Pariksha Sathi

Class 12 Organic Chemistry

Solved Questions — Examples, In-text & Exercises

कक्षा 12 कार्बनिक रसायन — हल किए गए प्रश्न

Units 6 – 10 · Bilingual: English + हिन्दी

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Pariksha Sathi — Class 12 Organic Chemistry: Solved Questions · Hindi + English

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यह एक स्वतंत्र अध्ययन-पुस्तिका है; किसी बोर्ड या पाठ्यपुस्तक प्रकाशक द्वारा प्रकाशित या अनुमोदित नहीं है।

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How to use / कैसे पढ़ें: Each question is in a shaded box with its number (**Ex** = worked example). The answer follows under the dashed line; a Hindi line explains the key idea.
हर प्रश्न छायांकित बॉक्स में उसके क्रमांक के साथ है; उत्तर डैश रेखा के नीचे है; हिन्दी पंक्ति मुख्य कारण समझाती है।

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।

Unit 6 : Haloalkanes & Haloarenes

हैलोऐल्केन एवं हैलोऐरीन — Solved Questions (Examples + Intext + Exercises)

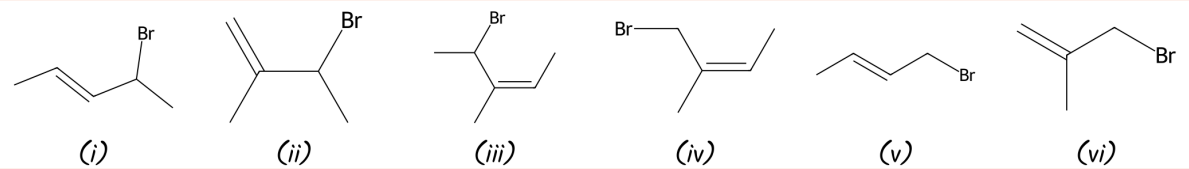
A. Solved Examples (हल किए गए उदाहरण)

Ex 6.1 **Draw all eight structural isomers of $C_5H_{11}Br$, name each by the IUPAC system and say whether it is a 1°, 2° or 3° bromide.**
$C_5H_{11}Br$ के आठ संरचनात्मक समावयवी, उनके IUPAC नाम और 1°/2°/3° वर्ग बताइए।

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 **Give the IUPAC name of each of these bromoalkenes.** इन ब्रोमोऐल्कीनों के IUPAC नाम लिखिए।



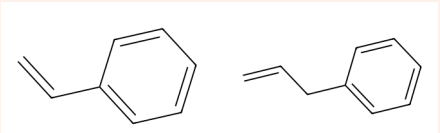
(i) (ii) (iii) (iv) (v) (vi)

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 **Free-radical monochlorination of 2-methylbutane, $(CH_3)_2CHCH_2CH_3$, is carried out. List every monochloro structural isomer that can form.**
2-मेथिलब्यूटेन के मोनोक्लोरीनीकरण से बनने वाले सभी समावयवी बताइए।

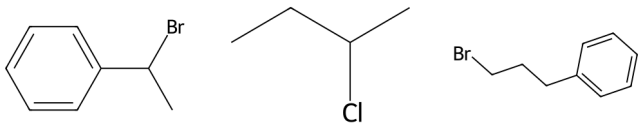
Ans. / उत्तर: The molecule has **four different types of H** → four monochloro isomers: अणु में चार प्रकार के H हैं → चार समावयवी।
$(CH_3)_2CHCH_2CH_2Cl$ · $(CH_3)_2CHCH(Cl)CH_3$ · $(CH_3)_2C(Cl)CH_2CH_3$ · $ClCH_2CH(CH_3)CH_2CH_3$

Ex 6.4 **Predict the product of each addition: (i) styrene ($C_6H_5CH=CH_2$) + HBr (ii) but-1-ene ($CH_3CH_2CH=CH_2$) + HCl (iii) allylbenzene ($C_6H_5CH_2CH=CH_2$) + HBr in presence of peroxide.** उत्पाद बताइए।



(i) styrene (iii) allylbenzene

Ans. / उत्तर:



(i) (ii) (iii)

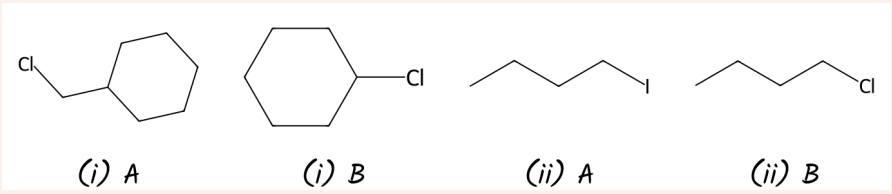
(i) **1-Bromo-1-phenylethane** — Markovnikov addition (stable benzylic carbocation). (ii) **2-Chlorobutane** (Markovnikov). (iii) **1-Bromo-3-**

phenylpropane — peroxide (Kharasch) effect gives anti-Markovnikov product.
(iii) में परॉक्साइड के कारण मार्कोनीकॉफ़-विरोधी योग होता है।

Ex 6.5 **Why does an alkyl halide give mainly an alkyl cyanide with KCN, but mainly an isocyanide with AgCN?**
KCN से सायनाइड और AgCN से आइसोसायनाइड क्यों?

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 each pair, which compound reacts faster by the S_N2 path? (i) A = (chloromethyl)cyclohexane, B = chlorocyclohexane (ii) A = 1-iodobutane, B = 1-chlorobutane** कौन S_N2 में तेज़?



(i) A (i) B (ii) A (ii) B

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 **Arrange in order of reactivity for S_N1 and for S_N2: (i) the four bromobutane isomers (ii) $C_6H_5CH_2Br$, $C_6H_5CH(C_6H_5)Br$, $C_6H_5CH(CH_3)Br$, $C_6H_5C(CH_3)(C_6H_5)Br$** S_N1 व S_N2 क्रम बताइए।

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 **State which member of each pair is chiral and which is achiral: (i) $CH_3CH(Br)OH$ and CH_3CHBr_2 (ii) pentan-2-ol and pentan-3-ol (iii) 2-bromobutane and 1-bromobutane** काइरल/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 **Chlorine pulls electrons away from the ring, yet it sends an incoming electrophile to the ortho and para positions. Explain.**
Cl इलेक्ट्रॉन-आकर्षी होकर भी ऑर्थो/पैरा निर्देशक क्यों?

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 **Draw the structure 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 बनाइए।

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 **When an alcohol is converted to an alkyl iodide using KI, why is H_2SO_4 avoided?**
KI के साथ H_2SO_4 क्यों नहीं?

