"Smiles" Reaction. The entropy of activation for k_s (Table IV) is close to zero consistent with a unimolecular process. Table I indicates that the 2-hydroxynaphthalene-1-sulfonate is about 50-fold more reactive than the 1-hydroxynaphthalene-2-sulfonate. This could be due to the lower pK of the 1-hydroxy group (4.88 as opposed to 6.14); a smaller factor could arise from peri interactions in the naphthalene-1-sulfonate not present in the naphthalene-2-sulfonate constraining the aryl group to be close to the 2-oxy anion.

(21) A preliminary report of part of this work: Thea, S.; Guanti, G.; Hopkins, A.; Williams, A. *J. Am. Chem. Soc.* **1982**, *104*, 1128.

Acknowledgment. We are grateful to CNR and Ministero della Pubblica Istruzione (Italy) and SERC (UK) for financial support. Part of this work was carried out during tenure of a Ciba-Geigy Senior Fellowship (AW). We thank C. Palmero and C. Pernigotti for their assistance with some of the experiments.

Supplementary Material Available: Tables for analytical and physical data for the substrates and details of molecular orbital and nonbonding calculations (4 pages). Ordering information is given on any current masthead page.

Stabilization Demands of Diethyl Phosphonate Substituted Carbocations as Revealed by Substituent Effects

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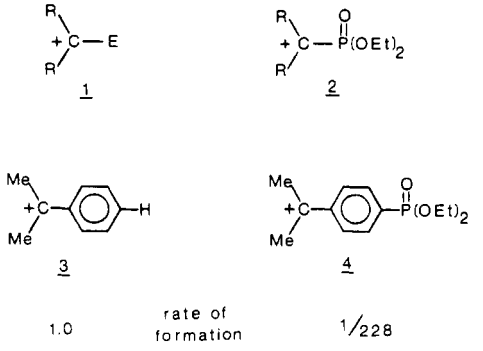
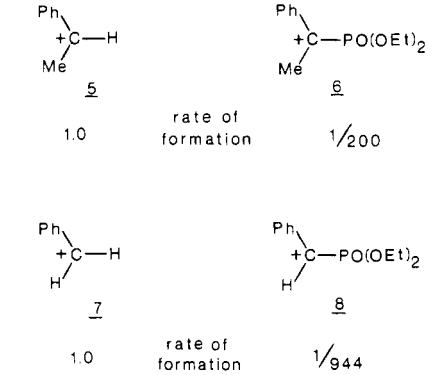
Trifluoroethanolyses of a series of mesylate derivatives of diethyl (1-aryl-1-hydroxymethyl)phosphonates, **9**, gave a Hammett ρ value of −10.1 in the electron donor substituent region. This value was slightly less than the value of −11.6 seen in the corresponding benzyl mesylates, $ArCH_2OMs$, **12**, in hexafluoroisopropyl alcohol. These data suggest that the demand for aryl group stabilization in the intermediate phosphoryl-substituted cation **10** does not surpass that of the α-H analogues, the benzyl cations. Some other factor must therefore account for the relative ease of formation of cations **10**, which have the electronegative diethyl phosphonate group attached directly to the cationic center. The likely factor is an offsetting cation stabilizing feature associated with the diethyl phosphonate group. The Hammett plots for both mesylates **9** and **12** show a break, with decreased ρ values (−6.1 and −5.1, respectively) being observed in the electron-withdrawing region of the plot. Solvent effect studies on **9**-*m*-F suggested that a change to "borderline behavior" is the origin of the break in the Hammett plot. A mechanistic change to the k_Δ process could be ruled out. The triflate derivative of diethyl (1-hydroxyethyl)phosphonate, **14**, gave mixtures of substitution and elimination products on solvolysis. Solvent effect studies indicated a largely nucleophilic mechanism, while isotope effect studies were in line with some cationic character in the transition state in the highly ionizing, nonnucleophilic hexafluoroisopropyl alcohol solvent. Ion pair formation or the S_N2 (intermediate) mechanism could rationalize the behavior of **14** in more highly ionizing solvents.

Our interest in electronegatively substituted carbocations of general type **1**[1,2] has led us to generate certain phosphoryl-substituted cations **2**. The diethyl phosphonate group is strongly electron withdrawing (σ = 0.52).[3] Cation **4** forms 228 times less readily than the cumyl cation **3** (σ^+ = 0.50). Surprisingly, cation **6** could be generated



quite readily (only 200 times more slowly than the α-H analogue **5**). This was unexpected since a potent electron-withdrawing group was attached directly to the cationic center of **6**. Naively, one might expect that the effect of this group would be to retard the rate to a much greater extent in **6** than in **4**, where the cationic center is insulated from the diethyl phosphonate group by a phenyl ring. This phenomenon, i.e., relatively small rate retardations on attachment of $PO(OEt)_2$ directly to a cationic center, appeared to be general. Cation **8** formed only 944 times less readily than the α-H analogue, the benzyl cation **7**.



Why does the diethyl phosphonate group, attached directly to the cationic center of **6** or **8**, have such a small rate retarding effect relative to hydrogen? A potential

(1) For a discussion of the chemistry of cation **1**, where E = COR, see: Creary, X. *Acc. Chem. Res.* **1985**, *18*, 3–8.
(2) Creary, X.; Geiger, C. C.; Hilton, K. *J. Am. Chem. Soc.* **1983**, *105*, 2851–8.
(3) Tsvetkov, E. N.; Lobanov, D. I.; Isosenkova, L. A.; Kabachnik, M. I. *J. Gen. Chem. USSR (Engl. Transl.)* **1969**, *39*, 2126–32. An earlier value of 0.60 has been reported. See: Freedman, L. D.; Jaffe, H. H. *J. Am. Chem. Soc.* **1955**, *77*, 920–1.

