ALDEHYDE & KETONE (Part-II)

By

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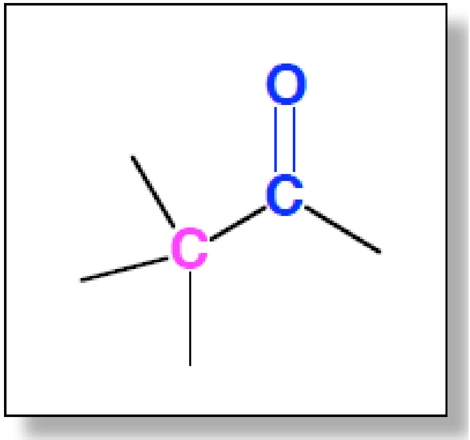
Chemical properties of Aldehydes and Ketones

☐ The reactions of aldehydes and ketones can be divided into two main categories:

1) Reactions of the carbonyl group **2) Reactions involving the α-carbon**



1) Reactions of the carbonyl group

The reactions of carbonyl compounds are one of the most important class of synthetically useful reaction in organic chemistry.

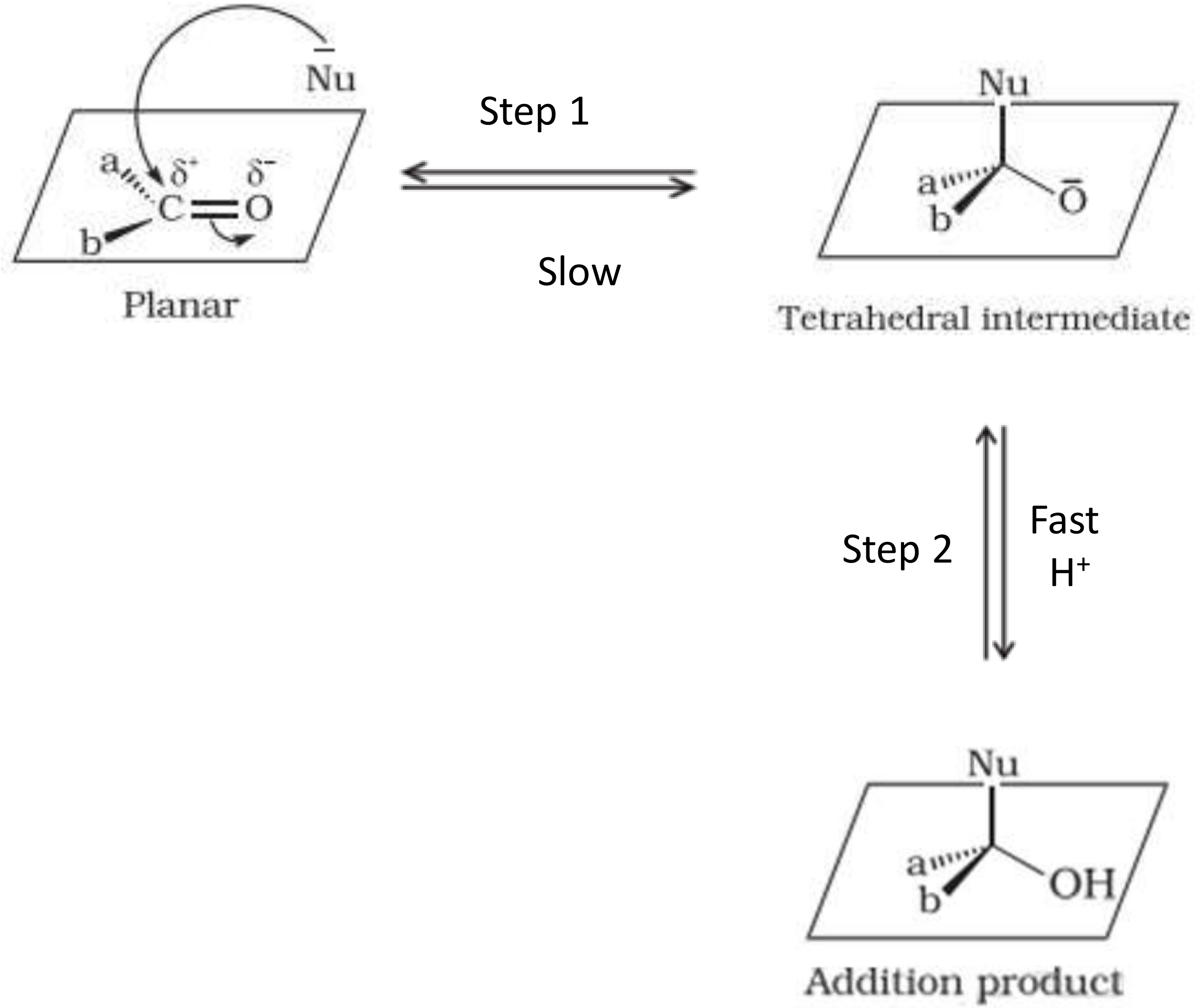
The reactions of carbonyls can be broadly classified as the direct **nucleophilic addition reactions** wherein a nucleophile adds to the carbonyl carbon atom.