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।

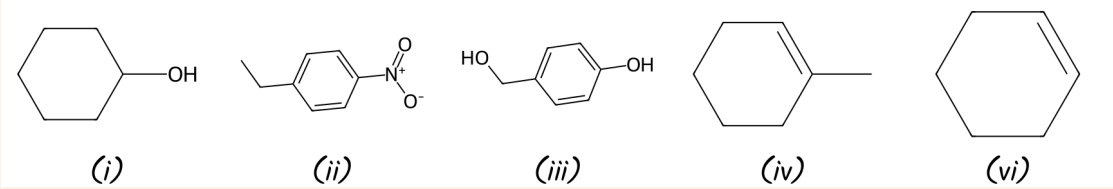
6.3 **Draw all the dichloro derivatives of propane.** प्रोपेन के सभी डाइक्लोरो व्युत्पन्न बनाइए।

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 **Which isomer of C_5H_{12}, on chlorination in light, gives (i) only one monochloride (ii) three monochlorides (iii) four monochlorides?** C_5H_{12} का कौन-सा समावयवी?

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 **Give the main monohalo product: (i) cyclohexanol + $SOCl_2$ (ii) 1-ethyl-4-nitrobenzene + Br_2, heat or UV (iii) 4-(hydroxymethyl)phenol + HCl, heat (iv) 1-methylcyclohexene + HI (v) CH_3CH_2Br + NaI (vi) cyclohexene + Br_2, heat or UV** *मुख्य उत्पाद बताइए।*



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

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 **Put in increasing order of boiling point: (i) chloromethane, dibromomethane, bromomethane, bromoform (ii) 1-chlorobutane, isopropyl chloride, 1-chloropropane** *क्वथनांक का बढ़ता क्रम।*

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।

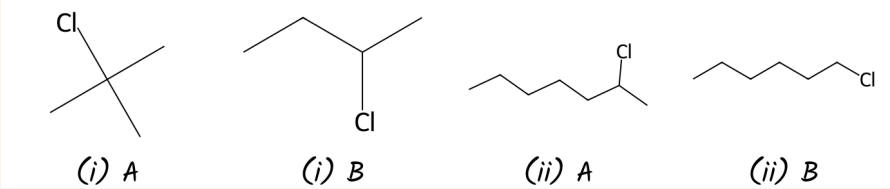
6.7 **For each pair, which halide reacts faster by S_N2? Give a reason. (i) 1-bromobutane / 2-bromobutane (ii) 2-bromobutane / 2-bromo-2-methylpropane (iii) 1-bromo-3-methylbutane, $(CH_3)_2CHCH_2CH_2Br$ / 1-bromo-2-methylbutane, $CH_3CH_2CH(CH_3)CH_2Br$**

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 **Which member of each pair undergoes S_N1 faster? (i) A = 2-chloro-2-methylpropane, B = 2-chlorobutane (ii) A = 2-chloroheptane, B = 1-chlorohexane** S_N1 में कौन तेज़?



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–E, R and R′: (a) bromocyclohexane + Mg (dry ether) → A; A + H_2O → B. (b) R–Br + Mg (dry ether) → C; C + D_2O → CH_3CHDCH_3. (c) R′–X + Na (ether) → 2,2,3,3-tetramethylbutane; R′–X + Mg → D; D + H_2O → E.** A से E, R व R′ पहचानिए।

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 Write the IUPAC name and classify (alkyl / allylic / benzylic 1°, 2°, 3°, vinylic or aryl): (i) $(CH_3)_2CHCH(Cl)CH_3$ (ii) $CH_3CH_2CH(CH_3)CH(C_2H_5)Cl$ (iii) $CH_3CH_2C(CH_3)_2CH_2I$ (iv) $(CH_3)_3CCH_2CH(Br)C_6H_5$ (v) $CH_3CH(CH_3)CH(Br)CH_3$ (vi) $CH_3C(C_2H_5)_2CH_2Br$ (vii) $CH_3C(Cl)(C_2H_5)CH_2CH_3$ (viii) $CH_3CH=C(Cl)CH_2CH(CH_3)_2$ (ix) $CH_3CH=CHC(Br)(CH_3)_2$ (x) p-$ClC_6H_4CH_2CH(CH_3)_2$ (xi) m-$ClCH_2C_6H_4CH_2C(CH_3)_3$ (xii) o-$BrC_6H_4CH(CH_3)CH_2CH_3$

IUPAC नाम लिखकर वर्गीकृत कीजिए।

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-$ClC_6H_4CH_2CH(CH_3)_2$	1-Chloro-4-(2-methylpropyl)benzene	Aryl
(xi) m-$ClCH_2C_6H_4CH_2C(CH_3)_3$	1-Chloromethyl-3-(2,2-dimethylpropyl)benzene	1° benzylic
(xii) o-$BrC_6H_4CH(CH_3)CH_2CH_3$	1-Bromo-2-(1-methylpropyl)benzene	Aryl

6.2 **IUPAC names please: (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 **Draw: (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 **Of CH_2Cl_2, $CHCl_3$ and CCl_4, which has the largest dipole moment?**
सबसे अधिक द्विध्रुव आघूर्ण किसका?

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} is unaffected by chlorine in the dark, but in bright sunlight it gives just one monochloro product, C_5H_9Cl. What is it?**
हाइड्रोकार्बन पहचानिए।

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 all the isomers of C_4H_9Br.** C_4H_9Br के समावयवी लिखिए।

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 **Give equations to make 1-iodobutane starting from (i) butan-1-ol (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 is an ambident nucleophile? Illustrate with one example.**
उभयदंती नाभिकस्नेही क्या है?

Ans. / उत्तर: Nucleophiles having **two nucleophilic centres** (can attack through two different atoms). Example: **cyanide ion** $[:C{\equiv}N:]^- \leftrightarrow [:C{=}N:]^-$ 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 member of each pair reacts faster with OH^- by S_N2? (i) CH_3Br / CH_3I (ii) $(CH_3)_3CCl$ / 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 **Sodium ethoxide in ethanol removes HX from each halide below. Write every alkene that can form and mark the major one: (i) 1-bromo-1-methylcyclohexane (ii) 2-chloro-2-methylbutane (iii) 3-bromo-2,2,3-trimethylpentane** *सभी ऐल्कीन लिखिए, मुख्य उत्पाद बताइए।*

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 **Carry out these conversions: (i) ethanol → but-1-yne (ii) ethane → bromoethene (iii) propene → 1-nitropropane (iv) toluene → benzyl alcohol (v) propene → propyne (vi) ethanol → ethyl fluoride (vii) bromomethane → propanone (viii) but-1-ene → but-2-ene (ix) 1-chlorobutane → n-octane (x) benzene → biphenyl** *रूपांतरण कीजिए।*

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:** $CH_3Br \xrightarrow{-KCN} CH_3CN$

$-CH_3MgBr$, ether→ $(CH_3)_2C{=}NMgBr$ $-H_3O^+$→ CH_3COCH_3

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

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

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

6.12 **Give reasons: (i) chlorobenzene has a smaller dipole moment than cyclohexyl chloride (ii) alkyl halides are polar yet do not mix with water (iii) Grignard reagents must be made under dry conditions** कारण बताइए।

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 **State the uses of Freon-12, DDT, carbon tetrachloride and iodoform.** उपयोग लिखिए।

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 **Give the main 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 (aqueous 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 **Show the mechanism by which 1-bromobutane reacts with KCN in aqueous ethanol to give pentanenitrile (n-BuCN).** क्रियाविधि लिखिए।

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 each set by S_N2 reactivity: (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 **Which is hydrolysed more readily by aqueous KOH: $C_6H_5CH_2Cl$ or $C_6H_5CHClC_6H_5$?** कौन आसानी से जल-अपघटित?

