Registry No.—I, 25975-83-1; II, 25169-61-3; III, 25975-85-3; IV, 25169-69-1; V, 25975-87-5; VI, 25975-88-6.

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Stereochemistry of Solvolytic Cyclization of the 5-Hexenyl System. Acetolysis of Methyl-5-hexenyl *p*-Bromobenzenesulfonates[1a]

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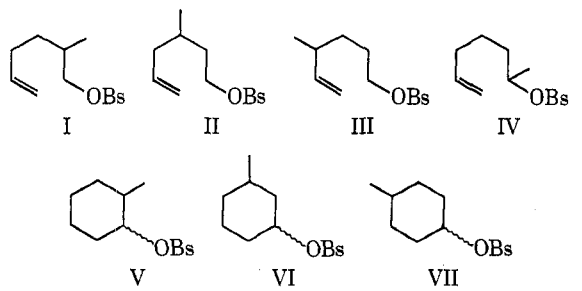
The rates and products of acetolysis of 2-, 3-, and 4-methyl-5-hexenyl *p*-bromobenzenesulfonates are reported, as well as the products of acetolysis of *cis*- and *trans*-2-, 3-, and 4-methylcyclohexyl and 6-hepten-2-yl *p*-bromobenzenesulfonates, thus furnishing data for comparison of π- and σ-route products for the three secondary methylcyclohexyl cations. As found in most previous instances for secondary carbonium ions, the π route yields less than half as much elimination product as the σ route. The stereochemistry of the substitution products from the π-route reactions strongly implies cyclization through a chairlike conformation and very rapid reaction of the resulting chair cyclohexyl cation with solvent.

Solvolytic cyclization of 5-hexenyl systems to cyclohexyl cations, the so-called π route[2] to these cations, has received considerable study,[3,4] and even synthetic use.[5] It is usually assumed that the cyclohexyl cation produced in these cyclizations is in a chair conformation, and Johnson and Harding have presented rather compelling evidence that this is the case for the mechanistically similar acid-catalyzed cyclization of 4-(3-butenyl)-3-cyclohexenol systems.[6] However, it was not at all clear that simpler, more flexible, 5-hexenyl systems should necessarily yield only the chair form of the cation in reactions involving intramolecular displacement of the leaving group by the π bond. It was therefore felt important to examine a simple system, employing a relatively innocuous marker, a methyl group, for detection of the preferred conformation of cyclization. At the same time it was hoped that presence of such a marker might help show other differences in product formation from π- and σ-route cyclohexyl cations. To this end, the rates and products of acetolysis of 2-, 3-, and 4-methyl-5-hexenyl *p*-bromobenzenesulfonates (I, II, and III) were determined, as well as the acetolysis products of 6-hepten-2-yl *p*-bromobenzenesulfonate (IV) and cis and trans isomers of 2-, 3-, and 4-methylcyclohexyl *p*-bromobenzenesulfonates (V, VI, and VII).



I II III IV

V VI VII

a, cis

b, trans

Results and Discussion

The products of acetolysis of all the brosylates are given in Table I. Because of the many components present in the product mixtures a rather elaborate method of analysis was necessary. Three separate analyses were performed on each product mixture. First, the initial pentane extract (see Experimental Section) was subject to gc analysis using a silver nitrate–ethylene glycol column which effectively separated 1-methylcyclohexene from 3- and 4-methylcyclohexene as well as "baseline" separating all the other hydrocarbons. (The separation of 3- and 4-methylcyclohexene could not be completely achieved and their yields are lumped together in Table I.) Secondly, a suitable internal standard was added to the pentane extract and the solution analyzed on a "UC-W98" (silicone rubber) column. This column separated all acetates (except certain of the cyclic ones from each other) and acyclic olefins (dienes) from cyclic ones. Finally, the product mixtures were subjected to lithium aluminum hydride reduction to convert acetates to alcohols and the resulting product mixture analyzed either with a glycerol column or a combination column composed of a forecolumn of THEED (tetrahydroxyethylethylenediamine) preceding a diglycerol column. Certain pairs of alcohols could not be separated on any columns tried. These were *trans*-3- and *cis*-4-methylcyclohexanol and *cis*-3- and *trans*-4-methylcyclohexanol. This is unfortunate, but in several instances the peak in question was collected, its ir spectrum being measured, and shown to be at least predominantly the expected isomer and not that resulting from hydride shift. All results shown in Table I are the average of at least two separate experiments. As mentioned previously,[7] the reproducibility in measurement of peak areas was no worse than $\pm 10\%$ for small peaks

(1) (a) Supported in part by the National Science Foundation (Grant GP-5658); (b) Alfred P. Sloan Research Fellow, 1968–1970. Author to whom correspondence should be addressed.

