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Synthesis and Transformation of [Difluoro(phenylseleno)methyl]-trimethylsilane

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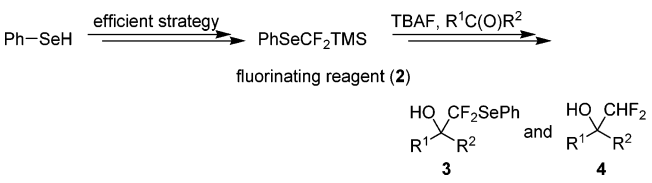

A novel and efficient strategy was developed to synthesize [difluoro(phenylseleno)methyl]trimethylsilane ($PhSeCF_2$-TMS, **2**), which was further utilized as a nucleophilic difluoromethylating reagent to incorporate the difluoro-(phenylseleno)methyl ($PhSeCF_2$) group into carbonyl compounds in good yields. The resulting $PhSeCF_2$-containing alcohols **3** could be conveniently converted into corresponding difluoromethyl alcohols **4** by a radical deselenylation.

The application of fluorinated organosulfur compounds as useful synthetic intermediates has evoked a widespread interest in the construction of fluorinated building blocks. Prakash and co-workers have reported the preparation of difluoromethyl phenyl sulfone and its applications as a difluoromethyl anion equivalent, a selective difluoromethylene dianion equivalent, as well as a difluoromethylidene equivalent.[1] In addition, bromodifluoromethyl phenyl sulfide ($PhSCF_2Br$) has also been demonstrated to be a highly versatile *gem*-difluoromethylene building block via the reaction of difluorophenylsulfanyl radical with olefins.[2] However, very little attention has been paid to the fluoroselenium compounds. It is well-known that sulfur and selenium have similar chemical reactivity, but differ in size, electronegativity, and nucleophilicity.[3] Based on the aforementioned cases, we are very interested in the reactivity of fluoroselenium compounds. In our opinion, [difluoro(phenylseleno)methyl]-trimethylsilane ($PhSeCF_2TMS$, **2**) would be a versatile nucleophilic difluoromethylating reagent although there is no corresponding report on its synthesis. First, the phenylseleno group is a useful reactive functionality, which can be easily removed after the desired synthetic steps and oxidative elimination of the phenylseleno moiety have been successfully exploited for the introduction of the double bond into organic molecules.[4] Second, the oxidative deselenylation leading to olefins proceeds relatively lower temperature than the corresponding organosulfide.[4a] Finally, reduction of the phenylseleno group to a hydrogen can be readily and directly achieved by traditional treatment with Bu_3SnH or by treatment with Raney-nickel under hydrogen.[5,6] These procedures have the advantage over the corresponding phenylthio group, which is removed by oxidation (H_2O_2 or CrO_3) followed by reductive desulfonylation (Na/Hg or Na/EtOH).[7]

We envisaged that silane **2** could react with carbonyl compounds to give β-hydroxy selenides. Recently, the synthesis of β-hydroxy selenides has gained extensive attention due to its applications as the versatile building blocks. The β-hydroxy selenides can be prepared either by regioselective ring-opening of epoxides with nucleophilic benzeneselenolate or tributylstannyl phenylselenolate ($Bu_3SnSePh$) in the presence of $BF_3{\cdot}Et_2O$ or by treatment of benzaldehydes with phenylseleno methyl or ethyl anion.[8,9] Enolates derived from ketones could condense with (phenylseleno)acetaldehyde, providing another synthetic route to β-hydroxy selenides.[10] The unique chemical properties of β-hydroxy selenides have been successfully employed for the introduction of double bond by elimination of PhSeOH.[9a,10] On the other hand, the oxidation of β-hydroxy selenides with *m*-CPBA and oxone can lead to a facile formation of epoxides.[9b,11]

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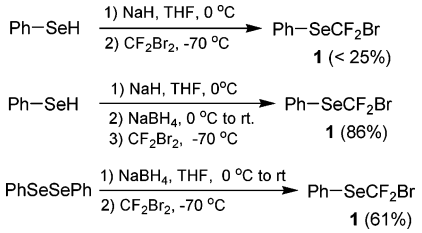
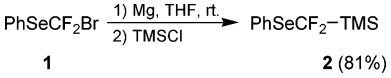
SCHEME 1



