nique employed under complete proton decoupling conditions produces singlets lying in a wider range of chemical shifts and may be a general-purpose approach to most conformational problems of organic chemistry. Its real accuracy (probably, not worse than 20%) is, in these cases, satisfactory for qualitative estimates.

Acknowledgment. We thank Dr. A. A. Borisenko for the valuable discussion of the quantitative aspects of the nmr analysis.

References and Notes

(1) This paper has been partially presented at the XIth European Congress on Molecular Spectroscopy, Tallin, USSR, 1973.

(2) See, *e.g.*, (a) E. L. Eliel, N. L. Allinger, S. J. Angyal,and C. A. Morrison, "Conformational Analysis," Interscience, New York, N.Y., 1965; (b) J. A. Hirsch in "Topics in Stereochemistry," Vol. I, Interscience, New York, N.Y., 1967; (c) F. R. Jensen, C. H. Bushweller, and B. H. Beck, *J. Amer. Chem. Soc.*, **91**, 344 (1969); (d) F. A. Bovey, E. W. Anderson, F. P. Hood, and R. L. Kornegay, *J. Chem. Phys.*, **40**, 3099 (1964); (e) F. R. Jensen and C. H. Bushweller in "Advances in Alicyclic Chemistry," Vol. 3, H. Hart and G. J. Karabatsos, Ed., Academic Press, New York, N.Y., 1971, and referencê cited therein.

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(4) (a) C. W. Buchanan, D. A. Ross, and J. B. Stothers, *J. Amer. Chem. Soc.*, **88**, 4301 (1966); (b) B. V. Cheney and D. M. Grant, *ibid.*, **89**, 5319 (1967); (c) J. B. Roberts, F. J. Weigert, J. I. Kroschwitz, and H. J. Reich, *ibid.*, **92**, 1338 (1970); (d) T. Pehk and E. Lippmaa, *Org. Magn. Resonance*, **3**, 679 (1971); (e) D. K. Dalling and D. M. Grant, *J. Amer. Chem. Soc.*, **89**, 6612 (1967).

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(7) See also, e.g., (a) H.-J. Schneider, T. Keller, and R. Price, *Org. Magn. Resonance*, **4**, 907 (1972); (b) A. D. Litmanovitch, N. A. Plate, N. M. Sergeyev, O. A. Subbotin, and T. I. Usmanov, *Dokl. Acad. Nauk SSSR*, **210**, 114 (1973); (c) F. A. L. Anet and V. Basus, *J. Amer. Chem. Soc.*, 95, 4423 (1973).

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(10) In this case, the ring inversion is nondegenerate, *i.e.*, $k_{ae} \neq k_{ea}$ where k_{ae} is the rate constant for the axial-to-equatorial transformation. Previously, nondegenerate ring inversion has been studied by Bovey, *et al.*,[2d] for fluorocyclohexane by using ^{19}F nmr.

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(13) As for the stereochemical aspects of ^3J ($^{13}C-^{19}F$) coupling constants, see also (a) F. J. Weigert and J. D. Roberts, *J. Amer. Chem. Soc.*, **93**, 2361 (1971); (b) J. B. Grutzner, M. Jautelat, J. B. Dence, and J. D. Roberts, *ibid.*, **92**, 7107 (1970).

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Silver(I)-Catalyzed Valence Isomerization of Substituted 1,8-Bishomocubanes. Stereochemical Aspects[1]

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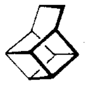
Contribution from the Evans Chemical Laboratories, The Ohio State University, Columbus, Ohio 43210. *Received August 6, 1974*

Abstract: The preparation of the 4-methyl- and 4-acetoxymethyl-substituted *cis*-9,10-dicarbomethoxypentacyclo[4.4.0.0^{2,5}.0^{3,8}.0^{4,7}]decanes **10a** and **10b** was effected by acetone-sensitized photocyclization of diene anhydrides **18**, methanolysis, and esterification with diazomethane. The diene anhydrides are the sole adducts obtained upon reaction of the monosubstituted cyclooctatetraenes with maleic anhydride. These unsymmetrical bishomocubanes offer the possibility for concomitant operation of four different Ag$^+$-catalyzed rearrangements leading to two isomeric snoutane diesters. The distal isomer **16** is shown to be formed preferentially (82% when R = CH_3; 65% when R = CH_2OAc) in both instances. X-Ray analysis of dibrosylate **21** was utilized to establish unequivocally the structural assignment. Chemical correlation of the two major products was realized through the trimethylsnoutane **23**. Ultimate mechanistic deduction of this complicated bond reorganization must account for the stereochemical bias evidenced in this study.

