copper(III) complex. The marked difference in behavior suggests that there are important aspects about the pathway of electron-transfer reactions which need exploration.

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Registry No. $Cu^{I}(dpmp)_2^{3-}$, 72251-87-7; $Cu^{I}(dmp)_2^{+}$, 21710-12-3; $Cu^{III}(H_{-3}G_4)^-$, 57692-61-2; $Cu^{III}(H_{-3}A_4)^-$, 68628-66-0; $Cu^{III}(H_{-3}V_4)^-$, 62959-93-7; $Cu^{III}(H_{-3}AG_3)^-$, 69088-03-5; $Cu^{III}(H_{-2}G_3)$, 69814-94-4; $Cu^{III}(H_{-2}A_3)$, 69042-71-3; $Cu^{III}(H_{-2}Leu_3)$, 69042-72-4; $Cu^{III}(H_{-3}G_3a)$, 62801-36-9; $Cu^{III}(H_{-3}PG_2a)$, 24212-63-3; $Cu^{III}(H_{-3}G_3AOCH_3)$, 69042-73-5; $Cu^{III}(H_{-2}G_2BA)$, 69814-95-5; $Cu^{II}(dpmp)_2^{2-}$, 72244-80-5; $Ir^{IV}Cl_6^{2-}$, 16918-91-5; $Cu^{III}(H_{-2}GA_2)$, 69814-92-2.

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Synthesis and Structural Isomerism of Some (Silylamino)phosphine Oxides[1]

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The reactions of various (silylamino)phosphines with molecular oxygen and with *tert*-butyl trimethylsilyl peroxide have been investigated. The silyl peroxide was found to be a milder and more generally effective oxidant than O_2. Depending upon the steric bulk of the nitrogen substituents in the starting (silylamino)phosphine, the oxidation products were either the structurally rearranged siloxyphosphinimines $Me_3SiN{=}P(R)MeOSiMe_3$ (**1**, R = Me; **2**, R = Ph) and $t\text{-}BuN{=}PMe_2OSiMe_3$ (**3**) or the (silylamino)phosphine oxides $\overline{Me_2SiCH_2CH_2SiMe_2N}\text{–}P(O)Me_2$ (**4**) and $RMe_2SiN(Me)P(O)Me_2$ (**5**, R = Me; **6**, R = *t*-Bu). In one case where two different silyl groups were present, the disproportionation products $RMe_2SiN{=}PMe_2OSiMe_2R$ (**1**, R = Me; **7**, R = *t*-Bu) were obtained. Proton, ^{13}C, and ^{31}P NMR spectroscopic data are reported for the new oxidation products.

Introduction

The derivative chemistry of (silylamino)phosphines such as $(Me_3Si)_2NPMe_2$ is dominated by a combination of two factors: the ease of oxidation of the P^{III} center to various P^{V} forms and the ease of Si–N bond cleavage in the presence of nucleophiles. This second feature often gives rise to structurally rearranged products from reactions which would be straightforward or routine when considered solely within the realm of organophosphorus chemistry. For example, while treatment of $(Me_3Si)_2NPMe_2$ with MeI readily yields the expected phosphonium salt, subsequent dehydrohalogenation with *n*-BuLi (eq 1) results in the formation of the (silylmethyl)phosphinimine derivative[2] rather than a phosphorus ylide. Similar [1,3] silyl shifts are sometimes observed in the reactions of (silylamino)phosphines with silyl azides (eq 2).[3] The factors which appear to influence the course of these reactions have been discussed in earlier papers.[2,3]

$$[(Me_3Si)_2NP^+Me_3]I^- \xrightarrow{n\text{-BuLi}} Me_3SiN{=}PMe_2CH_2SiMe_3 \qquad (1)$$

$$R(Me_3Si)NPMe_2 \xrightarrow[-N_2]{Me_3SiN_3} RN{=}PMe_2N(SiMe_3)_2 \qquad (2)$$

