Collegedunia NCERT Solutions

Step-by-step solutions, alternate methods & exam tips for Class 12 Chemistry

Chapter 8: Aldehydes, Ketones and Carboxylic Acids

About this Chapter

This chapter studies the chemistry of the **carbonyl group** ($C{=}O$): **aldehydes** ($RCHO$), **ketones** ($R_2C{=}O$) and **carboxylic acids** ($RCOOH$). We learn IUPAC nomenclature, the bonding and polarity of the carbonyl, preparation methods (oxidation, ozonolysis, Rosenmund, Stephen, Etard, Gattermann-Koch, Friedel-Crafts), and the central reactions: nucleophilic addition (with HCN, $NaHSO_3$, alcohols, amines), oxidation (Tollens', Fehling), reduction (Clemmensen, Wolff-Kishner), **aldol condensation** and the **Cannizzaro reaction**. For acids we study acidity trends (pK_a), the carboxylate resonance and the HVZ reaction.

Topics covered: Carbonyl structure • IUPAC naming • Preparations • Nucleophilic addition • Tollens'/Fehling • Aldol • Cannizzaro • Clemmensen/Wolff-Kishner • pK_a trends

Quick Formula Sheet

Carbonyl polarity:
$C^{\delta+}{=}O^{\delta-}$; nucleophile attacks C

Cyanohydrin:
$R_2C{=}O + HCN - R_2C(OH)CN$

Tollens' test:
$RCHO + 2\,[Ag(NH_3)_2]^+ + 3\,OH^- - RCOO^- + 2\,Ag\,(v) + 4\,NH_3 + 2\,H_2O$

Aldol (base, OH⁻):
$2\,CH_3CHO \longrightarrow CH_3CH(OH)CH_2CHO$

Cannizzaro:
$2\,HCHO - [conc \cdot OH^-]\,CH_3OH + HCOO^-$

Carboxylate resonance lowers pK_a;
$-I$ groups raise acidity, $+M/^{+}I$ groups lower it.

Chapter 8 Exercises

Q 8.1 **What is meant by the following terms? Give an example of the reaction in each case.**

(i) Cyanohydrin (ii) Acetal (iii) Semicarbazone

(iv) Aldol (v) Hemiacetal (vi) Oxime
(vii) Ketal (viii) Imine (ix) 2,4-DNP-derivative (x) Schiff's base

SOLUTION

Concept used. Each name in this question labels a specific addition or condensation product of a carbonyl ($C{=}O$) with a nucleophile. The carbonyl carbon carries a partial positive charge, $C^{\delta+}{=}O^{\delta-}$, so a nucleophile Nu^- attacks the carbon while O becomes O^-; protonation of the oxygen then gives the neutral adduct. We name each product, write its general structure, and give one balanced example.

> **☞ How to read the names**
>
> The suffix tells you the nucleophile: *-cyanohydrin* (from HCN), *-hemiacetal/-acetal* (from ROH), *-imine/-oxime/-semicarbazone* (from $R{-}NH_2$ derivatives), *-DNP derivative* (from 2,4-dinitrophenylhydrazine).

Step 1. **Cyanohydrin**: an α-hydroxynitrile formed when HCN adds across the carbonyl. General structure $R_2C(OH)CN$. Example with acetone:

$$(CH_3)_2C{=}O + HCN -[KCN/HCl]\,(CH_3)_2C(OH)CN.$$

Useful because the nitrile $-CN$ can be hydrolysed later to a α-hydroxy acid.

Step 2. **Acetal**: a *gem*-dialkoxy compound, $R{-}CH(OR)_2$, formed when an aldehyde reacts with two equivalents of an alcohol in the presence of dry HCl. The intermediate is a hemiacetal. Example with ethanal:

$$CH_3CHO + 2\,C_2H_5OH -[\text{dry HCl}]\,CH_3CH(OC_2H_5)_2 + H_2O.$$

Step 3. **Semicarbazone**: the condensation product of a carbonyl with semicarbazide ($H_2N{-}NH{-}CO{-}NH_2$). General structure $R_2C{=}N{-}NH{-}CO{-}NH_2$. Example:

$$CH_3COCH_3 + H_2N{-}NH{-}CO{-}NH_2 - (CH_3)_2C{=}N{-}NH{-}CO{-}NH_2 + H_2O.$$

A useful crystalline derivative used to characterise ketones.

Step 4. **Aldol**: a β-hydroxy aldehyde (or ketone) formed when two carbonyl molecules with an α-hydrogen combine under dilute base. General structure $R{-}CH(OH){-}CH(R){-}CHO$. Example with ethanal:

$$2\,CH_3CHO -[\text{dil}\cdot NaOH]\,CH_3CH(OH)CH_2CHO\ (\text{3-hydroxybutanal}).$$

Step 5. **Hemiacetal**: an α-alkoxy alcohol, $R{-}CH(OH)(OR)$, formed by addition of *one* mole of alcohol to an aldehyde. It is the intermediate on the way to an acetal. Example:

$$CH_3CHO + C_2H_5OH \xrightleftharpoons{\text{dry HCl}} CH_3CH(OH)(OC_2H_5).$$

Step 6. **Oxime**: condensation product with hydroxylamine NH_2OH. Structure $R_2C{=}N{-}OH$. Example:

$$CH_3COCH_3 + NH_2OH - (CH_3)_2C{=}N{-}OH + H_2O.$$

Step 7. **Ketal**: a *gem*-dialkoxy compound derived from a *ketone*, $R_2C(OR)_2$. Example with propanone and ethylene glycol:

$$(CH_3)_2C{=}O + HOCH_2CH_2OH - [\text{dry HCl}]\ (CH_3)_2C(OCH_2CH_2O) + H_2O.$$

Step 8. **Imine** (Schiff's base when R = aryl): product with a primary amine RNH_2, structure $R_2C{=}N{-}R$. Example:

$$CH_3CHO + C_2H_5NH_2 - CH_3CH{=}N{-}C_2H_5 + H_2O.$$

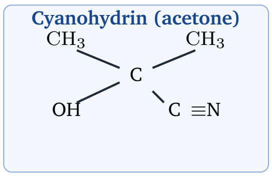
Step 9. **2,4-DNP-derivative**: 2,4-dinitrophenylhydrazone, the orange/yellow crystalline product with 2,4-dinitrophenylhydrazine $(2{,}4{-}(NO_2)_2C_6H_3{-}NH{-}NH_2)$. Example with ethanal:

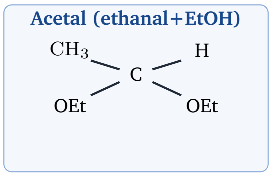
$$CH_3CHO + H_2N{-}NH{-}C_6H_3(NO_2)_2 - CH_3CH{=}N{-}NH{-}C_6H_3(NO_2)_2 + H_2O.$$

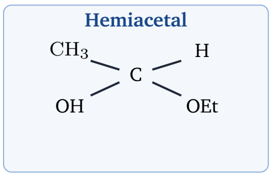
Step 10. **Schiff's base**: the imine formed when an aldehyde or ketone reacts specifically with an *aromatic* primary amine such as aniline. Structure $R_2C{=}N{-}Ar$. Example:

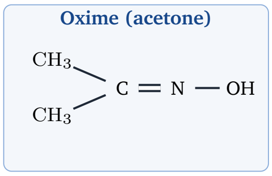
$$C_6H_5CHO + C_6H_5NH_2 - C_6H_5CH{=}N{-}C_6H_5 + H_2O.$$

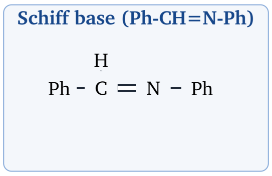
Visual structures of the key derivatives:

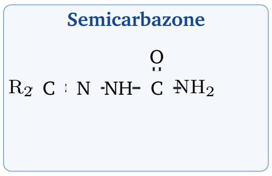

Cyanohydrin (acetone)


Acetal (ethanal+EtOH)


Hemiacetal


Oxime (acetone)


Schiff base (Ph-CH=N-Ph)


Semicarbazone

> **Final Answer:** Each derivative is a nucleophilic addition (or addition–elimination) product of $C{=}O$, with the nucleophile and the product tabulated above.

★ Why these derivatives matter

Crystalline derivatives (oximes, semicarbazones, 2,4-DNPs) have sharp melting points and are used to identify carbonyl compounds. Acetals and ketals are stable to base but cleave in dilute acid: they serve as protecting groups for $C{=}O$ during multi-step synthesis.

✗ Hemiacetal is unstable, acetal is stable

The hemiacetal $R{-}CH(OH)(OR)$ has both $-OH$ and an alkoxy group on the same carbon and usually exists in equilibrium with the parent aldehyde (cyclic sugars like glucose are an exception). Drive off the water with more ROH in dry HCl and you get the stable acetal $R{-}CH(OR)_2$. Students often write the hemiacetal as the final product; the equilibrium lies on the carbonyl side unless water is removed.

☞ Spot the nucleophile from the suffix

The CBSE pattern is simple: *-cyanohydrin* ↔ HCN; *-(hemi)acetal/-ketal* ↔ ROH; *-imine/-Schiff base* ↔ RNH_2; *-oxime* ↔ NH_2OH; *-hydrazone/-DNP* ↔ $H_2N{-}NHR$; *-semicarbazone* ↔ $H_2N{-}NHCONH_2$. Memorise the nucleophile, not the product structure, and you can re-derive every adduct in seconds.

EXPERT'S SOLUTION *: Pranav Sharma, M.Sc Chemistry, IIT Kanpur*

Picture-first. Every derivative in this list is a nucleophile adding to the same electrophile, the carbonyl carbon. The carbon is $C^{\delta+}$; nucleophile forms the new C–Nu bond; oxygen becomes $-OH$; if the nucleophile carries an NH next to the new bond, that NH kicks the OH out as water and we get a $C{=}N$.

Grouping by mechanism:

- Simple addition (stop at the tetrahedral adduct): cyanohydrin (HCN), hemiacetal (ROH, one equiv).
- Addition then substitution by a second nucleophile: acetal, ketal (two equivs of ROH with dry HCl).
- Addition–elimination ($C{=}O \rightarrow C{=}N$): imine, oxime, semicarbazone, 2,4-DNP, Schiff base (all nitrogen nucleophiles with an $N{-}H$).

Alternative approach (the electrophilicity–steric–resonance trio). Three independent factors decide how easily each nucleophile can land on the carbonyl carbon: (a) how positive that carbon already is (electrophilicity), (b) how crowded its two faces are (steric), and (c) whether the carbonyl is part of a π system that gives away positive charge to a neighbour (resonance). For HCHO all three are favourable, so it forms every adduct in this list at room temperature. For a hindered or resonance-stabilised carbonyl (e.g. amide $R{-}CO{-}NH_2$, ester $R{-}CO{-}OR$), the same nucleophiles struggle. Reading any new substrate through this trio is faster than memorising case-by-case.

Concept linkage: α-H acidity, tautomerism and oxidation/reduction. Each adduct here keeps the original carbonyl carbon's oxidation state intact (it is still C^{+1} in an aldehyde-derived adduct). That is the bridge to Q 8.7 (aldol, which needs α-H acidity), to Q 8.20 (oxidation of $-CHO$ to $-COOH$) and to Q 8.15 (Clemmensen / Wolff–Kishner, which take the carbon two oxidation states down). Recognising "addition only" vs "oxidation" vs "reduction" is the first sort you do on any carbonyl reagent.

☞ Why $2{,}4-(NO_2)_2-C_6H_3-NHNH_2$ instead of plain H_2N-NH_2?

Plain hydrazine gives a hydrazone, but the product is often a high-boiling liquid hard to isolate. The two $-NO_2$ groups deactivate the aniline-style NH_2 towards over-reaction and make the hydrazone a bright orange/yellow crystalline solid with a sharp melting point. That is why 2,4-DNP is the reagent of choice for carbonyl characterisation.

Step 1. Cyanohydrin: $(CH_3)_2C{=}O + HCN - (CH_3)_2C(OH)CN$. An industrial precursor to methyl methacrylate (Plexiglas monomer).

Step 2. Acetal vs hemiacetal: $CH_3CHO + C_2H_5OH \rightleftharpoons CH_3CH(OH)(OC_2H_5)$ (hemiacetal), then $+ C_2H_5OH, -H_2O \rightarrow CH_3CH(OC_2H_5)_2$ (acetal).

Step 3. Semicarbazone, oxime and 2,4-DNP follow the same addition–elimination: $R_2C{=}O + H_2N{-}X - R_2C{=}N{-}X + H_2O$ with $X = NHCONH_2, OH, NH{-}C_6H_3(NO_2)_2$ respectively.

Step 4. Aldol: the α-carbanion of one CH_3CHO attacks the carbonyl carbon of a second CH_3CHO to give $CH_3CH(OH)CH_2CHO$. This is the only entry on the list that builds a new $C{-}C$ bond.

Step 5. Imine / Schiff: same addition–elimination but with a primary amine. When the amine is aromatic ($C_6H_5NH_2$, aniline) the imine is called a Schiff's base.

Exam relevance. The CBSE 2024 and 2023 board papers both asked one-mark identifications of cyanohydrin and 2,4-DNP products, and a three-mark question on the differentiation of oxime vs Schiff base. Knowing the nucleophile-suffix pairing (see exam tip above) gives you the answer in under a minute.

Memory hook. *One-shot* addition for HCN / single ROH. *Two-shot* substitution for full acetal/ketal. *Eliminate water* whenever the nucleophile is an amine derivative. Aldol is the odd one out: a carbon nucleophile, so the new bond is $C{-}C$.

Final Answer: Definitions plus one balanced equation per term, as in the main solution.

