

Nucleophilic Reactivity of the Carbon–Carbon Double Bond. III. A Comparison of the Solvolytic Behavior of 5-Hexenyl and Cyclopentylcarbinyl *p*-Nitrobenzenesulfonates¹

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The acetolysis of 5-hexenyl *p*-nitrobenzenesulfonate proceeds 1.7 times as fast as that of *n*-hexenyl *p*-nitrobenzenesulfonate, in contrast to 4-pentenyl *p*-nitrobenzenesulfonate, which is only 0.72 times as fast as the saturated analog. The acetolysis of 5-hexenyl *p*-nitrobenzenesulfonate at 80.8° in the presence of 1.6 equiv. of sodium acetate yielded 83.7% 5-hexenyl acetate, 4.7% cyclohexene, and 11.6% cyclohexyl acetate, none of these products undergoing any further reaction when subjected separately to the reaction conditions. Without the sodium acetate, acetic acid added to the double bond at this temperature and the chief product was a high-boiling material, presumably 1,5-diacetoxyhexane, along with 2% cyclohexene, 42% cyclohexyl acetate, and 8% 5-hexenyl acetate. Cyclopentylcarbinyl *p*-nitrobenzenesulfonate, which undergoes acetolysis 3.5 times as fast as *n*-hexenyl, gives cyclohexene and cyclohexyl acetate as the principal products. Since the acetolyses of these two sulfonates might proceed to cyclohexane derivatives by way of the same intermediate ion XI, formed by the π -route in the one case and the σ -route in the other, the product compositions from the two have been quantitatively compared. The ratio of cyclohexene to cyclohexyl acetate in the product, under the same conditions, is 0.40 from 5-hexenyl, 3.4 from cyclopentylcarbinyl, and 6.7 from cyclohexyl *p*-nitrobenzenesulfonate. Possible reasons for these large differences are discussed.

Introduction

As indicated in the previous discussions,²⁻⁴ the activity of the carbon–carbon double bond as an internal nucleophilic reagent varies enormously with its geometry, substitution, and position in the molecule. The two preceding papers have dealt with double bonds in the 5,6-position which have the advantage of symmetrical location relative to the ionizable center, and of being at least disubstituted. As part of a survey of double bonds located in an ordinary carbon chain, we have investigated the solvolytic behavior of 4-pentenyl and 5-hexenyl *p*-nitrobenzenesulfonates. Finding a minor amount of acceleration and ring closure attending the acetolysis of the latter compound, we have compared it as to rate and products with two other compounds which also solvolyze to cyclohexane derivatives, namely the *p*-nitrobenzenesulfonates of cyclohexanol and of cyclopentylcarbinol.

(1) Presented at the 100th Annual Meeting of the National Academy of Sciences, Washington, D. C., April 1963.

(2) P. D. Bartlett, *Ann.*, **653**, 45 (1962).

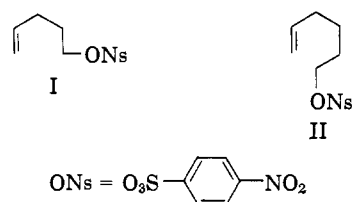
(3) Part I of this series: P. D. Bartlett, S. Bank, R. J. Crawford, and G. H. Schmid, *J. Am. Chem. Soc.*, **87**, 1288 (1965).

(4) Part II: P. D. Bartlett, and G. D. Sargent, *ibid.*, **87**, 1297 (1965).

Results

All the alcohols involved in this work are well known, and attention was centered on careful purification of materials and accurate quantitative accounting of products. The characterization and analysis of these compounds is summarized in Tables III and IV, and the calibration of the columns under the conditions of the vapor phase chromatographic separations is summarized in Table V.

Preliminary solvolysis of 4-pentenyl (I) and 5-hexenyl (II) *p*-nitrobenzenesulfonates in pure acetic acid showed addition of acetic acid to the double bond,



apparently catalyzed by the accumulating sulfonic acid, competing with or following solvolysis. When I was heated under reflux in acetic acid for 5 hr. (about 6 half-lives), the product consisted of nearly equal amounts of 4-pentenyl acetate and an ill-defined mixture of materials having about twice the retention time of 4-pentenyl acetate. Solvolysis of I in the presence of excess sodium acetate, however, yielded only 4-pentenyl acetate.

