6.68–7.78 (m, 4 H), 12.07 (s, 1 H), 15.12 (s, 1 H). Anal. Calcd for $C_{14}H_{18}O_3$: C, 71.77; H, 7.74. Found: C, 72.02; H, 8.17.

3-Hydroxy-1-(2-hydroxyphenyl)-5-phenylpenta-2,4-dien-1-one (8): NMR ($CDCl_3$) δ 6.30 (s, 1 H), 6.42–7.80 (m, 11 H), 12.40 (s, 1 H), 15.02 (br s, 1 H). Anal. Calcd for $C_{17}H_{14}O_3$: C, 76.68; H, 5.30. Found: C, 76.48; H, 5.37.

3-Hydroxy-1-[5-(allyloxy)-2-hydroxyphenyl]-3-(5-bromo-2-furyl)prop-2-en-1-one (10): NMR ($CDCl_3$) δ 4.56 (d, J = 4 Hz, 2 H), 5.15–6.40 (m, 3 H), 6.50 (d, J = 3 Hz, 1 H), 7.08–7.46 (m, 5 H), 10.50 (s, 1 H), 14.10 (br s, 1 H).

3-[4-(2-Propenyl)cyclohexenyl]-3-hydroxy-1-[5-(allyloxy)-2-hydroxyphenyl]prop-2-en-1-one (11): NMR ($CDCl_3$) δ 1.78 (br s, 3 H), 1.92–2.60 (m, 7 H), 4.50 (d, J = 5 Hz, 2 H), 4.75 (br s, 2 H), 5.12–6.15 (m, 3 H), 6.21 (s, 1 H), 6.80–7.35 (m, 4 H), 11.80 (s, 1 H), 15.40 (s, 1 H). Anal. Calcd for $C_{21}H_{24}O_4$: C, 74.09; H, 7.11. Found: C, 74.07; H, 7.17.

Acknowledgment. We thank the Alfred P. Sloan Foundation for partial support of this work.

Registry No. 1, 90554-75-9; 2, 40815-75-6; 3, 90554-76-0; 4, 90554-77-1; 5, 90554-78-2; 6, 90541-51-8; 7, 90554-79-3; 8, 39103-35-0; 9, 39103-33-8; 10, 90554-80-6; 11, 90554-81-7; HO-C_6H_4-o-Ac, 118-93-4; $CH_3(CH{=}CH)_2COCl$, 90554-82-8; CH_3COCl, 75-36-5; n-$C_5H_{11}COCl$, 142-61-0; $CH_2{=}CHCOCl$, 814-68-6; PhCH=CHCOCl, 102-92-1; PhCOCl, 98-88-4; $BrC{=}CHCH{=}C(COCl)O$, 26726-16-9; $CH_2{=}C(CH_3)CHCH_2CH{=}C(COCl)CH_2CH_2$, 90554-83-9; $CH_3CH{=}CHCOCl$, 10487-71-5.

Hard Acid and Soft Nucleophile Systems. 9.[1] Cleavage of Activated Carbon–Carbon Double Bonds with a Hard Lewis Acid and Ethanethiol

Kaoru Fuji,* Takeo Kawabata, Manabu Node, and Eiichi Fujita

Institute for Chemical Research, Kyoto University, Kyoto 611, Japan

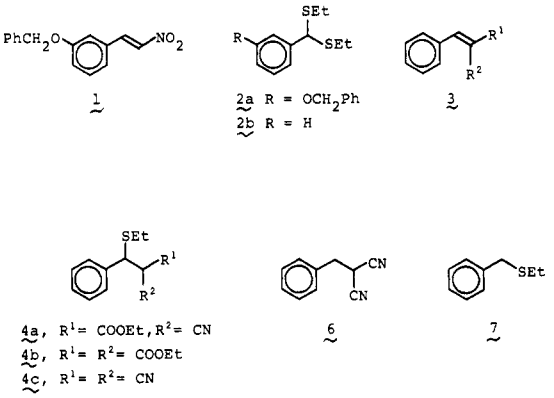
Received February 8, 1984

The principle of hard and soft acids and bases (HSAB)[2] has played an important role in understanding the chemoselectivity of reactions[3,4] and in the development of new reactions. Recently we have reported cleavage reactions of a variety of carbon–oxygen bonds of ethers[5] and esters[6] using combinations of a hard acid and a soft nucleophile. Coordination of a hard acid with the oxygen atom, which is a hard base, activates the carbon–oxygen bond followed by attack of a soft nucleophile on the carbon atom, which is regarded as a soft acid, to accomplish a carbon–oxygen bond cleavage. As both the pulling factor and the pushing factor are indispensable in this type of reactions, the transition state is situated between S_N1 and S_N2 displacement at the carbon atom in the mechanistic spectrum.

