CHAPTER - II

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INTRODUCTION :

The Chemistry of β-diones and their metal complexes is well understood.

The difference in the enolization characteristics of α-diones and β-diones has an obvious effect on co-ordinating ability of α-diones. In the ligand displacement reaction of low valent metal complexes, the acyclic α-diones behave as the four electron donors.[1-5] The reaction of o-quinone and related cyclic α-diones with the low valent metal complexes however, display the oxidative addition reaction leading to an increase in the oxidation state of the metal ion by +2, and a simultaneous reduction of α-dione to the respective catecholate derivative.[6-12] Ortho-Quinone and other related cyclic α-diones yield the o-semiquinolate complexes also under appropriate experimental conditions.[13-17]

Reactions of α & β-diones with different primary amines lead to the formation of Schiff bases.[18] α and β diones react with primary amines in the presence of metal ions to form a diimine complex[19] or a tetraimine complex[20] depending on the reaction conditions and the metal ions.

The reactions of α-diones (dl-2,3 bornane dione) in the presence of metal salts such as copper(II), cobalt(II), nickel(II) chlorides and iodides with primary amines (n-butyl amine, aniline, o-toludine, m-toludine and α-naphthylamine) lead to the formation of a new series of ligands (Schiff base) which could not be synthesized or made with difficulty in the absence of metal ions.[21,22]

α-Diones are known to condense with primary aromatic diamines in the presence of metal ions to form complexes containing macrocyclic ligands.[23-29] The condensation of α-dione with 1,3-diaminopropane and 1,2-diaminoethane in absence of metal ions resulted in the formation of a tarry intractable mass, while in the presence of metal ions like nickel(II), copper(II), iron(II) the reactions yield the 1,2 diimine or tetraimine complexes.[19,20]

The α-diimine obtained with decomposition of copper intermediate complex could be prepared and used as separate ligands.[22] α-Diimines have different co-ordination modes. Similar to α diones each imine group can act as a 2-electron donor and in the trans α-diimine each imino group can act as a separate monodentate ligand. In addition to the 6-co-ordination mode, the α-diimine moiety also has 4-delocalised π-electrons on the diimine skeleton available for π co-ordination. This type of π bonding reflects in the infra-red spectra showing large low field shift of the νC=N frequency.[30]

σ-σ'Bidentate co-ordination mode for α-diimines is common with low valent metal ions such as chromium(0), molybdenum(0), tungstan(0), manganese(0), rhenium(I), iron(0), nickel(0), divalent metal ions such as palladium(II), rhodium (II), iron(II), zinc(II), manganese(II) and chromium(III), iron(III) and molybdenum(III)[31,32].

The brief summary of the chemistry of α-diones given above suggests that the study of the stereo-electronic factors associated with the chemical reactions of α-diones will be promising with reference to the following points :

1) α-dione as a four electron donor
2) Reduction of α-dione to α-diolate
3) Formation of semiquinolate from α-dione
4) Complex formation reaction involving keto group
5) Chemical reaction of keto group in α-diones.

OBJECTIVE :

Although a vast information is available on the interaction of β-diones with metal ions, the study on the interactions of α-diones with metal ions is comparatively scanty. The diketone (2,3 bornanedione, cis benzil, cis furil) behave as four electron donor. The imine of 2,3 bornanedione behave as monodentate[18,19,21] as well as bidentate[22] ligand. The imine formation at both carbonyl groups were not observed during this reaction.

METHODOLOGY :

In the present work, α-diones, such as dl-2,3 bornane-dione was prepared. The metal-imine complexes with α-diones are prepared by using Cu(II), Co(II) and Ni(II) and other monoamines such as aniline, toludine, α-naphthyl amine.

