described above; evaporation of solvent from the benzene extract under reduced pressure left crude **10** (R = Me) as a colorless oil: IR (film) 3060, 2950, 2840, 1578, 1475, 1438, 1120, 1075, 1055, 960, 740, and 690 cm^{-1}. This oil was dissolved in THF (14 mL) containing water (5 mL) and hydrogen chloride (36.5% solution, 1 mL), and the solution was stirred at 25 °C for 0.5 h. Water (100 mL) was then added and the product was extracted with benzene (3 × 50 mL). The extract was washed with water (3 × 30 mL) and dried over $MgSO_4$. Evaporation of the solvent left a pale yellow oil which was purified by column chromatography [silica gel, hexane–dichloromethane (1:1) as eluant] to give pure **11** (0.63 g, 3.1 mmol, 62% total isolated yield): IR (film) 3080, 2950, 2850, 2750, 1710, 1578, 1478, 1437, 1150, 1022, 740, and 690 cm^{-1}.

Acknowledgment. We thank Dr. T. Mitsudo of Kyoto University for ^{13}C NMR measurement of *erythro*- and *threo*-**7**.

Registry No. **1** (R′ = Me), 51533-22-3; **1** (R′ = Et), 73090-26-3; **1** (R′ = *i*-Pr), 73090-27-4; **2**, 73090-28-5; **3**, 73090-29-6; **4**, 73090-30-9; **5** (R = Ph), 63603-28-1; **5** (R = *n*-Bu), 73090-31-0; **5** (R = *n*-Hex), 63603-31-6; **6** (R = *n*-Bu), 73090-32-1; **6** (R = *n*-Hex), 63603-32-7; *erythro*-**7**, 73090-33-2; *threo*-**7**, 73090-34-3; **8** (R = H, R′ = Me), 73090-35-4; **8** (R = H, R′ = Et), 73090-36-5; **8** (R = R′ = Me), 73090-37-6; **8′**, 69310-37-8; **9** (R = R′ = Me), 73090-38-7; **10** (R = Me), 73090-39-8; **10** (R = Et), 71338-47-1; cyclohexene, 110-83-8; cyclopentene, 142-29-0; cyclooctene, 931-88-4; styrene, 100-42-5; 1-hexene, 592-41-6; 1-octene, 111-66-0; *cis*-2-butene, 590-18-1; *trans*-2-butene, 624-64-6; $CH_3(CH_2)_5SeCN$, 60669-47-8; PhSeCN, 2179-79-5; $PhCH_2SeCN$, 4671-93-6; H_2O, 7732-18-5; acrylaldehyde, 107-02-8; crotonaldehyde, 4170-30-3; vinyl acetate, 108-05-4; 3-(phenylseleno)propyl chloride, 73090-40-1; MeOH, 67-56-1; EtOH, 64-17-5; *i*-PrOH, 67-63-0; AcOH, 64-19-7; *trans*-2-methoxycyclohexyl hexyl selenide, 73090-41-2; *trans*-2-methoxycyclohexyl benzyl selenide, 73090-42-3; CuCl, 7758-89-6; $CuCl_2$, 7447-39-4; $CuBr_2$, 7789-45-9; $NiCl_2$, 7718-54-9; $NiBr_2$, 13462-88-9.

Fluoride Ion Elimination–Addition Reactions. Synthesis of 2,2-Difluoroethenyl Phenyl Selenide and 2,2,2-Trifluoroethyl Phenyl Selenide

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2-Chloro-2,2-difluoroethyl phenyl selenide (**1**) reacts with KF and a catalytic amount of 18-crown-6 to give 2,2-difluoroethenyl phenyl selenide (**3**) and 2,2,2-trifluoroethyl phenyl selenide (**4**). The latter is formed by an elimination–addition sequence. 2-Bromo-2,2-difluoroethyl phenyl selenide (**2**) under the same conditions gives only **3**. The olefin **3** is highly reactive toward nucleophiles. Sulfide, sulfone, and keto analogues of **1** react with KF/18-crown-6 by a similar elimination–addition sequence, affording the corresponding 2,2,2-trifluoroethyl derivatives.

Organoselenium compounds,[1] including vinyl selenides,[2] are popular reagents for organic synthesis. It seemed that vinyl selenides having fluorine or fluorinated substituents on the olefinic portion should be highly reactive and have useful properties for the construction of fluorinated organic compounds. In an effort to prepare the previously unknown 2,2-difluoroethenyl phenyl selenide (**3**), an unusual fluorination process employing "naked fluoride ion"[3] which proceeds by elimination–addition was uncovered. In this paper, the synthesis of **3** and the details of this fluorination process are described.

