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Kinetic Analysis of the Silver(I)-Catalyzed 1,8-Bishomocubane–Snoutane Rearrangement[1]

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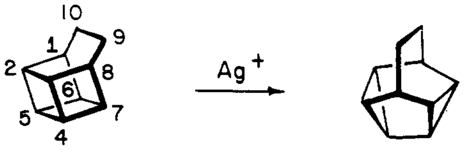
Abstract: Upon treatment with catalytic amounts of silver perchlorate in anhydrous benzene, 1,8-bishomocubanes substituted exclusively at the remote 9,10-position, at the C_4 corner, at both C_4 and C_5 and at C_2,C_3 experience clean isomerization to the structurally related snoutane in essentially quantitative yield. All reactions proceed with adherence to the second-order catalytic rate law $-d[\text{bishomocubane}]/dt = k_{Ag}[\text{bishomocubane}][AgClO_4]$. However, preequilibrium complex formation operates and it is argued that such intermediate complexation is a prelude to rearrangement rather than an inconsequential *cul de sac*. The rates of isomerization are decreased by electron-withdrawing groups and enhanced by donor substituents. Barring steric factors which give evidence of developing when both C_4 and C_5 carry functional groups, the rates can be correlated by a $\Sigma\sigma^*{}_{4\,\text{corner}}$ relationship defined by $\log (k_{Ag}/k^0{}_{Ag}) = \Sigma\sigma^*{}_{4\,\text{corner}}(\rho'^* + \rho''^*)$ where ρ'^* relates to the rate determining rearrangement step and ρ''^* to the equilibrium. From the data, it is seen that the C_4 corner substituent is not called upon at the transition state to interact directly with unit positive charge ($\Sigma\rho^* = -1.72$). Arguments are advanced which demonstrate the implausibility of concerted and oxidative additive mechanisms. Rather, the bond switching process is considered to be triggered by electrophilic attack at the C_2–C_5 bond with direct formation of a delocalized cyclopropylcarbinyl cation. Such edge argentation accounts for all available kinetic data and conforms to theoretical conclusions that attack by Ag^+ at an edge bond is energetically preferable to bidentate coordination with one of the cubyl surfaces.

In this paper we describe an investigation of the kinetics of silver(I)-promoted rearrangement of variously substituted pentacyclo[4.4.0.0^{2,5}.0^{3,8}.0^{4,7}]decanes (1,8-bishomocubanes, *e.g.*, **1**). In the course of these reactions, the four multiply fused cyclobutane rings in **1** enter into bond reorganization to provide isomeric pentacyclo[4.4.0.0^{2,4}.0^{3,8}.0^{5,7}]decanes (snoutanes, *e.g.*, **2**) constructed in part of pairs of cyclopropane and cyclopentane rings. Since **2** gives every indication of being less strained than **1**,[4] these transformations proceed in accord with prevailing relative thermodynamic stabilities. While the generality of such reactions has been rather extensively examined,[1,5] there have appeared no data concerning its kinetics. Rate data are available on related transformations of mono- and disubstituted cubanes, but, because of the very special molecular architecture of the cubane nucleus, differentiation between attack at one of the six possible faces or 12 possible edges is exceedingly intricate at best. Any detailed mechanistic analysis is thereby rendered complicated. Introduction of a 1,8-ethano bridge as in **1** (or 1,8-methano linkage as in homocubanes) serves to restrict relevant transition metal ion attack to only two surfaces ($C_{2,3,4,5}$ and $C_{4,5,6,7}$). In the parent hydrocarbon (**1**), the number of possibilities is reduced further by one-half for reasons of symmetry.



1 **2**

Current interest in these rearrangement processes has been heightened by the important question of whether relaxation of orbital symmetry constraints operates in the presence of the metal with concerted bond switching the result[5a,6] or whether one or more stepwise mechanisms play the determining role. A clear distinction between bidentate coordination[7] or edge argentation[8] by Ag^+ would similarly constitute a major advance in the field. In an effort to gain meaningful information relating to these questions, we have examined in kinetic terms the effect of substituting the bishomocubyl framework: (a) exclusively at the remote bridge (C_9,C_{10}) not involved directly in the structural reorganization; (b) at the C_4 corner with attendant dissymmetric consequences;[1] (c) at both C_4 and C_5 in order to address the question of cumulative or multiplicative rate acceleration; and (d) at C_2 and C_3 for direct comparison with the data in c.

Experiments with 9,10-Disubstituted Bishomocubanes. For the preparation of compounds **1** and **4–6**, the known diester **3** was subjected to a variety of conventional reactions (Scheme I). All end products, the pmr spectra of which are in full agreement with the structural assignments, were extensively purified prior to kinetic analysis. The $AgClO_4$-catalyzed rearrangements were conducted in anhydrous benzene solution at 40° using either pmr spectroscopy or vpc techniques to follow the progress of the reactions. The rates of isomerization of **1** and **3–6** follow the second-order catalytic rate law

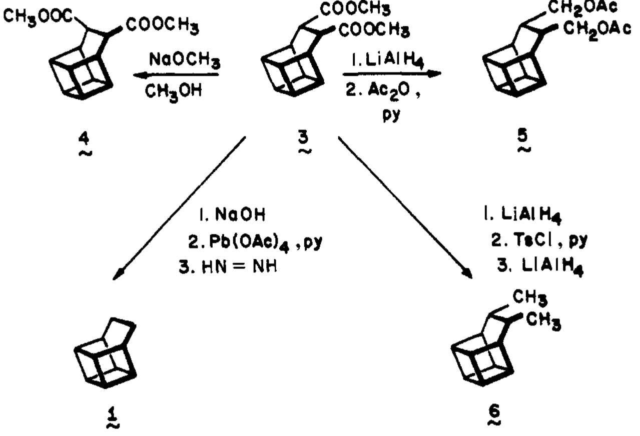
$$-d[\text{bishomocubane}]/dt = k_{Ag}[\text{bishomocubane}][AgClO_4]$$

i.e., all were cleanly first-order in both substrate and silver ion concentrations.[9] Under the conditions employed, with the bishomocubane generally in substantial excess over Ag(I), the observed kinetics were pseudo-first-order. Values of k_{Ag} as compiled in Table I were computed by least-

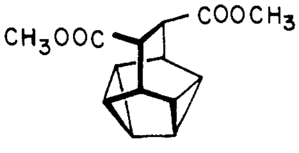
Table I. Isomerization Rate Date ($AgClO_4$, C_6H_6, 40°)

Compd	Method of analysis	k_{Ag}, M^{-1} sec^{-1}	Rel rate	$\Sigma\sigma^*_{4\ corner}$
1	Vpc	2.85×10^{-2}	24	0.78
3	Pmr	2.23×10^{-3}	1.9	1.50
4	Pmr	1.2×10^{-3}	1.0	1.50
5	Vpc	3.72×10^{-3}	3.1	1.24
6	Vpc	2.50×10^{-2}	21	0.74

Scheme I



squares methods from the slopes of first-order plots. In each instance, the related snoutane (**2**, **7**, or **8**) was produced in essentially quantitative yield. The revealing features of their pmr spectra which include proper distributions of high field cyclopropyl absorptions conform expectedly with spectra of previously available snoutanes.



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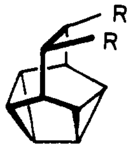


8a, R = COOCH3
b, R = CH2OAc
c, R = CH3

The rate-determining step of these rearrangements is therefore such as to involve one molecule of bishomocubane and one atom of Ag^+. Since no departures from this pattern were encountered, the formation of snoutanes may be quantitatively described by one of the following general schemes (eq 1-3). We are of the opinion that complex formation

$$\text{bishomocubane} + Ag^+ \xrightarrow[\text{(no intermediates)}]{} \text{snoutane} + Ag^+ \tag{1}$$

$$\text{bishomocubane} +$$

$$\begin{tikzcd} & \text{[complex]} \arrow[dr] & \\ Ag^+ \arrow[ur, "a", "\text{slow}"'] \arrow[dr, "b"'] & & \text{snoutane} + Ag^+ \\ & \text{[intermediate(s)]} \arrow[ur] & \end{tikzcd} \tag{2}$$

$$\text{bishomocubane} +$$

$$\begin{tikzcd} & & \text{[intermediate(s)]} \arrow[d] \\ Ag^+ \arrow[r, shift left, "k_1"] & \text{[complex]} \arrow[l, shift left, "k_{-1}"] \arrow[ur, "k_2"] \arrow[r] & \text{snoutane} + Ag^+ \end{tikzcd} \tag{3}$$

$$k_{-1} > k_2$$

cannot be rate determining (option a of eq 2). Not only are exchange phenomena involving Ag^+-benzene[11] and phosphinosilver complexes[12] known to be very rapid but interactions of Ag^+ with bicyclo[1.1.0]butanes are not kinetically limiting as well.[10] Also, complexation of the metal ion in the above examples is certain to be more favorable than expected from interaction with a bishomocubyl or homocubyl derivative. To differentiate option b of eq 2 and/or its concerted alternative (eq 1) from mechanism 3, one is required to determine rates of isomerization as a function of hydrocarbon concentration. Adherence to eq 3 would give a rate law defined by eq 4 which corresponds to a necessarily non-linear dependence of rate on concentration.[13] Thus, although a direct relationship exists between [bishomocubane] and rate at low substrate concentrations, this state of affairs gradually transmutes into a zero-order dependence at the higher concentration levels. Adherence to eq 1 and 2 would, in contrast, provide a linear plot throughout the entire concentration range. At the experimental level, one is constrained to examine hydrocarbons exclusively in this fashion since incremental increases in the concentration of more polar substrates would lead concomitantly to unwanted changes in solvent polarity. Consequently, recourse was made to basketane (**1**), and the kinetic runs were carried out in cyclohexane-benzene mixtures such that the volume per cent of benzene was the same for all runs. Although curvature in the plot of $-d[\mathbf{1}]/dt$ *vs.* [**1**] was clearly evident, it did not prove possible to obtain a reliable value for the preequilibrium constant K due to an unexplainable inadequate level of consistency in certain of the measurements. While no difficulty was encountered in obtaining satisfactory duplicate runs at low substrate concentrations, somewhat larger variations than acceptable were noted at the higher concentrations. Further study of this system was abandoned when Ward found it possible to assess the preequilibrium constant for 4-methylhomocubane as 0.19.[14]

$$-\frac{d[\text{bishomocubane}]}{dt} = \frac{k_2K[\text{bishomocubane}][AgClO_4]}{K[\text{bishomocubane}] + 1} \tag{4}$$

These findings denote in the homocubyl example, and by extension in other related molecules, that a preequilibrium process is operating. As will be discussed later, however, its direct relevance to the isomerization process should be treated with reservation, at least at present (see Discussion), in view of the possibility that the complex may be a *cul de sac*, that is

$$\text{complex} \overset{K}{\rightleftharpoons} \text{bishomocubane} + Ag^+ \xrightarrow{k_2} \text{snoutane} \tag{5}$$

No pmr spectral changes accompany incremental addition of Ag^+ to a bishomocubane such as **3** dissolved in benzene-d_6. Rather, as the concentration level of silver(I) ion is increased, only enhanced conversion to the snoutane is witnessed. This contrasts with analogous spectral titration experiments involving, for example, Ag^+ [15] and Hg^{2+} [16] with olefins and demonstrates that under our conditions there is no appreciable accumulation of either an Ag^+-bishomocubane complex or a species which may be otherwise considered a reaction intermediate.

