Mesylate Derivatives of α-Hydroxy Phosphonates. Formation of Carbocations Adjacent to the Diethyl Phosphonate Group

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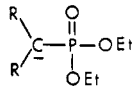
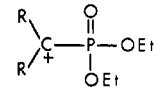
Abstract: Mesylates **3–6** have been prepared and reacted in a variety of solvents. Product, rate, and solvent effect studies implicate carbocationic intermediates in these solvolyses despite the electron-withdrawing $PO(OEt)_2$ group. Mesylate **3** gave exclusive substitution products. Optically active **3** gave racemic products on trifluoroacetolysis. α-Deuterium isotope effects were also in line with a cationic intermediate. Mesylate **4** gave some elimination product, **27**, along with the substitution product **28**, also via a cationic intermediate. Mesylates **5** and **6** gave exclusive elimination products. A β-deuterium isotope effect study gave a k_{H_6}/k_{D_6} value of 2.8. This isotope effect, along with a small m value (0.45), suggested the intermediacy of a reversibly formed ion pair which subsequently loses a proton. This mechanism represents the merging of the classical E1 mechanism and the $E2_{C^+}$ mechanism, the latter representing the cationic counterpart of the $E1_{cb}$ mechanism. Analysis of the solvolysis rates of **3** and **4** led to the conclusion that cationic intermediates are formed quite easily. Reasons are suggested for this unexpectedly facile generation of cations adjacent to the potent electron-withdrawing $PO(OEt)_2$ substituent.

The diethyl phosphonate substituent, $PO(OEt)_2$, is usually considered to possess electron-withdrawing properties. The σ_p value associated with this group is 0.52.[1] This group is also known to stabilize carbanions. This allows facile generation of anions such as **1** that are commonly used in the Emmons–Wadsworth modification of the Wittig reaction.[2]



1

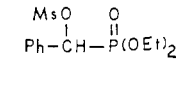


2

In view of recent interest in carbocations substituted with electron-withdrawing substituents,[3-8] we wanted to evaluate the effect of the diethyl phosphonate substituent on carbocation stability. Since σ and σ^+ values can differ substantially, we wanted to determine the σ^+ value for $PO(OEt)_2$. We also wanted to determine the effect of placing this group directly on a cationic center as in **2**. Can such carbocations be generated? What are their fates under solvolytic conditions? In order to answer such questions, mesylates **3–6** were prepared. Reported here are results of studies on these systems.

Results and Discussion

Synthetic Aspects. Mesylates **3–6** were all prepared from alcohol precursors available by the general method[9] shown in



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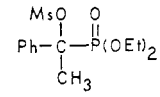

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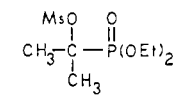

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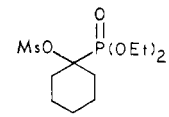

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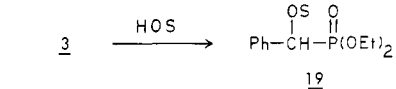
Scheme I. Condensation of diethyl trimethylsilyl phosphite with the appropriate aldehyde or ketone gave the silated alcohols **8–11**. Desilylation was accomplished with 10^{-3} M trifluoroacetic acid in methanol. Mesylate **3** was prepared from **12** by the Servis procedure[10] using mesyl chloride and triethylamine. This mesylation procedure was not successful for the preparations of **4**, **5**, and **6**. However, these mesylates could be prepared by a two-step procedure modeled after the Coates tosylation procedure.[11] Treatment of alcohols **13–15** with CH_3SOCl and triethylamine led to the sulfinate esters **16–18** (Scheme II). These were readily oxidized to the corresponding mesylates by using *m*-chloroperbenzoic acid.

Solvolytic Studies on 3. Mesylate **3** reacts in a variety of solvents to give exclusively the substitution product **19**. Rate data are



19

given in Table I. Immediately apparent is the fact that solvolyses are facile despite the electron-withdrawing group. The results of a solvent effect study are illustrated in Figure 1. Rates of solvolysis of **3** correlate well[12] with solvolysis rates of 2-adamantyl

(1) Tsvetkov, E. N.; Lobanov, D. I.; Isosenkova, L. A.; Kabachnik, M. I. *j. Gen. Chem. USSR (Engl. Transl.)* **1969**, *39*, 2126–2132. An earlier σ value of 0.60 has been reported. See: Freedman, L. D.; Jaffé, H. H. *J. Am. Chem. Soc.* **1955**, *77*, 920–921.

(2) (a) Wadsworth, W. S., Jr.; Emmons, W. D. *J. Am. Chem. Soc.* **1961**, *83*, 1733–1738. For related studies, see: (b) Horner, L.; Hoffman, H.; Wippel, H. G.; Klahre, G. *Chem. Ber.* **1959**, *92*, 2499–2505. (c) Pommer, H. *Angew. Chem.* **1960**, *72*, 911–915. (d) Seus, E. J.; Wilson, C. V. *J. Org. Chem.* **1961**, *26*, 5243–5244.

(3) (a) Creary, X. *J. Org. Chem.* **1979**, *44*, 3938–3945. (b) Creary, X. *J. Am. Chem. Soc.* **1981**, *103*, 2463–2465. (c) Creary, X.; Geiger, C. *Ibid.* **1982**, *104*, 4151–4162.

(4) Bégué, J.-P.; Charpentier-Morize, M. *Acc. Chem. Res.* **1980**, *13*, 207–212.

(5) (a) Gassman, P. G.; Talley, J. J. *J. Am. Chem. Soc.* **1980**, *102*, 1214–1216. (b) Gassman, P. G.; Talley, J. J. *Ibid.* **1980**, *102*, 4138–4143. (c) Gassman, P. G.; Saito, K.; Talley, J. J. *Ibid.* **1980**, *102*, 7613–7615. (d) Olah, G. A.; Arvanaghi, M.; Prakash, G. K. S. *Ibid.* **1982**, *104*, 1628–1631.

(6) (a) Koshy, K. M.; Tidwell, T. T. *J. Am. Chem. Soc.* **1980**, *102*, 1216–1218. (b) Jansen, M. P.; Koshy, K. M.; Mangru, N. N.; Tidwell, T. T. *Ibid.* **1981**, *103*, 3863–3867. (c) Allen, A. D.; Jansen, M. P.; Koshy, K. M.; Mangru, N. N.; Tidwell, T. T. *Ibid.* **1982**, *104*, 207–211.

(7) (a) Liu, K.-T.; Sheu, C.-F. *Tetrahedron Lett.* **1980**, 4091–4094. (b) Liu, K.-T.; Kuo, M.-Y.; Shu, C.-F. *J. Am. Chem. Soc.* **1982**, *104*, 211–215.

(8) (a) Paddon-Row, M. N.; Santiago, C.; Houk, K. N. *J. Am. Chem. Soc.* **1980**, *102*, 6561–6563. (b) Paddon-Row, M. N.; Houk, K. N.; Tidwell, T. T. *Tetrahedron Lett.* **1982**, 383–386.

(9) Novikova, Z. S.; Mashoshina, S. N.; Sapozhnikova, T. A.; Lutsenko, I. F. *J. Gen. Chem. USSR (Engl. Transl.)* **1971**, *41*, 2655–2660.

(10) Crossland, R. K.; Servis, K. L. *J. Org. Chem.* **1970**, *35*, 3195–3196.

(11) Coates, R. M.; Chen, J. E. *Tetrahedron Lett.* **1969**, 2705–2707.

(12) Although data have been given in ethanol, this point has not been included in the plot. The Y_{OTs} value for this solvent sometimes appears anomalous; i.e., we[3c] and others[6a] have often observed rates in ethanol that are faster than expected on the basis on this Y_{OTs} value. Cumyl chloride solvolyses[13] in ethanol are also faster than in acetic acid despite the smaller Y_{OTs} value of ethanol. A reviewer has suggested that the deviation seen in ethanol may be due to the onset of a k_s process. This would be consistent with the increased nucleophilicity of this solvent. Experiments are under way to test this suggestion.

