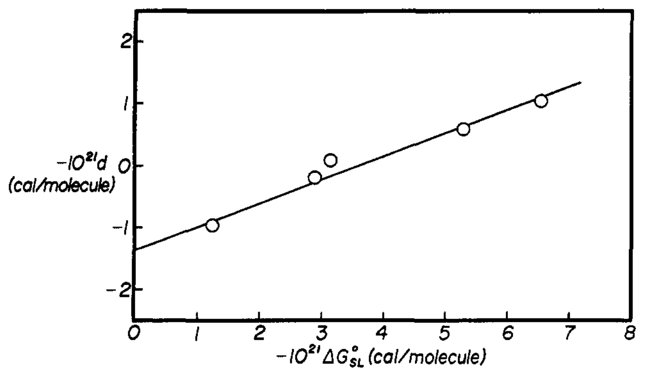

Figure 4. Relationship between d, the vertical deviation of experimental standard free-energy change from the maximal overlap area correlation line,[1] against $\Delta G°_{SL}$, the free-energy change extrapolated to zero surface tension.

treatment therefore suggests that the minimum stability of a complex in water is given by $kA + b$, or 1.4×10^{-21} cal/molecule less than that predicted by the average line. In fact, of the 50 complexes correlated earlier,[1] none falls below this lower limit.

This connection between the surface tension correlation and the overlap area correlation is evident in eq 4, as noted by Sinanoğlu.[2b] The quantity $c'\Delta(v_i^{2/3})$ can be considered an "effective surface area"; then, if a series of interactants is studied in a single solute, a plot of $\Delta G°$ against this effective surface area should reveal a dependence. In fact, the maximal overlap area correlation[1] is just such a plot, whose slope is 64 dyn/cm (close to γ_l for water, 72 dyn/cm, and even closer to γ_l for the usual experimental solvent, water containing a small percentage of acetonitrile) and deviations from which were attributed to specific interaction effects. The systems studied in the present paper and the preceding series[1,3] therefore seem suitable for further tests of Sinanoğlu's theory of solvent effects, the results thus far being derived independently of the theory and being fully consistent with it.

Acknowledgment. This study was supported in part by a General Research Support Grant from the National Institutes of Health, and in part by a grant from the Upjohn Co.

Solvolyses in the Bishomocubane System. Multistep Rearrangements within Ion Pairs[1,2]

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Received May 10, 1971

Abstract: The products, rates, and activation parameters of the acetolysis of 1,1'-bishomocubyl methanesulfonate (Ia) have been determined. In turn, the rates of acetolysis of the newly formed methanesulfonates III and IVa have been determined. In the acetolysis of Ia, 61% of it underwent rearrangement with internal return to slower solvolyzing isomers. The formation of the internal-returned *endo*-methanesulfonates suggests ionization to bridged-ion pairs, followed by frontside collapse. From the slow rates of reaction of IIa, IIIa, and IVa, the extensive skeletal rearrangement with internal return of Ia requires rearrangements occurring within ion pairs. Of special significance is the fact that internal return of Ia to Va involves rebonding of the methanesulfonate group four carbons removed from its original bonding position. The rate of acetolysis of Ia is $10^{2.9}$–$10^{4.1}$ times faster than predicted for unassisted acetolysis. [If the pentacyclodecyl cations are indeed bridged, the formation of isomeric acetates of the nucleus requires both frontside and backside migration (of adjacent carbon–carbon bonds to the electron-deficient center).]

With the discovery of the intramolecular photocycloaddition, in recent years a wide variety of substituted polycyclic cage compounds have been synthesized.[3] Some of the material prepared has been subjected to detailed solvolytic studies[4,5] and, indeed, the study of the pentacyclo[5.3.0^{2,5}.0^{3,9}.0^{4,8}]decane system II has aided our understanding of the possible involvement of symmetrical bridged cations in rearrangement processes.[5a] In a preliminary communication from this laboratory,[2] the product analysis data from the acetolysis of pentacyclo[4.4.0.0^{2,5}.0^{3,8}.0^{4,7}]dec-9-yl methanesulfonate (Ia), commonly called 1,1'-bishomocubyl methanesulfonate, was reported. To fully evaluate the significance of this extensive series of rearrangements the system underwent, more detailed product and kinetic investigations of the acetolysis of Ia as well as that of the related *endo*-1,2-bishomocubyl methane-

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(1) This work was supported in part by Grant No. GP 8700, National Science Foundation.

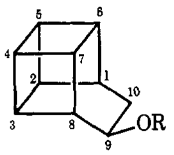
(2) For a preliminary publication of these results, see W. G. Dauben and D. L. Whalen, *J. Amer. Chem. Soc.*, **88**, 4739 (1966).

(3) For an excellent review, see W. L. Dilling, *Chem. Rev.*, **66**, 384 (1966).

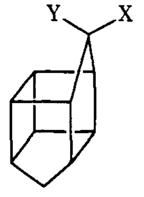
(4) W. G. Dauben and C. H. Schallhorn, *J. Amer. Chem. Soc.*, **93**, 2254 (1971).

