NCERT Solutions
Organic Chemistry

Class 12 · Units 6 – 10 · Examples + Intext + Exercises

कक्षा 12 कार्बनिक रसायन — सभी उदाहरण, पाठ्यनिहित व अभ्यास प्रश्नों के हल

Bilingual: English + हिन्दी

How to use / कैसे पढ़ें: Every question is in a red box with its NCERT number (**Ex** = solved example). Questions with structures are shown exactly as in the book. Answers are under the green dashed line; the Hindi line explains the key idea.
हर प्रश्न लाल बॉक्स में NCERT क्रमांक के साथ है; संरचना वाले प्रश्न पुस्तक से लिए गए चित्र के रूप में हैं। उत्तर हरी रेखा के नीचे; हिन्दी पंक्ति मुख्य कारण समझाती है।

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Exam tip: In conversions, write every reagent and condition over the arrow (e.g. $\xrightarrow{NaNO_2/HCl,\ 273\ K}$) — marks are given for each step.
रूपांतरण में हर तीर पर अभिकर्मक व परिस्थिति लिखें — हर चरण के अंक मिलते हैं।

Unit 6 : Haloalkanes & Haloarenes

हैलोऐल्केन एवं हैलोऐरीन — NCERT Solutions (Examples + Intext + Exercises)

A. Solved Examples (हल किए गए उदाहरण)

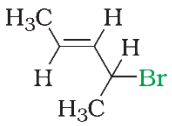
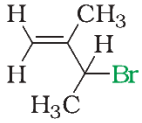
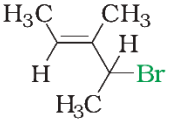
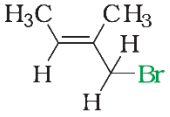
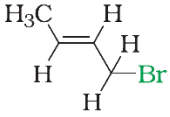
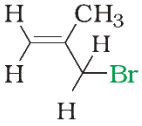
Ex 6.1 **Draw the structures of all the eight structural isomers that have the molecular formula $C_5H_{11}Br$. Name each isomer according to IUPAC system and classify them as primary, secondary or tertiary bromide.**

$C_5H_{11}Br$ के आठों संरचनात्मक समावयवी लिखें, IUPAC नाम दें तथा 1°, 2°, 3° में वर्गीकृत करें।

Ans. / उत्तर:

Structure	IUPAC name	Type
$CH_3CH_2CH_2CH_2CH_2Br$	1-Bromopentane	1°
$CH_3CH_2CH_2CH(Br)CH_3$	2-Bromopentane	2°
$CH_3CH_2CH(Br)CH_2CH_3$	3-Bromopentane	2°
$(CH_3)_2CHCH_2CH_2Br$	1-Bromo-3-methylbutane	1°
$(CH_3)_2CHCH(Br)CH_3$	2-Bromo-3-methylbutane	2°
$(CH_3)_2C(Br)CH_2CH_3$	2-Bromo-2-methylbutane	3°
$CH_3CH_2CH(CH_3)CH_2Br$	1-Bromo-2-methylbutane	1°
$(CH_3)_3CCH_2Br$	1-Bromo-2,2-dimethylpropane	1°

Ex 6.2 **Write IUPAC names of the following:** निम्नलिखित के IUPAC नाम लिखिए:

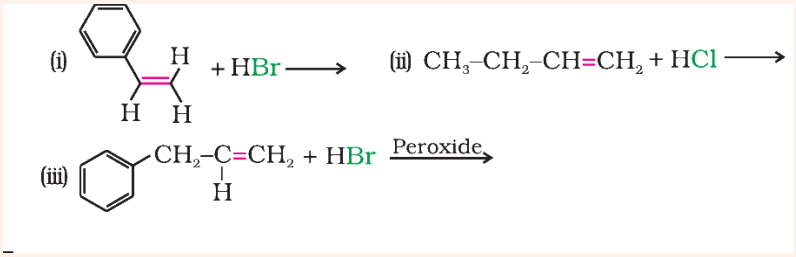
(i) 
(ii) 
(iii) 
(iv) 
(v) 
(vi) 

Ans. / उत्तर: (i) 4-Bromopent-2-ene (ii) 3-Bromo-2-methylbut-1-ene (iii) 4-Bromo-3-methylpent-2-ene
(iv) 1-Bromo-2-methylbut-2-ene (v) 1-Bromobut-2-ene (vi) 3-Bromo-2-methylpropene

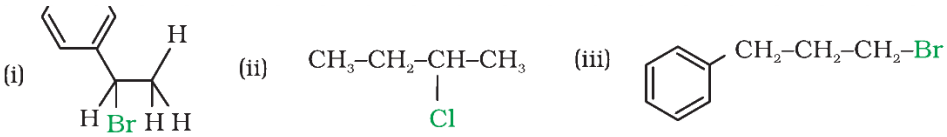
Ex 6.3 **Identify all the possible monochloro structural isomers expected to be formed on free radical monochlorination of $(CH_3)_2CHCH_2CH_3$.**
$(CH_3)_2CHCH_2CH_3$ के मुक्त मूलक मोनोक्लोरीनीकरण से बनने वाले सभी समावयवी पहचानिए।

Ans. / उत्तर: The molecule has **four different types of H** → four monochloro isomers: *अणु में चार प्रकार के H हैं → चार समावयवी।*
$(CH_3)_2CHCH_2CH_2Cl$ · $(CH_3)_2CHCH(Cl)CH_3$ · $(CH_3)_2C(Cl)CH_2CH_3$ · $ClCH_2CH(CH_3)CH_2CH_3$

Ex 6.4 **Write the products of the following reactions:** *उत्पाद लिखिए:*



Ans. / उत्तर:



(i) **1-Bromo-1-phenylethane** — Markovnikov addition (stable benzylic carbocation). (ii) **2-Chlorobutane** (Markovnikov). (iii) **1-Bromo-3-phenylpropane** — peroxide (Kharasch) effect gives anti-Markovnikov product.
(iii) में परॉक्साइड के कारण मार्कोनीकॉफ़-विरोधी योग होता है।

Ex 6.5 **Haloalkanes react with KCN to form alkyl cyanides as main product while AgCN forms isocyanides as the chief product. Explain.**
KCN से ऐल्किल सायनाइड पर AgCN से आइसोसायनाइड क्यों बनता है?

Ans. / उत्तर: KCN is **ionic** → gives free CN^-; attack mainly through **carbon** because the C–C bond formed is more stable than C–N → **R–CN**. AgCN is mainly **covalent** (Ag–C bond); only the lone pair on **nitrogen** is free to attack → **R–NC** (isocyanide).
KCN आयनिक — C से आक्रमण (R–CN); AgCN सहसंयोजी — केवल N का एकाकी युग्म मुक्त, इसलिए R–NC।

Ex 6.6 **In the following pairs, which would undergo S_N2 reaction faster?** कौन S_N2 में तेज़?



Ans. / उत्तर: (i) **Cyclohexylmethyl chloride** ($C_6H_{11}CH_2Cl$) — it is a 1° halide (less hindered) whereas chlorocyclohexane is 2°.

(ii) **1-Iodobutane** — I^- is a better leaving group (larger size, weaker C–I bond).

प्राथमिक हैलाइड कम त्रिविम बाधा के कारण तेज़; I^- श्रेष्ठ अवशिष्ट समूह।

Ex 6.7 **Predict the order of reactivity in S_N1 and S_N2 reactions: (i) the four isomeric bromobutanes (ii) $C_6H_5CH_2Br$, $C_6H_5CH(C_6H_5)Br$, $C_6H_5CH(CH_3)Br$, $C_6H_5C(CH_3)(C_6H_5)Br$**

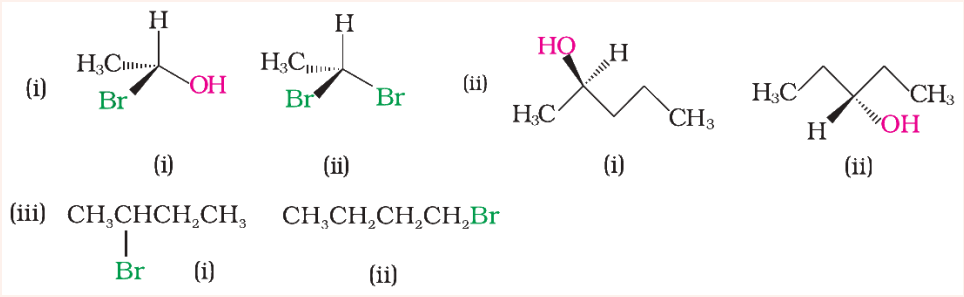
Ans. / उत्तर: (i) **S_N1:** $CH_3CH_2CH_2CH_2Br < (CH_3)_2CHCH_2Br < CH_3CH_2CH(Br)CH_3 < (CH_3)_3CBr$; **$S_N2$:** exactly the reverse.

(ii) **S_N1:** $C_6H_5C(CH_3)(C_6H_5)Br > C_6H_5CH(C_6H_5)Br > C_6H_5CH(CH_3)Br > C_6H_5CH_2Br$; **$S_N2$:** reverse.

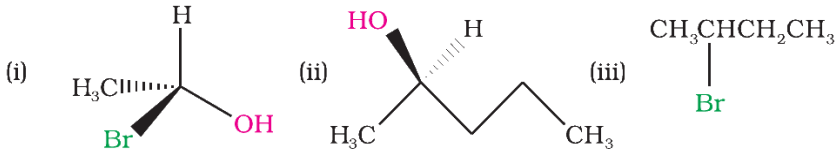
Reason: S_N1 depends on carbocation stability (3° > 2° > 1°; two phenyls stabilise by resonance); S_N2 depends on steric hindrance (phenyl is bulkier than methyl).

S_N1 — कार्बोधनायन का स्थायित्व; S_N2 — त्रिविम बाधा। इसलिए दोनों क्रम उलटे हैं।

Ex 6.8 **Identify chiral and achiral molecules in each pair:** काइरल व अकाइरल पहचानिए:



Ans. / उत्तर:



Chiral (one C with four different groups): (i)-(i) $CH_3CH(Br)OH$, (ii)-(i) pentan-2-ol, (iii)-(i) 2-bromobutane.

Achiral: (i)-(ii) CH_3CHBr_2 (two Br same), (ii)-(ii) pentan-3-ol (two ethyl same),

(iii)-(ii) 1-bromobutane (no stereocentre).
चार भिन्न समूहों वाला कार्बन हो तो काइरल; दो समूह समान हों तो अकाइरल।

Ex 6.9 **Although chlorine is an electron withdrawing group, yet it is ortho-, para- directing in electrophilic aromatic substitution reactions. Why?**
Cl इलेक्ट्रॉन-आकर्षी होते हुए भी ऑर्थो/पैरा निर्देशक क्यों है?

Ans. / उत्तर: Cl withdraws electrons by **−I effect** → destabilises the arenium ion → ring is **deactivated** (reactivity controlled by −I). But Cl donates its lone pair by **+R (resonance)**, which stabilises the carbocation formed by attack at **ortho and para** positions (a resonance form has + charge on the C bearing Cl, stabilised as a chloronium ion). So **orientation is controlled by resonance** → o/p.
−I प्रभाव से वलय निष्क्रिय, पर +R (अनुनाद) प्रभाव ऑर्थो/पैरा आक्रमण वाले कार्बोधनायन को स्थायी करता है — इसलिए ऑर्थो/पैरा निर्देशक।

B. Intext Questions (पाठ्यनिहित प्रश्न)

6.1 **Write structures of: (i) 2-Chloro-3-methylpentane (ii) 1-Chloro-4-ethylcyclohexane (iii) 4-tert-Butyl-3-iodoheptane (iv) 1,4-Dibromobut-2-ene (v) 1-Bromo-4-sec-butyl-2-methylbenzene.**
संरचनाएँ लिखिए।

Ans. / उत्तर: (i) $CH_3-CH(Cl)-CH(CH_3)-CH_2-CH_3$
(ii) Cyclohexane ring with −Cl at C-1 and $-CH_2CH_3$ at C-4 ($Cl-C_6H_{10}-C_2H_5$)
(iii) $CH_3CH_2-CH(I)-CH[C(CH_3)_3]-CH_2CH_2CH_3$
(iv) $BrCH_2-CH=CH-CH_2Br$
(v) Benzene ring: C-1 −Br, C-2 $-CH_3$, C-4 $-CH(CH_3)CH_2CH_3$

6.2 **Why is sulphuric acid not used during the reaction of alcohols with KI?**
ऐल्कोहॉल व KI की अभिक्रिया में H_2SO_4 क्यों नहीं लेते?

Ans. / उत्तर: H_2SO_4 converts KI to HI and, being an **oxidising agent**, oxidises HI to I_2: $2KI + H_2SO_4 \rightarrow 2KHSO_4 + 2HI$; $2HI + H_2SO_4 \rightarrow I_2 + SO_2 + 2H_2O$. So no HI is left to form R–I. A non-oxidising acid like **H_3PO_4** is used.
H_2SO_4 ऑक्सीकारक है — HI को I_2 में बदल देता है; इसलिए H_3PO_4 प्रयोग करते हैं।

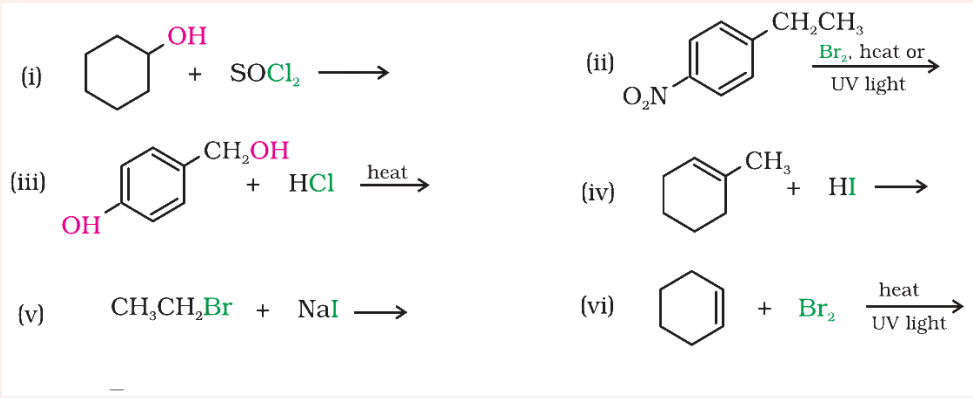
6.3 **Write structures of different dihalogen derivatives of propane.**
प्रोपेन के सभी डाइहैलोजन व्युत्पन्न लिखिए।

Ans. / उत्तर: $CH_3CH_2CHCl_2$ (1,1-dichloropropane) · $CH_3CCl_2CH_3$ (2,2-dichloropropane) · $ClCH_2CHClCH_3$ (1,2-dichloropropane) · $ClCH_2CH_2CH_2Cl$ (1,3-dichloropropane)

6.4 **Among the isomeric alkanes C_5H_{12}, identify the one that on photochemical chlorination yields (i) a single monochloride (ii) three isomeric monochlorides (iii) four isomeric monochlorides.**

Ans. / उत्तर: (i) **Neopentane**, $(CH_3)_4C$ — all 12 H equivalent.
(ii) **n-Pentane**, $CH_3CH_2CH_2CH_2CH_3$ — three kinds of H (C1/C5, C2/C4, C3).
(iii) **Isopentane (2-methylbutane)**, $(CH_3)_2CHCH_2CH_3$ — four kinds of H.
जितने प्रकार के समतुल्य H, उतने मोनोक्लोराइड।

6.5 **Draw the structures of major monohalo products:** *मुख्य उत्पाद लिखिए:*



Ans. / उत्तर: (i) Chlorocyclohexane (+ SO_2 + HCl)
(ii) $O_2N-C_6H_4-CH(Br)CH_3$ — 1-(1-bromoethyl)-4-nitrobenzene (benzylic H replaced)
(iii) $HO-C_6H_4-CH_2Cl$ — 4-(chloromethyl)phenol (only the alcoholic –OH is replaced; phenolic –OH is not)
(iv) 1-Iodo-1-methylcyclohexane (Markovnikov)
(v) CH_3CH_2I (Finkelstein)
(vi) 3-Bromocyclohexene (allylic substitution with Br_2/heat or UV)
(ii) व (vi) में मुक्त मूलक प्रतिस्थापन — बेंज़िलिक/ऐलिलिक H प्रतिस्थापित होता है।

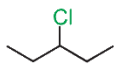
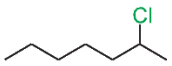
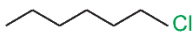
6.6 **Arrange in increasing order of boiling points: (i) Bromomethane, Bromoform, Chloromethane, Dibromomethane (ii) 1-Chloropropane, Isopropyl chloride, 1-Chlorobutane.**

Ans. / उत्तर: (i) Chloromethane < Bromomethane < Dibromomethane < Bromoform
(ii) Isopropyl chloride < 1-Chloropropane < 1-Chlorobutane
आण्विक द्रव्यमान बढ़ने पर क्वथनांक बढ़ता है; शाखन से घटता है।

6.7 **Which alkyl halide from the following pairs would react more rapidly by an S_N2 mechanism? (i) $CH_3CH_2CH_2CH_2Br$ or $CH_3CH_2CH(Br)CH_3$ (ii) $CH_3CH_2CH(Br)CH_3$ or $(CH_3)_3CBr$ (iii) $(CH_3)_2CHCH_2CH_2Br$ or $CH_3CH_2CH(CH_3)CH_2Br$**

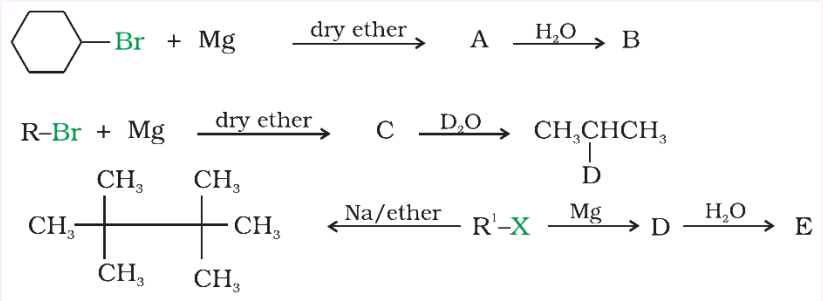
Ans. / उत्तर: (i) **$CH_3CH_2CH_2CH_2Br$** (1°, less hindered).
(ii) **$CH_3CH_2CH(Br)CH_3$** (2° is less hindered than 3°).
(iii) **$(CH_3)_2CHCH_2CH_2Br$** — its branch (CH_3) is farther from the C–Br carbon, so less steric hindrance.
S_N2 में जितनी कम त्रिविम बाधा, उतनी तेज़ अभिक्रिया।

6.8 **In the following pairs, which compound undergoes faster S_N1 reaction?**

(i)  and  (ii)  and 

Ans. / उत्तर: (i) **2-Chloro-2-methylpropane** (tert-butyl chloride) — forms the more stable 3° carbocation.
(ii) **2-Chloroheptane** — forms a 2° carbocation (more stable than the 1° from 1-chlorohexane).
S_N1 में जितना स्थायी कार्बोधनायन, उतनी तेज़ अभिक्रिया।

6.9 **Identify A, B, C, D, E, R and R' in the following:**



Ans. / उत्तर: A = **cyclohexylmagnesium bromide**, $C_6H_{11}MgBr$; B = **cyclohexane** (Grignard + H_2O → RH).
Since C + D_2O gives CH_3CHDCH_3, C = **$(CH_3)_2CHMgBr$** and R = **isopropyl** (R–Br =

2-bromopropane).

Wurtz product is 2,2,3,3-tetramethylbutane = $(CH_3)_3C-C(CH_3)_3$, so R^1 = **tert-butyl**, $R^1-X = (CH_3)_3CX$.

D = **$(CH_3)_3CMgX$**; E = **$(CH_3)_3CH$** (2-methylpropane).

