470 *Organometallics* 1988, 7, 470–474

Synthesis, Characterization, and Catalytic Properties of Poly(methyl(1-oxypyridin-3-yl)siloxane)

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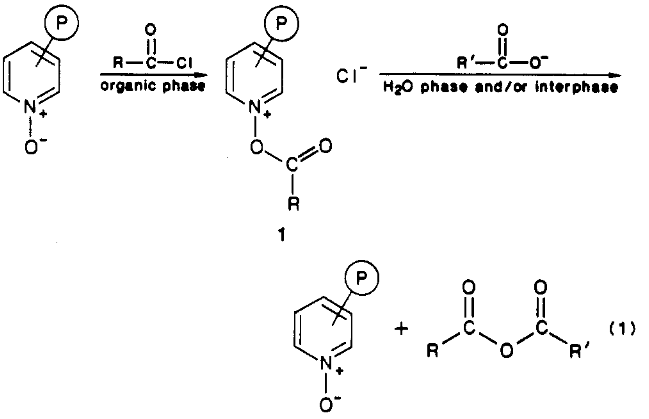
Received July 8, 1987

3-(Methyldichlorosilyl)pyridine (**2**) was synthesized by metalation of 3-bromopyridine with *n*-BuLi at −76 °C followed by reaction with excess $MeSiCl_3$. Compound **2** was polymerized by hydrolysis in aqueous ammonia to give hydroxyl-terminated poly(methylpyridin-3-ylsiloxane) (**3**). Species **3** was converted to the trimethylsiloxyl end-blocked polymer (**4**) with a mixture of $(Me_3Si)_2NH$ and Me_3SiCl. Polymer **4** was N-oxidized with $m\text{-}ClC_6H_4CO_3H$ to give **5**. Species **2**–**5** were characterized by IR and ^1H NMR spectra. The MS of **2** and the thermal analysis (DSC and TGA) of **3**–**5** are discussed. 3-(Trimethylsilyl)pyridine 1-oxide (**6**), 1,3-dimethyl-1,3-bis(1-oxypyridin-3-yl)disiloxane (**7**), and **5** were effective catalysts for conversion of benzoyl chloride to benzoic anhydride (yields ≥ 80%) in well-stirred suspensions of dichloromethane/aqueous $NaHCO_3$ (1.0 M) and for hydrolysis of diphenyl phosphorochloridate in aqueous $NaHCO_3$ (2.0 M). The latter had a half-life of less than 10 min at 23 °C. These results were compared to those obtained with pyridine 1-oxide (**8**) and poly(4-vinylpyridine 1-oxide) (**9**) as catalysts.

Introduction

Pyridine 1-oxide and solid-state polymers containing pyridine and 1-oxypyridinyl groups have been shown to serve as extremely active and selective nucleophilic catalysts in transacylation reactions.[1,2] A unique aspect of these catalysts and water-soluble homopolymer analogues is their ability to facilitate the synthesis of symmetrical or unsymmetrical acid anhydrides in high yield in aqueous/organic suspensions (i.e. inverse phase-transfer catalysis).[2] A distinctive feature of these reactions is the transport of an intermediate 1-(acyloxy)pyridinium ion (**1**), which is generated in the organic phase from pyridine 1-oxide species and an acyl chloride, to the aqueous phase where a subsequent reaction with a carboxylate ion gives the anhydride, which migrates rapidly and almost quantitatively into the organic phase. Fife et al. have suggested that the phase-transfer process includes an interphase component as evidenced by the selective transport of the more lipophilic ion of a competing pair of carboxylate ions at the water/organic medium interface.[1a] In order to probe further the question of interfacial activity and transport facility (i.e. rates and selectivity of reaction), it was desirable to design an organic soluble–water insoluble catalyst which can effect transacylation at the mixed-solvent interface without partitioning into the aqueous layer. We have recently reported the synthesis and characterization of disiloxanes containing the pyridinyl and 1-oxypyridinyl substituent.[3-5] These compounds are hydrophobic and have a low partition coefficient in CH_2Cl_2/H_2O suspensions. We now wish to describe the synthesis and characterization of 3-(methyldichlorosilyl)pyridine (**2**), hydroxy-terminated poly(methylpyridin-3-ylsiloxane) (**3**), trimethylsiloxyl-terminated poly(methylpyridin-3-ylsiloxane) (**4**), and the *N*-oxide of **4** (**5**), the latter of which fulfills the above-mentioned solubility and partitioning coefficient criteria. We also wish to report preliminary results from an investigation that compares the catalytic effectiveness of 3-(trimethylsilyl)pyridine 1-oxide (**6**), 1,3-dimethyl-1,3-bis(1-oxypyridin-3-yl)disiloxane (**7**), and **5** with pyridine 1-oxide (**8**) and poly(4-vinylpyridine 1-oxide) (**9**) in hydrolysis and other transacylation reactions of carboxylic and phosphoric acid chlorides.



