addition of 0.15 equiv of $Eu(fod)_3$ to the NMR sample of **23** in C_6D_6: $\Delta\delta$ 0.07 (H_a), 0.05 (H_b), 0.12 (H_c), 0.46 (H_d, H_e, and H_f), 0.19 (H_g), 0.07 (H_h), 0.06 (H_i and H_j), 0.23 (H_k and H_l), 0.05 (H_m), 0.05 (H_n). These data provided a clear assignment of the resonances due to H_g and H_h. Since H_g is closer to the carbonyl than H_h, the multiplet between δ 2.54 and 2.29 that exhibited the larger shift was assigned to H_g.

The trans,trans stereochemistry assigned to dienone **23** follows from two complementary NOE experiments. In the ^1H NMR spectrum of **23** in C_6D_6 with 0.15 equiv $Eu(fod)_3$ present, the signal for H_f overlaps with the signals for H_d and H_e. However, the signals for H_f, H_g, and H_h are well separated from each other. Since neither H_d or H_e will show an NOE when H_g or H_h is saturated, any enhancement of the H_d–H_e–H_f multiplet under these conditions can be attributed to H_f. Irradiation of H_g has no effect on this multiplet. However, saturation of H_h produces an approximately 50% increase in the intensity of the H_d–H_e–H_f signal. It follows that H_f is trans to H_g and cis to H_h.

3-(Dideuteriomethylene)spiro[5.6]dodeca-1,4,9-triene (32). A solution of **6** (800 mg, 4.59 mmol) in anhydrous ether (35 mL) was treated with a solution of *n*-butyllithium (6.43 mmol) and (trideuteriomethyl)triphenylphosphonium bromide (2.64 g, 7.34 mmol) in ether (100 mL) according to the procedure employed for the preparation of **5** from **6**. Kugelrohr distillation (70 °C, 0.05 mm) of the crude product provided **32** (669 mg, 84% yield) as a colorless liquid. The ^1H and ^{13}C NMR spectra of the distilled product were identical with those of the undeuterated olefin **5** with the following exceptions: ^1H NMR δ ($CDCl_3$) 4.80 ($C{=}CH_2$, absent); ^{13}C NMR δ ($CDCl_3$) 111.3 (exocyclic methylene C, absent).

Pyrolysis of 32. Pyrolysis of **32** was carried out at 450 °C according to the general procedure described above for flash-vacuum pyrolysis. Purification of the crude oil by GLC (10 ft × 0.25 in. 10% FFAP column, 135 °C) gave **32** and *cis,cis*-2-(dideuteriomethylene-5-methylene-7-vinylbicyclo[4.3.0]non-3-ene (**33**) as a colorless oil. The ^1H and ^{13}C NMR spectra of the GLC isolated product **33** were identical with those of the undeuterated hydrocarbon **11** with the following exceptions: ^1H NMR δ ($CDCl_3$) 5.01 and 4.96 (H_c and H_d, absent); ^{13}C NMR δ ($CDCl_3$) 111.5 (C-10, absent).

Acknowledgment. This work was supported by grants from the National Science Foundation (CHE-81-01212 and CHE-8318345). We are grateful to Dr. D. W. Brown for constructive conversations.

Registry No. **5**, 99018-47-0; **6**, 99018-48-1; **7**, 1614-73-9; **8**, 17328-87-9; **9**, 2401-88-9; **10**, 99018-49-2; **11**, 99018-50-5; **21**, 99018-51-6; **22**, 99018-52-7; **23**, 99018-53-8; **32**, 99018-54-9; **33**, 99018-55-0; **35**, 7148-07-4; **36**, 5473-11-0; **37**, 99018-56-1; (trideuteriomethyl)triphenylphosphonium bromide, 1787-44-6; cyclopentanone, 120-92-3; pyrrolidine, 123-75-1; piperidine, 110-89-4; methyl vinyl ketone, 78-94-4; 2,3-dichloro-5,6-dicyano-1,4-benzoquinone, 84-58-2; methyltriphenylphosphonium bromide, 1779-49-3; acrolein, 107-02-8.

The Nature of Cationic Intermediates Derived from α-Thiophosphoryl and α-Thiocarbonyl Mesylates. Neighboring Thiophosphoryl and Thiocarbonyl Participation

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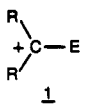
Received August 13, 1985

A series of mesylate derivatives of α-hydroxy thiophosphonates, $RCH(OMs)PS(OEt)_2$ (**8**), have been prepared. These mesylates can react by k_c processes under solvolytic conditions if cation stabilizing groups such as *p*-anisyl or *p*-thioanisyl groups are present. However, under conditions of appropriate electron demand, mesylates **8** can react by k_Δ processes involving thiophosphoryl participation. The cyclic intermediate ions capture acetic acid at phosphorus and lead ultimately to α-thio acetate derivatives of phosphonates. This overall transformation converts the P=S function to the P=O group. Rates of acetolyses of **8** can exceed those of the *O*-phosphoryl analogues by large factors when k_Δ processes are involved (as expected for anchimerically assisted processes). Mesylate derivatives of α-hydroxy thio esters, $R_2C(OMs)CSOCH_3$ (**9**), can also react by k_Δ processes as shown by enhanced rates relative to simple ester analogues. The substrate (*R*)-(−)-$PhCH(OMs)CSOCH_3$ (**38**) gives an acetolysis product that is largely retained, while **9** (R = Me) gave a large fraction of a rearranged product. These data all argue in favor of neighboring thiocarbonyl participation in **8**, giving cyclized intermediate cations. The behavior of mesylates **8** and **9** can therefore be quite different from that of the corresponding *O*-phosphoryl and carbonyl analogues. Neighboring group participation in **8** and **9** accounts for the differences. The contrasting behavior of **8** and **9** also argues *against* neighboring phosphoryl or carbonyl participation in solvolyses of mesylate derivatives of α-hydroxy phosphonates or α-keto mesylates.

Our studies[1] and those of others[2-5] have firmly established the existence of carbocations of general type **1** where the group E is formally electron withdrawing relative to hydrogen. Such intermediates **1** can be generated under



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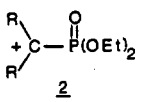

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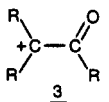

3

(1) For examples of cation **1** where E = $PO(OEt)_2$, see: (a) Creary, X.; Geiger, C. C.; Hilton, K. *J. Am. Chem. Soc.* **1983**, *105*, 2851–2858. (b) Creary, X.; Underiner, T. L. *J. Org. Chem.* **1985**, *50*, 2165–2170. For a discussion of the chemistry of cation **1**, where E = COR, and leading references, see: (c) Creary, X. *Acc. Chem. Res.* **1985**, *18*, 3–8. (d) Creary, X. *J. Am. Chem. Soc.* **1984**, *106*, 5568–5577. (e) Creary, X.; Geiger, C. C. *Ibid.* **1982**, *104*, 4151–4162.

(2) Begue, J.-P.; Charpentier-Morize, M. *Acc. Chem. Res.* **1980**, *13*, 207–212. (b) Charpentier-Morize, M. *Bull. Soc. Chim. Fr.* **1974**, 343–351.

(3) (a) Gassman, P. G.; Tidwell, T. T. *Acc. Chem. Res.* **1983**, *16*, 279–285. (b) Gassman, P. G.; Talley, J. J. *J. Am. Chem. Soc.* **1980**, *102*, 1214–1216; (c) *Ibid.* **1980**, 2138–2143. (d) Gassman, P. G.; Saito, K.; Talley, J. J. *Ibid.* **1980**, 7613–7615. (e) Gassman, P. G.; Guggenheim, T. L. *J. Org. Chem.* **1982**, *47*, 3023–3026.

(4) (a) Tidwell, T. T. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 20–32. (b) Allen, A. D.; Ambridge, I. C.; Che, C.; Micheal, H.; Muir, R. J.; Tidwell, T. T. *J. Am. Chem. Soc.* **1983**, *105*, 2343–2350. (c) Allen, A. D.; Jansen, M. P.; Koshy, K. M.; Mangru, N. N.; Tidwell, T. T. *Ibid.* **1982**, *104*, 207–211. (d) Jansen, M. P.; Koshy, K. M.; Mangru, N. N.; Tidwell, T. T. *Ibid.* **1981**, *103*, 3863–3867.

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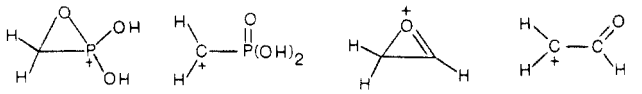
Table I. Product Ratios in Acetolyses of Mesylates 10

substituent	% ArCH(OAc)PS(OEt)$_2$ 18	% ArCH(SAc)PO(OEt)$_2$ 16
p-OCH_3	100	0
p-SCH_3	100	0
3,4-Me_2	17	83
p-Me	13	87
p-H	0	100
m-F	0	100
p-CF_3	0	100

solvolytic conditions as well as by other methods. We have presented evidence for the solvolytic generation of phosphoryl-substituted cations **2**[1a,b] and carbonyl-substituted cations **3**.[1c] Initially surprising was the fact that **2** and **3** could be solvolitically generated quite readily relative to the α-H analogues. The diethyl phosphonate and carbonyl groups did not appreciably slow the rate of formation of carbocations **2** and **3** relative to the α-H analogues despite the presence of these electron-withdrawing groups attached directly to the cationic center.

