

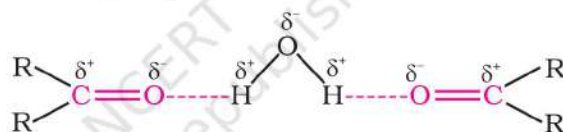
## 12.3 Physical Properties

The physical properties of aldehydes and ketones are described as follows.

Methanal is a gas at room temperature. Ethanal is a volatile liquid. Other aldehydes and ketones are liquid or solid at room temperature. The boiling points of aldehydes and ketones are higher than hydrocarbons and ethers of comparable molecular masses. It is due to weak molecular association in aldehydes and ketones arising out of the dipole-dipole interactions. Also, their boiling points are lower than those of alcohols of similar molecular masses due to absence of intermolecular hydrogen bonding. The following compounds of molecular masses 58 and 60 are ranked in order of increasing boiling points.

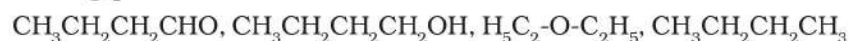
	b.p.(K)	Molecular Mass
n-Butane	273	58
Methoxyethane	281	60
Propanal	322	58
Acetone	329	58
Propan-1-ol	370	60

The lower members of aldehydes and ketones such as methanal, ethanal and propanone are miscible with water in all proportions, because they form hydrogen bond with water.



However, the solubility of aldehydes and ketones decreases rapidly on increasing the length of alkyl chain. All aldehydes and ketones are fairly soluble in organic solvents like benzene, ether, methanol, chloroform, etc. The lower aldehydes have sharp pungent odours. As the size of the molecule increases, the odour becomes less pungent and more fragrant. In fact, many naturally occurring aldehydes and ketones are used in the blending of perfumes and flavouring agents.

Arrange the following compounds in the increasing order of their boiling points:



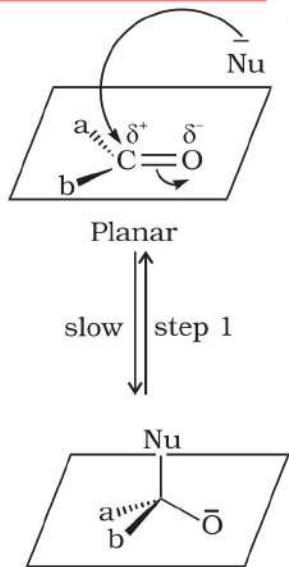
The molecular masses of these compounds are in the range of 72 to 74. Since only butan-1-ol molecules are associated due to extensive intermolecular hydrogen bonding, therefore, the boiling point of butan-1-ol would be the highest. Butanal is more polar than ethoxyethane. Therefore, the intermolecular dipole-dipole attraction is stronger in the former. *n*-Pentane molecules have only weak **van der Waals forces**. Hence increasing order of boiling points of the given compounds is as follows:



### Example 12.2

### Solution

## 12.4 Chemical Reactions



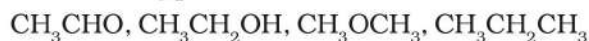
Tetrahedral intermediate

Addition product

**Fig.12.2:** Nucleophilic attack on carbonyl carbon

### Intext Question

**12.3** Arrange the following compounds in increasing order of their boiling points.



Since aldehydes and ketones both possess the carbonyl functional group, they undergo similar chemical reactions.

### 1. Nucleophilic addition reactions

Contrary to electrophilic addition reactions observed in alkenes (refer Unit 13, Class XI), the aldehydes and ketones undergo nucleophilic addition reactions.

#### (i) Mechanism of nucleophilic addition reactions

A nucleophile attacks the electrophilic carbon atom of the polar carbonyl group from a direction approximately perpendicular to the plane of  $sp^2$  hybridised orbitals of carbonyl carbon (Fig. 12.2). The hybridisation of carbon changes from  $sp^2$  to  $sp^3$  in this process, and a tetrahedral alkoxide intermediate is produced.

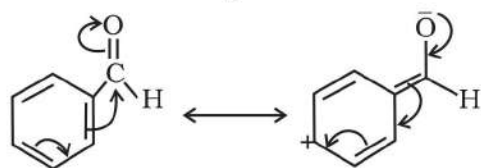
This intermediate captures a proton from the reaction medium to give the electrically neutral product. The net result is addition of  $\text{Nu}^-$  and  $\text{H}^+$  across the carbon oxygen double bond as shown in Fig. 12.2.

#### (ii) Reactivity

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

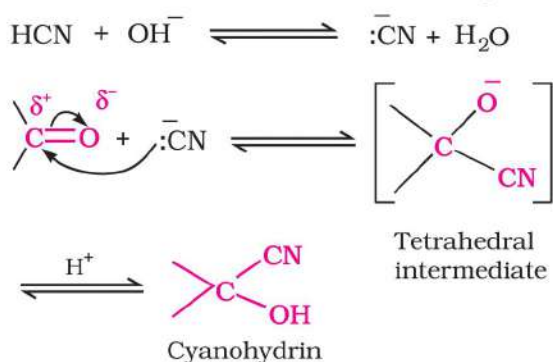
**Example 12.3** Would you expect benzaldehyde to be more reactive or less reactive in nucleophilic addition reactions than propanal? Explain your answer.

