

are more dependent on detailed calculations will not be surveyed here.²²⁻²⁴

Support of this research by the National Science Foundation and by the U. S. Army Research Office (Durham) is gratefully acknowledged.

(22) Recently an interesting review of the Woodward-Hoffmann rules has appeared as well as a discussion of the "Dewar-Zimmerman

rules": N. T. Anh, "Les Regles de Woodward Hoffmann," Ediscience, Paris, 1970.

(23) Applications of the Möbius-Hückel concept to photochemistry are presently not discussed in detail due to space limitations. For leading references see ref 24.

(24) (a) H. E. Zimmerman, *Angew. Chem., Int. Ed. Engl.*, **8**, 1 (1969); (b) H. E. Zimmerman and P. S. Mariano, *J. Amer. Chem. Soc.*, **91**, 1718 (1969); (c) H. E. Zimmerman and A. C. Pratt, *ibid.*, **92**, 6259, 6267 (1970); H. E. Zimmerman, D. F. Juers, J. M. McCall, and B. Schröder, *ibid.*, **93**, 3662 (1971); H. E. Zimmerman, P. Hackett, D. F. Juers, J. M. McCall, and B. Schröder, *ibid.*, **93**, 3653 (1971); H. E. Zimmerman and A. A. Baum, *ibid.*, **93**, 3646 (1971).

Catalysis of Strained σ Bond Rearrangements by Silver(I) Ion

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The capability of Ag^+ to form coordination complexes with unsaturated and aromatic molecules is now widely recognized.¹ In contrast, unsuccessful attempts to prepare alkylsilver compounds date back to the middle of the last century² and, with few exceptions, these difficulties persist to the present time.³

Chief among the factors behind the often fleeting existence of such substances is their low thermal stability. Alkenylsilver compounds, which likewise share this tendency for facile decomposition, were isolated for the first time approximately 15 years ago.⁴ The appreciably greater stability of alkynylsilver compounds has enabled them to be known for over a century.⁵

Very recently, the unique capability of certain transition metals to catalyze so-called "symmetry-forbidden" reactions under exceedingly mild conditions has been recognized. Examples of the phenomenon are the facile $[\pi 2_s + \pi 2_s]$ dimerization⁶ of norbornadiene (**1**) under the influence of zerovalent iron,⁷ nickel,⁸ and cobalt catalysts.⁹ Another is the $\text{Fe}(\text{CO})_5$ -catalyzed suprafacial 1,3-sigmatropic shift of hydrogen (a $[\sigma 2_s + \pi 2_s]$ change)⁶ in **2**;¹⁰ the epimeric alcohol **3** is unaffected.

(1) (a) R. N. Keller, *Chem. Rev.*, **28**, 229 (1941); (b) M. A. Bennett, *ibid.*, **62**, 611 (1962).

(2) (a) G. B. Buckton, *Justus Liebigs Ann. Chem.*, **109**, 225 (1859); (b) J. A. Wanklyn and L. Carius, *ibid.*, **120**, 70 (1861).

(3) An excellent recent review of organosilver chemistry has appeared: C. D. M. Beverivizk, G. J. M. van der Kerk, A. J. Lensink, and J. G. Noltes, *Organometal. Chem. Rev., Sect. A*, **5**, 218 (1970).

(4) F. Glockling, *J. Chem. Soc.*, 716 (1955); 3640 (1956).

(5) (a) C. Liebermann, *Justus Liebigs Ann. Chem.*, **135**, 268 (1865). (b) For a review, see A. M. Sledkov and L. Yu. Ukhin, *Usp. Khim.*, **37**, 1750 (1968); *Chem. Abstr.*, **70**, 11731k (1969).

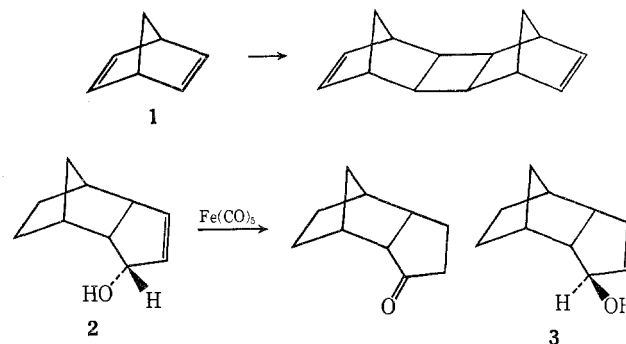
(6) For an explanation of this terminology and a listing of the applications thereof, consult R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Verlag Chemie, Weinheim/Bergstr., Germany, 1970.

(7) (a) C. W. Bird, D. L. Colinese, R. C. Cookson, J. Hudec, and R. O. Williams, *Tetrahedron Lett.*, 373 (1961); (b) P. W. Jolly, F. G. A. Stone, and K. MacKenzie, *J. Chem. Soc.*, 6416 (1965).

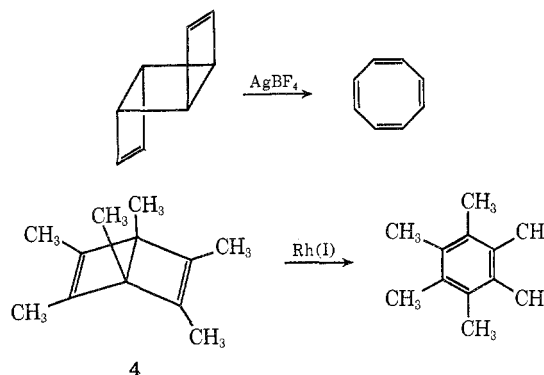
(8) (a) C. W. Bird, R. C. Cookson, and J. Hudec, *Chem. Ind. (London)*, 20 (1960); (b) G. N. Schrauzer and S. Eichler, *Chem. Ber.*, **95**, 2764 (1962).

(9) D. R. Arnold, D. J. Trecker, and E. B. Whipple, *J. Amer. Chem. Soc.*, **87**, 2596 (1965).

(10) F. G. Cowherd and J. L. von Rosenberg, *ibid.*, **91**, 2157 (1969).



