the rate, results in a relatively large uncertainty in the enthalpy and entropy of activation for this compound (Table I).

1,1,1-Triphenyl-2-propanol. 1,1,1-Triphenyl-2-propanone was reduced with lithium aluminum hydride in ether. There was obtained a 94% yield, m.p. 100.5–101.0°. Recrystallized from petroleum ether (b.p. 90–100°), the product exhibited m.p. 101.2–102.0°.

Anal. Calcd. for $C_{21}H_{20}O$: C, 87.45; H, 6.98. Found: C, 87.47; H, 6.87.

1,1,1-Triphenyl-2-propyl Tosylate. 1,1,1-Triphenyl-2-propanol proved to be exceptionally difficult to convert into its tosylate. The following procedure yielded the product in low yield and a number of successive preparations were required to obtain sufficient ester for the acetolysis study.

1,1,1-Triphenyl-2-propanol, 5.0 g., was dissolved in 10 g. of dry pyridine and treated with 6.5 g. of *p*-toluenesulfonyl chloride. The reaction mixture was maintained in a cold room at 20°F. for 5 days, then at 38°F. for 5 days, and finally at room temperature for 3 days. The reaction mixture was treated with ice water in the usual manner and the aqueous mixture was extracted four times with 50-ml. portions of chloroform. The chloroform extract was washed with water, 1 *M* sulfuric acid, cadmium chloride (10%) solution, sodium bicarbonate, water, and dried over anhydrous magnesium sulfate. Evaporation of the chloroform yielded 3.9 g. of a heavy brown oil, from which the tosylate was extracted with petroleum ether (b.p. 30–60°). The product was obtained from a 1:1 mixture of petroleum ether and ethyl ether by cooling to −78°. The white crystals exhibited m.p. 77–77.5°.

Anal. Calcd. for $C_{28}H_{26}SO_3$: C, 76.00; H, 5.92. Found: C, 75.72; H, 6.08.

Rate of Acetolysis. The small quantity of 1,1,1-triphenyl-2-propyl tosylate made it desirable to run the rates of acetolysis on a semimicro scale. The solvent was first tested by carrying out rate determinations at 70.0 utilizing the usual conditions: k_1 for isopropyl tosylate $2.10 \pm 0.04 \times 10^{-5}$ sec.$^{-1}$, and for isopropyl brosylate $6.92 \pm 0.03 \times 10^{-5}$ sec.$^{-1}$.[46] The semimicro procedure, utilizing 0.011 *M* solutions of the tosylate in the acid, yielded 2.09 ± 0.22 for isopropyl tosylate, and 7.6 ± 0.22 for isopropyl brosylate. These were considered to represent satisfactory checks and the procedure was then applied to 1,1,1-triphenyl-2-propyl tosylate.

(46) S. Winstein and E. Grunwald, *J. Am. Chem. Soc.*, **70**, 846 (1948), report k_1 6.90 and 6.98 × 10^{-5} sec.$^{-1}$.

Nucleophilic Reactivity of the Carbon–Carbon Double Bond. I. Solvolytic Ring Closure of 2-(Δ³-Cyclopentenyl)ethyl and 1-(Δ³-Cyclopentenyl)-2-propyl Arenesulfonates

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Contribution from the Converse Memorial Laboratory, Harvard University, Cambridge, Massachusetts. *Received July 24, 1964*

The double bond in 2-(Δ³-cyclopentenyl)ethyl tosylate and p-nitrobenzenesulfonate participates directly in the solvolysis of these esters, as shown not only by the direct formation of exo-norbornyl acetate as the product in acetic acid, but also by rate ratios from 5.8 in 50% aqueous ethanol to 640 in formic acid as the cyclopentenylethyl ester is compared with its saturated cyclopentylethyl analog. No O^{18} scrambling occurs when the p-nitrobenzenesulfonate of 2-(Δ³-cyclopentenyl)ethanol-O^{18} is recovered after 1 half-life in acetic acid. Endo-norbornyl p-nitrobenzenesulfonate is formolyzed at a rate similar to that of 2-(Δ³-cyclopentenyl)ethyl p-nitrobenzenesulfonate, but is not formed to an appreciable extent in the formolysis of the latter.[18,29] The acetolysis of 1-(Δ³-cyclopentenyl)-2-propyl p-nitrobenzenesulfonate has been studied. In the presence of enough sodium acetate to neutralize the strong acid produced, a mixture of unrearranged acetate and a cyclic product believed to be 6-methyl-exo-2-norbornyl acetate is obtained. In acetic acid without added sodium acetate, the initial product rearranges rapidly into 1-methyl-exo-norbornyl acetate. The factors governing the reduced "driving-force" ratio in the secondary case are discussed.

Introduction

It was observed long ago[1,2] that when a nucleophilic displacement reaction is made to occur intramolecularly, the rate of the reaction passes through two maxima when the nucleophile is separated from the seat of the displacement by one and by three carbon atoms. At both locations the reactivity of the nucleophile, as judged by successful competition with outside reagents, appears greater than in bimolecular reactions between comparable molecular species. Examples involving sulfur[3,4] and nitrogen[1,2] atoms are familiar. There are also cases where considerable nucleophilic reactivity is displayed intramolecularly by a nucleophile too weak to give the corresponding reaction under bimolecular conditions. An example is the substantial driving force afforded by the iodine atom in *trans*-2-iodocyclohexyl *p*-toluenesulfonate,[5] although alkyl iodides

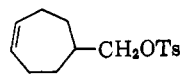
(1) G. Salomon, *Trans. Faraday Soc.*, **32**, 153 (1936).
(2) P. D. Bartlett, S. D. Ross, and C. G. Swain, *J. Am. Chem. Soc.*, **69**, 2971 (1947).
(3) A. G. Ogston, *Trans. Faraday Soc.*, **44**, 45 (1948).
(4) P. D. Bartlett and C. G. Swain, *J. Am. Chem. Soc.*, **71**, 1406 (1949).
(5) S. Winstein, E. Grunwald, and L. L. Ingraham, *ibid.*, **70**, 821 (1948).

do not show an ability to be further alkylated by such reagents as methyl tosylate. The successive discovery of the participation in displacement reactions of such neighboring groups as halogen,[6] acetoxyl,[7] benzamido,[8] and alkyl thio[4,9] set the stage historically for the elegant contributions of the last decade to valence theory through the study of bridged or "nonclassical" ions.[10]

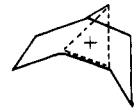
The unsymmetrical homoallylic systems[11-13] were extensively explored before those in which the double bond was situated at a greater distance from the ionizing center. Nevertheless, there were indications that the latter should possess interest from the rate maxima alluded to above for the closure of five- or six-membered rings.

Methoxy- and dimethoxyphenyl groups were shown to participate in ionization with five- and six-membered ring formation[14] in favorably constituted compounds, and Corey and Sauers[15] extended these observations to the double bond in citronellyl, 7-methyl-6-octen-1-yl, and 6-methyl-5-hepten-1-yl tosylates, which underwent formolysis with rate enhancement and (in the first and third cases) cyclization.