Compound II likewise yielded a high-boiling fraction on acetolysis in the absence of sodium acetate. In one experiment an acetic acid solution 0.175 *M* in II and 0.01 *M* in perchloric acid was allowed to react at 79.4° for 34 hr., about 4 solvolytic half-lives, and then analyzed both on an LAC-446 column and on one of diisodecyl phthalate. There were nine peaks on the vapor chromatogram; 35% of the material had the long retention times characteristic of the diacetates, 42% was cyclohexyl acetate, 2% was cyclohexene, and 8% was 5-hexenyl acetate. Control experiments showed that these solvolysis products were not themselves stable in acetic acid containing 0.01 *M* perchloric acid, and therefore detailed product studies were made in acetic acid containing enough sodium acetate to neutralize the sulfonic acid produced. All the identified products were separately shown to suffer no change under these experimental conditions. Bicyclo[3.1.0]hexane was not formed in the acetolysis of 5-hexenyl *p*-nitrobenzenesulfonate.

The products of acetolysis of 5-hexenyl *p*-nitrobenzenesulfonate are shown in Table I. In three runs in the presence of excess sodium acetate the cyclization amounted to 16.3, 18, and 18.7%. With 0.3 *M*

Table I. Summary of Product Runs, Acetolysis

Temp., °C	Time, hr.	(RX)	(NaOAc)	(LiClO ₄)	% Recovery	Analysis					
						A, cyclohexane	B, Cyclohexyl acetate	A/B	5-Hexenyl acetate	1-Methylcyclopentene ^a	Cyclopentylcarbinyl acetate
(a) From hexenyl <i>p</i> -nitrobenzenesulfonate											
80.8	86	0.17	0.271	0	94	4.7	11.6	0.40	83.7	0	0
80.8	86	0.17	0.271	0.03	98	5.5	13.2	0.42	81.3	0	0
80.8	86	0.17	0.271	0.30	98	14.7	17.9	0.82	67.4	0	0
80.8	34	0.17	None	0	55	2	42	0.05	8	0	0
(b) From cyclopentylcarbinyl <i>p</i> -nitrobenzenesulfonate											
80.8	52.3	0.18	0.271	0	83	61.9	18.0	3.4	0	15.1	5.1
80.8	52.3	0.18	0.271	0.03	80	62.3	18.8	3.3	0	14.1	4.9
80.8	52.3	0.18	0.271	0.30	90	68.5	15.4	4.4	0	13.8	2.3
80.8	64.5	0.18	0.271	None	83	60	20	3	0	12	0
80.8	64.5	0.18	None	None	78	4	88	0.045	0	8	0
(c) From cyclohexyl <i>p</i> -nitrobenzenesulfonate											
80.8	0.7	0.17	0.271	0	82	87	13	6.7	0	0	0

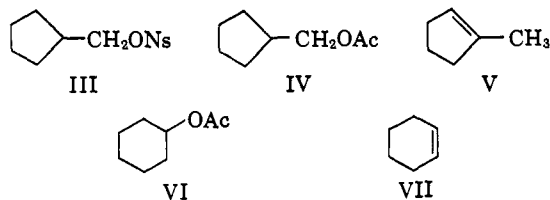
^a In two v.p.c. analyses with direct injection of solvolysis product, 1-methylcyclopentene and methylenecyclopentane were found in amounts of 9 and 4%, respectively, in the first, and 10 and 3% in the second. After extraction the methylenecyclopentane appeared to be converted (as in the other analyses) into 1-methylcyclopentene.

Table II. Summary of Kinetic Runs, 79.5°, HOAc

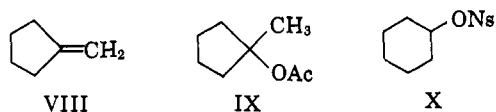
<i>p</i> -Nitrobenzenesulfonate	Concn., <i>M</i>	(NaOAc)	$k \times 10^5$, sec. ⁻¹	<i>b</i>	<i>k/k</i> _{hexyl}
<i>n</i> -Hexyl	0.02	0	1.02	13.8	
		0	1.01		
		0	0.99		
		0.0355	1.43		
		0.0355	1.58		
5-Hexenyl	0.02	(0.0309 <i>M</i> LiClO ₄)	1.29	8.9	1.72
		0	1.71		
		0	1.75		
		0.0355	2.25		
		0	0.72		
4-Pentenyl	0.02	0	0.72	13	0.72
		0	0.72		
		0.0355	1.07		
		0.0355	1.03		
		0	3.50		
Cyclopentylcarbinyl	0.02	0	3.50	1.4	3.47
		0	3.48		
		0.0355	3.68		
		0.0355	3.54		
		0	103		
Cyclohexyl	0.02	0	102	1.6	102
		0	102		
		0.0355	108		
		0.0355	108		
		0.0355	108		

lithium perchlorate present in addition, the cyclization rose to 32.6%, and the ratio of cyclohexene to cyclohexyl acetate doubled.

