Valence Isomerization of Homocubanes. Reversible Complex Formation and Kinetic Substituent Effects Operating during Silver (I)-Induced Bond Reorganization[1]

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Abstract: To probe the effect of such groups as phenyl, vinyl, cyclopropyl, and ethoxy on the rate of Ag$^+$-catalyzed homocubyl rearrangements, the isomerizations of 4-substituted homocubanes were compared with those of model compounds where direct resonance interaction in the transition state was not anticipated. In contrast to the kinetic behavior of homocubane and its 4-CH_3, 4-CH_2OAc, 4-$COOCH_3$, and 4-CH_2OCH_3 derivatives which conform to a linear σ^* free energy relationship ($\rho^* = -2.33$), the first four compounds isomerize more rapidly than expected on this basis. The 4-*tert*-butyl substituent affects bond switching by a steric parameter and the k_{Ag} in this instance is smaller than projected. Placement of a deuterium atom or a CD_3 group at C_4 gives rise to a small inverse kinetic deuterium isotope effect ($k_H/k_D = 0.97$) in each instance. Introduction of a second substituent at C_5 does not lead to acceleration of the bond switching process. The contributions of C_9 substitution to the overall isomerization rate have also received limited scrutiny. All of these catalyzed reactions follow a second-order rate dependence with incursion of preequilibrium complex formation. Adherence to Michaelis-Menten kinetics was demonstrated for 4-methylhomocubane (**6**). Several synthetic approaches were devised for the preparation of the various homocubanes and these are detailed. The rearrangements produce norsnoutanes exclusively and in essentially quantitative yield. On the basis of these diverse findings, the bond switchings appear to proceed by Ag$^+$-induced electrophilic ring opening of the less substituted edge bonds. Solvolytic reactions of cyclopropylcarbinyl and cyclobutyl derivatives serve as mechanistic prototypes.

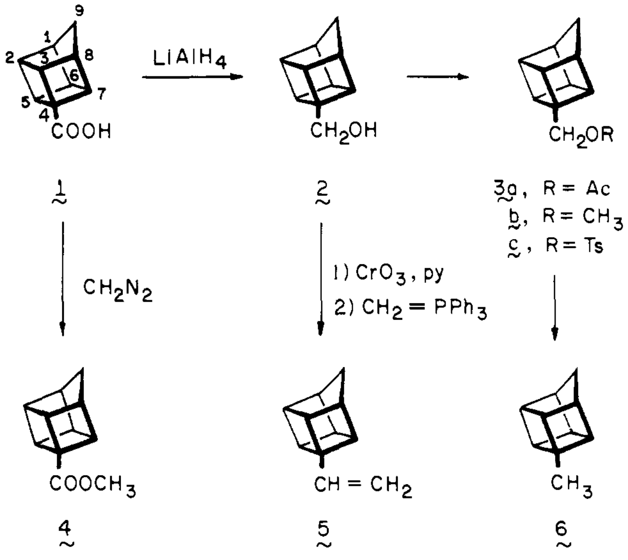
In previous papers of this series,[4] a detailed kinetic and product analysis of Ag$^+$-catalyzed 1,8-bishomocubane isomerizations was reported. After allowing for inductive contributions from the remote C_9,C_{10} substituents and steric effects, we concluded that a substantial portion of the rate enhancement or retardation in 4- and 4,5-substituted derivatives was contributed by a single corner functional group, although not to an extent such that direct interaction with full unit positive charge operates. However, the magnitude of resonance effects on these rearrangements was not evaluated owing to serious synthetic limitations. Because of this, we were led to investigate the response to transition metal catalysis of the next lower homolog of this highly strained system where it was believed that greater synthetic flexibility would be available. The parent homocubane molecule was known,[5] and a number of 4- and 9-substituted derivatives of this hydrocarbon had already made their appearance.[5-7] However, facile general routes to yet more diversely functionalized homocubane derivatives were still lacking.

In this paper we develop various synthetic approaches to such molecules and describe experimental scrutiny of several revealing aspects of their Ag(I)-catalyzed rearrangement. Specifically detailed are such matters as: (1) establishment of rapid and reversible homocubane–Ag$^+$ complex formation prior to rearrangement, (2) kinetic consequences of C_4 substitution by groups capable of resonance interaction, (3) deuterium isotope effect studies, and (4) contributions of C_9 substituents to the overall isomerization rate and to product stereochemistry.[8]

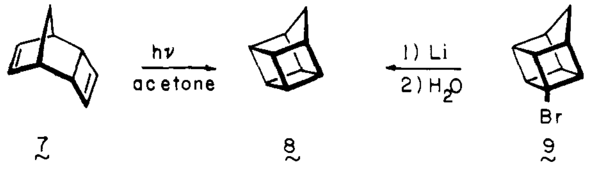
Results

Synthesis and Product Studies. With the development of an efficient synthesis of homocubane-4-carboxylic acid (**1**),[9] a convenient starting point was available for the preparation of 4-substituted derivatives **2–6**. The various chemical manipulations employed conform to standard practice and are summarized in Scheme I without further discussion.

Scheme I

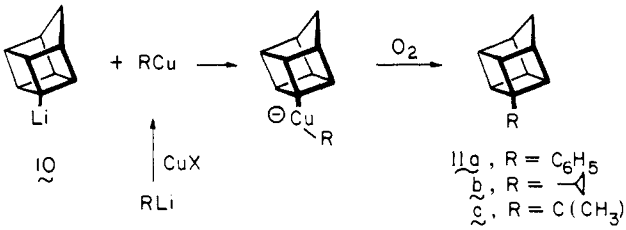


Two avenues to the parent hydrocarbon (**8**) were examined. The first of these is based on the familiar $_{\pi}2_s + _{\pi}2_s$ photocyclization reaction. Irradiation of **7**, available from the condensation of cyclobutadiene with cyclopentadiene,[10] in acetone solution under conditions of triplet sensitization, afforded **8** in 20% overall yield. However, this procedure was costly and tedious, and we found it preferable to gain access to **8** by subjecting **1** to a modified Hunsdiecker reaction[5c] followed by halogen–metal exchange of bromide **9** and quenching of the organolithium intermediate in water (47%).



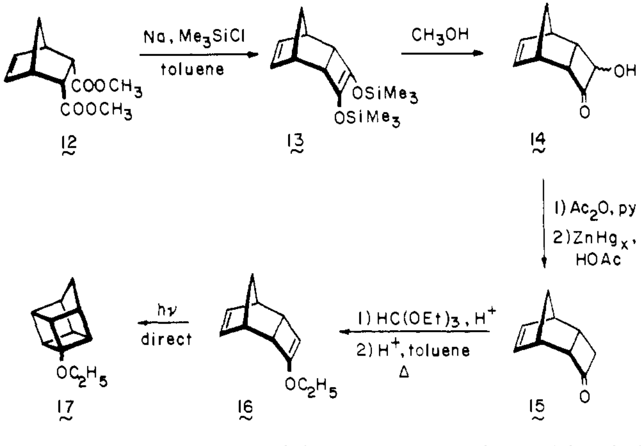
The oxidation of organohomocubylcuprates with molecular oxygen has made available several monosubstituted homocubanes which would otherwise have been unavailable for study (Scheme II). Such oxidative coupling reactions of copper(I) ate complexes, first examined by Whitesides,[11] were hampered somewhat by their heterogeneous nature and the direct dependence of yield on the steric nature of the organic ligand. Also, utilization of purified cuprous iodide was mandatory in the present instance since the commercial copper reagent was found to promote significant amounts of ring opening of the resulting homocubane to a substituted diene of type **7**.[12] No systematic attempt was made to maximize yields; however, we have noted that phenylcopper is best prepared using cuprous bromide. Under these conditions, the isolated yield of **11a** rose to 10%. The methyl (**6**), cyclopropyl (**11b**), and *tert*-butyl (**11c**) derivatives were obtained in yields of 20, 9, and 5%, respectively, after purification by vpc methods.

Scheme II



For the preparation of 4-ethoxyhomocubane (**17**), endo diester **12** was subjected to acyloin cyclization under the conditions specified by Bloomfield.[13] When the 3,4-bis[trimethylsiloxy]tricyclo$[4.2.1.0^{2,5}]$nona-3,7-diene (**13**) so obtained[7b] was hydrolyzed in methanol, a near quantitative yield of α-hydroxycyclobutanone **14** was obtained. Acetylation of **14** and subsequent reduction with amalgamated zinc in acetic acid led to the known[14] cyclobutanone **15** (Scheme III). In our hands, direct reduction of acyloin **14** in this fashion proved unsuccessful. Ketalization of **15** with ethyl orthoformate and subsequent treatment of the ketal with a catalytic amount of *p*-toluenesulfonic acid in refluxing toluene provided enol ether **16**. Subsequently, thermolysis of the ketal at *ca.* 165° in a vpc injection port was found to give **16** more conveniently on a small scale and in a higher state of purity. The structure of **16** was established by a combination of spectral and chemical evidence. The enol ether shows in its pmr spectrum (CCl_4) signals for the distinctively different olefinic protons at δ 5.67–5.80 (m, 2) and 4.34 (br s, 1), the ethoxy group at 3.61 (q, $J = 7$ Hz, 2) and 1.17 (t, $J = 7$ Hz, 3), the methine protons at 2.30–2.75 (m, 2) and 2.89–3.14 (m, 2), and the methylene pair at 1.35–2.00 (m, 2). Chemical confirmation of the assignment was derived from its direct photocyclization (at 2537 Å) to **17**. More conventional sensitized (acetone) conditions led to rather rapid disappearance of **16**, but at least three photoproducts made their appearance. Their identities were not investigated.

Scheme III



Samples of homocubanes **18–20** were generously provided to us by Dr. R. Miller.[7b] However, the need persisted for a 4,5-dialkylhomocubane, particularly the dimethyl derivative, for direct kinetic comparison with **6**. A uniquely satisfactory route to this hydrocarbon (**24**) was realized by dimethylation of readily accessible sulfone **21** and subsequent lithium aluminium hydride-promoted ring contraction of the α-sulfonyl carbanion derived from intermediate **22** (Scheme IV). Further details of this general synthetic procedure for the synthesis of 1,2-disubstituted cyclobutenes have appeared elsewhere.[15] When irradiated in benzene-acetone (1:1) with a bank of 3000-Å lamps from a Rayonet reactor for 24 hr, **23** was cleanly converted to the desired **24**. The definitive spectral data for **24** include the pmr spectrum which clearly reveals the symmetry of the molecule.

