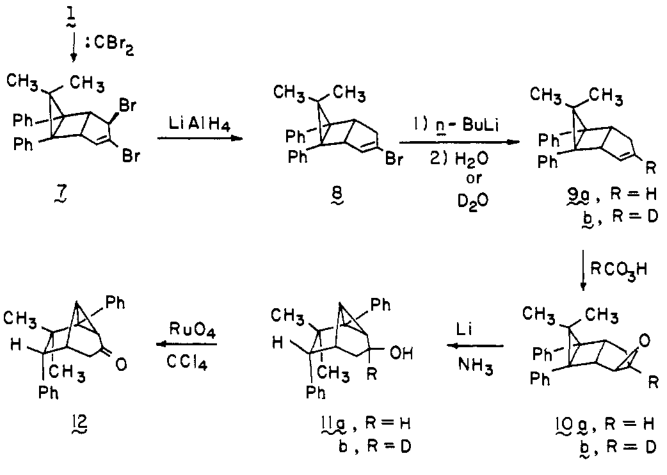
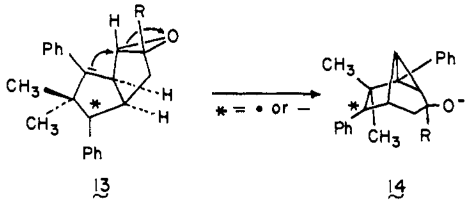
The hydroxyl group in **3** has been assigned the exo orientation on the strength of the multiplicity and coupling constant of the α-hydroxyl proton.[10a] The endo stereochemistry of the 4-phenyl substituent was deduced from the coupling constant of H_4 with H_3 ($J = 3.6$ Hz) characteristic of an *exo*-norbornyl proton[10b] and this assignment was supported by the finding that **3** reacts with triphenylphosphine dibromide[11] to give dibromide **6**, mp 142.5–143.5°,[3] whose detailed structure was established by three-dimensional X-ray analysis.[12]

Further insight into the generality and mechanism of the title reaction was gained from examination of the behavior of unsymmetrical epoxides **10a** and **10b**. These were available by conversion of **1** to dibromide **7** by reaction with dibromocarbene, followed by lithium aluminum hydride reduction, metal–halogen interconversion, and addition of water or deuterium oxide. The nmr spectrum ($CDCl_3$, 60 MHz) of hydrocarbon **9a** exhibits singlet resonances at δ 7.22 (10 H, aryl), 1.57 (3 H, methyl), and 0.73 (3 H, methyl), multiplets of area 1 at 5.8, 5.55, 3.3, and 2.85, and a two-proton mutiplet at 2.35.[14] When derived epoxide **10a** was subjected to the action of lithium in liquid ammonia, **11a**, mp 131–132°,[3] was obtained in 95% yield. The nmr spectrum of the latter compound shows the presence of ten aryl protons (s, δ 7.3) and two methyl groups (s, 1.19 and 0.73) in addition to an endo α-hydroxyl proton adjacent to a methylene group (t, $J = 5.5$ Hz, 5.06). The methylene and methine protons appear together with the OH peak as two groups of multiplets centered at 2.85 (4 H) and 1.72 (3 H). In like fashion, **10b** led uniquely to **11b** (nmr analysis). Ruthenium tetroxide oxidation gave ketone **12**, mp 151–152.5°.[3]



The nonindiscriminant deuterium labeling pattern in **11b** reveals that the epoxide ring does not experience initial reduction in this reaction since highly regiospecific C–O bond cleavage is not expected.[15] It must be concluded, therefore, that the cyclopropyl bond common to the two phenyl substituents is ruptured with overwhelming kinetic preference. The generation of radical anion **13** (or its dianion equivalent)[2] is followed by backside attack on the proximate C–O bond with formation of a cyclopropane ring. The ultimate protonation of anion **14** to position the phenyl substituent



in an endo stereodisposition presumably stems from control by kinetic factors.[16] The cyclopropane ring in **14** presumably is protected from further reduction because of electrostatic factors.

While this study relates specifically to the preparation of tricyclic alcohols having exo stereochemistry, the utilitarian nature of intramolecular reactions triggered by the reductive cleavage of cyclopropane rings is conceivably multifarious. Other aspects of this new synthetic method are receiving attention in these laboratories.

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ketones. This subject has recently been surveyed briefly by M. N. Rerick in "Reduction," R. L. Augustine, Ed., Marcel Dekker, New York, N. Y., 1968, Chapter 1.

