

mp 156–157°). The ir spectrum (KBr) was identical with authentic material prepared by Eguchi.³⁵

Bis-2,4-dinitrophenyl Oxalate-Hydrogen Peroxide Plus Substrates. A. **Acenaphthylene.** A solution of 69.4 mg (2 mmol) of hydrogen peroxide (98%) in 1 ml of dimethoxyethane was added to a suspension of 844 mg (2 mmol) of DNPO and 1.54 g (10 mmol) of acenaphthylene in 16 ml of the same solvent. After 3.5 hr, no further light was obtained when aliquots were treated with rubrene. Chloroform was added and the mixture was treated with saturated sodium bicarbonate. Evaporation, chromatography of the residue on Woelm acidic alumina, and recrystallization of the material eluted after acenaphthylene (benzene-pentane, 1:9) yielded 1.6 mg

(0.01 mmol, 0.5% based on the DNPO) of the trans dimer, mp 303–305° (sealed tube) (lit.³² mp 305°, sealed tube). Only traces of the cis isomer were seen.

B. **Anthracene.** Treatment of anthracene similar to that outlined above yielded anthraquinone (14%); anthracene 9,10-endoperoxide may also have been formed (identified by tlc).

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Photochemistry of Alkenes. Direct Irradiation in Hydroxylic Media¹

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Abstract: The photochemical behavior of a series of alkenes and cycloalkenes on direct irradiation in hydroxylic media has been studied and compared with the sensitized behavior of these same olefins under similar conditions. On irradiation in methanol 1-methylcyclohexene, -heptene, and -octene (**1b–d**) underwent photoprotonation, in complete analogy with their behavior on sensitized irradiation. In the case of 1-methylcyclohexene (**1b**) the photoproducts **3b** and **4b** were obtained in identical ratios on direct and sensitized irradiation, and labeling studies involving irradiation of **1b** in methanol-*O-d* showed that **3b** and **4b** were formed with extensive incorporation of deuterium, as observed earlier on sensitized irradiation. This parallel behavior between direct and photosensitized irradiation is consistent with the involvement of a *trans*-cycloalkene intermediate for the photoprotonation process, as previously proposed. By contrast, 1-methylcyclopentene (**1a**) did not undergo photoprotonation on irradiation in methanol. Comparison of the cycloalkenyl alcohols **6a** and **b** showed that the cyclohexenyl alcohol **6b**, but not the cyclopentenyl homolog **6a**, underwent fragmentation to **3** on either direct or sensitized irradiation, in concert with our earlier proposal that the photofragmentation process involves an initial protonation of the cycloalkene. A novel photochemical process was observed for tetraalkyl-substituted olefins on direct irradiation in hydroxylic media. Thus 1,2-dimethylcyclopentene (**14**) afforded a mixture of the photoproducts **15–18** on irradiation in methanol; 2,3-dimethyl-2-butene (**20**) yielded the products **24–27**, and bicyclohexylidene (**32**) gave the products **33–35**. The trisubstituted analog 2-methyl-2-butene (**36**) underwent much slower reaction but provided the analogous products **37–43**. 1,2-Dimethylcyclohexene (**8**) exhibited mixed behavior, affording the products **9–11** *via* photoprotonation and the mixture of products **9–13** *via* the new pathway. More extensive studies with 2,3-dimethyl-2-butene (**20**) showed that the rate of reaction is dependent upon the medium, decreasing in the order aqueous CH₃CN ~ CH₃OH > C₂H₅OH > *n*-C₄H₉OH. In less reactive media, competing isomerization of **20** to the photoproducts **24**, **28**, and **29** occurred; in nonhydroxylic media these were the principal photoproducts. Deuterium labeling studies involving irradiation of **20** in methanol-*O-d* revealed that the ethers **26** and **27** were formed without significant deuterium incorporation, whereas formation of the hydrocarbon products **24** and **25** was accompanied by extensive deuterium incorporation. These results are interpreted in terms of nucleophilic trapping of the Rydberg excited state **21a** or the radical-cation intermediate **21b**. The mechanistic ramifications of this interpretation are discussed.

Previous studies in these laboratories⁴ and others⁵ have shown that on sensitized irradiation in hydroxylic media cyclohexanes, -heptenes, and -octenes afford a mixture of photoproducts which result from an initial light-induced protonation of the olefin (*cf.* **1b–d**

(1) Presented in part as a plenary lecture at the Third International Symposium on Photochemistry, St. Moritz, Switzerland, July 1970; see *Pure Appl. Chem.*, **24**, 585 (1970).

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(4) (a) P. J. Kropp and H. J. Krauss, *J. Amer. Chem. Soc.*, **89**, 5199 (1967); (b) P. J. Kropp, *ibid.*, **91**, 5783 (1969).

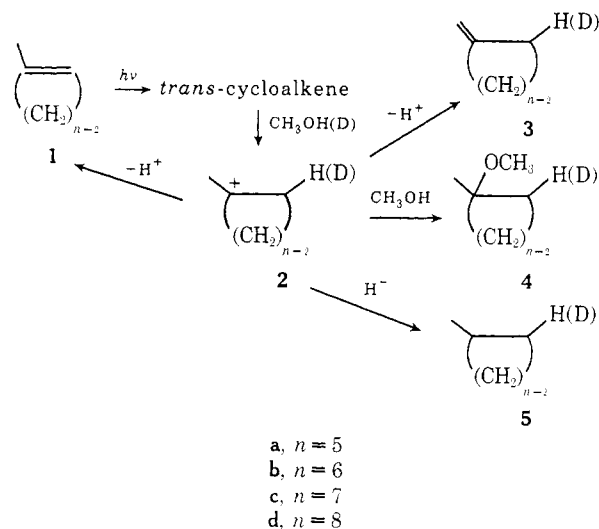
(5) (a) For reviews, see J. A. Marshall, *Accounts Chem. Res.*, **2**, 33 (1969); (b) J. A. Marshall, *Science*, **170**, 137 (1970).

→ **2b–d**). In striking contrast, cyclopentenenes and other highly constrained cyclic olefins exhibit radical behavior on irradiation under similar conditions,^{4b,6} whereas large-ring cyclic and acyclic olefins exhibit only cis ⇌ trans isomerization. Exocyclic olefins, such as the methylenecycloalkanes **3**, exhibit no observable photobehavior, although they probably also undergo an undetected cis ⇌ trans isomerization under these conditions. The unique behavior of cyclohexenes, -heptenes, and -octenes leading to photoprotonation has been attributed^{4,5} to initial cis ⇌ trans isomeri-

(6) R. R. Sauers, W. Schinski, and M. M. Mason, *Tetrahedron Lett.*, 4763 (1967).

zation of the olefin followed by protonation of the resulting highly strained trans isomer (Scheme I), a pro-

Scheme I



cess which is facilitated by the concomitant relief of strain in this intermediate.⁷ The divergent behavior exhibited by cyclopentene and other highly constrained olefins is thought to be associated with the inability of these olefins to undergo $\text{cis} \rightarrow \text{trans}$ isomerization; the radical-type behavior exhibited in these cases probably originates from intermolecular reaction by the $^3(\pi, \pi^*)$ excited state itself.^{4b} Large-ring cyclic, exocyclic, and acyclic olefins, on the other hand, can readily undergo $\text{cis} \rightleftharpoons \text{trans}$ isomerization, and there is no driving force for the resulting trans isomer, which has no severe strain in these cases, to undergo protonation.

If, as proposed, the photoprotonation process involves a highly strained ground-state *trans*-cycloalkene intermediate as the immediate precursor to the carbocation, it should be possible to achieve photoprotonation by direct irradiation as well, since olefins are known to undergo $\text{cis} \rightleftharpoons \text{trans}$ isomerization on direct irradiation in the liquid phase.⁸ We wish in this paper to describe the photobehavior of a series of olefins on direct irradiation in hydroxylic media and to compare this behavior with that exhibited by the same olefins under similar conditions on sensitized irradiation. In addition, a novel photoprocess uncovered during the course of this study and thought to involve intermolecular trapping of the first Rydberg excited state of olefins will be described.

Results

Photoprotonation. The results from sensitized irradiation of 1-methylcyclohexene, -heptene, and -octene (**1b–d**) are summarized in Table I. As previously observed,^{4a} the carbocation **2** resulting from the initial photoprotonation process undergoes the competing reactions outlined in Scheme I: (a) deprotonation to afford the exocyclic olefin **3** and regenerated starting olefin **1**, (b) nucleophilic trapping by solvent to afford the methyl ether **4**, and (c) hydride abstraction to afford

(7) There is precedent that highly twisted, strained olefins exhibit enhanced basicity; see J. A. Marshall and H. Faubl, *J. Amer. Chem. Soc.*, **92**, 948 (1970).

(8) See, for example, H. Yamazaki and R. J. Cvetanović, *ibid.*, **91**, 520 (1969).

Table I. Irradiation of Cycloalkenes **1** in Methanol^a

Olefin (<i>n</i>)	Conditions ^b	Time, hr	Yield, % ^c			
			1	3	4	5
1a (5)	Direct	9	39	<i>d</i>	<i>e</i>	<i>d</i>
	Direct, H ⁺	9	30	2	<i>f</i>	6
	Sensitized	15	38	5	<i>g</i>	10
	Sensitized, H ⁺	15	20	7	<i>g</i>	16
1b (6)	Direct	8	5	28	29	2 ^h
	Sensitized	11	17	42	41	<i>d</i>
1c (7)	Direct, H ⁺	5	9	2	71	2
	Sensitized, H ⁺	8	33	<i>d</i>	62	<i>d</i>
1d (8)	Direct	6	68	<i>i</i>	<i>g</i>	<i>i</i>
	Direct, H ⁺	6	27	<i>i</i>	47	<i>i</i>
	Sensitized	6	63	<i>i</i>	<i>g</i>	<i>i</i>
	Sensitized, H ⁺	6	25	<i>i</i>	37	<i>i</i>

^a Irradiations were conducted as described in the Experimental Section using 110-ml solutions containing 21 mmol of olefin and, where applicable, 3.0 ml of *p*-xylene as sensitizer. ^b Sensitized, Vycor filter sleeve employed; H⁺, solution contained 0.25% sulfuric acid. ^c Determined by gas chromatographic analysis of aliquots removed from the irradiation mixture. ^d Trace. ^e Ether fraction consisted of at least four poorly resolved components obtained in 10% yield. ^f Ether fraction consisted of at least four poorly resolved components obtained in 22% yield. ^g None detectable on comparison with an authentic specimen. ^h Four additional products observed in 14% total yield. ⁱ Not determined.

the reduced product **5**.⁹ As shown in Table I, these same products **3–5** were obtained on direct irradiation of olefins **1b–d** under similar conditions.^{10,11} Moreover, the ratio **3b/4b** of the major products obtained from 1-methylcyclohexene (**1b**) (1.02 and 0.97 from the sensitized and direct runs, respectively) was identical within experimental error for the two sets of conditions.