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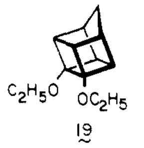

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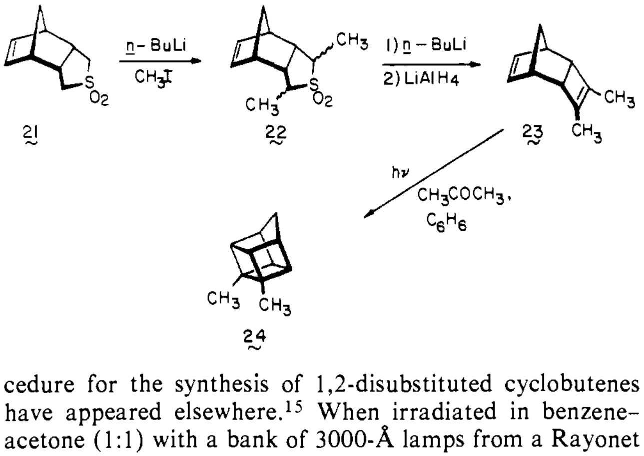
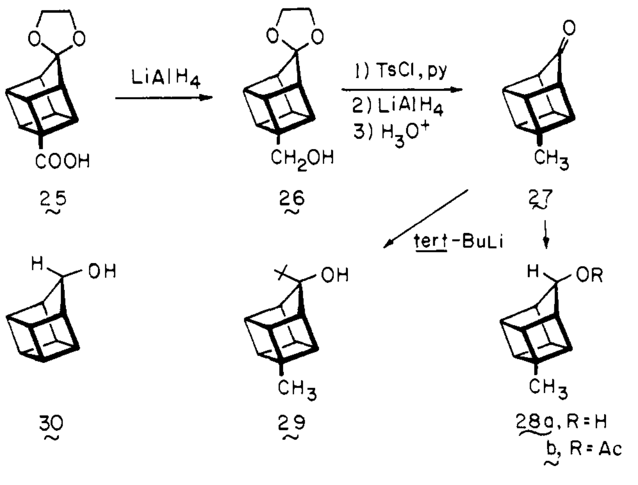
Scheme IV



In an effort to assess contributions of C_9 substituents to the kinetic behavior of homocubyl systems, we have also given attention to a series of four compounds defined by **28a, 28b, 29,** and **30** (Scheme V). Ready access to 4-methylhomocubanone was achieved by treating carboxylic acid **25**[5c] sequentially with lithium aluminum hydride, *p*-toluenesulfonyl chloride in pyridine, a second equivalent of hydride, and aqueous acid. The conversions of **27** to both **28** and **29** were routine.

Scheme V



At this point, it remained to prepare the deuterated homocubanes **31** and **32**. To this end, 4-lithiohomocubane was

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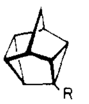
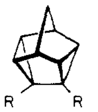
treated with deuterium oxide and the conversion of **1** to **3b** was repeated but with lithium aluminum deuteride as the reducing agent. A high level of deuterium enrichment was attained in both instances such that determination of the isotope effect associated with Ag(I)-catalyzed isomerization was entirely feasible.

Addition to these various homocubanes of catalytic amounts of silver ion resulted in their quantitative conversion (pmr analysis) to norsnoutanes **33–35**. In all cases except **4**, the rearrangements proceeded readily at 25–40° within several hours. The low reactivity of **4** necessitated the use of higher temperatures (123°, 12 hr) to achieve comparable results. Pentacyclo[4.3.0.0^{2,4}.0^{3,8}.0^{5,7}]nonane (**33g**) is a well-known hydrocarbon which has been prepared by a number of varied routes.[16] Its pmr spectrum is sufficiently distinctive that it serves nicely as the prototype for the mono- (**33**) and disubstituted derivatives (**34**).



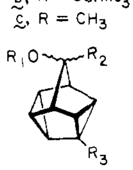
33

a, R = CH_2OH
b, R = CH_2OAc
c, R = CH_2OCH_3
d, R = $COOCH_3$
e, R = $CH{=}CH_2$
f, R = CH_3
g, R = H
h, R = C_6H_5
i, R = –◁
j, R = $C(CH_3)_3$
k, R = OC_2H_5
l, R = $OSiMe_3$
m, R = D
n, R = CD_3



34

a, R = OC_2H_5
b, R = $OSiMe_3$
c, R = CH_3



35

a, $R_1 = R_2 = H$; $R_3 = CH_3$
b, $R_1 = Ac$; $R_2 = H$; $R_3 = CH_3$
c, $R_1 = H$; $R_2 = C(CH_3)_3$; $R_3 = CH_3$
d, $R_1 = R_2 = R_3 = H$

With the exception of homocubanol (**30**), the C_9 functionalized homocubanes **28a, 28b,** and **29** were transformed into nonseparable mixtures of proximal and distal isomers **35**. The isomer ratios in the individual cases were seen by pmr integration of relevant signals to be 2.3, 2.0, and 1.77, respectively.[17]

Demonstration of Reversible Homocubane–Ag$^+$ Complexation. Kinetic study of the silver perchlorate catalyzed rearrangement of the most synthetically accessible homocubyl hydrocarbon, *i.e.*, **6**, showed its rate of disappearance in anhydrous benzene solution to be linear when log $[6]_0/[6]_t$ was plotted *vs.* 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 $AgClO_4$.

$$k_{cat} = \frac{2.303 \log [6]_0/[6]_t}{[AgClO_4]_t} \qquad (1)$$

To substantiate the kinetic order in the homocubane, the half-life method was employed and it was observed that the half-life of **6** is independent of initial concentration. Thus the catalyzed rearrangement is a second-order process dependent upon the concentrations of both **6** and Ag$^+$ ion, and the isomerization then proceeds in strict accordance with the second-order catalytic rate law given in eq 2.

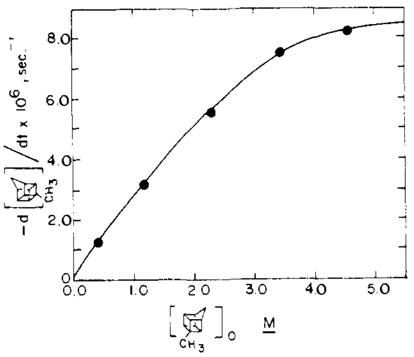


Figure 1. Initial rates of conversion of 4-methylpentacyclo[4.3.0.0^{2,5}.0^{3,8}.0^{4,7}]nonane (**6**) to **33e** as a function of the concentration of **6**. All runs were performed at 40° in 3.03 × 10^{-4} *M* silver perchlorate solutions consisting of 30% benzene and 70% cyclohexane-**6** (v:v).

$$-\frac{d[6]}{dt} = k_{Ag}[6][AgClO_4] \qquad (2)$$

A study of the initial rates of conversion of **6** to **33f** as a function of the concentration of **6** revealed a nonlinear variation in rate as revealed in Figure 1. This behavior accords with a linear kinetic dependence on [**6**] at low homocubane concentrations with gradual progression toward a zero-order dependence at higher concentration levels, and is identical in form with many enzyme-catalyzed reactions. As a consequence, the bond switching is seen to follow the terms of eq 3 and 4 if, as appears to be the case,[4b] complex formation is a direct prelude to norsnoutane production.[21]

$$\text{homocubane} + Ag^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{complex} \xrightarrow[\text{slow}]{k_2} \ ? \longrightarrow \text{norsnoutane} + Ag^+ \qquad (3)$$

$$\frac{d[\text{norsnoutane}]}{dt} = \frac{k_2K[\text{homocubane}][Ag^+]}{K[\text{homocubane}] + 1} \qquad (4)$$

From eq 4 it is possible to calculate the equilibrium constant for 4-methylhomocubane–Ag(I) complex formation as 0.19 at 40°. The extent of this complexation is seen to be rather substantial if one considers that it must operate in competition with the Ag$^+$-benzene equilibrium.

Kinetic Details and Some Mechanistic Implications. Kinetically, the rates of conversion of all 4-substituted homocubanes to the isomeric norsnoutanes (**33**) conformed to eq 2 when determined in anhydrous benzene at 40.3° (Table I). Due to the highly depressed isomerization rate of

Table I. Isomerization Rate Data for 4-Substituted Homocubanes ($AgClO_4$, anhydrous C_6H_6, 40°)

Compd	4-Substituent	Method of analysis	k_{Ag}, M^{-1} sec^{-1}	k_{rel}	σ^* [b]
17	$-OC_2H_5$	Vpc	3.69×10^{-1}	501	+1.68[c]
5	$-CH{=}CH_2$	Vpc	3.40×10^{-2}	46	+0.65[f]
11b	–◁	Vpc	2.53×10^{-2}	34	*d*
11a	$-C_6H_5$	Vpc	1.66×10^{-2}	23	+0.60
2	$-CH_2OH$	Vpc	8.49×10^{-3}	12	+0.56
18	$-OSiMe_3$	Pmr	7.17×10^{-3}	9.7	*d*
6	$-CH_3$	Vpc	7.15×10^{-3}	9.7	0.00
3b	$-CH_2OCH_3$	Vpc	1.10×10^{-3}	1.5	+0.64
8	–H	Vpc	7.36×10^{-4}	1.0	+0.49
11c	$-C(CH_3)_3$	Vpc	2.88×10^{-4}	0.39	−0.30
3a	$-CH_2OAc$	Vpc	7.39×10^{-5}	0.10	+1.01[e]
4	$-COOCH_3$	Vpc	1.83×10^{-7} [a]	0.00025	+2.00

[a] Extrapolated from data obtained at higher temperatures. [b] From R. W. Taft in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., Wiley, New York, N. Y., 1956, Chapter 13, unless otherwise noted. [c] M. Charton, *J. Org. Chem.* **29**, 1222 (1964). [d] Data not available. [e] G. F. Koser, *Chem. Commun.*, 388 (1971). [f] J. Hine and W. C. Bailey, Jr., *J. Amer. Chem. Soc.*, **81**, 2075 (1959); E. Euranto, *Ann. Univ. Turku., Ser. A1*, 42 (1960).

ester **4** under these conditions, its kinetic behavior was assessed at 122.8, 130.7, and 142.8° and extrapolation to a rate constant at 40° made on the basis of the activation parameters ($\Delta H^* = 23.9$ kcal/mol; $\Delta S^* = -13.1$ eu). The successful correlation realized between logarithmic values of k_{Ag} for 4-substituted bishomocubanes and $\Sigma\sigma^*{}_{4\,corner}$[4b] suggested that similar treatment of the kinetic data would be feasible here. Because C_4 is the unique site of structural alteration in these monosubstituted homocubanes, a simple plot against the appropriate Taft σ^* constant should define a straight line. In fact, a linear correlation is followed except for the *tert*-butyl derivative (**11c**) because of steric complications and for 4-phenyl- (**11a**), 4-vinyl- (**5**), and 4-ethoxyhomocubane (**17**) which isomerize too rapidly to conform to this type of reactivity dependence (Figure 2). If these four points are neglected, ρ^* as defined by the method of least squares is -2.33 ($r = 0.995$).[22] σ^* values for the cyclopropyl and trimethylsiloxy groups are to our knowledge presently unknown. Notwithstanding, the rate measurements suggest that the cyclopropyl substituent promotes, like phenyl, considerably greater acceleration than that expected on the basis of purely inductive contributions. The trimethylsiloxy derivative **18** isomerizes 50 times more slowly than ethoxyhomocubane (**17**).

