of the C_α–C_β bond. Put another way, in cyclic systems the intramolecular oxidative addition becomes a strained bicyclic process. The results for alkylation of 3-OH with MeLi (~55% syn and 45% anti γ-alkylation) indicate that both routes are involved in this case.

There is a discrepancy in our mechanistic proposals that evidently results from oversimplification.[11] Both intramolecular (eq 3) and intermolecular oxidative additions (Scheme V) are thought to give S_N2' (σ-allyl)copper(III) complexes exclusively. However, the intermediates derived by the two routes show different behavior and clearly differ in some unknown way. The complex involved in the cyclic process gives γ-alkylation product only.[5] In this case there is no evidence for isomerization to the (π-allyl)copper(III) complex (9). On the other hand, when the σ-allyl complex results from the intermolecular route, reductive elimination is accompanied by varying amounts (depending on the type of nontransferred ligand[1,3,8]) of isomerization to the π-allyl complex, which results in loss of regiochemistry. The difference in the σ-allyl complexes may be a matter of differences in aggregation or configuration of square-planar copper(III) complexes.

Experimental Section

Materials. (*S*)-(−)-α-Methyl-γ-phenylallyl alcohol (3-OH),[5] mp 57–59 °C, $[\alpha]^{30}_D$ −30.9° (*c* 5.2, $CHCl_3$) (88% ee), and (*N*-methyl-*N*-phenylamino)tri-*n*-butylphosphonium iodide[3] were prepared as reported earlier. Cuprous iodide was purified and solutions of methyllithium in ether and *n*-butyllithium in hexane were standardized by methods that have been described.[6] Authentic samples of alkylation products in Schemes II and IV and GC and spectral properties of these were available from an earlier study.[6]

Alkylation of (*S*)-(−)-3-OH with *n*-Butyllithium. In the experiment outlined in Scheme II, a stirred solution of 580 mg (3.9 mmol) of the above (*S*)-(−)-3-OH in 10 mL of dry THF at −40 °C was treated with 3.9 mmol of *n*-BuLi in 2.36 mL of hexane. The resulting lithium alkoxide solution was chilled to −78 °C and added (cannula) to a suspension of 746 mg (3.9 mmol) of CuI in 10 mL of dry THF which in turn was prepared in a nitrogen-flushed 100-mL flask equipped with a stirrer and septum. The mixture was stirred for 2.5 h at ca. −20 °C, the resulting homogeneous yellow solution was chilled to −78 °C, and 3.9 mmol of *n*-BuLi in hexane was added (this is step 3 in eq 1). After 10 min, 1.70 g (3.9 mmol) of (*N*-methyl-*N*-phenylamino)tributylphosphonium iodide in 16 mL of dry DMF was added. The resulting brown solution was stirred for 2.5 h at −20 °C and 3 h at room temperature after which the reaction was quenched with 20 mL of saturated aqueous NH_4Cl. The organic layer was separated and the remainder was extracted with ether. The extracts were combined, dried ($MgSO_4$), and concentrated by fractional distillation (Vigreux column). Vacuum distillation of the residue gave 0.57 g (78%) of clear colorless oil, bp 80–83 °C (1.4 mm). The composition of this product was determined by capillary GC (94 ft, UCON LB 550X, 130 °C and 299 ft, QF-1, 130 °C),[6] and components were identified by comparison of retention times with those for authentic samples.[6]

Diimide reduction of 0.50 g of the above product[5] gave 0.48 g (95%) of a colorless oil, bp 68–70 °C (1.5 mm). Spectral properties and capillary GC showed this to be mainly 4-phenyloctane (5). Purification by preparative GC (10 ft × $^3/_8$ in., 30% UCON on Chromosorb P, 130 °C) gave a pure sample of 5 that had the same IR and NMR spectral properties and GC retention time as those for an authentic sample of *dl*-5.[5] This sample of 5 had $[\alpha]^{25}_D$ −2.05° (*c* 5.91, *n*-hexane), which corresponds to 24% ee.[5]

