absence of a band at 1375 cm^{-1} showed absence of a methyl radical.

The MS of a lower boiling fraction [76° (9.8 mm)] showed molecular tions at m/e 176, 178, and 180 in the ratios corresponding to two chlorine atoms. The data correspond to $C_8H_{10}Cl_2$. The ir spectrum showed strong bands at 650–750 cm^{-1} for C–Cl stretch and strong bands at 800–1000 cm^{-1} for C–Cl stretch and olefin. Two bands were observed in the C=C stretch region. No methyl was indicated at 1380 cm^{-1} while CH_2 bonding was observed at 1450 cm^{-1}. On the assumption that the product consisted of two isomers (17 and 18), the NMR integrals were consistent with 18 as the major component. NMR spin decoupling revealed that the doublet δ 5.75 was coupling with the proton at δ 3.18. The integral was then found to be consistent with 85% 18 and 15% 17.

Registry No.—**3**, 22118-81-6; **7**, 52890-15-0; **8**, 55681-91-9; **9**, 55681-92-0; **10**, 55681-93-1; **12**, 17219-57-7; **13**, 55681-94-2; **14**, 52026-52-5; **15**, 51951-45-2; **16**, 55681-95-3; **17**, 52026-53-6; **18**, 22024-03-9; *cis*-dichoroethylene, 156-59-2; trichloroethylene, 79-01-6; tetrachloroethylene, 127-18-4; propene, 115-07-1; ethylene, 74-85-1; 2-pentene, 109-68-2; 1-octene, 111-66-0; cyclohexene, 110-83-8.

Supplementary Material Available. Additional ir, MS, and NMR data for compounds **3**, **9**, **10**, **14**, **16**, **17**, and **18** will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $4.50 for photocopy or $2.50 for microfiche, referring to code number JOC-75-2430.

References and Notes

(1) Presented before the Division of Organic Chemistry at the 162nd National Meeting of the American Chemical Society, Washington, D.C., Sept 1971. The reaction is described in L. Schmerling, U.S. Patent 3,406,210 (Oct 15, 1968). The structures of the products presented in the patent have since been found to be erroneous; the correct structures are presented in this paper.

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(10) See paragraph at end of paper regarding supplementary material.

Photochemistry of Alkenes. IV. Vicinally Unsymmetrical Olefins in Hydroxylic Media[1]

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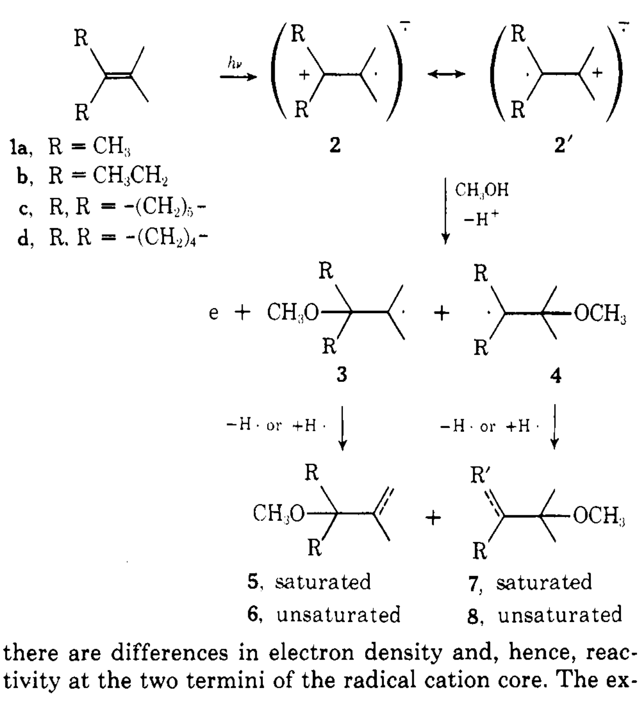
The photochemical behavior of the vicinally unsymmetrical tetrasubstituted olefins **1b–d** in methanol was studied. Each olefin afforded a mixture of saturated and unsaturated ethers **5–8** and hydrocarbons **11–13**. There was no strong dominance in the direction of nucleophilic attack on the excited states from olefins **1b–d**. Isopropylidenenorbornane (**14**) afforded a complex mixture, with the ether **15** and 2-*endo*-isopropylnorbornane (**16**) as the major products. Evidence for the presence of ejected electrons was obtained using sulfur hexafluoride as an electron trap.

