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STEREOCHEMISTRY OF ACETOLYSIS OF 2-OCTYL *p*-TOLUENESULFONATE[1]

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SOLVOLYSES of secondary alkyl systems frequently fall in the "borderline" region of solvolytic behavior in which controversy about detailed mechanism still exists. Especially interesting is the reaction of simple secondary alkyl sulfonates in acetic acid in which various criteria suggest a limiting mechanism.[4] Surprisingly, the only published stereochemical studies of such a system come from Kenyon's group[5] who obtained only the qualitative result of substantial net inversion of configuration in the reaction of 2-butyl or 2-octyl *p*-toluenesulfonate with acetic acid. We report here a more detailed study of the latter system which has revealed unexpected facets of this reaction.

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[2] Alfred P. Sloan Fellow, 1958-1962.

[3] Woodrow Wilson Fellow, 1958-1960; United States Rubber Company Fellow, 1960-1961.

[4] A. Streitwieser, Jr., *Chem. Rev.* 56, 571 (1956).

[5a] J. Kenyon, H. Phillips and V. P. Pittman, *J. Chem. Soc.* 1935, 1072; [b] M. P. Balfe, W. H. F. Jackman and J. Kenyon, *ibid.* 1954, 965.

The results of a number of acetolysis experiments are summarized in Table I. The product octyl acetate was distilled material which was examined for purity by gas chromatography and for optical activity. The activity was corrected for the presence of small amounts of non-ester impurities (e.g., solvent) and the percent inversion is recorded relative to 2-octyl acetate produced by reaction of the tosylate with tetraethylammonium acetate. The product ester generally also showed the presence of isomeric octyl acetates, mostly 3- with some 4-, whose quantities are recorded as "percent rearrangement." Further studies of these rearrangement products will be published elsewhere; suffice it to say here that the rearrangement is in part intramolecular and stereospecific. In some cases, 2-octyl acetate was isolated by gas chromatography; the percent net inversion of these samples is given in the final column of Table I.

In some experiments, octyl tosylate was recovered from an incomplete solvolysis. Because it is difficult to separate this oil completely from octyl acetate without jeopardizing its optical purity, it was allowed to solvolyze in absolute ethanol and the product ethyl octyl ether was examined. Ethanolysis of 2-octyl tosylate has been shown to go with complete inversion of configuration.[6]

The results show variable amounts of racemization which can be due in only small part to the action of the liberated toluenesulfonic acid on the ester product or to the addition of

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[6] A. Streitwieser Jr. and A. C. Waiss, Jr., J. Org. Chem. 27, 290 (1962).

TABLE I

Acetolyses of 0.2 M 2-Octyl Tosylate at 75°

run No.	time hrs.	No. of half-lives	added salt	% net apparent inversion	% rearrangement[a]	% net inversion of purified 2-OcOAc
73[b]	4.75	1.4	-	94	1.5	
154	8.7	2.5	-	88	4.0	93
49	27	$\sim$6[c]	-	88	4.3	
61[d]	28	$\sim$6[c]	-	93	4.6	
65	260	75	-	40	18.4	
54	26	>7	0.2M LiOAc	78	2.1	
57[e]	3	1.4	0.1M LiOTs	85	2.1	
155	5.5	2.5	0.1M LiOTs	75	4.6	78
56	5	$\sim$5	0.2M LiOTs	58	3.3	
50	26	12	0.1M LiOTs	56	8.5	
78[f]	1.5	2.2	0.1M $LiClO_4$	37	8.9	
152	1.7	2.5	0.1M $LiClO_4$	34	11.3	36

[a] Obtained from ratio of gas chromatography peak areas of isomeric octyl acetates to that for 2-octyl acetate. Estimated error is ±5% of number listed.

[b] Recovered unreacted tosylate was 7.5% racemized and 0.9% rearranged.