In 1960 LeNy[16] found that Δ^4-cycloheptenylmethyl *p*-toluenesulfonate (I) underwent acetolysis at least 30-times as fast as the corresponding saturated compound and yielded a single cyclic acetate whose configuration



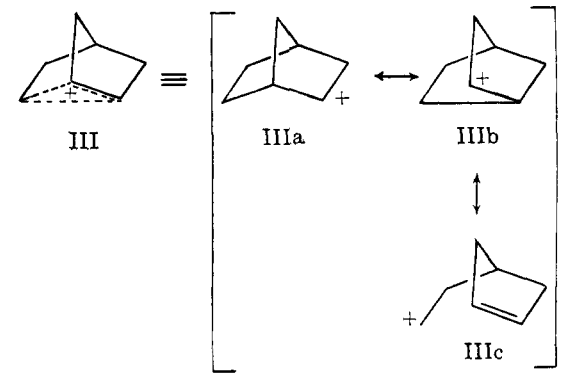
I



II

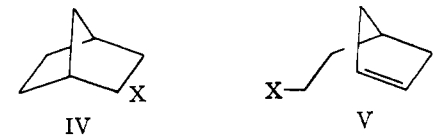
was uniquely consistent with the intervention of the bridged ion II. In the following year Lawton[17] showed that 2-(Δ^3-cyclopentenyl)ethyl *p*-nitrobenzenesulfonate (V, X = ONs) is solvolyzed in glacial acetic acid at a rate 95 times that of the saturated analog, producing *exo*-norbornyl acetate as the sole product. Bartlett and Bank[18] independently investigated the corresponding tosylate in three solvolyzing solvents. Other important examples have been observed by Goering and Closson[19] and by Winstein and Carter.[20]

The commonly written representation (III) for the 2-norbornyl bridged cation can be recast in valence bond notation (IIIa–c), each limiting structure corresponding to a possible starting material from which the ion may be formed. Winstein has proposed the general term "π-route" to distinguish the formation of



III IIIa IIIb IIIc

a bridged ion from compound V by participation of the π-electrons of the double bond, from the σ-route, in which the three-center, electron-deficient bond of III is formed by σ-delocalization from starting materials IV.



IV V

a, X = OTs
b, X = ONs
c, X = OAc
d, X = OH

The present paper and succeeding ones of this series will describe our experiments designed to explore the conditions under which the double bond exerts large or small nucleophilic driving forces upon the ionization process.

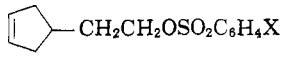
Results

The 2-(Δ^3-cyclopentenyl)ethanol (Vd) was prepared from Δ^3-cyclopentenyl bromide, both by reaction of the Grignard reagent with ethylene oxide and by reduction of 2-(Δ^3-cyclopentenyl)acetic acid prepared by alkylation of cyanoacetic ester, as was done by Lawton[17] starting with Δ^3-cyclopentenyl tosylate. The alcohol was characterized as its phenylurethan, m.p. 59–60°, and by its infrared and n.m.r. spectra. 1-(Δ^3-Cyclopentenyl)-2-propanol (VIId) was prepared by lithium aluminum hydride reduction of the corresponding ketone, which in turn was made both by the reaction of methylmagnesium bromide and cadmium chloride with Δ^3-cyclopentenylacetyl chloride and from Δ^3-cyclopentenyl bromide and acetoacetic ester. The phenylurethan of 1-(Δ^3-cyclopentenyl)-2-propanol melted at 83.5–84.5°.

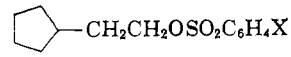
2-(Δ^3-Cyclopentenyl)ethyl Sulfonates (Va and Vb). Table I summarizes the results of rate studies of the solvolysis of the tosylate and *p*-nitrobenzenesulfonate of this primary alcohol (U) and of its saturated analog (S). Our preliminary study[18] included three solvents chosen for their similar values of the Grunwald–Winstein solvent parameter *Y*, but a considerable range of solvent basicity: 50% aqueous ethanol, 50% aqueous acetic acid, and formic acid. The mixed solvents are unnecessarily awkward for product studies, and the solubility of the starting material in 50% acetic acid leaves something to be desired. Accordingly, in our later work we have made rate measurements chiefly in anhydrous acetic and formic acids, using both the

(6) S. Winstein and H. J. Lucas, *J. Am. Chem. Soc.*, **61**, 2345 (1939).
(7) S. Winstein and R. E. Buckles, *ibid.*, **64**, 2780, 2787 (1942).
(8) S. Winstein, L. Goodman, and R. Boschan, *ibid.*, **72**, 2311 (1950).
(9) R. C. Fuson, C. C. Price, and D. M. Burness, *J. Org. Chem.*, **11**, 477 (1946).
(10) For a review see A. Streitwieser, "Solvolytic Displacement Reactions," McGraw-Hill Book Co., Inc., 1962, pp. 126–157, 181–187; *Chem. Rev.*, **56**, 698 (1956).
(11) P. Bruylants and A. Dewell, *Bull. Acad. Roy. Sci. Belg.*, [V] **14**, 140 (1928).
(12) T. A. Favorskaya and S. A. Fridman, *J. Gen. Chem. USSR*, **15**, 421 (1945).
(13) S. Winstein and R. Adams, *J. Am. Chem. Soc.*, **70**, 838 (1948).
(14) S. Winstein, R. Heck, S. Lapporte, and R. Baird, *Experientia*, **12**, No. 4, 138 (1956); R. Heck and S. Winstein, *J. Am. Chem. Soc.*, **79**, 3105, 3114 (1957).
(15) C. K. Sauers, Thesis, University of Illinois, 1957, p. 31 ff.
(16) G. LeNy, *Compt. rend.*, **251**, 1526 (1960).
(17) R. G. Lawton, *J. Am. Chem. Soc.*, **83**, 2399 (1961).
(18) P. D. Bartlett and S. Bank, *ibid.*, **83**, 2591 (1961).
(19) H. L. Goering and W. D. Closson, *ibid.*, **83**, 3511 (1961).
(20) S. Winstein and P. Carter, *ibid.*, **83**, 4485 (1961).

Table I. Rate Constants of Solvolysis of U and S in Various Solvents



U



S

Solvent	Temp., °C.	S or U	X	Method[a]		$k \times 10^4$, sec.$^{-1}$
Ethanol–water, 50% v./v.,	70.13	U	CH_3	Cond.		3.36
$Y = 1.66$	70.13	U	CH_3	Vis.		3.37
	70.13	S	CH_3	Cond.		0.58
	70.13	S	CH_3	Vis.		0.61
	70	k_U/k_S			5.7	
Acetic acid, anhydrous	100.85	U	CH_3	Vis		4.17
$Y = -1.65$	100.85	U	CH_3	Vis.		4.20
	61.85	U	CH_3	Vis.		0.106
	59.8	U	CH_3	(Extrap.)		0.085
	100.85	S	CH_3	Vis.		0.0563
	100.85	S	CH_3	Vis.		0.0564
	100.85	k_U/k_S	CH_3	Vis.	74	
	70.13	U	NO_2	Vis.		2.58
	70.13	U	NO_2	Vis.		2.65
	70.13	U	NO_2	Vis.		2.80
Acetic acid, anhydrous	61.83	U	NO_2	Vis.		1.31
	119.62	S	NO_2	Vis.		2.55
	119.62	S	NO_2	Vis.		2.57
Acetic acid, anhydrous	100.85	S	NO_2	Vis.		0.623
	100.85	S	NO_2	Vis.		0.625
	61.85	U	k_{NO_2}/k_{CH_3}	Vis.	12.4	
	100.85	S	k_{NO_2}/k_{CH_3}	Vis.	11.1	
Formic acid, anhydrous,	59.85	U	CH_3	Pot.		8.8
$Y = 2.05$	50.10	U	CH_3	N.m.r.		4.6
	50.10	U	CH_3	Cond.		4.23
	50.10	U	CH_3	Pot.		4.01
Formic acid, 97%	50.10	U	CH_3	Cond.		3.74
Formic acid, anhydrous	25.47	U	NO_2	Pot.		2.69
	80.4	S	NO_2	Pot.		1.61
	80.4	S	NO_2	Pot.		1.51
	70.13	S	NO_2	Vis.		0.624
	70.13	S	NO_2	Pot.		0.645
	50.10	S	NO_2	Pot.		0.0767
	25.47	S	NO_2	(Extrap.)		0.0042
	25.47	k_U/k_S	NO_2		640	

