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Exchange reactions of organotin and organosilicon compounds with vinylic fluorine

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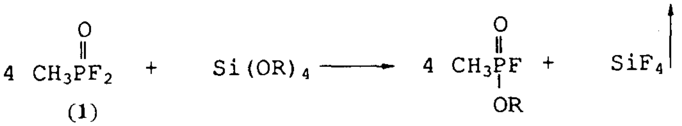
Abstract

Compounds carrying reactive fluorine atoms, such as methylphosphonic difluoride and perfluoroisobutene, undergo facile exchange with organosilanes and stannanes. Reactions with protic nucleophiles also yield similar products. To account for the products formed and observed reactivity differences, appropriate mechanisms are proposed. The reactions described herein have considerable synthetic utility.

Introduction

The present work is an extension of an earlier report from our laboratory [1] on the development of an innovative procedure for the synthesis of alkyl phosphonofluoridates using an exchange reaction between methyl phosphonic difluoride and organosilicon esters:



$$4\ \underset{(1)}{CH_3\overset{\overset{O}{\|}}{P}F_2} + Si(OR)_4 \longrightarrow 4\ CH_3\underset{\underset{OR}{|}}{\overset{\overset{O}{\|}}{P}}F + SiF_4\uparrow \qquad (1)$$

Its advantages are that (1) a solvent is not required and (2) the only byproduct of their action is a gaseous fluorinated silane which evolved as the phosphonofluoridate is formed. To broaden the scope of its usefulness and application, this procedure is now extended to reagents other than silicon.

Results and discussion

Of the elements below silicon in Group IVA, the organotin reagents have received the most attention from the synthetic organic chemistry viewpoint. As a result of our earlier success with organosilicon reagents, we have now explored the use of organotin esters in exchange reactions with compounds

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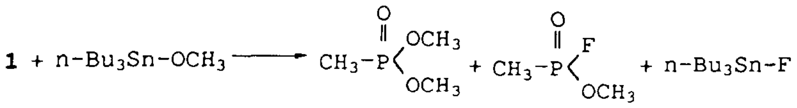
carrying reactive fluorine atoms. Upon mixing an equimolar amount of **1** and tributyltin methoxide (**2**), an exothermic reaction immediately ensued and a solid material formed in the reaction mixture. Extraction of the mixture with carbon tetrachloride, and the usual processing of the extract furnished 67% dimethyl methylphosphonate (**3**), 10% of methyl methylphosphonofluoridate (**4**) and 19% starting material:

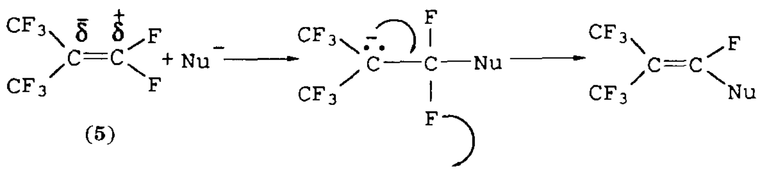


$$\mathbf{1} + n\text{-}Bu_3Sn\text{-}OCH_3 \longrightarrow CH_3\text{-}P(O)(OCH_3)_2 + CH_3\text{-}P(O)(F)(OCH_3) + n\text{-}Bu_3Sn\text{-}F \qquad (2)$$

(**2**) (**3**) (**4**)

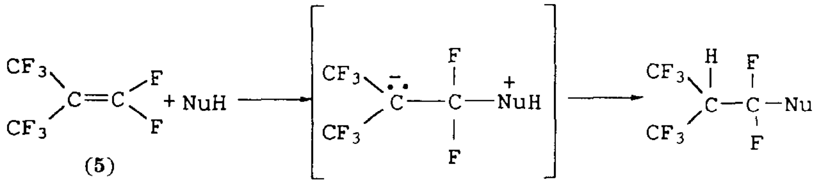
The yields, however, have not been optimized. None the less, the higher yields of **3** indicate enhanced reactivity of **2** towards exchange with organotin reagents than with organosilicon reagents. Since the secondary reaction produces the diester product, this reaction does not appear to be particularly useful for the routine synthesis of the alkyl phosphonofluoridates.