Highly strained cyclobutane compounds of the 1,8-bishomocubane (**1**),[3] homocubane (**2**),[3a,c,4] cubane (**3**),[5] secocubane (**4**),[3a,6] and *syn*-tricyclooctane (**5**)[7] types are so constructed that they are capable of rapid quantitative rearrangement in the presence of transition metal catalysts.[8] The bond reorganizations are of two extreme types: (a) that promoted by Ag(I) (4d^{10}) and related metal ions having appreciable σ electron acceptor ability which results in thermodynamically favorable dicyclobutane–dicyclopropane bond switching; (b) that induced by transition metals such as Rh(I) (4d^{8}) with decided capacity for oxidative addition which effects cleavage of one of the four-membered rings to a diolefin. Attached ligands are known to contribute also to the course of reaction.[9] Diester **6** is a rather typical example.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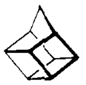
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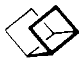
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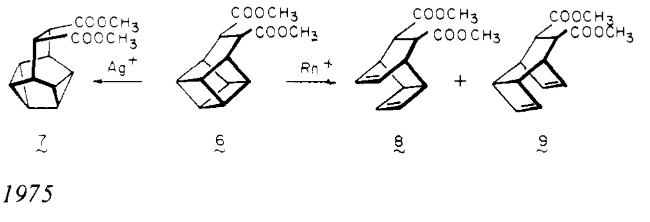


7 **6** **8** **9**

As a consequence of the high levels of p character in the strained σ bonds of **1–6**, appreciable interaction with such metal ions can take place.[10] In the rhodium complex catalyzed reactions, the rate-determining step is presently viewed, at least in certain cases,[5a,11] as the opening of a carbon–carbon bond and formation of Rh(III) intermediates whose ultimate fragmentation returns catalyst and affords diene product. If this mechanistic conclusion is generally relevant, the stepwise rather than concerted nature of such rearrangements has no bearing whatsoever on the question of direct release of symmetry-imposed restrictions to the retro (2 + 2) cycloaddition.[12] The detailed course of the entirely different structural change brought about by silver(I) ion, in contrast, remains the subject of considerable dispute. In brief, suggestions have ranged the gamut from fully concerted pathways triggered by suitable silver–cyclobutane orbital interaction,[7] to a stepwise oxidative addition pathway patterned upon the behavior of rhodium,[10c,13] as well as to simple Ag^+-induced electrophilic rupture of an appropriate bond in the strained molecule.[6a] What was known with certainty at the outset of the present detailed investigation was that such catalyzed bond relocations exhibit little if any kinetic dependence upon additive incremental strain effects[6] but that electronic perturbations have a marked influence on the rates of isomerization.[4b,5] These experimental findings were obviously quite limited in their scope and, as a consequence, the data could not rigorously distinguish between the several mechanistic alternatives.

No attention had yet been paid to the stereochemical aspects of such isomerizations. Consequently, as a prelude to rather detailed kinetic studies,[10a,14] our attention was directed to an examination of the stereochemistry of the Ag^+-catalyzed 1,8-bishomocubane–snoutane rearrangements[15] in anticipation that some light would be shed on this complex problem. As will be seen, phenomenological distinction between the various possible mechanisms cannot be achieved on the basis of stereochemical analysis alone, nor did we expect to achieve this. However, a decided preference for formation of the respective distal isomers is witnessed and, interestingly, this bias operates without regard for whether the corner C_4 substituent is an alkyl group or an oxygen-containing functionality.[16]

