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SYNTHESIS AND HYDROLYSIS OF FLUOROPYRIDINYL CONTAINING CHLOROSILANES

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Summary

2-Fluoro-3-dimethylchlorosilylpyridine (**A**) and 3-fluoro-4-dimethylchlorosilylpyridine (**B**) were synthesized from the corresponding fluoro-lithio-pyridines and dimethyldichlorosilane at −76°C. The liquid products were unstable on standing. **A** and **B** were hydrolyzed in aqueous ammonia at room temperature to give disiloxanes which are stable crystalline solids. The new compounds were characterized by IR, ^{1}H NMR and MS.

Introduction

It has been shown recently that monomers and polymers containing pyridine and pyridine 1-oxide function as basic and nucleophilic catalysts with unparalled activity in, for example, transacylation reactions of derivatives of carbon, sulfur and phosphorus acids [1–7]. These reactions are carried out effectively in immiscible solvent mixtures (e.g. H_2O/organic solvent emulsions) involving phase transfer catalysis methodology where the polymeric catalyst is soluble in the aqueous phase [7–9]. It is desirable to examine the effect of such reactions using organic soluble-water insoluble catalysts. Toward this goal we have explored the feasibility of placing the pyridine moiety on silicon monomers which can serve as precursors in the synthesis of hydrophobic siloxane derivatives. Thus, we now wish to report the preparation, characterization and hydrolysis of the first pyridinyl containing functional silanes by the reaction of lithiopyridine intermediates with chlorosilanes.

Experimental

Solvents and reagents were purified by drying over a suitable dehydrating agent followed by distillation. Infrared spectra were obtained using a Perkin–Elmer 283

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spectrometer with KBr discs. ^{1}H NMR spectra were recorded on a Varian EM360A spectrometer in $CDCl_3$ (or other suitable solvent). Mass spectra (EI/CI) were obtained at 70 eV on either a Finnigan MAT 4500 or Kratos MS-80RS spectrometers equipped with a gas chromatograph. Elemental analyses were carried out by Galbraith Laboratories, Inc., Knoxville, TN 37921 or MicAnal, Tucson, AZ 85717.

Synthesis of 2-fluoro-3-chlorodimethylsilylpyridine (A)

Dry diisopropylamine (DIPA, 19.3 g, 0.189 mol) in dry THF (75 ml) was stirred under argon at −76°C in a 250 ml 3-neck round-bottom flask fitted with a dropping funnel, mechanical stirrer and a low temperature thermometer. n-BuLi (75 ml, 2.51 *M* in hexane) mixed with THF (15 ml) was added dropwise. The mixture was stirred for 20 min at −76°C and 2-fluoropyridine (Olin Corporation, 18.7 g, 0.189 mol) dissolved in THF (45 ml) was added slowly. The resulting yellow suspension was stirred for 30 min at −76°C and poured under argon into a jacketed dropping funnel cooled with dry ice/acetone. The suspension was added dropwise to an excess of Me_2SiCl_2 (609 g, 4.72 mol) at −76°C under argon. The mixture was stirred for an additional 30 min and allowed to warm slowly to room temperature overnight. Volatile solvents and unreacted Me_2SiCl_2 were removed under vacuum at room temperature. The residual material was flash distilled to remove volatile products from salts. The distillate was distilled twice to give a colorless liquid **A** (19.3 g; 54%; b.p. 33–35°C/0.5 Torr). IR (cm^{-1}, rel. int.): 3090w, 3040w, 3005sh, 2960m, 2900sh, 2820w, 2750w, 2710w, 2690w, 1970w, 1900m, 1860w, 1780w, 1720m, 1625m, 1585s, 1550m, 1425sh, 1440m, 1390vs, 1330s, 1280w, 1250s, 1230s, sh, 1210m, 1135m, 1075m, 980w, 930w, 850s, 790vs, 760sh, 690m, 650m, 640w, 505sh, 490s, 480sh, 460m. ^{1}H NMR (δ(TMS), mult., J (Hz), H^n): 8.33, mc, H^6; 8.10, mc, H^4; 7.33, d/d/d, 7/5/3, H^5; 0.70, d, 1.2 (CH_3/F), H^{Me}; Area ratio: $H^{Me}/H^{4,5,6}$, 2.0 (Fig. 1); MS (*m/e*, %*b*, ion): 191/189, 11/31, M^+; 176/174,

