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Fluoride-mediated selective cross-coupling reactions of alkyl halides and trimethyl(perfluoroalkyl)silanes, Me_3SiR_f ($R_f = CF_3$, C_2F_5) in the absence of any catalysts

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Abstract

A temperature range of −18 °C to room temperature was found to be effective for selective fluoride-mediated cross-coupling reactions of trimethyl(perfluoroalkyl)silanes, Me_3SiCF_3 and $Me_3SiC_2F_5$, and alkyl halides, RX (X = Br, I) in the absence of any catalyst.

Keywords: Trimethyl(trifluoromethyl)silane; Trimethyl(pentafluoroethyl)silane; Cross-coupling; Fluoride

1. Introduction

Reactions of trimethyl(perfluoroalkyl)silanes are widely applied in organic and element organic synthesis with a variety of substrates [1]. Among these reactions, additions to heteromultiple bonds [2], formation of trifluoromethyl chalcogenates [3] as well as nucleophilic halide substitutions in the field of element organic chemistry [4] have most intensively investigated by our groups. However, direct C–C couplings of perfluoroorgano especially trifluoromethyl groups to non- or less-activated carbon atoms, i.e. alkyl groups, have not been achieved so far. In two recent papers [5,6], it has been pointed out that attempted C–C coupling using alkyl halides and trimethyl(trifluoromethyl)silane were unsuccessful under the conditions chosen [5] but were successful in the case of alkyl triflates [6]. Other methods applicable for adapting trifluoromethyl groups to organic kernels by halide substitution require the involvement of copper intermediates [7,8] in some cases generated from trialkyl(trifluoromethyl)silanes [9,10]. It should be noted that in one publication fluoride (TBAF)-mediated fluoroalkylation of MeI had been achieved using the reagent $Me_3SiCF_2C{\equiv}CPh$ "to give $MeCF_2C{\equiv}CPh$ albeit in low yield" [11]. Approaches to obtain trifluoromethyl alkanes are reactions of carboxylic acids and sulphur tetrafluoride [12] and of alkylthio derivatives and bromine trifluoride [13] while examples using the "Swarts procedure" are rare [14].

2. Results and discussion

In this paper, we report an efficient and selective approach to convert readily accessible alkyl halides ($C_nH_{2n+1}X$; X = Br, I) **1** into the corresponding 1,1,1-trifluoroalkanes ($C_nH_{2n+1}CF_3$) **2** and 1,1,1,2,2-pentafluoroalkanes ($C_nH_{2n+1}C_2F_5$) **3** (Scheme 1).

As model compounds, we chose ethyl iodide **1a**, ethyl bromide **1b**, 1-octyl iodide **1c**, 1-dodecyl iodide **1d**, 1-iodo-3-chloro-propane **1e**, 1,3-diiodo-propane **1f**, *i*-propyl iodide **1g**, cyclohexyl iodide **1h**, *t*-butyl chloride **1i** and *t*-butyl iodide **1k** in reactions with trimethyl(trifluoromethyl)silane. The influence of the fluoride source, either $[NMe_4]F$, $[TAS][Me_3SiF_2]$ or $[Cs(15\text{-crown-}5)_2]F$, appears to be negligibly small, while the use of CsF (without addition of a crown ether) or [K(18-crown-6)]F effected an increased formation of CF_3H and further fluorine containing by-products. Glyme (1,2-dimethoxyethane, DME) and diethylether turned out to be the solvent of choice, while reactions in THF or EtCN yielded CF_3H as the major products. In reactions with trimethyl(pentafluoroethyl)silane

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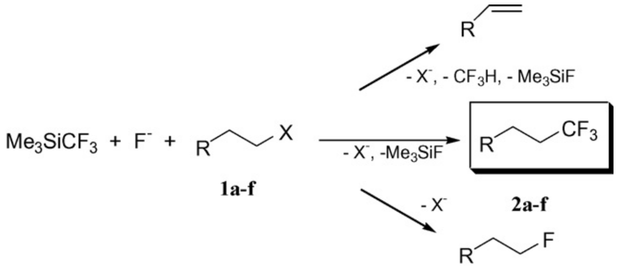
$$\underset{\mathbf{1}}{C_nH_{2n+1}X} + Me_3SiCF_3 + [Cat]F \longrightarrow \underset{\mathbf{2}}{C_nH_{2n+1}CF_3} + Me_3SiF + [Cat]X$$

$X = Br, I; Cat = NMe_4, S(NMe)_3, Cs(15\text{-}Crown\text{-}5)_2$

$$\underset{\mathbf{1}}{C_nH_{2n+1}I} + Me_3SiC_2F_5 + [Cs(15\text{-}Crown\text{-}5)_2]F \longrightarrow \underset{\mathbf{3}}{C_nH_{2n+1}C_2F_5} + Me_3SiF + [Cs(15\text{-}Crown\text{-}5)_2]I$$

Scheme 1. General reaction equations.



