Solvolytic Generation of α-Sulfonyl and α-Sulfinyl Carbocations

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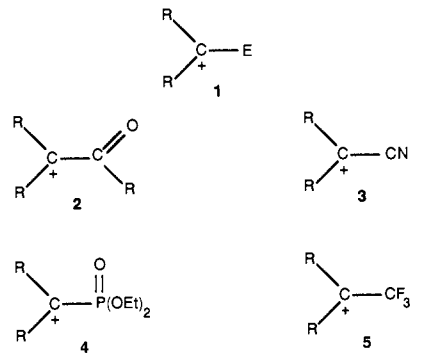
Abstract: A series of mesylates of general type $ArC(CH_3)(SO_2Ph)OMs$, **14**, have been prepared and studied under solvolytic conditions. The Hammett ρ value in methanol is −7.98. A solvent effect study on **14b**, where Ar = p-$CH_3C_6H_4$, gave a good correlation with Y_{OTs} values and an m value of 0.85. These data were interpreted in terms of the involvement of α-sulfonyl-substituted carbocations, which have a large demand for aryl group stabilization. In solvolyses of **14b**, capture of the α-sulfonyl carbocation by acetic or trifluoroacetic acid gave simple substitution products which could be isolated. In alcohol solvents subsequent unimolecular loss of benzenesulfinate ion from the initially formed α-alkoxy sulfone led ultimately to the formation of ketones or ketals. Analogous loss of benzenesulfinate from the primary product is also seen on prolonged reaction of **14b** in carboxylic acid solvents. Solvolyses of a series of α-bromo sulfoxides of general structure $ArC(CH_3)(SOPh)Br$, **35**, also proceed via the intermediacy of carbocations. The demand for aryl stabilization in these α-sulfinyl cations is also quite large as evidenced by the ρ value of −7.18 in triflouroethanol. The trifluoroethanolysis rate of **35b**, where Ar = p-$CH_3C_6H_4$, is 1.4×10^5 times slower at 25 °C than that of the α-H analogue $ArCH(CH_3)Br$, **29**. This, along with the large negative ρ value, implies that the interaction of the sulfur nonbonding electrons with the adjacent cationic center is of minimal importance in the α-sulfinyl carbocation derived from **35b**. These data conflict with previous suggestions that α-sulfinyl cations are greatly stabilized by the sulfur nonbonding electrons. Suggestions are offered to explain this apparent conflict. The relative reactivities of a series of bromides containing electron-withdrawing groups have been determined in the common solvent trifluoroethanol in order to evaluate the effect of these groups on the rate of carbocation generation. The relative reactivity order for solvolyses of substrates of general type p-$CH_3C_6H_4C(CH_3)BrE$, where E is an electronegative group, is COPh > $PO(OEt)_2$ > CN > SOPh > CF_3 > SO_2Ph.

Over the past 10 years, extensive studies have appeared in which cations of general type **1**, where the group E is formally electron withdrawing, have been generated.[1-5] Interest in such cations stems from the belief that such cations should be intrinsically destabilized due to the attachment of an electronegative group to an electron-deficient center. This belief has proven to be somewhat naive. Certain cations of general type **1** (i.e., cations **2-4**, where E = COR, CN, and $PO(OEt)_2$) can be generated solvolytically much more rapidly than might be anticipated on the basis of the electronegative properties of these groups.[1,3] These substituents appear to possess some cation stabilizing feature. On the other hand, when the substituent E is CF_3, the effect of this electronegative group appears to be largely inductively destabilizing, as evidenced by greatly repressed rates of solvolytic generation of cations of type **5**.[4,5a,b]



We have been interested in the effects of the electronegative sulfonyl group on electron-deficient intermediates. We have measured the effect of a benzylic SO_2CH_3 group on the rate of the methylenecyclopropane rearrangement which proceeds via a radical-like transition state.[6] A limited number of studies on cationic sulfonyl-containing systems have also appeared. A study by Bordwell and Mecca[7] suggested the involvement of the ion pair **7** in bimolecular substitution reactions of the allylic sulfone **6**. Meyers and Hua[8a] have suggested that the α-halo sulfones **8** can undergo solvolytic reactions involving sulfonyl-substituted carbocations **9**. Our interest in carbocations substituted with electron-withdrawing groups has led us to attempt to determine, in a more quantitative fashion, the effect of the sulfonyl group on carbocations when directly attached to the electron-deficient center as in **10**. We also wanted to examine the effect of the less oxidized sulfoxide group on the cationic center in **11**. Such intermediates have been suggested in the past in the α-halogenation of sulfoxides.[9] They have also been suggested in reactions of phen-

(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.* **184**, *106*, 5568-5577. (e) Creary, X.; Geiger, C. C. *Ibid.* **1982**, *104*, 4151-4162. For E = $PS(OEt)_2$, see: (f) Creary, X.; Mehrsheikh-Mohammadi, M. E. *J. Org. Chem.* **1986**, *51*, 7-15.

(2) Bégué, 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) **1980**, *102*, 2138-2143. (d) Gassman, P. G.; Saito, K.; Talley, J. J. *Ibid.* **1980**, *102*, 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.

(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) Liu, K.-T.; Wu, Y. W. *J. Chem. Res., Synop.* **1984**, 408-409. (c) Takeuchi, K.; Kitagawa, T.; Okamoto, K. *J. Chem. Soc, Chem. Commun.* **1983**, 7. (d) Hopkinson, A. C.; Dao, L. H.; Dupperrouzel, R.; Maleki, M.; Lee-Ruff, E. *Ibid.* **1983**, 727-728. (e) McDonald, R. N.; Tabor, T. E. *J. Am. Chem. Soc.* **1967**, *89*, 6573-6578. (f) McDonald, R. N.; Steppel, R. N. *Ibid.* **1970**, *92*, 5664-5670. (g) Olah, G. A.; Prakash, G. K. S.; Arvanaghi, M. *Ibid.* **1982**, *104*, 1628-1631. (h) Olah, G. A.; Prakash, G. K. S.; Arvanaghi, M.; Krishnamurthy, V. V.; Narang, S. C. *Ibid.* **1984**, *106*, 2378-2380.

(6) Creary, X.; Mehrsheikh-Mohammadi, M. E. *J. Org. Chem.* **1986**, *51*, 1110-1114.

(7) Bordwell, F. G.; Mecca, T. G. *J. Am. Chem. Soc.* **1972**, *94*, 2119-2121.

(8) (a) Meyers, C. T.; Hua, H. D. *Phosphorus Sulfur* **1979**, *6*, 197-198. (b) Meyers, C. T. *Topics in Organic Sulfur Chemistry*; Tisler, M., Ed.; University Press: Ljubljana, Yugoslavia, 1978; pp 207-260.

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Table I. Solvolysis Rates of Substrates in Various Solvents

