Trifluoroacetolysis of 2-Phenylethyl *p*-Toluenesulfonate[1,2]

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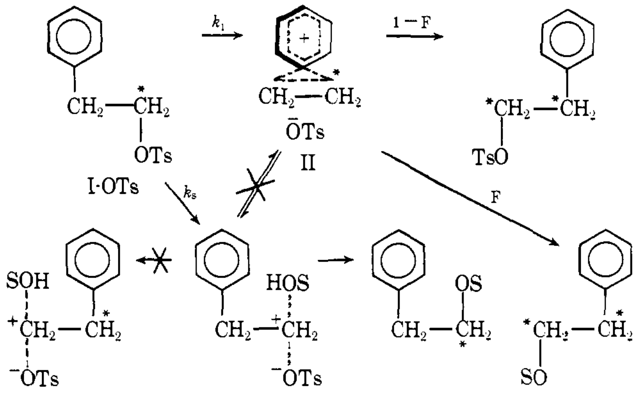
Abstract: A study was carried out to determine the amount of ion-pair return attending the trifluoroacetolysis of 2-phenylethyl tosylate and the kinds of salt effects associated with this system. A special salt effect was observed upon the addition of sodium trifluoroacetate and common ion rate depression upon the addition of tetra-*n*-butylammonium tosylate. The $k_{\mathrm{ext}}{}^0$ obtained by extrapolation of the special salt effect curve to zero salt concentration was somewhat less than the k_1 determined by deuterium scrambling. Thus, the trifluoroacetolysis of 2-phenylethyl tosylate can be explained with the involvement of three carbonium ion species: intimate ion pairs, solvent-separated ion pairs, and dissociated ions.

For some years Winstein and coworkers have discussed the solvolysis of 2-phenylethyl tosylate, PhEtOTs (I-OTs),[4–7] which is marginal with respect to neighboring phenyl participation in terms of a competition between anchimerically unassisted ionization (k_s) and anchimerically assisted ionization (k_Δ). The latter leads to the "nonclassical" phenyl-bridged or "ethylenephenonium"[8–10] cation. From kinetic criteria, the k_Δ/k_s ratio in the solvolysis of PhEtOTs was judged[4,5] to be low in ethanol (EtOH) and acetic acid (AcOH) and substantial in formic acid (HCOOH).

In AcOH, Coke's[11] elegant work with carbon-14 labeled PhEtOTs has made available quantitative values for F, k_Δ, and k_s, where $(1 - F)$ represents the fraction of ion-pair return associated with the k_Δ process. At 90° Coke finds that Fk_Δ is 29.6% of the titrimetric rate constant, k_t, k_s being 70.4%. The value of F is 0.318; therefore, k_Δ/Fk_Δ is 3.15. Assuming Fk_Δ leads to product with retention of configuration and k_s to product with inversion, Snyder[12] observed good agreement between Coke's rearrangement results and his own observations on the stereochemistry of acetolysis of *threo*-1,2-dideuterio-2-phenylethyl brosylate.

Regarding salt effects on the acetolysis of I-OTs, only a slight increase in the titrimetric rate constant was observed by Fainberg and Winstein[13] when lithium perchlorate was added to the acetolysis of I-OTs. This was attributed to a normal salt effect. The absence of a dramatic special salt effect can now be explained with reference to the work of Coke[11] and Lee.[14] From Coke's more recent work, one can calculate that $k_1/k_t = (k_\Delta + k_s)/(Fk_\Delta + k_s) = 1.6$ for the acetolysis of I-OTs at 90°. It is evident that even if the salt eliminated all the ion-pair return, the rate increase would be a mere 60%. Lee and coworkers[14] probed for the special salt effect in the acetolysis of I-OTs by measuring the change in the ratio of per cent rearrangement in starting material to per cent rearrangement in product, with the addition of $LiClO_4$. It turns out that the ratio measured in the presence of KOAc, 0.4, decreases to 0.2 with the addition of $LiClO_4$. They concluded that perchlorate ion is trapping a bridged intermediate and thus preventing some return to scrambled starting material. On the other hand, the rearrangement ratio increased from 0.4 to about 0.5 with the addition of added NaOTs, suggesting a greater fraction of return when common anion is present. It appears, then, that in the acetolysis of PhEtOTs the k_Δ route is accompanied by both internal and external return.

Scheme I



According to Lee, *et al.*,[14,15] formolysis of carbon-14 labeled PhEtOTs in the presence of 0.5 *M* potassium formate produced PhEtOCHO which was 45% rearranged. The rearrangement ratio (rearrangement in recovered ROTs–rearrangement in ROCHO) was 0.06 (after 1 half-life) increasing to 0.11 in the presence of 0.5 *M* NaOTs. From these data Fk_Δ is estimated to be 90% of k_t with very little ion-pair return ($1/F = 1.06$) accompanying solvolysis. There is, however, some return from dissociated species. These observations are characteristic of formolyses of arenesulfonates which lead to bridged ions.[16,17]

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[2] (a) Some aspects of this work were published in preliminary form. See A. Diaz, I. L. Reich, and S. Winstein, *J. Amer. Chem. Soc.*, **90**, 6546 (1968); (b) taken in part from the Ph.D. Thesis of I. L. Reich, University of California at Los Angeles, 1969.

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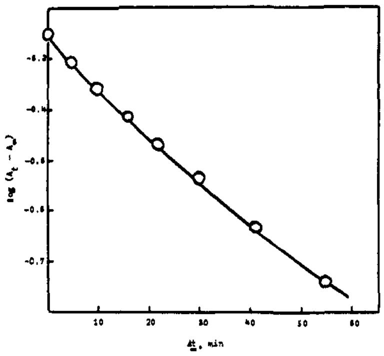

Figure 1. Log $(A_t - A_\infty)$ *vs.* Δt for 2-phenylethyl tosylate trifluoroacetolysis at 75.0°.

