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SYNTHESIS AND CHARACTERIZATION OF PYRIDINYLDISILOXANES AND THEIR BIS-*N*-OXIDES

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Summary

2- (**A**) and 3-dimethylchlorosilylpyridine (**B**) were synthesized by reaction of the corresponding lithiopyridines with dimethyldichlorosilane at −76 °C. The products were hydrolyzed in aqueous ammonia at room temperature to give the respective disiloxanes (**C** and **D**) which are stable, colorless distillable liquids. The dimers were characterized by IR, ^{1}H NMR and MS. The principal by-products of the syntheses were the *bis*-substituted derivatives. Additionally, the bis-*N*-oxide of **D** was prepared by reaction with *m*-chloroperoxybenzoic acid and characterized by IR, ^{1}H NMR and MS.

Introduction

Water soluble monomers and polymers containing pyridine and pyridine 1-oxide groups have been shown to serve as extremely active and selective nucleophilic catalysts in a variety of organic reactions: e.g. transacylation of derivatives of carbon, sulfur and phosphorus acids [1–7]. A unique aspect of these catalysts is their ability to facilitate the synthesis in high yield of extremely water sensitive materials (e.g. acid anhydrides) in aqueous/organic solvent suspensions by product phase transfer [8–10]. It is desirable to examine the effect of such reaction using organic soluble-water insoluble (i.e. 'inverse' phase transfer) catalysis. Toward this goal we have explored the feasibility of bonding the pyridine moiety to silicon monomers which serve as precursors to hydrophobic siloxane derivatives. We have recently described the synthesis and characterization of monofunctional fluoropyridinylsilanes and their respective disiloxanes [11]. We now wish to report the synthesis and properties of the 2- and 3-dimethylchlorosilylpyridine (**A** and **B**, respectively), their disiloxanes (**C** and **D**) and the bis-*N*-oxide of **D** (**G**).

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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 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 spectrometer equipped with a gas chromatograph. Elemental analyses were carried out by Galbraith Laboratories, Inc., Knoxville, TN 37921 or MicAnal, Tucson, AZ 85717.

*Synthesis of 3-dimethylchlorosilylpyridine (**B**)*

To a magnetically stirred solution of n-butyllithium (2.51 *M* in hexane, 50 ml) in dry ether (80 ml) under argon at −76 °C in a 250 ml round-bottom flask was added slowly a solution of 3-bromopyridine (20.0 g, 0.126 mol) in ether (40 ml). The mixture was stirred for 1 h. The resulting yellow suspension was added under argon to a jacketed dropping funnel cooled with dry ice and acetone. The suspension was added dropwise to excess Me_2SiCl_2 (129 g, 0.983 mol) at −76 °C under argon in a 1 l round-bottom flask. The mixture was stirred for an additional hour and allowed to warm slowly to room temperature overnight. Volatile solvents and unreacted Me_2SiCl_2 were removed under vacuum. The residue was flash distilled under vacuum (0.05 torr) to remove volatile products from solids. The distillate was distilled to give a colorless liquid, **B** (12.8 g; 59%; b.p. 42–46 °C at 0.5 torr). IR (cm^{-1}): $\nu(SiCH_3)$, 1265 s; ν(SiC), 795 vs; ν(ring), 705 s, 550 vs, 450 m; ν(SiCl), 505 vs. ^{1}H NMR (δ, mult., J (Hz), H^n, Area): 8.70, mc, H^2, 1; 8.51, d/d, 5/2, H^6, 1; 7.42, mc, $H^{4,5}$, 2; 0.27, s, H^{Me}, 6. Anal. Found: Cl, 19.37. $C_7H_{10}ClNSi$ calcd.: Cl, 20.65%.