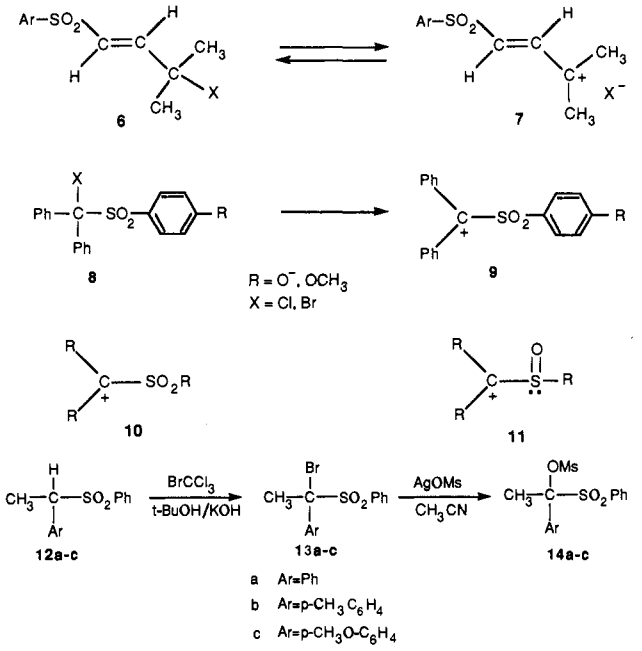
substrate	solvent[a]	temp, °C	k, s^{-1}
14a (*p*-H)	MeOH	100.0	1.21×10^{-4}
		80.0	1.42×10^{-5}
		25.0[b]	9.09×10^{-9}
14b (*p*-CH_3)	MeOH	25.0	1.78×10^{-6}
	CD_3CO_2D	60.0	1.32×10^{-4}
		40.0	1.05×10^{-5}
		25.0[b]	1.26×10^{-6}
	TFE	25.0	2.57×10^{-4}
	HCO_2H	25.0	3.07×10^{-3}
	HFIP	25.0	8.88×10^{-3}
	TFA	25.0	4.39×10^{-2}
14c (*p*-CH_3O)	MeOH	25.0	1.40×10^{-2}
35a (*p*-H)	TFE	95.0	1.06×10^{-4}
		75.0	1.27×10^{-5}
		25.0[b]	1.85×10^{-8}
35b (*p*-CH_3)	TFE	25.0	4.45×10^{-6}
	HCO_2H	25.0	1.60×10^{-5}
35c (*p*-CH_3O)	TFE	25.0	7.41×10^{-3}
13b (α-SO_2Ph)	TFE	120.0	8.45×10^{-5}
		100.0	1.43×10^{-5}
		25.0[b]	2.29×10^{-9}
29 (α-H)	TFE	10.4	1.59×10^{-1}
		14.2	2.33×10^{-1}
		17.9	3.21×10^{-1}
		25.0[b]	6.05×10^{-1}
30 (α-COPh)	TFE	25.0	2.34×10^{-2}
31 (α-$PO(OEt)_2$)	TFE	25.0	1.85×10^{-3}[c]
32 (α-CN)	TFE	25.0[d]	2.47×10^{-4}
33 (α-CF_3)	TFE	80.0	1.24×10^{-4}
		60.1	2.11×10^{-5}
		25.0[b]	5.26×10^{-7}
43	*i*-PrOH	25.0	1.96×10^{-1}
22a (*p*-SO_2Ph)	EtOH	90.0	3.55×10^{-4}
		70.0	5.29×10^{-5}
		25.0[b]	2.91×10^{-7}
22b (*p*-SO_2CH_3)	EtOH	90.0	2.78×10^{-4}
		70.0	4.09×10^{-5}
		25.0[b]	2.18×10^{-7}
23a (*p*-SOPh)	EtOH	25.0	4.52×10^{-6}
23b (*p*-$SOCH_3$)	EtOH	25.0	4.59×10^{-6}
56	TFE	25.0	9.23×10^{-4}
57	TFE	25.0	2.82×10^{-6}

[a] MeOH, 0.025 M Et_3N in methanol; EtOH, 0.025 M Et_3N in ethanol; 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); TFA, trifluoroacetic acid. [b] Extrapolated rate. [c] Estimated from the rate of the corresponding trifluoroacetate derivative **57** in TFE at 25 °C assuming a bromide/trifluoroacetate rate ratio of 656. This is the measured ratio for **29** and the trifluoroacetate derivative **56**. [d] Reference 3e.

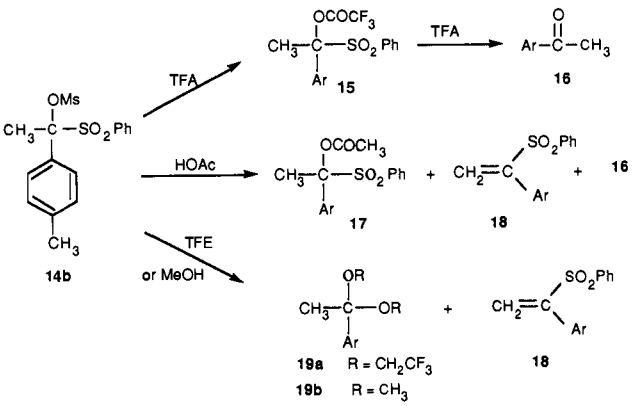
oxysulfoxonium tetrafluoroborate,[10] in acid-catalyzed reactions of phenyldiazomethyl sulfoxide,[11] and in reactions of certain α-iodo sulfoxides.[11,12] However, there are few quantitative data which would allow one to speculate on the relative stability of such sulfinyl-substituted cations. Of special interest was an evaluation of the effect of the nonbonding electron pair on rates of formation of cation **11**.

Results and Discussion

Generation of α-Sulfonyl Carbocations. A series of bromides of general type **13** were prepared from the sulfones **12** by the bromination procedure developed by Meyers.[8] These bromides proved to be relatively unreactive in solvolytic studies and were therefore converted to the corresponding mesylates **14** by treatment with silver mesylate in acetonitrile.



The solvolysis of **14b** was examined in detail. Trifluoroacetolysis gave the trifluoroacetate **15** as well as *p*-methylacetophenone, **16** (where Ar = *p*-$CH_3C_6H_4$). Analogous ketone products have also been observed in solvolysis of **8**.[8] The *p*-methylacetophenone is a secondary product which arises from the primary product **15**. The formation of this secondary product can be monitored when a pure sample of **15** is placed in trifluoroacetic acid. Conversion to *p*-methylacetophenone occurs with a half-life of 380 minutes at 25 °C. Some **16** is also formed from **15** under the aqueous workup conditions. Acetolysis results are similar in that the major products are the simple substitution product **17** and *p*-methylacetophenone, **16**. However a small amount (15%) of the elimination product **18** is formed at the higher temperature of the acetic acid solvolysis. In trifluoroethanol and methanol (buffered with triethylamine), the solvolysis products are the ketals **19a** and **19b**, respectively, along with a smaller amount of the elimination product **18**. None of the simple substitution product was observed, even at short reaction times.



Solvolysis rates of **14b** (Table I) are quite dependent on solvent ionizing power. Reaction in the highly ionizing CF_3CO_2H is 3.5 $\times 10^4$ times faster than in acetic acid-d_4. The effect of solvent on reaction rate is shown graphically in Figure 1. The correlation of rate with Y_{OTs} values[13] is good ($r = 0.997$), and the response to solvent ionizing power is large ($m = 0.85$). These data support the involvement of a cationic intermediate of general type **10**, where the potent electron-withdrawing SO_2Ph group is directly attached to the electron-deficient carbon. More specifically, we suggest that under solvolytic conditions, **14b** undergoes loss of

(9) (a) Durst, T.; Tin, K. C.; Marcil, M. J. V. *Can. J. Chem.* **1973**, *51*, 1704–1712. (b) Bory, S.; Tett, R.; Moreau, B.; Marquet, A. *C. R. Sequences Acad. Sci., Ser. C* **1973**, *276C*, 1323–1326. (c) Klein, J.; Stollar, H. *J. Am. Chem. Soc.* **1973**, *95*, 7437–7444.

(10) Shimagaki, M.; Tsuchiya, H.; Ban, Y.; Oishi, T. *Tetrahedron Lett.* **1978**, 3435–3438.

(11) Venier, C. G.; Wing, F. A., Jr.; Barager, H. J., III. *Tetrahedron Lett.* **1980**, 3159–3162.

(12) Reutrakul, V.; Panyachotipun, C.; Hahbvajanawong, V.; Sotheeswaran, S. *Tetrahedron Lett.* **1984**, 1825–1828.

(13) Schadt, F. L.; Bentley, T. W.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1976**, *98*, 7667–7674.

