Registry No.—Tri-*t*-butyl phosphate, 20224-50-4; cyclohexylammonium di-*t*-butyl phosphate, 20224-52-6; triisopropyl phosphate, 513-02-0; pinacol phosphonate, 16352-18-4; methyl pinacol phosphite, 14812-60-3; methylpinacol phosphate, 7443-26-7; *t*-butyl pinacol phosphate, 20224-35-5-; pinacol phosphoric acid, 13882-05-8; triallyl phosphate, 1623-19-4; tri-*t*-butyl phosphite, 15205-62-6.

Acknowledgment.—This work was generously supported by the National Institutes of Health under Grant 07965-03.

Pentacyclodecane Chemistry. V. The Synthesis and Acetolysis of *syn*- and *anti*-Pentacyclo[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]dec-6-yl *p*-Toluenesulfonate. Evidence Concerning the Intermediacy of Bridged Carbonium Ions[1]

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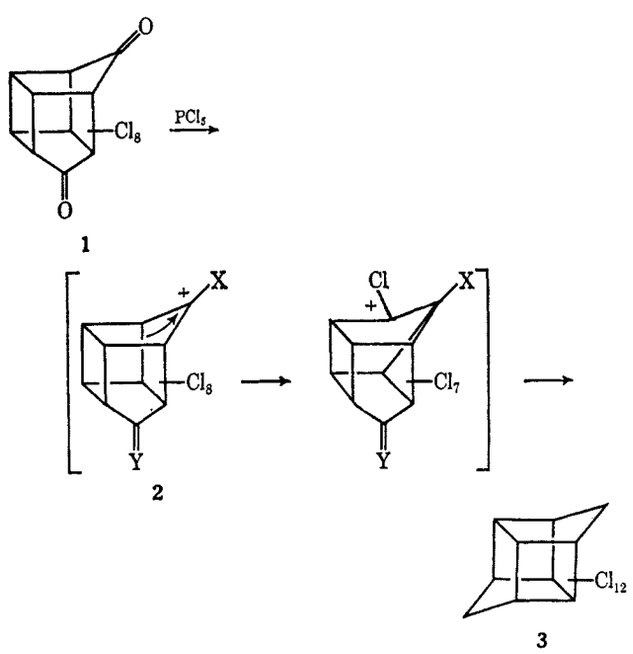
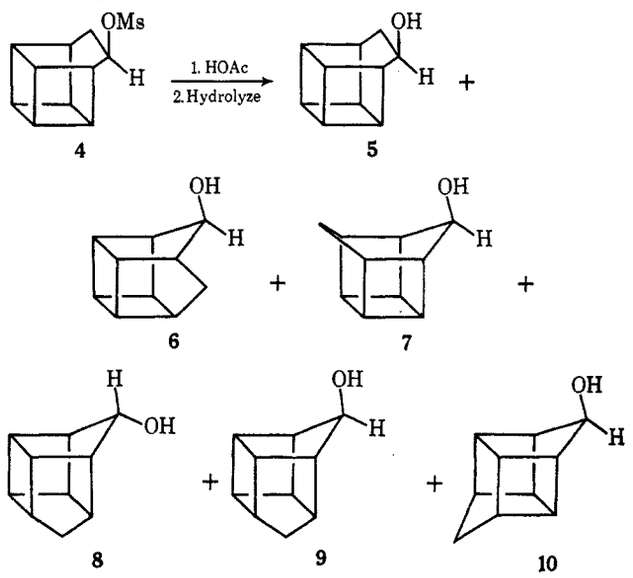
The *syn* and *anti* isomers of pentacyclo[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]decan-6-ol were synthesized by irradiation of *syn*- and *anti,endo*-tricyclo[5.2.1.0^{2,6}]deca-4,8-dien-3-ol, respectively, in acetone solution. Solvolysis of the *syn*-pentacyclodecyl tosylate in unbuffered acetic acid gave almost exclusively the unrearranged *syn* acetate. Acetolysis of the *anti* tosylate gave mainly the rearranged pentacyclo[5.3.0.0^{2,6}.0^{3,9}.0^{4,8}]dec-6-yl acetate accompanied by 15% of unrearranged *anti* acetate. Internal return with rearrangement occurred with the *anti* tosylate. The rates of acetolysis of the *syn* and *anti* tosylates were measured; rate accelerations of 1.3×10^4 and 5×10^3, respectively, over those predicted for unassisted solvolysis were calculated from Schleyer's equation. Reduction of pentacyclo[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]decan-6-one with sodium borohydride, lithium aluminum hydride, and lithium tri-*t*-butoxyaluminum hydride gave 76–80:24–20 ratios of *syn* and *anti* alcohols, respectively. The rate of borohydride reduction was determined, and an attempted correlation with the solvolysis rates was made. Equilibration of the *syn* and *anti* alcohols with aluminum isopropoxide–acetone gave a 50:50 mixture. The solvolysis reactions are best interpreted in terms of bridged carbonium ion intermediates, although other explanations cannot be ruled out entirely.

The unsymmetrical perchloro diketone **1** has been reported to rearrange to the symmetrical chlorocarbon **3** on reaction with phosphorus pentachloride.[2] The



X = $OPCL_4$ or Cl, Y = 0 or Cl_2

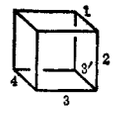
most reasonable pathway for this 1,3- to 1,4-bishomocubyl[3] rearrangement involves a carbonium ion mechanism[4] in which a 1,2-alkyl migration occurs in one of the cations **2**. A related reaction involving the acetolysis of the 1,1-bishomocubyl mesylate **4** was also recently reported.[5] Interestingly, this reaction generates all of the five possible bishomocubyl carbon skeletons **5–10**,[3,6]



(1) Part IV: W. L. Dilling and C. E. Reineke, *Tetrahedron Lett.*, 2547 (1967). A preliminary account of this work is presented in this paper.

(2) (a) P. E. Eaton, Ph.D. Thesis, Harvard University, 1960; (b) G. W. Griffin and A. K. Price, *J. Org. Chem.*, **29**, 3192 (1964).

(3) The numbering for the bishomocubane system of nomenclature refers to the shortest path along the edges of a cube between the positions of the two methylene bridges. Thus the five possible bishomocubanes are as follows: pentacyclo[4.4.0.0^{2,5}.0^{3,8}.0^{4,7}]decane, 1,1-bishomocubane; pentacyclo[4.4.0.0^{2,5}.0^{3,9}.0^{4,7}]decane, 1,2-bishomocubane; pentacyclo[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]decane, 1,3-bishomocubane; pentacyclo[4.4.0.0^{2,5}.0^{3,9}.0^{4,8}]decane, 1,3′-bishomocubane; pentacyclo[5.3.0.0^{2,6}.0^{3,9}.0^{4,8}]decane, 1,4-bishomocubane.



(4) M. S. Newman and L. L. Wood, Jr., *J. Amer. Chem. Soc.*, **81**, 4300 (1959).

(5) W. G. Dauben and D. L. Whalen, *ibid.*, **88**, 4739 (1966).

(6) The stereoisomers **8** and **9** were only isolated as a mixture and were not identified individually.[5]

TABLE I

NMR DATA FOR PENTACYCLODECANOLS[a]

Alcohol	—CHOH—	—C—H	O—H	—CH₂—
syn **8**	−4.04[b] (1.0)[c]	−3.2 to −2.1 (−)[d]	−2.28 (−)[d]	−1.66,[e] −1.41[e] (2.0)
anti **9**	−4.28[f] (1.0)	−3.1 to −2.2 (7.9)	−2.08 (1.0)	−1.62[g] (1.0), −1.20[g] (1.0)
10	−4.08 (1.0)	−3.1 to −2.3 (8.0)	−2.15 (1.0)	−1.39 (2.0)

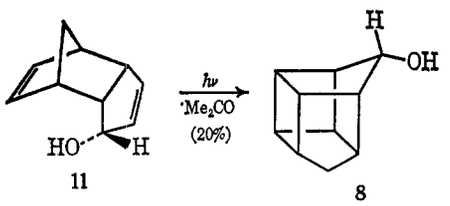
[a] $CDCl_3$ solution. [b] Ppm from internal TMS (δ). [c] Relative peak areas in parentheses. [d] Total relative area 9.0. [e] Doublet, J_{gem} = 10.8 cps, with further splitting evident. [f] Triplet, $J \sim 1.5$ cps. [g] Doublet, J_{gem} = 11.0 cps.

presumably *via* a series of carbonium ion rearrangements.[5]

The original purpose of the work described in this paper was the examination of the 1,3-bishomocubyl cation to 1,4-bishomocubyl cation rearrangement. The solvolysis of tosylate esters was chosen as the method for generating the 1,3-bishomocubyl cation. After this work was underway, it became apparent that this system was ideal for studying the possible intermediacy of bridged carbonium ions.

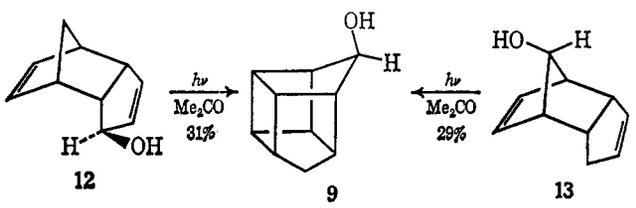
Results

syn-Pentacyclo[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]decan-6-ol[7] (**8**) was synthesized by the acetone photosensitized ring closure[8] of *endo,syn*-tricyclo[5.2.1.0^{2,6}]deca-4,8-dien-3-ol[9] (**11**).[10,11]



11 **8**

In a similar manner, the *anti* isomer **9** was prepared by irradiation of both the *anti*-3-dienol[9] **12** or the *syn*-10-dienol[9] **13** in acetone solution.

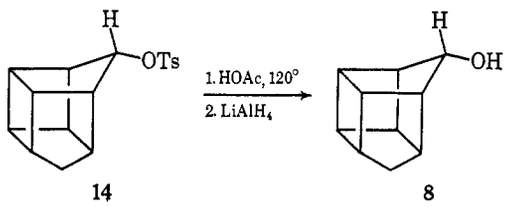


12 **9** **13**

The infrared, nuclear magnetic resonance (nmr), and mass spectra[13] (see Experimental Section) were entirely consistent with the assigned structures. All attempts to separate mixtures of the isomeric alcohols **8** and **9** were unsuccessful. Therefore, analyses of mixtures of these alcohols were made by nmr spectroscopy. The spectral data are given in Table I along with those for the symmetrical alcohol **10**. Of particular value for analysis were the signals for the proton on the hydroxyl-bearing carbon atoms (C-6). Also, the two isomers showed distinctly different AB quartet patterns for the methylene group.

