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SURVEY IN SYNTHESIS AND REACTIONS OF IMINE COMPOUNDS

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ABSTRACT

In this review paper .information about schiff bases ,methods of synthesis , reactions , properties, stability , using as catalysis in various reactions in most of organic reactions ,named reactions , Deils-Alder reaction , pericycli reaction , cyclo addition reaction which containing schiff bases , applications .

KEYWORDS: Anil, Azomethine, Formazan, Addition of Imine

INTRODUCTION

(Imine Compounds): Schiff Bases The class of organic compounds containing the azomethine (–HC=N–) group in their Structure is called imine compounds or the molecule containing carbon nitrogen (HC=N)(Double bond is called as mine or alternatively a Schiff base. It was first prepared by

German chemist Hugo Schiffand therefore, is referred to as Schiff base. These compounds Are prepared by the condensation reaction of carbonyls (aldehydes orketones) with primary amine .Usually, the Schiff bases obtained by the reaction of primary amines with aldehydes And Ketones Primary amines with simple R group give imines, which rapidly decompose Dimerize or polymerize. The stability of Schiff bases can be enhanced by insertion of an Aryl group in amines. Generally, aldehydes are more reactive than ketones and order of their reactivity is 1o<2o<3o He electrophilic carbon atoms of aldehydes and ketones can be targets of nucleophilic attack by amines. .The end result of this reaction is a compound in which the C=O double bond is replaced by a C=N double bond. This type of compound is known as an imine, or Schiff base.

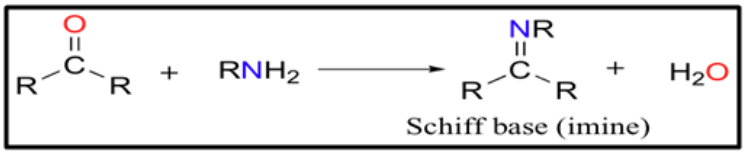


Figure 1

Mechanistically, the formation of an imine involves two steps. First, the amine nitrogen acts as a nucleophile, attacking the carbonyl carbon. This is closely analogous to hemiacetal and hemiketal formation.

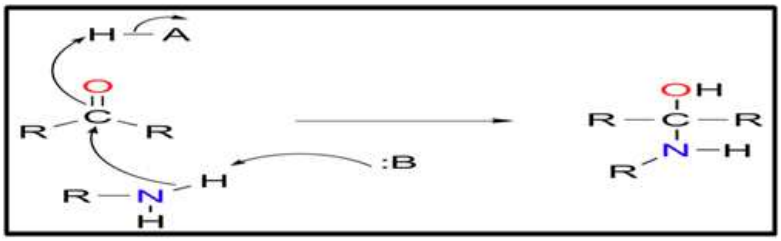


Figure 2

Based on your knowledge of the mechanism of acetal and ketal formation, you might expect that the next step would be attack by a second amine to form a compound with a carbon bound to two amine groups – the nitrogen version of a ketal.Instead, what happens next is that the nitrogen is deprotonated, and the electrons from this N-H bond 'push' the oxygen off of the carbon, leaving us with a C=N double bond (an imine) and a displaced water molecule.

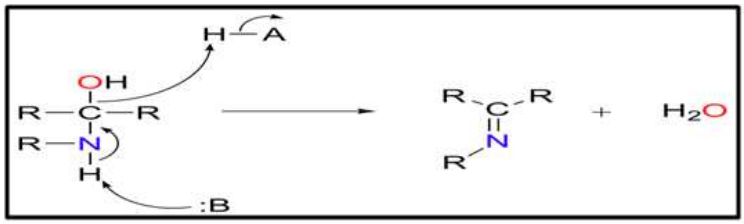


Figure 3

The conversion of an imine back to an aldehyde or ketone is a hydrolysis, and mechanistically is simply the reverse of imine formation:

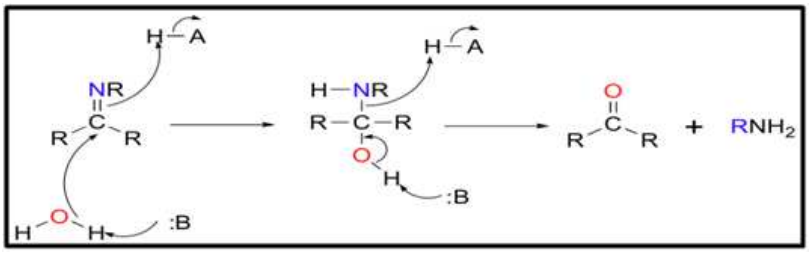


Figure 4

Hydrazones are close relatives to imines, but are not abundantly in biological molecules. Hydrazones are formed in reactions between aldehydes/ketones and hydrazines, a functional group containing a nitrogen-nitrogen bond.

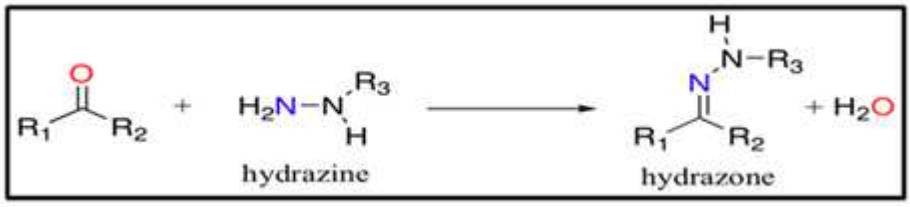


Figure 5

Guanafuracin, a known antibiotic compound, is a hydrazone, and can be prepared easily by combining equimolar amounts of the appropriate aldehyde and hydrazine:

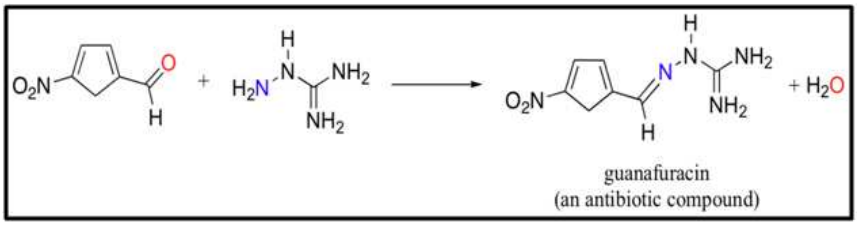


Figure 6

The mechanism for hydrazone formation is analogous to that of imine formation.

Pyridoxal Phosphate Coenzyme Links to Enzymes by A Schiff Base

Schiff base (imine) formation is a very important reaction in biological chemistry. One example involves the chemistry of pyridoxal phosphate (PLP), a derivative of pyridoxine, commonly known as vitamin B6.

Figure 7

But for know what you need to know is that PLP binds to a number of specific enzymes and plays a critical role in helping these enzymes to catalyze their reactions. Most enzymes that interact with PLP catalyze reactions involved in the metabolism of amino acids.

Notice that PLP has an aldehyde group. In many PLP-dependent enzymatic reactions, one of the first things that happens is that PLP forms a Schiff base link with a lysine residue on the enzyme.

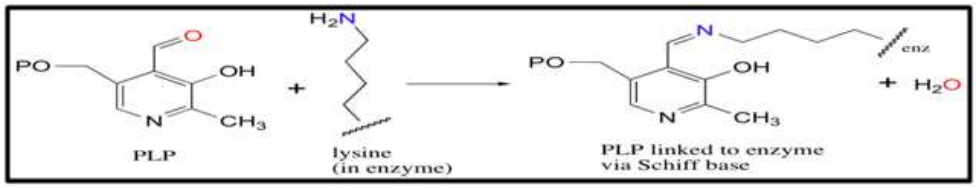


Figure 8

Often, the next step is what could be called a Schiff base transfer: the PLP is transferred from the enzyme lysine to the nitrogen of the amino acid substrate.

