Sudan university of Science and Technolgy

Department of chemistry

AThesis Submined In Partial Fulfilliment of the sRequirment of B.SC Degree In chemistry

Preparation of Di aryl gly oxime

Perpared by

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Supervisor

Uz. Fathi Abbas Omer

2014

بسم الله الرحمن الرحيم

قال تعالى:

(قل لو كان البحر مدادا لكلمات ربي لنفد البحر قبل أن تنفد كلمات ربي ولو جئنا بمثله مددا)

سوره الكهف الأيه (109)

Dedication

I dedicate this project to

My parents

family

sister

Acknowledgements

We would like to express my sincere appreciation to my superviser

Uz. Fathi Abbas Merghani for his lucide desigen of this research

and help throughout his work.

Abstract

Benzoin were prepared from aromatic aldehyde and ,their derivaties , this reaction catalyze by thiamine hydro chloride, then benzoin was oxidized by nitric acid to produce benzil, the benzil were reacted with hydroxyl amine to produce oxime, the oxime were change to β type , which are then reacted with metal ion to show their complexing properties.

مستخلص البحث

في هذا البحث تم تحضير مركب البنزوين من الالدهيد الاروماتي ومشتقاته وتم استخدام هيدروكلوريد السيامين كعامل حفاز, تمت اكسده البنزوين بواسطه حمض النتريك لانتاج البنزل , وتفاعل البنزل مع امين هيدروكسيل ونتج مركب الأوكسيم, وحول هذا الناتج لمركب اوكسيم من النوع بيتا, و تفاعل مع ايون المعدن لمعرفه خصائص المعقدات.

Content

1-Introduction

1-1 ALDEHYDE:

Many fragrances are aldehydes An **aldehyde** is an organic compound containing a formyl group. This functional group, with the structure R-CHO, consists of a carbonyl center (a carbon double bonded to oxygen) bonded to hydrogen and an R group,[1] which is any generic alkyl or side chain. The group without R is called the **aldehyde group** or **formyl group**. Aldehydes differ from ketones in that the carbonyl is placed at the end of a carbon skeleton rather than between two carbon atoms. Aldehydes are common in organic chemistry(2)..

1-1-1 Structuer:

Aldehyde contain the carbonyl group, C O, and are often referred to collectively as carbonyl compounds. It is the carbonyl group that largely determines the chemistry of aldehydes.

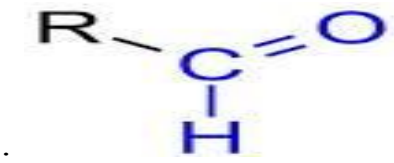
It is not surprising to find that aldehydes resemble each otherclosely in most of their properties. However, there is a hydrogen atom attached to the carbonyl group of aldehydes.

aldehydes are quite easily oxidized, aldehydes are usually more reactive toword nucleophilic addition the characteristic reaction of carbonyl compounds(1).

Let us examine the structure of the carbonyl group. Carbonyl carbon is joined to three other atoms by a bonds; since these bonds utilize sp2 orbitals(1).

they lie in a plane, and are 120 apart. The remaining/? orbital of the carbon

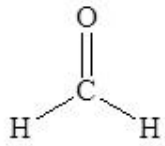
overlaps a p orbital of oxygen to form a π bond; carbon and oxygen are thus



joined by a double bond. The part of the molecule immediately surrounding
carbonyl carbon is flat; oxygen, carbonyl carbon, and the two atoms directly
attached to carbonyl carbon lie in a plane.
The electrons of the carbonyl double bond hold together atoms of quite
different electronegativity, and hence the electrons are not equally shared; in
particular, the mobile -n cloud is pulled strongly toward the more electronegativeatom, oxygen. The facts are consistent with the orbital picture of the carbonyl group.
Electron diffraction and spectroscopic studies of aldehydes and ketones show that carbon, oxygen, and the two other atoms attached to carbonyl carbon lie in a plane; the three bond angles of carbon are very close to 120.\The large dipole moments (2.3-2.8 D) of aldehydes and ketones indicate that the electrons or the carbonyl group arc quite unequally snared. We shall see how the physical and chemical properties of aldehydes and ketones are determined by the structure) the carbonyl group(1).

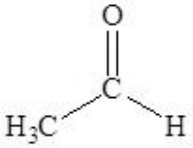
1-1-2 Nomenclature

The common names of aldehydes are derived from the names of the corresponding carboxyiic acids by replacing -ic add by -aldehyde.
The IUPAC names of aldehydes follow the usual pattern. The longest chain
carrying the CHO group is considered the parent structure and is named by replacing the -e of the corresponding alkane by -al. The position of a substituent is indicated by a number, the carbonyl carbon always being considered as C-l.
Here, as with the carboxylic acids, we notice that C-2 of the IUPAC name corresponds to alpha of the common name(1).



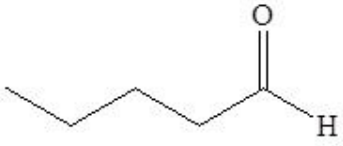
Methanal

(Formaldehyde)



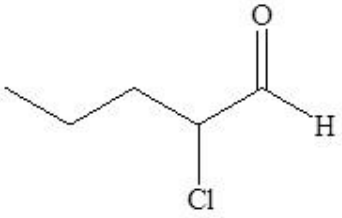
Ethanal

(Acetaldehyde)



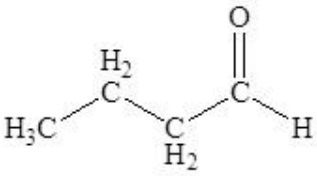
Pentanal

(Valeraldehyde)



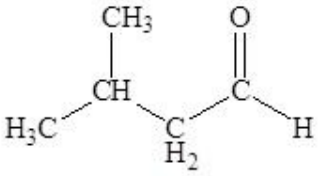
2-Chloropentanal

(a-Chlorovaleraldehyde)



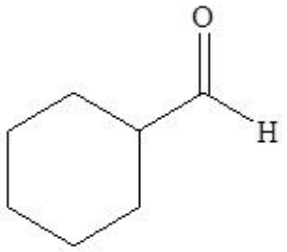
Butanal

(Butyraldehyde)

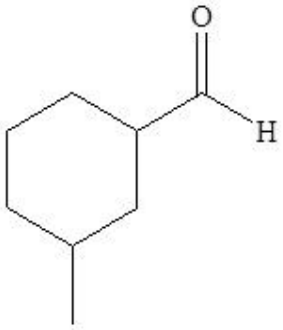


3-Methylbutanal

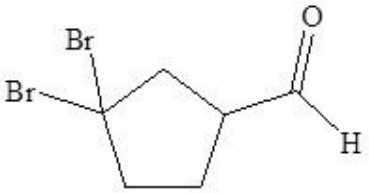
(isovaleraldehyde)



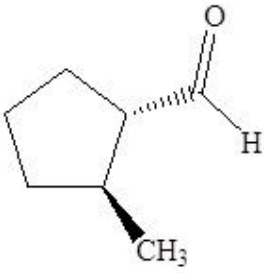
Cyclohexanecarbaldehyde



3-Methylcyclohexanecarbaldehyde



3,3-Dibromocyclopentanecarbaldehyde



trans-2-methylcyclopentanecarbaldehyde

1-1-3 physical properties:

The polar carbonyl group makes aldehydes are polar compounds,
and hence they have higher Boiling point that non-polar compounds or comparable molecular weight. By themselves, they are not capable Of intermolecular hydrogen bonding since they contain hydrogen bonded only to carbon; as a result they have lower boiling points than comparable alcohols or carboxylic acids. For example, compare -butyraldehyde (b.p, 76)
with n-pentane (b.p. 36) and ethyl ether (b.p. 35) on the one hand, and with n-butyl alcohol (b.p. 118) and propionic acid (b.p. 141) on the other.
The lower aldehydes are appreciably soluble in water, presumably
because of hydrogen bonding between solute and solvent molecules; borderline solubility is reached at about five carbon. Aldehydes are soluble in the usual organic solvents(1).

