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Homoallyl−Cyclopropylcarbinyl Cation Manifold. Trimethylsilyl versus Aryl Stabilization

Xavier Creary,* Benjamin D. O'Donnell, and Marie Vervaeke

Department of Chemistry and Biochemistry, University of Notre Dame, Notre Dame, Indiana 46556

creary.1@nd.edu

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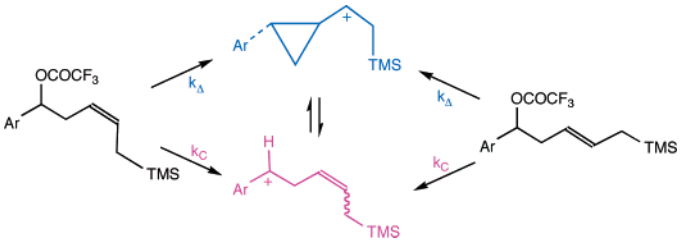

A series of *E*- and *Z*-1-aryl-5-trimethylsilyl-3-buten-1-yl trifluoroacetates were solvolyzed in CD_3CO_2D, and rates of reaction as well as products derived from these reactions were determined. Hammett plots showed a break, which was indicative of a mechanistic change from a k_C process when the most electron-donating substituents were attached to the aryl group to a k_Δ process involving formation of cyclized β-silyl carbocation intermediates for electron-withdrawing groups. In the case of *p*-CH_3O substitution (a k_C extreme), the cationic intermediate captures solvent (95%) or loses a proton (5%). In the case of *m*-CF_3 substitution (a k_Δ extreme), the β-silyl cation intermediate desilylates to give vinylcyclopropane products. Substituents with intermediate electronic properties give more complex product mixtures. Solvolysis of pure *Z*-trifluoroacetate (*p*-CH_3) gives small amounts of *E*-trifluoroacetate (*p*-CH_3) along with the *E*-substitution product. This isomerization suggests that the cyclized β-silyl cation can isomerize and then reopen to a classical aryl-stabilized cation. By way of contrast, B3LYP/6-31G* computational studies show only cyclized β-silyl cations as energy minima. Open k_C cations are higher-energy nonminimum energy structures.

Introduction

Stabilization of carbocations **1** by adjacent silicon is quite dramatic, and this phenomenon has been extensively studied quantitatively by Lambert.[1] This stabilization by β-silyl groups is due to a favorable interaction between the cation vacant p-orbital and the adjacent C−Si σ-bond. We have shown that a similar interaction occurs in carbenes **3**, and this interaction leads to facile rearrangement of carbenes **3** to alkenes **4** via silicon migration.[2] Taylor has recently developed a synthesis of vinylcyclopropanes **6** from **5**.[3] It was suggested that "activation" of **5** leads to neighboring double bond participation and subsequent formation of the β-silyl-stabilized carbocation **8**. Subsequent loss of the trimethylsilyl group ultimately leads to the vinylcyclopropanes **6**. Use of enantiomerically pure alcohols **5** led, in some cases, to enantiomerically pure cyclopropanes **6**,[3a] whereas in other cases, there was loss of enantioselectivity.[4]

In light of our interest in carbocation chemistry,[5] the phenomenon of neighboring group participation,[6] and the

(1) (a) Lambert, J. B.; Wang, G.-t.; Finzel, R. B.; Teramura, D. H. *J. Am. Chem. Soc.* **1987**, *109*, 7838. (b) Lambert, J. B.; Chelius, E. C. *J. Am. Chem. Soc.* **1990**, *112*, 8120. (c) Lambert, J. B. *Tetrahedron* **1990**, *46*, 2677. (d) Lambert, J. B.; Liu, X. *J. Organomet. Chem.* **1996**, *521*, 203. (e) Lambert, J. B.; Zhao, Y.; Emblidge, R. W.; Salvador, L. A.; Liu, X.; So, J. H.; Chelius, E. C. *Acc. Chem. Res.* **1999**, *32*, 183.

(2) (a) Creary, X.; Wang, Y.-X. *J. Org. Chem.* **1994**, *59*, 1604−1605. (b) Creary, X.; Jiang, Z.; Butchko, M.; McLean, K. *Tetrahedron Lett.* **1995**, *37*, 579. (c) Creary, X.; Butchko, M. A. *J. Org. Chem.* **2001**, *66*, 1115. (d) Creary, X.; Butchko, M. A. *J. Org. Chem.* **2002**, *67*, 112.

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(4) Melancon, B. J.; Perl, N. R.; Taylor, R. E. *Org. Lett.* **2007**, *9*, 1425−1428.

(5) Creary, X. *Chem. Rev.* **1991**, *91*, 1625.

(6) (a) Creary, X.; Mehrsheikh-Mohammadi, M. E. *J. Org. Chem.* **1986**, *51*, 7. (b) Creary, X.; Aldridge, T. *J. Org. Chem.* **1988**, *53*, 3888.

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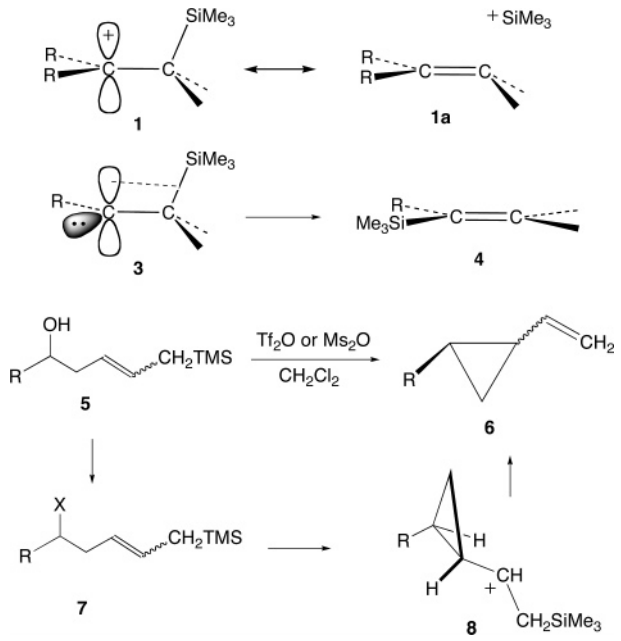
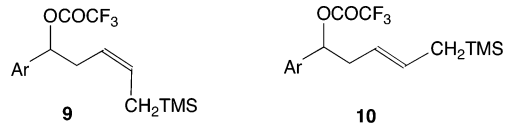


effect of silicon on adjacent electron-deficient reactive intermediates,[2] we have turned our attention to the reactions of a series of *cis*-trifluoroacetates **9** and *trans*-trifluoroacetates **10**. It was our intent to determine, by kinetic studies, the mechanistic details of reactions of these substrates under solvolytic conditions. When loss of enantioselectivity occurs in formation of **6**, what are the reasons? Is there a mechanistic change from the k_Δ to the k_C process, and if so, where does this change occur? Reported here are the results of kinetic studies on **9** and **10** as well as computational studies on related β-silyl-substituted carbocations.

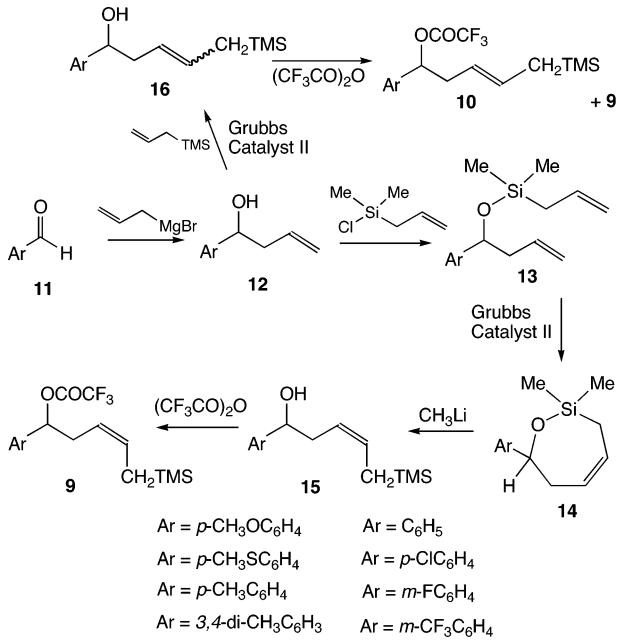


Results and Discussion

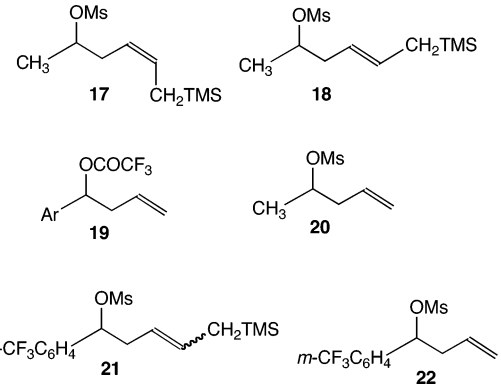
Synthetic Aspects. The pure *cis*-trifluoroacetates **9** were prepared using the methodology in Scheme 1 developed by the Taylor group.[3a−c] Silylation of the homoallylic alcohols **12** with allyldimethylsilyl chloride followed by intramolecular olefin metathesis gave silyl ethers **14** which were cleaved to the pure *cis*-alcohols **15**. The *trans*-trifluoroacetates **10** were prepared using a cross-metathesis reaction of **12** with allyltrimethylsilane.[3a] The inseparable mixture of alcohols **16** was converted to a mixture of trifluoroacetates **10** and **9** (*E*/*Z* ratio = 3). Fortunately, the ^{1}H NMR signals due to the trimethylsilyl groups of **10** and **9** are cleanly separated. This permits facile determination of solvolysis rates of the *trans*-trifluoroacetates **10** using this mixture. For comparison purposes, the mesylates **17**, **18**, and **21** were also prepared and studied along with the substrates **19**, **20**, and **22**, which contain double bonds not activated by trimethylsilyl groups.

Kinetic Studies. Rates of reaction of trifluoroacetrates and mesylates were measured in CD_3CO_2D containing 1.5 equiv of 2,6-lutidine and were monitored by 600 MHz ^{1}H NMR spectroscopy. Rate data are summarized in Table 1, and the corresponding Hammett plots for the data are shown in Figures 1 and 2. Immediately apparent is the fact that these plots are

SCHEME 1



not linear. These breaks in the Hammett plots for solvolyses of substrates **9** and **10** are indicative of changes in the mechanism as substituents change from electron-withdrawing to electron-donating.[7] The slope of the Hammett plot for *cis*-trifluoroacetates



9 in Figure 1 is −6.4 for the most electron-donating substituents, and this is indicative of a relatively high demand for stabilization of the cationic intermediate by the aryl substituent, i.e., a k_C mechanism. On the other hand, the reduced slope of −2.5 for the more electron-withdrawing substituents is indicative of a different cationic intermediate with less demand for aryl group stabilization, i.e., a k_Δ mechanism. Analogous behavior is observed for the *trans*-isomers **10** in Figure 2.

Silylated/Unsilylated Rate Ratio. A comparison of the acetolysis rates of **9** and **10** with that of the homoallylic trifluoroacetates **19** is informative. The silylated substrates **9** and **10** are all more reactive than the unsilylated analogues **19**. The *p*-OCH_3 derivatives of **9** and **10** are twice as reactive as **19** (*p*-OCH_3), and this indicates that the double bond in **19** (*p*-OCH_3) is slightly more inductively electron-withdrawing than are the nonparticipating double bonds in **9** (*p*-OCH_3) and **10** (*p*-OCH_3). However, there is a smooth increase in the **9**/**19** and **10**/**19** rate ratios as substituents become more electron-

(7) Gassman, P. G.; Fentiman, A. F. *J. Am. Chem. Soc.* **1970**, *92*, 2549.

TABLE 1. Solvolysis Rate Constants for Substrates in CD_3CO_2D

substrate	temp (°C)	k (s^{-1})[a]
9 (*m*-CF_3)	80.0	1.81×10^{-5}
	60.0	2.25×10^{-6}
	25.0[b]	3.0×10^{-8}
9 (*m*-F)	80.0	3.64×10^{-5}
	60.0	4.52×10^{-6}
	25.0[b]	6.1×10^{-8}
9 (*p*-Cl)	65.0	3.15×10^{-5}
	45.0	3.22×10^{-6}
	25.0[b]	2.4×10^{-7}
9 (*p*−H)	60.0	3.29×10^{-5}
	40.0	3.34×10^{-6}
	25.0[b]	4.9×10^{-7}
9 (*p*-CH_3)	25.0	2.96×10^{-6}
9 (3,4-di-CH_3)	25.0	4.61×10^{-6}
9 (*p*-SCH_3)	25.0	5.92×10^{-5}
9 (*p*-OCH_3)	25.0	7.77×10^{-4}
10 (*m*-CF_3)	80.0	3.60×10^{-5}
	60.0	4.17×10^{-6}
	25.0[b]	4.8×10^{-8}
10 (*m*-F)	80.0	7.50×10^{-5}
	60.0	9.01×10^{-6}
	25.0[b]	1.1×10^{-7}
10 (*p*-Cl)	65.0	6.02×10^{-5}
	45.0	6.23×10^{-6}
	25.0[b]	4.8×10^{-7}
10 (*p*-H)	60.0	7.21×10^{-5}
	40.0	7.38×10^{-6}
	25.0[b]	1.1×10^{-6}
10 (*p*-CH_3)	25.0	6.82×10^{-6}
10 (3,4-di-CH_3)	25.0	1.12×10^{-5}
10 (*p*-SCH_3)	25.0	7.58×10^{-5}
10 (*p*-OCH_3)	25.0	7.77×10^{-4}
17	25.0	3.27×10^{-5}
18	25.0	5.47×10^{-5}
19 (*p*-OCH_3)	25.0	3.88×10^{-4}
19 (*p*-SCH_3)	25.0	2.81×10^{-5}
19 (3,4-di-CH_3)	25.0[b]	7.8×10^{-7}
19 (*p*-H)	25.0[b]	6.0×10^{-9}
20	25.0[b]	5.1×10^{-8}
***cis*-21**	25.0	2.48×10^{-3}
***trans*-21**	25.0	4.75×10^{-3}
22	25.0	5.73×10^{-6}

[a] Maximum standard deviation in duplicate runs was ±2%. [b] Extrapolated from data at higher temperatures.

TABLE 2. Silylated/Unsilylated Rate Ratios in Solvolyses in CD_3CO_2D at 25 °C

substituent	**9**/**19**	**10**/**19**
p-OCH_3	2.0	2.0
p-SCH_3	2.1	2.7
3,4-di-CH_3	5.9	14.3
p-H	83	183
m-CF_3	433[a]	830[b]

[a] This is the *cis*-**21**/**22** mesylate ratio. [b] This is the *trans*-**21**/**22** mesylate ratio.

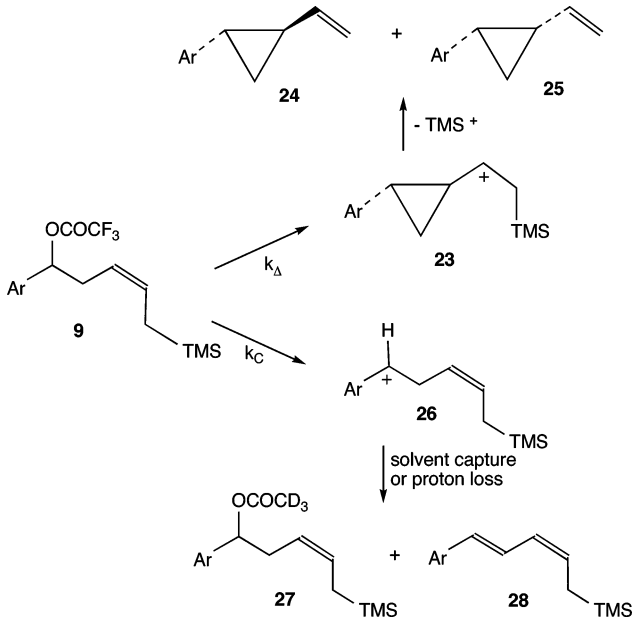
withdrawing (Table 2). This is attributed to the onset of neighboring double bond participation in **9** and **10**, which leads to increasing anchimeric assistance as substituents become more electron-withdrawing.[8] In the case of the strongly electron-withdrawing *m*-CF_3 substituent, the silylated/unsilylated ratio was determined for the corresponding mesylates because the trifluoroacetates are quite unreactive. Although both *E*- and *Z*-mesylates **21** are highly reactive substrates in CD_3CO_2D (half-lives of 146 and 280 s, respectively), they can be prepared and

(8) Brown, H. C. *The Nonclassical Ion Problem*; Plenum Press: New York, 1977.

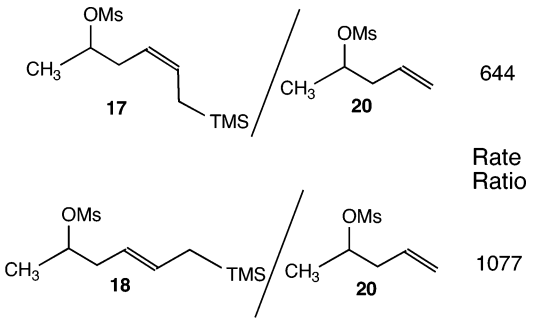
TABLE 3. Product Ratios from Solvolyses of 9 in CD_3CO_2D

substrate	**24**	**25**	**27**	**28**	**29**
9 (*m*-CF_3)	95	5	0	0	0
9 (*m*-F)	95	5	0	0	0
9 (*p*-Cl)	91	6	3	0	0
9 (*p*-H)	86	5	7	1	1
9 (*p*-CH_3)	52	2	36	5	5
9 (3,4-di-CH_3)	44	2	43	6	5
9 (*p*-SCH_3)	6	0	89	3	2
9 (*p*-OCH_3)	0	0	95	5	0

SCHEME 2



studied. They are 433 and 830 times faster reacting, respectively, than the mesylate **22** that has no silyl group. Anchimeric assistance in **21** is becoming much more pronounced due to increased demand for cation stabilization by the participating double bonds in **21**. Finally, if one replaces the cation stabilizing aryl group with a simple methyl group, as in mesylates **17** and **18**, the silylated/unsilylated ratio reaches values of 644 and 1077.[9]



Product Studies. The products derived from solvolyses of **9** in CD_3CO_2D are shown in Table 3, and they are quite dependent on the substituent. The electron-withdrawing *m*-CF_3 and *m*-F substituents lead to exclusively cyclized products **24** and **25**,

(9) Note that the acetolysis rate of unsilylated mesylate **20** is somewhat assisted by the homoallylic double bond, as revealed by the formation of small amounts of cyclopropane products from **20**.

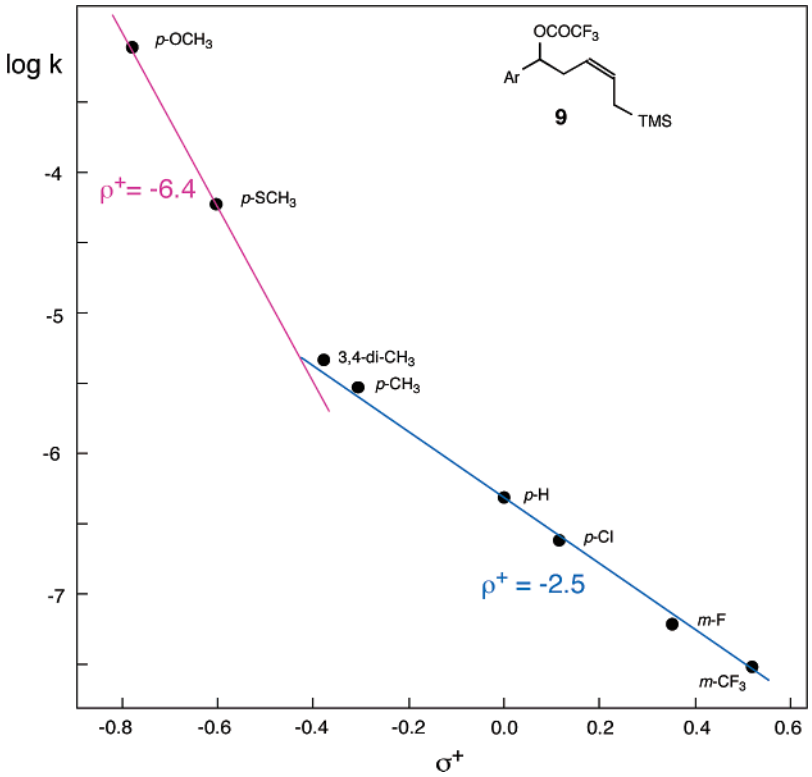


FIGURE 1. Plot of log *k* for reaction of **9** at 25 °C in CD_3CO_2D vs σ^+.

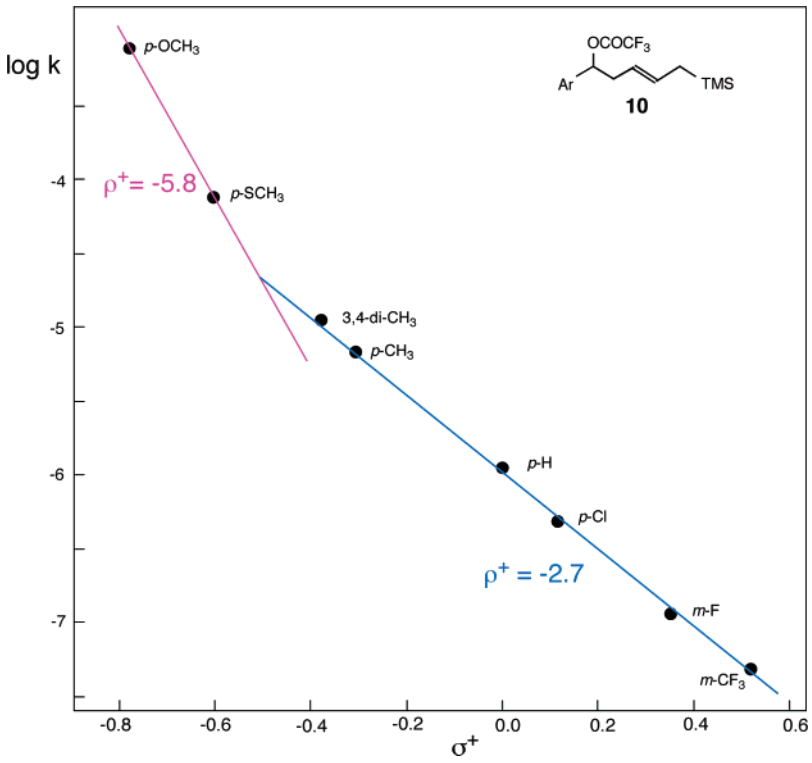


FIGURE 2. Plot of log *k* for reaction of **10** at 25 °C in CD_3CO_2D vs σ^+.

and this is indicative of solvolysis proceeding completely via the k_Δ pathway (cation **23**). The aliphatic analogues **17** and **18** are also k_Δ substrates which give the completely cyclized products *trans*- and *cis*-1-methyl-2-vinylcyclopropane. With *p*-Cl and *p*-H substituents, one begins to see small amounts of products **27** and **28** that are not cyclized. These products are derived from the capture of acetic acid or proton loss from an open carbocation **26** (the k_C process; Scheme 2). They assume increasing importance with *p*-CH_3, 3,4-di-CH_3, and *p*-SCH_3 substitution. In the case of **9** (*p*-OCH_3), there is no cyclized vinylcyclopropane product; i.e., the k_Δ process is bypassed in favor of the k_C solvolysis route.

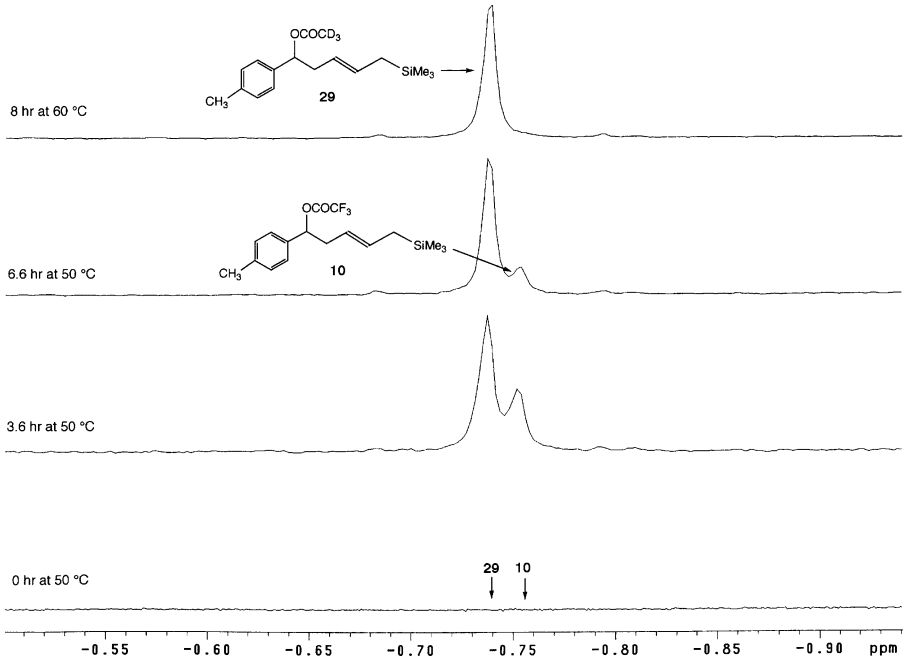


FIGURE 3. Evolving upfield region of ^{1}H NMR spectra during solvolysis of **9** (*p*-CH_3) in CD_3CO_2D showing the developing TMS groups of **10** (*p*-CH_3) and **29** (*p*-CH_3).

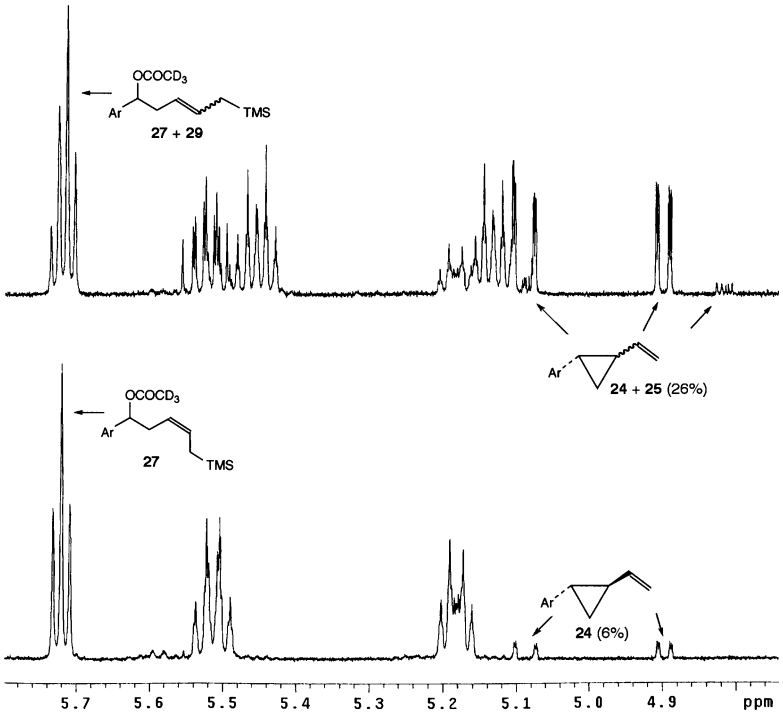
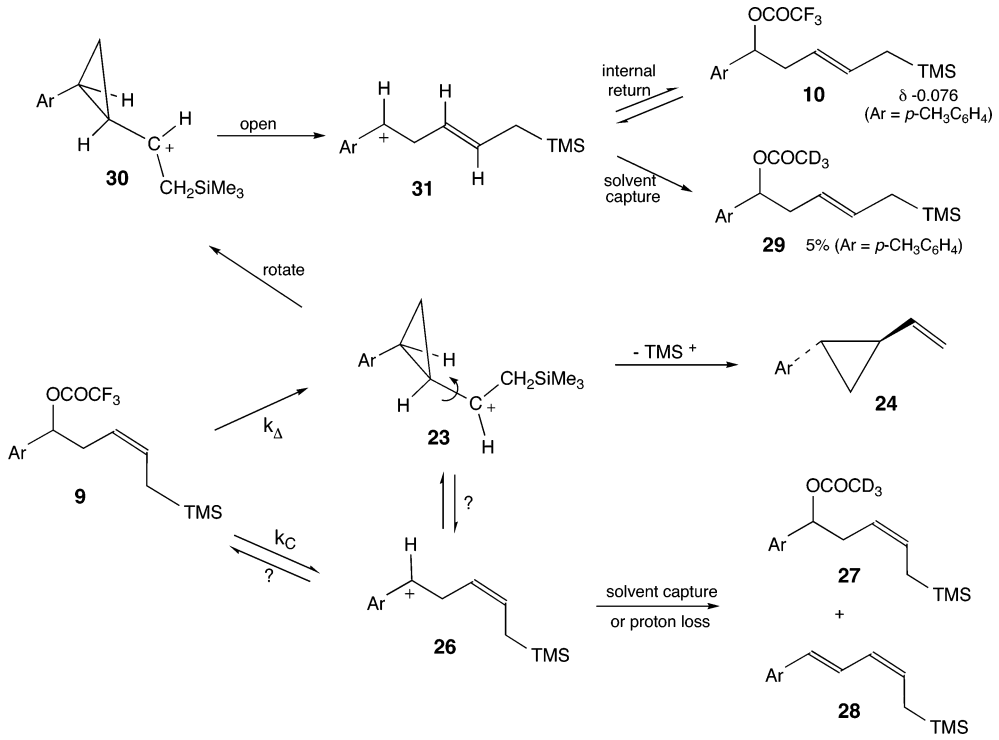


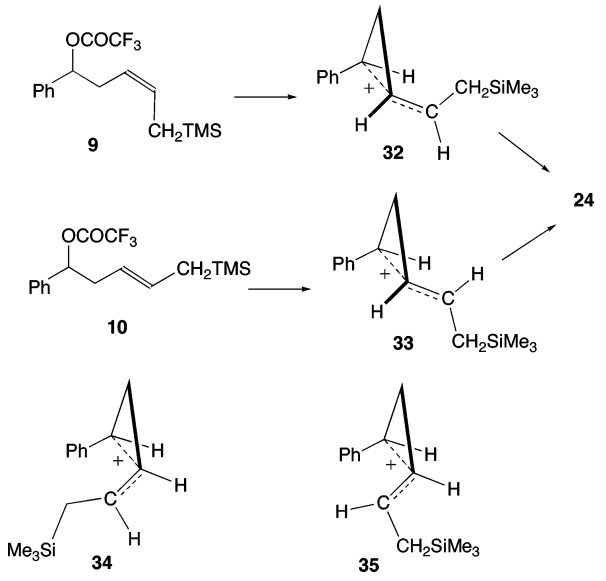
FIGURE 4. ^{1}H NMR spectra of solvolysis products from *cis*-**9** (*p*-SCH_3) in CD_3CO_2D (bottom) and from a 24:76 mixture of *cis*-**9** (*p*-SCH_3) and *trans*-**9** (*p*-SCH_3) (top).

Careful examination of the products formed when pure *cis*-trifluoroacetates **9** (*p*-H, *p*-CH_3, 3,4-di-CH_3, and *p*-SCH_3) react in CD_3CO_2D shows the presence of small amounts (1−5%) of *trans*-acetates **29**. What is the origin of these isomerized products? Careful monitoring of these reactions by ^{1}H NMR offers an explanation. Figure 3 shows a portion of the evolving upfield region of the ^{1}H NMR spectrum during solvolysis of *cis*-**9** (*p*-CH_3). Note that there is no trace of *trans*-**10** (*p*-CH_3) at the beginning of the reaction. However, as the reaction proceeds, there is a buildup of a small amount of *trans*-**10** (*p*-CH_3) at −0.076 ppm, which is slightly more reactive than *cis*-**9** (*p*-CH_3). It is suggested that the source of *trans*-acetate **29** (which appears at −0.074 ppm) is isomerization of *cis*-**9**. The mechanism of this isomerization is suggested in Scheme 3. The k_Δ process leads to the cyclized cation **23**. In this cation, the large β-silicon stabilization results in a small barrier to rotation about the C3−C4 bond and isomerization to **30** can occur. Competing with loss of trimethylsilyl from **30** is reopening of cation **30** to the aryl-stabilized cation **31**, which now has a trans double bond configuration. Internal return of the trifluoroacetate

SCHEME 3



ion accounts for the transient appearance of *trans*-**10** (*p*-CH_3), and solvent capture leads to the *trans*-acetate **29**.

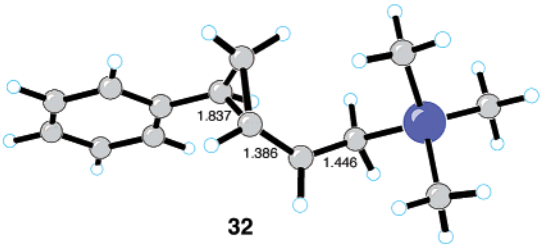


A question arises as to the ability of closed cation **23** and open cation **26** to interconvert. In view of the suggestion that closed cation **30** can open to **31**, it is a likely possibility that **23** can open to **26**. This suggestion is relevant to the observation of Taylor,[4] who observed some loss of enantiomeric purity when optically active **5** (R = C_6H_5, *p*-$CH_3C_6H_4$) was cyclized to the vinylcyclopropanes **24** via in situ conversion to the mesylate. A clean k_Δ process should lead to *complete* inversion at the ionization center. However, competing opening of **23** (Ar = C_6H_5, *p*-$CH_3C_6H_4$) to achiral **26** and reclosure could account for partial loss of enantiomeric purity in the product **24**. Competing k_C ionization of **9** to give achiral **26** followed by closure to give racemic **23** or internal return to give racemic starting material are other processes that would lead to loss of optical purity in **24**.

Precise ratios of products derived from solvolyses of *trans*-trifluoroacetates **10** are somewhat more difficult to measure because samples of **10** used for study all contained approximately 25% of the *cis*-trifluoroacetates **9**. However, the *trans*-trifluoroacetates **10** gave slightly more cyclized vinylcyclopropanes **24** and **25** than the *cis*-trifluoroacetates **9**, which is consistent with the slightly greater rate enhancements due to the competing k_Δ processes. For example, Figure 4 shows a comparison of the vinylcyclopropanes formed from pure *cis*-**9** (*p*-SCH_3) (bottom; 6%) with the vinylcyclopropanes formed from a 24:76 mixture of **9**/**10** (top; 26%). This means that 32% vinylcyclopropanes would be produced from "pure" *trans*-**10** (*p*-SCH_3). The kinetic data, which show that *trans*-**10** (*p*-SCH_3) reacts 2.7 times faster than **19** (*p*-SCH_3), are consistent with a small k_Δ component in the rate of *trans*-**10** (*p*-SCH_3).

Computational Studies. B3LYP/6-31G* computational studies[10] have been carried out to shed light on the cationic intermediates involved in these studies. These calculations show two minimum-energy structures (**32** and **33**) that could be potentially derived from *cis*-trifluoroacetate **9** and *trans*-trifluoroacetate **10**. These cations would produce the major solvolysis product, *trans*-vinylcyclopropane **24**. The cation **33** (derived from **10**) lies 1.4 kcal/mol lower in energy than the cation **32** (derived from **9**). This energy difference is in line with the slightly faster solvolyses rates of *trans*-isomers **10** relative to *cis*-isomers **9** when the k_Δ process dominates. Both cations **32** and **33** show elongated cyclopropane bonds (1.837 and 1.787 Å, respectively). These cations are best described as partially closed homoallyic cations, where cyclopropane bond formation is more extensive than in the cation **36** where there

(10) Frisch, M. J. et al. *Gaussian 03*, revision C.01; Gaussian, Inc.: Wallingford, CT, 2004.



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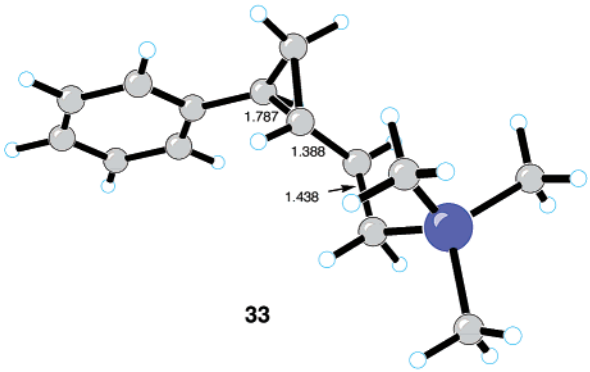

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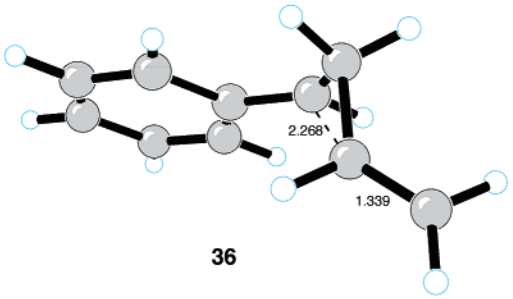

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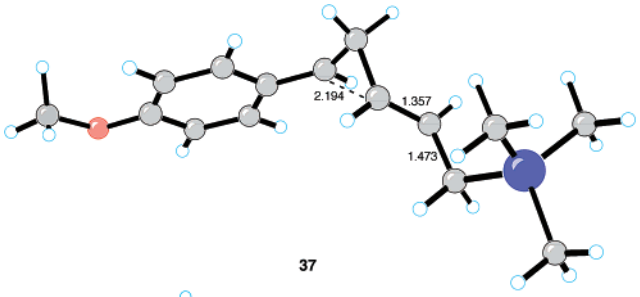

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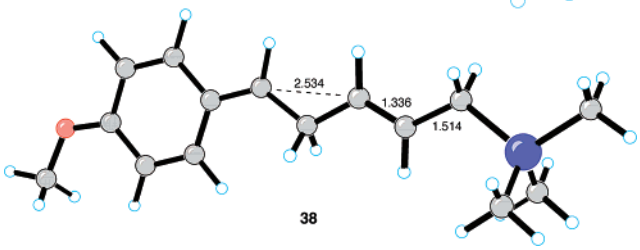

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is no silicon to stabilize the cationic intermediate. However, cyclopropane bond formation, although more advanced than in cation **36**, is still less than complete. β-Silyl stabilization of the B3YLP/6-31G* cations **32** and **33** is insufficient to completely offset phenyl stabilization. As expected on the basis of steric factors, the related cations **34** and **35** that would lead to *cis*-vinylcyclopropanes **25** lie 7.0 and 2.3 kcal/mol higher in energy than **33**, respectively.

It is interesting to note that no minimum-energy structures can be found that would correspond to the open cation **26**. Even in the case of the *p*-OCH_3-substituted cation **37**, there is still significant cyclopropane bond formation (C1−C3 bond = 2.194 Å) as well as silyl stabilization of this cation. Thus all cations have varying degrees of both aryl and trimethylsilyl stabilization. If one introduces artificial constraints into the calculation to prevent cyclization (by fixing the C^+−C2−C3−C4 dihedral angle in **38** at 180°), then the resultant *p*-OCH_3-stabilized benzylic cation **38** (not an energy minimum) is 11.2 kcal/mol less stable than the closed form **37**. Although this computational picture sheds some light on the mode of cation stabilization, open structures corresponding to **26** are all higher in energy at the B3LYP/6-31G* level and do not correspond to energy minima. However, we believe that distinct open and closed ions that can interconvert are the better mechanistic picture of what happens in solution. The Hammett plots in Figures 1 and 2 support this view of distinct open cations **26** and closed cations **23**, as does the formation of small amounts of *trans*-acetates **29** from pure *cis*-trifluoroacetates **9**. The gas-phase nature of the computational studies may account for the discrepancy with solution results.

Conclusions

The nonlinear Hammett plot in the solvolyses of trifluoroacetates **9** and **10** in CD_3CO_2D is indicative of a change in mechanism as substituents vary from electron-donating to electron-withdrawing. Thus, *p*-OCH_3 substitution leads to a k_C mechanism involving unassisted formation of an open carbocation **26** that undergoes solvent capture or proton loss. At the other mechanistic extreme, *m*-CF_3 substitution results in a k_Δ process as the silyl-substituted double bond assists in the ionization process to form a closed β-silyl carbocation **23**. This β-silyl cation suffers desilylation to give vinylcyclopropanes. This relatively simple mechanistic picture is complicated by the apparent interconversion of open and closed cations **26** and **23**, as evidenced by the formation of small amounts of *trans*-**10** and *trans*-**29** during the solvolysis of pure *cis*-**9** with certain substituents. In agreement with rate data, computational studies at the B3LYP/6-31G* level show that the closed cation **33** derived from trans double bond participation in **10** (Ar = C_6H_5) is 1.4 kcal/mol more stable than cation **32** derived from *cis*-**9** (Ar = C_6H_5). Open cations **26** are not energy minima at the B3LYP/6-31G* computational level even when Ar = *p*-CH_3-OC_6H_4. This computational finding is in conflict with conclusions based on the nonlinear Hammett plots that implicate discrete open as well as closed cations from **9** and **10** depending on aryl substitution.

Experimental Section

Preparation of Silyl Ethers 13. General Procedure. A solution of the appropriate homoallylic alcohol **12** (5 mmol) (prepared by reaction of allylmagnesium chloride with the corresponding benzaldehyde **11**) in CH_2Cl_2 containing 10 mmol of Et_3N and 5 mmol of imidazole was cooled to −10 °C, and 6 mmol of allyldimethylsilyl chloride in CH_2Cl_2 was added dropwise. The mixture was allowed to warm to room temperature. and after 1 h, the mixture was transferred to a separatory funnel with 25 mL of ether. The mixture was washed with cold water and cold dilute HCl solution. The organic phase was dried over a mixture of Na_2SO_4 and $MgSO_4$ and filtered, and the solvent was removed using a rotary evaporator. The residue was distilled to give the silyl ethers **13**. The following procedure is representative.

Reaction of 688 mg of alcohol **12** (Ar = C_6H_5) with 940 mg of Et_3N and 316 mg of imidazole in 8 mL of CH_2Cl_2 with 719 mg of allyldimethylsilyl chloride gave 834 mg of **13** (Ar = C_6H_5) (73%) (bp 61−62 °C) (0.1 mm). ^{1}H NMR of **13** (Ar = C_6H_5) ($CDCl_3$) δ 7.34−7.22 (m, 5 H), 5.76 (m, 1 H), 5.71 (m, 1 H), 5.06−5.00 (m, 2 H), 4.83 (m, 1 H), 4.81 (m, 1 H), 4.69 (d of d, J = 7.6, 5.3 Hz, 1 H), 2.48 (m, 1 H), 2.40 (m, 1 H), 1.55 (t, J = 1.2 Hz, 1 H), 1.54 (t, J = 1.2 Hz, 1 H), 0.45 (s, 3 H), 0.43 (s, 3 H). ^{13}C NMR of **13** (Ar = C_6H_5) ($CDCl_3$) δ 144.7, 135.2, 128.1, 127.2, 125.9, 117.0, 113.6, 75.1, 45.1, 24.9, −1.9, −2.0. Exact mass (CI) calcd for $C_{15}H_{23}OSi$ 247.1518, found 247.1488.

Preparation of Cyclic Silyl Ethers 14. General Procedure. A solution of approximately 3 mmol of silyl ether **13** in 30 mL of freshly distilled CH_2Cl_2 was stirred at room temperature as 20−30 mg of Grubbs second-generation catalyst, tricyclohexylphosphine-(1,3-bismesityl-4,5-dihydroimidazol-2-ylidene)(benzylidine) ruthenium dichloride, was added in one portion. The mixture was either stirred at room temperature or refluxed. The progress of the reaction was monitored by removal of small portions and analysis by ^{1}H NMR. An additional 25 mg of catalyst was added if the reaction ceased to progress. On completion of the reaction, the CH_2Cl_2 was removed using a rotary evaporator and the residue was taken up into hexanes and filtered through a small amount of silica gel to remove the insoluble catalyst. Solvent removal gave the crude silyl ethers **14** that were used without further purification. The following procedure is representative.

Reaction of 649 mg of silyl ether **13** (Ar = C_6H_5) in 28 mL of CH_2Cl_2 with 20 mg of Grubbs second-generation catalyst for 5 h at room temperature followed by the addition of 30 mg of fresh catalyst and reaction for 3 h at room temperature gave, after filtering through 2 g of silica gel, 424 mg of **14** (Ar = C_6H_5) (74%) as a clear oil. ^{1}H NMR of **14** (Ar = C_6H_5) ($CDCl_3$) δ 7.38 (m, 2 H), 7.34 (m, 2 H), 7.24 (m, 1 H), 5.93 (m, 1 H), 5.69 (m, 1 H), 5.02 (d of d, J = 9.7, 1.6 Hz, 1 H), 2.67 (m, 1 H), 2.38 (d of d of d, J = 15.4, 7.7, 1.8 Hz, 1 H), 1,87 (d of d of d, J = 15.0, 7.7, 1.8 Hz, 1 H), 1.54 (d of d, J = 15.0, 7.7 Hz, 1 H), 0.23 (s, 3 H), 0.22 (s, 3 H). ^{13}C NMR of **14** (Ar = C_6H_5) ($CDCl_3$) δ 145.5, 128.9, 128.2, 126.9, 126.5, 125.3, 74.8, 39.9, 18.5, −0.1, −2.0. Exact mass (FAB) calcd for $C_{13}H_{18}OSi$ 218.1127, found 218.1140.

Preparation of Alcohols 15. General Procedure. A solution of approximately 1 mmol of silyl ether **14** in 5−8 mL of anhydrous tetrahydrofuran was cooled to −78 °C, and 1.5 equiv of 1.6 M methyllithium in ether was added dropwise. The solution was allowed to warm to room temperature, and stirring was continued for 1 h. The solution was re-cooled to −30 °C, and water was added. The mixture was transferred to a separatory funnel using ether, and the organic extract was separated, washed with water and saturated NaCl solution, and dried over $MgSO_4$. The solvent was removed using a rotary evaporator, and the residue was chromatographed on silica gel. The product **15** was eluted with 10% ether in hexanes. The following procedure is representative.

Reaction of 344 mg of silyl ether **14** (Ar = C_6H_5) in 8 mL of THF with 1.4 mL of 1.6 M methyllithium in ether gave, after chromatography on 5.5 g of silica gel, 310 mg of alcohol **15** (Ar = C_6H_5) (84%).[11] ^{1}H NMR of **15** (Ar = C_6H_5) ($CDCl_3$) 7.40−7.34 (m, 4 H), 7.28 (m, 1 H), 5.62 (m, 1 H), 5.31 (m, 1 H), 4.70 (d of d, J = 8.2, 5.2 Hz, 1 H), 2.53 (m, 1 H), 2.43 (m, 1 H), 2.07 (br s, 1 H), 1.55 (m, 1 H), 1.49 (m, 1 H), 0.01 (s, 9 H). ^{13}C NMR of **15** (Ar = C_6H_5) ($CDCl_3$) δ 144.3, 129.5, 128.4, 127.5, 125.8, 122.3, 74.0, 37.1, 18.8, −1.8.

Preparation of Trifluoroacetates 9 and 19. General Procedure. A solution of approximately 0.3 mmol of the appropriate alcohol **15** or **12** in 2 mL of ether containing 1.5 equiv of 2,6-lutidine was cooled to −10 °C, and 1.3 equiv of trifluoroacetic anhydride was added dropwise. The mixture was allowed to warm to 10 °C and after 5 min was re-cooled to −10 °C. Water was then added, and the mixture was rapidly transferred to a separatory funnel using ether. The ether extract was washed with cold dilute HCl solution, $NaHCO_3$ solution, and saturated NaCl solution and and dried over $MgSO_4$. After filtration, the ether solvent was removed using a rotary evaporator to give the crude trifluoroacetates that were used without further purification. These trifluoroacetates **9** and **19** were all stored in ether at −20 °C. The following procedures are representative.

Reaction of 82 mg of alcohol **15** (Ar = p-$CH_3C_6H_4$) and 55 mg of 2,6-lutidine in 2 mL of ether with 95 mg of trifluoroacetic anhydride gave 108 mg of trifluoroacetate **9** (Ar = p-$CH_3C_6H_4$) (95%) as an oil. ^{1}H NMR of **9** (Ar = p-$CH_3C_6H_4$) ($CDCl_3$) δ 7.26 (d, J = 8.0 Hz, 2 H), 7.19 (d, J = 8.0 Hz, 2 H), 5.83 (d of d, J = 8.1, 6.3 Hz, 1 H), 5.55 (m, 1 H), 5.14 (m, 1 H), 2.75 (m, 1 H), 2.56 (m, 1 H), 2.35 (s, 3 H), 1.46 (m, 2 H), 0.0 (s, 9 H). ^{13}C NMR of **9** (Ar = p-$CH_3C_6H_4$) ($CDCl_3$) δ 156.8 (q, J = 286 Hz), 138.8, 135.0, 130.0, 129.4, 126.7, 120.1, 114.6 (q, J = 42 Hz), 80.5, 33.6, 21.2, 18.9, −1.8. Exact mass (FAB) calcd for $C_{17}H_{23}F_3O_2Si$ 344.1419, found 344.1424.

Reaction of 121 mg of alcohol **12** (Ar = C_6H_5) and 142 mg of 2,6-lutidine in 3 mL of ether with 240 mg of trifluoroacetic anhydride gave 180 mg of trifluoroacetate **19** (Ar = C_6H_5) (90%) as an oil. ^{1}H NMR of **19** (Ar = C_6H_5) ($CDCl_3$) δ 7.42−7.33 (m, 5 H), 5.93 (d of d, J = 8.1, 5.6 Hz, 1 H), 5.69 (m, 1 H), 5.18−5.11 (m, 2 H), 2.77 (m, 1 H), 2.67 (m, 1 H). ^{13}C NMR of **19** (Ar = C_6H_5) ($CDCl_3$) δ 156.8 (q, J = 286 Hz), 137.6, 131.9, 129.0, 128.8, 126.5, 119.4, 114.6 (q, J = 42 Hz), 79.6, 40.4. Exact mass (FAB) calcd for $C_{12}H_{11}F_3O_2$ 244.0711, found 244.0711.

Preparation of Alcohols 16. These substrates were prepared using the olefin cross-metathesis procedure of Taylor.[3a] Alcohols **16** were formed as a 3:1 mixture of *E*/*Z* stereoisomers, which were converted directly to the corresponding trifluoroacetate mixture **9** and **10**. The following procedure is representative.

A solution of 480 mg of 4-penten-2-ol, 2.55 g of allyltrimethylsilane, and 38 mg of catalyst in 40 mL of CH_2Cl_2 was refluxed for 1 h. After solvent removal, chromatography on 6 g of silica gel gave 602 mg of a 3:1 mixture of *E*- and *Z*-1-trimethylsilyl-5-hydroxy-hex-2-ene.[12]

Preparation of Mesylates 17, 18, and 20−22. General Procedure. A solution of approximately 5 mmol of the appropriate alcohol in 3−4 mL of CH_2Cl_2 containing 1.3 equiv of CH_3SO_2Cl was cooled to −50 °C, and 1.5 equiv of Et_3N was added dropwise. The mixture was allowed to warm to 10 °C and after 5 min was re-cooled to 0 °C. Cold water was then added, and the mixture was rapidly transferred to a separatory funnel using ether. The ether extract was rapidly washed with cold dilute HCl solution, $NaHCO_3$ solution, and saturated NaCl solution and dried over $MgSO_4$. After filtration, the solvents were removed using a rotary evaporator to give the crude mesylates that were used without further purification. These mesylates were all stored in ether at −20 °C. The following procedures are representative.

Reaction of 110 mg of a 3:1 mixture of *E*- and *Z*-1-trimethylsilyl-5-hydroxy-hex-2-ene and 95 mg of CH_3SO_2Cl in 3 mL of CH_2Cl_2 with 97 mg of Et_3N gave 146 mg (92% yield) of a mixture of mesylates **17** and **18**. These mesylates decomposed on prolonged standing at room temperature and were therefore stored in ether solution at −20 °C.

Reaction of 99 mg of 4-penten-2-ol and 144 mg of CH_3SO_2Cl in 3 mL of CH_2Cl_2 with 178 mg of Et_3N gave 165 mg (87% yield) of mesylate **20**.[13] ^{1}H NMR of **20** ($CDCl_3$) δ 5.79 (m, 1 H), 5.18 (m, 1 H), 5.16 (m, 1 H), 4.83 (sextet, J = 6.3 Hz, 1 H), 3.00 (s, 3 H), 2.47 (m, 1 H), 2.41 (m, 1 H), 1.43 (d, J = 6.3 Hz, 3 H). ^{13}C NMR of **20** ($CDCl_3$) δ 132.4, 119.1, 79.1, 40.9, 38.7, 20.8.

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Reaction of 19 mg of alcohol **16** (Ar = *m*-$CF_3C_6H_4$) and 11 mg of CH_3SO_2Cl in 1.5 mL of CH_2Cl_2 with 10 mg of Et_3N gave a mixture of mesylates **21**. Mesylates **21** are highly reactive substances that decompose at room temperature or on standing in $CDCl_3$ at room temperature. NMR spectra in $CDCl_3$ were recorded at 5 °C. Samples of **21** were stored in ether at −20 °C, and solvents were rapidly removed when preparing samples for kinetic studies.

Reaction of 133 mg of alcohol **12** (Ar = *m*-$CF_3C_6H_4$) and 97 mg of CH_3SO_2Cl in 3 mL of CH_2Cl_2 with 103 mg of Et_3N gave 164 mg (91% yield) of mesylate **22**. ^{1}H NMR of **22** ($CDCl_3$) δ 7.65−7.61 (m, 2 H), 7.58 (d, J = 8 Hz, 1 H), 7.54 (t, J = 8 Hz, 1 H), 5.71 (m, 1 H), 5.62 (d of d, J = 7.7, 6.0 Hz, 1 H), 5.16 (m, 1 H), 5.14 (m, 1 H), 2.81 (s, 3 H), 2.80 (m, 1 H), 2.66 (m, 1 H). ^{13}C NMR of **22** ($CDCl_3$) δ 139.3, 131.4, 131.3 (q, J = 32 Hz), 130.1, 129.5, 125.8 (q, J = 3.7 Hz), 123.8 (q, J = 272 Hz), 123.4 (q, J = 3.8 Hz), 119.9, 82.3, 41.4, 39.0. Exact mass (FAB) calcd for $C_{12}H_{13}F_3O_3S$ 294.0537s, found 294.0534.

Solvolyses of Trifluoroacetates and Mesylates in CD_3CO_2D. Kinetic Studies. Rate constants reported in Table 1 were all determined using 500 or 600 MHz ^{1}H NMR spectroscopy. A solution was prepared by dissolving approximately 5 mg of the appropriate substrate in 400 mg of CD_3CO_2D containing approximately 1.5 equiv of 2,6-lutidine. (The CD_3CO_2D is hygroscopic, and care was taken to keep the solvent dry.) A sample was sealed in an NMR tube. For runs at 25 °C, the tube was placed in the probe of an NMR set at 25.0 °C. At appropriate time intervals, the tube was analyzed by ^{1}H NMR, and relative areas due to starting trifluoroacetate or mesylate and products were measured. For slower runs, the tube was placed in a constant temperature bath at 25.0 °C between readings and then rapidly transferred to the 25.0 °C NMR probe.

For runs at higher temperature, the tube was placed in a constant temperature bath at the appropriate temperature. After allowing 20 s for temperature equilibration, the tube was kept in the bath for a long period of time (minimum of 1 h) relative to the time needed for the temperature to equilibrate. At appropriate time intervals, the tube was then rapidly quenched in a water bath at 15 °C and rapidly analyzed by ^{1}H NMR at ambient temperature. The amount of further reaction during the 10 min necessary to carry out the NMR analysis was insignificant (less than 0.1%).

In the case of trifluoroacetates **9**, the rate of disappearance of the triplet at approximately δ 5.9−6.0 was monitored. For trifluoroacetates **19** (Ar = *p*-$CH_3OC_6H_4$ and *p*-$CH_3SC_6H_4$), the rate of disappearance of the CH_3 singlets at δ 3.78 and 2.45 was monitored. In the case of all other trifluoroacetates **10** (which contained about 25% of the *cis*-isomer **9**), the rate of disappearance of the upfield TMS singlet at δ −0.07 to −0.09 due to **10** was monitored. Typical data illustrating this method are given as Supporting Information. In the case of trifluoroacetates **19**, the rate of disappearance of the doublet of doublets at δ 5.9−6.0 was monitored. For mesylates **17** and **18**, the rates of disappearance of the CH_3SO_3R singlets at δ 3.025 and 3.017 were monitored. For mesylates **20** and **22**, the rates of disappearance of the CH_3SO_3R singlets at δ 3.022 and 2.914 were monitored. For mesylates **21**, the rates of disappearance of the CH_3SO_3R singlets at δ 2.921 (*Z*-isomer) and 2.886 (*E*-isomer) were monitored. First-order rate constants for the disappearance of substrates were calculated by standard least-squares procedures. Correlation coefficients were all greater than 0.9999. The maximum standard deviation in duplicate runs was ±2%.

Solvolyses of Trifluoroacetates 9 in CD_3CO_2D. Product Studies. A solution of the appropriate trifluoroacetate **9** in CD_3CO_2D containing 1.5 equiv of 2,6-lutidine was kept at the appropriate temperature for 10 half-lives. The mixture was then analyzed by 600 MHz ^{1}H NMR for the relative amounts of each product. Cyclopropane products **24** (Ar = C_6H_5) and **25** (Ar = C_6H_5) were identified by NMR spectral comparison with authentic samples.[14] Substitution product **27** (Ar = C_6H_5) was identified by spectral comparison with an authentic sample of undeuterated **27**, prepared by acetylation of **15** (Ar = C_6H_5) with acetic anhydride. Traces products **28** (Ar = C_6H_5)[15] and **29** (Ar = C_6H_5) were identified by NMR spectral comparison with authentic samples. Products from other solvolyses were identified by spectral analogy. Typical spectra of products are shown as Supporting Information.

Computational Studies. Ab initio molecular orbital calculations were performed using the Gaussian 03 series of programs.[10] Structures of **32**, **33**, **36**, and **37** were characterized as minima via frequency calculations that showed no negative frequencies.

Supporting Information Available: Complete ref 10; the B3LYP/6-31G* calculated structures, energies, and Cartesian coordinates of **32**, **33**, and **36**−**38**; ^{1}H and ^{13}C NMR of compounds **13**−**15**, **9** (Ar = C_6H_5), **9** (Ar = *p*-$CH_3C_6H_4$), **9** (Ar = *p*-ClC_6H_4), **17** and **18**, **19** (Ar = C_6H_5), and **20**−**22**; evolving ^{1}H NMR spectra during reaction of **9** in CD_3CO_2D; as well as ^{1}H NMR spectral data used in the determination of the rate of **10** (Ar = C_6H_5) in CD_3CO_2H. This material is available free of charge via the Internet at http://pubs.acs.org.

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