

Salt Effects in the Stereochemistry of Acetolysis of 2-Octyl *p*-Toluenesulfonate¹

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Acetolysis of 2-octyl *p*-nitrobenzenesulfonate in the presence of lithium tosylate gives some 2-octyl tosylate with inversion of configuration. Kinetic studies of acetolysis of 2-octyl, *n*-butyl, and benzyl *p*-nitrobenzenesulfonates with lithium tosylate show a degree of conversion to alkyl tosylate relative to solvolysis of comparable magnitude in the three cases. Racemization and rearrangement in the presence of lithium perchlorate are also reported. The results are interpreted on the basis of ion-pair displacement mechanisms.

In studies of the stereochemistry of acetolysis of 2-octyl tosylate (2-OcOTs) it was found that the solvolytic displacement reaction itself proceeded with complete inversion of configuration but a concomitant racemization of the starting tosylate apparently involves a reaction with the liberated sulfonic acid.³ Preliminary experiments⁴ showed that the presence of lithium tosylate (LiOTs) caused increased racemization; hence, this more detailed study was undertaken.

Results and Discussion

Lithium Tosylate. The results of acetolysis experiments at 75° in the presence of LiOTs are summarized in Table I. Addition of LiOTs causes increased racemization of the product 2-octyl acetate (2-OcOAc). This feature is shown in the summary in Table II which compares the 2-OcOAc purified by g.c. produced during the first 2.5 half-lives (82% reaction) with and without salt. Part of this increased racemization came from racemization of the acetate after formation and from increased involvement of octenes (*vide infra*), but most of the effect resulted from increased concurrent racemization of the 2-OcOTs (Table III). The stereochemistry of the recovered tosylate was determined by ethanolysis as in the preceding paper.³ Note that on both the run without salt and with added LiOTs, the recovered unreacted 2-OcOTs was more racemized than the acetolysis product. This increased racemization with added alkali tosylate suggested a direct reaction of the displacement type; this suggestion was verified with the use of 2-octyl *p*-nitrobenzenesulfonate (2-OcONs).

This ester was prepared in the usual way from optically active 2-octanol and *p*-nitrobenzenesulfonyl chloride in pyridine. Its optical purity relative to the starting alcohol was established as in the case of 2-octyl tosylate by displacement with tetraethylammonium acetate in acetone. Kinetic experiments (*vide infra*) with

Table I. Effect of Salts on Stereochemistry of Acetolysis of 2-Octyl Tosylate at 75°

Run	Time, hr.	No. of half-lives ^a	Net apparent inversion, ^b %	Rearr. octyl acetates, %
0.1 M LiOTs				
50	26	12	56.2	8.5
56 ^c	5	~5	58.3	3.3
57 ^d	3	1.4	85.0	2.1
155	5.5	2.5	74.7 ^e	4.6
0.1 M LiClO ₄				
70	26	38	9.8	32.9
75	2.5	3.7	30.4	11.7
78 ^f	1.5	2.2	36.8	8.9
152	1.7	2.5	33.6 ^g	11.3
165 ^h	0.7	1.0	...	11.0

^a At 75° the time of the first half-life with 0.1 M LiOTs is 132 min., with 0.1 M LiClO₄, 41 min. ^b Corrected for nonester impurities but not for rearranged octyl acetates. ^c 0.2 M LiOTs. ^d Recovered starting material was 27.6% racemized and 1.9% rearranged. ^e Purification by g.c. gave 99.8% pure 2-octyl acetate of 77.5% net inversion. ^f Recovered tosylate was 17.6% racemized and 3.2% rearranged. ^g Purification by g.c. gave 99.0% pure 2-octyl acetate of 35.9% net inversion. ^h Run in acetic acid-*d* with racemic tosylate; recovered tosylate was 2.6% rearranged.

Table II. Stereochemistry of 2-Octyl Acetate after 2.5 Half-Lives at 75°

Run	Salt	Racem. of purified 2-OcOAc, %	Rearr., %
154 ^a	None	6.7	4.0
155	0.1 M LiOTs	22.5	4.6
152	0.1 M LiClO ₄	64.1	11.3

^a See ref. 3.

Table III. Stereochemistry of Recovered Octyl Tosylate from Partial Acetolyses at 75°

Run	Salt	No. of half-lives	Recovered tosylate, %		Product 2-Octyl acetate, %	
			Racem.	Rearr.	Racem. ^b	Rearr.
73 ^a	None	1.4	7.5	0.9	5	1.5
57	0.1 M LiOTs	1.4	27.6	1.9	13	2.1
78	0.1 M LiClO ₄	2.2	17.6	3.2	54	8.9

^a See ref. 3. ^b Corrected for presence of rearranged esters assuming these to be racemic.

racemic ester showed that acetolysis with added LiOTs gives downward drifting rate constants indicative of conversion of 2-OcONs to the less reactive 2-OcOTs. Accordingly, a 0.2 M solution of optically active 2-OcONs in acetic acid saturated in LiOTs (about 0.1 M) was interrupted after partial solvolysis at 50°. The recovered sulfonate esters were solvolyzed in ethanol to

(1) This research was supported in part by a grant from the National Science Foundation.

