# Synthesis and Characterisation of some Organo(imino-oxy)silanes

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Oximes form monomeric complexes, $\mathrm{Me}_n\mathrm{Si(ON{:}CR^1R^2)}_{4-n}$ ($n$ = 0—3), which appear to be tetrahedral, except for the derivatives, $\mathrm{Me_3SiON{:}CHR}$ (R = 2-pyridyl or 4-pyridyl) which appear to be five-co-ordinate.

IN CONTRAST to amino- and alkoxy-silanes [1] few organo(dialkylimino-oxy)silanes have been reported.[2] Oxime derivatives of B, Al, Ga, In, Tl,[3] Sn,[4] and Ti [5] have been studied.

Oxime derivatives of silicon(IV) were prepared by routes (1)—(6).

$$\mathrm{Me}_n\mathrm{SiCl}_{4-n} + (4-n)\mathrm{HON{:}CR^1R^2} + (4-n)\mathrm{Et_3N} \xrightarrow[100-105^\circ]{\text{PhH, reflux}} \mathrm{Me}_n\mathrm{Si(ON{:}CR^1R^2)}_{4-n} + (4-n)\mathrm{Et_3N,HCl} \quad (1)$$

($\mathrm{R^1}$ = Me or Et, $\mathrm{R^2}$ = Me, Et, $\mathrm{Pr^n}$, $\mathrm{Pr^i}$, $\mathrm{Bu^n}$ or $\mathrm{Bu^i}$ when $n = 1$; $\mathrm{R^1}$ = H, Me or Et, $\mathrm{R^2}$ = Me, Et, $\mathrm{Pr^n}$, $\mathrm{Pr^i}$, $\mathrm{Bu^n}$ or $\mathrm{Bu^i}$ when $n = 2$; $\mathrm{R^1}$ = H, Me, or Et, $\mathrm{R^2}$ = Et, $\mathrm{Pr^n}$, $\mathrm{Pr^i}$, $\mathrm{Bu^n}$, $\mathrm{Bu^i}$, 2-pyridyl, 4-pyridyl or $\mathrm{R^1 = R^2 = [CH_2]_4}$ when $n = 3$).

$$\mathrm{Me_2Si(OEt)_2 + 2HON{:}CR^1R^2} \xrightarrow[105-110^\circ]{\text{PhH, Na, reflux}} \mathrm{Me_2Si(ON{:}CR^1R^2)_2 + 2EtOH} \quad (2)$$

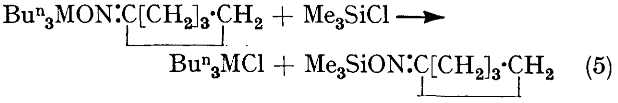
($\mathrm{R^1}$ = Me; $\mathrm{R^2}$ = Me or Et)

$$\mathrm{Me_3SiNEt_2 + HON{:}CR^1R^2} \longrightarrow \mathrm{Me_3SiON{:}CR^1R^2 + Et_2NH} \quad (3)$$

($\mathrm{R^1}$ = H, Me or Et; $\mathrm{R^2}$ = Me, Et, $\mathrm{Pr^n}$, $\mathrm{Pr^i}$ or $\mathrm{R^1 = R^2 = [CH_2]_4}$)

$$\mathrm{SiCl_4 + 4C_5H_5N + 4HON{:}CR^1R^2} \xrightarrow[\text{reflux, }105-110^\circ]{\text{PhH,}} \mathrm{Si(ON{:}CR^1R^2)_4 + 4C_5H_5N,HCl} \quad (4)$$

($\mathrm{R^1}$ = Me, $\mathrm{R^2}$ = Me or Et)



$$\mathrm{Bu^n_3MON{:}C[CH_2]_3{\cdot}CH_2 + Me_3SiCl} \longrightarrow \mathrm{Bu^n_3MCl + Me_3SiON{:}C[CH_2]_3{\cdot}CH_2} \quad (5)$$

(M = Ge or Sn)

$$\mathrm{NaON{:}CMe_2 + Me_3SiCl} \xrightarrow[\text{reflux}]{\text{light petroleum}} \mathrm{Me_3SiON{:}CMe_2 + NaCl} \quad (6)$$

The products were generally colourless, mobile, moisture-sensitive volatile liquids, monomeric in solution. Although regeneration of the parent oximes occurred readily, a catalyst ($\mathrm{ZnCl_2}$) was necessary to bring this about for compounds with bulky alkyl groups. A decrease in the readiness of compounds to undergo this cleavage was in the order $\mathrm{Pr^nHC{:}NOH > Me_2C{:}NOH > MeEtC{:}NOH > Et_2C{:}NOH \simeq MePr^nC{:}NOH > MePr^iC{:}NOH}$. Although reaction of tetraethoxysilane with acetoxime gave only the trioximinosilane, tetra(dimethylimino-oxy)silane resulted from reaction of silicon(IV) chloride and acetoxime in the presence of pyridine or triethylamine. The trimethyl(imino-oxy)silane, $\mathrm{Me_3SiON{:}CMeEt}$, reacts with acetyl chloride as shown in reaction (7).

