cis-**Cyclodec-3-en-1-one.** Oxidation[3] of *cis*-cyclodec-3-en-1-ol gave a 62% yield of the desired ketone: ir (neat) 3000, 2930, 2860, 1660, 1475, 1435, 1335, 1285, 1200, 1162, 1035, 848, and 724 cm^{-1}; nmr (δ, CCl_4) 5.3–5.9 (m, 2), 3.0 (d, J = 7 Hz, 2), 2.0–2.6 (m, 4), 1.8–1.2 (m, 8).

Anal. Calcd for $C_{10}H_{16}O$: C, 78.89; H, 10.59. Found: C, 78.93; H, 10.54.

cis-**1-Vinylcyclodec-3-en-1-ol.** The procedure used was the same as for the trans series and gave a 54% yield of the desired vinyl alcohol: ir (neat) 3480, 3050, 2950, 2845, 1480, 1455, 995, 885, 795, 730, 718, and 700 cm^{-1}; nmr (δ, CCl_4) 5.92, 5.16, 4.95 (ABC pattern, J = 1.5, 10, and 18 Hz, 3), 5.3–5.7 (m, 2), 1.1–1.8 (m, 15).

Anal. Calcd for $C_{12}H_{20}O$: C, 79.94; H, 11.18. Found: C, 79.76; H, 11.17.

cis-**1-Trimethylsiloxy-1-vinylcyclodec-3-ene (10c).** The method outlined for **10t** was also used to give a 61% yield (after preparative gc) of **10c**: ir (neat) 3120, 3025, 2980, 2860, 1470, 1435, 1410, 1250, 1062, 918, 835, and 750 cm^{-1}; nmr (δ, CCl_4) 5.85, 5.09, 4.99 (ABC pattern, J = 1.5, 10, and 18 Hz, 3), 5.2–5.6 (m, 2), 1.2–3.0 (m, 14), and 0.08 (s, 9).

Anal. Calcd for $C_{15}H_{28}OSi$: C, 71.36; H, 11.18. Found: C, 71.52; H, 11.06.

Thermolyses were run in the gas phase in evacuated Pyrex ampoules as described previously.[3] The products were hydrolyzed[3,16] and separated by gc on columns A and C.

Structural Assignments. The thermolyses of **10c** and its corresponding alcohol give a set of products with gc and spectral data that are analogous to the corresponding data for the products formed from the nine-membered ring case examined earlier. The products from **10t** and its alcohol were the same as for the cis cases except that the ratio of **12c** and **12t** was approximately reversed. The spectra of the products are listed below.

cis-**Cyclodec-5-en-1-one (12c):** ir (neat) 3050, 2980, 2920, 1700, 1460, 1445, 1430, 1365, 1162, 1100, 1010, and 693 cm^{-1}; nmr (δ, CCl_4) 5.1–5.4 (m, 2), 2.2–2.6 (m, 4), 1.0–2.2 (m, 14).

Anal. Calcd for $C_{12}H_{20}O$: C, 79.94; H, 11.18. Found: C, 79.90; H, 11.03.

trans-**Cyclodec-5-en-1-one (12t):** ir (neat) 3120, 2970, 2920, 1705, 1445, 1365, 1160, 1072, and 982 cm^{-1}; nmr (δ CCl_4) 4.9–5.1 (m, 2), 2.2–2.4 (m, 4), 1.0–2.2 (m, 14).

Anal. Calcd for $C_{12}H_{20}O$: C, 79.94; H, 11.18. Found: C, 79.74; H, 11.06.

4-Vinylcyclodecanone (11): ir (neat) 3090, 2920, 2860, 1690, 1620, 1460, 1425, 1410, 1360, 1250, and 905 cm^{-1}; nmr (δ, CCl_4) 5.57 (m, 1), 4.91 (d, J = 18 Hz, 1), 4.86 (d, J = 8 Hz, 1), 1.2–2.6 (m, 17); mass spectrum m/e 180.151 (calcd m/e for $C_{12}H_{20}O$, 180.151).

Dodeca-1,11-dien-3-one: nmr (δ, CCl_4) 5.5–6.4 (m, 4), 4.7–5.1 (m, 2), 2.3–2.6 (m, 2), 1.9–2.3 (m, 2), and 1.1–1.8 (m, 10).

Kinetic Experiments. A series of ampoules were heated in either a fused salt bath maintained by a Bailey Model 124 proportional controller or in an aluminum block oven regulated by a Cole Palmer Model 1300 proportional controller. All runs for **10c** used the fused salt bath. The runs for **10t** used both and it was established that both devices gave the same rate at the same measured temperature. Each sample was hydrolyzed[16] and analyzed on columns D and E. The data were treated as before.[3]

Acknowledgment. We thank Research Corporation for Cottrell Research Grant support.

(16) S. Friedman and M. L. Kaufman, *Anal. Chem.*, **38**, 144 (1966).

Substituent Effects on the Generation, Structural Rearrangement, and Deargentation of Argento Carbonium Ions. A Kinetic and Product Study of the Silver(I)-Catalyzed Isomerization of C_1-Functionalized Tricyclo[4.1.0.$0^{2,7}$]heptanes[1]

Leo A. Paquette and Gerald Zon[2]

Contribution from the Department of Chemistry, The Ohio State University, Columbus, Ohio 43210. *Received July 26, 1973*

Abstract: The $AgClO_4$-promoted isomerizations of 1-isopropyl-, 1-*tert*-butyl-, several 1-methoxymethyl-, and 1-(2-methoxyethyl)tricyclo[4.1.0.$0^{2,7}$]heptanes have been examined in detail. Evidence is presented that 1,2-hydride and alkyl shift to argento carbonium ion centers from suitably constructed side chains competes favorably with migration of the allylic cyclohexene hydrogen. The distributions of products from these derivatives have been compared to those of the parent hydrocarbon and several methyl congeners. An increase in effective steric bulk of the 1 substituent leads to an increase in type γ rearrangement (leading to bicyclo[3.2.0]hept-6-enes) at the expense of type α bond reorganization (1,3-cycloheptadiene production). Deuterium isotope effect studies for 1-methoxymethyl-d_2-tricyclo[4.1.0.$0^{2,7}$] heptane have demonstrated that, although the β' rearrangement is overwhelmingly favored in this instance, fractionation factors very similar to those previously found for the 1-trideuteriomethyl example were measured, signifying that the rate-determining steps in both cases were comparable. Kinetic data also support these conclusions. An overall mechanistic picture is presented which provides a reasonable explanation of the fact that cis enol ethers dominate over their trans counterparts when the type β' mechanism is operative.

The ability of the bicyclo[1.1.0]butane ring system to undergo transition metal catalyzed isomerizations is well documented.[3] The multiplicity of reaction manifolds available to such molecules is exemplified by the behavior of tricyclo[4.1.0.$0^{2,7}$]heptane deriva-

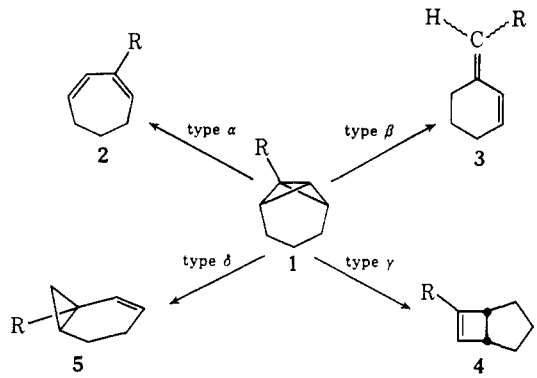
(1) Part XX of the series dealing with Ag^+-catalyzed rearrangements. For the previous paper, see L. A. Paquette and M. J. Kukla, *J. Chem. Soc., Chem. Commun.*, 409 (1973).

(2) National Institutes of Health Postdoctoral Fellow, 1972–1973.

(3) Reviews of this subject are available: L. A. Paquette, *Accounts Chem. Res.*, **4**, 280 (1971); *MTP (Med. Tech. Publ. Co.) Int. Rev. Sci. Org. Chem., Ser. One*, in press.

tives (1) when exposed to Ag^+ salts. Four rearrangement pathways may be followed depending upon the degree and nature of ring substitution (Chart I).[4,5]

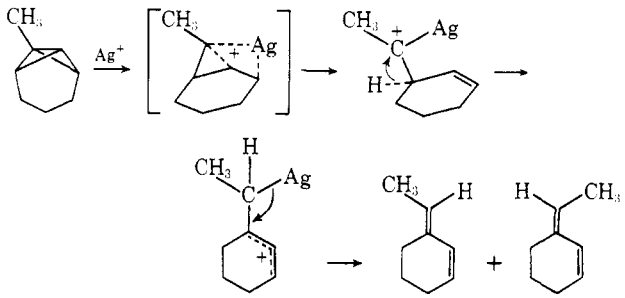
Chart I. Bond Reorganizations of Tricyclo[4.1.0.0^{2,7}]heptanes Catalyzed by Silver(I) Ion



The type α transformation, frequently encountered and reasonably well understood, is apparently initiated by electrophilic attack of Ag^+ at an edge bond with ensuing fission of the diametrically opposed C–C bond and ultimate heterolysis of the C–Ag linkage. The type δ process is rarely encountered when Ag^+ is utilized as catalyst and has not yet been examined in mechanistic detail. Accompanying papers[6] address themselves to the type γ pathway and, consequently, discussion of this rearrangement is deferred to those reports.

Incursion of the type β rearrangement is seen upon alkyl substitution of one or both bridgehead sites in **1**, and experimental evidence indicates that argento carbonium ions intervene in these isomerizations.[7] To the extent that tertiary metal-bonded carbocations of this type can be produced, this pathway may be kinetically favored, unless untoward steric effects gain importance. The generalized mechanism is outlined in Chart II.

Chart II. Mechanism of the Type β Rearrangement as Exemplified by 1-Methyltricyclo[4.1.0.0^{2,7}]heptane

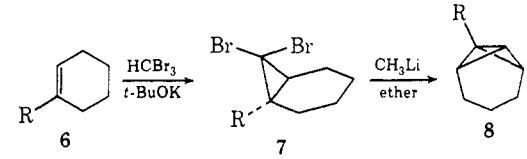


Until now, all studies of the β mechanism have concerned argento carbonium ions with methyl and 2-cyclohexenyl ligands attached to the metal-bonded carbon atom. Such ions have shown an exclusive tendency for 1,2 shift of the indicated allylic hydrogen, perhaps because of high energy restrictions associated with hydrogen migration from the methyl substituent. Hence, no information was available concerning migratory aptitudes to an argento carbocation center. Furthermore, the factors controlling the proportions of alkylidenecyclohexene isomers (**3**) were not understood. We therefore examined the effect of structural changes at the ionization center. Direct modification of the point where product-determining steps are located was expected to affect the reaction channels available to the argento carbonium ion. Since substituent alterations likewise affect the reaction environment, it was anticipated that the associated steric and electronic perturbations would provide mechanistic information about the generalized type β rearrangement as well as argento carbonium ions.

Results

1-Isopropyl- and 1-*tert*-Butyltricyclo[4.1.0.0^{2,7}]heptanes (8a and 8b). Attempts to extend the bridgehead alkylation method developed by Closs[8] and thus prepare **8a** by reaction of 1-lithiotricyclo[4.1.0.0^{2,7}]heptane with isopropyl bromide were unsuccessful. The synthesis of **8a** and also **8b** was, however, achieved by extension of the procedure developed by Moore,[9,10] involving conversion of 1-isopropyl- (**6a**) and 1-*tert*-butylcyclohexene (**6b**) to dibromonorcaranes **7a** and **7b** and treatment of these intermediates with methyllithium in ether (Chart III).

Chart III. Synthesis of 1-Alkyltricyclo[4.1.0.0^{2,7}]heptanes



a, R = $CH(CH_3)_2$; b, R = $C(CH_3)_3$

Rearrangement of **8a** was induced with silver perchlorate in anhydrous benzene solution at 40° (22 hr). The major product (66%) was identified as **9** (Chart IV) from its pmr spectrum which featured a pair of three proton doublets (J = 6.5 Hz) for the diastereotopic methyl groups in addition to absorptions due to two bridgehead hydrogens and one vinyl proton. This spectral-based assignment for **9** and that for 2-isopropyl-1,3-cycloheptadiene (**10**, 8%) were simultaneously confirmed by quantitative photoisomerization of the latter diene into **9**. Comparison of the vinylic proton signals in the pmr spectrum of **11** (10%) with those of *syn*- and *anti*-1-ethylidenecyclohexene[4e] gave indication that this product was of the indicated syn stereochemistry. An attempt to prepare *syn*- and *anti*-**11** by reaction of isobutylidenetriphenylphosphorane with 2-cyclohexen-1-one was without success. Hydro-

(4) (a) L. A. Paquette, G. R. Allen, Jr., and R. P. Henzel, *J. Amer. Chem. Soc.*, **92**, 7002 (1970); (b) L. A. Paquette, S. E. Wilson, and R. P. Henzel, *ibid.*, **93**, 1288 (1971); (c) L. A. Paquette, R. P. Henzel, and S. E. Wilson, *ibid.*, **93**, 2335 (1971); (d) L. A. Paquette and S. E. Wilson, *ibid.*, **93**, 5934 (1971); (e) L. A. Paquette, S. E. Wilson, R. P. Henzel, and G. R. Allen, Jr., *ibid.*, **94**, 7761 (1972); (f) L. A. Paquette, S. E. Wilson, and R. P. Henzel, *ibid.*, **94**, 7771 (1972); (g) L. A. Paquette, R. P. Henzel, and S. E. Wilson, *ibid.*, **94**, 7780 (1972); (h) G. Zon and L. A. Paquette, *ibid.*, **95**, 4456 (1973).