(2) S. Winstein and P. Carter, *J. Amer. Chem. Soc.*, **83**, 4485 (1961).

(3) P. D. Bartlett, W. D. Closson, and T. J. Cogdell, *ibid.*, **87**, 1308 (1965).

(4) (a) P. D. Bartlett, E. M. Nicholson, and R. Owyang, *Tetrahedron Suppl.*, **8**, 399 (1966). (b) W. S. Trahanovsky and M. P. Doyle, *J. Amer. Chem. Soc.*, **89**, 4867 (1967); W. S. Trahanovsky and M. P. Doyle, *Chem. Commun.*, 1021 (1967).

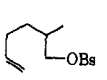
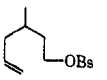
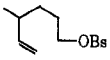
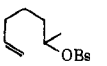
(5) W. S. Johnson, *Accounts Chem. Res.*, **1**, 1 (1968).

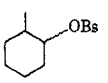
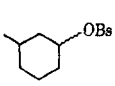
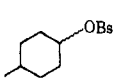
(6) W. S. Johnson and J. E. Harding, *J. Org. Chem.*, **32**, 478 (1967).

(7) S. A. Roman and W. D. Closson, *J. Amer. Chem. Soc.*, **91**, 1701 (1969).

TABLE I

ACETOLYSIS PRODUCTS OF METHYL-5-HEXENYL AND METHYLCYCLOHEXYL BROSYLATES[a]

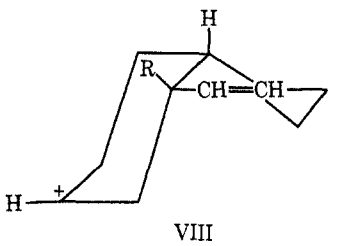
	Methyl-5-hexenyl Brosylates			
	% yield of			
				
trans-2-Methylcyclohexyl acetate		0.6	20.9	
cis-2-Methylcyclohexyl acetate		0.5	4.2	
trans-3-Methylcyclohexyl acetate		5.8	0.8	3.1
cis-3-Methylcyclohexyl acetate		38.5	1.4	6.3
trans-4-Methylcyclohexyl acetate	3.5			
cis-4-Methylcyclohexyl acetate	17.0			
1-Methylcyclohexyl acetate			1.1	
3- and 4-methylcyclohexene	11.4[b]	20.8[b]	5.4[c]	5.3[b]
1-Methylcyclohexene	1.9	1.8	6.7	
Cyclopentylmethylcarbinyl acetate			2.1	
Alkenes related to above			1.4	
Unrearranged acetate	21.2	32.2	56.0	38.2
Acyclic dienes	38.3			43.8
Other	5.7[d]	(5.3)[e]		3.1[f]
Total cyclic alkenes	13.3	22.6	13.5	5.3
Total cyclic acetates	20.5	45.4	30.5	9.4
% cyclization	34	68	44	15
% recovery	99	93	90	99.5

	Methylcyclohexyl Brosylates					
	% yield of					
						
	cis	trans	cis	trans	cis	trans
trans-2-Methylcyclohexyl acetate	0.5	7.6	0.3	0.3		
cis-2-Methylcyclohexyl acetate	0.2	12.0	0.1	0.8		
trans-3-Methylcyclohexyl acetate	0.4	0.6	22.3	6.1		
cis-3-Methylcyclohexyl acetate	0.1	1.2	2.8	15.9		
trans-4-Methylcyclohexyl acetate					12.0	2.3
cis-4-Methylcyclohexyl acetate					9.4	19.6
1-Methylcyclohexyl acetate	11.0	2.9	0.5	0.9		
3- and 4-methylcyclohexene	3.1[c]	26.1[c]	71.0[b]	71.7[b]	76.1[b]	78.1[b]
1-Methylcyclohexene	84.7	44.7	3.0	4.3	2.5	
Cyclopentylmethylcarbinyl acetate		1.8				
Alkenes related to above		3.1				
Total alkenes	88	74	74	76	79	78
Total acetates	12	26	26	24	21	22
% recovery	89	99	98	90	98	98

[a] Reactions carried out at 100°; [ROBs] = 0.1 *M*; [NaOAc] = 0.15 *M*. [b] Major component is 4-methylcyclohexene. [c] Major component is 3-methylcyclohexene. [d] 2-Methyl-5-hexen-2-yl acetate. [e] 3-Methyl-5-hexenyl chloride; not included in calculation of total yield. [f] Two or more unidentified components eluting near unrearranged acetate.