Q 8.2 **Name the following compounds according to the IUPAC system of nomenclature:**

(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-$OHC-C_6H_4-CHO$

SOLUTION

Concept used. The IUPAC name of a carbonyl is built in four steps:

1. identify the principal characteristic group ($-COOH$ $-CHO$ $C{=}O$; it gets the lowest locant and the suffix);
2. find the longest continuous carbon chain that contains it;
3. number from the end nearer the principal group so that this group, then unsaturation, then substituents, all get the lowest locants;
4. list substituents alphabetically with their locants in front of the parent name.

For aldehydes the suffix is -*al* and the CHO carbon is always C-1. For ketones the suffix is -*one* and the $C{=}O$ carbon gets the lowest locant. For carboxylic acids the suffix is -*oic acid* and the $COOH$ carbon is C-1.

> ☞ **Locant rule**
>
> First lowest set goes to the principal group's suffix carbon, then to unsaturation, then to substituents in alphabetic order. Ties are broken at the first point of difference.

Step 1. (i) $CH_3CH(CH_3)CH_2CH_2CHO$. Longest chain ending at CHO: five carbons (pentanal). Numbering from CHO: $C_1(CHO)-C_2(H_2)-C_3(H_2)-C_4(H)(CH_3)-C_5(H_3)$. A methyl sits at C-4. **Name:** **4-Methylpentanal**.

Step 2. (ii) $CH_3CH_2COCH(C_2H_5)CH_2CH_2Cl$. Principal group is the ketone $C{=}O$. Longest chain through it: take the $-C_2H_5$ side to extend the chain. Numbering to give the carbonyl the lowest locant gives $C_1(H_3)-C_2(H_2)-C_3({=}O)-C_4(H)-C_5(H_2)-C_6(H_2Cl)$, with an ethyl branch at C-4. **Name:** **6-Chloro-4-ethylhexan-3-one**.

Step 3. (iii) $CH_3CH{=}CHCHO$. Four carbons, CHO is C-1, double bond C-2 to C-3, more stable as *trans* (*E*). **Name:** **But-2-enal** (commonly *E*-but-2-enal, crotonaldehyde).

Step 4. (iv) $CH_3COCH_2COCH_3$. Two ketones in a five-carbon chain at C-2 and C-4. **Name:** **Pentane-2,4-dione**.

Step 5. (v) $CH_3CH(CH_3)CH_2C(CH_3)_2COCH_3$. Carbonyl at C-2; carbon skeleton: methyl, C(=O), C(CH3)2, CH2, CH(CH3), CH3. Substituents: two methyls at C-3, one at C-5; parent hexan-2-one. **Name:** **3,3,5-Trimethylhexan-2-one**.

Step 6. (vi) $(CH_3)_3CCH_2COOH$. Parent butanoic acid (four carbons in the principal chain). Two methyls at C-3. **Name:** **3,3-Dimethylbutanoic acid**.

Step 7. (vii) p-$OHC-C_6H_4-CHO$. Both $-CHO$ groups are substituents on benzene; we use the multiplying prefix *di* and the suffix -*dicarbaldehyde*. **Name:** **Benzene-1,4-dicarbaldehyde** (terephthalaldehyde).

> **Final Answer:** (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.

☞ Quick locant check

After numbering, add up the locants of the principal group and the substituents. Swap direction; if the new sum is smaller, you had the direction wrong. With ties, alphabetical priority decides.

EXPERT'S SOLUTION *: Aanya Iyer, Ph.D Organic Chemistry, IISc Bangalore*

Strategic angle. Skim each structure for the highest-priority suffix-bearing group ($-\mathrm{COOH}$ beats $-\mathrm{CHO}$ beats $\mathrm{C{=}O}$). Anchor it at the lowest locant, then read the chain out as a substituent list plus suffix.
Alternative approach (priority table). When several functional groups appear in the same molecule, the IUPAC seniority order is
$-\mathrm{COOH} > -\mathrm{COOR} > -\mathrm{CONH_2} > -\mathrm{CN} > -\mathrm{CHO} > \mathrm{C{=}O} > -\mathrm{OH} > -\mathrm{NH_2}$. Only the highest-ranked group earns the suffix; every other group falls back to a prefix (*oxo*- for a ketone $\mathrm{C{=}O}$, *formyl*- for an aldehyde $-\mathrm{CHO}$, *cyano*- for $-\mathrm{CN}$, etc.). The first scan of any new compound should be this priority sort.
Concept linkage. Each name fixes the connectivity, which in turn fixes the reactivity. Pentane-2,4-dione (iv) has two α-Hs between the carbonyls (the methylene), so its pK_a is unusually low (~ 9) — that links straight into the enol–enolate chemistry of Q 8.7. The 3,3,5-trimethylhexan-2-one (v) has *no* α-H on the C-3 side (quaternary carbon), so the aldol enolate forms only on the methyl side; this matters in later questions.

Step 1. (i) Pentanal with a methyl on C-4: **4-Methylpentanal**. Locants 1 (CHO) and 4 ($\mathrm{CH_3}$) sum to 5; numbering the other way gives 1 (CHO) and 2 ($\mathrm{CH_3}$) sum 3, but that puts CHO at the wrong end of the chain — recall CHO is always at C-1 so the only legal numbering is from CHO.

Step 2. (ii) Six-carbon ketone, Cl at C-6, $\mathrm{C_2H_5}$ branch on C-4: **6-Chloro-4-ethylhexan-3-one**. The ketone wins the lowest locant (3); alphabetical order "chloro" before "ethyl" is read.

Step 3. (iii) Four-carbon α, β-unsaturated aldehyde: **(E)-But-2-enal**. *trans* configuration is more stable due to lower steric strain.

Step 4. (iv) Symmetrical 1,3-diketone: **Pentane-2,4-dione** (acetylacetone). The methylene between two C=O groups is unusually acidic ($pK_a \approx 9$).

Step 5. (v) Six-carbon ketone with gem-dimethyl at C-3 and methyl at C-5: **3,3,5-Trimethylhexan-2-one**. Locants $\{2, 3, 3, 5\}$ beat any alternative numbering.

Step 6. (vi) Branched neopentyl acid: **3,3-Dimethylbutanoic acid**. Four-carbon parent because $-\mathrm{COOH}$ must be C-1.

Step 7. (vii) Two aldehydes para on benzene: **Benzene-1,4-dicarbaldehyde**. Both CHO groups keep the carbon, so they appear as “carbaldehyde”, not “-al”.

Exam relevance. CBSE awards full marks only for IUPAC names with the correct locant set, hyphenation and capitalisation. A common 1-mark trap is asking the name of $CH_3COCH_2COCH_3$ — many write “2,4-pentanedione” but the locants 2,4 must precede a hyphen on the parent (*pentane-2,4-dione*, not *2,4-pentanedione*).
Why this matters. Naming locks in the structure; once you write the name correctly, you know how each reagent will hit the molecule (which α-H is there, where steric crowding is, where the polar group sits).

Final Answer: Same set of seven IUPAC names as above.

Q 8.3 **Draw the structures of the following compounds.**
(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

SOLUTION

Concept used. To draw a structure from a name, reverse the naming algorithm: (1) draw the parent chain with the principal group at C-1 (or its lowest locant), (2) place substituents at their indicated locants, and (3) add stereochemistry / unsaturation as the locants specify.

Step 1. (i) **3-Methylbutanal**: butanal is $CH_3CH_2CH_2CHO$ with CHO as C-1. A methyl on C-3 gives

$$(CH_3)_2CH-CH_2-CHO.$$

Step 2. (ii) **p-Nitropropiophenone**: propiophenone is $C_6H_5-CO-C_2H_5$ (phenyl ethyl ketone). Putting $-NO_2$ *para* on the ring gives

$$O_2N-C_6H_4-CO-CH_2CH_3 \quad (\textit{para-}).$$

Step 3. (iii) **p-Methylbenzaldehyde**: a $-\mathrm{CHO}$ on benzene and a $-\mathrm{CH_3}$ *para*:

$$\mathrm{CH_3{-}C_6H_4{-}CHO} \quad (\textit{para-}, p\text{-tolualdehyde}).$$

Step 4. (iv) **4-Methylpent-3-en-2-one**: parent pentan-2-one is $\mathrm{CH_3{-}CO{-}CH_2{-}CH_2{-}CH_3}$. A double bond between C-3 and C-4, and a methyl on C-4, gives

$$\mathrm{CH_3{-}CO{-}CH{=}C(CH_3){-}CH_3} \equiv \mathrm{(CH_3)_2C{=}CH{-}COCH_3} \quad (\text{mesityl oxide}).$$

Step 5. (v) **4-Chloropentan-2-one**: pentan-2-one with Cl on C-4:

$$\mathrm{CH_3{-}CO{-}CH_2{-}CHCl{-}CH_3}.$$

Step 6. (vi) **3-Bromo-4-phenylpentanoic acid**: pentanoic acid with Br at C-3 and a phenyl at C-4:

$$\mathrm{CH_3{-}CH(C_6H_5){-}CH(Br){-}CH_2{-}COOH}.$$

Step 7. (vii) **p,p'-Dihydroxybenzophenone**: benzophenone is $\mathrm{C_6H_5{-}CO{-}C_6H_5}$. Hydroxyls *para* on each ring:

$$\mathrm{HO{-}C_6H_4{-}CO{-}C_6H_4{-}OH} \quad (\textit{both para}).$$

Step 8. (viii) **Hex-2-en-4-ynoic acid**: six-carbon acid with a double bond C2=C3 and a triple bond C4≡C5:

$$\mathrm{CH_3{-}C{\equiv}C{-}CH{=}CH{-}COOH}.$$

Final Answer: Structures (i)–(viii) as written above.

✗ Position of the principal group

In a ring system the CHO, $\mathrm{C{=}O}$ or COOH that sits *on* the ring is always implied at C-1 of the substituent-bearing ring (e.g. benzaldehyde, benzoic acid). The “para” locant in (ii), (iii), (vii) refers to position 4 relative to that C-1.

EXPERT'S SOLUTION : *Rohit Kapoor, M.Tech Chemical Engineering, IIT Delhi*

Strategic angle. Build each skeleton as parent + decorations. Pick the parent (butanal, pentan-2-one, pentanoic acid, benzaldehyde, benzophenone) and pin the principal group at C-1 or lowest locant. Then drop on substituents.

Alternative approach (skeleton-first). For any name, first sketch the bare carbon chain or ring (the parent), then add the principal group at the locant given, and only after that hang on the substituents. This forces you to keep the carbon count correct. Try it on (viii): hex = 6 carbons + COOH at C-1 + double bond 2–3 + triple bond 4–5, and you get the structure in three pen strokes.

> ☞ **Reading *para*, *ortho*, *meta* on benzene**
>
> For benzene compounds the ring carbon bearing the principal group is implicitly C-1. *Ortho* = C-2, *meta* = C-3, *para* = C-4. So p-nitrobenzaldehyde is 4-nitrobenzaldehyde; p-methylbenzaldehyde is 4-methylbenzaldehyde. Treat "p-" as a shorthand for "4-" in mono-substituted benzene derivatives.

Step 1. (i) Parent butanal $\mathrm{C_1HO{-}C_2H_2{-}C_3H_2{-}C_4H_3}$; add CH_3 at C-3 to get $\mathrm{OHC{-}CH_2{-}CH(CH_3){-}CH_3}$, i.e. isovaleraldehyde.

Step 2. (ii) Propiophenone is $PhCOC_2H_5$; p-NO_2 gives $\mathrm{O_2N{-}C_6H_4{-}CO{-}C_2H_5}$, a yellow crystalline solid.

Step 3. (iii) Benzaldehyde with p-methyl is p-tolualdehyde, $\mathrm{4\text{-}CH_3{-}C_6H_4{-}CHO}$, the precursor to terephthalic acid.

Step 4. (iv) Pentan-2-one with C3=C4 and a methyl on C-4: $\mathrm{(CH_3)_2C{=}CH{-}COCH_3}$ (mesityl oxide). This is the α,β-unsaturated ketone from diacetone alcohol.

Step 5. (v) Pentan-2-one + Cl at C-4: $\mathrm{CH_3COCH_2CHClCH_3}$. The C-4 chlorine is at the γ position relative to the carbonyl.

Step 6. (vi) Pentanoic acid with phenyl at C-4 and Br at C-3: $\mathrm{CH_3CH(C_6H_5)CHBrCH_2COOH}$.

Step 7. (vii) Benzophenone with OH para on each ring: $\mathrm{HO{-}C_6H_4{-}CO{-}C_6H_4{-}OH}$ (used as a UV-absorbing sunscreen ingredient).

Step 8. (viii) Hexanoic acid with C2=C3 and C4≡C5: $\mathrm{CH_3C{\equiv}CCH{=}CHCOOH}$. A conjugated en-ynoic acid.

Exam relevance. Structure-from-name questions reward neat, unambiguous bond drawings. Always show the double/triple bonds explicitly (don't compress them into $\equiv$ on a typed linear formula in your answer sheet).

Why this matters. Practising structure drawing in both directions (name → structure, structure → name) fixes IUPAC priorities firmly in mind.

> **Final Answer:** Eight structures as listed above.

Q 8.4 **Write the IUPAC names of the following ketones and aldehydes. Wherever possible, give also common names.**

(i) $\mathrm{CH_3CO(CH_2)_4CH_3}$ **(ii)** $\mathrm{CH_3CH_2CHBrCH_2CH(CH_3)CHO}$

(iii) $\mathrm{CH_3(CH_2)_5CHO}$ **(iv)** $\mathrm{Ph{-}CH{=}CH{-}CHO}$

(v) Cyclopentyl-CHO (vi) Ph−CO−Ph

SOLUTION

Concept used. Same rules as Q 8.2: identify the principal group, the longest chain containing it, number to give it the lowest locant, then list substituents alphabetically. Common names follow older but still accepted patterns (e.g. *cinnamaldehyde*, *heptanal* as oenanthaldehyde).