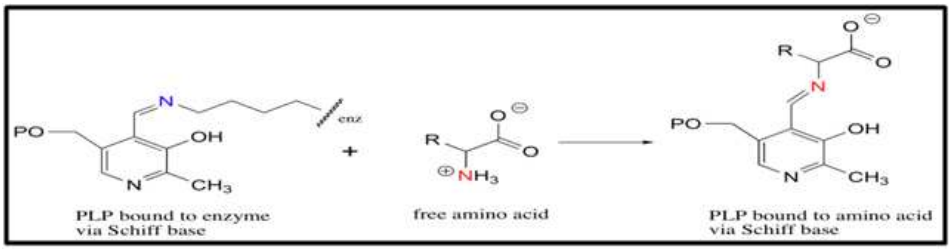


Figure 9

Schiff Base Formation in Aldolase Reactions

Another important example of Schiff base formation in biological chemistry involves carbon-carbon bond-forming reactions catalyzed by enzymes called aldolases. In an aldol reaction, two carbonyl-containing compounds condense to form a single molecule. A key step in this process is the formation of a Schiff base between one of the reactants and a lysine in the active site of the enzyme. For example, when plants convert carbon in the form of CO2 into carbohydrate, one of the early reactions that takes place is the condensation of the four-carbon sugar erythrose-4-phosphate (E4P) with dihydroxyacetone phosphate (DHAP) to form the seven-carbon sugar sedoheptulose-1,7-bisphosphate:

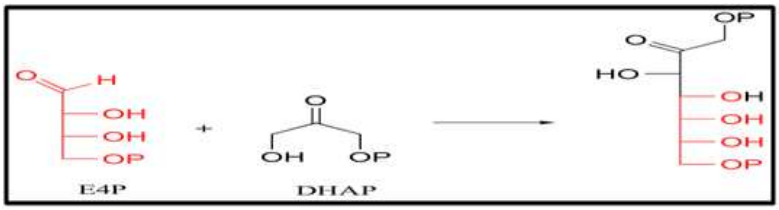


Figure 10

The DHAP substrate binds to the enzyme first, and forms a Schiff base with a specific active site lysine residue:

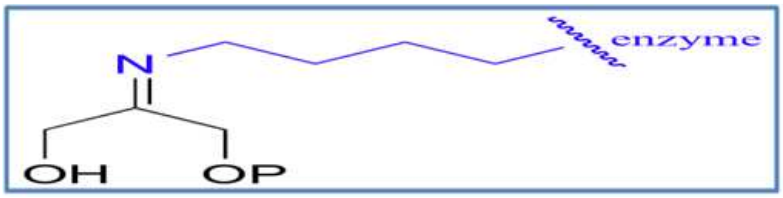


Figure 11

And see how formation of the Schiff base is a critical part of the enzyme's catalytic strategy.

Tetrahydrofolate is A Donor Acceptor of Single-Carbon Groups

Tetrahydrofolate, a coenzyme that is derived from folic acid (one of the B vitamins), participates in an interesting variation on the acetal / Schiff base mechanistic pattern. Serine hydroxymethyltransferase catalyzes the reversible conversion of the amino acids glycine and serine:

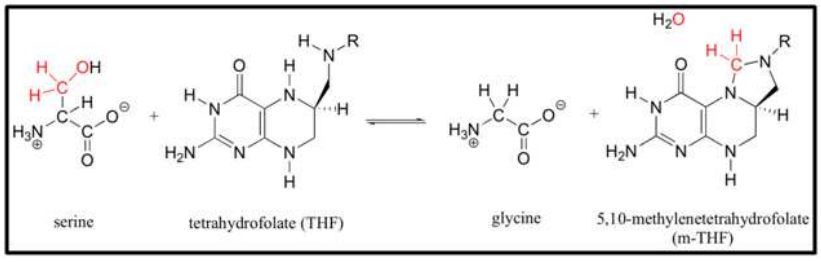


Figure 12

More than one mechanism has been proposed for this reaction, but one likely pathway involves free formaldehyde as an intermediate. In the serine to glycine direction, the formaldehyde intermediate is incorporated into tetrahydrofolate through the formation of what could be termed a 'cyclic nitrogen acetal' in the resulting 5,10-methylene-tetrahydrofolate. Notice that THF in this reaction serves as an acceptor of a single carbon group - in this case, formaldehyde.