Also, Pettit and his coworkers have demonstrated that the thermally forbidden $[\sigma 2_s + \pi 2_s]$ ring opening of certain cyclobutenes (disrotatory motion)⁶ occurs readily in the presence of silver(I) ion.¹¹ The smooth rhodium(I)-catalyzed valence isomerization of **4** to hexamethylbenzene further illustrates the impressive alteration in transformation restraints attainable under such conditions.¹²



The remarkable capability of these metals to promote such transformations is thought to be a result of the

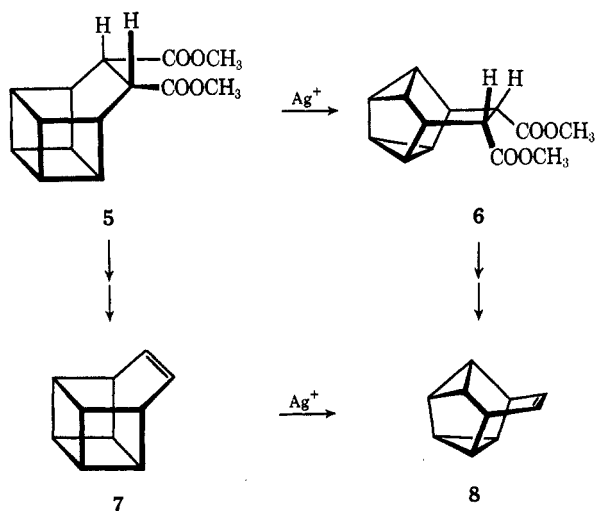
(11) W. Merk and R. Pettit, *ibid.*, **89**, 4787 (1967).

(12) (a) H. Hogeveen and H. C. Volger, *Chem. Commun.*, 1133 (1967); H. C. Volger and H. Hogeveen, *Recl. Trav. Chim. Pays-Bas*, **86**, 830 (1967).

properties of their d orbitals. As exemplified above, substantial attention has been given to the interactions which develop between such catalysts and transforming olefin ligands. We reasoned that just as a species such as Ag^+ coordinates with an olefinic π bond, so it should complex with σ bonds endowed with substantial p character. Accordingly, a study of transition metal promoted rearrangements of molecules constructed only of strained σ bonds promised significant rewards. Our activity in this area, albeit at an early stage, is summarized in this Account.

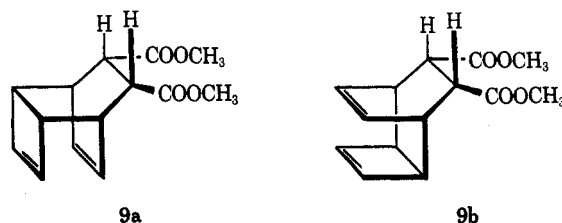
The [$\sigma 2_a + \sigma 2_a$] Skeletal Isomerization of Caged Molecules

Suggestive evidence that silver(I) ion could successfully catalyze skeletal bond reorganizations in caged molecules existed at the start of our work. Thus, examination of Furstoss and Lehn's report¹³ dealing with the synthesis of several 1,1'-bishomocubyl derivatives, and particularly pentacyclo[4.4.0.0^{2,5}.0^{3,8}.0^{4,7}]dec-9-ene (basketene, **7**), revealed wide discrepancies in physical and spectral properties with those reported almost simultaneously by the Masamune¹⁴ and Dauben¹⁵ groups. Although all three synthetic approaches closely paralleled each other, the French team was noted to have purified their samples of diester **5**, a key intermediate, by column chromatography on silica gel-silver nitrate (10%). Under these conditions, rapid conversion to **6** was inadvertently and unknowingly achieved.¹⁶ Subsequent hydrolysis and oxidative bis-decarboxylation of **6** gave rise without further structural change to pentacyclo[3.3.2.0^{2,4}.0^{3,7}.0^{6,8}]dec-9-ene (snoutene, **8**)^{17,18} rather than basketene (**7**).¹³ These

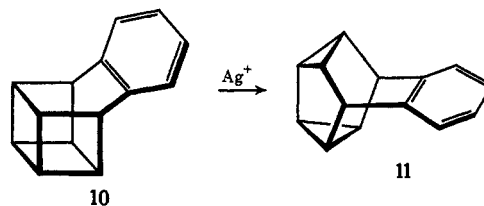


two hydrocarbons possess identical melting points (61–62°) but significantly different infrared and nmr spectra.

In point of fact, addition of several crystals of silver fluoroborate to dilute deuteriochloroform solutions of **5** at nmr probe temperatures ($\sim 40^\circ$) results in rapid quantitative conversion to **6**.¹³ The spectrum of **6** displayed in Figure 1 was recorded immediately subsequent to the introduction of the silver salt to the sample of **5** whose spectrum appears in the lower section of the illustration. The total elapsed time was less than 3 min. When **5** is heated at 275° in an evacuated tube, [$\sigma 2_s + \sigma 2_s$] thermal retrogression to **9a** and **9b** is observed.¹⁵ At 235° under 1 atm of nitrogen, **6** is formed in addition to the dienes.¹⁹ These observations suggest that no symmetry-allowed concerted thermal rearrangement pathway is directly available to **5**.



The cubyl skeletal rearrangement is now known to be a general reaction type. For example, benzobasketene (**10**), although stable to 350° in a flow system (gas phase), is transformed quantitatively to benzosnoutene (**11**) during 1 hr at room temperature upon exposure of dilute CDCl_3 solutions to AgBF_4 .¹⁶ Alternatively, the



same transformation can be achieved with equal efficiency by elution of **10** through a column of silica gel impregnated with silver nitrate. The conversion of basketene (**7**) to snoutene (**8**) is much less rapid and efficient, presumably because of extensive π -complex formation between the silver ion and the double bond.

Homocubane (**12**) and cubane (**14**) similarly rearrange to norsnoutane (**13**) and pentacyclo[3.3.0.0^{2,4}.0^{3,7}.0^{6,8}]octane (cuneane, **15**), respectively.^{16,20} In all the cases studied to this time, the isomerizations are seen to follow the second-order catalytic rate law $-d[\text{cage compound}]/dt = k_{\text{Ag}}[\text{cage compd}][\text{Ag salt}]$. A comprehensive evaluation of substituent, steric, and electronic effects, together with an analysis of solvation

similarity of this molecule with the anterior prolongation of the head of various animals such as the crocodile.¹⁷

(19) W. G. Dauben, M. G. Buzzolini, C. H. Schallhorn, D. L. Whalen, and K. J. Palmer, *Tetrahedron Lett.*, 787 (1970).

(20) L. Cassar, P. E. Eaton, and J. Halpern, *J. Amer. Chem. Soc.*, 92, 6366 (1970). The name "cuneane" (from the Latin *cuneus*, a wedge) was adopted by these authors because of the wedge-shaped structure of the hydrocarbon.

(13) R. Furstoss and J.-M. Lehn, *Bull. Soc. Chim. Fr.*, 2497 (1966).

(14) S. Masamune, H. Cuts, and M. G. Hogben, *Tetrahedron Lett.*, 1017 (1966).