(less than 10% of total peak area in gc spectrum) and about ±2% for larger peaks.

Johnson and Harding concluded that the carbonium ion VIII reacts with solvent formic acid in the conformation shown, and reacts faster than the octalin ring system can undergo inversion.[6] Whiting has also suggested that carbonium ions in hydroxylic solvents react considerably faster than rotation about carbon–carbon single bonds.[8] Berson and coworkers have noted in several publications that certain bicyclic carbonium ions must react by internal bond migration while still retaining a "memory" of the conformation of the starting material.[9] Thus, one can conclude that the products from a carbonium ion reaction in hydroxylic media may reveal the conformation of the cation. If we assume, after Johnson and Harding,[6] that solvent attack occurs mostly from the direction of least steric hindrance and if we make the reasonable assumption that the methyl group will tend to be located in the least hindered position during cyclization of the 5-hexenyl system and thus in the newly formed cyclohexyl cation,



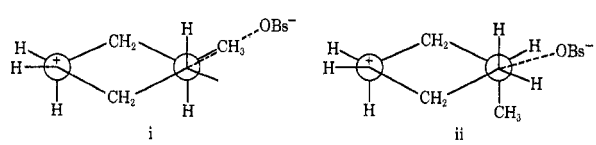
VIII

(8) M. C. Whiting, *Chem. Brit.*, **2**, 482 (1966).

(9) See J. A. Berson, R. G. Bergman, G. M. Clarke, and D. Wege, *J. Amer. Chem. Soc.*, **91**, 5601 (1969), and previous papers in this series.

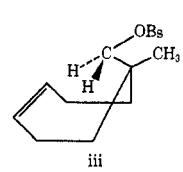
then one should be able to predict the configuration of the principle substitution product for each methyl-5-hexenyl system for any given conformation during cyclization. For a chair conformation, the predictions would be *cis*-4-methylcyclohexyl acetate from I,[10] *cis*-3-methylcyclohexyl acetate from II, *trans*-2-methylcyclohexyl acetate from III, and *cis*-3-methylcyclohexyl acetate from IV. The data from Table I show that these *are* the major cyclic substitution products in each case by rather sizable factors: 83% *cis* for I, 87% *cis* for II, 83% *trans* for III, and ~67% *cis* for IV. Thus, if we wish to assume a common conformation for cyclization of these minimally substituted 5-hexenyl derivatives, it must be chairlike. The minor product, in each case, can arise from axial attack of solvent on the preferred chair conformer of the cation, from reaction of small amounts of higher energy conformers, or both. The near identity in yields of the major isomeric substitution products from I, II, and III (~84%) makes our original assumption[10] that the eclipsing interaction in I would force the methyl predominantly axial look very good. In fact, the methyl group in the cation from I appears to be as predominantly axial as those in the cations from II and III are equatorial. This would be expected if the eclipsing interaction in I is as large (3.9 kcal/mol) as claimed in III[10] and if the free energy difference between "axial" and "equatorial" methyl during cyclization of the methyl-5-hexenyl derivatives is approximately the same as for cyclohexane (~1.7 kcal/mol).[12] The similarity in yields of product apparently derived from equatorial solvent attack on the more stable chair conformer in these systems to that observed by Johnson and Harding for equatorial attack (83%) of formic acid on ion VIII (R = H)[6] is interesting, but may be only coincidental.[13]

(10) In cyclization of 2-methyl-5-hexenyl brosylate (I) through a chair conformation the methyl group must either eclipse the brosylate as in i, or be oriented axially as in ii. Felkin and coworkers[11] have concluded that a



i ii

similar eclipsing interaction during solvolytic cyclization of 1-methyl-Δ^4-cycloheptenylmethyl brosylate (iii) raises the activation energy for the



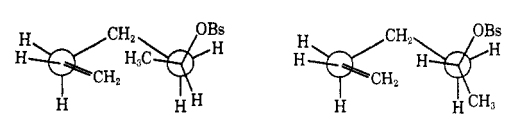
iii

process by 3.9 kcal/mol. While the 5-hexenyl cyclization may differ somewhat from that of iii, we feel that the eclipsing interaction should be large enough in i to make ii preferred and thus lead to formation of *cis*-4-methylcyclohexyl acetate if I cyclizes through a chair conformation.