2) Reactions involving the α-carbon

An important and versatile family of reactions of carbonyl arise due to the acidity of the alpha-C-H groups. Upon treatment with a base, such compounds are capable of yielding a very useful nucloeophile, known as enolate. The chemistry of enolates are widely exploited for the generation of C-C bonds in various reaction.

Nucleophilic Addition Reactions

- Contrary to electrophilic addition reactions observed in alkenes, the aldehydes and ketones undergo nucleophilic addition reactions.
- A nucleophile attacks the electrophilic carbon atom of the polar carbonyl group from a direction approximately perpendicular to the plane of sp^2 hybridized orbitals of carbonyl carbon.
- The hybridization of carbon changes from sp^2 to sp^3 in this process, and a tetrahedral alkoxide intermediate is produced.
- This intermediate captures a proton from the reaction medium to give the electrically neutral product. The net result is addition of Nu^- and H^+ across the carbon oxygen double bond.



Step 1

Slow

Step 2

Fast

H^+

Figure: Nucleophilic attack on carbonyl carbon

Comparison of reactivity of CHO & C=O towards Nu$^-$

Aldehydes are generally more reactive than ketones in nucleophilic addition reactions due to steric and electronic reasons. Sterically, the presence of two relatively large substituents in ketones hinders the approach of nucleophile to carbonyl carbon than in aldehydes having only one such substituent. Electronically, aldehydes are more reactive than ketones because two alkyl groups of ketones reduce the electrophilicity of the carbonyl carbon more effectively than aldehydes.

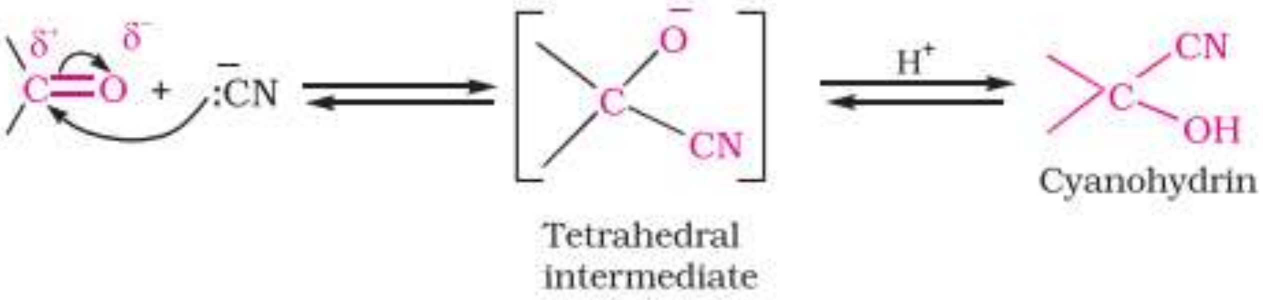
Nucleophilic Addition- Elimination Reactions

