41, 1279 (1976); (f) I. Hasegawa, M. Watabe, H. Aoyama, and Y. Omote, *Tetrahedron,* **33,** 485 (1977).

(18) (a) R. A. Schneider and J. Meinwald, *J. Am. Chem. Soc.,* **89,** 2023 (1967); (b) R. H. Hesse, *Adv. Free-Radical Chem.,* **1,** 83 (1969); (c) P. J. Wagner, P. A. Kelso, A. E. Kemppainen, and R. G. Zepp, *J. Am. Chem. Soc.,* **94,** 7500 (1972).

(19) There are in fact two different chair transition states possible for these hydrogen transfers corresponding to the *cis*- and *trans*-decalin analogues described on p 2028 of ref 18a. The *trans*-decalin analogue is shown but the conclusions are the same regardless of which one is used. The structures depicted were constructed from models using the standard bond lengths for cyclohexanone and the bond lengths for the uracil cycloadducts determined by x-ray crystallography.[3b]

(20) For a discussion of the dramatic effect of a heteroatom on biradical behavior see P. J. Wagner and M. J. Thomas, *J. Am. Chem. Soc.,* **98,** 241 (1976).

(21) General procedures: Melting points were taken in open capillaries in a Thomas-Hoover Unimelt apparatus and are uncorrected. Infrared spectra were taken in the indicated phase on Perkin-Elmer Model 137 or 467 spectrophotometers. Proton magnetic resonance spectra were recorded in the indicated solvent at 60 and 100 MHz on Varian A-60A and Jeolco MH-100 instruments. ^{13}C NMR spectra were measured on a Bruker HX-90. Spectra are reported in δ units with reference to internal tetramethylsilane. Mass spectra were obtained with an AEI-MS9 spectrometer using an ionizing potential of 70 eV. All irradiations were carried out with Corex-filtered light from a 450-W Hanovia medium-pressure source. The vessel containing the reaction mixture was held at −5 to 0 °C with an acetone-ice bath and a dry ice reflux condenser. Gas chromatographic analyses in the 1,3-dimethyl systems were performed on a 5 ft by $^1/_8$ in. column of 3% SE-30 on 100/120 mesh Varaport 30 (110–150 °C), while analyses on the unmethylated systems were performed on a 13 ft by $^1/_8$ in. column of 5% SE-30 on DMSC-treated 60/80 mesh Chromosorb G at 185 °C. Preparative scale gas chromatography utilized either a 20 ft by $^3/_8$ in. column of 5% DMSC-treated 60/80 mesh Chromosorb G (column A) or a 12 ft by $^1/_4$ in column of 20% Carbowax 20M on 60/80 Chromosorb P at 220 °C (column B). Elemental analysis was performed by Scandinavian Microanalytical Laboratory, Herlev, Denmark, or Heterocyclic Chemical Corp., Harrisonville, Mo., on sublimed or molecularly distilled pure samples.

(22) F. J. Weigert and J. D. Roberts, *J. Am. Chem. Soc.,* **92,** 1347 (1970).

(23) D. K. Dalling and D. M. Grant, *J. Am. Chem. Soc.,* **89,** 6612 (1967).

Copper(I) Catalysis of Olefin Photoreactions. Photorearrangement and Photofragmentation of Methylenecyclopropanes

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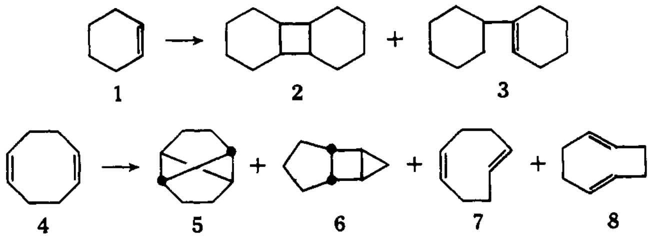
Contribution from the Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106. *Received December 27, 1976*

Abstract: Methylenecyclopropanes, 7-methylenebicyclo[4.1.0]heptane (**14**) and 8-methylenebicyclo[5.1.0]octane (**15**), undergo a variety of novel carbon skeletal reorganizations upon photolysis (254 nm) in the presence of copper(I) trifluoromethanesulfonate. Thus, **14** gives bicyclo[4.2.0]oct-1(8)-ene (**17**), *unsym*-pentamethyleneallene (**18**), 3-vinylcyclohexene (**19**), and 1-vinylcyclohexene (**20**); and **15** gives bicyclo[5.2.0]non-1(9)-ene (**22a**), bicyclo[5.2.0]non-1-ene (**22b**), *unsym*-hexamethyleneallene (**23**), and bicyclo[6.1.0]non-1-ene (**24**). Photofragmentation products, acetylene, and cyclohexene (**1**) or cycloheptene (**21**) are also obtained from **14** or **15**, respectively. The fate of the olefinic methylene group was traced by determining the position of deuterium labeling in the products from copper(I)-promoted photorearrangement of 7-(dideuteriomethylene)bicyclo[4.1.0]heptane (**16**).

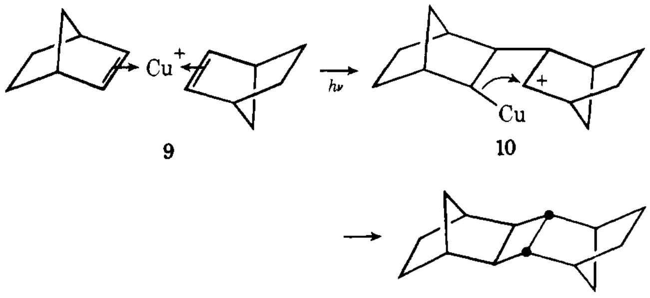
Introduction

Copper(I) salts promote a large variety of olefin photoreactions including both inter-[1] and intramolecular[2,3b] [2 + 2] cycloadditions to give cyclobutanes (e.g., **2** and **5**), and cis–trans isomerization[3] (e.g., **4** → **7** and **8**). Products of other less general reaction types (e.g., **3** and **6**) have also been found. Some mechanistic details of these reactions are known. Thus, there is evidence that initial cis–trans isomerization to yield copper complexes of reactive *trans*-cycloolefin intermediates may be important in some [2 + 2] cycloadditions (e.g., **1** → **2** and **4** → **5**).[1b,3b] A recent investigation of the mechanism of some intermolecular, copper(I)-catalyzed [2 + 2] photocycloadditions showed that these photodimerizations involve photoexcitation of a 2:1 olefin–Cu(I) complex, and that both C═C bonds *must be coordinated to the same Cu(I)* to undergo photodimerization.[1b] However, the precise nature of the olefin–catalyst–light interaction responsible for reaction remains unknown.