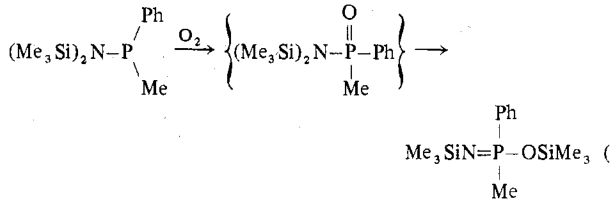
$$R = t\text{-Bu},\ t\text{-BuMe}_2\text{Si}$$

The direct oxidation of (silylamino)phosphines may also involve silyl migration since, in one previous report,[4] the siloxyphosphinimine **1** was obtained when dry O_2 was bubbled through a solution of $(Me_3Si)_2NPMe_2$ (eq 3). We report here the results of a more detailed study in which several (silylamino)phosphines were treated either with O_2 or with the nonradical oxidizing agent *tert*-butyl trimethylsilyl peroxide, $t\text{-}BuO_2SiMe_3$. The purpose of this study was twofold: (1) to determine if similar steric and electronic effects are operative in these oxidations as were found in the rearrangements involving the phosphorus ylides (eq 1) and imines (eq 2) and (2) to find a milder and safer oxidizing agent than O_2 for carrying out these reactions.

$$(Me_3Si)_2NPMe_2 \xrightarrow{O_2} \underset{\mathbf{1}}{Me_3SiN{=}PMe_2OSiMe_3} \qquad (3)$$

Results and Discussion

Reactions with O_2. When dry oxygen was bubbled through a dichloromethane solution of [bis(trimethylsilyl)amino]methylphenylphosphine for 2.5 h at room temperature, the product obtained (eq 4) in 59% yield was the rearranged siloxyphosphinimine **2**. Thus, one *P*-phenyl substituent does not prevent the oxidation from taking a course similar to that followed by the dimethyl analogue (eq 3).[4] Two phenyl groups on phosphorus are sufficient, however, to prevent oxidation since we observed no reaction, under the same conditions, between O_2 and $(Me_3Si)_2NPPh_2$. Alternatively, the diphenyl analogue of **1** and **2** has been prepared by another procedure and it also exists in the phosphinimine form.[5]



$$(Me_3Si)_2N\text{–}P(Ph)(Me) \xrightarrow{O_2} \left\{(Me_3Si)_2N\text{–}P(=O)(Ph)(Me)\right\} \longrightarrow Me_3SiN{=}P(Ph)(Me)\text{–}OSiMe_3 \qquad (4)$$

2

Including compound **2**, the new derivatives prepared in this study were either liquids of low volatility or low-melting solids which were purified by fractional distillation and characterized by ^1H and ^{13}C NMR spectroscopy and elemental analysis (Table I). The structure of **2** is confirmed by the observation of two distinct signals for the Me_3Si groups in both the ^1H and ^{13}C NMR spectra. The substantial P–C coupling constant of 3.5 Hz for one of the Me_3Si groups is also indicative of the $Me_3SiN{=}P$ linkage.[2-6]

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[1] Taken in part from the Ph.D. dissertation of J. C. Wilburn, Duke University, Durham, N.C., 1978.

[2] Wilburn, J. C.; Neilson, R. H. *Inorg. Chem.* **1979**, *18*, 347.

[3] Wilburn, J. C.; Wisian-Neilson, P.; Neilson, R. H. *Inorg. Chem.* **1979**, *18*, 1429.

[4] Wilburn, J. C.; Neilson, R. H. *Inorg. Chem.* **1977**, *16*, 2519.

[5] Neilson, R. H.; Jacobs, R. D.; Scheirman, R. W.; Wilburn, J. C. *Inorg. Chem.* **1978**, *17*, 1880.

[6] Buchner, W.; Wolfsberger, W. *Z. Naturforsch., B* **1974**, *29*, 328.