(2) Woodrow Wilson Fellow, 1958-1960; United States Rubber Co. Fellow in Chemistry, 1960-1961.

(3) A. Streitwieser, Jr., T. D. Walsh, and J. R. Wolfe, Jr., *J. Am. Chem. Soc.*, **87**, 3682 (1965).

(4) We are indebted to Mr. A. C. Waiss, Jr., for these experiments.

give 2-octyl ethyl ether (2-OcOEt) which was 97% pure and whose rotation showed 68% net retention of configuration relative to the starting alcohol. The sulfonic acids isolated from the ethanolysis were 78% *p*-toluenesulfonic acid (TsOH) and 22% *p*-nitrobenzenesulfonic acid (NsOH); that is, the octyl sulfonates submitted to ethanolysis contained 22% of the unreacted *p*-nitrobenzenesulfonate. Since this ester may be assumed to contribute inverted ether to the total ethanolysis product,⁵ the observed partial net retention indicates that the octyl tosylate itself has a configuration relative to the starting 2-OcONs corresponding to 120% inversion. However, because the 2-OcONs racemizes during acetolysis, this number is too high. Using the optical activity of the 2-OcOAc acetolysis product as a measure of the average activity of the 2-OcONs during acetolysis it follows that the 2-OcOTs is produced with $110 \pm 16\%$ net inversion of configuration. We next inquired if this is a normal SN2 displacement reaction and responded with some kinetic studies.

Kinetics. The stereochemical studies were run on solutions ($\sim 10^{-1} M$) substantially more concentrated than those normally used in kinetic studies (10^{-2} – $10^{-3} M$). Normal titrimetric acetolysis kinetics of 2-OcOTs under these conditions gave integrated, first-order rate constants which rose steadily with time. This increase undoubtedly reflects the positive salt effect of the liberated sulfonic acid. Following Fainberg and Winstein⁶ this salt effect may be represented as

$$k = k^0[1 + b(\text{salt})] \quad (1)$$

If [TsOH] = x ,

$$\frac{dx}{dt} = k^0[1 + bx][x_\infty - x] \quad (2)$$

This mixed-order equation is conveniently handled by integrating as follows

$$\frac{1}{t} \ln \frac{x_\infty - x_0}{x_\infty - x} = k^0 + \frac{bk^0}{t} \int_0^t x dt \quad (3)$$

A plot is made of the quantity on the left of eq. 3 for each point vs. $1/t \int_0^t x dt$ as determined from graphical integration to give a straight line whose intercept yields k^0 and whose slope divided by k^0 gives b . Note that for a true, first-order process, the quantity in the left of eq. 3 is constant. The results of this technique are summarized in Table IV. The b value for the first two

Table IV. Salt Effects in Acetolysis of 2-Octyl Tosylate at 75°

[2-OcOTs], mole/l.	Salt	$10^4 k^0$, sec. ⁻¹	b , l./mole
0.206	None	5.44	1.6
0.183	0.1 M LiOTs	8.18	1.8
0.186	0.1 M LiClO ₄	24.6	3.4

runs is that for *p*-toluenesulfonic acid and is relatively small (1.7). The b value for LiOTs is determined from

(5) A. Streitwieser, Jr., and A. C. Waiss, Jr., *J. Org. Chem.* **27**, 290 (1962).

(6) A. H. Fainberg and S. Winstein, *J. Am. Chem. Soc.*, **78**, 2763 (1956).

the first two k^0 values as 5.0. Similarly, b for LiClO₄ is determined as 35. These values appear to be typical; for example, Fainberg and Winstein⁷ report b values for acetolysis of 3,3-dimethyl-2-butyl tosylate of 30–34 for LiClO₄ and 3.0–3.4 for TsOH.

However, the apparent normalcy of these salt effects does not contribute to the question of whether the conversion of 2-OcONs to 2-OcOTs is a normal, direct displacement reaction superimposed on solvolysis. In principle, such a displacement reaction would be independent of solvolysis and could be detected by a kinetic study, but the magnitude of the salt effects on the solvolysis rate shows that in practice such a dissection would be rather difficult. Instead, we used a different approach by examining the effect of substrate structure on the relative rates of displacement and solvolysis; that is, we looked at the acetolysis kinetics in the presence of LiOTs, 2-OcONs, *n*-butyl *p*-nitrobenzenesulfonate (BuONs), and benzyl *p*-nitrobenzenesulfonate (BzONs). These systems were chosen because primary systems undergo direct displacement reactions more readily than secondary alkyl derivatives.⁸ If the reaction of 2-OcONs with LiOTs in acetic acid is a normal SN2 process, we expect its rate relative to solvolysis to be much higher for the *n*-butyl case and of intermediate magnitude for benzyl.

