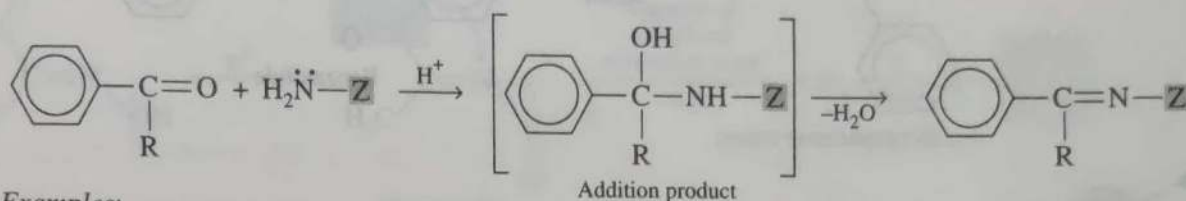
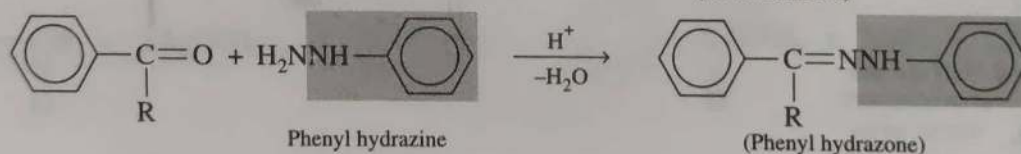
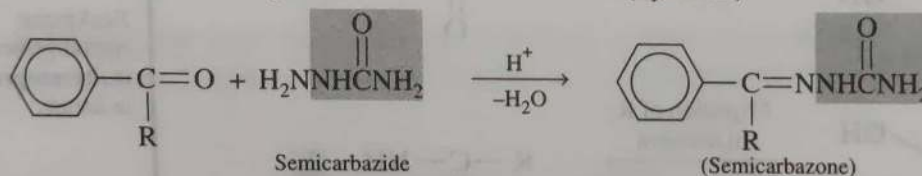
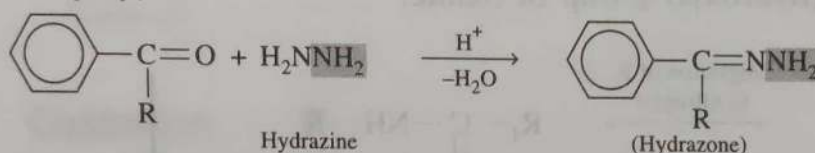
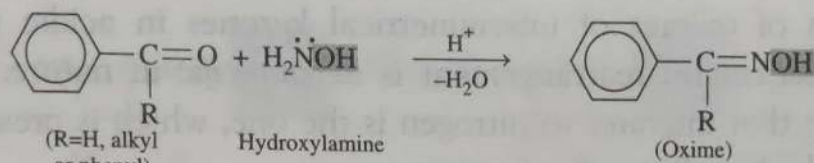


(ii) **Reaction with ammonia derivatives.** The ammonia derivatives include hydroxylamine, hydrazine, semicarbazide, phenylhydrazine, and 2,4-dinitrophenylhydrazine. The nucleophilic addition of ammonia derivatives to carbonyl compounds in acidic medium results in the formation of addition products, which undergo elimination of water to give corresponding solid crystalline products that have sharp melting points. The reactions are as follows:

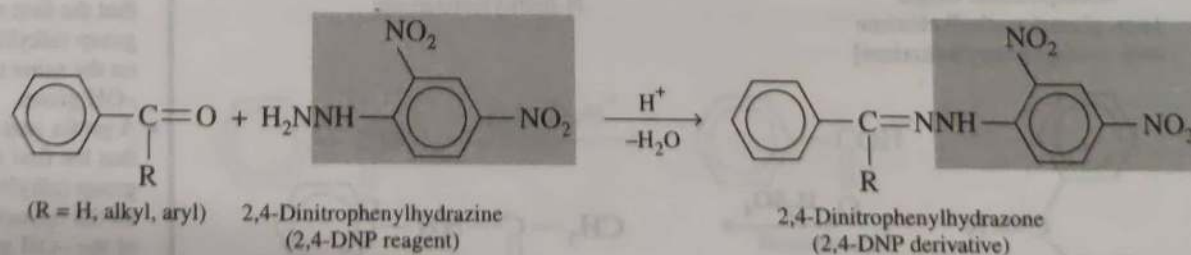
General reaction with ammonia derivatives



Examples:



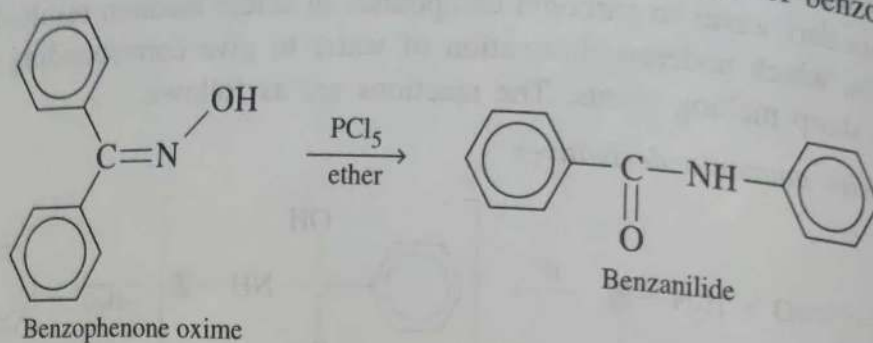
The reaction of carbonyl compounds with 2,4-dinitrophenylhydrazine (known as DNP reagent) results in the formation of yellow/orange crystalline product and is used as a *qualitative test for the detection of carbonyl compounds*.



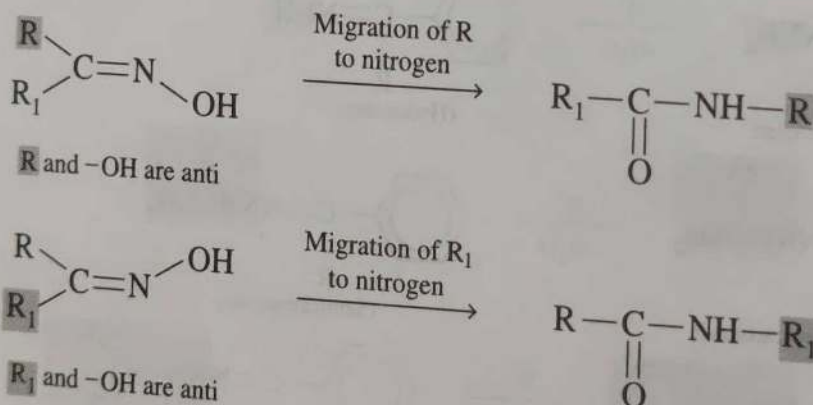
Beckmann rearrangement

The reaction of ketones with hydroxylamines results in the formation of ketoximes. The ketoximes ($\text{R}_2\text{C}=\text{NOH}$) in presence of acidic catalysts such as PCl_5 in ether, H_2SO_4 , P_2O_5 , BF_3 , SOCl_2 , SO_3 , and

so on undergo rearrangement to form N-substituted amides. This reaction is known as Beckmann rearrangement. The reaction was first observed by Beckmann in case of benzophenone oxime.