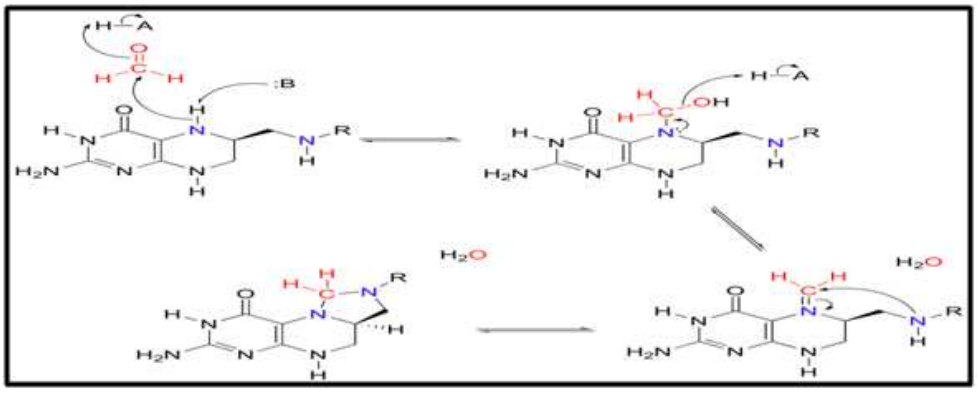


Figure 13

Ethyl diazoacetate react with N-benzylidene aniline to yield Aziridine:

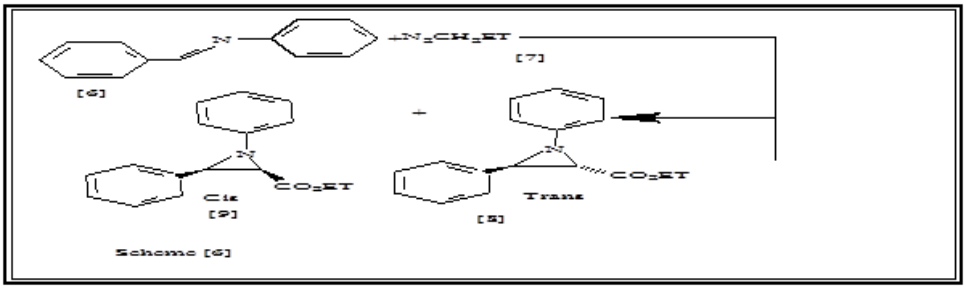


Figure 14

Benzylidene –aniline reacts with dichlorocarbene by [1+2] cyclo addition reaction to give 2,2- dichloro -1,3-diphenylaziridine :

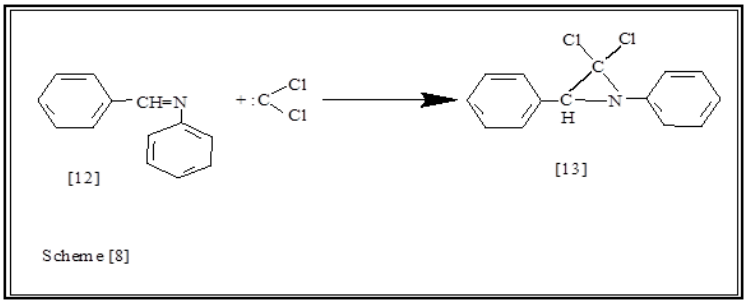
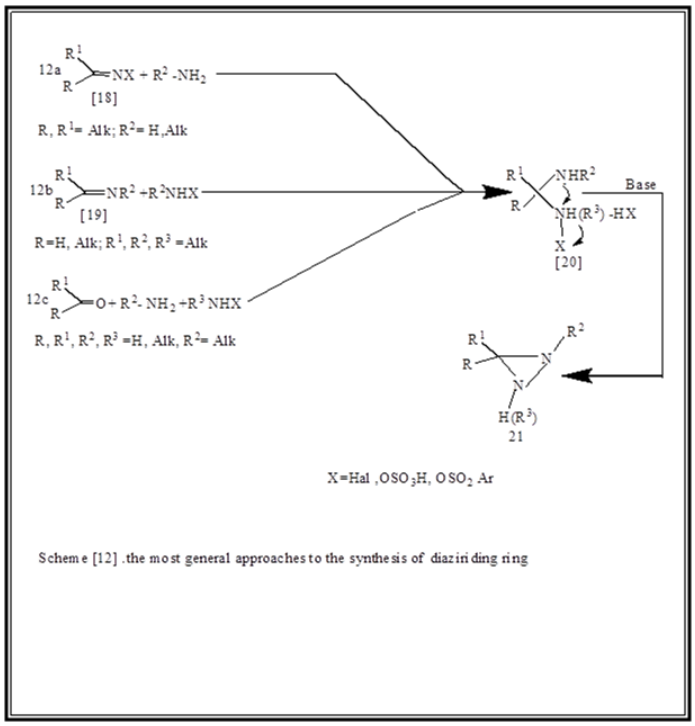