In an attempt to determine the mode by which **2** derives stabilization, theoretical studies have been carried out.[6] These studies suggest that cyclized ion **4** is substantially



4 **5** **6** **7**

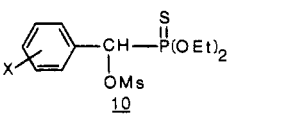
more stable than the open form, **5**. Earlier studies[7] have also suggested that the cyclized ion **6** is favored over the open α-keto cation **7**. Despite these calculations, we have obtained no experimental evidence for the involvement of cyclized forms of **2** and **3**.[8] Indeed, we have suggested[1a] that carbonyl π-conjugation is an important source of stabilization in **3**, while polarization of the large substituent may contribute unexpected stabilization to **2**.[1a] In an attempt to further evaluate the possibility of the intervention of cyclized ions in reactions potentially leading to electron-deficient carbocations, a series of mesylates of general structure **8** and **9** have been prepared. These systems have a neighboring sulfur-containing group. It is also well established[8a,9] that neighboring sulfur in sulfide systems is a very good participating group. In mesylates **8** and **9**, a somewhat different type of sulfur participation

8 **9**

involving the neighboring thiophosphoryl or thiocarbonyl group would lead to the thio analogues of **4** and **6**. We wanted to compare the behavior of these substrates **8** and **9** with the analogous phosphoryl and carbonyl systems to evaluate the importance of cyclized ions as intermediates. Reported here are the results of these studies.

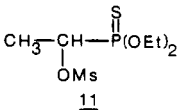
Results and Discussion

Reactions of α-Thiophosphoryl-Substituted Substrates. Mesylates **10** and **11** as well as the trifluoroacetate



10

a X = p-OMe e X = p-H
b X = p-SMe f X = m-F
c X = 3,4-di-CH_3 g X = p-CF_3
d X = p-CH_3



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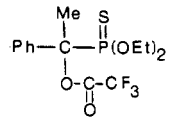
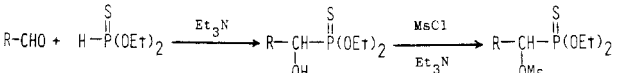


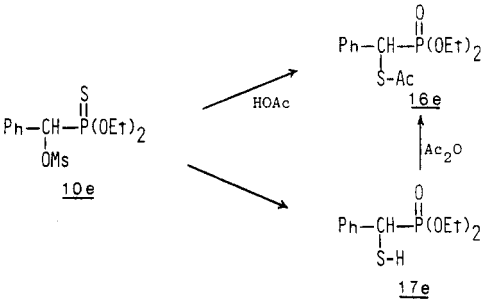
12

12 have been prepared. The triethylamine catalyzed condensation of the appropriate aldehyde, **13**, with diethyl thiophosphonate (**14**) gave the α-hydroxy thiophosphonates **15**,[10] which were converted to the corresponding mesylates in a straightforward fashion. Condensation of acetophenone with **14**, followed by reaction with trifluoroacetic anhydride, gave the trifluoroacetate **12**.



13 **14** **15** **10** and **11**

A summary of products of reaction **10** in acetic acid is given in Table I, while Table II contains rate data. The unsubstituted mesylate **10e** (X = *p*-H) solvolyzed in acetic acid (1% acetic anhydride) to give the product **16e** in



which the sulfur-containing thiophosphoryl group had been converted to the oxygen analogue. The rate of reaction of **10e** was quite solvent-dependent, with large rate increases being observed in more highly ionizing solvents. The *m* value[11] was 0.71. In 70% aqueous acetone, the deacetylated thiol **17e** was the exclusive product formed. Closer examination of the acetolysis of **10e** by ^{31}P NMR showed that the thiol **17e** (^{31}P = 24.7 ppm) is the primary reaction product. Under the reaction conditions, the thiol

(5) For further examples and leading references, see: (a) Liu, K.-T.; Kuo, M.-Y.; Sheu, C. F. *J. Am. Chem. Soc.* **1982**, *104*, 211–215. (b) Takeuchi, K.; Kitagawa, T.; Okamoto, K. *J. Chem. Soc., Chem. Commun.* **1983**, 7. (c) Hopkinson, A. C.; Dao, L. H.; Dupperrouzel, R.; Maleki, M.; Lee-Ruff, E. *Ibid.* **1983**, 727–728. (d) McDonald, R. N.; Tabor, T. E. *J. Am. Chem. Soc.* **1967**, *89*, 6573–6578. (e) McDonald, R. N.; Steppel, R. N. *Ibid.* **1970**, *92*, 5664–5670. (f) Olah, G. A.; Prakash, G. K. S.; Arvanaghi, M. *Ibid.* **1982**, *104*, 1628–1631. (g) Olah, G. A.; Prakash, G. K. S.; Arvanaghi, M.; Krishnamurthy, V. V.; Narang, S. C. *Ibid.* **1984**, *106*, 2378–2380.

(6) Pasto, D. J. *J. Org Chem.* **1985**, *50*, 1014–1018.

(7) Nobes, R. H. Bouma, W. J.; Radom, L. *J. Am. Chem. Soc.* **1983**, *105*, 309–314.

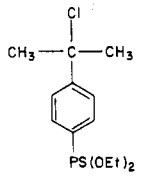
(8) Formation of larger rings by neighboring carbonyl participation is well documented. For leading references, see: (a) Capon, B. *Q. Rev. Chem. Soc.* **1964**, *18*, 45–111. (b) Pasto, D. J.; Serve, M. P. *J. Am. Chem. Soc.* **1965**, *87*, 1515–1521. (c) Ward, R. W.; Sherman, Jr., P. D. *Ibid.* **1968**, *90*, 3812–3817.

(9) For leading references, see: (a) Gunderman, K. D. *Angew. Chem., Int. Ed. Engl.* **1963**, *2*, 674–683. (b) Eliel, E. L.; Knox, D. E. *J. Am. Chem. Soc.* **1985**, *107*, 2946–2952.

(10) This reaction is based on the analogous reaction of diethyl phosphite with aldehydes and ketones. See: (a) Overberger, C. G.; Sarlo, E. *J. Org. Chem.* **1961**, *26*, 4711–4712. (b) Kharasch, M. S.; Mosher, R. A.; Bengelsdorf, I. S. *Ibid.* **1960**, *25*, 1000–1006. (c) Baraldi, P. G.; Guarneri, M.; Moroder, F.; Pollini, G. P.; Simoni, D. *Synthesis* **1982**, 653–655. For a reported base-catalyzed condensation of **14** with ketones, see: (d) Shagidullin, R. R.; Rizpolozhenskii, N. I.; Mukhametov, F. S.; Lipatova, I. P.; Vachugova, L. I. *Bull. Acad. Sci. U.S.S.R. Div. Chem. Sciences* **1972**, *21*, 2728–2730.

(11) This *m* value is based on Y_{OTs} solvent ionizing power values. See: Schadt, F. L.; Bentley, T. W.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1976**, *98*, 7667–7674.

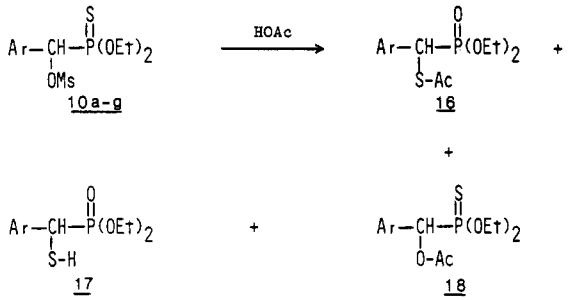
Table II. Solvolysis Rates of Substrates in Various Solvents

substrate	solvent[a]	temp, °C	k, s^{-1}
10a (*p*-MeO)	HOAc	25.0	6.14×10^{-2}
	MeOH	25.0	5.74×10^{-2}
10b (*p*-MeS)	HOAc	25.0	6.63×10^{-3}
	MeOH	25.0	6.17×10^{-3}
10c (3,4-Me_2)	HOAc	25.0	8.95×10^{-5}
10d (*p*-Me)	HOAc	25.0	5.56×10^{-5}
10e (*p*-H)	HOAc	25.0	5.78×10^{-6}
	EtOH	65.0, 45.0, 25.0[b]	1.41×10^{-4}, 1.59×10^{-5}, 1.35×10^{-6}
	TFE	25.0	6.25×10^{-4}
	HCO_2H	25.0	1.65×10^{-3}
	HFIP	25.0	9.21×10^{-3}
10f (*m*-F)	HOAc	65.0, 45.0, 25.0[b]	7.59×10^{-5}, 6.94×10^{-6}, 4.62×10^{-7}
10g (*p*-CF_3)	HOAc	80.0, 60.0, 25.0[b]	1.03×10^{-4}, 1.08×10^{-5}, 1.02×10^{-7}
$CH_3CH(OMs)PS(OEt)_2$ (11)	HOAc	100.0	7.83×10^{-5}
$CH_3CH(OMs)PO(OEt)_2$	HOAc	100.0	7.41×10^{-10} [c,d]
$PhC(OCOCF_3)((Me)PS(OEt)_2)$ (12)	HOAc	100.0	1.92×10^{-4}
	HCO_2H	45.0	6.71×10^{-5}
Ph-$C(OCOCF_3)(Me)PO(OEt)_2$ (55)	HOAc	100.0	1.42×10^{-5}
p-$MeOC_6H_4CH(OMs)PO(OEt)_2$	MeOH	25.0	6.95×10^{-2}
p-$MeSC_6H_4CH(OMs)PO(OEt)_2$	HOAc	25.0	6.96×10^{-3}
p-$CH_3C_6H_4CH(OMs)PO(OEt)_2$	HOAc	65.0, 50.0, 25.0[b]	1.73×10^{-4}, 2.95×10^{-5}, 1.04×10^{-6}
$PhCH(OMs)PO(OEt)_2$	HOAc	25.0[b,c]	3.32×10^{-7}
m-$FC_6H_4CH(OMs)PO(OEt)_2$	HOAc	25.0[b,c]	5.72×10^{-11}
$PhCH(OMs)CSOCH_3$ (38)	HOAc	25.0	3.22×10^{-5}
$PhCH(OMs)COOCH_3$ (40)	HOAc	25.0[b,f]	1.02×10^{-8}
$CH_3C(MsO)(CH_3)CSOCH_3$ (39)	HOAc	25.0	1.28×10^{-5}
$CH_3C(MsO)(CH_3)COOCH_3$ (45)	HOAc	25.0[b,g]	1.57×10^{-9}
 37	EtOH	25.0	3.84×10^{-6}

[a] HOAc: 0.05 M NaOAc in acetic acid containing 1% acetic anhydride. EtOH; 0.025 M 2,6-lutidine in absolute ethanol. MeOH; 10^{-3} M Et_3N in methanol. 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). [b] Extrapolated rate. [c] Reference 1b. [d] Assuming rate of ROTf = 10^5 × rate of ROMs. [e] Reference 1a. [f] Reference 1e. [g] Reference 1d.

