[CONTRIBUTION FROM THE WESTINGHOUSE RESEARCH LABORATORIES]

# Preparation and Properties of Some Negatively-substituted Organosilanes

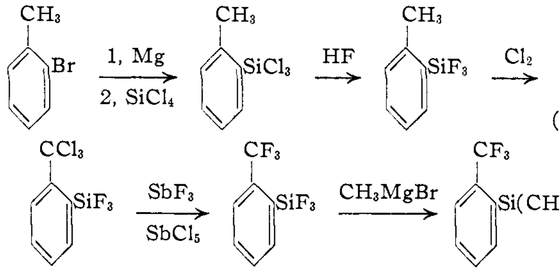
BY LAWRENCE W. FROST

RECEIVED JANUARY 27, 1956

The preparations of several organosilanes containing fluorinated organic groups are reported, together with their dielectric constants, dissipation factors, viscosities and usual physical properties. The preparations and physical properties are also given for the precursors which have not been previously reported. Melting points of mixtures of 4-chloro-3-(trifluoromethyl)-phenyltrimethylsilane and bis-[4-chloro-3-(trifluoromethyl)-phenyl]-dimethylsilane are also reported.

Several (trifluoromethyl)-phenylsilanes have been prepared to be used in a study of stable liquids of high dielectric constant. This paper reports the preparation and some physical properties of these compounds and of some of their precursors.

3-(Trifluoromethyl)-phenyltrimethylsilane, 4-chloro-3-(trifluoromethyl)-phenyltrimethylsilane, and bis-[4-chloro-3-(trifluoromethyl)-phenyl]-dimethylsilane were prepared from chlorotrimethylsilane or dichlorodimethylsilane and the appropriate substituted phenylmagnesium bromide. 3-Trifluoromethylbenzyltrimethylsilane was prepared from 3-trifluoromethylbenzylmagnesium chloride and chlorotrimethylsilane. Because of the difficulty of obtaining 2- and 4-bromo-(trifluoromethyl)-benzene, 2-(trifluoromethyl)-phenyltrimethylsilane was prepared by the following reaction scheme and 4-(trifluoromethyl)-phenyltrimethylsilane by a similar one in which the chlorination and the first fluorination steps were interchanged.



(1)

Attempts to prepare 2-(trichloromethyl)-phenyltrichlorosilane by chlorination of 2-methylphenyltrichlorosilane were unsuccessful, presumably because of steric hindrance. A similar hindrance has been observed in attempts to prepare 1,2-bis-(trichloromethyl)-benzene.[1] The chlorination of 2-methylphenyltrifluorosilane, however, proceeded easily to give 2-(trichloromethyl)-phenyltrifluorosilane.

The conversion of 4-(trichloromethyl)-phenyltrichlorosilane to 4-(trifluoromethyl)-phenyltrifluorosilane can be done in one step, but better yields were obtained by a two-step process with purification of the intermediate (trichloromethyl)-phenyltrifluorosilane.

Physical properties are given in Tables I and II for those compounds which have not been reported previously.

The high dielectric constant of bis-[4-chloro-3-(trifluoromethyl)-phenyl]-dimethylsilane made it of interest in this program, but it was unsuitable because of its high melting point. Consequently, several mixtures were made of this compound with various proportions of 4-chloro-3-(trifluoromethyl)-phenyltrimethylsilane, and their melting points were determined from warming curves. Attempts to use cooling curves were less successful because of supercooling and very slow crystallization. The phase diagram obtained is shown in Fig. 1. Data in the region between 60 and 90% of 4-chloro-3-(trifluoromethyl)-phenyltrimethylsilane were not obtained because all efforts to induce crystallization of these mixtures failed. The eutectic point appears to be at approximately 90% 4-chloro-3-(trifluoromethyl)-phenyltrimethylsilane, with a melting point of about −41°.