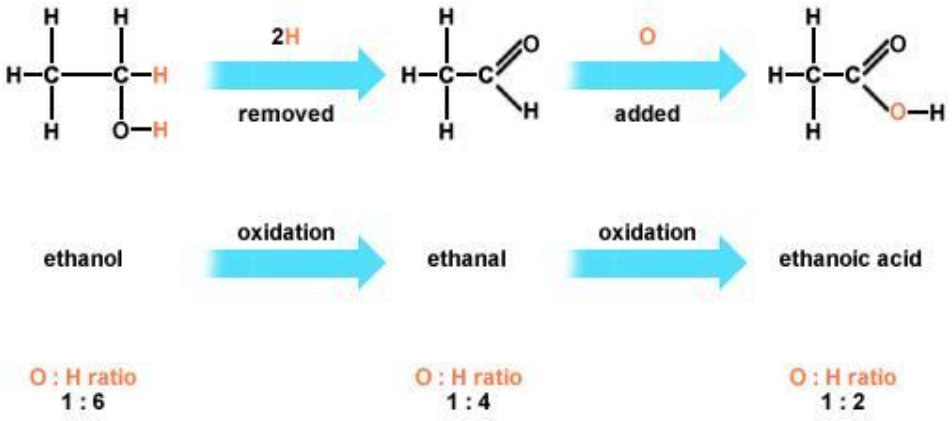
Name	M.P,c	B.P,C	Solub,g/100g H2O
Formaldehyde	-92	-21	V.sol
Acetaldehyde	-121	20	∞
Propionaldehyde	-81	49	16
n-Butyraldehyde	-99	76	7
n-Valeraldehyde	-91	103	SL.s
Heptaldehyde	-42	155	.1
Benzaldehyde	-26	178	.3
Phenaylacetaldehyde	194	SL.s	
m-tolualdehyde	199		

(1)

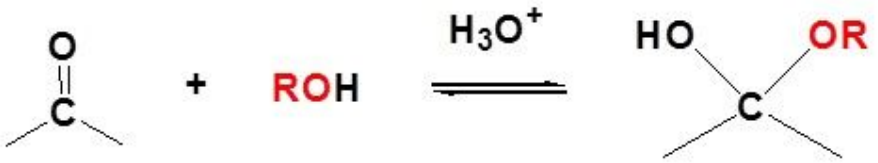
1-1-4-Chemical properties:

1-1-4-1-reaction with alcohol:

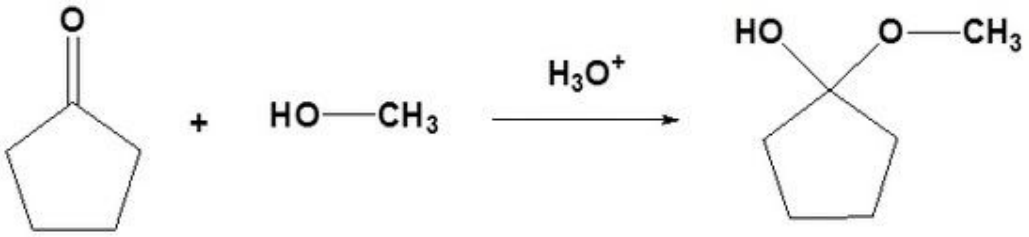
Alcohols add to the carbonyl group of aldehydes in the presence of anhydrous acids to yield acetals.
The reaction is carried out by allowing the aldehyde to stand with an excess of the anhydrous alcohol and a little anhydrous acid, usually hydrogen chloride. In the preparation of ethyl acetals the water is often removed as it is formed by means of the azeotrope of water, benzene, and ethyl alcohol (b.p. 64.9, Sec. 15.6). (Simple kctals are usually difficult to prepare by reaction of ketones with alcohols, and are made in other ways.)(1):

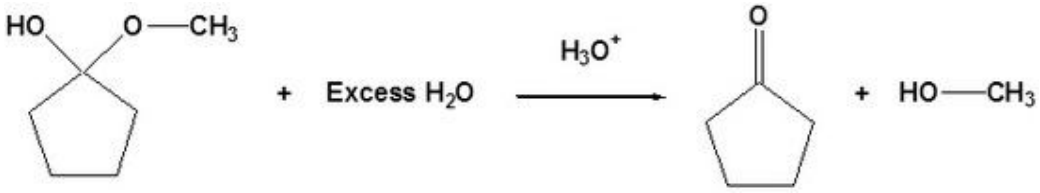


EXAMPLE;



Aldehyde or Ketone **Hemi-Acetal**





1-1-4-2-reaction with water:

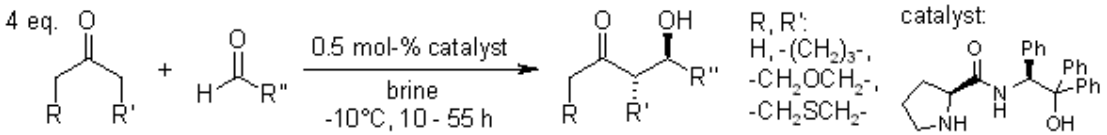
the addition of water to a carbonyl group, specifically the aldehyde carbonyl group in acetaldehyde. The overall reaction (from reactants to products) is:

- EXAMPLE:

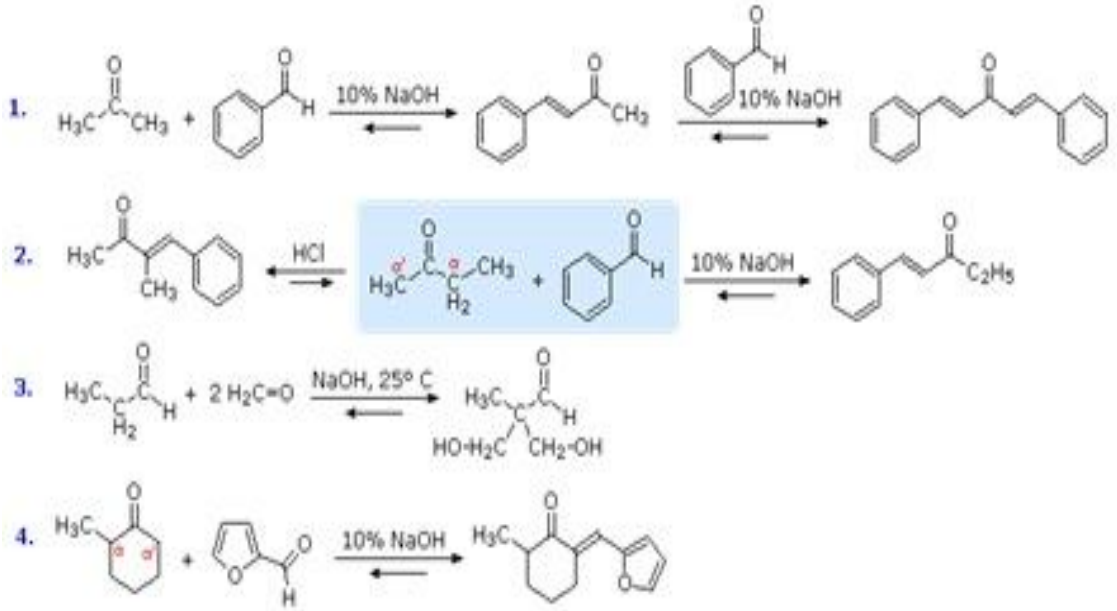
This type of reaction is known as an addition reaction. The name fits, because the product is the sum (or adduct) of the reactants. Addition reactions occur typically with functional groups which include *pi* bonds. Functional groups which include pi bonds are called *unsaturated* functional groups because some of the atoms in them have fewer than the maximum number of sigma bonds. For contrast, those which have no pi bonds do have the maximum number (four for carbon) of sigma bonds and are called *saturated*. (Take another look at the table of functional groups inside the front cover of Brown and note which ones are unsaturated.)

