.31 (br s, 4, CH$_2$-1 and -7), 7.94 (m, 3, CH-3 and CH$_2$-5), 8.29 (br s, 3, CH$_3$-6), 8.34 (t, 3, J = 1.0 Hz, CH$_3$-2), 8.98 (d, 3, J = 7.0 Hz, CH$_3$-3); mass spectrum, *m/e* (relative intensity) 138.1405 (calcd for C$_{10}$H$_{18}$, 138.1408), 138 (2), 123 (16), 110 (10), 109 (12), 96 (8), 95 (31), 83 (12), 82 (55), 81 (25), 79 (7), 71 (6), 70 (97), 69 (28), 68 (24), 67 (76), 65 (5), 56 (7), 55 (83), 54 (9), 53 (19), 51 (5), 43 (10), 42 (20), 41 (100), 39 (38).

1-(2,3-Dimethyl-2-butenyl)-1-methylcyclopropane (22), the major component of peak D, was obtained as a colorless liquid: ν_{max} 3068, 2991, 2914, 2859, 1448, 1380, 1370, 1007 cm^{-1}; ^{1}H NMR τ 7.96 (s, 2, CH$_2$-1′), 8.34 (s, 9, CH$_3$-2′, -3′, and -3′), 9.08 (s, 3, CH$_3$-1α), 9.68 (d with further fine splitting, 2, J = 7.2 Hz, CH-2α and -3α), 9.84 (d with further fine splitting, 2, J = 7.2 Hz, CH-2β and -3β); mass spectrum, *m/e* (relative intensity) 138.1405 (calcd for C$_{10}$H$_{18}$, 138.1408), 138 (13), 123 (10), 110 (5), 94 (6), 93 (33), 92 (5), 91 (5), 83 (68), 82 (27), 81 (23), 79 (10), 77 (6), 69 (8), 67 (39), 65 (6), 56 (6), 55 (100), 53 (14), 44 (13), 43 (13), 41 (50), 39 (29).

Diene 20 was obtained from peak E.

C. Irradiation in Methanol. A 110-mL methanolic solution containing 2.76 g of olefin was irradiated as described abover for 1.5 h. Preparative gas chromatography as outlined in part A yielded **20**–**24** and **26**. Late eluents from column C, which were a complex mixture of methyl ethers (30%), were not further investigated.

Irradiation of *cis*-2,6-Dimethyl-2,6-octadiene (27c). A. In Pentane. A 110-mL pentane solution containing 2.76 g of olefin was irradiated as described above from 3 h. Gas chromatographic analysis (column C, 80 °C) afforded five major peaks and at least seven minor peaks. The constitutents of the major peaks were collected and rechromatographed on column B (70 °C).

1,1-Dimethyl-2-(1,2-dimethyl-2-propenyl)cyclopropane (30) was obtained from peak A as a colorless liquid: ν_{max} 3083 (sh), 3069 (sh), 3054, 2964, 2943, 2871, 1644, 1454, 1378, 1124, 1072, 1020, 889 cm^{-1}; ^{1}H NMR τ 5.28 (m, 2, CH$_2$-3′), 8.25 (s with fine splitting, 3, CH$_3$-2′), 8.37 (m, 1, CH-1′), 8.89 (d, 3, J = 6.5 Hz, CH$_3$-1′), 8.96 (s, 3, CH$_3$-1α), 8.99 (s, 3, CH$_3$-1β), 9.52 (m, 2, CH-2α and -3α), 10.09 (m, 1, CH-3β); mass spectrum, *m/e* (relative intensity) 138.1409 (calcd for C$_{10}$H$_{18}$, 138.1408), 138 (3), 123 (33), 109 (6), 95 (36), 82 (64), 81 (30), 79 (5), 70 (13), 69 (72), 67 (91), 55 (28), 53 (14), 43 (11), 41 (100), 39 (32).