Results

Phenylselenenyl chloride or bromide added cleanly to vinylidene fluoride, giving the adducts **1** and **2**, respectively, in over 90% yield. A single regioisomer was obtained in both cases. **1** was treated with 7 equiv of anhydrous potassium fluoride in acetonitrile containing 0.3 equiv of 18-crown-6 at 60 °C to effect elimination of HCl. The reaction was monitored by GLPC. The data, summarized in Figure 1, showed the disappearance of the peak assigned to **1** and the corresponding appearance of a new peak. This second peak reached a maximum and then began to decrease with the appearance of a third component. The products were subsequently isolated and identified in pure form as the desired olefin **3** and the trifluoride **4**, respectively. In contrast, reaction of **2** with KF under identical conditions gave only **3**. No trace of **4** was detected after a 260-min reaction time.

$$PhSeX + CH_2{=}CF_2 \rightarrow PhSeCH_2CF_2X \quad \begin{matrix}\mathbf{1},\ X = Cl\\ \mathbf{2},\ X = Br\end{matrix}$$

$$\mathbf{1} \xrightarrow[\text{18-crown-6, acetonitrile}]{KF} \underset{\mathbf{3}}{PhSeCH{=}CF_2} \rightarrow \underset{\mathbf{4}}{PhSeCH_2CF_3}$$

$$\mathbf{2} \xrightarrow[\text{18-crown-6, acetonitrile}]{KF} \mathbf{3}$$

In preparative-scale experiments, both **3** and **4** were isolated in pure form. Reaction of **1** with excess KF and catalytic 18-crown-6 in refluxing acetonitrile gave about 80% **4** and 20% **3**. Since **3** and **4** have virtually identical boiling points, pure **4** was isolated by selective destruction of **3**. Treatment of the crude product with ethanolic potassium hydroxide for a few minutes at room temperature resulted in conversion of **3** to higher boiling materials. The trifluoride could be distilled from this mixture in 78% isolated yield. Pure **3** was isolated in 85% yield from the reaction of **2**. The olefin is a colorless distillable liquid which can be stored for months in a sealed vial in the freezer. It is stable to neutral water and can be briefly

(1) H. J. Reich, *Acc. Chem. Res.*, **12**, 22 (1979); D. L. J. Clive, *Tetrahedron*, **34**, 1049 (1978).
(2) S. Raucher and G. A. Koolpe, *J. Org. Chem.*, **43**, 4252 (1978); M. Sevrin, W. Dumont, and A. Krief, *Tetrahedron Lett.*, 3835 (1977); *Angew. Chem., Int. Ed. Engl.*, **16**, 541 (1977); M. Sevrin, J. N. Denis, and A. Krief, *Angew. Chem., Int. Ed. Engl.*, **17**, 526 (1978); S. Raucher, *J. Org. Chem.*, **42**, 2950 (1977); T. Kauffmann, R. Joussen, and A. Woltermann, *Angew. Chem., Int. Ed. Engl.*, **16**, 709 (1977); J. V. Comasseto and N. Petragnani, *J. Organomet. Chem.*, **152**, 295 (1978).
(3) C. L. Liotta in "Synthetic Multidentate Macrocyclic Compounds", R. M. Izatt and J. J. Christensen, Eds., Academic Press, New York, 1978.

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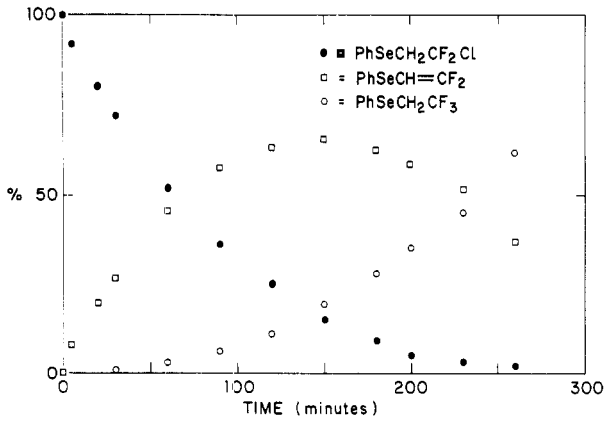
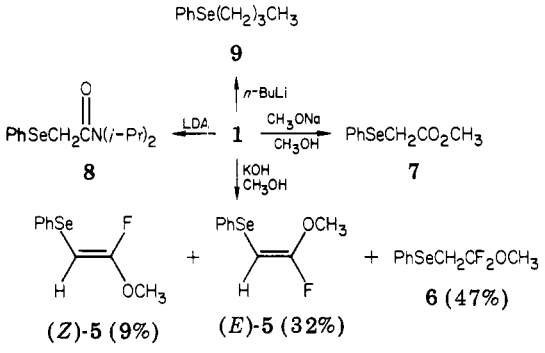