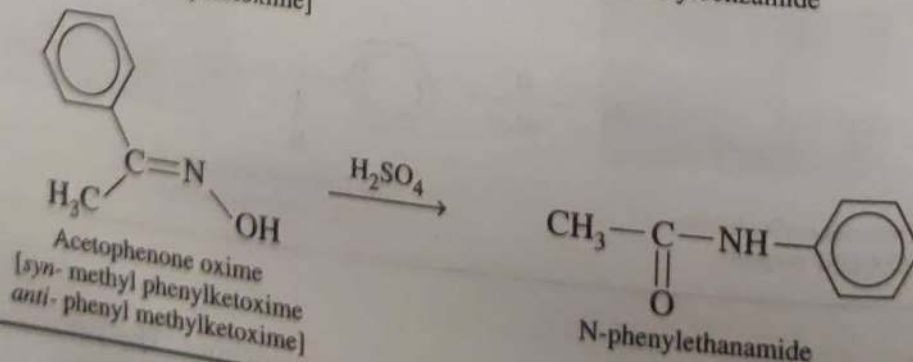
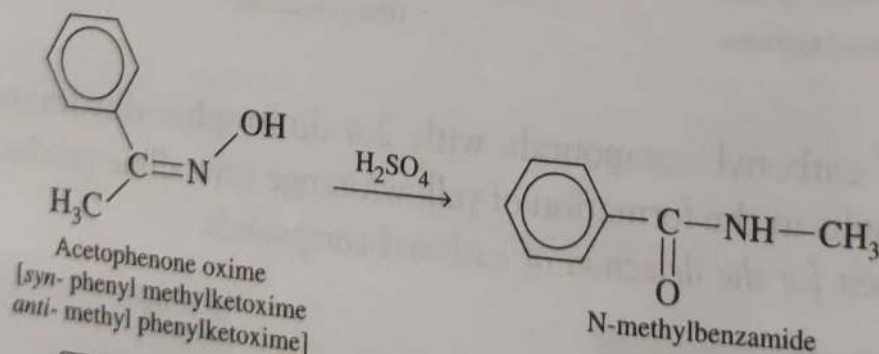


The reaction of oximes of unsymmetrical ketones in acidic medium revealed the fact that Beckmann rearrangement is *stereospecific* in nature. During rearrangement the group that migrates to nitrogen is the one, which is present at a position anti- to $-OH$ (hydroxyl) group of oxime.



Beckmann rearrangement is **Stereospecific** in nature.

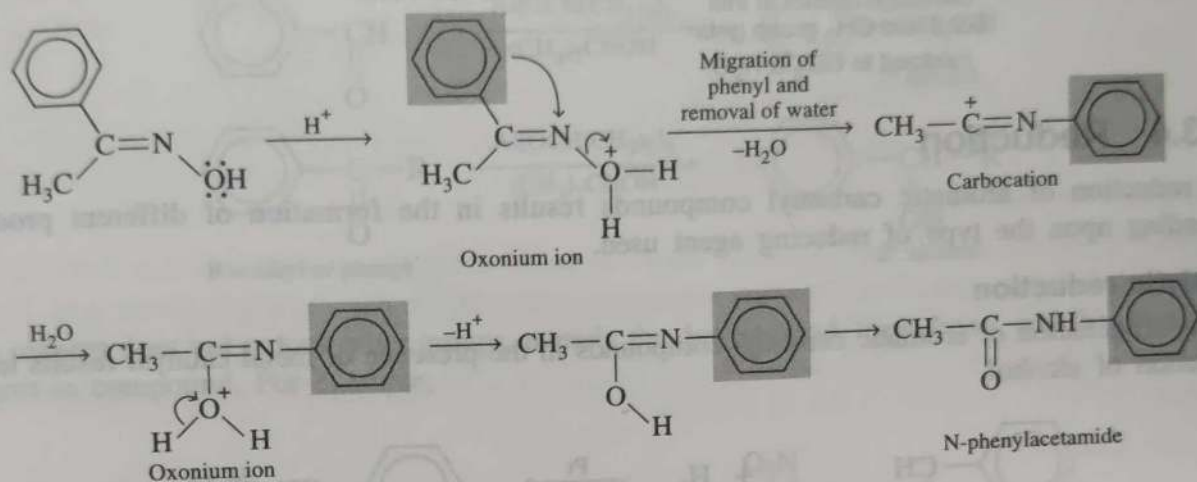
For example,



The general method of naming ketoximes makes use of the prefixes *syn*- and *anti*-.

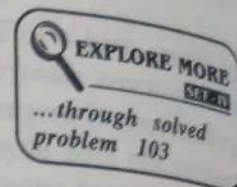
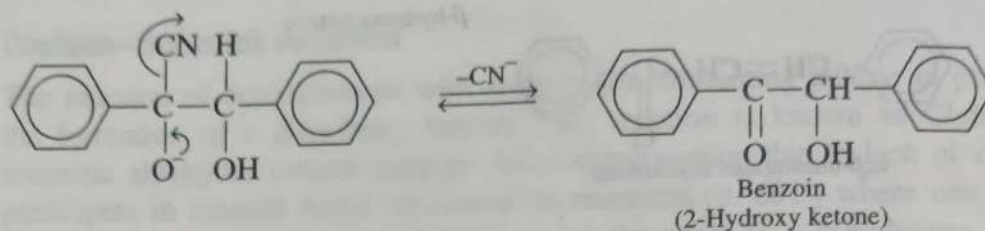
- A prefix *syn*- indicates that the first named group (alkyl/aryl) is on the same side as the $-OH$ group.
- A prefix *anti*- indicates that the first named group (alkyl/aryl) is on the opposite side of the $-OH$ group.

Mechanism of Beckmann rearrangement. It is an *intramolecular rearrangement* (1,2-shift) reaction. The rate of reaction is accelerated in presence of more nucleophilic migration groups. The mechanism for this oxime-amide rearrangement, in case of acetophenone oxime, in presence of an acid catalyst is as follows:



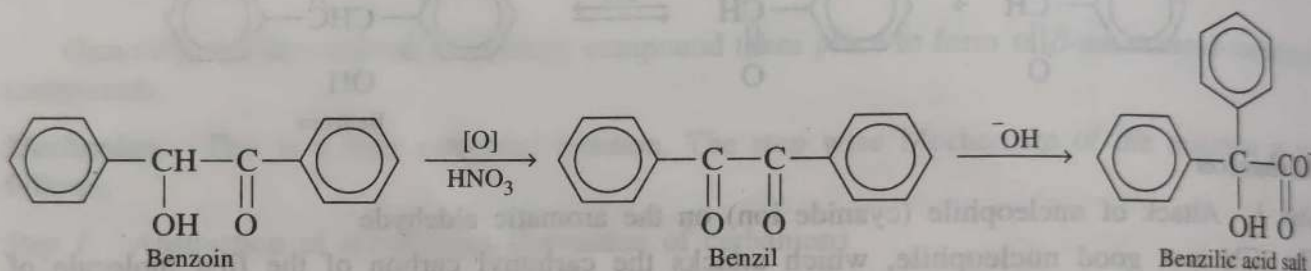
Step 3. loss of CN^- (formation of benzoin)

The CN^- is a good nucleophile as well as a good leaving group. Rapid loss of CN^- results in the formation of benzoin, a 2-hydroxy ketone.



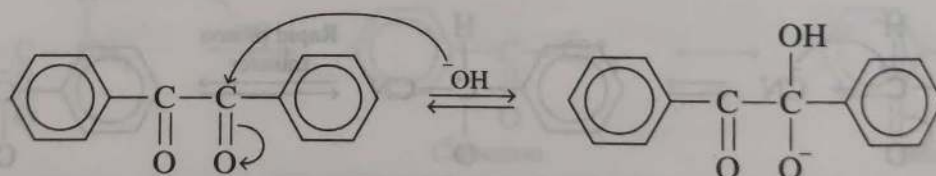
Benzil-Benzilic acid rearrangement

The condensation of benzaldehyde in the presence of cyanide ion (benzoin condensation) results in the formation of benzoin. Oxidation of benzoin (2-hydroxy ketone) results in the formation of benzil, a diketone. Benzil, in presence of a base undergoes a rearrangement reaction to form benzilic acid, an α -hydroxy acid.



