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Reaction of the Ruppert–Prakash reagent with perfluorosulfonic acids

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ABSTRACT

A new property of Me_3SiCF_3 to undergo C–F bond activation upon interaction with perfluorosulfonic acids is described. The reaction is catalyzed by titanium tetrachloride and affords difluoromethyl perfluorosulfonates in good yields.

1. Introduction

The Ruppert–Prakash reagent (Me_3SiCF_3) [1] has found extensive applications as a convenient equivalent of trifluoromethyl carbanion in reactions with carbonyl compounds, imines, and heteroatom-centered electrophiles [2]. The key feature of these processes is the activation of the silane with a Lewis base followed by transfer of the CF_3-group from pentacoordinate complex to an electrophilic species [3].

At the same time, reactions of Me_3SiCF_3 under conditions of acidic activation have remained virtually unexplored [4]. Indeed, there is only one reported example of the process of this type, the interaction of Me_3SiCF_3 with sulfur trioxide leading to Me_3SiOTf through the insertion of SO_3 into C–Si bond [5].

Herein we report a new property of the Ruppert–Prakash reagent to undergo concomitant C–F and C–Si bond activation in the presence of perfluorosulfonic acids.

2. Results and discussion

Within the context of our studies on the reactivity of silyl triflates bearing perfluorinated group [6] we attempted the preparation of silyl triflate **1** by reaction of Me_3SiCF_3 with triflic acid with the hope to effect the protonation of Me_3SiCF_3 at the methyl group [7] (Scheme 1, path a). The reaction was performed by addition of Me_3SiCF_3 to 2.0 equivalents of triflic acid without solvent at −20 °C followed by stirring at room temperature for 1 h.

Analysis of the reaction mixture by ^1H and ^{19}F NMR spectroscopy indicated that none of silane **1** was formed. Instead, difluoromethyltriflate **2a** and Me_3SiF were observed as the major products together with a small amount of Me_3SiOTf (path b). The rest of material was unreacted Me_3SiCF_3 and triflic acid.

Despite the fact that the reaction occurs exothermically upon mixing, it does not go to completion at room temperature even for a longer period (Table 1, entry 2). To achieve complete conversion of starting silane the reaction has to be performed with at least two equivalents of triflic acid at 40–45 °C affording difluoromethyltriflate **2a** in 80% yield after distillation (entry 3) [8].

It was found that the presence of catalytic amounts (1–5 mol%) of Lewis acid provides significant rate acceleration (Table 1, entries 4–12). Boron tribromide gave quite clean reactions, while $AlCl_3$ and $BF_3{\cdot}OEt_2$ had virtually no influence on the process. With antimony pentafluoride the reaction was most violent though decreased yield of difluoromethyltriflate was observed. Titanium tetrachloride turned out to be most efficient Lewis acid leading to rapid and clean reactions. Under optimal conditions the desired product was obtained within 1 h with only 1.2 equivalents of triflic acid (entry 12).

Other perfluorosulfonic acids were also involved in reaction with the Ruppert–Prakash reagent affording corresponding difluoromethylsulfonates **2b,c** in reasonable yields (Scheme 2). Disappointingly, non-fluorinated methanesulfonic acid proved to be absolutely unreactive under similar conditions.

Of special note is the facile C–F bond activation in M_3SiCF_3 occurring with perfluorosulfonic acids, while for conventional fluorocarbons the use of superacidic systems such as HF/SbF_5 or CF_3CO_2H/SbF_5 has been reported [9]. Only recently it was shown that activation of C–F bond in CF_3-substituted aromatics can be induced by large excess of triflic acid [10].

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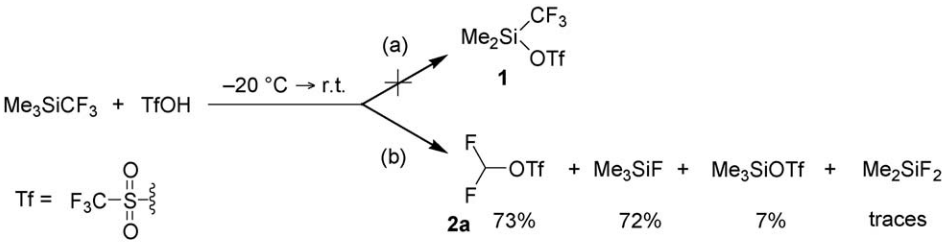


Scheme 1.

Table 1
Reaction of Me_3SiCF_3 with TfOH.