C. Exercises (अभ्यास प्रश्न)

6.1 Name the following halides according to IUPAC system and classify them as alkyl, allyl, benzyl (primary, secondary, tertiary), vinyl or aryl halides.
IUPAC नाम दें और ऐल्किल, ऐलिल, बेंज़िल (1°/2°/3°), वाइनिल या ऐरिल में वर्गीकृत करें।

Ans. / उत्तर:

Compound	IUPAC name	Class
(i) $(CH_3)_2CHCH(Cl)CH_3$	2-Chloro-3-methylbutane	2° alkyl
(ii) $CH_3CH_2CH(CH_3)CH(C_2H_5)Cl$	3-Chloro-4-methylhexane	2° alkyl
(iii) $CH_3CH_2C(CH_3)_2CH_2I$	1-Iodo-2,2-dimethylbutane	1° alkyl
(iv) $(CH_3)_3CCH_2CH(Br)C_6H_5$	1-Bromo-3,3-dimethyl-1-phenylbutane	2° benzylic
(v) $CH_3CH(CH_3)CH(Br)CH_3$	2-Bromo-3-methylbutane	2° alkyl
(vi) $CH_3C(C_2H_5)_2CH_2Br$	1-Bromo-2-ethyl-2-methylbutane	1° alkyl
(vii) $CH_3C(Cl)(C_2H_5)CH_2CH_3$	3-Chloro-3-methylpentane	3° alkyl
(viii) $CH_3CH=C(Cl)CH_2CH(CH_3)_2$	3-Chloro-5-methylhex-2-ene	Vinylic
(ix) $CH_3CH=CHC(Br)(CH_3)_2$	4-Bromo-4-methylpent-2-ene	3° allylic
(x) $p\text{-}ClC_6H_4CH_2CH(CH_3)_2$	1-Chloro-4-(2-methylpropyl)benzene	Aryl
(xi) $m\text{-}ClCH_2C_6H_4CH_2C(CH_3)_3$	1-Chloromethyl-3-(2,2-dimethylpropyl)benzene	1° benzylic
(xii) $o\text{-}BrC_6H_4CH(CH_3)CH_2CH_3$	1-Bromo-2-(1-methylpropyl)benzene	Aryl

6.2 **Give the IUPAC names of: (i) $CH_3CH(Cl)CH(Br)CH_3$ (ii) $CHF_2CBrClF$ (iii) $ClCH_2C{\equiv}CCH_2Br$ (iv) $(CCl_3)_3CCl$ (v) $CH_3C(p\text{-}ClC_6H_4)_2CH(Br)CH_3$ (vi) $(CH_3)_3CCH{=}CClC_6H_4I\text{-}p$**

Ans. / उत्तर: (i) 2-Bromo-3-chlorobutane (ii) 1-Bromo-1-chloro-1,2,2-trifluoroethane (iii) 1-Bromo-4-chlorobut-2-yne (iv) 2-(Trichloromethyl)-1,1,1,2,3,3,3-heptachloropropane (v) 2-Bromo-3,3-bis(4-chlorophenyl)butane (vi) 1-Chloro-1-(4-iodophenyl)-3,3-dimethylbut-1-ene

6.3 **Write the structures of: (i) 2-Chloro-3-methylpentane (ii) p-Bromochlorobenzene (iii) 1-Chloro-4-ethylcyclohexane (iv) 2-(2-Chlorophenyl)-1-iodooctane (v) 2-Bromobutane (vi) 4-tert-Butyl-3-iodoheptane (vii) 1-Bromo-4-sec-butyl-2-methylbenzene (viii) 1,4-Dibromobut-2-ene**

Ans. / उत्तर: (i) $CH_3CH(Cl)CH(CH_3)CH_2CH_3$ (ii) $Br\text{-}C_6H_4\text{-}Cl$ (1,4) (iii) $Cl\text{-}C_6H_{10}\text{-}C_2H_5$ (1,4 on cyclohexane)
(iv) $ICH_2\text{-}CH(C_6H_4Cl\text{-}o)\text{-}CH_2CH_2CH_2CH_2CH_2CH_3$ (v) $CH_3CH(Br)CH_2CH_3$ (vi) $CH_3CH_2CH(I)CH[C(CH_3)_3]CH_2CH_2CH_3$ (vii) ring: 1-Br, 2-CH_3, 4-$CH(CH_3)CH_2CH_3$ (viii) $BrCH_2CH{=}CHCH_2Br$

6.4 **Which one of the following has the highest dipole moment? (i) CH_2Cl_2 (ii) $CHCl_3$ (iii) CCl_4**
किसका द्विध्रुव आघूर्ण सबसे अधिक है?

Ans. / उत्तर: **CH_2Cl_2** ($\mu \approx 1.60$ D). In CH_2Cl_2 the two C–Cl dipoles add up with the C–H dipoles. In $CHCl_3$ the three C–Cl dipoles partly cancel ($\mu \approx 1.04$ D). CCl_4 is perfectly symmetrical (tetrahedral) → **$\mu = 0$**.
CH_2Cl_2 में द्विध्रुव जुड़ते हैं; $CHCl_3$ में आंशिक रूप से निरस्त; CCl_4 सममित, $\mu = 0$।

6.5 **A hydrocarbon C_5H_{10} does not react with chlorine in dark but gives a single monochloro compound C_5H_9Cl in bright sunlight. Identify the hydrocarbon.**

Ans. / उत्तर: C_5H_{10} fits C_nH_{2n} (alkene or cycloalkane). No reaction with Cl_2 in dark → **no C=C** → cycloalkane. Only one monochloro product → all 10 H are equivalent → **cyclopentane**.
अंधेरे में Cl_2 से अभिक्रिया नहीं — द्विबंध नहीं; एक ही मोनोक्लोरो उत्पाद — सभी H समतुल्य → साइक्लोपेंटेन।

6.6 **Write the isomers of the compound having formula C_4H_9Br.**

Ans. / उत्तर: $CH_3CH_2CH_2CH_2Br$ (1-bromobutane) · $CH_3CH_2CH(Br)CH_3$ (2-bromobutane; exists as two enantiomers) · $(CH_3)_2CHCH_2Br$ (1-bromo-2-methylpropane) · $(CH_3)_3CBr$ (2-bromo-2-methylpropane)

6.7 **Write the equations for the preparation of 1-iodobutane from (i) 1-butanol (ii) 1-chlorobutane (iii) but-1-ene.**

Ans. / उत्तर: (i) $CH_3CH_2CH_2CH_2OH + KI \xrightarrow{-95\%\ H_3PO_4,\ \Delta} CH_3CH_2CH_2CH_2I + KH_2PO_4 + H_2O$ (or red P / I_2)

(ii) $CH_3(CH_2)_3Cl + NaI \xrightarrow{\text{dry acetone}} CH_3(CH_2)_3I + NaCl\downarrow$ (Finkelstein)

(iii) $CH_3CH_2CH{=}CH_2 + HBr \xrightarrow{\text{peroxide}} CH_3(CH_2)_3Br \xrightarrow{NaI,\ \text{dry acetone}} CH_3(CH_2)_3I$

6.8 **What are ambident nucleophiles? Explain with an example.**
उभयदंती नाभिकस्नेही क्या हैं? उदाहरण दीजिए।

Ans. / उत्तर: Nucleophiles having **two nucleophilic centres** (can attack through two different atoms). Example: **cyanide ion** $[:C{\equiv}N:]^-$ ↔ $[:C{=}N:]^-$ attacks through C → alkyl cyanide (R–CN, with KCN) or through N → isocyanide (R–NC, with AgCN). Similarly **nitrite ion** –O–N=O: through O → alkyl nitrite (R–O–N=O, KNO_2); through N → nitroalkane (R–NO_2, $AgNO_2$).

दो आक्रमण-केंद्र वाले नाभिकस्नेही — जैसे CN^- (C या N से) और NO_2^- (O या N से)।

6.9 **Which compound in each pair will react faster in S_N2 reaction with –OH? (i) CH_3Br or CH_3I (ii) $(CH_3)_3CCl$ or CH_3Cl**

Ans. / उत्तर: (i) **CH_3I** — I^- is a better leaving group (weaker C–I bond). (ii) **CH_3Cl** — no steric hindrance; $(CH_3)_3CCl$ is highly hindered.

(i) आयोडाइड श्रेष्ठ अवशिष्ट समूह; (ii) मेथिल पर त्रिविम बाधा नहीं।

6.10 **Predict all the alkenes that would be formed by dehydrohalogenation of the following halides with sodium ethoxide in ethanol and identify the major alkene: (i) 1-Bromo-1-methylcyclohexane (ii) 2-Chloro-2-methylbutane (iii) 2,2,3-Trimethyl-3-bromopentane**

Ans. / उत्तर: (i) **1-Methylcyclohexene (major)** + methylenecyclohexane (minor). The two ring β-carbons are equivalent, so they give the same alkene.

(ii) $CH_3C(Cl)(CH_3)CH_2CH_3$ → **2-methylbut-2-ene (major)**, $(CH_3)_2C{=}CHCH_3$, +

2-methylbut-1-ene (minor), $CH_2=C(CH_3)CH_2CH_3$.

(iii) $(CH_3)_3C-C(Br)(CH_3)-CH_2CH_3$ (C-2 has no H) → **3,4,4-trimethylpent-2-ene (major)**, $(CH_3)_3C-C(CH_3)=CH-CH_3$, + 2-ethyl-3,3-dimethylbut-1-ene (minor), $(CH_3)_3C-C(=CH_2)CH_2CH_3$.

ज़ैतसेव नियम: अधिक प्रतिस्थापित ऐल्कीन मुख्य उत्पाद।

6.11 How will you bring about the following conversions? *निम्न रूपांतरण कैसे करेंगे?*

Ans. / उत्तर: (i) **Ethanol → but-1-yne:** $C_2H_5OH \xrightarrow{-SOCl_2} C_2H_5Cl$; $HC\equiv CH \xrightarrow{-NaNH_2} HC\equiv C^-Na^+ \xrightarrow{-C_2H_5Cl} HC\equiv C-CH_2CH_3$

(ii) **Ethane → bromoethene:** $C_2H_6 \xrightarrow{-Br_2,\ h\nu} C_2H_5Br \xrightarrow{-alc.\ KOH} CH_2=CH_2 \xrightarrow{-Br_2/CCl_4} BrCH_2CH_2Br \xrightarrow{-alc.\ KOH\ (1\ mol)} CH_2=CHBr$

(iii) **Propene → 1-nitropropane:** $CH_3CH=CH_2 \xrightarrow{-HBr,\ peroxide} CH_3CH_2CH_2Br \xrightarrow{-AgNO_2} CH_3CH_2CH_2NO_2$

(iv) **Toluene → benzyl alcohol:** $C_6H_5CH_3 \xrightarrow{-Cl_2,\ h\nu} C_6H_5CH_2Cl \xrightarrow{-aq.\ KOH} C_6H_5CH_2OH$

(v) **Propene → propyne:** $CH_3CH=CH_2 \xrightarrow{-Br_2/CCl_4} CH_3CHBrCH_2Br \xrightarrow{-alc.\ KOH} CH_3CBr=CH_2 \xrightarrow{-NaNH_2} CH_3C\equiv CH$

(vi) **Ethanol → ethyl fluoride:** $C_2H_5OH \xrightarrow{-PCl_5} C_2H_5Cl \xrightarrow{-AgF\ (Swarts)} C_2H_5F$

(vii) **Bromomethane → propanone:** $CH_3Br \xrightarrow{-KCN} CH_3CN \xrightarrow{-CH_3MgBr,\ ether} (CH_3)_2C=NMgBr \xrightarrow{-H_3O^+} CH_3COCH_3$

(viii) **But-1-ene → but-2-ene:** $CH_3CH_2CH=CH_2 \xrightarrow{-HBr} CH_3CH_2CH(Br)CH_3 \xrightarrow{-alc.\ KOH,\ \Delta} CH_3CH=CHCH_3$ (Zaitsev)

(ix) **1-Chlorobutane → n-octane:** $2CH_3(CH_2)_3Cl + 2Na \xrightarrow{-dry\ ether} CH_3(CH_2)_6CH_3 + 2NaCl$ (Wurtz)

(x) **Benzene → biphenyl:** $C_6H_6 \xrightarrow{-Br_2/FeBr_3} C_6H_5Br$; $2C_6H_5Br + 2Na \xrightarrow{-dry\ ether} C_6H_5-C_6H_5 + 2NaBr$ (Fittig)

6.12 Explain why (i) the dipole moment of chlorobenzene is lower than that of cyclohexyl chloride? (ii) alkyl halides, though polar, are immiscible with water? (iii) Grignard reagents should be prepared under anhydrous conditions?

Ans. / उत्तर: (i) In chlorobenzene the C–Cl carbon is sp^2 (more electronegative than sp^3), so the C–Cl bond is less polar. Also, because of resonance the lone pair of Cl is delocalised into the ring, giving the C–Cl bond partial double-bond character and an opposing dipole. So μ(chlorobenzene) < μ(cyclohexyl chloride).

sp^2 कार्बन अधिक विद्युतऋणी तथा अनुनाद के कारण C–Cl की ध्रुवता कम।

(ii) To dissolve, the strong **H-bonds between water molecules** must be broken; the new attractions formed between haloalkane and water are weaker and release less energy. So haloalkanes are immiscible. जल के H-बंध तोड़ने की ऊर्जा, नए आकर्षण से मिलने वाली ऊर्जा से अधिक।

(iii) Grignard reagents are very reactive and react with any proton source, even moisture: $RMgX + H_2O \rightarrow RH + Mg(OH)X$. So they are made in **dry ether**. नमी से RH बन जाता है, इसलिए निर्जल परिस्थिति।

6.13 Give the uses of freon 12, DDT, carbon tetrachloride and iodoform.

Ans. / उत्तर: **Freon-12 (CCl_2F_2):** refrigerant, air-conditioning, aerosol propellant.
DDT: insecticide — against malaria-carrying mosquitoes and typhus-carrying lice.
CCl_4: manufacture of refrigerants, aerosol propellants and CFCs; solvent; earlier as cleaning fluid, spot remover and fire extinguisher.
Iodoform (CHI_3): earlier used as an antiseptic (due to free iodine released).
फ़्रियॉन — प्रशीतक; DDT — कीटनाशी; CCl_4 — विलायक, CFC निर्माण; आयोडोफ़ॉर्म — पूतिरोधी।

6.14 Write the structure of the major organic product: (i) $CH_3CH_2CH_2Cl + NaI$ (acetone, heat) (ii) $(CH_3)_3CBr + KOH$ (ethanol, heat) (iii) $CH_3CH(Br)CH_2CH_3 + NaOH$ (water) (iv) $CH_3CH_2Br + KCN$ (aq. ethanol) (v) $C_6H_5ONa + C_2H_5Cl$ (vi) $CH_3CH_2CH_2OH + SOCl_2$ (vii) $CH_3CH_2CH=CH_2 + HBr$ (peroxide) (viii) $CH_3CH=C(CH_3)_2 + HBr$

Ans. / उत्तर: (i) $CH_3CH_2CH_2I$ (ii) $(CH_3)_2C=CH_2$ (elimination) (iii) $CH_3CH(OH)CH_2CH_3$ (iv) CH_3CH_2CN (v) $C_6H_5OC_2H_5$ (Williamson) (vi) $CH_3CH_2CH_2Cl$ (+ SO_2 + HCl) (vii) $CH_3CH_2CH_2CH_2Br$ (anti-Markovnikov) (viii) $CH_3CH_2C(Br)(CH_3)_2$ (Markovnikov)

6.15 Write the mechanism of the following reaction: n-BuBr + KCN $\xrightarrow{-EtOH-H_2O}$ n-BuCN

Ans. / उत्तर: KCN is ionic → gives CN^-, which attacks through C. 1-Bromobutane is a 1° halide → **S_N2** (one step):

$N\equiv C:^- + CH_3CH_2CH_2-CH_2-Br \rightarrow [N\equiv C^{\delta-}\cdots CH_2(C_3H_7)\cdots Br^{\delta-}]^{\ddagger} \rightarrow N\equiv C-CH_2CH_2CH_2CH_3 + Br^-$

CN^- attacks from the side opposite to Br (backside attack); the C–C bond forms

as the C–Br bond breaks; in the transition state C is bonded to five groups. Rate = $k[n\text{-BuBr}][CN^-]$.

S_N2: CN^- पीछे से आक्रमण करता है, एक ही चरण में C–CN बनता और C–Br टूटता है।

6.16 **Arrange the compounds of each set in order of reactivity towards S_N2 displacement: (i) 2-Bromo-2-methylbutane, 1-Bromopentane, 2-Bromopentane (ii) 1-Bromo-3-methylbutane, 2-Bromo-2-methylbutane, 2-Bromo-3-methylbutane (iii) 1-Bromobutane, 1-Bromo-2,2-dimethylpropane, 1-Bromo-2-methylbutane, 1-Bromo-3-methylbutane**

Ans. / उत्तर: (i) 1-Bromopentane > 2-Bromopentane > 2-Bromo-2-methylbutane
(ii) 1-Bromo-3-methylbutane > 2-Bromo-3-methylbutane > 2-Bromo-2-methylbutane
(iii) 1-Bromobutane > 1-Bromo-3-methylbutane > 1-Bromo-2-methylbutane > 1-Bromo-2,2-dimethylpropane
1° > 2° > 3°; और शाखा C–Br के जितनी पास, बाधा उतनी अधिक।

6.17 **Out of $C_6H_5CH_2Cl$ and $C_6H_5CHClC_6H_5$, which is more easily hydrolysed by aqueous KOH?**

Ans. / उत्तर: **$C_6H_5CHClC_6H_5$**. Hydrolysis goes by S_N1; the carbocation $(C_6H_5)_2CH^+$ is stabilised by resonance with **two** phenyl rings, so it forms more easily than $C_6H_5CH_2^+$.
दो फ़ेनिल समूहों से कार्बोधनायन अधिक स्थायी — S_N1 तेज़।

6.18 **p-Dichlorobenzene has higher m.p. than those of o- and m-isomers. Discuss.**

Ans. / उत्तर: p-Dichlorobenzene is **symmetrical**, so its molecules pack closely and fit better in the crystal lattice → stronger intermolecular forces → more energy is needed to melt it. (Boiling points are nearly the same for all three.)
पैरा-समावयवी सममित — क्रिस्टल जालक में अच्छी तरह फ़िट, इसलिए गलनांक अधिक।

6.19 **How the following conversions can be carried out?**

Ans. / उत्तर: (i) **Propene → propan-1-ol:** $CH_3CH{=}CH_2 \xrightarrow{-HBr,\ peroxide} CH_3CH_2CH_2Br \xrightarrow{aq.\ KOH} CH_3CH_2CH_2OH$
(ii) **Ethanol → but-1-yne:** as in 6.11 (i).
(iii) **1-Bromopropane → 2-bromopropane:** $\xrightarrow{alc.\ KOH} CH_3CH{=}CH_2 \xrightarrow{HBr} CH_3CH(Br)CH_3$

(iv) **Toluene → benzyl alcohol:** as in 6.11 (iv).

(v) **Benzene → 4-bromonitrobenzene:** $C_6H_6 \xrightarrow{Br_2/FeBr_3} C_6H_5Br \xrightarrow{\text{conc. } HNO_3/H_2SO_4} p\text{-}BrC_6H_4NO_2$ (major; Br is o/p directing)

(vi) **Benzyl alcohol → 2-phenylethanoic acid:** $C_6H_5CH_2OH \xrightarrow{SOCl_2} C_6H_5CH_2Cl \xrightarrow{KCN} C_6H_5CH_2CN \xrightarrow{H_3O^+} C_6H_5CH_2COOH$

(vii) **Ethanol → propanenitrile:** $C_2H_5OH \xrightarrow{PCl_5} C_2H_5Cl \xrightarrow{KCN} C_2H_5CN$

(viii) **Aniline → chlorobenzene:** $C_6H_5NH_2 \xrightarrow{NaNO_2/HCl,\ 273\text{-}278\ K} C_6H_5N_2^+Cl^- \xrightarrow{Cu_2Cl_2/HCl} C_6H_5Cl$ (Sandmeyer)

(ix) **2-Chlorobutane → 3,4-dimethylhexane:** $2CH_3CH(Cl)CH_2CH_3 + 2Na \xrightarrow{\text{dry ether}} CH_3CH_2CH(CH_3)\text{-}CH(CH_3)CH_2CH_3$ (Wurtz)

(x) **2-Methyl-1-propene → 2-chloro-2-methylpropane:** $(CH_3)_2C{=}CH_2 + HCl \rightarrow (CH_3)_3CCl$ (Markovnikov)

(xi) **Ethyl chloride → propanoic acid:** $C_2H_5Cl \xrightarrow{KCN} C_2H_5CN \xrightarrow{H_3O^+} C_2H_5COOH$

(xii) **But-1-ene → n-butyl iodide:** $\xrightarrow{HBr,\ \text{peroxide}} CH_3(CH_2)_3Br \xrightarrow{NaI,\ \text{dry acetone}} CH_3(CH_2)_3I$

(xiii) **2-Chloropropane → 1-propanol:** $\xrightarrow{\text{alc. } KOH} CH_3CH{=}CH_2 \xrightarrow{HBr,\ \text{peroxide}} CH_3CH_2CH_2Br \xrightarrow{\text{aq. } KOH} CH_3CH_2CH_2OH$

(xiv) **Isopropyl alcohol → iodoform:** $CH_3CH(OH)CH_3 + 4I_2 + 6NaOH \xrightarrow{\Delta} CHI_3\downarrow + CH_3COONa + 5NaI + 5H_2O$

(xv) **Chlorobenzene → p-nitrophenol:** $C_6H_5Cl \xrightarrow{\text{conc. } HNO_3/H_2SO_4} p\text{-}ClC_6H_4NO_2 \xrightarrow{\text{(i) NaOH, 443 K (ii) } H^+} p\text{-}HOC_6H_4NO_2$

(xvi) **2-Bromopropane → 1-bromopropane:** $\xrightarrow{\text{alc. } KOH} CH_3CH{=}CH_2 \xrightarrow{HBr,\ \text{peroxide}} CH_3CH_2CH_2Br$

(xvii) **Chloroethane → butane:** $2C_2H_5Cl + 2Na \xrightarrow{\text{dry ether}} C_4H_{10} + 2NaCl$ (Wurtz)

(xviii) **Benzene → diphenyl:** as in 6.11 (x).

