diethylene glycol in increments until no more dissolved at room temperature in the dark. With the cessation of stirring, the solution cooled a few degrees, and fresh crystals appeared, assuring saturation. The clear solution was decanted. Attempts to prepare the solution with diethylene glycol that was not freshly distilled always resulted in a brown to gray solution.

An aqueous solution made with 10.5 g. of the saturated silver nitrate in diethylene glycol and 50 ml. of water was dispersed on 30 g. of 60–80 mesh F. & M., Chromosorb P. Methyl alcohol could not be used as a dispersion diluent because it precipitated silver nitrate. The water was removed by vacuum desiccation for 120 hr. until no more water condensed in the vacuum line trap in 24 hr. Seventy milliliters of this packing filled 10 ft. of 0.25-in. tubing. The column is limited to operation at temperatures below 70° by loss of the solvent at significantly higher temperature.

Kinetic Experiments. The dry acetic acid used for these studies was prepared by distilling commercial acetic acid from triacetyl borate.[32] Solutions of sodium acetate in acetic acid were prepared by dissolving accurately weighed amounts of sodium carbonate in acetic acid, and then adding an equivalent amount of acetic anhydride to destroy the water formed. Solu-

(32) L. F. Fieser, "Experiments in Organic Chemistry," D. C. Heath and Co., Chicago, Ill., 1957, p. 281.

tions of perchloric acid in acetic acid were standardized against sodium acetate in acetic acid, prepared as described above.

The solvolysis reactions were followed by means of the ampoule technique. Approximately 5.5 ml. of the acetic acid solution of the nosylate (*ca.* 0.02 *M*) was placed in each ampoule. The ampoules were placed in the oil bath and withdrawn at appropriate intervals. The acid formed was then determined by titration of a 5.00-ml. aliquot with 0.025 *N* sodium acetate in acetic acid, using brom phenol blue as indicator. In cases where the reaction was carried out in the presence of excess acetate ion, a measured amount of standard perchloric acid in acetic acid was added to the aliquot, which was then back titrated with sodium acetate solution. The reactions were followed to about 85% of completion. The titer of "infinity" samples (those heated for 10 or more half-lives) was usually within 2% of the theoretical value.

Nucleophilic Reactivity of the Carbon–Carbon Double Bond. IV.[1] The Effect of Chain Elongation. 3-(Δ³-Cyclopentenyl- and 3,4-dimethyl-Δ³-cyclopentenyl)-propyl p-Nitrobenzenesulfonates

Paul D. Bartlett, Walter S. Trahanovsky, Donald A. Bolon, and George H. Schmid
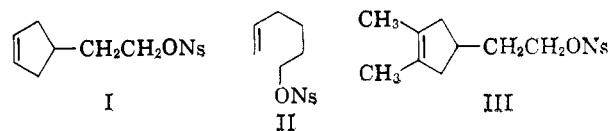
Contribution from the Converse Memorial Laboratory of Harvard University, Cambridge, Massachusetts 02138. Received November 12, 1964

In contrast to 2-(Δ³-cyclopentenyl)ethyl p-nitrobenzenesulfonate (I), 3-(Δ³-cyclopentenyl)propyl p-nitrobenzenesulfonate (IV) is acetolyzed without cyclization and without appreciable acceleration by the double bond. However, 3-(3,4-dimethyl-Δ³-cyclopentenyl)propyl p-nitrobenzenesulfonate (V) undergoes acetolysis at 60° 3.2 times faster than a saturated model compound, yielding, in the presence of 0.2 N sodium acetate, the structurally related acetate XI (42%), and the two olefins 1,7-dimethylbicyclo[3.2.1]octene-6 (IX, 32%) and 1-methyl-7-methylenebicyclo[3.2.1]octane (X, 25%) (the products being determined at 50°, and being nearly the same at 100°). These facts show that the elongation of the chain from ethyl to propyl brings about a decrease by a factor of 600 in the rate of the anchimerically assisted acetolysis. The sources of this difference lie partly in entropy, but mostly in energy factors. These are discussed.
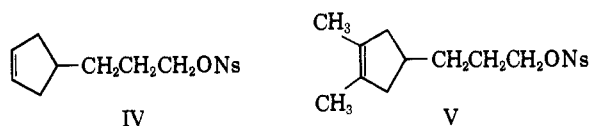
(1) Previous papers in this series: (a) P. D. Bartlett, S. Bank, R. J. Crawford, and G. H. Schmid, *J. Am. Chem. Soc.*, **87**, 1288 (1965); (b) P. D. Bartlett and G. D. Sargent, *ibid.*, **87**, 1297 (1965); (c) P. D. Bartlett, W. D. Closson, and T. J. Cogdell, *ibid.*, **87**, 1308 (1965).
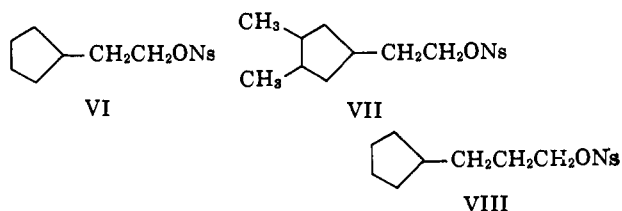
Introduction