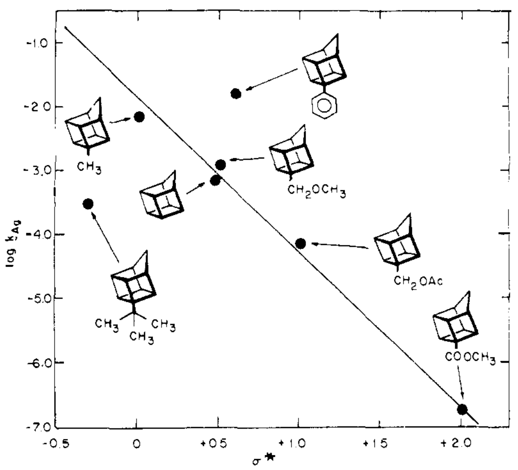


Figure 2. Correlation of log k_{Ag} with σ^* for various 4-substituted homocubanes.

Since the kinetic behavior of **3a**, **3b**, **4**, **6**, and **8** conforms to a linear free energy relationship and because σ^* is defined as characteristic of chemical change occurring at a *single* reaction site, multicenter reactivity (defined as a mechanistic crossover from reaction at one cubyl corner to that at another) in progressing through this series (σ^* range of 0.0 to +2.00) can be excluded.[24] Specifically, this means that the same bond or bonds of the strained carbon framework comprise the reaction center, despite substantial electronic modification of the substituent. Also, although the observed ρ^* value is appreciably negative, it does not appear compatible with the development of full unit positive charge on the corner atom directly adjacent to the substituent in the rate-determining step. In such an event, ρ^* would be expected to be substantially more negative.[4b]

When those substituents capable of resonance interaction with cationic centers are included, the catalytic rate constants are seen to vary over approximately six powers of ten (Table I).

The kinetic behavior of the 4,5-disubstituted homocubanes **19**, **20**, and **24** provides an informative test of additive substituent effects and cumulative steric influences at the two corners remote from the methano bridge. As can be seen from Table II, introduction of a second identical group at C_5 contributes little additional acceleration and, in fact, leads to small kinetic decelerations for the dimethyl and diethoxy examples. A similar reactivity profile is evidenced in the bishomocubyl series[4b] and can be comprehended in terms of steric factors acting to impede the necessary approach of Ag^+ to the reactive sites.

Secondary Deuterium Isotope Effects. Secondary deuterium isotope effects have been extensively employed in organic mechanistic studies, particularly in the area of solvolysis reactions, to probe the level of carbonium ion character in the transition state.[25] Usually, the effects are comparatively small and it is clear that only gross changes rather than small variations are significant. Nevertheless, force constant perturbations in the rate-determining step, probably arising from a blending of hyperconjugative and steric interaction mechanisms, can provide useful information concerning transition state vibrational frequencies if used with care.

Table II. Isomerization Rate Data for 4,5-Disubstituted Homocubanes ($AgClO_4$, anhydrous C_6H_6, 40.3°)

Compd	k_{Ag}, M^{-1} sec^{-1}	k_{rel} **8**	$k_{rel}{}^{monosubst}$ (R)	$k_{rel}{}^{disubst}$
19	2.7×10^{-1}	1.0	489 ($-OC_2H_5$)	367
20	1.12×10^{-2}	1.0	9.7 ($-OSiMe_3$)	15.2
24	6.44×10^{-3}	1.0	9.7 ($-CH_3$)	8.7

As concerns homocubane-*4-d* (**31**), two kinds of deuterium isotope effect can in principle operate during the isomerization to **33m**. The first of these involves cleavage of the C_3–C_4 bond and would be of the α type. Alternatively, Ag^+-induced rupture at C_2–C_5 would generate a β type interaction. In both instances, carbon is the leaving group and the distinction relates to the site of isotopic substitution as it is varied from the immediate vicinity of reaction (α) to an adjacent carbon atom (β). The rearrangement of **31** to **33m** at 40.3° in an azeotropically dried benzene solution of silver perchlorate was quantitatively assayed by gas chromatography in tandem with isomerization of its nonlabeled counterpart (**8**) under identical conditions. Seven such determinations showed a rearrangement isotope effect $k_{Ag_H}/k_{Ag_D} = 0.97 \pm 0.03$. Thus, a negligible kinetic contribution is provided by the deuterium atom at C_4 in the activated complex. If the α effect, usually taken as a measure of the geometric structure of the transition state, is operative, then the fractionation factor points up that cleavage of the C_3–C_4 bond does not result in a major hybridization change. Incursion of the β effect, normally taken as a measure of the carbonium ion character of the transition state, could be inconsequential owing to geometrically enforced angular restrictions which would preclude possible overlap of the C–D bond with relevant orbitals of the homocubyl nucleus.[26]

An explanation for the slightly inverse nature of k_{Ag_H}/k_{Ag_D} could follow from other considerations. Since **31** undergoes bond switching in accordance with eq 4 with the result that the overall rate constant is the product of an equilibrium constant and a rate constant ($k_H = k_2K$), the true isotope effect is given by the expression

$$k_{Ag_H}/k_{Ag_D} = (K_H/K_D)(k_{2_H}/k_{2_D}) \qquad (5)$$

Thus the overall partitioning is the product of an equilibrium isotope effect and a kinetic isotope effect. As seen by Cram and his coworkers, small and inverse isotope effects can be obtained when this condition prevails.[27]

Under comparable conditions 4-trideuteriomethylhomocubane (**32**) was found to exhibit a similar low inverse isotope effect (k_{Ag_H}/k_{Ag_D}) of 0.970 ± 0.005. This virtual lack of a kinetic fractionation factor (0.01 per atom D) is consistent with the conclusion arrived at on the basis of substitu-

Table III. Isomerization Rate Data for 9-Substituted Homocubanes ($AgClO_4$, anhydrous C_6H_6, 40.3°)

Compd	k_{Ag}, M^{-1} sec^{-1}	k_{rel} *vs.* **6**	k_{rel} *vs.* **8**
28a	4.85×10^{-3}	0.68	
28b	6.51×10^{-4}	0.091	
29	1.26×10^{-4}	0.018	
30	9.67×10^{-4}		1.3

ent effects, namely that the kinetic acceleration by the 4-methyl group is chiefly inductive in nature such that hyperconjugative electron release from the CD_3 group has a negligible impact on rate.

Rearrangements of C_9 Substituted Derivatives. Bridge substitution of the homocubyl ring system with electron withdrawing groups is expected to retard the rate of Ag^+-catalyzed rearrangement through long range inductive withdrawal.[4b] Where a 9-OH group is concerned, the resulting σ^* value of approximately +0.20[28a] is sufficiently close to zero that only small effects are expected. In the case of **28a** a 30% rate decrease relative to **6** is witnessed in agreement with previous findings.[4b] On the other hand, homocubanol (**30**) isomerizes some 30% more rapidly than homocubane (Table III). Acetylation of **28a** to give **28b**, thereby approximately doubling inductive electron withdrawal to C_9 ($\sigma^* \approx +0.36$),[28b] promotes further (sevenfold) deceleration.

The 9-*tert*-butylhomocubanol **29** was studied for several reasons. Firstly, the *tert*-butyl substituent is adequately removed from the reaction center to contribute very weakly, if at all, by inductive electron donation (estimated σ^* −0.04).[28c] However, the steric bulk it contributes to the upper surfaces of the homocubyl nucleus is reminiscent of that operating in *tert*-butylnorbornadiene (**36**)[30] and the *syn*- and *anti*-7-*tert*-butylnorbornenes (**37** and **38**).[31] In **37**, for example, formation of a π complex with Ag^+ is completely deterred for obvious steric reasons. Hydrocarbon **38** does form a silver complex but with a K_{eq} of only 20.8, representing a 2.4-fold reduction in complex stability relative to that of norbornene (K_{eq} = 49.5).[31] Incorporation of a *tert*-butyl group into a homocubane at C_9 should accordingly preclude backside attack of Ag^+ at C_2 and C_3 (if such were to operate) while simultaneously forcing C_9 in closer proximity to C_6 and C_7, with the effect that approach from those directions will likewise be more sterically encumbered than usual. Also, given the knowledge that carbomethoxy groups at C_9 and C_{10} in bishomocubanes are capable of causing an imbalance in the favored direction of approach by Ag^+, we would also expect longer range effects to be felt in **29**. In actuality, **29** rearranges 38 times more slowly than **28a**. The effect of *tert*-butyl substitution is therefore rather convincingly revealed in kinetic terms.

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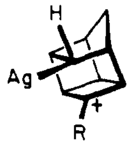
Discussion

Four fundamental characteristics of the Ag(I)-catalyzed homocubane–norsnoutane rearrangement are now recognized: (a) a homocubane–Ag^+ complex is produced in a rapid preequilibrium step as revealed by a second-order rate profile which adheres to Michaelis–Menten kinetics; (b) log k_{Ag}'s of 4-substituted homocubanes obey an excellent linear correlation with σ^* provided that the substituents are incapable of steric interaction with the transition metal reagent or resonance interaction with a developing cationic center; (c) deuterium isotope effects at C_4 are negligible; and (d) remote C_9 substituents exert an appreciable effect on rate. From the values of k_{Ag} in Table I the spread in reactivity between **4** and **17** is seen to be on the order of 10^7. Adherence to a fully synchronous bond switching scheme would require the rate-determining step to acquire minimal ionic character, such that compression of electronic perturbational effects into a rather narrow scale should result. As a consequence, the phenomenologically wide variations in rate cannot plausibly derive from a concerted process arising through direct strained bond interaction with the metal nor can effects of this sort be adequately accounted for in preequilibrium terms alone, since differences in K would never approach this order of magnitude.

In our view, an oxidative-addition mechanism is ruled out on the basis of arguments presented earlier[4b] and because of the widely divergent kinetic response of these same homocubanes to Rh(I) catalysis.[12] Rather, the data argue for a pathway having a transition state endowed with carbonium ion character. Failure to observe kinetic secondary isotope effects of any conseqence appears to rule out a completely free (open) carbonium ion intermediate such as **39** and argues in favor of a delocalized species such as **40** or **41**. Cation **41** would arise from electrophilic ring opening of an edge bond remote from the substituent and should be distinguishable from transition state model **40**.