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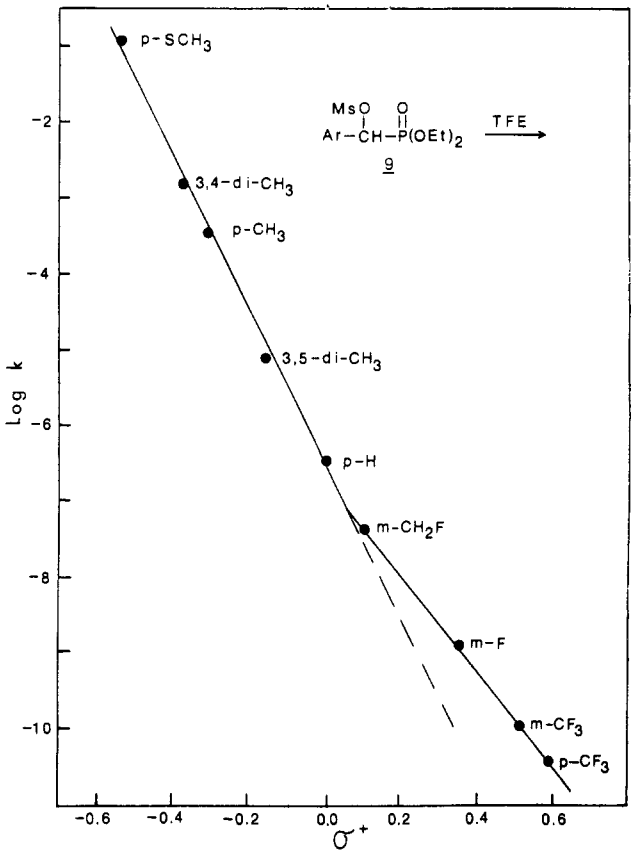


Figure 1. A plot of log k for solvolysis of **9** vs. σ^+.

cation stabilizing interaction between the diethyl phosphonate group and the directly attached cationic center was suggested.[2] Another possible explanation involves increased charge delocalization into the aromatic ring to offset the effect of the electronegative substituent. Forms such as **8a** could be more important in stabilizing **8** than in stabilizing the hydrogen analogues **7a**. In an attempt

7a 8a

to determine the reasons behind the unexpectedly rapid rate of formation of cations **2**, the extent of charge delocalization into the aromatic ring of cation **8** has been probed by way of substituent effects. Reported here are results of these studies.

Results and Discussion

Substituent Effects in Solvolyses of Benzylic Systems. A series of mesylates **9** have been prepared and solvolyzed in trifluoroethanol. Rate data are presented in Table I and graphically in Figure 1. The Hammett plot, using σ^+ values, shows a break. The large ρ value (−10.1) in the electron donor region of the plot is quite consistent with a cationic intermediate, **10**, having high electron demand. How does the demand for substituent stabilization (ρ value) in **10** compare with the α-H analogues, the substituted benzyl cations? Previous substituent effect studies on benzyl tosylates in acetone–water[4] show curved plots which are not straightened even by application of the Brown σ^+ constant.[5] These nonlinear plots are apparently a result of the susceptibility of these primary systems to solvent nucleophilicity. Solvolysis in relatively nucleophilic

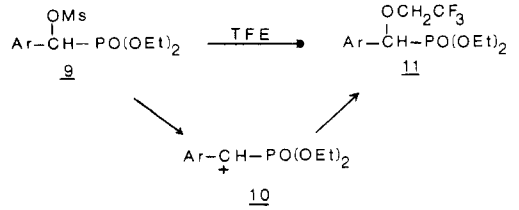


Table I. Solvolysis Rates of Substrates in Various Solvents

compd	solv[a]	temp, °C	k, s^{-1}
9-p-SCH_3	TFE	25.0	1.02×10^{-1}
9-3,4-$(CH_3)_2$	TFE	25.0	1.42×10^{-3}
9-p-CH_3	TFE	25.0	3.24×10^{-4}
9-3,5-di-CH_3	TFE	25.0	7.70×10^{-6}
9-p-H	TFE	25.0[b,c]	3.32×10^{-7}
9-m-CH_2F	TFE	100.0	1.00×10^{-4}
		80.0	1.72×10^{-5}
		25.0[b]	4.10×10^{-8}
9-m-F	TFE	120.0	4.17×10^{-5}
		100.0	7.20×10^{-6}
		80.0[b]	1.02×10^{-6}
		25.0[b]	1.26×10^{-9}
	HOAc	140.0	5.54×10^{-5}
		120.0	8.94×10^{-6}
		80.0[b]	1.27×10^{-7}
	HCO_2H	95.0	9.73×10^{-5}
		80.0[b]	1.97×10^{-5}
		75.0	1.12×10^{-5}
	HFIP	80.0	8.85×10^{-6}
	TFA	80.0[b]	3.37×10^{-4}
		75.0	2.02×10^{-4}
		70.0	1.19×10^{-4}
9-m-CF_3	TFE	150.0	3.87×10^{-5}
		120.0	3.76×10^{-6}
		25.0[b]	1.12×10^{-10}
9-p-CF_3	TFE	165.4	3.30×10^{-5}
		140.0	5.57×10^{-6}
		25.0[b]	4.28×10^{-11}
12-3,5-$(CH_3)_2$	HFIP	8.7	8.01×10^{-2}
		15.0	1.45×10^{-1}
		20.0	2.19×10^{-1}
		25.0[b]	3.36×10^{-1}
12-m-CH_3	HFIP	25.0	4.73×10^{-2}
12-p-H	HFIP	25.0	8.83×10^{-3}
12-m-CH_2F	HFIP	25.0	3.44×10^{-4}
12-m-CF_3	HFIP	90.0	4.24×10^{-4}
		70.5	1.16×10^{-4}
		25.0[b]	2.99×10^{-6}
12-p-CF_3	HFIP	95.0	2.24×10^{-4}
		75.0	5.94×10^{-5}
		25.0[b]	9.96×10^{-7}
14	EtOH	100.0[b]	7.35×10^{-4}
		80.0	1.57×10^{-4}
		70.0	6.93×10^{-5}
		60.0	2.78×10^{-5}
	HOAc	100.0	7.41×10^{-5}[d]
	TFE	140.0	8.66×10^{-5}
		120.0	1.87×10^{-5}
		100.0[b]	3.45×10^{-6}
	HCO_2H	100.0	8.05×10^{-5}
	HFIP	120.0	2.44×10^{-5}
		100.0	4.24×10^{-6}
14-d_4	EtOH	70.0	6.59×10^{-5}
	HCO_2H	100.0	6.85×10^{-5}
	HFIP	120.0	1.91×10^{-5}