*Synthesis of 1,1,3,3-tetramethyl-1,3-bis(3-pyridinyl)disiloxane (**D**)*

B (8.5 g, 0.05 mol) was placed in a 50 ml round-bottom flask. Aqueous ammonia (~ 50 ml, 30%) was added slowly with vigorous stirring. The mixture became turbid. Addition was continued until no further turbidity developed. The mixture was extracted with several portions (~ 20 ml) of toluene. The toluene fractions were combined, dried over anhydrous K_2CO_3 and filtered. Toluene was removed under vacuum to give a clear yellow liquid. The liquid was distilled twice under vacuum to give a clear colorless liquid **D** (5.2 g, 72%; b.p. 125–128 °C at 0.2 torr). IR (cm^{-1}): $\nu(SiCH_3)$, 1260 s; ν(SiOSi), 1050 vs; br, ν(SiC), 790 vs; ν(ring), 715 s, 620 s, 460 s. ^{1}H NMR (δ, mult., J (Hz), H^n, Area): 8.70 mc, H^2, 1; 8.55, d/d, 5/2, H^6, 1; 7.73, d/t, 7/1, H^4, 1; 7.15, d/d, 7/5; H^5, 1; 0.25, s, H^{Me}, 6. The GC-MS (EI/CI) spectrum of **D** is summarized in Table 1. Anal. Found: C, 58.86; H, 6.91; N, 9.71; Si, 19.65. $C_{14}H_{20}N_2OSi_2$ calcd.: C, 58.29; H, 6.99; N, 9.71; Si, 19.47%. **D** is soluble in organic solvents and only slightly soluble (4% by H_2O/CH_2Cl_2 partition) in water. **D** reacts with gaseous HCl to precipitate **D** · 2HCl as a salt insoluble in organic solvents.

*Synthesis of 1,1,3,3,-tetramethyl-1,3-bis(2-pyridinyl)disiloxane (**C**)*

The procedure is identical to that described for **B** and **D**. Typically n-BuLi (0.123 mol), 2-bromopyridine (0.135 mol) and Me_2SiCl_2 (2.5 mol) in ether solution were combined to give a product (**A**) which decomposed on heating under vacuum. Thus the intermediate, 2-dimethylchlorosilylpyridine, was not isolated as a pure substance. The mixture was hydrolyzed with aqueous ammonia and the product was extracted with toluene. Distillation gave a clear colorless liquid, **C** (8.1 g, 46%; b.p. 103–105 °C at 0.1 torr). IR (cm^{-1}): $\nu(SiCH_3)$, 1270 s; $\nu(SiOSi)$, 1070 vs, br. ^1H NMR (δ, mult., J (Hz), H^n, Area): 8.68, d/t, 5/1, H^6, 1; 7.4, mc, $H^{4,5}$, 2; 7.0, mc, H^3, 1; 0.48, s, H^{Me}, 6. The GC-MS (EI/CI) spectrum is summarized in Table 1. Anal. Found: C, 58.00; H, 6.80; N, 10.01; Si, 19.50%. $C_{14}H_{20}N_2OSi_2$ calcd.: C, 58.29; H, 6.99; N, 9.71; Si, 19.47%.

The GC-MS (EI/CI) spectra of the principal by-products in the synthesis of **A** and **B**, $(2\text{-}C_5H_4N)_2SiMe_2$ (**E**) and $(3\text{-}C_5H_4N)_2SiMe_2$ (**F**) respectively, are given in Table 1.

Synthesis of 1,1,3,3-tetramethyl-1,3-bis(3-pyridinyl 1-oxide)disiloxane (G)

In a typical experiment **D** (0.58 g, 2.0 mmol) was dissolved in CH_2Cl_2 (5 ml) in a 50 ml round bottom flask. *m*-Chloroperoxybenzoic acid (0.69 g, 4.0 mmol) dissolved in CH_2Cl_2 (10 ml) was added to **D**. The mixture was stirred in air overnight at ambient temperature. Aqueous K_2CO_3 (saturated) was added until no further precipitate formed. The white solids were removed by filtration and were washed with CH_2Cl_2 (5 ml). The solution was dried by filtering through a bed of anhydrous K_2CO_3. Residual solvent was removed by evaporation under vacuum to give a pale brown liquid **G** (0.54 g, 84%). IR (cm^{-1}): $\nu(SiOSi)$, 1060 vs, br; $\nu(N^+\text{–}O^-)$, 1260 vs, 790 s. ^1H NMR (δ, mult., Area, H^n) 8.23, mc, 1, $H^{2,6}$; 7.32, mc, 1, $H^{4,5}$; 0.35, s, 3, H^{Me}. MS (EI, 70 eV; m/e, $\%b$, ion): 320, 42, $M^{+\cdot}$; 305, 17, $(M-15)^+$; 304, 35, $(M-16)^+$; 303, 100 $(M-17)^{+\cdot}$; 287, 33, $(M-33)^+$; 78, 60, $(M-242)^+$. Anal. Found: C, 52.62; H, 6.43; N, 8.86; Si, 17.42. $C_{14}H_{20}N_2O_3Si_2$ calcd.: C, 52.46; H, 6.29; N, 8.74; Si, 17.53%.