Table I also shows the products when cyclopentylcarbinyl *p*-nitrobenzenesulfonate (III) is subjected to acetolysis under the same conditions. The products found are the unrearranged acetate (IV), 1-methylcyclopentene (V), cyclohexyl acetate (VI), and cyclohexene (VII). The products IV and V, as well as VI and VII, were unchanged in control experiments in



which they were held under the conditions of reaction. The contrary was true of methylenecyclopentane (VIII),



which was converted into a mixture of 1-methylcyclopentene (V) and 1-methylcyclopentyl acetate (IX). V, found on vapor chromatographic analysis, may have come in part from IX, and both may have been formed by way of VIII in the solvolysis.⁵

The acetolysis of cyclohexyl *p*-nitrobenzenesulfonate (X), also reported in Table I, yielded only cyclohexene (87%) and cyclohexyl acetate (13%).

Table II summarizes rate studies, made at the single temperature 79.5°, of the acetolysis of *n*-hexyl, 4-pentenyl, 5-hexenyl, cyclopentylcarbinyl, and cyclohexyl *p*-nitrobenzenesulfonates. In the absence of

(5) G. LeNy, *Compt. rend.*, **250**, 368 (1960), at the same temperature reported 71% of VII, 15% of VI, 9% of IV, and traces of V and IX. Her results differed slightly from ours in the direction of more ring expansion (86% vs. 80%) and a higher ratio of VII to VI (4.7 vs. 3.4).

added reagents, the ratios k/k_{hexyl} for these compounds are 0.72 for 4-pentenyl, 1.72 for 5-hexenyl, 3.47 for cyclopentylcarbonyl, and 102 for cyclohexyl nitrobenzenesulfonate. The first figure shows that for an ionizable compound with a nonparticipating double bond in the 4,5-position, there is a small retarding effect on ionization, due presumably to the adverse inductive effect arising out of the dipole produced by the bond between sp^2 - and sp^3 -hybridized carbon atoms.

In each case mild acceleration results from the addition of sodium acetate. In the table the magnitude of this acceleration has been expressed in the form of a tabulated value for b in the equation⁶ $k = k_0(1 + b(\text{NaOAc}))$. In the case of *n*-hexyl *p*-nitrobenzenesulfonate the accelerating effect of sodium acetate is 55% greater than that produced by lithium perchlorate, although the latter salt normally exerts greater kinetic neutral salt effects than the former. This, together with the almost 10-fold drop in the value of b for the branched sulfonate III and the secondary X, appears consistent with the view that the acetate is superposing direct S_N2 displacement upon the solvolysis.

Discussion

In three instances we have obtained measurements of the retardation due to a double bond or a benzene ring under conditions where the absence of participation has been established. For Δ^3 -cyclopentenyl bromide $k_u/k_s = 0.257$; for 2-(3-indanyl)ethyl *p*-nitrobenzenesulfonate it is 0.59⁸; and now for 4-pentenyl *p*-nitrobenzenesulfonate this ratio is found to be 0.72. It therefore seems possible that the acceleration noted in the solvolysis of 5-hexenyl *p*-nitrobenzenesulfonate, above, is produced over an opposing inductive effect whose magnitude might be estimated to provide a more accurate knowledge of the driving force involved. It is impossible to make this small correction with any assurance in view of the large number of conformations available to the 5-hexenyl compound and the importance of relative orientation in the interaction of two dipoles. We might guess at a figure of 0.76 for $k_u(\text{unassisted})/k_s$ in the case of II by taking the square root of the 2-(3-indanyl)ethyl figure and disregarding orientation; or we might look at the minimum-energy conformations of I and II, the extended forms, assume the angle between the interacting dipoles in the transition state to be the same in I and II, and from the distance d_I and d_{II} between the centers of the C-O and single bond-double bond dipoles arrive at an estimated work increment equal to $(d_I/d_{II})^3 RT \ln 0.72 = 0.422 RT \ln 0.72$, which would give $k_u(\text{unassisted})/k_s = 0.87$. The latter estimate is based on more closely related compounds. We shall use it, although the correction is small in comparison to completely unknown factors such as ground-state⁹ and transition-state solvation and populations of conformational states.

An estimate of the fraction of assisted solvolysis under the conditions of the product run in Table Ia,

(6) S. Winstein, E. Clippinger, A. H. Fainberg, and G. C. Robinson, *J. Am. Chem. Soc.*, **76**, 2597 (1954).

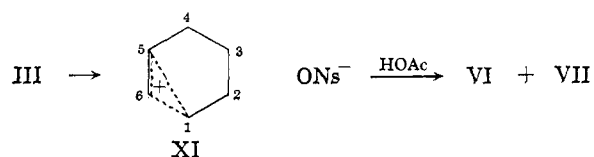
(7) P. D. Bartlett and M. R. Rice, *J. Org. Chem.*, **28**, 3351 (1963).

