Some new chemistry of perfluoro-t-butylsilver

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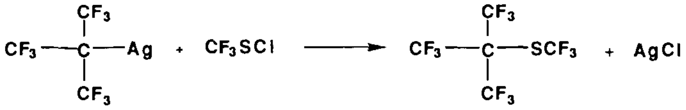
Abstract

Perfluoro-t-butylsilver, prepared by the reaction of silver fluoride with perfluoroisobutene, has been used to prepare new perfluoro-t-butyl derivatives in good yield.

Introduction

In 1968 Miller and Burnard [1] reported the preparation of perfluoroalkylsilver compounds from the nucleophilic addition of silver fluoride to fluoroalkenes. Using perfluoropropene and silver fluoride dissolved in acetonitrile, perfluoroisopropylsilver was formed in good yield. Since then, silver fluoride has been found to add to a wide variety of unsaturated fluorocarbons including perfluoro-2-butyne [2], tetrafluoroallene [3] and perfluoro-2-methyl-2-pentene [4]. A combination of silver trifluoroacetate and cesium or potassium fluoride has been employed in place of silver fluoride in reactions with perfluoroisobutene and perfluorocyclobutene [5].

In these studies, the perfluoroalkylsilver compounds have usually been treated with iodine or bromine to afford products resulting from the addition of IF or BrF across the double bond. There have been no reports of reactions of these compounds with pseudo-halides such as cyanogen bromide or trifluoromethylsulphenyl chloride. We chose to study the reaction of perfluoroisobutene (**1**) with silver fluoride and the subsequent reaction of perfluoro-t-butylsilver (**2**) with the aforementioned pseudo-halides.



$$CF_3-\underset{\underset{\textstyle CF_3}{|}}{\overset{\overset{\textstyle CF_3}{|}}{C}}-Ag + CF_3SCl \longrightarrow CF_3-\underset{\underset{\textstyle CF_3}{|}}{\overset{\overset{\textstyle CF_3}{|}}{C}}-SCF_3 + AgCl \qquad (1)$$

2 **3**

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Experimental

General procedures

WARNING! Because of the high toxicity of perfluoroisobutene by the inhalation route, efficient fume hoods should be used when performing experiments using this compound. ^{19}F NMR spectra were recorded on a Varian FT-80A or Varian XL-200 spectrometer. The external reference used for the ^{19}F NMR spectra was CCl_3F. A positive chemical shift value (δ, ppm) is taken downfield from the external reference. Mass spectra were obtained on a Finnigan model 5100 GC/MS equipped with a silica 25 m×0.31 mm (i.d.) SC-54 capillary column (J&W Scientific, Rancho Cordova, CA). Routine GLC separations were accomplished using a Hewlett–Packard 5890A gas chromatograph equipped with a J&W Scientific (Folsom, CA) 30 meter DB5 0.53 mm (i.d.) column. IR spectra were obtained using a Nicolet Model 10-DX FR-IR spectrometer. A Lauda RCS6 refrigerated circulating bath was used to cool the distillation condenser to −20 °C in all distillations where the desired product was expected to boil below 50 °C. Perfluoroisobutene was used as received from Armageddon Chemical Company (Durham, NC). Silver fluoride was obtained from PCR Inc. (Gainesville, FL) and was ground with a mortar and pestle in a dry-bag before use. Acetonitrile was distilled from calcium hydride prior to use.

Preparation of perfluoro-t-butyl trifluoromethyl sulfide (3) (nc)

