Schiff Base Complexes of Boron — Synthesis of Boron Complexes of Dibasic Tridentate Schiff Bases Derived from o-Hydroxyacetophenone & Hydroxyalkylamines

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Dibasic tridentate Schiff bases having the donor system ONO have been shown to form (OEt)B(SB) and B(SB) (SBH) types of derivatives where, SBH- and freshly prepared compounds have been found to be monomers in boiling benzene and non-electrolytes in non-aqueous system ONO have been shown to form (OEt)B(SB) and B(SB) (SBH) in 1:1 and 1:2 molar ratios respectively. The freshly prepared compounds have been found to be monomers in boiling benzene and non-electrolytes in dimethyl formamide. The infrared spectra show coordination of boron to oxygen of the phenolic or alcoholic group as well as nitrogen of the azomethine group.

SCHIFF base complexes of boron of the type BXS. SBH in which the Schiff bases act as neutral monodentate ligands, have been reported in literature. In this paper preparation and characterization of tetracoordinated boron complexes of bifunctional tridentate Schiff bases derived from o-hydroxyacetophenone and 2-hydroxyethylamine, 2-hydroxy-1-propylamine and 1-hydroxy-2-butyamine have been reported.

Triethyloxyborane was prepared by the interaction of boric acid (S. Merek) with absolute alcohol in benzene and removing water azotropically. It was freshly distilled before use.

Schiff bases were synthesized from o-hydroxyacetophenone and hydroxyalkylamines as described earlier. These were also distilled before use.

(i) o-Hydroxyacetophenone-2-hydroxyethylamine — Yellow solid, m.p. 96°C, b.p. 149-50°/0.1 mm (Found: C, 66-97, H, 7-56, N, 7-72. Req'd for C9H9NO2: C, 67-01, H, 7-31, N, 7-81%).

(ii) o-Hydroxyacetophenone-2-hydroxy-1-propylamine — Yellow solid, m.p. 91°, b.p. 164-65°/1.2 mm (Found: C, 68-12, H, 7-67, N, 7-34. Req'd for C11H12NO2: C, 68-37, H, 7-82, N, 7-25%).

(iii) o-Hydroxyacetophenone-1-hydroxy-2-butylamine — Highly viscous yellow liquid, b.p. 137-38°/0.3 mm (Found: C, 69-27, H, 8-19, N, 6-71%. Req'd for C13H14NO2: C, 69-55, H, 8-27, N, 6-76%).

Preparation of Schiff base derivatives of boron — Schiff base derivatives of boron were prepared by refluxing triethyloxyborane and the ligands in 1:1, 1:2 or 2:3 molar ratios in dry benzene under a column packed with Raschig rings until the whole of alcohol liberated during the reaction was distilled off azotropically with benzene. The alcohol liberated was estimated oxidimetrically. The products that crystallized out from dry benzene were dried in vacuo. The characterization data of the complexes are given in Table 1.

Exchange reactions of 1:1 derivatives with tertiary butanol — A weighed amount of ethoxyboron Schiff base 1:1 derivative was dissolved in hot dry benzene and to this excess of t-butanol added. The contents were refluxed under a column and the ethanol liberated was collected azotropically. After the complete exchange of the ethoxy group had taken place, the excess of solvent was distilled off and the products crystallized from the same solvent (Table 2) and finally dried in vacuo (0.05 mm).

Analysis — Boron in triethyloxyborane was estimated as described in the literature and in the case of complexes the following method was used:

A weighed amount of the sample was treated with methanol in the presence of 2-3 drops of conc. sulphuric acid. The methyl borate so produced was distilled off over a fractionating column and collected into a receiver flask having distilled water. The boric acid formed was then titrated against standard sodium hydroxide solution in the presence of manninol using phenolphthalein as indicator. Nitrogen was estimated by Kjeldahl's method.

The product obtained from 2:3 molar ratio reaction is always a mixture of 1:1 and 1:2 derivatives. This may probably be due to the steric requirements of the third ligand moiety, coming in between the two boron atoms in the probable structure. In general, the 1:1 and 1:2 molar ratio reactions may be depicted by the following equations:

B(OEt)3 + SBH2- → (OEt)B(SB)- + 2EtOH

B(OEt)3 + 2SBH2- → B(SB)2 + 3EtOH

All these derivatives are yellowish, crystalline solids and non-volatile in nature. These are stable in open atmosphere but when treated with water these get hydrolysed, except the 1:2 derivatives which remain as such even after prolonged refluxing with water. Tertiary amines like pyridine or triethylamine do not react with these derivatives indicating the stable tetracoordinated state of boron in these derivatives due to the coordination of nitrogen of the ligand moiety to boron through a dative bond. The ebullioscopic determinations of molecular weights in boiling benzene show 1:1 and 1:2 derivatives to be monomers and can thus possibly be represented by the tentative structures (I) and (II) respectively.

