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NOVEL SYNTHESIS OF ORGANO- TRI- AND DI-FLUOROSILANES WITH AQUEOUS HYDROFLUORIC ACID

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WE wish to report the conversion of organo- tri- and di-chlorosilanes to their fluoro-analogs in excellent yields via reaction with aqueous 48% hydrofluoric acid.

It is well-known[2] that halosilanes react readily with water to yield either hydroxysilanes or siloxanes, depending on experimental conditions and molecular structure, with mono-, di-, and tri-halosilanes showing increasing activity in that order. For this reason it has been

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[1] All work reported was performed at the Aeronautical Research Laboratory.

[2] E. C. Rochow, An Introduction to the Chemistry of the Silicones 2nd. ed. John Wiley and Sons, Inc., New York, N. Y., (1951) p. 9, 24; V. Bazant, V. Chvalovsky and J. Rathousky, Silikony, Statni Nakakladatelstvi Tech. Lit., Prague, Czechoslovakia, (1954) p. 98, 148.

customary to use anhydrous conditions for the preparation of fluorosilanes.[3]

In 1951, Marans, *et. al.*[4] reported that aqueous hydrofluoric acid may be used with the less readily hydrolyzable organoalkoxysilanes and tri-alkylmonochlorosilanes to yield the corresponding fluoro compounds. We have now found, surprisingly enough, that similar conditions can be applied to di- and tri-chlorosilanes which ordinarily hydrolyze extremely rapidly. In fact, in the presence of excess concentrated aqueous hydrofluoric acid, hydrolysis products of halosilanes have *not* been isolated by us.

A two-phase mixture of 25.0 g. (0.153 mole) of freshly distilled ethyltrichlorosilane (bp. 96.5 at 745 mm.) and 95 g. of 48% hydrofluoric acid, representing 2.28 moles of HF for a five-fold equivalents ratio, was shaken at 0° in a polyethylene bottle. (No significant reaction was

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[3a] H. S. Booth, et al, *J. Amer. Chem. Soc.* **68**, 2650 ff (1946);

[b] J. Gierut, F. J. Sowa and J. A. Nieuwland, *J. Amer. Chem. Soc.* **58**, 786 (1936);

[c] F. J. Sowa, U. S. Patents 2,527,233 (1950) and 2,477,704 (1949);

[d] A. E. Newkirk, *J. Amer. Chem. Soc.* **68**, 2736 (1946);

[e] E. A. Flood, *J. Amer. Chem. Soc.* **55**, 1735 (1933);

[f] W. H. Pearlson, T. J. Brice and J. H. Simons, *J. Amer. Chem. Soc.* **67**, 1769 (1945);

[g] E. Schnell, *Monatsh.* **88**, 1004 (1957).

[4] N. S. Marans, L. H. Sommer and F. C. Whitmore, *J. Amer. Chem. Soc.* **73**, 5127 (1951).

observed in the absence of agitation.) The evolved vapors of reaction product, all of which came over in the first hour, were condensed in a dry-ice trap and proved to be essentially pure ethyltrifluorosilane, bp. -5° (Lit. value, bp. -4.4°)[5]; $d_4^{-76.5}$ 1.227; (found: F, 49.1.[6] $C_2H_5F_3Si$ requires F, 49.9). Yields in two parallel runs were 88% and 90%, respectively.

Analogously, 26.4 g. (0.125 mole) of phenyltrichlorosilane (bp. 197 - 199° at 737 mm.) and 78.0 g. of 48% hydrofluoric acid (containing 1.875 moles of HF) were vigorously agitated at 0° for two hours. The phases were separated in a plastic burette and the organic layer washed with water, dried over anhydrous sodium sulfate and the excess hydrogen fluoride absorbed with sodium fluoride. Yield of crude phenyltrifluorosilane was 17.2 g. (85% of theory) boiling at 98 - 104° at 737 mm. (Lit. value, bp. 101 - 102°,[3f] 101.8°)[5]; n_D^{22} 1.4103; (found: F, 35.0.[6] $C_6H_5F_3Si$ requires F, 35.1).

A similar experiment with doubled quantities and, in addition, 200 ml. of n-pentane as diluent gave 83% yield of phenyltrifluorosilane.

The analogous reaction of 63.3 g. (0.25 mole) of diphenyldichlorosilane, in 200 ml. of n-pentane, with 50.0 g. (2.50 moles) of 48% aqueous hydrofluoric acid gave 43.5 g. (86.5%) of diphenyldifluorosilane, bp. 260 - 265° at 737 mm. (Lit. value, bp. 246 - 247°,[3f] 252° estimated)[5]; n_D^{25} 1.5536; (found: F, 17.09.[6] $C_{12}H_{10}F_2Si$ requires F, 17.25).

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[5] H. J. Emeleus and C. J. Wilkins, <u>J. Chem. Soc.</u> 454 (1944).

[6] Analyzed by volumetric method of reference 4.

Under similar conditions to the above, hexaphenyldisiloxane was not cleaved to give triphenylfluorosilane. This suggests that siloxane formation may not take place prior to establishment of the silicon-fluorine bond and that either direct halogen substitution or, possibly, interaction with the initial hydrolytic products of the chlorosilane may provide the mechanistic route. More work remains to be done to elucidate the scope, limitations and mechanism of this interesting and convenient procedure.