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 **Why does p-dichlorobenzene melt at a higher temperature than its o- and m-isomers?** पैरा का गलनांक अधिक क्यों?

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 would you convert: (i) propene → propan-1-ol (ii) ethanol → but-1-yne (iii) 1-bromopropane → 2-bromopropane (iv) toluene → benzyl alcohol (v) benzene → 4-bromonitrobenzene (vi) benzyl alcohol → 2-phenylethanoic acid (vii) ethanol → propanenitrile (viii) aniline → chlorobenzene (ix) 2-chlorobutane → 3,4-dimethylhexane (x) 2-methylpropene → 2-chloro-2-methylpropane (xi) ethyl chloride → propanoic acid (xii) but-1-ene → 1-iodobutane (xiii) 2-chloropropane → propan-1-ol (xiv) propan-2-ol → iodoform (xv) chlorobenzene → p-nitrophenol (xvi) 2-bromopropane → 1-bromopropane (xvii) chloroethane → butane (xviii) benzene → biphenyl (xix) tert-butyl bromide → isobutyl bromide (xx) aniline → phenyl isocyanide**

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:** $C_6H_6 \xrightarrow{-Br_2/FeBr_3} C_6H_5Br \xrightarrow{-conc.\ HNO_3/H_2SO_4} p\text{-}BrC_6H_4NO_2$ (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:** $2CH_3CH(Cl)CH_2CH_3 + 2Na \xrightarrow{-dry\ ether} CH_3CH_2CH(CH_3)\text{–}CH(CH_3)CH_2CH_3$ (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:** $\xrightarrow{-HBr,\ peroxide} CH_3(CH_2)_3Br$

$\xrightarrow{-NaI,\ dry\ acetone} CH_3(CH_2)_3I$

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

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

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

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

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

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

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

6.20 **An alkyl chloride gives an alcohol with aqueous KOH but an alkene with alcoholic KOH. Explain.** जलीय व ऐल्कोहॉली KOH में अंतर समझाइए।

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 **A primary bromide C_4H_9Br (a) gives (b) with alcoholic KOH; (b) adds HBr to give (c), an isomer of (a). With sodium, (a) gives (d), C_8H_{18}, which is not the product obtained from n-butyl bromide and sodium. Find (a) and write all equations.**

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 heated with alcoholic KOH (ii) bromobenzene reacts with Mg in dry ether (iii) chlorobenzene is hydrolysed (iv) ethyl chloride reacts with aqueous KOH (v) methyl bromide reacts with Na in dry ether (vi) methyl chloride reacts with KCN? क्या होता है?

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

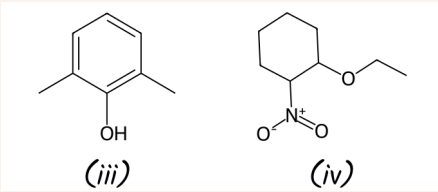
(vi) $CH_3Cl + KCN \rightarrow CH_3CN$ (ethanenitrile) + KCl

Unit 7 : Alcohols, Phenols & Ethers

ऐल्कोहॉल, फ़ीनॉल एवं ईथर — Solved Questions (Examples + Intext + Exercises)

A. Solved Examples (हल किए गए उदाहरण)

Ex 7.1 **IUPAC names please: (i) $CH_3CH(Cl)CH(CH_3)CH(CH_3)CH_2OH$ (ii) $(CH_3)_2CH-O-CH_2CH_3$ (iii) and (iv) as drawn:** IUPAC नाम लिखिए।



(iii) (iv)

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 **Write the structure and IUPAC name of the product of: (a) catalytic hydrogenation of butanal (b) hydration of propene with dilute H_2SO_4 (c) propanone + CH_3MgBr, then 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 **Put in increasing order of boiling point: (a) pentan-1-ol, butan-1-ol, butan-2-ol, ethanol, propan-1-ol, methanol (b) pentan-1-ol, n-butane, pentanal, ethoxyethane** क्वथनांक का बढ़ता क्रम।

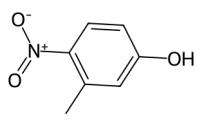
Ans. / उत्तर: (a) Methanol < ethanol < propan-1-ol < butan-2-ol < butan-1-ol < pentan-1-ol (b.p. rises with size; branching lowers it).
(b) n-Butane < ethoxyethane < pentanal < pentan-1-ol (van der Waals < weak dipole < dipole–dipole < H-bonding).
आकार बढ़ने पर क्वथनांक बढ़ता; शाखन से घटता; H-बंध वाले का सबसे अधिक।

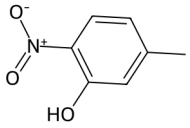
Ex 7.4 **Arrange by increasing acidity: propan-1-ol, 2,4,6-trinitrophenol, 3-nitrophenol, 3,5-dinitrophenol, phenol, 4-methylphenol.** अम्लता का बढ़ता क्रम।

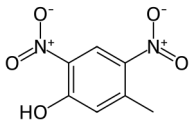
Ans. / उत्तर: Propan-1-ol < 4-methylphenol < phenol < 3-nitrophenol < 3,5-dinitrophenol < 2,4,6-trinitrophenol.
Alcohols are weaker than phenols; $-CH_3$ (electron donating) decreases acidity; each $-NO_2$ (electron withdrawing) increases it, most at o/p.
मेथिल अम्लता घटाता, नाइट्रो बढ़ाता है; जितने अधिक NO_2, उतना प्रबल अम्ल।

Ex 7.5 **Draw the major product(s) of: (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).