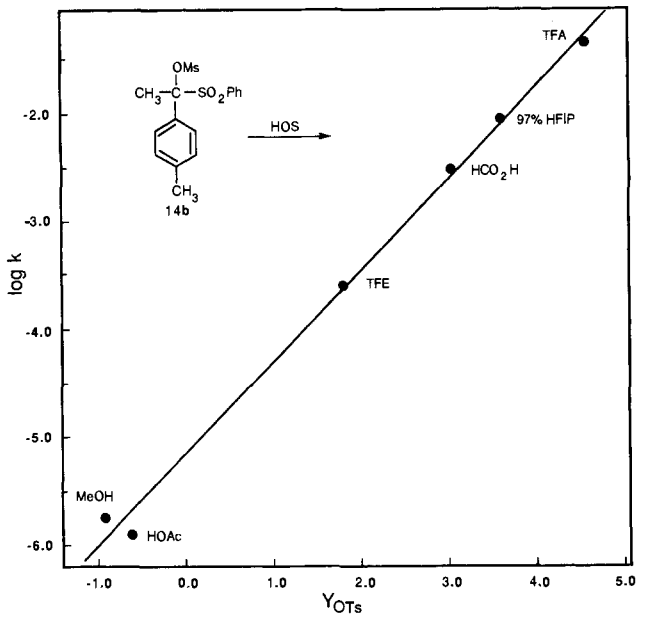
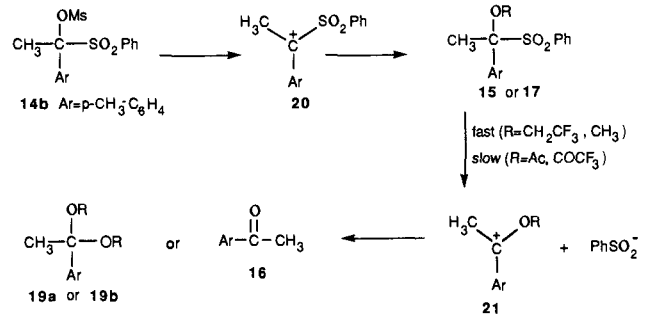
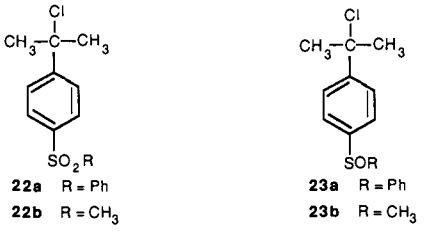


Figure 1. Plot of log k for solvolysis of **14b** vs. Y_{OTs}.

methanesulfonate ion giving the α-sulfonyl cation **20**. In trifluoroacetic and acetic acids, solvent capture gives the observed substitution products **15** and **17** which can be isolated. Proton loss from the cation **20** accounts for the small amount of the elimination product **18**. Loss of sulfinate ion from **15** or **17** in a unimolecular process[14] can subsequently occur to give the cationic intermediate **21** (R = $COCF_3$, $COCH_3$), which leads ultimately to *p*-methylacetophenone in carboxylic acid solvents. In alcohol solvents, this secondary loss of sulfinate ion is quite rapid due to the relative stability of the resultant alkoxy-substituted cation **21**. Hence no simple substitution products can be detected. Alcohol capture of **21** (R = CH_3, CH_2CF_3) leads to the observed ketal products **19**.



Sulfonyl Group Rate Effects. In order to gain some insights into the electron-withdrawing properties of the sulfonyl group, σ^+ values were determined for the *p*-SO_2Ph and *p*-SO_2CH_3 groups by solvolysis of the corresponding cumyl chlorides **22a** and **22b** in ethanol. Rate data are given in Table I, and σ^+ values for these

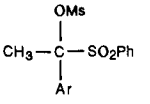
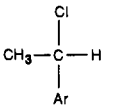
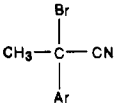
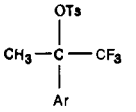
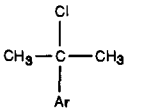
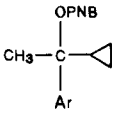
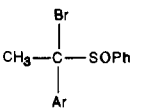


(14) For a study of the reactivity of sulfinate as a leaving group in carbocation-forming processes, see: (a) Creary, X. *J. Org. Chem.* **1985**, *50*, 5080–5084. For leading references on sulfinate as a leaving group in other mechanistic processes, see ref 1–9 of this paper. See also: Issari, B.; Stirling, C. J. M. *J. Chem. Soc., Perkin Trans. 2* **1984**, 1043–1051. Marshall, D. R.; Thomas, P. J.; Stirling, C. J. M. *J. Chem. Soc., Perkin Trans. 2* **1977**, 1898–1909.

Table II. σ^+ Values for Electron-Withdrawing Groups

substituent	σ^+	ref
p-SO_2Ph	0.670	this work
p-SO_2CH_3	0.697	this work
p-SOPh	0.416	this work
p-$SOCH_3$	0.414	this work
p-CO-*t*-Bu	0.293	1e
p-COPh	0.406	1e
p-CO_2CH_3	0.466	19a
p-$PO(OEt)_2$	0.505	1a
p-$PS(OEt)_2$	0.431	1f
p-CF_3	0.596	19a
p-CN	0.659	19b

Table III. Summary of ρ^+ Values

substrate	solvent	ρ^+	ref
 **14**	MeOH	−8.0	this work
 **24**	90% acetone	−4.95	16
 **25**	TFE	−6.70	3e
 **26**	80% EtOH	−6.85 (−7.46) (−10.3 for bromide)	5a 5b
 **27**	90% acetone	−4.54	19a
 **28**	80% acetone	−2.78	15
 **35**	TFE	−7.2	this work

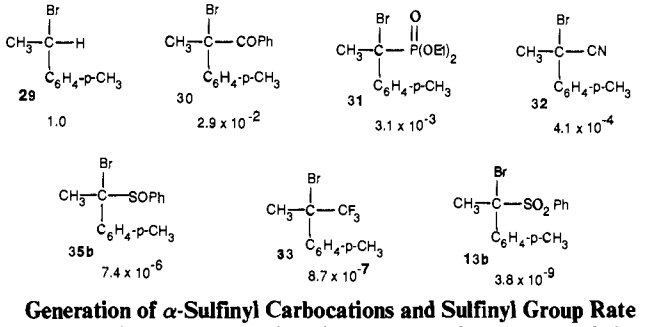
and related substituents are summarized in Table II. σ^+ values for *p*-SO_2Ph and SO_2CH_3 in ethanol are 0.670 and 0.697, respectively. These groups are therefore even more destabilizing when placed in the para position of a cumyl cation than are the CF_3 (σ^+ = 0.596) and the cyano substituents (σ^+ = 0.659).

Attention was next turned to rate effects of the sulfonyl group on the formation of α-sulfonyl carbocations where the sulfonyl group is directly attached to the cationic center. Rates of methanolysis of **14**, where Ar = C_6H_5 and *p*-$MeOC_6H_4$, were also determined (Table I). These data give a Hammett ρ^+ value of −8.0 for methanolysis of **14**. Other pertinent ρ^+ values are sum-

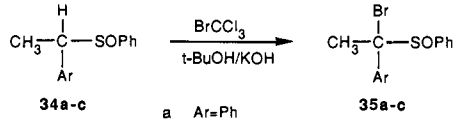
marized in Table III. These ρ^+ values give some measure of the demand for aryl group stabilization in the transition state for solvolyses of these substrates. Although the comparisons involve different solvents and leaving groups, certain trends are apparent. Carbocation stabilizing groups such as cyclopropyl lead to a reduced ρ^+ value (−2.78)[15] relative to the α-H analogue **24** where the ρ^+ value is −4.95.[16] The ρ^+ value of −8.0 seen for **14** is substantially larger (in absolute value) than the value of −4.95 seen in solvolyses of the α-H analogue **24**. This very large negative ρ^+ value is consistent with an extremely large demand for aryl stabilization in sulfonyl-substituted carbocations. The ρ^+ value for **14** exceeds that of the α-cyano analogue, **23**, and even the α-trifluoromethyl analogue, **26**.

A direct comparison of the effect of a variety of electronegative groups on solvolytic reactivity has been made. Analogues of substrates **30–33** have been previously investigated, and presumably these substrates solvolyze via k_c processes involving cations of general type **1**. However no complete comparison of the effect of various electronegative groups is available due to the variation of leaving groups and solvents employed in previous studies. To allow such a direct comparison of substrates containing electronegative groups, rates were measured in the common solvent trifluoroethanol. The aryl substituent chosen was p-$CH_3C_6H_4$, and the common leaving group was bromide. At 25 °C, the α-sulfonyl substrate **13b** is 2.6×10^8 times less reactive than the α-H analogue **29**. The SO_2Ph group is therefore the most rate retarding of the electronegative substituents reported to date, as evidenced by the fact that the solvolytic rate of the α-CF_3-substituted system **33** exceeds that of the α-bromo sulfone **13b** by a factor of 2.3×10^2. These rate comparisons suggest that the major effect of the SO_2Ph group is inductive in nature and that this effect is quite destabilizing with respect to carbocationic centers. No offsetting stabilizing effect is apparent as in the case of α-carbonyl cations, **2**, or α-cyano cations, **3**.