(10) (a) J. J. Tufariello and D. W. Rowe, *J. Org. Chem.*, **36**, 2057 (1971); (b) P. Laszlo and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **86**, 1171 (1964), and pertinent references cited therein.

(11) G. A. Wiley, R. L. Hershkowitz, B. M. Rein, and B. C. Chung, *ibid.*, **86**, 964 (1964).

(12) J. Clardy, personal communication. Details of this analysis and a mechanism for this reaction will be elaborated upon in the full paper. Suffice it to say at this time, however, that the replacement of hydroxyl by bromine is proposed to proceed chiefly with retention[13] and that C_2 in **3** becomes C_7 in **6**.

(13) J. P. Schaefer and D. W. Weinberg, *J. Org. Chem.*, **30**, 2635, 2639 (1965).

(14) In the spectrum of **9b**, the peak at δ 5.8 was seen to be lacking.

(15) H. C. Brown, S. Ikegami, and J. Kawakami, *J. Org. Chem.*, **35**, 3243 (1970).

(16) A. F. Thomas, R. A. Schneider, and J. Meinwald, *J. Amer. Chem. Soc.*, **89**, 68 (1967).

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Evidence for Autocatalysis in the Silver(I)-Promoted Reactions of Bicyclobutanes with Methanol[1]

Sir:

It is presently recognized that the interaction of bicyclobutanes with silver(I) salts in anhydrous nonprotic media (*e.g.*, benzene) promotes interesting structural bond reorganizations, whereas similar reaction in protic solvents (*e.g.*, methanol) leads instead to ready solvent incorporation.[2–4] In those examples where the same bond is initially cleaved under both sets of conditions, interception of appropriate organosilver intermediates has been claimed.[3] When a different bond experiences initial rupture, the transition metal has been given the role of catalyzing a different rearrangement process.[4] We now wish to report several pieces of evidence which demonstrate collectively the previously unrecognized but fundamental fact that *silver(I) promoted reactions of*

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(1) Silver(I) Ion Catalyzed Rearrangements of Strained σ Bonds. XVII. For the previous paper, see L. A. Paquette, R. S. Beckley, D. Truesdell, and J. Clardy, *Tetrahedron Lett.*, in press.

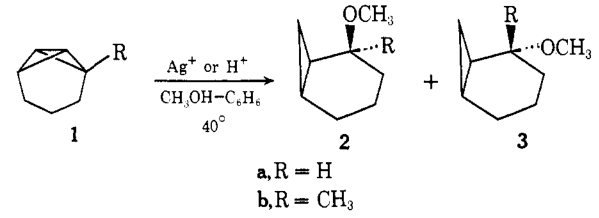
(2) (a) L. A. Paquette, *Accounts Chem. Res.*, **4**, 280 (1971); (b) L. A. Paquette and S. E. Wilson, *J. Amer. Chem. Soc.*, **93**, 5934 (1971); (c) L. A. Paquette, R. P. Henzel, and S. E. Wilson, *ibid.*, **93**, 2335 (1971).

(3) M. Sakai, H. H. Westberg, H. Yamaguchi, and S. Masamune, *ibid.*, **93**, 4611 (1971), and earlier papers by the Alberta group.

(4) P. G. Gassman and T. Nakai, *ibid.*, **94**, 5497 (1972).

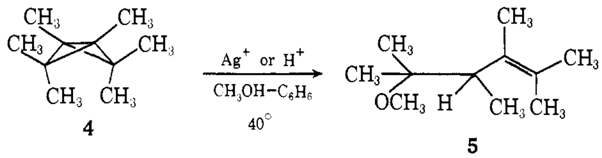
bicyclobutanes in methanol deviate significantly from normal second-order kinetic behavior and follow instead an autocatalytic pathway accompanied by acid production.

A plot for **1a** which follows the concentration of developing **2a** and **3a** *vs.* time defines a curve which demonstrates clearly the exponential rate of ether production (Figure 1). A decrease in the molarity of Ag^+ or bicyclobutane increased the time required for onset of the exceedingly rapid segment of reaction, whereas a concentration increase in either reagent had the reverse effect. The process was not significantly affected by a change from $AgClO_4$ to AgO_3SCF_3 and therefore appears to be independent of the nature of the gegenion.



