JOC Article

Preparation of Tri- and Difluoromethylsilanes via an Unusual Magnesium Metal-Mediated Reductive Tri- and Difluoromethylation of Chlorosilanes Using Tri- and Difluoromethyl Sulfides, Sulfoxides, and Sulfones

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A new and efficient method for the preparation of tri- and difluoromethylsilanes using magnesium metal-mediated reductive tri- and difluoromethylation of chlorosilanes is reported using tri- and difluoromethyl sulfides, sulfoxides, and sulfones. The byproduct of the process is diphenyl disulfide. Since phenyl trifluoromethyl sulfone, sulfoxide, and sulfide are readily prepared from trifluoromethane (CF_3H) and diphenyl disulfide, the method can be considered to be catalytic in diphenyl disulfide for the preparation of (trifluoromethyl)trimethylsilane (TMS−CF_3) from non-ozone-depleting trifluoromethane.

Introduction

The introduction of the trifluoromethyl (CF_3) and the difluoromethyl (CF_2H) groups into organic molecules has gained increasing attention due to the potential use of trifluoromethylated and difluoromethylated compounds in materials science and medicinal and agricultural chemistry.[1] Although there are few approaches to achieve this goal, fluoride-induced trifluoromethylation or difluoromethylation with organosilicon reagents (R_fSiR_3, $R_f = CF_3, CF_2H$) has been considered a straightforward and reliable method.[2] (Trifluoromethyl)trimethylsilane (TMS−CF_3), first developed by us[2b] in 1989 as a nulceophilic trifluoromethylating reagent of choice under mild conditions, is widely used and also works with enolizable carbonyl compounds. Recently developed nucleophilic trifluoromethylation methods are inefficient in the case of enolizable systems.[3]

TMS−CF_3 was first prepared by Ruppert et al. in 1984,[4] and since then, several other procedures have been developed by us and others via both chemical and electrochemical methods during the last two decades.[5] However, all of these methods have some drawbacks. First of all, they all use bromotrifluoromethane (CF_3Br) or iodotrifluoromethane (CF_3I)[3a] as a source for the trifluoromethyl group. Trifluoromethyl halides, particularly CF_3Br, in general are ozone depleting, and recently their manufacture and use have been regulated. Second, these procedures need special apparatus and well-controlled reaction conditions, and the product yields vary widely. Finally, none of the reported methods are amenable for the preparation of structurally diverse trifluoromethylsilanes. Compared with trifluoromethylation, little is known about nucleophilic difluoromethylation.[2f] This is mainly due to the lack of general and efficient methods for the preparation of difluoromethylsilanes.[6]

We now wish to report a new general and efficient method for the preparation of both trifluoromethylsilanes and difluoromethylsilanes using unusual magnesium metal-mediated reductive tri- and difluoromethylation of various chlorosilanes. Magnesium metal-promoted reactions through an electron-transfer process have attracted

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[1] (a) Hiyama, T., Eds. *Organofluorine Compounds. Chemistry and Applications*; Springer: New York, 2000. (b) Banks, R. E., Smart, B. E., Tatlow, J. C., Eds. *Organofluorine Chemistry-Principles and Commercial Applications*; Plenum Press: New York, 1994. (c) Welch, J. T., Eshwarakrishman, S., Eds. *Fluorine in Bioorganic Chemistry*; Wiley: New York, 1991. (d) Liebman, J. F., Greenberg, A., Dolbier, W. R., Jr., Eds. *Fluorine-Containing Molecules. Structure, Reactivity, Synthesis, and Applications*; VCH: New York, 1988.

[2] (a) Prakash, G. K. S.; Yudin, A. K. Chem. Rev. **1997**, *97*, 757. (b) Prakash, G. K. S.; Krishnamuti, R.; Olah, G. A. *J. Am. Chem. Soc.* **1989**, *111*, 393. (c) Yudin, K. Y.; Prakash, G. K. S.; Deffieux, D., Bradley, M.; Bau, R.; Olah, G. A. *J. Am. Chem. Soc.* **1997**, *119*, 1572. (d) Krishnamurti, R.; Bellew, D. R.; Prakash, G. K. S. *J. Org. Chem.* **1991**, *56*, 984. (e) Broicher, V.; Geffken, D. *Tetrahedron Lett.* **1989**, *30*, 5243. (f) Hagiwara, T.; Fuchikami, T. *Synlett* **1995**, 717.

[3] (a) Recently, CF_3I was also reported as a trifluoromethylating reagent: Ait-Mohand, S.; Takechi, N.; Medebielle, M.; Dolbier, W., Jr. *Org. Lett.* **2001**, *3*, 4271. (b) Motherwell, W. B.; Storey, L. *Synlett* **2002**, 646. (c) Billard, T.; Langlois, B. R.; Blond, G. *Eur. J. Org. Chem.* **2001**, 1467. (d) Billard, T.; Bruns, S.; Langlois, B. R. *Org. Lett.* **2000**, *2*, 2101. (e) Russell, J.; Roques, N. *Tetrahedron* **1998**, *54*, 13771.

[4] Ruppert, I.; Schlich, K.; Volbach, W. *Tetrahedron Lett.* **1984**, *25*, 2195.

[5] (a) Pawelke, G. *J. Fluorine Chem.* **1989**, *42*, 429. (b) Krishnamurti, R.; Bellew, D. R.; Prakash, G. K. S. *J. Org. Chem.* **1991**, *56*, 984. (c) Aymard, F.; Nedelec, J.-Y.; Perichon J. *Tetrahedron Lett.* **1994**, *35*, 8623. (d) Prakash, G. K. S.; Deffieux, D.; Yudin, A. K.; Olah, G. A. *Synlett* **1994**, 1057. (e) Ramaiah, P.; Krishnamurti, R.; Prakash, G. K. S. *Org. Synth.* **1995**, *72*, 232. (f) Grobe, J.; Hegge, J. *Synlett* **1995**, 641.

