6.20 (w), 6.96, 7.51, 8.33, 8.50, and 9.61 μ; nmr ($CDCl_3$) τ 4.19 (1 H, d of d, $J = 6.5$, 2 Hz), 4.38 (1 H, m), 6.33 (3 H, s), 6.2–6.6 (1 H, s), 7.2–8.2 (4 H, m).

1-Carbomethoxycyclopentene (22). The procedure used was a modification[30] of the literature procedures.[31,32] 2-Carbomethoxycyclopentanone was reduced with sodium borohydride to 2-carbomethoxycyclopentanol, bp 83–91° (1.3 mm). Dehydration of the alcohol with phosphorus pentoxide in benzene afforded a mixture of carbomethoxycyclopentenes which was equilibrated by treatment with methanolic sodium methoxide. Distillation afforded impure **22**, bp 71–75° (33 mm) [lit. bp 63–65° (10 mm),[31] 52° (12 mm)[33]]. Purification by preparative vpc at 120° on a 10 ft × 1/4 in. 25% DEGS on 60–80 Chromosorb P column gave pure **22**.

3-Carbomethoxycyclopentene (23). 3-Chlorocyclopentene was prepared by the method of Moffett[34] and was converted to the Grignard reagent and subsequently to cyclopentene-3-carboxylic acid by the method of Jørgensen and Berg.[35] Esterification with diazomethane afforded 3-carbomethoxycyclopentene (**23**), bp 66–67° (26 mm) [lit. bp 60–65° (15 mm),[31] 46° (10 mm)[35]].

Acknowledgment. We are indebted to the National Science Foundation for a grant which supported this investigation.

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[30] H. D. Scharf and F. Korte, *Chem. Ber.*, 97, 2425 (1964).

[31] S. J. Rhoads, J. K. Chattopadhyay, and E. E. Waali, *J. Org. Chem.*, **35**, 3352 (1970).

[32] K. V. Bokil and B. S. Nargund, *Proc. Indian Acad. Sci., Sect. A*, **11**, 409 (1940).

[33] M. Hanack and H. J. Schneider, *Tetrahedron*, **20**, 1863 (1964).

[34] R. B. Moffett, "Organic Syntheses," Collect. Vol. IV, Wiley, New York, N. Y., 1963, p 238.

[35] S. B. Jørgensen and A. Berg, *Acta Chem. Scand.*, **20**, 2192 (1966).

The Effect of Methyl Substitution on the Competitive Rearrangements of Tricyclo[4.1.0.0^{2,7}]heptanes by Silver(I) Ion. Product and Kinetic Considerations[1,2]

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Abstract: The Ag(I)-catalyzed rearrangements of tricycloheptane (**1a**), the 1- and 2-methyl homologs, and the 1,2-, 1,7-, and 2,6-dimethyl derivatives have been investigated. Kinetic studies relating to the relative rates of formation of 1,3-cycloheptadienes have revealed an interesting dependence on the position and number of methyl substituents. These same features control the product distribution; whereas the placement of methyl groups at C-2 and C-6 does not alter the propensity of the strained hydrocarbon for C-1,2 and C-3,4 bond cleavage, substitution at the bridgehead sites introduces considerable complexity. The formation of Ag^+–tricycloheptane complexes has been demonstrated by kinetic methods. The implications of these results as they relate to mechanism are briefly discussed.

Bicyclo[1.1.0]butanes, the most highly strained of the two-ring carbocyclic compounds,[4] have enjoyed a preeminent position in alicyclic chemistry since the successful synthesis of the first authentic derivative in 1959.[5] Of the various known transformations of these molecules, those resulting from metal ion catalyzed isomerization are certainly among the most intriguing.[6] The complex ground-state molecular changes of bicyclobutanes have now been meaningfully placed on a reasonable theoretical foundation;[7] at the outset of our study of the metal-catalyzed rearrangements of this class of hydrocarbons, even the basic theory allowing one to consider possible mechanisms was replete with confusing predictions. As a result, the present investigation began with two goals—first, elucidation of the types of skeletal isomerizations which tricyclo[4.1.0.0^{2,7}]heptanes would undergo under conditions of Ag^+ catalysis, and second, determination of the extent to which suitable placement of alkyl groups on this system would affect the rate of rearrangement and the product distribution.

Tricyclo[4.1.0.0^{2,7}]heptane (1).[8] Addition of **1a**, the archetype of *endo,endo*-2,4-disubstituted-bicyclobutanes, to anhydrous silver fluoroborate in deuteriochloroform at 40° resulted within minutes in quantitative conversion to *cis,cis*-1,3-cycloheptadiene (**2a**). When the hydrogen atoms positioned at C_1 and C_3 were replaced by deuterium as in **1b**,[9] *cis,cis*-1,3-cycloheptadiene-*2,3-d*$_2$ (**2b**)

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[1] Part XII of the series dealing with Ag^+-catalyzed rearrangements. For the previous paper, see L. A. Paquette and G. Zon, *J. Amer. Chem. Soc.*, **94**, 5096 (1972).

[2] Various aspects of this work have been presented at the Meeting of the Chemical Institute of Canada, Halifax, Nova Scotia, May, 1971, the 22nd National Organic Chemistry Symposium, Ann Arbor, Mich., June, 1971, and the Second Belgian Chemical Society Symposium on Small Rings and Activated Multiple Bonds, Louvain, Belgium, Sept 1971.

[3] (a) National Institutes of Health Postdoctoral Fellow, 1970–1971; National Science Foundation Postdoctoral Fellow, 1971–1972; (b) National Science Foundation Graduate Trainee, 1970–1972; (c) Senior Education Awardee, American Cyanamid Co., 1969–1970.

[4] (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).

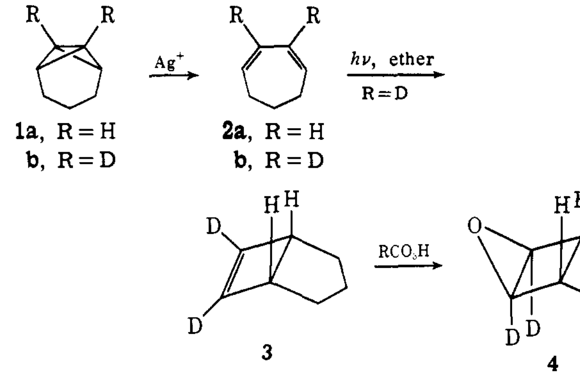
[5] (a) K. B. Wiberg and R. P. Ciula, *ibid.*, **81**, 5261 (1959); (b) K. B. Wiberg, *Advan. Alicycl. Chem.*, 2, 185 (1968).

[6] For a review of the status of this field in late 1970, see L. A. Paquette, *Accounts Chem. Res.*, **4**, 280 (1971).

[7] (a) G. L. Closs and P. E. Pfeffer, *J. Amer. Chem. Soc.*, **90**, 2452 (1968); (b) K. B. Wiberg and G. Szeimies, *ibid.*, 92, 571 (1970); (c) L. A. Paquette, G. R. Allen, Jr., and M. J. Broadhurst, *ibid.*, **93**, 4503 (1971).

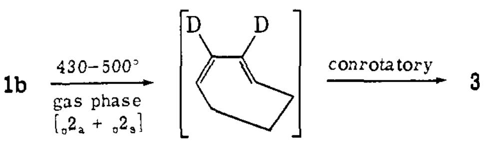
[8] These results were first disclosed in a preliminary communication: L. A. Paquette, G. R. Allen, Jr., and R. P. Henzel, *ibid.*, 92, 7002 (1970).

[9] P. G. Gassman and G. D. Richmond, *ibid.*, 92, 2090 (1970).



was similarly produced in high yield. Assignment of the precise deuterium positioning in **2b** (although clearly sp^2 bonded) could not be achieved on the basis of the nmr spectrum because the four olefinic protons of **2a** appear as a pseudosinglet at δ 5.74 in CDCl$_3$. Indirect deduction of the deuterium substitution pattern in **2b** was realized, however, by photolysis in ether solution.[10] The isolated bicyclo[3.2.0]hept-5-ene was found to be labeled exclusively as **3**. Further confirmation was derived by epoxidation of **3**; as expected, the resulting epoxide was devoid of >C*H*O– absorption at δ 3.47 (CDCl$_3$).[11,12]

The nature of this rearrangement and the facility with which it occurs contrast markedly with the conditions required for thermal bond reorganization of **1a**. Only when heated above 300° does this bicyclobutane suffer isomerization; because *cis*-bicyclo[3.2.0]hept-6-ene is formed under these conditions, *cis,trans*-1,3-cycloheptadiene has been justifiably postulated as the requisite intermediate.[14] 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 bicycloheptene proved to be identical in all respects with **3**.



With respect to the Ag$^+$-catalyzed rearrangement of **1a**, *cis*-bicyclo[3.2.0]hept-6-ene could be readily dismissed as a possible intermediate because of its stability to the reaction conditions for long periods of time. Additionally, the intervention of *cis,trans*-1,3-cycloheptadiene 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 is deposited as a stable complex.[15]

Table I. Pyrolysis of Tricyclo[4.1.0.0^{2,7}]heptane-*1,7*-d_2 (**1b**)

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

[a] 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.

Given the above data, one is faced with the currently fashionable question of whether orbital symmetry concepts are applicable in this instance. Since the conversion of **1** to **2** is the *formal* result of a $[{}_{\sigma}2_{a} + {}_{\sigma}2_{a}]$ bond reorganization,[17] a reaction mode which is symmetry forbidden from substrates in their ground states but photochemically allowed,[17] the question of a concerted catalyzed reaction must be considered. Such an eventuality could conceivably arise if silver(I) ion were interacting with the p-rich orbitals of the strained hydrocarbon to alter the electronic nature of certain

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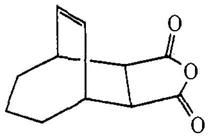
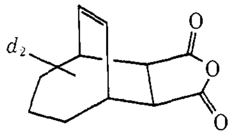
(10) (a) W. G. Dauben and R. L. Cargill, *Tetrahedron*, **12**, 186 (1961); (b) O. L. Chapman, D. J. Pasto, G. W. Borden, and A. A. Griswold, *J. Amer. Chem. Soc.*, **84**, 1220 (1962).