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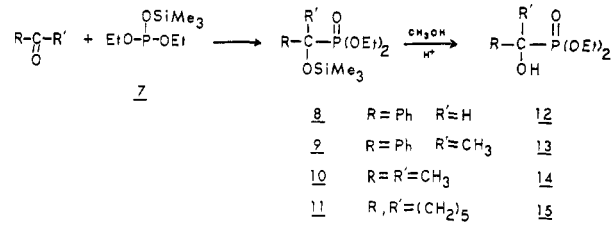
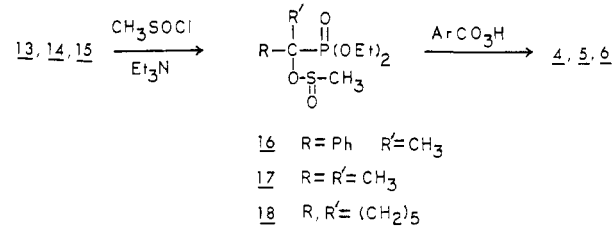
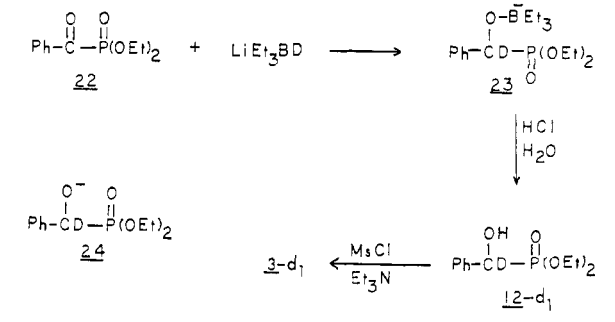
Scheme I



Scheme II



Scheme III



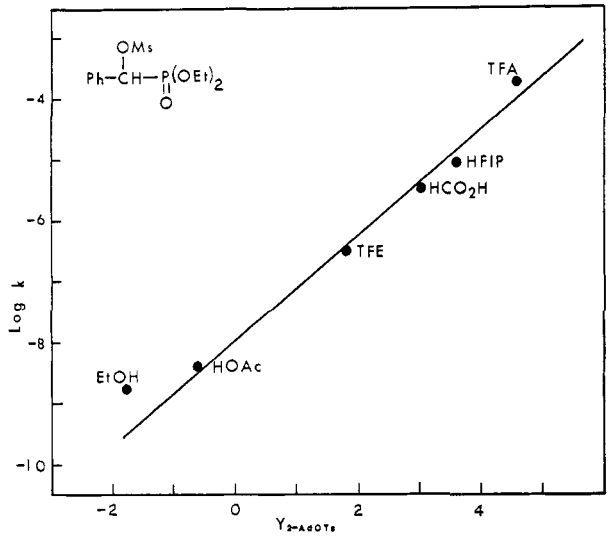


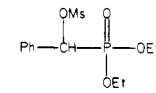
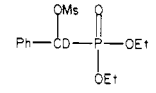
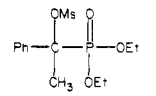
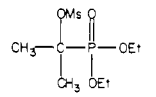
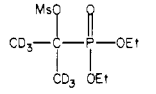
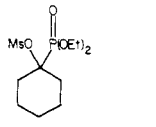
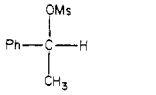
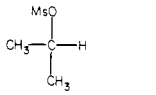
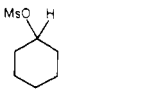
Figure 1. Plot of log k for the solvolysis of **3** in various solvents vs. log (k/k_0) for the solvolysis of 2-adamantyl tosylate ($Y_{2\text{-Ad-OTs}}$).

tosylate, a secondary system that Schleyer suggests solvolyzes by a k_c process.[14] The large rate increases with increasing solvent ionizing power (m = 0.88, correlation coefficient 0.994) is indicative of a cationic intermediate and is inconsistent with a k_s process.

(13) Okamoto, Y.; Inukai, T.; Brown, H. C. *J. Am. Chem. Soc.* **1958**, *80*, 4972–4976. The half-life for solvolysis of cumyl chloride in ethanol is 29 min at 25 °C. We have found a half-life of 56 min for solvolysis in acetic acid at 25 °C. Similar trends are seen with substituted cumyl chlorides.

(14) (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*, 2538–2540. (b) Fry, J. L.; Harris, J. M.; Bingham, R .C.; Schleyer, P. v. R. *Ibid.* **1970**, *92*, 2540–2542. (c) Schleyer, P. v. R.; Fry, J. L.; Lam, L. K. M.; Lancelot, C. J. *Ibid.* **1970**, *92*, 2542–2544.

Table I. Solvolysis Rates of Mesylates in Various Solvents

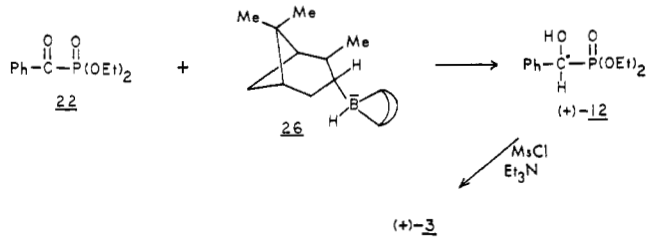
compd	solvent[a]	T, °C	k, s^{-1}	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$
	EtOH	120.1	8.46×10^{-5}		
		100.0	1.36×10^{-5}	25.7	−12.3
		25.0[b]	1.76×10^{-9}		
(3)	HOAc	110.0	1.39×10^{-4}	27.3	−5.4
		100.0	4.81×10^{-5}		
		90.0	1.82×10^{-5}		
		25.0[b]	3.78×10^{-9}		
	CF_3CH_2OH	80.0	1.51×10^{-4}	22.6	−12.4
		70.0	5.53×10^{-5}		
		60.0	2.06×10^{-5}		
		25.0[b]	3.32×10^{-7}		
	HCO_2H	50.0	9.20×10^{-5}	24.2	−2.2
		25.0	3.59×10^{-6}		
	HFIP	25.0	9.35×10^{-6}		
	CF_3CO_2H	25.0	1.91×10^{-4}		
	HOAc	100.0	4.15×10^{-5}		
	CF_3CH_2OH	70.0	4.71×10^{-5}		
	HCO_2H	50.0	7.62×10^{-5}		
(3-d_1)					
	EtOH	25.0	2.25×10^{-5}		
	HOAc	25.0	8.47×10^{-5}		
	CF_3CH_2OH	25.0	1.47×10^{-2}		
(4)					
	EtOH	120.0	1.46×10^{-4}	27.5	−6.8
		100.0	2.11×10^{-5}		
		25.0[b]	1.52×10^{-9}		
(5)					
	HOAc	120.0	2.10×10^{-4}	29.4	−1.1
		100.0	2.65×10^{-5}		
		25.0[b]	9.80×10^{-10}		
	CF_3CH_2OH	100.0	1.11×10^{-4}	25.9	−7.8
		80.0	1.46×10^{-5}		
		25.0[b]	1.37×10^{-8}		
	HCO_2H	90.0	2.01×10^{-4}	27.5	0.0
		70.0	2.10×10^{-5}		
		25.0[b]	4.13×10^{-8}		
	CF_3CO_2H	70.0	7.18×10^{-5} [c]	25.3	−3.9
		50.0	6.79×10^{-6} [c]		
		25.0[b]	2.29×10^{-7}		
	HOAc	100.0	9.23×10^{-6}		
	HCO_2H	90.0	7.38×10^{-5}		
	CF_3CO_2H	70.0	2.58×10^{-5} [c]		
(5-d_6)					
	CF_3CH_2OH	60.0	1.39×10^{-4}	24.1	−4.1
		40.0	1.28×10^{-5}		
		25.0[b]	1.73×10^{-6}		
(6)					
Ph-CH_2OMs	HFIP	25.0	9.23×10^{-3} [d]		
	EtOH	25.0	4.48×10^{-3}		
	CF_3CO_2H	25.0	5.6×10^{-5} [d]		
	CF_3CH_2OH	70.0	1.74×10^{-4}	22.5	−10.3
		50.0	2.12×10^{-5}		
		25.0	1.03×10^{-6}		

[a] See Experimental Section for a description of the solvent including the buffer employed. [b] Extrapolated rate. [c] Initial rate. The first-order plot showed slight curvature over 70% reaction. See Experimental Section. [d] Reference 3c.

