Photochemistry of Cycloalkenes. III. Ionic Behavior in Protic Media and Isomerization in Aromatic Hydrocarbon Media[1]

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Abstract: On irradiation in methanol in the presence of one of the aromatic hydrocarbon photosensitizers benzene, toluene, or xylene, 1-methylcyclohexene (**1b**) and -heptene (**1c**) were each converted to a mixture of the corresponding exocyclic isomer **2** and tertiary methyl ether **3**. Similarly (±)-*p*-menth-1-ene (**5**) and the ethyl analog **8** afforded the exocyclic isomers **6** and **9** and the ether mixtures **7** and **10**, respectively, whereas (+)-3-carene (**11**) gave the 3(10) isomer **12** and a mixture of the three ethers **13a–15a**. In aqueous *t*-butyl alcohol the analogous alcohols **13b–15b** were formed, along with **12**. 4-Isopropylcyclohexene (**16**) afforded the mixture of four ethers **17**, whereas the dienes **18** and **20** gave selectively the ethers **19** and **21**. The methoxy analog **22** gave the ketal **23**. In acetic acid 1-methylcyclohexene (**1b**) afforded the acetate **4b**. In *t*-butyl alcohol isomerization of **1b** to the exocyclic olefin **2b** predominated over ether formation; the rate of conversion was slower than in methanol, but was facilitated by the addition of 1% sulfuric acid. By contrast to the foregoing examples, no isomerization or ether formation was observed with the larger ring homolog 1-methylcyclooctene (**1d**), the acyclic analog 3,5-dimethyl-3-heptene (**24**), the exocyclic olefins **2b** and **2d**, or the conformationally rigid olefin α-cedrene (**27**). 1-Methylcyclopentene (**1a**) afforded principally the dihydro derivative, 1-methylcyclopentane. Deuterium labeling studies with (±)-*p*-menth-1-ene (**5**) confirmed an ionic mechanism for both the isomerization and the ether formation reactions. The isomerization reaction was also observed in aromatic hydrocarbon solvents in the absence of added protic media, despite the necessary difference in mechanism. On irradiation in benzene, toluene, xylene, or mesitylene 1-methylcyclohexene (**1b**) and -heptene (**1c**) were each converted to the corresponding exocyclic isomer **2**. Likewise, (±)-*p*-menth-1-ene (**5**), the ethyl analog **8**, and (+)-3-carene (**11**) afforded the exocyclic isomers **6, 9,** and **12**, respectively. On the other hand, neither the larger ring olefin 1-methylcyclooctene (**1d**) nor the acyclic analog 3,5-dimethylhept-3-ene (**24**) exhibited any detectable double-bond migration. Photodimerization competed effectively with isomerization in the case of 1-methylcyclohexene (**1b**), but not -heptene (**1c**). By contrast, the principal product from 1-methylcyclopentene (**1a**) was methylcyclopentane. Labeling studies revealed that the isomerization of (±)-*p*-menth-1-ene (**5**) to the 1(7) isomer **6** in benzene or xylene involves principally an intermolecular loss of hydrogen from C-7 and incorporation at C-2, with the newly incorporated hydrogen apparently coming from olefin rather than solvent. The mechanistic implications of these results are discussed.

One of the simplest and most abundant chromophores available for photochemical study is that of ethylene and its many alkyl-substituted derivatives. Previous investigations of alkene photochemistry, although many in number, have been limited principally to photosensitization studies with acyclic systems.[2] Aside from photoaddition to the sensitizer in certain cases, the only general pattern of behavior to emerge has been *cis–trans* isomerization, a transformation which apparently occurs as a consequence of the preferred orthogonal conformation of the triplet states of acyclic olefins.[3,4]

It was the purpose of the present study to investigate the behavior of five-, six-, and seven-membered cycloalkenes, in which *cis → trans* isomerization of the double bond should be a high-energy, if not structurally pro-

hibited, process.[5] Surprisingly, cycloalkene photochemistry has enjoyed only limited study, except for a few instances in which either photodimerization or photoaddition to the sensitizer was the only observed course of reaction.[4,6,7] In the present communication the intriguing photochemical behavior of cycloalkenes in protic solvents is described,[8] followed by a discussion of a similar study conducted in aromatic hydrocarbon solvents.

Results

Protic Media. Since cycloalkenes have intense ultraviolet absorption only at rather low wavelengths, it is generally desirable to employ a photosensitizer in studying their photochemical behavior. For this purpose benzene, toluene, and xylene were chosen since

(1) (a) Part II: P. J. Kropp, *J. Am. Chem. Soc.*, 89, 3650 (1967). (b) For a preliminary description of the present work, see P. J. Kropp, *ibid.*, 88, 4091 (1966).

(2) For examples of photosensitized *cis–trans* isomerization of acyclic alkenes see, among many others, (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) G. S. Hammond, J. Saltiel, A. A. Lamola, N. J. Turro, J. S. Bradshaw, D. O. Cowan, R. C. Counsell, V. Vogt, and C. Dalton, *J. Am. Chem. Soc.*, 86, 3197 (1964); (d) A. C. Testa, *J. Org. Chem.*, 29, 2461 (1964); (e) H. Morrison, *Tetrahedron Letters*, 3653 (1964); *J. Am. Chem. Soc.*, 87, 932 (1965); (f) R. F. Borkman and D. R. Kearns, *ibid.*, 88, 3467 (1966); (g) C. Moussebois and J. Dale, *J. Chem. Soc., Sect. C*, 260 (1966), and references cited therein.

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

(4) *cis–trans* isomerization has also been reported as the only photosensitized transformation for larger ring cycloalkenes such as 1,5,9-cyclododecatriene [H. Nozaki, Y. Nisikawa, Y. Kamatani, and R. Noyori, *Tetrahedron Letters*, 2161 (1965)] and 1,3-cyclooctadiene [R. S. H. Liu, *J. Am. Chem. Soc.*, 89, 112 (1967)].

(5) *trans*-Cyclooctene has long been known as a relatively stable, isolable compound: K. Ziegler and H. Wilms, *Ann.*, 567, 1 (1950). 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.

(6) See, for example, (a) D. Scharf and F. Korte, *Tetrahedron Letters*, 821 (1963); *Chem. Ber.*, 97, 2425 (1964); (b) H. H. Stechl, *Angew. Chem. Intern. Ed. Engl.*, 2, 743 (1963); (c) D. R. Arnold, R. L. Hinman, and A. H. Glick, *Tetrahedron Letters*, 1425 (1964); (d) D. R. Arnold, D. J. Trecker, and E. B. Whipple, *J. Am. Chem. Soc.*, 87, 2596 (1965); (e) R. Srinivasan and K. A. Hill, *ibid.*, 88, 3765 (1966).

(7) The report of F. J. McQuillin and J. D. Parrack, *J. Chem. Soc.*, 2973 (1956), which constitutes an exception to this general pattern, is discussed in detail below.

(8) Analogous results from a parallel study have recently been reported by J. A. Marshall and R. D. Carroll, *J. Am. Chem. Soc.*, 88, 4092 (1966).

their triplet energies (81–84 kcal/mole)[9] are well above those of alkenes (~70–82 kcal/mole).[10]

In general it was discovered that on photosensitized irradiation in alcoholic media 1-alkylcyclohexenes and -heptenes (1) are readily converted to a mixture of the exocyclic isomer 2 and a tertiary ether 3.[11] The relative amounts of exocyclic olefin 2 and ether 3 formed are dependent upon both the ring size and, as will be discussed below, the nature of the solvent. The behavior of the series of 1-methylcycloalkenes 1 in methanol under identical irradiation conditions is summarized in Table I. 1-Methylcyclohexene (1b) gave approximately

Table I. Irradiation of 1-Methylcycloalkenes (1) in Methanol–Xylene[a]

Olefin (n)	Time, hr	Yield, %[b] 1	2	3
1a (5)	12	59[c]	8	e
1b (6)	8	13	33	44
1c (7)	8	33	d	62
1d (8)	20	72	e	e
2b (6)	8	e	70	e
2d (8)	8	e	56	e

[a] Irradiations were conducted as described in the Experimental Section using 150-ml methanolic solutions containing 31 mmoles of olefin and 3.0 ml of xylene. [b] Determined by gas chromatographic analysis of aliquots removed from the irradiation mixture. [c] Methylcyclopentane obtained in 24% yield. A peak corresponding in retention time to ethylene glycol was also observed. [d] Trace. [e] None detectable on comparison with authentic specimens prepared independently.

equal amounts of exocyclic olefin 2b and ether 3b, whereas 1-methylcycloheptene (1c) gave predominantly the ether product 3c. By contrast, 1-methylcyclopentene (1a) reacted more slowly than either of the two higher homologs and afforded principally methylcyclopentane; no significant amount of the ether 3a could be detected.[12] In yet a third type of behavior, 1-methylcyclooctene (1d) showed no tendency for isomerization, ether formation, or reduction under these conditions but merely underwent slow disappearance on continued irradiation.[13] Through control experiments the exocyclic

(9) (a) D. F. Evans, *J. Chem. Soc.*, 2753 (1959); (b) D. R. Kearns, *J. Chem. Phys.*, 36, 1608 (1962), and references cited therein.