There are no corresponding synthetic procedures for [difluoro(phenylseleno)methyl]trimethylsilane ($PhSeCF_2$-TMS, **2**). We propose that it could be prepared from halodifluoromethyl phenyl selenides. In 1995, Uneyama and co-worker reported a new access to difluoromethylene compounds by an electrochemical procedure, in which bromodifluoromethyl phenyl selenide ($PhSeCF_2Br$) was furnished as a byproduct.[12] However, there were no detailed characterization data and synthetic procedure of $PhSeCF_2Br$ in their report. Herein, we described a novel and efficient preparation of $PhSeCF_2Br$ by the reaction of selenophenol with CF_2Br_2 in the presence of sodium borohydride. The difluoromethylating reagent $PhSeCF_2TMS$ was then synthesized by the coupling reaction of $PhSeCF_2Br$ and TMSCl. The transformation of $PhSeCF_2TMS$ was studied with nucleophilic addition to various aldehydes and ketones, and the resulting α,α-difluoro-*β*-hydroxy selenides were also deselenylated to give the corresponding difluoromethyl alcohol.

In 1981, Suda and Hino first reported the preparation of bromodifluoromethyl phenyl sulfide ($PhSCF_2Br$) in 58% yield by the reaction of thiophenol with CF_2Br_2 in aprotic solvents, and they suggested that the difluorocarbene intermediate was involved in the formation of $PhSCF_2Br$.[13] Later on, this reaction was improved by the addition of dibenzo-18-crown-6 as a catalyst to increase the yield.[2,14] Inspired by their work,[2,13,14] we attempted to prepare fluoroselenide ($PhSeCF_2Br$) by their methodology. Selenophenol was first treated with sodium hydride in THF followed by addition of CF_2Br_2 at −70 °C. Unfortunately, the yield of the desired product **1** was below 25%. Diphenyl diselenide (PhSeSePh) (major byproduct), difluoromethyl phenyl selenide ($PhSeCF_2H$), and diphenylseleno compounds ($PhSeCF_2SePh$) were formed as the byproducts. Thus, how to improve the yield of product **1** rendered us to investigate this reaction in detail. Reduction of the byproducts was the key to improve the yield of desired product **1**. It was reported that PhSeSePh was a common nucleophilic reagent, and it could be easily transferred into phenylseleno anion under the reduction of sodium borohydride.[15] Thus, we supposed that the addition of $NaBH_4$ might prevent the generation of PhSeSePh or convert the resulting PhSeSePh into $PhSe^-$, which could take part in the reaction again (Scheme 1). Thus, selenophenol was first treated with sodium hydride, followed by sequential addition of $NaBH_4$ and CF_2Br_2. Just as anticipated, $NaBH_4$ did prevent the generation of PhSeSePh and our desired product $PhSeCF_2Br$ was provided in 86% yield. Based on this result, we considered that PhSeSePh could also be used for the preparation of $PhSeCF_2Br$. Treatment of PhSeSePh with $NaBH_4$ in THF followed by addition of CF_2Br_2 successfully furnished the desired product $PhSeCF_2Br$ in 61% yield, which further confirmed the important role of $NaBH_4$ in the reaction between PhSeH/NaH and CF_2Br_2.

SCHEME 2



Trifluoromethyltrimethylsilane (CF_3TMS) is a good reagent to introduce a trifluoromethyl group into electrophilic compounds.[16] Therefore, [difluoro(phenylseleno)-methyl]trimethylsilane ($PhSeCF_2TMS$, **2**) would also be expected as a novel and efficient fluorination reagent to incorporate $PhSeCF_2$ group into organic compounds via nucleophilic addition. To the best of our knowledge, magnesium metal-mediated reductive fluoroalkylation of halosilane is the efficient route for synthesis of fluoroalkyltrimethylsilane, just as the recent synthesis of $PhSCF_2TMS$ by Prakash and co-workers.[17] Thus, $PhSeCF_2$-TMS **2** was prepared in 81% yield by the reaction of $PhSeCF_2Br$, magnesium and chlorotrimethylsilane (TMSCl) (Scheme 2). In our experiment, we found that the sequence of adding raw materials had a distinct influence on the result. If TMSCl was added before $PhSeCF_2Br$, the reaction would be complicated. The proper procedure was to treat $PhSeCF_2Br$ with Mg turnings at first in THF at room temperature, followed by slow addition of TMSCl via a syringe.