Kinetic measurements in solvents more polar than benzene were not feasible because of the intrinsic capability of such solvents to complex competitively with Ag^+ in their own right and thereby reduce significantly the levels of "available Ag^+." No evidence for rearrangement was found when these bishomocubanes were exposed to perchloric acid; consequently, conventional acid catalysis is not operative.

The rates of rearrangement are seen to be decreased by electron-withdrawing substituents at the remote 9,10-positions (Table I). The relative kinetic order signals the importance of long range inductive effects in such systems, and we have considered the possibility that these isomerizations may be significantly affected by electronic influences at all four corners of a reactive cyclobutane face. For the bishomocubanes **1** and **3-6**, the C_2, C_3, C_6, and C_7 atoms are viewed to be substituted by C-C-R groups and the $\Sigma\sigma^*_{4\,\text{corner}}$ values are readily calculated with the knowledge that removal of a substituent by one CH_2 unit from its site of influence reduces the σ^* for that group by a factor of 0.36.[17] The values of σ^* have been taken from Taft[17] and Hine[18] with the exception of that for $-CH_2OAc$ which has been estimated recently by Koser to be +1.01.[19] As an example 2(σ^* C-C-$COOCH_3$) + 2(σ^* H) or 2(+0.26) + 2(+0.49) = +1.50. These effects may be combined as in eq 6

$$\log \frac{k_{Ag}}{k^0_{Ag}} = \Sigma\sigma^*_{4\,\text{corner}}(\rho'^* + \rho''^*) \qquad (6)$$

where ρ'^* relates to the rate-determining rearrangement step and ρ''^* to the ubiquitous preequilibrium. Both phenomena should be attenuated or accelerated by substituent modification, although not necessarily with the same logarithmic slope. The plot of log k_{Ag} *vs.* $\Sigma\sigma^*_{4\,\text{corner}}$ in Figure 1 is seen to provide a linear correlation of excellent precision (r = 0.985) with a slope $\Sigma\rho^*$ of −1.64.

At this point, it is useful to recall that whereas the two relevant cyclobutyl surfaces of **1** and **4** are identical, those in **3**, **5**, and **6** differ by virtue of the 9,10-substitution. The small difference in k_{Ag} for esters **3** and **4** suggests that inversion of configuration at C_9 has little kinetic consequence. Although our preceding stereochemical study[1] would suggest that one face of **3**, **5**, and **6** is more susceptible to attack than the other, the $\Sigma\sigma^*_{4\,\text{corner}}$ term assays only inductive contributions. Equation 6 has been simplified for the latter examples but comparable adherence to this expression can be expected, particularly since only a rather narrow range of $\Sigma\sigma^*_{4\,\text{corner}}$ values (0.74-1.50) is involved (Table I).

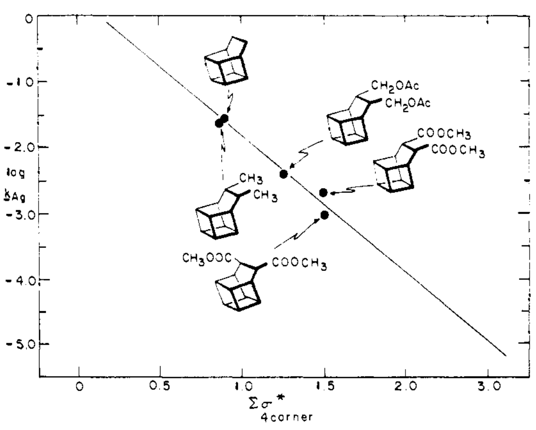


Figure 1. Correlation of log k_{Ag} with $\Sigma\sigma^*_{4\,\text{corner}}$ for **1** and **3-6**.

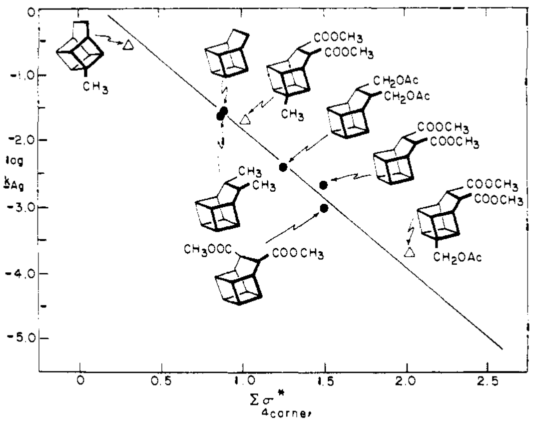
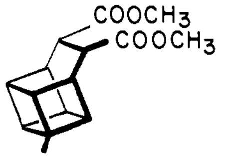


Figure 2. Extension of log $k_{Ag}/\Sigma\sigma^*_{4\,\text{corner}}$ correlation to include one corner substituent.

The Kinetic Consequences of C_4 Substitution. To develop further the correlation between the logarithms of k_{Ag} and $\Sigma\sigma^*_{4\,\text{corner}}$, the rates of Ag^+-catalyzed rearrangement of several 4-substituted bishomocubanes were examined. Compounds **9** and **10** were already available,[1] and hydrocarbon **11** was prepared by sequential hydrolysis, lead tetraacetate-promoted oxidative decarboxylation, and diimide reduction of **9**. Several attempts to expand this range of corner substituents were uniformly unsuccessful. For example, although the Diels-Alder reaction of neat methoxycyclooctatetraene (**13a**) with maleic anhydride took place at room temperature, the adduct proved very sensitive to hydrolysis and the unserviceable keto anhydride **14** was invariably obtained during purification. Cyclopropylcyclooctatetraene (**13b**), prepared in high yield by reaction of lithium dicyclopropylcopper with bromocyclooctatetraene, was converted to **15** without untoward incident, but attempts to achieve photochemical cyclization have failed. Further study of the phenyl (**16**) and carbomethoxy derivatives (**17**) was similarly thwarted by an inability to effect light induced $\pi2 + \pi2$ closure to the respective cubyl anhydrides (Scheme II).



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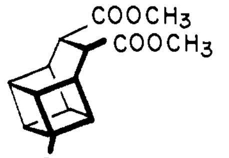

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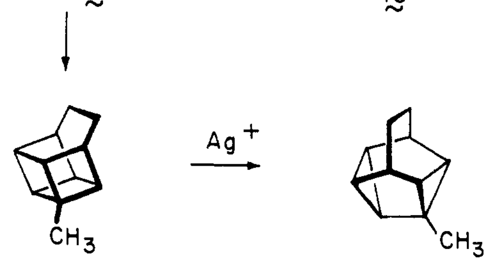

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Scheme II

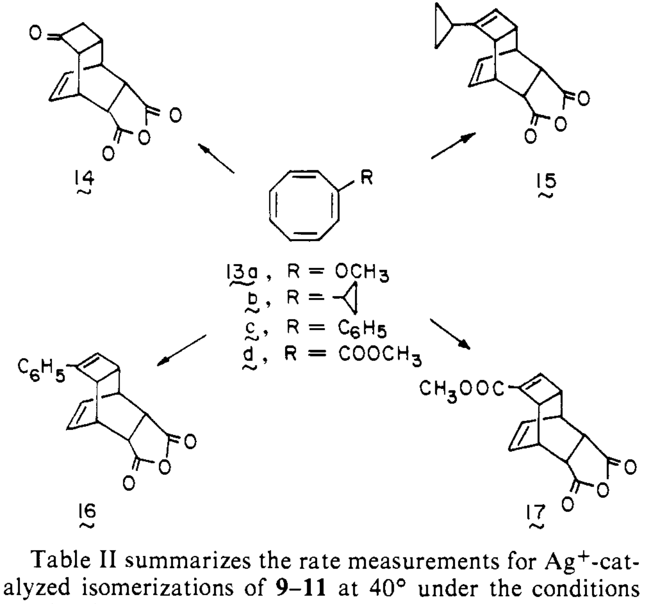


Table II summarizes the rate measurements for Ag^+-catalyzed isomerizations of **9-11** at 40° under the conditions previously described. Inspection of Figure 2 reveals that superimposition of these three additional points upon the ear-

Table II. Kinetic Data for Isomerization of C_4 Substituted Bishomocubanes ($AgClO_4$, C_6H_6, 40°)

Compd	Method of analysis	k_{Ag}, M^{-1} sec^{-1}	Rel rate[a]	$\Sigma\sigma^*_{4\ corner}$
9	Vpc	2.00×10^{-2}	16.7	+1.01
10	Pmr	3.06×10^{-4}	0.25	+2.02
11	Vpc	2.98×10^{-1}	248	+0.20

[a] k_{rel} for 4 = 1.0.

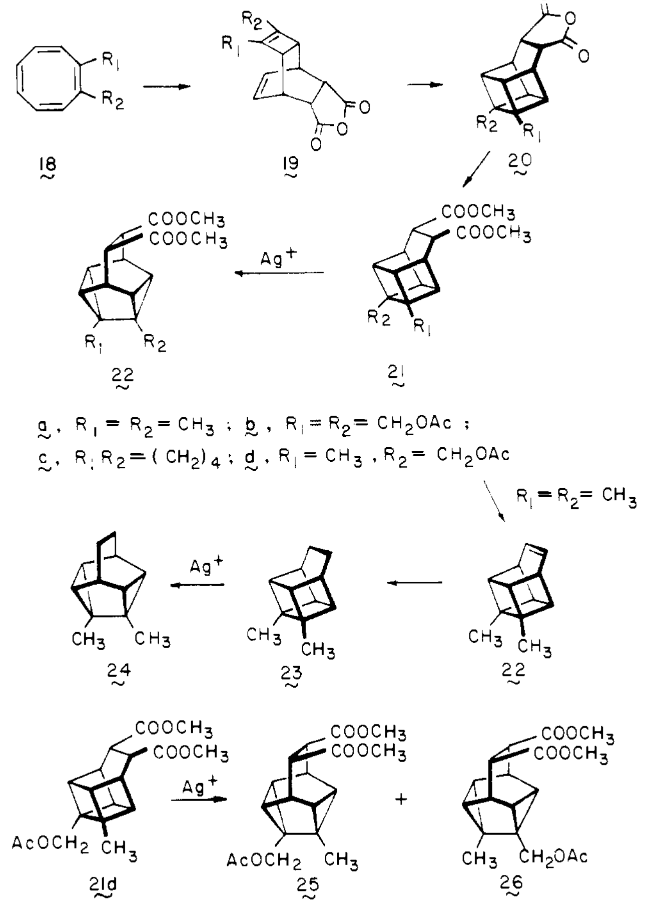
lier data does not result in significant deviation from the existing straight line. The correlation coefficient (0.987) remains highly acceptable and the least-squares slope ($\Sigma\rho^*$) defined by the eight points is only slightly more negative (−1.72). Obviously, therefore, the data remain correlatable under the terms of eq 6; several important trends are thereby unveiled. Firstly, methyl substitution at C_4 in **3** (giving **9**) and in **1** (leading to **11**) serves to promote acceleration of these isomerization reactions by a factor of 9–10. Also, in that pair of examples (**3** and **10**) which permits evaluation of the effect of C_4-CH_2OAc substitution, a sevenfold rate retardation is evidenced. On the basis of the $\Sigma\rho^*$ value of −1.72, it would appear that the corner substituent is not called upon at the rate determining transition state to interact directly with *unit* positive charge as, for example, that approaching full carbonium ion character on the adjacent carbon atom. Were this the case, a more highly negative ρ^* value would be expected if those reactions and equilibrium processes which result in development of cationic character at an immediately neighboring position are valid analogies (average ρ^* of −3.3 to −4.3).[17,20] Rather, the observed polar substituent effect is closer in magnitude to the ρ^* values of approximately 1.7 (sign dependent upon sign of charge) observed for equilibria in which unit formal charge is produced on an atom two atoms removed from the substituent.[17,21] However, this similarity may be quite fortuitous since $\Sigma\rho^*$ may actually comprise a composite value of kinetic and equilibrium ρ^* values if complex formation is a prelude to rearrangement. Given this conformity to eq 6, the two parameters should be additive and reinforcing in the same direction. In a recent assessment of electronic contributions by substituents on the argentation equilibria of alkenyl alkyl ethers, Fueno and coworkers plotted log K *vs.* σ_m and realized a linear correlation with the enormously negative slope (ρ) of −5.07.[22] In actuality, therefore, the kinetic ρ^* term could be more positive than −1.72, although it is not possible on the basis of the present data to estimate what this value might be. Notwithstanding, several different limiting descriptions of the rate-determining transition state to the title rearrangement can now be envisaged which accommodate the above data (see Discussion Section).

