77. *Derivatives of Monosilane. Part III. The Fluoromonosilanes.*

By H. J. Emeléus and A. G. Maddock.

Experiments on the fluorination of certain halogenated silanes are described. Mono-, di-, and tri-fluoromonosilane have been prepared and characterised.

Two fluoromonosilanes are on record. Tetrafluoromonosilane or silicon tetrafluoride was known to Scheele and has been exhaustively studied by a number of other workers since. Trifluoromonosilane or silicofluoroform has been described in but three previous papers. Ruff and Albert (*Ber.*, 1905, **38**, 53, 2222) prepared silicofluoroform by the action on silicochloroform of titanium tetrafluoride. The product was analysed, and characterised by determination of the m. p. and b. p. Those authors also described a thermal decomposition involving the formation of silicon tetrafluoride, silicon, and hydrogen. Later, Booth and Stillwell (*J. Amer. Chem. Soc.*, 1934, **56**, 1531) prepared silicofluoroform by reaction between silicochloroform and antimony trifluoride.

They revised Ruff and Albert's physical data and reported that silicofluoroform suffered a slow disproportionation, giving silicon tetrafluoride and monosilane, even at very low temperatures. A further observation bearing on the fluorosilanes was Moissan and Smiles's report (*Compt. rend.*, 1902, **134**, 1549) that disilane reacts vigorously with sulphur hexafluoride to give undetermined products.

Direct fluorination, either by a diluted fluorine stream or by the use of those fluorinating agents, such as cobaltic fluoride, which act by virtue of a small dissociation pressure of fluorine, seemed unlikely to yield the partly fluorinated monosilanes. It was therefore decided to investigate the fluorination of the chloro- and iodo-monosilanes by mercurous, silver, and antimony fluorides.

EXPERIMENTAL.

Most of the reactions now described were carried out in a Stock-type universal vacuum apparatus. The mercurous fluoride was prepared according to Henne and Renoll (*J. Amer. Chem. Soc.*, 1938, **60**, 1060). Silver fluoride solution was prepared by dissolution of silver carbonate in 40% hydrofluoric acid solution in the dark, the solution being evaporated in a platinum dish in diffuse daylight with constant stirring. Thus prepared, silver fluoride was obtained as an orange-brown, granular powder, possessing great activity as a fluorinating agent. The antimony trifluoride used was a commercial product purified by sublimation in a platinum apparatus. Mono- and di-chloromonosilane were prepared as described by Emeléus and Miller (J., 1939, 819) · equal volumes of tensimetrically pure hydrogen chloride and monosilane were heated for 24 hours at 100° in a globe in the presence of anhydrous aluminium chloride, and the products were separated by a series of fractional distillations and condensations. Trichloromonosilane (silicochloroform) was formed as a minor product in this reaction, but its preparation in this manner was uneconomical. It was prepared in larger quantities by the action of hydrogen chloride on silicon at 400°; the gases formed were condensed in an acetone–solid carbon dioxide bath, and the trichloromonosilane separated from the silicon tetrachloride, first by a fractional distillation at atmospheric pressure with a long still head, and subsequently by further fractional distillations and condensations in the vacuum apparatus. Mono- and di-iodomonosilane were prepared by a method already described (J., 1941, 353).

The fluorination of silicochloroform by means of antimony trifluoride as described by Booth and Stillwell (*loc. cit.*) was first investigated with a view to determine some further details of the reaction mechanism. The silicochloroform was prepared as described above, the final purification consisting of a distillation at − 70° followed by a condensation at −80°. The product was found to be tensimetrically identical with that of Booth and Stillwell. 2·093 G. of this product were distilled backwards and forwards at room temperature (10—15°) for 3 hours over 5 g. of antimony trifluoride in the presence of 0·2 c.c. of antimony pentachloride; investigation of the products then showed that 1·95 c.c. of hydrogen had been formed. During the fluorination a black film formed over the walls of the vessel and the surface of the antimony trifluoride; this was examined and shown to be metallic antimony. The formation of the film is due to the appreciable volatility of antimony trifluoride at room temperature: such a metallic film has been shown to be formed in all cases with antimony trifluoride where oxidising fluorination is possible, the probable reaction being represented by the equation $6SiHCl_3 + 8SbF_3 = 3H_2 + 6SiF_4 + 2Sb + 6SbCl_3$, *i.e.*, it may be measured by the hydrogen and silicon tetrafluoride formed. The ratio 1 : 2 of these gases was verified experimentally.

