(^{15}N)phenylalanine and the appropriate ^{13}C-enriched amino acid.[5] On the basis of ^{13}C NMR measurements, approximately 60% of the phenylalanine amides were ^{15}N labeled (data not shown). The loss of the ^{15}N label is attributed to the action of transaminases. Proton and nitrogen chemical shifts were correlated with forbidden echo spectroscopy as described previously.[5]

Figure 1A shows a portion of the ^{1}H–^{15}N forbidden echo spectrum of (^{15}N)phenylalanine-labeled T4 lysozyme. This region of the two-dimensional spectrum has three peaks, corresponding to three phenylalanine amide protons and labeled peaks d, b, and c as described in our earlier work.[5] Figure 1B shows the same region of the ^{1}H–^{15}N two-dimensional spectrum of a sample labeled with (^{15}N)phenylalanine and (1-^{13}C)leucine. Although the line width and ^{13}C–^{15}N spin–spin coupling are of the same order of magnitude ($\sim$17 Hz), one can readily see that peak c appears as a poorly resolved doublet in consecutive traces. The four remaining Phe amide resonances are unchanged. On this basis we assign peak c to amide resonance of the Leu 66-Phe 67 peptide.

We have introduced two other ^{13}C labels along with (^{15}N)-phenylalanine into the T4 lysozyme and the results are summarized in Table I. Incorporation of (1-^{13}C)valine affects signal a corresponding to Phe 104, which is situated adjacent to a valine residue. Similarly, Phe 114 adjoins Gly 113, and insertion of (1-^{13}C)glycine into the protein alters the resonance d.

Peaks e and b are unaffected by any of the ^{13}C-enriched amino acids and hence correspond to the resonances of Phe 4 and Phe 153. These can be assigned on the basis of their solvent exchange properties and the known secondary and tertiary structure at these positions as established by X-ray crystallography. Phe4 is in a solvent-exposed region of the protein while Phe 153 is found in an α-helical region. As demonstrated in our earlier work, peak e exchanges rapidly with D$_2$O ($t_{1/2} \sim$ 1 h, pD 5.5, 4 °C) and is assigned to phenylalanine 4. In contrast, peak b exchanges slowly ($t_{1/2} \sim$ 1 week) and is assigned to Phe 153. The other slowly exchanging amides (Phe67 and Phe104) are also in α-helical regions while the other fast exchanging amide at residue 114 is in a solvent-exposed region.

Heteronuclear difference decoupling can be added to the standard saturation–recovery experiment for the determination of longitudinal (T_1) relaxation rates. Subtraction of T_1 data sets with on- and off-resonance ^{15}N decoupling produces difference spectra which contain only the signals from protons bonded to the uncommon isotope. The T_1 values for the amide protons of the phenylalanine residues are listed in Table I. The values for Phe 67, Phe 104, Phe 114, and Phe 153 are determined to be 300 ± 30 ms. The signal at 7.74 ppm assigned to Phe4 has a slower rate of 420 ± 50 ms, indicative of a location in a region of unique flexibility or dipolar environment. This is consistent with the three-dimensional structure of T4 lysozyme as deduced by X-ray methods, where the atoms of Phe4 exhibit greater disorder than any of the other phenylalanine sites.[11]

These studies demonstrate that selective ^{15}N and ^{13}C labeling of T4 lysozyme permits the observation and unambiguous assignment of the ^{1}H and ^{15}N NMR resonances of specific amide units. However, since the line widths and ^{13}C–^{15}N couplings are similar in magnitude, it is unlikely that this approach will be useful for proteins much larger than lysozyme (18.7 kdaltons). Armed with these assignments, the structure and dynamics of T4 lysozyme can be probed by using NMR resonance lifetime and solvent exchange measurements.