(5) (a) W. L. Dilling, R. A. Plepys, and R. D. Kroening, *ibid.*, **91**, 3404 (1969); W. L. Dilling, C. E. Reineke, and R. A. Plepys, *J. Org. Chem.*, **34**, 2605 (1969), and previous papers in series; (b) P. von R. Schleyer, J. J. Harper, G. C. Dunn, V. J. D. Pasquo, and J. R. E. Hoover, *J. Amer. Chem. Soc.*, **89**, 698 (1967); (c) J. C. Barborak and R. Pettit, *ibid.*, **89**, 3080 (1967); (d) for a general review, see R. E. Leone and P. von R. Schleyer, *Angew. Chem., Int. Ed. Engl.*, **9**, 860 (1970).

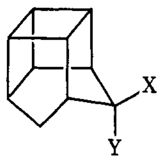
sulfonate (IIIa)[6] and *endo,sym*-1,3-bishomocubyl methanesulfonate (IVa[6]) were undertaken. During the course of these studies, a similar detailed study of the related *unsym*-1,3-bishomocubane system of IIe and IIf was reported,[5a] and these results when combined with those obtained in the present study permit a thorough evaluation of the nature of the intermediates (or activated complexes) encountered in the rearrangement of this highly strained cage system.



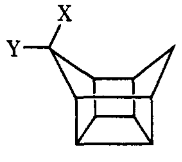
Ia, R = SO_2CH_3
Ib, R = Ac
Ic, R = H



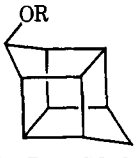
IIa, X = OSO_2CH_3; Y = H
IIb, X = H; Y = OSO_2CH_3
IIc, X = OAc; Y = H
IId, X = H; Y = OAc
IIe, X = OH; Y = H
IIf, X = H; Y = OH



IIIa, X = H; Y = OSO_2CH_3
IIIb, X = OSO_2CH_3; Y = H
IIIc, X = H; Y = OAc
IIId, X = OAc; Y = H
IIIe, X = H; Y = OH
IIIf, X = OH; Y = H



IVa, X = OSO_2CH_3; Y = H
IVb, X = H; Y = OSO_2CH_3
IVc, X = OAc; Y = H
IVd, X = H; Y = OAc
IVe, X = OH; Y = H
IVf, X = H; Y = OH



Va, R = SO_2CH_3
Vb, R = Ac
Vc, R = H

1,1′-Bishomocubyl methanesulfonate (Ia) was synthesized by reaction of the corresponding alcohol Ic with methanesulfonyl chloride and triethylamine in benzene. Because of its high reactivity, the product, a clear oil, was used without further purification for solvolytic studies. The similarities of the nmr spectra of the methanesulfonate and the alcohol from which it was made suggest that the product possesses structure Ia, and that a structural rearrangement had not occurred under reaction conditions. This conclusion was further verified by lithium aluminum hydride reduction of the methanesulfonate synthesized from 1,1′-bishomocubanol (Ic) to the known 1,1′-bishomocubane.[7]

Table I. First-Order Rate Constants and Activation Parameters for Acetolysis of Methanesulfonate Esters Ia, IIIa and IVa

Compd	Temp, °C	$k \times 10^4$, sec^{-1}	$\Delta H^{\ddagger}$, kcal/mole	$\Delta S^{\ddagger}$, eu
Ia	25.04 ± 0.01	36.1 ± 0.6[a]	20.4	−1.3
	35.00 ± 0.03	114 ± 2.5[a]		
IIIa	65.06 ± 0.03	*Ca.* 2.4		
IVa	65.06 ± 0.03	0.103 ± 0.001[a,b]	27.6	0.0
	75.06 ± 0.03	0.335 ± 0.005[a,b]		

[a] Average of two runs; rate constants were calculated by nonlinear least-squares analyses. Errors are expressed in units of standard deviation. [b] Observed infinity titer is 94% of theoretical infinity titer.

The rate of acetolysis of Ia exhibited first-order kinetics (see Table I) and the experimental infinity titer for acetolysis of Ia at 25° was 38–39% of the calculated theoretical infinity titer.[8] This low infinity titer suggests that 61–62% of Ia underwent internal return to slower solvolyzing isomers (Scheme I). The product mixture from acetolysis was separated by column chromatography into an acetate ester fraction and a methanesulfonate ester fraction. Sodium–ammonia reduction of the methanesulfonate fraction yielded a mixture of alcohols containing 45% of *endo*-1,2-bishomocubanol (IIIe), 45% of *endo,sym*-1,3-bishomocubanol (IVe), 7% of IIe and IIf,[9] and 3% of 1,4-bishomocubanol (Vc). Hydrolysis of the acetate fraction produced an alcohol mixture of different composition, consisting of 10% of Ic, 6% of IIe, 9% of IIf, 5% of IIIe, 55% of IVe, and 15% of Vc.

The structures for the pentacyclodecanols IIe, IIf, and Vc were assigned by comparing ir spectra of glpc-collected samples with those of appropriate authentic samples.[5,10,11] Although IIIe and IVe could not be separated on glpc, an nmr spectrum of the mixture exhibited absorbances at τ 5.94 (quartet, C*H*OH, J = 2.6 and 7.0 Hz) and 6.11 (triplet, C*H*OH, J = 4.0 Hz). The quartet at τ 5.94 for an α hydrogen requires an unsymmetrical structure. Since only five saturated pentacyclic decane structures exist (I–V), and the two unsymmetrical alcohols IIe and IIf are known compounds, the quartet signal must be due to one of the remaining unsymmetrical pentacyclodecanols IIIe or IIIf. Treatment of this alcohol with aluminum isopropoxide produced a new isomer. The new isomer was assigned the more stable exo structure IIIf, since models indicate a severe 1,3 interaction between Y and the endo hydrogen of the methylene group in IIIe. Such nonbonding interaction would be relieved in the exo isomer.