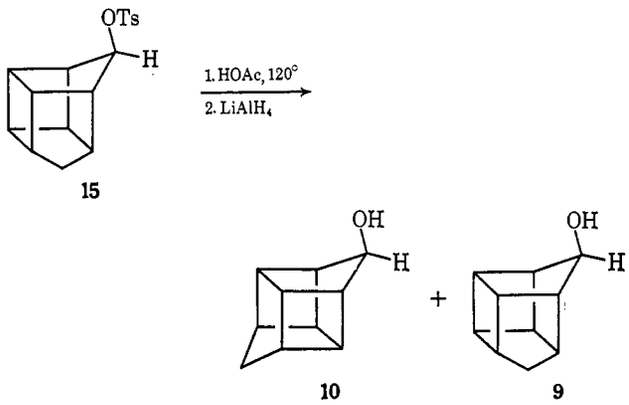
The acetates and tosylates of the alcohols **8** and **9** were prepared by standard procedures. The infrared, nmr, and mass spectra were consistent with the assigned structures. The differences in the nmr spectra of the alcohols **8** and **9** noted above were also observed in the spectra of the acetates and tosylates.

Preparative acetolysis of the *syn* tosylate **14** in unbuffered acetic acid at 120° for 10 half-lives, followed by lithium aluminum hydride reduction of the acetate product, gave the *syn* alcohol **8** in 94% over-all yield.



14 **8**

There could have been as much as 4% of both the *anti* alcohol **9** and the symmetrical alcohol **10** present in the *syn* alcohol **8** produced in this reaction. No concrete evidence for the formation of either **9** or **10** was obtained other than a gas chromatography (gc) peak with a retention time corresponding to the symmetrical alcohol **10**. The product from unbuffered acetolysis of the *anti* tosylate **15** at 120° for 10 half-lives was also reduced with lithium aluminum hydride. This product mixture consisted mainly (85%) of the rearranged symmetrical alcohol **10** and 15% unrearranged *anti* alcohol **9**. The presence of several per cent *syn* alcohol **8** would not have been detected in this product mixture. The over-all yield (75%) was not so high in this reaction as that described above from the *syn* tosylate **14**. Some black carbonaceous material was also formed in



15 **10** **9**

(7) The terms *syn* and *anti* refer to the position of the functional group with respect to the second methylene bridge (C-10).

(8) (a) G. O. Schenck and R. Steinmetz, *Chem. Ber.*, **96**, 520 (1963), have reported the acetone-sensitized ring closure of *endo*-dicyclopentadiene to pentacyclo[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]decane. (b) For other related ring closures see W. L. Dilling, *Chem. Rev.*, **66**, 384 (1966).

(9) R. B. Woodward and T. J. Katz, *Tetrahedron*, **5**, 70 (1959).

(10) Although the structural formulas in this paper show only one enantiomer, all the compounds capable of existing as optical isomers were actually racemic mixtures.

(11) The *syn* alcohol **8** has also been prepared by Cookson and coworkers[12] by the acetone-sensitized irradiation of *endo,anti*-tricyclo[5.2.1.0^{2,6}]deca-3,8-dien-10-ol.

(12) R. C. Cookson, J. Hudec, and R. O. Williams, *J. Chem. Soc., C*, 1382 (1967).

(13) See W. L. Dilling and M. L. Dilling, *Tetrahedron*, **23**, 1225 (1967), for the mass spectra of related compounds.

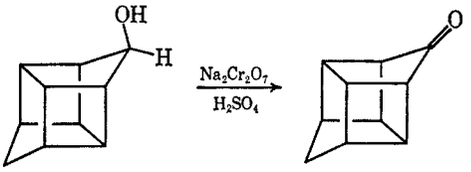
TABLE II

ACETOLYSIS RATES OF PENTACYCLODECYL TOSYLATES

Tosylate	Temp, °C	Rate constant (sec^{-1})[a]	$\Delta H^{\ddagger}$ (kcal/mol)[b]	$\Delta S^{\ddagger}$ (eu)[b]
syn **14**	120.0 ± 0.1	2.82 ± 0.04 × 10^{-4}	27.3 ± 1.0	−5.9 ± 1.6
	110.0 ± 0.1	1.10 ± 0.02 × 10^{-4}		
	25	3.0 × 10^{-9}		
anti **15**	130.0 ± 0.1	1.18 ± 0.04 × 10^{-4}		
	120.0 ± 0.1	5.07 ± 0.21 × 10^{-5}	25.8 ± 2.4	−13.2 ± 4.1
	25	1.0 × 10^{-9}		

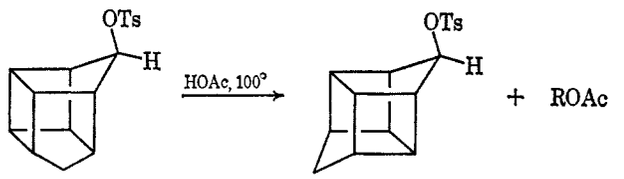
[a] Standard deviation given.[16] [b] Statistical error given.[17]

the acetolysis of the *anti* tosylate **15**. The symmetrical alcohol **10** was identified by spectral comparison with an authentic sample[5] as well as oxidation to the known ketone **16**.[2b,5] Acetolysis of the *anti* tosylate **15** at



10 **16**

100° for slightly less than 1 half-life (28% acetate isolated) gave approximately equal amounts of recovered *anti* tosylate **15** (30%) and rearranged symmetrical tosylate **17** (30%). The symmetrical tosylate



15 **17**

17 was identified by comparison of its nmr spectrum with that of an authentic sample.[14] No evidence (nmr, infrared) for any olefinic products was detected in the acetolysis of ether tosylate **14** or **15**.

The solvolysis rate data for tosylates **14** and **15** in unbuffered acetic acid are summarized in Table II.[15-17]

In order to use Schleyer's equation[18] relating the predicted unassisted solvolysis rate of secondary tosylates with strain effects, one needs an accurate measure of the carbonyl infrared stretching frequency of the corresponding ketone. The pertinent infrared absorption bands of ketone **18** are given in the Experimental Section. The splitting in the carbonyl region is assumed to be due to Fermi resonance.[19] Presumably the mode in resonance with $\nu_{C=O}$ is the first overtone of the band at 862 cm^{-1}. In order for a first overtone to be in Fermi resonance with a fundamental, two requirements must be met. One is that the first overtone must be of the same symmetry species as the fundamental with which it is in resonance. Since the ketone **18** has no formal symmetry elements, all modes belong to the same symmetry species. The second requirement is that the fundamental of the mode whose overtone is in Fermi resonance with $\nu_{C=O}$ must be a motion which has sizable components in a direction perpendicular to the motion of $\nu_{C=O}$. The fundamental at 862 cm^{-1} is likely to be a mode in which the carbon atoms adjacent to the carbonyl group expand symmetrically (ν "*sym* C–C–C"), thus fulfilling the second requirement. The frequency 862 cm^{-1} is reasonable for this vibration, although this assignment must be regarded as speculative. The band at 862 cm^{-1} has two satellites at 849 and 879 cm^{-1} which we assume make up a Fermi-resonance triplet. Therefore the two main Fermi-resonance hybrids near 1700 cm^{-1} will also be slplit into triplets. This is observed; the strongest component at 1763 cm^{-1} has reasonably spaced satellites at 1783 and 1742 cm^{-1}; the component at 1697 cm^{-1} has satellites at 1670 and 1720 cm^{-1} (shoulder ?). The first-order correction for Fermi resonance was made by using the approximation of Longseth and

$$\omega^0 = \frac{\omega_a + \omega_b}{2} \pm \frac{\omega_a - \omega_b}{2}\left(\frac{A_a - A_b}{A_a + A_b}\right)$$

Lord,[20] where the two values of ω^0 are the unperturbed frequencies, ω_a (1762.7 cm^{-1}) and ω_b (1697.2 cm^{-1}) are the observed frequencies, and A_a and A_b are the respective integrated band intensities (for which the peak-height intensities were substituted, A_a 1.15, A_b 0.05). The calculated values of ω^0 are 1729.9 ± 29.9 cm^{-1}. Therefore, $\nu_{C=O}$ (unperturbed) = 1759.8 cm^{-1} (or 1760 cm^{-1} to nearest cm^{-1}), and 2ν "*sym* C–C–C" (unperturbed) = 1700 cm^{-1}. The calculated frequency for the first overtone of the fundamental at 862 cm^{-1}, assuming a harmonic oscillator, is 1724 cm^{-1}. The anharmonicity is therefore 1.4%, an entirely reasonable amount. The values of the torsional angles, ϕ_i (both 60° in **14** and **15**), needed to use Schleyer's equation[18] were determined by examination of molecular models of the *syn* and *anti* tosylates **14** and **15**. The differences in the nonbonded ground-state and transition-state strain energies, GS-TS strain (**14** 0.4; **15**, 0.3), was estimated by a comparison of models of the tosylates **14** and **15** with models of various similar compounds for which Schleyer[18] has calculated strain energies.

Reduction of the pentacyclodecanone **18** with various hydride reducing agents gave primarily the *syn* alcohol **8** accompanied by smaller amounts of the *anti* epimer **9** in ratios of 3–4:1 (Table III).

(14) S. F. Brown, Senior Thesis, Princeton University, 1967.

(15) These data are slightly revised from those given in our original communication[1] owing to a different method of data treatment.

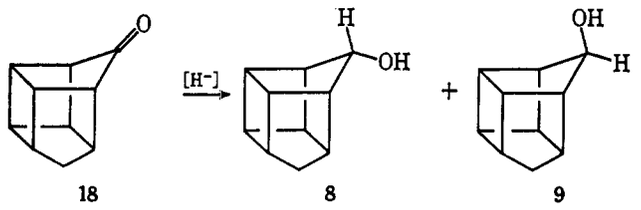
(16) E. L. Crow, F. A. Davis, and M. W. Maxfield, "Statistics Manual," Dover Publications, Inc., New York, N. Y., 1960, p 164.

(17) E. L. Purlee, R. W. Taft, Jr., and C. A. DeFazio, *J. Amer. Chem. Soc.*, **77**, 837 (1955).

(18) P. von R. Schleyer, *ibid.*, **86**, 1854 (1964).

(19) R. C. Cookson, E. Crundwell, R. R. Hill, and J. Hudec, *J. Chem. Soc.*, 3062 (1964).

(20) *Cf.* R. Ryason and M. K. Wilson, *J. Chem. Phys.*, **22**, 2000 (1954).