[a] Methods indicated are conductometric (cond.) and titration with visual indicator (vis.) or potentiometrical (pot.).

liquid tosylate Va and the crystalline *p*-nitrobenzenesulfonate Vb reported by Lawton.[17] Rate studies were made conductometrically, by titration with visual indicators, and potentiometrically, and in one case by following the disappearance of the n.m.r. signal due to protons on unsaturated carbon. Through rigid control of water content the rates in anhydrous formic acid have been made reproducible, and our preliminary rate constants in this solvent have been revised. The saturated *p*-nitrobenzenesulfonate proved much more satisfactory than the tosylate for formolysis rate measurements. Our most reliable measurement of the rate ratio k_U/k_S in formic acid is obtained by dividing the measured rate constant for solvolysis of the unsaturated *p*-nitrobenzenesulfonate at 25.47° by the extrapolated rate constant for the saturated *p*-nitrobenzenesulfonate at the same temperature. This rate ratio now appears to vary from 5.8 for the tosylates in 50% ethanol ($Y = 1.66$) to 640 for the *p*-nitrobenzenesulfonate in anhydrous formic acid. The same ratio for the tosylates in glacial acetic acid ($Y = -1.65$) is 74 at 100.85°.

In acetic acid the unsaturated *p*-nitrobenzenesulfonate Vb is solvolyzed faster than the tosylate Va by a factor of 12.4 at 61.85°; for the saturated esters at 100.85° the factor is 11.1. The very different ways in which the solvolysis rates of the saturated and unsaturated sulfonates depend upon solvent constitute an instructive example of an often-discussed feature of solvolysis. The sharply distinguishable SN2 and SN1 displacement mechanisms involving a nucleophilic solute give way to more subtle gradations in the polymolecular[21,22] process of reaction with the solvent.[23,24] For methyl bromide,[25] solvolysis is more than 100 times as fast in 50% ethanol as in formic acid, while for *t*-butyl chloride the order of effectiveness of these solvents is reversed. The relative effects of these two media, which differ so in nucleophilic character, may serve to characterize different substrates as to relative importance of cation solvation in their solvolysis mechanisms. Table II lists log ($k_{50\%\ \text{ethanol}}/k_{\text{formic acid}}$) for 2-($\Delta^3$-cyclopentenyl)ethyl and 2-cyclopentylethyl *p*-toluenesulfonates, and for some simple halides as reported by Swain, Mosely, and Bown.[25] The figures for the new compounds were determined from the measurements of this paper and ref. 18, with short extrapolations where necessary to bring the measurements in different solvents to a common temperature,

(21) N. Farinacci and L. P. Hammett, *J. Am. Chem. Soc.*, **59**, 2542 (1937).
(22) P. D. Bartlett and R. W. Nebel, *ibid.*, **62**, 1345 (1940).
(23) S. Winstein, E. Grunwald, and H. W. Jones, *ibid.*, **73**, 2700 (1951).
(24) C. G. Swain and R. B. Mosely, *ibid.*, **77**, 3727 (1955).
(25) C. G. Swain, R. B. Mosely, and D. E. Bown, *ibid.*, **77**, 3733 (1955).

Table II. Dependence of Solvolysis Rate Upon Solvent

Substrate	log ($k_{50\%\ \text{ethanol}}$/$k_{\text{formic acid}}$)
Methyl bromide	2.19
Ethyl bromide	1.73
2-Cyclopentylethyl tosylate	1.03
Isopropyl bromide	1.00
t-Butyl chloride	−0.39
2-(Δ^3-Cyclopentenyl)ethyl tosylate[18]	−0.5

the saturated tosylate and *p*-nitrobenzenesulfonate being interconverted with a rate factor of 11.

In the continuum of solvation requirements, our saturated and unsaturated sulfonates are seen to correspond closely with isopropyl bromide and *t*-butyl chloride, respectively. In all solvents tested the double bond increases the rate of solvolysis and decreases the importance of nucleophilicity in the solvent; that is to say, the double bond participates in the solvolysis in such a way as to make the developing cation in the transition state more self sufficient. In any one solvent the ratio k_U/k_S indicates how much this shifted character of the transition state improves the utilization of that solvent in solvolysis. This improved utilization is greatest in those solvents which are deficient in cation-solvating power.

The similarity of the 2-(Δ^3-cyclopentenyl)ethyl sulfonates to *t*-butyl chloride means that the Grunwald–Winstein solvent parameter *Y* should be an appropriate measure of solvent ionizing power to correlate the solvolysis rate of this unsaturated ester. From the rates of solvolysis of the unsaturated ester in acetic and formic acids at 59.85°, we calculate the value of *m* to be 0.54.

Our product studies[18] showed that the product of solvolysis in 50% acetic acid, which accounted for 92% of the material, consisted of a 60–40 mixture of *exo*-norbornyl acetate and *exo*-norborneol.

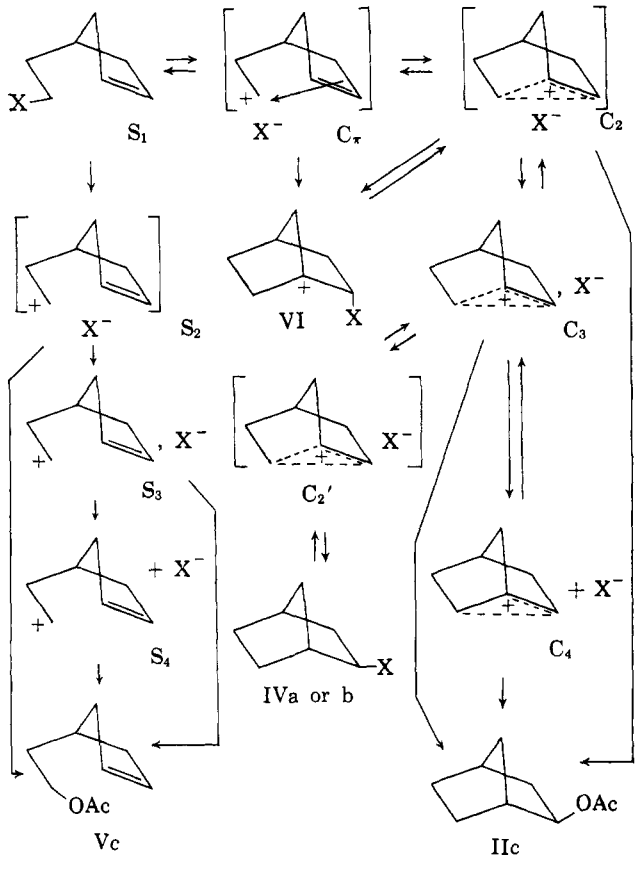
Any detailed view of the mechanism must take account of various ways in which the assisted ionization of the starting material may not be the sole rate-determining step. Chart I indicates what the situation might be if every complicating feature is present which has been identified in any related instance. The subscripts 1–4 denote the successive stages in solvolysis according to Winstein's general scheme: starting material, tight ion pair, solvent-separated ion pair, free ions. The S series corresponds to "unassisted" ionization (assisted only by solvent).[26] The C series refers to ionization with participation of the carbon–carbon double bond. In each series the possibility is considered that product may be formed directly from member 2, 3, or 4. A species C_π is included in which the bonding between the primary carbon atom and the double bond is considered to be more ionic and less firm than in C_2; this possibility is considered by analogy with the rapidly and loosely formed π-complexes

(26) The writing of primary carbonium structures for S_2, S_3, and S_4 is not intended to assign extreme charge-localized character to these intermediates. We believe, as indicated above, that the transition state in such a solvolysis can be approximated by an SN1, SN2, or Doering–Zeiss[27,28] type of formulation, the geometry being similar in all and the charge distribution varying by degrees from case to case.