Almost all covalent bonds have more or less hard–soft dissymmetry as well as charge dissymmetry. Thus, carbon–heteroatom bonds as well as carbon–oxygen bonds are cleaved with an appropriate combination of a hard acid and a soft nucleophile.[7] This account describes the cleavage of carbon–carbon double bonds bearing activating group(s) with a hard Lewis acid and ethanethiol.[8]

Results and Discussion

A combination of boron trifluoride etherate and ethanethiol has proved to be effective for deblocking the benzyl protecting group of alcohols and phenols.[9] However, attempted deblocking of 1 with this reagent resulted in the formation of an unexpected product **2a** in 48% yield,[10] by



cleavage of the carbon–carbon double bond. A similar reaction occurred to afford **2b** in 88% yield when a styrene derivative **3a** was treated with boron trifluoride etherate and ethanethiol at room temperature for 8 days (Table I, entry 1). In order to find a more effective catalyst for the cleavage, we examined other Lewis acids. Except for lanthanide chlorides (entries 6–8), the harder a Lewis acid is, the greater activity it possesses. The order of the activity of metal halides (entries 2–5) corresponds to that of their reported hardness.[11] Rare earth chlorides are hard Lewis acids[11] and have been reported to be effective catalysts for acetalization of aldehydes.[12] However, no double-bond cleavage occurred with rare earth chlorides, but the reaction ceased at the Michael addition stage, giving **4a** in some cases (entries 6 and 7). This might be attributed to their weak Lewis acidities.[13] It appears that the double-bond cleavage requires a hard acid that also has strong Lewis acidity. Aluminum chloride and bromide are satisfactory Lewis acids in this respect.

The double bond in styrene derivatives **3b–h** was cleaved under similar reaction conditions to afford **2b** in fair to good yields. Attempted reaction of nitroolefins **3b** and **3c** with aluminum chloride resulted in the formation of an unidentifiable mixture of products. Ethyl cinnamate did not give **2b** with aluminum chloride or bromide in ethanethiol and dichloromethane at room temperature after 2.5 h but furnished ethyl 3-(ethylthio)-3-phenylpropionate[14]

(1) For part 8 in this series, see: Node, M.; Kawabata, T.; Ohta, K.; Watanabe, K.; Fujimoto, M.; Fujita, E.; Fuji, K. *J. Org. Chem.*, in press.
(2) Pearson, R. G. *J. Am. Chem. Soc.* **1963**, *85*, 3533.
(3) For a review, see: (a) Pearson, R. G. "Hard and Soft Acids and Bases"; Dowden, Hutchinson, & Ross Inc.; Stroudsberg, 1973. (b) Ho, T.-L. "Hard and Soft Acids and Bases Principle in Organic Chemistry"; Academic Press: New York, 1977.
(4) For a recent example, see: Semmelhack, M. F.; Tamura, R. *J. Am. Chem. Soc.* **1983**, *105*, 4099.
(5) (a) Node, M.; Hori, H.; Fujita, E. *J. Chem. Soc., Perkin Trans. 1* **1976**, 2237. (b) Node, M.; Nishide, K.; Fuji, K.; Fujita, E. *J. Org. Chem.* **1980**, *45*, 4275. (c) Node, M.; Ohta, K.; Kajimoto, T.; Nishide, K.; Fujita, E.; Fuji, K. *Chem. Pharm. Bull.* **1983**, *31*, 4178.
(6) (a) Node, M.; Nishide, K.; Sai, M.; Fuji, K.; Fujita, E. *J. Org. Chem.* **1981**, *46*, 5163. (b) Node, M.; Nishide, K.; Ochiai, M.; Fuji, K.; Fujita, E. *Ibid.* **1981**, *46*, 5163.
(7) Node, M.; Kawabata, T.; Ohta, K.; Watanabe, K.; Fuji, K.; Fujita, E. *Chem. Pharm. Bull.* **1983**, *31*, 749.
(8) For a preliminary report, see: Fuji, K.; Kawabata, T.; Node, M.; Fujita, E. *Tetrahedron Lett.* **1981**, *22*, 875.
(9) Fuji, K.; Ichikawa, K.; Node, M.; Fujita, E. *J. Org. Chem.* **1979**, *44*, 1661.
(10) Fuji, K.; Kawabata, T.; Fujita, E. *Chem. Pharm. Bull.* **1980**, *28*, 3662.
(11) Klopman, G. *J. Am. Chem. Soc.* **1968**, *90*, 223.
(12) Luche, J.-L.; Gemol, A. L. *J. Chem. Soc., Chem. Commun.* **1978**, 976.
(13) Gemol, A. L.; Luche, J.-L. *J. Org. Chem.* **1979**, *44*, 4187.