(xix) **tert-Butyl bromide → isobutyl bromide:** $(CH_3)_3CBr \xrightarrow{\text{alc. } KOH} (CH_3)_2C{=}CH_2 \xrightarrow{HBr,\ \text{peroxide}} (CH_3)_2CHCH_2Br$

(xx) **Aniline → phenyl isocyanide:** $C_6H_5NH_2 + CHCl_3 + 3KOH\ (alc.) \xrightarrow{\Delta} C_6H_5NC + 3KCl + 3H_2O$ (carbylamine)

6.20 **The treatment of alkyl chlorides with aqueous KOH leads to the formation of alcohols but in the presence of alcoholic KOH, alkenes are major products. Explain.**

Ans. / उत्तर: In **aqueous** solution KOH gives highly hydrated OH^- ions, which act as a **nucleophile** → substitution → alcohol. **Alcoholic** KOH contains alkoxide ions (RO^-), a **stronger base**, which removes a β-hydrogen → **elimination** → alkene.
जलीय KOH: OH^- नाभिकस्नेही → प्रतिस्थापन (ऐल्कोहॉल)। ऐल्कोहॉली KOH: RO^- प्रबल क्षारक → β-H हटाकर विलोपन (ऐल्कीन)।

6.21 **Primary alkyl halide C_4H_9Br (a) reacted with alcoholic KOH to give compound (b). Compound (b) is reacted with HBr to give (c) which is an isomer of (a). When (a) is reacted with sodium metal it gives compound (d), C_8H_{18} which is different from the compound formed when n-butyl bromide is reacted with sodium. Give the structural formula of (a) and write the equations for all the reactions.**

Ans. / उत्तर: Since (d) is not n-octane, (a) is the branched 1° halide: **(a) = $(CH_3)_2CHCH_2Br$** (1-bromo-2-methylpropane).
$(CH_3)_2CHCH_2Br \xrightarrow{\text{alc. KOH}}$ **(b)** $(CH_3)_2C=CH_2$ (2-methylpropene)
$(CH_3)_2C=CH_2 + HBr \rightarrow$ **(c)** $(CH_3)_3CBr$ (2-bromo-2-methylpropane, Markovnikov) — an isomer of (a)
$2(CH_3)_2CHCH_2Br + 2Na \xrightarrow{\text{dry ether}}$ **(d)** $(CH_3)_2CHCH_2CH_2CH(CH_3)_2$ (2,5-dimethylhexane) + 2NaBr

6.22 **What happens when (i) n-butyl chloride is treated with alcoholic KOH (ii) bromobenzene is treated with Mg in the presence of dry ether (iii) chlorobenzene is subjected to hydrolysis (iv) ethyl chloride is treated with aqueous KOH (v) methyl bromide is treated with sodium in the presence of dry ether (vi) methyl chloride is treated with KCN?**

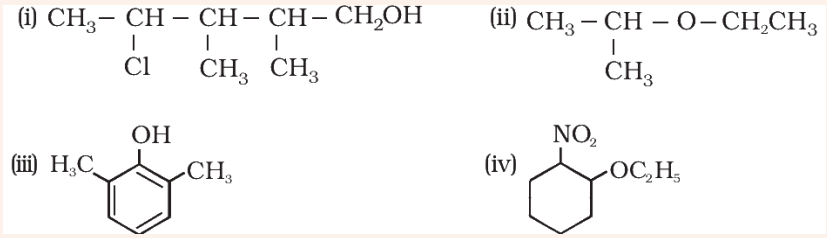
Ans. / उत्तर: (i) $CH_3CH_2CH_2CH_2Cl + KOH(alc.) \rightarrow CH_3CH_2CH=CH_2$ (but-1-ene) + $KCl + H_2O$
(ii) $C_6H_5Br + Mg \xrightarrow{\text{dry ether}} C_6H_5MgBr$ (phenylmagnesium bromide)
(iii) $C_6H_5Cl \xrightarrow{\text{(i) NaOH, 623 K, 300 atm (ii) } H^+} C_6H_5OH$ (phenol)
(iv) $C_2H_5Cl + KOH(aq) \rightarrow C_2H_5OH$ (ethanol) + KCl
(v) $2CH_3Br + 2Na \xrightarrow{\text{dry ether}} CH_3-CH_3$ (ethane) + 2NaBr
(vi) $CH_3Cl + KCN \rightarrow CH_3CN$ (ethanenitrile) + KCl

Unit 7 : Alcohols, Phenols & Ethers

ऐल्कोहॉल, फ़ीनॉल एवं ईथर — NCERT Solutions (Examples + Intext + Exercises)

A. Solved Examples (हल किए गए उदाहरण)

Ex 7.1 **Give IUPAC names of the following compounds:** IUPAC नाम दीजिए:



Ans. / उत्तर: (i) 4-Chloro-2,3-dimethylpentan-1-ol (ii) 2-Ethoxypropane (iii) 2,6-Dimethylphenol (iv) 1-Ethoxy-2-nitrocyclohexane

Ex 7.2 **Give the structures and IUPAC names of the products expected from: (a) catalytic reduction of butanal (b) hydration of propene in the presence of dilute sulphuric acid (c) reaction of propanone with methylmagnesium bromide followed by hydrolysis.**

Ans. / उत्तर: (a) $CH_3CH_2CH_2CHO \xrightarrow{H_2/Pd} CH_3CH_2CH_2CH_2OH$ — **Butan-1-ol**

(b) $CH_3CH{=}CH_2 \xrightarrow{H_2O/H^+} CH_3CH(OH)CH_3$ — **Propan-2-ol** (Markovnikov)

(c) $CH_3COCH_3 \xrightarrow{(i)\ CH_3MgBr\ (ii)\ H_2O} (CH_3)_3COH$ — **2-Methylpropan-2-ol**

Ex 7.3 **Arrange in increasing order of boiling points: (a) Pentan-1-ol, butan-1-ol, butan-2-ol, ethanol, propan-1-ol, methanol (b) Pentan-1-ol, n-butane, pentanal, ethoxyethane.**

Ans. / उत्तर: (a) Methanol < ethanol < propan-1-ol < butan-2-ol < butan-1-ol < pentan-1-ol (b.p. rises with size; branching lowers it).

(b) n-Butane < ethoxyethane < pentanal < pentan-1-ol (van der Waals < weak dipole < dipole–dipole < H-bonding).

आकार बढ़ने पर क्वथनांक बढ़ता; शाखन से घटता; H-बंध वाले का सबसे अधिक।

Ex 7.4 **Arrange in increasing order of acid strength: Propan-1-ol, 2,4,6-trinitrophenol, 3-nitrophenol, 3,5-dinitrophenol, phenol, 4-methylphenol.**

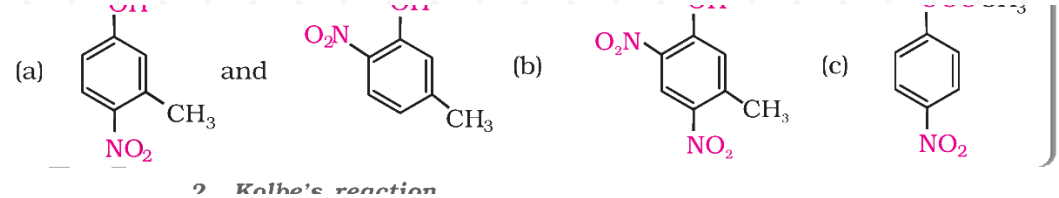
Ans. / उत्तर: Propan-1-ol < 4-methylphenol < phenol < 3-nitrophenol < 3,5-dinitrophenol < 2,4,6-trinitrophenol.

Alcohols are weaker than phenols; $-CH_3$ (electron donating) decreases acidity; each $-NO_2$ (electron withdrawing) increases it, most at o/p.

मेथिल अम्लता घटाता, नाइट्रो बढ़ाता है; जितने अधिक NO_2, उतना प्रबल अम्ल।

Ex 7.5 **Write the structures of the major products expected from: (a) mononitration of 3-methylphenol (b) dinitration of 3-methylphenol (c) mononitration of phenyl methanoate.**

Ans. / उत्तर: The combined o/p-directing influence of $-OH$ and $-CH_3$ decides the position (the site between the two groups is crowded).

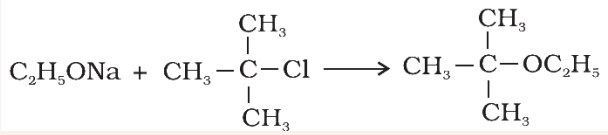


2 Kolbe's reaction

(a) 3-Methyl-4-nitrophenol and 5-methyl-2-nitrophenol (b) 5-Methyl-2,4-dinitrophenol (c) The $-O-CO-$ group is o/p directing; para product is major (less steric hindrance).

$-OH$ व $-CH_3$ दोनों ऑर्थो/पैरा निर्देशक हैं; दोनों के बीच वाली स्थिति भीड़ वाली है।

Ex 7.6 **The following is not an appropriate reaction for the preparation of t-butyl ethyl ether. (i) What would be the major product? (ii) Write a suitable reaction for the preparation of t-butyl ethyl ether.**



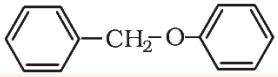
Ans. / उत्तर: (i) **2-Methylprop-1-ene**, $(CH_3)_2C=CH_2$. C_2H_5ONa is a strong nucleophile and a **strong base**; with a 3° halide, elimination dominates over substitution.

(ii) $(CH_3)_3C-ONa + CH_3CH_2Cl \rightarrow (CH_3)_3C-O-CH_2CH_3 + NaCl$ (halide must be 1°).

तृतीयक हैलाइड से ऐल्कीन बनती है; इसलिए तृतीयक भाग एल्कॉक्साइड में और प्राथमिक भाग हैलाइड में रखें।

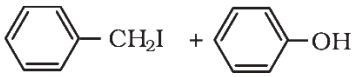
Ex 7.7 **Give the major products formed by heating each of the following ethers with HI.**

(i) $CH_3-CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2-O-CH_2-CH_3$ (ii) $CH_3-CH_2-CH_2-O-\underset{\displaystyle CH_3}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}}-CH_2-CH_3$

(iii) 

Ans. / उत्तर:

(i) $CH_3-CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2OH + CH_3CH_2I$ (ii) $CH_3CH_2CH_2OH + CH_3CH_2-\underset{\displaystyle CH_3}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}}-I$

(iii) 

(i) 2-Methylbutan-1-ol + iodoethane — both groups 1°, so I^- attacks the smaller ethyl (S_N2).

(ii) Propan-1-ol + 2-iodo-2-methylbutane — the 3° group forms a stable carbocation (S_N1), so it becomes the iodide.

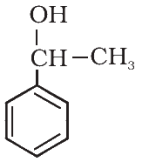
(iii) Iodomethylbenzene (benzyl iodide) + phenol — aryl–O bond is not broken; benzylic carbocation is stable.

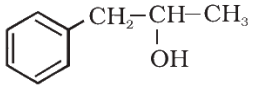
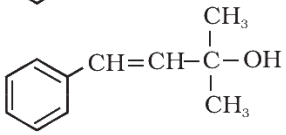
छोटा समूह आयोडाइड (S_N2); तृतीयक/बेंज़िलिक समूह आयोडाइड (S_N1); फ़ीनॉल कभी हैलाइड नहीं बनता।

B. Intext Questions (पाठ्यनिहित प्रश्न)

7.1 **Classify the following as primary, secondary and tertiary alcohols.** **7.2** **Identify allylic alcohols in the above examples.**

(i) $CH_3-\underset{\displaystyle CH_3}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}}-CH_2OH$ (ii) $H_2C=CH-CH_2OH$

(iii) $CH_3-CH_2-CH_2-OH$ (iv) 

(v)  (vi) 

Ans. / उत्तर: **Primary:** (i), (ii), (iii) **Secondary:** (iv), (v) **Tertiary:** (vi)

Allylic alcohols: (ii) $H_2C=CH-CH_2OH$ and (vi) — –OH is on the sp^3 carbon next

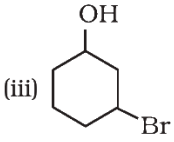
to C=C.

-OH वाले कार्बन पर कितने कार्बन जुड़े हैं, उससे 1°/2°/3°; द्विबंध के बगल वाले कार्बन पर -OH = ऐलिलिक।

7.3 Name the following compounds according to IUPAC system.

(i) $CH_3-CH_2-\underset{\displaystyle CH_2Cl}{\underset{|}{CH}}-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2OH$

(ii) $CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2-\underset{\displaystyle OH}{\underset{|}{CH}}-CH_2OH$

(iii) 

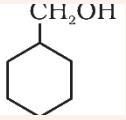
(iv) $H_2C=CH-\underset{\displaystyle OH}{\underset{|}{CH}}-CH_2-CH_2-CH_3$

(v) $CH_3-\underset{\displaystyle CH_3}{\underset{|}{C}}=\underset{\displaystyle Br}{\underset{|}{C}}-CH_2OH$

Ans. / उत्तर: (i) 4-Chloro-3-ethyl-2-(1-methylethyl)butan-1-ol (ii) 2,5-Dimethylhexane-1,3-diol (iii) 3-Bromocyclohexanol (iv) Hex-1-en-3-ol (v) 2-Bromo-3-methylbut-2-en-1-ol

7.4 Show how are the following alcohols prepared by the reaction of a suitable Grignard reagent on methanal?

(i) $CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2OH$

(ii) 

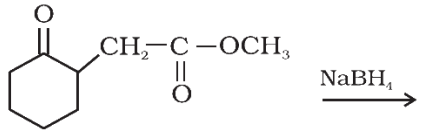
Ans. / उत्तर: (i) $(CH_3)_2CHMgBr + HCHO \rightarrow (CH_3)_2CHCH_2OMgBr \xrightarrow{-H_2O} (CH_3)_2CHCH_2OH + Mg(OH)Br$

(ii) $C_6H_{11}MgBr$ (cyclohexylmagnesium bromide) + $HCHO \rightarrow C_6H_{11}CH_2OMgBr \xrightarrow{-H_2O} C_6H_{11}CH_2OH$ (cyclohexylmethanol)

मेथेनैल + RMgX → $R-CH_2OH$ (प्राथमिक ऐल्कोहॉल)।

7.5 Write structures of the products of the following reactions:

(i) $CH_3-CH=CH_2 \xrightarrow{H_2O/H^+}$

(ii) 

(iii) $CH_3-CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CHO \xrightarrow{NaBH_4}$

Ans. / उत्तर: (i) $CH_3CH(OH)CH_3$ (propan-2-ol, Markovnikov)

(ii) Only the ring ketone is reduced; the ester is **not** reduced by $NaBH_4$ → methyl 2-(2-hydroxycyclohexyl)ethanoate (ring C=O → CH-OH, $-CH_2COOCH_3$ unchanged)

(iii) $CH_3CH_2CH(CH_3)CH_2OH$ (2-methylbutan-1-ol)

$NaBH_4$ केवल ऐल्डिहाइड/कीटोन को अपचयित करता है, एस्टर को नहीं।

7.6 **Give structures of the products when each alcohol reacts with (a) HCl–$ZnCl_2$ (b) HBr (c) $SOCl_2$: (i) Butan-1-ol (ii) 2-Methylbutan-2-ol**

Ans. / उत्तर: (i) (a) $CH_3CH_2CH_2CH_2Cl$ (slowly, on heating) (b) $CH_3CH_2CH_2CH_2Br$ (c) $CH_3CH_2CH_2CH_2Cl$

(ii) (a) $(CH_3)_2C(Cl)CH_2CH_3$ (immediately) (b) $(CH_3)_2C(Br)CH_2CH_3$ (c) $(CH_3)_2C(Cl)CH_2CH_3$

7.7 **Predict the major product of acid catalysed dehydration of (i) 1-methylcyclohexanol and (ii) butan-1-ol.**

Ans. / उत्तर: (i) **1-Methylcyclohexene** (more substituted alkene).

(ii) A mixture of but-1-ene and but-2-ene; **but-2-ene is major** because the 1° carbocation rearranges (hydride shift) to a more stable 2° carbocation, which then loses H^+ (Zaitsev).

प्राथमिक कार्बोधनायन, हाइड्राइड विस्थापन से द्वितीयक बनता है — इसलिए ब्यूट-2-ईन मुख्य।

7.8 **Ortho and para nitrophenols are more acidic than phenol. Draw the resonance structures of the corresponding phenoxide ions.**

Ans. / उत्तर: In **p-nitrophenoxide**, besides the usual forms with the negative charge at o/p ring carbons, there is an extra form in which the charge reaches the $-NO_2$ oxygen:

$^-O-C_6H_4-N(=O)O^-$ ... ↔ $O=C_6H_4=N^+(O^-)O^-$ (quinonoid form: ring C=O at C-1, C=N at C-4, both O of nitro carry negative charge).

In **o-nitrophenoxide** the same quinonoid form exists with C=N at C-2.

This extra delocalisation onto the electronegative O of $-NO_2$ makes o-/p-nitrophenoxide more stable than phenoxide, so o-/p-nitrophenols are more acidic. (m-NO_2 cannot take the charge by resonance.)

ऑर्थो/पैरा पर NO_2 होने से ऋणावेश NO_2 के ऑक्सीजन तक पहुँचता है — फ़ीनॉक्साइड अधिक स्थायी, अम्लता अधिक।

7.9 **Write the equations involved in (i) Reimer–Tiemann reaction (ii) Kolbe's reaction.**

Ans. / उत्तर: (i) $C_6H_5OH + CHCl_3 + aq.\ NaOH \xrightarrow{340\ K} o\text{-}(NaO)C_6H_4CHCl_2$ (substituted benzal chloride) $\xrightarrow{-NaOH} o\text{-}(NaO)C_6H_4CHO \xrightarrow{H^+}$ **$o\text{-}HOC_6H_4CHO$ (salicylaldehyde)**

(ii) $C_6H_5OH \xrightarrow{NaOH} C_6H_5ONa \xrightarrow{(i)\ CO_2,\ 400\ K,\ 4\text{–}7\ atm\ (ii)\ H^+}$ **o-HOC_6H_4COOH (salicylic acid)**

7.10 Write the reactions of Williamson synthesis of 2-ethoxy-3-methylpentane starting from ethanol and 3-methylpentan-2-ol.

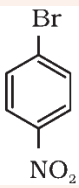
Ans. / उत्तर: $C_2H_5OH + HBr \rightarrow C_2H_5Br + H_2O$

$CH_3CH_2CH(CH_3)CH(OH)CH_3 + Na \rightarrow CH_3CH_2CH(CH_3)CH(ONa)CH_3 + ½H_2$

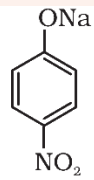
$CH_3CH_2CH(CH_3)CH(ONa)CH_3 + C_2H_5Br \rightarrow CH_3CH_2CH(CH_3)CH(OC_2H_5)CH_3 + NaBr$

प्राथमिक भाग (एथिल) हैलाइड बनाता है, द्वितीयक भाग एल्कॉक्साइड — ताकि विलोपन न हो।

7.11 Which of the following is an appropriate set of reactants for the preparation of 1-methoxy-4-nitrobenzene and why?

(i) 

+ CH_3ONa

(ii) 

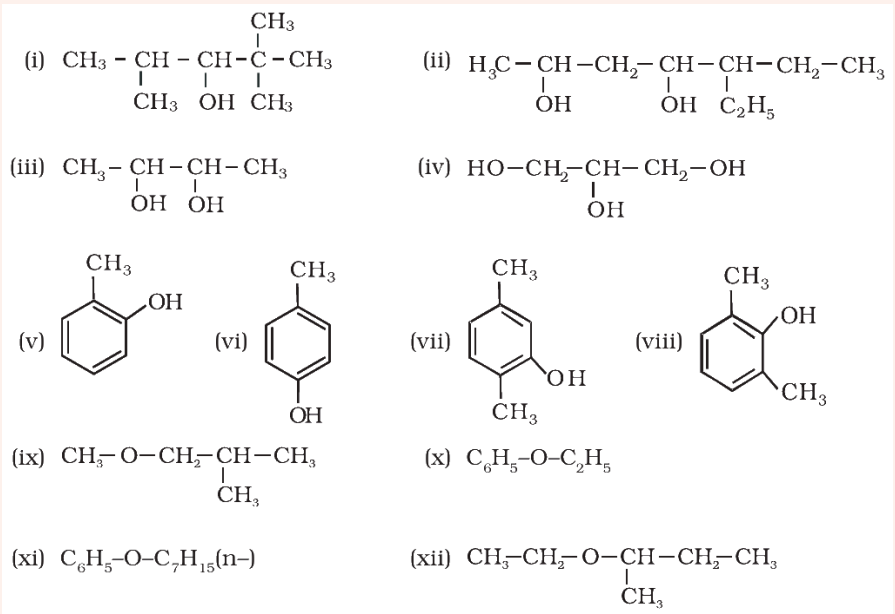
+ CH_3Br

Ans. / उत्तर: Set (ii) — sodium 4-nitrophenoxide + CH_3Br. Here the nucleophile (phenoxide) attacks the sp^3 carbon of CH_3Br by S_N2. In set (i), Br is on an sp^2 aryl carbon, whose C–Br bond has partial double-bond character and does not undergo nucleophilic substitution easily.

