363. *The Ethoxyfluorosilanes.*

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A rapid disproportionation of diethoxydichlorosilane into the mono- and the tri-ethoxy-compound has been observed. *Ethoxytrifluorosilane* has been prepared by reaction of the corresponding chloro-compound with antimony trifluoride. It disproportionates at room temperature. Triethoxyfluorosilane can be prepared from triethoxychlorosilane and antimony trifluoride and is stable up to 100°. Diethoxydifluorosilane exists at room temperature only in equilibrium with the mono- and the tri-ethoxy-compound.

The ethoxychlorosilanes $SiCl_3{\cdot}OEt$, $SiCl_2(OEt)_2$, and $SiCl(OEt)_3$ were first described by Friedel and Crafts (*Ann. Chim. Phys.*, 1863, **9**, 11) but the fluorine analogues of these compounds were unknown until recently. A brief report of their preparation by the fluorination of the chloro-compounds was published by Heal (*Nature*, 1946, **158**, 672). Peppard, Brown, and Johnson (*J. Amer. Chem. Soc.*, 1946, **68**, 76) have also prepared di- and tri-ethoxyfluorosilane by the reaction of ethyl orthosilicate with antimony trifluoride and antimony pentachloride.

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* Designated in the tables as 54 and 57, respectively.

They failed, however, to observe the disproportionation of diethoxydifluorosilane, and this communication, beside describing an alternative preparative method and some of the physical properties of these compounds, clarifies the question of their disproportionation.

Friedel and Crafts (*loc. cit.*) described the three ethoxychlorosilanes as stable substances which had definite boiling points, and were obtained by heating mixtures of ethyl orthosilicate and silicon tetrachloride in the molecular proportions 1 : 3, 1 : 1, and 3 : 1. Pellini, however, stated that the products of these reactions could not be separated by distillation (*Gazzetta*, 1915, **45**, 380). In an attempt to repeat this preparation of diethoxydichlorosilane, the product, when distilled, has been found to consist largely of the mono- and the tri-ethoxy-compound, which boiled at the temperatures given by Friedel and Crafts. The middle fraction, on repeated distillation, resolved itself progressively into the last two derivatives according to the equation $2SiCl_2(OEt)_2 \rightleftharpoons SiCl_3{\cdot}OEt + SiCl(OEt)_3$. With rapid distillation, using an efficient column, it is probable that diethoxydichlorosilane would show a definite boiling point, and the discrepancy between the results of Friedel and Crafts and of Pellini may be due to different conditions of distillation. A similar explanation may be given for the fact that Peppard, Brown, and Johnson (*loc. cit.*) were able to isolate diethoxydifluorosilane whereas the experiments described below show that this substance disproportionates readily.

Ethoxytrifluorosilane was prepared from antimony trifluoride and the corresponding chloro-compound, from which it differed by showing a ready disproportionation at room temperature. The product of this reaction contained silicon tetrafluoride and other ethoxyfluorosilanes and was purified by fractional condensation in a Stock vacuum apparatus. The disproportionation probably occurred according to the equation $2SiF_3{\cdot}OEt \rightleftharpoons SiF_2(OEt)_2 + SiF_4$. The diethoxy-compound is itself unstable (see below) and, at equilibrium, only about one-third of the monoethoxy-compound is decomposed. The boiling point of ethoxytrifluorosilane, extrapolated from vapour-pressure data, is about −7°, the vapour-pressure equation being $\log p = 8{\cdot}17 - 1400/T$. The latent heat of vaporisation is 6400 cals./mol., Trouton's constant 24·1, the melting point −122°, and the liquid density at −63° 1·32 g./c.c. An uncertainty occurs in the vapour-pressure data because of the possibility of slow disproportionation in the liquid.

