CHAPTER 19

ALDEHYDES AND KETONES

After completing this lesson, you will be able to:

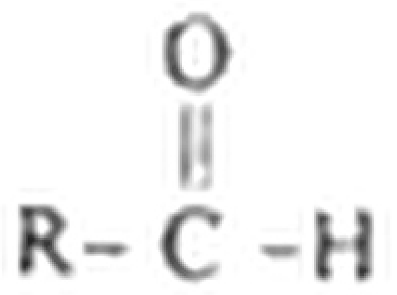
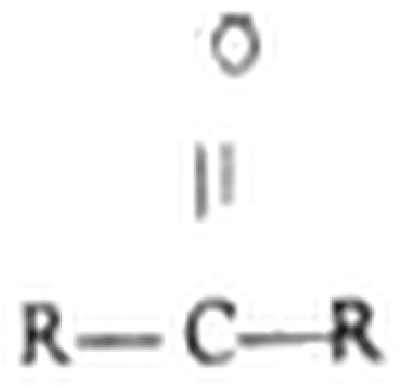
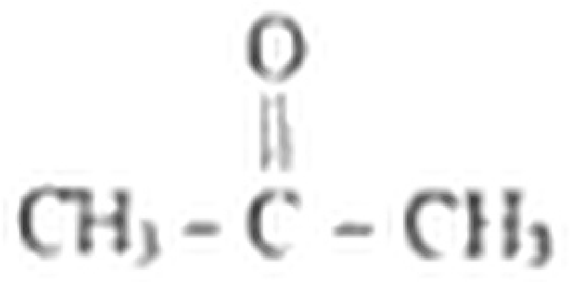
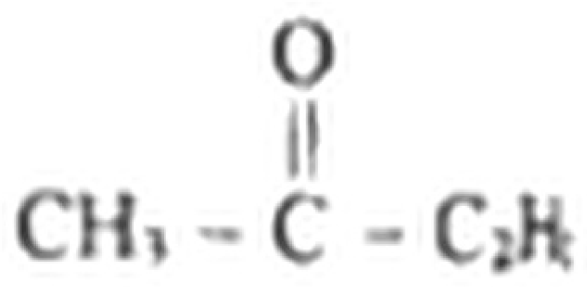
- Explain nomenclature and structure of aldehydes and ketones.
- Discuss the preparation of aldehydes and ketones by ozonolysis of alkene, hydration of alkynes, oxidation of alcohols and Friedel Craft's acylation of aromatics. (Applying) Describe reactivity of aldehydes and ketones and their comparison. (Analyzing)
- Describe acid and base catalyzed nucleophilic addition reaction of aldehydes and ketones. (Applying)
- Discuss the chemistry of aldehydes and ketones by their reduction to hydrocarbon alcohols, by using carbons neuclophiles nitrogen nucleophiles oxygen nucleophilic (Applying]
- Describe oxidation reactions of aldehydes and ketones. (Applying)
- Describe isomerism in aldehydes des and ketones. (Understanding)

QI. What are aldehydes and ketones?

Answer

Organic compounds containing the carbonyl functional group are called aldehydes and ketones.

Aldehydes	Ketones
(I) Functional Group	
In aldehydes, the C-atom of carbonyl group is directly attached to at least One H-atom.	In ketones, the C-atom of carbonyl group is bonded to two carbon atoms called ketonic group

(2) General Formula	
he homologous series of aldehydes have general formula $C_nH_{2n}O$.	The homologous series of ketones have general formula $C_nH_{2n}O$.
(3) General Formula Structure	
n aldehyde may be represented by the general formula structure  $R-\overset{\overset{O}{\|}}{C}-H$	ketone may be represented by the general formula structure  $R-\overset{\overset{O}{\|}}{C}-R$
(4) Occurrence	
Aldehydes groups are present in most sugars. hey are the principal constituents of a number of essential oils used as fragrances d flavors.	ketonic group is present in camphor and fructose.
(5) Examples	
(i) H-CHO (Formaldehyde) (ii) CH_3-CHO (Acetaldehyde)	 $CH_3-\overset{\overset{O}{\|}}{C}-CH_3$ (ii)  $CH_3-\overset{\overset{O}{\|}}{C}-C_2H$ Acetone Methyl ethyl ketor

Q2. Give nomenclature of aldehydes and ketones.

Answer

a) Common names

An aldehyde is named after the name of carboxylic acid obtained on its oxidation, the ending —ic acid is replaced by "aldehyde", e.g.,

H

|

HC = O Formaldehyde

H

|

$CH_3 - C = O$ Acctzldehyde

For naming substituted aldehyde, the chain is labeled by using a, p, y…etc. the carbon next to carbon of the carbonyl group is indicated by 'a' and so on.

b) IUPAC Names

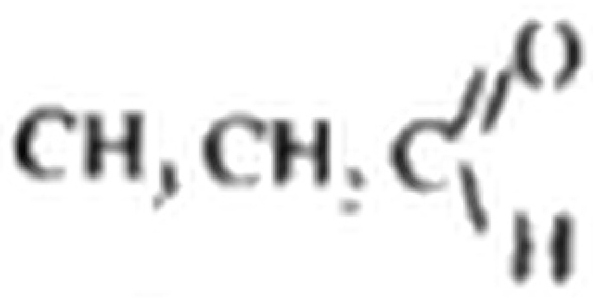
I. The longest carbon chain containing the aldehydic group is taken as the parent hydrocarbon.

2. The ending e of the alkane is replaced by al

3. The numbering starts from the carbon atom of the carbonyl group. The carbon atom of aldehydic group is always carbon number I.

4. The position of the substituent is indicated by numbers which is written before their number.

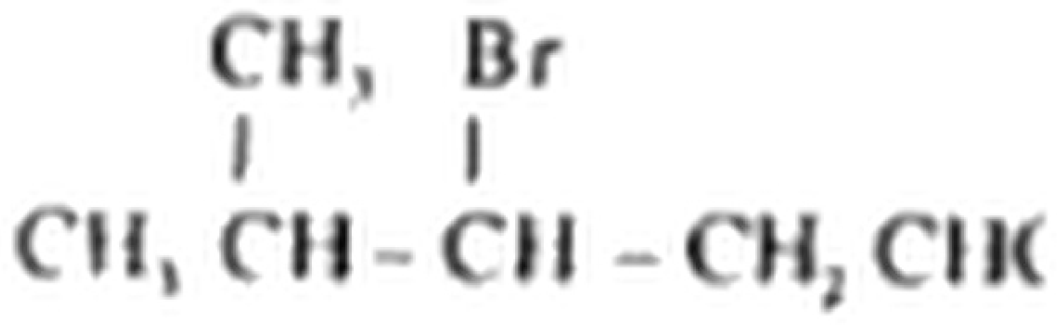
Examples:



Propanal

$Cl - CH_2CHO$

2-chloro ethanal



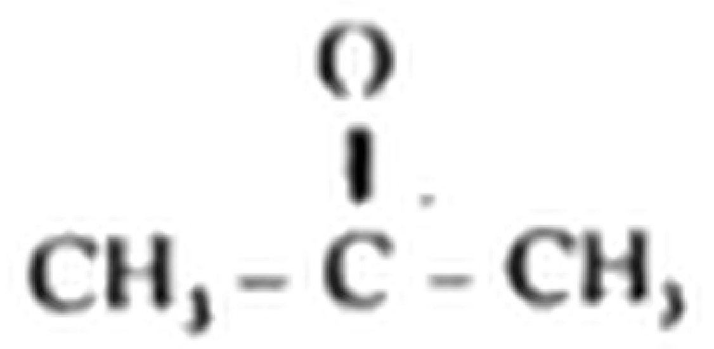
$CH_3\overset{CH_3}{\overset{|}{C}H} - \overset{Br}{\overset{|}{C}H} - CH_2CHO$

(3-bromo-4-methyl pentanal-1)

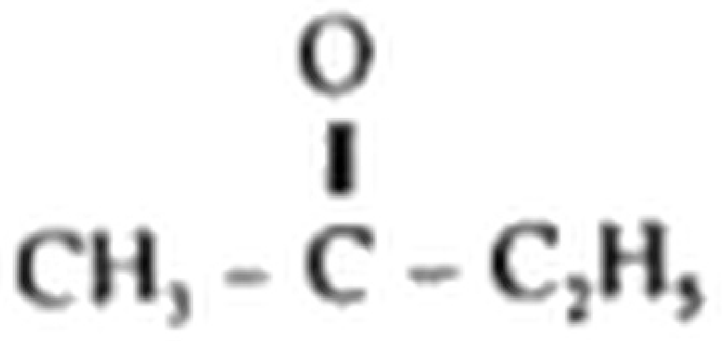
Ketones:

a) Common names:

Ketones are names by adding the word ketone after writing the names of alkyl or aryl group linked to carbonyl carbon in alphabetical order.

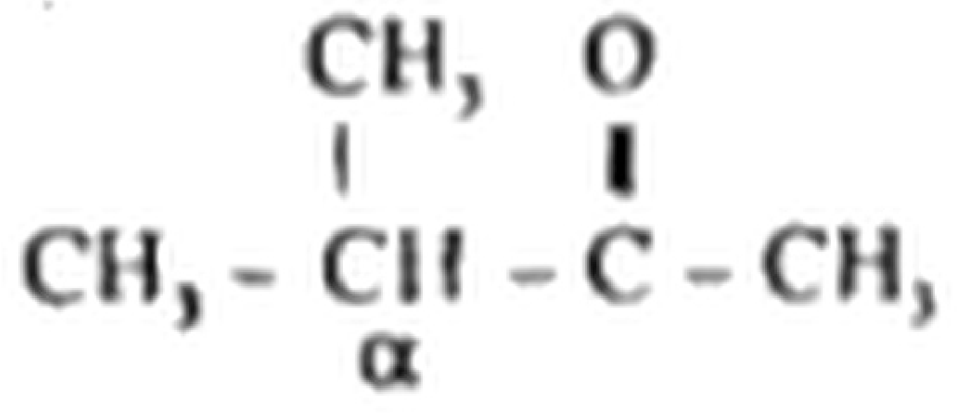

$CH_3-\overset{O}{\overset{\|}{C}}-CH_3$

Dimethyl Ketone
(Acetone)

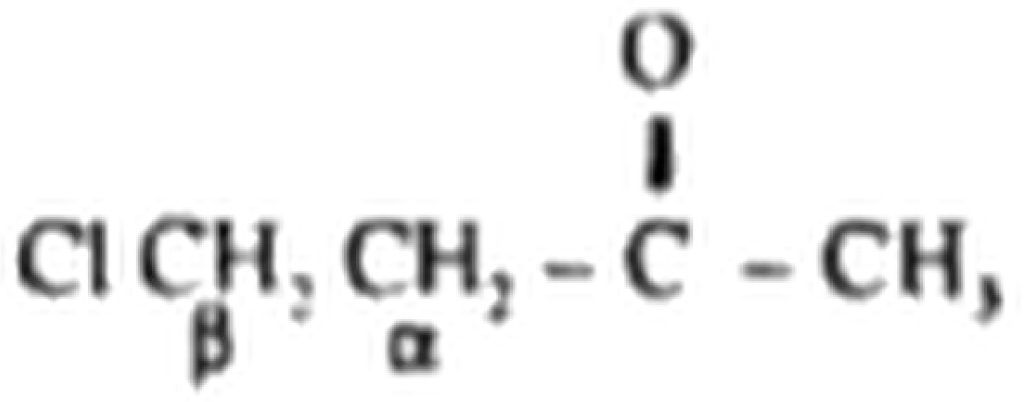

$CH_3-\overset{O}{\overset{\|}{C}}-C_2H_5$

Ethyl methyl
Ketone

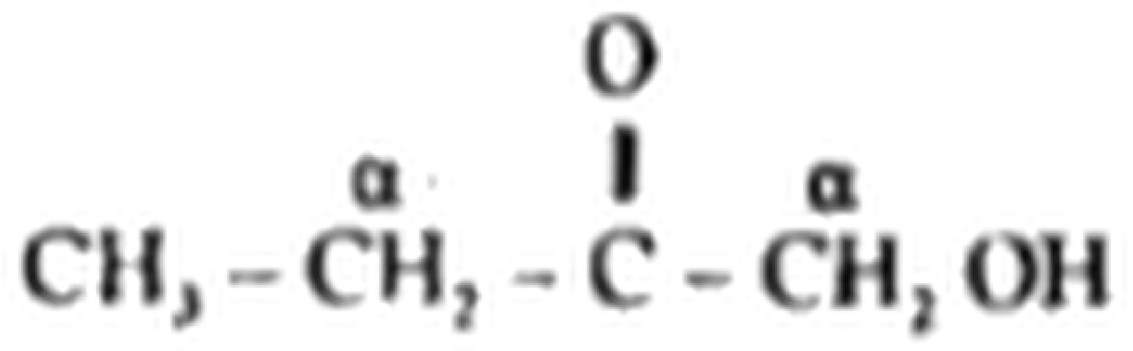
Substituted ketones are named by labeling the chain using a, p, y ..,etc, the carbon next to carbon of carbonyl group is indicated by 'a' and so on, e.g.


$CH_3-\underset{\alpha}{\overset{CH_3}{\overset{|}{CH}}}-\overset{O}{\overset{\|}{C}}-CH_3$

Methyl α–methyl ethyl Ketone


$Cl\underset{\beta}{CH_2}\underset{\alpha}{CH_2}-\overset{O}{\overset{\|}{C}}-CH_3$

Methyl β–chloroethyl ketone


$CH_3-\overset{\alpha}{CH_2}-\overset{O}{\overset{\|}{C}}-\overset{\alpha}{CH_2}OH$

α–hydroxyl–methyl ethyl ketone.

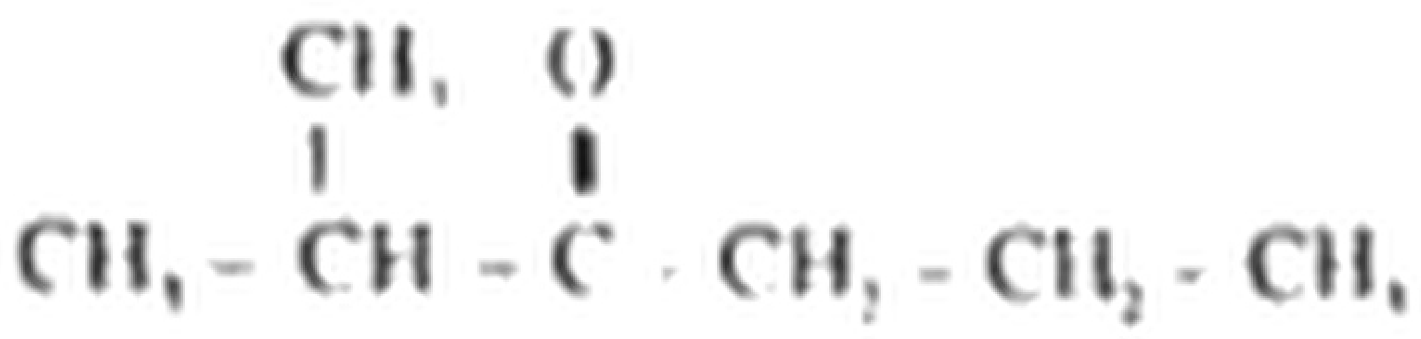
(b) IUPAC Names:

The longest chain containing the carbonyl group is taken a parent hydrocarbon.

The ending e of hydrocarbon is replaced by one

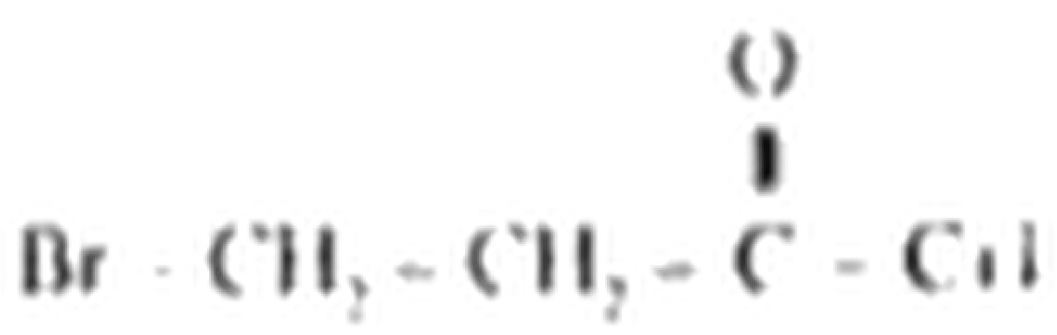
The numbering starts from the end that gives the carbonyl carbon the lower number. In cyclic ketones, carbonyl carbon is number I

The positions of substituent are indicated by numbers before their names.



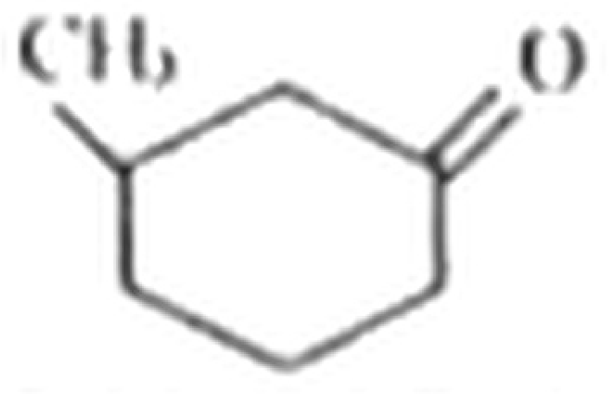
$CH_3-\overset{\overset{CH_3}{|}}{CH}-\overset{\overset{O}{\|}}{C}-CH_2-CH_2-CH_3$

2-methyl-3-hexanone

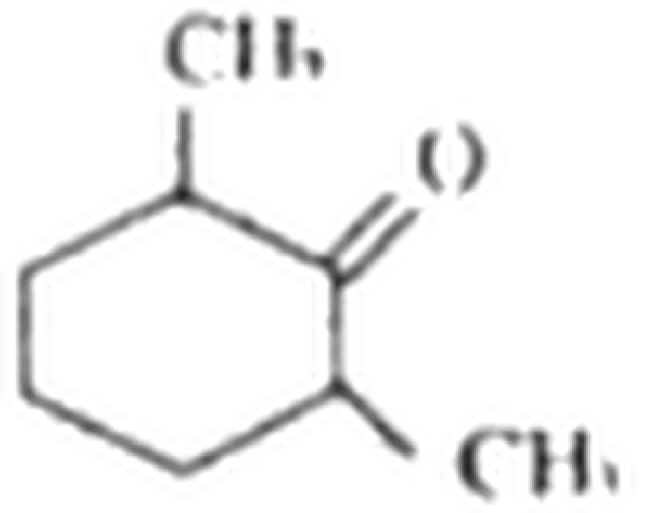


$Br-CH_2-CH_2-\overset{\overset{O}{\|}}{C}-CH_3$

4-bromo-2-butanone



3-Methyl Cyclo
hexanone



2, 6 dimethyl cycl
hexanone

Q3. Give Physical Properties of aldehydes of ketones.