Powdered silver fluoride (23.2 g, 0.183 mol) was transferred to a three-necked round-bottomed flask equipped with a gas inlet tube, mechanical stirrer and a dry-ice condenser. Freshly distilled acetonitrile (150 ml) was added to the flask followed by 43.6 g (0.128 mol) of perfluoroisobutene. After stirring for 1 h at ambient temperature, the flask was cooled in an ice-water bath while 26.3 g (0.193 mol) of trifluoromethylsulfenyl chloride (Armageddon Chemical Co, Durham, NC) was added with efficient stirring as a thick white precipitate (silver chloride) formed. The volatile components were separated from the reaction mixture by flash distillation into a dry-ice/acetone cooled receiver. After warming the distillate to room temperature, two layers were observed and separated. The bottom layer, containing the desired product, was distilled through a 6″ helipac (nichrome) column to yield 33.25 g (56.8%) of the desired product **3** (b.p., 65–67.5 °C). ^{13}C NMR: δ 65.2 [m, $^2J_{C-F}=31$ Hz, $^3J_{C-F}=2$ Hz, 1C, $(CF_3)_3\mathit{C}SCF_3$], 120.4 [q, $^1J_{C-F}$]=289 Hz, 3C, $(\mathit{C}F_3)_3C$], 126.6 [q, $^1J_{C-F}=312$ Hz, 1C, $(CF_3)_3CS\mathit{C}F_3$]; ^{19}F NMR: $\delta-39.5$ [m, $^5J_{C-F}=6.8$ Hz, 3F, $-SC\mathit{F}_3$], -66.1 [q, $^5J_{C-F}=6.8$ Hz, 9F, $(C\mathit{F}_3)_3CSCF_3$]. Mass spectrum (EI): $C_5F_{12}S^+$, 320 (14); $C_5F_{11}S^+$, 301 (100); $C_4F_7S^+$, 213 (46); $C_2F_3S^+$, 113 (17); CF_3^+, 69 (23). IR: 1280 (vs), 1225 (m), 1207 (w), 1195 (m), 1175 (m), 1105 (s), 1060 (m), 1040 (m), 765 (w) cm^{-1}.

Preparation of perfluoro-t-butyl bromide (4) [6]

Into a three-necked round-bottomed flask, equipped with a mechanical stirrer, gas-inlet tube, and a dry-ice condenser, was placed 18.9 g (0.149

mol) of ground silver fluoride and 75 ml of freshly distilled acetonitrile. After adding 29.9 g (0.149 mol) of perfluoroisobutene, the reaction mixture was stirred for 1 h at ambient temperature. The reaction flask was then cooled (ice–water bath) before cyanogen bromide (16.0 g, 0.149 mol) dissolved in 75 ml of acetonitrile was added dropwise. The volatile components were separated from the reaction mixture by a flash distillation under reduced pressure. Subsequent purification by distillation using a 4″ column packed with helipac nichrome turnings afforded 19.49 g (43.8%) of **4** (b.p., 43–45 °C) which was isolated as a crystalline solid. ^{13}C NMR: δ 57.5 [m, $^{2}J_{C-F}=31.9$ Hz, 1C, $[(CF_3)_3\mathit{C}Br]$, 119.8 [q, $^{1}J_{C-F}=287$ Hz, 3C, $(\mathit{C}F_3)_3CBr]$; ^{19}F NMR: $\delta-66.4$ (s, 9F). Mass spectrum (EI): $C_4F_9Br^+$, 300 (5) and 298 (6); $C_4F_8Br^+$, 279 (50); $C_3F_5Br^+$, 210 (63); $C_3F_4Br^+$, 191 (72); $C_2F_5{}^+$, 131 (96); $CF_3{}^+$, 69 (100). IR: 1280 (vs), 1220 (s), 965 (s), 937 (m), 760 (w), 723 (m), and 540 (w) cm^{-1}.

Preparation of perfluoro-t-butyl trifluoromethyl disulfide (6) (nc)

