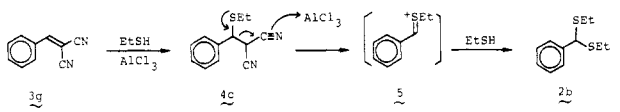
Table I. Double-Bond Cleavage of 3

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.

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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.

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

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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,

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(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).

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Table I. Reactions of Substrates with "Anhydrous" TBAF[a]

substrate	reaction time, h	temp, °C	method of preparation	fluoro compound GLC yield, %) [isolated yield,[b] %]	other products (GLC yields, %) [isolated yields, %]
CH_2=$CHCH_2Br$	0.1	25	A	CH_2=$CHCH_2F$ [85]	
$C_6H_5CH_2Br$[c]	8	25	D	$C_6H_5CH_2F$ (100) [66]	$C_6H_5CH_2OH$ (5)
$(C_6H_5)_3CCl$	6	40	B	$(C_6H_5)_3CF$ [65]	$(C_6H_5)_3COH$ [17]
$Br(CH_2)_7CH_3$	<1	25	C	$F(CH_2)_7CH_3$ (48) [35]	CH_2=$CH(CH_2)_5CH_3$ (12) $HO(CH_2)_7CH_3$ (40)
$TsO(CH_2)_7CH_3$	<1	25	C	$F(CH_2)_7CH_3$ (98) [57]	CH_2=$CH(CH_2)_5CH_3$ (trace) $HO(CH_2)_7CH_3$ (trace)
$CH_3CHBr(CH_2)_5CH_3$	<1	25	C	$CH_3CHF(CH_2)_5CH_3$ (10)	octenes [69[e]] (90)[d]
$CH_3(OTs)CH(CH_2)_5CH_3$	<1	25	C	$CH_3CHF(CH_2)_5CH_3$ (58) [52]	octenes $CH_3(OH)CH(CH_2)_5CH_3$ (32)[f] (7)
(−)-(*R*)-$CH_3(OTs)CH(CH_2)_5CH_3$	<1	25	C	(+)-$CH_3CHF(CH_2)_5CH_3$ (58) [54]	octenes $CH_3CH(OH)(CH_2)_5CH_3$ (33) (9)
C_6H_5COCl	<1	25	C	C_6H_5COF [81]	

[a] All spectral data (^1H and ^{19}F NMR, IR) of the isolated products were consistent with the assigned structures. [b] In small-scale preparations, isolated yields are underestimated. [c] The same result was obtained with benzyl chloride when carrying out the reaction for 12 h at 40 °C. [d] Only 2-octene. [e] Isolated as the dibromo compounds. [f] The ratio of 1-octene to 2-octene was 1:2.

significant improvements in methods and reagents, including the use of KF–18-crown-6 complex,[8] phase-transfer catalysis,[9,13] ion-exchange resins,[10] "spray-dried" KF,[11] and phosphorane salts[12] have allowed fluoride ion exchange more efficiently and conveniently and under milder conditions. Tetraalkylammonium fluorides have been shown to effect substitution of halides or tosylates in various solvents,[13–19] with high yields being obtained at solvent reflux temperatures[15,16,18] or with substrates activated toward nucleophilic substitution.[13,17,19]

Recently, Sharma and Fry reported an ^1H and ^{19}F NMR study of the products formed on heating commercial tetrabutylammonium fluroide (TBAF) trihydrate under high vacuum.[20] They found that on heating the salt at 77 °C, decomposition to tetrabutylammonium bifluoride, tributylamine, and 1-butene occurred. However, when the salt was warmed at 40 °C under high vacuum, almost anhydrous TBAF could be prepared. We found that this material, henceforth referred to as "anhydrous" TBAF, contained 0.1–0.3 molar equiv of water (by ^1H NMR). We had independently prepared "anhydrous" TBAF, which is an oil at room temperature, and employed it *without solvent* to prepare 3-fluoro-3-phenyldiazirine and 3-fluoro-3-phenoxydiazirine from the corresponding bromo- or chlorodiazirines.[21]

In this paper, we examine the reactivity of "anhydrous" TBAF with a range of halo- or tosyl-substituted organic compounds (containing allylic; benzylic; primary, secondary, and tertiary sp^3 or activated sp^2 carbon) (Table I). We also compare the stereochemistry of fluoride ion substitution by "anhydrous" TBAF with that found using other reagents.[12a]

From Table I, it can be seen that reaction of organohalides and tosylates with "anhydrous" TBAF gives yields of the corresponding fluoro compounds comparable to or higher than other methods of fluoride ion displacement as found in ref. 2–7. Most significantly, these yields are achieved at lower temperatures and shorter reaction times.