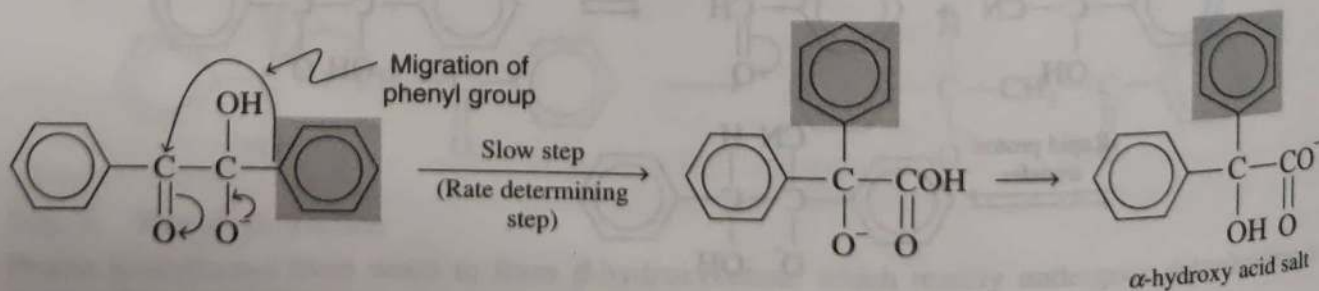
Mechanism

Step 1. Attack of nucleophile (base OH^-) on carbonyl carbon

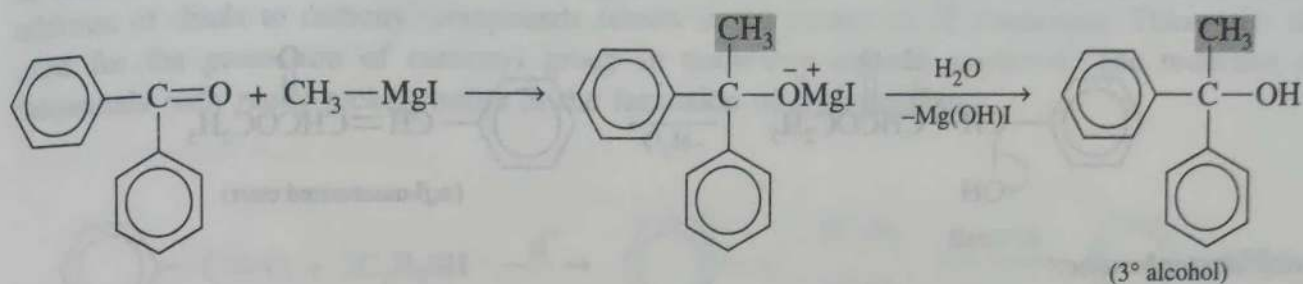


Step 2. Migration of phenyl group to carbonyl carbon (intramolecular carbanion addition)

The phenyl group along with its shared electron pair migrates to the carbonyl carbon. Phenyl behaves as carbanion and its addition occurs on carbonyl carbon to form α -hydroxy acids.



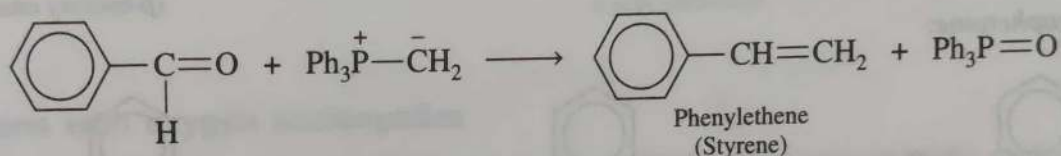
with benzophenone:



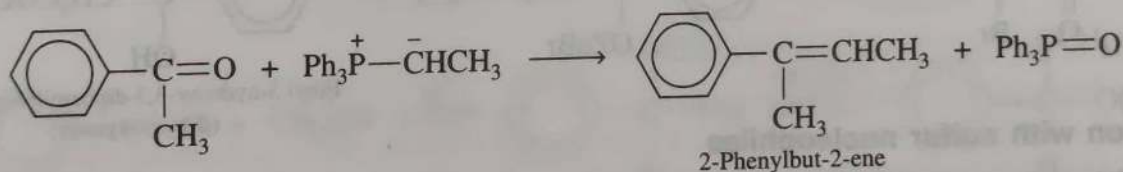
Aromatic aldehydes and ketones undergo similar reactions with methyllithium.

(iii) **Wittig reaction.** As discussed earlier (Section 17.3.2; p. 582), Wittig reaction involves reaction of phosphorous ylides with carbonyl compounds to form alkenes. The reaction proceeds via the formation of the *betaine* intermediate in the following manner:

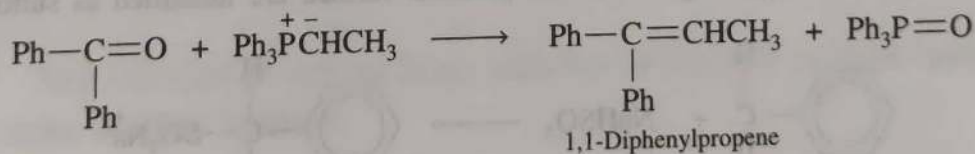
with benzaldehyde:



with acetophenone:

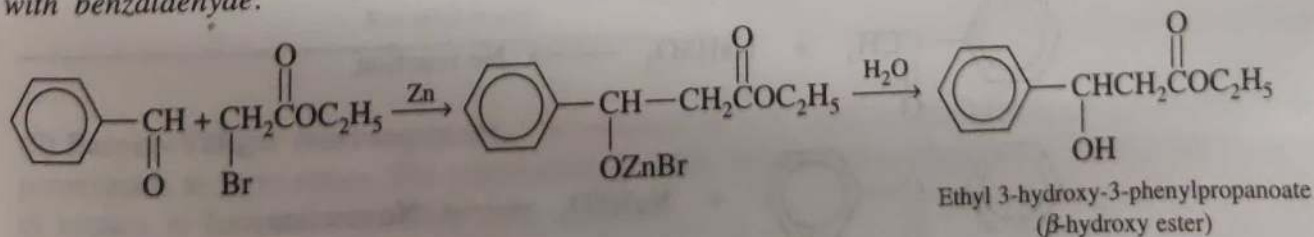


with benzophenone:

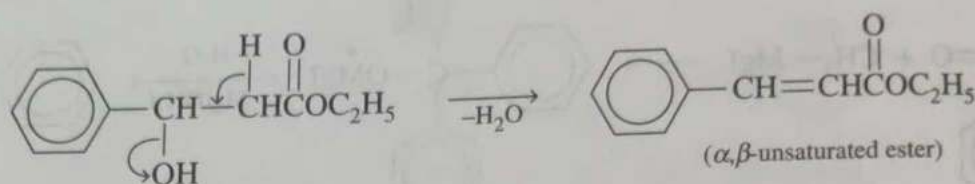


(iv) **Reformatsky reaction.** Reaction of aromatic aldehydes and ketones with α -haloesters in the presence of zinc to form β -hydroxyesters is known as **Reformatsky reaction**. The reaction proceeds via the formation of an organozinc derivative (for mechanism refer Section 17.3.2; p. 584).

