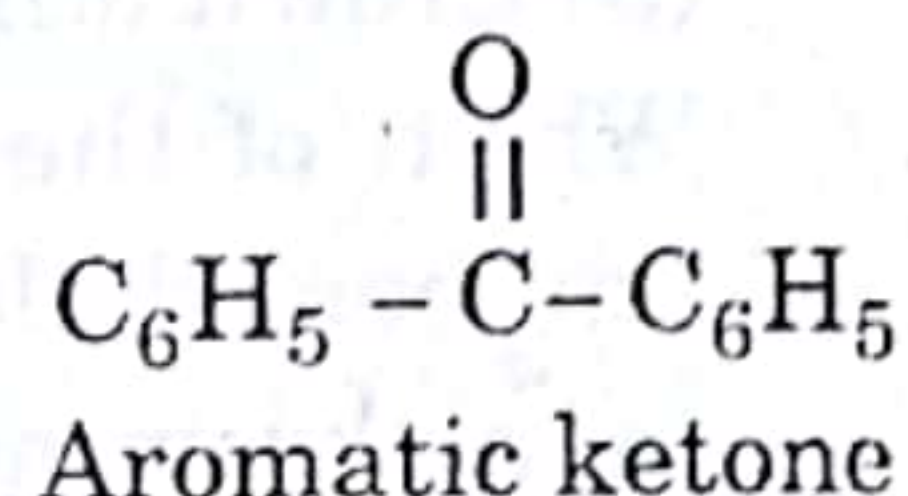
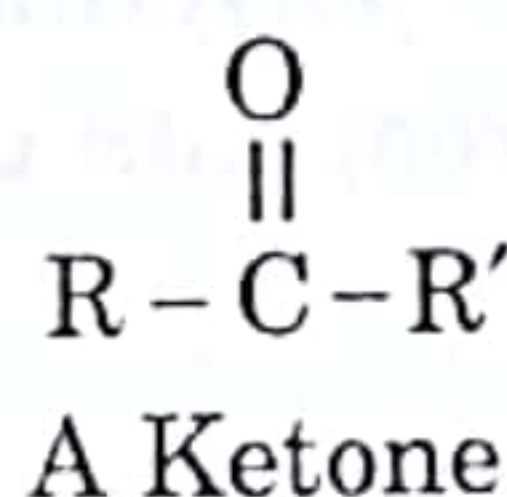
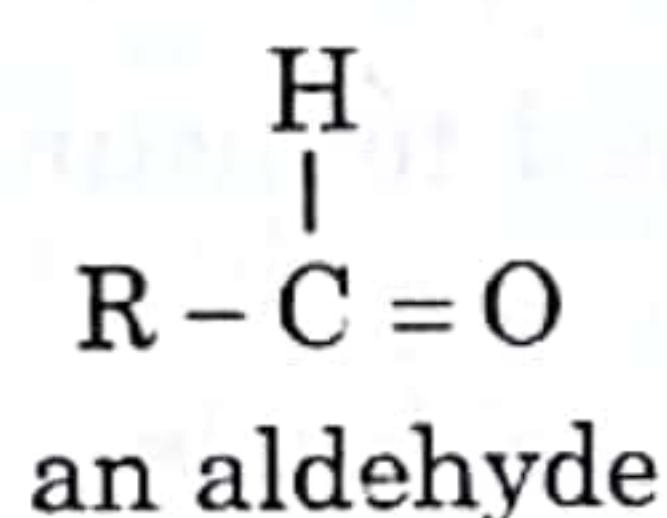
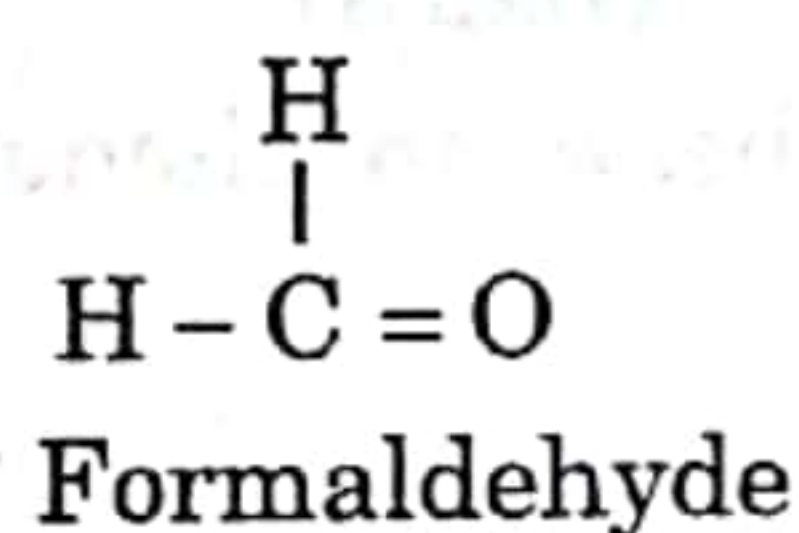


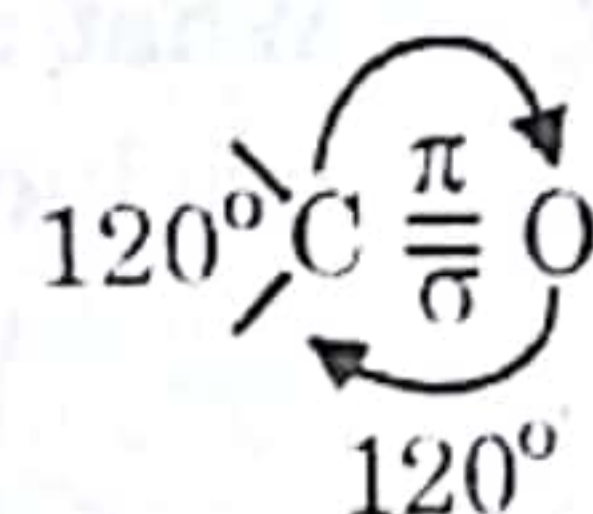
Both aldehydes and ketones contain carbonyl group, >C=O in their molecules. In aldehydes, the carbonyl carbon is bonded to at least one hydrogen atom, while in ketones the carbonyl carbon is always bonded to two other carbon atoms (i.e., two

alkyl groups). The characteristic functional group of aldehyde is $\text{-}\overset{\text{O}}{\parallel}{\text{C}}\text{-H}$ which is known as a **formyl group** and always occurs at the end of a chain. The general formula for aldehyde is RCHO (in formaldehyde, R is H). The characteristic functional group of ketones is >C=O , which is commonly called **keto group** and always occurs inside a chain. The general formula for ketones is RCOR' , where R and R' may be aliphatic or aromatic; they may be same or different.



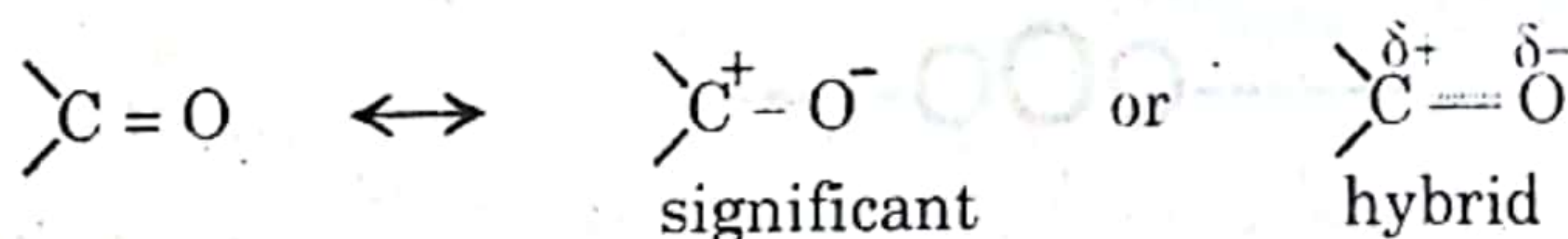
10.1 Structure and Reactivity of the Carbonyl Group

The carbonyl carbon is sp^2 hybridized. Thus carbonyl carbon, and the three atoms attached to it, lie in the same plane. The bond angles between the three attached atoms are approximately 120° . The unhybridized p -orbital of the carbon overlaps with the oxygen p -orbital, giving rise to a π bond between them.



Geometry of the carbonyl group

Oxygen being more electronegative pulls the mobile π electrons towards itself. As a result, the carbonyl group becomes highly polar, with a partial positive charge on the carbon atom and a partial negative charge on the oxygen atom. The polar nature of the carbonyl group can be represented by the following resonance structures:



The polarity of the carbonyl group is manifested in the physical and chemical properties of aldehydes and ketones. The physical consequences of the polarity of the carbonyl group is that carbonyl compounds generally have high dipole moments (the dipole moments of acetaldehyde and acetone are 2.70 D and 2.85D), and have higher boiling points than hydrocarbons of the same molecular masses.

(i) The chemical consequences of the polarity of the carbonyl group is that the positively charged carbon is readily attacked by electron-rich nucleophiles. In fact, the reactivity of carbonyl group towards nucleophiles is due to the ability of the carbonyl oxygen to accommodate the negative charge that develops as a result of such an attack. The reactivity of the carbonyl group towards nucleophilic addition

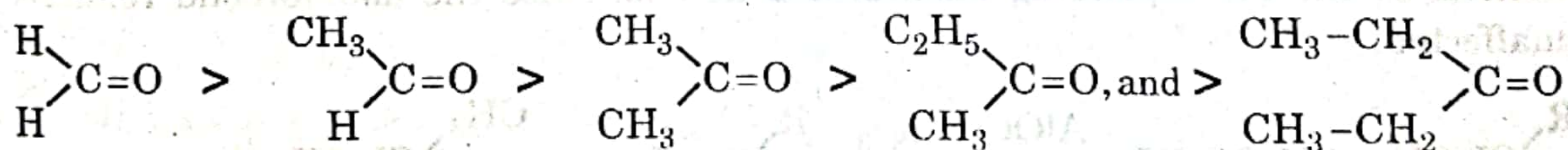
reactions is mainly influenced by (a) electronic factors, and (b) steric factor.

(a) **Electronic Factors.** The ease of attack of a nucleophile on the carbonyl carbon depends upon the magnitude of positive charge on the carbonyl carbon. **Electron-attracting** α -substituents such as nitro or halogen if present, would increase the positive character of the carbonyl carbon and thus facilitate the attack of nucleophile, while the **electron-donating groups** such as alkyl groups attached to the carbonyl group would decrease the positive charge of carbonyl carbon and thus make it susceptible to nucleophilic attack. In fact, the susceptibility of the carbonyl group to nucleophilic attack is due to the ability of the oxygen atom to accommodate the negative charge that develops as a result of the attack. Though an aryl group is electron attracting by inductive effect but due to resonance aryl groups decrease the positive charge of carbonyl carbon. Thus the net result is the deactivation of the carbonyl group due to the attachment of aryl groups.

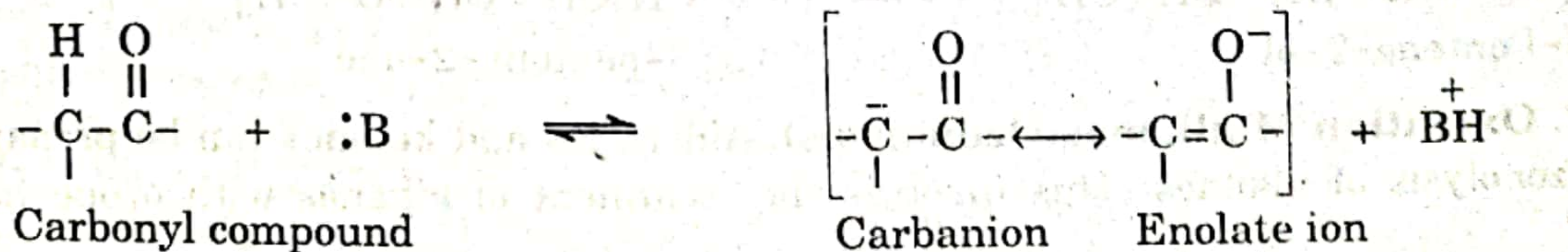


The reactivity of the carbonyl group decreases with increasing size of R's and with electron donation by R. Electron-attracting R's increase the reactivity of carbonyl ($\text{C}=\text{O}$) group.

(b) **Steric Effect.** Carbon in the carbonyl group is trigonal planar and the three atoms or groups attached to the carbonyl carbon lie in one plane and have angles of 120° between one another. When a nucleophile attacks at the carbonyl carbon, the carbon begins to acquire a tetrahedral configuration at the transition state and thus the groups bonded to the carbonyl group come closer to each other. Therefore, more bulky groups will interfere with each other to a greater degree, thus destabilizing the transition state and resultantly the reactivity of carbonyl group will decrease. Thus, because of steric effect aldehydes are more reactive than ketones. Cyclic ketones are more reactive than aliphatic analogues ketones because alkyl groups have greater freedom of motion and produce greater steric hindrance in the transition state for addition whereas in cyclic systems, rigidity of structure prevents any such motion. Thus we anticipate decreasing reactivity with increasing alkyl substituents would be as follows:



(ii) Another important characteristic of the carbonyl group is that it increases the acidity of an α -hydrogen, i.e., hydrogen attached to an α -carbon. This is because when a carbonyl compound loses an α -proton, the anion that is produced is *stabilized by resonance*. The negative charge of the anion is delocalized.



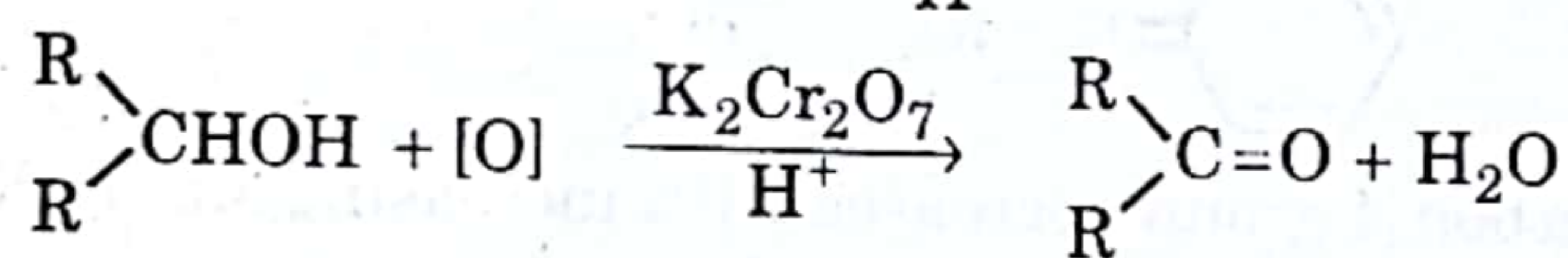
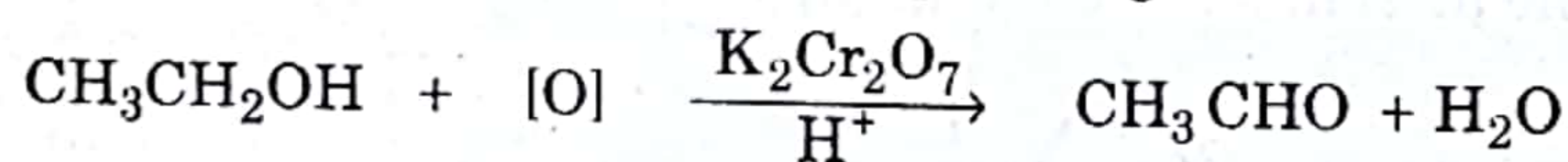
Because of the greater stability of the enolate ion than the carbanion, the resonance stabilized anion is often called an **enolate ion**.

The carbonyl group favours the ionization of the α -hydrogen by accommodating the negative charge of the resulting anion by delocalization over to oxygen, and thus increases its acidity.

In fact, it is the ability of the oxygen atom to accommodate the negative charge which is the real cause of the nucleophilic reactions at the carbonyl group, and the reactions at the α -carbon atom.

10.2 Methods of preparation of Aldehydes and ketones

1. Oxidation of Alcohols. Aldehydes and ketones can be prepared by the controlled oxidation of primary and secondary alcohols respectively using an acidified solution of potassium dichromate or potassium permanganate.

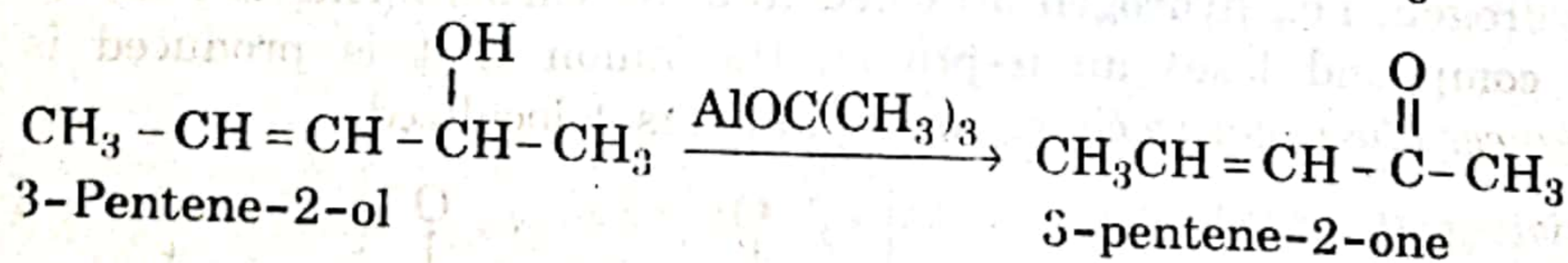
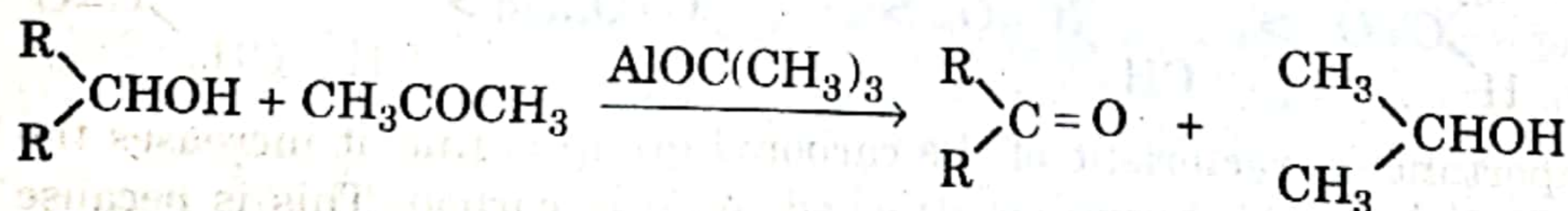


Secondary alcohol

Ketone

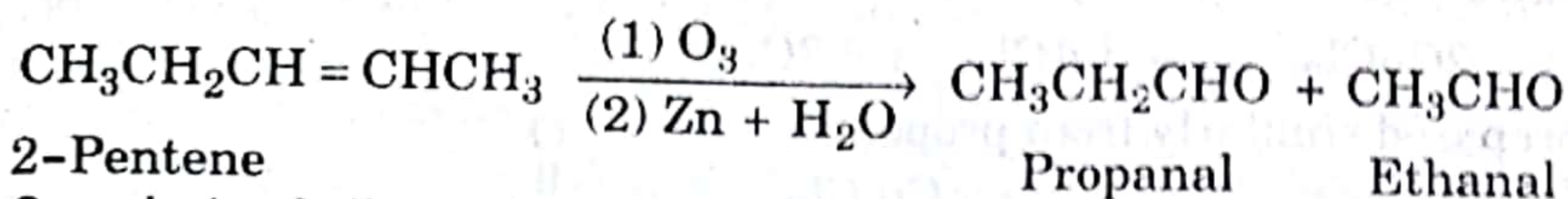
Aldehydes are very easily oxidized to carboxylic acids but ketones are resistant toward oxidation. Therefore, oxidation method is applicable for the preparation of ketones only. However, low boiling aldehydes than alcohols which may be easily removed by distillation or steam distillation, before they are further oxidized into carboxylic acids, can be prepared by oxidation methods.

Alternatively, ketones can be obtained from secondary alcohols by **Oppenauer oxidation**. In this method, the appropriate secondary alcohol is refluxed with excess of acetone in the presence of a weakly basic catalyst usually aluminium tertiary butoxide, $\text{AlOC}(\text{CH}_3)_3$. The net reaction is the dehydrogenation of the alcohol, and at the same time acetone present in the mixture is reduced to isopropyl alcohol. This method is particularly useful for oxidizing unsaturated alcohols to the corresponding unsaturated ketone, since the double bond remains unaffected.

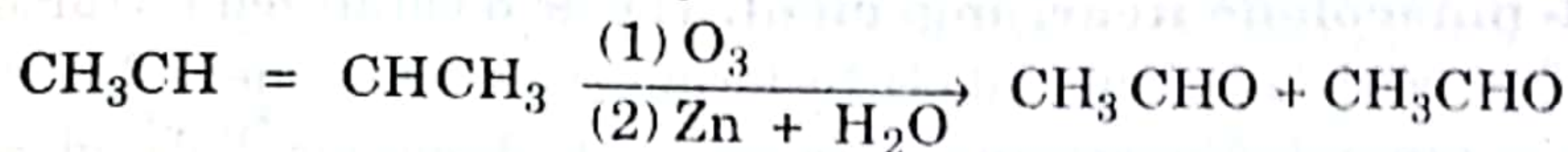


2. Oxidation of alkenes (Ozonolysis). Aldehydes and ketones can be prepared by ozonolysis of alkenes. This involves the treatment of alkenes with ozone to form

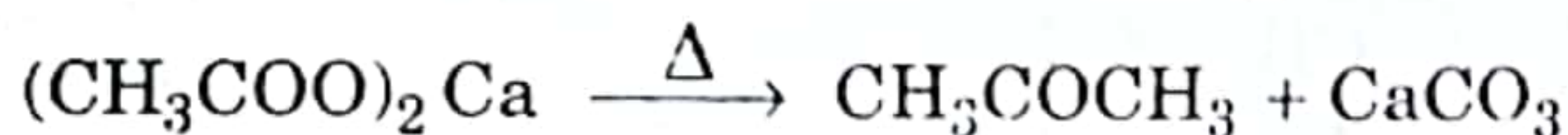
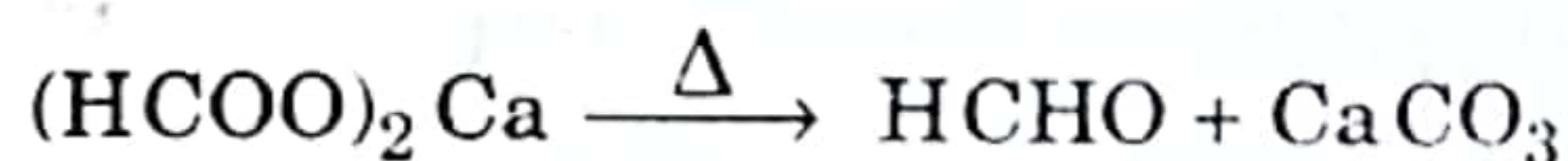
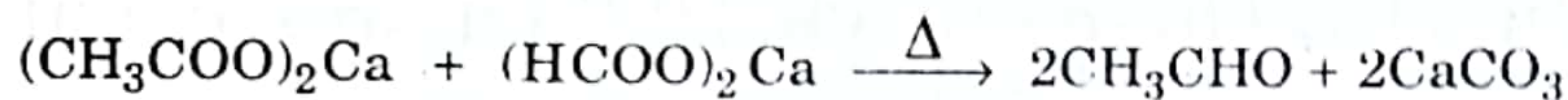
ozonides, which are not isolated because they are often explosive in dry state. The ozonides are reduced with $\text{Zn} + \text{H}_2\text{O}$ to form aldehydes and ketones.



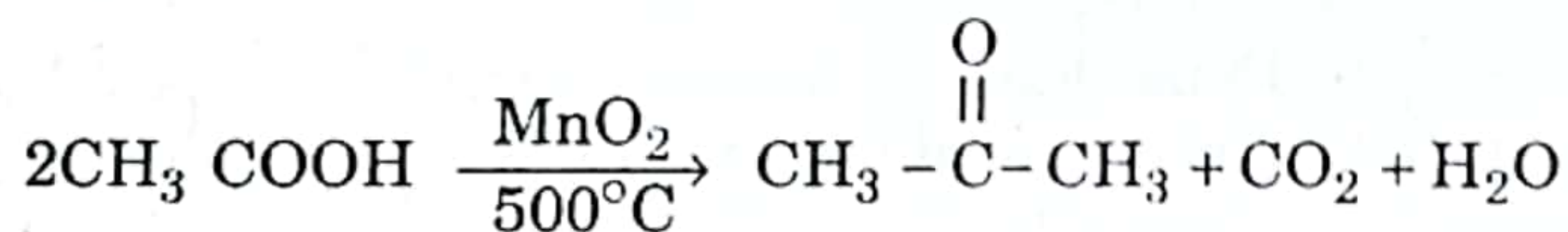
Ozonolysis of alkenes is not a good preparative method for aldehydes and ketones, since a mixture of carbonyl compounds is produced. However, if the starting alkene is symmetrical, only one carbonyl compound will be obtained.