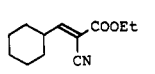
0022-3263/84/1949-3214$01.50/0

in 60% yield. Although it has been reported that nucleofugalities[15] in alkene-forming eliminations are not related to the pKa of the conjugate acid of the leaving group,[15] whether the reaction ceases at the Michael addition stage or proceeds further to afford **2b** seems to depend upon the pKa value of the carbon nucleofuge in this case. Those compounds with a leaving group of smaller pKa than diethyl malonate (pKa ~13[17]) can be cleaved with combination systems listed in Table I.

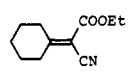
A possible reaction pathway of the double-bond cleavage involves the Michael addition of ethanethiol followed by a retro-aldol cleavage of the resulting single bond as shown in Scheme I. Reaction of **3g** with ethanethiol without Lewis acids gave the addition product **4c**, which was then converted to **2b** under the reaction conditions. These facts suggest the formation of a Michael adduct at the first stage. Intervention of the Michael adduct is also inferred from the results in Table I (entries 6, 7, and 16).

Both an S_N1 mechanism as shown in Scheme I and a direct attack of ethanethiol in the S_N2 sense are plausible for conversion of **4c** into **2b**. To discriminate between these two possibilities, **6**[18] was treated with 3 molar equiv of aluminum chloride in ethanethiol at 0 °C for 40 min without any generation of the expected product **7**.[19] This indicates that the sulfur substitutent is necessary for the elimination of an active methylene compound. Thus, direct replacement is not involved in the conversion of **4** into the dithioacetal **2b**.

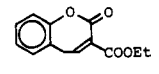
This type of the double-bond cleavage reaction can be applied not only for styrene derivatives but also for double bonds activated by electron-withdrawing groups in aliphatic compounds. Thus treatment of **8**, **9**, or a cyclic



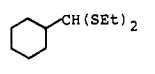
8



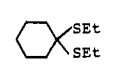
9



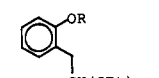
10



11



12



13a R = $COCH_2COOEt$
13b R = H

compound **10** with aluminum chloride and ethanethiol for 0.2, 5, and 0.5 h afforded **11**, **12**, and **13a** in 66%, 48%, and 81% yields, respectively. As the dithioacetal **13a** was unstable, it was characterized as the phenol **13b** after hydrolysis.

Experimental Section

Melting points were determined on a micro hot stage and are uncorrected. IR spectra were recorded with a JASCO A-202 spectrophotometer. ^1H NMR spectra were obtained with a Varian T-60 spectrometer or a JEOL JNM-FX100 spectrometer, and chemical shifts are reported in parts per million relative to internal Me_4Si. High-resolution mass spectra were determined on a JEOL JMS-DX300 mass spectrometer. GLC analyses were performed on a Shimadzu Model GC-4CM chromatograph.

Materials. Compounds **3a**,[20] **3b**,[21] **3c**,[22] **3d**,[20] **3e**,[23] **3f**,[23] **3g**,[20] **3h**,[20] and **9**[24] are known.