These results are consistent with a mechanism in which the photoproducts **3–5** originate *via* protonation of a common *trans*-cycloalkene intermediate, which can be generated by the sensitized or direct irradiation of the olefin **1**. Moreover, additional support for photoprotonation as the principal photoprocess in direct irradiation of **1b** was provided by the finding that irradiation in methanol-*O-d* afforded the ether **4b** with substantial incorporation of deuterium (4% *d*₀, 85% *d*₁, and 11% *d*₂)¹² as observed previously on sensitized irradiation.^{4,13}

(9) In our initial studies (ref 4a) no photoprotonation was observed for 1-methylcyclooctene (**1d**). The present studies have revealed that **1d** undergoes photoprotonation in methanol if the acidity of the medium is enhanced by the addition of low levels of mineral acid; note also H. Kato and M. Kawanisi, *Tetrahedron Lett.*, 865 (1970).

(10) In both the direct and sensitized irradiations of 1-methylcyclooctene a photoproduct was observed which achieved a photostationary state of 1–2% and which was preferentially extracted from the reaction mixture with silver nitrate. This latter behavior suggests that the observed intermediate may be the trans isomer; see A. C. Cope, R. A. Pike, and C. F. Spencer, *J. Amer. Chem. Soc.*, **75**, 3212 (1953).

(11) Both the sensitized and direct irradiation photoprotonation processes have been found to be sensitive to what are apparently minor impurities in some of the methanol and olefin samples employed, but the resulting vagarious behavior can be eliminated by the addition of 0.25% sulfuric acid. (Control studies have shown that the olefins **1b–d** do not undergo acid-catalyzed protonation under these conditions in the absence of light.) Recent studies have shown that some commercial specimens of methanol contain one or more impurities which generate an acidic photoproduct when methanol is employed as a solvent for photochemical experiments: P. J. Kropp and E. M. Dexheimer, manuscript in preparation. See also J. A. Marshall and J. P. Arrington, *J. Org. Chem.*, **36**, 214 (1971); S. J. Cristol, G. A. Lee, and A. L. Noreen, *Tetrahedron Lett.*, 4175 (1971); and G. Roussi and R. Beugelmans, *ibid.*, 1333 (1972).

(12) Multiple incorporation of deuterium into products of the photoprotonation process at high levels of conversion is a regular occurrence and is to be expected, since proton loss from the carbocation **2** to regenerate starting olefin **1** results in the formation of deuterated olefin **1**. This material, on recycling through the photoprotonation process, affords products **3–5** which are multiply labeled.

In contrast to the cycloalkenes **1b-d**, the cyclopentenyl analog **1a** failed to exhibit parallel behavior on direct and sensitized irradiation. As reported earlier^{4b,6} **1a** does not undergo sensitized photoprotonation in methanol and the ether product **4a** is not formed. However, on direct irradiation **4a** is formed, but along with three additional ether products which are unsaturated.¹⁴ The formation of both saturated and unsaturated ethers on direct irradiation is not characteristic of the photoprotonation process, but rather, as detailed below, parallels a new photochemical process displayed as well by other olefins such as the acyclic analog 2-methyl-2-butene (**36**). Thus it appears that the photoprotonation process has a parallel, marked dependence on ring size that limits it to cyclohexenes, -heptenes, and -octenes in both the direct and sensitized modes of reaction.

Photofragmentation. A process closely related to photoprotonation is the previously observed photofragmentation of a homoallylic alcohol.¹⁵ An additional example of this process was provided in the current work by the sensitized fragmentation of **6b**¹⁶ to methylenecyclohexane (**3b**) (Table II). This reaction,

Table II. Irradiation of Cycloalkenes **6a**

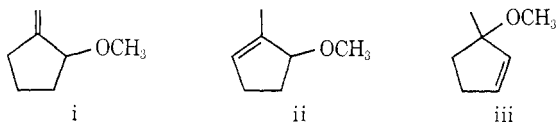
Olefin (<i>n</i>)	Solvent	Time, hr	Yield, % ^b	
			6	3
6a (5)	Benzene ^c	26	64	<i>d, e</i>
	Pentane	14	72	<i>d, e</i>
6b (6)	Benzene ^c	26	40	18 ^e
	Pentane	14	56	44

^a Irradiations were conducted in sealed quartz tubes as described in the Experimental Section using solutions containing 105 mg of olefin and 1.05 g of solvent. ^b Determined by gas chromatographic analysis. ^c Vycor filter sleeve employed. ^d None detectable on comparison with an authentic specimen. ^e A number of unidentified higher molecular weight products was obtained.

which probably proceeds *via* an initial photoprotonation process followed by collapse of the resulting carbo-

(13) The product mixture from direct irradiation of 1-methylcyclohexene (**1b**) exhibited a set of four gas chromatographic peaks in addition to those corresponding to photoproducts **3b-5b**. These minor products, which were not present in the sensitized irradiation mixtures, were formed as the principal products from direct irradiation of **1b** in ether or pentane and will be discussed in more detail separately in conjunction with a study of the photochemical behavior of olefins in non-hydroxylic media. In methanol-*O-d* they were formed without significant incorporation of deuterium. It thus appears that on direct irradiation in methanol **1b** undergoes two competing modes of photochemical reaction: a principal process involving photoprotonation and a minor process involving photoisomerization. The latter pathway becomes dominant in the absence of a proton source and is under further study.

(14) (a) By analogy to the behavior of 2-methyl-2-butene (**36**) as described below, these unsaturated ethers would have structures i-iii. Although the spectral properties of the mixture [nmr spectrum: τ 4.61 and 4.80 ($=CH-$), 5.06 ($=CH_2$), 6.04 (t, $J = 6$ Hz, CH_3OCHCH_2) and 6.80 (s, CH_3O)] are totally consistent with this composition, the individual ethers could not be isolated in sufficiently pure form to confirm these assignments. (b) A number of unidentified higher molecular weight products was also obtained.

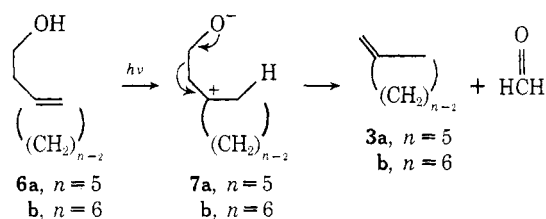


(15) P. J. Kropp and H. J. Krauss, *J. Amer. Chem. Soc.*, **91**, 7466 (1969).

(16) R. T. Arnold and J. F. Dowdall, *ibid.*, **70**, 2590 (1948).

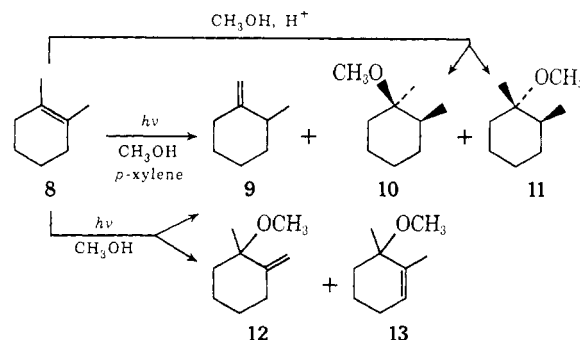
cation intermediate **7b** as depicted in Scheme II,¹⁷

Scheme II



should display the same ring-size dependence as the photoprotonation process itself. This was confirmed by the finding that the cyclopentenyl homolog **6a**¹⁸ failed to undergo detectable fragmentation to methylenecyclopentane (**3a**) under similar conditions. As shown in Table II, the photofragmentation process also occurred on direct irradiation, as seen by the conversion of **6b** to **3b**. Moreover, the usual ring-size dependence was seen to extend to the direct process, since the cyclopentenyl homolog **6a** failed to undergo fragmentation on direct irradiation. Thus the photoprotonation and photofragmentation processes display parallel ring-size effects in both the direct and sensitized modes of reaction.

Novel Behavior.¹⁹ Attempts to extend the direct irradiation photoprotonation process to the tetra-substituted analog 1,2-dimethylcyclohexene (**8**) lead to some surprising results. On *p*-xylene-sensitized irradiation **8** displayed behavior typical of a cyclohexene by affording the exocyclic isomer **9** and a mixture of the epimeric ethers **10** and **11**²⁰ (yields of 37, 10, and 21%, respectively),²¹ which were identical with the products of acid-catalyzed addition of methanol. However, direct irradiation of **8** gave not only the expected products **9-11** (**8**, **9**, and 15% yields, respectively) but also the unsaturated ethers **12** and **13**²² (2 and 5% yields, respectively).²³



It became more obvious that special behavior is exhibited by tetraalkyl-substituted olefins when it was

(17) Although shown as an intramolecular process in Scheme II, the photoprotonation step might also occur intermolecularly.

(18) R. T. Arnold, R. W. Amidon, and R. M. Dodson, *J. Amer. Chem. Soc.*, **72**, 2871 (1950).

(19) For a preliminary report of this portion, see E. J. Reardon, Jr., and P. J. Kropp, *ibid.*, **93**, 5593 (1971).