(11) The preparation of nonlabeled **4** has been reported: L. A. Paquette, A. A. Youssef, and M. L. Wise, *ibid.*, **89**, 5246 (1967).

(12) Because of the wide separation in chemical shifts of its various proton types, bicyclo[3.2.2]non-8-ene-6,7-dicarboxylic anhydride (i), formed by reaction of **2a** with maleic anhydride,[13] initially offered promise as a suitable probe for the deuterium labeling in **2b**. However, the requisite Diels–Alder cycloaddition requires such forcing conditions (refluxing xylene, 4 hr) that hydrogen–deuterium scrambling in **2b** *via* [1,5]-sigmatropic shifts becomes kinetically competitive with the [4 + 2] bonding process. As a result, the anhydride so produced (ii) is of little value for the desired analysis.



i



ii

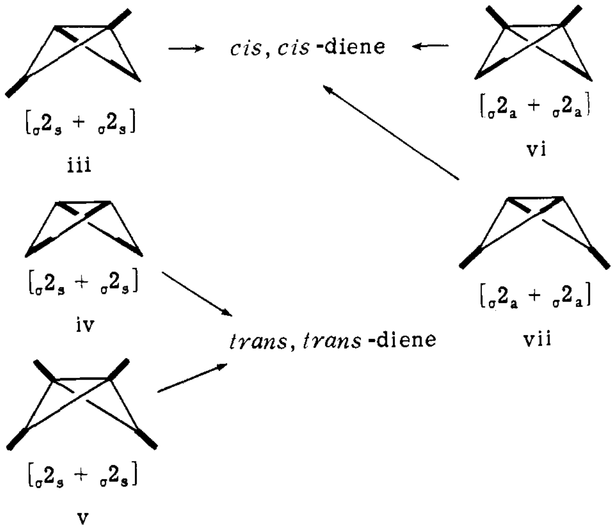
(13) E. P. Kohler, M. Tishler, H. Potter, and H. T. Thompson, *J. Amer. Chem. Soc.*, **61**, 1057 (1939).

(14) K. B. Wiberg and G. Szeimies, *Tetrahedron Lett.*, 1235 (1968).

(15) The stability of the silver nitrate complexes of *cis,trans*-1,3-cyclooctadiene[16a] and *cis,trans*-1,3-cyclononadiene[16b] has been recognized previously. The corresponding cis,cis isomers do not give rise to such complexes.

(16) (a) A. C. Cope and C. L. Bumgardner, *J. Amer. Chem. Soc.*, **78**, 2812 (1956); (b) R. W. Fawcett and J. D. Harris, *J. Chem. Soc.*, 2673 (1954).

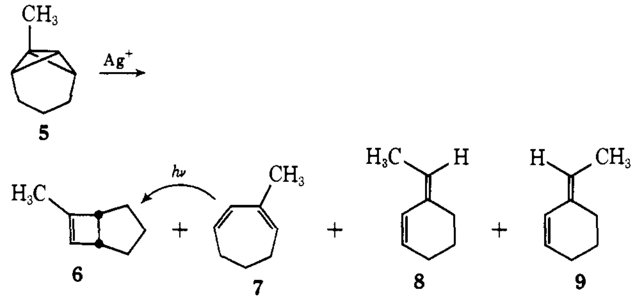
(17) R. B. Woodward and R. Hoffmann, *Angew. Chem.*, **81**, 797 (1969); *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969). Originally,[8] we described the net change involved in the conversion of **1** to **2** as a $[{}_{\sigma}2_{s} + {}_{\sigma}2_{s}]$ process. Subsequently, this terminology was strongly criticized by Masamune[18] who claimed that our notation was incorrect in that $[{}_{\sigma}2_{s} + {}_{\sigma}2_{s}]$ cleavage leads only to *trans,trans*-1,3-cycloheptadiene. This author failed to realize that in actuality bicyclobutanes can experience three distinctly different $[{}_{\sigma}2_{s} + {}_{\sigma}2_{s}]$ changes, and while we were addressing ourselves to mode iii, he apparently had focused his attention uniquely on iv or v. We have since altered our description to $[{}_{\sigma}2_{a} + {}_{\sigma}2_{a}]$ in view of the fact that use of either bond cleavage mode (*cf.* vi and vii) gives the identical answer and hence further ambiguity is avoided.



(18) M. Sakai, H. Yamaguchi, H. H. Westberg, and S. Masamune, *J. Amer. Chem. Soc.*, **93**, 1043 (1971).

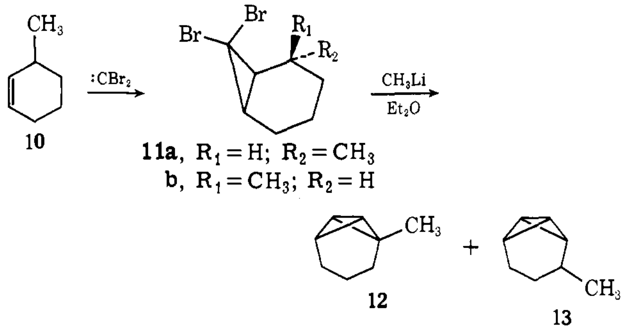
requisite orbitals.[19] Alternatively, the observed dramatic lowering of transition state energy (see below) could be associated with a very special mechanistic role played by Ag^+ in which its anticipated electrophilic properties could lead to the generation of discrete metal-bonded intermediates endowed with unique chemical reactivity. The combined experimental evidence presented in this and the succeeding two papers[20] will serve to provide a definitive distinction in favor of the latter eventuality.

1-Methyl- and 2-Methyltricyclo[4.1.0.0^{2,7}]heptanes (5 and 12).[21] The possible perturbing influence of incremental alkyl substitution upon the Ag^+-catalyzed tricycloheptane rearrangement was first evaluated with the readily available 1-methyl derivative **5**.[22] When **5** was treated with $AgClO_4$ (0.136 *M*) in anhydrous benzene at 40°, there was produced a mixture of four isomeric hydrocarbons, each of which in turn was found to be stable to the reaction conditions. Initial preparative scale vpc separation of this mixture on an OV-17 column (5% on Chromosorb G) at 100° led to the isolation of pure **6** (first to elute) and **7** (second component). The product of shortest retention time was identified as bicycloheptene **6** (44.3%) on the basis of its nmr spectrum ($CDCl_3$) which displays a lone olefinic (m, δ 5.64) and two allylic protons (m, 2.88–3.17) in addition to absorptions due to the methylene hydrogens (m, 6, 0.87–1.84) and the methyl group (m, 1.60). The structure of **7** (26.4%) follows from its nmr spectrum (see Experimental Section) and its ready photoisomerization to **6**. The last component proved to be a mixture of ethylidenecyclohexenes (29.3%); when reinjected onto a 20-ft QF-1 column (5% on Chromosorb G) at 100°, these isomers were cleanly separated and a cis:trans ratio of approximately 4:1 was revealed. The ultraviolet and nmr spectra of **8** and **9** were identical with those previously reported for these substances.[23]



5, **6**, **7**, **8**, **9**

The 2-methyl derivative **12** was conveniently prepared from 3-methylcyclohexene (**10**) by adaptation of the method of Moore.[24] Addition of dibromocarbene to **10** afforded in good yield an inseparable mixture of the *cis*- and *trans*-2-methyl-7,7-dibromobicyclo[4.1.0]heptanes (**11**). Direct treatment of **11** with methyllithium in ether at 0° yielded a mixture of **12** (~90%) and the isomeric 3-methyltricyclo[4.1.0.0^{2,7}]heptane (**13**, ~10%). The spectral properties of these hydrocarbons, which were separable on the OV-17 column, are in full accord with the assigned structures. In all likelihood, **12** results directly from **11a** since the derived carbene is uniquely constructed in a stereochemical sense for kinetically controlled insertion into the adjacent tertiary C–H bond. The other dibromide (**11b**) leads to a carbene intermediate capable only of insertion into a secondary C–H bond and as a result serves only as the precursor to **13**.

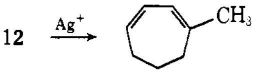


10

11a, $R_1 = H$; $R_2 = CH_3$
b, $R_1 = CH_3$; $R_2 = H$

12 **13**

The rearrangement of **12** catalyzed by 0.206 *M* $AgClO_4$ in dry benzene at 40° led exclusively to **14**.



14

The nmr spectrum of **14** is sufficiently different from that of **7** to define the molecule as the alternative possible methyl-1,3-cycloheptadiene in which the alkyl group is necessarily bonded to sp^2-hybridized carbon.

Clearly, the positioning of a methyl group at C_1 of the tricycloheptane nucleus exerts a much greater effect on the direction of the Ag^+-catalyzed rearrangement than does a like substituent at C_2, an observation which must be adequately accounted for in the final mechanistic analysis.

1,2-, 1,7-, and 2,6-Dimethyltricyclo[4.1.0.0^{2,7}]heptanes (28, 21, and 17). Synthesized by the analogous reaction of 1,3-dimethylcyclohexene (**15**) with dibromocarbene and subsequently with methyllithium in ether, 2,6-dimethyltricyclo[4.1.0.0^{2,7}]heptane (**17**) is rearranged directly by Ag^+ to 1,4-dimethyl-1,3-cycloheptadiene (**19**). The presence of the methyl groups at the termini of the conjugated diene unit in **19** is consistent with its ready photoisomerization to **20**. The nmr spectrum of **20** (in $CDCl_3$) shows two olefinic hydrogen atoms as a singlet at δ 5.81, a broad methylene proton envelope of area 6 at 0.84–1.71, and a second singlet (6 H) at 1.04 due to the methyl groups.

The preparation of **21** was effected by the dimethylation of **1a** as previously described.[21] Isomerization of **21** as above was found to produce **22** (80%) and **23** (20%). Assignment of structure to **22** is based on its nmr spectrum and its independent synthesis from 2-methyl-2-cyclohexenone (**24**) and ethylidenetriphenylphosphorane.

Elemental analysis of **23** indicated it to be an isomer of tricycloheptane **21**. The nmr spectrum in $CDCl_3$ dis-

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[19] For a recent review of the theoretical aspects of metal catalysis consult F. D. Mango, *Advan. Catal.*, **20**, 291 (1969).