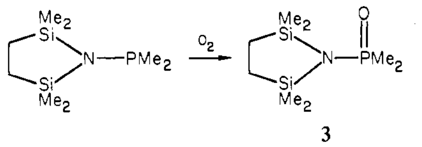
0020-1669/80/1319-0413$01.00/0

Table I. Preparative, Analytical, and NMR Spectroscopic Data for Oxidation Products

	NMR spectra[a]					prepn[b]			anal.[c]	
compd	signal	$\delta(^1H)$	J_{PH}	$\delta(^{13}C)$	J_{PC}	reacn time	% yield	bp, °C (torr)	% C	% H
$Me_3SiN{=}P(Ph)MeOSiMe_3$	Me_3SiN	−0.02		3.54	3.5	8.5 days	78	90–93 (0.5)	52.31	8.86
2	Me_3SiO	0.15		1.43		(2.5 h)	(59)		(52.13)	(8.75)
	MeP	1.41	14.0	21.08	96.4					
$Me_2\overline{SiCH_2CH_2SiMe_2N}P(O)Me_2$	Me_2Si	0.26		0.41	0.6	(2 h)	(64)	78–82 (0.2)	40.69	9.67
3	CH_2	0.76		7.96	5.9				(40.82)	(9.42)
	Me_2P	1.38	13.0	20.14	84.2					
t-$BuN{=}PMe_2OSiMe_3$	Me_3Si	0.19		1.14		9 days	51	62–63 (7.0)	48.99	10.82
4	Me_2P	1.34	13.2	19.88	98.3				(48.83)	(10.93)
	Me_3C	1.11		34.58	12.8					
	$Me_3\mathit{C}$			50.84	6.1					
$Me_3SiN(Me)P(O)Me_2$	Me_3Si	0.18		1.34		4 days	84	50 (0.01)	40.37	10.37
5	Me_2P	1.28	13.0	16.69	84.2			mp 45–46	(40.20)	(10.12)
	MeN	2.40	13.0	30.66						
t-$BuMe_2SiN(Me)P(O)Me_2$	Me_2Si	0.19		3.86		12 days	87	71 (0.10)	48.64	11.01
6	Me_2P	1.30	13.0	15.51	85.5			mp ca. 25	(48.83)	(10.93)
	Me_3C	0.96		26.03						
	$Me_3\mathit{C}$			18.72						
	MeN	2.44	13.0	31.07						
$OSiMe_2(t\text{-}Bu)$ t-$BuMe_2SiN{=}PMe_2$	Me_2SiN	0.02		−1.04	2.4	5 days	62[d]	87–90 (1.25)	52.08	11.36
7	Me_2SiO	0.32		−3.04					(52.29)	(11.28)
	Me_2P	1.53	13.0	21.42	95.8					
	Me_3CSi	0.92		25.69						
		1.00		26.83						
	$Me_3\mathit{C}SiN$			19.01	4.6					
	$Me_3\mathit{C}SiO$			24.04						

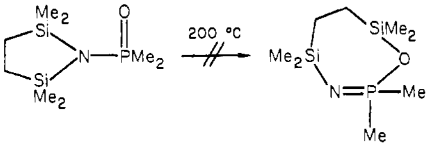
[a] Chemical shifts in ppm downfield from external Me_4Si; coupling constants in Hz. Solvents: ^1H, CH_2Cl_2; ^{13}C, $CDCl_3$. [b] Values in parentheses are for O_2 reactions; others are for t-BuO_2SiMe_3 reactions. [c] Calculated values in parentheses. [d] Estimated yield based upon disproportionation of t-$BuMe_2SiNPMe_2OSiMe_3$.

