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MONOFLUORINATION OF SOME DIHYDROSILANES

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SUMMARY

The heterogeneous fluorination of diethylsilane, ethylvinylsilane and divinylsilane with SbF_3 was studied by measuring the yields of the fluorinated products as a function of reaction time. As the reactions proceed, the monofluorinated species (two of them are new compounds) exhibit maxima in their percentage yields with respect to time. The proton NMR and IR spectra of the three silanes and their six fluorinated products are reported.

INTRODUCTION

Organofluorosilanes have been successfully synthesized from halides, ethers, and amines with common fluorinating agents such as metal fluorides, hydrofluoric acid, boron trifluoride, and others [1,2]. However, the degree of fluorination is difficult to control in these systems. On the other hand, the synthesis of organofluorosilicon hydrides involves either unusual fluorinating agents or tedious multistep methods with few exceptions [1]. Bulkowski _et_ _al_. [3] employed Ph_3CBF_4 under mild conditions to quantitatively convert $SiH_2(CH_3)_2$ to $SiHF(CH_3)_2$ and $SiH_2(C_2H_5)_2$ to $SiHF(C_2H_5)_2$. Finch _et_ _al_. [4] used PF_5 to partially fluorinate silicon compounds of the form $RSiH_3$ to give $RSiH_2F$ and $RSiHF_2$. SbF_5 intercalated in graphite was used by Corriu _et_ _al_. [5] to fluorinate a methoxysilicon hydride to the

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corresponding fluorosilicon hydride. In the present work, we are reporting a kinetic approach to the monofluorination of some dihydrosilanes. An extremely common fluorinating agent, SbF_3, was used to convert SiH_2RR' to $SiHFRR'$ and SiF_2RR'. However, kinetic measurements in the form of product yields versus time have been performed in order to search for the optimum conditions under which the yields of the monofluorinated organosilicon hydrides can be maximized.

The dihydrosilanes employed in this study include $SiH_2(C_2H_5)_2$, $SiH_2(C_2H_5)(CH{=}CH_2)$ and $SiH_2(CH{=}CH_2)_2$. The synthesis of their difluorinated products: $SiF_2(C_2H_5)_2$, $SiF_2(C_2H_5)(CH{=}CH_2)$ and $SiF_2(CH{=}CH_2)_2$ have all been previously reported [3,6-10]. Among the monofluorinated compounds of the three silanes, only $SiHF(C_2H_5)_2$ is known [3,7]. During the process of the present kinetic monofluorination studies all six of the possible fluorinated products of the three dihydrosilanes, including two new compounds, $SiHF(CH{=}CH_2)_2$ and $SiHF(C_2H_5)(CH{=}CH_2)$, were prepared and characterized.

EXPERIMENTAL

Chemicals

Diethylsilane was obtained from PCR. Dichloroethylvinylsilane and trichlorovinylsilane were from Petrarch Systems Inc. Lithium aluminium hydride (LAH) and vinyl magnesium bromide in tetrahydrofuran (THF), 1.0 molar, were obtained from Alfa Products. Antimony trifluoride was from Matheson, Coleman and Bell. It was dried to various degrees and stored in a dessicator. Antimony pentachloride was obtained from PCR. All reagents were used without further purification.

Synthesis of ethylvinylsilane and divinylsilane

Ethylvinylsilane was synthesized by the reaction of dichloroethylvinylsilane (dissoved in diglyme) with LAH at a reduced pressure of 5 torr. Products were collected in traps Gas chromotography was used for final purification.

Divinylsilane was synthesized by the reduction of dichlorodivinylsilane with LAH with a similar procedure. However, dichlorodivinylsilane was freshly prepared from the reaction of vinyl magnesium bromide (in THF) with trichlorovinylsilane (in anhydrous diethyl ether).

Treatment of antimony trifluoride

Antimony trifluoride is very hydroscopic and was therefore dried before use. Varying degrees of dryness were achieved with various procedures. Visible water was removed by heating above its melting point of 292°C. A final state of dryness was achieved through extensive heating of the liquid SbF_3. After drying, the SbF_3 was ground to a powder with mortar and pestle and stored in the presence of a drying agent.

