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# Preparation of 1,1,2-trifluoro-2-trimethylsilylethylene

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## Abstract

1,1,2-Trifluoro-2-trimethylsilylethylene can be readily prepared *via* the Cu(I)Br catalyzed silylation of the 1,1,2-trifluoroethenylzinc reagent with $Me_3SiCl$. The reaction is easily scaled-up, isolation of the trifluorovinylsilane is facile, and the procedure can be readily adapted to other trialkyl halosilanes.

*Keywords:* Fluorinated vinyl silanes; 1,1,2-Trifluoroethenylzinc; 1-Bromo-1,2,2-trifluoroethene

## 1. Summary

Fluorine-containing silanes are important synthons in synthetic organic chemistry. Trifluoromethyltrimethylsilane is a useful trifluoromethylation agent that has become the standard for the introduction of a "$CF_3$" group [1]. The corresponding 1,1,2-trifluoro-2-trialkylsilylethene (**1**) is an equally important synthon for the introduction of a trifluorovinyl group into organic compounds [1]. Similar to other fluorinated vinylsilanes, in the presence of a dry fluoride ion source, (**1**) efficiently transfers the $F_2C{=}CF$-group to carbonyl compounds to yield the corresponding carbinol (after hydrolysis) [1–3]. Compound (**1**) also reacts with $Bu_3SnCl$ or $Bu_3SnOSnBu_3$ in the presence of fluoride ion to transfer the trifluorovinyl group and provide a mild, useful preparation of fluorinated vinyl stannanes [4,5]. With related fluorine-containing vinyl silanes, the stannane preparation was demonstrated to be stereospecific [5]. Similar fluoride ion catalyzed transfer reactions were utilized by Japanese workers to prepare a difluoroacetylene-containing polymer which exhibited high conductivity [6]. In related work, Russian workers prepared unsaturated perfluorinated compounds *via* transfer of the trifluorovinyl group to perfluoroolefins and perfluoroazaalkenes [7]. Reaction of $SO_3$ with (**1**) has been employed for the synthesis of unsaturated silyl sulfonates, such as $F_2C{=}CFSO_2OSiR_3$, which on hydrolysis, gives $F_2C{=}CFSO_3H$ [8,9]. Compound (**1**) can be readily converted to (*Z*)- or (*E*)-$HFC{=}CFSiR_3$ *via* reduction with lithium aluminum hydride or trimethyltin hydride [10–13]. These hydrovinylsilanes can be readily converted to other useful fluorinated vinyl synthons [14,15]. Compound (**1**) can also be converted to the corresponding epoxide *via* oxidation with perfluoro-*cis*-2,3-dialkyloxaziridines [16].

Traditionally, (**1**) has been prepared *via* the reaction of chlorotrimethylsilane with either trifluorovinyllithium [10,17,18] or the corresponding trifluorovinyl Grignard reagent [19]. Normant modified these earlier procedures *via* in situ low temperature formation/capture of trifluorovinyllithium with $R_3SiCl$. His modified procedure permitted easy scale-up of the reaction and avoided the low-temperature large scale per generation of the unstable trifluorovinyllithium. However, it did not avoid the use of low-temperatures. Moreover, the use of $Me_3SiCl$ presented serious isolation problems and silanes, such as $Et_3SiCl$ and $C_6H_5Me_2SiCl$, were utilized to permit easy separation of (**1**) from solvent and $RLi/F_2C{=}CFX$ exchange products [20]. To avoid this separation problem, two alternative preparations of $F_2C{=}CFSiMe_3$ have been reported: (1) an electrochemical silylation method from $F_2C{=}CFBr$ and $Me_3SiCl$ [21,22]; and (2) the reaction of $F_2C{=}CFBr$ and hexaethylphosphorus triamide, $(Et_2N)_3P$, with $Me_3SiCl$ [23,24]. While the Grignard and lithium methodology suffer from lack of reagent stability and require generation at low temperatures, the electrochemical methodology requires expensive cells and the $(Et_2N)_3P$ method the use of the expensive and toxic phosphorus reagent.

