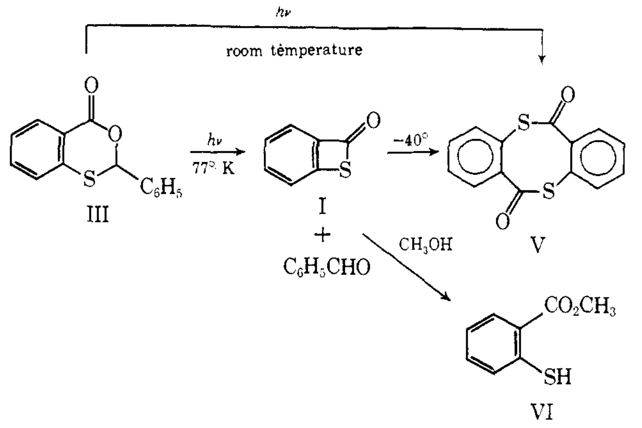
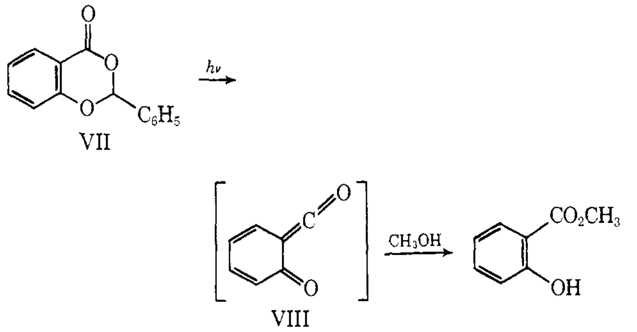


(VI).[7] The infrared spectrum and the formation of VI identify the intermediate as 2-thiobenzpropiolactone (I).

The facile synthesis of 2-thiobenzpropiolactone (I) from III led us to attempt the synthesis of the parent benzpropiolactone (II). Irradiation of VII at 77°K



gave rise to a ketene band (2118 cm^{-1}) but no bands which could be attributed to the β-lactone. Irradiation of VII in methanol at room temperature gave methyl salicylate. This latter result suggests that the ketene observed at low temperature may be VII.

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(7) Ethyl 2-mercaptobenzoate has been observed in the irradiation of III at room temperature in the presence of ethanol.[2]

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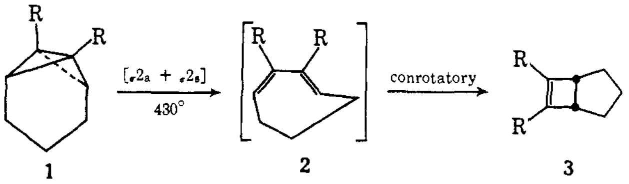
Silver(I) Ion Catalyzed Rearrangements of Strained σ Bonds. IV. The Fate of Tricyclo[4.1.0.0^{2,7}]heptane[1,2]

Sir:

Earlier studies in this laboratory have elaborated upon the remarkable facility with which Ag$^+$ can induce thermally disallowed $[_{\sigma}2_{a} + {}_{\sigma}2_{a}]$ skeletal isomerizations of homocubyl and 1,1′-bishomocubyl systems.[1,3] We now report an extension of this fascinating development to bicyclo[1.1.0]butane derivatives.

Despite the fact that the bicyclobutane ring system possesses a remarkably high strain energy (63–68 kcal/mol[4]), thermal reorganization of its derivatives requires elevated temperatures, usually in excess of 150°.[5,6] The activation energy for isomerization to butadiene resides in the vicinity of 41–43 kcal/mol.[5a,7] Nevertheless, the highly stereoselective nature of the reaction provides compelling evidence that the process is a concerted $[_{\sigma}2_{s} + {}_{\sigma}2_{a}]$ chemical transposition.[5d,e] In particular, such observations have revealed that electronic factors clearly outweigh thermodynamic considerations in determining the stereochemistry of the diene product.

A case in point is tricyclo[4.1.0.0^{2,7}]heptane (**1a**) which affords *cis*-bicyclo[3.2.0]hept-6-ene (**3a**) when heated above 300°. *cis,trans*-1,3-Cycloheptadiene (**2a**) justifiably has been postulated as the requisite intermediate.[5d] The gas-phase pyrolysis of **1b**, performed during the course of the present study (Table I), is likewise best accommodated by this mechanism. The resulting *cis*-bicyclo[3.2.0]hept-6-ene was deuterated



a, R = H; **b**, R = D

Table I. Pyrolysis[a] of Tricyclo[4.1.0.0^{2,7}]heptane-*1,7-d$_2$* (**1b**)

		Composition of pyrolysate, %		
Temp, °C	Yield, %	**3b**	Recovd **1b**	1,3-Cycloheptadiene[b]
430	86	50	32	18
440	91	56	16	28
490	91	33	10	57
500	91	5	10	85

[a] Gas-phase conditions under a nitrogen atmosphere at 12–16 mm in a quartz tube (28 cm × 16 mm) packed with quartz chips. [b] The 1,3-cycloheptadiene-d_2 had undergone virtually complete deuterium scrambling *via* consecutive [1,5]-sigmatropic hydrogen shifts, as established by nmr analysis of the hydrocarbon and its maleic anhydride adduct.