In the present work, dl-bornane 2,3 dione (dl-camphorquinone) a typical α-dione, is selected for the analysis of the reactions of α-diones. There are some interesting features of camphorquinone reported in the literature,[33]

1) The rotatory dispersion spectra of d-comphorquinone in n-hexane for different mole fractions display an iso-rotation point.[33]
2) An enormous solvent effect on the ^1H n.m.r. signals associatedd with the methyl protons at C_8, C_9 and C_{10} is displayed.
3) The polarization of these methyl protons through space is also envisaged.[34]
4) The direct condensation of camphorquinone with aniline gives a product with an imino group at C_3 without affecting[35,36] the keto group at C_2.

Camphorquinone is structurally related to camphenilone[37]. The mechanistic study of the racemization of d-camphenilone suggests the homoenolization reaction as an intermediate step[37,38]. It is therefore expected that the possible homoenolization reaction may be an intermediate step in the reactions of low valent metal complexes with camphorquinone leading to the skletal rearrangement.

The reaction of camphorquinone with complexes containing metal atom in the low oxidation state is expected to involve the oxidative addition reaction affording camph-2-ene-2,3 diolate complelexes. This reaction may proceed through the homoenolization of camphorquinone. Camphorquinone also co-ordinate as a neutral ligand behaving as a four electron donor. The structural determination of metal complexes obtained from these reactions and of ligands separated from the metal complexes will help for the determination of mechanism involved in these reactions.

The condensation reactions of camphorquinone with primary amines suggest that the steric factors affect the carbonyl group at C_2 from participating in imine formation. It is envisaged that the co-ordination of the carbonyl groups in the camphorquinone may modify the steric factors associated with the free ligand. The nature of metal ion and 'R' group in RNH_2 both will control the imine formation. Therefore, it is profitable to study the imine condensation reaction of camphorquinone in the presence of metal ions using different amines. By this reaction three types of complexes are formed under different conditions :

1) Complex containing imine group at C_3 position similar to that reported in the literature.[35,36]
2) Complex containing imino group at C_2 position.
3) Complex containing imino groups both at C_2 and C_3 positions.

Complex containing imine group at C_2 position, clearly shows that the steric factor which inhibit the formation of imine at C_2 minimizes in presence of metal ions and hence it may be the case of homogeneous catalytic reaction.

The mixed imine formation could be obtained by first condensing C_3 carbonyl group by one monoamine and condensation of second carbonyl in presence of metal ions. This type of reaction gives metalimine complex as well as the diimine which could be difficult to obtain in the absence of metal ions.

EXPECTED RESULTS :

The imine condensation reaction of camphorquinone will be carried out by using different amines in the presence of transition metal ions for analysing the stereo-electronic factors associated with the carbonyl group at C_2 and$_3$ in the camphorquinone.

The α-dione used in this study is camphorquinone and different amines condensed are, such as, aniline, nitroaniline, o-toluidine, m-toluidine, p-toluidine, α-naphthylamine, ethyl amine, butyl amine, propyl amine etc. in the presence of various metal ions such as chromium(III), iron(III), manganese(II), zinc(II), nickel(II), cobalt(II) copper(II) under different experimental conditions, so as to get an insight into the steric involvement of dl-2,3 bornane dione.

The steric factors involved in the imine condensation reaction of α- dione (dl-2,3 bornane dione) are modified in the presence of metal ions. The 2-imine and 2,3-diimine of 2,3-bornane dione which could not be otherwise obtained under normal conditions of organic reactions are prepared using the appropriate metal ions[5].

The role of the co-ordinated metal ion was probably to minimise the stereoelectronic differences between the axial methyl groups and on co-ordination both groups at C_2 and C_3 would have more or less similar reactivity. So the complexes in which the group at C_2 and C_3 co-ordinated the imine reaction took place at these groups.

The condensation reactions carried out in the present work of dl-2,3 bornanedione clearly indicate that C_2 position sterically hindered in the imine formation. The α-dimine was obtained from a reaction only if the condensation was carried in the presence of copper(II) ion.

The synthesis of mixed diimines with dl-2,3 bornanedione could be prepared by first isolating the Schiff base containing the imine at C_3 position with a monoamine taking care to amide transamination.

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