Dithioacetal 2b. General Procedure for the Double-Bond Cleavage. To a mixture of a Lewis acid (3 molar equiv) in ethanethiol (1 mL) was added a solution of a starting material (0.5 mmol) in dichloromethane (1 mL) with ice-cooling under argon. After being stirred for the time shown in Table I, the reaction mixture was poured into ice–water and extracted with dichloromethane. The organic layer was washed with brine, dried over Na_2SO_4, and evaporated to give dithioacetal **2b**.[25] The yield was determined by GLC on a 10% FFAP column (1 m × 3 mm) at 170 °C with 1,4-dimethylnaphthalene as an internal standard.

Ethyl 3-(Ethylthio)-2-cyano-3-phenylpropionate (4a). Entry 6 in Table I. To a stirred mixture of $YbCl_3 \cdot 6H_2O$ (580 mg, 1.5 mmol) in ethanethiol (1 mL) was added a solution of **3a** (100 mg, 0.5 mmol) in dichloromethane (1 mL) with ice-cooling, and it was stirred at room temperature for 96 h. The reaction mixture was then poured into aqueous Na_2CO_3 and extracted with dichloromethane. The organic layer was dried over Na_2SO_4 and evaporated to yield oily **4a** quantitatively: ^1H NMR ($CDCl_3$) δ 1.18 (t, 6 H, J = 7 Hz), 2.45 (q, 2 H, J = 7 Hz), 2.48 (q, 2 H, J = 7 Hz), 3.7–4.5 (m, 4 H), 7.2–7.6 (m, 5 H); IR (neat) 2995, 2260, 1735, 1600, 1500 cm^{-1}; high-resolution mass spectrum, calcd for $C_{14}H_{17}NO_2S$ (M^+) m/e 263.0979, obsd 263.0976.

3-(Ethylthio)-2-cyano-3-phenylpropanenitrile (4c). A solution of **3g** (4.5 g, 29 mmol) in ethanethiol (20 mL) was stirred for 120 h. Evaporation of ethanethiol yielded **4c** quantitatively: mp 41–44 °C (from isopropyl alcohol); ^1H NMR ($CDCl_3$) δ 1.23 (t, 3 H, J = 8 Hz), 2.59 (q, 2 H, J = 8 Hz), 4.15, 4.33 (AB d, each 1 H, J = 7 Hz), 7.39 (s, 5 H): IR ($CHCl_3$) 2990, 2260, 1590, 1500 cm^{-1}; high-resolution mass spectrum, calcd for $C_{12}H_{12}N_2S$ (M^+) m/e 216.0721, obsd 216.0731. Anal. Calcd for $C_{12}H_{12}N_2S$: C, 66.64; H, 5.59; N, 12.95. Found: C, 66.92; H, 5.50, N, 13.38.

Ethyl 2-Cyano-3-cyclohexylacrylate (8). The Knoevenagel condensation[26] of cyclohexanecarboxaldehyde (12.3 g, 0.11 mol) with ethyl cyanoacetate (11.3 g, 0.10 mol) afforded **8** (19.5 g, 94%): bp 98–99 °C (0.3 torr); ^1H NMR ($CDCl_3$) δ 1.35 (t, 3 H, J = 7 Hz), 0.9–2.1 (m, 10 H), 2.4–3.0 (m, 1 H), 4.28 (q, 2 H, J = 7 Hz), 7.41 (d, 1 H, J = 10 Hz); IR (neat) 2940, 2230, 1725, 1620 cm^{-1}; high-resolution mass spectrum, calcd for $C_{12}H_{17}NO_2$ (M^+) m/e 207.1260, obsd 207.1283. Anal. Calcd for $C_{12}H_{17}NO_2$: C, 69.54; H, 8.27; N, 6.76. Found: C, 69.99; H, 8.40; N, 7.00.