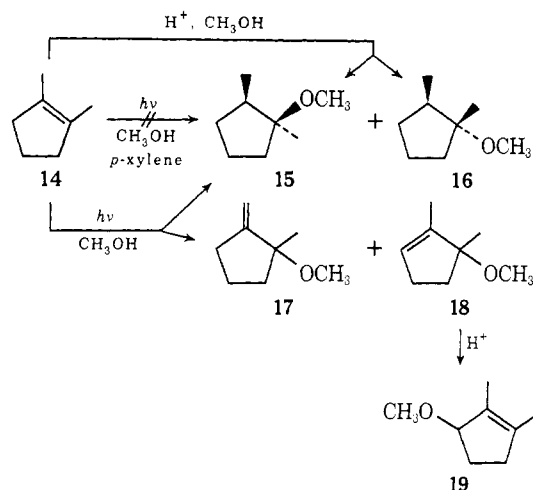
(20) W. Hueckel and S. K. Gupta, *Justus Liebigs Ann. Chem.*, **685**, 105 (1965).

(21) Two products having gas chromatographic retention times identical with 2,3-dimethylcyclohexene and *trans*-1,2-dimethylcyclohexene were also observed in trace quantities.

(22) The complete characterization of all novel compounds is summarized in the Experimental Section.

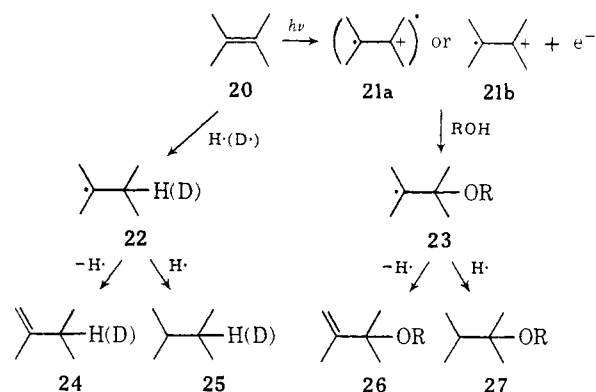
(23) In addition, a poorly resolved mixture of at least five unidentified hydrocarbon photoproducts was formed in approximately 6% total yield. In all of the irradiations described in this section a number of unidentified higher molecular weight products was also formed, each in low yield.

found that the cyclopentenyl analog **14** also underwent ether formation on irradiation in methanol to afford a mixture of the saturated ethers **15** and **16** (3 and 8% yields, respectively) and the unsaturated ethers **17** and **18** (7 and 15%, respectively).^{24,25}



By contrast, **14** displayed normal behavior for a cyclopentene on sensitized irradiation and afforded no ether products. Similarly, the acyclic analog **20** gave a mixture of the ethers **26** and **27** ($R = CH_3$) and the hydrocarbons **24** and **25** on direct irradiation in methanol (see Table III and Scheme III) but afforded none of

Scheme III



methanol resulted in initial formation of bicyclohexylidene (**32**) and ether **33**. The former product, in turn, underwent secondary reaction to afford products **33–35**. However, the photoconversion of cyclohexylcyclohexene (**30**) in methanol proved to be very slow, and **30** underwent only 17% conversion under conditions where bicyclohexylidene (**32**) underwent complete conversion. Thus the lack of any observable amount of **30** indicates that, surprisingly, it is not a significant photoproduct from **32**.

Sensitized irradiation of **30** likewise afforded bicyclohexylidene (**32**) and ether **33**, but under these conditions **32** was photostable and did not undergo secondary reaction. The unsaturated ether **34** was prepared independently by sensitized irradiation of 1,1'-bicyclohexenyl (**31**).

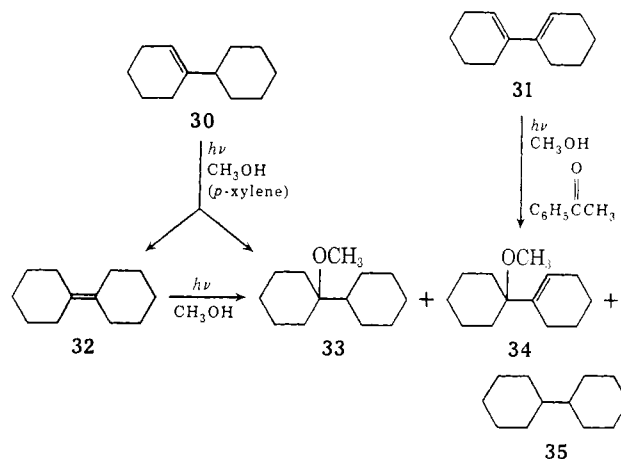
Table III. Irradiation of 2,3-Dimethyl-2-butene (**20**)^a

Solvent	Time, hr	Yield, % ^b							
		20	24	25	26	27	28	29	
H ₂ O, CH ₃ CN ^c	4	3	1.5	1	23	16	d	d	
CH ₃ OH	2	44	4	11	20	20	e	e	
	4	6	4	16	30	37	e	e	
CH ₃ OH/ ^f	128	42	1	2	2.5	3	d	d	
CH ₃ OH, (C ₂ H ₅) ₂ O ^g	2	71			18	6			
C ₂ H ₅ OH	4	35	5	6	20	12	e	e	
	8	3	5.5	6.5	23	16	e	e	
n-C ₄ H ₉ OH	4	60	5	3	10	2	1	1	
	16	5	11	7	23	10	4	4	

^a Unless otherwise indicated, irradiations were conducted as described in the Experimental Section using 200-ml solutions containing 3.40 g of olefin. ^b Determined by gas chromatographic analysis of aliquots removed from the reaction mixture and calculated relative to a saturated hydrocarbon internal standard. ^c 30% aqueous solution. ^d None detectable. ^e Trace. ^f A circular array of 16 G8T5 lamps, which emit principally at 253.7 nm, was used as the light source. The slowness of the reaction under these conditions is due in large part to the very small absorption by **20** at this wavelength. ^g 1:3.

these products on sensitization with *p*-xylene. In aqueous acetonitrile alcohols **26** and **27** ($R = H$) were obtained, along with the hydrocarbons **24** and **25**.

Finally, the analogous exocyclic olefin bicyclohexylidene (**32**) afforded the ethers **33** and **34** and bicyclohexyl (**35**) (yields of 8, 23, and 34%, respectively). This system is complicated by the fact that one of the expected, but unobserved, products, cyclohexylcyclohexene (**30**), is photolabile. Thus irradiation of **30** in



Thus tetraalkyl-substituted olefins exhibit photobehavior on direct irradiation in hydroxylic media which is superficially similar to the photoprotonation process in that both hydrocarbon and ether products are obtained but which is clearly different in that (a) both saturated and unsaturated ether products are formed, (b) there is no dependence on ring size, and (c) parallel behavior is not exhibited on sensitized irradiation.

Another major deviation from the photoprotonation process was the finding that irradiation of **20** in methanol-*O-d* resulted in extensive incorporation of deuterium in the hydrocarbon products **24** and **25** but only minor incorporation in the ethers **26** and **27** ($R = CH_3$), as outlined in Table IV.²⁶

(24) In addition a mixture of at least three unidentified hydrocarbon photoproducts was formed in approximately 15% yield.

(25) The ether **18** showed a marked propensity for undergoing allylic rearrangement to the isomer **19** during work-up and isolation procedures.

(26) The isotopic compositions listed in Table IV for the ethers **26** and **27** ($R = CH_3$) are possibly subject to large error since they had to be based on the $M - 31$ peaks. Qualitatively it can be concluded that these products are formed with low levels of deuterium incorporation.

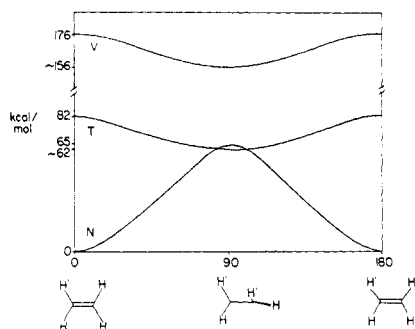


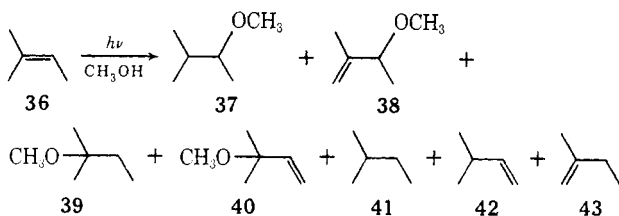
Figure 1. Potential energy curves for the twisting of the N, T, and V states of ethylene.

Table IV. Deuterium Analysis of Photoproducts from Irradiation of 2,3-Dimethyl-2-butene (20) in Methanol-*O-d*

	Isotopic composition, % ^a				
	20	24	25	26 ^b (R = CH ₃)	27 ^b (R = CH ₃)
<i>d</i> ₀	88	22	8	73	74
<i>d</i> ₁	9	62	73	19	21
<i>d</i> ₂	2	14	16	5	5
<i>d</i> ₃	1	2	3	3	0

^a Determined by mass spectroscopic analysis based on the molecular ion peak. ^b Based on the M - 31 peak.

The novel behavior is markedly sensitive to the degree of alkyl substitution. The trisubstituted analog 2-methyl-2-butene (36) undergoes much slower reaction in methanol than does 20 under the same conditions and after 72 hr was only 80% converted, affording principally a mixture of the ethers 37–40^{27–29} and the hydrocarbons 41–43 (combined yields of 14.5 and 42%, respectively).



The new behavior is also markedly sensitive to the nature of the medium. This can be seen in Table III by the decrease in rate of disappearance of 20 on going from aqueous acetonitrile through the homologous series of alcohols from methanol to 1-butanol. Likewise there is a decrease in rate on dilution of the methanolic solution with ether.³⁰

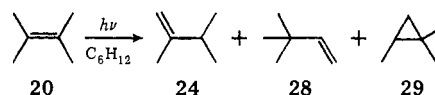
tion. However, it is not clear from the available data whether the low levels of deuterium incorporation listed in the table indicate an alternative mechanistic pathway for the formation of 26 and 27 which involves deuterium incorporation or whether they represent inherent errors in the method of analysis.