Results and discussion

2- (**A**) and 3-dimethylchlorosilylpyridine (**B**) were synthesized by the reaction of analogous lithiopyridines, which were prepared in situ from n-BuLi and the corresponding bromopyridine, with excess dimethyldichlorosilane (Scheme 1). Whereas **B** is a stable colorless liquid which can be purified by distillation, **A** decomposes on heating under vacuum. Thus **A** was not isolated and characterized as a pure substance. Both compounds are extremely sensitive to moisture and readily evolve HCl on standing to precipitate the quaternary salts. Moreover, bis-pyridinyl substituted by-products (i.e. Py_2SiMe_2) were detected by ^1H NMR and GC-MS.

The IR spectrum of **B** exhibits a strong band at 505 cm^{-1} which is characteristic of the Si–Cl stretching vibration found in triarylchlorosilanes [12]. Absorptions at 705, 550 and 450 cm^{-1} are consistent with r-, t- and y-ring vibrational modes analogous to those found in mono-, di- and triphenylsilane derivatives [13].

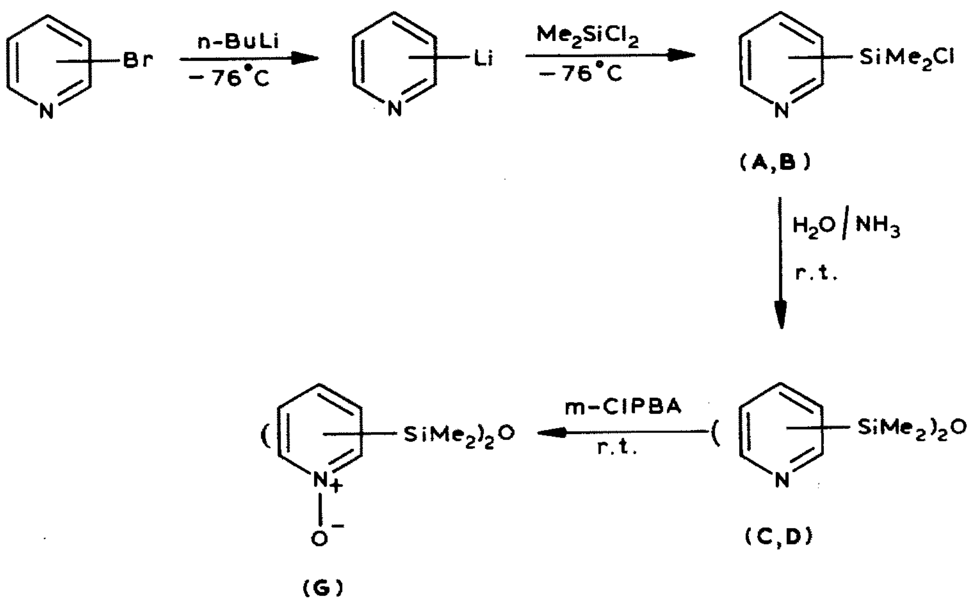
The ^1H NMR spectrum of **B** contains a singlet at high field (0.27 ppm) assigned to the methyl protons on silicon. The pattern of signals for **B** at low fields (7–9 ppm), although complex owing to multiple coupling, is comparable to other 3-substituted pyridines [14].

Disiloxanes **C** and **D** are obtained by the alkaline (NH_3) hydrolysis of precursor derivatives (Scheme 1). The products are stable, vacuum distillable liquids which are soluble in organic solvents and partition only slightly (4%) in water-CH_2Cl_2

TABLE 1

PRINCIPAL IONS IN THE EI/CI MASS SPECTRA OF $(2\text{-}C_5H_4NSiMe_2)_2O$ (C), $(3\text{-}C_5H_4NSiMe_2)_2O$ (D), $(2\text{-}C_5H_4N)_2SiMe_2$ (E) AND $(3\text{-}C_5H_4N)_2SiMe_2$ (F) AT 70 eV