1 2 3

4 5 6 7 8

Olefin photoreactions which are catalyzed by salts of copper(I) are especially interesting since the salts form well-characterized olefin complexes,[4] and since the olefin-metal interaction undoubtedly plays a key role in the photochemical process. An organocopper(I) carbenium ion **10** was suggested as a possible intermediate for the photodimerization of norbornene which gives **11** from the 2:1 olefin copper complex **9**.[1a]



9 10

11

The present study of photolysis of methylenecyclopropanes in the presence of copper(I) was inspired by the organocopper(I) carbenium ion hypothesis. Thus, copper catalysis of olefin photoreactions may involve preliminary photocupration, that is, light-induced transformation of a η^2-copper(I) olefin complex into a η^1-β-copper(I) carbenium ion intermediate. This would produce either cyclopropyl (**12**) or cyclo-

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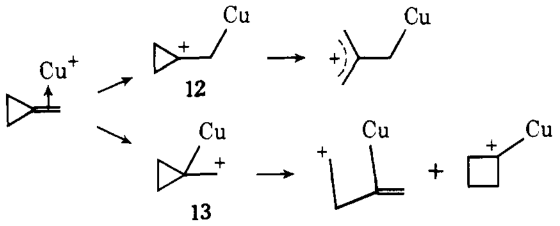
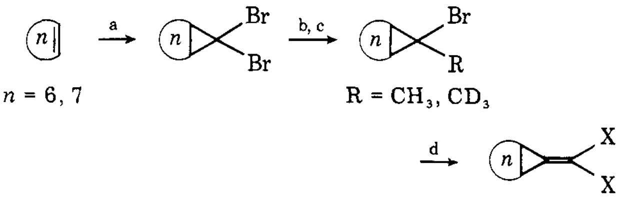


propylcarbinyl (**13**) carbenium ion intermediates from a methylenecyclopropane. Skeletal rearrangements might then ensue via well-known reactions of these types of carbenium ions.[5,6] We now report that the photochemistry of methylenecyclopropanes is characterized by a plethora of novel molecular transformations involving such carbon skeletal reorganizations.

Results

Synthesis of Methylenecyclopropanes. Alkylation of a 1-lithiocyclopropyl bromide[7] was employed for the preparation of 7-methylenebicyclo[4.1.0]heptane (**14**), 8-methylenebicyclo[5.1.0]octane (**15**), and the deuterated analogue **16**. Thus the dibromocarbene adducts[8] of cyclohexene and cycloheptene were metalated at −90 °C, and the resulting monolithium derivatives were alkylated with CH_3I or CD_3I. Subsequent dehydrobromination with potassium *tert*-butoxide in dimethyl sulfoxide gave **14**, **15**, and **16** isomerically pure. A previous synthesis of **14** and **15** via pyrolysis of the sodium salt of the corresponding cyclopropylcarbinyl toluenesulfonylhydrazone gave **14** and **15** in admixture with the isomeric bicyclo[(*n* + 1).1.0]alkene-1.[9]

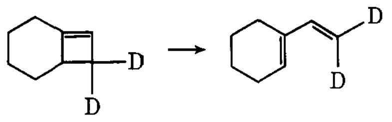


14, n = 6, X = H
15, n = 7, X = H
16, n = 6, X = D

a, $CHBr_3$/*t*-BuOK; b, *n*-BuLi/−90 °C; c, RI; d, *t*-BuOK/Me_2SO

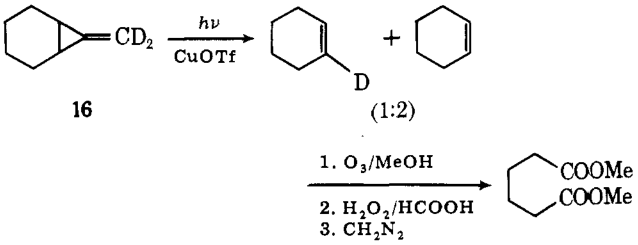
Copper-Catalyzed Photorearrangement and Photofragmentation. Irradiation (254 nm) of **14** with copper(I) trifluoromethanesulfonate–benzene complex, $(CuOTf)_2\cdot C_6H_6$,[4] in ether solutions gave cyclohexene (**1**), acetylene, bicyclo[4.2.0]oct-1(8)-ene (**17**), and *unsym*-pentamethyleneallene (**18**) as major products along with traces of 3-vinylcyclohexene (**19**) and 1-vinylcyclohexene (**20**). The retention times of all products were identical with those of authentic samples by gas-liquid phase chromatography. Methylenecyclopropane **14** and all photoproducts were stable under the conditions of analysis though **17** did isomerize to **20** if the injector temperature was set too high (vide infra). Proton magnetic resonance spectra of **1** and **17–20** were identical with those of authentic samples.[10] No reaction occurred without irradiation or upon irradiation in the absence of CuOTf, and the reaction stopped abruptly upon cessation of irradiation. Since the copper catalyst contains 0.5 equiv of benzene, **14** was irradiated in the presence of benzene alone (no CuOTf). No reaction occurred. The ratio of the products **1** and **17–20** was monitored from 24 to 70% conversion of **14** and found to be 1.00 (**17**):0.41 (**18**): 0.14 (**19**):0.10 (**20**) (±0.01) while that of cyclohexene (**1**) varied gradually from 1.8 after 24% conversion of **14** to 1.4 after 70% conversion.

A similar photorearrangement of the deuterium-labeled derivative **16** gave deuterium-labeled derivatives of **17–20** as shown in the equation above. The position of deuterium substitution in **18**-d_2, **19**-d_2, and **20**-d_2, but not **17**-d_2, is evident from a comparison of their ^{1}H NMR spectra with those of the unlabeled analogues (see Experimental Section). The deuterium substitution pattern in **17**-d_2 was demonstrated by conversion to **20**-d_2 upon vapor phase pyrolysis in a sealed tube.

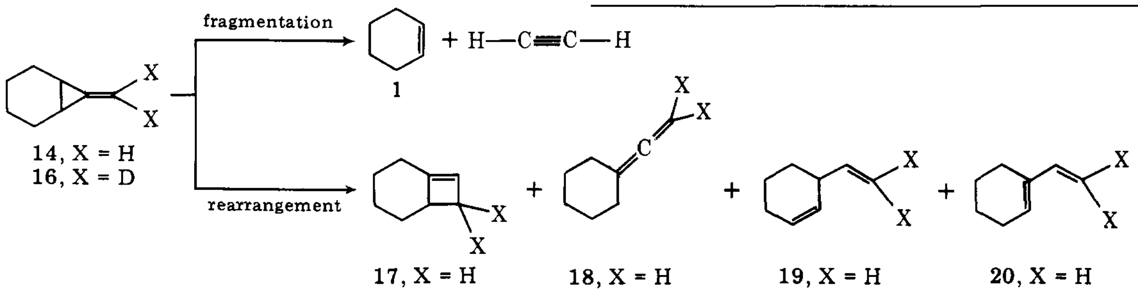


17-d_2 20-d_2

The cyclohexene produced by CuOTf-catalyzed photofragmentation of **16** was shown by mass spectrometric analysis to contain some deuterium (Table I). The mass spectrum of this product is understandable in terms of an approximately 1:2 mixture of d_1 and d_0 cyclohexene. The ^{1}H NMR spectrum of this product shows a vinyl to methylene proton absorption ratio of 1.6:8, suggesting a concentration of deuterium label in the vinyl positions. This spectrum is also understandable in terms of an approximately 1:2 mixture of 1-deuteriocyclohexene and unlabeled cyclohexene, respectively. The absence of deuterium label in the methylene positions of the cyclohexene produced from **16** was confirmed by conversion to dimethyl adipate which was deuterium free according to mass spectrometric comparison with authentic undeuterated dimethyl adipate.