- An addition-elimination reaction is a two-stage substitution reaction in which addition reaction is followed by an elimination reaction.
- Important examples of nucleophilic addition-elimination reactions as follows:

1) Addition of hydrogen cyanide (HCN)

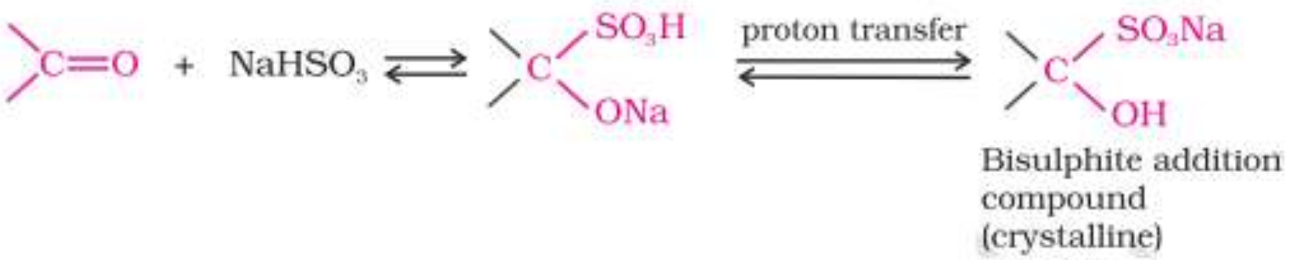
Aldehydes and ketones react with hydrogen cyanide (HCN) to yield cyanohydrins. This reaction occurs very slowly with pure HCN. Therefore, it is catalysed by a base and the generated cyanide ion (CN-) being a stronger nucleophile readily adds to carbonyl compounds to yield corresponding cyanohydrin.

$$HCN + OH^{-} \rightleftharpoons :\overline{C}N + H_2O$$



2) Addition of sodium hydrogensulphite

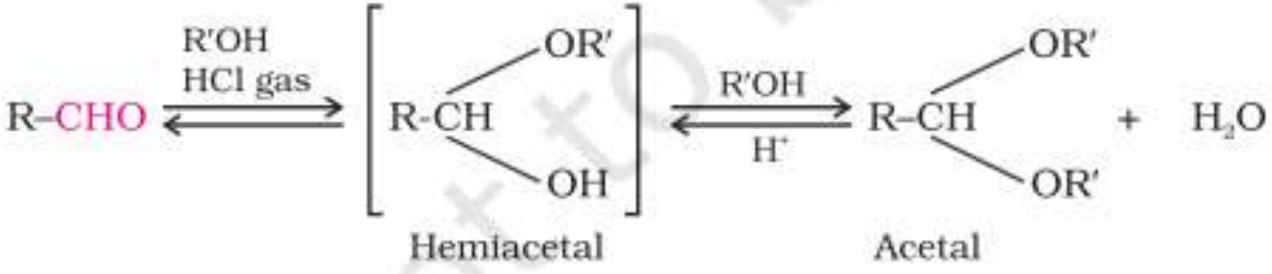
Sodium hydrogensulphite adds to aldehydes and ketones to form the addition products. The position of the equilibrium lies largely to the right hand side for most aldehydes and to the left for most ketones due to steric reasons. The hydrogensulphite addition compound is water soluble and can be converted back to the original carbonyl compound by treating it with dilute mineral acid or alkali. Therefore, these are useful for separation and purification of aldehydes.



Bisulphite addition compound (crystalline)