Sulfonate esters with a double bond in the 5,6-position relative to the sulfonate group undergo acetolysis with participation of the double bond and formation of cyclic products.[1] In 2-(Δ³-cyclopentenyl)ethyl p-nitrobenzenesulfonate (I) the solvolysis rate assisted by the double bond is about 75 times greater than that of Δ⁵-hexenyl p-nitrobenzenesulfonate (II), while in the dimethylated compound III this ratio rises to about 2850. Both facts have been interpreted as supporting a transition state in which, for minimum energy requirement, the positive charge in the incipient cation is distributed as evenly as possible between the two carbon atoms of the original double bond.

Stuart-type models suggest that the homolog of I, 3-(Δ^3-cyclopentenyl)propyl p-nitrobenzenesulfonate (IV), might cyclize with the introduction of less angle strain

CH₂CH₂CH₂ONs
IV

CH₃
CH₂CH₂CH₂ONs
CH₃
V

than in the case of I. This consideration prompted investigation of both IV and its dimethyl derivative V. Since previous work showed an insignificant difference between the methylated and unmethylated 2-cyclopentylethyl nitrobenzenesulfonates VI and VII, the unmethylated compound VIII was used as a standard of reference in the present work for both the methylated and unmethylated sulfonates.

CH₂CH₂ONs
VI

CH₃
CH₂CH₂ONs
CH₃
VII

CH₂CH₂CH₂ONs
VIII

Results

3-(Δ^3-Cyclopentenyl)propanol was prepared by the hydroboration of 4-allylcyclopentene, which in turn was prepared by coupling the Δ^3-cyclopentenyl Grignard reagent with allyl chloride. The dimethylated p-nitrobenzenesulfonate V was made from the previously[1b] described 3,4-dimethyl-Δ^3-cyclopentene-1-carboxylic acid by the sequence shown in Chart I.

Chart I

CH₃
COOH
CH₃
$\xrightarrow{\text{LAH}}$
CH₃
CH₂OH
CH₃
$\xrightarrow{\text{TsCl}}$

CH₃
CH₂OTs
CH₃
$\xrightarrow{\text{NaCH(COOEt)}_2}$

CH₃
CH₂CH
CH₃
COOEt
COOEt
$\xrightarrow[\text{2, HCl}]{\text{1, NaOH}}$

CH₃
CH₂CH
CH₃
COOH
COOH
$\xrightarrow{\Delta}$

CH₃
CH₂CH₂COOH
CH₃
$\xrightarrow{\text{LAH}}$
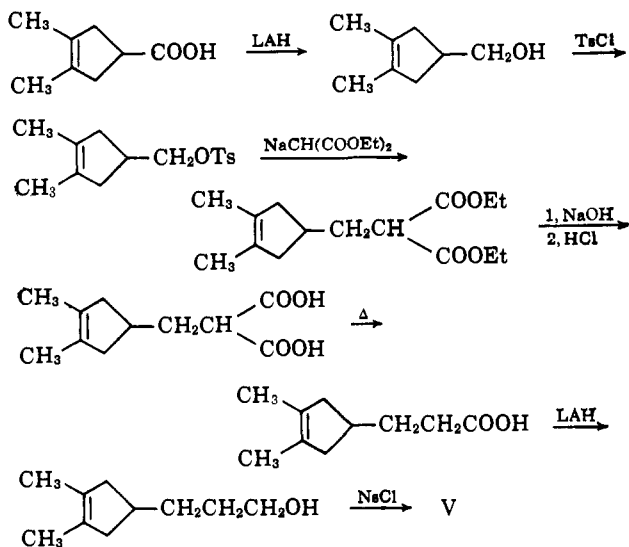
CH₃
CH₂CH₂CH₂OH
CH₃
$\xrightarrow{\text{NsCl}}$ V

Table I lists the rate constants determined for the acetolysis of 3-(Δ^3-cyclopentenyl)propyl p-nitrobenzenesulfonate, reasonable agreement being found between titrimetric and conductometric methods of following the reaction. The ratio k_u/k_s between the rate constants for the unsaturated and saturated sulfonates is 1.1 at 100.85° and 1.2 at 119.6°. Since this result suggested a slight participation of the double bond in the ionization process, we sought to magnify the effect by measuring formolysis rates of the same two esters. As shown in Table II, k_u/k_s is essentially unity in formic acid at 80°.