1-1-4-3-reaction with ketone:

This process begins with the irreversible generation of the kinetic enolate, e.g. by employing a sterically hindered lithium amide base such as LDA (lithium diisopropylamide). With an unsymmetrically substituted ketone, such a non-nucleophilic, sterically-demanding, strong base will abstract a proton from the least hindered side. Proton transfer is avoided with lithium enolates at low temperatures in ethereal solvents, so that addition of a second carbonyl partner (ketone or aldehyde) will produce the desired aldol product.

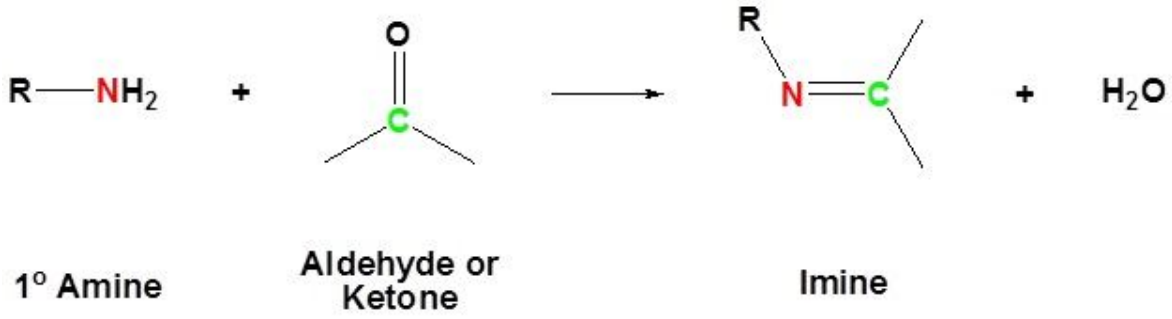


Example:*



1-1-4-4-reaction with primary amine:

- aldehydes and ketones react with a range of primary amine derivatives to give substituted imines.
- The derivatives with ammonia are too unstable to be isolated but can be reduced *in situ* to amines.
- The mechanism of these type of reactions is shown on the previous page.
- The reaction of 2,4-dinitrophenylhydrazone (2,4-DNP or Brady's reagent) is used as a laboratory test for aldehydes and ketones since the products precipitate as yellow to red solids(3)..



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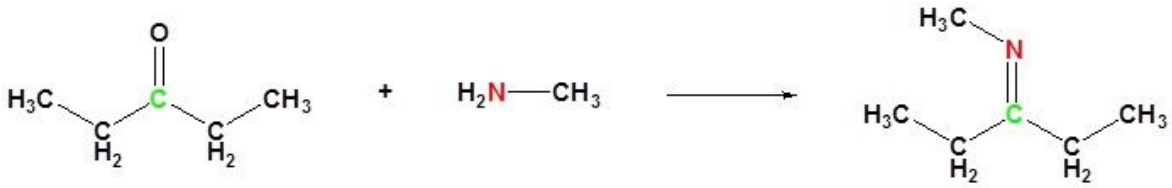
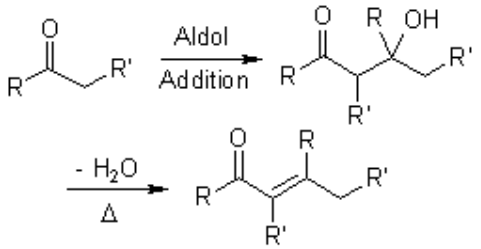


1-1-4-5- aldol condensation:



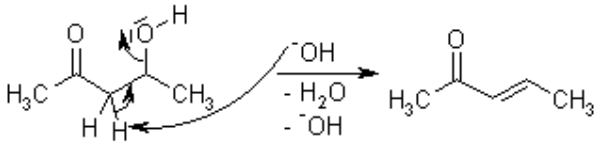
In some cases, the adducts obtained from the Aldol Addition can easily be converted (in situ) to α,β-unsaturated carbonyl compounds, either thermally or under acidic or basic catalysis. The formation of the conjugated system is the driving force for this spontaneous dehydration. Under a variety of protocols, the condensation product can be obtained directly without isolation of the aldol.

The aldol condensation is the second step of the Robinson Annulation.

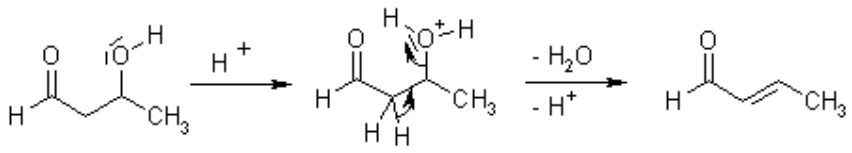
Mechanism of the Aldol Condensation

For the addition step see Aldol Addition:

Base catalyzed condensation :



Acid catalyzed condensation :



(23)

1-1-4-6-Benzion:

Benzoin (**Figure 1**) is an alpha-hydroxy ketone or a ketol, which forms as a crystalline solid.[1] This molecule is of vital importance to the synthetic process. It not only has importance as a parent molecule, but is also a key intermediate and precursor.[2] Benzoin is a chiral compound that appears in entantiomeric form, this crucial property provides stereoselectivity to its reactions and allows for the formation of non-symmetrical molecules.[2]
One of the compound's most critical uses comes from its ability to be oxidized easily into benzil (**Figure 2**), a photoinitiator of major importance to polymer chemistry. Benzil can be used to harden polymer coating, which can be used commercially and biologically.[3,4] Benzoin is formed from benzaldehyde through the formation of a new carbon to carbon bond(19).

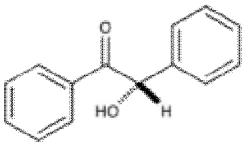


Figure 1. Structure of chiral benzoin

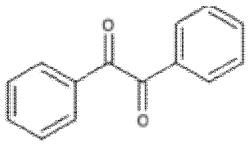


Figure 2. Structure of benzil

Condensation reactions are used often in organic chemistry, as they have the ability to join several compounds resulting in the formation of one large product. This is accomplished through the formation of a new bond. [5] These reactions are commonly used in polymer chemistry, they can elongate chains with no disruption to side group functionality, simply adding monomers.This type of polymerization has major commercial uses as it is often used in the synthesis of nylons and polyesters.[4] Carbonyl condensations, those that use carbonyls as reagents are of the most important types of condensations. These reactions have significant biological importance; several metabolic processes require condensation reactions. They are also one of the most general ways of forming carbon to carbon bonds, which are crucial to organic chemistry as few reactions have this ability.[5]

Benzoin condensation is one of the oldest carbon to carbon bond forming reactions in organic chemistry, that has major use as a model for specific catalysis.[6] The reaction has been used synthetically for over a century to create the parent molecule benzoin from two equivelants of benzaldehyde.[6,7] Traditionally the reaction was catalyzed by the cyanide

ion, however in the last thirty years it has been discovered that thiazolium salt species (**Figure 3**), most commonly in the form of thiamine hydrochloride or vitamin B_1 (**Figure 4**) can function analogously in a much greener way, seen in schema 1.