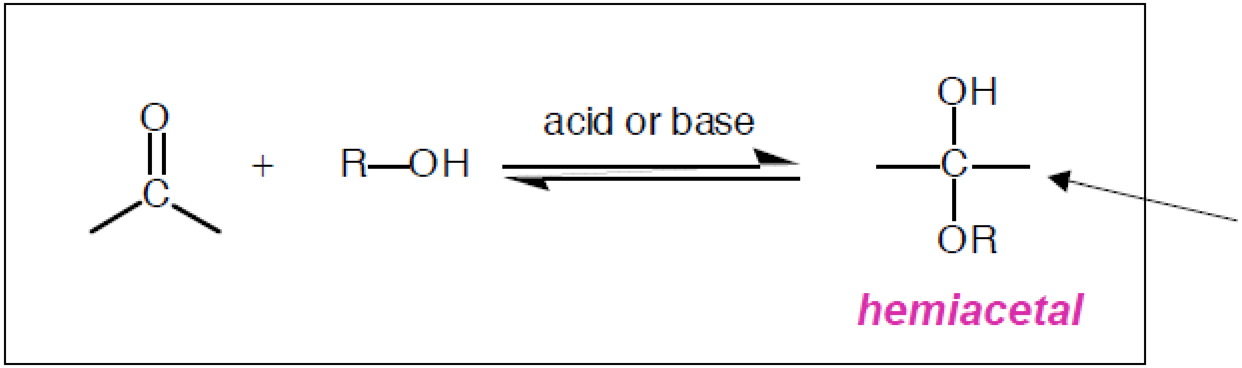
3) Addition of alcohols

Aldehydes react with one equivalent of monohydric alcohol in the presence of dry hydrogen chloride to yield alkoxyalcohol intermediate, known as hemiacetals, which further react with one more molecule of alcohol to give a gem-dialkoxy compound known as acetal.



❖ Formation of Hemiacetals

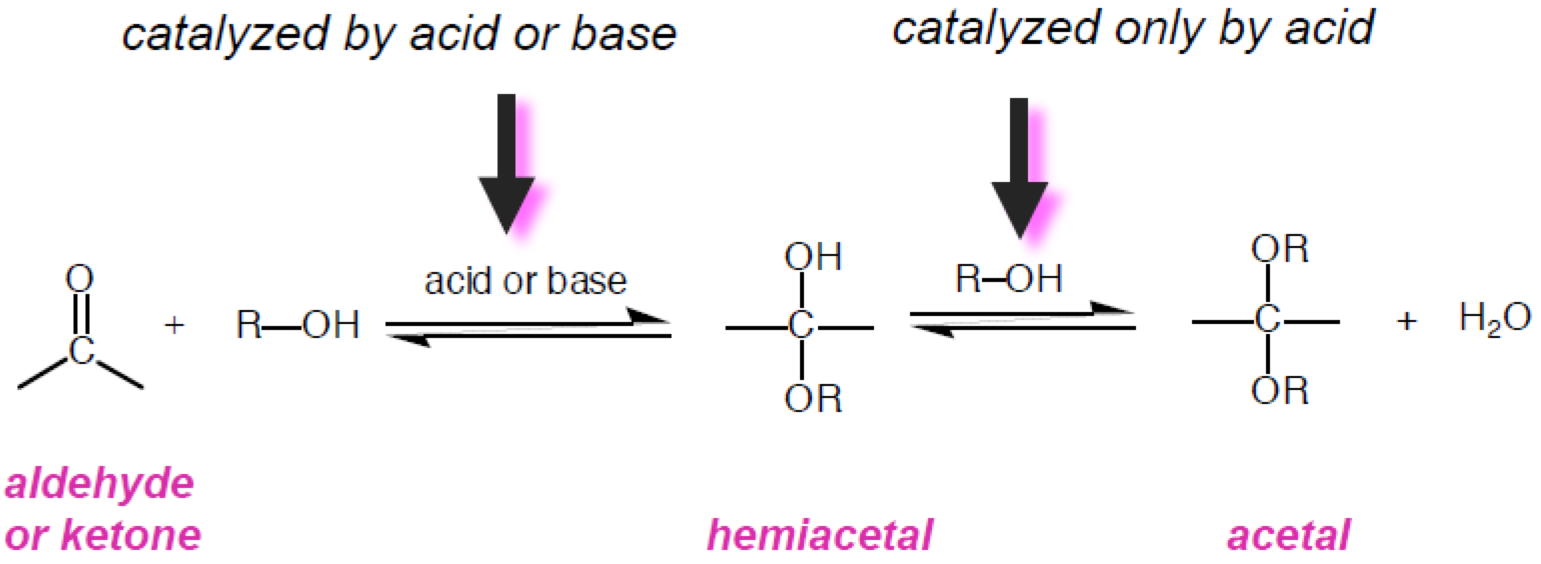
- When an alcohol adds reversibly to an aldehyde or ketone, the product is called a hemiacetal. Hemiacetals are formed in both acid- and base-catalyzed reactions.
- Hemiacetals are unstable
- Hemiacetals undergo further reversible reactions under acidic conditions only. This reaction involves carbocation chemistry.