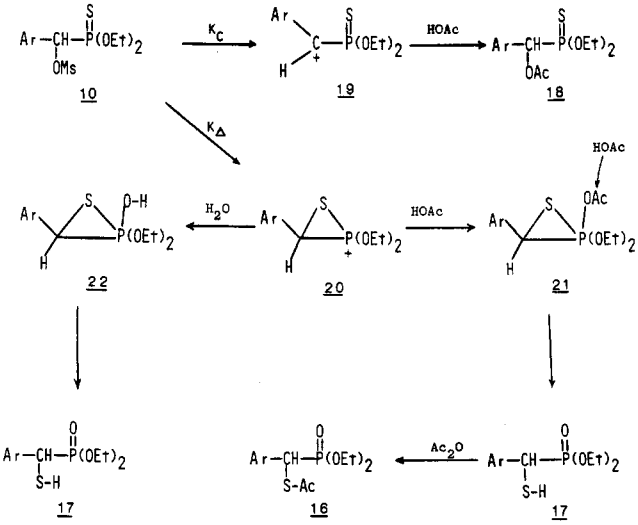
17e is converted to the acetylated product **16e** (^{31}P = 23.3 ppm).

In contrast, the *p*-methoxy and the *p*-(thiomethoxy) substrates **10a** and **10b** gave exclusively the simple unrearranged substitution products **18a** and **18b** on acetolysis. The *p*-methyl substrate **10d** gave a mixture of unrearranged substitution product **18d** (13%) along with the rearranged product **16d** (87%). Smaller amounts of the



thiol **17d** could also be observed at shorter reaction times. As in the case of the unsubstituted thiophosphonate **10e**, completely rearranged products are seen in acetolysis of the electronegatively substituted substrates **10f** and **10g**.[12]

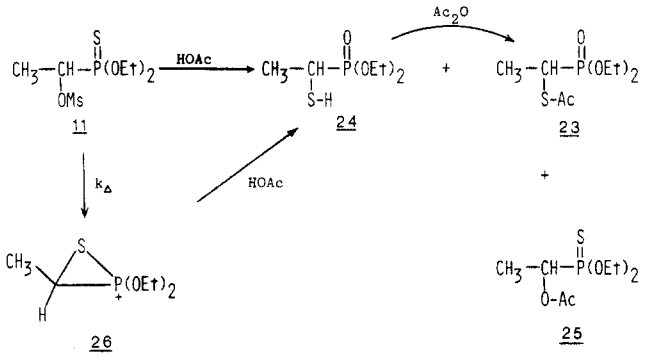
The following scheme is proposed to account for these observed products. The unrearranged acetates **18** are suggested to arise via a k_c process involving the thiophosphoryl substituted cation **19**. In the case of mesylates **10c–g**, a k_Δ process involving neighboring thiophosphoryl participation can compete with the k_c process. In the case of the more electron-withdrawing substituents, the k_Δ process can be the exclusive process. The intermediate cyclized ion **20** is suggested to undergo solvent capture at phosphorus giving **21**. Opening of **21** (an anhydride-like substrate) by nucleophilic attack at the acetyl group would lead to the thiol **17** and acetic anhydride. Acetylation of **17** by the acetic anhydride would give the final product **16**.[13] In the aqueous acetone solvolysis of **10e**, the rear-



(12) In contrast to the clean solvolyses of **10e** in acetic acid and aqueous acetone, solvolyses in alcohol solvents gave a complex product mixture which was not further characterized.

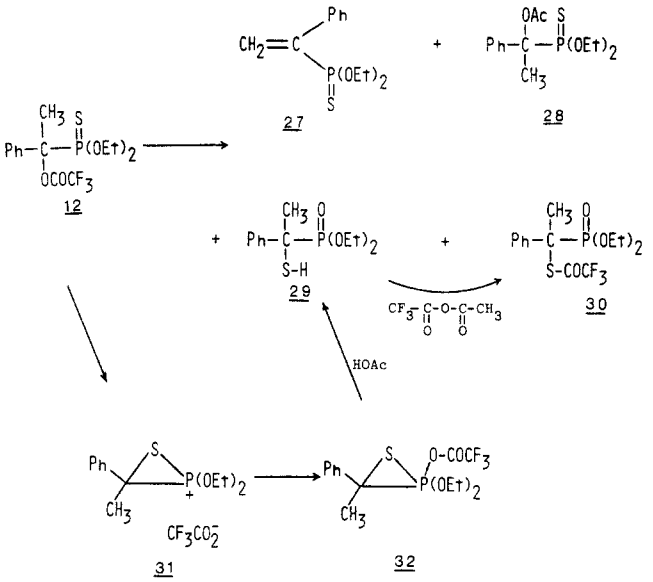
ranged product **17e** can be produced directly from **22**, the product of reaction of **20** with water.

Acetolysis of **11** also gave the rearranged products **23** and **24**, along with a trace of the simple substitution product **25**. The thiol **24** was also formed in the aqueous acetone solvolysis of **11**. These rearranged products are derived from the cyclized ion **26**. A small amount of acetic acid capture at carbon in **26** may account for the formation of **25**. The unrearranged product may also arise from a



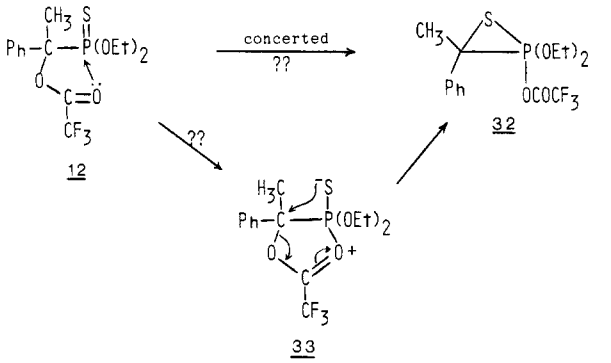
competing k_s process.[14]

Acetolysis of the trifluoroacetate **12** at 100 °C followed a slightly different course. Two unrearranged products, **27** and **28**, were formed in minor amounts, along with the

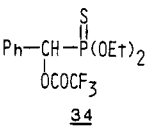


major products **29** and **30**. The minor products **27** and **28** are suggested to arise via proton loss and solvent capture of a k_c derived thiophosphoryl-substituted cation. The major rearranged products **29** and **30** are suggested to be derived from a competing k_Δ produced ion pair, **31**. This ion pair suffers internal return of trifluoroacetate at phosphorus giving **32**, rather than acetic acid capture. Cleavage of **32** with acetic acid would give the thiol **29** and acetic trifluoroacetic anhydride. Trifluoroacetylation of **29** with this mixed anhydride would give the observed major product **30**.

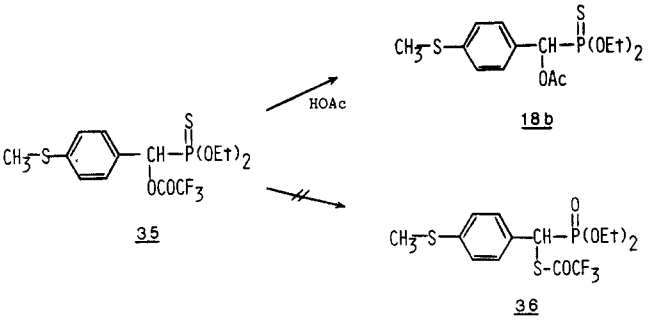
An alternative mechanism that should be considered involves the formation of **32** by nucleophilic attack of the carbonyl group of **12** on phosphorus to give **33**, followed by nucleophilic attack of sulfur on carbon. A conceptually similar mechanism would involve concerted nucleophilic attack of sulfur in **12** on carbon and internal migration of the trifluoroacetate group to give **32** directly. These al-



ternative mechanisms are considered unlikely based on the following data. The rate of reaction of **12** is substantially faster in the more highly ionizing formic acid solvent than in acetic acid. This is consistent with a mechanism involving heterolytic cleavage of the carbon–oxygen bond in **12** forming a cationic intermediate and inconsistent with the concerted mechanism for formation of **32**. Additionally, the analogous trifluoroacetate **34** has been prepared

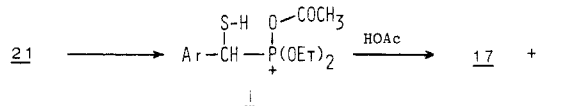


and it solvolyzes in acetic acid at a far slower rate than **12**. This also points to rate-limiting carbon–oxygen bond heterolysis in acetolysis of **12**. The additional methyl substitution in **12** stabilizes the transition state leading to **31**, as expected in a cationic k_Δ process. If the alternative mechanisms operated in acetolysis of **12**, then the unmethylated analogue **33** should have reacted at a comparable or faster rate than **12**. As a final piece of evidence in favor of the ionic pathway for the reaction of **12**, the trifluoroacetate **35** has been prepared and reacted in acetic acid at 100 °C. This substrate gave only the simple acetate substitution product **18b**, presumably via a k_c process as



suggested for the analogous mesylate **10b**. If internal nucleophilic attack of the trifluoroacetate carbonyl group at phosphorus was an important process, then **35** would have given the rearranged thiotrifluoroacetate **36**. This is not seen since carbon–oxygen bond breaking in an ionic process is the favorable process. We therefore have no evidence in favor of the mechanistic alternatives to the suggested ion pair pathway for rearrangement of **12** to **29**. It is suggested that recapture of trifluoroacetate can occur

(13) Alternatively one could envisage opening of **21** to give i and



eventually acetic anhydride. Such an intermediate i could be the source of the acetylated product **16**.