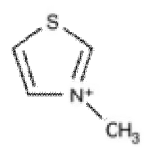


Figure 3. Basic structure of thiazolium salt

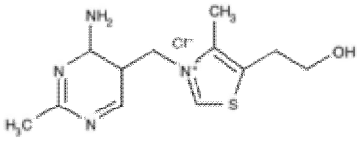
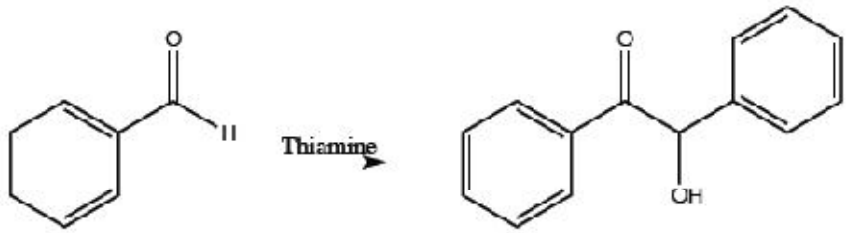


Figure 4. Structure of vitamin B_1



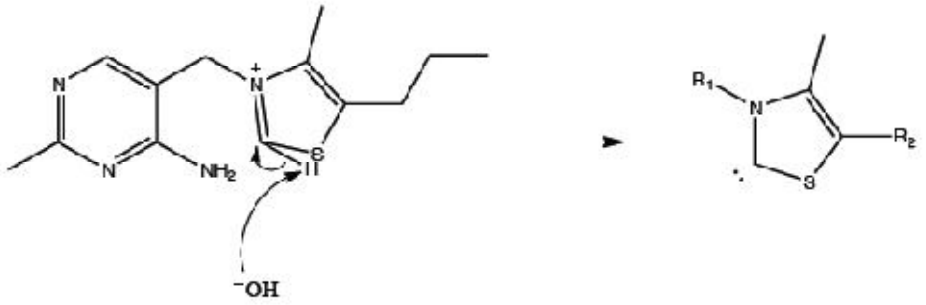
benzaldehyde

2-hydroxy-1,2-diphenylethanone
(Benzoin)

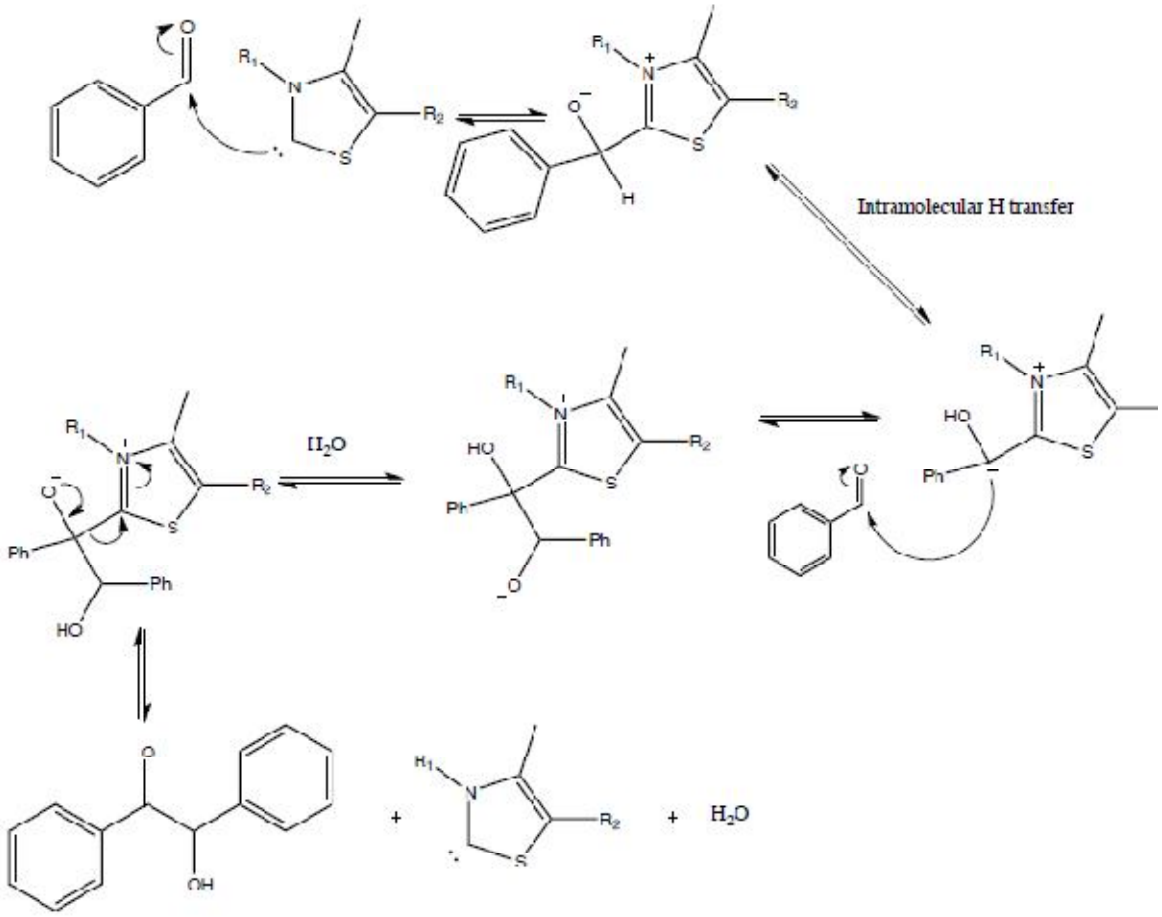
Mechanism

Step 1: Deprotonation of the thiamine:

NaOH attacks thiamine and deprotonates it. It is a condensation, since a molecule of H_2O is released. There is a formation of a carbine, which is very reactive.



Step 2: nucleophile attack of the benzaldehyde by the deprotonated thiamine:

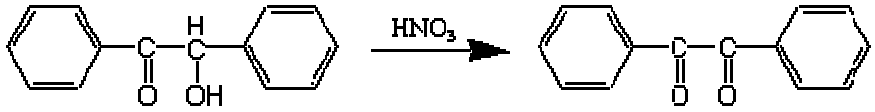


Benzoin is a parent compound to other types of aromatic ketols formed through benzoin condensation. The purpose of this lab was to synthesize benzoin from two equivelants of benzaldehyde in the most essential type of benzoin condensation. Thiamine was used as the catalyst, it is a natural product and a much safer method than the cyanide ion which is highly toxic. Thiamine-dependent enzymes are a biologic necessity. This condensation provides an example of metabolic condensations catalyzed by thiamine.[6] The success of the reaction can be quantified through NMR and IR spectroscopy of the product(19).

1-1-5-Oxidation of Benzion:

The oxidative transformation of benzoin to benzil has been accomplished by the use of a wide variety of reagents or catalysts and different reaction procedures. The conventional oxidizing agents yielded mainly benzaldehyde or/and benzoic acid and only a trace amount of benzil. The limits of practical utilization of these reagents involves the use of stoichiometric amounts of corrosive acids or toxic metallic reagents, which in turn produce undesirable waste materials and required high reaction temperatures. (4)

Starting with the α-hydroxyketone benzoin (prepared in **Part 1**), you will prepare an oxidation product, benzil, which is an α-diketone.



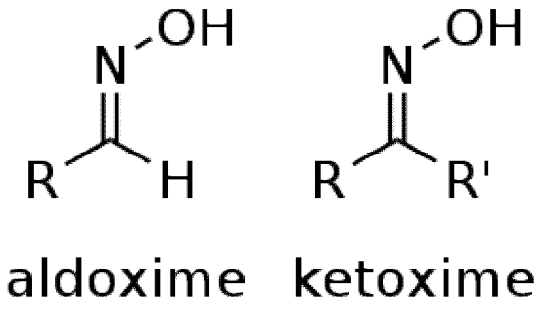
Benzoin Benzil

This oxidation can easily be done with a variety of mild oxidizing agents, including Fehling's solution (an alkaline cupric tartrate complex) or copper(II) sulfate in pyridine. In addition, benzoin could be oxidized by sodium dichromate, but the yield of benzil is lower because some of the benzoin is converted back into benzaldehyde following cleavage of the bond between the two oxidized carbon atoms, which is activated by the phenyl rings, producing benzoic acid as the final product. In this experiment, due to ease of use and consistent results, we will use nitric acid as the oxidizing agent.

