Selective Electrosynthesis of (Trimethylsilyldifluoro)methylbenzene, a $PhCF_2^-$ Precursor; Conditions for a Molar Scale Preparation without HMPA

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Abstract: Electrochemical reductive silylation of trifluoromethylbenzene by the sacrificial anode technique selectively led, in a THF/DMPU mixture instead of THF/HMPA and according to the charge passed, to the corresponding mono-, bis- or tris-trimethylsilyl derivatives, respectively $PhCF_2TMS$, $PhCF(TMS)_2$ and $PhC(TMS)_3$. This reaction, without any chemical equivalent, was extended to a molar scale synthesis, using a tubular flow cell.

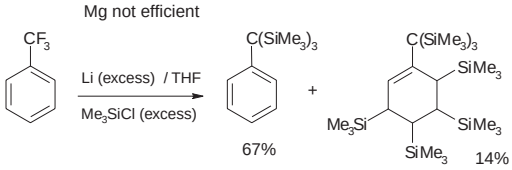
Key words: (trimethylsilyldifluoro)methylbenzene, bis(trimethylsilylfluoro)methylbenzene, molar scale electrosynthesis, sacrificial anode, tubular flow cell, (phenyldifluoro)methyl anion precursor

Developing convenient synthetic routes for the introduction of fluorinated groups in organic molecules is still an attractive challenge because of the specific chemical and biochemical properties of fluorinated compounds and their applications as biologically active drugs and agrochemicals.[1,2] Among the chemical methods for the introduction of perfluoroalkyl groups into various types of carbonyl containing organic compounds, the use of silyl reagents such as Ruppert's reagent (CF_3SiMe_3)[3] constitutes a very valuable synthetic procedure as shown by Olah and Prakash.[4] Concerning the introduction of the $PhCF_2$ group, only one publication[5] has been reported, probably because no practical method of preparation of the corresponding synthon, (trimethylsilyldifluoro)methylbenzene, $PhCF_2SiMe_3$ ($PhCF_2TMS$), has ever been described.

We report here the first synthesis of $PhCF_2TMS$ via an electrochemical reduction, in the presence of trimethylchlorosilane, of the readily available trifluoromethylbenzene (TFMB) according to the intensiostatic sacrificial anode process. Our first results[6] were obtained using HMPA as a cosolvent; but looking ahead to a really preparative scale synthesis, the different chemical and electrochemical parameters were re-examined to find the best electrolysis conditions avoiding the use of HMPA and selectively leading, in only one operation, to one mole of $PhCF_2TMS$ or, if required, $PhCF(TMS)_2$.

The chemical access to $PhCF_2TMS$ was very recently described, in 1997, by M.Yoshida et al.[5] through the reduction of (chlorodifluoro)methylbenzene with an excess of samarium iodide in the presence of trimethylchlorosilane in a benzene/HMPA mixture as a solvent. The starting product, $PhCF_2Cl$, non-commercially available, was prepared by reacting benzene with bis(chlorodifluoroacetyl) peroxide.

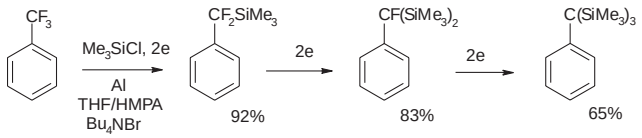
The method we developed uses the intensiostatic sacrificial anode process in an undivided cell. Through this method, (trifluoromethyl)trimethylsilane was successfully selectively synthesized from bromotrifluoromethane.[7,8] With regards to the chemical route[3] which involves the expensive tris(diethylamino)phosphine, the electrochemical method constitutes a valuable improvement. But compared to the reduction of the C–Br bond in CF_3Br (Ep = –1.7V/SCE),[15] the reduction of the C–F bonds in TFMB occurs at much more cathodic potentials (–2.61, –2.84 V/SCE respectively at Hg/DMF + Bu_4NI[9a] or –2.68, –2.80, –2.90 V/SCE respectively at Au/DMF + Bu_4NBr [9b]) and the chemical metal reduction methods are not convenient for the synthesis of $PhCF_2SiMe_3$. For example, we found that Mg/THF/HMPT was not efficient and the Me_3SiCl/Li/THF reagent[10] directly leads to a mixture of trisilylated and persilylated products (Scheme 1) without any chemoselectivity. Recently a new chemical synthesis of CF_3TMS by reduction of CF_3Br with aluminium powder in NMP as a solvent, in an autoclave, was reported.[11] We tried to adopt the latter conditions to synthesize $PhCF_2TMS$ from TFMB, but without any success.