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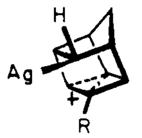

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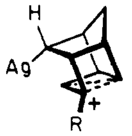
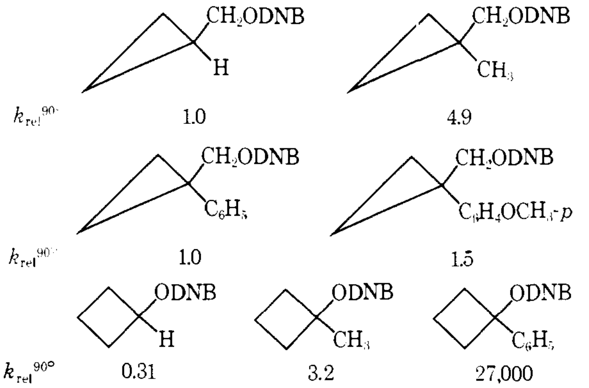
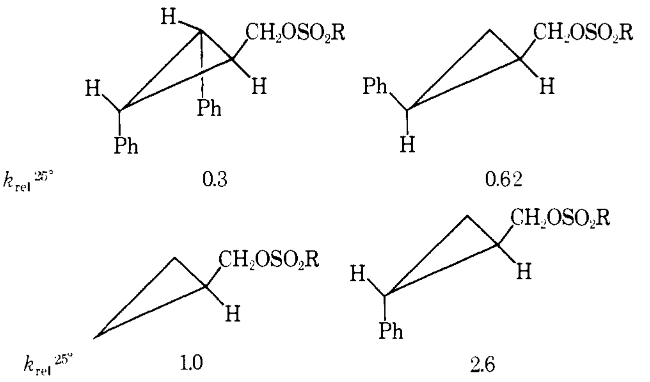


41

In a formal sense, the rearrangements of homocubanes to norsnoutanes correspond to cyclobutyl → cyclopropylcarbinyl ring contractions. At this point, it becomes important to ask whether the electronic nature of the intermediates in the Ag^+-catalyzed isomerizations can be described in terms of simpler prototypes. Previous kinetic studies of the solvolytic reactions of 1-substituted cyclopropylcarbinyl and cyclobutyl derivatives[32] have, for example, generated several intriguing facts: (a) ionization of 1-phenyl- and 1-*p*-anisylcyclopropylcarbinyl dinitrobenzoates is unassisted by the aryl group; (b) the substantial acceleration accorded 1-phenylcyclobutyl dinitrobenzoate points up a transition state with features approaching that of a benzylic cation; and (c) the activated complexes in (a) and (b) bear no resemblance to each other.



What has become equally clear from the small spread in rate constants for a series of 2-phenyl-[32,33] and 2-methylcyclopropylcarbinyl derivatives[32,34] is that these solvolysis transition states concentrate only low or moderate levels of excess positive charge at the ring β-methylene carbons in these examples (compare **42**). The usual rate enhancing effect of a phenyl substituent in such cases is seen to be reduced below the level of electronic transmission by methyl groups perhaps because geometric factors are not conducive to the full operation of conjugative effects and the stereoelectronically independent inductive effect attains a more preeminent position. No solvolytic studies appear to have been carried out on 2-arylcyclobutyl systems.



In agreement with our earlier conclusion, the level of acceleration exhibited, for example, by 4-phenyl- and 4-cyclopropylhomocubane[35] cannot be equated with the involvement of an intermediate such as **39**. To distinguish between **40** and **41**, it becomes necessary to address the question of site selectivity in silver ion complexation and to assess whether the R group is at the pivot (*cf.* **40**) or terminus (as in **41**) of a push-pull electronic situation with Ag^+ playing the acceptor role. If argentation constant data for olefin-silver(I) complexation were to serve as relevant analogy,[36a] then approach of the transition metal ion to the more substituted edge bond might be favored, particularly when R is small and electron donating, because of the higher levels of electron density in the adjoining edge bond. In Table IV is collected a series of relative stability constants which reveals, however, that incremental alkyl substitution does result in measurable increases in complex stability.[36b] However, these effects are not large and could seemingly be reversed by electronic factors in nonplanar systems such as cubyl derivatives.

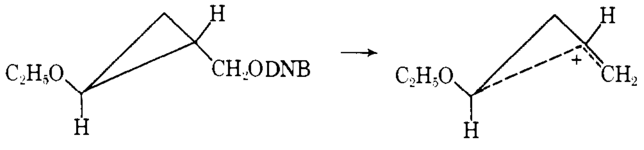
Table IV. Relative Stability Constants of Alkene-Silver(I) π Complexes[a]

π complex	Rel stability constant
$\underset{\overset{\downarrow}{Ag^+}}{CH_2{=}CH_2}$	1.0
$\underset{\overset{\downarrow}{Ag^+}}{CH_3CH{=}CH_2}$	0.41
$\underset{\overset{\downarrow}{Ag^+}}{(CH_3)_2C{=}CH_2}$	0.18
$\underset{\overset{\downarrow}{Ag^+}}{(CH_3)_2C{=}C(CH_3)H}$	0.36
$\underset{\overset{\downarrow}{Ag^+}}{(CH_3)_2C{=}C(CH_3)_2}$	0.005

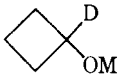
[a] M. A. Muhs and F. T. Weiss, *J. Amer. Chem. Soc.*, **84**, 4697 (1962).

If cleavage of the C_3-C_4 bond does operate, why should cations such as **39** be bypassed? A good reason for this might be that release of ring strain is already advanced in the transition state with the result that bond shifting as in **40** becomes operative at the onset of edge bond rupture.[37] Not only would there be an energetic advantage to partial electronic relocation in this fashion which would presumably serve to lower ΔG^* but charge dispersal would accrue as well. Our assessment of **41** is quite similar. Importantly, both models are predicted to show a $\Sigma\sigma^*_{4\,\mathrm{corner}}$ dependence on rate as required by the bishomocubyl data.[4b]

The accelerating effects of such substituents as phenyl, cyclopropyl, vinyl, and ethoxy all appear to be of too low an order to be rationalized in terms of model **40**, although there are few clear guidelines for estimating what the orders of magnitude should be. Schleyer and Van Dine have reported[34] that the *trans*-2-ethoxycyclopropylcarbinyl derivative **42** solvolyses at a rate 940 times faster than the parent system, as a likely consequence of the intervention of homoallylic delocalization as in **43**. Are the rather comparable accelerative effects exhibited by **42** and 4-ethoxyhomocubane (501-fold) purely coincidental, or do they arise from the structural similarities of the hypothetical intermediates **43** and **41** ($R = OC_2H_5$)? At this point further consideration of the deuterium isotope effect data would seem worthwhile. Both **31** and **32** exhibit small and inverse values of k_H/k_D. In studies carried out by Borcic, Sunko, and their coworkers,[38] *positive* fractionation factors were observed for solvolysis of methanesulfonates **44-47** where the carbon atoms bearing the isotopic label are not at a "terminus" position in the charge delocalized intermediate (compare **40**). When this situation does arise as in **48-50**, the fractionation factors are seen to be *inverse*.[38] Comparative evaluation of the structural features of those carbocations generated upon

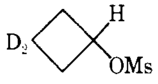


42 **43**



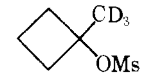
44

k_H/k_D 1.103



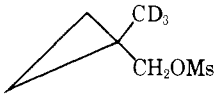
45

1.077



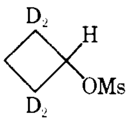
46

k_H/k_D 1.068



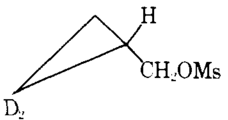
47

1.007



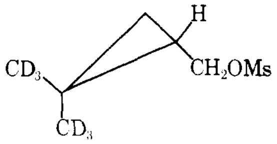
48

k_H/k_D 0.928



49

k_H/k_D 0.963



50

0.983

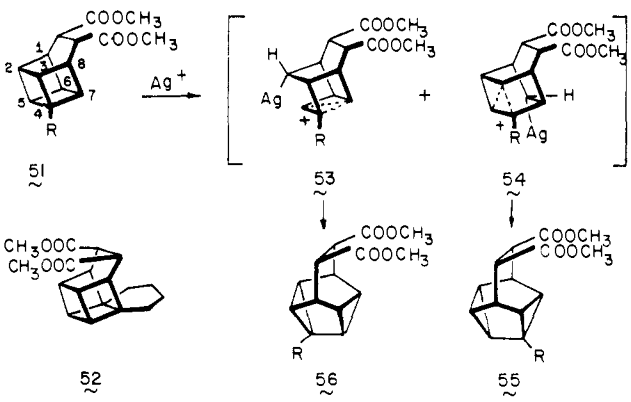
ionization of these three methanesulfonates and **41** (R = H and CD_3) provides a number of striking similarities.

In view of the difficulty inherent in examining transition states in general, and of two so closely related as **40** and **41** in particular, the effect of substitution at different sites could very well also be a suitable criterion for distinction between these activated complexes. Examination of the data for rearrangement of the 4,5-disubstituted derivatives **19, 20,** and **24** denotes that the second corner substituent is ineffective at promoting acceleration. Rationalization of these findings in terms of transition state model **40** would predict a greater than twofold increase in rate owing to the statistical doubling of reaction sites[39] and to a kinetic contribution from the C_5 (now fully substituted) site. Although some impedance to electrophilic attack by Ag^+ at the C_3–C_4 bond by the additional substituent at C_5 is expected, this should not be a monumental deterrence to Ag^+ complexation and subsequent bond switching. The estimated magnitudes of the composite influences appear to fall short in accounting for the observed rate decelerations (Table II).

In contrast, the effect of C_5 substitution on **41** brings into play a direct 1,2-interaction between Ag^+ and the second R group which was not already operational in the monosubstituted counterparts. Steric factors should thereby be magnified in the 4,5-disubstituted examples. Additionally, development of charge at C_5 should profit only slightly by substitution at that site with an electron-donating group if the solvolytic work of Roberts[32] provides erstwhile analogy. By these criteria, the second substituent should contribute to the kinetic profile more by its sheer steric bulk than by its potential for electronic transmission.

Finally, the stereochemical outcome of the isomerization of bishomocubanes substituted as in **51** can be convincingly accounted for on the basis of **41**. It will be recalled that distal isomer **56** is formed preferentially without regard to certain substituent variation at C_4.[4a] To accommodate these findings in terms of transition state model **40** would require that Ag^+-induced cleavage of the substituted edge bond closer to the carbomethoxy groups (*i.e.*, C_4–C_7) be more facile than that of the similar bond more remote from the substituted ethano bridge (C_3–C_4). However, the kinetic behavior of the 2,3-tetramethylene bishomocubyl diester **52** and such 9-substituted homocubanes as **29** provides indication that approach of Ag^+ is more effective when occurring from the sterically unencumbered direction. As shown in Scheme VI, this apparent inconsistency is obviated when electrophilic attack at the less substituted edge bonds operates as in **53** and **54**. The linear σ^* correlation of Figure 2 is also well accommodated by this mechanistic pathway.

Scheme VI



We emphasize that the sum of existing data causes Scheme VI to be a plausible mechanism for the Ag^+-catalyzed rearrangement of cubyl systems. Whether this working hypothesis stands the test of time or not, the unusual capacity of silver(I) ion to function as a rather exclusive type of electrophilic reagent and possible extrapolations of the findings to yet new areas are vividly apparent.