Answer

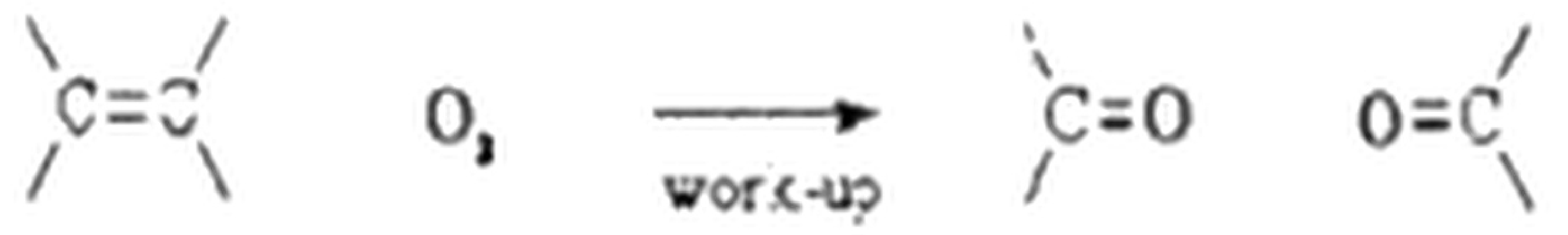
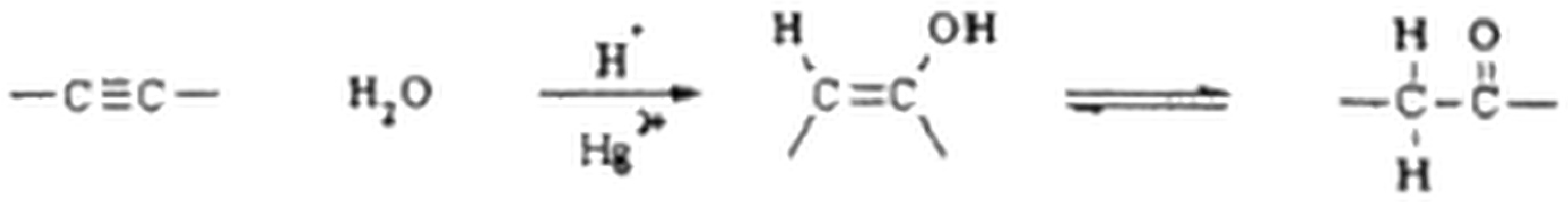
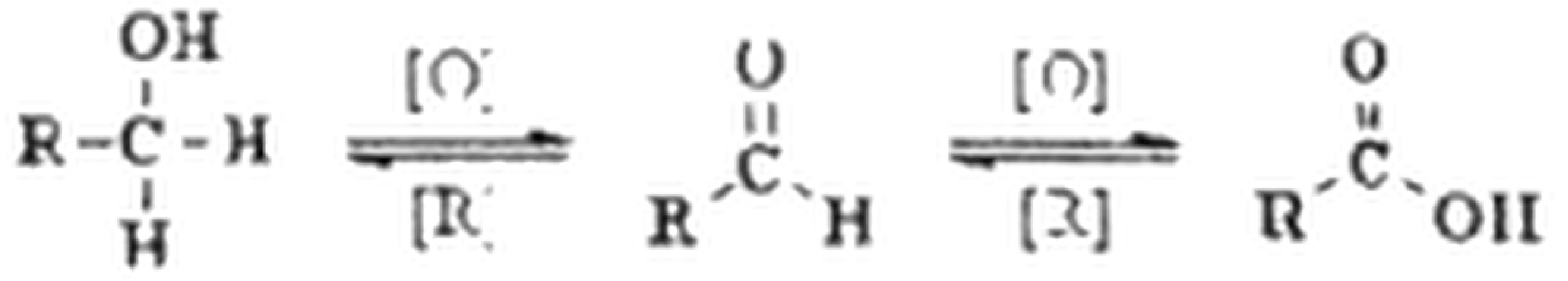
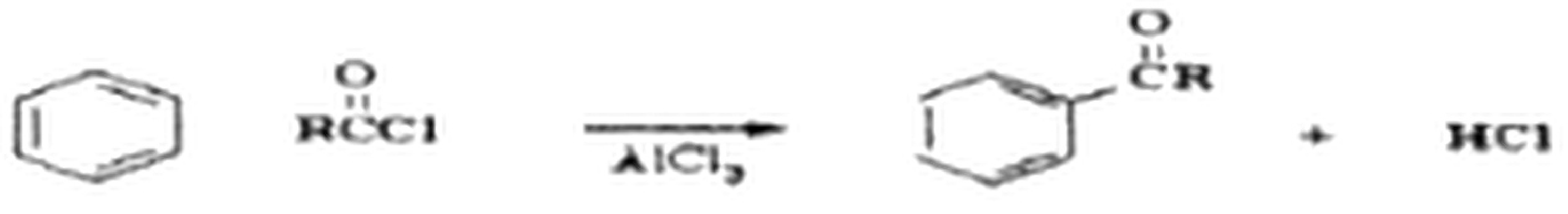
I) The polar nature of the C=O (due to the electronegativity difference of the atoms) means dipole-dipole interactions will occur.

2) Though C=O cannot hydrogen-bond to each other, the C=O can accept hydrogen bonds from hydrogen bond donors (e.g. water, alcohols). The implications of these effects are:

o higher melting and boiling points compared to analogous alkanes o lower boiling points than analogous alcohols o more soluble than alkanes but less soluble than alcohols in aqueous media

Q4. Give Preparations of Aldehydes and Ketones.

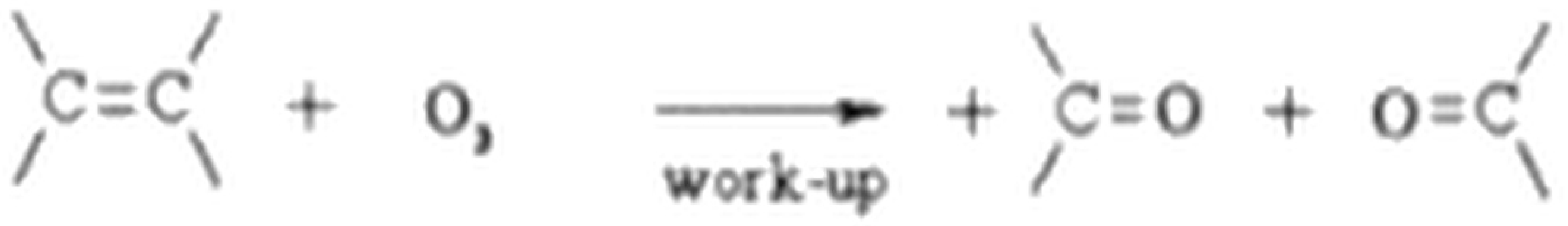
Answer

Ozonolysis of Alkenes	
Hydration of Alkynes	
Oxidation of Alcohols	
Friedel-Crafts Acylation of Aromatics	

Q5. Give reactions of ethane with ozone along with mechanism.

Answer

Ozonolysis of Alkenes



Reaction type: Electrophilic Addition

Elaboration

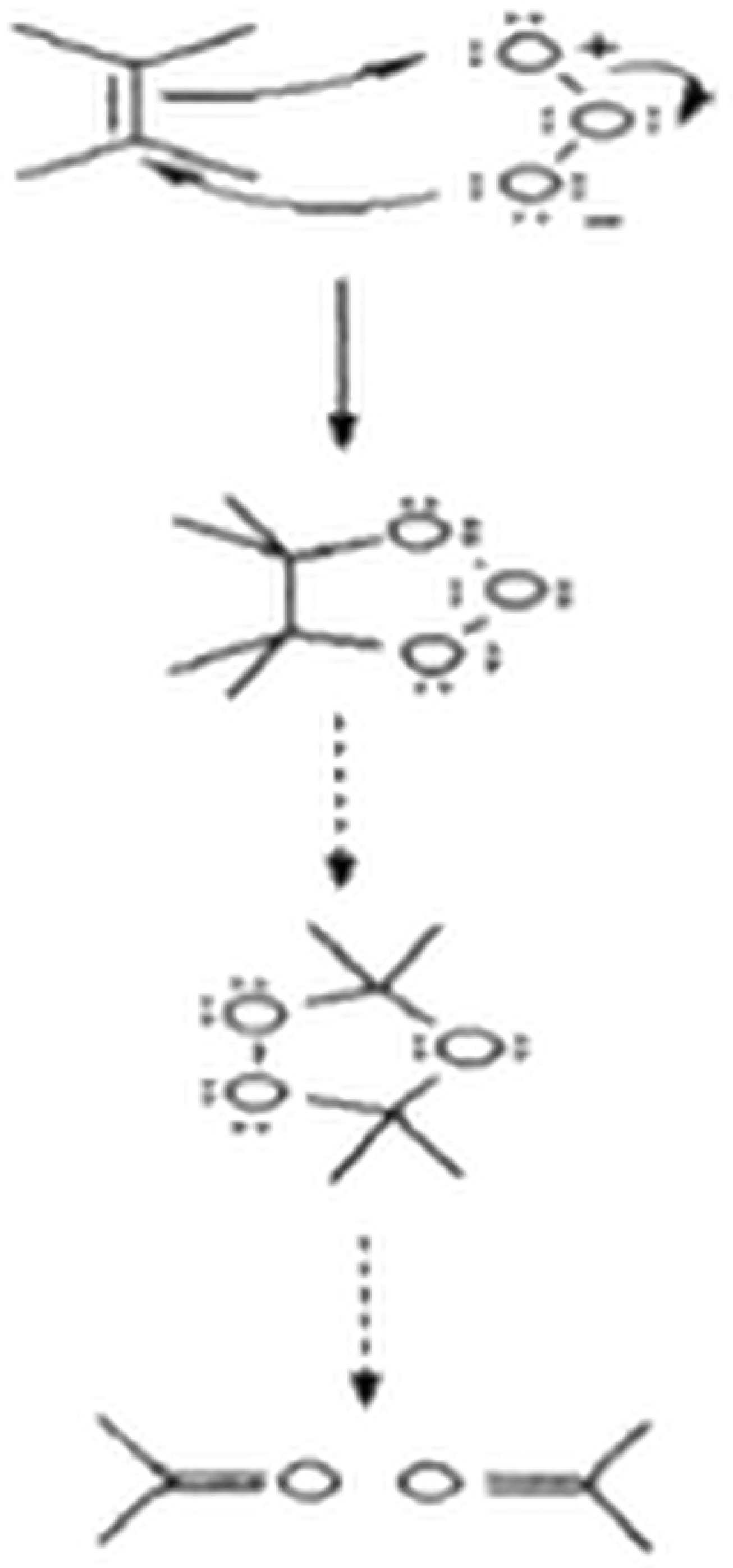
1. Overall transformation: C=C to 2C=O

2. Reagents: ozone, O_3, followed by a reducing work-up, usually Zn in acetic acid.

3. It is convenient to view the process as cleaving the. alkene into two carbonyl compounds:

4. The substituents on the C=O depend on the substituents on the C=C.

MECHANISM FOR REACTION OF ALKENES WITH O_3



Step 1:

The electrons act as the nucleophile, attacking the ozone at the electrophilic terminal O, A second C-O is formed by the nucleophilic O attacking the other end of the C=C.

step 2:

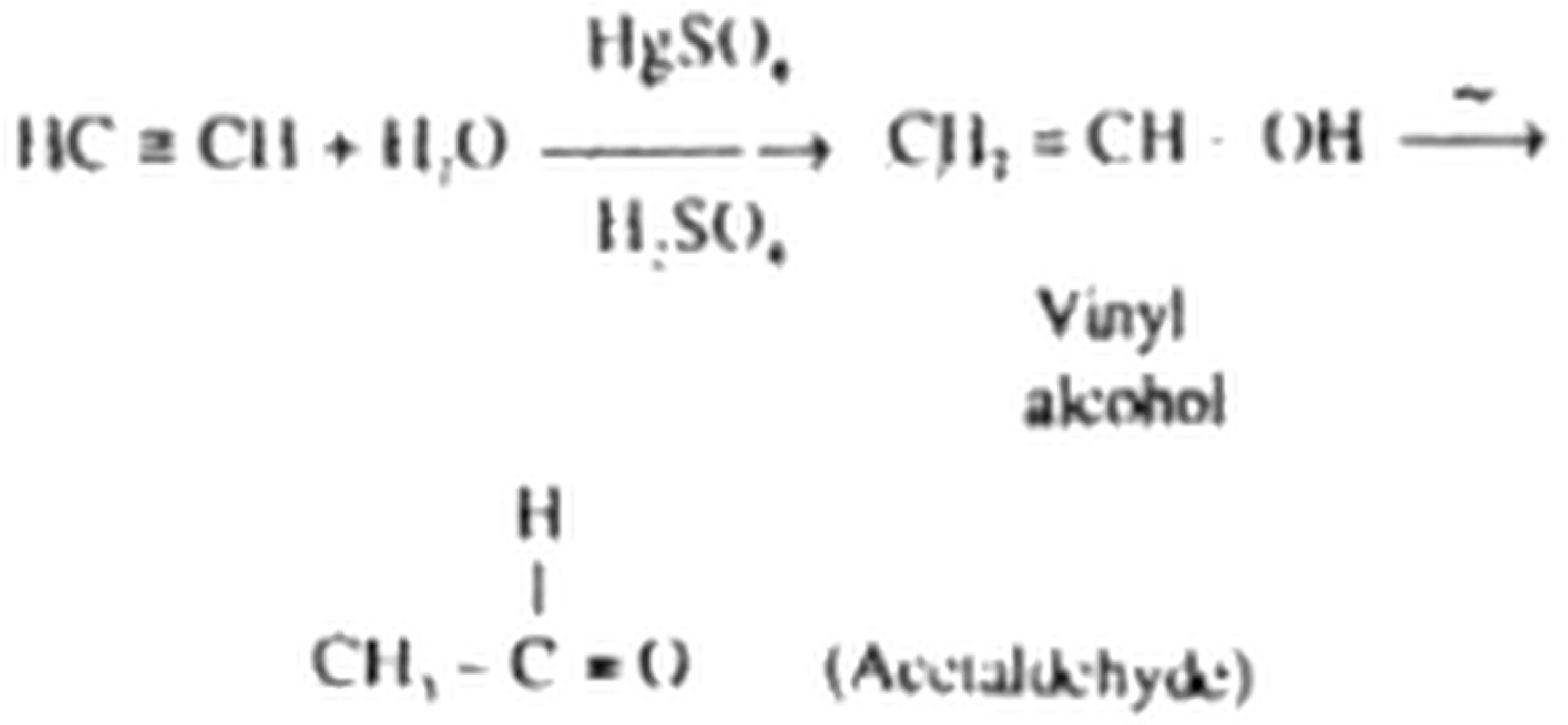
The cyclic species called the molozonide rearranges to the ozonide.

Step 3:

On work-up (usually Zn / acetic acid) the malozonide decomposes to give two carbonyl compounds.

Hydration of Alkynes

Water adds on to alkynes in the presence of dil. H_2SO_4 and $HgSO_4$ to produce an aldehyde or ketone. Enol forms as intermediate which isomerizes into aldehydes or ketones, e.g.,

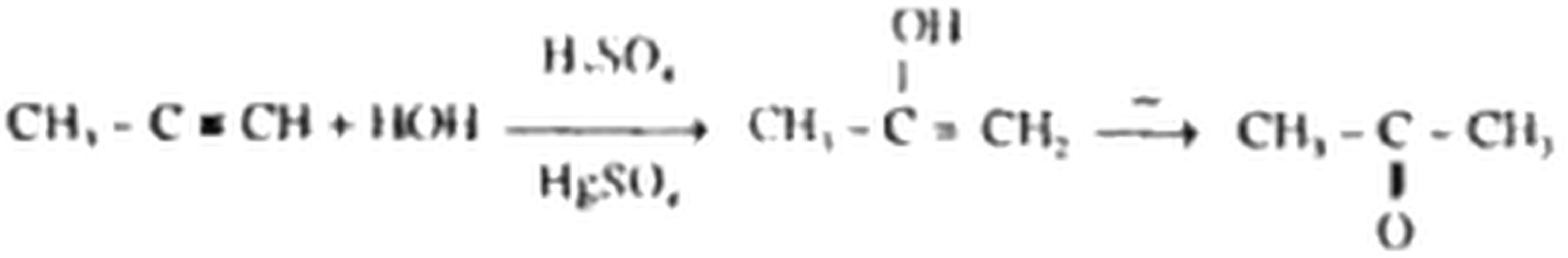


$$HC \equiv CH + H_2O \xrightarrow[H_2SO_4]{HgSO_4} CH_2 = CH - OH \xrightarrow{\sim} CH_3 - \overset{\overset{\displaystyle H}{|}}{C} = O$$

Vinyl alcohol

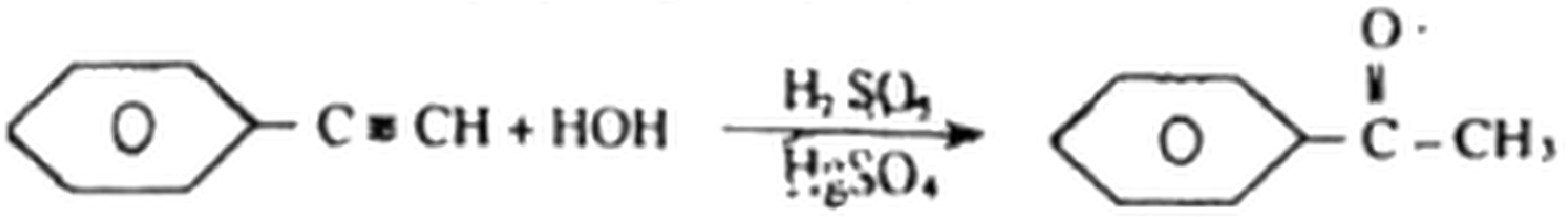
(Acetaldehyde)

Propyne gives acetone:



$$CH_3 - C \equiv CH + HOH \xrightarrow[HgSO_4]{H_2SO_4} CH_3 - \overset{\overset{\displaystyle OH}{|}}{C} = CH_2 \xrightarrow{\sim} CH_3 - \underset{\underset{\displaystyle O}{\|}}{C} - CH_3$$

This reaction is useful for preparing methyl aryl ketones



(Acetophenone)

Oxidation of Primary and Secondary Alcohols

Primary alcohols are oxidized to aldehydes by (i) warming with acidic dichromate solution (ii) Jone reagent (Cr0₃ + dil. H₂SO4 + acetone) (iii) Sarett reagent (CrO₃ in pyridine)

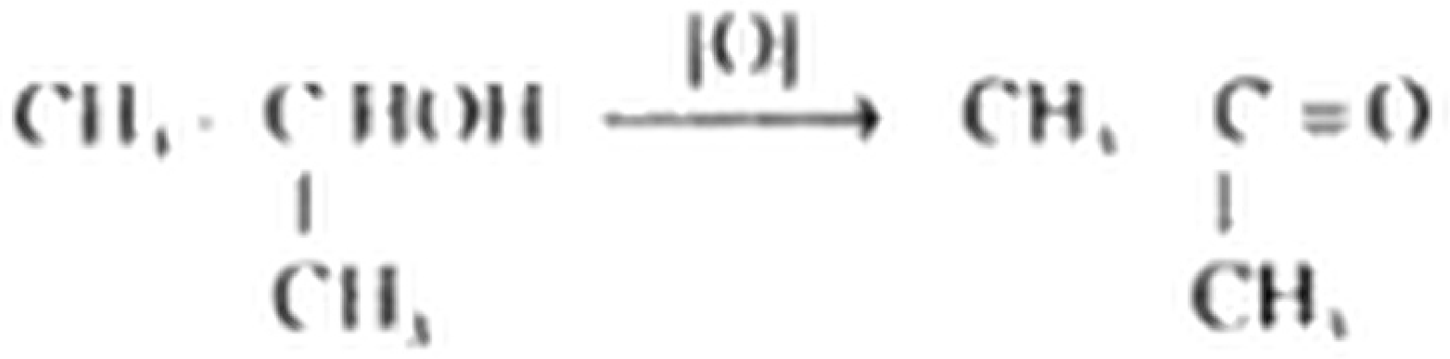
$$CH_3CH_2CH_2CH_2OH \xrightarrow[Na_2Cr_2O_7]{Conc.\ H_2SO_4} CH_3CH_2CH_2CHO$$

Butanol Butanal

$$C_6H_5CH_2OH \xrightarrow[reagent]{Sorett} C_6H_5CHO$$

$$n - C_7H_{15}CH_2OH \xrightarrow[reagent]{Jone} n - C_7H_{15}CHO$$

Non-aqueous solvents are employed to avoid further oxidation. Secondary alcohols are oxidized to ketones.



$$CH_3-\underset{\displaystyle CH_3}{\underset{|}{C}}HOH \xrightarrow{[O]} CH_3\ \underset{\displaystyle CH_3}{\underset{|}{C}}=O$$

Q6. Friedel-Crafts Acylation of Benzene.