[6] Although several different (difluoromethyl)silanes are documented in the literature, their preparations give low yields or need high-cost precursors such as TMS−CF_2Cl. See reports: (a) Liu, E. K. S.; Lagow, R. J. J. *Organomet. Chem.* **1978**, *145*, 167. (b) Broicher, V.; Geffken, D. J. *Orgnomet. Chem.* **1990**, *381*, 315. (c) Buerger, H.; Moritz, P. *J. Organomet. Chem.* **1992**, *427*, 293. (d) Fuchikami, T.; Ojima, I. *J. Organomet. Chem.* **1981**, *212*, 145.

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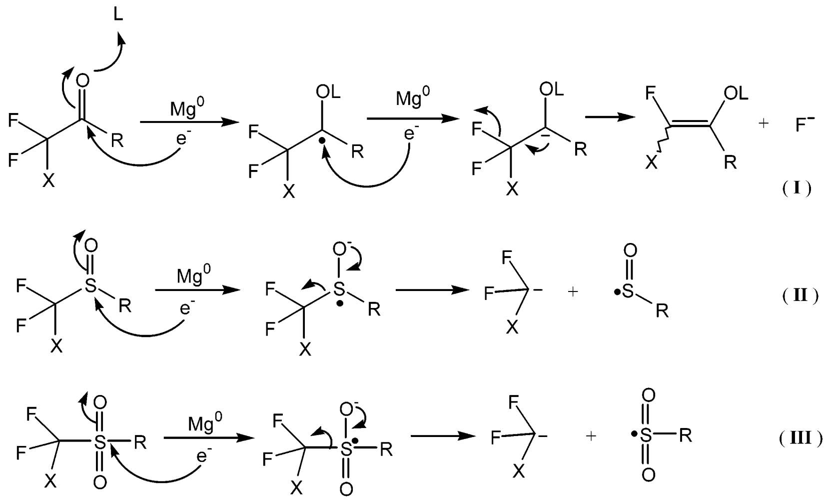
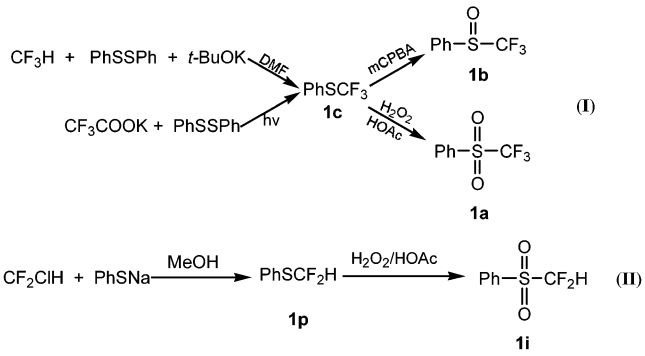
SCHEME 1[a]



[a] X = F, H; L = electrophiles such as trimethylsilyl group or magnesium cation, etc.

increasing interest recently, including C−F bond cleavage of trifluoromethyl ketones (Scheme 1, eq I),[7] trifluoroacetates,[8] trifluoromethylimines,[9] *p*-bis(trifluoromethyl) benzene[10] and difluoromethyl ketones,[11] O-silylation of tertiary alcohols,[12] cross-coupling of carbonyl compounds with TMSCl,[13] and C-acylation of aromatic α,β-unsaturated carbonyl compounds.[14] However, the magnesium metal-mediated reduction of trifluoromethyl and difluoromethyl sulfones or sulfoxides still has not been explored, and we felt that it may exhibit some different, interesting aspects as related to the well-known reductive C−F bond cleavage of tri- and difluoromethyl ketones.[7,11] In the trifluoromethyl and difluoromethyl sulfones or sulfoxides, due to the strong electron-withdrawing effect of CF_3 and CF_2H groups, the bond between the pseudohalide and the sulfur atom is sufficiently polarized by the pseudohalide group bearing substantial negative charge. Thus, when the electrons are transferred from magnesium metal to the sulfones and sulfoxides, reductive cleavage of the C−S bond to generate anionic CF_3^- or CF_2H^- species was anticipated over the C−F bond fission (Scheme 1, eqs II and III). Moreover, the phenyl trifluoromethyl sulfone **1a** or the sulfoxide **1b** can also be conveniently prepared from non-ozone depleting precursors such as trifluoromethane (CF_3H) or trifluoroacetate (Scheme 2, I),[15] and the difluoromethyl phenyl sulfone **1i** can be obtained using known methods (Scheme 2, II).[16] Furthermore, with these sulfones and sufoxides, the bond between sulfur and aromatic carbon is also hard to cleave, resulting in the expected regioselective bond fission. With these considerations in mind, we have embarked on the study of magnesium-mediated reductive trifluoromethylation and difluromethylation of various chlorosilanes and have found a long sought after simple, efficient method for the preparation of diverse trifluoromethylsilanes and difluoromethylsilanes.

SCHEME 2



Results and Discussion

Reaction of sulfone **1a** with 3 equiv of maganesium metal[17] and the chlorotriethylsilane in DMF solution at 0 °C gave exclusively (trifluoromethyl)triethylsilane, the only product detected by ^{19}F NMR. After workup and purification, (trifluoromethyl)triethylsilane **3d** was isolated in 95% yield. Diphenyl disulfide (PhSSPh) was also collected as a byproduct. TMS−CF_3 was also prepared similarly in quantitative conversions as identified by ^{19}F NMR.

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[7] Amii, H.; Kobaiyashi, T.; Hatamoto, Y.; Uneyama, K. *Chem. Commun.* **1999**, 1323.

[8] Amii, H.; Kobaiyashi, T.; Uneyama, K. *Synthesis* **2000**, 2001.

