Photochemistry of Cycloalkenes. V. Effects of Ring Size and Substitution[1]

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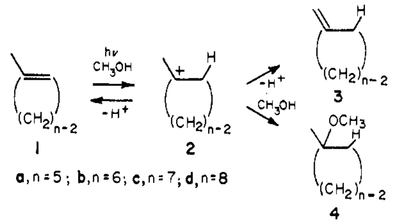
Abstract: The effects of ring size and substitution on the photochemical behavior of cyclic olefins have been investigated. Cyclohexene and -heptene undergo photosensitized addition of methanol in a fashion similar to that of the 1-methyl and 1-methoxyl analogs, but only in the presence of added mineral acid. Photoprotonation of the 1-phenyl derivatives **9b** and **c** can be readily effected in methanol by either direct irradiation or sensitization with acetophenone, but in either case added acid is required. By contrast, 1-methylcyclopentene showed no tendency to undergo photoprotonation under conditions in which 1-methylcyclohexene underwent extensive protonation. The photoproducts from 1-methylcyclopentene, methylenecyclopentane and methylcyclopentane, apparently arise *via* a radical process. Radical behavior is also exhibited by 2-norbornene (**12**), which affords a mixture of norbornanemethanol (**16**), 2,2′-binorbornane (**17**), and norbornane (**18**), as well as the photodimers **13** and **14**. Analogous behavior is exhibited by the 2-methyl derivative **22**, which affords a mixture of 2-methylnorbornane (**23**), 2-methylenenorbornane (**24**), and the mixture of methanol adducts **25**. Extension of the study to other bicyclic systems revealed that bicyclo[2.2.2]oct-2-ene (**8**) is photostable in acidic methanol, the bicyclo[3.1.1]hept-2-ene analog α-pinene (**28**) undergoes isomerization to *cis*-ocimene (**29**) under a variety of conditions, and the homologous bicyclo[3.2.1]oct-2-ene (**35**) undergoes facile photoprotonation in acetic acid or acidic methanol or *t*-butyl alcohol. Thus, aside from the two exceptions of bicyclo[2.2.2]oct-2-ene (**8**) and α-pinene (**28**), the photochemical behavior of cyclic olefins is a subtle function of the degree of flexibility available about the double bond, with radical behavior being exhibited by more highly constrained olefins and ionic behavior by olefins having approximately the same flexibility as cyclohexene or -heptene. The mechanistic implications of these results are discussed.

Recent studies have shown that irradiation of alcoholic solutions of 1-alkylcyclohexenes and -heptenes (*cf.* **1**) in the presence of aromatic hydrocarbon photosensitizers such as benzene, toluene, or xylene results in protonation of the double bond followed by three competing processes: (a) formation of the corresponding exocyclic isomer **3**, (b) addition of solvent to afford a tertiary cycloalkyl ether (**4**), and (c) regeneration of the starting olefin **1**.[2,3] By contrast, larger ring cycloalkenes and their acyclic analogs, which are well known to undergo facile *cis–trans* photoisomerization,[4] show no evidence of either isomerization or ether formation under these conditions.[2] The difference in behavior of these various systems is thus apparently related to the relative ease with which the carbon skeleton can accommodate an orthogonally oriented π,π^* triplet species and, perhaps, a *trans*-substituted double bond, although it is not clear from the available data which of these species is the reactive intermediate.[2] We wish now to report additional studies on the effects of substitution and ring size which considerably extend the previous results and afford important information on the mechanism of the photoprotonation reaction.



Unsubstituted Cycloalkenes. In contrast to the corresponding 1-methylcycloalkenes **1**, the unsubstituted analogs **5** undergo very inefficient protonation on irradiation in xylene–methanol mixtures. As shown in Table I, in the case of cyclohexene competing cyclodimerization is the major course of reaction. Dimerization is likewise the only observable reaction for cycloheptene but is a significantly slower process in this case.[5]

Table I. Irradiation of Cycloalkenes **5**[a]

Olefin (*n*)	Solvent	Sensitizer	Time, hr	Yield, %[b] **5**	**6**	Dimer
5b (6)	CH_3OH	Xylene	8	17	*c*, *d*	72[e]
	H^+, CH_3OH[f]	Xylene	4	*c*	62[d]	*c*
	H^+, CH_2OH[f]	Toluene	4	12	61	*c*
	Xylene	Xylene	8	3		88
5c (7)	CH_3OH	Xylene	8	65	*c*	20
	H^+, CH_3OH[f]	Xylene	4	13	51	*g*
	Xylene	Xylene	8	33		9
5d (8)	CH_3OH	*m*-Xylene	8	50	*h*	
	H^+, CH_3OH[f]	*m*-Xylene	4	59	*h*	

[a] Irradiations were conducted as described in the Experimental Section using 150-ml solutions containing 31 mmoles of olefin and, where applicable, 3.0 ml of sensitizer. Unless otherwise indicated, a commercial mixture of xylene isomers was employed. [b] Determined by gas chromatographic analysis of aliquots removed from the irradiation mixture. [c] None detectable by comparison with an authentic specimen. [d] Analysis complicated by overlap of peaks corresponding to **6b** and xylene. [e] A peak corresponding in retention time to cyclohexane and in area to a 2% yield was also observed. [f] Contained 1% sulfuric acid. [g] Trace; three additional peaks representing a 21% yield of unidentified high-boiling products were also observed. [h] No detectable volatile products.

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[1] (a) Part IV: P. J. Kropp and H. J. Krauss, *J. Org. Chem.*, **32**, 3222 (1967); (b) for a preliminary report of a portion of the present work, see P. J. Kropp, *J. Amer. Chem. Soc.*, **89**, 3650 (1967).

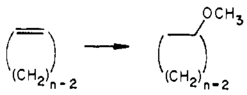
[2] P. J. Kropp and H. J. Krauss, *ibid.*, **89**, 5199 (1967).

[3] J. A. Marshall and R. D. Carroll, *ibid.*, **88**, 4092 (1966).

[4] See, for example, the discussion by R. B. Cundall, *Progr. Reaction Kinetics*, **2**, 165 (1964).

[5] This difference in propensity between cyclohexene and cycloheptene for undergoing photodimerization is consistent with that previously observed for the 1-methyl analogs **1b** and **c**.[2]

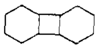
However, a slight increase in the acidity of the medium accomplished by the simple addition of 1% sulfuric acid resulted in a complete change in behavior, with ionic addition to afford the ethers **6b** and **c** becoming the major course of reaction.[6] However, even under the conditions of added sulfuric acid, cyclooctene was relatively stable and failed to undergo any detectable ionic addition. Thus, the same ring size effects observed with the 1-alkyl derivatives apparently operate in the unsubstituted series as well.



5 6

a, n=5; b, n=6; c, n=7; d, n=8

The dimeric material from cyclohexene could be separated gas chromatographically into three fractions which were present in relative amounts of 1:2.1:1.1. A mass spectrum of the combined fractions exhibited the expected intense peak at *m/e* 164, and the nmr spectrum had no significant absorption below τ 7.6. On the basis of these data it is assumed that the fractions represent three of the four possible stereoisomers of the familiar cyclobutane-type product **7** as previously obtained from other cycloalkenes,[7] but this point requires further investigation.



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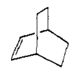

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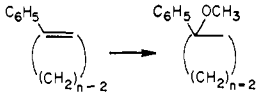
1-Phenylcycloalkenes. The photochemical behavior of the corresponding 1-phenyl derivatives **9** was also examined. In this case an external photosensitizer was not required since the molecule contains a chromophore which absorbs strongly in an accessible region of the ultraviolet spectrum.