(10) (a) The 0–0 $S_0 \rightarrow T_1$ absorption band of ethylene has been assigned at 3484 A (82 kcal/mole): D. F. Evans, *J. Chem. Soc.*, 1735 (1960). The spectroscopic triplet-state energies of other monoolefins are not well established. However, it can be assumed that they will decrease with increasing numbers of alkyl substituents about the double bond; see R. S. Mulliken, *J. Chem. Phys.*, 33, 1596 (1960), and R. E. Rebbert and P. Ausloos, *J. Am. Chem. Soc.*, 87, 5569 (1965). As discussed below, twisting about the double bond of acyclic alkenes results in a lowering of the triplet energy. (b) For a recent demonstration of the transfer of triplet energy from benzene to cyclohexene, see R. B. Cundall and P. A. Griffiths, *Chem. Commun.*, 194 (1966). The possibility of singlet energy transfer occurring is remote since E_{S_1} for benzene (112 kcal/mole) is substantially below that of cycloalkenes (>125).

(11) A considerable amount of polymer formation occurred when benzene was employed as the photosensitizer. This is consistent with the recent report by D. Bryce-Smith and A. Gilbert, *ibid.*, 643 (1966), that olefins such as cyclooctene initiate the phototelomerization of benzene. In general, it was observed that the use of toluene or xylene resulted in faster reaction and gave less evidence for polymer formation. For a quantitative measure of the relative efficiencies of these three materials in sensitizing the destruction of (±)-p-menth-1-ene (5), see ref 8.

(12) The behavior of 1-methylcyclopentene (1c), which resembles that of 2-norbornene and 2-methyl-2-norbornene, has been discussed separately; see ref 1a.

(13) In all cases extended irradiation resulted in a slow disappearance of each of the olefinic components. This is probably attributable, at least in part, to addition of the olefin to the aromatic hydrocarbon

isomers 2b and 2d were found to be stable to the irradiation conditions, affording neither the corresponding endocyclic isomer 1 nor the ether 3.

1a, $n = 5$
b, $n = 6$
c, $n = 7$
d, $n = 8$

2

3, R = CH₃
4, R = Ac
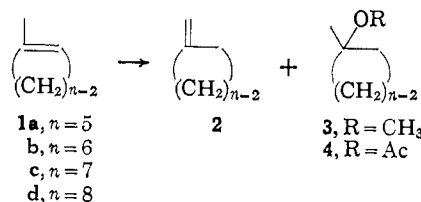
The reaction was successfully extended to a number of other 1-alkylcyclohexene derivatives, and in each case both the exocyclic isomer and an ether adduct were obtained. Thus (±)-p-menth-1-ene (5) afforded (±)-p-menth-1(7)-ene (6) and a 1:1.7 (trans:cis) mixture of the epimeric 1-p-menthyl ethers 7a and 7b (Table II).[14,15]

Table II. Irradiation of (±)-p-Menth-1-ene (5) in Methanol–Xylene[a]

Time, hr	Yield, %[b] 5	6	7a	7b
8	5	36	16	27
8[c]	41	21	16	23
8[d]	51	19	12	16

[a] Irradiations were conducted as described in the Experimental Section during 150-ml solutions containing 1.00 g of olefin and 15 ml of xylene. [b] Determined by gas chromatographic analysis of aliquots removed from the irradiation mixture. [c] Contained 1.5 ml of morpholine. [d] Solution 0.006 M in sodium acetate.

In similar fashion the ethyl analog 8[16] gave, in a comparable ratio, the exocyclic isomer 9 and the epimeric ethers 10.

5

6

7a, R = OCH₃; R' = CH₃
b, R = CH₃; R' = OCH₃

8

9

10
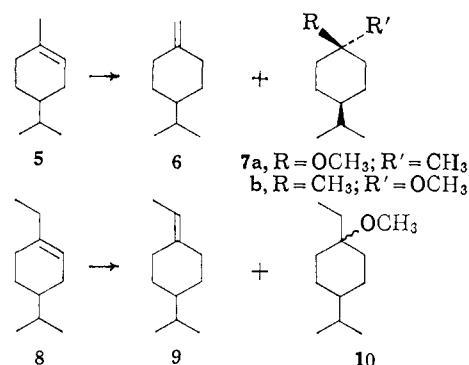
Particularly interesting behavior was exhibited by (+)-3-carene (11), which was converted to the 3(10) isomer 12 and a mixture of three tertiary ethers (13a–15a) (Table III). The identity of two of the ethers was easily established by conducting the irradiation in aqueous t-butyl alcohol, under which conditions the corresponding alcohols (13b–15b) were obtained in similar relative amounts.[17] The major and minor

sensitizer; see K. E. Wilzbach and L. Kaplan, *J. Am. Chem. Soc.*, 88, 2066 (1966), and D. Bryce-Smith, A. Gilbert, and B. H. Orger, *Chem. Commun.*, 512 (1966).

(14) W. Hückel and P. Heinzelmann, *Ann.*, 687, 82 (1965).

(15) See ref 8 for stereochemical assignments of the epimeric ethers. The photochemical isomeric ratio was quite different from that obtained by acid-catalyzed addition of methanol to 5, in which the trans isomer 7a heavily predominated (~4:1).

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

(17) In some runs with aqueous t-butyl alcohol, in which benzene

11 → **12** +

13a, R = CH₃
b, R = H

14a, R = CH₃
b, R = H

15a, R = CH₃
b, R = H
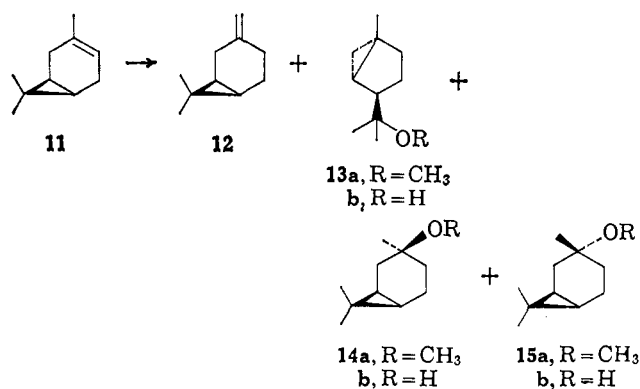
alcoholic products were found to be identical in every respect with authentic specimens of (+)-3β- (**14b**)[18] and (+)-3α-caranol (**15b**),[19] respectively. An analogous assignment of the structures **14a** and **15a** to the principal and minor ether products, respectively, is corroborated by the similarities of their spectral data, relative yields, and relative gas chromatographic retention times with those of the corresponding alcohol photoproducts.

Table III. Irradiation of (+)-3-Carene (**11**)[a]

Solvent–sensitizer	Time, hr	Yield, %[b]				
		11	12	13	14	15
CH₃OH–C₆H₆	16	38	18	10	12	3
CH₃OH–C₆H₄(CH₃)₂	8	35	23	12	17	3
(H₂O–(CH₃)₃COH)–C₆H₆[c]	8	52	13	7	14	4

[a] Irradiations were conducted as described in the Experimental Section using 150-ml solutions containing 1.00 g of olefin and 15 ml of sensitizer. [b] Determined by gas chromatographic analysis. [c] Contained 60 ml of water.

The remaining ether and alcohol likewise have similar properties. The nmr spectrum of the ether shows multiplets at τ 9.46 and 9.80 for two cyclopropyl methylene protons, indicating that the product has retained a cyclopropane ring, but not within the framework of the carane skeleton. This immediately brings to mind the structure **13a**, based on the recent observation that development of positive character at C-3 of certain carane derivatives results in rearrangement to the bicyclo[3.1.0]hexane system.[20] This assignment is supported both by additional features of the nmr spectrum, which show the presence of an additional tertiary cyclopropyl proton (τ 9.18) and three methyl groups which are shifted somewhat downfield (a six-proton singlet at 8.84 and a three-proton singlet at 8.90), and by the similarity of the nmr data with those of other bicyclo[3.1.0]hexanes previously obtained from carane derivatives.[20]

was employed as the photosensitizer, a fourth alcohol was obtained which exhibited spectral data consistent with those reported for the alcohol **i**, recently obtained by irradiation of benzene in an aqueous medium: E. Farenhorst and A. F. Bickel, *Tetrahedron Letters*, 5911 (1966). See also L. Kaplan, J. S. Ritscher, and K. E. Wilzbach, *J. Am. Chem. Soc.*, **88**, 2881 (1966).


i
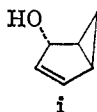
(18) H. Kuczynski and K. Piatkowski, *Roczniki Chem.*, **31**, 59 (1957).
(19) H. Kuczynski and Z. Chabudzinski, *ibid.*, **34**, 177 (1960).
(20) P. J. Kropp, *J. Am. Chem. Soc.*, **88**, 4926 (1966).