Similar irradiation of **15** in the presence of CuOTf gave cycloheptene (**21**), acetylene, bicyclo[5.2.0]non-1(9)-ene (**22a**), *unsym*-hexamethyleneallene (**23**), and bicyclo[6.1.0]non-1-ene (**24**) as major products. A small yield of bicyclo[5.2.0]non-1-ene (**22b**) was also obtained. Acetylene was identified by GLC comparison with an authentic sample. Cycloheptene (**21**) and bicyclo[6.1.0]non-1-ene (**24**)[9] were characterized by the identity of their GLC retention times and ^{1}H NMR spectra with those of authentic samples. The struc-



14, X = H
16, X = D

17, X = H
17-d^2, X = D

18, X = H
18-d^2, X = D

19, X = H
19-d^2, X = D

20, X = H
20-d^2, X = D

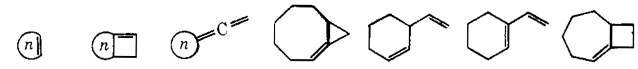
Table I. Parent Region of the Mass Spectra of 1-d_0 and 1-d_n

Compd	m/e	Rel intensity 81	82	83	84
1-d_0		25	63	6	0
1-d_n		23	67	40	3

Table II. 100-MHz ^{1}H NMR Spectra of **16** and **21** in CCl_4

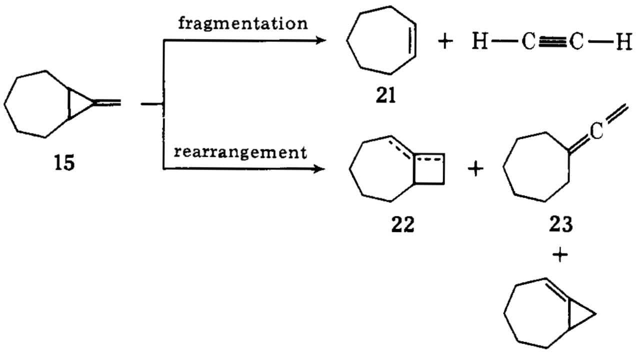
unsym-Pentamethyleneallene (**18**)	4.45 (2 H)	2.07 (4 H)	1.53 (6 H)
unsym-Hexamethyleneallene (**23**)	4.44 (2 H)	2.19 (4 H)	1.56 (8 H)

Table III. Relative Yields of Photolysis Products from **14** and **15**



1, 21 **17, 22a** **18, 23** **24** **19** **20** **22b**

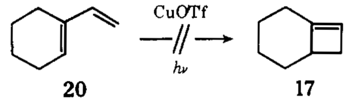
Methylenecyclopropane	**1**, $n = 6$ **21**, $n = 7$	**17**, $n = 6$ **22a**, $n = 7$	**18**, $n = 6$ **23**, $n = 7$	**24**	**19**	**20**	**22b**
	Rel product yields						
$n = 6$ (**14**)	49	31	13		4	3	
$n = 7$ (**15**)	30	45	7	12			6



15 **21** **22** **23** **24**

ture **23** was assigned on the basis of its ^{1}H NMR spectrum. The ^{1}H NMR spectra of **23** and **18** are very similar (Table II). The vinyl proton absorption is a quintet, $J = 2.4$ Hz, for both **18** and **23**. The bicyclo[5.2.0]nonenes **22a** and **22b** were identified by spectral and GLC comparison with samples prepared by an unambiguous synthesis (vide infra). The relative yields of products **21–24** after 55% conversion of **15** are given in Table III along with similar data for photolysis of **14**.

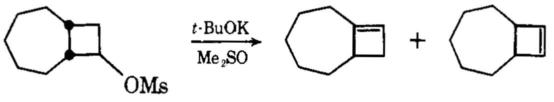
Since copper salts catalyze photocyclization of 1,3-butadiene to give cyclobutene,[2] we examined the possibility that cyclobutene **17** might be produced indirectly from **14** via copper(I)-catalyzed photocyclization of the 1,3-diene **20**. A mixture of **16** (i.e., **14**-d_2) and **20** (3:2) was irradiated in ether solution with CuOTf. Mass spectral analysis of the **17** produced showed it to be greater than 94% **17**-d_2. Also **20** alone



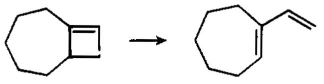
20 **17**

was irradiated in ether solution with CuOTf. No **17** was produced. Thus, photocyclization of **20**, which would give **17**-d_0, is not an important pathway for formation of **17** from **14**. Photocyclization of **20** did occur upon irradiation (254 nm) in acetone solution to give a low yield of **17** as the major isomerization product (see Experimental Section).

Synthesis of Bicyclo[5.2.0]nonenes. An approximately equimolar mixture of bicyclo[5.2.0]non-1(9)-ene (**22a**) and bicyclo[5.2.0]non-8-ene (**22c**) was obtained by treatment of 8-methanesulfonyloxybicyclo[5.2.0]nonane (**25**) with potassium *tert*-butoxide in dimethyl sulfoxide (Me_2SO) at 20 °C. The olefin **22a** exhibits a one-proton ^{1}H NMR absorption at δ 5.56 compared with a one-proton absorption at δ 5.42 for the analogous cyclobutene **17**. Additional proof for the structure assigned to **22a** was obtained by rearrangement to 1-vinylcycloheptene (**26**) upon vapor-phase pyrolysis in a sealed tube.

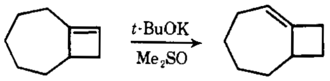


25 **22a** **22c**



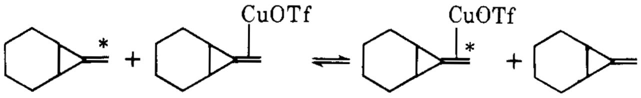
22a **26**

The olefin **22c** exhibits a two-proton absorption at δ 6.00 compared with δ 6.08 for the analogous cyclobutene, bicyclo[4.2.0]hex-7-ene.[10] Bicyclo[5.2.0]non-1-ene (**22b**) was obtained by potassium *tert*-butoxide catalyzed allylic rearrangement of **22a** in Me_2SO at 35 °C. In contrast, **22c** did not undergo any rearrangement even after prolonged heating in the presence of potassium *tert*-butoxide in Me_2SO. The ^{1}H NMR spectrum of **22b** exhibits a one-proton absorption at δ 5.21 (t, $J = 2.4$ Hz).



