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EXCHANGE REACTIONS OF ORGANOTIN AND ORGANOSILICON COMPOUNDS WITH MILD FLUORINATING AGENTS

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A diverse group of compounds bearing labile fluorine atoms have been found to undergo similar exchange reactions with various organosilanes and stannanes. For example, methylphosphonic difluoride, boron trifluoride etherate, and perfluoroisobutene all react with both organosilicon and organotin alkoxides to give products resulting from the exchange of fluoride for an alkoxide group. In contrast to reactions involving the use of protic nucleophiles that may yield these products, hydrogen fluoride is not formed as a by-product in these systems. Organotin compounds have been found to be more reactive than their silicon based analogs. Mechanisms are proposed to account for the products and the reactivity differences observed in these systems. These reactions have proven useful for the routine synthesis of various compounds.

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PREFACE

The work described in this report was authorized under Project No. 1C162622A554, Chemical Munitions. This work was started in September 1986 and completed in October 1988. The experimental data are recorded in laboratory notebooks 84-0145 and 87-0026.

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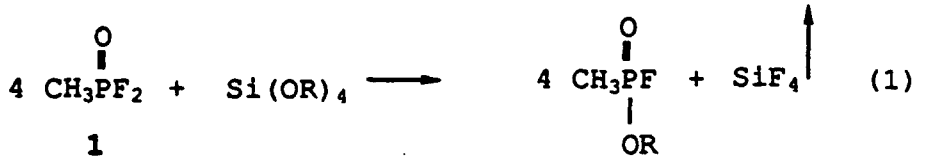
EXCHANGE REACTIONS OF ORGANOTIN AND ORGANOSILICON COMPOUNDS WITH MILD FLUORINATING AGENTS

1. INTRODUCTION

The Chemical Research, Development and Engineering Center (CRDEC) has an ongoing responsibility to prepare, purify, and characterize samples of the alkylphosphonofluoridates and other compounds containing fluorine for use in various research programs. Since our earlier report[1] on the discovery of a new procedure for the synthesis of the alkylphosphonofluoridates involving the use of organosilicon esters in an exchange reaction with methylphosphonic difluoride (**1**) (Eq.1), we have attempted to



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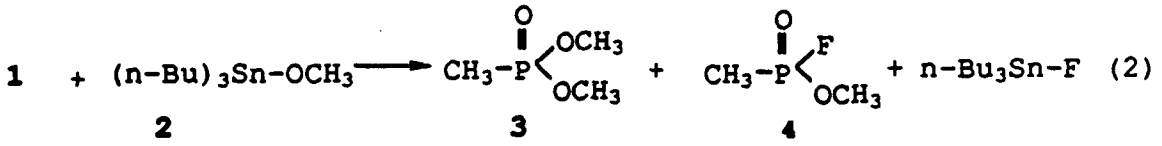
apply this methodology to other novel systems.

The advantages of this method over previous syntheses for the alkylphosphonofluoridates are that a solvent is not needed and the only by-product from the reaction is a gaseous fluorinated silane that evolves from the reaction mixture as the phosphonofluoridate product is formed. We have now explored this new synthetic methodology for the synthesis of other compounds bearing fluorine atoms, to attempt to broaden the spectrum of reactivities observed through the use of similar reagents based upon atoms other than silicon.

2. RESULTS AND DISCUSSION

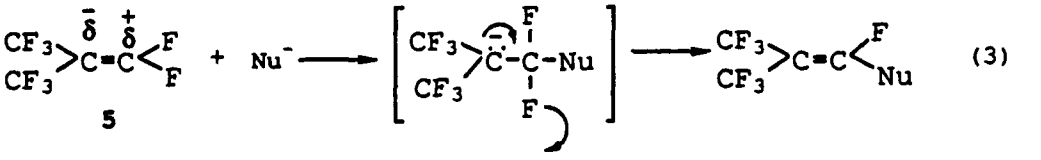
Of the elements below silicon in group IVA of the periodic table, the organic compounds of tin have received the most attention. Accordingly, we decided to explore the use of organotin esters in exchange reactions with compounds bearing labile fluorine atoms, such as **1**. Upon mixing an equimolar amount of **1** and tributyltin methoxide (**2**), an exothermic reaction immediately ensued and a solid material formed in the reaction mixture. After extraction of the mixture with carbon tetrachloride, and the usual processing of the extract, ^{31}P NMR analysis revealed that the solution was composed of 67% dimethyl

methylphosphonate (**3**), 10% of methyl methylphosphonofluoridate (**4**), and 19% of unreacted **1** (Eq.2). The yields have not been

