ml) was treated with an anhydrous solution (50 μl) of $AgClO_4$ in benzene (0.179 *M*) and heated at 40° for 15 hr. Work-up as before and vpc analysis revealed the presence of **48** (83.1%), **49** (3.9%), **50** (6.3%), and **51** (6.7%). *In situ* pmr analysis of the reaction mixture showed **48** and **49** to lack the vinyl ether absorptions at δ 5.88 and 4.31 (for **48**) and 6.34 and 4.74 (for **49**); no evidence for $-CH_2O-$ absorption for **50** and **51** was detected. For **48** *m/e* 140.1172 (calcd for $C_9H_{12}D_2O$ *m/e* 140.1170).

Acknowledgment. Support of this work by the National Science Foundation is gratefully acknowledged.

Stereospecificity and Regioselectivity Attending Type γ Rearrangement of 1,3-Disubstituted Tricyclo[4.1.0.0^{2,7}]heptanes under Conditions of Ag(I) Catalysis[1]

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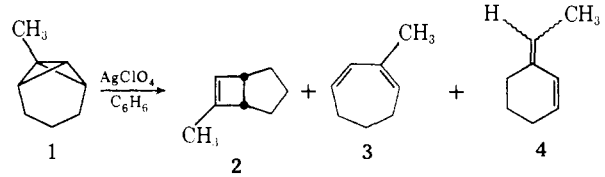
Abstract: To probe the stereospecificity and regioselectivity of the type γ process, Ag(I)-catalyzed rearrangement of the 1,3-dimethyl- and 3-methoxy-1-methyltricyclo[4.1.0.0^{2,7}]heptane epimeric pairs has been studied. All four strained ring compounds undergo high levels of type γ isomerization leading predominantly to substituted bicyclo[3.2.0]hept-6-ene products. By independent synthesis, we have assigned structures to these products. Analysis of the data reveals that the stereoproximally substituted tricycloheptanes give rise only to 2-*exo*-bicycloheptenes while the stereodistal pair isomerizes uniquely to 2-endo isomers. In addition to its overwhelming stereoselectivity, the title rearrangement is also notably regioselective, the 6-methyl isomers arising 1.5 (in the dimethyl series) to 4.0 (for the 3-methoxyl pair) more rapidly than their 7-methyl counterparts. The study thus furnishes the first stereochemical insight into this particular transition metal catalyzed transformation. Several mechanistic inferences are derived.

Although 1-methyltricyclo[4.1.0.0^{2,7}]heptane (**1**) is isomerized 2.2 times faster than the parent hydrocarbon by $AgClO_4$ in anhydrous benzene at 40°,[3] the role of the methyl substituent is far greater than providing small kinetic acceleration. Whereas tricyclo[4.1.0.0^{2,7}]heptane rearranges exclusively by the type α pathway[1] to give 1,3-cycloheptadiene in quantitative yield, **1** affords chiefly **2** (44%) together with **3** (26%) and **4** (29%, syn/anti = 4:1) under identical conditions.[3] Adherence to second-order kinetics and analysis of deuterium isotope effects in these reactions[4] have contributed to formulation of simplified mechanisms for these rearrangements. There now exists appreciable data to support the mechanistic interpretations advanced for the α and β isomerization processes.[1,4,5]



Later stereochemical investigations[6] as well as more recent kinetic and product studies[1] have shown, however, that the original concept of the γ bond reorganization[4,7] were oversimplified and equivocal.

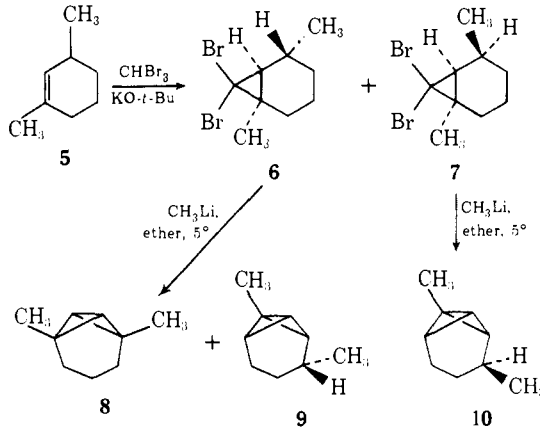
One of the more powerful ways to study a rearrangement reaction is to gain evidence relating to the stereochemistry of the process. Owing to the requirement that an alkyl group be positioned at C_1 of the tricycloheptane nucleus to effectuate the γ rearrangement, structural variation was relegated to the available positions on the trimethylene bridge. Our interest centered specifically on 1,3-disubstituted tricycloheptanes because of their relative accessibility, the possibility of establishing with minimal difficulty the structures of the anticipated bicyclo[3.2.0]hept-6-ene (type γ) products, and, most importantly, their potential ability to distinguish between several possible isomerization pathways. Furthermore, the C_3 substituents are positioned sufficiently remote from the bicyclobutane part structure so that direct perturbation of the usual transitory intermediates was not expected. We now detail experimental evidence showing that such labeling of the tricycloheptane framework unveils the *complete* stereoselectivity and *moderate* regioselectivity of the type γ rearrangement. Other phenomena which have an effect on this particular isomerization pathway and a comprehensive mechanistic profile are to be considered in the ensuing paper.[8]

(1) Silver(I) Ion Catalyzed Rearrangements of Strained σ Bonds. XXI. The previous paper is L. A. Paquette and G. Zon, *J. Amer. Chem. Soc.*, **96**, 203 (1974).
(2) National Institutes of Health Postdoctoral Fellow, 1972–1973.
(3) (a) L. A. Paquette, S. E. Wilson, R. P. Henzel, and G. R. Allen, Jr., *J. Amer. Chem. Soc.*, **94**, 7761 (1972); (b) L. A. Paquette, R. P. Henzel, and S. E. Wilson, *ibid.*, **93**, 2335 (1971).
(4) (a) L. A. Paquette, S. E. Wilson, and R. P. Henzel, *J. Amer. Chem. Soc.*, **94**, 7771 (1972); (b) L. A. Paquette and S. E. Wilson, *ibid.*, **93**, 5934 (1971).
(5) (a) M. Sakai and S. Masamune, *J. Amer. Chem. Soc.*, **93**, 4610 (1971); (b) M. Sakai, H. H. Westberg, H. Yamaguchi, and S. Masamune, *ibid.*, **93**, 4611 (1971).
(6) G. Zon and L. A. Paquette, *J. Amer. Chem. Soc.*, **95**, 4456 (1973).
(7) P. G. Gassman and T. J. Atkins, *J. Amer. Chem. Soc.*, **94**, 7748 (1972).
(8) L. A. Paquette and G. Zon, *J. Amer. Chem. Soc.*, **96**, 224 (1974).

Results

Synthesis. Preparation of the isomeric 1,3-dimethyltricycloheptanes **9** and **10** was effected by a method modeled on the synthesis of the parent ring system.[9] Treatment of 1,3-dimethylcyclohexene (**5**) with dibromocarbene gave a 66:34 mixture of *anti*- (**6**) and *syn*-1,5-dimethyl-7,7-dibromobicyclo[4.1.0]heptanes (**7**),[3a] preparative vpc separation of which was realized with the use of UCON 50HB 2000 Polar stationary phase (Chart I). The stereochemical assignments to **6** and **7**

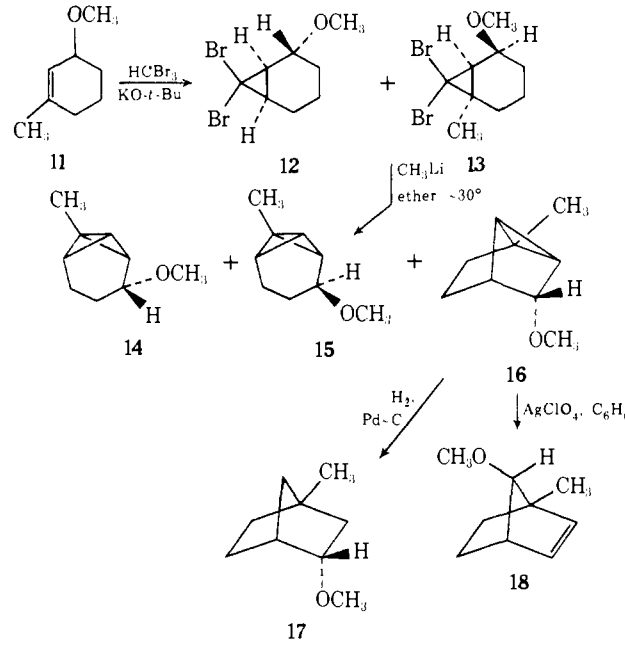
Chart I. Synthesis of the Isomeric 1,3-Dimethyltricyclo[4.1.0.0^{2,7}]heptanes



follow from steric considerations anticipated for the :CBr_2 addition[10] and from the subsequent intramolecular cyclization reactions of the individual isomers. When exposed to ethereal methyllithium at 5°, **6** was transformed into a 90:10 mixture of tricycloheptanes **8**[3a] and **9**. Owing to the very rapid rate of silver(I)-catalyzed rearrangement of **8** in benzene (exclusive type α isomerization to give 1,4-dimethyl-1,3-cycloheptadiene[3a]), treatment of the mixture of carbenoid insertion products with $AgClO_4$ under controlled conditions led to isolation of pure **9** after separation from the cycloheptadiene. Starting with **7**, a high level of stereoselectivity was observed in the ring closure, with the result that the distal isomer **10** was produced in good yield. The structural assignments are supported by pmr data. As expected,[3,4] the pair of spectra reflect a number of similarities with H_2 and H_6 being the most strongly deshielded protons and the bridgehead methyl singlet absortion appearing downfield of the C_3 methyl doublet.

