to the filtrate and the resulting solution was heated at 60 °C under argon for 2 h and then at 25 °C for 18 h. The volatiles were removed in vacuo and the residue was taken up in CH_2Cl_2, washed well with H_2O, dried over Na_2SO_4, and concentrated to give 2.3 g of a semisolid. Flash chromatography on 300 mL of silica gel with 20% EtOAc/hexane gave 1.64 g of pure triacetate (2.9 mmol) (64% yield) as a yellow solid: mp 177–179 °C (hexane); IR (KBr) 1775, 1740, 1718, 1170 cm^{-1}; NMR δ 0.05 (s, 3 H), 0.15 (s, 3 H), 0.80 (s, 9 H), 2.02 (s, 3 H), 2.20 (s, 3 H), 2.40 (s, 3 H, 2.43 (s, 3 H), 3.05 (d, 1 H, J = 16 Hz), 3.40 (d, 1 H, J = 16 Hz), 6.29 (s, 1 H), 7.35 (m, 2 H), 7.80 (m, 2 H), 8.20 (s, 2 H).

Anal. Calcd for $C_{31}H_{36}O_8Si$: C, 65.93; H, 6.43. Found: C, 66.10; H, 6.81.

***cis*-2-Acetyl-2-[[(1,1-dimethylethyl)dimethylsilyl]oxy]-2,3,5,10-tetrahydro-5,10-dioxo-1*H*-cyclopent[*b*]anthracene-1,4,11-triol 1,4,11-Triacetate (30).** To a stirred solution of 1.13 g (2.00 mmol) of anthracine **29** in 30 mL of glacial acetic acid at 25 °C under argon was added dropwise over 5 min a solution of 800 mg (8.0 mmol) of CrO_3 in 5 mL of H_2O. After stirring for 15 min, the dark solution was carefully poured into a stirred saturated solution of $NaHCO_3$ (100 mL). The organics were extracted into ethyl acetate, washed repeatedly with bicarbonate solution, dried over Na_2SO_4, filtered, and concentrated to give 1.2 g of an orange oil. Crystallization from hexane gave 720 mg (1.18 mmol) of a yellow solid. The mother liquors were chromatographed on silica gel with 20% ethyl acetate/hexane to give an additional 160 mg of product, 1.45 mmol total (72% yield): mp 110–112 °C; IR (KBr) 1775, 1750, 1715, 1675, 1175 cm^{-1}; NMR δ 0.05 (s, 3 H), 0.12 (s, 3 H), 0.90 (s, 9 H), 2.13 (s, 3 H), 2.28 (s, 3 H), 2.33 (s, 3 H), 2.36 (s, 3 H), 3.12 (d, 1 H, J = 16 Hz), 3.50 (d, 1 H, J = 16 Hz), 6.30 (s, 1 H), 7.70 (m, 2 H), 8.10 (m, 2 H).

Anal. Calcd for $C_{31}H_{34}O_{10}Si$: C, 62.61; H, 5.76. Found: C, 62.93; H, 5.63.

Glycoside Coupling of Protected Daunosamine to Diol 26b. A stirred solution of 326 mg (0.60 mmol) of 2,3,6-trideoxy-1,4-di-*O*-*p*-nitrobenzoyl-3-trifluoroacetamido-α-L-*lyxo*-hexopyranose[17] in 10 mL of dry CH_2Cl_2 at 0 °C under argon was treated with gaseous HCl for 3 min. After standing at 25 °C for 10 min, the *p*-nitrobenzoic acid was removed by filtration and the filtrate was concentrated to dryness yielding 200 mg (ca. 100%) of glycosyl chloride **31**. The chloro sugar (0.60 mmol), diol **26b** (140 mg, 0.44 mmol), and powdered anhydrous $CaCO_3$ (200 mg, 2.0 mmol) were vigorously stirred in 10 mL of dry CH_2Cl_2 under argon while a solution of 154 mg (0.60 mmol) of silver trifluoromethanesulfonate (AgTF) in 5 mL of dry THF was added over a 5-min period. The diol appeared to dissolve and the mixture darkened as addition of AgTf progressed. After stirring for 15 min at 25 °C, TLC (40% EtOAc/hexane) showed two mobile products, R_f 0.50 and R_{f_B} 0.42 with only a trace of starting diol remaining. The reaction mixture was filtered and filtrate was dried over Na_2SO_4. Concentration in vacuo gave 450 mg of a light brown foam. Preparative TLC on eight 20 cm × 20 cm (0.5 mm) silica gel plates with 25% EtOAc/hexane gave 75 mg of isomer A and 60 mg of isomer B. Both isomers gave similar spectra which indicated some decomposition upon chromatography. Isomer A was purified by precipitation from CH_2Cl_2 with hexane: IR (KBr) 3475, 1740, 1715, 1675, 1540 cm^{-1}; NMR δ 1.18 (d, 3 H, J = 7 Hz), 2.25 (m, 3 H), 2.38 (s, 3 H), 3.10 (s, 2 H), 3.60 (m, 1 H), 4.20 (q, 1 H, J = 7 Hz), 4.60 (m, 1 H), 5.35 (m, 2 H), 5.85 (s, 1 H), 6.96 (d, 1 H, J = 7 Hz, NH), 7.60 (m, 2 H), 7.85 (m, 2 H), 8.12 (s, 4 H), 8.35 (s, 2 H).

Effect of the α-Trifluoromethyl Moiety on the Solvolysis of Allylic Sulfonates

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A series of allylic sulfonates bearing aryl substituents on the 2-position and/or trifluoromethyl groups on the 1- and/or 3-positions has been studied under solvolytic conditions in 2,2,2-trifluoroethanol. Nonarylated 1,3-di(trifluoromethyl)-substituted allylic sulfonates did not solvolyze in a conventional manner but instead gave products diagnostic of a complex isomerization–cleavage process. Mono(trifluoromethyl)-substituted allylic sulfonates solvolyzed by normal paths to give k_H/k_{CF_3} ratios of 2×10^6 and 4×10^4 for the substitution at the 1- and 3-positions, respectively. No evidence for 1,3-π interactions was discerned.

Introduction

The study of carbocation intermediates that are destabilized by strongly electron-withdrawing substituents has recently drawn the attention of several groups.[2-8] We have been especially interested in evaluating the influence that these destabilizing substituents have on several classical solvolytic systems.[2,3a] For example, the α-cyano group produced rate retardations relative to α-H (k_H/k_{CN}) of

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(2) (a) Gassman, P. G.; Doherty, M. M. *J. Am. Chem. Soc.* **1982**, *104*, 3742. (b) Gassman, P. G.; Talley, J. J. *Tetrahedron Lett.* **1981**, *22*, 5253. (c) Gassman, P. G.; Saito, K. *Ibid.* **1981**, *22*, 1311. (d) Gassman, P. G.; Talley, J. J. *J. Am. Chem. Soc.* **1980**, *102*, 4138. (e) Gassman, P. G.; Saito, K.; Talley, J. J. *Ibid.* **1980**, *102*, 7613. (f) Dixon, D. A.; Charlier, P. A.; Gassman, P. G. *Ibid.* **1980**, *102*, 3957. (g) Gassman, P. G.; Talley, J. J. *Ibid.* **1980**, *102*, 1214. (h) Gassman, P. G.; Guggenheim, T. L. *J. Org. Chem.* **1982**, *47*, 3023.

(3) (a) Gassman, P. G.; Tidwell, T. T. *Acc. Chem. Res.* **1983**, *16*, 279. Tidwell, T. T. *Angew. Chem., Int. Ed. Engl.*, in press. (b) Allen, A. D.; Ambidge, I. C.; Che, C.; Michael, H.; Muir, R. J.; Tidwell, T. T. *J. Am. Chem. Soc.* **1983**, *105*, 2343. (c) Allen, A. D.; Shahidi, F.; Tidwell, T. T. *Ibid.* **1982**, *104*, 2516. (d) Allen, A. D.; Jansen, M. P.; Koshy, K. M.; Mangru, N. N.; Tidwell, T. T. *Ibid.* **1982**, *104*, 207. (e) Jansen, M. P.; Koshy, K. M.; Mangru, N. N.; Tidwell, T. T. *Ibid.* **1981**, *103*, 3863. (f) Koshy, K. M.; Roy, D.; Tidwell, T. T. *Ibid.* **1979**, *101*, 357. (g) Koshy, K. M.; Tidwell, T. T. *Ibid.* **1980**, *102*, 1216.

(4) (a) Liu, K.-T.; Kuo, M.-Y.; Sheu, C.-F. *J. Am. Chem. Soc.* **1982**, *104*, 211. (b) Liu, K.-T.; Sheu, C.-F. *Tetrahedron Lett.* **1980**, *21*, 4091.

(5) (a) Creary, X. *J. Org. Chem.* **1979**, *44*, 3938. (b) Creary, X. *J. Am. Chem. Soc.* **1981**, *103*, 2463. (c) Creary, X.; Geiger, C. C. *Ibid.* **1982**, *104*, 4151. (d) Begue, J.-P.; Charpentier-Morize, M. *Acc. Chem. Res.* **1980**, *13*, 207.

(6) (a) Olah, G. A.; Arvanaghi, M.; Prakash, G. K. S. *J. Am. Chem. Soc.* **1982**, *104*, 1628. (b) Olah, G. A.; Prakash, G. K. S.; Arvanaghi, M. *Ibid.* **1980**, *102*, 6640. (c) Olah, G. A.; Mo, Y. K. *Adv. Fluorine Chem.* **1972**, *7*, 69. (d) Olah, G. A.; Pittman, C. U., Jr. *J. Am. Chem. Soc.* **1966**, *88*, 3310.

(7) (a) Poulter, C. D.; Rilling, H. C. *Acc. Chem. Res.* **1978**, *11*, 307. (b) Poulter, C. D.; Satterwhite, D. M.; Rilling, H. C. *J. Am. Chem. Soc.* **1976**, *98*, 3376. (c) Astrologes, G. W.; Martin, J. C. *Ibid.* **1977**, *99*, 4400.

(8) (a) Paddon-Row, M. N.; Houk, K. N.; Tidwell, T. T. *Tetrahedron Lett.* **1982**, *23*, 383. (b) Paddon-Row, M. N.; Santiago, C.; Houk, K. N. *J. Am. Chem. Soc.* **1980**, *102*, 6561. (c) Moffat, J. B. *Chem. Phys. Lett.* **1980**, *76*, 304. (d) Reynolds, W. F.; Davis, P.; Taft, R. W.; Topsom, R. D. *Tetrahedron Lett.* **1981**, *22*, 1795.

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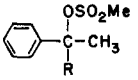
approximately 10^3 in system I where R and R′ cannot provide resonance stabilization.[2b-e,g] That the rate retardations are considerably less than might be predicted has been attributed to mesomeric stabilization, as in II. The importance of structure II is supported by theoretical studies.[2f,8] When the charge on I can be delocalized by R and R′, the k_H/k_{CN} rate ratio ranges up to 10^6.[2b,d]

I II

Whereas resonance contributor II can substantially attenuate the inductive destabilization of the α-cyano moiety, no such moderating effect is possible with the α-trifluoromethyl substituent in system III. In fact, Tidwell[3]

III

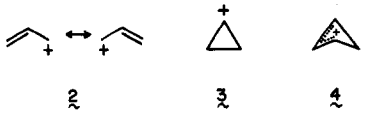
and Liu[4] have reported that the α-trifluoromethyl group gives rise to k_H/k_{CF_3} rate ratios in the range of 10^5–10^7 for tertiary sulfonate esters and 2×10^3–5×10^5 for the corresponding secondary systems. For tertiary systems, the trifluoromethyl rate retardations generally exceed those of the α-cyano group by ca. 10^3 and are more consistent with the magnitude of carbocation destabilization expected when only inductive effects are considered. Recent ab initio calculations[8a] predict that while the cyano and trifluoromethyl groups both have large destabilizing effects on α-carbocations, the cyano group is a much weaker destabilizer than the trifluoromethyl group. Likewise, the γ^+ treatment,[9] which is a quantitative method for assessing the ability of a substituent to influence the rate of formation of a carbocation, again establishes that the trifluoromethyl group is more destabilizing than the cyano group.[3a,c,d,g] A direct comparison between the benzylic sulfonates **1a** and **1b** gives a k_{CN}/k_{CF_3} rate ratio of ca. 2×10^3.[2h,3d,3g] In studies of allylic systems, Poulter et al.[7a,b]



1a, R = CN
1b, R = CF_3

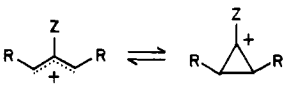
found a k_{CH_3}/k_{CF_3} rate ratio of 5×10^5. Independently of Poulter's work, we studied the solvolyses of several trifluoromethyl-substituted allylic triflates. In addition to documenting the expected rate retardations, we were also interested in studying the effect that trifluoromethyl substitution would have on the allylic charge distribution.

In the simple Hückel molecular orbital representation of the allyl cation (**2**), the positive charge is equally, *and totally*, dispersed to the terminal carbons, C_1 and C_3.



2 **3** **4**

These results have been critically analyzed,[10] and with few exceptions,[10d,h] more sophisticated calculations have predicted that a more accurate representation of **2** would distribute some positive charge to C_2. 1,3-π-Allylic interactions, leading in the extreme to the cyclopropyl cation (**3**), represent one means by which the allylic carbocation can redistribute charge from C_1 and C_3 to C_2. However, with the exception of the cyclobutenyl system, **4**,[11,12] there is no experimental evidence for 1,3 interactions in simple acyclic allylic systems.[10b,13] The ultimate consequence of 1,3-π-allylic interactions is closure to the cyclopropyl cation. The solvolytic relationship between the cyclopropyl system, **6**, and the allylic system, **5**, has been well-documented.[14,15] Since the allyl cation has been variously



5 **6**

calculated to be 35–49 kcal/mol lower in energy than the isomeric cyclopropyl cation,[16] both the propensity for cyclopropyl ring opening and the absence of 1,3-π interactions in simple allylic systems is understandable. However, consideration of the substituted allyl and cyclopropyl carbocations, **5** and **6**, respectively, shows that a judicious choice of substituents (R and Z) could radically alter their relative energies. Specifically, when R is a strongly electron-withdrawing substituent, **5** should be destabilized relative to **6**, while an electron-releasing substituent, Z, would be expected to lower the energy of **6** considerably more than it would lower the energy of **5**. These qualitative considerations have been supported by calculations that predict that electron-releasing substituents ought to not only lower the energy of **6** relative to **5**[16a] but also increase 1,3-π interactions.[17a] Furthermore, Liberles,[17b] using INDO and MINDO calculations, predicted that electron-releasing substituents at the termini of allylic cations favor **5** over **6**.

There exists a substantial amount of experimental support for the aforementioned considerations. Solvolysis of the cyclopropyl derivatives **7** gave rise to significant amounts of cyclopropyl products.[18] The electropositive

(9) (a) Traylor, T. G.; Ware, J. C. *J. Am. Chem. Soc.* **1967**, *89*, 2304. (b) Peters, E. N. *Ibid.* **1976**, *98*, 5627. (c) Peters, E. N. *J. Org. Chem.* **1977**, *42*, 1419. (d) McManus, S. P.; Harris, J. M. *Ibid.* **1977**, *42*, 1422.

(10) (a) Muller, N.; Mulliken, R. S. *J. Am. Chem. Soc.* **1958**, *80*, 3489. (b) Streitwieser, A., Jr.; Nair, P. M. *Tetrahedron* **1959**, *5*, 149. See also: Streitwieser, A. "Molecular Orbital Theory for Organic Chemists"; Wiley: New York, 1961, and references cited therein. (c) Chalvet O.; Daudel, R. *J. Chim. Phys.* **1952**, *49*, 629. (d) Brickstock, A.; Pople, J. A. *Trans. Faraday Soc.* **1954**, *50*, 901. (e) Hoyland, J. R.; Goodman, L. *J. Chem. Phys.* **1962**, *36*, 12. (f) Colpa, J. P.; MacLena, C.; Mackor, E. L. *Tetrahedron* **1963**, *19*, *Suppl. 2*, 65. (g) Hoffmann, R. *J. Chem. Phys.* **1964**, *40*, 2480. (h) Isaacs, N. S. *Tetrahedron* **1969**, *25*, 3555. (i) Navangyl, H. V.; Blatz, P. E. *J. Am. Chem. Soc.* **1973**, *95*, 1508. (j) Simonetta, M.; Heilbronner, E. *Theor. Chim. Acta* **1964**, *2*, 228.

(11) (a) Kiefer, E. F.; Roberts, J. D. *J. Am. Chem. Soc.* **1962**, *84*, 784. (b) Katz, T. J.; Gold, E. H. *Ibid.* **1964**, *86*, 1600. (c) Olah, G. A.; Staral, J. S.; Spear, R. J.; Liang, G. *Ibid.* **1975**, *97*, 5489.

(12) Corey, E. J.; Pirkle, W. H. *Tetrahedron Lett.* **1967**, 2255. See also: Eisenbarth, P.; Maas, G.; Regitz, M. *J. Am. Chem. Soc.* **1983**, *105*, 5134.

(13) (a) Olah, G. A.; Clifford, P. R.; Halpern, K.; Johanson, R. G. *J. Am. Chem. Soc.* **1971**, *93*, 4219. (b) Griffin, R. H.; Jewett, J. G. *Ibid.* **1970**, *92*, 1104. (c) Olah, G. A.; Spear, R. J. *Ibid.* **1975**, *97*, 1539.

(14) Sorensen, T. S.; Rauk, A. In "Pericyclic Reactions"; Marchand, A. P., Lehr, R. E., Eds.; Academic Press: New York, 1977; Vol. 2, pp 1–17.

(15) (a) Schleyer, P. v. R.; Sliwinski, W. F.; Van Dins, G. W.; Schöllkopf, U.; Paust, J.; Fellenberger, K. *J. Am. Chem. Soc.* **1972**, *94*, 125. (b) Sliwinski, W. F.; Su, T. M.; Schleyer, P. v. R. *Ibid.* **1972**, *94*, 133. (c) DePuy, C. H. *Acc. Chem. Res.* **1968**, *1*, 33.

(16) (a) Radom, L.; Hariharan, P. C.; Pople, J. A.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1973**, *95*, 6531. (b) Clark, D. T.; Armstrong, D. R. *Theor. Chim. Acta* **1969**, *13*, 365. (c) Merlet, P.; Peyerimhoff, S. D.; Buenker, R. J.; Shih, S. *J. Am. Chem. Soc.* **1974**, *96*, 959.

(17) (a) Carpenter, B. K. *J. Chem. Soc., Perkin Trans. 2* **1974**, 1. (b) Liberles, A.; Kang, S.; Greenberg, A. *J. Org. Chem.* **1973**, *38*, 1922.