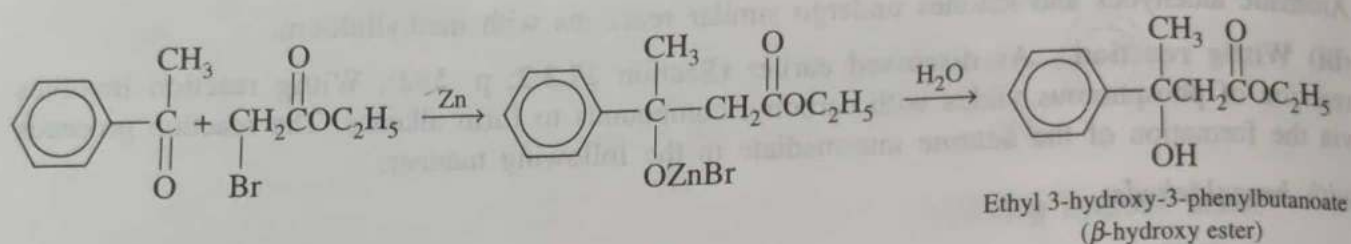
with benzaldehyde:



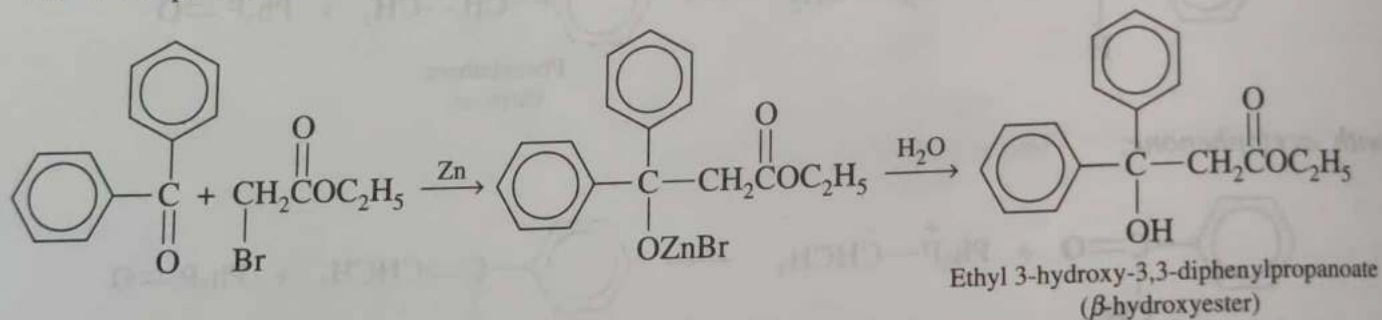
In aryl aldehydes, at times after the hydrolysis, elimination occurs and the product is an α,β -unsaturated ester.



with acetophenone:

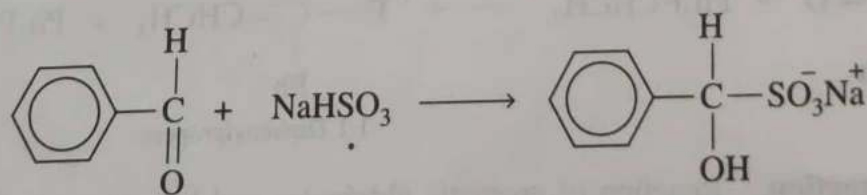



with benzophenone:

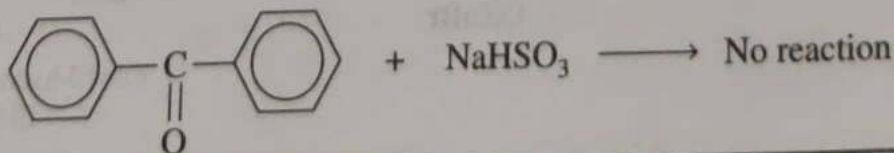
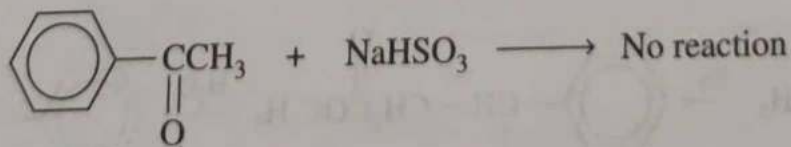


Reaction with sulfur nucleophiles

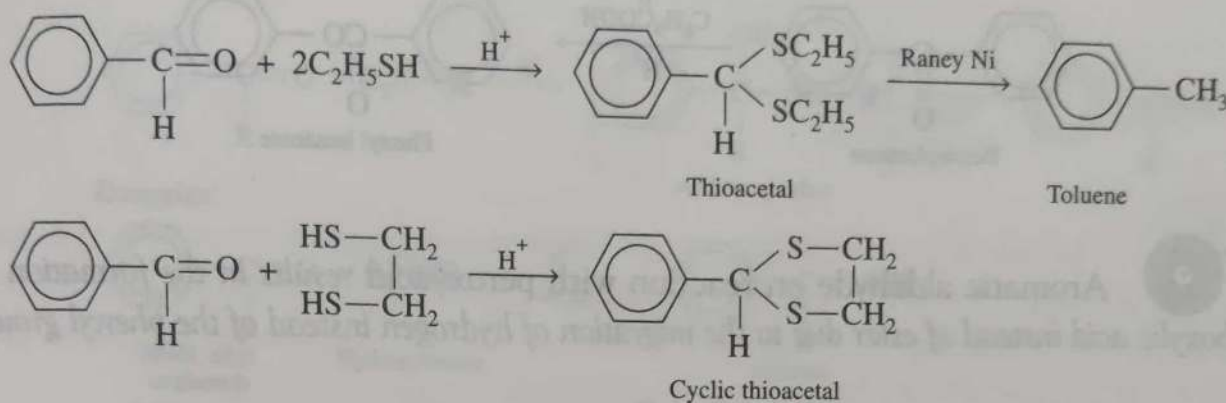
(i) **Addition of sodium bisulfite.** Aromatic aldehydes react with sodium bisulfite to form bisulfite addition product (adduct). The attack of sodium bisulfite occurs through sulfur, which is a better nucleophile compared to oxygen (p. 592). The products formed are identified as sulfonates.



 Aryl ketones do not give addition product (adduct) with sodium bisulfite due to steric factors.

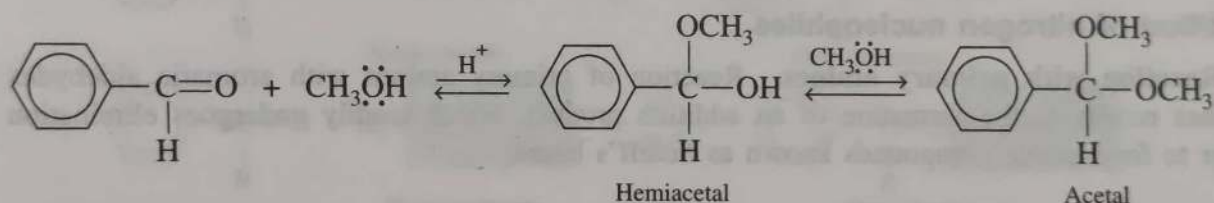



(ii) **Addition of thiols.** The reaction of carbonyl compound with thiols is much faster compared to reaction with alcohol due to high nucleophilicity of sulfur compared to oxygen. Acid catalyzed addition of thiols to carbonyl compounds results in the formation of *thioacetals*. Thioacetals are used for the protection of carbonyl group in multi-step organic synthesis. The reduction of thioacetals with Raney nickel results in the formation of hydrocarbons.

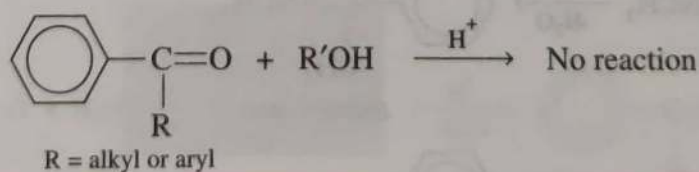


Reactions with oxygen nucleophiles

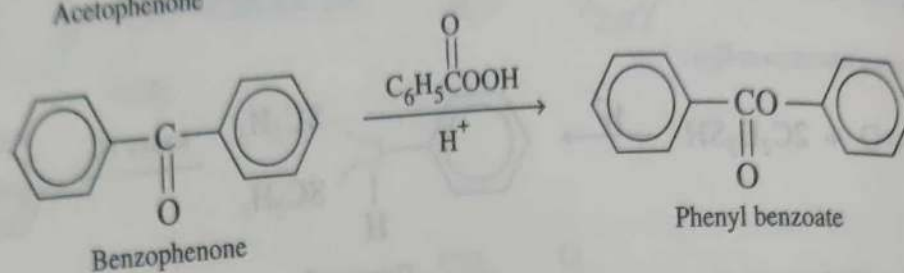
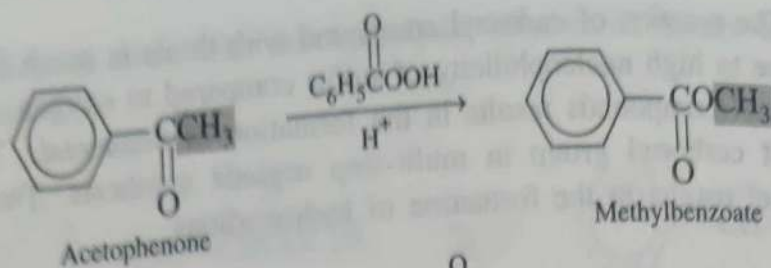
(i) **Addition of alcohol.** Aromatic aldehydes undergo addition of alcohol in acidic medium to form *hemiacetal*, which further adds another molecule of alcohol resulting in the formation of *acetal*.