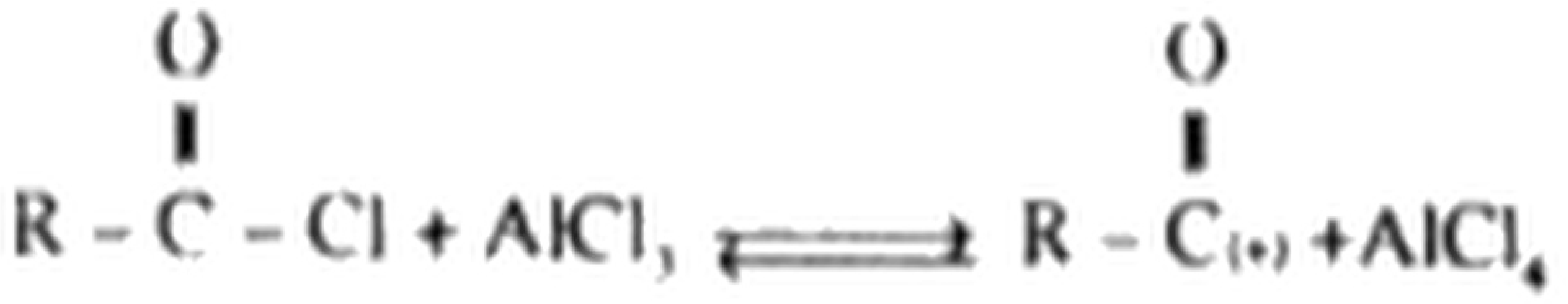
Answer

It is the substitution of acyl group in an organic compound in the presence of AlC13 or some other Lewis acid

$$C_6H_6 + R-\underset{\displaystyle O}{\underset{\|}{C}}-Cl \overset{AlCl_3}{\rightleftharpoons} C_6H_5COR + HCl$$

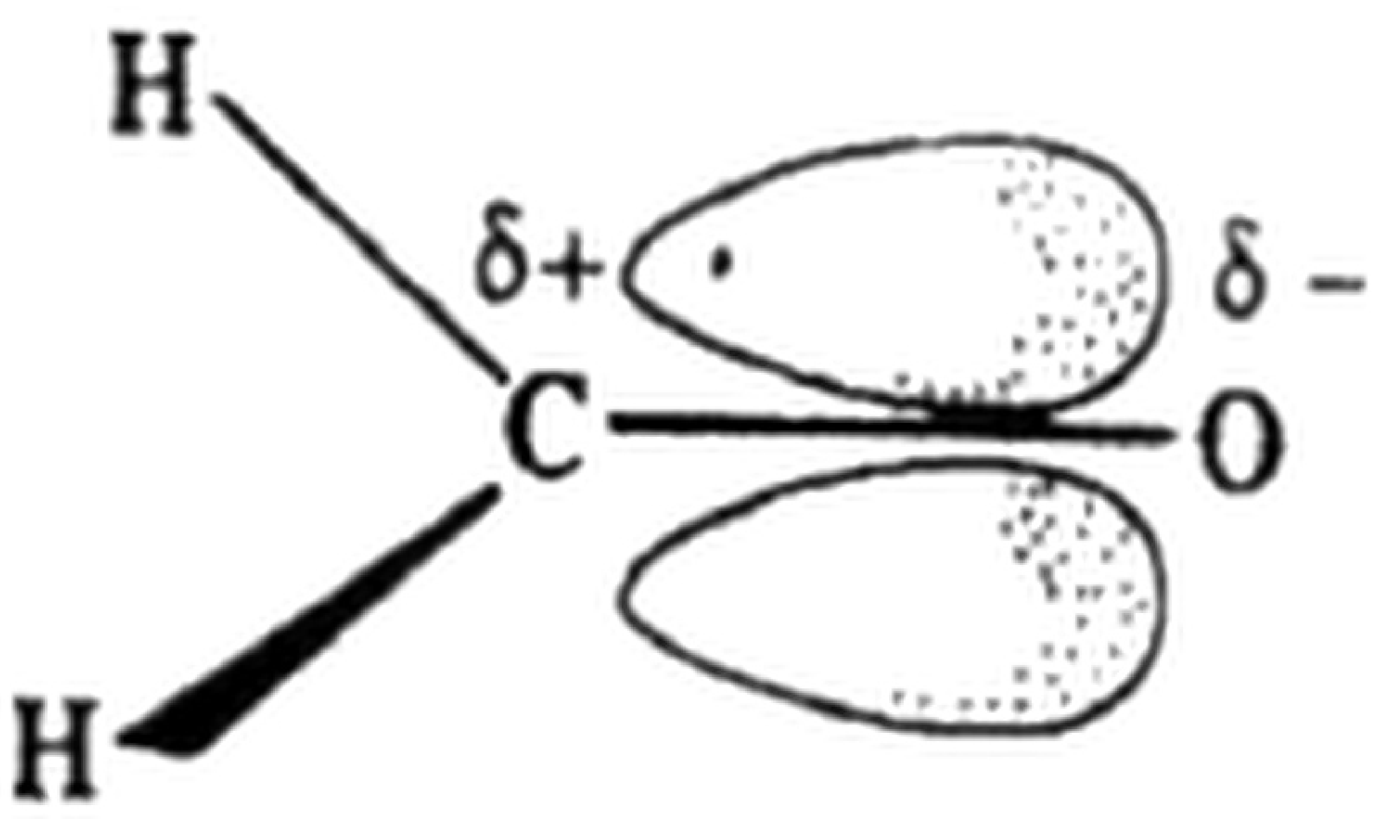
(Alkyl aryl ketone)

$AlCl_3$ generates acylenium ion (electrophile) which is substituted in the aromatic ring



$$R-\overset{\displaystyle O}{\overset{\|}{C}}-Cl + AlCl_3 \rightleftharpoons R-\overset{\displaystyle O}{\overset{\|}{C}}_{(+)} + AlCl_4$$

Reactivity:



The double bond of the carbonyl group has a o-bond and a It-bond. As oxygen is more electronegative, it attracts the it-electrons to itself. This attraction makes the carbonyl group a polar group.

The oxygen atom has a partial negative charge on it and the carbon atom has partial positive charge. The electron cloud is pulled more strongly by the oxygen atom than the carbon atom. It makes oxygen atom nucleophile and carbon atom becomes electrophile.

Q7. Give different reactions of aldehydes and ketones.

Answer

Nucleophilic Addiction

There are two types of nucleophilic addition reactions of carbonyl compounds.

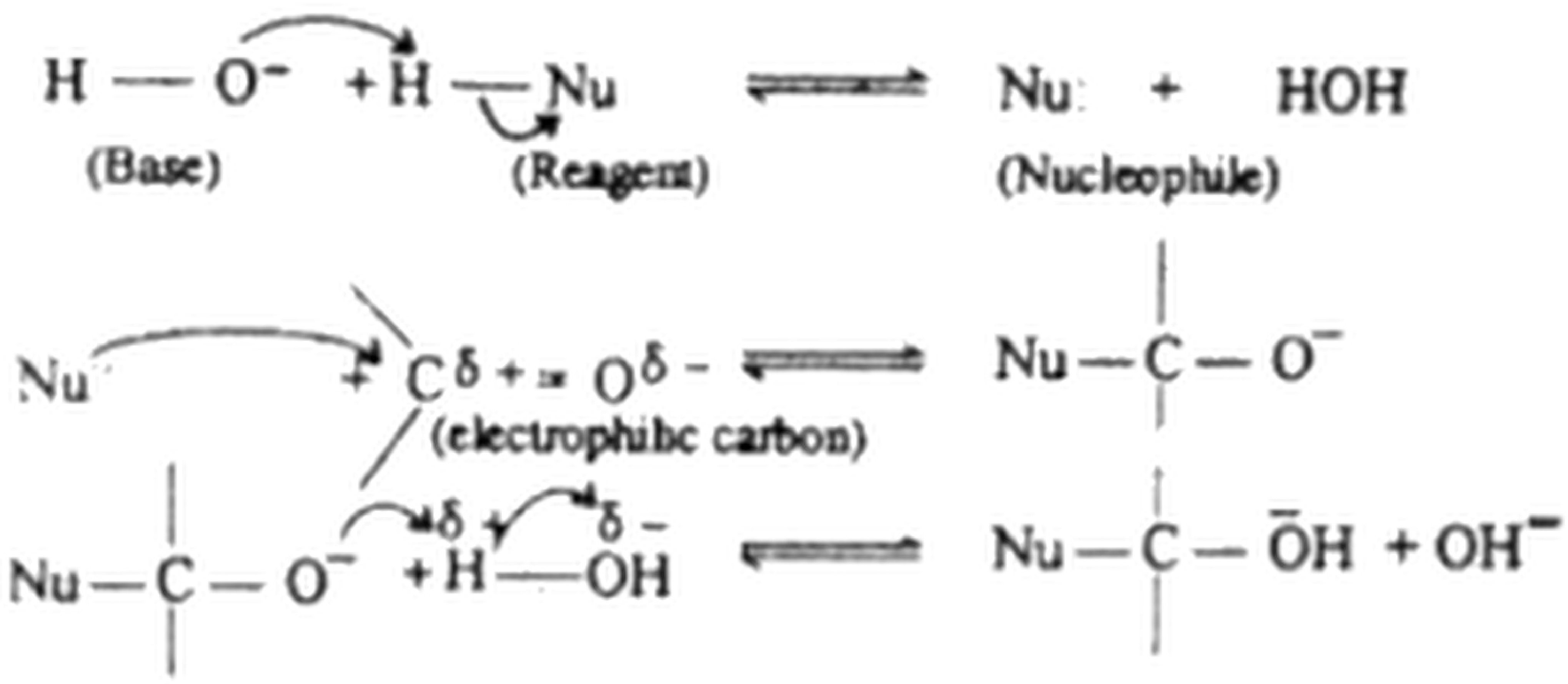
i) Base catalyzed nucleophilic addition reaction

ii) Acid catalyzed nucleophilic addition reaction

i) Base Catalyzed

A base catalyzed nucleophilic addition reaction takes place with a strong nucleophilic reagent. The base reacts with the reagent ad generates the nucleophile. The addition is initiated by the attack of a nucleophile on the electrophilic carbon of the carbonyl group. The general mechanism of the reaction is as follows:

General Mechanism



There are five types of base catalyzed nucleophilic addition reactions of carbonyl compounds.

I) Addition of hydrogen cyanide

2) Addition of Grignard's reagent

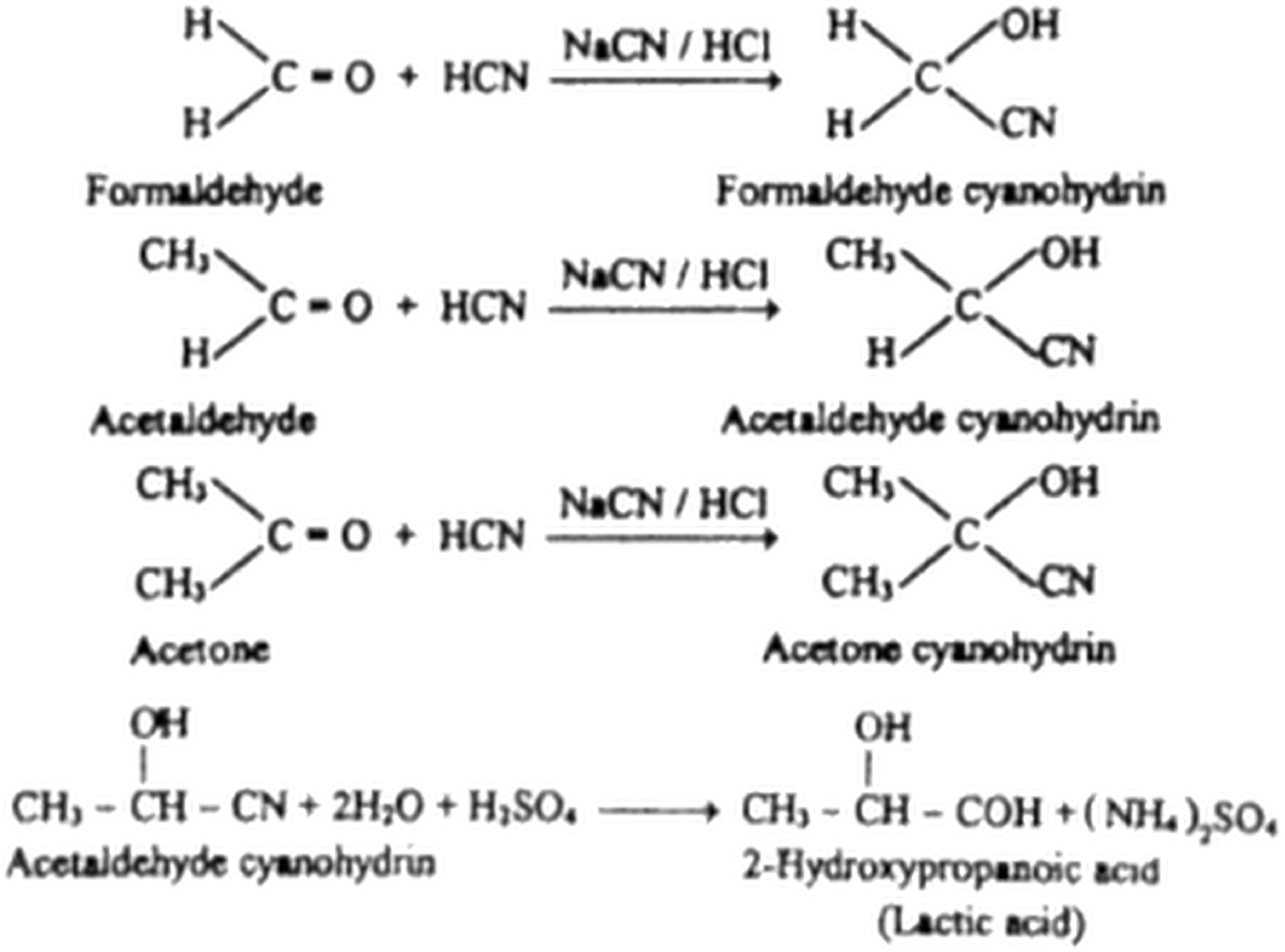
3) Addition of sodium bisulphate

4) Condensation reactions

5) Holoform reactions

1) Addition of hydrogen cyanide

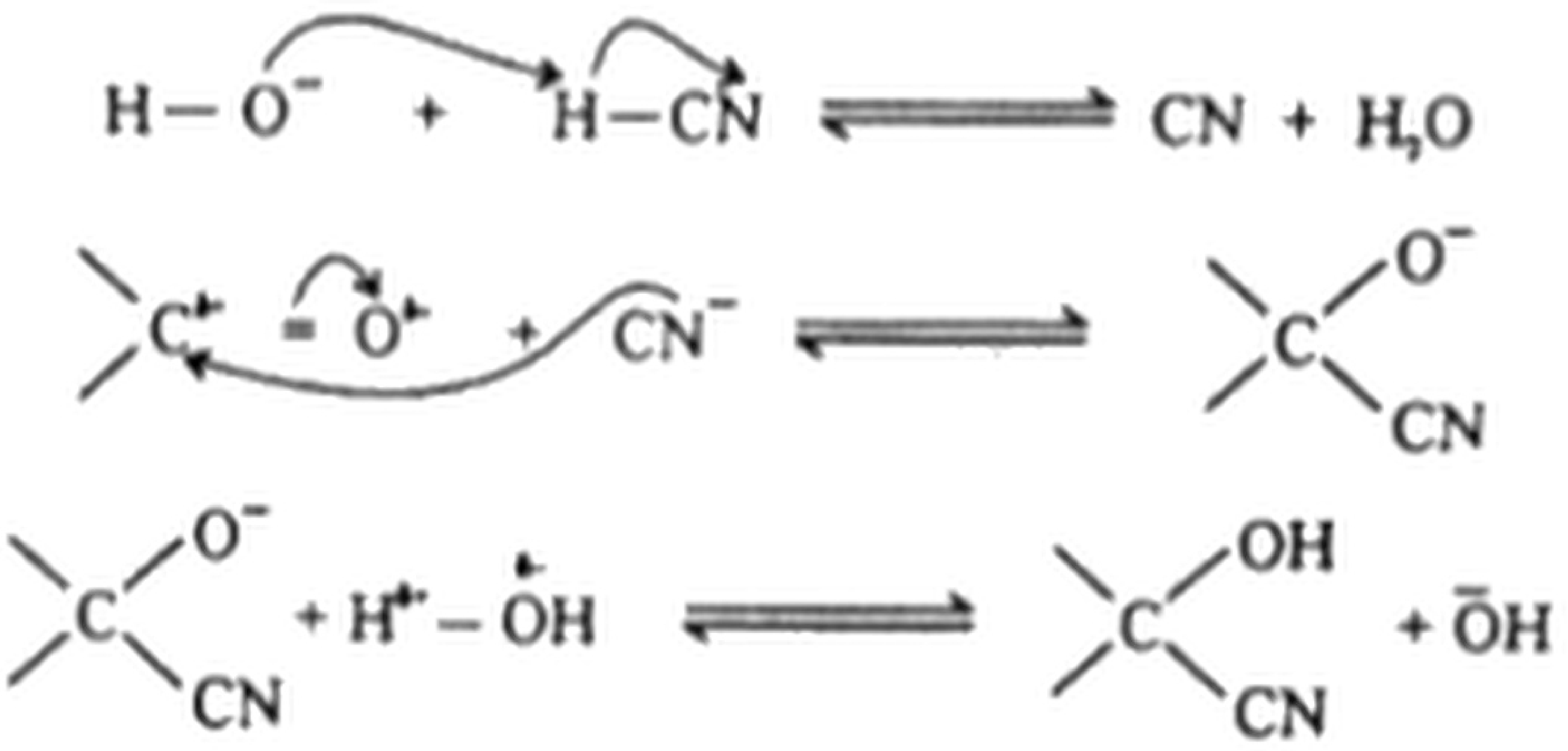
Hydrogen cyanide adds to aldehydes and ketones to form cyanohydrins. The acid generates HCN form sodium cyanide in HCl.



The reaction is based in the synthesis of a hydroxyl acid that contains one carbon atom more than the number of carbon atoms in the starting aldehydes or ketones.

Mechanism

The reaction is base catalyzed. The base (OR) generates cyanide ions which act as nucleophile. The mechanism of the reaction is as follows:



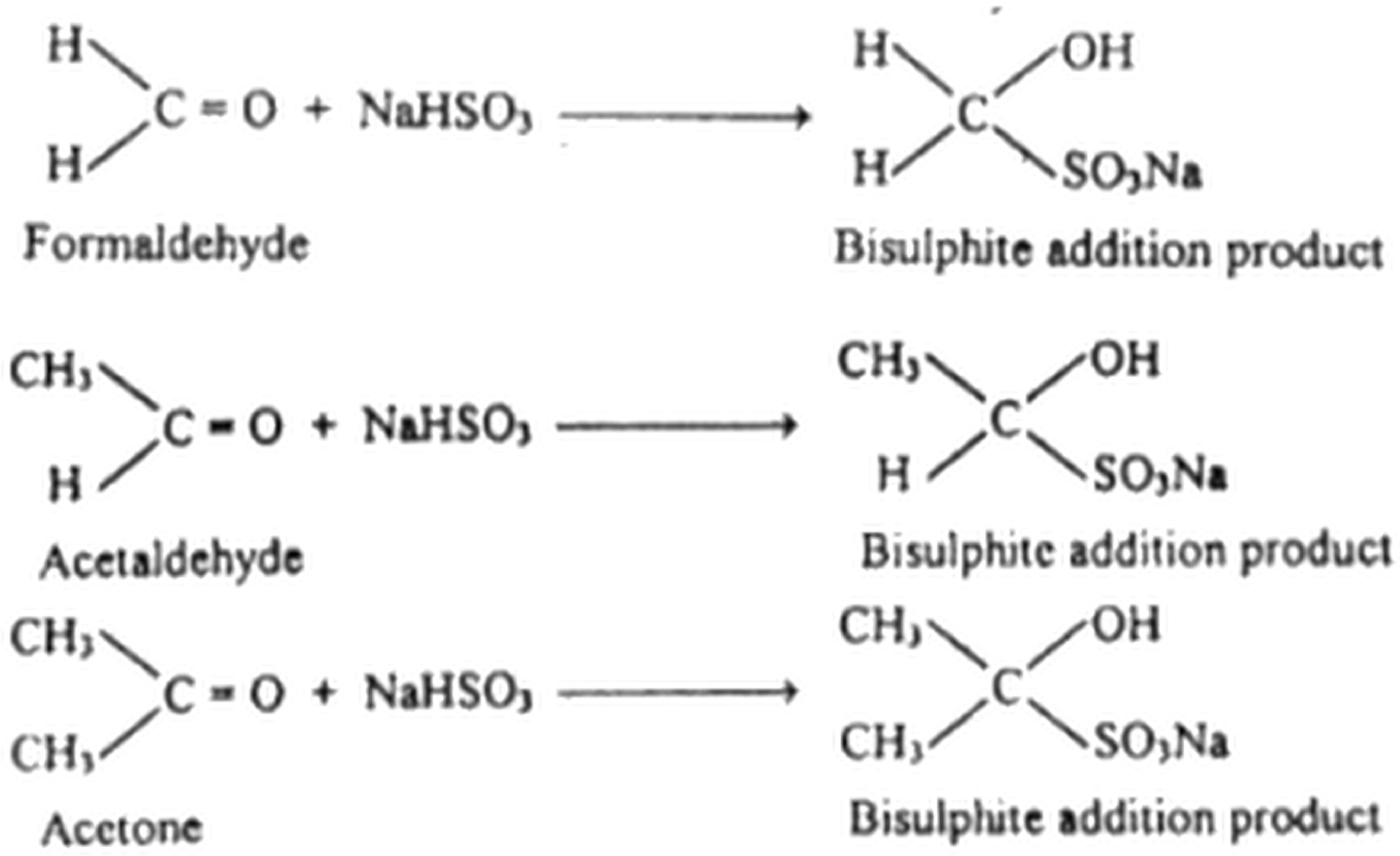
The hydroxide ion liberated in the formation of cyanohydrin reacts with undissociated hydrogen cyanide and produces more cyanide ions, which in turn react with more carbonyl compound.

1) Addition of Grignard's reagent

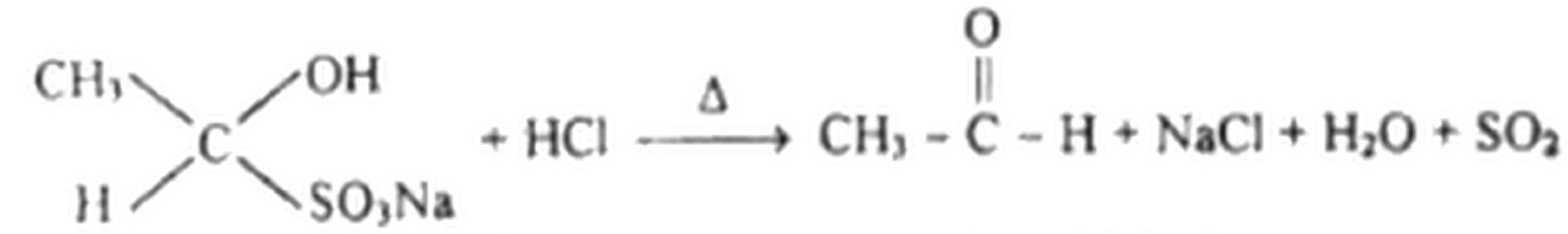
Grignard's reagents add to aldehydes and ketones to form adduct which on hydrolysis with a dilute mineral acid give alcohols. (Chapter 17)

2) Addition of sodium bisulphate

Aldehydes and small methyl ketones react with a saturated aqueous solution of sodium bisulphate to form a crystalline white precipitate of sodium bisulphate adduct.