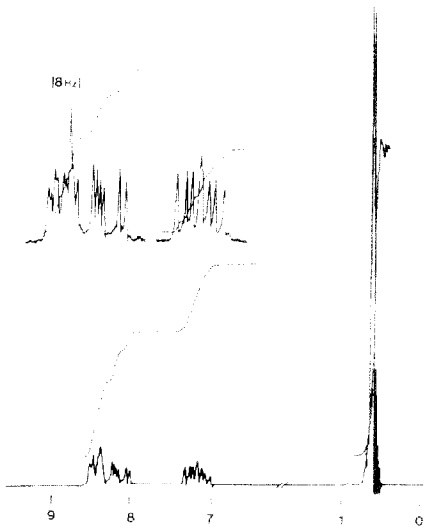


Fig. 1. 60 MHz ^{1}H NMR spectrum of 2-fluoro-3-chlorodimethylsilylpyridine (**A**).

35/100, $(M - Me)^+$; 154, 6, $(M - Cl)^+$; 138, 15, $(M - Cl - CH_2)^+$; 99/97, 15/41, $MeSiClF^+$; 92, 71, ?. Anal. Found: Cl, 18.62; $C_7H_9ClFNSi$ calc: Cl, 18.89%. **A** is soluble in organic solvents and extremely sensitive to moisture.

Hydrolysis of A

A 250 ml round bottom flask equipped with a dropping funnel and a mechanical stirrer was charged with **A** (74 mmol) and toluene (20 ml). Aqueous ammonia (30 ml, 30%) was added dropwise with vigorous stirring. After addition, the toluene layer was separated and the aqueous layer was extracted with several 20 ml portions of toluene. The toluene fractions were combined and dried over anhydrous $KHCO_3$. After filtration, the toluene was removed under vacuum. The resulting pale yellow fluid was distilled under vacuum to give a colorless liquid which solidified to colorless needles (**B**) on standing at ambient temperature. Yield: 56%; m.p. 41–42°C; b.p. 142–145°C/0.4 Torr; IR (cm^{-1}, rel. int.): 3120w, 3080m, 3050m, 2950m, 2900m, 2030w, 1965w, 1940w, 1900w, 1760w, 1615sh, 1585s, 1560s, 1535w, 1445w, 1390vs, 1305m, 1290m, 1260s, 1235s, 1215s, 1140s, 1060vs, br, 850s, 820sh, 795vs, 765m, 710s, 665m, 650m, 565m, 535w, 495m, 485m, 450m, 400m, 375m. ^1H NMR ($\delta(CH_2Cl_2)$, mult., J(Hz) H^n): 8.15, mc, H^6; 7.83, mc, 9/2, H^4; 7.10, d/d/d, ~ 7/4/3, H^5; 0.33, d, ~ 1, H^{Me}; Area ratio: $H^{Me}/H^{4,5,6}$, 2.0; MS (m/e, $\%b$, ion): 324, < 1, $M^{+\cdot}$; 310, 34, $(M - CH_2)^{+\cdot}$; 309, 100, $(M - CH_3)^+$; 231, 19, ?; 213, 31, $(M - CH_3 - C_5H_3NF)^+$; 155, 10, $(C_5H_3NFSiMeO)^+$; CI(CH_4): m/e, 325. Anal. Found: C, 51.92, H, 5.51; F, 11.36; N, 8.72; Si, 17.69; $C_{14}H_{18}F_2N_2OSi_2$ calc: C, 51.82; H, 5.59; F, 11.71; N, 8.63; Si, 17.31%. **B** is soluble in organic solvents and insoluble in water.