(5) (a) M. Sakai, H. Yamaguchi, H. H. Westberg, and S. Masamune, *J. Amer. Chem. Soc.*, **93**, 1043 (1971); (b) M. Sakai and S. Masamune, *ibid.*, **93**, 4610 (1971); (c) M. Sakai, H. H. Westberg, H. Yamaguchi, and S. Masamune, *ibid.*, **93**, 4611 (1971).

(6) (a) G. Zon and L. A. Paquette, *J. Amer. Chem. Soc.*, **96**, 215 (1974); (b) L. A. Paquette and G. Zon, *ibid.*, **96**, 224 (1974).

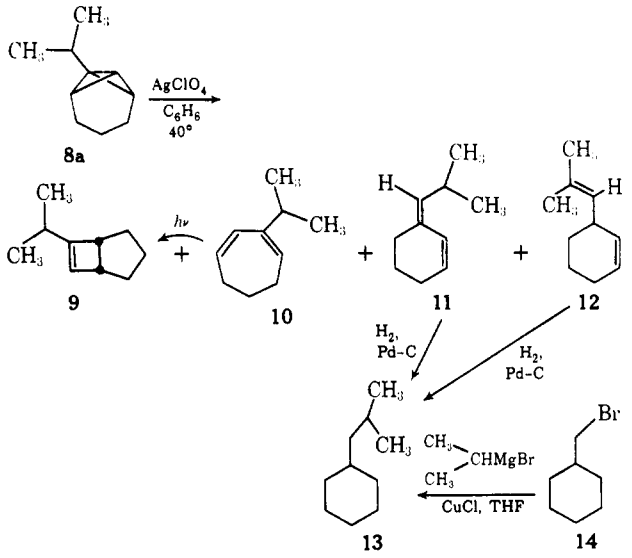
(7) For a recent theoretical consideration of the bonding in argento carbonium ions, see R. Noyori, *Tetrahedron Lett.*, 1691 (1973).

(8) G. L. Closs and L. E. Closs, *J. Amer. Chem. Soc.*, **85**, 2022 (1963).

(9) W. R. Moore, H. R. Ward, and R. F. Merritt, *J. Amer. Chem. Soc.*, **83**, 2019 (1961); W. R. Moore and B. J. King, *J. Org. Chem.*, **36**, 1877, 1882 (1971).

(10) W. R. Moore, private communication. These two hydrocarbons were in fact synthesized by Professor Moore by this method well before we became interested in them for this work. We are grateful to Professor Moore for his advice in this area.

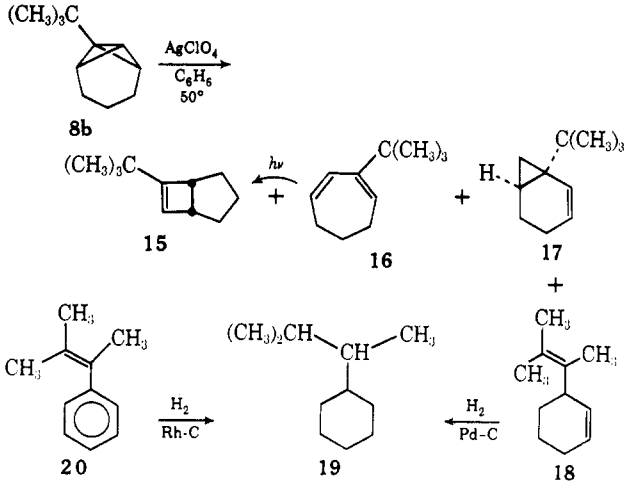
Chart IV. Products of the Ag^+-Catalyzed Rearrangement of **8a**



genation of **11** did, however, give a saturated hydrocarbon identical with an independently synthesized sample of isobutylcyclohexane (**13**). The last major volatile component showed principal pmr absorptions characteristic of three olefinic, one doubly allylic, and two allylic protons, as well as two nonequivalent sp^2-bonded methyl groups consistent with structure **12**. Catalytic hydrogenation of **12** similarly led exclusively to **13**. The origin of **12** can be explained by hydride shift of the tertiary isopropyl hydrogen to the argento carbonium ion center.

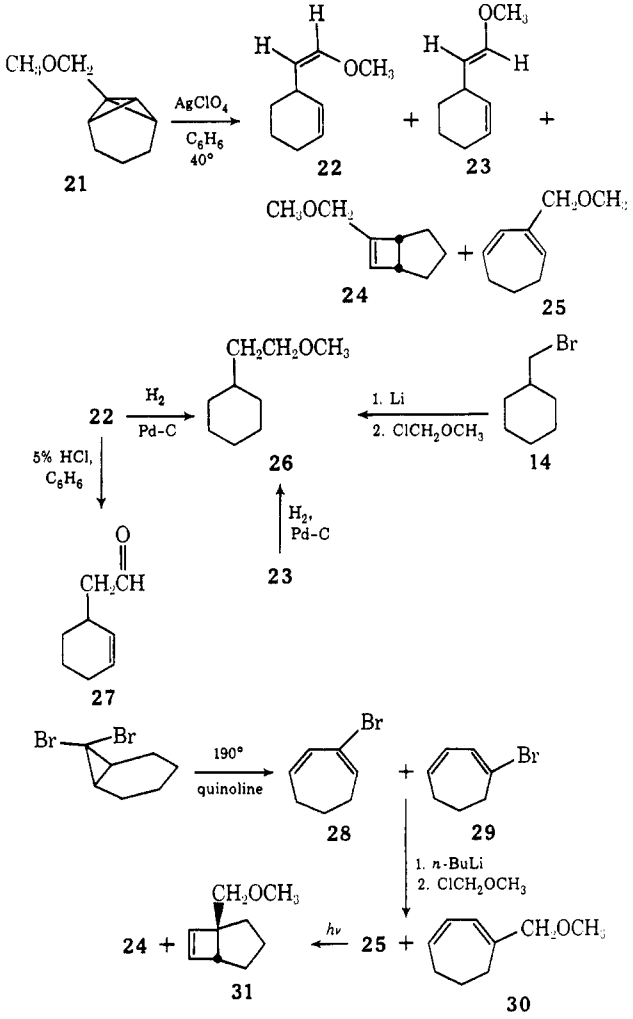
tert-Butyl derivative **8b** also underwent rearrangement in the presence of Ag^+ to a four-component mixture. In this instance the overwhelming product was 6-*tert*-butylbicyclo[3.2.0]hept-6-ene (**15**, 92%) (Chart V), the result of type γ bond reorganization.

Chart V. Products of the Ag^+-Catalyzed Rearrangement of **8b**



The pmr spectrum of **15** features the lone olefinic (δ 5.50) and pair of bridgehead protons (3.10 and 2.81) characteristic of this ring system. Further elaboration of this assignment was derived from the photoisomerization of **16** which was itself obtained in 4% yield after careful vpc isolation. The third component exhibited two cyclopropyl proton pmr multiplets (δ 0.39–0.76) and an olefinic proton doublet (6.08, 1 H, J = 10 Hz) and multiplet (5.32–5.56, 1 H) in addition to the *tert*-butyl singlet (0.84, 9 H) and a broad high field envelope of area 5 (2.2–1.3). These signals are sufficiently

Chart VI. Products of the Ag^+-Catalyzed Rearrangement of **21**



similar to a number of other 2-norcarenes[11] to define the molecule as **17** (2%). The least rapidly eluted component was identified as the methyl migrated diene **18** (2%) on the basis of its pmr spectrum and its catalytic reduction over 5% Pd–C to give 2-cyclohexyl-3-methylbutane (**19**), the independent synthesis of which was effected from known α,β,β-trimethylstyrene (**20**).

The 1-Methoxymethyltricyclo[4.1.0.0^{2,7}]heptane Series. Because these observations indicated that 1,2 shift of the allylic cyclohexene hydrogen to the argento carbocation center could be rendered competitive with hydride migration from an adjacent isopropyl group and Wagner–Meerwein methyl shift from a *tert*-butyl substituent, we sought to maximize this alternative migratory phenomenon. The substituent chosen for investigation was the methoxymethyl group since hydride shift from the methylene carbon to the adjoining electron-deficient organometallic center would eventuate in formation of a stabilized oxonium ion.[12]

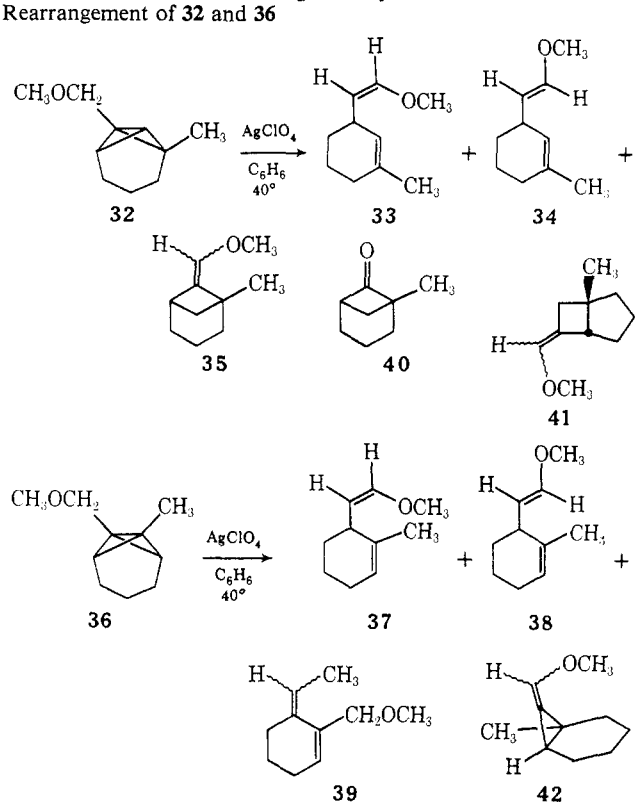
The preparation of **21** was effected by lithiation of the parent hydrocarbon with *n*-butyllithium and tetramethylethylenediamine (TMEDA) and subsequent addition of chloromethyl methyl ether. When **21** was treated with a solution of $AgClO_4$ in anhydrous benzene at 40°, there was produced a mixture of four isomeric products, each of which in turn was shown to be stable to the reaction conditions (Chart VI). The gross struc-

(11) L. A. Paquette and S. E. Wilson, *J. Org. Chem.*, 37, 3849 (1972).
(12) See, for example, J. Hine and J. Rosscup, *J. Amer. Chem. Soc.*, 82, 6115 (1960).

tures of **22** (88%) and **23** (3%) are consistent with the spectral evidence and individual catalytic hydrogenation to 2-cyclohexylethyl methyl ether (**26**). Whereas **22** and **23** are nonconjugated dienes as revealed by the presence of a doubly allylic proton in both pmr spectra, they are differentiated from each other by the coupling constants of the olefinic protons in the enol ether moiety. For **22**, J = 6.0 Hz whereas the same spin–spin interaction is twice as large for **23** (J = 12.5 Hz). Also, in the isomer with the β-vinyl proton and oxygen function trans (*i.e.*, **22**), the position of the vinyl proton resonance is at higher field (δ 4.31) than is the case when these same groups are cis disposed (4.74). These criteria have previously found application in assigning stereochemistry to enol ethers.[13] Additionally, acid-catalyzed hydrolysis of **22** gave aldehyde **27**. The minor products **24** (4%) and **25** (4%) were shown to exhibit pmr spectra identical with those of authentic samples prepared as shown in Chart VI.