(14) The rapid solvolysis rate of **11** relative to the *O*-phosphoryl analogue argues against a competing k_s process of comparable magnitude to the k_Δ process.

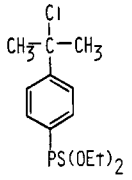
Table III. Comparison of Solvolysis Rates of Thiophosphoryl and Phosphoryl-Substituted Systems

substrate	solvent	$PS(OEt)_2/PO(OEt)_2$ rate ratio
p-$MeOC_6H_4CH(OMs)P(=X)(OEt)_2$	CH_3OH	0.83
p-$MeSC_6H_4CH(OMs)P(=X)(OEt)_2$	HOAc	0.95
p-$CH_3C_6H_4CH(OMs)P(=X)(OEt)_2$	HOAc	53
$PhCH(OMs)P(=X)(OEt)_2$	HOAc	1.53×10^3
m-$FC_6H_4CH(OMs)F(=X)(OEt)_2$	HOAc	8.08×10^3
$CH_3CH(OMs)P(=X)(OEt)_2$	HOAc	1.06×10^5 [a]
$PhC(OCOCF_3)(Me)P(=X)(OEt)_2$	HOAc	13.5

[a] Assuming rate of ROTf = $10^5 \times$ rate of ROMs.

at the phosphorus atom of **31** (or **20**) since this anion is more nucleophilic than mesylate. While undetected internal return of mesylate at phosphorus in **20** may occur, this process would probably be reversible and lead ultimately to **16**. The fact that the major product in the acetolysis of **12** (the thiotrifluoroacetate **30**) is not derived from capture of acetic acid (or acetate ion) implies that one never proceeds much beyond the tight ion pair stage before internal return of trifluoroacetate occurs.

Kinetic Studies on α-Thiophosphoryl-Substituted Substrates. In order to establish the electronic properties of the thiodiethyl phosphonate group, its effect on the solvolysis rate of the substituted cumyl chloride **37** has



37

been measured. The σ^+ value for $PS(OEt)_2$ (determined from the data in Table III) is 0.43, indicating that this group is slightly less electron withdrawing than $PO(OEt)_2$ ($\sigma^+ = 0.50$).[1a] With this in mind, results of kinetic studies on **10–12**, as well as for related substrates, are given in Table II. A comparison of the effect of $PS(OEt)_2$ and $PO(OEt)_2$ attached directly to a potential cationic center has been made in Table III. Mesylates **10a** and **10b**, which are proposed to solvolyze by k_c processes, are quite comparable in reactivity to the phosphoryl analogues which also react by a k_c mechanism. However, the thiophosphoryl substrates **10e**, **10f**, and **11** are all substantially more reactive than the phosphoryl analogues. These direct comparisons suggest that rates of **10e**, **10f**, and **11** are anchimerically assisted as expected in a k_Δ process leading to cyclized ions such as **20**. The rates for **10d** and **12** are also enhanced (but to a much smaller degree) (Table III) relative to their phosphoryl analogues. This is in line with the suggested k_Δ process with a superimposed k_c pathway of smaller magnitude.

Application of the tool of increasing demand[15] also provides conclusive evidence for the onset of thiophosphoryl participation in **10** containing less electron-donating substituents. Examination of a Hammett plott (Figure 1) reveals a sharp break in the plot, characteristic of a mechanistic changeover. The ρ value of −7.15 in the electron-donating region is characteristic of a cation with relatively high electron demand. The substrates **10c** and **10d** fall in the region of mechanistic changeover. This is in line with the mixture of rearranged and unrearranged

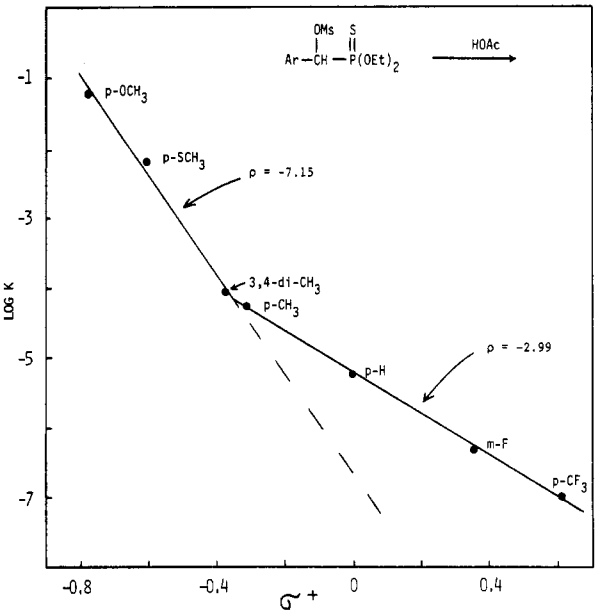
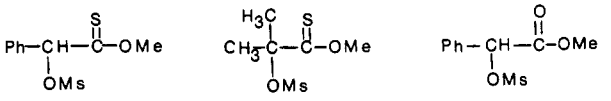


Figure 1. Plot of log k for acetolysis of **10** vs. σ^+.

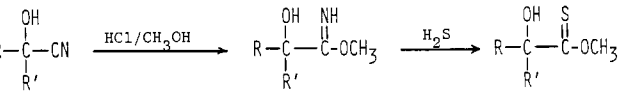
products observed in acetolyses of these two substrates. The substantially lower ρ value of −2.99 for the electronegative substituents is consistent with less demand for aryl stabilization due to the onset of neighboring thiophosphoryl participation. This dramatic break in the Hammett plot, along with the relative reactivity data, as well as the rearranged products in solvolyses of **10c–g**, **11**, and **12** point conclusively to the intervention of cyclized ions **20**, **27**, and **31**.

Reactions of α-Thiocarbonyl-Substituted Substrates. In view of the ability of the thiophosphoryl group to interact in a neighboring group fashion with a developing cationic center, attention was next turned to the thiocarbonyl group. The mesylates **38** and **39** were pre-



38 **39** **40**

pared from the cyanohydrins, mandelonitrile, and acetone cyanohydrin, respectively, by conversion to the imino esters **40**, followed by reaction with H_2S.[16] Reaction of the resultant α-hydroxy thionesters **41** with mesyl chloride–triethylamine gave the desired mesylates.



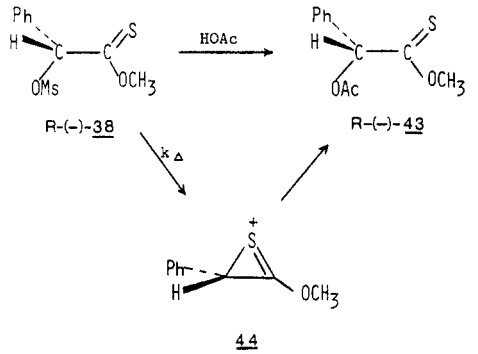
41 **42**

Acetolysis of **38** gave only the substitution product **43**. However, the rate of reaction exceeded that of the simple ester analogue **40** by a factor of 3.2×10^3. This suggested the possibility of neighboring thiocarbonyl participation. Therefore the stereochemistry of this reaction was investigated. (*R*)-(−)-mandelonitrile was converted to (*R*)-(−)-**42** (R = Ph, R′ = H), which was in turn converted to an optically active mesylate (*R*)-(−)-**38**. Acetolysis of (*R*)-(−)-**38** gave an optically active acetate, (*R*)-(−)-**43**, with 54% net retention. It is therefore suggested, on the basis of the

(15) For the classic example of the onset of a k_Δ process as a result of increasing electron demand, see: (a) Gassman, P. G.; Fentiman, A. F., Jr. *J. Am. Chem. Soc.* **1970**, *92*, 2549–2551. See also: (b) Brown, H. C. "The Nonclassical Ion Problem"; Plenum Press: New York, 1977.