Table I. Rate Constants for Acetolysis of 3-(Δ^3-Cyclopentenyl)propyl p-Nitrobenzenesulfonate (IV) and of 3-Cyclopentylpropyl p-Nitrobenzenesulfonate (VIII)

Com-pound	Temp., °C.	[NaOAc], M	$k \times 10^6$ sec.$^{-1}$
IV	70.31	None	0.408
IV	70.31	None	0.460
IV	79.44	None	1.22
IV	79.44	None	1.05
IV	100.85	None	8.77
IV	100.85	None	8.26
IV	100.85	0.03	10.65
IV	100.85	0.03	10.31
IV	119.60	None	39.5
IV	119.60	None	39.7
IV	119.60	0.03	47.7
VIII	100.85	None	7.79
VIII	100.85	None	7.57
VIII	100.85	0.03	10.15
VIII	100.85	0.03	10.00
VIII	119.60	None	34.2
VIII	119.60	None	32.3

Table II. Rate Constants for Formolysis of 3-(Δ^3-Cyclopentenyl)-propyl p-Nitrobenzenesulfonate (IV) and 3-Cyclopentylpropyl p-Nitrobenzenesulfonate (VIII) by the Potentiometric Method

Sul-fonate	Temp., °C.	$k \times 10^4$ sec.$^{-1}$
VIII	79.7	1.91
IV	80.4	1.85
IV	79.7	1.91

The product of acetolysis of a sample of 3-(Δ^3-cyclopentenyl)propyl p-nitrobenzenesulfonate, isolated in 91.5% yield, had an infrared spectrum identical with that of 3-(Δ^3-cyclopentenyl)propyl acetate prepared directly from the alcohol. Vapor phase chromatography on a diisodecyl phthalate column at 150° gave a single peak. Another column, diethylene glycol adipate with 2% of phosphoric acid (85%), at 150°, gave two cleanly separated peaks, the first of which, comprising 29% of the whole, appeared to be saturated from the absence of absorption at 3.24 and 14.5 μ in its infrared spectrum. The second peak was the unchanged acetate. From the fact that authentic 3-(Δ^3-cyclopentenyl)propyl acetate gave the same two peaks, and in different proportions, on chromatography over the same column, we think it likely that the first peak results from the action of phosphoric acid at 150° on the acetate, and was not present in the solvolysis product.

We have not yet explored the implications of this possible surface-catalyzed reaction of the acetate. Some unsuccessful experiments were carried out in an attempt to cyclize the p-nitrobenzenesulfonate in ionizing but nonnucleophilic media. Starting material was recovered after 30 days at room temperature in dimethyl sulfoxide, and after 30 and 50 days in Freon 113. After being sealed for five days in liquid sulfur dioxide at room temperature, 66% of the starting material was recovered together with intractable polymeric product. After 17 days the product was a black, amorphous solid. A solution of 0.0991 M lithium perchlorate in diethyl ether at 95° produced a dark, viscous oil in 46 hr.

For the kinetic studies of the dimethylated unsaturated sulfonate V a spectroscopic method was used after it was found to afford accurate rate measurements on samples of 4 mg. of substrate. Table III lists the rate constants for V compared with those for VIII. The two methyl groups (which in the case of the cyclopentenylethyl compounds resulted in k_{III}/k_I being 38) have now produced a substantial driving force from the double bond ($k_u/k_s = k_V/k_{VIII}$) of 3.9-fold at 70° and of 4.5 at 100°.
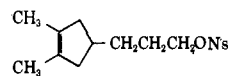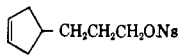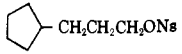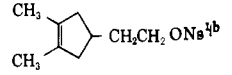
Table III. Rate Constants for Acetolysis of 3-(3,4-Dimethyl-Δ³-cyclopentenyl)propyl p-Nitrobenzenesulfonate (V) and 3-Cyclopentylpropyl p-Nitrobenzenesulfonate (VIII) by the Spectroscopic Method in Presence of 0.03 M Sodium Acetate

Sulfonate	Temp., °C.	$k \times 10^6$ sec.⁻¹
V	46.26	0.172
V	70.39	2.37
V	70.53	2.66
V	100.43	43.8
V	100.86	43.9
V[a]	100.86[a]	47.8[a]
VIII	70.05	0.578
VIII	70.57	0.630
VIII	100.35	9.66
VIII	100.39	9.62

[a] Conductivity method used; no added sodium acetate.