The formation of **2** presumably involves a [1,3] silyl migration from nitrogen to oxygen in the initially formed (silylamino)phosphine oxide (eq 4) although no direct evidence for such an intermediate has been obtained. NMR spectra recorded as the reaction proceeds consist only of peaks assignable to the starting phosphine and the rearranged product. A few (silylamino)phosphine oxides have, in fact, been reported,[7-10] lending support to speculation about their intermediacy in reactions such as eq 3 and 4. One example of a reversible [1,3] silyl shift has been described.[11] These systems have the common feature of containing only a single silyl substituent, but, as part of our study, we have prepared a (disilylamino)phosphine oxide (eq 5). Compound **3** is a waxlike solid which could be recovered unchanged after heating in a sealed ampule at 200 °C for 18 h (eq 6). It is concluded that the five-membered ring is sufficiently stabilizing to prevent the structural isomerization from occurring even under severe conditions. This behavior is quite different from that of the isoelectronic ylide system[2] in which the only isolated product was the structurally isomeric seven-membered ring $Me_2\overline{SiCH_2CH_2SiMe_2CH_2PMe_2N}$. The greater nucleophilicity of the ylide probably accounts for this difference in reactivity.



3

(5)



(6)

We have also studied the oxidation of other (silylamino)phosphines, but the results were much less straightforward. Indeed, it is probably more surprising that the above reactions proceeded so cleanly since the oxidation of simple phosphines is notoriously complex.[12] The *N*-alkyl derivatives $Me_3SiN(R)PMe_2$ (R = Me, t-Bu) were oxidized by O_2 (as evidenced by the characteristic[13] increase of the P–C–H coupling constant), but no identifiable products could be isolated. Hexamethyldisiloxane was observed in the ^1H NMR spectra, indicating that more than simple oxidation was taking place. The unsymmetrical (disilylamino)phosphine t-$BuMe_2Si(Me_3Si)NPMe_2$ also oxidized to give a complex mixture of products among which $(Me_3Si)_2O$, $Me_3SiN{=}PMe_2OSiMe_3$, and possibly t-$BuMe_2SiN{=}PMe_2OSiMe_2(t\text{-}Bu)$ were identified by ^1H NMR spectroscopy. Even more confusing is the fact that the less hindered compound t-$BuMe_2SiN(Me)PMe_2$ did not react with oxygen under the same reaction conditions.

Clearly, the direct oxidation of (silylamino)phosphines is, with a few exceptions (**1**–**3**), not a general synthetic route to (silylamino)phosphine oxides or the isomeric siloxyphosphinimines. The utility of the method is further complicated by its hazardous nature (see Experimental Section) which prevents the use of large quantities of reagents.

Reactions with t-BuO_2SiMe_3. In view of these shortcomings, it was necessary to search for other reagents which would be generally useful for the oxidation of (silylamino)phosphines. Only aprotic oxidizing agents can be used in these systems due to the high reactivity of the Si–N bond, thus precluding the

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(7) Keat, R. *J. Chem. Soc. A* **1970**, 1795.
(8) Roesky, H. W.; Glere, H. H. *Z. Naturforsch., B* **1970**, *25*, 773.
(9) Glidewell, C. *J. Organomet. Chem.* **1976**, *108*, 335.
(10) Neilson, R. H.; Kusterbeck, W. A. *J. Organomet. Chem.* **1979**, *166*, 309.
(11) Hodgson, P. K. G.; Katz, R.; Zon, G. *J. Organomet. Chem.* **1976**, *117*, C63.
(12) Hays, H. R.; Peterson, D. J. *Org. Phosphorus Compd.* **1972**, *3*, 341.
(13) Mavel, G. *Annu. Rep. NMR Spectrosc.* **1973**, *5B*, 1.

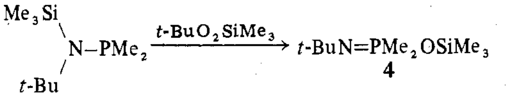
use of many oxidants commonly employed in organophosphorus chemistry.[12] Dimethyl sulfoxide, which readily converts the dichlorophosphine $t\text{-BuMe}_2\text{SiN(Me)PCl}_2$ to the corresponding oxide,[10] was unreactive toward the organo substituted (silylamino)phosphines utilized in this study.