18 8 9

TABLE III

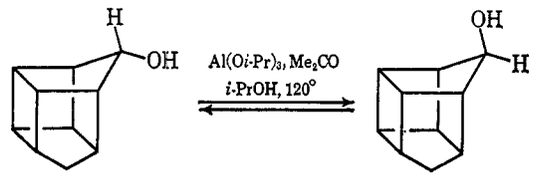
HYDRIDE REDUCTIONS OF PENTACYCLODECANONE 18

Reducting Agent	Solvent	—Product distribution, %— *syn* 8	*anti* 9
$NaBH_4$	MeOH	76 ± 1	24 ± 1
$LiAlH_4$[a]	Et_2O	80 ± 1	20 ± 1
$LiAl(O\text{-}t\text{-}Bu)_3H$	Et_2O	80 ± 1	20 ± 1

[a] Data from ref 13. Cookson and coworkers[12] also reported an 80:20 ratio for this reaction.

The rate of sodium borohydride reduction of the ketone **18** in 2-propanol at 0° was found to be 0.144 ± 0.007 M^{-1} sec^{-1}. Using the 76:24 ratio (Table III), one calculates partial rate factors of 11.0 × 10^{-2} M^{-1} sec^{-1} for hydride attack from the *anti* direction to produce the *syn* alcohol **8** and 3.5 × 10^{-2} M^{-1} sec^{-1} for attack from the *syn* direction to produce the *anti* alcohol **9**.

Equilibration of the epimeric alcohols **8** and **9** with aluminum isopropoxide and acetone in 2-propanol at 120° gave equal amounts of the two isomers within experimental error (50 ± 1:50 ± 1).[21]



8 9

Discussion

The skeletal rearrangement which occurs on solvolysis of the *anti* tosylate **15** shows that the 1,3-bishomocubyl cation can rearrange to the 1,4-bishomocubyl cation if the stereochemistry of the leaving group is appropriate. This observation lends support to the mechanism proposed above for the rearrangement which occurs on chlorination of the diketone **1**. Also, one step in the mechanism proposed by Dauben and Whalen[5] for the rearrangements occurring on solvolysis of the 1,1-bishomocubyl mesylate **4** is substantiated by this observation.

The fact that distinctly different products are formed on acetolysis of the *syn* and *anti* tosylates **14** and **15** shows that none or very little of a common intermediate is formed in the two reactions. This observation rules out any free or symmetrically solvated (*i.e.* free of leaving group effects) nonbridged carbonium ions as intermediates. A planar sp^2 carbonium ion carbon atom is assumed although a suggestion has been made that the structurally similar 7-norbornyl cation may be nonplanar.[22]

(21) Our previously reported[1] distribution for this equilibrium was in error.

The products from acetolysis of the tosylates **14** and **15** are easily rationalized on the basis of stereospecific rearrangements dictated by the stereochemistry of the tosylate group; *i.e.*, only rear-side 1,2-alkyl migrations are permitted (Scheme I). It is also clear that combination of the cation with the nucleophile must occur from the front side. The 1,3-bishomocubyl acetates **19** and **21** and the 1,4-bishomocubyl acetate **22** are not the only products which could conceivably be formed under the above specified requirements (Scheme I). Rearrangement *via* path b would lead to a 1,2-bishomocubyl derivative **20** while path d would lead to a 1,3′ derivative **23**. No evidence for the formation of any products other than **19**, **21**, and **22** was obtained. This lack of rearrangement to products having the carbon skeletons of **20** and **23** (and to the 1,1-bishomocubyl skeleton as in **5**) is entirely reasonable when one considers the relative amounts of strain present in these systems as judged by an examination of molecular models. The order of decreasing strain in the bishomocubyl carbon skeletons is probably 1,1 > 1,2 > 1,3′ > 1,3 > 1,4 owing to the 1,1 system having four cyclobutane rings fused together, the 1,2 system having three cyclobutane rings fused about a single carbon atom, the 1,3′ system having three cyclobutane rings fused in a linear arrangement, the 1,3 system having two cyclobutane rings fused, and the 1,4 system having two isolated cyclobutane rings. Dauben and Whalen's[5] results starting from the 1,1-bishomocubyl system are thus entirely reasonable.

With the data at hand, we have no evidence concerning the rearrangement of the *syn* tosylate **14** to the enantiomeric carbon skeleton (Scheme I). Work is currently under way to test this point. It is conceivable that the *syn* acetate **19** formed in this reaction arises simply by a substitution reaction proceeding with retention of configuration without any skeletal rearrangement, although we favor a reaction involving rearrangement (see below). Solvolysis of 7-norbornyl tosylate or brosylate leads to a high degree of retention without skeletal rearrangement in the formation of the 7-norbornyl product.[22,23]

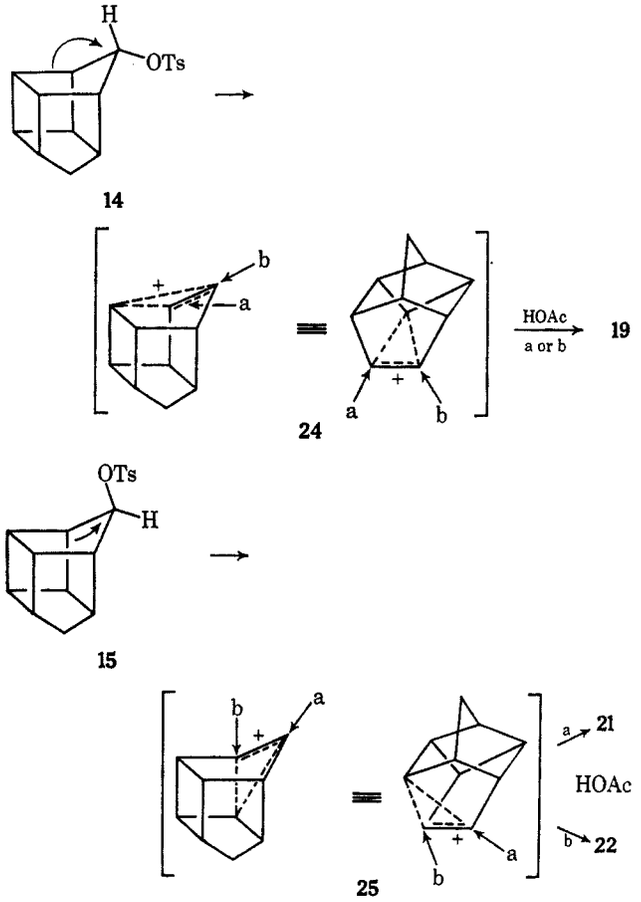
Reasonably good first-order kinetics were obtained for the acetolysis of the *anti* tosylate **15** up to 80–90% completion of the reaction, even though considerable rearrangement to the 1,4-bishomocubyl tosylate **17** occurred during acetolysis. The infinity titrations were also in good agreement with the theoretical values. These results imply that the acetolysis rate for the 1,4-tosylate **17** is nearly the same as that for the *anti* 1,3-tosylate **15**. Unpublished work by Schleyer and Brown shows this to be true; $k_{1,4}^{120°}$ = 6.86 × 10^{-5} sec^{-1}.[14] The low material balance (75%) and blackening of the reaction mixture on acetolysis of the *anti* tosylate **15** may indicate some ring opening to olefinic products followed by polymerization or decomposition.

The simplest and most consistent explanation for the stereochemical results of the solvolyses of the

(22) (a) F. B. Miles, *J. Amer. Chem. Soc.*, **90**, 1265 (1968); (b) P. G. Gassman, J. M. Hornback, and J. L. Marshall, *ibid.*, **90**, 6238 (1968). See however (c) J. E. Williams, Jr., R. Sustmann, L. C. Allen, and P. von R. Schleyer, *ibid.*, **91**, 1037 (1969).

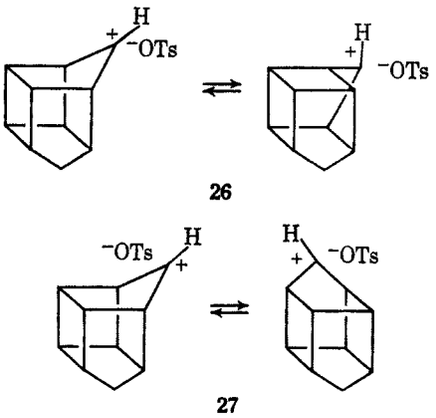
(23) (a) P. G. Gassman and J. M. Hornback, *ibid.*, **89**, 2487 (1967); (b) F. B. Miles, *ibid.*, **89**, 2488 (1967).

epimeric tosylates **14** and **15** is the intermediacy of the bridged ions **24** and **25**.[24]



The observed stereochemical retention in these substitution reactions could not have been due to S–O bond cleavage,[25] as evidenced by the fact that the acetates **19**, **21**, and **22** were the primary reaction products, not the alcohols **8**, **9**, and **10**. The concept of rapidly equilibrating nonbridged ions[26] (free or symmetrically solvated) does not appear to give a reasonable explanation, since one of the nonbridged ions (Scheme I) from both tosylates is the same (assuming a planar sp^2 carbonium ion); thus the same products would be expected from either tosylate, and such is not the case. The only apparent way for this explanation to be valid is for the equilibration between the two nonbridged cations to be faster than the C-6 carbon–hydrogen bending vibration, a situation which for all practical purposes would be the same as a vibrating bridged ion. A steric effect cannot be invoked in these bishomocubyl cations as the reason for the observed stereochemistry, as has been done for the 2-norbornyl system.[24f] Studies on hydride reduction of 1,3-bishomocubanone **18** and equilibration of the *syn* and *anti* alcohols **8** and **9** (see below) show that both faces of the carbonium ion at C-6 should be readily accessible to approach by a nucleophile.

An alternative explanation, which is not so easily dismissed, is the intermediacy of two sets of rapidly equilibrating nonbridged ion pairs **26** and **27**, which could be generated from the tosylates **14** and **15** respectively. Thus no common intermediate would be



formed from the two tosylates **14** and **15** if these ion pairs were the intermediates. One must still have some mechanism to account for the almost exclusive retention of configuration in these reactions, results which are opposite to those usually observed for SN1 reactions where complete racemization does not occur. Even with the α-phenylneopentyl system, where one might expect some net retention due to steric hindrance to rearside attack, the stereochemical result is 10% net inversion.[27] Two phenomena are possible to account for the observed retention. One involves rearrangements which are so rapid that solvent molecules are not able to attack the cation center on the side opposite the tosylate anion.[28,29] The second explanation for retention involves assistance by the anion to the acetic acid molecule attacking from the front side. This type of explanation has been offered for the net retention observed with several arylmethyl *p*-nitrobenzoates;[30] a process approximating an SNi reaction is apparently responsible for this retention.[31] However, the stereospecificity was much lower in these reactions than that which we observed, even though the *p*-nitrobenzoate anion is a stronger base than the tosylate anion.