Our previous finding that 1,2-dimethyltricyclo[4.1.0.0^{2,7}]heptane experiences type β rearrangement by regiospecific cleavage of the central and more highly substituted edge bond[4e] suggested that a comparison of the reactivities of **21** and **32** would be informative. Upon exposure to anhydrous $AgClO_4$ in benzene, **32** underwent isomerization chiefly to **33** (81%) and **34** (5%) (Chart VII). Thus, the reaction involving 1,2-

Chart VII. Products of the Ag^+-Catalyzed Rearrangement of **32** and **36**



hydride shift away from the methoxymethyl group gave indications of being general. An unexpected third product was also isolated in 12% yield. Its infrared spectrum (ν_{max} 1715 cm^{-1}) indicated the material to be an enol ether; the pmr data were in accord with this part structure and revealed further that the molecule possessed single olefinic (δ 5.77) and allylic hydrogens (3.2–3.0). From among the plausible structural possibilities, **42** is considered least compatible with the spectral evidence since the cyclopropyl bridgehead proton would be characterized by an unreasonably low field chemical shift. Of the two isomeric bicycloheptane possibilities, **41** was discounted by its independent synthesis from reaction of methoxymethylenetriphenylphosphorane with the cyclobutanone.[14] Because **41** exhibits an additional allylic methylene absorption at 2.44–2.18 (2 H), a set of signals lacking in the original product, its other methyl bridgehead isomer can also be excluded. Only enol ether **35**, which is differentiated from the others by virtue of an unconjugated cyclobutane methylene group, exhibits structural features consistent with the spectral evidence.[15] Unfortunately, reaction of ketone **40**[16] with $CH_3OCH{=}P(C_6H_5)_3$ failed to give **35**. Consequently, although **35** does remain the most consistent formulation, the assignment must be considered tentative.

The trends in the case of **32** were, like **21**, to produce large amounts of the cis enol ether and lesser quantities of the trans isomer. In contrast to **21**, **32** gave at best trace quantities of 1,3-cycloheptadiene (type α) and bicycloheptene (type γ) products.

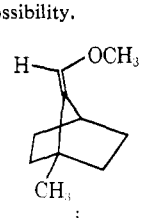
The final compound to be examined was **36**, selected because of the known propensity[4e] of structurally related 1,7-dimethyltricycloheptane for exclusive type β (80%) and γ (20%) rearrangement. When **36** was exposed to benzene–$AgClO_4$ solutions, no type γ bond reorganization took place. Rather, both possible type β processes operated exclusively with attack from the methoxymethyl direction being favored 16-fold over that at the bridgehead methyl center. On the basis of careful integration of vpc curves, the relative product distributon was shown to be 55% **37**, 38% **38**, 6% **39**, and 1% of an unknown minor component. The structural assignments in this instance follow from extensive spectral evidence (see Experimental Section).

1-(2-Methoxyethyl)tricyclo[4.1.0.0^{2,7}]heptane. Should the unprecedented reactivity patterns of **21**, **32**, and **36** be the result of ether oxygen proximity to the argento carbonium ion center, then insulation of the methoxyl substituent by an additional methylene group should result in a return toward "normal" reactivity. Inasmuch as **43** could be synthesized by sequential reaction of 1-lithiotricyclo[4.1.0.0^{2,7}]heptane with ethylene oxide and methyl iodide, we examined its skeletal rearrangement under conditions of Ag^+

(13) H. O. House and V. Kramar, *J. Org. Chem.*, **28**, 3362 (1963); H. O. House, L. J. Czuba, M. Gall, and H. D. Olmstead, *ibid.*, **34**, 2324 (1969); F. Bohlmann, C. Arndt, and J. Starnick, *Tetrahedron Lett.*, 1605 (1963).

(14) P. W. Jeffs and G. Molina, *J. Chem. Soc., Chem. Commun.*, 3 (1973).

(15) Enol ether i also is compatible in overall structure with the available spectral evidence. On mechanistic grounds, however, i must be judged to be a remote possibility.



i

(16) K. Wiberg and G. W. Kline, *Tetrahedron Lett.*, 1043 (1963); F. Nerdel, D. Frank, and H. Marshall, *Chem. Ber.*, **100**, 720 (1967); S. W. Baldwin and E. H. Page, Jr., *J. Chem. Soc., Chem. Commun.*, 1337 (1972).

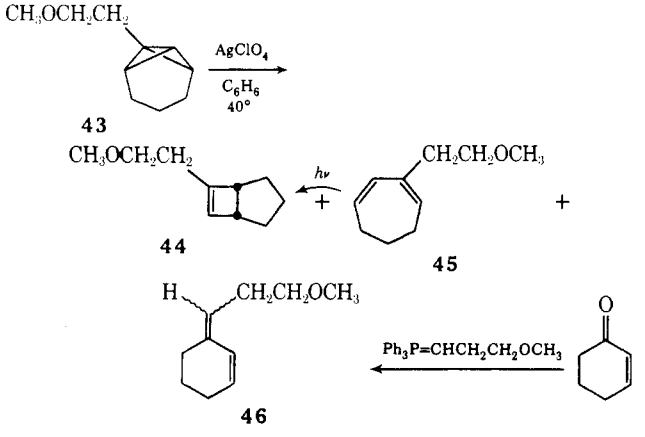
Table I. Comparative Rates of Rearrangement of Various Tricycloheptanes ($AgClO_4$, anhydrous C_6H_6, 40.0°)

Tricyclo-heptane	Initial rates of overall disappearance, k_{cat}, M^{-1} sec^{-1}	k_{rel}	Normalized isomerization rate constants k_i, M^{-1} sec^{-1} Type α	Type β	Type γ	Type δ	Type β'
	2.27×10^{-3}	17	2.27×10^{-3}				
	5.70×10^{-3}	43	1.5×10^{-3}	1.67×10^{-3}	2.52×10^{-3}		
8a	2.14×10^{-3}	16	1.7×10^{-4}	2.1×10^{-4}	1.41×10^{-3}		2.3×10^{-4} [a]
8b	1.31×10^{-4}	1	3.93×10^{-6}		1.21×10^{-4}	2.62×10^{-6}	2.62×10^{-6} [b]
21	6.71×10^{-3}	51	2.64×10^{-4}		2.75×10^{-4}		5.93×10^{-3} [c] 2.43×10^{-4} [d]
43	3.35×10^{-3}	26	6.70×10^{-4}	9.05×10^{-4}	1.77×10^{-3}		
32	1.17×10^{-1}	900					9.44×10^{-2} [e] 6.10×10^{-3} [f]
36	2.04×10^{-4}	1.6		1.31×10^{-5}			1.11×10^{-4} [g] 7.71×10^{-5} [h]

[a] Relates to formation of **12**. [b] Relates to formation of **18**. [c] Pertains to production of cis enol ether **22**. [d] Pertains to production of trans enol ether **23**. [e] For generation of cis isomer **33**. [f] For generation of trans isomer **34**. [g] Applies to extent to which cis isomer **37** was formed. [h] Applies to extent to which trans isomer **38** was formed.

catalysis. Three compounds were produced, the major (54%) component being identified as **44** (Chart VIII).

Chart VIII. Products of the Ag^+-Catalyzed Rearrangement of **43**



Approximately one-fifth (19%) of the mixture consisted of cycloheptadiene **45**. The remaining component is considered to be **46** (27%), vpc and pmr analysis of which suggests it to be a 4:1 mixture of syn and anti isomers. Ultraviolet irradiation of **45** led exclusively to **44**, and **46** was prepared independently by Wittig reaction of 3-methoxypropylidenetriphenylphosphorane on 2-cyclohexenone (syn:anti ≈ 1:4).

Expectation that the more remote oxygen atom in **43** would not effect mechanistic repercussions significantly different from those engendered by a simple 1-alkyl substituent was indeed realized. The reactivity profile for 1-methyltricycloheptane is such that structures comparable to **44–46** are obtained in very similar yield (44, 26, and 29%, respectively).[4e] Consequently, the hydride donating ability of the CH_2OCH_3 side chain must underlie the mechanistic changeovers observed for **21**, **32**, and **36**.

Kinetics Considerations. All of the tricycloheptanes examined in this study underwent rearrangement at convenient rates when exposed to anhydrous benzene solutions of silver perchlorate maintained at 40.0 ± 0.1° (Table I). The pseudo-first-order data reveal that the spread of relative rates of initial overall disappearance for **1** (R = H), **1** (R = CH_3), **8a**, **8b**, **21**, and **43** vary by no more than a factor of 50. This rather consistent kinetic behavior points to the minimal effect which such factors as major alterations in steric accessibility to the bicyclobutane ring by Ag^+ (compare **1**, R = H and **8b**) and possible changes in the site of preferential complexation (compare **1**, R = CH_3 and **21**) have on the *total* rate profile. Placement of an additional methyl group at C_2 (compare **21** and **32**), in contrast, results in acceleration in the reactivity of the tricycloheptane. When both bridgehead sites are substituted as in **36**, the rate of isomerization is decelerated, an observation consistent with the behavior of 1,7-dimethyltricycloheptane.[3e,6b]

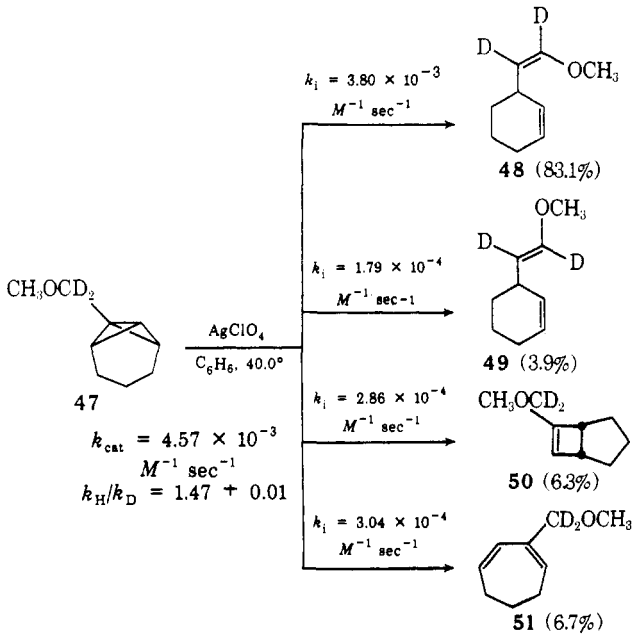
More revealing from the mechanistic standpoint are the variations in product distribution which arise upon alteration of the C_1 substituent. For example, whereas **1** (R = H) isomerizes solely by the type α pathway, bridgehead substitution by methyl (**1**, R = CH_3) alters this kinetically preferred conversion to 1,3-cycloheptadiene product and promotes competitive rearrangement of the type β and γ varieties. In fact, in this particular case the γ isomerization mode is favored over the other two by a factor of almost 2. These same reactivity features are exhibited by the 1-isopropyl (**8a**) and 1-*tert*-butyl derivatives (**8b**), with the latter evincing the slowest kinetic profile presumably as a consequence of steric factors.

When analyzed from the product composition direction, the divergent behavior is magnified further. Thus, as the size of the C_1 group is increased from H to CH_3, $CH(CH_3)_2$, and $C(CH_3)_3$, the type γ process becomes increasingly important (0, 44, 66, and 92, respectively). This mechanistic changeover occurs chiefly at the expense of the type α isomerization which is seen to drop off progressively through the series: 100, 26, 8, and 3%. These observations are consistent with the assumption that bond reorganization leading to bicycloheptene product arises by initial attack of Ag^+ on that face of the tricycloheptane nucleus more remote from the C_1 site. This point is to be elaborated upon later.[6]

Attack of Ag^+ at one of the more hindered edge bonds is now believed to promote concurrent cleavage of the central bond with generation of an intermediate argento carbonium ion. In accord with this mechanism, the rates of type β (and type B′)[17] isomerization are found to regress with incremental steric enlargement of the C_1 substituent. Progression through the series **21**, **1** (R = CH_3), **8a**, and **8b** demonstrates the decelerations in question. The approximately fourfold kinetic advantage enjoyed by **21** over **1** (R = CH_3) can be accounted for on the basis of complexation of Ag^+ to the methoxyl oxygen which reduces effective bulk and delivers the catalyst to the requisite area of reaction. It is interesting that in **36** where the ether oxygen has been further insulated from the bicyclobutane ring the combined type β and β' isomerization rate returns to a more normal value.

Deuterium Isotope Effect Studies. Rearrangement of dideuterated methoxymethyltricycloheptane **47** at 40.0 ± 0.1 ° in an azeotropically dried benzene solution of $AgClO_4$ proceeded with a k_{cat} of 4.57×10^{-3} M^{-1} sec^{-1}. The isotope effect for overall rate of disappearance of **47** is therefore $k_H/k_D = 1.47$, a value which compares favorably with that (1.21) observed for the 1-trideuteriomethyl derivative.[4f] Only minor changes in product distribution were noted (Chart IX). Rate

Chart IX. Products and Normalized Rate Constants Arising from Ag^+-Catalyzed Rearrangement of **47**



constant normalization and direct comparison with the rate constants derived from **21** revealed that the isomerizations leading to both **48** and **49** exhibit fractionation factors which are significantly positive, while those giving rise to **50** and **51** are inverse.

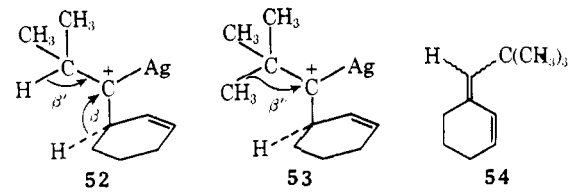
The data relating to enol ethers **48** and **49** reveal two significant facts. Firstly, the isotope effect values are, in keeping with the expected hyperconjugative effect of a $-CD_2-$ group, attached directly to the highly developed argento carbonium center in the rate-determining transition state. Secondly, the presence of both deuterium atoms on the enol ether double bonds attests to the operation of the 1,2-hydride shift.