Bisulphite on heating a dilute mineral acid (HCl or H2S04) regenerates the parent aldehydes or ketone.


Bisulphite addition product

Acetaldehyde

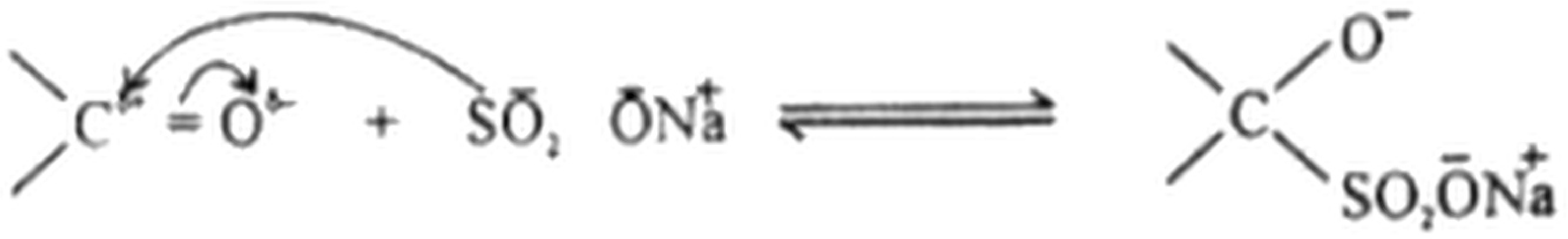
The reaction is used for the separation and purification of carbonyl compounds from non-carbonyl compounds such as alcohols.

Mechanism

Sodium bisulphate ionizes to form sulphate ions.

$$NaHSO_3 \rightleftharpoons S^-O_2 - O^- + H^+ + Na^+$$

The sulphite in acts as a nucleophile, since the sulphur atom is more nucleophilic than oxygen, a C-S bond is formed.



Proton is attached to the negatively charged oxygen atom to form bisulphate addition product.


Bisulphite addition product

Ketones in which both alkyl groups are larger than methyl do not react with sodium bisulphite.

1) Condensation reactions

The reaction in which two molecules of the same or different compounds combine to form a new compound with or without the elimination of a small molecule like H20 or NH3 are called condensation reactions.

a) ALDOL CONDENSATION

Definition:

Aldol condensation is a reaction in which two molecules of same or different carbonyl compound containing α-hydrogen (hydrogen attached to the carbon atom next to carbonyl group) combine together to from aldol or ketol, which usually loses water molecule.

Mild Alkaline conditions:

Aldol condensation takes place under mild alkaline conditions, for example in the presence of sodium carbonate, sodium bicarbonate, barium hydroxide, dilute sodium hydroxide or an alkoxide in low concentration.

Types:

Aldol condensation can occur:

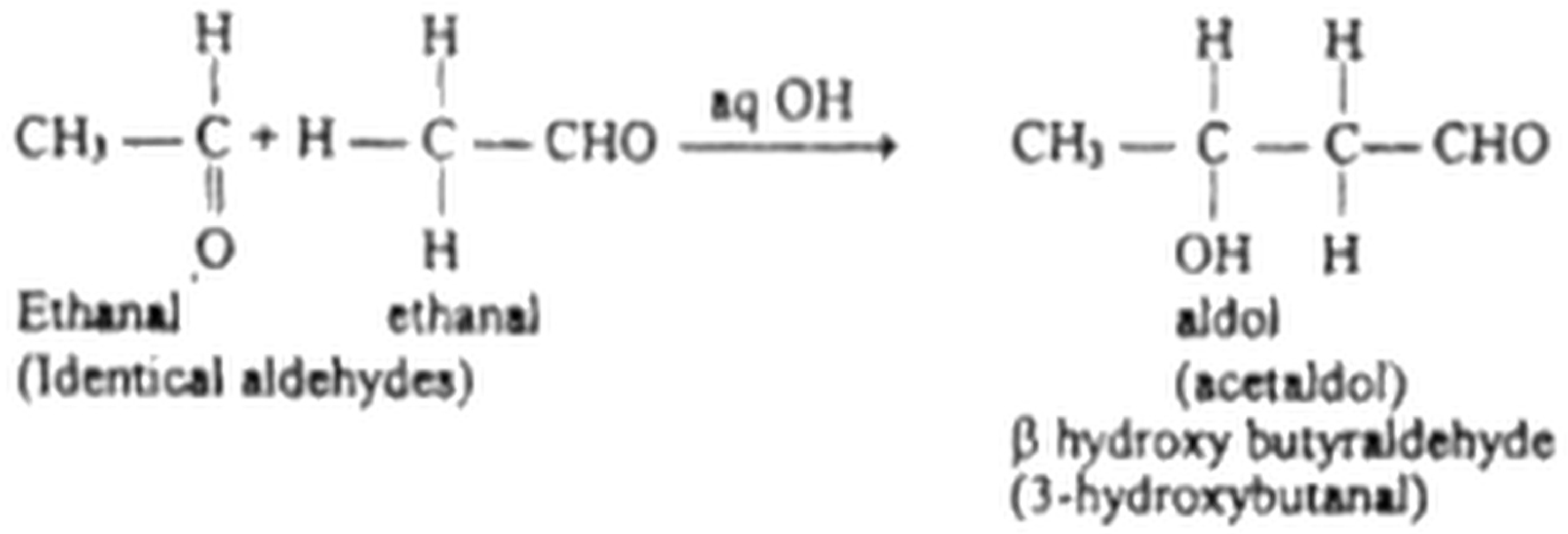
i) Between two aldehydes (identical or different)

ii) Between an aldehyde and a ketone

iii) Between two ketones (identical or different)

i) Condensation between two aldehydes:

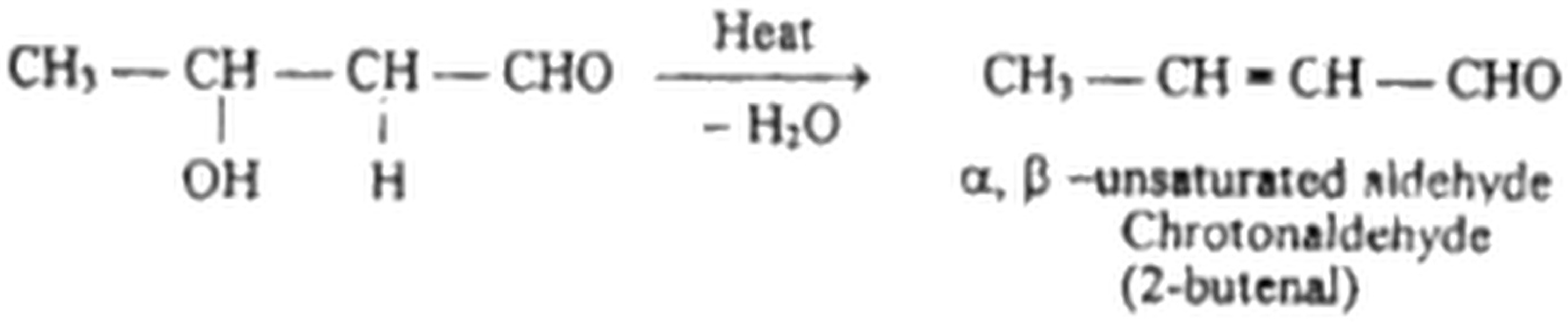
(a)



$$CH_3-\overset{H}{\underset{O}{C}} + H-\overset{H}{\underset{H}{C}}-CHO \xrightarrow{aq\ OH} CH_3-\overset{H}{\underset{OH}{C}}-\overset{H}{\underset{H}{C}}-CHO$$

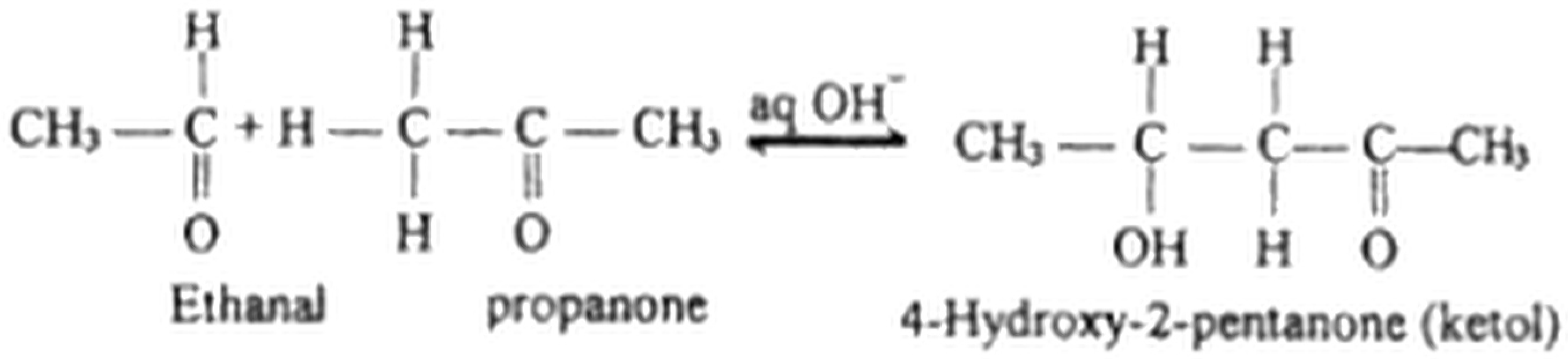
On heating aldol loses a molecule of water to form α, β-unsaturated aldehyde

(b)



$$CH_3-\underset{OH}{CH}-\underset{H}{CH}-CHO \xrightarrow[-H_2O]{Heat} CH_3-CH=CH-CHO$$

(ii) Condensation between aldehyde and ketone:



$$CH_3-\overset{H}{\underset{O}{C}} + H-\overset{H}{\underset{H}{C}}-\underset{O}{C}-CH_3 \xrightleftharpoons{aq\ OH^-} CH_3-\overset{H}{\underset{OH}{C}}-\overset{H}{\underset{H}{C}}-\underset{O}{C}-CH_3$$

Mechanism of Aldol Condensation:

Following steps are involved in aldol condensation.

I) Removal of a proton from α—carbon of aldehyde/ketone by base:

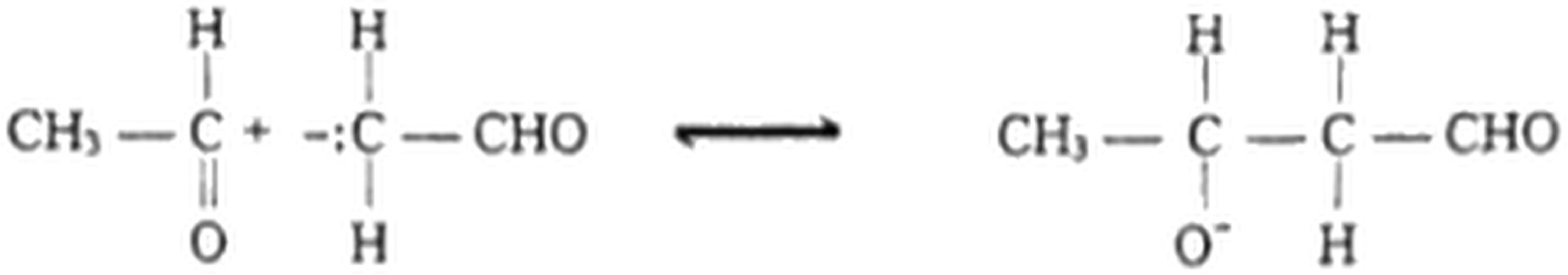
(Formation of nucleophile)

$$HO^- + H-\overset{H}{\underset{H}{C}}-CHO \longrightarrow HOH + {}^-:\overset{H}{\underset{H}{C}}-CHO$$

Carbanion (nucleophile)

2) Attack of nucleophile on carbonyl carbon to form alkoxide ion:

(Formation of alkoxide ion)

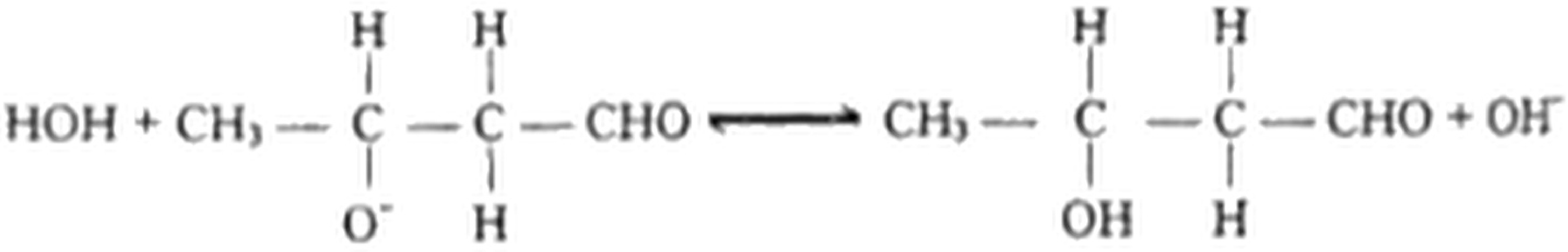


$$CH_3-\overset{H}{\underset{\underset{O}{\|}}{C}} + {}^-:\overset{H}{\underset{H}{C}}-CHO \longrightarrow CH_3-\overset{H}{\underset{O^-}{C}}-\overset{H}{\underset{H}{C}}-CHO$$

(alkoxide ion)

3) Removal of proton from water by alkoxide ion:

(Formation of aldol)



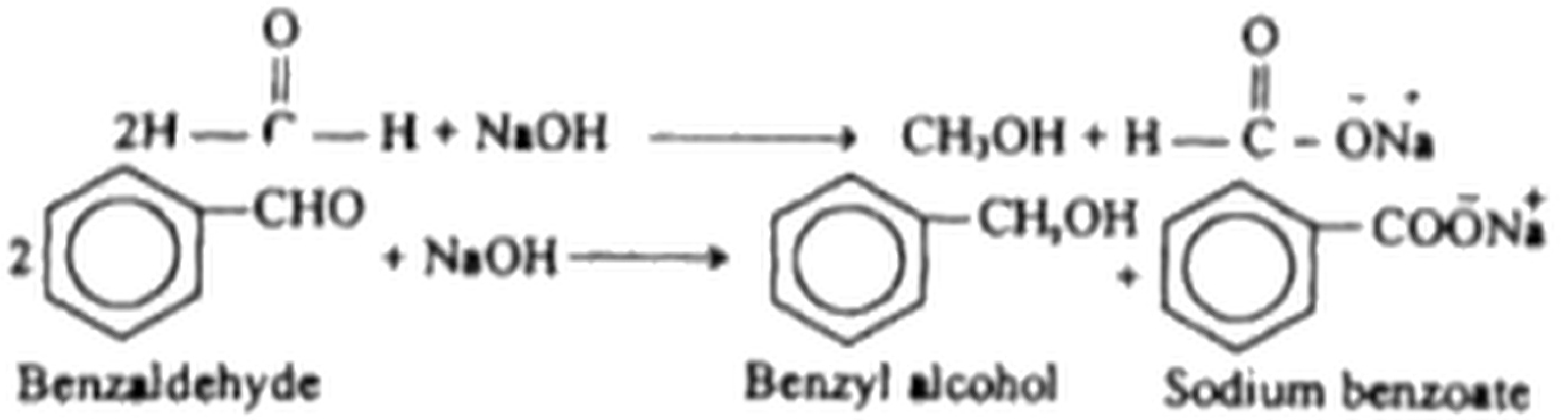
$$HOH + CH_3-\overset{H}{\underset{O^-}{C}}-\overset{H}{\underset{H}{C}}-CHO \longrightarrow CH_3-\overset{H}{\underset{OH}{C}}-\overset{H}{\underset{H}{C}}-CHO + OH^-$$

b) Cannizzaro's Reaction:

Aldehydes having no α-hydrogen atoms undergo Cannizzaro's reaction. It is a disproportionate (self-oxidation-reduction) reaction.

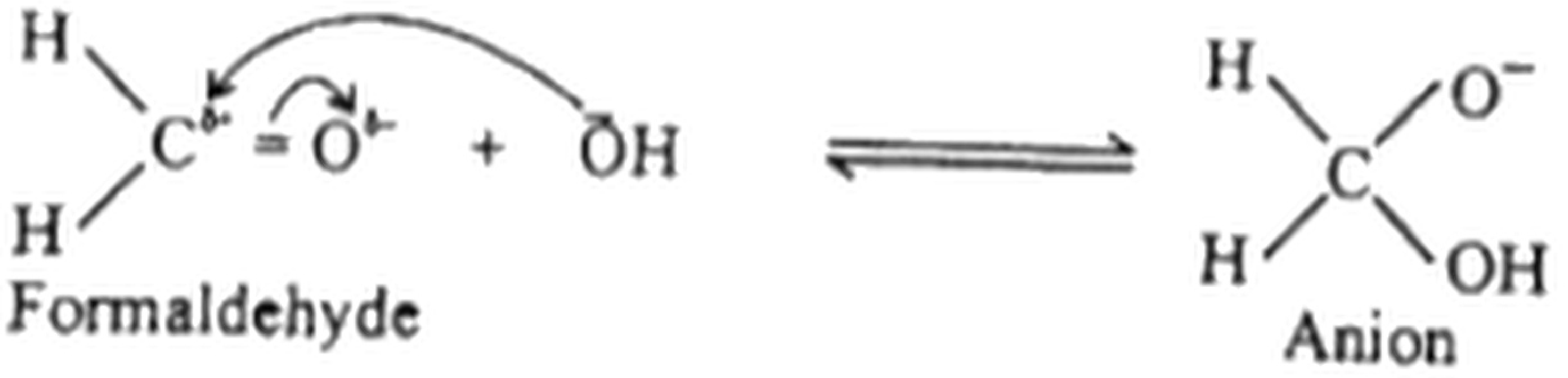
Two molecules of the aldehyde are involved.

One molecule is reduced into corresponding alcohol and the other is oxidized into the acid (in the salt form). The reaction carried out with 50 percent aqueous solution of sodium hydroxide at room temperature.

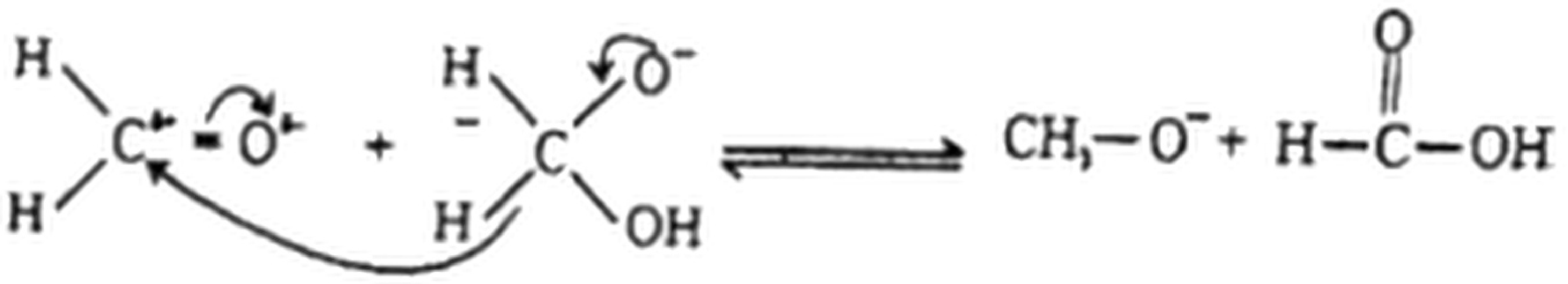


Mechanism of Cannizzaro's Reaction:

The hydroxide ion acts as a nucleophile. It attaches on the electrophilic carbonyl carbon to form a complex anion.