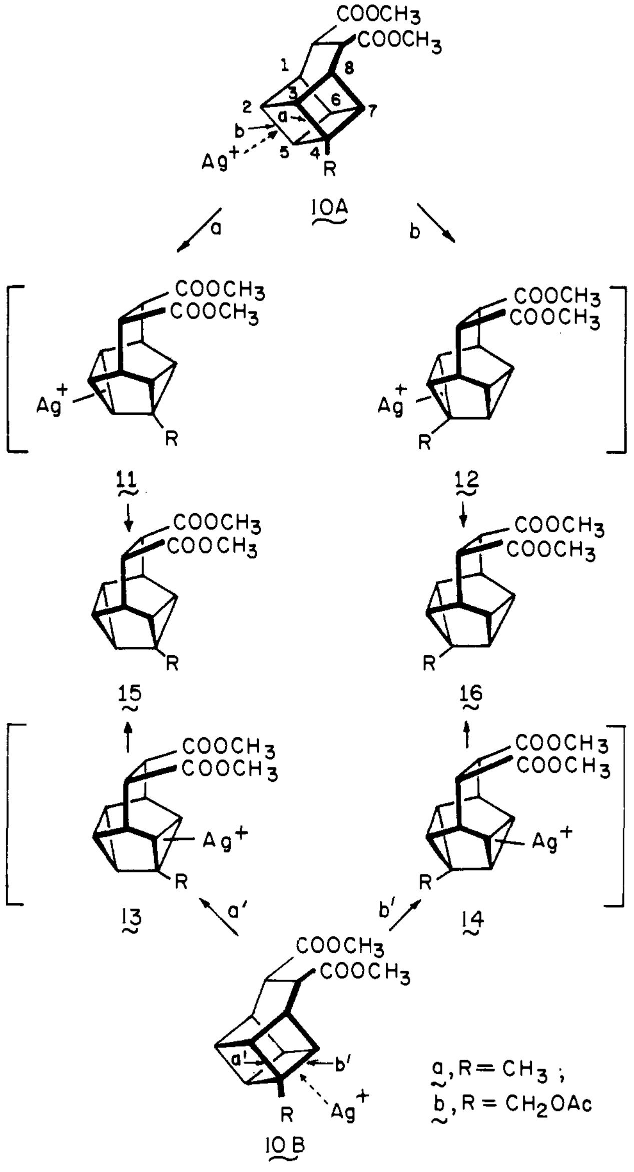
The unsymmetrical structure which results upon monosubstitution of a cis 9,10-disubstituted 1,8-bishomocubane at C_4 as in **10** generates the possibility that four distinct pathways can operate competitively. Depending upon the direction of approach adopted by Ag^+, one of four edge bonds can be called upon to initiate the rearrangement process. Attack at the more highly substituted bond (a) in **10A** leads to proximal positioning of the R and carbomethoxy groups in the snoutane product (as in **15**), whereas the same reaction course in **10B** (now involving bond b′) gives rise to distal isomer **16** (Scheme I). Similar interweaving of product-forming steps likewise operates when the less substituted peripheral bonds b and a′ undergo analogous interaction. The prevailing situation can be expressed mathematically as

$$d(\mathbf{15})/dt \sim k_a + k_{a'}$$

$$d(\mathbf{16})/dt \sim k_b + k_{b'}$$

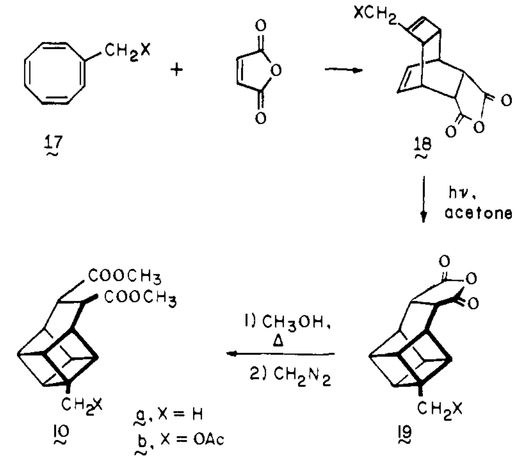
It is important to recognize that the sole structural feature which distinguishes **10A** from **10B** is the spatial orientation of the 9,10-substituents. The combined nature of these groups as well as R could affect the preequilibrium so as to direct Ag^+ complexation to one or the other cyclobutane face. Should approach toward the $C_{2,3,4,5}$ face be favored as a consequence, for example, of the minimization of steric factors, reaction channels passing through **11** and/or **12** would gain significance. Conversely, if favorable coordination of the donor atoms in the substituent triad to Ag^+ operates, then **13** and/or **14** could arise preferentially. During these transformations, the $C_{4,5}$ bond must rotate by approximately 90° in either of two directions relative to the remainder of the carbon framework. The hypothetical structures **11–14** are meant to represent conceptual snapshots of each system after completion of the rearrangement but prior to return of Ag^+ to the catalyst pool. For lack of specific information, the metal-hydrocarbon interaction is formulated as a loose complexation. Possible R···Ag^+ interactions are thereby made evident.

Scheme I



The synthesis of diesters **10a** and **10b**, patterned after the earlier experiments of Lehn,[17] Masamune,[18] and Dauben,[19] revolved about the crucial fact that methyl- and acetoxymethylcyclooctatetraene (**17a,b**) both undergo Diels–Alder cycloaddition with dienophiles of moderate reactivity *via* their 7-substituted bicyclo[4.2.0]octatriene valence tautomers.[20] Acetone-sensitized photocyclization of adducts **18** proceeded with moderate efficiency to give cubyl anhydrides **19** which were acceptably purified by chromatography on "activated" silica gel (Scheme II). Under less controlled conditions, hydrolysis to the corresponding diacids became a serious unwanted problem. Methanolysis and subsequent diazomethane treatment of the carboxylic acid esters afforded **10**. In larger scale photochemical reactions, small

Scheme II

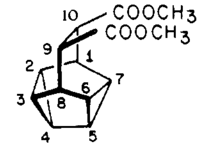


amounts of unclosed diene anhydride were seen to contaminate the bishomocubyl product. Customarily, attempts to effect purification by fractional crystallization at this stage failed. However, treatment of the impure diesters **10** dissolved in aqueous acetone with an excess of 2% potassium permanganate solution and then chromatography on a small amount of silica gel served effectively to remove the diene impurity. Methyl derivative **10a** is a white crystalline solid which exhibits pmr signals in $CDCl_3$ at δ 3.62 (s, 6), 2.63-3.28 (m, 9), and 1.15 (s, 3). The spectral features of **10b**, a colorless oil, are likewise fully compatible with the structural assignment (see Experimental Section).