Scheme 1 Chemical Reduction of Trifluoromethylbenzene (TFMB)

On the contrary, despite close reduction potentials, the electrochemical route allows strict control of the silylation steps, without chemical equivalent, just by controlling the charge passed (Scheme 2). The dynamic GC analysis of the TFMB silylation throughout the electrolysis in a THF/HMPA mixture, with an Al anode, clearly shows the stepwise mechanism as a function of the charge passed (Figure 1). Optimal conditions could be determined as 2.1, 4.3, 6.3 $F \cdot mol^{-1}$ for the mono-, di- and trisilylated products

respectively. $PhC(TMS)_3$ could also be prepared by electroreduction of TFMB in the same conditions after passing 6.3 F·mol^{-1} with a 65% isolated product yield.



Scheme 2 Electrochemical Reduction of Trifluoromethylbenzene

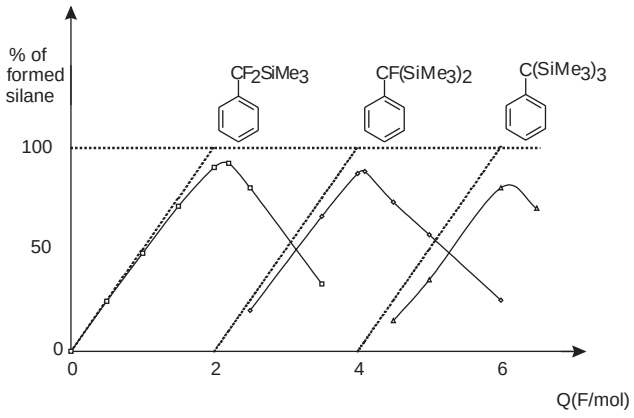


Figure 1 Dynamic GC Analysis of the Stepwise Silylation of Trifluoromethylbenzene

But in the previous case, the main disadvantage was the use of HMPA as a cosolvent. By varying the experimental parameters such as the nature of the solvent, the cosolvent, the supporting electrolyte and the nature of the anode metal, we tried to find the best conditions for the electrosynthesis of either $PhCF_2TMS$ or $PhCF(TMS)_2$. Because the changes that occur with different cathode materials (stainless steel, carbon cloth, aluminium) are rather insignificant, they are not reported here. The influence of the other parameters (solvent, cosolvent, supporting electrolyte, and anode metal) was determined by comparing the results of the corresponding electrolysis performed in standard conditions: 70 mL cell, 0.25 dm^2 stainless steel cathode, constant current density j = 0.4 A/dm^2 (i = 100 mA), TFMB: 0.2 mol·L^{-1}, TMSCl: 1.0 mol·L^{-1} (5 equiv), and very efficient magnetic stirring). Two reaction parameters were studied: the conversion rate ***C*** of TFMB into $PhCF_2TMS$ and $PhCF(TMS)_2$, and the chemoselectivity ***M*/*D*** of the monosilylation compared to the disilylation after having passed 2.4 F·mol^{-1}. The GC yields were determined using nonane as an internal standard.

Cosolvents were used without specific drying and the required electrolysis time for passing 2.4 F.mol^{-1} was calculated from the end of the preelectrolysis, when hydrogen evolution stopped. This hydrogen evolution resulted from the reduction of hydrogen chloride, which is formed by the hydrolysis of trimethylchlorosilane (used in a five fold excess compared to TFMB) from the traces of water present in the electrolytic medium. The different results (± 5% accuracy) are listed in Table 1. Considering the conversion rate, THF appears to be the best solvent. Highly polar solvents (NMP, DMF) provide good conduction but their own reduction, favoured by the electrophilic assistance of TMSCl, occurs in competition with the reduction of TFMB and the conversion rate of the latter remains very low. The selectivity towards the monosilylation is excellent probably because the reduction of the solvent occurs preferentially to that of $PhCF_2TMS$.

It appeared that the nature of supporting electrolytes introduced at the beginning of the electrolysis had an influence on the conversion and protonation rate as well as on the selectivity. The importance of the supporting electrolyte in the course of an electrolysis is well known.[12] However, taking into account the fact that, in the sacrificial anode technique, a large amount of metallic salts, working themselves as supporting electrolyte, is formed during the electrolysis, an interpretation of these results would require a specific research.

