Fluorinated Tertiary Thio- and Selenoethers from the Reaction of Sulfenyl or Selenenyl Chloride with Perfluoropropene Dimers in the Presence of Alkali Fluoride

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Synopsis. Perfluoro(1,1-dimethylbutanide) anion generated from hexafluoropropene dimers and alkali fluorides in dry *N,N*-dimethylformamide, reacts with arenesulfenyl or areneselenenyl chloride to give the corresponding aryl perfluoro(1,1-dimethylbutyl) sulfides or selenides in low to good yields.

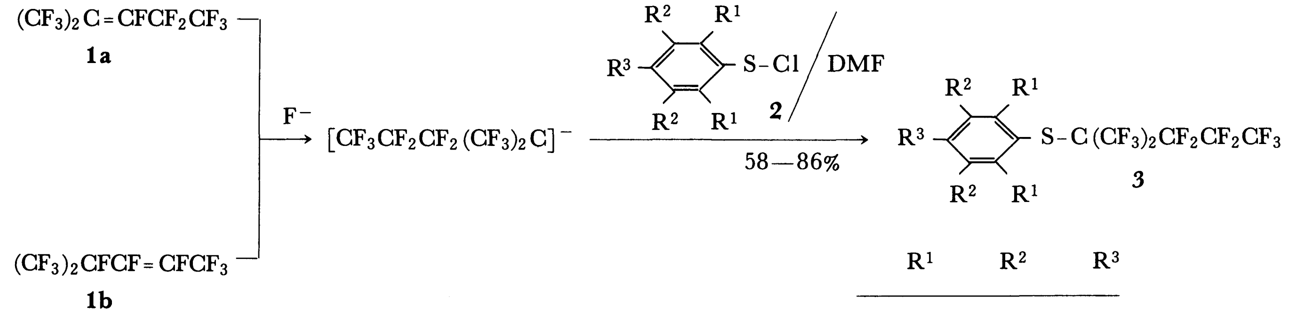
Fluorinated organic sulfides find uses as fungicides, insecticides, and surface-active agents. The usual procedures for the preparation of aryl perfluoroalkyl sulfides involve the alkylation of arenethiolates with perfluoroalkyl iodides,[1] reaction of aryl iodides[2] or arenediazonium salts[3] with metal perfluoroalkanethiolates, and photochemical reaction of arenethiols[4] or diaryl disulfides[5] with perfluoroalkyl iodides. Thermal decomposition of trifluoromethylazosulfonylarenes in the presence of diaryl disulfides[6] and reaction of aryl perfluoroalkyliodonium compounds with sodium arenethiolates[7] also lead to aryl perfluoroalkyl sulfides. In most of these cases, however, reactions are limited to the synthesis of fluorinated sulfides of short or straight alkyl chains. The synthesis of tertiary perfluoroalkyl sulfides is quite difficult, because the nucleophilic displacement of halogen atom from tertiary carbon is not feasible with perfluoro compounds.

In the present paper, we wish to report that aryl perfluoroalkyl sulfides of branched side chains can be easily obtained by the reaction of arenesulfenyl chlorides with perfluoroalkenes in the presence of alkali fluorides.[8] We used perfluoro(2-methyl-2-pentene) (**1a**) and perfluoro(4-methyl-2-pentene) (**1b**) as perfluoroalkenes, since these are inexpensive commercial products obtained by the dimerization of hexafluoropropene.[9]

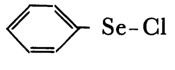
When alkene **1a** or **1b** is stirred with potassium fluoride in dry *N,N*-dimethylformamide (DMF) at 50—60 °C, perfluoro(1,1-dimethylbutanide) anion is generated and smoothly reacts with arenesulfenyl chloride (**2**) to afford the corresponding aryl perfluoro(1,1-dimethylbutyl) sulfides (**3**) in 58—86% yields, which are of interest as additives to some organic fluids.[10]

