the initial concentration of *t*-butyl bromide, x is the concentration of acid at any time, t, and k is the specific first-order rate constant. The value of k was taken as the slope of the best visual straight line defined by a plot of $\ln[(a)/(a-x)]$ *vs.* t. In the 24.1% water-in-ethanol solvent, where a check was made, the calculated and experimental infinity titers were identical within experimental error. In the 1.00% water-in-ethanol solvent, rates were followed to *ca.* 20% reaction, and in the 24.1% water-in-ethanol solvent, to *ca.* 75% reaction.

No test of the first-order nature of these solvolyses was considered necessary, and all solutions were approximately 0.100 molal in alkyl bromide. The averaged results of the kinetic investigations are given in Table I. All kinetic runs were made in triplicate on solutions involving different batches of solvent, so the uncertainties in the reported rate constants include the uncertainties involved in reproducing the compositions of the solvents.

Vapor Density Measurements and Distribution Coefficients.—With ethyl and isopropyl bromides, the apparatus for the vapor density measurements consisted of a stainless steel bomb and a stainless steel sampler of known volumes. The sampler was fitted at both ends with monel diaphragm valves and could be attached to the bomb or, alternatively, could be integrated into the flow system of a Fisher–Gulf Partitioner. In a vapor density determination, the evacuated sampler was attached to the bomb and an aliquot of a solution of the appropriate alkyl bromide in the appropriate solvent was injected into the bomb through a silicone rubber port. The apparatus was immersed in the constant temperature bath until temperature and vapor equilibria were established, and the valve between the sampler and the bomb was opened for a period of time sufficient for the re-establishment of vapor equilibrium. The valve then was closed, the apparatus was removed from the constant temperature bath, and the sampler was disengaged from the bomb and integrated into the flow system of the vapor-phase chromatography unit. The contents of the sampler were swept into the unit, and the area produced by the alkyl bromide in the resulting chromatogram was recorded. The vapor density corresponding to this area was read from a calibration curve of vapor density *vs.* area established by the same procedure in the same apparatus on the same day. Analyses for ethyl bromide were carried out at 35° on a 10-ft. column of 0.25-in. copper tubing packed with paraffin oil on firebrick. Analyses for isopropyl bromide were carried out at 65° on a composite column consisting of a 10-ft. length of 0.25-in. copper tubing packed with dimethylsulfolane on firebrick, connected in series with a similar piece of tubing packed with paraffin oil on firebrick. Helium was the eluting gas in all cases.

The vapor density measurements with *t*-butyl bromide were carried out in a glass apparatus. The sampler was fitted with a rubber port and was attached, *via* a large-bore stopcock, to a ground glass joint by which it could be joined to the bomb. The bomb was fitted with a rubber port and with a ground glass joint for connection to the sampler. In operation, the assembled apparatus, with the sampler evacuated and the stopcock closed, was immersed in the constant temperature bath. The sample solution was injected into the bomb through the rubber port, and the whole apparatus was rocked, gently, to aid the establishment of equilibrium between the vapor and the solution. After equilibrium was established, the stopcock was opened, and after the system again had reached equilibrium, it was closed. The sampler was then disengaged from the bomb, 10 ml. of water was injected into the sampler through the rubber port, and the sampler was shaken for a period of time ascertained to be sufficient for the complete hydrolysis of the *t*-butyl bromide. The contents of the sampler were then titrated to the phenolphthalein end-point with standard sodium hydroxide. The moles of base consumed was taken as equal to the moles of *t*-butyl bromide initially present in the sampler, and the vapor density was calculated from this value and the known volume of the sampler. With the 24.1% water-in-ethanol solvent, significant reaction occurred during the measurements. With this solvent, two vapor density measurements were made in succession, and the values obtained were extrapolated back to the time of mixing of the solution to give the approximate vapor density above the solution at 0% reaction. In these cases, no great precision was expected nor obtained; five values so obtained had an average deviation of ±20% from the mean.

All vapor density measurements were made on solutions which were approximately 0.100 molal in alkyl bromide. The distribution coefficients were calculated with the aid of equation 5 from the measured vapor densities and the known compositions of the solutions. The averaged values of the distribution coefficients are given in Table I. Each value represents the average of at least three determinations involving different batches of solvent; hence the uncertainties in the reported distribution coefficients include the uncertainties involved in reproducing the compositions of the solvents.

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CHICAGO 37, ILL.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

The Solvolysis of *cis*-5-Cyclodecen-1-yl *p*-Toluenesulfonate in Acetic Acid and Ethanol

BY HARLAN L. GOERING, HERBERT H. ESPY[1] AND WILLIAM D. CLOSSON[2]

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Acetolysis of *cis*-5-cyclodecen-1-yl *p*-toluenesulfonate at 20° results in the formation of *ca.* 0.8 equivalent of *p*-toluenesulfonic acid by a clean first-order process. Ethanolysis gives about 0.9 equivalent of acid. The remainder of the *p*-toluenesulfonic acid is liberated at higher temperatures. Since the original *p*-toluenesulfonate was homogeneous this behavior shows that solvolysis is accompanied by rearrangement to a relatively unreactive product. The ratio of rearrangement to solvolysis is not affected by the presence of *p*-toluenesulfonate ion which indicates that the rearrangement is intramolecular. The rearrangement product from the acetolysis liberates *p*-toluenesulfonic acid at a measurable rate at 80°. The kinetic behavior of this material indicates that two rearrangement products (tosylates) are formed. The first-order rate of solvolysis of *cis*-5-cyclodecen-1-yl *p*-toluenesulfonate is larger than that of cyclodecyl *p*-toluenesulfonate by factors of seven for acetolysis and ten for ethanolysis. Rates of acetolysis of the four isomeric 1-decalyl *p*-toluenesulfonates are reported.

Introduction

Kinetic and product studies have shown that in several systems solvolysis involves participation by π-electron-containing substituents one or more carbon atoms removed from the reaction center. Such participation results in anchimeric acceleration[3] in the cholesteryl,[4] *anti*-7-norbornenyl,[5]

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[1] Carbide and Carbon Fellow 1955–1956; du Pont Summer Research Fellow, 1956.

[2] Wisconsin Alumni Research Foundation Fellow, 1956–1957.

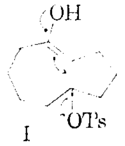
[3] S. Winstein, C. R. Lindegren, H. Marshall and L. L. Ingraham, THIS JOURNAL, **75**, 147 (1953).

[4] S. Winstein and R. Adams, *ibid.*, **70**, 838 (1948); M. Simonetta and S. Winstein, *ibid.*, **76**, 18 (1954).

[5] S. Winstein, M. Shatavsky, C. Norton and R. B. Woodward, *ibid.*, **77**, 4183 (1955); S. Winstein and M. Shatavsky, *ibid.*, **78**, 592 (1956).

exo-5-norbornenyl,[6] arylalkyl[7] and benzcycloöcten-3-yl[8] systems. Product studies also indicate that solvolysis involves participation by the carbon-carbon double bond or aryl group in these systems.