Each of the cosolvents led to excellent conversion rates. The selectivity *M*/*D* is slightly better for HMPA and DMPU (**3a**,**3c**). But for the final choice, HMPA, the best of the cosolvents, was left aside because of its presumed

Table 1 Influence of Chemical and Electrochemical Parameters on the Conversion Rate and the Chemoselectivity of the Electrosilylation of TFMB for 2.4 F·mol^{-1} of Charge

			Conversion rate C (%)	Selectivity M/D (%)[a]
Solvent[b] (TDA-1, NBu_4Br)	THF	**1a**	100	85/10
	DME	**1b**	90	70/5
	NMP	**1c**	10	100/0
	DMF	**1d**	5	100/0
Supporting electrolyte[b] (THF, DMPU)	NBu_4Br	**2a**	95	90/5
	NBu_4BF_4	**2b**	90	75/15
	NBu_4PF_6	**2c**	70	90/10
	Aliquat 336	**2d**	90	75/5
	CF_3SO_3Li	**2e**	95	80/15
	$(CF_3SO_2)_2NLi$	**2f**	70	85/15
	$AlCl_3$/LiCl	**2g**	95	80/5
Cosolvent[b] (THF, NBu_4Br)	HMPA	**3a**	100	92/8
	TDA-1	**3b**	100	85/10
	DMPU	**3c**	95	90/5
	DMI	**3d**	100	80/15
	TMEDA	**3e**	100	85/15
	NMP	**3f**	85	75/5
Anode (THF, cosolvent, NBu_4Br)	Al (HMPA)	**4a**	100	92/8
	Al (TDA-1)	**4b**	100	85/10
	Mg (HMPA)	**4c**	100	83/17
	Mg (TDA-1)	**4d**	100	65/25

[a] The difference to 100% is due to protonation products.
[b] THF : tetrahydrofurane, DME : dimethoxyethane, NMP : N-methylpyrrolidinone, DMF : dimethylformamide, HMPA : hexamethylphosphoramide, TDA-1 : tris(3,6-dioxaheptyl)amine, DMPU : 1,3-dimethyl-3,4,5,6-tetrahydro-2(1*H*)-pyrimidinone, DMI : 1,3-dimethyl-2-imidazolidinone, TMEDA : tetramethylethylenediamine, Aliquat 336 : methyltrioctylammonium chloride.

toxicity whereas DMPU was preferred to TDA-1 because it leads to better extraction and purification conditions. Nevertheless an electrolysis with TDA-1 as a cosolvent was also performed in a tubular flow cell at a 50 g scale. The influence of the DMPU concentration was studied as shown in Figure 2 where the $PhCF_2TMS$ yield is correlated to the ratio (number of DMPU moles)/(number of Al^{3+} moles formed by oxidation of the aluminium rod).

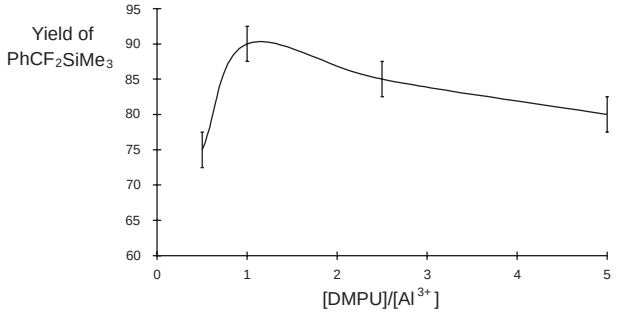


Figure 2 Yield of $PhCF_2TMS$ Depending on the ratio [DMPU]/[Al^{3+}]

According to this curve, the best yield was reached for one mole of DMPU per mole of Al^{3+}. This observation corresponds to the fact that the Al salts own only one free coordination site. Therefore, to insure a good conduction, 1.3 moles of cosolvent per mole of Al^{3+} were used. Increasing the cosolvent concentration led to a drop in the TFMB conversion rate presumably because of the competitive reduction of DMPU itself.

With regard to the anode metal, the conversion rate is 100% either with aluminium or magnesium. But, an abnormally high anodic current efficiency appeared with the latter, showing a chemical participation of the electrochemically scoured magnesium with a consequently important loss of selectivity as reported in Table 1.[6,13]

In the same conditions but with a 2.0 mol·L^{-1} TMSCl concentration, $PhCF(TMS)_2$ was obtained from TFMB in 70% yield after having passed 4.8 F·mol^{-1}. A better yield (85%) was reached by electrolysis of $PhCF_2TMS$ itself after the passage of 2.4 F·mol^{-1} of charge.

From these results, we determined the conditions for a molar scale synthesis using a tubular flow cell[14](Figure 3) fitted with an aluminium anode and a stainless steel cathode constituting the cell body.