In contrast to the triplet manifold of simple alkenes, in which just one excited state (π,π*) is clearly low lying, there are two, and possibly three, excited states in the singlet manifold which are low lying and close in energy. Assignment of two of these as π,π* and π,R(3s) is now widely accepted,[3] and the presence of a π,σ* state of similar energy has also been proposed.[3b] Studies in these laboratories have been directed toward elucidating the *chemical* properties of these excited states and the effects of structure and environment on their reactivities.

It has recently been reported from these laboratories that tri- and, particularly, tetrasubstituted alkenes exhibit novel photochemical behavior which appears to involve the π,R(3s) Rydberg excited state.[1,4] This state arises from promotion of one of the π electrons to a large molecular orbital similar in size and shape to a 3s atomic orbital. As depicted by **2** and **2′**, this process generates radical cation character in the π core of the molecule. In the case of 2,3-dimethyl-2-butene (**1a**) the excited state **2a** is trapped nucleophilically in hydroxylic media to afford a mixture of saturated and unsaturated ethers, as exemplified in Scheme I.[4] This reaction is of mechanistic interest, as it represents one of the first observations of the chemical behavior of the π,R(3s) excited state in solution. Little is known about the π,R(3s) state, including the important question of whether in vicinally unsymmetrical systems there are differences in electron density and, hence, reactivity at the two termini of the radical cation core. The ex-

Scheme I

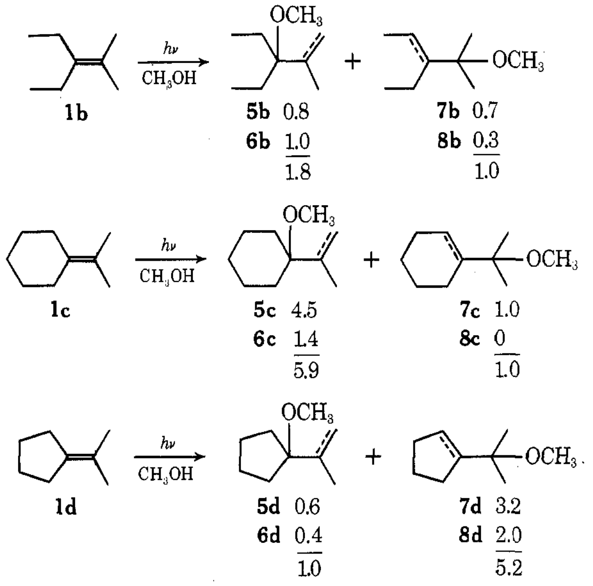


amples initially reported involved olefins having vicinal symmetry about the double bond;[4] in these systems nucleophilic attack at either end of the bond would afford the same radical intermediate (i.e., **3** = **4**). We wish now to describe additional insight into the chemical behavior of the π,R(3s) excited state gained by a study of the series of vicinally unsymmetrical olefins **1b–d.** Previous studies have shown that decreasing the ring size in this series on going from acyclic to six-membered to five-membered strongly affects the photochemical behavior in nonnucleophilic media.[5]

Results

The results from irradiation of these olefins in methanol are summarized in Table I and Scheme II. Each olefin afforded a mixture of saturated and unsaturated ethers **5–8.** Ethers **5** and **7** in each series were obtained independently by acid-catalyzed addition of methanol to the corresponding olefin **1**. Ethers **5b** and **7c** were also prepared independently by methylation of the corresponding alcohol. The remaining ethers were characterized by means of their spectral data, as outlined in the Experimental Section. Each olefin also afforded a mixture of saturated (**12**) and unsaturated hydrocarbons (**11** and **13**), which were identified by spectral data and comparison with authentic specimens. It is assumed that **5–8** and **11–13** are all primary products, since there was no significant change in their relative amounts during the course of reaction, except for a slow loss of the unsaturated products on extended irradiation.

Scheme II



Scheme III

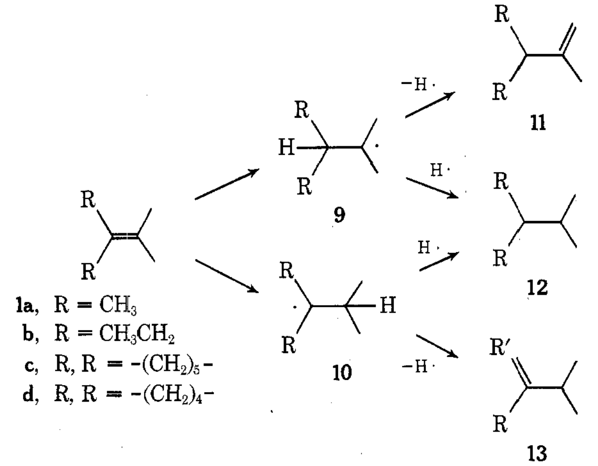


Table I
Irradiation of Alkenes 1 in Methanol[a]