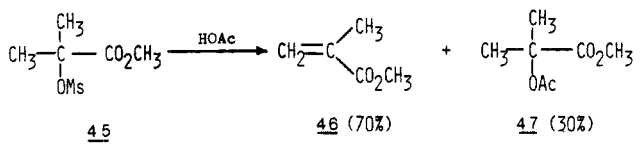
(16) For leading references on the preparation of thion esters from imino esters and hydrogen sulfide, see: Reid, E. E. "Organic Chemistry of Bivalent Sulfur"; Chemical Publishing Co., Inc.: New York, 1962. For a procedure related to the preparation of **42**, see: Vinkler, P.; Thimm, K.; Voss, J. *Justus Liebigs Ann. Chem.* **1976**, 2083–2093.

rate and stereochemical data, that **38** solvolyzes via a k_Δ process giving the cyclic intermediate **44**. Opening of **44**

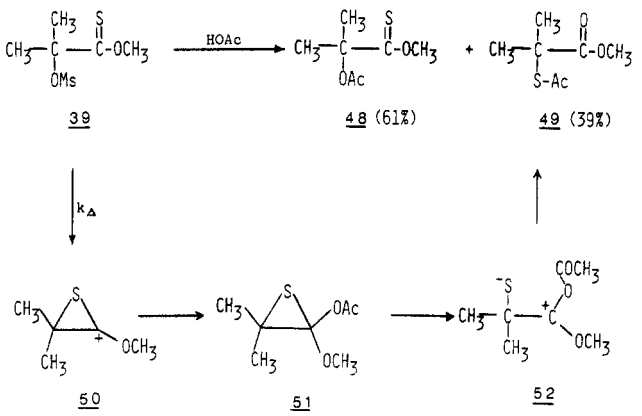


with inversion at carbon accounts for the net retention observed in this reaction. It is uncertain why the reaction is not completely stereospecific since (*R*)-(−)-**43** is optically stable in acetic acid under the reaction conditions. Partial racemization of the α-hydroxy thionester **42** (or the mesylate **38**) may have occurred under the conditions used to prepared (*R*)-(−)-**38**.[17]

Acetolysis of mesylate **39** strongly contrasted with that of the simple ester analogue **45**. The thio ester **39** was much more reactive (8.2×10^3) than the ester **45**. Acetolysis of **45** gave mainly the elimination product **46** by

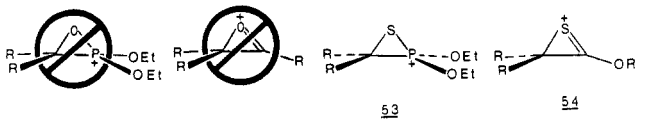


proton loss at an ion pair stage.[1c] However, the thio analogue **39** gave the simple substitution product **48** (61%) as well as the rearranged product **49** (39%). No trace of elimination product is seen in acetolysis of **39**. On the basis of the enhanced rate of **39** relative to the simple ester analogue **45**, the formation of the rearranged product **49**,



and the lack of elimination product from **39**, a k_Δ process is also suggested for acetolysis of **39**. Solvent capture of the intermediate ion **50** can occur at the tetracoordinate carbon with ring opening to give the substitution product **48**. Alternatively solvent capture at the trigonal carbon of **50** followed by ring opening and acetyl group transfer would give the rearranged product **49**. No rearranged products are formed from the cyclic ion **44** suggesting that the tetracoordinate ring carbon in **44** is more prone to nucleophilic attack than the comparable carbon in **50**. This may represent a steric phenomenon or may reflect a greater propensity for solvent attack at a benzylic carbon.

Summary and Conclusions. The thiophosphoryl-substituted mesylates **10a,b** solvolyze by k_c mechanisms. However, when substituents are less electron donating than *p*-methoxy and *p*-(thiomethoxy), k_Δ processes involving cyclic ions **20** can begin to compete. This is supported by the observation of structurally rearranged products, large rate enhancements relative to the phosphoryl analogues, and a sharp break in a Hammett plot. Mesylate **11** and trifluoroacetate **12** also react by a k_Δ pathway involving cyclized ions **27** and **31**. The thiocarbonyl-substituted mesylates **38** and **39** also react by way of cyclized cations **44** and **50**, respectively. Rate enhancements relative to the simple ester analogues, the formation of a product with net retention of configuration, and the observation of a structurally rearranged product from **12** support this conclusion. The behavior of thiophosphoryl- and thiocarbonyl-substituted mesylates is therefore substantially different in terms of rates, stereochemistry, and products formed from that of the analogous phosphoryl and carbonyl analogues. The involvement of cyclized ions from thiophosphoryl and thiocarbonyl substrates provides a viable explanation. The contrasting behavior of α-keto mesylates and mesylate derivatives of α-hydroxyphosphonates provides further evidence for the *lack of* such intermediates in solvolytic reactions of these latter substrates. The ease of formation of sulfur-containing three membered ring systems, relative to the oxygen analogues, provides a rational for the facile formation of ions such as **53** and **54** in contrast to their oxygen analogues.



Experimental Section

Gas Chromatographic analyses were carried out on a Hewlett-Packard 5750 chromatograph with flame ionization detector using a 6 ft 5% SE-30 on Chromosorb G column. A Varian 920 chromatograph was used for sample isolation. NMR spectra were recorded on a Varian EM 390, a MagnaChem A-200, or a Nicolet NB 300 spectrometer. Infrared spectra were recorded on a Perkin-Elmer 727B spectrometer. Titrations were carried out on a Metrohm E576 automatic recording titrator. Optical Rotations were obtained on a Rudolph Autopol III automatic polarimeter.

Reaction of Aromatic Aldehydes with Diethyl Hydrogen Thiophosphonate. General Procedure. A mixture of the appropriately substituted benzaldehyde (1.0 equiv), $HPS(OEt)_2$ (1.0 equiv), and triethylamine (0.2–0.4 equiv) was heated at 55–60 °C for 2 h. The reactions were monitored by NMR to ensure complete reaction. On completion of the reaction, the Et_3N catalyst was removed by evacuation of the flask with stirring at 0.1 mm. The solid products were slurried with pentane and collected. The products which did not crystallize were used as oils and directly converted to the mesylates. Yields ranged from 97% to 100%. The following procedure is typical.

A mixture of 1.34 g of freshly distilled benzaldehyde, 1.95 g of diethyl hydrogen thiophosphonate,[18] and 0.34 g of triethylamine was heated with stirring in a stoppered flask at 55–60 °C for 2 h. The Et_3N was removed under vacuum and the residue was cooled in a freezer. The solid which crystallized was slurried with Skelly F and collected to give 3.20 g (97%) of the α-hydroxy thiophosphonate **15** (R = Ph), mp 37–39 °C. NMR ($CDCl_3$) δ 7.6–7.2 (5 H, m), 4.95 (1 H, d, J = 8 Hz), 4.4–3.6 (4 H, m), 3.42 (1 H, br s), 1.27 (3 H, t, J = 7 Hz), 1.09 (3 H, t, J = 7 Hz). Anal.

(17) The optical purity of (*R*)-(−)-**42** and (*R*)-(−)-**38** was not determined. The fact that two preparations of (*R*)-(−)-**42** in pyridine gave products of differing rotations suggests that racemization can be a facile process in these systems. The related system (*R*)-(−)-**43** readily racemizes in pyridine. See the experimental section.

(18) Pelchowicz, Z. *J. Chem. Soc.* **1961**, 241–243.

Calcd for $C_{11}H_{17}O_3PS$: C, 50.76; H, 6.58. Found: C, 50.55; H, 6.39.

Reaction of Acetaldehyde with Diethyl Hydrogen Thiophosphonate. A mixture of 3.00 g of $HPS(OEt)_2$ and 5 g of acetaldehyde was cooled in an ice bath and 0.50 g of Et_3N was added dropwise. The mixture was stirred at room temperature in a stoppered flask for 18 h. The excess acetaldehyde and Et_3N were removed under aspirator pressure, and the residue was distilled to give 3.50 g (91%) of **15** (R = CH_3), bp 59–60 °C (0.07 mm). NMR ($CDCl_3$) δ 4.35–4.05 (4 H, m), 3.98 (1 H, q, J = 7 Hz), 3.90 (1 H, br s), 1.42 (3 H, d of d, J = 19, 7 Hz), 1.33 (6 H, t, J = 7 Hz).

Reaction of Acetophenone with Diethyl Hydrogen Thiophosphonate. A mixture of 1.20 g of acetophenone and 1.61 g of $HPS(OEt)_2$ was heated with 0.50 g of Et_3N at 60–65 °C for 24 h. The reaction was periodically monitored by NMR which after 24 h, showed a 1:1 equilibrium mixture of acetophenone and the product diethyl (1-phenyl-1-hydroxyethyl)thiophosphonate. The flask was heated at 60 °C and evacuated at 0.05 mmHg to remove the unreacted triethylamine and starting materials. The crude product weighed 1.30 g (47%) and was converted without purification to the trifluoroacetate. NMR ($CDCl_3$) δ 7.8–7.2 (5 H, m), 4.3–3.8, (4 H, m), 3.37, (1 H, br s), 1.80 (3 H, d, J = 17 Hz), 1.24 (3 H, t, J = 7 Hz), 1.17 (3 H, t, J = 7 Hz).

Preparation of Mesylates 10. General Procedure. The appropriate α-hydroxy thiophosphonate **15** was dissolved in 20 parts of methylene chloride at −30 to −40 °C and 1.8–2.0 equiv of methanesulfonyl chloride was added Triethylamine (2.0–2.3 equiv) was added dropwise to the mixture which was then allowed to warm to 0 °C. The mixture was taken up into ether, washed with water, dilute HCl, and saturated NaCl solution, and dried over $MgSO_4$. The solvents were removed by rotary evaporator leaving the mesylates **10**. Yields of crude products ranged from 95% to 100%. The following procedure is typical.

A solution of 255 mg of **15** (R = p-$CF_3C_6H_4$) and 134 mg of CH_3SO_2Cl in 10 mL of CH_2Cl_2 was cooled to −40 °C and 139 mg of Et_3N was added dropwise. After warming to 0 °C, a workup as described above followed. Solvent removal using a rotary evaporator left 318 mg of crude **10g** (Ar = p-$CF_3C_6H_4$). On cooling in a freezer, the product crystallized. The solid was slurried with cold Skelly F and collected giving 273 mg (86%) of **10g** (Ar = p-$CF_3C_6H_4$), mp 65–67 °C. NMR ($CDCl_3$) δ 7.68 (4 H, s), 5.83 (1 H, d, J = 13 Hz), 4.4–3.8 (4 H, m), 2.98, (3 H, s), 1.29 (3 H, t, J = 8 Hz), 1.21 (3 H, t, J = 8 Hz). Anal. Calcd for $C_{13}H_{18}F_3PO_5S_2$: C, 38.42; H, 4.46. Found: C, 38.06, H, 4.23.