The preferred trifluorovinylsilane is $F_2C{=}CFSiMe_3$. The use of a small alkyl group on silicon drastically reduces steric hindrance to attack by nucleophiles, such as fluoride ion. Consequently, transfer of the trifluorovinyl group is accelerated and the transfer processes can be accomplished under milder conditions, both with $F_2C{=}CFSiMe_3$ and other synthons derived from $F_2C{=}CFSiMe_3$. Herein, we describe a straightforward approach to the title compound using thermally stable vinyl zinc and copper reagents. All reagents are commercially

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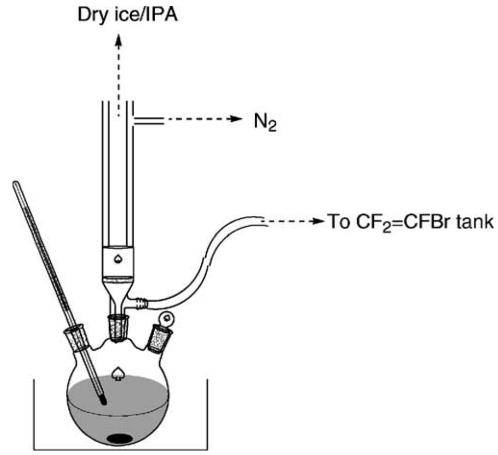
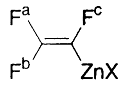


Fig. 1. Condensation of 1-bromo-1,2,2-trifluoroethene using a dry ice condenser.

available, low temperature processes are avoided, no electrochemical cells needs to be constructed, toxic reagents are avoided, and the overall scheme provides for each work-up and isolation of trifluorovinyltrimethylsilylethene.

## 2. Preparation of 1,1,2-trifluoroethenyl zinc—a general procedure

A 1 l three necked round bottomed flask was equipped with a PTFE coated magnetic stir bar, dry ice condenser cooled with dry ice and isopropanol attached to a source of nitrogen, rubber septum and thermometer. The flask was charged with 16.23 g (249.69 mmol) of activated zinc powder[1] and 250 ml of *dry* DMF.[2] 1-Bromo-1,2,2,-trifluoroethene (34 g, 210.67 mmol)[3] was added dropwise *via* the dry ice condenser (Fig. 1). The reaction generally initiated after a short induction period and was exothermic.[4] After the addition of the ethene was completed, the reaction mixture was stirred at room temperature for 3 h. $^{19}$F NMR analysis of the reaction mixture indicated that the zinc reagent was the major product, with trace quantities of trifluoroethene and starting material. The concentration of the zinc reagent was calculated to be 0.62 M,[5,6] while the conversion was 74%. In all subsequent trials, the yield of the zinc reagent prepared following the above procedure ranged from 65 to 75%.



$^{19}$F NMR (DMF solvent, $PhCF_3$ reference): −96.3 ppm (dd, $J_{ab} = 93$ Hz, $J_{ac} = 33$ Hz, 1F$^a$); −130.6 ppm (dd, $J_{bc} = 104$ Hz, $J_{ab} = 93$ Hz, 1F$^b$); −195.0 ppm (dd, $J_{bc} = 104$ Hz, $J_{ac} = 33$ Hz, 1F$^c$) [25].

## 3. Preparation of 1,1,2-trifluoro-2-trimethylsilylethene

A 250 ml three necked round bottomed flask equipped with a side arm, PTFE coated magnetic stir bar, cold water condenser attached to a nitrogen-T, thermometer, and rubber septum was charged with the zinc reagent prepared above (154 mmol) (Fig. 2, Scheme 1). To this zinc reagent was added 34.9 g (323 mmol, 2.1 equivalents) of dry chlorotrimethylsilane.[7] The system was placed in an ice water bath. Then, 2.2 g (15 mmol, 0.10 equivalent) of copper(I) bromide[8] was added all at once to the reaction mixture. After the addition of the copper(I) bromide was complete, the reaction

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[1] Zinc was activated by stirring 50 g of zinc powder with 500 ml of distilled water. To this slurry was added ~10 ml of concentrated hydrochloric acid drop-wise till the metal began to coagulate. After stirring the slurry for about 20 min, the zinc was washed repeatedly with water (3 ml × 500 ml), acetone (3 ml × 250 ml) and finally with ether (3 ml × 100 ml). The activated zinc powder, which had a silvery white appearance, was dried under full vacuum for at least 8 h. This activated zinc powder can be stored either under an atmosphere of nitrogen or vacuum for ~1 month. The zinc powder can also be activated by Knochel's method, cf. [25].

[2] Stirred over calcium hydride overnight and distilled under reduced pressure. The dried DMF was stored in amber bottles over 4 Å MS.

[3] Weight calculated by weighing the tank before and after the addition.

[4] When the reaction was carried out on a larger scale, it is advisable to add part of the 1-bromo-1,2,2-trifluoroethene, wait until the reaction initiates, and then bleed the remaining ethene slowly into the reaction mixture. This avoids an uncontrollable exotherm. If the reaction does not initiate, the stirring is stopped; and the zinc is allowed to settle, and ~0.2 ml of chlorotrimethylsilane is added. Once the surface of the reaction mixture turns pale yellow, the reaction has initiated and stirring is again commenced. Freezing of the gas inside the condenser and thus blocking it is avoided by using dry ice/isopropanol as the cooling mixture. The temperature of this mixture is −78 °C, much higher than the freezing point of 1-bromo-1,2,2-trifluoroethene. In the unlikely event of an uncontrollable exotherm, rapid pressure build-up is prevented by both the nitrogen flowing through the reaction flask as well as efficient cooling of the condenser.

