Topics
Aldehydes, Ketones and Haloalkanes
Aldehydes and Ketones

Aldehydes are molecules with the general formula $R-\overset{\text{O}}{\text{C}}-\overset{\text{H}}{\text{H}}$, where $R$ can be $H$, alkyl, or aryl groups. Ketones are molecules with the general formula $R-\overset{\text{O}}{\text{C}}-\overset{\text{R'}}{\text{R}}$, where $R$ and $R'$ are alkyl or aryl groups.

Aldehydes and ketones are called carbonyl compounds.
Structure of Carbonyl Group

Carbonyl group contains one sigma and one pi bond. Both carbon and oxygen atoms are in $sp^2$ hybridised state.
Naming of aldehydes and ketones

According to IUPAC:

Aldehydes are named by replacing ‘e’ of the corresponding alkane by suffix ‘al’.

Ketones are named by replacing ‘e’ of the alkane by suffix ‘one’.

Aldehyde group is always at terminal hence position is normally not mentioned.

In ketones we use position of carbonyl group whenever it is needed.
<table>
<thead>
<tr>
<th>Nomenclature</th>
<th>Molecular Formula</th>
<th>Common Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>R–CH₂–CH₃</td>
<td>CH₃-CH₂-CH₃</td>
<td>Propane</td>
</tr>
<tr>
<td>R–CH–CHO</td>
<td>CH₃-CH₂-CHO</td>
<td>Propanal</td>
</tr>
<tr>
<td>R–CO–R'</td>
<td>CH₃-CO-CH₃</td>
<td>Propanone</td>
</tr>
<tr>
<td>Alkane</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Alkanal</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Alkanone</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Preparation of Aldehydes and Ketones

By oxidation of alcohols:-

Using acidified $\text{K}_2\text{Cr}_2\text{O}_7$

Primary alcohols oxidises to aldehydes

Secondary alcohols oxidises to ketones

$\text{RCH}_2\text{OH} + [\text{O}] \rightarrow \text{Aldehyde} + \text{H}_2\text{O}$

$\text{RCHOHR'} + [\text{O}] \rightarrow \text{Ketone} + \text{H}_2\text{O}$
By Oppenauer Oxidation

Secondary alcohols on refluxing with excess of acetone in the presence of aluminium tertiary butoxide forms ketones.

\[ \text{RCHOH}_2\text{R} + \text{CH}_3\text{COCH}_3 \rightarrow \text{RCOR}' + \text{CH}_3\text{CHOHCH}_3 \]

Ketone
From calcium salts of fatty acids (Pyrolysis)

Aldehydes are obtained by dry distilling calcium salts of fatty acids with calcium formate.

Ketones are obtained by dry distillation of fatty acids other than calcium formate.
<table>
<thead>
<tr>
<th>Calcium salts</th>
<th>Aldehyde / Ketone</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcium formate</td>
<td>HCHO (fromaldehyde)</td>
</tr>
<tr>
<td>Calcium formate + Calcium acetate</td>
<td>CH₃CHO (Acetaldehyde)</td>
</tr>
<tr>
<td>Calcium formate + Calcium benzoate</td>
<td>C₆H₅CHO (Benzaldehyde)</td>
</tr>
<tr>
<td>Calcium acetate</td>
<td>CH₃COCH₃ (Acetone)</td>
</tr>
<tr>
<td>Calcium benzoate</td>
<td>C₆H₅COC₆H₅ (Benzophenone)</td>
</tr>
<tr>
<td>Calcium acetate + Calcium benzoate</td>
<td>C₆H₅COCH₃ (Acetophenone)</td>
</tr>
</tbody>
</table>
By Rosenmund’s Reduction

Acid chlorides are reduced to aldehydes by reducing with hydrogen in the presence of palladium supported over \( \text{BaSO}_4 \).

\[
\text{RCOCl} + \text{H}_2 \overset{140{\degree}C}{\longrightarrow} \text{RCHO} + \text{HCl}
\]
By Friedel – Craft’s reaction

Acetophenone is obtained by this method.

\[ C_6H_6 + CH_3COCl \xrightarrow{\text{heat}} \text{Anhy.}AlCl_3 \rightarrow C_6H_5COCH_3 + HCl \]
By Etard’s reaction

When toluene is oxidised with chromyl chloride in CCl₄, benzaldehyde is formed. Even CrO₃ brings about this reaction.

\[
\text{C}_6\text{H}_5\text{CH}_3 + [O] \xrightarrow{\text{CrO}_2\text{Cl}_2 / \text{CCl}_4} \text{C}_6\text{H}_5\text{CHO} + \text{H}_2\text{O}
\]

Toluene  Benzaldehyde
Properties of Aldehydes and Ketones

1. Lower members are soluble in water and higher members are insoluble. The solubility decreases with increase in size of alkyl groups.