Figure 15

Diaziridinecan be synthesized by an intramolecular SN1 cyclization of N- X –animal , which can be obtained through any of three methods,(i) An interaction of primary amines with the product of carbonyl compounds and aminating reagents such as hydroxyl aminao- sulfonic acid (HASA),(ii) an interaction of imine with aminatingreagents ,(iii) mixing of three components (carbonyl compounds , primary amines andaminating reagents) .



Scheme [12] .the most general approaches to the synthesis of diaziridingring

Figure 16

Dr. Nagham described reaction ofoxazepine with hydrazine to result 3- phenyl -4- (4- methyl benzene) -1,2 -4- triazocine -5, 8 –dione , which reacted with oxalic acid to produce 3- phenyl 1-4- (4-methyl phenyl)-1, 2- bicycle (diazetidine -3,4 –dione)-1,2,4- triazocine -5,8- dione as a four-membered ring :

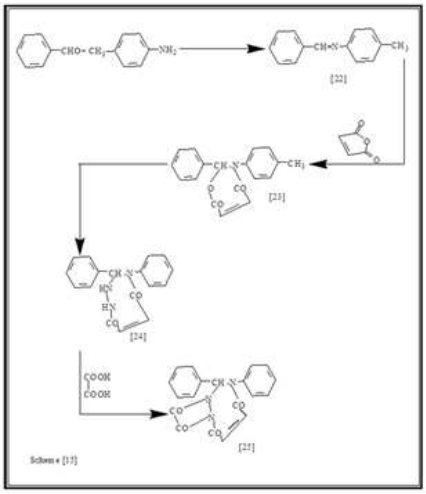


Figure 17

The reaction between hydrazine and P- methoxybenzaldehyde resulting 1,2- diazetidinederivative:

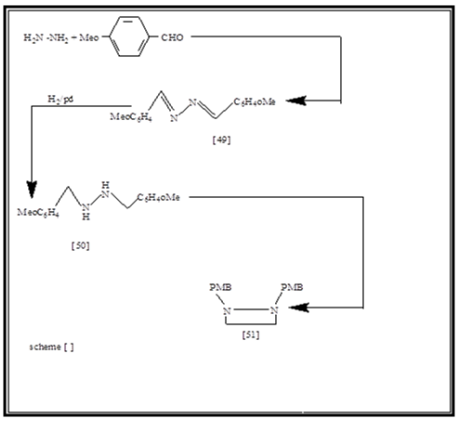


Figure 18

Fahmyl et. Al. Synthesied2-indolylarylindine hydrazones from reaction of 2-indolylcarbohydraziedwithdifferent aromatic and/or heterocyclic aldehydes, cyclocondensation of compound with thioglycolic acid give the corresponding 2-aryl-3-(2-indolylamide) thiazolidin-4-ones :

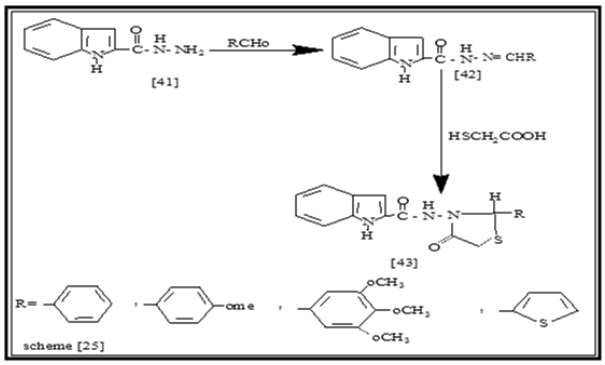


Figure 19

Kasimogullari et .al synthesized 3,3- (1,4- phenylene) bis(2-aryl- thiazolidin -4- one) by the reaction of thioglycollic acid with aldimines :