Peak B (21.1%) was one peak on columns A, B, and C yet possessed a ^{1}H NMR spectrum which indicated a mixture of at least two compounds. The major component (80%) was identified as ***cis*-1-methyl-1-(3-methyl-2-butenyl)-2-methylcyclopropane (28c)**: ^{1}H NMR τ 4.79 (t with further fine splitting, 1, J = 7 Hz, CH-2′), 7.98 and 8.12 (2 d, 2, J = 7 Hz, CH$_2$-1′), 8.27 (s, 3, trans CH$_3$-3′), 8.38 (s, 3, cis CH$_3$-3′), 8.92 (d, 3, J = 6 Hz, CH$_3$-2β), 9.04 (s, 3, CH$_3$-1α), 9.54 (m, 2, CH-2α and -3α), 10.11 (m, 1, CH-3β).

2,3,6-Trimethyl-1,5-heptadiene (29) was obtained from peak C as a colorless liquid: ν_{max} 3070, 3064, 2923, 2912, 1641, 1449, 1374, 895 cm^{-1}; ^{1}H NMR τ 4.89 (m, 1, CH-5), 5.29 (s with fine splitting, 2, CH$_2$-1), 7.94 (br m, 3, CH-3 and CH$_2$-4), 8.31 (s with fine splitting, 6, CH$_3$-2 and trans CH$_3$-6), 8.39 (s, 3, cis CH$_3$-6), 9.00 (d, 3, J = 6.4 Hz, CH$_3$-3) [lit.[23] ν_{max} (film) 1650, 890, 830 cm^{-1}; ^{1}H NMR (CCl$_4$) τ 5.0 (br, 1), 5.4 (s, 2), 7.85 (m, 1), 8.0 (m, 2), 8.35 (s, 6), 8.45 (s, 3), 9.05 (d, 3).

Diene 27c was recovered from peak D as a colorless liquid.

***trans*-2,6-Dimethyl-2,6-octadiene (27t)** was obtained from peak E as a colorless liquid: ν_{max} 3021, 2966, 2916, 2858, 1670, 1445, 1377, 1105, 830 cm^{-1}; ^{1}H NMR τ 4.81 (m, 2, CH-3 and -7), 7.97 (br s, 4, CH$_2$-4 and -5), 8.31 (s, 3, trans CH$_3$-2), 8.39 (s with fine splitting, 6, cis CH$_3$-2 and CH$_3$-6), 8.43 (d, 3, J = 7.2 Hz, CH$_3$-7).

B. In Methanol. A quartz tube (1-cm diameter) containing 145 mg of olefin (freshly distilled from LiAlH$_4$ and then collected by preparative gas chromatography from column A) and 5 mL of methanol was irradiated under an atmosphere of nitrogen in a Rayonet reactor for 120 h. Gas chromatographic analysis (column C, 80 °C) afforded two major peaks and three minor ones (<0.1%). None of the minor peaks was present in the chromatogram from the full-arc irradiation described in part A. The major peaks were the starting olefin (65%) and its trans isomer (**27t**, 35%).

C. Sensitized. A 110-mL methanolic solution containing 2.76 g of olefin and 2.2 g of *p*-xylene was irradiated for 8 h as described above with the use of a Corex filter. Gas chromatographic analysis (column C, 80 °C) revealed the presence of a 1:1 ratio of cis and trans isomers of 2,6-dimethyl-2,6-octadiene.

***cis*-3,7-Dimethyl-1-methoxy-2,6-octadiene (31c). A. Synthesis.** A solution of 15.4 g (0.100 mol) of *cis*-3,7-dimethyl-2,6-octadien-1-ol and sodium hydride (24 g of a 50% mineral oil suspension, 0.50 mol) in ether

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(22) W. Kimel, J. D. Surmatis, J. Weber, G. O. Chase, N. W. Sax, and A. Ofner, *J. Org. Chem.*, **22**, 1611 (1957).