In keeping with earlier results,[4f] the formation of **50** exhibits virtually a nil isotope effect as demanded by the original mechanistic conclusions wherein the C_1 carbon atom assumes negligible positive charge in the product-determining step of kinetic consequence. Since in the type α rearrangement which provides **51** the side chain likewise remains effectively insulated from the reaction site, the small inverse fractionation factor obtained in this instance is again compatible with the existing mechanistic model.

Discussion

Structural Requirements for Incursion of the Type β' Pathway. Relative Migratory Aptitudes to Argento Carbonium Ion Centers. Earlier it was noted that the presence of a bridgehead alkyl group on an edge bond of a tricycloheptane experiencing electrophilic attack by Ag^+ undergoes concomitant breakage of the central bond (the type β mechanism, Chart II) rather than subsequent rupture of a diametrically opposed edge bond. The chief controlling factor is assumedly[4f] the greater stability of the *tertiary* argento carbonium ions.

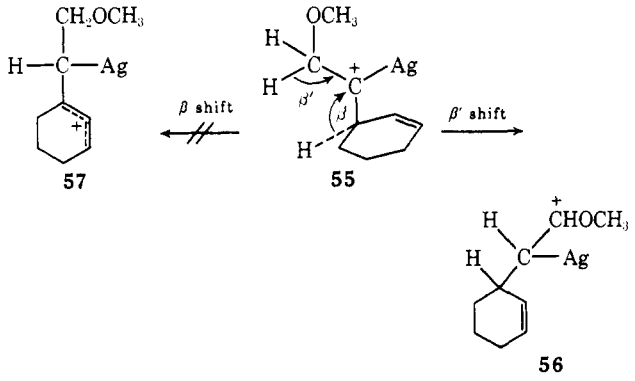
In our initial studies, product distributions gave evidence that 1,2-hydride shift of the allylic cyclohexene hydrogen to the cationic center was overwhelmingly preferred to hydride migration away from the methyl substituent (see Chart II). In the case of 1-isopropyltricycloheptane **8a**, the identity and nature of the product distributions require incursion of a second competing process involving hydride shift from the isopropyl group. Given the relative distribution of dienes **11** (10%) and **12** (11%), we infer that the type β and β' migrations in intermediate **52** are virtually isoenergetic. In the analogous argento carbonium ion derived from **8b** (*i.e.*, **53**), the migratory ability of a methyl substituent from the *tert*-butyl group exceeds that of the cyclohexene hydrogen by a factor equal to, or greater than, 4. This value is a lower limit, the accuracy of which is founded in part upon the amount of **18** produced (2%) and in part upon our experimentally



derived awareness that two very minor rearrangement products (0.5% each), present in concentrations too low to enable characterization, did also arise in this isomerization. It is well within the realm of possibility that one of these substances is **54**, although this need not be so.

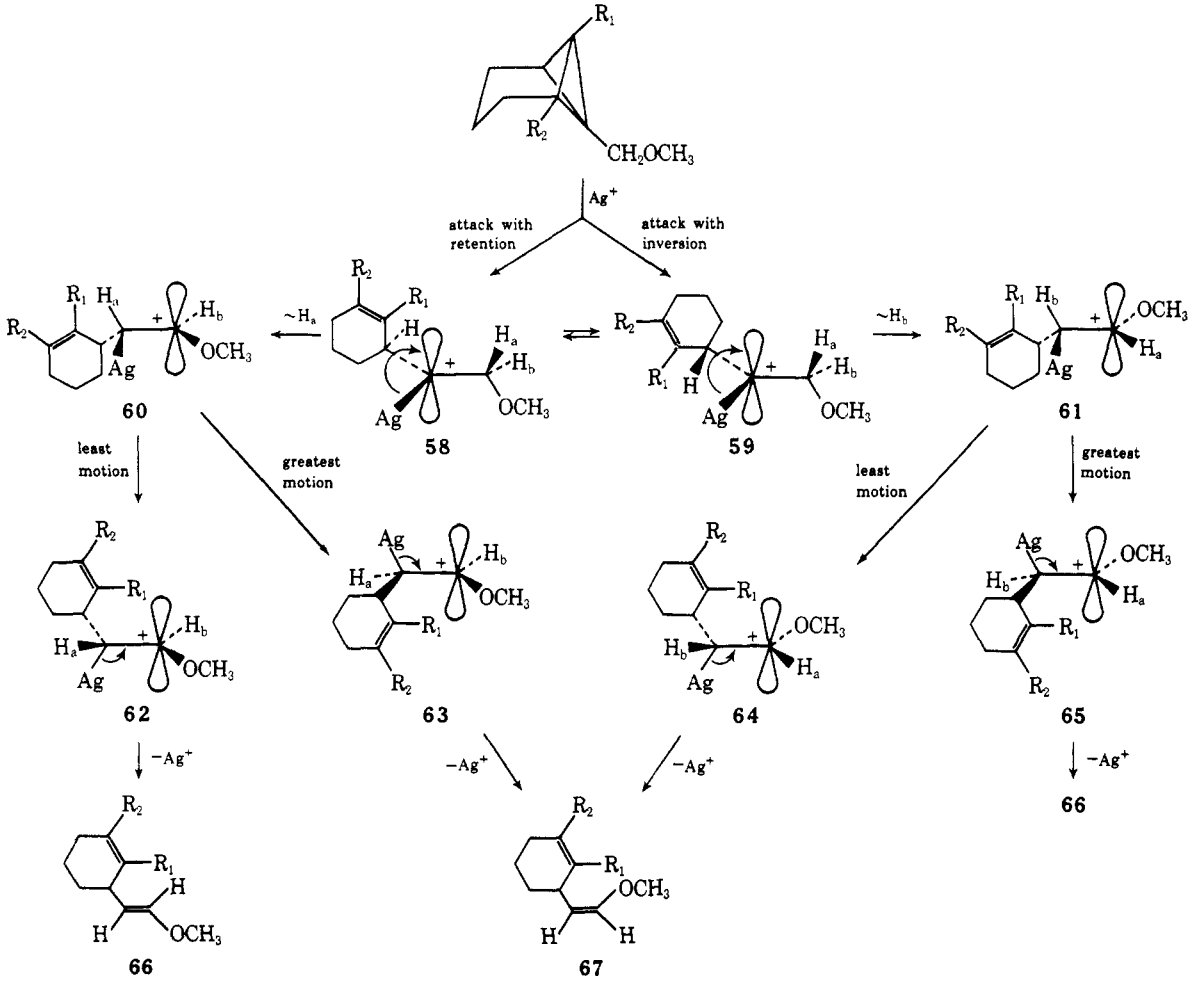
The question now arises as to whether the relative stabilities of the tertiary carbonium ions formed by migration of hydrogen or methyl in **52** and **53** are of major importance in determining the relative migratory aptitudes observed for these systems. On the basis of partial rate factors for migration of a wide spectrum of

(17) Type β' processes are herein defined for convenience as those bond reorganization pathways which proceed (as in the pure β examples) *via* intermediate argento carbonium ions. The differentiating feature is that subsequent hydride or alkyl shift to the electron-deficient center occurs from the direction opposite to that involving the allylic cyclohexene hydrogen atom.



three methoxymethyltricycloheptanes (**21**, **32**, and **36**) examined suggest that the transition states for the two possible 1,2 shifts receive significant stabilization from the newly developing carbonium ion center. Using **21** as the prototype, we reason that the initial product of rearrangement is argento carbonium ion **55**, which is not only characterized by its propensity for exclusive β'-hydride shift but must also derive extra transition state stabilization for this reaction manifold from the oxonium character of **56**. Since both rearrangements involve hydride shift, the driving force underlying the exoergic **55** → **56** reaction can be attributed most economically to the stability of **56**.

Chart X. Mechanistic Refinement of the Type β' Rearrangement with Stereochemical Detail



substituents in neopentyl solvolyses,[18] and particularly in the case of phenyl[18a] and cyclopropyl groups,[18d] it appears that stabilization of the transition state by delocalization of positive charge developing at the quaternary neopentyl carbon is small compared to the stabilization gained by cyclopropyl or phenyl migration. If the assumption is allowed that the type β and β' products are formed under conditions of kinetic control,[19] then the product distributions observed in the

Stereochemistry of Enol Ether Formation. Analysis of the Deargentation Process. An interesting finding was that rearrangement according to the β' mechanism led to a marked preponderance of the less stable geometric isomer. This was most evident in the methoxymethyl derivatives where the cis enol ethers dominated by substantial margins (**22**/**23** = 29; **33**/**34** = 16; **37**/**38** = 1.4). Insight into a kinetic basis can be gained by examining the structures of the intermediates which intervene along the β' reaction manifold. It is of interest to know whether Ag^+ attacks C_1 of the tricycloheptane with retention (to give initially **58**) or with inversion (providing **59**, see Chart X). Although clarification of this issue has remained elusive, we point out that this pair of argento carbonium ions is easily interrelatable by rotation of a single C–C σ

(18) (a) R. Heck and S. Winstein, *J. Amer. Chem. Soc.*, **79**, 3432 (1957); (b) E. N. McElrath, R. M. Fritz, C. Brown, C. Y. LeGall, and R. B. Duke, *J. Org. Chem.*, **25**, 2195 (1960); (c) R. S. Bly and R. T. Swindell, *ibid.*, **30**, 10 (1965); (d) Y. E. Rhodes and T. Takino, *J. Amer. Chem. Soc.*, **92**, 5270 (1970).

(19) This assumption seems justified from a number of points of view. Some of the more convincing evidence includes the far greater prominence of the thermodynamically less stable enol ethers **22**, **33**, and **37** relative to their trans counterparts (**23**, **34**, and **38**, respectively).

bond, such that the question of directional specificity in electrophilic attack by the transition metal ion becomes irrelevant.

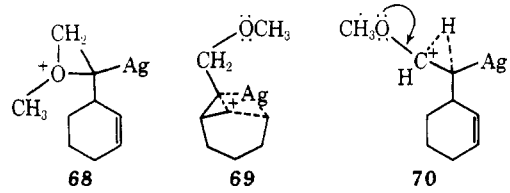
Examination of molecular models indicates that migration of one or the other diastereotopic $-CH_2O-$ hydrogen (H_a or H_b) effects generation of carbocations **60** and **61**, respectively, which differ significantly in nonbonded steric interactions. Should the activation for either hydride shift pathway be much larger than the barrier to interconversion between conformers **58** and **59**, the ratio of **60** and **61** will depend only on the difference between the transition-state energies (the "Curtin–Hammett principle").[20] The fact that Ag^+ is bulkier than an unsubstituted cyclohexene ring (**60**, **61**, $R_1 = R_2 = H$) may be sufficient to promote favored migration of H_b, at least to the extent that the greater relative stability of **61** (compared to **60**) is reflected in the transition state for its formation. The highly substituted nature of the metal-bond carbon in **60** and **61** raises the possibility that deargentation, the process by which Ag^+ is returned to the medium, operates under the control of ponderal factors and proceeds preferably in that direction which requires minimal rotation of this center. As illustrated in Chart X, **61** would selectively pass through **64** to give cis enol ether **67**, while **60** would eject Ag^+ from rotamer **62** to afford **66**. In summary it is possible that the predominance of **67** arises because of the kinetically favored intervention of **61** and **64**, the competing process involving **60** → **62** → **66**.

Some measure of support for this rationale is gained by examining the increasing steric bulk of the cyclohexene moiety in these structures. In the case of **32** for example, the situation arises in which $R_2 = CH_3$ and $R_1 = H$. This change is not as drastic as witnessed with **36** which forms intermediates wherein $R_1 = CH_3$ and $R_2 = H$. These structural modifications provide a useful series in which the nonbonded interactions generated by the cyclohexene substituent gradually approximate those engendered by the silver atom. As a consequence, the energy difference between **58** and **59**, originally maximized when $R_1 = R_2 = H$, is progressively minimized such that when $R_1 = CH_3$ and $R_2 = H$ these intermediates become internally encumbered to roughly comparable degrees. Since the ponderal effects associated with bond rotation in **60** and **61** are not relaxed, the increasing bulkiness of the cyclohexene ring could serve to increase the relative amount of **60** and ultimately trans enol ether **67** which is produced. The observed decreasing selectivity (29:16:1.4) is satisfactorily accounted for in these terms.

Factors Controlling Product Distribution. The fact that increases in effective size of the substituent in 1-substituted tricycloheptanes leads to a rapid dropoff in type α isomerization with a concomitant enhancement of type γ rearrangement suggests that the formation of bicycloheptenes occurs when Ag^+ attacks the tricycloheptane from the C_7 direction.[6]

A further interesting comparison emerges from analysis of the product distributions which arise from Ag^+-catalyzed rearrangement of **1** ($R = CH_3$), **21**, and **43**. The methyl and 2-methoxyethyl systems show a great deal of similarity in partitioning of the available bond reorganization pathways. Thus, the relative proportions of α, β, and γ products from **1** ($R = CH_3$) are 26, 29, and 44%, respectively,[4e] whereas for **43** the values are 20, 27, and 53%. Seemingly, therefore, the inherent steric differences between these two substituents are not sufficient to promote significant mechanistic changeover which is already clearly evident upon isopropyl substitution (8, 21, and 66%).