"Anhydrous" TBAF behaves not only as a potent source of nucleophilic fluoride but also as a potent base. Elimination of HBr is the dominant reaction on treatment of 2-bromooctane with TBAF, while elimination of HOTs is

(3) Benzyl fluoride has been prepared from benzyl bromide by a variety of methods with yields ranging from 30% to 70%. See footnote 7 of ref 8 and ref 8–12.

(4) Alkyl fluorides have been prepared in yields ranging from 20% to 50% from alkyl halides and alkyl *p*-toluenesulfonates and KF in a variety of solvents. See also footnote 8 of ref 8 and ref 8–12.

(5) 2,4-Dinitrofluorobenzene has been prepared in 92% yield by heating the corresponding chloride with KF in the absence of solvent at 190–200 °C for 7 h. The same conversion has been reported in the presence of KF–18-crown-6 complex (ref 8, yield not reported) and in 51–98% yield with KF, CsF, or RbF at 195 °C for 2 h in a variety of solvents (see footnote 11 of ref 8). See also ref 9 and 11.

(6) Benzoyl fluoride has been prepared from benzoyl chloride in 80–98% yield by a number of reagents including zinc fluoride in pyridine (Sekiya, A.; Ishikawa, N. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 1267), KF in acetonitrile with poly(ethylene glycol) (*M*, 300–600) as phase-transfer catalyst (Kitasume, T.; Ishikawa, N. *Chem. Lett.* **1978**, 183), KF–18-crown-6 (Cuomo, J.; Olofson, R. A. *J. Org. Chem.* **1979**, *44*, 1016), pyridine–HF (Olah, G. A.; Welch, J. T; Vankar, Y. D.; Nojima, M.; Kerekes, J.; Olah, J. A. *J. Org. Chem.* **1979**, *44*, 3872), (dialkylamino)sulfur trifluoride (Markovskii, L. N. Pashinnik, V. E. Synthesis **1975**, 801), and KF in the prepsence of a phase-transfer reagent (ref. 13). See also, ref 11.

(7) Fluorotriphenylmethane has been prepared from Ph_3CX (X = Cl or Br) by heating with ammonium fluoride in CH_3CN at 70 °C (Lichstein B. M.; Woolf, C. Ger. Offen. 2105907, 26 Aug 1971; *Chem. Abstr.* **1971**, *95*, 117983*n*).

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Table II. ^1H and ^{19}F NMR Spectral Data

compound	δ_H of CHF or CH_2F obsd	δ_H of CHF or CH_2F lit.	δ_F obsd	δ_F lit.	$^2J_{H-F}$, Hz obsd	$^2J_{H-F}$, Hz lit.
3-fluoropropene	4.85		−216.7	−216.0[a]	46.3	48.0[a]
fluorotriphenylmethane			−126.2	−126.7[a]		
1-fluorooctane	4.35	4.2[b]	−218.5	c	45.7 ($^3J_{H-F}$ = 23.3)	c
2-fluorooctane	4.50	4.3[b] 4.5[d]	−172.5	−165[d,e]	46.0	
benzyl fluoride	5.32	5.3[b]	−206.4	−206.3[a]	48.5	49[a]
benzoyl fluoride[f]			−17.7			

[a] Weigert, F. J. *J. Org. Chem.* **1980**, *45*, 3476. [b] Friedrich, E. C.; De Luca, G. *J. Organomet. Chem.* **1982**, *226*, 143. [c] In a, the δ_F value for 1-fluorobutane is given as −218.6 and $^2J_{H-F}$ = 48.2 and $^3J_{H-F}$ = 25.0. [d] Reference 12a. [e] In a, the δ_F value for 2-fluoropentane is −172.8. [f] IR $\nu_{C=O}$ at 1810 cm^{-1} (lit. 1810 cm^{-1}, Green, J. H. S.; Harrison, D. J. *Spectrochim. Acta* **1977**, *33A*, 583).