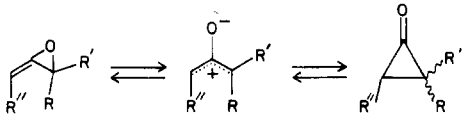
substituents Z appear to have prevented ring opening by stabilizing **6**. More dramatically, Jöngejan et al. were able to prepare the stable ions **8a** and **8b**, and, in agreement

7a, Z = SPh, X = Cl
7b, Z = c-C_3H_5, X = OTs

8a, X = NMe_2^+, R = H
8b, X = NMe_2^+, R = Me
9a, X = O, R = H
9b, X = O, R = Me

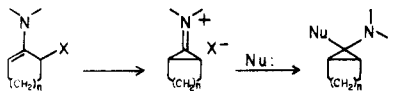
with the considerations cited above, the methylated derivative, **8b**, was much more susceptible to ring opening.[19] Similarly, dimethylcyclopropanone **9b** was much more labile than was **9a**.[20] Olah observed that electron-donating substituents at the 1- and 3-positions of the cyclobutenyl cation reduced or eliminated 1,3-π overlap.[21]

Finally, there are several examples wherein cyclopropyl products have been produced from bona fide or postulated allylic precursors. The isomerization of allene oxides **10** to cyclopropanones **11** via the *postulated* oxyallyl species **12**[22] and the conversion of α-halo enamines **13** into the



10 **12** **11**

cyclopropyl products **14**[23] both involve strongly electron-releasing substituents (*Z*; viz., **5** → **6**). Other examples

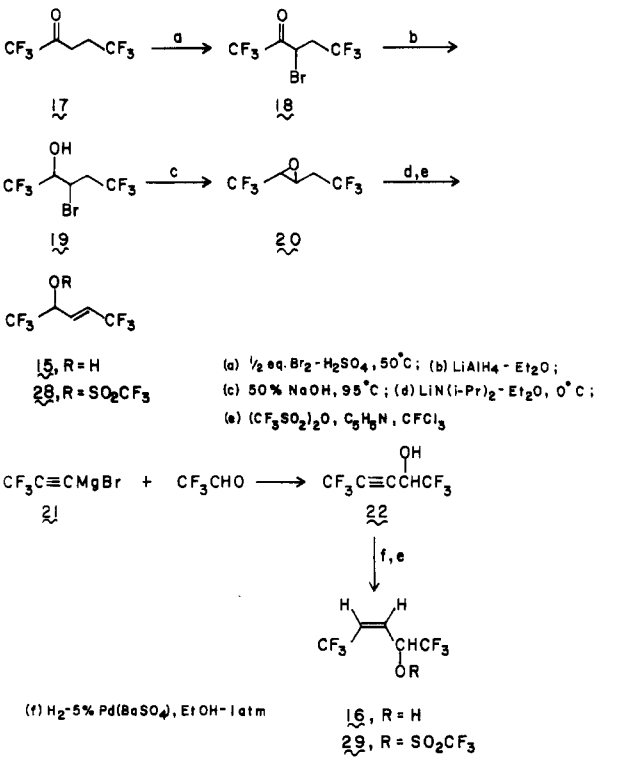


13, n = 1,2 **14**

of apparent ring closure of an allylic species are those of Corey and Pirkle[12] and of Aue and Helwig,[24] where the former case utilized cyclobutenyl 1,3-π interaction as the driving force behind cyclization and the latter fortuitously employed strategic substitution.

Given this background, we were extremely interested in studying the effect of the strongly electron-withdrawing trifluoromethyl substituents (R) on the allylic cation **5**. Could **5** be induced to undergo cyclization to **6**? In the absence of cyclization, would the degree of 1,3-π interaction be observably increased? In an effort to answer these and other questions, a series of trifluoromethyl-substituted allylic triflates was prepared and solvolyzed, and the results are reported below.

Scheme I

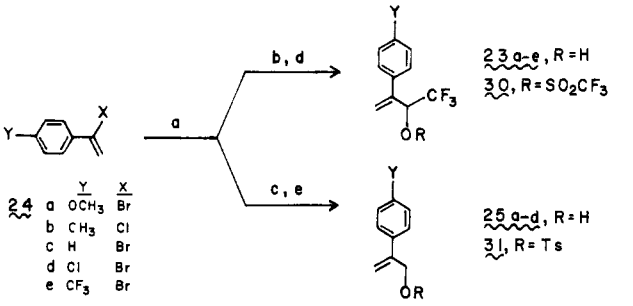


17 **18** **19** **20** **21** **22**

15, R = H
28, R = SO_2CF_3

16, R = H
29, R = SO_2CF_3

Scheme II



	Y	X
a	OCH_3	Br
b	CH_3	Cl
c	H	Br
d	Cl	Br
e	CF_3	Br

24

23a-e, R = H
30, R = SO_2CF_3

25a-d, R = H
31, R = Ts

Synthesis

The synthesis of (*E*)- and (*Z*)-1,1,1,5,5,5-hexafluoropent-3-en-2-ol (**15** and **16**, respectively) is outlined in Scheme I. Bromination of the hexafluoro ketone **17**[25] in concentrated sulfuric acid[26] afforded the bromo ketone **18** in 89% yield. Lithium aluminum hydride reduction of **18** produced a 67% yield of the bromohydrin **19**, which, when added dropwise to hot 50% sodium hydroxide, gave an 85% yield of the hexafluoro epoxide **20**. Treatment of **20** with lithium diisopropylamide in ethyl ether gave a 51% yield of the expected[27] (*E*)-allyl alcohol **15**.

The corresponding *Z*-isomer **16** was readily prepared in two steps. Trifluoropropynyl-Grignard (**21**)[28] and tri-

(18) (a) Landgrebe, J. A.; Becker, L. W. *J. Am. Chem. Soc.* **1967**, *89*, 2505. (b) Howell, R. A.; Jewett, J. G. *Ibid.* **1971**, *93*, 798. (c) Schöllkopf, U.; Ruban, E.; Tonne, P.; Riedell, K. *Tetrahedron Lett.* **1970**, 5077. (d) Masuda, T.; Furukawa, N.; Oae, S. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 2659. See also: Brown, H. C.; Gundu Rao, C.; Ravindranathan, M. *J. Am. Chem. Soc.* **1978**, *100*, 7946.

(19) (a) Jöngejan, E.; van Tilborg, W. J. M.; Dusseau, C. H. V.; Steinberg, H. *Tetrahedron Lett.* **1972**, 2359. (b) Jöngejan, E.; Steinberg, H.; deBoer, Th. J. *Ibid.* **1976**, 397.

(20) Turro, N. J.; Hammond, W. B. *J. Am. Chem. Soc.* **1967**, *89*, 1028.

(21) Olah, G. A.; Staral, J. S.; Spear, R. J.; Liang, G. *J. Am. Chem. Soc.* **1975**, *97*, 5489.

(22) For a review of this area, see: L'abbê, G. *Angew. Chem., Int. Ed. Engl.* **1980**, 276.

(23) (a) Reference 19b and references cited therein. (b) Blazejewski, J. C.; Cantacazene, D.; Wakselman, C. *Tetrahedron* **1973**, *29*, 4233. (c) Jöngejan, E.; Steinberg, H.; deBoer, Th. J. *Synth. Commun.* **1974**, *4*, 11. (d) Vilsmaier, E.; Tröger, W. *Synthesis* **1980**, 463. (e) Vilsmaier, E.; Scheiber, L. *Ibid.* **1980**, 465.

(24) Aue, D. H.; Helwig, G. S. *Chem. Commun.* **1975**, 604.

(25) Holbrook, G. W.; Pierce, O. R. *J. Org. Chem.* **1961**, *26*, 1037.

(26) McBee, E. T.; Hathaway, C. E.; Roberts, C. W. *J. Am. Chem. Soc.* **1956**, *78*, 4053.

(27) Cope, A. C.; Heeren, J. K. *J. Am. Chem. Soc.* **1965**, *87*, 3125.

(28) Henne, A. L.; Nager, J. *J. Am. Chem. Soc.* **1952**, *74*, 650.

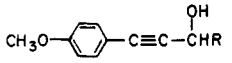
Table I. Rates of Trifluoroethanolysis of 3-Aryl-1,1,1-trifluorobut-3-en-2-yl Triflates (30a–e)[a]

compd	temp, °C (±0.01 °C)	rate, s^{-1}	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu	k_H/k_{CF_3}[c,d]
30a	95.00	$(1.45 \pm 0.02) \times 10^{-3}$			
	80.00	$(4.54 \pm 0.00) \times 10^{-4}$			
	65.00	$(1.08 \pm 0.07) \times 10^{-4}$			
	25.00[b]	1.54×10^{-6}	20.73 ± 0.79	−15.6 ± 2.3	1.71×10^6
30b	90.00	$(9.55 \pm 0.20) \times 10^{-4}$			
	75.00	$(2.57 \pm 0.00) \times 10^{-4}$			
	60.00	$(6.15 \pm 0.10) \times 10^{-5}$			
	25.00[b]	1.25×10^{-6}	21.29 ± 0.02	−14.1 ± 0.1	2.87×10^6
30c	95.00	$(1.00 \pm 0.01) \times 10^{-3}$			
	80.00	$(3.01 \pm 0.01) \times 10^{-4}$			
	65.00	$(7.59 \pm 0.01) \times 10^{-5}$			
	25.00[b]	1.09×10^{-6}	20.61 ± 0.30	−16.7 ± 0.9	2.11×10^6
30d	95.00	$(5.36 \pm 0.01) \times 10^{-4}$			
	80.00	$(1.45 \pm 0.01) \times 10^{-4}$			
	65.00	$(3.49 \pm 0.09) \times 10^{-5}$			
	25.00[b]	3.89×10^{-7}	21.82 ± 0.01	−14.6 ± 0.0	2.53×10^6
30e	95.00	$(3.24 \pm 0.10) \times 10^{-4}$			
	80.00	$(7.38 \pm 0.10) \times 10^{-5}$			
	65.00	$(1.74 \pm 0.10) \times 10^{-5}$			
	25.00[b]	1.38×10^{-7}	23.39 ± 0.75	−11.4 ± 2.1	

[a] The reactions were run at 0.003–0.005 M and were buffered with 1.5 equiv of 2,6-lutidine. [b] Extrapolated from higher temperatures. [c] The rate ratio was obtained from $10^6(k_{31a-d}/k_{30a-d})_{25\,°C}$. [d] The k_{OTf}/k_{OTs} ratio of 10^6 was selected from among several published values that span the range $10^{4.3}$–$10^{6.0}$ (ref 2g, 3b, and 46). The upper value was selected because it represents a *measured* rate difference obtained on trifluoroethanolysis of the triflate and tosylate of the secondary alcohol 1-phenyl-2,2,2-trifluoroethanol (ref 3b), a system closely related to **30**.

fluoroacetaldehyde[29] combined to give ca. 70% of the propargyl alcohol **22**. Hydrogenation over palladium on barium sulfate gave, after fractionation, 83% of the desired alcohol **16**. All attempts to prepare either **15** or **16** with strongly electron-donating substituents at the center of the allylic system failed.[30]

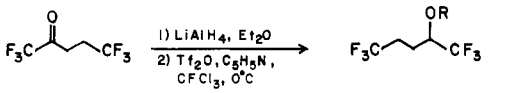
In order to study the degree of charge distribution at the central carbon of the allylic carbocation, a series of 2-aryl-1-(trifluoromethyl)allyl alcohols, **23**, was prepared as shown in Scheme II. Conversion of the α-halostyrenes **24** to the corresponding Grignard or lithio derivatives and subsequent addition of trifluoroacetaldehyde gave the desired alcohols **23**. The parent allylic substrates **25** were obtained by substituting gaseous formaldehyde for trifluoroacetaldehyde. With the exceptions of the preparations of **23a** and **25a**, the reactions in Scheme II proceeded without complication. Both **23a** and **25a** were contaminated with the propargyl alcohols **26** and **27**, respectively, suggesting that dehydrobromination of **24a** by *n*-butyllithium was competitive with transmetalation.



26, R = CF_3
27, R = H

The trifluoromethyl-substituted alcohols **15**, **16**, and **23** were converted to their corresponding trifluoromethanesulfonate (triflate) esters **28–30**, respectively, by the action of trifluoromethanesulfonic anhydride and pyridine in trichlorofluoromethane (Freon-11). The alcohols **25** were converted to the less reactive tosylates **31** by treating an ethereal solution of **25** with *p*-toluenesulfonyl chloride in the presence of powdered potassium hydroxide.

Finally, as a model compound, the saturated analogue of **15** and **16**, the hexafluoro alcohol **32**, was prepared by lithium aluminum hydride reduction of **17** and was converted to its triflate, **33**, in the usual manner.



17 **32**, R = H; **33**, R = SO_2CF_3

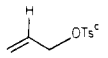
Solvolysis Studies

Table I lists the rates of solvolysis of the triflates **30a–e** in anhydrous 2,2,2-trifluoroethanol (TFE). Table II lists the solvolysis rates of the tosylates **31a–d** in the same solvent. Anhydrous TFE was selected as the solvent of choice because of its low nucleophilicity,[31] high ionizing power,[31e,32] and relatively weak acidity (pK_a = 12.37).[32,33] Although trifluoroacetic acid is considerably less nucleophilic than TFE, it was deemed unsatisfactory because of its known addition to the styryl system.[34] The kinetics of the solvolysis of the triflates **28** and **29** could not be accurately determined because more than 1 mol of acid was liberated during the reaction. All of the solvolyses were buffered with 2,6-lutidine, and the rates were determined by the conductimetric method.[35]

Prior to the trifluoroethanolysis of **29**, the saturated model system **33** was studied. Whereas Dafforn and Streitwieser[36] reported that trifluoroethanolysis of iso-

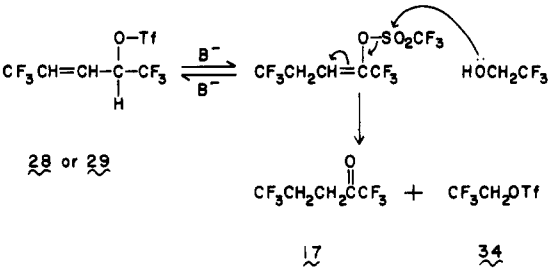
(29) Pierce, O. R.; Kane, T. G. *J. Am. Chem. Soc.* **1954**, *76*, 300.
(30) For a description of these efforts, see: Harrington, C. K., Ph.D. Thesis, The Ohio State University, Columbus, OH, 1976; *Diss. Abstr. B* **1976**, *37*, 2248.
(31) (a) Trahanovsky, W. S.; Doyle, M. P. *Tetrahedron Lett.* **1974**, 2155. (b) Bergstrom, R. G.; Wall, G. H.; Zollinger, H. *Ibid.* **1974**, 2957. (c) Schadt, F. L.; Schleyer, P. v. R. *Ibid.* **1974**, 2355. (d) Raber, D. J.; Dukes, M. D.; Gregory, J. *Ibid.* **1974**, 667. (e) Schadt, F. L.; Bentley, T. W.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1976**, *98*, 7667.
(32) Shiner, V. S., Jr.; Dowd, W.; Fisher, R. D.; Hartshorn, S. R.; Kessik, M. A.; Milakofsky, L.; Rapp, M. W. *J. Am. Chem. Soc.* **1969**, *91*, 4838.
(33) Ballinger, P.; Long, F. A. *J. Am. Chem. Soc.* **1959**, *81*, 1050.
(34) Allen, A. D.; Rosenbaum, M.; Seto, N. O. L.; Tidwell, T. T. *J. Org. Chem.* **1982**, *47*, 4234.
(35) For a detailed evaluation of the use of conductimetric methods for determining solvolytic rate constants, see: McDonald, R. N.; Davis, G. E. *J. Org. Chem.* **1973**, *38*, 138.

Table II. Rates of Trifluoroethanolysis of 2-Arylprop-2-en-1-yl Tosylates (31a-d)[a]

compd	temp, °C (±0.01 °C)	rate, s^{-1}	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu
31a	95.00	$(5.93 \pm 0.04) \times 10^{-4}$		
	80.00	$(2.13 \pm 0.01) \times 10^{-4}$		
	65.00	$(7.69 \pm 0.00) \times 10^{-5}$		
	25.00[b]	2.63×10^{-6}	16.13 ± 0.43	−29.9 ± 1.2
31b	95.00	$(5.48 \pm 0.08) \times 10^{-4}$		
	80.00	$(2.03 \pm 0.01) \times 10^{-4}$		
	65.00	$(8.27 \pm 0.01) \times 10^{-5}$		
	25.00[b]	3.59×10^{-6}	14.87 ± 0.80	−33.5 ± 2.3
31c	95.00	$(3.70 \pm 0.09) \times 10^{-4}$		
	80.00	$(1.39 \pm 0.02) \times 10^{-4}$		
	65.00	$(5.46 \pm 0.05) \times 10^{-5}$		
	25.00[b]	2.30×10^{-6}	15.05 ± 0.60	−33.8 ± 1.7
31d	95.00	$(1.91 \pm 0.1) \times 10^{-4}$		
	80.00	$(7.41 \pm 0.03) \times 10^{-5}$		
	65.00	$(2.60 \pm 0.03) \times 10^{-5}$		
	25.00[b]	9.84×10^{-7}	15.72 ± 0.09	−33.3 ± 0.2
	95.00	$(4.15 \pm 0.04) \times 10^{-4}$		
	80.00	$(1.53 \pm 0.00) \times 10^{-4}$		
	65.00	$(4.54 \pm 0.05) \times 10^{-5}$		
	25.00[b]	1.21×10^{-6}	17.57 ± 0.58	−26.7 ± 1.6

[a] The reactions were run at 0.003–0.005 M and were buffered with 1.5 equiv of 2,6-lutidine. [b] Extrapolated from higher temperatures. [c] For preparation, see Sendeya, R. V.; Vizgert, R. V.; Mikhalevick, M. K. *Org. React.* **1970**, *7*, 227.