$$\mathrm{Me_3SiON{:}CMeEt + CH_3COCl} \longrightarrow \mathrm{Me_3SiCl + MeEtC{:}NO{\cdot}OCCH_3} \quad (7)$$

Although $\mathrm{Et_3Si{-}O{-}N{:}CMe_2}$ underwent only partial hydrolysis in 5% HCl during 7 h under reflux, the corresponding methyl analogue was completely hydrolysed after 1 h under the same conditions. The ease of hydrolysis of such compounds appears to be in the order. $\mathrm{Me_3SiON{:}CR^1R^2 < Me_2Si(ON{:}CR^1R^2)_2 < Me_2Si(ON{:}CR^1R^2)_3 < Si(ON{:}CR^1R^2)_4}$.

*I.r. Spectra.*—Tentative i.r. assignments have been

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[3] J. R. Jennings and K. Wade, *J. Chem. Soc.* (*A*), 1967, 1333; I. Pattison and K. Wade, *ibid.*, 1968, 2618.

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made on the basis of published data.[6-8] The i.r. spectra of the organo(imino-oxy)silanes show absorptions at 1618—1650 (C:N stretch), 1250 (CH sym deform.), 910—940, (NO stretch), 840—920 ($\nu_a$SiO), 700—710 ($\nu_s$SiO), 670—810 ($\nu_a$SiC), and 580—670 $cm^{-1}$ ($\nu$SiC). In silatranes,[9] lowering of $\nu_s$(Si–C) to 609—620 $cm^{-1}$ is attributed to the intramolecular $(Si \leftarrow N)$ co-ordination. For organo(imino-oxy)silanes this absorption occurs in the range 600—670 $cm^{-1}$ and agrees with that found for alkylalkoxysilanes.[7a] The possibility of $sp^3d$ or $sp^3d^2$ hybridisation of the silicon atom, therefore, appears to be ruled out in these derivatives. For trimethyl(imino-oxy)silanes of the type $RCH{:}NOSiMe_3$ (R = 2-pyridyl or 4-pyridyl), $\nu_s$(Si–C) was in the range 580—590 $cm^{-1}$; very weak absorption at *ca.* 661 $cm^{-1}$ was attributed to silicon–nitrogen stretching vibrations, this suggests intramolecular $(Si \leftarrow N)$ co-ordination with five-co-ordinated silicon atom.

*N.m.r. Spectra.*—The $^1H$ n.m.r. spectra are consistent with an increase in the *syn*-form (estimated from signal intensities) upon silylation of the aldoximes. Signals attributable to $CH_3Si$ and the methyl group adjacent to the oximino-group in ketoximes and their complexes appeared as singlets.

The n.m.r. spectra of alkyl alkoxysilanes[10] indicate that inductive electron withdrawal and $(p \longrightarrow d)\pi$-bonding of oxygen to silicon both contribute to the electron densities in the molecules. Increase in deshielding of the Si–CH protons with successive introduction of the electronegative oximino-group, might be due either to inductive effects of the oximino-groups or to steric factors.

## EXPERIMENTAL

General experimental procedures are given below. Details of other experiments performed in a similar way to those described together with the details of the physical characteristics of the products obtained (m.p.s, b.p.s, elemental analyses, $n_D$ valves, and i.r. and $^1H$ n.m.r. spectroscopic data) are deposited with the N.L.L. as Supplementary Publication no. 20429 (8 pp).*

Moisture was rigorously excluded. Oximes were prepared by standard methods. Freshly distilled halogenosilanes, aminosilanes, alkoxysilanes and anhydrous benzene were used. Molecular weights were determined ebullioscopically in benzene and refractive indices with an Abbé refractometer. Nitrogen was estimated by the Kjeldahl procedure. Ethanol was estimated by oxidation with N-potassium dichromate in 12·5% sulphuric acid.[11] Silicon was estimated as $SiO_2$.[12] I.r. spectra were recorded as thin liquid film using, KBr optics (Perkin-Elmer 337) and NaCl optics (Perkin-Elmer 237). $^1H$ N.m.r. spectra were recorded in $CCl_4$, $CHCl_3$ or $CCl_4$–$CH_2Cl_2$) at 60 and 100 MHz, on Varian Associate models A-60 and HR-100 spectrometers with $SiMe_4$ as internal standard.

A number of the products have been prepared by alternative routes.

*Reactions of Organochlorosilanes with Oximes in the Presence of Triethylamine or Pyridine.*—Appropriate organochlorosilane was added dropwise with shaking to a cooled benzene solution of the ligand and a stoicheiometric amount of triethylamine or pyridine. The reaction mixture was then refluxed for a period dependent upon the nature of the organochlorosilane used (*e.g.* trimethylchlorosilane 1 h, dimethyldichlorosilane 2 h, methyltrichlorosilane 6 h). The precipitated triethylamine hydrochloride or pyridinium salt was filtered off and the solvent was distilled. The product was then purified by distillation.

