tensor.[15] It should be noted that temperature studies of the type described here are necessary to test critically the various theories. The equations of Jesson and of McGarvey can both give reasonable agreement with observed room temperature shifts. It is only when the temperature data are available that the deficiencies of the former set are experimentally demonstrable.

(15) W. D. Horrocks, Jr., *Inorg. Chem.*, 9, 690 (1970).

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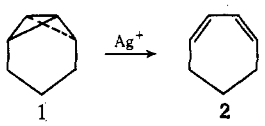
Silver(I) Ion Catalyzed Rearrangements of Strained σ Bonds. V. Stereochemical and Kinetic Analysis of the Isomerization of Bicyclo[1.1.0]butanes[1]

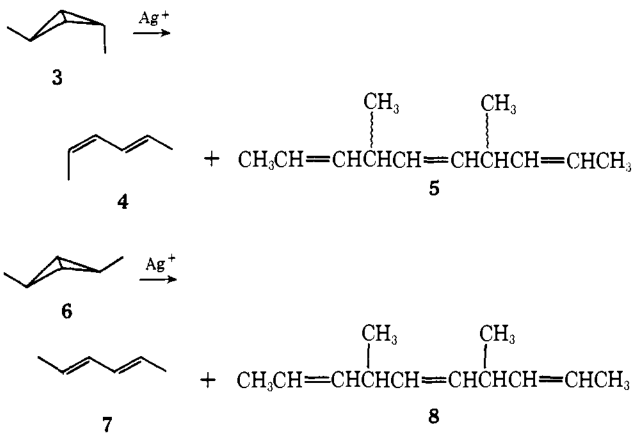
Sir:

Recent reports from this and other laboratories have described the remarkable capability of silver(I) ion to promote facile $[{}_{\sigma}2_a + {}_{\sigma}2_a]$ skeletal rearrangement of cubyl,[2] homocubyl,[3] 1,1′-bishomocubyl,[3,4] and secocubyl systems.[5] We have also described the ready isomerization of tricyclo[4.1.0.0^{2,7}]heptane (1) to *cis*,*cis*-1,3-cycloheptadiene (2) under similar conditions.[1]



It is to be specifically noted that all Ag$^+$-catalyzed reactions examined to the present time have dealt with molecules possessing high levels of structural rigidity. Accordingly, concerted catalyzed reactions in these instances need not necessarily be free (for steric reasons) to proceed along *competitive* symmetry-allowed and -forbidden pathways. Such considerations have caused van der Lugt[6] to conclude that "orbital symmetry seems not relevant for explaining the lowering of the energy of activation of forbidden reactions catalyzed by a transition metal." Resolution of this issue was deemed imperative and we have therefore examined the stereochemical course of the Ag$^+$-catalyzed isomerization of two structurally unconstrained hydrocarbons, the *endo,exo*- (3) and *exo,exo*-2,4-dimethylbicyclo[1.1.0]butanes (6).[7] During this study, unequivocal evidence has been gained that bicyclobutanes rearrange to 1,3-dienes preferentially by a formal $[{}_{\sigma}2_a + {}_{\sigma}2_a]$ pathway; that is to say that excited-state behavior (in the orbital symmetry sense) is exhibited even in those cases where the alternative stereochemical products are of comparable energy content. Also, in-depth kinetic studies of the conversion of 1 to 2 have now resolved the question of the intervention of silver–bicyclobutane complexes.

Addition of 3 to anhydrous silver fluoroborate in deuteriochloroform at ~40° (nmr probe conditions) resulted in highly stereospecific conversion to *cis,trans*-2,4-hexadiene (4, 62%—containing 0–1% 7) and to dimer formation (5, two isomers in a ratio of 1:1, 38%).[8] The related exo,exo derivative 6 led analogously to dienes 4 and 7 (14%, ratio 1:3) and dimers 8 (two different isomers in a ratio of 1.5:1, 86%).[8] Kinetic measurements relating to the rates of disappearance of 1, 3, and 6 are listed in Table I. The assigned structures to dimers 5 and 8 (of differing geometric and configurational stereochemistry) follow convincingly from their high-resolution mass spectra, their nmr features, and independent catalytic hydrogenation to 4,7-dimethyldecane.[9] These "dimers" do not arise from any of the combinations diene + diene, diene + cyclobutene, cyclobutene + cyclobutene, and cyclobutene + bicyclobutane; in actuality, 4 and 7 as well as *cis*- (9) and *trans*-3,4-dimethylcyclobutenes (10)[10] are stable to the reaction conditions. Consequently, 9



$$CH_3CH{=}CH\overset{CH_3}{\overset{|}{C}}HCH{=}CH\overset{CH_3}{\overset{|}{C}}HCH{=}CHCH_3$$

Table I. Isomerization Rate Data (C_6H_6 Solution)[a]

Hydrocarbon	$AgClO_4$, N	T, °C	k_{Ag}, M^{-1} sec^{-1}	Rel rate
1	7.86×10^{-2}	30.00	9.8×10^{-4}	
	7.86×10^{-2}	40.00	2.8×10^{-3}	1
	3.43×10^{-2}	50.00	6.8×10^{-3}	
3	4.03×10^{-2}	40.1	6.5×10^{-3}	2.3
6	2.02×10^{-2}	40.1	1.4×10^{-2}	5

[a] These rate data pertain to the initial rate of disappearance of bicyclobutane.