(a)


(a)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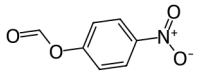

(c)

(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 **A student tries to make tert-butyl ethyl ether from C_2H_5ONa and $(CH_3)_3CCl$. (i) What will actually be the main product? (ii) Suggest a correct pair of reactants.** *मुख्य उत्पाद क्या होगा? सही अभिकारक सुझाइए।*

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 **Each ether is heated with HI. Give the main products: (i) $CH_3CH_2CH(CH_3)CH_2-O-CH_2CH_3$ (ii) $CH_3CH_2CH_2-O-C(CH_3)_2CH_2CH_3$ (iii) $C_6H_5CH_2-O-C_6H_5$** *HI के साथ उत्पाद बताइए।*

Ans. / उत्तर: (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)

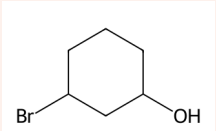
7.1 & 7.2 **Classify as 1°, 2° or 3° alcohols, and pick out the allylic ones: (i) $(CH_3)_3C-CH_2OH$ (ii) $CH_2=CH-CH_2OH$ (iii) $CH_3CH_2CH_2OH$ (iv) $C_6H_5-CH(OH)-CH_3$ (v) $C_6H_5-CH_2-CH(OH)-CH_3$ (vi) $C_6H_5-CH=CH-C(CH_3)_2OH$** *1°/2°/3° और ऐलिलिक पहचानिए।*

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 **Give IUPAC names: (i) $CH_3CH_2CH(CH_2Cl)CH(CH_2OH)CH(CH_3)_2$ (ii) $(CH_3)_2CHCH_2CH(OH)CH(CH_2OH)CH_3$ (iii) the cyclic alcohol drawn below (iv) $CH_2=CH-CH(OH)-CH_2CH_2CH_3$ (v) $(CH_3)_2C=C(Br)-CH_2OH$**



(iii)

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

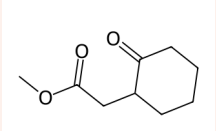
7.4 **Using methanal and a suitable Grignard reagent, how would you prepare (i) 2-methylpropan-1-ol, $(CH_3)_2CHCH_2OH$ (ii) cyclohexylmethanol, $C_6H_{11}CH_2OH$?**

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 + $RMgX \rightarrow R-CH_2OH$ (प्राथमिक ऐल्कोहॉल)।

7.5 **Give the products: (i) $CH_3CH=CH_2 + H_2O/H^+$ (ii) the keto-ester drawn below + $NaBH_4$ (iii) $CH_3CH_2CH(CH_3)CHO + NaBH_4$**

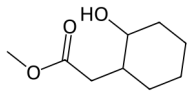


(ii)

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)



(ii)

(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 the product of (a) $HCl–ZnCl_2$ (b) HBr (c) $SOCl_2$ with (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 What is the main product when (i) 1-methylcyclohexanol (ii) butan-1-ol is dehydrated with acid?

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 o- and p-Nitrophenols are stronger acids than phenol. Show this using resonance structures of their phenoxide ions. अनुनाद संरचनाओं से समझाइए।

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

7.10 Starting from ethanol and 3-methylpentan-2-ol, make 2-ethoxy-3-methylpentane by Williamson synthesis.

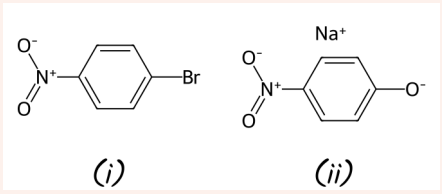
Ans. / उत्तर: $C_2H_5OH + HBr \rightarrow C_2H_5Br + H_2O$

$CH_3CH_2CH(CH_3)CH(OH)CH_3 + Na \rightarrow CH_3CH_2CH(CH_3)CH(ONa)CH_3 + \frac{1}{2}H_2$

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

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

7.11 **To make 1-methoxy-4-nitrobenzene, which pair is correct, (i) or (ii), and why?** *कौन-सा युग्म सही है और क्यों?*

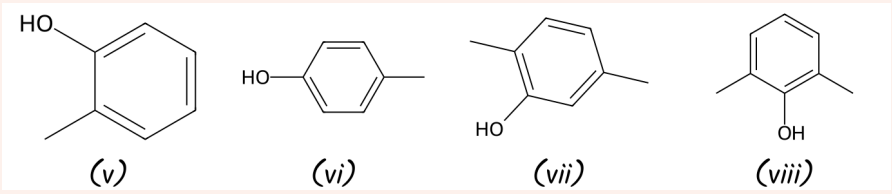


(i) 1-bromo-4-nitrobenzene + CH_3ONa (ii) sodium 4-nitrophenoxide + CH_3Br

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 **Give IUPAC names: (i) $CH_3CH(CH_3)CH(OH)C(CH_3)_2CH_3$ (ii) $CH_3CH(OH)CH_2CH(OH)CH(C_2H_5)CH_2CH_3$ (iii) $CH_3CH(OH)CH(OH)CH_3$ (iv) $HOCH_2CH(OH)CH_2OH$ (v)–(viii) the phenols drawn below (ix) CH_3–O–$CH_2CH(CH_3)CH_3$ (x) C_6H_5–O–C_2H_5 (xi) C_6H_5–O–C_7H_{15}(n) (xii) CH_3CH_2–O–$CH(CH_3)CH_2CH_3$**



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 **Draw: (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 and name all alcohols with formula $C_5H_{12}O$. (ii) Classify each as 1°, 2° or 3°.** $C_5H_{12}O$ के सभी ऐल्कोहॉल।

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 **Why does propanol boil at a higher temperature than butane?** प्रोपेनॉल का क्वथनांक ब्यूटेन से अधिक क्यों?

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 **Why are alcohols more soluble in water than hydrocarbons of similar molar mass?** ऐल्कोहॉल अधिक विलेय क्यों?

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 **Explain hydroboration–oxidation with an example.** हाइड्रोबोरेशन–ऑक्सीकरण उदाहरण सहित।

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 **Draw and name all monohydric phenols of formula C_7H_8O.**

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

7.8 **In steam distillation of a mixture of o- and p-nitrophenol, which isomer distils over, and why?** कौन-सा समावयवी भाप-वाष्पशील है और क्यों?

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 **Write the equations for making 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 the equation for making 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 **Show the mechanism of acid-catalysed hydration of ethene to ethanol.** *क्रियाविधि लिखिए।*

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 **Using only benzene, conc. H_2SO_4 and NaOH, write the steps to make phenol.**

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 to make: (i) 1-phenylethanol from an alkene (ii) cyclohexylmethanol from an alkyl halide by S_N2 (iii) pentan-1-ol from an 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 **Write two reactions showing that phenol is acidic. How does its acidity compare with ethanol?** फ़ीनॉल की अम्लता — दो अभिक्रियाएँ, एथेनॉल से तुलना।

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 **Why is o-nitrophenol a stronger acid than o-methoxyphenol?** कारण बताइए।

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 **How does an –OH group on a benzene ring activate the ring for electrophilic substitution?** –OH वलय को कैसे सक्रिय करता है?