relative rate in TFE at 25 °C

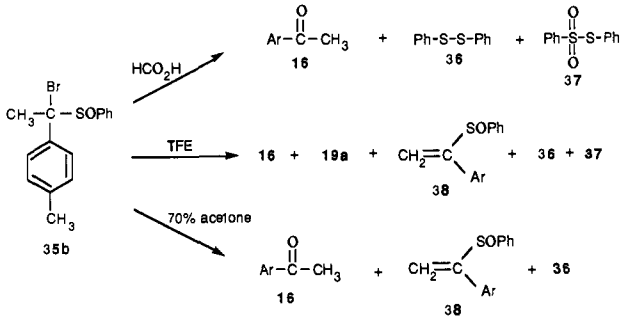


Generation of α-Sulfinyl Carbocations and Sulfinyl Group Rate Effects. With an improved understanding of the effect of the sulfonyl group, SO_2Ph, on carbocation stability and reactivity, attention was turned to the effect of the sulfinyl group, SOPh, on carbocations. A series of α-sulfinyl bromides **35** were prepared from the corresponding sulfoxides **34** by a bromination procedure analogous to that previously used to prepare the α-bromo sulfones

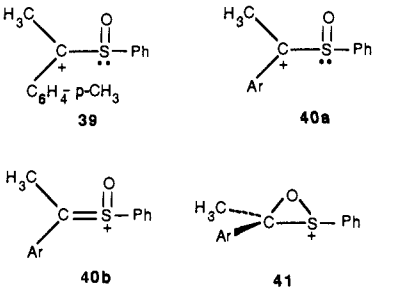


a Ar=Ph
b Ar=p-CH_3-C_6H_4
c Ar=p-CH_3O-C_6H_4

13. Despite the relatively low yields, the α-bromo sulfoxides **35** could be isolated. Solvolysis of **35b** (a mixture of diastereomers) in formic acid gave no simple substitution product. p-Methylacetophenone, **16**, was produced as well as diphenyl disulfide, **36**, and phenyl benzenethiosulfonate, **37**. These later two products are produced undoubtedly from loss of the benzenesulfinyl group and dimerization–disproportionation of the resultant PhS(O)H under the reaction conditions. Analogous products were seen in trifluoroethanol, where ketal **19a**, ketone **16**, and the elimination product **38** were formed (2.3:1.3:1 ratio) along with **36** and **37**. In 70% aqueous acetone (buffered with triethylamine) p-methylacetophenone, **16**, and the elimination product **38** were produced (6.1:1 ratio) along with diphenyl disulfide, **36**.



The products derived from solvolysis of **35b** are consistent with the involvement of cation **39**. The rate of solvolysis of **35b** in formic acid (Y_{OTs} = 3.04) is much greater than in acetic acid (Y_{OTs} = −0.61) as is expected for a reaction involving a cationic intermediate.[17] Solvent capture of **39** followed by subsequent



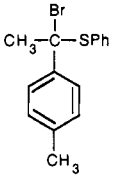
processes involving loss of the sulfinyl group would account for the observed products. In order to gain some insights into the effect of the sulfinyl group on solvolytically generated cations, the σ^+ values for the SOPh and $SOCH_3$ groups were determined in ethanol from the solvolysis rates of the cumyl chlorides **23a** and **23b**. As can be seen from Table II, these groups in the para position are electron withdrawing relative to hydrogen but less so than the more oxidized sulfone groups. In the case of the bromides **35a–c**, where the electron-withdrawing SOPh group is attached directly to the developing cationic center, the Hammett ρ^+ value was determined by measuring trifluoroethanolysis rates. In the case of **35b**, both diastereomers reacted at comparable rates as determined by monitoring the reaction in formic acid by NMR. The ρ^+ value based on these three substrates is −7.2. Pertinent comparisons can be seen in Table III. The ρ^+ value for **35** is quite large and indicative of a very large transition-state demand for aryl stabilization. We therefore conclude that the sulfinyl group is not very effective in alleviating the demand for charge delocalization into the aryl group. The demand for aryl stabilization in solvolysis of **35** is comparable to that of the CF_3-containing substrate **26**. This indicates that a conjugative interaction as represented by **40b** is *not* very important in stabilization of this α-sulfinyl carbocation. Solvolytic processes involving neighboring group participation of the adjacent oxygen atom, leading to **41**, are also considered unlikely due to the magnitude of the ρ^+ value.[19]

A direct comparison of the solvolysis rate of **35b** with those of the analogous bromides also supports these conclusions. The

(15) Peters, E. N.; Brown, H. C. *J. Am. Chem. Soc.* **1973**, *95*, 2397–2398.
(16) Tsuno, Y.; Kusuyama, Y.; Sawada, M.; Fujii, T.; Yakawa, Y. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 3337.
(17) Temperatures of about 90 °C are necessary to acheive solvolysis of **35b** in HOAc at convenient rates. Determination of precise solvolysis rate constants was difficult due to a competing sulfoxide pyrolysis reaction at these temperatures.
(18) Solvolysis of substrates in which neighboring thiophosphoryl participation is important results in a relatively small ρ value of only −2.99. See ref 1f.
(19) (a) Okamoto, Y.; Inukai, T.; Brown, H. C. *J. Am. Chem. Soc.* **1958**, *80*, 4972–4976. (b) Brown, H. C.; Okamoto, Y. *Ibid.* **1958**, *80*, 4979–4987.

sulfinyl-containing substrate **35b** is far less reactive (5.2×10^3) than the carbonyl-containing analogue **30** despite the comparable σ^+ values for these two groups. We conclude that, unlike the α-carbonyl cation[1c-e] derived from **30**, the α-sulfinyl cation is not stabilized by a conjugative interaction. The α-sulfinyl cation is produced from **35b** even less readily than the α-cyano cation forms from **32**. Sulfur nonbonding electron pair conjugation cannot be very important as a stabilizing feature in cations such as **40**. We speculate that this lack of stabilization by the sulfoxide nonbonding electron pair is due to the fact that the sulfur atom in sulfoxides already carries significant positive charge. Sulfoxides are probably best represented as dipolar structures. Conjugation as in **40b**, involving electrons in a sulfur sp^3 hybrid orbital, is probably not effective since these electrons are more strongly attached to the positively charged sulfoxide sulfur atom than are nonbonding electrons in a sulfide group.

A comparison of the solvolysis rate of the unoxidized α-bromo sulfide **42** with those of the α-H analogue **29** and the oxidized analogues **13b** and **35b** is instructive. The α-bromo sulfide **42** is far too reactive for its rate to be measured in trifluoroethanol. Therefore we have attempted to estimate its solvolytic rate in trifluoroethanol in the following fashion. The α-chloro sulfide **43** has been prepared and is found to solvolyze in the poorly



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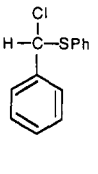
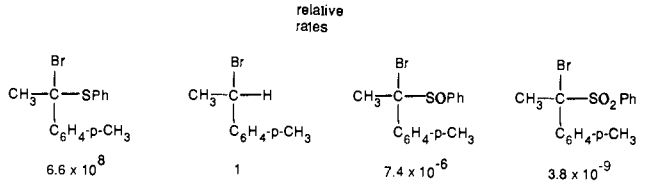
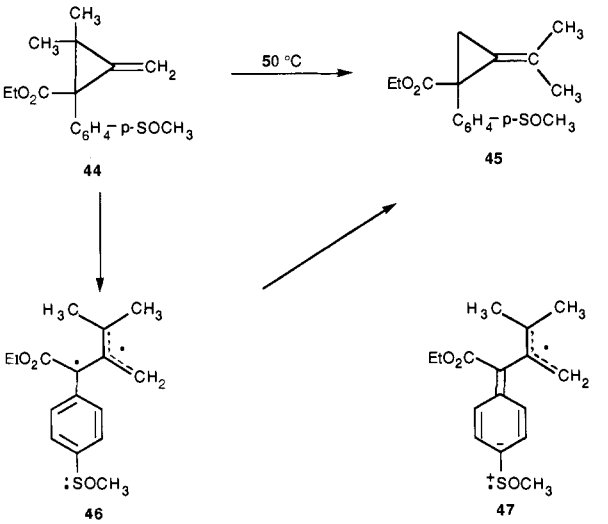


43

ionizing solvent isopropyl alcohol with a half-life of 3.54 s at 25 °C. One can crudely estimate the rate of **42** if one assumes a bromide/chloride reactivity ratio of 14,[20] a Winstein–Grunwald *m* value of 0.85 for solvolysis of **43**, an α-CH_3 rate-enhancing effect of 10^3,[21] and a *p*-CH_3 rate-enhancing effect of 10;[22] then the calculated trifluoroethanolysis rate of **43** at 25 °C is 4×10^8 s^{-1}. While this value involves large extrapolations and should not be taken literally, it does imply that α-SPh substitution enhances solvolysis rates by an enormous factor (approaching 10^9) relative to the α-H analogue. Oxidation of α-SPh to α-SOPh results in a rate reduction of approximately 10^{14}. Further oxidation of SOPh to α-SO_2Ph results in a further rate reduction of 1.9×10^3. This much smaller rate reduction is presumably due to the somewhat greater electron-withdrawing properties of SO_2Ph relative to SOPh as reflected by their corresponding σ^+ values. The first oxidation of sulfide to sulfoxide is the process which removes the conjugative ability of the sulfur nonbonding electrons. It is our view that further oxidation of sulfoxide to sulfone simply increases the electron-withdrawing properties of the substituent with no effect on the conjugative properties which have already been essentially destroyed in the sulfoxide.