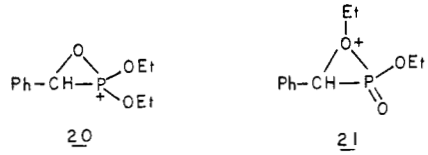
Table II. Kinetic α-Deuterium Isotope Effects in Solvolyses of **3** and **3-d_1**

solvent	T, °C	k_H/k_D
HOAc	100	1.16 ± 0.01
CF_3CH_2OH	70	1.17 ± 0.01
HCO_2H	50	1.21 ± 0.01

Scheme IV



It is conceivable that solvolysis of **3** occurs by a k_Δ process involving cationic intermediates such as **20** or **21**. In order to

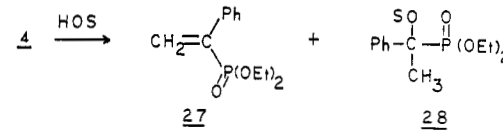


support or rule out such intermediates, an α-deuterium isotope effect study was carried out. α-Deuterium isotope effects have been used in the past as an empirical criterion for mechanistic determination in solvolytic processes. We have therefore prepared the deuterated mesylate **3-d_1** as shown in Scheme III. Reduction of **22** with lithium triethylborodeuteride gave **23** in which the initial reduction product is presumably strongly coordinated to triethylborane. This avoids the potential problem of fragmentation of alkoxide **24** to benzaldehyde and the anion of diethyl phosphite.[15] An acidic workup liberates the deuterated alcohol **12-d_1** under conditions where the mixture never becomes basic. The water solubility of **12-d_1** allows for facile separation from the trialkylborane byproduct. The deuterated product, **12-d_1**, was converted to the corresponding mesylate, **3-d_1**, and solvolytic rates were determined. Table II gives results of these α-deuterium isotope effect studies. Values are 1.16, 1.17, and 1.21, respectively, in acetic acid, trifluoroethanol, and formic acid.

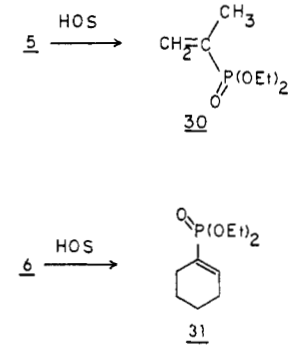
Shiner[16] has suggested a maximum k_H/k_D value of 1.23 for solvolysis of sulfonate esters at 25 °C. This value is indicative of a limiting (k_c) process. Ordinarily the α-deuterium isotope effect decreases with increasing temperature.[17] A value of around unity (or slightly inverse) is indicative of a k_s process.[16] Neighboring group participation[18] or significant solvent participation[16] will also result in a lowering of the α effect from the maximum value. The α-deuterium isotope effects for **3** and **3-d_1** appear to be approaching the maximum value suggested by Shiner as temperature decreases. The isotope effects of 1.16 at 100 °C and 1.17 at 70 °C compare favorably with the values of 1.15 and 1.17 seen for 2-adamantyl tosylate[17] at 100 and 75 °C, respectively. If one accepts the α-deuterium isotope effect as a mechanistic criterion, then our data strongly suggest that solvolysis of mesylate **3** is a limiting k_c process, involving cation **25** as a discrete in-

termediate. In line with the solvent effect study, the isotope effect study also rules out any significant solvent assistance. Ions such as **20** or **21** are also inconsistent with the α-deuterium isotope effect since it is known that neighboring group participation results in a decreased α effect.

Scheme V



Scheme VI



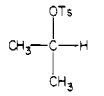
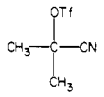
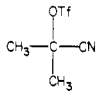
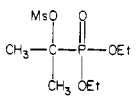
In order to further substantiate the intermediacy of **25** and to rule out any k_Δ processes, optically active mesylate (+)-**3** was prepared as shown in Scheme IV. Reduction of **22** with the chiral trialkylborohydride **26**,[19] derived from (+)-α-pinene, 9-BBN, and *tert*-butyllithium, gave an optically active product in which (+)-**12** predominated.[20] This optically active product was converted to the optically active mesylate, (+)-**3**. Solvolysis of this optically active mesylate in trifluoroacetic acid gave a completely racemic trifluoroacetate product. Additionally, the racemization rate exceeded the solvolytic rate by a factor of 2. Acetolysis of (+)-**3** gave an acetate product with a rotation of −2.5°. Acetylation of (+)-**12** with acetic anhydride gave an acetate with a rotation of +13.6°. Therefore, acetolysis gave a slight excess of the *inverted* acetate product. Analogous studies with (−)-**3** led to the same conclusion.

These studies using optically active **3** argue against k_Δ processes involving ions such as **20** and **21**. If such ions were involved, then products of overall retained configuration would have been formed (assuming ions such as **20** or **21** maintain their structural integrity). The racemic product in trifluoroacetolysis is completely consistent with the intermediacy of **25** and rules out anchimerically assisted, k_Δ, or solvent assisted, k_s, processes. The somewhat faster racemization rate (than solvolysis) suggests that internal return can occur at an ion-pair stage. The slightly inverted product in acetolysis also argues against ions such as **20** and **21**. Solvent capture of ion **25** at an earlier ion-pair stage would account for the partially inverted product in acetic acid.[21]

Solvolytic Studies on 4. Mesylate **4** proved to be quite reactive. At room temperature, **4** gave a mixture of elimination product **27** and substitution produce **28**, with **28** being the major product

(15) Such a fragmentation has precident. See: Hata, T.; Hashizume, A.; Nakajima, M.; Sekine, M. *Tetrahedron Lett.* **1978**, 363–366.
(16) Shiner, V. J., Jr.; Rapp, M. W.; Pinnick, H. R., Jr. *J. Am. Chem. Soc.* **1970**, *92*, 232–233 and references therein.
(17) Harris, M. J.; Hall, R. E.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1971**, *93*, 2551–2553.
(18) Eliason, R.; Tomič, M.; Borčić, S.; Sunko, D. E. *Chem. Commun.* **1968**, 1490–1491.
(19) Krishnamurthy, S.; Vogel, F.; Brown, H. C. *J. Org. Chem.* **1977**, *42*, 2534–2536.
(20) Midland's recently developed chiral trialkylborohydride, derived from (−)-nopol benzyl ether, 9-BBN, and *tert*-butyllithium, also gave an optically active product on reaction with **22**. The extent of assymetric induction was approximately the same as with **26**, but (−)-**12** predominated. See: Midland, M. M.; Kazubski, A. *J. Org. Chem.* **1982**, *47*, 2495–2496. The enantiomeric purity of these products was not determined.
(21) A reviewer has suggested that an ion such as **20** (or **21**) that opens to **25** (or an intermediate structure) cannot be ruled out. Although we feel that this is inconsistent with the data, we include this possibility.
(22) Leffek, K. T.; Llewellyn, J. A.; Robertson, R. E. *Can. J. Chem.* **1960**, *38*, 2171–2177.
(23) Streitwieser, A., Jr.; Dafforn, G. A. *Tetrahedron Lett.* **1969**, 1263–1266.

Table III. A Summary of β-Deuterium Isotope Effects

substrate	k-H_6/k-D_6	mechanistic conclusion	ref
	1.55 (H_2O) 2.12 (CF_3CO_2H)	significant solvent assistance rate-limiting ionization (k_c)	22 23
	2.19 (CF_3CH_2OH)	rate-limiting ionization (k_c) (E1)	5a
	3.80 (various solvents)	rate-limiting elimination after ion-pair formation ($E2_{R^+}$)	6b
	2.87 (HOAc) 2.73 (HCO_2H) 2.78 (CF_3CO_2H)[a]	proton elimination at an ion-pair stage; internal return and elimination rates comparable	this work

[a] Based on initial rates. See Experimental Section.

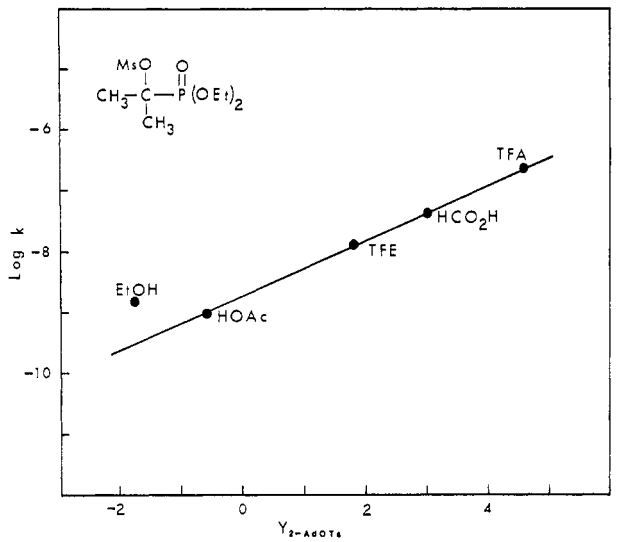
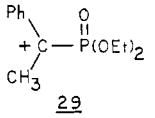


Figure 2. Plot of log k for the solvolysis of **5** in various solvents vs. $Y_{2\text{-Ad-OTs}}$.