9 10

a, n=5; b, n=6; c, n=7; d, n=8

Table II. Irradiation of 1-Phenylcycloalkenes **9**[a]

Olefin (*n*)	Solvent	Time, hr	Yield, %[b] 9	Yield, %[b] 10
9a (5)	CH_3OH	1	13	
	CH_3OH, H^+ [c]	1	10	
	CH_3OH, H^+ [d]	1	14	
9b (6)	CH_3OH	2	22	13
	H^+, CH_3OH [c]	2	*e*	80
	H^+, CH_3OH [c,f]	2	99	*e*
	H^+, CH_3OH[c,f,g]	2	3	95
9c (7)	CH_3OH	2	5	*e*
	H^+, CH_3OH[c]	2	8	79
9d (8)	H^+, CH_3OH[c]	2	52	
	H^+, CH_3OH[d]	2	39	

[a] Irradiations were conducted as described in the Experimental Section using 75-ml methanolic solutions containing 9.5 mmoles of olefin. [b] Determined by gas chromatographic analysis of aliquots removed from the irradiation mixture. [c] Contained 1% sulfuric acid. [d] Contained 4% sulfuric acid. [e] None detectable by comparison with an authentic specimen. [f] Pyrex filter employed. [g] Contained 12.5 mmoles of acetophenone.

As shown in Table II, irradiation of each of the members of the homologous series **9a–d** in methanol resulted in rapid loss of the starting material to afford an unidentified white precipitate which is assumed to be dimeric or polymeric material; there was no appreciable formation of any volatile products.[8a] However, in analogy with the unsubstituted analogs **1b** and **1c**, irradiation of 1-phenylcyclohexene (**9b**) and -heptene (**9c**) in the presence of 1% sulfuric acid resulted in an efficient formation of the ionic addition products **10b** and **c**.[6,8b] On the other hand, even with 4% levels of added sulfuric acid neither the cyclopentene **9a** nor the cyclooctene analog **9d** afforded any detectable amount of the ether **10a** or **d**.

The addition of methanol could also be effected by photosensitization. Irradiation of 1-phenylcyclohexene (**9b**) in acidified methanol solution containing acetophenone with light filtered through Pyrex readily afforded the ether **10b**. Since there was no disappearance of the starting olefin under identical conditions in the absence of acetophenone, it can be assumed that transfer of energy from acetophenone has occurred. Hence, photoprotonation of 1-phenylcyclohexene (**9b**) and, presumably, -cycloheptene (**9c**) can occur *via* the olefin triplet, as has been proposed for 1-alkylcycloalkenes.[2,3] However, it is not clear from these data whether photoprotonation accomplished by direct irradiation of phenylcycloalkenes involves a singlet or triplet excited species.

1-Methylcyclopentene. The failure of 1-phenylcyclopentene (**9a**) to undergo addition of methanol is consistent with our earlier finding that irradiation of 1-methylcyclopentene (**1a**) under conditions in which the cyclohexyl and heptyl homologs **1b** and **1c** are rapidly transformed into a mixture of the corresponding exocyclic olefin **3** and ether **4** resulted instead in a slow conversion to a mixture of methylenecyclopentane (**3a**) and methylcyclopentane (**11**) without any detectable formation of the ether **4a**.[2] It was not clear at that time whether these latter products are, in fact, a result of initial protonation of 1-methylcyclopentene to afford the carbonium ion **2a** followed by competing deprotonation to give **3a** and hydride transfer to afford **11**, a somewhat different course of events than those leading to **3** and **4** from the cyclohexyl and -heptyl analogs **1b** and **c**, or a result of an entirely different mechanism involving something other than initial protonation. Insight into this question has now been provided by an experiment in which an equimolar mixture of 1-methylcyclopentene (**1a**) and -hexene (**1b**) was irradiated in a xylene–methanol-O-*d* mixture. As shown in Chart I,

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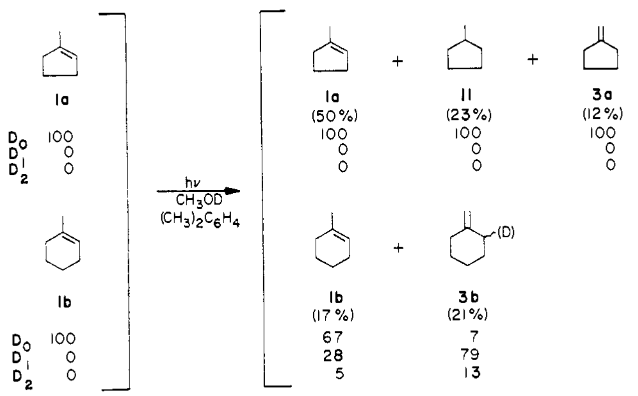
[6] The appropriate control experiments showed that there was no reaction under identical conditions in the absence of light.

[7] See, for example, (a) D. Scharf and F. Korte, *Tetrahedron Lett.*, 821 (1963); *Chem. Ber.*, 97, 2425 (1964); (b) H. H. Stechl, *Angew. Chem. Intern. Ed. Engl.*, 2, 743 (1963); (c) D. R. Arnold, R. L. Hinman, and A. H. Glick, *Tetrahedron Lett.*, 1425 (1964); (d) R. Srinivasan and K. A. Hill, *J. Amer. Chem. Soc.*, **88**, 3765 (1966); (e) D. R. Arnold, D. J. Trecker, and E. B. Whipple, *ibid.*, 87, 2596 (1965). The latter authors cite unpublished results in which the photosensitized cyclodimerization of cyclohexene was also observed, but no experimental details are provided.

[8] (a) Polymerization is reported to be the dominant photochemical reaction of styrene in solution; see J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," John Wiley & Sons, Inc., New York, N. Y., 1966, p 505. (b) Precedent for the photoprotonation of a 1-arylcyclohexene can be found in the photohydration of ergot alkaloids; see A. Stoll and W. Schlientz, *Helv. Chim. Acta*, 38, 585 (1955), and H. Hellberg, *Acta Chem. Scand.*, 11, 219 (1957). This reaction similarly requires acidic conditions.

Chart I



both the resulting methylenecyclohexane (**3b**) and the recovered 1-methylcyclohexene (**1b**) had undergone extensive incorporation of deuterium, whereas neither the recovered 1-methylcyclopentene (**1a**) nor the resulting methylcyclopentane (**11**) and methylenecyclopentene (**3a**) had incorporated any detectable amount of deuterium.[9,10] From these data it must be concluded that 1-methylcyclopentene (**1a**) fails to undergo photoinduced protonation and, presumably, reacts *via* a radical mechanism as discussed below.

2-Norbornene (12) and 2-Methyl-2-norbornene (22). Although substantially more reactive than 1-methylcyclopentene (**1a**), 2-norbornene (**12**), and its 2-methyl derivative **22** show similar radical-type behavior. Irradiation of 2-norbornene in xylene–methanol resulted in no detectable formation of 2-norbornyl methyl ether.[11] Instead, as indicated in Table III and Chart II, a complex mixture of products resulted which included the *exo-trans-endo* and *exo-trans-exo* cyclodimers **13** and **14**,[7a,e] norbornane (**18**), a mixture of the 2-*exo*- and -*endo*-methanol adducts **16a**, 2,2′-binorbornane (**17**),[7a] and ethylene glycol.[6,12] Analogous results were obtained in xylene–2-propanol except for an increase in the ratio of the radical-type products **16**–**19** relative to the cyclobutane dimers **13** and **14**. On the other hand, irradiation in a *t*-butyl alcohol–xylene mixture or in benzene solution, conditions under which no readily abstractable hydrogens are available, afforded the dimers **13** and **14** as the only products present in significant amount.[13] In toluene or xylene solution, the dimers **13** and **14** were accompanied by 2,2′-binorbornane (**17**) and the benzylic derivatives **20** and **21**. By contrast, 2-norbornene showed no tendency to undergo photoreaction in methanol solution in the absence of a sensitizer.