Figure 1. Reaction of 1 with potassium fluoride and 18-crown-6 in acetonitrile at 60 °C. Percent composition of mixture measured by GLC with 4-nitrotoluene as internal standard.

handled in the air without change.

Reaction of 1 with potassium fluoride was strongly inhibited by the presence of potassium bromide under catalytic crown ether conditions. Reaction of 1 with 7 equiv of KF, 1 equiv of KBr, and 0.05 equiv of 18-crown-6 in acetonitrile at 80 °C required over 30 h for complete disappearance of 1. After 48 h, the mixture consisted of 58% **3** and 42% **4** by GLPC.

Other base systems failed to yield **3** even when run to partial conversion. Treatment of 1 with excess methanolic potassium hydroxide at room temperature afforded the methoxy-substituted olefins **5** and the methanol adduct **6**. These products formed rapidly when **3** was treated



under the same conditions. Reaction of 1 with sodium methoxide in methanol or lithium diisopropylamide in THF gave the ester **7** or the amide **8**. 1 reacted with *n*-butyllithium in ether at −70 °C with exclusive attack on selenium, giving phenyl *n*-butyl selenide (**9**). Tertiary amine bases (triethylamine, Dabco, Proton Sponge) in hydrocarbon solvents failed to react with **1**.

The above results suggested a study on the conversion of additional substrates having activated β-chloro-β,β-difluoroethyl groups to difluorovinyl or trifluoroethyl groups using potassium fluoride. The known[4] sulfide **10** was

$$PhSCl + CH_2{=}CF_2 \rightarrow \underset{\mathbf{10}}{PhSCH_2CF_2Cl} + \underset{\mathbf{10a}}{PhSCF_2CH_2Cl}$$

$$\mathbf{10} \xrightarrow[\text{18-crown-6, } CH_3CN]{KF} \underset{\mathbf{11}}{PhSCH{=}CF_2} \rightarrow \underset{\mathbf{12}}{PhSCH_2CF_3}$$

$$\mathbf{10} \xrightarrow{CrO_3} \underset{\mathbf{13}}{PhSO_2CH_2CF_2Cl} \xrightarrow[\text{18-crown-6, } CH_3CN]{KF} \underset{\mathbf{14}}{PhSO_2CH_2CF_3}$$

(4) V. A. Korin'ko, Y. A. Serguchev, and L. M. Yagupol'skii, *Zh. Org. Khim.*, 11, 1268 (1975).

prepared by adding phenylsulfenyl chloride to vinylidene fluoride. Varying amounts of the isomeric sulfide **10a** were also obtained. Reaction of **10** with KF and catalytic 18-crown-6 in acetonitrile gave olefin[5] **11** and trifluoride[4] **12**. Oxidation of **10** with chromium trioxide gave the β-chloro-β,β-difluorosulfone[4] **13**. Reaction of **13** with KF under similar conditions gave the trifluoroethylsulfone[4] **14** in 71% yield. In this case, the difluoro olefin intermediate was not detected.

The β-chloro-β,β-difluoro ketone **15** was prepared by

$$RC(O)Cl + CH_2{=}CF_2 \xrightarrow{AlCl_3}$$

$$\underset{\mathbf{15},\ R = t\text{-}BuCH_2}{\underset{\mathbf{17},\ R = CH_3}{RC(O)CH_2CF_2Cl}} \xrightarrow[\text{18-crown-6, } CH_3CN]{KF} \underset{\mathbf{18},\ R = CH_3}{\underset{\mathbf{16},\ R = t\text{-}BuCH_2}{RC(O)CH_2CF_3}}$$

aluminum chloride catalyzed addition of *tert*-butylacetyl chloride to vinylidene fluoride.[6] Treatment of **15** with excess KF and catalytic 18-crown-6 in acetonitrile at room temperature afforded the corresponding trifluoroethyl ketone in 64% isolated yield. No intermediate was detected by GLPC during the reaction. Similarly, ketone[6] **17** was converted to 4,4,4-trifluoro-2-butanone[7] (**18**).