The Eyring equation has been fitted to the rates at different temperatures and the best values of enthalpy and energy of activation are listed in Table IV, together

Table IV. Activation Parameters for Acetolysis of 3-(3,4-Dimethyl-Δ³-cyclopentenyl)propyl p-Nitrobenzenesulfonate (V) in Comparison with Related Compounds

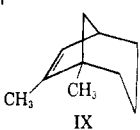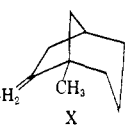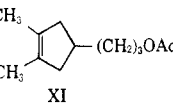| Sulfonate	$k \times 10^6$ (60°)	ΔH*, kcal.	ΔS*, e.u.
V CH₃⟩⟨CH₃⟩—CH₂CH₂CH₂ONs	0.88	23.5	-11.9
IV ⟨⟩—CH₂CH₂CH₂ONs	0.16	23.8	-14.2
VIII ⟨⟩—CH₂CH₂CH₂ONs	0.21	22.6	-16.9
III CH₃⟩=⟨CH₃⟩—CH₂CH₂ONs[4b]	429.3	20.6	-7.8

with the rate constants extrapolated or interpolated to 60° for comparison of the compounds with one another. Both unsaturated compounds with propyl side chains have appreciably *higher* activation enthalpies for acetolysis than does the saturated reference compound, while the strongly assisted solvolysis of the ethyl compound III has a *lower* enthalpy of activation. Thus the ratio k_u/k_s is not independent of temperature. If it were, we might be puzzled by the fact that this ratio is greater than unity for IV at 100° and above although all other indications of anchimeric assistance are absent. At 60°, where most of our other comparisons have been made, this ratio is 0.77 for IV, a normal value in the absence of appreciable participation of the double bond.

Comparing V directly with III we find that the elongation of the chain from two to three carbon atoms reduces the rate at 60° by a factor of 488, and reduces the *assisted* rate (best approximated here by $k_V - k_{IV}$) by a factor of about 600. Thus other properties of these two systems are much more important than the difference in total angle strain between the bicyclo[2.2.1]heptane and the bicyclo[3.2.1]octane.

In the product study of the solvolysis of V three products were identified: 1,7-dimethylbicyclo[3.2.1]-octene-6 (IX), 1-methyl-7-methylenebicyclo[3.2.1]octane (X), and 3-(3,4-dimethyl-Δ³-cyclopentenyl)propyl acetate (XI), in the relative amounts shown in Table V.

Table V. Products of the Acetolysis of 3-(3,4-Dimethyl-Δ³-cyclopentenyl)propyl p-Nitrobenzenesulfonate (0.1 M) in the Presence of 0.2 M Sodium Acetate
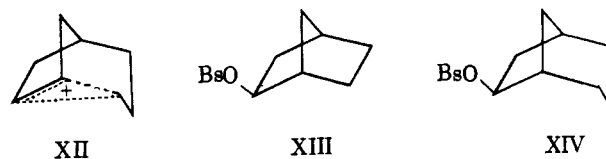
Temp., °C.	Products, %		
	IX	X	XI
50	32	25	42
100	33	28	39

The acetate XI was the only acetate present and was identified by comparison (v.p.c. retention time and n.m.r. spectrum) with authentic synthetic material. The n.m.r. spectra of the hydrocarbons IX and X are quite distinctive and uniquely consistent with the structures shown.

Discussion

The activation parameters show that of the 600-fold rate difference between the assisted rates of III and V, the enthalpy difference leads to a factor of about 60 while the entropy difference is responsible for about a factor of 10. Thus the slowness of V cannot be attributed simply to the increased number of random conformations of the chain, which would be a pure entropy effect.
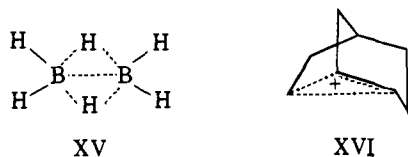
Some idea of the energy changes involved in the formation of the expected bridged ion XII can be had from the fact that the acetolysis of *exo*-2-norbornyl brosylate

XII   XIII   XIV

XIII at 50° is 370 times that of *exo*-6-bicyclo[3.2.1]-octyl brosylate (XIV).[2] Entropy of ring closure would appear to cancel out in this comparison as nearly as possible, and we conclude that the release of angle and eclipsing strain in bicyclo[3.2.1]octyl compounds relative to the norbornyl is more marked in the ground state than in the transition state for solvolysis by 3.8 kcal. To the extent to which the transition state resembles the bridged ion it might be expected to have less angle strain than the starting material itself. In diborane (XV), which has two three-center electron-de-

(2) H. L. Goering, personal communication.

ficient bonds analogous to that in the norbornyl cation, the bridging hydrogen atoms have a B–H distance of 1.33 Å., 12% longer than the singly bound hydrogen atoms.[3] If the bonds represented by single dotted

XV   XVI

lines in XII and the norbornyl cation are substantially longer than the normal covalent C–C bond, the strain at the other bond angles in the ion is considerably lessened, while the bridgehead strain at C-1 may be eliminated by the entirely different geometrical requirements of the three-center bond. This is probably a large part of the reason why anchimeric assistance in I is so marked despite the almost endothermic nature of the bicyclic ring closure. Similarly, the strained norbornyl brosylate XIII gains more in forming a bridged ion than the less strained bicyclooctyl brosylate XIV.