Cyclohexenes bearing no substituents on the double bond also undergo methanol addition, but somewhat less efficiently. Lacking the directive influence of the 7-CH₃ group of p-menth-1-ene (**5**), 4-isopropylcyclohexene (**16**) affords a mixture of four ethers (**17**), apparently arising from both cis and trans addition in both directions across the double bond. In the case of 1,4-cyclohexadienes the addition reaction exhibits a rather interesting selectivity which could find synthetic application. Thus, 1-ethyl-1,4-cyclohexadiene (**18**) undergoes predominant addition to the trisubstituted double bond to give the tertiary ether **19**. In the case of p-mentha-1,4-diene (**20**) addition occurs more rapidly to the methyl-substituted double bond, affording **21** as the predominant product.[21,22] The addition reaction is extendable to cycloalkenes bearing substituents other than alkyl groups on the double bond. The methoxy analog **22**, for example, afforded the methyl ketal **23** in 60% yield.

16 → **17**

18 → **19**

20 → **21**

22 → **23**
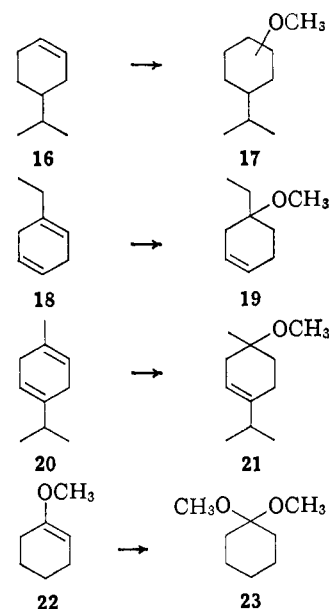
It was noted earlier that neither the isomerization nor addition reactions occurred with 1-methylcyclooctene (**1d**) or the exocyclic olefins **2b** and **2d**. Similarly it was found that neither reaction is extendable to the acyclic analog **24**, which on irradiation in methanol–xylene underwent slow disappearance without the formation of any detectable amount of the ether **25** or the terminal olefin **26**.[13] Under these conditions the isomer **26** was

24 ⇸ **25**

26 **27**
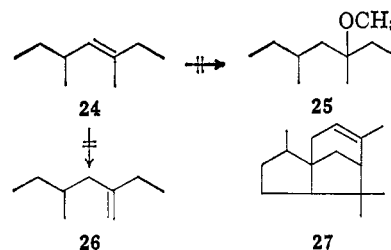
sufficiently stable that its formation would have been detectable to within 1%. Also relatively inert under these conditions was the conformationally rigid olefin

(21) Several minor olefinic and ether products were obtained from **20** which were not investigated.
(22) The photoproducts **19** and **21**, still being cyclohexenes, are themselves photochemically labile and undergo further reaction on extended irradiation.

α-cedrene (27) from which no detectable ether or isomerization products were formed.

Additional insight was afforded by a series of irradiations conducted with 1-methylcyclohexene (1b) under a variety of conditions, as summarized in Table IV. Direct irradiation of a methanolic solution of 1b in the absence of a photosensitizer led to a slow accumulation of the ether 3b and exocyclic olefin 2b (Table IV, entry 2). The use of acetophenone as a photosensitizer in place of xylene also afforded the photoproducts 2b and 3b, but with an accompanying rapid disappearance of the starting olefin (entry 3).[23] Thus the isomerization and ether formation reactions do not require aromatic hydrocarbon photosensitizers (or any sensitizer at all), but much more efficient reaction is achieved by using them.

Table IV. Irradiation of 1-Methylcyclohexene (1b)[a]

Entry	Solvent	Time, hr	Yield, %[b] 1b	2b	3b	4b
1	CH₃OH	8	4	30	63	..
2	CH₃OH[c]	8	73	9	7	..
3	CH₃OH[d]	4	18	6	13	..
4	CH₃OH[e]	8	8	41	31	1
5	(C₂H₅)₂NH	18	26	f	..	..
6	CH₃CO₂H	8	~40[g]	~20[g]	..	30
7	(CH₃)₃COH	7	33	5	..	..
8	(CH₃)₃COH, H⁺ [h]	12	34	46	..	..
9	C₆H₅CH₂OH[c]	6	8	56	..	..

[a] Irradiations were conducted as described in the Experimental Section using 150-ml solutions containing 31 mmoles of olefin and 3.0 ml of xylene. [b] Determined by gas chromatographic analysis of aliquots removed from the irradiation mixture. [c] Xylene omitted. [d] Xylene replaced with 3.0 ml of acetophenone. [e] Saturated with sodium acetate. [f] Trace. [g] Estimated; gas chromatographic peak overlapped by solvent peak. [h] Contained 1.5 ml of sulfuric acid.

Neither the isomerization nor ether formation reaction was inhibited noticeably by the addition of sodium acetate as a buffer to a methanolic solution of 1-methylcyclohexene (1b) or (±)-p-menth-1-ene (5). The addition of 1% morpholine in the case of 5 caused a slight retardation in the over-all rate of reaction and a small, but apparently real, increase in the ratio of isomerization to ether formation. On the other hand, irradiation of 1b in diethylamine–xylene led only to a slow disappearance of starting material, with no detectable isomerization occurring.

The substitution of acetic acid for methanol afforded 1-methylcyclohexyl acetate (4b), along with the usual isomerization product 2b. When methanol was replaced with t-butyl alcohol, 1b gave principally the olefin 2b and only a trace of ether product. The reduced amount of ether formation is probably attributable to the increased steric bulk of the alcohol. The use of t-butyl alcohol–sensitizer solutions would be a method of choice for isomerizing 1-alkylcycloalkenes to their thermodynamically less stable exocyclic analogs[24] were

(23) It is well known that ketonic photosensitizers afford a number of photoproducts from olefins that arise from oxetane formation, extraction of allylic hydrogen atoms, and radical additions to the olefin. For a recent study of the array of products from the irradiation of various carbonyl compounds in cyclohexene, see J. S. Bradshaw, J. Org. Chem., 31, 237 (1966).

(24) A. C. Cope, D. Ambros, E. Ciganek, C. F. Howell, and Z. Jacura, J. Am. Chem. Soc., 82, 1750 (1960), have reported the following equilibrium constants, determined at 25° in acetic acid containing p-toluenesulfonic acid: 1b/2b 240 and 1c/2c 74.

it not for the fact that the over-all rate of reaction is significantly reduced in going from methanol to t-butyl alcohol. Based on the assumption that this is due, at least in part, to the lower acidity of t-butyl alcohol, several irradiations were conducted in this solvent in the presence of 1% sulfuric acid. These conditions resulted in a rate of reaction comparable to that observed with methanol and gave predominantly the isomerization product. A somewhat more convenient method for the isomerization proved to be the use of benzyl alcohol as solvent, which requires neither an added sensitizer nor acid catalysis.[25]

Labeling Studies. Ionic Mechanism. In going from an endocyclic olefin such as p-menth-1-ene (5) to the exocyclic isomer 6 there is necessarily a loss of one hydrogen substituent from the 7-CH₃ group and a gain of one substituent at C-2. It is conceivable that this transformation could occur via an intramolecular C-7 → C-2 hydrogen shift. However, the foregoing experimental data can be more consistently explained in terms of an alternative mechanism, outlined in Scheme I, which simultaneously accounts for both the isomerization and ether formation reactions. It is proposed that on irradiation in a protic medium, HY, 1-alkylcyclohexenes and -heptenes (I) undergo initial protonation to afford a carbonium ion intermediate II, which is subsequently susceptible to three competing reactions: (a) elimination to exocyclic olefin III, (b) nucleophilic attack by solvent to give adduct IV, or (c) regeneration of starting olefin I.[26] The relative importance of the elimination and substitution processes would, as has been observed experimentally, be expected to be a function of such factors as ring size, substitution pattern, and acidity and nucleophilicity of the solvent. A more detailed consideration of the light-induced protonation step itself is delayed until the Discussion. However, convincing support for the principal features of Scheme I, which was obtained through labeling studies conducted with (±)-p-menth-1-ene (5), will now be described.