[a] HOAc; 0.05 M NaOAc in acetic acid containing 1% acetic anhydride. TFE; 0.025 M 2,6-lutidine in trifluoroethanol. HCO_2H; 0.05 M sodium formate in anhydrous formic acid. HFIP; 97% hexafluoroisopropyl alcohol and 3% water (by weight) containing 0.05 M 2,6-lutidine. TFA; 0.2 M sodium trifluoroacetate in trifluoroacetic acid containing 0.5% trifluoroacetic anhydride. [b] Extrapolated rate. [c] Reference 2. [d] Initial rate; the first-order plot is curved upwards.

(4) Kochi, J. K.; Hammond, G. S. *J. Am. Chem. Soc.* **1953**, *75*, 3445–51.
(5) Okamoto, Y.; Brown, H. C. *J. Org. Chem.* **1957**, *22*, 485–94.

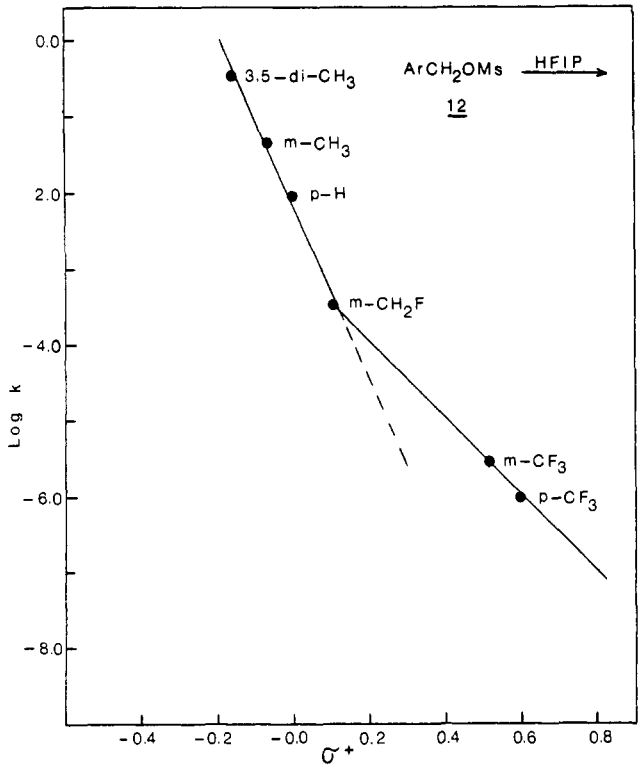
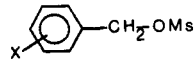


Figure 2. A plot of log k for solvolysis of benzyl mesylates, **12** vs. σ^+.

solvents is not completely limiting,[6] and solvent nucleophilicity becomes more important as the suubstituent becomes more electronegative.

Solvolyses of a series of benzyl mesylates, **12**, were therefore carried out in 97% hexafluoroisopropyl alcohol,



12

a solvent of high ionizing power and low nucleophilicity,[7] to determine the ρ value for benzyl cation formation under more limiting conditions. A plot is shown in Figure 2. A curve break is still observed. However, in the electron donor portion of the plot, the ρ value is −11.6, one of the largest values seen to date. This ρ value is *larger than* the value seen for **9**. On the basis of these ρ values, we conclude that, in solvolyses of **9**, there is no major increase in demand for aryl stabilization relative to the α-H analogues.[8] Therefore cations **10** owe their unexpected stability to some feature other than increased aryl group charge delocalization.

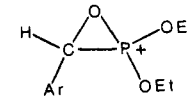
The break observed in Figures 1 and 2 must now be addressed. For benzyl mesylates (Figure 2) we conclude that, in the electron-withdrawing portion of the plot, there is still significant nucleophilic solvent participation, even in the relatively nonnucleophilic HFIP solvent. There is still substantial charge development in solvolyses of the electronegatively substituted benzyl mesylates as shown by the substantial ρ value of −5.1. However these results show that increased solvent participation is a mechanistic change which can cause a break in a Hammett plot despite the cationic nature of the solvolyses of the entire set of substrates.

Table II. A Summary of HFIP/HCO_2H Rate Ratios

substrate	HFIP/HCO_2H ratio	ref
2-adamantyl tosylate	3.7	10
9 (Ar = Ph)	2.6	2
cyclohexyl tosylate	0.45	7b, 11b
9-*m*-F	0.45	this work
sec-butyl tosylate	0.29[a]	7b, 11b
isopropyl tosylate	0.065	7b, 11b
14	0.052	this work
methyl tosylate	0.017	10

[a] 100% hexafluoroisopropyl alcohol.