In the study of III it was difficult to control the elimination of acetic acid from the cyclic product acetate during vapor chromatography, but it was shown that the direct product consisted of acetates, not olefins. In the present case the n.m.r. study of the solvolytic product indicated that the olefins were produced under the conditions of solvolysis for five solvolytic half-lives. It is very likely that elimination occurred directly from the first ionic intermediate, since excess sodium acetate was present and strong acid, which might have re-ionized the acetates, was not allowed to accumulate. The fact that the cyclic product from V is entirely olefins, while that from III is entirely acetates, must be due to the fact that the norbornyl ring strain is more unfavorable to a trigonally hybridized carbon atom in the ring than is the lesser strain in the bicyclo-[3.2.1]octyl ring. This would then be an unusually sensitive example of an effect well recognized as between five- and six-membered rings.[4] (Here the difference is between two five-membered rings of differing degrees of distortion.)

The presence of the methyl groups evidently retards the 2,7-hydride shift which in a related case[2] converts ion XII into XVI. In the absence of large energy differences between XII and XVI, either one should be stabilized by making one of the charged carbon atoms tertiary, as is the case here.

The above considerations suggesting that the ion XII is not under more strain, but is probably under less, than the norbornyl cation, and that the same is true of the respective transition states in solvolysis, leaves a factor of at least 60 (deduced from the activation parameters) to be accounted for, corresponding to 2.9 kcal. by which the solvolysis of V requires more energy input than that of III. If we arrange a model of III for best access of the double bond to C-1 of the ethyl group, preparatory to a nucleophilic displacement on C-1, every C–C bond with free rotation is in a perfectly staggered conformation. If we similarly arrange a model of V for closest approach of C-1 to the center of the double bond, C-2 and C-3 are in the eclipsed conformation. The energy of producing this eclipse from the conformation of lowest energy, if equal to the rotational barrier in ethane (2.7–3.0 kcal.),[5] would account for the difference in activation enthalpy between III and V. This estimated figure should be corrected upward because the bond in question more resembles the 2,3-bond of butane than the freer one of ethane. Offsetting this is a downward correction since the collinearity of displacing and displaced groups in the model is improved by introducing some staggering into the propyl chain, resembling that which a model shows for bicyclo[3.2.1]octane itself. This improved collinearity in turn is at the expense of increased angle strain in the propyl side chain and involves making the staggering at C-1,2 and between C-3 and the ring less perfect.

The less favorable entropy of activation for acetolysis of V compared to III reflects the larger number of conformations in the ground state which are unsuitable for reaction.

In order to isolate the direct product of acetolysis and avoid possible acid-induced rearrangements, sodium acetate was present in all the product studies. As observed in previous cases, this superposes a displacement reaction (S_N2) by acetate ion upon the assisted and unassisted solvolysis. It has been observed[6] that in 0.2 M sodium acetate the S_N2 reaction is about 1.5 times as fast as the unassisted acetolysis. An approximate calculation then predicts that the fraction of bicyclic product at 60° will be equal to

$$k_\Delta/(k_\Delta + k_s + k_{SN^2}) =$$
$$7.2/(7.2 + 2.09 + 3.14) = 0.58$$

where k_Δ is the rate constant for solvolysis assisted by the double bond and k_s is the rate constant for unassisted solvolysis, approximated by the rate constant for solvolysis of the saturated ester. This is near the observed value of 60%.

Further work is in progress on the role of conformational factors in solvolytic ring closures.

Experimental

1-Allyl-Δ^3-cyclopentene. Magnesium (2.43 g., 0.1 g.-atom) and ether (50 ml., absolute) was placed in a 300-ml. flask with the usual equipment. A nitrogen atmosphere was maintained throughout the reaction. Δ^3-Cyclopentenyl bromide (14.7 g., 0.1 mole) in ether (50 ml., absolute) was added at such a rate as to maintain gentle reflux. When all of the bromide was added, the mixture was heated at reflux for 2 hr. and then allowed to cool.

The paddle stirrer was removed and replaced by a tube reaching almost to the bottom of the flask. The Grignard solution was pumped through this tube and through a fritted glass filter into another flask under positive nitrogen pressure. The residual magnesium was rinsed twice with ether. The solution was cooled in an ice bath.