The isomerization of **10a** with 0.0161 *M* silver perchlorate in anhydrous benzene at 40° gave a two-component product mixture in a ratio of 82:18 as determined by expanded scale pmr (C_6D_6 solution) and normal vpc integrations. Careful chromatography on silver nitrate (10%)-impregnated alumina led to isolation of the major snoutane isomer in pure form. Fractions enriched in the minor rearrangement product (to *ca.* the 40% level) were also obtained. Attempts to ascertain by means of appropriate lanthanide shift pmr experiments the respective structures of these compounds were inconclusive. As summarized in Table I, complications arising from the near identical effect of the $Eu(fod)_3$ reagent upon H_1 and H_5 caused this technique to be unsatisfactory for this purpose.

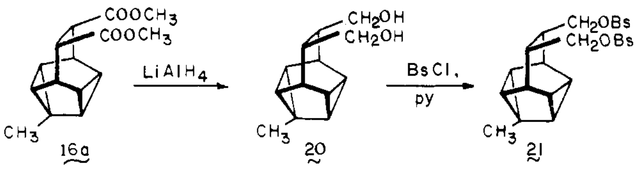
To obtain the desired datum, the pure major component was converted to the related dibrosylate by sequential lithium aluminum hydride reduction and reaction with *p*-bromobenzenesulfonyl chloride in pyridine (Scheme III). The distal stereochemistry of **21** was verified unequivocally by three-dimensional X-ray crystal structure analysis.[16,21]

Table I. Lanthanide Shift Data (CCl_4 solution, 100 MHz)

Compound	Proton	ν^a	$\Delta\nu^b$
	OCH_3	454	240
	$H_{9,10}$	585	406
	$H_{1,8}$	429	269
	$H_{2,3}$	180	88
	$H_{6,7}$	344	243
	$H_{4,5}$	157	56
16a	OCH_3	467	255
	$H_{9,10}$	595	421
	$H_{1,8}$	438	276
	$H_{2,3}$	168	88
	$H_{6,7}$	349	254
	H_5	144	64
	CH_3	102	23
15a	OCH_3	472	260
	$H_{9,10}$	597	423
	$H_{1,8}$	440	278
	$H_{2,3}$	181	101
	$H_{6,7}$	325	238
	H_4	145	65
	CH_3	86	7
16b	OCH_3	402	189
	$H_{9,10}$	464	287
	$H_{1,8}$	391	226
	$H_{2,3}$	247	151
	$H_{6,7}$	317	219
	H_5	270	165
	CH_2	651	399
	CH_3	482	361
15b	OCH_3	373	160
	$H_{9,10}$	427	250
	$H_{1,8}$	391	226
	$H_{2,3}$	174	77
	$H_{6,7}$	360	260
	H_4	270	165
	CH_2	619	367
	CH_3	451	330

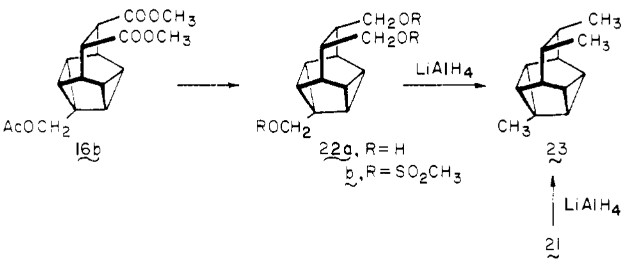
[a] In Hz. [b] The difference in Hz of the proton chemical shift in the absence of $Eu(fod)_3$ and with a Eu/substrate ratio of 1.0 (extrapolated from data at other concentrations). Were the $\cos^2\theta$ term not important, $\Delta\nu$ would be roughly proportional to $1/R^3$. This is seemingly not observed.

Scheme III



The rearrangement of **10b** occurs quantitatively under comparable conditions to afford two snoutane products in a 65:35 ratio (pmr analysis). Chromatography of this mixture on activated silica gel effected their separation. Elucidation of structure in the case of the major component was achieved by its conversion to trimethylsnoutane **23** by a series of conventional transformations (Scheme IV). Since the hydrocarbon so produced was identical in all respects to the compound obtained from hydride reduction of **21**, the major 4-acetoxysnoutane diester is necessarily the distal isomer **16b**.