Experimental Section

Solvents and reagents were purified by drying over a suitable dehydrating agent followed by distillation. Infrared spectra were obtained by using either a Perkin-Elmer 283 or Nicolet 5DXB spectrometer with KBr plates. ^1H NMR spectra were recorded on a Varian EM360-A spectrometer in $CDCl_3$ with CH_2Cl_2 or TMS as a reference. Mass spectra (EI) were observed at 70 eV with a Kratos MS-80RS spectrometer equipped with a gas chromatograph. Elemental analyses were carried out by MicAnal Organic Microanalysis, Tucson, AZ 85717. Thermal analysis was carried out with a Perkin-Elmer Series 7 thermogravimetric analyzer and differential scanning calorimeter. Since products **2**–**4** are fluids, sealed solution pans were used in DSC measurements. Molecular weight measurements were obtained by size exclusion chromatography using a Waters R401 differential refractometer and ASI ultragel (10^3, 10^4 Å) columns.

Synthesis of Trimethylsiloxyl End-Blocked Poly(methyl(1-oxypyridin-3-yl)siloxane) (5). To a magnetically stirred solution of *n*-BuLi (75 mL, 2.45 M in hexane, 0.184 mol) diluted with anhydrous diethyl ether (120 mL) at −76 °C in a 500-mL round-bottom flask was added dropwise 3-bromopyridine (32.3 g, 0.202 mol) dissolved in diethyl ether (75 mL). The resulting yellow suspension was stirred for an additional 30 min at low temperature and poured under argon into a dropping funnel which

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[†] On leave from the Synthetic Materials Research Institute of Tianjin (PRC).

(1) (a) Fife, W. K.; Xin, Y. *J. Am. Chem. Soc.* **1987**, *109*, 1278. (b) Fife, W. K.; Zhang, Z.-d. *J. Org. Chem.* **1986**, *51*, 3744. (c) Fife, W. K.; Zhang, Z.-d. *Tetrahedron Lett.* **1986**, *27*, 4933. (d) Fife, W. K.; Zhang, Z.-d. *Ibid.* **1986**, *27*, 4937.

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was jacketed and cooled with dry ice/acetone. The suspension was added slowly under argon with vigorous stirring to an excess of $MeSiCl_3$ (~700 g, 4.7 mol) at −76 °C in a 2-L round-bottom flask. After addition, the reaction mixture was allowed to warm to room temperature overnight. Volatile solvents and unreacted $MeSiCl_3$ were removed under vacuum at ambient temperature. The higher boiling materials were separated from solid residues by flash distillation. Subsequent column distillation (bp 71–73 °C (0.85 torr)) gave a colorless liquid (**2**, 9.6 g, 40%) which was soluble in organic solvents and extremely sensitive to moisture. IR (cm^{-1}, relative intensity): 3120 w, 3080 m, 3030 s, 3000 m, 2970 m, 2940 m, 2905 m, 2870 w, 2060 w, 2020 w, 1980 w, 1945 w, 1925 w, 1890 vw, 1855 w, 1750 w, 1575 vs, 1560 s, 1470 s, 1400 s, 1390 s, 1360 s, 1265 s, 1250 m, 1200 s, 1170 s, 1140 s, 1070 m, 1035 s, 1025 s, 1010 w, 840 w, 790 vs, br, 760 s, 710 vs, 670 w, 625 s, 550 vs, 505 vs, 455 m, 375 vs. ^1H NMR (δ, multiplicity, J (Hz), relative area, H^n): 8.57, d/d, 2/1, 1.0, H^2; 8.33, d/d, 5/2, 1.1, H^6; 7.60, d/t, 8/2, 1.0, H^4; 6.88, d/d/d, 8/5/1, 1.0, H^5; 0.60, s, 3.1, H^{Me}. MS (m/e, % b, ion): 195/193/191, 6.2/32/11, $M^{\cdot +}$; 180/178/176, 12/67/100, $(M - 15)^+$; 117/115/113, 2.7/13/20, $(M - 78)^+$; 78, 16, $(M - SiMeCl_2)^+$; 65/63, 9.7/24, $SiCl^+$.

