Organic and Biological Chemistry

The Stereochemistry of Bicyclo[3.2.1]octane. XV. The Acetolysis of Constrained Cyclohexyl Tosylates[1]

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Abstract: The apparent first-order rates of the acetolyses of 3,3,5,5-tetramethylcyclohexyl (III) and *exo*- and *endo*-3-bicyclo[3.2.1]octyl tosylates (VIII and IX) have been measured. The relative rates referred to cyclohexyl tosylate at 25° of III, VIII, and IX are 2:13:140. The structures of the olefins and acetates isolated indicated that no hydride shift had occurred. Compound VIII afforded bicyclo[3.2.1]octene-2 and *endo*-3-bicyclo[3.2.1]octyl acetate, whereas from IX the *exo*-acetate was also formed. These results are discussed in the light of current ideas on solvolysis.

In earlier papers,[4-8] 3,3,5,5-tetramethylcyclohexanone (I) and bicyclo[3.2.1]octanone-3 (V) have been discussed as models for the reflex effect[4-6] and its inverse.[7,8] However, of far more significance is the fact that the C_3 tosylates of bicyclo[3.2.1]octane are homologs of the corresponding 2-norbornyl esters. Therefore, comparison between them should be pertinent to the nonclassical ion problem because although both structures appear to be architecturally very similar, only in the former structure should σ-bond participation be reliably absent.[9] Furthermore, 3,3,5,5-tetramethylcyclohexyl tosylate, on account of geometric resemblance, should behave similarly to the *exo*-3-bicyclo[3.2.1]octyl tosylate. In addition to these steric features, the operation of hyperconjugative, transannular, and conformational effects could conceivably occur.

Accordingly, the tosylates of 3,3,5,5-tetramethylcyclohexanol (II) and *exo*- and *endo*-3-bicyclo[3.2.1]octanols (VI and VII) were prepared and acetolyzed. The kinetics of the acetolysis were measured and the composition and structure of the products were determined.

Results and Discussion

Conformations of Ground States. The configurations and conformations of the *exo*- and *endo*-3-bicyclo[3.2.1]octanols (VI and VII) and the conformation of 3,3,5,5-tetramethylcyclohexanol (II) were readily obtained from their nuclear magnetic resonance spectra. Tosylates and acetates gave spectra similar to those of the parent alcohols (Table I). The chemical shifts and coupling constants of the alcohols were found to be sensibly constant between 0 and 120°. It is worth remarking that the *gauche* coupling constants of the methine protons of the *exo* alcohol and its derivatives have appreciably different values ($J_{ae} \sim 6.0$ Hz) to those found for the *endo* epimers ($J_{ea} \sim J_{ee} \sim 3.0$ Hz). This configurational effect, first noticed by Anet,[10] is quite general[11] and permits configurational assignment of fixed ring cyclohexanols. Further, there are significant differences between the comparable coupling constants J_{aa} and J_{ae} of *exo*-3-bicyclo[3.2.1]octanol and its flexomer 3,3,5,5-tetramethylcyclohexanol which may spring from the differential operation of the reflex effect.[12]

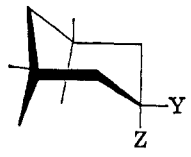
Table I. Chemical Shifts and Coupling Constants of the Methine Proton of Cyclohexyl Derivatives[a]