Alkene 1	Time, hr	Yield, %[b] 1	5	6	7	8	11	12	13
1a[c]	4	6	37	30				16	4
1b	6	31	13	16	11	5	1	10	*d*
1c	16	25	25	7.5	5.5	*e*	4	11	
1d	8	10	4	2.5	21	13	1	17	5

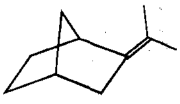
[a] Irradiations were conducted as described in the Experimental Section. [b] Determined by gas chromatographic analysis relative to an internal standard on aliquots removed from the reaction mixture. [c] See ref 4. [d] Trace. [e] None detectable.

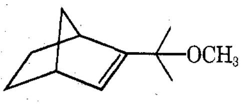
Table II
Irradiation of 2,3-Dimethyl-2-butene (1a) in Methanol in the Presence of Sulfur Hexafluoride[a]

[1a], mol/l	Time, hr	[F$^-$], mol/l
2.0×10^{-1}	3	2.4×10^{-3}
2.0×10^{-1}	5	2.9×10^{-3}
None	3	5.4×10^{-4}
None	5	7.0×10^{-4}

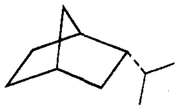
[a] Irradiations were conducted as described in the Experimental Section.

In connection with these and other studies the photochemical behavior of isopropylidenenorbornane (**14**) was also examined. On irradiation in methanol **14** afforded a complex mixture of hydrocarbon and ether products, of which the ether **15** and 2-*endo*-isopropylnorbornane (**16**) were identified as principal components.


14



15


16

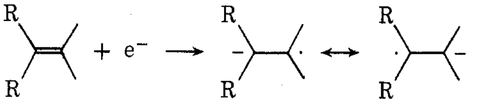
An important contribution from the present study was the observation of the presence of free electrons during the irradiation of olefin **1a** in methanol obtained using sulfur hexafluoride, a highly efficient specific electron scavanger which has been widely used in radiochemical and photochemical studies.[6] Sulfur hexafluoride undergoes decomposition to fluoride ions on electron capture in methanolic solution, making it a convenient probe for free electrons.[7] As detailed in Table II, irradiation of **1a** in methanol saturated with sulfur hexafluoride resulted in the generation of fluoride ions at concentrations substantially greater than those generated by the slow light-induced decomposition of sulfur hexafluoride under these conditions, in support of the presence of free electrons in the irradiation mixture.

Discussion

Ether Products. As can be seen from Scheme II, the excited states of olefins **1b–d** did not undergo nucleophilic attack at either end with equal facility. Moreover, there was a change from predominant attack at the ring end for **1c**, to more nearly equal degrees of attack at both ends for **1b**, to dominant attack at the *gem*-dimethyl end for **1d**. This pattern does not correlate with the observed regioselectivity of acid-catalyzed addition of methanol to these olefins, which shifts from a 17:1 predominance of **7b** over **5b** to a lesser 4.4:1 predominance of **7c** over **5c** to a 1.1:1 reversed predominance of **5d** over **7d**. Likewise it is contrary to the increasingly preferred photoreaction in nonnucleophilic media at the ring end of the double bond in going from **1b** to **1c** to **1d**.[5] However, since the photoproduct ratios are not large, the transition state energies for attack at either end apparently differ by less than 1 kcal/mol. The direction of attack will be controlled by several factors, including the relative contributions from resonance forms **2** and **2′**, differences in steric hindrance, and differences in stability of the resulting radicals **3** and **4**. The low selectivities observed suggest that these differences are either small or offsetting.

Hydrocarbon Products. Nucleophilic trapping of the π,R(3s) state should be accompanied by ejection of the excited electron, which no longer has a place in the π system to which to return. The present observation of electron trapping by sulfur hexafluoride confirms the presence of free electrons. In the absence of trapping by sulfur hexafluoride the resulting free electron might be trapped by either the solvent or unreacted starting olefin. The rate for electron capture is generally greater for olefins[8] than methanol,[9] but this advantage is offset by differences in concentration, leaving comparable probabilities for either mode of capture. Electron trapping by methanol results in the generation of hydrogen atoms (eq 1)[9] which, on capture by unreacted starting olefin **1**, would lead to the hydrocarbon photoproducts **11–13** as outlined in Scheme III. Alternatively, electron capture by olefin **1** (eq 2) would afford the

$$e^- + CH_3OH \longrightarrow CH_3O^- + H\cdot \qquad (1)$$



(2)

1 17

radical anion **17**, which on protonation by methanol would give rise to the same radical intermediates **9** and **10** and thence to the hydrocarbon products **11–13**. Both of these routes are consistent with the observed incorporation of deuterium in products **11a** and **12a** on irradiation of 2,3-dimethyl-2-butene (**1a**) in methanol-*O-d*.[4,10]

Work continues in elucidating further the chemical properties of the π,R(3s) excited states of alkenes.