Compound 10. To a solution of α-tetralone (1.24 g, 8.5 mmol) in chloroform (6 mL) was added a solution of m-chloroperbenzoic acid (2.52 g, 14 mmol) in chloroform (6 mL) during a period of 1.5 h, and the reaction mixture was stirred at room temperature for 20 h followed by reflux for 1.5 h. Crystals resulting from standing for 2 days were filtered off. The filtrate was diluted with chloroform, washed successively with 20% aqueous $NaHSO_3$, 10% aqueous $NaHCO_3$, and brine, dried over Na_2SO_4, and evaporated. Distillation of the residue afforded a pale yellow oil (bp 94–112 °C (1.2 torr), 1.0 g), a tetrahydrofuran (THF) (5 mL) solution of which was added dropwise to a solution of lithium diisopropylamide (LDA) (7.4 mmol) in THF (5 mL) at −78 °C under nitrogen. After being stirred for 15 min at the same temperature, ethyl chlorocarbonate (0.66 mL, 6.8 mmol) was added in one portion. After the reaction mixture was stirred for 2 h, it was added to a solution of LDA (7.4 mmol) in THF (5 mL) at −78 °C under nitrogen followed by stirring for 15 min. To this mixture was added a THF (5 mL) solution of phenylselenyl chloride (1.3 g, 6.8 mmol). The mixture was stirred for 2 h, poured into 1 N HCl (60 mL), and extracted with a 1:1 mixture of ether–pentane. The organic layer was washed with brine, dried over Na_2SO_4, and evaporated to leave a residue. Chromatography over a silica gel column (15% ethyl acetate–hexane) followed by recrystallization

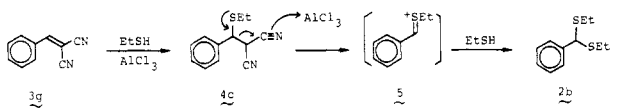
(14) Faust, G.; Verny, M.; Vessiere, R. *Bull. Soc. Chim. Fr.* **1975**, 2707.
(15) Stirling, C. M. *Acc. Chem. Res.* **1979**, *12*, 198.
(16) Stirling, C. M.; Varma, M. *J. Chem. Soc., Chem. Commun.* **1981**, 553.
(17) House, H. O. "Modern Synthetic Reactions", 2nd ed.; Benjamin: Menlo Park, CA, 1972; pp 494.
(18) Wallenfels, K.; Ertel, W.; Friedlich, K. *Liebigs Ann. Chem.* **1973**, 1663.
(19) Langler, R. F. *Can. J. Chem.* **1976**, *54*, 498.
(20) Pratt, E. F.; Werble, E. *J. Am. Chem. Soc.* **1950**, *72*, 4638.
(21) Gairand, C. B.; Lappin, G. R. *J. Org. Chem.* **1953**, *18*, 1.
(22) Hass, H. B.; Susie, A. G.; Heider, R. L. *J. Org. Chem.* **1950**, *15*, 8.
(23) Phillips, W. M.; Currie, D. J. *Can. J. Chem.* **1969**, *47*, 3137.
(24) Hein, R. W.; Astle, M. J.; Schelton, J. R. *J. Org. Chem.* **1961**, *26*, 4874.
(25) Ong, B. S. *Tetrahedron Lett.* **1980**, *21*, 4225.
(26) Jones, G. *Org. React. (N.Y.)* **1967**, *15*, 204.

Table I. Double-Bond Cleavage of 3

entry	compound	R^1	R^2	reaction conditions: Lewis acid[a]	time, h	temp[h]	yield of 2b, %
1	3a	COOEt	CN	$BF_3{\cdot}OEt_2$[b]	192	rt	88
2	3a	COOEt	CN	$AlBr_3$	0.3	rt	94
3	3a	COOEt	CN	$AlCl_3$	0.5	rt	84
4	3a	COOEt	CN	$FeCl_3$	96	rt	70
5	3a	COOEt	CN	$ZnCl_2$	78	rt	13
6	3a	COOEt	CN	$YbCl_3{\cdot}6H_2O$	96	rt	0[c]
7	3a	COOEt	CN	$LaCl_3{\cdot}7H_2O$	168	rt	0[d]
8	3a	COOEt	CN	$CeCl_3$	48	rt	0[e]
9	3b	NO_2	Me	$BF_3{\cdot}OEt_2$[f]	1	rt	48
10	3c	NO_2	Et	$BF_3{\cdot}OEt_2$[f]	0.5	0 °C	52
11	3d	COMe	COMe	$AlCl_3$	0.25	0 °C	87
12	3e	COMe	COOEt	$AlCl_3$	0.5	0 °C	78
13	3f	COOEt	COMe	$AlCl_3$	0.3	0 °C	83
14	3g	CN	CN	$BF_3{\cdot}OEt_2$[b]	156	rt	61
15	3g	CN	CN	$AlCl_3$	0.25	0 °C	100
16	3h	COOEt	COOEt	$BF_3{\cdot}OEt_2$	72	rt	71[g]
17	3h	COOEt	COOEt	$AlCl_3$	0.5	0 °C	94