Preparation of Mesylate 11. By use of the procedure described for the preparation of **10**, reaction of 2.45 g of **15** (R = CH_3) and 2.60 g of CH_3SO_2Cl in 40 mL of CH_2Cl_2 with 2.80 g of Et_3N at −40 °C gave 3.19 g (93%) of mesylate **11** as a clear oil. NMR ($CDCl_3$) δ 4.91 (1 H, pentuplet, J = 7 Hz), 4.35–4.05 (4 H, m), 3.12 (3 H, s), 1.64 (3 H, d of d, J = 18, 7 Hz), 1.34 (6 H, t, J = 7 Hz). Anal. Calcd for $C_7H_{17}O_5PS_2$: C, 30.43; H, 6.20. Found: C, 30.26; H, 5.94.

Preparation of Trifluoroacetate 12. A solution of 1.00 g of diethyl(1-phenyl-1-hydroxyethyl)thiophosphonate in 6 mL of pyridine was cooled in an ice bath as 1.80 g of trifluoroacetic anhydride was added dropwise. The mixture was stirred at room temperature for 2 h and then taken up into 15 mL of ether and 15 mL of Skelly F. The mixture was washed with cold water, cold 10% HCl, and saturated NaCl solution, and dried over $MgSO_4$. The solvents were removed using a rotary evaporator and the residue was distilled to give 1.20 g (89%) of **12**, bp 94–97 °C (0.025 mm). NMR ($CDCl_3$) δ 7.38 (5 H, br s), 4.3–3.8 (4 H, m), 2.27 (3 H, d, J = 17 Hz), 1.25 (3 H, t, J = 7 Hz), 1.23 (3 H, J = 7 Hz). Anal. Calcd for $C_{14}H_{18}F_3O_4PS$: C, 45.41; H, 4.90. Found: C, 44.89; H, 4.84.

Preparation of Trifluoroacetate 55. By use of a procedure analogous to the preparation of **12**, reaction of 0.54 g of diethyl(1-phenyl-1-hydroxyethyl)phosphonate[1a] in 3 mL of pyridine with 0.65 g of trifluoroacetic anhydride gave 0.70 g (94%) of **55**, bp 85–86 °C (0.02 mm). NMR ($CDCl_3$) δ 7.5–7.3 (5 H, m), 42–3.9 (4 H, m), 2.253 (3 H, d, J = 15 Hz), 1.255 (3 H, t, J = 7 Hz), 1.242 (3 H, t, J = 7 Hz).

Preparation of Trifluoroacetate 35. By use of a procedure analogous to the preparation of **12**, reaction of 0.38 g of **15** (R = p-$CH_3SC_6H_4$) in 5 mL of pyridine with 0.54 g of trifluoroacetic anhydride gave 0.52 g (100%) of **35**. NMR ($CDCl_3$) δ 7.6–7.2 (4 H, AA'BB' quartet), 6.23 (1 H, d, J = 10 Hz), 4.4–3.8 (4 H, m), 2.48 (3 H, s), 1.24 (3 H, t, J = 7 Hz), 1.21 (3 H, t, J = 7 Hz).

Preparation of 37.[19] Potassium diethyl thiophosphite was prepared by the dropwise addition of 2.70 g of $HPS(OEt)_2$ to a solution of 0.60 g of potassium on 180 mL of distilled (from sodium) ammonia. The blue color disappeared as the last drops of $HPS(OEt)_2$ were added. p-Iodocumyl alcohol (2.69 g) was added to the solution under nitrogen. The clear solution was irradiated in a Griffin-Srinivasan photochemical reactor using "350-nm" lamps for 5.5 h. Periodically, the frost was removed from the flask. The ammonia was allowed to evaporate and an aqueous workup with ether extraction followed. The ether extract was dried over $MgSO_4$ and the solvent was removed by using a rotary evaporator. The residue (2.70 g) which consisted of a mixture of p-iodocumyl alcohol, cumyl alcohol, and p-(diethylthiophosphono)cumyl alcohol, was chromatographed on 30 g of silica gel and eluted with increasing amounts of ether in Skelly F. Cumyl alcohol eluted first (with 95% Skelly–5% ether) followed by a mixture of cumyl alcohol and p-iodocumyl alcohol. Next a mixture of p-iodocumyl alcohol and p-(diethylthiophoshono)cumyl alcohol eluted as the amount of ether was increased to 25%. Finally 1.02 g (34%) of p-(diethylthiophosphono)cumyl alcohol eluted as a clear oil with 25% ether. NMR ($CDCl_3$) δ 8.06–7.55 (4 H, m), 4.3–4.0 (4 H, m), 1.75 (1 H, br s), 1.60 (6 H, s), 1.32 (6 H, t, J = 7 Hz).

Thionyl chloride (1.20 g) was added to 0.55 g of p-(diethylthiophosphono)cumyl alcohol at 0 °C. The mixture was stirred at room temperature for 20 min and excess $SOCl_2$ was removed under aspirator pressure. The residue was taken up into ether, washed with cold water and saturated NaCl solution, and dried over $MgSO_4$. The solvent was removed by using a rotary evaporator leaving 0.57 g (100%) of **37** as a clear oil. NMR ($CDCl_3$) δ 8.1–7.6 (4 H, m), 4.3–3.9 (4 H, m), 2.00 (6 H, s), 1.30 (6 H, t, J = 7 Hz).

Preparation of PhCH(OH)CSOMe (42, R = Ph; R′ = H). A solution of 1.315 g of mandelonitrile and 2.00 g of methanol in 35 mL of anhydrous ether was cooled in an ice bath and HCl gas was bubbled into the solution for 15 min. The flask was stoppered and kept at room temperature for 16 h. The solvent was then removed by using a rotary evaporator and the residue was dissolved in 35 mL of pyridine. The mixture was cooled in an ice bath, and H_2S gas was bubbled into the solution for 1 h. After being stirred at room temperature for 5 h, the mixture was taken up into ether and washed with 2 portions of water, 10% HCl solution, and saturated NaCl solution and dried over $MgSO_4$. The solvent was removed by using a rotary evaporator, leaving 1.03 g of a mixture consisting of 3 parts of **42** (R = Ph, R′ = H) and 1 part methyl mandelate. This mixture was chromatographed on 20 g of silica gel and eluted with 95% Skelly F–5% ether. The thio ester eluted immediately, giving 0.721 g (40%) of pure **42** (R = Ph, R′ = H). NMR ($CDCl_3$) δ 7.7–7.3 (5 H, m), 5.22 (1 H, d, J = 6 Hz), 4.28 (1 H, d, J = 6 Hz), 4.16 (3 H, s). Anal. Calcd for $C_9H_{10}O_2S$; C, 59.32; H, 5.53. Found; C, 59.50; H, 5.18.

Preparation of (*R*)-(−)-PhCH(OH)CSOMe (42). This alcohol was prepared by using a procedure analogous to that used to prepare the racemic **42** (R = Ph, R′ = H) but starting with (*R*)-(−)-mandelonitrile.[20] (*R*)-(−)-PhCH(OH)CSOMe was chromatographed to remove the methyl mandelate impurity. One preparation of (*R*)-(−)-**42** gave $[\alpha]^{24}_D$ −70.3° (c 1.5, CH_2Cl_2). A second preparation of (*R*)-(−)-**42** gave $[\alpha]^{24}_D$ −52.4° (c 3, CH_2Cl_2).

Preparation of Mesylate 38. A solution of 0.52 g of **42** (R = Ph, R′ = H) and 0.63 g of mesyl chloride in 20 mL of CH_2Cl_2 was cooled to −30 °C and 0.65 g of Et_3N was added dropwise. After warming to 0 °C, a standard workup as described above followed. Solvent removal using a rotary evaporator gave 0.73 g (98%) of mesylate **38** as an oil. NMR of **38** ($CDCl_3$) δ 7.7–7.3 (5 H, m), 6.20 (1 H, s), 4.12 (3 H, s), 2.97 (3 H, s).

Preparation of Mesylate (*R*)-(−)-38. This mesylate was prepared from (*R*)-(−)-**42** by using a procedure analogous to that used to prepare the racemic **38**. In the preparation from (*R*)-(−)-**42**

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with $[\alpha]^{24}_D$ −70.3°, (*R*)-(−)-**38** had $[\alpha]^{24}_D$ −22.5° (*c* 1.5, CH_2Cl_2). In the preparation from (*R*)-(−)-**42** with $[\alpha]^{24}_D$ −52.4°, (*R*)-(−)-**38** had $[\alpha]^{24}_D$ −15.9° (*c* 4, CH_2Cl_2).

Preparation of $Me_2C(OH)CSOMe$ (42, R = R′ = Me). A solution of 4.20 g of acetone cyanohydrin and 10 g of methanol in 50 mL of anhydrous ether was cooled in an ice bath under nitrogen and HCl gas was bubbled through the solution for 30 min. After it was allowed to stand at room temperature for 16 h, the solvent was removed by using a rotary evaporator. The solid residue was suspended in 50 mL of ether and cooled in an ice bath, and a solution of 13.2 g of Na_2CO_3 in water was added dropwise. After stirring for 15 min, the ether phase was dried over $MgSO_4$. Solvent removal using a rotary evaporator gave 2.70 g of a mixture of imino ester (90–95%) and methyl α-hydroxyisobutyrate (5–10%).