Another criterion usually employed in elucidating the mechanism of reactions involving σ participation is rate enhancement.[32] The major problem encountered in these arguments, as well as in the present study, is trying to decide what the rate would be in the absence of participation or anchimeric assistance. Since the

(24) For reviews of the bridged-ion problem, see (a) A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 126; (b) J. A. Berson, "Molecular Rearrangements," Part 1, P. deMayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, p 111; (c) P. D. Bartlett, "Nonclassical Ions," W. A. Benjamin, Inc., New York, N. Y., 1965; (d) G. D. Sargent, *Quart. Rev.*, **20**, 301 (1966); (e) B. Capon, M. J. Perkins, and C. W. Rees, "Organic Reaction Mechanisms, 1965," Interscience Publishers, New York, N. Y., 1966, p 1; "Organic Reaction Mechanisms, 1966," Interscience Publishers, New York, N. Y., 1967, p 1; (f) H. C. Brown, *Chem. Brit.*, 199 (1966); *Chem. Eng. News*, **45**, No. 7 86 (1967); (g) G. A. Olah, *ibid.*, **45**, No. 14, 77(1967); (h) H. L. Goering and G. N. Fickes, *J. Amer. Chem. Soc.*, **90**, 2848, 2856, 2862 (1968).

(25) See (a) C. W. Shoppee and G. A. R. Johnston, *J. Chem. Soc.*, 3261 (1961), (b) C. A. Bunton and Y. F. Frei, *ibid.*, 1872 (1951).

(26) (a) H. C. Brown, K. J. Morgan, and F. J. Chloupek, *J. Amer. Chem. Soc.*, **87**, 2137 (1965); (b) H. C. Brown, R. Bernheimer, C. J. Kim, and S. E. Scheppele, *ibid.*, **89**, 370 (1967).

(27) S. Winstein and B. K. Morse, *ibid.*, **74**, 1133 (1952).

(28) (a) P. S. Skell and R. J. Maxwell, *ibid.*, **84**, 3963 (1962); (b) G. J. Karabatsos, R. A. Mount, D. O. Rickter, and S. Meyerson, *ibid.*, **88**, 5651 (1966); (c) H. C. Brown and M. H. Rei, *ibid.*, **86**, 5008 (1964).

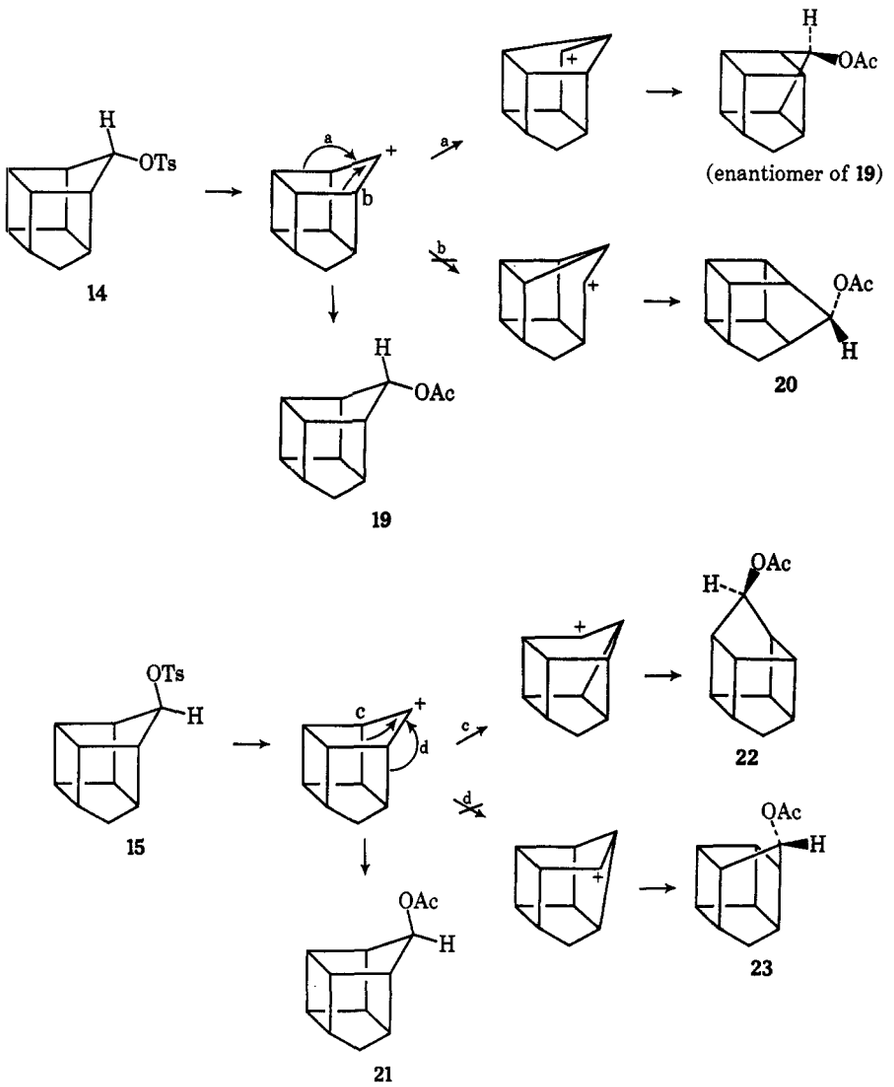
(29) If the rearrangement is truly this fast, it would appear that the ions involved would be essentially single vibrating bridged ions.

(30) (a) H. L. Goering and S. Chang, *Tetrahedron Lett.*, 3607 (1965); (b) H. L. Goering, R. G. Briody, and J. F. Levy, *J. Amer. Chem. Soc.*, **85**, 3059 (1963).

(31) H. Hart and H. S. Eleuterio, *ibid.*, **76**, 1379 (1954).

(32) P. von R. Schleyer, *ibid.*, **86**, 1856 (1964).

SCHEME I



6-pentacyclodecyl system contains the 7-norbornyl nucleus, one might choose the latter as a model[18,33] for predicting the unassisted rate for the former. On this basis, the rate accelerations for both the *syn* and *anti* tosylates **14** and **15** at 25° are *ca.* 10^5–10^6.[34] However, the carbonyl stretching frequency of 7-norbornanone is 1773 cm^{-1} [33] while that for 6-pentacyclodecanone **18** is only 1760 cm^{-1}. Because the carbonyl stretching frequency is sensitive to and reflects the C–CO–C bond angle, and ionization of the corresponding tosylate system is inhibited by a small C–C–C angle, the 7-norbornyl system may not be a good model. Schleyer[18] has developed an equation which utilized the carbonyl frequency of the ketone corresponding to the secondary tosylate in question as well as several other strain factors for calculating unassisted solvolysis rates. The calculated unassisted solvolysis rate constants at 25° for the *syn* and *anti* tosylates **14** and **15** are 2.3×10^{-13} sec^{-1} and 1.9×10^{-13} sec^{-1}, respectively, which correspond to rate acceleration factors of 1.3×10^4 and 5×10^3, respectively. It appears to us that Schleyer's equation is the best model for estimating unassisted solvolysis rates at the present time, although the use of this correlation has come under attack.[36]

Another means of detecting unexpectedly high solvolysis rates is a correlation between these rates and the rates of sodium borohydride reduction of the corresponding ketones.[37] Such a correlation is shown in Figure 1. All of the data except those for the two pentacyclodecyl systems are taken from Brown and Muzzio's paper.[37] This series of bicyclic compounds, excluding the pentacyclodecyl systems and those for which anchimeric assistance is believed to be operative in solvolysis, such as *anti*-7-norbornenyl, show at best a qualitative relationship between the rates of solvolysis and borohydride reduction as pointed out by these authors. The correlation line drawn between the cyclopentyl and 7-norbornyl compounds, as suggested by these authors, is one which gives a reasonable locus for the remaining points. Using this correlation line, one calculates rate accelerations of 320 and 1300 respectively for acetolysis of the *syn* and *anti* tosylates

(33) C. S. Foote, *J. Amer. Chem. Soc.*, **86**, 1853 (1964).

(34) The rate of acetolysis of 7-norbornyl tosylate at 25° is 6.4×10^{-15} sec^{-1}.[35]

(35) S. Winstein, M. Shatavsky, C. Norton, and R. B. Woodward, *J. Amer. Chem. Soc.*, **77**, 4183 (1955).

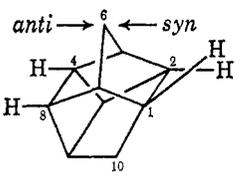
(36) H. C. Brown, I. Rothberg, P. von R. Schleyer, M. M. Donaldson, and J. J. Harper, *Proc. Nat. Acad. Sci.*, **56**, 1653 (1966).

(37) H. C. Brown and J. Muzzio, *J. Amer. Chem. Soc.*, **88**, 2811 (1966).

14 and **15**. However, owing to the poor correlation in general for the points in Figure 1, we cannot state unequivocally, based on this correlation, whether or not there is anchimeric assistance to ionization in the solvolysis of the 1,3-bishomocubyl systems.

It appears to us that the kinetic data indicates the possibility of anchimeric acceleration in the solvolyses of the tosylates **14** and **15**, but that an unambiguous answer cannot be given at the present time. The stereochemical results appear to us to be most consistent with and most simply explained by the intermediacy of bridged cations. However we cannot rule out certain other possibilities such as two noninterconverting sets of rapidly equilibrating non-bridged ion pairs.

The predominance of *anti* attack in the hydride reductions of the ketone **18** can be rationalized by an examination of molecular models. Due to the methylene group at C-10, the hydrogen atom on C-1 projects upward toward the methylene bridge at C-6. The other three hydrogen atoms at C-2, -4, and -8 lie essentially in the plane described by C-2, -4, and -8.



This steric approach control[38] in these reductions is expected because of the strained nature of the sp^2 carbon atom (C-6) in the ketone **18**, which would lead to a transition state similar to the reactants. On the other hand, the 50:50 distribution obtained on equilibration of the alcohols **8** and **9** indicates equal thermodynamic stability for the two isomers, *i.e.*, very little or no effect of the C-1 hydrogen atom. The hydride reductions are expected to be more sensitive to steric effects than the equilibration, owing to a perpendicular attack of the reducing agent on the carbonyl carbon atom. The actual energy differences ($\Delta\Delta F^{\ddagger}$) in the two modes of reduction are not great, *ca.* 0.7–0.8 kcal/mol.