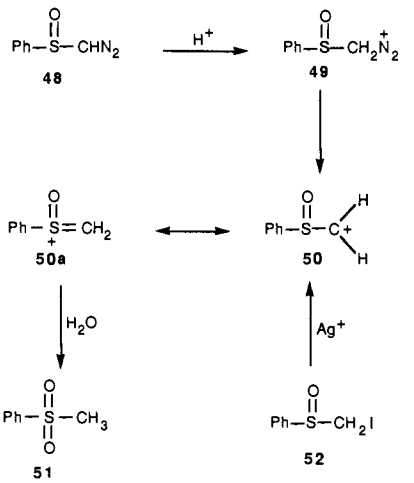
Related studies in the free radical area support our findings that the sulfinyl group does not act as an electron-donor group.[6] The captodative effect is a free radical stabilizing feature in which the combination of electron-donor and electron-acceptor substituents attached to a radical center exerts a synergistic stabilizing effect.[23] We have found[6] that there is no additional captodative stabilization in the transition state of the methylenecyclopropane rearrangement of **44** to **45**, which proceeds through the biradical **46**. If the sulfinyl group were capable of acting as an elec-



44 **45** **46** **47**

tron-donor group, then, in conjunction with the electron-withdrawing carboethoxy group, a captodative rate-enhancing effect would have been observed in the rearrangement of **44**. We have concluded that the sulfinyl group does *not* stabilize free radicals via a donor type of mechanism as pictured in **47**.

How do these findings fit with other studies where α-sulfinyl cations have been suggested? A study by Venier et al. on the acid-catalyzed decomposition of the diazo compound **48** suggested the involvement of cation **50**, which is stabilized as in **50a**.[11] This



cation captures water at sulfur and gives phenyl methyl sulfone, **51**. Silver-assisted solvolysis of **52** also gave **51** via **50**. The intermediate generated from **49** and **52** captures water at sulfur while the intermediate formed in the reaction of the α-bromo sulfoxides **35** gives products derived from solvent capture at carbon. Our studies suggest that the cations **40** do not derive significant stabilization from the adjacent sulfur, while it is suggested that **50** is substantially stabilized by the sulfinyl group. Indeed, if the directly attached PhSO group is cation destabilizing as our study indicates, then a cation such as **50** would be less stable than a methyl cation.

How do we resolve these conflicting interpretations of experimental results? Our data are completely consistent with the

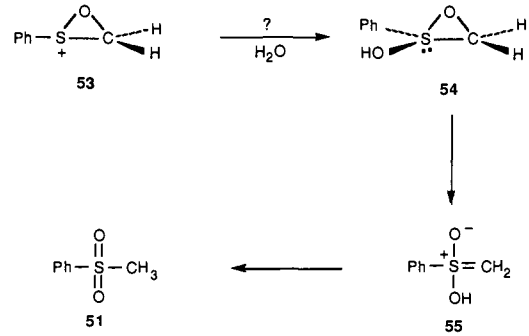
(20) This bromide/chloride reactivity ratio is taken from: Noyce, D. S.; Virgilio, J. A. *J. Org. Chem.* **1972**, *37*, 2643–2647.

(21) For a discussion of the α-CH_3/α-H ratio and leading references, see: Fry, J. L.; Harris, J. M.; Bingham, R. C.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1970**, *92*, 2540–2542. The α-CH_3/α-H ratio of 10^3 used for estimating the rate of **42** is a conservative estimate.

(22) This would correspond to a ρ value of −3.2 for solvolysis of substituted analogues of **43**.

(23) For a review and leading references, see: Viehe, H. G.; Janousek, Z.; Merényi, R. *Acc. Chem. Res.* **1985**, *18*, 148–154. The captodative effect is also referred to as merostabilization of "push–pull" stabilization. For further leading references, see: Leigh, W. J.; Arnold, D. R.; Humphreys, R. W. R.; Wong, P. C. *Can. J. Chem.* **1980**, *58*, 2537–2549.

involvement of the α-sulfinyl cations **40**, which do not derive any stabilization from the adjacent sulfoxide group. Previous literature[11] suggests that cations of type **50** are stabilized to a rather large extent by the sulfoxide group. One explanation for this apparent conflict is the possibility that the extreme demand for stabilization in **50** results in a changeover of the sulfoxide moiety from an electron-withdrawing to an electron-donating group (via resonance as in **50a**). In aryl-stabilized cations such as **39**, due to decreased electron demand, the sulfoxide would exert purely its electronegative effect. If this explanation is correct, then the sulfoxide group is capable of an enormous change in its response to a developing adjacent positive charge. In one case, i.e., cation **40**, it is quite destabilizing relative to α-H, while in the other case, i.e., cation **50**, it is quite stabilizing relative to hydrogen. We are aware of no precedent for a response change of this magnitude. An alternative suggestion to account for the conflicting data interpretations is the possibility that cation **50** is not actually involved. The cyclized form **53** has not previously been considered, and there is no evidence which precludes its involvement in the reactions of **49** and **52**. Capture of water at the sulfur of **53**



followed by ring opening and tautomerism would give the sulfone product **51** found in these reactions. In any case, further studies are necessary to allow one to distinguish between ion **50** and the cyclized form **53**. These studies should help to clear up the conflict with existing literature created by our current findings on the ability of the sulfinyl group to interact with an adjacent cationic center.

Conclusions. The α-mesyloxy sulfones **14** solvolyze giving products and rate data consistent with the involvement of α-sulfonyl cations of general type **10**. These cations form at much slower rates than the α-H analogues. The sulfonyl group is even more inductively destabilizing with respect to an adjacent cationic center than is the CF_3 group as evidenced by relative rates of cation formation and demand for aryl stabilization as reflected by ρ^+ values. The less oxidized α-sulfinyl cations of general type **11** can also be solvolytically generated from the α-bromo sulfoxides **35**. These cations also form at greatly reduced rates relative to the α-H analogues despite the potential for stabilization involving the sulfur nonbonding electrons. Oxidation of a sulfide function to sulfoxide results in an enormous rate reduction for formation of the α-substituted carbocation. Further oxidation of sulfoxide to sulfone gives a much smaller rate slowdown for carbocation formation. Stabilization of α-sulfinyl cations as in **40b** does not appear to be important. The series of bromides of general type p-$CH_3C_6H_4C(CH_3)BrE$, where the group E is an electronegative group, has been solvolyzed in the common solvent trifluoroethanol in order to compare the effect of various groups on rates of generation of electron-deficient carbocations. The relative reactivity order for formation of these aryl-stabilized carbocations containing the various electronegative groups E is COPh > $PO(OEt)_2$ > CN > SOPh > CF_3 > SO_2Ph.

Experimental Section

Preparation of Sulfones 12. General Procedure. A solution of the appropriate sulfide $ArCH(CH_3)SPh$ (prepared by reaction of the appropriate chloride with sodium thiophenoxide in ethanol) in 10 parts of CH_2Cl_2 was cooled to 0 °C, and 2.1 equiv of *m*-chloroperbenzoic acid was added slowly in small portions. After stirring for 2 h at room temperature, the mixture was taken up into ether and washed with a mixture of NaOH, NaI, and $Na_2S_2O_3$. The organic extract was dried over $MgSO_4$, and the solvent was removed by using a rotary evaporator. The crude sulfones **12** were slurried with pentane and collected on a Buchner funnel. The following procedure is representative.