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(1) Paper IV: L. A. Paquette, G. R. Allen, Jr., and R. P. Henzel, *J. Amer. Chem. Soc.*, 92, 7002 (1970).

(2) L. Cassar, P. E. Eaton, and J. Halpern, *ibid.*, 92, 6366 (1970).

(3) L. A. Paquette and J. C. Stowell, *ibid.*, 92, 2584 (1970).

(4) (a) L. A. Paquette, *ibid.*, 92, 5765 (1970); (b) W. G. Dauben, M. G. Buzzolini, C. H. Schallhorn, D. L. Whalen, and K. J. Palmer, *Tetrahedron Lett.*, 787 (1970); (c) R. Askani, *ibid.*, 3349 (1970).

(5) L. A. Paquette, R. S. Beckley, and T. McCreadie, submitted for publication.

(6) W. Th. A. M. van der Lugt, *Tetrahedron Lett.*, 2281 (1970).

(7) G. L. Closs and P. E. Pfeffer, *J. Amer. Chem. Soc.*, 90, 2452 (1968).

(8) Percentage compositions were determined by quantitative integration of nmr spectra. Vpc analysis was utilized to establish the ratio of dimers and dienes. The structures assigned to dienes 4 and 7 are based on comparison of spectral data with authentic samples obtained from Chemical Samples Co., Columbus, Ohio. Additionally, nmr spectra are identical with those provided by Dr. R. Srinivasan (IBM), whom we thank.

(9) Authentic 4,7-dimethyldecane was synthesized by catalytic hydrogenation (10% Pd/C, CH_3OH, 50°, 50 psig) of 4,7-dimethyl-5-decyne-4,7-diol (K + K Laboratories) according to the method of R. J. Tedeschi, *J. Org. Chem.*, 27, 2398 (1962).

(10) R. E. K. Winter, *Tetrahedron Lett.*, 1207 (1965). We thank Professor Winter for a sample of 9 and directions for an improved synthesis of 10.

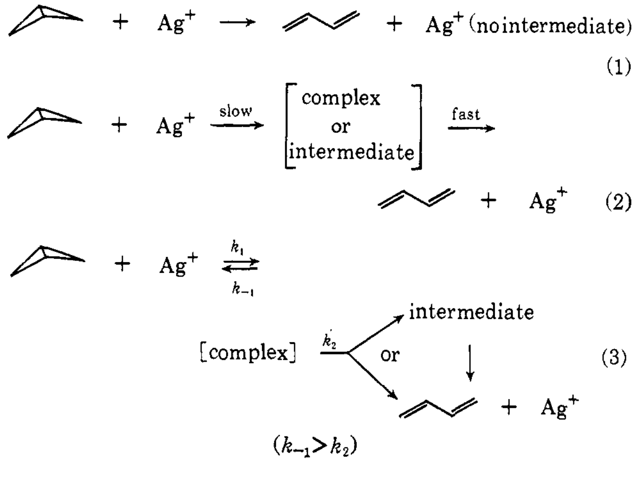
and **10** can be eliminated as intermediates during these transformations. It has not yet proven possible to confirm the first of the remaining two alternatives, *i.e.*, bicyclobutane + bicyclobutane; however, the capability of "cross-breeding" a 2,4-hexadiene of improper stereochemistry with a bicyclobutane in the presence of Ag$^+$ has been demonstrated. New "dimers" are formed in the reaction mixtures. The mechanism of "dimer" formation is presently being examined.

The above results indicate that the Ag$^+$-induced skeletal rearrangement of bicyclobutanes is formally a [$_{\sigma}2_a$ + $_{\sigma}2_a$] bond reorganization even in those derivatives which are free of secondary structural constraints. Since this stereochemical pathway is the reverse of that followed on thermolysis,[7] the Ag$^+$-catalyzed rearrangements are clearly not governed by the same electronic considerations which control their thermal isomerizations.