Experimental Section

Infrared spectra were obtained on carbon tetrachloride solutions with a Perkin-Elmer 421 grating spectrophotometer. Gas chromatographic analyses were performed on an Aerograph 90-P or a Hewlett-Packard 5750 instrument using 10 ft × 0.25 in. columns packed with (A) 20% Carbowax 20M, or (B) 20% SE-30 on 60–80 mesh Chromosorb W, or a 20 ft × 0.25 in. column packed with (C) 20% β,β'-oxydipropionitrile on 60–80 mesh Chromosorb P. Nuclear magnetic resonance spectra were determined on carbon tetrachloride solutions with a Jeolco C-60HL or Varian XL-100 spectrometer, using 0.3% tetramethylsilane as an internal standard. NMR data are reported in the following manner: multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, and m = unresolved multiplet); integration; coupling constant (given in hertz); and assignment. Mass spectra were obtained using an AEI MS-902 spectrometer; *m/e* values reported include the parent ion peak, if detectable, and other significantly large peaks appearing above *m/e* 55. Unless otherwise indicated, all irradiations were conducted using a Hanovia 450-W medium-pressure mercury arc and a water-cooled quartz immersion well. The solution was purged with nitrogen 5–10 min before irradiation. Vigorous stirring during irradiation was effected by a magnetic stirring bar. For product isolation the solution was added to water semisaturated with sodium chloride and continuously extracted with pentane. After removal of the pentane by distillation, the products were isolated gas chromatographically.

3-Ethyl-2-methyl-2-pentene (1b). A. Irradiation. A 100-ml methanolic solution containing 2.24 g of olefin was irradiated as described above for 6 hr. Gas chromatographic analysis (A and C) revealed partial recovery of olefin **1b** and formation of several hydrocarbon and four ether products. Isolation by gas chromatographic preparative methods afforded **3-ethyl-2-methyl-1-pentene (11b)** and **3-ethyl-2-methylpentane (12b)**, which each had spectral properties and gas chromatographic retention times identical with those of commercial samples. The remaining hydrocarbon products were not isolated.

3-Methoxy-3-ethyl-2-methylpentane (5b) was obtained as a colorless liquid: ν_{max} 2962, 2938, 2880, 2825, 1459, 1379, 1170, 1142, 1070, and 900 cm^{-1}; NMR spectrum τ 6.85 (s, 3, CH_3O–); MS *m/e* 129.1282 (calcd for $C_8H_{17}O$, 129.1280), 115 (83), 101 (100), 83 (25), and 59 (58). This material was identical with a specimen prepared independently as described below.

Isolation of the major ether product afforded **3-methoxy-3-ethyl-2-methyl-1-pentene (6b)** as a colorless liquid: ν_{max} 3092, 2971, 2882, 2827, 1640, 1450, 1379, 1161, 1149, 1123, 1082, 1058, 1029, 936, 919, and 901 cm^{-1}; NMR spectrum τ 4.95 and 5.05 (2 m, 2, CH_2=), 6.97 (s, 3, CH_3O–), and 9.27 [t, 6, $(CH_3CH_2)_2C$–]; MS *m/e* 142.1356 (calcd for $C_9H_{18}O$, 142.1358), 113 (100), 101 (18), 81 (22), and 55 (23).

2-Methoxy-3-ethyl-2-methylpentane (7b) was obtained as a colorless liquid: ν_{max} 2934, 2875, 2825, 1458, 1377, 1361, 1187, 1155, 1139, 1080, 1061, and 830 cm^{-1}; NMR spectrum τ 6.85 (s, 3, CH_3O–), and 8.93 [s, $(CH_3)_2C$–]; MS *m/e* 129.1277 (calcd for $C_8H_{17}O$, 129.1280), 83 (5), 73 (100), 59 (4), and 55 (8). This material was identical in retention time and spectral properties with a sample prepared as described below.