(3) See W. N. Lipscomb, *Advan. Inorg. Chem. Radiochem.*, 1, 119 (1959).
(4) H. C. Brown, R. S. Fletcher, and R. B. Johannesen, *J. Am. Chem. Soc.*, 73, 212 (1951).
(5) K. S. Pitzer, *Discussions Faraday Soc.*, 10, 66 (1951); E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p. 124 ff.
(6) W. S. Trahanovsky, unpublished work in this laboratory.

Allyl bromide (12.1 g., 0.1 mole) in ether (50 ml., absolute) was added to the cold Grignard solution over a 0.5-hr. period with stirring. The reaction was allowed to stir and warm to room temperature for 12 hr. During this time a heavy red oil separated.

Saturated ammonium chloride solution (100 ml.) was added slowly to the reaction, with attendant cooling, followed by water (100 ml.). The organic layer was separated and dried ($MgSO_4$). The ether solution was filtered and the ether removed under vacuum. The residue was distilled at atmospheric pressure giving crude allyl-Δ^3-cyclopentene (4.35 g., 40.3%, b.p. 118–122°). This was redistilled giving pure material (b.p. 121–121.5°). *Anal.* Calcd. for C_8H_{12}: C, 88.81; H, 11.19. Found: C 88.56, H, 11.39.

3-(Δ^3-Cyclopentenyl)propanol was prepared from 1-allyl-Δ^3-cyclopentene by the Brown hydroboration method.[7] The crude product, obtained in 48% yield, b.p. 97–108° (24 mm.), was redistilled, b.p. 112–112.5° (26 mm.). *Anal.* Calcd. for $C_8H_{14}O$: C, 76.19; H, 11.11. Found: C, 75.91, H, 11.18. The 60-Mc. n.m.r. spectrum was similar in appearance to that of 2-(Δ^3-cyclopentenyl)ethanol. It had peaks at δ 5.57 (unsaturation), 5.0 (OH), 3.50 (α-hydrogen), 2.20 (broad, ring), and 1.49 (β and γ of side chain).

The *acetate* was prepared from the alcohol and acetic anhydride in excess pyridine in 44% yield, b.p. 113–115° (20 mm.). *Anal.* Calcd. for $C_{10}H_{16}O_2$: C, 71.43; H, 9.52. Found: C, 70.87, H, 9.73. The purity was greater than 95% by vapor chromatography, in which it was employed as a reference compound.

The *p-nitrobenzenesulfonate* was prepared by the method of Streitwieser, in 55% yield, m.p. 56–57°. *Anal.* Calcd. for $C_{14}H_{17}O_5NS$: C, 54.02; H, 5.47; N, 4.50. Found: C, 54.20, H, 5.76, N, 4.19. The n.m.r. spectrum in $CDCl_3$ had peaks at δ 8.37 (aryl), 5.71 (unsaturation), 4.26 (α), and unresolved absorption from 2.5–1.4 (ring and side chain).

3,4-Dimethyl-Δ^3-cyclopentene carboxylic acid was prepared as described previously.[1b]

3,4-Dimethyl-Δ^3-cyclopentenylmethanol was prepared by the lithium aluminum hydride reduction of 22.4 g. (0.160 mole) of the acid by the procedure of Nystrom and Brown.[8] The crude material was distilled under reduced pressure to give 15.3 g. (76%) of product as a light yellow oil, b.p. 50–55° (1 mm.); $\nu_{max}^{CCl_4}$ (cm.$^{-1}$) 3600 (m), 3350 (s-broad), 2900 (s-broad), 1450 (s), 1390 (s), and 1040 (s-broad); n.m.r. spectrum (CCl_4) contained peaks at δ 3.4 (multiplet, $-CH_2-OH$), 1.55 (singlet, 2 $-CH_3$), and multiplet centered at 2.2 for ring protons; $n^{25}D$ 1.4748. *Anal.* Calcd. for $C_8H_{14}O$: C, 76.13; H, 11.18. Found: C, 75.71, H, 11.37.

2-(3,4-Dimethyl-Δ^3-cyclopentenyl)propionic Acid. The tosylate of 3,4-dimethyl-Δ^3-cyclopentenylmethanol was prepared by the method of Tipson.[9] A quantity of 31 g. (0.111 mole, 96%) of crude tosylate was obtained.