[a] 3 molar equiv were used unless otherwise stated. [b] 20 molar equiv. [c] Addition product 4a was obtained quantitatively. [d] A 1:1 mixture of 4a and the starting material was obtained. [e] The starting material was recovered quantiatively. [f] 10 molar equiv. [g] The Michael adduct 4b was obtained in 28% yield. [h] rt = room temperature.

Scheme I



from dichloromethane–hexane gave a crystalline product (998 mg), which was oxidized with hydrogen peroxide followed by elimination according to the reported method[27] to afford **10** (590 mg, 30%): mp 77–81 °C (from isopropyl alcohol); ^1H NMR ($CDCl_3$) δ 1.24 (t, 3 H, J = 7 Hz), 3.53 (d, 2 H, J = 8 Hz), 4.21 (q, 2 H, J = 7 Hz), 7.0–7.5 (m, 4 H), 7.79 (t, 1 H, J = 8 Hz); IR ($CHCl_3$) 2995, 1750, 1490, 1270 cm^{-1}; high-resolution mass spectrum, calcd for $C_{13}H_{12}O_4$ (M^+) m/e 232.0735, obsd 232.0733.

Double-Bond Cleavage of 8. This was performed according to the general procedure, and the yield (66%) of the product **11** was determined by GLC on a 10% FFAP column (1 m × 3 mm) at 175 °C with 1-methylnaphthalene as an internal standard. A part of the product was purified by distillation to afford dithioacetal **11**: bp 101–102 °C (1 torr); ^1H NMR ($CDCl_3$) δ 1.25 (t, 6 H, J = 7 Hz), 1.0–2.1 (m, 11 H), 2.63 (q, 4 H, J = 7 Hz), 3.64 (d, 1 H, J = 4 Hz); IR (neat) 2930, 1445 cm^{-1}. Anal. Calcd for $C_{11}H_{22}S_2$: C, 60.48; H, 10.15. Found: C, 60.52; H, 10.33.

Double-Bond Cleavage of 9. The general procedure applied to **9** afforded the dithioacetal **12**,[28] whose yield (48%) was obtained by GLC on a 10% FFAP column (1 m × 3 mm) at 170 °C with 1,4-dimethylnaphthalene as an internal standard.

Double-Bond Cleavage of 10. The reaction was carried out by using 37 mg (0.16 mmol) of **10** according to the general procedure. The crude product was purified by preparative thin-layer chromatography on Kieselgel $60F_{254}$ with ethyl acetate–hexane (1:2) to give oily dithioacetal **13a** (46 mg, 81%): ^1H NMR ($CDCl_3$) δ 1.20 (t, 6 H, J = 8 Hz), 1.32 (t, 3 H, J = 7 Hz), 2.59 (q, 4 H, J = 8 Hz), 3.06 (d, 2 H, J = 7 Hz), 3.63 (s, 2 H), 3.91 (t, 1 H, J = 7 Hz), 4.28 (q, 2 H, J = 7 Hz), 6.9–7.5 (m, 4 H); IR ($CHCl_3$) 2990, 1740, 1450 cm^{-1}.