(15) W. G. Dauben and D. L. Whalen, *ibid.*, 3743 (1966); W. G. Dauben, C. H. Schallhorn, and D. L. Whalen, *J. Amer. Chem. Soc.*, 93, 1446 (1971).

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

(17) L. A. Paquette and J. C. Stowell, *ibid.*, 93, 2459 (1971).

(18) The overly cumbersome proper names for **7** and **8** have caused the indicated trivial names to be used for simplicity. The name "basketene," originally suggested by Masamune,¹⁴ is derived from the obvious shape of the molecule. Likewise, the name "snoutene," taken from the medieval English word "snoute," pertains to the structural

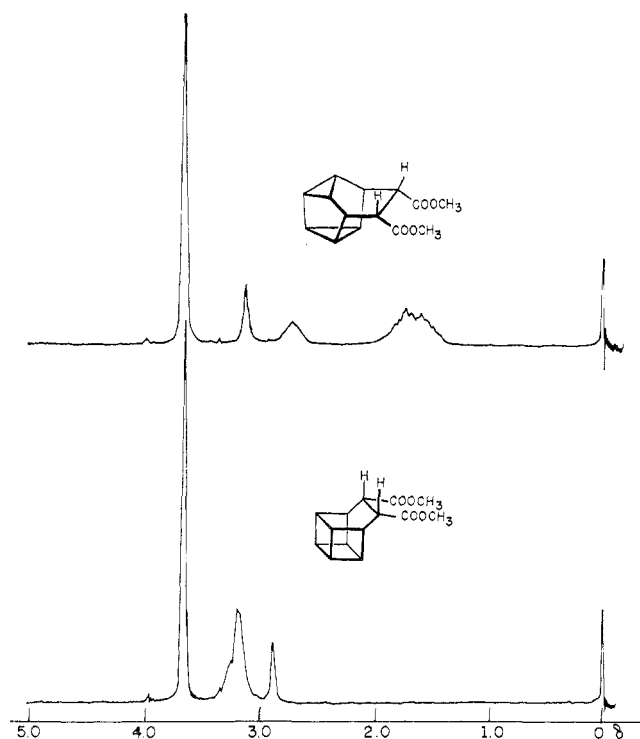
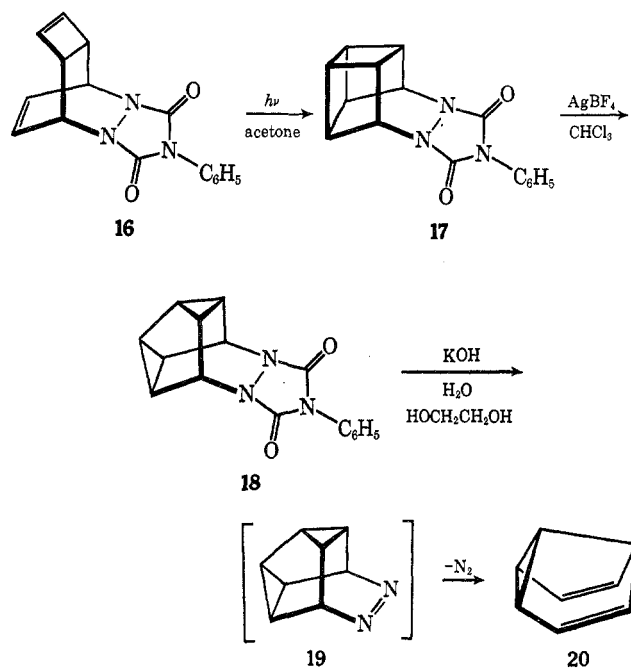
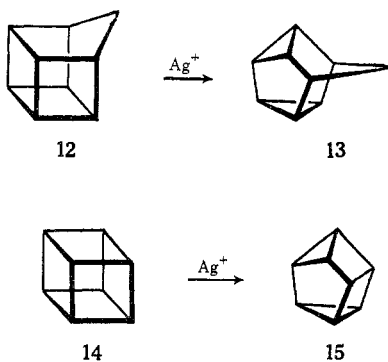


Figure 1. Lower curve: 60-MHz nmr spectrum of **5** in CDCl_3 . Upper curve: 60-MHz nmr spectrum of **6** recorded immediately after addition of catalytic amounts of AgBF_4 to the sample employed in recording the spectrum in the lower section.



The driving force behind these interesting pericyclic changes is the relief of steric strain estimated to be in the order of 35–50 kcal/mole.²³ If the cubyl rearrangements are concerted, that is, if migrating carbon a (*cf.* **21**) begins to bond to carbon c simultaneously with the

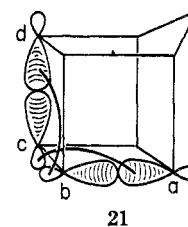


factors and an in-depth kinetic study, remain to be completed.

In one particularly noteworthy synthetic application of such silver(I) ion catalyzed rearrangements, the heretofore elusive $(\text{CH})_8$ hydrocarbon semibullvalene (**20**) can now be readily prepared in gram quantities.^{21,22} The sequence consists of initial acetone-sensitized photocyclization of the readily available *N*-phenylurazole diene **16**, silver fluoroborate catalyzed rearrangement of the bishomocubyl system **17** so produced, and hydrolysis of **18** with excess KOH in aqueous ethylene glycol at $\sim 100^\circ$. The liberated hydrazone undergoes rapid mild air oxidation to diazaspoutene (**19**) which decomposes readily (retrograde homo-Diels-Alder mechanism) with loss of nitrogen and formation of **20**.

(21) L. A. Paquette, *J. Amer. Chem. Soc.*, **92**, 5765 (1970).

(22) A minor variant of this synthetic scheme has also recently appeared: R. Askani, *Tetrahedron Lett.*, 3349 (1970).



bonding of d to b, then centers b and c must both participate with inversion of configuration in order to maintain the hydrogen atoms attached to these carbons on the outer periphery of the developing structure. In other words, the rearrangements are the formal result of $[\sigma_{2a} + \sigma_{2a}]$ transpositions and understandably symmetry forbidden for purely thermal conversions.