[9] Mae, M.; Amii, H.; Uneyama, K. *Tetrahedron Lett.* **2000**, *41*, 7893.

[10] Amii, H.; Hatomoto, Y.; Seo, M.; Uneyama, K. *J. Org. Chem.* **2001**, *66*, 7216.

[11] Prakash, G. K. S.; Hu, J.; Olah, G. A. *J. Fluorine Chem.* **2001**, *112*, 357−362.

[12] Nishigachi, I.; Kita, Y.; Watanabe, M.; Ishino, Y.; Ohno, T.; Maekawa, H. *Synlett* **2000**, 1025.

[13] Ishino, Y.; Maekawa, H.; Takenchi, H.; Sukata, K.; Nishiguchi, I. *Chem. Lett.* **1995**, 829.

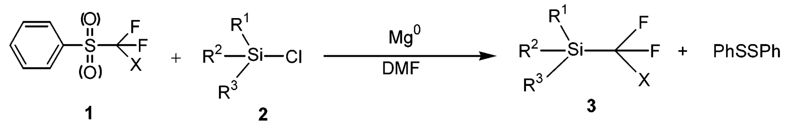
[14] Ohno, T.; Sakai, M.; Ishino, Y.; Shibata, T.; Maekawa, H.; Nishiguchi, I. *Org. Lett.* **2001**, *3*, 3439.

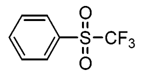
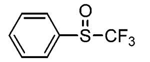
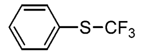
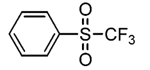
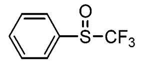
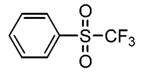
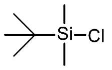
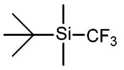
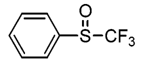
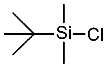
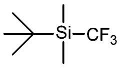
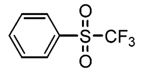
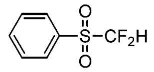
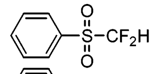
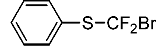
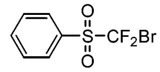
[15] Trifluoromethyl phenyl sulfide, sulfoxide, and sulphone are all commercially available. A number of reports on their preparation have appeared in the literature. For recent reports, see: (a) Russell, J.; Roques, N. *Tetrahedron* **1998**, *54*, 13771. (b) Gerard, F.; Jean-Mannel, M.; Laurent, S.-J. *Eur. Pat. Appl.* **1996**, EP 733614, 13 pp. (c) Chen, Q.-Y.; Duan, J.-X. *Chem. Commun.* **1993**, 918. (d) Yang, J.-J.; Kirchmeier, R. L.; Shreeve, J. M. *J. Org. Chem.* **1998**, *63*, 2656.

[16] (a) Hine, J.; Porter, J. *J. Am. Chem. Soc.* **1960**, *82*, 6178. (b) Hine, J.; Porter, J. *J. Am. Chem. Soc.* **1957**, *79*, 5493. (c) Stahly, G. P. *J. Fluorine Chem.* **1989**, *43*, 53.

[17] Commercial magnesium turnings were used without special pretreatment.

TABLE 1. Preparation of Trifluoromethylsilanes and Difluoromethylsilanes through Mg^0-Mediated Reductive Cleavage of C−S Bonds



entry	sulfur compound **1**	chlorosilane **2**	temperature[a]	time (h)[b]	product **3**	yields (%)[c]
a		Me_3SiCl	0°C ~ r t.	0.5 ~ 2	Me_3SiCF_3	100 (83)
b		Me_3SiCl	0°C ~ r.t.	0.5 ~ 2	Me_3SiCF_3	100 (81)
c		Me_3SiCl	r. t.	4	Me_3SiCF_3	45
d		Et_3SiCl	0°C ~ r.t.	1.3	Et_3SiCF_3	100 (95)
e		Et_3SiCl	r. t.	0.5	Et_3SiCF_3	98
f			-30°C ~ r. t.	3		75 (57)
g			r. t.	0.5		73
h		$(Me_3Si)_3SiCl$	-40 °C ~ r.t.	0.5	$(Me_3Si)_3SiCF_3$	85 (62)
i		Me_3SiCl	0°C	1.5	Me_3SiCF_2H	90 (76)
j		Et_3SiCl	-40 °C ~ r.t.	3	Et_3SiCF_2H	59 (51)
k		Me_3SiCl	r.t.	1.0	$PhSCF_2Si(CH_3)_3$	86 (85)
l		Me_3SiCl	0°C ~ r.t.	0.5	$Me_3SiCF_2CF_2SiMe_3$ $Me_3SiCF_2SiMe_3$	76 (55) 18