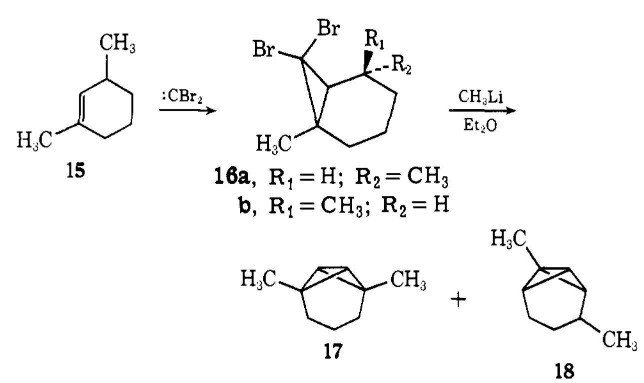
[20] (a) L. A. Paquette, S. E. Wilson, and R. P. Henzel, *J. Amer. Chem. Soc.*, **94**, 7771 (1972); (b) L. A. Paquette, R. P. Henzel, and S. E. Wilson, *ibid.*, 94, 7780 (1972).

[21] The rearrangement of **5** has been previously noted: L. A. Paquette, R. P. Henzel, and S. E. Wilson, *ibid.*, **93**, 2335 (1971).

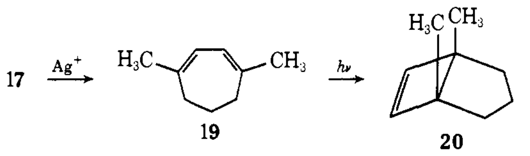
[22] G. L. Closs and L. E. Closs, *ibid.*, **85**, 2022 (1963).

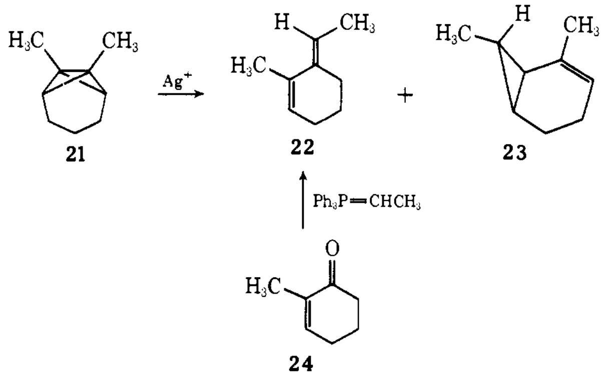
[23] P. D. Bartlett, *Quart. Rev., Chem. Soc.*, **24**, 473 (1970). We thank Professor Bartlett for providing us with copies of the nmr spectra. The assignments in the paper by Bank, *et al.* [S. Bank, C. A. Rowe, A. Schriesheim, and L. A. Naslund, *J. Org. Chem.*, **33**, 221 (1968)] should be reversed.

[24] (a) W. R. Moore, H. R. Ward, and R. F. Merritt, *J. Amer. Chem. Soc.*, **83**, 2019 (1961); (b) W. R. Moore and B. J. King, *J. Org. Chem.*, **36**, 1877, 1882 (1971).

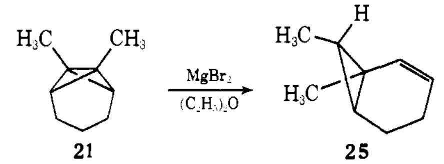


16a, $R_1 = H$; $R_2 = CH_3$
b, $R_1 = CH_3$; $R_2 = H$



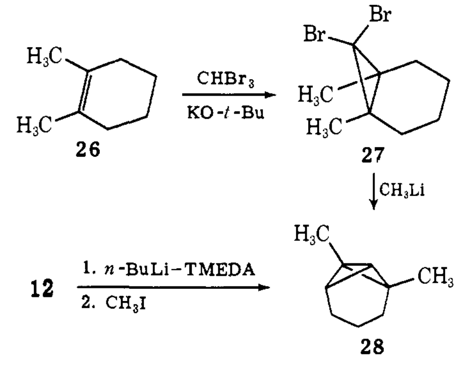


plays the lone olefinic proton as a multiplet positioned at δ 5.00–5.23. The predictably complex patterns due to the two methyl groups are seen to overlap in the 0.58–1.20 region. The remaining portion of the spectrum consists of a multiplet of area 7 at 1.48–2.46 assignable to the combination of two methylene groups and three cyclopropyl protons. In addition to conforming closely in detail to the chemical shift and multiplicity features anticipated for a norcarene substituted as in **22**,[25] the presence of only one olefinic proton unequivocally serves to remove alternative assignment **25** from further consideration. This structure has previously been advanced by Masamune and coworkers as the minor product (20%) in this rearrangement reaction.[26] Further elaboration of our assignment was derived from the preparation of **25** upon exposure of **21**

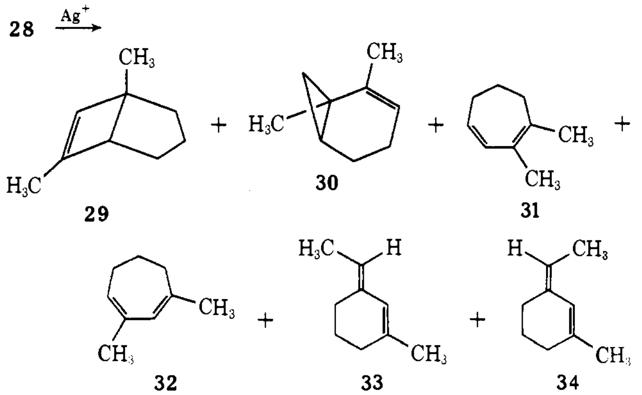


to the action of anhydrous magnesium bromide in ether.

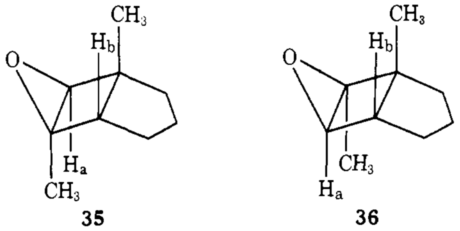
Two routes were utilized in the synthesis of 1,2-dimethyltricyclo[4.1.0.0^{2,7}]heptane (**28**). The first involved treating **12** with *n*-butyllithium–tetramethylethylenediamine in pentane followed by methyl iodide, and the second, preferred chiefly because of its adaptability to larger scale preparations, consisted of the methyllithium-promoted cyclization of dibromide **27**. The Ag(I)-catalyzed rearrangement of **28** provided a



rich assortment of isomeric hydrocarbons. These were isolated and identified on the basis of spectral evidence and chemical correlation.



The major product (52%) was identified as 1,6-dimethylbicyclo[3.2.0]hept-6-ene (**29**) by conversion into epoxide **35** with *m*-chloroperbenzoic acid. In the nmr spectrum of this substance, H_a appears as a singlet at δ 3.42 denoting the lack of coupling between H_a and H_b. This observation served to differentiate **35** from



epoxide **36** where coupling between H_a and H_b would result in splitting of the H_a absorption into a doublet.[10] Indeed, when a mixture of **31** and **32** (which could not be separated or well distinguished by nmr and ir methods) was photolyzed and subsequently epoxidized, a mixture of epoxides resulted as determined by nmr analysis. The J_{AB} coupling constant in **36** was noted to be 2.9 Hz. On the basis of careful integration of the H_a region, the ratio of **36**:**35** in this mixture was calculated to be 85:15. Accordingly, the amounts of **31** and **32** produced during rearrangement of **28** were estimated to be 10 and 2%, respectively.

Authentic diene **31** was conveniently produced by acid-catalyzed dehydration of alcohol **38**. The conversion to **31** is apparently the result of a cyclopropyl-

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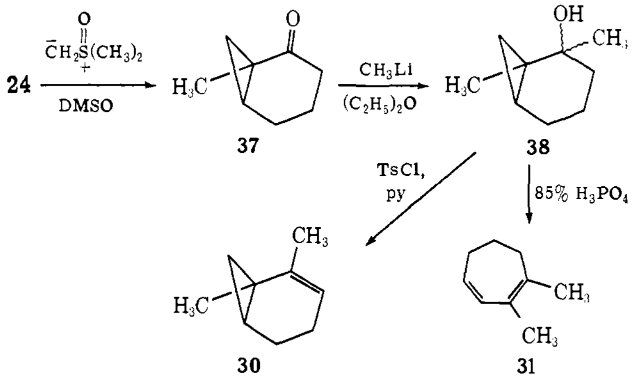
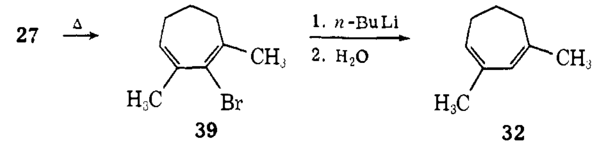
[25] For a detailed discussion of the preparation and nmr analysis of substituted norcarenes, consult L. A. Paquette and S. E. Wilson, *J. Org. Chem.*, in press.

[26] M. Sakai, H. H. Westberg, H. Yamaguchi, and S. Masamune, *J. Amer. Chem. Soc.*, 93, 4611 (1971).

carbinyl to homoallylic cation rearrangement and ultimate deprotonation. Isomeric dimethylcycloheptadiene (**32**) was also readily available by thermal dehydrobromination of dibromocyclopropane (**27**) and reduction of the resulting vinyl bromide (**39**) by sequential metalation with *n*-butyllithium and hydrolysis. Worthy of mention is the fact that cycloheptadienes **31** and **32** exhibit nearly identical nmr and ir spectra which makes differentiation on that basis virtually impossible. Conversion to epoxides **35** and **36** does serve, however, as a convenient means of unequivocal identification.





Substituted norcarene **30**, isolated in 8% yield, was prepared unequivocally by dehydration of **38** with *p*-toluenesulfonyl chloride in pyridine solution at 90°.

