122. *Some New Ethyl and Phenyl Silicon Fluorides.*

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Ethyl- and phenyl-substituted silicon fluorides of the types $SiRF_3$ and SiR_2F_2 have been prepared, thereby completing the series of ethyl and phenyl derivatives of silicon tetrafluoride. The new compounds are obtained in high yield from the corresponding chlorides by the action of zinc fluoride, and they are also produced by the action of hydrogen fluoride on the oxy-compounds.

The resistance of the compounds to hydrolysis rises rapidly with increase in the number of organic groups.

Comparatively few organo-substituted fluorides of non-metals are known, the majority having been prepared either by the action of hydrogen fluoride on the appropriate oxide or from the simple fluoride by substitution. Only trisubstituted silicon fluorides have been described; triethylfluorosilane has been prepared by both of the above methods (Flood, *J. Amer. Chem. Soc.*, 1933, **54**, 1735; Gierut, Sowa, and Nieuland, *ibid.*, 1936, **58**, 897), and the triphenyl and the tribenzyl derivative by the second method (Medox and Kotelkov, *J. Gen. Chem. U.S.S.R.*, 1937, **7**, 2007; Medox, *ibid.*, 1938, **8**, 291). We now describe the *mono-* and *di-ethyl-* and *-phenyl-silicon fluorides*, the completion of the series $SiEt_nF_{4-n}$ and $SiPh_nF_{4-n}$ providing information for a group study.

These compounds are readily prepared in high yield from the chlorides by conventional procedure, there being no evidence of disruption of the Si–C bond during the reaction. They are also formed by reaction of hydrogen fluoride (generated in the reaction mixture) with the appropriate siliconic acids, $(R\cdot SiO_2H)_x$, or silicones, $(SiR_2O)_x$; yields differ widely, but this alternative procedure provided confirmation of purity and identity of the products.

The reactivity of the compounds towards hydrolysing agents falls sharply as the number of organic groups increases, the behaviour of the series being as follows :

$SiEtF_3$	Immediately hydrolysed by water; reaction probably incomplete.
$SiPhF_3$	Immediately hydrolysed by water; reaction incomplete.
$SiEt_2F_2$ $SiPh_2F_2$	Very slight hydrolysis with water, but rapid decomposition with alkalis.
$SiEt_3F$	High resistance to hydrolysis; undecomposed by sodium in liquid ammonia (Gierut, Sowa, and Nieuland, *loc. cit.*).
$SiPh_3F$	High resistance to hydrolysis (Medox and Kotelkov, *loc. cit.*).

Such behaviour could not entirely be ascribed to steric factors, for the effect in the chloride series is much less pronounced. Substituted germanium halides and analogous aliphatic types show a broadly parallel trend.

There is a regular decrement in boiling point, of 34° per halogen atom, on passing from ethylchlorosilanes to ethylfluorosilanes : the difference is somewhat lower in the phenyl series. Phenyltrifluorosilane and diphenyldifluorosilane (b. p.'s 101·8°, 252°) are both slightly more volatile than their carbon analogues (b. p.'s 102·4°, and 260°, decomp.).

Experimental.

The required silicon chlorides were prepared by interaction of Grignard reagents with silicon tetrachloride as described by Kipping and his colleagues. Oxy-compounds were obtained by hydrolysis of the chlorides, no attempt being made to secure them in any particular degree of hydration. Ethylsiliconic acid separated when ethyltrichlorosilane was stirred into cold water; it was washed under running water, dried overnight at 120°, and finely powdered. Phenylsiliconic acid, prepared similarly, was dried for 2½ hours at 150°. Diethylsilicone was obtained by decomposing the dichloride with aqueous sodium hydrogen carbonate; it separated as a clear yellow oil and was used directly.

Ethyltrichlorosilane and diethyldichlorosilane are converted into the corresponding fluoro-compounds by the fluorides of zinc, lead, and antimony, but the first is best for preparative purposes because the action of antimony trifluoride is too vigorous and that of lead fluoride too sluggish. For the conversion of the phenylchloro- into the phenylfluoro-silanes zinc and antimony fluorides are equally useful.

Metallic fluorides used were of reagent quality, dried at 120—130°.