Compd	Signal due to methine resonance (C*H*–OH)
	exo
VI	Septuplet at 3.75 ppm, $J_{aa} = 10.5$, $J_{ae} = 6.0$ Hz
VIII	Septuplet at 4.60 ppm, $J_{aa} = 10.5$, $J_{ae} = 6.0$ Hz
X	Septuplet at 4.93 ppm, $J_{aa} = 10.5$, $J_{ae} = 6.1$ Hz
	endo
VII	Quintuplet at 3.95 ppm, $J_{ea} = J_{ee} = 3.0$ Hz
IX	Poorly resolved band at 4.75 ppm, width at half-height = 9.0 Hz
XI	Quintuplet at 4.97 ppm, $J_{ae} = J_{ee} = 3.2$ Hz
	Tetramethyl
II	Nonet at 3.80 ppm, $J_{aa} = 11.3$ Hz, $J_{ae} = 4.2$ Hz
III	Nonet at 4.76 ppm, $J_{aa} = 11.0$ Hz, $J_{ae} = 4.2$ Hz
IV	Nonet at 5.02 ppm, $J_{aa} = 11.1$ Hz, $J_{ae} = 4.2$ Hz

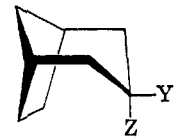
[a] In CCl_4 solution at 37°.

From an examination of a Dreiding model,[13] it appears that the inescapable and apparently severe 1,3-

(1) For an earlier paper in the series, see C. W. Jefford and E. H. Yen, *Tetrahedron*, **23**, 4549 (1967). For a preliminary communication, see C. W. Jefford, J. Gunsher, and B. Waegell, *Tetrahedron Letters*, 2333 (1965).
(2) Holder of a traineeship from the National Science Foundation, Washington, D. C.
(3) Work submitted by J. G. in partial fulfillment of the requirements for the Ph.D. degree at Temple University.
(4) B. Waegell and G. Ourisson, *Bull. Soc. Chim. France*, 495, 496, 503 (1963).
(5) B. Waegell, P. Pouzet, and G. Ourisson, *ibid.*, 1821 (1963).
(6) B. Waegell, *ibid.*, 855 (1964).
(7) C. W. Jefford and B. Waegell, *Tetrahedron Letters*, 1981 (1963).
(8) B. Waegell and C. W. Jefford, *Bull. Soc. Chim. France*, 844 (1964).
(9) Sargent has noted the advantages of the bicyclo[3.2.1]octyl skeleton as a test model and at the same time has lamented its neglect in comparison with its lower homolog: G. D. Sargent, *Quart. Rev.* (London), **20**, 358 (1966).
(10) F. A. L. Anet, *J. Am. Chem. Soc.*, **84**, 1053 (1962).
(11) N. Bhacca and D. H. Williams, *ibid.*, **86**, 2742 (1964).
(12) J. B. Lambert, *ibid.*, **89**, 1836 (1967).
(13) W. Büchi, Glasapparatefabrik, Flawil, Switzerland.



I, Y, Z = O
II, Y = OH; Z = H
III, Y = OTs; Z = H
IV, Y = OAc



V, Y, Z = O
VI (*exo*), Y = OH; Z = H
VII (*endo*), Y = H; Z = OH
VIII (*exo*), Y = OTs; Z = H
IX (*endo*), Y = H; Z = OTs
X (*exo*), Y = OAc; Z = H
XI (*endo*), Y = H; Z = OAc

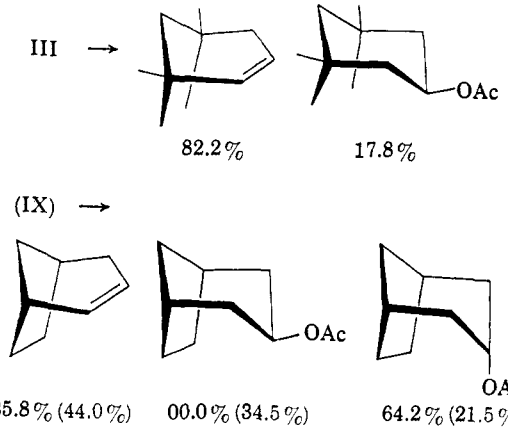
dimethyl steric interaction in II could result in the generation of twist boat conformations. Similarly, the interaction of the *endo*-hydroxyl group with the ethane bridge in VII could, but to a lesser degree than in II, also lead to a *regular* boat conformation.[14,15] However, it can be safely concluded from the nmr data that the cyclohexane portions of the alcohols, and by extension their tosylates and acetates, are locked firmly in the chair conformations under the conditions of solvolysis and that contributions of boat conformations to ground-state populations are negligible.[16]