TABLE I

PHYSICAL PROPERTIES OF SOME NEGATIVELY SUBSTITUTED SILANES

| Compound | B.p., °C. | M.p., °C. | $n^{25}D$ | $d^{25}_4$ |
|---|---|---|---|---|
| 2-$(CH_3)$-$C_6H_4$-$SiCl_3$ | 226.7 | −25 to −26 | 1.5336 | 1.306 |
| 2-$(CH_3)$-$C_6H_4$-$SiF_3$ | 130.8 | <−78 | 1.4278 | 1.190 |
| 2-$(CCl)_3$-$C_6H_4$-$SiF_3$ | 229.0 | −9 to −10 | 1.4997 | 1.562 |
| 2-$(CF_3)$-$C_6H_4$-$SiF_3$ | 138.0 | −36 to −38 | 1.3876 | 1.435 |
| 2-$(CF_3)$-$C_6H_4$-$Si(CH_3)_3$ | 185.5 | <−78 | 1.4561 | 1.089 |
| 4-$(CCl_3)$-$C_6H_4$-$SiCl_3$ | ... | 67.5–68.0 | .... | ... |
| 4-$(CCl_3)$-$C_6H_4$-$SiF_3$ | 212.2 | 5–5.5 | 1.4833 | 1.510 |
| 4-$(CF_3)$-$C_6H_4$-$SiF_3$ | 118.6 | − 3 to −4 | 1.3783 | 1.399 |
| 4-$(CF_3)$-$C_6H_4$-$Si(CH_3)_3$ | 180.7 | −23 | 1.4403 | 1.052 |
| 3-$(CF_3)$-$C_6H_4$-$Si(CH_3)_3$ | 175.1 | <−78 | 1.4413 | 1.053 |
| 3-$(CF_3)$-$C_6H_4$-$CH_2$-$Si(CH_3)_3$ | 195.6 | <−78 | 1.4451 | 1.034 |
| 4-Cl-3-$(CF_3)$-$C_6H_3$-$Si(CH_3)_3$ | 213.9 | −34.1 | 1.4663 | 1.166 |
| $(CH_3)_2[$4-Cl-3-$(CF_3)$-$C_6H_3]_2Si$ | 326.2 | 45.4 | 1.5077[a] | 1.375[a] |

[a] Supercooled liquid.

## Experimental

**Purification of Liquid Products.**—Each of the methylsilanes was purified by distilling the combined product from several similar runs through a 4-ft. Podbielniak Hyper-Cal column and collecting a center fraction of less than 0.5° boiling range. The analyses and most of the physical properties were determined on this sample. The sample for electrical properties was further purified by allowing it to stand in contact with powdered activated clay for several hours and then filtering.

The reactive intermediates were not highly purified on a large scale, since the crude materials were satisfactory to use in further reactions. In each case, a small sample of the product was purified by distillation through a 90-cm. column packed with glass helices to give material for analysis and the determination of physical properties.

**Physical Properties.**—Melting and boiling points were determined in the usual way, using mercury thermometers above −36° and a calibrated alcohol thermometer below that.

Viscosities were determined with calibrated Ostwald–Fenske viscometers in an oil-bath held within 0.05° of the indicated temperature.

Electrical properties were determined by the method of Berberich,[2] using a modification of the original cell design, in which the glass spacers are eliminated.

---

(1) O. Scherer, W. Schumacher and F. Muller, U. S. Patent 2,121,330 (1938).

(2) L. J. Berberich, *Ind. Eng. Chem., Anal. Ed.*, **17**, 582 (1945).