Discussion

The powerful basicity and nucleophilicity of fluoride ion generated by solubilization of potassium fluoride with crown ethers in organic solvents[3,8] or under other unsolvated conditions[9] are well-known Thus, formation of olefin **3** under these conditions is not surprising. Subsequent conversion of **3** to **4** presumably involves nucleophilic ad-

$$\underset{\mathbf{3}}{PhSeCH{=}CF_2} + F^- \rightarrow PhSe\bar{C}HCF_3 \xrightarrow{H^+} \underset{\mathbf{4}}{PhSeCH_2CF_3}$$

dition of fluoride ion to the difluoromethylene end of the olefin followed by quenching of the carbanion by a proton. The proton source may be the bihalide ion generated in the elimination step.

The striking effect of bromide ion on the course of these reactions may derive from the relative solubilities of the potassium halide salts in 18-crown-6/acetonitrile (KBr > KCl > KF).[10]

Elimination of HCl from 1 by fluoride ion is inhibited by the presence of KBr. Apparently bromide ion is a weaker base under these conditions and also suppresses the concentration of the active base (fluoride ion) by preferentially associating with the potassium ion–crown ether complex. Since the crown ether is present in only catalytic amounts, the concentration of fluoride ion in solution in the presence of bromide ion must be very small. The ultimate formation of the trifluoromethyl group must derive from its greater thermodynamic stability relative to CF_2Br or CF_2Cl since the concentrations of both Cl^- and Br^- must be greater than F^- during the addition step and since there is little difference in the relative nucleophilicity of F^-, Cl^-, and Br^- under these conditions.[10] The synthetic results, clean formation of **3** from **2** and **4** from **1**, may

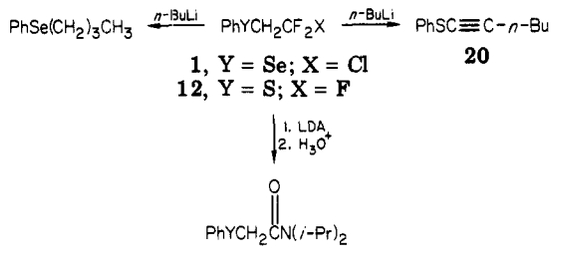
(5) T. Nakai, K. Tanaka, and N. Ishikawa, *Chem. Lett.*, 1263 (1976).
(6) I. L. Knunyantz, R. N. Sterlin, L. N. Pinkina, and D. L. Dyatkin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 296 (1958); *Chem. Abstr.*, **52**, 12754e (1960).
(7) R. N. Haszeldine, *J. Chem. Soc.*, 1261 (1954).
(8) C. L. Liotta and H. P. Harris, *J. Am. Chem. Soc.*, **96**, 2250 (1974).
(9) T. Ando and J. Yamawaki, *Chem. Lett.*, 45 (1979); J. H. Clark, *J. Chem. Soc., Chem. Commun.*, 798 (1978); D. Landini, F. Montanari, and F. Rolla, *Synthesis*, 428 (1974); J. Pless, *J. Org. Chem.*, **39**, 2644 (1974); Y. S. Klausner and M. Chorev, *J. Chem. Soc., Perkin Trans. 1*, 626 (1977).
(10) C. L. Liotta and E. E. Grisdale, *Tetrahedron Lett.*, 4205 (1975).

result from a fortuitous balance of factors, namely, a greater rate of elimination of HX from **2** relative to **1** plus the more pronounced inhibition of both elimination and addition by the bromide ion generated from **2** relative to the chloride ion generated from **1**. A more thorough understanding of these processes would require a detailed kinetic study, a formidable undertaking in view of the many equilibria which must be occurring under these conditions.

The formation of **5** and **6** from **1** with potassium hydroxide in methanol is also likely to involve elimination to the olefin **3** followed by nucleophilic addition to this highly electrophilic species and either protonation of the carbanion or elimination of fluoride ion. Under more strongly basic conditions ($NaOCH_3/CH_3OH$), **5** could lose HF to form the acetylenic ether **19**. Hydrolysis of this compound under the acidic workup conditions would give the observed ester **7**.

This latter process offers a relatively simple two-step synthesis of useful[1] α-phenylselenoacetates from phenylselenenyl chloride and vinylidene fluoride.