To show the labile nature of the ethoxy group in 1:1 derivatives, exchange reactions with tertiary butanol have been carried out and the results are given in Table 2. All the resulting derivatives are yellow, non-distillable solids and monomeric in nature in boiling benzene.
Table 1 — Reactions of Triethoxyborane with the Schiff Bases

<table>
<thead>
<tr>
<th>Sl No.</th>
<th>B(OEt) (g)</th>
<th>Schiff base (g)</th>
<th>Molar ratio</th>
<th>Refluxing time (hr)</th>
<th>Product and characteristics</th>
<th>m.p. °C</th>
<th>Ethanol found (Calc.)</th>
<th>Found (%)</th>
<th>Mol. wt found (Calc.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.46</td>
<td>C₁₈H₂₈N₂O₂</td>
<td>1:1</td>
<td>6</td>
<td>B(OEt) (C₁₈H₁₁N₂O₄)</td>
<td>139</td>
<td>0.87</td>
<td>4.62</td>
<td>6.08</td>
</tr>
<tr>
<td>2</td>
<td>0.96</td>
<td>C₁₈H₂₈N₂O₂</td>
<td>1:2</td>
<td>8</td>
<td>B(C₁₈H₁₁N₂O₄) (C₁₈H₁₄N₂O₄)</td>
<td>122</td>
<td>0.85</td>
<td>2.92</td>
<td>7.56</td>
</tr>
<tr>
<td>3</td>
<td>1.78</td>
<td>C₁₈H₂₈N₂O₂</td>
<td>1:1</td>
<td>7</td>
<td>B(OEt) (C₁₈H₁₁N₂O₄)</td>
<td>138</td>
<td>1.15</td>
<td>4.32</td>
<td>5.73</td>
</tr>
<tr>
<td>4</td>
<td>1.06</td>
<td>C₁₂H₁₅N₂O₂</td>
<td>1:2</td>
<td>10</td>
<td>B(C₁₂H₁₄N₂O₄) (C₁₂H₁₄N₂O₄)</td>
<td>116</td>
<td>0.93</td>
<td>2.71</td>
<td>3.52</td>
</tr>
<tr>
<td>5</td>
<td>1.67</td>
<td>C₁₂H₁₅N₂O₂</td>
<td>1:1</td>
<td>7</td>
<td>B(OEt) (C₁₂H₁₅N₂O₄)</td>
<td>166</td>
<td>1.02</td>
<td>4.09</td>
<td>5.29</td>
</tr>
<tr>
<td>6</td>
<td>0.58</td>
<td>C₁₂H₁₅N₂O₂</td>
<td>1:2</td>
<td>12</td>
<td>B(C₁₂H₁₄N₂O₄) (C₁₂H₁₄N₂O₄)</td>
<td>113</td>
<td>0.53</td>
<td>2.49</td>
<td>3.36</td>
</tr>
</tbody>
</table>

A comparison of the IR spectra (ν_max throughout in cm⁻¹) of the ligands with their corresponding boron derivatives reveals that most of the peaks remain unchanged. Weak and broad absorption bands in the 3300-3100 region due to the hydrogen bonded νOH or NH and observed in the spectra of the Schiff bases disappear altogether in the spectra of the corresponding derivatives, showing the chelation of boron through both oxygen and nitrogen atoms of the ligand moiety. In 1:2 derivatives, however, the presence of a band in the 3300-3100 region indicates that one of the functional groups of the second ligand moiety remains uncoordinated.

In the spectra of the ligands, a strong band in the 1620-1600 region may be assigned to νC=N over-lapping with νC=C. This band splits into two bands in the spectra of the derivatives and one of these shifts to the higher frequency side (~1650) leaving the other almost unchanged. The shifted band may probably be due to νC=N as the coordination of boron causes an increase in the bond order of C=N bond. The strong band ~1332 observed in the spectra of the triethoxyborane and assigned to ν₅B=O⁻, however, disappears in the spectra of the derivatives. This, further, substantiates the coordination of boron to nitrogen through a dative bond and accordingly there is a decrease in the double bond character in the B=O bond. The molar conductance values for these derivatives in dimethylformamide range over 12-20 ohm⁻¹ cm² mol⁻¹, indicating their non-electrolytic nature.

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References