In a typical hydrolysis experiment, **2** (0.97 g, 5.07 mmol) was placed in a round-bottom flask containing a magnetic stirring bar. The flask was placed in a ambient temperature bath and deionized water (6 mL) was added slowly with vigorous stirring. As aqueous ammonia (30%) was added dropwise to the clear solution, a turbidity developed. When no further turbidity occurred (~2–3 mL), the contents of the flask were transferred to a test tube and centrifuged to separate the water phase from the oil phase. The water was removed with a syringe, and the residual oil was dried under vacuum at 45 °C for 4 h to give a clear colorless viscous fluid (**3**, 0.85 g). IR (cm^{-1}, relative intensity): 3500–3100 s, br, 3070 w, 3020 m, 2990 w, 2960 m, 2900 w, 1930 w, 1740 w, 1650 w, br, 1575 s, 1560 m, 1470 m, 1395 s, 1340 sh, 1330 m, 1265 s, 1225 w, 1195 m, 1135 s, 1070 vs, br, 920 s, 790 s, br, 710 s, 630 sh, 625 m, 600 w, 550 w, 475 s, 430 s, 380 m. ^1H NMR (δ, $w_{1/2}$, H^n): 8.6, 20, $H^{2,6}$; 7.6, 30, H^4; 7.1, 20, H^5; 0.22, 15, H^{Me}. Area: $H^{2,6}$, 1.0; $H^{4,5}$, 1.1; H^{Me}, 1.5. Anal. Calcd for C_6H_7NOSi repeat group or cyclic oligomer: C, 52.52; H, 5.14; N, 10.21. Found: C, 51.20; H, 5.14; N, 9.81. **3** is soluble in organic solvents and is ≥95% retained in CH_2Cl_2 from a vigorously stirred H_2O/CH_2Cl_2 mixture.

Compound **3** was end-blocked by using the following procedure. Typically, **3** (0.5 g) was dissolved in $CHCl_3$ (5 mL) in a 25-mL round-bottom flask fitted with a reflux condenser. $(Me_3Si)_2NH$ (1 mL) and Me_3SiCl (0.2 mL) were dissolved in $CHCl_3$ and added to **3**. The mixture was stirred and refluxed for a minimum of 16 h. The solution was then filtered through a bed of anhydrous K_2CO_3. Volatile materials were evaporated under vacuum to give a clear, colorless fluid (**4**, 0.5 g). IR (cm^{-1}, relative intensity): 3130 w, 3070 w, 3020 m, 2990 w, 2955 s, 2890 w, 1930 w, 1740 w, 1650 w, br, 1575 s, 1560 s, 1470 m, 1395 s, 1340 sh, 1330 m, 1260 s, 1220 w, 1195 m, 1135 s, 1070 vs, br, 870 s, 845 s, 785 s, 760 sh, 710 s, 620 m, 540 w, 470 s, 430 s, 380 m. ^1H NMR (δ, $w_{1/2}$, H^n): 8.6, 18, $H^{2,6}$; 7.7, 20, H^4; 7.1, 18, H^5; 0.21, 8, H^{Me}; −0.07, 5, H^{Me_3}. Area ratio calcd for $Me_3Si(OSi(3\text{-}Py)Me)_{8.4}OSiMe_3$: $H^{2,6}$: H^4: H^5: H^{Me}: H^{Me_3}, 2:1:1:3:2.1. Found: 2:1:1:2.8:2; MW^{NMR}, 1340; MW^{GPC}, 1400. $\bar{M}_n$ depended on the reaction conditions and post-heat treatment.

Polymer **4** can be N-oxidized in the following manner. For example, **4** ($\bar{M}_n$ 830, $x = 5$, 0.34 g) was dissolved in CH_2Cl_2 (3 mL) and placed in a 25-mL round-bottom flask with a magnetic stirring bar. *m*-Chloroperoxybenzoic acid (0.44 g) dissolved in CH_2Cl_2 (7 mL) was added. The mixture was stirred at room temperature for 16 h. Aqueous saturated K_2CO_3 solution was added dropwise until neutral. The mixture was filtered, and the organic layer was separated and dried overnight with anhydrous K_2CO_3. The solution was filtered, and CH_2Cl_2 was vacuum evaporated to give a pale yellow oil (**5**, 0.2 g). IR (cm^{-1}, relative intensity): 3110 m, 3080 m, 2960 s, 2905 w, 2475 w, 2230 w, 1660 w, br, 1610 m, 1585 m, 1560 m, 1465 s, 1405 s, 1300 m, 1255 s, 1235 sh, 1170 m, 1122 s, sh, 1060 vs, br, 1015 s, sh, 940 m, 915 m, 870 sh, 845 s, 780 s, 735 sh, 700 w, 680 s, 640 w, 555 m, 515 w, 490 m, 475 w, 450 s, 425 s, 375 w, 350 m. ^1H NMR (δ, H^n): 8.3, $H^{2,6}$; 7.3, $H^{4,5}$; 0.3, H^{Me}; 0.05, H^{Me_3}; Area Ratio Calcd for $x = 5$: $H^{2,6}$: $H^{4,5}$: H^{Me}: H^{Me_3}, 1:1:1.5:1.8. Found: 1:1:3.2 (combination of $H^{Me} + H^{Me_3}$).