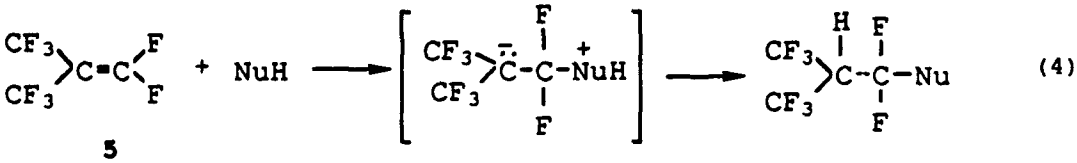


optimized. Nonetheless, it is apparent from the high percentage yield of the diester formed in this reaction that **2** is much more reactive toward the exchange reaction with **1** and **4** than are the alkoxy silanes. Because of the secondary reaction with the alkyl alkylphosphonofluoridate leading to the diester product, this reaction does not appear useful for the routine synthesis of the alkyl alkylphosphonofluoridates.

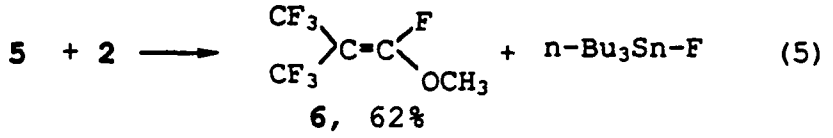
It is possible that the high reactivity of **2** may make it useful in exchange reactions in other systems. One such compound that has received much attention is perfluoroisobutene (**5**).[2] The reactions of unsaturated fluorocarbons are strikingly different from their hydrocarbon analogs. Whereas the chemistry of olefinic hydrocarbons is dominated by reactions with electrophiles, the perfluoro olefins are reactive toward nucleophiles. There are two main types of reactions which perfluoro olefins undergo in the presence of nucleophiles. One type is the addition-elimination reaction, in which the nucleophile adds to the more electropositive carbon of the double bond to give an intermediate carbanion, which eliminates fluoride to give an intermediate carbanion which in turn eliminates fluoride to give the product bearing the nucleophile (Eq.3). The other type involves a



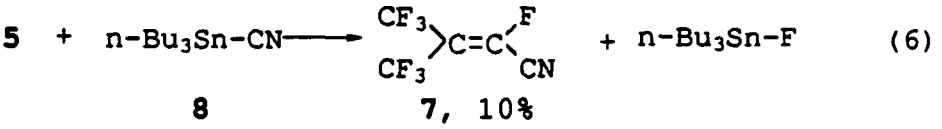
reaction with a protic nucleophile to give a dipolar intermediate, which undergoes an internal proton transfer. The reaction effectivelv adds HNu across the double bond (Eq.4).



It was found that **2** did indeed react with **5** to give the product resulting from what appears to be an addition-elimination reaction.In this case however, the actual mechanism may proceed via elimination from a dipolar intermediateof the type shown in Eq.4. The product **6** was formed in a 62% isolated yield upon adding **2** to a solution of **5** in xylene at 0 - 5 °C, followed by purification by distillation (Eq.5).