**Solution** The carbon atom of the carbonyl group of benzaldehyde is less electrophilic than carbon atom of the carbonyl group present in propanal.



The polarity of the carbonyl group is reduced in benzaldehyde due to resonance as shown below and hence it is less reactive than propanal.

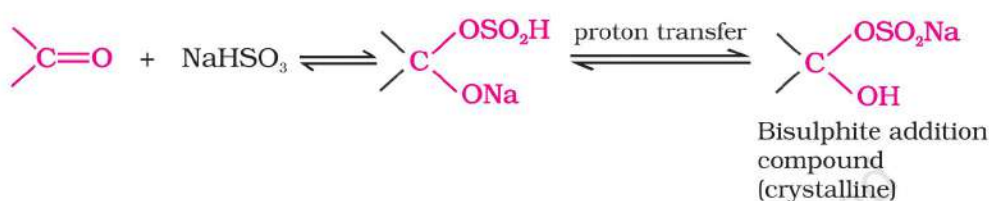
(iii) Some important examples of nucleophilic addition and nucleophilic addition-elimination reactions:



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

Cyanohydrins are useful synthetic intermediates.

(b) *Addition of sodium hydrogensulphite*: Sodium hydrogensulphite adds to aldehydes and ketones to form the addition products.

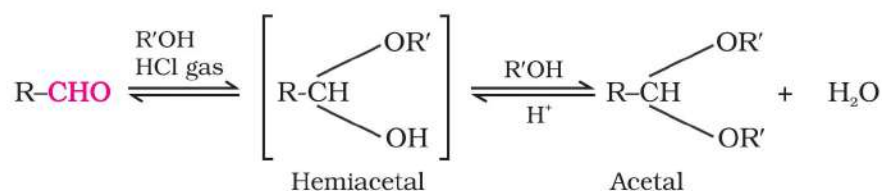


The position of the equilibrium lies largely to the right hand side for most aldehydes and to the left for most

ketones due to steric reasons. The hydrogensulphite addition compound is water soluble and can be converted back to the original carbonyl compound by treating it with dilute mineral acid or alkali. Therefore, these are useful for separation and purification of aldehydes.

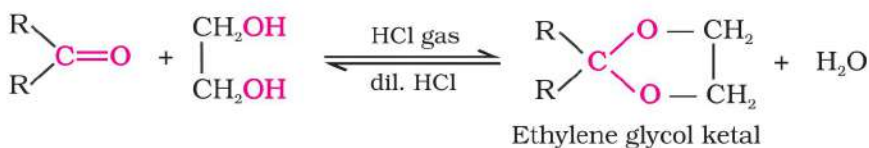
(c) *Addition of Grignard reagents*: (refer Unit 11, Class XII).

(d) *Addition of alcohols*: Aldehydes react with one equivalent of monohydric alcohol in the presence of dry hydrogen chloride to yield alkoxyalcohol intermediate, known as hemiacetals, which further react with one more molecule of alcohol to



give a *gem*-dialkoxy compound known as acetal as shown in the reaction.

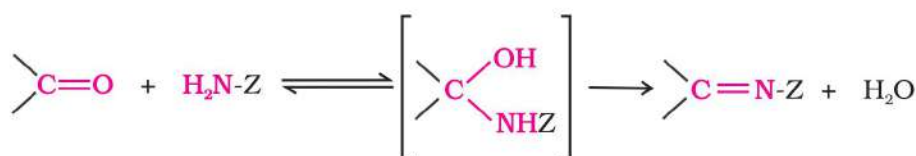
Ketones react with ethylene glycol under similar conditions to form cyclic products known as ethylene glycol ketals.



Dry hydrogen chloride protonates the oxygen of the carbonyl compounds and therefore, increases the electrophilicity of the carbonyl carbon facilitating

the nucleophilic attack of ethylene glycol. Acetals and ketals are hydrolysed with aqueous mineral acids to yield corresponding aldehydes and ketones respectively.

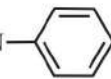
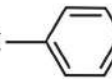
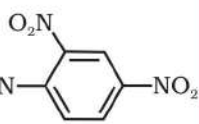
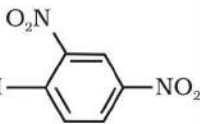
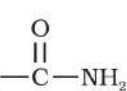
- (e) *Addition of ammonia and its derivatives*: Nucleophiles, such as ammonia and its derivatives  $\text{H}_2\text{N-Z}$  add to the carbonyl group of aldehydes and ketones. The reaction is reversible and catalysed by acid.



