Tetrahedron Letters Vol. 21, pp 4091 - 4094 0040-4039/80/1015-4091$02.00/0

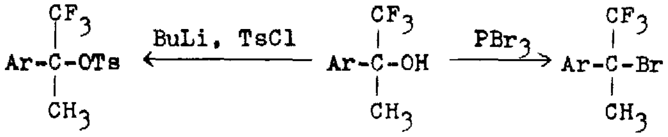
SOLVOLYSIS OF 1-ARYL-1-(TRIFLUOROMETHYL)ETHYL TOSYLATES. EVIDENCE FOR AN EXTREMELY HIGH ELECTRON DEMAND CARBENIUM ION INTERMEDIATE DUE TO THE PRESENCE OF α-TRIFLUOROMETHYL SUBSTITUENT

Kwang-Ting Liu* and Ching-Fen Sheu
Department of Chemistry, National Taiwan University
Taipei, Republic of China

Summary The rate-retarding effect of α-trifluoromethyl group observed in the solvolysis of 1-aryl-1-(trifluoromethyl)ethyl tosylates is so profound that a very large negative ρ^+ value, -8.82, is resulted and the 1-phenyl derivative becomes even less reactive than benzyl tosylate.

Although the importance of the effect of strong electron-withdrawing substituents β to reaction centers in solvolysis has been realized for more than a decade,[1] the α-effect of such substituents did not receive attention until very recently.[2,3,4] Gassman and Talley observed a rate-retarding factor of 3.5×10^3 for α-cyano group in 2-cyano-2-propyl tosylate vs. 2-propyl tosylate.[3] Larger retarding effect were found for trifluoromethyl group, 1.1×10^5 to 2.3×10^6, in 2-propyl and 2-phenylethyl tosylates,[4] and for 2-oxo-group, 2×10^7, in exo-3-methyl-endo-3-norbornyl tresylate.[2] We wish to report here the results of our independent study on the solvolysis of 1-aryl-1-(trifluoromethyl)ethyl tosylates (I), in which a largest negative ρ^+ value recorded to date for solvolysis is resulted and the tertiary tosylate Ic is even less reactive than the primary benzyl tosylate.

1-Aryl-1-(trifluoromethyl)ethanols, IIa-IIf, were prepared from Grignard addition of the corresponded arylmagnesium bromide to 1,1,1-trifluoroacetone. The alcohols were then converted into tosylates Ib-If, and bromides IIIa-IIIb, by conventional methods. The rates of solvolysis were determined by the



$$\mathrm{Ar{-}C(CF_3)(CH_3){-}OTs} \xleftarrow{\text{BuLi, TsCl}} \mathrm{Ar{-}C(CF_3)(CH_3){-}OH} \xrightarrow{\mathrm{PBr_3}} \mathrm{Ar{-}C(CF_3)(CH_3){-}Br}$$

Ar			
Ar = p-$CH_3OC_6H_4$	(Ia)	(IIa)	(IIIa)
= p-$CH_3C_6H_4$	(Ib)	(IIb)	(IIIb)
= C_6H_5	(Ic)	(IIc)	
= p-ClC_6H_4	(Id)	(IId)	
= m-ClC_6H_4	(Ie)	(IIe)	
= p-$CF_3C_6H_4$	(If)	(IIf)	

titrimetric method in duplicate. Since the tosylate Ia was too unstable for convenient preparation and was too reactive for an accurate measurement of rate, the bromide IIIa was employed instead, and the rate for IIIb was also measured for comparison. The pertinent data are listed in Table I.

Table I. Rates of Solvolysis of 1-Aryl-1-(trifluoromethyl)ethyl Derivatives

Substrate	Solvent	k, s^{-1} T_1 (°C)	T_2(°C)	25°C
Ia	80% EtOH			5.08[a]
IIIa	80% EtOH			1.29×10^{-4}
Ib	80% EtOH			1.73×10^{-4}
IIIb	80% EtOH	3.83×10^{-5}(100)	2.83×10^{-6}(75)	4.40×10^{-9} [b]
Ic	HOAc	5.92×10^{-4}(100)	3.83×10^{-5}(75)	4.12×10^{-8} [b]
	80% EtOH	3.47×10^{-4}(75)	2.05×10^{-5}(50)	7.57×10^{-7} [b]
	70% EtOH			1.95×10^{-6}
	60% EtOH			5.24×10^{-6}
	HCOOH			4.80×10^{-4}
Id	80% EtOH	2.38×10^{-4}(75)	1.32×10^{-5}(50)	4.56×10^{-7} [b]
Ie	80% EtOH	4.38×10^{-4}(125)	4.38×10^{-5}(100)	4.48×10^{-9} [b]
If	80% EtOH	3.85×10^{-4}(125)	3.08×10^{-6}(100)	1.27×10^{-10}[b]

[a] Calculated by multiplying the rate of IIIa by a factor of 3.94×10^4(Ib/IIIb).

[b] Calculated from data at higher temperature.

