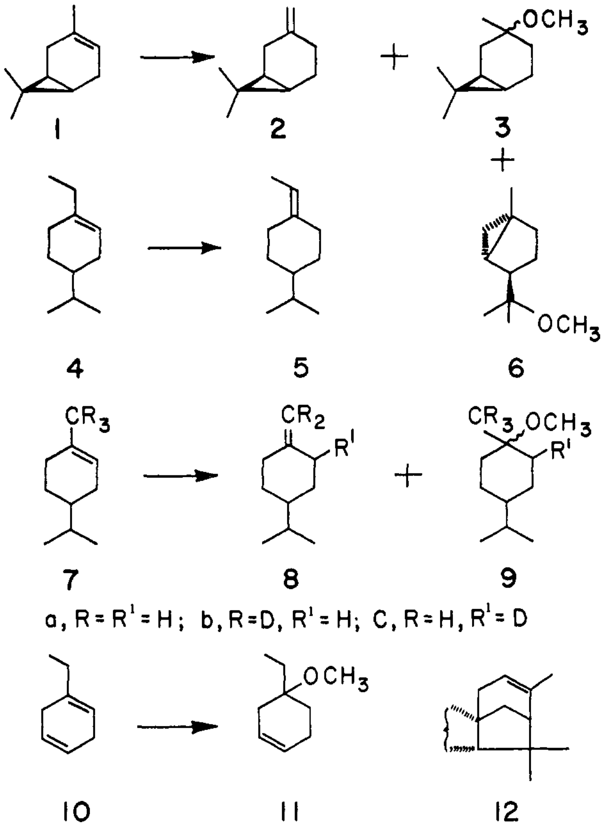
presence of alcohols, the entering hydrogen atom is incorporated in the form of a proton; irradiation of **7a** in benzene–methanol-O-*d* gives **8c** (along with **9c**), in which the newly incorporated hydrogen atom has been abstracted from oxygen rather than carbon.



a, R = R$^1$ = H; b, R = D, R$^1$ = H; c, R = H, R$^1$ = 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.

**Acknowledgment.** The able technical assistance of Messrs. H. J. Krauss and T. R. Walker is gratefully acknowledged.

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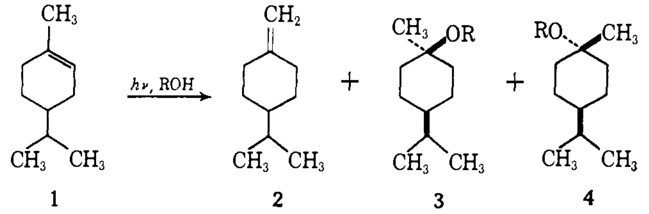
## The Photochemically Initiated Addition of Alcohols to 1-Menthene. A New Type of Photochemical Addition to Olefins

*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).

**Table I.** Sensitized Photolyses of 1-Menthene in Alcohol Solvents

| Entry | ROH | Sensitizer | $k$, sec$^{-1}$, at 25–30° $^{a}$ | Composition after 6 hr, % 1 | 2 | 3 | 4 |
|---|---|---|---|---|---|---|---|
| 1 | $CH_3OH$ | None | $1.3 \times 10^{-5}$ | 75 | 9.5 | 6.0 | 9.5 |
| 2 | $CH_3OH$ | Toluene | $6 \times 10^{-5}$ | 26 | 29 | 18 | 27 |
| 3 | $CH_3OH$ | Xylene$^{b}$ | $13 \times 10^{-5}$ | 6.0 | 34 | 24 | 37 |
| 4 | $CH_3OH$ | Xylene$^{b,c}$ | $5 \times 10^{-5}$ | ... | ... | ... | ... |
| 5 | $CH_3CH_2OH$ | Xylene$^{b}$ | $11 \times 10^{-5}$ $^{d}$ | 10 | 40 | 21 | 28 |
| 6 | $(CH_3)_2CHOH$ | Xylene$^{b}$ | $9 \times 10^{-5}$ | 12 | 61 | 10 | 17 |
| 7 | $(CH_3)_3COH$ | Xylene$^{b}$ | $0.7 \times 10^{-5}$ | 84$^{e}$ | 16$^{e}$ | ... | ... |
| 8 | $H_2O$$^{f}$ | Xylene$^{b}$ | $8 \times 10^{-5}$ | 17 | 23 | 26 | 33 |

[a] Reactions were carried out on 5 g of **1** in 400 ml of ROH containing 4 ml of the sensitizer. The rate constants were calculated from the disappearance of **1** as measured by gas chromatography using *ca.* 5% of a 1:1 mixture of *cis*- and *trans*-menthane as an internal standard. Owing to inherent design limitations of the reactor, constant temperature could not be maintained. [b] A mixture of isomers. [c] Oxygen was bubbled through the reaction mixture. [d] Average of two runs. [e] Interpolated from 4- and 8-hr points. [f] A 50% solution of aqueous *t*-butyl alcohol was used.