(27) (a) E. L. Gustus and P. G. Stevens, *J. Amer. Chem. Soc.*, **55**, 378 (1933); (b) A. V. Topchiev and N. F. Bogomolova, *Dokl. Akad. Nauk SSSR*, **88**, 487 (1953); *Chem. Abstr.*, **48**, 2567 (1954); (c) M. Verzele, M. Acke, and M. Anteunis, *J. Chem. Soc.*, 5598 (1963).

(28) (a) A. Reyckler, *Bull. Soc. Chim. Belg.*, **21**, 71 (1907); (b) A. W. Smith and C. E. Boord, *J. Amer. Chem. Soc.*, **48**, 1512 (1926); (c) S. Weinstein and L. L. Ingraham, *ibid.*, **74**, 1160 (1952); (d) T. W. Evans and K. R. Edlund, *Ind. Eng. Chem.*, **28**, 1186 (1936); (e) I. N. Nazarov, I. N. Azerbaev, and V. N. Rakcheva, *Zh. Obshch. Khim.*, **18**, 407 (1948); *Chem. Abstr.*, **43**, 113 (1949).

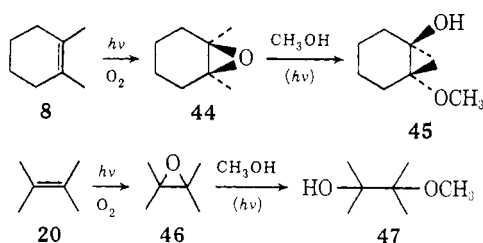
(29) (a) A. J. Ultee, *Recl. Trav. Chim. Pays-Bas*, **68**, 352 (1949); (b) Kh. V. Baylan, *Zh. Obshch. Khim.*, **21**, 720 (1951); *Chem. Abstr.*, **46**, 8946 (1952); (c) S. Weinstein and L. Goodman, *J. Amer. Chem. Soc.*, **76**, 4373 (1954).

In aprotic media 20 undergoes instead a slow isomerization to a mixture of the isomers 24, 28, and 29.³¹



However, appropriate control studies showed that none of the photoproducts 24, 28, or 29 serves as a precursor to the ethers 26 or 27 (R = CH₃) in methanol. In 1-butanol, in which the rate of conversion to photoproducts 24–27 is slow, appreciable amounts of the isomers 28 and 29 were formed. Although much less efficient because of the weak absorption by the olefin, the photo-reaction of 20 in methanol also occurred at 253.7 nm to afford a mixture of the photoproducts 24–27 similar to that obtained on irradiation with the full mercury arc.

When the irradiation of either 1,2-dimethylcyclohexene (8) or 2,3-dimethyl-2-butene (20) was carried out in the presence of oxygen the usual products 9–13 and 24–27 were formed. However, also obtained were the methoxy alcohols 45 and 47.³²



Discussion

Photoprotonation and Photofragmentation. It is generally agreed that alkenes undergo *cis* ⇌ *trans* isomerization on direct irradiation because the V, ¹(π, π*), excited state undergoes rapid vibrational relaxation to an orthogonal geometry in a manner similar to that exhibited by the corresponding triplet state T, as depicted in Figure 1 for ethylene. Internal conversion of this orthogonal species to the ground state (N) potential energy surface is followed by vibrational decay to afford the *cis* and *trans* isomers with approximately equal probability.

The occurrence of both photoprotonation and photofragmentation is consistent with, and supports, the earlier proposal⁴ that these processes involve initial *cis* → *trans* isomerization of the olefin followed by protonation of the resulting *transoid* intermediate, the latter step being driven by relief of strain. An alternative possibility that the direct irradiation photoprotonation and photofragmentation processes involve prior decay of the excited olefin to the triplet manifold does not seem likely since singlet–triplet intersystem crossing of olefins apparently does not compete effectively with internal conversion to the ground state.³³ A third possibility that the species undergoing protona-

(30) In all of our runs the photoproduct ratio 26/27 (R = CH₃) decreased with irradiation time. This may be due in part to a secondary reaction by the unsaturated ether 26 (R = CH₃) since a control experiment revealed that it undergoes slow disappearance under the irradiation conditions.

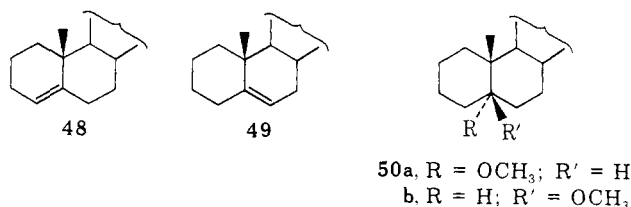
(31) Unpublished from these laboratories.

(32) J. S. Littler and W. A. Waters, *J. Chem. Soc.*, 2767 (1960).

(33) J. Saltiel, J. D'Agostino, E. D. Megarity, L. Metts, K. R. Neuberger, M. Wrighton, and O. C. Zafiriou, *Org. Photochem.*, **3**, 1 (1973).

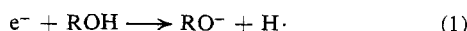
tion is a singlet excited state in the case of direct irradiation and a triplet excited species in the sensitized runs likewise does not seem probable since, as discussed below, the lowest lying singlet and triplet excited states of olefins are not of the same electronic configuration^{34, 35} and, hence, might be expected to show different chemical behavior.

In contrast to our observation that cycloalkenes afford identical results on direct and sensitized irradiation under otherwise identical conditions is a report that steroidal olefins of types **48** and **49** exhibit stereochemically different photobehavior depending on the mode of excitation.³⁶ Thus, although either direct or sensitized irradiation of **48** or **49** in methanol affords principally the 5-methoxy addition product **50**, benzene-sensitized irradiation gives only the 5 β epimer **50b** whereas direct irradiation affords both the 5 α and β epimers **50a** and **b**.³⁶



Although the origin of this discrepancy is not clear, it is conceivable that the sensitized addition process is forced to be stereoselective (involving the 5 β face) because the normally less hindered 5 α side is rendered inaccessible by the remaining presence of the sensitizer molecule.³⁷ By contrast, in the direct irradiation process both faces of olefins **48** and **49** are accessible to the methanol solvent.

Novel Behavior. As shown in Scheme III, the products obtained from direct irradiation of tetra-substituted olefins such as **20** in polar media are readily accounted for in terms of a radical-cation intermediate of type **21b** that undergoes nucleophilic trapping by the solvent to afford the alkoxy radical **23**, and subsequent loss or gain of H \cdot to give **26** or **27**, respectively.³⁸ The hydrocarbon products **24** and **25** could arise *via* attack of H \cdot on the starting olefin **20** as indicated in Scheme III. The source of H \cdot could be from reaction of the ejected electron with solvent (eq 1)³⁹ or transfer from



·CH₂OH. This is corroborated by the finding that irradiation of **20** in methanol-*O-d* resulted in extensive incorporation of deuterium in the hydrocarbon products

(34) A. J. Merer and R. S. Mulliken, *Chem. Rev.*, **69**, 639 (1969).

(35) F. H. Watson, Jr., A. T. Armstrong, and S. P. McGlynn, *Theor. Chim. Acta*, **16**, 75 (1970); F. H. Watson, Jr., and S. P. McGlynn, *ibid.*, **21**, 309 (1971).

(36) H. C. de Marcheville and R. Beugelmans, *Tetrahedron Lett.*, 1901 (1969).

(37) For a similar suggestion that the presence of the sensitizer molecule affects the stereochemical course of the photosensitized dimerization of 2-norbornene, as compared with the direct irradiation process, see D. R. Arnold and V. Y. Abrayits, *Mol. Photochem.*, **2**, 27 (1970).

(38) (a) Electron ejection is a precedented photochemical phenomenon in other systems and its possible extension as a more general photochemical phenomenon has been suggested; see J. Saltiel, *Surv. Progr. Chem.*, **2**, 239 (1964). (b) Efficient nucleophilic trapping of radical cations is precedented; see R. N. Adams, *Accounts Chem. Res.*, **2**, 175 (1969).

(39) A. Habersbergerova, Lj. Josimovic, and J. Teply, *Trans. Faraday Soc.*, **66**, 656, 669 (1970).

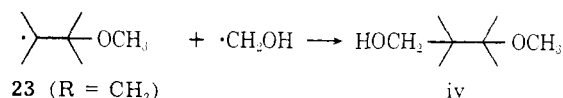
24 and **25** but only minor incorporation in the ethers **26** and **27** (R = CH₃).⁴⁰

In addition to accounting for the observed products, the involvement of a radical-cation intermediate is also consistent with the dependence of this type of photo-behavior on the degree of substitution of the olefin and dielectric constant of the medium. However, it is not consistent with the observation of reaction at 253.7 nm (4.88 eV), albeit slow at least partly because of the very weak absorption by the olefin at this wavelength. Unfortunately the ionization potentials of olefins in solution are unknown. However, the ionization potential of **20** in the gas phase is reported to be 8.30 eV,⁴¹ and it can be estimated from the Born equation that this would be lowered in solution by approximately 2 eV. Although this is only an approximation, it is doubtful that the ionization potential is lowered to the 4.88 eV level necessary to account for reaction at 253.7 nm.

A more attractive alternative is that reaction occurs *via* the first Rydberg excited state, R(3s), represented by **21a**. In the R(3s) \leftarrow N transition a π electron is promoted to a molecular orbital so large that the resulting excited state is expected to display behavior resembling that of a radical cation.³⁴ Nucleophilic trapping of this Rydberg species prior to electron demotion followed by loss of the excited electron would afford the same radical intermediate **23** as obtained by nucleophilic trapping of the radical cation **21a**. Unfortunately little is known about the lifetime of the Rydberg excited state in solution, but it is not unreasonable that nucleophilic trapping would be competitive with electron demotion in undiluted hydroxylic solvents. Likewise, little is known about the chemical behavior of the Rydberg excited state,⁴² and the present observations appear to represent the first report of the behavior in solution.