While increased solvent participation in the electron-withdrawing region is also an attractive explanation for the break in Figure 1, there is another possibility which must be considered. The onset of a k_Δ route, giving the cyclic ion **13**, could account for the decreased slope for electronegative substitutents.[9] A specific substrate, 9-*m*-F (*m*-F; $\sigma^+ = 0.35$) in this region has been examined in detail in an attempt to differentiate between these two possibilities.



13

Rate behavior of mesylate 9-*m*-F (Ar = *m*-FC_6H_4) has been examined as a function of solvent ionizing power, Y_{OTs}.[10] Data are presented in Table I. In contrast to the behavior of **9** (Ar = Ph) ($m = 0.88$; $r = 0.994$), mesylate 9-*m*-F gave a poorer correlation with Y_{OTs} values and overall smaller rate increases with solvent ionizing power ($m = 0.62$; $r = 0.947$). Mesylate 9-*m*-F appears to be reflecting the importance of solvent ionizing power *as well as solvent nucleophilicity*. These solvent effects do not support the k_Δ process leading to **13**. If such a cationic intermediate were involved, rate data should not reflect solvent nucleophilicity and the correlation with Y_{OTs} should have remained high.

The behavior of 9-*m*-F is becoming "borderline" as revealed by the decreased m value and decreased correlation with Y_{OTS}. A comparison of data at 80 °C shows that the rate is *slower* in HFIP than in HCO_2H despite the higher ionizing power of the former solvent. In an attempt to determine where mesylate 9-*m*-F falls in the k_c–k_s reactivity spectrum,[11] the HFIP/HCO_2H rate ratio was examined. Table II lists these values for 9-*m*-F as well as for additional substrates. The value for 9-*m*-F of 0.45 is less than the values for 2-adamantyl tosylate, a k_c substrate,[12] and for **9** (Ar = Ph), a substrate also reacting via a virtually limiting mechanism.[2] The reduced value for

(6) For a discussion and leading references, see: Harris, J. M.; Mount, D. L.; Smith, M. R.; Neal, W. C., Jr.; Dukes, M. D.; Raber, D. J. *J. Am. Chem. Soc.* **1978**, *100*, 8147–56.

(7) (a) Schadt, F. L.; Schleyer, P. v. R.; Bentley, T. W. *Tetrahedron Lett.* **1974**, 2335–8. (b) Bentley, T. W.; Bowen, C. T.; Morten, D. H.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1981**, *103*, 5466–75.

(8) The implicit assumption is that ρ values in TFE and HFIP will be comparable. In support of this assumption, a limited rate study of **9** in 97% HFIP (*p*-H, $k = 9.35 \times 10^{-6}$ s^{-1}; *p*-CH_3, $k = 1.54 \times 10^{-2}$ s^{-1}; 3,4-$(CH_3)_2$, $k = 6.94 \times 10^{-2}$ s^{-1}) gave a comparable ρ value of −10.3.

(9) For the classic example of the onset of a k_Δ process as a result of increasing electron demand, see: Gassman, P. G.; Fentiman, A. F., Jr. *J. Am. Chem. Soc.* **1970**, *92*, 2549–51.

(10) Schadt, F. L.; Bentley, T. W.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1976**, *98*, 7667–74.

(11) For a discussion of the k_c–k_s reactivity spectrum, see ref 6 and 10. See also: (a) Raber, D. J.; Neal, W. C., Jr.; Dukes, M. D.; Harris, J. M.; Mount, D. L. *J. Am. Chem. Soc.* **1978**, *100*, 8137–46. (b) Bentley, T. W.; Schleyer, P. v. R. *Ibid.* **1976**, *98*, 7658–66.

(12) (a) Fry, J. L.; Lancelot, C. J.; Lam, L. K. M.; Harris, J. M.; Bingham, R. C.; Raber, D. J.; Hall, R. E.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1970**, *92*, 2538–40. (b) Fry, J. L.; Harris, J. M.; Bingham, R. C.; Schleyer, P. v. R. *Ibid.* **1970**, 2540–42. (c) Schleyer, P. v. R.; Fry, J. L.; Lam, L. K. M.; Lancelot, C. J. *Ibid.* **1970**, *92*, 2542–44.

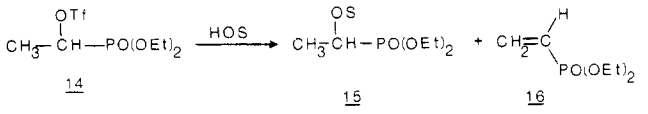
Table III. Product, Rate, and Isotope Effect Data for Solvolysis of 14

solv	% 15	% 16	k_{rel} (100 °C)	$k_{14}/k_{14\text{-}d_4}$
EtOH	98	2	213	1.05
HOAc	94	6	21.5	
TFE	44	56	1.0	
HCO_2H	90	10	23.3	1.18
HFIP	10[a]	90[a]	1.23	1.27

[a] 100% hexafluoroisopropyl alcohol.

9-*m*-F is a result of differing responses of this substrate, relative to 9 (Ar = Ph), to solvent ionizing power and solvent nucleophilicity. As can be seen from Table II, as nucleophilic character of the solvolysis mechanism increases, the HFIP/HCO_2H ratio decreases. The closer to the purely nucleophilic end of the reactivity spectrum, the greater becomes the importance of HCO_2H nucleophilicity. At the k_c limit, solvent ionizing power becomes more important. The HFIP/HCO_2H ratio for 9-*m*-F is comparable to that of cyclohexyl and 2-butyl tosylates. The solvolysis mechanism for these later substrates is not completely limiting and is classified as "borderline". Therefore the HFIP/HCO_2H rate ratio criterion suggests that mesylate 9-*m*-F also falls in the "borderline" region in solvents such as HCO_2H and TFE. We therefore conclude that the break in Figure 1 is due to the increased importance of the nucleophilic character of TFE as the substituent becomes more electronegative. However, there remains substantial cationic character in the transition state for solvolyses of all of these substrates. The nature of the precise mechanism for solvolysis of the "borderline" substrate 9-*m*-F will be subsequently discussed.

