

SYNTHESIS AND SPECTROSCOPIC STUDIES OF SOME NEW DIORGANOBIS(IMINOXY)SILANES

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Summary

Novel silicon derivatives of the type $\text{MePhSi}(\text{ON}=\text{CR}^1\text{R}^2)_2$ and $\text{Ph}_2\text{Si}(\text{ON}=\text{CR}^1\text{R}^2)_2$ have been prepared, and their reactions with acetyl chloride, acetic anhydride and diorganodichlorosilane examined.

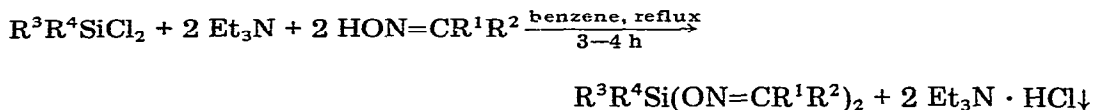
Introduction

A large number of oxime derivatives containing R_3Si moieties have been prepared and investigated in this and other laboratories [1], but there are few reports on compounds of the type $\text{R}_2\text{Si}(\text{ON}=\text{CR}^1\text{R}^2)_2$ [2].

The interesting results of studies of compounds of the type $\text{R}_3\text{SiON}=\text{CR}^1\text{R}^2$ [2] and $\text{Me}_2\text{Si}(\text{ON}=\text{CR}^1\text{R}^2)_2$ [2] encouraged us to examine oxime derivatives containing diorganosilyl group moieties, and we describe below the preparation and properties of some new methylphenyl- and diphenyl-diiminoxysilanes.

Results and discussion

Diphenyl- and methylphenyl-diiminoxysilanes were prepared by refluxing the diorganodichlorosilane with oxime in 1 : 2 molar ratio in the presence of an excess of triethylamine (~15–20% excess) in benzene:

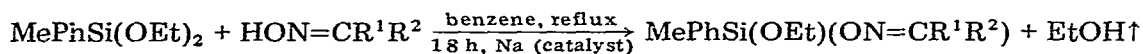


($\text{R}^1, \text{R}^2 = \text{Me, Me; Me, Et; Et, Et; Me, Pr; Me, Ph; H, Me; H, Ph; R}^3 = \text{Me or Ph; R}^4 = \text{Ph}$).

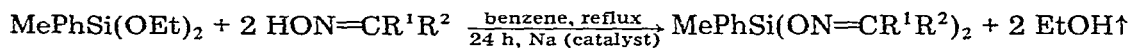
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An alternative route to diorganoiminoxysilanes involves treatment of methylphenyldiethoxysilane with an oxime, such as acetoxime in 1 : 1 or 1 : 2 molar ratio. Reaction is very sluggish in the absence of a catalyst, but can be forced to completion by use of metallic sodium as catalyst.

Methylphenylethoxyiminoxysilane was obtained when methylphenyldiethoxysilane and acetoxime were brought into reaction in equimolar ratio with subsequent removal of ethanol azeotropically during 18 h.



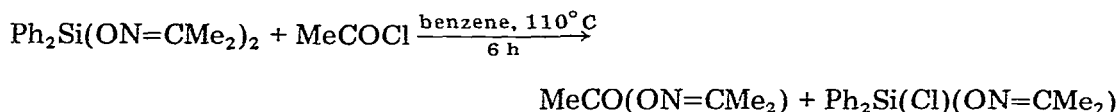
When this reaction was carried out under identical conditions with 1 : 2 molar quantities of reactants, 24 h were required for completion:



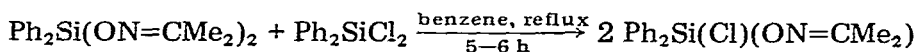
All these new organodiiminoxysilanes are colourless to reddish or green volatile solids or liquids. These are susceptible to hydrolysis, soluble in common organic solvents, and monomeric in refluxing benzene.

Reactions of diiminoxydiphenylsilane

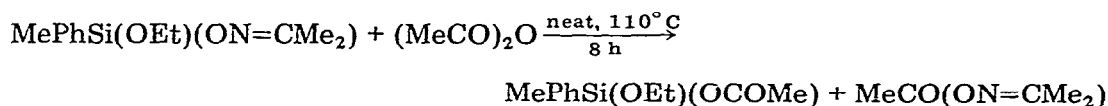
Treatment of $\text{Ph}_2\text{Si}(\text{ON}=\text{CMe}_2)_2$ with acetyl chloride gave the oxime ester and $\text{Ph}_2\text{Si}(\text{Cl})(\text{ON}=\text{CMe}_2)$.