(8) In this ratio k_s is for 2-(3,4-dimethylcyclopentyl)ethyl *p*-nitrobenzenesulfonate: P. D. Bartlett and G. D. Sargent, ref. 4.

(9) E. M. Arnett, P. M. Duggleby, and J. J. Burke, *J. Am. Chem. Soc.*, **85**, 1350 (1963).

line 1, with an average sodium acetate concentration of 0.186, is $(1.72 - 0.87)/[1.72(1 + 8.4 \times 0.186)] = 0.85/(1.72 \times 2.57) = 19.2\%$ of the total reaction (assisted + unassisted + S_N2), all the acceleration by acetate being assumed to be due to direct displacement. The sum of the cyclohexene and cyclohexyl acetate found is 16.3% of the total products. In similar fashion the accelerated solvolysis observed for III (ignoring any differences in rate between saturated primary *p*-nitrobenzenesulfonates and the small effect of sodium acetate on the rate) would lead us to expect a product of which $(3.47 - 0.87)/3.47$ or 75% should consist of cyclohexene and cyclohexyl acetate. The figure observed is 80%, consistent with the view that rate acceleration is associated with rearrangement here as it is with cyclization in the case of II.

The conversion from either II or III to cyclohexyl products involves the formation of a new carbon-carbon bond. In the case of solvolysis of III the cation must pass through a stage resembling XI, whether this be a mere transition state or a molecular species representing an energy minimum.



Special circumstances allowed us to conclude in part II⁴ that the bridged transition state was symmetrical and, since it was formed from symmetrical starting material, that it must therefore be the transition state leading to a symmetrical first intermediate. No such special circumstances exist in the present case, where the transition state must in any case be very unsymmetrical. In view of the uncertainty about the stability of XI, and the fact that assisted solvolysis seems to lead only to cyclohexene and cyclohexyl acetate, the simplest view might appear to be that both 5-hexenyl and cyclopentylcarbonyl *p*-nitrobenzenesulfonates, with or without a stabilized ion XI, are converted to the cyclohexyl cation XII in the process of



anchimerically assisted solvolysis.

That the "classical" cyclohexyl cation XII is indeed a stabler structure than XI would be anticipated from the strained and unsymmetrical structure of the latter, and is consistent with the fact that cyclohexyl *p*-nitrobenzenesulfonate (X) solvolyzes 59 times as fast as 5-hexenyl (II) and 29 times as fast as cyclopentylcarbonyl *p*-nitrobenzenesulfonate (III). However, if free XII were a common intermediate in all cases, then the products with six-membered rings (cyclohexene and cyclohexyl acetate) must be formed *after* the formation of XII and must necessarily arise in the same ratio from the starting materials II, III, and X. Table I shows that this is far from being the case; the ratio of cyclohexene to cyclohexyl acetate is in fact 0.40, 3.4, and 6.7, respectively, in these three cases. The variation is more than 16-fold. The six-membered ring products are therefore *not* formed from a single common

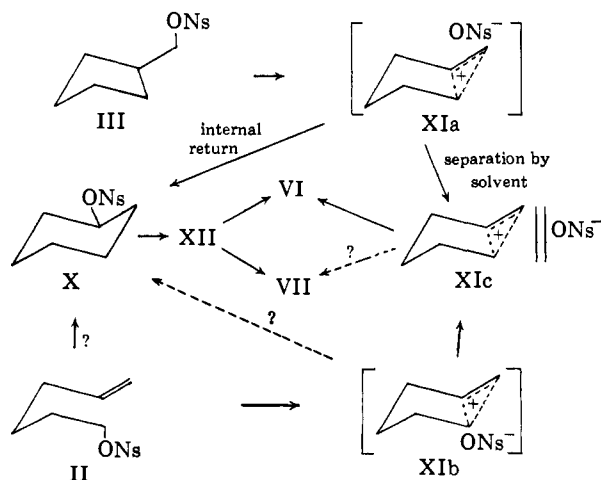
intermediate in any two of the three cases. The reaction path divides before the free cyclohexyl cation is formed. This requires the occurrence of ionic *intermediates* which are different in some degree when formed from hexenyl, cyclopentylcarbonyl, or cyclohexyl *p*-nitrobenzenesulfonates.

We have, then, a reaction of undoubtedly ionic character in which three starting materials give a common pair of products in such different ratios that the reaction paths must differ in some important respect. It would, of course, be possible to retreat into the most complicated explanation of all, namely, that there are six independent transition states and no common intermediates. We prefer to look for some meaning in the analogies and distinctions between this case and those of parts I and II. In acetic acid some of the chemistry of solvolysis is determined not by free ions but by ion pairs.¹⁰ The following scheme is not uniquely required by the evidence, but it keeps at a minimum the number of *ad hoc* assumptions which are necessary to explain the facts.