A point worthy of note is that the ethane bridge in the bicyclo[3.2.1]octane skeleton acts as a conformational anchor which is superior in some respects to the traditional *t*-butyl group. When *t*-butyl is used as anchor, the cyclohexane portion is often not sufficiently constrained for the exclusion of boat forms.[17,18] Moreover, the one-point attachment of the *t*-butyl group still allows considerable torsional freedom to the chair.[19]

Preparative Acetolyses. The compositions of the products formed from the buffered acetolysis of III, VIII, and IX were analyzed and the results are shown in Scheme I. 3,3,5,5-Tetramethylcyclohexyl tosylate (III) behaves very much like the epimeric 3,3,5-trimethylcyclohexyl tosylates[20] in that there is no fragmentation[21] and no migration by methyl or hydride groups. Olefin formation occurs to a high degree, much more so than in the case of the bicyclic compounds, but to about the same extent as that found for the 4-*t*-butylcyclohexyl tosylates.[22,23]

The bicyclic tosylates VIII and IX reveal interesting differences in behavior. The *exo*-tosylate VIII furnishes bicyclo[3.2.1]octene-2 and a sole substitution product, the *endo*-acetate XI. This result is qualitatively similar to that obtained in the acetolysis of *trans*-4-*t*-butylcyclohexyl arenesulfonate.[22,23] However, olefin formation is much less for VIII, probably due to the diminished flexibility of the cyclohexane ring caused by the ethane bridge.

Scheme I. Acetolysis Products Obtained from III, VIII, and IX



The substitution product must have arisen by exclusive back-side attack of solvent at C_3. Complete inversion, the absence of epimeric products, and the nonoccurrence of hydride shift can be adequately rationalized in terms of a back-side solvated intimate ion pair of short lifetime compared to that required for molecular relaxation processes.[22,24]

It is interesting to reflect that if the ethane bridge were effective in impeding back-side solvation of C_3, then solvolysis should give at least some SN1 product, *i.e.*, epimeric acetates.

Acetolysis of the *endo*-bicyclic tosylate IX afforded, in addition to bicyclo[3.2.1]octene-2, both *exo*- and *endo*-acetates X and XI, but no products indicative of hydride shift. This result resembles that found for the acetolysis of *cis*-4-*t*-butylcyclohexyl arenesulfonate, except that in the latter case appreciable hydride shift also occurs.[22,23] The solvolysis of the *endo*-tosylate IX undoubtedly proceeds *via* back-side attack of solvent on C_3 as in the *exo* case, but the appearance of both *exo*- and *endo*-acetates points to a longer lifetime of the solvated ion pair with respect to molecular relaxation. This is reasonable in view of the readier solvolysis of the *endo*- IX compared to *exo*-tosylate VIII. This time, formation of some *endo*-acetate provides further evidence that there may be something amiss with current notions regarding the importance of steric hindrance in deciding product stereochemistry in solvolysis reactions.

From time to time it has been asserted that bridged bicyclic systems have unusual steric requirements.[25] Indeed, the *exo* side of norbornene is particularly prone to attack by a variety of reagents,[26] from which it has been inferred that the *endo* side is sterically protected. In particular, the exclusive formation of *exo* product on solvolysis of *exo*-2-norbornyl sulfonate esters has been attributed to "steric hindrance to *endo* snbtution."[25,27]

(14) It appears from nmr data that in α derivatives of tropine,[15] the chair is considerably flattened by the interaction between the ethane bridge and the 3α substituent. Deformation to this extent in the structurally similar *endo*-3-bicyclo[3.2.1]octanol is presumably minimized by the buttressing effect of the tetrahedral C_8 atom.