When $\text{Ph}_2\text{Si}(\text{ON}=\text{CMe}_2)_2$ was refluxed with Ph_2SiCl_2 in equimolar ratio in benzene for 5–6 h, exchange of iminoxy and chloro groups occurred:



Methylphenyliminoxyethoxysilane was brought into reaction with neat acetic anhydride



Distillation of the products gave the oxime ester and methylphenylethoxyacetoxysilane, indicating cleavage of the Si—O bond of $\text{Si}=\text{O}-\text{N}=\text{CMe}_2$ in preference to that of $\text{Si}-\text{O}-\text{Et}$.

IR spectra

The IR spectra of the new diorganoiminoxysilanes show a weak to medium intensity band in the region $1625-1640 \text{ cm}^{-1}$ which may be attributed to the C=N stretch [3–5]. Strong bands characteristic of phenyl groups attached to silicon [6–8] appear at 1124 ± 2 , 1429 ± 2 , 723 ± 4 and $698 \pm 2 \text{ cm}^{-1}$. An

intense, sharp band in the region $1256\text{--}1265\text{ cm}^{-1}$ corresponds to Si-CH_3 deformation [6] while an absorption in the region $815\text{--}760\text{ cm}^{-1}$ is assigned to the methyl rocking and Si-C stretching mode [6]. A very intense band in the region $900\text{--}940\text{ cm}^{-1}$ is attributed to the N-O stretching mode [4]. An absorption of medium intensity in the region $830\text{--}870\text{ cm}^{-1}$ can be tentatively assigned to $\nu_a(\text{Si-O})$ stretching [9]. Strong absorption bands in the region $1020\text{--}1050\text{ cm}^{-1}$ are probably associated with the Si-O-N bond but in the parent methyl ketoximes the CH_3 non-planar [3] deformations are generally observed in the region $1030\text{--}1100\text{ cm}^{-1}$.

PMR spectra

Earlier PMR studies on oximes [10] and *O*-organometal oximes [11] indicated separation of the resonances for the protons on the carbon atoms next to the $>\text{C=N-O}$ group when an aromatic solvent was present or when the oxime molecule contained an aromatic substituent. In order to examine the influence of the silylphenyl group on the PMR signals of silylated oximes, the proton magnetic resonance spectra of some diphenyl- and methylphenyl-diiminoxysilanes were studied. The PMR spectral data are reported in Table 1, together with assignments for the peaks. The main features are: (i) separation of the lines for methylene and/or methyl protons of the alkyl groups attached to the imino carbon atom is observed even in non-aromatic solvents such as carbon tetrachloride; (ii) two multiplets with an integrated ratio of 2 : 3 appear in the region τ 2.0–3.0, and are assignable to the aromatic protons of the silylphenyl group. The *meta* and *para* protons (τ 2.5–3.0) are more highly shielded [12] than the *ortho* protons; (iii) replacement of chlorine atoms from methylphenyl-dichlorosilane by the iminoxy groups causes shielding of the silylmethyl protons by ~ 0.50 ppm. This is probably due to the combined effect of the lower electronegativity of the iminoxy groups compared with a chlorine atom, and the possibility of $p_\pi\text{--}d_\pi$ bonding (from the iminoxy oxygen to the silicon atom), which restores the electron density on the silicon atom.

Experimental

Rigorous precautions were taken to exclude moisture during the syntheses. Freshly-distilled diorganodichlorosilanes, diorganodiethoxysilanes, anhydrous benzene, and triethylamine were used. Oximes were prepared by standard methods [13].

Nitrogen was estimated by the Kjeldahl method, ethanol by oxidation with 1 *N* potassium dichromate in 12.5% sulphuric acid [14], and silicon as SiO_2 .

IR spectra were recorded as liquid films or Nujol mulls on a Perkin–Elmer model 337 spectrometer. The PMR spectra were measured on a Perkin–Elmer R12B spectrometer, in CCl_4 .

Preparation of methylphenyl- and diphenyl-diiminoxysilanes

(a) To an equimolar mixture of appropriate oxime and triethylamine ($\sim 10\text{--}20\%$ excess) in benzene (20 ml), the calculated quantity of methylphenyl- or diphenyldichlorosilane was added dropwise. An exothermic reaction took place, with immediate separation of solid $\text{Et}_3\text{N} \cdot \text{HCl}$. The mixture was refluxed for