It is important to establish that the symmetry element (C_{2v}) required to analyze the rearrangement does not bisect the bonds which are made or broken in the course of the bond reorganization. As a result, the symmetry element *per se* is not useful in analyzing the nature of the interactions operative under these circumstances.²⁴ In the present instance, it is expedient to evaluate the geometric demands by resorting to Prentice-Hall molecular models. In the seemingly operational pathway (**21**), the rear lobes of the indicated σ bonds to carbons b and c must enlarge to enable rear-

(23) This estimate is based on the *very approximate assumption* that the total strain energy should approximate the sum of the strain energies of the composite fused rings [K. B. Wiberg, *Advan. Alicyclic Chem.*, **2**, 185 (1968)]. In the present context, the rearrangement is seen to entail the conversion of two bicyclo[2.2.0]hexane residues ($E_s \approx 2 \times 53$ kcal/mole) to two bicyclo[3.1.0] moieties ($E_s = 2 \times 31$ kcal/mole).

(24) Reference 6, pp. 31–36.

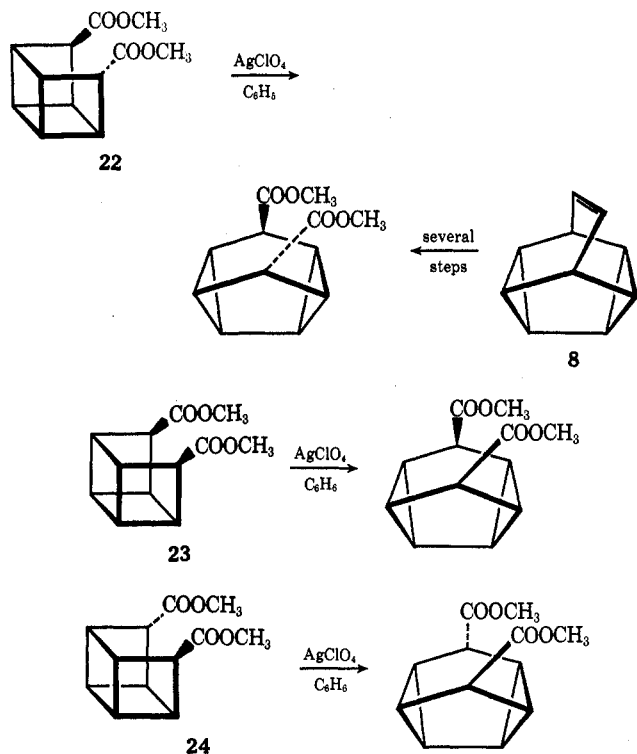
side bonding to occur readily. The facility of such rehybridization in the presence of silver ion may be the result of d-orbital interaction with the strained σ bonds to produce new occupied molecular orbitals with symmetry properties compatible with an allowed isomerization.

It must be borne in mind, however, that the stereochemical consequences of the cubyl rearrangements may be the result of high levels of structural rigidity in these structures such that competitive pathways are not geometrically feasible. Other (nonconcerted) mechanistic possibilities do exist,²⁵ and various tests of these alternatives are under active study at the present time.

The Rearrangement of Secocubane Derivatives

The [$\sigma_{2a} + \sigma_{2a}$] rearrangement is not confined to totally caged molecules. The somewhat less strained diesters **22–24**, which lack one of the cubane bonds, have also been found to undergo facile bond reorganization in the presence of Ag^+ .^{26,27} The skeletal changes are stereospecific and therefore the carbon atoms bearing the carbomethoxy groups cannot be involved directly in the *effective* complexation to silver ion.

Compounds **22–24** offer an opportunity to evaluate the effect of incremental degrees of ring strain on rearrangement rate. Kinetic measurements performed with AgClO_4 solutions in anhydrous benzene at 40° are cited in Table I; the rates for two cubyl esters are added for comparison.

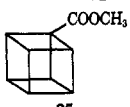
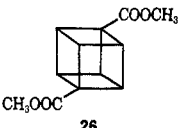


(25) For example, the theory of oxidative addition has been advanced by the Chicago group: J. E. Byrd, L. Cassar, P. E. Eaton, and J. Halpern, *Chem. Commun.*, 40 (1971).

(26) L. A. Paquette, R. S. Beckley, and T. McCreddie, *Tetrahedron Lett.*, in press.

(27) H. H. Westberg and H. Ona, *Chem. Commun.*, 248 (1971).

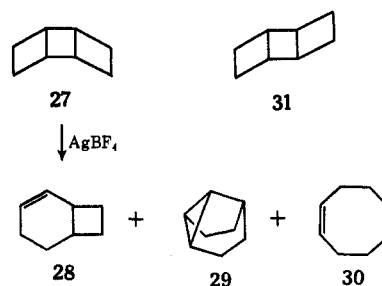
Table I
Rate Constants at 40° (AgClO_4 , C_6H_6)

Ester	k_{Ag} , $M^{-1} \text{sec}^{-1}$	Relative rate
22	8.0×10^{-5}	4.5
23	4.6×10^{-5}	2.5
24	4.3×10^{-5}	2.4
	5.5×10^{-3} ^a	310
	1.8×10^{-5} ^a	1

^a Taken from ref 20.

Examination of molecular models reveals that the secocubane to secocuneane rearrangement occurs with substantial steric decompression of the two endo substituents. This steric strain relief is *not* reflected in the rate of rearrangement of **22**. In actuality, the three secobutyl esters and the more strained 1,4-dicarboxymethoxycubane (**26**) all rearrange at comparable rates. We interpret this insensitivity to inherent molecular destabilization to mean that a concerted rearrangement is not operative. Clearly, if alleviation of strain were operative at the individual transition states for these very similar reactions, the rate sequence would be **26** > **22** > **23** > **24**, but this is not observed. Rather, the rate-determining step is probably the result of Ag^+ -induced rupture of a C–C bond on the cubic surface. If so, rate accelerations should be greater, the greater the availability of electron density at the site of bond cleavage. In accordance with this proposal, the rate constants for Ag^+ -induced rearrangement of cubane, **25**, and **26** are 17,000:310:1, respectively.²⁰ The far greater influence exerted by electronic effects appears reconcilable at this time only with a stepwise mechanism. We plan to elaborate on this point in the future.