the dominant side reaction with 2-octyltosylate.[22] Hydrolysis of the starting halide or tosylate to the corresponding alcohol is a significantly side reaction on treatment of benzyl bromide, chlorotriphenylmethane, or 1-bromooctane with "anhydrous" TBAF. This is presumably due to the remaining traces of moisture in the reagent which are rendered highly nucleophilic by the fluoride ion. For the same reason organofluorocompounds susceptible to alkaline hydrolysis (e.g., benzyl fluoride, 3-fluoropropene) required a nonaqueous workup in order to maximize yields. Unlike other methods of fluoride ion displacements which readily yield 2,4-dinitrofluorobenzene from chloro-2,4-dinitrobenzene, reaction of "anhydrous" TBAF with the latter compound gives a stable Meisenheimer complex from which only a poor yield (ca. 5%) of 2,4-dinitrofluorobenzene was obtained.[23]

Reaction of "anhydrous" TBAF with (−)-2-octyltosylate gives (+)-2-fluorooctane in good yield (see Table I) and having an optical purity ($[\alpha]^{20}_{589}$ (neat) +14.2°)[24] higher than that previously reported for 100% (+)-2-fluorooctane ($[\alpha]^{20}_{589}$ (neat) +13.6°).[12a] The value and sign of the specific rotation indicates that this reaction proceeds cleanly via an S_N2 mechanism.

Experimental Section

General Methods. Proton NMR spectra were normally recorded with a Varian T-60 spectrometer; chemical shifts are given in δ units, downfield from internal Me_4Si, and were determined in CCl_4 solution, or CCl_4 with added acetone-d_6, where the compound was insoluble in pure CCl_4. ^{19}F NMR spectra were recorded on a Varian CFT-20 spectrometer at 74.844 MHz in $CDCl_3$; chemical shifts are given in δ units downfield from internal $CFCl_3$. Analytical GLC was performed on a Varian Model 3700 gas chromatograph equipped with a Varian 4270 integrator and a 50-ft 10% SE-30 capillary column. High-pressure liquid chromatography was performed on a Waters Associates instrument equipped with a C-18 reversed-phase column. The eluent was CH_3CN at a flow rate of 1 mL/min. The optical rotations were determined at 20 °C in a thermostated 1-dm cell on a Perkin-Elmer Model 141 spectropolarimeter.

Chlorotriphenylmethane, chloro-2,4-dinitrobenzene, 3-bromopropene, benzyl bromide, 1- and 2-bromooctane, and benzoyl chloride were obtained from Aldrich and were used as received. 1- and (±)-2- and (−)-2-octanol tosylates were prepared from the corresponding octanols (Aldrich) by Streitweiser's procedure.[26]

Details of the preparations of some representative fluoro compounds are outlined below. All relevant spectral data (^1H and ^{19}F NMR, IR) of the products are collected in Table II.

"Anhydrous" TBAF. TBAF·$3H_2O$ (Aldrich) was heated in a round-bottomed flask with magnetic stirring at 40–45 °C under high vacuum (<0.1 mmHg). After several hours, the sample liquified. Heating was continued until the sample lost 20% of its original weight (usually ca. 48 h). The resulting "anhydrous" TBAF contained 0.1–0.3 molar equiv of water (by ^1H NMR) and ca. 10% of tetrabutylammonium bifluoride (by comparison of the doublet at δ −146 [J = 123 Hz] to the singlet at δ −99 [TBAF] in the ^{19}F NMR spectrum). This oil must be used immediately.

3-Fluoropropene (Method A). 3-Bromopropene (400 mg, 3.3 mmol) was added to "anhydrous" TBAF (ca. 10 mmol) at room temperature with stirring. The reaction was complete in 2–5 min (as judged by the formation of solid tetrabutylammonium bromide). The flask was then warmed to 45 °C to liquefy the reaction mixture, and the product was collected in a weighed gas trap by entrainment in a stream of dry nitrogen. The yield of pure 3-fluoropropene was 170 mg (85%).