Experimental Section

Melting points are corrected and boiling points are uncorrected. Proton magnetic resonance spectra were obtained on Varian A60-A, Varian HA-100, and Jeolco MH-100 spectrometers; apparent splittings are given in all cases. Infrared spectra were determined on Perkin-Elmer Model 137 and 467 instruments. Mass spectra were recorded on an AEI-MS9 spectrometer at an ionization potential of 70 eV. Elemental analyses were performed by the Scandinavian Microanalytical Laboratory, Herlev, Denmark. Preparative and analytic vpc work was done on a Varian-Aerograph A90-P3 instrument equipped with a thermal conductivity detector. Kinetic measurements were achieved with the acid of Hewlett-Packard 5750 unit (flame ionization detector) equipped with an electronic integrator.

4-Hydroxymethylpentacyclo[4.3.0.$0^{2,5}$.$0^{3,8}$.$0^{4,7}$]nonane (2). To 1.3 g (0.034 mol) of lithium aluminum hydride in 60 ml of anhydrous ether was added with stirring a solution of 5.0 g (0.031 mol) of homocubane-4-carboxylic acid (**1**)[9] in 60 ml of anhydrous ether. Upon completion of the addition, the mixture was stirred at room temperature for 2 hr and heated to reflux for 3 hr. With cooling, water was introduced until a white granular precipitate formed. The solid was separated by filtration, the dried filtrate was evaporated, and the residue was distilled to give 3.73 g (82%) of **2** as a colorless oil, bp 65-67° (0.05 mm). For analysis a sample was further purified by vpc on a 5 ft × 0.25 in. 5% Carbowax 20 M column (Chromosorb G) at 140°: δ_{TMS} ($CDCl_3$) 3.60 (s, 2), 3.0-3.5 (m, 7), 2.0 (s, 1), 1.7 (s, 2).

Anal. Calcd for $C_{10}H_{12}O$: C, 81.04; H, 8.16. Found: C, 80.87; H, 8.35.

4-Acetoxymethylpentacyclo[4.3.0.$0^{2,5}$.$0^{3,8}$.$0^{4,7}$]nonane (3a). A solution containing 400 mg (2.7 mmol) of **2** and 1 ml of acetic anhydride in 5 ml of pyridine was heated on a steam bath for 2 hr. After standing overnight, the solution was poured into water and the product was extracted with ether. The combined organic layers were washed with water, 6 *N* hydrochloric acid, and water, then dried and evaporated. Molecular distillation at a bath temperature of 100-120° and 20 mm afforded 480 mg (93%) of **3a** as a colorless sweet smelling liquid. Purification was achieved on the Carbowax 20 M column at 115°: δ_{TMS} ($CDCl_3$) 4.1 (s, 2), 2.9-3.4 (m, 7), 2.1 (s, 3), 1.6 (s, 2).

Anal. Calcd for $C_{12}H_{14}O_2$: C, 75.76; H, 7.42. Found: C, 75.74; H, 7.63.

4-Methoxymethylpentacyclo[4.3.0.$0^{2,5}$.$0^{3,8}$.$0^{4,7}$]nonane (3b). Approximately a tenfold molar excess of diazomethane in ether was added to an ether solution containing 600 mg (4.0 mmol) of **2,** and a few drops of boron trifluoride etherate were introduced. The mixture was filtered and the filtrate was washed with saturated sodium bicarbonate solution, dried, and evaporated. Molecular distillation of the residue at 80-100° (bath temperature) and 20 mm gave 630 mg (97%) of **3b,** a sample of which was purified on the Carbowax 20 M column at 80°: δ_{TMS} ($CDCl_3$) 3.45 (s, 2), 3.55 (s, 3), 3.15 (m, 7), 1.7 (s, 2).

Anal. Calcd for $C_{11}H_{14}O$: C, 81.44; H, 8.70. Found: C, 81.34; H, 8.80.

4-*p*-Toluenesulfonyloxymethylpentacyclo[4.3.0.0.^{2,5}.$0^{3,8}$.$0^{4,7}$]nonane (3c). A solution of 910 mg (6.1 mmol) of **2** and 1.5 g (7.8 mmol) of *p*-toluenesulfonyl chloride in 15 ml of dry pyridine was stored at 0° for 2 days, poured onto ice, and filtered. The solid was dissolved in ether and this solution upon drying and evaporation furnished 630 mg (34%) of **3c,** white crystals: mp 75-76° (from ether); δ_{TMS} ($CDCl_3$) 7.2-8.0 (m, 4), 4.1 (s, 2), 2.9-3.4 (m, 7), 2.5 (s, 3), 1.7 (s, 2).

Anal. Calcd for $C_{17}H_{18}O_3S$: C, 67.52; H, 6.00. Found: C, 67.43; H, 6.20.

4-Carbomethoxypentacyclo[4.3.0.$0^{2,5}$.$0^{3,8}$.$0^{4,7}$]nonane (4). To 600 mg (3.7 mmol) of **1** in 20 ml of anhydrous ether was added ethereal diazomethane until its yellow color persisted. The excess reagent was destroyed by warming on a steam bath. The liquid residue was molecularly distilled at 50-60° (bath temperature) and

0.1 mm to furnish 600 mg (92%) of **4:** δ_{TMS} ($CDCl_3$) 3.65 (s, 3), 3.2–3.55 (m, 7), 1.7 (s, 2).

Anal. Calcd for $C_{11}H_{12}O_2$: C, 74.98; H, 6.86. Found: C, 74.57; H, 6.95.

4-Vinylpentacyclo[4.3.0.0^{2,5}.0^{3,8}.0^{4,7}]nonane (5). Chromium trioxide (2.6 g, 26 mmol) was added to a stirred solution of dichloromethane (65 ml) and pyridine (4.1 g, 52 mmol). The resulting burgundy solution was stirred for 15 min.[40] To this was added 640 mg (4.3 mmol) of **2** in 5 ml of dichloromethane. After 15 min the solution was decanted and the residue was washed with ether (two 100-ml portions). The combined organic layers were washed with 5% sodium hydroxide solution (three 100-ml portions), 5% hydrochloric acid, 5% aqueous sodium bicarbonate solution (100 ml), and brine (100 ml). After drying and solvent removal, the residue was distilled to give 250 mg (40%) of the aldehyde as a clear liquid: bp 74° (1.0 mm): ν_{max} 2980, 2915, 2840, 2800, 2710, 1695 cm^{-1}; δ_{TMS} ($CDCl_3$) 9.57 (s, 1), 3.07–3.75 (m, 7), 1.70 (br s, 2).

n-Butyllithium (0.75 ml, 1.65 mmol) in pentane was added to a stirred suspension of methyltriphenylphosphonium iodide (665 mg, 1.65 mmol) in 30 ml of ether. After 25 min, the solution was yellow and homogeneous. After cooling to 5°, the solution was treated with 240 mg (1.65 mmol) of the aldehyde dissolved in 5 ml of ether. A white precipitate formed immediately. The mixture was refluxed overnight, cooled, and filtered. The ether was removed by distillation through a short column and the residue was extracted with pentane. The combined pentane layers were washed with water, dried, and carefully evaporated. Final purification by preparative vpc on a 13 ft × 0.25 in. 10% Carbowax column at 120° afforded 55 mg (23%) of **5:** δ_{TMS} ($CDCl_3$) 5.93–6.27 (m, 1), 5.12 (m, 1), 4.77–5.02 (m, 1), 3.18 (br s, 7), 1.68 (br s, 2).

Anal. Calcd for $C_{11}H_{12}$: C, 91.61; H, 8.39. Found: C, 91.54; H, 8.71.

4-Methylpentacyclo[4.3.0.0^{2,5}.0^{3,8}.0^{4,7}]nonane (6). A solution of 1.58 g (5.25 mmol) of **3c** in 100 ml of anhydrous ether was added dropwise to a stirred slurry of lithium aluminum hydride (600 mg, 16 mmol) in 100 ml of the same solvent. After being heated at reflux for 5 hr, the mixture was cooled and treated dropwise with water until a granular precipitate formed. The filtrate was evaporated and the residue molecularly distilled (60° and 20 mm) to yield 450 mg (65%) of **6:** δ_{TMS} ($CDCl_3$) 2.7–3.4 (m, 7), 1.65 (m, 2), 1.1 (s, 3).

Anal. Calcd for $C_{10}H_{12}$: C, 90.85; H, 9.15. Found: C, 90.97; H, 9.09.

Pentacyclo[4.3.0.0^{2,5}.0^{3,8}.0^{4,7}]decane (8). A. Photocyclization of Diene 7.[41] Cyclobutadieneiron tricarbonyl (3.00 g, 15.6 mmol) and cyclopentadiene (2.06 g, 31.2 mmol) were dissolved in 300 ml of acetone and cooled in an ice bath. Ceric ammonium nitrate (32.0 g, 60.0 mmol) was added over a 15-min period with stirring. After an additional 30 min, the solution was poured into 1 l. of aqueous sodium chloride solution and extracted with pentane. The dried pentane layers were subjected to spinning band distillation to remove solvent, and the residue was vacuum transferred into a Dry Ice–acetone cooled trap at 20 mm. Preparative vpc isolation (10 ft × 0.25 in. 5% SF-96 column at 75°) gave 709 mg (39%) of *endo*-tricyclo[4.2.1.0^{2,5}]nona-3,7-diene (**7**): mp 31–37°; δ_{TMS} ($CDCl_3$) 6.00 (s, 2), 5.91 (t, 2), 3.05 (m, 2), 2.65 (m, 2), 1.92 (m, 1), 1.53 (m, 1).

A solution of **7** (500 mg) in 350 ml of acetone was irradiated with a 450-W Hanovia lamp through Pyrex for 2.5 hr. The acetone was removed by spinning band distillation and the residue was purified by vpc on the SF-96 column at 75°. There was obtained 100 mg (20%) of **8:** mp 104–105° (lit.[5b] mp 104–105°); δ_{TMS} ($CDCl_3$) 3.25 (br m, 8), 1.68 (s, 2).

B. Halogen–Metal Exchange of Bromide 9. A mixture of 1.0 g (6.2 mmol) of **1** and 1.0 g (5 mmol) of red mercuric oxide in 25 ml of dry 1,2-dibromoethane was heated to 75°. A solution of 1.1 g (6.9 mmol) of bromine in 10 ml of the same solvent was added to the stirred mixture during 1 hr. Upon completion of the addition, heating at 75° was maintained for an additional hour and the mixture was cooled and extracted with 10% sodium hydroxide solution until a yellow solid was no longer present. The organic phase was washed with water, dried, and freed of 1,2-dibromoethane by distillation through a short Vigreux column at 20 mm. The residue was chromatographed on alumina (elution with petroleum ether) and the liquid so obtained was molecularly distilled to give 440 mg (36%) of **9** as a colorless liquid; δ_{TMS} ($CDCl_3$) 3.5 (m, 7), 1.75 (s, 2).