The lower limit of inherent ring strain required for rearrangement is yet to be established. In this regard, however, Pettit has recently observed that treatment of *syn*-tricyclooctane (**27**) with 0.25 *M* AgBF_4 in acetone at 56° results in rapid (~ 1 min) conversion to a mixture of bicyclooctene **28**, tetrahydrosemibullvalene (**29**), and 1,5-cyclooctadiene (**30**) in the ratio 18:80:2, respectively.²⁸ Under identical conditions, *anti*-tri-

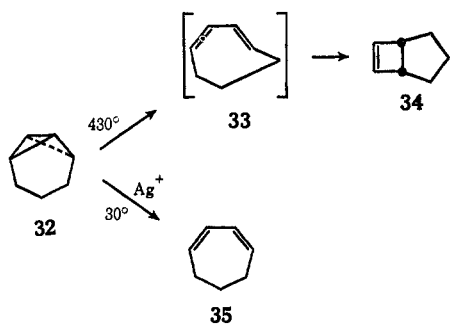


cyclooctane (**31**) has been found not to react after 5 days! The lack of reactivity of **31** has been attributed to the inability of Ag^+ to form a three-center bond in this instance.²⁸

Ring Cleavage of Bicyclo[1.1.0]butanes

The bicyclo[1.1.0]butanes, parents of the interesting bicyclo[$x.1.0$]alkane series of compounds, exhibit unique physical and chemical properties,²⁹ presumably as a result of the high strain energy of the molecules (63–68 kcal/mole).³⁰ Despite the facts that the activation energies for their thermal reorganization to butadienes are 41–43 kcal/mole³¹ and that elevated temperatures (150–430°) are required, the highly stereoselective nature of such isomerizations provides compelling evidence that they are concerted [$\sigma_2s + \sigma_2a$] changes.³² These observations denote that electronic considerations necessarily dominate thermodynamic factors in determining the stereochemistry of the diene.

As noted by Closs,^{32a} symmetrically labeled bicyclobutanes can in principle undergo three sterically different modes of ring opening. As a result, product analysis can readily provide quantitative information on the mechanistic pathway(s) operative during bond reorganization. A case in point is tricyclo[4.1.0.0^{2,7}]heptane (**32**) which affords *cis*-bicyclo[3.2.0]hept-6-ene (**34**) when heated above 400°. The highly reactive *cis,trans*-1,3-cycloheptadiene (**33**) has been implicated as the intermediate;^{32b} this interpretation is supported by deuterium labeling studies.³³ In dramatic contrast, **32** undergoes quantitative rearrangement exclusively to



cis,trans-1,3-cycloheptadiene (**30**) when treated with silver ion at ambient temperatures.³³

The rates of disappearance of **32** and other bicyclobutanes, like the cubyl systems, follow the second-order catalytic rate law $-d[\text{bicyclobutane}]/dt = k_{\text{Ag}}[\text{bicyclo}$

(28) J. Wristers, L. Brenner, and R. Pettit, *J. Amer. Chem. Soc.*, **92**, 7499 (1970).

(29) K. B. Wiberg, *Advan. Alicyclic Chem.*, **2**, 185 (1968).

(30) (a) R. B. Turner, P. Goebel, W. von E. Doering, and J. F. Coburn, Jr., *Tetrahedron Lett.*, 997 (1965); (b) R. B. Turner, P. Goebel, B. J. Mallon, W. von E. Doering, J. F. Coburn, Jr., and M. Pomerantz, *J. Amer. Chem. Soc.*, **90**, 4315 (1968); (c) K. B. Wiberg, G. M. Lampman, R. P. Ciula, D. S. Connor, P. Schertler, and J. Lavanish, *Tetrahedron*, **21**, 2749 (1965); (d) K. B. Wiberg and R. A. Fenoglio, *J. Amer. Chem. Soc.*, **90**, 3395 (1968).

(31) (a) H. M. Frey and I. D. R. Stevens, *Trans. Faraday Soc.*, **61**, 90 (1965); (b) J. P. Chesick, *J. Phys. Chem.*, **68**, 2033 (1964).

(32) (a) G. L. Closs and P. E. Pfeffer, *J. Amer. Chem. Soc.*, **90**, 2452 (1968); (b) K. B. Wiberg and G. Szeimies, *Tetrahedron Lett.*, 1235 (1968).

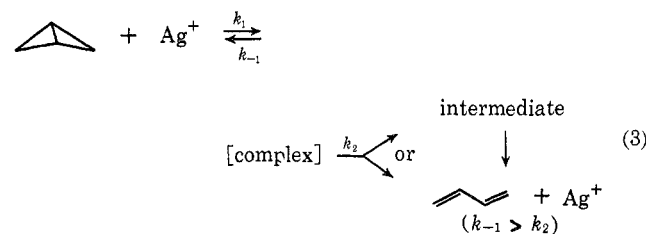
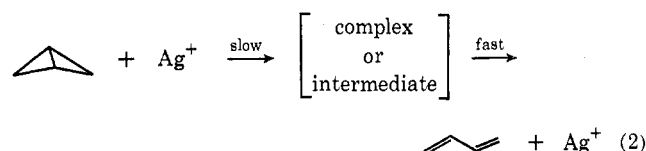
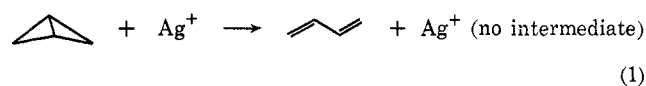
(33) L. A. Paquette, G. R. Allen, Jr., and R. P. Henzel, *J. Amer. Chem. Soc.*, **92**, 7002 (1970).

Table II
Isomerization Rate Data (C_6H_6 Solution)^a

Hydrocarbon	AgClO_4 , <i>N</i>	Temp, °C	k_{Ag} , $M^{-1} \text{sec}^{-1}$	Relative rate
32	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}	
36	4.03×10^{-2}	40.1	6.5×10^{-3}	2.3
39	2.02×10^{-2}	40.1	1.4×10^{-2}	5

^a L. A. Paquette, S. E. Wilson, and R. P. Henzel, *J. Amer. Chem. Soc.*, **93**, 1288 (1971).

butane][AgClO_4]. Kinetic data relating to measurements made with anhydrous silver perchlorate in dry benzene solution are grouped in Table II. In accord with the kinetic order, one of the following mechanisms (eq 1–3) must serve to describe the reaction. 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 and phosphinosilver complexes are known to be very rapid.³⁴ 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 mechanism 3, it becomes necessary only to measure the rates of isomerization (**32** was utilized) as a function of bicyclobutane concentration. The variation in rate is nonlinear (Figure 2) and can be expressed by the rate law

$$-\frac{d[\text{bicyclobutane}]}{dt} = \frac{k_2 K [\text{bicyclobutane}] [\text{AgClO}_4]}{K [\text{bicyclobutane}] + 1} \quad (4)$$

Adherence to eq 4, which signifies that the rate varies linearly with [bicyclobutane] at low substrate concentrations but is zero order in bicyclobutane at higher concentration levels, provides convincing evidence for mechanism 3. Mechanisms 1 and 2 cannot be operative since they demand a linear dependence of rate on bicyclobutane concentration and such is not observed.

(34) See Table II, footnote a.