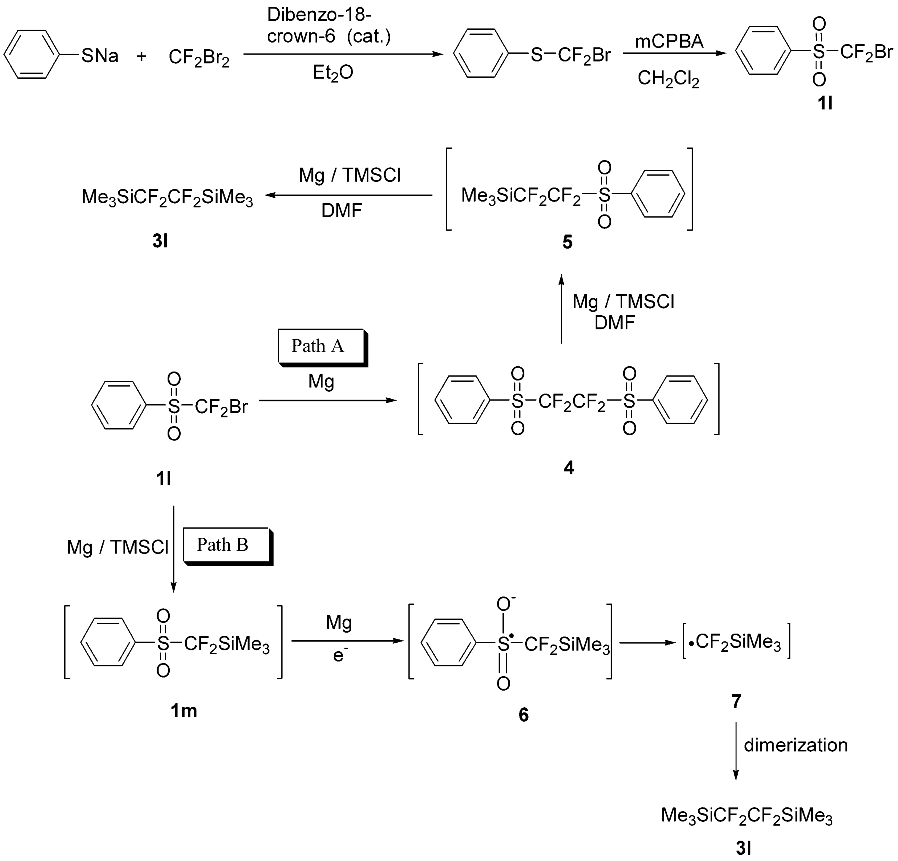
[a] Reaction temperature control is crucial due to the exothermic nature of the reaction. Larger-scale reactions normally need lower temperatures. [b] Reaction time may vary according to the different reaction scales. [c] Yields were determined by ^{19}F NMR, and data in parentheses are isolated yields.

The reaction works equally well for diverse types of chlorosilanes with tri- and difluoromethyl sulfones or sulfoxides (see Table 1). In the case of phenyl trifluoromethyl sulfide **1c** (entry c), the reaction was sluggish, indicating that the fluoroalkyl carbon−sulfur bond is not efficient in accepting the electron from the Mg metal. This was also confirmed by the fact that for the sulfide **1k**, the Barbier product **3k** (entry k) was produced in high yield without the C−S bond cleavage. In the case of bromodifluoromethyl phenyl sulfone **1l** (entry l), 1,2-bis(trimethylsilyl)-1,1,2,2-tetrafluoroethane **3l** was generated as the major product. This indicates that a Barbier-type coupling intermediate $[PhS(O)_2CF_2CF_2S(O)_2Ph]$ **4** is presumably formed, which is subsequently transformed into **3l** via a similar reductive fluoroalkylation process (see Scheme 3, path A).

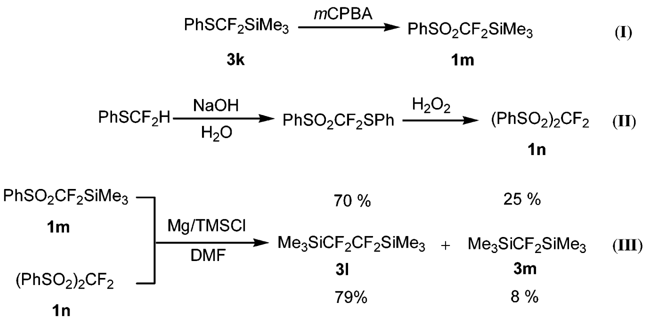
It is also possible that an alternative Barbier-type coupled intermediate **1m** is formed, which can generate the trimethylsilyldifluoromethyl radical species **7** that homocouples to produce **3l** (Scheme 3, path B). The likelihood of path B was supported by the experimental result that, under similar reaction conditions using Mg and TMSCl in DMF, both sulfone **1m** ($PhSO_2CF_2SiMe_3$) and disulfone **1n** ($PhSO_2CF_2O_2SPh$) readily produce compound **3l** in good yields (Scheme 4).

It should also be mentioned that the use of several reducing metals such as zinc, aluminum, indium, sodium, and lithium was explored to replace magnesium as the reducing agent, among which only zinc worked but only with a low yield of products (~30%). Other reducing or electron-donating reagents such as samarium iodide (SmI_2) and tetrakis(dimethylamono)ethylene were also investigated to no avail. Attempts to improve the reactivity of phenyl trifluoromethyl sulfide **1c** via electrochemistry using magnesium or zinc rod as the sacrificial anode and platinum as the cathode in DMF were also unsuccessful. DMF is not the only solvent required for this reaction. Other solvents such as THF can also be used, although it needs prolonged reaction times. This indicates there is no need to invoke CF_3^-/DMF adduct[15a] as the