Exhaustive Substitution of the Remote Bishomocubyl Corners (C_4 and C_5). Comparison of the rates of isomerization of 4-substituted bishomocubanes with unsubstituted and 4,5-disubstituted derivatives bearing like functionality on the bridge (C_9 and C_{10}) should in principle permit resolution of the question surrounding involvement of one or both corner sites in the rate limiting step. Were the rearrangement concerted or dependent upon comparable levels of metal ion coordination simultaneously at C_4 and C_5, a multiplicative rate acceleration (electron donor substituents) or deceleration (electronegative groups) should result since the two relevant sites would be equally affected. Such equal sharing between the two appended substituents will so stabilize the transition state that the observed rate factor should be approximately the square of the kinetic enhancement or retardation found for the single substituent. Cumulative acceleration effects of this type, promoted in particular by methyl substitution, have previously been described for solvolysis reactions of Δ^3-cyclopentenylethyl,[23] β-arylalkyl,[24a] and *anti*-7-norbornenyl derivatives,[24b] peracetic acid oxidations of alkenes,[25] brominations of olefins,[26] and carbene additions to double bonds.[27]

Contrariwise, if bond switching is assisted exclusively or principally by a single substituent as for example in a stepwise process, the difference in rates between the mono- and disubstituted bishomocubanes should be twofold, the additive effect arising from the mere statistical doubling of reaction sites. This very different substitution effect has been witnessed in the solvolytic behavior of 1,4-dihydrobenzyl tosylates where primary assistance to ionization comes from only one of the two double bonds[28] and in the acid-catalyzed hydration of simple alkenes where the rate-determining step involves protonation to give classical carbonium ions.[29]

Of the five 4,5-disubstituted bishomocubanes examined, four (**21a–d**) contain cis disposed carbomethoxy groups at C_9C_{10}; dimethylbasketane **23** was the unique hydrocarbon of this subset. All were prepared by the now conventional route which is outlined in Scheme III. In each instance, preparative scale Ag(I)-catalyzed rearrangement of **21a–c** and **23** was found to give rise in high yield to single snoutane isomers, the structural identities of which were established spectroscopically and by elemental analysis (see Experimental Section). Owing to the less symmetrical nature of **21d**, its isomerization led to two snoutanes (**25** and **26**) in a ratio of approximately 60:40 (pmr analysis). Because of limited quantities of this material, these products were not separated, and no specific formulation beyond **25** or **26** is advanced for the major component.

Scheme III



In all cases, good pseudo-first-order kinetic behavior obtained under the conditions employed. The catalytic rate constants for overall conversion to snoutanes (k_{Ag}) were

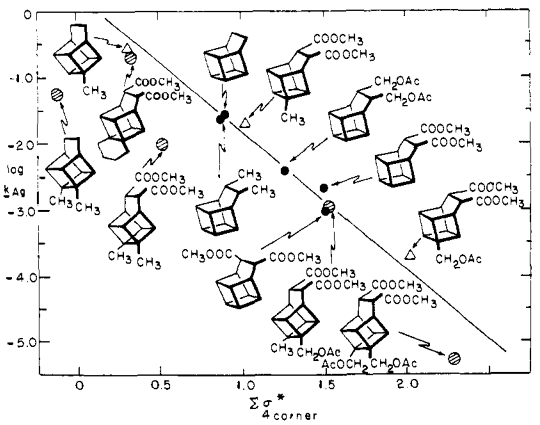


Figure 3. Composite correlation of log k_{Ag} with $\Sigma\sigma^*_{4\,corner}$ for the variously substituted bishomocubanes.

again measured at 40° using silver perchlorate in anhydrous benzene (Table III). It was immediately clear from inspection of the kinetic data and Figure 3 that neither of the predescribed conditions apply. For example, whereas C_4 methyl substitution of cis diester **3** to give **9** results in a ninefold kinetic acceleration, the 4,5-dimethyl derivative **21a** isomerizes at a rate 0.45 times that of **9**! The same reactivity is evidenced for the hydrocarbons basketane (**1**), 4-methylbasketane (**11**), and 4,5-dimethylbasketane (**23**) which rearrange with relative catalytic rate constants of 1.0:10.4:1.9, respectively. Further evidence to the fact that the 4,5-disubstituted bishomocubanes undergo bond switching more slowly than expected comes from the behavior of the bis(acetoxymethyl) derivative **21b**. We have already indicated that one acetoxymethyl group causes a rate retardation of 7.29 (compare **3** and **10**). In the context of a multiplicative kinetic situation, **21b** should isomerize at a rate some $(7.29)^2 = 53.1$ times slower than **3**. Additive kinetic influences project a rate retardation of approximately 15. Actually, a 412-fold deceleration prevails. This lack of adherence by **21a**, **21b**, and **23** to eq 6 is understandable on the basis of steric factors which now impede the requisite approach of Ag^+ ion to either of the two cubyl surfaces or, more specifically, to the environment of C_4 and C_5. The net effect is to displace the catalytic rate constants of these bishomocubanes well below the line defined by the previous $\Sigma\rho^*$ slope (see Figure 3).

Whereas the behavior of **21a** is such that only a fourfold acceleration is observed relative to **3**, the tetramethylene bridged derivative **21c** undergoes quantitative conversion to snoutane **22c** at a rate 100 times faster than **3**. We presently attribute this enhanced rate of isomerization of **21c** to a diminution of steric factors resulting from annulation, to an increase in ground state strain engendered by the additional ring, or to a combination of these two factors.

The situation where the corner substituents are methyl and acetoxymethyl (*cf.* **21d**) is an interesting one. Under normal circumstances, the contribution of the methyl group should be enhancing by a factor of approximately 9, *i.e.*, $k_{Ag}(\mathbf{9})/k_{Ag}(\mathbf{3})$. The acetoxymethyl group, on the other hand, is rate retarding and with **10** as the point of reference this deceleration should be on the order of 7. Assuming an additive substituent effect, **21d** should isomerize more slowly than **3** by a factor of about 1.5. As shown in Table III, **21d** actually rearranges 2.1 times slower than **3** and is the 4,5-disubstituted compound whose rate conforms best to the slope previously established (Figure 3). When the group of five compounds defined by **21a–d** and **23** is analyzed as an isolated subset according to eq 6, least-squares analysis provides a line of slope −1.56 having a correlation coefficient of 0.946. However, as already seen, a number of factors do not remain constant in this series, and a linear function is not to be expected. This point is brought home more clearly when these data are incorporated with the rate constants measured in the earlier phases of this study. That the restrictions produced by 4,5-disubstitution generally result in substantial kinetic deviations is clear from the poor *r* value (0.926) obtained from the entire data set of 13 points ($\Sigma\rho^* = -1.56$).

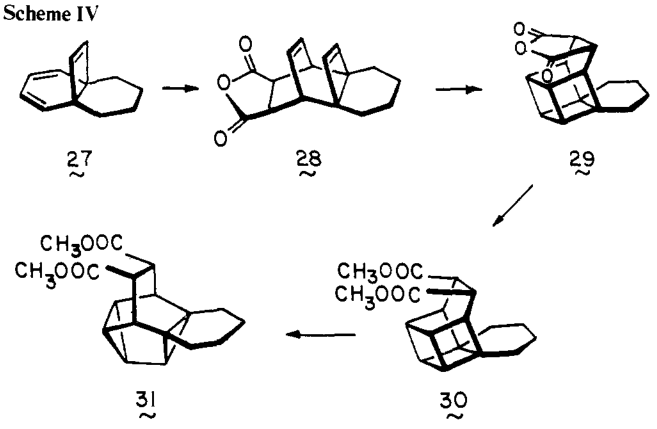
Table III. Kinetic Data for Isomerization of C_4,C_5 Disubstituted Bishomocubanes ($AgClO_4$, C_6H_6, 40°)

Compd	Method of analysis	k_{Ag}, M^{-1} sec^{-1}	Rel rate[a]	$\Sigma\sigma^*_{4\,corner}$
21a	Vpc	9.07×10^{-3}	7.6	+0.52
21b	Pmr	5.41×10^{-6}	0.0045	+2.54
21c	Vpc	2.31×10^{-1}	193	+0.32
21d	Pmr	1.04×10^{-3}	0.87	+1.53
23	Vpc	5.41×10^{-2}	45	+0.20

[a] k_{rel} for **4** = 1.0.

Synthesis and Isomerization of a 2,3-Annulated Bishomocubane. We have inferred from results described in the previous section that the kinetic behavior of the 4,5-tetramethylene derivative **21c** is seemingly anomalous. Consideration of possible pathways for the bishomocubyl to snoutane rearrangement (see Discussion) led us to undertake the preparation of an isomer of **21c** in which the additional ring is transposed from C_4,C_5 to two other corners of the cubyl surface, *viz.*, the C_2 and C_3 positions. The desired diester (**30**) was synthesized conveniently by Diels–Alder cycloaddition of maleic anhydride to [4.4.2]propella-2,4,11-triene (**27**) which proceeds *via* endo attack[30] to furnish anhydride **28**. Confirmation of adduct stereochemistry was achieved by sensitized photocyclization in acetone solution with formation of **29**. Methanolysis and diazomethane esterification of this anhydride completed the sequence (Scheme IV).