Note: this bond to carbon indicates that it may be either to an alkyl group or to hydrogen.

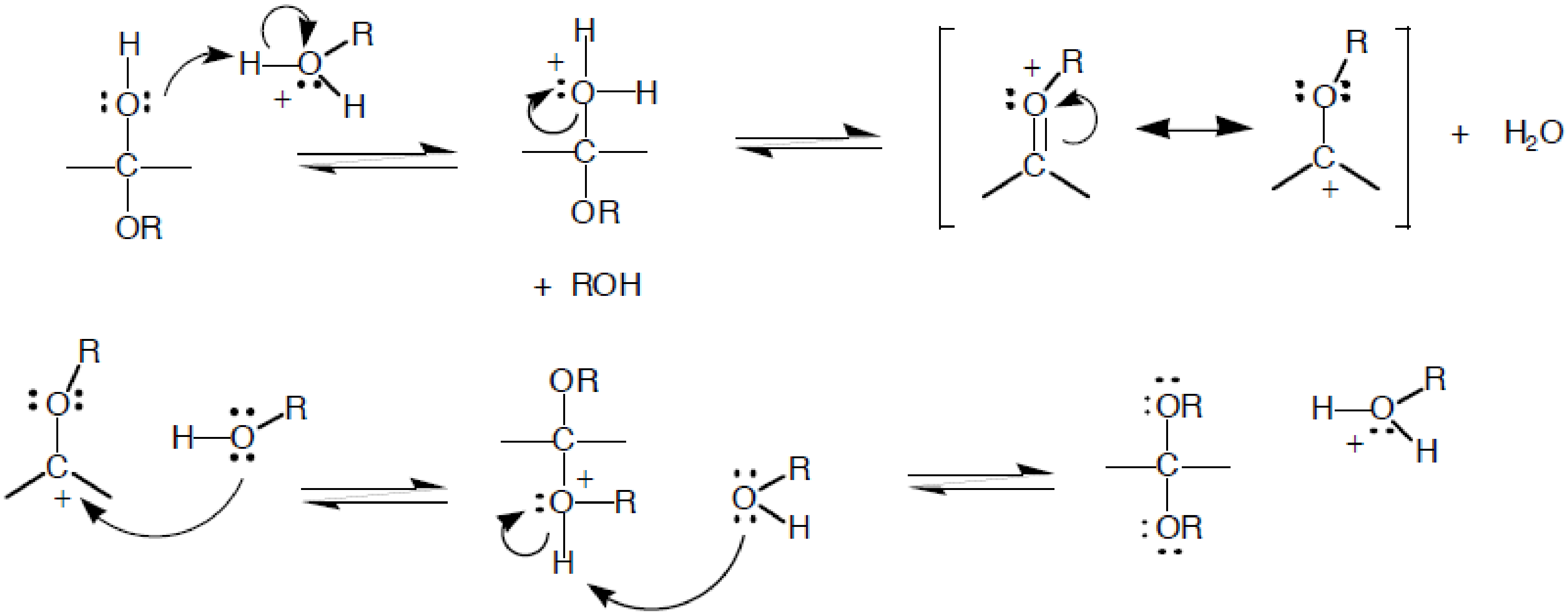
❖ Formation of Acetals

- Hemiacetals react further with alcohols under acidic conditions to form **acetals.**