Following the same procedure, 3-methoxy-1-methylcyclohexene (**11**) was treated with dibromocarbene to give a 95:5 mixture of dibromonorcaranes **12** and **13**.[10] When an ethereal solution of this mixture was treated with methyllithium at −30°, dehalogenation occurred with formation of a trio of methyl ethers (Chart II). The major component (67%) was identified as **14** on the basis of its pmr spectrum. In particular, the presence of the tricyclo[4.1.0.0^{2,7}]heptane nucleus was supported by the appearance of multiplets of area 1 each at δ 2.54–2.23 and 2.23–1.93 due to the two dissimilar "wing" protons and at 1.23–0.89 due to the bridgehead hydrogen.[3,4] The minor product (5%) was identified as **15** as a result of the similarities of its pmr features to those of **14**. Spectral differentiation between the isomers can be achieved principally on the basis of the chemical shift (in C_6D_6) of the C_1-methyl singlet in **15** which appears δ 0.04 upfield relative to the corresponding peak in **14**.

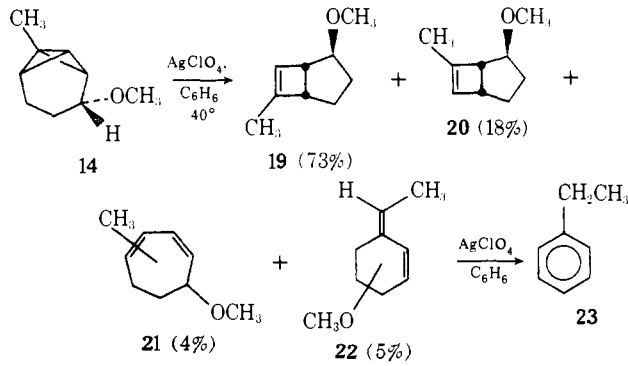
Chart II. Synthesis of the Isomeric 3-Methoxy-1-methyltricyclo[4.1.0.0^{2,7}]heptanes



The third substance (28%) was established as the product of carbenoid C–H insertion into the syn C_4–H bond by its very characteristic pmr features and chemical degradation.[11,12] When subjected to catalytic hydrogenation over Pd/C in ethanol at 1 atm, for example, **16** was transformed quantitatively to *endo*-1-methyl-3-methoxynorbornane (**17**). Additionally, **16** experiences ready Ag^+-promoted isomerization to **18**.

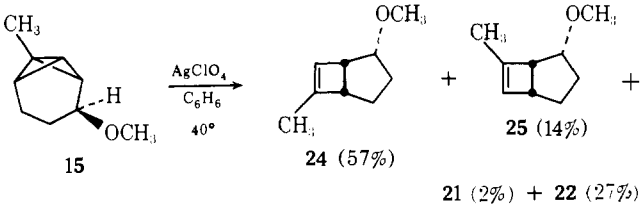
Isomerization of the Epimeric 3-Methoxy-1-methyltricycloheptanes. The results of the $AgClO_4$-promoted rearrangement of **14** and **15**, shown in Charts III and IV, respectively, give immediate recognition of the fact that the type γ pathway is significantly favored. Scrutiny of the relative product distribution from **15** *vs.* time revealed the percentage composition to remain essentially invariant during most of the reaction. However, after approximately 2 half-lives, four additional

Chart III. Products of the Ag^+-Catalyzed Isomerization of **14**



(9) W. R. Moore, H. R. Ward, and R. F. Merritt, *J. Amer. Chem. Soc.*, **83**, 2019 (1961).
(10) D. Seyferth and V. A. Mai, *J. Amer. Chem. Soc.*, **92**, 7412 (1970).
(11) L. A. Paquette and G. Zon, *J. Amer. Chem. Soc.*, **94**, 5096 (1972).
(12) Full details of the chemical degradation of **16** and its behavior toward Ag^+ catalysis will appear elsewhere.

Chart IV. Products of the Ag^+-Catalyzed Isomerization of **15**



15 **24** (57%) **25** (14%) 21 (2%) + **22** (27%)

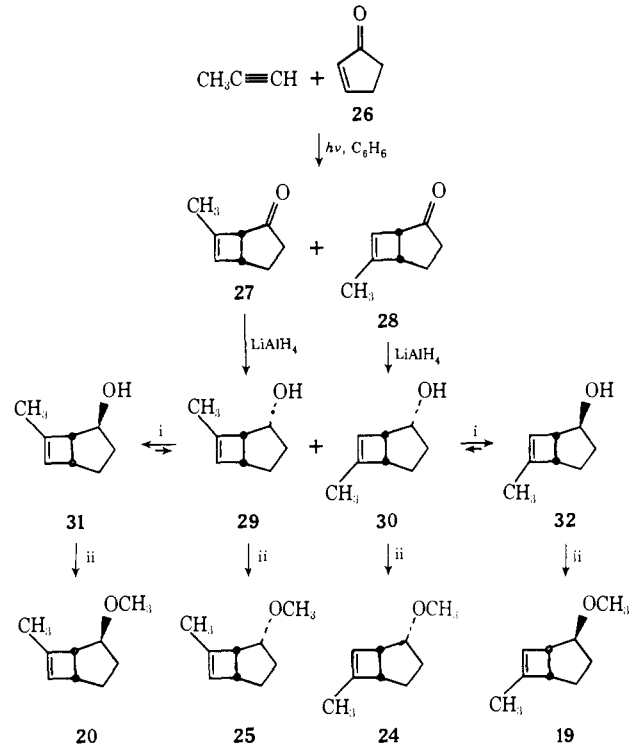
minor components made their appearance. These substances are believed to be secondary reaction products arising from further Ag^+ (or H^+) catalyzed rearrangement of the mixture initially produced. This suggestion was tested in the case of **22** which afforded ethylbenzene upon prolonged exposure to the reaction conditions. This precedented[11,13] transition metal promoted elimination of methanol substantiates further the structural assignment for **22**.

Significantly, the four isomeric bicyclo[3.2.0]heptenes **19**, **20**, **24**, and **25** proved stable to the medium utilized in their production. Accordingly, we conclude that they are formed under conditions of kinetic control. Independent synthesis of these diastereomers was achieved in moderate yield by extension of a photochemical reaction studied by Eaton[14] who found that photoexcited conjugated cyclic ketones are prone toward 2 + 2 cycloaddition to alkynes. When 2-cyclopentenone (**26**) was irradiated with propyne in benzene solution (450-W Hanovia lamp, Pyrex optics), two major products characterized as **27** and **28** were formed (Chart V).[15] Lithium aluminum hydride reduction of the individual ketones proceeded with steric approach control[17] to give endo alcohols **29** and **30**. The degree of stereospecificity was $\geq 95\%$ in favor of exo hydride delivery. The gross structures are consistent with the spectral evidence and their equilibration[18] to mixtures enriched in the exo counterparts upon treatment with aluminum isopropoxide in isopropyl alcohol containing acetone at 105–110°. For the isomer pair **31**/**29** the observed ratio was 59:41, whereas **32** and **30** were partitioned to a greater extent (78:22).[19]

The 60-MHz pmr spectra for each pair of *exo*- and *endo*-2-methoxybicycloheptenes exhibited strikingly different absorption patterns for the downfield 2-methine proton, as a consequence of the differences in dihedral angle relationships to H_1 and the methylene proton pair at C_3.[20] The relevant signal for **19** and **20** was seen as a somewhat broadened "singlet" while that arising from **24** and **25** appeared as a wide-spaced multiplet.[21]

(13) G. Zon, unpublished observations.
(14) P. E. Eaton, *Accounts Chem. Res.*, **1**, 50 (1968).
(15) This same photocycloaddition has been carried out a number of years ago by Professor Eaton and we thank him for his helpful comments regarding the structural assignments.[16]
(16) See also K. E. Hine and R. F. Childs, *J. Chem. Soc., Chem. Commun.*, 145 (1972).
(17) H. C. Brown and J. Muzzio, *J. Amer. Chem. Soc.*, **88**, 2811 (1966), and references cited therein.
(18) L. A. Paquette, G. V. Meehan, and S. J. Marshall, *J. Amer. Chem. Soc.*, **91**, 6779 (1969), and relevant references listed therein.
(19) No attempt was made to determine whether or not these mixtures represent equilibrium values.
(20) L. A. Paquette, *Tetrahedron Lett.*, 2027 (1963); *J. Amer. Chem. Soc.*, **86**, 500 (1964); O. L. Chapman and E. D. Hoganson, *ibid.*, **86**, 498 (1964).
(21) The greater signal width in those isomers having cis-oriented H_1/H_2 stereochemistry arises chiefly from the dihedral angle relationship of these two protons (0°) which will expectedly[22] give rise to an estimated coupling constant of 8–9 Hz. In contrast, the much larger dihedral angle (~109°) which exists when these same protons are transfused will result in a spin–spin interaction of only 1–3 Hz.

Chart V. Independent Synthesis of the Diastereomeric 2-Methoxy-6- and -7-methylbicyclo[3.2.0]hept-6-enes



i = $Al(i\text{-}C_3H_7O)_3$, $i\text{-}C_3H_7OH$, $(CH_3)_2CO$, 105–110°
ii = (1)NaH, DMF; (2)CH_3I

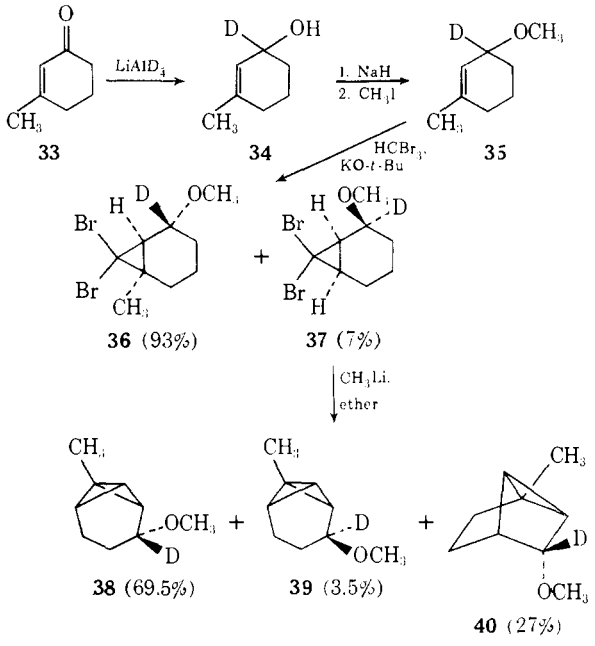
Compound **20** may further be differentiated from **19** by the chemical shift of its 2-methine hydrogen which is downfield shifted relative to that in **19** by 5 Hz. In addition, differentiation between all four isomers was possible by gas chromatographic techniques, and the latter were used extensively to define product composition.