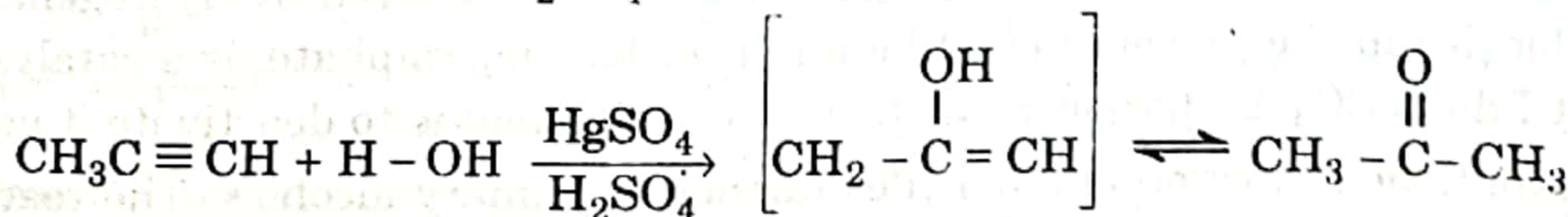
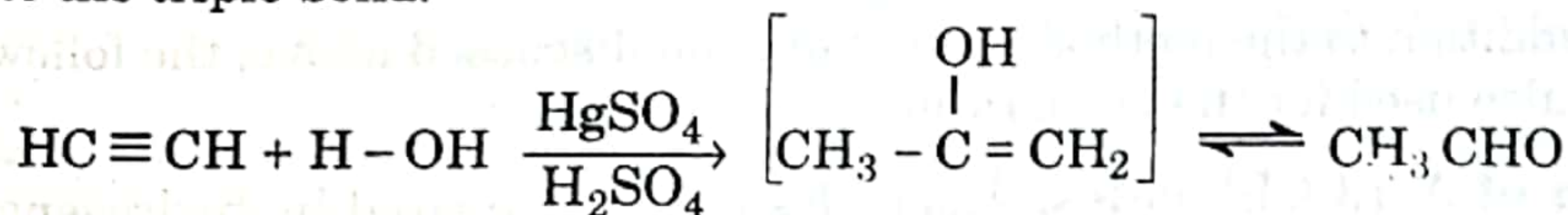
3. Pyrolysis of calcium salts of carboxylic Acids. Dry distillation of calcium salts of carboxylic acids yields a variety of carbonyl compounds depending on the nature of carboxylic acid used. A mixture of calcium formate and the calcium salt of any other carboxylic acid yields an aldehyde; calcium formate alone gives formaldehyde. Calcium salt of a carboxylic acid other than formic acid gives a symmetrical ketone.



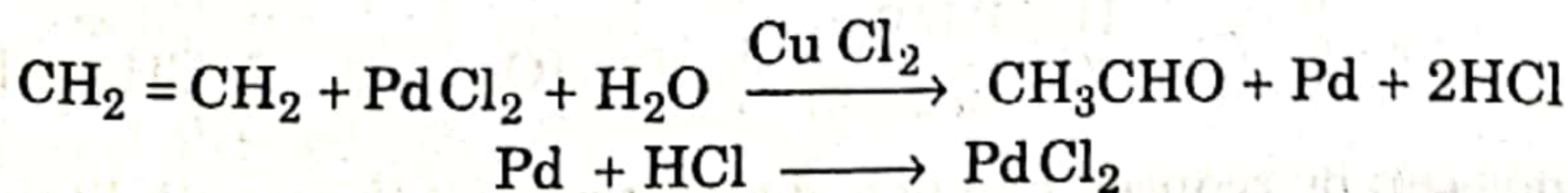
Pyrolysis of carboxylic acids can also be achieved by passing their vapours over manganese dioxide or thorium oxide.



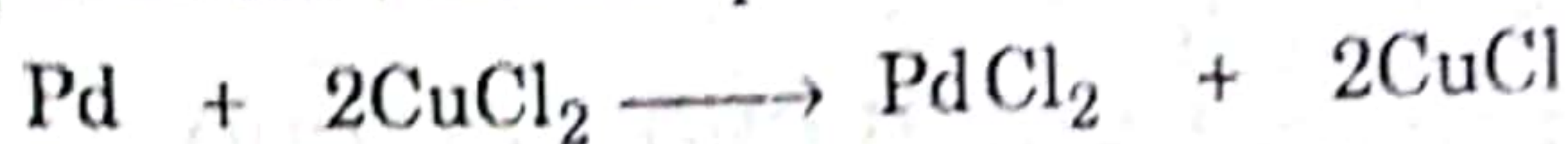
4. Hydration of Alkynes. Hydration of acetylene yields acetaldehyde. Hydration of alkynes, other than acetylene, yield ketones. Alkynes add water in the presence of mercuric sulphate and sulphuric acid to form an unstable vinyl alcohol, which rearranges rapidly to an aldehyde or a ketone. It involves Markovnikov's addition of water to the triple bond.



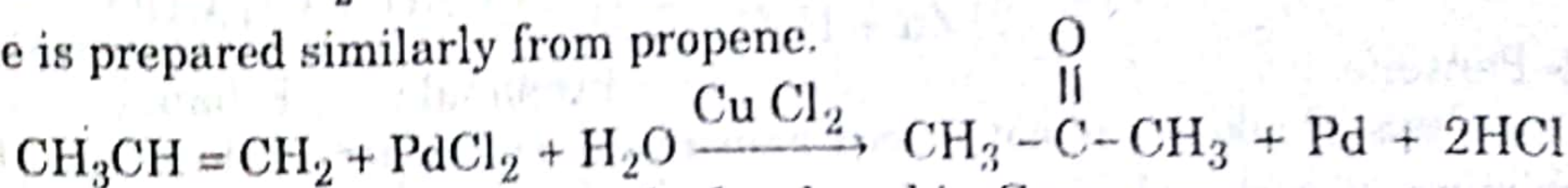
5. Wacker's Process. This process involves the treatment of an alkene with an acidified aqueous solution of palladium chloride and cupric chloride. For example,



The cupric chloride promotes the second reaction, enhancing the reconversion of the palladium back into palladium chloride.

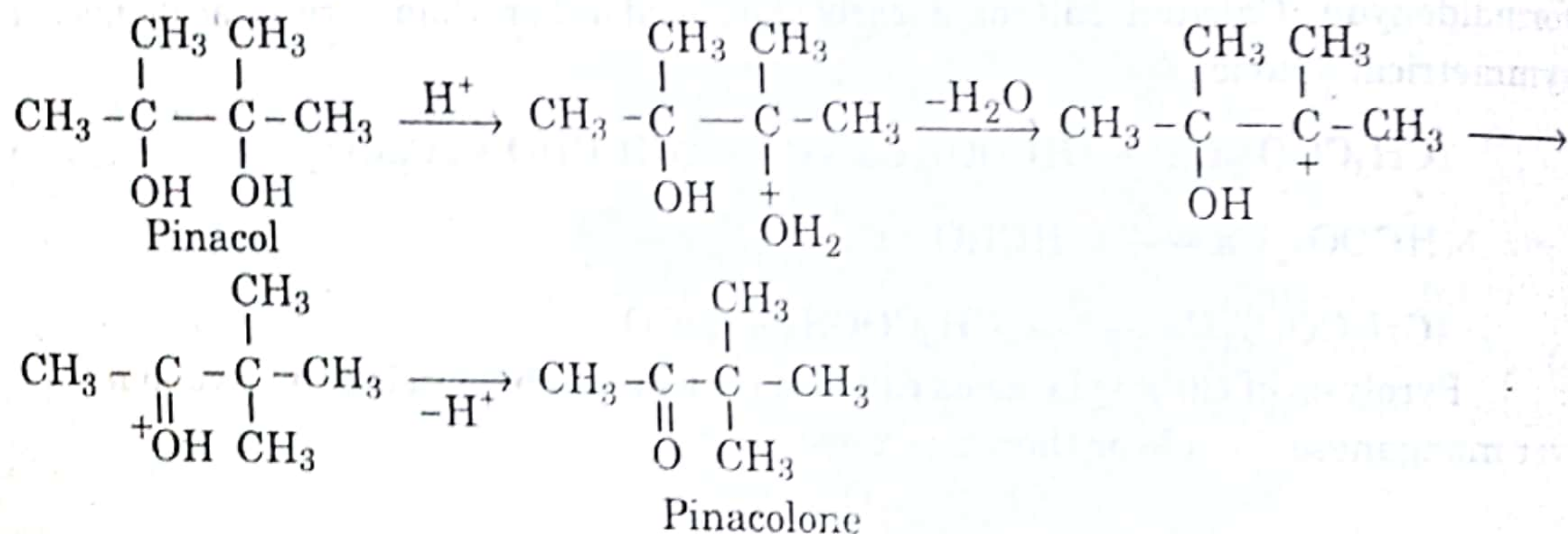


Acetone is prepared similarly from propene.

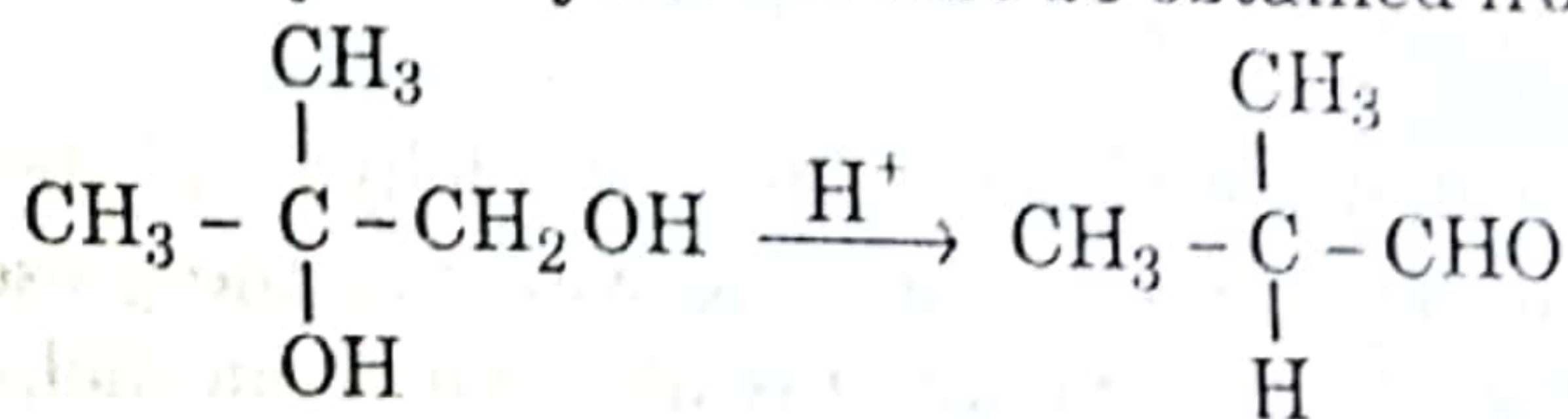


This method has been recently developed in Germany.

6. From pinacol- pinacolone Rearrangement. The acid catalyzed intramolecular rearrangement of pinacol (2,3-butanediol) to form pinacolone (methyl tert-butyl ketone) is known as pinacol- pinacolone rearrangement. When vic-diols (glycols) are treated with acids, they can be rearranged to give aldehydes or ketones. This reaction is called the **pinacol rearrangement**; the reaction gets its name from the typical compound pinacol $(\text{CH}_3)_2\text{COHCOH}(\text{CH}_3)_2$ which is rearranged to pinacolone, $(\text{CH}_3)_3\text{CCOCH}_3$.



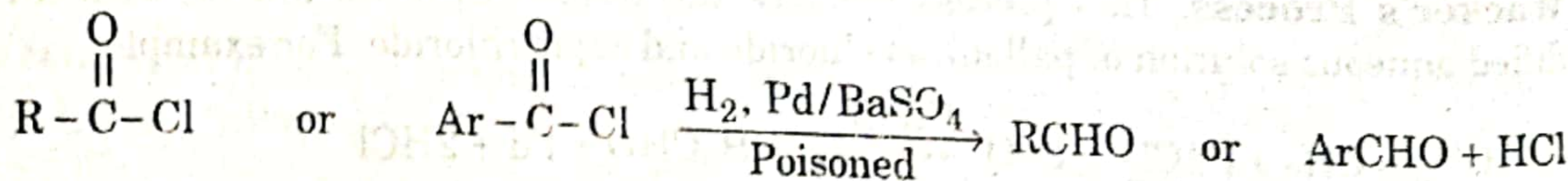
Similarly aldehydes can also be obtained from vic-diols.



Preparation of Aldehydes

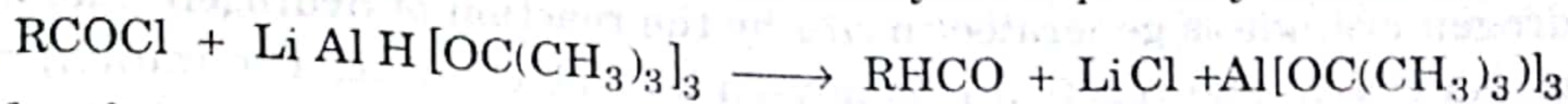
In addition to the methods of preparation discussed above, the following methods are also used for the preparation of aldehydes.

7. Reduction of Acid Chlorides. Aldehydes can be prepared by hydrogenation of acid chlorides in the presence of palladium over barium sulphate as a catalyst. The catalyst Pd/BaSO_4 is "poisoned" with sulphur or quinoline to deactivate it partially and prevent the reduction of aldehydes further to primary alcohols. The reaction is called **Rosenmund reduction**.

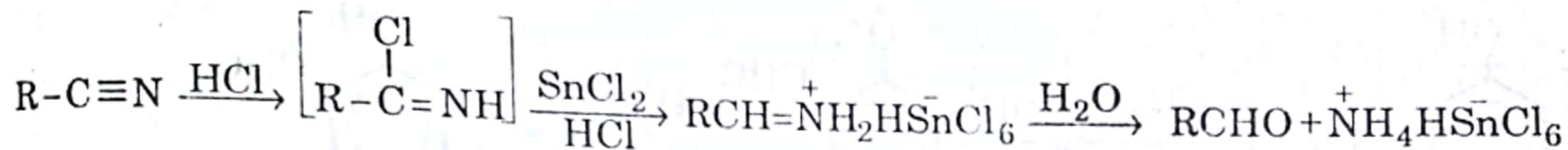


Acid chlorides can be reduced to aldehydes by treating them with lithium tri-

tert butoxyaluminium hydride, $\text{LiAlH}[\text{OC}(\text{CH}_3)_3]_3$, which is much less reactive than LiAlH_4 , and therefore does not reduce the aldehydes to primary alcohols.

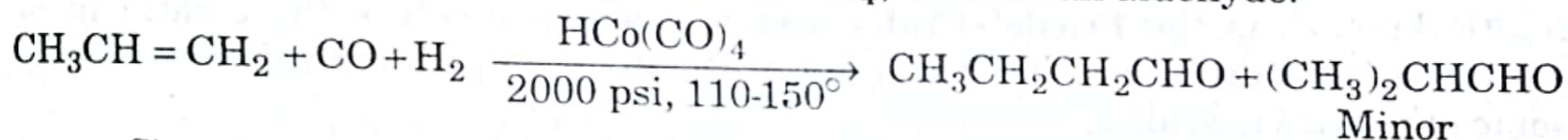


8. Reduction of Nitriles. Nitriles on treatment with stannous chloride and hydrogen chloride yield aldehydes. The reaction which is known as **Stephen reaction**, involves the reduction of the nitriles to produce immonium salts as intermediates, which are readily hydrolysed to yield aldehydes. Stephen reaction is applicable for the synthesis of both aliphatic and aromatic aldehydes, but it is more useful for the aromatic aldehydes.



9. Hydroformylation of terminal alkene (Oxo Reaction)

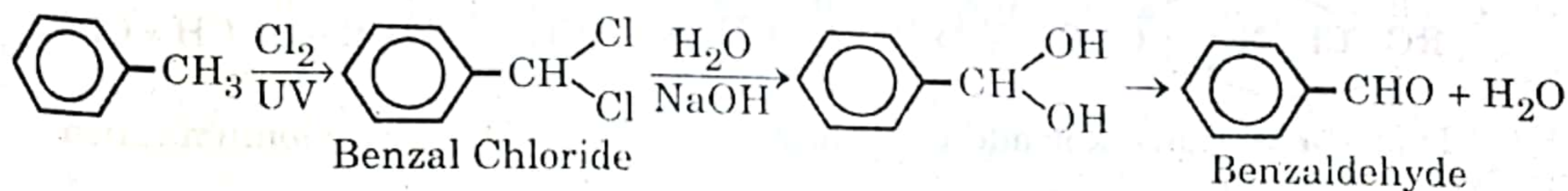
In this process, a terminal alkene reacts with carbon monoxide and hydrogen in the presence of a cobalt catalyst, $\text{HCo}(\text{CO})_4$, to form an aldehyde.



Since the net result of the reaction is the addition of an hydrogen atom, $-\text{H}$, and a formyl group, $-\text{CHO}$ across the double bond, the reaction is called **hydroformylation**.

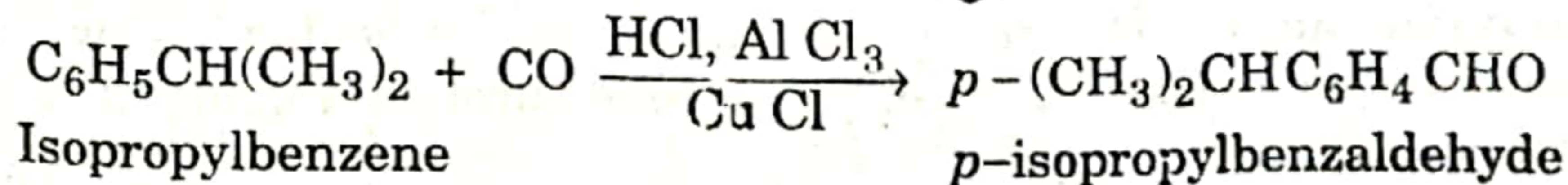
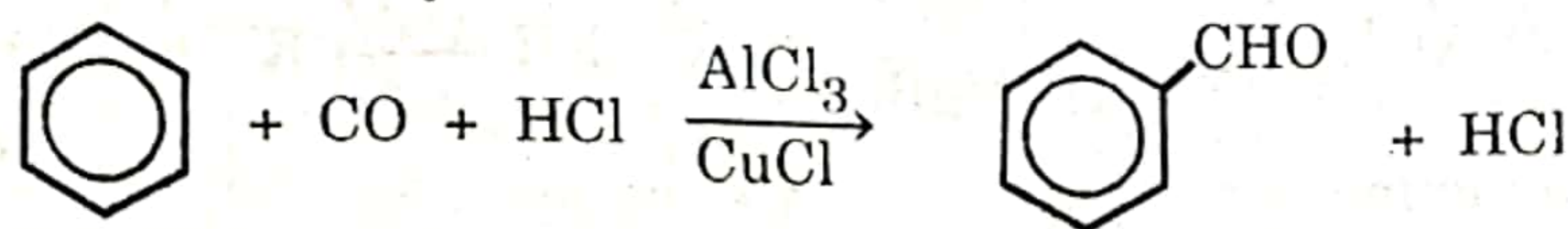
Special Methods for the preparation of Aromatic Aldehydes

10. Hydrolysis of geminal dihalides (i.e., Benzal chloride). The geminal dihalides produced by the side-chain halogenation of alkylbenzene (toluene) on basic hydrolysis yields aromatic aldehyde.

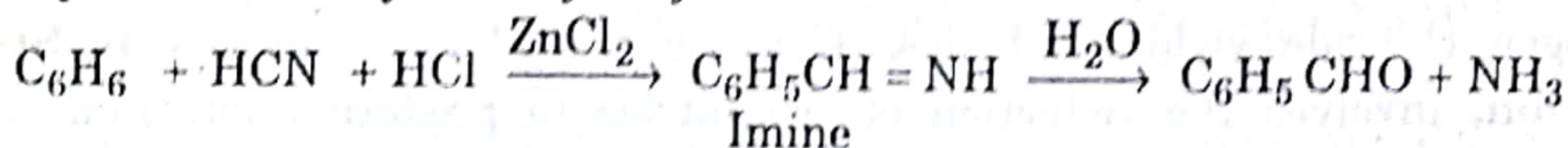


11. Formylation (Introduction of $-\text{CHO}$ group)

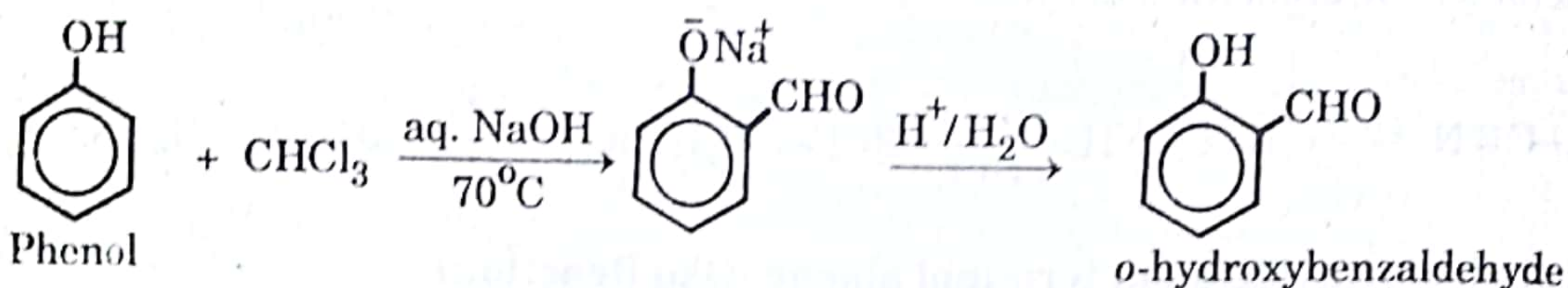
(a) **By Gatterman - Koch reaction.** A mixture of carbon monoxide and hydrogen chloride is passed through an aromatic hydrocarbon in the presence of AlCl_3 containing a trace of CuCl to form an aromatic aldehyde. The reaction is similar to the Friedel - crafts acylation.



(b) Gatterman Reaction. Gatterman - Koch reaction was modified by Gatterman who used hydrogen cyanide in place of poisonous CO as the source of formyl group. The hydrogen cyanide is generated *in situ* by the reaction of hydrogen chloride with NaCN or $Zn(CN)_2$. The reaction is catalysed by zinc chloride. The initially formed an imine yields an aldehyde on hydrolysis.

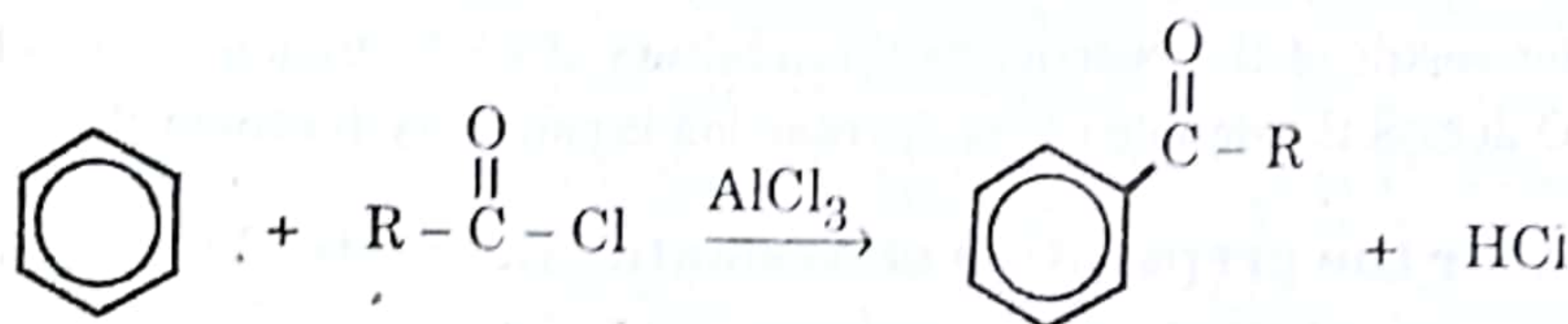


(c) By Reimer-Tiemann reaction. A phenolic aldehyde can be prepared by the treatment of a phenol with aqueous alkali followed by acid hydrolysis.

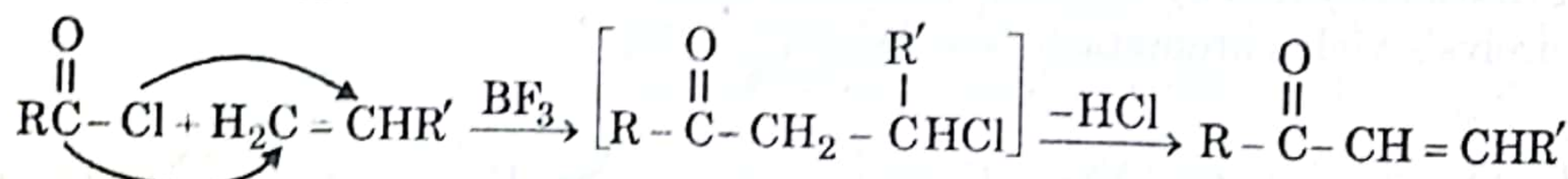


Special Methods for the preparation of ketones

12. Friedel-Crafts Acylation. One of the most important method of preparing aromatic ketones is the Friedel-Crafts acylation which involves the treatment of aromatic compounds with acid chlorides or acid anhydride in the presence of $AlCl_3$ or some other Lewis acid.