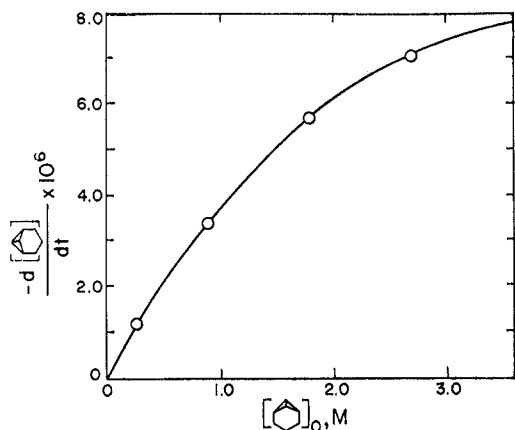


Figure 2. Initial rates of conversion of tricyclo[4.1.0.0^{2,7}]heptane (**32**) to **35** as a function of the concentration of **32**. All runs were performed at 40° in $2.02 \times 10^{-3} M$ silver perchlorate solutions consisting of 70% benzene–30% cyclohexane (v/v) and **32**.

The experimentally derived equilibrium in the case of **32** ($K = k_1/k_{-1} = 0.19 \pm 0.05$) indicates that complex formation is substantial. The activation parameters associated with the isomerization of **32**, $\Delta H^\ddagger = 18.2$ kcal/mole, $\Delta S^\ddagger = -12.4$ eu., and $\Delta G^\ddagger = 22.0$ kcal/mole, are in complete accord with the establishment of a preequilibrium and rate-determining rearrangement of the complex or a later intermediate.

Accordingly, bicyclobutane–silver(I) complexes are definitive intermediates in the catalyzed rearrangements. This conclusion is further supported by the strong dependence of the measurable second-order rate constant on the identity of the solvent (Table III).³⁵ An increase in the complexing power of the medium results in a proportionate diminution in “free” silver(I) available for catalytic purposes, an effect which is reflected in k_{Ag} . The phenomenon is particularly striking when acetonitrile is employed as solvent.

It should be noted that **32** is again a molecule of great structural rigidity. Arguments may be advanced to support the contention that this catalyzed reaction is not necessarily free, because of steric constraints, to proceed along competitive symmetry-allowed and -forbidden paths.³⁶ In an attempt to resolve this question, the behavior of *endo,exo*-(**36**) and *exo,exo*-2,4-dimethylbicyclo[1.1.0]butane (**39**) in the presence of Ag^+ was examined.³⁴ In the case of **36**, highly stereospecific conversion to *cis,trans*-2,4-hexadiene (**37**) was observed. Interestingly, an equal mixture of two dimers (**38**) accompanied the diene.^{36a} For **39**, diene formation was only stereoselective, giving **37** and **40** in a ratio of 1:3; in this instance, however, dimer formation was most efficient. The mechanism of dimer formation is not fully understood. The product dienes and *cis*- and *trans*-3,4-dimethylcyclobutene are stable to the reaction conditions.³⁴

The above results indicate that the Ag^+ -induced

(35) L. A. Paquette and S. E. Wilson, unpublished observations.

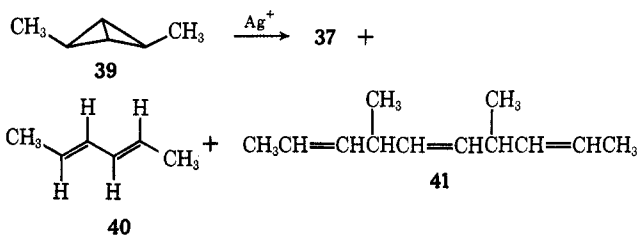
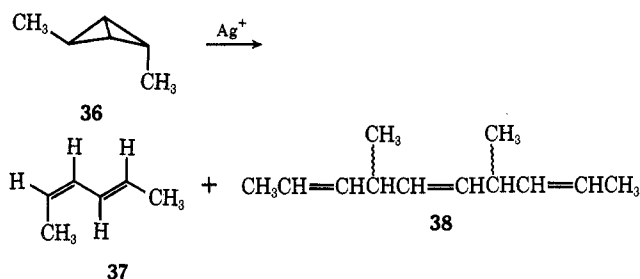
(36) W. Th. A. M. van der Lugt, *Tetrahedron Lett.*, 2281 (1970).

(36a) NOTE ADDED IN PROOF. M. Sakai, H. Yamaguchi, H. H. Westberg, and S. Nasamuni have suggested that these dimers are due to acid-catalyzed phenomena: *J. Amer. Chem. Soc.*, **93**, 1043 (1971).

Table III
Silver Perchlorate Catalyzed Isomerization Rate Data
for **32** in Various Solvents (40.00°)

Solvent	$k_{Ag}, M^{-1} \text{ sec}^{-1}$	Dielectric constant	Stability constant
C_6H_6	2.8×10^{-3}	2.3	$K_1 = 0.38^a$ $K_2 = 0.67^a$
CH_3COCH_3	2.5×10^{-3}	21.2	$K_1 = -0.85^a$
CH_3CN	No reaction	37.5	$\beta_2 = 1.23^a$
CH_3NO_2	1.6×10^{-1}	37.5	$K_1 \geq -3$

^a L. G. Sillén and A. E. Martell, *Chem. Soc. Spec. Publ.*, No. 17 (1964).



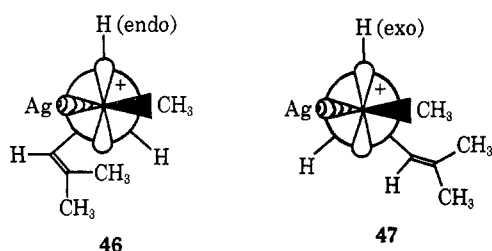
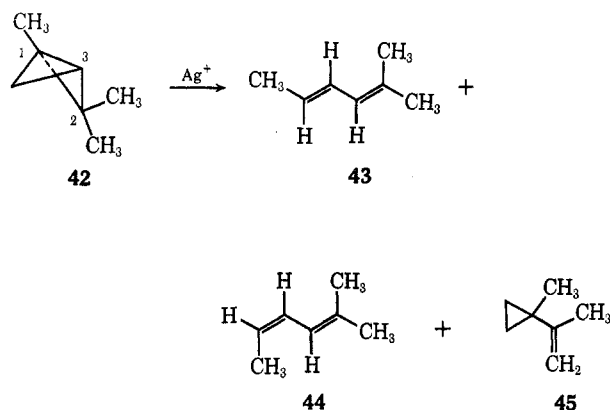
skeletal rearrangement of bicyclobutanes is characteristically a [$\sigma_{2a} + \sigma_{2a}$] bond reorganization even in those derivatives which are free of secondary structural constraints. Since the stereochemical pathways are the reverse of those followed on thermolysis,³² the Ag^+ -catalyzed rearrangements would appear not to be governed by the same electronic considerations which control their thermal isomerizations. However, stereospecificity by itself does not constitute proof for the concertedness of a reaction. In fact, more recent studies³⁷ have provided evidence that the 1:1 bicyclobutane–silver complexes are not transformed directly to products, but rather that discrete intermediates, implicated on circumstantial evidence to be argento carbonium ions, intervene, at least in certain cases.