Although **1a** appears to react more smoothly than **1b**, the yields of the common product **3** do not differ appreciably after appropriate duration of time. Tertiary structures of perfluoroalkyl chains are confirmed by ^{19}F NMR spectrum ($CFCl_3$) of **3a**, which exhibits absorptions due to CF_3 groups at δ 61.1 and 80.2 and those due to CF_2 groups at δ 104.3 and 121.3 with an intensity ratio of 6:3:2:2. Cesium fluoride is excellent as a source of fluoride ion, but it can be replaced by cheaper potassium fluoride without significant decrease in yields. Perfluoroalkene **1b** is known to isomerize into the thermodynamically more stable isomer **1a** in the presence of fluoride ion.[11] Both **1a** and **1b** are known to react with arenethiolates to give a complicated mixture of fluorinated vinylic sulfides.[12]

The present procedure is extended to the preparation of phenyl perfluoro(1,1-dimethylbutyl) selenide (**5**). Benzeneselenenyl chloride (**4**), generated in situ by the chlorinolysis of diphenyl diselenide with sulfuryl chloride, reacted with perfluoro(1,1-dimethylbutanide) anion in DMF at room temperature to give the expected selenide **5** in a low yield. The conversion is



	R1	R2	R3
a	H	H	H
b	H	H	CH_3
c	CH_3	H	CH_3
d	CH_3	CH_3	H
e	CH_3	CH_3	CH_3
f	H	H	Cl



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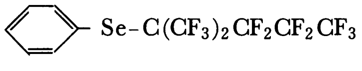

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Table 1. Aryl Perfluoro(1,1-dimethylbutyl) Sulfides Obtained

Sulfide 3	Bp (θ_b/°C)/mmHg[a]	Yield[b] %	IR (KBr)[c] cm^{-1}	^{1}H NMR (CCl_4/TMS)[d] δ(ppm)	MS (20 eV)[e] m/z (%)	Elementary analysis/%	
						Found	Calcd
3a	108/27	75	1335, 1210—1225, 1115, 965, 755, 710	7.33—7.50 (m, 3H), 7.68—7.80 (m, 2H)	428 (M^+, 48), 109 (100)	C: 33.56 H: 1.08	33.66 1.18
3b	132/28	60	1335, 1210—1250, 1115, 965, 820, 735, 710	2.41 (s, 3H), 7.16 (d, 2H; J=8.4 Hz), 7.60 (d, 2H; J=8.4 Hz)	442 (M^+, 32), 123 (100)	C: 35.55 H: 1.63	35.31 1.60
3c	155/27	86	1335, 1210—1245, 1115, 950, 820, 730, 710	2.27 (s, 3H), 2.54 (s, 6H), 6.92 (s, 2H)	470 (M^+, 12), 151 (100)	C: 38.14 H: 2.39	38.31 2.36
3d	96/0.22	80	1335, 1210—1245, 1115, 820, 735, 710	2.24 (s, 6H), 2.52 (s, 6H), 7.03 (s, 1H)	484 (M^+, 29), 165 (100)	C: 39.85 H: 2.70	39.68 2.71
3e	115/0.2 (51—53)[f]	59	1335, 1205—1260, 1115, 960, 820, 730, 710	2.22 (s, 9H), 2.58 (s, 6H)	498 (M^+, 17), 179 (100)	C: 40.88 H: 3.05	40.97 3.03
3f	132/34	58	1480, 1335, 1210—1250, 1115, 1095, 965, 830	7.37 (d, 2H; J=8.4 Hz), 7.68 (d, 2H; J=8.4 Hz)	462 (M^+, 25), 143 (100)	C: 30.88 H: 0.80	31.15 0.87

a) Bulb-to-bulb distillation (1 mmHg=133.322 Pa). b) Isolated yields based on **2** are not optimized. c) Measured on a Hitachi 260-10 spectrophotometer and only prominent peaks indicated. d) Recorded at 60 MHz using a Hitachi R-600 spectrometer. e) Obtained on a Hitachi M-80B spectrometer. f) Melting point.