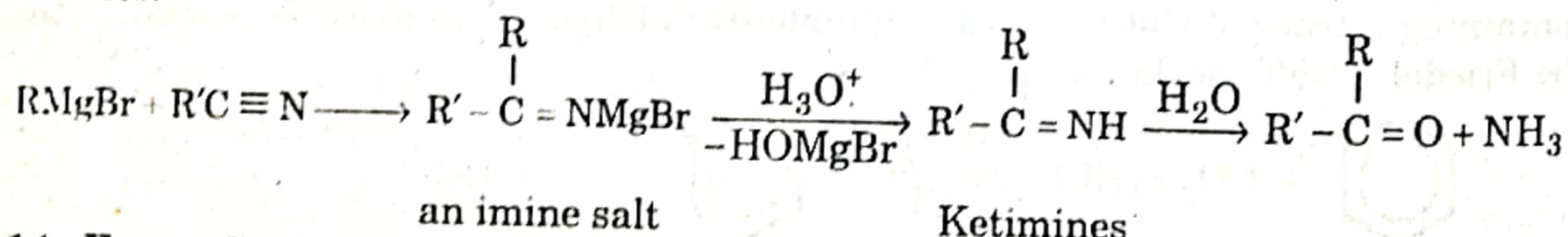


Acylation of Alkenes:

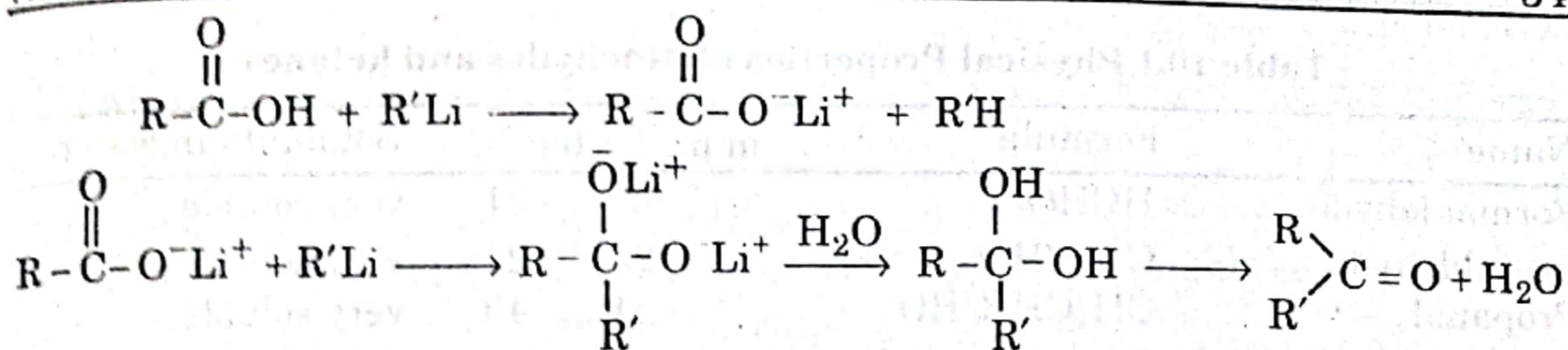


This is a Markovnikov addition initiated by $RC^+ = \ddot{O}$, an acylium cation.

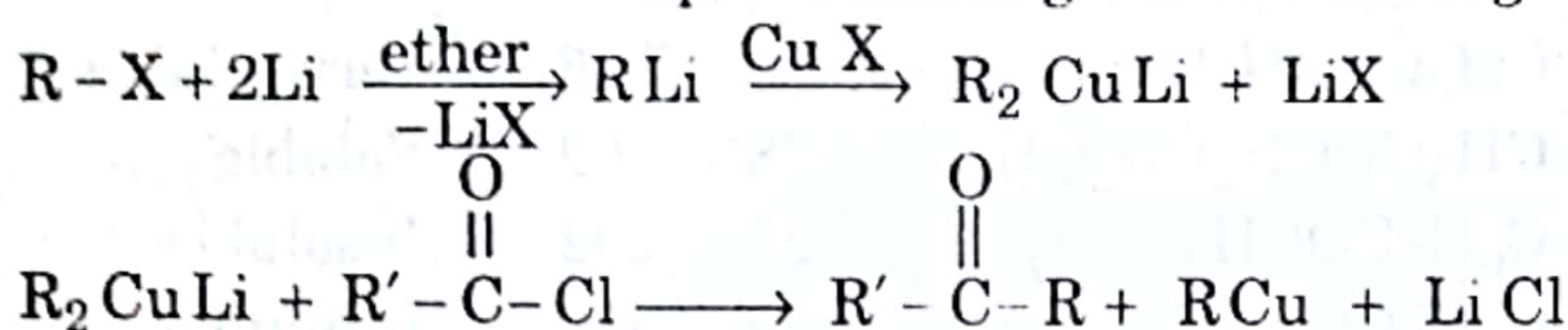
13. By addition of Grignard reagent to nitriles. Grignard reagents add to nitriles to give addition products (adduct) which on hydrolysis leads to ketimines which are unstable, under the reaction conditions and are rapidly hydrolyzed to ketones.



14. From Carboxylic acids. The reaction of a carboxylic acid with two molar equivalents of an alkyl- or aryllithium yields a ketone through a gem-diol which loses water spontaneously.

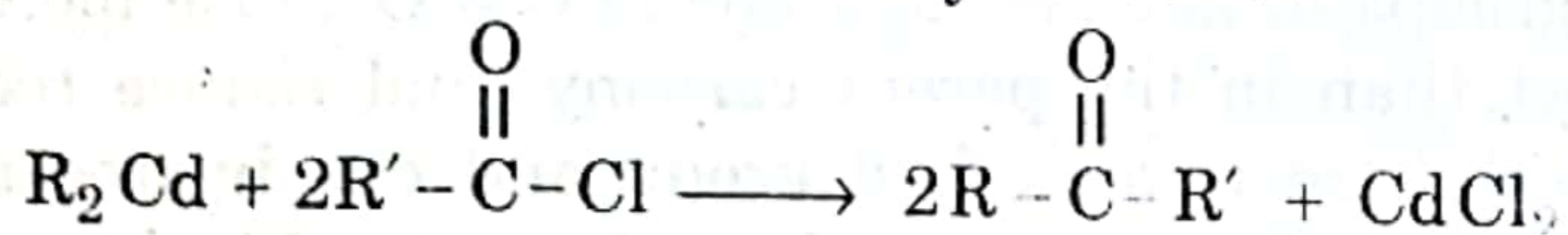
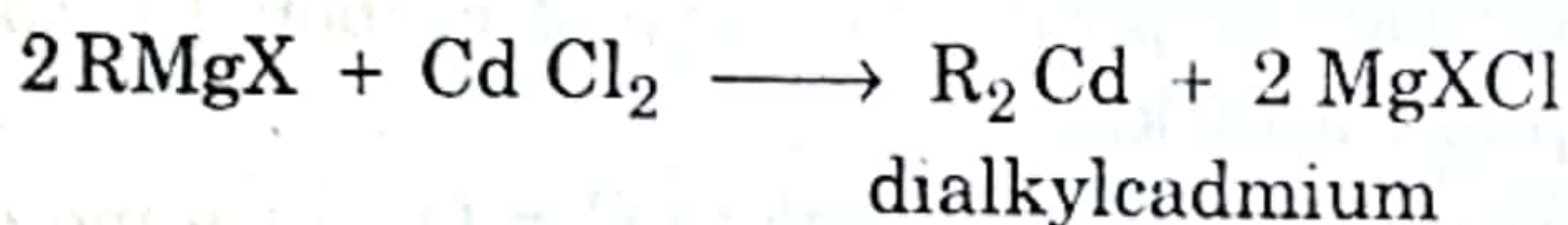


15. By the Reaction of Organocuprates with Acid chlorides. When an ether solution of lithium organo cuprate is treated with an acid halide at -78°C , a ketone is produced. Lithium organocuprates, R_2CuLi or Ar_2CuLi are produced by treating alkyl or aryl halides with lithium metal to form alkyllithium or aryllithium, which on further treatment with a cuprous halide gives lithium organocuprates.



16. By the Reaction of Organocadmium Compounds with Acid Chlorides.

Grignard reagents and alkyllithium are too reactive toward ketones to be used to prepare ketones from acid chlorides or esters because Grignard reagents react with acid chlorides or ester to yield tertiary alcohols. However, if a Grignard reagent is first converted to dialkyl or diaryl cadmium by treating it with anhydrous CdCl_2 . Dialkyl or diaryl cadmium thus produced on treatment with an acid chloride gives a ketone in good yield. This is because the organocadmium compounds are too unreactive toward ketones to attack the product, but they are reactive enough toward acid chlorides to form ketones.



10.3 Physical properties of Aldehydes and ketones

Lower aldehydes and ketones are colourless liquids except formaldehyde which is a gas. Pure aromatic ketones are solids.

The carbonyl group of aldehydes and ketones is polar in nature; therefore aldehydes and ketones have higher boiling points than hydrocarbons and other non-polar substances of comparable molecular masses. However, since aldehydes and ketones cannot form strong hydrogen bonds between their molecules, they have lower boiling points than corresponding alcohols.

Lower aldehydes and ketones are soluble in water due to the formation of hydrogen bonds with water molecules, but higher members containing more than five carbons are generally insoluble in water.

Lower aldehydes possess unpleasant smell, while some aromatic aldehydes obtained from natural sources have very pleasant fragrances. Ketones have pleasant

sweet odours.

Table 10.1 Physical Properties of Aldehydes and ketones

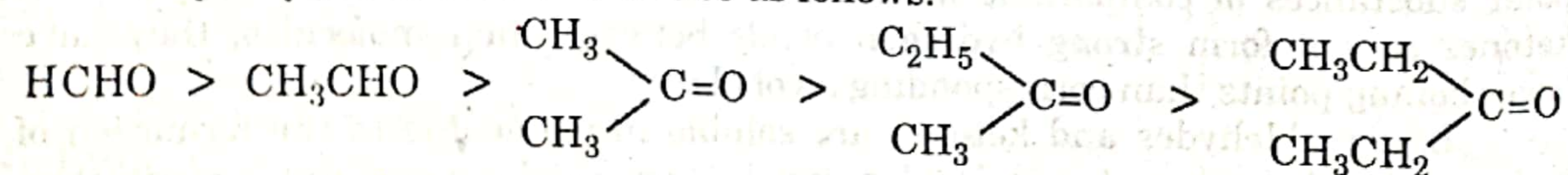
Name	Formula	m.p., °C	b.p. °C	Solubility in water
Formaldehyde	HCHO	-92	-21	very soluble
Acetaldehyde	CH ₃ CHO	-125	21	very soluble
Propanal	CH ₃ CH ₂ CHO	-81	49	very soluble
Butanal	CH ₃ (CH ₂) ₂ CHO	-99	76	Soluble
Pentanal	CH ₃ (CH ₂) ₃ CHO	-91.5	102	slightly soluble
Benzaldehyde	C ₆ H ₅ CHO	-57	178	slightly soluble
Phenylacetaldehyde	C ₆ H ₅ CH ₂ CHO	33	193	slightly soluble
Acetone	CH ₃ COCH ₃	-95	56.1	very soluble
Butanone	CH ₃ COCH ₂ CH ₃	-86	79.6	very soluble
2 - Pentanone	CH ₃ COCH ₂ CH ₂ CH ₃	-78	102	Soluble
Acetophenone	C ₆ H ₅ COCH ₃	21	202	Insoluble
Benzophenone	C ₆ H ₅ COC ₆ H ₅	48	306	Insoluble

10.4 Comparison of reactivity of aldehydes and Ketones

Aldehydes are more reactive than ketones because of the inductive effect and steric effect.

Inductive effect: In aldehydes, the hydrogen atom bonded to the carbonyl carbon disfavours the stability of the carbonyl group as the effect of hydrogen atom is to withdraw electrons. It would increase the positive character of the carbonyl carbon and thus facilitate the attack of nucleophile. On the other hand, in ketones both the alkyl groups are electron releasing group due to inductive effect and thus stabilizes the carbonyl group and would decrease the positive charge of carbonyl carbon and thus make it susceptible to nucleophilic attack.

Steric effect. Bulky groups in ketones adjacent to C = O cause more steric strain in the addition product than in the parent carbonyl and reduce reactivity toward addition. In aldehydes there is one alkyl group and one hydrogen atom attached to the carbonyl carbon ; but in ketones in place of one small hydrogen atom there is one relatively bulky alkyl or aryl group. Thus, due to steric factors also aldehydes are more reactive than ketones. Cyclic ketones are generally more reactive than their open chain analogous because in open chain compounds the alkyl groups have considerably more freedom of motion and produce greater steric hindrance in the transition state for addition. Thus we anticipate decreasing reactivity with increasing alkyl substituents would be as follows:



A characteristic structural difference between an aldehyde and a ketone is that an aldehyde contains a hydrogen atom directly attached to the carbonyl carbon atom, whereas no such hydrogen is present in ketones. Because of this structural

difference, aldehydes are oxidized easily, whereas ketones are oxidized only with difficulty.

Aldehydes undergo an addition polymerization while ketones do not undergo polymerization.

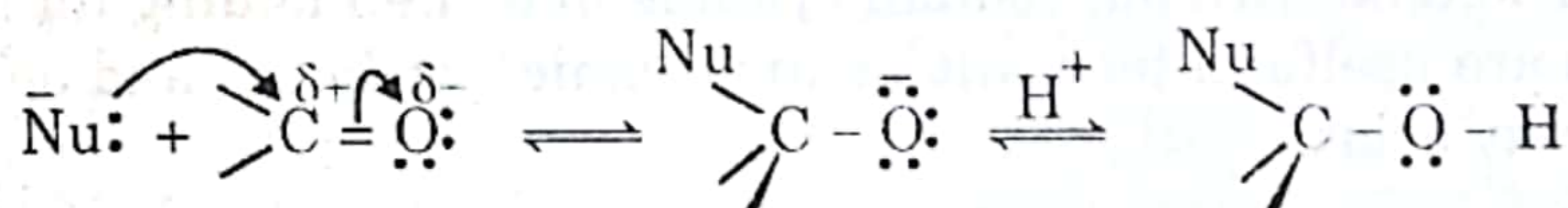
10.5 Reactions of Aldehydes and ketones

The reactions of aldehydes and ketones can be divided into three types.

- A. Nucleophilic addition to the carbon - oxygen double bond.
- B. Reactions due to the α -hydrogen atom of aldehydes and ketones.
- C. Oxidation Reactions

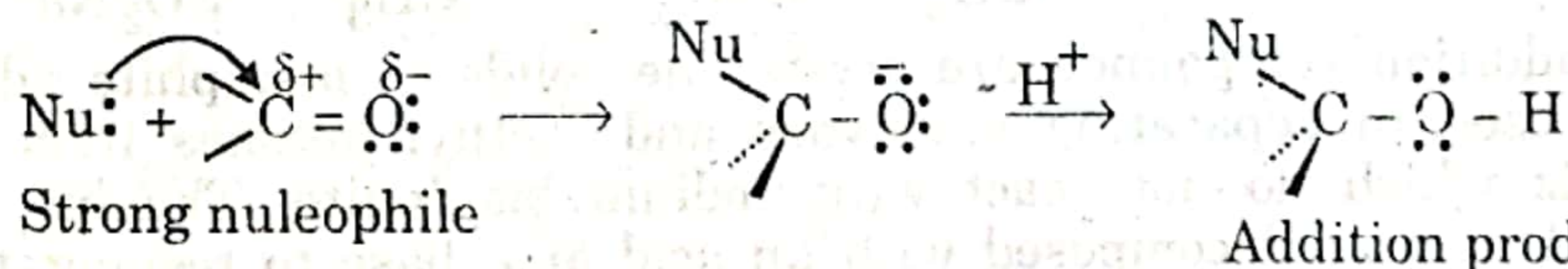
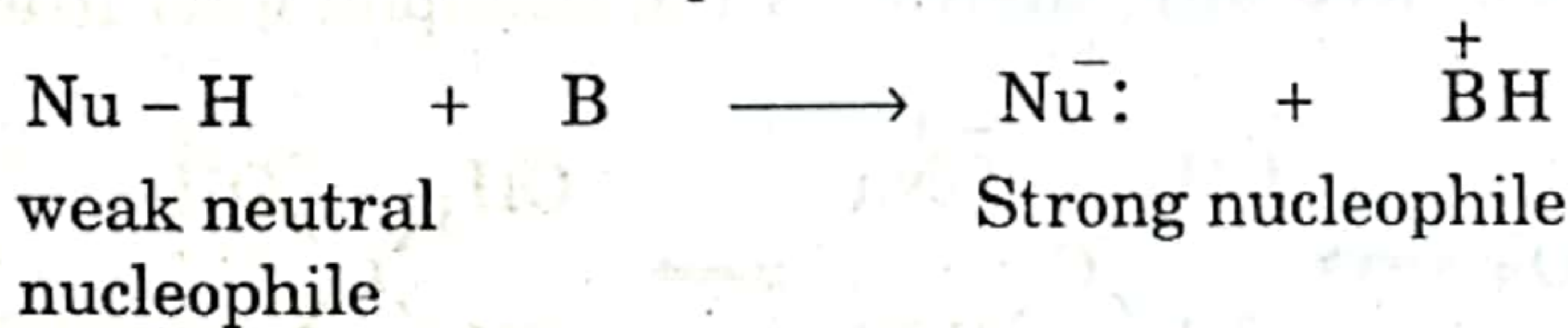
A. Nucleophilic Addition Reactions

The carbonyl group of aldehydes and ketones is a highly polar group. Addition on carbon-oxygen double bond may be initiated either by the attack of a nucleophile on the positively charged carbonyl carbon or by the attack of electrophile on the negatively charged oxygen of carbonyl group. When the reagent is a strong nucleophile, the nucleophile usually attacks the positively charged carbonyl carbon to form a new bond. As the new bond is formed, the electron pair of the carbon-oxygen π bond goes to the carbonyl oxygen, which acquires a negative charge. In the second step, the electrophile (usually a proton) attacks the negatively charged oxygen to form the addition product.

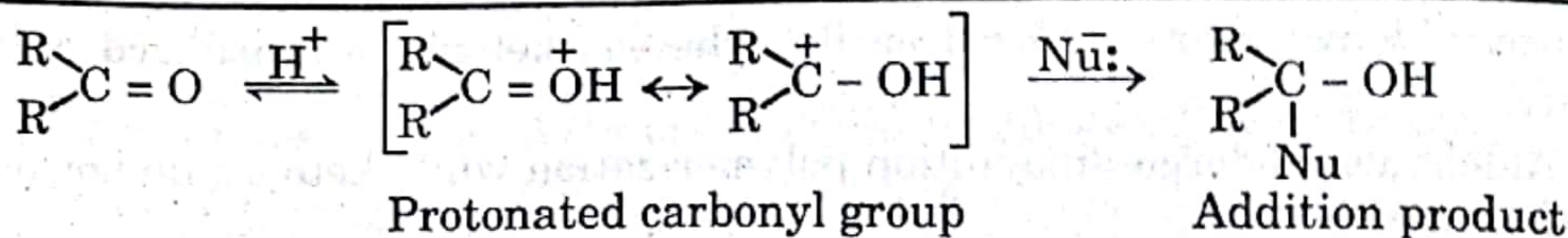


Addition product

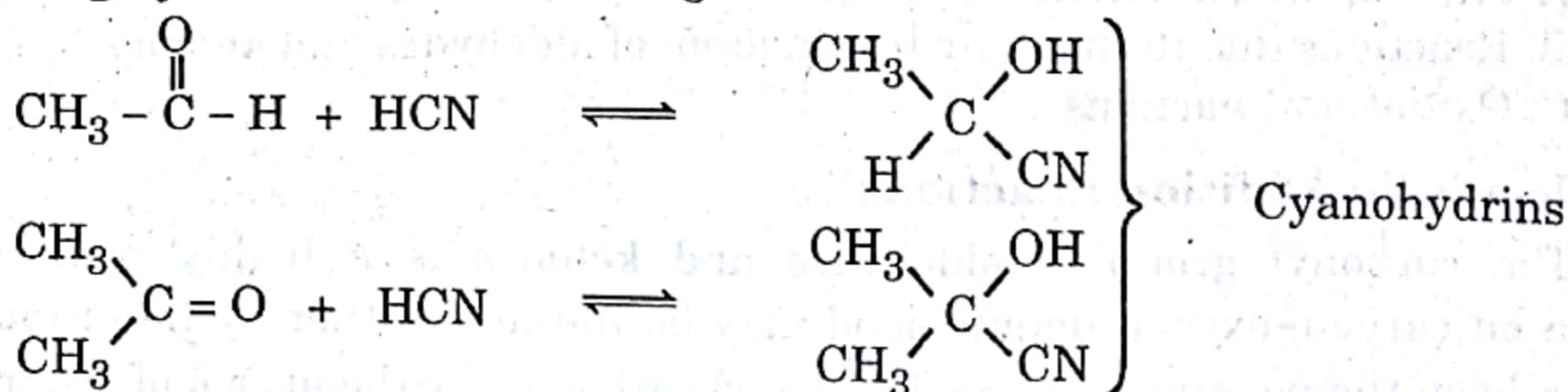
1. Base-Catalysed Nucleophilic Addition. Bases convert a weak neutral nucleophile to a strong one by removing a proton. The strong nucleophile ($\bar{\text{Nu}}:$) then attacks the positively charged carbonyl carbon to form a new bond and thus oxygen acquires a negative charge. The electrophile (H^+) attacks the negatively charged oxygen to form the addition product.



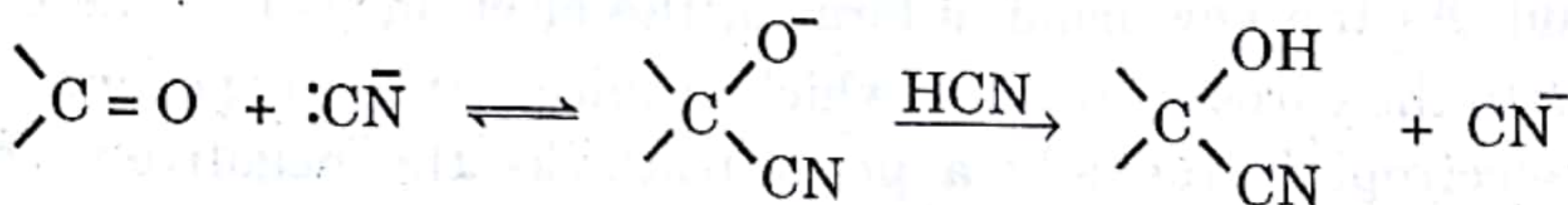
2. Acid-Catalysed Addition. This mechanism operates when carbonyl compounds are treated with reagents that are *strong acids* but *weak nucleophiles*. In the first step, the acid attacks the negatively charged carbonyl oxygen to give protonated carbonyl group, which is resonance stabilized. In the second step, the nucleophile attacks the protonated carbonyl group to form the addition product.



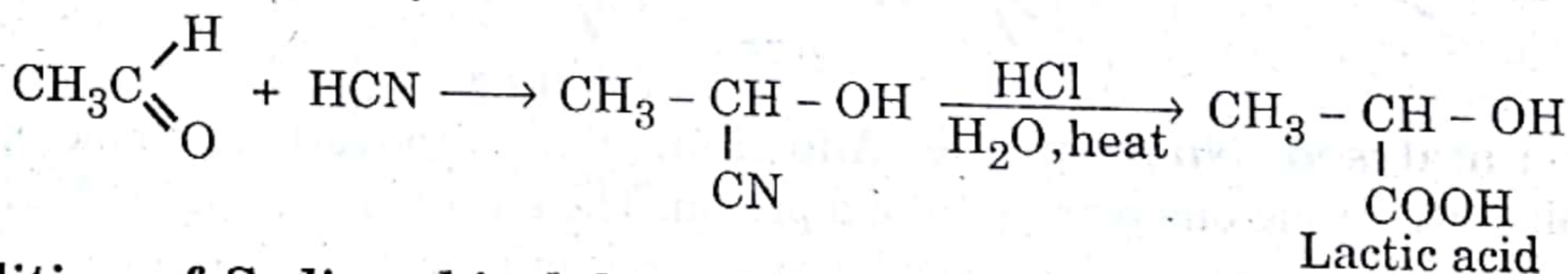
1. Addition of Hydrogen Cyanide. Hydrogen cyanide adds to the carbonyl group of aldehydes and most ketones to form Cyanohydrins. Ketones in which the carbonyl group is highly hindered do not undergo this reaction.



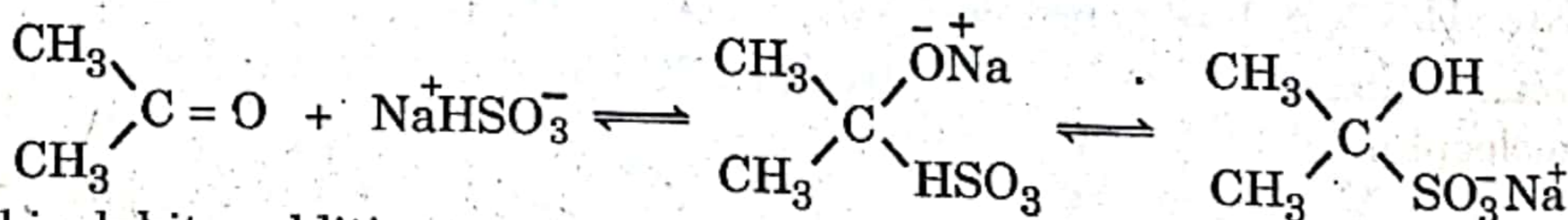
HCN is a weak acid, but the cyanide ion is a strong nucleophile. Therefore, cyanohydrin formation is initiated by a nucleophile attack by the cyanide ion on the carbonyl carbon.



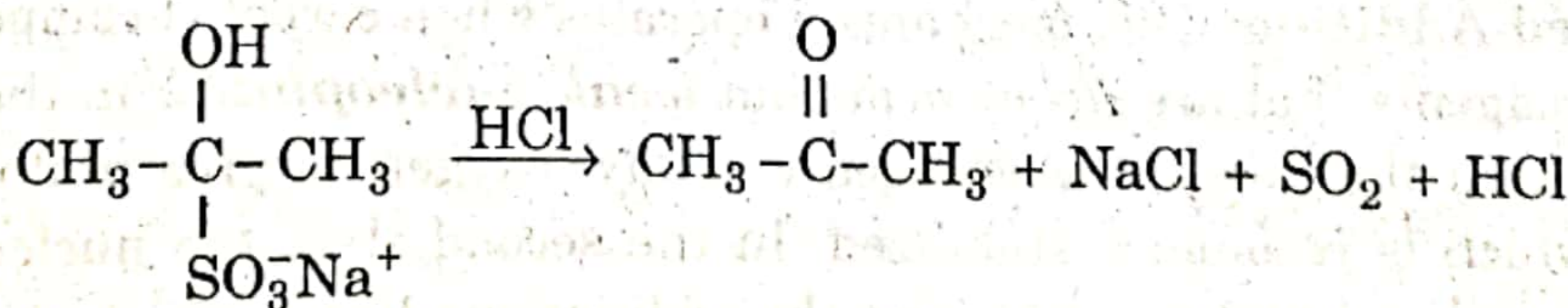
HCN is a very poisonous gas, and is generated *in situ* (in the reaction mixture) by mixing the aldehyde or ketone with aq. sodium cyanide and then adding dil HCl or H_2SO_4 . Cyanohydrins are useful intermediates in Organic synthesis and on acidic hydrolysis give α -hydroxy acids.



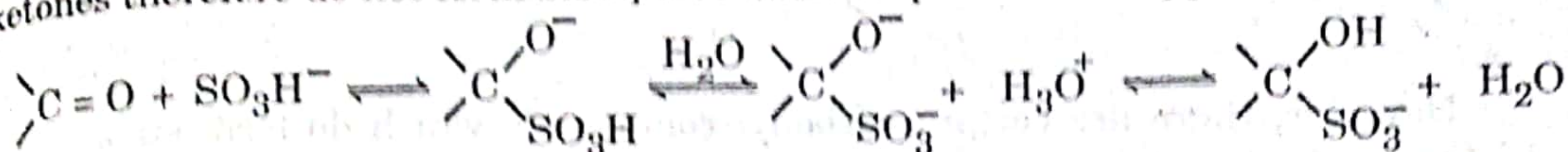
2. Addition of Sodium bisulphite. Aldehydes and methyl ketones react with a saturated aqueous solution of sodium bisulphite to give crystalline addition products. The reaction does not need any catalyst as the bisulphite ion itself is a strong nucleophile.



Since bisulphite addition compounds are crystalline solids, a bisulphite addition reaction is often used in separating aldehydes and methyl ketones from other organic compounds which do not react with sodium bisulphite. The bisulphite addition compounds can be decomposed with an acid or a base to regenerate the carbonyl compounds.

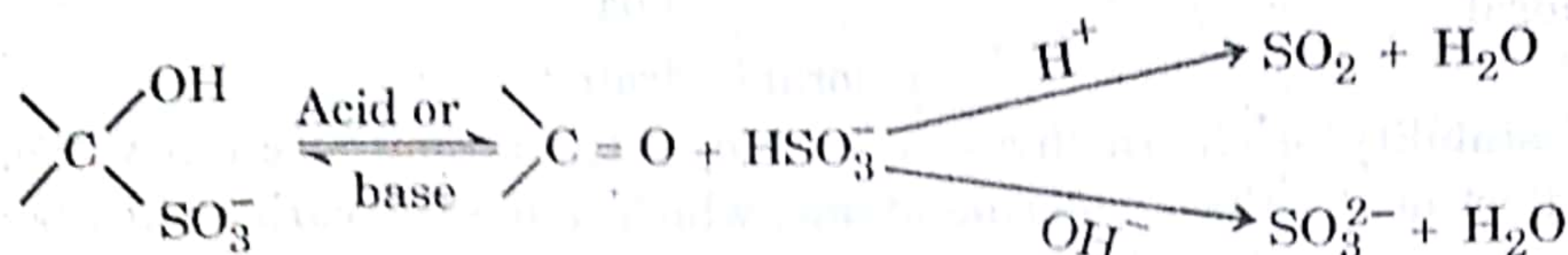


The addition of bisulphite is very sensitive to steric hindrance; most higher ketones therefore do not form bisulphite addition products in appreciable amounts.



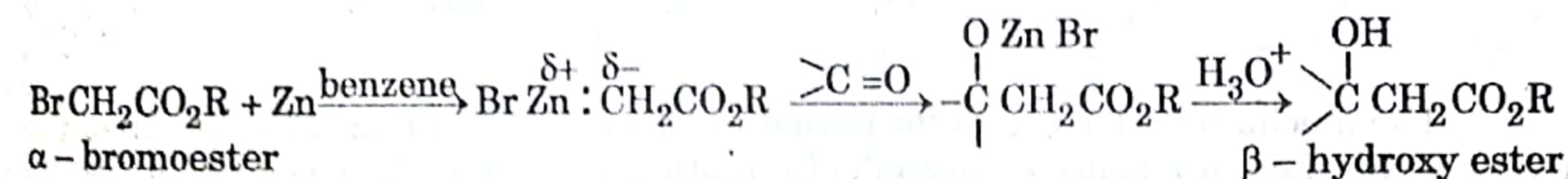
The reaction involves a nucleophilic attack by the sulphur atom of the bisulphite ion, at the carbonyl carbon, followed by a sequence of proton exchanges with the solvent.

The bisulphite addition products of the carbonyl compounds can be decomposed back to the aldehydes or ketones from which they were formed, on treatment with strong acids or bases.

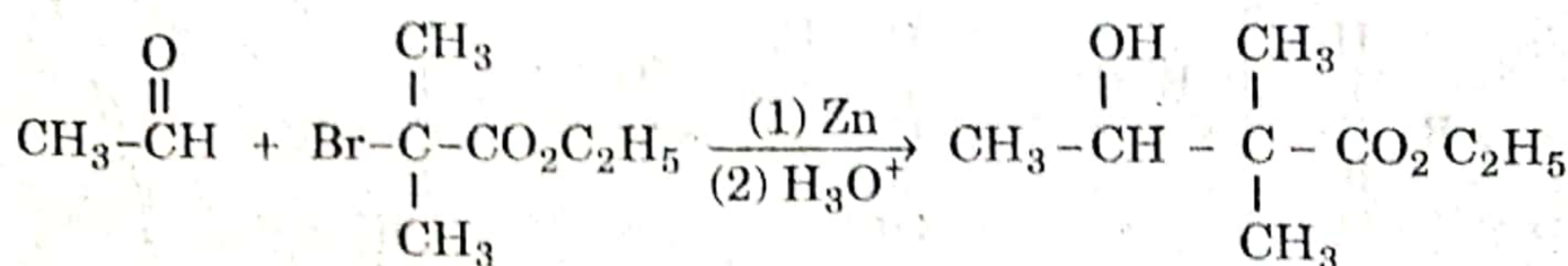
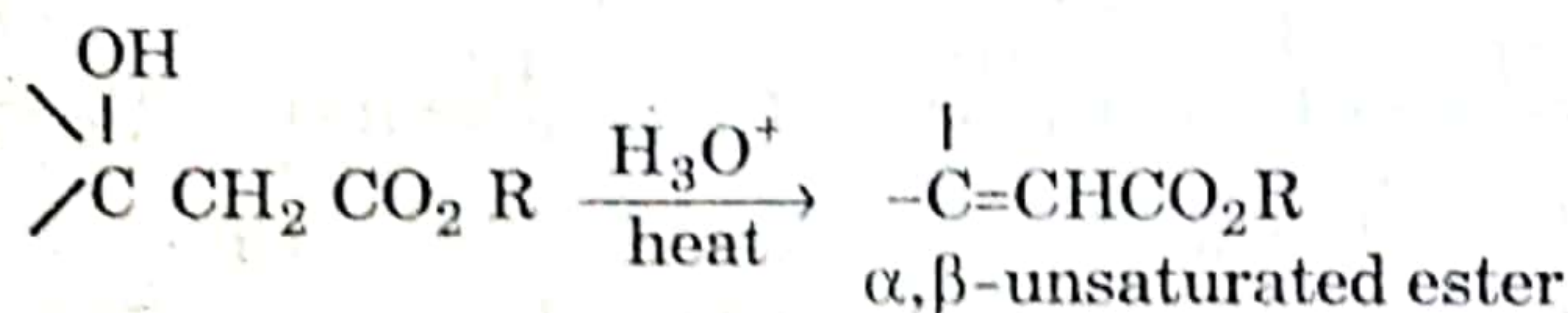


3. Addition of Grignard Reagents. (See reactions of Grignard reagents in Chapter 8, Alkyl halides and preparation of alcohols in Chapter 9).

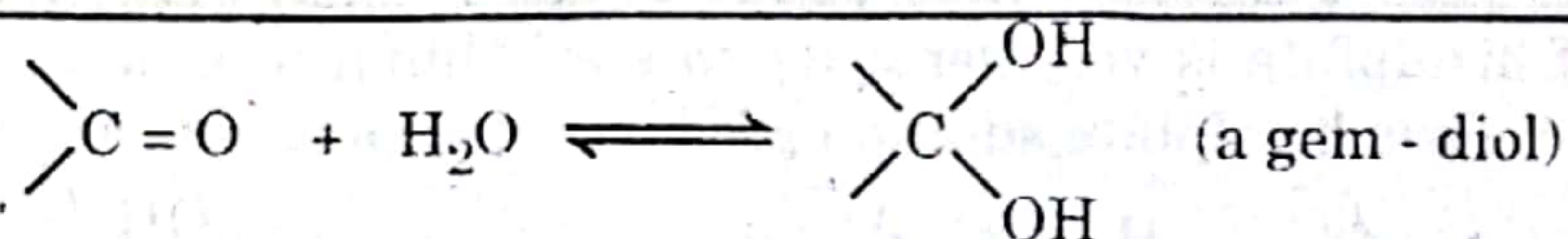
4. Reformatsky Reaction. The Reformatsky reaction resembles the reaction of Grignard reagents with aldehydes and ketones. In this reaction an aldehyde or ketone is treated with an α -bromo ester in the presence of zinc metal usually in benzene. The initial product is a zinc alkoxide which on hydrolysis yields β -hydroxy ester. The intermediate in the reaction appears to be an organozinc reagent that adds to the carbonyl group in a manner analogous to that of a Grignard reagent.



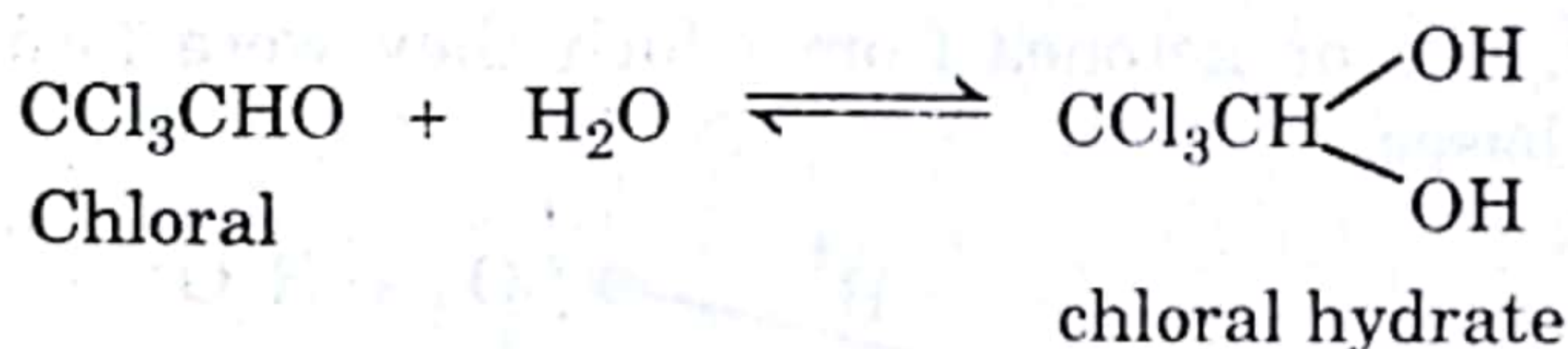
The β -hydroxy esters are easily dehydrated to α,β -unsaturated esters.



5. Addition of water. Aldehydes and ketones react with water to form gem-diols, which are generally too unstable to be isolated. The reaction is very much affected by electronic and steric factors.

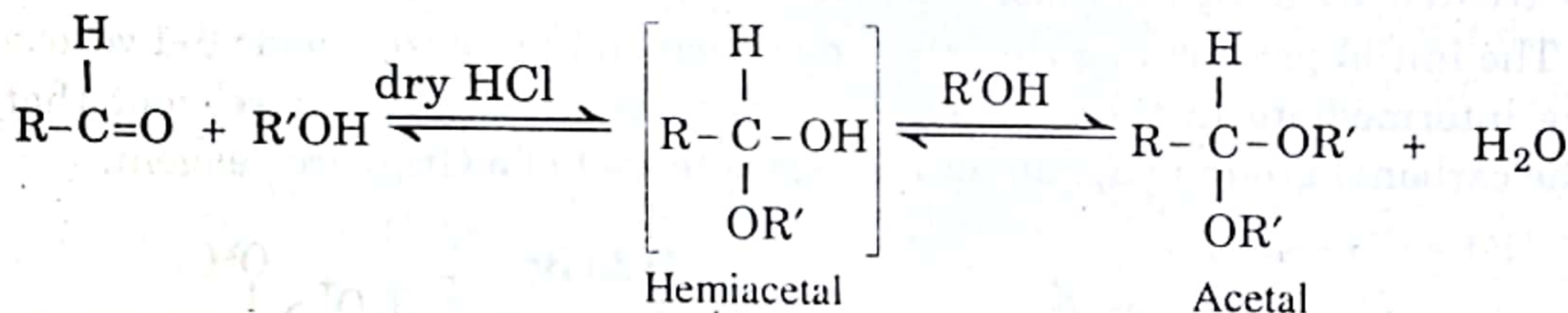


However, there are certain carbonyl compounds which do form stable gem-diols. One of the best known carbonyl compound is trichloroacetaldehyde, commonly called **chloral**. Chloral reacts with water to form crystalline chloral hydrate (m. p. 57°C) with the evolution of heat.

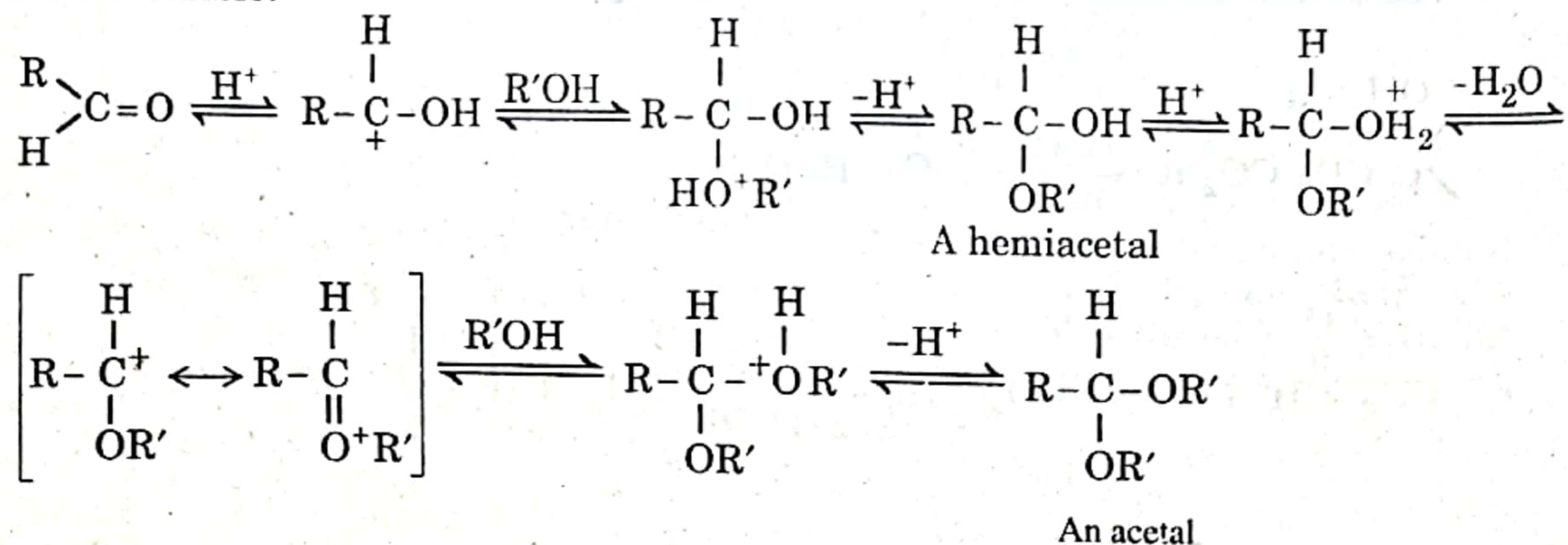


The stability of chloral hydrate is due to the strong electron withdrawing inductive effect of the three chlorine atoms, which make the carbonyl carbon more electron-deficient and thus can accommodate the two hydroxyl group.

6. Addition of Alcohols (formation of Acetals). Alcohols react with aldehydes in the presence of anhydrous HCl to give unstable addition products called **hemiacetals**. These hemiacetals react further with alcohols to form **acetals** (gem-diethers).

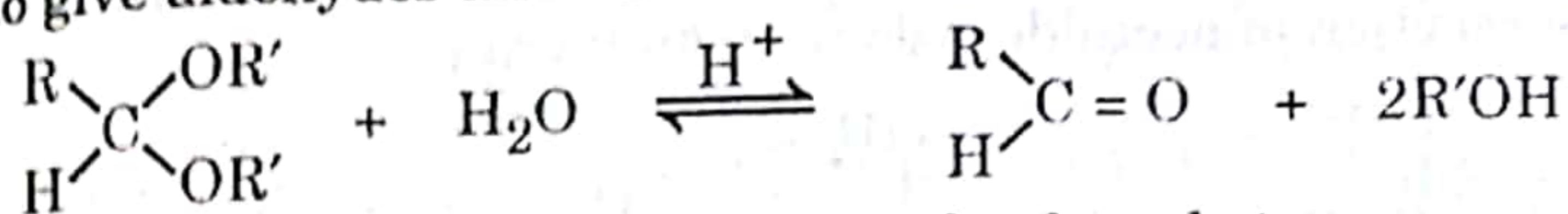


The mechanism for acetal formation involves acid-catalyzed formation of the hemiacetal, then an acid-catalyzed elimination of water, followed by a second addition of alcohol molecule. All steps in the formation of an acetal from an aldehyde are reversible.

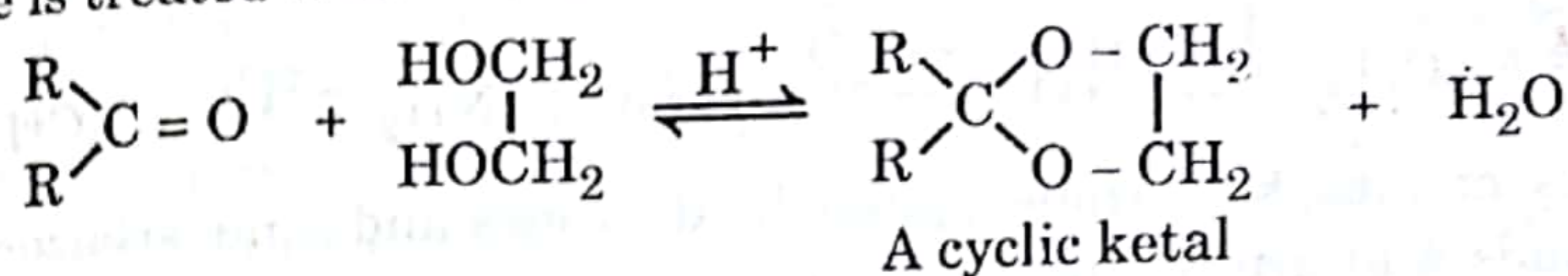


Acetal and hemiacetal formation is affected strongly by steric hindrance. Large groups in aldehydes as well as in alcohols will retard the reaction. Acetals are

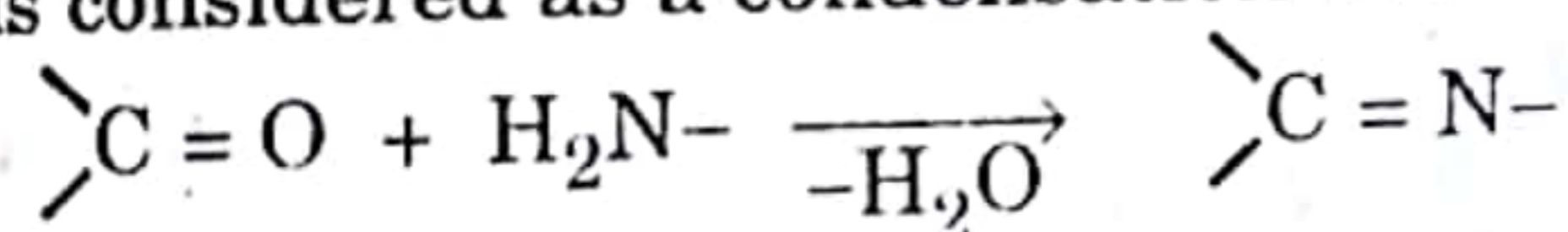
stable in neutral or basic media. The acetals undergo hydrolysis by dilute mineral acids to give aldehydes and alcohols.



