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**CHAPTER - IV**

**ROLE OF METAL IONS IN REACTIONS OF  
DL-CAMPHORQUINONE WITH AMINES**

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CHAPTER - IVROLE OF METAL IONS IN REACTIONS OFdl-CAMPHORQUINONE WITH AMINESINTRODUCTION :

Forster<sup>1</sup> noted that d-camphorquinone on reaction with aniline it forms an imino group at C<sub>9</sub> position as it is sterically least crowded. The reaction of d-camphorquinone with 1,3 propanediamine in the presence of nickel nitrate<sup>2</sup> gives a complex having imino group at C<sub>3</sub> position. But, when d-camphorquinone reacts with ortho-phenylenediamine both the carbonyl groups at C<sub>2</sub> and C<sub>3</sub> participate in an imine formation giving d-camphorquinoxaline<sup>3</sup>. The effect of R group (in RNH<sub>2</sub>) on the imine formation reaction would therefore enlighten the steric effect in dl-camphorquinone. Further these reactions are carried out in presence of metal ions. Due to the presence of metal ion it is possible to separate the Schiff base complexes.

RESULTS AND DISCUSSION :

The direct reaction of dl-camphorquinone with n-butyl amine gave a product (V-A) which showed a single band due to  $\gamma$ C=O and  $\gamma$ C=N. Its <sup>1</sup>H n.m.r. spectrum showed three signals of equal intensity at 0.77, 0.94 and 1.05 p.p.m. which were assigned to the methyl groups at C<sub>10</sub>, C<sub>8</sub>, C<sub>9</sub> respectively. On

the basis of analytical data and Forster's<sup>1</sup> suggestion tentatively it was assigned that the imine formation is at C<sub>3</sub> position in Fig.I compound (VA).

When this condensation reaction was carried out in the presence of metal ion the product obtained was different. When one mole of nickel chloride was treated with two moles of dl-camphorquinone and four moles of n-butyl amine a single complex (19) was separated. On its chemical analysis it was clear that one nickel ion had coordinated, with one ligand moiety obtained from dl-camphorquinone. The product obtained from this reaction had an imine group in every ligand. However, its <sup>1</sup>H n.m.r. showed three signals of equal intensity in addition to the three signals obtained in complex (VA). The later complex showed three signals at 0.82, 0.97 and 1.01 p.p.m. This clearly indicates that when the condensation of dl-camphorquinone with n-butyl amine was carried out in the presence of nickel(II), either the C<sub>2</sub> or C<sub>3</sub> carbonyl group in the camphorquinone participated in the formation of Schiff base. These additional three signals would be associated to compound (VB) which had an imine group at C<sub>2</sub>. I.R. spectrum showed the band at the higher frequency (1766 cm<sup>-1</sup>) which was assigned to νC=O in compound (VB Fig.I). Compound (VA) and (VB) are the isomers. But we were not able to separate these isomeric imines (VA) and (VB) (fig.1) by the chromatographic techniques or solubility differences.

The complex (19) was the mixture of two isomeric complexes having the configurations (A) and (B) (fig.2). Infrared spectrum of the complex (19) showed two bands at 1728 and 1738  $\text{cm}^{-1}$  due to  $\nu\text{C}=\text{O}$ . Its  $^1\text{H}$  n.m.r. spectrum showed the broad signals due to the paramagnetic nature of the complex in the solution. Due to steric factors in dl-camphorquinone we get imine at  $\text{C}_3$  position on condensation of camphorquinone and amine. These steric factors are minimised due to the presence of metal ion in the condensation reaction. The condensation reactions were carried out in the presence of different metal ions to analyse whether it would be possible to separate the isomeric imines.

These condensation reactions were carried out in presence of copper(II), cobalt(II), nickel(II) chlorides using different amines such as n-butyl amine, aniline o-toludine, p-toludine, m-toludine.

The complexes prepared were classified into two groups such as class I,  $\text{LMX}_2$  and Class II  $\text{L}_2\text{MX}_2$  (where L being the Schiff base and X being the halide group). (fig.3). Infra-red spectra in the region 1755-1630  $\text{cm}^{-1}$  were obtained due to class I and class II complexes. Since  $\nu\text{C}=\text{O}$  for class II complexes was not much shifted from that observed for free ligand, the carbonyl group in these complexes was not participated in co-ordination (or metal-oxygen bond was weak).

In class I complexes, infrared spectra shift to lower

frequency and there was decrease in the intensity which indicated that the carbonyl group in these complexes was participated in metal-ligand bonding<sup>4</sup>. The intensity of  $\nu\text{C}=\text{N}$ <sup>5</sup> was comparatively high. The Schiff base in the class I complexes behaved as a bidentate ligand and in the class II complexes it's behaviour was as a monodentate ligand. The class I complexes were four co-ordinated, the metal ion in class II complexes displayed four co-ordination number. The halide groups are participated in metal-ligand bonding and probably behaved as a monodentate ligand. The complexes of both the class are soluble in organic solvents such as benzene and chloroform.

