

UNCONVENTIONAL REACTIONS OF TRIMETHYL(TRIFLUOROMETHYL)SILANE

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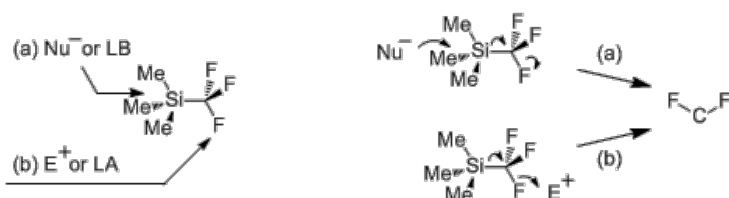
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Abstract: Reactions of trimethyl(trifluoromethyl)silane which do not result in nucleophilic transfer of CF_3 -group are discussed.

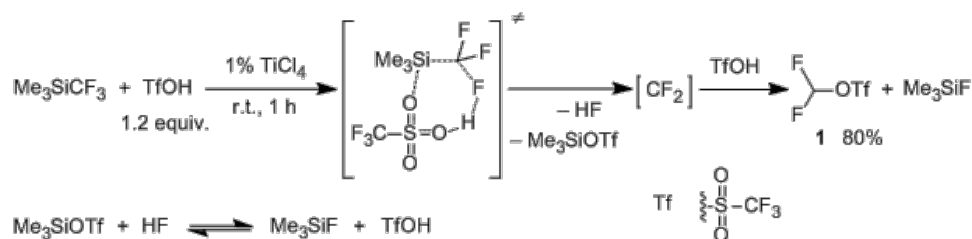
Keywords: trimethyl(trifluoromethyl)silane, difluorocarbene.

Trimethyl(trifluoromethyl)silane (Me_3SiCF_3 , the Ruppert-Prakash reagent) has found widespread applications for nucleophilic trifluoromethylation reactions [1]. Indeed, Me_3SiCF_3 serves as a source of CF_3 -carbanion towards wide variety of electrophilic fragments such as $\text{C}=\text{X}$ bonds, heteroatom-centered electrophiles, and transition metal complexes. The general feature of all these processes is that they proceed in the presence of an appropriate Lewis basic activator (typically fluoride), which interacts with the silicon atom generating highly reactive five-coordinate species. Herein we highlight reactions of Me_3SiCF_3 of other types, which likely proceed by different mechanisms or lead to products different from products of nucleophilic trifluoromethylation.

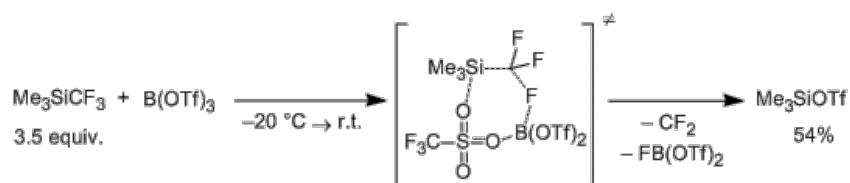
Considering reactivity of Me_3SiCF_3 , two sites of its molecule can be attacked by nucleophilic and electrophilic reagents. Nucleophiles (or Lewis bases) readily approach the silicon atom that induces fission of $\text{Si}-\text{C}$ bond (path a). The probable site for approach of electrophiles (or Lewis acids) is the fluorine atom and this pathway is expected to lead to the cleavage of strong $\text{C}-\text{F}$ bond (path b). Both pathways, in principle, can give the same difluorocarbene species.



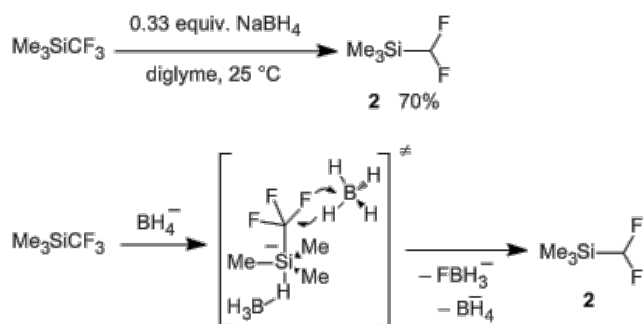
While Me_3SiCF_3 is relatively stable to the action of protic acids, it readily reacts with triflic acid under solvent-free conditions to give difluoromethyltriflate **1** along with fluorotrimethylsilane [2]. It was suggested that in this reaction the proton abstracts the fluoride from CF_3 -group accompanied by transfer of the Me_3Si -group to the triflate fragment generating the difluorocarbene. The latter is rapidly trapped by triflic acid to give the product **1**. At the same time, HF and silyltriflate, which were formed at the step of carbene generation, provide fluorotrimethylsilane. The reaction of Me_3SiCF_3 with TfOH is accelerated by Lewis acids, and best results were achieved using catalytic amount (1 mol %) of titanium tetrachloride. The Lewis acid may either increase acidity of TfOH , or accelerate equilibrium interaction of HF and silyltriflate.



The reaction of Me_3SiCF_3 with boron triflate leads to the formation of silyl triflate [2]. It is likely that in this case, similar to reaction with TfOH , the fission of $\text{C}-\text{F}$ and $\text{C}-\text{Si}$ bonds occurs in a concerted manner with extrusion of difluorocarbene.