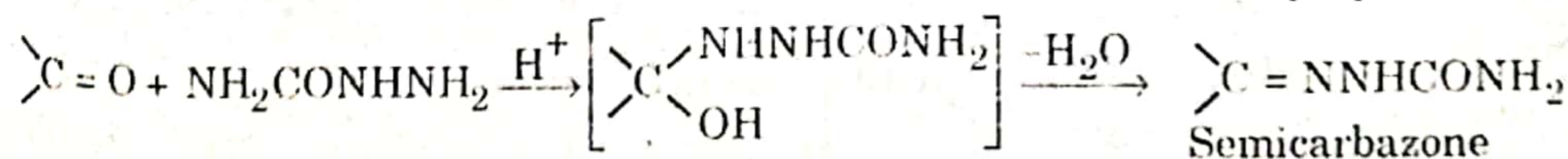
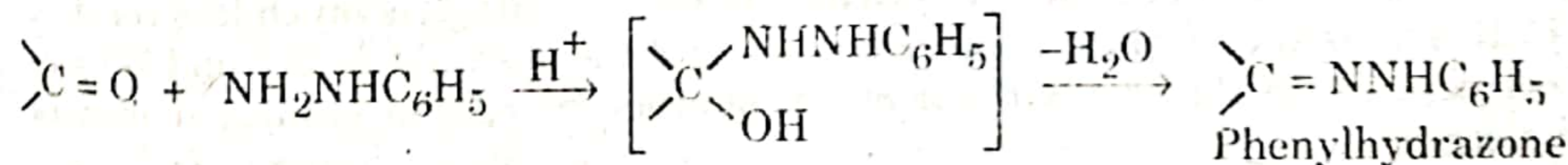
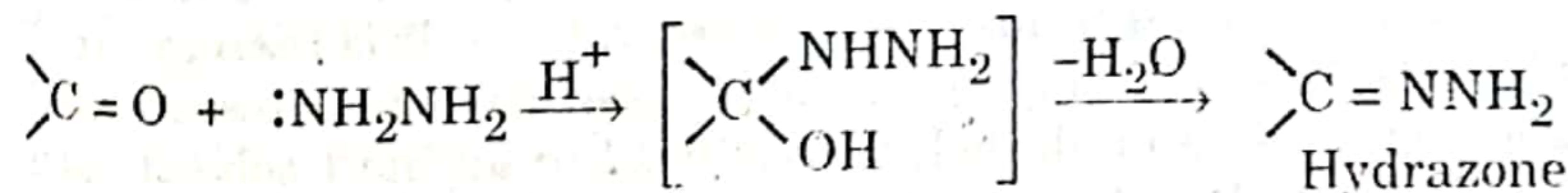
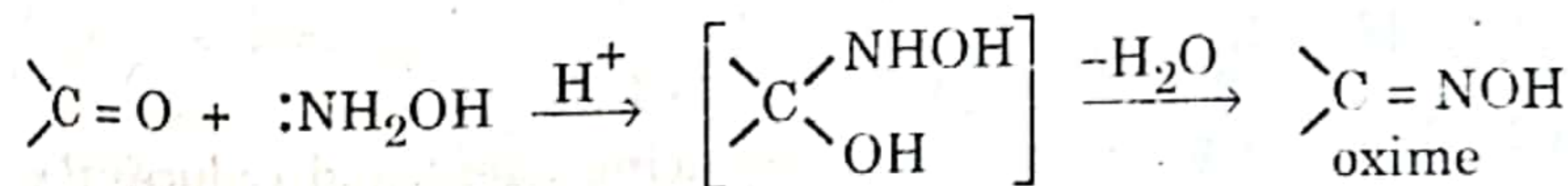
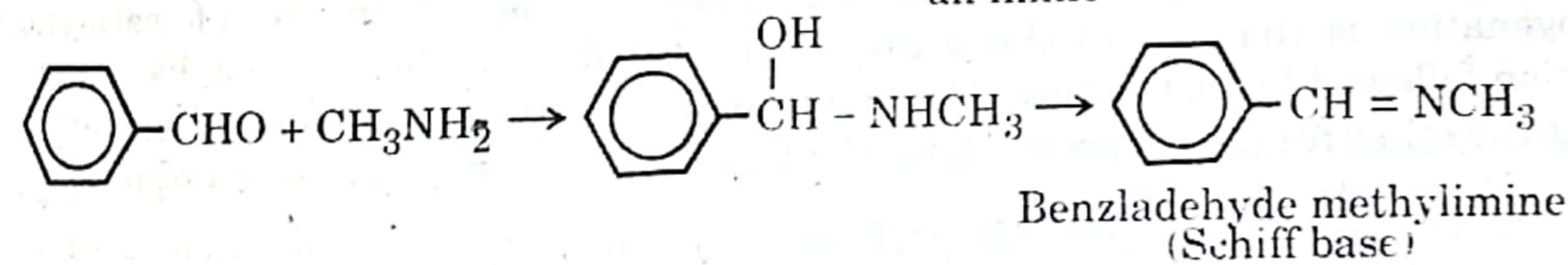
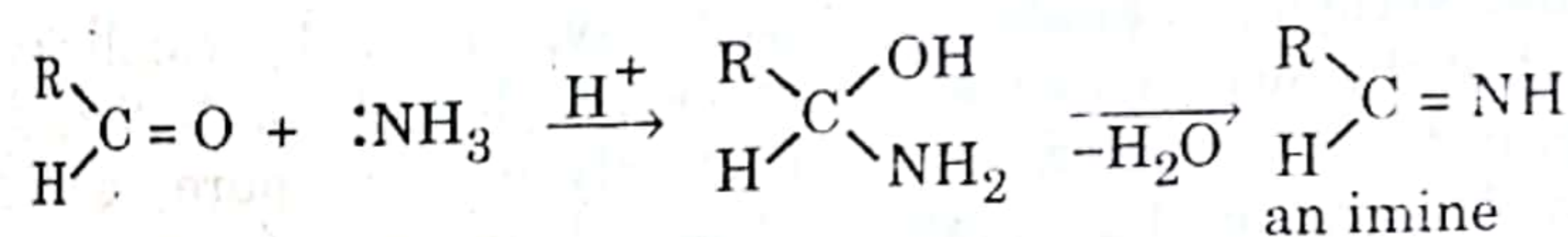
Ketal formation is not favoured when ketones are treated with simple alcohols and gaseous HCl. Cyclic ketal formation is favoured, however, when a ketone is treated with an excess of 1,2-diol in the presence of a trace of acid.



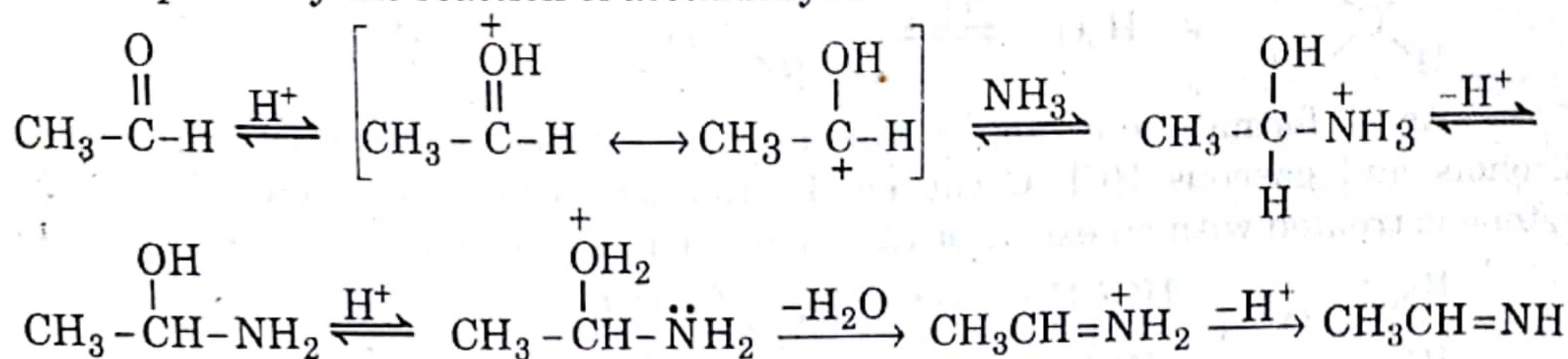
7. Addition of ammonia and its derivatives (Formation of Imines). Ammonia and its derivatives such as primary amine (RNH_2), hydroxylamine (NH_2OH), hydrazine (NH_2NH_2), phenylhydrazine ($\text{C}_6\text{H}_5\text{NHNH}_2$) and semicarbazide ($\text{NH}_2\text{CONHNH}_2$) react with aldehydes and ketones to form the corresponding unstable addition products, which lose a water molecule to form the stable **imine** derivatives, >C=N- , having a carbon-nitrogen double bond. The overall reaction can be thus considered as a condensation reaction of the type:



The reactions of the carbonyl compounds with various ammonia derivatives are shown below:

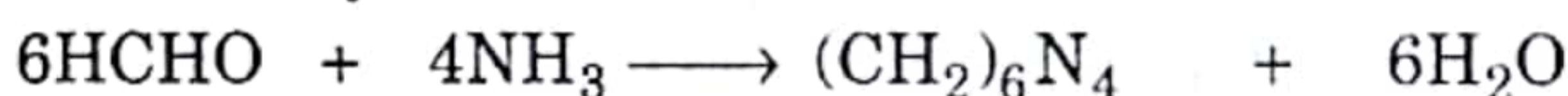


All these reactions are usually catalyzed by acids. Addition involves the nucleophilic attack on the protonated carbonyl group to form the addition product, as exemplified by the reaction of acetaldehyde with ammonia:



The products, oximes, hydrazones, phenylhydrazones and semicarbazones are crystalline compounds and are useful for the characterization and identification of aldehydes and ketones. 2,4-Dinitrophenylhydrazine is a particular useful reagent because it forms insoluble coloured (yellow to red) crystalline hydrazones with the carbonyl compounds. The other important utility of these products, especially oximes and semicarbazones, on heating with dilute acids give back the corresponding compounds. Therefore, these reactions are used for the separation and purification of aldehydes and ketones from other organic compounds.

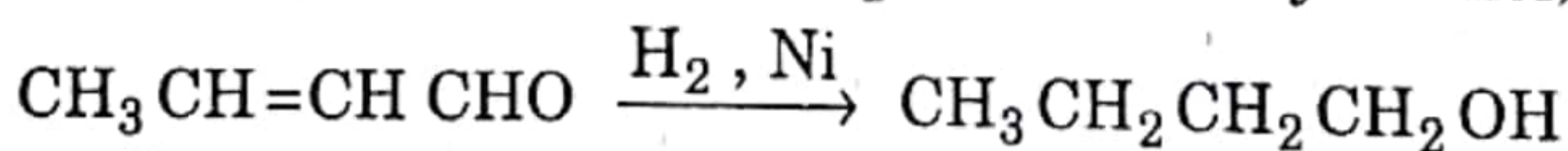
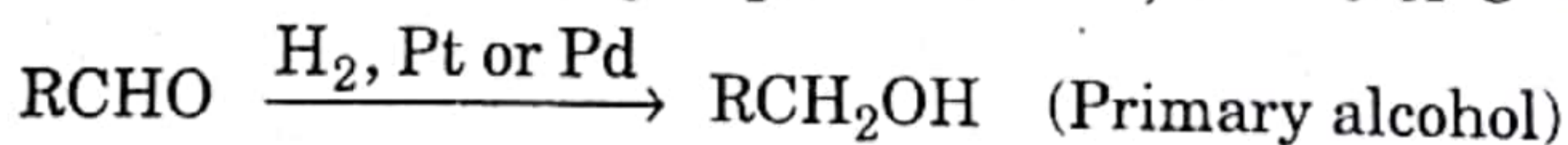
Formaldehyde reacts with ammonia to form hexamethlene tetramine.



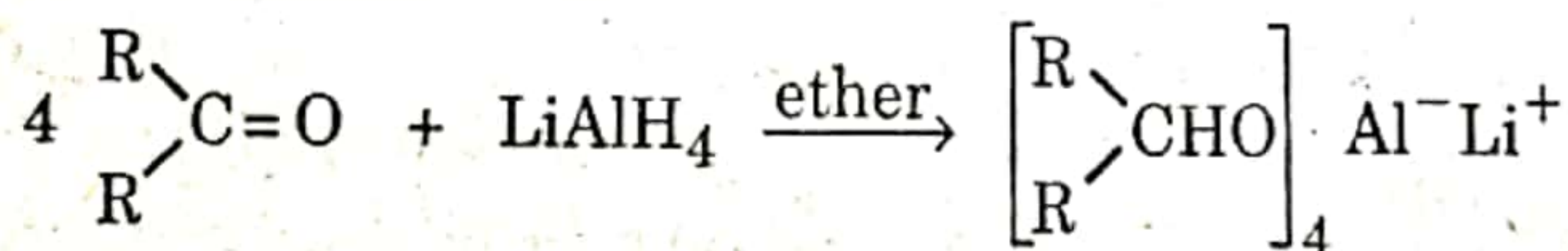
8. Reduction of Aldehydes and ketones

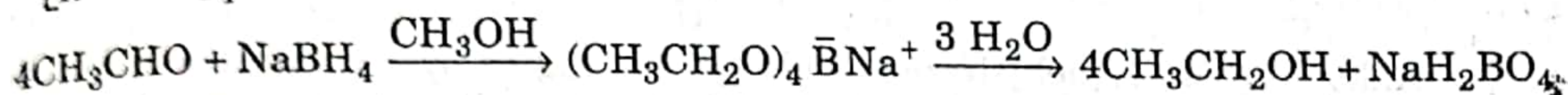
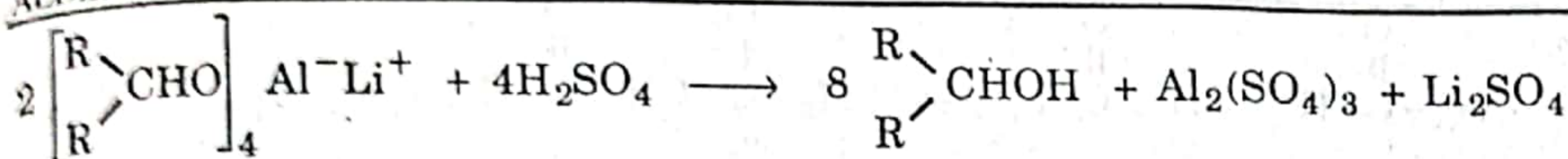
(a) Reduction to Alcohols: Aldehydes and ketones are easily reduced to the corresponding primary and secondary alcohols, respectively, either by catalytic hydrogenation or by the use of chemical reducing agents such as LiAlH_4 or NaBH_4 .

Catalytic hydrogenation is carried out in inert solvent or in pure liquid employing finely divided Ni, Pt or Pd catalyst. The advantage of catalytic hydrogenation is that the products can be separated from the catalyst by simple filtration followed by distillation. The main disadvantage of catalytic hydrogenation is that the other functional groups like ($\text{C}=\text{C}$, $\text{C}\equiv\text{C}$ or $\text{C}\equiv\text{N}$) are also reduced.



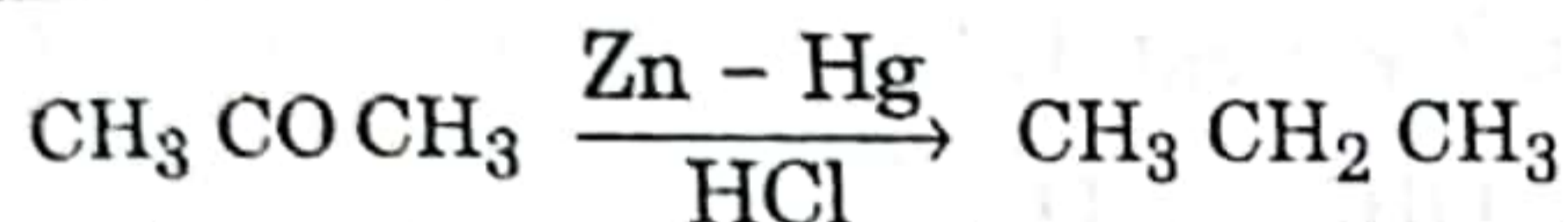
Lithium aluminium hydride is a very powerful reducing agent and reduces the carbonyl groups of aldehydes, ketones, acids and acid derivatives. It is therefore, not selective for aldehydes and ketones only. It is highly sensitive to moisture and hydrolytic solvents such as water and alcohol, so it is used in an inert solvent such as ether. On the other hand, **sodium borohydride**, (NaBH_4), is much less reactive than LiAlH_4 and is therefore more selective, and reduces only aldehydes and ketones to the corresponding alcohols without effecting other functional groups. It may be used in alcohols.



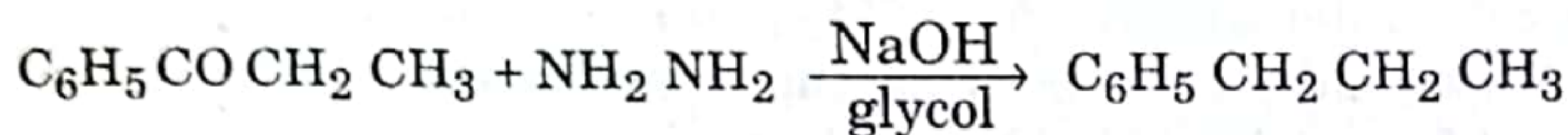


(b) **Reduction to Hydrocarbons.** There are several methods of reducing the carbonyl group, >CO- , of aldehydes and ketones to methylene group, $\text{-CH}_2\text{-}$. The two most important methods are (i) The Clemmensen reduction, and (ii) The Wolff-kishner reduction.

(i) **Clemmensen reduction** involves refluxing the aldehyde or ketone with zinc amalgam and HCl.

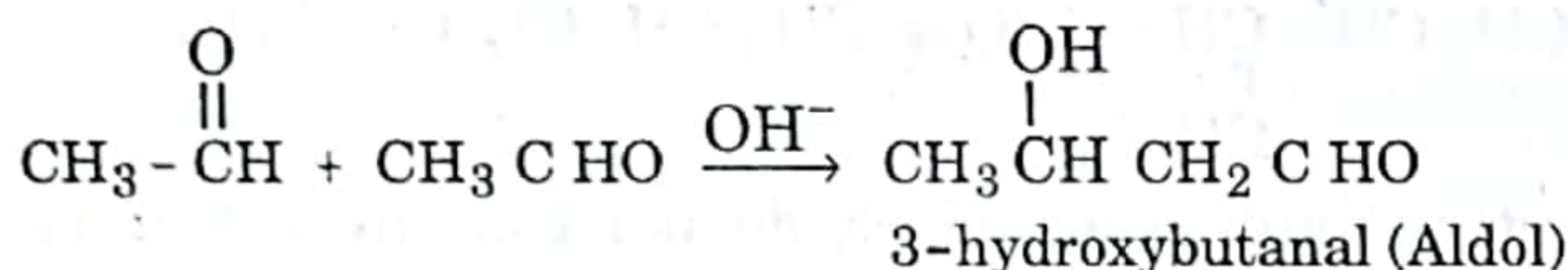


(ii) **Wolff-Kishner reduction** involves heating the aldehyde or ketone with hydrazine and a base (usually NaOH or KOH) in ethylene glycol or N, N-dimethyl formamide.



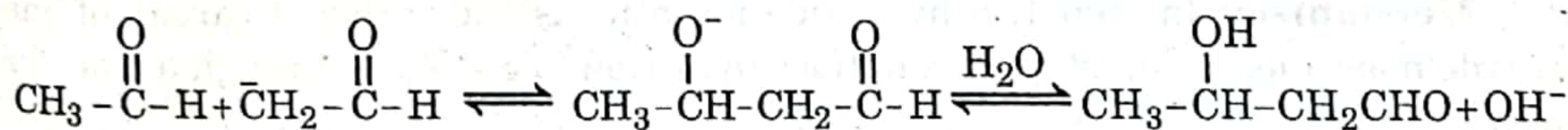
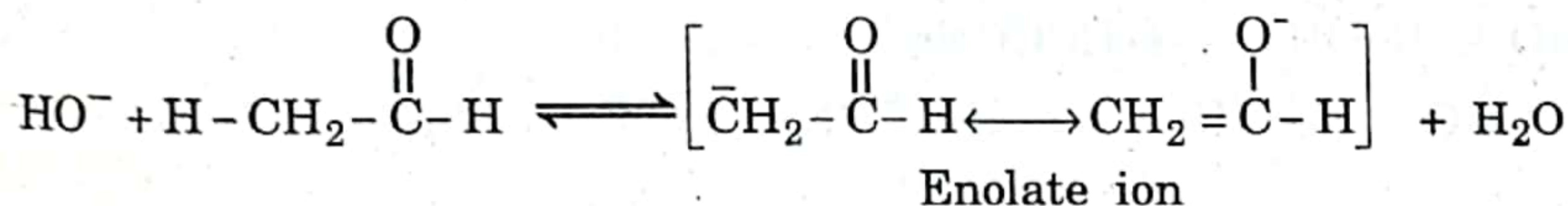
B. Reactions due to α -hydrogen atom

9. Aldol condensation. In the presence of a base or dilute acid two molecules of aldehydes or ketones containing α -hydrogen condense together to form β -hydroxyaldehydes or β -hydroxy ketones, generally known as **aldols**, which is both an aldehyde and alcohol. This reaction is called **aldol condensation**.

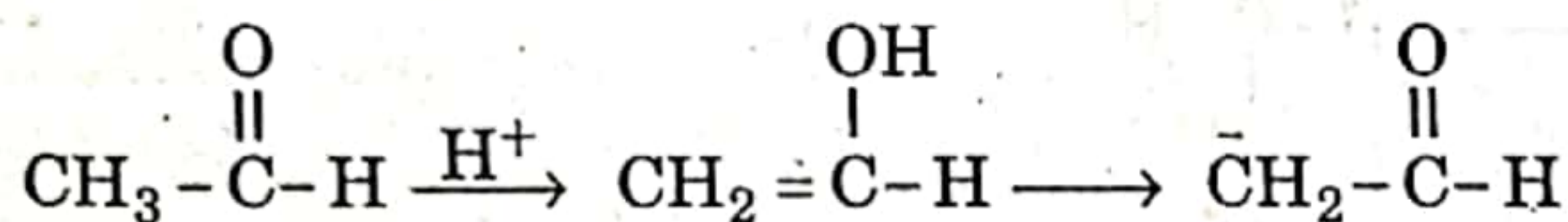


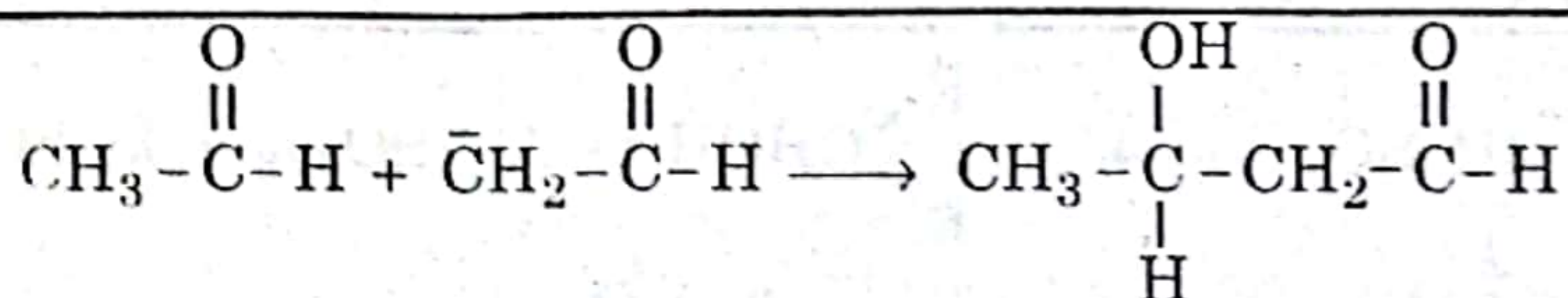
Mechanism:

In the first step hydroxyl ion removes a proton from the α -carbon to form enolate ion. In the second step, the enolate ion attacks the carbonyl carbon of another unionized aldehyde molecule to produce the anion of a β -hydroxy aldehyde which accepts a proton from the solvent water giving a β -hydroxy aldehyde.

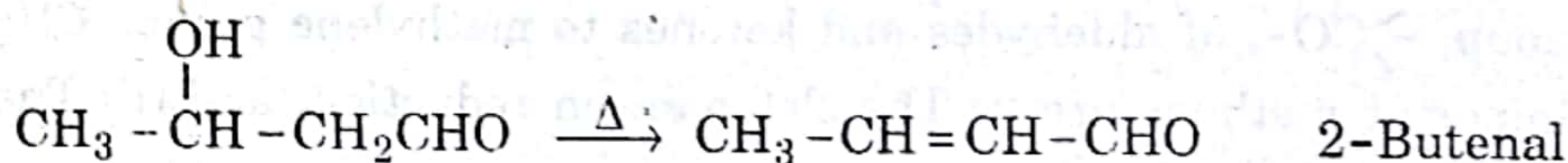


Acid catalyzed aldol condensation of aldehydes proceeds as follow:

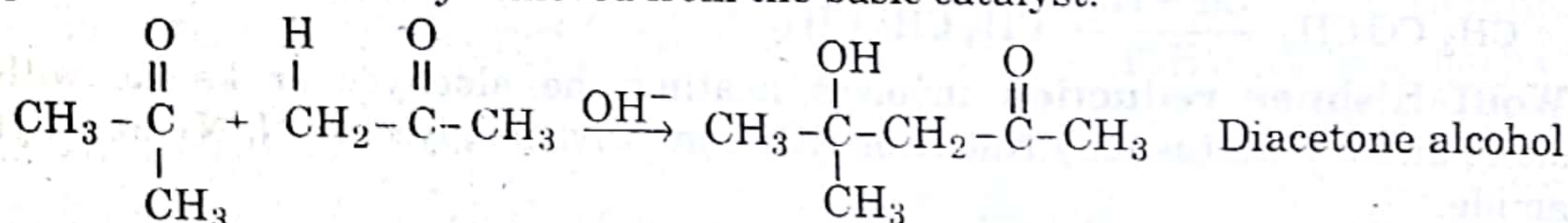




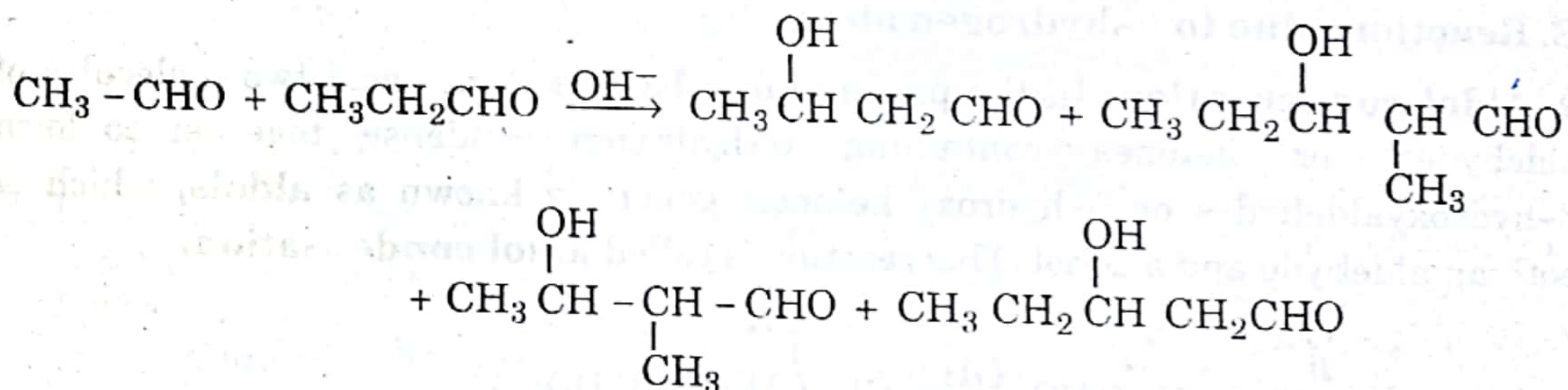
Aldols are easily dehydrated either by heating or by treatment with dilute acid to form α, β -unsaturated aldehyde. For example,



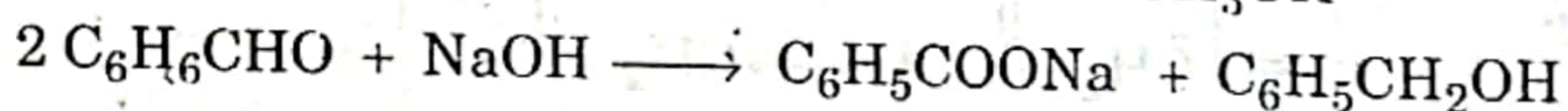
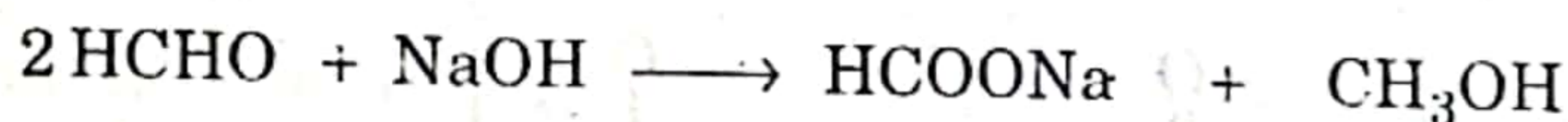
Aldol condensations are reversible, and with ketones the equilibrium is unfavourable for the condensation product. To effect condensation of ketones, the product is continuously removed from the basic catalyst.



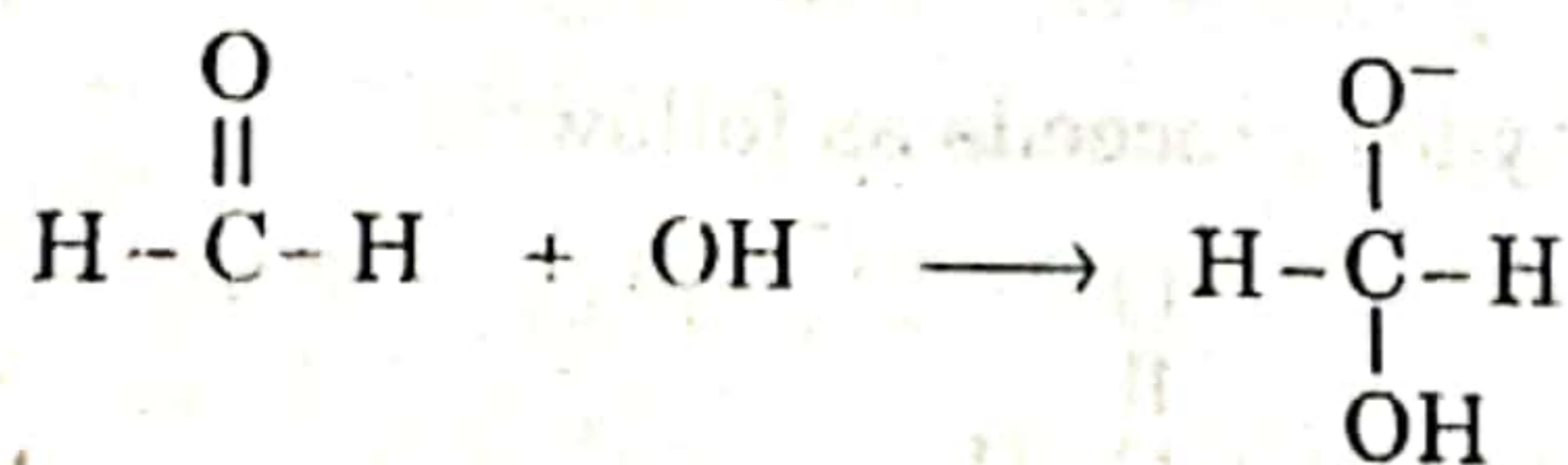
A mixture of two aldehydes, both having α -hydrogens, on treatment with a base gives a mixture of four possible aldol products.

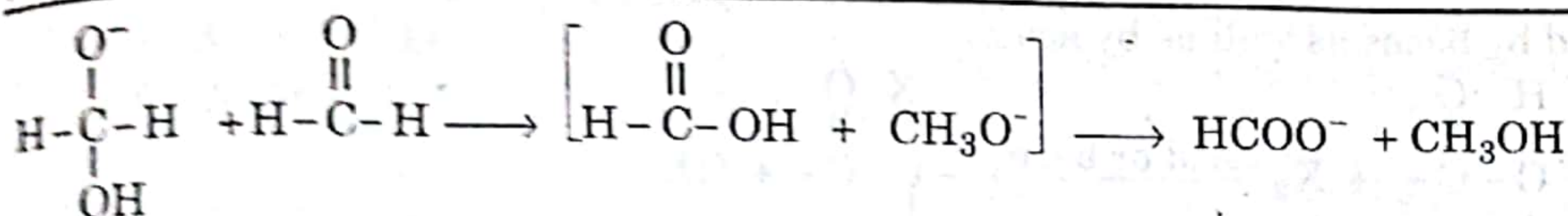


10. Cannizzaro's Reaction. Aldehydes which do not contain α -hydrogen (e.g., methanal and benzaldehyde) do not undergo aldol condensation reaction with alkali. However, when such aldehydes are treated with concentrated alkali, they undergo a disproportionation (self oxidation and reduction) reaction. One half of the total aldehyde is oxidized to the corresponding carboxylic acid and the other half is reduced to the primary alcohol. The reaction is known as Cannizzaro's reaction.

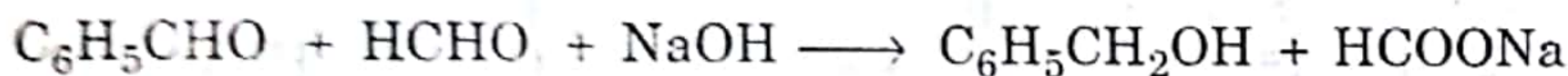


Mechanism: In step 1, a hydroxide ion attacks the carbonyl carbon of one aldehyde molecule, and in step 2, oxidation-reduction takes place through a transfer of a hydride ion.

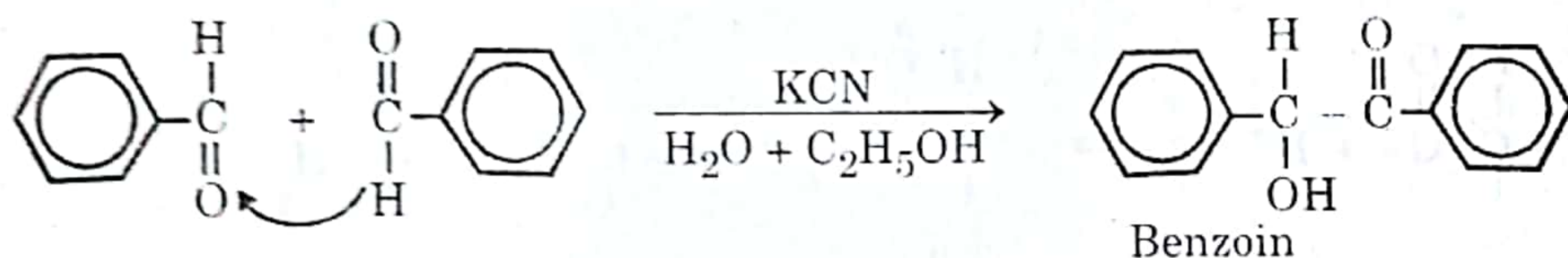




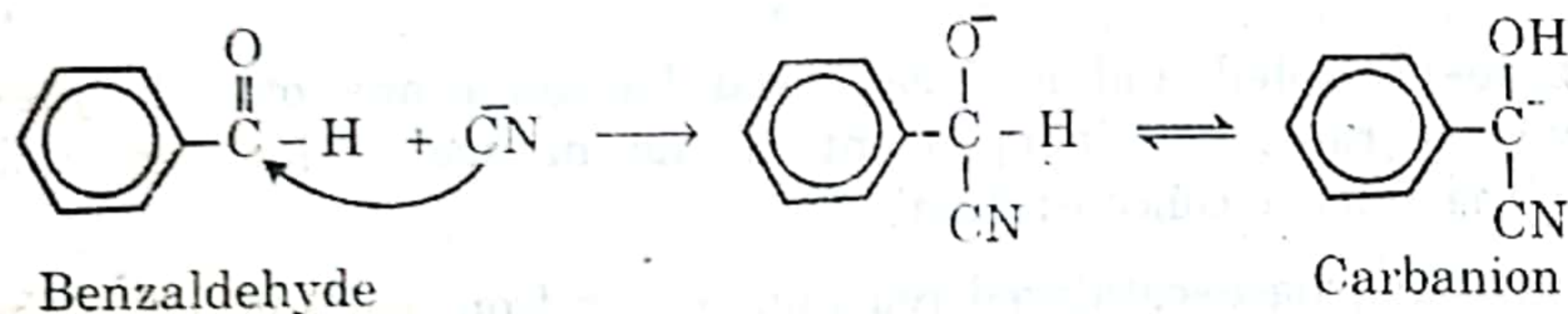
If a mixture of formaldehyde and some other aldehyde without α -carbon, is treated with a strong alkali, formaldehyde will be oxidized into formate ion and the other aldehyde will be reduced to corresponding alcohol. This reaction is known as crossed Cannizzaro's reaction.



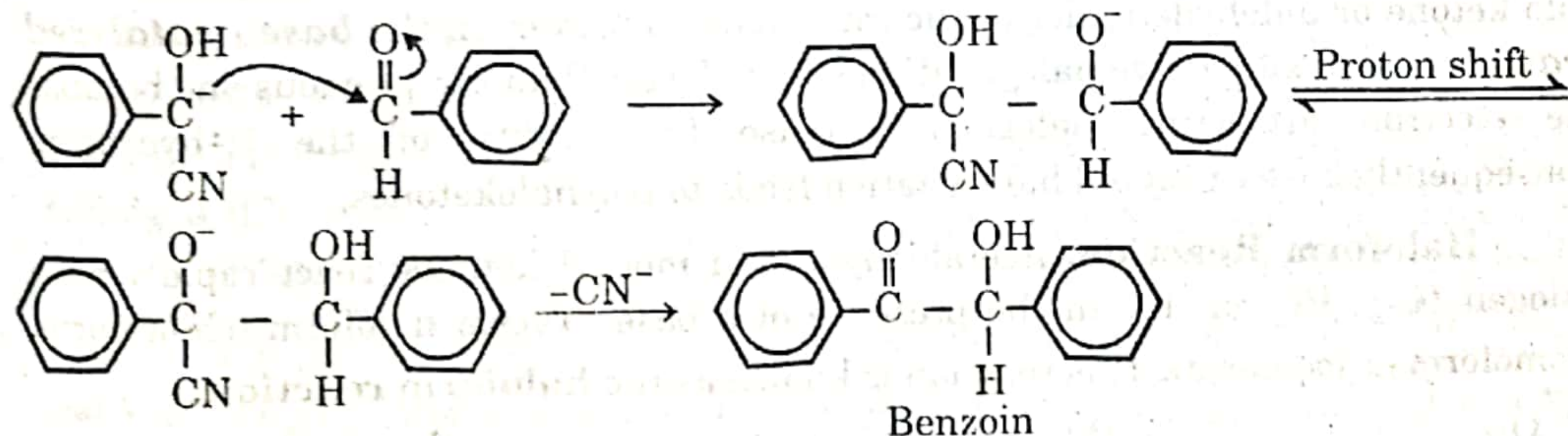
11. Benzoin Condensation. The benzoin condensation involves the treatment of benzaldehyde with certain other aromatic aldehyde in the presence of boiling aqueous alcoholic KCN (or Na CN), that undergo a condensation reaction to form α -hydroxyketones, generally known as **benzoin**, and the reaction is called **benzoin condensation**. For example, benzaldehyde reacts with alcoholic KCN to form benzoin. Notice that two molecules of benzaldehyde take part in the reaction.



Mechanism. The cyanide ion attacks the carbonyl group and enables the formation of carbanion.

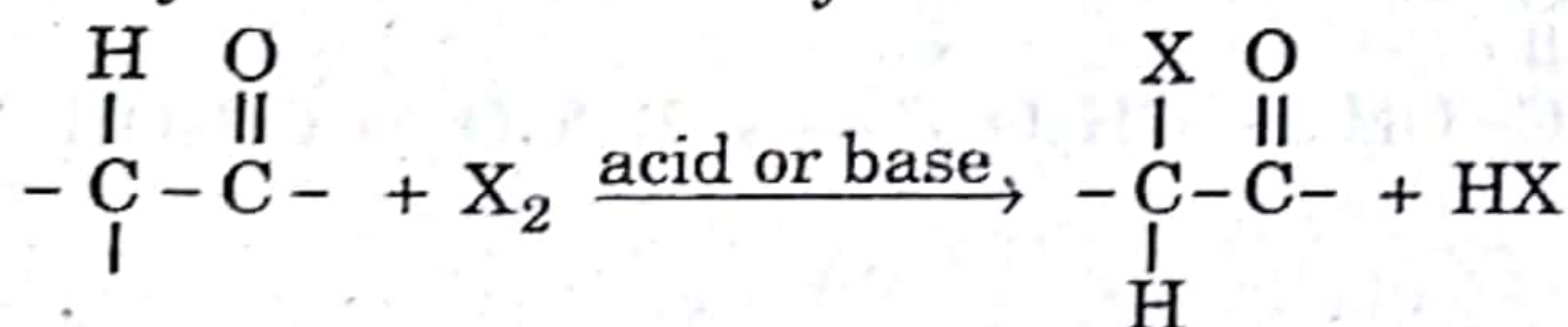


The carbanion can then react with another benzaldehyde molecule. Subsequent proton-transfer and loss of the cyanide ion gives benzoin.

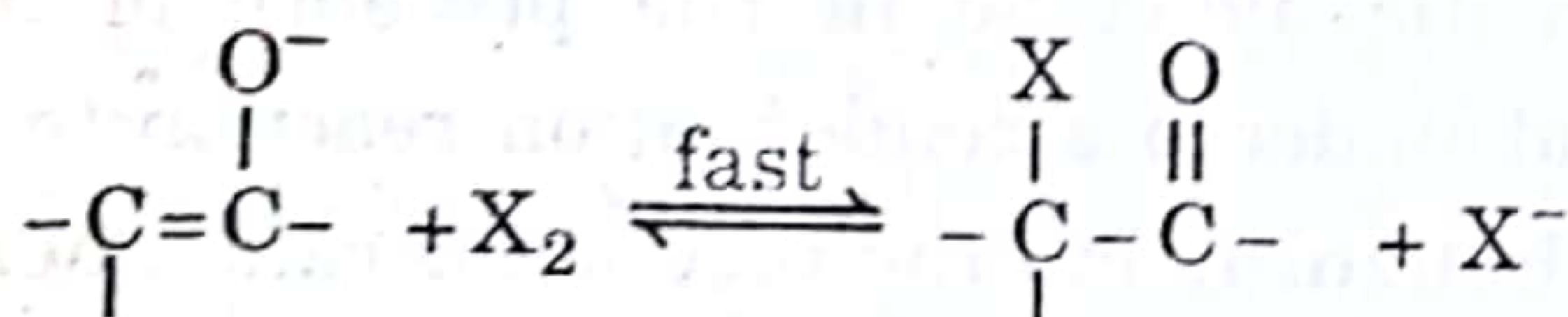
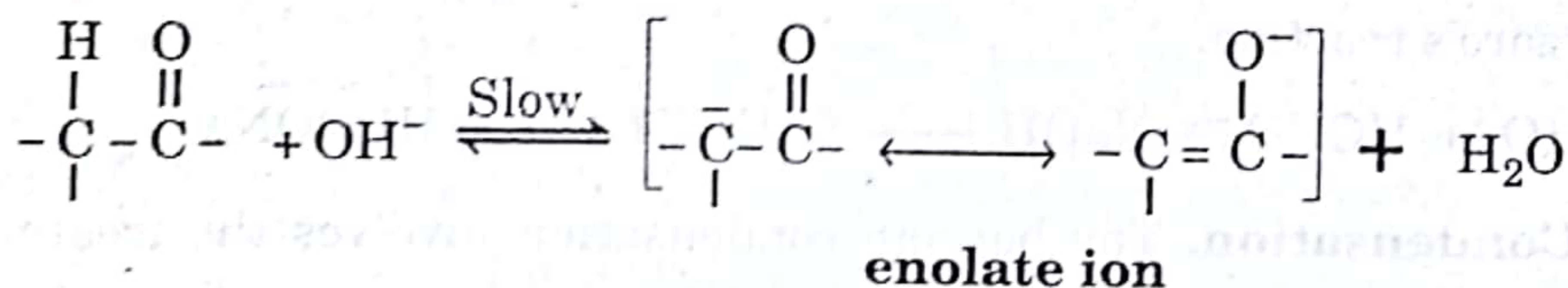


12. Halogenation. Aldehydes and ketones that have an α -hydrogen react rapidly with halogens (Cl_2 , Br_2 , or I_2) by substitution at the α -carbon. The halogenation is

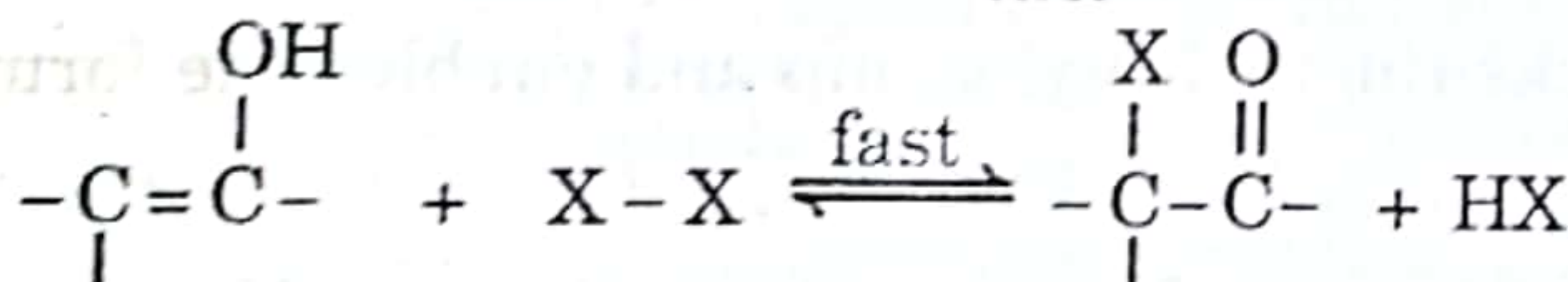
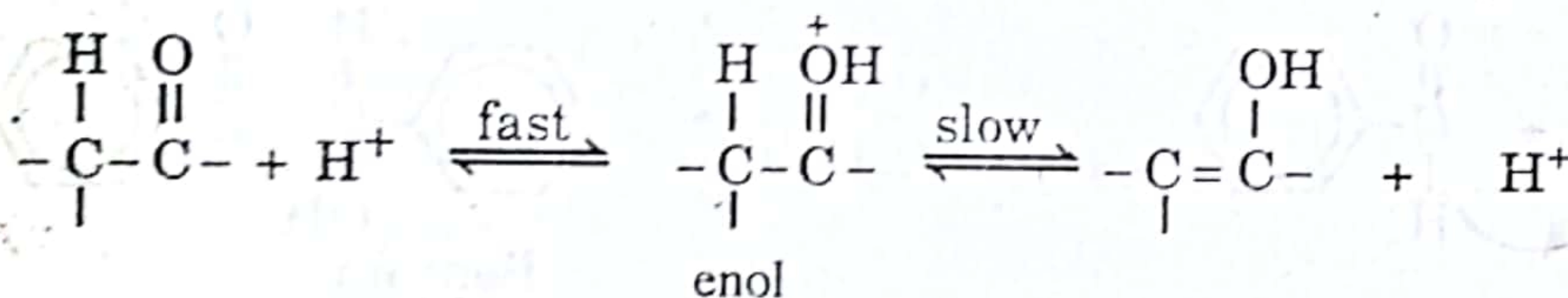
catalyzed by bases as well as by acids.



Mechanism. In the presence of bases, halogenation takes place through the slow formation of enolate ion, followed by the rapid reaction of the enolate ion with halogen.



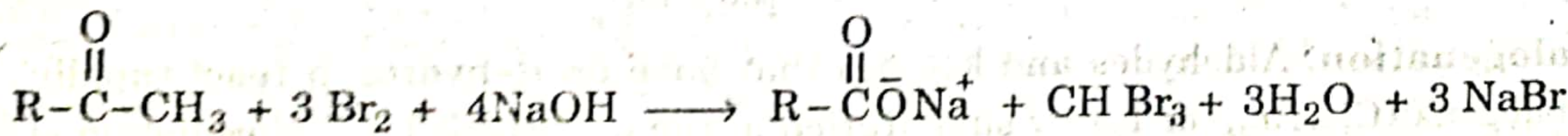
In the presence of acids, halogenation takes place through slow formation of an enol followed by the rapid reaction of the enol with the halogen.



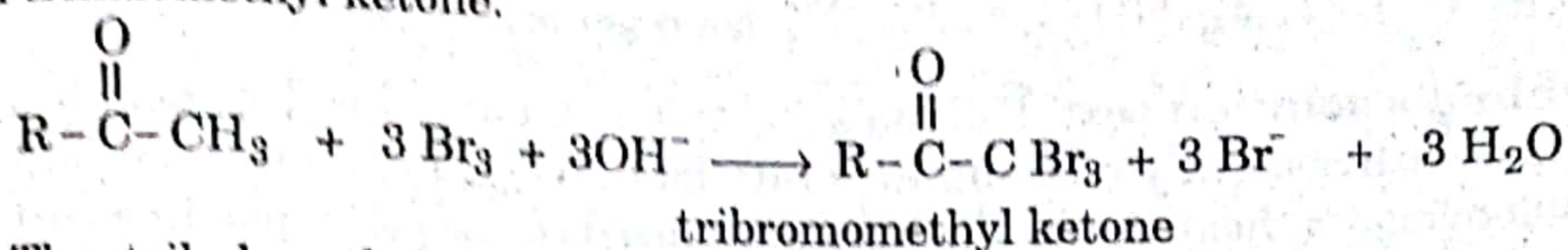
Both base-promoted and acid-catalyzed halogenations of aldehydes and ketones show that rates are independent of the nature of halogen and also independent of the halogen concentration.

The acid - and base-catalyzed reactions differ from each other in the fact that in the acid-catalyzed halogenation, each successive halogenation step is normally slower than the previous one. It is therefore possible to prepare mono-halo ketone or aldehyde under acidic conditions. However, in the **base-catalyzed reaction**, each successive halogenation step is faster than the previous one because the electron attracting halogens increase the acidity of the α -hydrogen. Consequently base catalyzed halogenation leads to polyhaloketones,

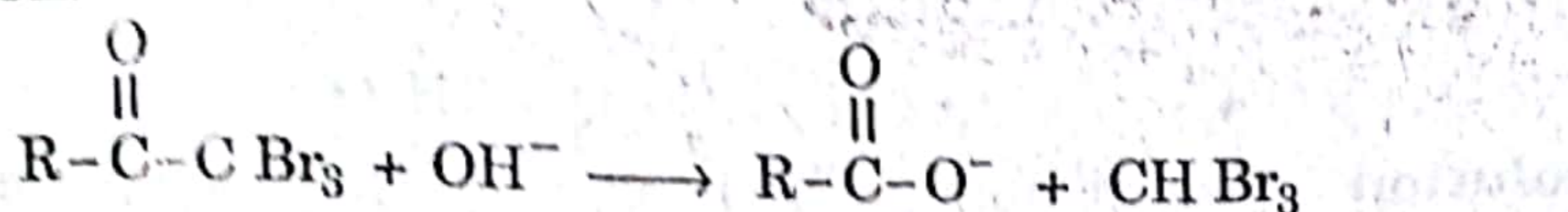
Haloform Reaction. Acetaldehyde and methyl ketones react rapidly with halogen (Cl_2 , Br_2 or I_2) in the presence of a base to form haloform (chloroform, bromoform or iodoform). This reaction is known as the **haloform reaction**.



A methyl ketone undergoes base catalyzed halogenation at the methyl carbon to form trihalomethyl ketone.

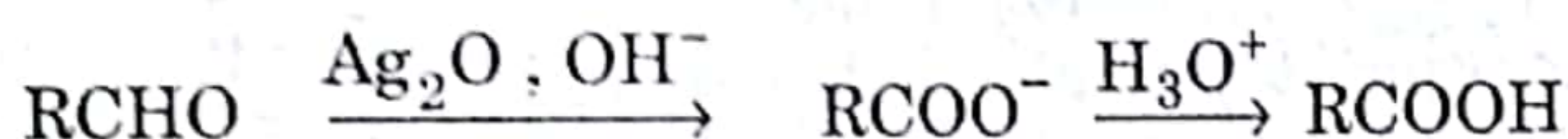
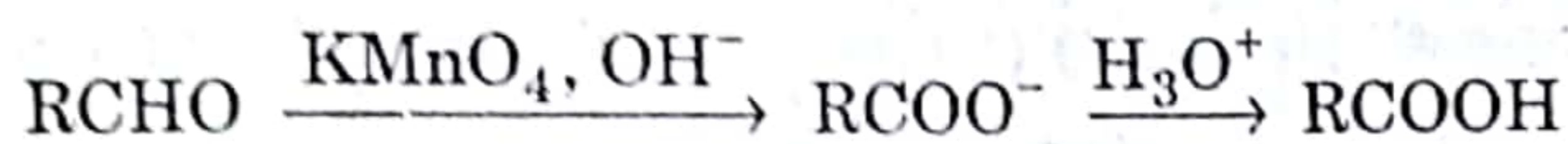


The trihalomethyl ketone reacts further with the hydroxide ion to form carboxylate ion and trihalomethane. The overall reaction is known as **haloform reaction**.