Fluorination of dihydrosilanes

The fluorination cell was a pyrex glass tube with a diameter of 30 mm and a length of 230 mm. This tube was equipped with an O-ring joint in the middle and a stopcock at the top.

The fluorination cell was opened at the O-ring joint and 1.0 g SbF_3 was placed in the bottom. Three to five drops of $SbCl_5$ were placed in the cell at this time, when used. The cell was then closed, connected to the vacuum line and evacuated. Liquid nitrogen was used during evacuation when $SbCl_5$ was present. A measured amount of dihydrosilane with known pressure and volume in the range of 0.2 mmol was introduced and the cell was closed. The pressure of the silanes was measured with a pressure transducer. An exothermic reaction between the reactants was observed to take place at room temperature. A gradual formation of an antimony mirror was also noted which was formed much more rapidly in the presence of $SbCl_5$.

Samples, three to five percent of the reaction system in size, were withdrawn at the time of reactant introduction and at various intervals throughout the time of the reaction.

The sample withdrawing process was carried out by equilibrating a known volume with the vapor phase of the fluorination cell. Aliquots continued to be withdrawn until the parent and the intermediate product were nearly consumed. The numbe of aliquots taken for analysis varied from five to ten.

Product analysis

The inital analysis and product separation of the sample aliquots were made with gas chromatography. A 10-ft dimethylsulfolane column at 24 ± 2 °C with a helium flow rate of 30.0 ± 0.2 ml/min was used for this purpose. The general pattern observed was that the amount of the parent compound decreased as the reaction proceeded; an intermediate product was produced, and its yield exhibited a maximum; and a final product eventually appeared and increased with time. The observed retention times were in the range of 15-17 minutes for the three parent compounds, 33-34 minutes for the three intermediate products, and 45-52 minutes for the three final products. These products were trapped individually during elution and identified by NMR and IR. The three intermediate products were shown to be the monofluorosilanes, and the three final products were shown to be the difluorosilanes.

RESULTS AND DISCUSSION

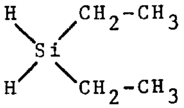
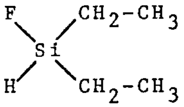
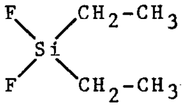
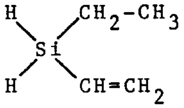
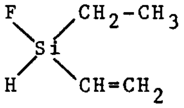
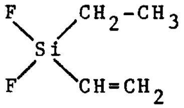
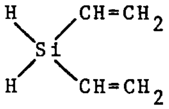
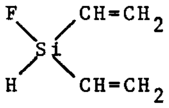
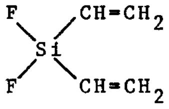
NMR spectra

The NMR spectra of the three parent compounds, the three intermediate compounds, and the three final compounds have been obtained on a Varian EM-390, 90 Hz spectrometer. Carbon tetrachloride was used as a solvent, and TMS was the internal standard. Approximately 0.1 mmol of each compound was used. Due to the high vapor pressure of the compounds the NMR tubes were sealed with high vacuum techniques.

The proton chemical shifts for the nine compounds are listed in Table 1. The silicon-, vinyl-, methylene-, and methyl-protons show their characteristic chemical shifts with the influence of the silicon and fluorine atoms displayed.

TABLE 1

NMR spectra of dihydrosilanes and their fluorinated products

Compound	Chemical shift, δ (ppm)			
	Si-H	$Si-CH=CH_2$	$Si-CH_2-$	$-CH_3$
	3.60		0.70	1.00
	4.60		0.85	1.10
			0.85	1.10
	3.85	5.95	0.75	1.00
	4.80	6.10	0.80	1.10
		6.10	0.85	1.10
	4.20	6.20		
	4.80	6.20		
		6.20		

The chemical shifts of the Si-H protons have δ values in the range of four. The presence of the fluorine on the silicon introduces a strong influence to the proton in the Si-H bond causing a downfield shift of 0.6-1.0 ppm. Because of the spin-spin coupling of the proton with fluorine, the resonance absorption of the proton inserting on the silicon splits into two equal peaks with a J_{HF} value of 52.2 Hz. This coupling is consistent with the previously observed J_{HF} values in various fluorosilanes [11,12].