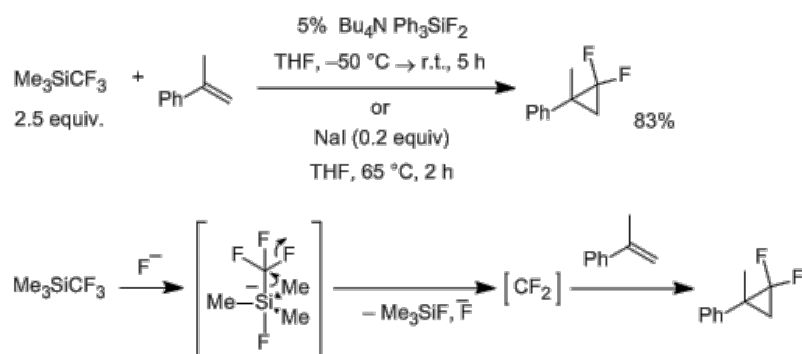


Sodium borohydride reacts with Me_3SiCF_3 in diglyme at room temperature affording (difluoromethyl)trimethylsilane **2** in good yield [3]. Of special note is that at least three from four hydrides are effectively used thereby allowing to employ substoichiometric amount (0.33 equiv.) of NaBH_4 . This procedure allows straightforward to access to silane **2**, which is more difficult to synthesize by other methods. Concerning reaction mechanism, it was proposed that Me_3SiCF_3 is activated by borohydride anion that leads to the elongation of $\text{Si}-\text{CF}_3$ bond and increase of negative charge on CF_3 -group that, in turn, elongates $\text{C}-\text{F}$ bond. Subsequent substitution of fluorine by hydride and regeneration of BH_4 -anion completes the formation of silane **2**.



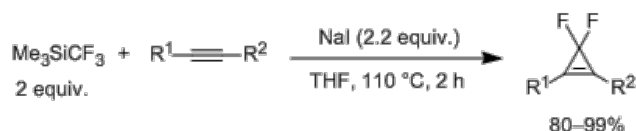
It was recently demonstrated that Me_3SiCF_3 can be used as efficient source of difluorocarbene [4]. Thus, treatment of alkenes and Me_3SiCF_3 with catalytic amount of tetrabutylammonium difluorotriphenylsiliconate in tetrahydrofuran results in the formation of difluorocyclopropanes. The reaction proceeds under mild conditions but efficiently works only for electron rich alkenes — this is a typical phenomenon for reactions of difluorocyclopropane.

In this process, the fluoride ion attacks the silicon to give five-coordinate complex, which generates difluorocarbene either by synchronous decomposition (as shown) or through the intermediate formation of free trifluoromethyl carbanion. At the final step, the difluorocarbene is trapped by the olefin.

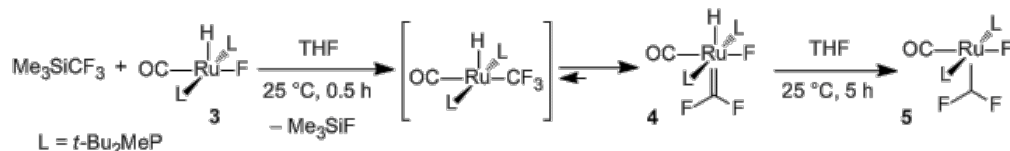


In alternative procedure, Me_3SiCF_3 is activated by sodium iodide (20 mol %) at elevated temperature (65°C). This protocol has wider scope compared to fluoride-catalyzed procedure, and it was applied to difluorocyclopropanation of various styrenes. Though authors did not suggest the mechanistic scheme, it can be proposed that attractive interaction between the iodide ion and silicon inducing polarization of Si-CF₃ bond may play important role in this process.

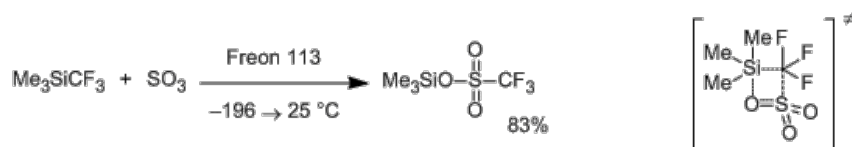
The system $\text{Me}_3\text{SiCF}_3/\text{NaI}$ was used for the cyclopropanation of alkynes [4]. The reaction is performed in a sealed tube at 110 °C and affords difluorocyclopropanes in high yields.



The reaction of Me_3SiCF_3 with complexes of transition metals in the presence of fluoride or alkoxide anions is frequently employed to generate stable species with the CF₃-group attached to metal such as Cu, Ni or Pd [5]. However, when similar transfer of the CF₃-group was applied to Ru, Os and Rh complexes, the formation of difluorocarbene complexes was observed [6]. For example, reaction of Me_3SiCF_3 with ruthenium complex **3** occurred rapidly to give compound **4**, which could be isolated in crystalline state. It was suggested that **4** is produced from initially generated Ru-CF₃ intermediate. Though compound **4** is stable in non-polar solvents, in tetrahydrofuran it slowly undergoes rearrangement into difluoromethyl-substituted complex **5**. The overall transformation of **3** to **5** corresponds to the insertion of difluorocarbene into Ru-H bond.



Sulfur trioxide interacts with Me_3SiCF_3 to give the product of insertion of SO₃ between the silicon and the CF₃-group [7]. The reaction was carried out at -196 to 25°C in Freon 113 (1,1,2-trichloro-1,2,2-trifluoroethane). The authors did not propose the mechanism of this intriguing reaction. Nevertheless, it seems likely that extremely high electrophilic character of the sulfur trioxide is the key factor responsible for this transformation. Direct attack of sulfur at the CF₃-group with simultaneous transfer of the Me₃Si-group to the oxygen atom through four-membered transition state cannot be excluded.



As follows from the reactions outlined above, Me_3SiCF_3 has diverse reactivity extending beyond conventional nucleophilic trifluoromethylation. In all processes discussed herein either the CF_3 -group or Si-CF_3 bond is involved. It would be a new direction in the chemistry of Me_3SiCF_3 if some reactions not affecting Si-CF_3 fragment are discovered.

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