Table III. Conditions for Isolation of Compounds by Gas Chromatography

Compd	Column	Column temp, °C	Detector temp, °C	Injector temp, °C	He flow, ml/min	Retention time, min
4a	A	90	200	170	100	12
4b	A	90	200	170	100	9
4c	A	90	200	170	100	12
4d	A	90	200	170	100	12.5
4e	A	90	200	170	100	9
4f	A	90	200	170	100	12
5	C	90	160	130	100	9.5
6 + 7	A	110	130	135	100	14
7	A	115	200	165	100	11
8	D	100	230	150	100	7
9	B	60	100	70	100	19

Irradiation of 1 in Dimethylacetylene. A solution of **1** (90 mg) in 15 ml of dimethylacetylene was sealed under nitrogen in a Pyrex tube and irradiated with a G.E. sunlamp for 2 hr. The tube was cooled, opened, and the dimethylacetylene distilled to give a yellow residue which must be kept cold and analyzed immediately. Preparative gas chromatography yielded 30 mg (36%) of a colorless, very sensitive liquid (**8**).

Anal. (precise mass[35]) Calcd for $C_{12}H_{16}$: 160.125194. Found: 160.125262.

Irradiation of 1 in Benzene. The diazo compound made from 5 g of tosylhydrazone (method B) was dissolved in 1 l. of dry, degassed benzene. Nitrogen was continually bubbled through the solution which was irradiated with two G.E. sunlamps for 12 hr. The yellow benzene solution was concentrated at the water pump and the brown residue immediately cooled and chromatographed. Collection of the first major peak gave a few milligrams of a low-melting solid, mp 40–42°.

Photochemical Stability of 4e and 4f. Compound **4f** (3 mg) was dissolved in 1 ml of a cyclohexene solution of **1**. The solution was made up so that the concentration of **1** was approximately that used in the stereochemical experiments. The solution was sealed under nitrogen in a Pyrex tube and irradiated with a G.E. sunlamp for 3 hr. The tube was cooled, opened, and the contents were analyzed on column A. No isomerization or loss of **4f** could be detected. A similar experiment showed the stability of **4e**. Adducts were formed with cyclohexene but these have not been carefully characterized. Spectra indicate the presence, as would be expected, of the products of addition to the double bond and insertion into the allylic carbon–hydrogen bond.

Pyrolysis of 9. Compound 9 (10 mg) was dissolved in 0.5 ml of carbon tetrachloride (0.5% tetramethylsilane added) and sealed under nitrogen in an nmr tube. The tube was heated in a water bath at 100°. Analysis by nmr revealed the complete rearrangement of 9 to **10** in 86 min.

Anal. (precise mass) Calcd for $C_{14}H_{16}$: 184.125194. Found: 184.125175.

Relative Rates of Addition of 2 to Olefins. Solutions of **1** in pairs of olefins were prepared by dissolving 5 mg of carefully purified **1** (method A with wash and redistillation) in 1 ml of one olefin and 1 ml of another. The solutions were sealed under nitrogen in Pyrex tubes and irradiated with two G.E. sunlamps for 2 hr. Analyses were performed on column A. Relative thermal conductivities of the adducts were determined by injecting known mixtures of adducts and comparing the known ratios with those obtained by integration of the gas chromatograms. The data from the irradiations were corrected accordingly.

Irradiation of 1 in *cis*-4-Methyl-2-pentene and Hexafluorobenzene. A solution of **1** (5 mg) in 1 ml of *cis*-4-methyl-2-pentene and 1 ml of hexafluorobenzene (73 mole % hexafluorobenzene) was sealed under nitrogen in a Pyrex tube and irradiated for 10 hr with a G.E. sunlamp. Analysis on column A showed that addition had proceeded to give 94% **4f** and 6% **4e**.

Acknowledgment. We are grateful to Mr. Ronald Hochman for experimental assistance.

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[35] Mass spectra were measured on an AEI-MS-9 mass spectrometer. We thank the National Science Foundation for providing funds for the purchase of this instrument through Grant GP-5200. The instrument Laboratory at Princeton is supported in part by Biomedical Sciences Support Grant FR-07057.

Photochemistry of Cycloalkenes. VI. Intramolecular Additions[1]

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Contribution from The Procter & Gamble Company, Miami Valley Laboratories, Cincinnati, Ohio 45239. *Received February 27, 1969*

Abstract: The effect of the availability of an intramolecular proton source on the photochemical behavior of three simple olefin systems (**9**, **20**, and **22**) was studied. Photosensitized irradiation of the norbornenes **9a–c** in methanol or benzene solution afforded principally three tricyclic ethers to which the structures **10a–c** are assigned. This intramolecular addition of the hydroxyl group of an alcohol to the norbornene chromophore is in marked contrast to the exclusive reaction with the α-CH bond previously observed for intermolecular photoreactions of norbornenes with alcohols. An attempt to induce an analogous photoprotonation of an acyclic olefin through the introduction of an intramolecular proton source was made by irradiation of the allyl cyclohexanol **20**. However, photosensitized irradiation under a variety of conditions led to a slow disappearance of **20** without the concomitant formation of a cyclic ether such as **21**; thus, there are still no examples of the photoprotonation of an acyclic olefin. Photosensitized irradiation of the cyclohexenyl alcohol **22** afforded methylenecyclohexane (**2**) and acetaldehyde, which presumably arose *via* photoprotonation and subsequent fragmentation as shown in **23**. In *m*-xylene solution the resulting acetaldehyde underwent photoaddition to the solvent to afford the alcohol **25**. The relationship of these results to the intermolecular photochemical behavior of cycloalkenes observed previously is discussed.

Recent studies have shown that the photochemical behavior of cyclic olefins generally falls into three distinct classes depending upon ring size. The first class is represented by cyclohexenes and -heptenes, which on photosensitized irradiation in protic media

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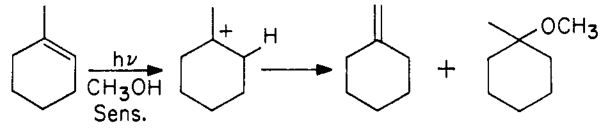
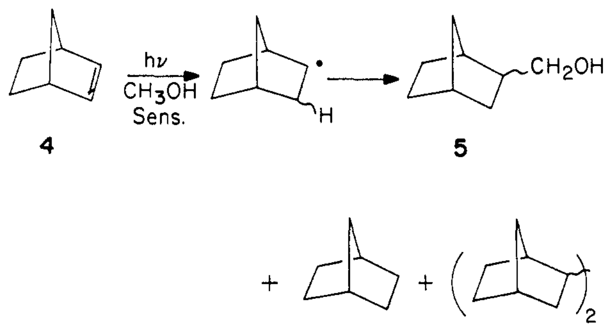
[1] (a) Part V: P. J. Kropp, *J. Amer. Chem. Soc.*, **91**, 5783 (1969); (b) presented in part before the Photochemistry Symposium of the Organic Chemistry Division, Abstracts, 155th National Meeting of the American Chemical Society, San Francisco, California, April 3, 1968, P-86.

undergo efficient protonation.[1-3] Thus photosensitized irradiation of 1-methylcyclohexene **1** in methanol affords a mixture of methylenecyclohexane (**2**) and the methyl ether **3**.[2] The second class is represented by larger ring cyclic olefins, as well as acyclic olefins, which undergo *cis–trans* photoisomerization under these conditions but exhibit no tendency to undergo protonation.[2] Yet a third type of behavior is exhibited by smaller ring cyclic olefins, such as 2-norbornene (**4**) and 1-methylcyclopentene, which display instead radical-type behavior.[1a,4] Thus photosensitized irradiation of 2-norbornene (**4**) in methanol affords a mixture of 2-norbornanemethanol (**5**), norbornane (**6**), and 2,2′-binorbornane (**7**), which apparently arise *via* an initial hydrogen-radical abstraction from the solvent.[1a]

It is clear that the photochemical behavior of cycloalkenes parallels the ability of the olefin to accommodate *cis–trans* isomerization about the double bond. With acyclic and large-ring cyclic olefins, in which *cis–trans* isomerization is readily accommodated, this process occurs to the exclusion of intermolecular reactions with protic media. On the other hand, with small-ring cyclic olefins such as 2-norbornene (**4**), in which little twisting about the double bond is conceivable, intermolecular reaction is seen, but only in the form of hydrogen-atom abstraction. The reactive species in this case is presumably the π,π^* triplet. The identity of the reactive species in the case of cyclohexenes and -heptenes, in which intermolecular reaction is seen in the form of protonation, is less clear. There is sufficient flexibility in this case to permit relaxation of the π,π^* triplet to an orthogonal geometry,[5] but it is also conceivable that intersystem crossing to a highly strained (and hence highly reactive) ground-state *trans*-olefin might occur. Hence *a priori* either the π,π^* triplet or a ground-state *trans*-olefin might be considered as the species undergoing protonation.[6]