Scheme IV



Silver perchlorate-catalyzed rearrangement of **30** in anhydrous benzene at 40° proceeded with a catalytic rate constant (k_{Ag}) of 3.76×10^{-4} M^{-1} sec^{-1} (vpc method) to give exclusively the snoutane **31**. Consequently, the following kinetic interrelationships hold

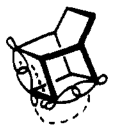
$$k_{Ag}(\mathbf{30}) = 0.17k_{Ag}(\mathbf{3})$$

$$k_{Ag}(\mathbf{21c}) = 104k_{Ag}(\mathbf{3}) = 614k_{Ag}(\mathbf{30})$$

Not only is the enhanced driving force to rearrangement found for **21c** lacking but **30** also isomerizes almost six times *less rapidly* than **3**. The first finding is not surprising and would appear to provide convincing evidence that much of the electron deficiency which develops during rearrangement occurs at C_4 and/or C_5 such that these sites are the most sensitive to substituent alteration. The causative factors underlying the sixfold slower isomerization rate of **30** relative to **3** are less obvious. We are of the opinion that approach of Ag^+ toward the $C_{2,3,4,5}$ surface of **30** and particularly toward the C_2 and C_3 corners of this cyclobutane ring will be seriously impeded for obvious steric reasons. If approach to the two available surfaces of parent diester **3** by Ag^+ were equally facile, then steric blockade of one of these avenues as in the case of **30** should result in halving of the original catalytic rate constant. However, symmetry considerations require that the cis oriented carbomethoxy groups at positions 9 and 10 generate interactions which create an imbalance in the reactivity levels of the two cubyl faces of **3**. If the kinetic behavior of **30** can be taken as prototypical for 2,3-disubstituted bishomocubyl diesters, then the sixfold rate reduction could be ascribed to a generally more effective approach of Ag^+ from that direction anti to the ester groups in sterically unconstrained situations.

Discussion

The Implausibility of a Concerted Mechanism. Four extreme possibilities can be delineated for the mechanism of Ag^+-catalyzed cubyl rearrangements. One of these, the concerted alternative, has been the subject of much theoretical speculation because of the possibility that such isomerizations could represent examples of symmetry-forbidden processes which become allowed as a result of orbital interaction with the metal. In the first paper of this series,[5a] we pointed out that if conventional restraints to thermal bond reorganization are contravened in this manner, the requisite geometric changes could take place formally by way of the $_{\sigma}2_a + {}_{\sigma}2_a$ electrocyclic reaction illustrated by **32**. However, the hypothetical concerted process need not be restricted to this specific interaction, since the allowed pericyclic $_{\sigma}2_s + {}_{\sigma}2_s + {}_{\sigma}2_s$ transformation epitomized by **33** can likewise account for the structural change.[31] In particular, note should be taken of the fact that the double inversion in **32** and the triple retention in **33** are not distinguishable on the basis of ultimate stereospecificity. In terms of requisite metal perturbation, however, they are widely different. Model **32** requires that the silver ion interact with an edge bond *other than the C_4,C_5 linkage* with probable involvement of both forward coordination and back-donation between the C–C σ bonding and antibonding orbitals and the atomic orbitals of Ag^+ in a fashion analogous to that proposed by Chatt for C–C π bond complexation with silver ion.[32,33] In **33**, perturbation by the metal is necessarily directed to the C_4,C_5 bond. Relaxation of strain at this center by simple charge transfer with development of higher p character in the σ bond could be accompanied by resultant weakening and provide snoutane by synchronous spatial orientation (as shown).



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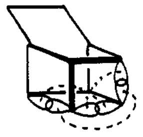

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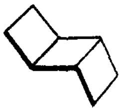
Experimentally, model **33** does not conform to the observed influence of alkyl substitution on the rate of isomerization. If interaction of Ag^+ with the C_4,C_5 bond were a necessary prelude to bond switching, then substitution at these positions with a methyl group as in **9** or **11**, two methyl groups as in **21a** and **23**, or a tetramethylene chain (**21c**) would not be expected to result in kinetic acceleration as is evidenced. In fact, the additional bracket in **21c** is seemingly adequate to deter all approach to the C_4,C_5 bond. Yet this ester isomerizes 100 times faster than **3**. Additionally, the 2,3-tetramethylene bishomocubyl diester (**30**) which is so constructed as to permit relatively unconstrained access to the C_4,C_5 bond is more than 600 times less reactive than isomer **21c**.

The operation of a concerted mechanism akin to **32** is more difficult to rule out rigorously on the basis of the experiments reported herein. However, data on homocubanes to be described in a companion paper[14b] and other pieces of circumstantial evidence make this mechanism also quite unlikely. (1) If rearrangement is concerted, the rate determining step should be minimally affected by alterations in the electronic nature of the substituent, and it then becomes difficult on this basis to understand the source of the appreciable rate enhancements witnessed for those C_4 groups such as phenyl, cyclopropyl, vinyl, ethoxy, and the like, which are capable of resonance interaction with a cationic center. (2) These rearrangements may be conducted in alcoholic or aqueous alcoholic media without solvent entrapment of intermediates,[30a,c,34] and it may be argued that they consequently bear the mark of concerted processes. Obviously, this conclusion does not necessarily follow since an ionic mechanism would simply require that rearrangement of intermediate carbocations be fast with respect to their reactions with solvent. In fact, this precise situation prevails in the stepwise Ag^+-promoted ionic rearrangements of bicyclo[1.1.0]butanes[10,35] where supportive evidence for ionic processes was originally claimed on the basis of methyl ether formation in methanol solution.[36] Later, however, ether formation was shown to be a side reaction having no bearing *per se* on the isomerization mechanisms.[37] (3) Pettit and coworkers have observed *anti*-tricyclooctane (**34**) to be totally inert toward silver fluoroborate in acetone at 56° for 5 days.[38] In contrast, syn isomer **35** is completely isomerized in approximately 1 min under identical conditions. The reactivity of **35** was attributed to a concerted bond migration resulting from Ag^+–hydrocarbon interaction as in **36**. The fact that **34** is inert toward Ag^+ was taken as substantiation of the concerted nature of this reaction because these workers were of the opinion that a stepwise carbonium ion pathway should not discriminate between the two systems. However, Gleiter, Heilbronner, and coworkers[39] have recently demonstrated by photoelectron spectroscopy that the high-lying σ orbitals of **34** and **35** have quite different electronic properties such that their primary interactions with Ag^+ could well be widely divergent. Consequently, their differing response to the action of Ag^+ can be interpreted in terms other than concertedness.



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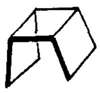

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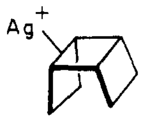


36

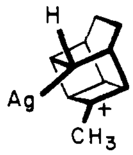
Consideration of the Oxidative Addition Pathway. Eaton and Halpern were the first to suggest the possibility that the action of Ag(I) may parallel that of rhodium(I) and promote skeletal rearrangement by initial insertion into a σ bond to yield a dialkylsilver(III) derivative which then experiences stepwise conversion to the related biscyclopropane derivative.[40] The same concept has also been invoked recently to account for Ag^+-catalyzed quadricyclane rearrangements.[41] Pettit has argued against such a scheme,[38] claiming that there is little driving force for silver to attain a formal oxidation state of +3. We share this latter opinion.

Examination of the energy requirements for the $(n - 1)$d

→ *n*p transition of Rh(I) (~1.60 eV) and Ag(I) (9.94 eV)[42] reveals an enormous difference in promotion energy between the two metals. Also, whereas rhodium is known to form a wide range of stable Rh(III) complexes with various ligands, compounds of the Ag(III) oxidation state are very rare.[43] Even silver alkyls are notoriously unstable and must be considered as high energy species in their own right.[44]

Given these clear indications of high endothermicity for the involvement of Ag(III) species, it seems rather improbable that complete insertion of Ag^+ into a bishomocubyl edge bond is operating as the rate determining step. Rather, the strong oxidizing character of silver(I), which compares favorably to that of thallium(III), can be expected to be the dominant feature and to promote bond heterolysis with generation of intermediate carbonium ions.[8]

The Electrophilic Ring Opening Process and the Question of Site Selectivity. All considerations of electrophilic C_4-C_5 bond cleavage can be immediately dismissed because the cationic intermediate so produced cannot reasonably rearrange to snoutane product. The reactivity of **21c** serves as the experimental basis for rejection of this pathway as well. In a symmetrical bishomocubane such as **1**, the reaction centers of consequence are seen to be the four equivalent edge bonds labeled C_2-C_5, C_3-C_4, C_4-C_7, and C_5-C_6. When this nucleus is substituted with a methyl group at C_4 as in **11**, the resulting structural perturbation is such that two quite different pairs of σ bonds are presented to the Ag^+ catalyst. Whereas attack at the more extensively substituted C_3-C_4 or C_4-C_7 sites would lead to 1-substituted cyclobutyl carbonium ion **37** or its delocalized counterpart **38**, heterolytic cleavage of the C_2-C_5 or C_5-C_6 bonds would likely provide the cyclopropylcarbinyl system **39**. The electrophilic ring opening is viewed as proceeding uniformly with retention of configuration at the metal bonded carbon and conforms to the stereochemistry anticipated for electron transfer within the Ag^+-σ bond complex.[33]



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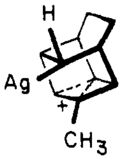

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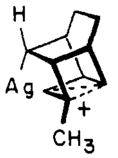


39

At issue of course is the question of which bond rupture is preferred kinetically. The experimental facts are that **11** rearranges 10.4 times faster than **1** and that correspondence with the terms of eq 6 is maintained. This correlatibility implies that the transition state has little resemblance to a 1-substituted cyclobutyl cation such as **37** where resonance effects would have greater impact[14] and a more negative ρ^* should present itself. Owing to the paucity of kinetic data on metal catalyzed rearrangements, it becomes necessary to make recourse to more conventional systems for rate comparisons. Evidence has been presented by Roberts which reveals that 1-methyl substitution of cyclobutyl 3,5-dinitrobenzoate gives rise to a tenfold level of kinetic acceleration.[45] An equally important comparison is that of various methylcyclopropylcarbinyl derivatives with the parent system, for the derived transition state structures could be indicators of the extent of methyl stabilization to be expected in **38** and **39**. Schleyer has noted that the ring methyl groups have a remarkably constant enhancing effect; in addition, the influence is multiplicative, each additional alkyl substituent increasing the rate independent of the number and location of its neighbors.[46] As a consequence of the near identical rate enhancements in the two series, it becomes immediately obvious that the methyl group is not a probe of sufficient capability to resolve alone the question of site selectivity. Those synthetic difficulties outlined earlier have precluded access to more highly varied C_4 substituted bishomocubanes. This problem could be circumvented in the homocubyl series and evidence subsequently accummulated in favor of **39**. However, further discussion of this point is deferred to that paper.[14b]

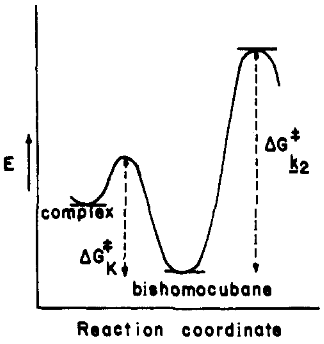


Figure 4. Reaction profile for inconsequential complex formation.