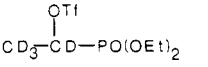
Solvolytic Studies on Triflate 14. The importance of aryl stabilization in cations 10 is apparent. Can the aryl group in 10 be replaced by a simple alkyl group such as methyl? This group has a γ^+ value[13] of 0.77–0.79 and hence would correspond to a substituent even more electronegative than *p*-CF_3. The behavior of triflate 14 was therefore examined. Solvolyses of 14 gave solvent-dependent mixtures of substitution and elimination products 15 and 16. Table I gives rates, and Table III summarizes



14 15 16

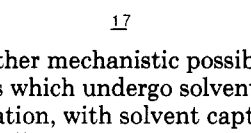
product data. The amount of elimination product increases as solvent nucleophilicity decreases. The rate is fastest in ethanol, the most nucleophilic and least ionizing of the solvents investigated. The slowest rate is observed in HFIP, the least nucleophilic and highest ionizing solvent in the series. Data was not obtained in TFA since 14 proved to be quite unreactive in this solvent. These kinetic results support a mechanism of highly nucleophilic character and argue against any k_Δ process. A k_Δ process should have given faster rates in the more highly ionizing solvents. One therefore concludes that further increasing electron demand by replacing the aryl group of 9 with methyl, as in 14, still does not result in the onset of a k_Δ process.

Where in the k_c–k_s reactivity spectrum does solvolysis of triflate 14 lie? Is the mechanism completely nucleophilic or is there some cationic character? Secondary deuterium isotope effects and the HFIP/HCO_2H rate ratio criterion have been applied in an attempt to answer these questions. Triflate 14-d_4 was prepared. Kinetic results are summarized in Table III. The values given represent a combination of α and β effects,[14] both of which should be smaller for nucleophilic solvolyses and larger for solvolyses with cationic character. The isotope effect in ethanol of 1.05 is in line with a transition state possessing little cationic character. However the value of 1.18 in HCO_2H suggests increasing cationic character in this more highly ionizing solvent. The largest effect (1.27) is seen in HFIP and is indicative of some degree of cationic character in the transition state for solvolysis of 14 in this highly ionizing, nonnucleophilic solvent. The HFIP/HCO_2H ratio also suggests some cationic character in solvolyses of 14. The value of 0.052 is somewhat larger than the value of 0.017 seen for methyl tosylate,[10] a model substrate for a purely nucleophilic solvolysis, but less than the value seen for 9-*m*-F. Some caution, however, is in order concerning interpretation of this ratio. The HFIP/HCO_2H rate ratio is probably not a precise indicator of the extent of cationic character in a reaction, but only a rough indicator, to be used in conjunction with some other criterion for assigning mechanism. Hence the HFIP/HCO_2H value for 14, which is in the region of isopropyl tosylate, a borderline substrate, should not be used by itself to suggest completely analogous mechanisms. While the extent of cationic character in solvolysis of 14 may not be as great as for isopropyl tosylate, the data point to some degree of transition-state charge development for reaction in the more highly ionizing solvents.



14-d_4

The question of the precise mechanism for solvolysis of 14 (as well as 9-*m*-F) has not been addressed other than in terms of a transition state with "cationic character". The isotope effect data for 14 in HFIP rule out a concerted elimination to account for the major product 16. A concerted elimination would involve a primary isotope effect and hence a much larger value would have been observed. The S_N2 (intermediate) mechanism of Bentley and Schleyer,[7b,10,11b] which involves nucleophilically assisted ion pair formation, as in 17 and 18, remains a possibility.



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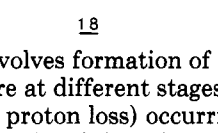

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Another mechanistic possibility involves formation of ion pairs which undergo solvent capture at different stages of solvation, with solvent capture (or proton loss) occurring at earlier ion pair stages in more nucleophilic solvents.[15] While we have our prejudices, any attempt to assign precise mechanisms will probably have to await resolution of the mechanistic controversy concerning borderline substrates.

It appears, based on the isotope effect data, that the amount of charge development in solvolyses of 14 in HOAc

(13) (a) Peters, E. N. *J. Org. Chem.* **1977**, *42*, 1419–22. McManus, S. P. Harris, J. M. *Ibid.* **1977**, *42*, 1422–7.

(14) For a discussion of α-deuterium isotope effects in solvolves, see: (a) Shiner, V. J., Jr.; Rapp, M. W.; Pinnick, H. R., Jr. *J. Am. Chem. Soc.* **1970**, *92*, 232–3 and references therein. For a discussion of β-effects, see: (b) Shiner, V. J., Jr.; Buddenbaum, W. E.; Murr, B. L.; Lamaty, G. J. *J. Am. Chem. Soc.* **1968**, *90*, 418–26. (c) Shiner, V. J., Jr. In "Isotope Effects in Chemical Reactions"; Collins, C. J., Bowman, N. S., Eds.; Van Nostrand-Reinhold: New York, 1970.

(15) (a) Humski, K.; Sendijarevic, V.; Shiner, V. J., Jr. *J. Am. Chem. Soc.* **1973**, *95*, 7722-28. (b) *Ibid.* **1976**, *98*, 2865–8. (c) Seib, R. C.; Shiner, V. J., Jr.; Sendijarevic, V.; Humski, K. *Ibid.* **1978**, *100*, 8133–37.

and HFIP is greater than in solvolysis of ethyl tosylate.[16] This could be a result of greater response of ethyl tosylate to solvent nucleophilicity due to decreased steric requirements relative to the more hindered **14**. It may also be reflecting the ability of the diethyl phosphonate group to stabilize adjacent positive charge by some mechanism. The fact that aryl delocalization of charge does not account for the unexpectedly high rate of formation of cations **5** and **7** also points to the diethyl phosphonate group as a potential cation stabilizing group under appropriate conditions of electron demand. Studies are continuing in an attempt to determine the precise nature of this cation-stabilizing effect by this formally electron-withdrawing group.