Experimental Section

Melting points were determined in capillary tubes and are corrected. Boiling points are not corrected. Infrared spectra were recorded using a Perkin-Elmer 337 double grating spectrometer by Mr. F. L. Beman and coworkers. The precision infrared carbonyl frequencies of the ketone **18** were measured directly with the optical read-out on a Beckman IR-9 spectrometer by Dr. W. J. Potts, Jr., and coworkers. Nuclear magnetic resonance (nmr) spectra were obtained by Mr. Beman and coworkers with a Varian A-60 spectrometer. The chemical shifts are reported in ppm (δ) relative to internal tetramethylsilane. Mass spectral analyses were performed by Mrs. W. L. Dilling and coworkers with a magnetically scanning 90° sector spectrometer using an electron ionizing voltage of 75 eV and a vaporizer temperature of 200° unless specified otherwise. High resolution mass spectra were obtained by Dr. L. A. Shadoff with a Consolidated Electrodynamics 21-110B spectrometer. Microanalyses were determined by Mr. L. E. Swim and coworkers. Gas chromatographic (gc) analyses were performed with a F & M 500 gas chromatograph. Thin layer chromatographic analyses were performed by Dr. N. E. Skelly.

(38) *Cf.* H. O. House, "Modern Synthetic Reactions," W. A. Benjamin, Inc., New York, N. Y., 1965, pp 28–32.

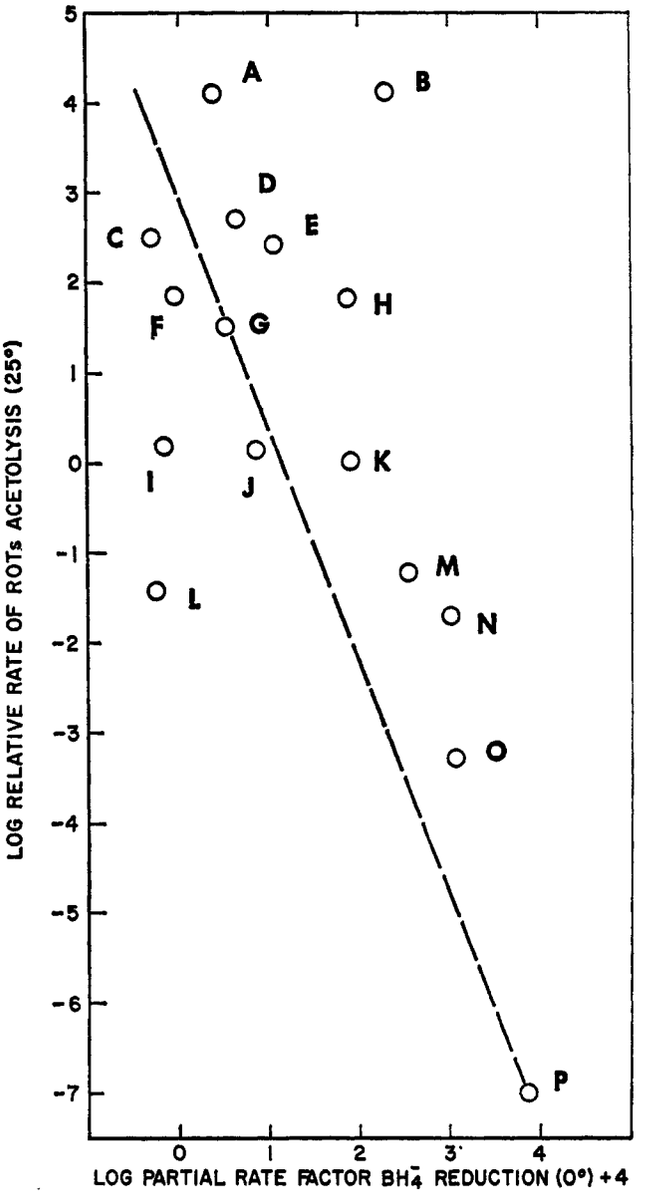
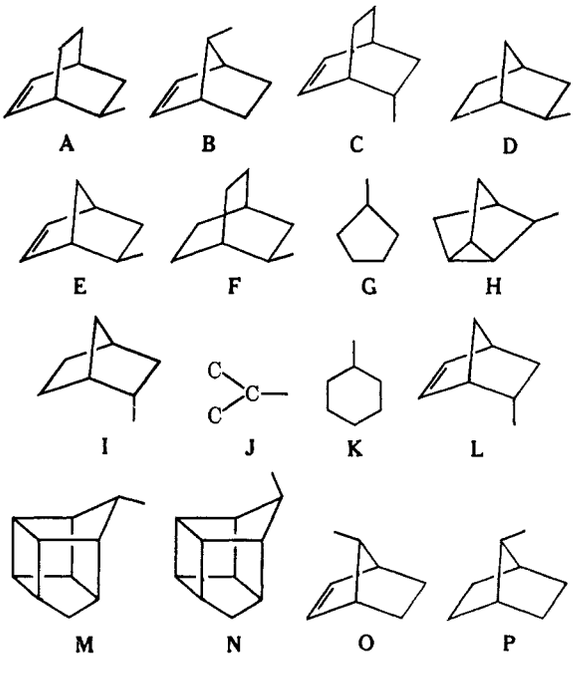


Figure 1.—Plot of logarithms of the relative rates of tosylate acetolysis *vs.* the logarithms of the partial rate factors for borohydride reduction.



endo,syn-**Tricyclo[5.2.1.0^{2,6}]deca-4,8-dien-3-ol** (11).—The first preparations of this material were made by the lithium aluminum hydride reduction of *endo*-tricyclo[5.2.1.0^{2,6}]deca-4,8-dien-3-one (**28**).[9] In some cases products resulting from reduction of the conjugated double bond occurred. These side products could be eliminated by using aluminum hydride in place of lithium aluminum hydride.

A slurry of aluminum hydride[39] in ether was prepared by adding aluminum chloride (0.4 g, 3 mmol) in small portions to a stirred mixture of lithium aluminum hydride (0.38 g, 10 mmol) in 50 ml of dry ether.

To this stirred slurry of aluminum hydride and lithium chloride, a solution of the ketone **28** (0.50 g, 3.4 mmol) in 10 ml of ether was added dropwise. The reaction mixture was stirred for 0.5 hr at room temperature and hydrolyzed by the cautious addition of 5 ml of water followed by 15 ml of 5 *N* hydrochloric acid. The ether layer was separated, washed with water, and dried ($MgSO_4$). Evaporation of the solvent and sublimation of the residue at 100° (0.5 mm) afforded 0.38 g (76%) of dienol **11**. Analysis by gc (column A, 10-ft × 0.25-in. 20% Apiezon L on 60–80 mesh Chromosorb WAW, 150°, helium flow rate 150 ml/min) showed only one peak for the alcohol **11**. The infrared and nmr spectra were identical wth those of a sample prepared by the lithium aluminum hydride reduction; the mixture melting point was not depressed.

syn-**Pentacyclo[5.3.0^{2,5}.0^{3,9}.0^{4,8}]decan-6-ol** (8).—A solution of the *syn* dienol **11** (3.8 g, 26 mmol) in 140 ml of redistilled acetone was purged with a slow stream of purified nitrogen for 1.5 hr. The solution was irradiated with a 450-W Hanovia medium pressure mercury arc lamp (type 679 A) through a 9700 Corex filter. The reaction was followed by gc analysis (column A, 225°, 40 ml/min): **11**, R_t 7.7 min; **8**, R_t 9.7 min. After irradiation for 1.5 hr, the conversion of **11** to **8** was essentially complete. An additional 6.3 g (43 mmol) of the alcohol **11** was completely reacted after 2 hr of similar treatment. The acetone was removed *in vacuo* from the combined reaction mixtures to give 10.7 g of a viscous yellow oil. This crude product was sublimed twice at 110° (0.5 mm) and recrystallized once from hexane to give 2.0 g (20%) of crystalline product **8**. Further recrystallization gave a sample: mp 175–176° (lit.[12] mp 180–181°); $\nu_{max}^{CCl_4}$ 3640 (w), 3340 (m, br), 2975 (s), 2860 (m), 1455 (w), 1340 (m) cm^{-1}; $\nu_{max}^{CS_2}$ 1290 (m), 1264 (m), 1245 (m), 1206 (w), 1196 (m), 1162 (m), 1129 (m), 1080 (s), 1047 (s), 1030 (m), 1018 (m), 951 (w), 941 (m), 889 (w), 878 (w), 846 (w), 835 (m), 800 (w), 789 (w), 768 (w), 698 (m), 619 (w), 547 (w), 520 (w), 481 (w) cm^{-1}. Nmr spectral data are given in Table I. The mass spectrum was consistent with that reported previously.[13]

Anal. Calcd for $C_{10}H_{12}O$: C, 81.04; H, 8.16; mol wt, 148. Found: C, 81.4; H, 8.09; mol wt, 148 (mass spectroscopy).

anti-**Pentacyclo[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]decan-6-ol** (9).—A solution of *endo,anti*-tricyclo[5.2.1.0^{2,6}]deca-4,8-dien-3-ol[9] (12) (10.0 g, 67.6 mmol) in 150 ml of acetone was irradiated as described above for the *syn* isomer. The reaction was also followed by gc analysis as described for the *syn* isomer: **12**, R_t 8.2 min; **9**, 9.7 min. After irradiation for 6.5 hr, the conversion of **12** to **9** was essentially complete. The acetone was removed to give 12.8 g of viscous yellow oil containing some crystalline material. Sublimation twice at 100° (0.5 mm) gave 5.1 g of soft white crystals. Recrystallization once from hexane gave 3.1 g (31%) of the alcohol **9**, mp 145–155°. Additional recrystallization gave a sample: mp 164–166° (lit.[12] mp 171–172°); $\nu_{max}^{CCl_4}$ 3640 (w), 3340 (m, br), 2975 (s), 2860 (m), 1455 (w), 1340 (m) cm^{-1}; $\nu_{max}^{CS_2}$ 1297 (m), 1245 (m), 1202 (m), 1185 (m), 1090 (s), 1078 (s), 1052 (s), 1031 (m), 1010 (w), 980 (w), 953 (w), 948 (m), 926 (m), 899 (w), 879 (w), 847 (w), 806 (w), 779 (w), 768 (w), 708 (m), 636 (w), 553 (w), 502 (w), 462 (w) cm^{-1}. Nmr spectral data are given in Table I. The mass spectrum was consistent with that reported previously.[13]

Anal. Calcd for $C_{10}H_{12}O$: C, 81.04; H, 8.16; mol wt, 148. Found: C, 81.2; H, 8.15; mol wt, 148 (mass spectrometry).

