



FORMATION OF 4-HYDROXY SUBSTITUTED PYRAZOLINE FROM CHALCONE EPOXIDE ON TREATMENT WITH SUBSTITUTED HYDRAZINE

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Abstract:

Metal complex formation may be considered to be due to the displacement of a proton from the ligand by metal causing a drop in the pH values of the solution. Equilibrium constants are related to the complex formation. The stepwise formation of mononuclear, binary and tertiary complexes may be described by a set of equilibrium constants. The change in concentration caused by a complex formation are reflected in the potential of a well chosen electrode where electrode reaction must be reversible. The electrode potential is well defined function of the concentration of the ion to be determined. Rossotti¹ have given a method for calculation of stability constants of complexes by pH-metry (Potentiometry). Calvin and Bjerrum² also followed pH-metric technique for study of stability constant of metal complexes. Martell and Calvin³ have done potentiometric study of metal complexes of a large variety of polycarboxylic acids, oximes and phenols. Various experimental methods are also used for determination of composition, and stability constant of complexes, such as potentiometric (pH-metry) method, spectrophotometry, polarography, ion exchange method, kinetic measurements, colorimetric and extraction methods. The number of methods are related with only to a well defined group of equilibrium system and so their application is restricted. Potentiometric technique is more suitable but it requires that electrode reaction must be reversible. The law of mass action strictly determines the concentration of the reactants and products in every reversible chemical reaction. The numerical values of equilibrium constant depends on the concentration.

Key Words : Chalcone , Epoxide, Metal, Complexes, Solution, Ligand

INTRODUCTION

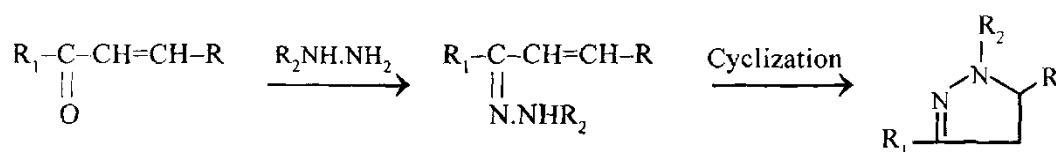
Since the last four decades, considerable research has been done on the study of complexes in solutions.^{4,5} Two or more simple species each having capability of independent existence when undergoes association, the resulting species formed is called 'complex' known as 'metal complex'. The group transfer reactions, bond formation, bond cleavage are the natural process which have been processed by metal complex formation. Metal complexes not only being the reacting molecules together to give activated complexes⁶ .but also polarized electrons from the ligand towards metal. Metal complexes plays very important role in several industrial processes in which catalysis is carried out by metal complexes. A well known catalytic polymerization by metal complex is Ziegler-Natta polymerisation by aluminum and titanium complexes as a catalyst. Dr. K. Zeigler of Germany and Prof. G. Natta of Italy, jointly awarded a Nobel Prize in 1963 for this development.

Many experimental methods have been devised to obtain quantitative data on a complex formation and calculation methods have been developed for the evaluation of stability constant from data. The tremendous development in inorganic chemistry due to main factor involved in this upswing was undoubtedly the wide-ranging research relating to the co-ordination chemistry. Co-ordination compounds play very important role in numerous chemical and biological systems. The importance become clear when one realise that chlorophyll, which is vital to photosynthesis in plants is a magnesium complex and that haemoglobin which carries oxygen to animal cells is an iron complex. Studies on enzymes have shown that the site of reaction in biological system is frequently a complex metal ion. Several industrial processes depend directly on catalysis by metal complexes.