(11) C. Chuit, F. Colard, and H. Felkin, *Chem. Commun.*, 118 (1966).

(12) E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis," Wiley, New York, N. Y., 1965, p 44.

(13) The one instance where the observations do not fit so well is that of the 3-methylcyclohexyl cation derived from IV. Rather than a 5:1 ratio in favor of the predicted cis acetate, only a 2:1 ratio was observed. The yield of cyclic acetate is only 9% in this case, and the identification of both acetate products rests only on gc retention times and peak enrichment techniques. However, assuming the identifications and ratio measurements are correct, the cation from IV seems clearly less selective either in production of the two possible chair conformations or in the subsequent substitution reactions. There would seem little reason for diminished selectivity in the substitution process, but there are some serious steric interactions for IV in conformations leading to a chair cation. If, after Chuit, Colard, and Felkin,[11] we assume colinearity of incoming and leaving groups is necessary during the displacement, the two conformations of IV necessary to produce a chair cation would be iv and v. In iv the methyl must nearly eclipse the adjacent



iv v

methylene; in v it must be oriented pseudo-axially. It seems rather plausible that IV may cyclize at least partly through some nonchair conformation where the 1-methyl substituent can avoid some of the steric interactions apparent in iv and v.

(14) (a) H. L. Goering and R. F. Myers, *J. Amer. Chem. Soc.*, **91**, 3386 (1969); H. L. Goering and W. D. Closson, *ibid.*, **83**, 3511 (1961). (b) W. D. Closson and G. T. Kwiatkowski, *Tetrahedron Lett.*, 6435 (1966). (c) P. E. Peterson and R. J. Kamat, *J. Amer. Chem. Soc.*, **91**, 4521 (1969).

One troublesome aspect of interpreting π-route product mixtures is the question of internal return, which could result in formation of σ-route type products from π-route reactions. Since the methylcyclohexyl brosylates all react at least an order of magnitude faster than the primary 5-hexenyl derivatives, their formation during acetolysis of I, II, and III would be difficult to detect. Since one does see internal return in π-route reactions in kinetically favorable situations[14] one must consider it for these. Using the yield of one or more of the olefins (predominant products from σ-route reaction) as the limiting factor, one may estimate upper-limits for internal return for each of the methyl-5-hexenyl system for both cyclic systems related to it. In most cases the upper limit on internal return is quite high, 40–50%. This may be at least partly due to the necessity of lumping 3- and 4-methylcyclohexene together as one product, the one used as the limiting factor in all but one case. The situation for 4-methyl-5-hexenyl brosylate (III) is more meaningful, since here 1-methylcyclohexene could be reliably used as the limiting factor. The upper limits on internal return for III turn out to be only 18% for *cis*-2-methylcyclohexyl brosylate (Ia) and 34% for *trans*-Vb. After "correction" for maximum possible internal return to Va and Vb, the only striking change in the product mixture from III is the lack of 1-methylcyclohexene and its effect on the acetate–olefin ratio. This, of course, may be only an artifact of "correction." In fact, since everything else seems to be produced in the π-route reaction of III, even after "correction," it would seem reasonable that some 1-methylcyclohexene should be produced. Making the simple assumption that the amount of 1-methylcyclohexene from π-route reaction should be about half the amount of 3-methylcyclohexene (proportional to the number of β hydrogens) lowers the upper limits on internal return to Va and Vb to 11% and 21%, respectively. If we assume that this is typical for π-route reactions of 5-hexenyl systems, then internal return does not represent a major reaction pathway for the π-route cations (say, 25% at most) and does not have a serious effect on the composition of the observed product mixture, or the conclusions drawn from them.