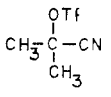
(Scheme V). The high reactivity of **4** prevented a complete solvent effect study. However, data in acetic acid and trifluoroethanol are consistent with a k_c process (m = 0.93) involving cation **29**.



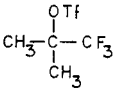
29

This cation suffers elimination or solvent capture. In light of the absence of k_Δ processes in solvolysis of **3**, it is highly unlikely that such processes could be involved in solvolyses of **4**.

Solvolytic Studies on 5 and 6. Solvolyses of mesylate **5** in all solvents gave the elimination product **30** exclusively. Mesylate **6** also gave only the elimination product **31** (Scheme VI). This type of behavior (exclusive elimination) is also seen in solvolyses of **32** and **33**. As before, solvolyses are unexpectedly facile (when



32



33

compared to isopropyl and cyclohexyl mesylates). Mechanistic possibilities range from a concerted elimination to a stepwise sequence involving cationic intermediates. Figure 2 shows the results of a solvent effect study in solvolysis of **5**. The m value (0.45) is smaller than expected for rate-limiting ionization.

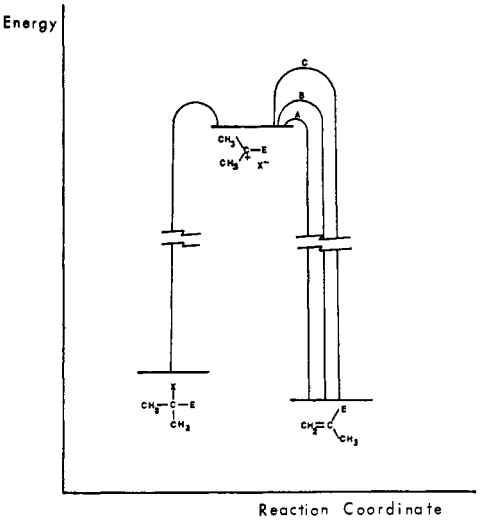


Figure 3. Potential energy surfaces for alkene formation via a cationic intermediate.

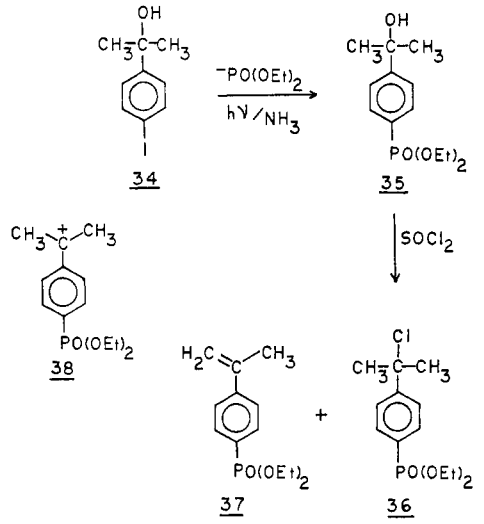
However, a carbocation intermediate cannot be ruled out by this less than limiting m value.

In order to gain further insight into the solvolysis mechanism for **5**, the deuterated analogue **5**-d_6 was prepared from acetone-d_6 and the β-deuterium isotope effect was measured. Table III summarizes data for **5** and related substrates and is quite revealing. The β-d_6 isotope effect for **5** is larger than expected for rate-limiting ionization as in the case of isopropyl tosylate in CF_3CO_2H and **32** in trifluoroethanol. It is, however, smaller than the value of 3.80 seen for **33**, which Tidwell suggests undergoes rate-limiting elimination at an ion-pair stage. On the basis of the β-d_6 value of about 2.8, we suggest the mechanistic scheme shown below. We suggest that a cationic intermediate is reversibly formed; i.e., the rate of proton elimination (k_2) at an ion-pair stage is comparable in magnitude to internal return (k_{-1}).

$$\text{R–OMs} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{R}^+\text{–}^-\text{OMs} \xrightarrow[-\text{H}^+]{k_2} \text{alkene}$$

A graphical representation contrasting the behavior of **5** with that of **32** and **33** is given in Figure 3. Path A represents the case where ionization is rate limiting. The β-deuterium isotope effect (due to C–H vs. C–D hyperconjugation) is "normal". This is the path followed when E = CN. In path B, the transition-state energies for both ionization and proton elimination steps are comparable in energy ($k_2 \approx k_{-1}$). The β-deuterium isotope effect should be slightly greater than normal due to a superimposed primary isotope effect during proton elimination. There should also be some correlation of rate with solvent Y value since, by the proposed mechanism, cation formation is also important. This

Scheme VII



is the suggested pathway when E = $PO(OEt)_2$. In path C, the proton elimination step is rate limiting. The β-deuterium isotope effect is greater than normal due to a superimposed hyperconjugative isotope effect on the primary isotope effect in the elimination. The correlation of rate with solvent ionizing power is not necessarily high since proton elimination is rate limiting. This is the path followed when E = CF_3. These pathways represent the possible mechanisms for elimination reactions involving carbocationic intermediates. The interpretation presented can account for the observed solvent and isotope effects seen in the solvolyses of **5**, **32**, and **33**.

While the mechanism represented by path C has been sporadically suggested,[6b,24,25] it is usually not included in the general scheme for elimination reactions. The process represented by path C can be considered the cationic counterpart of the E1cb elimination mechanism where loss of the leaving group is rate limiting. We suggest the term $E2_{R^+}$ to describe this cationic elimination reaction. The rate-limiting step is unimolecular in carbocation and unimolecular in base (solvent, counterion, or added base). Just as the E1cb reaction exists at one extreme of the elimination spectrum, it is reasonable that the $E2_{R^+}$ mechanism should exist at the other extreme. The elimination reaction therefore includes the E1cb, E2, E1, and the $E2_{R^+}$ spectrum. Solvolysis of **5** would represent the point where the E1 and $E2_{R^+}$ mechanisms are merging.

Effect of the Diethyl Phosphonate Group on Rates. In order to evaluate the electron-withdrawing properties of $PO(OEt)_2$, the σ_p^+ value for this substituent was determined. The requisite cumyl chloride was prepared as shown in Scheme VII. The photoinitiated $S_{RN}1$ reaction of *p*-iodocumyl alcohol (**34**) with potassium diethyl phosphite[26] gave **35**. This product was converted to a 3.6:1 mixture of chloride **36** and alkene **37** by treatment with thionyl chloride. Solvolysis of **36** in ethanol gave an extrapolated rate of 1.73×10^{-6} s^{-1} at 25 °C. This is 228 times slower than the unsubstituted cumyl chloride and corresponds to a σ^+ value of 0.505.

In light of this large rate-retarding factor of $PO(OEt)_2$ on the formation of the substituted cumyl cation **38**, it is interesting to examine the effect of removing the phenyl group and placing this group directly on an incipient cationic center. Cations **25** and **29** represent such systems. The solvolysis **3** in hexafluoroisopropyl alcohol (HFIP) is 987 times slower than that of benzyl mesylate in HFIP (where solvolysis of benzyl mesylate should be close to limiting). Solvolysis of **4** in ethanol is 200 times slower than that of α-phenethyl mesylate. We consider these rate-retarding factors unexpectedly small. They are only comparable in magnitude to the effect in the cumyl cation **38**, where the incipient cationic center is insulated from the diethyl phosphonate group by the aromatic ring. Normally the effect of an insulating aromatic ring is to attenuate the effect of a substituent on a solvolysis rate. For example, *p*-methyl substitution increases the solvolysis rate of cumyl chloride[27] by a factor of 27, while methyl substitution for hydrogen attached directly to a cationic center gives rate increases from 10^5 to 10^8.[28] In light of these considerations, the unattenuated diethyl phosphonate group in mesylates **3** and **4** might be expected to slow solvolysis rates by very large factors relative to model systems. This is not the case. Therefore, some other feature must partially offset the large expected rate-retarding effect of $PO(OEt)_2$. Some potential rate-enhancing features are considered below.