Brandes and Blaschette[14] have shown that *tert*-butyl trimethylsilyl peroxide, $t\text{-BuO}_2\text{SiMe}_3$, reacts smoothly with triphenylphosphine to afford high yields of triphenylphosphine oxide. This report and the commercial availability of the silyl peroxide prompted us to attempt similar oxidations of (silylamino)phosphines. Accordingly, when equimolar quantitites of $(\text{Me}_3\text{Si})_2\text{NPMe}_2$ and the peroxide were allowed to react in CH_2Cl_2 at room temperatures, the ^{1}H NMR spectrum of the mixture showed complete reaction after 18 h (eq 7). Subsequent fractional distillation gave compound **1** in 81% yield as compared to 49% from the direct oxidation method (eq 3). The phenylmethylphosphine $(\text{Me}_3\text{Si})_2\text{NP(Ph)Me}$ reacted similarly but more slowly (reaction time of ca. 8.5 days) to afford compound **2** in 78% yield.

$$(\text{Me}_3\text{Si})_2\text{NPMe}_2 + t\text{-BuO}_2\text{SiMe}_3 \xrightarrow[25\ ^\circ\text{C}]{\text{CH}_2\text{Cl}_2} \underset{\mathbf{1}}{\text{Me}_3\text{SiN=PMe}_2\text{OSiMe}_3} + t\text{-BuOSiMe}_3 \quad (7)$$

The silyl ether, $t\text{-BuOSiMe}_3$, is a volatile, easily removed byproduct which was identified by ^{1}H NMR spectroscopy. As was the case for the O_2 reaction, monitoring the reaction by ^{1}H NMR was useful for following its progress, but no signals assignable to a phosphine oxide intermediate were observed.

In contrast to the complexity of their reactions with O_2, the *N*-alkyl-substituted (silylamino)phosphines reacted slowly (over ca. 4–12 days) but cleanly with $t\text{-BuO}_2\text{SiMe}_3$ to afford oxidation products (eq 8 and 9) which were readily isolated and characterized. The rearranged structure of compound **4** is assigned on the basis of the similarity of its ^{13}C NMR spectrum to those obtained on related compounds containing the *tert*-butylimino substituent on phosphorus.[2,3] The P–N–C and P–N–C–C coupling constants of 6.1 and 12.8 Hz, respectively, are particularly diagnostic. On the other hand, when a less bulky group (i.e., Me) is present on nitrogen, there is strong evidence that the products of the oxidation (eq 9) are simply the (silylamino)phosphine oxides **5** and **6**. First, the observed ^{31}P chemical shifts (for **5**, −45.2 ppm; for **6**, −45.7 ppm)[15] are in good agreement with the value of −44.1 ppm reported for the model compound $\text{Me}_2\text{NP(O)Me}_2$.[16] The rearranged phosphinimines **1**, **2**, and **4** have quite different ^{31}P chemical shifts of −13.5,[17] −8.8, and −10.7 ppm, respectively. Second, compounds **5** and **6** have much higher boiling points than the phosphines from which they were prepared. Conversely, the rearranged compounds **1**, **2**, and **4** which do not contain the very polar phosphoryl moiety are actually somewhat more volatile than their phosphine precursors. Third, the ylide analogues of **5** and **6** in which a P=CH_2 function replaces the P=O bond also do not rearrange but instead give products resulting from attack on the solvent by the highly reactive ylide center.[2]