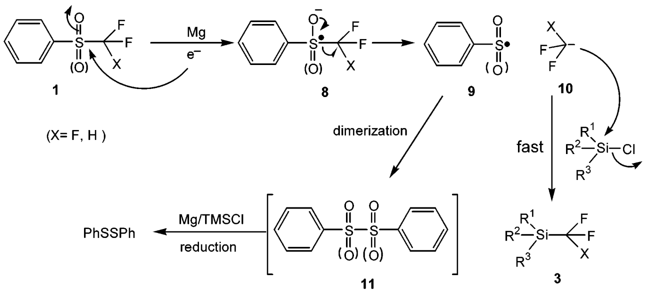
SCHEME 3



SCHEME 4



SCHEME 5



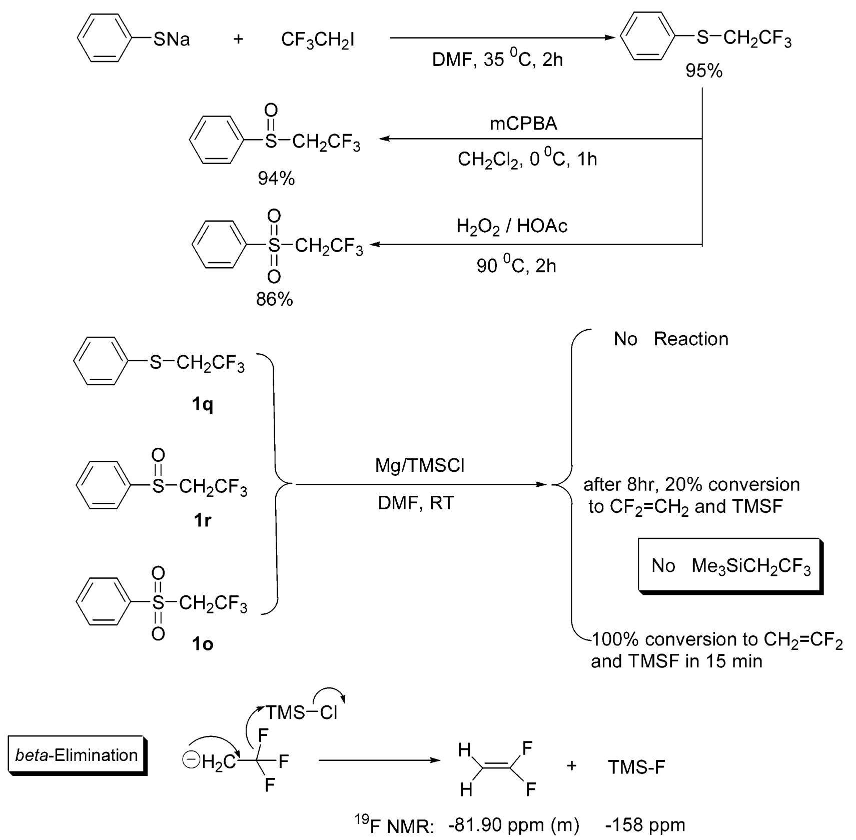
intermediate for these reactions. On the other hand, methyl phenyl sulfone in the presence of magnesium and TMSCl under similar conditions did not produce any tetramethylsilane.

Concerning the mechanism, we propose that a single electron transfer from magnesium metal to sulfones or sulfoxides facilitates a reductive cleavage of the C−S bond to form anionic tri- and difluoromethyl species and a sulfur-containg radical species (see Scheme 5). This mechanism provides a working model for this novel type of trifluoromethylation and difluoromethylation. The isolation of PhSSPh as a byproduct further confirms the possibility of the sulfur radical species. This mechanism is also supported by the fact that, when we used 2,2,2-trifluoroethyl phenyl sulfone [$PhS(O)_2CH_2CF_3$] **1o** as the reactant with Mg and TMSCl under similar reaction conditions, 1,1-difluoroethene was produced readily. Obviously, 1,1-difluoroethene was obtained through the β-elimination of the fluoride (F^-) from the in situ-generated anionic species ($CF_3CH_2^-$) from **1o** via a smilar mechanism as described above (Scheme 6). Scheme 6 also shows that in the case of 2,2,2-trifluoroethyl phenyl sulfone, sulfoxide, and sulfide, the order of reactivity is sulfone > sufoxide > sulfide.

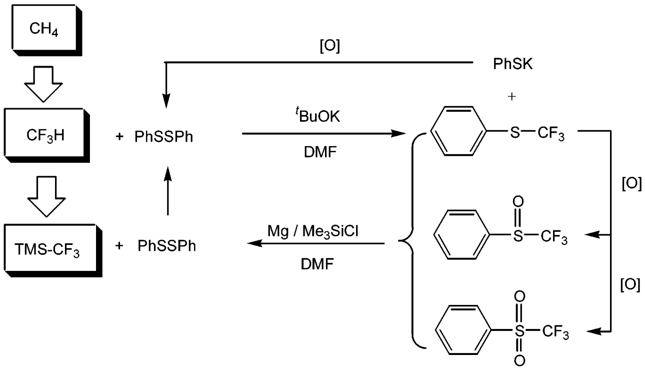
It should also be mentioned that methyl trifluoromethyl sulfone ($CH_3SO_2CF_3$) also reacts with magnesium metal and TMSCl in DMF to produce TMS−CF_3 in moderate yields (~40% over a period of 20 h at room temperature). However, the reaction appears to be sluggish. This indicates that the aromatic ring conjugation in **1a** is important to facilitate the initial electron transfer process.

The reductive fluoroalkylation chemistry was also attempted with other electrophiles such as aldehydes, ketones, allyl bromide, benzyl chloride, or tributyltin chloride with no success. Even tributyltin hydride and allyltrimethylsilane showed no reactivity. The reason for such a behavior is not clear.

SCHEME 6



SCHEME 7



It is well-known that the phenyl trifluoromethyl sulfone **1a** and sulfoxide **1b** can be readily prepared from trifluoromethane (manufactured from methane[18]) and diphenyl disulfide.[19] Since in our fluoroalkylation process, diphenyl disulfide is produced as a reductive byproduct, the presently developed method provides a novel and useful catalytic pathway (in diphenyl disulfide) for the production of (trifluoromethyl)silanes from trifluoromethane and chlorosilanes (see Scheme 7).

Conclusion

In conclusion, we have developed a versatile and new non-Freon-based method for the preparation of a number of (trifluoromethyl)silanes and (difluoromethyl)silanes via a magnesium metal-mediated reductive S−C bond cleavage process of trifluoromethyl and difluoromethyl sulfones, sulfoxides, and sulfides. The method can be considered to be catalytic with respect to the diphenyl disulfide since the starting phenyl trifluoromethyl sulfones, sulfoxides, and sulfides are themselves readily prepared using non-ozone-depleting trifluoromethane[28] and diphenyl disulfide.