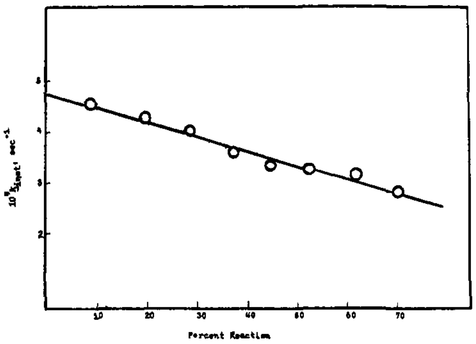

Figure 2. k_{inst} *vs.* per cent reaction for trifluoroacetolysis of 2-phenylethyl tosylate at 75.0°; intercept = 4.76×10^{-4} sec^{-1}.

Quite recently trifluoroacetic acid (CF_3COOH) with its very low nucleophilicity and relatively high ionizing power[18-25] has become an important solvolyzing solvent which gives rise to k_Δ/k_s ratios much higher than in HCOOH. Thus, Nordlander and Deadman[24] have observed that PhEtOTs solvolyzes more than a thousand times as rapidly as does ethyl tosylate (EtOTs) in CF_3COOH and leads to completely scrambled product. Consistently, Jablonski and Snyder[25] have shown that the stereochemical outcome of such trifluoroacetolysis of 1,2-dideuterio-2-phenylethyl tosylate leads to complete retention of configuration in the product. These observations are indicative of the intermediacy of a nonclassical phenyl-bridged cation in the trifluoroacetolysis of PhEtOTs. We now wish to present the results of an investigation that deals with the amount of ion-pair return and the kinds of salt effects associated with the trifluoroacetolysis of this system.

Results

The rates of trifluoroacetolysis of PhEtOTs at 75.0° were measured spectrophotometrically at various ROTs concentrations from 0.001 to 0.40 *M*. Integrated first-order rate constants were calculated according to eq 1, where A_0 is the absorbance at zero time and A_∞

$$k = \frac{2.303}{t} \log \frac{A_0 - A_\infty}{A_t - A_\infty} \qquad (1)$$

is the absorbance at infinity. At ROTs concentrations of 0.0030–0.02 *M*, the integrated first-order rate constants show a downward drift of about 20% from 10 to 70% reaction. A sample rate run for PhEtOTs with 0.00822 *M* ROTs is shown in Table I. At extremes of low (0.00183 *M*) and high (0.402 *M*) ROTs concentrations there was no detectable drift.

An attempt was made to determine the true rate constant in the cases where a drift was observed. Instantaneous rate constants for each rate point were calculated according to eq 2, where the quantity d log $(A_t - A_\infty)/\mathrm{d}t$ was obtained by measuring the slope of a plot of log $(A_t - A_\infty)$ *vs.* Δt with a tangent meter at each rate point. The calculated instantaneous rate

$$k_{inst} = 2.303 \frac{\mathrm{d} \log (A_t - A_\infty)}{\mathrm{d}t} \qquad (2)$$

constants were then plotted against per cent reaction. This plot was extrapolated to 0% reaction by a least-squares treatment of the k_{inst} points to give k_t^0. In general, good linearity of the points was observed, the least-squares line reproducing the k_{inst} points with an average deviation of *ca.* 2%. The plots derived from the rate run tabulated in Table I are shown in Figures 1 and 2.

Table I. Trifluoroacetolysis of 2-Phenylethyl *p*-Toluenesulfonate[a] at 75.0°

Δt, min	A_t[b]	% reaction[c]	$10^4 k$, sec^{-1}	$10^4 k_{inst}$, sec^{-1}
0	0.736	8.8		4.57
4.8	0.671	19.4	4.28	4.26
9.8	0.651	28.6	4.16	4.03
15.8	0.562	37.3	3.93	3.59
21.8	0.517	44.7	3.79	3.32
29.8	0.469	52.4	3.64	3.25
40.8	0.411	61.9	3.54	3.15
54.8	0.360	70.3	3.40	2.81
d	0.178			
		$k_{av} = (3.82 \pm 0.26) \times 10^{-4}$ sec^{-1}		

[a] 0.00822 *M*. [b] At 272.5 mμ. [c] Assuming that *A* at $t = 0$ is 0.790 (calculated using the extinction coefficient of PhEtOTs). [d] After 10 half-lives.

Table II contains a listing of the average integrated rate constants (k_{av}) for rate runs at various concentrations of ROTs. At the highest ROTs concentration, 0.40 *M*, the measured *k* has no downward drift. The average rate constant is 2.31×10^{-4} sec^{-1}. At the more diluted ROTs concentration (0.02–0.003 *M*), the rate constants are uniformly increasing as one proceeds to lower tosylate concentrations. In each run. k_t^0 is higher than the integrated *k* for the early 10% reaction point which is in turn higher than k_{av}. For runs with 0.008–0.003 *M* ROTs, the k_t^0 values average to $(4.86 \pm 0.12) \times 10^{-4}$ sec^{-1} with good agreement. The k_{av} for the lowest ROTs concentration used was 4.38×10^{-4} sec^{-1} and the integrated *k* for 10% reaction was 4.60×10^{-4} sec^{-1}. The drift in this run was too slight to do a proper extrapolation.

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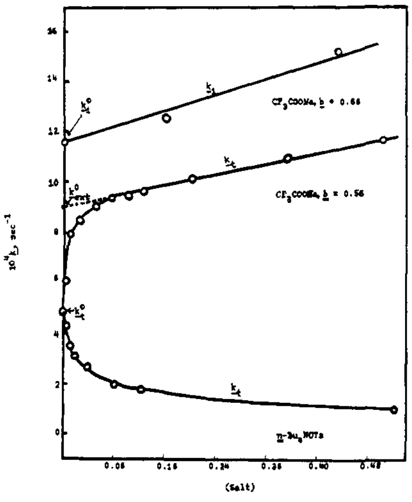


Figure 3. Salt effects in the trifluoroacetolysis of 2-phenylethyl tosylate at 75.0°.