Alkylation of (*S*)-(−)-3-OH with Methyllithium. The procedure for the experiment outlined in Scheme IV was the same as that above except that *n*-BuLi was replaced by MeLi in step 3. The alkylation product, bp 67–69 °C (8.8 mm), was isolated in 63% yield. The composition was determined by capillary GC (94 ft, UCON LB 550X, 80 °C and 196 ft, UCON LB 550X, 80 °C), and components were identified by comparison of retention times with those for authentic samples.[6]

Diimide reduction[5] of 0.27 g of the above product gave 0.23 g (84%) of 2-phenylpentane (7) contaminated with ~3% 3-methyl-1-phenylbutane. Purification by preparative GC (10 ft × $^3/_8$ in., 30% UCON on Chromosorb P, 65 °C) gave a homogeneous sample of 7 that had the same spectral properties (IR, NMR) and retention time as those for an authentic sample of *dl*-7.[5] This sample had $[\alpha]^{20}_D$ 0.49° (*c* 3.51, *n*-hexane), which corresponds to 2.5% ee[5].

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A Synthesis of 2-Fluoro-2-alkenes[1]

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A three-step method for the synthesis of 2-fluoro-2-alkenes from the parent methyl ketones has been developed. The yields of the sequence are fair, and no contamination of the products by the isomeric 2-fluoro-1-alkenes can be detected.

The reactivity of vinylic fluorides is a relatively unexplored area in organic synthesis. It has been clearly recognized that the substitution of a fluorine atom for a hydrogen atom can dramatically affect the physiological fate of biologically active molecules.[3] However, there has been limited exploration of the synthetic utility of selectively fluorinated molecules. Recent reports have shown vinylic fluorides to be highly regioselective in their reactions with electrophiles.[4–7] In particular, vinylic fluorides are more

(1) In memory of Professor Guido H. Daub, University of New Mexico, 1920–1984.
(2) Camille and Henry Dreyfus Teacher-Scholar, 1982–1987.
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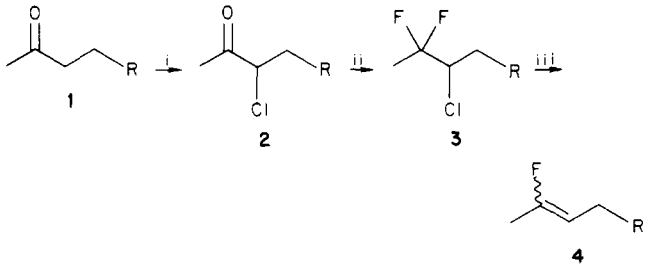
0022-3263/85/1950-1599$01.50/0

Table I

ketone	% yield of 2	% yield of 3	% yield of 4 in reduction[a]			
			Zn/Cu couple	Zn/Ag couple	Zn/Cu couple $BrCH_2CH_2Br$	$Mg/BrCH_2CH_2Br$
1a, R = C_6H_5	72	83	60	64	58	77 (55)
1b, R = $(CH_2)_2CO_2Me$	40	75	20	48	44	sluggish
1c, R = CH_2CO_2Et	57	64	87		40	sluggish
1d, R = CH_2CO_2Me	51	44			44	

[a] All Zn/Cu and Zn/Ag couple reactions were performed in dimethylformamide at 95 °C. Mg reduction was run in tetrahydrofuran or ether (ether yield in parenthesis) at 25 °C.

Scheme I



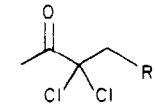
(i) $CuCl_2 \cdot 2H_2O$, LiCl, DMF, 50 °C, 48 h; (ii) $(Et)_2NSF_3$, CH_2Cl_2, 25 °C, 96 h; (iii) Zn/Cu or Zn/Ag couple, DMF, 95 °C.

nucleophilic than trisubstituted olefins[5] and electrophiles attack β to the fluorine to generate a carbocation intermediate that is stabilized by back-bonding with the fluorine atom.[8]

A number of approaches to the vinylic fluoride moiety have been developed. They involve (1) the elimination of the elements of HF from a difluoro compound with alumina,[9] (2) the reductive elimination of fluoride and halide from an α-halo *gem*-difluoride with a metal reducing agent,[10-13] (c) the ring opening of *gem*-chlorofluorocyclopropanes,[14] (d) the condensation reactions of aldehydes and ketones with fluorinated nucleophiles,[15,16] and (e) the photochemical ring cleavage of 2-fluoro-2-methylcyclopentanone.[6] This note describes the regiospecific synthesis of 2-fluoro-2-alkenes from the parent methyl ketones by a three-step sequence that proceeds in modest overall yield.