TABLE II

VISCOSITIES AND ELECTRICAL PROPERTIES OF SOME NEGATIVELY SUBSTITUTED SILANES

| Compound | Dielectric constant, 25° 60 cy. | 1000 cy. | 100 × tan δ, 25° 60 cy. | 1000 cy. | Viscosity, cstks. 37.8° | 98.9° |
|---|---|---|---|---|---|---|
| 2-$(CF_3)C_6H_4Si(CH_3)_3$ | 5.98[a] | | 0.22[a] | | 1.235 | 0.593 |
| 4-$(CF_3)C_6H_4Si(CH_3)_3$ | 7.34[b] | | .32[b] | | 0.935 | .496 |
| 3-$(CF_3)C_6H_4Si(CH_3)_3$ | 6.74[c] | 6.73 | 2.46[c] | 0.16 | 1.026 | .524 |
| 3-$(CF_3)C_6H_4CH_2Si(CH_3)_3$ | 7.50[a] | 7.50[a] | 0.24[a] | .02[a] | | |
| 4-Cl-3-$(CF_3)C_6H_3Si(CH_3)_3$ | 9.75 | 9.75 | .09 | .01 | 1.650 | .719 |
| $(CH_3)_2$[4-Cl-3-$(CF_3)$-$C_6H_3]_2Si$ | 10.35[d] | 10.35[d] | .19[d] | .02[d] | | |

[a] 28°, [b] 24°, [c] 100 cy., [d] supercooled liquid.

**Trichloro-2-methylphenylsilane.**—A Grignard reagent was prepared from 513 g. of 2-bromotoluene, 73 g. of magnesium and 1 liter of anhydrous ethyl ether. The resulting solution was added slowly, with stirring, to 680 g. of tetrachlorosilane. An exothermic reaction occurred, with the formation of a white precipitate. After the addition, stirring was continued for 15 hours at room temperature. The mixture was filtered, and the precipitate was washed with ether. The filtrate and washings were combined and distilled to give 361 g. (53%) of trichloro-2-methylphenylsilane, b.p. 84–90° (5 mm.).

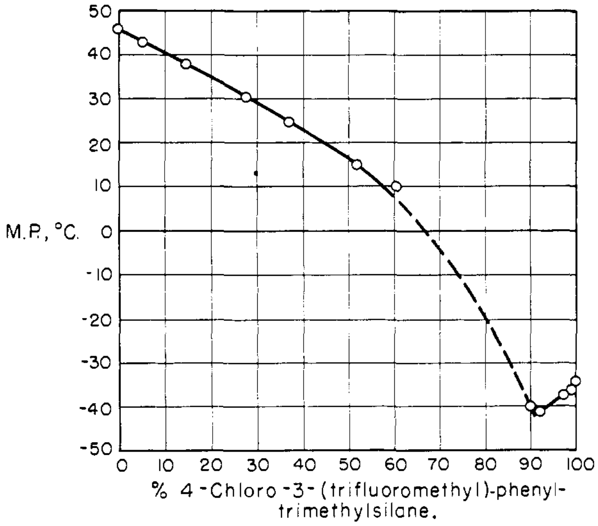


Fig. 1.—Melting points of mixtures of 4-chloro-3-(trifluoromethyl)-phenyltrimethylsilane and bis-[4-chloro-3-(trifluoromethyl)-phenyl]-dimethylsilane.

*Anal.* Calcd. for $C_7H_7Cl_3Si$: Cl, 47.3. Found: Cl, 47.0, 47.4.

**Trifluoro-2-methylphenylsilane.**—2-Methylphenyltrichlorosilane (477 g.) was placed in a stainless steel flask equipped with a stainless steel stirrer, a copper reflux condenser, and a copper inlet tube reaching to the bottom of the flask. Anhydrous hydrogen fluoride (360 g.) was added slowly through the inlet tube while the mixture was stirred without heating. The reaction was mildly exothermic. The product was allowed to stand over sodium fluoride to remove dissolved hydrogen fluoride, and was then distilled to give 265 g. (71%) of trifluoro-2-methylphenylsilane, b.p. 124–126°.

*Anal.* Calcd. for $C_7H_7F_3Si$: F, 32.3. Found: F, 32.2, 32.6.