Numbers of enzymes responsible for reaction in biological systems are frequently a complex metal ion, vitamin B₁₂ is co-complex when ligand get attached to the metal atom by more than one donor atom in such a way as to form a heterocyclic ring, this is known as chelation. The co-ordination compound so obtained is known as chelates. Various organic and inorganic chelating agents are useful in the detection and determination of inorganic ions. Chelating agents sometimes forms inner complexes with metal ions which are sparingly soluble and are used in gravimetric estimation of metal ions. Unnatural chelating agents are used in biological system for destruction of organisms by chelation of essential metal and bacteriocidal and fungicidal action.

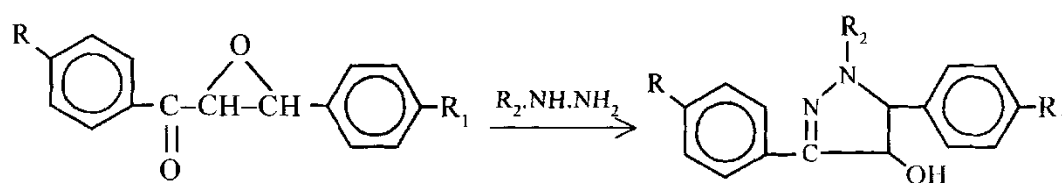
No other branch of chemistry has, in recent years received the concentrated study with fruitful results as the area encompassed by co-ordination chemistry. This science is passing through such a state of rapid advancement that many of the ideas and theories of the past four decades have already been either discarded or modified.

Reaction



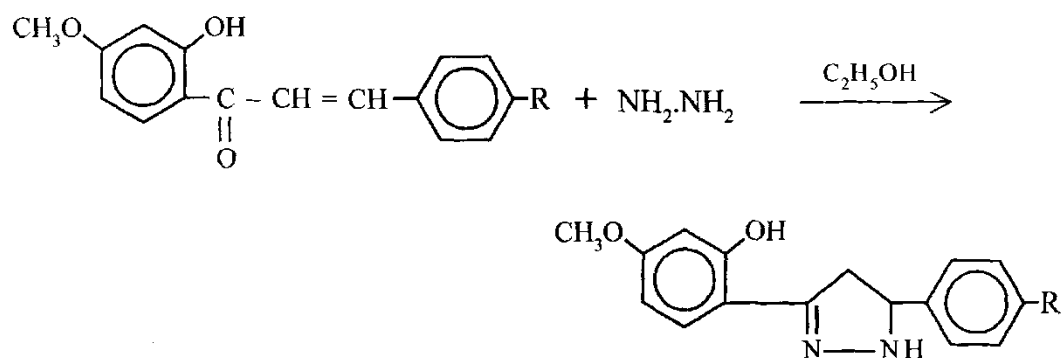
Substituted hydrazine's and chalcones under normal condition give hydrazone derivatives. The cyclization take place with the formation of substituted pyrazoline from chalcone and hydrazine or substituted hydrazine under only vigorous condition.

Sammour has reported the formation of 4-hydroxy substituted pyrazoline from chalcone epoxide on treatment with substituted hydrazine.