The TGA and DSC data for **3**–**5** are given in Figures 1 and 2, respectively.

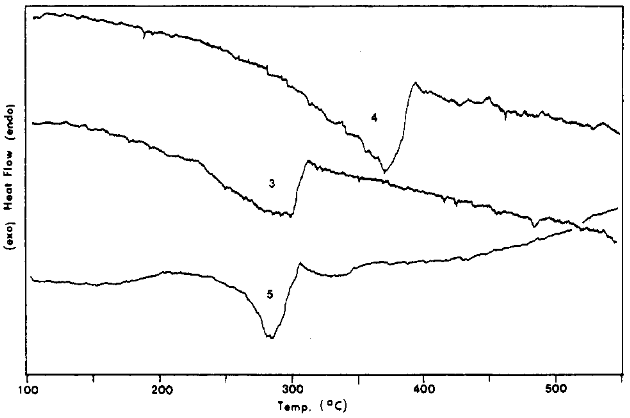


Figure 1. TGA of hydroxyl terminated (**3**), trimethsiloxyl end-blocked (**4**), and trimethylsiloxyl end-blocked/N-oxidized (**5**) poly(methylpyridin-3-ylsiloxane) (heating rate, 40 °C/min) under argon.

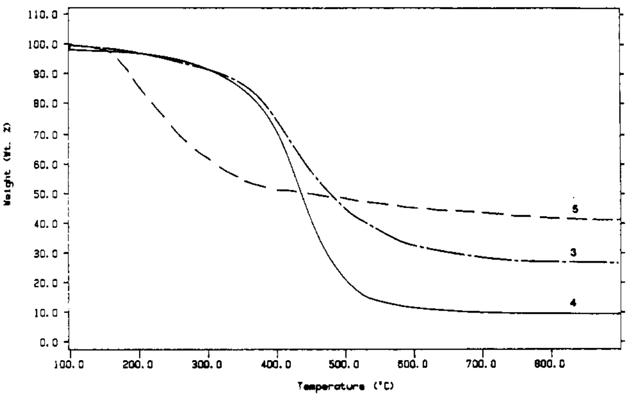


Figure 2. DSC of hydroxyl terminated (**3**), trimethylsiloxyl end-blocked (**4**), and trimethylsiloxyl end-blocked/N-oxidized (**5**) poly(methylpyridin-3-ylsiloxane) (heating rate, 20 °C/min) under argon.

Catalysis of Transacylation Reactions. Hydrolysis of Benzoyl Chloride. Two-phase mixtures containing 4 mmol of benzoyl chloride, 2.5 equiv of sodium bicarbonate, 0.10 equiv of catalyst (**5**–**9**), 10 mL of deionized water, and 10 mL of dichloromethane were stirred vigorously with a 1-in. Teflon-coated magnetic stirring bar for 10–240 min at room temperature (22–23 °C). After the reaction was completed, the organic layer was separated, washed twice with 10 mL of 2.0 M hydrochloric acid and then with 10 mL of 10% aqueous potassium carbonate, dried over anhydrous potassium carbonate, and rotary evaporated to obtain benzoic anhydride (mp 41–42 °C; recrystallized from ethyl acetate–hexane). Completeness of reaction was documented by IR spectral analysis (δ_{CO} = 1785, 1725 cm^{-1}; no band at 880 cm^{-1}). The water layer from the reaction mixture was acidified with 2.0 M hydrochloric acid, and the organic material was taken up in 15 mL of dichloromethane. The dichloromethane layer was separated, dried over anhydrous magnesium sulfate, and rotary evaporated to obtain benzoic acid (mp 120–122 °C; recrystallized from water). Results are summarized in Table I.

Hydrolysis of Diphenyl Phosphorochloridate. A mixture of 1 mmol of diphenyl phosphorochloridate, 5.0 equiv of sodium bicarbonate, 0.10 equiv of catalyst (**5**–**9**) dissolved in 10 drops of methanol, and 10 mL of deionized water was stirred at room temperature for 30 min as described above. The unreacted organic-soluble diphenyl phosphorochloridate was recovered by extraction with dichloromethane (3 × 10 mL), and the neutral and acidic fractions were isolated by the procedure described above. All products were then characterized by IR spectral analysis. The results are summarized in Table I.