We also found that ethanol (entry 5) and 2-propanol (entry 6) likewise added to 1-menthene (**1**) under the same conditions affording the ethers **3b**, **4b**, **3c**, and **4c**. In *t*-butyl alcohol (entry 7) the isomerization reaction greatly outweighed ether formation and no more than trace amounts of the *t*-butyl ethers **3d** and **4d** could be detected by gas chromatography, even after 18-hr reaction times. Interestingly, the isomerization was substantially slower in this solvent. In aqueous *t*-butyl alcohol hydration of 1-menthene (**1**) took place readily, giving alcohols **3e** and **4e**[7] (entry 8).

The stereochemical assignments for ethers **3** and **4** were made on the basis of the data presented in Table II. Supporting chemical evidence for the methyl and ethyl ethers comes from our isolation of **3a** and **3b** as the predominant products (**3**:**4** $\simeq$ 3.5:1) of acid-catalyzed alcohol additions to 1-menthene under equilibrating conditions (8–9-day reaction times).

**Table II.** Properties of Isomeric Ethers **3** and **4**

| Ether | *H*–C–O– $\delta_{TMS}^{CCl_4}$, ppm | Quaternary $CH_3$$^{a}$ $\delta_{TMS}^{CCl_4}$, ppm | $\Delta W_{1/2}$, Hz | Relative retention time$^{b}$ |
|---|---|---|---|---|
| **3a** | 3.08 | 1.03 | 0.30 | 1 |
| **4a** | 3.13 | 1.10 | 0.60 | 1.4 |
| **3b** | 3.27$^{c}$ | 1.03 | ...$^{d}$ | 1 |
| **4b** | 3.37$^{c}$ | 1.09 | ...$^{d}$ | 1.6 |
| **3c** | 3.67$^{e}$ | 1.08 | 0.38 | 1 |
| **4c** | 3.80$^{e}$ | 1.10 | ...$^{f}$ | 1.4 |

[a] *Cf.* K. L. Williamson, T. Howell, and T. A. Spencer, *J. Am. Chem. Soc.*, **88**, 325 (1966). [b] Expressed as the retention time of **4** divided by the retention time of **3** on a 10% DC-550 silicone oil on 60–80 Chromosorb W Column. [c] A quartet, $J = 7.0$ Hz. [d] Not measured because of overlapping with the $CH_2CH_3$ triplet. [e] A septet, $J = 6.0$ Hz. [f] Not measured because of overlapping with the isopropyl doublets.

The facts which emerge from these and related findings[8] suggest a reaction pathway involving the olefin's triplet state which, perhaps because of excessive steric strain, gives way to an intermediate possessing carbonium ion character in its subsequent reactions. The strain factor appears essential to the reaction since the exocyclic olefin **2** shows no tendency to give ethers **3** and **4**. The slight preponderance of ether **4** fits well with the expectation of a kinetically controlled addition to the double bond of 1-menthene or the related carbonium ion.

We are using these mechanistic concepts as guide lines in exploring new synthetic applications of photochemically initiated addition reactions to olefins. We have thus far found that 1-methylcyclohexene and 1-methylcycloheptene undergo both the isomerization and the addition reaction and that the former readily affords 1-methylcyclohexyl acetate upon irradiation in acetic acid with xylene as the photosensitizer.

**Acknowledgment.** We appreciate the complete cooperation and kind assistance offered by Dr. P. J. Kropp in this and related work. Partial support by Eli Lilly and Company through an unrestricted research grant is gratefully acknowledged.

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[7] Authentic material (a 3:2 mixture of **3e** and **4e**) was prepared from 4-isopropylcyclohexanone and methyllithium.

[8] P. J. Kropp, *J. Am. Chem. Soc.*, **88**, 4091 (1966).

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## Ionic Organoboranes. II.[1] Cesium Tropenylium Undecahydroclovododecaborate. Cage–Ring Interactions in $C_7H_6B_{10}H_9^-$ and $C_7H_6B_{12}H_{11}^-$ Ions[2]

*Sir:*

The purpose of this paper is threefold: (1) to report the synthesis of the tropenylium[3] undecahydroclovododecaborate anion (I), (2) to confirm our proposed[1] structure for the tropenylium nonhydroclovodecaborate anion (II), and (3) to demonstrate the direction and extent of electronic interaction between the cage and ring in such compounds.

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[1] Paper I: K. M. Harmon, A. B. Harmon, and A. A. MacDonald, *J. Am. Chem. Soc.*, **86**, 5036 (1964).

[2] Work supported by the National Science Foundation and the Petroleum Research Fund.

[3] The tropenylium substituent nomenclature has been discussed.[1]