The 3-methylethylidenecyclohexenes **33** (14%) and **34** (14%) were not separated but the relative amounts of the isomers in the mixture could satisfactorily be determined by integration of H_2 in **33** (δ 5.85) and **34** (δ 6.12).[27]

Kinetic Details. To more fully understand the mechanistic details involved in the Ag^+-catalyzed rearrangements of the tricycloheptanes, the kinetic behavior of a number of representative examples was studied. In the particular case of parent hydrocarbon **1a**, its rate of disappearance in a standardized anhydrous benzene solution of silver perchlorate was observed to be linear when log $[\mathbf{1a}]_0/[\mathbf{1a}]_t$ was plotted against time. A twofold increase in the $AgClO_4$ concentration resulted in doubling the slope of such a plot; furthermore, essentially the same value for k_{cat} was obtained from eq 1 irrespective of the concentration of

$$k_{cat} = \frac{2.303 \log [\mathbf{1a}]_0/[\mathbf{1a}]_t}{[AgClO_4]_t} \quad (1)$$

$AgClO_4$ (Table II). To substantiate the kinetic order in tricycloheptane, the half-life method was employed and it was observed that the half-life of **1a** is independent of initial concentration. Thus, the catalyzed rearrangement is a second-order process dependent upon the concentrations of both tricycloheptane and Ag^+ ion.

Table II. Isomerization Rate Data for **1a** in Anhydrous Benzene Solution[a]

Run no.	$[AgClO_4]$, N	T, °C	k_{Ag}, M^{-1} sec^{-1}
1	7.86×10^{-2}	30.00	9.9×10^{-4}
2	7.86×10^{-2}	30.00	9.7×10^{-4}
3	8.45×10^{-2}	40.00	2.28×10^{-3}
4	8.45×10^{-2}	40.00	2.22×10^{-3}
5	8.45×10^{-2}	40.00	2.30×10^{-3}
6	8.45×10^{-2}	40.00	2.26×10^{-3}
7	3.93×10^{-2}	50.00	7.0×10^{-3}
8	3.93×10^{-2}	50.00	7.0×10^{-3}
9	3.93×10^{-2}	50.00	6.4×10^{-3}
10	7.86×10^{-2}	50.00	6.7×10^{-3}
11	7.86×10^{-2}	50.00	6.7×10^{-3}

[a] These rate data pertain to the initial rate of disappearance of **1a**.

Table III. Solvent Effects on the $AgClO_4$-Catalyzed Rearrangement of **1a** (40.0°)

Solvent	Dielectric constant	k_{Ag}, M^{-1} sec^{-1}	Stability constant[a]
C_6H_6	2.3	2.3×10^{-3}	$K_1 = 0.38$; $K_2 = 0.67$
CH_3COCH_3	21.2	2.3×10^{-3}	$K_1 = -0.85$
CH_3CN	37.5	Very slow	$\beta_2 = 1.23$
CH_3NO_2	37.5	1.9×10^{-1}	$(K_1 \approx -3)$[b]

[a] Values taken from A. E. Martell, *Chem. Soc., Spec. Publ.*, No. 17 (1964). [b] Approximated on the basis of the value for nitrobenzene.

The rates of rearrangement of **1a** in a variety of solvents are shown in Table III. The wide variations in rate are seen not to correspond to changes in the dielectric constant of the media, but rather with the intrinsic capability of a given solvent to complex with Ag^+. Accordingly, solvent effects in such reactions are not useful probes of mechanism; rather, they serve to dramatize the importance of "available Ag^+" to the success of the bond reorganizations. However, it was clear that a standardized set of conditions had to be adopted for consistency; accordingly, anhydrous solutions of silver perchlorate in benzene were employed in all subsequent work.

In view of the fact that **1a** (and all other bicyclobutanes examined[20,28]) rearranges in strict accordance to the second-order catalytic rate law given in eq 2, one

$$-\frac{d[\text{bicyclobutane}]}{dt} = k_{Ag}[\text{bicyclobutane}][AgClO_4] \quad (2)$$

of the following general schemes must serve to describe the rearrangement process (eq 3, 4, or 5). Adherence to eq 4 would require that complex formation be rate determining. However, this theory did not seem tenable since exchange phenomena involving Ag^+-benzene[29] and phosphinosilver complexes[30] are known to be very rapid, and complexation of the transition metal in these particular examples is certain to be more favorable than expected from interaction with a bicyclobutane ring.[31] On the other hand, the *direct*

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[27] The nmr spectra of **33** and **34** were kindly made available to us by Professor Bartlett (see ref 23).

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

[29] Nmr line broadening techniques disclose that solutions as high as 0.4 M $AgClO_4$ in benzene (20–60°) undergo ligand exchange $[(C_6H_6)_x\text{-}Ag^+ + C_6H_6{}^0 \rightleftharpoons (C_6H_6)_{x-1}C_6H_6{}^0Ag^+ + C_6H_6]$ at a rate greater than 10^5 sec^{-1}. We thank Professor G. Gordon for these data in advance of publication and for helpful discussions relating to the kinetic profile.

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

[31] 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 hydrocarbon *without* the scission of any bonds. The demonstrated facile *reversible* formation of such complexes cannot be reconciled with a cleavage recombination phenomenon.

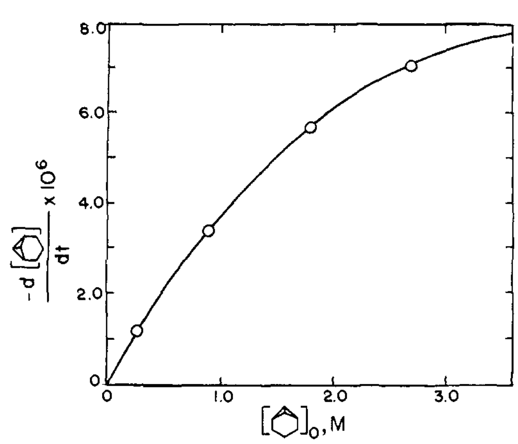
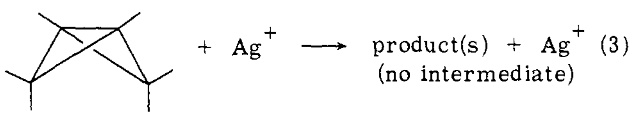
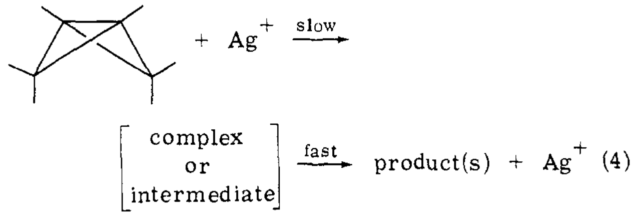
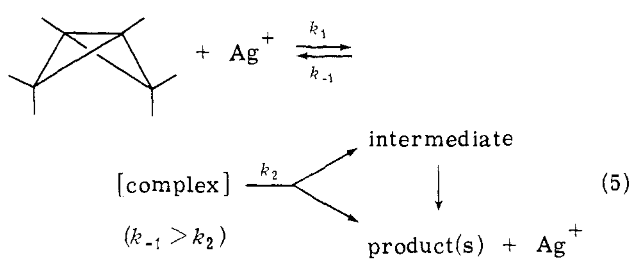


Figure 1. Initial rates of conversion of tricyclo[4.1.0.0^{2,7}]heptane (1a) to 1,3-cycloheptadiene (2a) as a function of the concentration of 1a. All runs were performed at 40° in 2.02 × 10^{-3} *M* silver perchlorate solutions consisting of 70% benzene and 30% cyclohexane–1a (v/v).







formation of a covalently bonded organosilver intermediate[32] could indeed be slow. To differentiate pathway 4 and/or its concerted alternative (eq 3) from mechanism 5, it becomes necessary only to measure the rates of isomerization as a function of hydrocarbon concentration. As Laidler[33] has succintly pointed out, adherence to eq 5 would give a rate law which can be expressed as in eq 6 which corresponds to a nonlinear

$$-\frac{d[\text{tricycloheptane}]}{dt} = \frac{k_2K[\text{tricycloheptane}][\text{AgClO}_4]}{K[\text{tricycloheptane}] + 1} \qquad (6)$$

variation in rate typified by Figure 1. This is due to a linear dependence of [tricycloheptane] on rate at low substrate concentrations which gradually transmutes into a zero-order dependence at higher concentration levels. Adherence to eq 3 and 4 would, in contrast, provide a linear plot throughout the entire concentration range.

From eq 6 it is possible to calculate the equilibrium constant for tricycloheptane–silver(I) complex formation. For **1a**, the experimentally derived value of K is 0.29 ± 0.05,[34] whereas for the 1-methyl derivative **5** the preequilibrium constant is 1.0 ± 0.1. These data suggest convincingly that silver(I) complexes are intermediates in such catalyzed rearrangements,[35] *i.e.*, mechanism 5 must apply. Additionally, the extent of complex formation is indeed substantial for it must operate in competition with the Ag$^+$–benzene equilibrium.

The activation parameters associated with the isomerization of **1a**, $\Delta H^{\ddagger} = 18.5$ kcal/mol, $\Delta S^{\ddagger} = -11.5$ eu, and $\Delta F^{\ddagger} = 22.1$ kcal/mol, are in complete accordance with the establishment of a preequilibrium and rate-determining rearrangement of such a complex.[36] It now remains to elucidate the intimate details by which the multifarious (when applicable) bond reorganizations to the various product types take place.[20]

Structural Considerations The ratios of rearrangement products (where relevant) were determined quantitatively by gas chromatographic or nmr methods (see Experimental Section). The yields of products were consistently high (>95% in nonpreparative runs).

Meaningfully, tricycloheptanes **1a**, **12**, and **17** give rise exclusively and quantitatively to 1,3-cycloheptadienes when exposed to Ag$^+$. It is mechanistically significant that positioning of one or more methyl substituents at the "wing" positions (C_2 and C_6) of the tricycloheptane nucleus does not result in alteration of the rearrangement mode adopted by the parent hydrocarbon. However, such alkyl substitution does influence in an intriguing way the kinetically favored conversion to 1,3-cycloheptadienes. Thus, the 2-methyl derivative **12** rearranges ten times faster than **1a** and 2,6-dimethyl congener **17** experiences a 2450-fold enhancement in the structural reorganization rate (Table IV). Although comment on these kinetic features is to be reserved for the ensuing paper,[20a] we point out at this time that the large rate difference observed between **1a** and **12** on the one hand and **17** probably reflects a mechanistic crossover in the latter system.