(15) R. J. Bishop, G. Fodor, A. R. Katritzky, F. Soti, L. E. Sutton, and F. J. Swinbourne, *J. Chem. Soc., Sect. C*, 74 (1966).

(16) For bicyclo[3.2.1]octane, a *regular* boat form is only attainable through an energetic transition state in which *five* carbon atoms are coplanar.

(17) R. D. Stolow, *J. Am. Chem. Soc.*, 83, 3722 (1961).

(18) E. W. Garbisch and D. B. Patterson, *ibid.*, 85, 3228 (1963).

(19) The nmr signal due to the methine (C_1) signal of *cis*- and *trans*-4-*t*-butylcyclohexanols is broad in contrast to the well-defined multiplets seen for compounds II, VI, and VII. The lack of resolution could arise from the lack of rigidity of the molecular fragments bearing the protons concerned (*cf.* A. H. Lewin and S. Winstein, *ibid.*, 84, 2464 (1962), and ref 10).

(20) H. P. Fischer, C. A. Grob, and W. Schwarz, *Tetrahedron Letters*, 25 (1962); *Helv. Chim. Acta*, 47, 1385 (1964).

(21) F. C. Whitmore and E. E. Stahly, *J. Am. Chem., Soc.*, 55, 4153 (1933); 67, 2158 (1945).

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

(23) S. Winstein and N. J. Holness, *J. Am. Chem. Soc.*, 77, 5562 (1955).

(24) S. Winstein, B. Appel, R. Baker, and A. Diaz, "Organic Reaction Mechanisms," Special Publication No. 19, The Chemical Society, London, 1965, p 109.

(25) (a) H. C. Brown, "The Transition State," Special Publication No. 16, The Chemical Society, London, 1962, p 154; (b) H. C. Brown, K. J. Morgan, and F. J. Chloupek, *J. Am. Chem. Soc.*, 87, 2137 (1965), footnote 73; (c) H. C. Brown, *Chem. Brit.*, 2, 199 (1966).

(26) G. D. Sargent, *Quart. Rev.* (London), 20, 344 (1966).

Table II. Acetolysis Rates of Constrained Cyclohexyl *p*-Toluenesulfonates

Tosylate	Temp, °C	k_1, sec^{-1}	ΔH, kcal	ΔS, eu
exo-3-Bicyclo-[3.2.1]octyl (VIII)	25.0[a]	4.87×10^{-7}	25.6	−2.4
	50.0	9.71×10^{-6}		
	70.0	1.07×10^{-4}		
	90.0	7.71×10^{-4}		
endo-3-Bicyclo-[3.2.1]octyl (IX)	25.0[a]	5.32×10^{-6}	22.8	−6.2
	50.0	1.12×10^{-4}		
	70.0	8.87×10^{-4}		
	90.0	5.52×10^{-3}		
3,3,5,5-Tetra-methylcyclo-hexyl (III)	25.0[a]	8.59×10^{-8}	27.4	1.0
	50.0	3.27×10^{-6}		
	70.0	3.96×10^{-5}		
	90.0	3.55×10^{-4}		

[a] Calculated rates.

(IX) is quite large. The fact that IX acetolyses six times more slowly than expected could be due to two reasons. It could mean in the present case that the (GS − TS) term in the Foote–Schleyer–Halford equation is much too big. The operation of the reflex effect could offset some of this interaction by bending C_3 away from the ethane bridge. Alternatively, it could mean that either ionization in the solvolytic step is incomplete or simply that the tosylate anion does *not* find a propitious avenue of departure. This is another way of saying that the correlation equation should contain a term for steric hindrance to ionization. It has already been suggested that such a term must be introduced before rates can be meaningfully calculated for bridged structures such as 2-norbornyl derivatives.[25c] Inspection of a Dreiding model of bicyclo[3.2.1]-octane