In Table II are given the overall rates of acetolysis for I, II, and III, as well as for the unsubstituted system, 5-hexenyl brosylate. Also included are estimated

TABLE II
EFFECTS OF METHYL GROUPS ON RATES OF ACETOLYSIS OF 5-HEXENYL BROSYLATES[a]

Brosylate	10^5k, sec^{-1}	Approximate rate of cyclization, 10^5k, sec^{-1}[b]
5-Hexenyl	4.29 ± 0.04	1.1[c]
2-Methyl-5-hexenyl	2.55 ± 0.01[d]	0.87
3-Methyl-5-hexenyl	10.2 ± 0.1[e]	6.95
4-Methyl-5-hexenyl	5.65 ± 0.03[f]	2.5

[a] At 100°; [ROBs] = 0.03 *M*, [NaOAc] = 0.035 *M*. [b] Estimated using per cent cyclizations from Table I. See also ref 15. [c] Estimated using data from ref 14. [d] $\Delta H^* = 24.4$ kcal/mol; $\Delta S^* = -14.5$ eu. [e] $\Delta H^* = 24.9$ kcal/mol; $\Delta S^* = -10.1$ eu. [f] $\Delta H^* = 24.9$ kcal/mol; $\Delta S^* = -11.0$ eu.

rates of cyclization for each case.[15] The effects of the methyl groups on these rates of cyclization are fairly large and quite instructive. The increased ease of cyclization caused by a substituent on the chain is a well-known phenomenon (sometimes referred to as the "*gem*-dimethyl effect") and should not depend much on its positioning on the chain.[17] Here we find almost an order of magnitude variation. The difference in effect between II and III is probably due to the difference in ground state torsional interactions and rotational energy barriers between a methyl group adjacent to sp^2 carbon and to sp^3 carbon.[18] The 8.7-fold difference in k for I and II corresponds to a $\Delta\Delta F^*$ (at 100°) of about 1.5 kcal, remarkably close to the free energy difference between axial and equatorial methyl (1.7 kcal).[12] This kinetic effect provides rather pleasing confirmation of our postulation that I should be the only one of the systems to cyclize to a cyclohexyl cation with a predominantly axial methyl group.

The pattern of products from the σ-route reactions (Table I) agree quite well with those observed from *tert*-butyl substituted cyclohexyl systems by Whiting, Sicher, and coworkers,[19] a general pattern of greater amount of substitution for equatorial brosylates, predominant inversion of configuration during substitution, and considerable hydride-shift product (with predominant retention of configuration at the new site when substitution occurs) being observed. The large amount of inverted substitution product obtained from the predominantly equatorial brosylate (always more predominantly inverted than the corresponding axial brosylate products) supports the postulation of a non-chair transition state for solvolysis of "rigid" equatorial cyclohexyl brosylates.[19,20] As in most comparisons of π- and σ-route product mixtures, there is an almost complete reversal of elimination–substitution ratios between the two pathways to the "same" cyclohexyl cation. While this difference does not show up in the case of the more rigid bicyclic carbonium ions (where elimination is difficult in any case)[2,9,21] or apparently in the more stable benzylic cations,[7] this pattern seems almost characteristic for the simpler secondary monocyclic cations.[3,4,14b]

Experimental Section[22]

Materials.—The compounds used in this study were either obtained from commercial sources or prepared by standard techniques. Their physical properties, derivatives, or sources are listed below.

3-Methyl-5-hexen-1-ol had bp 73–74° (12 mm): n^{20}D 1.4407; nmr (CCl_4) δ 0.95 (dubulet, 3 H), 1.0–2.1 (multiplet, 5 H), 3.6 (triplet, 2 H), 4.1 (singlet, 1 H), 4.8–6.1 (multiplet, 3 H).

The α-naphthylurethan had mp 45–46° (petroleum ether).

Anal. Calcd for $C_{18}H_{21}O_2N$: C, 76.30; H, 7.47. Found: C, 76.60; H, 7.49.

2-Methyl-5-hexen-1-ol had bp 68° (12 mm), n^{20}D 1.4399 [lit.[23] bp 166–168° (736 mm), n^{22}D 1.4382]: nmr (CCl_4) δ 0.9 (doublet, 3 H), 1.0–2.3 (multiplet, 5 H), 3.4 (doublet, 2 H), 4.0 (singlet, 1 H), 4.7–6.2 (multiplet, 3 H).

The α-naphthylurethan had mp 45.6–47.5° (petroleum ether).

Anal. Calcd for $C_{18}H_{21}O_2N$: C, 76.30; H, 7.47. Found: C, 76.52; H, 7.47.