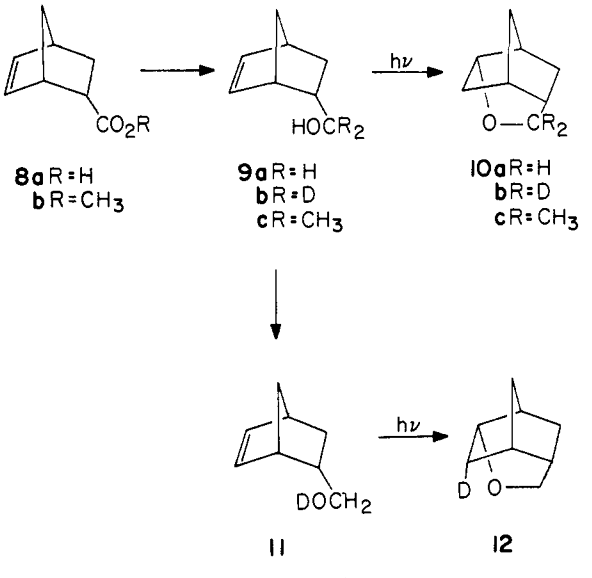


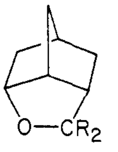
1 **2** **3**



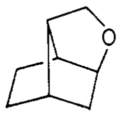
We wish now to consider the additional insight provided by examination of the photochemical behavior of the olefins **9a**, **20**, and **22**, each of which represents one of the abovementioned three classes of olefins and is potentially capable of undergoing *intramolecular* protonation.

5-Norbornene-2-*endo*-methanol (9a). Isomerically pure *endo*-alcohol **9a** was prepared from the *endo*-acid **8a** by esterification with diazomethane followed by reduction of the ester **8b** with lithium aluminum hydride. As shown in Table I, irradiation of **9a** in benzene solution resulted in disappearance of the starting olefin, accompanied by the formation of a single volatile photoproduct.[7] Isolation by preparative gas chromatography afforded the photoproduct as a high-melting (146–146.5°) colorless crystalline solid, which was found by elemental and mass spectral analysis to be isomeric with the starting material. Loss of the characteristic hydroxyl and olefinic absorptions in the infrared spectrum, accompanied by the appearance of a sharp band at 9.06 μ, suggested that a cyclic ether had been generated by intramolecular addition of the hydroxyl group to the double bond. However, the photoproduct was obviously quite different, as evidenced by melting point and spectral behavior, from either **13a**, the well-known product from acid-catalyzed cyclization of **9a**,[8] or **14**, the other known cyclic ether of this series.[9]





13a R=H
b R=CH₃



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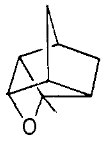

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Attempts to identify the photoether by acid-catalyzed cleavage or treatment with lithium aluminum hydride in refluxing N-ethylmorpholine afforded only recovered ether. Likewise, attempted oxidation to a lactone with chromic acid either afforded no reaction or gave a com-

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(2) P. J. Kropp and H. J. Krauss, *J. Amer. Chem. Soc.*, **89**, 5199 (1967).

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

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

(5) For a discussion of the relaxation of π,π^* triplets of simple olefins to orthogonal species, see R. B. Cundall, *Progr. Reaction Kinetics*, **2**, 165 (1964).

(6) The available data are consistent with either the π,π^* triplet or a *trans*-olefin as the proton abstracting species. The question of which is in fact the reactive species requires further study and is being pursued in several laboratories.

(7) The formation of this photoproduct has also been observed by R. R. Sauers and coworkers. We are indebted to Professor Sauers for discussion of their results prior to publication.

(8) H. A. Bruson and T. W. Riener, U. S. Patent 2,440,220 (1948); *Chem. Abstr.*, **42**, 5471 (1948).

(9) R. R. Sauers and P. E. Sonnet, *J. Org. Chem.*, **29**, 754 (1964).

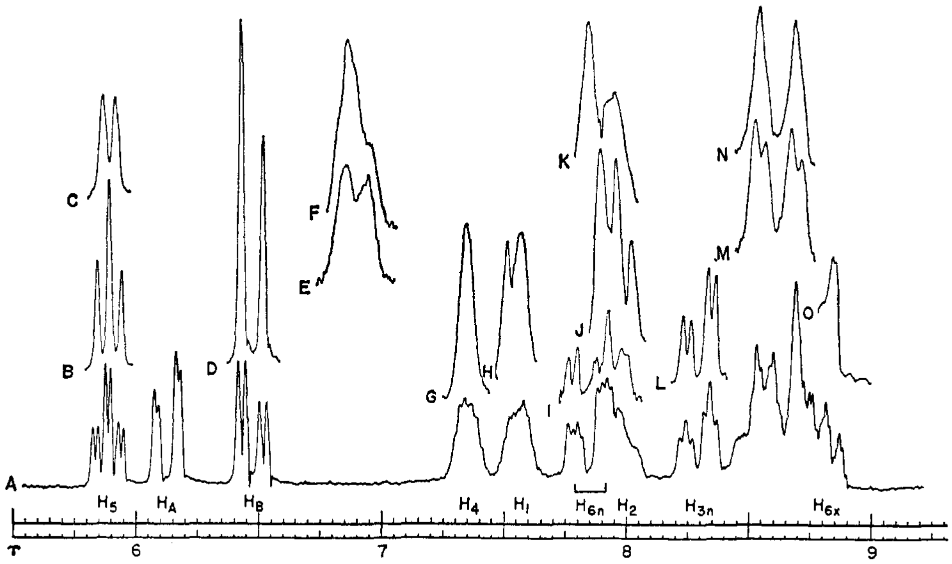

Figure 1. Nmr spectra of photoether **10a**: A, standard spectrum; B, H_5 band decoupled from H_1; C, H_5 band decoupled from H_1 and H_4; D, H_B band decoupled from H_2; E, expansion of one-half of H_A band; F, H_A band decoupled from H_{3x}; G, H_4 band decoupled from H_5; H, H_1 band decoupled from H_{6x}; I, H_{6n} and H_2 bands decoupled from H_1; J, H_2 band decoupled from H_B; K, H_{6n} and H_2 band decoupled from H_{6x}; L, H_{3n} band decoupled from H_4; M, Expansion of one-half of H_B band; N, H_B band decoupled from H_{6x}; O, H_{6x} band decoupled from H_5.

plex mixture of products. However, as described in the Experimental Section and summarized in Figure 1 and Table II, a detailed analysis of the nmr spectrum permitted assignment of the structure **10a** to the photoether.[10] It is interesting to note that many of the couplings observed for **10a** are quite different in magnitude from those normally encountered in the norbornane system. This can readily be seen in Table III, in which some of the data from **10a** are compared with that recently reported for a series of bridged norbornanes related to **13**.[11] The anomalies in the case of **10a** are undoubtedly attributable to the severe distortion imposed on the geometry of the norbornane system by the presence of C_2–C_5 bridging which causes C_2 and C_5 to be pulled toward each other with a concomitant upward displacement of C_3 and C_6 (*cf.*, Figure 2). This departure from normal geometry induces abnormal vicinal and long-range couplings which are consistent with predictions based on Dreiding models and which greatly strengthen a structural assignment for the photoether based on nmr data.

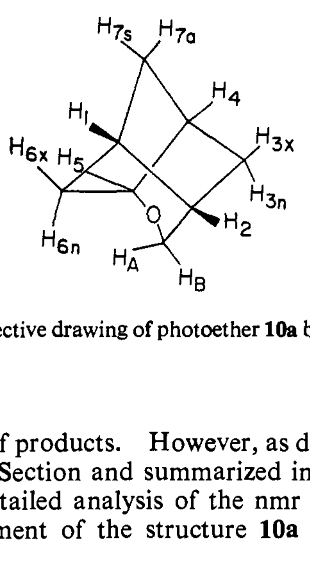

Figure 2. Perspective drawing of photoether **10a** based on Dreiding models.

Table I. Irradiation of the 5-Norbornene-2-*endo*-methanols **9a**–**9c** and **11**[a]

Olefin	Solvent	Sensitizer	E_T, kcal/mol	Time, hr	Yield, %[b] 9 or 11	Yield, %[b] 10 or 12
9a	C_6H_6	C_6H_6	84	10	14	43 (50)[c]
9a	CH_3OH	$(CH_3)_2C_6H_4$[d]	82	4	39	23 (38)
9a	C_6H_6	$C_6H_5COCH_3$[e]	74	4	36	22
9a	C_6H_6	C_6H_5CHO[e]	72	4	63	9
9a	C_6H_6	*e*		4	99	
9b	CH_3OH	$(CH_3)_2C_6H_4$[d]	82	4	9	51
9c	C_6H_6	C_6H_6	84	4	15	85 (100)
9c	CH_3OH	*m*-$(CH_3)_2C_6H_4$	82	2	22	65 (83)
11	CH_3OD	*m*-$(CH_3)_2C_6H_4$	82	4	14	3
11	C_6H_6	C_6H_6	84	8	33	21

[a] Irradiations were conducted as described in the Experimental Section using 150-ml solutions containing 3.0 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] Based on recovered starting material. [d] Commercial mixture of isomers. [e] Pyrex filter employed.

In connection with the analysis of the nmr spectrum of **10a**, it proved helpful to have the dideuterated analog **10b**. This derivative was readily obtained by reduction of the ester **8b** with lithium aluminum deuteride followed by irradiation of the resulting dideuterated alcohol **9b**.

The analogous dimethyl derivative **10c** was similarly obtained by irradiation of alcohol **9c**, prepared by treatment of ester **8b** with methylmagnesium bromide. Unfortunately the nmr spectrum of **10c** was not particularly useful in analyzing the spectrum of its unsubstituted analog **10a** because of differences in chemical shifts and coupling constants which apparently result from conformational changes induced by the presence of the two methyl substituents. However, the conversion of **9c** to **10c** did prove of interest because of its

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[10] Although the ethers **10** are properly named as derivatives of tricyclo[4.3.0.0^{3,8}]nonane, the norbornane numbering system has been employed as shown in Figure 2.

[11] K. C. Ramey, D. C. Lini, R. M. Moriarty, H. Gopal, and H. G. Welsh, *J. Amer. Chem. Soc.*, **89**, 2401 (1967). Although the introduction of a 2,6-methyleneoxy bridge introduces some distortion of the norbornane skeleton, this is relatively minor and, except for the 3n,7s and 5n,7a category, the coupling constants reported are similar to those observed in numerous other norbornane systems.

Table II. Analysis of Nmr Spectrum of Photoether **10a**[a]

Chemical shift, τ	Assignment	$\lvert J \rvert$, Hz 1	2	3n	3x[b]	4	5	6x[c]	7a	7s	A	B
5.89	5	2.0				5.1		5.1				
6.12	A				1.5							8.9
6.47	B		3.0					0.8			8.9	
7.34	4		*d*	2.5	*d*		5.1		*d*	*d*		
7.56	1		6.5				2.0	*e*	*d*	*d*		
7.72	6n	*e*						12[f]	3.5[g,h]			
7.94[f]	2	6.5			7.0[h]							3.0
8.27	3n				10.0[h]	2.5				3.0[g,h]		

[a] Based on single, double, and triple resonance spectra of photoethers **10a**, **10b**, and **12**. [b] Assigned at τ 8.62 on the basis of the frequency required to decouple from H_A. [c] Assigned at τ 8.83 on the basis of the frequency required to decouple from H_B and H_5. [d] A study of Dreiding models suggests that a coupling should be present, but the complexity of the spectra precluded an unequivocal observation of coupling. [e] The presence of coupling was observed but could not be measured because of the complexity of the spectra. [f] Estimated from the spectrum of **10b**. [g] Assignment based on the presence of a W pattern in molecular models. [h] Assignment not verified by decoupling.

Table III. Comparison of Coupling Constants

Type	Protons	$\lvert J \rvert$, Hz **10a**	**13**-type[a]
Geminal	3x,3n; 6x,6n	10.0–12	13.0–13.6
Vicinal	2,3x; 5,6x	5.1–7.0	10.0–10.8
	1,2; 4,5	5.1–6.5	4.0–5.0
	3n,4	2.5	0.5–0.8
Long-range	1,5	2.0	0.3–0.8
	3n,7s	3.0	1.3–2.2[b]
	6n,7a (5n,7a)	3.5	1.7–2.6[b]

[a] Based on various derivatives of **13**; see ref 11. [b] Couplings of 3–4 Hz have been reported in nonbridged norbornanes; see J. Meinwald and Y. C. Meinwald, *J. Amer. Chem. Soc.*, **85**, 2514 (1963).

facility. As can be seen in Table I, cyclization of **9c** proceeded approximately twice as fast as that of **9a** despite the fact that it involves the addition of a tertiary alcohol. Product yields were also substantially higher in the dimethyl series.

Even in methanol solution, under conditions in which 2-norbornene (**4**) affords the radical-type products **5–7** *via* hydrogen abstraction from methanol,[1a] **9a** underwent cyclization to the ether **10a**, although in this case the reaction was not as clean and additional photoproducts, including one having a retention time identical with that of the reduction product 2-norbornanemethanol (**5**), were also observed. In addition to benzene and xylene, which have high triplet excitation energies (82–84 kcal/mol), both acetophenone (E_T = 74 kcal/mol) and benzaldehyde (E_T = 72 kcal/mol) proved effective as photosensitizers for the conversion of **9a** to **10a**.

It was of particular interest to establish the location of the incoming proton in the photoether **9a**. This was accomplished by exchange of the hydroxyl proton of **9a** with deuterium oxide, followed by photocyclization of the resulting deuterated alcohol **11**. In the cyclization process the deuterium atom was found to be incorporated specifically at a single position which could be assigned by analysis of the nmr spectrum to the 6-*endo* position (*cf.*, **12**). Thus a *cis* addition of the –OH (or –OD) group across the double bond occurs during photocyclization. Exchange of the hydroxyl proton of **9a** for deuterium had a noticeable effect on the ease of cyclization. Thus the deuterated alcohol **11** afforded only small amounts of **12** in methanolic solution because of the rapid formation of competing radical-type products. Cyclization occurred more cleanly in benzene solution, in which the possibility of radical-type processes is greatly reduced because of the unavailability of readily abstractable hydrogen atoms, but even here cyclization was substantially slower than for **9a**.[12]

The cyclization of **9a** to **10a** can easily be pictured either as a highly concerted process or as a stepwise reaction involving an initial formation of the C_6–H bond followed by closure of the C_5–O bond. Unfortunately, the present data offer little insight concerning the timing of bond making and bond breaking. However, regardless of the timing of events, it is an important question to ask whether the cyclization involves a homolytic or heterolytic fission of the OH bond. Again, little information is available, but it is our preference to regard the addition process as ionic in view of the fact that it will occur with sensitizers having triplet excitation energies as low as 72 kcal/mol, which is substantially below the homolytic OH bond dissociation energy.[13,14] Moreover, radical abstraction of a hydrogen atom bonded to oxygen is rarely observed. However, facilitation of hydroxyl hydrogen abstraction in the case of **9a** because of its intramolecular availability cannot be ruled out.[15]

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(12) Similar isotope effects have been noted previously in the photoprotonation of cyclohexenes;[2] see also J. A. Marshall and M. J. Wurth, *J. Amer. Chem. Soc.*, **89**, 6788 (1967).

(13) Solution data are apparently not available, but the homolytic OH bond dissociation energy in the gas phase is generally taken to be 102 kcal/mol; see P. Gray and A. Williams, *Trans. Faraday Soc.*, **55**, 760 (1959).

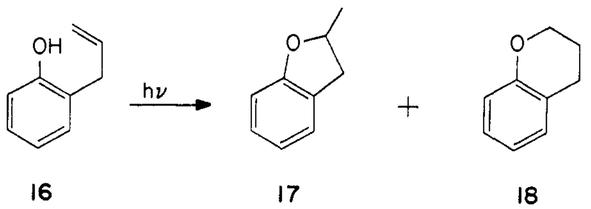
(14) Some precedence for ionic photoaddition to a 2-norbornene is offered by 2-phenyl-2-norbornene, which has been found to undergo photoprotonation in methanol, but reaction in this case involves a singlet species.[1a]

(15) Evidence for light-initiated hydroxyl–hydrogen abstraction from alcohols by flavins has recently been claimed and attributed to hydrogen bonding of the alcohol through the hydroxyl hydrogen to the flavin; see M. Green and G. Tollin, *Photochem. Photobiol.*, **7**, 129 (1968); see also W. M. Moore and C. Baylor, Jr., *J. Amer. Chem. Soc.*, **88**, 5677 (1966), and E. E. van Tamelen, J. I. Brauman, and L. E. Ellis, *ibid.*, **89**, 5073 (1967). However, the situation is somewhat different in the case of **9a**. Although intramolecular bonding of the hydroxyl hydrogen of **9a** to the π lobes of the double bond would appear from models to be quite favorable, the presence of intramolecular hydrogen bonding in **9a** could not be detected by infrared studies; see L. P. Kuhn, P. von R. Schleyer, W. F. Baitinger, Jr., and L. Eberson, *ibid.*, **86**, 650 (1964). Thus **9a** apparently has a preferred conformation in solution in which intramolecular hydrogen bonding is not favored. This suggests either that the photocyclization reaction results from molecules of **9a** which exist in the ground state (and initially in the excited state) in an intramolecularly hydrogen-bonded form but are present in too small a concentration to be observed by infrared studies, or that the π,π^* triplet of **9a** has a sufficient lifetime to permit rotation of the C_2–CH_2OH bond, thus allowing abstraction of the hydroxyl hydrogen to occur. This latter alternative is plausible in view of the fact that the π,π^* triplet of 2-norbornene **4** has a sufficiently long lifetime to undergo intermolecular reaction.[1a,4] On the other hand, the cleanness and facility of the conversion of **9c** to **10c** suggests that intramolecular hydrogen bonding can assist the cyclization process, for, in contrast to **9a**, the dimethyl

The conversion of **9a** to **10a** was not accompanied by any detectable alternative cyclization products. Although in some cases trace amounts of the cyclic ether **13a**,[8] presumably formed from acid-catalyzed cyclization of unreacted **9a**, were observed, under conditions of careful work-up there was no detectable formation of the ether **13a**. Likewise, acid-catalyzed cyclization afforded little or no detectable amount of the photoether **10a**. Thus the acid-catalyzed and light-initiated cyclizations each proceed quite specifically and afford opposite directions of addition across the double bond. This is perhaps not surprising since there are many differences in the two reactions. The acid-catalyzed cyclization involves an initial protonation of the double bond from the *exo* side[16a] and may be subject to thermodynamic control, whereas the photocyclization involves protonation from the *endo* side and is restricted to kinetic control.[16b] The fact that carbon–oxygen bond formation occurs at C_5 rather than C_6 in the photochemical cyclization may be attributable in part to relaxation of the π,π^* triplet norbornene chromophore to a partially twisted geometry.[17]

Attempts to effect an analogous photocyclization of the acid **8a** to a tricyclic lactone by irradiation in benzene solution were without success, as **8a** proved to be surprisingly unreactive under these conditions. Irradiation in xylene–methanol solution resulted in rapid disappearance of **8a** to afford a mixture of products, none of which appeared to be a lactone. On the other hand, irradiation of 5-*endo*-acetyl-2-norbornene resulted in a facile intramolecular cyclization to afford an oxetane[7] to which the structure **15** has recently been assigned.[18]

***trans*-2-Allylcyclohexanol (20).** Recently two separate research groups reported the light-induced cyclization of 2-allylphenols to bicyclic ethers,[19,20] as exemplified by the conversion of **16** to a 9:1 mixture of ethers **17** and **18**, respectively.[19] This reaction bears a formal analogy to the photoaddition of alcohols, water, and acetic acid to cyclic olefins,[2,3] in which either the π,π^* triplet of the olefin or a reactive intermediate derived from the olefin triplet abstracts a proton from the hydroxylic medium.[2] However, this latter photoaddition process has been found to be inapplicable in the case of acyclic olefins,[2] and the important question arises as to whether the cyclization of 2-allylphenols indicates that acyclic olefins are in fact capable of undergoing light-induced proton abstraction if an intramolecular proton source is available.[21] This question is particularly relevant in view of the photocyclization of **9a** to **10a**.



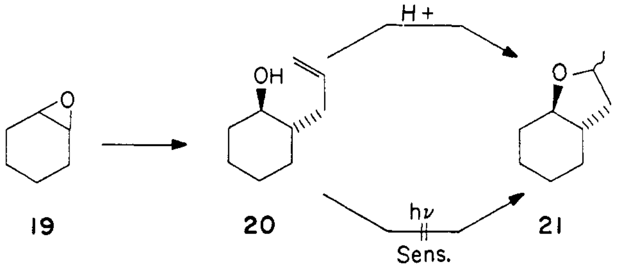
On the other hand, an alternative mechanism is conceivable for the photocyclization of 2-allylphenols which does not involve photoexcitation of the olefinic portion.[22] In light of the greatly enhanced acidity of the first excited states of phenols,[23] it is conceivable that cyclization involves instead an initial protonation of a ground-state allyl moiety by its excited phenol partner.

In order to study this question further, it was considdered desirable to eliminate the ambiguity introduced by the presence of the phenolic proton. Hence, the analogous cyclohexanol **20** was prepared by treatment of cyclohexene oxide (**19**) with allylmagnesium bromide[24] and was subjected to irradiation under a variety of conditions (Table IV). For purposes of comparison the corresponding bicyclic ether **21** was prepared by acid-catalyzed cyclization of **20**.[25] On irradiation in methanolic solution using either xylene or phenol as the photosensitizer there was no detectable conversion to **21**

Table IV. Irradiation of *trans*-2-Allylcyclohexanol (**20**)[a]

Solvent	Sensitizer	Time, hr	Yield, %[b] **20**	Yield, %[b] **21**
CH_3OH	$(CH_3)_2C_6H_4$[c]	8	84	*d*
H^+, CH_3OH[e]	*m*-$(CH_3)_2C_6H_4$	4	86	*f*
CH_3OH	C_6H_5OH	4	100	*d*
H^+, CH_3OH[e]	C_6H_5OH	4	77	3

[a] Irradiations were conducted as described in the Experimental Section using 150-ml solutions containing 3.00 g of **20** and 3.0 g of sensitizer. [b] Determined by gas chromatographic analysis of aliquots removed from the irradiation mixture. [c] Commercial mixture of isomers. [d] None detectable by direct comparison with an authentic specimen. [e] 1% Methanolic sulfuric acid. [f] Trace.



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derivative 9c has been found to exhibit detectable intramolecular hydrogen bonding; see M. Oki, H. Iwamura, T. Onoda, and M. Iwamura, *Tetrahedron*, 24, 1905 (1968).

(16) (a) A. Factor and T. G. Traylor, *J. Org. Chem.*, 33, 2607 (1968); (b) however, the possibility that acid-catalyzed cyclization of **9a** involves formation of the ether **10a** as a product of kinetic control followed by isomerization to **13** as a product of thermodynamic control is precluded by the finding that the ether **10a** is completely stable under conditions in which **9a** is converted to ether **13** in high yield with no detectable formation of **10a**.

(17) A study of Dreiding models using two adjacent trigonal carbon atoms to represent the triplet olefin suggests that twisting up to 30° could occur without excessive torsional strain.

(18) R. R. Sauers, W. Schinski, and M. M. Mason, *Tetrahedron Lett.*, 79 (1969).

(19) Gy. Frater and H. Schmid, *Helv. Chim. Acta*, 50, 255 (1967).

(20) W. M. Horspool and P. L. Pauson, *Chem. Commun.*, 195 (1967).

(21) 2-Allylphenol is one of the classical examples of intramolecular hydrogen bonding between a hydroxyl group and the π electrons of a double bond; see A. W. Baker and A. T. Shulgin, *J. Amer. Chem. Soc.*, 80, 5358 (1958).

(22) Allylphenols can be regarded as consisting of two separate chromophores. Direct irradiation should result in predominant absorption by the phenolic portion. If reaction does not occur from the S_1 state of this chromophore, intersystem crossing should occur to afford the phenol triplet (E_T = 84 kcal/mol), which in turn is capable of transferring triplet energy to the olefinic chromophore. This latter prediction has been verified, as described in the Experimental Section, by the finding that sensitized irradiation of 1-methylcyclohexene (1) in methanol solution with phenol afforded methylenecyclohexane (2) and the methyl ether 3 in yields comparable to those obtained under identical conditions using xylene as the photosensitizer.[2]

(23) See E. L. Wehry and L. B. Rogers, *J. Amer. Chem. Soc.*, 87, 4234 (1965), and references noted therein.

(24) R. L. Letsinger, J. G. Traynham, and E. Bobko, *ibid.*, 74, 399 (1952).

(25) (a) J. Colonge and F. Collomb, *Bull. Soc. Chim. Fr.*, 241, (1951); (b) S. E. Cantor and D. S. Tarbell, *J. Amer. Chem. Soc.*, 86, 2902 (1964).

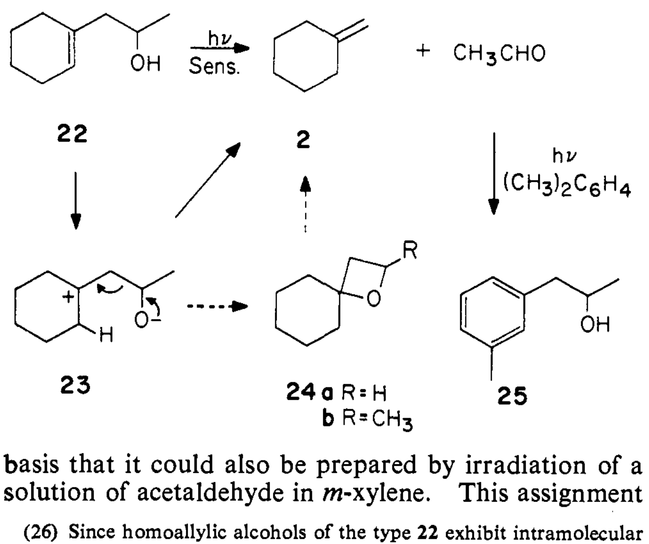
or any other volatile photoproduct. Under similar conditions but with the addition of 1% sulfuric acid trace amounts of **21** were generated. However, since control runs indicated similar behavior in the absence of light, there was again no observable photocyclization. Since **20** undergoes facile acid-catalyzed cyclization and since Dreiding models indicate no significant difference between **16** and **20** in availability of the hydroxyl proton to the double bond, these results suggest that photocyclization of 2-allylphenols does not involve proton abstraction by an excited olefinic chromophore. This was confirmed by the finding that photosensitized irradiation of 2-allylphenol (**16**) with acetophenone (E_T = 79 kcal/mol), an effective sensitizer for the photoprotonation of cyclic olefins,[1a-3] afforded no observed photoproducts, including no detectable amounts of the ethers **17** or **18**.

α-Methyl-1-cyclohexene-1-ethanol (22). In contrast to the hydroxy olefin **20**, in which the double bond is located in an acyclic environment, the cyclohexenyl alcohol **22** was expected to be capable of undergoing protonation to afford the intermediate **23**.[26] Ring closure would then afford the oxetane **24b**. However, as shown in Table V, irradiation of **22** in *m*-xylene or methanol–*m*-xylene solution afforded no detectable amounts of a photoproduct corresponding to the oxetane **24b** but gave instead methylenecyclohexane (**2**) in high yield.[27] Accompanying **2** were lesser amounts of an alcohol to which the structure **25** is assigned on the basis that it could also be prepared by irradiation of a solution of acetaldehyde in *m*-xylene. This assignment is supported by the nmr spectrum, which exhibited absorptions attributable to four aromatic protons (τ 2.9), two benzylic protons (τ 7.32), a single proton α to a hydroxyl group (τ 6.02), a methyl group attached to an aromatic ring (τ 7.68), and a methyl doublet (τ 8.79). The formation of **25** is assumed to occur *via* a secondary photochemical process involving abstraction of a benzylic hydrogen atom from xylene by excited acetaldehyde, followed by radical coupling.[28]

Table V. Irradiation of α-Methyl-1-cyclohexene-1-ethanol (**22**)[a]

Solvent	Sensitizer	Time, hr	Yield, %[b] 22	2	25
CH_3OH	m-$(CH_3)_2C_6H_4$	5	2	94	2
m-$(CH_3)_2C_6H_4$		4	14	70	24

[a] Irradiations were conducted as described in the Experimental Section using 150-ml solutions containing 3.00 g of **22** and, where applicable, 3.0 g of sensitizer. [b] Determined by gas chromatographic analysis of aliquots removed from the irradiation mixture.



The primary photoproducts from **22** are thus methylenecyclohexane (**2**) and acetaldehyde. Their formation could be accounted for by a thermal or photochemical decomposition of the oxetane **24b**. However, monitoring of the nmr spectrum of an irradiation of **22** conducted in benzene solution revealed the immediate formation of methylenecyclohexane (**2**) with no detectable formation of a photoproduct corresponding to **24b**.[29] Although highly strained oxetanes are known to be thermally labile,[28] it seems unlikely that **24b** should decompose spontaneously at 25–30°, the temperature of reaction, especially since the parent oxetane **24a** is an isolable compound that is stable to distillation at temperatures as high as 79°.[30] Although the possibility of a photochemical decomposition of **24b** is not precluded by the available data, there is no known precedent for such a process, and it seems more likely that the formation of methylcyclohexane (**2**) and acetaldehyde does not involve the intermediacy of **24b**. Instead the fragmentation of **22** can probably best be regarded as involving an initial photoprotonation followed by collapse of the resulting intermediate **23** as indicated.[26]

The photofragmentation of **22** to methylenecyclohexane (**2**) is formally a retro-Prins reaction and has an analogy in the thermal conversion of β-hydroxyolefins to give olefins and carbonyl compounds,[31] as illustrated by the pyrolytic conversion of the alcohol **26** to the terpineol **27**.[32] These reactions occur generally and are thought to proceed *via* a cyclic transition state.[31] However, some support for the proposed intervention of a protonation step in the photofragmentation process was found in the failure of the α-pinene derivative nopol (**28**) to undergo fragmentation. Irradiation of nopol (**28**) in either *m*-xylene or methanol–*m*-xylene solution resulted in a slow disappearance of the starting material with no detectable formation of β-pinene (**29**), a material which is known to be photostable under these conditions.[1a] Although nopol (**28**) exhibits intramolecular hydrogen bonding,[26] by analogy to α-pinene and other rigidly held olefins it would not be expected to undergo photoprotonation.[1a,33]

Summary. The conversion of 5-norbornene-2-*endo*-methanol (**9a**) to the cyclic ether **10a** demonstrates that the intramolecular availability of a hydroxyl hydro-

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[26] Since homoallylic alcohols of the type **22** exhibit intramolecular hydrogen bonding, photoprotonation could occur intramolecularly as shown; see C. R. Eddy, J. S. Showell, and T. E. Zell, *J. Amer. Oil Chem. Soc.*, **40**, 92 (1963). However, an analogous process involving intermolecular protonation is also conceivable.

[27] As discussed previously,[2] exocyclic olefins, in which the double bond is partially in an acyclic environment, are photochemically inert under these conditions.

[28] For several analogous photoadditions of aldehydes to diethyl ether, see J. Meinwald and R. A. Chapman, *J. Amer. Chem. Soc.*, **90**, 3218 (1968).

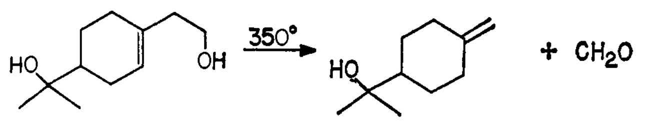
[29] Because of a continuous purging of the irradiation mixture with a stream of nitrogen, acetaldehyde was rapidly removed from the solution and was not observable in the nmr spectrum. However, the exit vapors gave a positive test with 2,4-dinitrophenylhydrazine reagent. Loss of acetaldehyde from solution also undoubtedly reduces the yield of adduct **25** from irradiations conducted in *m*-xylene.

[30] (a) H. B. Henbest and B. B. Millward, *J. Chem. Soc.*, 3575 (1960); (b) A. Rosowsky and D. S. Tarbell, *J. Org. Chem.*, **26**, 2255 (1961).

[31] See R. T. Arnold and G. Smolinsky, *J. Amer. Chem. Soc.*, **82**, 4918 (1960), and references cited therein.

[32] B. M. Mitzner and S. Lemberg, *J. Org. Chem.*, 31, 2022 (1966).

[33] The thermal behavior of nopol will be reported separately.



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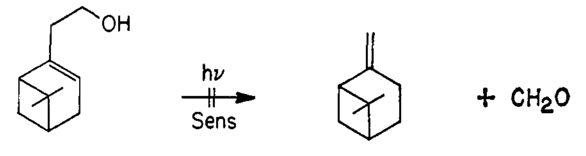

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gen can greatly alter the normal course of photoreaction of a cyclic olefin. The more rapid cyclization of the dimethyl derivative **9c** compared with **9a** suggests that intramolecular hydrogen bonding of the hydroxyl group to the olefinic chromophore facilitates the addition process. However, the photochemical inertness of *trans*-2-allylcyclohexanol (**20**) indicates that even the intramolecular availability of a proton (or hydrogen atom) source to an acyclic olefin is not sufficient to induce either proton or hydrogen atom abstraction. Thus cyclic olefins continue to stand apart from their acyclic counterparts in photochemical behavior. The conversion of α-methyl-1-cyclohexene-1-ethanol (**22**) to methylenecyclohexane (**2**), which most likely proceeds *via* intramolecular protonation, *cf.* **23**, is the first example of such a photofragmentation and suggests a number of additional applications for the photochemistry of cyclic olefins.

Experimental Section[34]

5-Norbornene-2-*endo*-methanol (9a). A. Preparation. The *endo* isomer **9a** was obtained in isomerically pure form by iodination of a commercial mixture of 5-norbornene-2-*exo*- and -*endo*-carboxylic acid followed by separation of the resulting iodolactone,[35] treatment with zinc and acetic acid,[36] esterification with diazomethane, and reduction with lithium aluminum hydride. The resulting colorless liquid was identical in every respect with the major component of a commercial mixture of 5-norbornene-2-*endo*- and *exo*-methanol isolated by preparative gas chromatography; each specimen exhibited an nmr spectrum identical with that recently published for **9a** except for the absence of the extraneous bands at τ 6.3 attributable to the *endo* isomer.[37]

B. Irradiation. 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. Irradiation of 9a as described in Table I followed by isolation of the principal photoproduct by preparative gas chromatography afforded **4-oxatricyclo[4.3.0.0^{3,8}]nonane** as colorless prisms, mp 146–146.5° (sealed capillary) after sublimation at 83–85° (760 mm); λ_{max} 9.06 μ; *m/e:* 124 (40), 95 (82), 81 (71), 80 (100), 79 (93), 67 (65), 66 (56), 55 (56), 41 (50), and 39 (51).

Anal. Calcd for $C_8H_{12}O$: C, 77.37; H, 9.74. Found: C, 77.3; H, 9.7.

C. Deuterium Exchange. A solution containing 3.00 g of alcohol **9a** in 200 ml of benzene was stirred overnight with 75 ml of deuterium oxide. After separation of the deuterium oxide and drying by azeotropic distillation, the benzene solution was adjusted to 150 ml and irradiated as described above. Isolation of the photoproduct by preparative gas chromatography afforded the ether **12** as colorless prisms, mp 146–147° (sealed capillary). The nmr spectrum was similar to that of photoether **10a** except for an attenuation of the H_{6n} band at τ 7.72. The isotopic composition was shown by mass spectral analysis to be 23% D_0 and 77% D_1.

5-Norbornene-2-methanol-α,α-d_2 (9b). A. Preparation. A solution containing 5.00 g of ester **8b** and 1.5 g of lithium aluminum deuteride in 25 ml of tetrahydrofuran was heated under reflux for 16 hr. Isolation in the usual manner afforded 4.92 g of alcohol **9b** as a colorless liquid, bp 60–62° (2.0 mm); λ_{max} 2.98, 4.54, and 4.76 μ. The nmr spectrum was identical with that for alcohol **9a** except for a severe attenuation of the multiplet at τ 6.5. Mass spectral analysis revealed an isotopic distribution of 4% D_1 and 96% D_2.

B. Irradiation. Irradiation of 3.00 g of alcohol **9b** as described in Table I followed by isolation of the principal photoproduct by preparative gas chromatography afforded photoether **10b** as colorless prisms, mp 150–150.5° (sealed capillary). Mass spectral analysis revealed the isotopic composition of 4% D_1 and 96% D_2.

Attempted Reactions with Photoether 10a. A. With Acid. A solution containing 200 mg of photoether **10a** and 3 mg of *p*-toluenesulfonic acid in 5 ml of benzene was heated under reflux in an atmosphere of nitrogen for 24 hr. Gas chromatographic analysis of the reaction mixture indicated an 86% recovery of **10a**. A peak corresponding in retention time to that of ether **13a** and in area to a 3% yield was observed but not further characterized. No additional products were observed. In a control run a solution containing 2.00 g of a commercial mixture of 5-norbornene-2-*endo*- and- 2-*exo*-methanol and 25 mg of *p*-toluenesulfonic acid in 15 ml of benzene was heated under reflux in an atmosphere of nitrogen for 24 hr. Gas chromatographic analysis of an aliquot removed from the reaction mixture revealed the formation of ether **13a** in 75% yield along with a 23% recovery of the starting alcohol mixture. A peak corresponding in retention time to that of ether **10a** and in area to less than a 2% yield was observed but not further characterized.

In a separate experiment a solution of 300 mg of photoether **10a** in 10 ml of methanol containing 1% sulfuric acid was heated under reflux in an atmosphere of nitrogen for 2 hr. Gas chromatographic analysis of an aliquot removed from the reaction mixture revealed no loss in starting material. The solution was then adjusted to 2% in sulfuric acid and refluxing was continued. After an additional 1 hr gas chromatographic analysis of an aliquot revealed no change. After an additional 5 hr gas chromatographic analysis showed the continued presence of 46% of the starting ether; there was no detectable formation of the ether **13a**.

B. With Lithium Aluminum Hydride. A solution containing 150 mg of photoether **10a** and 138 mg of lithium aluminum hydride in 20 ml of N-ethylmorpholine was maintained at 120° under an atmosphere of nitrogen for 7 days. Isolation in the usual manner afforded 152 mg of a colorless liquid which was shown by gas chromatographic analysis to consist principally (greater than 90%) of recovered starting material.

C. Oxidation. To a solution of 200 mg of photoether **10a** in 3 ml of acetone (freshly distilled from potassium permanganate) was added 2 ml of 8 *N* chromic acid solution and the resulting mixture was maintained overnight at 20°, during which time there was no appreciable change in color. Isolation in the usual manner afforded 203 mg of yellow crystals which were shown by spectral properties to be identical with starting material.

D. Cleavage with Boron Trifluoride. A solution of 156 mg of ether **10a** in 8 ml of acetic anhydride was cooled to 0°, 1.4 ml of boron trifluoride etherate was added, and the resulting mixture was maintained at 0° for 48 hr. The mixture was then poured over cracked ice and extracted with ether. The combined ether extracts were washed with saturated sodium bicarbonate solution and water, dried over saturated sodium chloride solution followed by anhydrous sodium sulfate, and concentrated by distillation to afford 160 mg of a pale yellow oil which exhibited strong absorption at 5.78 μ and which was shown by gas chromatographic analysis to consist of at least four components present in relative amounts of

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(34) 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 20% Carbowax 20M or 20% SE-30 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 P-1 and P-2 peaks were minimized by lowering the accelerating voltage (10–12 eV).

(35) C. D. Ver Nooy and C. S. Rondestvedt, Jr., *J. Amer. Chem. Soc.*, 77, 3583 (1955).

(36) C. S. Rondestvedt, Jr., and C. D. Ver Nooy, *ibid.*, 77, 4878 (1955).

(37) R. G. Foster and M. C. McIvor, *Chem. Commun.*, 280 (1967); see also J. A. Claisse and D. I. Davies, *J. Chem. Soc., B*, 679 (1967), and E. Pretsch, H. Immer, C. Pascual, K. Schaffner, and W. Simon, *Helv. Chim. Acta*, **50**, 105 (1967).

2:7:11:80. Isolation of the major component by preparative gas chromatography followed by short-path distillation at 112° (0.1 mm) afforded a colorless liquid, λ_{max} 5.75 and 8.08 μ; nmr spectrum: τ 5.43 (m, 1, >C*H*OAc), 6.14 (m, 2, –CH_2OAc), and 7.97 and 8.01 (2s, 6, CH_3CO_2–).[38] This material is tentatively identified as 5-acetoxynorbornane-2-methanol acetate. The presence of a complex quartet in the nmr spectrum at τ 9.34 indicated the presence of the 2-*endo* isomer,[36] but since this band integrated for only 0.4 proton the material was apparently principally the 2-*exo* isomer. An independent synthesis of this material was achieved by dissolving 5.00 g of a mixture of norbornane-2-*endo*- and -*exo*-methanol acetate in a mixture consisting of 98 ml of glacial acetic acid, 0.3 ml of water, and 0.1 ml of concentrated sulfuric acid and maintaining the resulting solution at 100° under an atmosphere of nitrogen for 16 hr according to the general procedure of Caldwell and Jackson.[39] The reaction mixture was concentrated to approximately 50 ml by distillation, and the residue was taken up in ether, exhaustively washed with saturated sodium bicarbonate solution and water, dried over saturated sodium chloride solution followed by anhydrous sodium sulfate, and concentrated by distillation to afford 5.12 g of a yellow liquid which displayed strong absorption at 5.78 μ and was shown by gas chromatographic analysis to consist of four components having the same retention times as the four products noted above except that they were present in relative amounts of 7:6:24:36. Isolation of the major component by preparative gas chromatography afforded a colorless liquid which exhibited infrared and nmr spectra almost identical with those of the major component noted above except for an almost complete absence of the multiplet at τ 9.34. This material is thus assumed to be 5-acetoxynorbornane-2-*exo*-methanol acetate.

α,α-Dimethyl-5-norbornene-2-*endo*-methanol (9c). A. Preparation. Treatment of a solution containing 52.2 g of a commercial mixture of 5-norbornene-2-*endo*- and -*exo*-carboxylic acid, methyl ester, in 100 ml of anhydrous ether with 260 ml of 3 *M* methylmagnesium chloride for 72 hr at 25° under an atmosphere of nitrogen in the general manner described previously[40] followed by isolation in the usual manner and distillation through an 18-in. spinning band column afforded 28.2 g of a 4.9:1 mixture of α,α-dimethyl-5-norbornene-2-*endo*- and -*exo*-methanol as a colorless liquid, bp 88–90° (20 mm); lit.[40] bp 92–93° (20 mm). Isolation of the major component by preparative gas chromatography afforded the *endo* isomer **9c** as a colorless liquid, λ_{max} 2.90 and 6.34 μ; nmr spectrum: τ 3.76 and 3.91 (2 q, 2, J_{AB} 5, $J_{AX} = J_{BX}$ 3, CH-5 and -6), 7.07 and 7.18 (2 br m, CH-1 and -4), 7.81 (m, 1, CH-2), 8.17 (m, 1, CH-3x), and 8.79 and 8.90 (2 s, 2CH_3–).[41]

Isolation of the minor component by preparative gas chromatography afforded the *exo* isomer as colorless prisms, mp 25.5–26°; λ_{max} 2.90 and 6.34 μ; nmr spectrum: τ 3.79 and 3.96 (2 q, 2, J_{AB} 5.2, $J_{AX} = J_{BX}$ 3, CH-5 and -6), 7.17 and 7.26 (2 br. s, 2, CH-1 and -4), and 8.75 and 8.80 (2 s, 2CH_3–).

B. Irradiation. Irradiation of 3.0 g of the above isomeric mixture as described in Table I resulted in a rapid disappearance of the *endo* isomer **9c** with no concomitant change in the amount of *exo* isomer present. Isolation of the single observed photoproduct by preparative gas chromatography followed by short-path distillation at 106–107° (12 mm) gave a colorless liquid tentatively identified as **5,5-dimethyl-4-oxatricyclo[4.3.0.0^{3,8}]nonane (10c)**, λ_{max} 9.10 μ; nmr spectrum: τ 6.02 (m, 1, CH-5, $J_{4,5} = J_{5,6x}$ 5, $J_{1,5}$ 2.5), 7.54 (m, 2, CH-1 and -4), 7.86 (m, 1, $J_{6n,6x}$ 12.5, $J_{6n,7a}$ 3.5, CH-6n), and 8.71 and 8.84 (2 s, 2CH_3–)[10]; *m/e:* 152 (4), 150 (29), 134 (74), 119 (58), 109 (56), 106 (32), 105 (35), 93 (81), 92 (30), 91 (100), 81 (58), 79 (59), 77 (39), 67 (42), and 66 (68).

Anal. Calcd for $C_{10}H_{16}O$: C, 78.89; H, 10.59. Found: C, 78.8; H, 10.6.

C. Acid-Catalyzed Cyclization. A solution containing 2.03 g of the above described isomeric mixture of α,α-dimethyl-5-norbornenemethanol and 25 mg of *p*-toluenesulfonic acid in 15 ml of benzene was heated under reflux in an atmosphere of nitrogen for 16 hr. The resulting solution was diluted with ether, washed with saturated sodium bicarbonate solution, dried over saturated sodium chloride solution followed by anhydrous sodium sulfate, and concentrated by distillation to give 2.10 g of a yellow liquid which was shown by gas chromatographic analysis to consist of four major components present in the ratio 1.0:2.0:2.4:1.2. The latter two components had retention times corresponding to the *exo* and *endo* isomers of the starting material, respectively. The first component appeared by infrared analysis to consist of dehydrated material and was not further characterized. Isolation of the second component by preparative gas chromatography afforded **2,2-dimethylhexahydro-3,5-methano-2H-cyclopenta[*b*]furan (13b)** as a colorless liquid, λ_{max} 8.72, 9.48, and 10.02 μ; nmr spectrum: τ 5.78 (t, 1, *J* 5.5, >CHO–), 7.12 (t, 1, *J* 4.5, bridgehead CH), and 8.76 and 8.84 (2 s, 6, 2CH_3–); *m/e:* 152 (1), 137 (100), 108 (39), 93 (48), 91 (20), 79 (36), 71 (38), 67 (34), and 66 (26); lit. λ_{max} 9.43 μ.[42]

Analysis of Nmr Spectrum of 10a. The nmr spectrum of photoether **10a** is shown in Figure 1A. The bridgehead protons H_1 and H_4 appeared as characteristic complex multiplets at τ 7.56 and 7.34.[10] In addition, the low-field region of the spectrum exhibited three one-proton absorptions assignable to the three protons adjacent to the ether oxygen (H_5, H_A, and H_B). Two of these latter bands appeared as the A and B portions of an ABX pattern (with additional long-range coupling) and are thus assigned to the methylene protons H_A and H_B; this led to assignment of the remaining band at τ 5.89 to the methine proton H_5. The assignments H_A and H_B were verified by examination of the spectrum of the dideuterated analog **10b**, which exhibited no bands corresponding to those assigned to H_A and H_B in the spectrum of **10a**.

Appearance of the methine proton H_5 in either spectrum as a triplet of doublets indicated the presence of strong coupling (5.1 Hz) with two other protons and weaker coupling (2.0 Hz) with yet a third proton. Two of the protons coupled with H_5 could be readily identified as the bridgehead protons by decoupling experiments. Irradiation at the frequency of the higher-field bridgehead multiplet removed the 2.0-Hz coupling to afford a triplet (Figure 1B), whereas simultaneous irradiation at the frequencies of both bridgehead multiplets removed in addition one of the 5.1-Hz couplings to afford a doublet (Figure 1C). Conversely, irradiation at the center of the H_5 band resulted in a substantial sharpening of the lower-field bridgehead multiplet (Figure 1G). On the basis that H_5 should exhibit stronger coupling with the closer bridgehead proton H_4, the multiplets at τ 7.34 and 7.56 were assigned to H_4 and H_1, respectively.[43]

Of the two bands arising from the methylene protons H_A and H_B the higher field doublet showed stronger secondary coupling (3.0 Hz). Inspection of Dreiding models revealed a dihedral angle between H_A and H_2 of approximately 85° and between H_B and H_2 of approximately 50°. Thus H_B should exhibit moderately strong coupling with H_2, whereas H_A should exhibit little or none. On this basis the higher-field band is assigned to H_B and the lower-field partner to H_A.[44]

H_2 was located by the finding that irradiation at τ 7.94 resulted in a collapse of the H_B quartet into a doublet (Figure 1D). Unfortunately the pattern at τ 7.94 is obscured by overlap with the high-field portion of H_{6n}. However, the basic appearance of this band as a triplet was seen in the spectrum of **10b**, in which there is no possible coupling of H_2 with H_B. A similar pattern was obtained from **10a** by decoupling H_2 from H_B (Figure 1J). The triplet pattern for H_2 in **10b** indicates the presence of approximately equal coupling (6.5–7.0 Hz) with two adjacent protons. One of these was identified as H_1 by the finding that irradiation of **10b** in the region of H_1 resulted in a collapse of the H_2 triplet pattern into that of a doublet.[45] The additional 7.0-Hz coupling with H_2 is assigned

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[38] Indicates multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, and m = unresolved multiplet), integration, and assignment. Coupling constants are given in hertz.

[39] J. R. Caldwell and W. J. Jackson, Jr., U. S. Patent 3,000,864 (1961).

[40] N. P. Sopoy, *Zh. Obshch. Khim.*, **25**, 2082 (1955); *Chem. Abstr.*, **50**, 8487 (1956).

[41] The remarkable diamagnetic shift of H_{3n} displayed by **9a**[37] is not shared by the homolog **9c**.

[42] F. D. Greene, M. L. Savitz, F. D. Osterholtz, H. H. Lau, W. N· Smith, and P. M. Zanet, *J. Org. Chem.*, **28**, 55 (1963).

[43] Irradiation at H_5 also effected a collapse of the band at τ 8.89 (Figure 10) and irradiation in the reverse manner collapsed the basic triplet pattern of H_5 to that of a doublet. On this basis it is assumed that the band at τ 8.89 represents the high-field half of the H_{6x} band.

[44] (a) The 1.5-Hz secondary coupling for H_A (*cf.*, Figure 1E) was removed by irradiation at τ 8.62 (Figure 1F). Since a Dreiding model of structure **10a** shows a reasonably planar W pattern between H_A and H_{3x}, the proton giving rise to this coupling is assigned as H_{3x}. (b) Additional coupling (0.8 Hz) is also exhibited by H_B (Figure 1M) which is removed by irradiation at τ 8.89 (Figure 1N). The band at this frequency has been assigned to H_{6x}.[43] This assignment is consistent with the fact that models show a potential overlap between the back orbitals of H_B and H_{6x}.

[45] Caution must be exercised in arriving at this conclusion, however, since the high-field portion of H_{6n} overlaps the H_2 band and H_{6n} is also coupled with H_1 (*cf.* Figure 1I).

to the vicinal proton H_{3x} on the basis of a dihedral angle of approximately 35° as indicated by Dreiding models.

The two remaining unassigned bands of the spectra of **10a** and **10b** which are clearly distinguishable as arising from single protons are those centered at τ 7.72 and 8.27. Each of these has a primary coupling of 10–12 Hz. Since a coupling of this magnitude would have to arise from a geminal proton, these bands are each assignable to one of the two methylene protons situated at C_3, C_6, or C_7. However, since the principal couplings of these two bands are not equal, the protons they represent must be attached to different carbon atoms. The higher field band was located at H_3 by the finding that irradiation at H_4 resulted in a collapse of the pair of triplets into a pair of doublets (Figure 1L). Conversely, the unidentified band at τ 7.72 was found to be coupled to the other bridgehead proton H_1 since irradiation at the frequency of H_1 resulted in collapse of the lower-field half into a doublet (Figure 1I). On this basis it is assigned as one of the H_6 protons, and, since the H_{6x} band had been previously located,[43] it was assigned specifically as H_{6n}. This assignment was corroborated by the finding that irradiation of the H_{6x} band resulted in a collapse of the basic doublet pattern of the τ 7.72 band (Figure 1K). Likewise, since H_{3x} had previously been assigned,[44a] the τ 8.27 band was specifically assigned to the H_{3n} position. The H_{3n} and H_{6n} bands each displayed an additional coupling of 3.0–3.5 Hz, which is probably attributable to W coupling with H_{7s} and H_{7a}, respectively.[46]

The foregoing analysis is consistent with the structural assignment **10a**.