Fluorotriphenylmethane (Method B). Chlorotriphenylmethane (930 mg, 3.3 mmol) was added to "anhydrous" TBAF (ca. 10 mmol) and stirred for 6 h at 40 °C under nitrogen. Ice water (15 mL) was added and the products were collected by suction filtration. After drying under high vacuum for 16 h, the crude solid was crystallized from hexane. The first crop of crystals (after standing for 24 h) was triphenylmethanol, 150 mg (17%), mp 162–164 °C. The second crop of crystals (after standing for 48–72 h) was fluorotriphenylmethane, 420 mg (48%), mp 102–104 °C (lit.[27] mp 103–104 °C). Evaporation of the mother liquor gave further impure fluorotriphenylmethane, 150 mg (17%), mp 94–96 °C.

(+)-2-Fluorooctane (Method C). (−)-2-Octanol tosylate (8.46 g, 30 mmol, α_D^{20} −7.78°: prepared from (−)-2-octanol α_D^{20} −8.00°) (ratio of rotation of tosylate:rotation of alcohol = 0.975, lit.[24] 0.98) was added to "anhydrous" TBAF (prepared from 18.9 g [60 mmol] of TBAF·$3H_2O$), and the mixture was stirred for 1 h. Water (50 mL) was added and the organic fraction was extracted with pentane (10 mL and then 4 × 5 mL). The pentane extracts were combined, washed with $CaCl_2$ solution, and then treated with bromine dropwise until the orange color remained. The excess bromine was removed by washing with 1 M aqueous thiosulfate, and the solution was dried with $MgSO_4$. The pentane was removed by distillation on a spinning-band column. The (+)-2-fluorooctane was collected by distillation under high vacuum into a gas trap held at −78 °C. The product (2.09 g, 54%) was >96% pure, the main impurity being 2-octanol (ca 2%). Final purification was achieved by distillation on a microspinning-band column (>99% pure by GLC); observed rotation, α +11.516°.

Benzyl Fluoride (Method D). Benzyl bromide (4.92 g, 29 mmol) was added to "anhydrous" TBAF (prepared from 11.525 g [36.6 mmol] of TBAF·$3H_2O$). A highly exothermic reaction ensued, warming the reaction mixture to 60 °C. After being stirred

(22) The observed influence of the leaving group on the direction of elimination caused by TBAF (1-alkene vs. 2-alkene, see Table I) is different from that reported by Ono (Ono, N. *Bull. Chem. Soc. Jpn.* **1971**, 44, 1369). He observed no effect on the 1-alkene/2-alkene ratio. The increase of this ratio observed upon changing Br for OTs is rather similar to the behavior observed when *t*-BuO$^-$ was used as base (Bartsch, R. A. *J. Org. Chem.* **1970**, *35*, 1336).

(23) This Meisenheimer complex is under further investigation in our laboratory and in the laboratory of Dr. J. H. Clark of York University, England. We thank Dr. Clark for helpful discussions on this topic.

(24) Calculated from the observed rotation by using the density of 1-fluorooctane in ref 25.

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for a further 8 h at 25 °C, the reaction mixture was triturated with dry pentane (5 × 25 mL). The pentane extracts were combined, and the solvent was removed by distillation on a spinning-band column. The resulting benzyl fluoride was distilled under reduced pressure in a Kugelrohr apparatus to yield 2.07 g (66%) of pure product.

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Registry No. TBAF, 429-41-4; CH_2=$CHCH_2Br$, 106-95-6; $C_6H_5CH_2Br$, 100-39-0; $(C_6H_5)_3CCl$, 76-83-5; $Br(CH_2)_7CH_3$, 111-83-1; $TsO(CH_2)_7CH_3$, 3386-35-4; $CH_3CHBr(CH_2)_5CH_3$, 557-35-7; $CH_3CH(OTs)(CH_2)_5CH_3$, 1028-12-2; (-)-(*R*)-$CH_3CH(OTs)(CH_2)_5CH_3$, 27770-99-6; C_6H_5COCl, 98-88-4; CH_2=$CHCH_2F$, 818-92-8; $C_6H_5CH_2F$, 350-50-5; $(C_6H_5)_3CF$, 427-36-1; $F(CH_2)_7CH_3$, 463-11-6; $CH_3CHF(CH_2)_5CH_3$, 407-95-4; (+)-$CH_3CHF(CH_2)_5CH_3$, 56772-74-8; C_6H_5COF, 455-32-3.