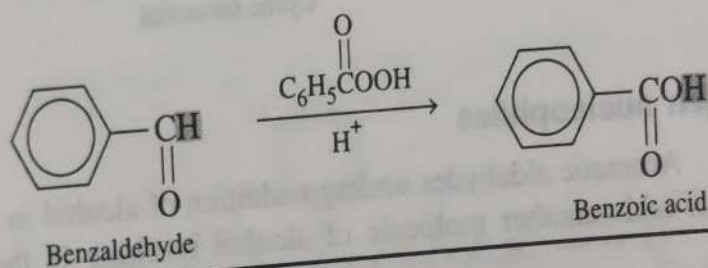
 Aryl ketones *do not* undergo addition of alcohol to form hemiketals and ketals because of steric reasons.

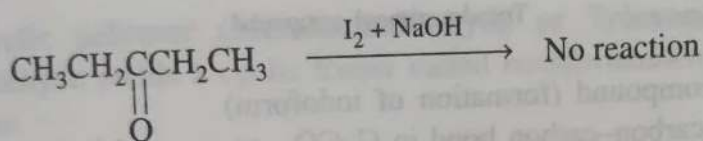
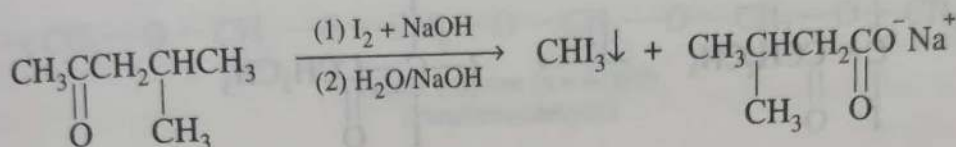
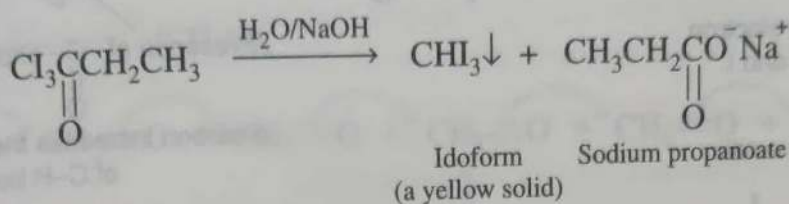
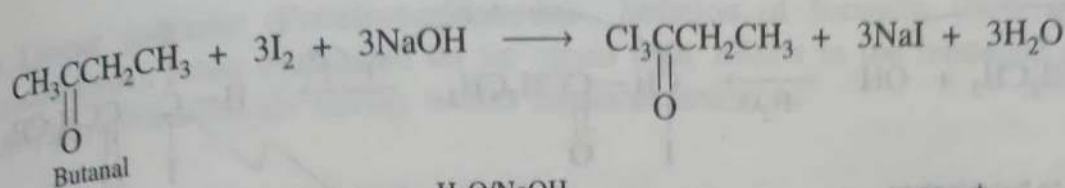


(ii) **Baeyer-Villiger rearrangement.** In presence of acid catalyst, the aromatic ketones react with peroxyacids to form esters. The mechanism (p. 587) involves the migration of alkyl or aryl group of ketones to form corresponding ester.



 Aromatic aldehyde on reaction with peroxyacid results in the formation of carboxylic acid instead of ester due to the migration of hydrogen instead of the phenyl group.



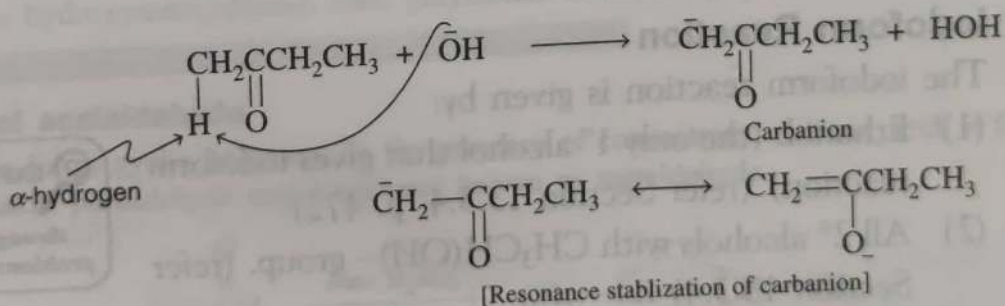


The reaction does not occur because the $\text{CH}_3\text{C}(=\text{O})$ -group is absent.

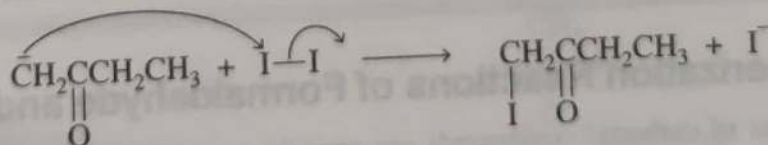
As discussed earlier in Section 13.3.4, p. 472, the iodoform reaction is also given by ethanol and secondary alcohols which have $\text{CH}_3\text{CH}(\text{OH})$ - group. In the first step, the $\text{CH}_3\text{CH}(\text{OH})$ - group is oxidized by sodium hypoiodite, NaOI (from $\text{NaOH} + \text{I}_2$) to CH_3CO - group and then the reaction proceeds as it does with carbonyl compounds.

Mechanism. The presence of CH_3CO - group is necessary for iodoform reaction. The $>\text{C}=\text{O}$ group is an electron withdrawing group which makes the α -hydrogens (CH_3 - group) acidic in nature.

Step 1. Abstraction of α -hydrogen by base (formation of carbanion)

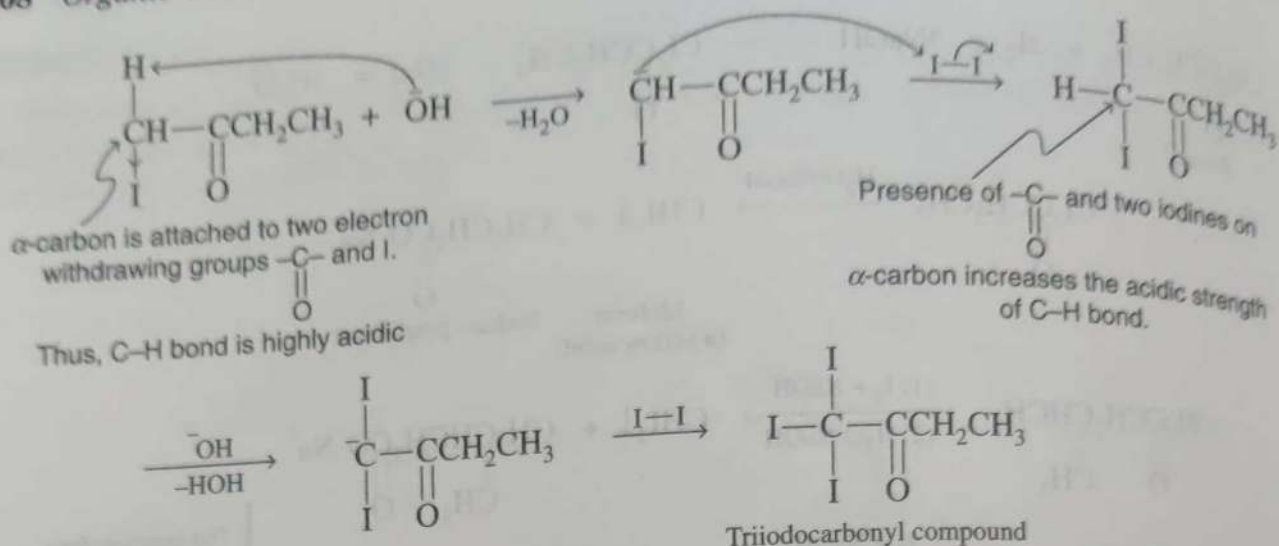


Step 2. Reaction of carbanion with iodine (formation of α -iodocarbonyl compound)