Into a 300 ml three-necked round-bottomed flask, equipped with a magnetic stir-bar, gas-inlet tube and a dry-ice condenser, was placed 8.66 g (0.068 mol) of finely ground silver fluoride and 75 ml of freshly distilled acetonitrile. After cooling the flask in an ice-water bath, 16.6 g (0.083 mol) of perfluoroisobutene was added. The reaction mixture was allowed to warm to ambient temperature and was magnetically stirred for 1 h. Then 6.6 g (0.2 mol) of sulfur was added and the reaction mixture was heated at 45–50 °C for 1 h. The reaction mixture was subsequently cooled to − 10–0 °C and 22.4 g (0.082 mol) of trifluoromethylsulfenyl chloride was slowly added. After allowing the reaction mixture to warm to room temperature, the volatile components were separated by flash distillation under reduced pressure. On warming to room temperature, two layers were observed and separated. The lower layer, consisting of the desired product, was purified by distillation using a 6″ column packed with nichrome helipac turnings to afford 19.0 g (79.5%) of the disulfide **6** (b.p., 101–102 °C). ^{13}C NMR: δ 65.6 [m, $^{2}J_{C-F}=25.4$ Hz, 1C, $(CF_3)_3\mathit{C}SSCF_3]$, 120.6 [q, 9F, $(\mathit{C}F_3)_3CSSCF_3]$, 126.9 [q, $^{1}J_{C-F}=320$ Hz, $(CF_3)_3CSS\mathit{C}F_3]$; ^{19}F NMR: δ -30.8 [s, 3F, $(CF_3)_3CSSC\mathit{F}_3]$, -11.7 [s, 9F, $(C\mathit{F}_3)_3CSSCF_3]$. Mass spectrum (EI): $C_5F_{12}S_2{}^+$, 352 (14); $C_5F_{11}S_2{}^+$, 333 (18); $CF_3S_2{}^+$, 133 (70); $CF_2S_2{}^+$, 113 (51); $CF_3{}^+$, 69 (100); $S_2{}^+$, 64 (58). IR: 1268 (vs), 1180 (vs), 1102 (vs), 972 (s), 960 (s), 926 (m), 757 (m), 724 (s), 542 (w), 444 (w) cm^{-1}.

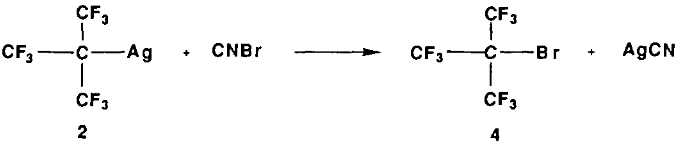
Results and discussion

We have successfully utilized silver fluoride in a reaction with **1** in order to prepare several new derivatives containing the perfluoro-t-butyl moiety. For example, after the formation of perfluoro-t-butylsilver (**2**), subsequent addition of trifluoromethylsulfenyl chloride yields the previously unknown unsymmetrical sulfide [eqn. (1)], perfluoro-t-butylmethyl sulfide (**3**), in good isolated yield (Table 1).

TABLE 1

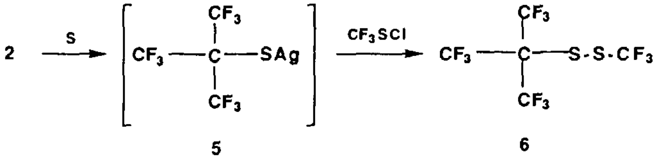
Isolated product yields of perfluoro-t-butyl derivatives

Reactants	Products	B.p. (°C)	Yield (%)
2 + CF_3SCl	**3**	65–67.5	56.8
2 + CNBr	**4**	43–45	43.8
5 + CF_3SCl	**6**	101–102	79.5



(2)

When cyanogen bromide is allowed to react with **2**, silver cyanide and perfluoro-t-butyl bromide (**4**) first reported by Aldrich *et al.* [6] are formed instead of perfluoro-t-butyl cyanide and silver bromide [eqn. (2)]. Apparently, the bromine atom is the more positive site in the cyanogen bromide molecule and it exhibits the typical ‘positive halogen’ reactivity.



(3)

Compounds such as **2** have been reported [5] to insert sulfur in the carbon to silver bond. We established that silver perfluorothio-t-butoxide (**5**) was indeed formed upon treatment of **2** with sulfur since it reacted with trifluoromethylsulfenyl chloride to form perfluoro-t-butyl trifluoromethyl disulfide (**6**) [eqn. (3)]. The disulfide **6** is, to our knowledge, the first known perfluorinated unsymmetrical disulfide.

Acknowledgement

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