Two different cosolvents, DMPU and TDA-1, were tested. With this cell, detecting the evolution of hydrogen during preelectrolysis is impossible, so the optimized electrolysis times were monitored by GC analysis (Table 2).

These results point out that two strategies can be carried out: if a selectivity close to 100% is required, only 2 F·mol^{-1} have to be passed, a recycling of TFMB being necessary; if a total conversion is preferred, 3.2 F·mol^{-1} have to be passed, $PhCF_2TMS$ and $PhCF(TMS)_2$ being separated by distillation. The latter option was chosen for the synthesis of 150 g (0.75 mol) of $PhCF_2TMS$.

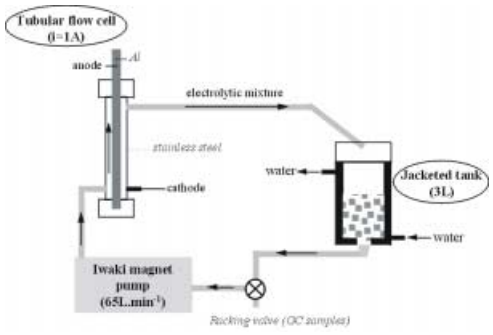


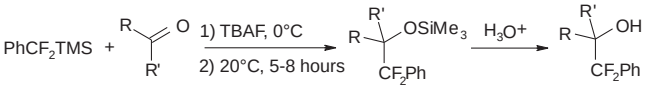
Figure 3 Tubular Flow Cell

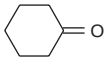
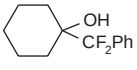
Table 2 Electrosynthesis of $PhCF_2TMS$ with TDA-1 and DMPU as Cosolvents in a Tubular Flow Cell; Influence of the Charge Passed (Electrolysis Time)

Cosolvent	Q(F.mol^{-1})	Electrolysis time (h)	C (%)	M/D (%)
TDA-1	2	55	53	100/0
	2.2	60.5	62	92/5
	2.8	77	82	85/10
	3.2	88	100	70/15
DMPU	2	55	66	95/5
	2.4	66	75	93/7
	2.8	77	86	88/12
	3.2	88	95	80/15

Finally, in order to decrease the proportions of TMSCl and solvent, and to increase the productive capacity of the cell, we performed an electrosynthesis in a 70 mL laboratory cell equipped with a stainless steel cathode (j = 0.4 A·dm^{-2}) and an aluminium anode in the following condi-

Table 3 Reaction of $PhCF_2TMS$ with Carbonyl Compounds



(RCOR')	Product	Yield %[a] ( )[b]	Literature [5]
PhCHO	PhCHOHCF2Ph	63(55)	70
$CH_3(CH_2)_6CHO$	$CH_3(CH_2)_6CHOHCF_2Ph$	66[c]	58
		60	

[a] Determined by ^{19}F spectroscopy based on $PhOCF_3$
[b] Yield of isolated product after separation by column chromatography on silicagel.
[c] This yield was reached using two equivalent of $PhCF_2TMS$.

tions: NBu_4Br (0.25 g) as the supporting electrolyte, THF (15 mL) as the solvent, DMPU (15 mL) as the cosolvent, and letting the molar ratio of TFMB/TMSCl = 1 (20 g; 2.0 mol·L^{-1} of TFMB and 14.7 g; 2.0 mol·L^{-1} of TMSCl). To avoid the protonation reaction that occurs at the end of the electrolysis due to the low concentration of the residual TMSCl, the current was stopped after passing 1.3 F·mol^{-1}. In these conditions, we acquired 13 g (65 mmol) of pure $PhCF_2TMS$.

An extrapolation of these conditions to a larger scale is in progress.

In order to check the ability of $PhCF_2TMS$ as a (difluorophenyl)methylating agent, we reacted three carbonylated compounds with this intermediate in the presence of TBAF according to Table 3:

It should be observed that in our conditions, the electrophile was used in stoichiometric proportions, instead of the large excess recommended by M. Yoshida et al.[5] With benzaldehyde and octanal, our results are in complete agreement with those of these authors. With cyclohexanone, the corresponding alcohol had never been described.

Therefore, without any chemical equivalent, this electrochemical procedure offers an easy, highly selective and safe, large scale method for the synthesis of $PhCF_2TMS$, a $PhCF_2^-$ equivalent, from the readily available trifluoromethylbenzene.