Results and Discussion

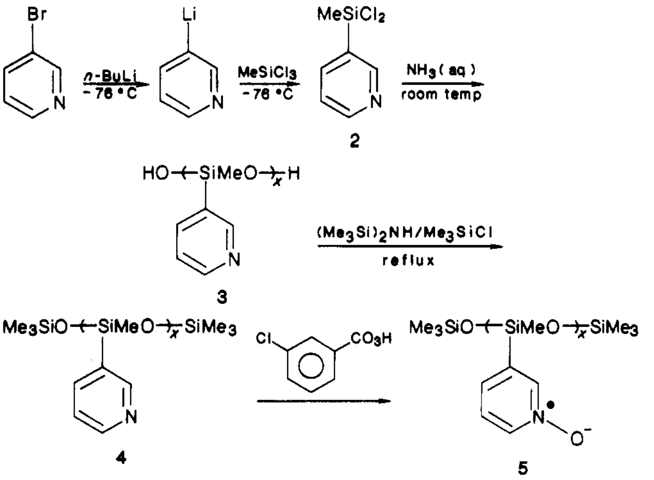
3-(Methyldichlorosilyl)pyridine (**2**) was synthesized by the reaction of 3-lithiopyridine, prepared in situ from

Table I. Catalysis of Transacylation Reactions of Benzoyl Chloride and Diphenyl Phosphorochloridate[a]

cat. (0.10 equiv)[b]	acid (%)	anhydride (%)	recovered acid chloride (%)
Benzoyl Chloride in CH_2Cl_2–1.0 M $NaHCO_3$			
	0.4	0.0	>90.0
8	42.0	49.4	1.6
9	8.3	81.0	0.7
6	4.9	91.6	1.5
7	8.1	79.1	2.0
5	5.0	89.3	3.0
Diphenyl Phosphorochloridate in 2.0 M $NaHCO_3$			
	14.2		72.6
8	22.4		71.9
9	39.2		47.3
6	72.3		22.9
7	66.0		23.5
5	85.9		10.7

[a] Reaction mixtures contained either 4 mmol of benzoyl chloride or 1 mmol of diphenyl phosphorochloridate. Reactions were run for 30 min at 22–23 °C. [b] **5**, poly(methyl(1-oxypyridin-3-yl)siloxane); **6**, 3-(trimethylsilyl)pyridine 1-oxide; **7**, 1,3-dimethyl-1,3-bis(1-oxypyridin-3-yl)disiloxane; **8**, pyridine 1-oxide; **9**, poly(4-vinylpyridine 1-oxide).

Scheme I



3-bromopyridine and *n*-butyllithium, with a large excess of methyltrichlorosilane at −76 °C (Scheme I). The product is a colorless distillable liquid which is soluble in aromatic, aliphatic, and chlorinated hydrocarbons and extremely sensitive to moisture and protonic solvents.

The infrared spectrum of **2** exhibits a pair of intense absorptions at 505 and 550 cm^{-1} characteristic of symmetric and asymmetric stretching vibrations, respectively, of the $SiCl_2$ group.[6] Bands at 710 (s)/760 (vs) and 455 (m) cm^{-1} are consistent with r- and t-ring vibrations, respectively, associated with Si–C ring modes observed in phenylsilanes.[7]

The chemical shifts, assignments, pattern of lines, and coupling constants in the aromatic region (6–9 ppm) of the 60-MHz ^1H NMR spectrum of **2** are comparable to known 3-substituted pyridines.[8] The methyl group protons on silicon appear as a sharp singlet at 0.60 ppm, indicating a normal anisotropic perturbation by the pyridine ring.

The mass spectrum of **2** exhibits polyisotopic ion clusters with relative abundances diagnostic of a dichloro compound for the molecular ions ($M^{\bullet+}$) and fragment ions $(M - Me)^+$ which contain the base peak, and $(M - py)^+$. The presence of an ion at *m/e* 78 (i.e. $(M - SiMeCl_2)^+$) suggests that the ion current can be carried by either the aromatic ring or the electrophilic metalloid. Conspicuous by its absence, but common to all silyl-substituted pyridines and their *N*-oxides,[3,4] is the $(M - HCN)^{\bullet+}$ ion which is characteristic of ring fragmentation elimination prominent in 3-substituted pyridines.[9]

Hydrolysis of **2** is carried out at room temperature by the slow addition of aqueous ammonia (Scheme I). The resulting hydroxyl end-functional polysiloxane (**3**) is dispersed as fine droplets in the medium and can be separated by centrifugation. When neat, **3** is a colorless viscous fluid with a molecular weight (1×10^3 to 1×10^4) dependent primarily on the length of time the polymer is heat-dried (e.g. <100 °C) under vacuum. Upon standing at room temperature for several weeks or heating for shorter periods of time above 100 °C, the fluid becomes a rubbery semisolid characteristic of a high molecular weight polymer resulting from chain-end condensation.