Step 1. (i) $CH_3CO(CH_2)_4CH_3 = CH_3COCH_2CH_2CH_2CH_2CH_3$. Seven carbons, ketone at C-2 from one end. **IUPAC:** **Heptan-2-one**; *common:* methyl *n*-pentyl ketone (or methyl amyl ketone).

Step 2. (ii) $CH_3CH_2CHBrCH_2CH(CH_3)CHO$. Number from CHO (C-1). Methyl at C-2, bromo at C-4, six-carbon parent (hexanal). **IUPAC:** **4-Bromo-2-methylhexanal**.

Step 3. (iii) $CH_3(CH_2)_5CHO$ has seven carbons in total with CHO as C-1. **IUPAC:** **Heptanal**; *common:* *n*-heptaldehyde / oenanthaldehyde.

Step 4. (iv) $Ph-CH=CH-CHO$. Three-carbon chain (propenal) with phenyl on C-3 and a C2=C3 double bond. **IUPAC:** **3-Phenylprop-2-enal** (*E*); *common:* cinnamaldehyde.

Step 5. (v) Cyclopentanecarbaldehyde: the $-CHO$ sits on a cyclopentane ring. **IUPAC:** **Cyclopentanecarbaldehyde**; no widely used common name.

Step 6. (vi) $Ph-CO-Ph$ is diphenyl ketone. **IUPAC:** **Diphenylmethanone**; *common:* benzophenone.

> **Final Answer:** (i) Heptan-2-one (methyl pentyl ketone) (ii) 4-Bromo-2-methylhexanal (iii) Heptanal (oenanthaldehyde) (iv) 3-Phenylprop-2-enal (cinnamaldehyde) (v) Cyclopentanecarbaldehyde (vi) Diphenylmethanone (benzophenone).

☞ Common-name ↔ IUPAC mapping

CBSE often asks the IUPAC name when the question gives a common name and vice versa. Keep this short table at the back of your mind: cinnamaldehyde = 3-phenylprop-2-enal; crotonaldehyde = but-2-enal; benzophenone = diphenylmethanone; oenanthaldehyde = heptanal; acetone = propan-2-one; mesityl oxide = 4-methylpent-3-en-2-one.

EXPERT'S SOLUTION *: Krishna Verma, Ph.D Organic Chemistry, IIT Madras*

Quick reading. For mixed cases like (i) and (iii), count from CHO or place the ketone at the lowest locant first. For (iv), note the styryl ($PhCH=CH^-$) group.
Alternative approach (count, then place). (a) count carbons in the principal chain

(including the suffix carbon); (b) place the principal group at the lowest possible locant; (c) read remaining substituents alphabetically with their locants. For (i) $CH_3COC_5H_{11}$, count = 7, ketone at C-2: heptan-2-one. For (vi) $PhCOPh$, count = 1 (the carbonyl carbon — the phenyls are substituents on it), suffix *-methanone*: diphenylmethanone.

> ☞ **Aldehydes attached to a ring carbon**
>
> When the $-CHO$ is on a ring carbon (cyclopentane, cyclohexane), name the ring as the parent and append *-carbaldehyde*. The aldehyde C is *not* counted in the ring's chain length. So cyclopentyl-CHO → cyclopentanecarbaldehyde, not 1-formylcyclopentane.

Concept linkage. The names anchor reactivity. Heptanal (iii) has α-H, so it does aldol; benzaldehyde-type compounds (no α-H, see Q 8.7) do Cannizzaro instead. Cinnamaldehyde (iv) has both a $C{=}C$ and a $C{=}O$ — selective reduction of $-CHO$ (NaBH$_4$ at low temperature) gives cinnamyl alcohol; selective $C{=}C$ hydrogenation (H$_2$/Pd) gives 3-phenylpropanal.

Step 1. (i) Heptan-2-one (methyl pentyl ketone). $M_w = 114$, used as a fragrance.

Step 2. (ii) 4-Bromo-2-methylhexanal. Two stereocentres at C-2 and C-4 (not asked, but worth noting).

Step 3. (iii) Heptanal (oenanthaldehyde). Six α-H total but only the two on C-2 take part in aldol.

Step 4. (iv) (E)-3-Phenylprop-2-enal (cinnamaldehyde). Conjugated α,β-unsaturated aldehyde; the aroma of cinnamon.

Step 5. (v) Cyclopentanecarbaldehyde. No common name in widespread use.

Step 6. (vi) Diphenylmethanone (benzophenone). No α-H, no $C{-}H$ that can transfer hydride either: stable to all the standard carbonyl reactions.

Exam relevance. Mixed naming questions test both IUPAC mechanics and recognition of trivial names. Two-mark questions typically ask one IUPAC + one common name; full marks need both.

Why this matters. The IUPAC name fixes the connectivity; the common name (cinnamaldehyde, benzophenone) is the everyday tag. Knowing both helps when reading literature.

> **Final Answer:** Same six pairs of names as the main solution.

Q 8.5 Draw structures of the following derivatives.

(i) The 2,4-dinitrophenylhydrazone of benzaldehyde

(ii) Cyclopropanone oxime

(iii) Acetaldehyde dimethylacetal

(iv) The semicarbazone of cyclobutanone

(v) The ethylene ketal of hexan-3-one

(vi) The methyl hemiacetal of formaldehyde

SOLUTION

Concept used. Each derivative is obtained from a parent carbonyl by a specific nucleophilic addition or addition–elimination (see Q 8.1). To draw it: locate the carbonyl carbon, replace $\mathrm{C{=}O}$ with the corresponding $\mathrm{C{=}N{-}X}$ (for hydrazone, oxime, semicarbazone) or with a tetrahedral $\mathrm{C(OR)_2}$ / $\mathrm{C(OH)(OR)}$ (for acetal/ketal/hemiacetal).

Step 1. (i) Benzaldehyde 2,4-DNP: replace $\mathrm{C{=}O}$ in PhCHO with $\mathrm{C{=}N{-}NH{-}Ar}$ where $\mathrm{Ar} = 2{,}4{-}(\mathrm{NO_2})_2\mathrm{C_6H_3}$.

$$\mathrm{C_6H_5{-}CH{=}N{-}NH{-}C_6H_3(NO_2)_2}.$$

Step 2. (ii) Cyclopropanone oxime: cyclopropanone is a three-membered ring with $\mathrm{C{=}O}$; the oxime replaces it with $\mathrm{C{=}N{-}OH}$. A cyclopropane ring with an exocyclic $\mathrm{{=}N{-}OH}$. Shorthand:

$$\mathrm{(CH_2)_2C{=}N{-}OH}\ (\text{exocyclic}).$$

Step 3. (iii) Acetaldehyde dimethylacetal: replace $\mathrm{CH_3CHO}$'s carbonyl by $\mathrm{CH(OCH_3)_2}$:

$$\mathrm{CH_3{-}CH(OCH_3)_2}.$$

Step 4. (iv) Cyclobutanone semicarbazone: replace $\mathrm{C{=}O}$ of cyclobutanone with $\mathrm{C{=}N{-}NH{-}CO{-}NH_2}$:

$$\mathrm{(CH_2)_3{-}C{=}N{-}NH{-}CO{-}NH_2} \quad (\text{4-membered ring at C}).$$

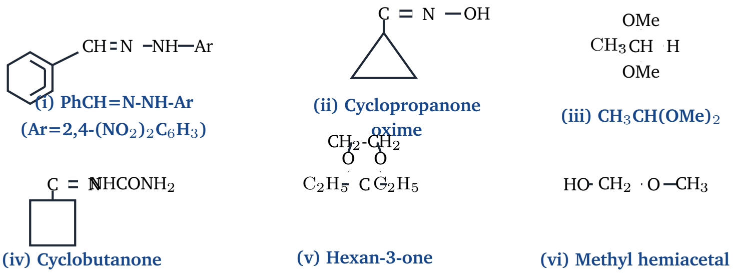
Step 5. (v) Hexan-3-one ethylene ketal: at C-3 of hexan-3-one $\mathrm{CH_3CH_2COC_2H_5}$ form a 1,3-dioxolane with ethylene glycol:

$$\mathrm{CH_3CH_2{-}C(OCH_2CH_2O){-}CH_2CH_3}.$$

Step 6. (vi) Methyl hemiacetal of formaldehyde: add one mole of $\mathrm{CH_3OH}$ to HCHO:

$$\mathrm{H{-}CH(OH)(OCH_3)} \equiv \mathrm{HOCH_2{-}OCH_3}.$$

Visual structures of the six derivatives:



(i) PhCH=N-NH-Ar (Ar=2,4-$(\mathrm{NO_2})_2\mathrm{C_6H_3}$)

(ii) Cyclopropanone oxime

(iii) $\mathrm{CH_3CH(OMe)_2}$

(iv) Cyclobutanone semicarbazone

(v) Hexan-3-one ethylene ketal

(vi) Methyl hemiacetal of HCHO

Final Answer: Structures (i)–(vi) as written.

★ Why these are useful

2,4-DNP and semicarbazone derivatives are coloured solids with sharp melting points (used to identify carbonyls). Acetals/ketals are *base-stable*, so they protect $C{=}O$ during multi-step reductions or organometallic additions and are removed later with dilute acid.

♥ Acetals/ketals as protecting groups

Suppose you must reduce a $-COOR$ to $-CH_2OH$ in a molecule that also has a $C{=}O$. $LiAlH_4$ would reduce both. Solution: protect $C{=}O$ as its ethylene ketal, reduce the ester, then hydrolyse the ketal back to $C{=}O$ with dilute acid. The ketal survives the strongly basic $LiAlH_4$ step because it has no electrophilic carbon. This is how modern multi-step synthesis tolerates many functional groups in one molecule.

EXPERT'S SOLUTION *: Diya Banerjee, Ph.D Organic Chemistry, IISc Bangalore*

Picture-first. Every derivative is a one-swap operation on the parent carbonyl. Draw the parent first, then swap.

Alternative approach (mechanism class shortcut). Three mechanism classes cover all six:

- Addition–elimination (nitrogen nucleophile, $C{=}O \rightarrow C{=}N$): 2,4-DNP (i), oxime (ii), semicarbazone (iv).
- Two-step substitution (oxygen nucleophile, 2 equiv ROH, $C{=}O \rightarrow C(OR)_2$): acetal (iii), ketal (v).
- One-step addition (one equiv ROH stops at the hemiacetal): (vi).

☞ Cyclic ketals are unusually stable

A ketal made with ethylene glycol or 1,3-propanediol (a *cyclic* ketal, i.e. 1,3-dioxolane or 1,3-dioxane) is far more stable than its open-chain cousin because the cyclic form has lower entropic cost — one ring instead of two free $-OR$ groups. This is why ethylene-glycol ketals are the standard $C{=}O$ protecting group in synthesis.

Concept linkage. The $C{=}N$ stretch of an oxime, semicarbazone or 2,4-DNP appears around $1620\,\mathrm{cm}^{-1}$, distinctly lower than the parent $C{=}O$ stretch near $1715\,\mathrm{cm}^{-1}$. So IR spectroscopy tells you instantly whether the derivative has formed. For acetals and hemiacetals, $C{=}O$ disappears completely (replaced by $C{-}O$ singles around $1100\,\mathrm{cm}^{-1}$) — another diagnostic.

Step 1. (i) $PhCH{=}N{-}NHC_6H_3(NO_2)_2$ (orange solid; m.p. $237\,°C$).

Step 2. (ii) Cyclopropane ring with exocyclic $=N{-}OH$. The ring strain leaves the oxime slightly less stable than an acyclic one.

Step 3. (iii) $CH_3CH(OCH_3)_2$. Used as a solvent and as an anhydrous source of acetaldehyde.

Step 4. (iv) Cyclobutane ring with exocyclic $=N-NH-CO-NH_2$.

Step 5. (v) Hexan-3-one with the C-3 sealed inside a 1,3-dioxolane. Standard $C=O$ protecting strategy for later $LiAlH_4$ steps.

Step 6. (vi) $HOCH_2OCH_3$ (methoxymethanol). Unstable in dilute acid — collapses back to $HCHO + CH_3OH$.

Exam relevance. 2-mark CBSE questions ask for the structural formula of one specified derivative given the parent carbonyl and nucleophile. Always show stereochemistry of the $C=N$ (*E/Z*) if asked, but the default is just the connectivity.

Why this matters. Recognising these on a spectrum (e.g. a strong $C=N$ stretch around $1620\,cm^{-1}$, no $C=O$ near $1715\,cm^{-1}$) confirms which derivative you have made.

> **Final Answer:** Six labelled structures, drawn as in the main solution.