(11) Weaver, L .H.; Matthews, B. W., submitted for publication in *J. Mol. Biol.*

Synthesis and Characterization of the Phosphinidene Borate Complexes [Li(Et$_2$O)$_2$PRBMes$_2$] and [Li(12-crown-4)$_2$][RPBMes$_2$]·THF, R = Ph, C$_6$H$_{11}$, or Mes (Mes = 2,4,6-Me$_3$C$_6$H$_2$): The First Structurally Characterized Boron–Phosphorus Multiple Bonds

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Received June 3, 1986

Although multiple bonding between boron and nitrogen[2] (and to a lesser degree carbon)[3] has been well established, there are no structurally characterized compounds in which boron is multiply bonded to a heavier main-group element. In this paper we report on the synthesis and characterization of a number of compounds in which boron is multiply bonded to phosphorus. These are the novel complexes [Li(Et$_2$O)$_2$RPBMes$_2$] (Mes = 2,4,6-Me$_3$C$_6$H$_2$; R = Ph, **1a**; R = C$_6$H$_{11}$, **1b**; R = Mes, **1c**) and the ion pairs [Li(12-crown-4)$_2$][RPBMes$_2$]·THF (R = Ph, **2a**; R = C$_6$H$_{11}$, **2b**; R = Mes, **2c**).

The synthesis of the title compounds involved the treatment of an Et$_2$O solution of Mes$_2$BPHR at 0 °C with 1 equiv of *t*-BuLi to give a solution of [Li(Et$_2$O)$_2$RPBMes$_2$]. Reduction of the volume and cooling afforded crystals of **1a**, **1b**, or **1c** in ca. 60% yield. Addition of 2 equiv of 12-crown-4 to **1a**, **1b**, or **1c** in ether gave yellow precipitates which were recrystallized from THF/Et$_2$O to give **2a**, **2b**, or **2c** in ca. 65% yield. Full synthetic details are given in the supplementary material.

The structures of three of the title compounds **1b**, **1c**, and **2c** were determined by X-ray crystallography.[4] The structures of **1c** (**1b** is very similar) and the anion of **2c** are illustrated in Figures 1 and 2. They show several interesting features. They are the first X-ray structures of monomeric compounds having a bond between planar boron and planar phosphorus centers. Furthermore, in **1b** and **1c**, these two planes C(1)C(10)BP and LiPBC(19) are almost coincident, having twist angles of 11.7° (**1b**) and 3.8° in (**1c**). For **2c** the atoms C(1)C(10)BPC(19) are virtually coplanar. The planarity of the phosphorus center, instead of the expected pyramidicity,[5] indicates the presence of only one stereochemically active lone pair at this site. The other available electron pair is presumably involved in multiple bonding to boron as indicated by the small twist angles. The eclipsed configuration in all three compounds is, of course, contrary to what is expected on steric grounds.

(1) A. P. Sloan Foundation Fellow, 1985–1987.

(2) Nöth, H.; Kölle, P. *Chem. Rev.* **1985,** *85,* 399. Nöth, H.; Weber, S.; Rasthofer, R.; Narula, Ch.; Konstantinov, A. *Pure Appl. Chem.* **1983,** 1453. Paetzold, P.; v Plotho, Ch.; Schmid, G.; Boese, R.; Schrader, B.; Bourgeard, D.; Pfeiffer, U.; Gleiter, R.; Schäfer, W. *Chem. Ber.* **1984,** *117,* 1089. Haase, M.; Klingebiel, U. *Angew. Chem., Int. Ed. Engl.* **1985,** *26,* 326. Haase, M.; Klingebiel, U.; Boese, R.; Polk, M. *Chem. Ber.* **1986,** *119,* 1117.

(3) Klusik, H.; Berndt, A. *Angew. Chem., Int. Ed. Engl.* **1983,** *22,* 877. Pachaly, B.; West, R. *J. Am. Chem. Soc.* **1985,** *107,* 1987. Glaser, B.; Nöth, H. *Angew. Chem., Int. Ed. Engl.* **1985,** *24,* 416. Bartlett, R. A.; Power, P. P. *Organometallics* **1986,** *5,* 1916.