Chart II

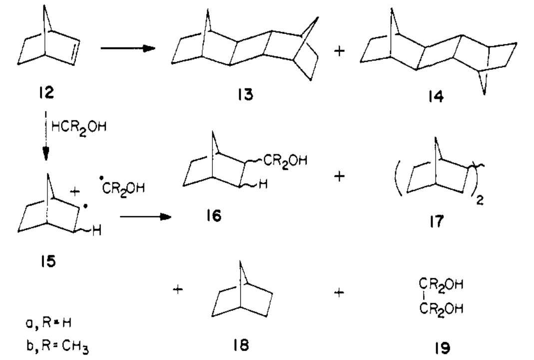
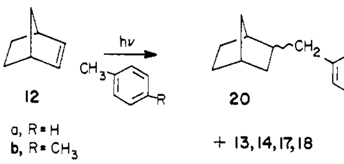


Table III. Irradiation of 2-Norbornene (**12**)[a]

Solvent	Sensitizer	Time, hr	Yield, %[b] **12**	**13**	**14**	**16/20**	**17**	**18**	**19/21**
CH_3OH	Xylene	4	1	26	3	24	11	8	28
CH_3OH	Naphthalene	7	77						
CH_3OH		8	88						
$(CH_3)_2CHOH$	Xylene	4	*c*	16	2	33	14	*c*	21
$(CH_3)_3COH$	Xylene	4	*c*	51	7		8	*c*	
Benzene	Benzene	8	37	22	3				
Toluene	Toluene	8	*c*	8	1	28	8	*c*	28
p-Xylene	*p*-Xylene	8	*c*	12	2	54	21	*c*	30

[a] Irradiations were conducted as described in the Experimental Section using 150-ml solutions containing 3.00 g of **12** and, where applicable, 3.0 ml of sensitizer. [b] Determined by gas chromatographic analysis of an aliquot removed from the irradiation mixture. The results reported are those of a typical run. [c] Not determined because of overlap by the solvent peak.



The cyclobutane dimers **13** and **14** were readily identified by comparison with authentic specimens obtained by acetone- or acetophenone-sensitized irradiation of 2-norbornene (**12**) as previously described,[7a,e] and the binorbornane **17** was identified by comparison with a sample obtained by Wurtz coupling of 2-norbornyl bromide.[7a,14] No successful method for separating the mixture of well-known *exo*- and *endo*-methanol adducts **16a** was found; however, the presence of the *endo* isomer in the mixture was readily apparent from the nmr spectrum, which displayed the high-field multiplet absorption at τ 9.36 that is characteristic of the 3-*endo* proton of 2-*endo*-norbornanemethanol.[15] Integration of the spectrum revealed an *exo*:*endo* ratio of 2.2:1. The 2-propanol adducts **16b** were obtained as two separable isomers in a 3.3:1 ratio, with the principal component again being the *exo* isomer. The benzylic derivative **20a** was obtained gas chromatographically as a poorly resolved mixture of two isomers present in an approximate ratio of 1.7:1. The mixture was easily characterized through its nmr spectrum, which exhibited absorptions corresponding to five phenyl protons at τ 2.88 and two benzylic protons as a multiplet at τ 7.5. The assignment was corroborated by the mass spectrum which displayed a parent ion peak at *m*/*e* 186 and in-

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[9] The detection limit for the presence of deuterium, which was determined mass spectrometrically, is estimated at less than 0.5%.

[10] The methyl ether **4b** was also obtained but was not subjected to deuterium analysis. It has previously been demonstrated that cyclohexyl ether formation is accompanied by deuterium incorporation.[2]

[11] Direct gas chromatographic comparison was made against a specimen of 2-*exo*-norbornyl methyl ether prepared by acid-catalyzed addition of methanol to 2-norbornene; see T. G. Traylor and A. W. Baker, *Tetrahedron Lett.*, No. 19, 14 (1959).

[12] Subsequent to the completion and preliminary report[1b] of our work in this area, R. R. Sauers, W. Schinski, and M. M. Mason [*ibid.*, 4763 (1967)] reported similar findings. The light-initiated addition of acetone to 2-norbornene (**12**) has also been reported; see ref 7a and W. Reusch, *J. Org. Chem.*, 27, 1882 (1962).

[13] The binorbornane **17** was also obtained in low yield in *t*-butyl alcohol–xylene mixtures, perhaps because of the availability of readily abstractable benzylic hydrogen atoms on xylene.

[14] The stereochemistries at C-2 and -2′ are unknown. Although samples obtained photochemically and by the Wurtz coupling appeared homogeneous by gas chromatography, minor variations in the nmr spectra suggest the possibility of stereoisomeric differences. Scharf and Korte report the presence of three isomers in the material obtained by acetone-sensitized irradiation of 2-norbornene.[7a]

[15] R. G. Foster and M. C. McIvor, *Chem. Commun.*, 280 (1967).

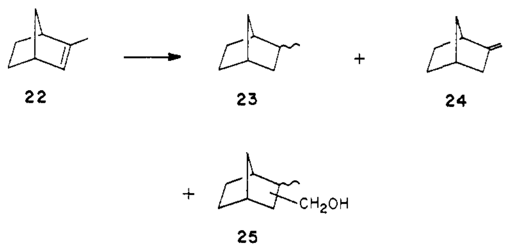
tense fragment ion peaks at m/e 91 and 95 corresponding to cleavage of the benzylic substituent. A mixture of the analogous adducts **20b** was obtained in *p*-xylene.

Parallel photochemical behavior was exhibited by the 2-methyl derivative **22**, except that the presence of the methyl substituent impeded the formation of dimeric products analogous to **13**, **14**, and **17**. As shown in Table IV, irradiation of **22** in xylene–methanol afforded principally a mixture of the methanol adducts **25**,[16] accompanied by smaller amounts of the dihydro derivative **23**, ethylene glycol, and the exocyclic isomer 2-methylenenorbornane (**24**). By contrast **24** displayed the usual photochemical stability which is now known to be characteristic of exocyclic olefins[2,3] and afforded neither **23** nor any other detectable volatile photoproduct.

Table IV. Irradiation of 2-Methyl-2-norbornene (**22**)[a]

Olefin	Solvent	Sensitizer	Time, hr	Yield, %[b] 22	23	24	25
22	CH_3OH	Xylene	4	11	24	6	44[c]
22	Xylene	Xylene	4	15	26	6	
24	CH_3OH	Xylene	4	*d*	*d*	82	*d*
24	Xylene	Xylene	4	*d*	*d*	93	

[a] Irradiations were conducted as described in the Experimental Section using 150 ml of solution containing 3.00 g of olefin and, where applicable, 3.0 ml of sensitizer. [b] Determined by gas chromatographic analysis of aliquots removed from the irradiation mixture. [c] Ethylene glycol also obtained in 13% yield. [d] None detectable by comparison with an authentic specimen.

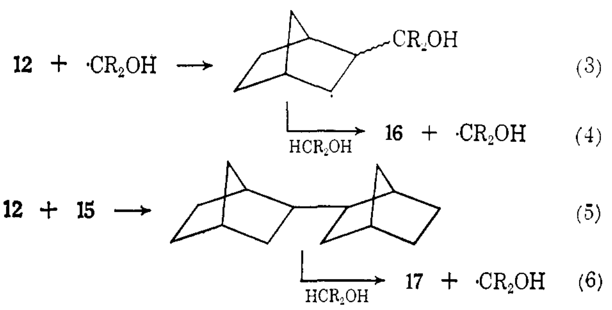


The formation of the cyclobutane dimers **13** and **14** in the presence of benzene, toluene, or xylene, combined with the lack of photoreaction under identical conditions except for the absence of the aromatic hydrocarbons, indicates that transfer of energy to 2-norbornene occurs under these conditions. Since the same two photodimers are formed in a similar ratio using acetophenone and other ketone sensitizers having high $S_1 \rightarrow T_1$ intersystem crossing efficiencies,[7a,e] it would appear that the transfer of energy generates a triplet 2-norbornene species. This is consistent with the relative triplet excitation energies of the aromatic hydrocarbons (81–84 kcal/mole) and 2-norbornene (~72 kcal/mole).[17]

The nature of the photoproducts **16–21** suggests the intervention of radical intermediates in their formation. It is our interpretation that these products arise *via* the initial abstraction of a hydrogen atom from the solvent as depicted in Chart II to generate the 2-norbornyl radical (**15**) and a solvent-derived radical as intermediates, followed by a series of chain reactions such as those outlined below. A similar series of reactions can be written to account for the formation of photoproducts **17**, **18**, **20**, and **21** in aromatic hydrocarbon solvents.