It is interesting to compare the chemistry of selenide **1** to that of sulfide **12**, described by Nakai and co-workers.[5,11]



Both react with LDA to give the corresponding amides after hydrolysis. However, the sulfide reacts with *n*-butyllithium to give the acetylenic thioether **20**, while **1** reacts with exclusive attack on the selenium to give phenyl butyl selenide. The propensity for attack by alkyllithiums on the selenium atom of selenides has been noted previously.[1]

Experimental Section

Phenylselenenyl chloride and diphenyl diselenide were used as received from Aldrich. Phenylsulfenyl chloride was prepared as described[12] from thiophenol and sulfuryl chloride. Potassium fluoride was dried overnight in a vacuum oven at 140 °C and then powdered with a mortar and pestle in a drybox immediately before use. Reagent-grade acetonitrile was distilled from calcium hydride and stored under N_2. 18-Crown-6 was used as received from PCR, Inc.

Proton NMR spectra were obtained on a Varian A-60 instrument with Me_4Si as internal standard. Fluorine NMR spectra were obtained on a Varian XL-100 instrument operated at 94.1 MHz, using $CFCl_3$ as internal standard. Negative chemical shifts refer to signals upfield from the standard. GLPC analyses were performed on a Hewlett-Packard 5700-A instrument with a 10 ft × 0.25 in. 10% SE-30 column at the indicated oven temperatures and with a helium carrier gas flow rate of 60 mL/min.

2-Chloro-2,2-difluoroethyl Phenyl Selenide (1). A 200-mL Hastelloy pressure vessel was charged with 19.1 g (0.10 mol) of phenylselenenyl chloride and 80 mL of methylene chloride. The vessel was closed, cooled in dry ice/acetone, evacuated, and charged with 13 g (0.20 mol) of vinylidene fluoride. The mixture was agitated overnight at 60 °C. After the mixture was cooled to room temperature, the excess vinylidene fluoride was vented. The vessel contents was concentrated on a rotary evaporator. Distillation of the residue through a short-path still gave 23.3 g (91%) of **1**: bp 66–67 °C (1.1 mm); ^1H NMR ($CDCl_3$) δ 3.57 (2 H, t), 7.1–7.7 (5 H, m); ^{19}F NMR ($CDCl_3$) δ −50.6 (t); exact mass, *m/e* calcd for $C_8H_7ClF_2Se$ 255.9369, found 255.9357.

2-Bromo-2,2-difluoroethyl Phenyl Selenide (2). Bromine (6.4 g, 0.04 mol) was added to a solution of 12.5 g (0.04 mol) of diphenyl diselenide in 80 mL of methylene chloride. This solution was transferred to a 200-mL Hastelloy pressure vessel which was closed, cooled in dry ice/acetone, evacuated, and charged with 10 g of vinylidene fluoride. The mixture was agitated overnight at 40 °C. After the mixture was cooled to room temperature and the excess vinylidene fluoride was vented, the vessel contents was concentrated on a rotary evaporator to an oil. Distillation of the oil through a short-path still gave 21.5 g (90%) of faintly yellow liquid: bp 71–73 °C (0.55 mm); ^1H NMR ($CDCl_3$) δ 3.70 (2 H, t), 7.1–7.7 (5 H, m); ^{19}F NMR ($CDCl_3$) δ −44.45 (t, J_{HF} = 15 Hz); exact mass, *m/e* calcd for $C_8H_7BrF_2Se$ 299.8864, found 299.8854.

2,2-Difluoroethenyl Phenyl Selenide (3). A mixture of 12.3 g (0.212 mol) of dry potassium fluoride, 2 g of 18-crown-6, 8.35 g (0.0278 mol) of **2**, and 150 mL of acetonitrile was heated under N_2 in an 80 °C oil bath for 5 h. The mixture was poured into 300 mL of ice water and extracted with methylene chloride (3 × 50 mL). The combined extracts were washed with water, dried ($MgSO_4$), and concentrated on a rotary evaporator to 5.8 g of faintly yellow oil. Distillation of the oil through a short-path still gave 5.2 g (85%) of colorless **3**: bp 35–36 °C (0.5 mm); ^1H NMR ($CDCl_3$) δ 5.18 (1 H, dd), 7.0–7.6 (5 H, m); ^{19}F NMR ($CDCl_3$) δ −75.5 (1 F, dd, J_{FF} = 24 Hz, J_{HF} = 2.4 Hz), −77.6 (1 F, t, J_{FF} = 24 Hz, J_{HF} = 21 Hz); exact mass, *m/e* calcd for $C_8H_6F_2Se$ 219.9602, found 219.9612.