(27) W. von E. Doering and H. H. Zeiss, *J. Am. Chem. Soc.*, **75**, 4733 (1953).

(28) A. Streitwieser, Jr., *Chem. Rev.*, **56**, 638 (1956).

Chart I



between olefins and strong acids, so different in their properties from the carbonium ions in whose formation they are often intermediates. *endo*-Norbornyl arylsulfonate (VI) is written in Chart I as a possibility by analogy with the interesting observation of Goering and Closson[19,29] that *internal return* in the ion pair from *cis*- or *trans*-5-cyclodecenyl *p*-nitrobenzoate in aqueous acetone leads to a rearranged *p*-nitrobenzoate representing over-all *cis* addition of carbon atom and ester group to the transannular double bond, although the main *solvolysis product* has the configuration corresponding to *trans* addition. In that instance the nitrobenzoate group rearranged with predominant retention of its carbonyl-O[18] label, indicating that the ion pair involved was the tight, nonsolvent-separated one.

This brings up a point to be considered in more detail in part III of this series. When a tight ion pair is formed directly from S_1, the immediate position of the anion is next to the primary carbon atom where it was originally attached and as favorable as possible for direct "frontside" attack, if any, on one of the carbon atoms of the original double bond (or for complete return to starting material). Such a location of the anion is intended to be shown in C_π and C_2, which then could yield internal return to *endo*-norbornyl sulfonate, while the tight ion pair C_2' has the anion in the normal position in which internal return to *exo*-norbornyl sulfonate is known to occur. It seems reasonable that, in the process of formation of C_3, this specificity of position of the anion will be lost, and from C_3 on the behavior should be only that characteristic of the known

(29) H. L. Goering, H. H. Espy, and W. D. Closson, *J. Am. Chem. Soc.*, **81**, 329 (1959).

norbornyl cation shown giving internal return through C_2' to IVa or b.

Chart I is shown, not through any fondness on our part for multiplying variables, but because it shows some reasonably documented possibilities by which internal nucleophilic attack by the double bond in 2-(Δ^3-cyclopentenyl)ethyl *p*-nitrobenzenesulfonate might not be the rate-determining step in the reaction as observed. Internal return from C_π or C_2 to S_1 would cause a later step to be rate determining, as would a rapid formation of *endo*-norbornyl ester (VI), whose solvolysis might then be rate determining. (The return from C_3 to IVa or b would not change the rate-determining step, since *exo*-norbornyl sulfonates are solvolyzed very much faster than the reaction we are measuring.)

endo-Norbornyl *p*-nitrobenzenesulfonate (VIb) was found to undergo formolysis at 25.47° with a rate constant of 3.62×10^{-4} sec.$^{-1}$, compared with 2.69×10^{-4} sec.$^{-1}$ for 2-(Δ^3-cyclopentenyl)ethyl *p*-nitrobenzenesulfonate (Vb). The first-order plot of the kinetic data for the latter was linear over 3 half-lives, and the starting material recovered after 1 half-life showed no contamination with *endo*-norbornyl *p*-nitrobenzenesulfonate. Therefore, the type of internal return with retention observed by Goering and Closson, which would lead to *endo*-norbornyl sulfonate in the present reaction, does not occur here.

To test for possible internal return from ion pairs of either series to starting material, 2-(Δ^3-cyclopentenyl)-ethanol-O^{18} was prepared and converted into its *p*-nitrobenzenesulfonate, which was solvolyzed in anhydrous acetic acid at 61.83°. At intervals up to 1 half-life the sulfonate was recovered and converted back into the alcohol by cleavage with sodium in liquid ammonia, a procedure which has been shown to occur without oxygen exchange.[30] Each sample of alcohol was analyzed for O^{18} as the recrystallized phenylurethan. The results are shown in Table III. There is

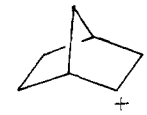
Table III. Isotopic Oxygen Content of 2-(Δ^3-Cyclopentenyl)ethanol Recovered from Its *p*-Nitrobenzenesulfonate during Acetolysis at 61.83°

Time, sec.	O^{18} content, determined on phenylurethan
0	0.378, 0.371
2000	0.393, 0.383
3500	0.384, 0.384
5200	0.376

no attenuation of the O^{18} content of the alcohol as there would be if ionization were followed by internal return to uncyclized starting material. This result may be an argument against a weakly cyclized species C_π as a stopping point in the ionization process. C_π would be closer in structure to uncyclized starting material than the usual norbornyl cation. As far as experimental detectability is concerned, we can drop C_π and VI from Chart I, and in the norbornyl system we cannot detect the separate existence of C_2 and C_2'. A contrary conclusion is reached in part III of this series concerning the bridged ion from Δ^5-hexenyl and cyclopentylmethyl sulfonates.

(30) D. B. Denney and E. J. Kupchik, *J. Am. Chem. Soc.*, **82**, 859 (1960).

To aid the discussion of some pertinent mechanistic questions, Chart I contains ten intermediate species. To include as an eleventh the "classical" norbornyl cation C*, with localized charge, would increase the



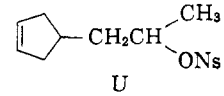
C*

number of postulated species, since it cannot be substituted for C_4, and its inclusion would explain no additional facts in the cases being studied. The need of a species C_4 in the solvolysis of norbornyl arylsulfonates has been clear for many years.[10,31] The importance of C* in deamination of norbornylamines is not entirely clear,[32,33] but to the extent to which it occurs its reaction pattern is different from that of the norbornyl cation normally intermediate in solvolysis.

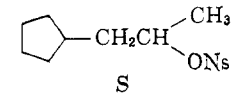
We shall show specifically in part II that the transition state in the solvolysis of S_1 and its 3-methyl and 3,4-dimethyl derivatives is affected symmetrically and about equally by the first and second methyl groups. The cationic carbon atom involved in the cyclization thus does not behave as it would if producing an ion of the C* type through an unsymmetrical transition state.

1-(Δ^3-Cyclopentenyl)-2-propanol. The secondary tosylate was less extensively investigated. Table IV

Table IV. Rate Constants for Acetolysis of U and S in Acetic Acid



U



S

Temp., °C.	S or U	Method[a]	$k \times 10^4$, sec.$^{-1}$
54.4	U	Cond.	2.85
54.4	U	Cond.	2.89
54.4	S	Vis.	1.30
54.4	S	Cond.	1.33
70.4	S	Cond.	7.94
54.4	k_U/k_S	2.18	

[a] Methods indicated are conductometric (cond.) and titration with visual indicator (vis.).

lists the kinetic results. As expected,[34] the driving-force ratio k_U/k_S is much less for ionization of the secondary than of the primary nitrobenzenesulfonates, being only 2.2 at 54.4°. This is expected because the unassisted ionization gains a great deal, and the assisted ionization little, through secondary character of the starting material. To compare the two systems we have made a short extrapolation of the rate data for the unsaturated primary nitrobenzenesulfonate, and a long extrapolation for the saturated primary ester, to 54.4°, with the result shown in Table V. The saturated secondary sulfonate is solvolyzed 138 times as fast as the primary; the secondary unsaturated

(31) S. Winstein and D. Trifan, *ibid.*, **74**, 1147, 1154 (1952).

(32) (a) J. A. Berson and D. A. Ben-Efraim, *ibid.*, **81**, 4094 (1959); (b) J. A. Berson and A. Remanick, *ibid.*, **86**, 1749 (1964).

(33) E. J. Corey, J. Casanova, Jr., P. A. Vatakencherry, and R. Winter, *ibid.*, **85**, 169 (1963).

(34) S. Winstein, B. K. Morse, E. Grunwald, K. C. Schreiber, and J. Corse, *ibid.*, **74**, 1113 (1952).