Scheme IV



In view of the demonstrated preference for formation of distal snoutane products **16** without regard for whether R is an alkyl or oxygen-containing substituent, attention becomes focused principally on pathways b and b′. The experimental findings indicate that one or both of these bond cleavages are decidedly favored over their counterparts a and a′ which, as noted earlier, lead instead to proximal isomers **15**. The question of whether **16** arises by competitive operation of pathways b and b′ or by predominant or exclusive involvement of one such initial bond cleavage is of prime mechanistic significance. Were the reaction course to proceed along avenue b, for example, it would suggest that Ag^+-induced cleavage of the *less substituted* distal bishomocubyl edge bond is most facile. Rearrangement along the b′ manifold in contrast demands initial rupture of the *most substituted* proximal bishomocubyl edge bond.

In either event, replacement of methyl by acetoxymethyl at C_4 is not a sufficient perturbation to cause a changeover in product distribution. Consequently, coordination effects such as those implicit in **12**, if operative, do not enhance the proportion of distal isomer. On the other hand, this structural alteration is entirely adequate to generate a meaningful kinetic change, the rate of rearrangement of **10a** being 64 times faster than that of **10b** at 40°.[14a] These data are, of course, not contradictory but point up simply the fact that electronic effects command an important kinetic relevance. Is the deceleration attending bond reorganization in **10b** the result of decreased capability by the $-CH_2OAc$ group to interact directly with an adjacent carbocationic center in a stepwise electrophilic process (ionic path b′)? Although at first glance this inference may seem entirely plausible, it hardly need be so. Due consideration to the other vitiating possibilities, concerted or otherwise, falls far short from ruling them off the limits of operational feasibility. Discussion of these implications is deferred to a later paper in this series. Suffice it to say that the ultimate mechanistic deduction must conform to the intriguing stereochemical bias uncovered in the present study.

Experimental Section

Melting points are corrected and boiling points are uncorrected. Proton magnetic resonance spectra were obtained with Varian A-60A, 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.

Methylcyclooctatetraene (17a). In a 500-ml three-necked flask fitted with an overhead stirrer, addition funnel, nitrogen inlet, and condenser was placed 100 ml of anhydrous ether. The flask was flushed with nitrogen and cooled to −73° in a Dry Ice–acetone bath. *n*-Butyllithium (35.2 ml of 1.45 *M* in hexane, 51 mmol) was added and a solution of bromocyclooctatetraene[22] (9.15 g, 50 mmol) in 50 ml of ether was slowly introduced. The solution was stirred for 2 hr at −55 to −60°, cooled to −73°, and treated dropwise with 13.2 g (93 mmol) of methyl iodide in 30 ml of the same solvent. After 16.5 hr at room temperature, additional ether was added to bring the volume to 400 ml and the mixture was poured into water (400 ml). The organic layer was washed with water, dried, and evaporated to give an oil, distillation of which afforded 4.78 g (81%) of methylcyclooctatetraene, bp 85–92° (72 mm) (lit.[23] bp 84.5° (67 mm)).

3-Methyltricyclo[4.2.2.0^{2,5}]deca-3,7-diene-9,10-dicarboxylic Anhydride (18a). A solution of 3.0 g (25.4 mmol) of **17a** and 3.0 g (30.6 mmol) of maleic anhydride in 16 ml of benzene was heated at reflux for 18 hr at which point approximately half of the solvent was evaporated in a stream of air. The residual solution was poured into 25 ml of ether, and the crystals which formed upon cooling were separated by filtration. Additional product was obtained by concentration of the mother liquors. The amount of white solid totaled 3.03 g (55%). Recrystallization from benzene–hexane gave **18a** as small white needles; mp 140–141° (lit.[23] mp 141.5–142.5°); δ_{TMS} ($CDCl_3$) 5.97–6.18 (m, 2, olefinic), 5.63 (m, 1, olefinic), 2.95–3.40 (m, 4), 2.48–2.83 (m, 2), 1.58 (br s, 3).

4-Methylpentacyclo[4.4.0.0^{2,5}.0^{3,8}.0^{4,7}]decane-9,10-dicarboxylic Anhydride (19a). A solution of 3.00 g (7.86 mmol) of **18a** in 300 ml of acetone was deaerated with a stream of nitrogen and then irradiated in a Rayonet reactor through quartz with 3000-Å lamps for 36 hr. The solvent was removed *in vacuo* and the residue was chromatographed on 100 g of activated silica gel (elution with 1:1 CCl_4:$CHCl_3$). There was obtained 737 mg (25%) of the photoproduct, recrystallization of which from hexane afforded white microcrystals, mp 69–72°. Similar results were realized when a Hanovia 200-W lamp source and Vycor filter were utilized: δ_{TMS} ($CDCl_3$) 2.50–3.50 (m, 9), 1.17 (s, 3); ν_{max} (Nujol) 1850, 1775 cm^{-1}.