(4) Crystal data at 130 K with Mo Kα (λ = 0.71069 Å) radiation: **1b**, monoclinic, *P*2$_1$/*c*, *Z* = 4, *a* = 16.512 (5) Å, *b* = 10.247 (3) Å, *c* = 20.489 (6) Å, β = 109.35 (2)°, *R* = 0.065, 364 parameters, 2475 unique observed data; **1c**, monoclinic, *Cc*, *Z* = 4, *a* = 21.717 (8) Å, *b* = 7.972 (3) Å, *c* = 23.683 (8) Å, β = 122.06 (2)°, *R* = 0.084, 359 parameters, 2320 unique observed data; **2c**, monoclinic, *C*2/*c*, 2 = 8, *a* = 35.408 (10) Å, *b* = 13.398 (4) Å, *c* = 20.697 (7) Å, β = 106.4 (2)°, *R* = 0.126, 337 parameters, 3183 unique observed data. The somewhat high *R* value for **2c** was due mainly to the disorder commonly found in the cations [Li(12-crown-4)$_2$]$^+$. This resulted in a significant reduction in the intensity of the data at 2θ values greater than ca. 40°. However, the anion [MesPBMes$_2$]$^-$ is not disordered and the bond distances and angles are normal and close to those seen in **1b** and **1c**.

(5) Compounds **1b** and **1c** could also be considered as lithium phosphides LiPX$_2$ with the expectation that these, as well as their As–Bi analogues, should be planar like their LiNX$_2$ counterparts. However, the only examples of monomeric heavier pnictide complexes of this type are [Li(THF)$_3$P(H)Mes] and [Li(1,4-dioxane)$_3$AsPh$_2$] and these are both *pyramidal* at the pnictogen. Thus the structures of both **1b** and **1c** are contrary to what is expected unless P–B multiple bonding is assumed: Bartlett, R. A.; Dias, H. V. R.; Hope, H.; Murray, B. D.; Olmstead, M. M.; Power, P. P. *J. Am. Chem. Soc.,* in press. Bartlett, R. A.; Olmstead, M. M.; Power, P. P.; Sigel, G., unpublished results.
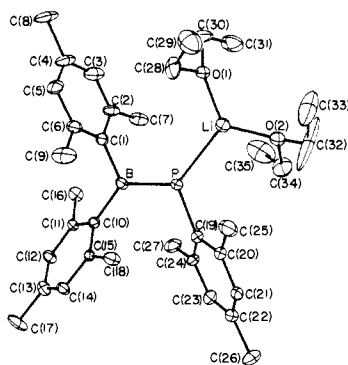
Figure 1. Important bond distances (Å) and angles (deg) for **1c**, values for **1b** are in brackets. PB = 1.823 (7) [1.832 (6)], PC (19) = 1.850 (10) [1.871 (6)], PLi = 2.451 (14) [2.454 (9)], BC (1) = 1.604 (14) [1.598 (8)], BC(10) = 1.593 (7) [1.598 (11)], LiO(1) = 1.899 (20) [1.951 (9)], LiO(2) = 1.893 (15) [1.957 (9)], BPC(19) = 111.7 (4) [108.2 (3)], BPLi = 126.9 (5) [127.1 (3)], LiPC(19) = 121.3 (3) [122.4 (3)], PBC(1) = 114.3 (5) [117.2 (4)], PBC(10) = 125.3 (7) [120.9 (4)], C(1)BC(10) = 120.3 (6) [121.9 (5)].
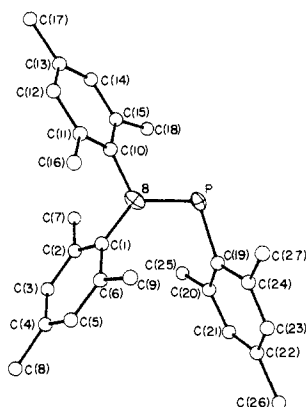

Figure 2. Important bond distances (Å) and angles (deg) for the anion of **2c**. BP = 1.835 (13), PC(19) 1.863 (10), BC(1) = 1.582 (15), BC(10) = 1.619 (15), BPC(19) = 108.2 (5), PBC(10) = 116.7 (7), C(1)BC(10) = 117.3 (10), PBC(1) = 126.0 (8).