Placement of at least one methyl group at a bridgehead site (*cf.* **5**, **20**, and **28**), in contrast, presents to the strained hydrocarbon the opportunity for more diversified rearrangement. Since both **5** and **28** do give rise to lesser amounts of 1,3-cycloheptadienes, it becomes possible to normalize their respective isomerization rates for inclusion in Table IV. When translated into terms of 1,3-cycloheptadiene production, it is seen that the logistics of alkyl substitution at C_1 and C_2 does not engender significant rate acceleration in this direction. Rather, the effect must be to enhance appreciably those bond reorganizations which are entirely nonoperative in **1a**, **12**, and **17**.

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[32] For a recent review of organosilver chemistry, see 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).

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

[34] This value was originally reported erroneously as 0.19 ± 0.05.[28]

[35] Although the possibility exists that the equilibria measured in this fashion relate to "dead end complex" formation, such an eventuality is considered to be unlikely in view of the customary high reactivity of bicyclobutane derivatives toward electrophilic reagents in general.

[36] At the present time, knowledge relating to the precise position of Ag$^+$ in such complexes and to the possible multiplicity of such sites is entirely lacking.

Table IV. Comparative Rates of Rearrangement of Tricycloheptanes to 1,3-Cycloheptadienes

Starting hydrocarbon	1,3-Cycloheptadiene	[AgClO$_4$], M	Method of analysis	k_{cat}, M^{-1} sec^{-1}	k_{rel}[b]
1a	**2a**	8.45×10^{-2}	Vpc	2.27×10^{-3}	1
5	7	8.06×10^{-2}	Vpc	1.5×10^{-3}[a]	0.67
12	**14**	1.61×10^{-2}	Nmr	2.26×10^{-2}	10
17	**19**	1.85×10^{-4}	Nmr	5.56×0.09	2450

[a] Adjusted rate constant. [b] These relative rates have not been corrected for statistical factors.

Summary and Conclusions

The above results reveal that the silver(I)-catalyzed rearrangements of tricycloheptanes deviate significantly from the pathway which operates on thermolysis.[7a,b] The distribution between various product types is particularly sensitive to alkyl substituents at the bridgehead centers; in such cases, the "normal" C-1,2 and C-3,4 bond cleavage exhibited by the parent system (**1a**) is displaced by preferential C-1,2 and C-1,3 bond breakage (leading to alkylidenecyclohexenes) and more deep-seated rearrangements (affording bicyclo[3.2.0] heptenes). The initial interaction with Ag$^+$ appears to be complex formation. Available experimental evidence suggests that the crucial step which dictates product composition follows upon, or is concomitant with, carbon–silver bond formation with subsequent isomerization in the various systems being strongly dependent upon relative carbonium ion stabilities. In most but not all situations,[20] the rupture of an edge bond seems rate determining. However, the striking kinetic behavior of **17** requires particular attention. Studies reported in the subsequent two papers[20] provide information which sheds light on the causative factors which underlie such contrasting behavior.

Experimental Section

Preparative Scale Rearrangement of 1a. A mixture of 2.93 g (31.2 mmol) of tricyclo[4.1.0.0^{2,7}]heptane (**1a**)[24a] and approximately 15 mg of silver fluoroborate in 15 ml of chloroform was stirred at room temperature with protection from light for 3 hr. The resulting mixture was passed through a column of neutral alumina (elution with pentane) to remove the inorganic material. The pentane and chloroform were removed by distillation at atmospheric pressure. Distillation of the residual liquid under partial vacuum afforded 2.47 g (85%) of 1,3-cycloheptadiene (**2a**): bp 53–55° (72–75 mm) [lit.[37] bp 55° (75 mm)]; $\delta_{\text{TMS}}^{\text{CDCl}_3}$ 5.80 (s, 4, olefinic), 2.17–2.58 (m, 4, allylic), and 1.58–2.08 (m, 2, methylene). This spectrum was identical with that of an authentic sample.

Preparative Scale Rearrangement of 1b. A. Direct Conversion to Bicyclo[3.2.0]hept-6-ene-*6,7-d*$_2$ (3). A solution of 152 mg of **1b**[9] in 0.5 ml of chloroform was treated with *ca.* 10 mg of silver tetrafluoroborate as before. After concentration of the eluted solution, 4 ml of ether was added and transfer to a quartz test tube was made. This solution was irradiated for 3 hr and 15 min with a 450-W Hanovia lamp housed in the customary quartz immersion well when the reaction was complete (vpc analysis). After careful evaporation of the major portion of the solvent, the remaining solution was subjected to preparative scale vpc purification to give 13.6 mg of **3**: $\delta_{\text{TMS}}^{\text{CDCl}_3}$ 3.18 (d, $|J|$ = 6.5 Hz, 2, allylic) and *ca.* 1.5 (m, 6, methylene). Less than 3% vinyl proton absorption was noted.

B. **Direct Conversion to Epoxide 4.** Processing of 199 mg of **1b** as in part A gave a solution of **3** to which was added dropwise a solution of 410 mg of *m*-chloroperbenzoic acid (89.5% assay) in 5 ml of chloroform. This solution was refluxed for 2 hr, cooled, washed in sequence with 20% sodium bisulfite, saturated sodium carbonate, and saturated sodium chloride solutions, dried, and concentrated with the aid of a small Vigreux column. Preparative scale vpc purification of the residue at 75° (5% SF-96 on Chromosorb G) furnished 58 mg of **4**: $\delta_{\text{TMS}}^{\text{CDCl}_3}$ 2.58 (m, 2, cyclobutylmethine) and 1.70 (m, 6, methylene).

Pyrolysis of 1b. A weighed amount of **1b** was vaporized in a nitrogen flow system at 12–16 mm. The gases were introduced into a quartz tube packed with quartz chips at the temperatures given in Table I. The effluent was condensed in a U tube chilled to −80° and analyzed by vpc (10% SF-96 on Chromosorb G) at 100°. The isolation of the bicycloheptene from preparative scale purifications showed it to be labeled exclusively as **3**.

1-Methyltricyclo[4.1.0.0^{2,7}]heptane (5). The contents of a 100-ml flask containing 55 ml of 1.45 *M* (0.080 mol) *n*-butyllithium in pentane, 10 g (0.086 mol) of *N,N,N',N'*-tetramethylethylenediamine (TMEDA), and 7.0 g (0.074 mol) of **1** were stirred for 10 hr under a nitrogen atmosphere. A white solid formed during this period. With the flask immersed in an ice bath, 5 ml (0.080 mol) of methyl iodide was added during 30 min. After being stirred for an additional 30 min, the reaction mixture was quenched with 25 ml of water and the separated organic layer was washed with 25 ml of saturated cupric sulfate solution to remove the residual TMEDA. The pentane solution was dried and the solvent was removed by distillation through a 10-cm Vigreux column. Distillation of the remaining liquid from sodium carbonate afforded 4.10 g (51%) of **5**, bp 62–66° (100 mm) [lit.[21] bp 66° (100 mm)]. For kinetic and product analysis work, pure **5** was obtained by preparative vpc using first a $^1/_4$ in. × 10 ft 10% SF-96 column at 125° and then a $^1/_4$ in. × 9 ft OV-17 column at 90°.

Preparative Scale Rearrangement of 5. To 15 ml of 0.136 *M* silver perchlorate in dry benzene was added 1.0 g (9.3 mmol) of **5**. A small quantity of a dark precipitate formed immediately. The mixture was heated to 50° for 2 hr and then quenched in 20 ml of saturated sodium chloride solution. The aqueous layer was extracted with 15 ml of pentane and the combined organic layer was dried and carefully distilled through a short Vigreux column at 100 mm to remove solvent. Initial preparative vpc separation on a $^1/_4$ in. × 9 ft 5% OV-17 column at 100° showed three components. The use of an internal standard (cycloheptatriene) in certain runs demonstrated the quantitative nature of this reaction. The first substance to elute was identified as **6** (44.3%): $\delta_{\text{TMS}}^{\text{CDCl}_3}$ 5.64 (m, 1, olefinic), 2.88–3.17 (m, 2, allylic), 0.87–1.84 (m, 6, methylenes), and 1.60 (s, 3, methyl).

Anal. Calcd for C_8H_{12}: C, 88.81; H, 11.19. Found: C, 88.94; H, 11.13.

The second component was assigned structure **7** (26.4%): $\delta_{\text{TMS}}^{\text{CDCl}_3}$ 5.72 (m, 3, olefinic), 1.6–2.5 (m, 6, methylene), and 1.78 (m, 3, methyl).

Anal. Calcd for C_8H_{12}: C, 88.81; H, 11.19. Found: C, 88.68; H, 11.27.

The last component (29.3%) was a mixture of isomers **8** and **9**. These were separated on a $^1/_4$ in. × 20 ft 5% QF-1 column at 100°. The syn isomer **8** eluted first: $\delta_{\text{TMS}}^{\text{CDCl}_3}$ 6.46 (m, 1), 5.59–6.04 (m, 1), 5.20 (m, 1), and 1.52–2.48 (m, 9, with maximum at 1.76).

The corresponding anti isomer **9** was subsequently obtained: $\delta_{\text{TMS}}^{\text{CDCl}_3}$ 6.05 (m, 1), 5.52–5.82 (m, 1), 5.29 (m, 1), and 1.52–2.51 (m, 9, with maximum at 1.71).

Photoisomerization of 7. A solution of 60 mg of **7** in 2 ml of ether contained in a quartz tube was irradiated with a 450-W Hanovia lamp housed in a water-cooled quartz well for 1.5 hr. The sole product (35 mg), collected by preparative vpc on the OV-17 column at 100°, was identical with **6** in all respects.