Sodium (2.6 g., 0.111 g.-atom), diethylmalonate, Eastman reagent grade (18.5 g., 0.115 mole), and 80 ml. of anhydrous ethanol was converted to a solution of sodium diethylmalonate by the procedure of Adams and Kamm.[10] Over a period of 45 min., the crude tosylate in 8 ml. of ethanol was added with stirring to the cool sodium dimethylmalonate. The mixture was refluxed for 3.5 hr. The ethanol was then removed under vacuum and the residue was treated with 100 ml. of water and 50 ml. of ether. The mixture was acidified with dilute sulfuric acid. The ether layer was separated and the aqueous layer was extracted twice with ether. After removing the ether from the combined ether solutions, the residue was treated with 90.0 g. (2.25 moles) of sodium hydroxide in 350 ml. of water. The mixture was refluxed for 9 hr. Then 100 ml. of water was added to the mixture and *ca.* 50 ml. of the solvent was distilled. The solution was cooled, washed with ether, then neutralized with concentrated hydrochloric acid. The mixture was extracted three times with ether and the ether solutions were combined, dried with magnesium sulfate, and filtered. Removal of the ether gave a very pale yellow crystalline solid. The crude diacid was dried under vacuum at 50° for 1 hr. and decarboxylated by the procedure of Johnson.[11] A quantity of 6.2 g. (34% based on tosylate) of a light yellow oil was obtained, $\nu_{max}^{CCl_4}$ 3000 cm.$^{-1}$ (broad), 1710 (s) cm.$^{-1}$

3-(3,4-Dimethyl-Δ^3-cyclopentenyl)-1-propanol was prepared by the lithium aluminum hydride reduction of the crude acid by the procedure of Nystrom and Brown.[8] The crude material was distilled, giving 2.8 g. (49%) of a light yellow oil, b.p. 74–77° (25–30 mm.); $\nu_{max}^{CCl_4}$ (cm.$^{-1}$) 3700 (w), 3350 (m-broad), 2900 (s), 1440 (m), 1050 (m-broad); n.m.r. spectrum (CCl_4) contained peaks at δ 3.78 (singlet, $-OH$), 3.50 (broad triplet, $-CH_2-O-$), 1.57 (singlet, $-CH_3$), plus broad multiplets centered around 2.17 and 1.48 accounting for the remaining protons; $n^{25}D$ 1.4747. *Anal.* Calcd. for $C_{10}H_{18}O$: C, 77.84; H, 11.76. Found: C, 77.08, H, 11.75.

3-(3,4-Dimethyl-Δ^3-cyclopentenyl)-1-propyl p-nitrobenzenesulfonate was prepared from 1.5 g (0.010 mole) of the corresponding alcohol and p-nitrobenzenesulfonyl chloride (Eastman, recrystallized from acetic acid, m.p. 79–80°) as previously described.[1] Recrystallization of the crude material from ether–pentane at $-25°$ yielded 1.55 g. (47%) of white crystals, m.p. 71–73°; $\nu_{max}^{CCl_4}$ (cm.$^{-1}$) 1590 (s) and 1350 (s) for $-NO_2$ and 1190 (s) for $-SO_2-$ with no $-OH$ bands; n.m.r. spectrum (CCl_4) showed peaks at δ 8.10 (quartet, aromatic protons), 4.02 (triplet, $-CH_2-OSO_2-$), 1.50 (singlet, $-CH_3$), and multiplets in appropriate places to account for the remaining protons. *Anal.* Calcd. for $C_{16}H_{21}NO_5S$: C, 56.62; H, 6.24; N, 4.13. Found: C, 56.49, H, 6.54, N, 4.42.

3-(3,4-Dimethyl-Δ^3-cyclopentenyl)-1-propyl acetate was prepared from the corresponding alcohol using acetic anhydride in pyridine. The crude product was purified by v.p.c. using a Carbowax basic column. N.m.r. spectrum (CCl_4) for this compound showed peaks at δ 3.84 (triplet, $-CH_2-O-CO-$), 1.85 (singlet, $-CO-CH_3$), and 1.50 (singlet, $=C(CH_3)-$).

3-Cyclopentyl-1-propanol was prepared by lithium aluminum hydride reduction of commercial cyclo-

(7) H. C. Brown and G. Zweifel, *J. Am. Chem. Soc.*, 82, 3222, 3223 (1960).
(8) R. F. Nystrom and W. G. Brown, *ibid.*, 69, 2548 (1947).
(9) R. S. Tipson, *J. Org. Chem.*, 9, 235 (1944).
(10) R. Adams and R. M. Kamm, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 250.
(11) W. S. Johnson, V. J. Bauer, J, L. Margrave, M. A. Frisch, L. H. Dreger, and W. N. Hubbard, *J. Am. Chem. Soc.*, 83, 606 (1961).

pentylpropionic acid by the procedure of Nystrom and Brown.[8] Cyclopentylpropanol was obtained in 60% yield, b.p. 109–109.5 (22 mm.); $\nu_{max}^{CCl_4}$ (cm.$^{-1}$) 3400 (s), 3000 (s), 1450 (s), 1050 (s-broad); n.m.r. spectrum contained peaks at δ 5.14 (singlet, –OH), 3.53 (triplet, –CH$_2$–O–), and broad multiplets centered around 1.54 accounting for the remaining protons. *Anal.* Calcd. for C$_8$H$_{16}$O: C, 75.00; H, 12.50. Found: C, 75.46, H, 12.55.