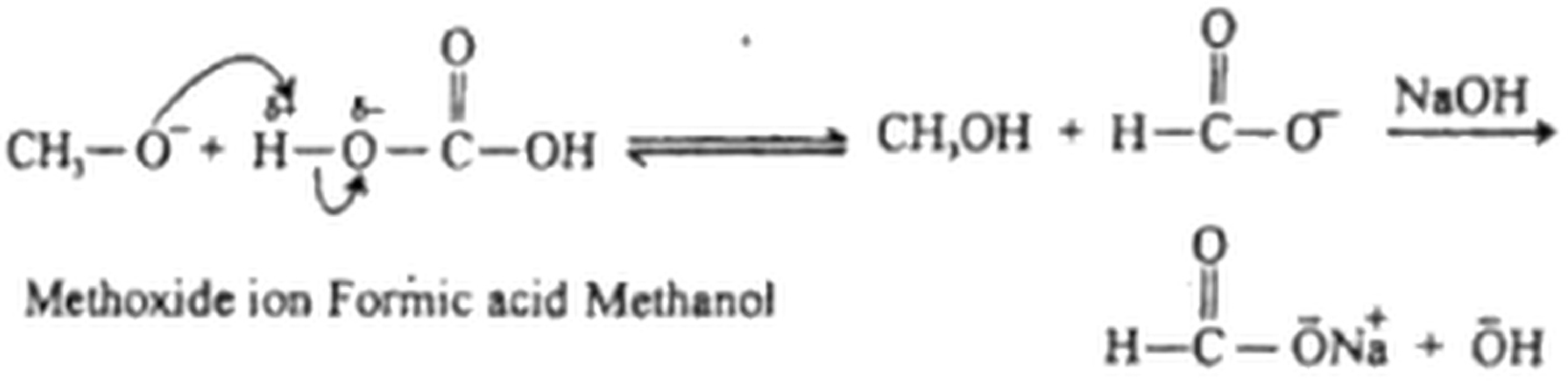
The anion transfers a hydride ion to second molecule of formaldehyde.



Formaldehyde Complex anion Methoxide ion Formic acid

The presence of the negative charge on oxygen of the anion helps in the loss of hydride ion.

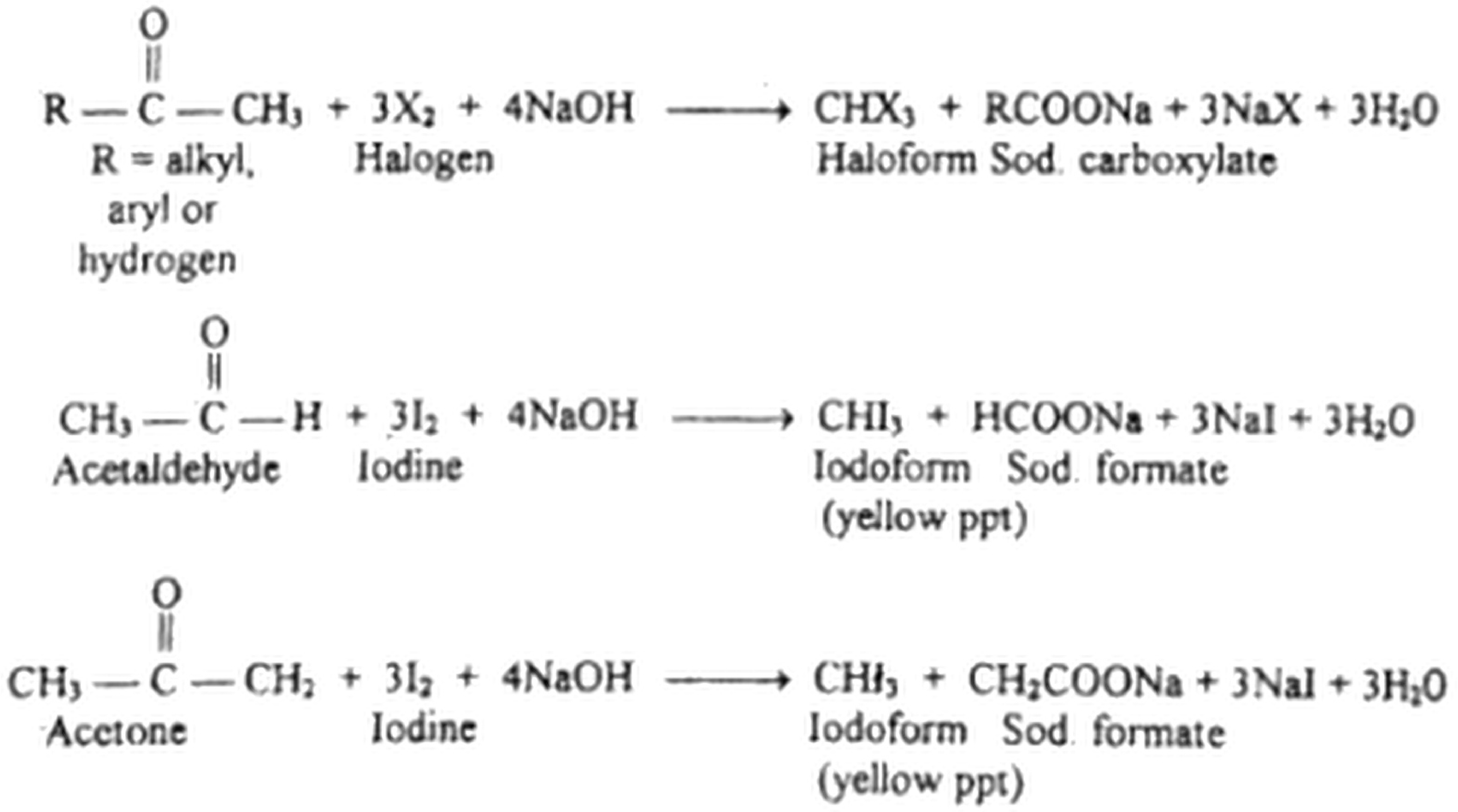
The methoxide ion acts as a base and abstracts a proton from formic acid to form methanol and formate ion.



The formate ion in the presence of alkali gives a salt of acid.

1) Haloform Reaction

Only acetaldehyde and methyl ketones react with halogens (Cl, Br, I) in the presence of sodium hydroxide to give haloform (chloroform, bromoform or iodoform) and sodium salt of the acid.

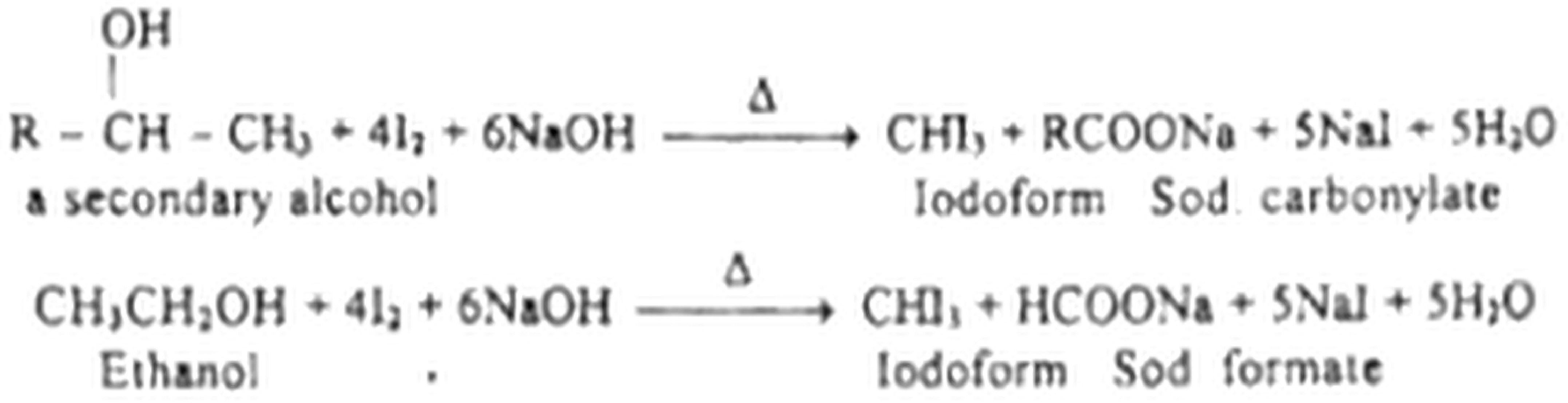


$$\underset{\substack{\text{R = alkyl,}\\ \text{aryl or}\\ \text{hydrogen}}}{R-\overset{\overset{O}{\|}}{C}-CH_3} + \underset{\text{Halogen}}{3X_2} + 4NaOH \longrightarrow \underset{\text{Haloform}}{CHX_3} + \underset{\text{Sod. carboxylate}}{RCOONa} + 3NaX + 3H_2O$$

$$\underset{\text{Acetaldehyde}}{CH_3-\overset{\overset{O}{\|}}{C}-H} + \underset{\text{Iodine}}{3I_2} + 4NaOH \longrightarrow \underset{\substack{\text{Iodoform}\\ \text{(yellow ppt)}}}{CHI_3} + \underset{\text{Sod. formate}}{HCOONa} + 3NaI + 3H_2O$$

$$\underset{\text{Acetone}}{CH_3-\overset{\overset{O}{\|}}{C}-CH_2} + \underset{\text{Iodine}}{3I_2} + 4NaOH \longrightarrow \underset{\substack{\text{Iodoform}\\ \text{(yellow ppt)}}}{CHI_3} + \underset{\text{Sod. formate}}{CH_2COONa} + 3NaI + 3H_2O$$

Secondary alcohols containing the methyl group also undergo this reaction. Ethanol is the only primary alcohol that gives this reaction.



$$\underset{\text{a secondary alcohol}}{R-\overset{\overset{OH}{|}}{CH}-CH_3} + 4I_2 + 6NaOH \xrightarrow{\Delta} \underset{\text{Iodoform}}{CHI_3} + \underset{\text{Sod. carbonylate}}{RCOONa} + 5NaI + 5H_2O$$

$$\underset{\text{Ethanol}}{CH_3CH_2OH} + 4I_2 + 6NaOH \xrightarrow{\Delta} \underset{\text{Iodoform}}{CHI_3} + \underset{\text{Sod formate}}{HCOONa} + 5NaI + 5H_2O$$

Halogen reaction, affords a convenient method for converting a methyl ketone to a carboxylic acid containing one carbon atom less than parent compound.

Iodoform Test:

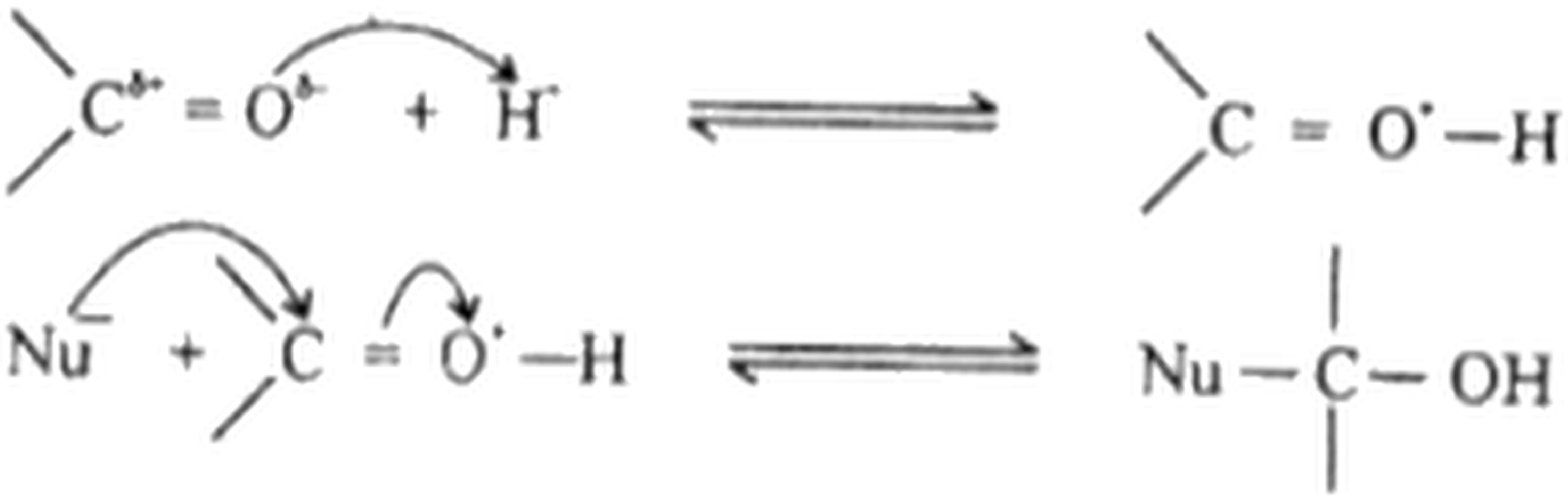
It is haloform reaction in which iodine and aqueous sodium hydroxide form water insoluble iodoform (a yellow solid). Iodoform test is used for distinguishing methyl ketones from other ketones. It is also used to distinguish ethanol form methanol and other primary alcohols. It can be used to distinguish acetaldehyde from other aldehydes.

ii) ACID CATALYSED NUCLEOPHILIC ADDITION REACTIONS

Acid catalyzed Addition Reactions

The addition is initiated by the proton liberated by the acid, which combines with the carbonyl oxygen. It increases the electrophilic character of the carbonyl carbon and the attack of the weaker nucleophile on the electrophilic carbon becomes easy.

The general mechanism of the reaction is as fallows.

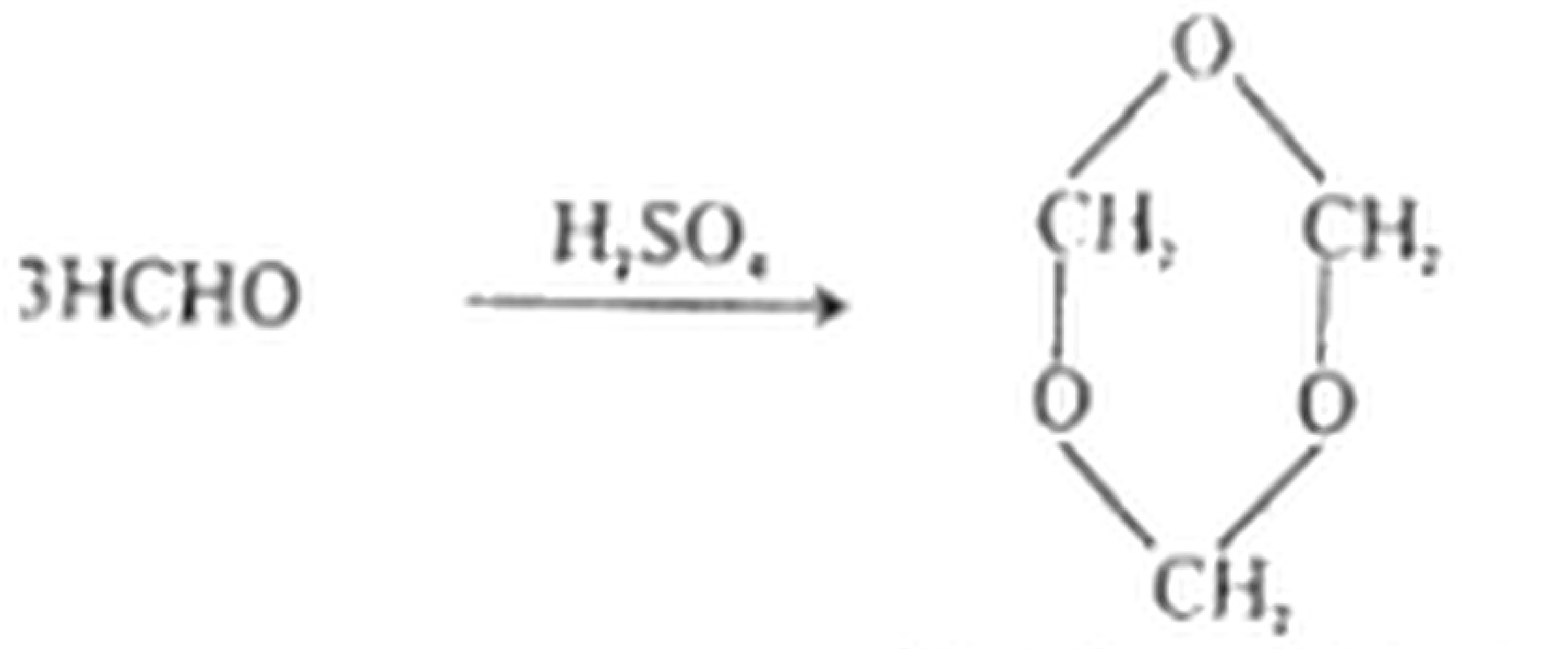


There are three types:

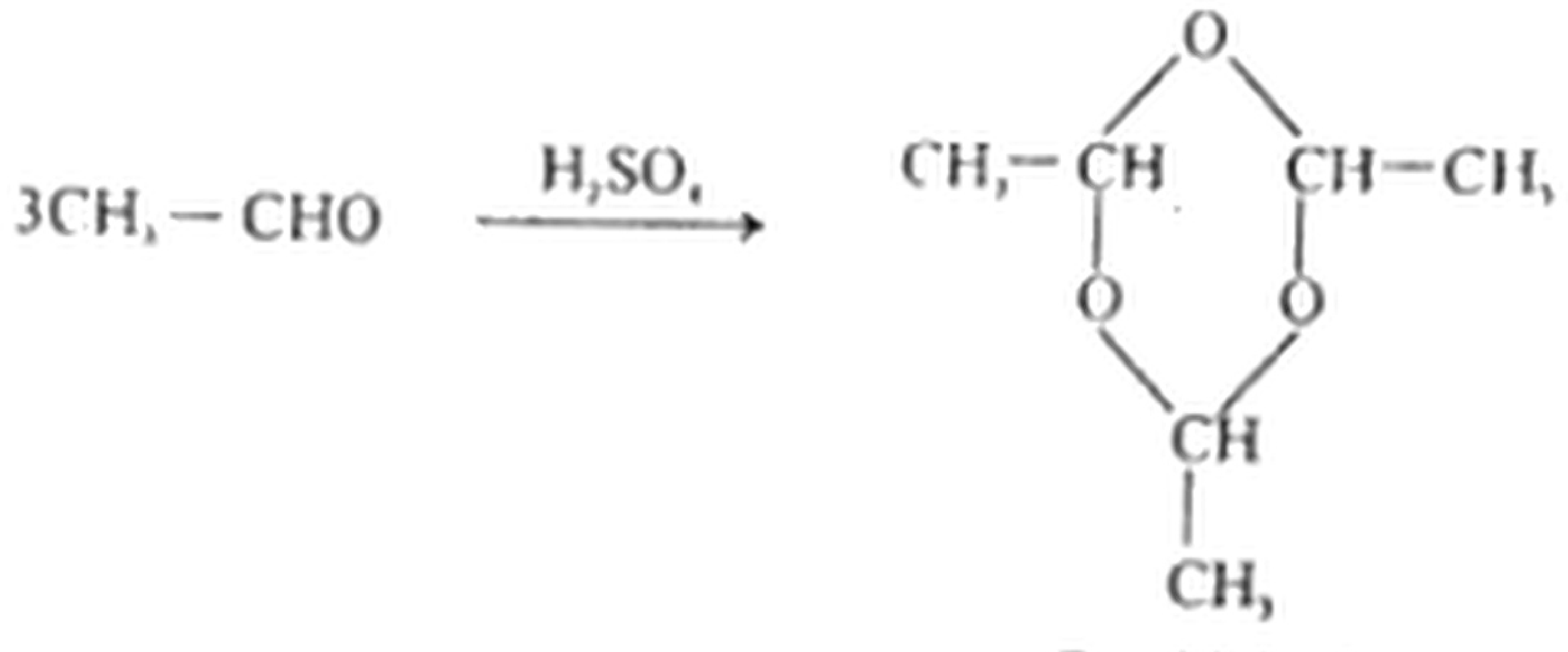
- I. Polymerization
- II. Addition of ammonia derivatives
- III. Addition of alcohols

Polymerization

Both formaldehyde and acetaldehyde polymerize in the presence of dil. H2S04 to give metaformaldehyde and paraldehyde.



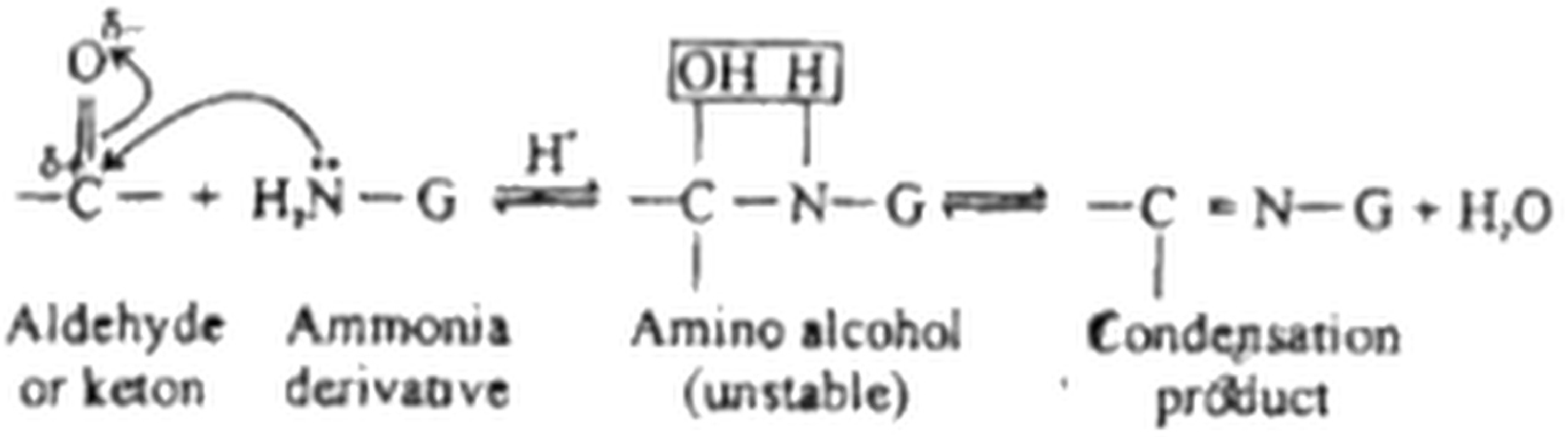
Metaformaldehyde



Paraldehyde

Addition of ammonia derivatives

Aldehydes and ketones react with ammonia derivatives,, G-NH2 to form compounds containing the group —C N — G. The reaction is known as condensation reaction or addition—elimination reaction because water is lost after addition occurs. The general reaction is given below.



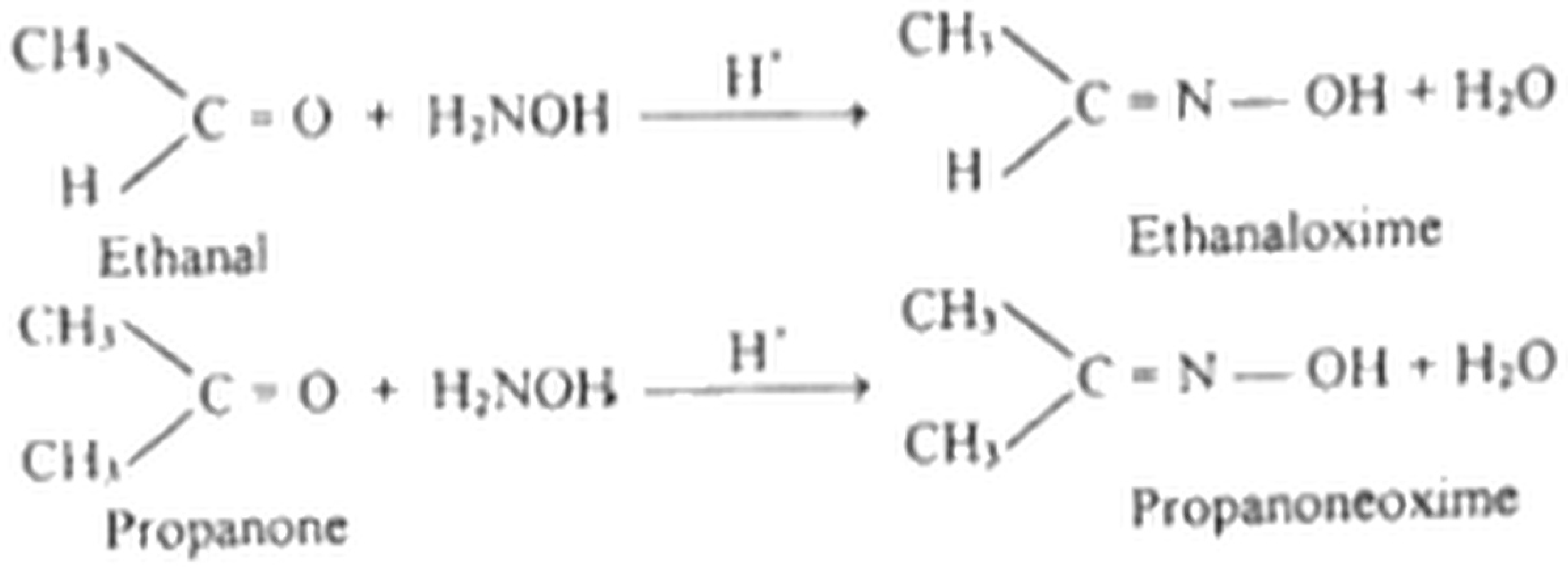
Where $G = \ddot{O}H, — \ddot{N}H_2 — \ddot{N}HC_6H_5, — \ddot{N}HCON_2$, etc

Specific Examples:

Some commonly used ammonia derivatives are hydroxylamine, NH20H, hydrazine, NH_2NH_2, phenylhydrazine, $C_6H_6NHNH_2$, semicarbazide, $NH_2NHCONH_2$, and 2,4- dinitrophenylhydrazine.

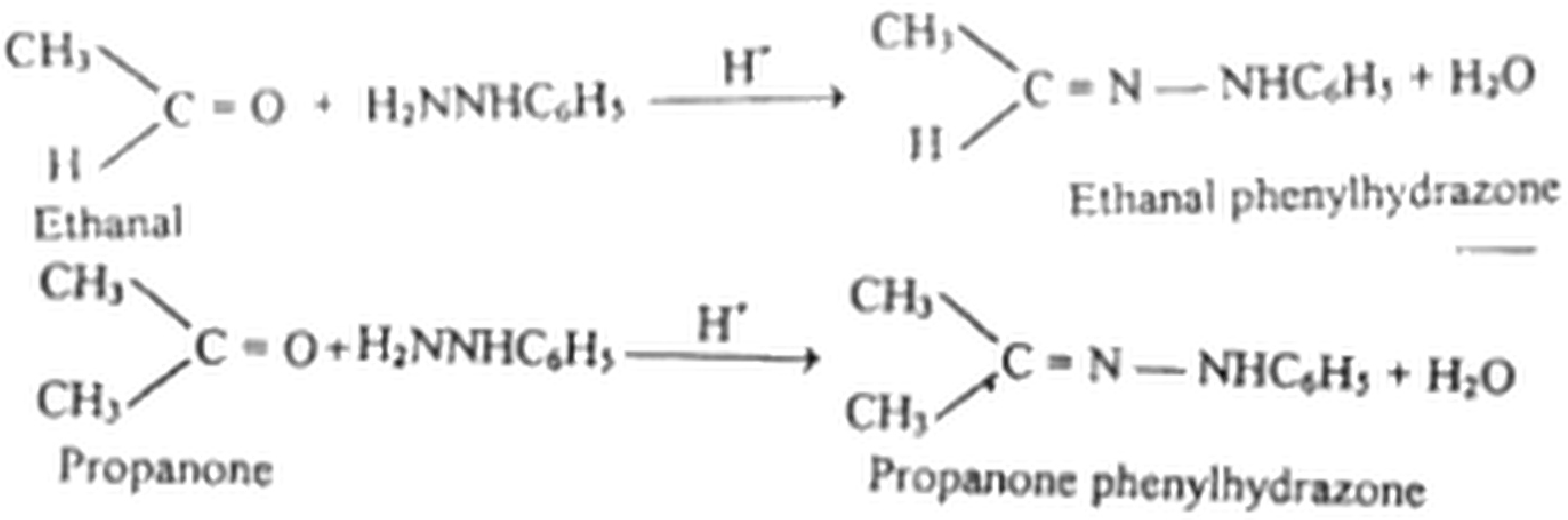
Reaction with hydroxylamine

Aldehydes and ketones react with hydroxylamine to form oximes in the presence of an acid.



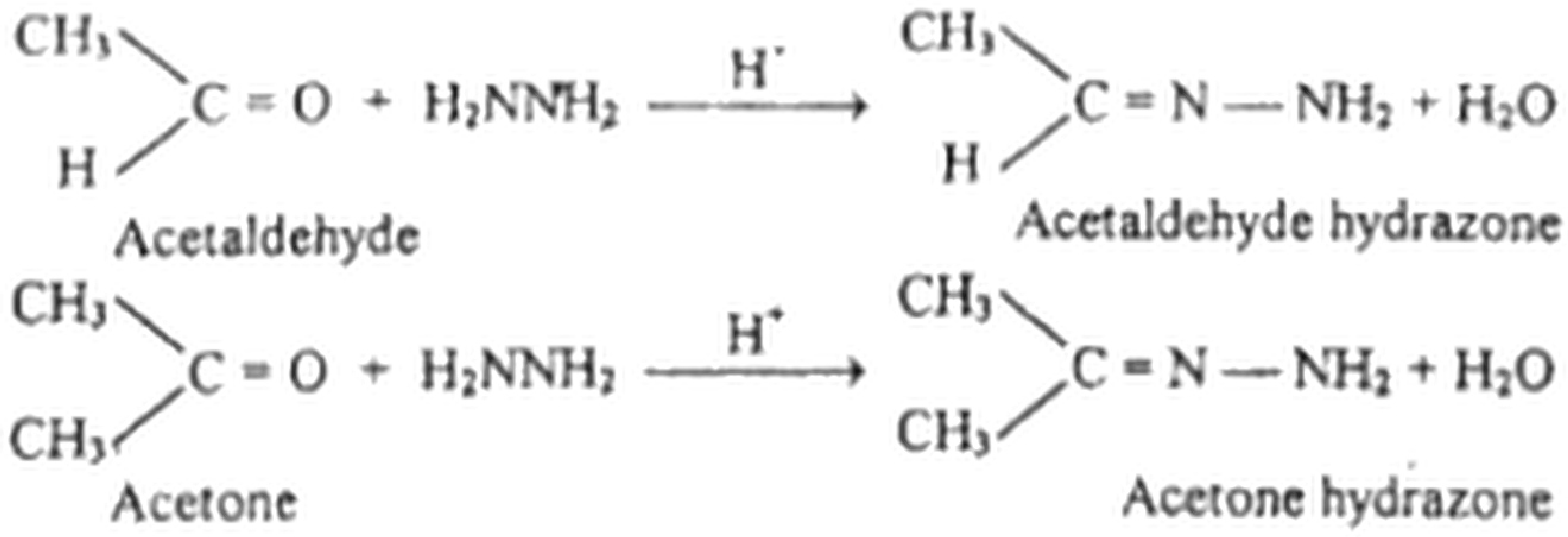
Reaction with Phenylhydrazone

Aldehydes and ketones react with phenylhydrazone to form phenylhydrazones in the presence of an acid.



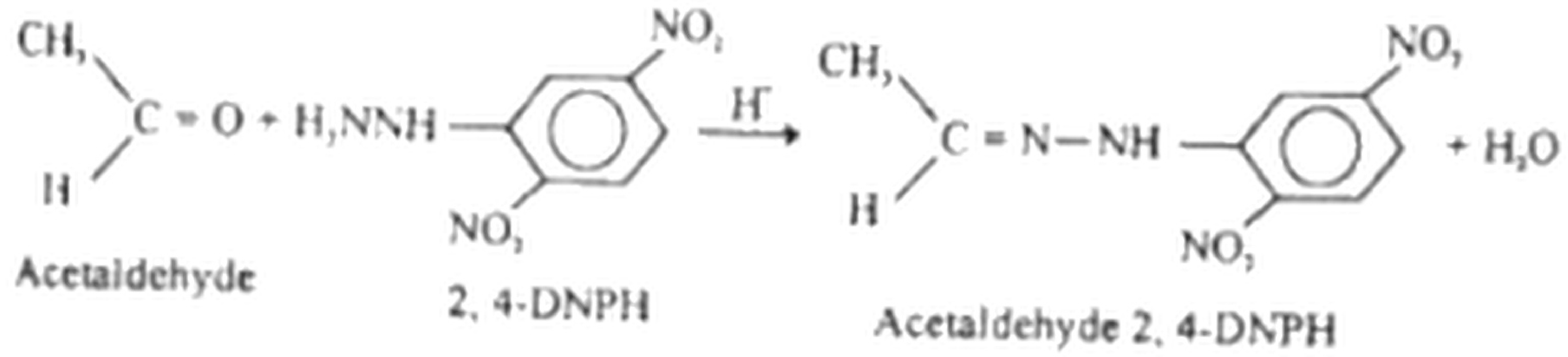
Reaction with hydrazine

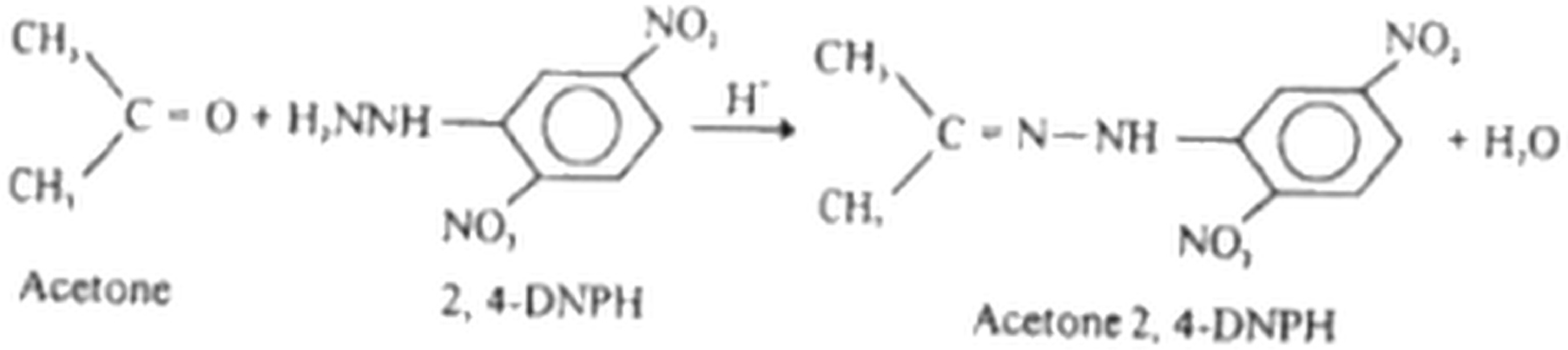
Aldehydes and ketones react with hydrazine to form hyrdazones in the presence of an acid.



Reaction with 2,4-dinitrophenylhydrazine

Aldehydes and ketones react with 2,4-dinitrophenylhydrazine to form 2,4dinitrophenylhydrazone in the presence of an acid.

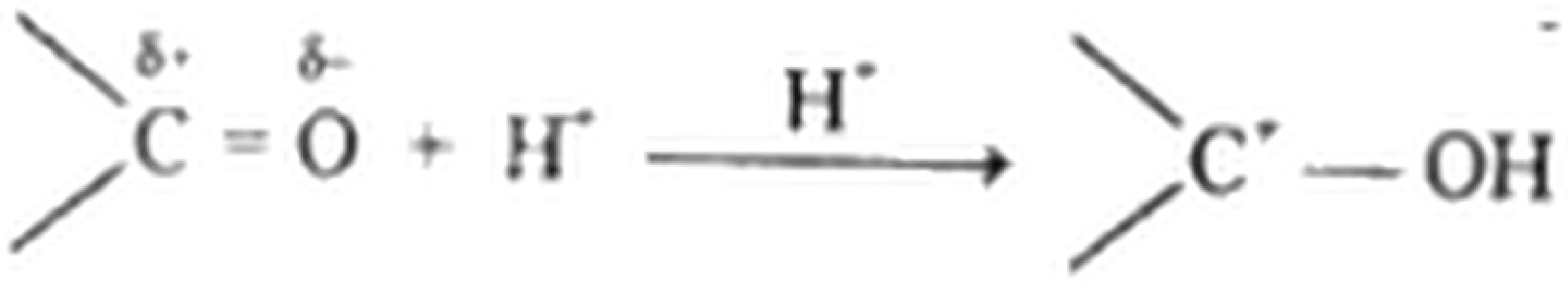




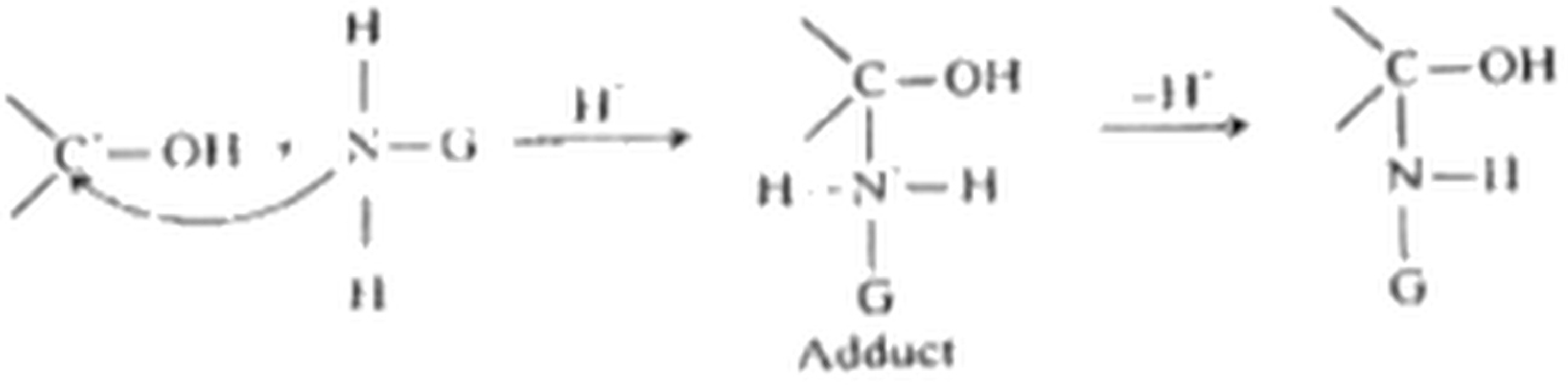
The reaction can be used for the identification of aldehydes and ketones because 2,4dinitrophenylhydrazones are usually yellow or orange crystalline solids.

Mechanism of the Reaction of ammonia derivatives

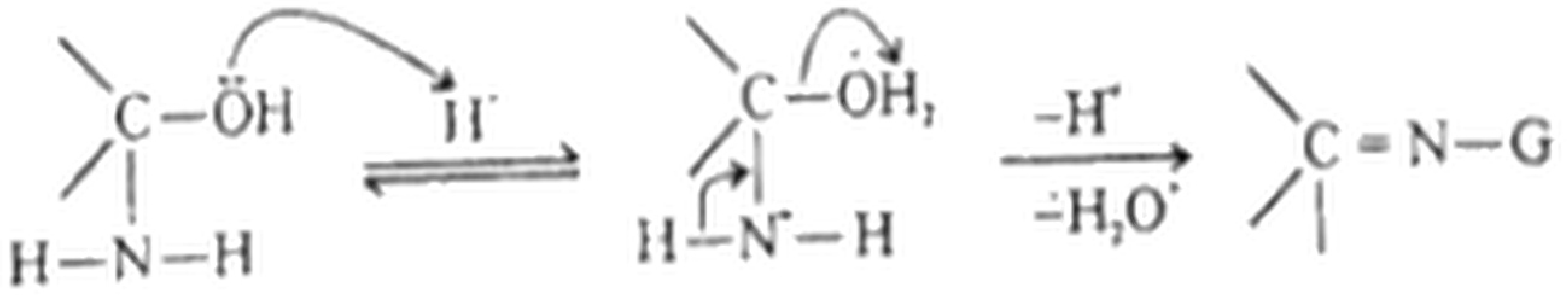
Step (i) Protonation of oxygen of the carbonyl group.



Step (ii) Nucleophilic attack of nitrogen of ammonia 'derivative on the electrophilic positively charged carbon and deprotonation of the adduct.



Step (iii) Protonation of oxygen of hydroxyl group followed by the removal of water.

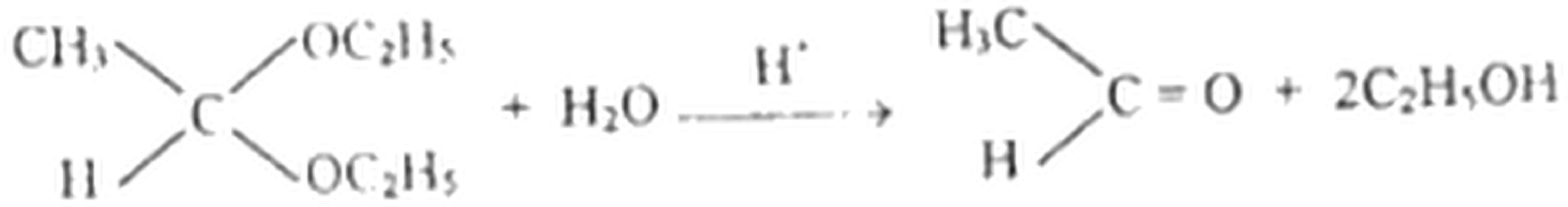


Addition of alcohols

Aldehydes combine with alcohols in the presence of hydrogen chloride gas to form acetals. The hydrogen chloride acts as a catalyst.

1, 1-Diethoxyethane

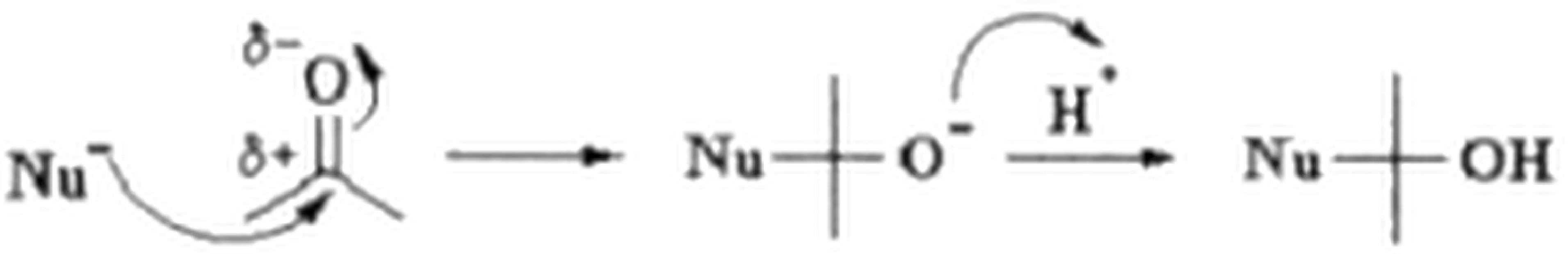
The reaction may be used to protect the aldehyde group against alkaline oxidizing agents. To regenerate aldehyde, the acetal is hydrolyzed in the presence of an acid.