The triplet absorbance at τ 6.11 was assigned to the symmetrical structure IVe. The endo configuration of IVe was assigned for the following reason. Oxidation of IVe with Jones reagent[12] produced the corresponding ketone VI, which, upon reduction with lithium aluminum hydride, yielded solely IVe. Models indicate

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[6] The systematic nomenclature for IIIa and IVa are *endo*-pentacyclo[$4.4.0.0^{2,5}.0^{3,9}.0^{4,7}$]dec-8-yl methanesulfonate and *endo*-pentacyclo[$4.4.0.0^{2,5}.0^{3,9}.0^{4,8}$]dec-7-yl methanesulfonate, respectively.

[7] W. G. Dauben and D. L. Whalen, *Tetrahedron Lett.*, 3743 (1966).

[8] Methanesulfonate ester Ia was isolated as an oil, and was not further purified because of its extreme reactivity. The oil was assumed to be 100% pure Ia for calculating the theoretical infinity titer.

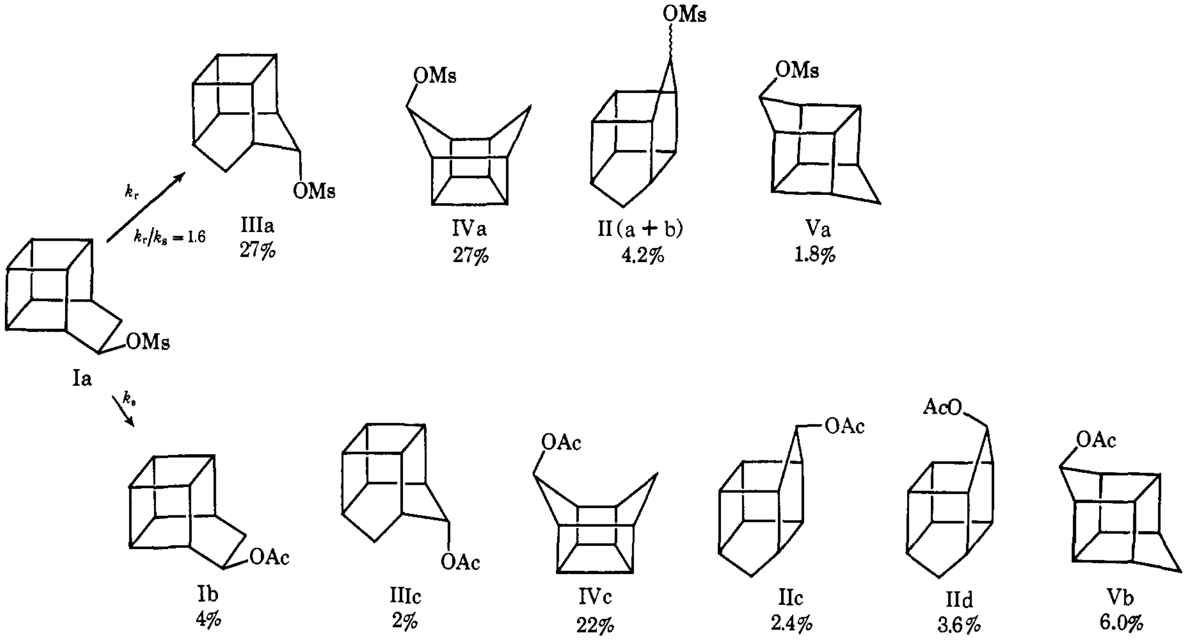
[9] Identified only by glpc retention time. The relative amounts of IIe and IIf in this fraction were not determined.

[10] A mixture of the two epimeric alcohols IIe and IIf in a 65:35 ratio, made by sodium borohydride reduction of pentacyclo[$5.3.0.0^{2,5}.0^{3,9}.0^{4,8}$]decan-6-one (see R. C. Cookson, J. Hudec, and R. Williams, *Tetrahedron Lett.*, 22, 29 (1960)) was kindly supplied by Professor K. Scherer, Jr.

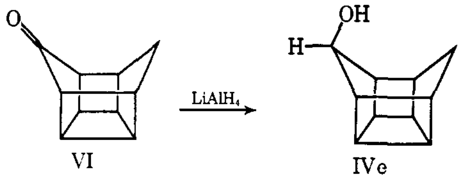
[11] G. Griffin and A. Price, *J. Org. Chem.*, 29, 3192 (1964).

[12] K. Bowden, I. Heilbron, E. R. G. Jones, and B. C. L. Weedon, *J. Chem. Soc.*, 39 (1946).

Scheme I

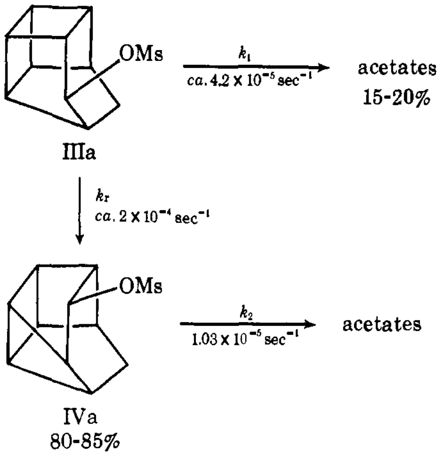


that attack of hydride reagent from the least-hindered side should give an endo hydroxyl group.



