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VINYLIC CATIONS FROM SOLVOLYSIS. IX. TRIFLUOROACETOLYSIS OF 1-ANISYL-2-METHYLPROPEN-1-YL ARYLSULFONATES

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A frequently considered[1-5] competing mechanism with the vinylic S_N1 solvolysis (eqn. 1) is a slow electrophilic addition-elimination,[6] followed by solvolysis of the saturated adduct (Ad_E-S_N) (eqn. 2). This route, which may operate even in aqueous ethanol,[2b] should

$$R^3R^2C{=}CR^1X \xrightarrow[-X^-]{\text{slow}} R^3R^2C{=}\overset{\oplus}{C}R^1 \xrightarrow{+Y^-} R^3R^2C{=}CR^1Y \qquad S_N1 \quad (1)$$

$$R^3R^2C{=}CR^1X \xrightarrow[+H^+]{\text{slow}} R^3R^2CH{-}\overset{\oplus}{C}R^1X \xrightarrow{+Y^-} R^3R^2CH{-}CR^1XY \xrightarrow{-HX} R^3R^2C{=}CR^1Y \quad Ad_E\text{-}S_N \quad (2)$$

be more important in the more acidic carboxylic acids. Since carbonium ions are formed by both routes, differentiation between them is not always easy. While the dominance of the S_N1 route is suggested by several criteria[4] for many systems, the autocatalysis in the unbuffered solvolysis of $AnCBr{=}CH_2$,[3] the log k - pH profile in the solvolysis of p-$H_2NC_6H_4CBr{=}CH_2$ in acidic media,[2b] and the k_{OBs}/k_{OTs} of ca. 0.3 for several formolyses of arylsulfonates[1a] point to the Ad_E-S_N mechanism for these systems. We wish now to report the operation of the S_N1 mechanism even in the highly acidic, highly ionizing and low nucleophilic trifluoroacetic acid (TFA).[7]

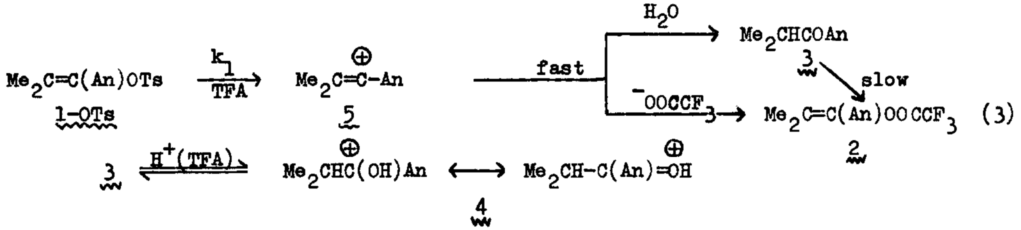
Trifluoroacetolysis of 1-anisyl-2-methylpropen-1-yl tosylate 1-OTs and brosylate 1-OBs in dry TFA (containing ≥2% of trifluoroacetic anhydride) gave only the corresponding trifluoroacetate 2.[8] However, in "dry" acid,[9] both 2 and anisyl isopropyl ketone 3 were formed, isolated and identified.[8] The percentage of 3 in the product from the "dry" acid was (by u.v.) 1-9%. Higher percentage was obtained by using "aged" acid and lower percentage from TFA which was kept for 24 hrs. with 1% of the anhydride. When the TFA is 0.1M in added water, 3 is formed in 28%.

Trifluoroacetolysis of 1-OTs and 1-OBs in unbuffered TFA gave a mixture with λ_{max} at 348 and 278 nm. In TFA containing 0.001M of $NaOOCCF_3$ λ_{max} is 274.5 nm, an absorption ascribed to 3 which has λ_{max} 262.5 nm (ε=16,700) and 275 nm (ε=10,300,sh) in cyclohexane. The maximum at 348 nm (with apparent ε=9,300) is formed also on dissolving 3 in TFA and is ascribed to the ion 4, formed by protonation of 3. For comparison, p-methoxyacetophenone has λ_{max} at 271.5 nm in EtOH,[10] 282 nm in 44% H_2SO_4,[11] and 340 nm in 95% H_2SO_4,[11] and we found λ_{max} 342.5 nm in TFA.[12] Apparently, the introduction of the weak base $NaOOCCF_3$ shifts the $3 \rightleftharpoons 4$ equilibrium towards 3.

The kinetics was followed spectrophotometrically at 348 nm and occasionally at 274.5 nm, and the same k_1 for 1-OTs was obtained at both wavelengths. The reaction was somewhat faster in the presence of $NaOOCCF_3$ and slightly slower in CF_3CO_2D (Table). For 1-OTs, $\Delta H^{\ddagger}$ = 20.3 Kcal/mole and $\Delta S^{\ddagger}$ = +6.4 e.u.