The observed proton ratios are also consistent with those expected from the structure of the nine compounds.

Infrared spectra

The IR spectra of diethylsilane, ethylvinylsilane, divinylsilane, and their six fluorinated products have been measured in the gas phase on a Sargent-Welch 3-200 Infrared Spectrophotometer. The spectra were taken with samples of 0.02 to 0.2 mmol of each compound in a cell with NaCl windows.

The wave numbers (in cm^{-1}) of the IR absorption peaks for the nine compounds are listed below.

$SiH_2(CH_2CH_3)_2$: 3160, 2960, 2920, 2880. 2820, 2740, 2125, 1460, 1420, 1235, 1130, 1085, 1015, 970-950, 850-830, 720.

$SiHF(CH_2CH_3)_2$: 3120, 2950, 2920, 2880, 2800, 2740, 2125, 1455, 1405, 1235, 1085, 1005, 970, 860-820, 710.

$SiF_2(CH_2CH_3)_2$: 3120, 2960, 2920, 2880, 2800, 2740, 1455, 1405, 1240, 1085, 1005, 970, 900-860, 750

$SiH_2(CH_2CH_3)(CH{=}CH_2)$: 3160, 3040, 3000, 2955, 2910, 2870, 2800, 2125, 1910, 1585, 1450, 1400, 1230, 1085, 1000, 960-930, 840, 710

$SiHF(CH_2CH_3)(CH{=}CH_2)$: 3160, 3040, 3000, 2955, 2910, 2870, 2780, 2125, 1920, 1585, 1450, 1400, 1230, 1085, 1000, 960, 860-830, 700

$SiF_2(CH_2CH_3)(CH\text{-}CH_2)$: 3160, 3040, 3000, 2955, 2910, 2870, 2800, 1930, 1585, 1450, 1400, 1240, 1085, 1000, 960, 870-905, 760

$SiH_2(CH{=}CH_2)_2$: 3170, 3050, 3000, 2960, 2890, 2420, 2270, 2140, 1915, 1720, 1590, 1400, 1260, 1130, 1010, 960-930, 860-830

$SiHF(CH{=}CH_2)_2$: 3040, 3000, 2940, 2140, 1920, 1585 1400, 1260, 1080, 1010, 955, 870, 820, 705

$SiF_2(CH{=}CH_2)_2$: 3040, 3000, 2940, 1930, 1585, 1400, 1260, 1080, 1000, 960, 910, 870, 750, 705.

The above listing shows that the spectra of the monofluorinated compounds are always similar to their corresponding parents. As expected, the Si-H absorption observed between 2140 to 2125 cm^{-1} is absent in the spectra of the difluorinated species. The spectra of the compounds containing double bonds always contain two characteristic absorptions at approximately 1910 and 1585 cm^{-1}. These absorptions are absent in the spectra of diethylsilane and its derivatives.

Rate of fluorination

The fluorination of the three dihydrosilanes was studied by measuring the yields of the fluorinated products as a function of reaction time. These kinetic results are shown in Figures 1-3 for diethylsilane, ethylvinylsilane, and divinylsilane, respectively. In Figures 1 and 3 results of different series of fluorination are included with the dryness of SbF_3 as the major variable. The effect of adding $SbCl_5$ on the reaction rate was also demonstrated by series of experiments in Figures 1 and 2. In all the figures the plotted yields of each species represent the mole percent of that component in the gaseous aliquot taken for analysis.

In essentially all the series shown in the figures, the parent compounds diminish to zero with reaction time while the monofluorinated products arise to maxima and then decrease. The difluorinated products show a gradual increase with time after an initial induction period.