Anal. Calcd for $C_{13}H_{12}O_3$: C, 72.21; H, 5.59. Found: C, 72.18; H, 5.64.

Dimethyl *cis*-4-Methylpentacyclo[4.4.0.0^{2,5}.0^{3,8}.0^{4,7}]decane-9,10-dicarboxylate (10a). A solution of **19a** (277 mg, 1.28 mmol) in 5 ml of anhydrous methanol was refluxed for 7 hr. Additional methanol was introduced to increase the volume to 15 ml and excess cold ethereal diazomethane was added. After standing overnight, the mixture was concentrated and the residual oil was triturated with pentane to induce crystallization. Recrystallization of the solid from hexane at −50° and then methanol–water gave 101 mg (28%) of **10a** as small white crystals: mp 51–53° (from methanol–water); ν_{max} (Nujol) 1740 cm^{-1}; δ_{TMS} ($CDCl_3$) 3.62 (s, 6), 2.63–3.28 (m, 9), 1.15 (s, 3).

Anal. Calcd for $C_{15}H_{18}O_4$: C, 68.69; H, 6.92. Found: C, 68.66; H, 6.87.

3-Acetoxymethyltricyclo[4.2.2.0^{2,5}]deca-3,7-diene-9,10-dicarboxylic Anhydride (18b). A solution of 3.17 g (18.0 mmol) of acetoxymethylcyclooctatetraene[24] and 2.20 g (22.4 mmol) of maleic anhydride in 15 ml of benzene was heated at reflux with stirring for 68 hr. A portion of the benzene was evaporated with a stream of air, ether was added, and this solution was cooled in a refrigerator. Filtration afforded 2.92 g (59%) of small white crystals, recrystallization of which from carbon tetrachloride gave pure **18b**; mp 112–113°; ν_{max} (Nujol) 1852, 1828, 1770, 1724 cm^{-1}; δ_{TMS} ($CDCl_3$) 6.07 (br t, 2), 5.90 (br s, 1), 4.47 (br s, 2), 3.03–3.50 (m, 4), 2.63–2.97 (m, 2), 2.07 (s, 3).

Anal. Calcd for $C_{15}H_{14}O_5$: C, 65.69; H, 5.15. Found: C, 65.43; H, 5.13.

4-Acetoxymethylpentacyclo[4.4.0.0^{2,5}.0^{3,8}.0^{4,7}]decane-9,10-dicarboxylic Anhydride (19b). A solution of 2.50 g (9.6 mmol) of **18b** in 375 ml of acetone was irradiated with continuous nitrogen purging for 6 hr with a 200-W Hanovia lamp housed in a quartz well fitted with a Vycor filter. Evaporation of the acetone and chromatography of the residual oil on activated silica gel (40 g, elution with carbon tetrachloride) gave 1.08 g (43%) of crystalline product. Pure **19b** was obtained by recrystallization from carbon tetrachloride as white crystals: mp 108.5–113°; δ_{TMS} ($CDCl_3$) 4.14 (s, 2), 2.92–3.50 (m, 9), 2.06 (s, 3).

Anal. Calcd for $C_{15}H_{14}O_5$: C, 65.69; H, 5.15. Found: C, 65.63; H, 5.19.

Dimethyl *cis*-4-Acetoxymethylpentacyclo[4.4.0.0^{2,5}.0^{3,8}.0^{4,7}]-decane-9,10-dicarboxylate (10b). It is of course most advantageous to effect the conversion of **18b** to **10b** with intermediate purification of anhydride **19b**. This need not be done, however, and the ensuing procedure illustrates our method of choice for removing residual uncyclized diene contaminant at this stage.

A solution of 900 mg (3.47 mmol) of impure **19b** (containing *ca.* 8% of **18b**) in 15 ml of anhydrous methanol was refluxed for 6 hr. The solution was cooled to 0° and treated with an excess of ethereal diazomethane. The diazomethane had evaporated after 4 hr at 25° and the residual methanol was removed *in vacuo*. A sample (413 mg) of the resulting oil was dissolved in 25 ml of acteone and treated with 10 ml (excess) of 2% aqueous potassium permanganate solution. The purple color persisted upon brief heating with a steam bath and stirring at room temperature for 1 hr. The mixture was poured into water and extracted with ether. The combined organic layers were dried, evaporated, and eluted through 20 g of silica gel with chloroform–carbon tetrachloride (3:7). There was isolated 213 mg of **10b** as a clear oil which was distilled (90–100° (0.3 mm)) for analysis: ν_{max} (neat) 1735 cm^{-1}; δ_{TMS} ($CDCl_3$) 4.12 (s, 2), 3.60 (s, 6), 3.07 (br s, 7), 2.86 (br s, 2), 2.03 (s, 3).