In an earlier paper[9] evidence was presented that the ethanolysis of 6-ketocyclodecyl *p*-toluenesulfonate involves acid-catalyzed enolization followed by rapid solvolysis of the enol (I) to give bicyclo[5.3.0]decan-2-one. The formation of bicyclic ketone and the rapid rate of solvolysis of I—the kinetic data indicate that I solvolyzes well over 10^3 times faster than cyclodecyl *p*-toluenesulfonate[9]—was attributed to participation by the enolic double bond as illustrated by the curved arrows in I. Scale models as well as other studies concerning transannular interactions[10,11] indicate that the proximity of the double bond and C_1 in the 5-cyclodecen-1-yl system is suitable for such participation.



I

II

In the present work we have examined the rates of ethanolysis and acetolysis of *cis*-5-cyclodecen-1-yl *p*-toluenesulfonate (II) to determine whether the transannular double bond has any effect on the solvolytic reactivity. Cope and co-workers[11] recently have reported that the solvolysis of II[12] in diethylaniline gives a mixture of 1,9- and *cis*-1,2-octalin. The apparently exclusive formation of bicyclo[4.4.0]decenes clearly shows that the double bond is indeed involved at some stage of the solvolysis under these conditions. An investigation of the products resulting from the solvolysis of II in hydroxylic solvents is in progress in another laboratory[13]; for this reason the present investigation was confined to the kinetics of solvolysis.

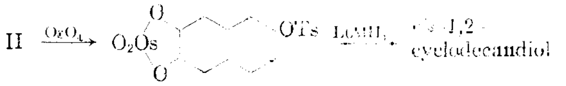
Results

The *cis*-5-cyclodecen-1-yl *p*-toluenesulfonate (II) used in the present work was prepared by a modification of the method described by Cope and co-workers.[11,12] Decalin was converted directly to 11-oxabicyclo[4.4.1]undec-1-yl acetate[14] which was hydrolyzed to 6-ketocyclodecanol. The keto alcohol was converted to trimethyl-6-hydroxycyclodecylammonium hydroxide which was converted to 5-cyclodecen-1-ol.[11]

The unsaturated alcohol obtained by this method was assumed previously[11] to be *trans*-5-cyclodecen-1-ol because of (a) the absorption at 10.18 μ in the infrared spectrum and (b) the method used to introduce the double bond. The absorption at 10.18 μ is indeed probably due to the presence of the *trans* isomer; however, it appears that the product is primarily the *cis* isomer. The *p*-toluenesulfonate II obtained in yields of up to 40% and *p*-chlorobenzoate (34% yield) are both derivatives of *cis*-5-cyclodecen-1-ol. The crude *p*-toluenesulfonate did not appear to contain any of the *trans* isomer. Presumably the *trans* isomer is considerably more reactive than the *cis* isomer and completely destroyed prior to isolation. The crude *p*-chlorobenzoate contained an isomer, probably *trans*-5-cyclodecen-1-yl *p*-chlorobenzoate, which was removed (but not purified) by recrystallization.

Pure *cis*-5-cyclodecen-1-ol was obtained by hydrolysis of the *p*-chlorobenzoate. Comparison of spectra showed that the pure *cis*-alcohol has a much lower absorption at 10.18 μ than the crude 5-cyclodecen-1-ol. The pure *cis*-alcohol was converted to II in 67% yield.

The configuration of the double bond in the unsaturated *p*-toluenesulfonate (II) was established by *cis* hydroxylation of the double bond (OsO_4) and removal of the *p*-toluenesulfonate group ($LiAlH_4$) as illustrated below.[15] The glycol resulting from the lithium aluminum hydride reduction was identified as the known[16] *cis*-1,2-cyclodecandiol. The formation of the *cis*- rather than the *trans*-glycol demonstrates beyond all reasonable doubt that the double bond in II has the *cis* configuration.



Acetolysis of *cis*-5-cyclodecen-1-yl *p*-toluenesulfonate (II) at 20° and 30° resulted in the formation of *ca.* 0.82 equivalent of *p*-toluenesulfonic acid by a clean first-order process, *i.e.*, the infinity titer observed after ten half-periods was about 82% of the calculated value. Subsequent heating of the reaction solutions at 80° for several hours increased the titer to the calculated value.

The first-order rate constants for the acetolysis of II at 20 and 30° were determined from the rate of acid formation which was measured by intermittent titration of the entire reaction mixture[17] with a standard solution of sodium acetate in anhydrous acetic acid. The "infinity titers" observed after ten half-periods at the reaction temperature were used to calculate the specific first-order constants. In each kinetic experiment the reaction was followed to about 75% completion and ten or more values of the constant were determined from appropriately spaced titrations. The rate constants determined in this way did not show any trends and were reproducible. A typical kinetic experiment which illustrates the first-order behavior of

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(6) J. D. Roberts, W. Bennett and R. Armstrong, THIS JOURNAL, **72**, 3329 (1950); J. D. Roberts and W. Bennett, *ibid.*, **76**, 4623 (1954); S. Winstein, H. M. Walborsky and K. C. Schreiber, *ibid.*, **72**, 5795 (1950).

(7) S. Winstein, *et al.*, *ibid.*, **79**, 756, 3105, 3114, 4238 (1957).

(8) R. Huisgen, *Angew. Chem.*, **69**, 341 (1957).

(9) H. L. Goering, A. C. Olson and H. H. Espy, THIS JOURNAL, **78**, 5371 (1956).

(10) H. J. Urech and V. Prelog, *Helv. Chim. Acta*, **40**, 477 (1957); N. J. Leonard, *Record Chem. Progress*, **17**, 243 (1956).

(11) A. C. Cope, R. J. Cotter and G. G. Roller, THIS JOURNAL, **77**, 3594 (1955).

(12) The double bond in II previously was assumed to have the *trans* configuration, ref. 11. In the present work it was shown that II is the *cis* isomer.

(13) A. C. Cope, private communication; see also reference 11.

(14) H. E. Holmquist, H. S. Rothrock, C. W. Theobald and B. E. Englund, THIS JOURNAL, **78**, 5339 (1956).

(15) This method for establishing the configuration was suggested by Drs. A. Eschenmoser and V. Prelog.

(16) (a) V. Prelog, K. Schenker and H. Günthard, *Helv. Chim. Acta*, **35**, 1598 (1952); (b) A. T. Blomquist, R. E. Burge and A. C. Sucsy, THIS JOURNAL, **74**, 3636 (1952).

(17) (a) P. D. Bartlett and C. G. Swain, *ibid.*, **71**, 1406 (1949); (b) H. L. Goering and K. L. Howe, *ibid.*, **79**, 6542 (1957).

the acetolysis is included in the experimental section and the results of the pertinent kinetic experiments are summarized in Table I. Some of the first-order constants (k) given in Table I are average values (and average deviations) of two or more independent experiments. The rest of the constants are average values (and average deviations) of ten or more determinations made during the experiment. When acid was allowed to accumulate (run 7) the rate was within experimental error of the rate observed when base was added at the outset (run 8). These experiments and the fact that reproducible rate constants were obtained show that the first-order rate of solvolysis is not disturbed by intermittent titration of the reaction mixture.