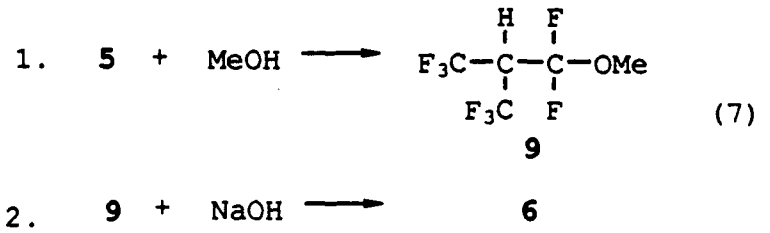


This reaction was also applied to a new synthesis of perfluoro β,β-dimethylacrylonitrile (**7**) (Eq.6), through the use of

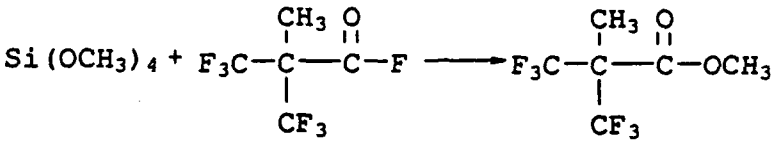


tributyltin cyanide (**8**) in a reaction with **5**. The nitrile **7** is a difficult compound to synthesize, and it has been the subject of synthetic study in the open literature as well as at CRDEC.[3,4] Compound **7** was obtained in an isolated yield of 10% using reaction conditions similar to those employed for the synthesis of **6** (Eq.5). It is not clear why the yield of **7** is so much lower than that of **6**. Perhaps **8** is less reactive than **2**. Even when a 20% excess of **8** was used in the reaction, a significant amount of **5** could be recovered from the reaction mixture.

The vinyl ether **6** is a valuable intermediate leading to useful monomers in polymer chemistry. A report by Misaki[5] describes the synthesis of **6** by a two step reaction sequence involving the addition of methyl alcohol across the double bond of **5** to give 1-methoxy-2-hydroperfluoroisobutane (**9**), followed by dehydrofluorination with sodium hydroxide to afford **6** (Eq.7).



The enhanced reactivity of organotin esters over their silicon analogs is also apparent from the reaction of **5** with tetramethoxy silane (**10**). In order to obtain products from the reaction of **5** with **10** it was necessary to heat the two compounds together in a bomb at 180 °C. Although the presence of the vinyl ether **6** was confirmed in the product mixture, the major product was identified as methyl α-methylhexafluoroisobutyrate (**12**). This compound is likely formed from an exchange reaction of **10** with α-methylhexafluoroisobutyryl fluoride (**11**) (Eq.8). The acid



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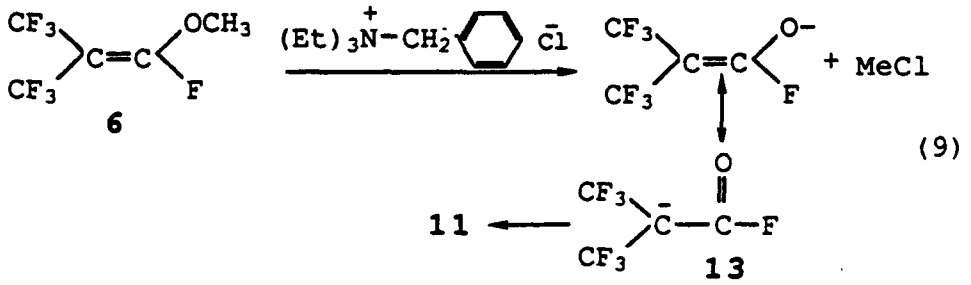
10 **11** **12**

fluoride **11** has been reported to result from the chloride ion induced rearrangement of **6**.[5] This rearrangement, induced by a phase transfer catalyst such as triethylbenzylammonium chloride, involves the demethylation of **6** to give methyl chloride and the anionic species **13**, followed by a methylation of the intermediate anionic species **13** with methyl chloride or **6** resulting in the formation of the acid fluoride **11** (Eq.9). In the tetramethoxy



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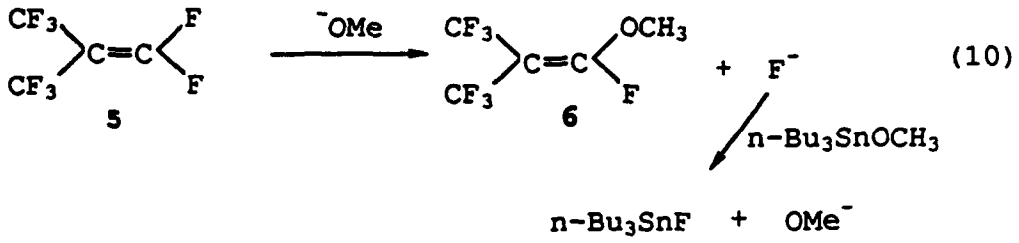
6 **13**

silane-perfluoroisobutene system the catalyst could be the fluoride anion coming from the decomposition of one of the fluorine-bearing compounds in the reaction or product mixture.