The rate data for Ic in different solvents provide a linear correlation with Y(2-AdOTs)[5] and a m value of 1.05 indicate the insignificance of solvent participation.[6,7] The same conclusion has also been reached by Koshy and Tidwell.[4] Interpolation to 97% trifluoroethanol (Y = 1.83) gave a rate constant for Ic of $4.87 \times 10^{-5}s^{-1}$, which was close to the observed one, $5.87 \times 10^{-5}s^{-1}$.[4] As compared with the rate data for benzyl tosylate, $5.17 \times 10^{-4}s^{-1}$,[8] in this very poorly nucleophilic solvent, it is evident that the solvolytic reactivity of the tertiary tosylate Ic is only about one-tenth of that of primary benzyl derivative.

It is more remarkably that the $\sigma^+\rho$ treatment gives a division into two lines (Fig. I), one for activating substituents with ρ value of -8.82, and the other for deactivating substituents with ρ value of -6.40. The observed ρ value of -8.82 is the most negative one for solvolysis recorded to date. Obviously, the carbenium ion intermediate is of very highly electron demand. The break in the $\sigma^+\rho$ plot suggests a change in mechanism. Solvent participation in this deactivating tertiary system is a possible candidate.[4] However, the unusually

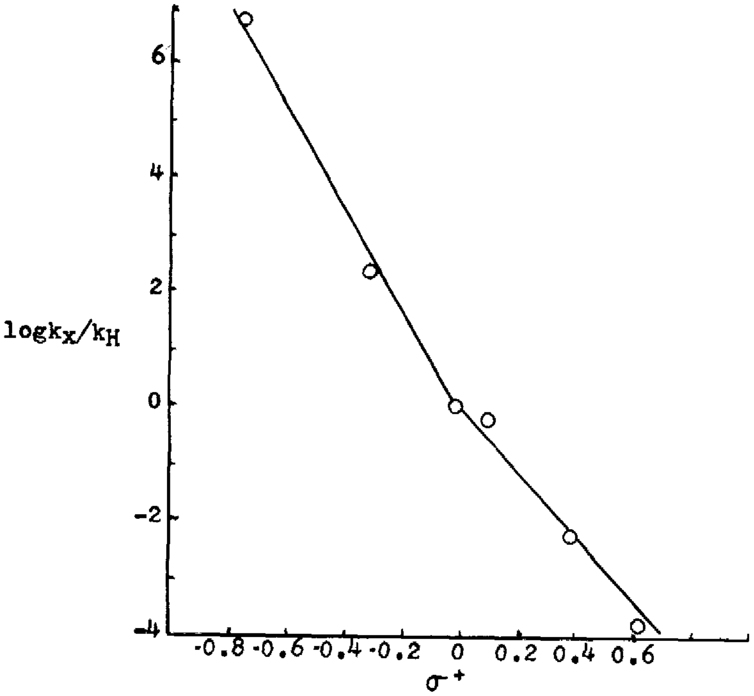


Fig. I Hammett-Brown plot for the solvolysis of 1-aryl-1-(trifluoromethyl)ethyl tosylates in 80% ethanol.

high tosylate/bromide rate ratio, 3.94×10^{4},[11] reveals that the back strain in the 1-aryl-1-(trifluoromethyl)ethyl system is very large and the intervention of solvent participation might be of less significant. Hydrogen participation might be an alternative explanation for the formation of a second line in the $\sigma^{+}\rho$ plot. Further study in this aspect is in progress.

Acknowledgement

We are indebted to the National Science Council for financial support.

References and Notes

1. For examples, see (a) R. Muneyoki and T. Yano, J. Am. Chem. Soc., **92**, 746 (1970); (b) J. B. Lambert anf A. G. Holocomb, ibid, **93**, 2994 (1971); (c) D. Lenoir, Tetrahedron Lett., 1563 (1974); (d) D. Farcasiu, J. Am. Chem. Soc., **98**, 5301 (1976).
2. X. Creary, J. Org. Chem., **44**, 3938 (1979). Tresylate denotes trifluoroethanesulfonate.
3. P. G. Gassman and J. J. Talley, J. Am. Chem. Soc., **102**, 1214 (1980).
4. K. M. Koshy and T. T. Tidwell, ibid, **102**, 1216 (1980).
5. F. L. Schadt, T. W. Bentley and P. v. R. Schleyer, ibid, **98**, 7667 (1976).
6. J. M. Harris, D. L. Mount and D. J. Raber, ibid, **100**, 3139 (1978)
7. H. C. Brown, M. Ravindranathan, F. J. Chloupek and I. Rothberg, ibid, **100**, 3143 (1978).
8. This value was estimated by dividing the rate constant for benzyl brosylate, $1.55 \times 10^{-3}s^{-1}$,[9] by a factor of 3 (the brosylate/tosylate ratio).[10]
9. J. M. Harris, D. L. Mount, M. R. Smith, W. C. Neal, Jr., M. D. Dukes and D. J. Raber, ibid, **100**, 8147 (1978).
10. S. Winstein and G. C. Robinson, ibid, **80**, 169 (1958).
11. The tosylate/bromide ratio for tertiary butyl system is about 5×10^{3}, see R. C. Bingham and P. v. R. Schleyer, ibid, **93**, 3189 (1971).

(Received in Japan 8 July 1980)