ऐरिल हैलाइड नाभिकस्नेही प्रतिस्थापन नहीं देता; इसलिए ऐरिल भाग फ़ीनॉक्साइड के रूप में लेते हैं।

C. Exercises (अभ्यास प्रश्न)

7.1 **Write IUPAC names of the following compounds:**



Ans. / उत्तर: (i) 2,2,4-Trimethylpentan-3-ol (ii) 5-Ethylheptane-2,4-diol (iii) Butane-2,3-diol (iv) Propane-1,2,3-triol (v) 2-Methylphenol (vi) 4-Methylphenol (vii) 2,5-Dimethylphenol (viii) 2,6-Dimethylphenol (ix) 1-Methoxy-2-methylpropane (x) Ethoxybenzene (xi) 1-Phenoxyheptane (xii) 2-Ethoxybutane

7.2 **Write structures of the compounds whose IUPAC names are: (i) 2-Methylbutan-2-ol (ii) 1-Phenylpropan-2-ol (iii) 3,5-Dimethylhexane-1,3,5-triol (iv) 2,3-Diethylphenol (v) 1-Ethoxypropane (vi) 2-Ethoxy-3-methylpentane (vii) Cyclohexylmethanol (viii) 3-Cyclohexylpentan-3-ol (ix) Cyclopent-3-en-1-ol (x) 4-Chloro-3-ethylbutan-1-ol**

Ans. / उत्तर: (i) $CH_3C(OH)(CH_3)CH_2CH_3$ (ii) $C_6H_5CH_2CH(OH)CH_3$ (iii) $HOCH_2CH_2C(OH)(CH_3)CH_2C(OH)(CH_3)CH_3$

(iv) Benzene ring: C-1 –OH, C-2 $-C_2H_5$, C-3 $-C_2H_5$ (v) $CH_3CH_2CH_2-O-CH_2CH_3$

(vi) $CH_3CH(OC_2H_5)CH(CH_3)CH_2CH_3$

(vii) $C_6H_{11}-CH_2OH$ (viii) $CH_3CH_2C(OH)(C_6H_{11})CH_2CH_3$ (ix) Five-membered ring with –OH at C-1 and C=C between C-3 and C-4 (x) $HOCH_2CH_2CH(C_2H_5)CH_2Cl$

7.3 **(i) Draw the structures of all isomeric alcohols of molecular formula $C_5H_{12}O$ and give their IUPAC names. (ii) Classify them as primary, secondary and tertiary.**

Ans. / उत्तर:

Structure	IUPAC name	Type
$CH_3CH_2CH_2CH_2CH_2OH$	Pentan-1-ol	1°
$CH_3CH_2CH_2CH(OH)CH_3$	Pentan-2-ol	2°
$CH_3CH_2CH(OH)CH_2CH_3$	Pentan-3-ol	2°
$(CH_3)_2CHCH_2CH_2OH$	3-Methylbutan-1-ol	1°
$CH_3CH_2CH(CH_3)CH_2OH$	2-Methylbutan-1-ol	1°
$(CH_3)_2C(OH)CH_2CH_3$	2-Methylbutan-2-ol	3°
$(CH_3)_2CHCH(OH)CH_3$	3-Methylbutan-2-ol	2°
$(CH_3)_3CCH_2OH$	2,2-Dimethylpropan-1-ol	1°

7.4 **Explain why propanol has higher boiling point than that of the hydrocarbon, butane?**

Ans. / उत्तर: Both have nearly the same molecular mass, but propanol molecules are associated by **intermolecular hydrogen bonding** (–O–H···O). Extra energy is needed to break these H-bonds. Butane has only weak van der Waals forces.
प्रोपेनॉल में अंतराअणुक H-बंध होते हैं; ब्यूटेन में केवल दुर्बल वान्डरवाल्स बल।

7.5 **Alcohols are comparatively more soluble in water than hydrocarbons of comparable molecular masses. Explain this fact.**

Ans. / उत्तर: Alcohols form **hydrogen bonds with water** molecules ($R–O–H\cdots OH_2$). Hydrocarbons cannot form H-bonds with water, so they are insoluble.
ऐल्कोहॉल जल से H-बंध बनाते हैं; हाइड्रोकार्बन नहीं।

7.6 **What is meant by hydroboration-oxidation reaction? Illustrate it with an example.**

Ans. / उत्तर: Addition of diborane $(BH_3)_2$ to an alkene gives a trialkylborane, which is oxidised by H_2O_2 in aqueous NaOH to an alcohol. Boron adds to the C with more H, so the net result is **anti-Markovnikov addition of water**.

$$3CH_3CH{=}CH_2 + BH_3 \rightarrow (CH_3CH_2CH_2)_3B \xrightarrow{-3H_2O_2,\ OH^-} 3CH_3CH_2CH_2OH + B(OH)_3$$

प्रोपीन से प्रोपेन-1-ऑल — मार्कोनीकॉफ़-विरोधी उत्पाद, उत्तम लब्धि।

7.7 **Give the structures and IUPAC names of monohydric phenols of molecular formula C_7H_8O.**

Ans. / उत्तर: o-$CH_3C_6H_4OH$ — **2-Methylphenol** (o-cresol) · m-$CH_3C_6H_4OH$ — **3-Methylphenol** (m-cresol) · p-$CH_3C_6H_4OH$ — **4-Methylphenol** (p-cresol)

7.8 **While separating a mixture of ortho and para nitrophenols by steam distillation, name the isomer which will be steam volatile. Give reason.**

Ans. / उत्तर: **o-Nitrophenol** is steam volatile. It has **intramolecular H-bonding** (between –OH and the adjacent $-NO_2$), so its molecules do not associate. p-Nitrophenol has **intermolecular H-bonding** → molecules associate → less volatile.
ऑर्थो में अंतःअणुक H-बंध — वाष्पशील; पैरा में अंतराअणुक H-बंध — अणु जुड़े, कम वाष्पशील।

7.9 **Give the equations of reactions for the preparation of phenol from cumene.**

Ans. / उत्तर: $C_6H_5CH(CH_3)_2$ (cumene) $\xrightarrow{-O_2\ (air)}$ $C_6H_5C(CH_3)_2-O-OH$ (cumene hydroperoxide) $\xrightarrow{-H^+/H_2O}$ $C_6H_5OH + CH_3COCH_3$

7.10 **Write chemical reaction for the preparation of phenol from chlorobenzene.**

Ans. / उत्तर: $C_6H_5Cl + NaOH \xrightarrow{-623\ K,\ 300\ atm} C_6H_5ONa \xrightarrow{-HCl} C_6H_5OH + NaCl$

7.11 **Write the mechanism of hydration of ethene to yield ethanol.**

Ans. / उत्तर: **Step 1** — protonation of alkene: $H_2O + H^+ \rightarrow H_3O^+$; $CH_2=CH_2 + H_3O^+ \rightarrow CH_3-CH_2^+ + H_2O$

Step 2 — nucleophilic attack of water on carbocation: $CH_3CH_2^+ + H_2O \rightarrow CH_3CH_2-O^+H_2$

Step 3 — deprotonation: $CH_3CH_2-O^+H_2 + H_2O \rightarrow CH_3CH_2OH + H_3O^+$
प्रोटॉनीकरण → कार्बोधनायन → जल का आक्रमण → प्रोटॉन निष्कासन।

7.12 **You are given benzene, conc. H_2SO_4 and NaOH. Write the equations for the preparation of phenol using these reagents.**

Ans. / उत्तर: $C_6H_6 + H_2SO_4$ (conc./oleum) $\rightarrow C_6H_5SO_3H + H_2O$
$C_6H_5SO_3H + NaOH$ (molten, fused) $\rightarrow C_6H_5ONa$ (+ Na_2SO_3, H_2O)
$2C_6H_5ONa + H_2SO_4$ (dil.) $\rightarrow 2C_6H_5OH + Na_2SO_4$

7.13 **Show how will you synthesise: (i) 1-phenylethanol from a suitable alkene (ii) cyclohexylmethanol using an alkyl halide by an S_N2 reaction (iii) pentan-1-ol using a suitable alkyl halide?**

Ans. / उत्तर: (i) $C_6H_5CH{=}CH_2$ (styrene) $\xrightarrow{H_2O/H^+}$ $C_6H_5CH(OH)CH_3$ (Markovnikov)

(ii) $C_6H_{11}CH_2Br + NaOH(aq) \xrightarrow{S_N2} C_6H_{11}CH_2OH + NaBr$

(iii) $CH_3(CH_2)_3CH_2Cl + KOH(aq) \rightarrow CH_3(CH_2)_3CH_2OH + KCl$

7.14 **Give two reactions that show the acidic nature of phenol. Compare acidity of phenol with that of ethanol.**

Ans. / उत्तर: $2C_6H_5OH + 2Na \rightarrow 2C_6H_5ONa + H_2\uparrow$ · $C_6H_5OH + NaOH \rightarrow C_6H_5ONa + H_2O$

Phenol ($pK_a \approx 10$) is about a **million times more acidic** than ethanol ($pK_a \approx 15.9$). Ethanol does not react with NaOH. Reasons: (i) –OH is on an sp^2 carbon, which withdraws electrons and makes O–H more polar; (ii) phenoxide ion is resonance-stabilised (charge delocalised over the ring), while ethoxide's charge is localised on O and is destabilised by +I of ethyl.

फ़ीनॉक्साइड अनुनाद से स्थायी; एथॉक्साइड नहीं — इसलिए फ़ीनॉल अधिक अम्लीय।

7.15 **Explain why is ortho nitrophenol more acidic than ortho methoxyphenol?**

Ans. / उत्तर: $-NO_2$ is **electron-withdrawing** (–I, –R): it stabilises the o-nitrophenoxide ion by delocalising the negative charge → more acidic. $-OCH_3$ is **electron-donating** (+R): it increases electron density on the phenoxide O and destabilises it → less acidic.

NO_2 इलेक्ट्रॉन खींचकर फ़ीनॉक्साइड स्थायी करता; OCH_3 इलेक्ट्रॉन देकर अस्थायी।

7.16 **Explain how does the –OH group attached to a carbon of benzene ring activate it towards electrophilic substitution?**

Ans. / उत्तर: The lone pair on O of –OH is delocalised into the ring (**+R effect**). Resonance forms place negative charge (high electron density) at the **ortho and para** positions. The electron-rich ring attracts electrophiles more strongly → activated, o/p-directing.

–OH का एकाकी युग्म अनुनाद से वलय में जाता है; ऑर्थो/पैरा पर इलेक्ट्रॉन घनत्व बढ़ता है।

7.17 **Give equations of the following reactions: (i) Oxidation of propan-1-ol with alkaline $KMnO_4$ (ii) Bromine in CS_2 with phenol (iii) Dilute HNO_3 with phenol (iv) Treating phenol with chloroform in presence of aqueous NaOH.**

Ans. / उत्तर: (i) $CH_3CH_2CH_2OH \xrightarrow{\text{alk. } KMnO_4} CH_3CH_2COO^-K^+ \xrightarrow{H^+} CH_3CH_2COOH$ (propanoic acid)

(ii) $C_6H_5OH + Br_2 \xrightarrow[273\ K]{CS_2} p\text{-}BrC_6H_4OH$ (major) + $o\text{-}BrC_6H_4OH$ (minor) + HBr

(iii) $C_6H_5OH \xrightarrow[298\ K]{\text{dil. } HNO_3} o\text{-}O_2NC_6H_4OH + p\text{-}O_2NC_6H_4OH$

(iv) Reimer–Tiemann: $C_6H_5OH + CHCl_3 + \text{aq. NaOH} \rightarrow$ (via benzal chloride) $\xrightarrow{H^+}$ salicylaldehyde ($o\text{-}HOC_6H_4CHO$)

7.18 **Explain the following with an example: (i) Kolbe's reaction (ii) Reimer–Tiemann reaction (iii) Williamson ether synthesis (iv) Unsymmetrical ether.**

Ans. / उत्तर: (i) **Kolbe's reaction:** sodium phenoxide reacts with CO_2 (a weak electrophile) to give salicylic acid after acidification. $C_6H_5ONa + CO_2 \xrightarrow[4\text{–}7\ atm]{400\ K;\ H^+} o\text{-}HOC_6H_4COOH$

(ii) **Reimer–Tiemann:** phenol + $CHCl_3$ + aq. NaOH introduces –CHO at the ortho position → salicylaldehyde.

(iii) **Williamson synthesis:** alkyl halide (preferably 1°) + sodium alkoxide/phenoxide → ether (S_N2). $CH_3CH_2Br + CH_3ONa \rightarrow CH_3CH_2OCH_3 + NaBr$

(iv) **Unsymmetrical (mixed) ether:** the two groups on O are different, e.g. C_2H_5–O–CH_3 (methoxyethane), C_6H_5–O–CH_3 (anisole).

कोल्बे — CO_2 से सैलिसिलिक अम्ल; राइमर-टीमन — $CHCl_3$ से सैलिसिलऐल्डिहाइड; विलियम्सन — RX + RONa; असममित ईथर — दोनों समूह भिन्न।

7.19 **Write the mechanism of acid dehydration of ethanol to yield ethene.**

Ans. / उत्तर: (conc. H_2SO_4, 443 K)

Step 1 (fast) — protonated alcohol: $CH_3CH_2OH + H^+ \rightleftharpoons CH_3CH_2O^+H_2$

Step 2 (slow, rate-determining) — carbocation: $CH_3CH_2O^+H_2 \rightleftharpoons CH_3CH_2^+ + H_2O$

Step 3 — loss of β-proton: $CH_3CH_2^+ \rightarrow CH_2{=}CH_2 + H^+$ (acid is regenerated; ethene is removed as formed)

7.20 **How are the following conversions carried out? (i) Propene → Propan-2-ol (ii) Benzyl chloride → Benzyl alcohol (iii) Ethyl magnesium chloride → Propan-1-ol (iv) Methyl magnesium bromide → 2-Methylpropan-2-ol.**

Ans. / उत्तर: (i) $CH_3CH=CH_2 + H_2O \xrightarrow{H^+} CH_3CH(OH)CH_3$

(ii) $C_6H_5CH_2Cl + NaOH(aq) \rightarrow C_6H_5CH_2OH + NaCl$

(iii) $C_2H_5MgCl + HCHO \rightarrow C_2H_5CH_2OMgCl \xrightarrow{-H_2O} CH_3CH_2CH_2OH$

(iv) $CH_3MgBr + CH_3COCH_3 \rightarrow (CH_3)_3COMgBr \xrightarrow{-H_2O} (CH_3)_3COH$

7.21 **Name the reagents used in the following reactions: (i) primary alcohol → carboxylic acid (ii) primary alcohol → aldehyde (iii) phenol → 2,4,6-tribromophenol (iv) benzyl alcohol → benzoic acid (v) dehydration of propan-2-ol → propene (vi) butan-2-one → butan-2-ol**

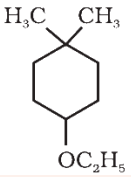
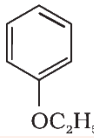
Ans. / उत्तर: (i) Acidified/alkaline $KMnO_4$ (or acidified $K_2Cr_2O_7$) (ii) PCC (pyridinium chlorochromate) or anhydrous CrO_3 (iii) Bromine water (iv) Acidified or alkaline $KMnO_4$ (v) 85% H_3PO_4 at 440 K (or conc. H_2SO_4) (vi) $NaBH_4$ or $LiAlH_4$ (or H_2/Ni)

7.22 **Give reason for the higher boiling point of ethanol in comparison to methoxymethane.**

Ans. / उत्तर: Ethanol molecules are associated by **intermolecular H-bonding**; methoxymethane has no H on oxygen, so it cannot form H-bonds among its own molecules (only weak dipole forces). Ethanol b.p. 351 K vs methoxymethane 248 K. एथेनॉल में H-बंध; मेथॉक्सीमेथेन में नहीं।

7.23 **Give IUPAC names of the following ethers:**

(i) $C_2H_5OCH_2-CH(CH_3)-CH_3$ (ii) $CH_3OCH_2CH_2Cl$ (iii) $O_2N-C_6H_4-OCH_3$ (p)

(iv) $CH_3CH_2CH_2OCH_3$ (v)  (vi) 

Ans. / उत्तर: (i) 1-Ethoxy-2-methylpropane (ii) 2-Chloro-1-methoxyethane (iii) 4-Nitroanisole (1-methoxy-4-nitrobenzene) (iv) 1-Methoxypropane (v) 1-Ethoxy-4,4-dimethylcyclohexane (vi) Ethoxybenzene

7.24 **Write the names of reagents and equations for the preparation of the following ethers by Williamson's synthesis: (i) 1-Propoxypropane (ii) Ethoxybenzene (iii) 2-Methoxy-2-methylpropane (iv) 1-Methoxyethane**

Ans. / उत्तर: (i) $CH_3CH_2CH_2ONa + CH_3CH_2CH_2Br \rightarrow CH_3CH_2CH_2OCH_2CH_2CH_3 + NaBr$

(ii) $C_6H_5ONa + C_2H_5Br \rightarrow C_6H_5OC_2H_5 + NaBr$

(iii) $(CH_3)_3CONa + CH_3Br \rightarrow (CH_3)_3COCH_3 + NaBr$ (not $(CH_3)_3CBr + CH_3ONa$, which gives alkene)

(iv) $CH_3CH_2ONa + CH_3Br \rightarrow CH_3CH_2OCH_3 + NaBr$

7.25 **Illustrate with examples the limitations of Williamson synthesis for the preparation of certain types of ethers.**

Ans. / उत्तर: (i) With **3° alkyl halides**, the alkoxide acts as a base and only alkene forms: $(CH_3)_3CBr + CH_3ONa \rightarrow (CH_3)_2C=CH_2 + CH_3OH + NaBr$. With 2° halides, elimination competes.

(ii) **Aryl halides** do not undergo nucleophilic substitution, so alkyl aryl ethers cannot be made from ArX + RONa: $C_6H_5Br + CH_3ONa \rightarrow$ no ether. (Use $C_6H_5ONa + CH_3Br$ instead.)

तृतीयक हैलाइड से ऐल्कीन; ऐरिल हैलाइड अभिक्रिया नहीं करते।

7.26 **How is 1-propoxypropane synthesised from propan-1-ol? Write mechanism of this reaction.**

Ans. / उत्तर: By acid dehydration at 413 K: $2CH_3CH_2CH_2OH \xrightarrow{\text{conc. } H_2SO_4,\ 413\ K} CH_3CH_2CH_2-O-CH_2CH_2CH_3 + H_2O$

Mechanism (S_N2): (1) $CH_3CH_2CH_2OH + H^+ \rightarrow CH_3CH_2CH_2O^+H_2$ (2) a second molecule of propanol attacks the protonated alcohol, water leaves: $C_3H_7OH + C_3H_7O^+H_2 \rightarrow C_3H_7-O^+(H)-C_3H_7 + H_2O$ (3) loss of $H^+ \rightarrow C_3H_7-O-C_3H_7$.

7.27 **Preparation of ethers by acid dehydration of secondary or tertiary alcohols is not a suitable method. Give reason.**

Ans. / उत्तर: 2° and 3° alcohols readily form stable carbocations and their bulky groups hinder S_N2 attack by another alcohol molecule. So **elimination predominates** and alkenes are formed instead of ethers.

द्वितीयक/तृतीयक ऐल्कोहॉल में विलोपन प्रबल — ईथर की जगह ऐल्कीन।

7.28 **Write the equation of the reaction of hydrogen iodide with: (i) 1-propoxypropane (ii) methoxybenzene (iii) benzyl ethyl ether.**

Ans. / उत्तर: (i) $CH_3CH_2CH_2OCH_2CH_2CH_3 + HI \rightarrow CH_3CH_2CH_2I + CH_3CH_2CH_2OH$ (with excess HI, the alcohol also gives propyl iodide)
(ii) $C_6H_5OCH_3 + HI \rightarrow C_6H_5OH + CH_3I$
(iii) $C_6H_5CH_2OC_2H_5 + HI \rightarrow C_6H_5CH_2I + C_2H_5OH$ (stable benzyl carbocation, S_N1)

7.29 **Explain the fact that in aryl alkyl ethers (i) the alkoxy group activates the benzene ring towards electrophilic substitution and (ii) it directs the incoming substituents to ortho and para positions.**

Ans. / उत्तर: The lone pair on O of –OR is delocalised into the ring (+R effect). (i) This increases electron density of the whole ring → **activated**. (ii) The resonance structures carry the negative charge at **ortho and para** positions, so electrophiles attack there.
–OR का एकाकी युग्म अनुनाद से वलय में → वलय सक्रिय; ऑर्थो/पैरा पर इलेक्ट्रॉन घनत्व अधिक।

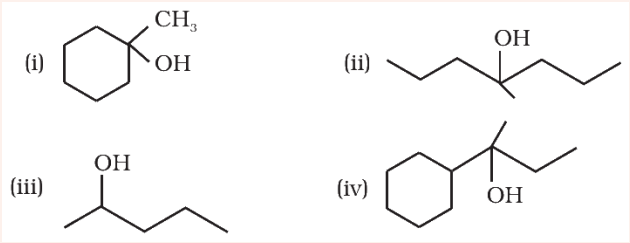
7.30 **Write the mechanism of the reaction of HI with methoxymethane.**

Ans. / उत्तर: **Step 1** — protonation: $CH_3-O-CH_3 + H-I \rightleftharpoons CH_3-O^+(H)-CH_3 + I^-$
Step 2 — S_N2 attack of I^-: $I^- + CH_3-O^+(H)-CH_3 \rightarrow CH_3I + CH_3OH$
Step 3 (excess HI, heat): $CH_3OH + HI \rightarrow CH_3O^+H_2 + I^- \rightarrow CH_3I + H_2O$

7.31 **Write equations of the following reactions: (i) Friedel–Crafts alkylation of anisole (ii) Nitration of anisole (iii) Bromination of anisole in ethanoic acid medium (iv) Friedel–Crafts acetylation of anisole.**

Ans. / उत्तर: (i) $C_6H_5OCH_3 + CH_3Cl \xrightarrow{anhyd.\ AlCl_3}$ 4-methylanisole (major) + 2-methylanisole (minor)
(ii) $C_6H_5OCH_3 \xrightarrow{conc.\ HNO_3 + H_2SO_4}$ 4-nitroanisole (major) + 2-nitroanisole (minor)
(iii) $C_6H_5OCH_3 + Br_2 \xrightarrow{CH_3COOH}$ p-bromoanisole (~90%, major) + o-bromoanisole (minor)
(iv) $C_6H_5OCH_3 + CH_3COCl \xrightarrow{anhyd.\ AlCl_3}$ 4-methoxyacetophenone (major) + 2-methoxyacetophenone (minor)