2. Aldehydes and ketones have higher boiling points than the alkanes due to presence of polar carbonyl groups. However they have lower boiling points than the corresponding alkanes due to absence of hydrogen bonding.
Chemical properties

**Addition reactions:**

Aldehydes and ketones undergo addition reactions with HCl, NaHSO$_3$ to form corresponding cynohydrines and bisulphites respectively.
Condensation reactions

Aldehydes and ketones undergo a number of condensation reactions with following reagents.

1. Hydroxyl amine (NH₂OH) – Oximes
2. Hydrazine (NH₂.NH₂) – Hydrazones
3. Phenylhydrazine (NH₂NHC₆H₅) – Phenyl hydrazones
4. Semicarbozide (NH₂NHCONH₂) – Semicarbazones
5. 2,4, dinitrophenylhydrazine – (Borsche’s reagent) – Orange yellow crystalline compound
With Grignard’s reagent

Formaldehyde + Grignard Reagent

Addition compound

Hydrolysis

Primary alcohols

Other aldehydes form secondary alcohols
Oxidation of aldehydes

Reducing property of aldehydes:

- Tollen’s reagent + $RCHO \xrightarrow{\text{heat}} RCOOH + \text{Ag}$

- Fehling’s solution + $RCHO \xrightarrow{\text{heat}} \text{Cu}_2\text{O}$ (red ppt)

- Benedict’s solution + $RCHO \xrightarrow{\text{heat}} \text{Cu}_2\text{O}$ (red ppt)
Oxidation of ketones

Ketones are difficult to oxidise. Hence, they do not reduce Tollen’s reagent, Fehling’s solution and Benedict’s reagent.

But strong oxidising agents like acidified KMnO$_4$ and K$_2$Cr$_2$O$_7$ oxidises to carboxylic acids with less number of carbon atoms.

In unsymmetrical ketones the keto group stays with the smaller alkyl group (Popoff’s rule).
Reduction of aldehydes and ketones

1. Aldehydes on reduction with Zn and dil. HCl, LiAlH$_4$ give primary alcohols. Ketones give secondary alcohols.

2. Clemmensen’s reduction:- When Aldehydes and Ketones are reduced with Zn – Hg/conc. HCl, hydrocarbons are formed.
Special reactions

Cannizzaro’s reaction:-

1. Aldehydes which do not contain $\alpha$ – hydrogen when treated with conc. NaOH undergo oxidation and reduction to give alcohol and sodium carboxylate

$$2C_6H_5CHO + NaOH \rightarrow C_6H_5CH_2OH + C_6H_5COONa$$
2. Aldol Condensation:-
Aldehydes and ketones having \( \alpha \) – hydrogen undergo self condensation in the presence of dil. NaOH forming \( \beta \) – hydroxy aldehydes or ketones.
3. **Perkin’s condensation**:

Benzaldehyde on heating with acetic anhydride in the presence of fused sodium acetate at 180$^\circ$C gives cinnamic acid (unsaturated) $C_6H_5CH=CHCOOH$

4. **Claisen condensation**:

Benzaldehyde reacts with acetaldehyde in the presence of dil. NaOH to form cinnamaldehyde. $C_6H_5CH=CH-CHO$
5. Benzoin condensation:

Benzaldehyde reacts with alcoholic KCN to form Benzoin.

\[ C_6H_5CH.OH.COC_6H_5 \]
Iodoform reaction:-
Aldehydes and ketones having CH3CO group react with Iodine and NaOH to form yellow crystalline ppt of iodoform. (E.g., acetaldehyde and acetone)

