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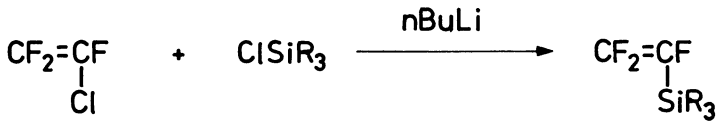
PRACTICAL SYNTHESIS AND POLYMERIZATION OF TRIFLUOROVINYLSILANES. A POSSIBLE PRECURSOR OF POLY(DIFLUOROACETYLENE)

Tamejiro HIYAMA,* Kiyoharu NISHIDE, and Michio OBAYASHI
Sagami Chemical Research Center, 4-4-1 Nishiohnuma, Sagamihara, Kanagawa 229

An improved procedure for the preparation of trifluorovinylsilanes was established which involved addition of butyllithium to a mixture of chlorosilanes and commercially readily available chlorotrifluoroethylene at -78 to -130 °C, and the resulting monomer was polymerized with a catalyst such as CsF or $(R_2N)_3S^+ F_2SiMe_3^-$ to give black metallic polymer which showed conductivity of 10^{-9} to 10^{-10} $\Omega^{-1}cm^{-1}$.

Polyacetylene, particularly doped one, is shown to have high electrical conductivity,[1] and have received rapidly growing attention, since these polymers are expected to have wide industrial applicability. However, the instability of polyacetylene under an aerial atmosphere sometimes interferes with practical applications. Of many experimental and theoretical attempts at the modifications,[2] a prediction presented by Yamabe, Fukui, Shirakawa, Ikeda, and their coworkers[3] is informative: poly(difluoroacetylene) should show much improved stability and characteristic electrical properties. The logical monomer difluoroacetylene[4] is, however, suspected to be extremely unstable and explosive,[5] though its polymerization and physical properties of the resulting polymer are recently claimed in patents without experimental details.[6] We reasoned that a monomer which may be converted to difluoroacetylene or its equivalent in situ before or after polymerization would be a safe alternative. Trifluorovinylsilane was chosen as the candidate in view of the anticipated facile elimination of fluorosilane due to large F-Si bond energy. Reported herein are practical synthesis of trifluorovinylsilanes and preliminary study on polymerization.

Trifluorovinylsilanes have been prepared by silylation of trifluorovinyllithium or -magnesium, which, in turn, is derived from trifluoroethylene or bromotrifluoroethylene.[7] These two starting fluoroethylenes are, however, relatively



expensive and sometimes hardly accessible. We found that commercially readily available chlorotrifluoroethylene was successfully transformed into the desired trifluorovinylsilanes in much improved yields simply by adding butyllithium to a mixture of chlorotrifluoroethylene and chlorotrialkylsilane at low temperature, whereby sequential Li-Cl exchange and spontaneous silylation of the resulting lithium carbenoid[8] took place selectively. A typical experimental procedure is illustrated for the preparation of triethyl(trifluorovinyl)silane. Chlorotrifluoroethylene (15.0 g, 0.129 mol) and then chlorotriethylsilane (16.1 g, 0.107 mol) were dissolved in a mixture of tetrahydrofuran (THF, 50 ml), diethyl ether (30 ml) and pentane (30 ml) at -130 °C (liquid nitrogen-pentane bath) under an argon atmosphere. To the resulting mixture was added butyllithium (1.60 mol/dm^3 hexane solution, 88 ml, 0.140 mol) drop by drop over a period of 1 h. After the addition was completed, the reaction mixture was gradually warmed to room temperature over 7.5 h, and the precipitated inorganic material was filtered off through a Celite pad. The filtrate was concentrated at atmospheric pressure using fractionation column, and the residue was distilled to give rise to triethyl(trifluorovinyl)silane (17.8

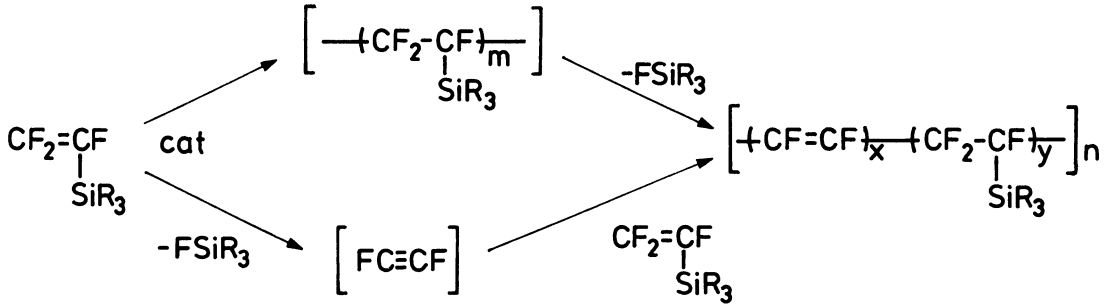
Table 1. Synthesis of Trifluorovinylsilanes