22a **22b**

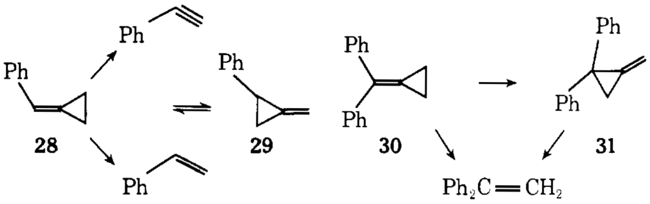
^{1}H NMR Characterization of CuOTf Complex of 14. The ^{1}H NMR spectrum of 7-methylenebicyclo[4.1.0]heptane (**14**) in the presence of CuOTf varied with the concentration of copper(I) relative to olefin (**14**). Thus, the vinyl proton resonance of **14** is shifted increasingly upfield as the relative concentration of CuOTf is increased (Figure 1). The linear dependence observed for the upfield shift as a function of relative concentration of copper(I) is presumptive evidence for the presence of only a single complexed species, namely, **27**, which rapidly transfers CuOTf to free olefin **14**.[4]



14 **27**

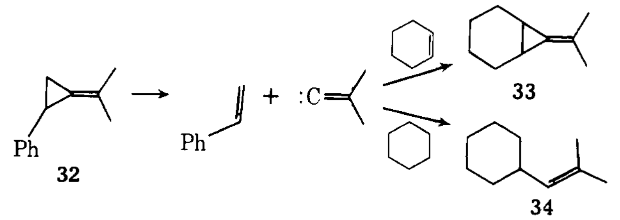
Discussion

Methylenecyclopropanes undergo a vast array of photochemical reactions upon irradiation (254 nm) in the presence of copper(I) trifluoromethanesulfonate as catalyst. Some of these reactions resemble those observed previously for direct or mercury-sensitized irradiation of methylenecyclopropanes. Thus, the arylmethylenecyclopropanes **28–31** are interconverted upon direct irradiation.[11] Photofragmentations are also observed with **28–31**. These photoreactions are not quenched



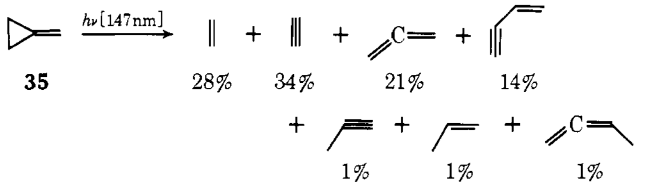
28 **29** **30** **31**

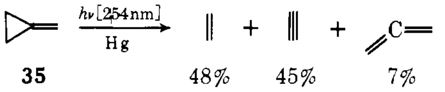
by piperylene, nor do they occur in sensitized irradiations. Therefore singlet excited states were postulated for the photoisomerizations and photofragmentations. Photofragmentation of **32** generates isopropylidenecarbene which can be



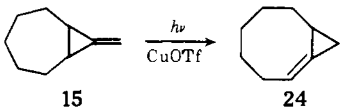
trapped with cyclohexene or cyclohexane to afford **33** or **34**, respectively.[12]

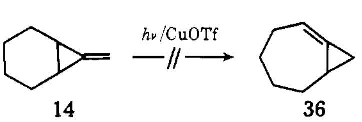
Direct irradiation of methylenecyclopropane (**35**) with high-energy (8.4 eV) ultraviolet light (147 nm) also leads to photofragmentation[13] to ethylene and acetylene. Other major products include allene and vinylacetylene. Mercury-sensitized photolysis of **35** results mainly in photofragmentation.[11a]

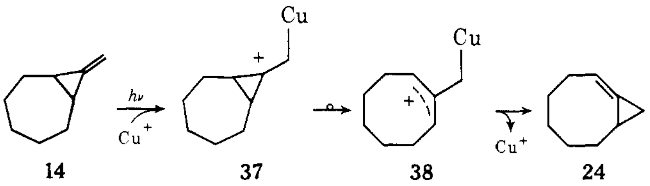




Interconversion of the isomeric methylenecyclopropanes **15** and **24** and photofragmentations yielding acetylene such as the production of **1** from **14** or **21** from **15** find analogy in the known reactions of electronically excited methylenecyclopropanes in the absence of CuOTf. The failure of **14** to give **36** in analogy with the **15** → **24** rearrangement is not surprising since the thermal equilibrium between these isomers favors **14** over **36** by 15:1.[9] In contrast, **24** is favored over **15** by 2:1 at equilibrium.[9] The present study does not provide a basis for presuming that these copper-catalyzed photoreactions are related mechanistically to any of the processes observed previously for electronically excited methylenecyclopropanes. One mechanistic alternative which should be considered involves organocopper(I) carbenium ion intermediates such as the cyclopropylcarbenium ion **37**. Electrocyclic ring opening of cyclopropylcarbenium ions to give allylcarbenium ions is a well-known process[5] which could give **38** from **37**. The observed product **24** could arise by 1,3-elimination of Cu$^+$ from **38**.







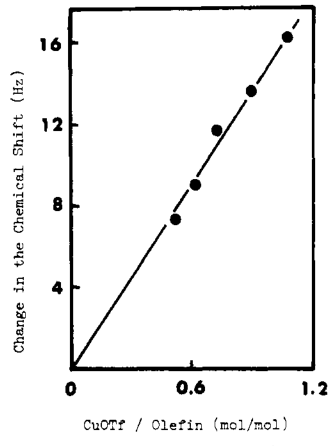
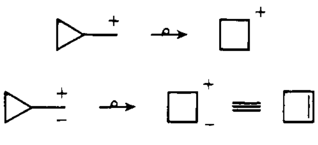
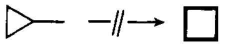


Figure 1. Upfield shift of δ 5.33 (vinyl proton) ^{1}H NMR absorption for **14** in the presence of CuOTf in acetone-d_6.

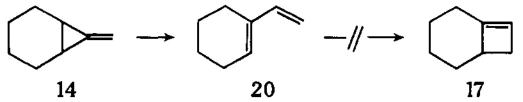
Photoisomerization of methylenecyclopropanes to give cyclobutenes such as **17** from **14** and **22a** from **15**, or methylenecyclobutanes such as **22b** from **15**, is unprecedented. The cyclopropylcarbinyl to cyclobutyl transformations observed in these copper-promoted photorearrangements are especially interesting. Ring expansion of cyclopropyl derivatives to give cyclobutyl derivatives generally involves generation and rearrangement of cyclopropylcarbinylcarbenes[14] or carbenium ions.[6] It is noteworthy that both of these types of reactive intermediates have a vacant orbital on the exocyclic carbon atom.