Scheme I
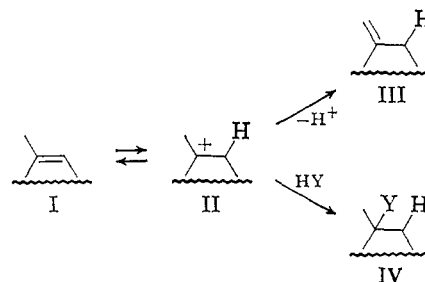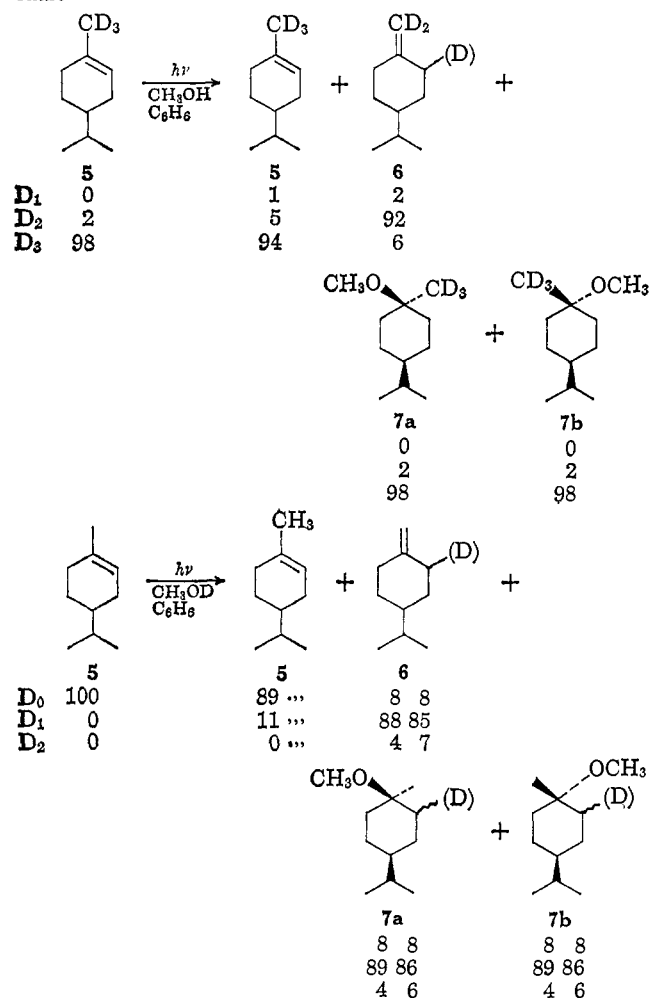

As shown in Chart I, irradiation of 5-7,7,7-d₃ afforded the ether products 7a and 7b with complete retention of deuterium, as determined mass spectroscopically; nmr data verified that the deuterium remained, at least principally, at C-7. On the other hand, the accompanying p-menth-1(7)-ene (6) was principally D₂, with no more than 6% of the isomerization 5 → 6 having possibly occurred via an intramolecular C-7 →

(25) An alternative method for effecting the endo → exo isomerization of a 1-alkylcyclohexene or -heptene involving irradiation in benzene, toluene, or xylene as sensitizer–solvent is discussed below.

(26) In the absence of alkyl substitution on the double bond, only the latter two processes would, of course, be applicable.

C-2 deuterium shift. The nmr spectrum again indicated that the retained deuterium remained at C-7.[27]

Chart I

	5	5	6
D_1	0	1	2
D_2	2	5	92
D_3	98	94	6

	7a	7b
	0	0
	2	2
	98	98

	5	5	6
D_0	100	89 ...	8 8
D_1	0	11 ...	88 85
D_2	0	0 ...	4 7

	7a	7b
	8 8	8 8
	89 86	89 86
	4 6	4 6

Complementary results were obtained by irradiating unlabeled 5 in methanol-O-*d*. The resulting ethers 7a and 7b and the isomerized olefin 6 were each predominantly monodeuterated. In an irradiation interrupted at only partial conversion, the recovered 5 had incorporated 11% deuterium, confirming that some return to starting material occurs after the protonation step. The gradual buildup of deuterium in the starting olefin is reflected further in some double labeling in each of the photoproducts 6, 7a, and 7b. In a second irradiation, continued until the starting olefin 5 had been totally consumed, the amount of double labeling increased. By contrast, irradiation of the acyclic analog 24 under similar conditions afforded recovered 24 which contained no detectable amount of deuterium.[28]

Aromatic Hydrocarbon Media. The photosensitized isomerization of a 1-methylcycloalkene to its exocyclic form in protic media is reminiscent of an earlier observation by McQuillin, *et al.*, that a mixture of α- (28) and β-eudesmol (29) was enriched in the β isomer on irradiation in benzene solution.[7] Despite the similarity in over-all result, however, it is obvious that the isomerization of 28 in benzene solution does not

(27) There was a small, but apparently real, loss of deuterium in recovered 5-*d₃* which suggests that some scrambling occurs in the ion II.

(28) Similarly, irradiation of 1-methylcyclopentene (1a) in xylene–methanol-O-*d* resulted in no detectable incorporation of deuterium in either the methylcyclopentane product or the recovered starting material; see ref 1a.

proceed *via* protonation, unless, perhaps, the hydroxyl proton of eudesmol itself serves as a proton source. It was thus of interest to undertake a detailed investigation of the photochemical behavior of 1-alkylcycloalkenes in aromatic hydrocarbon media.
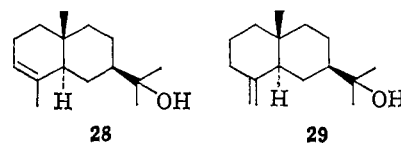
It was, in fact, found that irradiation of 1-alkylcyclohexenes or -heptenes in benzene, toluene, xylene, or mesitylene in the absence of any added hydroxylic material effects an isomerization of the double bond to the exocyclic position. Typical results from irradiation of the homologous series of 1-methylcycloalkenes 1a-d in xylene are summarized in Table V.

1	2

a, *n* = 5
b, *n* = 6
c, *n* = 7
d, *n* = 8
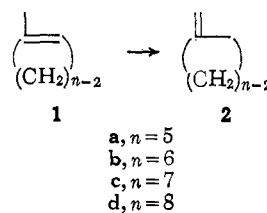
Many similarities to the photochemical behavior of these same materials in alcohol–aromatic hydrocarbon mixtures are apparent: (a) isomerization is exhibited by the six- and seven-membered ring systems but not by 1-methylcyclooctene (1d), which underwent only slow

Table V. Irradiation of 1-Methylcycloalkenes (1) in Xylene[a]

Olefin (*n*)	Time, hr	Yield, %[b]		
		1	2	Dimers
1a (5)	16	69[c]	10	..
1b (6)	8	11	26	46[d]
1c (7)	4	4	88	..
1d (8)	8	67	*e*	..
2b (6)	8	*e*	99	..

[a] Irradiations were conducted as described in the Experimental Section using 150-ml solutions containing 31 mmoles of olefin. [b] Determined by gas chromatographic analysis of aliquots removed from the irradiation mixture. The results reported are those of a typical run. [c] Methylcyclopentane formed in 19% yield. [d] Mixture of at least six components. [e] None detectable.

disappearance without any detectable formation of the exocyclic isomer 2d;[13] (b) 1-methylcyclopentene (1a), although photolabile, is significantly less reactive than either of the two next higher homologs 1b or 1c and afforded principally the dihydro derivative, 1-methylcyclopentane;[12] (c) the isomerization is a nonreversible process, in that the exocyclic olefins 2 are photostable under these conditions. Unlike the behavior in protic media there were, of course, no products of type IV resulting from addition of solvent to the olefin.

In further analogy with previous results in protic media it was found that isomerization occurred equally well with (±)-*p*-menth-1-ene (5), the ethyl analog 8, and (+)-3-carene (11) (see Table VI). However, the acyclic analog 24, like 1-methylcyclooctene (1d), was relatively stable to the irradiation conditions and exhibited no detectable isomerization to 26.

In marked contrast to the cyclopentene and -heptene homologs 1a and 1c, which showed only a negligible

Table VI. Irradiation of Olefins **5, 8, 11,** and **24**[a]

Olefin	Solvent	Time, hr	Product (yield, %[b])
5	Xylene	4	**5** (25), **6** (16)
8[c]	Benzene	16	**8** (21), **9** (16)
11	Benzene	8	**11** (66), **12** (21)
24[d]	Xylene	8	**24** (69), **26** (e)

[a] Irradiations were conducted as described in the Experimental Section using 150-ml solutions containing 3.00 g of olefin unless otherwise indicated. [b] Determined by gas chromatographic analysis of aliquots removed from the irradiation mixture. [c] 1.00 g. [d] 4.42 g. [e] None detectable.

loss of olefinic material, there was a consistently low recovery of volatile products from cyclohexene systems. This was traced in the case of 1-methylcyclohexene (**1b**) to the competing formation of a mixture of at least six difficultly separable high-boiling products having a molecular weight approximately twice that of **1b**. Dimerization was, in fact, the principal course of reaction for **1b**. Since the nmr spectrum of the mixture displays absorption below τ 7.5, it is apparent that the dimers are not all of the familiar cyclobutane type **30** previously obtained from other cycloalkenes;[6] complete characterization will have to await further study. The low recoveries from irradiation of **5** and **8** suggest that substantial dimerization of these olefins occurs as well, but this was not investigated. The higher recovery from irradiation of (+)-3-carene (**11**) indicates that dimerization is less extensive in this system.