[5] The NMR yield and concentration are calculated by addition of a known amount (usually 5 μl) of benzotrifluoride to 0.5 ml of the reaction mixture in an NMR tube. The NMR spectrum is obtained in the usual manner and the integral ratios are obtained as accurately as possible. The concentration is calculated by the following relation:

$$\left[\frac{0.041 \times 3}{a}\right] \times \frac{b}{0.5} = c$$

where '$a$' is the integral value of the standard, '$b$' the normalized integral value of the sample, and '$c$' the concentration of the sample in mmol/ml. The product of '$c$' and the total volume of the reaction mixture in ml gives the millimoles of the zinc reagent. This zinc reagent can be stored under nitrogen for at least 1 month with minimal loss of activity.

[6] It is important that the concentration of the zinc reagent be less than 1 M. Highly concentrated zinc reagents (typically greater than 1 M) do not readily exchange with copper (I) halides.

[7] Stirred over calcium hydride for 1 h, distilled at ambient pressure and used immediately.

[8] Copper (I) bromide was activated as follows: 50 g of copper (I) bromide was stirred with 20 ml of distilled water. To this slurry was added 50 ml of 48% hydrobromic acid. Once the copper (I) bromide had dissolved, it was re-precipitated by addition of ~500 ml of water. The precipitated copper (I) bromide was washed repeatedly with 500 ml portions of water till the washings were neutral to a pH paper. The copper (I) bromide was then washed with acetone (3 ml × 250 ml), ether (3 ml × 100 ml), and dried under full vacuum for at least 8 h. The off-white colored copper (I) bromide can be stored for at least 1 month in the absence of air or oxygen.

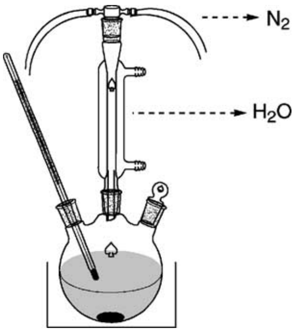
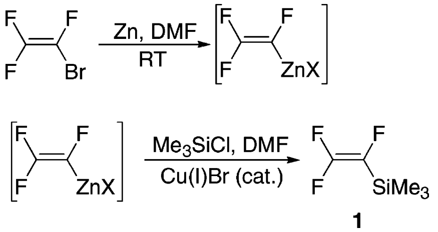
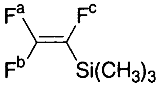


Fig. 2. Reaction of the vinyl zinc reagent with chlorotrimethylsilane and catalytic copper(I) bromide.



Scheme 1.

mixture was stirred overnight. Any solids were allowed to settle.[9] $^{19}$F NMR analysis of the reaction mixture indicated complete conversion of the zinc reagent to the vinyl silane. A small amount of trimethylsilyl fluoride (about 10%) was also formed. An amount of ethylene glycol corresponding to the molar excess of chlorotrimethylsilane (11 g, 171 mmol) was then added to the reaction mixture, to ensure that all the chlorotrimethylsilane was removed from the reaction mixture, thus making isolation of the final product more efficient. The reaction mixture was then stirred overnight. Flash distillation of the reaction mixture followed by slow, careful fractional distillation through a 6 in. Vigreaux column gave the vinyl silane as a clear, colorless liquid (21.2 g, 137 mmol, 65% isolated yield based on the starting vinyl bromide; bp = 69 °C). The major impurity, trimethylsilyl fluoride (about 10%), could not be separated,[10] but did not interfere in any subsequent reactions.



$^{19}$F NMR ($CDCl_3$ solvent, $CFCl_3$ reference): −88.7 ppm (dd, $J_{ab} = 71$ Hz, $J_{ac} = 25$ Hz, 1F$^a$); −117.6 ppm (dd, $J_{bc} = 115$ Hz, $J_{ab} = 71$ Hz, 1F$^b$); −199.5 ppm (dd, $J_{bc} = 115$ Hz, $J_{ac} = 25$ Hz, 1F$^c$) [20].

## Acknowledgements

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[9] It is important that any paramagnetic copper species be removed, otherwise they will broaden and distort the NMR spectral lines.

[10] This reaction has been carried out on a large scale in our laboratory (0.5–1.5 mol) by other co-workers using copper(I) iodide as the catalyst.