7.32 **Show how would you synthesise the following alcohols from appropriate alkenes?**



Ans. / उत्तर: All by acid-catalysed hydration (H_2O/H^+, Markovnikov):

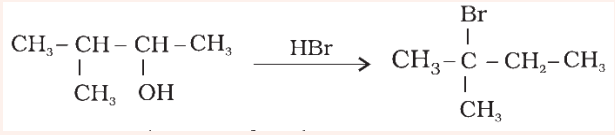
(i) 1-Methylcyclohexene → **1-methylcyclohexanol**

(ii) 4-Methylhept-3-ene → **4-methylheptan-4-ol**

(iii) Pent-1-ene → **pentan-2-ol** (pent-2-ene would give a mixture of pentan-2-ol and pentan-3-ol)

(iv) 2-Cyclohexylbut-2-ene (or 2-cyclohexylbut-1-ene) → **2-cyclohexylbutan-2-ol**

7.33 **When 3-methylbutan-2-ol is treated with HBr, the following reaction takes place. Give a mechanism for this reaction.**



Ans. / उत्तर: **Step 1** — protonation: $(CH_3)_2CH-CH(OH)-CH_3 + H^+ \rightarrow (CH_3)_2CH-CH(O^+H_2)-CH_3$

Step 2 — loss of water → 2° carbocation: $(CH_3)_2CH-C^+H-CH_3$

Step 3 — **1,2-hydride shift** from C-3 → more stable 3° carbocation: $(CH_3)_2C^+-CH_2-CH_3$

Step 4 — attack of Br^- → $(CH_3)_2C(Br)CH_2CH_3$ (2-bromo-2-methylbutane)

द्वितीयक कार्बोधनायन, हाइड्राइड विस्थापन से अधिक स्थायी तृतीयक में बदलता है।

Unit 8 : Aldehydes, Ketones & Carboxylic Acids

ऐल्डिहाइड, कीटोन एवं कार्बोक्सिलिक अम्ल — NCERT Solutions (Examples + Intext + Exercises)

A. Solved Examples (हल किए गए उदाहरण)

Ex 8.1 **Give names of the reagents to bring about the following transformations: (i) Hexan-1-ol to hexanal (ii) Cyclohexanol to cyclohexanone (iii) p-Fluorotoluene to p-fluorobenzaldehyde (iv) Ethanenitrile to ethanal (v) Allyl alcohol to propenal (vi) But-2-ene to ethanal**

Ans. / उत्तर: (i) $C_5H_5NH^+CrO_3Cl^-$ (PCC) (ii) Anhydrous CrO_3 (iii) CrO_3 in acetic anhydride, or 1. CrO_2Cl_2 2. H_2O (Etard) (iv) DIBAL-H, then H_2O (v) PCC (vi) O_3, then H_2O–Zn dust

Ex 8.2 **Arrange in increasing order of boiling points: $CH_3CH_2CH_2CHO$, $CH_3CH_2CH_2CH_2OH$, $H_5C_2–O–C_2H_5$, $CH_3CH_2CH_2CH_3$**

Ans. / उत्तर: $CH_3CH_2CH_2CH_3 < H_5C_2–O–C_2H_5 < CH_3CH_2CH_2CHO < CH_3CH_2CH_2CH_2OH$

Masses are similar (72–74). Butan-1-ol has H-bonding (highest); butanal is more polar than ethoxyethane (stronger dipole–dipole); butane has only van der Waals forces.

H-बंध > द्विध्रुव-द्विध्रुव > दुर्बल ध्रुवता > वान्डरवाल्स।

Ex 8.3 **Would you expect benzaldehyde to be more reactive or less reactive in nucleophilic addition reactions than propanal? Explain.**

Ans. / उत्तर: **Less reactive.** In benzaldehyde the C=O is in conjugation with the ring; resonance ($C_6H_5–CH=O \leftrightarrow {}^+C_6H_5=CH–O^-$) reduces the positive charge on the carbonyl carbon, making it less electrophilic than in propanal.

अनुनाद से कार्बोनिल कार्बन की इलेक्ट्रॉनस्नेहिता घटती है — बेंज़ैल्डिहाइड कम क्रियाशील।

Ex 8.4 **An organic compound (A), C_8H_8O, forms an orange-red precipitate with 2,4-DNP and gives a yellow precipitate on heating with iodine and NaOH. It neither reduces Tollens' or Fehling's reagent, nor decolourises bromine water or Baeyer's reagent. On drastic oxidation with chromic acid, it gives a carboxylic acid (B), $C_7H_6O_2$. Identify (A) and (B).**

Ans. / उत्तर: 2,4-DNP positive → C=O; Tollens'/Fehling negative → **ketone**; iodoform positive → **methyl ketone**; high unsaturation but no Br_2/Baeyer reaction → **aromatic ring**; oxidation gives $C_7H_6O_2$ = benzoic acid.

A = acetophenone, $C_6H_5COCH_3$; B = benzoic acid, C_6H_5COOH.

$C_6H_5COCH_3 + 3NaOI \rightarrow C_6H_5COONa + CHI_3\downarrow + 2NaOH$; $C_6H_5COCH_3 \xrightarrow{H_2CrO_4} C_6H_5COOH$

Ex 8.5 **Write chemical reactions to effect: (i) Butan-1-ol → butanoic acid (ii) Benzyl alcohol → phenylethanoic acid (iii) 3-Nitrobromobenzene → 3-nitrobenzoic acid (iv) 4-Methylacetophenone → benzene-1,4-dicarboxylic acid (v) Cyclohexene → hexane-1,6-dioic acid (vi) Butanal → butanoic acid**

Ans. / उत्तर: (i) $CH_3(CH_2)_3OH \xrightarrow{CrO_3\text{-}H_2SO_4} CH_3(CH_2)_2COOH$

(ii) $C_6H_5CH_2OH \xrightarrow{HBr} C_6H_5CH_2Br \xrightarrow{KCN} C_6H_5CH_2CN \xrightarrow{H_3O^+} C_6H_5CH_2COOH$

(iii) $m\text{-}O_2NC_6H_4Br \xrightarrow{Mg,\ ether} m\text{-}O_2NC_6H_4MgBr \xrightarrow{(i)\ CO_2\ (ii)\ H_3O^+} m\text{-}O_2NC_6H_4COOH$

(iv) $p\text{-}CH_3C_6H_4COCH_3 \xrightarrow{KMnO_4/KOH,\ \Delta;\ H^+} p\text{-}HOOCC_6H_4COOH$

(v) Cyclohexene $\xrightarrow{KMnO_4/H_2SO_4} HOOC(CH_2)_4COOH$

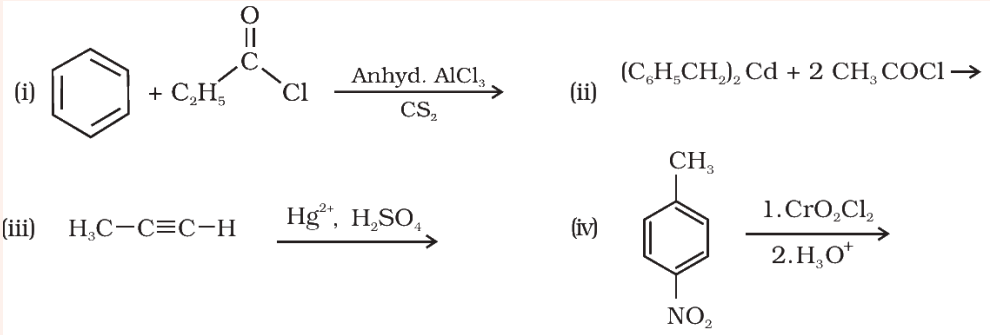
(vi) $CH_3CH_2CH_2CHO \xrightarrow{Tollens'\ reagent;\ H^+} CH_3CH_2CH_2COOH$

B. Intext Questions (पाठ्यनिहित प्रश्न)

8.1 **Write the structures of: (i) α-Methoxypropionaldehyde (ii) 3-Hydroxybutanal (iii) 2-Hydroxycyclopentanecarbaldehyde (iv) 4-Oxopentanal (v) Di-sec-butyl ketone (vi) 4-Fluoroacetophenone**

Ans. / उत्तर: (i) $CH_3CH(OCH_3)CHO$ (ii) $CH_3CH(OH)CH_2CHO$ (iii) cyclopentane ring with –CHO at C-1 and –OH at C-2 (iv) $CH_3COCH_2CH_2CHO$ (v) $CH_3CH_2CH(CH_3)\text{-}CO\text{-}CH(CH_3)CH_2CH_3$ (vi) $p\text{-}F\text{-}C_6H_4\text{-}COCH_3$

8.2 **Write the structures of products of the following reactions:**



Ans. / उत्तर: (i) $C_6H_5COCH_2CH_3$ — propiophenone (Friedel–Crafts acylation)

(ii) $2C_6H_5CH_2COCH_3$ (1-phenylpropan-2-one) + $CdCl_2$

(iii) CH_3COCH_3 — propanone (hydration of propyne; enol → ketone)

(iv) p-$O_2N-C_6H_4-CHO$ — 4-nitrobenzaldehyde (Etard)

8.3 **Arrange in increasing order of boiling points: CH_3CHO, CH_3CH_2OH, CH_3OCH_3, $CH_3CH_2CH_3$**

Ans. / उत्तर: $CH_3CH_2CH_3 < CH_3OCH_3 < CH_3CHO < CH_3CH_2OH$

8.4 **Arrange in increasing order of reactivity in nucleophilic addition: (i) Ethanal, Propanal, Propanone, Butanone (ii) Benzaldehyde, p-Tolualdehyde, p-Nitrobenzaldehyde, Acetophenone**

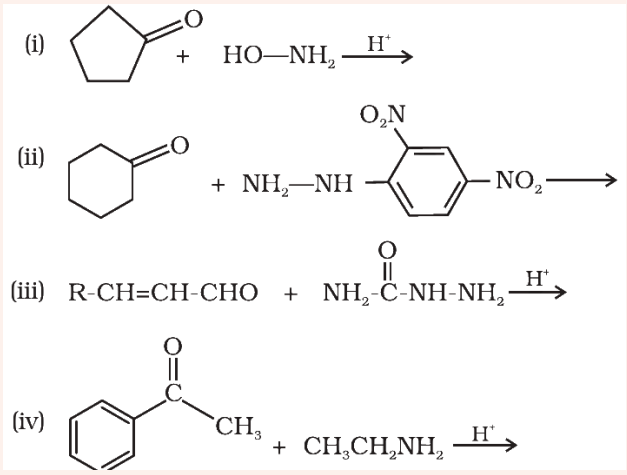
Ans. / उत्तर: (i) Butanone < Propanone < Propanal < Ethanal

(ii) Acetophenone < p-Tolualdehyde < Benzaldehyde < p-Nitrobenzaldehyde

Larger/more alkyl groups → more steric hindrance and +I → less reactive; $-NO_2$ (electron withdrawing) increases electrophilicity; $-CH_3$ decreases it.

त्रिविम बाधा व +I प्रभाव क्रियाशीलता घटाते; $-NO_2$ बढ़ाता है।

8.5 **Predict the products of the following reactions:**



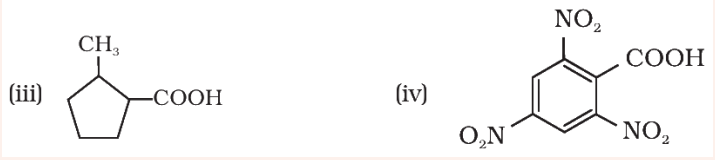
Ans. / उत्तर: (i) Cyclopentanone oxime ($C_5H_8=N-OH$)

(ii) Cyclohexanone 2,4-dinitrophenylhydrazone ($C_6H_{10}=N-NH-C_6H_3(NO_2)_2$)

(iii) $R-CH=CH-CH=N-NH-CO-NH_2$ (semicarbazone)

(iv) $C_6H_5C(CH_3)=N-CH_2CH_3$ (Schiff's base / substituted imine)

8.6 **Give the IUPAC names of the following compounds: (i) $PhCH_2CH_2COOH$ (ii) $(CH_3)_2C=CHCOOH$**



Ans. / उत्तर: (i) 3-Phenylpropanoic acid (ii) 3-Methylbut-2-enoic acid (iii) 2-Methylcyclopentanecarboxylic acid (iv) 2,4,6-Trinitrobenzoic acid

8.7 **Show how each of the following compounds can be converted to benzoic acid: (i) Ethylbenzene (ii) Acetophenone (iii) Bromobenzene (iv) Phenylethene (styrene)**

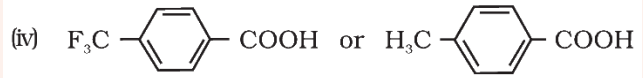
Ans. / उत्तर: (i) $C_6H_5CH_2CH_3 \xrightarrow{-KMnO_4/KOH,\ \Delta} C_6H_5COOK \xrightarrow{-H_3O^+} C_6H_5COOH$

(ii) $C_6H_5COCH_3 \xrightarrow{-KMnO_4/KOH,\ \Delta\ (or\ NaOI)} C_6H_5COO^- \xrightarrow{-H_3O^+} C_6H_5COOH$

(iii) $C_6H_5Br \xrightarrow{-Mg,\ dry\ ether} C_6H_5MgBr \xrightarrow{-(i)\ CO_2\ (ii)\ H_3O^+} C_6H_5COOH$

(iv) $C_6H_5CH=CH_2 \xrightarrow{-KMnO_4/KOH,\ \Delta} C_6H_5COOK \xrightarrow{-H_3O^+} C_6H_5COOH$

8.8 **Which acid of each pair would you expect to be stronger? (i) CH_3CO_2H or CH_2FCO_2H (ii) CH_2FCO_2H or CH_2ClCO_2H (iii) $CH_2FCH_2CH_2CO_2H$ or $CH_3CHFCH_2CO_2H$**

(iv) 

Ans. / उत्तर: (i) **CH_2FCO_2H** ($-I$ of F) (ii) **CH_2FCO_2H** (F more electronegative than Cl) (iii) **$CH_3CHFCH_2CO_2H$** (F closer to $-COOH$) (iv) **$F_3C-C_6H_4-COOH$** ($-CF_3$ withdraws, $-CH_3$ donates)

इलेक्ट्रॉन-आकर्षी समूह जितना प्रबल और $-COOH$ के जितना पास, अम्ल उतना प्रबल।

C. Exercises (अभ्यास प्रश्न)

8.1 **What is meant by the following terms? Give an example of the reaction in each case: (i) Cyanohydrin (ii) Acetal (iii) Semicarbazone (iv) Aldol (v) Hemiacetal (vi) Oxime (vii) Ketal (viii) Imine (ix) 2,4-DNP-derivative (x) Schiff's base**

Ans. / उत्तर: (i) **Cyanohydrin:** product of HCN addition to C=O ($-OH$ and $-CN$ on the same C). $CH_3CHO + HCN \xrightarrow{-OH^-} CH_3CH(OH)CN$

(ii) **Acetal:** gem-dialkoxy compound from an aldehyde + 2 mol alcohol (dry HCl). $CH_3CHO + 2CH_3OH \rightarrow CH_3CH(OCH_3)_2 + H_2O$

(iii) **Semicarbazone:** $>C=N-NH-CO-NH_2$, from C=O + semicarbazide. $(CH_3)_2CO + H_2NNHCONH_2 \rightarrow (CH_3)_2C=NNHCONH_2 + H_2O$

(iv) **Aldol:** β-hydroxy aldehyde from aldol reaction. $2CH_3CHO \xrightarrow{\text{dil. NaOH}} CH_3CH(OH)CH_2CHO$

(v) **Hemiacetal:** alkoxy alcohol from aldehyde + 1 mol alcohol. $CH_3CHO + CH_3OH \rightleftharpoons CH_3CH(OH)OCH_3$

(vi) **Oxime:** $>C=N-OH$, from C=O + hydroxylamine. $CH_3CHO + NH_2OH \rightarrow CH_3CH=NOH + H_2O$

(vii) **Ketal:** from ketone + diol (ethylene glycol), dry HCl. $(CH_3)_2CO + HOCH_2CH_2OH \rightarrow (CH_3)_2C(OCH_2CH_2O)$ (cyclic) $+ H_2O$

(viii) **Imine:** $>C=NH$, from C=O + NH_3. $CH_3CHO + NH_3 \rightarrow CH_3CH=NH + H_2O$

(ix) **2,4-DNP derivative:** 2,4-dinitrophenylhydrazone, a yellow/orange/red solid used to identify C=O. $CH_3CHO + H_2NNHC_6H_3(NO_2)_2 \rightarrow CH_3CH=NNHC_6H_3(NO_2)_2$

(x) **Schiff's base:** substituted imine >C=N–R from C=O + 1° amine. $C_6H_5CHO + C_6H_5NH_2 \rightarrow C_6H_5CH=NC_6H_5 + H_2O$

8.2 **Name the following compounds according to IUPAC system: (i) $CH_3CH(CH_3)CH_2CH_2CHO$ (ii) $CH_3CH_2COCH(C_2H_5)CH_2CH_2Cl$ (iii) $CH_3CH=CHCHO$ (iv) $CH_3COCH_2COCH_3$ (v) $CH_3CH(CH_3)CH_2C(CH_3)_2COCH_3$ (vi) $(CH_3)_3CCH_2COOH$ (vii) $OHCC_6H_4CHO$-p**

Ans. / उत्तर: (i) 4-Methylpentanal (ii) 6-Chloro-4-ethylhexan-3-one (iii) But-2-enal (iv) Pentane-2,4-dione (v) 3,3,5-Trimethylhexan-2-one (vi) 3,3-Dimethylbutanoic acid (vii) Benzene-1,4-dicarbaldehyde

8.3 **Draw the structures of: (i) 3-Methylbutanal (ii) p-Nitropropiophenone (iii) p-Methylbenzaldehyde (iv) 4-Methylpent-3-en-2-one (v) 4-Chloropentan-2-one (vi) 3-Bromo-4-phenylpentanoic acid (vii) p,p′-Dihydroxybenzophenone (viii) Hex-2-en-4-ynoic acid**

Ans. / उत्तर: (i) $(CH_3)_2CHCH_2CHO$ (ii) $p\text{-}O_2N\text{-}C_6H_4\text{-}COCH_2CH_3$ (iii) $p\text{-}CH_3\text{-}C_6H_4\text{-}CHO$ (iv) $(CH_3)_2C=CH\text{-}CO\text{-}CH_3$ (v) $CH_3CH(Cl)CH_2COCH_3$ (vi) $CH_3CH(C_6H_5)CH(Br)CH_2COOH$ (vii) $HO\text{-}C_6H_4\text{-}CO\text{-}C_6H_4\text{-}OH$ (both –OH para) (viii) $CH_3\text{-}C\equiv C\text{-}CH=CH\text{-}COOH$

8.4 **Write the IUPAC names of the following ketones and aldehydes; give common names where possible: (i) $CH_3CO(CH_2)_4CH_3$ (ii) $CH_3CH_2CHBrCH_2CH(CH_3)CHO$ (iii) $CH_3(CH_2)_5CHO$ (iv) Ph–CH=CH–CHO (v) cyclopentane–CHO (vi) PhCOPh**

Ans. / उत्तर: (i) Heptan-2-one — methyl n-pentyl ketone (ii) 4-Bromo-2-methylhexanal — γ-bromo-α-methylcaproaldehyde (iii) Heptanal — n-heptaldehyde (iv) 3-Phenylprop-2-enal — cinnamaldehyde (v) Cyclopentanecarbaldehyde (vi) Diphenylmethanone — benzophenone

8.5 **Draw structures of the following derivatives: (i) the 2,4-dinitrophenylhydrazone of benzaldehyde (ii) cyclopropanone oxime (iii) acetaldehyde dimethylacetal (iv) the semicarbazone of cyclobutanone (v) the ethylene ketal of hexan-3-one (vi) the methyl hemiacetal of formaldehyde**

Ans. / उत्तर: (i) $C_6H_5CH=N\text{-}NH\text{-}C_6H_3(NO_2)_2$ (2,4-) (ii) three-membered ring $(CH_2)_2C=N\text{-}OH$ (iii) $CH_3CH(OCH_3)_2$ (iv) four-membered ring $(CH_2)_3C=N\text{-}NH\text{-}$

$CO-NH_2$ (v) $CH_3CH_2-C(CH_2CH_2CH_3)<(O-CH_2-CH_2-O)$ (1,3-dioxolane ring) (vi) $HO-CH_2-OCH_3$

8.6 **Predict the products formed when cyclohexanecarbaldehyde reacts with: (i) PhMgBr and then H_3O^+ (ii) Tollens' reagent (iii) semicarbazide and weak acid (iv) excess ethanol and acid (v) zinc amalgam and dilute HCl**

Ans. / उत्तर: (i) $C_6H_{11}-CH(OH)-C_6H_5$ (cyclohexylphenylmethanol) (ii) $C_6H_{11}COO^-$ + $Ag\downarrow$ (silver mirror) (iii) $C_6H_{11}CH=N-NH-CO-NH_2$ (semicarbazone) (iv) $C_6H_{11}CH(OC_2H_5)_2$ (diethyl acetal) (v) $C_6H_{11}CH_3$ (methylcyclohexane, Clemmensen)

8.7 **Which of the following would undergo aldol condensation, which the Cannizzaro reaction and which neither? (i) Methanal (ii) 2-Methylpentanal (iii) Benzaldehyde (iv) Benzophenone (v) Cyclohexanone (vi) 1-Phenylpropanone (vii) Phenylacetaldehyde (viii) Butan-1-ol (ix) 2,2-Dimethylbutanal**

Ans. / उत्तर: **Aldol** (have α-H): (ii), (v), (vi), (vii). **Cannizzaro** (aldehydes without α-H): (i), (iii), (ix). **Neither:** (iv) benzophenone (ketone with no α-H), (viii) butan-1-ol (not a carbonyl compound).