Moreover, such rearrangements are unknown for cyclopropylcarbinyl radicals.[15]



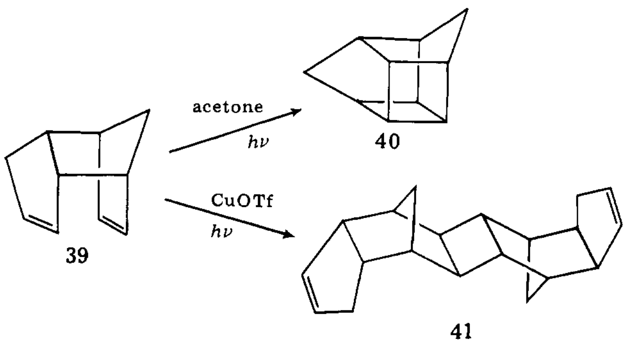
We ruled out the possibility of an indirect process for the production of **17** from **14** involving photocyclization of the 1,3-diene **20** (vide supra). Moreover, direct formation of all rearrangement products from a common precursor is supported by the constant ratio of product yields observed during the course of copper(I)-catalyzed photorearrangement of **14**. The rearrangement products are stable under the reaction conditions, and no stable intermediates were detected. The gradually diminishing yield of photofragmentation product, cyclohexene, most likely is due to secondary photoreactions which consume this product.[1b]

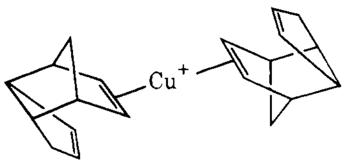


^{1}H NMR evidence shows that CuOTf forms a complex **29** with **14**. A similar complexation of **15** is assumed. Olefin complexes of CuOTf exhibit two strong UV absorption bands, one at 233-241 nm (ϵ_{max} 2500-3600) and one at 272-282 nm (ϵ_{max} 1500-2100).[16] Since no reaction occurs upon irradiation of the methylenecyclopropanes in the absence of CuOTf, the photoreactions of **14** and **15** must result from absorption of light by the corresponding Cu(I)-olefin complexes.

Differences are sometimes found between the products of photoreactions promoted by copper(I) and those promoted by triplet sensitizers. An important example is the production of 1-cyclohexylcyclohexene (**3**) in the photolysis of cyclohexene in the presence of copper(I)[1b] but not in the corresponding triplet-sensitized photolysis.[17] Another noteworthy contrast is found in the acetone-sensitized photolysis of *endo*-dicyclopentadiene (**39**)[18] to give intramolecular [2 + 2] cycloadduct **40** while CuOTf promotes intermolecular dimerization to give

41 and, at most, 1% of **40**.[1a] This is remarkable since the π bonds in **39** are intimately juxtaposed. A 2:1 complex **42** of this diene with CuOTf was isolated and shown to have copper coordinated with the exo face of the 8,9-C=C bond. If light absorption by **42** would produce an electronically excited free olefin, intramolecular cycloaddition seems unavoidable. However, photodimerization involves *only* the coordinated π bond of the diene. These examples of contrasting reactions suggest that *copper(I) is able to promote photochemical reactions of olefins in some manner other than triplet sensitization.*





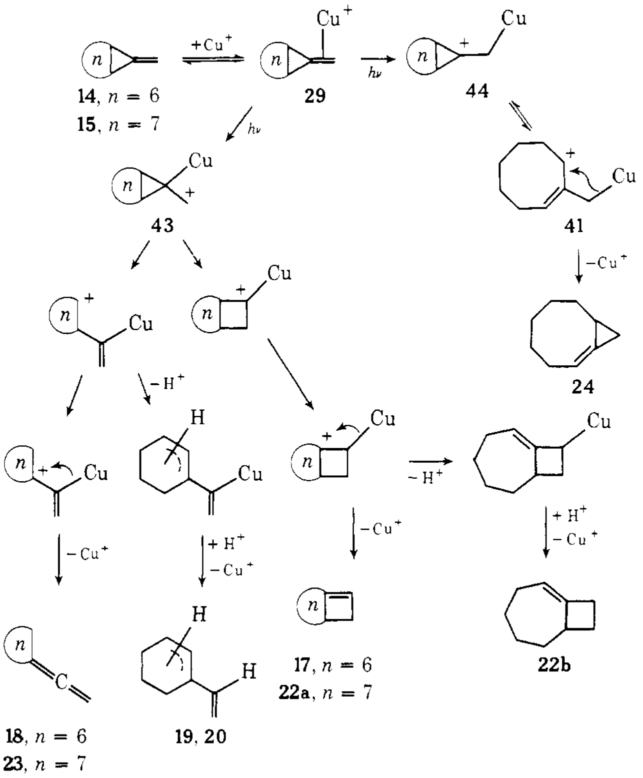
42

The photorearrangements observed for methylenecyclopropanes in the presence of CuOTf can be understood in terms of the organocopper(I) carbenium ion hypothesis (vide supra). Thus, the light-induced transformation of a η^2-copper(I)-olefin complex (e.g., **29**) into a η^1-β-copper(I)-carbenium ion intermediate (e.g., **43** or **44**) followed by well-known carbenium ion reactions *might* account for the copper(I)-catalyzed photorearrangements (Scheme I).[5,6] The position of deuterium substitution in the products of copper(I)-catalyzed photorearrangement of 7-(dideuteriomethylene)bicyclo[4.1.0]heptane (**16**) is in accord with this scheme.[19] Of course, *alternative mechanisms, e.g., involving excited state intermediates, have not been rigorously excluded.* However, copper-free excited state intermediates seem unlikely since many of the observed rearrangement types have never been found for electronically excited methylenecyclopropanes.

Conclusions

The photochemistry of methylenecyclopropanes in the presence of copper(I) is characterized by a plethora of novel molecular transformations involving carbon skeletal reorganizations. Some of these reactions are analogous to vapor phase photoreactions sensitized by mercury and liquid phase photoreactions of methylenecyclopropanes. However, many of the copper(I)-catalyzed reactions are unprecedented. Formation of cyclobutene and methylenecyclobutane products is especially interesting since cyclopropylcarbinyl to cyclobutyl transformations are unprecedented in organic photochemistry, and since such ring expansions generally involve generation and rearrangement of cyclopropylcarbinylcarbenes or carbenium ions. A detailed mechanism for copper(I) catalysis of methylenecyclopropane photorearrangements remains to be established. We believe that a mechanism for the light-catalyst-olefin interaction leading to rearrangement involving preliminary photocupration, light-induced transformation of a η^2-copper(I)-olefin complex into a η^1-β-copper(I) carbenium ion intermediate, deserves further serious consideration.