1-1-6-OXime:

An **oxime** is a chemical compound belonging to the imines, with the general formula $R^1R^2C{=}N\ O\ H$, where R^1 is an organic side-chain and R^2 may be hydrogen, forming an **aldoxime**, or another organic group, forming a **ketoxime**. O-substituted oximes form a closely related family of compounds. Amidoximes are oximes of amides with general structure RC(=NOH)(NRR').

Oximes are usually generated by the reaction of hydroxylamine and aldehydes or ketones. The term oxime dates back to the 19th century, a portmanteau of the words *oxygen* and *imine*.



aldoxime ketoxime

1-1-6-1-Structure and properties

Oximes exist as two geometric stereoisomers: a *syn* isomer and an *anti* isomer. Aldoximes, except for aromatic aldoximes, which exist only as *anti* isomers, and ketoximes can be separated almost completely and obtained as a *syn* isomer and an *anti* isomer.

Oximes have three characteristic bands in the infrared spectrum, at wavenumbers 3600 (O-H), 1665 (C=N) and 945 (N-O).[5]

In aqueous solution, aliphatic oximes are 10^2- to 10^3-fold more resistant to hydrolysis than analogous hydrazones.[6]

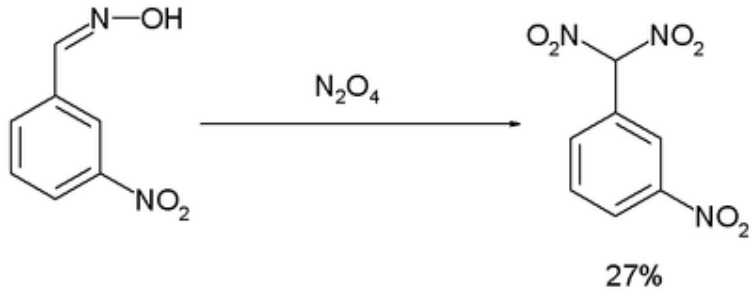
1-1-6-2-Reactions

The hydrolysis of oximes proceeds easily by heating in the presence of various inorganic acids, and the oximes decompose into the corresponding ketones or aldehydes, and hydroxylamines. The reduction of oximes by sodium metal, sodium amalgam, hydrogenation, or reaction with hydride reagents produces amines.[7] Typically the reduction of aldoximes gives

both primary amines and secondary amines; however, reaction conditions can be altered (such as the addition of potassium hydroxide in a 1/30 molar ratio) to yield solely primary amines.[8]

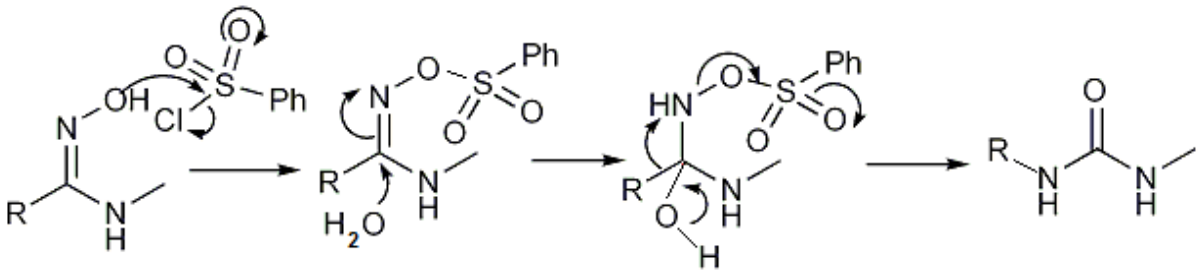
In general, oximes can be changed to the corresponding amide derivatives by treatment with various acids. This reaction is called Beckman rearrangement. In this reaction, a hydroxyl group is exchanged with the group that is in the anti position of the hydroxyl group. The amide derivatives that are obtained by Beckmann rearrangement can be transformed into a carboxylic acid by means of hydrolysis (base or acid catalyzed). And an amine by hoffman degradation of the amide in the presence of alkali hypoclorites at 80 degrees Celsius, the degradation is itself prone to side reactions, namely the formation of biurets or cyanate polymers., To avoid this side-reaction, strict temperature control is necessary; the reaction must be conducted at sufficient temperature to isomerise the cyanate to the isocyante. Also, good solvation is also crucial to be successful. Beckmann rearrangement is used for the industrial synthesis of caprolactam (see applications below).

The **Ponzio reaction** (1906)[9] concerning the conversion of *m*-nitrobenzaldoxime to *m*-nitrophenyldinitromethane with dinitrogen tetroxide was the result of research into TNT-like high explosives:[10]



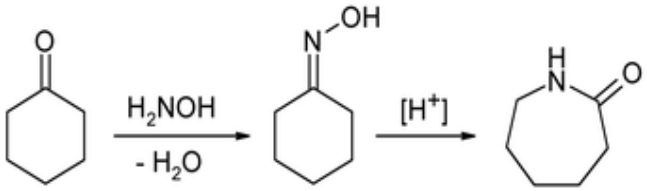
In the Neber rearrangement certain oximes are converted to the corresponding alpha-amino ketones.

Certain amidoximes react with benzenesulfonyl chloride to substituted ureas in the **Tiemann rearrangement**[11][12]



1-1-6-3-Uses

In their largest application, an oxime is an intermediate in the industrial production of caprolactam, a precursor to Nylon 6. About half of the world's supply of cyclohexanone, more than a billion kilograms annually, is converted to the oxime. In the presence of sulfuric acid catalyst, the oxime undergoes the Beckmann rearrangement to give the cyclic amide caprolactam:



1-1-6-4-Other applications

- Dimethylglyoxime ($dmgH_2$) is a reagent for the analysis of nickel and a popular ligand in its own right. In the typical reaction, a metal reacts with two equivalents of $dmgH_2$ concomitant with ionization of one proton.

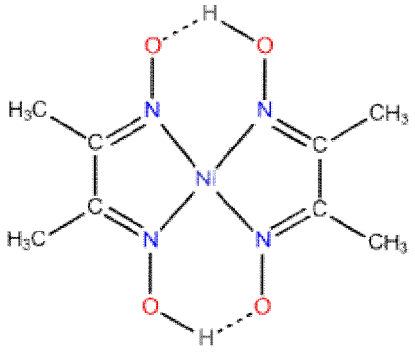


Figure. Structure of $Ni(dmgH)_2$.

- Oxime compounds are used as antidotes for nerve agents. A nerve agent inactivates acetylcholinesterase molecules by phosphorylation of the molecule. Oxime compounds can reactivate acetylcholinesterate by attaching to the phosphorus atom and forming an oxime-phosphonate, which then splits away from the acetylcholinesterase molecule. The most effective oxime nerve-agent antidotes are pralidoxime (also known as 2-PAM), obidoxime, methoxime, HI-6, Hlo-7, and TMB-4.[13] The effectiveness of the oxime treatment depends on the particular nerve agent used.[14]
- Perillartine, the oxime of perillaldehyde is used as an artificial sweetener in Japan, as it is 2000 times sweeter than sucrose.
- Salicylaldoxime is a chelator.[*citation needed*]
- Glyoxime, produced via the condensation of glyoxal with hydroxylamine,[15] forms highly energetic copper, lead and silver salts (copper, lead, and silver glyoximate, respectively).[16] However these compounds are too unstable to be of any commercial value.[*citation needed*]
- Diaminoglyoxime, a glyoxime derivative, is a key synthetic precursor, used to prepare various compounds, containing the highly reactive furazan ring.
- Methyl ethyl ketoxime is a skin-preventing additive in many oil-based paints.
- Some amidoximes like polyacrylamidoxime can be used to capture trace amounts of uranium from sea water[17][18]

2-Experimental and Result

2-1-Chemicals:

2-1-1-Solvent:

-Ethanol 95%

-Distelled water

-Benzen(mwt:78.11-Mfr by:ALPHA CHEMIKA-Grate:Gbr)

-2-1-2-Materials:

-Sodium hydroxide(mwt:40-Mfr by:PACKD FOR SERVICING LNDUSTR-Grate:Gbr).