The fluorinated products were separated by fractional distillation at −120° and by condensation at − 155° and in liquid nitrogen. The residue was further fractionated, and 0·750 g. of tensimetrically pure silicochloroform recovered. A head fraction from this separation was combined with the condensate at − 155°, and the mixture resolved by further fractionations into a less volatile fraction, consisting of partly fluorinated compounds, and a more volatile fraction (4·0 c.c.) characterised by vapour-pressure determinations as silicon tetrafluoride. The most volatile fraction was easily fractionated to tensimetric homogeneity, 158 c.c. of the product being obtained. Analysis by decomposition with sodium hydroxide showed it to consist of silicofluoroform. The freshly prepared product had a sharp m. p. and the mean of four determinations gave m. p. − 131·4° (ethylene thermometer). The following observations were made on the vapour pressure of the freshly isolated product:

Temp.	−105·0°	−108·0°	−110·0°	−112·5°	−114·0°	−117·0°
Press., mm. Hg	352	275	222	175	145	125

From these data the b. p. is − 95·0°, and the latent heat 4802 cals. Trouton's constant is 27·0, indicating considerable association in the liquid phase.

The steady decomposition by disproportionation at room temperature reported by Booth and Stillwell was observed, but this decomposition did not continue at the temperature of liquid nitrogen, as reported by these authors. The vapour pressure of the compound rises progressively and, in view of the disproportionation of difluoromonosilane reported below, it seems probable that the reaction is a simple disproportionation to monosilane and silicon tetrafluoride.

In the above experiment about 75% of the silicochloroform was converted into silicofluoroform, about 2% transformed into silicon tetrafluoride by oxidising fluorination, and the residual silicochloroform converted into partially fluorinated products, in particular dichloromonofluoromonosilane. These figures are calculated on the silicochloroform reacting and not on the quantity taken, 28% of which was recovered unchanged. In other experiments longer periods of reaction were allowed and in this way more complete conversion could be obtained. With 24 hours' treatment, all the silicochloroform reacted and 91% of the theoretical yield of silicofluoroform was obtained, but the extent of the oxidising side reaction also rose to 8%. In each case the reaction took place at room temperature.

In view of the satisfactory result of the above fluorination, the action of antimony trifluoride on tensimetrically pure dichloromonosilane (silylene chloride) was investigated. A preliminary test showed that a reaction took place at room temperature with considerable blackening of the antimony trifluoride, formation of an antimony mirror, and the evolution of hydrogen. A series of quantitative experiments were then carried out in which measured volumes of silylene chloride were fluorinated with an excess of antimony trifluoride in the presence of 10% of antimony pentachloride at room temperature for various times. The results were closely analogous to those with silicochloroform, but the reaction was rather slower and, if it was allowed to continue, progressively more oxidising fluorination took place. A reaction time of about 24 hours gave the greatest yields of silylene fluoride when using about 200 c.c. of dichloromonosilane with 5 g. of antimony trifluoride. The product, from such a preparation, was readily resolved into five fractions: (i) about 10%, calculated on the volume of silylene chloride taken, consisted of hydrogen; (ii) volatile at − 160°, was about 0·5%, and probably consisted of silicofluoroform from the oxidising fluorination; (iii) the largest, constituting about 90% by volume, volatile at − 130°, consisted of silylene fluoride and silicon tetrafluoride (80% and 10%, respectively) and traces of unidentified products assumed to be partly fluorinated compounds; (iv) a small fraction of about 8—9% of partly fluorinated compounds distilling at − 100°; (v) residue, 0·5—1%, of unchanged silylene chloride. Longer periods of fluorination increased the quantity of hydrogen and silicon tetrafluoride up to 30%. It is thus seen that under favourable conditions yields of silylene fluoride up to 80% could be obtained. The yield of the reaction could rapidly be determined by fractionation into the distillates mentioned above, and thence calculated from the volume of hydrogen formed and the volume of the third fraction. As a further check a sample of the third fraction was quantitatively decomposed with sodium hydroxide, silylene fluoride reacting according to the equation $SiH_2F_2 + 4NaOH = H_2O + 2H_2 + Na_2SiO_3 + 2NaF$. The silicon tetrafluoride reacts without production of a permanent gas. The presence of any chlorine derivatives in the product could be tested for in this hydrolysed mixture.