By the procedure described above, a solution of *endo,syn*-tricyclo[5.2.1.0^{2,6}]deca-3,8-dien-10-ol[9] (**13**) (6.2 g, 42 mmol) in 150 ml of acetone was irradiated for 2 hr. The gc retention time of **13** under conditions described in the preceding section was 8.2 min. Removal of the acetone gave 7.0 g of a yellow oil which partially crystallized on cooling. Sublimation at 80–90° (0.5–1.0 mm) and crystallization from pentane gave 1.81 g (29%) of crystals. Three additional recrystallizations of this material gave a sample of the alcohol **9**, mp 160–164°, showing infrared and nmr spectra identical with those reported above for **9**.

All attempts to separate mixtures of the isomeric alcohols **8** and **9** were unsuccessful. Crystallization from heptane and sublimation of an 80:20 mixture of **5** and **6** did not result in any fractionation.[13] The two alcohols had the same retention time on 17 different packed gc columns.[13] A mixture of **8** and **9** emerged as a single peak, R_t 28 min, from a 100 ft × 0.01 in. capillary column coated with 1,2,3-tris(2-cyanoethoxy)propane operated at 100°. Thin layer chromatography of the alcohol mixture on silica gel G with chloroform produced only one spot on development.

syn-**Pentacyclo[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]dec-6-yl Acetate** (19).—A 0.50-g (3.4 mmol) sample of the mixture of alcohols (80% **8**, 20% **9**) obtained from the lithium aluminum hydride reduction of the corresponding ketone **18**[13] was converted to the acetate mixture by stirring with 2 ml of acetic anhydride in 5 ml of pyridine at room temperature for 24 hr. The mixture was treated with 20 ml of water and extracted six times with 10 ml portions of pentane. The combined extracts were washed once with water, once with 10% hydrochloric acid, and again with water. After drying over anhydrous sodium sulfate, the pentane solution was decanted from the drying agent, and the pentane was removed under vacuum to give 0.58 g (90%) of acetates (80% **19**, 20% **21**): ν_{max}^{neat} 2980 (s), 2865 (w), 1740 (s), 1460 (w), 1380 (m), 1360 (w), 1277 (s), 1251 (s), 1231 (s), 1071 (m), 1042 (s) cm^{-1}; nmr spectrum (CCl_4), a broad singlet at −4.96 (0.21 H, –CHOAc– of **21**), a broad singlet at −4.70 (0.84 H, –CHOAc– of **19**), a broad multiplet at −3.1 to −2.3 with maximum intensity at −2.68 (8.0 H, –C(–)–H), a singlet at −1.97 (2.4 H, CH_3CO_2– of **19**), a singlet at −1.87 (0.6 H, CH_3CO_2– of **21**), and a pair of unsymmetrical doublets (with further ill-defined splitting) centered at −1.66 and −1.39 ppm (1.9 H, –CH_2– of **19**, J_{gem} = 11.0 cps, minor absorption for –CH_2– of **21** also visible, see following); mass spectrum, *m/e* 190 (M^+), 82 ($C_5H_6O^+$, base peak). Gc analysis (column A, 200°, 40 ml/min) showed a single peak, R_t 23.4 min.

anti-**Pentacyclo[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]dec-6-yl Acetate** (21).—As described above for the *syn* isomer, a solution of the *anti* alcohol **9** (0.50 g, 3.4 mmol) and 2 ml of acetic anhydride in 5 ml of pyridine was converted to 0.66 g (103%) of the *anti* acetate **21**: ν_{max}^{neat} 2980 (s), 2865 (w), 1740 (s), 1460 (w), 1380 (m), 1360 (w), 1298 (m), 1268 (s), 1251 (s), 1230 (m) 1219 (m), 1204 (m), 1077 (m), 1045 (s), 936 (m) cm^{-1}; nmr spectrum ($CDCl_3$), a broad singlet at −5.06 (0.9 H, –CHOAc–), a broad multiplet at −3.0 to −2.4 with maximum intensity at −2.79 and −2.65 (7.9 H, —C(–)–H), a singlet at −1.94 (3.1 H, CH_3CO_2), and a pair of unsymmetrical doublets (with further ill-defined splitting) centered at −1.66 and −1.25 ppm (2.1 H, –CH_2–, j_{gem} 11.0 cps); mass spectrum, *m/e* 82 ($C_5H_6O^+$, base peak).

Anal. Calcd for $C_{12}H_{14}O_2$: C, 75.76; H, 7.42; mol wt, 190. Found: C, 75.6; H, 7.16; mol wt, 190 (mass spectroscopy).

Gc analysis showed *ca.* 2% lower-boiling impurity.

syn-**Pentacyclo[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]dec-6-yl *p*-Toluenesulfonate** (14).—According to the method of Tipson,[40] the *syn* alcohol **8** (0.76 g, 5.1 mmol) and *p*-toluenesulfonyl chloride (1.0 g, 5.2 mmol) in 5 ml of pyridine were mixed at 0° and stirred at 0° for 1 hr. The mixture was stirred at room temperature for 2 hr, and then, while cooling in an ice bath, treated with 30 ml of water. The resulting milky mixture was extracted three times with 20-ml portions of methylene chloride, and the combined organic extracts were washed once with water, twice with 20-ml portions of 10% hydrochloric acid solution, and again with water. After drying over anhydrous sodium sulfate, the drying agent was removed by filtration, and the methylene chloride was removed *in vacuo* to give 1.35 g (87%) of crude *syn* tosylate **14**. Four recrystallizations from hexane gave a sample for analysis and kinetic studies: mp 64.5–65.5°; $\nu_{max}^{CCl_4}$ 2990 (m), 2940 (w), 2870 (w), 1375 (m), cm^{-1}; $\nu_{max}^{CS_2}$ 1192 (s), 1180 (s), 988 (s), 962 (m), 939 (m), 918 (m), 890 (m), 857 (s), 815 (m), 669 (s), 563 (s) cm^{-1}; nmr spectrum (CCl_4), a pair of unsymmetrial doublets centered at −7.74 and −7.28 (3.7 H, Ar–H, J_{vic} = 8.2 cps), a broad singlet at −4.50 (1.0 H, –CHOTs–), a singlet at −2.45 (Ar–CH_3) superimposed on a broad multiplet at −3.1 to −2.3

(39) M. J. Jorgenson, *Tetrahedron Lett.*, 559 (1962).

(40) R. S. Tipson, *J. Org. Chem.*, **9**, 235 (1944).

with maximum intensity at −2.65 (10.9 H total, —C(H)—), and a pair of unsymmetrical doublets (with further ill-defined splitting) centered at −1.65 and −1.37 ppm (2.4 H, $-CH_2-$, J_{gem} = 11 cps); mass spectrum (*ca.* 40°, direct probe sample introduction), *m/e* 130.0781 ($C_{10}H_{10}^+$, *m/e* calcd 130.0783, base peak).

Anal. Calcd for $C_{17}H_{18}O_3S$: C, 67.52; H, 6.00; S, 10.60; nuclidic mass, 302.0977. Found: C, 67.2; H, 5.88; nuclidic mass, 302.0980.

***anti*-Pentacyclo[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]dec-6-yl *p*-Toluenesulfonate (15).**—As described above for the *syn* isomer, 1.96 g (13.2 mmol) of the *anti* alcohol **9** and *p*-toluenesulfonyl chloride (2.7 g, 14 mmol) in 10 ml of pyridine were converted to 4.0 g of tosylate, obtained as a brown oil. Crystallization from hexane gave 3.6 g (90%) of crystalline tosylate, **15**, mp 61–70°. A sample was recrystallized for analysis and kinetic acetolysis: mp 78–78.5°; $\nu_{max}^{CCl_4}$ 2990 (m), 2740 (w), 2870 (w), 1375 (m) cm^{-1}; $\nu_{max}^{CS_2}$ 1190 (s), 1179 (s), 989 (s), 974 (m), 923 (s), 900 (m), 859 (m), 833 (m), 814 (m), 669 (m), 563 (s), cm^{-1}; nmr spectrum ($CDCl_3$), a pair of unsymmetrical doublets centered at −7.76 and −7.32 (3.9 H, Ar-**H**, J_{vic} 8.3 cps), a broad singlet at −4.85 (1.0 H, -CHOTs-), a singlet at −2.44 (Ar-CH_3) superimposed on a broad multiplet at −3.0 to −2.2 with maximum intensity at −2.68 and −2.56 (10.9 H total, —C(H)—), and a pair of unsymmetrical doublets centered at −1.60 and −1.19 ppm (2.2 H, $-CH_2-$, J_{gem} 11.0 cps); mass spectrum (*ca.* 40°, direct probe sample introduction), *m/e* 130 ($C_{10}H_{10}^+$, base peak).

Anal. Calcd for $C_{17}H_{18}O_3S$: C, 67.52; H, 6.00; S, 10.60; nuclidic mass, 302.0977. Found: C, 67.6; H, 5.80; nuclidic mass, 302.0983.

Preparative Acetolysis of *syn* Tosylate 14.—A solution of the *syn* tosylate **14** (0.89 g, 2.9 mmol) in 50 ml of glacial acetic acid was heated at 120° in a constant temperature bath for 7 hr (10 half-lives). After cooling to room temperature, the mixture was poured into 300 ml of water, and the cloudy mixture was extracted with methylene chloride (2 × 100 ml, 3 × 50 ml). This reaction was much cleaner, giving less insoluble material than was observed in the solvolysis of the isomeric *anti* tosylate **12** (see below). The combined extracts were washed with 5% sodium bicarbonate solution (100 ml, 50 ml) until the aqueous layer remained basic to bromophenol blue indicator, washed once with water (100 ml), and dried over anhydrous sodium sulfate. Removal of the drying agent by filtration and evaportion of the methylene chloride under vacuum gave 0.62 g of crude product. Infrared and nmr spectral analyses showed only acetate absorption; no tosylate or alcohol was detected. Gc analysis (column A, 175°, 40 ml/min) showed one major peak, R_t 37.4 min, with a slight shoulder, R_t *ca.* 34.5 min. Injection of a mixture of the crude solvolysis product and an authentic sample of the *syn* acetate **19** showed only one peak.