Scheme III



propyl triflate proceeded too rapidly to be measured, **33** was essentially unreactive at 140 °C and at 170 °C solvolyzed at a rate of less than 10^{-6} s^{-1}. Thus, in comparison to isopropyl triflate, the difference in free energy of activation ($\Delta\Delta G^{\ddagger}$) can be approximated to be 18–20 kcal/mol. These results are in good agreement with the work of Tidwell[3] and Liu.[4]

On the basis of the preliminary kinetic study of **33**, we were surprised to observe that, in buffered TFE, both **28** and **29** reacted rapidly at only 140 °C. The major product in both cases, which was isolated in 65% yield from **29**, was 1,1,1,5,5,5-hexafluoro-2-pentanone (**17**). No cyclopropyl products were found. The ketone, **17**, was shown to be identical with the previously prepared authentic sample. GC/mass spectral analysis of the minor products revealed the presence of 2,2,2-trifluoroethyl triflate (**34**), which was identified by comparison to the authentic material.[37] Control experiments showed that **28** and **29** did not react in the absence of 2,6-lutidine. The starting alcohol, **16**, was stable under the reaction conditions and was also stable in the presence of *p*-toluenesulfonic acid in ether at 35 °C. A proposed mechanism, which is consistent with the observed products and is precedented by the earlier works of Ball,[38a] Johncock,[38b] and Peterson,[38c] is shown in Scheme III. The work of Johncock,[38b] wherein he demonstrated that 1*H*,1*H*-perfluoroalkoxides effect S–O scission more readily than C–O scission in certain perfluoroalkyl triflates, is especially pertinent.

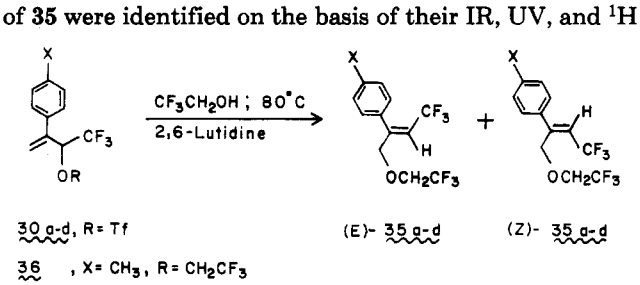
Table III. Summary of Products from the Trifluoroethanolysis of Triflates 30a-d

starting triflate	% yield[a] of **35**	Z/E[a,b] ratio
30a (X = OCH_3)	71	83/17
30b (X = CH_3)	60	84/16
30c (X = H)	61	88/12
30d (X = Cl)	69	92/8

[a] Product yields and isomer distributions were determined by VPC, using an internal standard method and a Hewlett-Packard Model 3370A integrator. [b] Control experiments demonstrated that (*E*)-**35** and (*Z*)-**35** were not interconverted under the reaction conditions.

The unexpected results obtained upon solvolyses of **28** and **29** suggested a greater opportunity for the formation of cyclopropyl products might be found in a system that combined less inductive destabilization with an electron-releasing substituent Z (cf. **5**) such as the aryl-substituted triflates, **30**.

Trifluoroethanolysis of the triflates **30a–d** proceeded by a mechanism obviously different than that proposed in Scheme III for **28** and **29**. The reactions proceeded cleanly and gave mixtures of the (*Z*)- and (*E*)-2-aryl-4,4,4-trifluorobut-2-en-1-yl ethers **35a–d**. Unlike **28** and **29**, solvolyses of **30a–d** produced no detectable trifluoroethyl triflate (**34**), but again, *there was no evidence of cyclopropyl products*. The products **35a–d** are clearly those of a classical allylic solvolysis. The results of the product studies are summarized in Table III. The *Z* and *E* isomers of **35** were identified on the basis of their IR, UV, and ^1H



and ^{19}F NMR spectra and their combustion analyses. The definitive *E* and *Z* stereochemical assignment was based on ultraviolet spectra.[39] The increased steric interaction

(36) Dafforn, G. A.; Streitwieser, A., Jr. *Tetrahedron Lett.* **1970**, 3159.
(37) Hansen, R. L. *J. Org. Chem.* **1965**, *30*, 4322.
(38) (a) Ball, S. S.; Andrews, L. J.; Keefer, R. M. *J. Org. Chem.* **1979**, *44*, 525. (b) Johncock, P. *J. Fluorine Chem.* **1974**, *4*, 25. (c) Peterson, P. E.; Indelicato, J. M. *J. Am. Chem. Soc.* **1968**, *90*, 6515.

Table IV. Trifluoroethanolysis of (*ZE*)-2-Aryl-4,4,4-trifluorobut-2-en-1-yl Triflates (37b–d)[a]

compd	temp, °C (±0.01 °C)	rate, s^{-1}	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu	k_H/k_{CF_3}[c,d]
37b	80.00	$(4.42 \pm 0.01) \times 10^{-3}$			
	65.00	$(1.12 \pm 0.02) \times 10^{-3}$			
	50.00	$(6.16 \pm 0.10) \times 10^{-4}$			
	25.00[b]	8.81×10^{-5}	14.21 ± 0.03	−29.4 ± 0.1	4.07×10^4
37c	80.00	$(3.54 \pm 0.10) \times 10^{-3}$			
	65.00	$(1.33 \pm 0.10) \times 10^{-3}$			
	50.00	$(4.40 \pm 0.10) \times 10^{-4}$			
	25.00[b]	5.66×10^{-5}	15.08 ± 0.16	−27.4 ± 0.5	4.06×10^4
37d	80.00	$(2.55 \pm 0.1) \times 10^{-3}$			
	65.00	$(9.96 \pm 0.1) \times 10^{-4}$			
	50.00	$(3.39 \pm 0.1) \times 10^{-4}$			
	25.00[b]	4.64×10^{-5}	14.60 ± 0.22	−29.4 ± 0.6	2.12×10^4

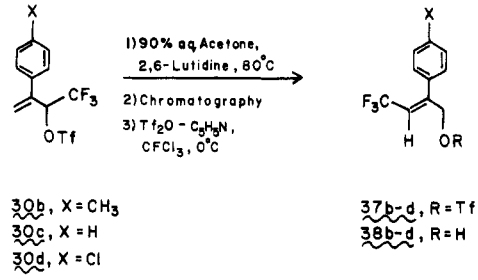
[a] The reactions were run at 0.003–0.005 M and were buffered with 1.5 equiv of 2,6-lutidine. [b] Extrapolated from higher temperatures. [c] The rate ratio was obtained from $10^6(k_{31b-d}/k_{37b-d})_{25}$. [d] See Table I, footnote *d* for an explanation of the k_{OTf}/k_{OTs} factor of 10^6.

between the trifluoromethyl and aryl groups of (*E*)-**35** relative to (*Z*)-**35** can be relieved by twisting the aryl ring out of the plane of the styryl olefin. The result of decreased conjugation produces a blue shift in the styryl A band. The A bands of the *E* isomers of **35a–d** all displayed a blue shift of 20–26 nm relative to their respective *Z* isomers.

It is interesting to note that the only solvolysis products of **30a–d** are those of abnormal allylic substitution (i.e., S_N2'). α-Halo substituents have been previously noted to favor abnormal substitution,[40a] presumably by inductively shifting π-electron density away from the γ-carbon. In fact, 1,1,1-trifluorobut-3-en-2-yl *p*-bromobenzenesulfonate was reported to react with nucleophiles almost exclusively by the S_N2' process.[40b] In order to establish the source of the products, (*E*)-**35** and (*Z*)-**35**, several control experiments were carried out. The alcohol **24b** was converted to the "normal" trifluoroethyl ether **36** by sequential treatment with sodium hydride and 2,2,2-trifluoroethyl triflate[37] in anhydrous dimethylformamide. When exposed to the solvolysis conditions, **36** did not rearrange to **35**. In principle, the triflates **30** could rearrange to the isomeric triflates **37** either via an intimate ion pair[41] or, as has recently been suggested by Jencks,[42] by a concerted sigmatropic rearrangement.[43] The rearranged triflates **37** might then be the precursors to the ethers **35**. Several experiments were carried out in order to test for this possibility.

Solvolyses of **30b–d** in 90% aqueous acetone gave rise to a mixture of the *E* and *Z* alcohols **38b–d**. The major *E* isomers were isolated by preparative gas chromatography and converted to the primary triflates **37b–d** by our usual method (Scheme IV). Trifluoroethanolysis of **37b–d** proceeded cleanly at a rate 50–100 times faster than observed for the secondary isomers **30b–d** (Table IV). The only products from **37b–d** were the expected[45] (*E*)-trifluoroethyl ethers, as determined by GC comparison with the authentic materials.

Scheme IV



30b, X = CH_3
30c, X = H
30d, X = Cl

37b-d, R = Tf
38b-d, R = H

Because of the aforementioned rate ratio (k_{37}/k_{30}), it was not feasible to stop the reactions of **30** to determine whether **37** was present. Instead, in order to test for a concerted rearrangement as suggested by Jencks,[42] the triflate **30b** in deuteriochloroform was heated to 85–90 °C for 2 h (equivalent to several half-lives) in an NMR tube and observed to be stable. To test for rearrangement via an intimate ion pair, **30b** was subjected to a similar experiment in the polar aprotic solvent acetonitrile-d_3. Again, there was no evidence for rearrangement to **37b**. Unfortunately, the slow decomposition of **30b** over the 2-h period slightly complicates the conclusions from the latter experiment.

A recent study by Tidwell[3b] of secondary carbocations destabilized by an α-CF_3, in strong ionizing nonnucleophilic solvents, argues convincingly for rate-limiting ionization to a cationic intermediate without participation by solvent (k_c) in secondary systems closely analogous to **30b–d**. In view of Tidwell's results, coupled with our own experiments, we believe that the ethers **35** most likely arise via a rate-limiting ionization of **30**, and the resulting ion pair then suffers exclusive attack by solvent at the γ-allylic carbon. If charge distribution is the chief factor determining product distribution and the solvent prefers to react with the carbon bearing the largest positive charge,[44] it is not surprising that the carbon γ to the trifluoromethyl, even though it is a primary carbon, should bear most of the positive charge. Interestingly, the *E*/*Z* ratio of the ethers **35a–d** varied systematically throughout the series. A reasonable explanation for this fact can be presented based on the data shown in Table V. α-Substituents on the styryl moiety result in steric inhibition to resonance which can be relieved by a skewing of the aromatic ring with respect to the ethylene moiety. With use of Suzuki's

(39) For a complete discussion of these principles, see: Suzuki, H. "Electronic Absorption Spectra and Geometry of Organic Molecules"; Academic Press: New York, 1967; pp 293–300.

(40) (a) de le Mare, P. B. D.; England, B. D.; Fowden, L.; Hughes, R. D.; Ingold, C. K. *J. Chem. Phys.* **1948**, *45*, 236. de le Mare, P. B. D.; Vernon, C. A. *J. Chem. Soc.* **1952**, 3325, 3328. (b) Pegolotti, J. A.; Young, W. G. *J. Am. Chem. Soc.* **1961**, *83*, 3258.

(41) For background on the theory of solvolysis reactions via variable involvement of ion pairs, see: (a) Bentley, T. W.; Schleyer, P. v. R. *Adv. Phys. Org. Chem.* **1977**, *14*, 1. (b) Harris, J. M. *Prog. Phys. Org. Chem.* **1974**, *11*, 89.

(42) (a) Jencks, W. P. *Acc. Chem. Res.* **1980**, *13*, 161. (b) Knier, B. L.; Jencks, W. P. *J. Am. Chem. Soc.* **1980**, *102*, 6789.

(43) For an early review of allylic isomerization reactions, see ref 44, pp 710–727.

(44) DeWolfe, R. H.; Young, W. G. In "The Chemistry of Alkenes"; Patai, S., Ed.; Interscience: New York, 1964; Chapter 10, pp 694–706.

(45) Young, W. G.; Sharman, S. H.; Winstein, S. *J. Am. Chem. Soc.* **1960**, *82*, 1376.

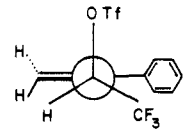
Table V. Ultraviolet Spectral Data of 23a-e and 25a-d and Their Calculated Interplanar Angles (θ)[a]

compd	λ_{max} (EtOH),[b] nm (log ϵ)	θ [a]
23a	251 (4.05)	37
23b	240 (4.04)	41
23c	234 (4.01)	44
23d	239	51
23e	236	43
25a	254 (4.11)	33
25b	246 (4.07)	32
25c	243 (4.11)	30
25d	247 (4.14)	38
p-$XC_6H_4(CH{=}CH_2)$		
X = OCH_3 [c]	260 (4.17)	0
X = CH_3 [c]	252 (4.23)	0
X = H[d]	248 (4.16)	0
X = Cl[e]	258	0
X = CF_3 [f]	250 (4.10)	0

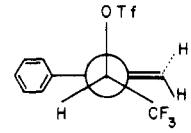
[a] Interplanar angle in degrees between the benzene ring and ethylene plane. [b] Styryl A band. [c] Roy, J. R.; Orchin, M. *J. Am. Chem. Soc.* **1959**, *81*, 305. [d] Overberger, C. G.; Tanner, D. *Ibid.* **1956**, *78*, 322. [e] Laitinen, H. A.; Miller, F. A.; Porks, T. D. *Ibid.* **1947**, *69*, 2707. [f] Trost, B. M.; Arndt, H. C. *Ibid.* **1973**, *95*, 5288.

method,[39] the value of the interplanar angle (θ) between the aromatic ring and the ethylene bond can be approximated, based on the position of the styryl A band. Table V presents the λ_{max} values and interplanar angles (θ) calculated for **23** and **25** and also shows the λ_{max} values for the parent styrenes.

The Newman projections **39** and **40** depict the rotamers that position the triflate group properly for maximum orbital overlap and that lead to (*E*)- and (*Z*)-**35**, respectively. The aryl–trifluoromethyl interaction in **39** can be



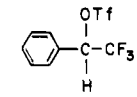
39



40

reduced by skewing the aromatic ring, while little relief is available from the trifluoromethyl–vinyl hydrogen steric interaction in **40**. As the aryl ring of **39** becomes more coplanar, i.e., as θ decreases, **39** will be relatively higher in its nonbonded interactional energy, and, hence, should lead to more of **40** and by extension more of (*Z*)-**35**. In fact, the calculated interplanar angles (θ) are qualitatively consistent with the trend in *E*/*Z* ratios shown in Table III.

With no detectable cyclopropyl products having arisen from solvolyses of the triflates **28–30** and **37**, we turned our attention to the kinetics of these solvolyses. The most obvious feature of the reaction kinetics was the expected large rate reduction provided by the trifluoromethyl group. The rate data in Tables I, II, and IV allow for the calculation of several new k_H/k_{CF_3} rate ratios. With the secondary triflates **30a–d**, the rate ratio is ca. 2×10^6, while with the primary triflates **37b–d**, the ratio is $(2–4) \times 10^4$. Interestingly, **30c** undergoes trifluoroethanolysis at a rate ca. 10^3 less than does a closely related secondary triflate, 1-phenyl-2,2,2-trifluoroethyl triflate (**41**).[3b] This result is significant, since the vinyl and phenyl groups are generally assumed to be quite similar in their ability to stabilize carbocations.[46,47] At the start of this study, we were concerned that solvent participation at an early stage in the solvolysis (k_S), either by an S_N2 or S_N2' process, might attenuate the degree of positive charge development. Tidwell's study of the aforementioned 1-aryl-2,2,2-trifluoroethyl tosylates (**41**) argues against a S_N2–k_S process



41

in **30**. Since intervention of a k_S pathway is known to accelerate solvolysis reactions relative to a pure k_c process,[41a,48e–g] the observation that **30c** reacted 10^3 times slower than did **41** provides supportive evidence against a k_S–S_N2' process.

The k_H/k_{CF_3} ratio cited for the triflates **30** is undoubtedly exaggerated because of an enhanced k_S component in the reference system, **31**. As a general rule, primary allylic substrates solvolyze with a high degree of nucleophilic solvent participation.[44,48d] However, the fact that crotyl chloride is 2000 times more reactive than allyl chloride[49] and that the γ-trifluoromethyl group of **37** produces a 20 000–40 000-fold decrease in solvolytic reactivity vs. **31** attests to a considerable positive charge in primary allylic substrates. Sneen and co-workers have presented compelling evidence for discrete ion pairs in allylic systems (including crotyl)[50a–c] and also in a closely related primary benzylic system.[50d]

The Grunwald and Winstein equation (eq 1) for analyzing nucleophilically solvent-assisted processes (k_S) has been widely used as a mechanistic probe.[41,48] In eq 1, k is the rate constant for solvolysis in any solvent and k_0 is the rate measured in 80% v/v ethanol/water; m is the sensitivity of the solvolysis of RX to solvent ionizing power Y and l is the sensitivity of RX to solvent nucleophilicity, N. Insight into the nature of our model system **31** was

$$\log (k/k_0) = lN + mY \quad (1)$$

obtained by solvolyzing **31b** in several ethanol/water mixtures. The results are summarized in Table VI.

When solvent nucleophilicity is kept relatively constant over a range of Y values, a reasonable approximation with aqueous ethanol solutions, eq 1 reduces to the original Winstein–Grunwald equation (eq 2). A plot of log k_{31b}

$$\log (k/k_0) = mY \quad (2)$$

(25 °C) vs. Y_{OTs}[48e] for the data in Table VI gives rise to an m_{OTs} for **31b** of 0.597 (corr = 0.9984). The response of **31b** to solvent ionizing power is comparable to that of isopropyl and benzyl tosylate.[48e] Since nucleophilic solvent assistance (k_S) has been previously calculated to enhance the trifluoroethanolysis of isopropyl tosylate by approximately an order of magnitude beyond a pure k_c process,[48e]

(46) Su, T. M.; Sliwinski, W. F.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1969**, *91*, 5386.

(47) Chwang, W. K.; Knittel, P.; Koshy, K. M.; Tidwell, T. T. *J. Am. Chem. Soc.* **1977**, *99*, 3395.

(48) (a) Grunwald, E.; Winstein, S. *J. Am. Chem. Soc.* **1948**, *70*, 846. (b) Winstein, S.; Grunwald, E.; Jones, H. W. *Ibid.* **1951**, *73*, 2700. (c) Winstein, S.; Fainberg, A. H.; Grunwald, E. *Ibid.* **1957**, *79*, 4146. (d) Bentley, T. W.; Schleyer, P. v. R. *Ibid.* **1976**, *98*, 7658. (e) Schadt, F. L.; Bentley, T. W.; Schleyer, P. v. R. *Ibid.* **1976**, *98*, 7667. (f) Bentley, T. W.; Bowen, C. T.; Morten, D. H.; Schleyer, P. v. R. *Ibid.* **1981**, *103*, 5466. (g) Pritt, J. R.; Whiting, M. C. *J. Chem. Soc., Perkin Trans. 2* **1975**, 1458.

(49) Vernon, C. A. *J. Chem. Soc.* **1954**, *423*, 4462.

(50) (a) Sneen, R. A.; Bradley, W. A. *J. Am. Chem. Soc.* **1972**, *94*, 6975. (b) Sneen, R. A.; Kay, P. S. *Ibid.* **1972**, *94*, 6983. (c) Sneen, R. A.; Carter, J. V. *Ibid.* **1972**, *94*, 6990. (d) Sneen, R. A.; Felt, G. R.; Dickason, W. C. *Ibid.* **1973**, *95*, 638.