The rate of trifluoroacetolysis was also measured at 50.0° for two ROTs concentrations. Activation parameters were calculated at the two ROTs concentrations from both k_{av} and k_t^0. The data are summarized in Table III. The $\Delta H^{\ddagger} = 19.5$ kcal/mol and $\Delta S^{\ddagger}$ −18 eu values are the same, within experimental error, whether calculated from rate constants at 0.02 M ROTs or 0.003 M ROTs. Likewise, the activation parameters calculated from k_{av} agree well with those calculated from k_t^0.

Table II. Rate Constants for the Trifluoroacetolysis of 2-Phenylethyl p-Toluenesulfonate and 2-Phenylethyl-$1,1$-d_2 p-Toluenesulfonate at 75.0°

ROTs, 10^2 M	10^4k, sec^{-1} [a] α-H$_2$	α-D$_2$	k_H/k_D
40	2.31 ± 0.08	2.14 ± 0.09	1.08
2.1	3.07 ± 0.19[b]	2.62 ± 0.11	1.17
0.82	3.91 ± 0.23	3.19 ± 0.14	1.23
0.32	4.07 ± 0.18	3.37 ± 0.09	1.21
"0.00" [c]	4.86 ± 0.15	3.82 ± 0.2	1.27

[a] The k_{av}'s were used at all concentrations except for the entry at "0.00" M ROTs where the extrapolated k_t^0's were used. Each value is the average of two or more runs. [b] Compare with 3.22 × 10^{-4} sec^{-1} extrapolated by Nordlander and Deadman[24] from data at lower temperatures using 0.050 M tosylate ester. [c] Error reflects the mean deviation of the k_{inst} points from the least-squares line.

Table III. Activation Parameters[a] for Trifluoroacetolysis of 2-Phenylethyl p-Toluenesulfonate

[ROTs], 10^2 M	Temp, °C	10^4k_{av}, sec^{-1}	$10^4k_t^0$, sec^{-1}
2.05	50.0	0.329 ± 0.035	0.383 ± 0.009
2.04	75.0	3.07 ± 0.19	3.95 ± 0.11
		$\Delta H^{\ddagger}_{av} = 19.1 \pm 1.4$ kcal/mol $\Delta S^{\ddagger}_{av} = -19.8 \pm 4.0$ eu at 75.0° $\Delta H^{\ddagger}_0 = 19.7 \pm 0.5$ kcal/mol $\Delta S^{\ddagger}_0 = -17.8 \pm 1.4$ eu at 75.0°	
0.324	50.0	0.426 ± 0.008	
0.332	75.0	4.16 ± 0.15	
		$\Delta H^{\ddagger} = 19.5 \pm 0.6$ kcal/mol $\Delta S^{\ddagger} = -18.1 \pm 1.7$ eu at 75.0°	

[a] Compare with $\Delta H^{\ddagger} = 20.2$ kcal/mol and $\Delta S^{\ddagger} = -16.8$ eu obtained by Nordlander and Deadman[24] using 0.050 M tosylate ester.

Table IV. Summary of k_t Values for the Trifluoroacetolysis of 2-Phenylethyl p-Toluenesulfonate with Added Salt at 75.0°

Salt, 10^2 M	10^4k, sec^{-1} k_t^0	k_{av}
n-Bu$_4$NOTs[a]		
0	4.86 ± 0.12	3.82 ± 0.26
0.492	4.29 ± 0.21	3.03 ± 0.16
1.015	3.47 ± 0.18	2.73 ± 0.17
1.815	3.04	2.48 ± 0.09
3.93	2.64	2.18 ± 0.11
8.08	1.96	1.84 ± 0.07
12.32	1.79	1.58 ± 0.15
52.3	0.94	0.91 ± 0.05
CF$_3$COONa[b]		
0.504[c]	6.06	4.91 ± 0.18
1.05[a]	7.91	5.75 ± 0.22
2.44	8.46	6.38 ± 0.71
5.10	9.03	7.57 ± 0.34
7.46	9.35	8.17 ± 0.25
7.70	9.35	8.86 ± 0.18
10.1	9.37	9.28 ± 0.09
12.6	9.66	9.54 ± 0.24
20.2	10.1	9.78 ± 0.11
35.4	11.0	10.7 ± 0.4
50.2	11.7	11.3 ± 0.4

[a] 0.0080–0.0085 M ROTs. [b] 0.020 M ROTs. [c] 0.00326 M ROTs.

The rates of trifluoroacetolysis of PhEtOTs in the presence of common-ion salt, tetra-n-butylammonium p-toluenesulfonate, were measured at 75.0°. The added concentration of n-Bu$_4$NOTs ranged from 0.0049 to 0.52 M. Here again, the integrated first-order rate constants drifted downward within a run and were treated as described above. As seen in Table IV, k_t^0 and k_{av} decrease uniformly in the presence of increasing amounts of added salt. In going from 0 to 0.52 M added n-Bu$_4$NOTs, k_t^0 is reduced from 4.86 × 10^{-4} sec^{-1} to 0.94 × 10^{-4} sec^{-1}, decreasing by more than a factor of five. This is shown in Figure 3 where k_t is plotted *vs.* added n-Bu$_4$NOTs.