The multiple bonding is also supported by the relatively short BP distances 1.832 (6) (**1b**), 1.823 (7) (**1c**), and 1.835 (13) Å (**2c**). Only a small number of complexes with BP bonds have been structurally characterized. However, the BP distances shown above are significantly shorter than 1.96 Å seen in boron phosphide.[6] Distances of ca. 1.93 Å have been seen in the adducts H$_3$PBH$_3$,[7a] Me$_3$PBH$_3$,[7a] Ph$_3$PBH$_3$,[7b] and the trimer [(Me$_2$PBH$_2$)].[8] Even longer bond lengths have been reported in [(Ph$_2$PBI$_2$)$_2$],[9] 2.01 Å, and in [(Me$_2$PBH$_2$)$_4$],[10] 2.08 Å. With very electronegative substituents on phosphorus, shorter BP distances (ca. 1.83 Å) were seen in F$_3$PBH$_3$[11] or F$_3$PB(BF$_2$)$_3$.[12] In these compounds, however, dπ–pπ bonding is believed to be involved in addition to the dative bond.[7a] In **1b**, **1c**, and **2c** the planarity of phosphorus and boron, the relatively short BP bonds,

and the eclipsed nature of both structures indicate considerable pπ–pπ overlap in addition to the σ-bond suggesting a substantial double-bond formulation.

The PB bonds in **1b**, **1c**, and **2c** may be compared to the silicon carbon double bond lengths of 1.764 (3) Å in [(Me$_3$Si)$_2$Si=C-(OSiMe$_3$)(adamantyl)] (twist angle 14.6°)[13] Å and 1.702 Å in [Me$_2$Si=C(SiMe$_3$)SiMe(t-Bu)$_2$].[14] The Schomaker–Stevenson method[15] predicts Si–C and B–P single-bond values of 1.88–1.90 Å and 1.95–1.98 Å. The fairly large disparity in these isoelectronic pairs is due to the large difference in EN for SiC compared to BP. Also the radius of boron is probably[16] 0.1 Å larger than that of carbon whereas the radius of phosphorus is 0.07 Å less than that of silicon.[16] Double bond values may be estimated at 8–9% less than the single bond value, i.e., 1.71–1.75 Å for Si=C[17] and 1.79–1.84 Å for B=P. The actual bond distances measured in **1b**, **1c**, and **2c** are within the predicted values (albeit on the higher end of the envelope) and consistent with a high degree of BP double-bond character. The removal of Li from phosphorus in **2c** has a relatively small effect on the structure.

The ^{31}P NMR spectra of **1a**, **1b**, and **1c** display broad singlets at 73.1, 70.05, and 55.5 ppm. The addition of 12-crown-4 to these solutions resulted in the downfield shift of these peaks to 103.6 (**2a**), 113.6 (**2b**), and 91.3 (**2c**) ppm. These types of shifts are similar to those seen when lithium derivatives of primary and secondary phosphines were treated with crowns.[18,19] However, both compounds of type **1** and **2** appear much further downfield, indicating a considerably deshielded phosphorus atom. The ^{11}B NMR spectra of **1a**, **1b**, and **1c** in ether appear as broad singlets at 65.4, 65.6, and 63.7 ppm relative to external BF$_3$·Et$_2$O. Insignificant changes in the spectra were observed when 12-crown-4 was added. The shifts are similar to those seen in other three coordinate Mes$_2$B-substituted compounds.[20]

In summary the compounds described display a considerable degree of BP multiple bonding and the B–P distances are very similar to that predicted for a double bond. A key factor in the facility of their synthesis is the use of two crowding mesityl groups at boron which effectively prevents further attack at this center.[21] Work on the further characterization of the title compounds and their heavier main group congeners is continuing.

(6) Perri, J. A.; La Placa, S.; Post, B. *Acta Crystallogr.* **1958**, *11*, 310.

(7) (a) Bryan, P. S.; Kuczkowski, R. L. *Inorg. Chem.* **1972**, *11*, 553. Hamilton, W. C. *Acta Crystallogr.* **1955**, 1986. (b) Huffman, J. C.; Skupinski, W. A.; Caulton, K. G. *Cryst. Struct. Commun.* **1982**, *11*, 1435.

(8) Hamilton, W. C. *Acta Crystallogr.* **1955**, *8*, 198.