Preparation and Properties of Ethyltrifluorosilane.—(1) Ethyltrichlorosilane (b. p. 98—99°) was dropped from a tap funnel on to zinc fluoride maintained at 55° in a flask which had been swept out with dry nitrogen. The gaseous product was passed through a water-cooled reflux condenser into a liquid-air trap attached to a vacuum fractionation system. The condensate, a snow-white solid melting to a sparkling liquid, was volatile in the vacuum line at −79° and almost completely retained by a trap at − 111°. Further fractionation narrowed the limits of the cut to −87° and −108°. The yield of tensimetrically pure product was 60% (0·2531 G. of the gas occupied 226·0 c.c. at 179 mm. and 18·0°, corresponding to *M*, 113·5. $C_2H_5SiF_3$ requires *M*, 114·1). The fluorine content of the *silane*, determined by titration of strong acid liberated on hydrolysis, was 49·95% (Calc.: 50·0%).

Vapour pressure values for ethyltrifluorosilane were as follows:

Temp.	−71·5°	−68·3°	−62·7°	−55·9°	−47·3°	−43·4°
V. p. (mm.)	15	20	30	48·5	84·5	107
Temp.	−34·1°	−26·9°	−18·0°	−10·3°	−7·5°	−5·2°
V. p. (mm.)	183	263·5	410	576.	650	725

The vapour pressure reaches 760 mm. at −4·4°, and the latent heat of vaporisation is 6181 cals./mol.

Gaseous ethyltrifluorosilane has a pungent smell and irritates the nose and throat intensely. It is readily inflammable, burning with a bright green-edged flame and forming a mist of silica. Hydrolysis with water is instantaneous, though the gas persists for a short time in moist air. The m. p. is −105° (pentane thermometer).

(2) A mixture of 12 g. of ethylsiliconic acid with 8 g. of calcium fluoride was gently warmed with 25 c.c. of concentrated sulphuric acid, so as to maintain a steady evolution of gas, the temperature being eventually raised to 120°. The gas was freed from hydrogen fluoride by passage through a solution of ethylsiliconic acid in sulphuric acid. It was collected in a liquid-air trap, and consisted of ethyltrifluorosilane (yield 25%) with a little silicon tetrafluoride, which was readily removed. Vapour-pressure values and the m. p. of the product were identical with those given in (1).

Preparation and Properties of Diethyldifluorosilane.—(1) Diethyldichlorosilane (b. p. 125—131°) was warmed to 60° with a 50% excess of zinc fluoride until reaction set in. The product (b. p. 60—61°) was removed through a fractionating column and purified by distillation in the vacuum line. The final cut lay between the limits −54° and −75°. Measurement of vapour density gave *M*, 123·6 [$(C_2H_5)_2SiF_2$ requires *M*, 124·1]. For analysis, the compound was absorbed in 2N-alkali, the solution diluted to 200 c.c. and faintly acidified with acetic acid, and the fluorine precipitated as calcium fluoride. The diethylsilicone remained in solution and did not interfere (Found: F, 29·9. $C_4H_{10}SiF_2$ requires F, 30·6%).

Vapour-pressure measurements by the static method gave the following values:

Temp.	−28·9°	−15·8°	−5·9°	+6·7°	+11·5°	23·4°	31·7°
V. p. (mm.)	9·5	25	41·5	80·5	103	189	263·5
Temp.	38·4°	45·6°	49·7°	55·0°	59·7°	60·9°	
V. p. (mm.)	345	450	521	625	726	760	

The latent heat of vaporisation is 7623 cals./mol.

Diethyldifluorosilane is a sparkling liquid with a faint smell reminiscent of that of oil of wintergreen. When added to water it sinks in oily drops, and only after 12 hours' standing does a thin film of hydrolysis products appear at the liquid interface. Alkaline reagents bring about very rapid hydrolysis. The compound does not attack glass at temperatures below its b. p. The m. p. is −78·7° ± 0·2°.

(2) 20 G. of the silicone were dissolved in 150 c.c. of concentrated sulphuric acid in a Pyrex flask, and 15 g. of calcium fluoride added. The flask was connected through liquid-air traps to the vacuum line. On gentle warming, a reaction set in and a layer of clear liquid soon accumulated on the surface of the reaction mixture. This liquid was distilled off and freed from silicon tetrafluoride by pumping at −70°. There were obtained 10 c.c. of product having b. p. 61—62° and m. p. −78°, in agreement with the values for diethyldifluorosilane (Found, acidimetrically: F, 30·4%).

Preparation and Properties of Phenyltrifluorosilane.—Chlorine was replaced by fluorine by means of zinc fluoride (50% excess) in a Kon-type flask. When once the reaction had been started by warming to about 60°, little further heating was necessary, the heat of the reaction distilling off the greater part of the lower-boiling product. This was twice redistilled from fresh zinc fluoride and then had b. p. 101·5°, the entire sample passing over within a range of 0·2°; yield 70%. Handled in contact with air, the substance attacks glass, but vacuum fractionation reduces the attack considerably. When kept in glass, it slowly formed a very involatile liquid, probably owing to action upon the glass. This made it always necessary to work with freshly distilled material.