In this context, the influence of the methoxymethyl group must necessarily be considered anomalous. For **21**, the product distribution is partitioned in a direction which greatly favors the type β' rearrangement manifold (4, 92, and 4%). This state of affairs may arise as a result of effective delivery of Ag^+ to one of the more highly substituted edge bonds through prior complexation with the proximate ether oxygen. This entropy advantage is presumably not accessible to **43** to a comparable degree because of the increased distances involved. The alternative possibility exists that the free energy decrease for the type β pathway finds its origin in argento carbonium ion stabilization such as illustrated in **68** or some sort of less well defined lone-pair stabilization typified by **69**. In any event, it is now



68 **69** **70**

clear that the presence of divalent oxygen in the immediate neighborhood of a transient argento carbonium ion has a favorable effect on its genesis.

Finally, the differing magnitude of k_H/k_D for formation of **48** and **49** (Chart IX), while revealing nonequivalent influences operative in the individual migrations, seemingly mitigates against rate-determining transition states involving synchronous hydride shift (*cf.* **70**). When compared to the fractionation factor determined for type β rearrangement of 1-trideuteriomethyltricycloheptane (1.21),[4f] roughly comparable rate-retarding effects are seen. In this latter example, no deuterium migration takes place. Consequently, these effects may be attributed chiefly to the rate-retarding inductive effect associated with carbocation generation adjacent to the isotopically labeled carbon atoms. Should entities such as **68** and **69** have any real existence, they could perhaps account for the somewhat larger magnitude of the isotope effect.

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; the cited absolute percentage compositions were obtained on this instrument. Kinetic determinations were carried out with the aid of a Hewlett-Packard 5750 unit (flame ionization detector) equipped with an electronic integrator. All rearrangements proceeded in essentially quantitative yield.

Rearrangement of 8a. A dry benzene solution (3.0 ml) of iso-

(20) E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill, New York, N. Y., 1962, pp 151, 152, 238.

merically pure (≥99%, vpc analysis) **8a**[10,21] (436 mg, 3.2 mmol) containing 0.54 mmol of silver perchlorate was heated at 40.0 ± 0.1° for 22 hr, treated with an excess of saturated sodium chloride solution, and extracted with pentane. Preparative scale vpc isolation on column A[22] (90°) led to collection of 200 mg (66% of the original mixture, vpc analysis) of the major product (**9**) and simultaneous collection of three extensively overlapping components (86 mg). Three additional minor components (0.5, 1.5, and 3.0%) were not isolated in quantities adequate for characterization. Careful separation of the above mixture on column B (45°) permitted isolation of pure **10** (8%), isomerically enriched **11** (10%, *ca.* 80% **11** and 20% **10**), and pure **12** (11%).

For **9**: $\delta_{TMS}^{CDCl_3}$ 5.67 (br s, 1 H_7), 3.21–2.73 (m, 2, H_1 and H_5), 2.41–1.89 (m, 1, $CH(CH_3)_2$), 1.89–1.14 (m, 6, ring methylenes), 0.99 (d, J = 6.5 Hz, 3, CH_3), and 0.97 (d, J = 6.5 Hz, 3, CH_3).

Anal. Calcd for $C_{10}H_{16}$: C, 88.16; H, 11.84. Found: C, 88.33; H, 11.96.

For **10**: $\delta_{TMS}^{CDCl_3}$ 6.00–5.54 (m, 3, olefinic), 2.64–2.3 (m, 1, $CH(CH_3)_2$), 2.3–2.04 (apparent quintet with 6 Hz spacing, 4, H_3 and H_7), 2.00–1.72 (apparent quartet with *ca.* 5–6-Hz spacing, 2, H_6), and 0.89 (d, J = 7.0 Hz, 6, $CH(CH_3)_2$). Calcd *m/e* 136.1252; obsd, 136.1253.

For **11**: $\delta_{TMS}^{CDCl_3}$ 6.38 (d with fine splitting, J = 10 Hz, 1, H_2), 6.12–5.56 (m, 1, H_3), 4.92 (d with fine splitting, J = 9 Hz, 1, >CH-*i*-Pr), 2.88–2.44 (m, 1, $CH(CH_3)_2$), 2.36–2.00 (m, 4, H_4 and H_6), 1.84–1.58 (apparent quartet with 6-Hz spacing, 2, H_5), and 0.89 (d, J = 7.0 Hz, 6, $CH(CH_3)_2$). Calcd *m/e* 136.1252; obsd, 136.1253.

For **12**: $\delta_{TMS}^{CDCl_3}$ 5.53 (q with additional fine splitting, 2, ring olefinic, $J_{AB} \cong 11$ Hz, $\Delta\nu_{AB} \cong 21$ Hz), 5.00 (d, J = 9 Hz with additional fine splitting, $J \cong 1$ Hz, side chain vinyl), 2.93 (br m, 1, doubly allylic), 2.08–1.84 (m, 2, allylic), 1.66 (d, J = 1 Hz, 3, CH_3), 1.61 (d, J = 1 Hz, 3, CH_3), and 1.84–0.85 (m, 4, methylenes). Calcd *m/e* 136.1252; obsd, 136.1254.

Photolysis of 10. A chilled (5°) ether solution (0.75 ml) of **10** (5 mg) was irradiated with a 450-W Hanovia mercury arc through quartz optics for 75 min. Vpc analysis on column A (125°) indicated the absence of **10** and the presence of essentially one (~90%) new product which exhibited the same retention time as **9**. Preparative vpc isolation (same conditions) of this component and subsequent pmr analysis confirmed it to be **9**.

Hydrogenation of 11. A solution of 5 mg of **11** in 5 ml of absolute ethanol was subjected to catalytic hydrogenation over 10 mg of 10% Pd–C at 1 atm in the usual manner. After 20 min, the filtered solution was diluted with water (5 ml) and extracted with pentane (2 × 1 ml). The major (*ca.* 80%) component was isolated by preparative vpc purification on column A (70°) and identified as **13** by comparison of its retention time and ir spectrum with that of authentic material (*vide infra*).

Hydrogenation of 12. Atmospheric catalytic hydrogenation of **12** (10 mg) as described for **11** led to rapid (*ca.* 10 min) consumption of 2 equiv of hydrogen. Following work-up, preparative vpc collection of the major (>95%) component gave a sample of **13** (5 mg, 50%) which was identified by comparison of its retention time and pmr–ir spectra with authentic material (*vide infra*).

Isobutylcyclohexane (13).[23] A solution of isopropylmagnesium bromide in anhydrous tetrahydrofuran (10 ml), prepared from 1.23 g (10 mmol) of isopropyl bromide and 300 mg (12 mg-at) of magnesium turnings, was added to 30 ml of tetrahydrofuran and 10 mg (0.1 mmol) of cuprous chloride was introduced at 4°. After dropwise addition of cyclohexylmethyl bromide (1.6 g, 9 mmol) in tetrahydrofuran (5 ml), the mixture was allowed to stir at ambient temperature for 22 hr. Water (30 ml) was added, and the combined pentane extracts (2 × 30 ml) were washed with water (3 × 30 ml) and brine (100 ml), and dried. Solvent was removed by careful atmospheric distillation. Preparative vpc analysis of the residual oil on column A (75°) led to collection of 70 mg (6%) of **13** which was identified by its pmr spectrum: $\delta_{TMS}^{CDCl_3}$ 1.80–0.90 (m, 14, methines and methylenes) and 0.82 (d, J = 6.0 Hz, 6, $CH(CH_3)_2$).[24]

Rearrangement of 8b. A solution of pure (>99%) **8b**[25] (387 mg, 2.6 mmol) and silver perchlorate (0.36 mmol) in anhydrous benzene (2 ml) was heated at 50.0 ± 0.1° for 18 hr, during which time a small amount of black precipitate was deposited. Preparative vpc (column A, 120°) of the quenched (aqueous sodium chloride) and extracted (pentane) reaction mixture led to collection of the three major components (ratio 92:5:2). Two trace components (*ca.* 0.5% each) were seen but not characterized.

The major and most rapidly eluting isomer was characterized as **15**; $\delta_{TMS}^{CDCl_3}$ 5.50 (s, 1, H_7), 3.10 (dd, *ca.* 3–4-Hz spacing, 1, H_1 or H_5), 2.81 (dd, *ca.* 3–4-Hz spacing, 1, H_1 or H_5), 2.0–0.8 (m, 6, methylenes), and 1.00 (s, 9, $C(CH_3)_3$). Further confirmation of the structural assignment was gained by photoisomerization of **16** (*vide infra*).

Anal. Calcd for $C_{11}H_{18}$: C, 87.93; H, 12.07. Found: C, 87.71; H, 11.91.

Identification of the slowest eluting product as **18**, after further vpc purification (column B, 45°), followed from its pmr spectrum and ultimate hydrogenation to **19** (*vide infra*); $\delta_{TMS}^{CDCl_3}$ 5.84–5.58 (m, 1, olefinic), 5.38 (d, J = 10 Hz, with additional fine splitting, 1, olefinic), 3.44–3.08 (br m, 1, doubly allylic), 2.18–1.44 (m, 6, methylenes), 1.65 (br s with fine splitting,[26] J = 1 Hz, 6, methyls), and 1.51 (br s with fine splitting,[26] J = 1 Hz, 3, methyl). For $C_{11}H_{18}$, *m/e* 150.1409 (calcd *m/e* 150.1408).

Vpc analysis of the original central fraction on the silver nitrate column (column B, 45°) showed it to consist of two fractions in a 60:40 ratio. These were readily separated under these conditions and the more rapidly eluting isomer was found to be 2-*tert*-butyl-1,3-cycloheptadiene (**16**) as revealed by its pmr spectrum and photoisomerization to **15** (*vide infra*). The less dominant substance has been tentatively assigned structure **17** from pmr and ir data.

For **16**: $\delta_{TMS}^{CDCl_3}$ 6.12–5.64 with apparent s at 6.03 (m, 3, $H_{1,3,4}$), 2.24–1.80 (m, 6, methylenes), and 1.04 (s, 9, $C(CH_3)_3$).

For **17**: $\delta_{TMS}^{CDCl_3}$ 6.08 (d, J = 10 Hz, with additional fine splitting, 1, H_2), 5.56–5.32 (m, 1, H_3), 2.20–1.28 (m, 5, $H_{4,5,6}$), 0.84 (s, 9, $C(CH_3)_3$), and 0.76–0.39 (m, 2, H_7); ν_{max}^{neat} 3070, 3035, 3005, 2960, 2860, 1640, 1465, 1365, 1150, and 690 cm^{-1}; for $C_{11}H_{18}$ *m/e* 150.1411 (calcd *m/e* 150.1408).

Photoisomerization of 16. An ether solution (0.75 ml) of **16** (6 mg) was irradiated as described above. Preparative vpc isolation (column A, 125°) of the lone photoproduct led to its identification as **15** on the basis of its retention time and pmr spectral comparison.

Hydrogenation of 18. A 3-mg sample of **18** was hydrogenated for 1 hr in the manner previous described. Vpc isolation (column A, 110°) indicated one product with a retention time equal to that of independently prepared **19**. This identification was confirmed by appropriate ir comparison.

2-Cyclohexyl-3-methylbutane (19). A solution of 10 g (0.068 mol) of **20**[26] in 100 ml of absolute ethanol containing 2.5 g of 5% rhodium on carbon was shaken in a Parr apparatus at 50 psig and 25°. After 18 hr, the filtered solution was concentrated. Vpc analysis (column A, 145°) indicated complete reduction, at which point a sample of **19** was collected: $\delta_{TMS}^{CDCl_3}$ 2.00–1.00 (br m, 13, methine and methylenes), 0.88, 0.78, and 0.73 (three d, J = 7.0 Hz, 9, CH_3).

Anal. Calcd for $C_{11}H_{22}$: C, 85.63; H, 14.37. Found: C, 85.64; H, 14.42.

1-Methoxymethyltricyclo[4.1.0.0^{2,7}]heptane (21). Tetramethylethylenediamine (380 mg, 3.3 mmol) was added under nitrogen to a magnetically stirred solution of *n*-butyllithium (3.3 mmol) in hexane (1.5 ml) which was cooled to 5°. A solution of tricyclo[4.1.0.0^{2,7}]heptane (310 mg, 3.3 mmol) in pentane (1 ml) was added and the mixture was stirred at room temperature for 24 hr. Pentane (1 ml) was added to the reaction mixture and a solution of chloromethyl methyl ether (0.25 ml, 3.3 mmol) in pentane (2 ml) was introduced at 5° during 3 min. After 0.5 hr at this temperature, the mixture was treated with 10 ml of saturated sodium bicarbonate solution and 2 ml of pentane and shaken in a separatory funnel.