30
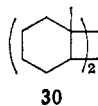
Both the rate of reaction and, in the case of cyclohexenes, the ratio of dimerization to isomerization were found to be dependent upon the choice of solvent. This is illustrated in Table VII for 1-methylcyclohexene (**1b**). In general, the fastest rates and cleanest products were obtained with xylene. In the case of benzene a yellow polymer invariably formed which coated the walls of the vessel and reduced the transmission of light.[11] In addition to the slower rate of reaction and contamination of the product with polymer, irradiation in benzene afforded by far the highest ratio of dimerization to isomerization.

Table VII. Irradiation of 1-Methylcyclohexene (**1b**) in Various Solvents[a]
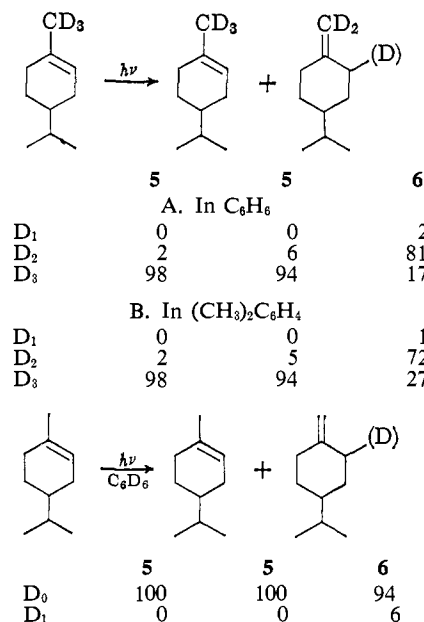
Solvent	E_T, kcal/mole	Time, hr	Yield, %[b] 1b	2b	Dimer[c]	Ratio dimer/2b
Benzene	84[d]	8	56	4	40	10
Toluene	83[e]	8	8	6	43	7.2
Xylene	81–82[f]	8	11	26	46	1.8
Mesitylene	80[f]	8	60	23	12	0.5
Acetone	~80[g]	4	53	4	i	...
Aniline	77	4	80	h	i	...
Benzonitrile	77[e]	4	73	1	i	...

[a] Irradiations were conducted as described in the Experimental Section using 150-ml solutions containing 31 mmoles of olefin. [b] Determined by gas chromatographic analysis of aliquots removed from the irradiation mixture. The results reported are those of a typical run. [c] Mixture of at least six components. [d] D. F. Evans, *J. Chem. Soc.*, 1351 (1957). [e] Reference 9a. [f] Reference 9b. [g] R. F. Borkman and D. R. Kearns, *J. Chem. Phys.*, **44**, 945 (1966). [h] None detectable. [i] Not analyzed.

Several attempts to effect the isomerization of 1-methylcyclohexene (**1b**) in other solvents were less rewarding (see Table VII). No isomerization was observed in aniline; in benzonitrile a very slow buildup of **2b** was accompanied by more rapid disappearance of starting material. A small amount of **2b** was obtained in acetone, but was again accompanied by a more rapid disappearance of starting material.[23]

Labeling Studies. Some insight into the mechanistic aspects of the isomerization reaction in aromatic hydrocarbon media was gained through a series of labeling studies. In the conversion of a 1-alkylcycloalkene to its exocyclic isomer, as in the rearrangement of (±)-p-menth-1-ene (**5**) to the 1(7)-isomer **6**, a hydrogen substituent must be lost from C-7 and one incorporated at C-2. *A priori* this could involve an intramolecular hydrogen shift. Although this was shown not to be the case in protic media, it seemed to be an attractive alternative for the isomerization conducted in aromatic hydrocarbon media, particularly benzene. However, as illustrated in Chart II, irradiation of **5**-7,7,7-d_3 in

Chart II

	5	5	6
	A. In C_6H_6		
D₁	0	0	2
D₂	2	6	81
D₃	98	94	17
	B. In $(CH_3)_2C_6H_4$		
D₁	0	0	1
D₂	2	5	72
D₃	98	94	27

	5	5	6
D₀	100	100	94
D₁	0	0	6

benzene afforded exocyclic material **6** which was found by mass spectroscopy to be mainly D_2. The nmr spectrum confirmed that C-7 had remained doubly deuterated. This predominant loss of one deuterium atom from the molecule clearly indicates that the principal mode of reaction involves an *intermolecular* transfer of hydrogen. The only obvious sources of hydrogen atoms are the benzene solvent or other molecules of olefin. That benzene serves as only a minor source, however, was demonstrated by the fact that irradiation of **5** in benzene-d_6 gave exocyclic olefin **6** containing only 6% D. These data appear to force the conclusion that the newly incorporated hydrogen atom is obtained primarily by destruction of a portion of the olefinic material. However, it is not clear whether the residual 17% D_3 material is attributable to the abstraction of deuterium atoms from the olefinic material being destroyed or to some competing intramolecular isomerization. When the irradiation of **5**-d_3 was conducted in xylene instead of benzene, the resulting isomer **6** contained a slightly *higher* percentage of D_3, *despite the presence of*

readily abstractable benzylic hydrogen atoms on the solvent. This suggests that abstraction from xylene does not occur very effectively, if at all.

Discussion

Protic Media. The rather remarkable photochemical lability of cyclohexenes and -heptenes in protic media has both synthetic and mechanistic interest. Synthetically, it represents a method for converting endocyclic olefins to their thermodynamically less stable exocyclic isomers. It also presents a means for promoting cationic behavior in neutral media under conditions of kinetic control. Moreover, it provides a method for selectively protonating cyclohexenes or -heptenes in the presence of exocyclic, acyclic, or larger ring cyclic olefins. The reaction should be extendable to the preparation of a wide variety of cycloalkyl derivatives besides ethers, alcohols, and acetates.

As for the mechanistic picture, it seems quite clear from the foregoing data that these reactions involve an ionic mechanism of the type outlined in Scheme I. Besides being supported by the labeling studies, this scheme is consistent with the observed formation of C–O bonds with alcohols, the Markovnikov direction of addition, the dependence of reaction rate upon acidity of the medium, and, in the case of dienes and **18** and **20**, selective addition to the double bond from which the more highly stabilized carbonium ion can be generated.[29]

There remain, however, the important questions of precisely which excited- or ground-state species is undergoing protonation and why protonation does not occur with exocyclic, acyclic, and larger ring cyclic olefins. Discussion of these points requires an initial consideration of why photosensitized *cis–trans* isomerization occurs in acyclic systems. It is generally accepted that severe repulsion between the electrons occupying the π and π^* orbitals of a π,π^* triplet olefin results in a preferred orthogonal conformation for the excited state.[3] This is illustrated for ethylene by Figure 1, in which the triplet energy level is plotted against the angle of twist about the double bond. On this basis it is assumed that vertical excitation to either the *cis* or *trans* π,π^* triplet is followed by a rapid relaxation to the orthogonally oriented species, from which $T_1 \rightarrow S_0$ intersystem crossing to either the *cis-* or *trans*-S_0 manifold can be easily achieved.[30]

Although acyclic and larger ring cyclic alkenes are relatively free to assume an orthogonal triplet geometry and isomerize to a ground-state *trans* olefin, incorporation of the double bond in a small ring places somewhat severe restrictions on the freedom to twist. As out-
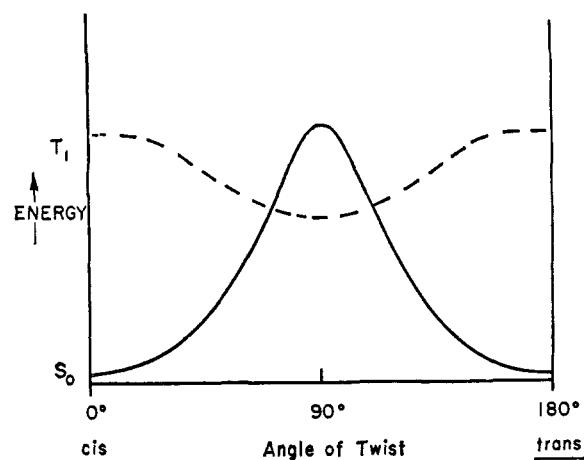

Figure 1. Potential energy curve for ethylene as a function of the angle of twist.

lined in Table VIII, examination of Dreiding models suggests that cyclohexene and its higher homologs are potentially capable of forming an orthogonal triplet but that such a large distortion should be prohibitive in the case of cyclopentene and other severely constrained olefins. Thus the marked change in photochemical behavior in going from a cyclohexene to a cyclopentene is probably related to the inability of the latter to exist as an orthogonally oriented π,π^* triplet, much less undergo *cis–trans* photoisomerization.[12]

Table VIII. Degree of Twist Available to Cycloalkene π,π^* Excited States as Estimated from Dreiding Models[a]

Cycloalkene	Twist, deg	Cycloalkene	Twist, deg
Cyclopentene	40	Cycloheptene	110
Cyclohexene	90	Cyclooctene	160

[a] Two adjacent trigonal atoms were used to represent the excited double bond.