The rates of trifluoroacetolysis of PhEtOTs increased significantly with the addition of sodium trifluoroacetate (0.0050–0.50 M). A downward drift was again observed within a run, this drift being much more pronounced at the lower concentrations of salt. The extrapolated and average rate constants with added CF$_3$COONa, measured at 75.0°, are listed in Table IV. The k_t values increase very steeply, at first, with increasing amounts of added salt. At about 0.075 M CF$_3$COONa the curve levels off and the subsequent points fall on a good straight line. The least-squares fit for this line provides a slope equal to 5.22 × 10^{-2} M^{-1} sec^{-1} and an intercept (k_{ext}^0) equal to (9.00 ± 0.06) 10^{-4} sec^{-1}. The concentration of CF$_3$COONa needed to increase the rate half-way from k_t^0 (4.86 × 10^{-4} sec^{-1}) to k_{ext}^0 (9.00 × 10^{-4} sec^{-1}) is *ca.* 0.006 M where the k_{ext}^0/k_t^0 ratio is 1.85. This is shown in Figure 3 where k_t is plotted against [CF$_3$COONa]. The linear portion of the curve in Figure 3 is fit by eq 3 where the b value is 0.56.

$$k_t = k_{ext}^0(1 + b[\mathrm{CF_3COONa}]) \qquad (3)$$

The effect of lithium perchlorate and lithium trifluoroacetate salts on k_t was measured at one or two concentrations and found to be similar to that of sodium trifluoroacetate. At 0.051 M salt, the average k with CF_3COOLi is slightly less than with CF_3COONa, the values being $(7.09 \pm 0.37) \times 10^{-4}$ sec^{-1} and $(7.57 \pm 0.34) \times 10^{-4}$ sec^{-1}, respectively. With 0.01 and 0.02 M added $LiClO_4$, the average k's are $(4.95 \pm 0.10) \times 10^{-4}$ sec^{-1} and $(6.81 \pm 0.36) \times 10^{-4}$ sec^{-1}, respectively. Both runs with CF_3COOLi and $LiClO_4$ show a detectable downward drift in the integrated k's within a run.

One rate run was done in the presence of 0.0474 M CF_3COONa and 0.0550 M NaOTs. The observed k_t is $(4.84 \pm 0.12) \times 10^{-4}$ sec^{-1} which is lower than the k_t observed with 0.0474 M CF_3COONa alone, *ca.* 9.0×10^{-4} sec^{-1} (see Figure 3).

The rates of trifluoroacetolysis of 2-phenylethyl-*1,1*-d_2 *p*-toluenesulfonate were measured at various ROTs concentrations. The observed kinetic behavior is qualitatively similar to that observed with the undeuterated ester; however, the effects are less pronounced. Table *II* summarizes the trifluoroacetolysis rates of PhEtOTs-α-d_2. The rates of trifluoroacetolysis of PhEtOTs-α-d_2 can be compared to those of the undeuterated tosylate at the same ROTs concentration in Table *II*. Each pair of rate runs used to determine k_H/k_D was done at the same time, under the same conditions.' The data seem to indicate an increase in the k_H/k_D ratio as one goes to lower ROTs concentration.

The total scrambling rate constant for trifluoroacetolysis of PhEtOTs-α-d_2 was determined by nmr. The reaction was followed using the intensity of the combined β-proton signals in the ROTs (δ 2.55 ppm) and $ROCOCF_3$ (δ 2.67 ppm), relative to the para-methyl signal at δ 7.92 ppm. Each run was sampled 3–5 times and the scrambling rate constants were calculated from eq 4, where I_0 is the intensity of the β

$$k_{1D} = 2.303 \log \frac{I_0 - I_\infty}{I_t - I_\infty} \qquad (4)$$

proton signals at time zero, I_∞ is the intensity at infinity, and I_t is the intensity at time t. The rates were done on 0.40 M ROTs solutions at 50.0 and 75.0°. The data are summarized in Table V.

Table V. Deuterium Scrambling Rates of 2-Phenylethyl-*1,1*-d_2 *p*-Toluenesulfonate in Trifluoroacetic Acid[a]

Temp, °C	CF_3COONa, M Init	 Av	$10^4 k_{1D}$, sec^{-1}
50.0	0	0	0.900 ± 0.005[b,c]
75.0	0	0	9.12 ± 0.16[b,c]
	0.25	0.16	9.92 ± 0.11
	0.50	0.43	12.0 ± 0.1

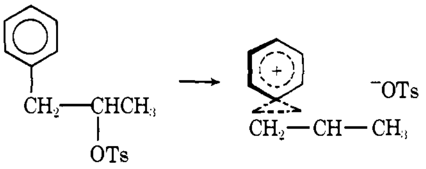
[a] 0.40 M ROTs. [b] Average of two runs. [c] $\Delta H^\ddagger = 20.0$ kcal/mol, and $\Delta S^\ddagger = -14.1$ eu.

A graph including all the various measured rate constants for the trifluoroacetolysis of PhEtOTs plotted against the concentration of added salt is shown in Figure 3.

Discussion

The total scrambling rate constant for PhEtOTs-α-d_2 in CF_3COOH as measured by nmr is 9.12×10^{-4} sec^{-1}. It was necessary to determine the k_H/k_D ratio in order to get at the ionization rate constants, k_1, of the undeuterated PhEtOTs. The measured k_{tH}/k_{tD} ratio varied with ROTs concentration where the highest ratio of 1.27 was obtained using the extrapolated rates. This value is probably the most nearly correct isotope effect. At the higher ROTs-α-d_2 concentrations, measurement of the isotope effect is complicated by ion-pair return which generates ROTs-α-H_2. With the assumption that k_{tH}^0/k_{tD}^0 is a good approximation for k_{1H}/k_{1D}, the scrambling rate constants were corrected to the protio ester using the value 1.27. Thus, $k_{1H} = 1.27 \times (9.12 \times 10^{-4}$ sec$^{-1}) = 11.6 \times 10^{-4}$ sec^{-1}. Unless specifically noted, for the remainder of the text k_1 refers to k for protio material (k_{1H}).

For the trifluoroacetolysis of PhEtOTs, k_1^0/k_t^0 or k_Δ/Fk_Δ has the value 2.39. Thus only 42% of the bridged phenonium ion pairs (II) produced give rise to solvolysis product while 58% regenerate covalent starting material. In this solvent, ion-pair return is less important than in the less ionizing solvent, acetic acid, where $k_\Delta/Fk_\Delta = 3.2$. The reverse behavior is observed with the more reactive secondary system, 1-phenyl-2-propyl OTs (III-OTs),[26] which also reacts *via* a bridged phenonium intermediate.[27] Here the k_Δ/Fk_Δ value is increased from 5.4 in acetic acid to 10.6 in trifluoroacetic acid.