Conclusions. A substituent effect study on a series of mesylates **9** in TFE gave a break in a Hammett plot. In the electron donor portion of the plot, the mechanism involves formation of electronegatively substituted cations **10**. The demand for aryl stabilization, as indicated by the ρ value, was not greater than in the α-H analogues. Increased charge delocalization into the aromatic ring of **10** was therefore not the reason for the unexpectedly rapid rate of formation of this class of cation. The break in the Hammett plot was interpreted in terms of the onset of increased nucleophilic solvent participation, i.e., borderline behavior in TFE. Cationic character remained "large" in all of these solvolyses. Solvolyses of triflate **14**, where methyl replaces aryl, resulted in even greater nucleophilic solvent involvement. In ethanol, the reaction was essentially S_N2 in character. In HCO_2H and HFIP, a transition state with some cationic character was implicated. Reaction of **14** in more highly ionizing nonnucleophilic solvents may involve ion pair formation or the S_N2 (intermediate)mechanism.

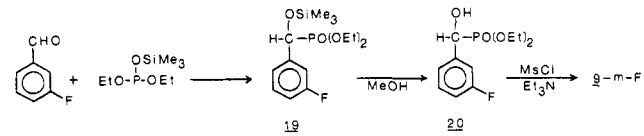
Experimental Section

Preparation of Mesylates 9. General Procedure. Diethyl trimethylsilyl phosphite[2,17] (1.1–1.2 equiv) was added to 1.0 equiv of the appropriately substituted benzaldehyde. After the initial exothermic reaction, the mixture was heated at 100 °C for 3–20 h to ensure complete reaction. The α-trimethylsiloxy phosphonates were then isolated by distillation at 0.05 mm. Yields ranged from 80 to 98%.

The α-trimethylsiloxy phosphonates obtained above (1 part) were dissolved in 10 parts of 10^{-3} M trifluoroacetic acid in absolute methanol. After standing for 3–15 h at room temperature, the solvent was removed by rotary evaporator. The crude α-hydroxy phosphonates were slurried with Skelly F and collected. Yields ranged from 94 to 98%.

The α-hydroxy phosphonates obtained above (1 part) were dissolved in 10 parts of methylene chloride and the mixture was to −30 °C. Methanesulfonyl chloride (1.4 equiv) was then added followed by dropwise addition of 2.0 equiv of triethylamine. After being warmed to 0 °C, the mixture was taken up into ether, washed with water, dilute HCl solution, and saturated NaCl solution, and dried over $MgSO_4$. For the more reactive mesylates, the workup was carried out rapdily by using cold solutions. After solvent removal by rotary evaporator, the solid mesylates were slurried with Skelly F and collected. Mesylate **9**-*m*-CH_2F remained an oil. Yields were essentially quantitative. Details of a typical preparation are given below.

Preparation of 9-*m*-F. Diethyl trimethylsilyl phosphite (3.10 g) was added to 1.64 g of *m*-fluorobenzaldehyde. After about 5 min, the flask was placed in an oil bath and heated at 100 °C for 2 h. A short-path distillation head was then attached. Distillation gave 4.31 g (97%) of the corresponding silylated α-hydroxy phosphonate **19**, bp 103–105 °C (0.07 mm).



19 20

Thirty milliliters of 0.001 M CF_3CO_2H in methanol was added to 4.31 g of **19**. The mixture was left at room temperature for 19 h, and the solvent was then removed by rotary evaporator. The white solid was slurried with Skelly F and collected on a Buchner funnel, giving 3.28 g (97%) of **20**: mp 74–75 °C. NMR ($CDCl_3$) δ 7.5–6.8 (4 H, m), 5.05 (1 H, d, J = 11 Hz), 4.90 (1 H, broad, exchanges with D_2O, shift is concentration dependent), 4.08 (4 H, quintet, J = 8 Hz), 1.27 (3 H, t, J = 8 Hz), 1.23 (3 H, t, J = 8 Hz). Anal. Calcd for $C_{11}H_{16}FO_4P$: C, 50.39; H, 6.15. Found: C, 49.97; H, 6.22.

A solution of 2.10 g of **20** in 15 mL of methylene chloride was cooled to −30 °C, and 1.28 g of CH_3SO_2Cl was added followed by dropwise addition of 1.68 g of Et_3N. After a workup as described above, 2.67 g (98%) of **9**-*m*-F was collected as a white solid: mp 37–39 °C; NMR ($CDCl_3$) δ 7.6–7.0 (4 H, m), 5.73 (1 H, d, J = 15 Hz), 4.19 (4 H, quintet, J = 8 Hz), 2.97 (3 H, s), 1.27 (6 H, overlapping triplets, J = 8 Hz). Anal. Calcd for $C_{12}H_{18}FO_6PS$: C, 42.35; H, 5.33. Found: C, 41.98; H, 5.30.