N.m.r. of reaction mixtures, quenched rapidly at 0° with CH_2Cl_2 - aqueous $NaHCO_3$ mixtures, showed that the 2 / 3 ratio is approximately constant along the reaction.[13] A much slower $2 \longrightarrow 3$ transformation (initial k_1=9.8. 10^{-7} sec^{-1} at 15.5°C, by u.v.) accompanies the solvolysis.[14]

The following mechanistic points suggest an S_N1 solvolysis via the vinyl cation 5, according to eqn. 3: (a) k_{1-OBs}/k_{1-OTs} = 2.27 at 15.5°C, a value close to the suggested value of ca. 3 for S_N1 reactions,[1a,15] which should be contrasted with the ratios 0.29-0.30 in HCO_2H for the Ad_E-S_N reaction.[1a] Our ratio is lower than those observed for 2 in trifluoroethanol (2.83), 50% AcOH-50% HCO_2H (3.56) or 70% acetone (5.03),[16] and may result from the solvent-dependency of σ_I values of the leaving group.[17] (b)The solvent isotope effect (SIE) $k_{CF_3CO_2H}/k_{CF_3CO_2D}$ = 1.07 is incompatible with a slow proton transfer according to the Ad_E-S_N mechanism.[5b] Reported SIE for TFA in detritiation and desilylation where proton transfers are rate determining are 1.75 and 6.2,respectively.[18] (c)The solvolysis rate of 1-OTs increases on addition of $NaOOCCF_3$ while the addition of



(3)

Table. Trifluoroacetolysis of 1-OTs and 1-OBs

Compound	T, °C	10^3k_1, sec^{-1}	Compound	T, °C	10^3k_1, sec^{-1}
1-OTs[a]	15.5	7.80±0.02	1-OTs[b,c]	15.5	8.81±0.23
1-OTs[b]	15.5	7.89±0.03	1-OBs[a]	15.5	17.7±0.07
1-OTs	25.1	26.7±0.15[d,e]	1-OTs	25.1	28.6±0.4[e]

[a] Measured at 347.5 nm. [b] Measured at 274.5 nm. [c] Solvent containing 0.053M $NaOOCCF_3$. [d] In CF_3CO_2D. [e] The amount of adventitious water in the O-H and in the O-D acids is similar, as judged by the percentage of 3 formed.

TFA to 1-hexene is slightly retarded in the presence of $NaOOCCF_3$.[19] (d)Extrapolation from the linear Winstein-Grunwald mY plot for the solvolysis of 1-OTs in $AcOH-HCO_2H$ mixtures ($m=0.68$)[16] gave Y=3.8 for TFA. This is reasonable in view of the values estimated from data in RCO_2H solvents for other systems: e.g., 3.6 for α-phenylethyl tosylate,[20a] 4.25 for k_Δ of n-propyl tosylate,[20b] and 3.05 for neopentyl tosylate.[20b] Although rate accelerations in TFA are frequently ascribed to enhanced neighboring group participation, we have yet no data on this question in our system.

The solvent effects on the solvolyses of 1 and related systems[21] will be soon reported

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6. For electron-attracting R^2 and R^3 the nucleophilic addition-elimination substitution (Z.Rappoport,Adv.Phys.Org.Chem.,7,1(1969)) competes with the S_N1 route in the presence of RS^- nucleophiles (Z.Rappoport and A. Gal, unpublished results).
7. Even if the S_N1 mechanism operates exclusively in TFA, extrapolation to other,less acidic solvents (e.g., AcOH) is not obvious. If the Winstein-Grunwald m value for

the Ad_E-S_N route is higher than m for the S_N1 route, the two mY lines may intersect and the Ad_E-S_N route may govern in the less acidic solvent.

8. All new compounds reported here gave satisfactory analyses and spectra.

9. Our "dry" TFA was obtained by distilling TFA from concentrated H_2SO_4. It contained adventitious water, and the rates were slightly dependent on the batch of TFA used. The amount of water was estimated from the percentage of **3** formed.

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12. In cyclohexane λ_{max} 225 nm (ε=17,800), 244 nm(ε=12,400) for **1-OTs**, and 235.5 nm(ε=27,200) for **1-OBs**. In cyclohexane **2** has λ_{max} 243.5 nm (ε=13,500) and in TFA it showed no maxima down to 260 nm, where solvent absorption becomes important.

13. Calculated from the ratio of the two methyl signals of **3** at δ 1.15 , 1.27 to those of **2** at δ 1.75, 1.78 in $CDCl_3$.

14. Neat **2** decomposes to **3** on standing. The decomposition in solution of vinyl acetates and formates to ketones was reported earlier (e.g., P.E.Peterson and J.E.Duddey, *J.Amer.Chem.Soc.*, *88*, 4990(1966); Z.Rappoport and Y.Apeloig, *ibid.*, *91*, 6734(1969)).

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