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 **Write equations for: (i) oxidation of propan-1-ol by alkaline $KMnO_4$ (ii) phenol + Br_2 in CS_2 (iii) phenol + dilute HNO_3 (iv) phenol + chloroform in 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) $C_6H_5OH + Br_2 \xrightarrow{CS_2,\ 273\ K}$ p-BrC_6H_4OH (major) + o-BrC_6H_4OH (minor) + HBr

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

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

7.18 **Explain with an example: (i) Kolbe's reaction (ii) Reimer–Tiemann reaction (iii) Williamson ether synthesis (iv) an unsymmetrical ether**
उदाहरण सहित समझाइए।

Ans. / उत्तर: (i) **Kolbe's reaction:** sodium phenoxide reacts with CO_2 (a weak electrophile) to give salicylic acid after acidification. $C_6H_5ONa + CO_2 \xrightarrow{400\ K,\ 4\text{–}7\ atm;\ H^+}$ o-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 **Show the mechanism by which ethanol is dehydrated by acid to 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 would you convert: (i) propene → propan-2-ol (ii) benzyl chloride → benzyl alcohol (iii) ethylmagnesium chloride → propan-1-ol (iv) methylmagnesium 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 a reagent for each change: (i) 1° alcohol → carboxylic acid (ii) 1° alcohol → aldehyde (iii) phenol → 2,4,6-tribromophenol (iv) benzyl alcohol → benzoic acid (v) propan-2-ol → propene (vi) butan-2-one → butan-2-ol**

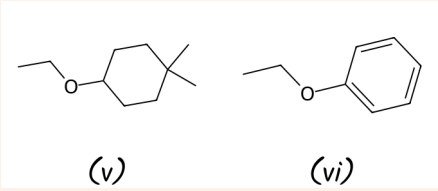
Ans. / उत्तर: (i) Acidified/alkaline $KMnO_4$ (or acidified $K_2Cr_2O_7$) (ii) PCC (pyridinium chlorochromate) or anhydrous CrO_3 (iii) Bromine water (iv) Acidified or alkaline $KMnO_4$ (v) 85% H_3PO_4 at 440 K (or conc. H_2SO_4) (vi) $NaBH_4$ or $LiAlH_4$ (or H_2/Ni)

7.22 **Why does ethanol boil at a much higher temperature than methoxymethane?** कारण बताइए।

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 these ethers: (i) $C_2H_5OCH_2CH(CH_3)CH_3$ (ii) $CH_3OCH_2CH_2Cl$ (iii) p-$O_2N-C_6H_4-OCH_3$ (iv) $CH_3CH_2CH_2OCH_3$ (v), (vi) as drawn**



(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 **By Williamson synthesis, give reagents and equations to make: (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 **Using examples, show where Williamson synthesis fails.** विलियम्सन संश्लेषण की सीमाएँ।

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 **Prepare 1-propoxypropane from propan-1-ol and show the mechanism.**

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

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 **Why is acid dehydration of 2° or 3° alcohols a poor way to make ethers?** *कारण बताइए।*

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 reaction of HI 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 **In alkyl aryl ethers, why does the –OR group (i) activate the ring and (ii) direct substituents to ortho/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 **Show the mechanism of the reaction between HI and 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 for anisole undergoing: (i) Friedel–Crafts alkylation (ii) nitration (iii) bromination in ethanoic acid (iv) Friedel–Crafts acetylation**

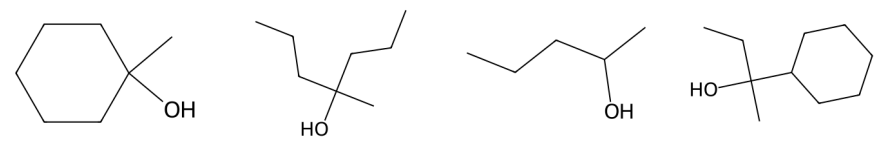
Ans. / उत्तर: (i) $C_6H_5OCH_3 + CH_3Cl \xrightarrow{\text{anhyd. } AlCl_3}$ 4-methylanisole (major) + 2-methylanisole (minor)

(ii) $C_6H_5OCH_3 \xrightarrow{\text{conc. } HNO_3 + H_2SO_4}$ 4-nitroanisole (major) + 2-nitroanisole (minor)

(iii) $C_6H_5OCH_3 + Br_2 \xrightarrow{CH_3COOH}$ p-bromoanisole (~90%, major) + o-bromoanisole (minor)

(iv) $C_6H_5OCH_3 + CH_3COCl \xrightarrow{\text{anhyd. } AlCl_3}$ 4-methoxyacetophenone (major) + 2-methoxyacetophenone (minor)

7.32 **From which alkene, and how, would you make each alcohol below?** उपयुक्त ऐल्कीन से कैसे बनाएँगे?



(i) (ii) (iii) (iv)

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 **3-Methylbutan-2-ol with HBr gives 2-bromo-2-methylbutane, $(CH_3)_2C(Br)CH_2CH_3$. Propose a mechanism. (Hint: a hydride shift turns the 2° carbocation into a 3° one.)**

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 — Solved Questions
(Examples + Intext + Exercises)

A. Solved Examples (हल किए गए उदाहरण)

Ex 8.1 **Name a reagent for each change: (i) hexan-1-ol → hexanal (ii) cyclohexanol → cyclohexanone (iii) p-fluorotoluene → p-fluorobenzaldehyde (iv) ethanenitrile → ethanal (v) allyl alcohol → propenal (vi) but-2-ene → ethanal** अभिकर्मक बताइए।

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 by increasing boiling point: $CH_3CH_2CH_2CHO$, $CH_3CH_2CH_2CH_2OH$, $C_2H_5–O–C_2H_5$, $CH_3CH_2CH_2CH_3$**

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 **Is benzaldehyde more or less reactive than propanal towards nucleophilic addition? Give a reason.** बेंज़ैल्डिहाइड अधिक या कम क्रियाशील?