4-Methyl-5-hexen-1-ol had bp 68° (12 mm), n^{22}D 1.4375: nmr (CCl_4) δ 1.0 (doublet, 3 H), 1.1–2.4 (multiplet, 5 H), 3.5 (triplet, 2 H), 4.6 (singlet, 1 H), 4.7–6.1 (multiplet, 3 H).

The α-naphthylurethan melted at 55.5–56° (petroleum ether).

Anal. Calcd for $C_{18}H_{21}O_2N$: C, 76.30; H, 7.47. Found: C, 76.29; H, 7.60.

6-Hepten-2-ol had bp 84–86° (60 mm), n^{20}D 1.4371 [lit.[24] bp 64–65° (13 mm), n^{18}D 1,4387): nmr (CCl_4) δ 1.1 (doublet, 3 H), 1.3–1.7 (multiplet, 4 H), 2.1 (multiplet, 2 H), 3.7 (multiplet, 1 H), 3.9 (singlet, 1 H), 4.8–6.1 (multiplet ,3 H).

Anal. Calcd for $C_7H_{14}O$: C, 73.76; H, 12.65. Found: C, 73.63; H, 12.36.

3-Methylhexan-1-ol had bp 135–140° (600 mm) [lit.[25] bp 168–169° (754 mm). The α-naphthylurethan melted at 44–46° (lit.[25] 45–47°).

2-Methyl-5-hexen-2-ol had bp 142–143° (760 mm) [lit.[26] bp 143–144° (760 mm)].

1-Methylcyclohexanol and cyclopentylmethylcarbinol were prepared on small scales by appropriate Grignard reactions, purified by small scale sublimative distillations and had ir and nmr spectra in complete agreement with structure.

cis-**3-Methylcyclohexanol** had bp 72–74° (15 mm), and its *p*-nitro benzoate melted at 45–46° (aqueous methanol) (lit.[27] mp 45.5–46.5°).

trans-**3-Methylcyclohexanol** was obtained from a mixture of the epimers by preparative gc. Its *p*-nitrobenzoate melted at 60–61° (lit.[28] mp 61.5–62.5°).

trans-**2-Methylcyclohexanol** had bp 82° (21 mm) [lit.[28] bp 75° (14 mm)]. The *p*-nitrobenzoate melted at 64–65° (aqueous methanol), (lit.[28] mp 64.5–65°).

(15) A referee has suggested that our product studies should have been carried out in acetic acid buffered with urea in the manner suggested by Trahanovsky, *et al.*,[16] in order to eliminate that fraction of acyclic product that arises from SN2 displacement by acetate ion. Unfortunately, urea does not completely inhibit further acid-catalyzed reactions of the acetolysis products, even cyclohexene being partly converted to cyclohexyl acetate under typical reaction conditions.[16] Since the stereochemistry of the substitution products were of prime concern in this study, a more effective buffering agent was necessary. However, since the bulk of the SN2 product must still come from attack by acetic acid at the concentration of acetate ion used in our product studies,[16] and since the acetate ion concentration was the same (0.15 *M*) in each case, the rates of cyclization stated in Table II and derived from the expression $k_{cyc} = k_{obs} \times$ fraction of cycl are at least proportional to the true cyclization rates in pure acetic acid and at best only slightly underestimated.

(16) W. S. Trahanovsky, M. P. Doyle, and P. D. Bartlett, *J. Org. Chem.*, **32**, 150 (1967).

(17) N. L. Allinger and V. Zalkow, *ibid.*, **25**, 701 (1960).

(18) (a) See ref 11, pp 19–21. (b) E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill, New York, N. Y., 1962, pp 133–134.

(19) (a) N. C. G. Campbell, D. M. Muir, R. R. Hill, J. H. Parish, R. M. Southam, and M. C. Whiting, *J. Chem. Soc. B*, 355 (1968). (b) M. Pánková, J. Sicher, M. Tichý, and M. C. Whiting, *ibid.*, 365 (1968). (c) M. Tichý, J. Hapala, and J. Sicher, *Tetrahedron Lett.*, 3739 (1969).

(20) V. J. Shiner and J. G. Jewett, *J. Amer. Chem. Soc.*, **87**, 1382 (1965).

(21) P. D. Bartlett, S. Bank, R. J. Crawford, and G. H. Schmid, *ibid.*, **87**, 1288 (1965), and subsequent papers in this series.