$$\mathbf{15} + HCR_2OH \longrightarrow \mathbf{18} + \cdot CR_2OH \tag{1}$$

$$\mathbf{12} + \cdot CR_2OH \longrightarrow \mathbf{15} + CR_2O \tag{2}$$



$$CR_2OH + CR_2O \longrightarrow \cdot OCR_2CR_2OH \xrightarrow{HCR_2OH} \mathbf{19} + \cdot CR_2OH \tag{7}$$

$$\mathbf{15} + \cdot CR_2OH \longrightarrow \mathbf{16} \tag{8}$$

$$\mathbf{15} + \mathbf{15} \longrightarrow \mathbf{17} \tag{9}$$

$$\mathbf{15} + \cdot CR_2OH \longrightarrow \mathbf{18} + CR_2O \tag{10}$$

$$2 \cdot CR_2OH \longrightarrow \mathbf{19} \tag{11}$$

Although the nature of the photoproducts strongly supports such a scheme for their formation, there are several alternatives which merit consideration. In the case of irradiations conducted in methanol, it is conceivable that the reaction is initiated by a photolytic decomposition of the solvent to form radical species such as $\cdot CH_2OH$, followed by trapping of these species by ground-state 2-norbornene (**12**) molecules, rather than abstraction of H· by a photoexcited 2-norbornene intermediate as proposed. Such a photolytic dissociation of methanol has been observed at low temperatures[18] and has been found to be enhanced by the presence of various aromatic compounds, including benzene.[18b] However, extended irradiation of 2-norbornene (**12**) in methanol in the absence of a photosensitizer afforded no detectable photoproducts. Moreover, a similar photostability was observed in the presence of naphthalene, which has a triplet excitation energy (61 kcal/mole) substantially below that of 2-norbornene (**12**) but which is reported to be equivalent to benzene in inducing the photolytic formation of $\cdot CH_2OH$ from methanol.[18b] Hence it is concluded that the 2-norbornene triplet is a required intermediate and that neither direct nor induced photolysis of methanol is a principal reaction pathway.

In the case of the formation of norbornane (**18**) there are two additional possibilities that reduction involves either (a) a transfer of hydrogen atoms from both the carbon and oxygen atoms of a solvent molecule (as represented formally by **26**) or (b) protonation of 2-norbornene (**12**) followed by a hydride transfer from solvent (*cf.* **12** → **27** → **18**).[19] However, these two possi-

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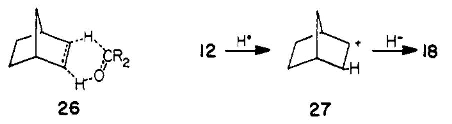
(16) A complex mixture consisting of at least four components was obtained.

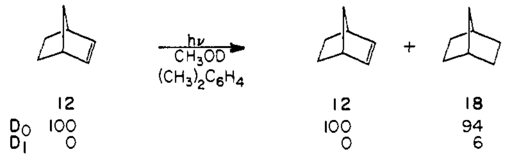
(17) (a) D. F. Evans, *J. Chem. Soc.*, 2753 (1959); (b) D. R. Kearns, *J. Chem. Phys.*, 36, 1608 (1962), and references cited therein; (c) D. R. Arnold, *Advan. Photochem.*, **6**, 301 (1968). See also ref 7a, c, and e.

(18) (a) P. J. Sullivan and W. S. Koski, *J. Amer. Chem. Soc.*, **85**, 384 (1963); (b) M. Ochiai, E. Mizuta, Y. Asahi, and K. Morita, *Tetrahedron*, **24**, 5861 (1968). (c) The formation of radical species, including $\cdot C(CH_3)_2OH$, on irradiation of 2-propanol at 254 nm has also been reported; see C. von Sonntag, *ibid.*, 24, 117 (1968).



bilities were ruled out as principal reaction pathways by the finding that xylene-sensitized irradiation of 2-norbornene (**12**) in methanol-O-*d* afforded, as shown in Chart III, norbornane (**18**) having only 6% incorpora-

Chart III



tion of deuterium and recovered 2-norbornene (**12**) which contained no detectable amount of deuterium.[9] Thus no significant amount of incorporation of the hydroxyl hydrogen has occurred.[20] This is completely consistent with the data on 1-methylcyclopentene (**1a**) described above, in which there was no detectable incorporation of deuterium in the formation of its photoproducts.

By analogy with these results and those from 1-methylcyclopentene (**1a**), it is concluded that the reduction of 2-methyl-2-norbornene (**22**) to 2-methylnorbornane (**23**) and its isomerization to 2-methylenenorbornane (**24**) also proceed *via* radical processes involving an initial hydrogen abstraction from the solvent. However, one important difference exhibited by 1-methylcyclopentene compared with 2-norbornene and its 2-methyl derivative is the lack of formation in the former case of a solvent adduct analogous to **16** or **25**.[21] This is probably attributable to the much greater susceptibility of 2-norbornene (**12**) (and presumably the 2-methyl analog **22**) for undergoing radical addition reactions compared with cyclopentene and its derivatives.[22] Thus reaction 3 may play a more prominent role than reaction 8 in the formation of adducts **16** and **25** and this, in turn, may well explain why 2-norbornene (**12**) and 2-methyl-2-norbornene (**22**) are consumed much more rapidly than 1-methylcyclopentene on photosensitized irradiation in hydrogen-donating solvents.

Bicyclo[2.2.2]oct-2-ene (8). It is apparent that the photochemical behavior of cycloalkenes is highly dependent upon the degree of twisting available about the double bond. To define more precisely the transition point in ring flexibility between radical and ionic behavior, the photochemical properties of the olefins **8**, **28**, and **35**, representing the bicyclo[2.2.2]oct-2-ene, bicyclo[3.1.1]hept-2-ene, and bicyclo[3.2.1]oct-2-ene systems, respectively, were examined.

As can be seen in Table V, bicyclo[2.2.2]oct-2-ene (**8**) proved to be essentially inert photochemically. Photosensitized irradiation in methanol solution under conditions in which 2-norbornene (**12**) was completely transformed to the mixture of photodimers and radical-type products **13**–**18** resulted in almost total recovery of **8**. Similarly, no ionic behavior was exhibited. Photosensitized irradiation in methanolic solution containing 1% sulfuric acid for 20 hr, under conditions in which cyclohexene undergoes substantial conversion to the ether **6b** in 4 hr, again resulted in essentially complete recovery of **8**. In neither case was there any appreciable formation of a photodimer or an ionic- or radical-type addition product.[23] As a further test of its photostability, **8** was irradiated in methanol-O-*d* containing 1% sulfuric acid-d_2; the recovered olefinic material was found to contain no detectable amount of deuterium.[9] This finding rules out the possibility that protonation was in fact occurring but that the resulting carbonium ion intermediate was simply undergoing reversal to the starting olefin (*i.e.*, **1** → **2** → **1**).

Table V. Irradiation of Bicyclo[2.2.2]oct-2-ene (**8**)[a]

Solvent	Sensitizer	Time, hr	Recovery, %[b]
CH_3OH	Toluene	8	93
H^+, CH_3OH[c]	Toluene	20	98
D^+, CH_3OD[d]	Toluene	8	100[e]

[a] Irradiations were conducted as described in the Experimental Section using 150-ml methanolic solutions containing 3.00 g of olefin and 3.0 ml of sensitizer. [b] Determined by gas chromatography of aliquots removed from the irradiation mixture. [c] Contained 1% sulfuric acid. [d] Contained 1% sulfuric acid-d_2. [e] 100% D_0.

α-Pinene (28). Substantially different behavior was exhibited by the bicyclo[3.1.1]heptene α-pinene (**28**). In contrast with bicyclo[2.2.2]oct-2-ene (**8**), α-pinene undergoes rapid reaction on sensitized irradiation in either xylene or xylene–methanol mixtures. However, there was no detectable formation of a photodimer or of ionic- or radical-type addition products. Instead, isomerization to the acyclic triene *cis*-ocimene (**29**) occurred.[24,25] At short reaction times this was the sole detectable photoproduct. However, on further irradiation **29** underwent rapid interconversion with the *trans* isomer **30** to afford an approximately 1:1 equilibrium mixture of **29** and **30**. After the mixture of ocimene isomers had reached the total yields of approximately 11–27% indicated in Table VI, extended irradiation resulted in continued loss of α-pinene without any significant increase in the total yield of the ocimenes. Control experiments revealed that this was attributable to a fairly rapid destruction of the ocimenes under these conditions to afford unidentified higher molecular weight products.[26] This problem was at least partially circumvented by the use of acetophenone as the photosensitizer in benzene solution; under these conditions substantially higher yields of the ocimenes were obtained.[27]

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(19) Evidence for this latter type of reduction in the case of 2-phenyl-2-norbornene has recently been observed in these laboratories (unpublished results); see also J. A. Marshall and A. R. Hochstetler, *Chem. Commun.*, 296 (1968), for a similar reduction of a cyclohexene.