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 **Compound A (C_8H_8O) gives an orange-red solid with 2,4-DNP and a yellow solid with I_2/NaOH. It does not reduce Tollens' or Fehling's reagent and does not decolourise bromine water or Baeyer's reagent. Strong oxidation with chromic acid gives acid B ($C_7H_6O_2$). Identify A and B.** A और B पहचानिए।

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 reactions for: (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 → hexanedioic acid (vi) butanal → butanoic acid**

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

(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 **Draw: (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) $CH_3CH_2CH(CH_3)–CO–CH(CH_3)CH_2CH_3$ (vi) $p\text{-}F–C_6H_4–COCH_3$

8.2 **Give the products: (i) benzene + C_2H_5COCl, anhydrous $AlCl_3/CS_2$ (ii) $(C_6H_5CH_2)_2Cd + 2CH_3COCl$ (iii) propyne ($CH_3C{\equiv}CH$) + Hg^{2+}/H_2SO_4 (iv) 4-nitrotoluene + 1. CrO_2Cl_2 2. H_3O^+** उत्पाद लिखिए।

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) $p\text{-}O_2N–C_6H_4–CHO$ — 4-nitrobenzaldehyde (Etard)

8.3 **Arrange by increasing boiling point: 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 by increasing reactivity towards nucleophilic addition: (i) ethanal, propanal, propanone, butanone (ii) benzaldehyde, p-tolualdehyde, p-nitrobenzaldehyde, acetophenone (think of steric and electronic effects)**

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 **Give the products: (i) cyclopentanone + NH_2OH (H^+) (ii) cyclohexanone + 2,4-dinitrophenylhydrazine (iii) R–CH=CH–CHO + semicarbazide (H^+) (iv) acetophenone + $CH_3CH_2NH_2$ (H^+)** उत्पाद बताइए।

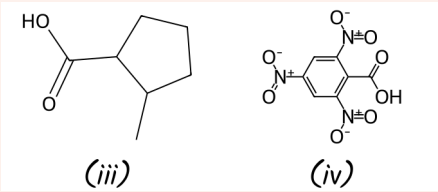
Ans. / उत्तर: (i) Cyclopentanone oxime ($C_5H_8{=}N{-}OH$)

(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 **IUPAC names: (i) $C_6H_5CH_2CH_2COOH$ (ii) $(CH_3)_2C{=}CHCOOH$ (iii), (iv) as drawn**



(iii) (iv)

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

8.7 **How can each be converted into benzoic acid? (i) ethylbenzene (ii) acetophenone (iii) bromobenzene (iv) 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 is the stronger acid in each pair? (i) CH_3COOH / CH_2FCOOH (ii) CH_2FCOOH / $CH_2ClCOOH$ (iii) $CH_2FCH_2CH_2COOH$ / CH_3CHFCH_2COOH (iv) 4-(trifluoromethyl)benzoic acid / 4-methylbenzoic acid** कौन अधिक प्रबल अम्ल?

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 **Explain each term with one reaction: (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** पदों को अभिक्रिया सहित समझाइए।

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 **IUPAC names: (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) p-OHC-C_6H_4-CHO**

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: (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-O_2N-C_6H_4-$COCH_2CH_3$ (iii) p-CH_3-C_6H_4-CHO (iv) $(CH_3)_2C=CH-CO-CH_3$ (v) $CH_3CH(Cl)CH_2COCH_3$ (vi) $CH_3CH(C_6H_5)CH(Br)CH_2COOH$ (vii) HO-C_6H_4-CO-C_6H_4-OH (both -OH para) (viii) $CH_3-C\equiv C-CH=CH-COOH$

8.4 **Give IUPAC (and common, if any) names: (i) $CH_3CO(CH_2)_4CH_3$ (ii) $CH_3CH_2CHBrCH_2CH(CH_3)CHO$ (iii) $CH_3(CH_2)_5CHO$ (iv) $C_6H_5-CH=CH-CHO$ (v) C_5H_9-CHO (-CHO on a cyclopentane ring) (vi) $C_6H_5COC_6H_5$**

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: (i) benzaldehyde 2,4-dinitrophenylhydrazone (ii) cyclopropanone oxime (iii) acetaldehyde dimethyl acetal (iv) cyclobutanone semicarbazone (v) the ethylene ketal of hexan-3-one (vi) the methyl hemiacetal of formaldehyde**

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

$(CH_2)_3C=N-NH-CO-NH_2$ (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 **What forms when cyclohexanecarbaldehyde reacts with: (i) C_6H_5MgBr, then H_3O^+ (ii) Tollens' reagent (iii) semicarbazide, weak acid (iv) excess ethanol, acid (v) Zn–Hg 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 **Sort into: aldol, Cannizzaro, or neither — and give the products: (i) methanal (ii) 2-methylpentanal (iii) benzaldehyde (iv) benzophenone (v) cyclohexanone (vi) 1-phenylpropanone (vii) phenylacetaldehyde (viii) butan-1-ol (ix) 2,2-dimethylbutanal** ऐल्डोल, कैनिज़ारो या कोई नहीं?

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) $2HCHO + \text{conc. } NaOH \rightarrow CH_3OH + HCOONa$

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

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

(v) 2 Cyclohexanone $\xrightarrow{\text{dil. NaOH}}$ 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) $2CH_3CH_2C(CH_3)_2CHO + \text{conc. } NaOH \rightarrow CH_3CH_2C(CH_3)_2CH_2OH + CH_3CH_2C(CH_3)_2COONa$

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

8.8 **Starting from ethanal, prepare (i) butane-1,3-diol (ii) but-2-enal (iii) but-2-enoic acid.**

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

(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 **A mixture of propanal and butanal can give four aldol products. Write their structures and names and state which aldehyde is the nucleophile and which the electrophile in each.**

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 **$C_9H_{10}O$ gives a 2,4-DNP derivative, reduces Tollens' reagent and shows the Cannizzaro reaction. Strong oxidation gives benzene-1,2-dicarboxylic acid. Identify it.** यौगिक पहचानिए।

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 **Ester A ($C_8H_{16}O_2$) is hydrolysed by dilute H_2SO_4 into acid B and alcohol C. Oxidising C with chromic acid gives B; dehydrating C gives but-1-ene. Write all 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**.

$CH_3CH_2CH_2COOCH_2CH_2CH_2CH_3 + H_2O \xrightarrow{\text{dil. } H_2SO_4} CH_3CH_2CH_2COOH + CH_3CH_2CH_2CH_2OH$

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

8.12 **Arrange in increasing order: (i) acetaldehyde, acetone, di-tert-butyl ketone, methyl tert-butyl ketone — reactivity with 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 **Suggest one simple test to tell apart: (i) propanal / propanone (ii) acetophenone / benzophenone (iii) phenol / benzoic acid (iv) benzoic acid / ethyl benzoate (v) pentan-2-one / pentan-3-one (vi) benzaldehyde / acetophenone (vii) ethanal / propanal** अंतर बताने का परीक्षण।

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 **Starting from benzene (any inorganic reagent; organic reagents with at most one carbon), prepare: (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 **In at most two steps, convert: (i) propanone → propene (ii) benzoic acid → benzaldehyde (iii) ethanol → 3-hydroxybutanal (iv) benzene → m-nitroacetophenone (v) benzaldehyde → benzophenone (vi) bromobenzene → 1-phenylethanol (vii) benzaldehyde → 3-phenylpropan-1-ol (viii) benzaldehyde → α-hydroxyphenylacetic acid (ix) benzoic acid → m-nitrobenzyl alcohol**

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

(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:** $C_2H_5OH \xrightarrow{PCC} CH_3CHO \xrightarrow{\text{dil. } NaOH} CH_3CH(OH)CH_2CHO$