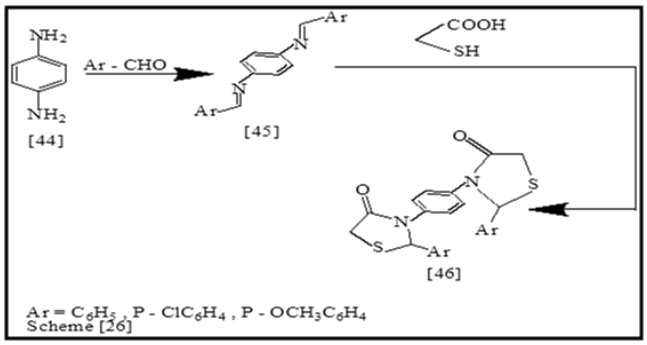


Figure 20

Anchal A synthesized 2- (4- hydroxyl phenyl) -3-(6- methoxy -1,3- benzothiazol -2-yl) -5- methyl -1,3-thiazolidin -4-one by reaction of 4-[6- methoxy -1,3- benzothiazole -2- yl) amino methyl]phenol with thiolatic acid :

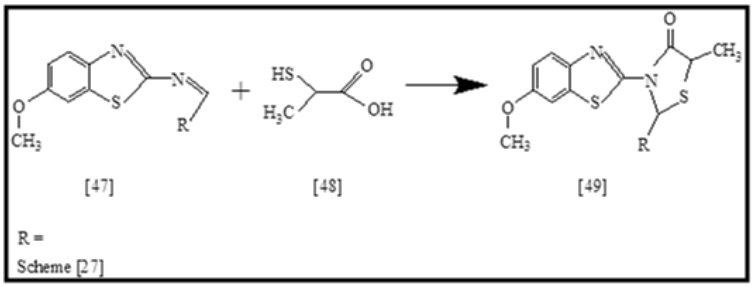


Figure 21

Madkour synthesized 6- bromo-3- [2-(4- chloro –phenyl) -4- oxo-1 ,3- thiazole-3- yl] -2- isopropyl -4(3H)- quinazolinone from the reaction of 3-aryliden amino -6- bromo -2- isopropyl -4(3H)- quinazolines with thio glycolic acid in dry benzene :

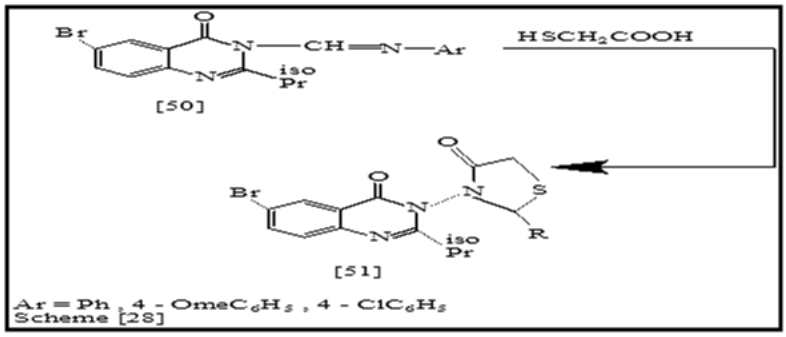


Figure 22

Mehdi et –al prepared (6- chloro- 2,3,5- triphenyl) -1,3- oxazine -4- one) [89] from reaction of (chloro carbonyl) phenyl ketene with N- benzilidene aniline :