**2-(Trichloromethyl)-phenyltrifluorosilane.**—2-Methylphenyltrifluorosilane (315 g.) was placed in a chlorination apparatus consisting of a 52 × 520 mm. test-tube supported vertically and provided with a fritted glass chlorine inlet reaching to the bottom, a cooling coil, a thermometer, a reflux condenser, and an external heater consisting of nichrome ribbon wound directly on the tube. Illumination was provided by two 15-watt blue fluorescent lamps in reflectors parallel to the tube and about 3 cm. from it. Chlorine was passed into the liquid at such a rate that the yellow color of dissolved chlorine was present only in the lower part of the tube, except during the induction period. The temperature was kept at 70–80° for six hours and was then raised to 125° for 11 hours. During the last several hours the reaction was very slow, and the liquid was kept saturated with chlorine. Air was passed through the liquid for 10 minutes to remove dissolved gases. The product was a yellow liquid weighing 498 g. (99%), which was essentially pure 2-(trichloromethyl)-phenyltrifluorosilane. A sample was found to distil at 70–78° (0.5 mm.).

*Anal.* Calcd. for $C_7H_4Cl_3F_3Si$: Cl, 38.1; F, 20.4; Si, 10.04. Found: Cl, 37.6, 37.6; F, 21.2, 21.0; Si, 9.76, 9.84.

**2-(Trifluoromethyl)-phenyltrifluorosilane.**—A mixture of 185 g. of powdered antimony(III) fluoride and 25 g. of antimony(V) chloride was stirred while 209 g. of 2-(trichloromethyl)-phenyltrifluorosilane was added slowly. An exothermic reaction occurred, with the formation of a red-orange complex. Heat was then applied to distil the product. The colorless distillate was redistilled to give 150 g. (87%) of 2-(trifluoromethyl)-phenyltrifluorosilane, b.p. 135–140°.

*Anal.* Calcd. for $C_7H_4F_6Si$: F, 49.6; Si, 12.20. Found: F, 49.6, 49.9; Si, 11.9, 12.0.

**2-(Trifluoromethyl)-phenyltrimethylsilane.**—2-(Trifluoromethyl)-phenyltrifluorosilane (230 g.) was stirred while 1950 ml. of a 1.7 *M* solution of methylmagnesium bromide in ethyl ether was added slowly. An exothermic reaction occurred, with refluxing and the formation of a sticky precipitate. When the addition was complete, heat was applied and refluxing was continued for two hours. The product was poured over a mixture of crushed ice and hydrochloric acid. The organic layer was separated and distilled. After the ether had been removed at atmospheric pressure, the pressure was reduced and 201 g. (92%) of 2-(trifluoromethyl)-phenyltrimethylsilane was obtained, b.p. 55° (5 mm.).

*Anal.* Calcd. for $C_{10}H_{13}F_3Si$: F, 26.1; Si, 12.85. Found: F, 26.6, 26.7; Si, 12.65, 12.51.

**4-(Trichloromethyl)-phenyltrichlorosilane.**—4-Methylphenyltrichlorosilane was prepared in 55% yield from 4-bromotoluene, magnesium and tetrachlorosilane. The observed boiling point of 94–95° (10 mm.) is in satisfactory agreement with the value of 210–215° reported by Pink and Kipping.[3]

4-Methylphenyltrichlorosilane (492 g.) was chlorinated in the apparatus used for the preparation of 2-(trichloromethyl)-phenyltrifluorosilane. In this case the temperature was held at 65° for eight hours and at 95–100° for 18 hours. The product crystallized on cooling to give 691 g. (96%) of essentially pure 4-(trichloromethyl)-phenyltrichlorosilane. A sample of this compound was recrystallized from anhydrous ethyl ether to give thick, transparent rods, m.p. 67.5–68.0°.

*Anal.* Calcd. for $C_7H_4Cl_6Si$: Cl, 64.8. Found: Cl, 64.6, 64.9.

**4-(Trichloromethyl)-phenyltrifluorosilane.**—A cylindrical nickel reactor was used, having a flat lid with a copper gasket, held in place by eight machine screws. A nickel stirrer, reflux condenser, thermometer well, and gas inlet tube were mounted in the lid, and an external heater was provided. 4-(Trichloromethyl)-phenyltrichlorosilane (553 g.) was placed in the reactor and stirred while 350 g. of anhydrous hydrogen fluoride was added through the inlet tube during 4.5 hours, the reaction temperature being kept at 25–75°. Air was blown through the mixture to remove dissolved

---

(3) H. S. Pink and F. S. Kipping, *J. Chem. Soc.*, **123**, 2830 (1923).

gases, and the liquid product was allowed to stand over sodium fluoride. It was distilled to give 430 g. (92%) of 4-(trichloromethyl)-phenyltrifluorosilane, b.p. 95–105° (20 mm.).