However, the enhanced reactivity of **2** should make it useful in exchange reactions in other systems such as perfluoroisobutene (**5**) [2]. It is known that perfluoro olefins are reactive towards nucleophiles via addition–elimination reactions such as:



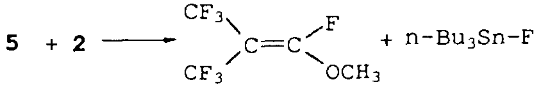
(**5**) (3)

or proton transfer such as:



(**5**) (4)

Trimethyltin methoxide (**2**) did react with **5** to give **6** (62% isolated yield) when **2** was added to a solution of **5** in xylenes at 0–5 °C:

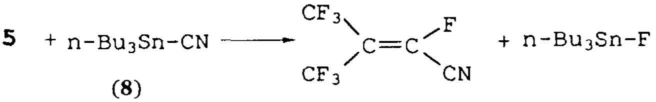


$$\mathbf{5} + \mathbf{2} \longrightarrow (CF_3)_2C{=}CF(OCH_3) + n\text{-}Bu_3Sn\text{-}F \qquad (5)$$

(**6**), 62%

Vinyl ether **6** is an extremely useful intermediate, which has been previously prepared by the addition of methanol to **5** followed by dehydrofluorination of 1-methoxy-2-hydroperfluoro-isobutane with sodium hydroxide [3].

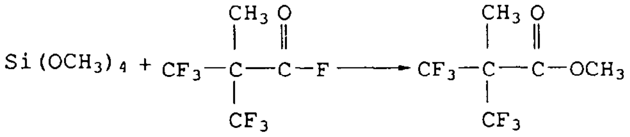
This reaction was then applied to a new synthesis of perfluoro-β,β-dimethylacrylonitrile (**7**) using tributyltin cyanide (**8**) in a reaction with **5**:



(**8**) (**7**), 10% (6)

Incidentally, **7** is a difficult compound to synthesize [4, 5]. Under the conditions used for the preparation of **6** (eqn. (5)), **7** was synthesized in 10% yield. It is not clear why the yield of **7** is so low compared with that of **6**. One reason may be that **8** is less reactive than **2**. For even a 20% excess of **8** did not significantly affect the yield of **7**. No disubstituted product, namely $(CF_3)_2C{=}C(CN)_2$, was observed in the reaction mixture.

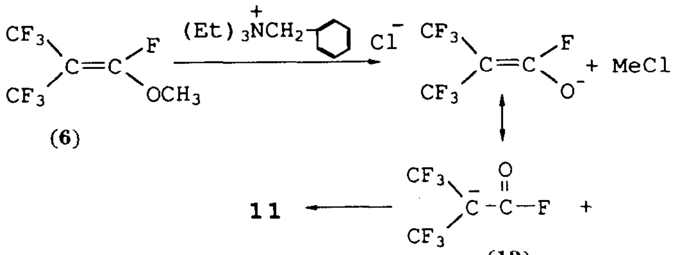
The fact that **5** reacts with tetramethoxysilane (**9**) only on heating at 180 °C clearly confirms the enhanced reactivity of organotin esters. Although the presence of **6** in the reaction mixture was confirmed, methyl α-methylhexafluoroisobutyrate (**11**) was the major product. Apparently, **11** must have resulted from methyl α-methylhexafluoroisobutyryl fluoride (**10**):



$$Si(OCH_3)_4 + CF_3-\underset{CF_3}{\overset{CH_3}{C}}-\overset{O}{\overset{\|}{C}}-F \longrightarrow CF_3-\underset{CF_3}{\overset{CH_3}{C}}-\overset{O}{\overset{\|}{C}}-OCH_3 \qquad (7)$$

(**9**) (**10**) (**11**)

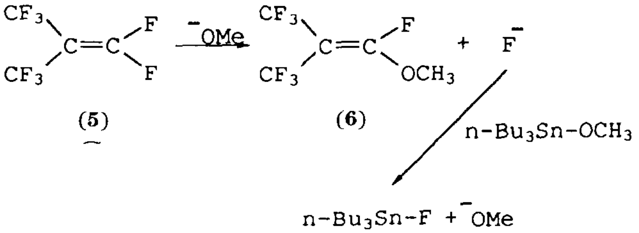
Since the formation of **11** via the chloride ion induced rearrangement of **6** has been reported [3] using a phase transfer catalyst such as benzyltriethylammonium chloride, this arrangement could cause the demethylation of **6** to an intermediate ionic species such as **12**. Methylation with CH_3Cl or with **6** must have resulted in **10**:



(**6**) (**12**) (8)

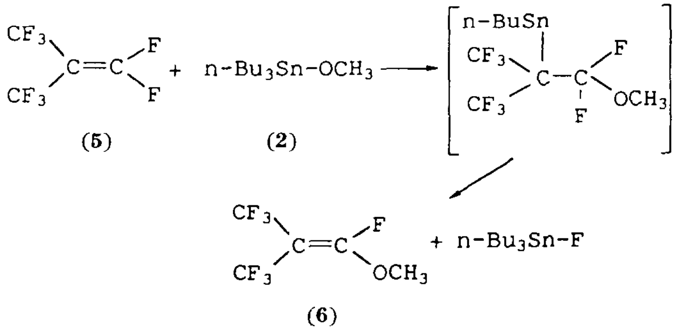
The fluoride ion, in splitting off the fluoro compounds in the reaction mixture, could have served as the catalyst for the conversion of **6** into **11**.