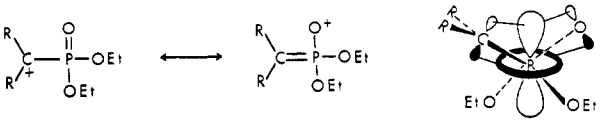
The kinetic α-deuterium isotope effect studies of **3**-d_1 and the studies on optically active **3** allow one to rule out neighboring group participation as a rate-enhancing feature. In view of the fact that there is no neighboring group participation in **3**, analogous k_Δ processes are considered unlikely for **4**.

A steric rate acceleration due to relief of ground-state strain has been considered. Such effects can be large in rigid bicyclic systems.[29] However, it is felt that, although the diethyl phosphonite substituent is a large group, steric rate acceleration cannot completely account for the unexpectedly rapid solvolysis rate of **3**. The ionization center still bears a hydrogen atom and hence is not extremely encumbered. It should be kept in mind that the carbon–phosphorus bond is longer (1.81 Å)[30] than a carbon–carbon bond. Therefore, the effective size of the diethyl phosphonate group should be smaller than that of a *tert*-butyl group.[31] However, accurate measurements on the size of the diethyl phosphonate group are not available. Therefore, we cannot rule out some steric rate enhancement. Such steric rate accelerations are probably small but could become important in systems that are more rigid and crowded than **3** and **4**.

The possibility of a stabilizing interaction between the diethyl phosphonate group and the cationic center must be considered. We have concluded that α-keto cations can derive some stabilization by a conjugative interaction with the carbonyl group as depicted in **39**. Gassman has concluded that α-cyano cations can

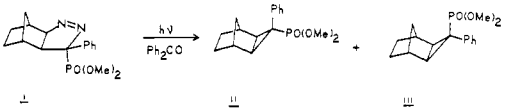
39 **40**

be stabilized in a similar manner as represented by **40**. Such a stabilizing interaction in cation **2a** could be represented by **2b**.



2a **2b** **2c**

(24) Fisher, R. D.; Seib, R. C.; Shiner, V. J., Jr.; Szele, I.; Tomić, M.; Sunko, D. E. *J. Am. Chem. Soc.* **1975**, *97*, 2408–2413.
(25) Seib, R. C.; Shiner, V. J., Jr.; Sendijarević, V.; Humski, K. *J. Am. Chem. Soc.* **1978**, *100*, 8133–8137.
(26) Bunnett, J. F.; Creary, X. *J. Org. Chem.* **1974**, *39*, 3612–3614.
(27) Brown, H. C.; Brady, J. D.; Grayson, M.; Bonner, H. W. *J. Am. Chem. Soc.* **1957**, *79*, 1897–1903.
(28) Fry, J. L.; Harris, J. M.; Bingham, R. C.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1970**, *92*, 2540–2542.
(29) Peters, E. N.; Brown, H. C. *J. Am. Chem. Soc.* **1975**, *97*, 2892–2895 and references therein.
(30) Samuel, G.; Weiss, R. *Tetrahedron* **1970**, *26*, 2995–3003.
(31) Data on the sensitized photolysis of pyrazoline i infers that phenyl and

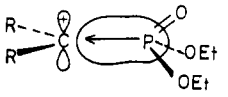


i ii iii

dimethyl phosphonate groups have comparable steric bulk. The biradical produced in the sensitized photolysis of i gave equal amounts of ii and iii where both the phenyl and dimethyl phosphonate groups can occupy the crowded syn position. See: Callot, H. J.; Benezra, C. *Can. J. Chem.* **1972**, *50*, 1078–1087.

However, the interaction represented by **2b** is fundamentally different from carbon or cyano conjugation. It must utilize a 3d orbital on phosphorus.[32] One possible d-orbital interaction (utilizing the d_{z^2} orbital) is illustrated by **2c**. The magnitude of the stabilization due to this type of interaction is not certain. Theoretical calculations may give some insight as to the importance of this stabilizing feature.

Another potential stabilizing feature attributable to phosphorus is its polarizability. It has been suggested that anions adjacent to sulfur (and presumably phosphorus) derive stabilization due to the polarizability of the large third-row atom.[33] If this is indeed the case, then cations adjacent to phosphorus should also be stabilized by a similar mechanism, which is illustrated in **2d**.



2d

Finally, the effect of the phenyl group on cations **25** and **29** must be considered. It is quite possible that some of the inductive destabilizing effect of the diethyl phosphonate group is offset by increased phenyl stabilization; i.e., increased electron demand results in increased charge delocalization by the aromatic ring.[34] Further studies are in progress to determine which of these factors (or combination thereof) are responsible for the unexpectedly facile generation of cations adjacent to the diethyl phosphonate group.

Conclusions. Cations adjacent to the electron-withdrawing $PO(OEt)_2$ substituent can be generated from mesylates **3** and **4**. This has been supported by large *m* values in a solvent effect study, a large α-deuterium isotope effect, and studies on an optically active system. Solvolytic rates are judged to be faster than expected on the basis of the σ^+ value of 0.505 for $PO(OEt)_2$. Increased phenyl charge delocalization, as well as a stabilizing effect by the adjacent inductively electron-withdrawing group on the cationic center, may account for these unexpectedly rapid rates. Solvolysis of mesylate **5** (and **6**) gave exclusive elimination product by a suggested mechanism involving reversible ion-pair formation followed by proton elimination. This mechanism represents the merging of the E1 and the mechanism that we have termed $E2_{R^+}$, the cationic analogue of the E1cb mechanism.[43]

Experimental Section

Gas chromatographic analyses were carried out on a Hewlett-Packard 5750 chromatograph with a flame ionization detector using a 5-ft 5% SE-30 on Chromosorb G column. A Varian 920 chromatograph was used for sample isolation. NMR spectra were recorded on Varian A-60A, EM 390, or XL-100 or Nicolet NB 300 spectrometers. Infrared spectra were recorded on a Perkin-Elmer 727B spectrometer. Mass spectra were recorded on an AEI Scientific Apparatus MS 902 spectrometer or on a Du Pont DP1 GC/MS system. Titrations were carried out with a Metrohm E576 automatic recording titrator.

Preparation of Diethyl Trimethylsilyl Phosphite (7).[35] Triethylamine (15.3 g) was added in one portion to a mixture of 14.0 g of diethyl phosphite and 16.4 of chlorotrimethylsilane in 100 mL of absolute ether. The mixture was stirred at reflux for 16 h. Pentane (150 mL) was then added, and the precipitated triethylamine hydrochloride was removed by rapid filtration through a Büchner funnel. The solvents were removed by a rotary evaporator, and 100 mL of pentane was added to the residue. After the mixture was filtered again, the solvent was again removed by a rotary evaporator. The residue was distilled. After a small forerun, 18.7 g (88%) of **7**,[35] bp 76–77 °C (20 mmHg), was collected. NMR (CCl_4): δ 3.77 (4 H, quintet, J = 7 Hz), 1.20 (6 H, t, J = 7 Hz), 0.19 (9 H, s).

Addition of 7 to Aldehydes and Ketones. General Procedure.[9] The appropriate aldehyde (benzaldehyde) or ketone (1.0 equiv) was added to diethyl trimethylsilyl phosphite (**7**) (1.0 equiv), and the mixture was heated in a sealed tube for 3 h at 110 °C. The tube was then opened, and the product was isolated by distillation.

Reaction of benzaldehyde with **7** gave 96% of **8**,[9,15] bp 93–94 °C (0.03 mmHg). NMR (CCl_4): δ 7.6–7.1 (5 H, m), 4.82 (1 H, d, J = 14 Hz), 3.92 (4 H, quintet, J = 7.2 Hz), 1.17 (6 H, t, J = 7.2 Hz), 0.08 (9 H, s).

Reaction of acetophenone with **7** gave 73% of **9**,[15] bp 101 °C (0.1 mmHg). NMR ($CDCl_3$): δ 7.6–7.1 (5 H, m), 4.3–3.7 (4 H, overlapping quintets, J = 7 Hz), 1.90 (3 H, d, J = 17 Hz), 1.4–1.0 (6 H, overlapping triplets, J = 7 Hz), 0.10 (9 H, s).

Reaction of acetone with **7** gave 63% of 10, bp 84–87 °C (1.4 mmHg). NMR (CCl_4): δ 4.07 (4 H, quintet, J = 7.2 Hz), 1.38 (6 H, d, J = 15 Hz), 1.30 (6 H, t, J = 7.2 Hz), 0.15 (9 H, s).