Since it had proved impossible to prepare diethoxydichlorosilane as an intermediate, the preparation of di- and tri-ethoxyfluorosilanes was attempted by treating triethoxychlorosilane with antimony trifluoride, when it was thought that some of the diethoxy-compound would be formed by disproportionation. From the mixture of products in this reaction two fractions (b. p. 70—110° and 110—145°) were distilled off at atmospheric pressure. The first of these probably contained an unstable diethoxydifluorosilane, the boiling point of which is given by Peppard, Brown, and Johnson as 83—83·5°. These authors did not observe the disproportionation of the diethoxy-compound, probably because their material was distilled only once through a long column. In the vacuum apparatus, however, six successive fractional condensations of a sample of the 70—110° fraction each yielded a mixture of the mono- and tri-ethoxy-compounds. In each operation the amount of each of these two compounds formed was about one-eighth of the total material treated. This amount did not diminish in relation to the main fraction with successive distillations. It was concluded that diethoxydifluorosilane changes quickly, after condensation, into an equilibrium mixture containing roughly three parts of diethoxydifluorosilane and one part of the mixed mono- and tri-ethoxy-derivatives. The analytical results for the final " diethoxydifluorosilane " condensate were approximately those for the pure compound, a result which is consistent with the presence of the two disproportionation products.

Pure triethoxyfluorosilane was isolated without difficulty by high-vacuum fractionation of the 110—145° fraction : it was condensed out at −40° and was a colourless liquid which fumed in moist air, was immediately hydrolysed by water to form gelatinous silica, and burnt with a luminous flame. The boiling point at 760 mm. was found by extrapolation of the vapour-pressure graph to be 134·6°, in reasonable agreement with the value given by Peppard, Brown, and Johnson (133—133·5°). The vapour-pressure equation was $\log p = 8{\cdot}040 - 2104/T$, the latent heat of vaporisation was 9620 cals./mol., and Trouton's constant 23·8. The compound set to a transparent glass when cooled, and its melting point was not determined. The vapour-pressure curve of a sample kept at 100° for 1 hour was completely unchanged, showing that the rate of disproportionation at this temperature is inappreciable.

The physical properties of the ethoxyfluorosilanes resemble closely those of the corresponding ethylfluorosilanes (Emeléus and Wilkins, *J.*, 1944, 454). The latter, however, do not disproportionate and are more resistant to hydrolysis : triethylfluorosilane, for example, is unattacked by cold water whereas the triethoxy-derivative is immediately hydrolysed. The tendency to disproportionate is greater in the ethoxyfluoro- than in the ethoxychloro-compounds. A further point of interest is that no catalyst is required for the reactions between antimony trifluoride and the ethoxychlorosilanes, whereas the reaction between antimony trifluoride and silicon tetrachloride does not occur unless a quinquevalent antimony compound is present. Fluorination of either of the stable ethoxychlorosilanes yields a mixture of the three ethoxyfluorosilanes, showing a partial breakdown of the C‒O‒Si bond system. Fluorination does not affect the C‒Si bonds in the ethyl chlorosilanes (Emeléus and Wilkins, *loc. cit.*) but it largely disrupts the Si‒O‒Si bonds in hexachlorodisiloxane (Booth and Osten, *J. Amer. Chem. Soc.*, 1945, **67**, 1092).

EXPERIMENTAL.

Ethoxytrichlorosilane and Triethoxychlorosilane.—It was intended to prepare each of the ethoxychlorosilanes separately, but the ready disproportionation of the diethoxy-compound, when its preparation was attempted, provided a method of obtaining the other two. Half-molar quantities of redistilled ethyl orthosilicate and silicon tetrachloride were mixed and heated in Carius tubes for three hours at 150°. The contents of the tubes were then distilled through an 8″ column. There were well-marked arrests in the rise of b. p. at 103° and 155°, the b. p.s given by Friedel and Crafts for mono- and tri-ethoxychlorosilanes, but no arrest at 136°, which is given as the boiling point of diethoxydichlorosilane. The middle fraction, which would contain the last compound, resolved itself into higher- and lower-boiling fractions in subsequent distillations, and after three successive distillations of the middle fraction the following quantities of the various products were isolated: $\mathrm{SiCl_3{\cdot}OEt}$, b. p. 102·5—104°, 31 g.; $\mathrm{SiCl_2(OEt)_2}$, b. p. 136—138°, 4 g.; $\mathrm{SiCl(OEt)_3}$, b. p. 154—156·5°, 48 g. A second preparation gave practically the same results.