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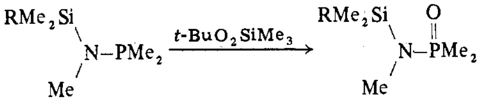
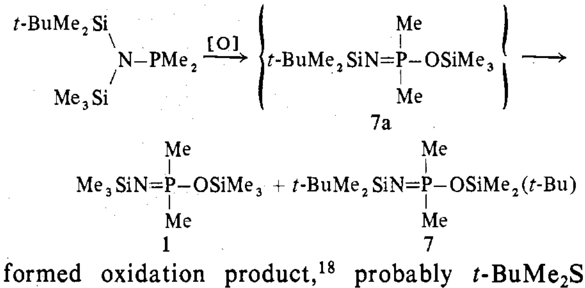
(8)



(9)

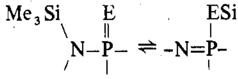
5, R = Me
6, R = *t*-Bu

The oxidation of the (disilylamino)phosphine $t\text{-BuMe}_2\text{Si(Me}_3\text{Si)NPMe}_2$ with the silyl peroxide also proved to be more straightforward than it was with oxygen. The reaction did, however, take a different course than those described above. The products isolated from the reaction mixture by fractional distillation were the bis(trimethylsilyl) compound **1** and the analogous bis(*tert*-butyldimethylsilyl) compound **7**. It is most likely that these symmetrically substituted compounds are formed via the disproportionation (eq 10) of some initially formed oxidation product,[18] probably $t\text{-BuMe}_2\text{SiN=PMe}_2\text{OSiMe}_3$ (**7a**). Proton NMR spectra obtained on the crude reaction product show major peaks which can be tentatively assigned to the mixed disilyl compound **7a**. This material decomposes slowly upon standing and more rapidly when distillation is attempted. Careful fractional distillation gave two clean fractions which were identified as compounds **1** and **7**. An intermediate fraction appeared to contain **7a** with significant amounts of the less volatile compound **7**. The reaction gave no detectable amounts of $(\text{Me}_3\text{Si})_2\text{O}$ or other cleavage products as were observed in the O_2 reaction of the same phosphine, further suggesting that **1** and **7** are formed by a disproportionation process. Interestingly this is the only example of an *inter*molecular silyl-exchange reaction among any of the Si–N–P systems which we have studied.



(10)

Conclusions. The oxidation of (silylamino)phosphines with *tert*-butyl trimethylsilyl peroxide and to a lesser extent with oxygen is an effective general synthetic route to various oxidation products. Depending upon the nature of the nitrogen substituents, these oxidation products may be the simple phosphine oxides (eq 5, 9), the siloxyphosphinimines (eq 4, 7, 8), or the disproportionation products (eq 10). The structural difference between the *tert*-butyl compound **4** and the *N*-methyl analogues **5** and **6** strongly suggests that sterically bulky substituents at nitrogen tend to favor the silyl migration process. A similar steric effect was found to be operative in the phosphinimines[3] and phosphorus ylides[2] (eq 11) which are isoelectronic with the (silylamino)phosphine oxides described herein. Taken in combination, the results of this and our previous studies[2,3] convincingly demonstrate the generality of the silyl migration phenomenon in Si–N–P systems. Moreover, the tendency for structural isomerization (eq 11) follows a trend ($\text{E} = \text{CH}_2 > \text{O} > \text{NR}$) which is consistent with the relative nucleophilic nature of the P=E functional groups.



$\text{E} = \text{O, NR, CH}_2$ (11)

Experimental Section

Caution. *The reaction of (silylamino)phosphines with oxygen is potentially hazardous.* In one experiment involving the reaction of $(\text{Me}_3\text{Si})_2\text{NPMe}_2$ (10 g) with O_2 in CH_2Cl_2 (10 mL), a *violent explosion* occurred without warning after the reaction had been in progress for ca. 30 min. The same synthesis[4] has been performed many

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(14) Brandes, D.; Blaschette, A. *J. Organomet. Chem.* **1975**, *99*, C33.

(15) Negative values represent downfield shifts from external H_3PO_4 reference.

(16) Mark, V.; Dungan, C. H.; Crutchfield, M. M.; Van Wazer, J. R. *Top. Phosphorus Chem.* **1967**, *5*, 347.