-Thiamine.

-vanillin(mw,t :152.15-Grate:Gbr –loba chemia put. Ltd ,107 wode house Road,mumbai400005.india). .
-Benzaldehyde(mwt106.12-Made in INDIA-Grate:Gbr).

-P-chloroBenzaldehye.

-Nitric acide.

-Hydroxyl amine (mwt:69.49-Mfr by:ALPHA CHEMIKA-Grate:Gbr).

2-2Appertaus:

-Conical flask(250ml)- Beaker(50ml, 100ml) –Round Bottome flask(50ml)- pipatte(10ml)- funnel- Glass rode.

2-3-Instrumental:

-IR

-Analytical plance

-Hot plate

2-4-Mothodes:

2-4-1-Prepration 0f Benzion:

1.5g of thamine hydrochloride was weighed in to aconical flask ,the solide was dissolved in to 2ml of water by swirling the flask, then 15ml of 95% ethanol was added,and the solution was swirled until it was homogeneous.

Then 4.5ml of aqueous sodium hydroxide solution was added,and the flask was swirled untial the bright yellow color coverted to bale yellow color.thenXg of benzaldehyde derivative was added to the flask, the conent of the flask was swirled until it was homogenous, then the flask was coopered and allowed it to stand in adark place for at least two days.

Then the solution was filtrated ,washed thed preciptate with cold water ,dried,weiged and calculated the percentage yield.

2-4-2-prepration of Benzil:

1g of curde benzion was weighed then added 5ml of concentrated nitric acid in to 50ml round bottomed flask ,the solution was heated on aboiling water bath with occasional shaking until evolution of oxide nitrogen.then pour the reaction mixture into 50ml of cold water in beaker,we stired well until the oil crystallises completely as yellow solide ,after the curd benzil was filtrated at pumped,and was washed it thorounghly with water to removed the nitric acid,the preciptate was dried ,weighed and calculated the percentade yeild.

2-4-3-prepration of oxime:

1g of hydroxyl amine hydrpchlorid was weighed and dissolved in to 10 ml of water ,6ml of3N sodium hydroxide solution was added ,0.50g of benzil sample was added ,the mixture was warmed on awater bath for20min ,then cooled in ice bath,filtrated the soution ,driedthe preciptate,weighed and calculated the percentage yeild.

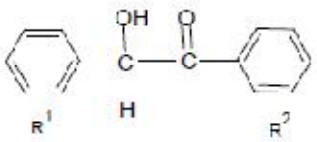
2-4-4-prepration of BetaBenzil monoxime:

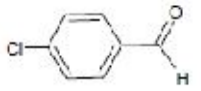
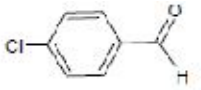
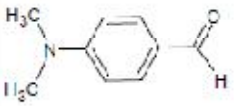
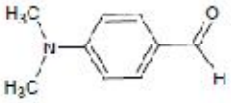
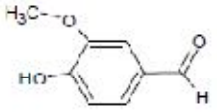
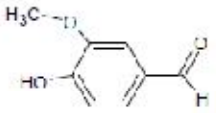
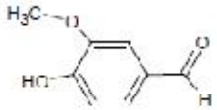
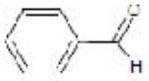
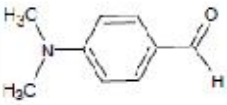
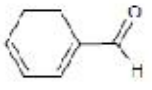
The alpha oxime is converted in to beta form by treatment with asolution of hydrogen chloride in benzen at room temperture.from benzen,solvate crystals which melt on rapid heating are obtained. removal of benzen of crystallisation in an oven and recrstallisation from carbon disulphide yeild pure beta benzilmomoxime.

2-5-Result:

2-5-1-percentage:

2-5-1-1Benzion:



R^1	R^2	Percentage
		69.85%
		80.80%
		84.1%
		86.72%
		85.01

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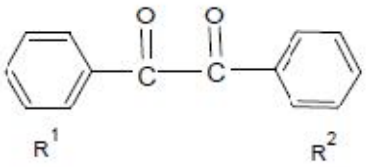
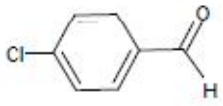
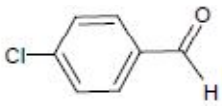
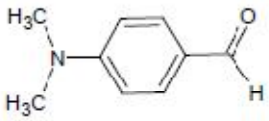
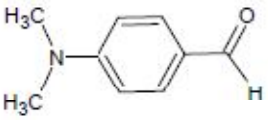
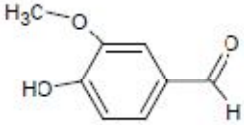
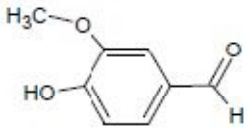
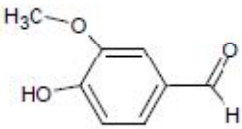
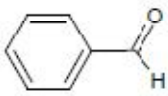
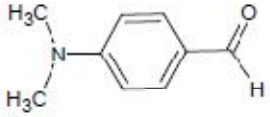
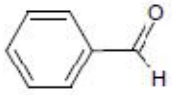


R^1	R^2	percentage
		79.55%
		84.84%
		88.9%
		90.9%
		87.8%

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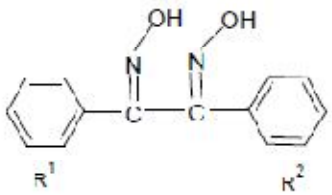
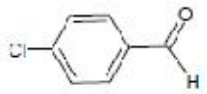
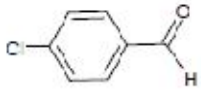
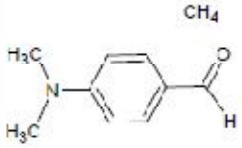
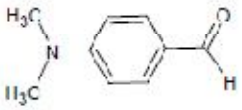
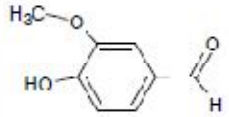
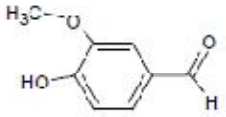
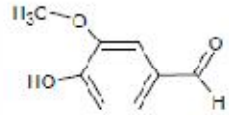
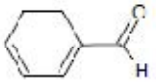
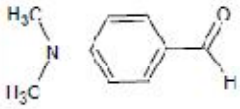
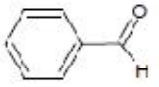
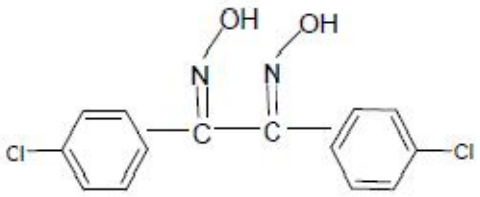


R^1	R^2	percentage
		82.73%
		89.76%
		92.72%
		96.39%
		92.85%

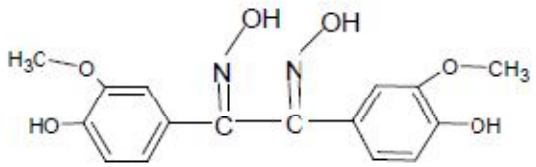
2-5-2-IR:

2-5-2-1:



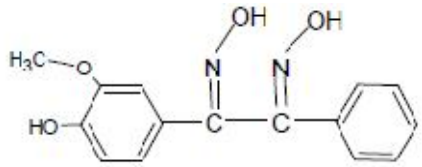
Functional group	Wave number /cm^{-1}
C-H st.vib	3091.68
O-H st.vib	3747.43
N-O st.vib	1666.38
C=C (Ar) st.vib	1585.38
C=N st.vib	1211.21
C-Cl st.vib	732.90