TABLE I

SOLVOLYSIS OF *cis*-5-CYCLODECEN-1-YL *p*-TOLUENESULFONATE

Run	Temp., °C.	[ROTs][a] 10^2 M	n[b]	Added salt[a] 10^2 M	10^5k, sec.$^{-1}$
		Ethanolysis			
1 A,B	20.05	0.9–1.0	2		4.42 ± 0.02
2		.818	1		4.44 ± .15[c]
3 A,B	29.97	.9–1.0	2		16.6 ± .1
4 A,B		.6–0.7	2		17.0 ± .4[d]
		Acetolysis			
5 A,B	20.05	0.9–1.0	2		16.5 ± 0.3
6 A-G	29.97	.9–1.0	7		62.6 ± .7
7		.890	1		60.3 ± .5[e]
8		.952	1		62.4 ± .3[f]
9		.949	1		64.3 ± .7[g]
10		.973	1		63.8 ± .8[h]
11		4.88	1		63.3 ± .5
12		0.913	1	5.14 NaOTs	63.4 ± .5
13		.950	1	0.82 $LiClO_4$	61.3 ± .8
14		.949	1	2.18 $LiClO_4$	66.6 ± 1.0
15		.892	1	3.13 $LiClO_4$	73.8 ± 0.9
16		.874	1	4.10 $LiClO_4$	78.7 ± 1.0
17		.902	1	5.24 $LiClO_4$	81.9 ± 0.9

[a] Initial concentrations. [b] Number of independent kinetic experiments. [c] The ampule technique was used in this experiment. [d] Tosylate prepared from alcohol obtained by reduction of 5-cyclodecenone was used in this experiment. [e] Determined from titrations after 1 and 2 half-lives; acid was allowed to accumulate between titrations. [f] Determined from two points; one-half of the calculated amount of titrant was added at the outset and one-fourth of the calculated amount was added after the first point. [g] The tosylate used in this experiment was recrystallized six times. [h] The tosylate used in this experiment was prepared from alcohol regenerated from the pure *p*-chlorobenzoate.

As shown by runs 13 to 17, addition of lithium perchlorate results in a positive salt effect. A plot of k *vs.* [$LiClO_4$] shows scatter but no indication of curvature and thus there is no evidence for a "special"[18] salt effect. The average deviation of the values of k from the best straight line is $< 3\%$ of k. Comparison of runs 6A-G, 12 and 17, shows that the salt effect of sodium *p*-toluenesulfonate, a common-ion salt, is very small compared to that of lithium perchlorate. The small salt effect of the common-ion salt is also apparent from the fact that the rate constants determined by the intermittent titration method did not show any trends. In runs without added salt the concentration of sodium *p*-toluenesulfonate varied from zero to about three-fourths of the initial concentration of II without affecting the rate to a detectable extent.

The relative effects of lithium perchlorate (b^{18b} is *ca.* 7) and the common-ion salt (b^{18b} is <1) are similar to those that have been observed for the acetolysis of other *p*-toluenesulfonates.[18] Apparently the small effect of the common-ion salt is not due to external return.[19] The present data show that the normal[18] salt effect of sodium *p*-toluenesulfonate is small and thus if external return were involved the addition or accumulation of the common ion would be expected to depress the rate.

Ethanolysis of II at 20 and 30° is similar to acetolysis in that less than an equivalent amount of acid is produced. In this case the observed "infinity titer" determined after ten half-lives at the reaction temperature is about 90% of the calculated value. The remainder of the acid is produced when the solutions are heated. The reactions were followed to about 75% completion and excellent first-order behavior was observed. A typical kinetic experiment is included in the experimental section and the pertinent experiments are summarized in Table I. The reactions were followed by intermittent titration of the entire reaction mixture with a standard solution of sodium ethoxide in ethanol. The sealed ampule technique was used in one experiment (run 2) and as indicated in Table I the rate constant agreed well with that obtained by the intermittent titration method; *cf.* runs 1 and 2.

The discrepancy between the observed and calculated "infinity titers" is due to the fact that solvolysis is accompanied by rearrangement to a relatively unreactive product. The process can be summarized as shown. In this scheme k_s

$$\text{solvolysis prod.} \xleftarrow{k_s} \text{II} \xrightarrow{k_r} \text{rearrangement prod.}$$

is the first-order constant for solvolysis and k_r is the first-order constant for rearrangement. The constants given in Table I are rate constants for the first-order disappearance of II and thus correspond to $k_r + k_s$. The rearrangement product does not solvolyze to a detectable extent during a period corresponding to ten half-periods for the solvolysis. Thus, rearrangement does not disturb the first-order rate of formation of solvolysis products. The titer is increased to the calculated value by heating the reaction mixtures to 80° or over for several hours. The amount of rearrangement can be determined readily from this increase in titer and the amount of solvolysis is measured by the "infinity titer" at 20 or 30°. The ratios of rearrangement to solvolysis, k_r/k_s, for various conditions are presented in Table II. Most of these values are average values (and average deviations) of two or more independent determinations. Some of the values included in the table were determined from "infinity titers" observed in the kinetic experiments and the titers of the reaction mixtures after heating. These values are not as accurate as those obtained from experiments designed to determine the ratios. In the latter experiments two or more aliquots of reaction mixture were heated at 30° for a period corresponding to ten half-periods for the solvolysis and two or

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(18) (a) A. H. Fainberg and S. Winstein, THIS JOURNAL, **78**, 2767 (1956); (b) **78**, 2763, 2780 (1956).

(19) S. Winstein, E. Clippinger, A. H. Fainberg, R. Heck and C. G. Robinson, *ibid.*, **78**, 328 (1956).

more aliquots were heated at 100° until the solvolysis of the unreactive rearrangement product was complete.

TABLE II

RATIO OF REARRANGEMENT TO SOLVOLYSIS OF *cis*-5-CYCLODECEN-1-YL *p*-TOLUENESULFONATE

Temp., °C.	[ROTs],[a] 10^2 M	n[b]	Added material 10^2 M	k_r/k_s
			Ethanolysis	
29.97	0.9	3		0.13 ± 0.01
	.7	2		.11 ± .01[c]
			Acetolysis	
20.05	0.9	2		0.18 ± 0.03[d]
29.97	.9	3		.22 ± .01
	.973	1		.16[d,e]
	.949	1		.18[d,f]
	5.0	4		.20 ± .01
	0.870	1	5.02 NaOTs	.22
	.872	1	5.13 $LiClO_4$	.20
	.9	2	1.0 NaOAc	.23 ± .01
	.9	3	2.0 NaOAc	.18 ± .03
	5.0	2	5.2 NaOAc	.154 ± .002
	0.898	1	1.10 HOTs	.18
	.949	1	2.20 HOTs	.21

[a] Initial concentration. [b] Number of independent experiments. [c] Determined using tosylate from alcohol prepared by reduction of the corresponding unsaturated ketone. [d] These values were calculated from data obtained in kinetic experiments. The accuracy is lower than in other cases and these values are intended to be a qualitative indication of k_r/k_s. [e] Determined using tosylate from alcohol regenerated from pure *cis*-5-cyclodecen-1-yl *p*-chlorobenzoate. [f] Determined using tosylate recrystallized four times from ethyl ether–pentane and twice from acetone–pentane.