The infrared spectrum of **3** is similar to that of **2**. Notable changes are (a) the disappearance of the $SiCl_2$ vibrations, (b) the appearance of a strong, broad band in the 1050–1100 cm^{-1} region characteristic of the Si–O–Si stretching vibration in siloxanes,[10] and (c) a strong broad band centered at 3200 cm^{-1} due to retained water superimposed on terminal OH groups. Attempts to completely remove the water with conventional drying agents or by azeotropic distillation with organic solvents were unsuccessful.

The ^1H NMR spectrum of **3** in $CDCl_3$ exhibits broad unresolved resonances in the aromatic region at positions similar to those found in the monomer. Broad signals with lack of resolution are consistent with magnetic nonequivalence of the methyl group protons resulting from a mixture of triad tacticities.

Species **3** can be end-blocked and simultaneously dehydrated by refluxing with a mixture of 1,1,1,3,3,3-hexamethyldisilazane and trimethylchlorosilane (Scheme I). Product **4** is a clear colorless viscous fluid that remains unchanged on standing or upon heating under vacuum or in air. Product **4** is soluble in organic solvents and immiscible with water.

The IR spectrum of **4** differs from **3** by the appearance of new bands at 845/870 cm^{-1} that are characteristic of the end-block $Si(CH_3)_3$ group. The intensity of the bands decreases with increase in polymer molecular weight, thus supporting the assignment. There is also a significant decrease in the OH absorption confirming an anhydrous polymer.

The principal difference between the ^1H NMR spectrum of **3** and **4** is the appearance of a singlet at −0.07 ppm in **4** which has been assigned to the terminal trimethylsiloxyl protons. The relative area of the peak decreases with increase in molecular weight. Thus, if the molecular weight is not to large (i.e. <10000), the ^1H NMR spectrum is a convenient method for determining the average degree of polymerization (viz. $A^{Me}/A^{Me_3} = 1.4$; $x = 8.3$; $\bar{M}_n$ 1300). The NMR data agree well with size exclusion chromatography ($\bar{M}_n$ 1400).

When **4** is treated with *m*-chloroperoxybenzoic acid, oxidation at the ring nitrogen occurs (Scheme I). The product **5** is a pale yellow viscous fluid which is soluble in organic solvents but immiscible with water. **5** has a par-

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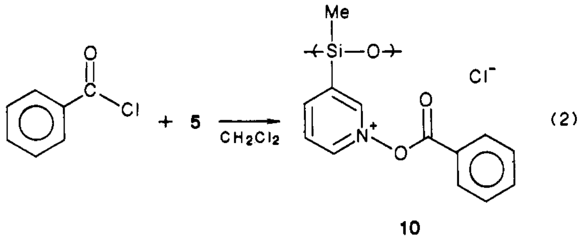
tition ratio of 24:1 in a CH_2Cl_2/H_2O medium. The IR spectrum of **5** gives direct evidence for the presence of the $N^+ - O^-$ bond with a characteristic stretching vibration at 1250 cm^{-1}.[11] The band is intense and broad, thus masking the much sharper CH_3 rocking modes in the same region. It is noteworthy that two new medium intensity absorptions occur in **5** at 920 and 940 cm^{-1}, which is a window in **4**. These are analogous to the bands assigned to $N^+ - O^-$ deformation modes at 800–900 cm^{-1} reported by Kireev et al.[11] and Shindo.[12]

A salient feature of the ^1H NMR spectrum of a low molecular weight oligomer of **5** is the appearance of two rather than three unresolved envelopes in the aromatic region. Similar spectral changes (i.e. the merging of $H^{3,4}$ protons and the upfield shift of $H^{2,6}$ protons by ~0.5 ppm) upon N-oxidation have been noted for other 3-substituted pyridines.[8] The position of the high-field methyl proton signals in **5** is comparable to that found in **4**.

The TGA of **3** and **4** ($x = 10$) under argon is given in Figure 1. Both polymers have approximately the same temperature at which the onset of weight loss occurs, presumably in part by depolymerization.[13,14] The larger residue fraction for the hydroxy-terminated species (28% vs 9%) may be a result of cross-linking by pyridinyl decomposition perhaps involving end-group (nucleophilic) attack at the 2-/6-positions of the ring. The TGA of **5**, however, indicates a lower onset of weight loss accompanied by a higher (40%) amount of residue. This suggests that the 1-oxide plays a significant role not only in chain scission but also in the cross-linking process.