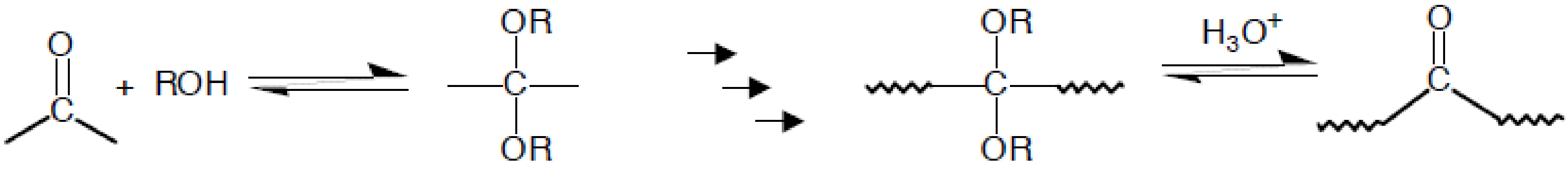
❖ Mechanism of Acetal Formation

- Under acidic conditions, some of the alcohol becomes protonated ROH_2^+.
- The hemiacetal OH oxygen abstracts a proton from ROH_2^+
- Loss of water gives a resonance-stabilized alkoxy carbocation.
- Nucleophilic attack by the alcohol on the carbocation occurs.
- Deprotonation by a further alcohol molecule produces the acetal.



❖ Acetals as Protecting Groups

- The reversibility of acetal formation along with the relative inertness of the RO-C-OR linkage make acetals useful as **protecting groups.**
- If the protecting group is more inert than the original functional group, then other reactions may be carried out with this molecule without worrying about altering or destroying the protecting group.
- When the other desired reactions are completed, the original group may be restored by carrying out the reverse of the reaction which introduced the protecting group.



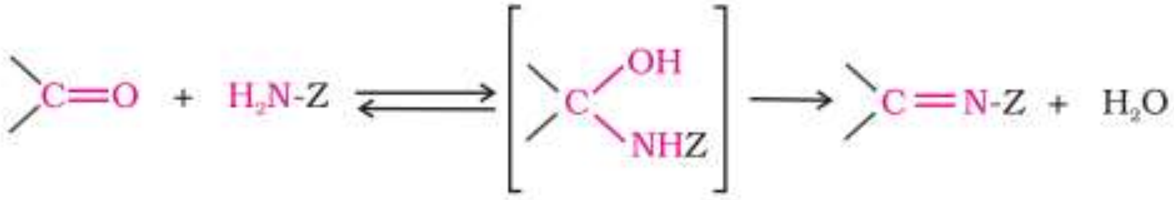
protection
(acetal formation)

further reactions

deprotection
(reverse of acetal formation)

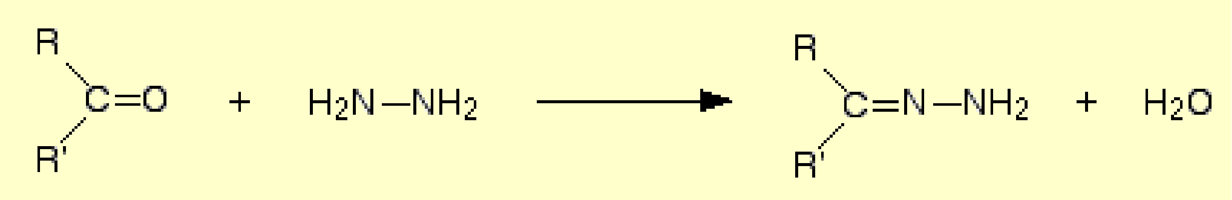
4) Addition of ammonia and its derivatives:

Nucleophiles, such as ammonia and its derivatives $H_2N\text{-}Z$ add to the carbonyl group of aldehydes and ketones. The reaction is reversible and catalysed by acid. The equilibrium favours the product formation due to rapid dehydration of the intermediate to form >C=N-Z