2,2,2-Trifluoroethyl Phenyl Selenide (4). A mixture of 17.5 g (0.3 mol) of dry potassium fluoride, 2 g of 18-crown-6, 11 g (0.043 mol) of **1**, and 100 mL of acetonitrile was refluxed under N_2 overnight. GLPC analysis (170 °C) showed a mixture of about 80% **4** and 20% **3**. The mixture was poured into 300 mL of water and extracted with methylene chloride (3 × 50 mL). The combined extracts were washed with water, dried ($MgSO_4$), and concentrated on a rotary evaporator to a dark liquid. The liquid was treated at room temperature with a solution of 3 g of KOH pellets dissolved in 50 mL of absolute ethanol. After being stirred for 15 min, the solution was poured into 200 mL of ice water and extracted with methylene chloride (2 × 100 mL). The combined extracts were washed with water, dried ($MgSO_4$), and concentrated on a rotary evaporator to 12.9 g of dark oil. Distillation through a 6-in. Vigreux column gave 7.97 g (78%) of colorless liquid: bp 32–34 °C (0.2 mm); ^1H NMR ($CDCl_3$) δ 3.28 (2 H, q), 7.1–7.7 (5 H, m); ^{19}F NMR ($CDCl_3$) δ −65.0 (t, J = 10.5 Hz); exact mass, *m/e* calcd for $C_8H_7F_3Se$ 239.9665, found 239.9668.

Reaction of 1 with Methanolic Potassium Hydroxide. A mixture of 20 g (0.078 mol) of **1**, 80 mL of methanol, and 7.8 g (0.12 mol) of KOH pellets was stirred at room temperature. After 1 h, an additional 6.8 g of KOH pellets was added. The mixture was stirred for a total of 2.5 h and then poured into 400 mL of ice water containing 15 mL of concentrated HCl. The aqueous solution was extracted with methylene chloride (3 × 100 mL). The combined extracts were washed with water, dried ($MgSO_4$), and concentrated on a rotary evaporator to 19.1 g of yellow oil. The product was distilled through a 1-ft spinning-band column of Teflon TFE fluorocarbon resin, giving 9.25 g (47%) of 2,2-difluoro-2-methoxyethyl phenyl selenide (**6**) [bp 68–70 °C (0.5 mm); ^1H NMR ($CDCl_3$) δ 3.27 (2 H, t), 3.48 (3 H, s), 7.1–7.7 (5 H, m); ^{19}F NMR ($CDCl_3$) δ −75.6 (t, J_{HF} = 10 Hz); exact mass, *m/e* calcd for $C_9H_{10}F_2OSe$ 251.9864, found 251.9829], 5.8 g (32%) of (*E*)-1-fluoro-1-methoxy-2-(phenylseleno)ethene ((*E*)-**5**) [bp 73–74 °C (0.5 mm); ^1H NMR ($CDCl_3$) δ 3.68 (3 H, s), 5.04 (1 H, d), 7.1–7.7 (5 H, m); ^{19}F NMR ($CDCl_3$) δ −76.9 (d, J_{HF} = 5 Hz); exact mass, *m/e* calcd for C_9H_9FOSe 231.9802, found 231.9784],

(11) K. Tanaka, S. Shiraishi, T. Nakai, and N. Ishikawa, *Tetrahedron Lett.*, 3103 (1978).
(12) D. H. Harpp, B. T. Friedlander, and R. A. Smith, *Synthesis*, 181 (1979).

and 1.6 g (9%) of (*Z*)-1-fluoro-1-methoxy-2-(phenylseleno)ethene ((*Z*)-**5**) [bp 81–83 °C (0.5 mm); ^{1}H NMR ($CDCl_3$) δ 3.63 (3 H, s), 4.63 (1 H, d), 7.1–7.7 (5 H, m); ^{19}F NMR ($CDCl_3$) δ −73.0 (d, J_{HF} = 30 Hz)].

Reactions of 3 and 4 with Base. A mixture of 2 g of KOH pellets and 20 mL of methanol was stirred under the KOH dissolved. A mixture (4 g) consisting of 54% of **3** and 46% of **4** by fluorine NMR was added. After 5 min, GLPC analysis showed complete disappearance of **3**. The mixture was poured into 100 mL of ice water containing 1 mL of concentrated HCl and extracted with methylene chloride (2 × 50 mL). The combined extracts were washed with water, dried ($MgSO_4$), and concentrated on a rotary evaporator to 3.7 g of colorless liquid. Fluorine NMR showed the presence of 52% **4**, 22% **6**, 18% (*E*)-**5**, and 7% (*Z*)-**5** as the only detectable components.