When attention was directed to the water washes of these reaction mixtures after total consumption of hydrocarbon, the aqueous solutions were found to be appreciably acidic. To illustrate, addition of silver perchlorate to **1a** in the methanol–benzene solvent system afforded, after addition of water, an aqueous phase exhibiting a pH of 5.2. The presence of both a bicyclobutane and silver ion is absolutely mandatory for acid formation, for in suitable control experiments involving $AgClO_4$ and solvent combination *but no hydrocarbon*, neutral water washes were consistently obtained. Solutions of pure bicyclobutanes in methanol likewise develop no acidity during this period of time.

However, because of the well-recognized lability of bicyclobutanes in acidic media, this observation prompted a comparative study of the effect on **1a**, **1b**, and **4** of approximately equivalent catalytic quantities of anhydrous silver perchlorate or 70% perchloric acid in 1:1 (v/v) methanol–benzene. In each instance, identical product mixtures were obtained in high yield.[5]



A number of other bicyclobutanes studied exhibited comparable behavior. Additionally, the product isotope effect for conversion of **1a** to 2-methoxybicyclo[4.1.0]heptane in $AgClO_4$–benzene (50%)–CH_3OH (25%)–CH_3OD (25%) has given a value for $k_H/k_D = 2.1 \pm 0.2$, which is approximately the magnitude expected for rate-determining proton transfer.[6] Replacement of the silver salt by $HClO_4$ gave the experimentally comparable value of $k_H/k_D = 1.7 \pm 0.3$. The deuterium incorporation was found to occur exclusively with retention of configuration paralleling earlier observations made under conditions of acid catalysis.[7]

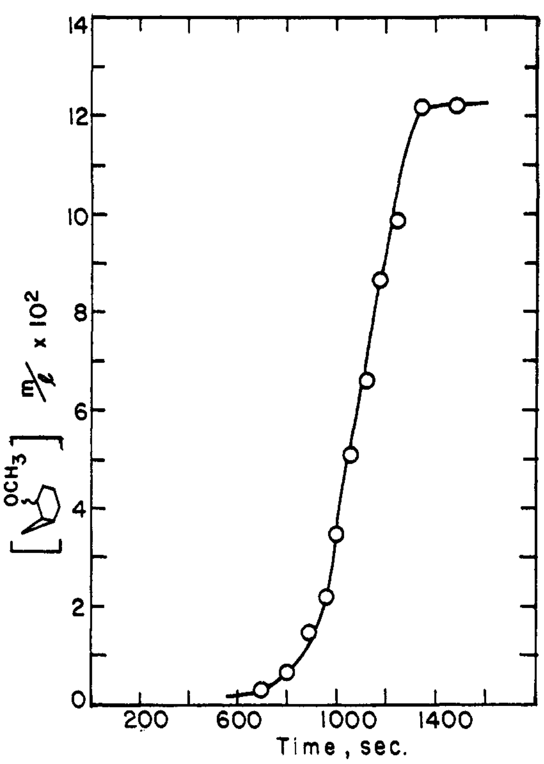
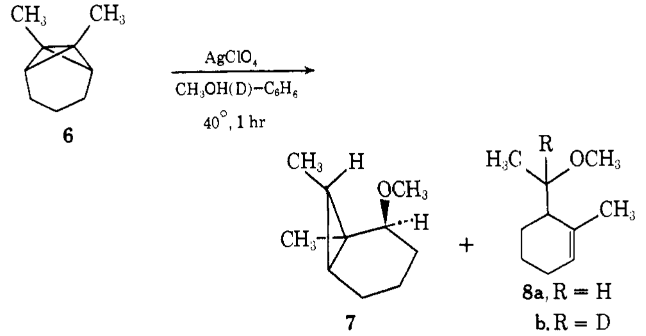
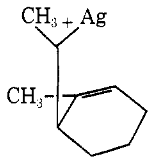


Figure 1. Plot of the concentration of developing 2-methoxybicyclo[4.1.0]heptanes realized upon treatment of **1a** (30 μl) with 1.0 ml of 4.7×10^{-3} *M* silver perchlorate (benzene solution) dissolved in 1.0 ml of methanol at 40.00°.