(23) S. Watanabe, K. Suga, and T. Fujita, *Synthesis*, 375 (1971).

was stirred for 10 min and then treated dropwise with 28.4 g (0.200 mol) of methyl iodide over a 10-min period according to the procedure outlined for the preparation of geranyl methyl ether.[24] The reaction mixture was stirred at room temperature for 48 h and then worked up in the usual manner. Distillation of the crude product afforded 15.7 g of ether **31c** as a colorless liquid: bp 93 °C (10 mm); ν_{max} 2968, 2917, 2857, 2818, 1665, 1447, 1383, 1377, 1184, 1098, 1016, 952, 913 cm^{-1}; ^{1}H NMR τ 4.63 (t, 1, J = 7.0 Hz, CH-2), 4.88 (br s, 1, CH-6), 6.08 (d, 2, J = 7.0 Hz, CH$_2$-1), 6.67 (s, 3, OCH$_3$), 7.91 (d, 2, CH$_2$-4 and -5), 8.23 (dd, 3, J = 2.2, 0.8 Hz, CH$_3$-3), 8.30 (s, 3, trans CH$_3$-7), 8.38 (s, 3, cis CH$_3$-7); mass spectrum, m/e (relative intensity) 168.1515 (calcd for $C_{11}H_{20}O$, 168.1514), 168 (17), 153 (7), 136 (32), 121 (48), 111 (20), 107 (14), 98 (30), 94 (14), 93 (92), 92 (16), 91 (19), 85 (25), 83 (12), 81 (24), 80 (33), 79 (22), 77 (14), 69 (100), 68 (38), 67 (39), 55 (14), 53 (15), 41 (82), 39 (18).

B. Irradiation. A 110-mL pentane solution containing 1.68 g of olefin was irradiated as described above for 2 h. Gas chromatographic analysis (column A, 98 °C) afforded seven peaks in addition to a number of early eluting peaks (approximately 11%) which were not further investigated. The constituents of the seven peaks were collected and rechromatographed on column B (110 °C).

3-(Methoxymethyl)-2,4,4-trimethyl-1,5-hexadiene (35) was obtained from peak A as a colorless liquid: ν_{max} 3072, 2970, 2924, 2895, 2876, 2811, 1639, 1460, 1450, 1415, 1379, 1363, 1119, 1004, 914, 896 cm^{-1}; ^{1}H NMR τ 4.12 (m, 1, CH-5), 5.08 (m, 4, CH$_2$-1 and CH$_2$-6), 6.53 and 6.54 (2 d, 2, J = 5.6, 9.0 Hz, CH$_2$OCH$_3$), 6.68 (s, 3, OCH$_3$), 7.74 (dd, 1, J = 5.6, 9.0 Hz, CH-3), 8.24 (s with fine splitting, 3, CH$_3$-2), 8.96 and 8.99 (2 s, 6, (CH$_3$)$_2$C-4); mass spectrum, m/e (relative intensity) 168.1512 (calcd for $C_{11}H_{20}O$, 168.1514), 168 (1), 153 (5), 136 (8), 125 (7), 123 (16), 121 (24), 107 (10), 99 (16), 93 (39), 85 (26), 81 (13), 80 (14), 79 (10), 69 (100), 68 (44), 67 (38), 55 (11), 53 (14), 45 (21), 44 (25), 41 (60), 40 (48), 39 (16).

2,6-Dimethyl-3-(methoxymethyl)-1,5-heptadiene (34) was obtained from peak B as a colorless liquid: ν_{max} 3076, 2974, 2920, 2895, 2875, 2826, 1643, 1450, 1375, 1193, 1120, 955, 890 cm^{-1}; ^{1}H NMR τ 4.91 (m, 1, CH-5), 5.16 and 5.24 (2 s with fine splitting, 2, CH$_2$-1), 6.64 (m, 2, C*H*$_2$OCH$_3$), 6.65 (s, 3, OCH$_3$), 7.66 (m, 1, CH-3), 7.90 (m, 2, CH$_2$-4), 8.30 (s, 6, CH$_3$-2 and trans CH$_3$-6), 8.39 (s, 3, cis CH$_3$-6); mass spectrum, m/e (relative intensity) 168.1512 (calcd for $C_{11}H_{20}O$, 168.1514), 168 (05), 153 (3), 136 (28), 125 (17), 123 (26), 121 (28), 107 (8), 99 (14), 95 (10), 94 (10), 93 (62), 92 (17), 91 (14), 85 (25), 81 (26), 80 (12), 79 (18), 77 (11), 69 (100), 68 (38), 67 (33), 55 (15), 53 (16), 45 (35), 43 (11), 41 (85), 39 (21).