(21) Nmr: $\delta_{TMS}^{C_6D_6}$ 2.20 (br s, 2, H_2 and H_6), 1.98 (heptet, J = 6.5 Hz, 1, $-CH(CH_3)_2$), 1.50–1.13 with maximum at 1.37 (7, H_7 and methylene protons), and 0.93 (d, J = 6.5 Hz, 6, $-CH(CH_3)_2$).

(22) The vpc columns employed in the preparative separations consisted of 0.25-in. (60 ml/min flow) or 0.125-in. (15 ml/min flow) Al tubing of varying lengths packed with the following stationary phases: A, 12 ft 8% Carbowax 20M on 60–80 mesh Chromosorb G; B, 6 ft 23% $AgNO_3$–glycerol (30:70) on 60–80 mesh firebrick; C, 12 ft 5% Carbowax 20M on NaOH-washed Chromosorb P (60–80 mesh); D, 10 ft 4.5% QF-1 on 60–80 mesh Chromosorb G; E, 10 ft 15% PMPE (5-ring) on Chromosorb W (DMCS, 80–100 mesh); F, 10 ft 5% Carbowax 20M on NaOH-washed Chromosorb P (60–80 mesh); G, 10 ft 10% Carbowax 20M on NaOH-washed Chromosorb P (60–80 mesh).

(23) This preparation of **13** was based on a report concerning analogous CuCl-catalyzed coupling reactions by M. Tamura and J. Kochi, *J. Amer. Chem. Soc.*, **93**, 1485 (1971).

(24) F. K. Signaigs and P. L. Cramer, *J. Amer. Chem. Soc.*, **55**, 3326 (1933).

(25) Nmr: $\delta_{TMS}^{CDCl_3}$ 2.41–2.18 (m, 2, H_2 and H_6), 1.40–1.15 (br s, 7, H_7 and methylenes), and 0.97 (s, 9, $-C(CH_3)_3$).

(26) For model systems in which similar homoallylic coupling of *ca.* 1.0–1.5 Hz is reported, see G. P. Newsoroff and S. Sternhell, *Aust. J. Chem.*, **19**, 1667 (1966).

The organic layer was washed with brine (10 ml), dried, and flash-vacuum distilled (0.2 mm) using a pot temperature of 100° and collecting all volatiles in a receiver cooled to −79°. Preparative vpc (column C, 90°) of the distillate yielded 136 mg (27%) of **21** as a fragrant colorless oil: $\delta_{TMS}^{C_6D_6}$ 3.63 (s, 2, CH_2OCH_3), 3.24 (s, 3, OCH_3), 2.30 (br, s 2, H_2 and H_6), 1.34 (br s, 6, methylenes), and 1.19 (t, J = 3 Hz, 1, H_7).

Anal. Calcd for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 78.09; H, 10.22.

Rearrangement of 21. A solution of **21** (94 mg, 0.7 mmol) in dry benzene (1.0 ml) was treated with an anhydrous solution of silver perchlorate (0.27 mmol) in benzene (1.5 ml) at 40° for 3 hr. Quenching and work-up followed the procedure employed above. Preparative vpc (column C, 105°) gave an analytically pure sample of **22** (60 mg, 64%) together with **23**, **24**, and **25**. Duplicate repetition of the above reaction on a smaller scale gave the following relative product distribution in the order of elution: 4 3% **24**, 88.4% **22**, 3.4% **23**, and 3.9% **25**.

For **22**: $\delta_{TMS}^{CDCl_3}$ 5.88 (dd, J = 6 and 1 Hz, 1, $=CHOCH_3$), 5.62 (br s, 2, cyclohexene olefinic), 4.31 (dd, J = 9 and 6 Hz, 1, $-CH=CHOCH_3$), 3.58 (s, 3, OCH_3), 3.48–3.00 (m, 1, doubly allylic), and 2.25–1.17 (m, 6, methylenes); ν_{max}^{neat} 3025, 2935, 2855, 1664, 1387, 1248, and 1113 cm^{-1}.

Anal. Calcd for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 77.97; H, 10.20.

For **23**: $\delta_{TMS}^{CDCl_3}$ 6.34 (d, J = 12.5 Hz, 1, $=CHOCH_3$), 6.00–5.54 (m, 2, cyclohexene olefinic), 4.74 (dd, J = 12.5 and 8.5 Hz, 1, $CH=CHOCH_3$), 3.50 (s, 3, OCH_3), 2.95–2.33 (m, 1, doubly allylic), and 2.17–1.33 (m, 6, methylenes).

Ethers **24** and **25** were identified by comparison of their pmr spectra with those of authentic samples (*vide infra*).

Control Experiments for Rearrangement of 21. Separate pmr samples of **24** (5 mg) and a mixture of **25** and **30** (5 mg, 65:35) in C_6D_6 (0.20 ml) were treated with an anhydrous solution (50 μl) of $AgClO_4$ in benzene (0.179 *M*) and heated at 40° for 6 hr. Pmr analysis indicated that no detectable changes had occurred under these conditions.

A solution of **22** (5 mg) in benzene (0.30 ml) with *o*-xylene as internal standard was mixed with a solution (0.45 ml) of anhydrous $AgClO_4$ in benzene (0.179 *M*) and heated at 40° for 23 hr. Work-up in the usual manner and vpc analysis (column C, 125°) revealed that only a trace amount of aldehyde **27** had formed, presumably due to the presence of traces of adventitious moisture.

Hydrogenation of 22. A solution of **22** (14.8 mg, 0.11 mmol) in absolute ethanol (2.0 ml) was added under 1 atm of hydrogen to a magnetically stirred suspension of 10% palladium on carbon (10 mg) in absolute ethanol (3.0 ml) which had been presaturated with hydrogen. The rapid uptake of hydrogen ceased after 10 min. After stirring the mixture for an additional 30 min, it was gravity filtered, diluted with pentane (2 ml), and shaken with water (5 ml). The separated aqueous layer was washed with pentane (3 ml) and the combined pentane layers were subjected to preparative vpc (column C, 105°). The only detectable component was collected (7.5 mg, 49%) and subsequently identified as **26** by comparison of retention time and pmr–ir spectra with those of authentic material (*vide infra*).

Hydrogenation of 23. Following the above procedure, 2 mg of pure **23** was similarly reduced to **26**. Identification was achieved by comparison of vpc retention times on three columns (C, 80°; D, 80°; E, 108°).

2-Cyclohexylethyl Methyl Ether (26). A solution of cyclohexylmethyl bromide (3.54 g, 20 mmol) in anhydrous ether (20 ml) was added over a period of 30 min to a magnetically stirred suspension of cut lithium wire (0.276 g, 40 mg-atoms) in ether using a water bath for cooling and an argon atmosphere. After addition, the mixture was stirred at ambient temperature for 1 hr and transferred by syringe to a predried flash which was equipped with a magnetic stirrer and serum cap. After cooling to 5°, an ether solution (5 ml) of chloromethyl methyl ether (1.80 g, 22 mmol) was introduced during 5 min and the reaction mixture was stirred at this temperature for an additional 45 min before addition of water (5 ml). The resulting mixture was washed twice with saturated aqueous sodium bicarbonate solution (50 ml) and then with brine (50 ml). The organic phase was dried and evaporated, and the residue (1.81 g) was vacuum distilled (much foaming!) to give a pale yellow distillate (650 mg), bp 50–70° (30 mm). Preparative vpc purification of a portion of this material gave **26**: ν_{max}^{neat} 2925, 2855, 1450, and 1121 cm^{-1}; $\delta_{TMS}^{CDCl_3}$ 3.57–3.33 (m, 2, CH_2OCH_3), 3.33 (s, 3, OCH_3), and 1.90–0.67 (m, 13).

Anal. Calcd for $C_9H_{18}O$: C, 75.99; H, 12.75. Found: C, 75.84; H, 12.81.

Acid-Catalyzed Hydrolysis of 22. A solution of **22** (15 mg) in benzene (0.5 ml) was vigorously stirred at room temperature with a solution of 5% aqueous hydrochloric acid. After 21 hr, the separated benzene layer was diluted with pentane (1 ml), washed with saturated sodium bicarbonate solution (2 ml), and dried. Vpc analysis (column C, 125°) indicated the presence of 11% unreacted **22** and a sole reaction product. The latter was collected and found to be an unpleasant smelling colorless oil (4.5 mg, 38%): ν_{max}^{neat} 3020, 2930, 2860, 2840, 2720, 1725, 1560, 1450, 1395, and 720 cm^{-1}; $\delta_{TMS}^{CDCl_3}$ 9.69 (apparent 6-line m, J = 1 Hz, 1, CHO), 5.60 (AB q with additional fine splitting, J_{AB} = 11 Hz, $\Delta\nu_{AB}$ = 11.6 Hz, 2, vinyl), 2.93–2.20 (m, 3, methine and CH_2CHO), 2.20–1.85 (m, 2, allylic methylene), and 1.85–1.13 (m, 4, methylenes); for $C_8H_{12}O$ *m/e* 124.0890 (calcd *m/e* 124.0888).

1- and 2-Methoxymethyl-1,3-cycloheptadienes (30 and 25). A solution of *n*-butyllithium (5.1 mmol) in hexane (2.3 ml) was added during 5 min to a magnetically stirred solution of a *ca.* 50:50 mixture of **28** and **29**[27] (800 mg, 4.6 mmol) in ether (8 ml) at 5° under nitrogen. After 8.5 hr at room temperature, the reaction mixture was cooled to 5° and chloromethyl methyl ether (1.2 g, 15 mmol) was added over a period of 3 min. After 25 min, the contents was poured into saturated aqueous sodium bicarbonate solution (30 ml) contained in a separatory funnel. After shaking, the separated organic layer was washed with brine (20 ml), dried, and flash-vacuum distilled (0.1 mm) at a pot temperature of 100° and using a receiver cooled to −79°. Preparative vpc (column C, 120°) led to simultaneous collection (due to extensive overlap) of the major (65%) and minor (35%) products. Based upon the photolysis results described below, the major and minor ethers were identified as **25** and **30**, respectively: $\delta_{TMS}^{CDCl_3}$ 6.02–5.74 (m, 3, olefinic), 3.85 (br s, 2, CH_2OCH_3), 3.29 (s, 3, OCH_3), 2.59–2.12 (m, 4, allylic), and 2.08–1.62 (m, 2, methylene). The spectrum in C_6D_6 was essentially the same as that in $CDCl_3$ except for the absorptions at 3.85 and 3.29 which now exhibited resonance doubling. The signals due to **25** appeared *ca.* 2 Hz to lower field than those of **30** and predominated by a factor of 2:1.

Anal. Calcd for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 78.07; H, 10.34.

1-Methoxymethyl- and 6-Methoxymethylbicyclo[3.2.0]hept-6-enes (31 and 24). An ether solution (2 ml) of the above mixture of **25** and **30** (24.6 mg) was placed in a stoppered quartz test tube and irradiated for 75 min at 5° with a 450-W Hanovia lamp housed in a water-cooled quartz immersion well. Vpc analysis (column C, 105°) indicated the absence of cycloheptadienes and the formation of two products. The minor (6.5 mg) and major (9.6 mg) components were collected (66%) and identified as **24** and **31**, respectively, from their characteristic pmr spectra.

For **31**: $\delta_{TMS}^{CDCl_3}$ 5.98 (s, 2, olefinic), 3.52 (s, 2, CH_2OCH_3), 3.37 (s, 3, OCH_3), 2.83 (d with fine splitting, J = 5 Hz, 1, bridgehead), and 2.08–0.85 (m, 6, methylenes). For $C_9H_{14}O$ *m/e* 138.1046 (calcd *m/e* 138.1044).

Anal. Calcd for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 78.15; H, 10.17.

For **24**: $\delta_{TMS}^{CDCl_3}$ 5.78 (br s, 1, olefinic), 3.82 (br s, 2, CH_2OCH_3), 3.34 (s, 3, OCH_3), 3.3–2.88 (m, 2, bridgeheads), and 1.97–0.83 (m, 6, methylenes). For $C_9H_{14}O$ *m/e* 138.1046 (calcd *m/e* 138.1044).

Anal. Calcd for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 78.03; H, 10.17.

1-Methoxymethyl-2-methyltricyclo[4.1.0.0^{2,7}]heptane (32). A 147-mg (1.3 mmol) sample of 2-methyltricyclo[4.1.0.0^{2,7}]heptane[4e] was lithiated and treated with chloromethyl methyl ether as described above. Preparative vpc (column C, 120°) of the flash-vacuum distillate afforded 20.5 mg (10%) of **32** as a colorless oil: $\delta_{TMS}^{C_6D_6}$ 3.72 (AB q, J_{AB} = 12 Hz, $\Delta\nu_{AB}$ = 25.8 Hz, 2, CH_2OCH_3), 3.25 (s, 3, OCH_3), 2.33–2.12 (m, 1, H_6), 1.83–0.85 with max at 1.34 (m, 7, methylenes and H_7), and 0.97 (s, 3, CH_3); calcd *m/e* 152.1201; found 152.1204.