To establish that **14** and **15** were not experiencing rearrangement by a Ag(I)-assisted methoxyl group ionization mechanism,[11] the isotopically labeled tricycloheptanes **38** and **39** were prepared (Chart VI). The products derived by rearrangement of **38** were separated and shown not only to be present in the same relative proportions as found with **14** but also to exhibit pmr spectra indicating that the methoxyl substituent had remained bonded to the isotopically labeled carbon in all cases. Insufficient quantities of **39** were available to permit spectral characterization of its individual rearrangement products. By analogy, however, it would seem that initial reaction of **39** with Ag^+ at C_3 is also contraindicated.

Rearrangement of the Epimeric 1,3-Dimethyltricycloheptanes. Isomerization of stereoproximal tricycloheptane **9** gave rise to six new hydrocarbons, the two major components of which were identified as the dimethylbicyclo[3.2.0]hept-6-enes **41** and **42** by means of pmr and vpc retention time comparisons with authentic samples prepared by photoisomerization of independently prepared 1,3-cycloheptadienes **43** and **44** (Chart VII). Realization that authentic, well-characterized samples of these dienes were required brought into being a study in which all possible isomeric 1,3- and 1,4-dimethyl substituted conjugated cycloheptadienes were synthesized. This was achieved by

(22) M. Karplus, *J. Chem. Phys.*, 30, 11 (1959).

Chart VI. Synthesis of Deuterium Labeled (3-*d*) 3-Methoxy-1-methyltricyclo[4.1.0.0^{2,7}]heptanes

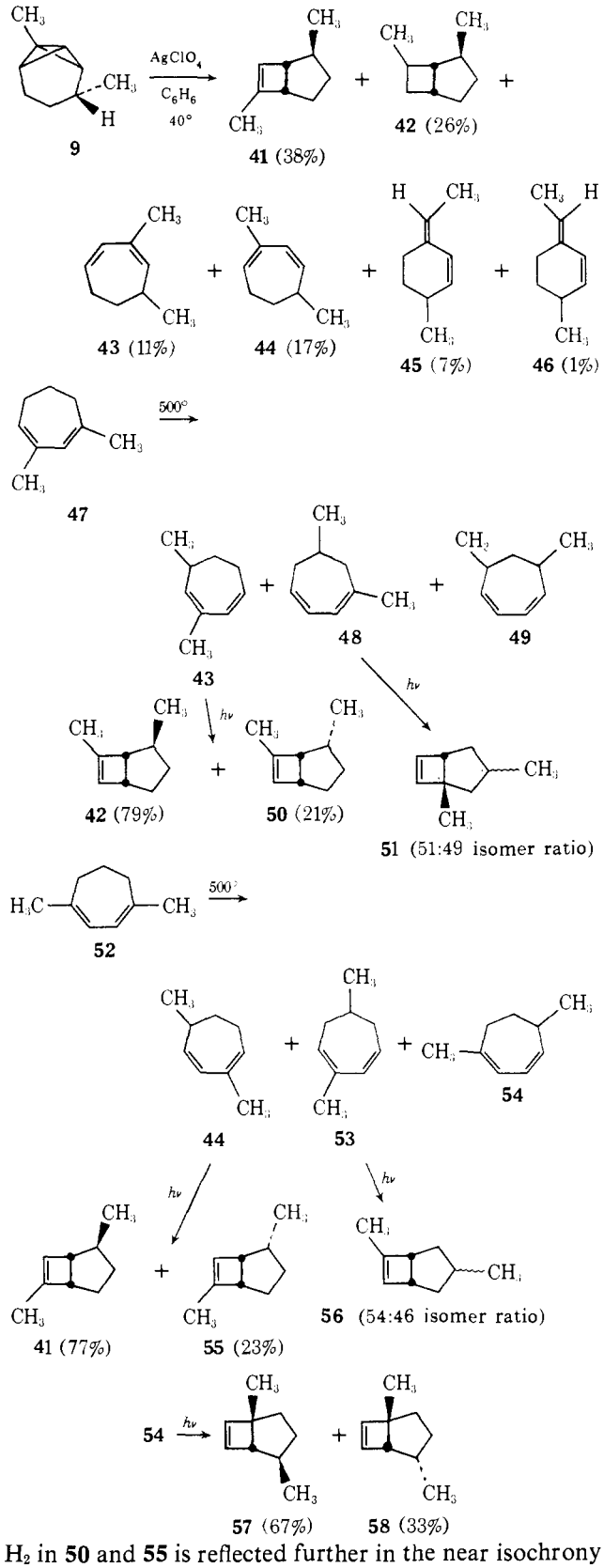


thermolyzing 1,3- (**47**) and 1,4-dimethylcycloheptdienes (**52**)[3a] (500°, gas phase) to induce 1,5-sigmatropic hydrogen migration. When short contact times (1–2 sec) were employed, pyrolysis of **47** was found to return 55% unchanged starting material and to give three additional isomers: **43** (12%), **48** (33%), and **49** (<1%). Hydrocarbon **48** displays a pmr spectrum featuring three olefinic protons, four allylic hydrogens, and the expected sp^2- and sp^3-bound methyl groups; its photoisomerization gave bicycloheptene **51**. The presence of three rather than four allylic protons in the pmr spectrum of **43** was uniquely consistent with the 2,7-dimethyl substitution pattern; irradiation of this diene afforded expectedly a pair of 2,7-dimethylbicycloheptenes. Like pyrolysis of **52** led to **52** (45%), **44** (12%), **53** (19%), and **54** (24%). Separation and characterization were again achieved by vpc methods, photochemical valence bond isomerization, and pmr analysis.

The configurational assignments to **41**, **42**, **50**, and **55** are founded on the following interpretation of rather distinctive pmr features. The two methyl groups in **50** and **55** are downfield shifted by *ca.* 0.28 ppm relative to those in **42** and **41**, respectively, and therefore are of the same configuration. Because the substituents at C_2 necessarily occupy pseudoaxial or pseudoequatorial orientations, these deshielding effects alone prove difficult to interpret. To illustrate, downfield shifts have been noted for equatorial substituents on cyclohexane rings, quasiaxial groups on cyclohexadiene rings, and R groups in *exo*-2-norbornyl derivatives.[23] Diagnostic structural information does follow from the fact that the 2-methyl signals for **50** and **55** are not clean doublets but mutliplets, consistent with virtual coupling of H_2 with the eclipsing H_1. In exo compounds **41** and **42**, H_1 and H_2 are orthogonal and accordingly give rise to a sharp doublet for the 2-methyl hydrogens (Table I).[24] The proximal nature of H_1 and

(23) L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, London, 1959.

Chart VII. Products of the Ag$^+$-Catalyzed Isomerization of **9**



H_2 in **50** and **55** is reflected further in the near isochrony (*ca.* 0 ppm) of their *bridgehead* protons as compared to the relatively large chemical shift differences (0.30–0.46 ppm) between these protons in **41** and **42**.[25]

(24) J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Pergamon Press, London, 1966, pp 814–816. We thank a referee for his comments on this subject.

(25) A likely consequence of the more comparable local environments of the two bridgehead protons in the endo series.

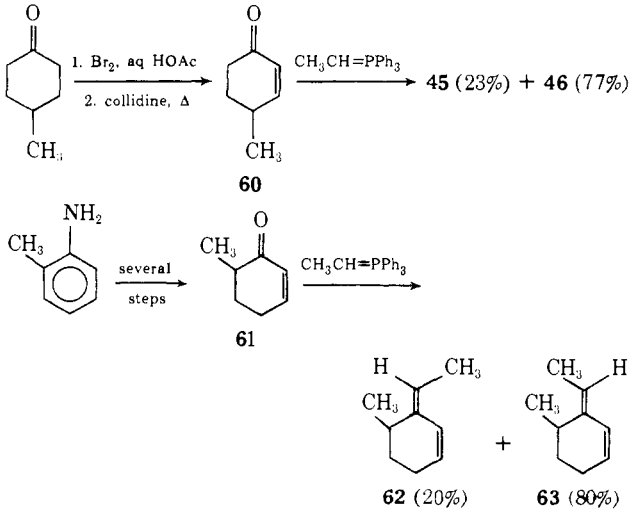
Table I. Experimental Data for Bicyclo[3.2.0]hept-6-ene Products Derived from Photoisomerization of the Dimethyl-1,3-cycloheptadienes