For electrolysis in a 70 mL cell, THF (SDS) was distilled over sodium-benzophenone ketyl. The cosolvents HMPA, DMPU (Fluka), TDA-1 (Aldrich) were used without any treatment. The supporting electrolytes were pumped off over 48 h at r.t.. Trimethylchlorosilane was distilled over Mg powder just before use. Gas chromatography was performed with a temperature-programmable Hewlett-Packard 5890A apparatus equipped with a 25 m × 0.25 μm CP-Sil 5CB capillary column. ^1H NMR spectra were recorded in $CDCl_3$ at 250 MHz with a Brucker AC 250 spectrometer, using residual $CHCl_3$ (δ = 7.27 ppm) as the internal standard. The signals are designated s (singlet), d (doublet), t (triplet), q (quartet), and m (multiplet). ^{13}C NMR spectra were obtained at 62.86 MHz with a Brucker AC 250 using $CDCl_3$ (δ = 77.70 ppm) as the internal standard. The signals are designated s (singlet), d (doublet), t (triplet), q (quartet), and m (multiplet). ^{29}Si NMR spectra were recorded in $CDCl_3$ at 39.73 MHz with a Brucker AC 200 spectrometer. ^{19}F NMR spectra were recorded in $CDCl_3$ at 282 MHz with a Brucker AC 200 spectrometer. Electron impact mass spectra were recorded at an ionisation voltage of 70 eV with a VG Micromass 16F spectrometer coupled with a gas chromatograph equipped with a 25 m × 0.25 μm CP-Sil capillary column. IR spectra were recorded with a Perkin Elmer 1420 spectrophotometer in pure liquids films (NaCl sheets). Elementary microanalyses were performed by the "Service Central de Microanalyses" of CNRS (France). Solvents, $PhCF_3$, NBu_4F in THF (1 mol·L^{-1}) are purchased from Aldrich, and SiO_2 (9385) from Merck.

(Trimethylsilyldifluoro)methylbenzene, $PhCF_2TMS$, in a 70 mL Laboratory Cell

(a) General Procedure with a 0.2 mol·L^{-1} TFMB Concentration

The electrolysis of magnetically stirred solutions was performed under nitrogen, in a previously described[6,13] undivided cell fitted with an aluminium rod as the anode and a concentric cylindrical stainless steel grid as the cathode. These two electrodes were previously chemically scoured by a 10% HCl solution, then rinsed out several times with distilled water and with acetone. The dried cell containing 0.8 mmol of supporting electrolyte: NBu_4Br (0.25 g), NBu_4BF_4 (0.25 g), NBu_4PF_6 (0.30 g), $(CF_3SO_2)_2NLi$ (0.22 g), CF_3SO_3Li (0.12 g), Aliquat 336 (0.31 g), $AlCl_3$ (0.10 g) + LiCl (0.03 g) was deaerated twice under vacuum and then with anhyd N_2. THF (55 mL), DMPU (1.8 mL, 14.9 mmol) or TDA-1 (4.8 mL, 14.9 mmol) and TMSCl (9 mL, 68.5 mmol) were introduced under light N_2 pressure. HCl resulting from the reaction between TMSCl and the residual H_2O was removed by preelectrolysing the solution (i = 0.1 A; j = 0.4 A.dm^{-2}). The other hydrolysis product, Me_6Si_2O, remains electrochemically inert. When evolution of H_2 ceased, TFMB (2 g, 13.7 mmol) was introduced through a septum by syringe. The electrolysis was then performed (i = 0.1 A; j = 0.4 A.dm^{-2}) over 9 hours, until the required charge (2.4 F·mol^{-1}) has been passed. The progress of the reaction was monitored by gas chromatography. At the end of the electrolysis, the mixture was poured into 250 mL of cold water. The organic layer was extracted with Et_2O (3 x 100 mL) and washed with cold H_2O (2 x 100 mL). After drying ($MgSO_4$), Et_2O was evaporated off. Fractional distillation over a Vigreux column gave with DMPU 1.9 g (70%) and with TDA-1 1.8 g (66%) of $PhCF_2TMS$; bp = 80 °C / 2.5 kPa.

(b) High Concentration Procedure

The cell, the electrodes and the solvent were prepared as described in the General Procedure. The dried cell containing NBu_4Br (0.25 g, 0.8 mmol) was deaerated twice under vacuum and then with anhyd N_2. THF (15 mL), DMPU (15 mL, 0.12 mol) and TMSCl (18 mL, 0.14 mol) were introduced under light N_2 pressure. After the preelectrolysis, the TFMB (20 g, 0.14 mol) was introduced through a septum by syringe. The electrolysis was then performed (i = 0.1 A; j = 0.4 A.dm^{-2}) over 48 hours, until the required charge (1.3 F·mol^{-1}) has been passed. The mixture was then treated as described in the General Procedure. Fractional distillation over a Vigreux column gave 7.2 g of unreacted TFMB and 13.1 g of pure $PhCF_2TMS$ (75% versus to converted TFMB), bp = 80 °C / 2.5 kPa.