[c] During these runs, the temperature of the bath dropped as much as 40° for an indeterminate time; hence, number of half-lives is an estimate.

[d] 0.02M OcOTs.

[e] Recovered tosylate was 28% racemized and 1.9% rearranged.

[f] Recovered tosylate was 18% racemized and 3.2% rearranged.

acetic acid to octene. Racemization resulted even in the presence of lithium acetate in which addition of acetic acid to alkene is precluded. Indeed, the amount of racemization in this case is substantially higher than in the absence of the lyate salt (22% vs. 12% for comparable reaction times). In course of this solvolysis, lithium acetate is converted progressively to lithium tosylate. Subsequent experiments show that lithium tosylate causes greatly increased amounts of racemization. These results suggest the possibility of a reaction between octyl tosylate and toluenesulfonic acid or lithium tosylate to produce racemized starting material.

In run 61, a more dilute solution (0.02 M) of 2-octyl tosylate in acetic acid was used to diminish any bimolecular reaction. The octyl acetate product shows less racemization (7%) than in the comparable run 49 at 0.2 M (12%) even before corrections for rearrangement are applied. More convincing is run 73 in which the unreacted 2-octyl tosylate recovered after 1.4 half-lives was 7.5% racemized compared to < 6% racemization of the 2-octyl acetate produced. Similarly, in run 57 with 0.1 M lithium tosylate after 1.4 half-lives, the recovered octyl tosylate was 28% racemized compared to < 15% for the 2-octyl acetate. Most of the apparent racemization is clearly due to racemization of starting material; the acetolysis reaction itself of 2-octyl tosylate proceeds with almost complete inversion of configuration.

2-Octyl p-nitrobenzenesulfonate (nitrosylate) solvolyzes several fold faster than the tosylate. An 0.2M solution of optically active 2-octyl nitrosylate in acetic acid containing about 0.1M lithium tosylate was maintained for about 4 half-lives (on the basis of initial rate). Unreacted sulfonate was isolated and was analyzed to be 22% octyl nitrosylate and 78% octyl tosylate. This material was allowed to solvolyze in absolute ethanol. The ethanolysis product when corrected for the contribution from nitrosylate demonstrated that the octyl tosylate was 110 ±16% inverted relative to starting octyl nitrosylate; that is, 2-octyl nitrosylate reacts with lithium tosylate in acetic acid to produce 2-octyl tosylate with essentially complete inversion of configuration.

At the salt concentrations used it is not possible to unravel kinetically a superposed direct displacement reaction from a solvolysis reaction because of large salt effects. The matter was examined in an alternate way; namely, by kinetic examination of acetolyses of 2-octyl, n-butyl and benzyl nitrosylates in the presence of 0.1M lithium tosylate. In all cases, the instantaneous first order rate constants diminish with time showing that alkyl nitrosylate is converted in part to more inert alkyl tosylate during the course of solvolysis. Because of the great difference in reactivities of these alkyl systems, these kinetics were run at different temperatures (25° for benzyl, 50° for 2-octyl, 100° for n-butyl). They are put in a common basis, however, by using as a reduced time scale, the extrapolated half-life at zero time. When the instantaneous first order rate constants are plotted on the same reduced time scale, Fig. 1 is obtained. This figure shows that the rate of conversion of nitrosylate to tosylate compared to the rate of acetolysis of nitrosylate is comparable for all