A mixture of (*E*)- and (*Z*)-**4-methoxy-3-ethyl-4-methyl-2-pentene (8b)** was obtained as a colorless liquid: ν_{max} 3057, 2978, 2934, 2880, 2824, 1459, 1376, 1361, 1168, 1145, 1069, and 894 cm^{-1}; NMR spectrum τ 4.53 (q, 1, J = 6.5 Hz, CH-3), 7.07 (s, 3, CH_3O–), 7.88 (q, 2, J = 7.5 Hz, CH_3CH_2–), 8.32 (d, 3, J = 6.5, CH_3-4), 8.79 [s, 6, $(CH_3)_2C$–], and 8.98 (t, 3, J = 7.5 Hz, CH_3CH_2–); MS *m/e* 142.1356 (calcd for $C_9H_{18}O$, 142.1358), 127 (93), 113 (37), 95 (34), 73 (100), 69 (26), and 67 (35).

B. Acid-Catalyzed Methanolysis. A solution containing 1 g of olefin **1b** and 10 drops of concentrated sulfuric acid in 30 ml of methanol was allowed to stand at room temperature for 18 days. The resulting solution was neutralized with sodium bicarbonate, diluted with water, and continuously extracted with pentane. The pentane solution was concentrated by distillation. Gas chromatographic analysis revealed the formation of two ether products in a 17:1.0 ratio. Isolation of the major component afforded ether **7b**. The second component had a retention time identical with that of ether **5b**.

Independent Synthesis of 3-Methoxy-3-ethyl-2-methylpentane (5b). A solution containing 3.5 g (20 mmol) of 2-methyl-3-ethyl-3-pentanol[11] in 25 ml of freshly distilled 1,2-dimethoxyethane was added dropwise to 1.33 g (20 mmol) of a 50% suspension of sodium hydride in oil, which had been washed with pentane, under nitrogen with stirring. After 6 hr 4.12 g (29 mmol) of methyl iodide was added dropwise to the solution in an ice bath. After addition, the mixture was stirred at 30° overnight. After cooling, the solution was diluted with 10 ml of water. The organic layer was collected and concentrated by distillation to afford 1.53 g (10.3 mmol, 53%) of ether **5b**, bp 75–76° (63 mm). This material was identical in every respect with that obtained photochemically as described above.

Isopropylidenecyclohexane (1c). A. Irradiation. A 100-ml methanolic solution containing 2.48 g (20 mmol) of olefin **1c**[12] was irradiated as described above for 16 hr. Gas chromatographic analysis (A and C) revealed a partial recovery of olefin **1c** and the formation of three hydrocarbon products and three ether products. Isolation by preparative gas chromatographic techniques (A and C) afforded **isopropylcyclohexane (12c)** which had spectral properties and a retention time identical with those of a commercial specimen. Isolation of the second component afforded **2-cyclohexylpropene (11c)** as a colorless liquid: ν_{max} 3091, 2935, 2860, 1645, 1453, 1375, 1108, and 891 cm^{-1} (lit.[13] ν_{max} 1650 and 883 cm^{-1}). The third hydrocarbon was not isolated.

1-Methoxy-1-isopropylcyclohexane (5c) was obtained as a colorless liquid: ν_{max} 2940, 2865, 2829, 1463, 1384, 1367, 1156, 1144, 1075, 940, 923, 912, and 804 cm^{-1}; NMR spectrum τ 6.88 (s, 3, CH_3O–) and 9.15 [d, 6, J = 7 Hz, $(CH_3)_2C$–]; MS *m/e* 156.1516 (calcd for $C_{10}H_{20}O$, 156.1514), 113 (100), and 81 (47). This material was identical in retention time and spectral properties with a sample prepared independently as described below.

1-Methoxy-1-(2′-propenyl)cyclohexane (6c) was obtained as a colorless liquid: ν_{max} 3090, 2938, 2861, 2825, 1638, 1447, 1148, 1079, 927, and 901 cm^{-1}; NMR spectrum τ 7.08 (s, CH_3O–), 5.10 (d, J = 10 Hz, vinyl); MS m/e 154.1359 (calcd for $C_{10}H_{18}O$, 154.1357), 139 (15), 113 (91), 111 (100), 81 (63), 79 (42), and 67 (22).

2-Methoxy-2-cyclohexylpropane (7c) was obtained as a colorless liquid: ν_{max} 2980, 2938, 2859, 2830, 1450, 1379, 1363, 1230, 1201, 1169, 1146, 1112, 1074, 889, and 854 cm^{-1}; NMR spectrum τ 6.87 (s, 3, CH_3O–) and 8.95 [s, $(CH_3)_2C$–]; MS m/e 141.1282 (calcd for $C_9H_{17}O$, 141.1279), 81 (27), 74 (27), 73 (100), 72 (34), and 59 (31). This material was identical in retention time and spectral properties with specimens prepared independently as described below.