(20) The small amount of deuterium incorporation observed in the formation of **18** could be accounted for by reaction 2 or 10.

(21) Likewise, sensitized irradiation of cyclopentene in methanol failed to produce any detectable cyclopentylmethanol; unpublished results.

(22) See J. Gresser, A. Rajbenbach, and M. Szwarc, *J. Amer. Chem. Soc.*, **83**, 3005 (1961).

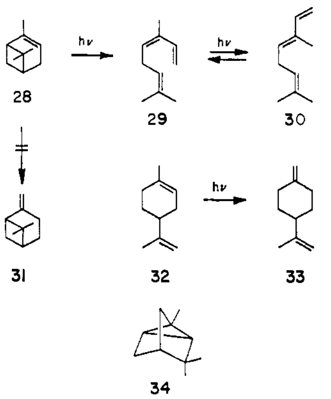
(23) A similar lack of dimer formation on irradiation of bicyclo-[2.2.2]oct-2-ene (**8**) in acetone solution was recently noted by H.-D. Scharf, *Tetrahedron*, **23**, 3057 (1967).

(24) For a preliminary report of this conversion from these laboratories in connection with another study, see W. F. Erman, *J. Amer. Chem. Soc.*, **89**, 3828 (1967).

(25) Subsequent to the completion of our work, G. Frank [*J. Chem. Soc., B*, 130 (1968)] has reported a similar finding.

(26) The rapid loss of the ocimene isomers in the presence of xylene may be caused by photoaddition of the olefins to xylene; see K. E. Wilzbach and L. Kaplan, *J. Amer. Chem. Soc.*, **88**, 2066 (1966), and D. Bryce-Smith, A. Gilbert, and B. H. Orger, *Chem. Commun.*, 512 (1966).

(27) However, as shown in Table VI, the rate of disappearance of α-pinene became significantly slower with increasing concentrations of the



It is noteworthy that with either xylene or acetophenone as sensitizer there is no detectable formation of the exocyclic isomer β-pinene (**31**). A control experiment revealed that (a) β-pinene is sufficiently stable under these conditions to have been detected if formed in less than 2% yield and (b) it does not serve as a precursor to either of the acyclic products.

Table VI. Irradiation of α-Pinene (**28**) and Related Olefins[a]

Olefin	Sensitizer	Solvent	Time, hr	Yield, %[b]				
				28	29	30	31	32
28	Xylene	Xylene	2	70	15	12	*c*	*c*
	Xylene	CH_3OH	2	72	5	6	*c*	*c*
	$C_6H_5COCH_3$	C_6H_6[d]	0.5	76	8	6	*c*	*c*
			2	49	19	18	*c*	*c*
			6	32	25	26	*c*	*c*
29	Xylene	Xylene	2	*c*	35	20	*c*	*e*
	Xylene	CH_3OH	2	*c*	28	30	*c*	*e*
	$C_6H_5COCH_3$	C_6H_6[d]	6	*c*	45	43	*c*	*e*
31	$C_6H_5COCH_3$	C_6H_6[d]	6	*c*	*c*	*c*	63	*c*
32	$C_6H_5COCH_3$	C_6H_6[d]	6	*c*	*c*	*c*	*c*	37[f]

[a] Irradiations were conducted as described in the Experimental Section using 150-ml solutions containing 3.00 g of olefin and, where applicable, 3.0 ml of sensitizer. Unless otherwise indicated, a commercial mixture of xylene isomers was employed. [b] Determined by gas chromatographic analysis of aliquots removed from the irradiation mixture. [c] None detectable by comparison with an authentic specimen. [d] Pyrex filter employed. [e] Not determined because a commercial sample of *cis*-ocimene was employed which contained limonene as an impurity. [f] *p*-Mentha-1(7),8-diene (**33**) also obtained in 13% yield.

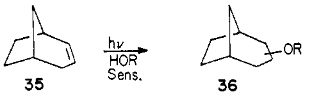
The conversion of α-pinene to *cis*- and *trans*-ocimene has previously been accomplished by direct irradiation.[28] However, the yields were low (3–5% for each isomer) and the ocimenes were accompanied by limonene (**32**) and cyclofenchene (**34**). In the present work there was no detectable formation of either limonene (**32**) or the exocyclic isomer *p*-mentha-1(7)-8-diene (**33**), to which limonene was found to undergo slow isomerization under the irradiation conditions. Likewise, there was no observable formation of cyclofenchene (**34**).[29] Thus the photosensitized reaction is much more specific than its direct irradiation counterpart. α-Pinene is also known to undergo isomerization to *cis*-ocimene on both pyrolysis and γ-ray radiolysis.[30] However, in each of these cases substantial quantities of limonene (**32**) are also formed. Thus the photosensitized rearrangement of α-pinene is a method of choice for preparing *cis*-ocimene free of limonene as a diluent, but it has the disadvantage of affording a photoequilibrated mixture of the *cis* and *trans* isomers.

Bicyclo[3.2.1]oct-2-ene (35). Homologous expansion of one of the single-carbon bridges of the bicyclo[3.1.1]heptene skeleton of α-pinene (**28**) to afford bicyclo[3.2.1]oct-2-ene (**35**) greatly enhances the degree of flexibility about the double bond, with the concomitant result that ionic photochemical behavior now becomes possible. As seen in Table VII, toluene-sensitized irradiation of **35** in acidified methanol or *t*-butyl alcohol resulted in formation of the methyl or *t*-butyl ethers **36a** and **36b**, typical products of ionic addition.[6] However, consistent with being only a disubstituted olefin, **35** exhibited little reactivity in the absence of added mineral acid. Although the ether products **36a** and **36b** appeared to be homogeneous by gas chromatographic analysis on several columns, the results from photoaddition of acetic acid suggest that they are probably isomeric mixtures. Irradiation of **35** in toluene–acetic acid readily afforded a mixture of acetates **36c**. Reduction of the crude acetate mixture with lithium aluminum hydride afforded a mixture of alcohols which displayed gas chromatographic peaks corresponding to the five bicyclooctanols **37–41**,[31] present in relative yields as indicated in Table VIII. The identity of the two major isomers **37** and **40** was confirmed through isolation by preparative gas chromatography and direct comparison

Table VII. Irradiation of Bicyclo[3.2.1]oct-2-ene (**35**)[a]

Solvent	Time, hr	Yield, %[b]	
		35	36
CH_3OH	8	82	
H^+, CH_3OH[c]	2	27	73
H^+, $(CH_3)_3COH$[c]	4	46	32
CH_3CO_2H	2	13	*d*

[a] Irradiations were conducted as described in the Experimental Section using 57 ml of a solution containing 1.5 g of olefin and 1.5 ml of toluene as a sensitizer. [b] Determined by gas chromatographic analysis of aliquots removed from the irradiation mixture. [c] Contained 1% sulfuric acid. [d] Not determined.



a, R = CH_3; **b**, R = $C(CH_3)_3$; **c**, R = $COCH_3$; **d**, R = H

Table VIII. Ionic Addition to Bicyclo[3.2.1]oct-2-ene (**35**)

Method	Relative yield, %[a]				
	37	38	39	40	41
CH_3CO_2H, $CH_3C_6H_5$, hν; $LiAlH_4$	69	5	6	17	3
H_2O, H^+ [b]	62	19	10	6	3
CH_3CO_2H, H^+; $LiAlH_4$[c]	9	39	40	10	2

[a] Determined by gas chromatographic analysis of crude product mixture; see ref 31. [b] A. F. Bickel, J. Knotnerus, E. C. Kooyman, and G. C. Vegter, *Tetrahedron*, 9, 230 (1960). [c] K. Alder, H. Krieger, and H. Weiss, *Chem. Ber.*, **88**, 144 (1955).