Since the bicyclobutanes rearrange according to the second-order catalytic rate law, $-d[\text{bicyclobutane}]/dt = k_{\text{Ag}}[\text{bicyclobutane}][\text{AgClO}_4]$, one of the following mechanisms will serve to describe the reaction (eq 1, 2, or 3). To satisfy eq 2, complex formation is required to be rate determining. However, this view does not appear tenable since exchange phenomena involving silver–benzene[11] and phosphinosilver complexes[12] are known to be very rapid.[13] On the other hand, the *direct* formation of an intermediate such as a σ-bonded species could indeed be slow. To differentiate mechanisms 1 and 2 from 3, it becomes necessary only to measure the rates of the isomerization (**1** was employed in this study) as a function of bicyclobutane concentration. As Laidler[14] has clearly pointed out, adherence to eq 3 would give a rate law which can be expressed as

$$\frac{-d[\text{bicyclobutane}]}{dt} = \frac{k_2K[\text{bicyclobutane}][\text{AgClO}_4]}{K[\text{bicyclobutane}] + 1} \qquad (4)$$

which corresponds to a nonlinear variation in rate typified by Figure 1. This is because the rate varies linearly with [bicyclobutane] at low substrate concentrations but becomes zero order in bicyclobutane at higher concentration levels. Adherence to eq 1 and 2 would, in contrast, provide a linear plot throughout the entire concentration range.



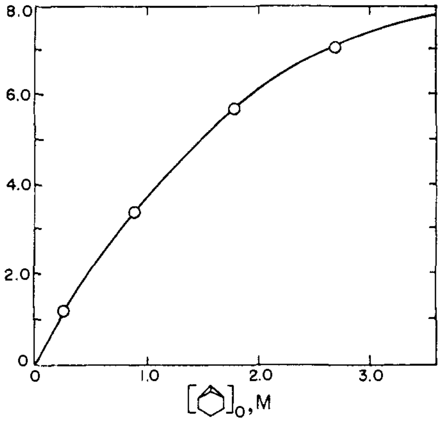


Figure 1. Initial rates of conversion of tricyclo[4.1.0.0^{2,7}]heptane (**1**) to 1,3-cycloheptadiene (**2**) as a function of the concentration of **1**. All runs were performed at 40° in 2.02 × 10^{-3} *M* silver perchlorate solutions consisting of 70% benzene and 30% cyclohexane-**1** (v:v).

Accordingly, bicyclobutane–silver(I) complexes are definitive intermediates in the catalyzed rearrangements, *i.e.*, mechanism 3 applies. In the example studied most thoroughly, it has proven possible to calculate from eq 4 the equilibrium constant for tricyclo[4.1.0.0^{2,7}]heptane–silver(I) complex formation. The experimentally derived value ($K = k_1/k_{-1} = 0.19 \pm 0.05$) reveals that the extent of complex formation is substantial. The activation parameters associated with the isomerization of **1**, $\Delta H^{\ddagger} = 18.2$ kcal/mol, $\Delta S^{\ddagger} = -12.4$ eu, and $\Delta F^{\ddagger} = 22.0$ kcal/mol, are in complete accordance with the establishment of a preequilibrium and rate-determining rearrangement of the complex. The subsequent intervention of σ-bonded Ag intermediates is not precluded. It now remains to elucidate the electronic details by which Ag$^+$ alters the orbital symmetry of the hydrocarbon portion of the complex or intermediate undergoing skeletal alteration; such studies are in progress.

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[11] Nmr line broadening techniques disclose that solutions as high as 0.4 *M* AgClO$_4$ in benzene (20–60°) undergo ligand exchange [$(C_6H_6)_x$-Ag$^+$ + $C_6H_6^0 \rightleftharpoons (C_6H_6)_{x-1}C_6H_6^0Ag^+ + C_6H_6$] at a rate greater than 10^5 sec^{-1}: G. Gordon, private communication.

[12] E. L. Muetterties, W. G. Peet, P. A. Wagner, and C. W. Alegranti, *Inorg. Chem.*, **9**, 2447 (1970).

[13] The term *complex* is used herein in its usual connotation, *viz.*, an attachment of the metal cation to one or more p-rich orbitals of the strained hydrocarbon *without* the scission of any bonds. The demonstrated facile *reversible* formation of such complexes ($K = 0.19$ corresponds to a $\Delta F^{\circ} \approx 1$ kcal/mol) cannot be reconciled with a cleavage–recombination phenomenon. We emphasize, however, that such complexes can in theory either rearrange directly to product(s) with liberation of Ag$^+$ or be transformed to a different species (intermediate) which subsequently rearranges to product(s).

[14] K. J. Laidler, "Chemical Kinetics," McGraw-Hill, New York, N. Y., 1950, pp 276–281.

[15] (a) National Institutes of Health Postdoctoral Fellow, 1970–1971; (b) National Science Foundation Graduate Trainee, 1970–1971.