In order to ascertain the mechanistic pathways by which Ia underwent acetolysis, it was necessary to prepare and study the solvolytic reactivity of IIIa and IVa; the solvolyses of IIa and IIb had been studied.[5a] *endo*-Methanesulfonate IIIa could not be isolated in pure form, only in a mixture of IIIa and IVa. However, an approximate rate of acetolysis of IIIa was determined in the following manner. The acetolysis rates of mixtures of IIIa and IVa, containing 50–80% of IIIa,[13] were determined titrimetrically at 65°. The apparent instantaneous rate constant drifted downward with time during the first part of the reaction, and the remainder of the reaction exhibited first-order kinetics. Isolation of unreacted mesylate after *ca.* 70% reaction produced relatively pure IVa,[14] thus indicating that IIIa is the more reactive isomer. A value for the rate of internal return (k_r) was estimated by isolating unreacted methanesulfonates (Scheme II) and observing the relative intensities of the infrared absorptions at 894 and 902 cm^{-1} due to IIIa and IVa, respectively. From this crude measurement, it was estimated that the half-life for conversion of IIIa to IVa was *ca.* 1 hr, corresponding to a value for k_r of 2.4×10^{-4} sec^{-1}. The initial titrimetric rate data for the mixture of IIIa and IVa were extrapolated to 100% IIIa. From these data and the value of k_r, an estimate of k_1 was found to be $\sim 4 \times 10^{-5}$. By comparison of k_r and k_1, the amount of internal return of IIIa to IVa can be estimated at 80–85%. The rate data and activation parameters for acetolysis of Ia, IIIa, and IVa are presented in Table I.

Scheme II. Acetolysis of IIIa at 65°



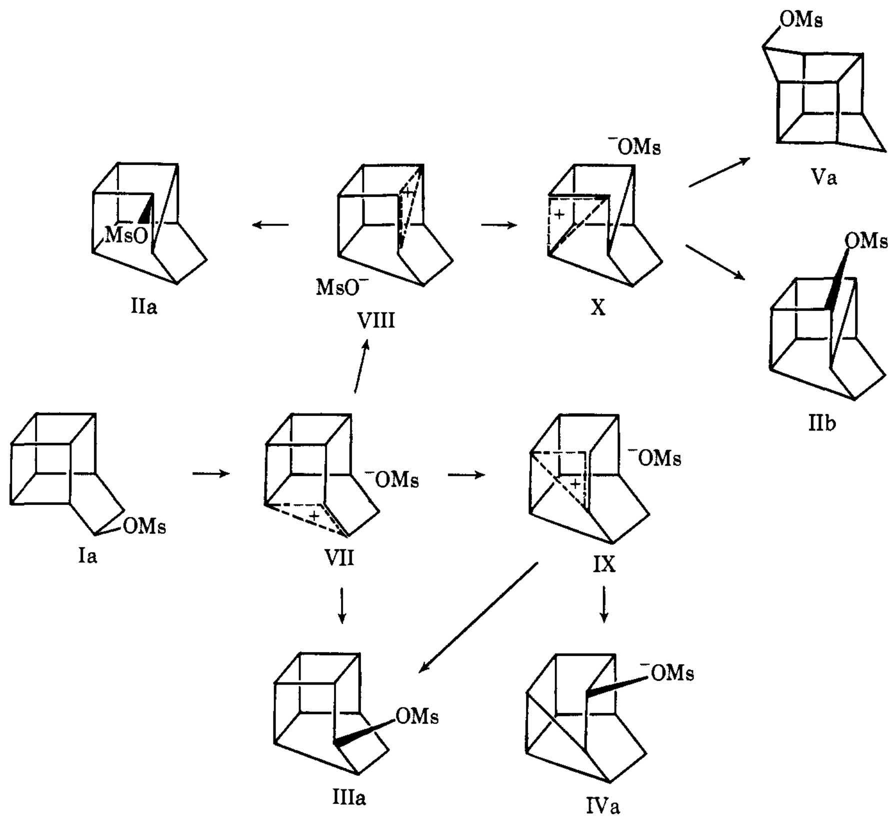
Formation of significant amounts of internal-returned *endo*-methanesulfonates IIIa and IVa in the acetolysis of Ia can be readily explained (Scheme III) by ionization to bridged ion pairs VII and IX, followed by frontside collapse of the methanesulfonate anion. A stepwise mechanism whereby Ia undergoes internal return only to IIIa, which in turn undergoes internal return to IVa, can be ruled out because of rate studies. *endo*-Mesylate IIIa is less reactive than Ia by a factor of 4400 and therefore the large amount of IVa produced after ten half-lives of reaction of Ia must come about directly from ion pairs as indicated in Scheme III. Since the reactivities of IIa, IIb, and IVa are all known to be at least 10^4 less than that of Ia, all internal-returned methanesulfonates formed in the acetolysis of Ia must come directly from Ia *via* an ion-pair mechanism, and not through covalent intermediates. Extensive skeletal rearrangements, presumably occurring within ion pairs, are required to obtain methanesulfonates Va, IIa, and (or) IIb. Of significance is the fact that internal return of Ia to Va involves rebonding of the methanesulfonate group four carbons removed from its original bonding position.[15]

(13) Isomer IIIa could be concentrated by crystallizing IVa from a mixture containing about equal amounts of IIIa and IVa.