(c) Large Scale Synthesis Using a Tubular Flow Cell

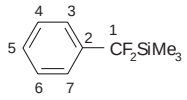
The electrolytic equipment previously described by Thiebault et al.[14] (Figure 3) comprises of: a 2 L jacketed tank cooled by H_2O at r.t., a 50 mL stainless steel cylinder (125 cm^2 surface area cathode) fitted with a 20 mm diameter aluminium rod (the anode) which constitutes the electrolytic cell, an Iwaki magnet pump which insures the circulation of the electrolytic medium (imposed flow = 65 L·min^{-1}) through the electrolytic cell, and a racking valve to take samples for GC analysis.

Before any electrolysis, both of the electrodes were previously scoured by a 10% HCl solution, fitted together and rinsed out by a circulating, in the whole setting, a dimethylformamide/acetic acid mixture (50/50), and then rinsed twice with commercial THF.

Solvents, cosolvents, TMSCl and supporting electrolyte were used without any treatment. TFMB (150 g, 0,5 mol·L^{-1}), TMSCl (600 mL, 2,5 mol·L^{-1}), DMPU (180 mL, 0.75 mol·L^{-1}) or TDA-1 (480 mL, 0,75 mol·L^{-1}), tetrabutylammonium bromide (6.5 g, 0,01 mol.L^{-1}) and THF (1.2 L) were introduced into the tank. The mixture was pumped into the electrolytic cell and an electric charge (i = 1 A, j = 0.45 A.dm^{-2}) was administered for the required time. The complete or partial conversion of TFMB according to the chosen option was monitored by GC. For example, for the complete conversion of 150 g of TFMB, it required 86 hours of electrolysis.

At the conclusion of the electrolysis, the mixture was transferred into a flask and volatile products (TMSCl in excess, THF and Me_6Si_2O) were evaporated off. The viscous residue was poured into 600 mL of a cold aq. HCl (2mol·L^{-1}) and the organic products were

extracted with Et_2O (3 × 200 mL). This solution was washed by iced H_2O (3 × 100 mL). After drying ($MgSO_4$), the solvent was evaporated off and $PhCF_2TMS$ was distilled; yield: 150 g (70%) with DMPU and 146 g (68%) with TDA-1.



^{1}H NMR: δ_H(TMS) = 0.21 (s, 9H), δ_H(Ar) = 7.26–7.45 (m, 5H).

^{13}C NMR: δ_C(TMS) = –4.9 (s), δ_{C5} = 128.3 (s), $\delta_{C3} = \delta_{C7}$ = 124.7 (t, $^3J_{C-F}$ = 8.0 Hz), $\delta_{C4} = \delta_{C6}$ = 128.8 (t, $^4J_{C-F}$ = 2.6 Hz), δ_{C1} = 134.5 (t, $^1J_{C-F}$ = 265.0 Hz), δ_{C2} = 138.3 (t, $^2J_{C-F}$ = 20.4 Hz).

^{29}Si NMR: δ_{Si} = 4.3 (t, $^2J_{Si-F}$ = 34.7 Hz).

^{19}F NMR: δ_F = –112.5 (s).

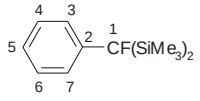
MS: *m*/*z* = 185 (M-15)$^+$, 127 (M-73)$^+$, 108 (M-92)$^+$, 93 (M-107)$^+$, 77 ($SiFMe_2^+$), 73 ($SiMe_3^+$).

Calculated (found) for $C_{10}H_{14}SiF_2$: C% = 59.96 (58.12), H% = 7.04 (7.04), F% = 18.97 (19.00).

The spectral data agree with those reported in the literature.[5]

[Bis(trimethylsilyl)fluoro]methylbenzene, $PhCF(TMS)_2$

The electrolysis (i = 0.1 A, j = 0.4 A·dm^{-2}) was performed as described in (a) with NBu_4Br (0.25 g, 0.8 mmol), DMPU (3.6 mL, 29.8 mmol), THF (55 mL), TMSCl (14.5 mL, 0.11 mol) and TFMB (2 g, 13.7 mmol) for 18 h until the required charge (4.8 F·mol^{-1}) has been passed. The workup of the mixture and isolation of $PhCF(TMS)_2$ were essentially similar to those described about $PhCF_2TMS$ (a); yield: 2.0 g (60%); bp = 130 °C / 4 kPa.