Reaction of cyclohexanone with **7** gave 91% of **11**,[9] bp 74–75 °C (0.03 mmHg). NMR ($CDCl_3$): δ 4.12 (4 H, quintet, J = 7 Hz), 2.1–1.3 (10 H, m), 1.32 (6 H, t, J = 7 Hz), 0.18 (9 H, s).

Desilylation of α-Siloxy Phosphonates 8–11. General Procedure. The appropriate α-siloxy phosphonate (1 part) was dissolved in a freshly prepared 10^{-3} M trifluoroacetic acid in methanol solution (10 parts). The reaction was monitored by gas chromatography. When no starting material remained (4–10 h), the methanol was removed by a rotary evaporator. α-Hydroxy phosphonates **12–14** were solids and were collected on a Büchner funnel, and **15** was isolated by distillation.

A quantitative yield of **12**,[9] mp 80–82 °C, was obtained; NMR ($CDCl_3$) δ 7.6–7.1 (5 H, m), 5.56 (1 H, br s, exchanges with D_2O, shift is concentration dependent), 5.00 (1 H, d, J = 12 Hz), 4.2–3.7 (4 H, m), 1.22 (3 H, t, J = 7 Hz), 1.18 (3 H, t, J = 7 Hz).

An 88% yield of **13**,[15] mp 74–75 °C, was obtained; NMR ($CDCl_3$) δ 7.8–7.2 (5 H, m), 4.17 (1 H, s), 4.3–3.7 (4 H, m), 1.79 (3 H, d, J = 16 Hz), 1.23 (3 H, t, J = 7 Hz), 1.19 (3 H, t, J = 7 Hz).

A 96% yield of **14**, bp 75–77 °C (0.08 mmHg), was obtained; NMR ($CDCl_3$) δ 4.16 (quintet, J = 7 Hz), 3.83 (1 H, d, J = 3 Hz), 1.42 (6 H, d, J = 15 Hz), 1.32 (6 H, t, J = 7 Hz).

A quantitative yield of **15**, mp 69–71 °C, was obtained; NMR ($CDCl_3$) δ 4.16 (4 H, quintet, J = 7 Hz), 2.74 (1 H, br s), 2.0–1.3 (10 H, m), 1.33 (6 H, t, J = 7 Hz).

Preparation of Mesylate 3. α-Hydroxy phosphonate **12** (0.80 g) was dissolved in 15 mL of methylene chhloride, and the solution was cooled to −50 °C. Mesyl chloride (0.53 g) was added followed by dropwise addition of 0.66 g of triethylamine. The mixture was warmed to 0 °C and then taken up into ether and water. The organic phase was washed with dilute hydrochloric acid and saturated sodium chloride solution and dried over $MgSO_4$. After filtration, the solvents were removed by a rotary evaporator. The crude mesylate **3** was an oil, which weighed 1.01 g (96%), and it was used without further purification; NMR ($CDCl_3$) δ 7.6–7.2 (5 H, m), 5.70 (1 H, d, J = 15 Hz), 4.4–3.7 (4 H, m), 2.82 (3 H, s), 1.30 (3 H, t, J = 7 Hz), 1.20 (3 H, t, J = 7 Hz).

Preparation of Methyl Sulfinate Esters 16–18. General Procedure. The α-hydroxy phosphonate (1 equiv) was dissolved in methylene chloride (10 parts), and the solution was cooled in an ice bath. Methanesulfinyl chloride[36] (2.0 equiv) was added in one portion followed by the dropwise addition of 2.3 equiv of triethylamine. After 15 min of stirring at 0 °C, the mixture was taken up into ether and water. The organic phase was washed with dilute hydrochloric acid and saturated sodium chloride and dried over $MgSO_4$. After filtration, the solvents were removed by a rotary evaporator. The sulfinate esters remained as oils. The yields of sulfinates **16**, **17**, and **18** were 91, 73, and 94%, respectively. The crude sulfinates were used directly in the next step.

Oxidation of Methyl Sulfinate Esters 16–18 to Mesylates 4, 5, and 6. General Procedure. A solution of the crude methyl sulfinate ester (1.0 equiv) in methylene chloride (10 parts) was stirred at room temperature as 1.27–1.30 equiv of *m*-chloroperbenzoic acid was added in one portion. The peracid was 85% pure. The solution warmed slightly, and the temperature was not allowed to exceed 35 °C. After about 10 min *m*-chlorobenzoic acid started to precipitate. After 2 h, the mixture was taken up into ether and aqueous sodium hydroxide (1.5 equiv) was added to the separatory funnel. After separating the aqueous extract, the organic phase was extracted with a solution of sodium iodide, sodium thiosulfate, and sodium hydroxide. After the organic phase was dried over $MgSO_4$ and filtered, the solvents were removed by a rotary evapo-

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(34) Evidence has been presented which indicates that the ability of a group to stabilize a cationic center can vary as a function of the "demand" at that center. See: (a) Gassman, P. G.; Fentiman, A. F. *J. Am. Chem. Soc.* **1970**, *92*, 2549–2551. (b) Brown, H. C. "The Nonclassical Ion Problem"; Plenum Press: New York, 1977.

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rator, leaving the corresponding mesylates.

The yield of **4** was 91%; NMR ($CDCl_3$) δ 7.8–7.3 (5 H, m), 4.3–3.7 (4 H, m), 3.07 (3 H, s), 2.34 (3 H, d, J = 16 Hz), 1.29 (3 H, t, J = 7 Hz), 1.21 (3 H, t, J = 7 Hz).

The yield of **5**, a very hydroscopic solid, was 74%; NMR ($CDCl_3$) δ 4.24 (4 H, quintet, J = 7 Hz), 3.11 (3 H, s), 1.88 (6 H, d, J = 16 Hz), 1.37 (6 H, t, J = 7 Hz). Mesylate **5**-d_6 was prepared in the same fashion (from acetone-d_6).

The yield of **6** was 80%; NMR ($CDCl_3$) δ 4.22 (4 H, quintet, J = 7 Hz), 3.14 (3 H, s), 2.7–1.5 (10 H, m), 1.36 (6 H, t, J = 7 Hz).

Solvolysis of Mesylates in Acetic Acid. General Procedure. The given mesylate was heated in a sealed tube in acetic acid containing 0.1 M NaOAc and 1% acetic anhydride for 10 half-lives. The ratio of sodium acetate to mesylate was approximately 1.3:1. The contents of the tube were taken up into ether, and solid Na_2CO_3 was added until the acetic acid was neutralized. A standard aqueous workup followed. After the solution was dried over $MgSO_4$ and filtered, the solvent was removed by a rotary evaporator. Details of individual solvolyses are given below.

Solvolyses of Mesylates in Trifluoroethanol. General Procedure. The given mesylate was heated (sealed tube) in trifluoroethanol containing 1.3 equiv of 2.6-lutidine for 10 half-lives. The tube contents were then taken up into ether, and the mixture was washed with dilute hydrochloric acid and saturated NaCl solution. After the solution was dried over $MgSO_4$ and filtered, the solvent was removed by a rotary evaporator. Details of individual solvolyses are given below.

Solvolysis of 3 in Acetic Acid. Mesylate **3** (309 mg) in 13 mL of HOAc for 16.5 h at 110 °C gave 215 mg (78%) of **19** (S = Ac); NMR ($CDCl_3$) δ 7.6–7.1 (5 H, m), 6.50 (1 H, d, J = 14 Hz), 4.3–3.7 (2 H, m), 2.14 (3 H, s), 1.26 (3 H, t, J = 7 Hz), 1.20 (3 H, t, J = 7 Hz).

Solvolysis of 3 in Trifluoroethanol. Mesylate **3** (253 mg) in 10 mL of trifluoroethanol for 20 h at 100 °C gave 240 mg (95%) of **19** (S = CH_2CF_3); NMR ($CDCl_3$) δ 7.7–7.3 (5 H, m), 4.80 (1 H, d, J = 15 Hz), 4.3–3.6 (4 H, m), 1.27 (3 H, t, J = 7 Hz), 1.21 (3 H, t, J = 7 Hz).