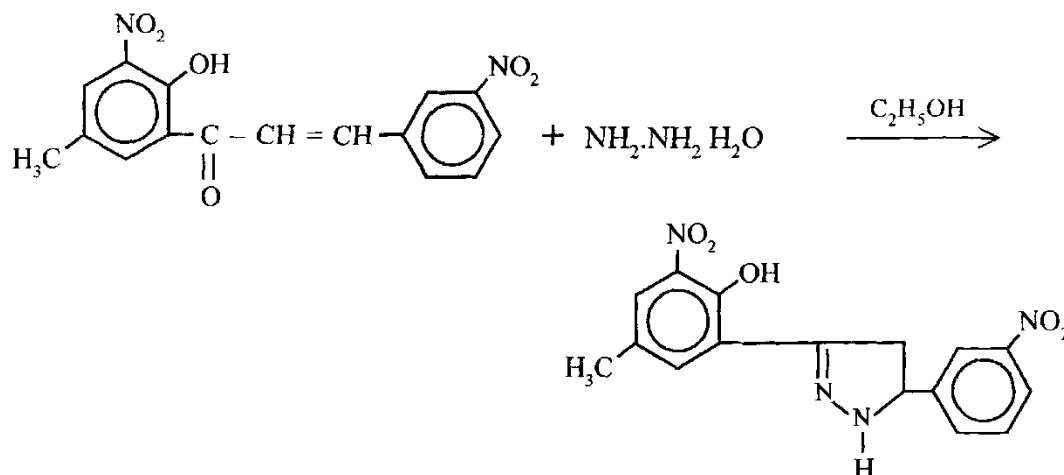


M.D. Ankiwala and H.B. Naik⁷ synthesized 1-phenyl-3-(2"-hydroxy-3"-bromo-4"-n-butoxy-5"-nitrophenyl-1-yl)-5-substituted phenyl-2-pyrazolines from corresponding chalcones and phenyl hydrazine in acetic acid and ethanol medium.

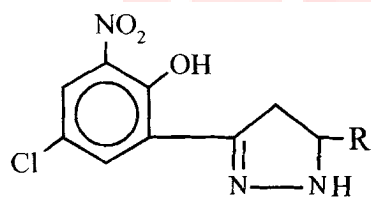
Sonare and Doshi⁸ synthesized 1-H-3-(2-hydroxy-4-methoxy)-phenyl-5-substituted pyrazolines and its derivatives by reaction of chalcone with hydrazine hydrates in ethanol.

Mechanism :

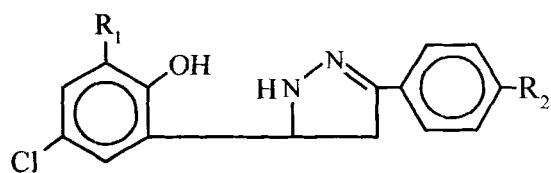
Raghuwanshi⁹ synthesized the 1-H-3-(2-hydroxy-3-nitro-5-methyl phenyl)-5-(3-nitrophenyl)-2-pyrazoline from 2'-hydroxy chalcone and hydrazine hydrate in ethanol.



1-H-3-(2'-hydroxy-5'-chloro-3'-nitrophenyl)-5-substituted phenyl-2-pyrazolines and their acetyl and benzoyl derivatives.



Ali et al¹⁰ have reported synthesis of isomeric \square^2 -pyrazolines and its derivatives from 2'-hydroxy chalcone.



Desai et al¹¹ have reported some new pyrazolines from 1-phenyl-2-pyrazolines, synthesized from chalcones by condensation with $\text{NH}_2.\text{NH}_2.\text{H}_2\text{O}$ and phenyl hydrazine.

Khadsan et al¹² synthesized and studied the antimicrobial activities of 3-(2-hydroxy-3-substituted-5-methylphenyl)-5-(3,4-methylene dioxyphenyl)-2-pyrazolines and its derivatives.

Joshi et al¹³ synthesized and studied the characterization and antimicrobial activity of some fluorinated pyrazolines.

Rathi¹⁴ synthesized and studied the characterization of pyrazolines prepared from 2-hydroxy-3,4-benzochalcones and substituted benzochalcones.

CONCLUSION:

Various methods for the synthesis of pyrazolines have been reviewed. The most convenient method of the synthesis of pyrazolines involve the action of hydrazine or phenyl hydrazine on α,β -unsaturated carbonyl compounds. hydrazine's or substituted hydrazine's reacts with substituted chalcones or flavones leading to the formation of pyrazolines. Pyridine has been widely used as reaction medium. The use of DMF, ethylenediamine and DMSO is also reported. With hydrazine in acetic acid, however N-acetyl pyrazolines are formed.

Literature survey reveals that 1-carboxamido pyrazolines and their derivatives were prepared by Utale¹⁵ We have resynthesized this 1-carboxamido pyrazolines and their derivatives for studying the physical properties.

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