The behavior of **42**, **48**, and **52** is illustrative. Exposure of **42** to $AgBF_4$ in chloroform solution results in quantitative conversion to dienes **43** and **44**, together with **45** in a ratio of 71:19:8.³⁷ This isomerization is most simply viewed as the result of C_1-C_2 and C_1-C_3 bond cleavage to afford the more highly substituted argento carbonium ion, and hydrogen migration from either or both of two possible conformations (**46** and **47**).³⁸ The rehybridization attending the formation of

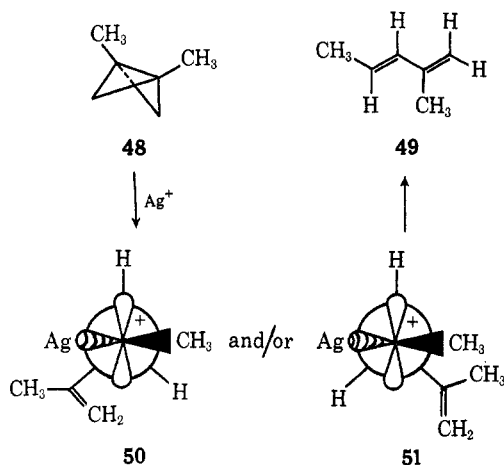
(37) L. A. Paquette, R. P. Henzel, and S. E. Wilson, *ibid.*, **93**, 2335 (1971).

(38) The question of the relative reactivities of the two conformations in this and other instances (cf. **50** and **51**, for example) is potentially resolvable. Because *exo* and *endo* hydrogen migration is particular to a given conformation, appropriate deuterium labeling and an analysis of the extent of H and D shift (correcting for isotope effects) should provide the requisite quantitative data.

the second double bond is in all likelihood thermodynamically controlled, in agreement with the predominance of **43**.



Similar treatment of **48** gives rise exclusively to diene **49**.³⁷ In this instance, the rehybridization which occurs subsequent to hydrogen migration in **50** and/or **51** is seen to lead uniquely to trans olefin for steric reasons.

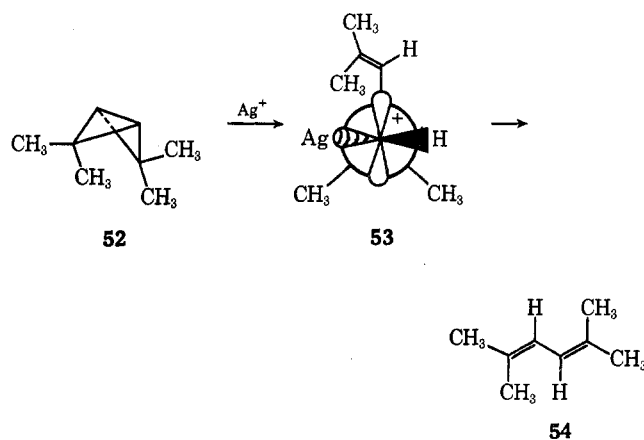


The essentially quantitative conversion of **52** to **54** under the previously stated conditions is also consistent with the intervention of argento carbonium ion **53**. In particular, the exclusivity of vinyl migration in **53** conforms to the greater migratory aptitude of vinyl (relative to alkyl) groups to cationic³⁹ (and also carbenoid⁴⁰) centers.

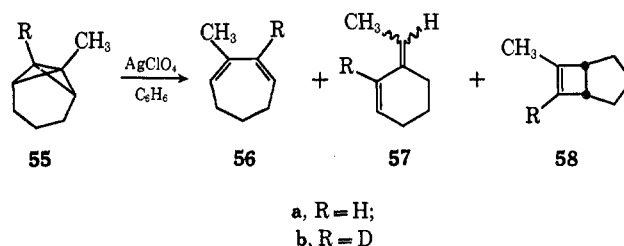
The effect of incremental alkyl substitution upon the course of bicyclobutane rearrangements is made strikingly evident in the tricyclo[4.1.0.0^{2,7}]heptane series. Whereas the parent hydrocarbon (**32**) affords only

(39) (a) Y. E. Rhodes and R. Takino, *J. Amer. Chem. Soc.*, **92**, 5270 (1970), and references therein; (b) R. S. Bly and R. T. Swindell, *J. Org. Chem.*, **30**, 10 (1965).

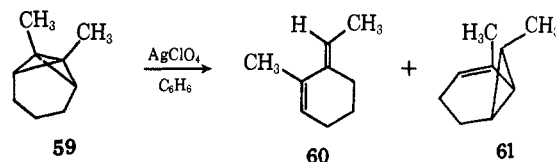
(40) A. R. Kraska, L. I. Cherney, C. G. Moseley, G. M. Kaufman, and H. Shechter, submitted for publication.



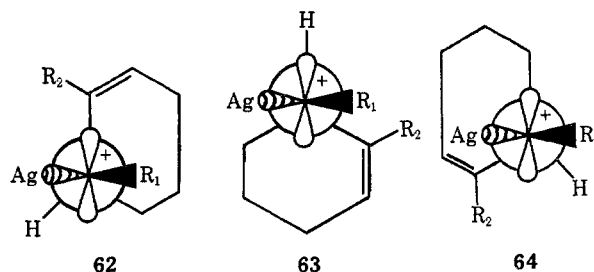
cis,cis-1,3-cycloheptadiene (**35**) when treated with AgClO_4 in benzene,³³ **55a** gives rise to a mixture of the four isomeric hydrocarbons **56a**, **57a**, and **58a** in the



ratio 29:29(syn-anti ratio of 4.5:1):42.³⁷ By rearranging **55b** in the same manner, ultimate positioning in **56-58** of the second tricycloheptane bridgehead carbon was revealed. Isomerization of **59** yields **60** (80%) and **61** (20%).³⁷