A sample, 0.58 g (3.1 mmol) of the crude solvolysis product, dissolved in 5 ml of dry ether, was added dropwise to a stirred slurry of 0.23 g (6 mmol) of lithium aluminum hydride in 10 ml of ether. After reaction for 16 hr at room temperature, the mixture was hydrolyzed with 0.5 ml of water and 1 ml of 5% sodium hydroxide solution. The insoluble salts were removed by filtration, and the filtrate was dried over anhydrous sodium sulfate. Removal of the ether under vacuum gave 0.41 g (94% from tosylate) of the *syn* alcohol **8** as shown by comparison of the infrared and nmr spectra with those of an authentic sample. The nmr spectrum indicated the possibility of the presence of up to 3–4% of the *anti* alcohol **9** by weak absorption at *ca.* −4.3 ppm. Gc analysis of the alcohol (column A, 175°, 40 ml/min) showed one major component corresponding by retention time (25.2 min) to the *syn* alcohol **8** and a minor component (*ca.* 4% of the total area) corresponding by retention time (23.2 min) to pentacyclo[5.3.0.0^{2,6}.0^{3,9}.0^{4,8}]decan-5-ol (**10**) (see below). The spectra of the crude product gave no indication of the identity of this minor component, and no further attempt at its identification was made.

Preparative Acetolysis of *anti* Tosylate 15. A. At 120° for 11 Half-lives. Pentacyclo[5.3.0.0^{2,6}.0^{3,9}.0^{4,8}]decan-5-ol (10).—A solution of 1.86 g (6.15 mmol) of the *anti* tosylate **15** in 100 ml of glacial acetic acid was heated in a constant temperature bath at 120° for 42 hr (11 half-lives). The dark reaction mixture was poured into 600 ml of water through a cotton filter to remove some of the black insoluble material present. The cloudy mixture was extracted with methylene chloride, and the combined organic extracts were washed with saturated sodium bicarbonate solution and with water, and then dried over anhydrous sodium sulfate. The drying agent was removed by filtration, and the methylene chloride removed under vacuum to give 0.93 g (80% yield) of an acetate as shown by the infrared spectrum. No tosylate or alcohol bands were observed in the infrared spectrum.

A sample of the product acetates (0.80 g, 4.2 mmol) in 5 ml of dry ether was added dropwise to a stirred slurry of 0.23 g (6 mmol) of lithium aluminum hydride in 15 ml of ether. After stirring at room temperature for 15 hr, the reaction mixture was hydrolyzed by the addition of 1 ml of 5% sodium hydroxide solution followed by 0.5 ml of water. The insoluble salts were removed by filtration, and the ether filtrate was dried over anhydrous sodium sulfate. The ether was removed by distillation to give 0.58 g (94% yield from acetate, 75% from tosylate) of crystalline alcohol product, mp 115–135°. Nmr analysis of this product showed it to be a mixture of 15% *anti* alcohol **9** and 85% pentacyclo[5.3.0.0^{2,6}.0^{3,9}.0^{4,8}]decan-5-ol (**10**) based on the resonances at −4.28 and −4.07 ppm, respectively. Gc analysis under conditions described in the preceding experiment showed two overlapping peaks with retention times of 23.6 min (**10**) and 25.2 min (**9**). The relative amounts were approximately the same as those shown by nmr analysis. Injection of a mixture of the reduction product and a known sample of the *anti* alcohol **9** caused enhancement of the minor peak. On a 10 ft × 0.25 in. Ucon Polar column at 200°, thered uction mixture showed two peaks with retention times of 44.7 and about 46.0 min. The retention time of the *anti* alcohol **9** was 46.1 min under identical conditions. The presence of several per cent *syn* alcohol **8** would not have been detected by nmr or gc.

Recrystallization of the alcohol mixture twice from pentane gave 0.23 g of alcohol **10** (containing 10% of the *anti* alcohol **9**): mp 143–144° (lit.[5] mp 137–140°); $\nu_{max}^{CCl_4}$ 3640 (w), 3330 (m, br), 2970 (s), 2920 (m), 2850 (m) cm^{-1}; $\nu_{max}^{CS_2}$ 1300 (m), 1272 (m), 1250 (m), 1085 (s), 1074 (s), 1050 (s), 1012 (m), 922 (m) cm^{-1}; nmr spectrum ($CDCl_3$), a broad singlet at −4.08 (0.90 H, -CHOH-) (0.10 H also appeared at −4.28 for **9**), broad multiplet at −3.1 to −2.3 with maximum intensity at −2.91, −2.70, and −2.51 (8.0 H, -C(H)—), a singlet at −2.15 (1.0 H, O-**H**), and a singlet at −1.39 ppm (2.0 H, $-CH_2-$) (minor absorption at −1.7 to −1.1 also appeared for **9**); mass spectrum, *m/e* 148 (M^+), 66 ($C_5H_6^+$, base peak). The infrared and nmr spectra were in agreement with the spectra of the symmetrical alcohol **10** provided by Professor W. G. Dauben.[5]

B. At 100° for One Half-life. Pentacyclo[5.3.0.0^{2,6}.0^{3,9}.0^{4,8}]-dec-6-yl *p*-Toluenesulfonate (17).—A solution of the *anti* tosylate **15** (1.0 g, 3.3 mmol) in 40 ml of acetic acid was heated at 100° for 22.5 hr. Work-up as in part A gave 0.80 g of a partially crystalline product mixture of tosylate and acetate as indicated by the infrared spectrum. The nmr spectrum ($CDCl_3$) if the mixture indicated the presence of both acetate and tosylate products and both the pentacyclo[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]decane and pentacyclo[5.3.0.0^{2,6}.0^{3,9}.0^{4,8}]decane skeletal systems. The relative peak areas were −7.9 to −7.2 ppm, 46.2 (due to 4 H), *anti* tosylate **15** and rearranged tosylate **17**; −4.85 ppm, 11.2 (1 H), *anti* tosylate **15** and rearranged acetate **22**; −4.64 ppm, 5.8 (1 H), rearranged tosylate **17**; −2.07 ppm, 8.0 (6 H), acetic anhydride; −1.97 ppm, 16.0 (3 H), rearranged acetate **22**; −1.8 to −1.5 and −1.3 to −1.1 ppm, ~15.8 (2 H), *anti* tosylate **15**; −1.5 to −1.3 ppm, ~19.2 (2 H), rearranged acetate **22** and rearranged tosylate **17**. The composition of this material was calculated from this data to be 32% (mol) *anti* tosylate **15**; 32% rearranged tosylate **17**; 29% rearranged acetate **22**; and 7% acetic anhydride. This material accounts for 89% of the starting tosylate **15**; yields are 30% recovered *anti* tosylate **15**, 30% rearranged tosylate **17**, and 28% rearranged acetate **22**. Based on unrecovered tosylates, these data indicate 40% acetolysis; the calculated value is *ca.* 48% based on an estimated rate constant of 8.2 × 10^{-6} sec^{-1} at 100°. The source of the acetic anhydride was the acetic acid solvent.

Recrystallization of the tosylate–acetate mixture three times from pentane gave a sample of crystalline tosylate, mp 59–62° (lit.[14] mp for **17**, 74–74.7°). The nmr spectrum ($CDCl_3$) indicated a 54:46 mixture of symmetrical tosylate **17** [broad singlets at −4.64, -CHOTs-, and −1.40 ppm, $-CH_2-$ (lit.[14] nmr in CCl_4, −4.58, −1.40 ppm)] and *anti* tosylate **15**. Infrared bands due to **17** not appearing in the spectrum of **15** were at 965 and 687 cm^{-1} (CS_2).

Oxidation of Alcohol 10. Pentacyclo[5.3.0.0^{2,6}.0^{3,9}.0^{4,8}]decan-5-one (16).—The alcohol **10** (0.23 g, 1.6 mmol), obtained above (90% pure), in 3 ml of ether was stirred for 2 hr at room temperature with 1 ml of a solution prepared by adding 5.0 g (16.8 mmol) of sodium dichromate dihydrate and 3.75 ml of 96% sulfuric acid to water to make a total volume of 25 ml.[41] The layers were separated, and the aqueous layer was extracted four times with 5-ml portions of ether. The combined ether extracts were washed once with saturated sodium bicarbonate solution, once with water, and dried over anhydrous sodium sulfate. Removal of the ether gave 0.15 g (63%) of crude product. Recrystallization from pentane gave light yellow crystals of the ketone **16**, mp 119–122° (lit. mp 120–122°,[5] 123°,[2b] 124.5–125.5°[14]); $\nu_{max}^{CCl_4}$ 2985 (m), 2930 (w), 2855 (w), 1755 (s) cm^{-1}; $\nu_{max}^{CS_2}$ 1260 (m), 1164 (m), 1156 (m), 1015 (w), 972 (w), 557 (m) cm^{-1}. The nmr spectrum was in good agreement with data reported in the literature.[5,42] The infrared and nmr spectra were in agreement with the spectra of the symmetrical ketone **16** provided by Professor W. G. Dauben.[5]

Procedure for Kinetic Acetolysis Runs.—The rates of acetolysis were determined titrimetrically by a procedure similar to that used by previous workers.[43] The acetic acid used for all kinetic work was prepared by refluxing with twice the calculate amount of acetic anhydride needed to react with the specified amount of water in the starting acid for 24 hr, and then distilling at a 10:1 reflux ratio through a 3-ft vacuum-jacketed Vigreux column. The middle cut, bp 115°, with 1% by weight added acetic anhydride, was used. The standard sodium acetate solution (4.03×10^{-3} *M*) was prepared by refluxing 106.7 mg of primary standard sodium carbonate in about 200 ml of the dry acetic acid and then diluting the resulting solution to 500 ml at room temperature in a volumetric flask. Ampoules were prepared for use by soaking them overnight in chromic acid cleaning solution. After being rinsed well with water, the ampoules were soaked in 10% aqueous ammonia solution, again rinsed well with water, and finally dried in an oven at 130° for several hours. The bromophenol blue indicator was used as a saturated solution in acetic acid. Tosylate samples were weighed into tared 25-ml volumetric flasks and diluted to volume with acetic acid. The samples were dissolved by shaking, and 2-ml aliquots were dispensed from a burette into 3-ml ampoules. The ampoules were sealed and placed in an oil bath maintained at the desired temperature (± 0.1°). After a temperature equilibration period of 5–10 min, the first ampoule was withdrawn at zero time, and succeeding ampoules were withdrawn at appropriate times. The withdrawn ampoules were allowed to cool to room temperature and opened. The contents were titrated to the yellow bromophenol blue end point with the standard sodium acetate solution. The tosylate concentrations and other pertinent data for the kinetic runs are presented in Table IV.