Q 8.6 **Predict the products formed when cyclohexanecarbaldehyde reacts with the following reagents.**

(i) PhMgBr and then H_3O^+

(ii) Tollens' reagent

(iii) Semicarbazide and weak acid

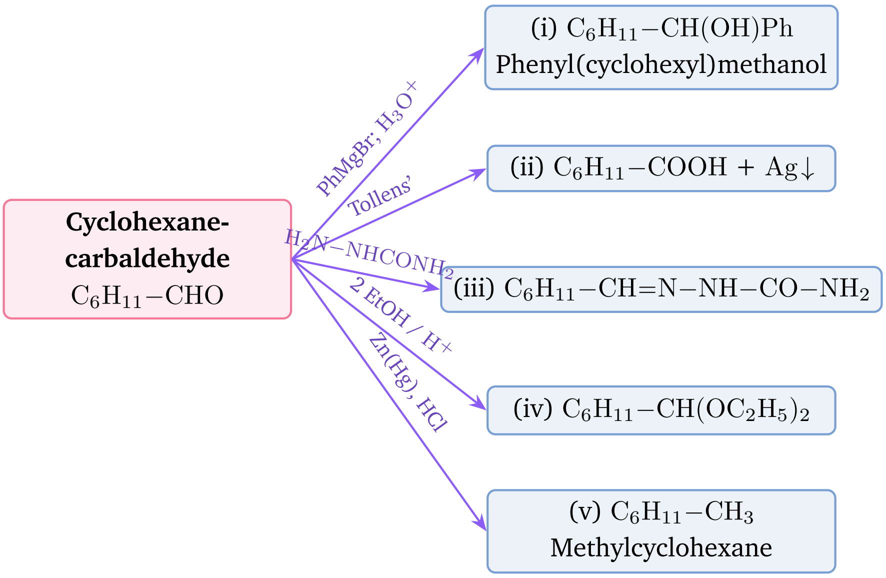
(iv) Excess ethanol and acid

(v) Zinc amalgam and dilute hydrochloric acid

SOLUTION

Concept used. Cyclohexanecarbaldehyde, $C_6H_{11}-CHO$, has the $-CHO$ on a cyclohexyl ring. Its carbonyl carbon is electrophilic and reacts with:

- Grignards $RMgX$, giving *secondary alcohols* after acidic workup.
- Tollens' reagent ($[Ag(NH_3)_2]^+$, mild oxidiser), giving the carboxylic acid (and a silver mirror).
- Semicarbazide ($H_2N-NH-CO-NH_2$) in weakly acidic medium, giving the semicarbazone (addition–elimination).
- Excess alcohol with dry acid, giving an acetal.
- Clemmensen reduction ($Zn(Hg)$, conc. HCl), reducing $C=O$ all the way to $-CH_2-$.



Step 1. (i) PhMgBr adds the phenyl to the carbonyl carbon; oxygen becomes O^-MgBr^+; aqueous workup protonates oxygen:

$$C_6H_{11}-CHO + PhMgBr - C_6H_{11}-CH(OMgBr)Ph -[H_3O^+]\ C_6H_{11}-CH(OH)Ph.$$

Product: **phenyl(cyclohexyl)methanol**, a secondary alcohol.

Step 2. (ii) Tollens' reagent oxidises $-CHO$ to $-COOH$ and deposits silver:

$$C_6H_{11}-CHO+2\,[Ag(NH_3)_2]^+ + 3\,OH^- - C_6H_{11}-COO^- + 2\,Ag\,(v) + 4\,NH_3 + 2\,H_2O.$$

Product: **cyclohexanecarboxylic acid** (silver mirror on the test tube).

Step 3. (iii) With semicarbazide and a trace of weak acid (pH 4–5), addition–elimination gives the semicarbazone:

$$C_6H_{11}-CHO + H_2N-NH-CO-NH_2 - C_6H_{11}-CH{=}N-NH-CO-NH_2 + H_2O.$$

Step 4. (iv) Excess ethanol with dry HCl: two moles of C_2H_5OH add and one water leaves:

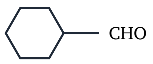
$$C_6H_{11}-CHO + 2\,C_2H_5OH -[\text{dry HCl}]\ C_6H_{11}-CH(OC_2H_5)_2 + H_2O.$$

Product: **cyclohexanecarbaldehyde diethyl acetal**.

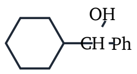
Step 5. (v) Clemmensen reduction takes $-CHO$ all the way to $-CH_3$:

$$C_6H_{11}-CHO -[Zn(Hg), HCl]\ C_6H_{11}-CH_3\ (\text{methylcyclohexane}).$$

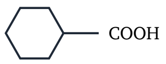
Structural drawings of cyclohexanecarbaldehyde and its products:



Cyclohexane-carbaldehyde

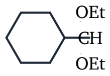


(i) Phenyl(cyclohexyl)methanol

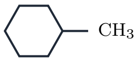


(ii) Cyclohexane-carboxylic acid

(iii) Semicarbazone



(iv) Diethyl acetal



(v) Methyl-cyclohexane

Reagents:
(i) PhMgBr / H_3O^+
(ii) Tollens'
(iii) $H_2N{-}NHCONH_2$
(iv) 2 EtOH / dry HCl
(v) Zn(Hg), HCl

> **Final Answer:** (i) Phenyl(cyclohexyl)methanol; (ii) cyclohexanecarboxylic acid; (iii) cyclohexanecarbaldehyde semicarbazone; (iv) diethyl acetal; (v) methylcyclohexane.

♥ Tollens' vs Fehling

Both oxidise $-\mathrm{CHO}$, but aromatic aldehydes (PhCHO) do *not* respond to Fehling. Cyclohexanecarbaldehyde is *aliphatic* (cyclohexyl is sp^3) and gives both Tollens' and Fehling positive.

✗ Don't mix up Clemmensen and Wolff–Kishner conditions

Both reduce $\mathrm{C{=}O} \rightarrow \mathrm{CH_2}$ but on opposite ends of the pH scale. Clemmensen uses $\mathrm{Zn(Hg)}$ in concentrated HCl (acidic); Wolff–Kishner uses $\mathrm{NH_2NH_2/KOH}$ in ethylene glycol (basic). Pick Clemmensen for base-sensitive substrates and Wolff–Kishner for acid-sensitive substrates. Writing the wrong combination ("$\mathrm{Zn/NaOH}$") is a routine -1 mark on board scripts.

EXPERT'S SOLUTION : *Aditya Mehta, M.Sc Chemistry, IIT Kanpur*

Picture-first. The substrate is an aliphatic aldehyde with an unhindered $\mathrm{C{=}O}$. So everything proceeds smoothly: addition with PhMgBr, oxidation with Tollens', condensation with semicarbazide, acetal formation with ethanol, and Clemmensen reduction.

Alternative approach (reagent-class sort). Sort each reagent by what it *does* to the carbonyl carbon's oxidation state and hybridisation:

- PhMgBr is a strong carbon nucleophile: adds C, leaves oxidation state unchanged, carbon becomes sp^3.
- Tollens' is a mild oxidiser: $-\mathrm{CHO} \rightarrow -\mathrm{COOH}$, oxidation state $\mathrm{C}^{+1} \rightarrow \mathrm{C}^{+3}$, still sp^2.
- Semicarbazide: addition–elimination, swaps $=\mathrm{O}$ for $=\mathrm{N}{-}\mathrm{NHCONH_2}$, sp^2 retained.
- Excess $\mathrm{ROH/H^+}$: addition-substitution, swaps $=\mathrm{O}$ for two $-\mathrm{OR}$, carbon becomes sp^3.
- Clemmensen: full reduction, $\mathrm{C}^{+1} \rightarrow \mathrm{C}^{-2}$, carbon becomes sp^3.

☞ Why Grignard gives a secondary alcohol here

Cyclohexanecarbaldehyde is an aldehyde (one H, one alkyl on the carbonyl C). Addition of a second alkyl/aryl group (from PhMgBr) gives a carbon with two alkyl/aryl groups + OH: a secondary alcohol. A formaldehyde substrate would have given a primary alcohol; a ketone substrate would have given a tertiary alcohol.

Concept linkage with carbonyl reactivity. The electrophilicity of an aldehyde carbon depends on (a) the absence of an extra alkyl ($+$I) donor, and (b) the absence of resonance donors. Here, cyclohexyl is just one $+$I alkyl — so the substrate is more reactive than acetone but less than formaldehyde. This matches the "aldehyde $>$ ketone" ladder you will use in Q 8.12 (i).

Step 1. (i) $C_6H_{11}-CH(OH)-Ph$: secondary alcohol from Grignard addition + protonation. Two-step mechanism (alkoxide intermediate, then aqueous workup).

Step 2. (ii) $C_6H_{11}-COOH$: silver mirror plus carboxylic acid. The mirror is silver(0) deposited on the inner test-tube wall.

Step 3. (iii) $C_6H_{11}-CH{=}N-NH-CO-NH_2$: cyclohexanecarbaldehyde semicarbazone. A crystalline solid with sharp m.p. used to identify the parent aldehyde.

Step 4. (iv) $C_6H_{11}-CH(OC_2H_5)_2$: the diethyl acetal. Bears two $-OEt$ on the same carbon.

Step 5. (v) $C_6H_{11}-CH_3$: methylcyclohexane. The deepest reduction available without breaking any $C-C$ bond.

Exam relevance. CBSE 2022 asked exactly this product-set question on a different aldehyde (propanal). Marks are split: 1 per product, with 1 extra mark for naming the named reaction (Clemmensen, Rosenmund, etc.). Always label the named reaction next to the arrow.

Why this matters. The same carbonyl carbon plays five different roles depending on the reagent: electrophile for Grignard, substrate for oxidation, substrate for addition–elimination, substrate for protection, substrate for reduction. The carbonyl is the most reagent-flexible functional group you meet in Class 12.

Final Answer: Five products as listed; methylcyclohexane from Clemmensen is the deepest reduction.

Q 8.7 **Which of the following compounds would undergo aldol condensation, which the Cannizzaro reaction, and which neither? Write the structures of the expected products of aldol condensation and Cannizzaro reaction.**

(i) Methanal (ii) 2-Methylpentanal (iii) Benzaldehyde

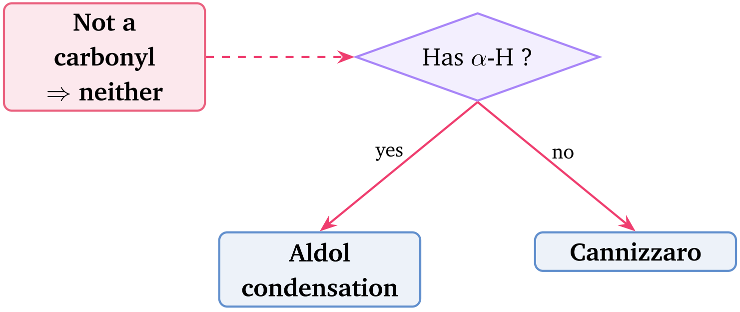
(iv) Benzophenone (v) Cyclohexanone (vi) 1-Phenylpropanone
(vii) Phenylacetaldehyde (viii) Butan-1-ol (ix) 2,2-Dimethylbutanal

SOLUTION

Concept used. Two simple rules decide:

- **Aldol condensation** requires at least one α-hydrogen on a carbonyl, because the base must abstract H^+ from the α-carbon to form the enolate nucleophile.
- **Cannizzaro reaction** happens only for carbonyls with *no* α-hydrogen: concentrated base then forces hydride transfer between two molecules, giving one alcohol and one carboxylate.

A compound that is not a carbonyl (e.g. butan-1-ol) does neither.



Step 1. (i) Methanal HCHO: no α-H ⇒ **Cannizzaro**:

$$2\,\mathrm{HCHO} -[\mathrm{conc}\cdot\ \mathrm{NaOH}]\ \mathrm{CH_3OH} + \mathrm{HCOO^-Na^+}.$$

Step 2. (ii) 2-Methylpentanal $CH_3CH_2CH_2CH(CH_3)CHO$: α-H present (on the $CH(CH_3)$) ⇒ **Aldol**, which on heating dehydrates to the α,β-unsaturated aldehyde $CH_3CH_2CH_2{-}C(C_3H_7){=}C(CH_3){-}CHO$ (2-methyl-3-propylhex-2-enal).

Step 3. (iii) Benzaldehyde C_6H_5CHO: no α-H ⇒ **Cannizzaro**:

$$2\,\mathrm{C_6H_5CHO} -[\mathrm{conc}\cdot\ \mathrm{NaOH}]\ \mathrm{C_6H_5CH_2OH} + \mathrm{C_6H_5COO^-Na^+}.$$

Step 4. (iv) Benzophenone $(C_6H_5)_2C{=}O$: no α-H. It is a ketone with no hydride-transferable $C{-}H$: **neither** aldol nor Cannizzaro.

Step 5. (v) Cyclohexanone: α-H on each α-CH_2 ⇒ **Aldol**; self condensation gives 2-(1-cyclohexenyl)cyclohexan-1-one (after β-elimination).

Step 6. (vi) 1-Phenylpropanone ($C_6H_5COCH_2CH_3$, propiophenone): α-H on the CH_2 ⇒ **Aldol**; the product is a β-hydroxy ketone that dehydrates to an α,β-unsaturated phenyl ketone.

Step 7. (vii) Phenylacetaldehyde ($C_6H_5CH_2CHO$): α-H on the benzylic CH_2 ⇒ **Aldol**; product (after dehydration) is 2,3-diphenylprop-2-enal.

Step 8. (viii) Butan-1-ol $CH_3CH_2CH_2CH_2OH$ is an alcohol, not a carbonyl: ⇒ **neither**.

Step 9. (ix) 2,2-Dimethylbutanal $(CH_3)_2C(C_2H_5)CHO$: the α-carbon is fully substituted (no α-H) $\Rightarrow$ **Cannizzaro**: With conc. OH^-:

$$2\,(CH_3)_2C(C_2H_5)CHO \longrightarrow$$

$$(CH_3)_2C(C_2H_5)CH_2OH + (CH_3)_2C(C_2H_5)COO^-Na^+.$$

> **Final Answer:** Aldol: (ii),(v),(vi),(vii). Cannizzaro: (i),(iii),(ix). Neither: (iv),(viii). Products as written.