Our approach (Scheme I) focused on the preparation and reductive elimination of a 3-chloro-2,2-difluoroalkyl moiety (**3**) to give the desired 2-fluoro-2-alkene (**4**).[10-13] The results of this effort are summarized in Table I.

Chlorination[17] of a methyl ketone ($CuCl_2 \cdot 2H_2O$, LiCl, DMF, 50 °C) afforded the desired 3-chloro-2-alkanone (**2**)[18] contaminated by small amounts of the 3,3-dichloro-2-alkanone (**5**). The bis-chlorinated material was easily removed by chromatography on silica gel.



5a, R = C_6H_5
b, R = $(CH_2)_2CO_2Me$
c, R = CH_2CO_2Et
d, R = CH_2CO_2Me

Geminal fluorination was accomplished according to established methods using (diethylamino)sulfur trifluoride[19] in dichloromethane. The process proved unremarkable, although chromatography on silica gel was again required to isolate the desired α-chloro *gem*-difluoride **3a-d**[20] from the dark brown reaction mixture.

The vicinal reduction of the α-chloro *gem*-difluorides (**3a-d**) proved to be less straightforward. A variety of reaction conditions left chloro difluoride **3c** unchanged, including zinc under ethanol reflux,[12] zinc under acetic acid reflux,[11] acid-washed zinc under ethanol reflux, and zinc amalgam in hot dimethylformamide (95 °C). Compounds **3a-d** were successfully reduced with either zinc/copper[21] or zinc/silver couple[22] in dimethylformamide at 95 °C (~4 days) to afford the corresponding vinylic fluorides **4a-d**.[18] The *E*/*Z* isomer ratios were insensitive to the reducing agent.

Reductions of chloro difluorides **3a-d** with zinc/copper couple entrained with 1,2-dibromoethane in hot dimethylformamide proceeded somewhat faster, although the yields proved comparable to those obtained without entrainment. The use of more reactive metal reducing agents offered no real improvement either. While magnesium metal[10] entrained with 1,2-dibromoethane in tetrahydrofuran smoothly reduced chloro difluoride **3a** in 77% yield at ambient temperature (55% yield in ether), the reaction proved sluggish for substrates containing an ester group (**3b** and **3c**). Lithium or calcium metal in liquid ammonia rapidly overreduced the chloro-difluorides, apparently to the olefin.[23] Thus, it would appear that the

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vicinal reduction step is best accomplished by use of a zinc/copper couple or a zinc/silver couple for the most general case.

These results demonstrate that the three step sequence described in Scheme I provides a regiospecific route to 2-fluoro-2-alkenes (4) from the corresponding methyl ketones 1 in modest overall yield (10–46%).

Experimental Section

General Data. Infrared spectra were determined on a Perkin-Elmer 1330 grating spectrophotometer. ^1H NMR spectra were determined at 60.00 MHz in $CDCl_3$, using a Varian EM 360L NMR spectrometer and are reported in parts per million (δ) relative to tetramethylsilane. ^{19}F NMR spectra were determined at 56.45 MHz in $CDCl_3/CFCl_3$, using a Varian EM 360L NMR spectrometer equipped with a fluorine probe and are reported in parts per million (δ) upfield relative to $CFCl_3$. Mass spectrometry was performed on a Finnigan 3200 GC/MS system. Combustion microanalyses were kindly done by Ms. Ruby Ju, Department of Chemistry, The University of New Mexico. (Diethylamino)sulfur trifluoride[24] was used without purification. The phrase "worked up in the usual fashion" means that the reaction mixture was diluted with water and extracted with ether, and the combined organic phases were washed with 10% $NaHCO_3$ and brine and dried over $MgSO_4$.