(i) $2HCHO + conc.\ NaOH \rightarrow CH_3OH + HCOONa$

(ii) $2CH_3CH_2CH_2CH(CH_3)CHO \xrightarrow{-dil.\ NaOH} CH_3CH_2CH_2CH(CH_3)-CH(OH)-C(CH_3)(CH_2CH_2CH_3)-CHO$ (3-hydroxy-2,4-dimethyl-2-propylheptanal)

(iii) $2C_6H_5CHO + conc.\ NaOH \rightarrow C_6H_5CH_2OH + C_6H_5COONa$

(v) 2 Cyclohexanone $\xrightarrow{-dil.\ NaOH}$ 2-(1-hydroxycyclohexyl)cyclohexanone $\xrightarrow{-\Delta,\ -H_2O}$ 2-cyclohexylidenecyclohexanone

(vi) $2C_6H_5COCH_2CH_3 \rightarrow C_6H_5CO-CH(CH_3)-C(OH)(C_6H_5)-CH_2CH_3$ (3-hydroxy-2-methyl-1,3-diphenylpentan-1-one)

(vii) $2C_6H_5CH_2CHO \rightarrow C_6H_5CH_2CH(OH)CH(C_6H_5)CHO$ (3-hydroxy-2,4-diphenylbutanal) $\xrightarrow{-\Delta}$ 2,4-diphenylbut-2-enal

(ix) $2CH_3CH_2C(CH_3)_2CHO + conc.\ NaOH \rightarrow CH_3CH_2C(CH_3)_2CH_2OH + CH_3CH_2C(CH_3)_2COONa$

α-H है → ऐल्डोल; ऐल्डिहाइड में α-H नहीं → कैनिज़ारो।

8.8 **How will you convert ethanal into the following compounds? (i) Butane-1,3-diol (ii) But-2-enal (iii) But-2-enoic acid**

Ans. / उत्तर: (i) $2CH_3CHO \xrightarrow{-dil.\ NaOH} CH_3CH(OH)CH_2CHO \xrightarrow{-NaBH_4} CH_3CH(OH)CH_2CH_2OH$

(ii) $2CH_3CHO \xrightarrow{\text{dil. NaOH}} CH_3CH(OH)CH_2CHO \xrightarrow{\Delta,\ -H_2O} CH_3CH=CHCHO$

(iii) $CH_3CH=CHCHO \xrightarrow{\text{Tollens' reagent}} CH_3CH=CHCOO^- \xrightarrow{H^+} CH_3CH=CHCOOH$

(Tollens' does not attack C=C)

8.9 **Write structural formulas and names of four possible aldol condensation products from propanal and butanal. In each case indicate which aldehyde acts as nucleophile and which as electrophile.**

Ans. / उत्तर:

Nucleophile (forms carbanion)	Electrophile	Aldol product
Propanal	Propanal	$CH_3CH_2CH(OH)CH(CH_3)CHO$ — 3-hydroxy-2-methylpentanal
Butanal	Butanal	$CH_3CH_2CH_2CH(OH)CH(C_2H_5)CHO$ — 2-ethyl-3-hydroxyhexanal
Propanal	Butanal	$CH_3CH_2CH_2CH(OH)CH(CH_3)CHO$ — 3-hydroxy-2-methylhexanal
Butanal	Propanal	$CH_3CH_2CH(OH)CH(C_2H_5)CHO$ — 2-ethyl-3-hydroxypentanal

जिस ऐल्डिहाइड का α-कार्बऋणायन बनता है, वह नाभिकस्नेही; जिसके C=O पर आक्रमण होता है, वह इलेक्ट्रॉनस्नेही।

8.10 **An organic compound $C_9H_{10}O$ forms 2,4-DNP derivative, reduces Tollens' reagent and undergoes Cannizzaro reaction. On vigorous oxidation, it gives 1,2-benzenedicarboxylic acid. Identify the compound.**

Ans. / उत्तर: 2,4-DNP + Tollens' → aldehyde; Cannizzaro → no α-H (–CHO on the ring); oxidation to phthalic acid → two groups ortho on benzene. Remaining C_2H_5 → **2-ethylbenzaldehyde**, $o\text{-}C_2H_5\text{-}C_6H_4\text{-}CHO$.

उत्तर: 2-एथिलबेंज़ैल्डिहाइड।

8.11 **An organic compound (A), $C_8H_{16}O_2$, was hydrolysed with dilute H_2SO_4 to give a carboxylic acid (B) and an alcohol (C). Oxidation of (C) with chromic acid produced (B). (C) on dehydration gives but-1-ene. Write equations.**

Ans. / उत्तर: (C) gives (B) on oxidation → same 4-C skeleton; (C) gives but-1-ene → (C) = **butan-1-ol**; (B) = **butanoic acid**; (A) = **butyl butanoate**.

$CH_3CH_2CH_2COOCH_2CH_2CH_2CH_3 + H_2O \xrightarrow{\text{dil. } H_2SO_4} CH_3CH_2CH_2COOH +$

$CH_3CH_2CH_2CH_2OH$

$CH_3(CH_2)_3OH \xrightarrow{H_2CrO_4} CH_3CH_2CH_2COOH$ · $CH_3(CH_2)_3OH \xrightarrow{conc.\ H_2SO_4,\ \Delta} CH_3CH_2CH{=}CH_2 + H_2O$

8.12 **Arrange in increasing order of the property indicated: (i) Acetaldehyde, Acetone, Di-tert-butyl ketone, Methyl tert-butyl ketone (reactivity towards HCN) (ii) $CH_3CH_2CH(Br)COOH$, $CH_3CH(Br)CH_2COOH$, $(CH_3)_2CHCOOH$, $CH_3CH_2CH_2COOH$ (acid strength) (iii) Benzoic acid, 4-Nitrobenzoic acid, 3,4-Dinitrobenzoic acid, 4-Methoxybenzoic acid (acid strength)**

Ans. / उत्तर: (i) Di-tert-butyl ketone < Methyl tert-butyl ketone < Acetone < Acetaldehyde

(ii) $(CH_3)_2CHCOOH < CH_3CH_2CH_2COOH < CH_3CH(Br)CH_2COOH < CH_3CH_2CH(Br)COOH$

(iii) 4-Methoxybenzoic acid < Benzoic acid < 4-Nitrobenzoic acid < 3,4-Dinitrobenzoic acid

(i) त्रिविम बाधा; (ii) −I प्रभाव (Br जितना पास, उतना प्रबल; +I वाली शाखा घटाती); (iii) $-NO_2$ बढ़ाता, $-OCH_3$ घटाता।

8.13 **Give simple chemical tests to distinguish between: (i) Propanal and Propanone (ii) Acetophenone and Benzophenone (iii) Phenol and Benzoic acid (iv) Benzoic acid and Ethyl benzoate (v) Pentan-2-one and Pentan-3-one (vi) Benzaldehyde and Acetophenone (vii) Ethanal and Propanal**

Ans. / उत्तर:

Pair	Test	Result
(i) Propanal / Propanone	Tollens' reagent	Propanal gives silver mirror; propanone does not (propanone gives iodoform)
(ii) Acetophenone / Benzophenone	Iodoform (I_2 + NaOH)	Acetophenone gives yellow CHI_3; benzophenone does not
(iii) Phenol / Benzoic acid	$NaHCO_3$ (or neutral $FeCl_3$)	Benzoic acid gives CO_2 effervescence; phenol does not (phenol gives violet colour with $FeCl_3$)
(iv) Benzoic acid / Ethyl benzoate	$NaHCO_3$	Benzoic acid effervesces; ester does not
(v) Pentan-2-one / Pentan-3-one	Iodoform	Pentan-2-one (CH_3CO-) gives yellow ppt; pentan-3-one does not
(vi) Benzaldehyde / Acetophenone	Tollens' (or iodoform)	Benzaldehyde gives silver mirror; acetophenone gives iodoform
(vii) Ethanal / Propanal	Iodoform	Ethanal gives yellow CHI_3; propanal does not

8.14 How will you prepare the following compounds from benzene? (any inorganic reagent and any organic reagent with not more than one carbon atom): (i) Methyl benzoate (ii) m-Nitrobenzoic acid (iii) p-Nitrobenzoic acid (iv) Phenylacetic acid (v) p-Nitrobenzaldehyde

Ans. / उत्तर: First: $C_6H_6 \xrightarrow{-CH_3Cl,\ anhyd.\ AlCl_3} C_6H_5CH_3$ (toluene)

(i) Toluene $\xrightarrow{-KMnO_4/KOH,\ \Delta;\ H^+} C_6H_5COOH \xrightarrow{-CH_3OH,\ conc.\ H_2SO_4} C_6H_5COOCH_3$

(ii) $C_6H_5COOH \xrightarrow{-conc.\ HNO_3 + conc.\ H_2SO_4} m\text{-}O_2NC_6H_4COOH$ (–COOH is meta-directing)

(iii) Toluene $\xrightarrow{-conc.\ HNO_3/H_2SO_4} p\text{-}O_2NC_6H_4CH_3$ (separate p-isomer) $\xrightarrow{-KMnO_4;\ H^+} p\text{-}O_2NC_6H_4COOH$

(iv) Toluene $\xrightarrow{-Cl_2,\ h\nu} C_6H_5CH_2Cl \xrightarrow{-KCN} C_6H_5CH_2CN \xrightarrow{-H_3O^+} C_6H_5CH_2COOH$

(v) p-Nitrotoluene $\xrightarrow{-CrO_2Cl_2/CS_2;\ H_3O^+\ (Etard)} p\text{-}O_2NC_6H_4CHO$

8.15 How will you bring about the following conversions in not more than two steps?

Ans. / उत्तर: (i) **Propanone → propene:** $CH_3COCH_3 \xrightarrow{-NaBH_4} CH_3CH(OH)CH_3 \xrightarrow{-conc.\ H_2SO_4,\ \Delta} CH_3CH{=}CH_2$

(ii) **Benzoic acid → benzaldehyde:** $C_6H_5COOH \xrightarrow{-SOCl_2} C_6H_5COCl \xrightarrow{-H_2,\ Pd\text{-}BaSO_4} C_6H_5CHO$ (Rosenmund)

(iii) **Ethanol → 3-hydroxybutanal:** $C_2H_5OH \xrightarrow{PCC} CH_3CHO \xrightarrow{dil.\ NaOH} CH_3CH(OH)CH_2CHO$

(iv) **Benzene → m-nitroacetophenone:** $C_6H_6 \xrightarrow{CH_3COCl,\ anhyd.\ AlCl_3} C_6H_5COCH_3 \xrightarrow{conc.\ HNO_3/H_2SO_4} m\text{-}O_2NC_6H_4COCH_3$

(v) **Benzaldehyde → benzophenone:** $C_6H_5CHO \xrightarrow{(i)\ C_6H_5MgBr\ (ii)\ H_3O^+} (C_6H_5)_2CHOH \xrightarrow{CrO_3\ (or\ PCC)} C_6H_5COC_6H_5$

(vi) **Bromobenzene → 1-phenylethanol:** $C_6H_5Br \xrightarrow{Mg,\ dry\ ether} C_6H_5MgBr \xrightarrow{(i)\ CH_3CHO\ (ii)\ H_3O^+} C_6H_5CH(OH)CH_3$

(vii) **Benzaldehyde → 3-phenylpropan-1-ol:** $C_6H_5CHO + CH_3CHO \xrightarrow{dil.\ NaOH,\ \Delta} C_6H_5CH{=}CHCHO \xrightarrow{H_2/Pd} C_6H_5CH_2CH_2CH_2OH$

(viii) **Benzaldehyde → α-hydroxyphenylacetic acid:** $C_6H_5CHO \xrightarrow{HCN} C_6H_5CH(OH)CN \xrightarrow{H_3O^+} C_6H_5CH(OH)COOH$

(ix) **Benzoic acid → m-nitrobenzyl alcohol:** $C_6H_5COOH \xrightarrow{conc.\ HNO_3/H_2SO_4} m\text{-}O_2NC_6H_4COOH \xrightarrow{B_2H_6;\ H_3O^+} m\text{-}O_2NC_6H_4CH_2OH$ (diborane does not reduce $-NO_2$)

8.16 Describe the following: (i) Acetylation (ii) Cannizzaro reaction (iii) Cross aldol condensation (iv) Decarboxylation

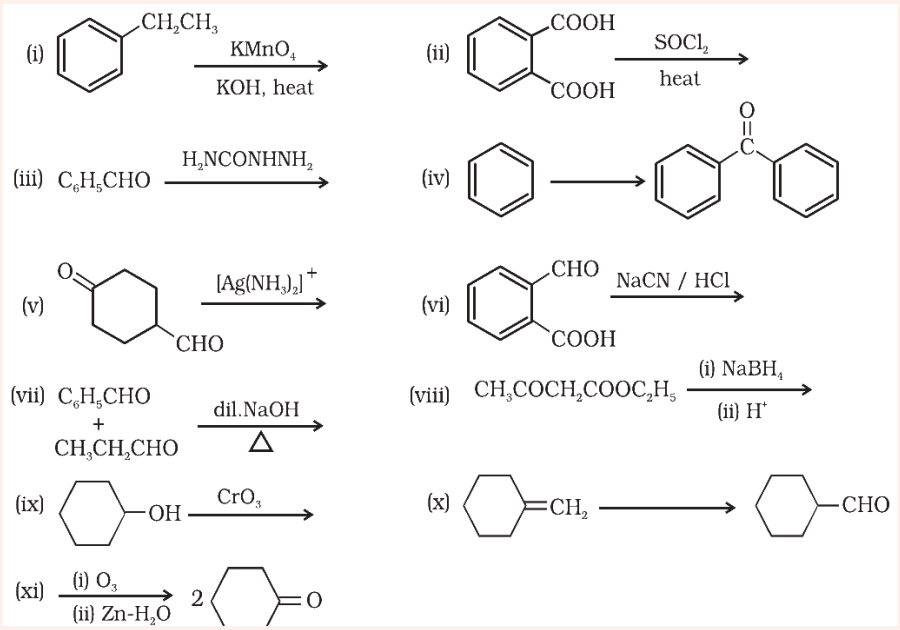
Ans. / उत्तर: (i) **Acetylation:** introduction of an acetyl group (CH_3CO-) into $-OH$, $-NH_2$ etc. using acetyl chloride or acetic anhydride (with pyridine/acid). $C_2H_5OH + CH_3COCl \rightarrow CH_3COOC_2H_5 + HCl$; $C_6H_5NH_2 + (CH_3CO)_2O \rightarrow C_6H_5NHCOCH_3 + CH_3COOH$

(ii) **Cannizzaro reaction:** aldehydes without α-H, heated with conc. alkali, undergo self oxidation–reduction (disproportionation): one molecule → alcohol, another → carboxylate. $2HCHO + \text{conc. } KOH \rightarrow CH_3OH + HCOOK$

(iii) **Cross aldol condensation:** aldol condensation between two different carbonyl compounds; if both have α-H, four products form. $CH_3CHO + CH_3CH_2CHO \xrightarrow{dil.\ NaOH}$ but-2-enal + 2-methylpent-2-enal + 2-methylbut-2-enal + pent-2-enal. With benzaldehyde (no α-H) one main product forms: $C_6H_5CHO + CH_3COCH_3 \rightarrow C_6H_5CH{=}CHCOCH_3$

(iv) **Decarboxylation:** loss of CO_2 when sodium salt of a carboxylic acid is heated with sodalime (NaOH : CaO = 3 : 1). $RCOONa + NaOH \xrightarrow{CaO,\ \Delta} R\text{-}H + Na_2CO_3$

8.17 **Complete each synthesis by giving missing starting material, reagent or products:**



Ans. / उत्तर: (i) C_6H_5COOK (potassium benzoate; benzoic acid after H^+)

(ii) o-$C_6H_4(COCl)_2$ — phthaloyl dichloride

(iii) $C_6H_5CH{=}N{-}NH{-}CO{-}NH_2$ — benzaldehyde semicarbazone

(iv) Reagent: C_6H_5COCl / anhyd. $AlCl_3$ (Friedel–Crafts acylation)

(v) 4-Oxocyclohexanecarboxylate (only –CHO is oxidised by Tollens'; ring ketone unaffected)

(vi) o-HOOC–C_6H_4–CH(OH)CN (cyanohydrin of the –CHO)

(vii) $C_6H_5CH{=}C(CH_3)CHO$ — 2-methyl-3-phenylprop-2-enal (cross aldol)

(viii) $CH_3CH(OH)CH_2COOC_2H_5$ — ethyl 3-hydroxybutanoate ($NaBH_4$ reduces only the ketone)

(ix) Cyclohexanone

(x) Reagents: (i) B_2H_6 (ii) H_2O_2/OH^- → cyclohexylmethanol; (iii) PCC → cyclohexanecarbaldehyde

(xi) Starting material: cyclohexylidenecyclohexane, $C_6H_{10}{=}C_6H_{10}$ (ozonolysis gives 2 cyclohexanone)

8.18 **Give plausible explanation: (i) Cyclohexanone forms cyanohydrin in good yield but 2,2,6-trimethylcyclohexanone does not. (ii) There are two $-NH_2$ groups in semicarbazide; only one is involved in forming semicarbazones. (iii) During preparation of esters from a carboxylic acid and an alcohol with acid catalyst, water or ester should be removed as soon as it is formed.**

Ans. / उत्तर: (i) In 2,2,6-trimethylcyclohexanone the three $-CH_3$ groups next to C=O cause **steric hindrance** to the attack of CN^- (and their +I effect lowers electrophilicity). Cyclohexanone has no such hindrance.
(ii) Semicarbazide is $H_2N-NH-CO-NH_2$. The $-NH_2$ attached to C=O has its lone pair **delocalised by resonance with C=O** (amide), so it is not nucleophilic. Only the $-NH_2$ attached to $-NH-$ is free to attack.
(iii) Esterification is a **reversible equilibrium**: $RCOOH + R'OH \rightleftharpoons RCOOR' + H_2O$. Removing a product shifts the equilibrium forward (Le Chatelier) and prevents hydrolysis of the ester.
(i) त्रिविम बाधा; (ii) एक $-NH_2$ का एकाकी युग्म C=O से अनुनाद में; (iii) उत्क्रमणीय अभिक्रिया — उत्पाद हटाने से साम्य आगे।

8.19 **An organic compound contains 69.77% carbon, 11.63% hydrogen and rest oxygen. Its molecular mass is 86. It does not reduce Tollens' reagent but forms an addition compound with sodium hydrogensulphite and gives positive iodoform test. On vigorous oxidation it gives ethanoic and propanoic acid. Write the possible structure.**

Ans. / उत्तर: O = 100 − 69.77 − 11.63 = 18.60%. Moles: C = 69.77/12 = 5.81, H = 11.63/1 = 11.63, O = 18.60/16 = 1.16 → ratio 5 : 10 : 1 → **$C_5H_{10}O$** (empirical mass 86 = molecular mass).
No Tollens' → ketone; $NaHSO_3$ addition + iodoform → methyl ketone (CH_3CO-); oxidation to $CH_3COOH + CH_3CH_2COOH$ → **pentan-2-one, $CH_3COCH_2CH_2CH_3$.**
उत्तर: पेंटेन-2-ओन।

8.20 **Although phenoxide ion has more number of resonating structures than carboxylate ion, carboxylic acid is a stronger acid than phenol. Why?**

Ans. / उत्तर: The carboxylate ion has **two equivalent** resonance structures, and the negative charge is on **two electronegative O atoms** — highly effective stabilisation. In phenoxide, the resonance structures are **not equivalent**, and in most of them the negative charge is on the **less electronegative carbon** atoms of the ring, so delocalisation is less effective. Hence carboxylate is more stable and carboxylic acid

is the stronger acid.
कार्बोक्सिलेट में ऋणावेश दो विद्युतऋणी O पर समान रूप से बँटा; फ़ीनॉक्साइड में असमान और कार्बन पर — इसलिए अम्ल अधिक प्रबल।

Unit 9 : Amines

ऐमीन — NCERT Solutions (Examples + Intext + Exercises)

A. Solved Examples (हल किए गए उदाहरण)

Ex 9.1 **Write chemical equations for: (i) reaction of ethanolic NH_3 with C_2H_5Cl (ii) ammonolysis of benzyl chloride and reaction of the amine so formed with two moles of CH_3Cl.**

Ans. / उत्तर: (i) $C_2H_5Cl + NH_3 \rightarrow C_2H_5NH_2 \xrightarrow{-C_2H_5Cl} (C_2H_5)_2NH \xrightarrow{-C_2H_5Cl} (C_2H_5)_3N \xrightarrow{-C_2H_5Cl} (C_2H_5)_4N^+Cl^-$

(ethanamine → N-ethylethanamine → N,N-diethylethanamine → tetraethylammonium chloride)

(ii) $C_6H_5CH_2Cl + NH_3 \rightarrow C_6H_5CH_2NH_2 + HCl$; $C_6H_5CH_2NH_2 + 2CH_3Cl \rightarrow C_6H_5CH_2N(CH_3)_2$ (N,N-dimethylphenylmethanamine) + 2HCl

Ex 9.2 **Write chemical equations for: (i) CH_3CH_2Cl into $CH_3CH_2CH_2NH_2$ (ii) $C_6H_5CH_2Cl$ into $C_6H_5CH_2CH_2NH_2$**

Ans. / उत्तर: (i) $CH_3CH_2Cl \xrightarrow{-KCN\ (alc.)} CH_3CH_2CN \xrightarrow{-LiAlH_4\ (or\ H_2/Ni)} CH_3CH_2CH_2NH_2$

(ii) $C_6H_5CH_2Cl \xrightarrow{-KCN\ (alc.)} C_6H_5CH_2CN \xrightarrow{-LiAlH_4} C_6H_5CH_2CH_2NH_2$

नाइट्राइल अपचयन से एक कार्बन अधिक वाली ऐमीन (श्रेणी आरोहण)।

Ex 9.3 **Write structures and IUPAC names of (i) the amide which gives propanamine by Hoffmann bromamide reaction (ii) the amine produced by Hoffmann degradation of benzamide.**

Ans. / उत्तर: (i) Hoffmann removes one C, so the amide has 4 C: $CH_3CH_2CH_2CONH_2$ — **butanamide**.

