Synthesis and characterization of benzilmonoxime complexes of organosilicon(IV)

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Complexes of the general formula Me₃SnL, Me₂SnL₂Cl₂ₙ and MeSnL₃Clₙ (where L=benzilmonoxime) have been prepared by reacting organosilicon(IV) chlorides with the sodium salt of the ligand (prepared in situ) in different molar ratios. These complexes have been characterised by elemental analyses, molecular weight determinations, conductivity measurements and spectral (IR, ¹H and ¹³C NMR) studies.

The peculiar behaviour of silicon(IV) and the vital role its complexes play in chemical and biological processes are of immense importance and are thought provoking in the realm of coordination chemistry¹. During the past few years, a plethora of references describing the organosilicon complexes of N, O and N, S donor Schiff bases have appeared in the literature²⁻⁵. Certain organosilicon compounds have been extensively used in chemical vapour deposition⁶ and in deoxygenation reactions in organic transformations⁷. However, little is known about the complexing behaviour of silicon with oxime. Oximes are important from biochemical point of view⁸. A recent review deals with complexes of oximes and oximato species, which are bidentate ligands capable of coordinating via oxygen and nitrogen⁹. Our continuing interest in the synthesis of biologically active complexes and in continuation to our recent report on organosilicon(IV)¹⁰⁻¹¹, have led us to synthesise and study the structural as well as other features of organosilicon(IV) complexes of benzilmonoxime.

**Experimental**

Chemicals and solvents used were dried and purified by standard methods¹² and moisture was excluded throughout the experimental manipulations. All the melting points are uncorrected. Methyl silicon chlorides i.e. Me₃SiCl, Me₂SiCl₂ and MeSiCl₃, were procured from E Merck or Aldrich and were used as such. Benzilmonoxime was prepared according to the literature method¹² and recrystallised before use. IR spectra were recorded on a Perkin-Elmer model 377 in the range of 4000-200 cm⁻¹. ¹H and ¹³C NMR spectra were obtained at 200 and 50 MHz, respectively (Bruker AC 200), in CDCl₃ as solvent. Chemical shifts were recorded in ppm (δ) relative to TMS as an internal standard. Microanalyses were performed by Coleman Carbon, Hydrogen and Nitrogen analysers for C, H and N respectively. Silicon and chlorine were estimated gravimetrically as SiO₂ and AgCl respectively, described elsewhere¹² and are in good agreement with the calculated values (Table I). The details concerning the molar conductance measurements are similar to those reported previously¹³. Molecular weights were measured on Knauer Vapour Pressure Osmometer in dilute (20 g litre⁻¹) CHCl₃ solution at room temperature.

**Reaction between Me₃SiCl and the sodium salt of benzilmonoxime in 1:1 molar ratio**

To a weighed amount of trimethylsilicon chloride (0.71 g, 6.54 mmol) in ~ 20 ml of dry isopropanol was added a calculated amount of sodium salt of the ligand, prepared by treating the ligand (1.47g, 6.54 mmol with sodium hydroxide in methanol), with dry isopropanol. The reaction was monitored by thin layer chromatography. The volatile component was distilled off and the residue was purified by recrystallisation in xylene.

**Scheme 1**

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mmol) with the sodium metal (0.15g, 6.54 mmol) in dry isopropanol ~ 20 ml. The reactants were refluxed for 4-6 h to ensure the completion of the reaction. Sodium chloride formed was filtered off and the excess solvent removed under reduced pressure to yield the desired product.

All other organosilicon(IV) complexes of benzilmonoxime were synthesised analogously. The pertinent data for this and other derivatives are listed in Table 1.

**Results and discussion**

Organosilicon(IV) derivatives of benzilmonoxime have been prepared as given in Scheme 1. These
reactions were found to be quite facile. Oxime being weak oxygen acid, reacts with the base and undergoes deprotonation.

All the newly synthesised compounds are solids, soluble in common organic and coordinating solvents. Molar conductance values reveal the non-electrolytic nature of the complexes indicating that the ligand is covalently bonded to silicon. Molecular weight determinations of these complexes in CHCl₃ solutions show their monomeric nature.

The characteristics bands in the IR spectra of benzilmonoxime at 3380-3260, 1670 and 1615 cm⁻¹ are assigned¹⁸ to ν(N-OH), ν(C=O) and ν(C=N), respectively. The free oxime band at 3380-3260 cm⁻¹ disappears in the complexes indicating deprotonation at the –OH end, thus providing an oxo coordination. This is also apparent from the non-electrolytic nature of the complexes. This fact is further supported by the appearance of ν(Si-O) modes at 1080-1060 cm⁻¹ in the spectra of the complexes. A strong band at 1615 cm⁻¹ for ν(C=N) in ligand is shifted to lower frequency by ~20 cm⁻¹ in the case of complexes, indicating the coordination of imino nitrogen to the silicon atom. In the literature a shift of this frequency to the higher¹⁸ as well as lower¹⁸ wave number and in some cases even no change has been noted¹⁸. A band at 1670 cm⁻¹ in the oxime due to carbonyl group does not show any discernible shift in the spectra of the complexes, suggesting its non-participation in coordination (Table 2).

The ¹H and ¹³C NMR spectral data are presented in Table 2. The proton signal due to the oxime group at δ 10.44 ppm in the free ligand¹⁷ disappears in the case of silicon complexes showing ligation of silicon to oxygen. The new proton signals at δ 0.28-0.67 ppm are due to methyl protons of the Me₃Si group. The resonances due to phenyl protons at δ 6.64-8.32 ppm remains almost unchanged in the complexes.

The ¹³C NMR spectra of the complexes are very much similar to that of the ligand except few new bands appear for methyl carbons bonded to silicon. The large shifts of >C=N carbon in the complexes clearly indicates coordination of imino nitrogen to the silicon atom¹⁹. The number of ¹³C NMR signals correspond to the number of chemically different carbon atoms present in these complexes (Table 2).

Based on the foregoing discussions a penta-coordinated trigonal bipyramidal geometry can be suggested around the silicon atoms as shown in Structure I:

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References