*Anal.* Calcd. for $C_7H_4Cl_3F_3Si$: Cl, 38.1; F, 20.4; Si, 10.04. Found: Cl, 37.2, 37.4; F, 21.8, 21.9; Si, 9.89, 10.05.

**4-(Trifluoromethyl)-phenyltrifluorosilane.**—A mixture of 99 g. of 4-(trichloromethyl)-phenyltrichlorosilane and 10 ml. of antimony(V) chloride was stirred while 127 g. of antimony(III) fluoride was added slowly. An exothermic reaction occurred, with the formation of a black, semi-solid mass. Heat was then applied, and a colorless distillate was collected. Redistillation gave 44 g. (63%) of 4-(trifluoromethyl)-phenyltrifluorosilane, b.p. 117–119°.

This method was inconvenient on a larger scale because of difficulty in stirring. The following preparation also gave better over-all yields.

A mixture of 215 g. of powdered antimony(III) fluoride and 25 g. of antimony(V) chloride was stirred while 280 g. of 4-(trichloromethyl)-phenyltrifluorosilane was added. The mixture was light colored, and little heat was evolved. Heat was applied, and 212 g. (92%) of colorless 4-(trifluoromethyl)-phenyltrifluorosilane, b.p. 110–120°, was distilled.

*Anal.* Calcd. for $C_7H_4F_6Si$: F (by hydrolysis), 24.8. Found: F (by hydrolysis), 24.5, 25.1.

**4-(Trifluoromethyl)-phenyltrimethylsilane.**—A Grignard reagent was prepared by bubbling bromomethane into a well-stirred mixture of 12.5 g. of magnesium turnings and 200 ml. of anhydrous ethyl ether until the magnesium had dissolved. A solution of 32 g. of 4-(trifluoromethyl)-phenyltrifluorosilane in 50 ml. of ethyl ether was then added slowly, with stirring. An exothermic reaction occurred, with refluxing. Heat was then applied, and refluxing was continued for one hour. The mixture was poured over a mixture of crushed ice and hydrochloric acid. The organic layer was then separated, washed with water, dried over calcium chloride, and distilled to give 27 g. (89%) of 4-(trifluoromethyl)-phenyltrimethylsilane, b.p. 113–114° (100 mm.).

*Anal.* Calcd. for $C_{10}H_{13}F_3Si$: F, 26.1; Si, 12.85. Found: F, 26.8, 26.8; Si, 12.88, 12.73.

**3-(Trifluoromethyl)-phenyltrimethylsilane.**—A reaction was carried out, using 48.6 g. of magnesium turnings, 450 g. of 3-bromo-(trifluoromethyl)-benzene and 217 g. of chlorotrimethylsilane in one liter of anhydrous ether. The Grignard reaction was first started, using the magnesium and a portion of the bromo compound and ether. When it had started, the rest of the ingredients were mixed and added, with stirring, at a rate to maintain a moderate reflux rate. When the addition was complete, heat was applied and refluxing continued for 24 hours. During this time the coupling reaction proceeded slowly as shown by the formation of a sticky precipitate and the fading of the dark brown color the Grignard reagent. The reaction mixture was then poured over a mixture of crushed ice and hydrochloric acid. The organic layer was separated, washed with water, dried over calcium chloride and distilled to give 302 g. (69%) of 3-(trifluoromethyl)-phenyltrimethylsilane, b.p. 75–80° (25 mm.).

*Anal.* Calcd. for $C_{10}H_{13}F_3Si$: F, 26.1; Si, 12.85. Found: F, 26.6, 26.9; Si, 12.76, 12.95.