***cis*-2-(Methoxymethyl)-1-methyl-1-(3-methyl-2-butenyl)cyclopropane (33c)** was obtained from peak C as a colorless liquid: ν_{max} 3061, 2973, 2922, 2868, 2814, 1447, 1408, 1376, 1200, 1106, 1015 cm^{-1}; ^{1}H NMR τ 4.80 (t, 1, J = 7.0 Hz, CH-2′), 6.59 (d, 2, J = 7.2 Hz, C*H*$_2$OCH$_3$), 6.64 (s, 3, OCH$_3$), 7.98 (d, 2, J = 7.0 Hz, CH$_2$-1′), 8.27 (s, 3, trans CH$_3$-3′), 8.38 (s, 3, cis CH$_3$-3′), 8.98 (s, 3, CH$_3$-1α), 9.12 (m, 1, CH-2α), 9.50 (dd, 1, J = 7.7, 4.7 Hz, CH-3α), 9.81 (dd, 1, J = 5.3 and 4.7 Hz, CH-3β); mass spectrum, m/e (relative intensity) 168.1512 (calcd for $C_{11}H_{20}O$, 168.1514), 168 (3), 136 (67), 123 (9), 121 (37), 112 (41), 111 (9), 107 (15), 105 (12), 99 (17), 97 (17), 96 (56), 95 (33), 94 (13), 93 (100), 92 (14), 91 (24), 82 (10), 81 (100), 80 (21), 79 (35), 77 (19), 71 (10), 69 (50), 68 (24), 67 (58), 65 (9), 55 (25), 53 (19), 45 (20), 43 (15), 41 (62), 39 (21).

Peak D afforded two peaks on column B; the ^{1}H NMR of the first peak (1%) indicated that it contained at least three compounds, two of which were probably the cis and trans isomers of **1-methoxy-3,5,5-trimethyl-2,6-heptadiene (57)**: ^{1}H NMR τ 4.12 (2 d, C*H*=CH$_2$), 5.08 (m, CH=C*H*$_2$), 6.08 (2 d, C*H*$_2$OCH$_3$), 8.23 (s, CH$_3$ cis to H and trans to CH$_2$OCH$_3$), 8.33 (s, CH$_3$ trans to H and cis to CH$_2$OCH$_3$).

The second peak of peak D yielded a colorless oil liquid which could clearly be seen from its ^{1}H NMR spectrum to be a 1.1:1 mixture of ***trans*-2-methoxy-1-methyl-1-(3′-methyl-2′-butenyl)cyclopropane (33t)** [^{1}H NMR τ 4.82 (t, 1, J = 7.0 Hz, CH-2′), 6.59 (m, 2, C*H*$_2$OCH$_3$), 6.64 (s, 3, OCH$_3$), 7.97 (m, 2 CH$_2$-1′), 8.28 (s, 3, trans CH$_3$-3′), 8.40 (s, 3, cis CH$_3$-3′), 8.96 (s, 3, CH$_3$-1α), 9.92 (m, 1, CH-3α)] and ***cis*-1,1-dimethyl-2-(4-methoxy-2-methyl-2-butenyl)cyclopropane (32c)** [^{1}H NMR τ 4.63 (*t*, 1, J = 6.8 Hz, CH-3′), 6.07 (d, 2, J = 6.8 Hz, C*H*$_2$OCH$_3$), 6.66 (s, 3, OCH$_3$), 7.97 (m, 2, CH$_2$-1′), 8.18 (s, 3, CH$_3$-2′), 8.93 and 8.96 (2 s, 6, (CH$_3$)$_2$C-1)].