With fluoroalkylated silane compound **2** in hand, we first studied the reaction of $PhSeCF_2TMS$ with aldehydes and ketones. The reaction was carried out with the catalysis of TBAF to provide the corresponding α,α-difluoro-*β*-hydroxy selenides **3**. It was reported the existence of a small amount of water in TBAF did not pose any serious problems in the trifluoromethylation of aldehydes and ketones with CF_3TMS, and use of anhydrous TBAF did not offer any advantages.[16] However, the existence of a small amount of water in TBAF lowered the yield of the desired alcohols **3** and led to $PhSeCF_2H$ as a byproduct in our experiments. This phenomenon was attributed to the electron-donating property of PhSe moiety, which resulted in more nucleophilic of $PhSeCF_2^-$ than CF_3^- anion and perfluoroalkyl anion. Addition of molecular sieves into the reaction mixture could successfully overcome this problem and the results were summarized in Table 1. Reactions of aldehydes (aromatic and aliphatic aldehydes, entries 1−4) with compound **2** proceeded well and gave the hydroxyl compounds **3a**−**e** in moderate to high yields. However, ketones provided the corresponding compounds **3e**,**f** in somewhat low yields (entries 5 and 6) along with a large amount of

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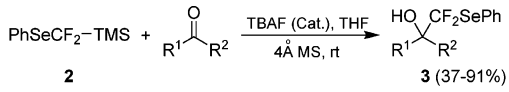
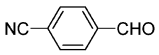
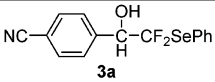
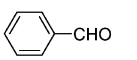
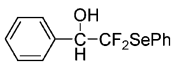
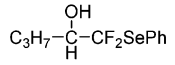
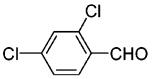
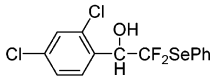
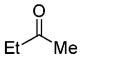
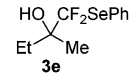
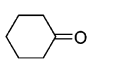
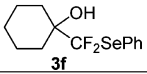
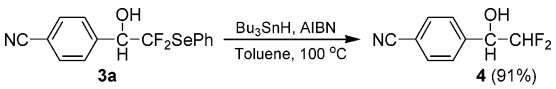
TABLE 1. Nucleophilic (Phenylseleno)difluoromethylation of Carbonyl Compounds with $PhSeCF_2$−TMC 2



Entry	Carbonyl Compounds	Product **3**	Yield (%)
1		 **3a**	91
2		 **3b**	64
3	C_3H_7CHO	 **3c**	78
4		 **3d**	73
5		 **3e**	49
6		 **3f**	37

SCHEME 3



byproduct $PhSeCF_2H$. In our opinion, the low yields of **3e**,**f** were caused by the low reactivity of ketone carbonyl group, which resulted in preferential reaction of fluoroalkylated silane **2** with water in TBAF.

α,α-Difluoro-β-hydroxy selenides can be further transferred into the corresponding difluoromethyl alcohols by a traditional radical deselenylation procedure. As a representative example, treatment of α,α-difluoro-β-hydroxy selenide **3a** with Bu_3SnH in the catalysis of AIBN provided the difluoromethyl alcohol **4** in 91% yield (Scheme 3). The resulting difluoromethyl alcohol is a highly useful compound for potential application.[18]

In conclusion, we described a novel and efficient synthesis of bromodifluoromethyl phenyl selenide ($PhSeCF_2Br$, **1**) by the addition of $NaBH_4$ to prevent the formation of diphenyl diselenide. [Difluoro(phenylseleno)methyl]-trimethylsilane ($PhSeCF_2TMS$, **2**) was conveniently prepared by the coupling reaction of $PhSeCF_2Br$ and TMSCl. The resulting fluoroalkylated silane **2**, in the presence of a fluoride initiator, could act as a "$PhSeCF_2^-$" equivalent and reacted with a series of aldehydes and ketones to furnish the corresponding α,α-difluoro-β-hydroxy selenides **3**, which could be deselenylated to afford difluoromethyl alcohols via a classical procedure. In our opinion, difluoroalkylation of carbonyl compounds with **2** provided an optional method for the preparation of wide ranges of α, α-difluoro-β-hydroxy selenides and difluoromethyl alcohols.