Solvolysis of 3 in Trifluoroacetic Acid. A 30-mg sample of **3** in 0.5 mL of CF_3CO_2H containing 0.5% trifluoroacetic anhydride and 0.2 M in sodium trifluoroacetate was kept at room temperature for 24 h. Periodic NMR monitoring showed the disappearance of **3** and formation of **19** (S = $COCF_3$); NMR (CF_3CO_2H) δ 7.55 (5 H, br s), 6.43 (1 H, d, J = 13 Hz), 4.28 (4 H, quintet, J = 7 Hz), 1.38 (6 H, t, J = 7 Hz). The NMR spectrum also showed a 3 H singlet at δ 3.18, which is assigned to sodium methanesulfonate. Attempts to separate **19** (S = $COCF_3$) from CF_3CO_2H by extraction procedures led to substantial hydrolysis of **19** (S = $COCF_3$) to **12**.

Preparation of *12*-d_1. A solution of 3.10 g of **22**[37] in 30 mL of ether was cooled to −78 °C as 15 mL of 1.0 M lithium triethylborodeuteride (Aldrich Chemical Co.) in tetrahydrofuran (THF) was added dropwise. At the end of the addition, the pale yellow color disappeared. A mixture of 1.3 mL of concentrated HCl, 15 mL of D_2O, and 15 mL of THF was then added dropwise at −78 °C. The mixture was warmed to 0 °C, and 30 mL of water was added. The mixture was transferred to a separatory funnel with ether. The aqueous phase was separated, and the organic phase was extracted with four additional 30-mL portions of water. The organic phase was discarded. The combined aqueous extracts were reextracted with 20 mL of ether. The water was then removed at reduced pressure (2 mmHg). The residue was taken up into 100 mL of ether, and the ether solution was washed with 10 mL of water and dried over $MgSO_4$. The solution was filtered, and the ether was removed by a rotary evaporator. The crude **12**-d_1, 1.02 g (33%), was slurried with pentane and collected on a Büchner funnel. The NMR of **12**-d_1 was identical with that of **12** except for the absence of the doublet at δ 5.00.

Mesylate **3**-d_1 was prepared (97%) by the same procedure used to prepare **3**. The NMR of **3**-d_1 showed no signal at δ 5.70.

Preparation of (+)-12. A solution of 5.56 g of (+)-α-pinene (Aldrich Chemical Co., $[\alpha]^{22}_D$ 47.1°), 15 mL of THF, and 75.8 mL of 0.5 M 9-BBN in THF (Aldrich) was refluxed for 3 h. Thirty milliliters of ether was then added. This solution, containing **26**,[19] was cooled to −78 °C as 19 mL of 2.0 M *tert*-butyllithium in pentane was added dropwise. After being stirred at −78 °C for 45 min, the solution was added, via a double-ended needle, to a mixture of 7.83 g of **22** in 75 mL of ether at −100 °C (frozen methanol slurry from liquid nitrogen). The mixture was then warmed to −30 °C and recooled to −78 °C, and 3.7 mL of concentrated HCl in 45 mL of THF was added dropwise. Sixty milliliters of water was added with rapid stirring. The remainder of the workup was analogous to that described in the preparation of **12**-d_1. The yield of (+)-**12** was 1.77 g (23%), $[\alpha]^{23}_D$ +9.9° (*c* 3.5, CH_3OH). The NMR spectrum was identical with that of **12**.

Mesylate (+)-**3** was prepared by the same procedure used to prepare **3**, $[\alpha]^{23}_D$ +20.2° (*c* 2.3, CH_2Cl_2).

Preparation of (−)-12. The procedure was identical with the preparation of (+)-**12** except for the use of nopol benzyl ether[20] in place of (α)-pinene. NB-Enantride, prepared from 4.22 g of nopol benzyl ether, 30 mL of 0.5 M 9-BBN, and 7.0 mL of 2.0 M *tert*-butyllithium, was added to a −100 °C mixture of 3.1 g of **22** in 30 mL of ether. The workup was as described for **12**-d_1 and (+)-**12**. The yield of (−)-**12** was 0.67 g (22%), $[\alpha]^{23}_D$ −9.0° (*c* 1.5, CH_2Cl_2). The NMR spectrum was identical with that of **12**.

Mesylate (−)-**3** was prepared by the same procedure used to prepare **3**, $[\alpha]^{23}_D$ −20.6° (*c* 2.8, CH_2Cl_2).

Solvolysis of (+)-3 in Trifluoroacetic Acid. A solution of 0.84 g of (+)-**3** in 16 mL of 0.2 M sodium trifluoroacetate in trifluoroacetic acid was rapidly transferred to a 2-dm polarimeter tube. The rotation was monitored as a function of time. The rotation fell to 0° with a half-life of approximately 33 min at 24 °C. As before, the product **19** (S = $COCF_3$) could not be isolated via an aqueous workup.

Solvolysis of (−)-3 in Acetic Acid. Mesylate (−)-**3** (620 mg) in 25 mL of HOAc for 35 h at 100 °C gave 476 mg (86%) of (+)-**19** (S = $COCH_3$), $[\alpha]^{23}_D$ +2.5° (*c* 3.2, CH_2Cl_2). The NMR spectrum of the product was identical with that of the inactive product.

Acetylation of (+)-12. Acetic anhydride (250 mg) was added to a solution of 295 mg of (+)-**12** in 3 mL of pyridine at room temperature. After 12 h at room temperature, the solution was taken up into ether and washed with water and dilute HCl. After the solution was dried over $MgSO_4$ and filtered, the solvent was removed by a rotary evaporator. The yield of (+)-**12** (R = $COCH_3$), $[\alpha]^{23}_D$ +13.6° (*c* 1.5, CH_2Cl_2) was 278 mg (80%).

A sample of (+)-**19** (R = $COCH_3$) in 0.05 M NaOAc in HOAc for 45 h at 100 °C showed no change in rotation.

Solvolysis of 4 in Acetic Acid. Mesylate **4** (235 mg) in 10 mL of acetic acid for 24 h at room temperature gave 100% of **27**[38] and **28** (S = $COCH_3$) in a 28:72 ratio. Samples of each product were isolated by preparative gas chromatography. NMR of **27** ($CDCl_3$): δ 7.7–7.2 (5 H, m), 6.33 (1 H, d of d, J = 22 Hz, J = 1.5 Hz), 6.17 (1 H, d of d, J = 46 Hz, J = 1.5 Hz), 4.13 (4 H, quintet, J = 7 Hz), 1.30 (6 H, t, J = 7 Hz). NMR of **28** (S = $COCH_3$) ($CDCl_3$): δ 7.6–7.2 (5 H, m), 4.3–3.8 (4 H, m), 2.18 (3 H, d, J = 15 Hz), 2.15 (3 H, s), 1.27 (3 H, t, J = 7 Hz), 1.21 (3 H, t, J = 7 Hz).

Solvolysis of 4 in Ethanol. Mesylate **4** (279 mg) in 10 mL of ethanol (0.1 M in 2,6-lutidine) at 35 °C for 24 h gave 98% of **27** and **28** (S = Et) in a 37:63 ratio. Samples of each product were isolated by preparative gas chromatography. NMR of **28** (S = Et) ($CDCl_3$): δ 7.6–7.2 (5 H, m), 4.3–3.8 (4 H, m), 3.7–3.1 (2 H, m), 1.86 (3 H, d, J = 16 Hz), 1.23 (6 H, t, J = 7 Hz).

Solvolysis of 4 in Methanol. Mesylate **4** (234 mg) in 9 mL of methanol (0.1 M in 2,6-lutidine) at 35 °C for 23 h gave 92% of **27** and **28** (S = CH_3) in a 17:83 ratio. Samples of each product were isolated by preparative gas chromatography. NMR of **28** (S = CH_3) ($CDCl_3$): δ 7.6–7.2 (5 H, m), 4.2–3.7 (4 H, m), 3.20 (3 H, s), 1.86 (3 H, d, J = 16 Hz), 1.22 (6 H, t, J = 7 Hz).

Solvolyses of 5 in Carboxylic Acids. Mesylate **5** (114 mg) in 10 mL of HOAc at 116 °C for 25 h gave a quantitative yield of **30**;[39,40] NMR ($CDCl_3$) δ 5.97 (1 H, d of multiplets, J = 22 Hz), 5.77 (1 H, doublet of quintets, J = 48 Hz, J = 1.8 Hz), 4.10 (4 H, quintet, J = 7 Hz), 1.93 (3 H, d of multiplets, J = 14 Hz), 1.33 (6 H, t, J = 7 Hz). Solvolysis of **5** in formic acid for 54 h at 78 °C also gave **30** as the only product by GC and NMR analysis. Solvolysis of **5** in trifluoroacetic acid for 26 h at 70 °C also gave **30** as the only product by NMR analysis. Absolute yields were not obtained in these latter two solvents.