Diene	Bicycloheptenes[a] Structure	Rel %	Vpc column[b]	Vpc conditions	Nmr data, δ
43	**42**	79	N	100°, 60 ml/min t_r = 16.7 min	(C_6D_6) 5.49 (br s with additional splitting, 1, olefinic), 3.06 (v br s, 1, bridgehead), 2.60 (br s, 1, bridgehead), 2.06–1.70 (m, 2), 1.46 (br s with additional splitting, 3, CH_3C=), 1.56–1.10 (m, 3), and 0.75 (d, J = 7 Hz, 3, >CHCH_3)
	50	21		t_r = 19.1 min	(C_6D_6) 5.62 (br s with additional splitting, 1, olefinic), 3.10–2.80 (m, 2, bridgeheads), 2.06–0.86 (m, 5), 1.61 (br s, 3, CH_3C=), and 1.04 (m, 3, >CHCH_3)
48	**51a**	51	N	100°, 60 ml/min t_r = 10.2 min	(C_6D_6) 5.83 (apparent s, 2, olefinic), 2.64 (d, J = 7 Hz, 1, bridgehead), 2.50–1.85 (m, 1, >CHCH$_3$), 1.25 (s, 3, bridgehead methyl), 0.99 (d, J = 7 Hz, 3, >CHCH_3), and 1.85–0.47 (m, 4, methylene)
	51b	49		t_r = 12.2 min	(C_6D_6) 6.05 (apparent s, 2, olefinic), 2.82–2.55 (m, 1, bridgehead), 2.53–2.05 (m, 1, >CHCH$_3$), 1.25 (s, 3, bridgehead methyl), 1.09 (d, J = 7 Hz, 3, >CHCH_3), and 2.05–0.95 (m, 4, methylene)
53	**56a**	54	N	100°, 60 ml/min t_r = 17.3 min	($CDCl_3$) 5.69 (br s with additional splitting, 1, olefinic), 3.18–2.86 (m, 2, bridgeheads), 2.42–1.95 (m, 1, >CHCH$_3$), 1.9–0.9 (m, 4, methylene), 1.61 (br s with additional splitting, 3, CH_3C=), and 1.05 (d, J = 7 Hz, 3, >CHCH_3)
	56b	46		t_r = 15.0 min	($CDCl_3$) 5.50 (br s with additional splitting, 1, olefinic), 2.97 (d, J = 7 Hz, 2, bridgeheads), 2.3–1.9 (m, 1, >CHCH$_3$), 1.9–1.2 (m, 2, methylene), 1.57 (br s with additional splitting, 3, CH_3C=), 1.25–0.60 (m, 2, methylene), and 0.98 (d, J = 6.5 Hz, 3 >CHCH_3)
44	**41**	77	K	30°, 15 ml/min t_r = 9.8 min	(C_6D_6) 5.52 (br s with additional splitting, 1, olefinic), 3.08–2.82 (m, 1, bridgehead), 2.62 (br s, 1, bridgehead), 1.44 (br s with additional splitting, 3, CH_3C=), 0.74 (d, J = 7.5 Hz, 3, >CHCH_3), and 2.1–0.94 (m, 5)
	55	23		t_r = 9.2 min	(C_6D_6) 5.58 (br s with additional splitting, 1, olefinic), 3.08–2.82 (m, 2, bridgeheads), 1.10–0.94 (m, 3, >CHCH_3), and 2.1–0.94 (m, 8)
54[c]	**57**	67	P	110°, 60 ml/min	($CDCl_3$) 5.8–6.0 (m, 2, olefinic), 2.28 (br s, 2, bridgehead), 2.15–1.15 (m, 5), 1.29 (s, 3, bridgehead methyl), and 0.80 (d, J = 7 Hz, >CHCH_3)
	58	33	P		($CDCl_3$) 5.8–6.0 (m, 2, olefinic), 2.65–2.45 (br m, 1, bridgehead), 2.15–1.15 (m, 5), 1.22 (s, 3, bridgehead methyl), and 0.91 (d, J = 7 Hz, >CHCH_3)

[a] For each bicycloheptene, calcd m/e (for C_9H_{14}) 122.1095; found 122.1097. [b] See ref 28 for description. [c] We thank Dr. Stanley E. Wilson for this experiment.

To characterize the two ethylidenecyclohexenes formed in the rearrangement of **9**, the four most likely structures were synthesized by Wittig reactions on 2-cyclohexenones **60** and **61** (Chart VIII). Each of the

Chart VIII. Independent Synthesis of the Isomeric Ethylidenecyclohexenes



dienes exhibits a doublet (J = 7 Hz) of area 3 for the sp^2-bound methyl group and the complementary quartet (J = 7 Hz) for the terminal vinyl proton. As previously recognized,[3e,26] the characteristically low field H_2 absorptions provide a convenient handle for determining the relative positioning of the two substituents of the exocyclic ethylidene group. In the present instance, isomers **45** and **62** exhibit deshielded H_2 absorptions at δ 6.33 and 6.34 and consequently are of syn stereochemistry. The shielding accorded to this same proton in **46** (δ 5.96) and **63** (5.92) identifies these hydrocarbons as belonging to the anti series. When comparison was made with the products of rearrangement of **9**, it was found that only **45** and **46** had been produced in relative yields of 12 and 2%.

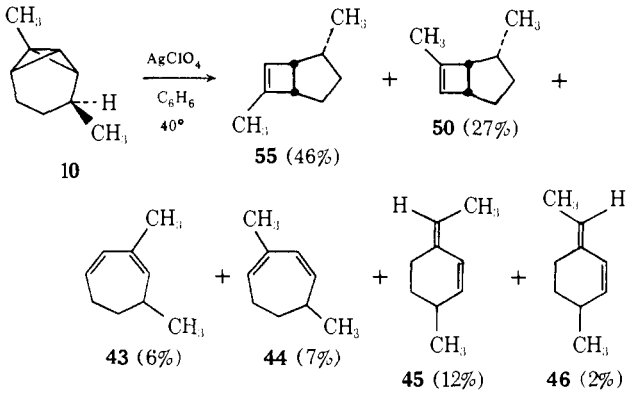
The rearrangement behavior of the distal 1,3-dimethyltricycloheptane isomer **10** was greatly expedited due to the availability of authentic samples. When treated with $AgClO_4$ in the conventional manner, **10** afforded the product mixture given in Chart IX. Vpc analysis showed that none of the *exo*-2-methylbicycloheptenes **41** and **42** was present, nor was there any detectable evidence for the formation of **62** and **63**.

Discussion

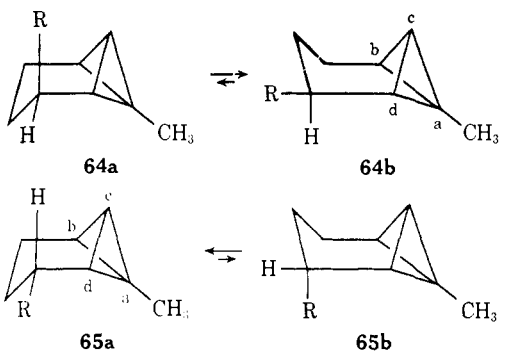
A relevant aspect of the present study is the dominance of type γ bicycloheptene derivatives. Intuitively, one might have expected that additional substitution at C_3 of the tricycloheptane ring system would not have greatly altered the distribution of products previously observed for the 1-methyl derivative (**1**) which rearranges by the type γ process to the extent of 44%. However, the proximal isomers **9** and **14**, in the presence of Ag^+, reproducibly isomerize to give combined

(26) P. D. Bartlett, *Quart. Rev., Chem. Soc.*, **24**, 473 (1970).

Chart IX. Products of the Ag^+-Catalyzed Isomerization of **10**



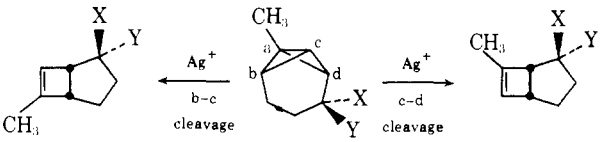
relative bicycloheptene yields of 64 and 91%, respectively. The distal isomers **10** and **15** exhibit greater internal consistency, their level of type γ rearrangement operating to the extent of 73 and 71%. Although these findings do not bear directly on the stereochemical issue, they suggest that conformational effects induced by the C_3 substituents (*cf.* **64** and **65**) may exercise a secondary influence on the kinetically preferred avenues of approach of the transition metal ion to the bicyclobutane moiety.



Since the objective of this research was to determine the overall stereochemistry of the type γ pathway, it is important to point out that such rearrangements give every indication of being totally stereospecific. Furthermore, the observed direction of stereospecificity necessarily excludes formal cleavage of the a–b or a–d bonds (*cf.* **64** and **65**) at the onset of rearrangement, since initial rupture of these bonds would eventuate in formation of bicycloheptenes possessing C_2 configuration opposite to that observed. This conclusion was expected from our earlier studies which interrelated the effect of increasing steric bulk at C_1 with mechanistic partitioning[1] and the unlikelihood that argento carbonium ion intervention would be bypassed in these instances despite the presence of an electron-donating bridgehead substituent which favors generation of such a species.[1,3,4,27]

The data also show the process beginning with cleavage of the central a–c bond and subsequent 1,3-hydride shift[4] to be inoperative. Under the terms of this mechanistic option, only bicycloheptenes with inverse C_2 stereochemical features would again arise, and this is not seen.

In contrast, the observations are consistent with a bimolecular reaction[8] between Ag^+ and the strained ring involving competitive edge attack at bonds b–c or



c–d and ultimate 1,2-carbon shift. Since the first pathway eventuates in the formation of 6-methylbicycloheptenes, while the latter gives rise to the 7-methyl isomers (with identical C_2 stereochemistry in either bicycloheptene), determination of the product distribution can serve as a direct measure of the regioselectivity of the process. The difference in the two modes of reaction lies significantly in favor of b–c breakage, the 6-methyl isomers being 1.5 (in the 3-methyl series) to 4.0 (for the 3-methoxy pair) more prevalent than their 7-methyl counterparts. This preferential rupture of the b–c linkage is kinetically dominant in the present examples likely owing to steric congestion engendered by the C_3 substituent which perturbs what otherwise would be isoenergetic reaction modes. The ensuing paper[8] addresses itself to the intimate details of the electronic reorganizations attending electrophilic attack by Ag^+ at the indicated positions.