A mixture of a considerable excess of lithium shot and **9** (60 mg) in 30 ml of anhydrous ether was heated to reflux under dry nitrogen for 2.5 hr. Another 100 mg (total 0.81 mmol) of **9** was added and reflux was resumed for 3 additional hr. After standing overnight at room temperature, the mixture was filtered and the filtrate washed with water. The aqueous phase was extracted with ether, and the combined organic layers were dried and concentrated by slow distillation through a Vigreux column. Preparative vpc purification of the concentrate on a 12 ft × 0.25 in. 15% PMPE 6-ring column (Chromosorb W) at 140° afforded 45 mg (47%) of **8,** mp 102–104°, identical to the solid obtained above.

4-Phenylpentacyclo[4.3.0.0^{2,5}.0^{3,8}.0^{4,7}]decane (11a). Phenyllithium in ether (prepared from 2.0 g of lithium wire and 9.0 g (57 mmol) of bromobenzene) was added to a slurry of commercial cuprous bromide (7.2 g, 50 mmol) in 10 ml of dry tetrahydrofuran at −78° under nitrogen. Warming to 0° resulted in formation of a red-black solution and a tarry precipitate. After 15 min, the solution was cooled to −78° and 4-homocubyllithium (from 8 ml of 2.0 *N tert*-butyllithium in pentane and 1.0 g (5.0 mmol) of **9**) in ether was introduced *via* cannula. The red solution was stirred for 1 hr at −78° and then oxidized for 10 min with a slow stream of oxygen. The solution was washed with aqueous ferrous sulfate and ammonium chloride solutions, dried, and carefully evaporated. Phenylhomocubane (92 mg, 10%) was isolated from a 3 ft × 0.25 in. 5% Carbowax 20 M column at 140°; δ_{TMS} ($CDCl_3$) 6.96–7.3 (m, 5), 3.24 (m, 7), and 1.70 (s, 2).

Anal. Calcd for $C_{15}H_{14}$: C, 92.74; H, 7.26. Found: C, 92.33; H, 7.45.

4-Cyclopropylpentacyclo[4.3.0.0^{2,5}.0^{3,8}.0^{4,7}]decane (11b). Cyclopropyllithium was prepared by the method of Seyferth.[42] Reaction of 3 g of cyclopropyl bromide with 0.6 g of lithium metal in 60 ml of dry ether gave a solution which titrated to 0.76 *N* active organolithium reagent.

4-Homocubyllithium (**10**) was prepared by halogen–metal exchange between *tert*-butyllithium (15 mmol) and bromide **9** (1.6 g, 8.0 mmol) in ether. No exchange seemingly occurred at −78°, but upon slowly warming to room temperature an exothermic reaction took place.

Cyclopropyllithium (45 ml, 35 mmol) in ether was added to a stirred slurry of purified cuprous iodide (5.0 g, 27 mmol) in tetrahydrofuran (10 ml) cooled to −78°. After 5 min, the homocubyllithium solution was introduced *via* cannula. The resulting solution was stirred at −78° for 1 hr and then oxidized by passing a slow stream of oxygen through the flask. The mixture was hydrolyzed with saturated ferrous sulfate solution and filtered. The organic layer was dried, and the low boiling components were removed by distillation through a short Vigreux column. Collection of **11b** from a 6 ft × 0.25 in. 10% Carbowax column at 110° afforded 63 mg (5%) of the hydrocarbon: δ_{TMS} (C_6H_6) 3.10 (m, 7), 1.76 (s, 2), 1.06 (m, 2), 0.48 (m, 3).

Anal. Calcd for $C_{12}H_{14}$: C, 91.08; H, 8.92. Found: C, 90.70; H, 9.16.

4-*tert*-Butylpentacyclo[4.3.0.0^{2,5}.0^{3,8}.0^{4,7}]decane (11c). Oxidation of the mixed cuprate obtained by treatment of 6.3 g (33 mmol) of purified cuprous iodide[43] with 35 mmol of *tert*-butyllithium at −78° followed by the addition of 8 mmol of 4-homocubyllithium (prepared by the exchange reaction of 1.6 g of **9** and 15 ml of 1.1 *N tert*-butyllithium) and work-up in the predescribed fashion afforded after collection from the Carbowax column 60 mg (5%) of **11c** as a clear colorless liquid: δ_{TMS} (C_6H_6) 3.00 (m, 7), 1.64 (br s, 2), 0.80 (s, 9).

Anal. Calcd for $C_{13}H_{18}$: C, 89.59; H, 10.41. Found: C, 89.48; H, 10.48.

***endo*-3,4-Bis(trimethylsiloxy)tricyclo[4.2.1.0^{2,5}]nona-3,7-diene (13).** To a vigorously stirred suspension of sodium (5.06 g, 0.22 g-atom) in toluene (300 ml) at reflux was added a solution of diester **12** (10.5 g, 0.05 mol) and chlorotrimethylsilane (27.2 g, 0.25 mol) in toluene (80 ml) during 3 hr. The resulting mixture was heated at reflux for an additional 10 hr, cooled, and filtered through Celite. The filtrate was concentrated under reduced pressure and the residue was distilled in a Kugelrohr apparatus at 80–85° and 0.05 mm to provide 12 g (82%) of **13** as an oil: δ_{TMS} ($CDCl_3$) 5.8–5.9 (t, $J \approx$ 1.5-2.0 Hz, 2), 2.45–2.85 (m, 4), 1.4–2.1 (m, 2), 0.17 (s, 18).

***endo*-Tricyclo[4.2.1.0^{2,5}]non-7-en-3-one (15).**[14] A 22.0-g (0.075 mol) sample of **13** was added dropwise to reagent grade anhydrous methanol (300 ml) at room temperature and after 15 min the solvent was removed under reduced pressure to afford **14** as a pale yellow solid (11.6 g, 100%) which was not purified further: δ_{TMS} ($CDCl_3$) 6.02-6.35 (m, 2), 4.38-4.68 (m, 1), 2.9-4.0 (m, 4), 1.35-1.90 (m, 2).

To a solution of **14** (11.6 g, 0.075 mol) in pyridine (30 ml) was added acetic anhydride (40 ml) dropwise at 0-10°. After stirring for 0.5 hr at room temperature, the mixture was added to ice (300 g) and extracted with ether (750 ml). The organic layer was separated, washed with 1 *N* hydrochloric acid, 1 *N* sodium hydroxide, and water, and dried. Evaporation gave 10.6 g of crude product which was doubly chromatographed on a short silica gel column (elution with ether-hexane) to give 8.4 g of a pale yellow oil: ν_{max} (neat) 1792, 1750, 1372, 1220, 1025 cm^{-1}; δ_{TMS} ($CDCl_3$) 6.04-6.30 (m, 2), 5.44 (dd, J = 3.5 and 8.0 Hz, 1), 3.04-3.80 (m, 4), 2.09 (s, 3), 1.67 (m, 2). The mass spectrum did not show a parent ion peak of sufficient intensity to measure; major ions were *m/e* 150, 84, 66, and 41.

To a solution of the acetoxy ketone (2.1 g, 11 mmol) in glacial acetic acid (250 ml) was added activated zinc dust[44] (60 g) and mercuric chloride (1.5 g). The resulting mixture was vigorously stirred at the reflux temperature for 24 hr under nitrogen. The warm reaction mixture was filtered and the cooled filtrate was treated with 0.9 equiv (based upon acetic acid) of aqueous sodium hydroxide. The aqueous mixture was extracted with dichloromethane (three 250-ml portions), and the combined organic layers were washed with brine and dried. After solvent removal, the residue was distilled in a Kugelrohr apparatus at 110° and 10 mm to give 1.02 g (70%) of **15** as a semisolid material: ν_{max} (CCl_4) 1781 cm^{-1}; δ_{TMS} ($CDCl_3$) 6.08-6.20 (m, 2), 3.55-3.90 (m, 1), 1.35-3.30 (series of m, 7).

***endo*-3-Ethoxytricyclo[4.2.1.0^{2,5}]nona-3,7-diene (16).** A mixture of ketone **15** (350 mg, 2.6 mmol), triethylorthoformate (470 mg, 3.1 mmol), and ethanol (0.3 ml) was treated with a small amount of atmosphere saturated with vapor from concentrated hydrochloric acid. The resulting solution was stirred for 1 hr at room temperature and subjected to distillation in a Kugelrohr apparatus to give 450 mg (82%) of the diethyl ketal: bp 60-65° (0.05 mm); δ_{TMS} ($CDCl_3$) 5.93-6.32 (m, 2), 3.38 and 3.31 (two q's, J = 7 Hz, 4), 1.35-3.15 (series of m, 8), 1.17 and 1.13 (t, J = 7 Hz, 6).

The diethyl ketal (2.10 g, 10.1 mmol) in toluene (40 ml) was treated with a benzene solution of *p*-toluenesulfonic acid (0.01 mmol) and the mixture was heated at reflux for 72 hr under nitrogen. Vpc analysis (6 ft × 0.25 in. 5% SE-30 on Chromosorb G, 120°) showed approximately 45% conversion to product. A portion of the mixture was purified by vpc to give pure **16:** δ_{TMS} ($CDCl_4$) 5.67-5.80 (m, 2), 4.34 (br s, 1), 3.61 (q, J = 7 Hz, 2), 2.30-2.75 and 2.89-3.14 (m, 4), 1.35-2.00 (m, 2), 1.17 (t, J = 7Hz, 3).

Calcd for $C_{11}H_{14}O$ *m/e* 162.1045; found, 162.1047.

An alternative preparation of **16** was achieved by thermolysis of the ketal in the injector port of the gas chromatograph heated to 175°.

4-Ethoxypentacyclo[4.3.0.0^{2,5}.0^{3,8}.0^{4,7}]nonane (17). Each of four quartz tubes was charged with crude **16** (300 mg) and cyclohexane (12 ml, distilled from lithium aluminum hydride). These solutions were purged for 10 min with nitrogen and irradiated in a Rayonet reactor equipped with 2537-Å lamps. After 17 hr, the conversion was approximately 20%. Irradiation was continued until only a small fraction of **16** remained. A significant amount of polymer had precipitated from solution. Volatile components were collected by vacuum distillation (up to 120° and 10 mm), and the single photoproduct was purified on the SE-30 column at 105°: δ_{TMS} (C_6D_6) 2.78-3.62 (m, 7), 1.56-1.75 (m, 2), 1.16 (t, J = 7 Hz, 3).

Anal. Calcd for $C_{11}H_{14}O$: C, 81.44; H, 8.70. Found: C, 81.37; H, 8.75.

4,5-Dimethylpentacyclo[4.3.0.0^{2,5}.0^{3,8}.0^{4,7}]nonane (24). A 200-μl sample of diene **23**[15] in 20 ml of acetone-benzene (1:1) was placed in a quartz tube and irradiated in a Rayonet reactor fitted with 3000-Å lamps. During 24 hr, smooth conversion to a single photoproduct occurred (vpc analysis). The solvent was removed by short path distillation and **24** was purified by vpc methods (6 ft × 0.25 in. 10% UCON, 75°); δ_{TMS} (C_6D_6) 3.2 (m, 2), 2.8 (m, 4), 1.67 (m, 2), 1.00 (s, 6).