(ii) Benzamide (7 C) → $C_6H_5NH_2$ — **aniline (benzenamine)**.

Ex 9.4 **Arrange in decreasing order of basic strength: $C_6H_5NH_2$, $C_2H_5NH_2$, $(C_2H_5)_2NH$, NH_3**

Ans. / उत्तर: $(C_2H_5)_2NH > C_2H_5NH_2 > NH_3 > C_6H_5NH_2$

ऐल्किल समूह (+I) क्षारकता बढ़ाते हैं; ऐनिलीन में एकाकी युग्म वलय से अनुनाद में — दुर्बल

क्षारक।

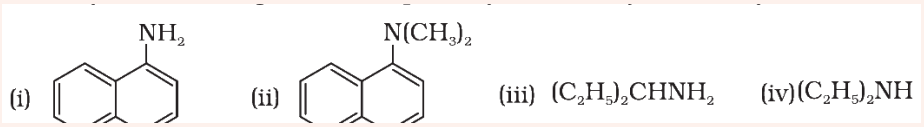
Ex 9.5 **How will you convert 4-nitrotoluene to 2-bromobenzoic acid?**

Ans. / उत्तर: $p\text{-}O_2N\text{-}C_6H_4\text{-}CH_3 \xrightarrow{-Br_2/FeBr_3}$ 2-bromo-4-nitrotoluene $\xrightarrow{-Sn/HCl}$ 3-bromo-4-methylaniline $\xrightarrow{-NaNO_2/HCl,\ 273\ K}$ diazonium salt $\xrightarrow{-H_3PO_2/H_2O}$ 2-bromotoluene $\xrightarrow{-KMnO_4/KOH;\ H^+}$ **2-bromobenzoic acid**

$-NO_2$ को $-NH_2$ बनाकर डाइऐज़ोनियम द्वारा हटाया गया; फिर CH_3 का ऑक्सीकरण।

B. Intext Questions (पाठ्यनिहित प्रश्न)

9.1 **Classify the following amines as primary, secondary or tertiary:**



Ans. / उत्तर: (i) 1-Naphthylamine — **1°** (ii) N,N-Dimethyl-1-naphthylamine — **3°**
(iii) $(C_2H_5)_2CHNH_2$ — **1°** (iv) $(C_2H_5)_2NH$ — **2°**

ऐमीन में वर्गीकरण N पर जुड़े समूहों की संख्या से होता है।

9.2 **(i) Write structures of different isomeric amines of molecular formula $C_4H_{11}N$. (ii) Write IUPAC names of all the isomers. (iii) What type of isomerism is exhibited by different pairs of amines?**

Ans. / उत्तर:

Structure	IUPAC name	Type
$CH_3CH_2CH_2CH_2NH_2$	Butan-1-amine	1°
$CH_3CH_2CH(NH_2)CH_3$	Butan-2-amine	1°
$(CH_3)_2CHCH_2NH_2$	2-Methylpropan-1-amine	1°
$(CH_3)_3CNH_2$	2-Methylpropan-2-amine	1°
$CH_3NHCH_2CH_2CH_3$	N-Methylpropan-1-amine	2°
$CH_3NHCH(CH_3)_2$	N-Methylpropan-2-amine	2°
$CH_3CH_2NHCH_2CH_3$	N-Ethylethanamine	2°
$(CH_3)_2NCH_2CH_3$	N,N-Dimethylethanamine	3°

(iii) **Position isomerism** (butan-1-amine / butan-2-amine), **chain isomerism** (butan-1-amine / 2-methylpropan-1-amine), **metamerism** (N-methylpropan-1-amine

/ N-ethylethanamine), **functional isomerism** (1° / 2° / 3° amines).

9.3 **How will you convert (i) benzene into aniline (ii) benzene into N,N-dimethylaniline (iii) Cl–$(CH_2)_4$–Cl into hexane-1,6-diamine?**

Ans. / उत्तर: (i) $C_6H_6 \xrightarrow{\text{conc. } HNO_3/H_2SO_4} C_6H_5NO_2 \xrightarrow{Sn/HCl \text{ (or } Fe/HCl)} C_6H_5NH_2$

(ii) Aniline (as above) $\xrightarrow{2CH_3Cl \text{ (or } CH_3I)} C_6H_5N(CH_3)_2$

(iii) $Cl(CH_2)_4Cl \xrightarrow{2KCN \text{ (alc.)}} NC(CH_2)_4CN \xrightarrow{LiAlH_4 \text{ (or } H_2/Ni)} H_2N(CH_2)_6NH_2$

9.4 **Arrange in increasing order of basic strength: (i) $C_2H_5NH_2$, $C_6H_5NH_2$, NH_3, $C_6H_5CH_2NH_2$, $(C_2H_5)_2NH$ (ii) $C_2H_5NH_2$, $(C_2H_5)_2NH$, $(C_2H_5)_3N$, $C_6H_5NH_2$ (iii) CH_3NH_2, $(CH_3)_2NH$, $(CH_3)_3N$, $C_6H_5NH_2$, $C_6H_5CH_2NH_2$**

Ans. / उत्तर: (i) $C_6H_5NH_2 < NH_3 < C_6H_5CH_2NH_2 < C_2H_5NH_2 < (C_2H_5)_2NH$

(ii) $C_6H_5NH_2 < C_2H_5NH_2 < (C_2H_5)_3N < (C_2H_5)_2NH$

(iii) $C_6H_5NH_2 < C_6H_5CH_2NH_2 < (CH_3)_3N < CH_3NH_2 < (CH_3)_2NH$

जलीय विलयन में +I प्रभाव, विलायकन और त्रिविम बाधा — तीनों मिलकर क्रम तय करते हैं।

9.5 **Complete the following acid-base reactions and name the products: (i) $CH_3CH_2CH_2NH_2 + HCl \rightarrow$ (ii) $(C_2H_5)_3N + HCl \rightarrow$**

Ans. / उत्तर: (i) $CH_3CH_2CH_2NH_3^+Cl^-$ — propylammonium chloride (ii) $(C_2H_5)_3NH^+Cl^-$ — triethylammonium chloride

9.6 **Write reactions of the final alkylation product of aniline with excess of methyl iodide in the presence of sodium carbonate solution.**

Ans. / उत्तर: $C_6H_5NH_2 \xrightarrow{CH_3I} C_6H_5NHCH_3 \xrightarrow{CH_3I} C_6H_5N(CH_3)_2 \xrightarrow{CH_3I} C_6H_5N^+(CH_3)_3I^-$ (N,N,N-trimethylanilinium iodide, the final product). Na_2CO_3 neutralises the HI formed at each step: $2HI + Na_2CO_3 \rightarrow 2NaI + H_2O + CO_2$.

9.7 **Write chemical reaction of aniline with benzoyl chloride and name the product.**

Ans. / उत्तर: $C_6H_5NH_2 + C_6H_5COCl \xrightarrow{\text{pyridine}} C_6H_5NHCOC_6H_5 + HCl$ — **N-phenylbenzamide (benzanilide)**

9.8 **Write structures of different isomers of C_3H_9N. Write IUPAC names of the isomers which will liberate nitrogen gas on treatment with nitrous acid.**

Ans. / उत्तर: $CH_3CH_2CH_2NH_2$ (propan-1-amine, 1°) · $(CH_3)_2CHNH_2$ (propan-2-amine, 1°) · $CH_3NHCH_2CH_3$ (N-methylethanamine, 2°) · $(CH_3)_3N$ (N,N-dimethylmethanamine, 3°)

Only 1° aliphatic amines liberate N_2: **propan-1-amine** and **propan-2-amine**. $RNH_2 + HNO_2 \rightarrow ROH + N_2\uparrow + H_2O$

9.9 **Convert (i) 3-methylaniline into 3-nitrotoluene (ii) aniline into 1,3,5-tribromobenzene.**

Ans. / उत्तर: (i) $m\text{-}CH_3C_6H_4NH_2 \xrightarrow{NaNO_2/HCl,\ 273\ K} m\text{-}CH_3C_6H_4N_2^+Cl^- \xrightarrow{HBF_4} m\text{-}CH_3C_6H_4N_2^+BF_4^- \xrightarrow{NaNO_2/Cu,\ \Delta} m\text{-}CH_3C_6H_4NO_2$

(ii) $C_6H_5NH_2 \xrightarrow{Br_2(aq)}$ 2,4,6-tribromoaniline $\xrightarrow{NaNO_2/HCl,\ 273\ K}$ diazonium salt $\xrightarrow{H_3PO_2/H_2O}$ 1,3,5-tribromobenzene

C. Exercises (अभ्यास प्रश्न)

9.1 **Write IUPAC names of the following compounds and classify them into primary, secondary and tertiary amines: (i) $(CH_3)_2CHNH_2$ (ii) $CH_3(CH_2)_2NH_2$ (iii) $CH_3NHCH(CH_3)_2$ (iv) $(CH_3)_3CNH_2$ (v) $C_6H_5NHCH_3$ (vi) $(CH_3CH_2)_2NCH_3$ (vii) $m\text{-}BrC_6H_4NH_2$**

Ans. / उत्तर: (i) Propan-2-amine — 1° (ii) Propan-1-amine — 1° (iii) N-Methylpropan-2-amine — 2° (iv) 2-Methylpropan-2-amine — 1° (v) N-Methylbenzenamine (N-methylaniline) — 2° (vi) N-Ethyl-N-methylethanamine — 3° (vii) 3-Bromobenzenamine (3-bromoaniline) — 1°

9.2 **Give one chemical test to distinguish between: (i) Methylamine and dimethylamine (ii) Secondary and tertiary amines (iii) Ethylamine and aniline (iv) Aniline and benzylamine (v) Aniline and N-methylaniline**

Ans. / उत्तर:

Pair	Test	Observation
(i) CH_3NH_2 / $(CH_3)_2NH$	Carbylamine ($CHCl_3$ + alc. KOH, heat)	Methylamine gives foul-smelling CH_3NC; dimethylamine does not
(ii) 2° / 3° amine	Hinsberg ($C_6H_5SO_2Cl$)	2° gives sulphonamide insoluble in alkali; 3° does not react
(iii) Ethylamine / Aniline	Azo-dye test: $NaNO_2$ + HCl at 273–278 K, then alkaline phenol/β-naphthol	Aniline gives orange/red dye; ethylamine gives N_2 bubbles, no dye
(iv) Aniline / Benzylamine	Azo-dye test (as above)	Aniline gives azo dye; benzylamine (aliphatic type) evolves N_2, no dye
(v) Aniline / N-Methylaniline	Carbylamine	Aniline gives foul smell (C_6H_5NC); N-methylaniline (2°) does not

9.3 Account for the following:

Ans. / उत्तर: (i) **pK_b of aniline > methylamine:** in aniline the lone pair on N is delocalised into the benzene ring (resonance) and is less available for protonation; aniline is more stable than the anilinium ion. In methylamine, +I of CH_3 increases electron density on N. So aniline is a weaker base (higher pK_b).

(ii) **Ethylamine soluble, aniline not:** ethylamine forms H-bonds with water; in aniline the large hydrophobic C_6H_5 group outweighs the H-bonding of $-NH_2$.

(iii) **Methylamine + $FeCl_3$ gives hydrated ferric oxide:** $CH_3NH_2 + H_2O \rightleftharpoons CH_3NH_3^+ + OH^-$; the OH^- ions precipitate Fe^{3+}: $FeCl_3 + 3OH^- \rightarrow Fe(OH)_3\downarrow$ $(Fe_2O_3{\cdot}xH_2O) + 3Cl^-$.

(iv) **m-Nitroaniline in nitration:** in strongly acidic nitrating mixture, aniline is protonated to the anilinium ion ($-NH_3^+$), which is meta-directing → ~47% m-nitroaniline.

(v) **No Friedel–Crafts:** aniline (Lewis base) forms a salt with $AlCl_3$ (Lewis acid); N gets a positive charge and strongly deactivates the ring.

(vi) **Aromatic diazonium salts more stable:** in ArN_2^+ the positive charge is delocalised over the benzene ring by resonance; aliphatic diazonium ions have no such stabilisation and decompose at once.

(vii) **Gabriel synthesis preferred:** it gives pure 1° amines, free from 2° and 3° amines (unlike ammonolysis).

(i) अनुनाद; (ii) बड़ा जलविरोधी फ़ेनिल; (iii) OH^- बनता है; (iv) ऐनिलिनियम आयन मेटा-निर्देशक; (v) $AlCl_3$ से लवण; (vi) अनुनाद स्थायित्व; (vii) शुद्ध प्राथमिक ऐमीन।

9.4 Arrange the following:

Ans. / उत्तर: (i) Decreasing pK_b: $C_6H_5NH_2 > C_6H_5NHCH_3 > C_2H_5NH_2 > (C_2H_5)_2NH$

(ii) Increasing basic strength: $C_6H_5NH_2 < C_6H_5N(CH_3)_2 < CH_3NH_2 < (C_2H_5)_2NH$

(iii) (a) p-Nitroaniline < Aniline < p-Toluidine (b) $C_6H_5NH_2 < C_6H_5NHCH_3 < C_6H_5CH_2NH_2$

(iv) Gas phase, decreasing: $(C_2H_5)_3N > (C_2H_5)_2NH > C_2H_5NH_2 > NH_3$ (only +I effect works)

(v) Increasing boiling point: $(CH_3)_2NH < C_2H_5NH_2 < C_2H_5OH$

(vi) Increasing solubility in water: $C_6H_5NH_2 < (C_2H_5)_2NH < C_2H_5NH_2$

9.5 How will you convert:

Ans. / उत्तर: (i) **Ethanoic acid → methanamine:** $CH_3COOH \xrightarrow{-NH_3,\ \Delta} CH_3CONH_2 \xrightarrow{-Br_2/NaOH} CH_3NH_2$

(ii) **Hexanenitrile → 1-aminopentane:** $CH_3(CH_2)_4CN \xrightarrow{-H_2O/H^+\ (partial\ hydrolysis)} CH_3(CH_2)_4CONH_2 \xrightarrow{-Br_2/NaOH} CH_3(CH_2)_4NH_2$

(iii) **Methanol → ethanoic acid:** $CH_3OH \xrightarrow{-PCl_5} CH_3Cl \xrightarrow{-KCN} CH_3CN \xrightarrow{-H_3O^+} CH_3COOH$

(iv) **Ethanamine → methanamine:** $C_2H_5NH_2 \xrightarrow{-HNO_2} C_2H_5OH \xrightarrow{-KMnO_4} CH_3COOH \xrightarrow{-NH_3,\ \Delta} CH_3CONH_2 \xrightarrow{-Br_2/NaOH} CH_3NH_2$

(v) **Ethanoic acid → propanoic acid:** $CH_3COOH \xrightarrow{-LiAlH_4} CH_3CH_2OH \xrightarrow{-PCl_5} C_2H_5Cl \xrightarrow{-KCN} C_2H_5CN \xrightarrow{-H_3O^+} C_2H_5COOH$

(vi) **Methanamine → ethanamine:** $CH_3NH_2 \xrightarrow{-HNO_2} CH_3OH \xrightarrow{-PCl_5} CH_3Cl \xrightarrow{-KCN} CH_3CN \xrightarrow{-LiAlH_4} CH_3CH_2NH_2$

(vii) **Nitromethane → dimethylamine:** $CH_3NO_2 \xrightarrow{-Sn/HCl} CH_3NH_2 \xrightarrow{-CHCl_3/alc.\ KOH} CH_3NC \xrightarrow{-H_2/Pt} CH_3NHCH_3$

(viii) **Propanoic acid → ethanoic acid:** $C_2H_5COOH \xrightarrow{-NH_3,\ \Delta} C_2H_5CONH_2 \xrightarrow{-Br_2/NaOH} C_2H_5NH_2 \xrightarrow{-HNO_2} C_2H_5OH \xrightarrow{-KMnO_4} CH_3COOH$

9.6 **Describe a method for the identification of primary, secondary and tertiary amines. Also write chemical equations.**

Ans. / उत्तर: **Hinsberg test** (benzenesulphonyl chloride, $C_6H_5SO_2Cl$):
· **1° amine**: $C_6H_5SO_2Cl + H_2N{-}C_2H_5 \rightarrow C_6H_5SO_2NHC_2H_5 + HCl$. The N–H is acidic (strong $-SO_2-$ group), so the product **dissolves in KOH**.
· **2° amine**: $C_6H_5SO_2Cl + HN(C_2H_5)_2 \rightarrow C_6H_5SO_2N(C_2H_5)_2 + HCl$. No H on N → **insoluble in alkali** (precipitate).
· **3° amine**: **no reaction**.
(Also: carbylamine test is positive only for 1° amines.)
1° — उत्पाद क्षार में विलेय; 2° — अविलेय; 3° — अभिक्रिया नहीं।

9.7 **Write short notes on: (i) Carbylamine reaction (ii) Diazotisation (iii) Hofmann's bromamide reaction (iv) Coupling reaction (v) Ammonolysis (vi) Acetylation (vii) Gabriel phthalimide synthesis**

Ans. / उत्तर: (i) **Carbylamine reaction:** 1° amines (aliphatic or aromatic) heated with $CHCl_3$ and alcoholic KOH give foul-smelling isocyanides; test for 1° amines. $R{-}NH_2 + CHCl_3 + 3KOH \rightarrow R{-}NC + 3KCl + 3H_2O$
(ii) **Diazotisation:** conversion of a 1° aromatic amine into a diazonium salt with $NaNO_2 + HCl$ at 273–278 K. $C_6H_5NH_2 + NaNO_2 + 2HCl \rightarrow C_6H_5N_2^+Cl^- + NaCl + 2H_2O$
(iii) **Hofmann bromamide reaction:** an amide with Br_2 and NaOH gives a 1° amine with one carbon less (alkyl/aryl group migrates from C=O carbon to N). $RCONH_2 + Br_2 + 4NaOH \rightarrow RNH_2 + Na_2CO_3 + 2NaBr + 2H_2O$
(iv) **Coupling reaction:** benzenediazonium chloride reacts with phenol (alkaline) or aniline (acidic) at the para position to give coloured azo compounds (dyes).
$C_6H_5N_2^+Cl^- + C_6H_5OH \xrightarrow{-OH^-} p\text{-}HOC_6H_4{-}N{=}N{-}C_6H_5$ (orange) $+ HCl$
(v) **Ammonolysis:** cleavage of C–X by NH_3: alkyl halide + ethanolic NH_3 in a sealed tube at 373 K gives a mixture of 1°, 2°, 3° amines and quaternary salt. $RX + NH_3 \rightarrow RNH_2 \rightarrow R_2NH \rightarrow R_3N \rightarrow R_4N^+X^-$
(vi) **Acetylation:** replacement of H of $-NH_2$ or >NH by CH_3CO- using acetyl chloride/acetic anhydride (pyridine). $C_6H_5NH_2 + (CH_3CO)_2O \rightarrow C_6H_5NHCOCH_3 + CH_3COOH$
(vii) **Gabriel phthalimide synthesis:** phthalimide + ethanolic KOH → potassium phthalimide; + R–X → N-alkylphthalimide; alkaline hydrolysis → pure 1° amine + phthalate. Not used for aromatic amines.