***trans*-1,1-Dimethyl-2(4-methoxy-2-methyl-2-butenyl)cyclopropane (32t)**, the major component of peak E, was obtained as a colorless liquid: ν_{max} 3055, 2987, 2941, 2922, 2891, 2869, 2818, 1667, 1447, 1372, 1120, 1105, 1091, 1020, 950, 908 cm^{-1}; ^{1}H NMR τ 4.55 (t, 1, J = 6.9 Hz, CH-3′), 6.02 (d, 2, J = 6.9 Hz, C*H*$_2$*OCH*$_3$), 6.65 (s, 3, OCH$_3$), 7.96 (d, 2, J = 6.8 Hz, CH$_2$-1′), 8.29 (s, 3, CH$_3$-2′), 8.96 and 8.97 (2 s, 6, (CH$_3$)$_2$C-1), 9.47 (m, 2, CH-2α and -3α), 10.06 (m, 1, CH-3β); mass spectrum, m/e (relative intensity) 153.1277 (calcd for $C_{10}H_{17}O$, 153.1279), 153 (4), 136 (26), 123 (25), 121 (65), 119 (11), 111 (14), 109 (12), 108 (12), 107 (30), 105 (13), 97 (29), 95 (39), 94 (22), 93 (75), 92 (18), 91 (30), 85 (100), 83 (13), 82 (12), 81 (60), 80 (30), 79 (48), 77 (24), 69 (98), 68 (30), 67 (52), 55 (52), 53 (25), 45 (36), 44 (24), 43 (26), 41 (100).

Diene 31c was recovered from peak F, and diene **31t** was obtained from peak G as a colorless liquid whose spectral data and gas chromatographic retention time were identical with those of an authentic sample whose preparation is described below.

***trans*-3,7-Dimethyl-1-methoxy-2,6-octadiene (31t). A. Synthesis.** A 7.7-g (0.05 mol) sample of *trans*-3,7-dimethyl-2,6-octadien-1-ol was treated in a manner identical with that described above to give 6.0 g of diene **31t** as a colorless liquid: bp 85 °C (4.2 mm); ν_{max} 2970, 2922, 2857, 2820, 1667, 1447, 1383, 1377, 1205, 1179, 1123, 1105, 1087, 952, 912 cm^{-1}; ^{1}H NMR τ 4.63 (t, 1, J = 7.0 Hz, CH-2), 4.88 (br s, 1, CH-6), 6.05 (d, 2, J = 7.0 Hz, CH$_2$-1), 6.66 (s, 3, OCH$_3$), 7.92 (m, 4, CH$_2$-4 and -5), 8.31 (s, 6, CH$_3$-3 and trans CH$_3$-7), 8.39 (s, 3, cis CH$_3$-7) [lit.[24] bp 92–97 °C (20 mm); ν_{max} 2899, 1667, 1445, 1374, 1205, 1176, 1124, 1105, 1087, 957, 914, 830 cm^{-1}; ^{1}H NMR τ 4.70 (t, J = 7 Hz, 1), 4.95 (br, 1), 6.12 (d, J = 7 Hz, 2), 6.74 (s, 3), 8.33 (s, 6), 8.40 (s, 3)].

B. Irradiation. A 110-mL pentane solution containing 1.6, g of olefin was irradiated as described above for 2 h. Gas chromatographic analysis (column A, 98 °C) revealed the same seven peaks as observed in the irradiation of the cis isomer, but in different proportions. As in the case of the cis isomer there were early eluting peaks (~11%) which were not further investigated. Analysis as previously described for the cis isomer revealed the presence of **31–35**.

Irradiation of 2-Methyl-2-heptene (36). A 110-mL methanolic solution containing 2.24 g of olefin was irradiated as described abover for 8 h. Gas chromatographic analysis (column B, 45 °C) revealed six early eluting peaks and five later peaks. The major peaks were collected and rechromatographed (column C, 70 °C).

2-Methylheptane (37), obtained in 2% yield from peak C, possessed a retention time and infrared spectrum identical with those of authentic 2-methylheptane prepared by hydrogenation of olefin **36** as described below.

2-Methyl-1-heptene (38) was obtained from peak E in 16% yield as a colorless liquid: ν_{max} 3075, 2960, 2933, 2875, 2862, 1648, 1450, 1475, 888 cm^{-1}; ^{1}H NMR τ 5.30 (br s, 2, CH$_2$-1), 7.99 (t, 2, J = 7.0 Hz, CH$_2$-3), 8.27 (br s, 3, CH$_3$-2), 9.10 (t, 3, J = 6. 2 Hz, CH$_3$-6).

Olefin 36 was recovered in 18% yield from peak F.