Experimental Section

All boiling points are uncorrected. Infrared spectra were obtained on a Perkin-Elmer Model 137 spectrophotometer and proton magnetic resonance spectra were recorded with Varian A-60A and HA-100 spectrometers as well as a Joelco MH-100 instrument. Apparent splittings are given in all cases. Mass spectra were obtained with a CEC-MS9 instrument at an ionization potential of 70 eV. Elemental analyses were performed by the Scandinavian Microanalytical Laboratory, Herlev, Denmark. Preparative and rough analytical vpc work was done on a Varian Aerograph A90-P3 instrument equipped with a thermal conductivity detector. Refined product composition data were obtained with the aid of a Hewlett-Packard 5750 unit (flame ionization detector) equipped with an electronic integrator.

***syn*- and *anti*-7,7-Dibromo-1,5-dimethylbicyclo[4.1.0]heptanes (6 and 7).** Dibromides **6** and **7** were prepared according to the procedure of Paquette, *et al.*,[3a] in 94% isolated yield. Preparative vpc using column A[28] (135°) led to separation of the major (**6**, 66%) and minor (**7**, 34%) isomers as greenish viscous oils which exhibited characteristic $>CHCH_3$ doublets in their 100-MHz pmr spectra ($CDCl_3$) at δ 1.17 and 1.24, respectively. In this manner, **6** was obtained with 1% cross-contamination from **7**; the anti isomer (**7**) proved to be of 85% isomeric purity.

Reaction of 7 with Methyllithium. A magnetically stirred ether solution (2 ml) of **7** (141 mg, 0.5 mmol, 85% purity) was cooled in an ice bath under a nitrogen atmosphere and treated dropwise with an ether solution (0.5 ml) of methyllithium (1.09 mmol). After 15 min, water (1 ml) was added and the separated aqueous layer was washed with ether (1 ml). The combined and dried ether layers were flash-vacuum distilled (60°, 5 mm) into a receiver cooled to

(27) L. A. Paquette, *Accounts Chem. Res.*, 4, 280 (1971).

(28) The following Al columns were employed during the course of this research: A, 6 ft × 0.25 in. 10% UCON 50HB 2000 Polar on 60–80 mesh Chromosorb G; B, 12 ft × 0.25 in. 5% Carbowax 20M on KOH-washed 60–80 mesh Chromosorb P; C, 6 ft × 0.25 in. 5% SE-30 on 60–80 mesh Chromosorb G; D, 6 ft × 0.25 in. 10% Carbowax 20M on 60–80 mesh Chromosorb G; E, 12 ft × 0.25 in. 5% OV-11 on 60–80 mesh Chromosorb G; F, 5 ft × 0.25 in. 3% SE-30 on 100–200 mesh Varaport #30; G, 12 ft × 0.25 in. 12% OV-11 on 80–100 mesh Chromosorb W; H, 10 ft × 0.125 in. 5% Carbowax 20M on KOH-washed Chromosorb P (60–80 mesh); I, 11 ft × 0.25 in. 15% QF-1 on 60–80 mesh Chromosorb W; J, 12 ft × 0.25 in. 10% Carbowax 20M on base-washed 60–80 mesh Chromosorb P; K, 20 ft × 0.125 in. 20% β,β'-oxydipropionitrile on 60–80 mesh Chromosorb P; L, 10 ft × 0.125 in. 1.5% QF-1 on 60–80 mesh Chromosorb G; M, 24 ft × 0.125 in. 1% SE-30 Hewlett-Packard "high efficiency" column; N, 24 ft × 0.25 in. 5% PMPE 5-ring on 60–80 mesh Chromosorb G; O, 6 ft × 0.25 in. 23% $AgNO_3$–glycerol (30:70) on 60–80 mesh Firebrick; P, 12 ft × 0.25 in. 5% PMPE 5-ring on 60–80 mesh Chromosorb G.

−78°. Preparative vpc of the distillate using column B[28] (70°) led to collection of 42 mg (69%) of an 85:15 mixture of **10** and **8**, from which **8** could be removed if desired by reaction with $AgClO_4$ in benzene (see below for **9**). For C_9H_{14} *m/e* 122.1097 (calcd *m/e* 122.1095); $\delta_{TMS}^{CDCl_3}$ 2.38–1.96 (m, 2, H_2 and H_6), 1.54 (s, 3, 1-CH_3), 0.85 (d, J = 5.5 Hz, 3, 3-CH_3), and 1.06–0.8 (m, 6).

Reaction of 6 with Methyllithium. Following essentially the same procedure as that described above, 256 mg (0.9 mmol) of **6** (99% purity) yielded 55 mg (50%) of a 90:10 mixture of **8** and **9**. This material was dissolved in dry benzene (1.0 ml) and added at 0° to a magnetically stirred anhydrous solution of $AgClO_4$ (0.036 mmol) in benzene (1 ml). The cooling bath was removed after 60 sec and the reaction mixture was stirred at ambient temperature for an additional 540 sec before quenching by addition of saturated aqueous sodium chloride solution (2 ml). After vigorous shaking and separation of the benzene layer, the aqueous layer was washed with pentane (0.5 ml) and the combined organic layers were dried. Preparative vpc using column C[28] (55°) gave 6 mg of pure **9**. For C_9H_{14}, *m/e* 122.1097 (calcd *m/e* 122.1095); $\delta_{TMS}^{CDCl_3}$ 2.22–1.84 (m, 2, H_2 and H_6), 1.42 (s, 3, 1-CH_3), 0.88 (d, J = 7.0 Hz, 3, 3-CH_3), and 8–0.6 (m, 6).

1-Methyl-1-cyclohexen-3-ol. Lithium aluminum hydride reduction of 1-methyl-1-cyclohexen-3-one[29] was achieved according to the procedure of Dauben and Berezin.[30] Distillation of the crude reduction product gave an 84% yield of the alcohol as a colorless oil, bp 83° (12 mm),[31] which proved to be ≥99% pure by vpc analysis on column D[28] (140°): $\delta_{TMS}^{CDCl_3}$ 5.60–5.37 (m, 1, olefinic), 4.17 (b vr s, 1, >CHO–), 2.94 (s, 1, OH), 2.35–1.10 (m, 6, methylenes), and 1.68 (m, 3, CH_3).

Anal. Calcd for $C_7H_{12}O$: C, 74.95; H, 10.78. Found: C, 74.51; H, 10.87.

1-Methoxy-3-methylcyclohex-2-ene (11). A solution of 118 g (1.05 mol) of 1-methyl-1-cyclohexen-3-ol in 100 ml of anhydrous dimethylformamide was added during 3.5 hr to a mechanically stirred suspension of sodium hydride (49 g, 2.04 mol) in the same solvent (550 ml). Upon completion of the addition, an additional 200 ml of solvent was added to facilitate stirring which was continued for 2.5 hr at room temperature. With ice cooling, a solution of 600 g (4.2 mol) of methyl iodide in 200 ml of dimethylformamide was slowly introduced and the resulting thick slurry was stirred overnight. Water (2 l.) was added and following pentane extraction (2 × 500 ml) the combined organic layers were washed with water (3 × 200 ml), dried, and distilled to afford 93 g (70%) of **11** as a colorless oil, bp 90–92° (70 mm), which was *ca.* 95% pure by vpc (column E,[28] 85°). Purification of a small sample of **11** was achieved by preparative vpc: $\delta_{TMS}^{CDCl_3}$ 5.65–5.43 (m, 1, olefinic), 3.72 (br s, 1, >CHO–), 3.33 (s, 3, OCH_3), 2.33–1.15 (m, 6, methylenes), and 1.68 (m, 3, CH_3).

Anal. Calcd for $C_8H_{14}O$: C, 76.14; H, 11.18. Found: C, 75.72; H, 11.15.

***syn*- and *anti*-7,7-Dibromo-5-methoxy-1-methylbicyclo[4.1.0]heptanes (12 and 13).** A magnetically stirred suspension of 35 g (0.28 mol) of **11** and 33.6 g (0.30 mol) of powdered potassium *tert*-butoxide in pentane (250 ml) was cooled to −30° and a solution of bromoform (70.4 g, 0.28 mol) in pentane (55 ml) was added at this temperature over 1.5 hr. Following complete addition, gradual warming to room temperature, and stirring for an additional 2 hr, water (125 ml) was added. The separated organic layer was washed with water (125 ml), dried, concentrated, and distilled to give 52.2 g (68%) of a pale yellow oil, bp 90–94° (0.8 mm), identified as a 95:5 mixture of **12** and **13** from its pmr spectrum and subsequent reaction with methyllithium (*vide infra*): $\delta_{TMS}^{CDCl_3}$ 3.43 (s, 3, OCH_3), 3.40–3.17 (m, 1, >CHO–), 1.47 (s, 3, CH_3), and 2.08–0.93 (m, 7); a singlet at 3.52 was attributed to the methoxyl group of **13**. An analytically pure sample of this mixture was obtained by preparative vpc using column F[28] (90°).

Anal. Calcd for $C_9H_{14}Br_2O$: C, 36.27; H, 4.74; Br, 53.62. Found: C, 36.13; H, 4.72; Br, 54.41.