(14) The structure of the less reactive methanesulfonate was assigned on the basis of similarities of its nmr spectrum with that of IVe.

(15) For internal return in which the anion migrates a considerable

Scheme III



The solvolytic reactivity of the 1,1′-bishomocubyl system at 25° is greater than that of cyclohexyl brosylate by a factor of 52,800 (Table II), and larger than that for 2-bicyclo[2.2.2]octyl brosylate by a factor of 996. A calculation of the expected nonassisted solvolysis rate by the methods of Foote[16a] and Schleyer[16b] indicates that Ia solvolyzes a factor of $10^{2.9}$–$10^{4.1}$ times faster than a suitable model that would fit the Foote–Schleyer correlations. The enhanced reactivity of Ia might, therefore, be attributed to anchimeric assistance by the neighboring σ bond (Scheme IV). The relief of the steric strain in going from Ia to such a transition state, which would imply significant electron delocalization between C-3, C-8, and C-9, provides a reasonable interpretation for the lowering of the transition state energy of Ia → XII, compared to ionization of Ia *without* assistance of the C(3)–C(8) bond. The C(3)–C(8)–C(7) bond angle of Ia can be estimated from X-ray data[17] to be 87°, and much of the angle strain introduced by this small angle would be relieved in the transition state of the reaction Ia → XII. The high reactivity of Ia relative to IIa and IIb, which also have a strained cyclobutane ring adjacent to an ionizing center, is most probably due to a much greater skeletal strain of Ia. A greater amount of this skeletal strain must be released in the transition state of Ia → VII compared to that released in the ionization of IIa or IIb.

Table II. Rates[a] of Acetolyses, 25°

Compound	k, sec^{-1}	k_{rel}
Cyclohexyl brosylate	1.71×10^{-7} [b]	1.0
exo-2-Norbornyl brosylate	8.79×10^{-5} [b]	514
endo-2-Norbornyl brosylate	2.52×10^{-7} [b]	1.5
Bicyclo[2.2.2]oct-2-yl brosylate	9.07×10^{-6} [c]	53.0
Ia	3.61×10^{-3}	52,800[g]
IIIa	*Ca.* 8.5×10^{-7} [d]	*Ca.* 12
IVa	3.64×10^{-8} [e]	0.53[g]
IIa (OTs)	3.0×10^{-9} [f]	0.053[g]
IIb (OTs)	1.0×10^{-9} [f]	0.018[g]
Homocubyl tosylate	8.53×10^{-9} [h]	0.15[g]

[a] All rate constants except for IIIa are titrimetric. [b] S. Winstein, B. K. Morse, E. Grunwald, H. W. Jones, J. Corse, D. Trifan, and H. Marshall, *J. Amer. Chem. Soc.*, **74**, 1127 (1952). [c] H. L. Goering and M. F. Sloan, *ibid.*, **83**, 1992 (1961). [d] Using the activation parameter of IVa, the rate at 25° was estimated. [e] Extrapolated from rate data at higher temperatures. [f] Reference 5. [g] The observed rates for acetolysis of methanesulfonate esters were assumed to be larger than the rates for the corresponding tosylate esters by a factor of 1.2; D. S. Noyce, B. Johnson, and B. Winstein, *J. Org. Chem.*, **34**, 463 (1969). The ratio $k_{(\text{ROBs})}/k_{(\text{ROTs})}$ was assumed to be 3. [h] P. von R. Schleyer, J. Harper, G. Dunn, V. DiPasquo, and R. Hoover, *J. Amer. Chem. Soc.*, **89**, 698 (1967); W. G. Dauben and E. Debus, unpublished results.

Although neighboring strained cyclobutane bonds might provide some "vertical" stabilization[18] of the transition state leading to a cation with positive charge located at C-9, formation of endo products IIIa and IIIc suggests that significant backside bonding at C-8 and C-9 must exist in the ion pair or intermediate (postulated as VII and XI, Scheme IV) leading to those products. Solvent must also be excluded from one side of

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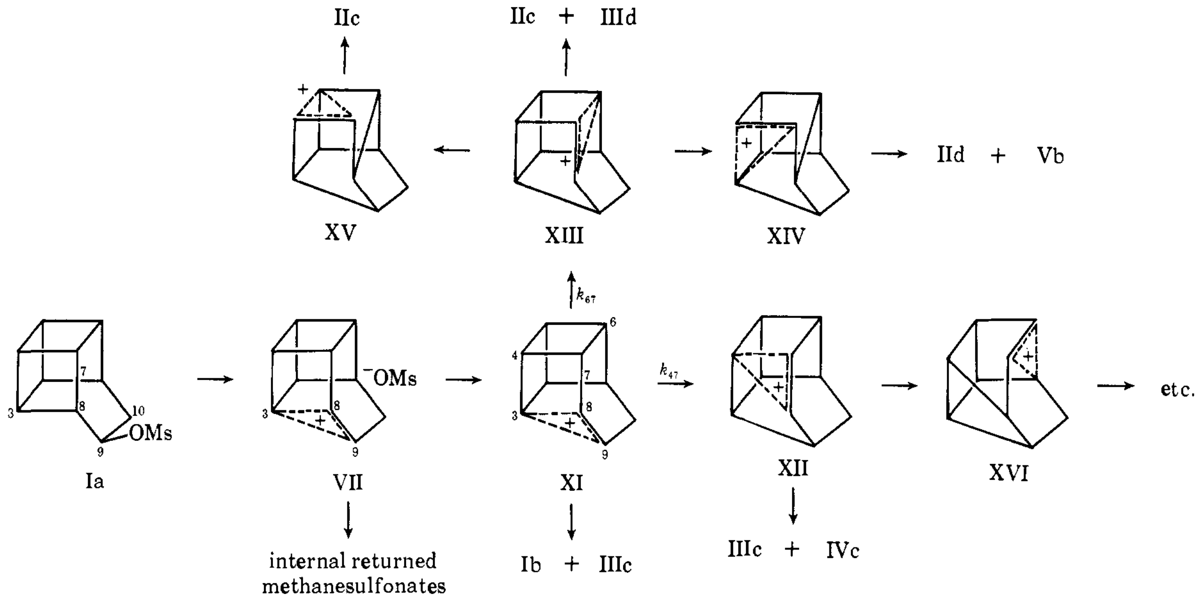
distance, see H. L. Goering and M. J. Degani, *J. Amer. Chem. Soc.*, **91**, 4506 (1969).