2-[2,2-Bis(ethylthio)ethyl]phenol (13b). A solution of **13a** (46 mg, 0.13 mmol) in dichloromethane (10 mL) was stirred with 2.0 g of neutral alumina (Alumina Woelm N, activity 1) for 6 h. Alumina was filtered off and washed with dichloromethane. The combined organic layer was evaporated followed by preparative TLC (ethyl acetate–hexane, 1:3) to afford oily **13b** (23 mg, 74%): ^1H NMR ($CDCl_3$) δ 1.22 (t, 6 H, J = 8 Hz), 2.64 (q, 4 H, J = 8 Hz), 3.17 (d, 2 H, J = 7 Hz), 4.06 (t, 1 H, J = 7 Hz), 5.8–6.0 (br s, 1 H), 6.7–7.3 (m, 4 H); IR ($CHCl_3$) 3590, 3300, 2940, 1590, 1455 cm^{-1}. Anal. Calcd for $C_{12}H_{18}OS_2$: C, 59.47; H, 7.49. Found: C, 59.73; H, 7.75.

Acknowledgment is made to the Ministry of Education, Science, and Culture, Japan, for support of this research under Grant No. 58570871.

Registry No. 2b, 7334-52-3; **3a**, 2169-69-9; **3b**, 18315-84-9; **3c**, 25695-90-3; **3d**, 4335-90-4; **3e**, 15802-63-8; **3f**, 15802-62-7; **3g**, 2700-22-3; **3h**, 5292-53-5; **4a**, 78614-61-6; **4c**, 78614-62-7; **8**, 90913-43-2; **9**, 6802-76-2; **10**, 90913-44-3; **11**, 76241-76-4; **12**, 27482-20-8; **13a**, 90913-45-4; **13b**, 90913-46-5; EtSH, 75-08-1; $BF_3{\cdot}OEt_2$, 109-63-7; $AlBr_3$, 7727-15-3; $AlCl_3$, 7446-70-0; $FeCl_3$, 7705-08-0; $ZnCl_2$, 7646-85-7; $YbCl_3$, 10361-91-8; $LaCl_3$, 10099-58-8; $CeCl_3$, 7790-86-5; cyclohexanecarboxaldehyde, 2043-61-0; ethyl cyanoacetate, 105-56-6; α-tetralone, 529-34-0; 4,5-dihydro-1-benzoxepin-2(3*H*)-one, 3041-17-6; ethyl chlorocarbonate, 541-41-3; ethyl 4,5-dihydro-2(3*H*)-oxo-1-benzoxepin-3-carboxylate, 90913-47-6.

(27) Reich, H. J.; Renga, J. M.; Reich, I. L. *J. Am. Chem. Soc.* **1975**, *97*, 5434.
(28) Rescli, A. *Ber.* **1927**, *60*, 1420.

"Anhydrous" Tetrabutylammonium Fluoride: A Mild but Highly Efficient Source of Nucleophilic Fluoride Ion

D. Phillip Cox,* Jacek Terpinski, and Witold Lawrynowicz

Department of Chemistry, Rutgers, The State University of New Jersey, New Brunswick, New Jersey 08903

Received February 8, 1984

A number of general and convenient reagents have been developed for the preparation of organic fluoro compounds.[1] Of the methods available, fluoride ion displacement of halides or tosylates has been widely used. However, these methods generally require high temperatures and/or long reaction times.[2-7] In the last ten years,

(1) For reviews, see: Gerstenberger, M. R. C.; Haas, A. *Angew. Chem.* **1981**, *93*, 659; *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 647. Clark, J. H. *Chem. Rev.* **1980**, *80*, 429. Sheppard, W. A.; Sharts, C. M. "Organic *Fluorine Chemistry*"; W. A. Benjamin: New York, 1969. Chambers, R. D. "Fluorine in Organic Chemistry"; Wiley-Interscience: New York, 1973. Forche, D. In Houben-Weyl, "Methoden der Organischen Chemie", Vol. 5/3, Mueller, E., Ed.; George Thieme Verlag: Stuttgart, 1962.
(2) 3-Fluoropropene (allyl fluoride) has been prepared by treatment of 3-bromopropene (allyl bromide) with KF in diethylene glycol at 140 °C (Puchnarevic, V. B.; Vcelak, J.; Voronkov, M. G.; Chvalovsky, V. *Collect. Czech. Chem. Commun.* 1974, *39*, 2616) and in 50% yield with KF in HMPT at 160 °C (Wakselman, C.; Warski, L.; Le Dren, A. *Bull. Soc. Chim. Fr.* **1969**, 334).

0022-3263/84/1949-3216$01.50/0