Solvolysis of 6 in Trifluoroethanol. Mesylate **6** (248 mg) in 10 mL of 0.1 M 2,6-lutidine in trifluoroethanol for 3.75 h at 100 °C gave 170 mg (99%) of **31**;[40] NMR ($CDCl_3$): δ 6.77 (1 H, br d, J = 23 Hz), 4.06 (4 H, quintet, J = 7 Hz), 2.4–1.9 (4 H, m), 1.9–1.5 (4 H, m), 1.32 (6 H, t, J = 7 Hz).

Preparation of 35. Potassium diethyl phosphite was prepared by the dropwise addition of 3.26 g of diethyl phosphite to 0.95 g of potassium in 150 mL of distilled (from sodium) ammonia. The blue color disappeared as the last drops were added. *p*-Iodocumyl alcohol[41] (2.00 g) was added to the solution under nitrogen. The mixture was irradiated in a

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Griffin–Srinivasan photochemical reactor using "350-nm" lamps for 4.5 h. The ammonia was allowed to evaporate under nitrogen, and an aqueous workup with ether extraction followed. The ether extract was dried over $MgSO_4$ and filtered, and the solvent was removed by a rotary evaporator. The final traces of solvent were removed at 0.1 mm, leaving 1.32 g (64%) of **35** as a clear oil. NMR ($CDCl_3$): δ 8.0–7.5 (5 H, m), 4.10 (4 H, quintet, J = 7 Hz), 3.03 (1 H, s), 1.58 (6 H, s), 1.30 (6 H, t, J = 7 Hz).

Preparation of 36. Thionyl chloride (280 mg) was added to 307 mg of **35** at 15 °C. After being stirred for about 30 min at room temperature, the mixture was taken up into ether. The ether was washed with water and dried over $MgSO_4$. After filtration, solvent removal by a rotary evaporator left 270 mg of a mixture of **36** and **37** in a 3.6:1 ratio as determined by NMR. NMR of **36** ($CDCl_3$): δ 8.0–7.5 (5 H, m), 4.13 (4 H, quintet, J = 7 Hz), 1.99 (6 H, s), 1.32 (6 H, t, J = 7 Hz). The elimination product **37** showed olefinic protons at δ 5.45 and 5.18 and a broad singlet (allylic methyl group) at δ 2.17. This mixture was used directly for titrimetric measurement of rate constants.

Mesylate Solvolyses. Kinetic Procedures. Solvolyses of the mesylates in Table I in acetic acid 0.05 M in NaOAc and containing 1% acetic anhdyride were carried out by using the sealed-ampule technique previously described.[42] Reactions were monitored for approximately 2 half-lives. Titrimetric end points were determined potentiometrically by titration with 0.01 M $HClO_4$ in HOAc, and infinity values were determined in duplicate. Correlation coefficients for rate constants were greater than 0.9999. Maximum standard deviations for duplicate runs were ±2% (±1% for α-deuterium isotope effect studies).

Solvolyses of **3**, **4**, and **5** in ethanol were carried out in absolute ethanol containing 0.025 M 2,6-lutidine. The sealed-ampule technique was used, and end points were determined by potentiometric titration of unreacted base with 0.01 M $HClO_4$ in ethanol. The solvolysis of α-phenethyl mesylate[10] in ethanol (no base added) was followed spectrophotometrically by monitoring the absorbance decrease at 221 nm.

Solvolyses of **3**, **5**, **6**, and cyclohexyl mesylate in trifluoroethanol were carried out in distilled trifluoroethanol containing 0.025 M 2,6-lutidine using sealed ampules. At given times, 2-mL aliquots were quenched by dilution with 4 mL of absolute ethanol. End points were determined by potentiometric titration with 0.01 M $HClO_4$ in ethanol. Solvolysis of **4** in trifluoroethanol (0.025 M Et_3N) was followed spectrophotometrically by monitoring the absorbance increase at 243 nm.

Solvolyses in formic acid were carried out in anhydrous formic acid containing 0.05 M sodium formate by using the sealed-ampule technique. At given times, 1-mL aliquots were quenched by dilution with **4** mL of acetic acid. End points were determined by potentiometric titration with 0.01 M $HClO_4$ in HOAc.

Solvolysis of **3** in hexafluoroisopropyl alcohol was carried out in 97% HFIP–3% water containing 0.05 M 2,6-lutidine. At given times, 1-mL aliquots were quenched by dilution with 4 mL of absolute ethanol. End points were potentiometrically determined by titration with 0.01 M $HClO_4$ in ethanol.

Solvolyses in trifluoroacetic acid were carried out with 0.20 M sodium trifluoroacetate in CF_3CO_2H containing 0.5% trifluoroacetic anhydride. Reactions were monitored by NMR spectroscopy. Trifluoroacetolysis of **3** was followed by monitoring the decrease in intensity of the methyl singlet due to the mesylate group as a function of time. The methyl singlet of the byproduct (sodium methanesulfonate) appears 0.17 ppm downfield from the methyl singlet in **3**. Trifluoroacetolysis of **5** and **5**-d_6 were also followed by monitoring the decrease in intensity of the methyl singlet due to the mesylate group. The sodium methanesulfonate methyl singlet appears 0.14 ppm upfield from the methyl singlet in **5**. The first-order plots for trifluoroacetolyses of **5** and **5**-d_6 showed a slight upward curvature over 70% reaction. Correlation coefficients were 0.9998 and 0.9991, respectively. Therefore, the rate constants given in Table I represent "initial" rate constants calculated from data over 32% and 28% reaction for **5** and **5**-d_6, respectively. When all of the data is used to calculate rate constants, the value of k-H_6/k-D_6 (Table III) is 3.06.

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Registry No. 3, 51761-45-6; (+)-**3**, 58166-93-4; (−)-**3**, 85166-94-5; **4**, 85166-79-6; **5**, 51761-43-4; **5**-d_6, 85166-90-1; **6**, 51761-46-7; **7**, 13716-45-5; **8**, 31675-43-1; **9**, 54599-18-7; **10**, 74152-47-9; **11**, 36240-43-4; **12**, 1663-55-4; (+)-**12**, 85185-11-1; (−)-**12**, 85166-92-3; **12**-d_1, 85166-91-2; (+)-**12** (R = $COCH_3$), 85166-96-7; **13**, 34881-11-3; **14**, 6632-88-8; **15**, 42763-00-8; **16**, 85166-80-9; **17**, 85166-81-0; **18**, 85166-82-1; **19** (S = AC), 16153-59-6; **19** (S = CH_2CF_3), 85166-83-2; **19** (S = $COCF_3$), 85166-84-3; (+)-**19** (S = $COCH_3$), 85166-95-6; **22**, 3277-27-8; **26**, 64081-12-5; **27**, 25944-64-3; **28** (S = $COCH_3$), 85166-85-4; **28** (S = Et), 63573-19-3; **28** (S = CH_3), 85166-86-5; **30**, 20170-34-7; **31**, 31651-16-8; **34**, 60514-82-1; **35**, 85166-87-6; **36**, 85166-88-7; **37**, 85166-89-8; EtOH, 64-17-5; CH_3ClO_2S, 124-63-0; CH_3SOCl, 676-85-7; HOAc, 64-19-7; CF_3CH_2OH, 75-89-8; CF_3CO_2H, 76-05-1; $LiEt_3BO$, 22560-16-3; HCO_2H, 64-18-6; HFIP, 29463-77-2; 9-BBN, 280-64-8; diethyl phosphite, 762-04-9; chlorotrimethylsilane, 75-77-4; benzaldehyde, 100-52-7; acetophenone, 98-86-2; acetone, 67-64-1; cyclohexanone, 108-94-1; *m*-chloroperbenzoic acid, 937-14-4; (+)-α-pinene, 7785-70-8; nopol benzyl ether, 74851-17-5; potassium diethyl phosphite, 54058-00-3.

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(43) **Note Added in Proof:** Ingold has suggested the term $E2_{C^+}$ to describe an acid catalyzed alcohol dehydration proceeding via rate limiting proton loss from a cationic intermediate. To avoid duplication of terms, we suggest that this nomenclature be used rather than $E2_{R^+}$. We thank T. T. Tidwell for pointing out this nomenclature of which we were not aware. See: Ingold, C. K. In "Structure and Mechanism in Organic Chemistry", 2nd ed.; Cornell University Press: Ithica, NY, 1969; p 955.