Reaction of 1 with Sodium Methoxide. A solution of 5.1 g (0.02 mol) of **1** in 20 mL of methanol was added over 20 min to a solution of 5.4 g (0.1 mol) of sodium methoxide in 30 mL of methanol at 0 °C. The mixture was allowed to warm to room temperature and stirred for 20 h. The mixture was poured into 150 mL of ice water containing 4 mL of concentrated HCl and extracted with methylene chloride (2 × 100 mL). The combined extracts were washed with water, dried ($MgSO_4$), and concentrated on a rotary evaporator to 4.6 g of oil. Distillation of the product gave 3.9 g (85%) of methyl (phenylseleno)acetate (**7**): NMR ($CDCl_3$) δ 3.47 (3 H, s), 3.60 (2 H, s), 7.1–7.7 (5 H, m); exact mass, *m/e* calcd for $C_9H_{10}O_2Se$ 229.9845, found 229.9826.

Reaction of 1 with *n*-Butyllithium. A solution of 2.6 g (0.01 mol) of **1** in 30 mL of ether was cooled to −70 °C. A solution of *n*-butyllithium in hexane (16 mL, 1.6 M, 0.026 mol) was added dropwise over 0.5 h, keeping the temperature below −70 °C. The resulting mixture was stirred at −70 °C for 0.5 h and then warmed to room temperature over 1 h. The solution was poured into 100 mL of ice water containing 5 mL of concentrated HCl. The ether layer was separated. The aqueous solution was extracted with 50 mL of ether. The combined ether extracts were dried ($MgSO_4$) and concentrated on a rotary evaporator to 2.4 g of phenyl *n*-butyl selenide.

Reaction of 1 with Lithium Diisopropylamide (LDA). A solution of 0.046 mol of LDA in 85 mL of THF/ether (prepared from diisopropylamine and methyllithium) was cooled to −70 °C, and a solution of 2.6 g (0.01 mol) of **1** in 10 mL of THF was added over 10 min. The solution was stirred for 2 h at −70 °C. The solution was poured into 200 mL of ice water containing 10 mL of concentrated HCl. The aqueous solution was extracted with ether (3 × 100 mL). The combined extracts were washed with water, dried ($MgSO_4$), and concentrated on a rotary evaporator to 2.7 g of dark oil. Bulb-to-bulb distillation at 0.5 mm gave 2.1 g of light yellow amide **8**: ^{1}H NMR ($CDCl_3$) δ 1.17 and 1.33 (12 H, br ds), 3.71 (2 H, s), 3.1–4.1 (2 H, m), 7.1–7.7 (5 H, m); exact mass, *m/e* calcd for $C_{14}H_{21}NOSe$ 299.0788, found 299.0797.

2-Chloro-2,2-difluoroethyl Phenyl Sulfide (10). An 80-mL Hastelloy pressure vessel was charged under N_2 with 14.5 g (0.1 mol) of phenylsulfenyl chloride and 30 mL of methylene chloride. The vessel was closed, cooled in dry ice/acetone, evacuated, and charged with 13 g (0.20 mol) of vinylidene fluoride. The mixture was agitated overnight at 60 °C. After the mixture was cooled to room temperature and vented to atmospheric pressure, the contents was concentrated on a rotary evaporator to 17.7 g of golden liquid. Short-path distillation gave 14.2 g (68%) of faintly yellow **10**: bp 58–60 °C (0.3 mm) [lit.[4] bp 61–62 °C (1 mm)]; ^{1}H NMR ($CDCl_3$) δ 3.62 (2 H, t), 7.1–7.6 (5 H, m); ^{19}F NMR ($CDCl_3$) δ −53.08 (t, J_{HF} = 12.5 Hz).

In some apparently identical preparations, the product was contaminated with varying amounts of its isomer **10a**, detected by the appearance of a triplet at δ 5.33 in the proton NMR spectrum.