Scheme 2. Possible reaction pathways of the attempted trifluoromethylation of alkyl halides.

after optimization of the reaction conditions using Me_3SiCF_3 only **1a**, **1c**–**1e** were used.

Taking into account, that carbon–carbon bond formation between C-nucleophiles and alkyl halides in most cases proceed via S_N2 reactions [15] products as outlined in Scheme 2 can be anticipated.

During our investigations, no evidence was found for alkyl fluorides which were formed in fluoride-mediated reactions of Me_3SiCF_3 with alkyl triflates [6].

Reaction conditions were optimized on the elaborated basis that the ratio of Me_3SiCF_3 to the corresponding fluoride source should be 1 to 1. The optimized temperature range as well as the stoichiometry was checked by using **1a**, **1c** and **1e** as alkyl halides. ^{19}F NMR and ^{1}H NMR spectroscopy was used to determine the relative ratios of the products. On the basis of these results, we recommend a temperature range from −18 °C to ambient temperature and a stoichiometric ratio of alkyl halide to trimethyl(trifluoromethyl)silane of 1:1.7 to be most efficient for quantitative and selective conversion of the chosen alkyl halides into the corresponding 1,1,1-trifluoroalkanes **2**, respectively 1,1,1,2,2-pentafluoroalkanes **3**. The results under optimized conditions are summarized in Table 1.

^{19}F NMR spectroscopic evidence was found for 1,1,1-trifluoro-2-methylpropane, $CF_3CH(CH_3)CH_3$ **2g** [16] in analogous reactions. Even under optimized conditions, no evidence for halide substitution was found in reactions of Me_3SiCF_3 with **1h**–**1k**. In these reactions (**1h**, **1k**), formal eliminations of CF_3H with formation of the corresponding alkenes appear to be the dominating processes (Scheme 3).

The main products of the reactions of **1h** and Me_3SiCF_3 detected by ^{19}F and ^{1}H NMR spectroscopy were CF_3H and cyclohexene. A similar reaction behaviour has to be attributed to **1k** by elimination of 2-butene.

Table 1
Perfluoroalkylation of **1** in absence of a catalyst

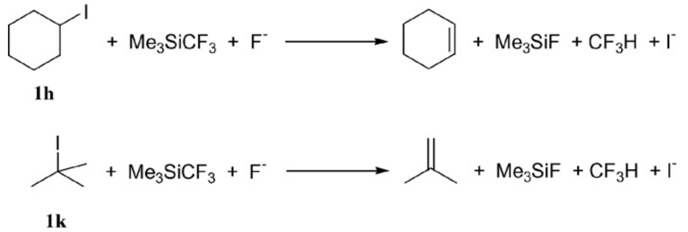
No.	RX **1**	Reaction time (h)	RR$_f$ **2**, **3**	Yields[a] (%)	Other products (%)
1	**1a**	1	**2a**	>98 (NMR) [21]	
2	**1b**	1	**2a**	>98 (NMR) [21]	
3	**1c**	1	**2c**	70 [22]	
4	**1d**	1.5	**2d**	78 [22]	
5	**1e**	1	**2e**	61[b] [23]	
6	**1f**	1	**2f**	45 (NMR[c])	$CF_3(CH_2)_3I$ (50); $CF_3CH_2CH{=}CH_2$ (5)
7	**1g**	1	**2g**	60 (NMR) [16]	$CH_3CH{=}CH_2$, **B**, **C**
8	**1h**	1	–	0	c-C_6H_{10} (100)
9	**1i**	16[d]	–	0	**B** (major product; >75%) [20]
10	**1k**	1	–	0	$(CH_3)_2C{=}CH_2$ (100)
11	**1a**	16	**3a**	>98 (NMR) [18]	
12	**1c**	16	**3c**	78	
13	**1d**	16	**3d**	82	
14	**1e**	16	**3e**	>98 (NMR)	

[a] Yields *vs.* **1**, in general. The values given are isolated yields in those cases (NMR) is missing. In all other cases (>98%), yields were calculated from ^{1}H NMR spectra integrating the "alpha"-CH_2 groups of ICH_2R and CF_3CH_2R in the reaction mixtures. Integrals were added and yields (%) were determined dividing the respective integral by the sum. The figure >98% means that the signal of the I(Br)CH_2-group was not detected.