TABLE 1
PMR SPECTRAL DATA FOR SOME ORGANOIMINOXYSILANES IN CARBON TETRACHLORIDE

Compound	Chemical shifts ^a (τ , ppm)				
	Si-CH ₃	Si-C ₆ H ₅	CH ₃ N=C	CH ₂ CH ₃ N=C	(CH ₂) _n N=C
MePhSi(ON=CHMe) ₂	9.46	2.10-2.90	8.10-8.40 ^b (centred at 8.25)	—	anti ^c (2.9-3.4) q, $J = 6$ Hz
MePhSi(ON=CMe ₂) ₂	9.46	2.10-2.90	8.10, 8.15	—	—
MePhSi(ON=CMeEt) ₂	9.42	2.10-2.90	8.08, 8.12	—	8.9 (t, $J = 7$ Hz)
Ph ₂ Si(ON=CMe ₂) ₂	—	2.10-3.00	8.10, 8.12	—	—
Ph ₂ Si(ON=CMeEt) ₂	—	2.10-3.00	8.14, 8.26	8.70-9.30 ^d (centred at 9.00)	7.30-8.08 (quintet, $J = 7$ Hz)
Ph ₂ Si(ON=CMePr ^H) ₂	—	2.10-3.00	8.18, 8.28	8.98-9.50 ^e	7.46-8.98 ^f
Ph ₂ Si(ON=CEt ₂) ₂	—	2.18-3.00	—	8.50-9.30 (multiplet)	7.30-8.20 (sextet, $J = 7$ Hz)

^a Downfield TMS: t, triplet; q, quartet. ^b Two doublets overlapping giving approximately a triplet ($J = 6$ Hz). ^c The azomethine *syn* proton is seen to be overlapping the phenyl C-H resonance. ^d Approximately two triplets ($J = 7$ Hz). ^e Two triplets overlapping giving approximately a quartet ($J = 7$ Hz). ^f Broad multiplet due to the methylene protons of the alkyl group attached to the imino carbon atom.

TABLE 2

REACTIONS OF DIORGANODICHLOROSILANES WITH OXIMES (1 : 2 MOLAR RATIO) IN THE PRESENCE OF TRIETHYLAMINE

Sample No.	Reagents	Product ^a (% yield)		Nature	B.p. (°C/mmHg)	Analysis found (calcd.) (%)		²⁸ n _D	
		R ³ R ⁴ SiCl ₂ R ³ , R ⁴ (g)	R ¹ R ² C=NOH R ¹ , R ² (g)			Et ₃ N (g)	Si		N
1	Ph, Ph (2.54)	Me, Me (1.46)	(2.06)	Ph ₂ Si(ON=CMe ₂) ₂ (78)	Yellow solid	196/3.0	8.56 (8.60)	8.36 (8.57)	—
2	Ph, Ph (2.54)	Me, Et (1.64)	(2.32)	Ph ₂ Si(ON=CMeEt) ₂ (77)	Yellow viscous liquid	178/0.6	7.88 (7.92)	7.78 (7.90)	1.5348
3	Ph, Ph (4.01)	Et, Et (3.15)	(4.27)	Ph ₂ Si(ON=CEt ₂) ₂ (60)	Yellow red viscous liquid	174/0.2	7.30 (7.34)	7.22 (7.32)	—
4	Ph, Ph (2.67)	Me, Pr (2.06)	(2.40)	Ph ₂ Si(ON=CMePr) ₂ (60)	Yellow viscous liquid	182/0.3	7.28 (7.34)	7.24 (7.32)	1.5290
5	Ph, Ph (2.66)	Ph, H (2.54)	(2.50)	Ph ₂ Si(ON=CPhH) ₂ (50)	Yellow green viscous liquid	188/0.2	6.62 (6.65)	6.35 (6.60)	1.5655
6	Ph, Ph (2.39)	Ph, Me (2.50)	(2.04)	Ph ₂ Si(ON=CMePh) ₂ (47)	Yellow green viscous liquid	197/0.1	6.19 (6.24)	5.98 (6.22)	—
7	Me, Ph (2.08)	Me, H (1.26)	(2.18)	MePhSi(ON=CMeH) ₂ (74)	Colourless liquid	106/0.9	11.82 (11.89)	11.75 (11.86)	1.5020
8	Me, Ph (1.62)	Me, Me (1.23)	(1.89)	MePhSi(ON=CMe ₂) ₂ (73)	Yellow liquid	114—118/1.0	10.56 (10.63)	10.40 (10.59)	1.5030
9	Me, Ph (1.24)	Me, Et (2.10)	(1.91)	MePhSi(ON=MeEt) ₂ (67)	Yellow liquid	138/1.8	9.57 (9.61)	9.30 (9.58)	1.4942
10	Me, Ph (1.01)	Et, Et (1.05)	(1.23)	MePhSi(ON=CEt ₂) ₂ (65)	Yellow liquid	146/1.3	8.69 (8.77)	8.43 (8.74)	1.4900
11	Me, Ph (1.17)	Me, Pr (1.13)	(1.26)	MePhSi(ON=CMePr) ₂ (65)	Yellow liquid	136/0.5	8.73 (8.77)	8.49 (8.74)	1.4892
12	Me, Ph (1.20)	Ph, H (1.50)	(1.45)	MePhSi(ON=CPhH) ₂ (52)	Yellow highly viscous liquid	183/0.9	7.76 (7.80)	7.52 (7.78)	—
13	Me, Ph (1.17)	Ph, Me (1.62)	(1.34)	MePhSi(ON=CPhMe) ₂ (50)	Yellow green viscous liquid	197/0.9	7.19 (7.24)	6.84 (7.22)	—

^a All compounds are monomeric in refluxing benzene.