Although formation of an orthogonal triplet and *cis* $\rightarrow$ *trans* isomerization should be available to cyclohexenes and -heptenes,[31] a resulting *trans*-cycloalkene should be extraordinarily strained; it is perhaps not unreasonable to expect that, if once formed in hydroxylic media, *trans*-cyclohexenes and -heptenes should seek immediate relief of strain by undergoing rapid protonation.[32]

While the above reasoning has served as a useful working hypothesis and is compatible with all of the available data, several alternative interpretations are available, such as the possibility that the π,π^* excited triplet species itself undergoes protonation rather than serving merely as a precursor to the proton-abstracting species.[33] The possibility that protonation involves

(29) Caution must be urged against carrying the analogy too close to ground-state chemistry, since the carbonium ion II will, at least initially, have much more vibrational energy and probably a different geometry than an analogous carbonium ion generated by simple protonation of a ground-state *cis* olefin. Moreover, the carbonium ion II reacts irreversibly in going to III and IV and in reverting to I, since III and IV are photochemically inert and regeneration of II from I requires transfer of another quantum of energy from the sensitizer. Thus kinetic rather than thermodynamic control prevails, and it is not surprising, for example, that the ratio of isomeric ethers **7a** and **7b** generated photochemically is quite different from that obtained by acid-catalyzed addition of methanol to **5**. Likewise, the irreversible formation of exocyclic olefin III permits its preparation from the thermodynamically more stable endocyclic isomer.

(30) In the event that the triplet excitation energy of the sensitizer is insufficient to effect a vertical transition of a *cis* or *trans* acceptor molecule to the corresponding *cis* or *trans* triplet, a nonvertical excitation leading directly to a lower energy twisted triplet species can apparently occur; see ref 2c.

(31) Note also that irradiation of 2-cyclohepten-1-one results in *cis–trans* isomerization: E. J. Corey, M. Tada, R. LaMahieu, and L. Libit, *J. Am. Chem. Soc.*, **87**, 2051 (1965), and P. E. Eaton and K. Lin, *ibid.*, **87**, 2052 (1965).

(32) See, for example, the extraordinary reactivity of even *trans*-2-cycloocten-1-one, as described by P. E. Eaton and K. Lin, *ibid.*, **86**, 2087 (1964).

(33) Some evidence that the availability of a *trans* intermediate is not a necessary condition for light-induced protonation of a cycloalkene has come from recent unpublished studies in these laboratories with norbornenes, in which *cis* $\rightarrow$ *trans* isomerization is structurally prohibited. Although norbornenes generally exhibit radical behavior,[1a]

an eximer formed between the photosensitizer and olefin is likewise not rigorously excluded; however, the fact that both ether and isomerization products are formed in the absence of a photosensitizer, albeit very slowly, indicates that eximer formation is not a necessary condition for reaction. It is also not known at this point what importance, if any, the availability of hydrogen bonding to the ground-state olefin prior to excitation plays in facilitating photoinduced protonation.

Regardless of the precise mechanistic details, the ether formation reaction can be placed in a rapidly expanding category of photochemical reactions involving ionic-type addition of an alcohol, water, or acetic acid across a carbon–carbon double bond. Previous examples have included cyclic dienes,[34] cycloalkenones,[35] and thymines and uracils.[36,37] The similarity of these reactions suggests the possibility of parallel mechanistic features in some, or perhaps even all, of these cases. It is hoped that future work will shed light on this important question.

Aromatic Hydrocarbon Media. Irradiation in appropriate aromatic hydrocarbon media provides an alternative method for the contrathermodynamic conversion of 1-alkylcyclohexenes and -heptenes to their corresponding exocyclic isomers. The procedure is particularly convenient for cycloheptenes but has the disadvantage in the case of cyclohexenes of substantial competing dimerization of the olefin. Therefore, in the latter case irradiation in benzyl alcohol or acidified *t*-butyl alcohol solution is a preferred method for effecting the isomerization. It is of interest to note that in protic media, such as methanol, little or no dimerization of 1-methylcyclohexene (1b) could be detected. Thus protonation in hydroxylic media competes effectively with dimerization, but hydrogen abstraction in aprotic media does not.

The similar dependence on ring size of the isomerization reaction in aromatic hydrocarbon media suggests mechanistic features parallel with those of the ionic behavior in protic media described in the preceding section, except that the reactive species undergoes hydrogen abstraction rather than protonation. As discussed above, the abstracting species might be either the orthogonally oriented π,π^* triplet intermediate or a highly strained, ground-state *trans*-cycloalkene; neither possibility is precluded by the available data. However, any detailed interpretation of the present results must simultaneously account for the facts that (a) on one hand, 1-methylcyclopentene (1a) and 2-methyl-2-norbornene, which are each incapable of forming an orthog-

onally oriented π,π^* triplet species, also show radical behavior but afford principally the corresponding saturated methylcycloalkane accompanied by only small amounts of exocyclic olefin;[1a] and (b) on the other hand, exocyclic, acyclic, and larger ring cyclic olefins, which are capable of readily forming both an orthogonal triplet and a relatively unstrained *trans* isomer, show no tendency to undergo either isomerization or reduction.

In addition to the related questions of the identity of the reactive species, the reasons for its particular behavior, and the origin of the hydrogen atoms which it abstracts, a host of other problems remain to be answered. These include why dimerization is sufficiently facile to compete with isomerization in the case of 1-alkylcyclohexenes but not -heptenes (or even -pentenes) and why the ratio of isomerization to dimerization is dependent on the nature of the solvent. The observed decreases in rate and in the relative amounts of dimerization in going from toluene to xylene and then to mesitylene are suggestive of a steric effect, but the possibility that the small decrease in triplet excitation energy through the series is an important factor cannot be discounted. It is hoped that further studies will provide some insight into these problems.

Experimental Section[38]

B. ($\pm$)-*p*-Menth-1-ene (5). From the irradiations described in Table II the following photoproducts were isolated by gas chromatography. ($\pm$)-*p*-Menth-1(7)-ene (6) was obtained as a colorless oil, λ_{max} 6.04 and 11.28 μ; nmr spectrum: τ 5.52 (s, 2, CH$_2$-7) and 9.20 (d, 6, $J = 6$, CH$_3$-9 and -10); *m/e*: 138, 123, and 109.[39] ($\pm$)-*trans*-1-*p*-Menthyl methyl ether (7a) was obtained as a colorless liquid with infrared spectrum identical with spectrum 5A of Hückel and Heinzelmann;[14] nmr spectrum: τ 6.86 (s, 3, OCH$_3$), 8.92 (s, 3, CH$_3$-7), and 9.13 (d, 6, $J = 6$, CH$_3$-9 and -10); *m/e*: 170, 155, 138, and 123.[15] ($\pm$)-*cis*-1-*p*-Menthyl methyl ether (7b)

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under special conditions ionic behavior has been observed. This does not necessarily preclude the intervention of a *trans* intermediate for cyclohexenes and -heptenes, however.

(34) (a) See G. Bauslaugh, G. Just, and E. Lee-Ruff, *Can. J. Chem.*, 44, 2837 (1966), and previous articles in the series; (b) W. G. Dauben and W. T. Wipke, *Pure App. Chem.*, 9, 539 (1964); (c) see also T. N. Huckerby, N. A. J. Rogers, and A. Sattar, *Tetrahedron Letters*, 1113 (1967).

(35) O. L. Chapman, J. B. Seija, and W. J. Welstead, Jr., *J. Am. Chem. Soc.*, 88, 161 (1966); T. Matsuura and K. Ogura, *ibid.*, 88, 2602 (1966); T. K. Hall, Ph.D. Dissertation, Iowa State University of Science and Technology, Ames, Iowa, 1965 [*Dissertation Abstr.*, 26, 5034 (1966)].

(36) See S. Y. Wang, *Federation Proc.*, 24, Suppl. 15, 71 (1965), and references cited therein.