[16] (a) C. S. Foote, *ibid.*, **86**, 1853 (1964); (b) P. von R. Schleyer, *ibid.*, **86**, 1853, 1855 (1964). The parameters used in the Schleyer correlation were: ν_{CO} 1715 (weighted average of absorptions at 1727 and 1709 cm^{-1}); ϕ, 0, 60; GS-TS, 0.4. Recent findings have shown that in all cases the k_s/k_c ratio is not unity; thus, the Foote–Schleyer correlation may be of limited usage (P. v. R. Schleyer, J. L. Fry, L. K. M. Lam, and C. J. Lancelot, *ibid.*, **92**, 2542 (1970).

[17] W. G. Dauben, C. H. Schallhorn, and D. L. Whalen, *ibid.*, **93**, 1446 (1971).

[18] N. A. Clinton, R. S. Brown, and T. G. Traylor, *ibid.*, **92**, 5228 (1970).

Scheme IV



the intermediate(s) leading to endo product IVc. Electron-delocalized intermediate XII (Scheme IV) satisfies this requirement.[19]

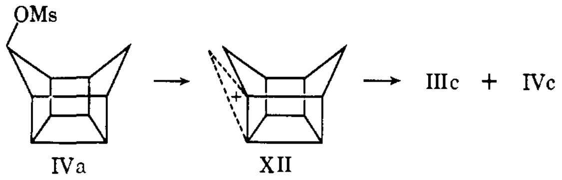
Isolation of acetates IIc, IId, and Vb in the acetolysis of Ia suggests that pentacyclic cations XIII, XIV, and XV are also intermediates, formed by further carbon–carbon bond migrations in intermediates XI and XII. Previous work by Dilling[5] has demonstrated that intermediate XV, generated by solvolysis of IIa (OTS), produces only product IIc. Also, generation of ion XIV from solvolysis of IIb (OTS) yields only products IId and Vb. These products are consistent with the bridged structures proposed.

If the pentacyclodecyl cations formed from solvolysis of Ia are indeed bridged, then two types of carbon–carbon bond migrations are possible: a frontside migration (*i.e.*, same side as carbon bridge), *i.e.*, XI → XII and XIII → XV, and a backside migration (*i.e.*, opposite side as carbon bridge), *i.e.* XI → XIII and XIII → XIV. A frontside migration would lead to retention of stereochemistry at one carbon atom (C-8 in XI → XII, Scheme IV), whereas a backside migration would provide inversion of stereochemistry at this same carbon atom (C-8 in XI → XIII, Scheme IV). These rearrangement processes would predict formation of all possible pentacyclodecyl acetate isomers in the product mixture if extensive rearrangement took place. The product mixture isolated suggests that frontside and backside migrations of carbon to an electron-deficient center (*i.e.*, k_{47} *vs.* k_{67} in Scheme IV) are competitive. Acetates IIId and IVd might therefore be expected in the product mixture. However, because of the complexity of the product distribution, small amounts of either isomer may have gone undetected. The isomeric acetates could also result from a symmetrically solvated classical ion.

Acetolysis of IVa in buffered acetic acid at 75° for 10 half-lives, followed by lithium aluminum hydride reduction of the acetate products, yielded 62% of IVe, 7% of IIIe, 10% of IIe and IIf,[20] 16% of Vc, 2% of an unidentified product with the same retention time as IIIf, and 3% of products with short retention times. Bishomocubanol (Ic) was not detected in the product mixture. A low infinity titer (94% of theoretical) suggests that some internal return to slower solvolyzing methanesulfonates occurs.

Ionization of mesylate IVa with anchimeric assistance would produce bridged ion XII, and collapse of solvent from the top side of this ion explains formation of the major acetate IVc with retained stereochemistry. However, at least several other intermediate ions must also be present to explain products IIc, IId, and Vb. Therefore, ion XII (see Scheme V) must also convert to ions XIII, XIV, and XV. The exact route(s) by which XII converts to XIII, XIV, and XV has not been ascertained. The synthesis and solvolysis of *exo,sym*-1,3-bishomocubanol (IVb) will cast more light on the skeletal rearrangement routes of pentacyclodecyl cations.