Synthesis of 3-fluoro-4-chlorodimethylsilylpyridine (C)

The procedure was the same as described for **A**. In a typical experiment n-BuLi (0.12 mol), DIPA (0.12 mol), 3-fluoropyridine (0.12 mol) and Me_2SiCl_2 (3.1 mol)

Fig. 2. 60 MHz ^1H NMR spectrum of 3-fluoro-4-chlorodimethylsilylpyridine (**C**).

were combined to give a 55% yield of distilled product (b.p., 63–64°C/1 Torr). IR (cm^{-1}, rel. int.): 3060m, 2970m, 2900w, 2100w, 2050w, br, 1960w, 1915w, 1880w, 1815w, 1750w, 1630w, 1585w, 1530m, 1475s, 1405s, 1335w, 1275s, 1260s, 1230s, 1220sh, 1200s, 1185sh, 1170s, 1155w, 1105s, 1095sh, 1055s, 915w, 850vs, 810vs, 800sh, 725m, 695s, 660s, 560s, 545s, 500s, br, 470m, 450s. ^{1}H NMR (δ(TMS), mult., J(Hz), H^n): 8.00, mc, $H^{2,6}$; 7.02, d/d, 6/4, H^5; 0.18, d, < 1, H^{Me}; Area ratio: $H^{Me}/H^{2,5,6}$, 2.0 (Fig. 2); Anal. Found: 18.50; $C_7H_9ClFNSi$ calc: Cl, 18.69%. **C** is soluble in organic solvents and extremely sensitive to moisture.

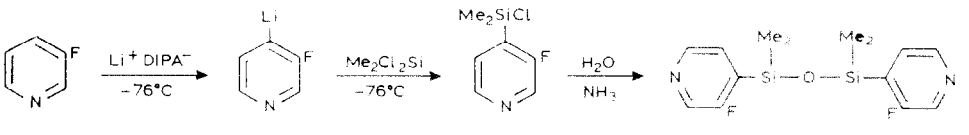
Hydrolysis of **C**

C (e.g. 22 mmol) was hydrolyzed in a manner similar to that described for **A**. The product **D** was purified by distillation to give a colorless liquid which solidified to needle crystals upon standing at 0°C. Yield: 73%; m.p. 35–37°C; b.p. 107–108°C/0.2 Torr; IR (cm^{-1}, rel. int.): 3050m, 2960m, 1595w, 1530m, 1475s, 1400s, 1270s, 1260s, 1240s, 1200s, 1180w, 1170m, 1105s, 1070vs, br, 910m, 840s, 800s, 720m, 710m, 690m, 650m, 560m, 545s, 475m, 450s; ^{1}H NMR ($\delta(CH_2Cl_2$ (ext)), mult., J(Hz), H^n): 8.18, mc, $H^{2,6}$; 7.17, d/d, 4.5/4.5, H^5; 0.20, d, 0.8, H^{Me}; Area: $H^{2,6}/H^5/H^{Me}$, 2/1/6; MS (m/e, %h, ion): 324, < 1, M^+; 310, 27, $(M-CH_2)^+$; 309, 100, $(M-CH_3)^+$; 231, 12, ?; 213, 32, $(M-CH_3-C_5H_3NF)^+$; 155, 46, $(C_5H_3NFSiMeO)^+$; 125, 27 $(C_5H_3NFSiH)^+$; CI(CH_4); m/e, 325. Anal. Found: C, 50.99; H, 5.66; N, 8.54. $C_{14}H_{18}F_2N_2OSi_2$ calc: C, 51.82; H, 5.59; N, 8.63%.