Fluorination of Ethoxytrichlorosilane.—Antimony trifluoride was well dried in a vacuum desiccator before use. The silane (30 g.) was added at the rate of about one drop per second to a 50% excess (45 g.) of antimony trifluoride in a bulb with a sealed-in tap-funnel. The bulb was continually shaken. The temperature rose to about 70° and the reaction mixture liquefied. The volatile products were led off through a water-cooled condenser to a trap cooled in liquid air, a stream of dry nitrogen being passed throughout the reaction. After the reaction, the contents of the low-temperature trap were pumped into the fractionating line of a Stock vacuum apparatus. *Ethoxytrifluorosilane* (Found: Si, 22·9, 21·2; F, 43·5, 42·0. $\mathrm{EtOSiF_3}$ requires Si, 21·5; F, 43·8%) was isolated by keeping the reaction product at a temperature at which the vapour pressure was 2—5 mm. and allowing the vapour to pass through a series of three traps in the vacuum apparatus kept at −80°, −110°, and −185°. The first removed less volatile ethoxyfluorosilanes, the monoethoxy-compound separated at −110°, and silicon tetrafluoride passed into the −185° trap. It was characterised by vapour-pressure measurements.

Preliminary experiments showed that the disproportionation of ethoxytrifluorosilane was fairly rapid at room temperature, but was inappreciable below about −20°. In the above method of separation decomposition of the liquid at −110° would be negligible, and the main source of contamination of the product was the decomposition during the vapour-pressure determinations. In measuring the vapour pressure of the compound, the sample was contained in a large bulb which was wholly immersed in the cooling bath and connected by a capillary to an external mercury manometer. In this way only the small amount of vapour in the capillary was at room temperature and readings were fairly steady. Temperatures were measured with an ammonia vapour pressure thermometer. The following data were obtained:

Temp.	−66·7°	−62·0°	−56·5°	−51·5°	−48·4°	−44·7°	−36·6°	−30·8°	−25·3°
V. p., mm.	19	34	49	68	85	105	178	253	315

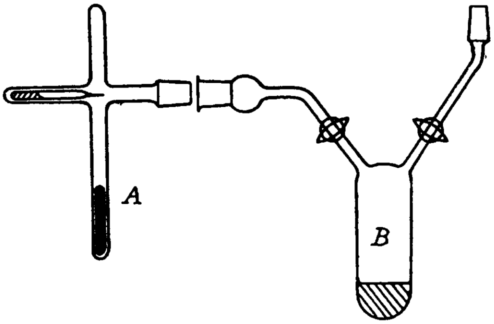
The m. p. determined by Stock's method ("The Hydrides of Boron and Silicon," p. 184) was −122° ± 1°. The liquid density of ethoxytrifluorosilane was measured by distilling a sample into a pyknometer at −63°, which was sealed off from the vacuum system and weighed. The volume at room temperature was determined by filling with mercury, correction being made for the expansion of the glass in calculating the density at −63°.

Fluorination of Triethoxychlorosilane.—Triethoxychlorosilane (30 g.) was mixed with a 60% excess of antimony trifluoride in a Kon flask, which was cooled in water while the reaction proceeded and then left to stand for some time. All products boiling up to 170° were distilled off at atmospheric pressure. The distillate was redistilled from a further 5 g. of antimony trifluoride, fractions boiling at 70—110° and 110—145° being collected. In both distillations gaseous products escaped. The two fractions were separately subjected to fractional condensation in the vacuum apparatus. In the case of the 70—110° fraction, which was believed to contain diethoxydifluorosilane, condensing traps at −30°, −75°, and −185° were used, the diethoxy-compound being removed at −75°. Unlike the monoethoxy-compound, which could be resubmitted to fractional condensation without appreciable condensates appearing in the traps at −80° or −185°, the diethoxy-compound when refractionated gave both mono- and tri-ethoxy-fractions, the proportions of which have already been mentioned. These substances reappeared in each fresh distillation and were formed at the temperature (*ca.* 0°) at which the substance was vaporised in order to submit it to fractional condensation in the low-temperature traps. The final "diethoxydifluorosilane" condensate had nearly the same analytical composition as pure diethoxydifluorosilane [Found: Si, 16·8; F, 23·6. Calc. for $\mathrm{SiF_2(OEt)_2}$: Si, 18·0; F, 24·3%].