(9) Bullen, G. J.; Mallinson, P. R. *J. Chem. Soc., Chem. Commun.* **1969**, 132.

(10) Goldstein, P.; Jacobson, R. A. *J. Am. Chem. Soc.* **1962**, *84*, 2457.

(11) Marriott, J. C.; Salthouse, J. A.; Ware, M. J.; Freedman, G. M. *J. Chem. Soc., Chem. Commun.* **1970**, 595.

(12) De Boer, B. G.; Zalkin, A.; Templeton, D. H. *Inorg. Chem.* **1969**, *8*, 836.

(13) Brook, A. G.; Nyburg, S. C.; Abdesaken, F.; Gutekunst, B.; Gutekunst, G.; Kallury, R. K. M. R.; Poon, Y. C.; Chang, Y.-M.; Wong-Ng, W. *J. Am. Chem. Soc.* **1982**, *104*, 5667. Nyburg, S. C.; Brook, A. G.; Abdesaken, F.; Gutekunst, G.; Wong-Ng, W. *Acta Crystallogr., Sect. C* **1985**, *C41*, 1632.

(14) Wiberg, N.; Wagner, G. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 1005. Wiberg, N.; Wagner, G.; Müller, G. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 229.

(15) Schomaker, V.; Stevenson, D. P. *J. Am. Chem. Soc.* **1941**, *63*, 37.

(16) See Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 4th ed.; Wiley: New York, 1980; p 289. This reference suggests that the covalent radius of boron is not well defined by probably lies between 0.85 and 0.90 Å. Table 6.1 in Huheey (Huheey, J. E. *Inorganic Chemistry*, 3rd ed.; Harper and Row: New York, 1983, p 258) gives 0.9 Å as the radius of boron. From 1.1 Å as the radius of phosphorus, assuming the range of 0.85–0.90 Å for B, with an 8% reduction for double bonding, a P–B double bond is predicted to be 1.79–1.84 Å. These methods also predict a value of ca. 1.74–1.77 Å for a B–P multiple bond which might be expected in a monomer of formula RPBR.

(17) Schaefer, H. F. *Acc. Chem. Res.* **1982**, *15*, 283.

(18) Zschunke, A.; Bauer, E.; Schmidt, H.; Issleib, K. *Z. Anorg. Allg. Chem.* **1982**, *495*, 115.

(19) Sigel, G.; Power, P. P., unpublished work.

(20) Brown, N. M. D.; Davidson, F.; Wilson, J. W. *J. Organomet. Chem.* **1981**, *209*, 1. Nöth, H.; Wrackmeyer, B. In *NMR—Basic Principles and Progress*; Diehl, P., Fluck, E., Kosfeld, R., Eds.; Springer Verlag: Berlin, 1978; Vol. 14.

(21) The use of the Mes$_2$B group has been pioneered elsewhere by Wilson and Pelter and co-workers: Wilson, J. W. *J. Organomet. Chem.* **1980**, *186*, 297. Brown, N. M. D.; Davidson, F.; Wilson, J. W. *J. Organomet. Chem.* **1980**, *185*, 277. Pelter, A.; Singaram, B.; Williams, L.; Nelson, J. W. *Tetrahedron Lett.* **1983**, *24*, 621. Pelter, A.; Briaden, G.; Roesser, R. *Tetrahedron Lett.* **1985**, *26*, 5097.

(22) **Note Added in Proof**: Reports involving formal B–P single bonds in the complexes [Mes(H)PB(Cl)(tmp)], [{MesPB(tmp)}$_2$], and [{(Et)$_3$CPB-(tmp)}$_2$] were published after this work had been submitted. In each case the phosphorus center is pyramidal and the B–P distances are 1.916 (3), 1.948 (3), 1.933 (2), and 1.916 (2) Å. See: Arif, A. M.; Cowley, A. H.; Pakulski, M.; Power, J. M. *J. Chem. Soc., Chem. Commun.* **1986**, 889. Kölle, P.; Nöth, H.; Paine, R. T. *Chem. Ber.* **1986**, *119*, 2681. These distances and geometries further support the multiple bonding formulation in complexes **1** and **2**. Also, Professors Cowley and Escudie have informed us that they have spectroscopically characterized compounds similar to **1** and **2** which differ only in the type of substituent. However, no X-ray structural characterizations have yet emerged.