B. Acid-Catalyzed Methanolysis. A solution containing 1 g of olefin **1c** and 10 drops of concentrated sulfuric acid in 20 ml of methanol was allowed to stand at room temperature for 11 days. The resulting solution was neutralized with sodium bicarbonate and continuously extracted with pentane. The pentane solution was concentrated by distillation. Preparative gas chromatographic techniques (C) afforded the two ether products **7c** and **5c** in a 4.4:1.0 ratio, each having retention times and spectral properties identical with those given above.

Independent Synthesis of 2-Methoxy-2-cyclohexylpropane (7c). 2-Cyclohexyl-2-propanol was prepared by the addition of methyllithium (60 ml of 2.2 *M* solution) dropwise to an ice-cold solution of cyclohexyl methyl ketone in 25 ml of anhydrous ether under nitrogen. After 1 hr of stirring at room temperature, 50 ml of water was added dropwise and the solution was stirred for an additional 1 hr. The reaction mixture was then extracted with ether and the combined ether extracts were dried over saturated sodium chloride solution followed by anhydrous sodium sulfate. Distillation afforded 7.98 g (56%) of 2-cyclohexyl-2-propanol, bp 42° (4 mm).

A solution containing 2.15 g (15 mmol) of 2-cyclohexyl-2-propanol in 50 ml of anhydrous ether was added dropwise with stirring to 0.81 g of a 50% suspension of sodium hydride in oil, which had been washed with pentane, under nitrogen. After 4 hr of stirring the solution was cooled in an ice bath and 2.41 g (17 mmol) of methyl iodide was added dropwise. After addition, the mixture was stirred at room temperature for 24 hr. The mixture was treated with 5 ml of water and extracted with three 25-ml portions of ether. The combined ether fractions were washed with a saturated sodium chloride solution, dried over anhydrous sodium sulfate, and concentrated by distillation. Isolation by preparative gas chromatography (C) afforded a specimen of **7c** which had spectral properties identical with those described above.

Isopropylidenecyclopentane (1d). A. Irradiation. A 100-ml methanolic solution containing 2.2 g of olefin **1d** was irradiated as described above for 8 hr. Gas chromatographic analysis (B and C) revealed a partial recovery of olefin **1d** and the formation of three hydrocarbon and four ether products. Isolation by preparative gas chromatographic techniques afforded **isopropylcyclopentane (12d)** which had a retention time and spectral properties identical with those of a commercial sample. **1-Isopropyl-1-cyclopentene (13d)** was obtained as a colorless liquid which had spectral properties identical with those of an authentic sample prepared by treatment of 2-cyclopentyl-2-propanol with *p*-toluenesulfonic acid.[14] **2-Cyclopentylpropene (11d)** was obtained as a colorless liquid, ν_{max} 3088, 2962, 2875, 1644, 1453, 1377, and 892 cm^{-1} (lit.[13] ν_{max} 1650 and 881 cm^{-1}).

1-Methoxy-1-isopropylcyclopentane (5d) and **2-methoxy-2-cyclopentylpropane (7d)** were obtained as colorless liquids which had the same retention times and spectral properties as the specimens prepared independently as described below. **1-Methoxy-1-(2′-propenyl)cyclopentane (6d)** was observed as one component of a mixture of the four ethers in an NMR spectrum (τ 5.10), but attempts to isolate the material were unsuccessful. **2-Methoxy-2-(1′-cyclopentenyl)propane (8d)** was obtained as a colorless liquid: ν_{max} 3058, 2981, 2934, 2850, 2823, 1462, 1442, 1372, 1359, 1258, 1167, 1143, 1072, 950, and 911 cm^{-1}; NMR spectrum τ 4.41 (m, –CH=), 6.90 (s, CH_3O–), and 8.70 [s, $(CH_3)_2C$–]; MS m/e 140.1203 (calcd for $C_9H_{16}O$, 140.1201), 125 (100), 109 (18), 95 (15), 93 (40), and 67 (20).

B. Acid-Catalyzed Methanolysis. A solution containing 1 ml of olefin **1d** and 6 drops of concentrated sulfuric acid in 10 ml of methanol was allowed to stand for 1 day. The solution was neutralized with sodium bicarbonate and extracted with pentane. The combined pentane extracts were washed with saturated sodium chloride solution, dried over anhydrous sodium sulfate, and concentrated by distillation. Preparative gas chromatographic techniques (A) afforded the ethers **5d** and **7d** in a 1.1:1.0 ratio.