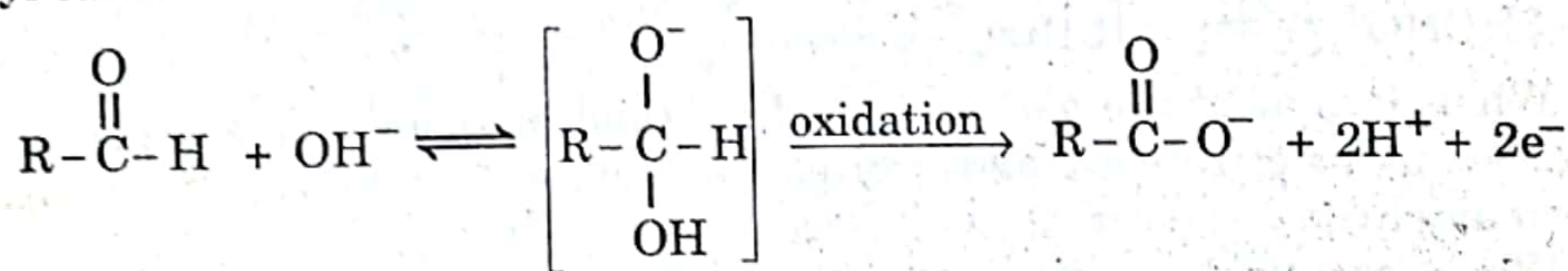


The haloform reaction is used as a characteristic test for the presence of acyl group, $-\text{COCH}_3$. Since the haloform reaction with iodine and NaOH gives a bright yellow precipitate of iodoform. This test is known as **iodoform test**.

13. Oxidation (Distinction between aldehydes and ketones). Ketones are difficult to oxidize, while aldehydes are easily oxidized to carboxylic acids containing the same number of carbon atoms as in parent aldehyde by strong oxidizing agents such as potassium permanganate, and they are also oxidized by mild oxidizing agents such as moist silver oxide.

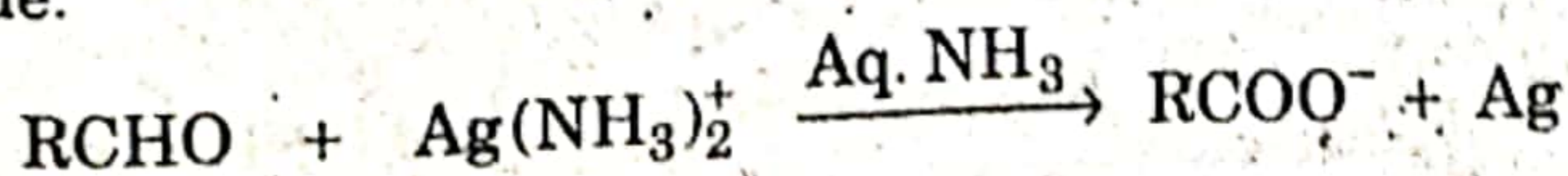


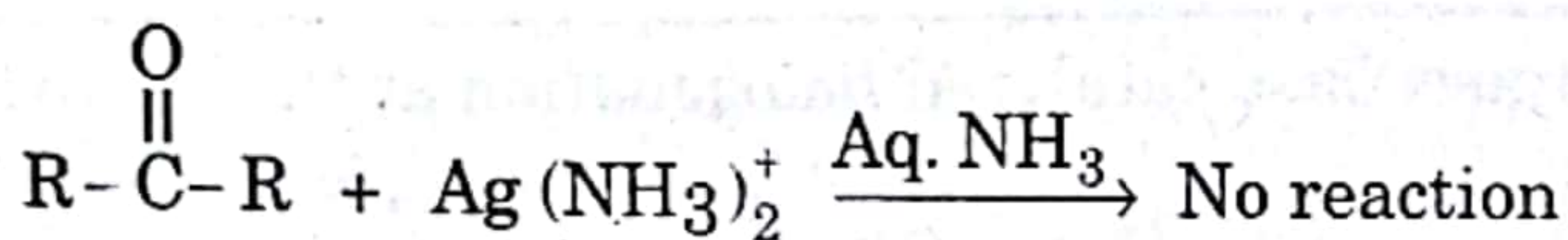
Oxidation of aldehydes occurs particularly readily in an alkaline solution and the reaction is initiated by the nucleophile attack of the hydroxide ion on the carbonyl carbon.



The ease of alkaline oxidation of aldehydes provides useful tests that differentiate aldehydes from ketones. These tests are:

(i) **Tollen's reagent test (Silver mirror test):** Tollen's reagent is ammoniacal silver nitrate which contains the silver diammine ion, $\text{Ag}(\text{NH}_3)_2^+$, and is prepared by adding a dilute solution of ammonia to a 5% solution of silver nitrate until the initially formed precipitate of silver hydroxide dissolves. When Tollen's reagent is added to an aldehyde and heated, the aldehyde is oxidized to acid, and the silver ion present in the Tollen's reagent is reduced to metallic silver which deposits on the walls of the test tube as silver mirror. This test indicates the presence of an aldehyde.



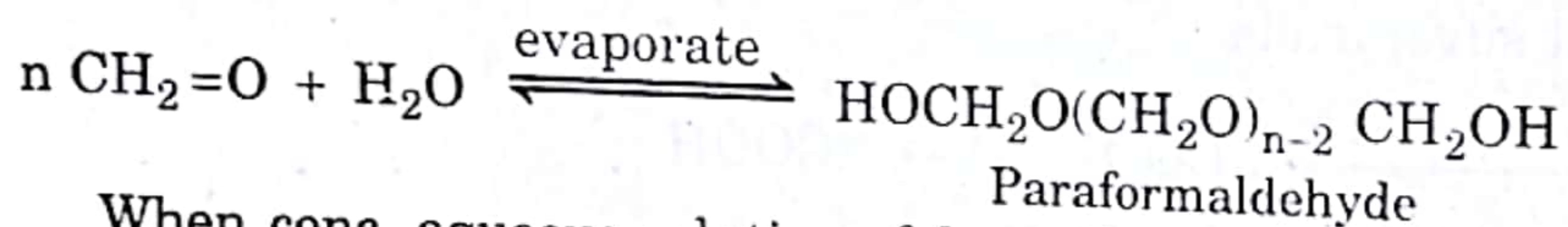


(ii) **Fehling's solution test.** Fehling's solution is an alkaline solution of cupric ion complexed with sodium potassium tartarate ions. When Fehling's solution is added to an aldehyde and heated, the aldehyde is oxidized to the corresponding carboxylate ion, the cupric ions present in the Fehling's solution is reduced to cuprous ions giving red-brick precipitates of Cu_2O , which indicates the presence of an aldehyde. Ketones do not give this test.

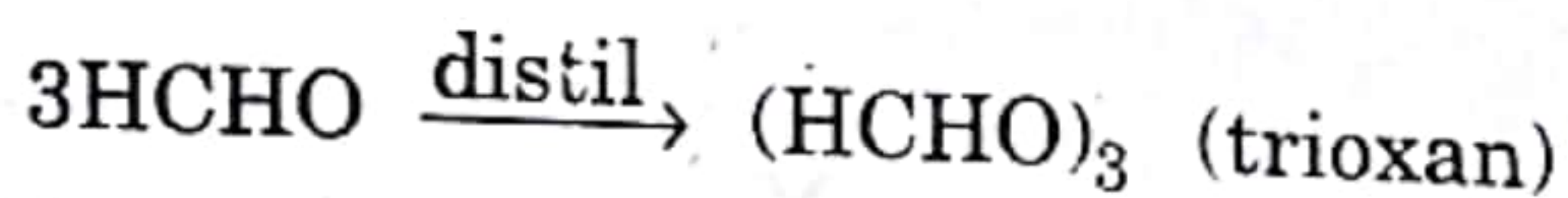
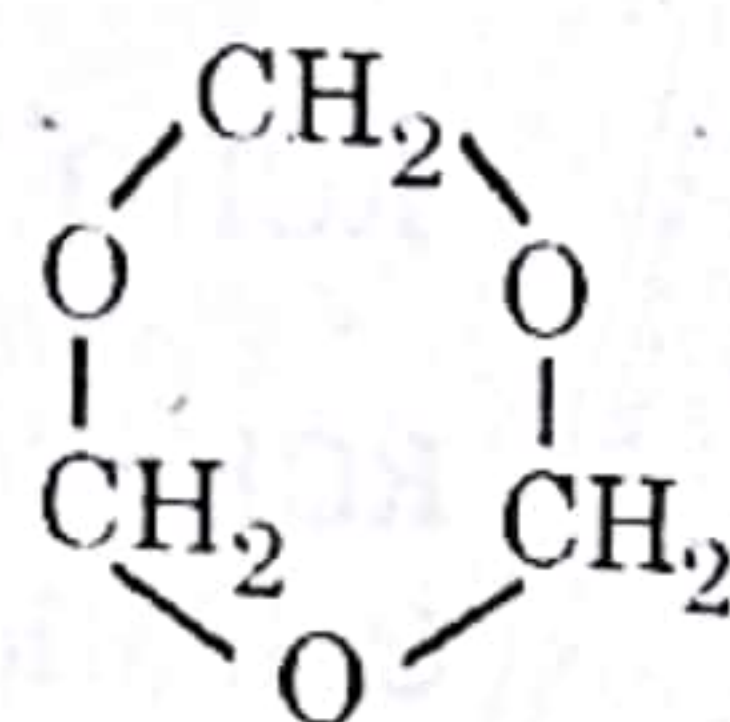


(iii) **Benedict's solution** is an alkaline solution of cupric ion complexed with citrate ion. It reacts in the same way as Fehling's solution.

14. Polymerization. Aldehydes undergo an addition polymerization, whereas ketones are not much susceptible to polymerization. Both linear and cyclic polymers are formed. When 40 percent solution of formaldehyde (*Formalin*) is evaporated to dryness, **paraformaldehyde** is formed. Paraformaldehyde reverts to formaldehyde on heating strongly. It is therefore a good source of gaseous formaldehyde for use in synthesis

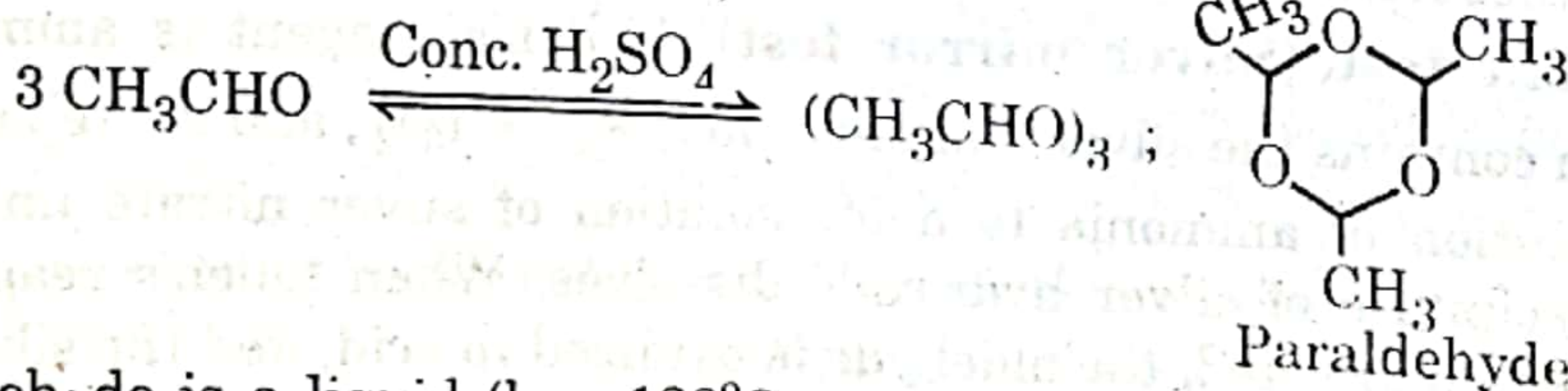


When conc. aqueous solution of formaldehyde containing 2% H_2SO_4 is distilled, a solid cyclic trimer of formaldehyde known as **trioxan** or **metaformaldehyde**, (m.p. 62°C), is obtained.



When formaldehyde gas is allowed to stand at room temperature, it slowly undergoes polymerization and forms a white solid called trioxan or metaformaldehyde.

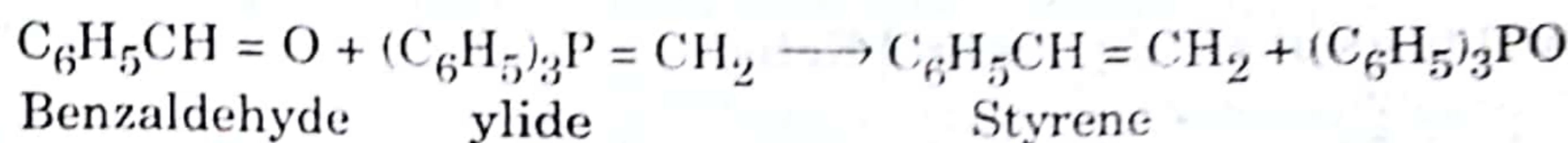
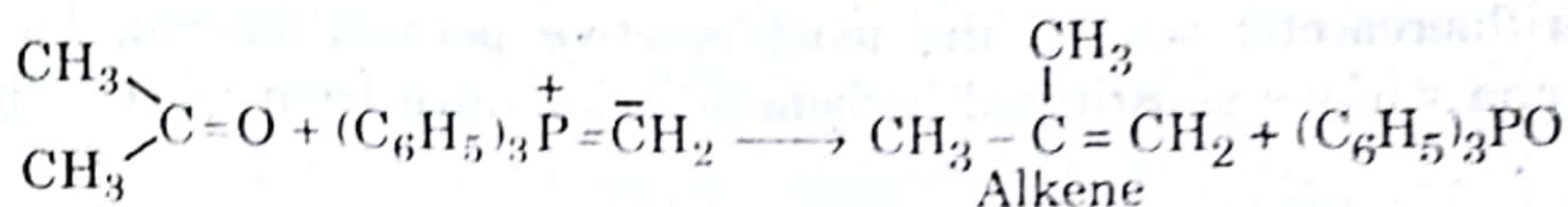
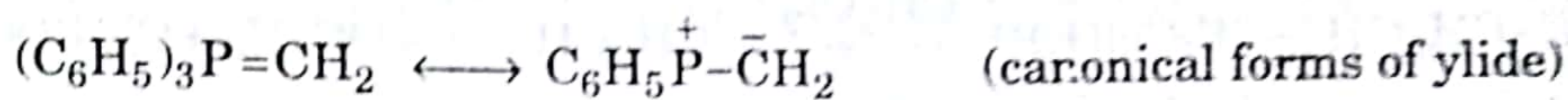
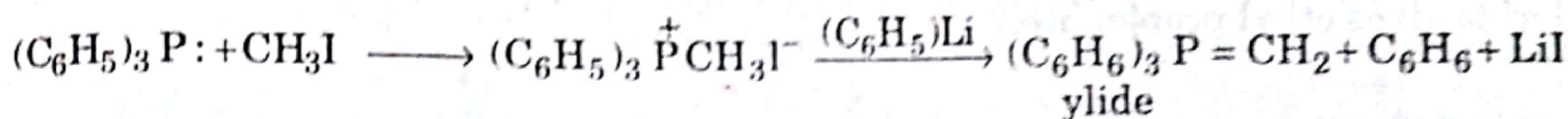
When acetaldehyde is treated with a small amount of H_2SO_4 at room temperature, a cyclic trimer known as **paraldehyde** is formed.



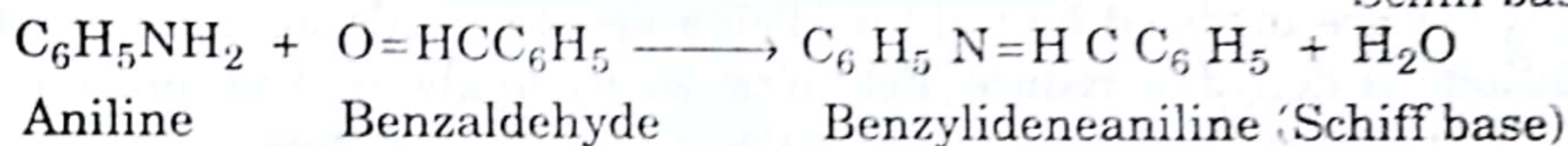
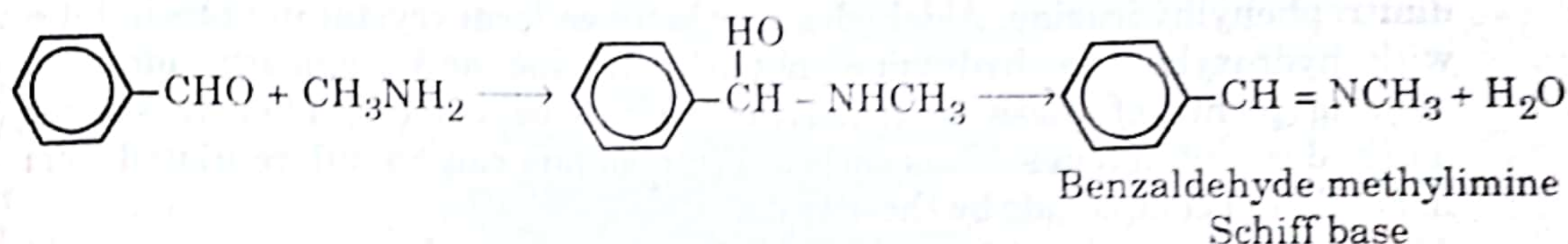
Paraldehyde is a liquid (b.p. 128°C) which on distillation in the presence of small amount of H_2SO_4 , yields acetaldehyde. Acetaldehyde also forms a solid 8-membered cyclic tetramer, metaldehyde (m.p. 246°C) that sublimes readily.

15. Wittig Reaction. Aldehydes and ketones react with phosphorus ylides,

prepared from primary alkyl halides and triphenylphosphine, to yield alkenes and triphenyl phosphine oxide. The reaction is known as **Wittig reaction**.

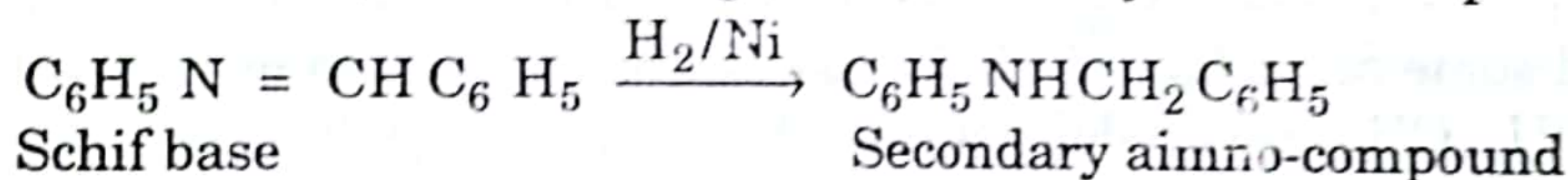


16. Schiff's Base. Aromatic aldehydes react with amines to give addition product, which is unstable, loses water molecule, to yield imine called **Schiff base**.



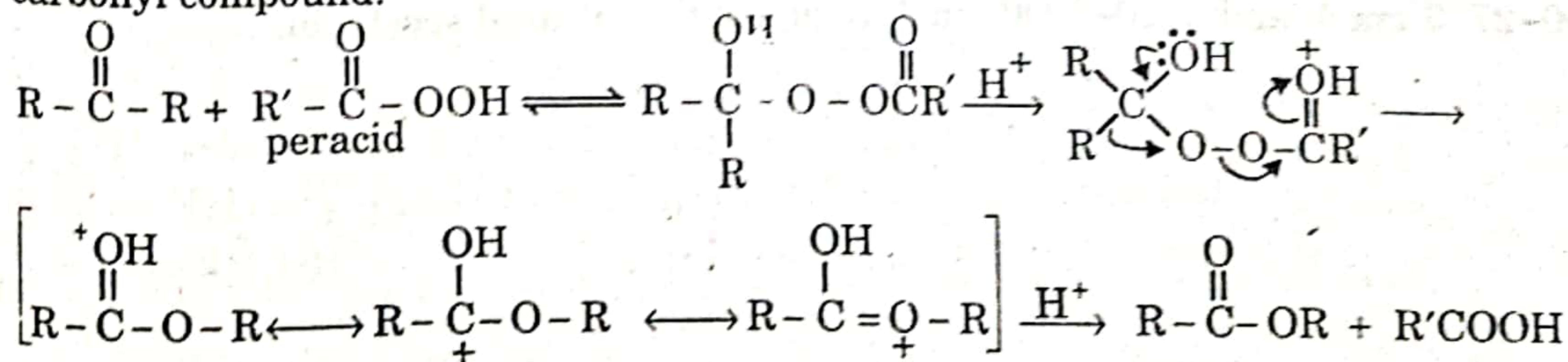
The schiff bases on hydrolysis easily give free amine. Their formation offers an easy method of protecting an amino - group before nitration.

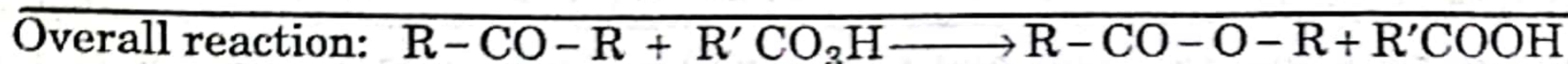
On reduction, a schiff base gives a secondary amino-compound.



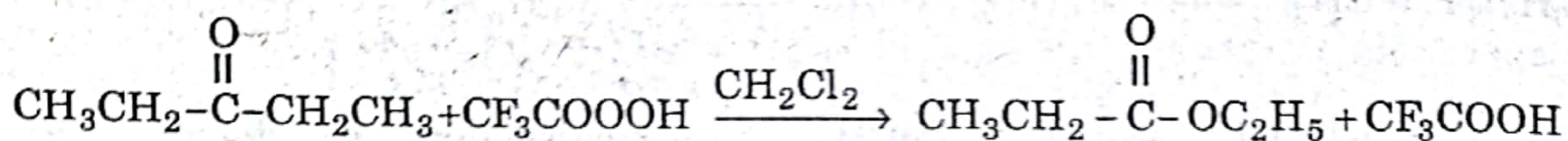
Schiff's Test. Dilute solutions of aldehydes when added to Schiff's reagent (rosaniline hydrochloride dissolved in water and its red colour decolourised by passing sulphur dioxide) restores its red colour. This is known as **Schiff's test** for aldehydes. Ketones do not give this test.

17. Baeyer-Villiger Oxidation. In the Baeyer Villiger oxidation, a ketone is oxidized by a per acid ($\text{R}'\text{CO}_3\text{H}$) to an ester. The key step in the mechanism is heterolytic dissociation of the O-O bond in an adduct from the peracid and a carbonyl compound.





Diethyl ketone when oxidized with trifluoroperacetic acid in methylene chloride gives ethyl propionate.



Peroxytrifluoroacetic acid is the most reactive peracid known, but both peracetic acid and various substituted perbenzoic acids have been used with good results.

10.6 Chemical tests of aldehydes and Ketones

A number of tests can be used to identify aldehydes and ketones. These tests are based on the chemical properties of aldehydes and ketones.

1. All aldehydes and ketones form coloured crystalline precipitates with 2,4-dinitrophenylhydrazine. Aldehydes and ketones form crystalline precipitates with hydroxylamine, hydrazine, phenylhydrazine and semicarbazide. The melting points of these solid derivatives can be used to identify specific aldehydes and ketones. Thus carbonyl compounds can be differentiated from noncarbonyl compounds by these tests.
2. Aldehydes are oxidized by mild oxidizing agents, while ketones resist mild oxidation. Aldehydes reduce Fehling's solution giving red precipitate of Cu_2O and form silver mirror with Tollen's reagent. Ketones generally do not give these tests, and therefore aldehydes can be differentiated from ketones.
3. Methyl ketones (and acetaldehyde) are readily oxidized by $\text{NaOI}(\text{NaOH} + \text{I}_2)$ to iodoform, CHI_3 and are thus easily detected by the iodoform test. Ethyl alcohol and some secondary alcohols that can be oxidized to methyl ketones, e.g., $-\text{CHOH}-\text{CH}_3$, give iodoform test.
4. Formaldehyde and other aldehydes can be differentiated by their reaction with NaOH . Formaldehyde gives Cannizzaro reaction and other aldehydes give aldol condensation reaction.

10.7 Spectroscopic Identification. The UV absorption spectrum of ketones show λ_{max} at 190 nm comes from the $\pi \rightarrow \pi^*$ transition. The infrared spectrum of carbonyl groups of aldehydes and ketones show strong $\text{>C}=\text{O}$ stretching bands at 1700-1750 cm^{-1} . The $-\text{CHO}$ group of aldehydes also shows two weak bands in the 2700-2775 cm^{-1} and 2820-2900 cm^{-1} region of the infrared spectrum.