(37) Other examples of ionic addition have also been reported, such as across carbon–carbon bonds in arylcyclopropanes [C. S. Irving, R. C. Petterson, I. Sarkar, H. Kristinsson, C. S. Aaron, G. W. Griffin, and G. J. Boudreaux, *J. Am. Chem. Soc.*, 88, 5675 (1966)] and [2.2]paracyclophane [R. C. Helgeson and D. J. Cram, *ibid.*, 88, 509 (1966)], but these cases appear to be less closely related mechanistically.

was obtained as a colorless liquid with an infrared spectrum identical withs pectrum 5B of Hückel and Heinzelmann;[14] nmr spectrum: τ 6.78 (s, 3, OCH₃), 8.84 (s, 3, CH₃-7), and 9.13 (d, 6, $J = 6$, CH₃-9 and -10); m/e: 170, 155, 138, and 123.[15]

C. (+)-3-Carene (11). From irradiation of (+)-3-carene[40] in methanol as described in Table III the following photoproducts were isolated. (+)-3(10)-Carene (12) was obtained as a colorless liquid by short-path distillation at 95° (6 mm); λ_{max} 6.06 and 11.34 μ; nmr spectrum: τ 5.44 (s, 2, CH₂-10), 9.05 and 9.11 (2s, 6, CH₃-8 and -9), and 9.3 (m, 2, CH-1 and -6) (*Anal.* Calcd for C₁₀H₁₆: C, 88.16; H, 11.84. Found: C, 88.3; H, 11.7). (+)-1-Methyl-4-*exo*-(2-methoxy-2-propyl)bicyclo[3.1.0]hexane (13a) was obtained as a colorless liquid by short-path distillation at 87–88° (8 mm); $[\alpha]^{27}_{5461} + 92°$ (c 1.20); λ_{max} 9.18 μ; nmr spectrum: τ 6.82 (s, 3, OCH₃), 7.65 (m, 1, CH-4), 8.83 and 8.84 (2s, 6, (CH₃)₂C<), 8.90 (s, 3, CH₃-1), and 9.18, 9.46, and 9.80 (3m, 3, CH-5 and CH₂-6); m/e: 168, 153, 137, 136, 122, and 121 (*Anal.* Calcd for C₁₁H₂₀O: C, 78.51; H, 11.98. Found: C, 78.4; H, 11.8). (+)-3β-Caranyl methyl ether (14a) was obtained as a colorless liquid by short-path distillation at 58–59° (2 mm); $[\alpha]^{27}_{5461} + 11°$ (c 1.44); λ_{max} 8.95 μ; nmr spectrum: τ 6.83 (s, 3, OCH₃), 8.82 (s, 3, CH₃-10), 9.02 and 9.03 (2s, 6, CH₃-8 and -9), and 9.4 (m, 2, CH-1 and -6); m/e: 137, 136, 134, 132, 122, 121, 120, and 119 (*Anal.* Calcd for C₁₁H₂₀O: C, 78.51; H, 11.98. Found: C, 78.3; H, 11.9). (+)-3α-Caranyl methyl ether (15a) was obtained as a colorless liquid by short-path distillation at 73° (3 mm); $[\alpha]^{27}_{5461} + 14°$ (c 1.46); λ_{max} 9.10 and 9.24 μ; nmr spectrum: τ 6.78 (s, 3, OCH₃), 8.88, 8.94, and 9.02 (3s, 9, CH₃-8, -9, and -10), and 9.3 (m, 2, CH-1 and -6) (*Anal.* Calcd for C₁₁H₂₀O: C, 78.51; H, 11.98. Found: C, 78.3; H, 11.8).

From irradiation of (+)-3-carene in aqueous *t*-butyl alcohol as described in Table III the following photoproducts, in addition to (+)-3(10)-carene (12), were isolated. (+)-1-Methyl-4-*exo*-(2-hydroxy-2-propyl)bicyclo[3.1.0]hexane (13b) was obtained as a colorless liquid, λ_{max} 2.90 μ; nmr spectrum: τ 7.82 (m, 1, CH-4), 8.78 and 8.84 (2s, CH₃-1 and (CH₃)₂C<), and 9.0–9.85 (m, 3, CH-5 and CH₂-6); m/e: 154.1356 (theory for C₁₀H₁₈O: 154.1358), 136, 121, and 119. (+)-3β-Caranol (14b) was obtained as long colorless needles, mp 71–72°, unchanged on admixture with an authentic specimen; infrared and nmr spectra identical with those of an authentic specimen.[18] (+)-3α-Caranol (15b) was obtained as a colorless liquid which exhibited infrared and nmr spectra identical with those of an authentic specimen.[19] On several occasions an additional alcohol was obtained to which the assignment bicyclo[3.1.0]hex-2-en-4-*exo*-ol is tentatively made; λ_{max} 2.95 and 6.28 μ; nmr spectrum: τ 3.82 and 4.54 (2d, 2, $J = 5$, CH-3 and -2), 5.62 (m, 1, CH-4), and 9.08 and 10.16 (2m, 2, CH₂-6).[17]

D. (±)-1-Ethyl-4-isopropylcyclohexene (8). A solution containing 1.00 g of 8[16] and 3 ml of xylene in 147 ml of methanol was irradiated for 8 hr in the usual fashion. Gas chromatographic analysis revealed the formation of olefin 9 (35%) and a 1.3:1 mixture of the epimeric ethers 10 (60%). Isolation by preparative gas chromatography gave the following materials. (±)-1-Ethylidene-4-isopropylcyclohexane (9) was obtained as a colorless liquid by short-path distillation at 80° (6 mm), λ_{max} 12.20 μ; nmr spectrum: τ 4.93 (q, 1, $J = 7$, =CHCH₃), 8.50 (d, $J = 7$, =CHCH₃), and 9.20 (d, 6, $J = 6$, (CH₃)₂CH-); m/e: 152, 137, 124, and 123. An identical specimen was obtained by treatment of 5.00 g (35.2 mmoles) of 4-isopropylcyclohexanone for 16 hr at 60° with a solution of ethylidenetriphenylphosphorane prepared by treatment of 25 ml of anhydrous dimethyl sulfoxide with 1.70 g (35.2 mmoles) of 54% sodium hydride dispersion in mineral oil at 60° for 2 hr followed by cooling to 0°, addition of 12.7 g of ethyltriphenylphosphonium bromide in 50 ml of anhydrous dimethyl sulfoxide, and stirring at 25° for 30 min (*Anal.* Calcd for C₁₁H₂₀: C, 86.76; H, 13.24. Found: C, 86.9; H, 13.1). (±)-1-Ethyl-4-isopropylcyclohexyl methyl ether (10) was a mixture of epimers obtained as a colorless liquid by short-path distillation at 74° (1 mm); nmr spectrum: τ 6.96 (epimer A) or 6.88 (epimer B) (s, 3, OCH₃) and 9.17 (d, 6, $J = 6$, (CH₃)₂CH-). (*Anal.* Calcd for C₁₂H₂₄O: C, 78.19; H, 13.13. Found: C, 77.9; H, 13.3).

E. 4-Isopropylcyclohexene (16). A solution containing 1.50 g of 16 and 15 ml of benzene in 135 ml of methanol was irradiated in the usual fashion for 18 hr. Gas chromatographic analysis revealed the presence of four isomeric ethers in a total yield of 24%, accompanied by recovered starting material (15%). The ether fractions were separated into two poorly resolved pairs of isomers by

preparative gas chromatography. Fraction A exhibited λ_{max} 9.12 μ; nmr spectrum: τ 6.8 (m, 1, CH₃OCH<), 6.88 (s, 3, OCH₃), and 9.22 (d, 6, $J = 6$, (CH₃)₂CH-). Fraction B exhibited λ_{max} 9.02 μ; nmr spectrum: τ 6.84 (s, 3, OCH₃), 7.12 (m, 1, CH₃OCH<), and 9.20 (d, 6, $J = 6$, (CH₃)₂CH-) (*Anal.* Calcd for C₁₀H₂₀O: C, 76.86; H, 12.90. Found: C, 76.8; H, 12.6).

F. 1-Ethyl-1,4-cyclohexadiene (18). A solution containing 3.05 g of 18 and 1.5 ml of xylene in 148.5 ml of methanol was irradiated in the usual fashion for 7 hr. Gas chromatographic analysis revealed the presence of ether 19 (6%) as the only detectable photoproduct, along with recovered starting material (65%). Isolation by preparative gas chromatography afforded a specimen of ether 19 which was identical in all respects with material obtained by the acid-catalyzed addition of methanol to 18 as described below.

G. *p*-Mentha-1,4-diene (20). A 150-ml methanolic solution containing 3.82 g of diene 20[41] and 3 ml of xylene was irradiated for 10 hr in the usual fashion. Gas chromatographic analysis revealed the presence of a principal photoproduct (34% yield) and recovered starting material (23%) along with several minor products.[21] Isolation of the major photoproduct on a preparative scale afforded a specimen of the ether 21 which was identical in all respects with material obtained by the acid-catalyzed addition of methanol to 20 as described below.

H. 1-Cyclohexen-1-yl Methyl Ether (22). A 150-ml methanolic solution containing 2.94 g of ether 22[42] and 3 ml of xylene was irradiated in the usual fashion for 15 hr, at which time the reaction mixture was shown to contain unreacted starting material (15% recovery) and 1,1-dimethoxycyclohexane (23) (60% yield). Isolation of the photoproduct by preparative gas chromatography afforded a specimen of 1,1-dimethoxycyclohexane which was identical in all respects with an authentic specimen.[42]

I. 3,5-Dimethyl-3-heptene (24). A solution containing 3.00 g of 3,5-dimethyl-3-heptene and 1.5 ml of xylene in 148.5 ml of methanol was irradiated in the usual fashion for 6 hr. Monitoring of the irradiation mixture by gas chromatographic analysis of aliquots removed periodically revealed only a slow destruction of the starting material, with no concomitant formation of any detectable amount of either the ether 25 or the olefin 26. After 6 hr 79% of the starting material remained.