Reaction of 3.00 g of p-$CH_3C_6H_4CH(CH_3)SPh$ in 25 mL of CH_2Cl_2 with 6.25 g of 85% *m*-chloroperbenzoic acid gave 3.40 g (99%) of sulfone **12b**: mp 109–110 °C; ^1H NMR ($CDCl_3$) δ 7.8–7.2 (m, 5 H), 7.07 (m, 4 H), 4.20 (q, J = 7.5 Hz, 1 H), 2.30 (s, 3 H), 1.72 (d, J = 7.5 Hz, 3 H).

Preparation of α-Bromo Sulfones 13. General Procedure.[8b] The appropriate sulfone **12** was dissolved by warming it in 2.8 parts of $BrCCl_3$ and 5 parts of *tert*-butyl alcohol. Powdered KOH (4.5 parts) was added in small portions to the stirred mixture held in a room temperature water bath. The reaction was exothermic. After 75 min, the mixture was taken up into CH_2Cl_2 and washed with water. The organic extract was dried over $MgSO_4$, and the solvent was removed by using a rotary evaporator. The crude products **13** were slurried with hexanes and collected on a Buchner funnel. The following procedure is representative.

Reaction of a solution of 6.53 g of sulfone **12b** in 18.45 mL of $BrCCl_3$ and 33.1 mL of *tert*-butyl alcohol with 29.7 g of powdered KOH gave 7.74 g (91%) of α-bromo sulfone **13b**: mp 126–128 °C; ^1H NMR ($CDCl_3$) δ 7.8–7.2 (m, 7 H), 7.2–6.9 (d, 2 H), 2.465 (s, 3 H), 2.359 (s, 3 H). Anal. Calcd for $C_{15}H_{15}BrO_2S$: C, 53.11; H, 4.46. Found: C, 52.92; H, 4.58.

Preparation of Mesylates 14. General Procedure. A solution of the appropriate α-bromo sulfone **13** (1 equiv) and 3 equiv of silver mesylate in dry acetonitrile was heated for a given period of time and protected from light. The mixture was then taken up into 50% ether–50% CH_2Cl_2 and washed with four portions of aqueous KCN and saturated NaCl solution. The organic extract was dried over $MgSO_4$, and the solvent was removed by using a rotary evaporator. Recrystallization of the residue from CH_2Cl_2–Skelly F gave the corresponding mesylates **14**. The following procedure is representative.

A solution of 1.515 g of α-bromo sulfone **13b** and 2.648 g of silver mesylate in 100 mL of acetonitrile was heated at reflux for 3 h. After a workup as described above and solvent removal, the residue was cooled to −20 °C. The solid which formed was recrystallized from 3 mL of CH_2Cl_2 and 6 mL of hexanes to give 0.770 g (49%) of mesylate **14b**: mp 91–93 °C dec; ^1H NMR ($CDCl_3$) δ 7.69–7.59 (m, 3 H), 7.50–7.43 (t, 2 H), 7.29–7.23 (d, 2 H), 7.16–7.10 (d, 2 H), 3.153 (s, 3 H), 2.434 (s, 3 H), 2.350 (s, 3 H). Anal. Calcd for $C_{16}H_{18}O_5S_2$: C, 54.22; H, 5.12. Found: C, 53.97; H, 5.23.

Reaction of 1.041 g of α-bromo sulfone **13a** and 1.866 g of silver mesylate in 18 mL of acetonitrile in sealed tubes at 125 °C for 3 h gave a large amount of the elimination product **18** (Ar = Ph) and a smaller amount of mesylate **14a** from which 88 mg (8%) of **14a** could be isolated.

Reaction of 340 mg of α-bromo sulfone **13c** and 605 mg of silver mesylate in 22 mL of acetonitrile at room temperature for 1 h gave 284 mg (81%) of mesylate **14c**, which crystallized from hexanes containing a small amount of ether at −20 °C. During solvent removal, the temperature was not allowed to exceed 0 °C. Mesylate **14c** readily decomposed on standing at room temperature and was stored at −80 °C. **14c**: ^1H NMR ($CDCl_3$) δ 7.80–7.45 (m, 5 H), 7.38 (d, 2 H), 6.88 (d, 2 H), 3.81 (s, 3 H), 3.14 (s, 3 H), 2.43 (s, 3 H). Mesylate **14c** decomposed on standing in $CDCl_3$.

Preparation of Cumyl Chlorides 22 and 23. The cumyl chlorides **22a** (p-SO_2Ph) and **22b** (p-SO_2CH_3) were prepared by treating the corresponding cumyl alcohols (prepared by oxidation of the corresponding sulfides with 2 equiv of *m*-chloroperbenzoic acid) with thionyl chloride by using procedures analogous to those previously described.

The cumyl chlorides **23a** (p-SOPh) and **23b** (p-$SOCH_3$) were prepared by oxidation of the corresponding p-(thioalkyl)cumyl chlorides with 1 equiv of *m*-chloroperbenzoic acid. The following procedure is representative. A solution of 650 mg of p-(thiomethoxy)cumyl alcohol in 10 mL of CH_2Cl_2 was cooled to 0 °C, and HCl gas was bubbled in for about 2 min. A slow stream of nitrogen was then bubbled through the mixture to remove the excess HCl. A solution of 0.616 g of 85% *m*-chloroperbenzoic acid in 5 mL of CH_2Cl_2 was then added dropwise to the cold solution. The mixture was then warmed to room temperature, and after 1 h, the mixture was taken up into ether. The mixture was then washed with NaOH solution and saturated NaCl solution and dried over $MgSO_4$. The solvent was removed by using a rotary evaporator, and the residue slowly crystallized. The solid was slurried with hexanes and collected to give 726 mg (93%) of **23b**: mp 54–56 °C; ^1H NMR ($CDCl_3$) δ 7.82–7.59 (AA'BB' quartet, 4 H), 2.753 (s, 3 H), 2.009 (s, 6 H).

Preparation of Sulfoxides 34. General Procedures. A solution of the appropriate sulfide $ArCH(CH_3)SPh$ in 10 parts of CH_2Cl_2 was cooled to 0 °C, and a solution of 0.95 equiv of *m*-chloroperbenzoic acid in CH_2Cl_2 was slowly added dropwise to the stirred solution. The mixture was then stirred at room temperature for 30 min and taken up into ether, and an aqueous workup followed. The organic extract was washed with

NaOH solution and dried over MgSO4. After solvent removal on a rotary evaporator, the solid mixture of diastereomeric sulfoxides was slurried with hexanes and collected on a Buchner funnel. The following procedure is representative.

Addition of a solution of 1.69 g of 85% *m*-chloroperbenzoic acid in 25 mL of CH_2Cl_2 to a solution of 2.22 g of *p*-$CH_3C_6H_4CH(CH_3)SPh$ in CH_2Cl_2 at 0 °C gave 1.95 g (82%) of sulfoxide **34b**: mp 70–78 °C, as a mixture of diastereomers; ^1H NMR ($CDCl_3$) δ 7.5–6.8 (m, 9 H), 4.02 (q, J = 7.2 Hz, CH of minor diastereomer), 3.77 (q, J = 7.2 Hz, CH of major diastereomer), 2.32 (s, 3 H), 1.67 (d, J = 7.2 Hz, CH_3 of major diastereomer), 1.54 (d, J = 7.2 Hz, CH_3 of minor diastereomer). The ratio of the two diastereomers was 1.95 to 1 as determined by NMR.

Preparation of α-Bromo Sulfoxides 35. General Procedure. The appropriate sulfoxide **34**, dissolved in a mixture of $BrCCl_3$ and *tert*-butyl alcohol, was treated with powdered KOH by using a procedure analogous to that used to prepare the α-bromo sulfones, **13**. On completion of the reaction, the mixture was taken up into CH_2Cl_2, washed with water and saturated with NaCl solution, and dried over $MgSO_4$. The solvent was removed on a rotary evaporator, and the residue was chromatographed on silica gel and eluted with 25% ether in hexanes. The following procedure is representative.

