
Synthesis of alkyl fluorosilanes by the reaction of alkyl chlorosilanes with pyridinium poly(hydrogen fluoride) at room temperature**K. R. Muddukrishna****Department of Inorganic and Physical Chemistry,
Indian Institute of Science,
Bangalore 560012 (India)****Abstract**

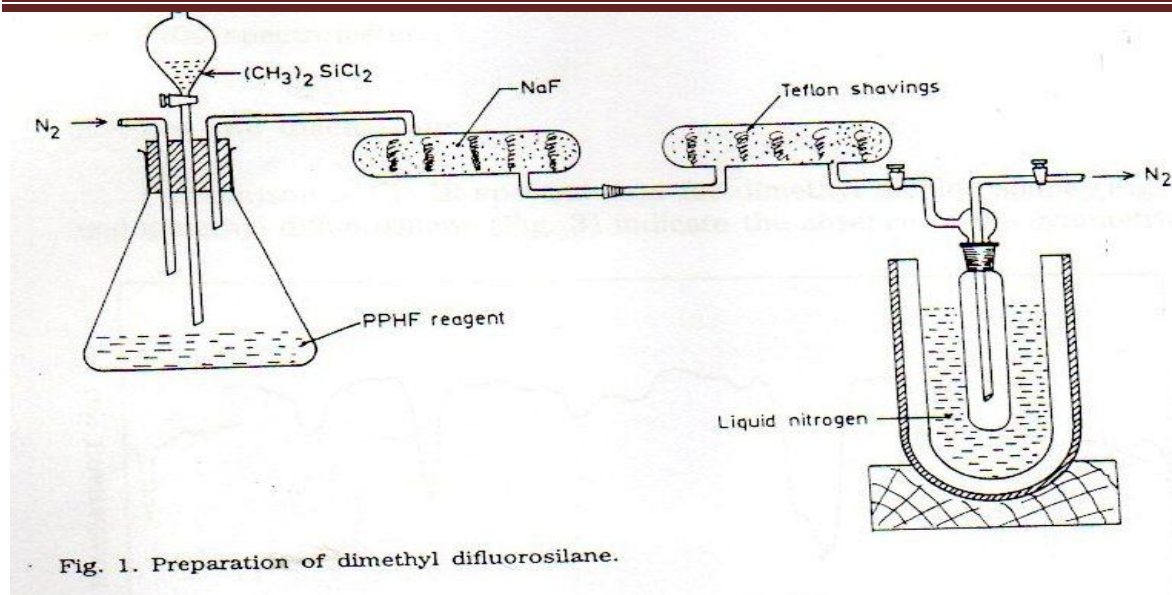
Dimethyl difluorosilane (DFS) has been prepared in high yield (80-90%) by the reaction of dimethyl dichloro-silane with pyridinium poly(hydrogen fluoride) at room temperature (25-35 °C). The gas has been characterised by IR and ¹⁹F NMR spectroscopy, molecular weight measurements and elemental analysis. The method has been extended to the preparation in high yields of monomethyl and trimethyl fluorosilanes.

Introduction

Alkyl fluorosilanes are a class of compound which possess a wide variety of industrial uses [1, 2]. Several methods of preparation are reported in the literature involving fluorination of alkyl chlorosilanes by a variety of fluorinating reagents such as ZnF₂ [3], anhydrous HF in concentrated sulphuric acid [4] and by passing alkyl aluminium halide vapour over an alkali metal fluorosilicate [5]. These preparations need high temperature, yields are low and in many cases a mixture of fluorosilanes are formed which call for further purification procedures. Recently, alkyl fluorosilanes have been prepared by treating alkyl silanes with nitronium tetrafluoroborate [6] at room temperature. We have recently utilized pyridinium poly(hydrogen fluoride) PPHF as an efficient fluorinating reagent [7, 8] and this has been extended to the fluorination of alkyl chlorosilanes at room temperature. The present reported method provides a rapid, one-pot reaction, followed by purification of the fluorosilane.

Experimental

Pyridinium poly(hydrogen fluoride) (30 ml) was placed in a three-neck stoppered polyethylene flask (250 ml), fitted with a dropper and provided with an outlet tube linked to two sodium fluoride towers and a receiver cooled in liquid nitrogen (See Fig. 1). A slow stream of nitrogen was used as the carrier gas thus avoiding moisture condensation. Dimethyl dichlorosilane



(6 ml) was added over a period of 45 min, an exothermic reaction occurring after each addition with a gas being evolved. The gas was passed through the NaF towers which removed the entrained HF and it was subsequently collected in the cooled receiver. The nitrogen stream was continued for 2h in total in order to recover all the evolved gas. The product was then sublimed into previously evacuated clean dry glass bulbs after removal of the non-condensable gases. The product was further purified by low-temperature fractional condensation and, the pure gas stored in glass bulbs.