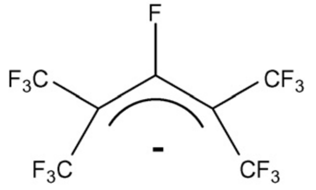
[b] Reaction in Et_2O; product contained ca. 15% Et_2O.

[c] NMR data correspond with literature values of related compounds (^{19}F and ^{1}H).

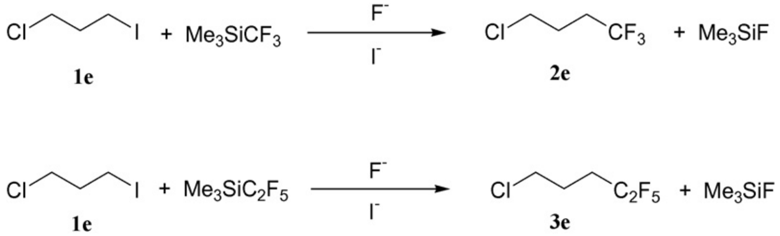
[d] After 1 h bis(15-crown-5)cesium 1,1,1,2,3,6,6,6-octafluoro-2,4,4,5,5-pentakis(trifluoromethyl)hexan-3-ide [20] is detected as the major product.



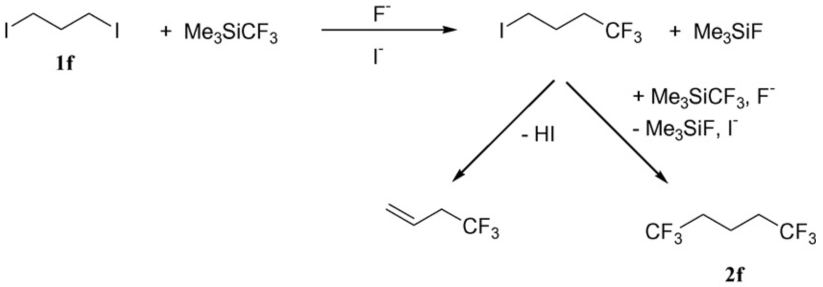
Scheme 3. Elimination processes in the reactions of **1h**, **1k** and Me_3SiCF_3.



Scheme 4. Schematic drawing of **B**.



Scheme 5. Reaction of **1e** and Me_3SiCF_3, respectively $Me_3SiC_2F_5$.



Scheme 6. Reaction of Me_3SiCF_3 and **1f**.

Fluorine-containing by-products such as **A**–**C** were detected in these spectra as signals of very low intensities but as major products in not optimized experiments with all model compounds and with **1i** even under optimized conditions (**1i** can be recovered unchanged). The fluorine-containing by-products $(CF_3)_3CCF_2R$ (**A**) ($\delta = -63.5$, t, 9F; -99.9, decet, 2F, $^4J_{F,F} = 11.4$ Hz) [17] and CF_3CF_2R (**C**) ($\delta = -85.5$, s, 3F; -119.8, t, 2F, $^3J_{F,H} = 18.4$ Hz) [18] are formulated exclusively on the basis of ^{19}F NMR spectroscopic data by comparison with relevant literature values [17,18] and those presented in this paper (reactions with $Me_3SiC_2F_5$; **3c**–**3e**). **A** and **C** seem to be characteristic products only in the reactions of Me_3SiCF_3 and **1**, while the formation of the 1,1,1,3,5,5,5-heptafluoro-2,4-bis(trifluoromethyl)-pentenide anion **B** [19,20] (Scheme 4) via the intermediately formed 1,1,1,2,3,6,6,6-octafluoro-2,4,4,5,5-pentakis(trifluoromethyl)hexan-3-ide anion appears to be typical for reactions of Me_3SiCF_3 with itself under the influence of fluoride ions in this temperature range [20]. A mechanistic approach for the formation of **B** is given elsewhere [20].