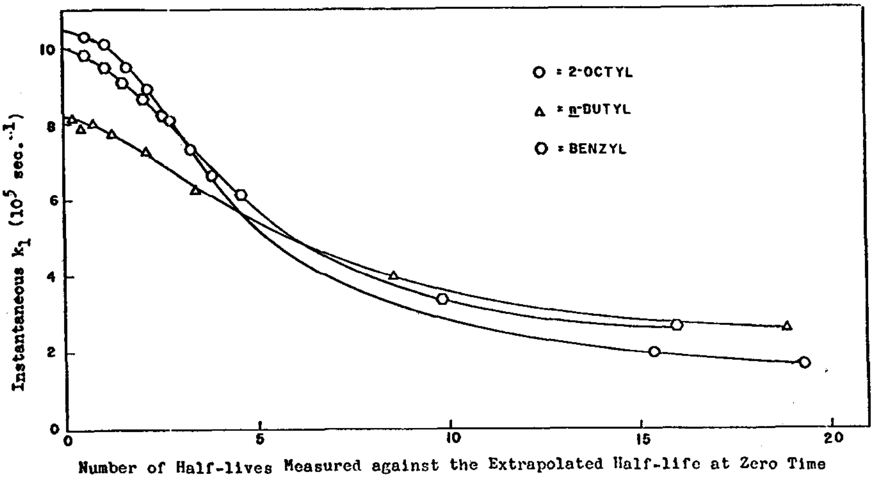

FIG. 1

Exchange of Various Nitrosylates with Lithium Tosylate

three systems. If the interconversion were a normal direct displacement reaction, we would have expected this reaction to be relatively much faster for the primary systems. The reaction seems instead to be an integral part of the acetolysis mechanism.

The results are completely explicable in terms of an ion-pair mechanism which, for 2-octyl tosylate, takes the form:

$$\begin{tikzcd}
\text{Oc–OTs} \arrow[r, shift left, "k_1"] & \text{Oc}^+\ \text{OTs}^- \arrow[l, shift left, "k_{-1}"] \arrow[r, shift left, "\overset{k_{ex}}{\text{Li}^+\text{X}^-}"] \arrow[d, "k_s"] & \text{X}^-\text{Oc}^+ \arrow[l, shift left, "k_{-ex}"] \arrow[r, shift left] \arrow[d] & \text{X–Oc} \arrow[l, shift left] \\
& \text{AcO–Oc} & \text{OcOAc} &
\end{tikzcd}$$

The initial ion-pair can return to starting material, react with solvent (with essentially complete inversion) or react with salt. The salt reaction probably involves an ion quadruplet; however, the observed inversion in these reactions requires that this ion quadruplet be written not as a cyclic structure, $\begin{array}{cc} X^- & Li^+ \\ Oc^+ & OTs^- \end{array}$ which suggests configuration retention but rather as the linear structure[7] $Li^+X^-Oc^+OTs^- \rightleftharpoons X^-Oc^+OTs^-Li^+$, in which migration of a lithium cation from one end to the other and subsequent fission would produce X^-Oc^+ with inversion. This structure suggests an interaction of both anions with the two lobes of the carbonium ion *p*-orbital as in the Doering-Zeiss formulation.[4,8] The ion-pair intermediates probably correspond also to Winstein's internal ion pairs.[9]

The observed rearrangements require an additional mode of reaction for the ion-pair intermediates:

$$R^+X^- \rightleftharpoons R'^+X^-$$

in which R'^+ is a rearranged carbonium ion. The results with added lithium perchlorate (Table I) also fit into this formulation. Ion-pair exchange yields an alkyl perchlorate in which rearrangements and net racemization are enhanced.

Finally, it should be mentioned that the results reported in this paper provide evidence concerning the nature

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[7] *cf.* E. D. Hughes, C. K. Ingold, S. F. Mok, S. Patai and Y. Pocker, *J. Chem. Soc.* 1957, 1265.

[8] W. E. Doering and H. H. Zeiss, *J. Am. Chem. Soc.* **75**, 4733 (1953).

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

and reactions of the ion-pair intermediates in carbonium ion solvolyses—they say little about their mode of formation. In particular, there should be no implication that acetolysis of primary alkyl sulfonates is limiting; nucleophilic participation by solvent is doubtless important for such cases, but intermediates apparently are formed that behave similarly to intermediates formed in secondary alkyl cases. Further discussion of the primary cases will be deferred to a subsequent paper.