Entry	TfOH, equiv.	Additive (mol %)	Time, h	Temperature, °C	Conversion, %[a]	Yield of **2a**, %[b]
1	1.5	–	3	40–45	71	[c]
2	2	–	18	r.t.	96	[c]
3	2	–	3	40–45	100	80
4	1.5	BBr_3 (5)	1	r.t.	91	[c]
5	1.5	BBr_3 (5)	18	r.t.	100	83
6	1.5	$AlCl_3$ (5)	1	r.t.	61	[c]
7	1.5	$AlCl_3$ (5)	18	r.t.	88	[c]
8	1.5	$BF_3{\cdot}OEt_2$ (5)	18	r.t.	98	[c]
9	1.5	SbF_5 (5)	1	r.t.	100	72
10	1.5	$TiCl_4$ (5)	1	r.t.	100	83
11	1.5	$TiCl_4$ (1)	2	r.t.	100	83
12	1.2	$TiCl_4$ (1)	1	r.t.	100	80

The last row is the most efficient procedure among all entries.

[a] Determined by ^{19}F NMR spectroscopy.

[b] After distillation.

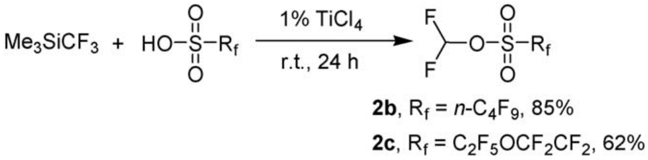
[c] The isolation of product was problematic, since unreacted Me_3SiCF_3 cannot be removed by distillation.

Concerning the mechanism of this reaction, it can be proposed that the final product is produced by protonation of difluorocarbene, which is generated either by stepwise or by concerted elimination of HF and Me_3SiOTf (Scheme 3).

To probe the stepwise mechanism, we evaluated other triflurомethylated compounds—$PhCF_3$ and $PhOCF_3$, which upon abstraction of fluoride anion would give phenyl and phenoxy stabilized carbocations. However, these substances proved to be absolutely unreactive in reaction with TfOH even in the presence of 5% of $TiCl_4$. Another argument against stepwise mechanism in the reaction of Me_3SiCF_3 is that the generation of carbocationic intermediate would be unfavorable since trimethylsilyl group does not exert significant cation-stabilizing effect on α-carbon atom [11].

These data suggest that the concerted pathway for the reaction of the Ruppert–Prakash reagent, involving simultaneous C–F and C–Si bond cleavage along with H–F and O–Si bond formation, is more likely.

The role of Lewis acids deserves special comment. It is expected that the Lewis acid interacts with triflic acid to give corresponding metal triflates [12,13]. Such highly Lewis acidic substance may accelerate the reaction of Me_3SiCF_3 with acid by one of the following ways. Thus, it may either increase the Bronsted acidity of the acid [14] or increase the rate of the equilibrium regeneration of triflic acid (Scheme 3, bottom equation). Another opportunity is that Lewis acid accelerates the generation of difluorocarbene from Me_3SiCF_3 through the activation of C–F bond.

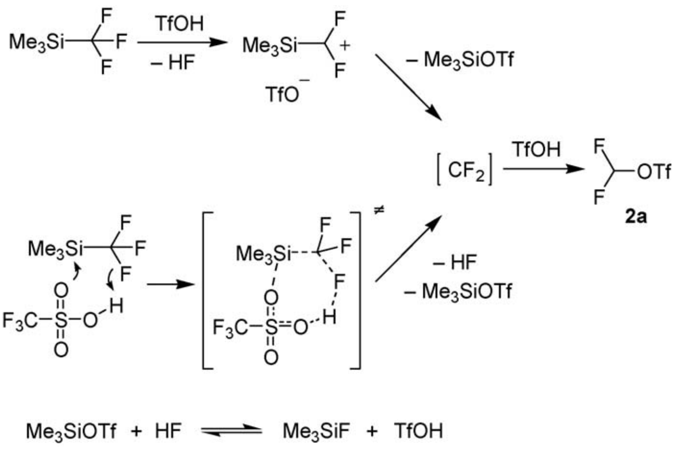


2b, $R_f = n\text{-}C_4F_9$, 85%
2c, $R_f = C_2F_5OCF_2CF_2$, 62%

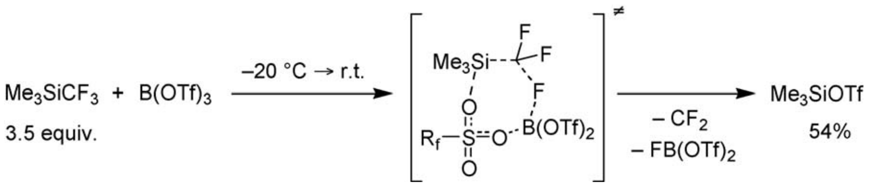
Scheme 2.