Anal. Calcd for $C_{11}H_{14}$: C, 90.35; H, 9.65. Found: C, 90.32; H, 9.61.

4-Hydroxymethylpentacyclo[4.3.0.0^{2,5}.0^{3,8}.0^{4,7}]nonan-9-one Cyclic Ethylene Ketal (26). A solution of 150 mg of **25**[5c] in 10 ml of anhydrous ether was treated with 100 mg of lithium aluminum hydride in 10 ml of the same solvent as previously described. Evaporation of the dried organic phase left 140 mg of **26** as a colorless oil (ν_{max} (neat) 3450 cm^{-1}) which was used without further purification to prepare the tosylate.

4-Methylpentacyclo[4.3.0.0^{2,5}.0^{3,8}.0^{4,7}]nonan-9-one (27). A solution of 2.0 g (9.7 mmol) of **26** in 30 ml of pyridine was cooled in an ice bath and 4.0 g (21 mmol) of freshly recrystallized *p*-toluenesulfonyl chloride was added. After 2 days at 0°, the mixture was poured into ice water and the solid was collected by filtration and dissolved in ether for drying purposes. Evaporation of this dried solution provided 1.8 g (52%) of the tosylate as white crystals, mp 93.5-95° (from ether).

Anal. Calcd for $C_{19}H_{20}O_5S$: C, 63.32; H, 5.59; S, 8.90. Found: C, 63.22; H, 5.63; S, 9.03.

A solution of 1.7 g (4.7 mmol) of the tosylate in 175 ml of anhydrous ether was added to 250 mg (6.6 mmol) lithium aluminum hydride in 50 ml of the same solvent and heated to reflux for 5 hr. Work-up in the predescribed fashion afforded 0.90 g (100%) of methyl ketal which was hydrolyzed directly.

A mixture of 800 mg (4.2 mmol) of ketal and 35 ml of 10% aqueous sulfuric acid was heated at 80° for 3 hr. The solution was cooled and diluted with saturated brine. Extraction with ether followed by washing of the combined organic layers with water and 10% sodium bicarbonate solution gave after drying and evaporation a yellow oil. Preparative vpc purification on a 5 ft × 0.25 in. 10% SE-30 column (Chromosorb G) at 110° provided 340 mg (55%) of **27:** δ_{TMS} ($CDCl_3$) 3.12 −3.70 (m, 5), 2.82-3.10 (m, 2), 1.19 (s, 3). The 2,4-dinitrophenylhydrazone melted at 162.5-164°.

Anal. Calcd for $C_{16}H_{14}N_4O_4$: C, 58.89; H, 4.32; N, 17.17. Found: C, 58.55; H, 4.60; N, 16.93.

4-Methylpentacyclo[4.3.0.0^{2,5}.0^{3,8}.0^{4,7}]nonan-9-ol (28a). A solution of 400 mg (2.7 mmol) of **27** in 10 ml of anhydrous ether was added dropwise to 100 mg (2.6 mmol) of lithium aluminum hydride in 10 ml of the same solvent. After 3 hr at reflux, work-up proceeded along the usual lines to give 280 mg (69%) of **28a** as white crystals: mp 56.5-58° (from pentane); δ_{TMS} ($CDCl_3$) 4.3 (m, 1), 2.75-3.6 (br m, 7), 1.85 (s, 1), 1.09 (s, 3).

Anal. Calcd for $C_{10}H_{12}O$: C, 81.04; H, 8.16. Found: C, 81.07; H, 8.16.

4-Methylpentacyclo[4.3.0.0^{2,5}.0^{3,8}.0^{4,7}]nonan-9-ol Acetate (28b). A solution containing 55 mg (0.37 mmol) of **28a** in 2 ml of pyridine was treated with 0.5 ml of acetic anhydride and heated on a steam bath for 30 min. The usual work-up and molecular distillation provided 50 mg (71%) of **28b** as a clear oil: δ_{TMS} ($CDCl_3$) 5.05 (m, 1), 2.8-3.5 (br m, 7), 1.95 (s, 3), 1.12 (s, 3).

Anal. Calcd for $C_{12}H_{14}O_2$: C, 75.76; H, 7.42. Found: C, 75.60; H, 7.48.

4-Methyl-9-*tert*-butylpentacyclo[4.3.0.0^{2,5}.0^{3,8}.0^{4,7}]nonan-9-ol (29). A solution of 190 mg (1.3 mmol) of **27** in 10 ml of anhydrous ether was cooled to −80° under a nitrogen atmosphere and 2.5 ml of 1.2 *N* *tert*-butyllithium in pentane was introduced. After 1 hr, the mixture was allowed to warm to room temperature and hydrolyzed by addition of water. The organic layer was dried and evaporated and the residual solid was sublimed at 0.2 mm (220 mg) followed by chromatography on silica gel (elution with 5% ether in hexane). The white solid melted at 63-64°: δ_{TMS} (C_6D_6) 2.70-3.60 (m, 7), 1.33 (m, 1), 1.07 (s, 3), 0.95 (s, 9).

Anal. Calcd for $C_{14}H_{20}O$: C, 82.30; H, 9.87. Found: C, 82.54; H, 9.72.

Pentacyclo[4.3.0.0^{2,5}.0^{3,8}.0^{4,7}]nonane-*4-d* (31). *tert*-Butyllithium (4.4 mmol) was added *via* syringe to 3 ml of dry ether in a flame dried flask under argon. After 30 min at −78°, 320 mg (1.6 mmol) of **9** was introduced and the solution was allowed to warm to room temperature where it became light orange in color and a white precipitate was deposited. The reaction was quenched with 1 ml of deuterium oxide. Preparative vpc purification on a 6 ft × 0.25 in. 15% Carbowax column at 125° provided 60 mg (32%) of **31.** The pmr spectrum lacked one proton from the multiplet at 3.25. The hydrocarbon affords a very weak parent ion and intense M − 1 peak. Because of this, the level of isotopic purity was difficult to establish; however, the extent of d_1 substitution was confidently estimated to be greater than 95% (pmr analysis).

4-Trideuteriomethylpentacyclo[4.3.0.0^{2,5}.0^{3,8}.0^{4,7}]nonane (32). An ethereal solution of **1** (1.3 g, 8.0 mmol) was added dropwise to

Table V. Experimental Data for the Pentacyclo[4.3.0.$0^{2,4}$.$0^{3,8}$.$0^{5,7}$]nonanes Derived from Ag^+-Catalyzed Rearrangements of the Homocubanes

Starting homocubane	Structure	Method	Time, hr (°C)	Isolated yield, %	vpc column (°C)	Pmr data, δ	Analytical data
2	**33a** (oil)	A	10 (25)	45	*a* (140)	($CDCl_3$) 3.75 (s, 2), 2.60 (m, 2), 2.05 (m, 6), 1.85 (m, 2)	Calcd for $C_{10}H_{12}O$: C, 81.04; H, 8.16. Found: C, 80.60; H, 8.10
3a	**33b** (oil)	A	10 (40)	60	*a* (120)	($CDCl_3$) 4.25 (s, 2), 2.65 (m, 2), 2.10 (m, 2), 1.85 (m, 2)	Calcd for $C_{12}H_{14}O_2$: C, 75,76; H, 7.42. Found: 75.75; H, 7.52
3b	**33c** (oil)	A	4 (40)	50	*a* (110)	($CDCl_3$) 3.50 (s, 2), 3.35 (s, 3), 2.60 (m, 2), 2.05 (m, 5), 1.85 (m, 2)	Calcd for $C_{11}H_{14}O$: 81.44; H, 8.70. Found: C, 81.28; H, 8.74
4	**33d** (mp 57–58°)	A	12 (123)	55	*b* (150)	($CDCl_3$) 3.70 (s, 3), 1.8–2.9 (series of m, 9)	Calcd for $C_{11}H_{12}O_2$: C, 74.98; H, 6.86. Found: C, 74.73; H, 6.92
5	**33e** (oil)	B	3 (40)	49	*c* (120)	(C_6D_6) 5.70–6.15 (H_x, 1), 4.83–5.18 (H_A, H_B, J_{AB} = 2.0 Hz, 2), 2.52–2.68 (m, 2), 1.77–2.27 (m, 7)	Calcd for $C_{11}H_{12}$: C, 91.61; H, 8.39. Found: C, 91.46; H, 8.43
6	**33f** (oil)	A	5 (25)	50	*d* (135)	($CDCl_3$) 2.60 (m, 2), 1.90 (m, 7), 1.30 (s, 3)	Calcd for $C_{10}H_{12}$: C, 90.85; H, 9.15. Found: C, 90.98; H, 9.11
8	**33g** (mp 87–88°)	C	20 (25)	50	*e* (75)	($CDCl_3$) 2.56 (br m, 2), 1.8–2.2 (m, 8)	*i*
11a	**33b** (oil)	B	3 (40)	50	*f* (125)	(C_6H_6) 2.70 (m, 2), 2.33 (m, 3), 2.12 (m, 2), 1.93 (m, 2). Phenyl protons were obscured by the solvent	Calcd for $C_{15}H_{14}$: C, 92.74; H, 7.26. Found: C, 92.48; H, 7.62
11b	**33i** (oil)	B	20 (40)		*c* (120)	(C_6H_6) 2.60 (m, 2), 1.94 (m, 6), 1.22 (m, 2), 0.34 (m, 4)	Calcd for $C_{12}H_{14}$: C, 91.08; H, 8.92. Found: C, 91.21; H, 9.25
11c	**33j** (oil)	B	48 (40)		*b* (100)	(C_6H_6) 2.50 (m, 2), 1.78 (m, 7), 0.94 (s, 9)	Calcd for $C_{13}H_{18}$: C, 89.59; H, 10.41. Found: C, 89.59; H, 10.36
17	**33k** (oil)	B	1 (40)		*g* (105)	(C_6H_4) 3.56 (q, J = 7 Hz, 2), 2.05–2.63 (br m, 5), 1.67–1.98 (m, 2), 1.53–1.67 (m, 2), 1.13 (t, J = 7 Hz, 3)	Calcd for $C_{11}H_{14}O$: C, 81.44; H, 8.70. Found: C, 81.38; H, 8.70
18	**33l**	B	Kinetic determinations only			(C_6H_6) 2.5 (m, 2), 2.1 (m, 3), 1.8 (m, 2), 1.55 (m, 2), 0.22 (s, 9)	*j*
19	**34a**	B	Kinetic determinations only			(CCl_4) 3.75 (center of AB, J_{AB} = 7 Hz, 4), 2.43 (m, 2), 2.13 (apparent t, J = 2 Hz, 4), 1.42 (m, 2), 1.15 (t, J = 7 Hz, 6)	*j*
20	**34b**	B	Kinetic determinations only			(C_6H_6) 2.24–2.54 (m, 2), 2.02–2.20 (m, 4), 1.28–1.40 (m, 2), 0.27 (s, 18)	*j*
24	**34c** (oil)	B	24 (40)	55	*h* (110)	(C_6H_6) 2.48 (m, 2), 1.8 (m, 4), 1.4–1.8 (m, 2), 1.12 (s, 6)	Calcd for $C_{11}H_{14}$, *m/e* 146.1095; found, 146.1098
28a	**35a** (oil)	A	3 (40)	93	*k*	(CCl_4) 4.08 (m, 1), 3.08 (s, 1), 2.40 (m, 2), 2.04 (br s, 2), 1.42–1.94 (series of m, 3), 1.37 and 1.30 (two s, total 3)	Calcd for $C_{10}H_{12}O$, *m/e* 148.0881; found, 148.0883
28b	**35b** (oil)	A	96 (40)	82	*k*	($CDCl_3$) 4.68 (m, 1), 2.54 (m, 2), 1.92 (m, 2), 1.83 (s, 3), 1.40–1.82 (m, 2), 1.30 and 1.27 (two s, total 3)	Calcd for $C_{12}H_{14}O_2$, *m/e* 190.0994; found, 190.0996
29	**35c** (oil)	A	90 (40)			(CCl_4) 2.40 (m, 2), 1.4–2.2 (m, 7), 1.36 and 1.32 (two s, total 3), 1.02 (s, 9)	Calcd for $C_{14}H_{20}O$, *m/e* 204.1514; found, 204.1513

[a] 5 ft × 0.25 in. 5% Carbowax 20 M on Chromosorb G. [b] 6 ft × 0.25 in. 20% Carbowax 20 M on Chromosorb W. [c] 13 ft × 0.25 in. 10% Carbowax 20 M on Chromosorb G. [d] 12 ft × 0.25 in. 25% PMPE 6-ring on Chromosorb W. [e] 5 ft × 0.25 in. 5% SF-96 on Chromosorb W. [f] 3 ft × 0.25 in. 10% Carbowax 20 M on Chromosorb G. [g] 6 ft × 0.25 in. 5% SE-30 on Chromosorb W. [h] 6 ft × 0.25 in. 10% UCON on Chromosorb G. [i] See ref 16. [j] Prepared independently and analyzed by Dr. Miller (see ref 7b). [k] Purified by molecular distillation at 0.1 mm.

450 mg (10.3 mmol) of lithium aluminum deuteride in the same solvent. The mixture was heated at reflux for 2 hr, cooled, and decomposed by addition of water. The usual work-up gave an oily residue which was molecularly distilled at 0.1 mm to give 470 mg (39%) of alcohol-d_2. To this material in 20 ml of dichloromethane containing 470 mg of triethylamine and cooled to −5° was added 400 mg of methanesulfonyl chloride during 10 min. After being stirred for 15 min at 0°, the mixture was poured into cold water. The organic phase was washed with cold 10% hydrochloric acid, cold saturated sodium bicarbonate solution, and cold brine. Drying and evaporation of solvent afforded 600 mg of mesylate which was dissolved in ether and added to 400 mg of lithium aluminum deuteride in ether. This mixture was refluxed for 5 hr, cooled, and decomposed by addition of 10% sodium hydroxide until a white granular precipitate formed. The dried organic layer was filtered and freed of solvent by distillation through a Vigreux column. The residue was purified by preparative vpc (12 ft × 0.25 in. 25% PMPE 6-ring column) at 105° to provide 104 mg (25%) of **32.** No methyl protons were evident in the pmr spectrum.

General Procedures for Preparative Scale Ag^+-Catalyzed Rearrangements (Table V). Method A. A solution of 50–100 mg of homocubyl derivative in 2–2.5 ml of 0.186 *M* silver perchlorate-benzene was stirred at 25-40° for several hours until completion of rearrangement. After addition of saturated brine, the benzene phase was dried and the product isolated by preparative vpc methods.

Method B. To a solution of the homocubane (15-30 mg) in benzene-d_6 (0.35 ml) contained in a pmr tube was added 10 μl of a solution of silver perchlorate in benzene (0.195 *M*). The resulting solution was heated at the appropriate temperature (tube sealed in the case of **4**) and the pmr spectrum was recorded at appropriate intervals to determine the extent of reaction. The work-up which followed was identical with that in procedure A.

Method C. The homocubane was dissolved in chloroform-*d* in a pmr tube. Approximately 2 mg of silver tetrafluoroborate was added and, upon completion of the rearrangement (pmr analysis), the solution was filtered through a small column of alumina and the product isolated by preparative vpc.

Determination of the Ag^+-6 Equilibrium Constant. All kinetic experiments were conducted in glassware which had been washed sequentially with nitric acid, distilled water, ammonium hydroxide, and distilled water. In a typical experiment, a known volume of 4-methylhomocubane (**6**) was weighed into the reaction vessel. The total volume was then brought to 0.70 ml by addition of the appropriate amount of 0.0193 *M trans*-decalin in cyclohexane. For those runs involving the highest concentration of **6**, 0.0799 *M trans*-decalin in cyclohexane was substituted for the less concentrated solution (to facilitate quantitative vpc assay). In this manner a known concentration of internal standard was introduced into the reaction mixture.

The solution was allowed to equilibrate at 40.3° and 0.30 ml of 1.01×10^{-3} *M* silver perchlorate-benzene solution was introduced, thus giving a solution 3.03×10^{-4} *M* in silver ion. The vessel was agitated to ensure complete mixing and then stoppered. Aliquots were removed at appropriate intervals and quenched by addition to saturated brine. The organic phase was separated, dried over anhydrous magnesium sulfate, and analyzed on the Hewlett-Packard instrument equipped with a 10 ft × 0.125 in. 15% PMPE 6-ring column (Chromosorb W, 65°). The isomerizations were followed to 3% conversion or less and equal molar responses to the flame ionization detector were assumed. A plot of the concentration of **33f** *vs.* time gave a straight line whose slope determined the initial rate of rearrangement.

General Procedure for the Determination of Catalytic Rate Constants by Pmr and Vpc Methods. Those procedures outlined in the preceding paper[4b] were followed without significant variation.

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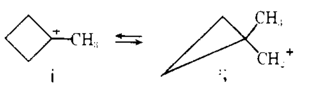

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Influence of Structural Features on the Course of Transition Metal Catalyzed 1,8-Bishomocubane Rearrangements[1]

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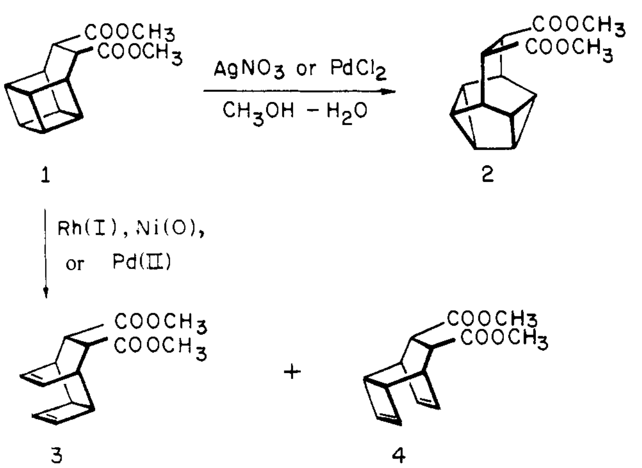
Abstract: Evidence is presented that the rearrangements of several 1,8-bishomocubane derivatives by various Rh(I) and Pd(II) catalysts are sensitive not only to the nature of the ligands attached to the metal but also to the level of substitution at the reaction site (C_4 and C_5). Thus, the level of snoutane production increases in the order $[Rh(NOR)Cl]_2 < PdI_2(PPh_3)_2 < PdCl_2(PPh_3)_2 < PdCl_2(PhCN)_2$ irrespective of the degree or nature of the bishomocubane substitution pattern. The observed effect is sometimes very large varying from 0 to 100% of snoutane during progression through this series of catalysts. This trend indicates decreased formation of snoutane as the metal ion is made softer. Also, as steric hindrance is gradually increased at the remote bishomocubyl corners, greater proportions of snoutane appear in the product mixture. The effect is significantly greater with $PdI_2(PPh_3)_2$ than for $[Rh(NOR)Cl]_2$ indicating that the palladium complex is more responsive in its catalytic action to these influences. Kinetic data point up the fact that steric retardation with $PdI_2(PPh_3)_2$ is a far more serious issue than it is with Ag(I) catalysis. The isomerizations appear to be less sensitive to electronic effects. Since the distribution of dienes derived from 9,10-disubstituted bishomocubanes is generally such that the endo isomer predominates, preferential approach from the direction proximal to these groups is kinetically favored in most (but not all) cases. Additional trends in these rearrangements are discussed.

Supplementing the previous stereochemical[4] and kinetic[5] investigation of Ag(I)-promoted bishomocubane–snoutane rearrangements, we here describe the considerably more varied behavior of such compounds toward Pd(II) and Rh(I) catalyst systems. Previously, Dauben had shown that reaction of diester **1** with $PdCl_2$ in aqueous methanol similarly led in quantitative yield to snoutane **2**.[6] However, Pd(II) complexes having ligands (*e.g.*, phosphites) which are strong π acceptors but weak σ donors were found to promote competing isomerization leading to moderate levels of **3** and **4**. With palladium complexes containing ligands of the σ donor–π acceptor type, *e.g.*, $PdI_2(PPh)_3$, essentially complete conversion to **3** and **4** was noted. The rearrangement of **1** to **3** and **4** likewise operates exclusively when $Ni(COD)_2$[8] and a series of Rh(I) complexes[6] are employed. These findings conform to earlier discoveries that Rh(I) catalysis leads to efficient cyclobutane–diolefin valence isomerization. Examples include the rearrangements of quadricyclane to norbornadiene,[9] hexamethylprismane to hexamethyl(Dewar benzene),[10] cubane to tricyclooctadiene,[11] and cuneane to semibullvalene.[12] The choice of catalysis mode is therefore seemingly predicated upon the ability of the metal ion for oxidative addition which facilitates the cyclobutane–diolefin transformation or for σ electron acceptance which favors conversion to snoutane.[6]



However, it was apparent when the present work was initiated that these mechanistic inferences had been drawn exclusively from substrates lacking substituents at the reaction site. A detailed examination of substituent effects as they affect the environment where reaction occurs, and consequently the reaction course as well, comprises the principal objective of this investigation. The only previous observation to be made on the subject of substituent influences is the response of carbomethoxycubane (**5**) to the catalytic effect of $[Rh(NOR)Cl]_2$.[11] At 40° in deuteriochloroform solution, **5** experiences isomerization to **6** and **7** at a rate 16 times slower than cubane and gives principally that diene