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STUDIES ON SCHIFF'S BASES CHELATES USING QUANTITATIVE ANALYSIS

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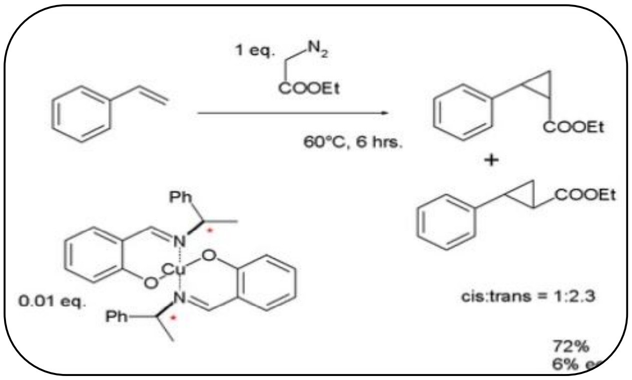
ABSTRACT

Schiff-bases are considered as a very important class of organic compounds, having wide applications in many biological aspects, proteins, visual pigments, enzymic aldolization and decarboxylation reactions. Moreover, some Schiff's bases and their metal complexes exhibit antibiotic, antiviral and antitumor agents, biological activity. They are also used as catalysts in polymer and dyes industry, beside some uses as antifertility and enzymatic agents.

KEYWORDS: *Schiff's base, Chelates, Quantitative analysis.*



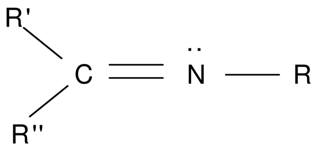
INTRODUCTION

An interesting application of Schiff's bases is their use as an effective corrosion inhibitor, which is based on their ability to spontaneously form a monolayer on the surface to be protected.[1-4]

In this article we have focused on the application of Schiff's bases in quantitative analytical chemistry.

Schiff's bases

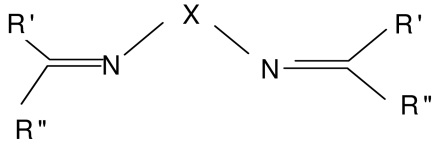
A Schiff base or Schiff's base is a type of chemical compounds containing a carbon-nitrogen double bond as functional group, where the nitrogen atom connected to aryl group or alkyl group (R) but not hydrogen. The Schiff base is synonymous with an azomethine. These compounds were named after Hugo Schiff and has the following general structure:



Where R stands for a phenyl or alkyl group which makes the Schiff base a stable imine.

This kind of ligands is able to coordinate metal ions through the imine nitrogen and another group, usually linked to the aldehyde. The chemists still prepare Schiff bases and nowadays active and welldesigned Schiff base ligands are considered ''privileged ligands''.[5]

The bridged Schiff's bases have the following structure which contains many functional groups able to change according to the purpose required.



Where R' = H or alkyl group
R" = phenyl or substituted phenyl, X = alkyl or aryl group

In fact, Schiff bases are able to stabilize many different metals in various oxidation states controlling the performance of metals in a large variety of useful catalytic transformations.[6]

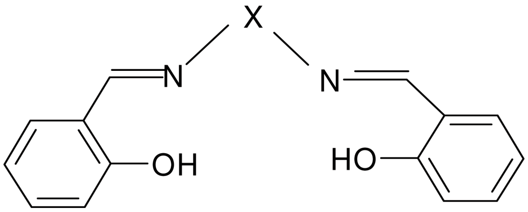
Most commonly Schiff bases have NO or N_2O_2-donor groups but the oxygen atoms can be replaced by sulphur, nitrogen, or selenium atoms.[4]

Although the Schiff bases are known to be good chelating agents, and easily prepared and characterized, little interest has been given to their uses for analytical purposes because of two serious drawbacks, they are insoluble in aqueous solutions and they decompose easily in acidic solutions, limiting their use to basic conditions.[7]

This family can be divided into two groups of symmetric and asymmetric Schiff's base. Salens and salophen can be symmetric or asymmetric but hydrazones are the members of the asymmetric Schiff's bases.