Reaction of 12 and 13 with Methyllithium. A magnetically stirred solution of 9.0 g (0.03 mol) of **12** and **13** (95:5) in ether (60 ml) was cooled to −30° and maintained at this temperature during addition of methyllithium (0.03 mol) in ether (18.5 ml) over a period of 0.5 hr. After 1 hr at room temperature, the cooled (5°) reaction mixture was treated with water (60 ml) and the separated organic layer was washed with brine (60 ml), dried, and concentrated by careful atmospheric distillation. Flash-vacuum distillation of the residue at 25° and 0.8 mm using a receiver cooled to −78° led to collection of volatiles (68% yield of products) which were separated and purified by careful preparative vpc columns G[28] (62°) and B[28] (100°). The three insertion products in order of elution were identified as **16** (28%), **14** (67%), and **15** (5%) from their characteristic pmr spectra and subsequent chemical transformations.[12]

For **14**, $\delta_{TMS}^{C_6D_6}$ 3.39–2.99 (m, 1, H_3), 3.20 (s, 3, OCH_3), 2.54–2.23 (m, 1, H_2 or H_6), 2.23–1.93 (m, 1, H_2 or H_6), 1.81–1.23 (m, 4, methylenes), 1.48 (s, 3, CH_3), and 1.23–0.89 (m, 1, H_7).

Anal. Calcd for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 78.39; H, 10.18.

For **15**, the 100-MHz pmr spectrum (C_6D_6-TMS) was essentially identical with that of **14** except for the C_1-methyl chemical shift which appears 4 Hz to higher field than that of the corresponding signal in **14**. For $C_9H_{14}O$ *m/e* 138.1046 (calcd *m/e* 138.1045).

For **16**: $\delta_{TMS}^{C_6D_6}$ 3.79–3.55 (dd with additional fine splitting, J = 7.5 and 2.5 Hz, 1, H_2), 3.01 (s, 3, OCH_3), 2.71–2.35 (m, 1, H_3), 1.99–1.56 (m, 6), and 1.00 (s, 3, CH_3).

Anal. Calcd for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 78.07; H, 10.22.

Ag(I)-Catalyzed Rearrangement of 14. Syn substituted tricycloheptane **14** (280 mg, 2 mmol) was added to an nmr tube containing an anhydrous solution of $AgClO_4$ in benzene (0.67 ml of 0.1877 *M*; 0.126 mmol; 6 mol %) and the resultant solution was heated at 40°. After 26 hr, pmr analysis of the pale yellow reaction mixture indicated that rearrangement was complete. Formation of a small amount of black precipitate was also in evidence. The reaction was quenched by shaking with saturated brine (6 ml) and extracted with pentane (3 × 5 ml). Vpc analysis (column G,[28] 100°) of the combined organic layers indicated the presence of three components subsequently identified as **19**/**20** (91%), **22** (5%), and **21** (4%).

The identity of **19** and **20** was confirmed by independent synthesis (*vide infra*) and the isomer distribution of 73:18 was obtained by repeated integration of the adequately separated >CHO– signals.

Anal. Calcd for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 78.21; H, 10.11.

The peak corresponding to **21** was composed of two 1,3-cycloheptadienes in approximately equal amounts as evidenced by the presence of two methoxy singlets of roughly equal intensity; $\delta_{TMS}^{C_6D_6}$ 6.10–5.40 (m, 3, olefinic), 3.97–3.50 (m, 1, >CHO–), 3.21 and 3.18 (two s, 3 total, OCH_3's), 2.35–1.45 (m, 4), and 1.72 (apparent q, J = 1 Hz, two CH_3's). For $C_9H_{14}O$ *m/e* 138.1042 (calcd *m/e* 138.1045).

For **22**: $\delta_{TMS}^{C_6D_6}$ 6.38 (br d, $J \approx$ 10 Hz, 1), 5.97–5.56 (m, 1), 5.36 (br q, J = 7 Hz, 1), 3.75–3.50 (br t, $J \approx$ 3 Hz 1, >CHO), 3.19 (s, 3, OCH_3), 2.70–1.70 (m, 4), and 1.62 (d, J = 7 Hz, 3, CH_3). For $C_9H_{14}O$ *m/e* 138.1042 (calcd *m/e* 138.1045).

Aromatization of 22. A solution of 6 mg of **15** in 0.2 ml of anhydrous benzene was kept at 40° for 48 hr after admixture with 0.40 ml of 0.188 *M* $AgClO_4$ in benzene. After the usual work-up, vpc analysis revealed that no **22** remained. The lone new component which was detected was identified as ethylbenzene (**23**) by comparison of retention times with those of an authentic sample on several columns.

Ag(I)-Catalyzed Rearrangement of 15. A solution of **15** (6 mg) in anhydrous benzene (0.20 ml) was treated as above with $AgClO_4$ in benzene (0.40 ml of 0.188 *M*). At various time intervals, aliquots of this solution were removed, quenched in the customary fashion with brine, and analyzed by flame ionization vpc on column H[28] (53°) previously shown not to cause detectable rearrangement of **15**. Products **24** and **25** were identified by comparison of their retention times (4.3 and 6.1 min, respectively) with those of authentic samples (*vide infra*). Products **21** and **22** exhibited retention times (14.1 and 16.0 min, respectively) equal to those compounds of identical structure obtained from the rearrangement of **14**. The relative product distribution was (in the order cited above) 57, 14, 2, and 27%. The *exo*-2-methoxybicycloheptenes **19** and **20** (t_r = 5.2 min) were not detected.

Photocyclization of 2-Cyclopentenone to Propyne. Propyne (8 ml, 0.14 mol), previously condensed at −78° under nitrogen in a graduated collection tube, was allowed to evaporate through a glass frit into a chilled flask containing 500 ml of benzene (magnetic stirring). The resultant solution was combined with 0.82 g (0.01

(29) M. W. Cronin and G. H. Riesser, *J. Amer. Chem. Soc.*, **75**, 1664 (1953).

(30) W. G. Dauben and G. H. Berezin, *J. Amer. Chem. Soc.*, **85**, 468 (1963).

(31) M. Mousseron, R. Jacquier, M. Mousseron-Canet, and R. Zagdown [*Bull. Soc. Chim. Fr.*, **19**, 1042 (1952)] have reported bp 80–85° (15 mm) for the "ethylenic alcohol" derived from sodium reduction of 1-methyl-1-cyclohexen-3-one. However, no analytical or spectroscopic data were reported for this alcohol which could be reoxidized to the starting enone.

mol) of 2-cyclopentenone[32] and irradiated while being stirred for 26 hr, using a 450-W Hanovia lamp, a water-cooled Pyrex immersion well, and a tightly stoppered photochemical cell which was externally cooled in a water bath. After removal of solvent by distillation through a 6-in. Vigreux column, the residue was flash-vacuum distilled at 0.8 mm into a receiver cooled to −78°. Vpc analysis of the distillate on column A[28] (120°) indicated the presence of recovered starting material (13%) and two major products with retention times of 14.6 (47%) and 21.4 min (23%) in addition to at least six minor by-products. Preparative vpc of the more rapidly (120 mg) and less rapidly (80 mg) eluting components of consequence permitted their identification as **27** and **28** when their ir spectra were compared to those provided by Professor Eaton.[15] Characteristic ir absorption frequencies for **27** are observed at 814 (m), 777 (m), and 756 (m) cm^{-1}, while those for **28** appear at 836 (m) and 782 (m) cm^{-1}. The pmr spectra of **27** and **28** are very similar except for the chemical shifts of the methyl and olefinic absorptions which appear (in CCl_4) at δ 1.70 (br s with fine splitting) and 6.00 (br s with fine splitting) for **27**, but at 1.78 and 5.80 for **28**. Remaining absorptions appear at δ 3.25 (m, 1, bridgehead), 2.97 (m, 1, bridgehead), and 2.9–1.7 (m, 4, methylenes).

endo-**2-Hydroxy-7-methylbicyclo[3.2.0]hept-6-ene (29).** A solution of **27** (147 mg, 1.20 mmol) in anhydrous ether (2.7 ml) was added to a magnetically stirred suspension of lithium aluminum hydride (90 mg, 2.37 mmol) in ether (1.8 ml) at 0°. After 1 hr at 25°, water (0.09 ml), 20% sodium hydroxide solution (0.09 ml), and more water (0.27 ml) were added sequentially. The white solid was collected by filtration through a plug of glass wool and was washed with ether (5 ml). Removal of ether on a rotary evaporator gave an approximately quantitative yield of product as a viscous colorless oil which was ≥95% pure by vpc analysis (column I,[28] 100°). This material was used without further purification: $\delta_{TMS}^{CDCl_3}$ 5.78 (br s with fine splitting, 1, olefinic), 4.10 (apparent q, J = 8 Hz, 1, H_2), 3.20–2.80 (m, 2, bridgeheads), 2.17–1.12 (m, 4, methylenes), 1.79 (br s with fine splitting, 3, CH_3), and 1.55 (s, 1, OH).

endo-**2-Hydroxy-6-methylbicyclo[3.2.0]hept-6-ene (30).** Similar hydride reduction of **28** gave a near quantitative yield of isomerically pure (≥95%, vpc column I[28]) **30**: $\delta_{TMS}^{CDCl_3}$ 5.79 (br s with fine splitting, 1, olefinic), 3.98 (apparent q, J = 8 Hz, 1, H_2), 3.17–2.80 (m, 2, bridgeheads), 2.27 (s, 1, OH), 1.67 (br s with fine splitting, 3, CH_3), and 2.10–1.00 (m, 4, methylenes).

exo-**2-Hydroxy-7-methylbicyclo[3.2.0]hept-6-ene (31).** An anhydrous isopropyl alcohol solution (5.6 ml) of unpurified **29** (149 mg, 1.20 mmol), anhydrous acetone (0.015 ml), and freshly distilled aluminum isopropoxide (0.83 g, 4.0 mmol) was sealed in a base-washed glass tube and heated at 105–110° for 65 hr. The cooled solution was treated with water (10 ml), and 15% sodium hydroxide solution (2-3 ml) was added with shaking to dissolve the flocculant white precipitate.[33] The resultant solution was extracted with methylene chloride (4 × 30 ml) and the combined organic layers were dried and concentrated. Vpc analysis (column I,[28] 100°) of the residue revealed it to be a 41:59 mixture of **29** (t_r = 18.6 min) and **31** (t_r = 22.3 min). Preparative vpc isolation (same conditions) gave 37 mg of pure **29** and 50 mg of pure **31** as viscous oils (58% overall yield based on **27**). For **31**: $\delta_{TMS}^{CDCl_3}$ 5.59 (br s with fine splitting, 1, olefinic), 4.12 (apparent d, J = 3 Hz, 1, H_2), 3.13 (m, 1, bridgehead), 2.91 (m, 1, bridgehead), 2.37 (s, 1, OH), 2.20–1.20 (m, 4, methylenes), and 1.62 (br s with fine splitting, 3, CH_3).