J. α-Cedrene (27). A solution containing 1.45 g of α-cedrene (27) and 13 ml of benzene in 137 ml of methanol was irradiated in the usual fashion for 16 hr. Analysis by gas chromatography revealed the presence of 55% unreacted starting material which was accompanied by no detectable photoproducts.

Acid-Catalyzed Preparation of Ethers. Comparison specimens of the ether photoproducts (or potential photoproducts) were prepared independently by treatment of 1 g of olefin with 10 ml of 10% methanolic sulfuric acid at 27° for 4–6 days. In this manner the following ethers were prepared. **1-Ethylcyclohex-3-en-1-yl methyl ether (19)** was obtained as a colorless liquid by short-path distillation at 76° (4 mm); λ_{max} 6.06 and 9.26 μ; nmr spectrum: τ 4.45 (m, 2, CH-3 and -4), 6.88 (s, 3, OCH₃), and 9.16 (t, 3, $J = 7$, ethyl CH₃) (*Anal.* Calcd for C₉H₁₆O: C, 77.09; H, 11.50. Found: C, 77.2; H, 11.4). *p*-**Menth-3-en-1-yl methyl ether (21)** was obtained as a colorless liquid by short-path distillation at 80° (3.5 mm); λ_{max} 8.82, 9.12, and 9.32 μ; nmr spectrum: τ 4.78 (m, 1, CH-3), 6.82 (s, 3, OCH₃), 8.86 (s, 3, CH₃-7), and 9.01 (d, 6, $J = 6$, CH₃-9 and -10) (*Anal.* Calcd for C₁₁H₂₀O: C, 78.51; H, 11.98. Found: C, 78.5; H, 11.8). **3,5-Dimethyl-3-heptyl methyl ether (25)** was obtained as a colorless liquid by short-path distillation at 72° (7 mm); λ_{max} 9.28 (br) μ; nmr spectrum: τ 6.96 (s, 3, OCH₃) and 8.96 (s, 3, CH₃CO<) (*Anal.* Calcd for C₁₀H₂₂O: C, 75.88; H, 14.01. Found: C, 75.8; H, 13.8). **1-Cyclooctyl methyl ether (3d)** was obtained as a colorless liquid by short-path distillation at 79° (3.5 mm); λ_{max} 9.26 μ; nmr spectrum: τ 6.88 (s, 3, OCH₃) and 8.92 (s, 3, CH₃-1). In a similar manner specimens of the previously reported **1-methyl-1-cyclopentyl (3a),[43] 1-methyl-1-cyclohexyl (3b),[44]** and **1-methyl-1-cycloheptyl methyl ethers (3c)[45]** were prepared.

2-Ethyl-4-methyl-1-hexene (26). A. Preparation. A 20.0-g (1.56 moles) portion of 5-methyl-3-heptanone was treated for 16 hr

(40) Generously supplied by Waldorf-Hoerner Paper Products Co., Missoula, Mont.

(41) Generously supplied by Dr. W. I. Fanta.
(42) Generously supplied by Dr. R. A. Damico.
(43) G. A. Lutz, A. E. Bearse, J. E. Leonard, and F. C. Croxton, *J. Am. Chem. Soc.*, 70, 4139 (1948); W. Hückel and E. Mögle, *Ann.*, 649, 13 (1961).
(44) W. Treibs, *Chem. Ber.*, 70B, 589 (1937).
(45) W. Hückel and J. Wächter, *Ann.*, 672, 62 (1964).

at 60° with a solution of methylenetriphenylphosphorane prepared by treatment of 50 ml of anhydrous dimethyl sulfoxide with 7.48 g (1.56 moles) of 54% sodium hydride dispersion in mineral oil at 60° for 2 hr followed by cooling to 0°, addition of 63.8 g of methyltriphenylphosphonium bromide in 100 ml of anhydrous dimethyl sulfoxide, and stirring at 25° for 30 min. Isolation by addition to water and extraction with pentane gave, on distillation at 90–91° (85 mm), 13.0 g (67% yield) of a colorless liquid, λ_{max} 6.10 and 11.26 μ; nmr spectrum: τ 5.35 (d, 2, CH₂-1) (*Anal.* Calcd for C_9H_{18}: C, 85.63; H, 14.37. Found: C, 85.9; H, 14.1).

B. Irradiation. A solution containing 3.00 g of **26** and 3 ml of xylene in 147 ml of methanol was irradiated in the usual fashion for 6 hr. Gas chromatographic analysis indicated a 95% recovery of olefin which, on collection, was identical in all respects with starting material.

Characterization of Dimeric Products from 1-Methylcyclohexene (3b). For the preparation of a larger quantity of the mixture of

dimeric products, a 150-ml solution containing 50 g of 1-methylcyclohexene (**3b**) in xylene was irradiated as described above for 45 hr. Continued irradiation effected no substantial increase in the amount of accumulated dimer. Removal of the solvent by distillation followed by final purification by preparative gas chromatography over SE-30 afforded a colorless liquid which exhibited six poorly resolved peaks on gas chromatography over Carbowax 20M; λ_{max} 6.08 and 11.26 μ; nmr spectrum: τ 5.40 (m) and 6.04 (m); *m/e*: 192, 187, 177, 163, 150, and 149.

Spiroconjugation

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Contribution No. 1320 from the Central Research Department, Experimental Station, E. I. du Pont de Nemours and Company, Wilmington, Delaware 19898. Received April 21, 1967
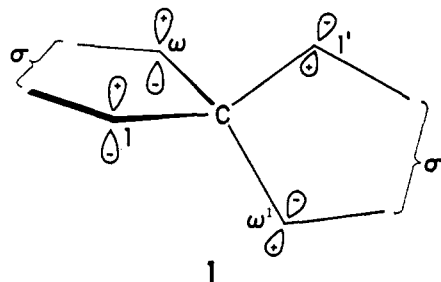
Abstract: When two perpendicular π systems are joined by a common tetrahedral atom, it is postulated that electronic delocalization will produce important and characteristic effects in the electronic spectrum and in chemical reactivity; this special case of homoconjugation has been called spiroconjugation. It will occur whenever four p centers are located by D_{2d} symmetry on atoms bonded to the tetrahedral center. The theory is developed and discussed; in this manner, *e.g.*, the properties of the spirenes, $(CH{=}CH)_mC(CH{=}CH)_n$, and the polyene ketals, $(CH{=}CH)_qC(OR)_2$, can be classified and predicted.

Homoconjugation has been a useful general concept to describe the interaction of systems of p orbitals which are separated by insulating atoms, and its effects seem most important in high-energy species (ions, transition states, and excited states). This paper discusses an extension of the idea of homoconjugation and draws attention to a class of structures in which this concept is expected to be particularly important.

Theory. When two π systems are held in perpendicular planes by a common atom of tetrahedral geometry (*e.g.*, the spiro configuration), the overlap between p orbitals on atoms bound directly to the insulating atom is considerable, and consequently exchange interactions may become significant. In a system of carbon atoms **1**, in which four p orbitals (χ_s) are perpendicular in pairs ($s = 1,\omega$ and $1',\omega'$) to the intersecting planes, σ and σ' (local D_{2d} symmetry), the overlap integral of two orbitals in different planes has about 20% of the value for adjacent p orbitals in planar π-electron molecules.[1] Exchange interactions can now remove the energy degeneracy, and symmetry requires the splitting to be $4\beta'$, where β' is the exchange integral between orbitals in different planes (Figure 1). We call such interaction about a tetrahedral center "spiroconjugation." [2,3]

1

Application of these considerations to molecules which contain perpendicular π systems joined by an insulating atom which is approximately tetrahedral predicts interesting consequences for which support is experimentally available. These consequences are solely determined by symmetry and geometry considerations, the former dictating what interactions are allowed and the latter measuring their magnitude. Since chemical and electronic spectral behavior is often reflected by the properties of the frontier molecular orbitals, it is instructive to develop the idea of spiroconjugation by determining its effect on the highest occupied (HOMO) and lowest vacant molecular orbitals (LVMO) of the constituent π systems.[4]

(1) For a tetrahedral carbon center and bonded (C–C) distances of 1.50 A, the overlap integral is $S_{spiro} = 0.042$, which amounts to 16% of $S_{\pi\pi} = 0.271$ (at 1.34 A) and 20% of $S_{\pi\pi} = 0.214$ (at 1.48 A) in planar systems.

(2) The p orbitals in **1** can be lone pairs or terminals of π systems. We have reserved the term spiroconjugation for the four-orbital case (1); however, it should be pointed out that the degeneracy of the two-

(1,1') and three-orbital (1,ω,1') cases is removed with smaller splittings of $2\beta'$ and $2\sqrt{2}\beta'$, respectively.

(3) In all calculations in this paper, a value $\beta'/\beta_0 = {}^1/_4$ was uniformly adopted as a matter of convenience, since the results do not depend on this choice in a significant way. In all orbital diagrams, the systems before and after allowance for spiroconjugation are shown in the left and right columns, respectively.