General Procedure for α-Chlorination of Ketones. A ketone (1, 50 mmol), LiCl (62.5 mmol), and $CuCl_2 \cdot 2H_2O$ (125 mmol) were dissolved in dimethylformamide (80 mL) and were heated to 50 °C for 48 h. The reaction was worked up in the usual fashion and the solvent removed under reduced pressure to give a yellow oil containing three components by TLC: the bischlorinated ketone (~10%), the desired monochlorinated ketone (~60%), and the starting ketone (~30%). Chromatography on silica gel afforded the desired chloroketone.

3-Chloro-4-phenyl-2-butanone (2a). Chlorination of **1a** afforded 3-chloro-4-phenyl-2-butanone (**2a**) in 58% yield and 3,3-dichloro-4-phenyl-2-butanone (**5a**) in 13% yield. **2a**: IR (λ_{max}^{film}) 3060, 3030, 2920, 1720, 1600, 1490, 1450, 1425, 1350, 1270, 1230, 1210, 1150, 1075, 1020, 930, 825, 750, 700 cm^{-1}. ^1H NMR ($CDCl_3$) δ 2.27 (s, 3 H), 3.00 (d of d, 1 H, J = 8, 14 Hz), 3.33 (d of d, 1 H, J = 6, 14 Hz), 4.37 (d of d, 1 H, J = 6, 8 Hz), 7.27 (s, 5 H); mass spectrum, m/e (relative intensity) 184/182 (M^+), 148/146 (100), 147/145, 103, 91, 77. Anal. Calcd for $C_{10}H_{11}ClO$: C, 65.76; H, 6.07. Found: C, 65.55; H, 5.98.

Methyl 5-Chloro-6-oxoheptanoate (2b). Chlorination of **1b**[25] afforded methyl 5-chloro-6-oxoheptanoate (**2b**) in 40% yield and methyl 5,5-dichloro-6-oxoheptanoate (**5b**) in 10% yield. **2b**: IR (ν_{max}^{film}) 2960, 1740, 1440, 1360, 1200, 1080, 1000, 980, 880, 850, 800 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.9 (m, 4 H), 2.1–2.4 (m, 5 H) including 2.31 (s), 3.65 (s, 3 H), 4.25 (d of d, 1 H, J = 6, 8 Hz); mass spectrum, m/e (relative intensity) 194/192 (M^+), 163, 162, 161, 160, 152, 150, 125, 120, 118, 87 (100). Anal. Calcd for $C_8H_{13}ClO_3$: C, 49.88; H, 6.80. Found: C, 50.03; H, 6.79.

Ethyl 4-Chloro-5-oxohexanoate (2c). Chlorination of **1c**[26] afforded ethyl 4-chloro-5-oxohexanoate (**2c**) in 57% yield and ethyl 4,4-dichloro-5-oxohexanoate (**5c**) in 10% yield. **2c**: IR (ν_{max}^{film}) 2980, 2940, 1720, 1430, 1370, 1360, 1300, 1250, 1200, 1090, 1020, 950, 850, 820, 800 cm^{-1}; H NMR ($CDCl_3$) δ 1.25 (t, 3 H, J = 8 Hz), 2.0–2.7 (m, 7 H) including 2.33 (s), 4.10 (q, 2 H, J = 8 Hz), 4.37 (d of d, 1 H, J = 6, 8 Hz); mass spectrum, m/e (relative intensity) 194/192 (M^+), 151, 149, 148, 147, 146, 145, 121, 119, 88 (100). Anal. Calcd for $C_8H_{13}ClO_3$: C, 49.88; H, 6.80. Found: C, 50.05; H, 6.75.

Methyl 4-Chloro-5-oxohexanoate (2d). Chlorination of **1d** afforded methyl 4-chloro-5-oxohexanoate (**2d**) in 51% yield and methyl 4,4-dichloro-5-oxohexanoate (**5d**) in 18% yield. **2d**: IR (ν_{max}^{film}) 2960, 1730, 1440, 1360, 1300, 1260, 1220, 1200, 1080, 1000, 890, 840, 800 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.00–2.70 (m, 7 H) including 2.33 (s), 3.68 (s, 3 H), 4.34 (d of d, 1 H, J = 6, 8 Hz); mass spectrum, m/e (relative intensity) 180/178 (M^+), 149, 148, 147, 146 (100), 138, 136, 121, 119. Anal. Calcd for $C_7H_{11}ClO_3$: C, 47.07; H, 6.21. Found: C, 47.13; H, 6.16.