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Experimental Section

Bromodifluoromethyl Phenyl Selenide (1). Method A. Under nitrogen atmosphere, phenylselenol (1.023 g, 6.5 mmol) was added dropwise to a stirred suspension of sodium hydride (303 mg, 7.6 mmol) in 10 mL of dry THF cooled in an ice bath. Then $NaBH_4$ (1.005 g, 26.5 mmol) was added to the yellow suspension. After an exothermic reaction ceased, the mixture was stirred at room temperature for 20 min and then cooled to −70 °C in a dry ice−acetone bath. Dibromodifluoromethane (2.5 mL, 27.3 mmol) was slowly added to the stirred solution. The reaction mixture was stirred for 10 min cooled in the dry ice-acetone bath, and then for 30 min at room temperature. During this period, the yellow suspension turned to a cream colored suspension. Ether and saturated aqueous NH_4Cl were added slowly to the reaction mixture, and the resulting mixture was partitioned. The aqueous layer was extracted with ether, and the organic layer combined was washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure to leave an oil, which was purified by column chromatography (*n*-pentane) to give **1** (1.594 g, 86%) as a colorless oil.

Method B. Under nitrogen atmosphere, $NaBH_4$ (100 mg, 2.64 mmol) was added to a stirred solution of diphenyl diselenide (103 mg, 0.33 mmol) in 2 mL of dry THF. Dry methanol (ca. 0.1 mL) was added slowly to the reaction mixture cooled in an ice bath until the bright yellow solution turned colorless. After an exothermic reaction ceased, the mixture was stirred at room temperature for 20 min and then cooled to −70 °C on a dry ice−acetone bath. Dibromodifluoromethane (0.25 mL, 2.73 mmol) was slowly added to the stirred solution. The reaction mixture was stirred for 10 min cooled in a dry ice−acetone bath and then stirred for 30 min at room temperature. Ether and saturated aqueous NH_4Cl were added slowly to the reaction mixture, and the resulting mixture was partitioned. The aqueous layer was extracted with ether, and the organic layer combined was washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure to leave an oil, which was purified by column chromatography (*n*-pentane) to give **1** (116 mg, 61%) as a colorless oil: ^1H NMR (300 MHz, $CDCl_3$) δ 7.40−7.45 (2H, m), 7.49−7.51 (1H, m), 7.76−7.78 (2H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 108.6 (t, $^1J_{CF}$ = 355 Hz), 126.1, 129.6, 130.6, 137.1; ^{19}F NMR (282 MHz, $CDCl_3/CFCl_3$) δ −18.43 (2F, s); IR (neat) ν 1579, 1477, 1441, 1089, 1078, 1058 cm^{-1}; MS (EI) *m/z* = 286 (M^+, 13), 207 (19), 157 (18), 127 (100), 77 (28); HRMS (EI) calcd for $C_7H_5F_2BrSe$ 285.8708, found 285.8721.

[Difluoro(phenylseleno)methyl]trimethylsilane (2). To a dry 25 mL Schlenk flask under nitrogen atmosphere were added Mg turnings (30 mg, 1.25 mmol) and $PhSeCF_2Br$ (143 mg, 0.5 mmol) in 2.5 mL of THF at room temperature. Subsequently, TMSCl (0.26 mL, 2.0 mmol) was added slowly via a syringe. The reaction mixture was stirred at room temperature for 30 min, and the starting substrate was completely consumed by TLC. The reaction mixture was then transferred to a flask via a syringe. Excess TMSCl was removed under reduced pressure. The residue was purified by silica gel chromatography (*n*-pentane) to give **2** (113 mg, 81%) as a pale yellow oil: ^1H NMR (300 MHz, CD_3COCD_3) δ 0.20 (9H, s), 7.40−7.43 (3H, m), 7.68−7.71 (2H, m); ^{13}C NMR (75 MHz, C_6D_6) δ −4.4, 124.3 (t, $^2J_{CF}$ = 4.2 Hz), 128.9, 129.0, 133.3 (t, $^1J_{CF}$ = 312.9 Hz), 137.3; ^{19}F NMR (282 MHz, CD_3COCD_3) δ −85.24 (2F, s); IR (neat) ν 3063, 2964, 1579, 1477, 1440, 1255, 1081, 1066 cm^{-1}; MS (EI) *m/z* = 280 (M^+, 38), 261 (68), 230 (50), 169 (69), 77 (100), 73 (945); HRMS (EI) calcd for $C_{10}H_{14}F_2SeSi$ 279.9997, found 280.0022; Anal. Calcd for $C_{10}H_{14}F_2SeSi$: C, 43.01; H, 5.05. Found: C, 43.38; H, 5.27.