^{1}H NMR: δ_H(TMS) = 0.23 (s, 18H), δ_H(Ar) = 7.08–7.40 (m, 5H).

^{13}C NMR: δ_C(TMS) = –2.2 (d, $^3J_{C-F}$ = 4.0 Hz), δ_{C1} = 99.7 (d, $^1J_{C-F}$ = 155.3 Hz), $\delta_{C3} = \delta_{C7}$ = 121. (d, $^3J_{C-F}$ = 13.6 Hz), $\delta_{C4} = \delta_{C6}$ = 124.2 (s), δ_{C5} = 128.0 (s), δ_{C2} = 144.5 (d, $^2J_{C-F}$ = 13.8 Hz).

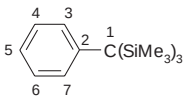
^{29}Si NMR: δ_{Si}= 3.69 ppm (d, $^2J_{Si-F}$ = 23.6 Hz).

^{19}F NMR: δ_F = –218.9 ppm (s).

MS: *m*/*z* = 239 (M-15)$^+$, 181 (M-73)$^+$, 162 (M-92)$^+$, 147 (M-107)$^+$, 77 ($SiFMe_2^+$), 73 ($SiMe_3^+$); Calculated (found) for $C_{13}H_{23}Si_2F$: C% = 61.35 (59.97), H% = 9.11(9.6), F% = 7.46 (7.15).

(Tristrimethylsilyl)methylbenzene, $PhC(TMS)_3$

Prepared under the same general conditions as $PhCF_2TMS$ with NBu_4Br (0.25 g, 0.8 mmol), DMPU (5.4 mL, 44.7 mmol), THF (55 mL), TMSCl (18 mL, 0.14 mol) and TFMB (2 g, 13.7 mmol).The electrolysis was performed for 27 h until the required charge (7.2 F·mol^{-1}) had been passed; yield: 2.1 g (50%); bp= 118 °C / 0.5 kPa, mp = 204 °C (EtOH), identical to $PhC(TMS)_3$ previously described in the literature.[10]



^{1}H NMR: δ_H(TMS) = 0.24 (s, 27H), δ_H(Ar) = 7.08–7.40 (m, 5H).

^{13}C NMR: δ_C(TMS) = 4.25 (s), δ_{C1} = 21.5 (s), δ_{C5} = 123.5 (s), $\delta_{C4} = \delta_{C6}$ = 127.5 (s), $\delta_{C3} = \delta_{C7}$ = 131.5 (s), δ_{C2} = 143.2ppm (s).

^{29}Si NMR: δ_{Si} = 1.20 (s).

MS: *m*/*z* = 308 (M·$^+$), 293 (M-15)$^+$, 73 ($SiMe_3^+$).

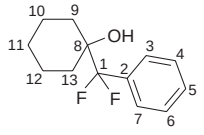
Calculated (found) for $C_{16}H_{32}Si_3$: C% = 62.25(60.92), H% = 10.36(10.36).

(Phenyldifluoro)methylation; General Procedure

To a ice cooled and stirred solution of $PhCF_2TMS$ (1 g, 5 mmol), in THF (4 mL), one equivalent of the carbonyl compound (0.5 equivalent in the case of octanal) and then 0.2 equivalent of TBAF (2 mL of a solution 1 mol·L^{-1} in THF) were introduced dropwise using a syringe. The resulting solution was stirred at 0 °C for 30 minutes and then at r.t. for 5 to 8 h (the conversion rate was monitored by GC). Afterwards, aq HCl (1mol·L^{-1}, 7 mL) was slowly added and stirred for 1 h. The mixture was then extracted with EtOAc (3 × 10 mL), the combined extracts were washed with brine, dried ($MgSO_4$) and evaporated in vacuo at r.t.

1-[difluoro(phenyl)methyl]cyclohexanol

Crude 1-[difluoro(phenyl)methyl]cyclohexanol (0.6 g, 2.6 mmol) was purified by column chromatography on silica gel with cyclohexane/EtOAc (95/5 v/v to 93/7 v/v) as the eluent to afford 0.58 g (50%) of pure alcohol as a colourless oil.



^{1}H NMR: δ_H(9–13) = 1.62 (m, 10H), δ_H(OH) = 2.02 (s, 1H), δ_H(Ar) = 7.39–7.52 (m, 5H).