In practice, acetolysis of each *p*-nitrobenzenesulfonate in the presence of LiOTs gave decreasing integrated first-order rate constants indicative of conversion of RONs to ROTs. The actual kinetics of the system is rather complex—we are dealing with relatively high concentrations and have salt effects with the salt changing during reaction. Nevertheless, a more quantitative idea of the relative rate of conversion was obtained from the following analysis.

$$\frac{d[\text{acid}]}{dt} = k_{\text{RONs}}[\text{RONs}] + k_{\text{ROTs}}[\text{ROTs}]$$

If [acid] = x , [RONs] + [ROTs] = $a - x$. Let [ROTs]/ $a - x = f$

$$\frac{dx/dt}{a - x} = [k_{\text{RONs}}(1 - f) + k_{\text{ROTs}}f]$$

$$\frac{d \ln (a - x)/dt}{k_{\text{RONs}}} = 1 - (1 - \frac{k_{\text{ROTs}}}{k_{\text{RONs}}})f \quad (4)$$

A plot was made of $\ln (a - x)$ vs. t . For a simple, first-order reaction, such a plot would be a straight line. In the present case it is curved; the slope was measured at various points with a Gerber "derivimeter" and f was obtained using eq. 4. This equation requires the solvolysis rate of RONs and the ratio, $k_{\text{ROTs}}/k_{\text{RONs}}$. The former was obtained from the integrated, first-order rate constant extrapolated to zero time; the latter was derived from points late in the reaction or from independent experiments. The values obtained for this rate ratio are: 2-Oc at 50°, $1/33$; benzyl at 25°, $1/26$; and *n*-Bu at 100°, $1/6$. Note that for this purpose, the results are comparatively insensitive to errors in this ratio. The solvolytic reactivities varied greatly and

(7) A. H. Fainberg and S. Winstein, *ibid.*, **78**, 2780 (1956).

(8) In many displacement reactions ethyl systems are ~40 times more reactive than isopropyl systems: cf. A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., (1963).

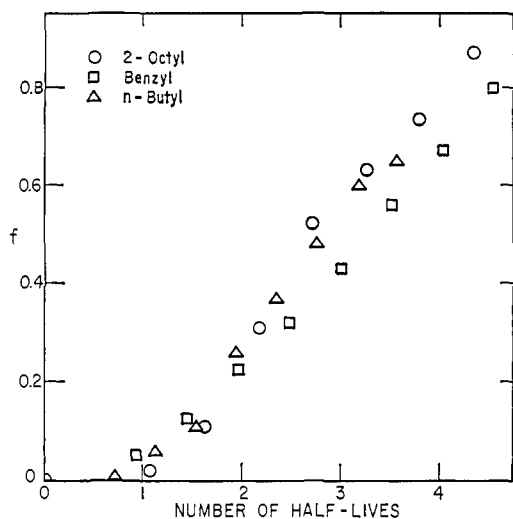
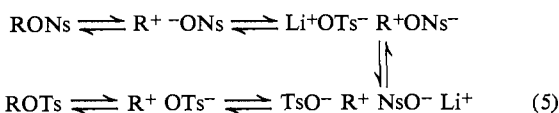


Figure 1. Fraction of unsolvolyzed alkyl *p*-nitrobenzenesulfonate converted to alkyl tosylate as a function of the extent of solvolysis.

different temperatures were required for convenient measurement; the extrapolated half-lives for solvolysis of RONs are: 2-Oc at 50°, 1.8 hr.; benzyl at 25°, 1.9 hr.; and *n*-Bu at 100°, 2.5 hr.

Values of *f* (amount of unsolvolyzed sulfonate converted to ROTs) as a function of the number of half-lives for solvolysis of RONs are shown in Figure 1. The curves are remarkably similar despite the great difference in structural types involved. In each case, after 2 half-lives for solvolysis of RONs, about 25% of the unsolvolyzed RONs was converted to ROTs. This independence of relative rate with structure provides compelling evidence that the displacement and solvolysis are not independent processes for all of these compounds but are part of the same reaction. In view of the significance of ion-pair intermediates in carbonium ion acetolysis reactions, we suggest that the conversion of 2-OcONs to 2-OcOTs is a displacement reaction on an ion pair intermediate which may be formulated as



If this mechanism applied to all three systems, it would be interesting that the competition of the $\text{R}^+ \text{ONs}^-$ ion pair intermediate for solvent and for LiOTs is so much the same for the three systems studied, but it should be recalled that the solvolyses were carried out under temperature conditions such that the reactions went at comparable speeds. The effect of temperature on the competition ratios would certainly be of interest but was not determined in the present study. Finally, we may mention that the ion-pair displacement mechanism agrees with that proposed recently by Weiner and Sneen for some solvolyses in partially aqueous solvents.⁹

Acetolysis of 2-Octyl Acetate and Octene. As summarized in Tables I and III, the OcOAc product of acetolysis is partially rearranged. The extent of rearrangement is more pronounced at long reaction times, undoubtedly because of the action of acid on

(9) H. Weiner and R. A. Sneen, *J. Am. Chem. Soc.*, **87**, 292 (1965).