We suppose that cyclohexyl *p*-nitrobenzenesulfonate, X, undergoes solvolysis *only* through the charge-localized cyclohexyl cation XII and its intimate and solvent-separated ion pairs, and that this reaction path leads to the ratio VII/VI = 6.7. In the solvolysis of cyclopentylcarbonyl *p*-nitrobenzenesulfonate III, the intimate ion pair XIa has the anion adjacent to the carbon atom to which it was initially attached; this is the position most favorable to internal return to cyclohexyl *p*-nitrobenzenesulfonate X. Such internal return is not detectable directly because X is solvolyzed 29 times as fast as III. Products from III are then formed partly *via* X and partly from the solvent-separated ion pair XIc and perhaps from free XI itself. Because XIc and XI are folded along the dotted diagonal and lack the mobility of XII, they are not geometrically favorable precursors for cyclohexene (see Chart I).

When 5-hexenyl *p*-nitrobenzenesulfonate (II) forms the intimate ion pair XIb, the anion is on the opposite side of the cation from the place it must reach in

Chart I



order to achieve internal return to X. Such internal return must at least require many more collisions for

(10) S. Winstein, E. Clippinger, A. H. Fainberg, and G. C. Robinson, *J. Am. Chem. Soc.*, **76**, 2597 (1954).

its occurrence from XIb than from XIa, if indeed it can happen at all. On the limiting assumption that XI can give no cyclohexene (case I), it would be concluded¹¹ that XIa gives internal return to X 89% of the time, while XIb gives only 33% of such internal return. If it be assumed that XIb is incapable of internal return (case II), and gives the observed 4.7% of cyclohexene directly, then XIa must still undergo 83% internal return to yield the observed results.

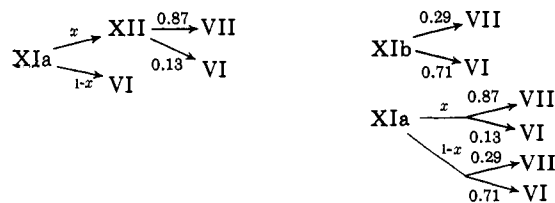
It is consistent with this hypothesis that lithium perchlorate at a concentration of 0.3 *M* doubled the proportion of cyclohexene found in the acetolysis of II (Table Ia, line 3). The decreased amount of cyclohexene in the presence of acid is of course due to secondary acid-catalyzed addition of acetic acid to the double bond.

Our original interest in studying 5-hexenyl *p*-nitrobenzenesulfonate was to locate the borderline between participation and nonparticipation of the double bond in solvolysis. As noted in part I,³ this borderline shifts with the solvent; assisted solvolysis (in the case of 2-(Δ^3 -cyclopentenyl)ethyl arylsulfonates) has a solvent dependence like that of *t*-butyl chloride, while unassisted solvolysis (represented there by 2-cyclopentylethyl sulfonates) has a solvent dependence like that of isopropyl bromide. This makes a difference of 1.53 log units in the relative effects of ethanol and formic acid on the rate, and a difference of about 8-fold in the ratio k_u/k_s between acetic and formic acids, when measured at temperatures of equal assisted rates in the two solvents.

In the case of 5-hexenyl *p*-nitrobenzenesulfonate we have confined our measurements to acetic acid. Recently Johnson and co-workers¹² have observed product ratios in the formolysis of 5-hexenyl *p*-nitrobenzenesulfonate which suggest that $k_{\text{assisted}}/k_{\text{unassisted}}$ at 75° is about 1.2 in 100% formic acid and 2.6 in 98% formic acid, compared with our corresponding figure of 0.2 in acetic acid at 80° from Table Ia, line 1. (This appears to be the best basis of comparison since rate constants were not reported in the formic acid work. Both product studies were made in the presence of the sodium salt of the solvent acid.) This is a 6-fold increase in the importance of the anchimeric assistance between anhydrous acetic and formic acids, not far from the expected factor.

In part II it was possible to isolate the effect of methyl substitution on the participating ability of the double bond, all factors of conformation and sym-

(11) For case I all the VII observed must come from internal return, and for XIa we have $0.87x = 61.9/(61.9 + 18.0) = 0.774$; $x = 0.774/0.87 = 89\%$, internal return with rearrangement. For XIb, $0.87x = 4.7/$



Case I

Case II

(4.7 + 11.6) = 0.29; $x = 0.29/0.87 = 33\%$. For case II we have $61.9/(61.9 + 18.0) = 0.774 = 0.87x + 0.29(1 - x)$; $0.58x = 0.774 - 0.29 = 0.48$; $x = 0.48/0.58 = 83\%$.