(22) Melting and boiling points are uncorrected. Nuclear magnetic resonance spectra (nmr) were measured at 60 MHz, using tetramethylsilane as internal standard. Preparative gas chromatography was carried out on an Aerograph A-90 gas chromatograph; analytical gas chromatography was performed using a Hewlett–Packard 5750 research chromatograph.

(23) R. Brettle and F. S. Holland, *J. Chem. Soc.*, 4836 (1962).

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(25) A. Dewael and A. Weckering, *Bull. Soc. Chim. Belges*, **33**, 495 (1924).

(26) J. K. Kochi, *J. Amer. Chem. Soc.*, **85**, 1958 (1963).

(27) W. Hückel and J. Kurz, *Chem. Ber.*, **91**, 1290 (1958).

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cis-**2-Methylcyclohexanol** was separated from a mixture of the epimeric alcohols by preparative gc and had spectroscopic properties in keeping with its structure. Its brosylate is described in Table III.

TABLE III

YIELDS, PROPERTIES, AND ACETOLYSIS EQUIVALENTS OF BROSYLATES

Brosylate	Yield, %	Mp, °C	Acetolysis equivalent Calcd	Acetolysis equivalent Found
2-Methyl-5-hexenyl (I)	70	Oil	333	343
3-Methyl-5-hexenyl (II)	60	Oil	333	342
4-Methyl-5-hexenyl (III)	70	Oil	333	335
5-Hepten-2-yl (IV)	58	Oil	333	338
3-Methylhexyl	74	Oil	335	341
5-Hexenyl	50	Oil	319	327
cis-2-Methylcyclohexyl (Va)	67	56–56.5	333	334
trans-2-Methylcyclohexyl (Vb)	80	48.5–49.5	333	334
cis-3-Methylcyclohexyl (VIa)	69	41.5–42.5	333	335
trans-3-Methylcyclohexyl (VIb)	87	54–54.5	333	335
cis-4-Methylcyclohexyl (VIIa)	72	86.5–87	333	333
trans-4-Methylcyclohexyl (VIIb)	82	48.5–49	333	334

4-Methylcyclohexanols.—Both cis and trans isomers were obtained in pure form from Aldrich Chemical Co.

p-**Bromobenzenesulfonates** were prepared in the usual manner. Solid *p*-bromobenzenesulfonates (brosylates) were purified by recrystallization from pentane at 0°; brosylates that were liquid at room temperature were purified by recrystallization from pentane at −50 to −80°. The yields, properties, and acetolysis equivalents are given in Table III.

Acetates of the alcohols were prepared on a small scale from the pure alcohols and acetic anhydride in pyridine. Pure samples were obtained by preparative gc in most cases, and all had ir and nmr spectra in agreement with assumed structure.

Product Analysis.—Solvolyses were carried out by heating a 0.10 *M* solution of brosylate in 0.15 *M* sodium acetate (in acetic acid) in a sealed ampule for at least ten half-lives at 100°. The reaction mixture was cooled, diluted with water, and continuously extracted with pentane for 24 hr. The pentane extract was carefully washed with water, dilute sodium bicarbonate solution, and saturated brine, and dried with anhydrous magnesium sulfate. Concentration was not necessary since the volume of pentane used was kept small, 30–40 ml. Products were analyzed directly from the dried pentane solution by gc on the following columns: (1) a 12 ft × 1/8 in. silver nitrate-ethylene glycol Chromosorb W acid washed 60–80 mesh column, for olefin determination; (2) a 6 ft × 1/8 in. 10% UC W-98 80–100 mesh column, for quantitative determination of olefin and acetate; (3) a 6 ft × 1/8 in. 15% diglycerol Anachrom 90–100 mesh with a 2 ft × 1/8 in. 20% THEED Chromosorb P 60–80 mesh fore column, or a 5 ft × 1/8 in. 25% glycerol Chromosorb P 60–80 mesh column, for alcohols from reduced acetate.

For all product analyses three general procedures were used.

1. **Olefin Determination.**—A small sample (0.5 λ) from the pentane extract was analyzed on the silver nitrate column operated at 30°. This column was effective in separating the isomeric methylcyclohexenes. 1-Methyl-cyclohexene eluted first followed by 4-methylcyclohexene and 3-methylcyclohexene. This was the same order observed by Gil-Av.[29] However, on several silver nitrate columns prepared according to his procedure, 4-methylcyclohexene and 3-methylcyclohexene could not be completely resolved. The 3 isomer always shouldered on the 4 isomer.