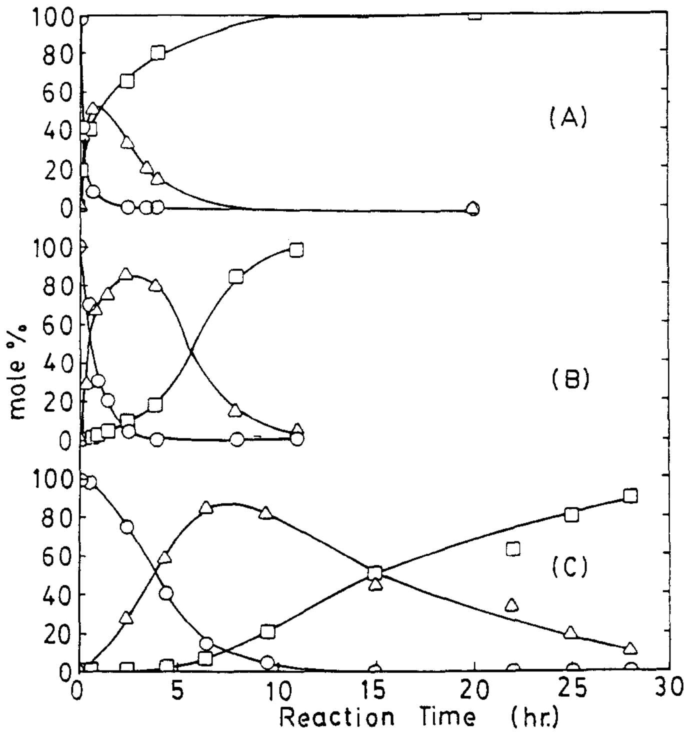


Fig. 1. Fluorination of $SiH_2(CH_2CH_3)_2$ by SbF_3: (A) with $SbCl_5$ added. (B) SbF_3 dried with extensive heating, (C) SbF_3 heated for 1 hour at about 300°C. ○ $SiH_2(CH_2CH_3)_2$, △ $SiHF(CH_2CH_3)_2$, □ $SiF_2(CH_2CH_3)_2$.

The effect of $SbCl_5$ on the fluorination was examined in two systems. Figures 1(A) and 1(B) show the effect of $SbCl_5$ for two series of the fluorination experiments with diethylsilane under otherwise identical conditions. The maximum yield of the monofluorinated product occurred at 2.5 hours when SbF_3 was used alone, while with the addition of $SbCl_5$ the maximum occurred at 0.7 hours. However, the maximum yield of the monofluorination product decreased from 90% to 50% with the addition of $SbCl_5$. In Figure 2 similar experimental comparison for ethylvinylsilane is shown. However, in this instance $SbCl_5$ caused extensive cleavage of the Si-C bond giving smaller molecules as products. Both of the fluorinated products were observed only in very low yields. It can be concluded that the addition of $SbCl_5$, although increasing the reaction rate, does not enhance the yield of the monofluorination product.