Scheme I



Experimental Section

General. All photolyses were conducted in cyclindrical quartz vessels which were cooled with an internal water-cooled finger. The reaction mixtures were stirred magnetically and irradiated externally with a Rayonet Photochemical Reactor (Southern New England Ultraviolet Co., Model RPR-100) equipped with 254-nm lamps. Preparative gas-liquid phase chromatography (GLC) was performed with a Varian Model 202B instrument equipped with a ¼ in. × 15 ft column filled with 15% Dow Corning (DC) 710 silicon oil on 60/80 Chromosorb W. The injector, detector, and column temperatures were always kept below 150 °C. Analytical GLC was performed with a Varian Model 1400 instrument equipped with a ⅛ in. × 15 ft column filled with 15% DC 710 on 80/100 Chromosorb P. Proton magnetic resonance spectra were recorded with a Varian A-60A or HA-100 FT spectrometer with tetramethylsilane as an internal standard and CCl_4 as solvent. Mass spectra were recorded with a Du Pont Model 21-094 GC-MS instrument with an interfaced computer. Microanalyses were performed by Chemalytics, Inc., Tempe, Ariz., and Par-Alexander Labs, South Daytona, Fla.

Materials. Diethyl ether solvent for photolyses was freshly distilled from lithium aluminum hydride under dry nitrogen immediately before use. Bicyclo[4.2.0]oct-1(8)ene (**17**),[10] *unsym*-pentamethyleneallene (**18**),[10] 3-vinylcyclohexene (**19**),[10] 1-vinylcyclohexene (**20**),[10] bicyclo[6.1.0]non-1-ene (**24**),[9] and copper(I) trifluoromethanesulfonate-benzene complex[4] were prepared by known procedures.

7-Methylenebicyclo[4.1.0]heptane (14). A three-neck 250-mL round-bottom flask equipped with a thermometer and serum cap and gas inlet adaptor was charged with 7,7-dibromobicyclo[4.1.0]heptane[8] (5.08 g, 20 mmol), MeI (5.68 g, 40 mmol), hexamethylphosphoric triamide (20 mL), and tetrahydrofuran (100 mL, freshly distilled from potassium benzophenone ketyl). The mixture was stirred magnetically under a blanket of dry nitrogen and cooled with a toluene slush bath (liquid nitrogen). Butyllithium (30 mmol) in hexane (18 mL) was added over 1 h. The resulting mixture was stirred at −45 °C for 40 min and then allowed to warm to room temperature. Ether (50 mL) was added and the solution was washed with water (2 × 150 mL), 10% HCl (2 × 150 mL), water (150 mL), and saturated aqueous $NaHCO_3$ (100 mL), and dried (Na_2SO_4). Distillation gave 7-

bromo-7-methylbicyclo[4.1.0]heptane, bp 80–85 °C (10 mm) (83%).

The bromide (3.7 g, 20 mmol) was added to a magnetically stirred solution of potassium *tert*-butoxide in dimethyl sulfoxide (50 mL, distilled from BaO) with ice-water bath cooling. After the exothermic reaction subsided, the mixture was stirred for 2 h at room temperature and then poured into water (300 mL) and extracted with pentane (2 × 100 mL). The organic solution was washed with water (5 × 100 mL), dried (Na_2SO_4), and distilled to give 7-methylenebicyclo[4.1.0]heptane (63%): bp 49–53 °C (10 mm); NMR (60 MHz) δ 1.1–1.40 (4 H, C-3, 4), 1.40–2.0 (6 H), 5.33 (2 H, t, J = 1.9 Hz, vinyl); mass spectrum (70 eV) *m/e* (rel intensity) 108 (8), 93 (100), 91 (22), 80 (35), 79 (79), 78 (12), 77 (26), 67 (16), 66 (10), 41 (13).

Anal. Calcd for C_8H_{12}: C, 88.82; H, 11.18. Found: C, 88.79; H, 11.12.

7-(Dideuterio)methylenebicyclo[4.1.0]heptane (16). The dideuterio analogue (**16**) of (**14**) was prepared similarly except that 40 mmol of CH_3I was replaced with 30 mmol of CD_3I. NMR (60 MHz) δ 1.1–1.40 (4 H, C-3, 4), 1.40–2.0 (6 H); mass spectrum (70 eV) *m/e* (rel intensity) 110 (11), 95 (100), 94 (38), 93 (42), 82 (58), 81 (77), 80 (60), 79 (52), 78 (27), 77 (17), 69 (21), 68 (16), 67 (23), 66 (16).

8-Methylenebicyclo[5.1.0]octane (15). The procedure of Doering and Hoffmann for the preparation of 7,7-dibromobicyclo[4.1.0]heptane was adapted for the synthesis of 8,8-dibromobicyclo[5.1.0]octane, bp 66–68 °C (0.03 mm), by substituting cycloheptene for cyclohexene in their procedure.[8] The dibromide was converted, as in the synthesis of **14** above, into the methylenecyclopropane (**15**), bp 50–52 °C (8 mm) (58% overall yield from the dibromide). NMR (60 MHz) δ 1.1–2.2 (12 H), 5.22 (2 H, s, vinyl); mass spectrum (70 eV) *m/e* (rel intensity) 122 (13), 107 (75), 105 (23), 94 (74), 93 (96), 92 (23), 91 (58), 81 (65), 80 (72), 79 (100), 78 (45), 77 (45), 68 (49), 67 (63), 66 (30), 65 (22).

Anal. Calcd for C_9H_{14}: C, 88.45; H, 11.55. Found: C, 88.82; H, 11.51.

Photolysis of 14 in the Presence of Copper(I). A solution of **14** (500 mg) and $(CuOTf)_2$-C_6H_6 (170 mg) in ether (15 mL) was irradiated for 12 h, and then poured into 10% NH_4OH (30 mL) and extracted with ether (2 × 20 mL). The combined extracts were washed with water (20 mL) and dried (Na_2SO_4). After removal of solvent by distillation, the products were separated by preparative GLC with a column temperature of 95 °C. Relative retention times follow: cyclohexene (**1**), 16; *n*-octane, 23; 3-vinylcyclohexene (**19**), 42; bicyclo[4.1.0]oct-1(8)-ene (**17**), 54; 7-methylenebicyclo[4.1.0]heptane (**14**), 59; *unsym*-pentamethyleneallene (**18**), 67; 1-vinylcyclohexene (**20**), 76. These products were characterized by the identity of their GLC retention times and ^{1}H NMR spectra with those of authentic samples.[10]

Bicyclo[4.1.0]oct-1(8)-ene (17). NMR (100 MHz) δ 0.76–1.28 (2 H), 1.28–2.76 (9 H), 5.43 (1 H, s, vinyl); mass spectrum (70 eV) *m/e* (rel intensity) 108 (41), 93 (77), 91 (21), 80 (26), 79 (100), 78 (15), 77 (31), 74 (29), 67 (20), 65 (14), 59 (38), 45 (20), 41 (20).

***unsym*-Pentamethyleneallene (18).** NMR (100 MHz) δ 1.53 (6 H, s), 2.07 (4 H, s, allylic), 4.45 (2 H, quintet, J = 2.4 Hz, vinylic); mass spectrum (70 eV) *m/e* (rel intensity) 108 (100), 94 (12), 93 (92), 91 (37), 80 (33), 79 (68), 78 (21), 77 (46), 74 (19), 67 (26), 65 (16), 59 (23).