Even though the reactions of **1** and **5** appear to be similar, the mechanistic pathways may in fact differ. Based on the catalytic effect of water on the reaction rate, a mechanism was proposed for the reaction of **1** with organosilicon esters [1]. An analogous mechanism involving the catalytic effect of free methoxide can be proposed for the fluoride ion thus generated, which in turn may then regenerate the reactive methoxide to form tributyltin fluoride:



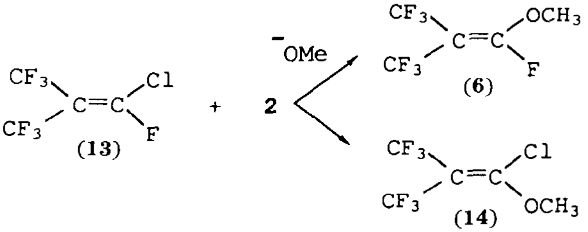
(9)

An alternative approach involves the addition of **2** to **5** to give the intermediate which subsequently eliminates tributyltin fluoride and furnishes **6**:



(10)

To see whether indeed the tin moiety played any role in the formation of the transition species leading to **6**, the reaction of 1-chloroperfluoroisobutylene (**13**) [6] with **2** was investigated. If the methoxide is involved in the reaction, as chloride is a better leaving group than fluoride, **6** should be the predominant product. Alternatively, if tin is involved in the transition state, the 1-chloro-1-methoxyperfluorobutylene (**14**) should be formed



(11)

and thus lend credence to the transition state involving the tin moiety (eqn. (10)).

Our results prove that products **6** and **14** are formed in almost equal amounts and thus provide definite evidence for the significant role and involvement of the transition state mechanism (eqn. (10)) and possibly in the reaction of **2** with **5** (eqn. (5)). Similar results were obtained using petroleum ether as a solvent.

Conclusion

Earlier it was shown that novel exchange reactions of organosilicon esters with methylphosphonic difluoride give high yields of the alkyl phosphonofluoridates [1]. Now we have extended this methodology through the use of organotin esters. Perfluoroisobutene yields products resulting from the exchange of fluorine atom for a methoxy or a cyano group. These syntheses may represent significant improvements over existing preparations.

Experimental details

General procedures

Warning! Because of the high toxicity of perfluoroisobutene by the inhalation route, efficient fume hoods should be used when performing experiments with this compound. ^{19}F and ^{13}C spectra were recorded on a Varian VXR-400S spectrometer using CCl_3F as an external reference (machine frequencies, 100.58 MHz (^{13}C), 376.29 MHz (^{19}F), 400 MHz (^{1}H)). A positive chemical shift value δ, (ppm) is taken downfield from the external reference. Mass spectra were obtained on a Finnigan model 5100 gas chromatograph–mass spectrometer equipped with a silica 25 m × 0.31 mm (inside diameter) SC-54 capillary column (J&W Scientific, Rancho Cordova, CA). Routine gas–liquid chromatography (GLC) separations were accomplished using a Hewlett–Packard 5890A gas chromatograph equipped with a 30 m DB-5 0.53 mm (inside diameter) column (J&W Scientific, Folsom, CA). IR spectra were obtained using a Nicolet model 10-DX Fourier transform IR spectrometer. Unless otherwise noted, the IR and nuclear magnetic resonance (NMR) spectra were run on the neat compound. Spinning-band distillations were carried out using a B/R-36T column (B/R Instrument Co., Pasadena, MD). A Lauda RCS6 refrigerated circulating bath was used to cool the distillation condenser to −20 °C in all distillations where the product was expected to boil below 50 °C. Perfluoroisobutene was used as received from Armageddon Chemical Company (Durham, NC). Tributyltin cyanide and tributyltin methoxide, obtained from Aldrich Chemical Company, were used as received. Acetonitrile was dried by refluxing over calcium hydride. Xylene was dried over sodium ribbon.