A solution of 1.75 g of sulfoxide **34b** in 10 g of $BrCCl_3$ and 12 mL of *tert*-butyl alcohol was treated with 14.5 g of powdered KOH. After the mixture stirred for 2 h at room temperature, an aqueous workup followed as described above. Chromatography on 25 g of silica gel gave an oil which was slurried with hot hexane. On cooling, the product crystallized giving 0.52 g (22%) of the α-bromo sulfoxides **35b**, mp 60–90 °C. Two diastereomers were present in a 1.24 to 1 ratio as determined by NMR: ^1H NMR ($CDCl_3$) δ 7.8–7.2 (m, 7 H), 7.5–6.9 (m, 9 H), 2.367 (s, 3 H), 2.289 (s, CH_3 of the major diastereomer), 2.173 (s, CH_3 of the minor diastereomer). Anal. Calcd for $C_{15}H_{15}BrOS$: C, 55.74; H, 4.68. Found: C, 54.47; H, 4.56.

Bromination of **34a** for 5 h at room temperature by using the above procedure gave 33% of **35a**. The ratio of diastereomers before chromatography was about 4 to 1. After chromatography the ratio was 20 to 1 with the CH_3 of the major diastereomer appearing at δ 2.34. The CH_3 of the minor diastereomer appeared at δ 2.23.

Bromination of **34c** for 15 min in an ice–water bath according to the above procedure gave the unstable α-bromo sulfoxide **35c**. After chromatography the ratio of the diastereomers of **35c** was 5.9 to 1 with the CH_3 of the major diastereomer appearing at δ 2.28. The CH_3 of the minor diastereomer appeared at δ 2.17. On standing for short periods of time in $CDCl_3$, **35c** decomposed.

Preparation of α-Bromo Ketone 30. A solution of lithium diisopropylamide (prepared by the addition of 2.1 mL of 2.5 M *n*-butyllithium in hexane to 0.59 g of diisopropylamine in 10 mL of tetrahydrofuran) was cooled to −78 °C, and a solution of 0.95 g of *p*-$CH_3C_6H_4CH(CH_3)COPh$ in 3 mL of THF was added dropwise. The mixture was warmed to −35 °C and recooled to −78 °C. A solution of 0.73 g of $ClSiMe_3$ in 5 mL of THF was added, and the mixture was warmed to room temperature. After 1 h at room temperature, the mixture was taken up to 50 mL of an ether–Skelly F mixture (50/50). The mixture was washed with cold water and saturated NaCl solution and dried over $MgSO_4$. The solvent was removed by using a rotary evaporator, and the mixture was distilled to give 1.10 g (87%) of the silyl enol ether derivative; bp 104–110 °C (0.04 mm), as a mixture of E and Z isomers.

A solution of 0.250 g of the silyl enol ether mixture prepared above in 3 mL of CH_2Cl_2 was cooled to −78 °C, and a solution of 0.145 g of Br_2 in 2 mL of CH_2Cl_2 was added dropwise. The mixture was allowed to warm to room temperature, and the solvent was removed at reduced pressure with the last traces being removed at 0.1 mm. The unstable α-bromo ketone **30** (0.253 g, 99%) remained as a light-yellow oil which was used immediately for kinetic studies without further purification: ^1H NMR ($CDCl_3$) δ 7.81–7.74 (d, 2 H), 7.45–7.07 (m, 7 H), 2.340 (s, 3 H), 2.209 (s, 3 H).

Preparation of 33. Bromide **33** was prepared according to a procedure analogous to that previously described.[5a] Reaction of *p*-$CH_3C_6H_4C(CH_3)(OH)CF_3$ with PBr_3 at 40 °C for 2 h as previously described gave only recovered starting alcohol and none of the bromide **33**. Reaction at 85–93 °c for 4 h gave the desired bromide **33**, bp 76–77 °C (2 mm), with spectral properties identical with those previously reported.

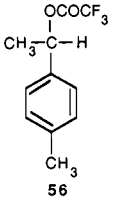
Preparation of α-Chloro Sulfide 43. A solution of 0.539 g of PhSCl in 10 mL of CH_2Cl_2 was cooled to −78 °C as a solution of 0.539 g of phenyldiazomethane in 3 mL of CH_2Cl_2 was added dropwise. Nitrogen evolution was instantaneous. On completion of the addition the color was completely discharged. The solvent was removed under reduced pressure, and the solid residue was distilled to give 0.740 g (85%) of the α-chloro sulfide **43**,[24] bp 115 °C (0.05 mm), which solidified on standing at −20 °C: ^1H NMR ($CDCl_3$) δ 7.8–7.0 (m, 10 H), 6.29 (s, 1 H).

Kinetics Procedures. Procedures were in certain cases analogous to those previously described.[1] However, determination of solvolysis rates of sulfones **14** was sometimes complicated by the secondary process in which benzenesulfinate is lost. Oxidation and/or disproportionation of the benzenesulfinic acid occurs at higher temperatures and, in some cases, prevented determination of rates by simple back-titration of unreacted buffering base as we have described previously.

The rates of solvolysis of **14a** and **14b** in methanol containing 0.025 M Et_3N were monitored by back-titration of the unreacted Et_3N with perchloric acid. Solvolysis of **14b** in TFE containing 0.025 M 2,6-lutidine was monitored by back-titration of the unreacted 2,6-lutidine with perchloric acid. Calculated infinity values were used due to the variable measured infinity values resulting from benzenesulfinate oxidation and/or disproportionation. Solvolysis of **14b** in HCO_2H containing 0.05 M sodium formate was monitored by back-titration of the unreacted sodium formate with perchloric acid. Solvolysis of **14b** in CD_3CO_2D containing pyridine as a buffering base was monitored by NMR by observing the disappearance of the methyl singlet at δ 3.15. Solvolyses of **14b** in 97% HFIP and in trifluoroacetic acid were monitored spectrophotometrically by observing the absorbance increase at 260 and 262.5 nm, respectively. Solvolysis of **14c** in methanol was monitored spectrophotometrically by observing the absorbance increase at 240 nm.

Determination of solvolysis rates of α-bromo sulfoxides **35** by acid titration procedures was also complicated by the fact that "infinity" values varied with time due to secondary reactions of the PhS(O)H produced in solvolysis. The solvolysis rate of **35a** in TFE containing 0.025 M 2,6-lutidine was therefore determined by aqueous titration of the bromide ion released as a function of time with aqueous silver nitrate. The solvolysis rates of **35b** in TFE containing 0.025 M 2,6-lutidine and in HCO_2H containing 0.05 M sodium formate were determined by back-titration of unreacted base with perchloric acid as previously described. Calculated infinity values were used. The solvolysis rate of **35c** in TFE containing 0.001 M Et_3N was monitored spectrophotometrically by observing the absorbance decrease at 237 nm. Clean first-order kinetic behavior was observed for **35a–c** despite the fact that measurements were made on the mixture of diastereomers described earlier. This is due to the fact that both diastereomers of **35b** appear to react at comparable rates, while **35a** and **35c** are reasonably free of the minor diastereomer.

Solvolysis rates for **29** and **30** in TFE, and for **43** in isopropyl alcohol, were monitored spectrophotometrically by observing absorbance changes at 201, 250, and 259 nm, respectively. Solvolysis rates of **33** in TFE containing 0.025 M 2,6-lutidine were monitored by back-titration of the unreacted 2,6-lutidine with perchloric acid as previously described. The solvolysis rate for trifluoroacetate **56** in TFE was determined spectrophotometrically at 228 nm. The solvolysis rate for trifluoroacetate **57** in TFE was determined by quenching the solvolysis mixture, removing the TFE solvent under vacuum, and analyzing it by NMR spectroscopy in $CDCl_3$.



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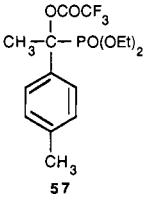

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Rate constants for all of the above procedures were calculated by the method of least squares. Correlation coefficients were all greater than 0.999 and in most cases greater than 0.9999. Rate constants given represent an average of at least two runs.

Solvolysis of Mesylate 14b in Trifluoroacetic Acid. Four milliliters of trifluoroacetic acid containing 0.2 M sodium trifluoroacetate was added to 145 mg of mesylate **14b** with rapid stirring. After 60 s the mixture was transferred with ether to 35 mL of cold saturated $NaHCO_3$ solution. After CO_2 evolution ceased, the organic phase was washed with another 40 mL of cold saturated $NaHCO_3$ solution and saturated NaCl solution and dried over $MgSO_4$. The solvent was removed on a rotary evaporator to give 124 mg of an oil. NMR analysis showed a mixture of the trifluoroacetate **15** (Ar = *p*-$CH_3C_6H_4$) and p-methylacetophenone, **16**. The oil was triturated with hexanes and cooled. The solid which formed was recrystallized from hexanes to give 77 mg (51%) of trifluoroacetate **15**: 113–114 °C; ^1H NMR (Ar = *p*-$CH_3C_6H_4$) $CDCl_3$ δ 7.78–7.65 (m, 3 H), 7.502 (t, J = 7.8 Hz, 3 H), 7.135 (d, J = 8.2 Hz, 2 H), 7.038 (d, J =

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8.2 Hz, 2 H), 2.356 (s, 3 H), 2.349 (s, 3 H); IR (Ar = p-$CH_3C_6H_4$) (CH_2Cl_2) $\nu_{C=O}$ 1800 cm^{-1}. In a separate experiment, heating a sample of mesylate **14b** in trifluoroacetic acid for 2 h at 55 °C gave only p-methylacetophenone, **16**.