Anal. Calcd for $C_{17}H_{20}O_6$: C, 63.74; H, 6.29. Found: C, 63.71; H, 6.39.

Ag^+-Catalyzed Rearrangement of 10a. A solution containing 403 mg (1.54 mmol) of **10a** in 4 ml of 0.0161 *M* silver perchlorate–benzene was sealed in a test tube and heated in a thermostated water bath at 40.3° for 28 hr. The contents were diluted with an equal volume of hexane and chromatographed on alumina (40 g) impregnated with silver nitrate (10%). Elution with benzene–hexane (1:1) afforded 376 mg (93%) of a mixture of **15a** and **16a** in a ratio of 18:82 (pmr integration of methyl signals). The first of the several chromatography fractions was dissolved in methanol (8 ml) and water was added to the cloud point. Refrigeration caused crystallization of 173 mg of colorless crystals, mp 52.5–56°. Recrystallization from the same solvent system gave pure **16a** as white plates, mp 55–56°; δ_{TMS} ($CDCL_3$) 3.53 (s, 6), 2.90 (s, 2), 2.58–

2.80 (m, 2), 1.58 (br s, 3), 1.33 (s, 3), 1.28 (br s, 2).

Anal. Calcd for $C_{15}H_{18}O_4$: C, 68.69; H, 6.92. Found: C, 68.67; H, 6.95.

Minor isomer **15a** was not obtained in pure form. Its pmr features were deduced by suitable overlay of spectra of fractions enriched in **15a** with that of pure **16a**. Details may be found in Table I.

4-Methyl-9,10-bis(hydroxymethyl)pentacyclo[4,4,0,$0^{2,4}$,$0^{3,8}$,$0^{5,7}$]decane Di-*p*-bromobenzenesulfonate (21). To a stirred slurry of 183 mg (4.8 mmol) of lithium aluminum hydride in 4 ml of anhydrous ether was added 260 mg (1.0 mmol) of **16a** in 4 ml of ether. After 2 hr at room temperature, saturated aqueous ammonium chloride solution was added, the precipitated salts were filtered, and these washed well with warm ether. The combined ether solutions were evaporated to give a white solid, recrystallization of which from hexane afforded 118 mg (82%) of diol **20** as small white crystals: mp 124–125°; δ_{TMS} ($CDCl_3$) 3.40–4.20 (m, 6), 2.07–2.43 (m, 4), 1.15–1.70 (m, 5), 1.32 (s, 3). When D_2O was added, the signal in the 3.40–4.20 region was washed out.

Anal. Calcd for $C_{13}H_{18}O_2$: C, 75.69; H, 8.80. Found: C, 75.59; H, 8.91.

A solution of 188 mg (0.74 mmol) of *p*-bromobenzenesulfonyl chloride in 1 ml of anhydrous pyridine was cooled in ice while 37 mg (0.18 mmol) of diol **20** was added. The solution was refrigerated for 4 days and poured onto 10 g of ice. Work-up in the usual fashion yielded 30 mg (26%) of **21** as white crystals: mp 137–138.5° dec (*ca.* 165°); δ_{TMS} ($CDCl_3$) 7.75 (s, 8), 3.95–4.30 (m, 4), 2.12–2.57 (m, 4), 1.12–1.70 (m, 5), 1.28 (s, 3).

Anal. Calcd for $C_{25}H_{24}Br_2O_6S_2$: C, 46.60; H. 3.75. Found: C, 46.59; H, 3.85.

Ag^+-Catalyzed Rearrangement of 10b. A solution of 1.05 g (3.42 mmol) of **10b** in 10 ml of 0.2 *M* silver perchlorate-benzene was sealed in a 20-ml test tube and heated at 40.0° in a thermostated water bath for 94 hr (>30 half-lives). The contents were washed with saturated sodium chloride solution and rapidly filtered through 7 g of silica gel (benzene elution) to give a clear oil which was carefully rechromatographed on 25 g of activated silica gel. Quantitative pmr measurements were accomplished prior to the second chromatography. Elution with 1–5% ether in benzene effected separation of the isomers. Fractions 21–24 (332 mg) contained only the major isomer **16b**. These were combined, and crystallization was effected from hexane to give **16b** as white needles: mp 109.5–111°; δ_{TMS} ($CDCl_3$) 4.23 (s, 2), 3.62 (s, 6), 3.03 (br s, 2), 2.68–2.90 (m, 2), 2.07 (s, 3), 1.50–1.85 (m, 5).

Anal. Calcd for $C_{17}H_{20}O_6$: C, 63.74; H, 6.29. Found: C, 63.85; H, 6.34.

Fractions 33–35 which contained minor isomer **15b** were combined (132 mg) to give a clear oil. Calcd for $C_{17}H_{20}O_6$, *m/e* 320.1260; found, 320.1259. Details of the pmr spectrum are summarized in Table I.