(12) W. S. Johnson, D. M. Bailey, R. Owyang, R. A. Bell, B. Jaques, and J. K. Crandall, *J. Am. Chem. Soc.*, **86**, 1959 (1964).

metry being held constant. In part IV a discussion will be given on the effect of conformational factors when substitution and symmetry at the double bond are held constant,¹³ and it will be shown that an increase by one CH₂ group in the length of the chain between an ionizing center and an actively participating double bond can reduce the rate of assisted ionization by a factor of 600. With this effect, we could easily account for a rapid decline of participation in going from 3-butenyl to 4-pentenyl sulfonates, and from 5-hexenyl to 6-heptenyl sulfonates.¹⁴ However, the increase in participation between 4-pentenyl and 5-hexenyl implies the entrance of another factor which is neither one of conformation nor one of substitution. We suggest that in the short, homoallylic systems the bridged ("bicyclobutonium") ion, though involving π -participation of the double bond, is necessarily unsymmetrical with more positive charge on the "distant" (cyclopropyl carbinyl) than on the "near" (cyclobutyl) carbon atom. In the highly participating double bond of 2-(Δ^3 -cyclopentenyl)ethyl sulfonates the anchimeric assistance reaches a maximum with perfect symmetry in the bridged ion. In 5-hexenyl sulfonates the important distances can be similar to those in 2-(Δ^3 -cyclopentenyl)ethyl, and the bridged ion gains in stability (compared to 4-pentenyl) as it acquires a greater approach to symmetrical charge distribution.

Experimental

4-Penten-1-ol. The method of Kharasch and Fuchs was used to prepare 4-pentenol.¹⁵ One modification made was to use three times as much ether for solvent as recommended. This made the reaction mixture much more fluid at critical stages. From 115 g. (1.50 moles) of allyl chloride, 40 g. (1.64 moles) of magnesium, and 100 g. (2.27 moles) of ethylene oxide was obtained 60 g. (0.696 mole, 46.4% based on allyl chloride) of 4-pentenol, b.p. 134–136°, n_{25}^D 1.4277 (lit.¹⁶ n_{20}^D 1.4290). Its 1-naphthylurethan was prepared, m.p. 61.8–62.5° (petroleum ether) (lit.¹⁶ m.p. 62.5–63.0°).

5-Hexen-1-ol. A solution of 10.5 g. (0.0704 mole) of 1-bromo-4-pentene (prepared from the tosylate and lithium bromide in acetone) was mixed with 5.5 g. (0.084 mole) of potassium cyanide in 25 ml. of ethylene glycol and heated at 100° with stirring for 2 hr. The solution was then cooled, diluted with water, and extracted with ether. The ether solution of the nitrile was concentrated and mixed with 40 ml. of 20% potassium hydroxide and heated at reflux for 22 hr. It was then washed with ether and acidified and the acid was extracted with ether. Distillation at 8 mm. yielded 5.87 g. (0.0514 mole, 73.0%) of 5-hexenoic acid, b.p. 92–95° at 8 mm. (lit.¹⁷ b.p. 101–105° at 13 mm.), n_{25}^D 1.4321–1.4325 (lit.¹⁷ n_{25}^D 1.4318).

To a suspension of 2.85 g. (75 mmoles) of lithium aluminum hydride in 100 ml. of dry tetrahydrofuran, 5.80 g. (50.8 mmoles) of 5-hexenoic acid was carefully added. The mixture was refluxed for 18 hr.,

(13) Part IV: W. S. Trahanovsky and P. D. Bartlett, *J. Am. Chem. Soc.*, **87**, 1314 (1965).

(14) G. H. Schmid, unpublished work.

(15) M. S. Kharasch and C. F. Fuchs, *J. Org. Chem.*, **9**, 359 (1944).

(16) M. F. Ansell and D. A. Thomas, *J. Chem. Soc.*, 1163 (1958).

(17) F. B. LaForge, N. Green, and W. A. Gersdorff, *J. Am. Chem. Soc.*, **70**, 3709 (1948).

and then the excess hydride was destroyed by careful addition of a large excess of dilute hydrochloric acid. The resulting solution was extracted with ether and the ether solution was washed with dilute acid and saturated brine, then dried and concentrated. Distillation at atmospheric pressure yielded 4.44 g. (44.3 mmoles, 87.3%) of 5-hexen-1-ol, b.p. ca. 140°, n_{25}^D 1.4318–1.4332 (lit.¹⁸ n_{25}^D 1.4335).

A small amount of this material was converted to its 1-naphthylurethan, m.p. 61.5–63.0° (petroleum ether) (lit.¹⁹ m.p. 62°).