1-Methoxy-1-isopropylcyclopentane (5d) was obtained as a colorless liquid: ν_{max} 2960, 2876, 2826, 1467, 1386, 1368, 1190, and 1080 cm^{-1}; NMR spectrum τ 6.94 (s, 3, CH_3O–), 8.39 [m, 9, $(CH_2)_4CH$–], and 9.12 [d, 6, J = 6.75 Hz, $(CH_3)_2C$–]; MS m/e 142.1355 (calcd for $C_9H_{18}O$, 142.1358), 113 (13), 99 (100), 81 (12), 69 (16), and 67 (78).

2-Methoxy-2-cyclopentylpropane (7d) was obtained as a colorless liquid: ν_{max} 2957, 2873, 2830, 1466, 1381, 1363, 1186, 1124, 1079, and 909 cm^{-1}; NMR spectrum τ 6.87 (s, 3, CH_3O–), 8.55 [m, 9, $(CH_2)_4CH$–], and 8.93 [s, 6, $(CH_3)_2C$–]; MS m/e 127.1120 (calcd for $C_8H_{15}O$, 127.1124), 95 (72), 69 (50), 67 (100), and 59 (33). The infrared spectrum was similar to that previously reported.[15]

2-Isopropylidenenorbornane (14). A. Irradiation. A 100-ml methanolic solution containing 2.72 g of olefin **14**, prepared by the general method of Kornblum et al.,[12,14] was irradiated as described above for 7 hr. Gas chromatographic analysis (B) revealed the formation of seven ether and several hydrocarbon products. The following two principal products were isolated by preparative techniques.

2-(2′-Methoxy-2′-propyl)-2-norbornene (15) was obtained as a colorless liquid: ν_{max} 3055, 2971, 2873, 2822, 1442, 1370, 1368, 1273, 1161, and 1069 cm^{-1}; NMR spectrum τ 4.19 (d, J = 3 Hz, olefinic), 6.88 (s, CH_3O–), 7.09 (m, bridgehead), 8.73 (s, CH_3–), and 8.75 (s, CH_3–); MS m/e 166.1354 (calcd for $C_{11}H_{18}O$, 166.1357), 151 (40), 123 (100), 108 (15), 107 (20), and 91 (42).

2-*endo*-Isopropylnorbornane (16) was obtained as a colorless liquid: ν_{max} 2950, 2869, 1462, 1450, 1381, 1362, and 1310 cm^{-1}; NMR spectrum τ 7.78 (m, bridgehead). This material was identical in retention time and spectral properties with an authentic sample obtained as described previously.[16]

Irradiation of 2,3-Dimethyl-2-butene (1a) in the Presence of Sulfur Hexafluoride. Through a solution containing 1.68 g (20 mmol) of 2,3-dimethyl-2-butene (**1a**) in 100 ml of methanol was bubbled nitrogen (15 min) followed by sulfur hexafluoride (10 min). Sulfur hexafluoride was slowly bubbled through the solution during the irradiation, which was carried out by the general procedure described above. After irradiation, 80 ml of the solution was diluted to 100 ml with distilled water. Fluoride concentrations were then determined from the potential of an Orion fluoride ion activity electrode (94-09) vs. a Fischer standard saturated calomel electrode with cracked glass junction as measured by a Beckman Century SS pH meter on expanded scale. A calibration curve was obtained using sodium fluoride in 80:20 methanol–water standard solutions. The results are summarized in Table II.

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Registry No.—**1a**, 563-79-1; **1b**, 19780-67-7; **1c**, 5749-72-4; **1d**, 765-83-3; **5b**, 55660-92-9; **5c**, 55660-93-0; **5d**, 55660-94-1; **6b**, 55660-95-2; **6c**, 55660-96-3; **7b**, 55660-97-4; **7c**, 55660-98-5; **7d**, 3275-02-3; (*E*)-**8b**, 55660-99-6; (*Z*)-**8b**, 55661-00-2; **8d**, 55661-01-3; **11c**, 2157-18-8; **11d**, 55661-02-4; **14**, 4696-14-4; **15**, 55661-03-5; **16**, 55661-04-6; 2-methyl-3-ethyl-3-pentanol, 55661-05-7; methyl iodide, 74-88-4; 2-cyclohexyl-2-propanol, 16664-07-6; methyllithium, 917-54-4; cyclohexyl methyl ketone, 823-76-7; sulfur hexafluoride, 2551-62-4.

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(7) Although sulfur hexafluoride normally yields six fluoride ions for each electron captured in methanolic solution, this ratio may not hold in the presence of olefinic material in view of the known reaction of the initially

formed intermediate, the sulfur pentafluoride radical, with alkenes; see H. W. Sidebotton, J. M. Tedder, and J. C. Walton, *Trans. Faraday Soc.*, **65**, 2103 (1969).