Compound	EI spectrum									CI (MH^+)
C	*m/e*	288	287	274	273	211	210	180	136	289
	%*b*	>1	>1	5	17	20	100	8	10	
	ion	$M^{+\cdot}$	$(M-1)^+$	$(M-14)^{+\cdot}$	$(M-15)^+$	$(M-77)^{+\cdot}$	$(M-78)^+$	$(M-108)^+$	$(M-152)^+$	
D	*m/e*	288	287	274	273	210	194	136		289
	%*b*	29	14	20	100	5	14	14		
	ion	$M^{+\cdot}$	$(M-1)^+$	$(M-14)^{+\cdot}$	$(M-15)^+$	$(M-78)^+$	$(M-94)^+$	$(M-152)^+$		
E	*m/e*	214	213	200	199	184	183	136		215
	%*b*	100	51	6	32	24	20	35		
	ion	$M^{+\cdot}$	$(M-1)^+$	$(M-14)^{+\cdot}$	$(M-15)^+$	$(M-30)^{+\cdot}$	$(M-31)^+$	$(M-78)^+$		
F	*m/e*	214	200	199	184	183	136			215
	%*b*	31	11	100	9	9	8			
	ion	$M^{+\cdot}$	$(M-14)^{+\cdot}$	$(M-15)^+$	$(M-30)^{+\cdot}$	$(M-31)^+$	$(M-78)^+$			



SCHEME 1

mixtures.

The IR spectrum of **D** is similar to that of **B** with the exception of the disappearance of the Si–Cl absorption and the appearance of a very intense and broad band at 1050 cm^{-1} identifiable with the Si–O–Si stretching vibration in disiloxanes. The spectrum of **C** has a equivalent band at 1070 cm^{-1} [15].

The ^1H NMR spectrum of **D** in the aromatic region gives a complex pattern of resonances due to long range proton–proton ring couplings and is recognizable as a pyridine compound with 3-substitution [14]. All ring protons are discernible and assignments were made by comparison with known 3-organopyridine derivatives. The assignment of protons in **C** is based on pattern recognition with analogous organopyridines [14].

Table 1 summarizes the GC-MS (EI/CI) data for **C**, **D** and the principal by-products of the substitution reaction; i.e. $(2\text{-}C_5H_4N)_2SiMe_2$ (**E**) and $(3\text{-}C_5H_4N)_2SiMe_2$ (**F**). The salient differences in the fragmentation pattern of **C** and **D** are (a) the presence of a noticeable molecular $(M)^{+\cdot}$ in **D** not seen in **C** and (b) a base peak corresponding to scission of the Me–Si bond, $(M-15)^+$, in **D** in contrast to scission of the C_5H_4N–Si bond, $(M-78)^+$, in **C**. The only noticeable difference in the MS of **E** and **F** is the base peak, which in **F** results from loss of Me and in **E** is the molecular ion. Interestingly, the ion $(M-HCN)^+$ usually present in the fragmentation of 2- and 3-substituted pyridines is not seen in **C**–**F** [16]. A similar observation was made for the fluoropyridinyl containing silanes and disiloxanes [11].

B can be oxidized to the corresponding bis-*N*-oxide (**G**) at ambient temperatures. **G** is a brown liquid which is soluble in organic solvents and only slightly soluble in water. **G** reveals a strong infrared band at 790 cm^{-1} characteristic of the N^+–O^- out-of-plane bending vibration in aromatic *N*-oxides [17]. In addition there is a very intense and broadened absorption at 1260 cm^{-1} diagnostic of the N^+–O^- stretching vibration which apparently overlaps a characteristically sharp CH_3–Si rocking vibration.

The ^1H NMR spectrum of **G** consists of two envelopes of peaks in the aromatic region corresponding to overlap of the H^2/H^6 (δ 8.23 ppm) and H^4/H^5 (δ 7.32 ppm) protons and a sharp singlet upfield assigned to H^{Me}. The chemical shifts of the upfield singlet in **B** and **G** are essentially the same. The H^2/H^6 protons in **G** are shifted upfield (ca. ~ 0.4 ppm) from analogous protons in **B**, presumably as a result of resonance interaction of the lone pairs of electrons on oxygen with the π orbitals of the ring. Similar shift changes have been observed for 3-methyl and other substituted pyridines compared to their *N*-oxides [14].

The MS of **G** indicates a prominent molecular ion (m/e 320) with fragmentation giving rise to the principal ions $(M-CH_3)^+$, $(M-O)^+$, $(M-OH)^{+\cdot}$ (base), $(M-O-OH)^+$ and $(Py)^+$. As with **C**–**F**, $(M-HCN)^{+\cdot}$ due to ring rupture, is not observed.

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