2-OcOAc. The several experiments which were run with 2-OcOAc to determine the extent of this effect are summarized in Table V. In run 67 the conditions simulate the end of a solvolysis; after 130 hr. the ester is only 6% rearranged. Rearrangement is more extensive in the presence of LiClO_4 (*vide infra*). Acid-catalyzed rearrangement of the ester can occur directly or *via* olefin as intermediate. In a kinetic run with optically active 2-OcOAc and 0.039 *M* HClO_4 in acetic acid at 75°, $k_{\text{racem}} = 1.8 \times 10^{-5} \text{ sec.}^{-1}$ whereas $k_{\text{rearr}} \cong 0.7 \times 10^{-5} \text{ sec.}^{-1}$, *i.e.*, racemization was more than twice as fast as rearrangement. Because elimination can give 1-octene, which would regenerate only 2-OcOAc, as well as 2-octene which, on readdition, would give 2- and 3-OcOAc, a factor of somewhat less than 2 would be expected. A mixture of 0.2 *M* mixed octenes, 0.2 *M* TsOH, and 0.1 *M* LiClO_4 in acetic acid at 75° reached an equilibrium mixture after 1 day and contained 12% octenes; the octyl acetate mixture in the equilibrium was 47% 2-OcOAc.

Direct evidence for some intramolecular rearrangement during reaction of 2-OcOAc with acid was obtained with optically active ester. The product of run 159, Table V, was separated into two fractions by preparative g.c. with a Tween Column.¹⁰ One fraction consisted almost entirely of 3-OcOAc, the other primarily of 2-OcOAc. From the analyses and rotations the 2-OcOAc has $\alpha_D 1.39^\circ$ or 64% of the rotation of the starting ester, whereas the 3-OcOAc has $\alpha_D 0.17^\circ$. (+)-2-Octanol (I) and (+)-3-octanol (II) have the same configurations.^{11,12} (+)-2-Octanol and



(+)-2-OcOAc have the same configuration,¹³ whereas (+)-3-OcOH and (-)-3-OcOAc are configurationally related.¹¹ Hence, the optically active 3-OcOAc produced by treatment of 2-OcOAc with acid must be derived by a net inversion of configuration. This result can be rationalized as in Chart I. (+)-2-OcOAc (X = OAc) can exist in two highly populated conformations, A and B. Rearrangement of A with inversion at both centers as shown yields 3-OcOAc with retention of configuration E, but involves a transition state for migration of hydrogen (C) which has *cis*-alkyl groups and is thus more strained than the corresponding transition state (D) which would arise from B and produce 3-OcOAc with net inversion of configuration F. The latter process is favored but apparently not by very much; the 3-OcOAc produced has about 13% of the optical purity of the starting 2-OcOAc.¹¹

Rearrangement during Solvolysis. The 2–5% rearrangement found for product ester after a solvolysis period of 3–6 hr. (runs 56, 57, and 155 in Table I)

(10) We are indebted to Dr. R. Teranishi of the Western Regional Research Laboratory, U. S. Department of Agriculture, for assistance in this separation.

(11) J. Kenyon, *J. Chem. Soc.*, **105**, 2226 (1914).

(12) K. Freudenberg, "Stereochemie," Book 2, Franz Deuticke, Leipzig, 1933, p. 695; J. A. Mills and W. Klyne, *Progr. Stereochem.*, **1**, 205 (1954).

(13) R. H. Pickard and J. Kenyon, *J. Chem. Soc.*, **105**, 830 (1914).