3-Vinylcyclohexene (19). NMR (100 MHz) δ 1.1–2.1 (6 H), 2.72 (1 H, C-3), 4.92 (1 H, d, J = 11 Hz, terminal vinyl), 5.00 (1 H, d, J = 6 Hz, terminal vinyl), 5.3–5.9 (3 H, m, vinyl).

1-Vinylcyclohexene (20). NMR (100 MHz) δ 1.63 (4 H, C-4, 5), 2.10 (4 H, C-3, 6), 4.80 (1 H, d, J = 10 Hz, terminal vinyl), 4.94 (1 H, d, J = 16 Hz, terminal vinyl), 5.66 (1 H, C-2 vinyl), 6.22 (1 H, dd, J = 10 and 16 Hz).

The ratio of products from **14** was monitored by removing aliquots (100 μL) from the reaction mixture periodically. The aliquots were shaken with ether (1 mL) and 10% NH_4OH (2 mL). The resulting copper-free organic solution was analyzed by GLC for products and starting material (which were all stable under the conditions of analysis) with *n*-octane as internal standard.

Acetylene. The photolysis of **14** was performed in a quartz tube 14 × 0.5 cm fitted with a stopcock 2 cm from the top with a rubber serum cap on the top. After photolysis to 18% completion (24 h) with the stopcock closed, the sample was cooled to −78 °C, the stopcock opened, and an excess of aqueous KCN added. After closing the stopcock, warming to room temperature, and shaking well, the mixture was again cooled to −78 °C, the stopcock opened, and a sample removed for analysis on a 5 ft × 1/8 in. Porapak Q column (temperature programmed 30–230 °C at a rate of 20 °C/min). Retention times obtained follow: acetylene, 0.9 min; ethyl ether, 3.9 min; benzene and cyclohexene, 5.3 min; and methylenenorcarane, 7.8 min. Yields were obtained by peak weighing, after calibration of the flame ionization VPC for the different response to acetylene and methylenenorcarane. Acetylene was formed in 13% yield based on reacted starting material, and cyclohexene in 67% yield.

Photolysis of 16 in the Presence of Copper(I). The d_2-methylenecyclopropane **16** was photolyzed in the presence of $(CuOTf)_2 \cdot C_6H_6$ as for **14** above. The ^{1}H NMR spectra of the **18**-d_2, **19**-d_2, and **20**-d_2 obtained allowed unambiguous assignment of the positions of deuterium labeling.

3,3-Dideuterio-1,1-pentamethyleneallene (18-d_2). NMR (60 MHz) δ 1.55 (6 H), 2.10 (4 H); mass spectrum (70 eV) *m/e* (rel intensity) 110 (58), 96 (16), 95 (36), 94 (17), 93 (28), 82 (18), 81 (32), 80 (21), 79 (30), 78 (18), 74 (38), 67 (14), 59 (50), 45 (35), 44 (17), 43 (14), 41 (27).

3-(β,β-Dideuterio)vinylcyclohexene (19-d_2). NMR (100 MHz) δ 1.0–2.2 (6 H), 2.72 (1 H, C-3), 5.4–5.8 (3 H, nonterminal vinyl).

1-(β,β-Dideuterio)vinylcyclohexene (20-d_2). NMR (100 MHz) δ 1.63 (4 H, C-4, 5), 2.10 (4 H, C-3, 6), 5.66 (1 H, s, C-2 vinyl), 6.20 (1 H, s, α vinyl). The ^{1}H NMR spectrum of the **17**-d_2 obtained did not allow unambiguous assignment of the position of deuterium.

Bicyclo[4.1.0]oct-1(8)ene-d_2. NMR (100 MHz) δ 0.76–1.28 (2 H), 1.28–2.76 (7 H), 5.43 (1 H, s, vinyl); mass spectrum (70 eV) *m/e* (rel intensity) 108 (2), 100 (41), 96 (16), 95 (49), 94 (39), 93 (37), 82 (31), 81 (50), 80 (47), 79 (78), 78 (31), 74 (52), 69 (16), 67 (14), 59 (64), 45 (44), 41 (26). This material was shown to be **7,7-dideuteriobicyclo[4.1.0]oct-1(8)ene (17-d_2)** by conversion to **20**-d_2 upon vapor phase pyrolysis in a sealed tube.

Degradative Analysis of Cyclohexene from 16. The partially deuterated cyclohexene (40 mg) (see text), obtained in the photolysis of the d_2-methylenecyclopropane **16**, in acetic acid (1 mL) and formic acid (0.5 mL) was stirred magnetically while an excess of ozone was bubbled through the reaction mixture at 0 °C. Then 30% hydrogen peroxide (1 mL) was added and the resulting mixture was boiled under reflux for 2 h. The product was extracted into ether (2 × 20 mL). The extract was washed with water and then extracted with saturated aqueous Na_2CO_3. After acidification of the aqueous extract with HCl, the product was taken up into ether (20 mL). The ether solution was dried ($MgSO_4$), and then treated with an excess of an ether solution of diazomethane. Solvent was removed by rotary evaporation to yield dimethyl succinate (85%) which exhibits a mass spectrum and ^{1}H NMR spectrum identical with that of deuterium-free, authentic dimethyl succinate.

Photolysis of 15 in the Presence of Copper(I). The methylenecyclopropane **15** was photolyzed in ether solution in the presence of $(CuOTF)_2 \cdot C_6H_6$ as for **14** above. The products were separated by preparative GLC with a column temperature of 120 °C. Relative retention times follow: cycloheptene (**21**), 0.27; cyclooctane, 0.63; 8-methylenebicyclo[5.1.0]octane (**15**), 1.00; bicyclo[5.2.0]non-1(9)ene (**22a**), 1.00; bicyclo[5.2.0]non-1-ene (**22b**), 1.17; *unsym*-hexamethyleneallene (**23**), 1.28; bicyclo[6.1.0]non-1-ene (**24**), 1.40. Cycloheptene (**21**) and bicyclo[6.1.0]non-1-ene (**24**) were characterized by the identity of their GLC retention times and ^{1}H NMR spectra with those of authentic samples[9] which were stable under the conditions of GLC analysis.

Bicyclo[6.1.0]non-1-ene (24). Mass spectrum (70 eV) *m/e* (rel intensity) 122 (25), 107 (64), 94 (61), 93 (89), 92 (12), 91 (38), 81 (59), 80 (65), 79 (100), 78 (15), 77 (36), 68 (43), 67 (54), 66 (21), 65 (14), 55 (16), 54 (15), 53 (29).

Though the starting material **15** and product **22a** were not separable by GLC, essentially pure **22a** was isolated from a photolysis reaction mixture which was produced after prolonged irradiation. The structures of the products **22a** and **22b** were assigned by spectral and GLC comparison with samples prepared by an unambiguous synthesis (vide infra) and in light of ^{1}H NMR spectral similarities between **22a** and the homologous bicyclic cyclobutene **17**. Both **22a** and **22b** were stable under the conditions of GLC analysis of the reaction product mixtures, though **22a** rearranged to **26** if the injector temperature was too high. Thus, the structure of **22a** was further confirmed by rearrangement upon vapor phase pyrolysis in a sealed tube (200 °C, 1 h) which gave compound **26**.