The data presented in Table II show that k_r/k_s is not affected by the addition of lithium perchlorate, toluenesulfonic acid or sodium *p*-toluenesulfonate. The ratio is somewhat lower for ethanolysis than for acetolysis and it appears that it is depressed by the addition of sodium acetate.

Samples of II derived from different batches of *cis*-5-cyclodecen-1-ol were used in the experiments summarized in Tables I and II. Various methods were used to purify different samples of the alcohol, *e.g.*, distillation, chromatography, recrystallization of a solid derivative, etc. All of the samples of II gave the same values for k_r/k_s (Table II) and k (Table I). The value of k_r/k_s was not changed by several recrystallizations of II. From these observations it is clear that the samples of II were not contaminated by an unreactive isomer. Thus the unreactive material is produced during the solvolysis. This is also shown by the fact that different values of k_r/k_s are obtained for acetolysis and ethanolysis.

It seemed likely that the unreactive *p*-toluenesulfonate formed by the rearrangement might be 1-decalyl *p*-toluenesulfonate or bicyclo[5.3.0]dec-2-yl *p*-toluenesulfonate. The four isomeric 1-decalols[20] and the corresponding *p*-toluenesulfonates[21] are known; however, the isomeric bicyclo[5.3.0]decan-2-ols are apparently unknown.[21d] Attempts to isolate the rearrangement product were unsuccessful and in order to obtain information concerning the identity of this material its rate of acetolysis at 80° was determined for comparison with the rates of acetolysis of the isomeric 1-decalyl *p*-toluenesulfonates.

Solutions of the rearrangement product were prepared by heating 0.05 M solutions of II at 30° for ten half-lives (calculated from k for run 11, Table I). After titration with 0.25 M sodium acetate in acetic acid the resulting solution (about 0.04 M sodium *p*-toluenesulfonate and 0.005 M rearrangement product) was distributed into ampules and the rate of acetolysis was determined in the usual manner. The apparent first-order rate constants determined from the rate of acetolysis showed a considerable downward trend. Apparently this behavior is due to the fact that the rearrangement product consists of two *p*-toluenesulfonates which solvolyze at different rates.

In Fig. 1 a plot of log [ROTs] *vs.* time is presented. This can be resolved into two straight lines by the method of Brown and Fletcher,[22] which indicates that two compounds are reacting simultaneously. The rate constant and initial concentration of the slower component (β-tosylate) are given by the slope and intercept of the straight line in Fig. 1. The rate of the fast component (α-tosylate) is obtained from a plot of log $[ROTs]_{total}$ − log $[ROTs]_\beta$ *vs.* time. These data show that α-tosylate and β-tosylate were present in about equal amounts at zero time. Since some of the α-tosylate solvolyzed during temperature equilibration, *i.e.*, before zero time on the plot, it is clear that rearrangement gives more α-tosylate than β-tosylate.

The rate constants for α-tosylate and β-tosylate, obtained by the method described above, are presented in Table III together with the rate constants for the four isomeric 1-decalyl *p*-toluenesulfonates. The rate constants for α-tosylate and β-tosylate have rather large uncertainties as would be expected since they were determined graphically from the rate of formation of the last 15% of the *p*-toluenesulfonic acid formed. In this connection it is noteworthy that these constants were reproducible; *cf.* run 18 and 19. It is even more significant that in a control experiment (run 23) the acetolysis of 0.01 M *trans–trans*-1-decalyl *p*-toluenesulfonate in the presence of 0.05 M sodium *p*-toluenesulfonate (*i.e.*, conditions which simulate those for the solvolysis of the rearrangement product) showed excellent first-order behavior.

Comparisons of the rate data in Table III suggest that β-tosylate is probably *cis–trans*-1-decalyl *p*-toluenesulfonate. These data also suggest that α-tosylate may be *cis–cis*-1-decalyl *p*-toluenesulfonate or *trans–cis*-1-decalyl *p*-toluenesulfonate. However, it is difficult to see how II could be converted to either of these two by an intramolecular process (see Discussion).

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[20] W. G. Dauben, R. C. Tweit and C. Mannerskantz, THIS JOURNAL, **76**, 4420 (1954).

[21] (a) W. Hückel, *Ber.*, **77B**, 805 (1944); (b) W. Hückel and R. Schwen, *Ann.*, **604**, 97 (1957); W. Hückel, O. Neunhoeffer, A. Gercke and E. Frank, *ibid.*, **477**, 99 (1930); (c) W. Hückel, H. Havekoss, K. Kumetat, D. Ullmann and W. Doll, *ibid.*, **533**, 128 (1938); (d) Note

ADDED IN PROOF.—One of the isomeric bicyclo[5.3.0]decan-2-ols has been described recently by A. C. Cope, M. Brown and H. Lee, THIS JOURNAL, **80**, 2855 (1958).

[22] H. C. Brown and R. S. Fletcher, *ibid.*, **71**, 1845 (1949).

TABLE III

ACETOLYSIS RATE CONSTANTS FOR REARRANGEMENT PRODUCTS AND 1-DECALYL *p*-TOLUENESULFONATES

Run	Compound	Temp., °C.	ROTs, 10^2 *M*	Salt, 10^2 *M*	10^5k, sec.$^{-1}$
18	α-Tosylate	79.65	0.3	3.7 NaOTs	121 ± 20[a]
18	β-Tosylate	79.65	.3		7.5 ± 0.5[a]
19	α-Tosylate	79.65	.3	0.8 NaOAc 3.7 NaOTs	123 ± 10[a]
19	β-Tosylate	79.65	.3		7.1 ± 0.6[a]
		1-Decalyl tosylate[b]			
20	*trans-trans*	99.82	1.0		16.5 ± 0.2
21		99.82	1.0	2.5 NaOTs	17.9 ± .1
22		79.65	1.0		1.63 ± .02
23		79.65	1.0	5.0 NaOTs	1.98 ± .04
24[c]	*trans–cis*	79.65	1.2		86 ± 1
25[c]		79.65	1.2	3.7 NaOTs	96 ± 1
26[c]	*cis–cis*	79.65	1.2		118 ± 2
27[c]		79.65	1.2	3.7 NaOTs	134 ± 3
28[c]		79.65	1.0	3.7 NaOTs 1.1 NaOac	135 ± 2
29[c]	*cis–trans*	79.78	1.28		6.81 ± 0.17
30[c]		79.78	1.28	3.7 NaOTs	7.59 ± 0.15

[a] Determined graphically from plots of log ROTS *vs.* time. [b] The indicated configurations refer to the C_9C_{10} and C_9C_1 hydrogen atoms. [c] These experiments were carried out in duplicate. The values of *k* are the average values of the two independent experiments.