Preparation of 1-methoxy-1,3,3,3-tetrafluoro-2-trifluoromethyl-1-propene (6) [3]

A three-neck flask of 100 ml capacity was equipped with a gas-tight mechanical stirrer, gas inlet tube, a dry ice–acetone cooled condenser and a pressure-equalized dropping funnel. The flask was charged with 40 ml of xylene. The reaction was cooled to ice temperature and perfluoroisobutene (20 g, 0.1 mol) was introduced into the reaction flask. A solution consisting of 28.8 ml (32.1 g, 0.1 mol) of tributyltin methoxide was added dropwise with good stirring. A white solid formed immediately. After addition was complete, the volatile liquid portion was flash distilled into a dry-ice–acetone cooled receiver under reduced pressure (1 Torr). The flash distillate was twice distilled through a 6 in. Vigreux column to give 14.0 g of **6** (b.p., 101–103 °C) (62%) with a purity of 94.3% as determined by GLC. ^{13}C NMR (acetonitrile) C(F)(OCH_3) δ: 163.8 (m, $J=307$ Hz, $J=2.5$ Hz); C(F)(O$\mathit{C}H_3$) δ: 58.6 (d, $J=13.9$ Hz); $\mathit{C}(CF_3)_2$ δ: 81.2 (d of sept, $J=25.3$ Hz, d, $J=35.5$ Hz); $\mathit{C}F_3$'s δ: 123.5, 123.8 (qt, $J=269$ Hz). ^{19}F NMR (acetonitrile) (CF_3)(*trans*) δ: -55.7 (q, $J=7.7$ Hz, $J=11.2$ Hz); (CF_3)(*cis*) δ: -56.0 (q, $J=7.7$ Hz, $J=26.6$ Hz); C–F δ: -63.2 (s). Mass spectrum (electron impact): $C_5H_3F_7O^+$, 212 (52); $C_5H_3F_6O^+$, 193 (100); $C_4F_6O^+$, 178 (5); $C_4F_5O^+$, 159 (52); $C_4F_6^+$, 150 (5); $C_2H_3F_3O^+$, 100 (5); $C_3H_3F_3O^+$, 93 (13); CF_3^+, 69 (43). IR ν_{max}: 2973.1 (vw), 1779.2 (vw), 1712.9 (vs), 1469.3 (m), 1374.8 (vs), 2324.8 (m), 1269.4 (s), 1220.2 (m), 1176.5 (vs), 1148.1 (m), 1110 (w), 1070 (vs), 995.7 (s), 762.2 (w), 717.4 (w) cm^{-1}.

Preparation of 1-cyano-1,3,3,3-tetrafluoro-2-trifluoromethyl-1-propene (7) [4, 5]

A flame-dried argon gas purged 1 l three-neck round-bottomed flask, equipped with a magnetic stirrer, gas inlet, immersed thermometer and a Dry Ice–alcohol cooled finger condenser terminating into a vented inert gas inlet tube, was first charged with tributyltin cyanide (53.30 g, 0.1686 mol) in a glove bag; then 500 ml of xylene was directly distilled into the reaction flask. The resulting solution was stirred at ambient temperature while perfluoroisobutene (**5**) (34.60 g, 0.1730 mol, 3% excess) was slowly sparged into the reaction flask. The reaction mixture temperature rose 10 °C over the period of addition. The reaction was accompanied by the formation of a deep-red color. After being heated at 30 °C for 1 h and at 50 °C for an additional hour, the reaction mixture was then flash distilled into a Dry Ice–alcohol cooled receiver. The crude material, containing **7**, 17.5% unreacted **5** and solvent, was first concentrated by distillation on a spinning-band column to remove **5**, which tends to codistil with **7**. The residue was distilled through a 6 in. silvered vacuum-jacketed distilling column filled with Helipack Nichrome packing and a reflux distilling condenser cooled with a refrigerated circulating bath at 0 °C. The product **7** distilled over at 51–53 °C to yield 3.35 g (9.60%). The GLC indicated the purity to be 98.6%. Mass spectrum (electron impact): $C_5F_7N^+$, 207 (10); $C_5F_6N^+$, 188 (30); $C_4F_3^+$, 181 (3), $C_4F_6^+$, 162 (10); $C_4F_3N^+$, 157 (5); $C_4F_4N^+$, 138 (60); $C_4F_3N^+$, 119 (5); $C_3F_3N^+$, 107 (4); $C_4F_2N^+$, 100 (37); $C_3F_3^+$, 93 (22); $C_2F_2N^+$, 76 (5); CF_3^+, 69 (100). IR ν_{max}: 2250.0 (w), 1682.2 (m), 1540.2 (vw), 1360.2 (vs), 1286.6 (m), 1249.4 (s), 1205.5 (vs), 1161.1 (w), 1003.7 (m), 942.2 (m), 757.9 (vw), 719.5 (w) cm^{-1}. ^{19}F NMR (xylene): $C\mathit{F}_3$(*trans*) δ: -61.6 (d of d, $J=7.5$, 7.8 Hz); $C\mathit{F}_3$(*cis*) δ: -60.8 (d of d, $J=7.2$, 23 Hz); $C\mathit{F}$ δ: -94.26 (d of d, $J=7.5$, 23 Hz).