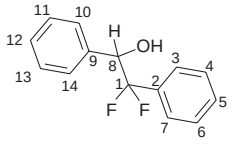
^{13}C NMR: δ_{C5} = 129.6 (s), $\delta_{C3} = \delta_{C7}$ = 127.1 (t, $^3J_{C-F}$ = 6.7 Hz), $\delta_{C4} = \delta_{C6}$ = 127.3 (s), δ_{C1} = 122.9 (t, $^1J_{C-F}$ = 249.4 Hz), δ_{C2} = 134.2 (t, $^2J_{C-F}$ = 26.7 Hz), δ_{C11} = 25.6 (s), $\delta_{C9} = \delta_{C13}$ = 30.3 (t, $^3J_{C-F}$ = 2.2 Hz), $\delta_{C12} = \delta_{C10}$ = 20.7 (s).

^{19}F NMR: δ_F = –111.4 (s).

MS: *m*/*z* = 226 (M·)$^+$(<1%), 127 ($PhCF_2$, 23%), 99 (C_6H_{10}OH, 100%), 81 (C_6H_9, 44.4%); Calculated (found) for $C_{13}H_{16}OF_2$: M = 226.117561 (226.116922)(–2.8 ppm).

2,2-Difluoro-1,2-diphenylethanol

Crude 2,2-difluoro-1,2-diphenylethanol (0.85 g, 3.6 mmol) was purified by column chromatography on silica gel with cyclohexane/EtOAc (95/5 v/v to 93/7 v/v) as the eluent to afford 0.52 g (61%) of pure alcohol as colourless crystals.



^{1}H NMR: δ_H(OH) = 2.45 (d, 1H), δ_H(8) = 5.01 (m, 1H), δ_H(Ar) = 7.20 (m, 10H).

^{13}C NMR: δ_{C9} = 135.7 (s), δ_{C2} = 133.7 (t, $^2J_{C-F}$ = 22.5 Hz), δ_{C5} = 130.0 (s), δ_{C12} = 128.6 (s), $\delta_{(C3, C4, C6, C7, C10, C11, C13, C14)}$ = 127.9 (m), δ_{C8} = 126.3 (t, $^2J_{C-F}$ = 7.5 Hz), δ_{C1} = 121.1 (t, $^1J_{C-F}$ = 247.5 Hz).

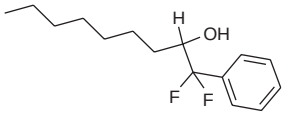
^{19}F NMR: δ_F (282 MHz, $CDCl_3$, from $PhOCF_3$) = –29.1 ppm (s), δ_F (282 MHz, THF with DMSO d^6 ext from $PhOCF_3$) = –22.5 ppm (d, 1F, J_{FF} = 252.8 Hz, J_{HF} = 28.2 Hz), δ_F = –28 ppm (d, 1F, J_{FF} = 252.8 Hz, J_{HF} = 28.2 Hz).

MS: *m*/*z* = 234 $(M^{\cdot})^+$(<1%), 214 (M-HF)(<1%), 127 ($PhCF_2$, 15%), 107 (Ph-CHOH, 100%), 105 (PhCO, 12%), 90 (PhCH, 4%), 79 (CF_2CHO, 64%), 77 (Ph, 43%), 51 (CF_2H, 13%).

The spectral data agree with those reported in the literature.[5]

1,1-Difluoro-1-phenylnonan-2-ol

Crude 1,1-difluoro-1-phenylnonan-2-ol was purified by column chromatography on silica gel with cyclohexane/EtOAc (95/5 v/v to 93/7 v/v) as the eluent to afford pure alcohol as colourless crystals.



^{19}F NMR: δ_F (282 MHz, THF with DMSO d^6 ext from $PhOCF_3$) = –24.15 (d, 1F, J_{FF} = 253.8 Hz, J_{HF} = 28.2 Hz), δ_F = –30.05 (d, 1F, J_{FF} = 253.8 Hz, J_{HF} = 28.2 Hz).

MS: *m*/*z* = 256 $(M^{\cdot})^+$(<1%), 129 (M-$PhCF_2$)(29%), 128 ($Me(CH_2)_6CHO$, 100%), 127 ($PhCF_2$, 44.7%), 111 (C_8H_{15}, 11.8%), 69 (C_5H_9, 55.3%), 55 (C_7H_{10}, 21%), 43 (C_3H_7, 15.8%), 28 (C_2H_4, 13%). The spectral data agree with those reported in the literature[5].

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