Table V. Acetolysis of 2-Octyl Acetate at 75°

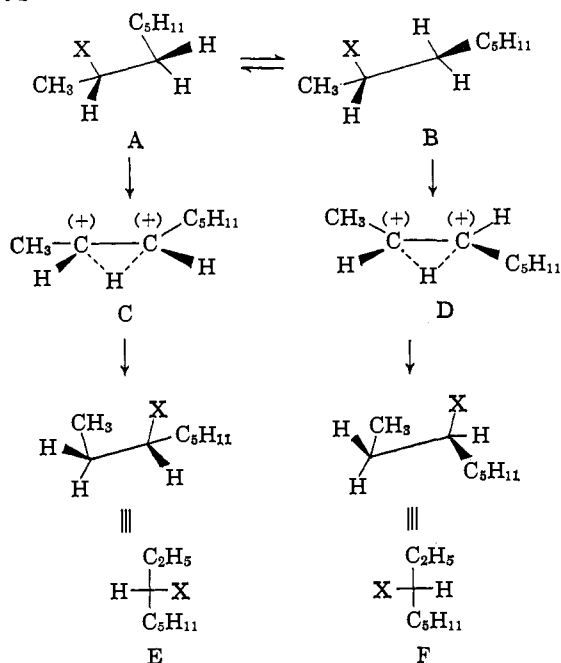
Run	[2-OcOAc], M	Addends	Time, hr.	Optical Activity, α_D (deg.) Start	Optical Activity, α_D (deg.) Product	Racem., %	Rearr., %
59	0.20	0.1 M LiOTs	3	-0.893	-0.846	5	0
59			26		-0.845	5	0
67	0.20	0.1 M LiOTs	130	-1.282	-0.737	43	~5.8 ^a
159	0.21	0.1 M TsOH 0.1 M LiClO ₄ 0.19 M TsOH	26	2.169	0.840 ^b	61 ^b	20.9
89	0.25	0.002 M HClO ₄	48	0.119 ^c	0.123 ^c	0	...
95	0.50	0.4 M LiClO ₄	73	0
99	0.50	0.04 M HClO ₄	192	48.6
99			240	48.4
99			528	48.5

^a Forerun of distillate showed 7.3% rearrangement; main fraction showed 5.2%. ^b The 2-OcOAc content is 36% racemized. See text. ^c Uncorrected rotations of the acetic acid solution.

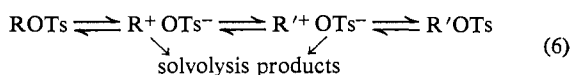
is far in excess of that expected from reaction of ester after its formation.

The extent of involvement of olefin in the rearrangement process was established by solvolysis in acetic

Chart I

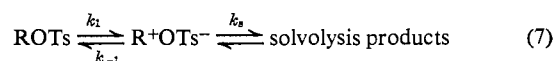


acid-*t*. A solution, 0.26 M in 2-OcOTs and 0.20 M in LiOTs, was maintained at 75° for 6.6 hr. (about 3 half-lives) and the ester products were examined with a gas chromatograph proportional-flow counter. The level of radioactivity in the products showed that 4% of the 2-OcOAc and 48% of the 3-OcOAc arose from acetolysis of octene intermediates.³ About half of the 3-OcOAc formed thus results from an intramolecular rearrangement during the acetolysis. This process may probably be depicted as in Chart I, with X = OTs. The intermediate carbonium tosylate ion pair can rearrange or react with solvent. In this respect it is noteworthy that unreacted tosylate always shows some degree of rearrangement (Tables I and III); hence, to the mechanism in eq. 5 we must add the process



These schemes contain the important implication that internal return exists in acetolysis of simple alkyl

sulfonates; hence, acetolysis rates as normally measured give composite rate constants that differ from simple ionization rates. That is, for the process

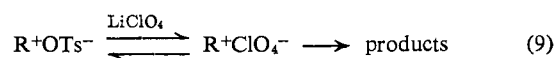


$$k_{\text{exptl}} = k_1 \times \frac{k_s}{k_{-1} + k_s} \quad (8)$$

The important ratio $k_s/(k_{-1} + k_s)$ could be obtained for simple systems from a careful study of the amount of rearrangement in the acetolysis products compared to the extent of rearrangement in the unreacted sulfonate as implied in eq. 6.

Lithium Perchlorate. Addition of LiClO₄ to the acetolysis of 2-OcOTs produces a rate acceleration which appears to be a normal salt effect (*vide supra*), but it also has an important effect on the products—racemization and rearrangement are more pronounced (Tables I, II, and III). In part, this effect comes from enhanced solvolysis of the product octyl acetate (Table VI), but this factor should still be comparatively minor at short reaction times. For example, in run 159, Table V, 2-OcOAc after 25 hr. with 0.1 M LiClO₄ and 0.19 M TsOH is 21% rearranged and 36% racemized; acetolysis of 2-OcOTs with 0.1 M LiClO₄ for only 1.7 hr. yields 2-OcOAc which is 64% racemized plus 11% of rearranged esters (run 152, Tables I and II).