3-Methoxy-2-methyl-1-heptene (39) was obtained in 4% yield from peak H as a colorless liquid: ν_{max} 3076, 2960, 2936, 2876, 2862, 2822, 1648, 1469, 1449, 1373, 1127, 1093, 902 cm^{-1}; ^{1}H NMR τ 5.07 (br s, 2, CH$_2$-1), 6.50 (m, 1, CH-3), 6.77 (s, 3, OCH$_3$), 8.35 (br s, 3, CH$_3$-2), 9.10 (br t, 3, J = 6.5 Hz, CH$_3$-6); mass spectrum, m/e (relative intensity) 142.1360 (calcd for $C_9H_{12}O$, 142.4358), 85 (100), 55 (32).

3-Methoxy-2-methylheptane (40) was obtained in 1% yield from peak I as a colorless liquid: ν_{max} 2961, 2933, 2876, 2822, 1468 1468, 1455, 1386, 1378, 1366, 1150, 995 cm^{-1}; ^{1}H NMR τ 6.63 (s, 3, OCH$_3$), 7.11 (m, 1, CH-3), 8.18 (m, 1, CH-2), 9.12 (dd, 6, J = 7.0, 2.0 Hz, (CH$_3$)$_2$C-2); mass spectrum, m/e (relative intensity) 144.1514 (calcd for $C_9H_{20}O$, 144.1514), 101 (100), 87 (58), 85 (21), 69 (87), 59 (17), 55 (39).

2-Methoxy-2-methylheptane (41) was obtained from peak K in 1% yield as a colorless liquid: ν_{max} 2962, 2935, 2877, 2865, 2830, 1470, 1460, 1383, 1367, 1215, 1086 cm^{-1}; ^{1}H NMR τ 6.80 (s, 3, OCH$_3$), 8.86 (s, 6, (CH$_3$)$_2$C-2), 9.10 (br t, 3, J 6.5 Hz, CH$_3$-6); mass spectrum, m/e (relative intensity) 129.1276 (calcd for $C_7H_{15}O$, 129.1274), 73 (100), 59 (12), 56 (14), 55 (16).

Hydrogenation of 2-methyl-2-heptene (36). A mixture of 200 mg of 2-methyl-2-heptene and 20 mg of 5% palladium-on-charcoal in 10 mL of methanol was stirred under a atmosphere of hydrogen for 3 h. The solution was filtered and the products extracted into pentane. The pentane was removed from the dried solution by distillation to yield 190 mg of **2-methylheptane (37)** as a colorless liquid: ν_{max} 2958, 2927, 2874, 2858 1462, 1379, 1361 cm^{-1}; ^{1}H NMR τ 9.13 (d, 6, J = 6 Hz, CH$_3$-1 and -2).

Irradiation of 2,3-Dimethyl-2-heptene (42). A 110-mL methanolic solution containing 2.5 g of olefin was irradiated as described above for 1 h. Gas chromatographic analysis (column C, 80 °C) afforded three early peaks and four late peaks whose constituents were collected and rechromatographed on column B.

2,3-Dimethylheptane (43) was obtained in 13% yield from peak A as a colorless liquid whose physical properties were identical with those of an authentic specimen prepared as described below.

The second peak (5% yield) appeared to be a mixture of **2,3-dimethyl-1-heptene (44)** and **2-methyl-3-methyleneheptane (45)** which could not be separated.

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(24) M. A. Schwartz and T. J. Dunn, *J. Am. Chem. Soc.*, **94**, 4205 (1972).

Olefin 42 was recovered in 29% yield from peak C.

2,3-Dimethyl-3-methoxyheptane (46) was obtained in 10% yield from peak D as a colorless liquid: ν_{max} 2962, 2947, 2876, 2826, 1467, 1385, 1379, 1369, 1089, 1073 cm^{-1}; ^{1}H NMR τ 6.86 (s, 3, OCH_3), 8.19 (m, 1, CH-3), 8.69 (m, 6, CH_2-4, -5, and -6), 9.01 (s, 3, CH_3-3), 9.12 and 9.16 (2 d, 6, $J = 6.8$ Hz, $(CH_3)_2C$-2); mass spectrum, m/e (relative intensity) 143.1438 (calcd for $C_9H_{19}O$, 143.1437), 143 (5), 126 (5), 116 (9), 115 (100), 113 (9), 102 (6), 101 (92), 85 (6), 84 (9), 83 (28), 73 (12), 71 (7), 70 (5), 69 (48), 67 (5), 59 (45), 57 (9), 55 (38), 45 (12), 43 (16), 41 (35), 39 (9).