III-OTs

The addition of CF_3COONa salt causes a steep increase in the rate of trifluoroacetolysis of PhEtOTs which gradually levels off at higher salt concentrations. This is characteristic of the special salt effect observed with $LiClO_4$ in the acetolysis of many systems.[28–32] Extrapolation of the linear portion of the special salt effect curve to zero concentration provides the value of k_{ext}^0 equal to 9.00×10^{-4} sec^{-1}. The values for k_{ext}^0/k_t^0 and k_1^0/k_{ext}^0 are 1.85 and 1.29, respectively, where the former gives a measure of the amount of ion-pair return coming from the solvent separated ion pair. The latter gives an estimate of the extent of involvement of the intimate ion pair. These quantities can be compared to the corresponding ones obtained for 1-phenyl-2-propyl OTs (III-OTs) in CF_3COOH,[26] where $k_{ext}^0/k_t^0 = 1.59$ and $k_1^0/k_{ext}^0 = 6.67$. It is striking that return from the intimate ion pair is much more important from the more stable intermediate generated from 1-phenyl-2-propyl tosylate whereas return from the solvent separate ion pair is approximately equal for both systems.

The special salt effect can be further characterized by the quantities $[CF_3COONa]_{1/2} = 6 \times 10^{-3}$ M and $b = 0.56$. The normal salt effect of CF_3COONa as measured by the b value is *ca.* 10 times smaller than for 1-

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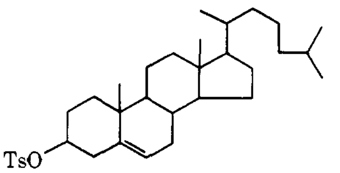
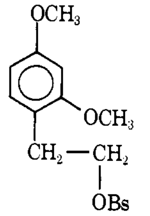
(32) S. Winstein, P. E. Klinedinst, Jr., and G. C. Robinson, *ibid.*, 83, 885 (1961).

phenyl-2-propyl OTs (b = 6.4). In acetolysis where the special salt effect was first noticed and investigated, the most commonly used special salt was $\mathrm{LiClO_4}$. With $\mathrm{LiClO_4}$ in AcOH the slope of the initial steeply ascending part of the special salt effect curve is greater than for $\mathrm{CF_3COONa}$ in $\mathrm{CF_3COOH}$, linearity setting in at lower concentrations. The quantity $[\mathrm{LiClO_4}]_{1/2}$ ranges from 8×10^{-5} to 3×10^{-3} M for the various β-arylalkyl esters examined.[28-31]

In the case of cholesteryl tosylate (IV)[29] and 2-(2,4-dimethoxyphenyl)ethyl brosylate (V)[29] other special salts besides $\mathrm{LiClO_4}$ were investigated, namely diphenylguanidinium acetate (DPGHOAc), LiOAc, NaOAc, and KOAc. With both IV and V, k_{ext}^0 was constant for all the various salts while the values of $[\mathrm{salt}]_{1/2}$ and b were quite specific for each salt. Thus, there was the same amount of ion-pair capture with all salts, but a variation in efficiency of capture among them. It was difficult to measure $[\mathrm{salt}]_{1/2}$ for the acetate salts since these salts are neutralized by the acid produced in acetolysis. An estimate of $[\mathrm{LiOAc}]_{1/2} = ca.\ 3 \times 10^{-3}$ M was obtained with V, where $[\mathrm{LiClO_4}]_{1/2} = 8 \times 10^{-5}$ M. Thus, $\mathrm{LiClO_4}$ is a much more efficient special salt than LiOAc in acetolysis, at least for V-OBs. Sodium, potassium, and lithium acetate show very small normal salt effects, *e.g.*, b is 2 for LiOAc in the solvolysis of V-OBs. The normal salt effects of acetate salts in $\mathrm{CF_3COOH}$ are comparable to those found in AcOH. However, an interesting contrast is that in the trifluoroacetolysis of PhEtOTs; $\mathrm{LiClO_4}$ does not show any greater efficiency as a special salt than $\mathrm{CF_3COONa}$ or $\mathrm{CF_3COOLi}$.



IV-OTs



V-OBs

Induced common-ion rate depression was observed by Winstein, *et al.*, in the acetolysis of every system which displays a special salt effect.[32] It was evident from one run done in the presence of both $\mathrm{CF_3\ COONa}$ and NaOTs that induced depression was also occurring in the trifluoroacetolysis of PhEtOTs. Induced common-ion depression was tested for by adding 0.055 M NaOTs to one run containing 0.047 M $\mathrm{CF_3COONa}$. This concentration of special salt is sufficient to raise k_t to 9.00×10^{-4} sec^{-1}, a value well above k_t^0 which is 4.86×10^{-4} sec^{-1}. Addition of common-ion salt at this $\mathrm{CF_3COONa}$ concentration does indeed cause depression of k_t to 4.84×10^{-4} sec^{-1}. Therefore, in $\mathrm{CF_3COOH}$ as in AcOH the ion pair of the special salt ($\mathrm{R^+ClO_4^-}$) can exchange with common-ion salt $\mathrm{Na^+}$ $\mathrm{OTs^-}$, thereby suppressing the special salt effect.

The downward drift of the integrated first-order solvolysis rate constants and the progressive rate depression with addition of increasing quantities of n-$\mathrm{Bu_4NOTs}$ show that common-ion rate depression is important in the trifluoroacetolysis of PhEtOTs. This indicates the presence of dissociated ions which can return to covalent ROTs as well as give rise to solvolysis product.