✗ Watch the α-carbon, not the chain length

Aldol/Cannizzaro depends on α-H availability, not on chain length. Even formaldehyde (one carbon) shows Cannizzaro because its α-position does not exist; 2,2-dimethylpropanal (5 carbons) also has no α-H and gives Cannizzaro.

EXPERT'S SOLUTION : *Tara Nair, Ph.D Organic Chemistry, IISc Bangalore*

Decision tree. For each compound: (a) Is it a carbonyl? If no → neither. (b) Does it have α-H? If yes → aldol; if no → Cannizzaro.

Alternative approach (aldol vs Cannizzaro decision). Both reactions need (i) a carbonyl and (ii) base. Aldol additionally needs an α-H so the base can deprotonate it; Cannizzaro additionally needs a transferable hydride (the $C-H$ of the $-CHO$ itself). A ketone like benzophenone has no α-H *and* no $C-H$ on the carbonyl carbon, so neither reaction runs. Run this two-question test on every compound: "Is there an α-H?" then "Is there a transferable $C-H$?"

☞ Crossed Cannizzaro and Cannizzaro of HCHO

When the substrate is a mixture of formaldehyde and another α-Hless aldehyde (e.g. HCHO + PhCHO), HCHO acts as the hydride donor (most easily oxidised) and the other aldehyde gets reduced. This "crossed Cannizzaro" is a clean way to convert PhCHO → $PhCH_2OH$ while sacrificing the cheap HCHO to formate.

- (i), (iii), (ix): no α-H $\Rightarrow$ Cannizzaro.
- (ii), (v), (vi), (vii): α-H present $\Rightarrow$ Aldol (gives β-hydroxy carbonyl, then dehydrates).
- (iv): no α-H but it is a ketone; benzophenone does not undergo Cannizzaro (no hydride donor); neither.
- (viii): alcohol, not a carbonyl; neither.

Concept linkage with α-H acidity and tautomerism. An aldehyde or ketone α-H has $pK_a \approx 20$, much more acidic than a simple alkane ($pK_a \approx 50$) because the resulting carbanion is delocalised onto the electronegative oxygen (enolate). The same enolate is the nucleophilic species in aldol. The keto–enol tautomerism is the structural underpinning: the enol form $\mathrm{R{-}C(OH){=}CH_2}$ is the protonated enolate, and the two forms interconvert in solution.

Step 1. Methanal: $2\,\mathrm{HCHO} -[\mathrm{OH}^-]\,\mathrm{CH_3OH} + \mathrm{HCOO}^-$. Disproportionation is fast; commercial HCOONa is made by exactly this Cannizzaro on industrial scale.

Step 2. Benzaldehyde: $2\,\mathrm{PhCHO} -[\mathrm{OH}^-]\,\mathrm{PhCH_2OH} + \mathrm{PhCOO}^-$. Classic Cannizzaro; product mix is 50:50 alcohol:carboxylate.

Step 3. 2,2-Dimethylbutanal: $2\,\mathrm{RCHO} -[\mathrm{OH}^-]\,\mathrm{RCH_2OH} + \mathrm{RCOO}^-$, $R = \mathrm{C(CH_3)_2C_2H_5}$.

Step 4. 2-Methylpentanal aldol (after β-elimination): 2-methyl-3-propylhex-2-enal.

Step 5. Cyclohexanone aldol: 2-(1-cyclohexenyl)cyclohexan-1-one.

Step 6. Phenylacetaldehyde aldol: 2,3-diphenylprop-2-enal.

Exam relevance. This is one of the most-asked CBSE board questions on the chapter. Expect a 5-mark variant where the question lists 4–5 compounds and asks for sorting + product structures + mechanism. Memorise the decision tree as a 30-second sort.
Why this matters. The single rule "no α-H = no enolate" tells you every time which test will fire. Aldol is the α-chemistry; Cannizzaro is the carbonyl-only chemistry.

> **Final Answer:** Aldol: (ii), (v), (vi), (vii); Cannizzaro: (i), (iii), (ix); Neither: (iv), (viii).

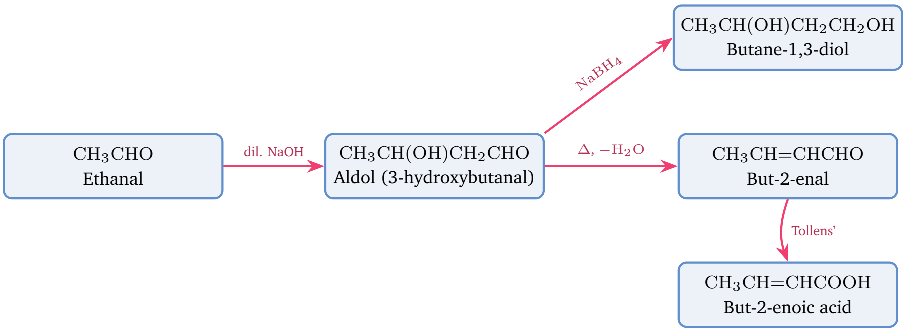
Q 8.8 How will you convert ethanal into the following compounds?

(i) Butane-1,3-diol (ii) But-2-enal (iii) But-2-enoic acid

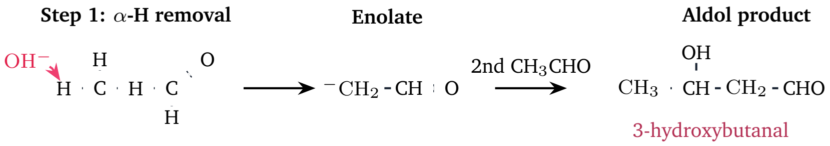
SOLUTION

Concept used. All three targets come from a self-aldol on ethanal ($\mathrm{CH_3CHO}$). The product 3-hydroxybutanal, $\mathrm{CH_3CH(OH)CH_2CHO}$, branches three ways:

- reduce both $-\mathrm{OH}$ and $-\mathrm{CHO}$ to alcohols $\rightarrow$ butane-1,3-diol;
- dehydrate the aldol $\rightarrow$ but-2-enal;
- oxidise but-2-enal's $-\mathrm{CHO} \rightarrow$ but-2-enoic acid.



Aldol mechanism (curly arrows):



Step 1. **Self-aldol on ethanal**. Dilute $NaOH$ removes an α-H from one CH_3CHO to give the enolate $^{-}CH_2CHO$; the enolate attacks a second CH_3CHO at its carbonyl carbon; protonation gives the aldol:

$$2\,CH_3CHO -[\text{dil}\cdot\ NaOH]\ CH_3{-}CH(OH){-}CH_2{-}CHO\ (\text{3-hydroxybutanal}).$$

Step 2. (i) **Butane-1,3-diol**: reduce the aldehyde of the aldol to a primary alcohol with $NaBH_4$ (or H_2/Ni):

$$CH_3CH(OH)CH_2CHO -[NaBH_4]\ CH_3CH(OH)CH_2CH_2OH.$$

Step 3. (ii) **But-2-enal**: dehydrate the aldol by warming; $-OH$ on C-3 and α-H on C-2 leave as water:

$$CH_3CH(OH)CH_2CHO -[\Delta]\ CH_3{-}CH{=}CH{-}CHO + H_2O.$$

Step 4. (iii) **But-2-enoic acid** (crotonic acid): oxidise the aldehyde of but-2-enal with mild oxidant (Tollens' or Ag_2O; avoid $KMnO_4$ which cleaves the $C{=}C$):

$$CH_3CH{=}CHCHO -[\text{Tollens} / Ag_2O]\ CH_3CH{=}CHCOOH.$$

> **Final Answer:** Aldol → (i) reduce → butane-1,3-diol; (ii) dehydrate → but-2-enal; (iii) oxidise (ii) → but-2-enoic acid.

☞ Pick the right oxidant

For an α, β-unsaturated aldehyde, use Tollens' or Ag_2O/NH_3 to oxidise $-CHO$ without touching the $C{=}C$. Acidic $KMnO_4$ or $K_2Cr_2O_7$ will cleave the double bond and ruin the carbon skeleton.

✗ Don't reduce the $C{=}C$ when you only want the $C{=}O$

For (i), use $NaBH_4$ (selective for $C{=}O$, leaves $C{=}C$ alone), not $H_{2/}Ni$ (reduces both). The aldol product still has only one $C{=}O$ to reduce (the $-CHO$); the $-OH$ is already an alcohol. Conversely for (ii), warming in mild base is enough — never use $H_2SO_{4/}\Delta$, which would re-protonate the carbonyl and drive the reverse aldol.

EXPERT'S SOLUTION *: Yash Joshi, M.Tech Chemical Engineering, IIT Bombay*

Quick reading. All three targets sit on the same family tree, with the aldol product $CH_3CH(OH)CH_2CHO$ as the trunk.

Alternative approach (Hell–Volhard–Zelinsky logic does not apply here, but selective oxidant choice does). For polyfunctional targets always ask: which functional group am I changing, and what do I leave alone? Here the trunk has $-OH$ and $-CHO$; each branch chooses one selective transformation: reduce $-CHO$ but keep $-OH$ (use $NaBH_4$), dehydrate but keep $-CHO$ (use Δ), or oxidise $-CHO$ but keep $C{=}C$ (use Tollens'). Selectivity is the central skill of multifunctional synthesis.

☞ How β-elimination dehydrates the aldol

After the aldol forms, gentle warming pulls an α-H and an $-OH$ off neighbouring carbons (E1cb-like): the carbonyl pulls its α-H, the hydroxide leaves, and a new $C{=}C$ forms conjugated with the existing $C{=}O$. The resulting α, β-unsaturated carbonyl is more stable than the aldol because of the new conjugation.

Step 1. Form the aldol: $2\,CH_3CHO -[\text{dil}\cdot\ NaOH]\ CH_3CH(OH)CH_2CHO$. Only a catalytic amount of NaOH is needed; too much base drives the system to the α, β-unsaturated product directly (Claisen–Schmidt-like).

Step 2. (i) Reduce both functional groups: $NaBH_4$ first reduces the CHO; the $C(OH)$ already exists. Net product $CH_3CH(OH)CH_2CH_2OH$. $NaBH_4$ in MeOH at room temperature is the textbook choice.

Step 3. (ii) Heat the aldol to drive off water across C-2,C-3 to give $CH_3CH{=}CHCHO$. The newly formed $C{=}C$ is conjugated with $C{=}O$ — the aldol product was higher in energy than this α, β-unsaturated aldehyde because of the lost conjugation; that is the driving force.

Step 4. (iii) Mild oxidation of (ii) with Tollens' converts $-CHO \rightarrow -COOH$ without touching the alkene. The $[Ag(NH_3)_2]^+$ complex is a mild $Ag(I)$ oxidiser that stops at the carboxylic acid stage.

Concept linkage — the aldol family tree. Starting from *any* aldehyde with α-H, the aldol gives a β-hydroxy carbonyl. Then four standard moves give four common targets: reduce → 1,3-diol; dehydrate → enal; oxidise → enoic acid; hydrogenate → saturated β-hydroxy ketone. Pattern fluency beats route-design.

Exam relevance. CBSE 2024 set a 3-mark version on propanal-to-2-methylpent-2-enal.

The marking scheme demands all three steps shown explicitly, with reagents above each arrow.

Why this matters. Recognising one "branch point" intermediate (the aldol product here) lets you reach a whole family of products in 2–3 steps instead of designing each route from scratch.

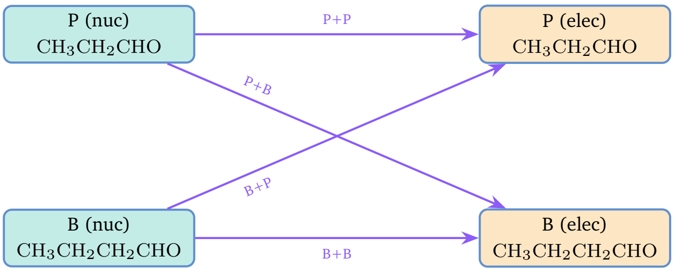
> **Final Answer:** Aldol → (i) butane-1,3-diol; (ii) but-2-enal; (iii) but-2-enoic acid.

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

SOLUTION

Concept used. In a crossed aldol between propanal (CH_3CH_2CHO, call it **P**) and butanal ($CH_3CH_2CH_2CHO$, call it **B**), either aldehyde can be the *enolate nucleophile* (its α-carbon attacks) or the *electrophile* (its carbonyl carbon is attacked). With two distinct aldehydes there are four nucleophile/electrophile combinations.

> ☞ **Why α-carbon is nucleophilic**
>
> A base removes an α-H to form a resonance-stabilised carbanion (the enolate). The negatively charged carbon attacks the carbonyl carbon of another aldehyde.



Step 1. **P (nuc) + P (elec)**: self-aldol of propanal. Enolate of CH_3CH_2CHO is $CH_3CH(-)CHO$. Attacks the carbonyl carbon of another propanal:

$$2\,CH_3CH_2CHO - CH_3CH_2{-}CH(OH){-}CH(CH_3){-}CHO$$

3-hydroxy-2-methylpentanal. After β-elimination: $CH_3CH_2{-}CH{=}C(CH_3){-}CHO$ **2-methylpent-2-enal**.

Step 2. **B (nuc) + B (elec)**: self-aldol of butanal. Enolate $CH_3CH_2CH(-)CHO$ attacks the carbonyl of another butanal:

$$2\,CH_3CH_2CH_2CHO - CH_3CH_2CH_2{-}CH(OH){-}CH(C_2H_5){-}CHO$$

3-hydroxy-2-ethylhexanal. After β-elimination:
$CH_3CH_2CH_2{-}CH{=}C(C_2H_5){-}CHO$ **2-ethylhex-2-enal**.