Table VI. Rates of Aqueous Enthanolysis of 2-(4-Methylphenyl)prop-2-en-1-yl Tosylate[a]

solvent (% EtOH)[b]	Y value[c]	temp, °C (±0.01 °C)	k, s^{-1}	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, eu
95	−1.17	65.00	8.59×10^{-4}		
		50.00	2.57×10^{-4}		
		35.00	4.51×10^{-5}		
		25.00[d]	1.57×10^{-5}	19.74 ± 1.56	−14.3 ± 4.4
80	0.0	65.00	1.55×10^{-3}		
		50.00	4.40×10^{-4}		
		35.00	9.30×10^{-5}		
		25.00[d]	3.29×10^{-5}	18.81 ± 0.65	−16.0 ± 2.0
70	0.47	65.00	2.14×10^{-3}		
		50.00	6.17×10^{-4}		
		35.00	1.17×10^{-4}		
		25.00[d]	4.05×10^{-5}	19.48 ± 1.14	−13.3 ± 3.5
62.5	0.81	65.00	$(2.19 \pm 0.00) \times 10^{-3}$		
		50.00	$(6.15 \pm 0.01) \times 10^{-4}$		
		35.00	$(1.40 \pm 0.01) \times 10^{-4}$		
		25.00[d]	5.01×10^{-5}	18.35 ± 0.34	−16.6 ± 1.0
50	1.29	65.00	4.18×10^{-3}		
		50.00	1.10×10^{-3}		
		40.00	3.68×10^{-4}		
		25.00[d]	7.03×10^{-5}	19.80 ± 0.04	−11.1 ± 0.1

[a] The reactions were run at 0.003–0.005 M buffered with 1.5 equiv of 2,6-lutidine. [b] Volume percent (v/v) ethanol/water. [c] Reference 48e. [d] Extrapolated from higher temperatures.

Table VII. Rates of Aqueous Ethanolysis of 2-Arylprop-2-en-1-yl Tosylates[a,b]

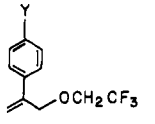
compd	temp, °C (±0.005 °C)	k, s^{-1}	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, eu
31c	65.00	$(1.98 \pm 0.01) \times 10^{-3}$		
	50.00	$(5.30 \pm 0.20) \times 10^{-4}$		
	35.00	$(1.24 \pm 0.00) \times 10^{-4}$		
	25.00[c]	4.36×10^{-5}	18.49 ± 0.03	−16.5 ± 0.1
31b	65.00	$(2.19 \pm 0.00) \times 10^{-3}$		
	50.00	$(6.15 \pm 0.10) \times 10^{-4}$		
	35.00	$(1.40 \pm 0.01) \times 10^{-4}$		
	25.00[c]	5.01×10^{-5}	18.35 ± 0.34	−16.6 ± 1.0
31d	65.00	$(1.70 \pm 0.02) \times 10^{-3}$		
	50.00	$(4.89 \pm 0.01) \times 10^{-4}$		
	35.00	$(1.16 \pm 0.00) \times 10^{-4}$		
	25.00[c]	4.23×10^{-5}	17.93 ± 0.27	−18.4 ± 1.0
31a	65.00	$(2.38 \pm 0.01) \times 10^{-3}$		
	50.00	$(6.81 \pm 0.06) \times 10^{-4}$		
	35.00	$(1.53 \pm 0.05) \times 10^{-4}$		
	25.00[c]	5.53×10^{-5}	18.31 ± 0.46	−16.6 ± 1.4

[a] 62.5% v/v ethanol/water. [b] The reactions were run at 0.003–0.005 M buffered with 1.5 equiv of 2,6-lutidine. [c] Extrapolated from higher temperatures.

extrapolation to **31b** suggests that the model system **31** most likely overstates the k_H/k_{CF_3} rate ratio in **30** by a comparable amount.[51]

Analysis of the activation parameters in Tables I, II, and IV supports the argument that the degree of nucleophilic solvent participation is greater in **31** than in **30**. Values of $\Delta S^{\ddagger}$ tend to show a systematic variation with mechanism. Usually, the values of $\Delta S^{\ddagger}$ are negative, and S_N2 reactions generally have numerically larger values than S_N1 reactions.[48f,52] The $\Delta S^{\ddagger}$ values for the primary tosylates **31** are 15–18 entropy units more negative than for the secondary triflates **30**, suggesting considerably more S_N2 character in the solvolysis of **31** than in the solvolysis of **30**. That the difference in $\Delta S^{\ddagger}$ is not due to a difference in leaving groups (OTs vs. OTf) is apparent by comparing the primary tosylates and triflates in Tables II and IV.

The kinetics for trifluoroethanolysis of the reference tosylates **31a–d** were previously recorded in Table II; the products, obtained in 93–100% yields, were the trifluoroethyl ethers **42**. The extrapolated rates at 25 °C correlated



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poorly with Brown's σ_p values[53a] ($\rho = -0.98 \pm 0.40$). A substantially improved correlation was obtained when σ_p was replaced with the inductive σ^0 values of Taft[53b] or van Bekkum[53c] ($\rho = -1.23 \pm 0.20$ and -1.39 ± 0.20, respectively). The basis for the use of σ^0 values was that many reactions cannot be mesomerically stabilized, and hence normal σ_p values for electron-releasing substituents are exalted. If any σ^+[53d] component is added to σ^0, the fit for **31a–d** rapidly deteriorates. Obviously, the reference to-

(51) This interpretive assessment of k_s in **31**, as opposed to a direct measurement by the methods described in ref 48e, results from the aforementioned reality that the reference k_c solvent, trifluoroacetic acid, is known to add to styrenes (ref 35).

(52) Hartshorn, S. R. "Aliphatic Nucleophilic Substitution"; Cambridge University Press: London, 1973; p 82.

(53) (a) McDaniel, D. H.; Brown, H. C. *J. Org. Chem.* **1958**, *23*, 420. (b) Taft, R. W.; Lewis, I. C. *J. Am. Chem. Soc.* **1959**, *81*, 5343. (c) van Bekkum, H.; Verkade, P. E.; Wepster, B. M. *Recl. Trav. Chim. Pays-Bas* **1959**, *78*, 815. (d) Brown, H. C.; Okamoto, Y. *J. Am. Chem. Soc.* **1958**, *80*, 4979.

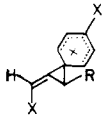
sylates appear to be responding solely to inductive effects.[54] Solvolysis of **31a–d** in 62.5% v/v ethanol/water[55] (Table VII) gave a σ^0 correlation of $\rho = -0.23 \pm 0.1$. Recalling the ρ of ca. −1.3 in trifluoroethanol, it is evident that the relatively nonnucleophilic TFE allows considerably more positive charge to develop in the transition state than is possible with aqueous ethanol. Reactions near the S_N2 end of the spectrum are well-known to experience less electron demand by the cationic center and, hence, be less sensitive to structural changes.[48f,52]

Analysis of the kinetic results shown in Table I for trifluoroethanolysis of **30a–e** showed a reasonable fit with σ_p and gave rise to a ρ of -1.33 ± 0.14. The correlation of the data with van Bekkum's inductive σ^0 values resulted in a ρ of -1.56 ± 0.11. We felt that minimal evidence for delocalization of positive charge to the 2-position of the allyl cation would be a demonstrable mesomeric contribution due to the aryl stabilization. Reactions involving resonance stabilization of a positive charge wherein the relative importance of the resonance interaction differs from that in a σ^+ relationship have been treated as a linear combination as in eq 3. Yukawa and Tsuno[57] rewrote eq 3 into the form of eq 4, where $a = \rho(1 - R)$ and $b = \rho R$.

$$\log (k/k_0) = a\sigma + b\sigma^+ \quad (3)$$

$$\log (k/k_0) = [(1 - R)\sigma + R\sigma^+]\rho \quad (4)$$

With the aid of a computer, R was allowed to vary so as to obtain the best fit of the data in Table I to eq 4. With use of Brown's σ_p and σ^+ values, an R of −0.26 was obtained. Thus, *the R term in eq 4 acted so as to remove the mesomeric contribution inherent in the σ_p constants!* When van Bekkum's σ^0 was used instead of σ_p, an R of 0.03 was obtained; for all practical purposes the fit was optimized by using only the inductive σ^0 constants. Indeed, the ρ values obtained for both **30** and **31** are remarkably reminiscent of the negative ρ values previously observed in several β-arylalkyl systems, prior to the onset of aryl participation.[58] In fact, even though there was no mesomeric stabilization provided to the allylic system, it is worth noting that there was also no evidence for aryl participation (k_Δ) in solvolysis of **30a** and **30b**. Such participation would lead to structure **43**. It should be noted that the analogous intermediate, **44**, has been invoked to explain the kinetics observed on bromination of 3-arylpropynes.[59]



43, R = CF_3, X = H
44, R = H, X = Br

The trifluoromethyl-substituted system **30** was somewhat more sensitive to aryl substitution than was the model system **31**. Two explanations can be proposed, neither of which requires the intermediacy of allylic charge delocalization to the central carbon. The most obvious explanation is that the decreased response of **31** is a result of the enhanced nucleophilic solvent participation in **31** relative to **30**. Increased S_N2 character decreases electron demand and reduces the degree of response to structural parameters.[48f,52] A second possible argument is based on electronic factors. Both **30** and **31** can be represented by the general structure **45**. Compounds such as **45** can be

45

treated by the linear free-energy relationship, eq 5, which

$$\log (k/k_0) = \gamma^+\rho + \sigma\rho' \quad (5)$$

is merely a combination of Peters' treatment for correlating groups adjacent to the cationic center[9] with the classical Hammett linear free-energy relationship.[53] If γ^+ was kept constant, eq 5 would reduce to the classical Hammett equation. However, there is ample experimental evidence that suggests that in any system ρ' is a function of γ^+. In solvolytic systems, as electron demand increases (i.e., $\gamma^+_{CF_3}$ vs. γ^+_H, or γ^+_{CN} vs. γ^+_H), ρ' becomes more responsive to changes in σ.[2h,3b,4a] In comparing systems **30** and **31**, the increased electron demand inherent in **30** would be expected to give rise to a more negative ρ than that observed in **31**.

In summary, allylic triflates that are disubstituted at the α- and γ-positions with trifluoromethyl groups did not solvolyze in the conventional manner but instead underwent a complex isomerization–cleavage reaction. Allylic triflates substituted with one trifluoromethyl group at either the α- or γ-position underwent trifluoroethanolysis at a theoretically reasonable rate, and, by extrapolation, gave k_H/k_{CF_3} rate ratios of ca. 2×10^6 and 4×10^4, respectively. While the trifluoromethyl group severely retarded the solvolyses of the aryl-substituted allylic triflates **30** relative to the unsubstituted parents **31**, there was no evidence for 1,3-π interaction as demonstrated by formation of cyclopropyl products. Likewise there was no evidence of mesomeric stabilization of charge at C-2 of the allylic system in **30**, as evidenced by linear free-energy correlations.

Experimental Section[60]

1,1,1,5,5,5-Hexafluoro-2-pentanone (17). A 500-mL, three-necked, round-bottomed flask, equipped with a Friedrichs condenser, a 60-mL constant-pressure addition funnel, and a magnetic stirring bar, was oven dried and allowed to cool under a flow of dry nitrogen. Under a positive nitrogen pressure, the flask was charged with 3.88 g (0.16 mol) of magnesium turnings, 150 mL of anhydrous ether, and an iodine crystal. A small portion of 29.2 g (0.165 mol) of 1-bromo-3,3,3-trifluoropropane[61] was added and the reaction was heated to reflux. After initiation, the remainder of the bromide was added at a rate sufficient to maintain a gentle reflux. After stirring for an additional 1 h, the solution was transferred under nitrogen to a dry 250-mL constant-pressure addition funnel. The addition funnel was attached to a 500-mL, three-necked, round-bottomed flask previously equipped with a reflux condenser and a mechanical stirrer and charged with 21.3 g (0.15 mol) of ethyl trifluoroacetate in 25 mL of anhydrous ether.

(54) For a brief discussion of a related study, without experimental details, see: Streitwieser, A. "Molecular Orbital Theory for Organic Chemists"; Wiley: New York, 1961; p 361.
(55) Y(62.5% v/v ethanol/H_2O) = Y(TFE) = 1.045; ref 50a and Shiner, V. J.; Dowd, W.; Fisher, R. D.; Hartshorn, S. R.; Kessick, M. A.; Milakofsky, L.; Rapp, M. W. *J. Am. Chem. Soc.* **1969**, *91*, 4838.
(56) Streitwieser, A., Jr. "Solvolytic Displacement Reactions"; McGraw-Hill: New York, 1962; pp 73–74.
(57) Yukawa, Y.; Tsuno, Y. *Bull. Chem. Soc. Jpn.* **1959**, *32*, 965, 967.
(58) Lancelott, C. J.; Cram, D. J.; Schleyer, P. v. R. In "Carbonium Ions"; Olah, G. A., Schleyer, P. v. R., Eds.; Wiley-Interscience: New York, 1972; Vol. 3, Chapter 27, pp 1370–1375.
(59) Pincock, J. A.; Somawardhana, C. *Can. J. Chem.* **1978**, *56*, 1164.
(60) Melting points and boiling points are uncorrected. Elemental analyses were performed by the Scandinavian Microanalytical Laboratory, Herlev, Denmark.
(61) Haszeldine, R. N. *J. Chem. Soc.* **1953**, 3371.

With ice cooling, the Grignard solution was added over a 1-h period. The reaction was stirred at 0 °C for another 5 h and finally stirred overnight at room temperature. The reaction was quenched by a dropwise addition of 20% (v/v) sulfuric acid. The layers were separated, and the aqueous phase was extracted with three 30-mL portions of ether. The combined extracts were washed with 500 mL of saturated sodium chloride, dried over anhydrous sodium sulfate, and filtered. A final drying with phosphorus pentoxide was required in order to completely remove all traces of moisture incorporated as the ketone hydrate. After the ethereal solution was decanted from the drying agent, the ether was removed by distillation through a 30-cm glass helices packed column. Fractional distillation of the residue afforded 17.7 g (62%) of pure **17**: bp 79–80 °C (lit. bp[25] 82 °C); IR (CCl_4) 1776, 1302, 1266, 1250, 1224, 1190, 1159, 1119, 1075, 992 cm^{-1}; ^1H NMR (CCl_4/Me_4Si) δ 1.49 (2 H, m), 1.94 (2 H, t, J = 9 Hz); ^{19}F NMR ($C_6H_5CF_3/CFCl_3$) δ 68.17 (t, J = 9 Hz), 80.4 (s).

3-Bromo-1,1,1,5,5,5-hexafluoro-2-pentanone (18). A 50-mL, three-necked, round-bottomed flask, equipped with a magnetic spin bar, a dry ice condenser, and a 10-mL constant-pressure addition funnel, was charged with 20 mL of concentrated sulfuric acid and 10 g (51 mmol) of 1,1,1,5,5,5-hexafluoro-2-pentanone (**17**). The flask was heated to 45 °C, and, over a 2-h period, 4.12 g (26 mmol) of bromine was added portionwise. (Liberated hydrogen bromide is reconverted into bromine in concentrated sulfuric acid.) The reaction was maintained at 45–50 °C for 8 h and finally allowed to stir at room temperature overnight. Any unreacted bromine was removed by heating the mixture to 60–70 °C, which caused the bromine to freeze on the dry ice condenser. The layers were separated, and the organic phase was stirred over anhydrous potassium carbonate. Fractional distillation afforded 11.10 g (89%) of the colorless bromo ketone **18**: bp 55–57 °C (ca. 170 mm). Usually, the bromo ketone was contamined with varying amounts of the unreacted starting ketone **17**, which was removed during a subsequent step. An analytical sample was obtained by preparative VPC on a 10 ft × $^3/_8$ in. 15% DEGS on 60/80 Chrom P column at 80 °C: IR (CCl_4) 1776, 1300, 1250, 1225, 1159, 1119, 1075, 1101 cm^{-1}; ^1H NMR (CCl_4/Me_4Si) δ 2.6–3.5 (2 H, m), 4.8 (1 H, d of d, J = 5 Hz, J' = 8 Hz); ^{19}F NMR ($C_6H_5CF_3/CFCl_3$) δ 65.97 (t, J = 10 Hz), 76.18 (s).

Anal. Calcd for $C_5H_3BrF_6O$: C, 22.00; H, 1.11. Found: C, 21.98; H, 1.27.

3-Bromo-1,1,1,5,5,5-hexafluoro-2-pentanol (19). A 250-mL, three-necked, round-bottomed flask, equipped with a magnetic stirring bar, a reflux condenser (equipped with a drying tube), and a 10-mL constant-pressure addition funnel, was charged with 100 mL of anhydrous ether and 0.28 g (7.5 mmol) of lithium aluminum hydride. To the stirred solution was added dropwise 6.0 g (22.3 mmol) of 3-bromo-1,1,1,5,5,5-hexafluoro-2-pentanone (**18**) over a 20-min period. The reaction mixture was allowed to stir for an additional 1 h, at which time any excess hydride was destroyed by the cautious dropwise addition of water, followed by the slow addition of 25 mL of 0.1 M sulfuric acid. The layers were separated, and the aqueous layer was extracted with three 20-mL portions of ether. The combined extracts were washed with saturated sodium chloride solution, dried over anhydrous calcium sulfate, and filtered. After removal of the ether by distillation, the residue was distilled through a 10-cm Vigreaux column to afford 4.0 g (67%) of **19** as a colorless liquid: bp 58–60 °C (ca. 50 mm). An analytical sample was obtained by preparative VPC on a 10 ft × $^3/_8$ in. 15% DEGS on 60/80 Chrom P column at 145 °C: IR (neat) 3571, 1401, 1374, 1261, 1190, 1155, 1094, 1056, 964, 922 cm^{-1}; ^1H NMR ($CDCl_3/Me_4Si$) δ 2.6–3.1 (3 H, m, 2 H after exchange with D_2O), 4.05 (1 H, m), 4.4 (1 H, t of d, J = 7 Hz, J' = 2 Hz).

Anal. Calcd for $C_5H_5BrF_6O$: C, 21.84; H, 1.83. Found: C, 21.92; H, 1.88.