Reaction of 10 with Potassium Fluoride. A mixture of 2.1 g (0.01 mol) of **10**, 4.1 g of potassium fluoride, 0.7 g of 18-crown-6, and 50 mL of acetonitrile was heated with vigorous stirring in a 60 °C oil bath. The course of the reaction was monitored by GLPC (oven temperature 175 °C) which showed the disappearance of the starting material peak at 7.8 min and the appearance of a new peak at 3.2 min, followed by the appearance of a second new peak at 3.4 min. After 3.4 h, the peak due to **10** had disappeared and the mixture was poured into 200 mL of ice water. The aqueous solution was extracted with methylene chloride (2 × 100 mL). The combined methylene chloride extracts were washed with water, dried ($MgSO_4$), and concentrated on a rotary evaporator to 1.62 g of dark oil. Kugelrohr distillation of the oil at 0.35 mm and 80 °C gave 0.9 g of colorless oil which showed a quartet at δ 3.38 (J = 10 Hz), a double doublet at δ 5.10 (J = 21 Hz, 1 Hz), and a multiplet at δ 7.1–7.5. The spectrum is consistent with a mixture of 25% **11** and 75% **12**.

Reaction of 13 with Potassium Fluoride. The sulfone **13** was prepared by chromium trioxide oxidation[4] of **10**. A mixture of 2.05 g (0.035 mol) of potassium fluoride, 0.4 g of 18-crown-6, 1.2 g (0.005 mol) of **13**, and 25 mL of acetonitrile was stirred in a 60 °C oil bath for 2 h. The mixture was poured into 100 mL of water and extracted with methylene chloride (3 × 25 mL). The combined extracts were washed with water, dried ($MgSO_4$), and concentrated on a rotary evaporator to 1.28 g of solid. Recrystallization from hot aqueous ethanol gave 0.79 g (71%) of the (trifluoroethyl)sulfone **14**: mp 107–109 °C (lit.[4] mp 109–110 °C); ^{1}H NMR ($CDCl_3$) δ 3.93 (2 H, q), 7.4–8.2 (5 H, m).

1-Chloro-1,1-difluoro-5,5-dimethyl-3-hexanone (15). *tert*-Butylacetyl chloride (26.9 g, 0.20 mol) was added over 0.25 h to a solution of 26.7 g (0.20 mol) of anhydrous aluminum chloride in 75 mL of chloroform at −10 °C. Vinylidene fluoride (16.6 g, 0.26 mol) was bubbled into the solution over 0.5 h. The solution was poured into 300 g of ice and 30 mL of concentrated HCl. The layers were separated, and the aqueous layer was extracted with 100 mL of chloroform. The combined chloroform solutions were washed with 100 mL of cold aqueous 5% KOH solution, dried ($MgSO_4$), and concentrated on a rotary evaporator to 29.2 of yellow oil. Distillation of the oil through a 6-in. column gave 20.8 g of **15**: bp 40–41 °C (0.2 mm); ^{1}H NMR ($CDCl_3$) δ 1.03 (9 H, s), 2.42 (2 H, s), 3.38 (2 H, t, J_{HF} = 12 Hz).

Reaction of 15 with Potassium Fluoride. A mixture of 9.93 g (0.05 mol) of **15**, 1 g of 18-crown-6, 14.5 g (0.25 mol) of potassium fluoride, and 70 mL of acetonitrile was stirred for 1 h at room temperature. GLPC analysis (150 °C) showed complete disappearance of the starting material and the appearance of a single new peak. The mixture was poured into 300 mL of ice water and extracted with methylene chloride (3 × 25 mL). The combined extracts were washed with water, dried ($MgSO_4$), and filtered. The filtrate was concentrated by distillation through a 6-in. column to remove methylene chloride. The residue was distilled, giving 5.8 g (64%) of the colorless (trifluoroethyl) ketone **16**: bp 59–60 °C (20 mm); ^{1}H NMR ($CDCl_3$) δ 1.03 (9 H, s), 2.41 (2 H, s), 3.20 (2 H, q, J_{HF} = 11 Hz).

Registry No. **1**, 73194-20-4; **2**, 73194-21-5; **3**, 73194-22-6; **4**, 73194-23-7; (*E*)-**5**, 73194-24-8; (*Z*)-**5**, 73194-25-9; **6**, 73194-26-0; **7**, 68872-84-4; **8**, 73194-27-1; **9**, 28622-61-9; **10**, 588-49-8; **10a**, 56354-30-4; **11**, 61698-70-2; **12**, 2262-07-9; **13**, 56354-38-2; **14**, 56354-44-0; **15**, 73194-28-2; **16**, 73194-29-3; phenylselenenyl chloride, 5707-04-0; vinylidene fluoride, 75-38-7; diphenyl diselenide, 1666-13-3; phenylsulfenyl chloride, 931-59-9; *tert*-butylacetyl chloride, 7065-46-5; KF/18-crown-6, 38348-17-3; Br_2, 7726-95-6.