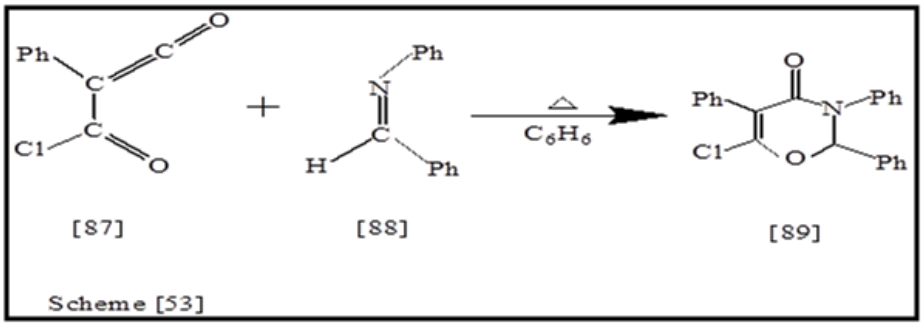


Figure 23

Archana et al described the reaction between halogen o substituted aldehydes and substituted primary amine yielding Schiff base , which converted into substituted – oxazine:

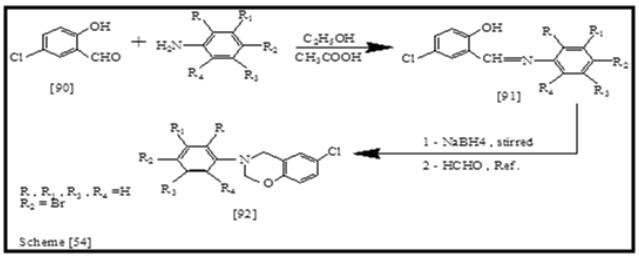


Figure 24

Dr. Nagham synthesized Bis(2- arabinose -5, 6- benzo -4- one -1,3- oxazine)

from reaction of Bis (1-arabinos amine) and salicylic acid:

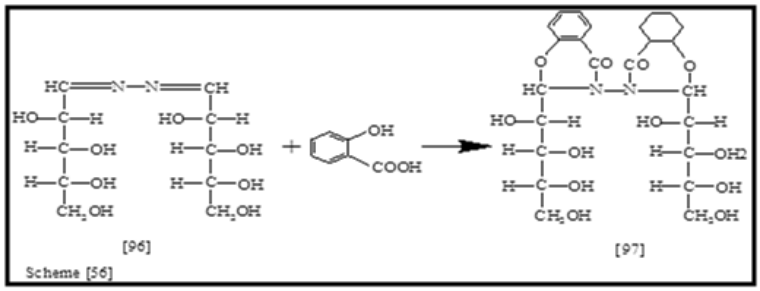


Figure 25

Dr. Nagham synthesized many schiff bases and azo groups called (formazan compound) to produce various membered rings .

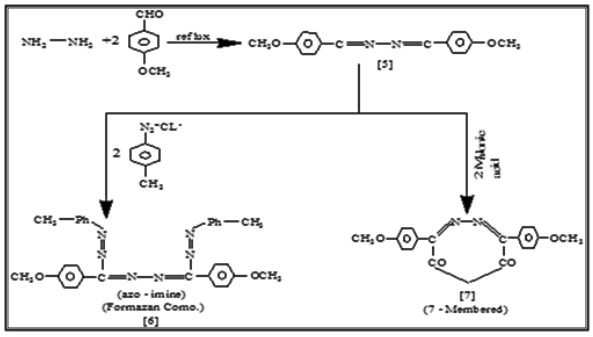


Figure 26

Dr. Nagham synthesized eight- membered rings from reaction of schiff base from

Melamine compound :

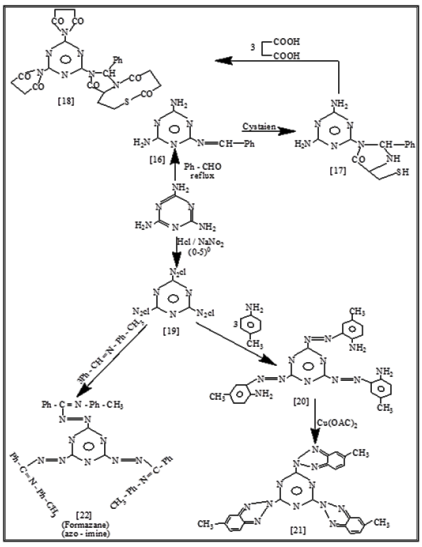


Figure 27

Dr. Nagham synthesized Ion-Complexes from coordination of schiff base (formazan)

