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Fluorodesilylations of fluorophenyltrimethylsilanes with elemental fluorine: discovery of a novel 1,2-migration of the trimethylsilyl group

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Abstract

The main product in the direct elemental fluorination of 4-fluorophenyltrimethylsilane was 1,4-difluorobenzene, produced by the *ipso* electrophilic substitution of the trimethylsilyl group. An unexpected product, 2,5-difluorophenyltrimethylsilane, was also formed as the result of a novel 1,2-migration of the trimethylsilyl group. The same trimethylsilyl 1,2-shifts were observed in the elemental fluorinations of 2-fluoro- and 2,4-difluoro-phenyltrimethylsilanes. We propose that the carbocations formed in the rearrangements were stabilised by the mesomeric effect of the α-fluorine and the greater stability of these intermediates provided the driving force for the trimethylsilyl group migrations. Although the main products in all of the fluorinations were the fluorodesilylated product, the reactions were not totally regioselective and some competing fluorodeprotonation also occurred in the reactions of 2-fluoro- and 2,4-difluoro-phenyltrimethylsilanes. The role of protic acids and Lewis acids in particular triflic acid, trifluoroacetic acid and boron trifluoride in a variety of co-solvents, respectively, was crucial in all the fluorinations we studied, experiments done in their absence gave very poor yields. Optimal conditions for fluorination of silylated substrates are described.

Keywords: Fluorination; Elemental fluorine; Desilylation; Rearrangements

1. Introduction

Fluoroaromatics constitute an enormously important area in chemistry because of their vast and diverse range of commercial applications [1–4]. Although their main use has been in the development of new pharmaceuticals and agrochemicals, they have also been utilised in liquid crystals, polymer chemistry, biomedical applications and even in dyes. In spite of the extensive work in this field, there is no simple method for the regioselective introduction of fluorine into aromatic compounds and researchers still rely on the traditional nucleophilic methods such as the Balz–Schiemann reaction and the 'Halex' process. More recent interest has focused on using electrophilic sources of fluorine to react with the electron rich aromatic ring system. Early examples of electrophilic fluorinating agents were the hypofluorites (ROF) [5], but because of their hazardous nature they have been surpassed by the fluoraza reagents (R^1NFR^2) [6]. This series of compounds are generally stable solids which can be stored and easily handled, and have been used successfully for the fluorination of nucleophilic substrates. Their major disadvantage is that they are very expensive reagents which typically contain only a small amount of active fluorine per mole of reagent. For example, in 1 kg of Selectfluor [7,8] there is only 53.6 g of active fluorine present. They are all synthesised using elemental fluorine and consequently it would be beneficial to be able to use elemental fluorine directly rather than indirectly.

One of the major problems of direct elemental fluorination is the tendency for fluorine to cleave homolytically because of its low bond dissociation energy. This, combined with the low activation energy for the hydrogen abstraction reaction, can start radical chain processes involving the highly reactive fluorine atom and results in low selectivity. For successful electrophilic aromatic substitution it is therefore essential to discourage the radical reactions by using low reaction temperatures, by diluting the substrate, as well as the fluorine and by using polar solvents to encourage heterolytic cleavage of the fluorine. Originally, Rozen et al. [9] used chloroform, acetic acid or nitromethane to enhance the polar processes, but more recently in the electrophilic substitution of aromatics, Conte et al. [10] discovered that the highest yields of monofluorinated products were obtained with more polar solvents in the following order of decreasing polarity.

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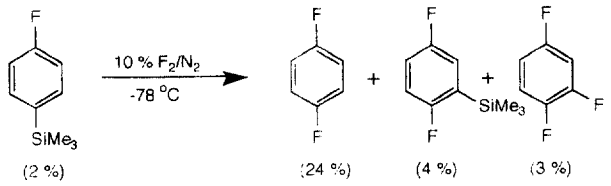
$CF_3CO_2H > CF_3CH_2OH > CH_3OH > CHCl_3 > CFCl_3$

Chambers et al. [11,12] and Purrington and Woodard [13] have also used protonic and Lewis acids, respectively, to promote the electrophilic fluorination of aromatics. The disadvantage of these reactions is that mixtures of isomers are produced, although Chambers et al. have overcome this by using two functional groups whose directional effects reinforce each other. Another method for achieving site selectivity is to metallate the substrate with a group IVb element, it is then possible to cleave the metal/metalloid–aryl bond with electrophilic fluorine to give the corresponding fluoroaromatic via *ipso* aromatic substitution [14–21]. The success of the halodemetallation is based on the weak metal/metalloid carbon bond and higher bond polarity compared to the corresponding carbon–hydrogen bond. Although the fluorination yields have been found to increase down the Group IVb elements [14], organostannanes are very toxic compounds and so we decided to investigate the electrophilic cleavage of aryl–silicon bonds for the synthesis of di- and tri-fluoroaromatics.

2. Results and discussion

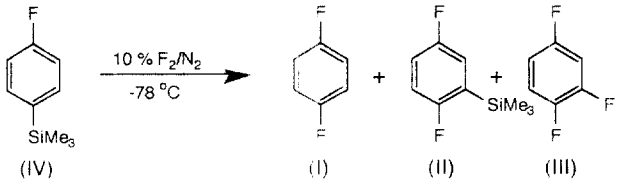
Although reasonable fluorodesilylation yields (20–30%) have been reported for the elemental fluorinations of 4-substituted phenyltrimethylsilanes [15,17], these yields were calculated from the amount of fluorine used, since much of the work was designed to incorporate ^{18}F for positron emission tomography (PET) studies. A large excess of substrate to fluorine (8–100 fold) was normally used to minimise fluorination on the phenyl rings of both starting materials and products. In contrast to this work, the direct elemental fluorination of 4-fluorophenyltrimethylsilane reported in Scheme 1 used a stoichiometric amount of fluorine and the yields were calculated from the amount of substrate used. The reaction was also carried out on a larger scale, using 12 mmol of substrate compared to 30–60 μmol used previously. Despite this, the 24% yield of fluorodesilylated product, 1,4,-difluorobenzene, is still comparable to the previous reports. However, preliminary experiments (Table 1) had shown that it is necessary to catalyse the fluorination with boron trifluoride to improve the yields. It is thought that the boron trifluoride is encouraging the electrophilic substitution of the trimethylsilyl group by polarising the F–F bond.

Scheme 1 also shows the formation of the by-products 2,5-difluorophenyltrimethylsilane and 1,2,4-trifluorobenzene. We propose that the 2,5-difluorophenyltrimethylsilane is produced by the trimethylsilyl group undergoing a 1,2-migration and a possible mechanism is shown in Scheme 2. It is well recognised that fluorine α to a positive charge can stabilise it because of its mesomeric effect giving rise to another resonance structure (VIA ↔ VIB). Hence carbocation (VI) is more stable than carbocation (V), which is also destabilised inductively by the β fluorine, and this is thought to be the



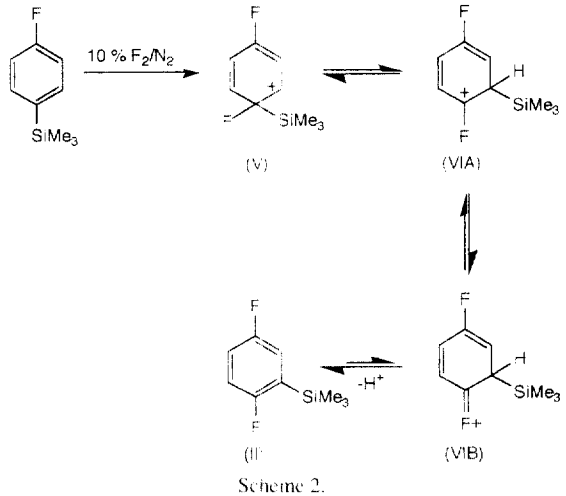
Scheme 1.

Table 1
Preliminary study on the elemental fluorination of 4-fluorophenyltrimethylsilane



Fluorination conditions	Yield			
	I	II	III	IV
(i) $CFCl_3$/MeOH (10%)	31	12	2	3
(ii) $CFCl_3$/MeOH (10%), KF (1 equiv.)	32	11	2	2
(iii) $CFCl_3$/DCM/MeOH (10%), BF_3–MeOH (1 equiv.)	43	12	5	6
(iv) $CFCl_3$/MeOH (10%), BF_3·$3CH_3CO_2$ (1 equiv.)	50	15	4	5

The yields were calculated from the gc and ^{19}F NMR spectra without using internal standards and so they were overestimated by a factor of two.



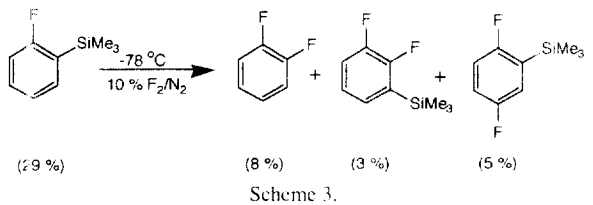
Scheme 2.

driving force for the trimethylsilyl 1,2-shift. The first 1,2-shift of a trimethylsilyl group on a benzene ring was reported by Seyferth and White [22] in 1979. When heated to 152°C in the presence of 2.3 mol% of trifluoroacetic acid, 1,2-bis(trimethylsilyl)benzene isomerised in 48 h to a mixture containing 1,3-bis(trimethylsilyl)benzene (93%) and 1,4-bis(trimethylsilyl)benzene (5%). The driving force for this

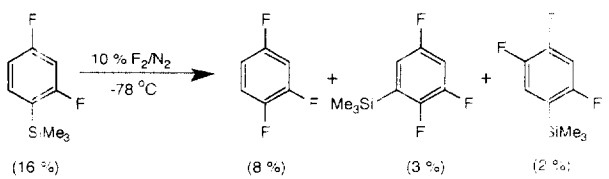
rearrangement was thought to be the steric repulsion between the vicinal trimethylsilyl substituents. Since then, there have been a few reports in the literature of 1,2-migrations of silyl groups accompanying proto- [23], chloro- [24] and bromodesilylations [24–26] in aromatic compounds but this paper is the first report of a silyl migration accompanying a fluorodesilylation.

In the elemental fluorination of 2-fluorophenyltrimethylsilane (Scheme 3), the main product was 1,2-difluorobenzene, but a significant amount of 2,5-difluorophenyltrimethylsilane was also produced by a competing fluorodeprotonation because of the strong *para*-directing effect of the fluorine substituent. Competing fluorodeprotonation reactions have been observed before, especially when the trimethylsilyl group is *para* to a strong electron-donating group, such as methoxy [15,17]. Of most interest however, was the production of 2,3-difluorophenyltrimethylsilane which confirmed that a 1,2-shift of the trimethylsilyl group was occurring in these reactions. A very similar result was obtained in the fluorodesilylation of 2,4-difluorophenyltrimethylsilane (Scheme 4). Again the main reaction was fluorodesilylation producing 1,2,4-trifluorobenzene, some competing fluorodeprotonation also occurred to give 2,4,5-trifluorophenyltrimethylsilane and 2,3,5-trifluorophenyltrimethylsilane was formed by the 1,2-trimethylsilyl migration.

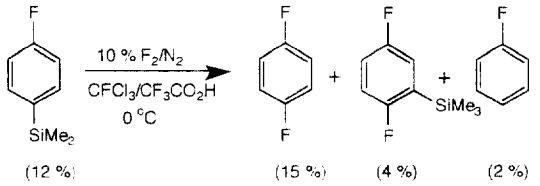
As the preliminary experiments (Table 1) had shown that the fluorodesilylations catalysed by $BF_3 \cdot 2CH_3CO_2H$ gave better yields of 1,4-difluorobenzene than the reactions catalysed by $BF_3 \cdot MeOH$, the effects of acid on the reaction were also investigated. When 4-fluorophenyltrimethylsilane was fluorinated in the mixed solvent system $CFCl_3/CF_3CO_2H$ (10%), a 15% yield of 1,4-difluorobenzene was achieved with 12% of the starting material left (Scheme 5). Notably, no 1,2,4-trifluorobenzene was produced and 4% of the 2,5-difluorophenyltrimethylsilane was formed, but some competing protodesilylation had occurred giving fluorobenzene (2%). Trifluoroacetic acid therefore seemed to be almost as good as boron trifluoride at promoting the *ipso* electrophilic substitution of the trimethylsilyl group and so the effect of the stronger acid, trifluoromethanesulphonic (triflic) acid, was also examined. In the same reaction using the mixed



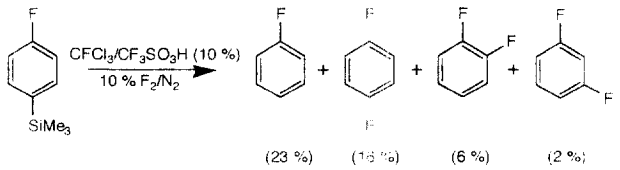
Scheme 3.



Scheme 4.



Scheme 5.



Scheme 6.

solvent system $CFCl_3/CF_3SO_3H$ (10%) all of the products were fluorobenzenes with no fluorophenyltrimethylsilanes present (Scheme 6). Protodesilylation had occurred giving fluorobenzene, which was then fluorinated to all three isomers of difluorobenzene. It was an extremely clean reaction and 1,4-difluorobenzene (16% yield) was the main isomer formed. Protonic acids therefore seemed to encourage the electrophilic fluorination of aromatics as efficiently as the Lewis acid catalyst boron trifluoride. At this stage it is unknown whether the mechanism is strong acid catalysis from their high polarity or whether hypofluorites (CF_3CO_2F, CF_3SO_3F) are formed from the acids in situ and then fluorinate the aromatics. However, these results are in agreement with the work reported by both Chambers et al. [11,12] and Conte et al. [10], who have independently insinuated that acids will become the best solvents for the direct elemental fluorination of aromatics in the future. Further work examining the potential of triflic acid in this new role will be described in a following paper.

3. Experimental

Proton (^1H) and carbon (^{13}C) NMR were recorded in $CDCl_3$ with a Bruker AC300 NMR spectrometer. Chemical shifts are reported in parts per million (δ in ppm) downfield from internal tetramethylsilane. Fluorine (^{19}F) NMR were recorded with a Jeol FX90Q spectrometer using $CDCl_3$ as a solvent with chemical shifts (δ in ppm) downfield from internal $CFCl_3$. Gas chromatographic analyses were performed on a Pye Unicam series 304 chromatograph with a WCOT fused silica coating CP-Sil 19CB column (50 m × 0.32 mm i.d.). The GC-MS were recorded on a Kratos Profile mass spectrometer in the electron impact mode.

Methanol was dried using dry magnesium turnings and dichloromethane was distilled over calcium hydride before being stored over 4 Å molecular sieves. Trichlorofluoromethane was also stored over 4 Å molecular sieves in a refrigerator. Ether refers to diethyl ether and was dried over sodium wire. All other chemicals were used as received from sup-

pliers. In the elemental fluorinations 10% fluorine in nitrogen premixed and provided by Air Products was used. The fluorine line was set up so that the 10% F_2/N_2 passed through a column of potassium fluoride, to remove any hydrogen fluoride present, before being regulated by a glass flow meter. The elemental fluorinations were conducted in a glass cylindrical reactor which had a side arm to allow the 10% F_2/N_2 to be bubbled through a sintered disc directly into the bottom of the reaction mixture. This left room in the middle of the flask for a Teflon paddle which was connected by a steel shaft to a vibro-stirrer motor and was used for efficient mixing. The reactor was also equipped with a thermocouple pocket and an exit port.

3.1. Preparation of 4-fluorophenyltrimethylsilane

Butyllithium (1.6 M in hexane, 36 cm^3, 58 mmol) in dry ether (30 cm^3) was added over 45 min under dry nitrogen to a stirred solution of 4-bromofluorobenzene (10.0 g, 57 mmol) in ether (50 cm^3) at −45°C. After stirring the reaction mixture for 80 min at −45°C, chlorotrimethylsilane (6.4 g, 59 mmol) in ether (30 cm^3) was added over 20 min and the mixture was allowed to warm to room temperature over 12 h. The solution was filtered to remove lithium chloride, washed with 5% $NaHCO_3$ solution and water and then dried ($MgSO_4$). The solvent was removed by rotary evaporation to leave the crude oil, which upon distillation under reduced pressure gave a colourless oil (6.0 g, 63% yield), bp 70–72°C at 20 mm Hg. δ_H(300 MHz, $CDCl_3$) 0.28 (9H, s, $Si(CH_3)_3$), 7.06 (2H, m, *o*-ArF), 7.51 (2H, m, *m*-ArF); δ_F(84 MHz, $CFCl_3$) −113.1 (1F, m, 4-F); δ_C(300 MHz, $CDCl_3$) −1.0 (s, $SiMe_3$), 114.9 (d, $^2J_{C-F}$ = 19.5 Hz), 135.2 (d, $^3J_{C-F}$ = 7.3 Hz), 135.9 (d, $^4J_{C-F}$ = 3.7 Hz), 163.6 (d, $^1J_{C-F}$ = 247.4 Hz); *m/z* (EI) 168 (M^+), 153 (M-Me)$^+$, 139 (M-Et)$^+$, 125 (M-SiMe)$^+$, 123 (M-Me_3)$^+$, 109 (M-$HSiMe_2$)$^+$, 91 (M-$FSiMe_2$)$^+$, 77 ($SiMe_2F$)$^+$.

3.2. Preparation of 2,4-difluorophenyltrimethylsilane

Using the same experimental method as above, 1-bromo-2,4,-difluorobenzene (10.0 g, 52 mmol) in ether (50 cm^3) was reacted with *n*-butyllithium (32.5 cm^3, 52 mmol) in ether (30 cm^3) at −78°C and then with chlorotrimethylsilane (6.5 g, 60 mmol) in ether (30 cm^3). Distillation at atmospheric pressure gave 2,4-difluorophenyltrimethylsilane (4.6 g, 47%) as a colourless oil, bp 164–166°C δ_H(300 MHz, $CDCl_3$) 0.30 (9H, d, J_{H-F} = 1 Hz, $Si(CH_3)_3$), 6.72 (1H, td, $^3J_{H-F}$ = 9 Hz, $^4J_{H-H}$ = 2 Hz), 6.85 (1H, td, $^3J_{H-F}$ = $^3J_{H-H}$ = 8.5 Hz, $^4J_{H-H}$ = 2 Hz), 7.34 (1H, m, *o*-ArSiMe$_3$); δ_F(84 MHz, $CFCl_3$) −97.8 (1F, m, 2-F), −109.8 (1F, m, 4-F); δ_C(300 MHz, $CDCl_3$) −1.1 (s, $SiMe_3$), 103.2 (dd, $^2J_{C-F}$ = 30.1, 24.1 Hz), 111.1 (dd, $^2J_{C-F}$ = 19.7 Hz, $^4J_{C-F}$ = 3.3 Hz), 121.7 (dd, $^2J_{C-F}$ = 30.8 Hz, $^4J_{C-F}$ = 3.5 Hz), 136.0 (dd, $^3J_{C-F}$ = 13.9, 9.3 Hz), 164.5 (dd, $^1J_{C-F}$ = 249.4 Hz, $^3J_{C-F}$ = 12.6 Hz), 167.7 (dd, $^1J_{C-F}$ = 242.1 Hz, $^3J_{C-F}$ = 12.0 Hz); *m/z* (EI) 186 (M^+), 171 (M-Me)$^+$, 151 (M-CH_2F)$^+$, 143 (M-SiMe)$^+$, 109 (M-$SiMe_2F$)$^+$, 105 (M-$SiMeF_2$)$^+$, 77 ($SiMe_2F$)$^+$.

3.3. Preparation of 2-fluorophenyltrimethysilane

It was not possible to synthesise 2-fluorophenyltrimethylsilane using lithium–bromine exchange because the 2-fluorophenyllithium intermediate was unstable at −78°C and eliminated lithium fluoride to form a benzyne, which subsequently reacted with 2-fluorophenyllithium to form 2-fluoro-2′-trimethylsilylbiphenyl. Therefore, to prepare 2-fluorophenyltrimethylsilane it was necessary to carry out a one-pot Grignard reaction to trap the 2-fluorophenylmagnesium bromide with chlorotrimethylsilane as soon as it was formed and so prevent the formation of biphenyls [27]. The crude oil was distilled under reduced pressure to give 2-fluorophenyltrimethylsilane (2.33 g, 20.3%), bp 68–70°C at 20 mm Hg. δ_H(300 MHz, $CDCl_3$) 0.32 (9H, d, J_{H-F} = 1 Hz, $Si(CH_3)_3$), 6.97 (1H, td, $^3J_{H-F}$ = $^3J_{H-H}$ = 8.5 Hz, $^4J_{H-H}$ = 0.8 Hz, *o*-ArF), 7.11 (1H, tt, $^3J_{H-H}$ = 7.5 Hz, $^4J_{H-H}$ = $^5J_{H-F}$ = 0.8 Hz, *p*-ArF), 7.35 (2H, m, *m*-ArF); δ_F(84 MHz, $CFCl_3$) −101.0 (1F, m, 2-F); δ_C(300 MHz, $CDCl_3$) −1.0 (s, $SiMe_3$), 114.7 (d, $^2J_{C-F}$ = 25.8 Hz), 123.8 (s), 131.2 (d, $^3J_{C-F}$ = 8.2 Hz), 135.1 (d, $^3J_{C-F}$ = 11.4 Hz), 167.5 (d, $^1J_{C-F}$ = 240.6 Hz); *m/z* (EI) 168 (M^+), 153 (M-Me)$^+$, 137 (M-C_2H_7)$^+$, 125 (M-SiMe)$^+$, 105 (M-SiMeHF)$^+$, 91 (M-$SiMe_2F$)$^+$, 77 ($SiMe_2F$)$^+$.

3.4. Elemental fluorination of 4-fluorophenyltrimethylsilane catalysed by BF_3·MeOH

The dried reaction vessel was charged with 4-fluorophenyltrimethylsilane (2 g, 12 mmol), $CFCl_3$ (63.5 cm^3), MeOH (10 cm^3) and DCM (25 cm^3). After bubbling nitrogen through the reaction mixture for 10 min, BF_3·MeOH (1.5 cm^3, 13 mmol) was added and the reaction mixture was cooled to −78°C. F_2/N_2 (10%) was then passed through the stirred solution at 1.3 l h^{-1} for 5 h (29 mmol F_2) at −78°C. The resulting reaction mixture was purged with nitrogen for 10 min and warmed to room temperature before washing the organics with 5% $NaHCO_3$ solution and water. The organics were dried ($CaCl_2$ and $MgSO_4$) and finally the $CFCl_3$ was distilled off (bp 23°C) to leave an oil. The products were analysed by a combination of GC, after addition of toluene as an internal standard, GC-MS and ^{19}F NMR, after addition of hexafluorobenzene as an internal standard to the crude reaction mixture. These techniques showed that the reaction mixture contained 1,4-difluorobenzene (24%): [δ_F(84 MHz, $CFCl_3$) −120.2 (2F, quint, $^3J_{F-H}$ = $^4J_{F-H}$ = 6 Hz, 1-F, 4-F); *m/z* (EI) 114 (M^+), 94 (M-HF)$^+$, 88 (M-C_2H_2)$^+$, 75 (M-HF_2)$^+$]; 2,5-difluorophenyltrimethylsilane (4%); [δ_F(84 MHz, $CFCl_3$) −108.3 (1F, dm, $^5J_{F-F}$ = 20 Hz, 2-F), −121.2 (1F, m, 5-F); *m/z* (EI) 186 (M^+), 171 (M-Me)$^+$, 143 (M-SiMe)$^+$, 109 (M-$SiMe_2F$)$^+$, 105 (M-$SiMeF_2$)$^+$, 77 ($SiMe_2F$)$^+$]; 1,2,4-trifluorobenzene (3%): [δ_F(84 MHz, $CFCl_3$) −116.1 (1F, m, 4-F), −133.8 (1F, m, 2-F),

−143.8 (1F, m, 1-F); *m/z* (EI) 132 (M^+), 101 $(M-F)^+$, 88 $(M-C_2HF)^+$, 81 $(M-CHF_2)^+$, 63 $(M-CF_3)^+$]; and 4-fluorophenyltrimethylsilane (2%).

3.5. Elemental fluorination of 2-fluorophenyltrimethylsilane catalysed by BF_3·MeOH

Using the same experimental procedure 10% F_2/N_2 was bubbled at 1 l h^{-1} for 2.75 h (12 mmol F_2) through 2-fluorophenyltrimethylsilane (1.35 g, 8 mmol) in $CFCl_3$ (64 cm^3), MeOH (10 cm^3), DCM (25 cm^3) and BF_3·MeOH (1 cm^3, 8.7 mmol) at −78°C. Analysis of the reaction mixture showed that it contained 1,2-difluorobenzene (8%); [δ_F(84 MHz, $CFCl_3$) −138.9 (2F, m, 1-F, 2-F); *m/z* (EI) 114 (M^+), 94 $(M-F)^+$, 88 $(M-C_2H_2)^+$, 75 $(M-HF_2)^+$, 63 $(M-CHF_2)^+$]; 2,3-difluorophenyltrimethylsilane (3%); [δ_F(84 MHz, $CFCl_3$) −127.9 (1F, d, $^3J_{F-F}$=21 Hz, 2-F) −139.8 (1F dd, $^3J_{F-F}$=21 Hz, $^3J_{F-H}$=8 Hz, 3-F); *m/z* (EI) 186 (M^+), 171 $(M-Me)^+$, 143 $(M-SiMe)^+$, 105 $(M-SiMeF_2)^+$, 77 $(SiMe_2F)^+$]; 2,5-difluorophenyltrimethylsilane (5%) and 2-fluorophenyltrimethylsilane (29%).

3.6. Elemental fluorination of 2,4-difluorophenyltrimethylsilane catalysed by BF_3·MeOH

Using the same experimental procedure, 10% F_2/N_2 was bubbled at 1 l h^{-1} for 6 h (27 mmol F_2) through 2,4-difluorophenyltrimethylsilane (2.24 g, 12 mmol) in $CFCl_3$ (63.5 cm^3), MeOH (10 cm^3), DCM (25 cm^3) and BF_3·MeOH (1.5 cm^3, 13 mmol) at −78°C. Analysis of the reaction mixture showed that it contained 1,2,4-trifluorobenzene (8%); 2,3,5-trifluorophenyltrimethylsilane (3%); [δ_F(84 MHz, $CFCl_3$) −116.6 (1F, m, 5-F), −133.0 (1F, m, 2-F), −134.3 (1F, m, 3-F); *m/z* (EI) 204 (M^+), 189 $(M-Me)^+$, 161 $(M-SiMe)^+$, 123 $(M-SiMeF_2)^+$, 103 $(M-SiMeHF_3)^+$]; 2,4,5-trifluorophenyltrimethylsilane (2%); [δ_F(84 MHz, $CFCl_3$) −103.5 (1F, m, 2-F), −133.0 (1F, m, 4-F), −145.0 (1F, m, 5-F); *m/z* (EI) 204 (M^+), 189 $(M-Me)^+$, 161 $(M-iMe)^+$, 127 $(M-SiMe_2F)^+$, 77 $(SiMe_2F)^+$]; and 2,4-difluorophenyltrimethylsilane (16%).

3.7. Elemental fluorination of 4-fluorophenyltrimethylsilane in $CFCl_3/CF_3CO_2H$ (10%)

The dried reaction vessel was charged with 4-fluorophenyltrimethylsilane (2 g, 12 mmol), $CFCl_3$ (180 cm^3) and CF_3CO_2H (20 cm^3) before cooling to 0°C. After being flushed with nitrogen for 10 min, 10% F_2/N_2 was bubbled at 1 l h^{-1} through the stirred mixture for 4 h (18 mmol F_2). The resulting reaction mixture was purged with nitrogen for 10 min and then warmed to room temperature. The reaction mixture was poured slowly into water and cooled in an ice bath before being neutralised with sodium bicarbonate. The organic layer was then washed with 10% $NaHCO_3$ solution and water, dried ($MgSO_4$) and the $CFCl_3$ distilled off to leave an oil. Analysis by GC, after addition of toluene as an internal standard, GC-MS and ^{19}F NMR spectroscopy, after addition of hexafluorobenzene as an internal standard, showed that the reaction mixture contained 1,4-difluorobenzene (15%); 2,5-difluorophenyltrimethylsilane (4%); fluorobenzene (2%); [δ_F(84 MHz, $CFCl_3$) −113.6 (1F, m, 1-F); *m/z* (EI) 96 (M^+), 70 $(M-C_2H_2)^+$, 63 $(M-H_2F)^+$]; and 4-fluorophenyltrimethylsilane (12%).

3.8. Elemental fluorination of 4-fluorophenyltrimethylsilane in $CFCl_3/CF_3SO_3H$ (10%)

Using the same experimental procedure as the fluorination in trifluoroacetic acid, 10% F_2/N_2 was bubbled at 1 l h^{-1} for 3 h (13 mmol) through 4-fluorophenyltrimethylsilane (2 g, 12 mmol) in $CFCl_3$ (180 cm^3) and CF_3SO_3H (20 cm^3) at −7°C. Analysis of the reaction mixture showed that it contained fluorobenzene (23%); 1,4-difluorobenzene (16%); 1,2-difluorobenzene (6%) and 1,3-difluorobenzene (2%); [δ_F(84 MHz, $CFCl_3$) −110.4 (2F, m, 1-F, 3-F); *m/z* (EI) 114 (M^+), 94 $(M-HF)^+$, 88 $(M-C_3H_2)^+$, 81 $(M-CH_2F)^+$, 75 $(M-F_2)^+$].

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