Although the reactions of **1** and **5** with the silicon and tin esters appear similar, the mechanisms leading to the products may be different. In the reaction of **1** with the silicon alkoxides, a mechanism was proposed to account for the observed catalytic effect of water on the reaction rate.[1] An analogous mechanism can be proposed for the reaction of **5** with **2** involving a catalytic amount of free methoxide anion, which takes part in the addition-elimination reaction with **2** to generate the product and

fluoride anion (Eq.10). The resulting fluoride anion can then



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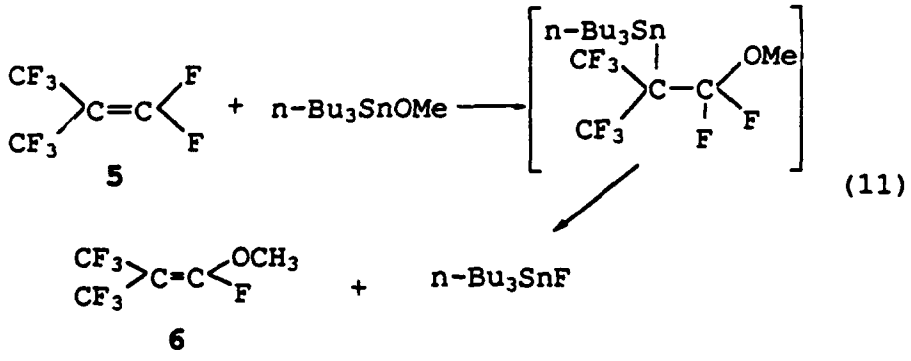
regenerate the reactive methoxide anion from the tributyltin moiety by nucleophilic attack and form the tribuytltin fluoride. An alternate mechanism is one involving the addition of **2** across the double bond to give an intermediate which eliminates tributyltin fluoride and the product **6** (Eq.11).



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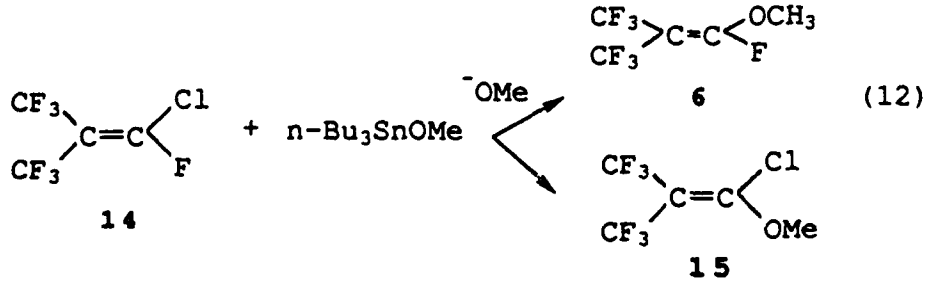
In order to determine if the tin moiety is involved in the transition state leading to the product **6**, the reaction of 1-chloroperfluoroisobutene (**14**)[6] with **2** was studied (Eq.12). If



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the mechanism of this reaction involves free methoxide, then **6** should be the predominant product since chloride is a better leaving group than fluoride. Alternatively, if the tin atom is

involved in the transition state, then the product of fluoride elimination, namely, 1-chloro-1-methoxyperfluoroisobutene (**15**) should be formed. Since the tin to fluorine bond is known to be a very strong bond, the formation of **15** would reasonably be expected to give credence to the transition state mechanism (Eq.11).

Our results show that products **6** and **15** are formed in almost equal amounts whether a polar or nonpolar solvent is used, as the reaction was carried out in both acetonitrile and petroleum ether with similar results. The formation of equal amounts of **6** and **15** provides evidence that the transition state mechanism (Eq.11) plays at the very least, a partial role in the reaction of **5** with **2** (Eq.5), and possibly the reaction of **5** with **8** as well (Eq.6).

3. EXPERIMENTAL SECTION

3.1 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. The machine frequencies used to generate the various spectra using the VXR-400S were: 100.58 MHz for ^{13}C spectra, 376.29 MHz for ^{19}F spectra and 400 MHz for ^{1}H spectra. 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 x 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 30 meter DB-5 0.53 mm(i.d.) column (J&W Scientific, Folsom, CA). IR Spectra were obtained using a Nicolet Model 10-DX FT-IR. Unless otherwise noted, the IR and 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.

3.2 The Preparation of 1-Methoxy-1,3,3,3-tetrafluoro-2-trifluoromethyl-1-propene (**6**).

A 100 ml. capacity three-neck flask was equipped with a gas-tight mechanical stirrer, gas inlet tube, 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 gm., 0.1 mol) was introduced into the reaction flask. A solution consisting of 28.8 ml (32.1 gm, 0.1 mol) of tributyltin methoxide in an equivalent volume of xylene was added dropwise with good stirring. A white solid formed immediately. After the addition was complete, the volatile liquid portion was flash distilled into a dry ice/acetone receiver under reduced pressure (1 mm). The flash distillate was twice distilled through a 6" Vigreux column to give 14.0 gm of **6**, b.p. 101-103 °C (62%) with a purity of 94.3% as determined by glc. ^{13}C NMR: (acetonitrile): $\underline{C}$-(F)(OCH_3) δ: 163.8 (d, 307 Hz, m, 2.5 Hz); C(F)($O\underline{C}H_3$) δ: 58.6 (d, 13.9 Hz); $\underline{C}(CF_3)_2$ δ: 81.2 (d of sept, 25.3 Hz, d,35.5 Hz) ; $\underline{C}F_3$'s δ: 123.5, 123.8 (qt, 269 Hz). ^{19}F NMR: (acetonitrile); $(CF_3)_{(trans)}$ δ: -55.7 (q,7.7 Hz, d, 11.2 Hz), $(CF_3)_{(cis)}$ δ: -56.0 (q, 7.7 Hz, d, 26.6 Hz); C-F δ: -63.2 (m). MS (EI): $C_5H_3F_7O^+$ 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: 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)

3.3 The Preparation of 1-Cyano-1,3,3,3-tetrafluoro-2-trifluoromethyl-1-propene (**7**).

A flame-dried, argon gas-purged one liter three-neck round bottom flask, equipped with magnetic stirrer, gas inlet, immersed

thermometer, and a dry ice/alcohol cooled finger condenser terminating into a vented inert gas inlet tube, was charged with tributyltin cyanide (53.30 gm, 0.1686 mol) in a dry glove bag under an inert atmosphere and 500 ml of dry xylene was then directly distilled into the reaction flask. The resulting solution was stirred at ambient temperature while perfluoroisobutene (34.60 gm, 0.1730 mol,3% xs) was slowly sparged into the reaction flask. The reaction temperature rose 10 degrees during the period of addition, accompanied by the formation of a deep red color. After the reaction mixture was heated at 30 °C for one hour and at 50 °C for an additional hour, it was then flash distilled at 60 °C/10 mm(Hg) into a dry ice/alcohol cooled receiver. The crude product, containing 17.5% unreacted **5**, **7**, plus solvent, was first concentrated by distillation on a spinning band column to remove **5**, which tends to co-distill with **7**. The residue was distilled through a 6" silvered vacuum jacketed distilling column filled with helipack nicrome 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 gm (9.60%). The glc indicated the purity to be 98.6%. MS(EI): $C_5F_7N^+$ 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: 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). ^{19}F NMR: (xylene); $CF_{3(trans)}$ δ: -61.6 (d of d, 7.5 Hz, 7.8 Hz), $CF_{3(cis)}$ δ: -60.8, (d of d, 7.2 Hz, 23 Hz); CF δ: -94.26 (d of d, 7.5 Hz, 23 Hz).

3.4 <u>The Preparation of α- Methylhexafluoroisobutyryl Fluoride (**11**)[5].</u>

A flame-dried argon gas-purged 10 ml capacity single-neck round bottom flask, equipped with a stir bar and a distillation unit terminating into a dry ice/alcohol cooled reciver, was charged with 7.40 gm 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 and the distillation head temperature gradually rose to 60-65 °C. The crude distillate was redistilled at 48-49 °C to give 5.0 gm of **11** (75%) (Lit. bp 48

°C).[5] The glc of the distillate indicated a purity of 97.5%.

3.5 The Preparation of Methyl α-Methylhexafluoroisobutyrate (**12**).

A flame-dried 5 ml heavy wall carius tube was charged with 0.512 gm of α-methyl hexafluoroisobuytyrl fluoride (**11**) (2.41 mmol) and 0.186 gm of tetramethoxy silane (1.21 mmol, 100% xs). After being cooled to -70 °C, evacuated to 90 mm, and sealed, the reaction was heated at 150 °C for 24 hr. 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: $\underline{C}H_3$-C δ: 12.6 (sept, 2.2 Hz); CH_3-$\underline{C}$ δ: 57.7 (sept, 27.6 Hz); $(\underline{C}F_3)_2$ δ: 123.1 (q, 284 Hz); -$\underline{C}$=O δ: 163.2 (s); -O$\underline{C}H_3$ δ: 53.0 (s). ^{19}F NMR: C$(C\underline{F}_3)_2$ δ: 70.1 (s). ^{1}H: $C\underline{H}_3$-C$(CF_3)_2$ δ: 1.0; -O$C\underline{H}_3$ δ: 3.2.

3.6 The Preparation of 1-Chloro-1-methoxy-2-trifluoromethyl-3,3,3-trifluoro-1-propene (**15**).

A flame-dried, argon gas-purged 250 ml capacity three-neck round bottom flask, equipped with a mechanical stirrer, immersed thermometer, self-compensating dropping funnel, and a reflux condenser terminating into a vented inert gas inlet, was charged with 75 ml of freshly distilled acetonitrile and 1-chloro-2-trifluoromethyl-1,3,3,3-tetrafluoro-1-propene[6] **14** (15.75 gm, 72.75 mmol). The flask was cooled to ice temperature and stirred while 22 ml of tributyltin methoxide (24.53 gm, 76.40 mmol, 5% xs) in 50 ml of freshly distilled acetonitrile was added dropwise. 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. A glc of the crude reaction mixture indicated that it contained a 1:1 mix of the 1-chloro **15** and the 1-fluoro methoxy compound **6**. The reaction mixture was flash distilled under reduced pressure into a dry ice/alcohol cooled reciever, and then twice distilled through a 6" nichrome wire packed vacuum jacketed column having a variable take-off head to give 2.20 gm of **15** (26.2%) bp 117-120 °C, 95.5% pure by glc. NMR: ^{13}C NMR: $\underline{C}F_3$'s, δ: 123.0, 123.3 (q, 272 Hz); CF_3-$\underline{C}$= δ: 101.1 (sept, 33.3 Hz); =$\underline{C}$-Cl(OCH_3) δ: 159.7 (m, 2.5 Hz); C

($O\underline{C}H_3$) δ: 60.8 (s) : ^{19}F; CF_{3cis} δ: -57.4 (q, 9.2 Hz), CF_{3trans} δ: -58.3, (q, 9.0 Hz). IR: 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).

4. CONCLUSIONS

Since our discovery of the novel exchange reactions of organosilicon esters with methylphosphonic difluoride to give high yields of the alkylphosphonofluoridates, we have developed new applications for this type of synthetic methodology. The wide range of reactivities observed with the silanes has been broadened through the use of organotin reagents. Perfluoroisobutene has also been shown to undergo these exchange reactions to yield products resulting from the exchange of a fluorine atom for a methoxy or a cyano group. These syntheses represent a new methodology for the synthesis of various compounds.

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