Schiff’s reagent test:-
Aldehydes give immediate pink colour but ketones do not.
Q1. The carbon atom of the carbonyl group is
1) $sp^2$ hybridised
2) $sp^3$ hybridised
3) $sp$ hybridised
4) $dsp^2$ hybridised
Answer: (1) $sp^2$ hybridised
Q2. Ketones can be prepared by
1) Clemmensen’s reduction
2) Rosenmund’s reduction
3) Oppenauer's oxidation
4) Cannizzaro's reaction
Answer (3) Oppenauer’s oxidation
Q3. Aldehydes are the first oxidation product of
1) Secondary alcohols
2) Primary alcohols
3) Tertiary alcohols
4) Dihydric alcohols
Answer (2) Primary alcohols
Q4. Ketones are the first oxidation products of
1) Primary alcohols
2) Secondary alcohols
3) Dihydric alcohols
4) Tertiary alcohols
Answer (2) Secondary alcohols
Q5. Which of the following will not be formed when calcium acetate is distilled with calcium benzoate

1) Acetone
2) Benzophenone
3) Acetophenone
4) Acetaldehyde

Answer (3) Acetophenone is formed
Q6. On heating calcium acetate and calcium formate, the major product formed is
1) CH₃COCH₃
2) CH₃CHO
3) HCHO + CaCO₃
4) CH₃CHO + CaCO₃
Answer (4) CH₃CHO + CaCO₃ is formed
Q7. Aldehydes and Ketones do not give addition reaction with

1) HCl
2) NaHSO$_3$
3) HCN
4) HCl aq

Answer (4) HCl aqueous
Q8. Aldehydes may be distinguished from ketones by the use of
1) Conc. H₂SO₄
2) Tollens’s reagent
3) Pyrogallol
4) Grignard reagent
Answer (2) Tollens’s reagent (aldehydes reduces it to Ag)
Q9. Which of the following does not undergo Cannizzaro’s reaction on heating with an alkali solution?

1) CCl$_3$CHO
2) (CH$_3$)$_3$C·CH·O
3) HCHO
4) C$_6$H$_5$·CHO

Answer (1) CCl$_3$CHO (because it will cleave in presence of base)

CCl$_3$CHO + NaOH $\rightarrow$ CHCl$_3$ + HCOONa
Q10. Aldol condensation will not occur in  
1) HCHO  
2) CH₃CH₂CHO  
3) CH₃COCH₃  
4) CH₃CHO  
Answer (1) HCHO (because it does not contain α – H atom)
Q11. In which of the following reactions, aromatic aldehyde is treated with acid anhydride in the presence of corresponding salt of the acid to give unsaturated aromatic acid
1) Friedel – Crafts reaction
2) Perkin’s reaction
3) Wurtz reaction
4) Kolbe’s reaction

Answer (2) Perkin’s reaction

\[
\text{C}_6\text{H}_5\text{CHO} + (\text{CH}_3\text{CO})_2\text{O} \rightarrow \text{C}_6\text{H}_5\text{CH}=\text{CHCOOH} + \text{CH}_3\text{COOH}
\]
Q12. Aldehydes and ketones can be reduced to corresponding hydrocarbons by
1) Refluxing with strong acids
2) Passing the vapours over heated lead oxide
3) Refluxing with zinc amalgam and conc. HCl
4) Refluxing it with strong alkali

Answer (3) Refluxing with zinc amalgam and conc. HCl (Clemmensen’s reduction)
Q13. The IUPAC name of $\text{CH}_3\text{COCHCHO}$ is

1) 3–methyl–3–formyl–2–propane
2) 2–methyl–3–oxobutanal
3) 2–acetylpropanal
4) 3–methylbutan–3–one–1–al

Answer (2) 2–methyl–3–oxobutanal
Q14. Identify the compound X and Y in the following reactions.

1) Benzoic acid and Calcium acetate
2) Benzaldehyde and Calcium formate
3) Benzoic acid and Sodium formate
4) Benzaldehyde and Sodium acetate

Answer (2)
Q15. Decreasing order of reactivity towards nucleophilic addition reactions for the following compound I) HCHO II) CH₃COCH₃ III) CH₃CHO IV) C₆H₅COCH₃ is

1) I > III > II > IV 
2) I > III > IV > II 
3) III > I > II > IV 
4) II > IV > III > I 

Answer (1) I > III > II > IV 
Steric hinderance to carbonyl group and +I effect of substituents decreases the reactivity 

\[ \text{HCHO} > \text{CH₃CHO} > \text{CH₃COCH₃} > \text{C₆H₅COCH₃} \]
Q16. Benzaldehyde can be prepared by the action of chromyl chloride on toluene dissolved in CS$_2$, the reaction is known as

1) Etard’s reaction
2) Hoffmann’s reaction
3) Schotten – Baumann reaction
4) Fittig’s reaction