exo-**2-Hydroxy-6-methylbicyclo[3.2.0]hept-6-ene (32).** Repetition of the above procedure using unpurified **30** (102 mg, 0.82 mmol) gave a 78:22 mixture (same vpc conditions as with **31**) of **32** (t_r = 22.5 min) and **30** (t_r = 27.1 min). Preparative vpc isolation afforded 51.4 mg of pure **32** and 19.2 mg of pure **30** as viscous oils (69% overall yield from **28**). The nmr spectrum of **32** was strikingly similar to that of **31**.

endo-**2-Methoxy-7-methylbicyclo[3.2.0]hept-6-ene (25).** A solution of **29** (55 mg, 0.44 mmol) in anhydrous dimethylformamide (3 ml) was added to excess sodium hydride (85 mg, 3.5 mmol) and the magnetically stirred mixture was heated at 40–50° for 1 hr after which time it was allowed to stir at ambient temperature overnight. Methyl iodide (1.14 g, 8.0 mmol) was added to the ice-cooled reaction mixture and stirring was continued at 25° for 3 hr before quenching with water (10 ml). Initial pentane (20 ml) extraction was followed by a second pentane (10 ml) wash of the aqueous layer and the combined organic phases were washed with water (4 × 3 ml) and dried. Solvent was removed by slow atmospheric distillation through a 6-in. Vigreux column and the residue was subjected directly to preparative vpc (column H,[28] 100°). There was obtained 30 mg (49%) of **25**: $\delta_{TMS}^{C_6D_6}$ 5.69 (br s with fine splitting, 1, olefinic), 3.46 (apparent q, J = 8 Hz, 1, H_2), 3.22 (s, 3, OCH_3), 3.70–2.70 (m, 2, bridgeheads), 1.78 (br s with fine splitting, 3, CH_3), 2.17–1.67 (m, 2, methylene), and 1.47–1.02 (m, 2, methylene).

Anal. Calcd for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 78.11; H, 10.25.

exo-**2-Methoxy-7-methylbicyclo[3.2.0]hept-6-ene (20).** Analogous O-methylation of **31** (57 mg) afforded **20** in 51% isolated yield after preparative vpc (same conditions: $\delta_{TMS}^{C_6D_6}$ 5.55 (br s with fine splitting, 1, olefinic), 3.50 (br s with fine splitting, 1, H_2), 3.27–2.98 (m, 2, bridgeheads), 3.14 (s, 3, OCH_3), 1.48 (br s with fine splitting, 3, CH_3), and 2.10–1.25 (m, 4, methylenes). For $C_9H_{14}O$ *m/e* 138.1047 (calcd *m/e* 138.1045). For elemental analysis (admixed with **19**), see above.

endo-**2-Methoxy-6-methylbicyclo[3.2.0]hept-6-ene (24).** Repetition of this procedure using 19.2 mg of **30** led to a 64% isolated yield of **24**: $\delta_{TMS}^{C_6D_6}$ 5.81 (br s with fine splitting, 1, olefinic), 3.38 (apparent q, J = 8 Hz, 1, H_2), 3.19 (s, 3, OCH_3), 3.18–2.63 (m, 2, bridgeheads), 1.47 (br s with fine splitting, 3, CH_3), 2.03–1.58 (m, 2, methylene), and 1.38–0.78 (m, 2, methylene). For $C_9H_{14}O$ *m/e* 138.1046 (calcd *m/e* 138.1045).

exo-**2-Methoxy-6-methylbicyclo[3.2.0]hept-6-ene (19).** When 49.4 mg of **32** was methylated as above, there was obtained a 42% yield of **19**: $\delta_{TMS}^{C_6D_6}$ 5.55 (br s with fine splitting, 1, olefinic), 3.43 (br s with fine splitting, 1, H_2), 3.27–2.95 (m, 2, bridgeheads), 3.14 (s, 3, OCH_3), 1.46 (br s with fine splitting, 3, CH_3), and 2.07–1.27 (m, 4, methylenes). For $C_9H_{14}O$ *m/e* 138.1047 (calcd *m/e* 138.1045). For elemental analysis (admixed with **20**) see above.

1-Methyl-1-cyclohexen-3-ol-*3-d* (34). This labeled alcohol was prepared from **33** in the same manner as its protium analog with substitution of lithium aluminum deuteride (2.0 g, 0.048 mol). Vpc analysis (column J,[28] 125°) confirmed the presence of one component, a sample of which was collected for mass spectrometric analysis. For $C_7H_{11}OD$ *m/e* 113.0949 (calcd *m/e* 113.0951).

1-Methoxy-3-methylcyclohex-2-ene-*1-d* (35). Unpurified **34** (*ca.* 0.109 mol) was converted to **35** according to the procedure used for the preparation of **11**. Distillation yielded 11.2 g (81%) of a colorless oil, by 80–82° (50 mm), identified as **35** by comparison of its pmr spectrum with that of **11**. For $C_8H_{13}OD$ *m/e* 127.1108 (calcd *m/e* 127.1107).

***syn*- and *anti*-7,7-Dibromo-5-methoxy-1-methylbicyclo[4.1.0]heptane-*5-d* (36 and 37).** Treatment of 11.2 g of **35** with dibromocarbene as before gave a crude (undistilled) reaction product, pmr analysis of which indicated that approximately 11% of **35** remained. Vacuum distillation yielded 19 g (75%) of pale yellow oil, bp 98–100° (0.8 mm), which was identified as a mixture of **36** (93%) and **37** (7%) by pmr analysis and particularly by integration of the two relevant methoxyl singlets.

Mass spectrometric analysis (70 eV) of this mixture did not show the presence of the expected parent ion isotope cluster at *m/e* 297, 299, and 301. However, the highest observable isotope cluster appeared at *m/e* 265, 267, and 269, presumably due to fragmentation of the parent ion into CH_3OH and $[C_8H_9DBr_2]\cdot^+$. This was confirmed by accurate mass measurement: for $C_8H_9D^{79}Br^{81}Br$ *m/e* 266.9190 (calcd *m/e* 266.9193).

Reaction of 36 and 37 with Methyllithium. When the **36/37** mixture was treated with methyllithium as before, flash-vacuum distillation yielded a colorless distillate, bp ≤25° (0.8 mm), which was shown by vpc analysis (column J,[28] 100°) to be an ether solution containing **40** (27.1%, t_r = 12.8 min), **38** (69.5%, t_r = 16.1 min), and **39** (3.5%, t_r = 20.2 min). Preparative vpc isolation using column G[28] (100°) led to the isolation of pure **40** and **38**. Ether **39** remained contaminated (*ca.* 50% purity) with **38** and was further purified by passage through column J[28] (100°). The sample of **39** so obtained (50 mg) contained only 8% of **38**. Products **38**–**40** were identified as $C_9H_{13}DO$ isomers by accurate *m/e* measurements and by pmr data. The combined yield of **40** and **38** was 67%.

For **38**, approximately the same spectrum as its protio analog (**14**) except for the absence of absorption at $\delta_{TMS}^{C_6D_6}$ 3.39–2.99 due to H_3 and the appearance of H_2 as a triplet (J = 3.5 Hz).

For **39**, approximately the same spectrum as **38** but with methoxyl and methyl singlets positioned 2 and 3 Hz (at 60 MHz), respectively, to lower field. In this isomer, H_2 is seen as an apparent quartet (J = 2–3 Hz).

(32) C. H. Depuy and K. L. Eilers, *Org. Syn.*, **42**, 38 (1962).

(33) Although acid work-up is generally used,[18] alkaline work-up was employed in the present case to preclude the risk of acid-catalyzed rearrangement.

For **40**, $\delta_{TMS}^{C_6D_6}$ 3.05 (s, 3, OCH_3), 2.52 (m, 1, H_3), 2.39–1.54 (m, 6), and 1.03 (s, 3, CH_3).

Ag(I)-Catalyzed Rearrangement of 9. A 7-mg (0.057 mmol) sample of **9** was allowed to react with anhydrous $AgClO_4$ (0.179 mmol) in benzene (1.10 ml) at 40.0 ± 0.1°. Upon completion of the rearrangement (*ca.* 12 hr), the reaction mixture was processed in the usual fashion. Analysis of the bicycloheptene and ethylidenecyclohexene compositions was achieved with column K[28] at 32° and column L[28] at 36° (15 ml/min), respectively, while separation of the cycloheptadiene isomers was attained with maximum efficienty on column K[28] operated at 61°. All products were identified by comparison of their vpc retention times with those of authentic samples (as well as all of the isomeric possibilities) under a variety of conditions. Integration of the various peak areas gave the following relative peak ratios: **41** (38), **42** (26%), **43** (11%), **44** (17%), **45** (7%), and **46** (1%).

Ag(I)-Catalyzed Rearrangement of 10. Essentially the same procedure described above for **9** was utilized for the analogous rearrangement of **10** (2.5 mg, 0.02 mmol). Separation and characterization of the three sets of constitutional isomers were again achieved readily by the previously indicated vpc techniques. The product composition consisted of **55** (46%), **50** (27%), **43** (6%), **44** (7%), **45** (12%), and **46** (2%).