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ocimenes. This was presumably due to competitive quenching of the acetophenone triplets by the ocimene isomers as they accumulated in the reaction mixture.

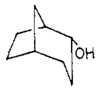
(28) R. Mayer, K. Bochow, and W. Zieger, *Z. Chem.*, **4**, 348 (1964).

(29) However, lack of an authentic specimen of cyclofenchene (**34**) for direct comparison precluded a conclusive verification of its absence.

(30) For a recent review, see D. V. Banthorpe and D. Whittaker, *Quart. Rev.* (London), 20, 373 (1966).

(31) W. Kraus, *Chem. Ber.*, 97, 2726 (1964).

with authentic specimens.[32,33] The ratio of bicyclooctan-2-ol and -3-ol products was further confirmed by chromic acid oxidation of the total alcohol mixture **36d** to afford a mixture of two ketones, present in relative yields of 80 and 20%, which were characterized as bicyclo[3.2.1]octan-2-one (**42**) and -3-one (**43**), respectively,



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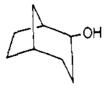

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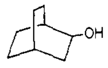

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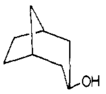

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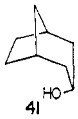

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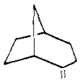

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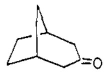

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by direct comparison with authentic specimens.[32–34]

In each of the irradiations of **35** the material recoveries were high and there was no indication of the formation of radical-type products. Likewise, there was no evidence for isomerization to bicyclo[2.2.2]oct-2-ene (**8**), which, if formed, would have been stable under the irradiation conditions.[35] The spectrum of positionally and stereochemically isomeric adducts which results suggests that the photoaddition process is stepwise, involving an initial protonation to afford the 2- and 3-bicyclo[3.2.1]octylcarbonium ions, with formation of the 2 ion apparently favored. This picture is in accord with what intuitively would also be expected for ground-state acid-catalyzed addition to **35**. However, it has been reported that acid-catalyzed hydration of **35** affords a bicyclo[3.2.1]octan-2-ol of unspecified stereochemistry[36] whereas addition of acetic acid affords bicyclo[2.2.2]octan-2-ol acetate as the sole isolated products, respectively.[37] However, repetition of these experiments in our hands followed by gas chromatographic analysis of the total crude product revealed the formation of isomers **37**–**41** in the relative amounts indicated in Table VIII. It is clear that neither method of addition is as selective as reported. Moreover, there are variations in relative yields of the various isomers, the origins of which are not obvious. It is of interest that the photochemical addition of acetic acid affords a reaction profile more closely resembling that obtained from acid-catalyzed hydration of **35** rather than that resulting from acid-catalyzed addition of acetic acid.

Discussion

As described above, replacement of the methyl substituent of the previously studied[2,3] 1-methylcycloalkenes **1** by hydrogen or phenyl has little effect on the correlation of photochemical reactivity with ring size; photoprotonation is observed for the cycloalkenes **5** and **9** having $n = 6$ or 7 but disappears in going to either larger or smaller ring sizes. However, there is apparently a marked attenuation in basicity of the reactive species derived from unsubstituted or phenyl-substituted cyclohexenes and -heptenes relative to those having electron-releasing alkyl or alkoxy substituents. Thus, for example, 1-methylcyclohexene (**1b**) and -cycloheptene (**1c**) and 1-methoxycyclohexene undergo efficient photoprotonation in methanol, whereas cyclohexene and -heptene and the phenyl derivatives **9b** and **c** require the enhanced acidity of methanol–sulfuric acid mixtures. There is, thus, a fine balance between the basicity of the reactive state and the acidity of the solvent for cyclohexenes and -heptenes in methanol which can be shifted either by introducing electron-releasing substituents on the double bond or by enhancing the acidity of the solvent through the addition of small amounts of mineral acid.

There is also a fine balance between ring size and type of photochemical behavior, with cyclopentenes and 2-norbornenes exhibiting radical behavior, cyclohexenes and -heptenes undergoing protonation, and larger ring cyclic, exocyclic, and acyclic olefins showing neither type of behavior. The radical behavior displayed by cyclopentenes and 2-norbornenes almost surely arises from the π,π^* triplet since the complicating possibility of intersystem crossing to a highly strained *trans* singlet species, present in cyclohexenes and -heptenes, is almost undoubtedly absent in such highly constrained olefins. The resulting hydrogen-atom abstraction is not an unexpected behavior for a species having unpaired electrons. The failure of larger ring cyclic, exocyclic, and acyclic olefins—in which the complicating possibility of a highly strained *trans* intermediate is again absent—to undergo hydrogen-atom abstraction under similar conditions is probably related to a shorter lifetime and perhaps also to a lower energy for the vibrationally relaxed π,π^* triplet in these cases.[38–40]

The failure of bicyclo[2.2.2]oct-2-ene (**8**), which is subject to approximately the same degree of constraint as 2-norbornene, to undergo hydrogen abstraction is probably due not to ring size, but to steric hindrance toward approach to the double bond.[41] On the other

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(32) P. Nedenskov, H. Heide, and N. Clauson-Kaas, *Acta Chem. Scand.*, **16**, 246 (1962).

(33) (a) B. Waegell and C. W. Jefford, *Bull. Soc. Chim. Fr.*, 844 (1964); (b) W. Kraus, *Chem. Ber.*, **97**, 2719 (1964).

(34) Under the gas chromatographic conditions employed[31] any bicyclo[2.2.2]octanone originating from **39** would not have been separated from bicyclo[3.2.1]octan-2-one (**42**).

(35) However, the limit for detection of **8** is estimated at 2–4%. The formation of small amounts of bicyclo[2.2.2]octan-2-ol (**39**) suggests that trace amounts of the corresponding olefin **8** may also have been generated.

(36) See Table VIII, footnote *b*.

(37) See Table VIII, footnote *c*.

(38) Although the energy levels of the vibrationally relaxed triplets of simple olefins have not been well defined, the available data suggest that E_T for 2-norbornene (~72 kcal/mole[17c]) is somewhat greater than E_T for 2-pentene (~62 kcal/mole[39]). Moreover, their geometry should differ rather considerably, as the 2-pentene triplet can readily become orthogonal whereas a study of Dreiding models suggests that the triplets for 2-norbornene and cyclopentene cannot twist beyond 30–40° without introducing excessive torsional strain.

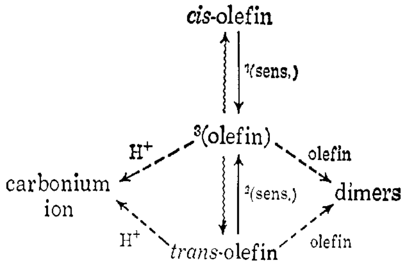
(39) G. S. Hammond, N. J. Turro, and P. A. Leermakers, *J. Phys. Chem.*, **66**, 1144 (1962); see also M. A. Golub and C. L. Stephens [*ibid.*, 70, 3576 (1966)], who report the photosensitized *cis–trans* isomerization of 2-octene with some sensitizers having triplet energies as low as 50 kcal/mole.

(40) W. H. Urry, F. W. Stacey, E. S. Huyser, and O. O. Juveland [*J. Amer. Chem. Soc.*, **76**, 450 (1954)] have reported that 1-hexene and 1-octene undergo radical-type addition of ethanol or 2-propanol on extended irradiation (96–168 hr) in the absence of a photosensitizer. This reaction, which can also be induced with *t*-butyl peroxide in the absence of light, apparently involves a radical-chain process. The available data do not indicate whether it originates from hydrogen-atom abstraction by an excited singlet or triplet olefin species or from light-induced formation and/or decomposition of trace peroxides. However, as shown in Table III, irradiation of 2-norbornene in methanol in the absence of a photosensitizer resulted in no detectable conversion to **13**–**19** under conditions in which it was totally consumed in half as much time in the presence of a photosensitizer.

hand, the failure of α-pinene (**28**) to undergo hydrogen abstraction is principally attributable to the availability of a facile intramolecular rearrangement pathway which is able to compete effectively with any potential intermolecular processes.