The mixture obtained above was dissolved in 50 mL of ether and H_2S gas was bubbled into the solution for 50 min. After the mixture was stirred for 2 h at room temperature, 20 mL of cold water was added and the ether phase was separated. After being dried over $MgSO_4$, the solvent was removed by using a rotary evaporator and the residue was distilled to give 1.00 g (15%) of **42** (R = R′ = Me), bp 43–45 °C (15 mm). The product contained about 3% of methyl α-hydroxyisobutyrate which could be removed by silica gel chromatography using Skelly F–ether (95/5) as an eluent. NMR ($CDCl_3$) δ 4.18 (3 H, s), 3.96 (1 H, s), 1.45 (6 H, s). Anal. Calcd for $C_5H_{10}O_2S$: C, 44.75; H, 7.51. Found: C, 44.12; H, 7.25.

Preparation of Mesylate 39. A solution of 0.417 g of **42** (R = R′ = Me) and 0.72 g of Et_3N in 10 mL of CH_2Cl_2 was cooled to 0 °C and 0.71 g of mesyl chloride was added dropwise. After 30 min at 0 °C, a standard aqueous workup followed as described above. Solvent removal using a rotary evaporator gave mesylate **39** contaminated with about 20% unreacted **42** (R = R′ = Me). The crude product was evacuated at 0.05 mm to remove the unreacted **42** leaving 0.350 g (53%) of **39** as an oil. NMR of **39** ($CDCl_3$) δ 4.17 (3 H, s), 3.06 (3 H, s), 1.82 (6 H, s).

Solvolyses of Mesylates in HOAc. General Procedures. The appropriate mesylate **10** was heated in a sealed tube in carefully dried HOAc containing approximately 1.3 equiv of NaOAc and 1% acetic anhydride for more than 10 half-lives. The contents of the tube were taken up into ether, washed with water, Na_2CO_3 or $NaHCO_3$ solution, and saturated NaCl solution, and dried over $MgSO_4$. After solvent removal using a rotary evaporator, the products were characterized by standard spectral methods. Details of specific solvolyses are given below.

Acetolysis of 10a (Ar = *p*-$MeOC_6H_4$). Reaction of 0.31 g of **10a** in 22 mL of HOAc for 30 min at room temperature gave 0.28 g (100%) of acetate **18a** as the only product. NMR ($CDCl_3$) δ 7.6–6.8 (4 H, AA′BB′ quartet), 6.19 (1 H, d, *J* = 11 Hz), 4.4–3.8 (4 H, m), 3.80 (3 H, s), 2.14 (3 H, s), 1.23 (3 H, t, *J* = 7 Hz), 1.16 (3 H, t, *J* = 7 Hz).

Acetolysis of 10d (Ar = *p*-MeC_6H_4). Reaction of 230 mg of **10d** in 16 mL of HOAc for 3 h at 50 °C and a workup as described above gave 205 mg of a mixture of **16d**, **17d**, and **18d**. Samples of **16d** and **18d** were isolated by silica gel chromatography (which did not completely separate **17d**). A pure sample of **17d** was isolated by gas chromatography. NMR, 300 MHz, of **16d** ($CDCl_3$) δ 7.4–7.1 (4 H, AA′BB′ quartet), 6.172 (1 H, d, *J* = 10.4 Hz), 4.2–3.8 (4 H, m), 2.338 (3 H, d, *J* = 1.6 Hz), 2.169 (3 H, s), 1.265 (3 H, t, *J* = 7.0 Hz), 1.198 (3 H, t, *J* = 7.0 Hz). This product was identical with a sample of **16d** produced by acetylation of **15** (R = *p*-MeC_6H_4) with acetic anhydride in pyridine. NMR, 300 MHz, of **18d** ($CDCl_3$) δ 7.36–7.08 (4 H, AA′BB′ quartet), 4.931 (1 H, d, *J* = 20.6 Hz), 4.2–3.7 (4 H, m), 2.342 (3 H, s), 2.313 (3 H, d, *J* = 1 Hz), 1.285 (3 H, t, *J* = 7.1 Hz), 1.136 (3 H, t, *J* = 7.1 Hz). NMR, 300 MHz, of **17d** ($CDCl_3$) δ 7.36–7.11 (4 H, AA′BB′ quartet), 4.24–3.75 (5 H, m), 2.606 (1 H, d of d, *J* = 10.6, 8.1 Hz), 2.332 (3 H, d, *J* = 1.6 Hz), 1.324 (3 H, doublet of triplets, *J* = 7.1, 0.6 Hz), 1.153 (3 H, doublet of triplets, *J* = 7.1, 0.6 Hz).

In a different run, acetolysis of 32 mg of **10d** in 0.7 mL of HOAc was followed by a rapid aqueous workup using $NaHCO_3$ to neutralize the acetic acid. Careful drying with $MgSO_4$ gave, after solvent removal, a mixture of **16d** and **18d** with no **17d**. The ratio of **16d** to **18d** was 13:87 as determined by 300-MHz NMR.

Acetolysis of 10e (Ar = C_6H_5). Reaction of 0.80 g of **10e** in HOAc for 24 h at 50 °C gave, after an aqueous workup using $NaHCO_3$, 0.75 g of the thioacetate **18e** as the only product. A separate experiment gave about 50% of the thiol **17e** along with the acetylated product **18e**. ^1H NMR of **18e** ($CDCl_3$) δ 7.5–7.2 (5 H, m), 4.97 (1 H, d, *J* = 21 Hz), 4.2–3.7 (4 H, m), 2.33 (3 H, s), 1.287 (3 H, t, *J* = 7.1 Hz), 1.120 (3 H, t, *J* = 7.1 Hz); ^{13}C NMR of **18e** ($CDCl_3$) δ 192.171, 135.281, 129.291 (d, *J* = 6 Hz), 128.535, 127.934, 63.483 (d, *J* = 7 Hz), 63.248 (d, *J* = 7 Hz), 42.959 (CH, d, *J* = 150 Hz), 29.992, 16.341 (d, *J* = 6 Hz), 16.144 (d, *J* = 6 Hz); IR of **18e** (CCl_4) 1707 cm^{-1}; ^1H NMR of **17e** ($CDCl_3$) δ 7.5–7.2 (5 H, m), 4.3–3.7 (5 H, m), 2.644 (1 H, d of d, *J* = 11, 8.3 Hz, exchanges with D_2O), 1.325 (3 H, t, *J* = 7.1 Hz), 1.126 (3 H, t, *J* = 7.1 Hz); ^{13}C NMR of **17e** ($CDCl_3$) δ 136.47, 128.74, 128.57, 127.95, 63.65 (d, *J* = 7 Hz), 63.50 (d, *J* = 7 Hz), 38.59, (CH, d, *J* = 146 Hz), 16.43 (d, *J* = 6 Hz), 16.21 (d, *J* = 6 Hz).

A separate reaction of **10e** in HOAc (0.05 M NaOAc and 1% acetic anhydride) was monitored by ^{31}P NMR. The ^{31}P signal for **10e** in acetic acid appears at δ 84.8. After 26 min at 60 °C, the spectrum showed new signals at δ 24.7 and 23.4 in a 10:1 ratio. These signals was identified as thiol **17e** and thioacetate **16e**, respectively, by comparison of chemical shifts with authentic samples. Continued heating led to complete disappearance of the signal at δ 84.8. The signal at δ 24.7 (**17e**) eventually began to decrease while the signal at δ 23.4 (**16e**) increased. Prolonged heating led to complete conversion of the signal at δ 24.7 to the signal at 23.4. A control experiment showed that treatment of an authentic sample of **17e** (produced in the aqueous acetone solvolysis described below) with acetic anhydride in acetic acid led to the disappearance of the signal at δ 24.7 and formation of a signal at δ 23.4.

Acetolysis of 10g (Ar = *p*-$CF_3C_6H_4$). Reaction of 160 mg of **10g** in 11 mL of HOAc for 19 h at 80 °C gave, after an aqueous workup using Na_2CO_3, 130 mg of **18g**. A trace of **17g** was also present in the crude mixture. NMR of **18g** ($CDCl_3$) δ 7.61 (4 H, s), 5.02 (1 H, d, *J* = 21 Hz), 4.4–3.7 (4 H, m), 2.36 (3 H, s), 1.29 (3 H, t, *J* = 7 Hz), 1.14 (3 H, t, *J* = 7 Hz).

Solvolysis of 10e (Ar = C_6H_5) in Aqueous Acetone. A solution of 135 mg of **10e** and 86 mg of 2,6-lutidine in 10 mL of 70:30 acetone/water (by volume) was heated at 60 °C for 16 h. The acetone was removed by using a rotary evaporator and the residue was taken up into ether and washed with dilute HCl and saturated NaCl solution. After being dried over $MgSO_4$, the solvent was removed by using a rotary evaporator leaving 99 mg (95%) of **17e**, which was identical with the sample described above.

Acetolysis of Mesylate 11. A solution of 326 mg of **11** in 13 mL of HOAc (0.10 M NaOAc) was heated in a sealed tube at 125 °C for 5 h. After a standard workup as described above, with $NaHCO_3$ washing, distillation gave 148 mg (49%) of a mixture of **23** and **25** bp 80–82 °C (0.05 mm) in a 12.6:1 ratio as determined by NMR. Samples of each product were isolated by preparative G.C. NMR of **23** ($CDCl_3$) δ 4.21–4.08 (4 H, m), 3.843 (1 H, doublet of quartets, *J* = 17.4, 7.4 Hz), 2.376 (d, *J* = 0.6 Hz), 1.501 (3 H, d of d, *J* = 16.8, 7.4 Hz), 1.326 (6 H, t, *J* = 7.1 Hz). NMR of **25** ($CDCl_3$) δ 5.319 (1 H, doublet of quartets, *J* = 5.5, 7.0 Hz), 4.28–4.07 (4 H, m), 2.121 (3 H, s), 1.461 (3 H, doublet of doublets, *J* = 18.5, 7.0 Hz), 1.313 (3 H, t, *J* = 7.1 Hz), 1.302 (3 H, t, *J* = 7.1 Hz). This product was identical with a sample of **25** produced by acetylation of **15** (R = CH_3) with acetic anhydride in pyridine.