Ring Opening of Epoxides with Morpholine–Borane

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The reductive ring opening of epoxides by borane is often both slow and complex.[1,2] However, Brown and co-workers have found the reaction to be accelerated by sodium and lithium borohydrides or by boron trifluoride etherate.[2,3] In the borohydride-catalyzed reduction of 1-methylcyclohexene oxide, the products were reported to be 74% *cis*-2-methylcyclohexanol and 26% 1-methylcyclohexanol.[3] In related examples the preferance for forming the less highly substituted alcohol was regularly evidenced.

The boron trifluoride catalyst also leads to the less substituted alcohol as the major product.[2] However, only epoxides substituted with one or more phenyl groups were reported to open with this Lewis acid catalyst. In contrast to the result reported above, 1-phenylcyclohexene oxide yields primarily *trans*-2-phenylcyclohexanol (82%) along with 18% of the cis isomer. It was conjectured that the function of the catalyst was to promote the rearrangement of the epoxide; the resulting carbonyl functional group then being reduced by the borane.

In the work described above, the solvent used was tetrahydrofuran, and borane was added in the form of its stable THF complex. However, this solvent system offers a practical difficulty in preparative applications in that THF forms an intractable polymer in the presence of boron trifluoride. In order to overcome the problem of product isolation posed by the polymer formation, it was decided to explore the utilization of other borane sources in solvent systems other than THF. In the course of this work it became evident that a number of exceptions existed to the previously published limitation of mandatory aryl substitution in the boron trifluoride catalyzed reaction. These results are reported here.

Results and Discussion

It has been known for some years that amine–borane complexes have the capability of reducing carbonyl compounds.[4] Consequently, it was desided to essay the epoxide reduction by using the morpholine–borane complex as a point of departure. When an ether solution of styrene oxide and an equivalent of morpholine–borane were treated at room temperature with an equivalent of boron trifluoride etherate, a quantitative yield of 2-phenylethanol was observed. Since only small amounts of material were being used in this study, no attempt was made to determine the stoichiometric requirements of the reaction. This result parallels the observations of Brown and Moon[2] with regard to the course of the reaction but avoids the undesireable formation of the THF polymer.

Subsequently, the same conditions were applied to the ring-opening of 1-methylcyclohexene oxide. The reaction product was analyzed by both C-13 and proton NMR. In contrast to the report for 1-phenylcyclohexene oxide above, the major product in this instance was the cis isomer of 2-methylcyclohexanol (84%). The minor product was 1-methylcyclohexanol (16%).

In this instance it was possible to test the hypothesis that rearrangement of the epoxide to the ketone precedes the reduction step. It was found, not unexpectedly, that boron trifluoride does cause such a rearrangement of the epoxide. The reduction of 2-methylcyclohexanone with borane in THF gave a mixture comprised of 83% *trans*-2-methylcyclohexanol along with 17% of the cis isomer. The same result was obtained in ether solutions of morpholine–borane and with morpholine–borane plus boron trifluoride. The fact that each of these various forms of borane leads mainly to the trans isomer while the epoxide reduction yields primarily the cis isomer rules out the prior rearrangement of the epoxide in this case.

As a comparison to the above result, the reduction of the epoxide from 2-ethyl-1-hexene was also carried out. The yield of crude product was 92%, and NMR analysis indicated that only 2-ethyl-1-hexanol was formed.

In contrast to the results above, the application of the above reduction to 2,3-epoxypropyl *p*-methoxyphenyl ether and to epichlorohydrin, respectively, led to the formation of the appropriate secondary alcohols, 1-(*p*-methoxyphenoxy)-2-propanol and 1-chloro-2-propanol. The latter was isolated only in 80% yield due to its water solubility.

Four cases were found in which reduction did not follow the desired course. The reduction of norbornene epoxide gave a very complex mixture in which neither the exo nor endo norbornol were evident. The ^{13}C NMR of this product suggested that the morpholine had become involved in the reduction process. It is also true that this very reactive epoxide polymerizes when reacted with boron trifluoride. Consequently, the matter was not further pursued. The epoxide from 1-butene also gave a complex mixture of products. There was a suggestion of 2-butanol in the proton NMR, but only products of low volatility were present. Since a green flame was produced on combustion, it seems likely that borate esters were produced. At the other extreme, the reduction of the syn epoxide of 5,8-diacetoxy-1,4-dihydro-1,4-ethanonaphthalene[5] was

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