General Procedure for Bis-Fluorination of α-Chloro Ketones. An α-chloro ketone (**2**, 10 mmol) was dissolved in anhydrous dichloromethane (5 mL) in an oven-dried flask under dry N_2. This solution was cooled to 0 °C and (diethylamino)sulfur trifluoride[25] (15 mmol, 1.5 equiv) was added via syringe over a 1-min period. The reaction mixture was allowed to warm to room temperature and stir for 96 h. The reaction was worked up in the usual fashion (water quench at 0 °C), and the solvent was removed under reduced pressure to give a brown oil containing at least five components by TLC, only one of which could be characterized. Chromatography on silica gel yielded the desired α-chloro *gem*-difluoride.

2-Chloro-3,3-difluoro-1-phenylbutane (3a). Fluorination of **2a** afforded 2-chloro-3,3-difluoro-1-phenylbutane (**3a**) in 83% yield. **3a**: IR (ν_{max}^{film}) 3080, 3040, 2950, 1900, 1875, 1810, 1670, 1600, 1500, 1450, 1400, 1360, 1200, 1080, 1040, 930, 850, 750, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.73 (t, 3 H, $J[CH_3,F]$ = 18 Hz), 2.70 (d of d, 1 H, J = 11, 15 Hz), 3.37 (d of d, 1 H, J = 4, 15 Hz), 3.7–4.3 (m, 1 H), 7.30 (s, 5 H); ^{19}F NMR ($CDCl_3/CFCl_3$) $\delta(F_1)$ –93.5, $\delta(F_2)$ –104.4, $J[CH_3,F_1] = J[CH_3,F_2]$ = 18.0 Hz, $J[H,F_1]$ = 5.2 Hz, $J[H,F_2]$ = 14.0 Hz, $J[F_1,F_2]$ = 257 Hz; mass spectrum, m/e (relative intensity) 206/204 (M^+), 109, 103, 92, 91 (100), 77.

Methyl 5-Chloro-6,6-difluoroheptanoate (3b). Fluorination of **2b** afforded methyl 5-chloro-6,6-difluoroheptanoate (**3b**) in 75% yield. **3b**: IR (ν_{max}^{film}) 3010, 2960, 1740, 1670, 1440, 1390, 1370, 1200, 1080, 930, 870, 820, 760, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.4–2.0 (m, 7 H) including 1.70 (t, $J[CH_3,F]$ = 18 Hz), 2.1–2.5 (m, 2 H), 3.73 (s, 3 H), 3.7–4.5 (m, 1 H); ^{19}F NMR ($CDCl_3/CFCl_3$) $\delta(F_1)$ –94.1, $\delta(F_2)$ –103.9, $J[CH_3,F_1] = J[CH_3,F_2]$ = 18.4 Hz, $J[H,F_1]$ = 8.0 Hz, $J[H,F_2]$ = 11.2 Hz, $J[F_1,F_2]$ = 260 Hz; mass spectrum, m/e (relative intensity) 216/214 (M^+), 183, 159, 101, 99 (100).

Ethyl 4-Chloro-5,5-difluorohexanoate (3c). Fluorination of **2c** afforded ethyl 4-chloro-5,5-difluorohexanoate (**3c**) in 64% yield. **3c**: IR (ν_{max}^{film}) 3000, 1740, 1450, 1400, 1380, 1360, 1200, 1040, 930, 860, 830, 740, 680 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.25 (t, 3 H, J = 8 Hz), 1.73 (t, 3 H, $J[CH_3,F]$ = 19 Hz), 2.0–3.7 (m, 4 H), 3.93 (m, 1 H), 4.17 (q, 2 H, J = 8 Hz); ^{19}F NMR ($CDCl_3/CFCl_3$) $\delta(F_1)$ –94, $\delta(F_2)$ –101, $J[CH_3,F_1] = J[CH_3,F_2]$ = 20.0 Hz, $J[H,F_1]$ = 8.0 Hz, $J[H,F_2]$ = 12.0 Hz, $J[F_1,F_2]$ = 255 Hz; mass spectrum, m/e (relative intensity) 216/214 (M^+), 196, 194, 189, 187, 171, 169 (100), 159.