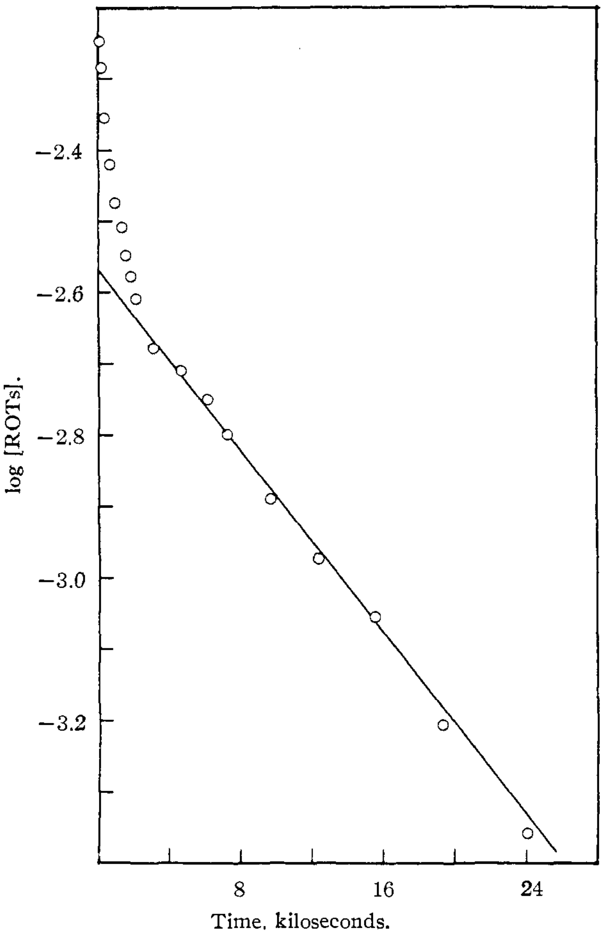

Fig. 1.—Acetolysis of products resulting from rearrangement of 5-cyclodecen-1-yl *p*-toluenesulfonate.

Discussion

It is of interest to compare the rates of solvolysis of *cis*-5-cyclodecen-1-yl *p*-toluenesulfonate (II) and cyclodecyl *p*-toluenesulfonate to determine if participation by the double bond in II is involved in the rate-determining step of the solvolysis. The first-order constants for acetolysis and ethanolysis of cyclodecyl *p*-toluenesulfonate at 20.11° are 2.42×10^{-5} sec.$^{-1}$ and 0.42×10^{-5} sec.$^{-1}$, respectively.[9] Thus II solvolyzes 10 times faster in ethanol and 7 times faster in acetic acid than cyclodecyl *p*-toluenesulfonate. Both compounds solvolyze faster in acetic acid than in ethanol, $k_{\mathrm{HOAc}}/k_{\mathrm{EtOH}} = 3.7$ for II and 5.8 for cyclodecyl *p*-toluenesulfonate, which indicates[23] that in each case the rate-determining step involves ionization (*i.e.*, a carbonium-ion mechanism) rather than nucleophilic participation by the solvent. The greater apparent rate of ionization of II than of the saturated analog may be due to participation by the double bond. However, a difference of this magnitude could be due to other factors, *e.g.*, conformational effects. The fact that the difference in reactivity is greater for ethanolysis than acetolysis suggests that it is probably due to participation by the double bond. The nucleophilic assistance, or driving force, resulting from such participation would be expected to be more important in the poorer ionizing solvent (ethanol). In this connection it is interesting to note that the anchimeric acceleration resulting from Ar_{1-3}[24] participation in the solvolysis of β-triphenylethyl *p*-toluenesulfonate is a little larger in ethanol than in acetic acid.[25]

The rearrangement which accompanies solvolysis also indicates that participation by the double bond is involved. Evidently the rearrangement involves "internal return"[19] from an ion-pair intermediate. The fact that the ratio of rearrangement to solvolysis, k_r/k_s, is not affected by the presence of a common-ion salt or lithium perchlorate indicates that rearrangement does not involve "external return" or "ion-pair return" from an "external"[19] ion-pair intermediate. The smaller value of k_r/k_s in ethanol than in acetic acid and the fact that this ratio for acetolysis is decreased by the addition of acetate ion is consistent with the idea that rearrangement involves "internal return." It has been observed[26] with other systems that the ratio of "internal return" to solvolysis is greater in acetic acid than in ethanol.

Participation by the double bond could result in the formation of either [4.4.0]- or [5.3.0]bicyclic products as illustrated by III. The enolic double bond in I participates so as to give rise to a [5.3.0]-bicyclic product as would be expected. However, it appears that II gives largely [4.4.0]bicyclic products. This is indicated by the formation of *cis*-1,2- and 1,9-octalin when II is solvolyzed in diethylaniline[11,27] and by the fact that one of the

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(23) S. Winstein and H. Marshall, THIS JOURNAL, **74**, 1120 (1952); S. Winstein, A. H. Fainberg and E. Grunwald, *ibid.*, **79**, 4146 (1957).

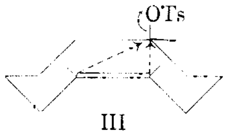
(24) S. Winstein, R. Heck, S. Lapporte and R. Baird, *Experientia*, **12**, 138 (1956).

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

(26) (a) S. Winstein and K. C. Schreiber, *ibid.*, **74**, 2165 (1952); (b) H. L. Goering, T. D. Nevitt and E. F. Silversmith, *ibid.*, **77**, 5026 (1955).

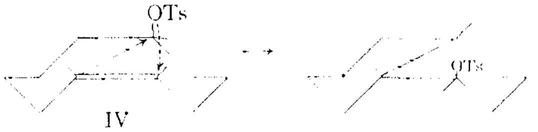
(27) It is not clear whether or not solvent participation is involved under these conditions.

products resulting from the intramolecular rearrangement (β-tosylate) appears to be *cis–trans*-1-decalyl *p*-toluenesulfonate and the other (α-tosylate) may be *cis–cis-* or *trans–cis*-1-decalyl *p*-toluenesulfonate.



III

It is interesting to note that the conversion of II to *cis–trans*-1-decalyl *p*-toluenesulfonate appears to be consistent with available information[26b,28] concerning the stereochemical relationship between products and reactants for rearrangements of this type, *i.e.*, intramolecular rearrangements involving "internal return." This conversion is illustrated by IV. It is difficult to visualize the conversion of II to *trans–cis-* or *cis–cis*-1-decalyl *p*-toluenesulfonate by an intramolecular process. For this reason it appears that α-tosylate may be a [5.3.0]- rather than a [4.4.0]bicyclic tosylate.