**3-(Trifluoromethyl)-benzyltrimethylsilane.**—A reaction was carried out with 195 g. of 3-(trifluoromethyl)-benzyl chloride, 130 g. of chlorotrimethylsilane and 36 g. of magnesium turnings in 500 ml. of anhydrous ether. After the Grignard reaction was started with the magnesium and part of the benzyl chloride, the remaining ingredients were mixed and added with stirring at such a rate that reflux was maintained. Stirring was continued for one hour after the addition was complete. The mixture was filtered and the filtrate was washed with water, dried over sodium sulfate, and distilled to give 151 g. (65%) of 3-(trifluoromethyl)-benzyltrimethylsilane, b.p. 90–95° (25 mm.).

*Anal.* Calcd. for $C_{11}H_{15}F_3Si$: F, 24.5; Si, 12.08. Found: F, 24.9, 25.0; Si, 12.04, 12.07.

**4-Chloro-3-(trifluoromethyl)-phenyltrimethylsilane.**—A reaction was carried out with 1038 g. of 4-bromo-2-(trifluoromethyl)-chlorobenzene, 98 g. of magnesium turnings and 490 g. of chlorotrimethylsilane in two liters of anhydrous ether, following the procedure of the preceding run except that the mixture was refluxed for 20 hours after the addition was complete. Distillation of the product gave 774 g. of 4-chloro-3-(trifluoromethyl)-phenyltrimethylsilane, b.p. 65–75° (5 mm.).

*Anal.* Calcd. for $C_{10}H_{12}ClF_3Si$: Cl, 14.05; F, 22.6; Si, 11.12. Found: Cl, 14.17, 14.18; F, 22.3, 22.8; Si, 10.89, 11.05.

**Bis-[4-chloro-3-(trifluoromethyl)-phenyl]-dimethylsilane.**—A reaction was carried out with 1038 g. of 4-bromo-2-(trifluoromethyl)-chlorobenzene, 258 g. of dichlorodimethylsilane and 100 g. of magnesium turnings in three liters of anhydrous ether, following the procedure of the preceding run except that the period of reflux was 12 hours. The dried product was distilled to give 590 g. (71%) of bis-[4-chloro-3-(trifluoromethyl)-phenyl]-dimethylsilane, b.p. 140–150° (1 mm.). This product later crystallized. A portion of it was recrystallized three times from methanol to give transparent rods, m.p. 45.8–46.2°.

*Anal.* Calcd. for $C_{16}H_{12}Cl_2F_6Si$: Cl, 17.00; F, 27.3; Si, 6.73. Found: Cl, 16.59, 16.65; F, 27.9, 28.1; Si, 6.99, 7.01.

**Acknowledgment.**—The author wishes to thank Dr. Thomas J. Hall for assistance in the preparations, Miss Mildred Rutter and Mr. H. C. Craig for the electrical measurements, and Mrs. E. J. Criner, Mr. J. F. Reed and Miss Marjorie Mistrik for analytical work.

PITTSBURGH 35, PENNA.

---

# COMMUNICATIONS TO THE EDITOR

## POLYPEPTIDES. IX. THE KINETICS OF STRONG-BASE INITIATED POLYMERIZATIONS OF AMINO ACID-N-CARBOXYANHYDRIDES

*Sir:*

It has been shown previously[1,2] that NaOH or $NaOCH_3$ initiation of γ-benzyl-L-glutamate-N-carboxyanhydride (BLGA) makes possible the preparation of very high molecular weight poly-γ-benzyl-L-glutamate (PBLG). In this communication, we report the results of kinetic measurements on this new polymerization method which indicate that base initiated polymerizations (a) proceed by a mechanism which does not require a proton in the initiator, (b) exhibit propagation constants many times those of primary amine initiated

---

[1] E. R. Blout, R. H. Karlson, P. Doty and B. Hargitay, THIS JOURNAL, **76**, 4492 (1954).

[2] E. R. Blout and R. H. Karlson, *ibid.*, **78**, 941 (1956).