Anal. Calcd for $C_{10}H_{16}O$: C, 78.90; H, 10.59. Found: C, 78.60; H, 10.54.

Rearrangement of 32. A solution of **32** (15 mg, 0.1 mmol) in dry benzene (0.50 ml) was mixed with an anhydrous solution (0.25 ml) of $AgClO_4$ in benzene (0.179 *M*) and the resultant solution was heated at 40° for 4.5 hr. After the predescribed sodium chloride quench and work-up, vpc analysis (column C, 120°) indicated (order of elution) the presence of **35** (12%), **33** (81%), and **34** (5%)

(27) D. G. Lindsay and C. B. Reese, *Tetrahedron*, **21**, 1673 (1965).

which were collected and identified from the following spectral data. Two more slowly eluting unknown products (1% and 0.5%) were also detected.

For **33**: ν_{max}^{neat} 3035, 3000, 2935, 2856, 2835, 1660, 1450, 1387, 1245, and 1110 cm^{-1}; $\delta_{TMS}^{CDCl_3}$ 5.87 (dd, J = 6 and 1 Hz, 1, =C*H*OCH$_3$), 5.26 (m, 1, ring olefinic), 4.29 (dd, J = 9 and 6 Hz, 1, C*H*=CHOCH$_3$), 3.58 (s, 3, OCH$_3$), 3.47–2.92 (m, 1, doubly allylic), and 2.17–0.95 with max as 1.69 (m, 9, methylenes and CH$_3$). For $C_{10}H_{16}O$ *m/e* 152.1200 (calcd *m/e* 152.1201).

Anal. Calcd for $C_{10}H_{16}O$: C, 78.90; H, 10.59. Found: C, 78.92; H, 10.57.

For **34**: ν_{max}^{neat} 3035, 3000, 2930, 2860, 2835, 1650, 1450, 1207, 1135, and 931 cm^{-1}. For $C_{10}H_{16}O$ *m/e* 152.1200 (calcd *m/e* 152.1201). The mass spectral fragmentation patterns for **34** and **33** were virtually identical.

For **35**: ν_{max}^{neat} 2945, 2860, 2830, 1715, 1695, 1450, 1220, and 1120 cm^{-1}; $\delta_{TMS}^{CDCl_3}$ 5.77 (br s, 1, olefinic), 3.56 (s, 3, OCH$_3$), 3.2–3.0 (m, 1, bridgehead), 2.0–1.5 (m, 8, methylenes), and 1.02 (s, 3, CH$_3$).

Anal. Calcd for $C_{10}H_{16}O$: C, 78.90; H, 10.59. Found: C, 78.61; H, 10.35.

1-Methoxymethyl-7-methyltricyclo[4.1.0.0^{2,7}]heptane (36). Lithiation and methoxymethylation of 1-methyltricyclo[4.1.0.0^{2,7}]-heptane[4e] (630 mg, 5.8 mmol) by the procedure described above and preparative vpc isolation (column C, 105°) of the flash-vacuum distillate yielded 260 mg (29%) of **36** as a colorless oil: ν_{max}^{neat} 2930, 2855, 2820, 1442, 1190, 1131, 1103, 981, and 909 cm^{-1}; $\delta_{TMS}^{C_6D_6}$ 3.51 (s, 2, C*H*$_2$OCH$_3$), 3.18 (s, 3, OCH$_3$), 2.01 (br s, 2, H$_2$ and H$_6$), 1.33 (br s, 6, methylenes), and 1.27 (s, 3, CH$_3$).

Anal. Calcd for $C_{10}H_{16}O$: C, 78.90; H, 10.59. Found: C, 78.75; H, 10.67.

Rearrangement of 36. A sample of **36** (140 mg, 0.9 mmol) was dissolved in an anhydrous solution (2.0 ml) of $AgClO_4$ in benzene (0.179 *M*) and the mixture was heated at 68° for 5 hr before quenching and work-up in the usual manner. Preparative vpc (column C, 120°) led to the collection (order of elution) of **37** (55%), **38** (38%), **39** (6%, 65:35 isomer mixture), and an unknown (1%).

For **37**: ν_{max}^{neat} 3030, 3000, 2930, 2855, 1670, 1659, 1447, 1388, 1247, and 1111 cm^{-1}; $\delta_{TMS}^{CDCl_3}$ 5.93 (d, J = 6 Hz, 1, =C*H*OCH$_3$), 5.44 (m, 1, ring olefinic), 4.32 (dd, J = 10 and 6 Hz, 1, C*H*=CHOCH$_3$), 3.58 (s, 3, OC*H*$_3$), 3.37–2.92 (m, 1, doubly allylic), 2.15–1.75 (m, 2, allylic), 1.75–1.28 (m, 4, methylenes), and 1.62 (s with fine splitting, 3, methyl).

Anal. Calcd for $C_{10}H_{16}O$: C, 78.90; H, 10.59. Found: C, 78.97; H, 10.60.

For **38**: ν_{max}^{neat} 3050, 3035, 3000, 2930, 2855, 2835, 1665, 1648, 1447, 1207, 1132, and 935 cm^{-1}; $\delta_{TMS}^{CDCl_3}$ 6.33 (d, J = 12.5 Hz, 1, =C*H*OCH$_3$), 5.47 (m, 1, ring olefinic), 4.71 (dd, J = 12.5 and 9 Hz, 1, C*H*=CHOCH$_3$), 3.51 (s, 3, OCH$_3$), 2.72–2.20 (br m, 1, doubly allylic), 2.20–1.8 (m, 2, allylic), 1.8–1.33 (m, 4, methylenes), and 1.53 (s with fine splitting, 3, methyl).

Anal. Calcd for $C_{10}H_{16}O$: C, 78.90; H, 10.59. Found: 78.89; H, 10.60.

For **39′**: ν_{max}^{neat} 2930, 2863, 2830, 1448, 1193, 1129, 1087, and 792 cm^{-1}; $\delta_{TMS}^{CDCl_3}$ 6.07–5.67 (m, 1, ring olefinic), 5.33 (br q, J = 7 Hz, 1, =C*H*CH$_3$), 4.12 (br s, 2, -CH$_2$O-), 3.34 (s, 3, OCH$_3$), 2.42–2.01 (m, 4, allylic), 2.0–1.5 (m, 2, methylene), and 1.82 (br d, J = 7 Hz, 3, methyl). For $C_{10}H_{16}O$ *m/e* 152.1202 (calcd *m/e* 152.1201).

For **39″**: ν_{max}^{neat} 3030, 2980, 2925, 2860, 2835, 1640, 1450, 1190, 1131, 1091, and 826 cm^{-1}; $\delta_{TMS}^{CDCl_3}$ 5.95–5.75 (m, 1, ring olefinic), 5.51 (br q, J = 7 Hz, 1, =C*H*CH$_3$), 4.04 (br s, 2, -CH$_2$O-), 3.33 (s, 3, OCH$_3$), 2.52–2.0 (m, 4, allylic), 2.0–1.42 (m, 2, methylene), and 1.72 (br d, J = 7 Hz, 3, methyl). For $C_{10}H_{16}O$ *m/e* 152.1202 (calcd *m/e* 152.1201).

1-Methylcyclopentene. The usual two-step procedure[28,29] for conversion of cyclopentanone to 1-methylcyclopentene *via* *p*-toluenesulfonic acid monohydrate catalyzed dehydration of 1-methylcyclopentanol was circumvented by use of the presently reported method which afforded a comparable yield based on starting cyclopentanone.

Cyclopentanone (84 g, 1.0 mol) was slowly added during 1 hr to an ether solution of methylmagnesium bromide which was prepared in the normal fashion from methyl iodide (170 g, 1.2 mol), magnesium turnings (29 g, 1.2 g-atoms), and anhydrous ether (500 ml). After the mixture was stirred at 25° for 12 hr, dilute aqueous hydrochloric acid (300 ml, 5 *N*) was slowly added with ice-bath cooling and after 1 hr of stirring the separated aqueous layer was extracted with ether (2 × 100 ml). The combined organic layers were washed with saturated aqueous sodium bicarbonate solution and brine, dried, and evaporated. The azeotropic distillate (bp 45–93°) was processed by separation of the water phase, washing with brine, drying, and redistillation. There was obtained 39 g (48%) of 1-methylcyclopentene.

7,7-Dichloro-1-methylbicyclo[3.2.0]heptan-6-one. Activated zinc dust[30] (26 g, 0.40 g-atom), 1-methylcyclopentene (12.5 g, 0.15 mol), and ether (150 ml) were stirred mechanically in a three-necked flask (250 ml) equipped with a condenser, nitrogen inlet, and addition funnel. Freshly distilled trichloroacetyl bromide (16 ml, 0.13 mol) in ether (15 ml) was slowly added (1 hr), during which time reflux was maintained (*Caution:* occasional vigorous frothing!). One hour after completion of the addition, the solid was removed by filtration and the filtrate was treated with saturated sodium bicarbonate solution until gas evolution ceased. After ether extraction (2 × 200 ml) of the aqueous slurry, the combined ether layers were washed with brine, dried, and concentrated. The dark orange residue was filtered through silica gel (ether) and then alumina (ether) and the resulting product (25 g, 30%) was used without further purification.[14]

1-Methylbicyclo[3.2.0]heptan-6-one. A magnetically stirred suspension of the impure dichloro ketone (7.5 g, *ca.* 0.04 mol) and zinc dust (50 g, 0.77 g-atom) in glacial acetic acid (75 ml) was heated at 100–110° for 2 hr. The cooled reaction mixture was filtered and the solid was washed thoroughly with benzene (3 × 50 ml). Water (750 ml) was added to the combined filtrates and the separated aqueous phase was extracted with benzene (3 × 100 ml). The combined benzene solutions were washed with saturated sodium bicarbonate solution and brine, and finally dried. Solvent removal gave 5 g (~100%) of a light brown oil that was identified as the desired ketone on the basis of its pmr spectrum.[12]

***syn-* and *anti*-6-Methoxymethylidene-1-methylbicyclo[3.2.0]heptane (41).** A hexane solution (0.5 ml) of *n*-butyllithium (1 mmol) was added to a magnetically stirred suspension of methoxymethyltriphenylphosphonium chloride (342 mg, 1 mmol) in ether (2 ml) and the red mixture was stirred at ambient temperature for 30 min. A solution of crude 1-methylbicyclo[3.2.0]heptan-6-one (124 mg, *ca.* 1 mmol) in ether (0.5 ml) was added and the mixture was refluxed for 18 hr before addition of saturated sodium bicarbonate solution (0.5 ml) and pentane (2 ml). The dried organic layer was flash-vacuum distilled (bath temperature 80° (0.1 mm)) and preparative vpc of the condensate (column A, 145°) yielded 30% of an approximate 1:1 mixture of *syn-* and *anti*-**41** as two extensively overlapped peaks: $\delta_{TMS}^{CDCl_3}$ 5.79–5.57 (m, 1, olefinic), 3.50 and 3.48 (two s in *ca.* 1:1 ratio, 3, two OCH$_3$), 2.95–2.55 (br m, 1, H$_5$), 2.44–2.18 (four-line m, 2, H$_7$), 1.95–1.30 (m, 6, H$_2$–H$_4$), and 1.22 (s, 3, methyl).

Anal. Calcd for $C_{10}H_{16}O$: C, 78.90; H, 10.59. Found: C, 78.86; H, 10.71.

Careful preparative re-vpc (column A, 120°) gave small quantities of each geometric isomer. For the more rapidly eluting component: ν_{max}^{neat} 2940, 2860, 2835, 1703, 1677, 1454, 1221, 1134, and 1103 cm^{-1}. For $C_{10}H_{16}O$ *m/e* 152.1203 (calcd *m/e* 152.1201). For the slower eluting component: ν_{max}^{neat} 2940, 2860, 2830, 1705, 1679, 1452, 1223, 1154, 1129, 1116, and 1101 cm^{-1}. Found *m/e* 152.1203.

1-(2-Methoxyethyl)tricyclo[4.1.0.0^{2,7}]heptane (43). According to the procedure described above, tricyclo[4.1.0.0^{2,7}]heptane (280 mg, 3 mmol), *n*-butyllithium (3 mmol), and TMEDA (350 mg, 3 mmol) were allowed to react at room temperature for 24 hr. Pentane (2 ml) was added, the reaction mixture was cooled to 5°, and ice-cold ethylene oxide (2 ml, 40 mmol) was introduced in one portion. Stirring was continued at 5° for 2 hr and at 25° for 3 hr before dilution with pentane (1 ml) and addition of cold methyl iodide (3 ml, 50 mmol) at 5°. After 2 hr, the cooling bath was removed and stirring was continued at room temperature for 15 hr. The reaction mixture was washed with water (3 × 10 ml) and brine (10 ml) before flash distillation *in vacuo* (0.2 mm) at 80°. Preparative vpc of the −80° condensate (column C, 105°) yielded 30 mg (7%) of **43**: $\delta_{TMS}^{C_6D_6}$ 3.33 (t, J = 6.5 Hz, 2, -CH$_2$O-), 3.13 (s, 3, OCH$_3$), 2.17 (br s, 2, H$_2$ and H$_6$), 2.02 (t, J = 6.5 Hz, 2, -C*H*$_2$CH$_2$O-), and 1.50–1.12 with maximum at 1.35 (m, 7, methylenes and H$_7$). For $C_{10}H_{16}O$ *m/e* 152.1204 (calcd *m/e* 152.1201).