In the above examples, uniformly rapid reaction obtained. In contrast, **6** reacted relatively slowly with anhydrous silver perchlorate in methanol–benzene (1:1) to give **7** (41%) and **8a** (51%).[5,8] When this reaction was performed in CH_3OD–C_6H_6, **8b** accounted for 84% of the product mixture. In this connection, although **7** is stable under the reaction conditions to silver ion in methanol, it does experience conversion to **8a** in acidic methanol; however, the extent to which the production of **8a** is partitioned between direct formation from **6** (*via* **9**[2b,c] and/or its H^+ equivalent) and secondary formation from **7** has not yet been completely established. By contrast, the formation of 1,3-





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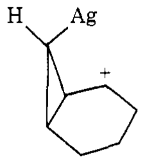

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(5) All new compounds were synthesized independently by unequivocal methods and were fully characterized in spectral and analytical detail.

(6) R. L. Schowen, *Progr. Phys. Org. Chem.*, **9**, 275 (1972).

(7) K. B. Wiberg and G. Szeimies, *J. Amer. Chem. Soc.*, **92**, 571 (1970).

(8) Interestingly, the sample of **8a** produced in the ring opening of **6** consisted of only one of the two possible diastereomers.

cycloheptadiene from **1a** by direct reaction with Ag^+ comprises only ~1% of the total reaction in methanol.

The change in product type exhibited by **5** on the one hand and **2**, **3**, and **7** on the other is fully consistent with established carbonium ion behavior and the relative stabilities of cyclopropylcarbinyl and homoallylic cations substituted to various degrees with alkyl groups.[9] In addition, the foregoing results demonstrate that effective complexation of Ag^+ with methanol appreciably reduces its capability to promote skeletal isomerization.[10] However, methanol and presumably other hydroxylic media appear unique in providing suitable conditions under which bicyclobutanes can react (at seemingly different rates depending upon substitution) with silver salts to form acid. Unlike the situation which perhaps prevails with rhodium(I) catalysts under certain conditions,[11] this acid is not introduced inadvertently on the catalyst or in the solvent, but arises from a chemical reaction of Ag^+ with methanol and the strained hydrocarbon. The mechanism of this uncommon process has not yet been established and remains currently an outstanding important question.

We caution, therefore, that the formation of cyclopropylcarbinyl ethers **2**, **3**, and **7** need not be the result of interception of intermediate silver cyclopropyl cations of type **10**.[3,4,11,12] The present data suggest that direct proton-mediated opening of the bicyclobutane constitutes a real possibility.

Acknowledgment. Partial financial support for this research was provided by the donors of the Petroleum Research Fund, administered by the American Chemical Society, whom we thank.

(9) For a leading reference, consult C. D. Poulter and S. Winstein, *J. Amer. Chem. Soc.*, **94**, 2297 (1972).

(10) A kinetic study of solvent effects on Ag^--catalyzed *isomerization* reactions of bicyclobutanes may be found in L. A. Paquette, S. E. Wilson, and R. P. Henzel, *ibid.*, **94**, 7771 (1972).

(11) W. G. Dauben and A. J. Kielbania, Jr., *ibid.*, **94**, 3669 (1972).

(12) The intermediacy of such cations in nonprotic solvents now appears well established with certain bicyclobutanes: ref 10; L. A. Paquette, R. P. Henzel, and S. E. Wilson, *J. Amer. Chem. Soc.*, **94**, 7780 (1972); relevant references cited in these papers.

(13) National Institutes of Health Postdoctoral Fellow, 1970–1971; National Science Foundation Postdoctoral Fellow, 1971–1972.

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

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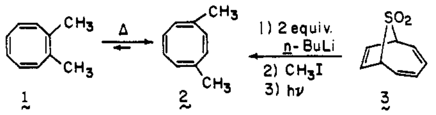
Degenerate Rearrangement and Isomerization of Disubstituted Cyclooctatetraenes under Conditions of Thermal Activation[1]

Sir:

Of the $(CH)_{10}$ hydrocarbons so far studied, six are presently recognized to exhibit a remarkable capability for degenerate bond reorganization at somewhat elevated temperatures.[2] In contrast, no substance of molecular formula $(CH)_8$ has yet been reported capable of undergoing interchange of its constituent atoms and bonds with regeneration of the same gross structure.[3,4] We now provide evidence which reveals that disubstituted cyclooctatetraenes can, in fact, partake of this same fascinating propensity for structural self-interconversion.