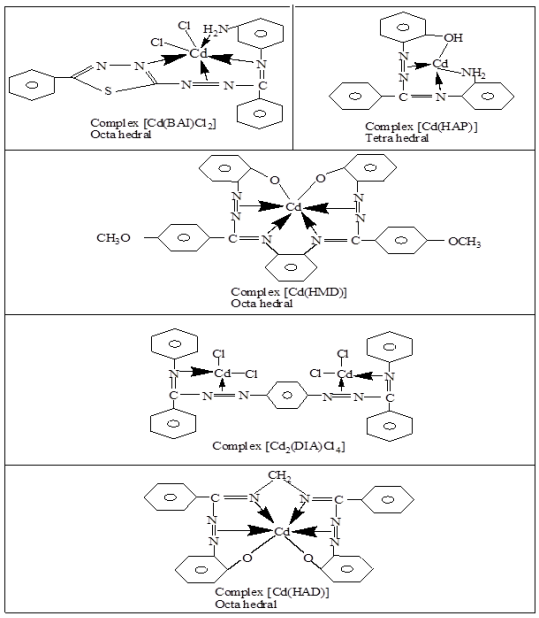


Figure 28

REFERENCES

1. S. George. , "Organic Chemistry" Mosby-Year Book . 1995 , Chp.14 , p. 589-649 (1995).
2. P. Sykes; "Agide Book to Mechanism in Oaganic Chemistry" , 5th Ed ., Longman, (1974) .
3. R. E. Brewster, W. E. McEwen; "Organic Chemistry" , Ch . 30ed Ed ., p.638 , (1971) .
4. B.A. Marry; "Organic Reaction Mechanism" , Ch . 1, Jon Willey sons , (2005) .
5. L.F. Fieser and K.L. Eilliamson , "Organic Experiment" 5th Ed ., DC . Heath and company Toronto, Canada, p. 270. (1983).

6. F. A.Carey and R. J. Sundberg "Advanced Organic Chemistry" part A:strures and Mechanisms, 2nded ., Plenum Press. New York, p. 243, (1983).
7. Nagham M Aljamali., As. J. Rech., 2014 , 7 ,9 , 810-838.
8. C.O.Wilson and O. Givold, "Text book of Organic Medicinal and pharmaceutical Chemistry", 5th Ed ., Pitman Medical Publishing Co. LTD, London coppy right. Cby. J. B. LippinCott Company (1966) .
9. Nagham M Aljamali., As. J. Rech., 2014 , 7 ,11.
10. Nagham M Aljamali., Int. J. Curr.Res.Chem.Pharma.Sci. 1(9): (2014):121–151.
11. Nagham M Aljamali., Int. J. Curr.Res.Chem.Pharma.Sci. 1(9): (2014):88- 120.
12. Y. Ju, D. Kumar, R. S. Varma, J. Org. Chem., 2006, 71, 6697-6700.
13. N. Iranpoor, H. Firouzabadi, B. Akhlaghinia, R. Azadi, Synthesis, 2004, 92-96.
14. Y. Liu, Y. Xu, S. H. Jung, J. Chae, Synlett, 2012, 2663-2666.
15. D. S. Bhalerao, K. G. Agamanchi, Synlett, 2007, 2952-2956.
16. Louis D. Quin and Tohn A. Tyrell, "Fundamentals of Heterocyclic Chemistry" 9th Ed.,Wiley , New York , (2010)
17. Paula YurkanisBruice , "Organic Chemistry " , 6th Ed., publishing as prentice hall, (2011) .
18. TheophilEicher and Siegfried Hauptmann, "The Chemistry Of Heterocycles" 2nd Ed., Wiley, (2003) .
19. Julio AlVarez–Builla , Juan Jose Vaquero and Jose Barluenga , "Moderen Heterocyclic Chemistry" , Wiley , (2011) .