Table V. Comparison of Acetolysis Rates at 54.4° of 2-(Δ^3-Cyclopentenyl)ethyl (IIIb) and 1-(Δ^3-Cyclopentenyl)-2-propyl (VIIb) *p*-Nitrobenzenesulfonates and Their Saturated Analogs

k (sec.$^{-1}$ × 10^4) for	Primary (III), extrapolated	Secondary (VII)	k_{VII}/k_{III}
Unsatd. (U)	0.83	2.87	3.5
Satd. (S)	0.0096	1.32	138
k_U/k_S	87	2.2	
$k_U - 0.7k_S$	0.82	1.95	(2.4)
$(k_U - 0.7k_S)/0.7k_S$	122	2.1	

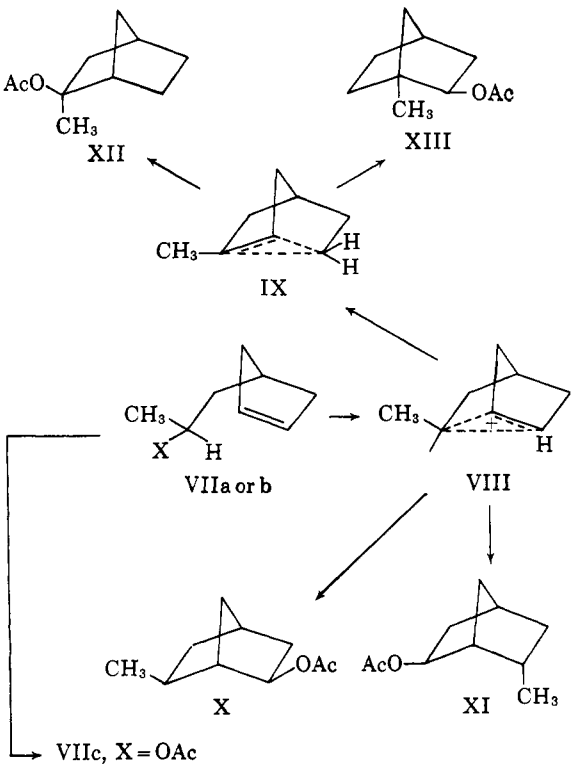
sulfonate is solvolyzed only 3.5 times as fast as the primary unsaturated.

In several examples to be reported in parts II and IV, those Δ^4- and Δ^5-unsaturated sulfonates which undergo acetolysis without any cyclization show acetolysis rates which are from 60 to 80% of those of the corresponding saturated compounds. This is the result of the small adverse effect of the sp^2–sp^3 dipole associated with the double bond. If, therefore, we want to estimate what portion of the observed solvolysis rate is due to unassisted local attack of solvent at the ionizable bond, we may well take about 70% of the rate of the saturated ester rather than the whole of it. The last two rows of Table V represent an attempt to compare the assisted and unassisted portions of the solvolysis rates, giving ratios $(k_U - 0.7k_S)/0.7k_S$ of 122 for the primary compound Vb and of 2.1 for the secondary compound VIIb. From work of Sargent in this laboratory (part II) we know that the substitution of a methyl group at position 3 in the cyclopentenyl ring brings about a 7-fold increase in the rate of acetolysis, all of it being anchimerically assisted. One might say that *in the transition state for assisted ionization each of the two carbon atoms of the cyclopentenyl double bond appears about three times as carbonium-ion-like as the carbon atom at which the ionization is taking place!*

The first product study of the acetolysis of the 1-cyclopentenyl-2-propyl *p*-nitrobenzenesulfonate in pure acetic acid led to a product which was principally a mixture of the known 1-methyl-*exo*-norbornyl acetate (XIII) and the unrearranged 1-(Δ^3-cyclopentenyl)-2-propyl acetate (VIIc) in the ratio of 2.6 to 1. The former product evidently resulted from rearrangement of the initial product of ring closure, which would be expected to be 6-methylnorbornyl cation (VIII).

By assuming that assisted and unassisted solvolyses lead to cyclized and uncyclized products, respectively, we should expect the ratio of XIII to VIIc in the product to be the same as the kinetic ratio, $(k_U - 0.7k_S)/0.7k_S$. The two numbers are in fact 2.6 and 2.1, respectively, which is satisfactory agreement within the limits of knowledge of the figure 0.7. The effect of the unneutralized sulfonic acid is apparently to prolong the life of ion VIII to permit its conversion into IX. It may do this by re-ionizing X or XI, but evidently not by re-ionizing VIIc, which would lead to an eventual total cyclization of the material.

A simple 6,2-hydride shift, rendered especially facile because it converts a secondary–secondary into a secondary–tertiary bridged ion, would convert VIII into IX. Each of these ions can combine with acetate ion to yield four different products (a total of eight)



of which only the four with *exo*-acetate are probable under solvolytic conditions.

Three more product studies were made with tosylate as starting material, and including in the solvolytic medium enough sodium acetate to neutralize the strong acid produced. In each case the principal cyclized product was an isomer different from XIII, and about 90% of the product consisted of a mixture of it and the uncyclized acetate VIIc. There were three other minor products. Table VI lists these product runs, with the ratio of principal cyclized to uncyclized product. It seems probable that sodium acetate has at least three effects upon the reaction: preventing re-ionization of the initial cyclic product by neutralizing the sulfonic acid produced; a salt effect, favorable to both assisted and unassisted ionization, but not necessarily in the same degree; and accelerated capture of the intermediate carbonium ions, shortening their lifetime. The greatly reduced proportion of cyclic product in the experiment with 3 *M* sodium acetate probably indicates competition of direct displacement by acetate ion with the solvolytic process.

Table VI. Effect of Sodium Acetate on Relative Amounts of Cyclization in Acetolysis of 1-(Δ^3-Cyclopentenyl)-2-propyl Sulfonates

Ester	*M*	NaOAc, *M*	Temp., °C.	Time, hr.	Ratio of products, cyclized/uncyclized
Nitrobenzene-sulfonate	0.185	None	55	12	2.6
Tosylate	0.857	1.2	55	12	2.0
Tosylate	0.64	0.97	50	20	1.7
Tosylate	0.20	3.0	80	19	0.59

Experimental

2-(Δ^3-Cyclopentenyl)ethanol from Ethylene Oxide. Δ^3-Cyclopentenyl bromide (15.7 g.)[35] was converted into a Grignard reagent and treated with 9.4 g. (2 molar equiv.) of ethylene oxide. The solution was heated under reflux overnight, hydrolyzed, dried, and the ether was removed. The product was isolated in a yield of 3.1 g. (23%) by vacuum distillation, b.p. 90–95° at 20 mm., $n^{25}D$ = 1.4699; phenylurethan, m.p. 59–60°.

Anal. Calcd. for $C_{14}H_{17}NO_2$: C, 72.70; H, 7.41; N, 6.06. Found: C, 72.53; H, 7.26; N, 6.06.

By Way of Cyclopentenylacetic Acid. Crude methyl Δ^3-cyclopentenylacetate (prepared by the method of Clinton and Laskowski[36]) in 50 ml. of anhydrous ether was added dropwise over a period of 15 min. to a mixture of 2.4 g. (0.064 mole) of lithium aluminum hydride in 150 ml. of anhydrous ether. The reaction mixture was allowed to stir at room temperature for 48 hr., then decomposed by the slow addition of 20 ml. of saturated sodium chloride solution. The ether layer was decanted from the salts and the salts were thoroughly washed with ether. The combined ether layer was dried over anhydrous magnesium sulfate. After filtering, the ether was removed on the steam bath. The residue was distilled at reduced pressure to give 4.5 g. of product, b.p. 82–85° at 15 mm. (63% yield from Δ^3-cyclopentenylacetic acid), $n^{25}D$ 1.4687. Lawton[17] reports b.p. 180–182°, $n^{25}D$ 1.4691.