Preparation of *m*-(Fluoromethyl)benzaldehyde. This aldehyde, used in the preparation of **9**-*m*-CH_2F, was prepared from *m*-(fluoromethyl)bromobenzene.[18] A solution of 5.59 g of *m*-(fluoromethyl)bromobenzene in 65 mL of THF was cooled to −78 °C, and 20 mL of 1.6 M butyllithium in hexane was added dropwise. After 1.75 h at −78 °C, a solution of 6.58 g of dimethylformanide in 12 mL of ether was added dropwise. The mixture was warmed to 0 °C, and 75 mL of water was added. The mixture was taken up into ether and washed with water and saturated NaCl solution, and dried over $MgSO_4$. After solvent removal using a rotary evaporator, the residue was distilled giving 3.07 g (75%) of *m*-(fluoromethyl)benzaldehyde: bp 114–116 °C (20 mm); NMR ($CDCl_3$) δ 10.12 (1 H, s), 8.1–7.4 (4 H, m), 5.48 (2 H, d, J = 48 Hz).

Preparation of Benzyl Mesylates, 12. The substituted benzyl mesylates, **12**, were prepared from the corresponding benzyl alcohols by reaction with mesyl chloride and Et_3N in methylene chloride using the same procedure as in preparation of mesylates **9**.

Preparation of Triflate 14. A solution of 1.10 g of diethyl (1-hydroxyethyl)phosphonate[19] in 13 mL of CH_2Cl_2 was cooled to −50 °C, and 0.79 g of 2,6-lutidine was added followed by 1.96 g of trifluoromethanesulfonic anhydride. The mixture was warmed to 0 °C and taken up into ether, and a rapid, standard aqueous workup followed using cold water, dilute HCl, and saturated NaCl solution. After being dried over $MgSO_4$, the solvent was removed by rotary evaporator and the residue was distilled to give 1.61 g (61%) of **14**, bp 72–75 °C (0.06 mm). The yield of **14** was quite dependent on the distillation rate. Rapid distilliation using a short-path head, warmed by a heat gun, gave highest yields: NMR ($CDCl_3$) δ 5.09 (1 H, quintet, J = 8 Hz), 4.22 (4 H, m), 1.69 (3 H, doublet of doublets, J = 16, 8 Hz), 1.36 (6 H, t, J = 8 Hz).

Preparation of Triflate 14-d_4. A mixture of 1.00 g of acetaldehyde-d_4 (Aldrich Chemical Co.) in 1 mL of ether and 3.95 g of diethyl trimethylsilyl phosphite was held at 0 °C for 30 min and then slowly warmed to 35 °C over 3.5 h. Distillation gave 4.52 g (93%) of diethyl (1-(trimethylsiloxy)ethyl)phosphonate-d_4. Desilylation of this material in 50 ml of 10-3 M trifluoroacetic acid in methanol gave 3.14 g of diethyl (1-hydroxyethyl)-phosphonate-d_4. This was converted to **14**-d_4 using the same procedure as described for preparation of **14**. The NMR showed no signals at δ 5.09 and 1.69.

Solvolyses of 9 in Trifluoroethanol. General Procedure. A solution of **9** in trifluoroethanol containing 1.2 equiv of 2,6-

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lutidine was heated for 10 half-lives in a sealed tube. The trifluoroethanol was removed by rotary evaporator, and the residue was taken up into ether, washed with dilute HCl solution, and dried over $MgSO_4$. After solvent removal by rotary evaporator, the products were characterized by standard spectral methods. The following procedure is representative.

A solution of 291 mg of **9**-*m*-F in 15 mL of TFE containing 128 mg of 2,6-lutidine was heated in sealed tubes for 31 h at 125 °C. Workup, as described above, gave 278 mg (94%) of **11** (Ar = *m*-FC_6H_4): NMR ($CDCl_3$) δ 7.6–6.9 (4 H, m), 4.82 (1 H, d, J = 16 Hz), 4.35–3.65 (6 H, m), 1.27 (3 H, t, J = 8 Hz) 1.23 (3 H, t, J = 8 Hz).

Solvolyses of 14. General Procedure. A solution of triflate **14** in the appropriate solvent containing 1.25 equiv of buffering base was heated for 10 half-lives in a sealed tube. The mixture was then taken up into ether, and a standard aqueous workup followed. For reactions in HOAc and HCO_2H, the mixtures were taken up into ether and washed with water and then with NaOH solution. After standard drying procedures, the solvent was removed by rotary evaporator. Products were separated by preparative gas chromatography and identified by standard spectral methods. The following procedure is representative.

A solution of 162 mg of triflate **14** in 7 mL of TFE containing 75 mg of 2,6-lutidine was heated in saled tubes at 139 °C for 25 h. After a standard workup using a minimal amount of water (**16** is appreciably soluble in water), the mixture was analyzed by 300-MHz NMR which showed **15** and **16** in a 39:61 ratio. NMR of **15** (S = CH_2CF_3) ($CDCl_3$): δ 4.3–3.8 (7 H, m), 1.457 (3 H, doublet of doublets, J = 17, 7 Hz), 1.353 (3 H, t, J = 7 Hz), 1.346 (3 H, t, J = 7 Hz). NMR of **16**[20] ($CDCl_3$) δ 6.4–6.0 (3 H, m), 4.099 (4 H, quintet, J = 7 Hz), 1.335 (6 H, t, J = 7 Hz).

Solvolyses of Mesylates and Triflates. Kinetics Procedures. Solvolyses of mesylates **9** were monitored by using the titrimetric methods previously described.[2,21] Maximum standard deviations in duplicate runs were ±3%. The very reactive **9**-*p*-SCH_3 was monitored spectrophotometrically by following the absorbance increase at 260 nm. Benzyl mesylates containing electron donor substituents were also monitored spectrophotometrically. Those containing electron-withdrawing substituents were monitored titrimetrically. Solvolysis rates of **9**-*m*-F in TFA were determined by NMR monitoring the disappearance of the carbinyl doublet of **9**-*m*-F and the appearance of the product trifluoroacetate. Solvolysis rates of **14** and **14**-d_4 were monitored titrimetrically. Maximum standard deviations for the isotope effect data were ±1.5%.