7,7-Dibromo-2-methylbicyclo[4.1.0]heptane (11). Bromoform (55.7 g, 0.22 mol) was added dropwise during 1 hr to a mechanically stirred suspension of 24.7 g (0.22 mol) of powdered potassium *tert*-butoxide and 19.2 g (0.20 mol) of 3-methylcyclohexene in 100 ml of pentane maintained at −15 to −30°. The mixture was allowed to warm gradually to room temperature with stirring over a 2-hr period, at which time water was added and the layers were separated. The aqueous phase was extracted twice with pentane and the combined organic layers were dried and concentrated. Distillation

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(37) A. C. Cope, T. A. Liss, and G. W. Wood, *J. Amer. Chem. Soc.*, 79, 6287 (1957).

gave 42.2 g (79%) of **11** as an inseparable mixture of isomers, bp 66–69° (0.5 mm). An analytical sample was obtained by preparative vpc purification on a $^1/_4$ in. × 5 ft 3% SE-30 column operated at 150°: $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 0.7–2.3 (m with sharp spike at 1.25).

Anal. Calcd for $C_8H_{12}Br_2$: C, 35.85; H, 4.51. Found: C, 35.94; H, 4.55.

Reaction of 11 with Methyllithium. Under a nitrogen atmosphere, 50 ml (55 mmol) of 1.1 *M* methyllithium in diethyl ether was added during 15 min to a solution of 10 g (39 mmol) of **11** in 100 ml of anhydrous ether maintained at −10°. Upon completion of the addition, the solution was stirred at room temperature for 1 hr and then carefully quenched with water (50 ml). The ether phase was washed with saturated aqueous sodium chloride solution, dried, and carefully evaporated through a short Vigreux column over a small amount of potassium carbonate. The remaining material was removed of high boiling impurities by vacuum transfer at 80° (15 mm) into a cold (−70°) trap. The two tricycloheptanes were separated by preparative scale vpc on a $^1/_4$ in. × 10 ft 5% OV-11 column at 85°. The first to elute was **12** (980 mg): $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 2.19–2.46 (m, 1), 1.18–1.49 with maximum at 1.29 (m, 8) and 1.04 (s, 3).

Anal. Calcd for C_8H_{12}: C, 88.81; H, 11.19. Found: C, 88.52; H, 11.06.

The second component (127 mg) gave an nmr spectrum consistent with **13**: $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 2.11–2.57 (m, 2), 1.11–1.72 (m, 7), and 0.87 (d, $|J| = 5.0$ Hz, 3).

Anal. Calcd for C_8H_{12}: C, 88.81; H, 11.19. Found: C, 88.73; H, 11.27.

Rearrangement of 12. Approximately 3 ml of 0.206 *M* silver perchlorate in dry benzene was allowed to equilibrate at 40° for 10 min at which point 500 mg of **12** was introduced by means of a syringe. After 2 hr, the reaction was quenched by the addition of 3 ml of saturated aqueous sodium chloride solution. Processing of the organic phase as above, followed by preparative vpc on the OV-11 column at 85°, resulted in the isolation of **14** (305 mg) as the only product: $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 5.49–5.87 (m, 3, olefinic), 2.13–2.53 (m, 4, allylic), 1.62–2.09 (m, 2, methylene), and 1.82 (s, 3, methyl).

Anal. Calcd for C_8H_{12}: C, 88.81; H, 11.19. Found: C, 88.68; H, 11.27.

7,7-Dibromo-1,5-dimethylbicyclo[4.1.0]heptane (16). Treatment of 20 g (0.18 mmol) of 1,3-dimethylcyclohexene (**15**) with 28 mg (0.25 mol) of potassium *tert*-butoxide and 65.7 g (0.25 mol) of bromoform as previously described afforded 43.2 g (84%) of **16**: bp 79–81° (0.5 mm); $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 1.00–2.04 (m with maximum at 1.40).

Anal. Calcd for $C_9H_{14}Br_2$: C, 38.33; H, 5.00. Found: C, 38.27; H, 4.97.

Reaction of 16 with Methyllithium. Treatment of a solution of 10 g (35.5 mmol) of **16** in 100 ml of dry ether with 40 ml (44 mm) of 1.1 *N* methyllithium as before furnished 2.80 g (64.6%) of a mixture of **17** and **18**. These components were not readily separable by vpc and were therefore analyzed as the mixture. The nmr spectrum of **17** (in $CDCl_3$) consisted of a multiplet (8 H) at δ 1.11–1.57 and a singlet (6 H) at 1.01. The spectrum of **18** displayed a multiplet (2 H) at δ 1.96–2.38, a singlet (3 H) at 1.57, a doublet ($|J| = 5.5$ Hz, 3) at 0.88, and a multiplet (6 H) at 0.69–1.65.

Anal. Calcd for C_9H_{14}: C, 88.45; H, 11.55. Found: C, 88.57; H, 11.40.

Rearrangement of 17. To 3 ml of 8.45×10^{-3} *M* silver perchlorate in anhydrous benzene was added 1.0 g of a mixture of **17** and **18**. The solution was cooled momentarily in an ice bath to counteract the exothermic reaction which occurred. After 1 min of reaction, 2 ml of saturated sodium chloride solution was added and the organic layer was separated and dried. Two substances were detected and collected using a $^1/_4$ in. × 10 ft 10% SF-96 column at 110°. The first compound (100 mg) was identified as unrearranged **18** by means of its spectra.

Anal. Calcd for C_9H_{14}: C, 88.45; H, 11.55. Found: C, 88.57; H, 11.40.

The second hydrocarbon (326 mg) was found to be 1,4-dimethyl-1,3-cycloheptadiene (**19**): $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 5.48 (s, 2), 2.10–2.43 (m, 4), 1.76 (s, 6), and 1.61–2.03 (m, 2).

Anal. Calcd for C_9H_{14}: C, 88.45; H, 11.55. Found: C, 88.08; H, 11.71.

1,5-Dimethylbicyclo[3.2.0]hept-6-ene (20). Irradiation of a solution containing 142 mg of **19** in 4 ml of ether for 1.5 hr as previously described afforded 81 mg of **20** after preparative scale vpc purification: $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 5.81 (s, 2), 0.84–1.71 (m, 6), and 1.04 (s, 6).

Anal. Calcd for C_9H_{14}: C, 88.45; H, 11.55. Found: C, 88.46; H, 11.76.

1,7-Dimethyltricyclo[4.1.0.0^{2,7}]heptane (21). Under a nitrogen atmosphere, 1.0 g (9.3 mmol) of **5**, 10 ml of 1.16 *M* (11.6 mmol) *n*-butyllithium in pentane, and 1.5 g (12.9 mmol) of TMEDA were allowed to react for 6 hr. In a dropwise manner, 2.0 g (14.1 mmol) of methyl iodide was added during 5 min while cooling in ice. Water (10 ml) and pentane (20 ml) were then cautiously added in that order. The organic layer was dried and the solvent was removed by distillation. Vacuum transfer as before at 100° allowed the collection of volatile components. Preparative scale vpc ($^1/_4$ in. × 10 ft 5% OV-17 column at 100°) afforded 423 mg of **21**: $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 1.86 (m, 2), 1.28 (s, 6), and 1.25 (m, 6).

Rearrangement of 21. To 5.0 ml of 8.45×10^{-3} *M* silver perchlorate in dry benzene was added 500 mg of **21** and the solution was heated to 50° for 6 hr. The usual work-up was followed by preparative scale vpc separation on the OV-17 column at 110°. The first component (42 mg) showed an nmr spectrum consistent with *exo*-2,7-dimethylbicyclo[4.1.0]hept-2-ene (**23**): $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 5.00–5.23 (m, 1), 1.48–2.46 (m, 7), and 0.58–1.20 (m, 6).

Anal. Calcd for C_9H_{14}: C, 88.45; H, 11.55. Found: C, 88.43; H, 11.59.

The second substance to elute (210 mg) was identical in all respects with **22** which was independently synthesized in the following manner.

***anti*-3-Ethylidene-2-methylcyclohexene (22).** Under a nitrogen atmosphere, 15 ml of 1.45 *M* *n*-butyllithium in hexane was added during 1 min to 8.3 g (20 mmol) of ethyltriphenylphosphonium iodide in 50 ml of dry tetrahydrofuran. To the resulting red solution was added 2.2 g (20 mmol) of 2-methylcyclohexenone (**24**) during 2 min. A precipitate formed immediately. After the mixture was heated at reflux for 6 hr, it was cooled, poured into 100 ml of pentane, filtered, and washed twice with water (50 ml). The dried organic layer was carefully evaporated and the product **22** was isolated by preparative vpc using a $^1/_4$ in. × 10 ft 10% SF-96 column at 125°. There was obtained 100 mg of **22**: $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 5.02–5.75 (m, 2), 1.50–2.52 (m, 12, with maximum at 1.77).

Anal. Calcd for C_9H_{14}: C, 88.45; H, 11.55. Found: C, 88.39; H, 11.64.

7,7-Dibromo-1,6-dimethylbicyclo[4.1.0]heptane (27) and 2-Bromo-1,3-dimethyl-1,3-cycloheptadiene (39). To a flask containing 23 g (0.21 mol) of 1,2-dimethylcyclohexene, 33.6 g (0.30 mol) of potassium *tert*-butoxide, and 200 ml of pentane maintained at −25° was added dropwise 76.0 g (0.30 mol) of bromoform. The mixture was stirred for 1 hr at room temperature. Approximately 150 ml of water was added and the organic phase was separated, washed with saturated aqueous sodium chloride solution, and dried. The solvent was evaporated and the residue was subjected to simple vacuum distillation whereupon 41.8 g of a distillate was obtained, bp 65–95° (0.5–4.0 mm). This distillate was dissolved in 200 ml of pentane and the resultant solution was cooled to −78° for 30 min. While still cold, the pentane solution was decanted leaving white crystals which were recrystallized from 80 ml of pentane. The crystals melted upon approaching room temperature. Excess solvent was removed *in vacuo* to give 16 g (27%) of a clear oil assigned structure **27**: $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 1.17–2.09 (m, 8) and 1.25 (s, 6).

The supernatant pentane solution was evaporated and the resultant oil was distilled to give two fractions: bp 68–72° (3.4 mm), 14.0 g, and bp 72–82° (3.4 mm), 5.3 g (total 46%). An analytical sample of **39** was obtained by vpc methods: $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 5.76–6.10 (m, 1), 1.79–2.16 (m, 6), and 2.03 (s, 6).

Anal. Calcd for $C_9H_{13}Br$: C, 53.75; H, 6.52. Found: C, 53.83; H, 6.60.