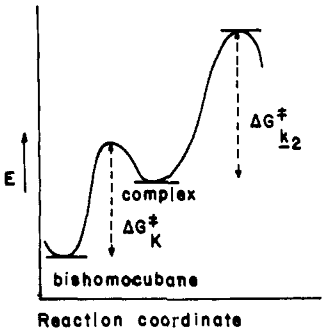
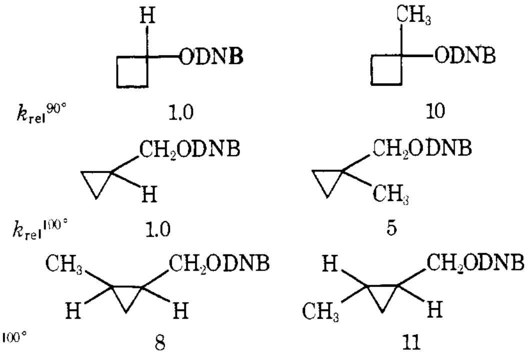
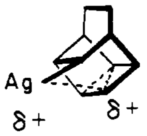


Figure 5. Reaction profile for intermediate complexation as a prelude to rearrangement.



The question now arises as to why 4,5-dimethyl substitution as in **21a** and **23** alters the kinetic profile in the observed manner. In terms of a stepwise mechanism, the rates of rearrangement of these bishomocubanes should be double (twice the probability) that of **9** and **11**, respectively, barring complicating factors such as increased steric interference to complexation. But **23** isomerizes 11 times more slowly than the extrapolated value and the factor for **21a** is only 4.4 times less rapid. In our estimation, these differences can be explained by changes in the magnitude of the preequilibrium constant *K* (see eq 6), its absolute value decreasing in proportion to the level of substitution.[47] This working hypothesis suggests that the preequilibrium is an integral part of the bond switching process and not associated with irrelevant complexation. The two mechanisms have differing reaction coordinates as seen in Figures 4 and 5. If the preequilibrium were a true *cul de sac*, the free energy term for rearrangement would derive from the ground state bishomocubane → transition state gap. The alternative situation is such that $\Delta G^*_{k_2}$ is determined from the energy level of the intervening complex. While the present data do not rigorously rule out operation of the mechanism defined by Figure 4, the relative kinetic order can best be rationalized in terms of the interrelationship of K and k_2 denoted by Figure 5.[48]

Finally, we note that the results from this study are in agreement with the suggestion advanced on theoretical grounds by Lehn and Wipff[49] that bond switching is initiated as a consequence of edge-on Ag^+ attack at the appropriate strained σ bond, a process referred to by us as edge argentation.[8] Symmetrical bidentate interaction with one of the cubyl surfaces[7] does not appear to direct the course of these Ag(I)-catalyzed reactions. Rupture of the complexed bond so as to position silver other than at C_4 or C_5 can then lead *via* cyclopropylcarbinyl rearrangement pathways and ultimate ejection of Ag^+ to snoutane product. But if electrophilic attack is concentrated at one edge bond, how does one explain the kinetic dependence on $\Sigma\sigma^*_{4\ \mathrm{corner}}$? We reason that because relaxation of the enormous strain inherent in the bishomocubyl system is quite apt to occur in the transition state and that a ready mechanism to achieve this is delocalization of the C_4C_7 electron pair as rupture of the C_2C_5 bond commences (see **40**), four corner atoms do simultaneously become intricately involved in positive charge dissipation at the rate-determining step. The unique and amusing aspect of this model is that the carbon atom foursome does not describe a cubyl surface but a portion of the perimeter.



40

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 aid of Hewlett-Packard 5750 unit (flame ionization detector) equipped with an electronic integrator.

Dimethyl *trans*-Pentacyclo[4.4.0.0^{2,5}.0^{3,8}.0^{4,7}]decane-9,10-dicarboxylate (4). To 20 ml of methanol was added a small pea of sodium. After the metal had reacted, 910 mg (3.67 mmol) of **3**[5c,d] was introduced and the solution was refluxed with protection from atmospheric moisture for 16 hr. The major portion of the solvent was removed *in vacuo*. Water and ether were added, and the organic phase was separated, washed with water, and dried. Evaporation left 880 mg (96.5%) of **4**, recrystallization of which from methanol gave white blades: mp 58.5-59°; δ_{TMS} ($CDCl_3$) 3.69 (s, 6), 2.90-3.45 (m, 10).

Anal. Calcd for $C_{14}H_{16}O_4$: C, 67.73; H, 6.50. Found: C, 67.68; H, 6.37.

***cis*-9,10-Bis(hydroxymethyl)pentacyclo[4.4.0.0^{2,5}.0^{3,8}.0^{4,7}]decane. A. Reduction of the Anhydride.** To a stirred slurry of 174 mg (4.5 mmol) of lithium aluminum hydride in 10 ml of anhydrous tetrahydrofuran was added 615 mg (3.0 mmol) of the bishomocubyl anhydride and the mixture was heated at reflux for 5 hr. Hydrolysis was achieved with a minimum of saturated aqueous ammonium chloride solution, and the aluminum salts were washed well with ether after filtration. Recrystallization of the organic residue from hexane gave 411 mg (71%) of white flakes, mp 104-110°. Further recrystallization from this solvent raised the mp to 108-110°: δ_{TMS} ($CDCl_3$) 4.18 (br s, 2), 3.58-3.92 (m, 4), 2.92-3.40 (m, 6), 2.50-2.88 (m, 2), 1.92-2.23 (m, 2).

Anal. Calcd for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39. Found: C, 74.85; H, 8.30.

B. Reduction of Diester 5. Reduction of 746 mg (3.0 mmol) of **3** with 176 mg (4.5 mmol) of lithium aluminum hydride in ether solvent (16 ml) according to the above procedure afforded 272 mg (47%) of diol, mp 104-110°, which was identical with the previous sample.

***cis*-9,10-Bis(acetoxymethyl)pentacyclo[4.4.0.0^{2,5}.0^{3,8}.0^{4,7}]decane (5).** A solution of 400 mg (2.08 mmol) of the diol in 5 ml of anhydrous pyridine and 3 ml of acetic anhydride was heated for 1.5 hr at 110° and allowed to stand overnight. The mixture was poured into 50 ml of cold water and extracted with ether (three 25-ml portions). The combined organic layers were washed with 3 *M* hydrochloric acid, water, and saturated sodium bicarbonate solution. Evaporation of the dried ether solution gave a clear oil which crystallized from pentane at −30° as white needles: mp 45-46° (457 mg, 80%); δ_{TMS} ($CDCl_3$) 4.15-4.38 (m, 4), 3.10-3.50 (m, 6), 2.72-3.10 (m, 2), 2.38-2.57 (m, 2), 2.20 (s, 6).

Anal. Calcd for $C_{16}H_{20}O_4$: C, 69.55; H, 7.30. Found: C, 69.76; H, 7.30.

***cis*-9,10-Bis(*p*-toluenesulfonyloxymethyl)pentacyclo[4.4.0.0^{2,5}.0^{3,8}.0^{4,7}]decane.** A solution of 1.915 g (10.1 mmol) of *p*-toluenesulfonyl chloride in 10 ml of anhydrous pyridine was treated with 449 mg (2.34 mmol) of diol and the mixture was refrigerated for 6 days. After pouring onto ice and water, there was deposited a solid which was filtered, washed well with water, and dried (436 mg, mp 95-120°). The product dissolved in benzene (15 ml) was decolorized with charcoal and crystallized by slowly adding 50 ml of hexane as the solution was refluxed. Cooling caused crystallization of shiny plates: mp 136-138° (238 mg, 35%); δ_{TMS} ($CDCl_3$) 7.75 (AB m, 8), 3.83-4.10 (m, 4), 2.55-3.30 (m, 8), 2.43 (s, 6), 1.87-2.22 (m, 2).

Anal. Calcd for $C_{26}H_{28}O_6S_2$: C, 62.38; H, 5.64. Found: C, 62.66; H, 5.57.

***cis*-9,10-Dimethylpentacyclo[4.4.0.0^{2,5}.0^{3,8}.0^{4,7}]decane (6).** A 173-mg portion of the ditosylate (0.35 mmol) was heated at reflux with 89 mg (2.3 mmol) of lithium aluminum hydride in 8 ml of ether for 16 hr. Work-up as previously described gave an oil which was purified by preparative gas chromatography (5 ft × 0.25 in. 5% SE-30 on Chromosorb G at 110°) to give 31 mg (56%) of **6**: δ_{TMS} ($CDCl_3$) 2.88-3.33 (m, 6), 2.30-2.63 (m, 2), 1.58-1.98 (m, 2), 0.70-0.95 (m, 6).

Anal. Calcd for $C_{12}H_{16}$: C, 89.94; H, 10.06. Found: C, 89.75; H, 9.95.

Snoutane, Pentacyclo[4.4.0.0^{2,4}.0^{3,8}.0^{5,7}]decane (2). A solution of **1** (25 mg) in benzene (0.6 ml) was treated with 50 μl of 0.195 *M* silver perchlorate in benzene and heated at 40° for 7.5 hr (>10 half-lives). The cooled solution was diluted with pentane and washed with brine and water. The organic layer was dried and the product was purified by preparative vpc (6 ft × 0.25 in. SE-30). There was obtained 20 mg of **2** as a white solid: mp 93.5° (sealed tube); δ_{TMS} ($CDCl_3$) 2.28-2.46 (m, 2), 1.37-1.77 (series of m, 10).

Anal. Calcd for $C_{10}H_{12}$: C, 90.85; H, 9.15. Found: C, 90.72; H, 9.10.

Dimethyl *trans*-Pentacyclo[4.4.0.0^{2,4}.0^{3,8}.0^{5,7}]decane-9,10-dicarboxylate (7). An 87-mg sample of **4** was added to a solution of silver perchlorate in benzene (1.0 ml of 0.195 *M*) and the mixture was heated at 40° for 15 hr (>10 half-lives), cooled, diluted with ether, and washed with brine and water. The organic layer was dried and evaporated to give 85 mg of an oil which crystallized. Recrystallization from isooctane gave **7** as white crystals: mp 77.0-78.0°; δ_{TMS} ($CDCl_3$) 3.72 (s, 6), 3.22-3.32 (m, 2), 2.72-3.00 (m, 2), 1.17-2.00 (m, 6).

Anal. Calcd for $C_{14}H_{16}O_4$: C, 67.73; H, 6.50. Found: C, 67.80; H, 6.61.

***cis*-9,10-Bis(acetoxymethyl)pentacyclo[4.4.0.0^{2,4}.0^{3,8}.0^{5,7}]decane (8b).** To a rapidly stirred slurry of 112 mg (0.58 mmol) of silver fluoroborate and 3 ml of chloroform was added 101 mg (0.37 mmol) of **5**. This mixture was stirred for 20 min at room temperature, diluted with 3 ml of carbon tetrachloride, and eluted through a short column of silica gel. Evaporation of the eluate gave **8b** as a crystalline material which was recrystallized from pentane (5 ml) at 0 to −55° and obtained as shiny plates: mp 35-37°; δ_{TMS} ($CDCl_3$) 4.12-4.35 (m, 4), 2.18-2.55 (m, 4), 2.08 (s, 6), 1.28-1.90 (m, 6).