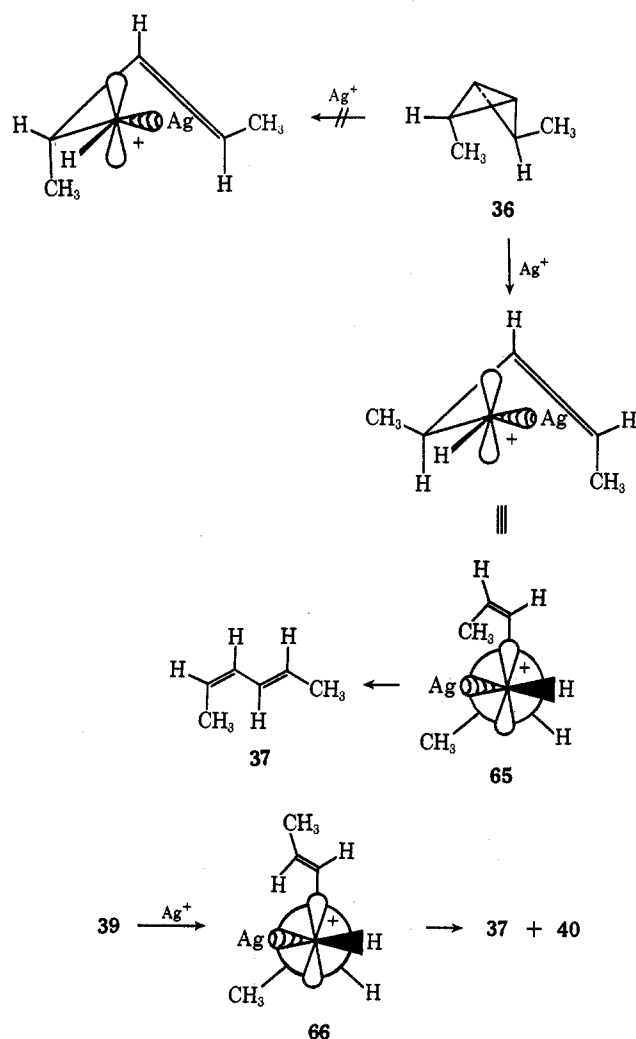


It would appear, therefore, that the operation of 1,2-vinyl shifts, 1,2-hydrogen migrations, or more deep-seated rearrangements is dependent upon the relative reactivities of conformations **62-64**. A study of various alternative substitution patterns (in progress) should throw more light on the controlling factors which are operative.



The argento carbonium ion hypothesis, which we are currently striving to confirm fully, can also serve to explain the stereoselectivity encountered in the Ag^+ -catalyzed rearrangements of **36** and **39**. Approach of Ag^+ to **36** from the less hindered direction (exo and proximal to the endo substituent) would lead *via* com-

plex formation to **65**. Subsequent vinyl migration in **65** and thermodynamic control in the requisite rehybridization at the migration terminus would mitigate against *cis,cis*-diene formation and furnish *cis,trans*-diene **37**. The lack of stereospecificity encountered



with **39** can likewise be explained by the assumption that vinyl migration to the neighboring argento carbonium ion in **66** proceeds normally to give a species, rehybridization of which now favors *trans,trans*-diene **40** over *cis,trans*-diene **37** by a factor of 3:1 for thermodynamic reasons.

Establishment of such a mechanism would, of course, mean that the stereochemical results noted above reflect not orbital symmetry control in the bond reorganization but rather a combination of steric, kinetic, and thermodynamic factors.

Of a particularly interesting nature, catalysis by Ag^+ eventuates in bond cleavage processes which are distinctly different (in unsymmetrical examples) from those which occur in the presence of rhodium, ruthenium, and related transition metal carbonyl catalysts.⁴¹

Rearrangement of Other Alicyclic Derivatives

A large number of additional silver(I)-catalyzed

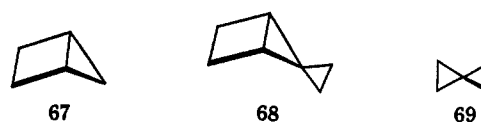
(41) P. G. Gassman and F. J. Williams, *J. Amer. Chem. Soc.*, **92**, 7631 (1970); P. G. Gassman, T. J. Atkins, and F. J. Williams, sub-

mitted for publication.
 (42) L. A. Paquette and R. C. West, unpublished observations.
 (43) B. C. Menon and R. E. Pincock, *Can. J. Chem.*, **47**, 3327 (1969).

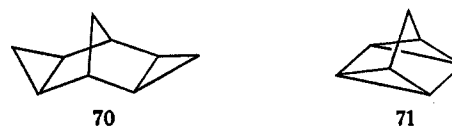
isomerizations will undoubtedly be discovered in the near future. Substantial emphasis is also expected to be placed on the catalytic effects of other transition metals. Such developments will be welcome, for they will constitute the essential experimental framework upon which the theory of such catalysis will be rationally based.

With specific regard to Ag^+ catalysis, it would appear that two essential features must be present in the molecule under consideration. The first of these is ring strain, since high levels of p character in the C-C bonds are necessary to bring the substrate into the metal coordination sphere; furthermore, relief of strain provides the ultimate driving force for rearrangement. However, ring strain alone is not sufficient. It appears equally essential that the substrate possess a geometry suitable for multicentered C-C σ -bond interaction with the metal ion during the reaction pathway.

Attention has already been called to the inertness of *anti*-tricyclooctane (**31**) to silver(I) ion. Likewise, the two bicyclo[2.1.0]pentanes **67** and **68** as well as spiro-



pentane (**69**) are stable to silver fluoroborate in chloroform despite their highly strained nature.⁴² Menon and Pincock⁴³ have noted that, whereas **70** is stable to silver nitrate at 25° and exhibits no noticeable complex formation under these conditions, quadricyclane (**71**) is rapidly isomerized to norbornadiene upon similar treatment.



It is of paramount importance to inquire about the extreme limits of structural features required for rearrangement. This we are attempting to do. However, because this question is intimately interwoven with the electronic energy levels of both the metal and the hydrocarbon and because the energy levels of the metal vary appreciably with the nature of the attached ligand, it is difficult at this time to predict the propensity of a given structural type for effective complexation, much less which rearrangement pathway will be followed if more than one is available.

I am especially indebted to my coworkers who have contributed so ably to the work cited in the references emanating from this laboratory. Their creativity, ingenuity, and industriousness have been vital factors in the development of our activity in this area. I wish also to acknowledge grant support from the donors of the Petroleum Research Fund, administered by the American Chemical Society, and fellowship support from the National Institutes of Health and the National Science Foundation.