(29) E. Gil-Av, J. Herling, and J. Shabtai, *J. Chromatogr.*, **1**, 508 (1958).

2. **Quantitative Determination of Olefin and Acetate.**—A measured amount of internal standard, chlorobenzene, was added to the pentane extract. Analysis was carried out on the UC-W-98 column programmed from 75 to 120° at 20°/min, the program was initiated 7 min after injection of the sample, and the upper temperature was maintained for 8 min after it had been reached. Molar response factors for standard solutions containing weighed amounts of olefin, acetate, and internal standard were determined in exactly the same way. In general the UC-W-98 column used in this was was effective in separating tertiary, secondary, and acyclic acetates. In addition 1-methylcyclohexene separated from its isomers and dienes separated from the cyclic olefins.

3. **Analysis of Alcohols.**—The pentane extract was treated with 0.5 g of lithium aluminum hydride and stirred for 1 hr. Reduction product was carefully worked up (in the usual way) and analyzed on the glycol columns operated at 95–100°. Secondary alcohols separated from tertiary alcohols and mixtures of epimeric methylcyclohexanols (except for the 3 and 4 systems) were completely resolved. Coupling the information gained from the three analyses enabled quantitative determination of olefin and acetate products.

All products were identified by comparing their gc retention times with authentic material and by collecting products, when feasible, and comparing their spectral properties with authentic samples. Product percentages (given in Table I) are the average of two or more analyses. A typical product analysis, that of the acetolysis products from III, is given below.

Products from the Acetolysis of 4-Methyl-5-hexenyl *p*-**Bromobenzenesulfonate.**—From 0.663 g (1.99 mmol) of the *p*-bromobenzenesulfonate in 20 ml of 0.15 *M* sodium acetate in acetic acid was obtained 1.72 mmol (90.6%) of product shown by gc analysis to consist of 6.8% 1-methylcyclohexene, 5.4% a mixture of 3- and 4-methylcyclohexene (predominantly the 3 isomer), 1.3% olefin which eluted before the methylcyclohexene isomers (thought to be a mixture of vinylcyclopentane, 1-ethylcyclopentene, and ethylidenecyclopentane), 1.0% 1-methylcyclohexyl acetate, 4.2% *cis*-2-methylcyclohexyl acetate, 20.9% *trans*-2-methylcyclohexyl acetate, 2.1% methylcyclopentylcarbinyl acetate, 0.9% *trans*-3-methylcyclohexyl acetate, 1.4% *cis*-3-methylcyclohexyl acetate, and 56.0% 4-methyl-5-hexenyl acetate.

Stabilities of acetolysis products to acetolysis conditions were tested by heating solutions of the compounds in question in acetic acid, containing sodium acetate and sodium brosylate in concentrations corresponding to those present at the end of the acetolysis product study, for a period corresponding to ten half-lives for the acyclic precursor, then isolation and analysis as described above. Most compounds showed no change, but methylenecyclohexane was partially converted to 1-methylcyclohexene (18.5%) and 1-methylcyclohexyl acetate (7.5%), 1-methylcyclohexyl acetate was partially converted to 1-methylcyclohexene (51%) and methylenecyclohexane (4%), and 1-methylcyclohexene yielded a small amount (3%) of 1-methylcyclohexyl acetate.

Kinetic experiments were performed using the ampoule technique as described previously.[7]

Registry No.—3-Methyl-5-hexen-1-ol, 25913-87-5; 3-methyl-5-hexen-1-ol (α-naphthylurethan), 25957-53-3; 2-methyl-5-hexen-1-ol, 25913-88-6; 2-methyl-5-hexen-1-ol (α-naphthylurethan), 25906-55-2; 4-methyl-5-hexen-1-ol, 25906-56-3; 4-methyl-5-hexen-1-ol (α-naphthylurethan), 25906-57-4; 6-hepten-2-ol, 24395-10-6; 3-methylhexan-1-ol, 13231-81-7; *cis*-3-methylcyclohexanol, 5454-79-5; I, 25906-60-9; II, 25906-61-0; III, 25906-62-1; IV, 25906-78-9; 3-methylhexyl brosylate, 25906-79-0; 5-hexenyl brosylate, 25906-80-3; Va, 25903-10-0; Vb, 10300-00-2; VIa, 25902-72-1; VIb, 25902-73-2; VIIa, 25902-74-3; VIIb, 25902-75-4.