1,2-Dimethyltricyclo[4.1.0.0^{2,7}]heptane (28). Method A. Methyllithium (40 ml of 1.1 *M* solution, 44 mmol) in diethyl ether was added during 45 min to 5.0 g (18 mmol) of **27** in 100 ml of anhydrous ether maintained at −20°. The flask contents were stirred for 15 min at room temperature and treated cautiously with water (~100 ml). The organic layer was washed with saturated aqueous sodium chloride solution, dried, and carefully evaporated through a short Vigreux column. The remaining liquid was vacuum transferred at 80° (20 mm) into a cold (−78°) trap. Subsequent vpc purification ($^1/_4$ in. × 10 ft 5% OV-17 column at 80°) resulted in isolation of 580 mg (27%) of **28**: $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 2.02–2.22 (m, 1), 1.49 (s, 3), 1.13–1.36 (m, 6), 1.02 (s, 3), and 0.89–1.09 (m, 1).

Anal. Calcd for C_9H_{14}: C, 88.45; H, 11.55. Found: C, 88.44; H, 11.54

Method B. Under a nitrogen atmosphere 721 mg (6.67 mmol) of **12** was pipetted rapidly into a solution consisting of 10 ml of 1.3 *M* *n*-butyllithium in pentane and 2.0 ml of tetramethylethylenediamine. Reaction was permitted to proceed at room temperature for 5 hr. In a dropwise manner, 1.0 ml of methyl iodide in 3 ml of pentane was added during 15 min. Addition of 20 ml of water and 20 ml of pentane was followed by washing the pentane layer with saturated aqueous cupric sulfate solution and drying. After careful distillation of the pentane, the residue was vacuum transferred at 90° (10 mm) into a cold (−78°) trap. Preparative vpc purification ($^1/_4$ in. × 10 ft 5% OV-11 column at 40°) led to the isolation of 320 mg (39%) of **28**.

Rearrangement of 28. Approximately 2 ml of 0.202 *M* silver perchlorate in benzene was equilibrated thermally at 40°. Into this solution was syringed 421 mg (3.45 mmol) of **28** resulting in immediate deposition of a small quantity of dark precipitate. After 45 min, 2 ml of saturated aqueous sodium chloride solution was added and the organic phase was dried. Product separation was then achieved gas chromatographically on the OV-11 column at 80°. The first product to elute (95.6 mg) was found to be 1,6-dimethylbicyclo[3.2.0]hept-6-ene (**29**): $\delta_{\text{TMS}}^{\text{CDCl}_3}$ 5.41–5.55 (m, 1), 2.36–2.65 (m, 1), 1.16–1.92 (m, 6), 1.51 (t, J = 1.5 Hz, 3), and 1.18 (s, 3).

Anal. Calcd for C_9H_{14}: C, 88.45; H, 11.55. Found: C, 88.38; H, 11.67.

The second component (11.3 mg) proved to be 1,2-dimethylbicyclo[4.1.0]hept-2-ene (**30**): $\delta_{\text{TMS}}^{\text{CDCl}_3}$ 5.05–5.30 (m, 1), 1.58–1.92 (m, 7), 1.13 (s, 3), 0.81–1.22 (m, 1), and 0.32–0.71 (m, 2).

Anal. Calcd for C_9H_{14}: C, 88.45; H, 11.55. Found: C, 88.35; H, 11.49.

The third fraction (23.8 mg) was shown to be a mixture of 1,2- (**31**) and 1,3-dimethyl-1,3-cycloheptadienes (**32**). The final fraction (52.3 mg) consisted of a mixture of **33** and **34**: $\delta_{\text{TMS}}^{\text{CDCl}_3}$ 6.12–6.29 (m, 0.5), 5.72–5.95 (m, 0.5), 4.99–5.46 (m, 1), and 1.50–2.44 (m, 12, with maximum at 1.73).

Photoisomerization and Epoxidation of the Mixture of 31 and 32. An ethereal solution of the **31**–**32** mixture (25 mg) was irradiated through quartz with a 450-W Hanovia mercury lamp for 3 hr. The ether was evaporated and *ca.* 5 ml of chloroform was added along with 160 mg (0.92 mmol) of *m*-chloroperbenzoic acid (89%). After being heated to 60° for 1.5 hr, the solution was washed twice with 20% aqueous sodium sulfite solution and then with aqueous sodium bicarbonate and sodium chloride solutions. After drying, the solution was carefully evaporated and the epoxide mixture (15 mg) was isolated by preparative vpc on the OV-17 column at 100°. The nmr spectrum indicated an 85:15 mixture of **36** and **35**: $\delta_{\text{TMS}}^{\text{CDCl}_3}$ 3.42 (s, 0.15), 3.38 (d, J = 2.9 Hz, 0.85), 1.40–2.18 (m, 7), 1.35 (s, 2.55), 1.31 (s, 0.45), 1.08 (s, 2.55), and 1.04 (s, 0.45).

1-Methylbicyclo[4.1.0]hexan-2-one (37). The procedure outlined by Fieser and Fieser[38] was followed using 9.0 g of 2-methylcyclohexenone, 22 g of trimethyloxosulfonium iodide, and 5 g of sodium hydride in mineral oil (57%). Vacuum distillation of the product resulted in the isolation of 6.6 g (65%) of **37**: bp 57–59° (3.4 mm); $\delta_{\text{TMS}}^{\text{CDCl}_3}$ 0.70–2.38 (m, 9) and 1.20 (s, 3).

Anal. Calcd for $C_8H_{12}O$: C, 77.38; H, 9.74. Found: C, 76.74; H, 9.84.

Addition of Methyllithium to 37. Dropwise addition of 1.5 g (12 mmol) of **37** dissolved in 3 ml of anhydrous ether to 12.5 ml of 1.2 *M* methyllithium (15 mm) maintained at −70° was achieved during 10 min. After being stirred at room temperature for 15 min, the solution was treated with 10 ml of water. The organic layer was washed with saturated aqueous sodium chloride solution, dried, and evaporated. The resulting colorless oil (**38**) was not further purified.

1,2-Dimethyl-1,3-cycloheptadiene (31). The oil obtained above was added dropwise over a 10-min period to 10 ml of 85% phosphoric acid previously heated to 60°. The entire system was kept under 3.5 mm pressure, conditions under which all volatile material was collected in a cold (−78°) trap during 15 min. Ether was added to the trap and this solution was washed with saturated aqueous sodium bicarbonate and dried. Preparative vpc on the OV-17 column at 95° resulted in isolation of 25 mg (2%) of **31**.

Anal. Calcd for C_9H_{14}: C, 88.45; H, 11.55. Found: C, 88.24; H, 11.68.

1,3-Dimethyl-1,3-cycloheptadiene (32). To a solution of 5.0 g (25 mmol) of **39** in 100 ml of ether at 0° was added 25 ml of 1.3 *M* (33 mmol) *n*-butyllithium in pentane over a 5-min period. The solution was stirred at 0° under nitrogen for 3 hr and then at ambient temperature for 3 hr. Following the careful addition of 100 ml of water, the ether layer was washed with brine and dried. After evaporation of the ether, the remaining volatile material was vacuum transferred at 80° (15 mm). Preparative vpc purification on the OV-17 column at 85° afforded 820 mg (30%) of **32**.

Anal. Calcd for C_9H_{14}: C, 88.45; H, 11.55. Found: C, 88.32; H, 11.50.

exo-**1,6-Dimethylbicyclo[3.2.0]hept-6-ene Oxide (35).** A solution of 86 mg (0.70 mmol) of **29** and 160 mg (0.92 mmol) of *m*-chloroperbenzoic acid (89%) in 3 ml of chloroform was heated to 60° for 2 hr. Work-up in the previously described fashion and preparative vpc purification ($^1/_4$ in. × 5 ft 10% SF-96 column at 100°) led to the isolation of 59 mg (61%) of **35**: $\delta_{\text{TMS}}^{\text{CDCl}_3}$ 3.42 (s, 1), 1.40–2.18 (m, 7, with maximum at 1.69), 1.31 (s, 3), and 1.04 (s, 3)

Anal. Calcd for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 78.07; H, 10.19.

exo-**1,7-Dimethylbicyclo[3.2.0]hept-6-ene Oxide (36).** An ethereal solution of 34 mg (0.28 mmol) of **31** was irradiated through quartz as before. A solution of the resulting cyclobutene and 80 mg of *m*-chloroperbenzoic acid (89%) in 3 ml of chloroform was heated to 60° for 2 hr. Work-up in the predescribed fashion gave 24 mg (61%) of **36**: $\delta_{\text{TMS}}^{\text{CDCl}_3}$ 3.38 (d, $|J|$ = 2.9 Hz, 1), 1.40–2.18 (m, 7), 1.35 (s, 3), and 1.08 (s, 3).

Anal. Calcd for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 78.30; H, 10.27.

1,2-Dimethylbicyclo[4.1.0]hept-2-ene (30). The oil obtained from the addition of methyllithium to 1.5 g of **37** was heated to 90° with 3.8 g (20 mmol) of *p*-toluenesulfonyl chloride in 20 ml of pyridine for 30 min. The pyridine solution was poured into 100 ml of water which in turn was washed with two 100-ml portions of ether. The combined ether layers were washed with dilute hydrochloric acid and saturated aqueous sodium bicarbonate solution, dried, and evaporated. Vacuum transfer of the residue at 80° (20 mm) gave a condensate in the −70° trap which was purified by preparative vpc on the OV-17 column at 95°. There was obtained 52 mg (4%) of **30**, identical in all respects with the sample isolated above.

General Procedure for the Determination of Rate Constants by Vpc Methods. The response factors for **1a** and **2a** were determined by preparing four standard solutions of different relative amounts of the two components in dry benzene. The linear plot of the molar ratios of **2a** to **1a** *vs.* the peak-area ratios of these isomers exhibited a slope of 0.923. This value was utilized as the response factor.