Analysis was carried out by decomposing an alcoholic solution of the compound with excess of standard alkali and back-titrating the excess, litmus being used as indicator (Found: F, 34·8; *M*, cryoscopic in benzene, 164·0, 168·7. $C_6H_5SiF_3$ requires F, 35·2%; *M*, 162·1). Attempts to determine the fluorine by precipitation as calcium fluoride gave low and erratic results. This was attributable to the fact that when the solution obtained by absorbing the substance in alkali was slightly acidified to promote complete precipitation of interfering phenylsiliconic acid, hydrolytic decomposition was reversed and re-formed phenyltrifluorosilane was lost through volatilisation.

Vapour-pressure values, determined statically below, and dynamically above, room temperature gave the b. p. as 101·8°/760 mm. and *L* as 8750 cals./mol. Data were as follows:

Temp.	−9·2°	+1·4°	+16·5°	35·8°	55·2°	72·2°	84·2°	92·1°	94·5°
V. p. (mm.)	6	10	24	60	147	279·5	428	557	619

Phenyltrifluorosilane is a colourless, inflammable liquid ($d_{4°}^{17°}$ 1·212) with a pungent and aggressive smell. It is quickly hydrolysed by water and alkalis, and in the air the smell of the compound soon gives way to that of hydrogen fluoride.

An attempt was made to isolate derivatives of phenyltrichlorosilane, in which only one or two atoms of chlorine had been replaced by fluorine. Powdered antimony trifluoride was added in quantities of about 2 g. to a large excess (50 g.) of the liquid. After each addition the mixture was carefully warmed to about 50° to initiate the reaction. When the reaction had ceased, the lower-boiling material which might have been expected to contain fluorochlorides was distilled off. The process was repeated several times and the total product carefully fractionated, but no indication of the presence of compounds of intermediate volatility was found.

Action of Hydrogen Fluoride on Phenylsiliconic Acid.—The reaction mixture, containing 21 g. of this acid, 25 g. of calcium fluoride, and 150 c.c. of concentrated sulphuric acid, was heated to 100° for 15 minutes, whereupon the volatile products were pumped off at about 5 mm., through a tube charged with equal parts of phenylsiliconic acid and phosphoric oxide, into a liquid-air trap. Small quantities of liquid and much silicon tetrafluoride were collected. Repetition of this procedure gave, in all, about 2 c.c. of liquid. This was fractionated in the vacuum line between $-30°$ and $-60°$, but even when freshly distilled it always appeared somewhat milky. The b. p. under atmospheric pressure was 99—103°. The material was completely free from chloride, but the fluorine content was 31·4% (Calc.: 35·2%), pointing to the presence of impurity. The low yield may have been due to sulphonation, or to oxidation of the Ph–Si bond by the sulphuric acid.

Preparation and Properties of Diphenyldifluorosilane.—This compound was also prepared by interaction of zinc fluoride with the corresponding chloride (b. p. 200—202°/45 mm.). The crude product, b. p. 156—160°/50 mm., was purified by two further distillations under reduced pressure. There was finally obtained a liquid passing over at 158° at 50 mm.; yield 55% [Found: F, 17·1; *M*, cryoscopic in benzene, 207·7, 210·1. $(C_6H_5)_2SiF_2$ requires F, 17·3%; *M*, 220·1]. It was particularly important that the diphenyldichlorosilane used should be free from diphenyl, as this impurity is of closely similar volatility to the fluorinated product.

Vapour pressures were as follows:

Temp.	119·4°	149·8°	169·3°	188·3°	194·5°	216·5°	236·6°	242·8°
V. p. (mm.)	12·5	36·5	73	138	163	313	515	603

The accuracy of the temperature measurement at higher temperatures is believed to be ± 0·4°. The equation $\log p = 8{\cdot}288 - 2839/T$ defines the vapour-pressure curve, from which the normal b. p. is calculated to be 252·0°.

Diphenyldifluorosilane is a colourless and rather viscous oil ($d_{4°}^{17°}$ 1·145) with a faint smell resembling that of anisole. It is not hydrolysed in moist air, and even in contact with water only a trace of hydrolysis product appears after a day or two, but ammonia and alkalis decompose it in a few seconds. The compound attacks glass slightly in the vicinity of the b. p.

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