Anal. Calcd for $C_{16}H_{20}O_4$: C, 69.55; H, 7.30. Found: C, 69.29; H, 7.26.

***cis*-9,10-Dimethylpentacyclo[4.4.0.$0^{2,4}$.$0^{3,8}$.$0^{5,7}$]decane (8c).** A solution of 71 mg (0.44 mmol) of **6** in 3 ml of 0.0051 *M* silver perchlorate in benzene was sealed in a vial and heated in a water bath at 40.0° for 18.5 hr (*ca.* 12 half-lives). The reaction mixture was washed with an equal volume of brine and partially concentrated after drying. Pure **8c** was obtained by vpc purification (5 ft × 0.25 in. 25% PMPE 6-ring on Chromosorb W, 40°) as a clear oil (39 mg, 55%); δ_{TMS} ($CDCl_3$) 1.82-2.25 (m, 4), 1.25-1.82 (m, 6), 0.88 (br d, J = 6.5 Hz, 3).

Anal. Calcd for $C_{12}H_{16}$: C, 89.94; H, 10.06. Found: C, 89.73; H, 9.92.

4-Methylpentacyclo[4.4.0.$0^{2,5}$.$0^{3,8}$.$0^{4,7}$]dec-9-ene. To a 3.0-g sample of **9**[1] was added sodium hydroxide (2.16 g) in water (100 ml). The resulting mixture was heated at 90° until a homogeneous solution was obtained. The cooled solution was acidified, extracted with dichloromethane, dried, and concentrated. Treatment of the residue with hexane afforded 1.61 g (6.9 mmol) of crude diacid which was not further purified.

Oxygen was bubbled through a solution of this diacid in pyridine (20 ml) for 15 min. After dried lead tetraacetate (6.1 g, 13.8 mmol) was added, the resulting mixture was stirred and heated in an oil bath at 65°. After several minutes, gas was evolved. Heating was continued for 5 min whereupon the mixture was cooled, poured into dilute nitric acid (20 ml of concentrated acid diluted with 150 ml of water), and extracted with pentane. The organic layer was washed with water, 5% sodium carbonate solution, and water. The dried solution was freed of pentane by distillation and the residue was Kugelrohr distilled at room temperature and 100 mm; δ_{TMS} ($CDCl_3$) 6.44-6.68 (m, 2), 3.52-3.82 (m, 2), 2.96-3.16 (m, 1), 2.24-2.72 (m, 4), 1.20 (s, 3).

Calcd for $C_{11}H_{12}$ m/e 144.0939; found, 144.0941.

4-Methylpentacyclo[4.4.0.$0^{2,5}$.$0^{3,8}$.$0^{4,7}$]decane (11). The crude methylbasketene in methanol (150 ml) was treated with potassium azodicarboxylate (10 g), cooled in an ice bath, and treated dropwise with acetic acid (10 ml) during a 1-hr period. After being stirred for several hours, the reaction mixture was added to water (100 ml) and the hydrocarbon was extracted with pentane. The pentane solution was dried and concentrated, and the residue was purified by preparative vpc (12 ft × 0.25 in. 8% Carbowax 20M on Chromosorb G, 115°). There was isolated 145 mg (15% overall) of **11** as a colorless oil: δ_{TMS} ($CDCl_3$) 2.47-3.08 (m, 7), 1.37-1.52 (m, 4), 1.08 (s, 3).

Anal. Calcd for $C_{11}H_{14}$: C, 90.35; H, 9.65. Found: C, 90.53; H, 9.65.

4-Methylpenacyclo[4.4.0.$0^{2,4}$.$0^{3,8}$.$0^{5,7}$]decane (12). A solution of **11** (25 mg) in benzene was treated as above at 40° with a catalytic quantity of silver perchlorate dissolved in the same solvent. Workup in the predescribed manner gave a single product which was purified by vpc methods (6 ft × 0.25 in. 15% SE-30 at 110°); 22 mg (88%); δ_{TMS} ($CDCl_3$) 2.17-2.45 (m, 2), 1.05-1.58 (m, 9), 1.27 (s, 3).

Anal. Calcd for $C_{11}H_{14}$: C, 90.35; H, 9.65. Found: C, 90.60; H, 9.69.

Reaction of Methoxycyclooctatetraene with Maleic Anhydride. A mixture of 135 mg (1.0 mmol) of methoxycyclooctatetraene (**13a**) and 100 mg (1.0 mmol) of maleic anhydride was sealed in a small tube. The solution which initially developed was seen to solidify. The tube was opened and the solid filtered and washed well with ether to give 70 mg of fine light yellow crystals. Recrystallization from chloroform furnished 29 mg (12%) of **14** as fine white crystals: mp 204-206°; $\nu_{\max}$ (Nujol) 1848, 1767 cm^{-1}; δ_{TMS} ($CDCl_3$) 6.35 (m, 2), 3.38-3.72 (m, 3), 2.87-3.32 (m, 3), 2.27-2.87 (m, 2).

Calcd for $C_{12}H_{10}O_4$ m/e 218; found, 218.

Cyclopropylcyclooctatetraene (13b). A solution of cyclopropyllithium,[50] prepared from cyclopropyl bromide (64.5 g, 0.53 mol) and lithium (10.0 g, 1.44 g-atoms), in 500 ml of ether was added portionwise to a stirred suspension of copper iodide[51] (24.0 g, 0.125 mol) in ether (300 ml) at −78°. The resulting mixture was allowed to warm to −25° with stirring where it was kept for 1.5 hr. A solution of bromocyclooctatetraene (11.2 g, 60 mmol) in ether (250 ml) was introduced dropwise at −50°, whereupon the reaction vessel was allowed to warm to room temperature.[52] After 45 min the mixture was chilled in an ice bath and saturated ammonium chloride was cautiously added. The ether layer was washed several times with water, dried, and evaporated. The residue was distilled at 35° and 0.05 mm in a Kugelrohr apparatus to afford 7.8 g (90%) of a yellow oil shown by vpc to be essentially pure **13b**. The pmr spectrum of a vpc purified sample in CCl_4 exhibited absorptions at 5.38-5.80 (m, 7), 1.13-1.63 (m, 1), and 0.35-0.70 (m, 4). Calcd for $C_{11}H_{12}$ m/e 144.0939; found, 144.0937.

Anal. Calcd for $C_{11}H_{12}$: C, 91.61; H, 8.39. Found: C, 91.43; H, 8.45.

3-Cyclopropyltricyclo[4.2.2.$0^{2,5}$]deca-3,7-diene-9,10-dicarboxylic Anhydride (15). A mixture of 7.0 g (49 mmol) of **13b**, 6.0 g (61 mmol) of maleic anhydride, 30 ml of toluene, and a small amount of hydroquinone was heated at reflux for 50 hr. Addition of ether to the cooled reaction mixture provided 6.5 g of yellow crystals which were taken up in methylene chloride and treated with activated charcoal. Recrystallization from dichloromethane–ether gave pure **15**: mp 140-141°; δ_{TMS} ($CDCl_3$) 5.88-6.10 (m, 2), 5.53 (br s, 1), 2.94-3.30 (m, 4), 2.43-2.73 (m, 2), 1.00-1.50 (m, 1), 0.30-0.78 (m, 4).

Anal. Calcd for $C_{15}H_{14}O_3$: C, 74.36; H, 5.83. Found: C, 74.16; H, 5.89.

3-Phenyltricyclo[4.2.2.$0^{2,5}$]deca-3,7-diene-9,10-dicarboxylic Anhydride (16). A mixture of 4.5 g (0.046 mol) of maleic anhydride and 25 ml of benzene was heated at reflux with stirring until solution was effected. Phenylcyclooctatetraene (**13c**, 7.2 g, 0.040 mol) was added and heating was continued for 18 hr. Cooling to 0° resulted in crystallization of the product which was filtered and washed well with three 25-ml portions of cold ether. There was obtained 7.70 g (69%) of **16**; mp 171-173° (lit.[53] mp 173-174°); δ_{TMS} ($CDCl_3$) 7.33 (s, 5), 5.77-6.27 (m, 3), 3.03-3.70 (m, 5), 2.65-2.95 (m, 1). This spectrum was identical with that of the title compound as published by Huisgen.[54]

3-Carbomethoxytricyclo[4.2.2.$0^{2,5}$]deca-3,7-diene-9,10-dicarboxylic Anhydride (17). To a refluxing stirred solution of maleic anhydride (635 mg, 6.50 mmol) in 5 ml of xylene was added 827 mg (5.10 mmol) of **13d** in 1 ml of the same solvent. The solution was refluxed for 40 hr and the greater portion of the xylene was evaporated with a stream of air. The product was finally filtered to give 850 mg (64%) of white powder which was recrystallized from methyl acetate (decolorizing charcoal) to leave 517 mg of **17** as small white flakes, mp 174.5-178.5°, which were not purified further when the photocyclization was seen to fail: δ_{TMS} 6.62 (br s, 1), 6.08 (br t, 2), 3.72 (s, 3), 2.97-3.65 (m, 5), 2.72-2.92 (m, 1).

3,4-Dimethyltricyclo[4.2.2.$0^{2,5}$]deca-3,7-diene-9,10-dicarboxylic Anhydride (19a). A stirred solution of 407 mg (3.08 mmol) of 1,2-dimethylcyclooctatetraene (**18a**),[55] a small amount of hydroquinone, and 440 mg (4.50 mmol) of maleic anhydride in 5 ml of benzene was heated at reflux for 43 hr. Upon cooling, crystallization occurred. Approximately half of the solvent was evaporated in an air stream and the cold solution was filtered. The precipitate was washed well with ether to give 260 mg of small white crystals. Evaporation of the filtrate gave an additional 48 mg of white crystals (total yield of 43%). Recrystallization from benzene gave material of mp 179-182° (lit.[56] mp 184.5-185.5°); δ_{TMS} ($CDCl_3$) 5.05 (m, 2), 3.01-3.49 (m, 4), 2.57 (s, 2), 1.48 ppm (s, 6).

4,5-Dimethylpentacyclo[4.4.0.$0^{2,5}$.$0^{3,8}$.$0^{4,7}$]decane-9,10-dicarboxylic Anhydride (20a). A solution of 2.0 g of **19a** in 400 ml of benzene-acetone (1:1) was deaerated with a stream of nitrogen and irradiated through quartz with a 450-W Hanovia lamp housed in a Vycor filter. After 10-12 hr, the solution was concentrated and the residue was triturated with small amounts of cold methanol to leach out yellow, oily material. In this manner, 18.7 g of **20a** was obtained from 23.9 g of **19a** (78%). No attempt was made to purify the product at this step.