Scheme V



Experimental Section

Melting points were determined in capillary tubes and are uncorrected. Combustion analyses were performed by the Microanalytical Laboratory, College of Chemistry, University of California at Berkeley.

Kinetics. A. Materials. Dry acetic acid was prepared by distillation from a solution containing 0.05 *M* acetic anhydride in glacial acetic acid. Additional acetic anhydride was added to the dry acetic acid so that the concentration was 0.01 *M*. Standard potassium acetate–acetic acid solution was prepared from analytical potassium carbonate and dry acetic acid.

B. Procedure. The rate of acetolysis of Ia was determined by the method of Wiberg and Hess.[21] Rates of acetolysis of IIIa

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(19) Rapidly equilibrating classical ions have also been invoked to explain the observed stereospecificity: H. C. Brown, K. J. Morgan, and F. J. Chloupek, *J. Amer. Chem. Soc.*, **87**, 2137 (1965).

(20) The glpc fraction containing IIe and IIf was collected, and its infrared spectrum was essentially identical with the infrared spectrum of a sample containing 60% of IIf and 40% of IIe.

(21) K. Wiberg and B. Hess, Jr., *J. Amer. Chem. Soc.*, **89**, 3015 (1967).

were determined, by the sealed ampoule[22] technique, in 0.01605 M potassium acetate–acetic acid solution. Aliquots were withdrawn from the rate bath and backtitrated with 0.01625 M perchloric acid–acetic acid solution to a bromphenol blue end point. Rate constants were calculated from nonlinear regression analysis of the data on a Wang 700 tabletop computer, with a program kindly written by Professor A. C. Hyman, University of Maryland, Baltimore County.

Pentacyclo[4.4.0.0^{2,5}.0^{3,8}.0^{4,7}]dec-9-yl Methanesulfonate (Ia). A solution of 6.06 g (40.9 mmol) of pentacyclo[4.4.0.0^{2,5}.0^{3,8}.0^{4,7}]decan-9-ol (Ic) and 4.73 g (41.3 mmol) of methanesulfonyl chloride[23] in 80 ml of benzene was cooled in an ice bath. To the stirred solution was added dropwise 4.70 g (46.5 mmol) of triethylamine over a period of several minutes. The reaction mixture was removed from the ice bath and allowed to stir at room temperature for 10 min. The mixture was filtered and the solid ammonium chloride was washed with benzene. The solvent was removed under aspirator pressure to yield 10.0 g of clear oil. A small sample of product was further freed from solvent by a stream of nitrogen: ir (CCl_4) 1348, 1172 cm^{-1}; nmr (τ, CCl_4) 5.20 (doublet of triplets, 1, J = 3.5, 9.5 Hz), 7.11 (s, 3).

Anal. Calcd for $C_{11}H_{14}O_3S$: C, 58.38; H, 6.24. Found: C, 58.38; H, 6.67.

The ester was unstable, and was used immediately after making.

Lithium Aluminum Hydride Reduction of Pentacyclo[4.4.0.0^{2,5}.0^{3,8}.0^{4,7}]dec-9-yl Methanesulfonate. Lithium aluminum hydride (150 mg, 3.95 mmol) was added to a solution of 154 mg (0.682 mmol) of Ia in 15 ml of dry ether, and the resulting mixture was stirred under reflux for 30 min. Excess lithium aluminum hydride was decomposed with water, and the ether solvent was carefully removed by distillation. The residue was filtered through 1.5 g of Woelm neutral alumina (activity III) with pentane, and the solvent was carefully removed to yield 44 mg (49.5%) of pentacyclo[4.4.0.0^{2,5}.0^{3,8}.0^{4,7}]decane, mp 99–103°, with ir and nmr spectra identical with that of the authentic sample.[7]

Product Analysis from Acetolysis of Pentacyclo[4.4.0.0^{2,5}.0^{3,8}.0^{4,7}]dec-9-yl Methanesulfonate (Ia). A. Isolation of Products. To a stirred solution of 3.36 g (0.041 mol) of anhydrous sodium acetate in 200 ml of glacial acetic acid was added 9.2 g (0.041 mol) of methanesulfonate Ia. The reaction mixture was allowed to stand at room temperature for 3.25 hr and was then diluted with 600 ml of water. The mixture was extracted three times with pentane (total 450 ml). The pentane extracts were combined and dried with anhydrous magnesium sulfate, and the solvent was removed to yield 7.15 g of product mixture.

The product was chromatographed on a column of 150 g of Woelm neutral alumina III. Elution of the column with 1 l. of pentane yielded 2.68 g (34.7%) of a complex acetate mixture, ir (CCl_4) 1727 cm^{-1}. Further elution of the column with 600 ml of benzene provided 3.77 g (40%) of internal returned methanesulfonate esters: ir (CCl_4) 1175 cm^{-1}; nmr (τ, CCl_4) 7.08 and 7.10 (singlets, approximately equal intensities), 7.56 and 7.59 (doublets, J = 13 Hz, approximately equal intensities). Recrystallization of this mixture twice from ether–petroleum ether (bp 30–60°) produced relatively pure IVa, mp 76–79° (contaminated with small amount of IIIa).

B. Analysis of Acetate Mixture. The acetate fraction was hydrolyzed with potassium hydroxide in methanol and the resulting alcohol mixture was analyzed on a 20% DEGS glpc column. The mixture was found to consist of 5% of an unidentified material, 15% of Vc, 15% of a mixture of IIe and IIf (40:60 ratio),[24] 10% of Ic, and 55% of IVe and IIIe (90:10 ratio). The spectral data of alcohol products and their corresponding ketones are given below.