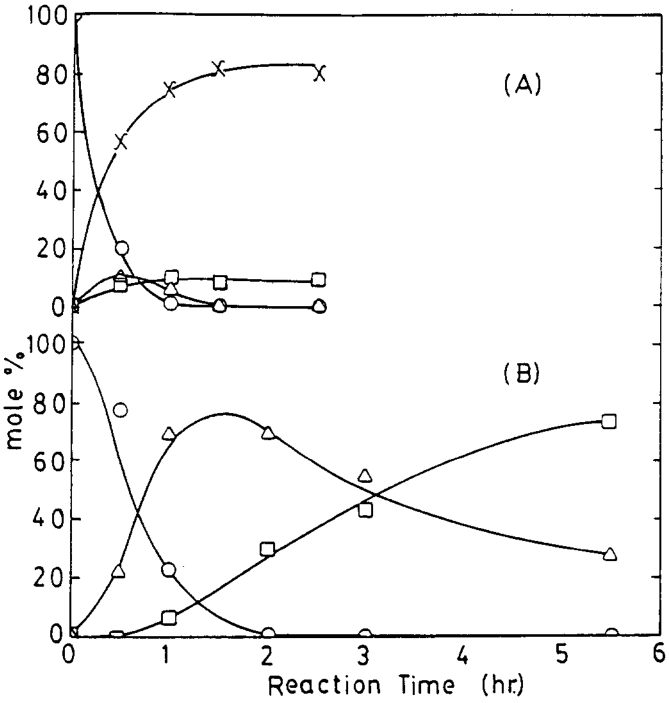


Fig. 2. Fluorination of $SiH_2(CH_2CH_3)(CH{=}CH_2)$ by SbF_3: (A) with $SbCl_5$ added, (B) SbF_3 dried with extensive heating,
○ $SiH_2(CH_2CH_3)(CH{=}CH_2)$, △ $SiHF(CH_2CH_3)(CH{=}CH_2)$,
□ $SiF_2(CH_2CH_3)(CH{=}CH_2)$, × $SiH_3CH_2CH_3$ and $SiH_3CH{=}CH_2$.

The effect of the dryness of SbF_3 upon the fluorination rate is represented in Figures 1 and 3. Four states of dryness for SbF_3 were employed in this portion of the study: Condition I, only visible water removed; Condition II, heated at about 300°C for 30 minutes; Condition III, heated at about 300°C for one hour; Condition IV, thoroughly dried with extensive heating. Figure 3 compares the fluorination results of divinylsilane with SbF_3 at three different conditions of dryness. As shown in Figure 3(C), fluorination by SbF_3 with only the visible water removed is a very slow process where the monofluorination product reaches only 30% after 25 hours. With SbF_3 in Condition II the yield of the monofluorination product reached a maximum of 70% in about 35 hours as il-

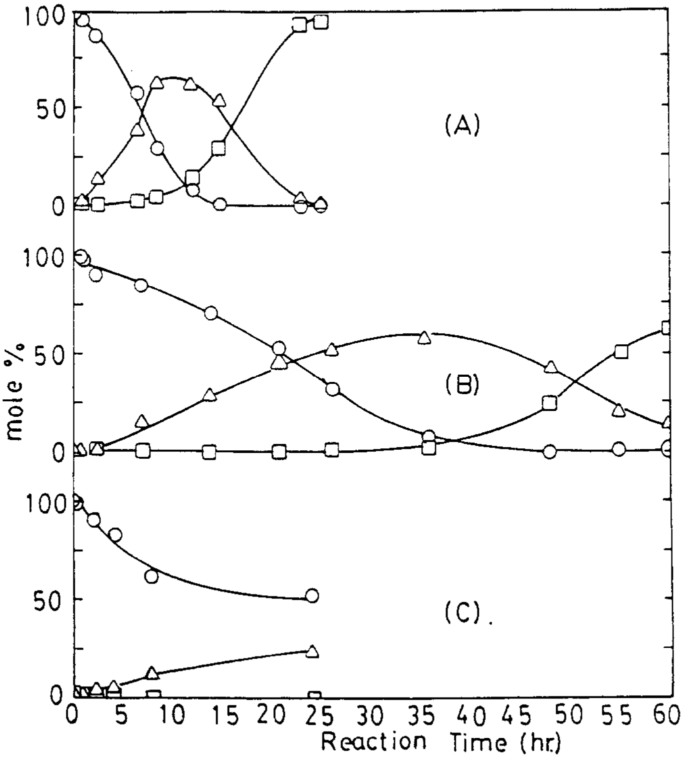


Fig. 3. Fluorination of $SiH_2(CH=CH_2)_2$ by SbF_3: (A) SbF_3 heated for one hour at about 300 °C, (C) SbF_3 heated for 30 minutes at about 300 °C, (C) SbF_3 with visible water removed. ○ $SiH_2(CH=CH_2)_2$, △ $SiHF(CH=CH_2)_2$, □ $SiF_2(CH=CH_2)_2$.

lustrated in Figure 3(B). It required more than 60 hours for the difluorination to be completed. Figure 3(A) shows the rate of fluorination with SbF_3 in Condition III. The monofluorination product reached a maximum of 70% at about 10 hours, and difluorination was complete in 25 hours. Similarly, Figures 1(B) and 1(C) compare fluorination rates for diethylsilane with SbF_3 in Conditions III and IV, respectively. For SbF_3 in Condition III, the yield of the monofluorination product reached a maximum of 85% in about seven hours, while for SbF_3 in Condition IV the corresponding maximum of 85% occurred in about 2.5 hours. The difluorination was essentially completed in 30 hours for SbF_3 in Condition III, and i 12 hours for SbF_3 in Condition IV. In summary, the displayed trends show that the drier the SbF_3, the faster the fluorination. However, regardless of the reaction rates the maximum yields reached by the monofluorination products remains fairly constant for each parent compound. Therefore, the dryness of SbF_3 does not alter the maximum yield of the monofluorinated compound--it only affects the time required to reach such maxima.