Cyclopentylcarbinol was prepared by LiAlH₄ reduction of 15.0 g. of cyclopentanecarboxylic acid (Aldrich Chemical Co., Milwaukee, Wis.). Distillation at 25 mm. yielded 10.9 g. (0.108 mole, 83.0%), b.p. 76–78° (lit.²⁰ b.p. 68–70° at 16 mm.), n_{25}^D 1.4572 (lit.²⁰ n_{25}^D 1.4570). The 1-naphthylurethan was prepared; m.p. 87–88° (petroleum ether) (lit.²⁰ m.p. 87.4–87.8°).

***p*-Nitrobenzenesulfonate Esters.** The *p*-nitrobenzenesulfonate esters required in these studies were prepared from the corresponding alcohols by the method of Streitwieser and Schaeffer.²¹ The yields, melting points, and recrystallization solvents are shown in Table III, and the analytical data are presented in Table IV.

Table III. Yields and Melting Points of Alkyl *p*-Nitrobenzenesulfonates

Ester	Yield, %	M.p., °C.	Recrystn. solvent
<i>n</i> -Hexyl	63.2	52–53	Ether–petroleum ether
4-Pentenyl	46.5	45–46	Ether–petroleum ether
5-Hexenyl	60.5	40–41	Ether–petroleum ether
Cyclopentanemethyl	68.2	92–93	Ethanol
Cyclohexyl	58.4	78–79	Benzene–petroleum ether

Table IV. Analytical Data for Alkyl *p*-Nitrobenzenesulfonates^a

Ester	Calcd., %		Found, %	
	C	H	C	H
<i>n</i> -Hexyl	50.16	5.97	50.34	5.91
4-Pentenyl	48.70	4.83	48.71	4.87
5-Hexenyl	50.51	5.30	50.22	5.33
Cyclopentanemethyl	50.51	5.30	50.33	5.26
Cyclohexyl	50.51	5.30	50.42	5.19

^a The analyses were performed by Dr. Stephen M. Nagy of the Microchemical Laboratory, Massachusetts Institute of Technology, Cambridge, Mass.

Acetate Esters. These were prepared on small scale from the corresponding alcohols with acetyl chloride and pyridine in ether solution according to the method of Sarel and Newman.²² 5-Hexenyl acetate, b.p. 72.0–72.5° at 22 mm., n_{25}^D 1.4210 (lit.²³ b.p. 169–170° at 704 mm., n_{20}^D 1.4241) was obtained in 61% yield. Cyclohexyl acetate was obtained from

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Dr. Shelton Bank, b.p. 170–172° (lit.²⁴ b.p. 172° at 752 mm.). Cyclopentyl acetate, b.p. 142–144°, n_D^{25} 1.4285 (lit.²⁴ b.p. 153° at 760 mm., n_D^{20} 1.4318), was prepared in 47% yield. 4-Pentenyl acetate, b.p. 132–134°, n_D^{25} 1.4161 (lit.²⁵ b.p. 46–47° at 12 mm., n_D^{25} 1.4159), was obtained in 35% yield. Cyclopentanemethyl acetate, b.p. 165–168°, n_D^{25} 1.4316 (lit.²⁵ b.p. 172.5° at 741 mm., n_D^{25} 1.4340), was obtained in 44% yield. 1-Methylcyclopentanol was prepared from cyclopentanone and methylmagnesium chloride by the method of Collins and Hammond,²⁶ 59% yield, m.p. 34.5–36.5° after sublimation (lit.²⁶ m.p. 35°). 1-Methylcyclopentyl acetate was obtained in 55% yield, b.p. 64° at 32 mm., n_D^{25} 1.4290 (lit.²⁷ b.p. 66–70° at 30 mm., n_D^{25} 1.4291).

Hydrocarbons. 1,5-Hexadiene and cyclohexene were used as obtained commercially. 1-Methylcyclopentene and methylenecyclopentane samples were kindly supplied by Professor A. C. Cope. Bicyclo[3.1.0]hexane, b.p. 81° at 767 mm., n_D^{25} 1.4366, was prepared by the method of Simmons and Smith²⁸ (lit.²⁸ b.p. 81–82°, n_D^{25} 1.4373).

Analyses of Products From Acetolysis Reactions. A sample of the *p*-nitrobenzenesulfonate of from 0.25 to 1.00 g. was dissolved in 5.0–20.0 ml. of dry acetic acid with or without added sodium acetate (*ca.* 1.8 moles). After a suitable period of reaction (2–10 half-lives) at 80°, the solution was cooled and diluted with about 10 volumes of water. The products could then be extracted with *n*-pentane directly or with ether after neutralizing to pH 5 (cooling). The volume of extraction solvent was kept small so that no concentration step was necessary prior to v.p.c. analysis. A measured amount of an internal standard, either *t*-butylbenzene or *n*-pentyl acetate, was added for quantitative analysis.