The thermal chemistry of cyclooctatetraene had its origins nearly 20 years ago when its fragmentation to styrene, benzene, ethylene, and acetylene was reported.[5] More recently, pyrolytic rearrangement of the parent hydrocarbon to dihydropentalene[6] and of the 1,3,5,7-tetramethyl[7] and octamethyl derivatives[8] to the corresponding semibullvalenes has been achieved. The latter reactions have been postulated to occur *via* bicyclo[3.3.0]octadienediyls,[9] intermediate species apparently involved also in the thermal isomerization of 5,6- to 5,11-disubstituted dibenzocyclooctatetraenes.[10] In the present study, this pathway has been found *not* to be of mechanistic significance.

To permit detection of the rearrangements, recourse was made to alkyl substitution. Thus, when **1**[11,12] was pyrolyzed in a flow system at 405–590° under nitrogen at 20–30 mm (contact time ~1 sec) and the resulting mixture of cyclooctatetraenes analyzed by vpc, ir, and nmr methods,[13] conversion to the 1,4-isomer **2** in proportion to the oven temperature was evidenced (Table I). Authentic **2** was prepared by dimethylation of **3**[14] and subsequent photoinduced sulfur dioxide extrusion.[15,16] Aromatic products were also formed in amounts paralleling the input of heat to the system. In a typical run involving **1** at 600°, for example, benzene (1.3%), toluene (96.2%), *p*-xylene (1.1%), and *o*-xylene (1.3%), but no *m*-xylene, were found in the volatile fraction.



Conditions analogous to those used above reconvert

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[1] This research was supported in part by the National Science Foundation (Grant No. GP-35344).

[2] For a current listing, see L. A. Paquette, M. J. Kukla, and J. C. Stowell, *J. Amer. Chem. Soc.*, **94**, 4920 (1972), footnote 3.

(3) This field has been exhaustively reviewed by L. T. Scott and M. Jones, Jr., *Chem. Rev.*, **72**, 181 (1972).

(4) The Cope rearrangement of a tetrabromotetramethyltricyclo-[$4.2.0.0^{2,5}$]octa-3,7-diene is, at least formally, an exception to this statement [R. Criegee and R. Huber, *Chem. Ber.*, 103, 1855 (1970)].

(5) I. Tanaka, *J. Chem. Soc. Jap., Pure Chem. Sect.*, **75**, 212 (1954); *Chem. Abstr.*, **48**, 4984*b* (1954).

(6) M. Jones, Jr., and L. O. Schwab, *J. Amer. Chem. Soc.*, **90**, 6549 (1968).

(7) H. E. Zimmerman and H. Iwamura, *ibid.*, **92**, 2015 (1970).

(8) R. Criegee and R. Askani, *Angew. Chem., Int. Ed. Engl.*, **7**, 537 (1968).

(9) Such intermediates have also been invoked in the thermal rearrangement of tricyclo[$3.3.0.0^{2,6}$]octa-3,7-diene to semibullvalene: J. Meinwald, D. Schmidt, and H. Tsuruta, *J. Amer. Chem. Soc.*, **91**, 5877 (1969); H. E. Zimmerman, J. D. Robbins, and J. Schantl, *ibid.*, **91**, 5878 (1969). See also W. T. Borden and A. Gold, *ibid.*, **93**, 3830 (1971).

(10) M. Stiles and U. Burckhardt, *ibid.*, **86**, 3396 (1964); M. Stiles, 19th National Organic Chemistry Symposium, Tempe, Ariz., June 1965, p 62.

(11) A. C. Cope and H. C. Campbell, *J. Amer. Chem. Soc.*, **73**, 3536 (1951).

(12) Full details of an improved synthesis of this hydrocarbon will appear elsewhere.

(13) Dimethyl derivatives 1 and 2 were separated on a 24 ft × 1/8 in. Hi-Pac column at 60° and could easily be distinguished by the chemical shifts of their methyl signals (δ 1.68 and 1.82 for 1; δ 1.75 for 2). Their solution infrared spectra differ significantly in the fingerprint region.

(14) Obtained by *m*-chloroperbenzoic acid oxidation of the related sulfoxide [A. G. Anastassiou and Y.-H. Chao, *Chem. Commun.*, 979 (1971)]. See also J. Gasteiger and R. Huisgen, *J. Amer. Chem. Soc.*, **94**, 6541 (1972).

(15) L. A. Paquette, R. E. Wingard, Jr., and R. H. Meisinger, *ibid.*, **93**, 1047 (1971).

(16) W. E. Konz, W. Hechtl, and R. Huisgen [*ibid.*, **92**, 4104 (1970)] have prepared 2 by yet another route.