Table III

Tosylate	$\nu_{C=O}$	(GS − TS) strain, kcal/mole	k_1, sec^{-1} (25.0°)	k_{rel} (calcd)	k_{rel} (obsd)
Cyclo-hexyl	1717.0	0	3.79×10^{-8}	0.562	1
III	1714.9	1.8[a,c]	8.59×10^{-8}	21.4	2.26
VIII	1714.0	1.8[a,c]	48.7×10^{-8}	28.2	12.8
IX	1714.0	3.8[b,c]	532×10^{-8}	851	140

[a] 1.8 kcal/mole = 2(CH_3–H) interactions (solvolytic value). [b] 3.8 kcal/mole = 2(CH_3–OTs) interactions (solvolytic value). [c] E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis," Interscience Publishers, Inc., New York, N. Y., 1962, Chapter 2.

It can now be seen that this interpretation cannot be correct in the light of the opposite stereochemical course exhibited by the solvolysis of *exo*-3-bicyclo-[3.2.1]octyl tosylate, the *endo* side of which appears to be just as hindered as that of the 2-norbornyl system.

Kinetics. The tosylates were acetolyzed following Winstein's procedure.[28] The rates were found to follow apparent first-order kinetics. They are listed in Table II together with their derived activation parameters.

Before discussing the solvolysis rates they have to be examined to see if they are "normal" by comparison with that of cyclohexyl tosylate. Normality can be reasonably estimated from a knowledge of the ground-state geometry of the tosylate and the carbonyl stretching frequency of the related ketone by means of the Halford–Foote–Schleyer equation.[29,30] Estimated and observed rates are tabulated in Table III. No startling divergences are seen. 3,3,5,5-Tetramethylcyclohexyl tosylate (III) solvolyses about ten times more slowly than expected. The discrepancy could mean that the value set for the interaction between the methyl groups and the methine hydrogen is too big. The agreement between observed and calculated rates for *exo*-3-bicyclo[3.2.1]octyl tosylate (VIII) is much better, which suggests that torsional relief of ground-state interactions, which should be less for VIII than for III, is probably the origin of the discrepancy.

The gap between calculated and observed rates for the acetolysis of *endo*-3-bicyclo[3.2.1]octyl tosylate reveals that the path of a group leaving from the *endo* side of C_3 undergoing hydridization change from sp^3 to sp^2 is obstructed by the ethane bridge. In much the same way, corresponding egress from C_2 of norbornane is similarly hampered, but, perhaps to a lesser degree.

The significant point which emerges from the present results, in spite of the possibility of similar steric hindrance to ionization in *endo*-3-bicyclo[3.2.1]octyl and *endo*-2-norbornyl arenesulfonates, is that the *exo*/*endo* rate ratio for the bicyclo[3.2.1]octyl tosylates is in the opposite order as that found in the 2-norbornyl system.[31,32] Accordingly, it would have to be concluded that some special effect (*e.g.*, anchimeric acceleration) must operate in the *exo* isomer of the latter system on solvolysis.

The present results of acetolysis parallel those recently reported for the ethanolysis of the epimeric 3-bicyclo[3.2.1]octyl tosylates[33] and chlorides.[34] The latter chlorides have been used by Grob as a homomorphous comparison for the ethanolysis of 3α- and -β-chloronortropine and -tropine.[35]

Experimental Section

All melting and boiling points are uncorrected. Microanalyses were performed by Dr. G. Robertson, Florham Park, N. J. The