There remains the important question of which is the reactive intermediate in the case of cyclohexenes and -heptenes. The possible processes in these two systems are outlined in Chart IV. In principle, either the olefin triplet or the ground-state *trans*-olefin might be the immediate precursor in the protonation and dimerization processes. Comparison with cyclopentenes and 2-norbornenes, in which only radical behavior is observed and only the olefin triplet can be involved, implies that photoprotonation of cyclohexenes and -heptenes involves the *trans*-olefin. However, since the vibrationally relaxed triplets of cyclohexene and -heptene probably differ in geometry and possibly in energy from the corresponding triplets of cyclopentene and 2-norbornene, this conclusion must be considered tentative.

Chart IV



It is of interest to note that the rate of disappearance of cyclohexene is not strongly dependent upon the acidity of the medium but the nature of the products is. Under sufficiently acidic conditions, the formation of cyclobutane-type dimers is completely quenched in favor of the formation of protonation products. By contrast, the rate of disappearance of cycloheptene is greatly accelerated in acidic media. The origin of this discrepancy lies in the reduced propensity of cycloheptenes for undergoing photodimerization.

Experimental Section[42]

Irradiations. A. General. Unless otherwise indicated, all irradiations were conducted with 150 ml of solution using a Hanovia 450-W, medium-pressure mercury arc and a water-cooled Vycor immersion well. Vigorous stirring of the reaction mixture was effected by the introduction of a stream of nitrogen through a jet opening in the bottom of the outer jacket. Starting materials were obtained commercially except for 1-phenylcycloheptene (**9c**),[43] 1-phenylcyclooctene (**9d**),[44] 2-methyl-2-norbornene (**22**),[45] and bicyclo[3.2.1]oct-2-ene (**35**),[46] which were prepared as previously described. Except where otherwise indicated a commercial mixture of *o*-, *m*-, *p*-xylene was employed. The progress of photochemical reactions was monitored by gas chromatographic analysis of aliquots removed periodically. Yields were determined by calibration against an internal hydrocarbon standard. The results are summarized in Tables I–VIII. For product identification the irradiation mixtures were concentrated on an 18-in. spinning-band column, and the individual components were isolated by preparative gas chromatography and characterized either as described below or by comparison with commercial specimens. None of the photochemical reactions reported occurred under identical conditions in the absence of ultraviolet light.

B. Cyclohexene and -heptene. From the irradiations described in Table I the following photoproducts were isolated. **Cyclohexyl methyl ether (6b)** was obtained as a colorless liquid: λ_{max} 9.05 μ; nmr spectrum τ 6.70 (s, 3, CH_3O-) and 6.89 (m, 1, $>CHO-$).[47] This material was identical in every way with an authentic specimen prepared by treatment of cyclohexanol with diazomethane.[48]

The **cyclohexene dimers** were obtained as a colorless liquid which on gas chromatographic analysis (A) afforded three peaks having relative areas of 1:2.1:1.1. The nmr spectrum of the combined fractions exhibited no absorption below τ 7.6; *m/e* 164 (7), 135 (7), 121 (8), 107 (7), 106 (7), 97 (7), 96 (13), 95 (17), 94 (7), 93 (11), 91 (19), 83 (26), 82 (94), 81 (40), 80 (12), 79 (23), 77 (9), 68 (20), and 67 (100).

Cycloheptyl methyl ether (6c) was obtained as a colorless liquid: λ_{max} 9.14 μ; nmr spectrum τ 6.72 (s, 4, CH_3O- and $>CHO-$). This material was identical in every respect with a specimen, bp 163°, prepared independently by treatment of cycloheptanol with diazomethane[48] (lit.[49] bp 160–165.5 and 162–163°).

C. 1-Phenylcyclohexene and -heptene (9b and c). From the irradiations described in Table II the following photoproducts were isolated. **Methyl 1-phenylcyclohexyl ether (10b)** was obtained as a colorless liquid by short-path distillation at 85–86° (0.4 mm): λ_{max} 6.24 and 9.32 μ; nmr spectrum τ 2.8 (m, 5, C_6H_5-) and 7.24 (s, 3, CH_3O-).

Anal. Calcd for $C_{13}H_{18}O$: C, 82.06; H, 9.54. Found: C, 82.2; H, 9.9.

Methyl 1-phenylcycloheptyl ether (10c) was obtained as a colorless liquid by short-path distillation at 88–90° (0.1 mm): λ_{max} 6.24, 9.20, and 9.30 μ; nmr spectrum τ 2.7 (m, 5, C_6H_5-) and 7.06 (s, 3, CH_3O-).

Anal. Calcd for $C_{14}H_{20}O$: C, 82.30; H, 9.87. Found: C, 82.7; H, 10.2.

D. 2-Norbornene (12). From the irradiations described in Table III the following photoproducts were obtained. *endo-trans-exo*-**Pentacyclo[8.2.1.1^{4,7}.0^{2,9},0^{3,8}]tetradecane (13)** was obtained as colorless plates from methanol: mp 38–39° (lit. mp 38–39° [7e] and 34° [7a]). The 60-Mhz nmr spectrum was identical with the one previously presented.[7e]

exo-trans-exo-**Pentacyclo[8.2.1.1^{4,7}.0^{2,9}.0^{3,8}]tetradecane (14)** was obtained as colorless plates from methanol, mp 63.5–65.5° (lit. mp 63.5–64°) [7e] and 62°. [7a] The material was identical in every respect with an authentic specimen prepared by cuprous chloride catalyzed photodimerization of 2-norbornene.[7e]

2-Norbornanemethanol (16) was obtained as a colorless liquid which had the same gas chromatographic retention time as a commercial mixture of the *exo* and *endo* isomers; phenylurethan, colorless needles from methanol, mp 124–124.5° (lit.[50] mp 110–110.5° for the *exo* isomer and 133–134° for the *endo* isomer). The nmr spectrum exhibited ABX multiplets centered at τ 6.66 and 6.43 with relative integrated areas of 2.2:1; these are assigned to the *exo* and *endo* isomers, respectively. The assignment of the *endo* isomer was confirmed by the presence of a multiplet at τ 9.36 having an integration one-half that of the band at τ 6.43.[15]

exo- **and** *endo*-**α,α-dimethyl-2-norbornanemethanol (16b)** were obtained as colorless liquids from two separate gas chromatographic (B) peaks having relative areas of 3.3:1 These were identical with authentic specimens obtained as described previously;[51] nmr

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[41] However, for a recent example of what appears to be an *intramolecular* hydrogen abstraction by a bicyclo[2.2.2]oct-2-ene, see W. Herz and M. G. Nair, *J. Amer. Chem. Soc.*, **89**, 5474 (1967).

[42] Infrared spectra were obtained on neat samples with a Perkin-Elmer Infracord spectrophotometer. Gas chromatographic analyses were performed on an Aerograph Model 90-P instrument using 10 ft × 0.25 in. columns packed with (A) 20% Carbowax 20M, (B) 20% SE-30, (C), 20% FFAP, or (D) 25% diglycerol on 60–80 mesh Chromosorb W. Nuclear magnetic resonance spectra were determined in chloroform-d_3 solution with a Varian Model HA-100 spectrometer, using tetramethylsilane as an internal standard. Mass spectra were obtained using an Atlas Model CH-4 or SM-1 spectrometer; for deuterium analyses the P − 1 and P − 2 peaks were minimized by lowering the accelerating voltage (10–12 eV). *J* values are given in hertz.

[43] H. Pines, A. Edeleanu, and V. N. Ipatieff, *J. Amer. Chem. Soc.*, **67**, 2193 (1945).

[44] A. C. Cope and A. A. D'Addieco, *ibid.*, **73**, 3419 (1951).

[45] K. Alder and H.-J. Ache, *Chem. Ber.*, **95**, 503 (1962).

[46] H. Krieger, *Suomen Kemistilehti, B*, **38**, 260 (1965).

[47] Indicates multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, and m = unresolved multiplet), integration, coupling constant (hertz), and assignment.

[48] E. Mueller and W. Rundel, *Angew. Chem.*, 70, 105 (1958).

[49] M. Verzele, M. Acke, and M. Anteunis, *J. Chem. Soc.*, 5598 (1963).