At first, this method of analysis gave anomalous results, but it was found that this was due to incomplete reaction of the alkali with the silylene fluoride, resulting in the formation of rather stable hyposilicates, such as Schwarz has described, which decompose on heating in water with the evolution of hydrogen. A more precise and standardised procedure eliminated this difficulty. About 15 c.c. of the silylene fluoride sample was distilled on to about 10 c.c. of previously degassed 30% sodium hydroxide solution cooled in liquid nitrogen and contained in a bulb tube closed by a tap. The tap was closed, and the alkali boiled for some time (30 mins.) by placing the vessel in water at 35—40°. The hydrogen formed was pumped off by a Töpler pump through a trap cooled in liquid nitrogen, and measured in the gas burette. The reaction was thus taken to completion.

Numerous quantitative preparations were subsequently carried out, and in all the yield of silylene fluoride was about 80% under the conditions described above. The isolation of pure silylene fluoride from the silicon tetrafluoride in the third fraction proved less easy than was expected. An initial mistake was made in supposing that silylene fluoride should be more volatile than silicon tetrafluoride. By following an attempted separation by the above method of analysis it was soon shown that this was not the case. Eventually by a series of fractional distillations at − 130°, combined with fractional condensations at − 143°, a pure sample of silylene fluoride was isolated. In view of the difficulty of this separation and the low yield of the fourth fraction no attempt was made to isolate a partially fluorinated product such as SiH_2ClF.

The analysis of the final product was made by hydrolysis in the manner described above, combined with a determination of the fluorine in the hydrolysed mixture by De Boer and Basant's method (*Z. anorg. Chem.*, 1926, **152**, 213). Analytical results are given below. Three determinations of the vapour density by direct weighing gave the values of 68·3, 68·5, 68·7 (Calc.: 68·0). The mean of four determinations of the m. p., using an ethylene thermometer, gave it as − 122·0°, and this was confirmed by the intersection of the two branches of the vapour-pressure curve determined in the usual manner by using ethylene and hydrogen chloride vapour-pressure thermometers. The data are given below, and lead to a b. p. of − 77·8° and a latent heat of 4751 cals. Hence Trouton's constant = 25·7, indicating considerable association in the liquid phase. This fact is in agreement with the anomalous b. p.

Vol. of SiH_2F_2 taken, c.c. at N.T.P.	Vol. of H_2 formed, c.c. at N.T.P.	H_2/SiH_2F_2.		Fluorine, %.	
		Found.	Calc.	Found.	Calc.
12·55	25·0	1·99	2·00	56·3	55·9
16·18	32·0	1·98	2·00	56·7	55·9
17·50	34·7	1·98	2·00	56·0	55·9

Temp.	− 85·2°	− 88·2°	− 88·5°	− 90·9°	− 93·0°	− 95·0°	− 97·7°	− 99·8°	−105·0°
Press., mm. Hg	463·0	417·4	396·3	332·1	296·0	250·3	197·3	169·0	121·4
Temp.	−106·9°	−112·2°	−116·2°	−118·1°	−120·8°	−124·2°	−129·3°	−132·5°	−134·5°
Press., mm. Hg	101·7	60·9	41·6	37·7	25·5	16·5	11·0	8·2	6·1

The difficulty in the separation of the silylene fluoride from the crude product made an investigation of alternative preparations desirable, and analogy with the corresponding carbon compounds suggested an attempt to fluorinate silylene iodide with silver or mercurous fluoride. However, in neither case was the result satisfactory. In the first case silylene iodide was allowed to melt in contact with silver fluoride cooled in ice, but even at this low temperature a violent reaction took place, giving a red flame and formation of a brown amorphous powder. A large volume of hydrogen was also formed. In the second case the silylene iodide reacted quite smoothly with the cooled mercurous fluoride, but a considerable volume of hydrogen was formed and by measurement of its volume a limit of 55% was set to the maximum possible yield of silylene fluoride. Further examination of this preparation was therefore postponed.