Salen

When two equivalents of salicylaldehyde are combined with a diamine, a particular chelating Schiff base is produced. The so-called Salen ligands with four coordinating sites and two axial sites open to ancillary ligands. Although the term Salen was used originally only to describe the tetradentate Schiff bases derived from ethylenediamine, the more general term Salen-type is used in literature to describe the class of [O,N,N,O] tetradentate Schiff base ligands.[5]



Salen compounds are insoluble in aqueous solutions and they decompose easily in acidic solutions, limiting their use to basic condition.

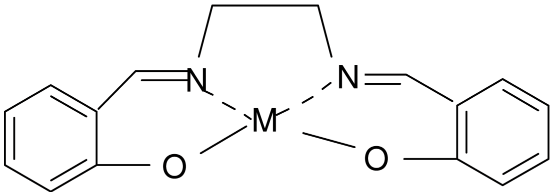
Salophen

Salophen or acetylparamidophenyl salicylate is a Schiff's base with non-toxic properties, which is an effective substitute for salicylic acid.

Hydrazones

Hydrazones are a class of organic compounds with the general structure of R2C=NNR2 which are related to ketones and aldehydes by the replacement of the oxygen with the NNR2 functional group. These compounds are commonly formed through the reaction of hydrazine with ketones or aldehydes. Schiff`s bases are able to coordinate metals through imine nitrogen, and there is a wide use of these metal complexes as catalysts.[5] In the last few years, various Schiff`s base complexes of transition metals including Mn(III), Fe(II), Ni(II), Cr(III), Ru(III) etc. have been used as the catalysts for epoxidation of olefins and as mono oxygen sources for catalyst to carry out oxygen transfer to the olefins.[6,7]

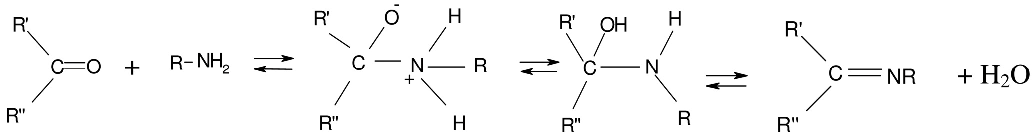
They are easy to synthesize (simply and cheaply) and multidentate. Substitution at the aromatic ring can modify the electronic and steric properties of the resulting complexes (fine-tuning) as it can form metal complexes of various sizes because of its open structure, as shown in the following structure.



Metal chelate of N,N'-Bis(salicylidene)ethylenediamine

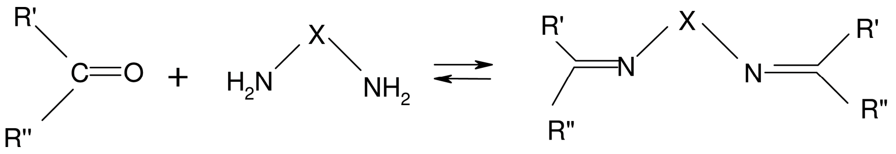
Synthesis

There are several reaction pathways to synthesise Schiff bases.[5Error! Bookmark not defined.,8,9] The most common is an acid catalysed condensation reaction of amine with an aldehyde or ketone under refluxing conditions (Scheme -1). The first step in this reaction is an attack of nucleophilic nitrogen atom of amine on the carbonyl carbon, resulting in a normally unstable carbinolamine intermediate. The reaction can reverse to the starting materials, or when the hydroxyl group is eliminated and a C=N bond is formed and the product is called imine. Many factors affect the condensation reaction, for example the pH of the solution as well as the steric and electronic effects of the carbonyl compound and amine. In acidic solutions the amine is protonated, thus cannot function as a nucleophile and the reaction cannot proceed. Furthermore, in very basic reaction conditions the reaction is hindered as sufficiently protons are not available to catalyse the elimination of the carbinolamine hydroxyl group. In general, aldehydes react faster than ketones in Schiff base condensation reactions as the reaction centre of aldehyde is sterically less hindered than that of ketone. Furthermore, the extra carbon of ketone donates electron density and thus makes the ketone less electrophilic compared to aldehyde.[4]



Scheme -1: Prepartion of Schiff's bases.