Indeed, it is known that C–F bond can be heterolitically activated with Lewis acids [15–17]. In particular, various polyfluoroolefins interact with boron triflate $B(OTf)_3$ to give products of substitution of a fluorine atom by TfO-group [16]. When we treated the Ruppert–Prakash reagent with boron triflate the only observable product was Me_3SiOTf, which was isolated with the yield of 54% (Scheme 4). We believe that in this case the reaction also proceeds in a concerted fashion with the expulsion of difluorocarbene and generation of another boron Lewis acid $FB(OTf)_2$. The latter species may further react with the silane providing, finally, boron trifluoride.

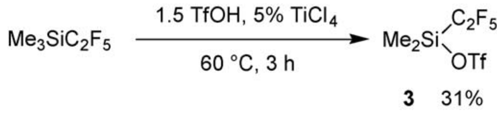
We also studied the behavior of pentafluoroethyl-substituted silane $Me_3SiC_2F_5$ in the presence of triflic acid (Scheme 5). The reaction was very slow furnishing silyl triflate **3** as a result of the protonation of the methyl group.



Scheme 3.



Scheme 4.



Scheme 5.

We briefly examined the reactivity of difluoromethyl triflate **2a** with typical nucleophiles. No reaction was observed with pyridine and triphenylphosphine for 24 h at room temperature (in $CDCl_3$, NMR control). With more nucleophilic N-methylimidazole the rapid decomposition of **2a** was noted to give several species, presumably, N-methylimidazolium fluoride and CF_3SO_2F. The inability of trilate **2a** to serve as alkylating reagent is similar to that of trifluoromethyl triflate [18] and 1,1-difluoroethyl triflate [19]. At the same time, such behavior stands in sharp contrast with that of difluoromethylsulfonium salts, which are competent difluoromethylating reagents [20].

In summary, a new reaction of the Ruppert–Prakash reagent proceeding upon interaction with perfluorosulfonic acids and affording difluoromethyl perfluorosulfonates has been described. The simultaneous C–F and C–Si bond activation is believed to be the key feature responsible for the efficiency of the reaction.

3. Experimental

3.1. General experimental procedures

All reactions were performed under an argon atmosphere. Commercially available silanes (P&M) and perfluorsulfonic acids (P&M, Aldrich) were purified by distillation. NMR spectra were recorded on a Bruker AM-300 or AC-200 instruments.

3.2. Reaction of Me_3SiCF_3 with perfluorosulfonic acids—general procedure

Titanium tetrachloride (11 μL, 0.1 mmol) was added dropwise to perfluorosulfonic acid (12 mmol) under vigorous stirring at room temperature, and the mixture was kept for 5 min. The homogeneous yellow solution was evacuated at 10–15 Torr until gas evolution ceased (ca. 5–10 min). The mixture was cooled to −20 °C, Me_3SiCF_3 (1.48 mL, 10 mmol) was added, and the mixture was kept for 2 min. The cooling bath was replaced first by ice/water bath, which was kept for 2 min, and then by water bath with 20 °C, and the mixture was stirred at room temperature (1 h for **2a** or 24 h for **2b,c**).

For the isolation of **2a**, volatile materials were distilled off under vacuum (100 Torr) in a cold trap (liq. nitrogen). The collected liquid contains **2a** and Me_3SiF in a molar ratio 1:1, which cannot be separated by small-scale distillation. The sample of **2a** containing traces of Me_3SiF was obtained by fractional distillation through a 15-cm column with glass filling.

For the isolation of **2b,c**, volatile materials (mostly Me_3SiF) were distilled off under vacuum (20 Torr). The residue was distilled off under vacuum (ca. 1 Torr, oil pump) in a cold trap (liq. nitrogen). The collected liquid contains compounds **2b,c**, which were >98% pure according to NMR spectroscopy. Subsequent vacuum distillation afforded analytically pure substances.

3.2.1. Difluoromethyl trifluoromethanesulfonate (2a)

B.p. 48.5–49 °C. ^1H NMR (300 MHz, $CDCl_3$), δ: 6.85 (t, 1H, $J = 67.9$, CHF_2). ^{13}C NMR (75 MHz, $CDCl_3$), δ: 115.0 (t, $J = 276.1$, CHF_2), 118.3 (qt, $J = 319.6$, 1.9, CF_3) ^{19}F NMR (282 MHz, $CDCl_3$), δ: −82.9 (d, 2F, $J = 67.9$, CHF_2), −75.2 (s, 3F, CF_3). Material contains ca. 1.5% of Me_3SiF, ^1H NMR, δ: 0.23 (d, $J = 7.1$); ^{19}F NMR, δ: −158.59 (deqaplet, $J = 7.1$).