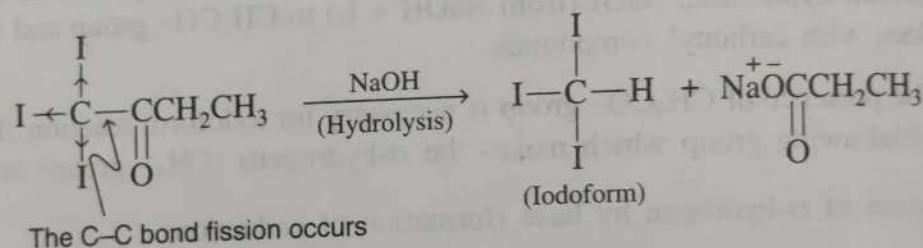


Step 3. Formation of triiodocarbonyl compound

The introduction of iodine (an electronegative species) further enhances the acidic character of α -hydrogens and their abstraction by base occurs more readily. The repetition of steps 1 and 2 occurs till all the α -hydrogens are replaced by iodine and a triiodocarbonyl compound is formed.



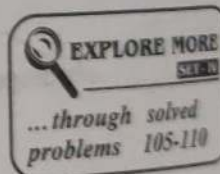
Step 4. Hydrolysis of triiodocarbonyl compound (formation of iodoform)
 In presence of an alkali, the cleavage of carbon-carbon bond in C-CO- occurs and is favoured by the presence of three electron withdrawing iodine atoms attached to α -carbon of carbonyl compound. As a consequence, iodoform is finally formed.



Iodoform Reaction

The iodoform reaction is given by:

- (1) Ethanol. (the only 1° alcohol that gives iodoform reaction) (refer Section 13.3.4, p. 472)
- (2) All 2° alcohols with $\text{CH}_3\text{CH}(\text{OH})-$ group. (refer Section 13.3.4)
- (3) Acetaldehyde. (the only aldehyde that gives iodoform reaction)
- (4) All methyl ketones (aliphatic and aromatic) with $\text{CH}_3\text{CO}-$ group.



17.3.6 Polymerization Reactions of Formaldehyde and Acetaldehyde

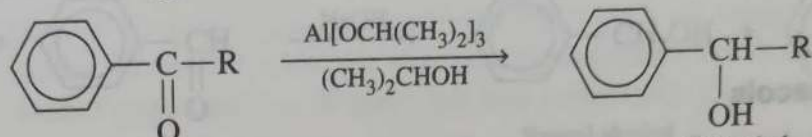
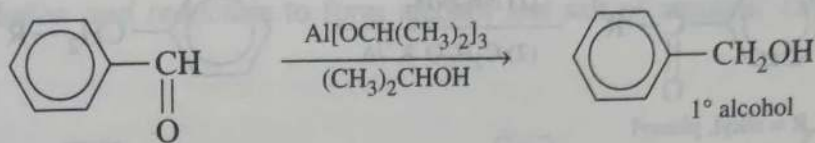
Some of the reactions of carbonyl compounds are specific to aldehydes only. One such reaction is *polymerization reaction*. Lower aldehydes are easily polymerized to form linear chain or cyclic polymers. During polymerization, the aldehyde units undergo addition at the polar carbonyl group. This section discusses the polymerization of formaldehyde and acetaldehyde.

Polymers of formaldehyde

Formaldehyde forms three polymers, namely paraformaldehyde, trioxane, and bakelite.

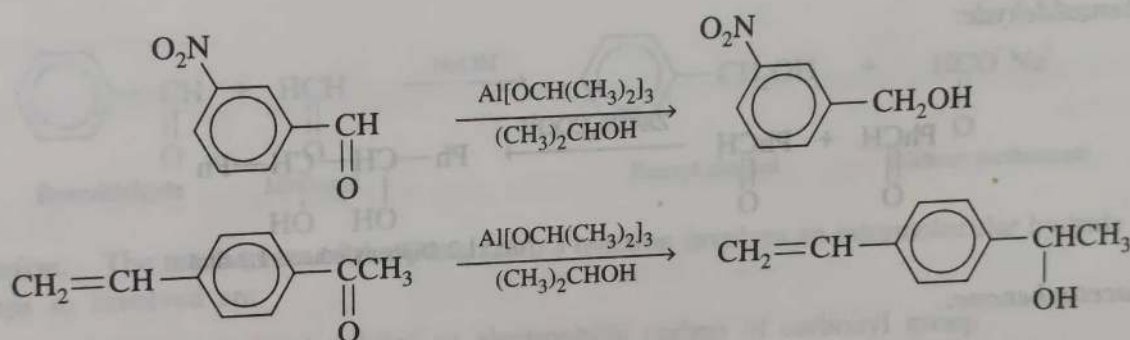
Meerwein-Ponndorf-Verley reduction

Aromatic carbonyl compounds on treatment with a solution of aluminium isopropoxide in isopropyl alcohol get reduced to alcohols.

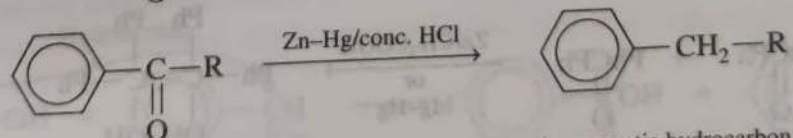
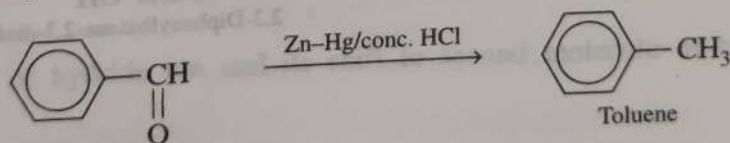


R = alkyl or phenyl

This reagent does not reduce other groups, namely the double bond, triple bond, and the nitro group present in compound. For example,

**Clemmensen reduction**

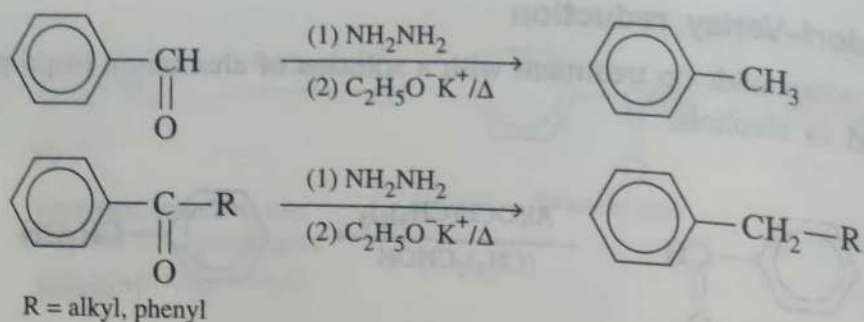
The carbonyl ($>\text{C}=\text{O}$) group of aromatic aldehydes and ketones can be reduced to methylene ($>\text{CH}_2$) group by zinc amalgam in a manner similar to aliphatic carbonyl compounds. This reaction is used for reducing carbonyl compounds, which are *sensitive to alkali*.