Vc showed the following: mp 137–140°; ir (CCl_4) 3610 cm^{-1}; nmr (τ, CCl_4) 6.03 (unresolved, 1), 6.9–7.8 (m, 8), 8.63 (unresolved, 2). Oxidation of Vc with Jones reagent[12] yielded pentacyclo[5.3.0.0^{2,6}.0^{3,9}.0^{4,8}]decan-5-one: mp 120–122° [lit.[11] mp 123°]; ir (CCl_4) 1821, 1795, 1751, 1698 cm^{-1}; nmr (τ, CCl_4) 6.67 (unresolved, 2), 7.24 (m, 4), 7.43 (unresolved, 2), 8.58 (t, 2, J = 1.4 Hz).

IIe and IIf showed the following: ir (CCl_4) 3610 cm^{-1}; nmr (τ, CCl_4) 5.78 and 6.06 (C*H*OH, ratio 60:40). Oxidation of IIe and IIf with Jones reagent produced pentacyclo[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]decan-6-one, mp 124–126° [lit.[10] mp 124–126°], with an ir spectrum identical with that of an authentic sample.

IVe showed the following: mp 223–225°; ir (CCl_4) 3610 cm^{-1}; nmr (τ, $CDCl_3$) 6.06 (t, 1, J = 4.0 Hz), 7.0 (m, 8), 7.40 (d, 1, J = 12.5 Hz), 8.88 (d, 1, J = 12.5 Hz further unresolved splitting). Weak absorption at τ 7.50 (d, J = 12.5 Hz) indicated that approximately 10% of IIIe was also present. See analysis of methanesulfonate mixture below. Oxidation of IVe with Jones reagent produced pentacyclo[4.4.0.0^{2,5}.0^{3,9}.0^{4,8}]decan-7-one: mp 180–182°; ir (CCl_4) 1739 cm^{-1}; nmr (τ, CCl_4) 6.67 (m, 6), 7.15 (m, 2), 8.11 (d, 1, J = 13 Hz), 8.62 (d, 1, J = 13 Hz), further unresolved splitting).

C. Analysis of Internal-Returned Methanesulfonate Mixture. A solution of 500 mg (21.7 mmol) of sodium in 40 ml of liquid ammonia[25] was prepared in a three-necked flask equipped with a Dry Ice condenser, fitted with a potassium hydroxide drying tube, and containing a magnetic stirring bar. A solution of 0.474 g (2.1 mmol) of internal-returned methanesulfonates in 25 ml of anhydrous ether was added, and the mixture was allowed to stir for $2^1/_3$ hr. The excess sodium was decomposed with solid ammonium chloride, followed by careful addition of 10 ml of water. The mixture was allowed to stir 1 hr at room temperature, and was diluted with water. The product was extracted into ether, the ether solution was washed with 5% hydrochloric acid, water, and saturated sodium chloride solution, and then dried over anhydrous magnesium sulfate. The solvent was removed and the residue sublimed at 125° (1 mm): yield 238 mg (78%); mp 214–217°; ir (CCl_4) 3623 cm^{-1}; nmr (τ, $CDCl_3$) 5.94 (quartet, C*H*OH, J = 2.6, 7.0 Hz), 6.11 (t, C*H*OH, J = 4 Hz), 7.40 (d, J = 12.5 Hz), 7.50 (d, J = 12.5 Hz). The triplet at τ 6.11 and doublet at 7.40 were also present in the nmr spectrum of the major product from hydrolysis of the solvolysis acetates, and therefore was attributed to the symmetrical structure IVe. The quartet at τ 5.94 and doublet at 7.50 were assigned to the endo unsymmetrical structure IIIe. Analysis of the sublimed alcohol mixture on glpc indicated also the presence of 7% of IIe and IIIf,[9] and 3% of Vc.

Aluminum Isopropoxide Epimerization of IIId. A mixture of 77 mg (0.57 mmol) of a mixture of alcohols IIIe and IVe, obtained from sodium–ammonia reduction of internal returned methanesulfonates above, was heated at 90° under nitrogen with 132 mg (0.66 mmol) of aluminum isopropoxide, 78 μl (1.1 mmol) of acetone, and 4 ml of isopropyl alcohol for 75 hr. The reaction solution was diluted with saturated sodium chloride solution and the product was extracted into ether; yield 65 mg (50%). Glpc analysis (20% DEGS column, 151°) of the product mixture indicated the presence of about 25% of a new product with a retention time different from that of IIIe and IVe. The doublet (J = 13 Hz) at τ 7.50 due to IIIe in the original reaction mixture was reduced to $\simeq$25% of the intensity of the doublet (J = 13 Hz) at τ 7.40 due to the α hydrogen of IVe. This result indicated that IIIe had undergone substantial isomerization to a new isomer, whereas IVe isomerized much more slowly under the conditions.

The new product was collected from glpc: mp 185–190°; ir (CCl_4) 3650, 3400 (broad) cm^{-1}; nmr (CCl_4) 6.05 (1 H, m), no olefinic absorption; molecular weight (mass spectrum) 148.

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[24] The ratio of IIe:IIf was determined by comparing the areas of the absorptions at τ 5.78 and 6.06; see ref 5.

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