As charted in Figure 2, the vapor-phase ultraviolet absorption spectra of monoolefinic hydrocarbons typically display two prominent bands above 6.2 eV, the spectral region utilized in the present study—an intense band with a maximum at 6.6–7.6 eV ($\epsilon \sim 10^4$) and, to the red, a weaker band with a maximum at 5.4–7.2 eV ($\epsilon \sim 10^3$).³⁴ The corresponding liquid-phase spectra are qualitatively similar. It is generally agreed that the former band represents the V \leftarrow N, (π, π^*), transition. Much confusion has surrounded the assignment of the latter band, but there is growing consensus that it represents an R(3s) \leftarrow N (Rydberg) transition.^{34, 35} As can be seen from Figure 2, both transitions are lowered in energy by increasing alkyl substitution, but the Rydberg transition is much more sensitive to substitution, having a slope similar to that of the ionization potentials. This similarity in slope is, of course, con-

(40) Also obtained on irradiation of **20** in methanol was the alcohol iv ($\sim 1\%$ yield), which probably arises as shown below.



(41) J. P. Teegan and A. D. Walsh, *Trans. Faraday Soc.*, **47**, 1 (1951).

(42) To the best of our knowledge there is only one example in which photochemical behavior has been assigned to an olefin Rydberg state. This assignment, involving various gas-phase fragmentations, was made by default when it was found that the reactions occurred under conditions in which there was no concomitant cis-trans isomerization; see P. Borrell and F. C. James, *ibid.*, **62**, 2452 (1966); P. Borrell and P. Cashmore, *ibid.*, **65**, 2412 (1969).

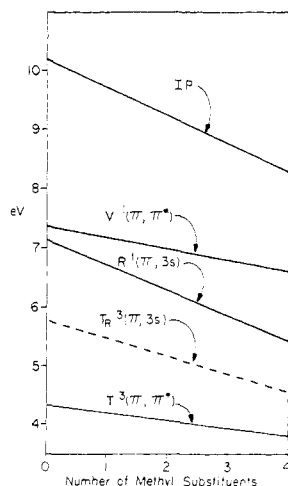


Figure 2. Observed (—) or predicted (---) vertical excitation energies for the π, π^* and Rydberg electronic levels of ethylene and its methyl-substituted derivatives and their ionization potentials (IP) (see ref 34).

sistent with the cation-radical character of the Rydberg excited state and, indeed, has been used as part of the argument in characterizing this transition as Rydberg in character.

The data gathered in Figure 2 are for the observed maxima of the $V \leftarrow N$ and $R \leftarrow N$ systems. Unfortunately the locations of the 0,0 bands for these two transitions are not known. This is a particularly complicated question since the spectroscopic V state of acyclic and larger-ring cyclic olefins can relax by ~ 20 kcal to a lower energy by undergoing twisting about the carbon-carbon bond. The present results strongly suggest that the lower, and hence reactive, singlet excited state is the Rydberg excited state in the case of tetraalkyl-substituted olefins. The lack of any significant degree of reaction *via* a Rydberg excited species in the case of less highly substituted olefins suggests that the lower excited species in these cases is the π, π^* excited state. The very inefficient Rydberg-type reaction in the case of the trisubstituted olefins 1-methylcyclopentene (**1a**) and 1-methyl-2-butene (**36**) suggests that in these cases the Rydberg excited state is nearly isoenergetic with, but perhaps slightly higher lying than, the V state. The marked emergence of the Rydberg excited state as lowest lying in the case of tetrasubstituted olefins is attributable to the greater sensitivity of this excited state to alkyl substitution.

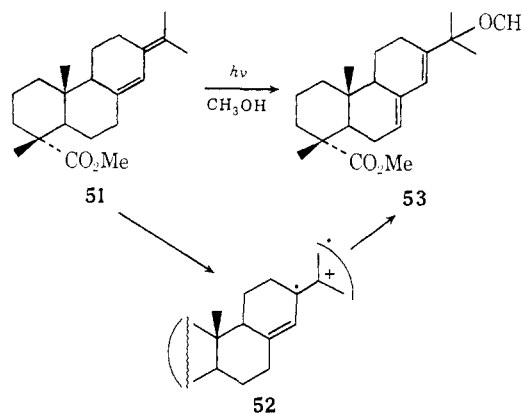
It has been suggested that the lower energy band of bicyclohexylidene (**32**) at 5.96 eV cannot be Rydberg in character because of its high intensity ($\epsilon \sim 5 \times 10^3$).⁴³ However, the similarity in photochemical behavior between **32** and other tetrasubstituted olefins implies a similarity in the nature of the reactive excited state and supports the assignment in this case as Rydberg. Moreover, it should be noted that the intensity of this band in the case of **32** is not significantly higher than that of other olefins and that the $R(3s) \leftarrow N$ may gain part of its intensity *via* vibronic stealing from the $V \leftarrow N$ transition.

Photoproducts **45** and **47** probably arise *via* light-initiated epoxidation of the starting olefins **8** and **20**, followed by acid-catalyzed methanolysis of the resulting

(43) P. A. Snyder and L. B. Clark, *J. Chem. Phys.*, **52**, 998 (1970).

epoxides **44** and **46**. The latter process is probably facilitated by the adventitious formation of acidic photoproducts which has been observed for many commercial specimens of methanol.¹¹ The initial photoepoxidation step is preceded.⁴⁴ Moreover, irradiation of **8** in hexane solution in the presence of oxygen afforded substantial quantities of the epoxide **44**.³¹

It is not yet clear how extensively ethylene derivatives will display the novel photobehavior observed here for olefins **8**, **14**, **20**, **32**, and **36**. However, one other example may be the recent observation that irradiation of the diene methyl neoabietate (**51**) in methanol affords the dienyl ether **53** rather than the usual type of mono-unsaturated product involving the formal addition of the elements of methanol across one of the double bonds.⁴⁵ In this case reaction may involve the Rydberg intermediate **52**. It is noteworthy that addition occurred to a tetrasubstituted ethylene unit in this case.



Our previous studies on the photoprotonation of olefins afforded several reactions having important synthetic applicability.⁴ The discovery of Rydberg behavior opens yet a new vista of synthetic applications, since trapping of the radical-cation-like intermediate with any one of a number of nucleophiles should be possible. Moreover, the reaction has the advantage of not being limited to certain cyclic systems. Further work is in progress to explore more fully the synthetic and mechanistic implications of this new reaction.

Experimental Section⁴⁶

Irradiations. Unless otherwise indicated, all irradiations were conducted using a Hanovia 450-W, medium-pressure mercury arc and a water-cooled quartz 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. The irradiations outlined in Table II were conducted in sealed quartz nmr tubes strapped to an immersion well. Irradiations at 254 or 350 nm were conducted using an RPR-100 Rayonet photochemical reactor equipped with a circular array of 16 G8T5 or

(44) R. C. Petterson, *Angew. Chem., Int. Ed. Engl.*, **9**, 644 (1970).

(45) J. C. Sircar and G. S. Fisher, *Chem. Ind. (London)*, 26 (1970).

(46) Infrared spectra were obtained on carbon tetrachloride solutions with a Perkin-Elmer infracord or 421 grating spectrophotometer. Gas chromatographic analyses were performed on an Aerograph 90-P or a Hewlett-Packard 5750 instrument using 10 ft \times 0.25 in. columns packed with (A) 20% Carbowax 20M, (B) 20% SE-30 on 60-80 mesh Chromosorb W, or (C) 20% β, β' -dioxypionitrile on 60-80 mesh Chromosorb P. Nuclear magnetic resonance spectra were determined in chloroform- d_3 or carbon tetrachloride solution with Varian HA-100 or Jeolco C-60HL spectrometers, using 0.3% tetramethylsilane as an internal standard. Mass spectra were obtained using an AEI MS-902 or a Hitachi RNU-6E spectrometer; in deuterium analyses the P-1 and P-2 peaks were minimized by lowering the accelerating voltage (12 eV). *m/e* values reported include the parent ion peak, if detectable, and other significantly large peaks appearing above *m/e* 55.

F8T5/BL lamps. Starting materials were obtained commercially except for 1-(2'-ethanol)cyclopentene (**6a**),¹⁸ 1-(2'-ethanol)cyclohexene (**6b**),¹⁶ and bicyclohexylidene (**32**).⁴⁷ The progress of photochemical reactions was monitored by gas chromatographic analysis of aliquots removed periodically, calculated relative to an internal hydrocarbon standard. Control runs showed that no reaction occurred in the absence of light. Results from irradiation of olefins **1** and **6** are outlined in Tables I and II.

1,2-Dimethylcyclohexene (8). A. **Sensitized Irradiation.** A solution containing 4.40 g of olefin **8**, 3.0 g of *p*-xylene, and 200 ml of methanol was irradiated as described above for 3 hr with the use of a Vycor filter. Gas chromatographic analysis (B) revealed the continued presence of olefin **8** (14% recovery) and the presence of three principal products. At least four other products were detected in trace amounts, two of which corresponded in retention times to **2,3-dimethylcyclohexene** and *trans*-**1,2-dimethylcyclohexane**. Isolation of the major component by a preparative gas chromatography afforded a colorless liquid which exhibited structural properties identical with that of a commercial specimen of **1-methylene-2-methylcyclohexane (9)**.

Isolation of the second major component afforded *trans*-**1,2-dimethylcyclohexyl methyl ether (10)** as a colorless liquid: ν_{\max} 1150, 1118, 1090, 1075, 928, 870, 854, and 780 cm^{-1} ; nmr τ 6.90 (s, 3, CH_3O), 8.92 (s, 3, CH_3-1), and 9.1 (m, 3, CH_3-2); m/e 142.1364 (calcd for $\text{C}_9\text{H}_{18}\text{O}$, 142.1358), 127, 99, 95, 85, 72, 69, 67, and 59.