1,1,1,5,5,5-Hexafluoro-2,3-epoxypentane (20). A 25-mL, three-necked, round-bottomed flask was equipped with a magnetic spin bar, a short-path distillation head, and a 10-mL constant-pressure addition funnel. The flask was charged with 12 g of a 50% (w/w) sodium hydroxide solution and heated to 95 °C. After addition of 1.90 g (7.0 mmol) of the bromohydrin **19** to the addition funnel, a vacuum of ca. 250 mm was applied to the entire system. The bromohydrin **19** was added to the hydroxide solution over a 2-min period, and the epoxide product **20** was spontaneously distilled from the reaction mixture along with appreciable quantities of water. The epoxide–water mixture was covered with powdered "Drierite" and redistilled to afford 1.12 g (85%) of **20**, bp 58–60 °C (250 mm), as a colorless liquid. An analytical sample was obtained by preparative VPC on a 10 ft × $^3/_8$ in. 15% DEGS on 60/80 Chrom P column at 75 °C: IR (CCl_4) 1351, 1295, 1258, 1190–1150, 922, 694 cm^{-1}; ^1H NMR (CCl_4/Me_4Si) δ 2.4–2.8 (2 H, m), 3.24–3.56 (2 H, m); ^{19}F NMR ($C_6H_5CF_3/CFCl_3$) δ 66.31 (t, J = 10 Hz), 69.48 (d, J = 7 Hz).

Anal. Calcd for $C_5H_4F_6O$: C, 30.92; H, 2.06. Found: C, 30.89; H, 2.13.

***trans*-1,1,1,5,5,5-Hexafluoropent-3-en-2-ol (15).** A 50-mL, side-armed flask equipped with a magnetic stirring bar, a reflux condenser, and a rubber septum was charged with 25 mL of anhydrous ether and 0.67 g (6.6 mmol) of diisopropylamine. With ice cooling and under a nitrogen atmosphere, the solution was treated with 1 equiv of commercial methyllithium. A 100-mL, side-armed flask, equipped as described above and blanketed with dry nitrogen, was charged with 1.16 g (6 mmol) of **20** and 15 mL of anhydrous ether. With ice cooling, the lithium diisopropylamide solution was added dropwise via syringe. The reaction was allowed to stand overnight at −5 °C. After addition of 25 mL of 1 N hydrochloric acid solution, the layers were separated, and the aqueous phase was washed with three 15-mL portions of ether. The combined ethereal solution was washed with 20 mL of 1 N hydrochloric acid and 20 mL of saturated sodium chloride solution and dried over anhydrous magnesium sulfate. After filtration, the ether was removed by distillation and the residue was distilled under reduced pressure. After an early fraction containing ether and some unreacted starting material, 0.59 g (51%) of the desired alcohol **15** was obtained as a colorless oil: bp 48–50 °C (50 mm). An analytical sample was obtained by preparative VPC on a 10 ft × $^3/_8$ in. 15% DEGS on 60/80 Chrom P column at 140 °C: IR (neat) 3460, 1698, 1325, 1274, 1183, 1160–1110, 966, 885 cm^{-1}; ^1H NMR ($CDCl_3/Me_4Si$) δ 1.70 (1 H, m, exchanges with D_2O), 4.63 (1 H, m), 6.30 (2 H, m); ^{19}F NMR ($C_6H_5CF_3/CFCl_3$) δ 66.03 (d, J = 6 Hz), 79.96 (d, J = 7 Hz).

Anal. Calcd for $C_5H_4F_6O$: C, 30.92; H, 2.06. Found: C, 30.69; H, 2.18.

1,1,1,5,5,5-Hexafluoropent-3-yn-2-ol (22). A solution of 0.154 mol of ethylmagnesium bromide (from 16.8 g of ethyl bromide) in 150 mL of anhydrous ether was prepared in a 500-mL, three-necked, round-bottomed flask. The flask was equipped with a Dewar condenser, and, over a 3-h period, 15.0 g (0.16 mol) of trifluoropropyne[62] was passed into the solution through a fritted gas dispersion tube. The solution was cooled to 0–5 °C and 0.16 mol of freshly generated trifluoroacetaldehyde[29] was condensed into the reaction. After the mixture was stirred for an additional 15 min, saturated ammonium chloride solution was added dropwise until the precipitated salts coagulated. The ethereal solution was decanted, the salts were washed twice with 20-mL portions of ether, and the combined ethereal solution was filtered and the ether was removed by distillation through a 30-cm glass helices packed column. The residue was distilled through a 10-cm glass helices packed column. The first fraction, bp 35–40 °C, accounted for 2.7 g and consisted largely of ether. A second fraction afforded 7.0 g of material of bp 41–89 °C consisting of ca. 70% of the desired alcohol **22** along with ether. A final fraction was constant boiling at 90–92 °C and afforded 17.0 g of ca. 90% pure **22**, contaminated with azeotropic ether. An analytical sample was obtained by preparative VPC with a 15% DEGS on 60/80 Chrom P column at 110 °C: n_D^{23} 1.3174; IR (CCl_4) 3690, 2320, 1370, 1351, 1198, 1163, 1083, 1005, 840, 706 cm^{-1}; ^1H NMR ($CDCl_3/Me_4Si$) δ 2.84 (1 H, m, exchanges with D_2O), 4.80 (1 H, m); ^{19}F NMR ($C_6H_5CF_3/CFCl_3$) δ 52.94 (d, J = 2.7 Hz), 80.14 (d, J = 5.5 Hz).

Anal. Calcd for $C_5H_2F_6O$: C, 31.27; H, 1.05. Found: C, 31.15; H, 1.16.

***cis*-1,1,1,5,5,5-Hexafluoropent-3-en-2-ol (16).** A 125-mL hydrogenation flask was charged with 200 mg of 5% palladium-on-barium sulfate and 25 mL of absolute ethanol and connected to an atmospheric pressure hydrogenation apparatus. After blanketing of the catalyst, 9.0 g (0.047 mol) of **22** was added in

(62) Finnegan, W. G.; Norris, W. P. *J. Org. Chem.* **1963**, *28*, 1139.

one portion. Hydrogen uptake was smooth and the reaction was monitored by analytical VPC (10 ft × $^1/_8$ in. 10% FFAP on 45/60 Chrom G; column T = 120 °C). Upon the first appearance of the fully saturated alcohol, the hydrogen source was removed and the solution was filtered through a Celite pad. The filtrate was poured into 125 mL of ice–water, and the colorless liquid that separated to the bottom was drawn off. The cold aqueous phase was washed with three 25-mL portions of Freon-11, and the combined organic phases were washed twice with 20-mL portions of cold water and then with 25 mL of saturated sodium chloride solution. The organic phase was dried over anhydrous sodium sulfate, and, after filtration, the Freon-11 was removed by distillation. The residue was flash distilled. Fractional distillation with a Nester-Faust NFA-200 annular still afforded 7.57 g (83%) of pure **16**: bp 67 °C (100 mm). An analytical sample was obtained by preparative VPC on a 10 ft × $^1/_4$ in. 10% FFAP on 45/60 Chrom G column at 120 °C: IR (neat) 3448, 1695, 1427, 1274, 1222, 1190, 1134, 1080, 1030, 877, 766, 733 cm^{-1}; ^{1}H NMR ($CDCl_3$/Me_4Si) δ 3.0 (1 H, m, exchanges with D_2O), 5.03 (1 H, m), 5.97 (2 H, m); ^{19}F NMR ($C_6H_5CF_3$/$CFCl_3$)[63] δ 60.23 (d of m, J = 7.5 Hz), 80.21 (m).

Anal. Calcd for $C_5H_4F_6O$: C, 30.92; H, 2.06. Found: C, 30.69; H, 2.18.

1,1,1,5,5,5-Hexafluoro-2-pentanol (32). A 50-mL, round-bottomed flask equipped with a magnetic spin bar and a reflux condenser was charged with 20 mL of anhydrous ether and 0.32 g (8.5 mmol) of lithium aluminum hydride. To this suspension was added, at room temperature, with stirring, 1.94 g (0.01 mol) of 1,1,1,5,5,5-hexafluoro-2-pentanone (**17**) in 8 mL of ether over a 30-min period. After being refluxed for 10 h, the reaction mixture was quenched by the addition of 1.0 mL of 10% sodium hydroxide solution. The resulting reaction mixture was filtered, the filtrate was dried over anhydrous sodium sulfate and filtered, and the ether was removed by distillation through a 15-cm glass helices packed column. Distillation of the residue afforded 1.94 g of a colorless oil: bp 60–62 °C (55 mm) [lit.[64] bp 108 °C (760 mm)]. The product was shown to be 95% pure by analytical VPC (contaminated only with ether) for a 95% yield: IR (CCl_4) 3705, 1300, 1255, 1180, 1157 cm^{-1}; ^{1}H NMR ($CDCl_3$/Me_4Si) δ 1.88 (2 H, m), 2.16 (1 H, s, exchanges with D_2O), 2.24 (2 H, m), 3.90 (1 H, m).

1-(Bromoethenyl)benzene (α-Bromostyrene 24c). Method A. The procedure of Nef[65] was used to prepare **24c** in 55% yield.

Method B. A cold solution of 7 g (68 mmol) of phenylacetylene in 15 mL of glacial acetic acid was treated with a large excess of anhydrous hydrogen bromide. The solution was poured into 150 mL of ether and neutralized by the cautious addition of 20% sodium carbonate solution. The layers were separated, and the aqueous phase was extracted with two 50-mL portions of ether. The combined ethereal extracts were washed with saturated sodium chloride solution, dried over anhydrous magnesium sulfate, and filtered, and the filtrate was concentrated on a rotary evaporator. The residue was taken up in 400 mL of 60–70 °C petroleum ether and the solution was passed through 90 g of Brockman, basic, activity I alumina. The column was further eluted with an additional 600 mL of petroleum ether. Concentration of the eluent afforded 7.0 g (56%) of **24c** as a colorless oil, which could be used without further purification: IR (neat) 1695, 1623, 1493, 1450, 1266, 1215, 1055, 1028, 888, 768, 696 cm^{-1}; ^{1}H NMR (CCl_4/Me_4Si) δ 5.77 (1 H, d, J = 2 Hz), 6.07 (1 H, d, J = 2 Hz), 7.30 (3 H, m), 7.53 (2 H, m).

3-Phenyl-1,1,1-trifluorobut-3-en-2-ol (23c). A 250-mL, three-necked, round-bottomed flask was equipped with a Hirschberg stirrer, a Dewar condenser, and a 10-mL addition funnel. Under a nitrogen atmosphere, the flask was charged with 90 mL of anhydrous ether and 0.485 g of finely cut lithium wire (70 mmol). With ice cooling and vigorous stirring, 6.4 g (35 mmol) of α-bromostyrene (**24c**) was added at such a rate that the temperature in the flask never exceeded 5 °C. After the mixture was stirred for an additional 2 h, 0.04 mol of trifluoroacetaldehyde was condensed into the reaction. The mixture was poured into 100 mL of 3% hydrochloric acid, the layers were separated, and the aqueous phase was extracted with three 30-mL portions of ether. The combined ethereal solutions were washed with saturated sodium chloride solution, dried over anhydrous calcium sulfate, and filtered, and the filtrate was concentrated on a rotary evaporator. The residue was chromatographed on 200 g of silica gel with 12% ether–88% 60–70 °C petroleum ether. Concentration of the product fractions and distillation of the residue afforded 2.00 g (33%) of high pure **23c**: bp 50–51 °C (0.1 mm). An analytical sample was obtained by preparative VPC on a 5% XF-1150 on 45/60 Chrom W column at 145 °C: n_D^{25} 1.4871; IR (neat) 3450, 1640, 1495, 1447, 1266, 1175, 1134, 1064, 1028, 933, 853, 777, 725, 698 cm^{-1}; ^{1}H NMR ($CDCl_3$/Me_4Si) δ 3.00 (1 H, br s, exchanges with D_2O), 4.88 (1 H, q, J = 7 Hz), 5.54 (1 H, br s), 5.62 (1 H, br s), 7.36 (5 H, s); ^{19}F NMR ($CDCl_3$/$CFCl_3$) δ 77.76 (d, J = 7 Hz); UV λ_{max}^{EtOH} 234 nm (log ϵ 4.01).

Anal. Calcd for $C_{10}H_9F_3O$: C, 59.40; H, 4.49. Found: C, 59.12; H, 4.57.

2-Phenylallyl Alcohol (25c). A 250-mL, three-necked, round-bottomed flask, equipped with a reflux condenser, a 60-mL addition funnel, and a magnetic stirring bar, was charged with 1.7 g (70 mmol) of magnesium. Under a flow of dry, oxygen-free nitrogen, the apparatus was dried with an electric heat gun. Upon cooling, the flask was charged with 50 mL of anhydrous tetrahydrofuran, a small iodine crystal, and 10–15 drops of ethyl bromide. After the reaction had initiated, 12.2 g (67 mmol) of α-bromostyrene (**24c**) in 15 mL of tetrahydrofuran was added dropwise over a 1-h period. The reaction was stirred an additional 30 min, refluxed for 30 min, and cooled to 25 °C. With continued stirring, 3 g (0.1 mol) of solid paraformaldehyde was added in one portion and the reaction was stirred for an additional 1 h. After addition of 30 mL of 20% ammonium chloride solution, the layers were separated, and the aqueous phase was extracted with three 40-mL portions of ether. The combined organic phase was washed with two 50-mL portions of water and once with 50 mL of saturated sodium chloride solution. The solution was dried over anhydrous magnesium sulfate and filtered, and the filtrate was concentrated on a rotary evaporator. The residue was distilled to afford 3.75 g (42%) of **25c**, bp 77–79 °C (0.25 mm) [lit.[66] bp 95–96 °C (1.5 mm)], as a colorless liquid.

4-(1-Bromoethenyl)chlorobenzene (24d). Method A. The procedure by Nef[65] for the preparation of α-bromostyrene (**24c**) was used to prepare **24d** from (*p*-chlorophenyl)acetylene[67] in 46% yield.

Method B. The procedure previously described for the preparation of **24c** (method B) was applied in the same manner to afford to afford **24d**, contaminated only with trace amounts of petroleum ether, in 69% yield: bp 48–50 °C (2.0 × 10^{-5} mm); IR (neat) 1590, 1484, 1395, 1209, 1092, 1052, 1008, 882, 825, 795, 715 cm^{-1}; ^{1}H NMR (CCl_4/Me_4Si) δ 5.65 (1 H, d, J = 2.2 Hz), 6.05 (1 H, d, J = 2.2 Hz), 7.1–7.7 (4 H, m).

Anal. Calcd m/e C_8H_6BrCl: 215.9342. Found: 215.9327.

3-(4-Chlorophenyl)-1,1,1-trifluorobut-3-en-2-ol (23d). The Grignard reagent of **24d** was prepared in a manner analogous to the procedure outlined for the preparation of **25c**. A slurry of 0.5 g of magnesium in 15 mL of tetrahydrofuran was treated dropwise with 4.4 g (20 mmol) of **24d** in 10 mL of tetrahydrofuran at 40–45 °C. The Grignard reagent was treated with 3 × 10^{-2} mol of gaseous trifluoroacetaldehyde. After addition of 25 mL of 20% ammonium chloride, the layers were separated, and the aqueous phase was washed with four 30-mL portions of ether. The combined organic phase was washed with 50 mL of saturated sodium chloride solution, dried over anhydrous magnesium sulfate, and filtered, and the filtrate was concentrated on a rotary evaporator. The residue was chromatographed on silica gel (25 g of silica/g of residue) with 10% ether–90% 60–70 °C petroleum ether (v/v). The alcohol fractions were combined and concentrated in vacuo, and the residue was distilled to afford 2.34 g (49%) of pure **23d**, bp 60–61 °C (10^{-5} mm), as a very light yellow oil. An analytical sample was obtained by preparative VPC on a 10 ft × $^1/_4$ in. 5% XF-1150 on 45/60 Chrom W column at 175 °C: IR (neat) 3420,

(63) Several of the compounds investigated gave complex fluorine magnetic resonance spectra due to through space ^{19}F–^{19}F coupling. A paper describing this phenomenon will be submitted for publication in the near future.

(64) Holbrook, G. W.; Pierce, O. R. *J. Org. Chem.* **1961**, *26*, 1037.

(65) Nef, J. V. *Justus Liebigs Ann. Chem.* **1899**, *308*, 264.

(66) Hatch, L. F.; Patton, T. L. *J. Am. Chem. Soc.* **1954**, *76*, 2705.

(67) Jacobs, T. L. *Org. React.* **1949**, *5*, 1.

1500, 1401, 1269, 1176, 1137, 1097, 1016, 935, 856, 836, 800, 767, 737, 722 cm^{-1}; ^1H NMR ($CDCl_3/Me_4Si$) δ 2.52 (1 H, d, J = 5 Hz, exchanges with D_2O), 4.93 (1 H, m), 5.63 (1 H, s), 5.71 (1 H, s), 7.33 (4 H, s); ^{19}F NMR ($CDCl_3/CFCl_3$) δ 77.79 (d, J = 7 Hz); UV λ_{max}^{EtOH} 239 nm.

Anal. Calcd for $C_{10}H_8ClF_3O$: C, 50.76; H, 3.41. Found: C, 50.81; H, 3.48.

2-(4-Chlorophenyl)allyl Alcohol (25d). A solution of the Grignard reagent derived from 4.34 g (0.02 mol) of α-bromo-p-chlorostyrene (**24d**) and 0.02 mol of magnesium in 20 mL of tetrahydrofuran was prepared in a manner analogous to that previously described in the preparation of **23d**. The solution was treated at 0 °C with 0.04 mol of gaseous formaldehyde and worked up as described in the preparation of **25c**. The residue was chromatographed on silica gel (25 g of silica gel/g of residue) with 12% ether–88% petroleum ether. The alcohol fractions were combined and concentrated. High-vacuum distillation afforded 1.77 g (53%) of pure **25d** as a very light yellow oil: bp 72–73 °C (10^{-6} mm); IR (neat) 3300, 1496, 1400, 1090, 1042, 1012, 908, 830 cm^{-1}; ^1H NMR ($CDCl_3/Me_4Si$) δ 1.7 (1 H, m, exchanges with D_2O), 4.5 (2 H, m), 5.27 (1 H, m), 5.36 (1 H, m), 7.05 (4 H, s); UV λ_{max}^{EtOH} 247 nm (log ϵ 4.14).

Anal. Calcd for C_9H_9ClO: C, 64.10; H, 5.38. Found: C, 64.12; H, 5.53.