Step 3. **P (nuc) + B (elec)**: enolate of propanal attacks the carbonyl of butanal:

$$CH_3CH_2CHO + CH_3CH_2CH_2CHO - CH_3CH_2CH_2{-}CH(OH){-}CH(CH_3){-}CHO$$

3-hydroxy-2-methylhexanal. After β-elimination:
$CH_3CH_2CH_2{-}CH{=}C(CH_3){-}CHO$ **2-methylhex-2-enal**.

Step 4. **B (nuc) + P (elec)**: enolate of butanal attacks the carbonyl of propanal:

$$CH_3CH_2CH_2CHO + CH_3CH_2CHO - CH_3CH_2{-}CH(OH){-}CH(C_2H_5){-}CHO$$

3-hydroxy-2-ethylpentanal. After β-elimination:
$CH_3CH_2{-}CH{=}C(C_2H_5){-}CHO$ **2-ethylpent-2-enal**.

> **Final Answer:** Four aldol products (after β-elimination): 2-methylpent-2-enal (P+P), 2-ethylhex-2-enal (B+B), 2-methylhex-2-enal (P-nuc, B-elec), 2-ethylpent-2-enal (B-nuc, P-elec).

☞ Crossed aldol selectivity

A clean crossed aldol needs one aldehyde with no α-H (e.g. formaldehyde, benzaldehyde) as the electrophile; otherwise you get all four products as here. Lithium enolates or kinetically controlled aldol-type condensations are used to overcome this.

EXPERT'S SOLUTION : *Ishaan Bhat, M.Sc Chemistry, IIT Kanpur*

Strategic angle. Label one aldehyde the nucleophile (its α-C attacks) and the other the electrophile (its C=O is attacked). With two aldehydes that both have α-H, you get $2 \times 2 = 4$ combinations.

Alternative approach (combinatorial). Number the aldehydes A and B, then enumerate *(nucleophile)+(electrophile)* pairs: AA, AB, BA, BB. Two of these are self-aldols and two are crosses. For each pair, the β-hydroxy product has the carbon chain of the electrophile extended at its carbonyl carbon by the α-carbon of the nucleophile.

☞ The C-C bond formed in aldol

The new C−C bond joins the α-carbon of the nucleophile to the carbonyl carbon of the electrophile. So in "P (nuc) + B (elec)", the propanal α-C (which is C-2 of propanal) connects to the butanal carbonyl carbon (which is C-1 of butanal). Trace this bond and the structural formula falls out.

Concept linkage — carbanion (enolate) reactivity. The α-H of a carbonyl has $pK_a \approx 20$; in dilute NaOH the equilibrium concentration of the enolate is small but enough to react. The aldol product's $-OH$ is then dehydrated on heating to give an α, β-unsaturated aldehyde with conjugation between $C{=}C$ and $C{=}O$, which lowers the molecule's energy. The same enolate logic governs Claisen, Reformatsky and Knoevenagel reactions.

Step 1. P+P aldol: $CH_3CH_2CH(OH)CH(CH_3)CHO \rightarrow$ 2-methylpent-2-enal. (Self-aldol of propanal.)

Step 2. B+B aldol: $CH_3CH_2CH_2CH(OH)CH(C_2H_5)CHO \rightarrow$ 2-ethylhex-2-enal. (Self-aldol of butanal.)

Step 3. P-nuc + B-elec: $CH_3CH_2CH_2CH(OH)CH(CH_3)CHO \rightarrow$ 2-methylhex-2-enal. (Cross product 1.)

Step 4. B-nuc + P-elec: $CH_3CH_2CH(OH)CH(C_2H_5)CHO \rightarrow$ 2-ethylpent-2-enal. (Cross product 2.)

Exam relevance. CBSE 2023 awarded 1 mark per correctly labelled product (4 marks total) plus 1 mark for explicitly identifying nucleophile vs electrophile in each case (5 marks total). Always label, don't just list.

Why this matters. The crossed aldol is a $C-C$ bond-forming reaction that builds complex aldehyde skeletons from simple ones; the selectivity problem here is a classic challenge in modern synthesis (Mukaiyama, Evans aldol).

> **Final Answer:** Four aldols / α, β-unsaturated aldehydes as listed.

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

SOLUTION

Concept used. The clues build up a unique aromatic aldehyde:

- *Forms 2,4-DNP and reduces Tollens'* $\Rightarrow$ the compound is an aldehyde $R-CHO$.
- *Cannizzaro* $\Rightarrow$ no α-H on the CHO $\Rightarrow$ the aldehyde sits directly on an aromatic ring, $Ar-CHO$.
- *Oxidation gives 1,2-benzenedicarboxylic acid* (phthalic acid) $\Rightarrow$ the side-chain on the ring oxidises to a $-COOH$ that sits *ortho* to the existing $-CHO$, and the existing $-CHO$ also oxidises to $-COOH$.

So the compound has $-CHO$ at one ring carbon and an *ortho* alkyl side chain that ends up as $-\mathrm{COOH}$. The molecular formula must be $C_9H_{10}O$.

Step 1. **Count atoms.** A benzene ring contributes C_6H_4 when di-substituted. Add $-\mathrm{CHO}$ and an alkyl group $-\mathrm{R}$; for the formula to be $C_9H_{10}O$ we need $\mathrm{R} + \mathrm{CHO} = C_3H_6O$. So $\mathrm{R} = -C_2H_5$ (ethyl). Skeleton: $C_6H_4(\mathrm{CHO})(C_2H_5)$.

Step 2. **Verify atoms**: $C_6 + 1 + 2 = C_9$; $H_4 + 1 + 5 = H_{10}$; O_1. ✓

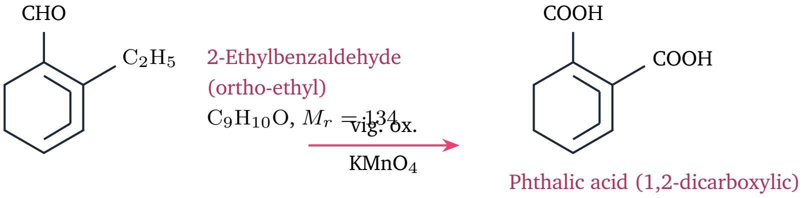
Step 3. Place the ethyl *ortho* to the CHO so that oxidation of both side chains gives *1,2-(ortho)* diacid (phthalic acid):

$$\text{o-}C_2H_5{-}C_6H_4{-}\mathrm{CHO} -[\mathrm{KMnO_4}, H^+]\ \text{o-}\mathrm{HOOC}{-}C_6H_4{-}\mathrm{COOH}.$$

Step 4. Confirm Cannizzaro: the CHO has no α-H (it sits directly on the aromatic ring) $\Rightarrow$ Cannizzaro is possible. ✓

Step 5. Sanity check Tollens'/2,4-DNP: both tests require only an intact $-\mathrm{CHO}$, present here. ✓

Structure of the identified compound:



> **Final Answer:** The compound is **2-ethylbenzaldehyde** (*o*-ethylbenzaldehyde), $C_6H_4(C_2H_5)(\mathrm{CHO})$ with C_2H_5 ortho to CHO.

★ Why *ortho*, not *meta* or *para*

Vigorous oxidation of an alkyl-aryl side chain (e.g. with hot $\mathrm{KMnO_4}$) gives an $\mathrm{Ar{-}COOH}$ on the ring carbon that was attached to the side chain. For *phthalic* acid (1,2-) we need the two COOH groups on adjacent ring carbons, so the ethyl must be *ortho* to the CHO.

♥ How phthalic acid features industrially

Phthalic acid is a precursor for plasticisers (DEHP), polyester resins (alkyd paints, glyptal) and dyes (phenolphthalein, fluorescein). Recognising it as a 1,2-disubstitution product on benzene is a recurring pattern in CBSE structure-elucidation problems. The 1,3-(isophthalic) and 1,4-(terephthalic) isomers map to different products: terephthalic acid is the monomer for PET bottles.

EXPERT'S SOLUTION : *Aditi Reddy, Ph.D Organic Chemistry, IISc Bangalore*

Structural observation. Three signposts:

- 2,4-DNP and Tollens' + Cannizzaro ⇒ aryl aldehyde $\mathrm{Ar{-}CHO}$.
- Vigorous oxidation gives phthalic acid (1,2-diacid) ⇒ two side chains *ortho* on benzene, both end up as COOH.
- $C_9H_{10}O$ leaves C_3H_6 outside the ring, split as $-\mathrm{CHO}$ + $-C_2H_5$.

Alternative approach (DoU first, then tests). Degree of unsaturation immediately tells you the ring + carbonyl count, so the skeleton is set before any test result is used. DoU $= (2C + 2 - H)/2 = 5$; four count for the aromatic ring (3 π + 1 ring), leaving 1 for a single $\mathrm{C{=}O}$. Now layer on the test results to choose between possible isomers.

☞ Vigorous $KMnO_4$ cuts side chains to the bone

Hot acidic $KMnO_4$ takes *any* aryl side chain that has at least one benzylic $\mathrm{C{-}H}$ (so $-CH_3$, $-CH_2R$, $-CHR_2$) all the way down to $-\mathrm{COOH}$ on the ring carbon. A $-CR_3$ (no benzylic H, like *tert*-butyl) is left untouched. So "vigorous oxidation gave one $-\mathrm{COOH}$" tells you there was one side chain with at least one benzylic H.

Step 1. DoU $= (2 \times 9 + 2 - 10)/2 = 5$. Four for the benzene ring + one for $\mathrm{C{=}O}$. ✓

Step 2. Place $-\mathrm{CHO}$ at C-1 (Cannizzaro ⇒ no α-H), $-C_2H_5$ at C-2 (ortho).

Step 3. Vigorous oxidation: $-\mathrm{CHO} \rightarrow -\mathrm{COOH}$ (the existing aldehyde) and $-CH_2CH_3 \rightarrow -\mathrm{COOH}$ (the ethyl loses both of its carbons except the one bonded to the ring; that ring carbon ends up as a $-\mathrm{COOH}$). Both ortho: phthalic acid.

Step 4. Confirm carbon count of products: ortho-diacid is $C_8H_6O_4$ — the original 9-carbon compound lost one carbon during ethyl oxidation. Always check loss/gain of carbon in side-chain oxidation.

Concept linkage — side-chain oxidation, hyperconjugation and Hammett. The reactivity of a benzylic $\mathrm{C{-}H}$ in $KMnO_4$ oxidation tracks the same hyperconjugation that makes toluene more easily oxidised than benzene (which is inert to $KMnO_4$). Electron-donating p-substituents accelerate side-chain oxidation; strong electron-withdrawers ($-NO_2$) slow it down. So the test "vigorous $KMnO_4$ cuts every benzylic side chain" is qualitatively right but rate-sensitive in practice.

Exam relevance. Structure-elucidation questions like this are a CBSE 5-mark staple. Marks split: 1 for molecular formula arithmetic, 1 for each functional-group test interpretation, 1 for the final structure. Show your atom-counting work explicitly.

Why this matters. Side-chain oxidation always cuts back to the ring carbon, no matter how long the alkyl. So an ortho-ethyl becomes an ortho-COOH, locking the substitution pattern.

Final Answer: Compound: **2-Ethylbenzaldehyde**.

Q 8.11 An organic compound (A) (molecular formula $C_8H_{16}O_2$) was hydrolysed with dilute sulphuric acid to give a carboxylic acid (B) and an alcohol (C). Oxidation of (C) with chromic acid produced (B). (C) on dehydration gives but-1-ene. Write equations for the reactions involved.

SOLUTION

Concept used. Acidic hydrolysis of an ester $R{-}COO{-}R$ gives a carboxylic acid $R{-}COOH$ (B) and an alcohol $R{-}OH$ (C). Two extra clues fix B and C:

- Oxidation of $R{-}OH$ to a *carboxylic acid* (with $CrO_{3/}H_2SO_4$, chromic acid) means $R{-}OH$ is a *primary* alcohol.
- Since B is the oxidation product of C, B is the carboxylic acid corresponding to C: $R{-}CH_2OH \rightarrow R{-}COOH$. So $R = R\,({-}CH_2)$ in atom count, i.e. B has the same carbon count as C.
- Dehydration of C gives but-1-ene $CH_3CH_2CH{=}CH_2$; therefore $C = CH_3CH_2CH_2CH_2OH$ (butan-1-ol; a primary butanol that dehydrates to terminal but-1-ene).

Step 1. Set (C) $= CH_3CH_2CH_2CH_2OH$. Oxidation with $CrO_{3/}H_2SO_4$:

$$CH_3CH_2CH_2CH_2OH -[CrO_3, H_2SO_4]\, CH_3CH_2CH_2COOH,$$

so (B) $= CH_3CH_2CH_2COOH$ (butanoic acid).

Step 2. Reconstruct (A). The ester of B and C is butyl butanoate:

$$(A) = CH_3CH_2CH_2{-}COO{-}CH_2CH_2CH_2CH_3.$$

Verify formula: $C_3H_7{-}COO{-}C_4H_9 = C_8H_{16}O_2$. ✓

Step 3. Acidic hydrolysis (dil. H_2SO_4):

$$CH_3CH_2CH_2COOC_4H_9 + H_2O \longrightarrow$$
$$CH_3CH_2CH_2COOH + CH_3CH_2CH_2CH_2OH.$$

Step 4. Oxidation of (C):

$$CH_3CH_2CH_2CH_2OH -[CrO_{3/}H_2SO_4]\, CH_3CH_2CH_2COOH.$$

Step 5. Dehydration of (C):

$$CH_3CH_2CH_2CH_2OH -[\mathrm{conc}\cdot\ H_2SO_4, 443\,K]\, CH_3CH_2CH{=}CH_2{+}H_2O\ (\text{but-1-ene}).$$

Final Answer: (A) butyl butanoate $C_3H_7COOC_4H_9$; (B) butanoic acid; (C) butan-1-ol.