R = alkyl, phenyl

Wolff-Kishner reduction

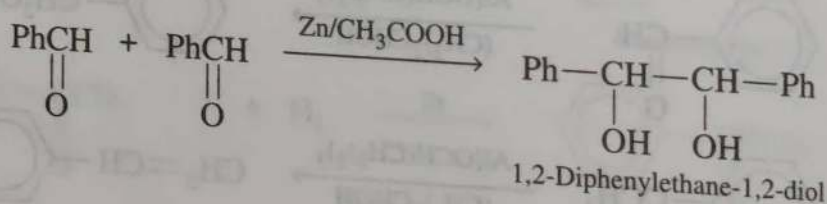
The carbonyl group ($>\text{C}=\text{O}$) of aromatic aldehydes and ketones can be reduced to methylene ($>\text{CH}_2$) group by reaction with hydrazine followed by hydrolysis with sodium or potassium ethoxide as in the case of aliphatic carbonyl compounds. The method is used for the reduction of carbonyl compounds that are *sensitive to acids*.



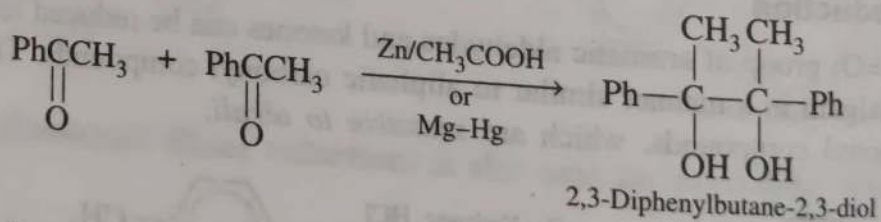
Reduction to pinacols

Aliphatic aldehydes do not form pinacols unlike aromatic aldehydes and ketones that form pinacols (di-*tert* 1,2-diols) on reduction. The reducing agent used in the process is zinc in acetic acid. Further in the presence of light and isopropanol as a solvent, benzophenone yields benzopinacol. The reaction is termed as *photochemical reduction of benzophenone*. The reaction with different aromatic carbonyl compounds are as follows:

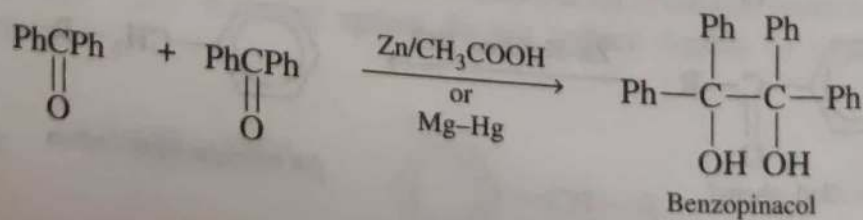
with benzaldehyde:



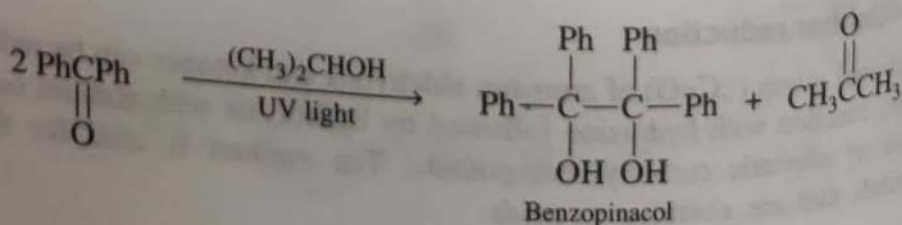
with acetophenone:



with benzophenone:



Alternatively,



17.4 REACTION OF α,β -UNSATURATED CARBONYL COMPOUNDS

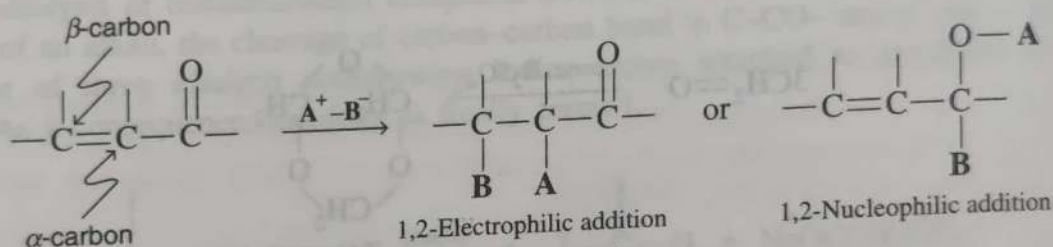
The *aldol condensation* is one of the methods used for preparation of α,β -unsaturated compounds. The α,β -unsaturated carbonyl compounds undergo reactions that are characteristics of $>C=C<$ and $>C=O$ systems. These compounds, may undergo addition reactions at $C=C$ or $C=O$ system which may occur in two ways to result in 1,2-addition products or 1,4-addition products.

Meaning of 1,2 and 1,4-addition

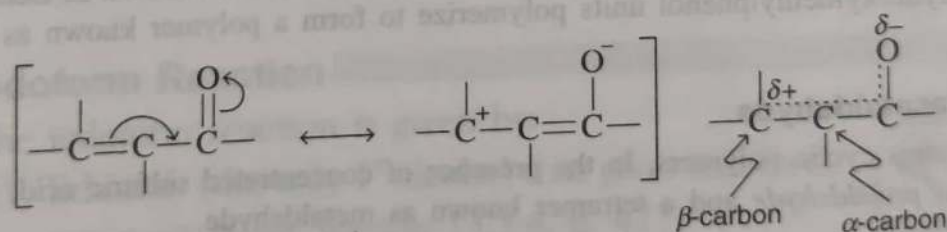
(Do not confuse with the numbering due to nomenclature)

- 1,2-Addition means the addition of reagent on any adjacent positions in the substrate.
- 1,4-Addition means the addition of one part of the reagent takes place on the substrate (position-1) followed by addition of other part of the reagent to the position-4, with respect to the first addition.

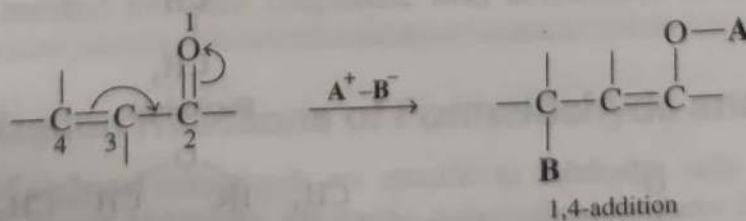
The 1,2-addition may occur as *electrophilic addition* or *nucleophilic addition* as depicted below:



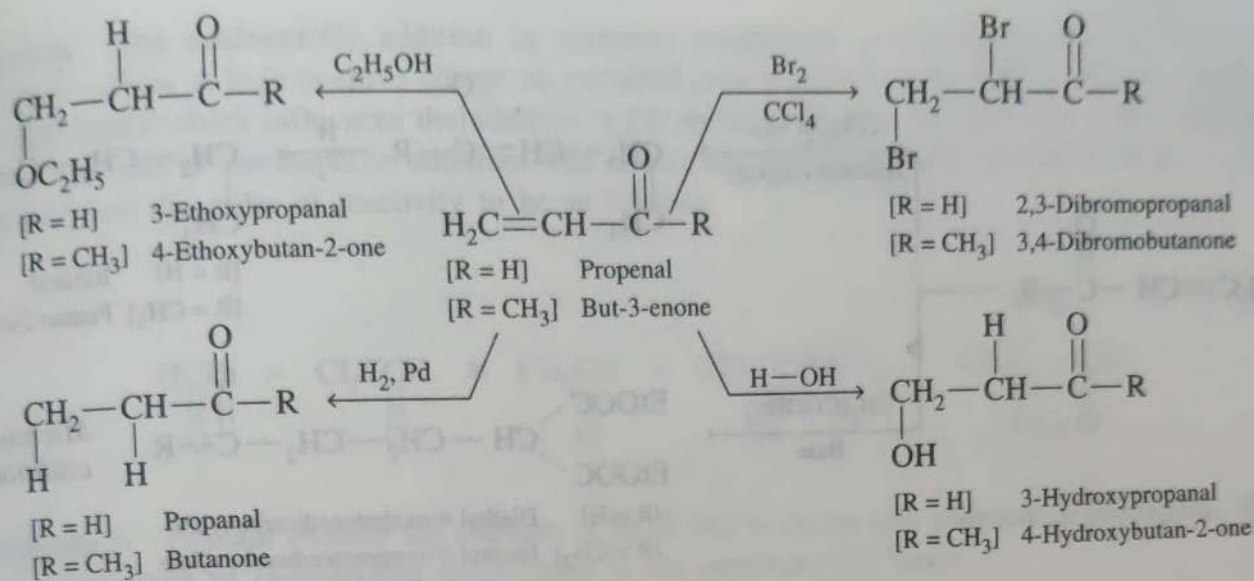
However, in these compounds the $C=C$ participates in delocalization with $C=O$ group. This delocalization results in 1,4-addition or conjugate addition in α,β -unsaturated carbonyl compounds.