Questions

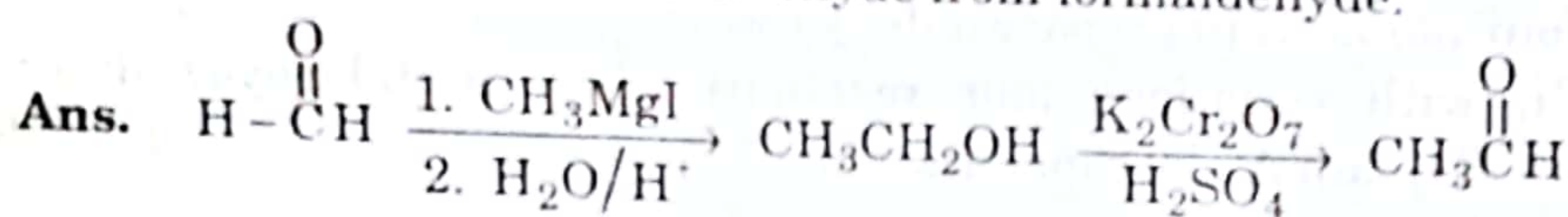
1. How will you synthesize ethyl phenyl ketone from each of the following substances: (i) Benzene (ii) Benzoyl chloride (iii) Benzaldehyde (iv) Benzoic acid (v) Benzotrile P.U. 2003
2. Write equations with conditions for the following conversions:
 - (i) Acetylene into Acetaldehyde
 - (ii) Acetyl chloride into Acetaldehyde
 - (iii) Toluene into Benzaldehyde
 - (iv) Acetone into propane P.U. 2003
3. What happens when:
 - (i) Formaldehyde is distilled with H_2SO_4
 - (ii) Acetophenone is heated with Br_2 in the presence of CH_3COOH .
 - (iii) Benzaldehyde is treated with $NaCN$:
 - (iv) Formaldehyde is treated with concentrated $NaOH$ solution. P.U. 2002
- 4.(a) Give four methods to prepare aldehydes.
 (b) Explain with equations four reactions where acetaldehyde differs from acetone. Explain Aldol condensation. P.U. 1985,92
5. How would you prepare:
 - (a) Aldehydes from acid chloride,
 - (b) Aldehydes from Grignard reagent.
 - (c) Ketones from organocadmium compounds. P.U.1988
6. Describe the following reactions:
 - (i) Aldol condensation
 - (ii) Cannizzaro's reaction
 - (iii) Haloform reaction
 - (iv) Addition of $C_6H_5NHNH_2$ to acetaldehyde
 - (v) Reformatsky reaction
 - (vi) Rosenmund reduction P.U.1984, 85, 94, 95,2001
7. Give three methods of preparation common for aldehydes and ketones and one method each for specific preparation of aldehydes and ketones. P.U.1982
8. How will you distinguish between acetaldehyde and acetone.
9. How will you distinguish between the following pairs of compounds.
 - (i) 2 - pentanone and 3 - pentanone
 - (ii) Formaldehyde and acetaldehyde
 - (iii) Butanal and 2 - butanone
10. What is the structure of carbonyl group? How does it react with :
 - (i) HCN ;
 - (ii) $NaHSO_3$;
 - (iii) NH_2OH
11. How are ketones prepared? Describe their important reactions.
12. How is acetaldehyde prepared in the laboratory?
 How does it reacts with the following reagents.
 - (i) $NaHSO_3$
 - (ii) HCN
 - (iii) $CH_3Mg Br$
 - (iv) NH_2OH
 - (v) Dilute $NaOH$
 - (vi) $Br_2/NaOH$

SHORT QUESTIONS

1. By rapid test tube reactions distinguish between
 (a) pentanal and 3-pentanone (b) diethyl ketone and methyl *n*-propyl ketone
 (c) Pentanal and 2,2-dimethyl propanal (d) 2-pentanol and 2-pentanone

Ans: (a) Pentanal, an aldehydes, gives a positive Tollen's test (Ag mirror), while 3-pentanone will not give this test.
 (b) Only methyl *n*-propylketone gives CHI_3 (yellow precipitate) on treatment with NaOH (iodoform test).
 (c) Unlike pentanal, 2,2-dimethyl propanal has no α -H and so does not undergo an aldol condensation. Pentanal in base gives a coloured solution.
 (d) Only the ketone, 2-pentanone gives a solid oxime with NH_2OH . Additionally, 2-pentanol is oxidized by CrO_3 (colour change is from orange-red to green). Both give a positive iodoform test.

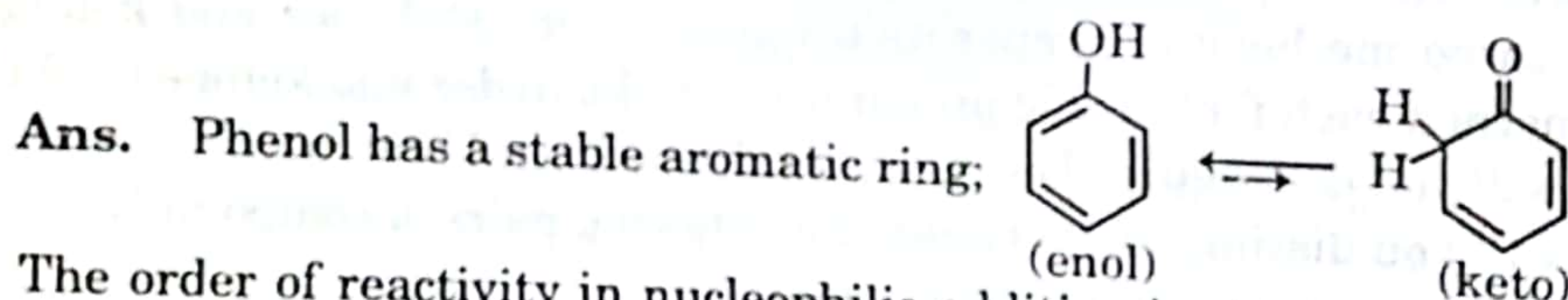
2. How will you synthesize acetaldehyde from formaldehyde.



3. What are similarities and differences between C=O and C=C bonds?

Ans. Both undergo addition reactions. They differ in that the C of C=O is more electrophilic than a C of C=C, because O is more electronegative than C. Consequently, the C of C=O reacts with nucleophiles. The C=C is nucleophilic and adds mainly electrophiles.

4. $\text{C}_6\text{H}_5\text{OH}$, an enol, is much more stable than its keto isomer, cyclohexa-2,4-diene-1-one. Why?



5. The order of reactivity in nucleophilic addition is: $\text{HCHO} > \text{RCHO} > \text{R}_2\text{C}=\text{O}$. Account for this order in terms of steric and electronic factors.

Ans. A change from a trigonal sp^2 to a tetrahedral sp^3C in the transition state is accompanied by crowding of the 4 group on C. Crowding and destabilization of transition state increase in the order: $\text{CH}_2\text{O} > \text{RCHO} > \text{R}_2\text{C}=\text{O}$.

Also, the electron releasing R's intensify the negative charge developing on O, which destabilizes the transition state and decreases reactivity.

6. Explain why only RCHO, methyl ketones (RCOCH_3) and cyclic ketones react with NaHSO_3 ?

Ans. SO_3^{2-} is a large ion and reacts only if C=O is not sterically hindered, as in the

case of RCHO , RCOCH_3 and cyclic ketones. Thus higher ketones do not form bisulphite addition products in appreciable amounts due to steric hindrance.

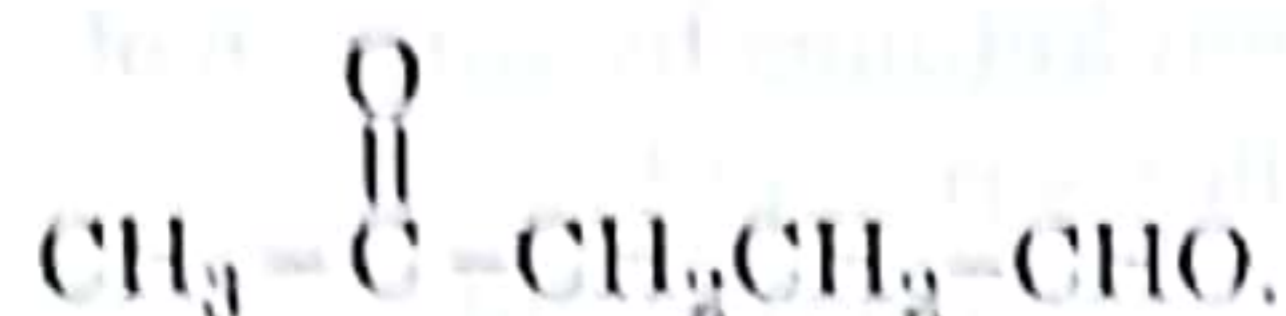
7. A compound ($\text{C}_5\text{H}_{10}\text{O}$), forms a phenylhydrazone, gives negative Tollen's and iodoform tests and is reduced to pentane. What is the compound?

Ans. Phenylhydrazone formation indicates a carbonyl compound. Since the negative Tollen's test rules out an aldehyde, the compound A must be a ketone. A negative iodoform test rules out the $\text{CH}_3\text{C}=\text{O}$ group, and the reduction product, pentane establishes the C's to be in a continuous chain. The compound is $\text{CH}_3\text{CH}_2\text{COCH}_2\text{CH}_3$.

8. A compound ($\text{C}_5\text{H}_{10}\text{O}_2$) is reduced to pentane. With H_2NOH it forms a dioxime and also gives positive iodoform and Tollen's tests. Deduce its structure.

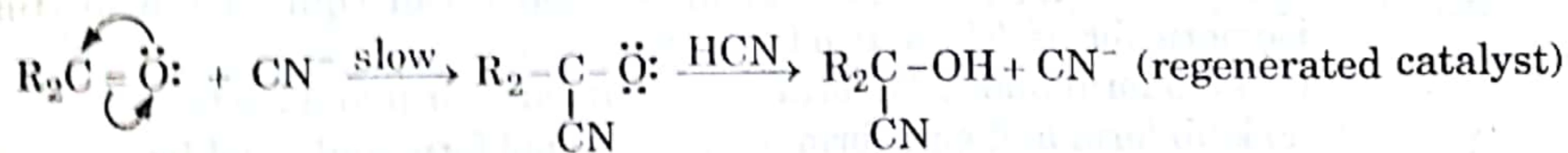
Ans. Reduction to pentane indicates 5 C's in a continuous chain. The dioxime

shows two carbonyl groups. The positive CHI_3 test points to $\text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-$, while the positive Tollen's test establish a $-\text{CH}=\text{O}$. The compound is



9. The rate of addition of HCN to $\text{R}_2\text{C}=\text{O}$ to form a cyanohydrin, $\text{R}_2\text{C}(\text{OH})\text{CN}$ is increased by adding a trace of NaCN . Explain.

Ans. HCN is a very poor nucleophile, but the cyanide ion is a strong nucleophile. Therefore, cyanohydrin formation is initiated by the CN^- ion on the carbonyl carbon and the rate-controlling step is the addition of CN^- .

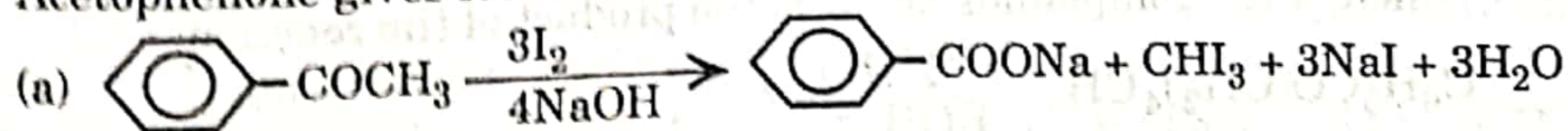


10. Explain why formation of oximes and other ammonia derivatives requires slightly acidic media ($\text{pH} \approx 3.5$) for maximum rate, while basic or more highly acid conditions lower the rate.

Ans. The carbonyl group becomes more electrophilic and reactive when converted by acid to its conjugate acid, $\text{>C}^+-\text{OH}$. In more strongly acid solutions ($\text{pH} < 3.5$) the unshared pair of electrons (the nucleophilic site) of N is protonated to give electrophilic $\text{H}_3\text{N}^+\text{G}^-$ ($\text{G}^- = -\text{OH}, -\text{NHC}_6\text{H}_5$ or NHCONH_2), a species which cannot react. In basic media there is no protonation of $\text{C}=\text{O}$.

11. How will you distinguish between acetophenone and benzophenone.

Ans. Acetophenone gives iodoform test. Benzophenone does not give this test

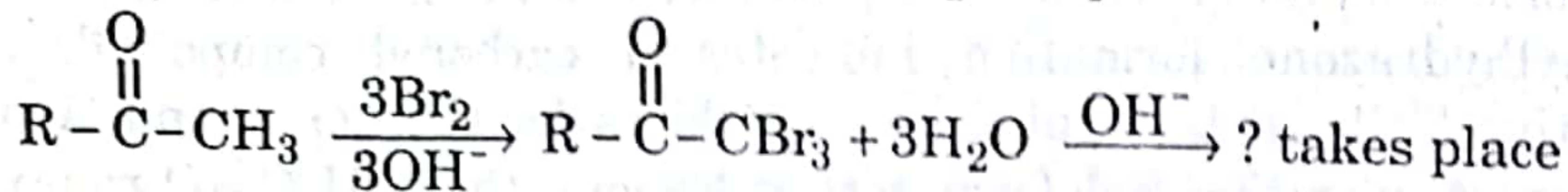


12. How will you distinguish between benzaldehyde and acetaldehyde?

Ans. Acetaldehyde gives Fehling's test and iodoform test. Benzaldehyde does not.

Multiple Choice Questions

1. Which of the following is the major organic product, when the reaction:



- (a) $R-\overset{\text{OH}}{\underset{\text{OCH}_3}{\text{C}}}-\text{CH}_3$ (b) $R-\overset{\text{OH}}{\underset{\text{H}}{\text{C}}}-\text{CH}_3$ (c) CHBr_3 (d) HO CBr_3 **Ans: (c)**

2. The reaction, $\text{CH}_3\text{CH}_2\overset{\text{O}}{\parallel}{\text{C}}\text{H} \xrightarrow[\text{H}_2\text{O}]{\text{NaOH}} \text{CH}_3\text{CH}_2\overset{\text{OH}}{\underset{\text{CH}_3}{\text{C}}}\overset{\text{O}}{\parallel}{\text{C}}\text{H}$; is generally called

- (a) Aldol condensation (b) Clemmensen reduction
(c) Oxidation (d) reduction **Ans: (a)**

3. Aldehydes may be distinguished from ketones by the use of

- (a) Hoffman reagent (b) Tollen's reagent
(c) Grignard reagent (d) Cannizzaro reagent **Ans: (b)**

4. Which reagent will react with benzaldehyde to yield a phenylhydrazone?

- (a) NH_2NH_2 (b) NH_2OH (c) $\text{C}_6\text{H}_5\text{NH}_2$ (d) $\text{C}_6\text{H}_5\text{NHNH}_2$ **Ans: (d)**

5. Which of the following tests is not used to identify aldehydes?

- (a) Tollen's test (b) Baeyer's test
(c) Benedict's test (d) the ammonia test **Ans: (b)**

6. Aldehydes and ketones exist in solution as an equilibrium mixture of two isomeric forms. These two forms are:

- (a) keto form and aldol form (b) aldol form and iso form
(c) keto form and enol form (d) enol form and aldol form **Ans: (c)**

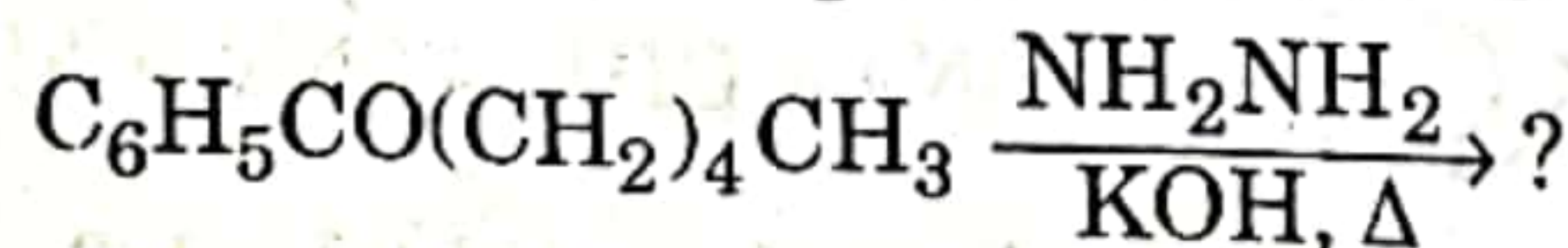
7. Which of the following reagents may not be used for the oxidation of aldehydes and ketones to organic acids?

- (a) $\text{Ag}(\text{NH}_3)_2^+$ (b) KMnO_4 (c) $\text{K}_2\text{Cr}_2\text{O}_7$ (d) LiAlH_4 **Ans: (d)**

8. Treating benzaldehyde with acetone in 20% NaOH at 100°C gives which compound as the main product?

- (a) $\text{C}_6\text{H}_5-\overset{\text{H}}{\text{C}}=\overset{\text{H}}{\text{C}}-\overset{\text{O}}{\parallel}{\text{C}}=\text{O}$ (b) $\text{C}_6\text{H}_5-\overset{\text{OH}}{\text{C}}-\text{CH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{OH}$
(c) $\text{C}_6\text{H}_5-\overset{\text{H}}{\text{C}}=\overset{\text{H}}{\text{C}}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_3$ (d) $\text{C}_6\text{H}_5-\text{CH}=\overset{\text{O}}{\parallel}{\text{C}}-\text{C}_6\text{H}_5$ **Ans: (c)**

9. Which of the compounds below is the product of the reaction:

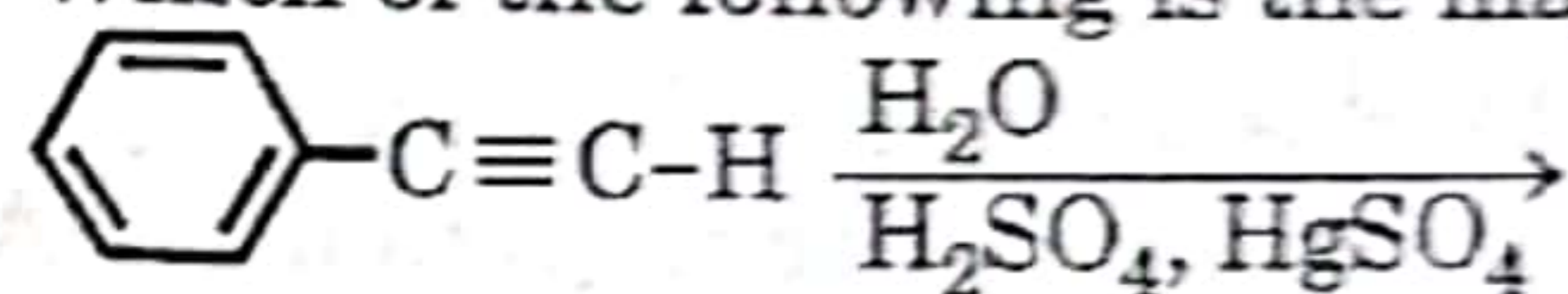


- (a) $\text{C}_6\text{H}_5\text{COH}(\text{CH}_2)_4\text{CH}_3$ (b) $\text{C}_6\text{H}_5(\text{CH}_2)_4\text{CH}_3$

- (c) $C_6H_5(CH_2)_5CH_3$ (d) $C_6H_5-OC(CH_2)_4CH_3$ **Ans: (c)**
10. The above reaction (Q.9) is known as a:
 (a) Clemmensen reduction (b) Rosenmund reduction
 (c) Friedel-Crafts reaction (d) Wolf-Kishner reduction **Ans: (d)**
11. In a nucleophilic addition reaction, when a nucleophile attacks the carbonyl carbon, the hybridization of carbon atom changes from:
 (a) sp^3 to sp^2 (b) sp^2 to sp^3 (c) sp^2 to sp (d) sp to sp^2 **Ans: (b)**
12. Which of the following compounds will not give iodoform test on treatment with $I_2/NaOH$?
 (a) 3-pentanone (b) acetaldehyde (c) Butanone (d) Acetone **Ans: (a)**
13. Which of the following compounds will not give Cannizzaro's reaction?
 (a) HCHO (b) CH_3CHO (c) $(CH_3)_3CHC$ (d) C_6H_5CHO **Ans: (b)**
14. Cannizzaro's reaction is given by
 (a) Aldehydes without an α -hydrogen (b) Aldehydes that contain α -hydrogen
 (c) Both aldehydes and ketones that have no α -hydrogen
 (d) Ketones without α -hydrogen **Ans: (a)**
15. Which of the following types of reactions the Cannizzaro's reaction is:
 (a) Oxidation reaction (b) Acid-base reaction
 (c) Self oxidation-reduction reaction (d) Reduction reaction **Ans: (c)**
16. Aldols on heating undergoes which process of the following?
 (a) Decomposition (b) Oxidation
 (c) disproportionation (d) dehydration **Ans: (d)**
17. Which of the following will not undergo aldol condensation?
 (a) Acetaldehyde (b) Benzaldehyde (c) Acetone (d) Propanaldehyde **Ans: (b)**
18. 3-Hydroxybutanal on heating yields:
 (a) 2-Butanone (b) 2-Butenal (c) Butanal (d) propanone **Ans: (b)**
19. A mixture of formaldehyde and benzaldehyde on treatment with aq. NaOH solution gives:
 (a) benzyl alcohol and sodium formate (b) benzyl alcohol and methanol
 (c) sodium benzoate and methanol
 (d) sodium benzoate and sodium formate **Ans: (a)**
20. Benzaldehyde on treatment with alc. KCN gives:
 (a) potassium benzoate (b) benzyl alcohol
 (c) benzoic acid (d) benzoin **Ans: (d)**
21. Benzaldehyde reacts with phosphorus ylide to yield triphenyl phosphine oxide and?
 (a) benzyl alcohol (b) benzoic acid (c) styrene (d) benzoin **Ans: (c)**
22. Which of the following reagents is a particularly useful reagent for the identification and characterization of carbonyl compounds?
 (a) hydrazine (b) 2,4-dinitrophenylhydrazine
 (c) semicarbazide (d) Sodium bisulphate **Ans: (b)**
23. Which of the following is the best method for preparing $(CH_3)_3COCH_3$?
 (a) $NaOCH_3 + (CH_3)_3CCl \rightarrow$ (b) $(CH_3)_3CH + CH_3OH \xrightarrow{H_2SO_4}$

(c) $(\text{CH}_3)_3\text{COK} + \text{CH}_3\text{OH} \rightarrow$ (d) $(\text{CH}_3)_3\text{COK} + \text{CH}_3\text{I} \rightarrow$ **Ans: (d)**

24. Which of the following is the major product of the reaction:



(a) $\text{HO}_3\text{S}-\text{C}_6\text{H}_4-\text{C}\equiv\text{C}-\text{H}$ (b) $\text{C}_6\text{H}_5-\text{C}(=\text{O})-\text{CH}_3$ (c) $\text{C}_6\text{H}_5-\text{CH}=\text{CH}_2$ (d) $\text{C}_6\text{H}_5-\text{CH}_2-\text{CHO}$ **Ans: (b)**

25. Which of the following reactions is analogous to Friedel-Crafts acylation with formyl chloride?

(a) Reimer-Tiemann reaction (b) Gatterman-Koch reaction
(c) Rosenmund reaction (d) Freund reaction **Ans: (b)**

26. Which of the following methods does not give aldehydes?

(a) Hydration of alkynes (b) Oxidation of primary alcohols
(c) Oxidation of secondary alcohols (d) Gatterman reaction **Ans: (c)**

27. Which type of the reaction is the formation of acetals from alcohols on treatment with aldehydes?

(a) Nucleophilic substitution (b) Electrophilic substitution
(c) Oxidation (d) Nucleophilic addition **Ans: (d)**

28. Which of the following reducing agent can reduce aldehydes and ketones directly to hydrocarbons?

(a) LiAlH_4 (b) $\text{H}_2 + \text{Ni}$ (c) $\text{Zn(Hg)} + \text{HCl}$ (d) $\text{H}_2 + \text{Pt}$ **Ans: (c)**

29. Which of the following pair of compounds can be distinguished by means of Tollen's reagent test?

(a) CH_3CHO and CH_3COCH_3 (b) CH_3COCH_3 and $\text{CH}_3\text{CH}_2\text{COCH}_3$
(c) CH_3COCH_3 and $\text{CH}_3\text{COOC}_2\text{H}_5$ (d) HCHO and CH_3CHO **Ans: (d)**

30. Which of the following reagents will give similar results for both butanal and butanone

(a) Tollen's reagent (b) $\text{I}_2 + \text{aq. NaOH}$
(c) Fehling's solution (d) 2,4-dinitrophenylhydrazene reagent **Ans: (d)**

31. What is the final product when propanone is treated with HCN , and the product formed is hydrolysed under acidic conditions?

(a) $\text{CH}_3\text{CH(OH)COOH}$ (b) $(\text{CH}_3)_2\text{C(OH)COOH}$
(c) $\text{CH}_3\text{CH}_2\text{COOH}$ (d) $\text{CH}_3\text{CH}_2\text{CH(OH)COOH}$ **Ans: (b)**

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