IV

It seems likely that the "internal" ion-pair intermediate(s) involved in the rearrangement is (are) common to both rearrangement and solvolysis as

$$\begin{tikzcd}
\text{II} \arrow[r, "k_1"] & \text{intermediate(s)} \arrow[r, "k_3"] \arrow[dl, "k_2"'] \arrow[d, "k_4"] & \beta\text{-tosylate} \\
\alpha\text{-tosylate} & \text{solvolysis product} &
\end{tikzcd}$$

As indicated, more than one "internal" ion-pair intermediate may be involved in the ionization, *i.e.*, the initially formed intermediate may rearrange to and perhaps be in equilibrium with other species of this same type. Only "internal" ion-pair intermediates are considered in the above scheme. Additional intermediates of the type described by Winstein and co-workers[19] are presumably involved in the conversion of the "intermediate(s)" to solvolysis product. The rate constants (k) in Table I correspond to k_1, and k_r and k_s are $k_1(k_2 + k_3)/(k_2 + k_3 + k_4)$ and $k_1k_4/(k_2 + k_3 + k_4)$, respectively.

There are several possible structures for the carbonium ion(s) involved in the ionization of II. Because the apparent anchimeric acceleration is small, one cannot rule out the possibility that ionization results in the formation of the *cis*-5-cyclodecen-1-yl cation which subsequently rearranges, *i.e.*, participation may not be involved in the rate-determining ionization. It seems more likely, however, that ionization results in the direct formation of a rearranged ion, *e.g.*, the *cis*-1-decalyl carbonium ion, or a non-classical carbonium ion.

Experimental

5-Cyclodecen-1-ol.—Commercial decalin was purified by passing it through a column of silica gel and converted directly to 11-oxabicyclo[4.4.1]undec-1-yl acetate, m.p. 102–104°, according to the method of Holmquist, *et al.*[14] The conversion (based on *cis*-decalin) was 1–2%. The ester was saponified by refluxing in aqueous methanol containing two equivalents of potassium hydroxide. After neutralization with acetic acid, two equivalents of hydroxylamine hydrochloride and two equivalents of sodium acetate were added together with enough water so that the refluxing solution was homogeneous. After refluxing for 0.5 hour the solution was concentrated under reduced pressure and chilled. An 82% yield (based on the acetate) of 6-hydroxycyclodecanone oxime separated which after recrystallization from aqueous methanol melted at 113–114° (lit.[29] m.p. 111–112°). The oxime was converted to 5-cyclodecen-1-ol, b.p. 91–93° (2 mm.), n^{25}D 1.5057 (lit.[11] b.p. 77–78° (0.25 mm.), n^{25}D 1.5030–1.5050), in 42% yield according to the method of Cope and co-workers.[11] The infrared spectrum of the product appeared to be indistinguishable from the published spectrum.[11] This product was assumed previously[11] to be *trans*-5-cyclodecen-1-ol. However, the present work shows that this product consists primarily of the *cis* isomer.

The alcohol was converted to the α-naphthylurethan which melted at 137.8 to 138.8° (aqueous ethanol).

Anal. Calcd. for $C_{21}H_{25}NO_2$: C, 77.98; H, 7.79. Found: C, 78.25; H, 7.70.

The phenylurethan melted at 111.5–112.5° (aqueous ethanol).

Anal. Calcd. for $C_{17}H_{23}NO_2$: C, 74.69; H, 8.48. Found: C, 74.37; H, 8.46.

The crude 5-cyclodecen-1-ol was converted to *cis*-5-cyclodecen-1-yl *p*-chlorobenzoate, m.p. 66–67° (pentane) (34% yield of pure product) by the method used previously[30] to convert alcohols to *p*-nitrobenzoate derivatives.

Anal. Calcd. for $C_{17}H_{21}ClO_2$: C, 69.73; H, 7.23. Found: C, 69.93; H, 7.20.

Pure *cis*-5-cyclodecen-1-ol, m.p. 43–44.3°, b.p. 91–93° (1.3 mm.), n^{25}D 1.5074, was obtained from the *p*-chlorobenzoate, m.p. 64–65°, as follows. A solution of 9.66 g. (0.033 mole) of ester in 150 ml. of methanol containing 7.3 g. (0.13 mole) of potassium hydroxide was refluxed for 4 hours. After concentration to near dryness under reduced pressure the residue was diluted with water and extracted with pentane. After drying (Na_2SO_4) the pentane was removed and the alcohol distilled. The crystalline product was purified further by recrystallization. The yield was 3.83 g. (75%).

The *p*-toluenesulfonate, m.p. 62–62.8°, obtained from this alcohol was identical with that obtained (in lower yield) from the crude 5-cyclodecen-1-ol.

***cis*-5-Cyclodecen-1-yl *p*-Toluenesulfonate** (II).—5-Cyclodecen-1-ol was converted to *cis*-5-cyclodecen-1-yl *p*-toluenesulfonate (II), m.p. 61.2–61.6° (ether-pentane) (lit.[11,12] m.p. 62.2–63.2°) in about 40% yield according to the method of Cope and co-workers.[11,12] This material had the correct composition (carbon–hydrogen analysis) and the average value of 10 determinations of the solvolysis equivalent was 309 ±2 (theory 308.4).

Samples of alcohol purified by various methods were converted to tosylate by this method. These samples of alcohol were purified by (a) fractionation, (b) chromatography on alumina and (c) regeneration from the *p*-chlorobenzoate, m.p. 66–67°. The *p*-toluenesulfonate derivatives of these samples of alcohols were used in the kinetic experiments.

The *p*-toluenesulfonate was also prepared from alcohol obtained by reduction of 5-cyclodecen-1-one[31] with lithium aluminum hydride. Alcohol prepared by this method gave erratic results, occasionally giving the desired product, m.p. 58–60°, sometimes giving only oily material and sometimes a product melting at 96–98°. The infrared spectra and rate constants for the material which melted at 58–60° were the same as those for the *cis*-5-cyclodecen-1-yl *p*-toluenesulfonate described above.

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[28] D. J. Cram, *et al.*, THIS JOURNAL, **76**, 28 (1954), and previous papers in this series.

[29] A. C. Cope, E. J. Cotter and G. G. Roller, *ibid.*, **77**, 3590 (1955).

[30] H. L. Goering and J. Blanchard, *ibid.*, **76**, 5405 (1954).

[31] A. C. Cope and G. Holzman, *ibid.*, **72**, 3062 (1950).

