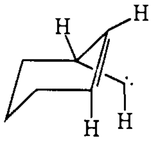
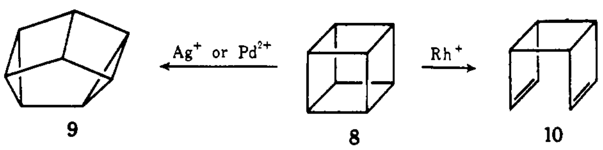
The rearrangements of **1**, especially those observed with noble metal catalysts similar to those used in catalytic hydrogenations, offer the first basis for a rational explanation of the complex reaction mixtures observed in the catalytic hydrogenation of highly strained ring systems. Generally, the reduction of derivatives of bicyclo[1.1.0]butane over the usual hydrogenation catalysts results in the cleavage of more than one bond of the highly strained polycyclic.[10] In view of the results discussed above, it seems reasonable to suggest that these multibond reductions may be due to rapid isomerization of the starting material followed by catalytic reduction of the resulting olefins. In support of this hypothesis, the products derived from the reduction of **1** over palladium on carbon[4] were the same as those obtained from the reduction of the olefins resulting from the isomerization of **1** by noble metal catalysts.

Mechanistically, the very clean isomerization of **1** to **4** by rhodium dicarbonyl chloride dimer differs significantly from the thermal and silver ion catalyzed isomerizations of **1**. Our isomerization clearly requires a hydrogen shift while both the thermal and silver ion catalyzed processes would appear to involve simple valence tautomerisms. These latter processes have been discussed in terms of concerted rearrangements.[11,12] At present insufficient data prohibit any decision about the concerted or nonconcerted nature of our rearrangement. However, it is interesting to note that the isomerization of **1** to **4** can be viewed as another example of a *formal* retro-carbene addition[14] in which the transition metal catalysts may facilitate the formation of a complex of **7**. A hydrogen shift would then give **4**.



7

In relation to the specificity of the various catalysts which we have investigated it is interesting to note that palladium(0) and platinum(IV) parallel rhodium(I) in their catalytic behavior. This is to be contrasted with the findings of Cassar, Eaton, and Halpern, who have reported[15] that the rearrangement of cubane (**8**) gives **9** with either silver(I) or palladium(II) but yields **10** with rhodium(I). The causes of this specificity are currently under investigation. We are also continuing to investigate the mechanism and scope of the transition metal catalyzed isomerizations of other highly strained ring systems.



Acknowledgment. We are indebted to the National Science Foundation and to the Alfred P. Sloan Foundation for support of this work.

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[10] For a listing of several examples of unusual reduction patterns for derivatives of bicyclo[1.1.0]butane, see K. B. Wiberg, *Advan. Alicyclic Chem.*, 2, 198 (1968).

[11] As described,[2] the conversion of 1 into 2 presumably occurs *via* initial opening of 1 to *cis,trans*-1,3-cycloheptadiene followed by subsequent closure of this diene to 2.

[12] At this time definitive evidence for the concerted nature of the silver ion catalyzed rearrangement of 1 has not been provided. The postulate of the "concertedness" of silver ion catalyzed isomerizations has been based on the specificity of the reaction.[3,13]

[13] L. A. Paquette and J. C. Stowell, *J. Amer. Chem. Soc.*, **92**, 2584 (1970); L. A. Paquette, *ibid.*, **92**, 5765 (1970).

[14] P. G. Gassman and F. J. Williams, *ibid.*, **92**, 7631 (1970).

[15] L. Cassar, P. E. Eaton, and J. Halpern, *ibid.*, **92**, 3515, 6366 (1970).

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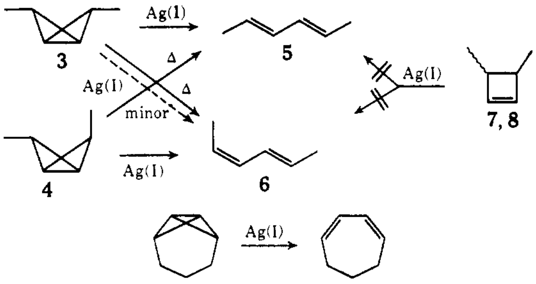
Silver(I)-Catalyzed Conversion of Bicyclobutanes to Butadienes. Concerning Stereospecificity

Sir:

The stereochemical consequence of a chemical reaction provides an important and very often decisive mechanistic probe. Metal-catalyzed rearrangements of organic molecules reported thus far[1] mainly involved systems in which the reaction centers were incorporated in the product in such a manner that only one mode of reaction was possible to explain the observed product and an alternative stereochemical pathway was structurally prohibited.[2] A question immediately arises. Is the reaction still stereospecific providing that energy contents of two possible isomeric products are comparable? We have searched for a system which would provide this particular stereochemical information. We wish to report herein that the bicyclobutane system undergoes nearly quantitative and largely (but not perfectly) stereospecific conversion to the corresponding butadiene system with the silver(I) ion at room temperature (Scheme I).