4,9,10-Tris(hydroxymethyl)pentacyclo[4,4,0,$0^{2,4}$,$0^{3,8}$,$0^{5,7}$]decane (22a). To a stirred slurry of 237 mg (6.25 mmol) of lithium aluminum hydride in 10 ml of anhydrous ether cooled in an ice bath was introduced a solution of **16b** (332 mg, 1.05 mmol) in 10 ml of ether. Processing in the predescribed fashion afforded 209 mg (89%) of **22a** as small white crystals, mp 131–133.5°, from chloroform–carbon tetrachloride; δ_{TMS} ($CDCl_3$-DMSO-d_6) 3.17–3.98 (m, 11), 1.18–2.50 (m, 7). Three protons in the 3.17–3.98 region were washed out with D_2O.

Anal. Calcd for $C_{13}H_{18}O_3$: C, 70.24; H, 8.16. Found: C, 70.09; H, 8.11.

4,9,10-Tris(methanesulfonyloxymethyl)pentacyclo[4,4,0,$0^{2,4}$,$0^{3,8}$,$0^{5,7}$]decane (22b). A mixture of 30 mg (0.14 mmol) of **22a** and 84 μl of triethylamine (previously refluxed with phthalic anhydride, distilled, and redistilled from potassium hydroxide) in 2.0 ml of anhydrous methylene chloride (distilled from phosphorus pentoxide) was stirred with ice-salt cooling while 51 mg (0.45 mmol) of freshly distilled methanesulfonyl chloride was added during 3 min. During the reaction, the triol dissolved. The mixture was stirred for 35 min, poured onto ice, and extracted with methylene chloride. The combined organic layers were washed with ice water, 3 *M* hydrochloric acid, saturated sodium bicarbonate solution, and brine. Drying and evaporation gave 50 mg (82%) of **22b** as an oil which was not further characterized. The pmr spectrum exhibited a characteristic singlet at δ 3.1 (in $CDCl_3$).

4,9,10-Trimethylpentacyclo[4,4,0,$0^{2,4}$,$0^{3,8}$,$0^{5,7}$]decane (23). A. **Hydride Reduction of 22b.** To a mixture of 50 mg (0.11 mmol) of **22b** and 3 ml of ether (insufficient solubility) was added a slurry of 48 mg (1.25 mmol) of lithium aluminum hydride in 2 ml of the same solvent. The mixture was stirred at reflux for 5 hr and at room temperature overnight. Hydrolysis with saturated ammonium chloride solution, extensive extraction of the insoluble aluminate salts, and careful evaporation of the combined filtrates gave an oil which was essentially homogeneous by vpc. Isolation from a 5 ft × 0.25 in. 25% PMPE-6 ring column (Chromosorb W) at 140° gave 3.5 mg (18%) of **23** as a colorless liquid identical by ir, pmr and vpc retention times with the authentic sample prepared below. Calcd for $C_{13}H_{16}$, *m/e* 174.1408; found, 174.1404.

B. Hydride Reduction of 21. A mixture of 154 mg (0.24 mmol) of dibrosylate **21** and 190 mg (5 mmol) of lithium aluminum hydride in 10 ml of ether was refluxed for 24 hr and worked up as above to give 11 mg (26%) of **23:** δ_{TMS} ($CDCl_3$) 1.72–2.35 (m, 4), 1.17–1.58 (m, 5), 1.32 (s, 3), 0.88–1.12 (overlapping m, 6). The hydrocarbon had a t_{ret} of 14 min. At longer retention times (>1 hr), a large peak was seen. Collection of this material returned 38 mg (77%) of diol **20**.

Anal. Calcd for $C_{13}H_{16}$: C, 89.59; H, 10.41. Found: C, 89.69; H, 10.30.

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

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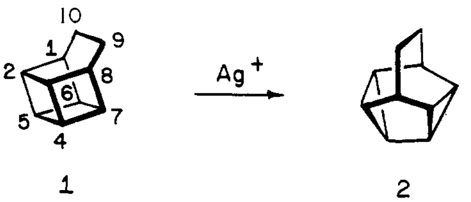
Abstract: Upon treatment with catalytic amounts of silver perchlorate in anhydrous benzene, 1,8-bishomocubanes substituted exclusively at the remote 9,10-position, at the C_4 corner, at both C_4 and C_5 and at C_2,C_3 experience clean isomerization to the structurally related snoutane in essentially quantitative yield. All reactions proceed with adherence to the second-order catalytic rate law $-d[\text{bishomocubane}]/dt = k_{Ag}[\text{bishomocubane}][\text{AgClO}_4]$. 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

$$-d[\text{bishomocubane}]/dt = k_{Ag}[\text{bishomocubane}][\text{AgClO}_4]$$

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-