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Registry No. **9**-*p*-SCH_3, 96258-44-5; **9**-3,4-$(CH_3)_2$, 96258-45-6; **9**-*p*-CH_3, 96258-46-7; **9**-3,5-$(CH_3)_2$, 96258-47-8; **9**-*p*-H, 51761-45-6; **9**-*m*-CH_2F, 96258-48-9; **9**-*m*-F, 96258-49-0; **9**-*m*-CF_3, 96258-50-3; **9**-*p*-CF_3, 96258-51-4; **11** (Ar = *m*-FC_6H_4), 96258-58-1; **12**-3,5-$(CH_3)_2$, 96258-52-5; **12**-*m*-CH_3, 96258-53-6; **12**-*p*-H, 55791-06-5; **12**-*m*-CH_2F, 96258-54-7; **12**-*m*-CF_3, 96258-55-8; **12**-*p*-CF_3, 96258-56-9; **14**, 96258-57-0; **14**-d_4, 96292-53-4; **15** (S = CH_2CF_3), 96258-61-6; **16**, 682-30-4; **19**, 96258-59-2; **20**, 96258-60-5; TFE, 75-89-8; HFIP, 920-66-1; TFA, 76-05-1; *p*-$SCH_3C_6H_4CHO$, 3446-89-7; 3,4-$(CH_3)_2C_6H_3CHO$, 5973-71-7; *p*-$CH_3C_6H_4CHO$, 104-87-0; 3,5-$(CH_3)_2C_6H_3CHO$, 5779-95-3; C_6H_5CHO, 100-52-7; *m*-$CH_2FC_6H_4CHO$, 96258-62-7; *m*-FC_6H_4CHO, 456-48-4; *m*-$CF_3C_6H_4CHO$, 454-89-7; *p*-$CF_3C_6H_4CHO$, 455-19-6; *p*-$SCH_3C_6H_4CH(OSiMe_3)PO(OEt)_2$, 96258-63-8; 3,4-$(CH_3)_2C_6H_3CH(OSiMe_3)PO(OEt)_2$, 96258-64-9; *p*-$CH_3C_6H_4CH(OSiMe_3)PO(OEt)_2$, 96258-65-0; 3,5-$(CH_3)_2C_6H_3CH(OSiMe_3)PO(OEt)_2$, 96258-66-1; $C_6H_5CH(OSiMe_3)PO(OEt)_2$, 31675-43-1; *m*-$CH_2FC_6H_4CH(OSiMe_3)PO(OEt)_2$, 96258-67-2; *m*-$CF_3C_6H_4CH(OSiMe_3)PO(OEt)_2$, 96258-68-3; *p*-$CF_3C_6H_4CH(OSiMe_3)PO(OEt)_2$, 96258-69-4; *p*-$SCH_3C_6H_4CH(OH)PO(OEt)_2$, 96258-70-7; 3,4-$(CH_3)_2C_6H_3CH(OH)PO(OEt)_2$, 96258-71-8; *p*-$CH_3C_6H_4CH(OH)PO(OEt)_2$, 79158-40-0; 3,5-$(CH_3)_2C_6H_3CH(OH)PO(OEt)_2$, 96258-72-9; $C_6H_5CH(OH)PO(OEt)_2$, 1663-55-4; *m*-$CH_2FC_6H_4CH(OH)PO(OEt)_2$, 96258-73-0; *m*-$CF_3C_6H_4CH(OH)PO(OEt)_2$, 86208-43-7; *p*-$CF_3C_6H_4CH(OH)PO(OEt)_2$, 96258-74-1; 3,5-$(CH_3)_2C_6H_3CH_2OH$, 27129-87-9; *m*-$CH_3C_6H_4CH_2OH$, 587-03-1; $C_6H_5CH_2OH$, 100-51-6; *m*-$CH_2FC_6H_4CH_2OH$, 96258-75-2; *m*-$CF_3C_6H_4CH_2OH$, 349-75-7; *p*-$CF_3C_6H_4CH_2OH$, 349-95-1; $Me_3SiOP(OEt)_2$, 13716-45-5; *m*-$CH_2FC_6H_4Br$, 456-43-9; CD_3CDO, 1632-89-9; HOAc, 64-19-7; HCO_2H, 64-18-6; EtOH, 64-17-5; diethyl (1-hydroxyethyl)phosphonate, 15336-73-9; diethyl (1-(trimethylsiloxy)ethyl)phosphonate-d_4, 96258-76-3; diethyl (1-hydroxyethyl)phosphonate-d_4, 96258-77-4.

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Nonstabilized Imidate Ylides by the Desilylation Method: A Route to the Pyrrolizidine Alkaloids Retronecine and Indicine

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Imidate ylides, members of the azomethine ylide family, are generated by desilylation of *N*-[(trimethylsilyl)methyl] imidate salts with CsF. This technique is used to prepare monoprotected retronecine **16** starting from butyrolactam. The route is improved over that described in our 1980 communication, in particular in the conversion of enamine ester **8a** into selenides **13** via selective 1,4 reduction with Dibal and in situ selenylation of the aluminum enolate. Synthetic *d,l*-**16** is converted predominantly into *d,l*-indicine by acylation with *d,l*-**19**.

During extensive studies which culminated in the early 1970's, Huisgen et al. established stabilized azomethine ylides as reactive intermediates which readily undergo cycloaddition reactions with dipolarophiles.[1] Many examples were reported of the synthesis of pyrroles, pyrrolines, and pyrrolizidines from suitable combinations of azomethine dipoles with acrylate- or propiolate-derived dipolarophiles. Nonstabilized azomethine ylides, on the other hand, could be generated in only a few specialized systems.[2] Their inaccessibility precluded synthetic ap-

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