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

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

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

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

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

8.16 **Write short notes on: (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). $C_2H_5OH + CH_3COCl \rightarrow CH_3COOC_2H_5 + HCl$; $C_6H_5NH_2 +$

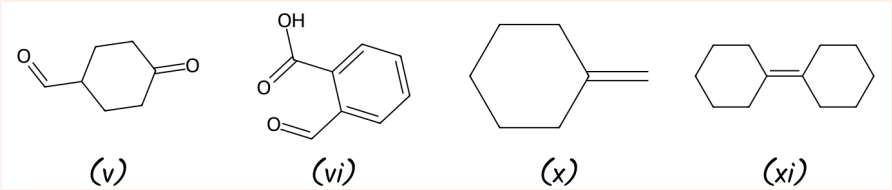
$(CH_3CO)_2O \rightarrow C_6H_5NHCOCH_3 + CH_3COOH$

(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. $CH_3CHO + CH_3CH_2CHO \xrightarrow{\text{dil. NaOH}}$ 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). $RCOONa + NaOH \xrightarrow{CaO,\ \Delta} R{-}H + Na_2CO_3$

8.17 **Fill in the missing reagent, starting material or product: (i) ethylbenzene + $KMnO_4/KOH$, heat → ? (ii) phthalic acid + $SOCl_2$, heat → ? (iii) $C_6H_5CHO + H_2NCONHNH_2$ → ? (iv) benzene + ? → benzophenone (v) 4-oxocyclohexanecarbaldehyde + Tollens' reagent → ? (vi) 2-formylbenzoic acid + NaCN/HCl → ? (vii) $C_6H_5CHO + CH_3CH_2CHO$, dil. NaOH, heat → ? (viii) $CH_3COCH_2COOC_2H_5$ + (i) $NaBH_4$ (ii) H^+ → ? (ix) cyclohexanol + CrO_3 → ? (x) methylenecyclohexane + ? → cyclohexanecarbaldehyde (xi) ? + (i) O_3 (ii) $Zn{-}H_2O$ → 2 cyclohexanone**



(v) (vi) (x) (xi)

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

(ii) $o\text{-}C_6H_4(COCl)_2$ — 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) $o\text{-}HOOC{-}C_6H_4{-}CH(OH)CN$ (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 **Explain: (i) cyclohexanone forms a cyanohydrin in good yield, but 2,2,6-trimethylcyclohexanone does not (ii) semicarbazide has two $-NH_2$ groups, but only one reacts to form a semicarbazone (iii) in acid-catalysed esterification, water or ester should be removed as it forms**
कारण बताइए।

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 **A compound has 69.77% C, 11.63% H and the rest O; molar mass 86. It does not reduce Tollens' reagent, forms a bisulphite addition compound, gives a positive iodoform test, and on strong oxidation gives ethanoic and propanoic acids. Suggest its 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 **Phenoxide has more resonance structures than carboxylate, yet carboxylic acids are stronger acids than phenol. Why?** कार्बोक्सिलिक अम्ल अधिक प्रबल क्यों?

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 — Solved Questions (Examples + Intext + Exercises)

A. Solved Examples (हल किए गए उदाहरण)

Ex 9.1 **Write equations for: (i) C_2H_5Cl with ethanolic NH_3 (ii) ammonolysis of benzyl chloride, followed by reaction of the amine 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 equations for: (i) $CH_3CH_2Cl \rightarrow CH_3CH_2CH_2NH_2$ (ii) $C_6H_5CH_2Cl \rightarrow C_6H_5CH_2CH_2NH_2$**

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 **Give the structure and IUPAC name of (i) the amide that gives propanamine by Hoffmann bromamide reaction (ii) the amine formed 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 basic strength: $C_6H_5NH_2$, $C_2H_5NH_2$, $(C_2H_5)_2NH$, NH_3** क्षारकता का घटता क्रम।

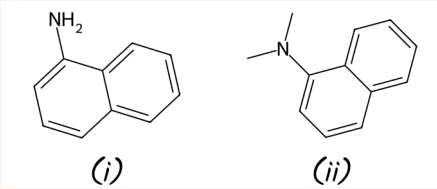
Ans. / उत्तर: $(C_2H_5)_2NH > C_2H_5NH_2 > NH_3 > C_6H_5NH_2$
ऐल्किल समूह (+I) क्षारकता बढ़ाते हैं; ऐनिलीन में एकाकी युग्म वलय से अनुनाद में — दुर्बल क्षारक।

Ex 9.5 **Convert 4-nitrotoluene into 2-bromobenzoic acid.** रूपांतरण कीजिए।

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 as 1°, 2° or 3°: (i), (ii) as drawn (iii) $(C_2H_5)_2CHNH_2$ (iv) $(C_2H_5)_2NH$** वर्गीकृत कीजिए।



(i) (ii)

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) Draw all isomeric amines of formula $C_4H_{11}N$. (ii) Name each by IUPAC. (iii) Which types of isomerism do they show?**

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 would you convert (i) benzene → aniline (ii) benzene → N,N-dimethylaniline (iii) Cl–$(CH_2)_4$–Cl → 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 by increasing 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 and name the products: (i) $CH_3CH_2CH_2NH_2 + HCl$ (ii) $(C_2H_5)_3N + HCl$**

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

9.6 **Aniline is treated with excess CH_3I in sodium carbonate solution. Write the reactions up to the final product.**

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

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

9.8 **Draw the isomers of C_3H_9N. Which of them give off N_2 with nitrous acid? Name them.**

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 → 3-nitrotoluene (ii) aniline → 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 **Give IUPAC names and classify as 1°, 2° or 3°: (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 **Suggest one chemical test to tell apart: (i) methylamine / dimethylamine (ii) a 2° / a 3° amine (iii) ethylamine / aniline (iv) aniline / benzylamine (v) aniline / N-methylaniline** अंतर बताने का परीक्षण।

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 **Explain why: (i) aniline has a higher pK_b than methylamine (ii) ethylamine dissolves in water but aniline does not (iii) aqueous methylamine precipitates hydrated ferric oxide from $FeCl_3$ (iv) nitration of aniline gives a lot of m-nitroaniline although $-NH_2$ is o/p-directing (v) aniline does not undergo Friedel–Crafts reaction (vi) aromatic diazonium salts are more stable than aliphatic ones (vii) Gabriel synthesis is preferred for making 1° amines** *कारण बताइए।*