9.8 **Accomplish the following conversions:**

Ans. / उत्तर: (i) **Nitrobenzene → benzoic acid:** $C_6H_5NO_2 \xrightarrow{-Sn/HCl} C_6H_5NH_2 \xrightarrow{-NaNO_2/HCl,\ 273\ K} C_6H_5N_2Cl \xrightarrow{-CuCN} C_6H_5CN \xrightarrow{-H_3O^+} C_6H_5COOH$

(ii) **Benzene → m-bromophenol:** $C_6H_6 \xrightarrow{-HNO_3/H_2SO_4} C_6H_5NO_2 \xrightarrow{-Br_2/FeBr_3} m\text{-}BrC_6H_4NO_2 \xrightarrow{-Sn/HCl} m\text{-}BrC_6H_4NH_2 \xrightarrow{-NaNO_2/HCl,\ 273\ K} m\text{-}BrC_6H_4N_2Cl \xrightarrow{-H_2O,\ warm} m\text{-}BrC_6H_4OH$

(iii) **Benzoic acid → aniline:** $C_6H_5COOH \xrightarrow{-NH_3,\ \Delta} C_6H_5CONH_2 \xrightarrow{-Br_2/NaOH} C_6H_5NH_2$

(iv) **Aniline → 2,4,6-tribromofluorobenzene:** $C_6H_5NH_2 \xrightarrow{-Br_2(aq)}$ 2,4,6-tribromoaniline $\xrightarrow{-NaNO_2/HCl,\ 273\ K}$ diazonium salt $\xrightarrow{-HBF_4}$ diazonium fluoroborate $\xrightarrow{-\Delta}$ 2,4,6-tribromofluorobenzene

(v) **Benzyl chloride → 2-phenylethanamine:** $C_6H_5CH_2Cl \xrightarrow{-KCN} C_6H_5CH_2CN \xrightarrow{-LiAlH_4} C_6H_5CH_2CH_2NH_2$

(vi) **Chlorobenzene → p-chloroaniline:** $C_6H_5Cl \xrightarrow{-HNO_3/H_2SO_4} p\text{-}ClC_6H_4NO_2 \xrightarrow{-Sn/HCl} p\text{-}ClC_6H_4NH_2$

(vii) **Aniline → p-bromoaniline:** $C_6H_5NH_2 \xrightarrow{-(CH_3CO)_2O,\ pyridine} C_6H_5NHCOCH_3 \xrightarrow{-Br_2/CH_3COOH} p\text{-}BrC_6H_4NHCOCH_3 \xrightarrow{-H_3O^+\ (or\ OH^-)} p\text{-}BrC_6H_4NH_2$

(viii) **Benzamide → toluene:** $C_6H_5CONH_2 \xrightarrow{-Br_2/NaOH} C_6H_5NH_2 \xrightarrow{-NaNO_2/HCl,\ 273\ K} C_6H_5N_2Cl \xrightarrow{-H_3PO_2} C_6H_6 \xrightarrow{-CH_3Cl,\ anhyd.\ AlCl_3} C_6H_5CH_3$

(ix) **Aniline → benzyl alcohol:** $C_6H_5NH_2 \xrightarrow{-NaNO_2/HCl,\ 273\ K} C_6H_5N_2Cl \xrightarrow{-CuCN} C_6H_5CN \xrightarrow{-LiAlH_4} C_6H_5CH_2NH_2 \xrightarrow{-HNO_2} C_6H_5CH_2OH$

9.9 **Give the structures of A, B and C in the following reactions:**

(i) $CH_3CH_2I \xrightarrow{NaCN} A \xrightarrow[\text{Partial hydrolysis}]{OH^-} B \xrightarrow{NaOH+Br_2} C$

(ii) $C_6H_5N_2Cl \xrightarrow{CuCN} A \xrightarrow{H_2O/H^+} B \xrightarrow[\Delta]{NH_3} C$

(iii) $CH_3CH_2Br \xrightarrow{KCN} A \xrightarrow{LiAlH_4} B \xrightarrow[0°C]{HNO_2} C$

(iv) $C_6H_5NO_2 \xrightarrow{Fe/HCl} A \xrightarrow[273\,K]{NaNO_2+HCl} B \xrightarrow[\Delta]{H_2O/H^+} C$

(v) $CH_3COOH \xrightarrow[\Delta]{NH_3} A \xrightarrow{NaOBr} B \xrightarrow{NaNO_2/HCl} C$

(vi) $C_6H_5NO_2 \xrightarrow{Fe/HCl} A \xrightarrow[273\,K]{HNO_2} B \xrightarrow{C_6H_5OH} C$

Ans. / उत्तर:

	A	B	C
(i)	CH_3CH_2CN	$CH_3CH_2CONH_2$	$CH_3CH_2NH_2$
(ii)	C_6H_5CN	C_6H_5COOH	$C_6H_5CONH_2$
(iii)	CH_3CH_2CN	$CH_3CH_2CH_2NH_2$	$CH_3CH_2CH_2OH$
(iv)	$C_6H_5NH_2$	$C_6H_5N_2^+Cl^-$	C_6H_5OH
(v)	CH_3CONH_2	CH_3NH_2	CH_3OH
(vi)	$C_6H_5NH_2$	$C_6H_5N_2^+Cl^-$	p-HOC_6H_4–N=N–C_6H_5 (p-hydroxyazobenzene)

9.10 **An aromatic compound 'A' on treatment with aqueous ammonia and heating forms compound 'B' which on heating with Br_2 and KOH forms 'C' of molecular formula C_6H_7N. Write the structures and IUPAC names of A, B and C.**

Ans. / उत्तर: $C_6H_7N = C_6H_5NH_2$, formed by Hoffmann reaction, so B is the amide with one more C and A is the acid.

A = C_6H_5COOH — benzoic acid (benzenecarboxylic acid)

B = $C_6H_5CONH_2$ — benzamide (benzenecarboxamide)

C = $C_6H_5NH_2$ — aniline (benzenamine)

$C_6H_5COOH \xrightarrow{-NH_3(aq),\ \Delta} C_6H_5CONH_2 \xrightarrow{-Br_2/KOH} C_6H_5NH_2$

9.11 **Complete the following reactions: (i) $C_6H_5NH_2 + CHCl_3 +$ alc. KOH → (ii) $C_6H_5N_2Cl + H_3PO_2 + H_2O$ → (iii) $C_6H_5NH_2 + H_2SO_4$(conc.) → (iv) $C_6H_5N_2Cl + C_2H_5OH$ → (v) $C_6H_5NH_2 + Br_2$(aq) → (vi) $C_6H_5NH_2 + (CH_3CO)_2O$ → (vii) $C_6H_5N_2Cl \xrightarrow{-(i)\ HBF_4\ (ii)\ NaNO_2/Cu,\ \Delta}$**

Ans. / उत्तर: (i) $C_6H_5NC + 3KCl + 3H_2O$ (phenyl isocyanide)

(ii) $C_6H_6 + N_2 + H_3PO_3 + HCl$

(iii) $C_6H_5NH_3^+HSO_4^-$ (anilinium hydrogensulphate) $\xrightarrow{-453-473\ K}$ p-$H_2NC_6H_4SO_3H$ (sulphanilic acid)

(iv) $C_6H_6 + N_2 + CH_3CHO + HCl$

(v) 2,4,6-Tribromoaniline (white ppt) + 3HBr

(vi) $C_6H_5NHCOCH_3$ (acetanilide) + CH_3COOH

(vii) $C_6H_5N_2^+BF_4^- \rightarrow C_6H_5NO_2 + N_2 + NaBF_4$

9.12 **Why cannot aromatic primary amines be prepared by Gabriel phthalimide synthesis?**

Ans. / उत्तर: The method needs nucleophilic substitution of the halide by the phthalimide anion. **Aryl halides do not undergo nucleophilic substitution** (C–X has partial double-bond character, sp^2 carbon), so the phthalimide anion cannot replace X in ArX.
ऐरिल हैलाइड नाभिकस्नेही प्रतिस्थापन नहीं देते।

9.13 **Write the reactions of (i) aromatic and (ii) aliphatic primary amines with nitrous acid.**

Ans. / उत्तर: (i) $C_6H_5NH_2 + NaNO_2 + 2HCl \xrightarrow{273\text{–}278\ K} C_6H_5N_2^+Cl^- + NaCl + 2H_2O$ (diazonium salt, stable in cold)

(ii) $R\text{–}NH_2 + HNO_2 \xrightarrow{NaNO_2 + HCl} [R\text{–}N_2^+Cl^-] \rightarrow R\text{–}OH + N_2\uparrow + HCl$
(unstable diazonium salt decomposes; N_2 is evolved quantitatively)

9.14 **Give plausible explanation: (i) Why are amines less acidic than alcohols of comparable molecular masses? (ii) Why do primary amines have higher boiling point than tertiary amines? (iii) Why are aliphatic amines stronger bases than aromatic amines?**

Ans. / उत्तर: (i) N is less electronegative than O, so the N–H bond is less polar than O–H and the amide ion (RNH^-) is less stable than the alkoxide ion (RO^-). So amines lose H^+ less easily.
(ii) 1° amines have two H on N and form intermolecular H-bonds; 3° amines have no H on N, so no H-bonding.
(iii) In aliphatic amines, the +I effect of alkyl groups increases electron density on N. In aromatic amines, the lone pair of N is delocalised into the benzene ring and is less available for protonation.
(i) N कम विद्युतऋणी; (ii) प्राथमिक में H-बंध; (iii) ऐलिफ़ैटिक में +I, ऐरोमैटिक में अनुनाद।

Unit 10 : Biomolecules

जैव-अणु — NCERT Solutions (Intext + Exercises; this unit has no solved examples)

A. Intext Questions (पाठ्यनिहित प्रश्न)

10.1 **Glucose or sucrose are soluble in water but cyclohexane or benzene (simple six membered ring compounds) are insoluble in water. Explain.**
ग्लूकोस/सुक्रोस जल में विलेय पर साइक्लोहेक्सेन/बेंज़ीन अविलेय क्यों?

Ans. / उत्तर: Glucose has five and sucrose has eight –OH groups, which form **hydrogen bonds with water**. Cyclohexane and benzene have no –OH (non-polar), so they cannot form H-bonds with water.
अनेक –OH समूह जल से H-बंध बनाते हैं; हाइड्रोकार्बन अध्रुवीय हैं।

10.2 **What are the expected products of hydrolysis of lactose?**

Ans. / उत्तर: $C_{12}H_{22}O_{11}$ (lactose) + H_2O → **β-D-galactose + β-D-glucose**
लैक्टोस → गैलेक्टोस + ग्लूकोस।

10.3 **How do you explain the absence of aldehyde group in the pentaacetate of D-glucose?**

Ans. / उत्तर: Glucose exists mainly as a cyclic hemiacetal (–OH of C-5 joined to C-1). In the pentaacetate, the C-1 –OH is also acetylated, so the ring cannot open to give a free –CHO. Hence the pentaacetate does not react with NH_2OH.
चक्रीय रूप में C-1 भी ऐसीटिलित — वलय खुल नहीं सकती, इसलिए मुक्त –CHO नहीं।

10.4 **The melting points and solubility in water of amino acids are generally higher than those of the corresponding halo acids. Explain.**

Ans. / उत्तर: Amino acids exist as **zwitter ions** ($H_3N^+–CHR–COO^-$). They are salt-like with strong electrostatic attractions → high m.p., and they are strongly solvated by water → high solubility. Halo acids have no such dipolar ionic structure.
ज़्विटर आयन — लवण जैसे गुण, उच्च गलनांक और जल में विलेयता।

10.5 **Where does the water present in the egg go after boiling the egg?**

Ans. / उत्तर: On boiling, the egg-white proteins are **denatured** (coagulate). The water present gets held (absorbed/adsorbed) in the coagulated protein through H-bonding, so it does not flow out.
विकृत (स्कंदित) प्रोटीन H-बंध द्वारा जल को अपने में बाँध लेता है।

10.6 **Why cannot vitamin C be stored in our body?**

Ans. / उत्तर: Vitamin C is **water soluble**; excess is readily excreted in urine, so it is not stored and must be taken regularly in the diet.
जल-विलेय — मूत्र के साथ निकल जाता है।

10.7 **What products would be formed when a nucleotide from DNA containing thymine is hydrolysed?**

Ans. / उत्तर: **β-D-2-Deoxyribose + phosphoric acid + thymine.**

10.8 **When RNA is hydrolysed, there is no relationship among the quantities of different bases obtained. What does this fact suggest about the structure of RNA?**

Ans. / उत्तर: There is no fixed base pairing (unlike A = T, G ≡ C in DNA), so RNA is **single-stranded**.
क्षारक युग्मन नहीं — RNA एकल रज्जुक है।

B. Exercises (अभ्यास प्रश्न)

10.1 **What are monosaccharides?**

Ans. / उत्तर: Carbohydrates that **cannot be hydrolysed** further into simpler polyhydroxy aldehyde or ketone units, e.g. glucose, fructose, ribose. (About 20 occur in nature.)
जिनका आगे जल-अपघटन न हो — ग्लूकोस, फ़्रक्टोस, राइबोस।

10.2 **What are reducing sugars?**

Ans. / उत्तर: Carbohydrates that **reduce Fehling's solution and Tollens' reagent** because they have a free aldehydic/ketonic group (or a free hemiacetal). All monosaccharides, maltose and lactose are reducing sugars; sucrose is not.
जो फ़ेहलिंग व टॉलेंस को अपचयित करें — सभी एकलशर्करा, माल्टोस, लैक्टोस।

10.3 **Write two main functions of carbohydrates in plants.**

Ans. / उत्तर: (i) **Storage of food/energy** as starch. (ii) **Structural material** — cellulose forms the plant cell wall.
(i) मंड के रूप में भोजन संग्रह (ii) सेलुलोस से कोशिका भित्ति।

10.4 **Classify into monosaccharides and disaccharides: Ribose, 2-deoxyribose, maltose, galactose, fructose and lactose.**

Ans. / उत्तर: **Monosaccharides:** ribose, 2-deoxyribose, galactose, fructose.
Disaccharides: maltose, lactose.

10.5 **What do you understand by the term glycosidic linkage?**

Ans. / उत्तर: The **oxide (–O–) linkage** joining two monosaccharide units, formed by loss of a water molecule, e.g. C1–C4 link in maltose, C1–C2 link in sucrose.
दो एकलशर्कराओं को जोड़ने वाला ऑक्सीजन बंध (जल निकलकर बनता है)।

10.6 **What is glycogen? How is it different from starch?**

Ans. / उत्तर: Glycogen is the storage carbohydrate of animals (**animal starch**), found in liver, muscles and brain (also yeast and fungi). Its structure is like amylopectin but **more highly branched**. Starch is the plant storage carbohydrate, made of amylose (unbranched, 15–20%) and amylopectin (branched, 80–85%).
ग्लाइकोजन जंतु मंड है — ऐमाइलोपेक्टिन जैसा पर अधिक शाखित; मंड पौधों में।

10.7 **What are the hydrolysis products of (i) sucrose and (ii) lactose?**

Ans. / उत्तर: (i) Sucrose → **D-(+)-glucose + D-(–)-fructose** (invert sugar) (ii) Lactose → **β-D-galactose + β-D-glucose**

10.8 **What is the basic structural difference between starch and cellulose?**

Ans. / उत्तर: Starch is a polymer of **α-D-glucose** (amylose: C1–C4, unbranched; amylopectin: C1–C4 chain with C1–C6 branches). Cellulose is a **straight-chain** polymer of **β-D-glucose** joined by C1–C4 glycosidic links.
मंड — α-ग्लूकोस; सेलुलोस — β-ग्लूकोस की सीधी श्रृंखला।

10.9 **What happens when D-glucose is treated with the following reagents? (i) HI (ii) Bromine water (iii) HNO_3**

Ans. / उत्तर: (i) Prolonged heating with HI → **n-hexane**, $CH_3(CH_2)_4CH_3$ (shows straight chain of 6 C).
(ii) Bromine water (mild oxidant) → **gluconic acid**, $HOOC-(CHOH)_4-CH_2OH$

(shows –CHO).
(iii) HNO_3 → **saccharic acid**, HOOC–$(CHOH)_4$–COOH (both –CHO and –CH_2OH oxidised; shows a 1° alcohol group).

10.10 Enumerate the reactions of D-glucose which cannot be explained by its open chain structure.

Ans. / उत्तर: (i) Despite having –CHO, glucose does not give **Schiff's test** and does not form the **$NaHSO_3$ addition product**.
(ii) Glucose **pentaacetate does not react with NH_2OH**, showing no free –CHO.
(iii) Glucose exists in two crystalline forms, **α (m.p. 419 K)** and **β (m.p. 423 K)**. These are explained by the cyclic (pyranose) hemiacetal structure.
शिफ़ परीक्षण नहीं, $NaHSO_3$ योगज नहीं, पेंटाऐसीटेट + NH_2OH नहीं, α व β रूप।

10.11 What are essential and non-essential amino acids? Give two examples of each type.

Ans. / उत्तर: Essential: cannot be synthesised in the body; must come from diet — e.g. valine, leucine (also lysine, isoleucine, phenylalanine...).
Non-essential: synthesised in the body — e.g. glycine, alanine (also glutamic acid, aspartic acid...).
आवश्यक — आहार से लेने पड़ते हैं; अनावश्यक — शरीर स्वयं बनाता है।

10.12 Define the following as related to proteins: (i) Peptide linkage (ii) Primary structure (iii) Denaturation

Ans. / उत्तर: (i) **Peptide linkage:** the amide bond –CO–NH– formed between the –COOH of one amino acid and the –NH_2 of another with loss of water.
(ii) **Primary structure:** the specific sequence of amino acids in a polypeptide chain.
(iii) **Denaturation:** loss of biological activity of a native protein when its H-bonds are disturbed by heat or change of pH; globules unfold and helices uncoil (2° and 3° structures destroyed, 1° intact), e.g. coagulation of egg white on boiling.

10.13 What are the common types of secondary structure of proteins?

Ans. / उत्तर: **α-Helix** and **β-pleated sheet**.

10.14 What type of bonding helps in stabilising the α-helix structure of proteins?

Ans. / उत्तर: Hydrogen bonding between the –NH group of each amino acid residue and the >C=O group of an adjacent turn of the helix (intramolecular).

10.15 **Differentiate between globular and fibrous proteins.**

Ans. / उत्तर:

Fibrous proteins	Globular proteins
Polypeptide chains run parallel, held by H-bonds and disulphide bonds; fibre-like	Chains coil around to give a spherical shape
Generally insoluble in water	Usually soluble in water
e.g. keratin (hair, wool, silk), myosin (muscles)	e.g. insulin, albumins

10.16 **How do you explain the amphoteric behaviour of amino acids?**

Ans. / उत्तर: In water, amino acids exist as zwitter ions, $H_3N^+-CHR-COO^-$. The $-COO^-$ group accepts a proton (reacts with acids) and the $-NH_3^+$ group donates a proton (reacts with bases). So they react with both acids and bases → **amphoteric**.

$H_3N^+CHRCOO^- + H^+ \rightarrow H_3N^+CHRCOOH$; $H_3N^+CHRCOO^- + OH^- \rightarrow H_2NCHRCOO^- + H_2O$

ज़्विटर आयन अम्ल और क्षार दोनों से अभिक्रिया करता है — उभयधर्मी।

10.17 **What are enzymes?**

Ans. / उत्तर: Enzymes are **biocatalysts**, almost all globular proteins, that catalyse biochemical reactions under mild conditions. They are highly specific for a reaction and substrate, needed in small amounts, and lower the activation energy (e.g. maltase, sucrase).

एंज़ाइम = जैव-उत्प्रेरक, गोलिकाकार प्रोटीन, अति विशिष्ट।

10.18 **What is the effect of denaturation on the structure of proteins?**

Ans. / उत्तर: H-bonds are broken; globules unfold and helices uncoil. The **secondary and tertiary structures are destroyed**, but the **primary structure remains intact**. The protein loses its biological activity.

10.19 **How are vitamins classified? Name the vitamin responsible for the coagulation of blood.**

Ans. / उत्तर: By solubility: (i) **fat-soluble** — A, D, E, K (stored in liver and adipose tissue); (ii) **water-soluble** — B-group and C (excreted in urine, must be supplied regularly). **Vitamin K** is responsible for blood coagulation.

वसा-विलेय (A, D, E, K) व जल-विलेय (B, C); रक्त का थक्का — विटामिन K।

10.20 **Why are vitamin A and vitamin C essential to us? Give their important sources.**

Ans. / उत्तर: **Vitamin A:** deficiency causes xerophthalmia (hardening of cornea) and night blindness. Sources: fish liver oil, carrots, butter, milk.
Vitamin C: deficiency causes scurvy (bleeding gums). Sources: citrus fruits, amla, green leafy vegetables.
A की कमी से रतौंधी; C की कमी से स्कर्वी।

10.21 **What are nucleic acids? Mention their two important functions.**

Ans. / उत्तर: Nucleic acids (DNA and RNA) are long-chain polymers of nucleotides (polynucleotides) present in the nucleus. Functions: (i) DNA is the chemical basis of **heredity** and can self-replicate during cell division; (ii) they direct **protein synthesis** (message in DNA, synthesis by RNA).
आनुवंशिकता का आधार और प्रोटीन संश्लेषण।

10.22 **What is the difference between a nucleoside and a nucleotide?**

Ans. / उत्तर: **Nucleoside** = nitrogenous base + pentose sugar (base at C-1′).
Nucleotide = nucleoside + phosphoric acid (phosphate at C-5′ of the sugar).
न्यूक्लियोसाइड = क्षारक + शर्करा; न्यूक्लियोटाइड = न्यूक्लियोसाइड + फ़ॉस्फ़ेट।

10.23 **The two strands in DNA are not identical but are complementary. Explain.**

Ans. / उत्तर: The two strands are held by H-bonds between **specific base pairs**: adenine always pairs with thymine and guanine with cytosine. So the sequence of one strand fixes the sequence of the other — they are complementary, not identical.
A–T तथा G–C का विशिष्ट युग्मन — इसलिए दोनों रज्जुक पूरक हैं।

10.24 **Write the important structural and functional differences between DNA and RNA.**

Ans. / उत्तर:

DNA	RNA
Sugar: β-D-2-deoxyribose	Sugar: β-D-ribose
Bases: A, G, C, **T**	Bases: A, G, C, **U**
Double-stranded helix	Single-stranded
Carries hereditary information; self-replicates	Carries out protein synthesis (m-RNA, r-RNA, t-RNA)

10.25 What are the different types of RNA found in the cell?

Ans. / उत्तरः (i) Messenger RNA (m-RNA) (ii) Ribosomal RNA (r-RNA) (iii) Transfer RNA (t-RNA)

All the best! शुभकामनाएँ!