As seen in Figure 3, k_t decreases markedly with the addition of n-$\mathrm{Bu_4NOTs}$. The decrease is quite sharp at lower salt concentrations and becomes less dramatic as the concentration of n-$\mathrm{Bu_4NOTs}$ is increased. At the highest concentration of added salt (0.52 M) used, k_t is still decreasing. There was no evidence of a minimum and subsequent increase (due to a normal salt effect) in the curve of k_t *vs.* n-$\mathrm{Bu_4NOTs}$ concentration. Since the slope of the curve is quite small at the highest n-$\mathrm{Bu_4NOTs}$ concentration, the value of k_t at 0.52 M salt is probably close to the minimum value. Using the b value of 0.56 of $\mathrm{CF_3COONa}$ as an approximation for the b value for n-$\mathrm{Bu_4NOTs}$ and $k_t = 0.94 \times 10^{-4}$ sec^{-1} at 0.52 M n-$\mathrm{Bu_4NOTs}$, k_t^{d}[28] was estimated with the aid of eq 5. This provides the value of 0.73×10^{-4} sec^{-1} which is an upper limit to k_t^{d} (k_t^{d} is defined in eq 9). The actual value may be slightly lower. Using this value, the ratio k_t^0/k_t^{d} can be approximated at 6.7. This indicates that in the trifluoroacetolysis of PhEtOTs at least 85% of the product trifluoroacetate is produced from dissociated ions. The remainder, 15% or less, comes from the solvent-separated ion pair.

$$k_t = k_t^{\mathrm{d}}[1 + b(n\text{-}\mathrm{Bu_4NOTs})] \qquad (5)$$

Although p-toluenesulfonic acid (HOTs) was not added to the trifluoroacetolysis to determine its efficiency in rate depression, the downward drift observed in the rate runs with no added salt indicated that HOTs was having a substantial effect. In fact, if one estimates the average concentration of HOTs in some of these runs, one can see that depression by HOTs is nearly as efficient as by n-$\mathrm{Bu_4NOTs}$. This is not surprising since it is possible that a significant amount of n-$\mathrm{Bu_4NOTs}$ may be present as HOTs in $\mathrm{CF_3COOH}$. Eaborn[33] observed that hydrogen chloride and, to a lesser extent, hydrogen bromide were evolved when lithium chloride and lithium bromide were dissolved in $\mathrm{CF_3COOH}$.

These results on common-ion rate depression can be contrasted with those observed in the acetolysis of some other systems. For cholesteryl tosylate (IV-OTs) and 2-(2,4-dimethoxyphenyl)ethyl tosylate (V-OTs) common-ion rate depression was probed with the addition of LiOTs.[28] In both these systems the maximum depression occurred already at the very low LiOTs concentration of *ca.* 0.007 M, yielding values of k_t^0/k_t^{d} equal to 1.20 and 1.57 for IV-OTs and V-OTs, respectively. For 2-p-anisylethyl tosylate in AcOH, common-ion rate depression was explored with the addition of n-$\mathrm{Bu_4NOTs}$, LiOTs, and HOTs.[34] The efficiency of these compounds in depressing the rate of solvolysis increased in going from HOTs to LiOTs to n-$\mathrm{Bu_4NOTs}$. This is what is expected since the fraction of dissociated species present in AcOH is greater for n-$\mathrm{Bu_4NOTs}$ than for LiOTs and LiOTs is in turn more dissociated than HOTs.[34] Thus, HOTs gave a k_t^0/k_t^{d} ratio of 1.39, LiOTs of 1.47, and n-$\mathrm{Bu_4NOTs}$ of 1.54.

It is interesting to note that a greater fraction of the rate of solvolysis of PhEtOTs in $\mathrm{CF_3COOH}$ can be depressed by n-$\mathrm{Bu_4NOTs}$ than in the case of III-OTs, IV-OTs, and V-OTs in AcOH, even though it takes a lot more n-$\mathrm{Bu_4NOTs}$ to effect maximum depression. At

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(33) C. Eaborn, P. M. Jackson, and R. Taylor, *J. Chem. Soc. B*, 613 (1966).

(34) P. E. Klinedinst, Jr., Ph.D. Dissertation, University of California at Los Angeles, 1959.

least 85% of the product is formed from dissociated ions in the trifluoroacetolysis of PhEtOTs, while in the acetolysis of III, IV, and V only 35, 36, and 17% of the product are formed from dissociated species, respectively.

The trifluoroacetolysis of PhEtOTs (ROTs) can be explained with the intermediacy of two ion pairs and dissociated ions. This is diagrammed below where A is the intimate ion pair, B is the solvent-separated ion pair, and C is a dissociated ion.

$$\begin{tikzcd}
\text{I-OTs} & \text{A} & \text{B} & \text{C} \\
\text{ROTs} \arrow[r, shift left, "k_1"] & \text{R}^+\text{OTs}^- \arrow[l, shift left, "k_{-1}"] \arrow[r, shift left, "k_2"] & \text{R}^+//\text{OTs}^- \arrow[l, shift left, "k_{-2}"] \arrow[r, shift left, "k_3"] \arrow[d, "k_s{}^B"] & \text{R}^+ + \text{OTs}^- \arrow[l, shift left, "k_{-3}"] \arrow[dl, "k_s{}^C"] \\
 & & \text{product} &
\end{tikzcd} \qquad (6)$$

Using the values $k_1 = 11.6 \times 10^{-4}$ sec^{-1} and $k_{\text{ext}}{}^0 = 9.00 \times 10^{-4}$ sec^{-1} in eq 7[16] provides the value 0.18 for

$$\frac{k_1}{k_{\text{ext}}{}^0} = 1 + \frac{k_{-1}}{k_2} \qquad (7)$$

the k_{-1}/k_2 ratio. It follows that 15% of the intimate ion pairs formed in the trifluoroacetolysis of PhEtOTs return to covalent starting material $(k_{-1}/k_{-1} + k_2)$ and 85% go on to the solvent-separated ion pair stage. From the above scheme one can write the following expression for $k_t{}^0$ when [OTs$^-$] approaches zero[28] (eq 8).

$$k_t{}^0 = k_1/1 + \frac{k_{-1}/k_2}{(k_s{}^B + k_3)/(k_{-2} + k_s{}^B + k_3)} \qquad (8)$$

On the other hand, when [OTs$^-$] is very large, the fully depressed rate constant $k_t{}^d$ is defined as in eq 9.[28,34]

$$k_t{}^d = \frac{k_1}{1 + \dfrac{k_{-1}/k_{-2}}{k_s{}^B/(k_{-2} + k_s{}^B)}} \qquad (9)$$

Using the values for k_1, $k_t{}^0$ (4.86×10^{-4} sec^{-1}), and k_{-1}/k_2 in eq 8 provides the values $(k_s{}^B + k_3)/(k_2 + k_s{}^B + k_3) = 0.129$ and $k_{-2}/(k_{-2} + k_s{}^B + k_3) = 0.871$. Using the values for k_1, $k_t{}^d$ (0.73×10^{-4} sec^{-1}), and k_{-1}/k_2 in eq 9 provides the value 81.7 for $k_{-2}/k_s{}^B$.