(27) H. C. Brown, *et al.*, *J. Am. Chem. Soc.*, **86**, 1246, 5008 (1964), and intervening papers.
(28) S. Winstein, E. Grunwald, and L. L. Ingraham, *ibid.*, **76**, 821 (1948).
(29) C. S. Foote, *ibid.*, **86**, 1853 (1964).
(30) P. von R. Schleyer, *ibid.*, **86**, 1854 (1964).
(31) (a) The comparable *exo*/*endo* rate ratio for the structurally related epimeric 6,6-dimethyl-2-norbornyl tosylates is 222;[31b] (b) P. von R. Schleyer, M. M. Donaldson, and W. E. Watts, *J. Am. Chem. Soc.*, **87**, 375 (1965).
(32) S. Winstein and D. Trifan, *ibid.*, **74**, 1147, 1154 (1952).
(33) P. F. Jackisch, Doctoral Dissertation, University of Michigan, 1965.
(34) C. A. Grob and A. Weiss, *Helv. Chim. Acta*, **49**, 2605 (1966).
(35) A. T. Bottini, C. A. Grob, E. Schumacher, and J. Zergenyi, *ibid.*, **49**, 2516 (1966).

nmr spectra were determined on a Varian A-60 spectrometer at *ca.* 35° using tetramethylsilane as an internal standard in roughly 10–20% solutions of carbon tetrachloride. Characteristic nmr data of most compounds are listed in Table I. The infrared spectra were determined on a Beckman IR-9 grating spectrophotometer or a Perkin-Elmer Infracord. The gas chromatograph (Model 700, F & M Scientific Corp., Avondale, Pa.) was equipped with a thermal conductivity detector. The chromatographic columns were 9 ft long × 0.25 in. in diameter packed with Tide (a household detergent, manufactured by Procter & Gamble, Cincinnati, Ohio) or 20% N,N-bis(2-cyanoethyl)formamide[36] on Chromosorb P (calcined diatomaceous earth of 60–80 mesh with a surface area of 4–6 m^2/g). Helium was used as the carrier gas (*ca.* 40 cc/min for analysis and 100 cc/min for preparation).

Preparation of Compounds as Reactants and for Comparison. Ketones I and V. In order to determine accurately the carbonyl stretching frequency of bicyclo[3.2.1]octanone-3 (V)[8,37] and tetramethylcyclohexanone (I),[38] they were purified *via* recrystallization of their semicarbazones to constant melting point. The ketone was regenerated by acid hydrolysis and liberated by steam distillation. Distillation afforded the pure ketone.

Alcohols II, VI, and VII. *exo*- and *endo*-3-bicyclo[3.2.1]octanols (VI and VII) were prepared according to our previously published procedure.[8] They have also been described (together with their tosylates) by Kraus in a later publication.[39] 3,3,5,5-Tetramethylcyclohexanol (II) was prepared by reduction of the parent ketone with lithium aluminum hydride.[38]

***p*-Toluenesulfonates III, VIII, and IX** were prepared by treating the alcohols with *p*-toluenesulfonyl chloride in pyridine solution. On work-up, an oil remained which was recrystallized from petroleum ether (bp 30–60 or 60–70°). Tosylates III, VIII, and IX were colorless solids with melting points of 88–91, 76–77, and 71–73°, respectively.

Anal. Calcd for $C_{17}H_{26}O_3S$ (III): C, 66.00; H, 8.15; S, 10.37. Found: C, 65.90; H, 8.50; S, 10.18.

Anal. Calcd for $C_{15}H_{20}O_3S$ (VIII and IX): C, 64.25; H, 7.19; S, 11.44. Found for VIII: C, 64.60; H, 7.47; S, 11.15. Found for IX: C, 64.35; H, 7.19; S, 11.34.

Acetates IV, X, and XI were prepared from the alcohols by heating them with acetic anhydride in excess pyridine for 15 min. Acetates IV, X, and *XI* were colorless oils which were purified by distillation and molecular microdistillation (*e.g.*, at 3 mm and a bath temperature of 90°).

Anal. Calcd for $C_{12}H_{22}O_2$ (IV): C, 72.67; H, 11.18. Found: C, 72.75; H, 10.90.

Anal. Calcd for $C_{10}H_{16}O_2$ (X and XI): C, 71.39; H, 9.59. Found for X: C, 71.94; H, 9.76. Found for XI: C, 71.00; H, 9.71.