Configuration of Double Bond in 5-Cyclodecen-1-yl *p*-Toluenesulfonate.—The configuration of the double bond in II (and thus in the alcohol and *p*-chlorobenzoate) was established as follows.[15] A solution of 1.23 g. (3.94 mmoles) of II and 3 ml. of dry pyridine in 7 ml. of dry tetrahydrofuran was chilled in a Dry Ice-bath. A solution of 1 g. (3.93 mmoles) of osmium tetroxide in 3 ml. of tetrahydrofuran was added to the chilled solution after which the resulting mixture was allowed to stand at −80° for four hours. The reaction mixture was poured into 150 ml. of cold anhydrous ether and chilled to −80° for 2 hours to precipitate the cyclic osmic ester. The osmic ester was separated by filtration, washed with ether and dissolved in 100 ml. of dry tetrahydrofuran. This solution was added slowly to a solution of 1 g. of lithium aluminum hydride in 80 ml. of tetrahydrofuran and the resulting solution was refluxed for 12 hours. After decomposition of the excess lithium aluminum hydride (dilute aqueous HCl) the reaction mixture was diluted with dilute hydrochloric acid. The resulting solution (just acid to congo red) was concentrated under reduced pressure to remove the organic solvent. The residue was diluted with 350 ml. of water and the resulting solution was extracted (ether) for 20 hours with a continuous extractor. After evaporation of the ether the residue was treated with 20 ml. of pentane and the crude solid cyclodecanediol was collected by filtration. This material was recrystallized from methanol–isopropyl ether mixture to constant melting point. In this way 0.128 g. (19%) of pure *cis*-1,2-cyclodecanediol, m.p. 138–139° (lit. 140°,[16a] 135–138°[16b]) was obtained. The infrared spectrum of this material (Nujol mull) appeared to be indistinguishable from the published spectrum[16a] of the *cis*-glycol.

1-Decalyl-*p*-toluenesulfonates.—The *trans-trans*-1-decalol, m.p. 60.4–60.7° (lit.[20] m.p. 58–59.5°), and *cis–cis*-1-decalol, m.p. 91.0–91.8° (lit.[20] m.p. 89–91.5°), were prepared by the methods described by Dauben and co-workers.[20] *trans-trans*-1-Decalyl *p*-toluenesulfonate, m.p. 98.3–98.7° (ether-pentane), solvolysis equivalent 308 (theory 308.4) (lit.[21a] m.p. 98°), and *cis–cis*-1-decalyl *p*-toluenesulfonate, m.p. 88–88.5°, solvolysis equivalent 310 (theory 308.4) (lit.[21b] m.p. 96–97°), were prepared from the alcohols by the method used to prepare II.[32]

trans-cis-1-Decalol was obtained as follows. *trans*-1-Decalone was converted to a mixture of *trans–cis*- and *trans-trans*-1-decalol by hydrogenation of an acetic acid solution (platinum oxide). The alcohols were cleanly separated by the chromatographic method described by Winstein and Holness[33] for separating equatorial (*trans-trans* isomer) and axial (*trans–cis* isomer) isomers. The pure *trans-cis* isomer melted at 48–48.5° (lit.[20] m.p. 49°) and was converted to *trans-cis*-1-decalyl *p*-toluenesulfonate which, after recrystallization from methanol, melted at 70.5–71.8° (lit.[31] m.p. 72°), solvolysis equivalent 311.6 (theory 308.4).

cis-trans-1-Decalol was prepared from *cis*-1-decalone by the method of Hückel and co-workers.[21c] The alcohol was purified by recrystallization of the *p*-nitrobenzoate derivative, m.p. 84.3–85.0° (lit.[21c] m.p. 86°). The alcohol was regenerated by hydrolysis[30] and converted directly to the *p*-toluenesulfonate derivative, m.p. 91–92° (methanol) (lit.[21c] m.p. 89–90°), solvolysis equivalent 311.6 ± 0.6 (theory 308.4).

The kinetic studies showed that the four 1-decalyl *p*-toluenesulfonates described above were homogeneous. The infinity titers, determined at 10 half-lives, did not increase when the solutions were heated.

Kinetic Experiments.—Anhydrous acetic acid was prepared by refluxing reagent grade glacial acetic acid with the calculated amount of acetic anhydride and a trace of sodium acetate followed by distillation. Anhydrous ethanol was prepared according to the method of Lund and Bjerrum.[34] Anhydrous lithium perchlorate was obtained from the G. F. Smith Chemical Co. and used without further treatment. Sodium *p*-toluenesulfonate (Eastman Kodak Co.) was dried for 2 hours at 100° before use.

A. Acetolysis.—A sufficient amount of II to give 25 ml. of reaction mixture of the desired concentration was placed in a 50-ml. reaction flask which was partially immersed in the thermostat. The reaction flask was equipped with a 5-ml. micro-buret and an exit tube attached to a calcium chloride drying tube. Twenty-five ml. of thermostated solvent was added to the reaction flask and the solution was titrated at intervals to the brom phenol blue end-point with 0.05 *M* sodium acetate in anhydrous acetic acid. In experiments using more concentrated solutions, *i.e.*, 0.05 *M*, 0.25 *M* titrant was used. The rate constants were calculated from the observed titers—the "infinity titer" was measured after 10 half-lives at the reaction temperature—by use of the integrated equation for a first-order reaction. A typical kinetic experiment is summarized in Table IV. In all of these experiments the observed "infinity titers" were about 82% of the calculated value. When the solutions were heated to 80° or over for several hours the titer was increased to within experimental error of the calculated value.

TABLE IV

ACETOLYSIS OF *cis*-5-CYCLODECEN-1-YL *p*-TOLUENESULFONATE AT 29.97° (RUN 6A)

Time, 10^{-3} sec.	[ROTs], 10^3 *M*	$10^5 k$, sec.$^{-1}$
0	6.88	
0.126	6.34	63.3
.219	6.00	62.7
.282	5.76	62.6
.461	5.14	63.2
.634	4.61	63.0
.790	4.25	62.4
.944	3.82	62.2
1.136	3.37	62.7
1.359	2.95	62.3
1.824	2.22	62.0
2.583	1.38	62.2
		62.6 ± 0.4

The ampule technique was used to determine the rates of acetolysis of the isomeric 1-decalyl *p*-toluenesulfonates.

B. Ethanolysis.—The rate of ethanolysis of II was determined in the same way as the rate of acetolysis except that the reaction mixtures were titrated to the brom thymol blue end-point with 0.05 *M* sodium ethoxide in anhydrous ethanol. In one experiment the ampule technique was used. A typical experiment is summarized in Table V.

TABLE V

ETHANOLYSIS OF *cis*-5-CYCLODECEN-1-YL *p*-TOLUENESULFONATE AT 20° (RUN 1A)

Time, 10^{-3} sec.	[ROTs], 10^3 *M*	$10^5 k$, sec.$^{-1}$
0	8.66	
3.055	7.74	4.32
4.850	7.23	4.39
6.725	6.78	4.34
9.350	6.15	4.40
12.035	5.55	4.45
14.690	5.11	4.41
17.450	4.68	4.40
20.040	4.29	4.41
22.805	3.96	4.39
27.440	3.48	4.36
30.875	3.16	4.35
36.335	2.67	4.52
		4.40 ± 0.04

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[32] The *cis–cis*-1-decalyl *p*-toluenesulfonate was prepared from alcohol which was recrystallized to constant melting point. The melting point of the tosylate was lower than that reported in the literature (ref. 21b). The melting point was lowered rather than raised by recrystallization. The crude *p*-toluenesulfonate prepared from pure alcohol melted at 88–88.5°. After two recrystallizations at low temperatures from ether–pentane mixtures the melting point was lowered to 83–84°. Recrystallization at high temperatures from petroleum ether (60–68°) resulted in a larger decrease in the melting point. The decrease in melting point was not accompanied by a change in the saponification equivalent. Difficulties in recrystallizing this compound have been mentioned previously (ref. 21b) and attributed to decomposition.