Thus, one can determine the fate of the solvent-separated ion pair intermediate. The largest fraction, 87%, returns to the intimate ion pairs $(k_{-2}/(k_{-2} + k_s{}^B + k_3))$, while 1.2% is captured by solvent and forms product from $(k_{-2}/k_s{}^B)$. By difference then, 11.8% of the intermediates dissociate to C.

The partitioning of the various intermediates in the trifluoroacetolysis of 1-phenylethyl tosylate is summarized in the scheme below. In trifluoroacetolysis of PhEtOTs in the absence of common ion (OTs$^-$) *ca.* 9% of the product trifluoroacetate arises from the solvent-separated ion pairs while the rest, 91%, arises from the dissociated species. Finally, the ratio of return to covalent ROTs to product formation of the ion pairs (R$^+$OTs$^-$ plus R$^+$//OTs$^-$) is given by $k_{-1}/(k_3 + k_s{}^B)$ or 15%/(11.8% + 1.2%) which equals 1.15. This indicates that *ca.* 54% of the ion-pair intermediates return to ROTs which agrees reasonably well with the estimate of 58% calculated from $k_1{}^0/k_t{}^0$.

$$\begin{tikzcd}
\text{ROTs} \arrow[r, shift left] & \text{R}^+\text{OTs}^- \arrow[l, shift left, "15\%"] \arrow[r, shift left, "85\%"] & \text{R}^+//\text{OTs}^- \arrow[l, shift left, "87\%"] \arrow[r, shift left, "11.8\%"] \arrow[d, "1.2\%"] & \text{R}^+ + \text{OTs}^- \arrow[l, shift left] \arrow[d] \\
 & & \text{product} & \text{product}
\end{tikzcd}$$

This behavior can be compared to the solvolytic behavior in the acetolysis of 2-*p*-anisylethyl tosylate (III).[16] The partitioning of the various intermediates in this system is summarized in the scheme below.

$$\begin{tikzcd}
\text{ROTs} \arrow[r, shift left] & \text{R}^+\text{OTs}^- \arrow[l, shift left, "8\%"] \arrow[r, shift left, "92\%"] & \text{R}^+//\text{OTs}^- \arrow[l, shift left, "95\%"] \arrow[r, shift left, "2.5\%"] \arrow[d, "2.8\%"] & \text{R}^+ + \text{OTs}^- \arrow[l, shift left] \arrow[d] \\
 & & \text{product} & \text{product}
\end{tikzcd}$$

In comparing the solvolytic behavior of the two systems, two significant differences are seen. First, the ion-pair intermediates show consistently more dissociation in CF_3COOH. Secondly, a much greater portion of the solvolysis product is derived from the solvent-separated ion pair in AcOH (see above). Thus, trifluoroacetic acid promotes dissociation relative to solvent capture of R$^+$//OTs$^-$ with 2-phenylethyl tosylate more than AcOH with 2-*p*-anisylethyl tosylate. This is in line with the previously observed less nucleophilic character[35] and greater dissociating ability[26] of trifluoroacetic acid solvent.

Whereas the solvolysis of PhEtOTs was marginal with respect to anchimeric assistance in EtOH, AcOH, and HCOOH, in CF_3COOH the solvolysis is overwhelmingly k_Δ, the k_Δ/k_s ratio being 23,000.[35] It is clear that the trifluoroacetolysis involves a stabilized phenonium ion. Thus, it is not surprising that PhEtOTs in CF_3COOH shows the same phenomena of internal return, special salt effect, and common-ion rate depression observed earlier in the acetolysis of various systems which give bridged phenonium ions.

Experimental Section

2-Phenylethyl *p*-toluenesulfonate was prepared in the usual way from 2-phenylethyl alcohol and crystallized from pentane: mp 36.5–37.0° (lit.[28] mp 35.5–36.6°).

Phenylethyl-*1,1*-d_2 *p*-toluenesulfonate. Material containing greater than 99% d_2 was kindly provided by Dr. J. Petrovich (mp 37.4–37.7°).

Sodium trifluoroacetate and lithium trifluoroacetate were made in trifluoroacetic acid by the addition of the appropriate amount of dry sodium carbonate or lithium carbonate followed by an equivalent amount of trifluoroacetic anhydride to react with the water formed.

Sodium *p*-toluenesulfonate was made in trifluoroacetic acid by the addition of the appropriate amount of dry sodium carbonate and toluenesulfonic acid followed by trifluoroacetic anhydride to react with the water formed.

Tetra-*n*-butylammonium *p*-toluenesulfonate was prepared as previously described: mp 71.5–72.5° (lit.[34] mp 73.5–74.5°).

Lithium Perchlorate. Lithium perchlorate trihydrate was dehydrated at 0.2 mm over phosphorus pentoxide using refluxing toluene as the heating agent.

Trifluoroacetic Acid. Trifluoroacetic acid (2 l.) and 50 ml of trifluoroacetic anhydride were refluxed for 1 hr. The solution was then distilled through a 2-ft vacuum-jacketed column packed with rings. The middle fraction was collected in a Schlenk flask and stored under nitrogen. After distillation 0.1% trifluoroacetic anhydride was added to the acid. Later batches of trifluoroacetic acid were treated with silver oxide prior to distillation as described by Eaborn.[33] There was no difference in the solvolysis rates of a number of *p*-toluenesulfonates in the trifluoroacetic acid which had been prepared by the two methods.