Dimethyl *cis*-4,5-Dimethylpentacyclo[4.4.0.$0^{2,5}$.$0^{3,8}$.$0^{4,7}$]decane-9,10-dicarboxylate (21a). The crude sample from above in 5 ml of anhydrous methanol was refluxed for 6 hr. After being cooled to 0° in an ice bath, this solution was treated with excess diazomethane in ether and refrigerated for 1 day. Evaporation gave an oil which crystallized under pentane. This product was dissolved in 5 ml of acetone and treated with 14 ml of 2% aqueous potassium permanganate solution in 2-ml portions. After addition of each aliquot, the solution warmed and the purple color was dissipated. After an hour at room temperature, the mixture was extracted with ether (two 25 ml portions), and the combined organic layers were washed with brine (two 25 ml portions), dried, and evaporated to give a clear oil. Chromatography on activated silica gel (elution with 30% chloroform in carbon tetrachloride) gave a white solid which was recrystallized from methanol–water to afford 30 mg (37%) of **21a** as white plates: mp 92–93.5°; δ_{TMS} ($CDCl_3$) 3.62 (s, 6), 2.55–3.17 (m, 8), 1.07 (s, 6).

Anal. Calcd for $C_{16}H_{20}O_4$: C, 69.55; H, 7.30. Found: C, 69.61; H, 7.30.

Dimethyl *cis*-4,5-Dimethylpentacyclo[4.4.0.0^{2,4}.0^{3,8}.0^{5,7}]decane-9,10-dicarboxylate (22a). A solution of 50 mg (0.18 mmol) of **21a** in 0.25 ml of benzene and 0.25 ml of 0.2 *M* silver perchlorate in benzene was prepared in a pmr tube. Occasional scanning of the spectrum indicated the isomerization to be approximately 50% complete after 20 min at 40°. The sample was then maintained at 40.0° in a constant temperature water bath for 150 min, chromatographed on silica gel (benzene elution), and crystallized from methanol–water to yield 38 mg of **22a** as small white crystals: mp 61.5–63.5°; δ_{TMS} ($CDCl_3$) 3.62 (s, 6), 2.98 (m, 2), 2.60–2.86 (m, 2), 1.15–1.65 (m, 4), 1.22 (s, 6).

Anal. Calcd for $C_{16}H_{20}O_4$: C, 69.55; H, 7.30. Found: C, 69.46; H, 7.27.

1,2-Diacetoxymethylcyclooctatetraene (18b). 1,2-Dihydroxymethylcyclooctateraene[55,57] (13.9 g, 85 mmol) was dissolved in acetic anhydride (60 ml) and the resulting solution was heated for 1 hr on a steam bath. The cooled reaction mixture was poured into 1 l. of ice water and extracted with benzene (two 500 ml portions). The organic phase was dried and evaporated, and the residual oil was distilled at 115° and 0.05 mm in a Kugelrohr apparatus: 16.0 g (75%); δ_{TMS} (CCl_4) 5.97 and 5.83 (br s, 6), 4.6 (ABq, 4), 2.03 (s, 6).

Anal. Calcd for $C_{14}H_{16}O_4$: C, 67.73; H, 6.50. Found: C, 67.48; H, 6.60.

3,4-Diacetoxymethyltricyclo[4.2.2.0^{2,5}]deca-3,7-diene-9,10-dicarboxylic Anhydride (19b). To a solution of **18b** (15.0 g, 60.5 mmol) in benzene (100 ml) was added maleic anhydride (7.6 g, 78 mmol) and a small amount of hydroquinone. The resulting mixture was heated at reflux for 24 hr. Removal of a portion of the benzene and addition of ether provided 18.8 g (90%) of a white crystalline solid: mp 139–140°; δ_{TMS} ($CDCl_3$) 5.92–6.10 (m, 2), 4.50 (s, 4), 3.04–3.40 (m, 4), 2.64–2.84 (m, 2), 2.05 (s, 6).

Anal. Calcd for $C_{18}H_{18}O_7$: C, 62.42; H, 5.24. Found: C, 62.22; H, 5.26.

Dimethyl *cis*-4,5-Diacetoxymethylpentacyclo[4.4.0.0^{2,5}.0^{3,8}.0^{4,7}]decane-9,10-dicarboxylate (21b). A solution of diene **19b** (7.5 g, 21.6 mmol) in acetone (400 ml) was purged with nitrogen and irradiated for 60 hr in a Rayonet reactor fitted with a bank of 3000-Å lamps. After the solvent was removed under vacuum, the residue was treated with methanol (50 ml) and the resulting solution was heated to reflux for 6 hr, diluted with ether, and treated with excess ethereal diazomethane. After 4 hr at room temperature, solvent was removed and the residue was chromatographed on silica gel (elution with chloroform–carbon tetrachloride mixtures). Fractions containing mixtures of the desired bishomocubane and uncyclized ester were combined and treated with an excess of potassium permanganate in 60% aqueous acetone for 1 hr. The aqueous phase was extracted several times with ether, and the combined organic layers were washed with brine and dried. Upon evaporation the residue was again chromatographed on silica gel and recrystallized from ether–hexane to provide 1.5 g of white crystalline **21b:** mp 80.5–81.5°; δ_{TMS} ($CDCl_3$) 4.20 (s, 4), 3.62 (s, 6), 3.03 (br s, 6), 2.88 (br s, 2), 2.04 (s, 6).

Anal. Calcd for $C_{20}H_{24}O_8$; C, 61.21; H, 6.17. Found: C, 61.26; H, 6.20.

Dimethyl *cis*-4,5-Diacetoxymethylpentacyclo[4.4.0.0^{2,4}.0^{3,8}.0^{5,7}]decane-9,10-dicarboxylate (22b). To bishomocubane **21b** (34.6 mg) in a pmr tube was added 300 μl of anhydrous 0.179 *M* silver perchlorate–benzene solution and the sample was degassed and sealed under vacuum. After 20 hr at 75° (no significant rearrangement after 22 hr at 40°), the solution was added to 20 ml of brine and extracted with dichloromethane. Evaporation of the dried organic layers provided 32 mg of **22b** as a white solid: mp 112–113°; δ_{TMS} ($CDCl_3$) 4.32 (m, 4), 3.64 (s, 6), 2.72–3.17 (m, 4), 2.06 (s, 6), 1.60–1.93 (m, 4).

Anal. Calcd for $C_{20}H_{24}O_8$: C, 61.21; H, 6.17. Found: C, 61.06; H, 6.23.

3,4-Tetramethylenetricyclo[4.2.2.0^{2,5}]deca-3,7-diene-9,10-dicarboxylic Anhydride (19c). A solution of 3.10 g (19.6 mmol) of 1,2-tetramethylenecyclooctatetraene (**18c**),[58] 3.00 g (30.7 mmol) of maleic anhydride, and a small amount of hydroquinone in 20 ml of toluene was flushed with nitrogen and heated in an oil bath at 110° for 70 hr. Much of the toluene was then removed in a stream of nitrogen. Some ether was added and the solution was cooled to give 1.75 g (35%) of fine white crystals. Recrystallization from benzene–hexane gave pure **19c:** mp 189.5–191°; δ_{TMS} ($CDCl_3$) 6.00 (m, 2), 3.10–3.33 (m, 2), 3.00–3.10 (m, 2), 2.75 (br s, 2), 1.40–2.05 (m, 8).

Anal. Calcd for $C_{16}H_{16}O_3$: C, 74.98; H, 6.29. Found: C, 74.72; H, 6.17.

Dimethyl *cis*-4,5-Tetramethylenepentacyclo[4.4.0.0^{2,5}.0^{3,8}.0^{4,7}]decane-9,10-dicarboxylate (21c). A solution of 700 mg (2.74 mmol) of **19c** in 350 ml of acetone was purged with nitrogen and irradiated with a 200-W Hanovia lamp in a quartz immersion well fitted with a Vycor filter for 15 hr. Evaporation of the solution gave a heavy oil which was dissolved in 50 ml of anhydrous methanol and heated at reflux for 4 hr. The solution was concentrated to one-half its volume, cooled to 0°, and treated with excess ethereal diazomethane. Chromatography on silica gel and selective destruction of uncyclized diester with aqueous permanganate as above, followed by a final purification on silica gel gave 28 mg of **21c** as fine white crystals: mp 62–64°; δ_{TMS} ($CDCl_3$) 3.46 (s, 6), 2.65–3.15 (m, 8), 1.13–1.82 (m, 8).

Anal. Calcd for $C_{18}H_{22}O_4$: C, 71.50; H, 7.33. Found: C, 71.55; H, 7.36.

Dimethyl *cis*-4,5-Tetramethylenepentacyclo[4.4.0.0^{2,4}.0^{3,8}.0^{5,7}]decane-9,10-dicarboxylate (22c). A 21-mg sample of **21c** in 1 ml of benzene was treated with a catalytic amount of silver fluoroborate for 20 min at 40°. The reaction mixture was poured into saturated sodium chloride solution and the organic layer was separated, dried, and evaporated. There was obtained an oil which was purified by preparative vpc isolation (2 ft × 0.25 in. Carbowax 20 M, 160°) and subsequent Kugelrohr distillation at 140° and 0.5 mm (6 mg); δ_{TMS} ($CDCl_3$) 3.60 (s, 6), 3.15 (br s, 2), 2.58–2.90 (m, 2), 1.25–1.75 (m, 8), 1.63 (m, 4).

Calcd for $C_{18}H_{22}O_4$ *m/e* 302.1518; found, 302.1520.

1-Acetoxymethyl-2-methylcyclooctatetraene (18d).[59] To a suspension of 1.4 g (30.8 mmol) of lithium aluminum hydride in 75 ml of ether was added slowly with stirring 7.1 g (36.8 mmol) of ethyl 2-methylcyclooctatetraenecarboxylate[60] dissolved in 50 ml of the same solvent. After 12 hr at room temperature, the mixture was treated sequentially with 1.4 ml of water, 1.4 ml of 20% sodium hydroxide solution, and 4.2 ml of water, filtered, and evaporated. There remained 5.45 g (100%) of the alcohol as a yellow liquid. The *p*-nitrobenzoate was prepared, mp 42–43° (from methanol).

Anal. Calcd for $C_{17}H_{15}NO_4$: C, 68.67; H, 5.08; N, 4.71. Found: C, 68.63; H, 5.15; N, 4.73.

A solution of 6.6 g (44.6 mmol) of this alcohol in 15 ml of acetic anhydride was heated for 1 hr on a steam bath. Excess acetic anhydride was removed *in vacuo* and the residue was distilled to give 7.35 g (87%) of **18d,** bp 90° (0.05 mm). A sample was further purified by vpc for analysis: δ_{TMS} ($CDCl_3$) 5.60–5.92 (m, 6), 4.58 (ABq, 2), 2.04 (s, 3), 1.37–1.90 (m, 3).

Anal. Calcd for $C_{12}H_{14}O_2$: C, 75.76; H, 7.42. Found: C, 75.42; H, 7.45.

3-Acetoxymethyl-4-methyltricyclo[4.2.2.0^{2,5}]deca-3,7-diene-9,10-dicarboxylic Anhydride (19d). To a solution of **18d** (7.35 g, 38.7 mmol) in 40 ml of benzene was added 5.05 g (51.5 mmol) of maleic anhydride and a small amount of hydroquinone and the resulting mixture was heated at reflux for 72 hr. The product was recrystallized from benzene–ether to provide 7.65 g (69%) of colorless crystals: mp 101–102.5°; δ_{TMS} ($CDCl_3$) 5.88–6.13 (m, 2), 3.00–3.33 (m, 4), 2.50–2.75 (m, 2), 2.03 (s, 3), 1.59 (s, 3).