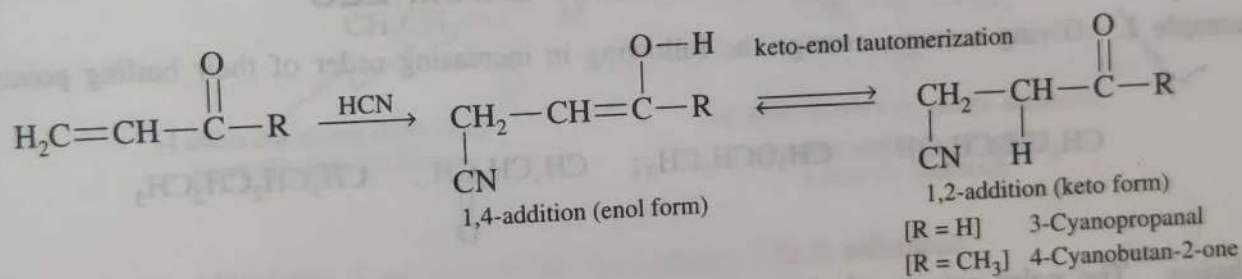
Due to resonance, during the addition of polar reagent the *electrophilic part* of the reagent add to carbonyl oxygen and *nucleophilic part* to β -carbon. The β -carbon is electrophilic due to electron withdrawing carbonyl group.



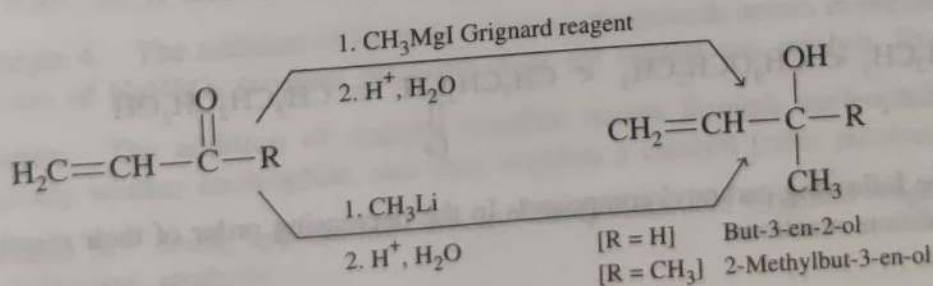
The reactions of α,β -unsaturated carbonyl compounds are summarized below by taking the examples of propenal ($R=H$) and but-3-enone ($R=CH_3$)




If the polar reagent has H⁺ as electrophile part, then 1,4-addition results in *enol* that rapidly *tautomerizes* to give a *keto* product, which is a 1,2-addition product. For example,



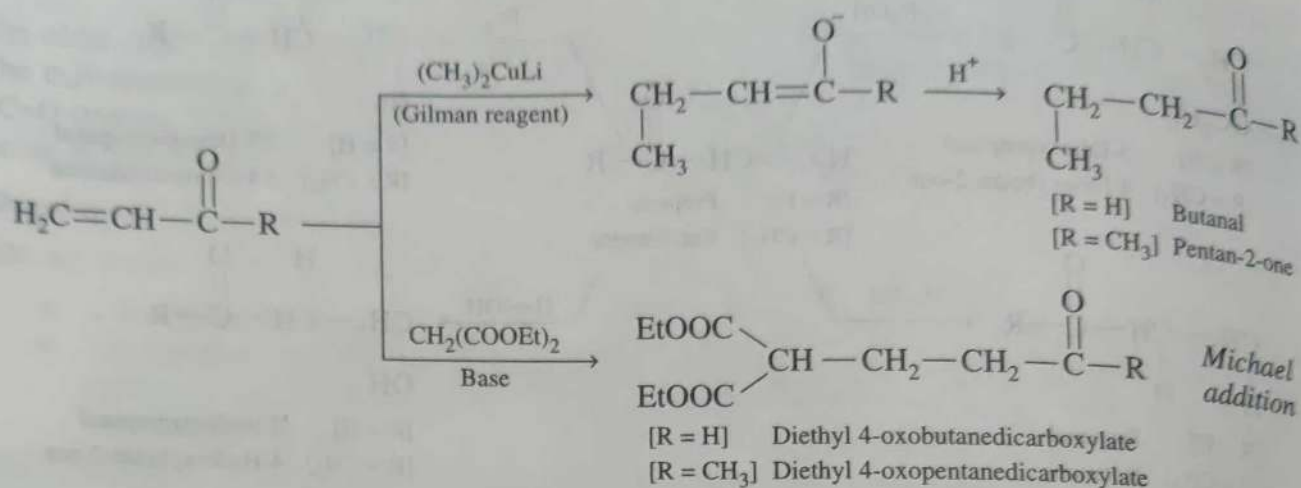
Strong nucleophilic reagents like Grignard reagent or organolithiums prefer to attack at carbonyl carbon to give usual 1,2-addition product.



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 problems 112-114

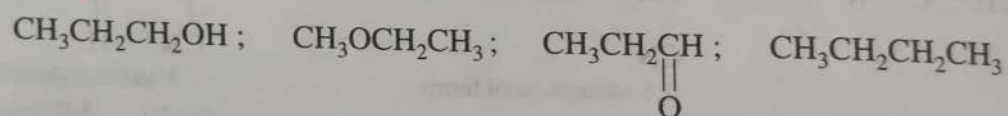
It is interesting to note that Grignard reagent not only attacks at carbonyl carbon (1,2-addition) but it may also attack at olefinic carbon (>C=C<; 1,4-addition) of α,β-unsaturated ketones.

✓ On the other hand the organolithium cuprates (Gilman reagent) and enolates being less basic, attack exclusively at β-carbon. The nucleophilic addition, of compounds with reactive methylene group like malonic ester or ethylacetoacetate, to α,β-unsaturated carbonyl compounds in presence of base (as catalyst) is known as **Michael addition**. The α,β-carboxylic acid esters or nitriles also undergo Michael addition reaction.

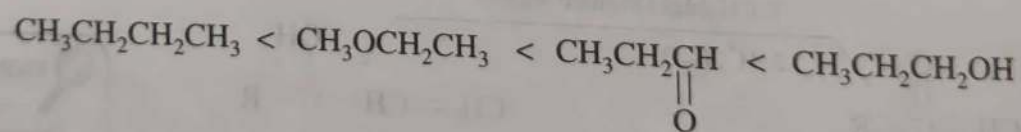


SELECTED SOLVED EXAMPLES

Example 1. Giving reasons, arrange the following in increasing order of their boiling points:



Solution. The polar compounds have higher boiling point compared to nonpolar compounds. Thus, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$ will have the lowest boiling point. Alcohol ($\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$) will have the highest boiling point due to hydrogen bonding. Carbonyl compounds have higher boiling points compared to ethers (refer Section 17.1.1). Therefore, the increasing order of boiling points is:



Example 2. Arrange the following carbonyl compounds in the decreasing order of their reactivity towards nucleophilic addition reactions:

