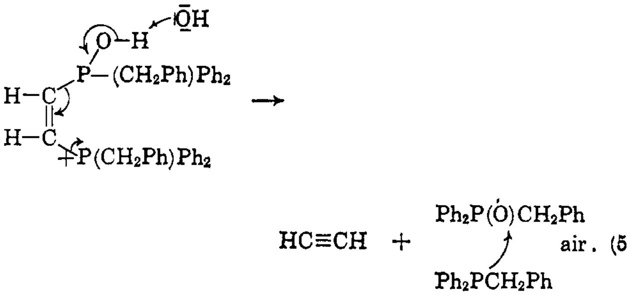
cess benzyl halide, respectively. Compound VI melted at 218–219° (MeOH–acetone). *Anal.* Calcd: Br, 14.1. Found: Br, 14.31. Compound VII melted at 333–335° (MeOH–CH_3CN).

Proton nmr spectra of VI in deuteriochloroform solution at 60 Mc show a doublet centered at τ 5.01 (J_{PCH} = 15 cps), two phenyl proton complexes at τ 2.9 and 2.4, and a peak at τ 1.5. In TFA the doublet is at τ 5.40. The ratio of phenyl and vinyl protons to methylene protons indicates a monophosphonium salt. The *trans* isomer of II[1] reacts with benzyl bromide in benzene to give an isomer of VI (mp 208–210°) with a doublet centered at τ 4.85 (J_{PCH} = 15 cps) and peaks at τ 2.85, 2.5, and 2.25. In TFA the doublet appears at τ 5.4, showing that isomerization takes place in this solvent.

Compound VII is insoluble in $CDCl_3$. A TFA solution gives a spectrum identical with that of the product from *trans*-II and excess benzyl bromide (mp 309–312°). This may be due to isomerization in the formation, but more likely, by TFA. The spectra show a doublet (separation = 14 cps) with a shallow complex in the middle centered at τ 5.25, and the phenyl–vinyl proton complex in the ratio of 1:8.

Basic hydrolysis of VII gave benzyldiphenylphosphine oxide and not the oxides of I (eq 5).



(5)

Acknowledgment. We acknowledge the support of this work by National Science Foundation Grant GP3823 and Petroleum Research Fund Grant 2326-Al,-4; Mr. Gordon Boudreaux of the Southern Regional Laboratories of the U. S. Department of Agriculture for obtaining the proton nmr data; Dr. M. M. Crutchfield of Monsanto Co. and Professor Claibourne Griffin of the University of Pittsburgh for obtaining the P^{31} nmr data; and the help given by Professor William L. Masterton of the University of Connecticut in obtaining the molecular weight data.

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Photochemical Behavior of Cycloalkenes

Sir:

Numerous studies have established that transfer of triplet energy to acyclic or macrocyclic olefins from suitable photosensitizers (having $E_T \geq 69$ kcal/mole) results in *cis–trans* isomerization of the double bond,[1] undoubtedly as a consequence of the preferred orthogonal conformation of triplet olefins.[2] By contrast, the photochemical behavior of smaller ring cyclic olefins, in which *trans* isomers are exceedingly strained,[3] has been little studied except for several reports of dimerization.[4] We wish to describe here two related light-induced reactions of cycloalkenes which appear to be widely applicable and are of both synthetic and mechanistic interest.

Irradiation of 1-alkylcycloalkenes in the presence of aromatic hydrocarbon photosensitizers (benzene, toluene, or xylene) has been found to induce isomerization to the analogous exocyclic olefins. Thus (+)-3-carene (**1**) is converted to (+)-3(10)-carene (**2**), (±)-1-menthene (**7a**) to (±)-1(7)-menthene (**8a**), and the ethyl analog **4**[5] to the exocyclic isomer **5**.[6,7] In the presence of alcohols there is a competing reaction leading to the formation of tertiary ethers. Thus in 9:1 methanol–xylene **7a** is converted to the *cis* (27% yield) and *trans* isomers (16%) of **9a**[8] as well as to the exocyclic olefin **8a** (36%). 1-Methylcycloheptene affords the analogous tertiary ether[9] (62% yield). (+)-3-Carene (**1**) gives (+)-3α- (3%) and (+)-3β-methoxycarane (**3**, 17%), the rearranged ether **6** (12%), and the olefin **2** (23%); in aqueous *t*-butyl alcohol–benzene the corresponding alcohols[10] are formed in a similar ratio.[11]

Unsubstituted cycloalkenes also undergo ether formation, but less efficiently. In an interesting example of the synthetic potential of this reaction, the diene **10** was found to give selectively the tertiary ether **11**. By contrast, the conformationally rigid cedrene (partial structure **12**), the acyclic olefin 3,5-dimethyl-3-heptene, and the exocyclic olefins **2** and **8a** are totally inert to addition or rearrangement under these conditions.

Labeling studies with **7b** have revealed that the transformation to **8** in benzene or benzene–methanol is principally *intermolecular*, resulting in the loss of 0.8–0.9 D and giving predominantly the D_2 product **8b** (along with **9b** in methanol). Moreover, at least in the

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[1] (a) R. B. Cundall, *Progr. Reaction Kinetics*, **2**, 165 (1964); (b) G. S. Hammond, N. J. Turro, and P. A. Leermakers, *J. Phys. Chem.*, **66**, 1144 (1962); (c) A. C. Testa, *J. Org. Chem.*, **29**, 2461 (1964); (d) H. Morrison, *Tetrahedron Letters*, 3653 (1964); *J. Am. Chem. Soc.*, **87**, 932 (1965); (e) H. Nozaki, Y. Nisikawa, Y. Kamatani, and R. Noyori, *Tetrahedron Letters*, 2161 (1965).

(2) See, for example, the discussion in ref 1a.

(3) Chemical evidence for the formation of the highly reactive *trans*-cycloheptene has been described: E. J. Corey, F. A. Carey, and R. A. E. Winter, *J. Am. Chem. Soc.*, **87**, 934 (1965). *trans*-Cyclohexene is unknown.

(4) See, for example (a) D. Scharf and F. Korte, *Tetrahedron Letters*, 821 (1963); (b) *Chem. Ber.*, **97**, 2425 (1964); (c) D. R. Arnold, R. L. Hinman, and A. H. Glick, *Tetrahedron Letters*, 1425 (1964); (d) D. R. Arnold, D. J. Trecker, and E. B. Whipple, *J. Am. Chem. Soc.*, **87**, 2596 (1965).

(5) G. Ohloff, G. Schade, and H. Farnow, *Chem. Ber.*, **90**, 106 (1957).

(6) This isomerization was apparently first observed by F. J. McQuillin and J. D. Parrack, *J. Chem. Soc.*, 2973 (1956), in the conversion of a mixture of α- and β-eudesmol to the pure β isomer by irradiation in benzene solution. However, the generality of this reaction was not recognized.

(7) Irradiations were conducted with a 450-w mercury lamp and a Vycor immersion apparatus containing 150 ml of solution and 1.00 g of olefin. Satisfactory analytical and spectral data were obtained for all new compounds.

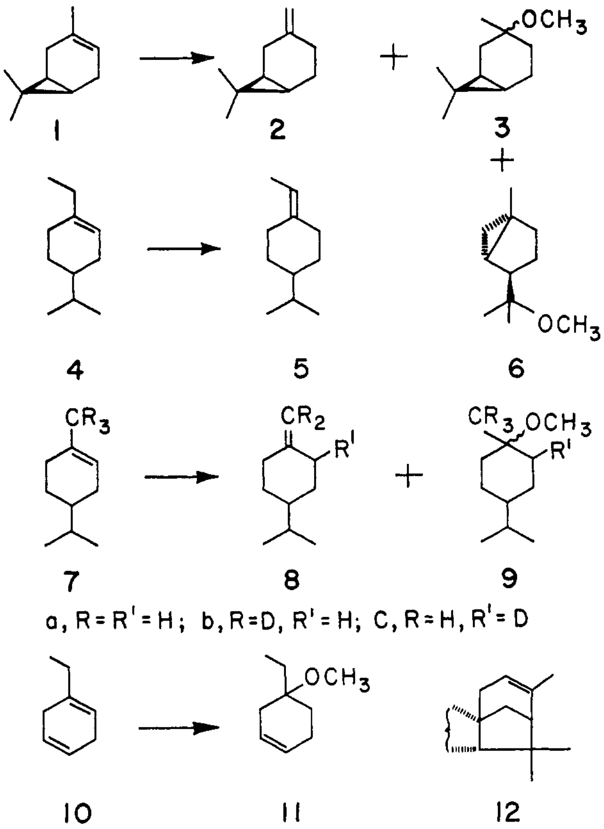
(8) (a) W. Hueckel and P. Heinzelmann, *Ann.*, **687**, 82 (1965). (b) The formation of the isomeric ethers **9a** from **7a** was first observed by J. A. Marshall and R. D Carroll, *J. Am. Chem. Soc.*, **88**, 4092 (1966), to whom the author is deeply indebted for discussion of their results prior to publication.

(9) W. Hueckel and J. Waechter, *Ann.*, **672**, 62 (1964).

(10) H. Kuczyński and K. Piatkowski, *Roczniki Chem.*, **31**, 59 (1957); H. Kuczyński and Z. Chabudziński, *ibid.*, **34**, 177 (1960). Several examples of rearrangement of the carane skeleton to that of bicyclo-[3.1.0]hexane resulting from the generation of positive character at C-3 have recently been observed (P. J. Kropp, *J. Am. Chem. Soc.*, in press.

(11) The ether products can also be obtained, but in lower yield, by irradiation of the various olefins under identical conditions except for the absence of a photosensitizer.

presence of alcohols, the entering hydrogen atom is incorporated in the form of a proton; irradiation of **7a** in benzene–methanol-O-*d* gives **8c** (along with **9c**), in which the newly incorporated hydrogen atom has been abstracted from oxygen rather than carbon.



a, R = R' = H; b, R = D, R' = H; C, R = H, R' = D

The incorporation of protons, the formation of C–O bonds with alcohols, and Markovnikov direction of addition are all typical of ionic rather than free-radical processes. Thus cycloalkenes join the growing roster of chromophores which exhibit photochemical behavior that is essentially ionic in character.[12] The isomerization and addition reactions may involve protonation of the cycloalkene triplet, followed by competing olefin and ether formation. However, the failure of acyclic and exocyclic olefins to exhibit similar behavior leads us *tentatively* to prefer an alternative mechanism in which it is assumed that intersystem crossing from an orthogonal cycloalkene triplet affords, in addition to regenerated *cis* olefin, a highly energetic *trans* intermediate which seeks relief of strain *via* protonation and subsequent elimination or ether formation.[13,14] Studies of the scope and mechanistic features of both the isomerization and addition reactions continue.

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(12) See, for example, discussion by P. J. Kropp, *J. Am. Chem. Soc.*, **86**, 4053 (1964), and references cited therein.

(13) This mechanism implies that acyclic, exocyclic, and large-ring endocyclic olefins, in which *cis–trans* isomerism is not sterically impeded, should not be expected to undergo facile double bond migration or alcohol addition. Likewise, small-ring or rigidly held cycloalkenes in which orthogonality cannot be achieved in the excited state should be unreactive.

(14) W. G. Dauben and W. T. Wipke, *Pure Appl. Chem.*, **9**, 539 (1964), have observed the addition of methanol across the 3,4-double bond of the diene 3,10-dimethyl-3,5-hexalin and have proposed a mechanism involving a vibrationally excited ground-state intermediate; see also C. C. Leznoff and G. Just, *Can. J. Chem.*, **42**, 2801 (1964). However, no previous examples of addition to an isolated carbon–carbon double bond have been reported.

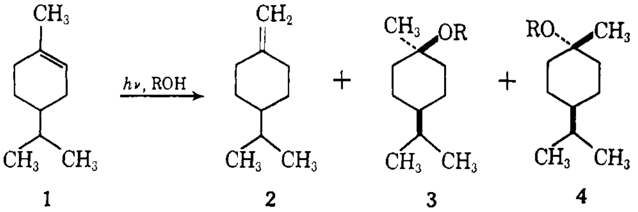
The Photochemically Initiated Addition of Alcohols to 1-Menthene. A New Type of Photochemical Addition to Olefins

Sir:

In connection with some projected synthesis projects we became interested in the photochemical isomerization of isolated carbon–carbon double bonds.[1] Initial studies, carried out with 1-menthene (**1**), have yielded unexpected and useful results which constitute the subject of this communication.

Irradiation[2] of 1-menthene (**1**) in methanol–benzene[3] (100:1) led to a slow buildup of the exocyclic isomer **2** and a more rapid buildup of two completely unexpected products, ethers **3a** and **4a.**[4] These materials were isolated by preparative gas chromatography and identified through comparison of their infrared and nmr spectra with those of authentic samples.[5]

Our subsequent investigations, outlined in Table I, showed that while the reactions also took place in the absence of a sensitizer (entry 1), benzene and particularly toluene and xylene served as effective promoters (entries 2 and 3). Furthermore, discontinuation of the irradiation after several hours caused all reactions to stop and no buildup of products was detected, even after 12 hr, thus ruling out the possibility of fortuitous acid catalysis. The addition of oxygen (entry 4)[6] to reactions in progress caused a marked rate retardation.



a, R=CH$_3$; b, R=CH$_3$CH$_2$;
c, R=(CH$_3$)$_2$CH; d, R=(CH$_3$)$_3$C;
e, R=H

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(1) *Cf.* F. J. McQuillin and J. D. Parrack, *J. Chem. Soc.*, 2973 (1956).

(2) A Hanovia 450-w high-pressure mercury vapor lamp (type L) was used with a water-jacketed Vycor immersion well.

(3) When the reaction was conducted in pure benzene according to the procedure of McQuillin and Parrack,[1] an opaque, insoluble polymer rapidly coated the immersion well. The use of methanol as a cosolvent alleviated this difficulty. We are indebted to Dr. P. J. Kropp for suggesting this modification and informing us of his work on the isomerization of (+)-3-carene and other olefins in the early stages of our own work.

(4) Certain *conjugated* dienes give unsaturated ethers upon irradiation in alcohol solvents. *Cf.* W. G. Dauben and W. T. Wipke, *Pure Appl. Chem.*, **9**, 539 (1964); G. Just and C. Pace-Asciak, *Tetrahedron*, **22**, 1069 (1966), and references therein. However, no previous examples of the type observed in this study with isolated carbon–carbon double bonds have appeared.

(5) Olefin **2** was obtained from 4-isopropylcyclohexanone and methylenetriphenylphosphorane. Acid-catalyzed addition of methanol to 1-menthene (**1**) afforded ethers **3a** and **4a**.

(6) D. W. Setser, D. W. Placzek, R. J. Cvetanović, and B. S. Rabinovitch, *Can. J. Chem.*, **40**, 2179 (1962).