The DSC data for **3**–**5** are given in Figure 2. The order of "stability" as judged from the exotherm maximum is **4** > **3** ≈ **5**. In order to identify the changes that occur during the heating process, we carried out a series of DSC experiments on **4** in which heating was terminated at different points along the thermogram; i.e. prior to, at, and post exothermic maximum. With the exception of the samples heated above 500 °C, the residues from **4** were clear viscous yellow fluids soluble in CH_2Cl_2. The IR spectrum of the soluble residues were almost identical with the unheated material, the only change being the appearance of a weak band at 940 cm^{-1}. A similar absorption has been noted previously for the *N*-oxide polymer, thus suggesting some N-oxidation by ambient air. Indeed, the band is not present when precautions are taken to exclude oxygen from the sample holder and the analyzer. The combination of SiC, SiOSi, and SiC_3 vibrations, increased viscosity and solubility in organic solvents of the residues, and the appearance of a weak broad exotherm suggests that heating to 450 °C promotes principally redistribution polymerization with little, if any, cross-linking. In contrast, if **4** is heated above 500 °C, the residue is a black insoluble solid with a relatively featureless IR spectrum containing broad bands in the SiOSi and SiC regions. The absence of ring modes and the appearance of a sharp band at 2350 cm^{-1}, which corresponds to the SiH vibration, implies that degradation involves cross-linking by pyridine ring decomposition and H migration. The latter is a well-known pathway in mass spectrometry of organosilanes.[15] Oligomers **3** and **5** give similar DSC results with decomposition at lower temperatures.

Compound **5** was found to be an effective catalyst for the conversion of benzoyl chloride to benzoic anhydride in well-stirred suspensions of dichloromethane–1.0 M aqueous sodium bicarbonate (Table I). The reaction is believed to involve formation of the poly((benzoyloxy)-pyridinium) intermediate, **10**, in the organic phase (eq 2),



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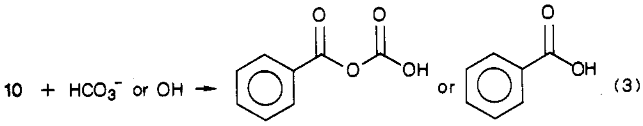
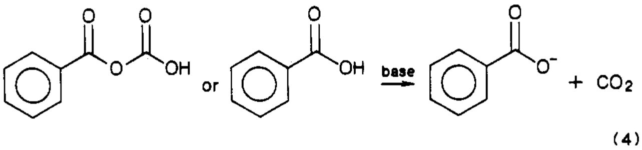
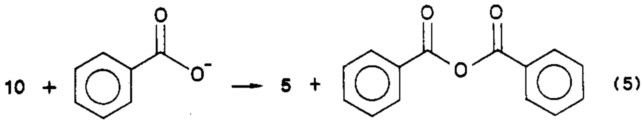




and **10** then quickly reacts with bicarbonate ion and/or hydroxide ion at the interface to form benzoate ion (eq 3 and 4). Apparently most of the benzoate ion is trapped by additional **10** in the organic layer or at the interphase to produce benzoic anhydride (eq 5), an example of normal PTC process.[16] The same result is observed for catalysis by 3-(trimethylsilyl)pyridine 1-oxide (**6**), the siloxane dimer (**7**), and the homopolymer of 4-vinylpyridine 1-oxide (**9**). Interestingly, catalysis by pyridine 1-oxide (**8**) furnishes nearly equal amounts of anhydride and hydrolysis product. This has been taken as evidence for a high proportion of inverse phase-transfer catalysis (IPTC), i.e., reaction between 1-(benzoyloxy)pyridinium ion and bicarbonate ion in the aqueous phase.[1a] It is particularly significant that water-soluble (**9**) and organic-soluble (**5**) polymeric catalysts behave quite similarly in two-phase media. This argues for a symmetry in catalysis at the interphase of the water–organic solvent suspension.



Hydrolysis of diphenyl phosphorochloridate (DPPC) in 2.0 M aqueous sodium carbonate is also believed to be a two-phase process. DPPC is quite insoluble in water and forms an insoluble second phase at the concentration employed (i.e. 0.10 M). It seems highly significant that the hydrophobic silicon-substituted pyridine 1-oxides (**5**–**7**) are much more effective catalysts than the hydrophilic pyridine 1-oxide and poly(4-vinylpyridine 1-oxide) (**8**, **9**). In fact, **5** is clearly the most effective catalyst we have examined for this reaction ($t_{1/2}$ < 10 min). Since derivatives of phosphoric acids are known to undergo substitution reactions via nucleophilic addition–elimination sequences[17] (eq 6), we believe that the initial step in hydrolysis of

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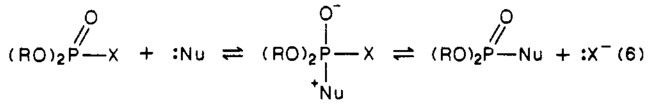

$$(RO)_2P(=O)-X + :Nu \rightleftharpoons (RO)_2P(O^-)(X)(^+Nu) \rightleftharpoons (RO)_2P(=O)-Nu + :X^- \quad (6)$$

DPPC occurs in the organic phase. Moreover, the relatively high catalytic activity of **5** provides strong evidence for the importance of association or binding between the hydrophobic catalyst and DPPC prior to the first catalytic step. It is noteworthy that polysiloxanes, long recognized and utilized because of their inertness and hydrophobicity, are now shown to be important platforms for chemical catalysis even in water-containing media provided they are appropriately functionalized.