Triethoxyfluorosilane [Found: Si, 15·6, 16·0; F, 10·3, 10·1. Calc. for $\mathrm{SiF(OEt)_3}$: Si, 15·4; F, 10·4%] was obtained without difficulty by high-vacuum fractionation of the 110—145° fraction. It was condensed out at −40°, with neighbouring traps at −10° and −185°. There was no evidence of disproportionation in this case. Vapour-pressure measurements were made with an isoteniscope, temperatures being measured with a standard mercury thermometer. Data are recorded below:

Temp.	17·6°	40·0°	60·1°	70·0°	79·2°	89·0°	100·7°
V. p., mm.	6·5	21	53	81	116	169	255

Analysis.—Silicon and fluorine were determined on the same sample. Each sample (0·2—0·4 g.) was distilled into a short, thin-walled weighing tube, which was sealed off from the vacuum system with a capillary neck. A file scratch was made at the base of this capillary, and the tube with its sample was weighed. The capillary was broken off in a special capillary-breaker (see figure, *A*), in which a weighted glass rod fell on to the capillary when the breaker was rotated on its ground joint. During this operation the capillary-breaker was evacuated and in communication with the hydrolysis bulb *B*, which contained potassium hydroxide solution (100% excess over that required to hydrolyse the sample), frozen in liquid air. The sample distilled on to the hydrolysing agent at once. The stopcock between hydrolysis bulb and capillary breaker was closed, and the bulb warmed in boiling water until the gelatinous silica at first precipitated had dissolved. The empty weighing tube and its capillary were weighed.



The hydrolysate was washed out of the bulb, and 4 g. of ammonium carbonate were added. After 24 hours most of the silica had separated, and was filtered off, washed with water, and dried. The filtrate was evaporated on a steam-bath, to decompose excess of ammonium carbonate. 3 C.c. of ammoniacal zinc oxide solution were added, and evaporation continued until the solution no longer smelled of ammonia. The precipitate of zinc oxide and silicate was filtered off, washed, and dissolved in a little concentrated hydrochloric acid. This solution was evaporated to dryness, and the residue baked at 130° for several hours. More acid was added, and the evaporation and baking repeated. After three such operations, the now insoluble silica was moistened with dilute hydrochloric acid, filtered off, washed, and dried. It was combined with the main silica precipitate, and ignited and weighed, to give the silicon content of the sample.

The fluoride in the filtrate from the zinc oxide precipitation was precipitated in a mixture of calcium fluoride and carbonate by adding a solution of 5 g. of hydrated calcium nitrate. The mixed precipitate was treated by the classical gravimetric procedure for fluorine analysis, the carbonate being removed by evaporations with acetic acid. After weighing, the calcium fluoride was converted into calcium sulphate, and this weighed as a check. The weights agreed well in all cases.

Disproportionation of Ethoxytrifluorosilane.—The following figures illustrate the disproportionation of this silane. 0·3694 G. of the purified compound was distilled into a 60-c.c. gas-weighing bulb, which was then left at room temperature for 18 hours: as judged from the speed of disproportionation observed, this time should have amply sufficed to allow the substance to come to equilibrium with its disproportionation products. The liquid did not vaporise quite completely. The pressure in the bulb was about one atmosphere. The entire contents of the bulb were then fractionally condensed in a series of traps at −75°, −120°, and −185°, so separating them into crude diethoxydifluorosilane, ethoxytrifluorosilane, and silicon tetrafluoride fractions. The middle fraction was redistilled in the same way, and the resulting −75° and −185° fractions combined with those first obtained. The combined −185° (silicon tetrafluoride) fraction was redistilled to remove a little ethoxytrifluorosilane, which was added to the main ethoxytrifluorosilane fraction. All fractions were then weighed, giving:

SiF_4	0·0592 g.	(−185°)
$SiF_3 \cdot OEt$	0·2225 g.	(−120°)
Heavy fraction [mainly $SiF_2(OEt)_2$]	0·0865 g.	(−75°)
Total	0·3682 g.	(99·7% recovery)

Calculation shows the composition of the heavy fraction to have been approximately $SiF_{1 \cdot 9}(OC_2H_5)_{2 \cdot 1}$. It probably consisted mainly of diethoxydifluorosilane, with some triethoxyfluorosilane.

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