Methyl 4-Chloro-5,5-difluorohexanoate (3d). Fluorination of **2d** afforded methyl 4-chloro-5,5-difluorohexanoate (**3d**) in 44% yield. **3d**: IR (ν_{max}^{film}) 3000, 2950, 1730, 1430, 1375, 1350, 1310, 1200, 1020, 1190, 920, 870, 840, 820 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.75 (t, 3 H, $J[CH_3,F]$ = 18 Hz), 2.0–3.7 (m, 4 H), 3.73 (s, 3 H), 3.8–4.3 (m, 1 H); ^{19}F NMR ($CDCl_3/CFCl_3$) $\delta(F_1)$ –94.4, $\delta(F_2)$ –102.0, $J[CH_3,F_1] = J[CH_3,F_2]$ = 20.0 Hz, $J[H,F_1]$ = 8.0 Hz, $J[H,F_2]$ = 12.0 Hz, $J[F_1,F_2]$ = 259 Hz; mass spectrum, m/e (relative intensity) 202/200 (M^+), 182/180, 171, 169, 145, 74, 65 (100).

Vicinal Reductions of α-Chloro *gem*-Difluorides. Method 1. Freshly prepared Zn/Cu couple[21] (4.8 g) was added to a rapidly stirring solution of α-chloro *gem*-difluoride (**3**, 5.0 mmol) in dimethylformamide (19 mL). The resulting slurry was heated to 95 °C under a reflux condenser. Additional Zn/Cu couple (2.4 g) was added every 24 h until the reaction was judged complete (GLC, 72 h). The reaction was worked up in the usual fashion, and the solvent was removed under reduced pressure to give a yellow oil. Chromatography on silica gel gave the desired vinylic fluoride as a mixture of *E* and *Z* isomers.

Method 2. The same as method 1 except that freshly prepared Zn/Ag couple[22] was used.

Method 3. The same as method 1 except that 10 drops of 1,2-dibromomethane were added at the beginning of the reaction and 10 additional drops of 1,2-dibromoethane were added with each addition of Zn/Cu couple.

Method 4. An oven-dried 10-mL round-bottom flask was charged with a solution of α-chloro *gem*-difluoride (**3**, 2.0 mmol) in anhydrous tetrahydrofuran or ether (4 mL). Magnesium turnings (20 mmol) and five drops of 1,2-dibromoethane were

(23) Reduction of methyl 5-chloro-6,6-difluoroheptanoate (**3c**) with Li or $Ca/NH_3(l)$ gave 5-hepten-1-ol by GC/MS.

(24) We wish to thank Dr. G. A. Boswell, Jr. (Du Pont), and Dr. T. H. Morton (University of California, Riverside) for helpful discussions and generous gifts of (diethylamino)sulfur trifluoride.

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added at 25 °C, and a visible reaction ensued. Two additional drops of 1,2-dibromoethane were added every 10 min until the reaction was judged complete (GLC, 4 h). The reaction was worked up in the usual fashion, and the solvent was removed under reduced pressure to give a yellow oil. Chromatography on silica gel gave the desired vinylic fluoride as a mixture of *E* and *Z* isomers.