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(1) Paper III: L. A. Paquette and J. C. Stowell, submitted for publication.

(2) Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for their partial support of this research.

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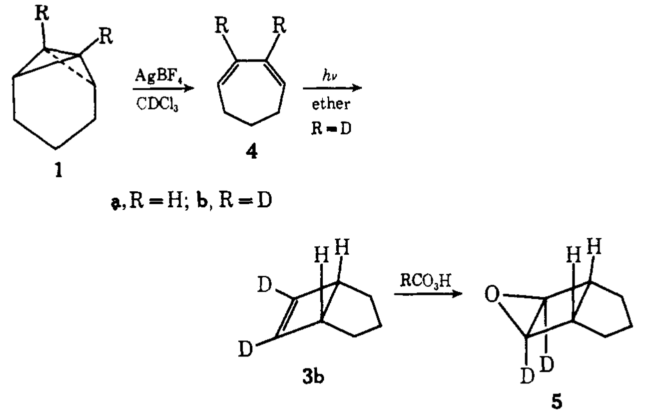
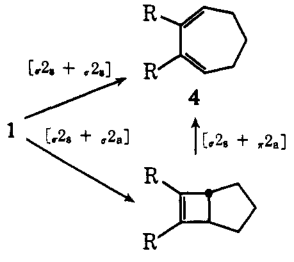
exclusively as in **3b** (absence of vinyl absorption at δ 5.86 in $CDCl_3$).[8]

In dramatic contrast, exposure of dilute $CDCl_3$ solutions of **1a** to catalytic amounts of silver fluoroborate at nmr probe temperatures (~40°) results within minutes in quantitative conversion to *cis,cis*-1,3-cycloheptadiene (**4a**). Bicyclic hydrocarbon **3a** was readily dismissed as a possible intermediate, since it is stable to the reaction conditions for long periods of time. Additionally, the intervention of **2a** was shown to be unlikely on the basis of the observation that *cis,trans*-1,3-cyclooctadiene is not subject to trans → cis isomerization under entirely comparable circumstances, but rather is deposited as a stable complex.[9] No complex formation is visible during the Ag^+-catalyzed rearrangement of **1**.

When **1b** was rearranged in this manner, *cis,cis*-1,3-cycloheptadiene-d_2 was similarly produced in high yield. However, because the four vinyl protons of **4a** appear as a pseudosinglet at δ 5.74 in $CDCl_3$, the deuterium substitution pattern had to be deduced indirectly. To this end, this diene was photolyzed in ether solution.[11] The isolated **3** was shown to be labeled exclusively as **3b**, thus unequivocally identifying the diene as **4b**. Further confirmation of the assignment was derived by epoxidation of the **3b** so produced. As anticipated, the resulting epoxide (**5**) was devoid of >C*H*O- absorption at δ 3.47 ($CDCl_3$).[12]



In view of these data, *it is clear that the rearrangement of* **1** *under conditions of* Ag^+ *catalysis is not governed by the same electronic considerations which control its thermal isomerization.* Rather, the conversion of **1** to **4**, if concerted, is required to be the formal result either of a direct symmetry disallowed $[{}_{\sigma}2_{s} + {}_{\sigma}2_{s}]$ bond reorganization, or of a two-step process involving initial thermally allowed $[{}_{\sigma}2_{s} + {}_{\sigma}2_{a}]$ rearrangement to *trans*-bicyclo[3.2.0]hept-6-ene (**6**) and subsequent $[{}_{\sigma}2_{s} + {}_{\pi}2_{a}]$ ring opening. The first alternative is very attractive for, in addition to being eminently feasible in the thermodynamic sense, it invokes a role for Ag^+ very similar to that observed in the rearrangements of cubyl systems.[1,3] The first step of the second alternative constitutes an example of a long recognized, but previously unrealized, thermally allowed rebonding pathway for bicyclobutanes.[4a,13] Unfortunately, thermodynamic analysis of this step is not possible in the present instance because of the unavailability of **6**. The purely thermal conversion of severely twisted **6** to **4** under very mild conditions would not be unexpected.



The capability of deciding between these alternatives exists and is presently under active investigation. Although the ultimate resolution of this question is of considerable direct importance to an understanding of the mechanistic role played by Ag^+ in this and other[14] bicyclobutane rearrangements, it is now evident that the observed dramatic lowering of transition-state energies is associated not only with relief of strain but also in a very fundamental way with interaction between the strained σ bonds and the atomic orbitals of the noble metal ion.

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(8) In addition, the ratio of bridgehead allylic protons to methylene hydrogens was precisely 1 :3.

(9) The stability of the silver nitrate complexes of *cis,trans*-1,3-cyclooctadiene[10a] and *cis,trans*-1,3-cyclononadiene[10b] has previously been recognized. The corresponding cis,cis isomers do not give rise to such complexes.

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Organosilicon Compounds Containing Monovalent Gold

Sir:

The current interest in the coordination chemistry of gold in its lower valency state[1,2] and of organogold species[3–7] prompts us to report some recent results on the organosilicon chemistry of gold.[8] The findings in

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