Rearrangement of 43. A 30-mg sample of **43** in C_6D_6 (0.25 ml) was heated with a solution (0.15 ml) of anhydrous $AgClO_4$ in

(28) G. Chavanne and L. Vogel, *Bull. Soc. Chim. Belg.*, **37**, 141 (1928).

(29) A. C. Cope, C. L. Bumgardner, and E. E. Schweizer, *J. Amer. Chem. Soc.*, **79**, 4729 (1957).

(30) W. T. Brady, H. G. Liddell, and W. L. Vaughn, *J. Org. Chem.*, **31**, 626 (1966).

benzene (0.179 *M*) at 40° for 24 hr. Following the usual work-up procedure, preparative vpc (column C, 120°) led to collection of **44** (54%), **45** (19%), and a 4:1 mixture of *syn*- and *anti*-**46** (27%) which were identified by their characteristic pmr spectra and various chemical interconversions (*vide infra*).

For **44**: $\delta_{TMS}^{CDCl_3}$ 5.58 (m, 1, olefinic), 3.48 (t, J = 6.5 Hz, 2, $-CH_2O-$), 3.33 (s, 3, OCH_3), 3.17–2.92 (m, 2, H_1 and H_5), 2.22 (br t, J = 6.5 Hz, 2, $-CH_2CH_2O-$), and 1.78–0.83 (m, 6, methylenes). For $C_{10}H_{16}O$ *m/e* 152.1203 (calcd *m/e* 152.1201).

For **45**: $\delta_{TMS}^{CDCl_3}$ 5.80–5.44 (m, 3, olefinic), 3.48–3.16 with maximum at 3.28 (m, 5, CH_2OCH_3), 2.40–2.04 (m, 6, allylic), and 2.00–1.64 (m, 2, methylene). For $C_{10}H_{16}O$ *m/e* 152.1203 (calcd *m/e* 152.1201).

For **46**: $\delta_{TMS}^{CDCl_3}$ 6.36 (d, J = 10 Hz, 1), 5.86–5.54 (m, 1), 5.16–4.88 (m, 1), 3.46–3.22 with maximum at 3.24 (m, 5, CH_2OCH_3), 2.52–1.96 (m, 6, allylic), and 1.82–1.60 (m, 2, methylene).

Photoisomerization of 45. A sample of **45** (1 mg) dissolved in ether (0.20 ml) was irradiated as described above. Vpc analysis revealed the absence of **45** and formation of **44** established on the basis of comparative retention times on three different columns.

***syn*- and *anti*-(3-Methoxypropylidene)-2-cyclohexene (46).** A magnetically stirred suspension of 3-methoxypropyltriphenylphosphonium chloride[31] (2.5 g, 6.8 mmol) in anhydrous tetrahydrofuran was heated to 60° and treated with *n*-butyllithium (6.8 mmol) in hexane (3.4 ml). After 3 hr at this temperature, 2-cyclohexen-1-one (300 mg, 3 mmol) was added and the mixture was refluxed for 18 hr. Brine (10 ml) was added after cooling and followng pentane extraction the combined organic layers were dried, concentrated and flash-vacuum distilled (160°, 0.05 mm). Preparative vpc of the condensate (column C, 125°) gave 50 mg (11%) of an analytically pure sample of *syn*- and *anti*-**46** (1:4).

Anal. Calcd for $C_{10}H_{16}O$: C, 78.90; H, 10.59. Found: C, 78.80; H, 10.60.

Gas Chromatographic Kinetic Analyses for $AgClO_4$-Catalyzed Rearrangements of Substituted Tricyclo[4.1.0.0^{2,7}]heptanes. General Procedure. All runs were performed at 40.0 ± 0.1° using a constant-temperature circulating water bath. Purified (preparative vpc) substrates were injected into solutions of $AgClO_4$–benzene that were thermally equilibrated for 20 min in a 1-dram screw-cap glass vial, which was equipped with a tight-fitting rubber septum. Differences in initial substrate and $AgClO_4$ concentrations were governed by substrate availability and lability toward rearrangement, respectively. Aliquots (50–100 μl) were quickly removed by syringe, shaken with saturated aqueous sodium chloride solution (1.5–2.0 ml) and pentane (50-100 μl), and stored at 0°. Vpc analyses of the supernatant organic layers were completed within 1–12 hr to minimize errors (due to product volatility), and were carried out with a Hewlett-Packard Model 5750 gas chromatograph in the flame-ionization mode. Peak areas were determined by the "cut-and-weigh" technique, using Xerox copies of the original traces, and were not corrected for differential flame-ionization sensitivities, due to the relatively small amount of samples available. Quantitative product distributions were derived from thermal conductivity measurements. Plots of ln ([substrate]$_i$/[substrate]$_t$) *vs.* time exhibited good linearity generally to greater than 3 half-lives and slopes were calculated from manually fitted straight lines. Values for individual catalytic rate constants (k_i) were calculated by multiplication of the overall catalytic rate constants (k_{cat}) by the experimentally determined (vpc) relative product percentages. Pertinent information regarding each substrate is detailed below. Overall and individual catalytic rate constants are summarized in Table I. The k_i values have been treated as pseudo-first-order reactions, an assumption believed to be valid in view of the kinetic behavior of the various tricycloheptanes where the individual pathways dominate.

A. 1-Methoxymethyltricyclo[4.1.0.0^{2,7}]heptane (21). Vpc analysis of six aliquots obtained over a period of 2000 sec (*ca.* 90% conversion) from the reaction of **21** (10 mg, 0.072 mmol) in $AgClO_4$–benzene (1.00 ml of 0.179 *M*) were carried out using column F (82°, 15 ml/min), on which **21** and all products (**22**–**25**) were separable. Due to the preponderance of *cis*-vinyl ether **22** in the product distribution, the relative ratios of **21**:**22** were measured with time. A duplicate kinetic run indicated good precision.

B. 1-Methoxymethyl-d_2-tricyclo[4.1.0.0^{2,7}]heptane (47). The complete procedure used for kinetic analysis of **47** was identical with that described above for **21**. Pairs of **21** and **47** kinetic analyses were run simultaneously to minimize errors in determination of the isotope effect.

C. 1-(2-Methoxyethyl)tricyclo[4.1.0.0^{2,7}]heptane (43). A solution of **43** (6.1 mg, 0.040 mmol) in dry benzene (100 μl) was injected into a preequilibrated $AgClO_4$–C_6H_6 (1.00 ml) solution and four aliquots were removed over a period of 3600 sec (*ca.* 87% conversion), after which time the relative ratio of **45**:**44** and **43** (overlapping peaks) were measured using column F (115°). The relative amount of **43** was readily computed by subtraction of the relative amount of **44** calculated from the product distribution measured after complete reaction (*ca.* 18 hr). Acceptable precision was obtained in a duplicate run (six aliquots).

D. 1-Methoxymethyl-2-methyltricyclo[4.1.0.0^{2,7}]heptane (32). Five aliquots were removed over a period of 1300 sec (*ca.* 92% conversion) from a reaction mixture of **32** (10 mg, 0.065 mmol) in $AgClO_4$–benzene (1.00 ml of 0.0179 *M*) and were analyzed on column F (95°). As in the case of **21**, the relative ratios of major product **33** to **32** and **35** (overlapping peaks) were monitored and translated to values of ln ([**32**]$_i$/[**32**]$_t$) by use of the product distribution measured after complete reaction (*ca.* 18 hr). A duplicate run was carried out to check precision.

E. 1-Isopropyltricyclo[4.1.0.0^{2,7}]heptane (8a). Reaction of **8a** (20 mg, 0.147 mmol) in $AgClO_4$–benzene (1.00 ml of 0.179 *M*) and removal of four aliquots over a period of 3600 sec (*ca.* 74% conversion) led to measurement of the relative ratio of **8a** and major product **9** (overlapped peaks) to **10**–**12** (overlapped peaks) peak areas, using column G (80°). These data were then transformed to ln ([**8a**]$_i$/[**8a**]$_t$) *vs.* time points in a manner analogous to that described above for **43**, and a duplicate run was carried out. It should be noted that determination of the product distribution after complete rearrangement required the use of preparative vpc collection and reinjection on a second ($AgNO_3$-coated) column. Consequently, additional possibility for accuracy errors is present in the product distribution (and hence k_i values) reported herein for **8a**.

Pmr Kinetic Analyses for $AgClO_4$-Catalyzed Rearrangements of Substituted Tricyclo[4.1.0.0^{2,7}]heptanes. General Procedure. Substrates **8b** and **36** were purified by preparative vpc immediately prior to use and reaction solutions were sealed (*in vacuo*) in precision-bore thin-walled nmr tubes. All runs were performed in the absence of light at 40.0 ± 0.1° using a constant-temperature circulating water bath, except for the relatively short periods of time (*ca.* 15 min) during transport to and from (*via* Dewar-bath at 39 ± 1°) pmr analysis at the ambient peak temperature (*ca.* 39 ± 2°, methanol calibration) of a Varian A60-A spectrometer. Kinetic plots exhibited acceptable linearity generally to greater than 3 half-lives and slopes were calculated from manually fitted straight lines. Specific details for each compound follow.

A. 1-*tert*-Butyltricyclo[4.1.0.0^{2,7}]heptane (8b). Over a period of *ca.* 43 hr (*ca.* 95% conversion), a sample of **8b** (28 mg, 0.187 mmol) in $AgClO_4$–benzene (0.300 ml of 0.179 *M*) was used to obtain six data points calculated directly from the relative peak heights of the individual $C(CH_3)_3$ singlets of **8b** and major product **15**. The usual data treatment led to the values given in Table I.

B. 1-Methoxymethyl-7-methyltricyclo[4.1.0.0^{2,7}]heptane (36). A sample of **36** (20 mg, 0.13 mmol) in dry benzene-d_6 (0.150 ml) and $AgClO_4$–benzene (0.150 ml of 0.179 *M*) was employed and five data points over a period of 48 hr (*ca.* 94% conversion) were obtained. Each data point was calculated by comparing the relative integrated signal intensities for the OCH_3 singlet of **36** *vs.* the two overlapping OCH_3 singlets for major products **37** and **38**.

1-Methoxymethyl-d_2-tricyclo[4.1.0.0^{2,7}]heptane (47). The same procedures as described above for **21** were employed using chloromethyl-d_2 methyl ether[32] (>95% d_2 by pmr). The pmr spectrum of **47** was essentially identical with that of **21** except for the absence of detectable absorption due to the CH_2OCH_3 protons at δ 3.63. For $C_9H_{12}D_2O$ *m/e* 140.1171 (calcd *m/e* 140.1170).

Rearrangement of 47. A 20-mg sample of **47** in benzene-d_6 (0.25

(31) Obtained by refluxing 1-chloro-3-methoxypropane [E. Haworth and W. H. Perkin, Jr., *J. Chem. Soc.*, **65**, 591 (1894)] and triphenylphosphine in benzene for 100 hr: mp 203–207°; $\delta_{TMS}^{CDCl_3}$ 8.00–7.40 (m, 15, aromatic), 4.10–3.42 (m, 4, $>\overset{+}{P}CH_2-$ and $-CH_2O-$), 3.20 (s, 3, OCH_3), and 2.40–1.70 (m, 2, $-CH_2CH_2O-$).

(32) The procedure reported by M. Schlosser [*Chem. Ber.*, **97**, 3219 (1964)] for the preparation of this substance was modified by replacement of DCl acidification with direct dichloromethane extraction of triphenylmethoxymethyl-α-d_2-phosphonium chloride and subsequent drying. In order to effect near complete D/H exchange, this phosphonium salt (*ca.* 85% d_2) was recycled a second time.

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.

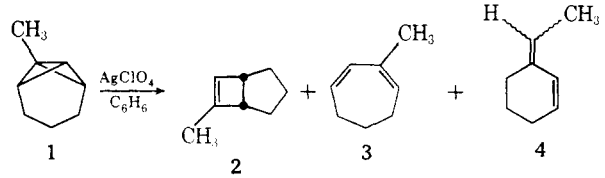
Stereospecificity and Regioselectivity Attending Type γ Rearrangement of 1,3-Disubstituted Tricyclo[4.1.0.0^{2,7}]heptanes under Conditions of Ag(I) Catalysis[1]

Gerald Zon[2] and Leo A. Paquette*

Contribution from the Department of Chemistry, The Ohio State University, Columbus, Ohio 43210. *Received July 26, 1973*

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).