2,3-Dimethyl-2-methoxyheptane (47) was obtained in 13% yield from peak E as a colorless liquid: ν_{max} 2967, 2935, 2876, 2864, 2827, 1467, 1384, 1372, 1364, 1144, 1088, 1073 cm^{-1}; ^{1}H NMR τ 6.83 (s, 3, OCH_3), 8.93 (s, 6, $(CH_3)_2C$-2), 9.10 (br t, 3, $J = 6.2$ Hz, CH_3-6), 9.15 (d, 3, $J = 6.2$ Hz, CH_3-3); mass spectrum, m/e (relative intensity) 143.1438 (calcd for $C_9H_{19}O$, 143.1439), 143 (4), 72 (5), 73 (100), 70 (10), 69 (10), 59 (6), 55 (11), 43 (9), 41 (16).

2,3-Dimethyl-3-methoxy-1-heptene (48) was obtained in 12% yield from peak F as a colorless liquid: ν_{max} 3093, 2962, 2940, 2876, 2827, 1643, 1370, 1168, 1126, 1090, 1073, 901 cm^{-1}; ^{1}H NMR τ 5.02 and 5.12 (2 s with further fine splitting, 2, CH_2-1), 6.91 (s, 3, OCH_3), 8.31 (s with further fine splitting, 3, CH_3-2), 8.75 (s, 3, CH_3-3), 9.10 (br t, 3, $J = 6.6$ Hz, CH_3-6); mass spectrum, m/e (relative intensity) 156.1513 (calcd for $C_{10}H_{20}O$, 156.1514), 156 (2), 141 (6), 124 (6), 115 (14), 109 (9), 100 (8), 99 (100), 95 (7), 83 (8), 82 (10), 81 (6), 73 (11), 69 (30), 67 (22), 59 (10), 55 (14), 45 (8), 43 (10), 41 (30), 39 (10).

2-Methoxy-2-methyl-3-methyleneheptane (49) was obtained in 7% yield from peak G as a colorless liquid: ν_{max} 3093, 2980, 2958, 2933, 2872, 2865, 2823, 1637, 1375, 1360, 1172, 1143, 1073, 800 cm^{-1}; ^{1}H NMR τ 4.97 and 5.04 (2 s with further fine splitting, 2, $=CH_2$), 6.94 (s, 3, OCH_3), 7.98 (br m, 2, CH_2-4), 8.54 (br m, 4, CH_2-5 and -6), 8.70 (s, 6, $(CH_3)_2C$-2), 9.06 (br t, 3, $J = 6.5$ Hz, CH_3-6); mass spectrum, m/e (relative intensity) 156.1513 (calcd for $C_{10}H_{20}O$, 156.1514), 156 (1), 141 (22), 124 (4), 109 (6), 100 (6), 99 (70), 83 (14), 82 (19), 81 (10), 73 (100), 72 (7), 69 (20), 67 (35), 55 (21), 53 (9), 43 (16), 41 (34), 39 (17).

Hydrogenation of 2,3-Dimethyl-2-heptene (42). A mixture of 200 mg of 2,3-dimethyl-2-heptene and 20 mg of 10% palladium-on-charcoal in 5 mL of methanol was stirred under an atmosphere of hydrogen for 2 h. The solution was filtered and the products extracted into pentane. The pentane was removed from the dried solution by distillation to yield 190 mg of 2,3-dimethylheptane (**43**) as a colorless liquid: ν_{max} 2960, 2931, 2875, 1462, 1385, 1375, 1365 cm^{-1}; ^{1}H NMR τ 9.14 and 9.21 (2 d, 6, $J = 6.4$ Hz, $(CH_3)_2C$-2), 9.18 (s, 3, CH_3-3).