Irradiation of 5-Acetyl-2-norbornene. A 150-ml benzene solution containing 3.00 g of a commercial mixture of 5-*exo*- and -*endo*-acetyl-2-norbornene (1.00:1.23) was irradiated as described above for 2 hr. Gas chromatographic analysis of an aliquot revealed the continued presence of a small amount of the *exo* and *endo* isomers (approximately 10% each) and the formation of a principal photoproduct (66% yield based on *endo* isomer). Isolation by preparative gas chromatography afforded a colorless liquid, λ_{max} 9.04, 10.18, and 11.80; nmr spectrum: τ 5.52 (q, 1, J 2.5 and 4, >CHO–), 7.36 (m, 2), 7.84 and 8.06 (2 m, 2), and 8.63 (s, 3, CH_3–); *m/e:* 136 (12), 91 (14), 80 (100), 79 (74), 78 (37), 77 (32), 66 (36), and 51 (14). This material has been assigned the oxetane structure **15**.[18]

Attempted Photocyclization of 5-Norbornene-2-*endo*-carboxylic Acid (8a). A solution containing 3.0 g of a commercial mixture of 5-norbornene-2-*endo*- and -*exo*-carboxylic acid and 3 ml of xylene made up to 150 ml with methanol was irradiated as described above for 4 hr. Gas chromatographic analysis of an aliquot revealed complete disappearance of the *exo* isomer and the continued presence of 21% of the *endo* isomer; there were no detectable volatile photoproducts.

In a second experiment 150 ml of a benzene solution containing 3.0 g of a commercial mixture of 5-norbornene-2-*endo*- and -*exo*-carboxylic acid was irradiated as described above for 7 hr. Gas chromatographic analysis of an aliquot revealed no change in the amount of either isomer present.

***trans*-2-Allylcyclohexanol (20). A. Preparation.** Treatment of cyclohexene oxide with allylmagnesium bromide as described previously[24] afforded alcohol **20** as a colorless liquid, bp 85–86° (8 mm); λ_{max} 2.95 and 6.10 μ; nmr spectrum: τ 4.20 and 4.95 (2 m, 3, $-CH{=}CH_2$), 6.76 (m, 1, CH-1), and 7.56 (m, 1, CH-2); 3, 5-dinitrobenzoate, colorless plates from petroleum ether, mp 70–71°; lit. bp 94–96° (15 mm)[24] and 95–98° (18 mm);[47] 3,5-dinitrobenzoate: *trans*, mp 69–70°[47] and *cis*, mp 106.5–107°.[48] This material exhibited only one peak on gas chromatographic analysis, and on the basis of the 3,5-dinitrobenzoate derivative is assumed to be the *trans* isomer **20**. However, the presence of a multiplet at τ 6.40 in the nmr spectrum with an area corresponding to 0.23 proton may indicate the presence of the *cis* isomer as an impurity.

B. Acid-Catalyzed Cyclization. A solution containing 500 mg of alcohol **20** and 15 mg of *p*-toluenesulfonic acid in 7 ml of benzene was heated under reflux in an atmosphere of nitrogen for 16 hr. The resulting solution was diluted with ether, washed with saturated sodium bicarbonate solution, dried over saturated sodium chloride solution followed by anhydrous sodium sulfate, and concentrated by distillation. Gas chromatographic analysis revealed the presence of two peaks present in the ratio 1:1.83 corresponding to recovered alcohol **20** and a new product, respectively. Isolation of the product by preparative gas chromatography followed by short-path distillation at 74° (3.0 mm) afforded **2-methyl-*trans*-octahydrobenzofuran (21)** as a colorless liquid, λ_{max} 9.32 μ; nmr spectrum: τ 5.85 and 6.87 (2 m, 2, CH-2 and -7a) and 8.76 (d, J 6, CH_3-2); lit. bp 75° (17 mm).[25a]

Anal. Calcd for $C_9H_{16}O$: C, 77.09; H, 11.50. Found: C, 77.3; H, 11.2.

C. Irradiation. Irradiation of alcohol **20** as outlined in Table IV afforded no observed photoproducts.

Irradiation of 2-Allylphenol (16). A 150-ml benzene solution containing 3.0 g of 2-allylphenol (**16**) was irradiated for 8 hr as described above. Gas chromatographic analysis of an aliquot revealed the presence of recovered starting material (24%) and three photoproducts (43, 3, and 1%). Isolation of the major product by preparative gas chromatography afforded a colorless liquid which exhibited spectral properties similar to those reported for 2-methyl-2,3-dihydrobenzofuran (**17**).[19] Similar irradiation through a Pyrex filter of a 150-ml benzene solution containing 3.0 g of 2-allyphenol (**16**) and 2.7 g of acetophenone for 8 hr was shown by gas chromatographic analysis of an aliquot to result in a 72% recovery of starting material with no detectable formation of the ether **17**. An unidentified photoproduct was observed in 4% yield.

α-Methyl-1-cyclohexene-1-ethanol (22). A. Preparation. Treatment of a solution containing 22.1 g of 1-cyclohexenylacetone in 50 ml of ether with 6.7 g of lithium aluminum hydride at 25° under an atmosphere of nitrogen for 22 hr followed by isolation in the usual manner and subsequent distillation through an 18-in. spinning-band column afforded 11.0 g of alcohol **22** as a colorless liquid, bp 56° (1.75 mm); λ_{max} 2.92 and 6.00 μ; nmr spectrum: τ 4.57 (s, 1, CH-2), 6.24 (sextet, 1, J 6, CH-α), and 8.88 (d, 3, J 6, CH_3-α).

Anal. Calcd for $C_9H_{16}O$: C, 77.09; H, 11.50. Found: C, 76.8; H, 11.3.

B. Irradiation. Alcohol **22** was irradiated as summarized in Table V. Methylenecyclohexane **2** was identified by direct comparison of samples isolated by preparative gas chromatography with a commercial specimen. Isolation of the minor photoproduct followed by short-path distillation at 122–123° (5.5 mm) afforded **3-*m*-tolyl-2-propanol (25)** as a colorless liquid, λ_{max} 2.95 μ; nmr spectrum: τ 2.9 (m, 4, aromatic CH), 6.02 (sextet, 1, J 6.5, CH-2), 7.32 (m, 2, CH_2-3), 7.68 (s, 3, aromatic CH_3–), and 8.79 (d, 3, J 6.0, CH_3-1); *m/e:* 150.1045 (calcd for $C_{10}H_{14}O$: 150.1045), 148 (26), 132 (49), 117 (84), 115 (26), 106 (84), 105 (91), 91 (84), 79 (21), 77 (30), 51 (20), 45 (20), and 43 (100).

Anal. Calcd for $C_{10}H_{14}O$: C, 79.95; H, 9.39. Found: C, 79.4; H, 9.4.

Irradiation of a solution containing 0.5 g of acetaldehyde in 75 ml of *m*-xylene for 2 hr as described above afforded the alcohol **25** in a 27% yield. A specimen isolated by preparative gas chromatography exhibited spectral behavior similar to that described above.

Irradiation of Nopol (28). A 150-ml solution of *m*-xylene containing 3.0 g of nopol (**28**) was irradiated as described above for 6 hr. Gas-chromatographic analysis revealed the continued presence of nopol (36% recovery) and the formation of a single detectable photoproduct (10%) which was not identified. There was no detectable formation of β-pinene.

Irradiation in a similar fashion of a 150-ml methanolic solution containing 3.0 ml of *m*-xylene and 3.0 g of nopol resulted in loss of the starting material and the formation in low yield of several unidentified photoproducts having retention times longer than that of nopol but with no detectable formation of β-pinene.

Use of Phenol as a Photosensitizer. A 75-ml methanolic solution containing 1.5 g each of 1-methylcyclohexene (**1**) and phenol was irradiated as described above for 2 hr. Gas-chromatographic analysis revealed the presence of methylenecyclohexane (**2**, 42% yield) and methyl 1-methylcyclohexyl ether (**3**, 44% yield).

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(46) Although in norbornanes *endo* protons normally absorb at higher field than their *exo* counterparts, the close approach of a nonbonded group may cause a substantial downfield shift; see, for example, W. G. Dauben and W. T. Wipke, *J. Org. Chem.*, **32**, 2976 (1967), and references cited therein. Since the H_{6n}–H_A internuclear distance in **10a** is 1.9 Å as measured by Dreiding models, the surprisingly lowfield position of H_{6n} may be due at least in part to compression by H_A. This is also consistent with the downfield position of H_A relative to H_B. No significant compression of H_{3n} is apparent from a study of models; the smaller downfield shift in this case may be due to an anisotropic effect of the oxygen bridge.

(47) R. Cornubert, G. Barraud, M. Cormier, M. Descharmes, and H. G. Eggert, *Bull. Soc. Chim. Fr.*, 400 (1955).

(48) P. Anziani, A. Aubry, G. Barraud, M.-M. Claudon, and R. Cornubert, *ibid.*, 408 (1955).