Supplementary Material Available: Experimental details for the synthesis of **1** and **2**, computer-generated drawing of **1b**, summary of data collection and refinement, and tables of atom coordinates and thermal parameters, bond distances and angles, and hydrogen coordinates (18 pages). Ordering information is given on any current masthead page.

Scheme I

Surprisingly Small Effect of an α-CF₃ for α-CH₃ Substitution on 1-(4-Methoxyphenyl)ethyl Cation Reactivity[1]

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Experimental studies on the effect of the strongly electron withdrawing α-CF₃ group on carbocation stability have been restricted to documenting the large rate-retarding effect on the rate constants for solvolysis by rate-determining carbocation formation.[2,3] Little is known about the effect on the reverse reaction of carbocation with nucleophiles; however, chemical intuition suggests that a highly destabilized α-CF₃-substituted cation will be more reactive than the α-CH₃ counterpart. I wish to report that, contrary to intuition, an α-CF₃ for α-CH₃ substitution at **1** has little effect on the rate constant for the reaction
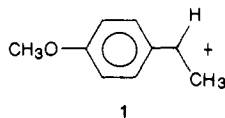
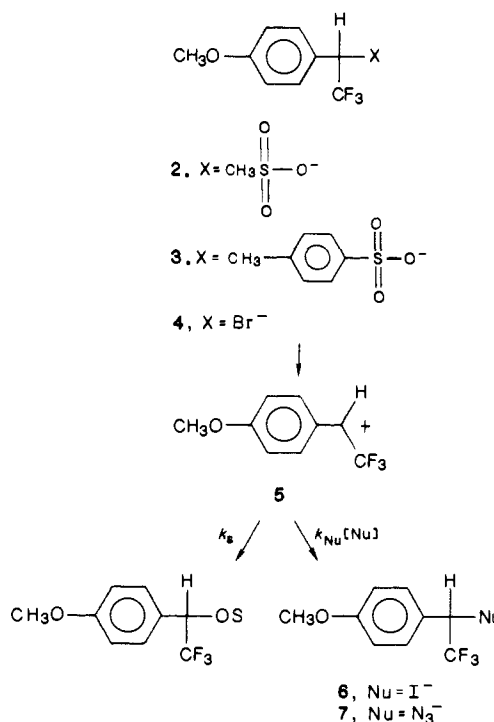of the 1-(4-methoxyphenyl)ethyl cation with aqueous trifluoroethanol.

The absorbance at 290 nm is constant during the solvolysis reaction of **2**[4,5] but increases during reaction of **2** in the presence

of NaI due to the formation of **6**.[5] This reaction is S_N1 because the pseudo-first-order rate constants for **6** formation change only slightly from 3.5×10^{-2} s⁻¹ at low [NaI] to 3.2×10^{-2} s⁻¹ at 0.5 M NaI where 98% of the product is **6**. The amount of **6** formed is proportional to $(A_f - A_0)$ where A_0 and A_f are the initial and final absorbances at 290 nm, respectively. The data obtained show a good fit to eq 1. The rate constant ratio for iodide and solvent

$$1/(A_f - A_0) = [1/(A_f - A_0)_{max}](1 + k_s/k_1[I^-]) \qquad (1)$$

reaction with **5**, $k_1/k_s = 85 \pm 6$ M⁻¹, is calculated from the slope and the intercept of a plot of $1/(A_f - A_0)$ against $1/[I^-]$. The amount of **6** (as measured by $A_f - A_0$ at 290 nm) formed at a constant NaI and **2** concentration decreases with increasing [NaN₃] due to the formation of **7**. The azide reaction is also S_N1 because the pseudo-first-order rate constants for **6** formation are independent of [N₃⁻].[6]

The relative concentrations of the adducts formed from the reaction of **2**, **3**,[2b] and **4**[7] with nucleophiles were determined from their absorbance at 254 nm, after separation by HPLC.[8] The following nucleophilic selectivities were calculated from product concentration data:[9] $k_I/k_s = 90$ M⁻¹ for the reactions of **2** and **3**; $k_{Br}/k_s = 37$ M⁻¹ for the reaction of **3**; $k_{az}/k_s = 95$ M⁻¹ for the reactions of **3** and **4**.