The *p*-toluenesulfonate, an oil, was prepared by the method of Tipson.[37] The analytical sample still contained alcohol and was only 91% pure by alkali equivalent after 10 half-lives.

Anal. Calcd. for a mixture of 88.7% tosylate and 11.3% alcohol: C, 62.13; H, 6.47. Found: C, 62.13; H, 6.57.

The infrared and n.m.r. spectra are consistent with this structure and composition. The *p*-nitrobenzenesulfonate melted at 65–66°. (Lawton[17] reports 65–67°.)

2-Cyclopentylethanol was prepared in two ways: (1) by the reaction of cyclopentylmagnesium bromide with ethylene oxide, by a procedure like that used for 2-(Δ^3-cyclopentenyl)ethanol, and (2) more satisfactorily by the reduction of commercially available cyclopentylacetic acid with $LiAlH_4$.

The product was distilled at reduced pressure to give 13.5 g. of product, b.p. 70–73° at 22 mm. (80.0% yield). Ipatieff[38] reports b.p. 179–181°.

Δ^3-Cyclopentenylacetone was prepared both directly from Δ^3-cyclopentenyl bromide and acetoacetic ester and by way of Δ^3-cyclopentenylmalonic ester and Δ^3-cyclopentenylacetyl chloride.

a. From Acetoacetic Ester. The potassium derivative from 9.0 g. of redistilled ethyl acetoacetate was treated in anhydrous *t*-butyl alcohol with 11.0 g. of Δ^3-cyclopentenyl bromide. The mixture was heated under reflux for 30 hr., the reaction being followed by titration of aliquots with 0.1 *N* HCl until 93% complete. The deep orange-colored oil, isolated by extraction between ether and water (sufficient of the latter to dissolve the potassium bromide), was hydrolyzed directly with 70 ml. of 5% sodium hydroxide. After stirring for 12 hr., the solution was acidified with 15 ml. of 50% sulfuric acid, added dropwise, and steam distilled through a Vigreux column. The 4 g. of clear, yellow oil resulting from the work-up was dried with calcium chloride and reduced to the secondary alcohol.

b. By Way of Δ^3-Cyclopentenylacetic Acid. The acid was prepared by a sequence described by Lawton.[17]

The potassium derivative made from 28.25 g. (0.25 mole) of distilled ethyl cyanoacetate in dry *t*-butyl alcohol was heated with stirring for 10 hr. with 18.37 g. of Δ^3-cyclopentenyl bromide. The cyclopentenylcyanoacetic ester was isolated by acidification with cold dilute hydrochloric acid and ether extraction. The oil, after drying with $MgSO_4$ and evaporation of the ether, was added to 61 g. of potassium hydroxide in 72 ml. of water and heated for 6 hr. at reflux.[39] Cyclopentenylmalonic acid was isolated as a crude solid by extraction.

The malonic acid, dissolved in 100 ml. of anhydrous pyridine, was heated under reflux for 30 min.[40] The cyclopentenylacetic acid was isolated by neutralization, ether extraction, drying with $MgSO_4$, and distillation, b.p. 120° (20 mm.), $n^{25}D$ 1.4640. The over-all yield from Δ^3-cyclopentenyl bromide was 48%. The acid had principal infrared absorptions at 3.29, 3.44, 3.53, 5.83, 6.96, 7.04, 7.61, 7.77, 8.14, and 14.81 μ, determined on the undiluted liquid. The *p*-bromophenacyl ester melted at 66–67°.

Anal. Calcd. for $C_{15}H_{15}BrO_3$: C, 55.74; H, 4.68. Found: C, 55.34; H, 4.77.

A Grignard reagent was prepared from 3.7 g. (0.154 g.-atom) of magnesium, a crystal of iodine, and 31.3 g. (0.180 mole) of methyl bromide in 200 ml. of anhydrous ether, at room temperature, after which 14.15 g. (0.077 mole) of anhydrous cadmium chloride was added. After 1 hr. of stirring, there was added a benzene solution containing the acid chloride prepared from 3.5 g. of Δ^3-cyclopentenylacetic acid and 4.96 g. of thionyl chloride. The mixture was stirred at room temperature for 1 hr. and refluxed for 3 hr. The Δ^3-cyclopentenylacetone was isolated as an oil by extraction, which was used directly in the next step.

1-(Δ^3-Cyclopentenyl)-2-propanol was prepared by $LiAlH_4$ reduction of Δ^3-cyclopentenylacetone, and obtained as a liquid, b.p. 74° at 10 mm., $n^{26}D$ 1.4651. The infrared and n.m.r. spectra of this material were consistent with the proposed structure. Vapor phase chromatography indicated that the purity of the alcohol was >99.8%. The phenylurethan was prepared, m.p. 87.5–88° (from *n*-hexane).

Anal. Calcd. for $C_{15}H_{19}NO_2$: C, 73.43; H, 7.80; N, 5.71. Found: C, 73.20; H, 8.05; N, 5.90.

(35) P. D. Bartlett and M. R. Rice, *J. Org. Chem.*, **28**, 3351 (1963). This preparation is a hazardous one, having produced a fire in this laboratory and shattering explosions in several other laboratories. It should be carried out only on a modest scale and with suitable precautions. See C. R. Johnson and J. C. Keiser, *Tetrahedron Letters*, 3327 (1964).

(36) R. O. Clinton and S. C. Laskowski, *J. Am. Chem. Soc.*, **70**, 3135 (1948).

(37) R. S. Tipson, *J. Org. Chem.*, **9**, 238 (1944).

(38) V. N. Ipatieff, W. W. Thompson, and H. Pines, *J. Am. Chem. Soc.*, **73**, 553 (1951).

(39) W. H. Miller, A. M. Dessert, and G. W. Anderson, *ibid.*, **70**, 500 (1948).

(40) W. S. Johnson, V. J. Bauer, J. L. Margrave, M. A. Fresch, L. H. Dreger, and W. N. Hubbard, *ibid.*, **83**, 612 (1961).

The *p*-nitrobenzenesulfonate ester was prepared in poor yield (20%) by the method given by Streitwieser and Schaeffer.[41] It was recrystallized from ether–petroleum ether (b.p. 30–60°) in the cold room and stored in the refrigerator. It melted just above room temperature. The *p*-toluenesulfonate melted at 32–35°.

The infrared spectrum of the alcohol, determined without solvent, showed peaks at 2.87, 3.20, 3.36, 3.47, 6.18, 6.88, 7.29, 7.41, 7.74, 8.89, 9.50, 9.78, 10.08, 10.78, 11.19, 11.42, 12.00, 12.22, 13.05, and 14.44 μ.

Its n.m.r. spectrum at 60 Mc. shows a narrow, 2-proton singlet at τ 4.40, a quartet (1H) centered at τ 6.26 with J = 7 c.p.s., a 1-proton singlet at τ 6.55, overlapping complex multiplets (7H) from τ 7.3 to 8.7, and a 3-proton doublet (J = 7 c.p.s.) at τ 8.83.

The over-all yield of 1-(Δ^3-cyclopentenyl)-2-propanol from 4-bromocyclopentene was 18–28% by way of acetoacetic ester, and 23% by way of Δ^3-cyclopentenylacetic acid.

1-(Cyclopentyl)-2-propanol. This material was prepared in 65% over-all yield from the commercially available (Aldrich Chemical Co.) 2-cyclopentylacetic acid. The alcohol had b.p. 82° at 16 mm., $n^{25}D$ = 1.4550.