*Reactions of Dimethyldiethoxy- and Tetraethoxy-silanes with Acetoxime in the Presence of Sodium in Benzene.*—Acetoxime (4·36 g), dimethyldiethoxysilane (4·42 g), benzene (50 ml) and a little sodium were azeotropically distilled during 18 h. The excess of solvent was then removed; the residue was distilled to give dimethyl(dimethylimino-oxy)silane b.p. 73—74°/4 mm, (60% yield).

Dimethyl(ethylmethylimino-oxy)silane was prepared similarly.

Similarly tetraethoxysilane (4·67 g) and acetoxime (6·56 g) gave a liquid, b.p. 98—100°/0·7 mm (60% yield) (Found: Si, 9·7%; N, 14·5%; *M*, 280. $C_{11}H_{23}N_3O_4Si$ requires, Si, 9·7%; N, 14·5%; *M*, 290).

*Preparation of Tetra(imino-oxy)silanes.*—Tetra(imino-oxy)silanes were prepared by reaction of silicon(IV) chloride and oximes in the presence of pyridine.

(i) Acetoxime (3·32 g) in benzene was added to silicon(IV) chloride (1·87 g), pyridine (4·01 g), and benzene. After the mixture had been refluxed for 4 h, the pyridinium salt was filtered off and the solvent was removed. The residue was distilled to give solid tetra(dimethylimino-oxy)silane, b.p. 128°/0·5 mm (60% yield) (Found: Si, 8·8%; N, 17·5%; *M*, 320. $C_{12}H_{24}N_4O_4Si$ requires Si, 8·85%; N, 17·7%; *M*, 316).

(ii) Similarly methyl ethyl ketoxime (7·69 g), silicon tetrachloride (3·74 g), and pyridine (8·10 g) yielded a liquid, b.p. 141·5—143·5°/0·6 mm (60% yield) (Found: Si, 7·4%; N, 14·9%; *M*, 375. $C_{16}H_{32}O_4N_4Si$ requires Si, 7·5%; N, 15·0%; *M*, 372).

*Synthesis of Trimethyl(imino-oxy)silanes.*—(1) Reaction of butyraldoxime (2·62 g) and trimethyl(diethylamino)silane (4·36 g) liberated diethylamine which was slowly distilled at a bath temperature of 100°. The remaining liquid was distilled (b.p. 40—42°/10 mm, 121—123°/760 mm) to give $Me_3SiON{:}CHPr^n$ (Found: Si, 17·5%; N, 8·8%; *M*, 161. $C_7H_{17}NOSi$ requires Si, 17·65%; N, 8·8%; *M*, 159). $n_D$ 1·4160 at 20 °C (lit.,[13] 1·4160 at 20 °C).

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* For details of Supplementary Publications see Notes to Authors No. 7, *J. Chem. Soc.* (*A*), 1970, Issue No. 20.

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(2) Trimethyl(dimethylimino-oxy)silane prepared similarly from acetoxime (1·46 g) and trimethyl(diethylamino)-silane (2·91 g) had b.p. 120—121°/760 mm (Found: Si, 19·25%; N, 9·6%; *M*, 147. $C_6H_{15}NOSi$ requires Si, 19·35%; N, 9·65%; *M*, 145).

(3) A mixture of trimethylchlorosilane (3·26 g) and sodium acetoximate (2·85 g) in light petroleum was refluxed for 0·5 h. The sodium chloride was filtered off; excess of solvent distilled and the residual liquid was distilled at 120—121°/760 mm.

(4a) Trimethylchlorosilane (1·20 g) was added to $Bu^n_3SnON{:}C_5H_8$ (3·88 g). The cool mixture was distilled to give $Me_3SiON{:}C_5H_8$, b.p. 64°/7·5 mm, (80% yield) and tri-n-butyltin chloride, b.p. 102°/0·5 mm (70% yield).

(4b) Similarly, trimethylchlorosilane (0·60 g) and $Bu^n_3GeON{:}C_5H_8$ (1·71 g) gave after refluxing for 1 h $Me_3SiON{:}C_5H_8$, b.p. 64°/7·5 mm (60% yield) and tri-n-butylgermanium chloride, b.p. 139—140°/13 mm.

*Reaction of Trimethyl(imino-oxy)silane with Acetyl Chloride.*—Acetyl chloride (1·68 g) was added to $Me_3SiON{:}CMeEt$ (3·35 g) cooled to 5 °C. After 1 h at room temperature the mixture was distilled to give trimethylchlorosilane (b.p. 57—57·5°/760 mm, 70% yield) and the *O*-acyl oxime ester (b.p. 75—76°/10 mm, 70% yield) identified by its i.r. spectrum (Found: N, 10·7%; *M*, 130. $C_6H_{11}N_1O_2$ requires: N, 10·85%; *M*, 129).

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