Experimental Section

(Trifluoromethyl)trimethylsilane (3a). Into a 250 mL dry Schlenk flask under an argon atmosphere were added 1.14 g of Mg turnings (47.5 mmol) and 11.8 g TMSCl (109 mmol) in 50 mL of DMF at 0 °C. After the mixture was stirred for 2 min, 4.62 g (23.8 mmol) of **1b** in 5 mL of DMF was added slowly via a syringe. The reaction mixture was stirred at room temperature at 0 °C for 30 min and then at room temperature for another 1.5 h until all the starting material was transformed into product **3a** (monitored by ^{19}F NMR). All the low-

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[18] Webster, J. L.; Lerou, J. J. U.S. Patent 5,446,218, 1995.

[19] PhS(O)CF_3 and PhS$(O)_2CF_3$ can be obtained by oxidation of $PhSCF_3$, which can be produced from CF_3H and PhSSPh. See ref 15.

[20] Li, X.; Jiang X.; Gong, Y.; Pan, H. *HuaXue XueBao* **1985**, *43*, 260.

[21] Burton, D. J.; Weimers, D. M. *J. Fluorine Chem.* **1981**, *18*, 573.

[22] (a) Hine, J.; Ghirardelli, R. G. *J. Org. Chem.* **1958**, *23*, 1550. (b) Nakai, T. et al. *J. Fluorine Chem.* **1977**, *9*, 89. (c) Long, Z.-Y.; Chen, Q.-Y. *J. Fluorine Chem.* **1998**, *91*, 95.

[23] Fuchigami, T.; Yamamoto, K.; Nakagawa, Y. *J. Org. Chem.* **1991**, *56*, 137.

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[25] Yamamoto, T.; Watanabe, H. *Jpn. Kokai Tokkyo Koho* **2001**, JP 2001039942.

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[28] Production and use of trifluoromethane (CF_3H) is not currently banned. However, it is known that this compound may have relatively high potential to cause greenhouse warming.

boiling fractions were collected under vacuum into a trap (cooled in liquid nitrogen), warmed to room temperature, and then washed with ice−water (50 mL x 3). After quick drying over activated molecular sieves, the organic mixture was fractionally distilled using a 30 cm long column to give 2.73 g (81% yield) product **3a**, bp 53−55 °C (lit.[2d] 55−55.5 °C). ^{1}H NMR (360 MHz, CDCl$_3$): δ 0.25 (s, 9H, CH$_3$). ^{13}C NMR (90 MHz, CDCl$_3$): δ −5.3 (s, CH$_3$); 131.7 (q, $^{1}J_{\mathrm{C-F}} = 321.8$ Hz, CF$_3$). ^{19}F NMR (338 MHz, CDCl$_3$): δ −67.2.

Similarly, compound **1a** was used to prepare **3a** in 82% isolated yield. Compound **1c** also could be used to prepare **3a**, but the reaction was found to be sluggish.

(Trifluoromethyl)triethylsilane (3d). Into a flame-dried Schlenk flask containing 1.03 g (43 mmol) of magnesium turnings and 30 mL of DMF under argon was added 3.0 g (14 mmol) of trifluoromethyl phenyl sulfone **1a** at 0 °C. After the mixture was stirred for 5 min, 6.45 g (43 mmol) of triethylsilyl chloride was added dropwise via syringe. The color of the reaction mixture slowly turned yellow. The progress of the reaction was monitored by ^{19}F periodically. After 1 h, the mixture was slowly warmed to room temperature over a 20 min period and the reaction mixture was washed with 50 mL of ice−water. After the excess Mg was removed, the solution was extracted with pentane (30 mL x 3). The pentane phase was washed carefully with cold 98% sulfuric acid (30 mL x 4) to remove most of the siloxane and silanol. Subsequently, the organic phase was washed with cold water (30 mL x 2), saturated aqueous NaHCO$_3$ solution (30 mL x 2), and water (20 mL x 2) and dried over anhydrous magnesium sulfate. The solvent was removed under vacuum (∼100 Torr), and the resulting crude product also contained PhSSPh as a byproduct (characterized by both GC-MS and NMR). The crude product was carefully purified by small-scale fractional distillation to give 2.48 g (95% yield) of (trifluoromethyl)triethylsilane **3d**, bp = 56∼58 °C/60 Torr (lit.[26] 52∼54 °C/10 Torr). GC-MS showed that its purity was higher than 96%. ^{1}H NMR (500 MHz, CDCl$_3$): δ 0.79 (q, $^{3}J_{\mathrm{H-H}} = 7.9$ Hz, 6H); 1.04 (t, $^{3}J_{\mathrm{H-H}} = 7.9$ Hz, 9H). ^{13}C NMR (125 MHz, CDCl$_3$): δ 0.79 (s, CH$_2$); 6.37 (s, CH$_3$); 132.19 (q, $^{1}J_{\mathrm{C-F}} = 323.5$ Hz, CF$_3$). ^{19}F NMR (470 MHz, CDCl$_3$): −61.30. ^{29}Si NMR (99 MHz, CDCl$_3$): δ 7.74 (q, $^{2}J_{\mathrm{Si-F}} = 32.0$ Hz). GC-MS (*m*/*z*): 184 (M$^+$), 155 (M − Et), 115(Et$_3$Si$^+$).