*Preparation of α-methylhexafluoroisobutyryl fluoride (**10**) [3]*

A flame dried argon purged single-neck round-bottomed flask of 10 ml capacity, equipped with a stir bar and a distillation unit terminating into a Dry Ice–alcohol cooled receiver, was charged with 7.40 g of **6** (35 mmol) and 339 mg of benzyltriethylammonium chloride (1.5 mmol, 4.3 mol.%). The stirred slurry was heated to 85–90 °C. The distillation head temperature gradually rose to 60–65 °C. The crude distillate was redistilled at 48–49 °C to give 5.0 g of **10** (75%) (48 °C [3]). The GLC indicated a purity of 97.5%.

*Preparation of methyl α-methylhexafluoroisobutyrate (**11**)*

A flame dried heavy-wall Carius tube of 5 ml capacity was charged with 512 mg of α-methylhexafluoroisobutyryl fluoride (**10**) (2.41 mmol) and 186 mg of tetramethoxysilane (1.21 mmol, 100% excess). After being cooled to −70 °C, the flask was evacuated to 90 Torr and sealed. The reaction mixture was heated at 150 °C for 24 h. Examination of the reaction mixture by ^{13}C, ^{19}F and ^{1}H NMR indicated that only the desired product, **11**, was present. ^{13}C NMR: $\mathit{C}H_3$–C δ: 12.6 (sept, $J=2.2$ Hz); CH_3–*C* δ: 57.7 (sept, $J=27.6$ Hz); $(\mathit{C}F_3)_2$ δ: 123.1 (q, $J=284$ Hz); ($-\mathit{C}=O$) δ: 163.2 (s); $-O\mathit{C}H_3$ δ: 53.0 (s). ^{19}F NMR: $C(C\mathit{F}_3)_2$ δ: 70.1 (s). ^{1}H NMR $C\mathit{H}_3-C(CF_3)_2$ δ: 1.0; ($-OC\mathit{H}_3$) δ: 3.2.

*Preparation of 1-Chloro-1-methoxy-2-trifluoromethyl-3,3,3-trifluoro-1-propene (**14**) (nc)*

A flame dried argon gas purged three-neck round-bottomed flask of 250 ml capacity, equipped with a mechanical stirrer, immersed thermometer, a self-compensating dropping funnel and a reflux condenser terminating into a vented inert gas inlet, was charged with 75 ml of acetonitrile and 15.75 g of 1-chloro-2-trifluoromethyl-1,3,3,3-tetrafluoro-1-propene (**13**) (72.75 mmol). The flask was cooled to ice temperature while 22.0 ml of tributyltin methoxide (24.5 g, 76.40 mmol, 5% excess) in 50 ml of freshly distilled acetonitrile was added with stirring. A heavy white precipitate formed immediately. After the addition was complete, the reaction mixture was stirred for an additional hour while coming to ambient temperature. GLC of the crude reaction mixture indicated that it contained a 1:1 mix of the 1-fluoro-1-methoxy compound (**6**) and the 1-chloro-1-methoxy compound (**14**). The material was flash distilled under reduced pressure into a Dry Ice–alcohol cooled receiver and then twice distilled through a 6 in Nichrome wire-packed vacuum column having a variable take-off head, to give 2.20 g of **14** (26.2%) (b.p., 117–120 °C) 95.5% pure by GLC. ^{13}C NMR: $\mathit{C}F_3$'s δ: 123.0, 123.3 (q, $J=272$ Hz); $CF_3-\mathit{C}=$ δ: 101.1 (sept, $J=33.3$ Hz); $=\mathit{C}-Cl(OCH_3)$ δ: 159.7 (m, $J=2.5$ Hz); $C(O\mathit{C}H_3)$ δ: 60.8 (s). ^{19}F NMR: (CF_3(*cis*)) δ: −57.4 (q, $J=9.2$ Hz), (CF_3(*trans*)) δ: −58.3, (q, $J=9.0$ Hz). IR ν_{max}: 3021(w), 2966(w), 2864(w) 2257(w), 1816(m), 1768(m), 1700(w), 1630(vs), 1457(s), 1338(vs), 1304(s), 1273(m), 1204(vs), 1151(vs), 1061(m), 991(s), 935(s), 848(s), 759(m), 738(m), 708(s), 635(vw), 545(vw), 471(vw) cm^{-1}.

Acknowledgments

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