(17) Volkholz, M.; Stelzer, O.; Schmutzler, R. *Chem. Ber.* **1978**, *111*, 890.

(18) A separate experiment showed that the starting phosphine does not disproportionate under comparable conditions.

times without incident with smaller quantities (ca. 3-5 g) of the phosphine. *The use of appropriate safety shields is essential.*

Materials and General Procedures. The (silylamino)phosphine reagents were prepared according to the published procedures.[2] *tert*-Butyl trimethylsilyl peroxide was purchased from Petrarch Systems, Inc., and used without further purification. Dichloromethane was distilled from P_2O_5 and stored over molecular sieves. Proton, ^{13}C, and ^{31}P NMR spectra were recorded on JEOL MH-100 and FX-60 spectrometers. Infrared spectra were obtained on a Perkin-Elmer 297 or Beckman IR-4250 spectrophotometer. Elemental analyses were performed by the Schwarzkopf Microanalytical Laboratory, Woodside, N.Y.

All reactions and other manipulations were carried out under an atmosphere of dry nitrogen. The following procedures are typical of those used in the oxidation of (silylamino)phosphines with O_2 or $t\text{-BuO}_2\text{SiMe}_3$. Preparative, analytical, and NMR spectroscopic data for all of the new compounds are summarized in Table I.

Preparation of *P*-Methyl-*P*-phenyl-*P*-(trimethylsiloxy)-*N*-(trimethylsilyl)phosphinimine (2). Oxygen, dried by passing slowly through a trap cooled to −78 °C, was bubbled through a solution of $(\text{Me}_3\text{Si})_2\text{NP(Ph)Me}$ (16.1 mmol) in CH_2Cl_2 (25 mL) at room temperature. As determined by ^1H NMR spectroscopy, the reaction was complete in about 2.5 h. After removal of solvent under vacuum, distillation afforded **2** as a colorless liquid (2.81 g, 59% yield; bp 90-93 °C (0.5 torr)).

Preparation of [(*tert*-Butyldimethylsilyl)methylamino]dimethylphosphine Oxide (6). *tert*-Butyl trimethylsilyl peroxide (23.0 mmol) was added to a stirred solution of $t\text{-BuMe}_2\text{SiN(Me)PMe}_2$ (23.0 mmol) in CH_2Cl_2 (25 mL) under a nitrogen atmosphere. The flask was tightly stoppered, and the mixture was allowed to stir at room temperature for 12 days during which time the progress of the reaction was periodically checked by ^1H NMR. After removal of the solvent and $t\text{-BuOSiMe}_3$ under reduced pressure, distillation afforded **6** as a colorless liquid (4.41 g, 87% yield, bp 59-64 °C (0.01 torr)) which partially solidified to needlelike crystals (mp ca. 25 °C). IR spectrum (neat liquid): 2950 (s), 2920 (s), 2890 (sh), 2850 (s), 1555 (m), 1410 (m), 1390 (sh), 1355 (w), 1290 (s), 1250 (s), 1190 (s, br), 1070 (s), 1050 (br, sh), 925 (s), 890 (s), 850 (s), 825 (s), 785 (s), 730 (s), 670 (m), 580 (w), 475 (w), 410 (m) cm^{-1}.