In a 1-dram vial (which had previously been painted black on its exterior surface to ensure protection from light) equipped with a septum was placed 1.0 ml of 8.45 × 10^{-2} *M* silver perchlorate in benzene (freshly titrated by the Volhard method). This solution was allowed to equilibrate at 40.00° for 20 min; 30 µl of **1a** was syringed into the vial and a timer was started. Six aliquots (each ~100 µl) were removed from the vial at given time intervals and quenched in 1 ml of saturated aqueous sodium chloride solution. The organic material was taken up in a small amount of pentane and a sample of this solution was injected into the gas chromatograph ($^1/_4$ in. × 10 ft 5% OV-17 column at 85°). The progress of the reaction was followed for about 4000 sec.

The areas of the peaks corresponding to **1a** and **2a** were measured by means of a planimeter. The area of the peak due to **2a** was multiplied by the response factor 0.923 to obtain a value for an equivalent amount of **1a**. A plot of log $[\mathbf{1a}]_0/[\mathbf{1a}]_t$ *vs.* time yielded a straight line for at least 1 half-life. In this case, four runs were conducted (see Table I). The average value of 2.27 ± 0.03 × 10^{-3} M^{-1} sec^{-1} is considered to be an accurate value for the Ag^+-catalyzed rearrangement of **1a**.

General Procedure for the Determination of Rate Constants by Nmr Methods. A Varian Associates A-60A spectrometer was employed in the recording of all spectra. Into an nmr tube was syringed 200 µl of standardized silver perchlorate–benzene solution. The tube was placed in the probe maintained at 40.1° for 10 min to achieve thermal equilibration. The tube was quickly removed and 20 µl of the tricycloheptane was added. After being inverted once, the tube was returned to the probe. A timer was started at the instant the tube was inverted. Integration of the appropriate tricycloheptane and product peaks was performed at given time intervals. A plot of log $[\text{tricycloheptane}]_0/[\text{tricycloheptane}]_t$ was usually curved and the rate constant was calculated from the (linear) slope exhibited by the initial points. The reported rate constants are averages of at least three runs.

Determination of the Ag^+–1a Equilibrium Constant. In a black-painted 1-dram vial equipped with a serum were syringed 600 µl of dry benzene, 100 µl of 2.02 × 10^{-2} *M* silver perchlorate–anhydrous benzene, 270 µl of dry cyclohexane, and 11.5 µl (9.7 × 10^{-3} g) of cyclooctane. This solution was permitted to equilibrate at 40.00° for 30 min. Subsequently, 30 µl of **1a** was introduced simultaneously with timer initiation. At given time intervals 100-µl aliquots were removed, quenched in saturated sodium chloride solution, taken up in pentane, and analyzed by vpc as before.

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[38] L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis," Vol. 1, Wiley, New York, N. Y., 1967, p 315.

By means of the internal standard, an accurate weight of the **2a** present could readily be determined by use of the formula

$$[\mathbf{2a}]_{\mathrm{wt}} = (9.7 \times 10^{-3}\ \mathrm{g})(0.981)\frac{[\mathbf{2a}]_{\mathrm{area}}}{[\mathrm{cyclooctane}]_{\mathrm{area}}}$$

The response factor 0.981 was arrived at from analyses of standard solutions containing known quantities of **2a** and cyclooctane. The concentrations of **2a** were calculated and plotted against time to obtain its rate of appearance.

This experiment was repeated using 100-, 200-, and 300-μl samples of **1a** in conjunction with 70-, 170-, and 270-μl decreases, respectively, in the volume of cyclohexane. In this manner, the total volume of the solution remained constant.

Determination of the Ag^+-5 Equilibrium Constant. Into a reaction vial were syringed 600 μl of dry benzene containing 0.925 mg of *cis*-decalin as an internal standard (from a standard solution of 77.1 mg of *cis*-decalin in 50 ml of benzene), 100 μl of 0.0161 *M* silver perchlorate in anhydrous benzene, and 270 μl of dry cyclohexane. The solution was allowed to equilibrate at 40.00° for 30 min and 30 μl of **5** was introduced. A timer was started and at given intervals 100-μl aliquots were removed, quenched in saturated sodium chloride solution, taken up in pentane, and analyzed by vpc methods ($^1/_8$ in. × 12 ft 5% OV-17 column at 90°).

By means of the internal standard, an accurate weight of 3-ethylidenecyclohexenes **8** and **9** could readily be determined by way of the equation

$$[\mathbf{8} + \mathbf{9}]_{\mathrm{wt}} = (9.25 \times 10^{-4}\ \mathrm{g})\frac{[\mathbf{8} + \mathbf{9}]_{\mathrm{area}}}{[cis\text{-decalin}]_{\mathrm{area}}}$$

This equation is based on the assumption of equal weight responses to the flame ionization detector. The concentrations of all products were then calculated with the knowledge that the ethylidenecyclohexene mixture comprises 29.3% of the product composition. The total concentration of products was plotted against time to obtain the rate of disappearance of **5**.

This experiment was repeated with 100- and 200-μl samples of **5** in conjunction with 70- and 170-μl decreases, respectively, in the volume of cyclohexane.

Method of Calculating K_{eq}. The equation of interest is given in eq 6; for simplicity, we let $R = -\mathrm{d[tricycloheptane]}/\mathrm{d}t$. At low concentrations of tricycloheptane, K[tricycloheptane] is assumed to be ≪1 and eq 6 reduces to

$$R = k_2K[\mathrm{tricycloheptane}][\mathrm{AgClO_4}] \qquad (7)$$

or

$$k_2K = \frac{R}{[\mathrm{tricycloheptane}][\mathrm{AgClO_4}]} \qquad (8)$$

Such a treatment provides a value for k_2K which will require modification only if the initial assumption is incorrect.

From eq 6, one can derive the following expression

$$K = \frac{k_2K[\mathrm{tricycloheptane}][\mathrm{AgClO_4}] - R}{[\mathrm{tricycloheptane}]R} \qquad (9)$$

K is then calculated at the various tricycloheptane concentration levels used in the experiments. If the calculated K disproves the original assumption (K[tricycloheptane] ≪ 1), then k_2K is recalculated by means of eq 6. Such a procedure gives rise to a new K from eq 9. This process is repeated until the value of k_2K, and of course the value of K, no longer change.

A sample set of calculations is provided below for **5**.

$$[\mathrm{AgClO_4}] = 1.6 \times 10^{-3}\ M$$

$$[\mathrm{tricycloheptane}] = 0.24\ M$$

$$R = 1.9 \times 10^{-6}\ \mathrm{mol/(l.\ sec)} = k_2K(0.24\ M)(1.6 \times 10^{-3}\ M) \qquad (10)$$

$$k_2K = 4.9 \times 10^{-3}\ \mathrm{l./(mol\ sec)}$$

For the run where [tricycloheptane] = 0.81 *M*, *R* was found equal to 4.2 × 10^{-6} mol/(l. sec). Therefore

$$K = \frac{(4.9 \times 10^{-3}\ \mathrm{l./(mol\ sec)})(0.81\ M)(1.6 \times 10^{-3}\ M) - 4.2 \times 10^{-6}\ \mathrm{mol/(l.\ sec)}}{(0.81\ \mathrm{l./(mol\ sec)}(4.2 \times 10^{-6}\ \mathrm{mol/(l.\ sec)}))} = 0.62\ M^{-1}$$

For the run where [tricycloheptane] = 1.6 *M*, *R* was found equal to 6.1 × 10^{-6} mol/(l. sec). Therefore

$$K = \frac{(4.9 \times 10^{-3}\ \mathrm{l./(mol\ sec)})(1.6\ M)(1.6 \times 10^{-3}\ M) - 6.1 \times 10^{-6}\ \mathrm{mol/(l.\ sec)}}{(1.6\ M)(6.1 \times 10^{-6}\ \mathrm{mol/(l.\ sec)})} = 0.65\ M^{-1}$$

Utilizing $K = 0.63\ M^{-1}$, substituting in eq 6, and solving for k_2K, we obtain for the point wherein [tricycloheptane] = 0.24 *M*

$$k_2K = \frac{(1.9 \times 10^{-6}\ \mathrm{mol/(l.\ sec)})(0.63\ M^{-1})(0.24\ M) + 1.9 \times 10^{-6}\ \mathrm{mol/(l.\ sec)}}{(0.24\ M)(1.6 \times 10^{-3}\ M)} = 5.8 \times 10^{-3}\ \mathrm{l./(mol\ sec)}$$

With the aid of eq 9, the values of K for the other two concentrations can now be realized.

$$K = \frac{(5.8 \times 10^{-3}\ \mathrm{l./(mol\ sec)})(0.81\ M)(1.6 \times 10^{-3}\ M) - 4.2 \times 10^{-6}\ \mathrm{mol/(l.\ sec)}}{(0.81\ M)(4.2 \times 10^{-6}\ \mathrm{mol/(l.\ sec)})} = 0.97\ M^{-1}$$

$$K = \frac{(5.8 \times 10^{-3}\ \mathrm{l./(mol\ sec)})(1.6\ M)(1.6 \times 10^{-3}\ M) - 6.1 \times 10^{-6}\ \mathrm{mol/(l.\ sec)}}{(1.6\ M)(6.1 \times 10^{-6}\ \mathrm{mol/(l.\ sec)})} = 0.99\ M^{-1}$$

Utilizing $K = 0.98\ M^{-1}$ and resubstituting in eq 6 as before, we derive $k_2K = 6.3 \times 10^{-3}$ l./(mol sec) and the following new values for K (K = 1.2 and 1.0 M^{-1}), thereby generating the value which finally accepted: 1.1 ± 0.1 M^{-1}.

Alternatively, a graphic solution can be realized with the same results by the method of Lineweaver and Burk.[39] As a result of the fact that the initial rate of rearrangement (V_0) = k_2[tricycloheptane][AgClO$_4$], eq 11 obtains; plotting of [tricycloheptane]/V_0

$$\frac{[\mathrm{tricycloheptane}]}{V_0} = \frac{[\mathrm{tricycloheptane}]}{k_2[\mathrm{AgClO_4}]} + \frac{1}{Kk_2[\mathrm{AgClO_4}]} \qquad (11)$$

vs. [tricycloheptane] affords the value of $1/Kk_2[\mathrm{AgClO_4}]$ on the [tricycloheptane]/V_0 axis intercept and the slope is $1/k_2[\mathrm{AgClO_4}]$.

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[39] H. Lineweaver and D. Burk, *J. Amer. Chem. Soc.*, **56**, 658 (1934).