2-5-2-2:



Functional group	Wave number /cm^{-1}
C-H st.vib	2966.31
C-H (Ar) st.vib	3122.54
O-H st.vib	3745.50
N-O st.vib	1616.24
C=C (Ar) st.vib	1533.30
C=N st.vib	1301.86
C-O st.vib	1249.79

2-5-2-3:



Functional group	Wave number /cm^{-1}
C-H st.vib	3006.82
C-H (Ar) st.vib	3093.61
O-H st.vib	3407.98
N-O st.vib	1535.23
C=C (Ar) st.vib	1569.95
C=N st.vib	1301.86
C-O st.vib	1191.93

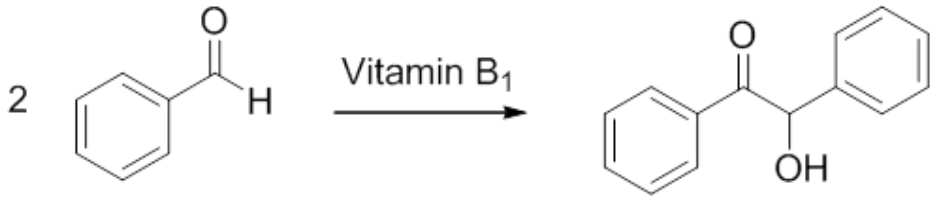
3-Discition

3-1-Benzion:

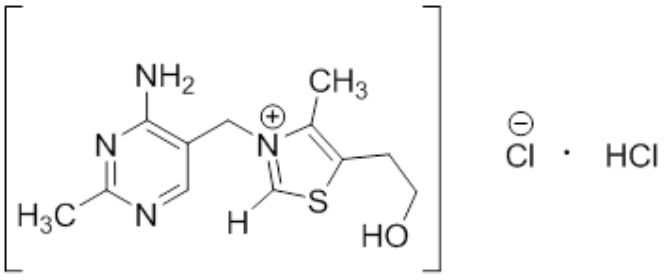
Benzoin is the precursor of the antiepileptic medicine, **Dilantin (Phenytoin)**.

Benzoin is also a white crystal **perfumery**. The DL-type is a hexagon monoclinic rhombic crystal. Both D-type and L-type are needle-shape crystals.

In this experiment, a benzoin condensation of benzaldehyde is carried out with a biological coenzyme, thiamine hydrochloride, as the catalyst(20).

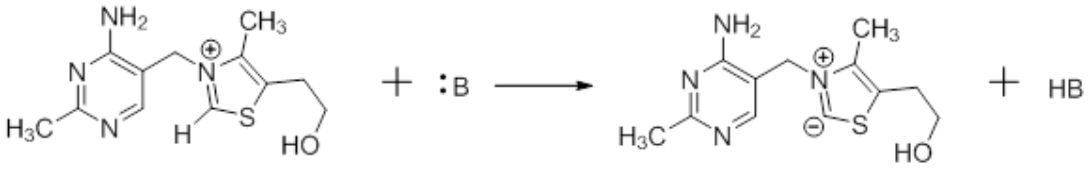


Vitamin B_1 is a coenzyme. It may replace the extremely toxic substance, sodium cyanide, as the catalyst, is benzoin condensation. The structure of Vitamin B_1 is as fallow:

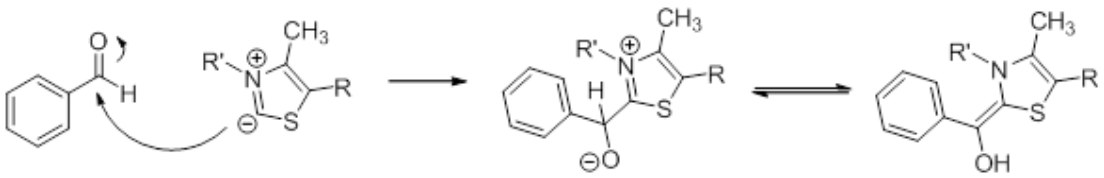


3-1-1-Mechanism

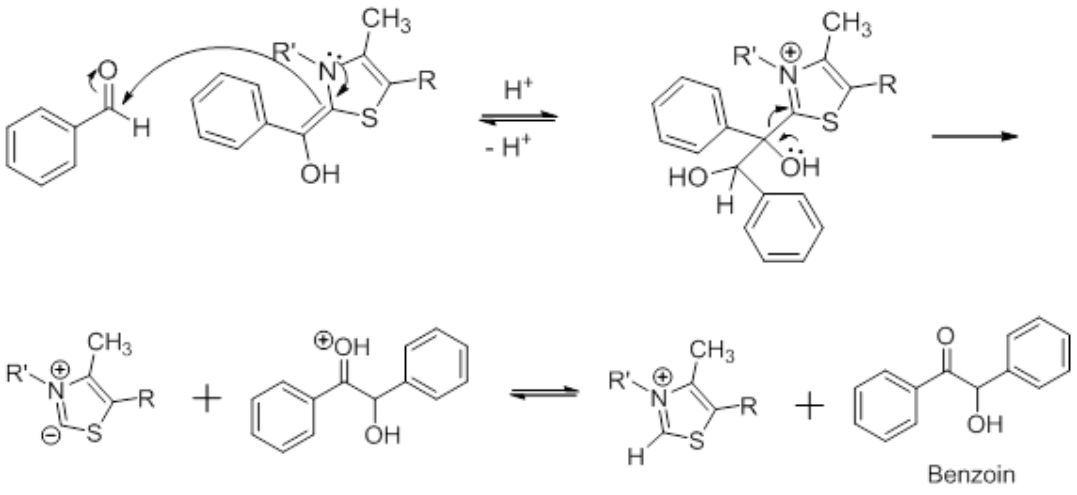
Step 1



Step 2



Step 3



Methoxy substituent are electron donating, which increases the electron density at the carbonyl carbon, which also makes it less electrophilic for the thiamine nucleophile to attack it.so the (benzion) reaction will no happen for those two.

The chloro substituent are electron withdrawing so the thiamine attack the carbonyl carbon impoluing proton transfer occurs to make

carbonanion .but since the chloro is electron withdrawing ,they cause the carbonanion to be less nucleophilic . the rate of the reaction is very slow in addition of the anion to second aldehyde.

The electron withdrawing group decrease the percentage of reaction and electron donating group increase ,the percentage of 4,4/- di Chloro benzion is equal 69.85%, the percentage 4,4/- N-N-di methyl amine benzion equal 80.80%, 3,3/ di methoxy-4,4/ di hydroxyl benzion is equal84.1%.when we mixed pure benzaldehyde with N,N di methyl amine benzaldehyde,the percentage of N,N di methyl amine benzion in this mixture 85.81%,the percentage of vaniline and benzaldehyde mixture is equal 86.7%.

3-2-Benzil:

Nitric acid readily oxide benzion to benzil (1,2-di phenyl 1,2-ethane dione), a di ketone ,it self bening reduced to (nitrous acid) which decompose to oxides of nitrogen + water .

Ph-CH (OH) –c= o-ph –[o] → phco-coph

$HNO_3 \rightarrow HNO_2 + [O]$

$2HNO_2 \rightarrow NO_2 + NO + H_2o$

Overall:

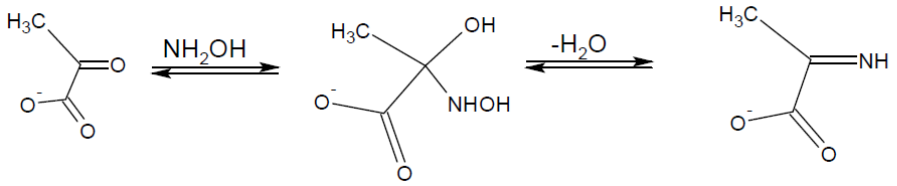
$2phcH\ (OH)\text{-}C{=}O\text{-}ph + 2HNO_3 \rightarrow 2Ph\text{-}co\text{-}co\text{-}ph + NO_2 + NO$ (21)

The electron donating group oxidized rapidly (3,3\ di-methoxy-4,4\di hydroxyl benzil the percentage equal88.9%) and electron withdrawing group less oxidized (4,4\- di chloro benzil equal 79.55%).