Answer (1) Etard’s reaction

$\text{C}_6\text{H}_5\text{CH}_3 + [\text{O}] \overset{\text{CrO}_2\text{Cl}_2/\text{CCl}_4}{\rightarrow} \text{C}_6\text{H}_5\text{CHO} + \text{H}_2\text{O}$
Q17. The end product in the reaction

\[
\text{CH}_3\text{COOH} \xrightarrow{\text{CaCO}_3} A \xrightarrow{\text{heat}} B \xrightarrow{\text{NH}_2\text{OH}} C
\]

1) Acetaldehyde oxime
2) Formaldehyde oxime
3) Methyl nitrate
4) Acetone oxime

**Answer (4) Acetone oxime**

A=\((\text{CH}_3\text{COO})_2\text{Ca}\), B=\(\text{CH}_3\text{COCH}_3\), C=Acetone oxime
Q.18 Acetone and acetaldehyde are
1) Functional isomers
2) Position isomers
3) Chain isomers
4) Not isomers

Answer (4) Not isomers

CH₃COCH₃ & CH₃CHO do not have same molecular formula
Q19. Benzaldehyde is different from aliphatic aldehydes in its reaction towards

1) Fehling’s solution
2) Schiff’s reagent
3) Tollen’s reagent
4) NaHSO₃ solution

Answer (1) Fehling’s solution (because benzaldehyde undergo Cannizzaro’s reaction due to presence of NaOH)
Q20. If formaldehyde and KOH are heated, we get

1) Ethyl formate
2) Acetylene
3) Methane
4) Methyl alcohol

Answer (4) Methyl alcohol

\[ 2\text{HCHO} + \text{KOH} \rightarrow \text{HCOOK} + \text{CH}_3\text{OH} \]
Haloalkanes (R-X)

Monohalogen derivatives of alkanes are called haloalkanes (alkyl halides)

Alkanes: $C_nH_{2n+2}$

Haloalkanes: $C_nH_{2n+1}X$
Classification

Based upon the type of carbon atom to which halogen atom is attached

$\text{CH}_3$-$^*$\text{CH}_2$-Cl $\text{CH}_3$-CH-Cl $\text{CH}_3$-C-Cl

Chloro ethane 2-chloropropane 2-chloro-2-methyl propane

Primary ($1^0$) Secondary ($2^0$) Tertiary ($3^0$)
Nomenclature of Haloalkanes

CH₃Cl – Chloromethane
CH₃CH₂Br – Bromoethane

Methods of preparation:
1. From alcohols:
   a. Action with halogen acid
   b. Action with phosphorus halides
   c. Action with thionyl chloride
Anhydrous HX + ZnCl₂ → R-X + H₂O

R-OH- + PX₃ → R-X + H₃PO₃

SOCl₂ → R-X + SO₂ + HX

Pyridine (Darzen’s Process)
2. From alkenes:

$$R-\text{CH}=\text{CH}_2 + \text{HX} \rightarrow R-\text{CH}-\text{CH}_3$$
\[ \text{NH}_3 \quad R-, \ R_2, R_3N, \ R_4NX \quad \text{NH}_2, \ \text{NH} \]

Alcohol

KOH

Alkene (dehydrohalogenation)

Ni

R - H (Alkane)

250 C

KCN

R - CN (Alkane nitrate cyanide)

Alcohol

Aq. CN

R - NC (Alkyl isocyanide)

Alcohol

Aq. KOH

R - OH (Alcohol)

Mg/dry ether

R - Mg - X

R - X

C\text{\textsubscript{6}}H\text{\textsubscript{5}} - X/dry ether

Na

Higher alkane Wurtz reaction

Alkyl benzene (Wurtz - Fittig's reaction)

(Friedal - Craft's reaction)

Anhydrous ZnCl\textsubscript{2}

Benzene

Dr.GSN
**Differences between $S_N$1 and $S_N$2 reactions**

<table>
<thead>
<tr>
<th>$S_N$1 Reactions</th>
<th>$S_N$2 Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>It is a two step reaction</td>
<td>It is a single step reaction</td>
</tr>
<tr>
<td>Rate of the reaction depends upon only the concentration of haloalkanes</td>
<td>Rate of the reaction depends upon the concentration of haloalkanes and nucleophile</td>
</tr>
<tr>
<td>It follows first order kinetics</td>
<td>It follows second order kinetics</td>
</tr>
<tr>
<td>The order of reactivity is $3^0&gt;2^0&gt;1^0&gt;\text{CH}_3$</td>
<td>The order of reactivity is $\text{CH}_3&gt;1^0&gt;2^0&gt;3^0$</td>
</tr>
<tr>
<td>Reaction is favoured by polar solvents</td>
<td>Reaction is favoured by non – polar solvents</td>
</tr>
<tr>
<td>Reaction takes place with weak bases</td>
<td>Reaction requires strong bases</td>
</tr>
<tr>
<td>Racemic mixture is obtained as the product</td>
<td>The product has inversion of configuration</td>
</tr>
</tbody>
</table>
Q21. Which of the following alkyl halides is unreactive in an $S_N2$ reaction?