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Transannular Photochemical Ring Closure of 1,2,5,6-Tetramethylenecyclooctane as a Synthetic Route to Small-Ring Propellanes

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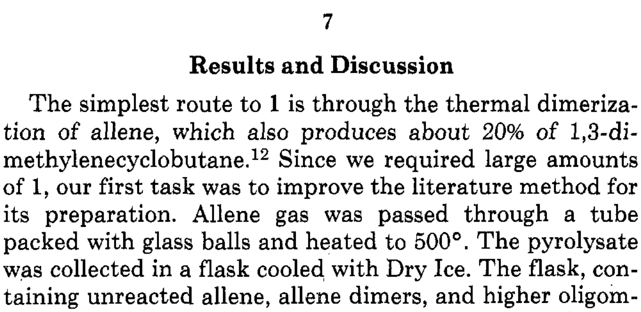
The synthesis of 2,6-dimethylene[3.3.2]propellane (**4**) in three steps and 12% overall yield from allene dimer **1** is reported. The key reaction is the formation of **4** by transannular photochemical ring closure of 1,2,5,6-tetramethylenecyclooctane (**3**). A chemical separation of **4** from isomers that are carried through the synthesis is described, which makes the purification of the intermediates (**1**–**3**) unnecessary. Compound **4** has been converted to the parent [3.3.2]propellane (**6**), which undergoes free-radical addition of bromine across the central bond to give **13**.

The synthesis of small-ring propellanes has been an area of considerable activity in recent years.[2] Theoretical interest in [2.2.2]propellane (**7**)[3] has given special stimulus to the preparation of this molecule. A derivative of **7** has been synthesized by Eaton and his coworkers through two successive ring contractions of [4.2.2]propellane-2-one.[4a] This key intermediate was prepared from the enol acetate of 1,3-cyclohexanedione by photoaddition of ethylene, base-catalyzed elimination of the elements of acetic acid, and photoaddition of a second molecule of ethylene.[4b] Evidence for the intermediacy of the parent compound (**7**) in the electrochemical reduction of 1,4-dibromobicyclo[2.2.2]octane[5] and in the mercury-sensitized photolysis of 1,4-dimethylenecyclohexane[6] has also been reported.

Our route[7] to the [2.2.2]propellane ring system took cognizance of the fact that photochemical ring closure in 1,4-dimethylenecyclohexane provided a formally attractive synthesis of **7**. However, since the ring in this diene prefers a chair conformation,[8] we anticipated that ring closure to **7** might be a rather inefficient process. Moreover, because short-wavelength light or a high-energy sensitizer would be required to excite the isolated double bonds in 1,4-dimethylenecyclohexane, it seemed possible that **7**, if formed, might undergo photoinitiated opening back to the starting material. Finally, were only small amounts of **7** to be formed, for either or both of the above reasons, its separation from unreacted starting material would be problematical. Therefore, we explored the route, outlined in Scheme I, which circumvented these difficulties by effecting photochemical ring closure in 1,2,5,6-tetramethylenecyclooctane (**3**).[9] Cyclooctane rings readily undergo 1,5-transannular reactions;[10] and excitation of **3**, either direct or sensitized, was expected to be easy because of the conjugated diene systems present in the molecule. Moreover, the methylene groups in the anticipated photocyclization product (**4**) could be ozonized to give **5**, a precursor of the parent [3.3.2]propellane (**6**) and, more important, a promising intermediate for the synthesis of **7**.[11] As indicated in Scheme I, a synthesis of **3** can be constructed by noting that **3** is the product of cyclobutene ring opening in **2**, which is in turn a dimer of 1,2 dimethylenecyclobutane (**1**). Thus our synthesis began with attempts to prepare **2** from **1**.

Scheme I



1 2 3

4, R = CH_2
5, R = O
6, R = H_2

7

Results and Discussion

The simplest route to **1** is through the thermal dimerization of allene, which also produces about 20% of 1,3-dimethylenecyclobutane.[12] Since we required large amounts of **1**, our first task was to improve the literature method for its preparation. Allene gas was passed through a tube packed with glass balls and heated to 500°. The pyrolysate was collected in a flask cooled with Dry Ice. The flask, containing unreacted allene, allene dimers, and higher oligomers, was then connected to the inlet of the heated tube and allowed to warm to room temperature. Only the allene distilled through the tube, and the pyrolysate was trapped in a second flask. The two flasks were then interchanged and the allene was cycled through the tube again.[13] Allene, recycled thus ten times, gave yields of dimers on the order of 25%. With further recycling even higher yields could be realized.