To examine reactivity and selectivity, reactions with 1,3-dihalogenated propanes **1e** and **1f** were carried out. These reactions give double information—firstly whether chloride replacement is possible (**1e**) and secondly whether allyl halide formation is dominating (**1e**, **1f**). Reactions of **1e** and Me_3SiR_f ($R_f = CF_3$, C_2F_5) under optimized conditions clearly exhibited that in these cases allyl chloride formation is nearly completely suppressed and iodide substitution appears selectively, while no evidence for chloride substitution is found (Scheme 5). 1-Chloro-4,4,4-trifluorobutane **2e** and 1-chloro-4,4,5,5,5-pentafluoropentane **3e** are selectively formed.

The situation changed using 1,3-diiodo propane **1f** as a reactant. In reactions of **1f** and Me_3SiCF_3 in molar ratios of 1:3.4 or 1:4, formation of 1,1,1,5,5,5-hexafluoro pentane **2f** is accompanied by formation of 1-iodo-4,4,4-trifluoro butane (up to 50%) and 1,1,1-trifluoro-3-butene (up to 5%) (Scheme 6). As a consequence of HI elimination, amounts of CF_3H are comparably high (Table 1).

3. Conclusion

Selective perfluoroalkylation of *n*-alkyl halides is possible with Me_3SiCF_3 and $Me_3SiC_2F_5$ in glyme or diethylether using $[Cs(15\text{-crown-}5)_2]F$ as a fluoride source without any additional catalyst in a conveniently accessible temperature range (−18 °C to ambient temperature, i.e. crushed ice/sodium chloride) to give the C–C coupling products in good yields. Other fluoride sources such as $[NMe_4]F$ and TASF are also suitable. Reactions with secondary and tertiary alkyl iodides suffer from HX elimination processes yielding mainly the corresponding alkenes and R_fH; alkyl chlorides appear to be non-reactive under those conditions.

4. Experimental

4.1. Materials and methods

All reactions were carried out in a dry argon (nitrogen) atmosphere using Schlenk techniques.

Me_3SiCF_3 was purchased from ABCR, $Me_3SiC_2F_5$ was prepared from C_2F_5I, Me_3SiCl and tetrakis(dimethylamino)ethen following the Petrov procedure [24]. CsF (Acros) was carefully dried prior to use. 15-Crown-5 was purchased from Fluka, alkyl halides from ACROS and used as received. All solvents were purified according to literature procedures [25].

Approximately 90 experiments for optimization of the conditions (Me_3SiCF_3) were carried out varying the fluoride source ($[NMe_4]F$, TASF, [K(18-crown-6)]F, CsF, $[Cs(15\text{-crown-}5)_2]F$), the solvent (THF, diglyme, DME, diethylether, propionitrile), the relative ratio Me_3SiCF_3 to fluoride (5:1 up to 1:2), the temperature range (−60 °C to ambient) and the ratio of **1** to Me_3SiCF_3 (5:1 to 1:2).

NMR spectra were recorded on a Bruker AC-200 spectrometer: ^1H (200.1 MHz) and ^{19}F (188.3 MHz) and $^{13}C\{^1H\}$ (50.3 MHz) NMR spectra. Chemical shifts are given in ppm relative to Me_4Si and CCl_3F as external standards. Acetone-d_6 was used as an external lock (5 mm tube) in reaction control measurements and for neat compounds while an original sample of the reaction mixture or the neat compound, respectively, was measured in a 4 mm insert. NMR data not reported so far for known compounds are added after the corresponding reference (cf. Table 1). EI mass spectra were run on a Finnigan MAT 95 spectrometer (20 eV).

4.2. General procedure (preparative scale)

A solution of 15 mmol of the corresponding alkyl halide **1** and 25.5 mmol Me_3SiR_f ($R_f = CF_3$, C_2F_5) in 50 mL of glyme was cooled on an ice-bath to −18 °C (ice/sodium chloride). Solid, carefully dried CsF (25.5 mmol) was added in one portion. Finally, 51 mmol 15-crown-5 were added. The temperature was allowed to reach room temperature over a period of approximately 1 h ($R_f = CF_3$) or 16 h ($R_f = C_2F_5$). $[Cs(15\text{-crown-}5)_2]I$ was filtered off and all easily volatile compounds were removed in vacuo. From the pale brown residues, oily compounds **2**, **3** were extracted with *n*-pentane or obtained as volatile derivatives after trap-to-trap condensation. Compounds were mainly analyzed by NMR spectroscopic means (in comparison with literature data) and in part by mass spectrometry.