1) Primary
2) Secondary
3) Tertiary
4) Methyl chloride

Answer (3) Tertiary alkyl halides react by $S_N1$ reaction (not $S_N2$)
Q22. On reaction with alcoholic KOH, 1 – chlorobutane gives

1) 1 – Butene
2) 2 – Butene
3) 1 – Butanol
4) 2 – Butanol

Answer (1) 1–Butene (dehydrohalogenation)

\[
\text{ClCH}_2\text{CH}_2\text{CH}_2\text{CH}_3 \xrightarrow{\text{KOH}} \text{CH}_2=\text{CHCH}_2\text{CH}_3
\]
Q23. Which of the following compounds will produce an isocyanide on treatment with alkyl halide?

1) NaCN
2) KCN
3) AgCN
4) HCN

Answer (3) AgCN

$RX + AgCN \rightarrow RNC + AgX$
Q24. $S_N1$ reaction of alkyl halide leads to
1) Retention of configuration
2) Racemisation
3) Inversion of configuration
4) None of these
Answer (2) Racemisation
Q25. Alkyl halides react with magnesium in dry ether to form
1) MgX₂
2) Grignard’s reagent
3) Alkene
4) Alkyne
Answer (2) Grignard’s reagent
RX + Mg → RMgX
Q26. Which of the following haloalkane is most reactive?

1) 1 – Bromopropane
2) 1 – Chloropropane
3) 2 – Bromopropane
4) 2 – Chloropropane

Answer (3) 2–Bromopropane

The order of reactivity for alkyl group is $3^0,2^0,1^0$ and for halogen $I > Br > Cl$
Q27. Which of the following statements about benzyl chloride is incorrect?

1) It is a lachrymatory liquid and answers Beilstein’s test
2) It gives a white precipitate with alcoholic silver nitrate
3) It is less reactive than alkyl halides
4) It can be oxidised to benzaldehyde by boiling with cupric nitrate solution

Answer (3), but benzyl chloride is more reactive than alkyl halides due to resonance
Q28. On heating a mixture of two alkyl halides with sodium metal in dry ether, 2–methyl propane was obtained. The alkyl halides are
1) Chloromethane and chloroethane
2) Chloromethane and 1–chloropropane
3) 2-Chloropropane and chloromethane
4) 2-Chloropropane and chloroethane
Answer (3)
$$(\text{CH}_3)_2\text{CHCl} + 2\text{Na} + \text{ClCH}_3 \rightarrow (\text{CH}_3)_2\text{CHCH}_3 + 2\text{NaCl}$$
Q29. The order of reactivities of methyl halides in the formation of Grignard’s reagent is

1) $\text{CH}_3\text{Br} > \text{CH}_3\text{I} > \text{CH}_3\text{Cl}$

2) $\text{CH}_3\text{Br} > \text{CH}_3\text{Cl} > \text{CH}_3\text{I}$

3) $\text{CH}_3\text{Cl} > \text{CH}_3\text{Br} > \text{CH}_3\text{I}$

4) $\text{CH}_3\text{I} > \text{CH}_3\text{Br} > \text{CH}_3\text{Cl}$

Answer (4), the order of reactivity is for the formation of Grignard’s reagent is $\text{CH}_3\text{I} > \text{CH}_3\text{Br} > \text{CH}_3\text{Cl}$
Q30. The name of the product obtained by the addition of HI to propene in the presence of peroxide catalyst is

1) 1-Iodopropane
2) 2-Iodopropane
3) 1-Iodopropene
4) Propyl iodide

Answer (2), \( \text{CH}_3\text{CH}=\text{CH}_2 + \text{HI} \xrightarrow{\text{peroxide}} (\text{CH}_3)_2\text{CHI} \)

It is Markownikov’s addition. HI does not undergo anti Markownikov’s addition.