Most of the effect stems from increased involvement of olefin. Using the same technique of solvolysis in acetic acid-*t* containing 0.10 M LiClO₄ and comparing product radioactivities, it was found that almost 30% of the 2-OcOAc and almost all of the 3-OcOAc produced arose through addition of solvent to olefin. This still leaves a substantial amount of racemization of 2-OcOAc which must arise during the solvolytic displacement reaction itself. It is noteworthy that that unreacted tosylate shows significantly more rearrangement and racemization than in the absence of salt, although the amounts are much less than for product acetate. These effects of LiClO₄ appear to be rationalized by the addition to the mechanisms in eq. 5 and 6 of the further ion-pair processes



Racemized acetate and elimination appear to be the principal products from solvolysis of the carbonium

perchlorate ion pair. Rearrangement may also be enhanced, but we have no direct evidence for this. This ion pair capture process is similar to that reported by Weiner and Sneen⁹ with sodium azide.

The difference in the chemistry of carbonium sulfonate and perchlorate ion pairs suggests that the latter are more ionic. Either these ion pairs have appreciable but varying covalent character or the perchlorate ion pairs tend more to become "solvent separated."¹⁴ In either case a carbonium ion is produced having an effectively greater positive charge to distribute within the organic molecule and resulting in enhanced rates of elimination and probably also of rearrangement. Enhanced molecular rotation and consequent racemization within such a "looser" ion pair is also understandable.

Other Systems. Ion-pair exchange reactions in solvolysis are undoubtedly general. In order to detect conveniently the effects of the unreacted tosylate, substrate and salt concentrations were used that exceed those in most solvolysis studies of a purely kinetic type. It seems clear that dilute solutions are essential in order to avoid these perturbations. This is true even when alkali acetate is used to neutralize the acid liberated; subsequent, acid-catalyzed reactions of solvolysis products are reduced or eliminated by this technique, but ion-pair exchange reactions may still be significant.

The kinetic results described above for *n*-butyl and benzyl *p*-nitrobenzenesulfonate in the presence of LiOTs show that ion pair exchange appears to be just as important for primary systems as for secondary. The exchange of β -phenylethyl tosylate with NaOTs described by Lee, *et al.*,¹⁵ should undoubtedly be interpreted also as an ion-pair reaction. The significant amounts of racemization observed in acetolyses of optically active 1-butyl-1-*d* *p*-nitrobenzenesulfonate¹⁶ and benzyl- α -*d* tosylate³ undoubtedly result from ion-pair exchange prior to reaction with solvent. Acetolysis of primary alkyl sulfonates has been described repeatedly as a solvolysis that involves significant nucleophilic participation by solvent.¹⁷ The arguments and logic used in leading to this description still hold true and for these primary systems we must consider the alternative mechanism in which a transition state containing a weak covalent bond to tosylate ion at the rear leads to the ion-pair intermediates discussed above and competes with a similar transition state involving an acetic acid molecule at the rear. There appears to be general agreement that such a nucleophilic contribution is small¹⁷ in acetolysis; hence, there should be comparatively little dependence on nucleophilicity. Thus, exchange in primary systems with lithium tosylate or lithium perchlorate by displacement could well be comparable in extent to exchange among ion pairs of secondary systems. However, the same arguments applied to acetolysis of secondary alkyl sulfonates lead to the conclusion that these are essentially limiting¹⁷; that is, if exchange in

these cases also came about by nucleophilic attack on substrate rather than on ion pairs, the contribution of nucleophilicity should now be much more important for primary systems, and the observed comparability of exchange rates among the various systems would not be expected. Thus, the present study does not weaken the accepted theory of limiting and nucleophilic solvolyses but does introduce significant complicating features.

Experimental¹⁸

Materials Used. Lithium *p*-toluenesulfonate was prepared in water from equivalent amounts of *p*-toluenesulfonic acid monohydrate and lithium carbonate and recrystallized from water.

*Anal.*¹⁹ Calcd. for LiC₇H₇O₃S: S, 18.00. Found: S, 18.01.

2-Octyl *p*-nitrobenzenesulfonate was prepared as for the tosylate using 2-octanol, α^{25}_D 4.000 \pm 0.007°, and a reaction time of 4 hr. A reaction time of 2 days gave octyl chloride. The light yellow oil had α^{25}_D 2.895 \pm 0.008°, and no absorption at 2.7–2.9 μ in the infrared.

*Anal.*¹⁹ Calcd. for C₁₄H₂₁NO₅S: N, 4.44. Found: N, 4.63; Cl, 0.13.

Benzyl *p*-nitrobenzenesulfonate was prepared by adding a solution of 21.55 g. (0.097 mole) of *p*-nitrobenzenesulfonyl chloride (Eastman, purified by extraction into hexane) in 125 ml. of tetrahydrofuran to a mixture maintained at –70° prepared from 12 g. (0.12 mole) of 25% sodium hydride dispersion in mineral oil and 10 ml. (0.097 mole) of redistilled benzyl alcohol in 150 ml. of ether by refluxing overnight. After additional stirring the mixture was filtered, the solvent was removed, and the residue (63% yield) was recrystallized from ether–pentane–hexane to give almost colorless crystals which decomposed without melting at 75°.