3-(4-Methylphenyl)-1,1,1-trifluorobut-3-en-2-ol (23b). A 500-mL, three-necked, round-bottomed flask, equipped with a reflux condenser, a 125-mL addition funnel, and a gas inlet adapter, was flushed with dry nitrogen and charged with 2.5 g of magnesium turnings and 100 mL of anhydrous tetrahydrofuran. After the reaction was initiated with 10–15 drops of ethyl bromide, a solution of 14.0 g (92 mmol) of α-chloro-p-methylstyrene (**24b**)[67] in 25 mL of tetrahydrofuran was added at a rate that sustained a reaction temperature of 40–45 °C. The solution was stirred an additional hour and treated with 0.1 mol of gaseous trifluoroacetaldehyde. After addition of 70 mL of 20% ammonium chloride solution, the layers were separated, and the aqueous phase was clarified by addition of 3 N hydrochloric acid until all the suspended salts dissolved. The aqueous phase was extracted with three 50-mL portions of ether, and the combined organic phase was washed thoroughly with three 30-mL portions of 1.5 N hydrochloric acid and once with 50 mL of saturated sodium chloride solution. The ethereal solution was dried over anhydrous magnesium sulfate and filtered, and the filtrate was concentrated in vacuo. The residue was chromatographed on 250 g of silica gel with 10% ether–90% petroleum ether (v/v). The alcohol fractions were combined and concentrated by rotary evaporation, and the residue was distilled to afford 4.83 g (25%) of pure **23b**, bp 68–70 °C (0.3 mm), as a colorless oil. An analytical sample was obtained by preparative VPC on a 10 ft × $^1/_4$ in. 5% XF-1150 on 45/60 Chrom W column at 155 °C: IR (neat) 3430, 1516, 1266, 1175, 1135, 1066, 950, 927, 855, 823 cm^{-1}; ^1H NMR ($CDCl_3/Me_4Si$) δ 2.37 (3 H, s), 2.44 (1 H, d, J = 7 Hz, exchanges with D_2O), 4.95 (1 H, m), 6.02 (2 H, m), 7.24 (4 H, m); ^{19}F NMR ($CDCl_3/CFCl_3$) δ 77.81 (d, J = 7 Hz); UV λ_{max}^{EtOH} 240 nm (log ϵ 4.04).

Anal. Calcd for $C_{11}H_{11}F_3O$: C, 61.11; H, 5.13. Found: C, 61.00; H, 5.22.

2-(4-Methylphenyl)allyl Alcohol (25b). A solution of 15.2 g (0.1 mol) of α-chloro-p-methylstyrene in 25 mL of tetrahydrofuran was added to 2.42 g (0.1 mol) of magnesium turnings in 70 mL of tetrahydrofuran to generate the Grignard reagent exactly as described for the preparation of **23b**. The Grignard solution was treated with 0.2 mol of gaseous formaldehyde and worked up as described in the preparation of **25c**. The crude residue was chromatographed on 300 g of silica gel with 12% ether–88% petroleum ether (v/v). The alcohol fractions were combined and concentrated by rotary evaporation, and the residue was sublimed in vacuo to afford 7.1 g (48%) of pure **25b** as a snow white crystalline solid: mp 50–52 °C. An analytical sample was obtained by recrystallization from cyclohexane followed by a second sublimation: mp 52–53 °C; IR (KBr) 3500–3100, 1517, 1126, 1107, 1042, 1015, 895, 825, 738 cm^{-1}; ^1H NMR ($CDCl_3/Me_4Si$) δ 1.9 (1 H, m, exchanges with D_2O), 2.34 (3 H, s), 4.48 (2 H, m), 5.23 (1 H, m), 5.37 (1 H, m), 6.84–7.40 (4 H, m); UV λ_{max}^{EtOH} 246 nm (log ϵ 4.07).

Anal. Calcd for $C_{10}H_{12}O$: C, 81.04; H, 8.16. Found: C, 81.01; H, 8.13.

4-(1-Bromoethenyl)anisole (24a). Compound **24a** was prepared in quantitative yield by the procedure of Rappoport and Apeloig.[68]

2-(4-Methoxyphenyl)allyl Alcohol (25a). A solution of 0.02 mol of freshly prepared α-bromo-p-methoxystyrene (**24a**) in 80 mL of anhydrous ether was cooled under an argon atmosphere to −70 °C. A few crystals of bipyridyl were added as an indicator, and 9.5 mL of 2.1 M n-butyllithium in hexane was added dropwise over a 10-min period. The solution was slowly warmed until the mixture became homogeneous and immediately recooled. If any precipitation from solution was observed upon recooling, the warming and cooling cycle was repeated until no more material precipitated upon cooling. The solution was warmed to −20 °C and treated with 2 equiv of gaseous formaldehyde. The reaction was quenched and worked up as previously described in the preparation of **25c**. Concentration of the ethereal solution afforded 2.78 g (85%) of a yellow solid, which melted over a wide range. The product was shown by high-pressure liquid chromatography (HPLC) to be a mixture of two alcohols. Chromatography on silica gel (70 g, 12% ether–88% petroleum ether) removed the nonpolar starting materials and began to separate the two alcohols. The fractions enriched in alcohol were combined. The combined fractions of the more polar alcohol were rechromatographed on 150 g of silica gel (same solvent) from which 530 mg of **25a** (greater than 95% pure) was obtained: mp 78.0–79.5 °C. The less polar alcohol was identified by spectral data and comparison to an authentic sample[69] as 3-(p-methoxyphenyl)propargyl alcohol (**27**). An analytical sample of **25a** was obtained by subliming the material from the last fractions collected from the column chromatography: mp 80–81 °C; IR (KBr) 3500–3100, 1612, 1515, 1254, 1186, 1110, 1055, 1037, 896, 835 cm^{-1}; ^1H NMR ($CDCl_3/Me_4Si$) δ 1.50–1.90 (1 H, m, exchanges with D_2O), 3.80 (3 H, s), 4.50 (2 H, br s), 5.24 (1 H, m), 5.36 (1 H, br s), 6.83 (2 H, d, J = 8 Hz), 7.36 (2 H, d, J = 8 Hz); UV λ_{max}^{EtOH} 254 nm (log ϵ 4.11).

Anal. Calcd for $C_{10}H_{12}O_2$: C, 73.14; H, 7.37. Found: C, 72.98; H, 7.31.

3-(4-Methoxyphenyl)-1,1,1-trifluorobut-3-en-2-ol (23a). A solution of 0.02 mol of **24a** in anhydrous ether was converted to the α-lithiostyryl derivative as described in the preparation of **25a**. The organolithium solution was treated with 0.03 mol of trifluoroacetaldehyde. The reaction was treated with 50 mL of 20% ammonium chloride solution, and the layers were separated. The aqueous phase was extracted with two 25-mL portions of ether, and the combined ethereal solution was washed with 50 mL of saturated sodium chloride solution. The organic solution was dried over anhydrous magnesium sulfate and filtered, and the filtrate was concentrated in vacuo to afford 2.4 g of yellow oil, which was shown to be a mixture of two alcohols by HPLC. Silica gel chromatography (50 g of silica/1 g of residue) with 6% ether–94% petroleum ether (v/v) was able to greatly enrich the mixture in the desired alcohol **23a**, and an analytical sample as well as material for solvolysis could be obtained by preparative VPC on a 10 ft × $^1/_4$ in. 5% XF-1150 on 45/60 Chrom W column at 180 °C. The minor, less polar alcohol was identified as 4-(4-methoxyphenyl)-1,1,1-trifluorobut-3-yn-2-ol (**26**) by comparison with an authentic sample.

Spectral data for **23a**: IR (neat) 3450, 1614, 1516, 1251, 1176, 1135, 1068, 1034, 852, 834 cm^{-1}; ^1H NMR ($CDCl_3/Me_4Si$) δ 2.59 (1 H, d, J = 6 Hz, exchanges with D_2O), 3.84 (3 H, s), 4.94 (1 H, m; q after D_2O exchange, J = 7 Hz), 5.58 (1 H, br s), 5.62 (1 H, br s), 6.90 (2 H, d, J = 9 Hz), 7.30 (2 H, d, J = 9 Hz); ^{19}F NMR ($CDCl_3/CFCl_3$) δ 77.76 (d, J = 7 Hz); UV λ_{max}^{EtOH} 251 nm (log ϵ 4.05).

Anal. Calcd for $C_{11}H_{11}F_3O_2$: C, 56.89; H, 4.78. Found: C, 56.58; H, 5.02.

4-(4-Methoxyphenyl)-1,1,1-trifluorobut-3-yn-2-ol (26). A solution of 2.0 g (15 mmol) of (p-methoxyphenyl)acetylene[70] in 5 mL of anhydrous ether was added dropwise at 25 °C to 10.5 mL of 1.44 M n-butyllithium in ether. The reaction was stirred for 2 h at 25 °C and then treated with a 10% excess of gaseous trifluoroacetaldehyde. After addition of 15 mL of 20% ammonium

(68) Rappoport, Z.; Apeloig, Y. *J. Am. Chem. Soc.* **1974**, *96*, 6428.
(69) Bohlmann, F.; Enkelmann, R. E.; Plettner, W. *Chem. Ber.* **1964**, *97*, 2118.
(70) Manchot, W. *Justus Liebigs Ann. Chem.* **1912**, *387*, 281.

chloride solution, enough 1 N hydrochloric acid was added to clarify the two layers. The layers were separated, and the aqueous phase was extracted with three 15-mL portions of ether. The combined organic layer was washed with 20 mL of saturated sodium chloride solution, dried over anhydrous magnesium sulfate, and filtered, and the filtrate was concentrated in vacuo. The residue was distilled to afford 2.80 g (81%) of **26** as a light yellow oil: bp 104–105 °C (0.6 mm). An analytical sample was obtained by preparative VPC on a 10 ft × $^1/_4$ in. 5% XF-1150 on 45/60 Chrom W column at 180 °C: IR (neat) 3420, 2222, 1613, 1510, 1252, 1182, 1140, 1075, 1030, 982, 831 cm^{-1}; ^{1}H NMR ($CDCl_3$/Me_4Si) δ 2.6 (1 H, m, exchanges with D_2O), 383 (3 H, s), 4.83 (1 H, m, collapses to q, J = 6 Hz after D_2O exchange), 6.83 (2 H, d, J = 9 Hz), 7.46 (2 H, d, J = 9 Hz).

Anal. Calcd for $C_{11}H_9F_3O_2$: C, 57.39; H, 3.94. Found: C, 57.47; H, 4.00.

4-(Trifluoromethyl)styrene.[71] A solution of 30 g (0.16 mol) of 1-[4-(trifluoromethyl)phenyl]ethanol[71] in 175 mL of anhydrous benzene was treated portionwise with 32 g of phosphorus pentoxide. The solution was refluxed for 30 min and the benzene solution was decanted. The solvent was removed by fractional distillation through a 15-cm glass helices packed column. The residue was fractionated through the same column to afford 12.3 g (45%) of pure 4-(trifluoromethyl)styrene, bp 67–68 °C (25 mm) [lit.[71] bp 66–68 °C (40 mm)]. Spectral data: IR (neat) 1620, 1402, 1325, 1165, 1125, 1068, 1011, 985, 917, 842 cm^{-1}; ^{1}H NMR (CCl_4/Me_4Si) δ 5.33 (H_a, d of d, J_{ac} = 11 Hz, $J_{ab} \leq$ 1 Hz), 5.75 (H_b, d of d, J_{bc} = 17 Hz, $J_{ab} \leq$ 1 Hz), 6.70 (H_c, d of d, J_{ac} = 11 Hz, J_{bc} = 17 Hz), 7.47 (4 H, m); ^{19}F NMR ($CDCl_3$/$CFCl_3$) δ 63.50 (s).

4-(1,2-Dibromoethyl)benzotrifluoride. A solution of 12.3 g (71 mmol) of 4-(trifluoromethyl)styrene in 75 mL of carbon tetrachloride was treated with 11.5 g of bromine (72 mmol) in 40 mL of carbon tetrachloride at 0 °C. The reaction was stirred and irradiated with a Hanovia utility lamp for 2 h. Unreacted bromine was removed by washing with 50 mL of 0.3 M sodium thiosulfate solution. The organic phase was washed twice with 50-mL portions of water and once with 50 mL of saturated sodium chloride and dried over anhydrous magnesium sulfate. The solution was filtered, and the filtrate was concentrated on the rotary evaporator to give 22.2 g (94%) of 4-(1,2-dibromoethyl)benzotrifluoride, which was used without further purification. An analytical sample was obtained by recrystallization from ethanol–water followed by sublimation: mp 48.0–48.5 °C; IR (KBr) 1429, 1267, 1225, 1207, 1173, 1118, 945, 835, 707 cm^{-1}; ^{1}H NMR ($CDCl_3$/Me_4Si) the aliphatic region of this material was characterized by its ABX spectrum; δ_a = 3.98, δ_b = 4.06, δ_x = 5.15; J_{ab} = −10.5 Hz, J_{ax} = 11.4 Hz, J_{bx} = 4.7 Hz, δ_{arom} = 7.59 (AB q, J = 9 Hz); ^{19}F NMR ($CDCl_3$/$CFCl_3$) δ 63.73 (s).

Anal. Calcd for $C_9H_7Br_2F_3$: C, 32.56; H, 2.13. Found: C, 32.48; H, 2.15.

4-(1-Bromoethenyl)benzotrifluoride (24e). A solution of 5 g (15 mmol) of 4-(1,2-dibromoethyl)benzotrifluoride in 75 mL of methanol was treated at 25 °C with 10 mL of 2 N potassium hydroxide solution and stirred for 10 additional min. The solution was concentrated on the rotary evaporator, and the residue was dissolved in 125 mL of ether. The ethereal solution was washed with three 25-mL portions of water and finally with 25 mL of saturated sodium chloride solution. After drying over anhydrous magnesium sulfate, the solution was filtered, and the filtrate was concentrated in vacuo. The residue (3.88 g, 100%) was a light yellow oil, which was pure by NMR analysis and was used without further purification: IR (neat) 1614, 1410, 1328, 1170, 1130, 1074, 1015, 893, 842 cm^{-1}; ^{1}H NMR ($CDCl_3$/Me_4Si) δ 5.83 (1 H, d, J = 2 Hz), 6.16 (1 H, d, J = 2 Hz), 7.73 (4 H, s); ^{19}F NMR ($CDCl_3$/$CFCl_3$) δ 63.76 (s).

Anal. Calcd m/e $C_9H_6BrF_3$: 251.9585. Found: 251.9606.

3-[4-(Trifluoromethyl)phenyl]-1,1,1-trifluorobut-3-en-2-ol (23e). A 50-mL, three-necked, round-bottomed flask, equipped with an addition funnel, a reflux condenser, and a gas inlet tube, was charged with 0.2 g of magnesium and 4 mL of anhydrous tetrahydrofuran. Under a dry, oxygen-free nitrogen atmosphere, a small iodine crystal and three drops of ethyl bromide were added, and after the reaction began, 2.1 g (8.4 mmol) of **24e** in 10 mL of tetrahydrofuran was added over a 30-min period. The reaction was stirred an additional hour and a 50% excess of trifluoroacetaldehyde was let into the reaction. The reaction was worked up as described in the preparation of **26**. The crude product, a viscous oil, was vacuum transferred at 10^{-5} mm. From the distillate, 50 mg of **23e** was obtained by preparative VPC on a 10 ft × $^1/_4$ in. 5% XF-1150 on Chrom W column at 150 °C: IR (neat) 3430, 1630, 1410, 1338, 1270, 1173, 1129, 1070, 1015, 938, 845 cm^{-1}; ^{1}H NMR ($CDCl_3$/Me_4Si) δ 2.42 (1 H, m, exchanges with D_2O), 4.96 (1 H, q, J = 7 Hz), 5.68 (1 H, s), 5.78 (1 H, s), 7.56 (4 H, AB q, J = 9 Hz); ^{19}F NMR ($CDCl_3$/$CFCl_3$) δ 63.69 (s), 77.77 (d, J = 7 Hz); UV λ_{max}^{EtOH} 236 nm.

Anal. Calcd m/e for $C_{11}H_8F_6O$: 270.0478. Found: 270.0496.

General Procedures for the Preparation of Triflates. Method A. In a general procedure, a solution of trifluoromethanesulfonic anhydride[72] in pyridine at 0 °C was treated with the requisite alcohol. As a general rule, 1 mL of pyridine was used for every 100 mg of alcohol, and a 50% molar excess of trifluoromethanesulfonic anhydride was used in every case. The pyridine reaction mixture was stored in the ice box for 48 h and then poured into 5 mL of ice water/1 mL of pyridine and extracted with ether. The ethereal extracts were washed with a 0.1 M potassium bisulfate solution until the washings remained acidic. The ethereal solution was washed with a saturated sodium bicarbonate solution and dried over anhydrous magnesium sulfate. After filtration, the filtrate was concentrated by distillation, and the residue was distilled.

Method B. In a general procedure, 1.1 mmol of trifluoromethanesulfonic anhydride in 1 mL of Freon-11 was treated at 0 °C with a solution of 1 mmol of the requisite alcohol and 1.1 mmol of pyridine in 1 mL of Freon-11. The reaction was stirred for 15–30 min at 0 °C and the mixture was filtered through a fritted disk covered with 1 g of silica gel. The precipitate was washed with three 2-mL portions of Freon-11 and the combined filtrate was concentrated in a mild vacuum. The triflates thus obtained were usually free of alcohol and of high purity.

2,2,2-Trifluoroethyl Trifluoromethanesulfonate (34). Method B was used to prepare **34** in 54% yield: bp 89–91 °C [lit.[37] bp 89–91 °C (740 mm)].

1,1,1,5,5,5-Hexafluoro-2-pentyl Trifluoromethanesulfonate (33). Method A was used to prepare **33** in 65% yield from 1,1,1,5,5,5-hexafluoro-2-pentanol (**32**): bp 48–50 °C (30 mm). An analytical sample was obtained by preparative VPC on a 10 ft × $^3/_8$ in. 15% DEGS on 60/80 Chrom P column at 120 °C: IR (CCl_4) 1433, 1300, 1287, 1266–1200, 1175, 1143, 1015, 942 cm^{-1}; ^{1}H NMR (CCl_4/Me_4Si) δ 2.28 (4 H, m), 5.04 (1 H, m); ^{19}F NMR ($CDCl_3$/$CFCl_3$)[63] δ 67.89 (t, J = 9 Hz), 77.80 (m), 75.39 (q, J = 3 Hz).

Anal. Calcd for $C_6H_5F_9O_3S$: C, 21.96; H, 1.54. Found: C, 22.15; H, 1.64.

***trans*-1,1,1,5,5,5-Hexafluoropent-3-en-2-yl Trifluoromethanesulfonate (28).** Compound **28** was prepared via method A in 51% yield from alcohol **15**: IR (CCl_4) 1470, 1295, 1244, 1220, 1163, 980, 909 cm^{-1}; ^{1}H NMR (CCl_4/Me_4Si) δ 5.9–6.4 (m).