3–4 h, triethylamine hydrochloride was filtered off, and solvent removed. The residual liquid on distillation under reduced pressure gave the iminoxysilane (Table 2).

(b) A solution containing acetoxime (1.24 g, 16.94 mmol), methylphenyldiethoxysilane (1.78 g; 8.5 mmol), benzene (ca. 35 ml) and a catalytic amount of sodium (0.0004 g) was refluxed, and the liberated ethanol removed azeotropically with benzene during 24 h. After removal of solvent, the residual liquid was distilled under reduced pressure to give $\text{MePhSi}(\text{ON}=\text{CMe}_2)_2$, b.p. 114–118°C/1.0 mm. (Found: N, 10.48; Si, 10.60; EtOH, 0.76 g (in the azeotrope). $\text{C}_{13}\text{H}_{20}\text{N}_2\text{O}_2\text{Si}$ calcd.: N, 10.59; Si, 10.63%. EtOH, 0.78 g.)

Preparation of methylphenyliminoxysilane

A mixture containing acetoxime (0.72 g, 9.81 mmol), methylphenyldiethoxysilane (2.06 g; 9.80 mmol), sodium metal (0.0005 g) was refluxed below a fractionating column and ethanol was removed azeotropically with benzene during 18 h. After removal of volatiles, distillation under reduced pressure gave $\text{MePhSi}(\text{OEt})(\text{ON}=\text{CMe}_2)$, b.p. 98°C/0.5 mmHg. (Found: N, 5.75; Si, 11.77; EtOH, 0.43 g (in the azeotrope). $\text{C}_{12}\text{H}_{19}\text{NO}_2\text{Si}$ calcd.: N, 5.90; Si, 11.84%; EtOH, 0.45 g.)

Reaction of diphenyldiiminoxysilane with acetyl chloride

A mixture of $\text{Ph}_2\text{Si}(\text{ON}=\text{CMe}_2)_2$ (1.27 g, 3.89 mmol) acetyl chloride (0.305 g, 3.88 mmol) and benzene (ca. 10 ml) was heated for 6 h at 110°C. Removal of the solvent followed by distillation under reduced pressure gave $\text{Ph}_2\text{SiCl}(\text{ON}=\text{CMe}_2)$, b.p. 153°C/0.9 mmHg (Found: N, 4.64; Si, 9.67, Cl, 12.18. $\text{C}_{15}\text{H}_{16}\text{ClNOSi}$, calcd.: N, 4.83; Si, 9.70; Cl, 12.24%) and oxime ester, b.p. 86°C/20 mmHg. (Found: N, 12.09. $\text{C}_5\text{H}_9\text{NO}_2$ calcd.: N, 12.20%.)

Interaction of diphenyldiiminoxysilane with diphenyldichlorosilane

To a benzene solution of $\text{Ph}_2\text{Si}(\text{ON}=\text{CMe}_2)_2$ (0.67 g, 2.04 mmol) was added Ph_2SiCl_2 (0.53 g, 2.04 mmol). The mixture was refluxed for 5–6 h and solvent removed in vacuo. Distillation of the residue under reduced pressure afforded $\text{Ph}_2\text{SiCl}(\text{ON}=\text{CMe}_2)$, b.p. 153°C/0.9 mmHg. (Found: N, 4.71; Si, 9.61; Cl, 12.15. $\text{C}_{15}\text{H}_{16}\text{ClNOSi}$ calcd.: N, 4.83; Si, 9.70; Cl, 12.24%.)

Interaction of methylphenylethoxyiminoxysilane with acetic anhydride

Methylphenylethoxyiminoxysilane (0.98 g, 4.13 mmol) and acetic anhydride (0.42 g, 4.12 mmol) were heated together at 110°C for 8 h. Distillation under reduced pressure gave $\text{MePhSi}(\text{OCOMe})(\text{OEt})$, b.p. 87–90°C/2.5 mmHg. (Found: Si, 12.48. $\text{C}_{11}\text{H}_{16}\text{O}_3\text{Si}$ calcd.: Si, 12.52%) and $\text{Me}_2\text{C}=\text{NOCOMe}$, b.p. 72–73°C/15 mmHg. (Found: N, 12.00. $\text{C}_5\text{H}_9\text{NO}_2$ calcd.: N, 12.20%.)

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