In a separate run, the reaction of **11** at 125 °C in CD_3CO_2D (commercial material which was not further dried) was monitored by NMR. The major product formed was the thiol **24**-d_1 (6 parts), along with a smaller amount of **23**-d_3 (1 part) and a trace of **25**-d_3.

Reaction of 110 mg of **11** in 10 mL of 70:30 vol/vol aqueous acetone for 2 days at 120–125 °C gave, after acetone removal using a rotary evaporator and a standard aqueous workup, 70 mg (89%) of **24**. NMR of **24** ($CDCl_3$) δ 4.26–4.13 (4 H, m), 3.05–2.84 (1 H, m), 2.051 (1 H, d of d, *J* = 8.3, 7.7 Hz), 1.531 (3 H, d of d, *J* = 17.1, 7.3 Hz), 1.354 (6 H, t, *J* = 7.1 Hz).

Acetolysis of Trifluoroacetate 12. Reaction of 265 mg of **12** in 20 mL of HOAc at 100 °C for 16 h gave 239 mg of a mixture of **27**, **28**, **29**, and **30** in a 10:1:30:70 ratio, respectively, as determined by 300-MHz NMR. Samples of each product were isolated by preparative GC. NMR of **27** ($CDCl_3$) δ 7.53–7.46 (2 H, m), 7.37–7.32 (3 H, m), 6.430 (1 H, d of d, *J* = 24.5, 1.4 Hz), 6.057 (1 H, d of d, *J* = 50.6, 1.4 Hz), 4.24–4.04 (4 H, m), 1.271 (3 H, t, *J* = 7.1 Hz); NMR of **28** ($CDCl_3$) δ 7.4–7.2 (5 H, m), 4.2–3.8 (4 H, m), 2.196 (3 H, d, *J* = 17.2 Hz), 2.156 (3 H, s), 1.256 (3 H, t,

J = 7 Hz), 1.215 (3 H, t, J = 7 Hz); IR of **28** (CCl_4) 1755 cm^{-1}, NMR of **29** ($CDCl_3$) δ 7.8–7.2 (5 H, m), 4.35–3.75 (4 H, m), 2.814 (1 H, d, J = 6 Hz), 2.014 (3 H, d, J = 15.3 Hz), 1.281 (3 H, t, J = 7 Hz), 1.182 (3 H, t, J = 7 Hz), NMR of **30** ($CDCl_3$) δ 7.74–7.64 (2 H, m), 7.42–7.28 (3 H, m), 4.15–3.84 (3 H, m), 3.76–3.61 (1 H, m), 2.286 (3 H, d, J = 15.7 Hz), 1.298 (3 H, doublet of triplets, J = 7.1, 0.5 Hz), 1.145 (3 H, doublet of triplets, J = 7.1, 0.5 Hz).

Acetolysis of Trifluoroacetate 35. A solution of 128 mg of **35** in 8 mL of HOAc was heated at 100 °C for 6 h. A standard workup gave 105 mg (95%) of acetate **18b** which was identical with a sample prepared by acetylation of **15** (R = $CH_3SC_6H_4$) with acetic anhydride in pyridine and the product of acetolysis of mesylate **10b**. NMR ($CDCl_3$) δ 7.6–7.1 (4 H, AA'BB' quartet), 6.18 (1 H, d, J = 17 Hz), 4.4–3.8 (4 H, m), 2.47 (3 H, s), 2.15 (3 H, s), 1.24 (6 H, overlapping doublet of triplets).

Acetolysis of Mesylate 38. Reaction of 101 mg of **38** in 9 mL of HOAc at 40 °C for 16 h gave, after a standard workup with Na_2CO_3 washing, 85 mg (97%) of PhCH(OAc)CSOMe (**43**), identical with a sample prepared by acetylation of **42** (R = Ph, R' = H) with acetic anhydride. NMR ($CDCl_3$) δ 7.7–7.3 (5 H, m), 6.21 (1 H, s), 4.05 (3 H, s), 2.16 (3 H, s).

Acetolysis of Mesylate 39. Reaction of 80 mg of **39** in 5 mL of HOAc at 50 °C for 14 h gave, after a standard workup with Na_2CO_3 washing, 59 mg (89%) of a mixture of **48** and **49** in a 61:39 ratio as determined by NMR. Samples of each product were isolated by preparative G.C. NMR of **48** ($CDCl_3$) δ 4.093 (3 H, s), 2.049 (3 H, s), 1.669 (6 H, s); IR of **48** (CCl_4) 1745 cm^{-1}; NMR of **49** ($CDCl_3$) δ 3.735 (3 H, s), 2.276 (3 H, s), 1.578 (6 H, s); IR of **49** (CCl_4) 1743, 1694 cm^{-1}.

Acetolysis of Mesylate (*R*)-(−)-38. Reaction of 369 mg of (*R*)-(−)-**38**, $[\alpha]^{24}_D$ −15.9°, in 27 mL of 0.05 M NaOAc in HOAc for 6 h 40 min at 40 °C gave, after a workup as described above, with $NaHCO_3$ washing, 295 mg of crude acetate. This product was chromatographed on 13 g of silica gel and eluted with 5% ether in Skelly F. The yield of chromatographed (*R*)-(−)-**43** was 269 mg (85%), $[\alpha]^{24}_D$ −15.7° (*c* 2.5, CH_2Cl_2). In a run using (*R*)-(−)-**38** with $[\alpha]^{24}_D$ −22.5°, acetolysis gave (*R*)-(−)-**43** with $[\alpha]^{24}_D$ −22.0°.

Preparation of (*R*)-(−)-43. A mixture of 249 mg of (*R*)-(−)-**42**, $[\alpha]^{24}_D$ −52.4°, 210 mg of acetic anhydride, and 0.2 mL of CH_2Cl_2 was stirred at room temperature, and 2 drops of a mixture of 78 mg of H_2SO_4 in 0.35 mL of acetic acid was added. After 2.5 h at room temperature, 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 chromatographed on 15 g of silica gel which gave 297 mg (93%) of (*R*)-(−)-**43**, $[\alpha]^{24}_D$ −29.3° (c 3, CH_2Cl_2). The NMR spectrum was identical with that of the racemic material. A sample of (*R*)-(−)-**43** in pyridine at room temperature racemized over a period of 18 h. A sample of (*R*)-(−)-**43** in 0.1 M NaOAc in HOAc, after 16 h at 40 °C and 5 days at room temperature, showed a rotation decrease of 10%.

Kinetic Procedures. Rates of most substrates in HOAc were measured using the titrimetric procedures previously described.[1a,b,21] Rates of **10a** and **10b** in HOAc were measured spectrophotometrically by monitoring the absorbance decrease at 257 and 280 nm, respectively. Injection of 15 μL of a solution of the appropriate mesylate in ether into 3 mL of HOAc initiated the kinetic run. Rates of acetolyses of the trifluoroacetates **12** and the *O*-phosphoryl analogue were monitored by gas chromatography using biphenyl as an internal standard using a procedure analogous to that previously described. Methanolysis rates of **10a**, **10b**, and *p*-$MeOC_6H_4CH(OMs)PO(OEt)_2$ were measured spectrophotometrically at 250, 284, and 248 nm, respectively. Rates of reaction of **10e** in ethanol, trifluoroethanol, and formic acid were measured titrimetrically by using previously described procedures. In formic acid and TFE, aliquots were quenched in cold HOAc and rapidly titrated. The rate of **10e** in 97% HFIP was measured spectrometrically at 223 nm.

Acknowledgment is made to the National Science Foundation (CHE-8305820) and to the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. We also acknowledge the NIH for a grant used to purchase the 300-MHz NMR spectrometer.

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Kinetic Isotope Effects in Hydrogen Atom Transfer Reactions between Benzylic Carbons

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Received August 9, 1985

The kinetic deuterium isotope effect for transfer of hydrogen from tetralin, dihydroanthracene, fluorene, diphenylmethane, triphenylmethane, and acenaphthene to the benzyl radical was measured at 170 °C. The range of values for the effect was from 6.5 to 8.0. Activation energy parameters were obtained for five of the hydrogen donors. The apparent difference between activation energies for deuterium or hydrogen transfer was ≥2 kcal/mol for triphenylmethane, diphenylmethane, and tetralin. Applications of several tests indicate that a tunnel effect plays a significant role in these hydrogen transfers.

The transfer of a hydrogen atom from a donor to an organic free radical is a fundamental reaction of widespread interest. A particular example is the transfer from a benzylic donor to the benzyl radical. The mechanistic details of such reactions are of special interest because both donor and acceptor are resonance-stabilized at the transition state. The absolute rate for hydrogen transfer must then be heavily influenced by the extensive bond deformations required to achieve resonance stabilization at both benzylic sites.

Kinetic deuterium isotope effects have frequently been used to probe the character of transition states. Jackson and O'Neill measured the deuterium isotope effect for transfer between toluene and benzyl radical.[1] They reported k_H/k_D = 6.7 at 168 °C and suggested that substantial tunneling can account for the large magnitude of

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