*Anal.*¹⁹ Calcd. for C₁₃H₁₁NO₅S: C, 53.23; H, 3.78; N, 4.78; S, 10.93. Found: C, 53.42; H, 4.08; N, 5.06; S, 10.83.

Solvolysis Reactions. The acetolyses of 2-OcOTs were run as in the preceding paper. The reaction of 2-OcONs with lithium tosylate was carried out by adding 85.12 g. of the ester prepared above to a saturated solution (~0.1 *M*) of excess LiOTs in 1300 ml. of acetic acid at 50°. After 470 min. (~4 half-lives) at this temperature, the mixture was poured into ice water to give 150 mg. of a yellow solid, m.p. 124.5–128.2°, which may be a diaryl sulfide but which was not identified. The separated organic liquid gave octyl acetates, b.p. 84.5° (10 mm.), α^{27}_D –2.253 \pm 0.006°, which were 4.3% rearranged by g.c. analysis. The aryl sulfonate ester residue was solvolyzed in ethanol to give ethyl octyl ethers obtained as two fractions, b.p. 65.8–67.2° (10 mm.), α^{23}_D 4.878 \pm 0.008°, 99.1% ethers with 3.3% rearrangement, b.p. 67.2° (10 mm.), α^{27}_D 5.027 \pm 0.010°, 99.8% ethers with 2.8% rearrangement.

The acidic, brown solid obtained by evaporation of the aqueous extracts of the ethanolysis products was analyzed and found to be 1.43% N and 16.81% S.

(14) S. Winstein, E. Clippinger, A. H. Fainberg, R. Heck, and G. C. Robinson, *J. Am. Chem. Soc.*, **78**, 328 (1956).

(15) C. C. Lee, R. Tkachuk, and G. P. Slater, *Tetrahedron*, **7**, 206 (1959).

(16) A. Streitwieser, Jr., and W. D. Schaeffer, *J. Am. Chem. Soc.*, **79**, 6233 (1957).

(17) See the summary and references cited in ref. 8.

(18) See also ref. 3.

(19) Analysis by Microanalytical Laboratory, University of California, Berkeley, Calif.

Assuming a two-component mixture, this analysis corresponds to 78% TsOH and 22% NsOH. 2-Octyl tosylate is so much less reactive than the *p*-nitrobenzenesulfonate that the octyl acetate acetolysis product may be assumed to come entirely from the latter sulfonate. The rotation of the product acetate serves as an approximate measure of the optical purity of the recovered octyl *p*-nitrobenzenesulfonate; that is, from the ratio of the optical activities of 2-octyl ethyl ether and 2-octyl acetate, 2.57, the recovered *p*-nitrobenzenesulfonate should give rise to ether of $\alpha_D (-2.30)(2.57) = -5.91 \pm 0.07^\circ$. Note that the ether formed actually had a positive rotation. From its rotation and the relative amounts of TsOH and NsOH produced, we deduce the rotation of the ether obtained by ethanolysis of the 2-OcOTs present as $\alpha_D 8.1 \pm 1.0^\circ$. 2-Octyl ethyl ether having the same configuration and optical purity of the starting 2-octanol would have $\alpha_D 7.35 \pm 0.21^\circ$; hence, the conversion of 2-OcONs to tosylate during acetolysis proceeds with $110 \pm 16\%$ inversion.

The product of run 70 (Table I) was separated into 2 fractions by g.c. (silicone, 0.5-in. column) and each fraction was analyzed by g.c. Relative retention times for peaks found were: fraction 1, 0.94 and 1.00; and fraction 2, 0.95, 1.00, and 1.08. Octyl acetates under these conditions give: 2-OcOAc, 1.08; 3-OcOAc, 1.00; and 4-OcOAc, 0.95. Infrared spectra of these fractions and of all other product mixtures were those of mixed isomeric octyl acetate.

Kinetic Studies. Solvolysis solutions were made up with the indicated materials and maintained in a thermostat held to $\pm 0.05-0.1^\circ$.

Sealed tubes containing aliquots were used, or aliquots were withdrawn periodically from a stoppered flask. The samples were quenched by cooling and titrated potentiometrically with sodium acetate in acetic acid using calomel and glass electrodes. The experimental data are given in Tables VI and VII. Acetolysis of 0.0075 *M* benzyl *p*-nitrobenzenesulfonate at $24.99 \pm 0.02^\circ$ gave $k = 6.68 \pm 0.04 \times 10^{-5} \text{ sec.}^{-1}$. This rate is 26 times that for the tosylate.²⁰

Table VI. Acetolysis of 2-OcOTs at 75°

0.1 <i>M</i> LiOTs		0.1 <i>M</i> LiClO ₄	
Time, sec.	Titer ^a	Time, sec.	Titer ^a
0	1.79	0	1.61
1808	6.10	1200	10.18
3600	1.55	2700	2.94
5400	2.09	3600	3.54
10980	3.33	5400	4.335
12710	3.62	7200	4.76
16200	4.08	10800	5.12
00	5.12	00	5.21

^a The first two points are 10-ml. aliquots titrated with 0.0534 *M* NaOAc; remaining points are 5-ml. aliquots titrated with 0.1781 *M* NaOAc.