In a separate experiment, 8.5 mg of trifluoroacetate **15**, isolated as described above, was dissolved in 0.5 mL of trifluoroacetic acid containing 0.2 M sodium trifluoroacetate in an NMR tube. The conversion of **15** to p-methylacetophenone, **16**, was monitored by 300-MHz NMR at 25 °C by observing the appearance of the two methyl signals of **16**, which appear downfield from the methyl signals of **15**. The first-order rate constant for this process is 3.05×10^{-5} s^{-1}. After completion of the reaction an authentic sample of p-methylacetophenone was added to the NMR tube to confirm its presence.

Solvolysis of Mesylate 14b in Acetic Acid. A solution of 74 mg of **14b** in 10 mL of HOAc containing 0.05 M NaOAc and 1% acetic anhydride was heated at 70 °C for 4 h. The mixture was then taken up into ether, the solution was washed with dilute NaOH solution and saturated NaCl solution, and the organic phase was dried over $MgSO_4$. The solvent was removed on a rotary evaporator, leaving 46 mg of a clear oil. Analysis by 300-MHz NMR showed the presence of acetate **17** (Ar = p-$CH_3C_6H_4$), the elimination product **18** (Ar = p-$CH_3C_6H_4$), and p-methylacetophenone, **16**, in a 25:15:60 ratio, respectively. Hexane was added to the oil which was cooled in a freezer. A solid crystallized, and the hexanes were decanted leaving 10 mg of acetate **17** (Ar = p-$CH_3C_6H_4$): IR (Ar = p-$CH_3C_6H_4$) (CH_2Cl_2) $\nu_{C=O}$ 1760 cm^{-1}; ^1H NMR (Ar = p-$CH_3C_6H_4$) ($CDCl_3$) δ 7.71-7.62 (m, 3 H), 7.466 (t, J = 7.8 Hz, 2 H), 7.13-7.02 (AA'BB' quartet, 4 H), 2.334 (s, 3 H), 2.277 (s, 3 H), 2.139 (s, 3 H). **18**: ^1H NMR (Ar = p-$CH_3C_6H_4$) ($CDCl_3$) δ 7.695 (d, 2 H), 7.526 (t, 1 H), 7.403 (t, 2 H), 7.212 (d, 2 H), 7.069 (d, 2 H), 6.596 (s, 1 H), 5.932 (s, 1 H), 2.315 (s, 3 H). p-Methylacetophenone, **16**, formed in the acetolysis was identified by NMR spectral comparison with an authentic sample.

Solvolysis of Mesylate 14b in Trifluoroethanol. A solution of 43 mg of **14b** in 6 mL of TFE containing 40 mg of Et_3N was kept at 25 °C for 7.5 h. The solvent was then removed on a rotary evaporator, and the residue was taken up into ether. The mixture was then washed with water, dilute KOH, and saturated NaCl and dried over $MgSO_4$. The ether was removed on a rotary evaporator to give 32 mg of a mixture of ketal **19a** (96%) and the elimination product **18** (4%). **19a**: ^1H NMR (Ar = p-$CH_3C_6H_4$) ($CDCl_3$) δ 7.43-7.35 (d, 2 H), 7.24-7.16 (d, 2 H), 3.90-3.66 (m, 4 H), 2.362 (s, 3 H), 1.666 (s, 3 H).

Solvolysis of Bromide 35b in Formic Acid. A solution of 258 mg of **35b** in 17 mL of formic acid containing 0.05 M sodium formate was heated at 55 °C for 5 h. The mixture was taken up into ether, washed with water, dilute Na_2CO_3, and saturated NaCl, and dried over $MgSO_4$. The solvent was removed on a rotary evaporator, and the residue was chromatographed on 6 g of silica gel and eluted with 5% ether in hexanes. Diphenyl disulfide, **36**, eluted first (41 mg) followed by p-methylacetophenone (75 mg, 70%), and finally the thiosulfonate **37**[25] (32 mg) eluted. These products were all identified by spectral comparison with authentic samples.

In a separate experiment, the reaction of 10 mg of **35b** in 0.7 mL of formic acid containing 0.05 M sodium formate was monitored directly by 300-MHz NMR at 45 °C. p-Methylacetophenone, **16**, was observed to form at the same rate that **35b** disappeared. No buildup of an intermediate could be observed. The two diastereomers of **35b** disappeared at rates which were identical within the limits of NMR determination.

Solvolysis of Bromide 35b in Trifluoroethanol. A solution of 170 mg of **35b** in 8 mL of TFE containing 0.075 M 2,6-lutidine was heated for 5 h at 60 °C. The solvent was removed on a rotary evaporator, and the residue was taken up into ether, washed with water and saturated NaCl, and dried over $MgSO_4$. NMR analysis showed the presence of ketal **19a** and p-methylacetophenone, **16**, along with the elimination product **38** in a 2.3:1.3:1 ratio, respectively. Also present were diphenyl disulfide, **36**, and the thiosulfonate **37**. The residue was chromatographed on 7 g of silica gel and eluted with 5% ether in hexanes. The initial fraction (61 mg) contained a mixture of ketal **19a** and diphenyl disulfide, **36**, which were identified by spectral methods and by comparison of gas chromatographic retention times with those of authentic samples. p-Methylacetophenone, **16** (32 mg, 45%), eluted next, followed by **37** (22 mg). The solvent polarity was then changed to 100% ether, and the elimination product **38** (28 mg, 22%) eluted: ^1H NMR (Ar = p-$CH_3C_6H_4$) ($CDCl_3$) δ 7.47-7.27 (m, 5 H), 7.09 (s, 4 H), 6.21 (s, 1 H), 5.88 (s, 1 H), 2.31 (s, 3 H).

Solvolysis of Bromide 35b in 70% Aqueous Acetone. A solution of 144 mg of **35b** in 5 mL of 70% aqueous acetone (by volume) containing 55 mg of Et_3N was heated at 70 °C for 46 h and at 80 °C for 16 h. The solvent was removed on a rotary evaporator, and the residue was taken up into ether, washed with water, dilute HCl, and saturated NaCl solution, and dried over $MgSO_4$. After solvent removal on a rotary evaporator, the residue (102 mg) was analyzed by NMR and gas chromatography, which showed p-methylacetophenone, **16**, and the elimination product **38** in a 86 to 14 ratio, along with diphenyl disulfide, **36**.

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Preparation and Regiospecific Cyclization of Alkenyllithiums[1]

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Abstract: A two-step, one-pot sequence has been developed that provides an anionic route to functionalized carbocycles containing five- or six-membered rings. Primary alkenyllithiums, which are prepared in excellent yield by metal-halogen interchange between the appropriate iodide and t-BuLi at -78 °C, are stable at low temperature. These species have been found to undergo regiospecific, and in several instances totally stereoselective, isomerization at elevated temperature to give a five- or six-membered ring bearing a CH_2Li moiety that may be functionalized with electrophiles. The more complex behavior of secondary alkenyllithiums is discussed.

The construction of C-C bonds is arguably the most important operation in organic synthesis. It is therefore not surprising that much recent interest has focused on the synthetic utility[2] of the highly regiospecific isomerization of 5-hexen-1-yl radicals to cyclopentylmethyl-containing products.[3] A major disadvantage of this otherwise powerful methodology is the fact that the product radical is difficult to trap in a controlled, intermolecular reaction to give a functionalized product.[2,4] A conceptually simple solution to this limitation of radical cyclizations would seem to be provided by the well-established tendency of various organometallic de-

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(1) Presented in part at the 190th National Meeting of the American Chemical Society, Chicago, IL, Sept 1985; ORGN 121.

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