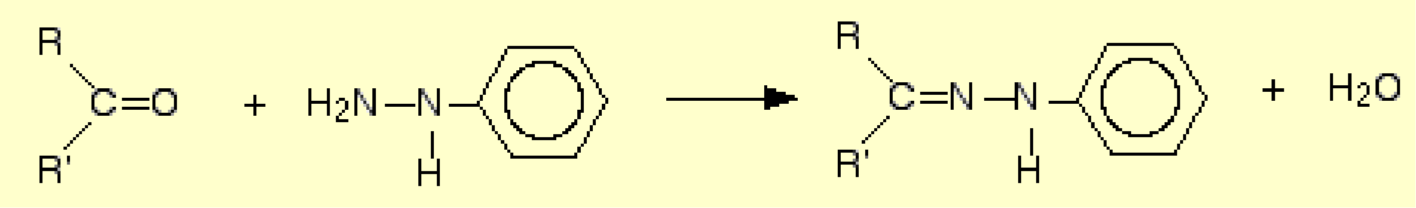
Z = Alkyl, aryl, OH, NH_2, C_6H_5NH, $NHCONH_2$, etc.

Reaction with hydrazine



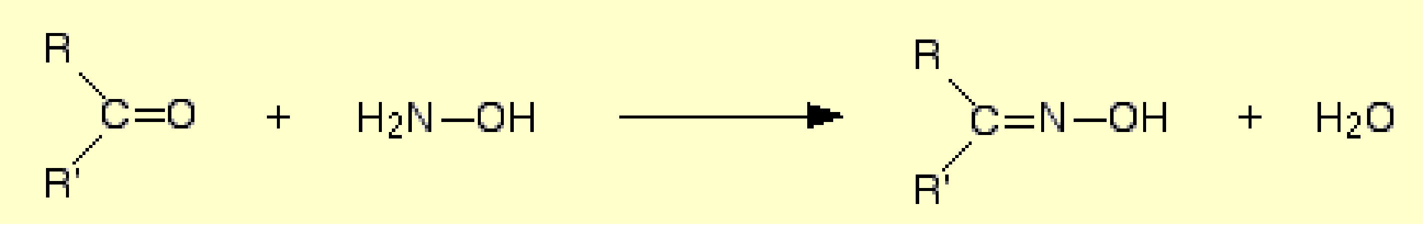
The product is a "hydrazone”

Reaction with phenylhydrazine



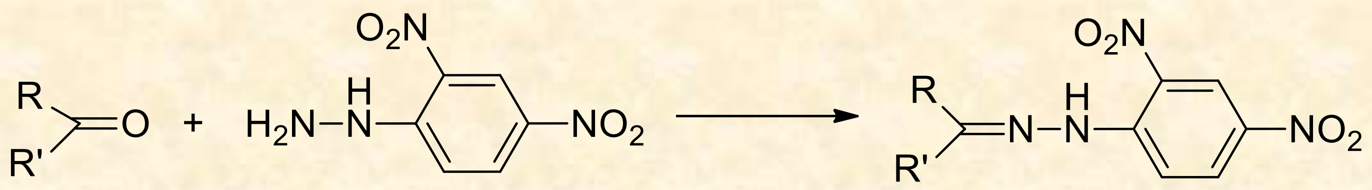
The product is a "phenylhydrazone"

Reaction with hydroxylamine



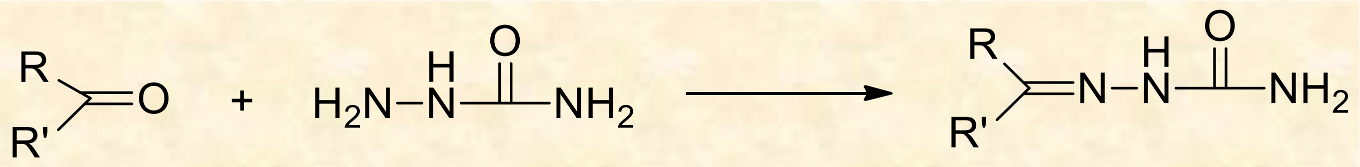
The product is an "oxime"

Reaction with 2,4-Dinitrophenyl hydrazine



The product is a " 2,4 Dinitrophenylhydrazone”

Reaction with Semicarbazide



The product is Semicarbazone