2,2-Difluoro-2-phenylseleno-1-(4′-cynaophenyl)ethanol (3a). A solution of $PhSeCF_2TMS$ (140 mg, 0.5 mmol) and 4-cynaobenzaldehyde (328 mg, 2.5 mmol) in 2.5 mL of THF was dried over MS-4 Å, after which TBAF (0.1 mL, 1 M solution in THF, containing ca. 5% water) was added. The resulting solution was stirred at room temperature for 2 h. Then a substantial amount of water was added, and stirring was continued for another 1 h. The mixture was extracted with ether (3 × 20 mL), and the combined extracts were washed with brine, dried over

Na_2SO_4, and evaporated. Purification of the residue with column chromatography [petroleum ether/EtOAc, 5/1 (v/v)] gave the corresponding alcohol **3a** (154 mg, 91%) as a pale yellow solid: mp 89 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.05 (1H, d, J = 3.0 Hz), 4.96−5.03 (1H, m), 7.32−7.68 (9H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 75.9 (t, $^2J_{CF}$ = 26 Hz), 112.9, 118.5, 123.2, 126.1 (t, $^1J_{CF}$ = 299 Hz), 128.6, 129.4, 129.8, 132.0, 137.2, 140.1; ^{19}F NMR (282 MHz, $CDCl_3$) δ −77.7 (1F, dd, $^2J_{FF}$ = 213 Hz, $^3J_{FH}$ = 6.9 Hz), −83.9 (1F, dd, $^2J_{FF}$ = 213 Hz, $^3J_{FH}$ = 15.8 Hz); IR (neat) ν 3433, 2963, 2235, 1578, 1475, 1440, 1056 cm^{-1}; MS (EI) m/z = 339 (M^+, 32), 208 (35), 132 (100), 127 (82), 77 (51); HRMS (EI) calcd for $C_{15}H_{11}NOF_2Se$ 338.9973, found 338.9961.

2,2-Difluoro-1-(4′-cynaophenyl)ethanol (4). A mixture of **3a** (30 mg, 0.09 mmol) and toluene (4 mL) was heated at 100 °C, followed by addition of a catalytic amount of AIBN (5 mg, 0.03 mmol) and tributyltin hydride (123 μL, 0.45 mmol). After being kept at 100 °C for 30 min, the mixture was cooled to room temperature and the solvent was evaporated, diluted with saturated NaF solution (10 mL), and filtered. The aqueous layer was extracted with EtOAc (3 × 10 mL). The combined organic extracts were washed with water (3 × 10 mL) and brine (10 mL), dried over Na_2SO_4, and evaporated. The residue was purified by column chromatography [petroleum ether/EtOAc, 2/1 (v/v)] to gave **4** (15 mg, 93%) as a pale yellow oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.86 (1H, br), 4.93 (1H, m), 5.75 (1H, td, $^2J_{FH}$ = 56 Hz, $^3J_{HH}$ = 4.8 Hz), 7.57−7.59 (2H, m), 7.69−7.72 (2H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 72.9 (t, $^2J_{CF}$ = 24.1 Hz), 115.2 (t, $^1J_{CF}$ = 245 Hz), 112.8, 118.4, 127.9, 132.3, 140.8; ^{19}F NMR (282 MHz, $CDCl_3$) δ −127.4 (1F, ddd, J = 286 Hz, 56 Hz, 9.6 Hz), −128.0 (1F, ddd, J = 286 Hz, 56 Hz, 9.6 Hz); IR (neat) ν 3433, 2234, 1507, 1407, 1076 cm^{-1}; MS (EI) m/z = 184 (M^+, 58), 132 (85), 104 (100), 77 (49); HRMS (EI) calcd for $C_9H_7NOF_2$ 183.0496, found 183.0507.

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Supporting Information Available: Characterization data for compounds **3b**−**f**, and ^{1}H NMR and ^{13}C NMR spectra of all of the compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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