3.2.2. Difluoromethyl 1,1,2,2,3,3,4,4,4-nonafluorobutane-1-sulfonate (2b)

B.p. 75–80 °C (bath temperature)/65 Torr. ^1H NMR (300 MHz, $CDCl_3$), δ: 6.85 (t, 1H, $J = 67.9$, CHF_2). ^{13}C NMR (75 MHz, $CDCl_3$), δ: 108.5 (tqtt, $J = 271.5$, 39.8, 32.6, 1.6, $\mathit{C}F_2CF_3$), 109.9 (tquint, $J = 271.5$, 31.0, $CF_2\mathit{C}F_2CF_2$), 114.5 (tt, $J = 302.7$, 36.5, CF_2S), 115.1 (t, $J = 276.2$, CHF_2), 117.3 (qtt, $J = 288.4$, 32.7, 1.5, CF_3). ^{19}F NMR (282 MHz, $CDCl_3$), δ: −129.7 (m, 2F, CF_2), −124.6 (m, 2F, CF_2), −113.4 (t, 2F, $J = 13.8$, CF_2), −85.9 (d, 2F, $J = 67.9$, CHF_2), −84.8 (t, 3F, $J = 9.5$, CF_3). Anal. Calcd for $C_5HF_{11}O_3S$ (350.11): C, 17.15; H, 0.29. Found: C, 17.29; H, 0.21.

3.2.3. Difluoromethyl 1,1,2,2-tetrafluoro-2-(pentafluoroethoxy)ethanesulfonate (2c)

B.p. 70–75 °C (bath temperature)/65 Torr. ^1H NMR (300 MHz, $CDCl_3$), δ: 6.84 (t, 1H, $J = 67.9$, CHF_2). ^{13}C NMR (75 MHz, $CDCl_3$), δ: 112.4 (tt, $J = 301.5$, 38.0), 114.1 (tq, $J = 288.9$, 44.4, $\mathit{C}F_2CF_3$), 115.0 (t, $J = 276.2$), CHF_2), 115.3 (tt, $J = 290.8$, 30.5), 115.7 (qt, $J = 285.3$, 40.5, $CF_2\mathit{C}F_3$). ^{19}F NMR (282 MHz, $CDCl_3$), δ: −115.0 (s, 2F, CF_2), −89.3 (t, 2F, $J = 12.7$, CF_2), −87.8 (s, 3F, CF_3), −83.1 (d, 2F, $J = 67.9$, CHF_2), −82.7 (t, 2F, $J = 12.7$, CF_2). Anal. Calcd for $C_5HF_{11}O_4S$ (366.11): C, 16.40; H, 0.28. Found: C, 16.59; H, 0.24.

3.3. Preparation of silyl triflate 3

Titanium tetrachloride (55 μL, 0.5 mmol) was added dropwise to TfOH (1.33 mL, 15 mmol) under vigorous stirring at room temperature, and the mixture was kept for 5 min. The homogeneous yellow solution was evacuated at 10–15 Torr until gas evolution ceased (ca. 5–10 min). Trimethylpentafluoroethylsilane (1.69 mL, 10 mmol) was added, the reaction flask was immersed in the bath preheated to 60 °C, and the mixture was stirred at this temperature for 3 h. The mixture was cooled to −20 °C, diluted with diethyl ether (1.56 mL, 15 mmol), and subjected to vacuum distillation (the addition of ether prior to distillation is necessary for the efficient separation of the product from excess triflic acid). Silyl triflate **3** was obtained in 31% yield, 0.988 g.

3.3.1. Dimethyl(pentafluoroethyl)silyl trifluoromethanesulfonate (3)

B.p. 83–85 °C/65 Torr. ^1H NMR (300 MHz, $CDCl_3$), δ: 0.79 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$), δ: −4.1 (m, $(CH_3)_2$), 115.5 (tq, $J = 270.1$, 42.4, $\mathit{C}F_2CF_3$), 118.4 (q, $J = 317.5$, O_2SCF_3), 119.8 (qt, $J = 284.2$, 29.6, $CF_2\mathit{C}F_3$). ^{19}F NMR (282 MHz, $CDCl_3$), δ: −135.8 (s, 2F, CF_2), −85.4 (s, 3F, CF_3), −80.1 (s, 3F, CF_3).

3.4. Reaction of Me_3SiCF_3 with $B(OTf)_3$

Triflic acid (0.89 mL, 10 mmol) was added dropwise to BBr_3 (834 mg, 3.33 mmol) at 0 °C. The mixture was kept for 10 min at room temperature, and dried in a vacuum of an oil pump. The resulting white solid was cooled to −25 °C and treated with Me_3SiCF_3 (1.72 mL, 11.66 mmol). The mixture was allowed to warm to room temperature and stirred for additional 1 h. Volatile materials were distilled off under vacuum (10 Torr) in a cold trap (−20 °C) to give 1.12 g of Me_3SiOTf (54% yield).

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