♥ Ester hydrolysis in everyday chemistry

Ester hydrolysis is the chemistry of fats and oils (saponification), lipase action in the stomach, the breakdown of aspirin to salicylic acid, and many industrial processes. Recognising a $C_8H_{16}O_2$ saturated formula as "ester or acid" is the first step of every problem of this type.

✗ Same carbon count is a hint, not a rule

The clue "oxidation of (C) gives (B)" fixes the carbon count of (B) = (C), but not the carbon count split between (B) and (C) in (A). Students often write a "methyl heptanoate" ($CH_3{-}OOC{-}C_6H_{13}$) and discover their alcohol can't dehydrate to but-1-ene. Always cross-check both clues (oxidation product and dehydration product) before committing to a structure.

☞ Two-step decoding

The fastest way to solve ester structure-elucidation problems: (1) Find the alcohol C from its alkene (the dehydration product points back to the parent alcohol's skeleton); (2) Oxidise C in your head to get B; (3) Combine B + C as an ester to get A; (4) Verify by molecular formula. Four short steps, never more.

EXPERT'S SOLUTION *: Sneha Patel, M.Sc Physical Chemistry, IIT Madras*

Quick reading. $C_8H_{16}O_2$, DoU $= 1 \Rightarrow$ one π-bond, so either ester or acid. "Hydrolyses to acid + alcohol" fixes it as an ester. The alcohol dehydrates to but-1-ene, fixing C = butan-1-ol. Then B = oxidation product of C = butanoic acid, so A is butyl butanoate.
Alternative approach (Saytzeff rule check). But-1-ene is the *less-substituted* alkene; if C were sec-butanol ($CH_3CH(OH)CH_2CH_3$), Saytzeff dehydration would give the *more*-substituted but-2-ene as the major product, not but-1-ene. So C must be a primary alcohol where the only possible alkene is the terminal one — butan-1-ol. This Saytzeff cross-check rules out the secondary isomer immediately.

Step 1. C: but-1-ene comes from $CH_3CH_2CH_2CH_2OH$ via $-H_2O$ (no rearrangement at 443 K).

Step 2. B: $CH_3CH_2CH_2CH_2OH -[CrO_3/H_2SO_4]\ CH_3CH_2CH_2COOH$. Chromic acid is a strong oxidiser: primary alcohol → carboxylic acid, secondary alcohol → ketone.

Step 3. A: connect B and C as an ester: $CH_3CH_2CH_2{-}COO{-}CH_2CH_2CH_2CH_3$ via Fischer esterification.

Step 4. Verify $C_8H_{16}O_2$: $C_3H_7COOC_4H_9 = C_8H_{16}O_2$. ✓ DoU $= 1$ matches the ester $C{=}O$.

Concept linkage with oxidation–reduction map. The

$\mathrm{R{-}CH_2OH} \to \mathrm{R{-}CHO} \to \mathrm{R{-}COOH}$ ladder is the standard oxidation map for primary alcohols. Mild oxidants (PCC, MnO_2) stop at the aldehyde; strong oxidants (CrO_3/H_2SO_4, hot acidic $\mathrm{KMnO_4}$) go to the carboxylic acid. Knowing which oxidant stops where is essential for selective synthesis.
Exam relevance. Three-step structure-elucidation problems are a classic CBSE 5-mark question. Show molecular formula verification (atom-counting) at the end — it earns a separate mark.
Why this matters. Pattern: *acid + primary alcohol of the same carbon count and the alcohol → alkene with terminal double bond* fixes the alcohol as the unbranched primary one.

> **Final Answer:** A: butyl butanoate; B: butanoic acid; C: butan-1-ol.

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

SOLUTION

Concept used. Two effects govern these orderings:

- *Reactivity of a carbonyl towards* HCN depends on (a) the electrophilicity of the carbonyl carbon, which is *lowered* by electron-donating alkyl groups (+I), and (b) the steric crowding around the carbonyl carbon, which blocks the approaching $\mathrm{CN^-}$. Both effects make the reaction *slower* as alkyl size grows.
- *Acid strength* is fixed by the stability of the conjugate base $\mathrm{R{-}COO^-}$. Electron-withdrawing groups ($-\mathrm{I}$, $-\mathrm{M}$) stabilise the anion and increase acidity; electron-donating groups ($+\mathrm{I}$, $+\mathrm{M}$) destabilise it and decrease acidity. Inductive effects fall sharply with distance.

Step 1. (i) Crowding and $+I$ both reduce HCN addition. Acetaldehyde ($\mathrm{CH_3CHO}$, one methyl) is least hindered; Acetone ($\mathrm{(CH_3)_2CO}$, two methyls) is more hindered; Methyl tert-butyl ketone ($\mathrm{(CH_3)_3C{-}CO{-}CH_3}$) has one bulky $\mathrm{C(CH_3)_3}$;

Di-tert-butyl ketone ($[(CH_3)_3C]_2C{=}O$) has two bulky groups. Increasing reactivity:

$$\text{Di-}t\text{-Bu ketone} < \text{Me-}t\text{-Bu ketone} < \text{Acetone} < \text{Acetaldehyde}.$$

Step 2. (ii) Effects on acid strength:

- $CH_3CH_2CH(Br)COOH$: $-Br$ on α-C, strong $-I$, closest to COOH $\Rightarrow$ most acidic.
- $CH_3CH(Br)CH_2COOH$: $-Br$ on β-C, $-I$ acts at one more bond, less acidic.
- $CH_3CH_2CH_2COOH$ (butanoic acid): no $-I$; mild $+I$ from the alkyl chain.
- $(CH_3)_2CHCOOH$ (isobutyric acid): the branched $(CH_3)_2CH^-$ has *more* $+I$ than the straight $CH_3CH_2CH_2{}^-$; destabilises $-COO^-$ *more* $\Rightarrow$ least acidic.

Increasing acid strength:

$$\begin{aligned}&(CH_3)_2CHCOOH < CH_3CH_2CH_2COOH\\&\qquad < CH_3CH(Br)CH_2COOH < CH_3CH_2CH(Br)COOH.\end{aligned}$$

Step 3. (iii) Effects on para/meta-substituted benzoic acids:

- $-NO_2$ is a strong $-I, -M$ group; 3,4-dinitro stabilises $-COO^-$ more than 4-nitro alone.
- $-OCH_3$ para is a $+M$ donor; it destabilises $-COO^-$ via resonance into the ring.

Increasing acid strength:

$$\text{4-Methoxybenzoic} < \text{Benzoic} < \text{4-Nitrobenzoic} < \text{3,4-Dinitrobenzoic}.$$

Final Answer: (i) Di-t-Bu ketone < Methyl t-Bu ketone < Acetone < Acetaldehyde.
(ii) $(CH_3)_2CHCOOH < CH_3CH_2CH_2COOH < CH_3CH(Br)CH_2COOH < CH_3CH_2CH(Br)COOH$.
(iii) 4-Methoxybenzoic < Benzoic < 4-Nitrobenzoic < 3,4-Dinitrobenzoic.

★ Carboxylate resonance and pK_a

Removing H^+ from $R{-}COOH$ produces $R{-}COO^-$, which is stabilised by resonance over two equivalent O atoms. Anything that pulls electron density away from this anion ($-I, -M$) stabilises it and lowers pK_a (stronger acid). Anything that pushes electron density in ($+I$, $+M$) raises pK_a (weaker acid).

✗ Inductive falls fast with distance

Many students write β-bromo and α-bromo acids as roughly equally acidic. Actually, the inductive effect of a halogen falls by a factor of ~ 3 for every σ-bond it must travel. Quantitatively: α-chlorobutanoic acid has $pK_a \approx 2.86$, β-chloro ≈ 4.05, γ-chloro ≈ 4.52; butanoic acid $pK_a = 4.82$. So α-substitution makes a $\sim 100\times$ stronger acid than β-substitution. Distance matters.

EXPERT'S SOLUTION *: Karan Gupta, B.Tech Chemical Engineering, IIT Bombay*

Strategic angle. For (i), $+I$ and steric crowding both *reduce* HCN addition. For (ii), the closer the $-$I group to COOH, the stronger the acid; alkyl $+I$ groups weaken the acid in proportion to branching. For (iii), score each substituent: $-OCH_3$ ($+M$, para) weakens; $-NO_2$ ($-I, -M$) strengthens.

Alternative approach (numerical pK_a ladder for acid strength). The qualitative orderings here follow from real pK_a values:

- Isobutyric acid $pK_a = 4.86$; butanoic acid $pK_a = 4.82$.
- β-bromobutanoic acid $pK_a \approx 4.0$; α-bromobutanoic acid $pK_a \approx 2.97$.
- 4-Methoxybenzoic $pK_a = 4.47$; benzoic acid $pK_a = 4.20$; 4-nitrobenzoic $pK_a = 3.41$; 3,4-dinitrobenzoic acid $pK_a \approx 2.8$.

Lower pK_a = stronger acid. Practise placing real numbers on the ladder and the qualitative ordering becomes obvious.

☞ $-I$ vs $+M$ on para-substituted benzoic acids

$-NO_2$ has both $-I$ and $-M$ effects — both pull electron density away from $-COO^-$, stabilising the anion strongly. $-OCH_3$ has $-I$ (small, oxygen is electronegative) *but* also a stronger $+M$ effect (the oxygen lone pair pushes into the ring); the net push destabilises $-COO^-$ when para, so the acid is weaker than benzoic acid.

Concept linkage with carbonyl reactivity. For (i), HCN addition rate $\propto$ electrophilicity of carbonyl C. Electrophilicity decreases as more $+$I alkyl groups crowd around it (alkyl donates into the empty π^* of C=O, and also blocks the approach of CN^-). This is the same logic as "aldehydes are more reactive than ketones towards nucleophilic addition".

Step 1. (i) Order: **Di-t-Bu ketone** (most hindered; kinetically dead) $<$ **Me-t-Bu ketone** $<$ **Acetone** $<$ **Acetaldehyde** (least hindered, fastest).

Step 2. (ii) Branched alkyl ($+I$ strongest) $<$ straight chain ($+I$ smaller) $<$ β-bromo ($-I$ at distance) $<$ α-bromo ($-I$ closest). Net: lowest pK_a for the α-bromo compound.

Step 3. (iii) $-OCH_3$ para ($+M$ destabilises anion) $<$ H (benzoic, no substituent) $<$ one $-NO_2$ ($-I, -M$ stabilises) $<$ two $-NO_2$ groups (additive $-I, -M$).

Exam relevance. Acid-strength ordering is asked almost every CBSE year. Marks split: 1 mark for the correct sequence, 1 mark for naming the dominant effect ($\pm I$, $\pm M$, steric,

etc.). Always state which effect dominates.
Why this matters. The Hammett substituent effect is one of the few quantitative tools for predicting reactivity from structure. The orderings here are the qualitative form of that idea.

> **Final Answer:** Three orderings as listed above.

Q 8.13 Give simple chemical tests to distinguish between the following pairs of compounds.
(i) Propanal and Propanone (ii) Acetophenone and Benzophenone
(iii) Phenol and Benzoic acid (iv) Benzoic acid and Ethyl benzoate
(v) Pentan-2-one and Pentan-3-one (vi) Benzaldehyde and Acetophenone
(vii) Ethanal and Propanal

SOLUTION

Concept used. We use functional-group tests:

- *Tollens' / Fehling's* detect $-CHO$ (aldehydes give positive; ketones do not).
- *Iodoform test* $(NaOH/I_2)$ gives a yellow precipitate of CHI_3 when the molecule has a $CH_3{-}CO^-$ group or a $CH_3{-}CH(OH)^-$ group adjacent.
- $NaHCO_3$ reacts only with carboxylic acids (fizz of CO_2); phenols are too weak.
- *Neutral* $FeCl_3$ gives violet colour with phenol but not with benzoic acid.

Step 1. (i) **Propanal vs Propanone**: Tollens'. Propanal (CH_3CH_2CHO) gives a silver mirror; propanone (CH_3COCH_3) does not.

Step 2. (ii) **Acetophenone vs Benzophenone**: Iodoform. Acetophenone $(C_6H_5COCH_3)$ has CH_3CO^- and gives yellow CHI_3; benzophenone $((C_6H_5)_2C{=}O)$ does not.

Step 3. (iii) **Phenol vs Benzoic acid**: $NaHCO_3$. Benzoic acid fizzes (CO_2); phenol does not. Or neutral $FeCl_3$: phenol gives violet; benzoic acid gives a buff precipitate of ferric benzoate.

Step 4. (iv) **Benzoic acid vs Ethyl benzoate**: $NaHCO_3$. Benzoic acid fizzes; ethyl benzoate $(C_6H_5COOC_2H_5)$ does not.

Step 5. (v) **Pentan-2-one vs Pentan-3-one**: Iodoform. Pentan-2-one $(CH_3COCH_2CH_2CH_3)$ has CH_3CO^- and gives CHI_3 (yellow); pentan-3-one $(C_2H_5COC_2H_5)$ has no methyl ketone group and gives no precipitate.

Step 6. (vi) **Benzaldehyde vs Acetophenone**: Tollens'. Benzaldehyde gives silver mirror; acetophenone does not.

Step 7. (vii) **Ethanal vs Propanal**: Iodoform. Ethanal (CH_3CHO) gives CHI_3; propanal (CH_3CH_2CHO) does not.