Chlorosilane	Reaction temp/°C	Reaction time/ h	Product (yield/%)	Bp or [Mp]/°C (Torr)
Et_3SiCl	-130	7.5	$CF_2=CFSiEt_3$ (85)	144
Et_3SiCl	-78	4	$CF_2=CFSiEt_3$ (86)	
nPr_3SiCl	-130	3.5	$CF_2=CFSinPr_3$ (93)	82-83 (15)
$PhMe_2SiCl$	-130	3	$CF_2=CFSiMe_2Ph$ (88)	82-83 (17)
$PhCH_2Me_2SiCl$	-130	8	$CF_2=CFSiMe_2CH_2Ph$ (93)	95-96 (20)
$Ph_2MeSiCl$	-130	5	$CF_2=CFSiMePh_2$ (79)	158-163 (17)
Et_2SiCl_2	-130	8	$(CF_2=CF)_2SiEt_2$ (71)	55-56 (19)
Et_2SiCl_2	-78	3	$(CF_2=CF)_2SiEt_2$ (88)	
Ph_2SiCl_2	-130	5	$(CF_2=CF)_2SiPh_2$ (88)	[48-49]
$PhSiCl_3$	-130	3	$(CF_2=CF)_3SiPh$ (52)	97-98 (17)

g, 85% yield) as a colorless transparent oil, bp 144 °C; ^{19}F NMR ($CDCl_3$- $CFCl_3$ standard): 87.15 ppm (dd, J = 70.5 and 26.8 Hz), 117.00 ppm (dd, J = 115.7 and 70.5 Hz), and 198.9 ppm (dd, J = 115.7 and 26.8 Hz); MS: m/z 196 (M^+). Found: C, 48.75; H, 7.71%. Calcd for $C_8H_{15}F_3Si$: C, 48.95; H, 7.70%.

Results with other chlorosilanes are summarized in Table 1. In addition to mono(trifluorovinyl)silanes, bis- and tris(trifluorovinyl)-substituted ones are now readily accessible. The reaction carried out at -78 °C, Dry-Ice/acetone temperature, with THF only for the reaction medium gave equal or better yields of products. Scaling up to 0.5 mol is effected at -78 °C without any problems. For example, triethyl(trifluorovinyl)silane was prepared in 69-71% yields under these conditions.

For polymerization of trifluorovinylsilanes, fluoride ion-releasing compounds were found to be effective catalysts. When triethyl(trifluorovinyl)silane (2.18 g) was heated at 180 °C in the presence of cesium fluoride (57 mg) for 10 days, black solid gradually precipitated. This material (214 mg) was insoluble in water, conc sulfuric acid, methanol, ethanol, dichloromethane, o-dichlorobenzene, dimethyl sulfoxide, or N,N-dimethylformamide even at the boiling temperature, but mostly soluble in hexamethylphosphoric triamide at 200-230 °C (ca. 20 mg/ml). It did not melt below 300 °C, whereupon the weight reduction started and continued up to 500 °C as measured by thermal gravimetry. IR (KBr): 1755 (br), 1630 (br), 1100 (br), 740, 480 cm^{-1}. The strong absorption at 1630 cm^{-1} suggests the presence of conjugated fluoro olefin moiety. Average molecular weight (GPC) was 1 - 1.2 x 10^4 (based on polystyrene). The polymer precipitated on the glass wall of the reaction vessel showed metallic luster and the conductivity of 8.5 x 10^{-9} $\Omega^{-1}cm^{-1}$. The conductivity did not change in air after 6 months. Elementary analysis revealed that triethylsilyl group was not eliminated completely, and the x : y ratio in the following formula is estimated to be 6 : 1.



R = Et, Me

cat = CsF, $(Et_2N)_3\overset{+}{S}\ F_2\bar{S}iMe_3$, $(Me_2N)_3\overset{+}{S}\ F_2\bar{S}iMe_3$

The fluoride ion catalyst is assumed to work for the polymerization of triethyl(trifluorovinyl)silane and elimination of fluorotriethylsilane from the polymer intermediate or, alternatively, for elimination of fluorotriethylsilane from triethyl(trifluorovinyl)silane to give difluoroacetylene which copolymerized with triethyl(trifluorovinyl)silane under the reaction conditions. Actually, fluorotriethylsilane was found to be present in the volatile material of the polymerization mixture (GC-MS). Tris(diethylamino)sulfonium and tris(dimethylamino)-sulfonium difluorotrimethylsilicate also were the effective catalysts for polymerization of trifluorovinyltrimethylsilane and triethyl(trifluorovinyl)silane, respectively, and gave similar polymers having conductivity of ca. 2×10^{-10} Ω^{-1} cm^{-1}. Although the conductivities of these polymers fall in the borderline of semiconductor and insulator, doping experiments are expected to improve the electric properties.

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