Olefins. Bicyclo[3.2.1]octene-2 was obtained by first hydrogenating 5-hydroxymethylnorbornene and then by heating the dihydro compound with 85% orthophosphoric acid at 160°.[40] 3,3,5,5-Tetramethylcyclohexene was prepared by heating the alcohol with potassium hydrogen sulfate.[38]

Acetolyses. Product Analysis. Weighed amounts of tosylate (*ca.* 0.5 g) and anhydrous potassium acetate (*ca.* 0.5 g) were placed in 50-ml ampoules. To each ampoule was added 50.00 ml of glacial acetic acid containing *ca.* 1% acetic anhydride. The ampoule was sealed and placed in a constant-temperature bath for at least ten half-lives. The ampoule was withdrawn from the bath, cooled to room temperature, and poured onto 100 g of ice–water. The aqueous solution was extracted with three 25-ml portions of ether (ethanol-free). The extracts were dried over anhydrous magnesium sulfate and filtered, and the volume was reduced to *ca.* 25 ml. If the volume was reduced to less than this amount, considerable loss of olefin occurred. This solution was then subjected to vpc analysis at 100° using a Tide column. The individual olefins and acetates were isolated by trapping the separate peaks. The collected materials were identified by comparing their retention times and infrared and nmr spectra with those of authentic samples.

Several preparative solvolyses and analyses were carried out for each tosylate at a particular temperature. The percentage compositions were normalized by dividing the peak areas by the square root of the molecular weight of the compound. The data in Scheme I represent the average of at least three experiments, the results of which were constant within ±2.5%.

Rate Measurements. The method was essentially that of Winstein.[28] Solutions of tosylate (0.03–0.05 *M*) in dry acetic acid (50 ml) containing 1% acetic anhydride were made up at room temperature. Eight aliquots of about 6 ml were sealed in ampoules and immersed together in a bath of mineral oil. The bath temperature was controlled thermostatically to ±0.01° (by a Sargent Thermonitor, catalog no. S-84810). Periodically ampoules were withdrawn and quenched in ice. The time at which the first ampoule was withdrawn was designated zero time (t_0). Portions (5 ml) of the ampoule contents were then titrated against standard sodium acetate in acetic acid using brom phenol blue as indicator. The concentration of the unreacted tosylate was obtained and its logarithm at time t was plotted against reaction time t. The apparent titrimetric first-order acetolysis rate constant was calculated from the resulting slope. Rate constants were determined by a least-squares fitting of the data.[41] Since the analytical precision was less than ±0.5% and solvolyses were followed to at least 70% completion, the error in the rate constants was reckoned as being no greater than ±1.5%.[42]

Acknowledgments. We are indebted to the National Science Foundation and the Petroleum Research Fund, administered by the American Chemical Society, for the financial support of this work. We wish to thank Drs. P. von R. Schleyer, D. Dalton, and R. M. Moriarty for helpful criticism.

(36) G. J. Frisone, *Nature*, **193**, 370 (1962).
(37) C. W. Jefford, *Proc. Chem. Soc.*, 64 (1963).
(38) G. Chiurdoglu and A. Maquestiau, *Bull. Soc. Chim. Belges*, **63**, 357 (1964).
(39) W. Kraus, *Chem. Ber.*, **97**, 2719 (1964).
(40) K. Alder and R. Reubke, *ibid.*, **91**, 1525 (1958).
(41) F. Daniels, J. H. Matthews, J. W. Williams, P. Bender, and R. A. Alberty, "Experimental Physical Chemistry," 5th ed, McGraw-Hill Book Co., Inc., New York, N. Y., 1956.
(42) S. W.Benson, "The Foundation of Chemical Kinetics," McGraw-Hill Book Co., Inc., New York, N. Y., 1960, pp 86–94.