The *p*-nitrobenzenesulfonate ester was prepared. It has a melting point just below room temperature. Vapor phase chromatography gives the purity of the alcohol as >99.8%.

endo-Norborneol was prepared in 79.5% crude yield by the lithium aluminum hydride reduction of norcamphor, m.p. of crude alcohol 81–100°. Sublimation gave material melting in a sealed tube at 150–151°.

1-Methyl-exo-norborneol was prepared according to the directions of Schleyer.[42]

endo-Norbornyl p-nitrobenzenesulfonate was prepared from 4.00 g. of *endo*-norborneol in 50 ml. of anhydrous pyridine and 8.84 g. of *p*-nitrobenzenesulfonyl chloride; yield 8.5 g. (80%) of twice recrystallized material, m.p. 94–95° (from pentane).

Product of Solvolysis of 2-(Δ^3-Cyclopentenyl)ethyl Tosylate in 50% Acetic Acid. The solution, after heating at 72° for 7 hr., was neutralized and extracted with ether. Evaporation gave an oil with an infrared spectrum corresponding to a mixture of *exo*-norbornyl acetate and *exo*-norborneol. Vapor phase chromatography, carried out on a carbitol column at 156–158°, showed two peaks in the ratio of 60 to 40, accounting for 92% of the material. The retention times of the major and minor components, 7.6 and 9.4 min., respectively, were identical with those of authentic *exo*-norbornyl acetate and *exo*-norborneol. All peaks varied in position by 0.2–0.5 min. with small changes in column temperature.

Saponification with potassium hydroxide converted the mixture to *exo*-norborneol, isolated by ether extraction and sublimation of the white crystalline product. The infrared spectrum was identical with that of authentic *exo*-norborneol.

Oxygen-18 Enriched Δ^3-Cyclopentenylacetic Acid. 3.0 g. (0.130 g.-atom) of sodium in small pieces was cautiously added to 50 ml. of 1.7 atom % oxygen-18 enriched water. After the sodium had reacted, 16.0 g. (0.114 mole) of methyl Δ^3-cyclopentenylacetate was added followed by enough absolute ethanol to make the solution homogeneous. The total volume was approximately 100 ml. The reaction mixture was heated under reflux for 45 hr. The ethanol was then removed by distillation. The residue was cooled and made acid by the addition of cold concentrated hydrochloric acid. The water solution was extracted with ether. The combined ether layers were washed with water and dried over anhydrous magnesium sulfate. The ether layer was filtered and the ether was removed on the steam bath. The residue was distilled at reduced pressure to give 12.0 g. of product (83.5% yield), b.p. 89–91° at 3 mm.

Oxygen-18 enriched 2-(Δ^3-cyclopentenyl)ethanol was prepared by lithium aluminum hydride reduction of oxygen-18 enriched Δ^3-cyclopentenylacetic acid by the method previously described; oxygen-18: 0.730 atom % excess.

Oxygen-18 enriched 2-(Δ^3-cyclopentenyl)ethyl p-nitrobenzenesulfonate was prepared from oxygen-18 enriched 2-(Δ^3-cyclopentenyl)ethanol and *p*-nitrobenzenesulfonyl chloride in the manner previously described.

Test for Oxygen-18 Scrambling during Solvolysis of Oxygen-18 Enriched 2-(Δ^3-Cyclopentenyl)ethyl p-Nitrobenzenesulfonate in Acetic Acid at 61.83 ± 0.01°. Excess oxygen-18 enriched 2-(Δ^3-cyclopentenyl)ethyl *p*-nitrobenzenesulfonate (8.0706 g.) was placed in 30 ml. of anhydrous acetic acid in a 50-ml. volumetric flask. The solution was cloudy at room temperature but quickly became homogeneous when placed in the oil bath at 61.83 ± 0.01°. After standing in the bath for approximately 10 min., the first sample was removed and added to a separatory funnel containing 100 ml. of ethyl ether and a solution of saturated sodium bicarbonate. The samples were removed as shown in Table VII. The time was taken as the first drop entered the quenching solution. After the violent reaction with sodium bicarbonate had ended, the layers were separated. The aqueous layer was extracted with ether. The combined ether layers were dried over anhydrous sodium carbonate. The ether solution of each sample was treated as follows. The ether solution was filtered and concentrated to a few milliliters. Addition of *n*-pentane caused the precipitation of 2-(Δ^3-cyclopentenyl)ethyl *p*-nitrobenzenesulfonate. The solutions were kept at −25° until ready for cleavage. The recovered 2-(Δ^3-cyclopentenyl)ethyl *p*-nitrobenzenesulfonate from each sample after collection was recrystal-

Table VII

Sample no.	Time, sec.	Vol. sample, ml.	Vol. satd. $NaHCO_3$ used
1	0	5	125
2	2000	5	125
3	3500	10	250
4	5200	10	250

(41) A. Streitwieser and A. Schaeffer, *J. Am. Chem. Soc.*, 79, 6236 (1957).

(42) P. von R. Schleyer, Thesis, Harvard University, 1956, p. 375.

lized, collected, and air-dried immediately before cleavage.

Cleavage of 2-(Δ^3-Cyclopentenyl)ethyl p-Nitrobenzenesulfonate Recovered from Solvolysis in Acetic Acid. The method used is that of Denney and Kupchik.[30] To 1.00 g. (0.0435 g.-atom) of sodium in approximately 150 ml. of liquid ammonia in a Dry Ice–acetone bath was added a solution of 1.0 g. (0.0034 mole) of 2-(Δ^3-cyclopentenyl)ethyl *p*-nitrobenzenesulfonate in about 25 ml. of anhydrous ethyl ether. The reaction mixture was allowed to stir in a Dry Ice–acetone bath for 3 hr. Solid ammonium chloride was added until the blue color faded and was followed by 25 ml. of water. After the ammonia had evaporated, 100 ml. of water was added. The aqueous layer was extracted with ether. The ether layer was placed in a weighed flask, and the ether was removed to constant weight. A slight excess of freshly distilled phenyl isocyanate was added, and the reaction mixture was allowed to stand at room temperature for about 15 min. The sides of the flask were scratched with a stirring rod until crystallization occurred. A small quantity of *n*-hexane was added to aid in collecting the solid. The solid was recrystallized twice from *n*-hexane, m.p. 62.0–62.5°. The infrared spectrum of each of the three samples was identical with that of the authentic phenylurethan. The phenylurethan samples were analyzed for O^{18} (Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.) with the results shown in Table III.

Product of Solvolysis of 1-(Δ^3-Cyclopentenyl)-2-propyl p-Nitrobenzenesulfonate. In Absence of Added Reagent. The sulfonate of 1-(Δ^3-cyclopentenyl)-2-propanol (0.2882 g.) was dissolved in 5.0 ml. of dry acetic acid and warmed to 55° for 12 hr. The strong acid was neutralized with 2.4 ml. of 0.35 *N* sodium acetate in acetic acid. The acetate product was obtained by continuous extraction with pentane. After slowly removing the solvent, an infrared spectrum of the oil was taken.

The oil was refluxed with 0.6 g. of potassium hydroxide in 20 g. of methanol for 6 hr. The alcoholic product was obtained by continuous extraction with pentane (6 hr.) and removing the pentane very slowly through a Vigreux column. Vapor phase chromatography of this material (Ucon polar 80°) showed it to be a mixture of 1-methyl-*exo*-norborneol and 1-(Δ^3-cyclopentenyl)-2-propanol in the ratio of 2.6 to 1. An infrared spectrum of a synthetic mixture of these proportions was identical with that of the reaction product.