Isolation of the minor component afforded *cis*-**1,2-dimethylcyclohexyl methyl ether (11)** as a colorless liquid: ν_{\max} 1128, 1085, 900, 870, and 825 cm^{-1} ; nmr τ 6.84 (s, 3, CH_3O), 8.97 (s, 3, CH_3-1), and 9.15 (3, d, $J = 6.5$ Hz, CH_3-2); m/e 142.1341 (calcd for $\text{C}_9\text{H}_{18}\text{O}$, 142.1358), 99, 95, 85, 72, 69, 67, 59, and 55. The infrared spectra obtained for the ethers **10** and **11** were identical with those previously reported.²⁰

Based on recovered starting material the three major products **9–11** were obtained in yields of 37, 21, and 10%, respectively.

B. **Acid-Catalyzed Addition of Methanol.** A solution containing 2.0 g of olefin **8** and 6 drops of concentrated sulfuric acid in 10 ml of methanol was allowed to stand at room temperature for 2 weeks. Gas chromatographic analysis revealed the presence of ethers **10** and **11** in a ratio of 3.4:1.0. Specimens collected by preparative gas chromatography afforded spectral data identical with that reported above.

C. **Direct Irradiation.** A solution containing 4.40 g of olefin **8** in 200 ml of methanol was irradiated as described above for 8 hr. Gas chromatographic analysis (B) revealed a 3% recovery of olefin **8**, the formation of **1-methylene-2-methylcyclohexane (9)** in 8% yield, and the formation of at least five additional hydrocarbon products in a total yield of 6%. In addition, four ether products were detected. Collection of the first and third to elute by preparative techniques (A) afforded *trans*- and *cis*-**1,2-dimethylcyclohexyl methyl ether (10 and 11)** in yields of 15 and 9%, respectively. Isolation of the second ether to elute afforded **1-methyl-2-methylene-cyclohexyl methyl ether (12)** in 4% yield as a colorless oil: ν_{\max} 3096, 1646, 1370, 1109, 1173, 1078, and 905 cm^{-1} ; nmr τ 5.11 and 5.22 (2 br s, 2, $\text{CH}_2=\text{CH}_2$), 7.00 (s, 3, CH_3O), and 8.80 (s, 3, CH_3-1); m/e 140.1200 (calcd for $\text{C}_9\text{H}_{16}\text{O}$, 140.1201), 125, 111, 109, 108, 95, 93, 91, 85, 79, 77, 72, and 67.

Isolation of the fourth ether afforded **1,2-dimethyl-2-cyclohexenyl methyl ether (13)** in 2% yield as a colorless liquid: nmr τ 4.43 (br s, 1, $\text{CH}-3$), 6.97 (s, 3, CH_3O), 8.42 (br s, 3, CH_3-2), and 8.81 (s, 3, CH_3-1); m/e 140.1198 (calcd for $\text{C}_9\text{H}_{16}\text{O}$, 140.1201), 125, 109, 108, 93, 91, 79, 77, and 67.

D. **Irradiation in the Presence of Oxygen.** A solution containing 2.28 g of olefin **8** in 100 ml of methanol was irradiated as described above for 3 hr except that the stream of nitrogen was replaced by oxygen. Gas chromatographic analysis revealed the formation of **1-methylene-2-methylcyclohexane (9)** (10%), five additional hydrocarbon products (6% total) and ethers **10–13** (21% total), an unidentified ether (1%), and **2-hydroxy-1,2-trans-dimethylcyclohexyl methyl ether (45)** (11%). Isolation of the last component by preparative techniques (A) afforded ether **45** as a colorless liquid: ν_{\max} 3628, 1180, 1084, 948, and 873 cm^{-1} ; nmr τ 6.87 (s, 3, CH_3O), 7.97 (br s, 1, OH), and 8.84 and 8.88 (2 s, 6, 2 CH_3); m/e 158.1303 (calcd for $\text{C}_9\text{H}_{18}\text{O}_2$, 158.1307), 143, 126, 125, 111, 98, 85, 84, 83, 72, 71, 59, and 55.

Material identical with that described above for ether **45** was obtained by treatment of 0.2 g of 1,6-dimethyl-7-oxabicyclo[4.1.0]-

heptane (**44**)⁴⁸ with 1.0 ml of methanol containing a small drop of sulfuric acid for 2 hr at room temperature followed by neutralization and isolation by preparative gas chromatographic techniques.

Independent Synthesis of Ethers 12 and 13. In accord with the general procedure previously described,⁴⁹ a solution containing 5.50 g of olefin **8**, 30 mg of rose bengal, and 25 ml of methanol was irradiated at 350 nm for 16 hr while oxygen was slowly bubbled through the solution. The solution was then concentrated under a stream of nitrogen. The resulting crude mixture of hydroperoxides was dissolved in 50 ml of ether, mixed with a solution containing 13 g of triphenylphosphine, and allowed to stand at room temperature for 4 days. The solvent was removed under reduced pressure, the residue slurried with pentane, and the pentane solution decanted and distilled through a short path to give 2.9 g of a colorless, viscous liquid, bp 65–69° (15 mm). Gas chromatographic analysis (A) revealed the presence of two principal components of this mixture. Isolation of the first component by preparative techniques afforded **1-methyl-2-methylene-cyclohexanol** as a colorless liquid: ν_{\max} 3616, 3095, 1648, 906, and 898 cm^{-1} ; nmr τ 5.16 and 5.44 (2 s, 2, $\text{CH}_2=\text{CH}_2$), 6.60 (s, 1, OH) and 8.73 (s, 3, CH_3); m/e 126.1040 (calcd for $\text{C}_8\text{H}_{14}\text{O}$, 126.1045), 111, 108, 97, 93, 91, 83, 79, 77, 71, 69, 67, 59, 58, and 55.

Isolation of the second component afforded **1,2-dimethyl-2-cyclohexenol** as a colorless liquid: ν_{\max} 3608 cm^{-1} ; nmr τ 4.70 (br s, 1, $\text{CH}-3$), 6.54 (s, 1, OH), 8.38 (s, CH_3-2), and 8.82 (s, 3, CH_3-1); m/e 126.1042 (calcd for $\text{C}_8\text{H}_{14}\text{O}$, 126.1045), 111, 108, 93, 91, 79, 77, 67, and 55.

The remainder of the above mixture of allylic alcohols was further purified by chromatography through 90 g of neutral activity III alumina. Elution with 1:9 benzene–hexane afforded a mixture of impurities. Elution with ether afforded 2.0 g of a mixture of the two allylic alcohols as a colorless liquid. In accord with the general procedure previously described,⁵⁰ a solution of this mixture in ether was stirred with 0.5 g of sodium hydride for 4 hr. A solution containing 11 g of methyl iodide in ether was added dropwise and the resulting mixture was stirred overnight at room temperature. Filtration through Celite afforded a pale yellow solution which was shown by a gas chromatographic analysis to consist of the ethers **12** and **13**. Isolation by preparative techniques afforded specimens of these ethers which exhibited spectral data identical with that reported above.

1,2-Dimethylcyclopentene (14). A. **Direct Irradiation.** A solution containing 1.0 g of olefin **14** in 100 ml of methanol was irradiated as described above for 3 hr. Gas chromatographic analysis revealed the presence of three unidentified hydrocarbon photoproducts, formed in approximately 15% total yield, and the ethers **15–18**, formed in yields of 8, 3, 7, and 15%, respectively. Isolation of each of these components by preparative gas chromatography afforded specimens having spectral properties identical with those described below.

B. **Acid-Catalyzed Addition of Methanol.** A solution containing 2.0 g of olefin **14** and 6 drops of concentrated sulfuric acid in 10 ml of methanol was allowed to stand at room temperature for 2 weeks. Gas chromatographic analysis (A) revealed the formation of two products in a 1.2:1.0 ratio. Isolation of the major component afforded *trans*-**1,2-dimethylcyclopentyl methyl ether (15)** as a colorless liquid: ν_{\max} 1091 and 1072 cm^{-1} ; nmr spectrum τ 6.97 (s, 3, CH_3O), 8.90 (s, 3, CH_3-1), and 9.13 (br d, 3, CH_3-2); m/e 128.1205 (calcd for $\text{C}_8\text{H}_{16}\text{O}$, 128.1201), 99, 86, 85, 81, 72, and 55.

Isolation of the minor product afforded *cis*-**1,2-dimethylcyclopentyl methyl ether (16)** as a colorless liquid: ν_{\max} 1129, 1088, and 1050 cm^{-1} ; nmr τ 6.95 (s, 3, CH_3O), 8.99 (s, 3, CH_3-1), and 9.18 (d, 3, $J = 6$ Hz, CH_3-2); m/e 128.1183 (calcd for $\text{C}_8\text{H}_{16}\text{O}$, 128.1201), 99, 86, 85, 81, 72, and 55.

C. **Independent Synthesis of Ethers 17–19.** A solution containing 5.00 g of olefin **14** and 30 mg of rose bengal in 25 ml of methanol was irradiated for 22 hr at 350 nm while a slow stream of oxygen was passed through the solution. Disappearance of the olefin was monitored by gas chromatographic analysis. Several replenishments of the dye were necessary. Reduction of the hydroperoxide mixture and isolation of the allylic alcohols were accomplished in the same manner as described above for the cyclohexyl homologs. The first component to elute was **1-methyl-2-methylene-cyclopentanol**, obtained as a colorless oil: nmr τ 5.07 and 5.25

(48) L. W. Trevoy and W. G. Brown, *J. Amer. Chem. Soc.*, **71**, 1675 (1949).

(49) K. Gollnick, *Advan. Photochem.*, **6**, 1 (1968).

(50) W. G. Dauben, J. H. Smith, and J. Saltiel, *J. Org. Chem.*, **34**, 261 (1969).

(47) D. H. R. Barton, E. H. Smith, and B. J. Willis, *Chem. Commun.*, 1226 (1970); N. J. Turro, P. A. Leermakers, and G. F. Vesley, *Org. Syn.*, **47**, 34 (1970).

(2 s, 2, $\text{CH}_2=\text{CH}$), and 8.75 (s, 3, CH_3 -1); m/e 112.0891 (calcd for $\text{C}_7\text{H}_{12}\text{O}$, 112.0888), 97, 95, 94, 93, 91, 84, 81, 79, 77, 72, 71, and 69.

The second component to elute gave an nmr spectrum consistent with **2,3-dimethyl-2-cyclopenten-1-ol**: τ 5.7 (m, 1, CH -1), 6.50 (br s, 1, HO), and 8.43 (s, 6, CH_3 -1 and -2).⁵¹ The remainder of the above mixture of allylic alcohols was treated with sodium hydride and methyl iodide as described above. The reaction mixture was filtered through Celite to give a yellow-green solution, which was concentrated by distillation. Gas chromatographic analysis revealed the presence of two components. Isolation of the first component by preparative techniques afforded a mixture of **1-methyl-2-methylenecyclopentyl methyl ether (17)** and **1,2-dimethyl-2-cyclopentenyl methyl ether (18)**: nmr spectrum for **17** τ 5.09 and 5.18 (2 s, $\text{CH}_2=\text{CH}$), 7.03 (s, CH_3O), and 8.81 (s, CH_3 -1); for **18** τ 4.59 (m, CH -3), 7.08 (s, CH_3O), and 8.81 (s, CH_3 -1).

Isolation of the second component afforded **2,3-dimethyl-2-cyclopentenyl methyl ether (19)** as a colorless liquid: ν_{max} 1380, 1349, 1188, and 1086 cm^{-1} ; nmr τ 5.91 (m, 1, CH -1), 6.87 (s, 3, CH_3O), and 8.43 (m, 6, CH_3 -2 and -3); m/e 126.1025 (calcd for $\text{C}_9\text{H}_{14}\text{O}$, 126.1045), 111, 95, 94, 93, 91, 80, 79, 78, 77, 69, 67, 66, and 65.

The above mixture of three allylic ethers was dissolved in methanolic hydrochloric acid. The solution turned bright green within 10 min. After 2 hr the reaction was quenched with sodium methoxide. Gas chromatographic analysis revealed the continued presence of the two major components. Isolation of the first component afforded ether **17** uncontaminated by ether **18**.

D. Photosensitized Irradiation. A solution containing 2.00 g of olefin **14** and 3 ml of *p*-xylene in 100 ml of methanol was irradiated as described above using a Vycor filter for 8 hr. There was a loss of **14** but no detectable formation of any volatile photoproducts.

2,3-Dimethyl-2-butene (20). **A. Direct Irradiation.** The results from direct irradiation of olefin **20** under a variety of conditions are summarized in Table III. The products were isolated by preparative gas chromatography. Alcohols **26** and **27** ($\text{R} = \text{H}$) were identified by direct comparison with commercial specimens. The following additional products were characterized.

Methyl 1,1,2-trimethyl-2-propenyl ether (26, $\text{R} = \text{CH}_3$) was obtained as a colorless liquid: ν_{max} 3097, 1644, 1376, 1361, 1170, 1147, 1075, and 901 cm^{-1} ; nmr τ 5.32 (s, 2, $\text{CH}_2=\text{CH}$), 7.12 (s, 3, CH_3O), 8.38 (s, 3, CH_3 -2), and 8.78 (s, 6, CH_3 -1); m/e 114.1041 (calcd for $\text{C}_7\text{H}_{14}\text{O}$, 114.1045), 99, 83, 82, 73, 69, and 67.

This material was identical in retention time and spectral properties with a specimen prepared independently by treatment of 2,3-dimethyl-3-buten-2-ol (**26, $\text{R} = \text{H}$**) with sodium hydride and methyl iodide as described above.

Methyl 1,1,2-trimethylpropyl ether (27, $\text{R} = \text{CH}_3$) was obtained as a colorless liquid: ν_{max} 1388, 1375, 1365, 1198, 1179, 1152, 1110, 1085, and 1064 cm^{-1} ; nmr τ 6.92 (s, 3, CH_3O), 8.26 (h, 1, $J = 6.5$ Hz, CH -2), and 8.99 (s, 6, CH_3 -1); m/e 101 and 73.

Anal. Calcd for $\text{C}_7\text{H}_{14}\text{O}$: C, 72.35; H, 13.88. Found: C, 72.49; H, 13.80.

This material was identical in retention time and spectral properties with a sample prepared independently by acid-catalyzed addition of methanol to olefin **20** following the general procedure described above.

3-Methoxy-2,2,3-trimethylbutan-1-ol was obtained as a colorless liquid: ν_{max} 3460, 2982, 2838, 1469, 1377, 1145, and 1059 cm^{-1} ; nmr τ 6.65 (s, 2, CH_2 -1), 6.80 (s, 3, CH_3O), 8.85 (s, 6, CH_3 -3), and 9.12 (s, 6, CH_3 -2); m/e 131.1073 (calcd for $\text{C}_7\text{H}_{16}\text{O}_2$, 131.1072), 115, 99, 84, 83, 74, 73, 69, 57, and 55.

2,3-Dimethyl-3-methoxy-2-butanol (47) was obtained as a colorless liquid: ν_{max} 3572, 1156, 1118, and 1068 cm^{-1} ; nmr τ 6.86 (s, 3, CH_3O), 7.70 (s, 1, OH), and 8.92 (s, 12, CH_3); m/e 117, 101, 85, 83, 73, 59, 57, and 55. This material was identical in every respect with a specimen obtained by acid-catalyzed methanolysis of 2,3-dimethyl-2-butene oxide (**46**).

Ethyl 1,1,2-trimethyl-2-propenyl ether (26, $\text{R} = \text{C}_2\text{H}_5$) was obtained as a colorless liquid: ν_{max} 3091, 1641, 1388, 1373, 1357, 1207,

1156, 1107, 1068, and 899 cm^{-1} ; nmr τ 5.20 (s, 2, $\text{CH}_2=\text{CH}$), 6.83 (q, 2, $J = 6.5$ Hz, $\text{CH}_3\text{CH}_2\text{O}$), 8.28 (s, 3, CH_3 -2), 8.73 (s, 6, 2 CH_3), and 8.90 (t, 3, $J = 6.5$ Hz, CH_3CH_2); m/e 128.1199 (calcd for $\text{C}_9\text{H}_{16}\text{O}$, 128.1201), 113, 87, 85, 83, 69, 67, 59, 57, and 55.

Ethyl 1,1,2-trimethylpropyl ether (27, $\text{R} = \text{C}_2\text{H}_5$) was obtained as a colorless liquid: ν_{max} 1390, 1374, 1364, 1173, 1153, 1118, 1098, and 1069 cm^{-1} ; nmr τ 6.68 (q, 2, $J = 6.5$ Hz, $\text{CH}_3\text{CH}_2\text{O}$), 8.25 (h, 1, $J = 6.5$ Hz, CH -2), 8.95 (t, 3, $J = 6.5$ Hz, CH_3CH_2), 8.83 (s, 6, 2 CH_3), and 9.13 (d, 6, $J = 6.5$ Hz, 2 CH_3); m/e 115, 87, 85, 69, and 59.

Anal. Calcd for $\text{C}_9\text{H}_{18}\text{O}$: C, 73.78; H, 13.93. Found: C, 73.77; H, 13.78.

This material was identical in every respect with a sample prepared independently by acid-catalyzed addition of ethanol to olefin **20**.

***n*-Butyl 1,1,2-trimethyl-2-propenyl ether (26, $\text{R} = n\text{-C}_4\text{H}_9$)** was obtained as a colorless liquid: ν_{max} 3087, 2979, 2930, 2866, 1635, 1446, 1368, 1356, 1286, 1149, 1068, 1028, 975, 895, and 727 cm^{-1} ; nmr τ 8.73 (s, 6, 2 CH_3 -1), 8.26 (m, 3, CH_3 -2), 6.84 (m, 2, $-\text{CH}_2\text{O}-$), and 5.08 (m, 2, $\text{CH}_2=\text{CH}$); m/e 156.1511 (calcd for $\text{C}_{10}\text{H}_{20}\text{O}$, 156.1514), 141, 115, 85, 84, 83, 59, 57, and 55.

This material was identical with a specimen prepared independently by a modification of the general procedure described above. A solution containing 1.00 g (10 mmol) of a commercial sample of 2,3-dimethyl-3-buten-2-ol (**26, $\text{R} = \text{H}$**) in 25 ml of freshly distilled diethylene glycol dimethyl ether was stirred for 2 hr with 840 mg (17.5 mmol) of a 50% suspension of sodium hydride in oil which had been washed with pentane. An additional 600 mg (12.5 mmol) of sodium hydride was washed with pentane and added, and stirring was continued for 1 hr. The resulting suspension was cooled in an ice bath and 3.68 g (20 mmol) of 1-iodobutane was added rapidly. After 15 min the reaction mixture was warmed to room temperature and then maintained at 34° for 24 hr. The mixture was diluted with water and extracted with pentane. The combined pentane extracts were dried over anhydrous sodium sulfate and concentrated by distillation. Isolation by preparative gas chromatography (**C**) afforded ether **26** ($\text{R} = n\text{-C}_4\text{H}_9$).

***n*-Butyl 1,1,2-trimethylpropyl ether (27, $\text{R} = n\text{-C}_4\text{H}_9$)** was obtained as a colorless liquid: ν_{max} 2961, 2933, 2874, 1465, 1390, 1372, 1364, 1170, 1152, 1081, and 730 cm^{-1} ; nmr τ 6.68 (m, 2, $-\text{CH}_2\text{O}-$); m/e 143.1434 (calcd for $\text{C}_9\text{H}_{18}\text{O}$, 143.1436), 115, 87, 85, 59, 57, and 55.

This material was identical with a specimen prepared independently by treatment of a commercial sample of 2,3-dimethylbutan-2-ol (**27, $\text{R} = \text{H}$**) with sodium hydride and 1-iodobutane using the modified general procedure described above.

B. Sensitized Irradiation. A solution containing 3.4 g of olefin **20** in 200 ml of methanol was irradiated through a Corex filter for 2 hr. No disappearance of the olefin occurred. *p*-Xylene (3.0 g) was added and the irradiation continued another 4 hr. Again, no disappearance of the olefin occurred.

Irradiation of Methyl 1,1,2-Trimethyl-2-propenyl Ether (26, $\text{R} = \text{CH}_3$). A solution containing 2.15 g of olefin **26** ($\text{R} = \text{CH}_3$) in 100 ml of ether was irradiated as described above for 8 hr. Gas chromatographic analysis revealed a slow loss of starting olefin (58% recovery) and the formation of a small peak (8% yield) having a retention time identical with ether **27** ($\text{R} = \text{CH}_3$). No other volatile products were observed.

Bicyclohexylidene (32). **A. Direct Irradiation.** A solution containing 3.10 g of olefin **32**⁴⁷ in 100 ml of methanol was irradiated as described above for 4 hr. Gas chromatographic analysis revealed a 5% recovery of **32** and the formation of photoproducts **33–35** in yields of 8, 22, and 32%, respectively. Isolation of the major components by preparative methods afforded **bicyclohexyl (35)** as a colorless liquid which was identical in every respect with a commercial specimen.

Isolation of the minor ether component afforded **1-bicyclohexyl methyl ether (33)** as a colorless liquid: ν_{max} 2933, 2858, 2828, 26721 1447, 1146, and 1078 cm^{-1} ; nmr τ 6.96 (s, 3, CH_3O); m/e 196.1800 (calcd for $\text{C}_{13}\text{H}_{24}\text{O}$, 196.1827), 164, 153, 113, 112, 97, 93, 85, 83, 82, 81, 79, 71, 69, 67, and 55.

Isolation of the major ether component afforded **1-(1'-bicyclohexenyl) methyl ether (34)** as a colorless liquid: ν_{max} 2937, 2861, 2826, 1447, 1145, 1078, 913, and 818 cm^{-1} ; nmr τ 4.54 (m, 1, CH -2'), and 7.16 (s, 3, CH_3O); m/e 194.1667 (calcd for $\text{C}_{13}\text{H}_{22}\text{O}$, 194.1671), 163, 162, 119, 105, 95, 91, 81, 79, 77, 67, 55, and 53.

B. Sensitized Irradiation. A 100-ml methanolic solution containing 3.01 g of olefin **32** and 20 g of *p*-xylene was irradiated as described above through a Vycor filter for 8 hr. Gas chromatographic analysis revealed a 98% recovery of the olefin.

(51) This component is certainly a result of rearrangement of the trisubstituted olefin 1,2-dimethyl-2-cyclopenten-1-ol on the gas chromatographic column since no trace of the latter was found here but its methyl ether was generated from this mixture. 1,2-Dimethyl-2-cyclopenten-1-ol has been prepared and found to be "extremely unstable" [see V. A. Mironov, S. N. Kostina, A. N. Elizarova, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 875 (1964); *Chem. Abstr.*, 61, 5532 (1964); V. A. Mironov, E. V. Sobolev, and A. N. Elizarova, *Tetrahedron*, 19, 1939 (1963)]. Additional components of the above mixture appeared to be epoxides and diols.

1-Cyclohexylcyclohexene (30). A. **Sensitized Irradiation.** A solution containing 3.28 g of olefin **30** and 3.0 g of *p*-xylene in 100 ml of methanol was irradiated through a Vycor filter for 16 hr. Gas chromatographic analysis revealed the formation of two principal products accompanied by a number of minor products. Isolation of the first principal component afforded bicyclohexylidene (**32**). Isolation of a second component afforded a specimen of the ether **33** which was identical in all respects with that described above. These products were formed in yields of 29 and 53%, respectively.

B. **Direct Irradiation.** A solution containing 3.00 g of olefin **30** and 0.5 ml of concentrated sulfuric acid in 100 ml of methanol was irradiated for 16 hr. Gas chromatographic analysis revealed the formation of ethers **33** and **34** (50 and 10% yields, respectively) along with an unresolved mixture of olefins **30** and **32** (33%).

Irradiation of 1,1'-Bicyclohexenyl (31). A 75-ml methanolic solution containing 1.5 g of olefin **31** and 1.5 g of acetophenone was irradiated for 6 hr through a Pyrex filter as described above. Gas chromatographic analysis revealed the formation of a single principal product. Isolation by preparative techniques afforded a specimen of ether **34** which was identical in every respect with that described above.

Irradiation of 2-Methyl-2-butene (36). A solution containing 3.01 g of olefin **36** in 200 ml of methanol was irradiated as described above for 72 hr. Gas chromatographic analysis revealed a 20% recovery of olefin **36** and the formation of three hydrocarbon products having retention times corresponding to **2-methylbutane (41)**, **3-methyl-1-butene (42)**, and **2-methyl-1-butene (43)** in yields of 4, 17, and 21%, respectively. In addition, the presence of four ether products was indicated. Isolation of the first component by preparative techniques (A) afforded **1,2-dimethylpropyl methyl ether (37)**²⁷ as a colorless liquid: ν_{\max} 1386, 1372, and 1100 cm^{-1} ; nmr τ 6.77 (s, 3, CH_3O), 7.05 (t, 1, $J = 7.5$ Hz, CH-1), 8.98 (d, 3, $J = 6$ Hz, CH_3 -1), and 9.12 (d, 6, $J = 7.5$ Hz, 2 CH_3 -2). This material was identical in all respects with a specimen prepared independently by the treatment of 8.8 g of 3-methyl-2-butanol with 4.8 g of a 50% suspension of sodium hydride in 30 ml of ether for 5 hr at 25°, followed by the addition of 15 g of methyl iodide and continued stirring overnight. Decanting of the reaction mixture followed by distillation afforded 3.70 g of a colorless liquid, bp 70–74°.

Isolation of the second ether component afforded **1,2-dimethyl-2-propenyl methyl ether (38)** as a colorless liquid: ν_{\max} 3080, 1650,

1371, 1115, 1095, 1078, and 901 cm^{-1} ; nmr τ 5.16 (br s, 2, $\text{CH}_2=$), 6.40 (q, 1, $J = 8$ Hz, CH-1), 6.87 (s, 3, CH_3O), 8.37 (br s, 3, CH_3 -2), and 8.82 (d, 3, $J = 8$ Hz, CH_3 -1); m/e 100.0886 (calcd for $\text{C}_{10}\text{H}_{12}\text{O}$, 100.0888), 85, 69, 59, and 55. This material was identical in all respects with a specimen prepared independently by the treatment of 8.6 g of 3-methyl-3-buten-2-ol with 4.8 g of 50% sodium hydride suspension and 15 g of methyl iodide as described above. Decanting and distillation afforded 3.70 g of a colorless liquid, bp 60–68°.

Evidence for the presence of the isomeric tertiary ethers **39** and **40** was obtained by comparison of the retention times of authentic specimens and the irradiation products on three (A–C) gas chromatographic columns. **1,1-Dimethylpropyl methyl ether (39)**²⁸ was prepared by the treatment of 4 ml of olefin **36** with 10 ml of methanol containing 7 drops of concentrated sulfuric acid for 1 month at 25°. Quenching of the reaction with an excess of sodium bicarbonate followed by filtration and distillation afforded a colorless liquid, bp 60–64°. Final purification by preparative gas chromatography afforded ether **39** as a colorless liquid: ν_{\max} 1380, 1365, 1189, and 1087 cm^{-1} ; nmr τ 6.92 (s, 3, CH_3O), 8.55 (q, 2, $J = 5$ Hz, CH_2 -2), 8.91 (s, 6, 2 CH_3 -1), and 9.17 (t, 3, $J = 5$ Hz, CH_3).

1,1-Dimethyl-2-propenyl methyl ether (40)²⁹ was prepared by treatment of 8.6 g of 1,1-dimethyl-2-propen-1-ol with 4.8 g of 50% sodium hydride and 15 g of methyl iodide as described above. Decanting and distillation afforded 4.6 g of a colorless liquid: bp 70–75°; ν_{\max} 3091, 3068, 1648, 1412, 1375, 1360, 1173, 1145, 1075, 1000, and 922 cm^{-1} ; nmr τ 4.2, 4.8, and 5.05 (3 m, 3, vinyl H), 6.93 (s, 3, CH_3O), and 8.75 (s, 2 CH_3 -1).

Gas chromatographic analysis revealed that ethers **37–40** were obtained in yields of 3, 10, 1, and 0.5%, respectively.

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Photochemical Transformations. VIII. Photosensitized Rearrangements of Some Acyclic Allylic Halides¹

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Abstract: Photosensitizer-mediated irradiations of a number of acyclic allylic chlorides (and of allyl bromide) have been conducted. In addition to the *cis*–*trans* isomerization anticipated for appropriate olefins, allylic (1,3-sigmatropic) rearrangements and rearrangements of allylic halides to halocyclopropanes (1,2-sigmatropic photocyclizations) were observed. Solvent effects on these rearrangements and upon the competing free-radical processes have been studied. Evidence for triplet photosensitization has been adduced and some quantum yield and quenching studies have been conducted. Possible reaction paths are considered for the photorearrangements.

As reported earlier,³ our interest in the preparation of bridged polycyclic compounds by the photo-induced di- π -methane rearrangement^{4,5} led us to the

irradiation of an acetone solution of **1**, anticipating the formation of **2**. Irradiation instead led to a mixture of the *exo* and *endo* epimers of **3**, a result which appeared to have no precedent in the photochemical literature, involving a process formally analogous to a Wagner–Meerwein rearrangement. As we had previously shown⁶ that **3** is substantially less stable than **1**,

(1) (a) Previous paper in series: S. J. Cristol and G. C. Schloemer, *J. Amer. Chem. Soc.*, **94**, 5916 (1972). (b) Portions of this work were presented in the James Flack Norris Award address at the 163rd National Meeting of the American Chemical Society, Boston, Mass., April 1972. (c) Other portions were described in a preliminary communication: S. J. Cristol and G. A. Lee, *J. Amer. Chem. Soc.*, **91**, 7554 (1969).

(2) (a) From the Ph.D. Thesis of G. A. L., 1971, NDEA Fellow; (b) from the Ph.D. Thesis of A. L. N., 1970.

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