[33] S. Winstein and N. J. Holness, THIS JOURNAL, **77**, 5562 (1955).

[34] H. Lund and J. Bjerrum, *Ber.*, **64**, 210 (1931).

In these experiments the "infinity titers" were about 90% of the theoretical value. Subsequent heating of the solution increased the titer to the calculated value.

C. Acetolysis of the Rearrangement Product.—Solutions of 0.05 *M* II in anhydrous acetic acid were thermostated at 30° for 4 hr. (12 half-lives for the solvolysis). These solutions were neutralized with 0.25 *N* sodium acetate in acetic acid and the resulting solutions were used for the kinetic experiments. The rate of acetolysis was measured by the ampule technique. The reactions were followed by potentiometric titration of aliquots with 0.01 *M* sodium acetate in acetic acid. The first-order rate constants calculated in the usual manner showed a downward trend as illustrated by Table VI. Plots of log [ROTs] *vs.* time, such as Fig. 1, were used after the manner of Brown and Fletcher, for the determination of the inital concentration and acetolysis rate constants (Table III) of the two components (α-tosylate and β-tosylate).[22]

In a control experiment the acetolysis of 0.01 *M trans-trans*-1-decalyl *p*-toluenesulfonate in the presence of 0.05 *M* sodium *p*-toluenesulfonate was followed by the method described above. The rate constants obtained did not show any trends.

D. Measurement of k_r/k_s.—Solutions of 0.1 *M* II were thermostated at 30° for 10–15 half-lives for the solvolysis. Aliquots were then titrated and the titers compared with those of aliquots that were heated for 15 hours at 90°. The ratio of the difference in titer to the titer after 10–15 half-lives at 30° is k_r/k_s.

TABLE VI

ACETOLYSIS OF REARRANGEMENT PRODUCT AT 79.65° IN THE PRESENCE OF 0.0362 *N* NaOTs AND 0.00812 *N* NaOAc

Time, 10^3 sec.	ROTs, 10^3 *M*	10^5k, sec.$^{-1}$	Time, 10^3 sec.	ROTs, 10^3 *M*	10^5k, sec.$^{-1}$
0	5.56		3.12	2.09	31.4
0.12	5.18	58.7	4.62	1.95	22.6
.42	4.40	55.6	6.12	1.78	18.6
.72	3.78	53.4	7.32	1.59	17.1
1.02	3.34	49.9	9.72	1.29	15.0
1.32	3.08	44.8	12.42	1.06	13.3
1.62	2.82	41.9	15.62	0.88	11.8
1.92	2.64	38.9	19.32	.62	11.4
2.22	2.46	36.6	24.12	.44	10.5

MADISON 6, WIS.

[CONTRIBUTION NO. 2352 FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY]

Hydrolysis of Diaryliodonium Salts

BY MARJORIE C. CASERIO, DONALD L. GLUSKER AND JOHN D. ROBERTS

RECEIVED MAY 28, 1958

The products of hydrolysis of some unsymmetrically substituted diphenyliodonium salts to phenols and aryl iodides have been identified and their distributions determined. The direction of cleavage has been found to be insensitive to the nature of the substituents, the solvent, catalysts, and the nature of the associated anion, fluoride, fluoroborate, *p*-toluenesulfonate or trifluoroacetate. A rate study has shown that hydrolysis is a complex reaction which is retarded by acid and catalyzed by cuprous copper and also by oxygen when dioxane–water is used as the solvent. Possible mechanisms are discussed.

Introduction

The kinetics of hydrolysis of diazonium salts in acidic aqueous solution has provided substantial evidence that a phenyl cation is an intermediate in the reaction.[1] This is a unique example of aromatic nucleophilic displacement by an SN1-type mechanism. The investigation here described was initially undertaken in the hope that alternative classes of aromatic compounds might be found to undergo nucleophilic displacement by similar mechanisms. At the outset, it was hoped that the hydrolysis of diaryliodonium salts might proceed with intermediate formation of a phenyl cation, by analogy with certain diazonium salt reactions.

$$(C_6H_5)_2I^{\oplus} \longrightarrow C_6H_5^{\oplus} + C_6H_5I$$

$$C_6H_5^{\oplus} + 2H_2O \longrightarrow C_6H_5OH + H_3O^{\oplus}$$

The work of Beringer,[2] Lewis[3] and Nesmeyanov,[4] on the reactions of diphenyliodonium salts has shown clearly how susceptible these salts are to attack by nucleophilic reagents by a variation of the SN2 mechanism. For example, only 6–15% hydrolysis occurs on refluxing aqueous solutions of diphenyliodonium chloride; the main reaction is one of attack by chloride ion to give chloro- and iodobenzenes.[2c] Therefore, substantial hydrolysis will not occur by either an SN1 or SN2 mechanism unless the nucleophilic character of the associated anion is negligibly small. It was for this reason that fluoride, fluoroborate, tosylate and trifluoroacetate iodonium salts were selected for investigation, since these anions possess little or no nucleophilic character, and consequently might allow hydrolysis to take place exclusively.

We hoped that a study of the products from hydrolysis of unsymmetrical iodonium salts would indicate the operative mechanism, since it was anticipated that substituents would strongly influence the product distributions in a manner which would allow a distinction to be made between reaction by an SN1 or SN2 mechanism. Thus, the products to be expected for SN2 hydrolysis of the 3-nitrodiphenyliodonium ion are *m*-nitrophenol and iodobenzene; in contrast, SN1 hydrolysis should give predominantly *m*-nitroiodobenzene and phenol.

Hydrolysis of Unsymmetrical Iodonium Salts.—In carrying out experiments designed to test some of the preceding hypotheses, the iodonium salts were refluxed with water for periods varying from a few hours to several days. In a few instances, aqueous dioxane and acetonitrile were used as solvents to prevent separation of an organic phase.

The hydrolysis of 4-methoxydiphenyliodonium

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(1) For leading references see E. S. Lewis, THIS JOURNAL, **80**, 1371 (1958), and also D. F. DeTar and D. I. Relyea, *ibid.*, **76**, 1680 (1954).

(2) (a) F. M. Beringer, A. Brierley, M. Drexler, E. M. Gindler and C. C. Lumpkin, *ibid.*, **75**, 2708 (1953); (b) F. M. Beringer and E. M. Gindler, *ibid.*, **77**, 3203 (1955); (c) F. M. Beringer, E. J. Geering, I. Kuntz and M. Mausner, *J. Phys. Chem.*, **60**, 141 (1956).

(3) E. S. Lewis and C. A. Stout, THIS JOURNAL, **76**, 4619 (1954).

(4) A. N. Nesmeyanov, L. G. Makarova and T. P. Tolstaya, *Tetrahedron*, **1**, 145 (1957), and references cited therein.