The Schiff bases obtained from the n-hexane washings of the complexes during the synthesis. By using analytical data of the Schiff bases separated from the complexes the nature of metal-ligand bonding in class(I) and class (II) complexes was analysed. The Schiff bases obtained from class (II) complexes showed three <sup>1</sup>H n.m.r. signals in the region 0.70 - 1.30 p.p.m. of equal intensity. Infrared spectra of these Schiff bases showed only one band due to  $\nu\text{C}=\text{O}$ . These results clearly showed that only one carbonyl group at one specific position had participated in the imine condensation reaction. We tentatively proposed the presence of an imine group at C<sub>3</sub> position in these compounds.

The Schiff bases separated from the class-I complexes showed two closely spaced  $\nu\text{C}=\text{O}$  group frequencies and a hump

was observed on a band associated with  $\nu\text{C}=\text{N}$ . The  $^1\text{H}$  n.m.r. spectra of these ligands showed three additional signals of equal intensity in the high field region corresponding to  $-\text{CH}_3$  group. These results suggested that the ligand separated from the class I complexes was a mixture of two isomeric imines. Thus, the one isomer containing an imine group at  $\text{C}_3$  position and the carbonyl group at  $\text{C}_2$  position was not participated in the condensation reaction and the other isomer containing an imine group at  $\text{C}_{(2)}$  and a carbonyl group at  $\text{C}_3$  position. Therefore it was very necessary to do a careful separation of complexes and of imines separated from the complexes.

The complexes prepared in the present work were found to decompose both on silica and neutral alumina column. Therefore, these isomers can be separated from the fractional crystallisation from different organic solvents. One of the two isomeric complexes was more soluble in benzene.

The washings of class II complexes gave only one imine, and its I.R. and  $^1\text{H}$  n.m.r. spectra were identical with those separated from the corresponding complexes. From n-hexane washings of class I complexes two imines (A) and (B) were separated [Fig.2]. From n-hexane washings of copper(II) complexes, two isomeric imines along with the other which did not show any band due to  $\nu\text{C}=\text{O}$  was obtained. It showed two strong bands due to  $\nu\text{C}=\text{N}$  group one at  $1708\text{ cm}^{-1}$  and the other in the region  $1662-1671\text{ cm}^{-1}$ . These results showed that there

was formation of an imine having two imino groups one at  $C_2$  and other at  $C_3$  position [fig.2]. However, such a complex having imine group both at  $C_2$  and  $C_3$  position was not detected both from the i.r. spectrum of the complexes and from the spectroscopic data of the ligands separated from the corresponding complexes.

The role of metal ion in the formation of isomeric imines seemed to be stereoelectronic. The difference in the polarisation of  $-CH_3$  groups at  $C_8$  and  $C_9$  positions by the groups at  $C_2$  and  $C_3$  positions was indicated from the solvent effect on  $^1H$  n.m.r. spectrum of d-camphorquinone. Such polarisation effects were also displayed by the Schiff bases separated in the present work. The decreasing trend of the difference of the shielding of the two axial methyl groups was as follows.

1-naphthylamine > phenylimine > 3-methyl phenylimine  
> 2 methyl phenylimine > n-butyl imine

The role of metal ion is to minimise the stereoelectronic difference between the axial methyl groups and on co-ordination both the groups at  $C_2$  and  $C_3$  would have more or less reactivity. In class I complexes the carbonyl groups at  $C_2$  and  $C_3$  were co-ordinated, the imine condensation reaction took place at these groups. The yield of isomer (B) was about 80 percent that of isomer (A). The difference in the yield was due to the difference in the stereoelectronic factors at

C<sub>2</sub> and C<sub>3</sub>.

In the imine condensation reaction of dl-camphorquinone with n-butyl amine and aniline in the presence of copper(II), a compound containing imine both at C<sub>2</sub> and C<sub>3</sub> (compound C) was separated, while the corresponding copper(II) complex was not separated. It seemed that the Schiff base formation reaction proceeded through a transition state consisting of a formation of a  $\alpha$ -diimine metal complex. The formation of Schiff base with formula (B) was also proceeded through a complex formation reaction.

Direct condensation reaction of dl-camphorquinone with amine gave a compound which had only one imine group at C<sub>3</sub> position whereas in presence of metal ions the compound obtained was having an imine group at C<sub>2</sub> and C<sub>3</sub> position. In these condensation reactions the proper care was taken to avoid the presence of micro amounts of metal ions for e.g., the condensation reaction of dl camphorquinone with aniline containing a small amount of copper(II) as an impurity gives a mixture of isomeric imines.

These results suggested that the condensation reactions of dl-camphorquinone and amine when carried out in presence of metal the product obtained was having imino groups at both C<sub>2</sub> and C<sub>3</sub>. The groups at C<sub>2</sub> and C<sub>3</sub> should participate in co-ordination for the formation of isomeric imines.

These reactions were the homogeneous catalytic reactions.



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