(*E*)- and (*Z*)-3-Fluoro-1-phenyl-2-butene (4a). Reduction of **3a** afforded a 35:65 mixture of the *E* and *Z* isomers of 3-fluoro-1-phenyl-2-butene (**4a**) in yields of 60% (method 1), 64% (method 2), 58% (method 3), and 77% (method 4). **4a**: IR (ν_{max}^{film}) 3040, 2910, 1700, 1600, 1490, 1430, 1380, 1310, 1270, 1210, 1140, 1080, 1060, 1020, 985, 925, 850, 790, 730, 690 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.87 (d of m, 3 H, $J[CH_3,F]$ = 18 Hz), 3.23/3.35 (d/d, 2 H, J = 8 Hz; *E* and *Z* isomers), 4.7–5.2 (1 H; *Z* isomer: d of t at δ 4.65, J_t = 8 Hz, J[H,F] = 37 Hz, *E* isomer: d of t at δ 5.17, J_t = 8 Hz, J[H,F] = 21 Hz), 7.23 (s, 5 H); ^{19}F NMR ($CDCl_3/CFCl_3$) $\delta(E)$ −94.2 (d of q, $J[CH_3,F]$ = 18 Hz and J[H,F] = 24 Hz), $\delta(Z)$ −104.8 (d of q, $J[CH_3,F]$ = 18 Hz, and J[H,F] = 44 Hz); mass spectrum, *m/e* (relative intensity) 150 (M^+), 135 (100) 129, 115, 91, 78, 77. Anal. Calcd for $C_{10}H_{11}F$: C, 79.97; H, 7.38. Found: C, 80.12; H, 7.14.

(*E*)- and (*Z*)-Methyl 6-Fluoro-5-heptenoate (4b). Reduction of **3b** afforded a 55:45 mixture of the *E* and *Z* isomers of methyl 6-fluoro-5-heptenoate (**4b**) in yields of 20% (method 1), 48% (method 2), and 44% (method 3). The reduction of **3b** according to method 4 never proceeded to completion. **4b**: IR (ν_{max}^{film}) 3000, 1720, 1440, 1350, 1160, 1080, 1030, 990, 910, 850, 730 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.5–2.5 (m, 9 H) including 1.83 (d, $J[CH_3,F]$ = 18 Hz), 3.63 (s, 3 H), 4.0–5.2 (1 H; *Z* isomer: d of t at δ 4.40, J_t = 7 Hz, J[H,F] = 39 Hz; *E* isomer: d of t at δ 4.90, J_t = 7 Hz, J[H,F] = 23 Hz); ^{19}F NMR ($CDCl_3/CFCl_3$) $\delta(E)$ −99.5 (d of q, $J[CH_3,F]$ = 20 Hz and J[H,F] = 24 Hz), $\delta(Z)$ −107.9 (d of q, $J[CH_3,F]$ = 20 Hz and J[H,F] = 44 Hz); mass spectrum, *m/e* (relative intensity) 150 (M^+), 135 (100), 129, 115, 91, 78, 77. Anal. Calcd for $C_8H_{13}FO_2$: C, 59.98; H, 8.18. Found: C, 60.00; H, 8.01.

Ethyl 5-Fluoro-4-hexenoate (4c). Reduction of **3c** afforded a 57:43 mixture of the *E* and *Z* isomers of ethyl 5-fluoro-4-hexenoate (**4c**) in yields of 87% (method 1) and 40% (method 3). The reduction of **3c** according to method 4 never proceeded to completion. **4c**: IR (ν_{max}^{film}) 3000, 1740, 1700 (shoulder), 1450, 1390, 1375, 1350, 1300, 1250, 1190, 1140, 1100, 1040, 1020, 860 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.25 (t, 3 H, J = 7 Hz), 1.87 (d, $J[CH_3,F]$ = 18 Hz), 2.33 (s, 4 H), 4.13 (q, 2 H, J = 7 Hz), 4.3–5.2 (1 H; *Z* isomer: d of t at δ 4.50, J_t = 8 Hz, J[H,F] = 40 Hz; *E* isomer: d of t at δ 5.00, J_t = 8 Hz, J[H,F] = 20 Hz); ^{19}F NMR ($CDCl_3/CFCl_3$) $\delta(E)$ −94 (d of q, $J[CH_3,F]$ = 18 Hz and J[H,F] = 22 Hz), $\delta(Z)$ −102 (d of q, $J[CH_3,F]$ = 18 Hz and J[H,F] = 38 Hz); mass spectrum, *m/e* (relative intensity) 160 (M^+), 115, 111, 89, 87, 86, 83, 73 (100). Anal. Calcd for $C_8H_{13}FO_2$: C, 59.98; H, 8.18. Found: C, 59.61; H, 7.81.