For preparation of the bridged Schiff's bases a diamine compound is required with two molecules of aldehyde or ketone according to the structure of the product of interest as in the following reaction.



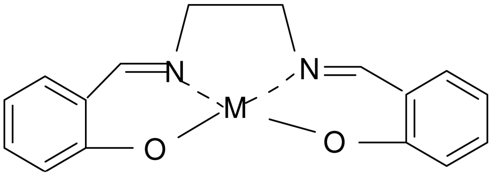
Scheme -2

Where R' = H or alkyl group
R" = phenyl or substituted phenyl
X = alkyl or aryl group

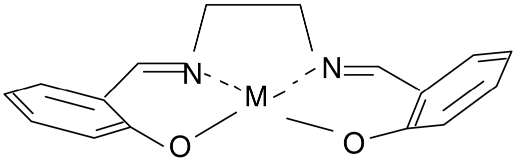
Metal salen complexes

Metal salen complexes have a tendency for square-planar geometry as the bridge between the imine moieties forces the cis-configuration around the metal centre, although in some cases a slightly distorted geometry towards tetrahedral form exists. When the metal complex has square-planar geometry, the metal ion is in the plane formed by the N2O2-donor atoms and the two axial positions are free for coordination with solvent or other molecules.[10,11]

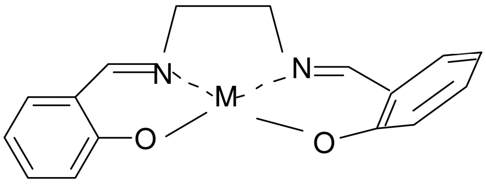
Metal salen complexes can have an umbrella, stepped, or planar molecular conformation (Figure- 1) due to folding of the six-numbered metallocycles and the metal center may deviate from the plane defined by the N2O2-donor atoms. The umbrella and stepped forms are the most common for salen complexes and the strictly planar conformation has been reported only for few complexes.[5]



Planar



Umbrella



Stepped

Fig.-1: Schematic presentations of planar, umbrella, and stepped molecular conformation of salen complexes.

Conformation of the ethylene-bridge is closely related to the overall conformation of the salen compound. Fully planar complexes might have an eclipsed conformation (N(1)– CH2–CH2–N(2) torsion angle ca. 0°) but usually the conformation is gauche. In gauche conformation the carbon atoms of the ethylene-bridge are on the opposite sides of the MN2O2-plane. The geometry around the metal centre in N,N'-bridged Schiff base complexes may be tuned by altering the length of the bridge, the molecular structure becomes more flexible as the number of methylene groups in the bridge increases.[12]

In the salen complexes, which prefer square-planar geometry, dioxygen is coordinated in one axial position and the other axial position is occupied by a base or solvent molecule.[13]

Applications of Schiff's bases chelates in quantitative analysis

Jungreis and Thabet[14] have reported several applications for Schiff' bases in qualitative and quantitative classical analyses. All these applications did not cover a wide area in analytical chemistry.

Advances in analytical techniques and the development and application of new analytical reagents are as important in trace analyses as the development of analytical instruments

A number of Schiff's base chelateing agents used for the detection of metal ions can also be applied for their quantitative determination. The procedures in most cases remain similar.

CONCLUSION

The main step in the above applications is the complex formation which depends mainly on pH, temperature, cation size, and the structure of the ligand. Optimisation of these factors to enhance the stability of the complex leads to high selectivity of the developed analytical method.

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