(1) Part of this work was completed during the author's tenure as the Herchel Smith Fellow at Cambridge University. Address correspondence to the University of Kentucky.

(2) (a) Gassman, P. G.; Tidwell, T. T. *Acc. Chem. Res.* **1982,** *16,* 279. (b) Allen, A. D.; Ambridge, I. C.; Che, C.; Michael, H.; Muir, R. J.; Tidwell, T. T. *J. Am. Chem. Soc.* **1983,** *105,* 2343. (c) Allen, A. D.; Jansen, M. P.; Koshy, K. M.; Mangru, N. N.; Tidwell, T. T. *J. Am. Chem. Soc.* **1982,** *104,* 207. (d) Liu, K.-T.; Kuo, M.-Y.; Shu, C.-F. *J. Am. Chem. Soc.* **1982,** *104,* 211. (e) Liu, K.-T.; Shu, C.-F. *Tetrahedron Lett.* **1980,** *21,* 4091. (f) Tidwell, T. T. *Angew Chem., Int. Ed. Engl.* **1984,** *23,* 20.

(3) A (4×10^5)-fold effect of the α-CF₃ substitution on k_{solv} for the reaction of 1-(4-methoxyphenyl)ethyl chloride in 50:50 water/trifluoroethanol at 25 °C is calculated from k_{solv} values of 20 and 5.6×10^{-5} s⁻¹, respectively, for reaction of the CH₃- and CF₃-substituted compounds. The former rate constant is calculated from the estimated rate constant for reaction in 80% aqueous acetone (Tsuno, Y.; Kusuyama, Y.; Sawada, M.; Fujii, T.; Yukawa, Y. *Bull. Chem. Soc. Jpn.* **1975,** *48,* 3337), a 2.6 unit different in *Y* values for the two solvents and an *m* value of 1.0 for S_N1 solvolysis (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. Fainberg, A. H.; Winstein, S. *J. Am. Chem. Soc.* **1956,** *78,* 2770), and the latter value from the rate constant reported here for reaction of **4** and an average k_{Br}/k_{Cl} ratio of 11 for the reaction of ring-substituted 1-phenylethyl bromides and chlorides (Richard, J. P.; Jencks, W. P. *J. Am. Chem. Soc.* **1984,** *106,* 1383).

(4) The reactions reported here were at 25 °C in 50:50 (v/v) water/trifluoroethanol and at constant ionic strength of 0.5 (NaClO₄).

(5) The mesylate was synthesized by adaptation of the published method for preparation of the tosylate.[2b] The compound was isolated as a highly reactive oil which contained variable small (<10%) amounts of unreacted 1-(4-methoxyphenyl)-2,2,2-trifluoroethanol. The compound showed the expected ¹H NMR spectrum in CDCl₃ with a C*H*CF₃ quartet at 5.77 ppm. Compound **6** was isolated by extraction from a solvolysis reaction mixture containing **2** and 0.5 M I⁻ into ether. The ¹H NMR spectrum in CDCl₃ showed a C*H*CF₃ quartet with a chemical shift of 5.34 ppm.

(6) Note that the pseudo-first-order rate constants for **6** and **7** formation and **2** disappearance must all be the same. Jencks, W. P. *Catalysis in Chemistry and Enzymology*; McGraw Hill: New York, 1969; p 571.

(7) Compound **4** was synthesized by bromination of the precursor alcohol with PBr₃[2d] and purified by vacuum distillation. The NMR, IR, and elemental analysis are in agreement with the chemical structure.

(8) Aliquots (50–200 μL) from the reaction mixture (~0.1 mM substrate) were analyzed as described previously.[12]

(9) Nucleophilic selectivities, k_{Nu}/k_s, were calculated from the slope and the intercept of a plot of $1/[area]_{RNu}$ against $1/[Nu]$, where $[area]_{RNu}$ is the integrated area of the HPLC peak for the nucleophilic adduct.