Silyl Peroxide Oxidation of $t\text{-BuMe}_2\text{Si(Me}_3\text{Si)NPMe}_2$. In a manner similar to that described above for the synthesis of **6**, equimolar quantities (29.0 mmol) of the reactants were allowed to stir in CH_2Cl_2 (25 mL) for 5 days at room temperature. Solvent removal left a colorless liquid residue which was tentatively characterized as mainly $t\text{-BuMe}_2\text{SiN}{=}\text{PMe}_2\text{OSiMe}_3$ by its ^1H NMR spectrum (20% v/v in CH_2Cl_2): Me_2Si singlet (δ 0.00), Me_3Si singlet (δ 0.33), *t*-Bu singlet (δ 0.90), and Me_2P doublet (δ 1.42, J_{PCH} = 13.5 Hz). Distillation gave three major fractions: (A) bp 34-43 °C (1.25 torr), 1.25 g, identified as $\text{Me}_3\text{SiN}{=}\text{PMe}_2\text{OSiMe}_3$ (**1**); (B) bp 62-66 °C (1.25 torr), 2.92 g, identified as mainly a mixture of fractions A and C along with some $t\text{-BuMe}_2\text{SiN}{=}\text{PMe}_2\text{OSiMe}_3$; (C) bp 67-90 °C (1.25 torr), 2.90 g, identified as $t\text{-BuMe}_2\text{SiN}{=}\text{PMe}_2\text{OSiMe}_2(t\text{-Bu})$ (**7**). The last portion of the distillate solidified in the condenser. This portion was combined with fraction C, and the mixture was redistilled to afford an analytically pure sample of **7** (bp 87-90 °C (1.25 torr)) as a low-melting slushy solid. After standing for 2 weeks, fraction B was shown by ^1H NMR to contain increased amounts of the disproportionation products **1** and **7**.

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Polymer-Anchored Metal Oxide Particles. 1. Superparamagnetic Magnetite Microcrystals Stabilized by Lignosulfonate

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Physical data are used to show that microcrystals (ca. 100 Å diameters) of magnetite can be stabilized by polymeric lignosulfonate. X-ray powder patterns indicate Fe_3O_4; line broadening in the patterns reflects the small size of the microcrystals. Magnetic susceptibility and ^{57}Fe Mössbauer results indicate that these materials are superparamagnetic and that the size of the magnetite microcrystals can be readily varied. Dissolution of these water-soluble magnetite-lignosulfonate solids gives ferrofluids and the magnetization of one of these ferrofluids has been measured.

Introduction

Ferrofluids consist of ca. 100 Å diameter particles of a magnetic solid (usually magnetite, Fe_3O_4) colloidally suspended in a carrier fluid.[2-4] Typical carrier fluids include hydrocarbons, water, fluorocarbons, esters, diesters, organometallics, polyphenyl ethers, and silicones. Surfactants such as oleic acid and other small molecules as well as a few polymers have been used to coat the surface of microcrystalline Fe_3O_4 to help prevent particle flocculation. At present, the only general approach used to synthesize ferrofluids involves placing the *bulk* magnetic compound, surfactant, and carrier liquid in a ball mill half-filled with steel balls and *grinding for 1-6 months.* It is of considerable interest, thus, to develop better synthetic approaches for ferrofluids, particularly since their unusual magnetic properties are finding applications in loudspeakers, zero-leakage seals, damping liquids, nonwearing electrical switches, artificial muscles,[2] magnetic inks,[5] ore separation,[6,7] and energy converters.[8]

In view of the desirability of identifying simple syntheses of ferrofluids, our interest was drawn to reports[9,10] that highly

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(1) A. P. Sloan Foundation Fellow, 1976-1978.
(2) Kaiser, R.; Rosensweig, R. E. Report CR-1407; NASA: Washington, DC, 1969; p 1.
(3) Moskowitz, R. *IEEE Spectrum* **1975**, *12* (3), 53.
(4) Khalafalla, S. E. *CHEMTECH* **1975**, 540.
(5) Kuhl, L.; Myers, R. A. *Sci. Am.* **1979**, April, 162.
(6) Andres, U. T. *Mater. Sci. Eng.* **1976**, *26*, 269.
(7) Khalafalla, S. E.; Reimers, G. W. *AIME Trans.* **1973**, *254*, 193.
(8) Rosensweig, R. E. *Int. Sci. Technol.* **1966**, 48.
(9) Briggs, W. S.; Kjargaard, N. J. U.S. Patent 4019995, April 26, 1977.

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