[50] J. A. Berson, J. S. Walia, A. Remanick, S. Suzuki, P. Reynolds-Warnhoff, and D. Willner, *J. Amer. Chem. Soc.*, **83**, 3986 (1961).

spectra, *exo*, τ 7.82 (m, 2, H-1 and -4) and 8.86 and 8.90 (two s, 2CH$_3$–); *endo*, τ 7.80 (m, 2, H-1 and -4) and 8.74 and 8.84 (two s, 2CH$_3$–).

2,2′-Binorbornane (17) was obtained as a colorless liquid having no nmr absorption below τ 7.7; *m/e* 190 (26), 161 (17), 123 (26), 122 (29), 121 (30), 108 (21), 107 (15), 95 (100), 94 (19), 93 (25), 81 (33), 80 (59), 79 (34), 67 (86), and 66 (45). This material was identical in every respect with an authentic specimen obtained through Wurtz coupling of 2-*exo*-bromonorbornane[7a] by treatment of 2.87 g (16.4 mmoles) of 2-*exo*-bromonorbornane with 3.77 g (16.4 mg-atoms) of sodium in 35 ml of toluene (dried over sodium) under reflux in an atmosphere of nitrogen for 16 hr.[14]

2-Benzylnorbornane (20a) was obtained as a colorless liquid by short-path distillation at 78–80° (0.6 mm): λ_{max} 6.20, 13.28, 13.80, and 14.34 μ; nmr spectrum τ 2.88 (m, 5, C$_6$H$_5$–), 7.5 (m, 2, –CH$_2$–), and 7.80 and 8.02 (two m, 2, H-1 and -4); *m/e* 186 (7), 96 (6), 95 (100), 91 (13), and 67 (13).

Anal. Calcd for $C_{14}H_{18}$: C, 90.26; H, 9.74. Found: C, 89.9; H, 10.0.

2-*p*-Xylylnorbornane (20b) was obtained as a colorless liquid by short-path distillation at 98° (0.1 mm): λ_{max} 12.22, 12.60, and 14.34 μ; nmr spectrum τ 3.10 (s, 4, C$_6$H$_4$–) and 7.75 (s, CH$_3$–); *m/e* 200 (14), 106 (14), 105 (19), 95 (100), and 67 (16).

Anal. Calcd for $C_{15}H_{20}$: C, 89.94; H, 10.06. Found: C, 89.9; H, 10.2.

Norbornane, ethylene glycol, pinacol, bibenzyl, and 4,4′-dimethylbibenzyl were characterized by direct comparison with commercial specimens.

E. **2-Methyl-2-norbornene (22).** From the irradiations described in Table IV the following photoproducts were obtained. **2-Methylnorbornane (23)** was obtained as a colorless liquid which was identical with an authentic specimen obtained by hydrogenation of 2-methyl-2-norbornene over 10% palladium on charcoal in acetic acid at atmospheric pressure;[45] nmr spectrum τ 9.08 (d, J = 6, CH$_3$–) with no absorption below 7.8.

2-Methylenenorbornane (24) was obtained as a colorless liquid which was identical in every respect with an authentic specimen prepared as described previously.[52]

2-Methylnorbornanemethanol (25) was obtained as a colorless liquid which exhibited four peaks on gas chromatographic analysis (B) similar in retention time to those afforded by a commercial sample: λ_{max} 3.0 μ; nmr spectrum τ 6.5 (m, 2, –CH$_2$O–).

F. **α-Pinene (28).** From the irradiations described in Table VI the following photoproducts were isolated. ***cis*-Ocimene (29)** was obtained as a colorless liquid which exhibited an infrared spectrum identical with that of an authentic specimen;[53] nmr spectrum τ 3.24 (q, 1, J_{trans} = 17, J_{cis} = 11, H-2), 4.8 (m, 4, 2H-1 and H-4 and -6), 7.19 (t, 2, $J_1 = J_2$ = 7, 2H-5), and 8.22, 8.34, and 8.40 (three s, 9, 3CH$_3$–).

***trans*-Ocimene (30)** was obtained as a colorless liquid which exhibited an infrared spectrum identical with that of an authentic specimen;[53] nmr spectrum τ 3.71 (q, 1, J_{trans} = 17, J_{cis} = 11, H-2), 4.62 (t, 1, $J_1 = J_2$ = 7, H-1), 4.7–5.2 (m, 3, H-1, -4, and -6), 7.25 (t, 2, $J_1 = J_2$ = 7, 2H-5), and 8.30, 8.36, and 8.42 (three s, 9, 3CH$_3$–).

***p*-Mentha-1(7),8-diene (33)** was obtained as a colorless liquid which exhibited an infrared spectrum identical with that of an authentic specimen;[53] nmr spectrum τ 5.36 and 5.42 (two s, 4, 2H-7 and -9) and 8.28 (s, 3H-10).

G. **Bicyclo[3.2.1]oct-2-ene (35).** From the irradiations described in Table VII the following photoproducts were isolated. **Bicyclo[3.2.1]octyl methyl ether (36a)** was obtained as a colorless liquid by short-path distillation at 86° (7.0 mm): λ_{max} 9.1 μ; nmr spectrum τ 6.72 (s, 4, CH$_3$OC(H)<).

Anal. Calcd for $C_9H_{16}O$: C, 77.09; H, 11.50. Found: C, 76.85; H, 11.55.

Bicyclo[3.2.1]octyl *t*-butyl ether (36b) was obtained as a colorless liquid by short-path distillation at 88° (1.75 mm): λ_{max} 9.32 μ; nmr spectrum τ 6.3 (m, 1, >CHO–), 7.85 (m, 2, H-1 and -5), and 8.75 (s, CH$_3$–); *m/e* 182 (4), 167 (1), 126 (14), 108 (33), 93 (22), 81 (36), 80 (100), 79 (99), 78 (17), 77 (23), 67 (77), 66 (58), 57 (58), 56 (73), 55 (40), 54 (26), and 53 (23)

Anal. Calcd for $C_{12}H_{22}O$: C, 79.06; H, 12.16. Found: C, 79.1; H, 12.1

Bicyclo[3.2.1]octyl acetate (36c) was obtained as a colorless liquid by short-path distillation at 85° (2.5 mm) which exhibited three peaks by gas chromatography (C): λ_{max} 5.74 and 8.1 μ; nmr spectrum τ 5.28 (m, 1) and 8.00 (s, CH$_3$CO–).

Anal. Calcd for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 71.5; H, 9.5.

Treatment of the total mixture of acetates with an excess of lithium aluminum hydride in ether solution overnight at 25° followed by the usual isolation procedure afforded a mixture of alcohols as a partially crystalline colorless mass. Gas chromatographic analysis (D) afforded peaks corresponding in retention time to the five bicyclooctanols **37–41** with relative areas as indicated in Table VIII. Isolation of the major component by preparative gas chromatography from a portion of the crude product afforded colorless prisms, mp 172–173° (sealed capillary), which were identified as ***cis*-bicyclo[3.2.1]octan-2-ol (37)** by direct comparison with an independently prepared sample;[32] lit.[54] mp 174–175 and 175.7–176.7°. Isolation of the second largest component afforded colorless prisms, mp 72–76° (sealed capillary), which were identified as ***trans*-bicyclo[3.2.1]octan-3-ol (40)** by spectral comparison with an authentic specimen;[33] lit. mp 116–117° [33a] and 114–115°.[33b]

Oxidation of a second portion (97 mg) of the crude mixture of alcohols with 0.17 ml of 4 *N* chromic acid according to the Jones procedure[55] afforded 96 mg of colorless crystals which were shown by gas chromatographic analysis (C or D) to consist of two components present in the ratio 2:8. Isolation of the minor component by preparative gas chromatography afforded colorless crystals, mp 137.5–139° (sealed capillary), which were identified as **bicyclo[3.2.1]octan-3-one (43)** by direct comparison with an independently prepared specimen;[33] lit. mp 132–133° [33a] and 144–145°.[33b] Isolation of the major component afforded colorless crystals, mp 118.5–120° (sealed capillary), which were identified as **bicyclo[3.2.1]octan-2-one (42)** by comparison with a commercial specimen.

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