The fate of SbF_3

It was observed that the gaseous products from the fluorination process contained essentially no H_2 and at most a trace amount of SiF_4. The latter product would supposedly be derived from the interaction of HF and the glass tubing. The absence of H_2 and HF as fluorination products indicates that the fluorination is likely to be in the form of exchange reactions such as:

$$SiH_2RR' + SbF_3 \rightarrow SiHFRR' + SbHF_2 \qquad (1)$$

$$SiHFRR' + SbF_3 \rightarrow SiF_2RR' + SbHF_2 \qquad (2)$$

$$SiH_2RR' + SbHF_2 \rightarrow SiHFRR' + SbH_2F \qquad (3)$$

However, the slow formation of the difluorinated product means that fluorination with SbF_3 is a stepwise process and that a single step difluorination reaction, as shown in (4), does not occur:

$$SiH_2RR' + SbF_3 \rightarrow SiF_2RR' + SbH_2F \qquad (4)$$

Another experimental observation was the formation of an antimony mirror on the wall of the reaction cell. However, its rate of formation was not quantitatively related to the rate of fluorination, indicating that the formation of metallic antimony is probably due to side reactions. It is conceivable that the antimony mirror was formed from the decomposition of the unstable SbH_3 [13] which was produced during the SbF_3 fluorination process. Since the material balance of the gaseous products in the analyzed aliquots leaves little room for other undetected gaseous products, the inclusion of any substantial amount of SbH_3 in the product spectrum is very unlikely. SbH_3 has a boiling point of -17.1°C and would be a gas under reaction conditions.

ACKNOWLEDGEMENT

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REFERENCES

1 C. Eaborn, Organosilicon Compounds, Butterworths, London (1969).

2 V. Bazant, V. Chvalovsky and Rathousky, Organosilicon Compounds, Vol. 1, Academic Press, New York (1965).

3 J.E. Bulkowski, R. Stacy and C.H. Van Dyke, J. of Organomet. Chem., 87 (1975) 137.

4 M.A. Finch, L.H. Marcus, C. Smirnoff, C.H. Van Dyke and N. Viswanathan, Syn. Inorg. Metal-Org. Chem., 103 (1971).

5 R.J.P. Corriu, J.M. Fernandez and C. Guerin, J. Organo met. Chem., 192 (1980) 347.

6 V.F. Mironov, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, (1962) 1884.

7 Sintez i Svoistva Monomerov, Akad. Nauk SSSR. Inst. Neffekhion Sintera, Sb. Robot 12-01 (Dvenadtsatoi) Kont. Po. Vysokomolekul. Seedin, 1962 (1964) 153 (Russ.).

8 M.G. Voronkov and Yu. I. Skori, (Inst. Silicate Chem. Leningrad) Izv. Akad. Nauk SSSR, Ser. Khim, 7 (1964) 1215.

9 A.P. Krishkov, V. A. Drozdov and I. Yu Orlova, Zh. Obshch. Khim., 36 (1966) 2014.

10 A. A. Yakubovich, S.P. Makarov and V.A. Ginsburg, Zhur. Obschechei Khim., 28 (1958) 1036.

11 E.A.V. Ebsworth and S.G. Frankiss, Trans. Faraday Soc., 63 (1967) 1574.

12 C.N. Banwell, J.N. Murrell, and M.A. Turpin, Chem. Commun., (1968) 1466.

13 J.D. Smith, in J.C. Bailar, H.J. Emeleus, Sir R. Nyholm and A.F. Trotman-Dickenson (Editors), Comprehensive Inorgánic Chemistry, Vol. 2, Pergamon Press, New York, 1st edn., 1973, p. 587.