Trifluoroacetic anhydride was distilled before use.

Kinetic Measurements in Trifluoroacetic Acid. Trifluoroacetolyses were followed spectrophotometrically using the method of

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(35) I. L. Reich, A. Diaz, and S. Winstein, *J. Amer. Chem. Soc.*, **91**, 5635 (1969).

Swain and Morgan[36] modified by Peterson.[37] Rates were done by this technique on tosylate ester concentrations ranging from 0.0015 to 0.40 *M*. The usual ampoule technique, using 5-ml aliquots, was employed.[38] The samples were quenched by delivering the aliquot into 95% ethanol. The absorbance of the ethanol solutions was measured at the sharp maximum at 272.5 mμ on a Cary Model 14M recording spectrophotometer. The quenched solutions were quite stable and no significant change in absorbance was found, after 1 hr, in most cases.

It was always necessary to dilute the trifluoroacetic acid sample prior to analysis (at least 0.5 ml of EtOH/5 ml of sample), the reason being that alkyl tosylates and tosylic acid not only have the same absorption maximum but also approximately the same extinction coefficient. When the sample contained less than 50% ethanol it was necessary to measure the absorbance immediately after the addition of the ethanol for the absorbance was found to decrease on standing, especially for the infinity point.

The extinction coefficient of 2-phenylethyl *p*-toluenesulfonate in 8% trifluoroacetic acid in 95% ethanol was 513. The infinity absorbances due to toluenesulfonic acid or sodium toluenesulfonate usually fell in the range 0.180–0.240, corresponding to a molar extinction coefficient of 125.

For the trifluoroacetolyses containing high concentrations of tetra-*n*-butylammonium tosylate, it was not possible to watch disappearance of the absorption of the ROTs for it was swamped by the absorption of the added tosylate salt. For concentrations of tetra-*n*-butylammonium tosylate greater than 0.1 *M*, it became necessary to extract the ROTs from the trifluoroacetic acid solution between pentane and water.[38] The pentane layer was evaporated to dryness and the residue was dissolved in 95% ethanol and then analyzed.

Nmr Studies in Trifluoroacetic Acid. Product studies and deuterium scrambling rates were performed in a sealed tube using *ca.* 0.4 ml of a 0.40 *M* solution of tosylate ester. The nmr tube was immersed in a constant temperature bath. At appropriate intervals it was withdrawn and cooled in ice and the nmr spectrum was recorded and integrated on an A-60 D Varian nmr spectrometer. The deuterium scrambling of 2-phenylethyl-*1,1*-d_2 tosylate was followed by measuring the decrease of the area of combined β proton signals in the ROTs (δ 2.55 ppm) and the ROCOF$_3$ (δ 2.67 ppm) from two protons to one.

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[36] C. G. Swain and C. R. Morgan, *J. Org. Chem.*, **29**, 2097 (1964)

[37] P. E. Peterson, R. E. Kelley, Jr., R. Belloli, and K. A. Sipp *J. Amer. Chem. Soc.*, 87, 5169 (1965).

[38] A. H. Fainberg and S. Winstein *ibid.*, 78, 2770 (1956).

Synthesis of the Tetracyclo[11.1.0.0^{3,5}.0^{7,9}]tetradecan-11-ols. Possible Heptahomotropylium Ion Precursors[1]

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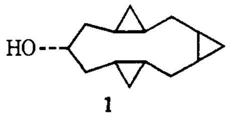
Corvallis, Oregon 97331. Received June 4, 1971

Abstract: The all-syn form of tetracyclo[11.1.0.0^{3,5}.0^{7,9}]tetradecan-11-ol, epi-**2**, has been synthesized by a route which utilizes a sequence of highly selective homoallylic ring expansions. Variations in the sequence allow synthesis of six related isomers and their corresponding ketones which were necessary for the structural assignment. The tosylate of epi-**1** is of interest as a possible precursor of the heptahomotropylium ion, **4**.

The present paper describes the synthesis of six previously unknown tetracyclo[11.1.0.0^{3,5}.0^{7,9}]tetradecan-11-ols, **1**, **2**, and **3**, and their epimers. The compounds are of considerable interest since epi-**1** is a possible precursor or heptahomotropylium ion, **4**. The primary synthetic goal was to obtain compound epi-**1**, but since it was totally unknown the other related compounds were necessary for spectral comparison. Accordingly, a route was devised which allowed modifications such that all six isomeric alcohols and their corresponding ketones could be obtained. The success of the scheme depends on three important observations which we have reported earlier.[4] The Simmons–Smith (SS) reactions[5] of medium sized ring allylic alco-



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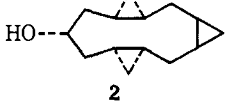

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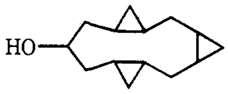
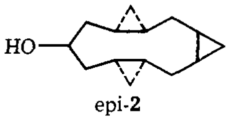


epi-**1**



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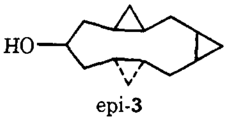
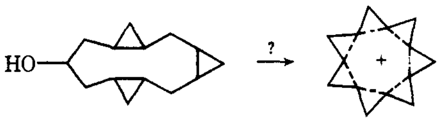


epi-**3**



epi-1 **4**

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[3] Deceased Nov 23, 1969.

[4] (a) M. Gasic, D. Whalen, B. Johnson, and S. Winstein, *J. Amer. Chem. Soc.*, **89**, 6382 (1967); (b) C. D. Poulter, E. C. Friedrich, and S. Winstein, *ibid.*, **91**, 6892 (1969); (c) C. D. Poulter, E. C. Friedrich, and S. Winstein, *ibid.*, **92**, 4274 (1970); (d) C. D. Poulter and S. Winstein, *ibid.*, **92**, 4284 (1970).

[5] H. E. Simmons, E. P. Blanchard, and R. D. Smith, *ibid.*, **86**, 1347 (1964), and references therein.