1-Vinylcycloheptene (26). NMR (100 MHz) δ 1.4–1.8 (6 H, C-4, 5, 6), 2.2 (4 H, C_3, 7), 4.82 (1 H, d, J = 11 Hz, trans-β-vinyl), 4.99

(1 H, d, $J = 17$ Hz, cis-β-vinyl), 5.79 (1 H, t, $J = 6$ Hz, C-2), 6.20 (1 H, dd, $J = 11, 17$ Hz, α-vinyl).

Anal. Calcd for C_9H_{14}: C, 88.45; H, 11.55. Found: C, 88.38; H, 11.50.

The structure of **23** was assigned on the basis of the similarity of its ^{1}H NMR spectrum with that of the homologous compound **18.**

***unsym*-Hexamethyleneallene (23).** NMR (100 MHz) δ 1.56 (8 H, s), 2.19 (4 H, allylic), 4.44 (2 H, quintet, $J = 2.4$ Hz, vinyl); mass spectrum (70 eV) *m/e* (rel intensity) 122 (100), 107 (53), 94 (54), 93 (73), 91 (32), 81 (58), 80 (51), 79 (97), 78 (14), 77 (35), 68 (50), 67 (44), 66 (15), 65 (12).

Anal. Calcd for C_9H_{14}: C, 88.45; H, 11.55. Found: C, 88.29; H, 11.62.

Synthesis of Bicyclo[5.2.0]nonenes. Bicyclo[5.2.0]nonan-8-one, prepared by the reported method[20] (3.0 g, 21 mmol), in dry methanol (50 mL) was cooled with an ice-salt bath and stirred magnetically. Sodium borohydride (0.6 g) was added in small portions over a period of 5 min. Then the mixture was warmed to room temperature and stirred for 10 h. Excess 2 N HCl was added to destroy excess hydride and the solvent was removed by rotary evaporation. The residue was taken up in water (20 mL) and the resulting mixture was extracted with ether (2 × 20 mL). The extract was washed with saturated aqueous $NaHCO_3$ (20 mL) and saturated aqueous NaCl (20 mL) and dried (Na_2SO_4). Solvent was stripped by rotary evaporation and the residual oil distilled to give the alcohol (2.5 g) in 83% yield: bp 123–128 °C (10 mm); ^{1}H NMR (60 MHz) δ 0.9–3.2 (15 H), 4.10 (1 H, q, $J = 7$ Hz, C-8).

A solution of this alcohol (2.5 g, 17.6 mmol) and methanesulfonyl chloride (2.0 g, 1.37 mL, 17.6 mmol) in methylene chloride (5 mL) was treated with pyridine (2.87 g, 3.0 mL, 37 mmol) dropwise over 30 min with magnetic stirring and ice-methanol bath cooling. Stirring was continued at 0 °C for 3 h. The resulting mixture was poured into ice-cold 10% HCl (25 mL) and extracted into ether (40 mL). The extract was washed with water (2 × 20 mL) and saturated aqueous $NaHCO_3$ (20 mL) and dried (Na_2SO_4). Solvent was stripped by rotary evaporation to give crude methanesulfonate **25:** ^{1}H NMR (60 MHz) δ 0.8–2.8 (14 H), 2.90 (3 H, s, CH_3), 4.89 (1 H, q, $J = 7$ Hz, C-8). This unstable product could not be purified by distillation and decomposed upon standing at room temperature for several days, and was therefore used immediately after preparation for the synthesis of the desired olefins.

The methanesulfonate **25** from 2.5 g (17.6 mmol) of the alcohol was added to a suspension of potassium *tert*-butoxide (11 g, 0.1 mol) in dry dimethyl sulfoxide (100 mL). The mixture was stirred at room temperature for 15 h. Then it was poured into ice water (200 mL) and the product was extracted into pentane (3 × 50 mL). The organic extracts were washed with water (3 × 50 mL) and dried (Na_2SO_4). Solvent was removed by distillation at atmospheric pressure and the residue was distilled under reduced pressure to give an approximately 1:1 mixture of bicyclo[5.2.0]nonenes **22a** and **22c** (1.4 g) in 65% overall yield from the alcohol, bp 58–71 °C (10 mm). Pure samples of the isomeric olefins were obtained by preparative GLC.

Bicyclo[5.2.0]non-1(9)-ene (22a). ^{1}H NMR (100 MHz) δ 1.0–2.5 (12 H), 1.6–1.8 (1 H, C-7), 5.56 (1 H, s, C-9 vinyl).

Anal. Calcd for C_9H_{14}: C, 88.45; H, 11.55. Found: C, 88.44; H, 11.64.

Bicyclo[5.2.0]non-8-ene (22c). ^{1}H NMR (100 MHz) δ 1.1–1.9 (10 H, C-2, 3, 4, 5, 6), 2.89 (2 H, d, $J = 11$ Hz, C-1, 7 allylic), 6.00 (2 H, s, C-8, 9 vinyl).

Anal. Calcd for C_9H_{14}: C, 88.45; H, 11.55. Found: C, 88.48; H, 11.49.

Bicyclo[5.2.0]non-1-ene (22b). The olefin **22a** (30 mg) and potassium *tert*-butoxide (200 mg) in dimethyl sulfoxide (5 mL) was stirred magnetically at 40 °C. After 3 h, 0.1 mL of the solution was added to 5 mL of water and the product extracted into pentane. GLC analysis of the resulting solution indicated an exactly 1.00:1.00 ratio of starting material **22a** to product **22b.** After 41 h, the entire reaction mixture was poured into ice water (30 mL) and the product was extracted into pentane (3 × 10 mL). The organic solution was washed with water (3 × 10 mL) and dried (Na_2SO_4). GLC analysis indicated a ratio of 0.10:1.00 for **22a** and **22b,** respectively. Solvent was removed by distillation at atmospheric pressure. A pure sample of **22b** was obtained by preparative GLC: ^{1}H NMR (100 MHz) δ 1.0–2.7 (12 H), 2.7–3.1 (1 H, C-7 allylic), 5.21 (1 H, t, $J = 2.4$ Hz, C-2 vinyl); mass spectrum (70 eV) *m/e* (rel intensity) 122 (54), 107 (72), 94 (66), 93 (94), 92 (13), 91 (39), 81 (58), 80 (68), 79 (100), 78 (21), 77 (41), 68 (43), 67 (57), 66 (28), 65 (19), 55 (19), 54 (20), 53 (32).

Anal. Calcd for C_9H_{14}: C, 88.45; H, 11.55. Found: C, 88.34; H, 11.53.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the Research Corporation for support of this research. We thank Professor M. S. Newman and Dr. V. J. Lee for spectra of *unsym*-pentamethyleneallene. We thank Professor J. D. Roberts for stimulating discussions.

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