Scheme I



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[1] Systems receiving current interest are: (a) fused cyclobutene (W. Merck and R. Pettit, *J. Amer. Chem. Soc.*, **89**, 4788 (1967)); (b) quadricyclene and similar compounds (H. Hogeveen and H. C. Volger, *ibid.*, **89**, 2486 (1967); F. D. Mango and J. H. Schachtschneider, *ibid.*, **89**, 2484 (1967); H. C. Volger, H. Hogeveen, and M. M. P. Gaasbeck, *ibid.*, **91**, 218 (1969); T. J. Katz and S. Cerefice, *ibid.*, **91**, 2404 (1969); L. Cassar and J. Halpern, *Chem. Commun.*, 1082 (1970)); (c) basketene (W. G. Dauben, M. G. Buzzolini, C. H. Schallhorn, and D. Whalen, *Tetrahedron Lett.*, 787 (1970); L. A. Paquette and J. C. Stowell, *J. Amer. Chem. Soc.*, **92**, 2584 (1970); H. H. Westberg and H. Ona, *Chem. Commun.*, in press); (d) cubane (L. Cassar, P. E. Eaton, and J. Halpern, *J. Amer. Chem. Soc.*, **92**, 3515, 6366 (1970)).

[2] For instance, consider the case where the metal ion departs from the rhodium(III)-quadricyclene (see ref 1b) complex to give norbornadiene as the final product. Whether the reaction may proceed or not through an intermediate which has lost the memory of orbital symmetry, the likely product will be norbornadiene.

Upon treatment with silver perchlorate (0.1–0.15 *M*) in benzene, bicyclobutane (**1**)[3] (0.3–0.5 *M*) itself was rearranged to afford butadiene (**2**). This conversion proceeded smoothly at room temperature and the yield of **2** was more than 90% at any stage of the reaction, based on the consumed amount of **1**.[4] *exo,exo*- and *endo,exo*-2,4-dimethylbicyclobutanes (**3**, **4**)[5] under the same conditions underwent largely stereospecific conversion into *trans,trans*- and *cis,trans*-2,4-hexadienes (**5**, **6**), respectively, and the results are tabulated below (Table I). No other C_6 products were observed during the course of reaction. Both *cis*- and *trans*-dimethylcyclobutanes (**7**, **8**)[6] as well as **5**, **6**, and *cis,cis*-2,4-hexadiene (**9**) were recovered unchanged under the above conditions with silver perchlorate. Therefore, **5**, **7**, **8**, and **9** and their silver complex are eliminated as intermediates during the conversion of **4** to **6**.

Table I. Product Distribution (%) of Ag(I)-Catalyzed Reaction of 2,4-Dimethylbicyclobutane[a]

Compd	5	6	Total yield, %	Temp, °C
3	78	22	89	26
3	77	23	95	5
4	5	95	99	26
4	1	99	99	5

[a] See ref 4.

The above results show that the silver(I)-catalyzed reaction of **3** and **4**, the former to the lesser extent, chooses a discrete stereochemical pathway and stereochemistries of the products are virtually the reverse of those obtained by thermolysis.[5] A prediction can be easily made that readily available tricyclo[4.1.0.0^{2,7}]heptane (**10**)[7] will provide *cis,cis*-cycloheptadiene (**11**). This was found to be the case (97% yield) and the intermediacy of *cis*-bicyclo[3.2.0]heptene-6 can be disregarded since it was shown to be stable under the reaction conditions.[8]

Numerous experiments have been reported to show at least superficially that metal catalysts remove the symmetry restriction on thermally disallowed processes. However, we believe that this communication is the first to demonstrate that the metal ion affects stereospecific reactions in systems with stereochemical alternatives and reverses the stereochemical course of the thermolysis. Because strong extrasymmetric factors[9] which could influence the stereochemistry of the products are not obvious at the present moment, it is suggested that this bicyclobutane–silver(I) reaction is to a large measure governed *at some stage* by the orbital symmetry of the whole system undergoing skeletal changes.[10,11] However, obviously the data presently available preclude further analysis of the reaction. Questions concerning the intermediacy of the bicyclobutane–silver(I) complex, its structure, the possibility of rearrangement of the ligand, and the timing (stage) of removal of silver from the systems must be answered before one can propose the manner in which the observed stereospecificity is controlled.