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: (i) by decreasing pK_b: $C_2H_5NH_2$, $C_6H_5NHCH_3$, $(C_2H_5)_2NH$, $C_6H_5NH_2$ (ii) by increasing basicity: $C_6H_5NH_2$, $C_6H_5N(CH_3)_2$, $(C_2H_5)_2NH$, CH_3NH_2 (iii) by increasing basicity: (a) aniline, p-nitroaniline, p-toluidine (b) $C_6H_5NH_2$, $C_6H_5NHCH_3$, $C_6H_5CH_2NH_2$ (iv) by decreasing gas-phase basicity: $C_2H_5NH_2$, $(C_2H_5)_2NH$, $(C_2H_5)_3N$, NH_3 (v) by increasing boiling point: C_2H_5OH, $(CH_3)_2NH$, $C_2H_5NH_2$ (vi) by increasing water solubility: $C_6H_5NH_2$, $(C_2H_5)_2NH$, $C_2H_5NH_2$**

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 **Convert: (i) ethanoic acid → methanamine (ii) hexanenitrile → 1-aminopentane (iii) methanol → ethanoic acid (iv) ethanamine → methanamine (v) ethanoic acid → propanoic acid (vi) methanamine → ethanamine (vii) nitromethane → dimethylamine (viii) propanoic acid → ethanoic acid**

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, with equations, to identify 1°, 2° and 3° amines.**
1°, 2°, 3° ऐमीन की पहचान की विधि।

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 **Short notes: (i) carbylamine reaction (ii) diazotisation (iii) Hofmann 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). $C_6H_5N_2^+Cl^- + C_6H_5OH \xrightarrow{-OH^-} p\text{-}HOC_6H_4\text{-}N{=}N\text{-}C_6H_5$ (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 **Carry out: (i) nitrobenzene → benzoic acid (ii) benzene → m-bromophenol (iii) benzoic acid → aniline (iv) aniline → 2,4,6-tribromofluorobenzene (v) benzyl chloride → 2-phenylethanamine (vi) chlorobenzene → p-chloroaniline (vii) aniline → p-bromoaniline (viii) benzamide → toluene (ix) aniline → benzyl alcohol**

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 **Identify A, B and C: (i) $CH_3CH_2I \xrightarrow{-NaCN} A \xrightarrow{-OH^-,\ partial\ hydrolysis} B \xrightarrow{-NaOH + Br_2} C$ (ii) $C_6H_5N_2Cl \xrightarrow{-CuCN} A \xrightarrow{-H_2O/H^+} B \xrightarrow{-NH_3,\ \Delta} C$ (iii) $CH_3CH_2Br \xrightarrow{-KCN} A \xrightarrow{-LiAlH_4} B \xrightarrow{-HNO_2,\ 0\ °C} C$ (iv) $C_6H_5NO_2 \xrightarrow{-Fe/HCl} A \xrightarrow{-NaNO_2+HCl,\ 273\ K} B \xrightarrow{-H_2O/H^+,\ \Delta} C$ (v) $CH_3COOH \xrightarrow{-NH_3,\ \Delta} A \xrightarrow{-NaOBr} B \xrightarrow{-NaNO_2/HCl} C$ (vi) $C_6H_5NO_2 \xrightarrow{-Fe/HCl} A \xrightarrow{-HNO_2,\ 273\ K} B \xrightarrow{-C_6H_5OH} C$**

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)	$C_6H_5NH_2$	$C_6H_5N_2^+Cl^-$	$p\text{-}HOC_6H_4\text{-}N{=}N\text{-}C_6H_5$ (p-hydroxyazobenzene)

9.10 **Aromatic compound A, heated with aqueous ammonia, gives B; B with Br_2 and KOH gives C, C_6H_7N. Give 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: (i) $C_6H_5NH_2 + CHCl_3$ + alc. KOH (ii) $C_6H_5N_2Cl + H_3PO_2 + H_2O$ (iii) $C_6H_5NH_2$ + conc. H_2SO_4 (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) $C_6H_5N_2Cl$ + (i) HBF_4 (ii) $NaNO_2/Cu$, Δ**

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) $\xrightarrow{453\text{–}473\ K}$ 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 can't Gabriel phthalimide synthesis make aromatic 1° amines?** *कारण बताइए।*

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 nitrous acid with (i) aromatic 1° amines (ii) aliphatic 1° amines.**

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 **Explain: (i) amines are weaker acids than alcohols of similar mass (ii) 1° amines boil higher than 3° amines (iii) aliphatic amines are stronger bases than aromatic amines** कारण बताइए।

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 — Solved Questions (Intext + Exercises; this unit has no worked examples)

A. Intext Questions (पाठ्यनिहित प्रश्न)

10.1 **Why do glucose and sucrose dissolve in water while cyclohexane and benzene, also six-membered rings, do not?** ग्लूकोस विलेय, 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 does lactose give on hydrolysis?** लैक्टोस के जल-अपघटन उत्पाद?

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

10.3 **Why does D-glucose pentaacetate show no free aldehyde group?** पेंटाऐसीटेट में –CHO क्यों नहीं?

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 **Why do amino acids have higher melting points and water solubility than the corresponding halo acids?**

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 **After an egg is boiled, where does its water go?** उबले अंडे का पानी कहाँ जाता है?

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 is vitamin C not stored in the body?** विटामिन C संग्रहित क्यों नहीं होता?

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 **A DNA nucleotide containing thymine is hydrolysed. What are the products?**

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

10.8 **RNA hydrolysis shows no fixed ratio between its bases. What does this tell us about RNA's structure?**

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 **Define monosaccharides.** एकलशर्करा क्या हैं?

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 is meant by reducing sugars?** अपचायी शर्करा क्या हैं?

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 **State two main roles 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 **Sort into monosaccharides and disaccharides: ribose, 2-deoxyribose, maltose, galactose, fructose, lactose.**

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

10.5 **What is a glycosidic linkage?** ग्लाइकोसिडिक बंध क्या है?

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, and how does it differ 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 **Give the hydrolysis products of (i) sucrose (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 key 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 reacts with (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 **List the facts about D-glucose that the open-chain structure cannot explain.** खुली श्रृंखला संरचना किन तथ्यों को नहीं समझा पाती?

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 **Distinguish essential from non-essential amino acids, with two examples of each.**

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, for 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 **Name the common secondary structures of proteins.**

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

10.14 **Which bonding holds the α-helix of a protein in shape?**

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 **Distinguish between globular and fibrous proteins.** गोलिकाकार व रेशेदार प्रोटीन में अंतर।

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 Why are amino acids amphoteric? *ऐमीनो अम्ल उभयधर्मी क्यों?*

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? *एंज़ाइम क्या हैं?*

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 How does denaturation affect protein structure?

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? Which vitamin is needed for blood clotting?

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 do we need vitamins A and C? Give their main 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? State 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 How does a nucleoside differ from 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 DNA strands are complementary, not identical. Explain.
DNA के रज्जुक पूरक क्यों हैं?

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 Give the main 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 Name the types of RNA found in cells.

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

All the best! शुभकामनाएँ!