(Trifluoromethyl)*t*-butyldimethylsilane (3f). Into a dry 250 mL Schlenk flask under an argon atmosphere were added 5.14 g of Mg turnings (214 mmol) and 32.3 g (214 mmol) of *tert*-butyldimethylsilyl chloride in 150 mL of DMF at −30 °C. Subsequently, 15.0 g (71.4 mmol) of **1a** in 10 mL of DMF was added slowly via a syringe. The reaction mixture was stirred at room temperature at −30 °C for 1 h and then at room temperature for another 2 h until all the starting material was consumed (^{19}F NMR showed that the conversion of **3f** was 75%). The reaction mixture was washed with ice−water, followed by extraction with pentane (30 mL x 4). The combined pentane phase was further washed carefully with cold 98% sulfuric acid (20 mL x 4) to remove most of the siloxane and silanol. Then, the pentane phase was washed with cold aqueous NaHCO$_3$ solution three times until pH paper indicated neutral pH. The pentane phase was dried over MgSO$_4$ and the solvent evaporated to give a crude product that was fractionally distilled to give 7.46 g of colorless liquid (95 °C/410 Torr), which turned to a transparent crystalline solid at room temperature (mp 52∼54 °C, sublimes), yield 57%. ^{1}H NMR (500 MHz, CDCl$_3$): δ 0.20 (s, 6H); 0.99 (s, 9H). ^{13}C NMR (125 MHz, CDCl$_3$): δ −8.8; 16.0; 26.0; 132.0 (q, $^{1}J_{\mathrm{C-F}} = 323.8$ Hz, CF$_3$). ^{19}F NMR (470 MHz, CDCl$_3$): δ −61.8. ^{29}Si NMR (99 MHz, CDCl$_3$): δ 8.4 (q, $^{2}J_{\mathrm{Si-F}} = 32.8$ Hz). GC-MS (*m*/*z*): 184 (M$^+$), 127 (M$^+$ − ^{t}Bu), 115 (M$^+$ − CF_3), 99 (M$^+$ − CF_3 − CH_3), 57 (*t*Bu$^+$). High-resolution GC-MS (EI): *m*/*z* calcd for C$_7$H$_{15}$F$_3$Si (M$^+$) 184.0895, found 184.0943.

Tris(trimethylsilyl)trifluoromethylsilane (3h). The procedure was similar to the above examples. Into 2 g (83 mmol) of Mg turnings and 1 g (4.76 mmol) of **1a** in 20 mL of DMF at −40 °C was slowly added 3 g (10.6 mmol) of tris(timethylsilyl)silyl chloride in 10 mL of DMF. The reaction mixture was then stirred at −40 °C for 1 h and between −40 and − 20 °C for another 2 h, until all the **1a** was consumed (monitored by ^{19}F NMR). The reaction mixture was washed with ice−water, followed by extraction with pentane (20 mL x 4). The pentane phase was washed with cold 98% sulfuric acid (10 mL x 3) to remove most of the siloxane and silanol and washed with cold aqueous NaHCO$_3$ solution three times until pH paper indicated neutral pH. After drying over MgSO$_4$ and solvent removal, the crude product was further purified by silica gel chromatography (pentane as the eluent) to give 0.93 g (62% yield) of solid product **3h** that sublimes at 50 °C/10 Torr. ^{1}H NMR (500 MHz, CDCl$_3$): δ 0.26 (s, 27 H). ^{13}C NMR (125 MHz, CDCl$_3$): δ 0.5 (s, CH$_3$); 136.8 (q, $^{1}J_{\mathrm{C-F}} =328.0$ Hz, CF$_3$). ^{19}F NMR (470 MHz, CDCl$_3$): δ −41.4. ^{29}Si NMR (99 MHz, CDCl$_3$): δ −66.8 (q, $^{2}J_{\mathrm{Si-F}} = 27.5$ Hz, 1 Si); −12.5 (q, $^{3}J_{\mathrm{Si-F}} = 4.6$ Hz, 3Si). GC-MS (*m*/*z*): 316 (M$^+$), 247 [(Me$_3$Si)$_3$Si$^+$], 69 (CF$_3$$^+$). High-resolution GC-MS (EI): *m*/*z* calcd for C$_{10}$H$_{27}$F$_3$Si$_4$ (M$^+$) 316.1142, found 316.1110.

(Difluoromethyl)trimethylsilane (3i). Into a mixture of 4.8 g (200 mmol) of Mg turnings, 28.93 g (266 mmol) of TMSCl, and 100 mL of DMF at 0 °C was added 12.80 g (66.7 mmol) of difluoromethyl phenyl sulfone (**1i**) in 10 mL of DMF slowly. The reaction mixture was stirred at 0 °C for 90 min until ^{19}F NMR showed that all the **1i** was consumed. All of the low-boiling species was separated out by bulb to bulb distillation, followed by washing with ice−water (30 mL x 3) and drying over molecular sieves. Fractional distillation (using a 30 cm long distillation column) afforded 4.96 g of product, bp 52 °C (lit.[2c] 50 °C), yield 76%. ^{1}H NMR (360 MHz, CDCl$_3$): δ 0.15 (s, 9H); 5.82 (t, $^{2}J_{\mathrm{H-F}} = 46.5$ Hz, 1H). ^{13}C NMR (90 MHz, CDCl$_3$): δ −5.4 (t, $^{3}J_{\mathrm{C-F}} = 2.8$ Hz); 123.9 (t, $^{1}J_{\mathrm{C-F}} = 254.7$ Hz). ^{19}F NMR (338 MHz, CDCl$_3$): δ −140.1 (d, $^{2}J_{\mathrm{F-H}} = 46.8$ Hz).

(Difluoromethyl)triethylsilane (3j). Into a mixture of 5 g (26 mmol) of difluoromethyl phenyl sulfone (**1i**), 1.9 g of Mg turnings (78 mmol), and 150 mL of DMF at −40 °C was slowly added 11.8 g (78 mmol) of chlorotriethylsilane. The reaction mixture was then stirred at temperatures between −40 and 10 °C over a 4 h period until ^{19}F NMR indicated that all the **1i** was consumed. Similar workup as above and fractional distillation gave 2.2 g of product **3j**,[27] bp 71 °C/56 Torr, yield 51%. ^{1}H NMR (500 MHz, CDCl$_3$): δ 0.72 (q, $^{3}J_{\mathrm{H-H}} = 8.0$ Hz, 6H); 1.02 (t, $^{3}J_{\mathrm{H-H}} = 8.0$ Hz, 9H); 5.95 (t, $^{2}J_{\mathrm{H-F}} = 46.0$ Hz, 1H). ^{13}C NMR (125 MHz, CDCl$_3$): δ 0.6 (s, CH$_2$); 6.7 (s, CH$_3$); 124.3 (t, $^{1}J_{\mathrm{C-F}} = 254.8$ Hz). ^{19}F NMR (470 MHz, CDCl$_3$): δ −137.6 (d, $^{2}J_{\mathrm{F-H}} = 45.8$ Hz). ^{29}Si NMR (99 MHz, CDCl$_3$): δ 3.3 (t, $^{2}J_{\mathrm{Si-F}} = 24.8$ Hz). GC-MS (*m*/*z*): 166 (M$^+$); 115 (Et$_3$Si$^+$); 51 (CF$_2$H$^+$).