4.2.1. 1,1,1-Trifluoro-n-nonane (2c) [22]

Oil. NMR: ^1H NMR (200.1 MHz, neat): 2.07 (m, 2H), 1.48 (m, 2H), 1.26 (broad s, 10 H), 0.84 (t, 3H); ^{19}F NMR (188.3 MHz, neat): −66.3 (t, $J = 11.4$ Hz); ^{13}C NMR (50.3 MHz, neat): 127.8 (q, $J = 276$ Hz), 33.6 (q, $J = 28$ Hz), 32.1, 29.6, 29.4, 29.0, 22.9, 22.2 (q, $J \approx 2$ Hz), 14.1. EIMS (EI, 20 eV, *m/z*): 182 (M^+).

4.2.2. 1,1,1-Trifluoro-n-tridecane (2d) [22]

Oil. NMR: ^1H NMR (200.1 MHz, neat): 1.97 (m, 2H), 1.49 (m, 2H), 1.25 (broad s, 18 H), 0.85 (t, 3H); ^{19}F NMR (188.3 MHz, neat): −66.9 (t, $J = 10.8$ Hz); ^{13}C NMR (50.3 MHz, neat): 125.9 (q, $J = 276$ Hz), 32.4 (q, $J = 29$ Hz), 30.8, 28.5 (2C), 28.4, 28.2 (2C), 28.1, 27.6, 21.5, 20.6 (q, $J \approx 2$ Hz), 12.4. EIMS (EI, 20 eV,): $m/z = 238$ (M^+).

4.2.3. 1,1,1,2,2-Pentafluoro-n-decane (3c)

Oil. NMR: ^1H NMR (200.1 MHz, neat): 1.94 (m, 2H), 1.53 (m, 2H), 1.27 (broad s, 10 H), 0.85 (t, 3H); ^{19}F NMR (188.3 MHz, neat): −86.2 (s, 3F), −118.8 (t, $J = 18$ Hz, 2F); ^{13}C NMR (50.3 MHz, neat): 119.3 (qt, $J = 284/37$ Hz), 115.7 (tq, $J = 251/37$ Hz), 31.7, 30.4 (t, $J = 22$ Hz), 29.1, 29.0 (2C), 22.4, 20.1 (t, $J \approx 3$ Hz), 13.3. EIMS (EI, 20 eV, *m/z*): 232 (M^+).

4.2.4. 1,1,1,2,2-Pentafluoro-n-tetradecane (3d)

Oil. NMR: ^1H NMR (200.1 MHz, neat): 1.85 (m, 2H), 1.50 (m, 2H), 1.22 (broad s, 18 H), 0.81 (t, 3H); ^{19}F NMR (188.3 MHz, neat): −86.2 (s, 3F), −118.5 (t, $J = 18$ Hz, 2F); ^{13}C NMR (50.3 MHz, neat): 118.7 (qt, $J = 285/37$ Hz), 115.0 (tq, $J = 251/37$ Hz), 31.4, 30.0 (t, $J = 22$ Hz), 29.12, 29.11, 29.04, 28.87, 28.85, 28.67, 28.55, 22.0, 19.6 (t, $J \approx 3$ Hz), 12.9. EIMS (EI, 20 eV, *m/z*): 288 (M^+).

4.2.5. 1,1,1,2,2-Pentafluoro-5-chloro-n-pentane (3e)

NMR: ^1H NMR (200.1 MHz, DME): 3.44 (t, $J = 6$ Hz, 2H), 2.15 (m, 2H), 1.99 (m, 2H); ^{19}F NMR (188.3 MHz, DME) −86.2 (s, 3F), −118.7 (t, $J = 17$ Hz, 2F).

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2a: δ_C (50.3 MHz, neat) 128.2 (q, $J = 277$ Hz); 27.7 (q, $J = 30$ Hz); 6.4 (q, $J \approx 2$ Hz).

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2e: δ_H (200.1 MHz, Et_2O) 3.51 (t, $J = 6$ Hz, 2H), 2.20 (m, 2H), 1.94 (m, 2H); δ_F (188.3 MHz, Et_2O) −66.6 (t, $J = 11.1$ Hz); δ_C (50.3 MHz, Et_2O) 126.1 (q, $J = 275$ Hz), 41.7, 30.1 (q, $J = 29$ Hz), 24.2 (q, $J \approx 3$ Hz).

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