Pyrolysis of 1,3-Dimethyl-1,3-cycloheptadiene (47). A 320-mg sample of **47**[33a,34] was introduced in a slow stream of nitrogen at 30 mm pressure into a quartz tube (28 cm × 16 mm) packed with quartz chips heated to 500° (contact time *ca.* 2 sec). The pale yellow pyrolysate (310 mg) was dissolved in pentane to separate small amounts of polymer. Analytical vpc (column M,[28] 70°) indicated the presence of four components in the relative ratio of 12, 33, 55, and <1%. Similar traces were obtained using columns H[28] (70°) and N[28] (130°). Collection of the three major components by preparative vpc on column N[28] (130°) led to their identification as **43**, **48**, and recovered **47** in their order of elution on the basis of their pmr spectra and subsequent photoisomerization. The minor pyrolysis product was assumed to be **49**.

For **43**: $\delta_{TMS}^{THF\text{-}d_8}$ 5.82–5.53 (m, 2, olefinic), 5.53–5.32 (m, 1, olefinic), 2.4–2.0 (m, 3, allylic), 1.72 (br s with fine splitting, 3, CH_3C=), 2.0–1.5 (m, 2, methylene), and 1.01 (d, J = 7.0 Hz, 3, >CHCH_3). For C_9H_{14} *m/e* 122.1097 (calcd *m/e* 122.1095).

For **48**: $\delta_{TMS}^{THF\text{-}d_8}$ 5.55 (br s, 3, olefinic), 2.5–1.9 (5, allylic and methine), 1.77 (br s, 3, CH_3C=), and 1.10–0.88 (m, 3, >CHCH_3). For C_9H_{14} *m/e* 122.1097 (calcd *m/e* 122.1095).

Pyrolysis of 1,4-Dimethyl-1,3-cycloheptadiene (52). Pyrolysis of **52**[33a,34] (270 mg) was performed in the same manner and the pale yellow pyrolysate (260 mg) was subjected directly to preparative vpc on column N.[28] The components were identified in their order of elution as **53** (19%), **44** (12%), **54** (24%), and recovered **52** (45%) from their pmr spectra and subsequent photoisomerization.

For **53**: $\delta_{TMS}^{THF\text{-}d_8}$ 5.83–5.38 (m, 3, olefinic), 2.6–1.8 (m, 5, allylic and methine), 1.72 (br s with fine splitting, 3, CH_3C=), and 0.92 (m, 3, >CHCH_3). For C_9H_{14} *m/e* 122.1097 (calcd *m/e* 122.1095).

For **44**: $\delta_{TMS}^{THF\text{-}d_8}$ 5.78–5.40 (m, 3, olefinic), 2.7–1.9 (m, 3, allylic), 1.9–1.4 (m, 2, methylene), 1.72 (apparent quintet, $J \approx 1.2$ Hz, 3, CH_3C=), and 1.00 (d, J = 7.0 Hz, 3, >CHCH_3). For C_9H_{14} *m/e* 122.1097 (calcd *m/e* 122.1095).

For **54**: $\delta_{TMS}^{CDCl_3}$ 5.54 (br s, 3, olefinic), 2.75–2.06 (m, 3, allylic), 1.97–1.48 (m, 2, methylene), 1.81 (br s, 3, CH_3C=), and 1.03 (d, J = 7.0 Hz, 3, >CHCH_3). For C_9H_{14} *m/e* 122.1097 (calcd *m/e* 122.1095).

Photoisomerization of the Dimethyl-1,3-cycloheptadienes. Typical Procedure. An ether solution (4 ml) of **44** (25 mg) was placed in a quartz test tube equipped with a tight-fitting rubber serum stopper, the tube was fastened to a water-cooled quartz immersion well, and the entire apparatus was placed in an ice–water bath (test tube was not completely submerged). After irradiation at approximately 5° for 2 hr with a Hanovia 450-W medium-pressure mercury arc, vpc analysis (column H,[28] 67°, 30 ml/min) indicated the absence of **44**. Preparative scale vpc isolation (one product peak, column N,[28] 100°) gave 18 mg (70%) of a colorless oil shown by subsequent analysis on column K[28] (30°) to be a 77:23 mixture of **41** and **55**. Spectral data and other relevant information are compiled in Table I.

4-Methyl-2-cyclohexen-1-one (60). The following procedure represents a modification of that reported by Ansell and coworkers.[35] A solution of distilled collidine (52.5 g, 0.43 mol) and unrectified 2-bromo-4-methylcyclohexanone (70 g, 0.37 mol)[36] was prepared in a 250-ml three-necked flask equipped with a magnetic stirring bar, thermometer, and reflux condenser, and the flask was placed in a preheated (100°) oil bath and rapidly heated (*ca.* 10 min) to 170°. An exothermic reaction began, the heating bath was removed, and the reaction maintained itself at approximately 185° for 5 min before cooling was noted. The reaction mixture was cooled in ice, dichloromethane (250 ml) was added, and the precipitated solids were removed by filtration. The dark filtrate was washed with water (2 × 60 ml), 10% hydrochloric acid (60 ml), saturated aqueous sodium bicarbonate solution (2 × 60 ml), and brine (60 ml). The dried organic layer was evaporated and the residue was fractionally distilled to give 17.8 g (44%) of **60** as a colorless liquid, bp 70–75° (12–15 nm) [lit.[35] bp 70–71° (14 mm)]. This material was utilized without further purification; nmr analysis revealed, however, the absence of detectable β,γ-unsaturated isomer.[37]

6-Methyl-2-cyclohexen-1-one (61). This ketone was obtained in 8% overall yield following the general procedure of Stork and White[38] which began by Birch reduction of *o*-toluidine. The compound was identified as **61** by its characteristic pmr spectrum.[37]

***syn*- and *anti*-4-Methyl-1-ethylidene-2-cyclohexene (45 and 46).** Under a nitrogen atmosphere, a solution of *n*-butyllithium in hexane (18 ml of 2.2 *M*, 0.04 mol) was added during 3 min to a magnetically stirred suspension of ethyltriphenylphosphonium iodide (16.8 g, 0.04 mol) in anhydrous tetrahydrofuran (100 ml). A solution of **60** (2.2 g, 0.02 mol) in the same solvent (25 ml) was introduced and the mixture was refluxed for 4.5 hr, cooled, poured into pentane (200 ml), and filtered through a glass wool plug. The filtrate was successively washed with water (3 × 100 ml), 3% hydrochloric acid (50 ml), saturated sodium bicarbonate solution (100 ml), and water (100 ml). After drying, the solution was concentrated by distillation through a 6-in. Vigreux column and the residue was flash-vacuum distilled (90° (3 mm)) into a cooled (−78°) receiver. Preparative vpc (column N,[28] 132°) of the distillate led to collection of the major (~90%) peak. Reinjection of this material onto column O[28] revealed it to be a 23:77 mixture of **45**:**46**. These were subsequently isolated and characterized. The combined yield of **45** and **46** was 21%.

For **45**: $\delta_{TMS}^{CDCl_3}$ 6.33 (dd, J = 10.0 and 2.0 Hz, 1, H_2), 5.60 (d with fine splitting, J = 10.0 Hz, 1, H_3), 5.13 (br q, J = 7.0 Hz, 1, vinyl), 2.74–1.46 (m, 4), 1.66 (br d, J = 7.0 Hz, 3, =CHCH_3), 1.46–1.11 (m, 1), and 1.00 (d, J = 7.0 Hz, 3, >CHCH_3). For C_9H_{14} *m/e* 122.1097 (calcd *m/e* 122.1095).

For **46**: $\delta_{TMS}^{CDCl_3}$ 5.96 (dd, J = 10.0 and 2 Hz, 1, H_2), 5.46 (d with fine splitting, J = 10.0 Hz, 1, H_3), 5.30 (br q, J = 7.0 Hz, 1, vinyl), 2.68–1.74 (m, 4), 1.66 (br d, J = 7.0 Hz, 3, =CHCH_3), 1.46–1.14 (m, 1), and 1.00 (d, J = 7.0 Hz, 3, >CHCH_3). For C_9H_{14} *m/e* 122.1097 (calcd *m/e* 122.1095).

Anal. Calcd for C_9H_{14}: C, 88.45; H, 11.55. Found: C, 88.09; H, 11.45.

***syn*- and *anti*-6-Methyl-1-ethylidene-2-cyclohexene (62 and 63).** Following the procedure described above, **61** (550 mg, 5 mmol) was refluxed with ethylidenetriphenylphosphorane (10 mmol) for 6 hr and yielded an oil which was isolated (20 mg, 3%) by preparative vpc on column N[28] (132°). Subsequent collection of the two isomerically pure components led to their identification as **62** (20%) and **63** (80%).

For **63**: $\delta_{TMS}^{CDCl_3}$ 5.92 (d with fine splitting, J = 10.0 Hz, 1, H_2), 5.72–5.44 (m, 1, H_3), 5.22 (br q, J = 7.0 Hz, 1, vinyl), 3.02–2.66 (m, 1), 2.30–1.94 (m, 2), 1.94–1.55 (m, 2), 1.68 (d, J = 7.0 Hz, 3, =CHCH_3), and 0.98 (d, J = 7.0 Hz, 3, >CHCH_3). For C_9H_{14} *m/e* 122.1097 (calcd *m/e* 122.1095).

For **62**: the spectrum was essentially the same as **63** and featured absorptions at $\delta_{TMS}^{CDCl_3}$ 6.34 (d with fine splitting, J = 10.0 Hz, 1, H_2) and 1.03 (d, J = 7.0 Hz, 3, >CHCH_3). For C_9H_{14} *m/e* 122.1097 (calcd *m/e* 122.1095).

Acknowledgment. This work was supported in part by the National Science Foundation whom we thank.

(34) Prepared by John A. Schwartz whom we thank.

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