The importance of hydrophobic binding interactions in facilitating catalysis in enzyme reactions is well-known. The impact of this phenomenon in the action of synthetic polymer catalysts for reactions such as described above is significant. A full investigation of a variety of monomeric and polymeric catalysts with nucleophilic catalytic sites is currently underway. They are being used to study the effect of polymer structure and morphology on catalytic activity in transacylation reactions.

Acknowledgment is made to Reilly Tar and Chemical Co. and the Dow Corning Corp. for partial support of this research. J.-m. X. and C.-x. T. express their sincerest gratitude to the Synthetic Materials Research Institute of Tianjin (PRC) for leaves-of-absences to carry out the research. We thank the National Science Foundation for financial support enabling the purchase of the thermal analysis equipment (Grant CHE84-10776).

Registry No. **2**, 108094-05-9; **6**, 17379-35-0; **7**, 111209-65-5; **8**, 694-59-7; **9**, 26715-00-4; diphenyl phosphorochloridate, 2524-64-3; benzoyl chloride, 98-88-4; benzoic acid, 65-85-0; benzoic anhydride, 93-97-0; 3-bromopyridine, 626-55-1.

Syntheses of *p*-Phenylene- and *p*-Biphenylene-Bridged Methylated Binuclear Ferrocenes

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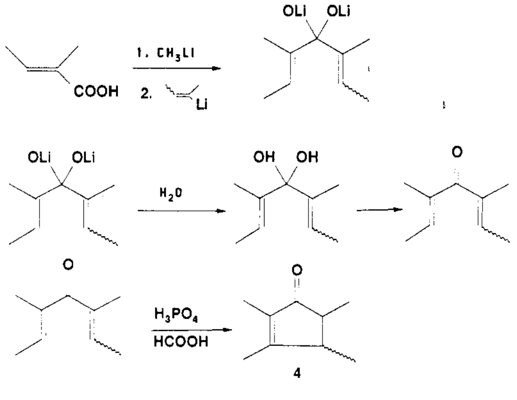
Received July 14, 1987

p-Phenylene and *p*-biphenylene-bridged methylated cyclopentadienyl rings were prepared. Reaction of the dilithio salts of the ligands with $(\eta^5\text{-}C_5Me_5)Fe(acac)$ provides cleanly ferrocenes bridged by *p*-phenylene and *p*-biphenylene groups. The electrochemistry of these compounds shows that a mixed-valence state is stabilized only in the *p*-C_6H_4-bridged species; if the bridge is extended to two aromatic rings, the individual ferrocenes do not interact. Methyl substitution on the ring increases the interaction between the metals centers as shown for $(\eta^5\text{-}C_5H_5)Fe[(\eta^5\text{-}C_5Me_4)C_6H_4(\eta^5\text{-}C_5Me_4)]Fe(\eta^5\text{-}C_5H_5)$, in which the mixed-valence state is less stable as compared with the analogous, fully methylated compound.

Introduction

Although bridged biferrocenes have been extensively investigated for their mixed-valence properties,[1] systematic variations in the bridging group, which could allow definition of the factors governing the Fe–Fe coupling, have generally not been used. We have recently adopted a general strategy for the synthesis of bridged biferrocenes different from the classical methods that involve the coupling of two ferrocene moieties.[2] Treatment of 2 equiv of $(\eta^5\text{-}C_5Me_5)Fe(acac)$ (acac = acetylacetonate) with the dilithium salt of a (cyclopentadienyl)–X–(cyclopentadienyl) linking ligand provides an efficient route to a variety of new biferrocenes joined by an unsaturated organic group X. We report herein the synthesis of new linked cyclopentadienyl ligands for which X = *p*-phenylene and *p*-biphenylene. These ligands were used to prepare biferrocenes, whose properties will also be discussed.

Scheme I



Results and Discussion

Synthesis and Characterization of *p*-Bis(3,4-dimethylcyclopentadienyl)phenylene (1), *p*-Bis(tetramethylcyclopentadienyl)phenylene (2), and *p*-Bis-

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