Characterisation of $(CH_3)_2SiF_2$

IR spectral data

The IR spectrum of the gas contained in a 10-cm gas cell was recorded by means of a Perkin-Elmer model 599 spectrometer over the spectral range $400\text{-}4000\text{ cm}^{-1}$.

^{19}F NMR spectroscopy

The NMR spectrum was recorded at room temperature using a FT 80 MHz spectrometer with the gas dissolved in carbon tetrachloride. CF_3COOH was used as the external standard.

Molecular weight determination

The molecular weight of the gas was determined by vapour density measurements.

Fluoride analysis

An aliquot of the gas was hydrolysed with sodium hydroxide (2 mol^{-1}) and the fluoride analysed spectrophotometrically [9] on a Hitachi UV-Vis No.3400 Spectrometer.

Results and discussions

Comparison of the IR spectral data for dimethyl dichlorosilane (fig.2) and dimethyl difluorosilane (Fig.3) indicate the absence of the symmetrical

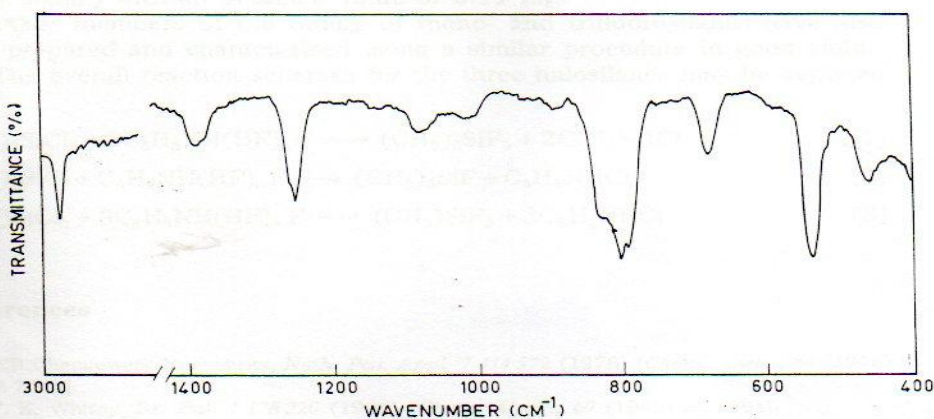


Fig. 2. IR spectrum of dimethyl dichlorosilane.

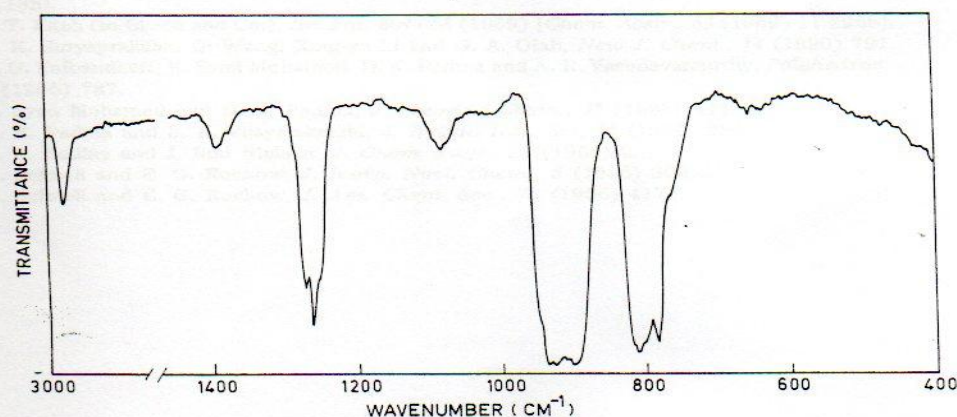


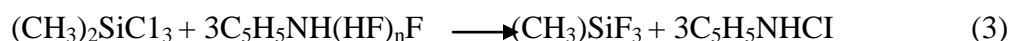
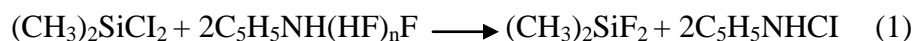
Fig. 3. IR spectrum of dimethyl difluorosilane.

Stretch and assymetrical stretching frequencies of the Si—Cl bond at 550 and 690 cm^{-1} respectively, and the appearance of new band at 900 and 950 cm^{-1} corresponding to Si—F vibrations in the spectrum for $(\text{CH}_3)_2\text{SiF}_2$ as reported in the literature [10].

The ^{19}F NMR spectrum indicated a singlet at -51.68 ppm in agreement with reported data [11, 12].

From gas density measurements, the observed molecular weight of the gas was 95.6 in close agreement to the expected value of 96 for dimethyl difluorosilane. This was further supported by analytical data for the fluoride, the expected amount of fluoride in solution being

9.35 mg (for 23.61 mg of gas taken) with an obtained value of 9.11 mg. Other members of the family of mono- and trifluorosilanes have also been prepared and characterised using a similar procedure in good yield. The overall reaction schemes for the three halosilanes may be depicted as:



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