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(3) Prepared according to the procedure reported by J. Bayless, L. Friedman, J. A. Smith, F. B. Cook, and H. Shechter, *J. Amer. Chem. Soc.*, **87**, 661 (1965).

(4) The yields reported herein are based on the integration of nmr signals and/or that of glpc peaks and are corrected to the relative sensitivity of the detector in the latter method. In both cases, cyclohexane was used as reference. The rate of rearrangement of **1**, **3**, **4**, and **10** at 40.7° varied directly with the initial Ag(I) concentration, being given by the expression $-d[\text{bicyclobutane}]/dt = k[\text{bicyclobutane}] \times [\text{AgClO}_4]_0$, and unaffected by the addition of the corresponding products, butadiene or its derivatives: **1**, $k = 5.2 \times 10^{-5}\ M^{-1}\ \text{sec}^{-1}$; **3**, 3.2×10^{-3}; **4**, 1.4×10^{-2}; **10**, 1.9×10^{-3}. A referee, apparently having attempted to repeat our experiments, informed us of the irreproducibility of our results in his laboratory. We earlier had similar experiences, but soon discovered that a trace of acid and possibly moisture are responsible for undesired side reactions. All the glassware including nmr tubes must be washed with dilute ammonia before drying and the reagent and solvent must be handled in a dry nitrogen atomosphere. The yields reported herein are the average of, at least, three runs and the absence of high molecular weight products (if present, presumably less than 5%) was confirmed by heating the glpc column (UC-W98) to 200°. The acid sensitivity of the bicyclobutane–Ag reaction was again confirmed after the referee's report.

(5) G. L. Closs and P. E. Pfeffer, *J. Amer. Chem. Soc.*, 90, 2452 (1968). We are grateful to Professor Closs for providing us with experimental details of the preparation of **3** and **4**.

(6) R. E. K. Winter, *Tetrahedron Lett.*, 1207 (1965).

(7) W. R. Moore, H. R. Ward, and R. T. Merritt, *J. Amer. Chem. Soc.*, **83**, 2019 (1961). For thermolysis of **10**, see K. B. Wiberg and G. Szeimies, *Tetrahedron Lett.*, 1235 (1968).

(8) After submission of this paper, this particular reaction (**10** to **11**) was reported by L. A. Paquette, G. R. Allen, Jr., and R. P. Henzel, *J. Amer. Chem. Soc.*, **92**, 7002 (1970). Clearly this example by itself provides no answer to the question raised in the text because of the expected thermodynamic instability of as yet unknown *cis,trans*-cycloheptadiene compared with **11** (see ref 2). These authors incorrectly viewed the reaction, if concerted, as $[{}_\sigma 2_s + {}_\sigma 2_s]$ which leads to *trans,-trans*-cyclohepta-1,3-diene. Obviously $[{}_\sigma 2_a + {}_\sigma 2_a]$ represents the net change of **10** in the orbital symmetry sense.

(9) J. A. Berson and S. S. Olin, *ibid.*, **92**, 1086 (1970).

(10) Theoretical arguments pertinent to this subject have already appeared (see ref 1a and 1b) and repetition is avoided.

(11) The degree of nonspecificity in the case of **3** demands special attention. It is also likely that the stereospecificity varies with the kind of metals employed and we have no intention of generalizing the present results to other metal-catalyzed reactions.

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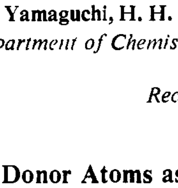
Effect of Thioether Donor Atoms as Nonbridging Ligands in the Reduction of Cobalt(III) Complexes by Iron(II)

Sir:

In a recent paper, Lane and Bennett reported a rate enhancement for the reduction of mercaptoacetatobis(ethylenediamine)cobalt(III) by chromium(II).[1] Recent work in our laboratories has demonstrated that the reduction of *s-cis*-dichloro(1,8-diamino-3,6-dithiaoctane)cobalt(III) perchlorate by iron(II) occurs at a rate 10^3 times more rapid than that for *cis*-$\text{Co(en)}_2\text{Cl}_2^+$ under comparable conditions. This represents the first quantitative study in which the nonbridging-ligand effect is evaluated for thioether donors positioned trans to a chloride–cobalt(III) bridge for reduction by iron(II).

Previous stereochemical studies have established the geometry of *s-cis*-Co(eee)Cl_2^+ as that shown below.[2]



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(1) (a) R. H. Lane and L. E. Bennett, *J. Amer. Chem. Soc.*, **92**, 1089 (1970). (b) k_{82} has been more recently determined to be in the order of $\sim 5 \times 10^6\ M^{-1}\ \text{sec}^{-1}$: L. E. Bennett, private communication.

(2) J. H. Worrell and D. H. Busch, *Inorg. Chem.*, **8**, 1563 (1969).