Owing to the instability of silicofluoroform (see above), the stability of silylene fluoride was examined. No appreciable change in the vapour pressure of a sample of silylene fluoride stored over mercury for 14 days was noticed; however, the vapour pressure of a sample of silylene fluoride stored in the same manner for two years (room temperature, 0—20°) was found to have risen considerably. A series of fractional condensations at − 160° resolved the mixture thereby formed into equal volumes of silicon tetrafluoride and monosilane. Complete disproportionation had therefore taken place: $2SiH_2F_2 = SiH_4 + SiF_4$.

The preparation of monofluoromonosilane or silyl fluoride by fluorination of silyl chloride by antimony trifluoride was next examined. Preliminary experiments showed that fluorination took place at room temperature, again with the formation of an antimony mirror and the evolution of hydrogen. In one of a number of quantitative experiments, 201 c.c. of silyl chloride were confined over 5 g. of antimony trifluoride mixed with 0·2 c.c. of antimony pentachloride for 24 hours at 12°; 45 c.c. of hydrogen and 142 c.c. of products volatile at − 130° were obtained. The residue, all of which distilled above − 80°, was shown tensimetrically to consist almost entirely of unchanged silyl chloride. This indicates a 79% yield of silyl fluoride in the more volatile fraction on the assumption that little silylene fluoride or silicofluoroform was formed. A similar conclusion was reached from the results of analysis of samples of the − 130° fraction by hydrolysis with sodium hydroxide. Longer periods of fluorination were again found to produce more hydrogen and consequently more oxidising fluorination.

The separation of pure silyl fluoride from the product of the above fluorination proved very difficult, and a degree of purity exceeding 98% could not be attained. It is thought that the isolation of silyl fluoride is rendered difficult by a slow disproportionation reaction which is more rapid than those observed with the other fluorides. It was, indeed, soon observed that samples stored at room temperature steadily increased in vapour pressure. Fractionations on quantities as large as 2 l. of gas were carried out, and a series of fractional distillations at − 140° with condensation of the silicon tetrafluoride proved most effective. The course of the fractionation was followed by vapour-density measurements and analysis. Attempts to obtain a more readily purified product by fluorination of silyl iodide by mercurous or silver fluoride were as unsuccessful as the experiments with silylene iodide: the results indeed were closely analogous. Analysis of the purest sample of silyl fluoride obtainable gave the results shown below.

Vol. of SiH_3F taken, c.c. at N.T.P.	Vol. of H_2 found, c.c. at N.T.P.	H_2/SiH_3F.		Fluorine, %.	
		Found.	Calc.	Found.	Calc.
21·2	62·4	2·94	3·00	40·8	38·0
17·1	50·1	2·93	3·00	41·0	38·0

Observed values of the vapour density were 51·0, 51·1 (Calc. : 50·5). A few points on the vapour pressure curve were determined, and are tabulated below.

Vap. press., mm. Hg	58	100	184	243	320	416
Temp.	−128·1°	−122·0°	−116·2°	−112·5°	−109·1°	−105·8°

The extrapolated b. p. is − 98·6°, and the latent heat 4500 cals. This gives 25·8 for Trouton's constant, again indicating the association of these compounds in the liquid phase.

The fluoromonosilanes appear, therefore, to be characterised by anomalous b. p.'s due to association in the liquid phase, caused presumably by hydrogen bonds, and by a pronounced tendency to disproportionation even at room temperature which is most marked in the case of silyl fluoride and silicofluoroform.

IMPERIAL COLLEGE, LONDON, S.W.7.

[*Received, December 8th,* 1943.]