3-3- Oxime:

If for example, the reaction at PH7 pyruvate anion(1) and hydroxylamine, NH_2OH, is followed by moitoring the infra-red spectrum of the reaction mixture, then the absorption characteristic of C=O (v_{max} 1710 Cm^{-1}) in the starting material(1) is found to disappear completely

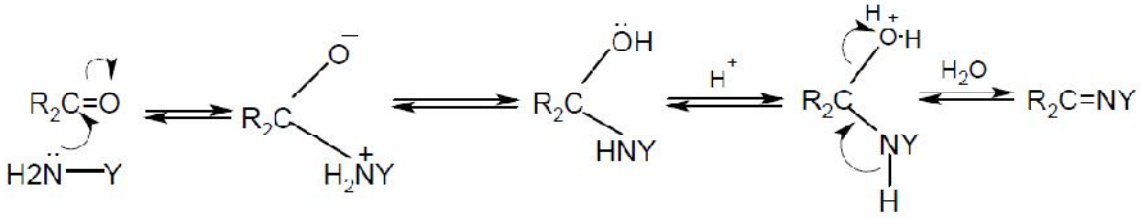
before any absorption characteristic of C=N (v_{max} 1400Cm^{-1}) in the product oxime (2) appears at all. Clearly an intermediate must thus be formed, and it seems probable that this is acarbinolamine (3,such a species has actually been detected by n.m.r. spectroscopy, in the reaction of MeCHO with NH_2OH) :



(1) (3) (2)

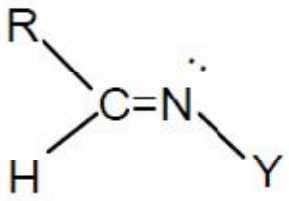
V_{max}1710cm^{-1} $^{V}_{max}$1400cm^{-1}

Increasing the acidity of the reaction mixture is found to decrease the rate at which C=O absorption disappears-: NH_2OH is beging progressively converted into $HN^{+}H_2OH$, which is not nucleophilic and to increase markedly the rate at which the C=N absorption appears increasing acid catalysis of the dehydration (3)-(2). This is compatible with a reaction pathway of the generate form:

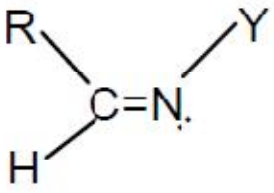


Strong nucleophiles such as NH_2OH (Y=OH) do not require catalysis of their initial addition to C=O, but weaker ones such as $phNHNH_2$(Y=PhNH) and $NH_2CONHNH_2$(Y=$NHCONH_2$) often require acid catalysis to activate the C=O group(cf.p.204,it is in fact general acid catalysis). Often, either the initial addition step or the dehydration step can be made rate- limiting at will, depending on the pH of the

solution. At neutral and alkaline pHs it is generally the dehydration, e.g.(3)-(2) that is slow and rate-limiting(cf. above),while at more acid pHs it is generallythe initial addition of the nucleophile, e.g.(1)-(3). That is slow and rate limiting. This clearly has significance in preparative and formation 0f such derivatives of carbonyl compounds tends to exhibit PH optuma the value depend ing on the nature of the particular carbonyl compound and of the ammonia derivative empoyed: thus for formation of an oxime from propanone, Me_2CO,the optimum pH is found to be ≈4.5. with aldehydes (and with unsymmertrical ketones ,RCO') there is ,of cours, the possibility of formation alternative syn and anti geometrical isomers:



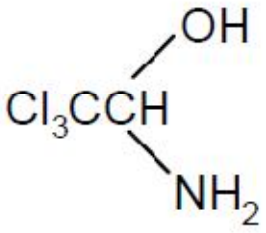
syn



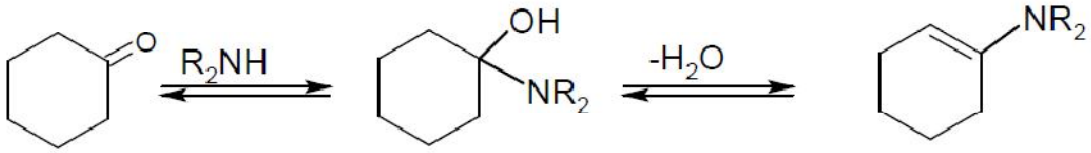
anti

It is found in practice that the syn isomer usually predominates.;with RCOR` this is the isomer in which Y is nearest to the smaller of the groups,R or R`.

Ammonia it self yeilds imines,$R_2C=NH$.with carbonyl compounds but these derivatives are unstable and react with each other to form polymers of varying size. The classical aldehyde ammonias are found to be hydrated cyclic trimers, but from aldehydes carrying powerfully electron-with drawing subtituents it is possible to isolate the simple ammonia adduct [4, cf.(3), and hydrates, p. 208, hemi-acetals, p. 209:



With RNH_2 the product are also imines ,these ,too ,are usually un stable unless one of the substituents on the carbonyl carbon atom is aromatic ,e.g .ArCH=NR- the stable products are then known Schift bases .With R_2NH, the initial adduct(5) cannot lose water in the normal way; some such species have been isolated but they are particularly stable. If, however , the adduct has any α-H atoms then a different dehydration can be made to take place yielding an enamine(6):



(5) (6)

Enamines are of some important as synthetic intermediates.(22).

4,4/-Chloro oxime percentage is equal 82.7%, 4,4/ di methyl amine oxime percentage is equal 89.8%, 3,3/ di methoxy-4,4/ -di hydroxyl oxime percentage is equal 92.7%,the percentage of 4,di methyl amine oxime is equal 92.85% and 3,methoxy 4, hydroxy oxime percentage is equal 96.39.

3-3-1- IR Spectroscopy:

Illustrates the spectrum of oxime sample with FT-IR transmission in the rang 4000-400cm^{-1} .the spectrum in 2-5-2-1 shows characteristies absorption association band with commom compound. The stretching

absorption beaks at 3091.68cm^{-1}, 3747.43$cm^{-1}$and 1122.49cm^{-1} corresponding to C-H,O-H and O-N groups respectively, also the spectra shows stretching absorption band at 1585.38$cm^{-1}$and 1211.21cm^{-1} corresponding to C=C(Ar) and C=N groups respectively, at 732.90cm^{-1} lead to C-CL group. The spectrum in 2-5-2-2 shows characteristies absorption ,the stretching absorption beaks at 3745.50cm^{-1}, 2966.31cm^{-1} and 3122.54cm^{-1} corresponding to O-H, C-H, C-H(Ar) groups respectively, while the spectra show stretching absorption beaks at 1533.30 and 1186.14 leads to C=C(Ar) and O-N groups respectively ,at 1301.86cm^{-1} appear C=N group, and at 1249.79cm^{-1} appear C-O group. The spectrum in 2-5-2-3 shows at 3407.98cm^{-1}, 3006.8cm^{-1} and 3093.61cm^{-1} corresponding to O-H, C-H ,C-H(Ar) stretching vibration respectively, also the shows stretching absorption at 1569.95cm^{-1}, 1301.86cm^{-1} and 997.13cm^{-1} leads to C=C(Ar),C=N, C-O groups.

3-4-Recommendation:

In this work five benzion, benzil and oxime products were prepared, the oxime were change to β type. Three of the oxime were illucidate with IR.

-Melting point of all prepared compound must be done.

-More illucidation spectra should be done such as H^1NMR, Ms.

-More complexing properties with other element is favoured.

-More reaction condition of complex formation should be done .

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