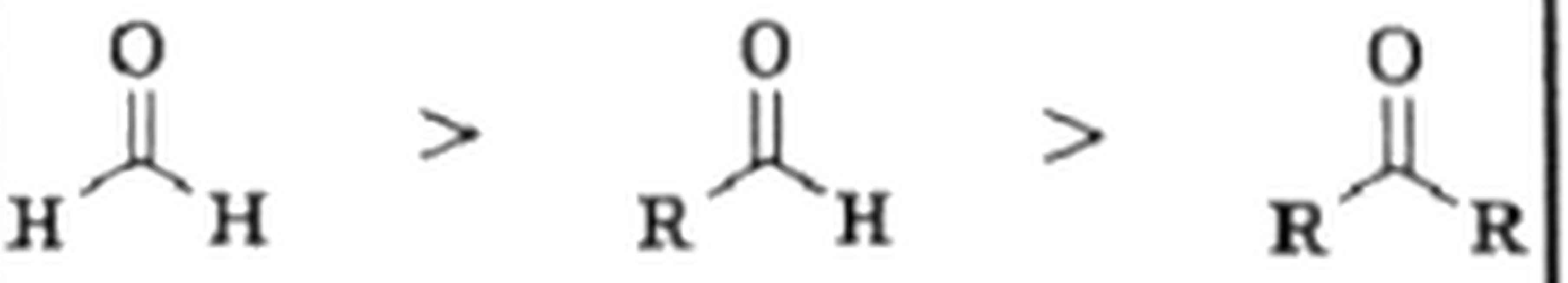
Note: Ketones do not react under these conditions.

19.6.2 Relative Reactivity

Overall a simple nucleophilic addition can be represented with curly arrows as follows:



The reactivity of aldehydes and ketones can be easily rationalized by considering the important resonance contributor which has charge separation with a +ve C and -ve O.

<table>
<tr><td colspan="2">In general the reactivity order towards nucleophiles is : aldehydes > ketones (see below)
The substituents have two contributing factors on the reactivity at the carbonyl C:</td></tr>
<tr><td>1. Size of the substituents attached to the C=O. Larger groups will tend to sterically hinder the approach of the Nucleophile.
2. The electronic effect of the substituent. Alkyl groups are weakly electron donating so they make the C in the carbonyl <i>less</i> electrophilic and therefore <i>less</i> reactive towards nucleophiles.</td><td></td></tr>
</table>

These trends are supported by the trends in the equilibrium data for the formation of hydrate.

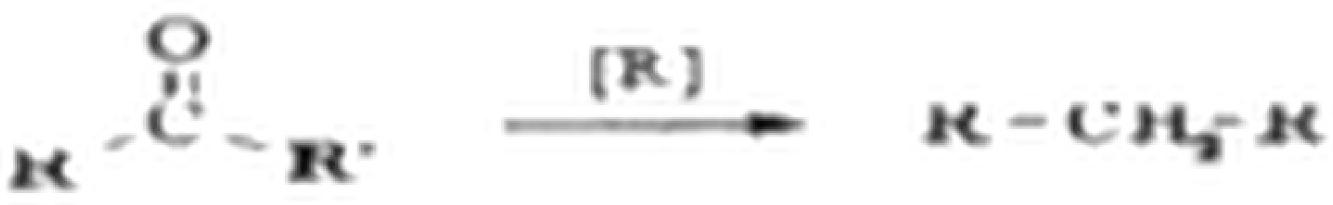
Carbonyl	K/ M^{-1}	% Hydrate	
methanol	41	99.96	
ethanal	1.8×10^{2}	50	
Carbonyl 2,2-dimethylpropanal	4.1 x 10-3	19	Hydrate
propanone	2.5 x 105	0.14	

(K = [hydrte]/C = O

Q8. Give Reduction reactions of Aldehydes and Ketones.

Answer

Reduction to Hydrocarbons



$$R-\overset{O}{\overset{\|}{C}}-R' \xrightarrow{[R]} R-CH_2-R$$

I) Clemmensen Reduction (acidic conditions)

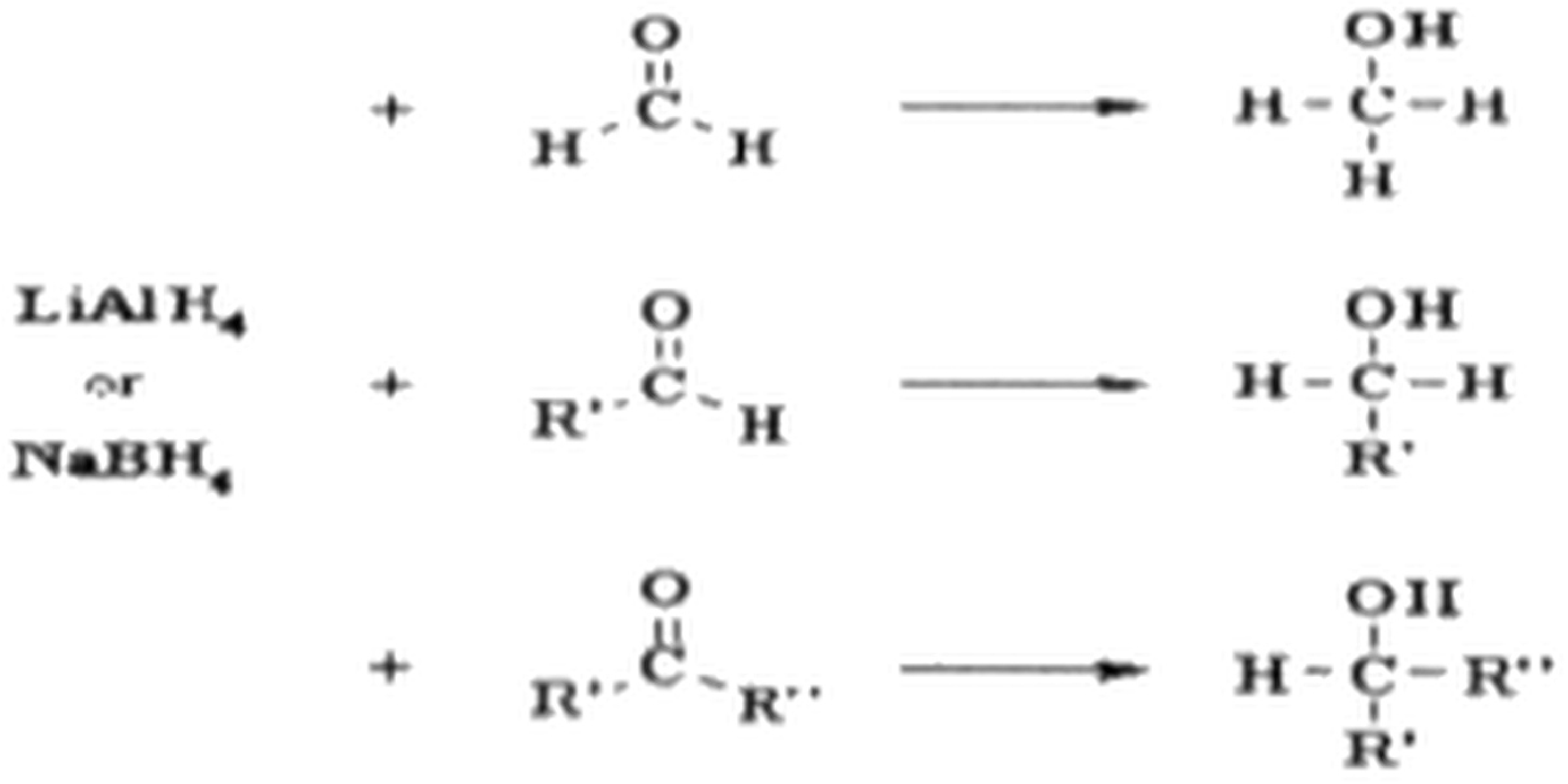
Zn(Hg) in HCl reduced the C=O into -CHz Wolff-Kishner Reduction (basic conditions)

2) NH_2NH_2 / KOH / ethylene glycol (a high boiling solvent) reduces the C=O into $-CH_2-$

Overview

- These reduction methods do not reduce C = C , or $—CO_2H$
- The choice of method should be made based on the tolerance of other functional groups to the acidic or basic reaction conditions.

3) Hydride Reductions of Aldehydes and Ketones



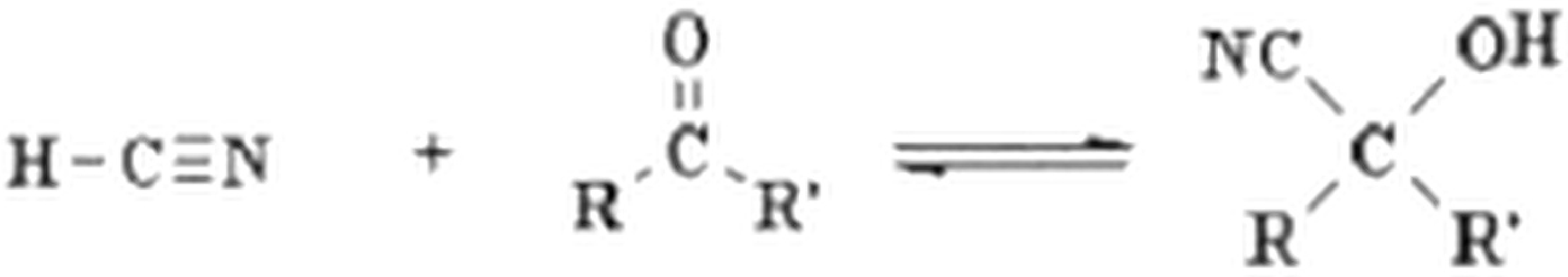
- Aldehydes and ketones are most readily reduced with hydride reagents.
- The reducing agents LiAlH4 and NaBH4 act as a source of (hydride ion).
- Overall 2 H atoms are added across the C=O to give H-C-O-H.

406 Star Key to Clm1istry 12 (Federal Board)

- Hydride reacts with the carbonyl group, C = O, in aldehydes or ketones to give alcohols.
- The substituents on the carbonyl tell the nature of the product alcohol.
- Reduction of methanal (formaldehyde) gives methanol.
- Reduction of other aldehydes gives primary alcohols.
- Reduction of ketones gives secondary alcohols.
- The acidic work-up converts an intermediate metal alkoxide salt into the desired alcohol via a simple acid base reaction.

Q9. Reactions of aldehydes of ketones using carbon nucleophiles.

Answer



- Cyanide adds to aldehydes and ketones to give a cyanohydrin.
- The reaction is usually carried out using NaCN or KCN with HCl.
- HCN is a fairly weak acid, but very toxic.

- The reaction is useful since the cyano group can be converted into other useful functional groups (-C02H or -CH2NH2)

11) Nucleophilic Addiction of Cyanide to an Aldehyde

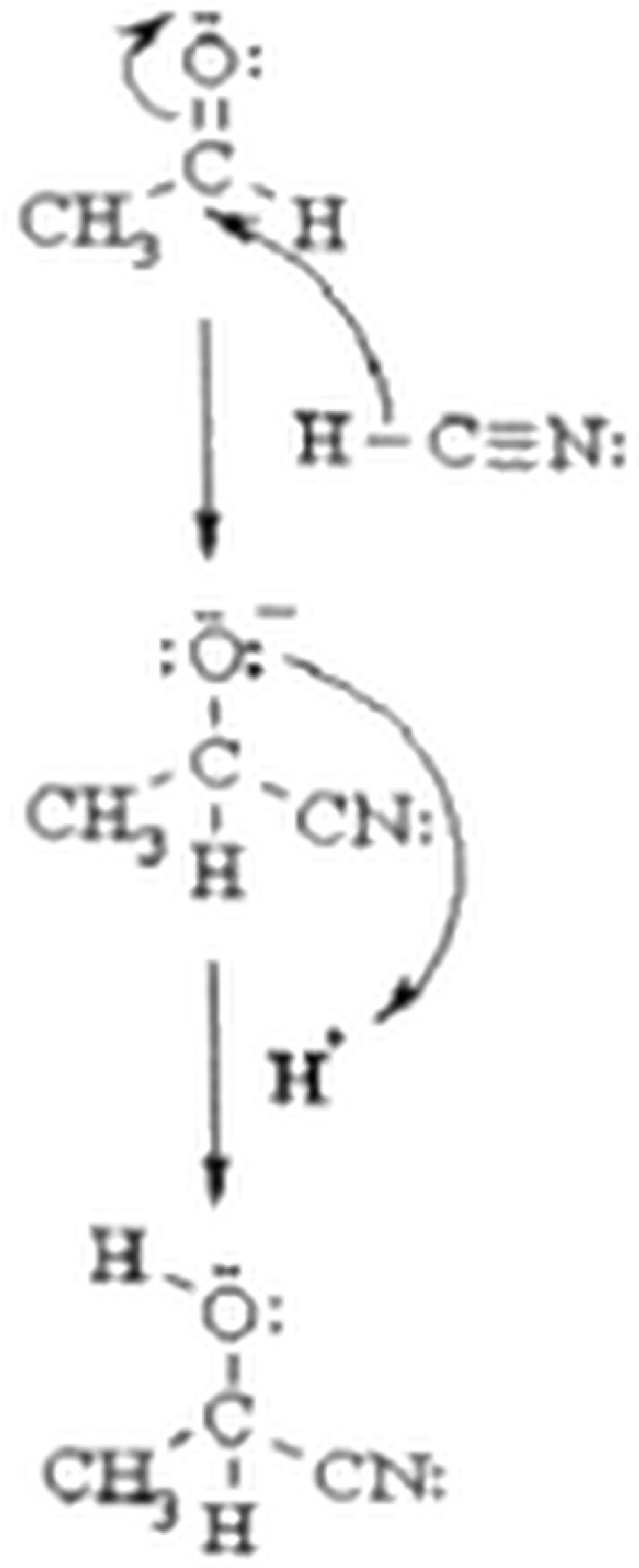
Step 1:

The nucleophilic C in the cyanide adds to the electrophilic C in the polar carbonyl group, electrons from the C=O move to the electronegative O creating an intermediate alkoxide.

Step 2:

An acid/base reaction. Protonation of the

alkoxide oxygen creates the cyanohydrin product.



iii) Using Nitrogen Nucleophiles

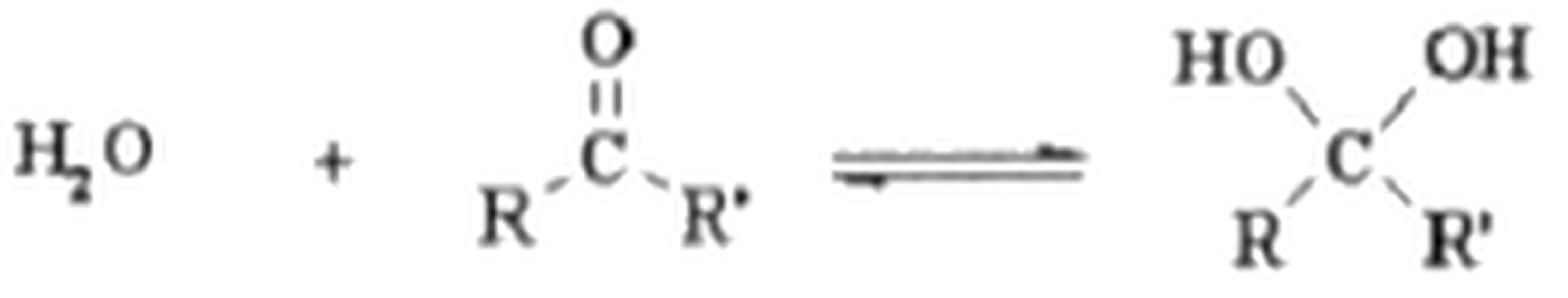
Reactions of Primary Amine derivatives

imine

- Primary amines, R-NH_2 or ArNH_2, undergo nucleophilic addition with aldehydes or ketones to give carbinolamines which then dehydrate to give substituted imines.
- The reactions are usually carried out in an acidic buffer to activate the C=O and facilitate dehydration but without inhibiting the nucleophile.
- Systems of the general type Z-NH_2 undergo this type of reaction and can be used

iv) Using Oxygen Nucleophiles

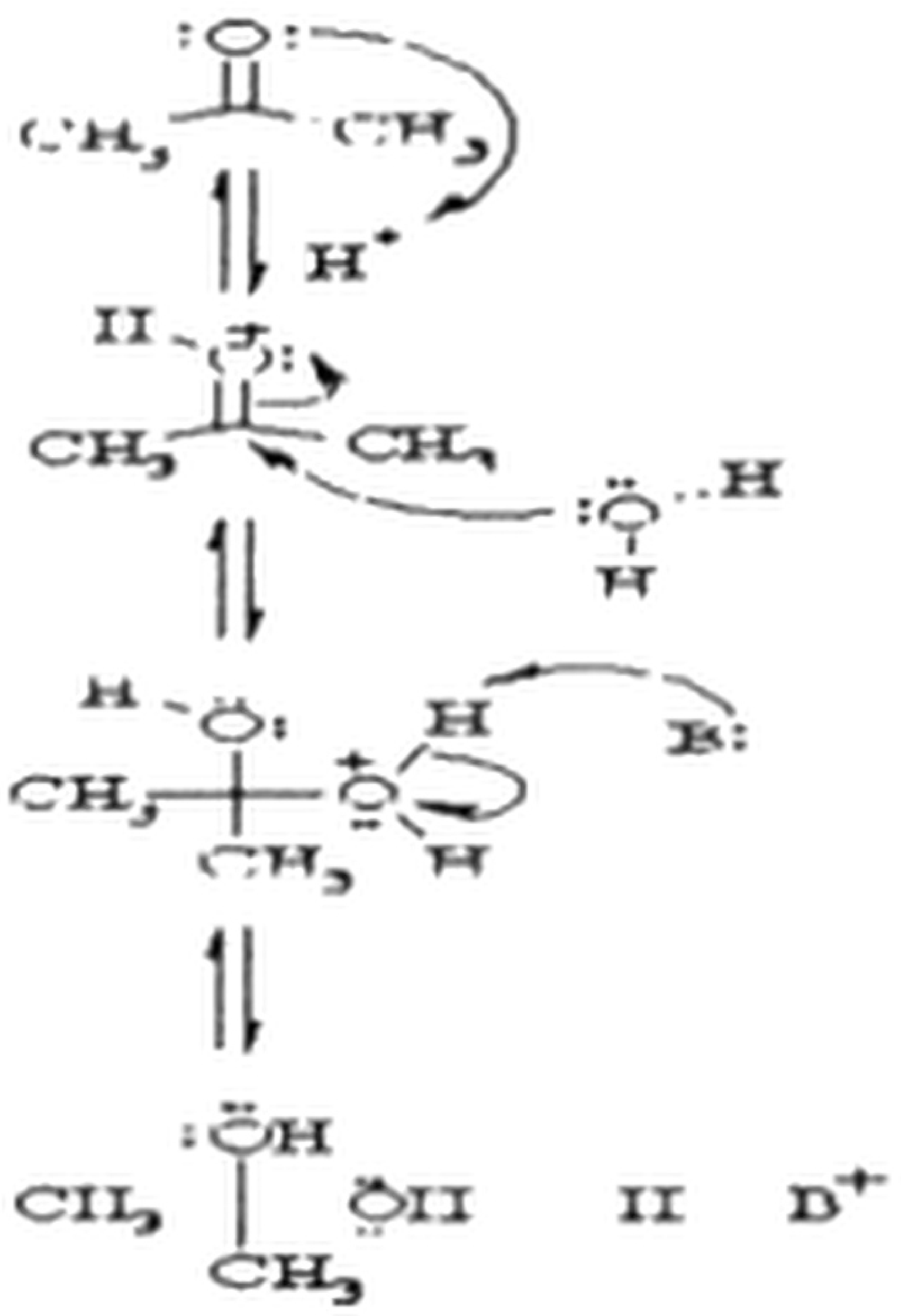
Formation of Hydrates



hydrate

- Aldehydes and ketones react with water to give I , I -geminal diols known as hydrates.
- In general, hydrates are not stable enough to be isolated as the equilibrium shifts back to starting materials.
- However, hydrates are the reactive species in the oxidation of aldehydes to acids.
- Understanding the mechanism is useful before looking at the very closely related reactions of alcohols.