TABLE IV

SUMMARY OF KINETIC ACETOLYSIS[a] DATA FOR *syn* TOSYLATE **14** AND *anti* TOSYLATE **15**

Run	Tosylate	Temp, °C	Initial concn, *M*	No. of points taken	% reaction followed	Infinity titration, % of theory
1	14	110	0.0164	8	76	97.4
2	14	110	0.0149	9	77	97.8
3	14	120	0.0159	10	79	95.8
4	14	120	0.0133	10	80	94.0
5	15	120	0.0194	6	53	90.4
6	15	120	0.0250	9	87	98.5
7	15	130	0.0216	10	88	101.8
8	15	130	0.0193	10	79	103.2

[a] Typical experimental data are presented in Table V.

The rate constants were obtained by the infinity titer method using the equation

$$2.303 \log \frac{A_\infty - A_0}{A_\infty - A_t} = k_t$$

TABLE V

KINETICS OF ACETOLYSIS OF *syn* TOSYLATE **14** AT 110.0 ± 0.1°

Run 1		Run 2	
Time, sec	Log $\frac{A_\infty - A_0}{A_\infty - A_t}$	Time, sec	Log $\frac{A_\infty - A_0}{A_\infty - A_t}$
556	0.0228	613	0.0342
929	0.0481	1262	0.0674
1485	0.0748	1781	0.0896
2576	0.1281	2423	0.1268
4341	0.2146	4105	0.2103
5991	0.3109	5514	0.2835
12400	0.5644	8701	0.4333
		12088	0.5962

where A_∞, A_0, and A_t are the number of milliliters of standard sodium acetate solution required for the titration of the aliquots after 10 half-lives (average of 2), at time zero, and at time t, respectively. The data from the duplicate runs were combined in a least squares analysis[16] to evaluate the rate constants (Table II).

Pentacyclo[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]decan-6-one (18).—Material for the infrared measurements was prepared by irradiation of *endo*-tricyclo[5.2.1.0^{2,6}]deca-4,8-dien-3-one (**1**)[9] as described by Cookson and coworkers.[12,44] Purification was achieved by column chromatography on Woelm acid-washed alumina, activity grade I, using hexane–ether as the eluent, followed by sublimation at 70° (9 mm), mp 126.5–127.5° (lit. mp 122–126°,[12] 124–126°,[44] 124.5–125.5°[2b]). Infrared spectra were recorded with 1.5% and 10% (wt/vol.) solutions: partial spectrum, $\nu_{max}^{CCl_4}$ (log I_0/I for 1.5% solutions), 1783.3 (0.50), 1762.7 (1.15) 1742.2 (0.30), ~1720 (0.04, shoulder), 1697.2 (0.05), 1670 cm^{-1} (0.007); $\nu_{max}^{CS_2}$ 879 (0.03), 862 (0.08), 849 cm^{-1} (0.03).

Lithium Tri-*t*-butoxyaluminum Hydride Reduction of Ketone 18.—A slurry of lithium tri-*t*-butoxyaluminum hydride was prepared by adding 1.90 g (25.6 mmol) of *t*-butanol to a mixture of 0.30 g (7.9 mmol) of lithium aluminum hydride in 100 ml of ether. To this stirred mixture there was added 0.50 g (3.4 mmol) of ketone **18** as a solution in 5 ml of ether. The reaction mixture was stirred at room temperature for 1 hr and then hydrolyzed by adding 5 *N* hydrochloric acid until the solids dissolved. The ether layer was separated, washed with water, and dried ($MgSO_4$). Evaporation of the solvent and sublimation of the residue afforded 0.25 g (50%) of a mixture of alcohols, mp 168–172°. Analysis by nmr indicated the composition to be 80 ± 1% *syn* isomer **8** and 20 ± 1% of the *anti* isomer **9**.

Sodium Borohydride Reduction of Ketone 18.—A solution of sodium borohydride (0.20 g, 5.3 mmol) in 10 ml of methanol was stirred in an ice bath at 0–5°. Over a period of 5 min, a solution of 0.50 g (3.4 mmol) of ketone **18** in 3 ml of methanol was added dropwise such that the temperature did not rise above 15°. The reaction mixture was warmed to room temperature and stirred overnight. Decomposition of the borates was accomplished by adding dilute hydrochloric acid. The alcohols were precipitated by dilution with water. The products were extracted with ether, washed with water, and dried. Evaporation of the solvent and sublimation at 100° (0.5 mm) afforded 0.30 g (60%) of a mixture of alcohols, mp 166–171°. Analysis by nmr indicated 76 ± 1% alcohol **8** and 24 ± 1% alcohol **9**.

Procedure for Sodium Borohydride Reduction Kinetics of Ketone 18.—The rate of reduction of this ketone was obtained relative to that of cyclohexanone. A solution was made up containing 0.381 g (3.93 mmol) of cyclohexanone, 0.490 g (3.36 mmol) of ketone **18**, and 0.187 g of *o*-dichlorobenzene (internal standard), and diluted to 10 ml with 2-propanol. This solution was cooled for 15 min in an ice–water bath and added quickly to a cold (0°), stirred solution of 0.045 g (1.2 mmol) of sodium borohydride in 10 ml of 2-propanol. At intervals of 1, 2, and 10 min, 0.3-ml aliquots were removed and quenched by placing in vials containing 3 drops of 5 *N* hydrochloric acid. The ketone–alcohol ratios were determined by gc (10 ft × 0.25 in. 20% Carbowax 20M on Chromosorb WAW, 175° isothermal for 21 min, then programmed at 11°/min to 225°, finally isothermal at 225°, 40 ml/min): R_t cyclohexanone, 11.0 min; cyclohexanol, 12.8 min; *o*-dichlorobenzene, 20.0 min; ketone

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18, 37.0 min; alcohols 8 and 9, 42.4 min. None of the starting materials or products were lost by other reactions to give nonvolatile products.

After a 1-min reaction, the ratio of cyclohexanone to cyclohexanol was 82.9:17.1, respectively. At the same time, the ratio of ketone 18 to the mixture of alcohols 8 and 9 was 18.5:81.5, respectively. After 2 min, the above ratios were 78.8:21.2 and 13.1:86.9. After 10 min, these ratios were 68.8:31.2 and 3.1:96.9. The relative rates were calculated by the equation below[45]

$$\frac{k_x}{k_y} = \frac{\log \frac{[X]_f}{[X]_i}}{\log \frac{[Y]_f}{[Y]_i}}$$

where i and f indicate initial and final. The relative rates were 8.97 after 1 min, 8.53 after 2 min, and 9.38 after 10 min.

The average relative rate for reduction of pentacyclodecanone 14 to cyclohexanone was 8.96 ± 0.43. Since the absolute rate for reduction of cyclohexanone at 0° is $1.61 \times 10^{-2}\ M^{-1}\ \text{sec}^{-1}$,[37] the calculated rate for 18 is $0.144 \pm 0.007\ M^{-1}\ \text{sec}^{-1}$.

Equilibration of *syn* 8 and *anti* 9 Alcohols.—According to the procedure of Wilcox and coworkers,[46] the reaction mixtures were made up in heavy-walled Pyrex tubes which were then frozen at −196° and sealed *in vacuo*. Each tube contained 100 mg (0.68 mmol) of alcohol, 300 mg (1.47 mmol) of aluminum isopropoxide, 20 μl (0.27 mmol) of acetone, and 2 ml of 2-propanol. The tubes were placed in a constant temperature oil bath at 120° and removed for analysis after the appropriate intervals. The reactions were worked up by pouring the contents of the tube into 5 ml of 5 *N* hydrochloric acid. This mixture was then diluted with water and the alcohols were extracted with two 20-ml portions of ether. The combined ether extracts were washed with water and dried ($MgSO_4$). The alcohols were recovered by evaporation of the ether and sublimation of the residue at 100° (0.5 mm). The recovery of the alcohols was *ca.* 75% in each run. The sublimate was analyzed by nmr. The two carbinol C–H (C-6) absorption peaks for 8 and 9 at −4.04 and −4.28 ppm, respectively, were recorded six times for each equilibration sample. The areas of the peaks were obtained by plainmeter integration and averaged. The results of these analyses are given in Table VI.

TABLE VI
ALUMINUM ISOPROPOXIDE EQUILIBRATION OF *syn* ALCOHOL 8 AND *anti* ALCOHOL 9

Starting alcohol	Equilibration time, hr	Distribution (%)[a] *syn* 8	*anti* 9
syn 8	95	51.2	48.8
	137	50.0	50.0
	169	50.3	49.7
anti 9	95	50.5	49.5
	168	50.0	50.0

[a] The range of precision in these values is ± 1%.

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Registry No.—**8**, 20446-30-4; **9**, 20446-31-5; **10**, 20446-32-6; **14**, 20446-33-7; **15**, 20446-34-8; **18**, 20446-29-1; **19**, 20446-35-9; **21**, 20440-15-7.

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Equilibration of *p*-Menthadienes in Acid and Base[1]

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Conditions are described for equilibrating the *p*-menthadienes with acid or base without getting appreciable amounts of the aromatization product, *p*-cymene. The equilibrium composition is given, and rate constants for the interconversions observed in acid and base are recorded and compared.

A great many studies have been reported involving acid-[3] and base-catalyzed[4] isomerizations of various substances to mixtures containing *p*-menthadienes. However, due to complicating side reactions, especially aromatization, equilibrium among the *p*-menthadienes appears to have been reached only in one case, involving potassium *t*-butoxide in dimethyl sulfoxide at 50°, which gave a 5:3:1 ratio of II, III, and V, respectively.[4c] In this study, only the three main constituents were identified, and the only rate constants given are for disappearance of starting materials. We wish to report a fuller analysis of the equilibrium composition, conditions for achieving it in acid and base with <10% of side reactions, and rate constants for many of the possible interconversions of the isomers.

Equilibrium was first reached with potassium *t*-butoxide in *t*-butanol at 200° for 8 hr. Starting from α-terpinene (II), 3,8-*p*-menthadiene (IV), or γ-terpinene (V), gas phase chromatography (gpc) gave virtually the same trace. Preparative gpc of the mixture in one case followed by spectral analysis and derivatization of the components showed the equilibrium mixture at 200° to contain the six isomers shown in Scheme I in the percentages indicated (relative to total diene = 100%; in a typical case, 1% of menthenes and 7% of *p*-cymene were also present). The stability order observed for the *p*-menthadienes can be rationalized in terms of the intrinsic stabilities of double bonds in various menthenes (Δ3 > 1Δ > Δ8 > the other three

(1) Taken in part from the B.S. Thesis of H. P. Klein, University of Illinois, 1963, and the M.S. Thesis of E. J. Salacinski, University of Arizona, 1966; presented at the 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., April 1967.

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