Results and discussion

2-Fluoro-3-dimethylchlorosilylpyridine (**A**) and 3-fluoro-4-dimethylchlorosilylpyridine (**C**) are readily synthesized by the reaction of the respective fluorolithiopyridines, which are prepared in situ from n-BuLi, diisopropylamine and a fluoropyridine, with excess dimethyldichlorosilane (Scheme 1). Fluoropyridines were used because of their high selectivity for substitution at the carbon α to the halogen [10]. The products are colorless, distillable liquids that are soluble in organic solvents and extremely sensitive to trace quantities of moisture to evolve HCl and precipitate the quaternary salt of the ring nitrogen. In addition to **A** and **C**, bis-pyridinyl substituted by-products and hydrolysis products (see later) were detected by ^{1}H NMR and MS.

Upon standing at room temperature in dry air, nitrogen or argon, **A** and **C** turn yellow and turbid and eventually become brown gelatinous materials suggesting a slow irreversible polymerization presumably through a reaction involving the pyridinyl rings [11].



SCHEME 1

The IR spectra of **A** and **C** exhibit a strong band near 500 cm^{-1} distinctive of the Si–Cl stretching vibration [12]. Absorptions at 690–700 and 450–460 cm^{-1} in both compounds are consistent with *r*- and *t*-ring modes, respectively, associated with Si–C ring stretching vibrations analogous to bands found in phenylsilanes [13]. Additionally the band near 555 cm^{-1} in **A** and 545 cm^{-1} in **C** are characteristic of the *y*-ring bending mode.

Salient regions of the ^1H NMR spectrum **A** are given in Fig. 1. The methyl group protons on silicon appear as an upfield doublet (0.7 ppm, J 1.2 Hz) owing to long range $^1H(Me)$–^{19}F coupling. A similar doublet occurs in **C** (0.2 ppm, $J \approx 1$ Hz). Comparable splitting has not been observed in related fluorophenyl substituted silanes [14]. The pattern of resonances for **A** in the aromatic region (7.3–8.3 ppm), although complex, is characteristic of substituted pyridines containing three adjacent protons with additional complexity arising from long range coupling to fluorine. Proposed assignments are based on spectra of comparable disubstituted pyridine derivatives [15]. Similarly, the downfield region for **C** exhibits a recognizable AX coupling pattern for 3,4-disubstituted pyridine with additional ^{19}F coupling to H^5 (i.e. d/d, $J = 5/5$; Fig. 2).

Disiloxanes **B** and **D** are obtained by the hydrolysis of **A** and **C** respectively, in aqueous ammonia (Scheme 1). The products are distillable liquids; and, when purified, they are relatively low melting, colorless crystalline solids which are soluble in organic compounds and slightly soluble in water.

The infrared spectra of **B** and **D** are similar to that of **A** and **C** with the exception of the disappearance of the Si–Cl absorption and the appearance of a very intense and broad band (**B**, 1060 **D**, 1070 cm^{-1}) characteristic of the Si–O–Si stretching vibrations in disiloxanes [16]. Except for small differences in chemical shift, the ^1H NMR spectra of **A** and **B**, and **C** and **D** are identical.

The GC/MS(EI) of **A** exhibits a prominent molecular ion (*m/e*, 191/189) characteristic of a polyisotopic monochloro derivative. The principle fragmentation route involves loss of the methyl group (*m/e* 176/174, parent) and chlorine (*m/e* 154), the ion current being carried by a pyridinyl containing species. Although molecular ions were not detected for **B** and **D** by electron impact methods (20–70 eV), molecular weights were confirmed by chemical ionization (*m/e*, 325). Fragmentation of **B** and **D** involves (a) loss of CH_3 (*m/e*, 309) and, subsequently, loss of F-Py (*m/e*, 213) and (b) H-Atom transfer (i.e. $M - 14$, *m/e* 310). Conspicuous by its absence is the $(M - HCN)^+$ ion usually present due to ring fragmentation of 3-substituted pyridines [17].

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