Acetolysis of 2-Octyl Acetate. The indicated solutions were maintained at $75 \pm 0.1^\circ$ for the specified time (Table VI). The solutions were worked up as usual and examined polarimetrically and by g.c.

(20) S. Winstein, E. Grunwald, and H. W. Jones, *J. Am. Chem. Soc.*, 73, 2700 (1951).

Table VII. Acetolysis of Alkyl *p*-Nitrobenzenesulfonates with 0.05 *M* LiOTs

2-Octyl ^a		<i>n</i> -Butyl ^b		Benzyl ^c	
Time, 10 ⁻³ sec.	Titer ^d	Time, 10 ⁻³ sec.	Titer ^d	Time, 10 ⁻³ sec.	Titer ^d
3.6	1.26	2.7	0.90	2.915	0.795
7.2	2.365	4.5	1.485	6.54	1.655
10.8	3.10	6.31	1.955	10.39	2.25
14.4	3.54	9.0	2.58	13.75	2.595
18.0	3.835	13.5	3.31	17.78	2.875
21.6	3.99	20.7	4.02	21.12	3.025
25.2	4.09	31.52	4.465	35.60	3.29
28.8	4.15	74.7	4.925	72.42	3.39
104.4	4.32	161.1	5.10	115.75	3.575
129.6	4.36	∞	5.17	167.15	3.54
172.8	4.41			275.11	3.63
∞	4.82			∞	3.67

^a At 50° . ^b At 100° . ^c At 25° . ^d Five-milliliter aliquots titrated with 0.1867 *M* NaOAc.

analysis. The product of run 159 was separated into two fractions by g.c. on a 10 ft. \times 1 in. Tween column at 135° . The first fraction was further separated to give 0.2 ml., $\alpha^{22,6D} 0.102 \pm 0.005^\circ$ (*l* 0.5), containing 96.2% octyl acetates of which 3.5% was 2-OcOAc and the remainder 3-OcOAc. The second fraction gave a solution, $\alpha^{22,4D} 1.037 \pm 0.004^\circ$, consisting of 19.4% solvent and 80.6% octyl acetates which were 91.7% 2-OcOAc and 8.3% 3-OcOAc.

Acetolysis of Octenes. An acetic acid solution 0.2 *M* in octenes,³ 0.2 *M* in TsOH, and 0.1 *M* in LiClO₄ and containing 2,2,4-trimethylpentane as an internal standard was maintained at 75° . Aliquots were withdrawn periodically and worked up as usual except that distillation was omitted. Olefin content relative to the standard was determined by g.c. on a silicone column and the isomeric octyl acetates were analyzed with a PDEAS column. Values remained essentially constant after 20 hr. when 13% of the original olefin remained and the acetates consisted of 47% 2-OcOAc.

Acetolyses in Acetic Acid-*t*. These were carried out and analyzed as in the preceding paper.³ The LiOTs run was 0.26 *M* in 2-OcOTs and 0.20 *M* in LiOTs maintained at 75° for 3 half-lives. Counts per unit area for the products were: 2-OcOAc, 171, 190, 202; 3-OcOAc, 1881, 2217, and 2153; X,³ 88,300, 104,000, and 106,000. The average value divided by the equivalent activity of the acetic acid-*t* used and multiplied by the isotope effect (~ 12) gives the actual degree of reaction with solvent³: 2-OcOAc, 0.05; 3-OcOAc, 0.48; and X, 23.

In the LiClO₄ run, a solution 0.21 *M* in 2-OcOTs and 0.10 *M* in LiClO₄ was maintained at 75° for 3 half-lives and worked up as usual. Since the extent of rearrangement is greater for this case it was possible to measure the radioactivity of the 4-OcOAc as well as the others. Counts per unit area were: 2-OcOAc, 1233 and 1250; 3-OcOAc, 4358 and 4264; and 4-OcOAc, 12,549 and 10,086. The average values give the following fractions for formation *via* addition of acetic acid to octene: 2-OcOAc, 0.29; 3-OcOAc, 1.00; and 4-OcOAc, 2.6. The high value for 4-OcOAc indicates that some molecules have gone through several cycles of addition and elimination and that, consequently, not all of the 3-OcOAc has come *via* olefin.