In the Presence of Sodium Acetate. The *p*-toluenesulfonate of 1-(Δ^3-cyclopentenyl)-2-propanol was used in this experiment. Solvolyses were carried out at 50, 55, and 80°, with results shown in Table V. In the 50° experiment, 1.8 g. of tosylate was dissolved in 10 ml. of previously dried acetic acid containing 0.8 g. of sodium acetate. The solution was sealed in a glass ampoule and heated at 50° for 20 hr. The products were isolated by neutralization of the solvent with cold aqueous sodium hydroxide and extraction with pentane, then complete saponification with 1 g. of potassium hydroxide in 20 g. of methanol under reflux for 12 hr. The alcoholic product, isolated by continuous pentane extraction of the acidified mother liquor, was subjected to vapor phase chromatography. In addition to the 5–7 short-time peaks characteristic of a concentrated pentane residue, there were five components, of which two, present in the ratio of 1.7 to 1, represented 91% of the product. The more strongly retained and minor component had a retention time identical with that of 1-(Δ^3-cyclopentenyl)-2-propanol. The other component was not identical with the bicyclic product (1-methyl-*exo*-2-norborneol) from the solvolysis without added sodium acetate.

The mixture of alcohols was subjected to column chromatography on alumina, leading to the isolation of the major component as a sublimable solid, eluted in the late pentane fractions, and of 1-(Δ^3-cyclopentenyl)-2-propanol, eluted by benzene–ether. The latter had an infrared spectrum identical with that of the starting alcohol. The former, which seems likely to be a 6-methyl-2-*exo*-norborneol, showed infrared absorption (in carbon tetrachloride) at 2.70, 2.81, 2.89 (w), 3.40 (vs), 6.80 (sh, m), 6.87 (sh, s), 6.95, 7.31 (s), 7.49 (m), 7.68 (s), 7.86 (m), 7.98, 8.07, 8.22 (w), 8.53 (s), 8.70 (w), 8.90 (sh), 9.04 (s), 9.40, 9.71 (w), 10.05 (m), 10.32 (w), 10.59, 10.71 (m), 11.01, 11.23, 11.50 (s), and 12.01 (w) μ.

Kinetic Method. a. Titrimetric rate constants were determined by the generally used procedure of sealing portions of the reacting solutions in glass ampoules, removing ampoules at chosen intervals from the thermostat bath, chilling, and titrating. Titrations in glacial acetic acid were performed with standard sodium acetate solution and bromophenol blue as indicator. For solvolyses in the presence of sodium acetate, standard perchloric acid solution in acetic acid was added first, then back titrated. The "infinity time" titer was determined from an ampoule which had been in the bath for 10 half-lives.

b. The conductometric rate constants were determined by placing a solution of approximately 50 mg. of the compound in 15 ml. of solvent in a conductivity cell which was placed in a constant-temperature bath. The resistance of the solution was taken at various time intervals by means of a conductivity bridge, Model RC 16B1, Industrial Instruments, Inc. The data were plotted according to the method of Frost and Pearson.[43a]

The rate constant was calculated from the slope of the best line drawn visually through the points.

c. The potentiometric rate constants were determined in a manner similar to the titrimetric rate constants. The only difference is that the end point of the titration was determined potentiometrically by the method of Winstein and Marshall rather than by a visual indicator.[44]

d. The n.m.r. rate constants were determined by placing a solution of approximately 1.0 g. of the compound in 10 ml. of solvent in a volumetric flask, which was placed in a constant temperature bath. At the various time intervals, an aliquot was withdrawn by means of a pipet and placed in a cold n.m.r. tube. The tubes were then placed in the freezer at −25° until they could all be analyzed. The n.m.r. spectra, with integrations, were taken on a Varian A-60 spec-

(43) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," 2d Ed., John Wiley and Sons, Inc., New York, N. Y., 1961: (a) p. 35, (b) p. 46.

(44) S. Winstein and H. Marshall, *J. Am. Chem. Soc.*, **74**, 1126 (1952).

trometer. The rate constant for the disappearance of vinyl protons was calculated in the usual manner.[43b]

Acknowledgment. We thank the National Science Foundation for support of this work.

Nucleophilic Reactivity of the Carbon–Carbon Double Bond. II. Solvolytic Ring Closure of 2-(3-Methyl- and 3,4-dimethyl-Δ^3-cyclopentenyl)ethyl *p*-Nitrobenzenesulfonates[1]

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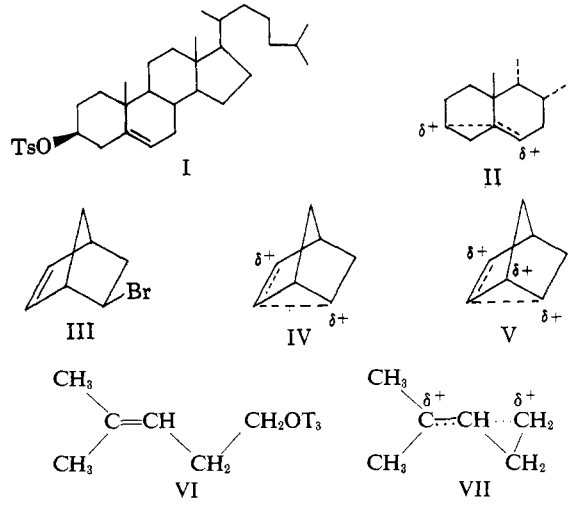
The two compounds in the title (XII and XIII), prepared according to Chart I, show acetolysis rates which are faster than that of the saturated reference compound XXXIII by factors of 600 and 3300, respectively. The similar accelerating effects of the first and second methyl groups show that the anchimeric assistance by the double bond is such as to place nearly equal amounts of positive charge simultaneously on the two originally doubly bonded carbon atoms. The products from XII and XIII, 2-methyl- and 1,2-dimethyl-exo-2-norbornyl acetates, respectively, have been isolated in good yield and their structures have been confirmed by synthesis. The effects of methyl substitution in solvolytic ring closure are compared with those in epoxidation and acid-catalyzed hydration as models for symmetrical and unsymmetrica ltransition states. 2-(2-Indanyl)ethyl p-nitrobenzenesulfonate (XIV) undergoes acetolysis more slowly than the saturated reference compound.

Introduction

In homoallylic (3-alkenyl) halides and sulfonates a carbon–carbon double bond often acts to accelerate ionization. In most such cases one end of the double bond (C-3) is nearer than the other to the seat of ionization, and it is the remote end of the double bond which appears (on the basis of product structure) to carry a good share of the charge. Examples are cholesteryl tosylate (I),[2] *exo*-2-norbornenyl bromide (III),[3] and 4-methyl-3-pentenyl tosylate (VI).[4] In these cases it has been inferred that the transition state and first intermediate in solvolysis involve an unsymmetrical participation of the double bond (II, IV, and VII, respectively). Although the norbornenyl cation readily undergoes rearrangements suggesting the symmetrical structure V[5] rather than IV, the incomplete redistribution of C-14 in the solvolysis of labeled norbornenyl derivatives[6] excludes V as the sole ionic intermediate, and even the representation V assigns different roles to the two carbon atoms of the double bond.



Among ionizable compounds which lead to cyclization by the π-route,[7] some of the greatest accelerations are noted in compounds having the double bond in the 5,6-position relative to the departing group and symmetrically placed, so that its two carbon atoms are equidistant from C-1 or nearly so. It is especially striking that the ratio of assisted to unassisted formolysis appears to be about 16 times as great for the symmetrically placed double bond of 2-(Δ^3-cyclopentenyl)ethyl *p*-nitrobenzenesulfonate (VIII)[7] as for the unsymmetrically placed one of 3-(Δ^2-cyclopentenyl)propyl *p*-nitrobenzenesulfonate (IX).[8] The most spectacular case of the effect of symmetry remains the contrast between the effect of the double bond on solvolysis rate in

anti-7-norbornenyl sulfonates ($k_{unsat}/k_{sat} = 10^{11}$)[9] and in *exo*-2-norbornenyl sulfonates ($k_{exo}/k_{endo} = 10^3$).[10]

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