incomplete even after prolonged reaction time. The product **5** is a photo-labile oil, which slowly decomposes on storage, even in a refrigerator, to form diphenyl diselenide. Reaction of **1a** with 2,4,6-trimethylbenzeneselenenyl chloride in the presence of an alkali fluoride also affords the corresponding selenide in a similar yield, but the product is unstable and soon begins to decompose on standing at room temperature. Introduction of methyl groups into aromatic rings appears to lower the stability of fluorinated tertiary selenoethers. Literature so far contains only few descriptions on the preparation of aryl perfluoroalkyl selenides; they are obtained either by photochemical reaction of areneselenols with trifluoromethyl iodide[13] or by treatment of trifluoromethaneselenenyl chloride with arylmagnesium bromides.[14]

In summary, the present method is a simple, efficient, and straightforward procedure for the preparation of various ring-substituted aryl tertiary perfluoroalkyl sulfides from readily accessible diaryl disulfides and commercially available perfluoroolefins.

Experimental

Perfluoro(2-methyl-2-pentene) (**1a**) and perfluoro(4-methyl-2-pentene) (**1b**) are commercial products available from NEOS Co. Ltd. (Kano-cho, Chuo-ku, Kobe 650, Japan). Diaryl disulfides are prepared by heating aryl iodides with copper(I) thiocyanate in hexamethylphosphoric triamide.[15] Diaryl diselenides are obtained by the alkaline decomposition of aryl selenocyanates.[16] Potassium fluoride is dried over phosphorus pentaoxide under reduced pressure at 100—120 °C prior to use.

Arenesulfenyl Chloride (2); General Procedure: To a stirred solution of diaryl disulfide (1 mmol) in dichloromethane (1 ml) is added dropwise sulfuryl chloride (1 mmol) at room temperature. Stirring is continued for 30 min to afford arenesulfenyl chloride **2** as a red solution, which is immediately used for the following reaction.

Aryl Perfluoro(1,1-dimethylbutyl) Sulfide (3); General Procedure: A mixture of perfluoro(2-methyl-2-pentene) **1a** (3.0 g; 10 mmol) and potassium fluoride (0.23 g; 4 mmol) in dry DMF (5 ml) is stirred at 50—60 °C for 3 h under nitrogen. Color gradually turns deep yellow. Then arenesulfenyl chloride **2** (2 mmol) is added dropwise and stirring is continued at this temperature for 1—2 h. After cooling the mixture is diluted with water and extracted with ether (3×10 ml). The organic extract is washed with brine, dried with sodium sulfate, and evaporated. The residual oil is chromatographed on silica gel (Wako Gel C-200) using hexane as eluent to give **3** in the yields given in the Table.

Perfluoro(1,1-dimethylbutyl) Phenyl Selenide (5): A mixture of perfluoroalkene **1a** (3.0 g; 10 mmol), potassium fluoride (0.23 g; 4 mmol) and DMF (5 ml) is stirred at 50—60 °C for 3 h under nitrogen. The resulting yellow liquid is cooled to room temperature and diphenyl diselenide (0.31 g; 1 mmol) followed by sulfuryl chloride (0.134 g; 1 mmol) is added with vigorous stirring. After stirring for 1 h, the reaction is quenched by the addition of water and the product is extracted with ether (3×10 ml). The combined extract is washed with brine, dried with sodium sulfate, and evaporated to leave an oily residue, which is chromatographed on silica gel (Wako Gel C-200) using hexane as eluent to give **5** as a pale yellow oil; yield, 0.195 g (21%). MS (20 eV) m/z (rel intensity) 476 (M^+, 3), 281 (8), 181 (46), and 157 (100); ^{1}H NMR (CCl_4): δ 7.33—7.50 (m, 3H) and 7.76—7.89 (m, 2H); IR (KBr) 3070, 1250—1210 (vs), 1150, 1100, 960, 820, 750, 730, and 710 cm^{-1}. Found: C, 30.12; H, 0.98%. Calcd for $C_{12}H_5F_{13}Se$: C, 30.34; H, 1.06%.

On standing, **5** gradually decomposes to separate diphenyl diselenide as yellow needles, mp 60—61 °C (lit,[17] mp 63 °C).

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