Methyl 5-Fluoro-4-hexenoate (4d). Reduction of **3d** afforded a 55:45 mixture of the *E* and *Z* isomers of methyl 5-fluoro-4-hexenoate (**4d**) in 44% yield (method 3). **4d**: IR (ν_{max}^{film}) 2900, 1740, 1710 (shoulder), 1440, 1390, 1365, 1320, 1200, 1180, 1140, 1100, 1035, 1000, 900, 850 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.87 (d, 3 H, $J[CH_3,F]$ = 18 Hz), 2.36 (s, 4 H), 3.70 (s, 3 H), 4.2–5.3 (1 H; *Z* isomer: d of t at δ 4.53, J_t = 8 Hz, J[H,F] = 38 Hz; *E* isomer: d of t at δ 5.00, J_t = 8 Hz, J[H,F] = 20 Hz); ^{19}F NMR ($CDCl_3/CFCl_3$): $\delta(E)$ = −98.1 (d of q,$J[CH_3,F]$ = 20 Hz and J[H,F] = 24 Hz); and δ(Z) = −106.1 (d of q,$J[CH_3,F]$ = 20 Hz and J[H,F] = 44 Hz); mass spectrum, *m/e* (relative intensity) 146 (M^+), 115, 87, 86 (100), 85, 74, 73. Anal. Calcd for $C_7H_{11}FO_2$: C, 57.52; H, 7.59. Found: C, 57.74; H, 7.74.

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Registry No. **1a**, 2550-26-7; **1b**, 2046-21-1; **1c**, 13984-57-1; **1d**, 13984-50-4; **2a**, 20849-77-8; **2b**, 95739-61-0; **2c**, 95739-62-1; **2d**, 64037-75-8; **3a**, 95739-63-2; **3b**, 95739-64-3; **3c**, 95739-65-4; **3d**, 95739-66-5; (*E*)-**4a**, 95739-67-6; (*Z*)-**4a**, 95739-68-7; (*E*)-**4b**, 95739-69-8; (*Z*)-**4b**, 95739-70-1; (*E*)-**4c**, 95739-71-2; (*Z*)-**4c**, 95739-72-3; (*E*)-**4d**, 95739-73-4; (*Z*)-**4d**, 95739-74-5; **5a**, 95739-75-6; **5b**, 95739-76-7; **5c**, 95739-77-8; **5d**, 95739-78-9; (diethylamino)sulfur trifluoride, 38078-09-0.

Coupling of Allylic Alcohol Epoxides with Sulfur-Stabilized Allylic Anions

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A study of the coupling of epoxy alcohol **15** with sulfur-stabilized allylic anions was undertaken as a route to dienes **16** and **17**. The allylic sulfone **9a** upon deprotonation with *n*-butyllithium in THF–HMPA undergoes smooth coupling with the epoxy magnesio alkoxide **15c** at −78 °C to give the sulfone diol **17** in high yield. Sulfone **9a** is prepared via allylic oxidation of geranyl phenyl sulfone with selenium dioxide–*tert*-butyl hydroperoxide (TBHP). Epoxy alcohol **15a** is secured by addition of propargylmagnesium bromide to methacrolein followed by silylation and selective epoxidation with $VO(acac)_2$–TBHP. A facile reaction is also observed with the lithiated sulfide **5b** and epoxide **15c** to afford the diol **16**. In contrast, the lithium salt **15b** of epoxy alcohol **15a** is only slowly attacked by the lithiated sulfide **5b** and not at all by the lithiated sulfone **9b**. The coupling products **16** and **17** are intermediates in a projected cembranolide synthesis.

Important new developments in epoxidation methodology have enhanced the status of allylic alcohol epoxides as synthetic intermediates.[1] These substances can now be prepared in high stereochemical purity from readily available precursors. As a result, epoxy alcohols have played increasingly key roles in stereocontrolled syntheses of diverse natural products and drugs,[1] polyols,[2a] and most recently, carbohydrates.[2b] In work to date, major emphasis has been placed on the epoxide function as a latent diol or methylcarbinol moiety. The direct utilization of epoxy

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