Anal. Calcd m/e for $C_5H_3F_6O_3S$ ($M^+ - CF_3$): 256.9707. Found: 256.9710.[73]

***cis*-1,1,1,5,5,5-Hexafluoropent-3-en-2-yl Trifluoromethanesulfonate (29).** Alcohol **16** was converted to **29** in 53% yield by using method B: IR (neat) 1695, 1439, 1362, 1282, 1235, 1220, 1176, 1143, 1053, 988, 877, 866, 766, 717 cm^{-1}; ^{1}H NMR (CCl_4/Me_4Si) δ 5.8–6.4 (m); ^{19}F NMR ($C_6H_5CF_3$/$CFCl_3$)[63] δ 61.14 (m), 75.77 (m), 77.78 (m).

Anal. Calcd m/e for $C_5H_3F_6O_3S$ ($M^+ - CF_3$): 256.9707. Found: 256.9711.[73]

3-Phenyl-1,1,1-triflurobut-3-en-2-yl Trifluoromethanesulfonate (30c). Compound **30c** was prepared in 87% yield by using method B: IR (neat) 1432, 1280, 1250, 1225, 1200, 1148, 1000, 887, 866, 775, 700 cm^{-1}; ^{1}H NMR ($CDCl_3$/Me_4Si) δ 5.84 (3 H, m), 7.39 (5 H, s); ^{19}F NMR ($CDCl_3$/$CFCl_3$)[63] δ 75.46 (q, $J \leq$

(71) Baldwin, J. G.; Kapicki, J. A. *J. Am. Chem. Soc.* **1970**, *92*, 4868.

(72) Burdon, J.; Farazmand, I.; Stacey, M.; Tallow, J. C. *J. Chem. Soc.* **1957**, 2574.

(73) Many of the trifluoromethanesulfonates prepared in this study did not store well at room temperature or above. As a result, elemental analyses were not obtained on these intermediates.

1 Hz), 76.31 (d of q, J = 7 Hz, $J' \leq$ 1 Hz).

Anal. Calcd m/e for $C_{11}H_8F_6O_3S$: 334.0097. Found: 334.0100.[73]

3-(4-Methylphenyl)-1,1,1-trifluorobut-3-en-2-yl Trifluoromethanesulfonate (30b). Method B was used to convert **23b** to **30b** in 97% yield: IR (neat) 1430, 1277, 1219, 1198, 1145, 997, 886, 820 cm^{-1}; ^{1}H NMR ($CDCl_3$/Me_4Si) δ 2.38 (3 H, s), 5.80 (3 H, m), 7.26 (4 H, s); ^{19}F NMR ($CDCl_3$/$CFCl_3$)[63] δ 75.45 (m), 76.33 (m, collapsed to d, J = 6 Hz, when 75.45 was irradiated).

Anal. Calcd m/e for $C_{12}H_{10}F_6O_3S$: 348.0254. Found: 348.0216.[73]

3-(4-Chlorophenyl)-1,1,1-trifluorobut-3-en-2-yl Trifluoromethanesulfonate (30d). Compound **30d** was obtained in 73% yield by using method B: IR (neat) 1600, 1497, 1431, 1280, 1250, 1222, 1148, 1000, 957, 887, 865, 831 cm^{-1}; ^{1}H NMR ($CDCl_3$/Me_4Si) δ 5.69 (1 H, q, J = 6 Hz), 5.76 (1 H, s), 5.80 (1 H, s), 7.28 (4 H, m); ^{19}F NMR ($CDCl_3$/$CFCl_3$)[63] δ 75.35 (m, collapsed to singlet when 76.17 was irradiated), 76.17 (m, collapsed to d, J = 6 Hz, when 75.35 was irradiated).

Anal. Calcd m/e for $C_{11}H_7ClF_6O_3S$: 367.9707. Found: 367.9707.[73]

3-(4-Methoxyphenyl)-1,1,1-trifluorobut-3-en-2-yl Trifluoromethanesulfonate (30a). Method B was used to prepare **30a** in 78% yield: IR (neat) 1612, 1518, 1430, 1275, 1230–1180, 1145, 1032, 992, 950, 884, 863, 831 cm^{-1}; ^{1}H NMR ($CDCl_3$/Me_4Si) δ 3.85 (3 H, s), 5.89 (3 H, m), 6.92 (2 H, d of m, J = 9 Hz), 7.32 (2 H, d of m, J = 9 Hz); ^{19}F NMR ($CDCl_3$/$CFCl_3$)[63] δ 75.48 (m), 76.22 (d of m, J = 6 Hz).

Anal. Calcd m/e for $C_{12}H_{10}F_6O_4S$: 364.0202. Found: 364.0245.[73]

3-[4-(Trifluoromethyl)phenyl]-1,1,1-trifluorobut-3-en-2-yl Trifluoromethanesulfonate (30e). When alcohol **23e** was treated as described in method B, stirring for 2–3 h was required in order to effect the formation of **30e** in 73% yield: IR (neat) 1625, 1432, 1330, 1280, 1225, 1200, 1172, 1139, 1069, 1000, 953, 888, 845 cm^{-1}; ^{1}H NMR ($CDCl_3$/Me_4Si) δ 5.75 (1 H, q, J = 6 Hz), 5.89 (1 H, s), 5.96 (1 H, s), 7.57 (4 H, AB q, J = 9 Hz); ^{19}F NMR ($CDCl_3$/$CFCl_3$)[63] δ 63.91 (s), 75.34 (q, J = 1.4 Hz), 76.23 (m).

Anal. Calcd m/e for $C_{12}H_7F_9O_3S$: 401.9970. Found: 401.9929.[73]

General Procedure Used for the Preparation of 2-Arylallyl Tosylates. An ethereal solution of 1 equiv of the requisite alcohol and 1 equiv of p-toluenesulfonyl chloride was cooled in an ice bath and treated in small portions with an excess of powdered potassium hydroxide. After stirring at 0 °C for an additional 45 min, or until a spatula that had been dipped into the reaction no longer smelled of tosyl chloride, the reaction was poured into ice water, and the layers were separated. The aqueous phase was washed twice with ether, and the combined organic extracts were washed with saturated sodium chloride solution. After drying over anhydrous magnesium sulfate and filtration, the solvent was stripped from the solution by rotary evaporation to afford a crystalline residue. The residue was dissolved in a minimum amount of 10% ether–pentane and treated with Norit. After removal of the Norit, the solution was slowly cooled to −70 °C, with scratching, until the tosylates began to crystallize. The majority of the solvent was removed with a filter stick and the remainder by evaporation in a vacuum oven.

2-Phenylprop-2-en-1-yl 4-Toluenesulfonate (31c). Compound **31c** was obtained in a 52% yield: mp 59–60 °C. An analytical sample was prepared by a second recrystallization from a minimum of warm cyclohexane: mp 60–61 °C; IR (KBr) 1357, 1187, 1174, 915, 848, 838, 817, 782, 713, 678, 665, 551, 530 cm^{-1}; ^{1}H NMR ($CDCl_3$/Me_4Si) δ 2.44 (3 H, s), 4.83 (2 H, br s), 5.30 (1 H, br s), 5.46 (1 H, br s), 7.20 (7 H, m), 7.66 (2 H, d, J = 8 Hz).

Anal. Calcd for $C_{16}H_{16}O_3S$: C, 66.63; H, 5.59. Found: C, 66.61; H, 5.60.

2-(4-Methylphenyl)prop-2-en-1-yl 4-Toluenesulfonate (31b). Compound **31b** was obtained in 68% yield as a fluffy white solid. Recrystallization from 10% ether–90% pentane (v/v) afforded an analytical sample: mp 80–81 °C; IR (KBr) 1596, 1517, 1371, 1358, 1193, 1189, 1172, 1093, 1019, 1005, 964, 941, 918, 845, 839, 824, 811, 792, 673, 660, 610, 550 cm^{-1}; ^{1}H NMR (CCl_4/Me_4Si) δ 2.34 (3 H, s), 2.44 (3 H, s), 4.83 (2 H, br s), 5.30 (1 H, s), 5.45 (1 H, s), 6.90–7.40 (6 H, m), 7.74 (2 H, d, J = 8 Hz).

Anal. Calcd for $C_{17}H_{18}O_3S$: C, 67.52; H, 5.99. Found: C, 67.37; H, 6.03.

2-(4-Chlorophenyl)prop-2-en-1-yl 4-Toluenesulfonate (31d). Compound **31d** was obtained in 70% yield as colorless needles. Recrystallization produced the analytical sample: mp 58.0–59.0 °C; IR (KBr) 1497, 1375, 1190, 1175, 1093, 1012, 966, 940, 925, 827, 811, 657, 552 cm^{-1}; ^{1}H NMR ($CDCl_3$/Me_4Si) δ 2.44 (3 H, s), 4.83 (2 H, br s), 5.36 (1 H, s), 5.5 (1 H, s), 7.16–7.39 (6 H, m), 7.7 (2 H, d, J = 8 Hz).

Anal. Calcd for $C_{16}H_{15}ClO_3S$: C, 59.53; H, 4.68. Found: C, 59.28; H, 4.83.

2-(4-Methoxyphenyl)prop-2-en-1-yl 4-Toluenesulfonate (31a). Recrystallization of crude **31a** from 10% ether–90% pentane (v/v) afforded pure **31a** in 62% yield: mp 78.0–79.5 °C; IR (KBr) 1611, 1515, 1475, 1372, 1360, 1295, 1257, 1191, 1175, 1095, 1032, 961, 942, 930, 909, 848, 833, 811, 692, 665, 563, 550 cm^{-1}; ^{1}H NMR ($CDCl_3$/Me_4Si) δ 2.45 (3 H, s), 3.80 (3 H, s), 4.88 (2 H, br s), 5.23 (1 H, br s), 5.44 (1 H, s), 6.81 (2 H, d, J = 9 Hz), 7.07–7.37 (4 H, m), 7.73 (2 H, d, J = 8 Hz).

Anal. Calcd for $C_{17}H_{18}O_4S$: C, 64.13; H, 5.70. Found: C, 64.25; H, 5.65.

Trifluoroethanolysis of 2-Arylallyl Tosylates (31a–d). General Procedure. A solution containing 7.5 × 10^{-4} mol of the appropriate tosylate in 15 mL of trifluoroethanol, buffered to 0.075 M with 2,6-lutidine, was blanketed with argon and sealed in a combustion tube. The solution was heated at 80 °C for 24 h, cooled, and transferred from the sealed tube to a 25-mL, round-bottomed flask. The trifluoroethanol was removed by distillation under reduced pressure (bp ca. 40 °C), and the residue was triturated with 8–10 mL of ether. The combined ethereal solutions were washed once with 10 mL of 2 N hydrochloric acid and once with 10 mL of saturated sodium chloride solution and dried over anhydrous magnesium sulfate. After filtration, the solution was concentrated on the rotary evaporator and taken up in 1 mL of ether, and the products were collected by preparative gas chromatography.

2-Phenyl-1-(2,2,2-trifluoroethoxy)prop-2-ene (42c). Trifluoroethanolysis of **31c** afforded **42c** in 98.5% yield. An analytical sample was obtained by preparative gas chromatography on a 10 ft × $^1/_4$ in. 10% SE-30 on 60/80 Chrom W column at 130 °C: IR (neat) 1281, 1164, 1127, 964, 779, 708 cm^{-1}; ^{1}H NMR ($CDCl_3$/Me_4Si) δ 3.85 (2 H, q, J = 9 Hz), 4.55 (2 H, br s), 5.37 (1 H, m), 5.61 (1 H, br s), 7.21–7.53 (5 H, m); ^{19}F NMR ($CDCl_3$/$CFCl_3$) δ 75.23 (t, J = 9 Hz).

Anal. Calcd for $C_{11}H_{11}F_3O$: C, 61.10; H, 5.12. Found: C, 61.19; H, 5.25.

2-(4-Methylphenyl)-1-(2,2,2-trifluoroethoxy)prop-2-ene (42b). Trifluoroethanolysis of **31b** afforded **42b** in 100% yield. An analytical sample was obtained by preparative VPC, using the same column as for **42c** at 150 °C: IR (neat) 1520, 1308, 1280, 1164, 1125, 1100, 1020, 966, 910, 825 cm^{-1}; ^{1}H NMR ($CDCl_3$/Me_4Si) δ 2.02 (3 H, s), 3.83 (2 H, q, J = 9 Hz), 4.53 (2 H, br s), 5.30 (1 H, m), 5.58 (1 H, br s), 7.05–7.50 (4 H, m); ^{19}F NMR ($CDCl_3$/$CFCl_3$) δ 74.79 (t, J = 9 Hz).

Anal. Calcd for $C_{12}H_{13}F_3O$: C, 62.60; H, 5.69. Found: C, 62.65; H, 5.82.

2-(4-Chlorophenyl)-1-(2,2,2-trifluoroethoxy)prop-2-ene (42d). Solvolysis of **31d** afforded **42d** in 93.5% yield. An analytical sample was obtained by preparative VPC as for **42c** with the oven at 155 °C: IR (neat) 1495, 1315, 1280, 1165, 1128, 1100, 1014, 965, 917, 834 cm^{-1}; ^{1}H NMR ($CDCl_3$/Me_4Si) δ 3.84 (2 H, q, J = 9 Hz), 4.50 (2 H, m), 5.20 (1 H, m), 5.44 (1 H, br s), 7.63 (4 H, s); ^{19}F NMR ($CDCl_3$/$CFCl_3$) δ 74.83 (q, J = 9 Hz).

Anal. Calcd $C_{11}H_{10}ClF_3O$: C, 52.71; H, 4.02. Found: C, 52.84; H, 4.15.

2-(4-Methoxyphenyl)-1-(2,2,2-trifluoroethoxy)prop-2-ene (42a). Compound **42a** was obtained in 93% yield from the solvolysis of **31a**. Preparative VPC with the column used for **42c** at 170 °C afforded an analytical sample: IR (neat) 1610, 1511, 1307, 1280, 1250, 1165, 1125, 1100, 1032, 961, 832 cm^{-1}; ^{1}H NMR ($CDCl_3$/Me_4Si) δ 3.83 (3 H, s), 3.83 (2 H, q, J = 9 Hz), 4.53 (2 H, br s), 5.28 (1 H, m), 5.54 (1 H, br s), 6.89 (2 H, d, J = 8 Hz), 7.43 (2 H, d, J = 8 Hz); ^{19}F NMR ($CDCl_3$/$CFCl_3$) δ 74.85 (t, J = 9 Hz).

Anal. Calcd for $C_{12}H_{13}F_3O_2$: C, 58.53; H, 5.32. Found: C, 58.46; H, 5.40.

Trifluoroethanolysis of 3-Aryl-1,1,1-trifluorobut-3-en-2-yl Triflates (30a–d). General Procedure. A solution of tri-

fluoroethanol which was 0.05 M in the appropriate triflate and 0.075 M in 2,6-lutidine was heated to reflux for 48–64 h. The reaction products were isolated as described above for the trifluoroethanolysis of the 2-arylallyl tosylates **31a–d**.

(*E*)- and (*Z*)-2-Phenyl-4,4,4-trifluorobut-2-en-1-yl 2,2,2-Trifluoroethyl Ether (35c). Solvolysis of **30c** afforded, as the only major products, (*E*)- and (*Z*)-**35c**. Analytical samples were obtained by preparative VPC on a 15% DEGS on 60/80 Chrom P column at 145 °C.

(*E*)-**35c**: IR (neat) 1685, 1280, 1222, 1170, 1135, 1055, 967, 760, 700, 668 cm^{-1}; ^1H NMR ($CDCl_3/Me_4Si$) δ 3.94 (2 H, q, J = 8.5 Hz), 4.33 (2 H, m), 6.03 (1 H, q of t, J = 8 Hz, J' = 2.2 Hz), 7.33 (5 H, m); ^{19}F NMR ($CDCl_3/CFCl_3$) δ 57.26 (d of t, J = 8 Hz, J' = 2.2 Hz), 75.05 (t, J = 8.5 Hz); UV λ_{max}^{EtOH} 226 nm (log ϵ 3.67).

Anal. Calcd for $C_{12}H_{10}F_6O$: C, 50.71; H, 3.55. Found: C, 50.50; H, 3.71.

(*Z*)-**35c**: IR (neat) 1660, 1348, 1270, 1190–1110, 1055, 1004, 968, 759, 692 cm^{-1}; ^1H NMR ($CDCl_3/Me_4Si$) δ 3.79 (2 H, q, J = 8.5 Hz), 4.77 (2 H, br s), 6.08 (1 H, q, J = 8.5 Hz), 7.46 (5 H, m); ^{19}F NMR ($CDCl_3/CFCl_3$) δ 56.83 (d, J = 8.5 Hz), 75.01 (t, J = 8.5 Hz); UV λ_{max}^{EtOH} 248 nm (log ϵ 4.01).

Anal. Calcd m/e for $C_{12}H_{10}F_6O$: 284.0635. Found: 284.0629.

(*E*)- and (*Z*)-2-(4-Methylphenyl)-4,4,4-trifluorobut-2-en-1-yl 2,2,2-Trifluoroethyl Ether (35b). (*E*)- and (*Z*)-**35b** were obtained from the solvolysis of **30b**. Analytical samples were obtained by preparative VPC, using the column described for **35c** at a temperature of 155 °C. (*E*)-**35b**: IR (neat) 1685, 1518, 1346, 1283, 1170, 1135, 1050, 967, 889, 826 cm^{-1}; ^1H NMR ($CDCl_3/Me_4Si$) δ 2.36 (3 H, s), 3.91 (2 H, q, J = 8.6 Hz), 4.30 (2 H, m), 5.98 (1 H, q of t, J = 8.2, J' = 2.6 Hz), 7.15 (4 H, AB q, J = 8.5 Hz); ^{19}F NMR ($CDCl_3/CFCl_3$) δ 57.16 (d of t, J = 8.3 Hz, J' = 2.6 Hz), 75.04 (t, J = 8.2 Hz); UV λ_{max}^{EtOH} 236 nm (log ϵ 3.82).

Anal. Calcd for $C_{13}H_{12}F_6O$: C, 52.35; H, 4.06. Found: C, 52.22; H, 4.23.

(*Z*)-**35b**: IR (neat) 1655, 1342, 1281, 1267, 1165, 1120, 807 cm^{-1}; ^1H NMR ($CDCl_3/Me_4Si$) δ 3.00 (3 H, s), 3.77 (2 H, q, J = 8.6 Hz), 4.73 (2 H, br s), 6.04 (1 H, q, J = 8.7 Hz), 7.28 (4 H, AB q, J = 8.5 Hz); ^{19}F NMR ($CDCl_3/CFCl_3$) δ 56.56 (d, J = 8.7 Hz), 74.99 (t, J = 8.6 Hz); λ_{max}^{EtOH} 257 nm (log ϵ 3.98).

Anal. Calcd m/e for $C_{13}H_{12}F_6O$: 298.0791. Found: 298.0811.