MECHANISM FOR THE ACID catalyzed FORMATION OF HYDRATES



Step 1:

An acid/base reaction. Since there is only a weak nucleophile, we need to activate the carbonyl by protonating on O.

step 2:

The nucleophilic O in the water attacks the electrophilic C in the CFO, breaking the 't bond and giving the electrons to the positive O.

Step 3:

An acid/base reaction. Deprotonation of the oxonium ion neutralizes the charge giving the hydrate.

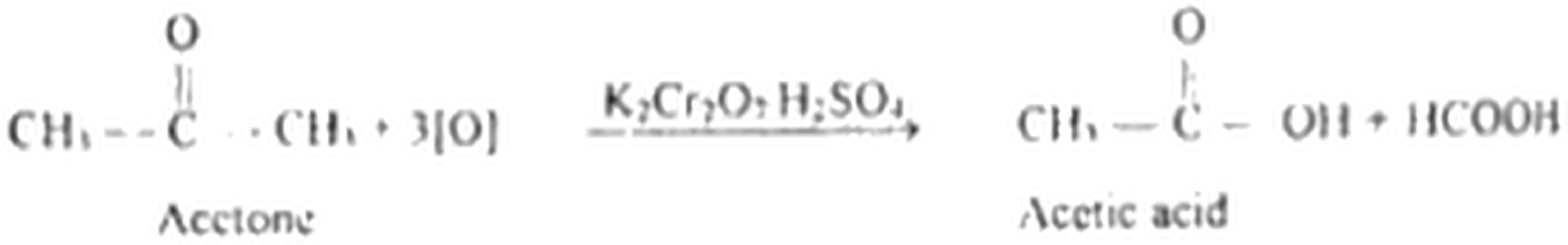
v) Oxidation Reactions

Oxidation of Aldehydes:

Mild oxidizing agents like Tollen's reagent, Fehling's solution and Benedict's solution easily oxidize aldehydes to carboxylic acids. They are also oxidized by strong oxidizing agents such as $K_2Cr_2O_7/H_2SO_4$, $KMnO/H_2SO_4$, and dilute nitric acid. The hydrogen atom attached to the carbonyl group in aldehydes is oxidized to OH group in these reactions.

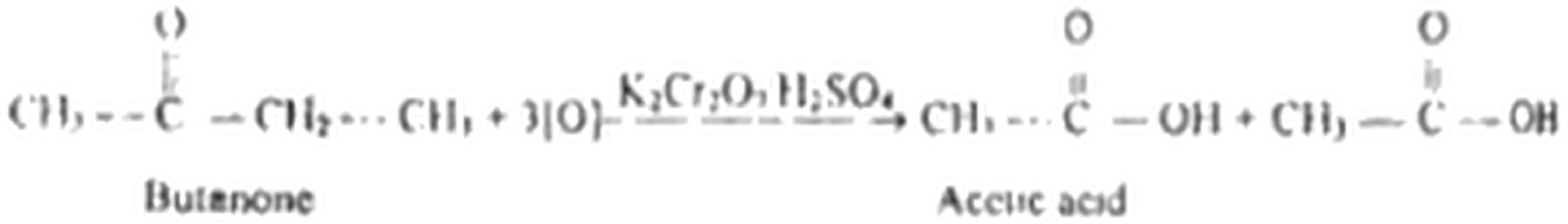
Oxidation of Ketones:

Ketones are only oxidized by strong oxidizing agents such as K_2Cr_2O/H_2SO_4, $KMnO/H_2SO_4$ and conc. HN03. The carbon atom joined to the smaller number of hydrogen atoms is oxidized. In case of symmetrical ketones only one carbon atom adjacent to the carbonyl group is oxidized and mixture of two carboxylic acids is always obtained.



$$\underset{\text{Acetone}}{CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3} + 3[O] \xrightarrow{K_2Cr_2O_7\,H_2SO_4} \underset{\text{Acetic acid}}{CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-OH} + HCOOH$$

However, in case of unsymmetrical ketones, the carbon atom joined to the smaller number of hydrogen atoms is preferentially oxidized and the carbonyl group remains with the smaller alkyl group.



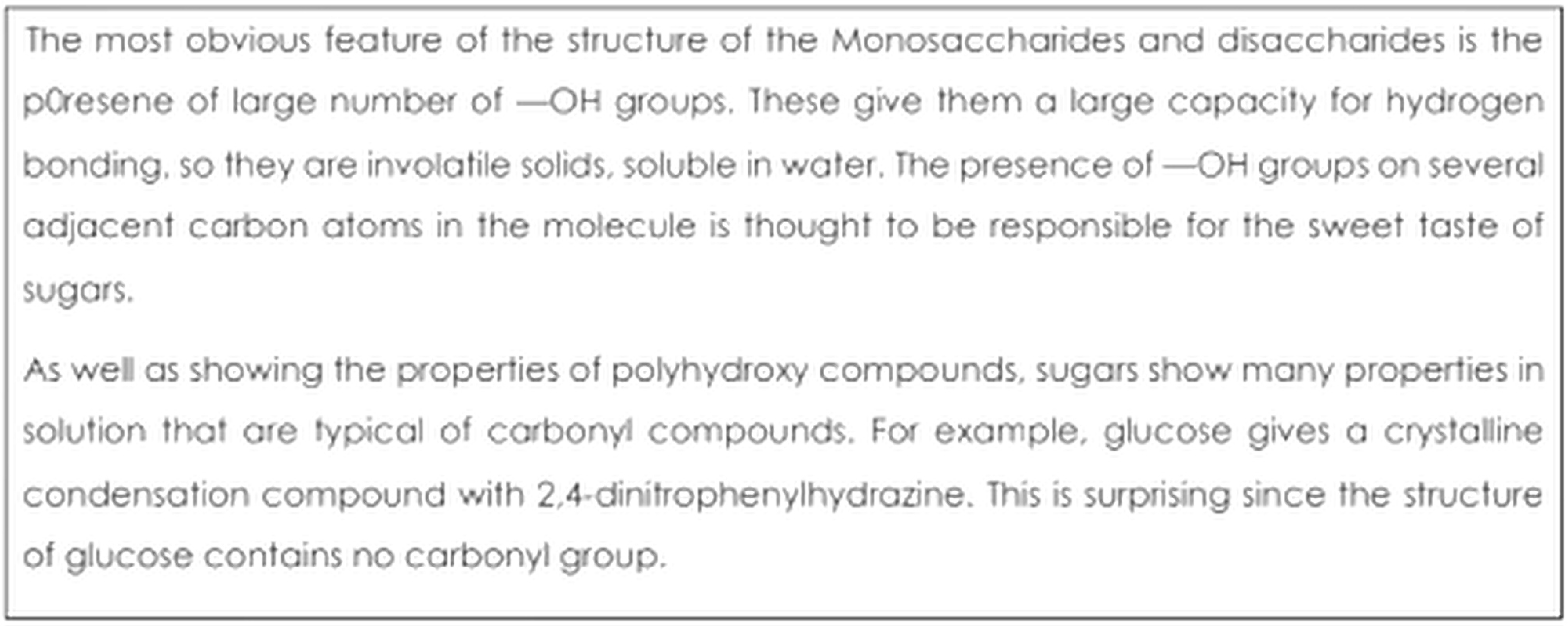
$$\underset{\text{Butanone}}{CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_2-CH_3} + 3[O] \xrightarrow{K_2Cr_2O_7\,H_2SO_4} \underset{\text{Acetic acid}}{CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-OH} + CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-OH$$

IMPORTANT INFORMATIONS

Sugars Glucose and Fructose — Naturally occurring carbonyl compounds

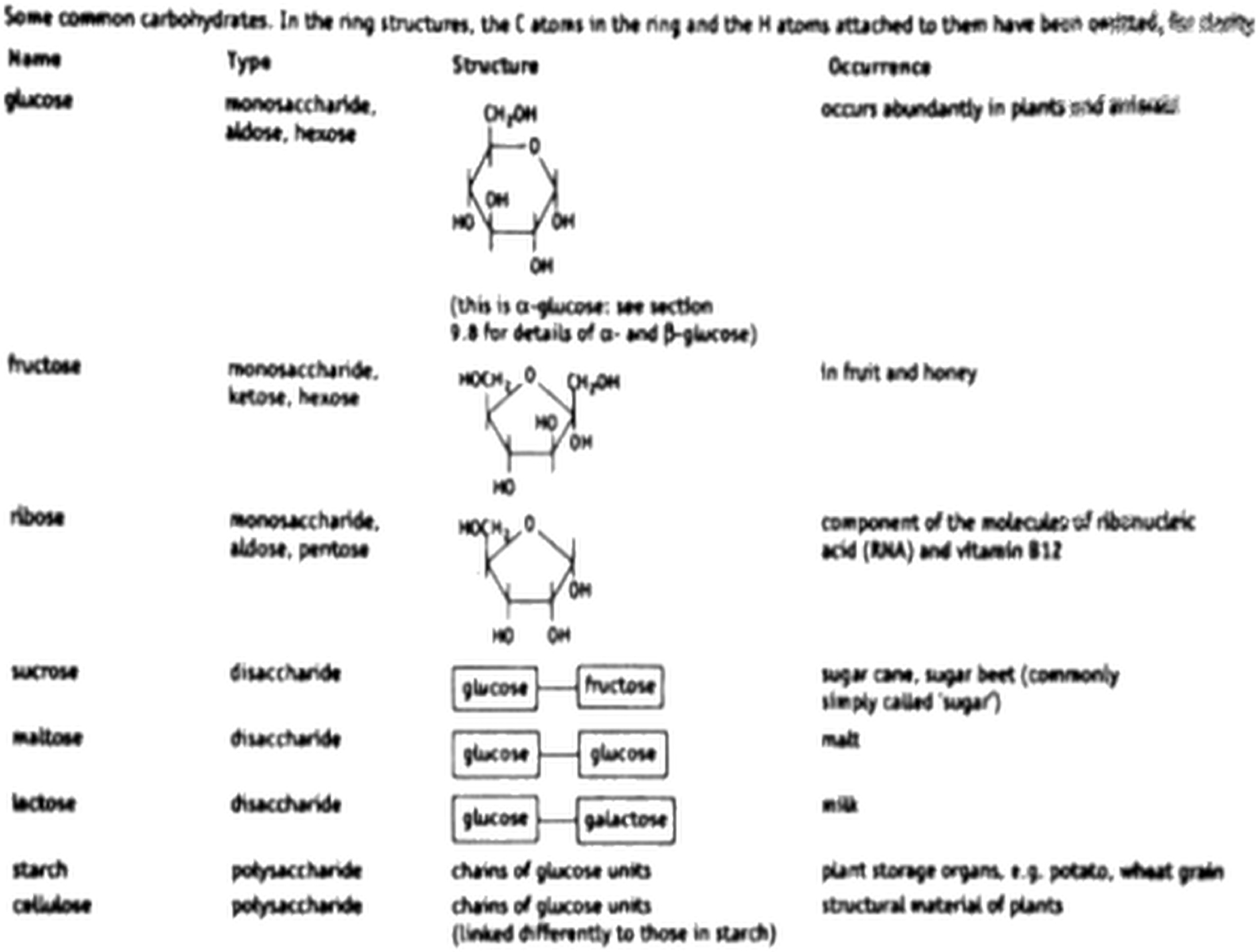
Sugars are sweet tasting soluble carbohydrates. Carbohydrates derive their name for the fact that they are composed of carbon, hydrogen and oxygen with H and O in the ratio of [illegible] as in water. Monosaccharides such as glucose are usually pentoses or hexoses, i.e. they contain 5 or 6 carbon atoms in their molecules. Disaccharides such as sucrose consist of two monosaccharide molecules joined by the elimination of a molecule of water. Polysaccharides such as starch are made up of many Monosaccharides units joined together. Notice that the Monosaccharides all have asymmetric molecules. They therefore exhibit optical isomerism.

The most obvious feature of the structure of the Monosaccharides and disaccharides is the presence of large number of —OH groups. These give them a large capacity for hydrogen bonding, so they are in volatile solids, soluble in water. The presence of —OH groups on several adjacent carbon atoms in the molecule is thought to be responsible for the sweet taste of sugars.



The most obvious feature of the structure of the Monosaccharides and disaccharides is the p0resene of large number of —OH groups. These give them a large capacity for hydrogen bonding, so they are involatile solids, soluble in water. The presence of —OH groups on several adjacent carbon atoms in the molecule is thought to be responsible for the sweet taste of sugars.

As well as showing the properties of polyhydroxy compounds, sugars show many properties in solution that are typical of carbonyl compounds. For example, glucose gives a crystalline condensation compound with 2,4-dinitrophenylhydrazine. This is surprising since the structure of glucose contains no carbonyl group.

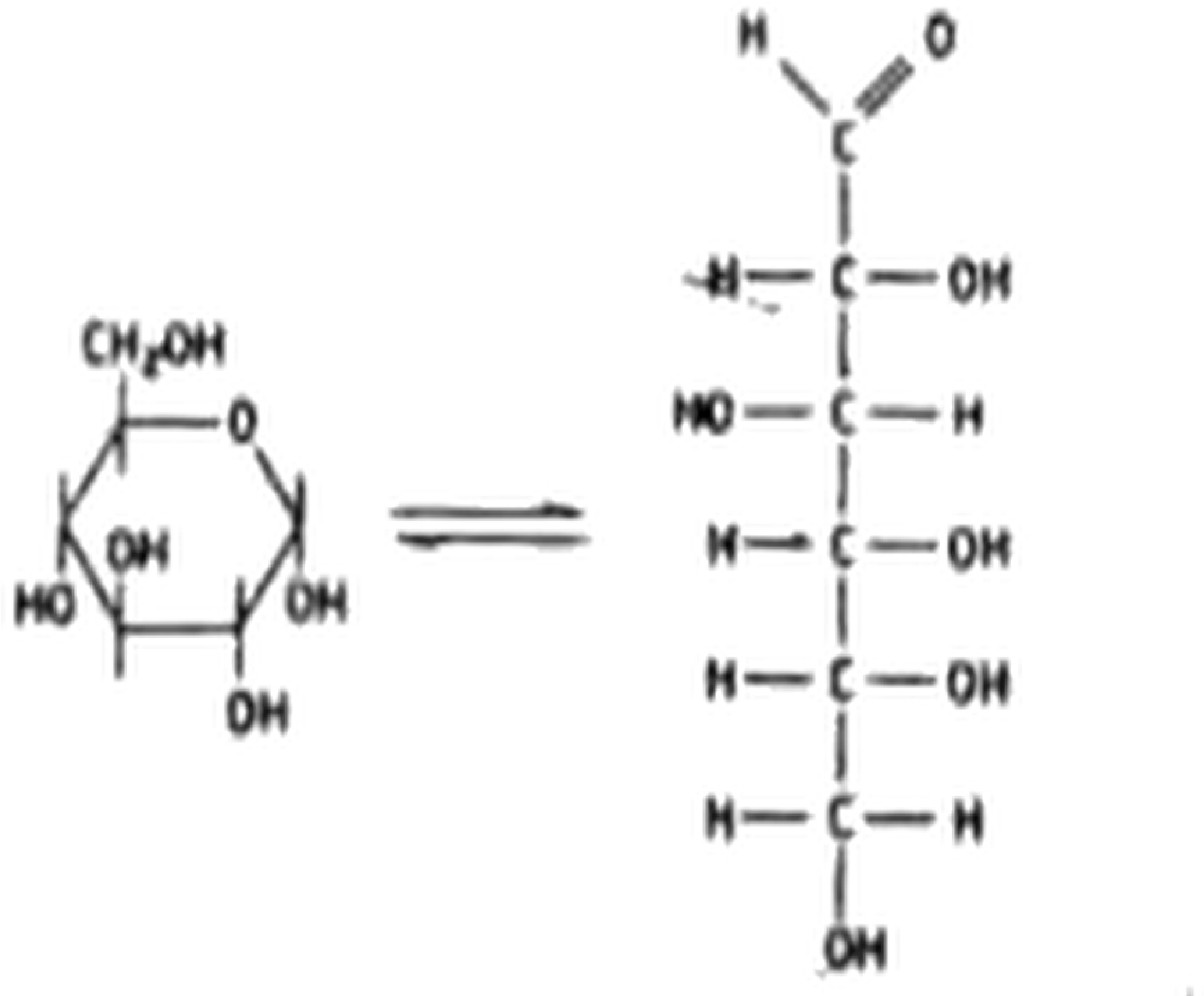


Some common carbohydrates. In the ring structures, the C atoms in the ring and the H atoms attached to them have been omitted, for clarity

Name	Type	Structure	Occurrence
glucose	monosaccharide, aldose, hexose	(this is α-glucose: see section 9.8 for details of α- and β-glucose)	occurs abundantly in plants and animals
fructose	monosaccharide, ketose, hexose		in fruit and honey
ribose	monosaccharide, aldose, pentose		component of the molecules of ribonucleic acid (RNA) and vitamin B12
sucrose	disaccharide	glucose — fructose	sugar cane, sugar beet (commonly simply called 'sugar')
maltose	disaccharide	glucose — glucose	malt
lactose	disaccharide	glucose — galactose	milk
starch	polysaccharide	chains of glucose units	plant storage organs, e.g. potato, wheat grain
cellulose	polysaccharide	chains of glucose units (linked differently to those in starch)	structural material of plants

The carbonyl properties possessed by glucose arise from the fact that in addition to its normal ring form it can exist as an open chain form.

Glucose — An example of aldehyde

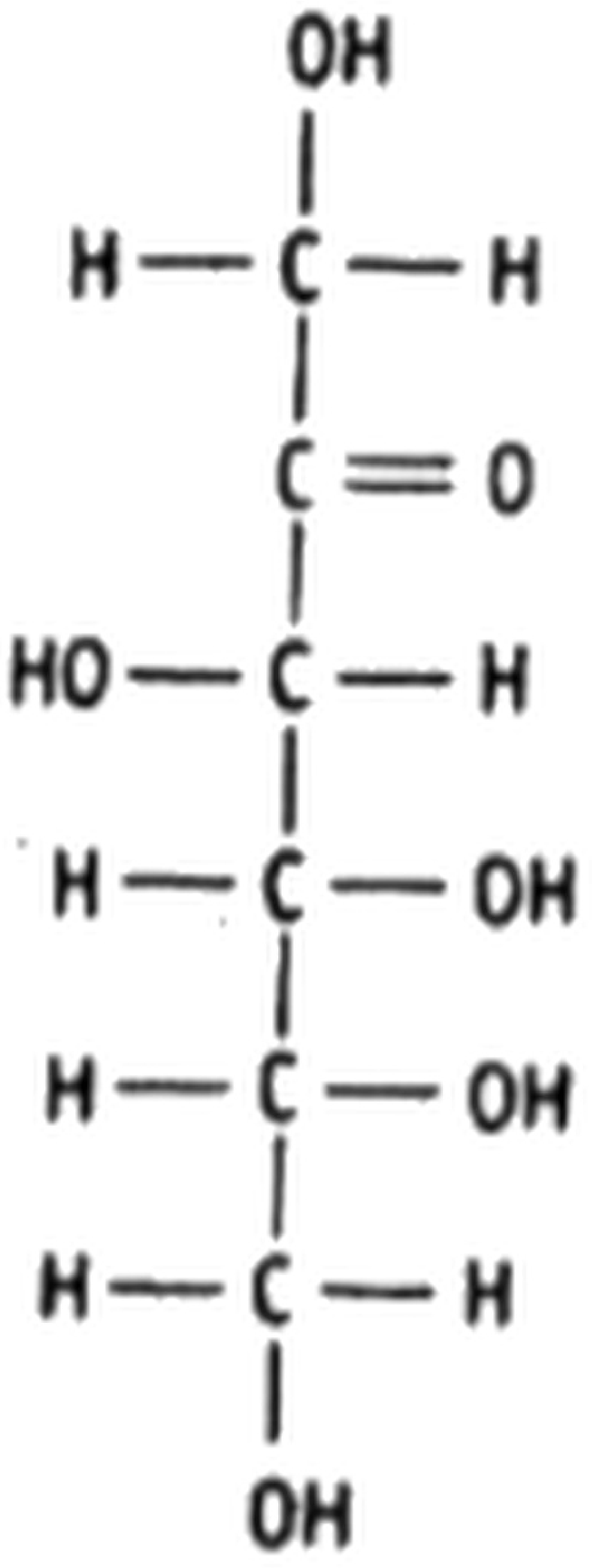


Ring form open-chain 6m

The two forms are readil inter-converted and in a ueous solution about 1% of lucose molecules exist in the open chain form. This form carries an aldehyde group, so glucose has several properties typical of an aldehyde. It is sometimes called an aldose. Thus, in addition to the condensation reaction already mentioned glucose shows the reducing properties typical of an aldehyde. The reduction of Fehling's solution (or Benedict's solution) is a standard test for glucose and other reducing sugars.

Fructose — An example of Ketone

The open chain form of fructose is



Fructose is therefore a ketose.

Why does the open chain form of glucose and other sugars change to the ring form? It is a result of the tendency of the carbonyl group to undergo nucleophilic addition. The nucleophile involved is the oxygen atom of one of the -OH group of the same molecule. An internal nucleophilic addition reaction occurs, forming a ring.