Anal. Calcd for $C_{16}H_{16}O_5$: C, 66.66; H, 5.59. Found: C, 66.53; H, 5.60.

Dimethyl *cis*-4-Acetoxymethyl-5-methylpentacyclo[4.4.0.0^{2,5}.0^{3,8}.0^{4,7}]decane-9,10-dicarboxylate (21d). A solution of diene **19d** (6.12 g, 21.3 mmol) in acetone (400 ml) was purged with nitrogen and irradiated for 5.5 days in a Rayonet reactor fitted with a bank of 3000-Å lamps. The acetone was evaporated and the residue in 50 ml of methanol was heated at reflux for 6 hr. Treatment with excess diazomethane and work-up in the predescribed fashion afforded 2.39 g (39%) of **21d** as a viscous colorless oil; δ_{TMS} ($CDCl_3$) 4.17 (s, 2), 3.62 (s, 3), 2.62–3.22 (m, 6), 2.05 (s, 3), 1.15 (s, 3).

Anal. Calcd for $C_{18}H_{22}O_6$: C, 64.65; H, 6.63. Found: C, 64.57; H, 6.64.

Dimethyl *cis*-4-Acetoxymethyl-5-methyl- (25) and *cis*-5-Acetoxymethyl-4-methylpentacyclo[4,4,0,0^{2,4},0^{3,8},0^{5,7}]decane-9,10-dicarboxylates (26). To a pmr sample of **21d** used for rearrangement kinetics was added brine and ether. The ether extract was dried and evaporated to give an essentially quantitative yield (>95%) of the mixture as a colorless viscous oil; δ_{TMS} (C_6H_6) 4.16 and 4.14 (overlapping s, 60:40 ratio, 2, $-CH_2O-$), 3.43 (s, 6), 2.50–3.00 (m, 4), 1.72 and 1.76 (s, 60:40 ratio, 3), 1.20 (br s, 3), 0.92–2.00 (m, 4).

Anal. Calcd for $C_{18}H_{22}O_6$: C, 64.65; H, 6.63. Found: C, 64.57; H, 6.81.

4,5-Dimethylpentacyclo[4,4,0,0^{2,5},0^{3,8},0^{4,7}]dec-9-ene (22). A mixture prepared from diester **21a** (16.5 g, 59.7 mmol), 10 ml of methanol, and 9.6 g of sodium hydroxide in 400 ml of water was heated at reflux for 2 hr, cooled, and acidified with concentrated hydrochloric acid. The precipitated diacid was filtered and dried (15.0 g, 100%).

A solution of this diacid (14.5 g, 58.5 mmol) in pyridine (195 ml) was treated with lead tetraacetate (51.8 g, 117 mmol) and a stream of oxygen as described in the preparation of the 4-methyl derivative. A portion of the residue obtained after work-up was purified for analytical purposes by vpc (12 ft × 0.25 in. Carbowax 20 M, 110°); δ_{TMS} ($CDCl_3$) 6.48 (m, 2), 3.42–3.84 (m, 2), 2.27 (m, 4), 1.13 (s, 3).

Anal. Calcd for $C_{12}H_{14}$: C, 91.08; H, 8.92. Found: C, 90.94; H, 8.93.

4,5-Dimethylpentacyclo[4,4,0,0^{2,5},0^{3,8},0^{4,7}]decane (23). The remaining crude basketene **22** was divided in two portions and each was treated with diimide using dipotassium azodicarboxylate (60 g) and acetic acid (56 ml) in methanol (1 l.). The residue so produced was sublimed in a closed system to provide 3.55 g (38% from the diacid) of pure **23**; mp 42–43°; δ_{TMS} ($CDCl_3$) 2.50 (s, 6). 1.40 (br s, 4), 1.00 (s, 6).

Anal. Calcd for $C_{12}H_{16}$: C, 89.94; H, 10.06. Found: C, 90.20; H, 10.05.

4,5-Dimethylpentacyclo[4,4,0,0^{2,4},0^{3,8},0^{5,7}]decane (24). A solution of **23** (50 mg) in benzene was treated with silver perchlorate–benzene solution and heated at 40° for ten half-lives as described above. The single product was purified by preparative vpc (6 ft × 0.25 in. 15% SE-30, 115°) and afforded 45 mg of **24**; δ_{TMS} ($CDCl_3$) 2.17–2.46 (m, 2), 1.38–1.50 (m, 4), 1.12–1.30 (m, 4), 1.19 (s, 6).

Anal. Calcd for $C_{12}H_{16}$: C, 89.94; H, 10.06. Found: C, 89.53; H, 10.22.

2,5-Tetramethylenetricyclo[4.2.2.0^{2,5}]deca-3,7-diene-9,10-dicarboxylic Anhydride (28).[61] A magnetically stirred solution of 790 mg (5.00 mmol) of [4.4.2]propella-2,4,11-triene (**27**)[62] and 491 mg (5.00 mmol) of maleic anhydride in 10 ml of anhydrous benzene was refluxed for 24 hr. The solvent was evaporated and the residue sublimed. Initially, unreacted maleic anhydride and a clean viscous oil formed on the cold finger (up to *ca.* 140° and 0.1 mm). Further heating gave 903 mg (71%) of **28** as off-white crystals. Recrystallization from benzene–hexane afforded pure anhydride: mp 181.5–182.5°; δ_{TMS} ($CDCl_3$) 6.12 (dd, J = 3.3 and 4.8 Hz, 2), 5.79 (s, 2), 3.28–3.42 (m, 2), 2.78–3.00 (m, 2), 1.32–1.85 (m, 8).

Anal. Calcd for $C_{16}H_{16}O_3$: C, 74.98; H, 6.29. Found: C, 74.92; H, 6.28.

2,3-Tetramethylenepentacyclo[4,4,0,0^{2,5},0^{3,8},0^{4,7}]decane-9,10-dicarboxylic Anhydride (29). A solution of 730 mg of **28** in 500 ml of acetone was purged with nitrogen and irradiated in a quartz tube with 3000-Å lamps in the Rayonet reactor for 88 hr. The solvent was removed *in vacuo* and the residue was heated to 50–60° and 0.1 mm for 1.5 hr to remove diacetone alcohol. This material was redissolved in acetone, and the solution was deoxygenated and irradiated for an additional 45 hr. Removal of the solvent and its photochemical by-products as before left a yellow oily solid. The substance was chromatographed on activated silica gel (elution with ethanol-free carbon tetrachloride:chloroform 1:1) and 381 mg (52%) of bishomocubyl anhydride, mp 192–193° (from benzene–hexane), resulted: δ_{TMS} ($CDCl_3$ 2.72–3.20 (m, 8), 1.43 (br s, 8).

Anal. Calcd for $C_{16}H_{16}O_3$: C, 74.98; H, 6.29. Found: C, 74.90; H, 6.38.

Dimethyl *cis*-2,3-Tetramethylenepentacyclo[4,4,0,0^{2,5},0^{3,8},0^{4,7}]decane-9,10-dicarboxylate (30). A solution of 200 mg (0.78 mmol) of **29** in 15 ml of anhydrous methanol was heated at reflux zomethane. Evaporation gave an oil which crystallized upon scratching under pentane. Recrystallization from pentane afforded **30** (180 mg, 76%) as small white needles; mp 69–70°; δ_{TMS} ($CDCl_3$) 3.83 (s, 6), 2.98–3.40 (m, 6), 2.68–2.93 (m, 2), 1.72 (s, 8).

Anal. Calcd for $C_{18}H_{22}O_4$: C, 71.50; H, 7.33. Found: C, 71.51; H, 7.38.

Ag^+-Catalyzed Rearrangement of 30. A 10-mg sample of **30** was dissolved in 2.55 ml of 0.1009 *M* silver perchlorate–benzene and the solution was kept at 40° for 1.5 days in the absence of light. Work-up in the predescribed fashion and preparative vpc isolation (4 ft × 0.125 in. 5% Carbowax 20 M Chromosorb G, 170°) gave pure **31**; δ_{TMS} ($CDCl_3$) 3.70 (s, 6), 3.07 (m, 2), 2.38 (m, 2), 0.95–1.95 (br m, 12).

Anal. Calcd for $C_{18}H_{22}O_4$ m/e 302.1518; found, 302.1520.

General Procedure for the Determination of Catalytic Rate Constants by Pmr Methods. Kinetic runs were carried out in benzene solution with either a circulating constant temperature water bath or the probe of a Varian Associates A60-A spectrometer maintained at 40.0°. The benzene was dried over calcium hydride and distilled from lithium aluminum hydride prior to use. Stock solutions of silver perchlorate (G. Frederick Smith Co.) in benzene were dried by distillation of the benzene–water azeotrope, and the silver ion concentration was determined by titration with standardized potassium thiocyanate.[63] The stock solutions were stored in amber glass bottles. A solution of the bishomocubane in dry benzene was prepared and measured volumetrically along with the silver perchlorate solution into a pmr tube. The tube was then inserted into the probe or the water bath, and spectra were recorded at measured time intervals. Integration of appropriate signals of the bishomocubane and snoutane was performed at the same time and plots of ln $a/(a - x)$ *vs.* time (sec) were linear. The slope of such lines, determined by the method of least squares, is equal to k_{Ag}.

General Procedure for the Determination of Catalytic Rate Constants by Vpc Methods. The bishomocubane and silver perchlorate solutions were mixed in a 1-dr vial (which had previously been painted black on its exterior surface to ensure protection from light) equipped with a septum. These solutions were allowed to equilibrate at 40.0° for 5–10 min. An accurate timer was started and aliquots were removed at suitable time periods. For the fast reactions, the substrate and silver perchlorate solutions were separately equilibrated and the timer was started immediately after mixing. Each aliquot was quenched in 1 ml of saturated aqueous sodium chloride solution and analysis of the dried organic layer was made on a Hewlett-Packard 5750 gas chromatograph. The areas of the relevant peaks were measured electronically and by planimetry.

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References and Notes

(1) Part XXVII of the series dealing with Silver(I) Ion Catalyzed Rearrangements of Strained σ Bonds. The preceding paper is L. A. Paquette and R. S. Beckley, *J. Amer. Chem. Soc.*, part XXVI.

(2) University Postdoctoral Fellow, 1970–1971; National Institutes of Health Postdoctoral Fellow, 1971–1972.

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(21) Examples include the protonation of amines having the general formula $RCH_2N(CH_3)_2$ ($\rho^- = -2.0$) (ref 20d), the ionization of carboxylic acids ($\rho^* = 1.7$) (ref 17, p 607), and the acid dissociation of alcohols, RCH_2OH ($\rho^* = 1.4$) (D. Ballinger and F. A. Lang, *J. Amer. Chem. Soc.*, **82**, 795 (1960)).

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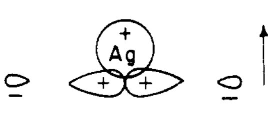
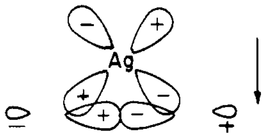


Ag(s) ← (C–C) σ



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