(*E*)- and (*Z*)-2-(4-Chlorophenyl)-4,4,4-trifluorobut-2-en-1-yl 2,2,2-Trifluoroethyl Ether (35d). (*E*)- and (*Z*)-**35d** were obtained from the trifluoroethanolysis of **30d**. Analytical samples were obtained by preparative VPC with the column used for **35c** at a temperature of 175 °C. (*E*)-**35d**: IR (neat) 1685, 1602, 1497, 1345, 1280, 1221, 1168, 1135, 1050, 1017, 966, 827 cm^{-1}; ^1H NMR ($CDCl_3/Me_4Si$) δ 3.93 (2 H, q, J = 8.5 Hz), 4.30 (2 H, m), 6.05 (1 H, q of t, J = 8.0 Hz, J' = 2.3 Hz), 7.28 (4 H, AB q, J = 8.6 Hz); ^{19}F NMR ($CDCl_3/CFCl_3$) δ 57.34 (d of t, J = 8.0 Hz, J' = 2.3 Hz), 75.01 (t, J = 8.5 Hz); λ_{max}^{EtOH} 228 nm (log ϵ 3.92).

Anal. Calcd for $C_{12}H_9ClF_6O$: C, 45.23; H, 2.85. Found: C, 45.53; H, 3.01.

(*Z*)-**35d**: IR (neat) 1496, 1340, 1279, 1167, 1128, 817 cm^{-1}; ^1H NMR ($CDCl_3/Me_4Si$) δ 3.79 (2 H, q, J = 8.6 Hz), 4.73 (2 H, br s), 6.06 (1 H, q, J = 8.5 Hz), 7.42 (4 H, s); ^{19}F NMR ($CDCl_3/CFCl_3$) δ 56.88 (d, J = 8.5 Hz), 74.98 (t, J = 8.6 Hz); λ_{max}^{EtOH} 254 nm (log ϵ 4.11).

Anal. Calcd m/e for $C_{12}H_9ClF_6O$: 318.0245. Found: 318.0205.

(*E*)- and (*Z*)-2-(4-Methoxyphenyl)-4,4,4-trifluorobut-2-en-1-yl 2,2,2-Trifluoroethyl Ether (35a). (*E*)- and (*Z*)-**35a** resulted from solvolysis of **30a**. Analytical samples were obtained by preparative VPC on a 10 ft × $^3/_8$ in. 15% DEGS on 60/80 Chrom P column at 185 °C. (*E*)-**35a**: IR (neat) 1679, 1615, 1515, 1280, 1254, 1175, 1135, 1052, 1032, 964, 834 cm^{-1}; ^1H NMR ($CDCl_3/Me_4Si$) δ 3.86 (3 H, s), 3.93 (2 H, q, J = 8.5 Hz), 4.33 (2 H, m), 5.98 (1 H, q of t, J = 8 Hz, J' = 2 Hz), 6.9 (2 H, d, J = 9 Hz), 7.2 (2 H, d, J = 9 Hz).

Anal. Calcd for $C_{13}H_{12}F_6O_2$: C, 49.69; H, 3.85. Found: C, 49.76; H, 3.96.

(*Z*)-**35a**: IR (neat) 1651, 1615, 1514, 1280, 1171, 1133, 827 cm^{-1}; ^1H NMR ($CDCl_3/Me_4Si$) δ 3.86 (3 H, s), 3.82 (2 H, q, J = 8.5 Hz), 4.72 (2 H, br s), 6.01 (1 H, q, J = 8 Hz), 7.22 (2 H, d, J = 8 Hz), 7.44 (2 H, d, J = 8 Hz).

Anal. Calcd m/e for $C_{13}H_{12}F_6O_2$: 314.0740. Found: 314.0746.

3-(4-Methylphenyl)-1,1,1-trifluorobut-3-en-2-yl 2,2,2-Trifluoroethyl Ether (36). A 25-mL, three-necked, round-bottomed flask, equipped with a magnetic stir bar, a reflux condenser, and a gas inlet adapter, was flushed with dry, oxygen-free nitrogen. To the flask was added 0.1 g of 50% sodium hydride–mineral oil dispersion which was washed with three 5-mL portions of ether. After the nitrogen flow had evaporated all of the ether, the flask was charged with 15 mL of dry dimethylformamide. With ice cooling, 0.43 g (2 mmol) of **23b** was added, and after hydrogen evolution had ceased, 0.69 g (3 mmol) of trifluoroethyl triflate was added in one portion. The reaction was refluxed for 12 h, cooled, poured into 50 mL of water, and extracted with four 15-mL portions of low-boiling petroleum ether. The extracts were washed with saturated sodium chloride solution, dried over anhydrous magnesium sulfate, and filtered, and the filtrate was concentrated in vacuo. The residue, 0.57 g, was found to be a mixture of the desired ether **36** and the starting alcohol **23b**. Pure **36** was obtained by preparative VPC on a 10 ft × $^1/_4$ in. 5% XF-1150 on 45/60 Chrom W column at 130 °C: IR (neat) 1518, 1280, 1175, 1146, 1042, 1018, 970, 820 cm^{-1}; ^1H NMR ($CDCl_3/Me_4Si$) δ 2.36 (3 H, s), 4.01 (2 H, q, J = 8.2 Hz), 4.74 (1 H, q, J = 6.2 Hz), 5.65 (1 H, s), 5.72 (1 H, s), 7.22 (4 H, AB q, J = 8 Hz); ^{19}F NMR ($CDCl_3/CFCl_3$) δ 75.14 (t, J = 8.2 Hz), 76.43 (d, J = 6.2 Hz).

Anal. Calcd for $C_{13}H_{12}F_6O$: C, 52.35; H, 4.06. Found: C, 52.25; H, 4.19.

Solvolysis of 3-Aryl-1,1,1-trifluorobut-3-en-2-yl Triflates (30a–d) in 90% Aqueous Acetone. General Procedure. A solution of 90% acetone–10% water (v/v) was prepared and buffered to 0.1 M in 2,6-lutidine. The appropriate triflates **30b–d** were individually dissolved in the solution to a concentration of 0.06–0.07 M, and the solutions were refluxed for 24 h. The majority of the acetone was removed by distillation and the residue was taken up in ether and washed with 1 N hydrochloric acid. After drying over anhydrous magnesium sulfate, the solutions were filtered and concentrated on the rotary evaporator to afford light yellow oils as residues. The major product, (*E*)-2-aryl-4,4,4-trifluorobut-2-en-1-ol, was isolated by preparative VPC on a 10 ft × $^1/_4$ in. 5% XF-1150 on 45/60 Chrom W column.

(*E*)-2-Phenyl-4,4,4-trifluorobut-2-en-1-ol (38c). Compound **38c** resulted from solvolysis of **30c**. An analytical sample was obtained by preparative VPC at an oven temperature of 140 °C: IR (neat) 3360, 1680, 1495, 1446, 1390, 1337, 1280, 1217, 1130, 1087, 751, 697 cm^{-1}; ^1H NMR ($CDCl_3/Me_4Si$) δ 1.8 (1 H, br s, exchanges with D_2O), 4.36 (2 H, m), 6.05 (1 H, q of t, J = 8 Hz, J' = 2 Hz), 7.23 (3 H, m), 7.37 (2 H, m).

Anal. Calcd m/e for $C_{10}H_9F_3O$: 202.0604. Found: 202.0607.

(*E*)-2-(4-Methylphenyl)-4,4,4-trifluorobut-2-en-1-ol (38b). Solvolysis of **30b** afforded as the major product (*Z*)-**38b**. An analytical sample was obtained by preparative VPC at 150 °C: IR (neat) 3360, 1686, 1518, 1286, 1228, 1215, 1140, 1090, 827, 816 cm^{-1}; ^1H NMR ($CDCl_3/Me_4Si$) δ 1.8 (1 H, s, exchanges with D_2O), 2.36 (3 H, s), 4.33 (1 H, m), 6.01 (1 H, q of t, J = 8.0 Hz, J' = 2.0 Hz), 7.16 (4 H, m); ^{19}F NMR ($CDCl_3/CFCl_3$) δ 56.97 (d of t, J = 8 Hz, J' = 2 Hz); UV λ_{max}^{EtOH} 228 nm.

Anal. Calcd for $C_{11}H_{11}F_3O$: C, 61.11; H, 5.13. Found: C, 60.90; H, 5.26.

(*E*)-2-(4-Chlorophenyl)-4,4,4-trifluorobut-2-en-1-ol (38d). Solvolysis of **30d** afforded (*Z*)-**38d** as the major product, which was obtained analytically pure by preparative VPC at 175 °C: IR (neat) 3370, 1680, 1600, 1493, 1280, 1218, 1132, 1088, 1017, 828 cm^{-1}; ^1H NMR ($CDCl_3/Me_4Si$) δ 1.66 (1 H, br s, exchanges with D_2O), 4.34 (2 H, m), 6.09 (1 H, q of t, J = 8 Hz, J' = 2.0 Hz), 7.17 (2 H, d, J = 8.7 Hz), 7.38 (2 H, d, J = 8.7 Hz).

Anal. Calcd m/e for $C_{10}H_8ClF_3O$: 238.0185. Found: 238.0224.

(*E*)-2-Phenyl-4,4,4-trifluorobut-2-en-1-yl Trifluoromethanesulfonate (37c). Method B, previously described for the preparation of triflates, converted **38c** into **37c** in 27% yield: IR (neat) 1682, 1420, 1283, 1249, 1221, 1140, 1085, 1056, 956, 755, 695 cm^{-1}; ^1H NMR ($CDCl_3/Me_4Si$) δ 5.09 (2 H, m), 6.05 (1 H, m), 7.22 (3 H, m), 7.38 (2 H, m).

Anal. Calcd m/e for $C_{11}H_8F_6O_3S$: 334.0098. Found: 334.0101.[73]

(*E*)-2-(4-Methylphenyl)-4,4,4-trifluorobut-2-en-1-yl Trifluoromethanesulfonate (37b). Method B was used to convert **38b** into **37b** in 47% yield: IR (neat) 1682, 1420, 1285, 1248, 1213, 1142, 1055, 958, 940, 847 cm^{-1}; ^1H NMR ($CDCl_3/Me_4Si$) δ 2.38 (3 H, s), 5.09 (2 H, m), 6.03 (1 H, q of t, J = 7.5 Hz, J' = 1.7 Hz), 7.18 (4 H, AB q, J = 8.5 Hz); ^{19}F NMR ($CDCl_3/CFCl_3$) δ 57.95 (d of t, J = 7.6 Hz, J' = 2.1 Hz), 75.48 (s).

Anal. Calcd m/e for $C_{12}H_{10}F_6O_3S$: 348.0254. Found: 348.0221.[73]

(*E*)-2-(4-Chlorophenyl)-4,4,4-trifluorobut-2-en-1-yl Trifluoromethanesulfonate (37d). Compound **37d** was obtained in 49% yield from **38d** by using method B: IR (neat) 1680, 1494, 1420, 1281, 1248, 1220, 1141, 1051, 960, 940, 835 cm^{-1}; ^1H NMR ($CDCl_3/Me_4Si$) δ 5.09 (2 H, m), 6.11 (1 H, q of t, J = 7.5 Hz, J' = 2 Hz), 7.20 (2 H, d, J = 8.7 Hz), 7.36 (2 H, d, J = 8.7 Hz).

Anal. Calcd m/e for $C_{11}H_7ClF_6O_3S$: 367.9709. Found: 367.9698.[73]

Determination of the Reaction Kinetics. Anhydrous trifluoroethanol purchased from Matheson Coleman and Bell was used directly without further purification. Solutions of the appropriate triflates or the tosylates were prepared at 0.003–0.005 M. The solutions were buffered with 2,6-lutidine at 0.0045–0.0075 M, respectively. The kinetics were determined conductimetrically in a 10-mL conductance cell, which was sealed for each run. The mathematical treatment of the rate data was that described by Bamford and Tippen where a weighted least-squares treatment was used to determine the first-order rate constants.[74]

Determination of Yields. The yields for the trifluoroethanolysis of triflates **30a–d** and tosylates **31a–d** were determined by VPC, using the method of internal standards. Two sealed tubes with a known amount of triflate or tosylate in trifluoroethanol, buffered with 2,6-lutidine, were solvolyzed for 8–10 half-lives. An exact amount of internal standard was added to each tube, and the product peak areas as compared to the area of the standard were determined with the aid of a Hewlett-Packard Model 3370A electronic integrator. Prior standardization of the solvolysis products vs. the internal standards allowed precise determination of the yields.

Determination of the Stability of 36 to the Reaction Conditions. A solution was prepared by dissolving 30 mg (0.1 mmol) of 3-(4-methylphenyl)-1,1,1-trifluorobut-3-en-2-yl 2,2,2-trifluoroethyl ether (**36**) in 10 mL of anhydrous trifluoroethanol (0.01 M), previously buffered to 0.005 M with 2,6-lutidine. To the solution was added 26 mg of 2,6-lutidinium trifluoromethanesulfonate (0.1 mmol) (prepared by adding trifluoromethanesulfonic acid to a solution of 2,6-lutidine in ether). The resulting solution was refluxed for a time equal to 10 half-lives. Monitoring the reaction by analytical VPC on a 10 ft × $^1/_8$ in. 5% XF-1150 on 45/60 Chrom W column and also a 10 ft × $^1/_8$ in. 15% DEGS on 60/80 Chrom P column showed no change in **36**.

Determination of the Stereochemical Stability of (*E*)- and (*Z*)-35b–d to the Reaction Conditions. The (*E*)-2-aryl-4,4,4-trifluorobut-2-en-1-yl 2,2,2-trifluoroethyl ethers **35b–d** were obtained pure by preparative VPC as described above. Trifluoroethanol solutions were prepared that were 0.01 M in each ether, 0.005 M in 2,6-lutidine, and 0.01 M in 2,6-lutidinium trifluoromethanesulfonate. The individual solutions were refluxed for a time equal to 10 half-lives, and no detectable isomerization was found.

In a related experiment, a solution of the triflate **30b** in trifluoroethanol, buffered with a 50% excess of 2,6-lutidine, was examined for product formation at 10%, 25%, 50% 75%, and 100% reaction. The ratio of (*E*)- and (*Z*)-**35b** was found qualitatively to be quite constant throughout the reaction.

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Registry No. **15**, 89619-07-8; **16**, 89619-09-0; **17**, 372-49-6; **18**, 89619-04-5; **19**, 89619-05-6; **20**, 89619-06-7; **22**, 89619-08-9; **23a**, 89618-98-4; **23b**, 89618-99-5; **23c**, 89619-00-1; **23d**, 89619-01-2; **23e**, 89619-02-3; **24a**, 29338-71-4; **24b**, 42107-37-9; **24c**, 98-81-7; **24d**, 89619-10-3; **24e**, 89619-13-6; **25a**, 89619-03-4; **25b**, 66520-90-9; **25c**, 6006-81-1; **25d**, 45941-96-6; **26**, 89619-11-4; **27**, 37614-59-8; **28**, 89619-15-8; **29**, 89619-16-9; **30a**, 89618-87-1; **30b**, 89618-88-2; **30c**, 89618-89-3; **30d**, 89618-90-6; **30e**, 89618-91-7; **31a**, 89618-92-8; **31b**, 89618-93-9; **31c**, 66303-64-8; **31d**, 89618-94-0; **32**, 2927-15-3; **33**, 89619-14-7; **34**, 6226-25-1; (*Z*)-**35a**, 89619-27-2; (*E*)-**35a**, 89619-28-3; (*Z*)-**35b**, 89619-23-8; (*E*)-**35b**, 89619-24-9; (*Z*)-**35c**, 89619-21-6; (*E*)-**35c**, 89619-22-7; (*Z*)-**35d**, 89619-25-0; (*E*)-**35d**, 89619-26-1; **36**, 89619-29-4; **37b**, 89618-95-1; **37c**, 89618-96-2; **37d**, 89618-97-3; **38b**, 89619-31-8; **38c**, 89619-30-7; **38d**, 89619-32-9; **42a**, 89619-20-5; **42b**, 89619-18-1; **42c**, 89619-17-0; **42d**, 89619-19-2; $H_2C{=}CHCH_2OTs$, 4873-09-0; p-$H_3COC_6H_4(CH{=}CH_2)$, 637-69-4; p-$H_3CC_6H_4(CH{=}CH_2)$, 622-97-9; $C_6H_5(CH{=}CH_2)$, 100-42-5; p-$ClC_6H_4(CH{=}CH_2)$, 1073-67-2; p-$F_3CC_6H_4(CH{=}CH_2)$, 402-50-6; 1-bromo-3,3,3-trifluoropropane, 460-32-2; ethyl trifluoroacetate, 383-63-1; ethyl bromide, 74-96-4; trifluoropropyne, 661-54-1; trifluoroacetaldehyde, 75-90-1; phenylacetylene, 536-74-3; formaldehyde, 50-00-0; (p-methoxyphenyl)acetylene, 768-60-5; 4-(trifluoromethyl)styrene, 402-50-6; 1-[4-(trifluoromethyl)phenyl]ethanol, 1737-26-4; 4-(1,2-dibromoethyl)benzotrifluoride, 89619-12-5.

(74) (a) "The Practice of Kinetics"; Bamford, C. H., Tippen, C. F. H., Eds.; Elsevier: New York, 1969; pp 364–377. (b) Weighting factor was $(C_\infty - C_t)^2$.

Vinylene 1,2-Bis(trifluoromethanesulfonates) from Azibenzils and Triflic Anhydride

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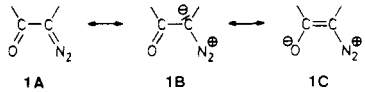
Trifluoromethanesulfonic anhydride reacts with azibenzil and its 4-Cl and 4-OMe derivatives (**2a–c**) to give predominantly 1,2-diarylvinylene 1,2-bis(trifluoromethanesulfonates) (*Z,E*)-**4a–c** besides small amounts of the corresponding benzils **5a–c**. The *Z* olefins are favored over their *E* isomers in all cases. The reaction begins with electrophilic attack on the oxygen of the diazo ketone by the anhydride; it represents a novel method of generating vinyl cations via vinyldiazonium ions.

According to their dominant resonance structures (**1A** ⇄ **1B** ⇄ **1C**), it is expected that α-diazo ketones exhibit ambident behavior toward electrophiles. C-Attack by the electrophile is the most frequently encountered reaction, with protons, acyl or silyl groups, metal ions, or halogen cations acting as electrophilic moieties.[1] Examples of O-attack include the kinetically controlled O-protonation,[2]



1A **1B** **1C**

(1) Regitz, M.; Maas, G. "Aliphatic Diazo Compounds"; Academic Press, in press.

0022-3263/84/1949-2273$01.50/0