3-Cyclopentyl-1-propyl p-nitrobenzenesulfonate was recrystallized from ether–pentane at –25°, m.p. 70.0–70.5°; n.m.r. spectrum (CDCl$_3$) showed peaks at δ 7.9 (quartet, aromatic protons), 4.0 (triplet, –CH$_2$–OSO$_2$–), and a broad multiplet for remaining protons.

Anal. Calcd. for C$_{14}$H$_{19}$O$_5$NS: C, 53.67; H, 6.07; N, 4.47. Found: C, 53.50, H, 5.87, N, 4.53.

Kinetic Measurements. The methods of following acetolyses by conductance and by titration have been previously described.[1c]

The acetolysis of *p*-nitrobenzenesulfonates in media containing a base was measured spectrophotometrically taking advantage of the absorption of alkyl *p*-nitrobenzenesulfonates (λ_{max} 250 mμ (ϵ 14,000 in cyclohexane)). The method was patterned after a spectrophotometric method used to follow the hydrolysis of methyl tosylate in water developed by Swain and Morgan.[12]

A solution of 100 ml. of acetic acid containing sodium acetate and approximately 4 mg. of nosylate was transferred to sealed tubes. The kinetic run was conducted in a conventional fashion and the contents of the tubes were analyzed as follows. Into a clean, but wet, 60-ml. separatory funnel having a teflon stopcock were pipetted 5 ml. of cyclohexane and 10 ml. of water. A tube was opened and 5 ml. of its contents was pipetted into the cyclohexane–water mixture. The mixture was shaken for at least 1 min. After standing for at least 5 min., the lower phase was removed. After at least 5 more min., the cyclohexane solution was pipetted into a Beckman DU cell and the optical density of the solution was measured at 250 mμ against pure cyclohexane. The accuracy of the method is confirmed by agreement of the acetolysis of 5-hexenyl nosylate determined by the spectrophotometric method and the titrimetric method and by the agreement of duplicate runs.

Calculation of rate constant, calculations of activation parameters, and calculation of rate constants at various temperatures from the activation parameters

(12) C. G. Swain and C. R. Morgan, *J. Org. Chem.*, 29, 2097 (1964).

were made using an IBM 1620 computer[13] and standard kinetic equations.

Product Studies. A quantity of 5 ml. of an acetic acid solution containing 0.2 *M* sodium acetate and 0.1 *M p*-nitrobenzenesulfonate was placed in a sealed tube and held at the given temperature for more than five solvolytic half-lives. The cooled tube was opened and its contents were transferred to a separatory funnel and shaken with 0.5 ml. of carbon tetrachloride and 20 ml. of water for 2 min. V.p.c. of the carbon tetrachloride solution (8-ft. carbowax column, He flow 50 ml./min., column temperature 100° from 0–17 min., 175° from 17 min. on) showed three main products at 11.0 (IX), 13.5 (X), and 48 min. (XI). The products were collected from the v.p.c. and their n.m.r. spectra were taken. The n.m.r. spectra were consistent with the expected products: (IX) 1,7-dimethylbicyclo[3.2.1]-6-octene, n.m.r. spectrum (CCl$_4$) showed peaks at δ 5.25 (singlet, —CH=C<), 2.38 (singlet, bridgehead hydrogen), 1.58 (singlet, C=C—CH$_3$), 0.94 (singlet, bridgehead methyl), and multiplets to account for the remaining protons; (X) 1-methyl-7-methylenebicyclo-[3.2.1]octane, n.m.r. spectrum (CCl$_4$) showed peaks at 4.62 (doublet, >C=CH$_2$), 2.25 (multiplet, allylic protons), 1.05 (singlet, bridgehead methyl); (XI) 3-(3,4-dimethyl-Δ^3-cyclopentenyl)-1-propyl acetate, n.m.r. spectrum and v.p.c. retention time were identical with that of an authentic sample.

The quantitative analysis of the products was carried out by n.m.r. Before extracting the acetic acid solution with carbon tetrachloride, a weighed amount (*ca.* 20 mg.) of bromobenzene was added. After extraction, the carbon tetrachloride solution was dried with magnesium sulfate and the n.m.r. of the solution was taken. The relative percentages of the three products were obtained from the integration of the three peaks at 5.3, 4.6, and 3.9. The areas of the products relative to the bromobenzene signal showed that 80% of the products was accounted for. This method of analysis was shown to be accurate by using known amounts of cyclohexene and amyl acetate in acetic acid.

(13) Programs were written by J. M. McBride, J. Wright, and S Nelsen.