The equilibrium favours the product formation due to rapid dehydration of the intermediate to form  $\text{>C=N-Z}$ .

Z = Alkyl, aryl, OH,  $\text{NH}_2$ ,  $\text{C}_6\text{H}_5\text{NH}$ ,  $\text{NHCONH}_2$ , etc.

**Table 12.2: Some N-Substituted Derivatives of Aldehydes and Ketones (>C=N-Z)**

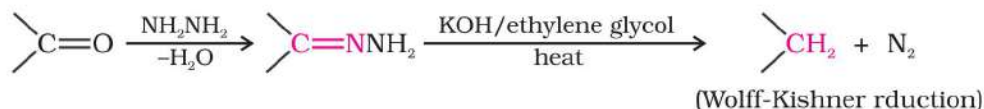
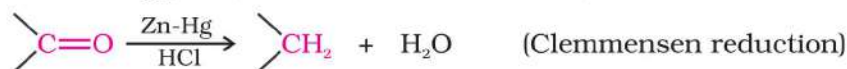
Z	Reagent name	Carbonyl derivative	Product name
-H	Ammonia	$\text{>C=NH}$	Imine
-R	Amine	$\text{>C=NR}$	Substituted imine (Schiff's base)
-OH	Hydroxylamine	$\text{>C=N-OH}$	Oxime
- $\text{NH}_2$	Hydrazine	$\text{>C=N-NH}_2$	Hydrazone
-HN- 	Phenylhydrazine	$\text{>C=N-NH-}$ 	Phenylhydrazone
-HN- 	2,4-Dinitrophenylhydrazine	$\text{>C=N-NH-}$ 	2,4 Dinitrophenylhydrazone
-NH- 	Semicarbazide	$\text{>C=N-NH-C(=O)-NH}_2$	Semicarbazone

\* 2,4-DNP-derivatives are yellow, orange or red solids, useful for characterisation of aldehydes and ketones.

## 2. Reduction

- Reduction to alcohols*: Aldehydes and ketones are reduced to primary and secondary alcohols respectively by sodium borohydride ( $\text{NaBH}_4$ ) or lithium aluminium hydride ( $\text{LiAlH}_4$ ) as well as by catalytic hydrogenation (Unit 11, Class XII).
- Reduction to hydrocarbons*: The carbonyl group of aldehydes and ketones is reduced to  $\text{CH}_2$  group on treatment with zinc-amalgam and concentrated hydrochloric acid [**Clemmensen**].

**reduction**] or with hydrazine followed by heating with sodium or potassium hydroxide in high boiling solvent such as ethylene glycol (**Wolff-Kishner reduction**).

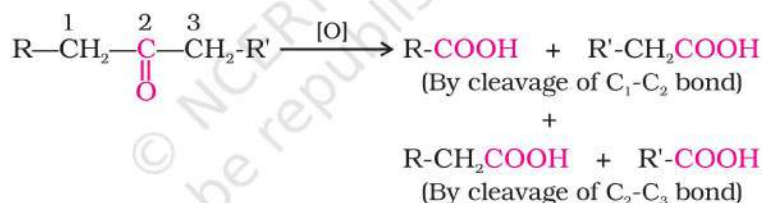


### 3. Oxidation

Aldehydes differ from ketones in their oxidation reactions. Aldehydes are easily oxidised to carboxylic acids on treatment with common oxidising agents like nitric acid, potassium permanganate, potassium dichromate, etc. Even mild oxidising agents, mainly Tollens' reagent and Fehlings' reagent also oxidise aldehydes.



Ketones are generally oxidised under vigorous conditions, i.e., strong oxidising agents and at elevated temperatures. Their oxidation involves carbon-carbon bond cleavage to afford a mixture of carboxylic acids having lesser number of carbon atoms than the parent ketone.

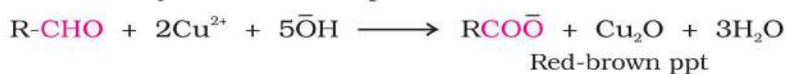


The mild oxidising agents given below are used to distinguish aldehydes from ketones:

(i) **Tollens' test:** On warming an aldehyde with freshly prepared ammoniacal silver nitrate solution (Tollens' reagent), a bright silver mirror is produced due to the formation of silver metal. The aldehydes are oxidised to corresponding carboxylate anion. The reaction occurs in alkaline medium.



(ii) **Fehling's test:** Fehling reagent comprises of two solutions, Fehling solution A and Fehling solution B. Fehling solution A is aqueous copper sulphate and Fehling solution B is alkaline sodium potassium tartarate (Rochelle salt). These two solutions are mixed in equal amounts before test. On heating an aldehyde with Fehling's reagent, a reddish brown precipitate is obtained. Aldehydes are oxidised to corresponding carboxylate anion. Aromatic aldehydes do not respond to this test.



Bernhard Tollens  
(1841-1918) was a  
Professor of Chemistry  
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