1,2-Bis(trimethylsilyl)-1,1,2,2-tetrafluoroethane (3l). Into a mixture of 0.42 g (17.5 mmol) of Mg turnings, 1.92 g (17.7 mmol) of TMSCl, and 10 mL of DMF was added 1.60 g (5.9 mmol) of bromodifluoromethyl phenyl sulfone **1l**. The reaction mixture was stirred at 0 °C for 30 min and then at room temperature for another 30 min until ^{19}F NMR showed that all the **1l** was consumed (the yield of **3l** was 76% and byproduct TMSCF$_2$TMS, 18% by ^{19}F NMR analysis). The reaction mixture was washed with ice−water followed by extraction with pentane (10 mL x 4). The pentane phase was washed with cold 98% sulfuric acid (10 mL x 3) to remove most of the siloxane and silanol. Then, the pentane solution was washed with cold aqueous NaHCO$_3$ solution three times until pH paper indicated a neutral pH. After drying over MgSO$_4$ and solvent removal, the crude product was further purified by fractional distillation and then recrystallization at −20 °C to give 0.40 g of crystalline product **3l**, mp 40∼42 °C, yield 55%. ^{1}H NMR (500 MHz, CDCl$_3$): δ 0.24 (s, 18H). ^{13}C NMR (125 MHz, CDCl$_3$): δ −4.0 (m, CH$_3$); 126.6 (tt, $^{1}J_{\mathrm{C-F}} = 265.0$ Hz; $^{2}J_{\mathrm{C-F}} = 45.9$ Hz). ^{19}F NMR (470 MHz, CDCl$_3$): δ −122.3.

Compound **3l** was also prepared by using PhSO$_2$CF$_2$O$_2$SPh (**1n**) or PhSO$_2$CF$_2$TMS (**1m**) as the starting material (see Scheme 4).

Phenyl (Trimethylsilyl)difluoromethyl Sulfide (3k). Into a mixture of 0.22 g (9.2 mmol) of Mg turnings, 1.99 g (18.3 mmol) of TMSCl, and 20 mL of DMF at room temperature was added 1.1 g (4.6 mmol) of bromodifluoromethyl phenyl sulfide **1k**. The reaction was stirred at room temperature for another 1 h. Excess TMSCl was removed under vacuum (~10 mmHg). The residue was washed with ice−water and then extracted with dichloromethane (20 mL x 3). The organic phase was further washed with brine and water successively and dried over $MgSO_4$. After solvent removal, the crude product was further purified by silica gel chromatography (pentane as eluent) to give 905 mg (85% yield) of product **3k** as a colorless liquid, bp 86~87 °C/4 Torr. ^1H NMR (500 MHz, $CDCl_3$): δ 0.25 (s, 9H); 7.37 (m, 3H); 7.59 (d, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ −4.2; 126.3 (t, $^3J_{C-F} = 4.1$ Hz); 128.8; 129.3; 134.0 (t, $^1J_{C-F} = 300.1$ Hz); 136.2. ^{19}F NMR (470 MHz, $CDCl_3$): δ −88.1 (s). ^{29}Si NMR (99 MHz, $CDCl_3$): 7.7 (t, $^2J_{Si-F} = 31.28$ Hz). IR (neat): 3064; 2965; 2904; 1884; 1585; 1475; 1441; 1414; 1307; 1255; 1076; 1025; 962; 884; 850; 825; 744; 703; 690; 631; 607; 496 cm^{-1}. GC-MS (m/z): 232 (M^+), 109 (PhS^+), 73 (Me_3Si^+). HRMS (DEI): m/z calcd for $C_{10}H_{14}F_2SSi$ (M^+) 232.0553, found 232.0545.

Phenyl (Trimethylsilyl)difluoromethyl Sulfone (1m). Phenyl (trimethylsilyl)difluoromethyl sulfide (**3k**) (2.0 g, 8.6 mmol) was oxidized with *m*CPBA (9.0 mmol) in 20 mL of CH_2Cl_2 initially at 0 °C, followed by stirring at room temperature overnight. After filtration, the filtrate was washed with Na_2SO_3 solution (10 mL x 3), $NaHCO_3$ solution (10 mL x 2), and water sequentially. After drying over $MgSO_4$ and solvent removal, the crude product was distilled to afford 1.2 g (51% yield) of product **1m** as a colorless liquid, bp 112~114 °C/1 Torr. ^1H NMR (500 MHz, $CDCl_3$): δ 0.44 (s, 9H); 7.61 (t, 2H); 7.74 (t, 1H); 7.95 (d, 2H). ^{19}F NMR (470 MHz, $CDCl_3$): δ −112.9. HRMS (DCI/NH_3): m/z calcd for $C_{10}H_{18}F_2NO_2SSi$ ($M + NH_4^+$) 282.0795, found 282.0787.

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Supporting Information Available: General experimental paragraph; ^1H, ^{13}C, ^{19}F, and ^{29}Si NMR spectra of compounds **3f**, **3h**, **3i**, and **3l**; and high-resolution mass spectra of compounds **3f**, **3h**, **3l**, and **1m**. This material is available free of charge via the Internet at http://pubs.acs.org.

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