An F. & M. Model 300 v.p.c. apparatus and an F. & M. Model 609, the latter having a flame ionization detector, were used. Some of the early analyses were performed on a 12-ft. column of 20% silicone grease on Chromosorb P or an 8-ft. column of Ucon P on Chromosorb. For reproducible analyses two columns were eventually used: (1) a 20-ft. diisodecyl phthalate column, for which we are indebted to Miss Kathleen Schueller, which was operated at 150° column and 180° inlet temperature with a helium flow rate of 40.7 ml./min., and (2) a 10-ft. silver nitrate–diethylene glycol column,²⁹ operated at 70° column and 130° inlet temperature, with a helium flow rate of 38.2 ml./min. The silver nitrate column was uniquely effective in separating cyclohexene, 1-methylcyclopentene, and methylenecyclopentane, but was more heat sensitive than the other column. Its chief drawback was that it gave incomplete separation of the two principal acetates, which were separated well by the diisodecyl phthalate column. For authentic samples of the possible solvolysis products, retention times were observed as shown in Table V. A standard solution

Table V. Calibration of Gas Chromatographic Columns

Sample	Retention time, min.	
	AgNO ₃ - DEG	DIDP column
1-Methylcyclopentene	6.9	6.4
Methylenecyclopentane	13.5	5.8
Cyclohexene	18.0	7.8
Cyclohexyl acetate	60.4	56.9
Cyclopentanemethyl acetate	62.4	60.6
5-Hexenyl acetate	73.3	45.8
<i>t</i> -Butylbenzene (standard)	28.3	47.0

containing 0.340 g. of *t*-butylbenzene, 0.380 g. of cyclohexyl acetate, and 0.319 g. of cyclohexene in 10.00 ml. of pentane solution was used to calibrate the chromatograms for registered areas, using the formula $fA_s/A_u = \text{moles S}/\text{moles U}$ where $f = \text{area factor}$, $A_s = \text{area measured for } t\text{-butylbenzene}$, and $A_u = \text{area measured for cyclohexyl acetate or cyclohexene}$. The two area factors were quite different. The one factor was used for all acetates and the other for all olefins.

In order to show that the extractive work-up procedure did not discriminate in favor of olefins or acetates, known amounts of cyclohexene and cyclohexyl acetate were dissolved in acetic acid, worked up, and analyzed by the usual procedure. The recoveries of the two substances were the same within 2%.

Some experiments were carried out to determine whether the reaction and extraction procedure led to further reaction of any of the products. Cyclopentanemethyl acetate and 5-hexenyl acetate in separate tests were unchanged (90% recovery) according to v.p.c. analysis after treatment with 0.271 *N* sodium acetate in acetic acid at 80.8° for a period of time comparable to the *p*-nitrobenzenesulfonate solvolysis period. Cyclohexene and cyclohexyl acetate, after similar treatment for 24 hr., were recovered and analyzed by v.p.c. qualitatively. Neither showed any conversion to known products. 1-Methylcyclopentyl acetate was partially converted to 1-methylcyclopentene in 24 hr. at the same conditions. Most interesting is the fact that methylenecyclopentane was converted into a mixture of 1-methylcyclopentyl acetate and 1-methylcyclopentene. This accords with the fact that its presence is indicated in product mixtures directly injected into the v.p.c. but not in extracted product mixtures.

Infrared spectra of v.p.c.-separated products were obtained by concentrating the sample, injecting the concentrate, and condensing the fractions in 2-mm. tubing at Dry Ice temperature. The spectra were compared to those of authentic material. In the case of 1-methylcyclopentene the spectrum was compared with the one in the API collection.³⁰

Preparation of Silver Nitrate–Diethylene Glycol Column.³¹ Diethylene glycol, the technical grade of the Union Carbide Chemicals Co., was treated with pellets of sodium and distilled. The central portion, boiling at 70–71° (1 mm.), with n_D^{25} 1.4458, was taken. Silver nitrate was added to a stirred solution of the

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(30) American Petroleum Institute, Project No. 44, Infrared Spectrum No. 1834.

(31) Directions for this column preparation were given by Dr. W. R. Moore.

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.

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

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In contrast to 2-(Δ^3 -cyclopentenyl)ethyl *p*-nitrobenzenesulfonate (I), 3-(Δ^3 -cyclopentenyl)propyl *p*-nitrobenzenesulfonate (IV) is acetolyzed without cyclization and without appreciable acceleration by the double bond. However, 3-(3,4-dimethyl- Δ^3 -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-(Δ^3 -cyclopentenyl)ethyl *p*-nitrobenzenesulfonate (I) the solvolysis rate assisted by the double bond is about 75 times greater than that of Δ^5 -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.