Irradiation of 1,5-Cyclooctadiene (50). A 110-mL solution of olefin (2.16 g) in pentane was irradiated for 4 h as described above. A heavy white precipitate was evident on the probe after 2 h and gas chromatographic analysis (column B, 65 °C) revealed little change from the 2- to 4-h aliquots. The constituents of the four major peaks were collected and rechromatographed (column C, 75 °C).

***trans*-1,2-Diethenylcyclobutane (53t)** was obtained from peak A in 1% yield as a colorless liquid: ν_{max} 3082, 2978, 2942, 2908, 2866, 1826, 1636, 1442, 1421, 1413, 991, 913 cm^{-1}; ^{1}H NMR τ 4.10 (m, 2, $(CH{=}CH_2)$-1 and -2), 5.04 (m, 4, $(CH{=}CH_2)$-1 and -2), 7.31 (br s, 2, CH-1 and -2), 8.14 (m, 4, CH_2-3 and -4) [lit.[25] ν_{max} (CCl_4) 3084, 3072, 2996, 2980, 2940, 2905, 2866, 1826, 1635, 1460, 1441, 1422, 1414, 1289, 1235, 1111, 990, 912 cm^{-1}; lit.[26] ^{1}H NMR τ 4.1–4.7 and 5.2–5.5 (m, 6), 7.6 (br, 2), 8.4 (m, 4).

***cis*-1,2-Diethenylcyclobutane (53c)** was obtained from peak B in 2% yield as a colorless liquid: ν_{max} 3080, 3001, 2979, 2947, 2913, 2865, 1636, 993, 912 cm^{-1}; ^{1}H NMR τ 4.06 (m, 2, $(CH{=}CH_2)$-1 and -2), 5.02 (m, 4, $(CH{=}CH_2)$-1 and -2), 6.88 (br s, 2, CH-1 and -2), 7.96 (m, 4, CH_2-3 and -4) [lit.[26] ^{1}H MR τ 3.8–4.7 and 5.0–5.5 (m, 6), 7.0–7.5 (br, 2), 8.0–8.7 (m, 4)].

***syn*-2-Ethenylbicyclo[3.1.0]hexane (51),** the first component of peak C, was obtained in 3% yield as a colorless liquid: ν_{max} 3070, 3037, 3003, 2948, 2933, 2865, 1638, 1469, 1451, 1027, 991, 911 cm^{-1}; ^{1}H NMR τ 4.14 (m, 1, $(CH{=}CH_2)$-2), 4.96 (m, 2, $(CH{=}CH_2)$-2), 7.25 (br s, 1, CH-2), 8.7 (m, 6, CH_2-3 and -4 and CH-5 and *exo*-CH-6), 9.74 (m, 2, CH-1 and *endo*-CH-6); mass spectrum, m/e (relative intensity) 108.0941 (calcd for C_8H_{12}, 108.0939), 108 (5), 107 (5), 94 (6), 93 (71), 91 (32), 80 (45), 79 (100), 78 (19), 77 (35), 67 (52), 66 (27), 65 (17), 54 (31), 53 (12), 52 (5) 51 (9), 41 (32), 39 (30) [lit.[12] ^{1}H NMR τ 4.31, 5.09, 7.28, 8.5, 9.83.

The syn stereochemistry was confirmed by hydrogenation to *syn*-2-ethylbicyclo[3.1.0]hexane.[16]

4-Ethenylcyclohexene (52), the second component of peak C, was obtained in 3% yield as a colorless liquid whose gas chromatographic retention times and spectral data were identical with those of a commercial sample.

Peak D (1%) contained four constituents which were not further investigated. Diene **50** was recovered in 79% yield as the major component of peak E.

Quantum Yield Determination. A solution of 235 mg (2.85 mmol) of freshly distilled diene **1** in 15 mL of pentane containing a hydrocarbon internal standard was deaerated for 15 min with nitrogen bubbling and irradiated for 32 h in a 1.4 cm × 21 cm Suprasil tube by using an RPR-100 Rayonet photochemical reactor equipped with a circular array of 16 RPR-1849 Å/2537 Å lamps. A quantum yield of 0.2 was determined for the formation of **2**, with the conversion of cycloheptene to methylenecyclohexane as actinometer.[27,28] No detectable isomerization was observed on irradiation of diene **1** for 150 h under similar conditions at 254 nm.

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