> **Final Answer:** (i) Tollens' (propanal +); (ii) Iodoform (acetophenone +); (iii) $NaHCO_3$ (benzoic acid +); (iv) $NaHCO_3$ (benzoic acid +); (v) Iodoform (pentan-2-one +); (vi) Tollens' (benzaldehyde +); (vii) Iodoform (ethanal +).

☞ Pick the most specific test

When two tests could work, prefer the one whose colour change or precipitate is unmistakable: silver mirror, yellow CHI_3, fizz with $NaHCO_3$, violet with neutral $FeCl_3$. Avoid ambiguous colour changes.

✗ Tollens' has limits Fehling doesn't share

Tollens' is positive for both aliphatic and aromatic aldehydes. Fehling's reagent, however, is positive *only for aliphatic aldehydes* — aromatic aldehydes like benzaldehyde give a *negative* Fehling test. Don't write "Benzaldehyde gives a red precipitate with Fehling" — it gives *no* precipitate. Similarly, α, β-unsaturated aliphatic aldehydes give a sluggish, partial Fehling response.

EXPERT'S SOLUTION *: Vivaan Singh, M.Sc Chemistry, IIT Kanpur*

Quick reading. Three tools cover the table:

- Tollens' (or Fehling) distinguishes $-CHO$ from no $-CHO$.
- Iodoform distinguishes CH_3CO^- / $CH_3CH(OH)^-$ from not.
- $NaHCO_3$ distinguishes $-COOH$ from $-OH$ / ester.

Alternative approach (functional-group signature card). Build a one-line mental signature for each test:

- Tollens': silver mirror (visible Ag^0 on inner wall), $R-CHO$ only.
- Fehling: brick-red Cu_2O precipitate, aliphatic $R-CHO$ only.
- Iodoform: yellow CHI_3 precipitate (m.p. 119 °C), CH_3CO-R or $CH_3CH(OH)-R$ only.
- $NaHCO_3$: brisk effervescence of CO_2, $R-COOH$ only.
- Neutral $FeCl_3$: violet/purple colour, phenols (and enols).

☞ **Mechanism of the iodoform test**

I_2 in NaOH triply iodinates the methyl group of a methyl ketone to give $R-CO-CI_3$; hydroxide then cleaves the $C-C$ bond, releasing the stable trihalomethanide CI_3^- (which picks up a proton to give iodoform CHI_3, a yellow solid). For $CH_3CH(OH)R$ substrates, $I_{2/}NaOH$ first oxidises the alcohol to the methyl ketone, then the same cleavage runs. This is why both functional groups give a positive iodoform.

Concept linkage with the oxidation/reduction map. Tollens' and Fehling are mild oxidants that take $-CHO \rightarrow -COOH$ without touching $C=C$. Iodoform is a haloform cleavage: a $C-C$ bond breaks, producing a carboxylate and the methyl ketone is shortened by one carbon. $NaHCO_3$ is purely acid-base. Knowing the chemistry (not just the observation) tells you which test to pick.

Step 1. Tollens' fires for: (i) propanal, (vi) benzaldehyde. Aliphatic propanal gives *both* Tollens' *and* Fehling; benzaldehyde gives only Tollens'.

Step 2. Iodoform fires for: (ii) acetophenone (has CH_3-CO^-), (v) pentan-2-one (has CH_3-CO^-), (vii) ethanal (has CH_3-CHO).

Step 3. $NaHCO_3$ fires for: (iii) benzoic acid (vs phenol), (iv) benzoic acid (vs ester).

Exam relevance. CBSE has asked this exact 7-pair question in 2018, 2020 and 2023. Marking: 1 mark per pair (must state the reagent *and* the visible observation). Write both. Saying "Tollens' positive" alone scores 0.5; saying "Tollens' — silver mirror with propanal, no change with propanone" earns full marks.
Why this matters. A small kit of three reagents distinguishes seven different aldehyde/ketone/acid/phenol pairs. Recognising what the test detects is more important than memorising each case.

Final Answer: Tests as above for all seven pairs.

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

SOLUTION

Concept used. "One-carbon reagent" means we may use CH_4, CH_3OH, CH_3Cl, CH_3COCl, CO, HCN, HCHO, etc., but not C_2H_5OH. The intermediates $C_6H_5CH_3$

(toluene) and C_6H_5COOH (benzoic acid) are workhorses because:

- $-CH_3$ on benzene is *ortho/para directing* and activates the ring.
- $-COOH$ is *meta directing* and deactivates the ring.
- Side-chain oxidation: $Ar{-}CH_3 -[KMnO_4]\, Ar{-}COOH$.

Step 1. (i) **Methyl benzoate** $C_6H_5COOCH_3$.

1. Friedel-Crafts methylation: $C_6H_6 + CH_3Cl -[AlCl_3]\, C_6H_5CH_3$ (toluene).
2. Side-chain oxidation: $C_6H_5CH_3 -[KMnO_4, OH^-, \Delta]\, C_6H_5COOH$.
3. Fischer esterification: $C_6H_5COOH + CH_3OH -[H^+]\, C_6H_5COOCH_3$.

Step 2. (ii) **m-Nitrobenzoic acid**. Convert benzene → toluene as above, then oxidise to benzoic acid. $-COOH$ is *meta* directing, so nitration places NO_2 at the 3-position: $C_6H_5COOH -[HNO_3/H_2SO_4]\, m\text{-}O_2N{-}C_6H_4{-}COOH$.

Step 3. (iii) **p-Nitrobenzoic acid**. Reverse the order: nitrate *toluene* first (since $-CH_3$ is o/p directing, the major product is *p*-nitrotoluene), then oxidise the methyl: $C_6H_5CH_3 -[HNO_3/H_2SO_4]\, p\text{-}O_2N{-}C_6H_4{-}CH_3 -[KMnO_4]\, p\text{-}O_2N{-}C_6H_4{-}COOH$.

Step 4. (iv) **Phenylacetic acid** $C_6H_5CH_2COOH$.

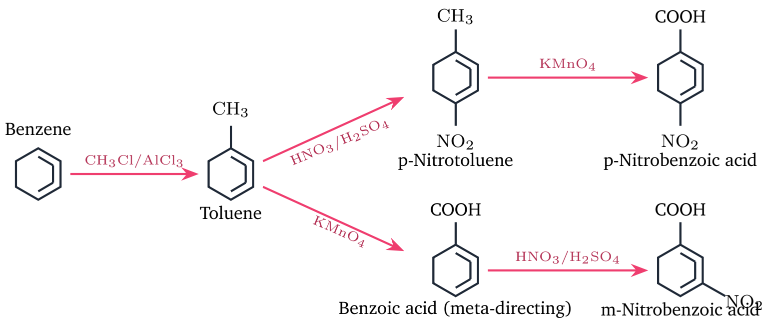
1. Methylate benzene → toluene.
2. Side-chain chlorination: $C_6H_5CH_3 + Cl_2 -[h\nu]\, C_6H_5CH_2Cl$ (benzyl chloride).
3. Nucleophilic substitution with KCN:
   $C_6H_5CH_2Cl + KCN - C_6H_5CH_2CN + KCl$.
4. Hydrolyse the nitrile: $C_6H_5CH_2CN \xrightarrow{H_3O^+,\ \Delta} C_6H_5CH_2COOH$.

Step 5. (v) **p-Nitrobenzaldehyde**.

1. Toluene → *p*-nitrotoluene (HNO_3/H_2SO_4, major *para*).
2. Side-chain dibromination:
   $p\text{-}O_2N{-}C_6H_4{-}CH_3 -[Br_2/h\nu, 2\,eq]\, p\text{-}O_2N{-}C_6H_4{-}CHBr_2$.
3. Hydrolysis of the gem-dihalide:
   $p\text{-}O_2N{-}C_6H_4{-}CHBr_2 + H_2O - p\text{-}O_2N{-}C_6H_4{-}CHO + 2\,HBr$.

Alternative: Etard reaction on *p*-nitrotoluene (CrO_2Cl_2 in CS_2) gives the chromium adduct which hydrolyses to the aldehyde.

Directing effect routes (key disconnection):



Final Answer: Five syntheses as written; the order (oxidise then nitrate vs nitrate then oxidise) is what controls *meta* (ii) versus *para* (iii).

♥ Directing-group sequencing

This question is really about choosing the right order so that the directing effect of the substituent points the next reagent to the desired position. *Oxidise then nitrate* when you want *meta*; *nitrate then oxidise* when you want *para*.

✗ Friedel–Crafts fails on strongly deactivated rings

You cannot Friedel–Crafts on nitrobenzene (or on benzoic acid) — the $-NO_2$ / $-COOH$ deactivate the ring so strongly that $AlCl_3$ doesn't push the electrophile onto it. So sequences like "nitrate benzene, then Friedel–Crafts methylate" fail. The correct order for (i) is methylate first (when ring is unsubstituted and reactive), oxidise, then esterify. Don't reverse Friedel–Crafts and oxidation.

EXPERT'S SOLUTION : *Riya Chatterjee, Ph.D Organic Chemistry, IIT Madras*

Strategic angle. Pin the central question: what directs the electrophile to the right position? $-CH_3$ on the ring is o/p directing (activator); $-COOH$ is meta directing (deactivator). This single rule decides every sequence.

Alternative approach (work backwards from the target). For each target, identify the last functional-group install:

- Methyl benzoate $\rightarrow$ esterify $COOH$ $\rightarrow$ make $COOH$ from CH_3 $\rightarrow$ start from benzene $\rightarrow$ toluene.
- m-Nitrobenzoic acid $\rightarrow$ nitrate benzoic acid (meta-direct) $\rightarrow$ make benzoic acid first.
- p-Nitrobenzoic acid $\rightarrow$ oxidise p-nitrotoluene (already-installed o/p-directing methyl decides para) $\rightarrow$ nitrate toluene.
- Phenylacetic acid $\rightarrow$ hydrolyse $-CN$ $\rightarrow$ install $-CN$ from $-Cl$ $\rightarrow$ benzylic chlorination of toluene.
- p-Nitrobenzaldehyde $\rightarrow$ hydrolyse $-CHBr_2$ or use Etard on p-nitrotoluene $\rightarrow$ nitrate toluene to install NO_2 para.

☞ Etard reaction in one line

CrO_2Cl_2 (chromyl chloride) in CS_2 converts $Ar-CH_3$ to a chromium–ester intermediate that on aqueous workup gives $Ar-CHO$. Stops cleanly at the aldehyde (because the intermediate is base-stable). Great for (v).

Concept linkage — the directing-effect map. Activators ($-CH_3$, $-OH$, $-NH_2$, $-OR$) are o/p directors; deactivators except halogens are meta directors. Halogens are an exception: deactivators but o/p directors. For multi-step benzene synthesis the rule is simple: install activators before running another electrophilic substitution; install deactivators last (or use them as meta-directors).

Step 1. (i) Friedel–Crafts methylation, then $\mathrm{KMnO_4}$ oxidation (side-chain to $-\mathrm{COOH}$), then Fischer esterification with $\mathrm{CH_3OH}/H+$.

Step 2. (ii) Get to benzoic acid first ($-\mathrm{COOH}$ meta-directs); nitrate (HNO_3/H_2SO_4) gives m-nitrobenzoic acid.

Step 3. (iii) Nitrate toluene first ($-\mathrm{CH_3}$ o/p-directs; *para* is the major thermodynamic product because of steric reasons); oxidise side chain second.

Step 4. (iv) Toluene → benzyl chloride ($\mathrm{Cl_2}/h\nu$, free-radical) $\rightarrow \mathrm{C_6H_5CH_2CN}$ (KCN, SN2) $\rightarrow \mathrm{C_6H_5CH_2COOH}$ (hydrolysis with aq. $\mathrm{H_2SO_4}$ or NaOH then acidify).

Step 5. (v) Toluene → p-nitrotoluene (nitration, o/p) → Etard (or double side-chain bromination with $\mathrm{Br_2}/h\nu$ then hydrolysis) gives p-nitrobenzaldehyde.

Exam relevance. Multi-step synthesis is a 5-mark CBSE classic. Marking scheme: 1 mark per correctly named reagent; candidates lose marks for forgetting to label "meta" or "para" explicitly under the structure.

Why this matters. Sequence matters as much as reagents in electrophilic aromatic substitution; one swap of order changes *meta* to *para* and the whole synthesis.

> **Final Answer:** Five-step routes as written; choice of order is the key synthetic decision.

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

(i) Propanone to Propene
(ii) Benzoic acid to Benzaldehyde
(iii) Ethanol to 3-Hydroxybutanal
(iv) Benzene to m-Nitroacetophenone
(v) Benzaldehyde to Benzophenone
(vi) Bromobenzene to 1-Phenylethanol
(vii) Benzaldehyde to 3-Phenylpropan-1-ol
(viii) Benzaldehyde to a-Hydroxyphenylacetic acid
(ix) Benzoic acid to m-Nitrobenzyl alcohol

SOLUTION

Concept used. Each two-step conversion uses one carbonyl or aromatic reaction followed by a workup transformation. Key named procedures used here:

- *Clemmensen reduction* $Zn(Hg)/HCl$: $C{=}O \rightarrow CH_2$.
- *Rosenmund reduction* $H_{2/}Pd{-}BaSO_4$: $RCOCl \rightarrow RCHO$.
- *Aldol condensation* of two carbonyls.
- *Grignard reaction*: $RMgX + R{-}CHO/R{-}CO{-}R \rightarrow$ alcohol.
- *Friedel-Crafts acylation*: $ArH + RCOCl/AlCl_3 \rightarrow ArCOR$.

Step 1. (i) **Propanone → Propene**.

$$(CH_3)_2C{=}O -[NaBH_4]\ (CH_3)_2CHOH -[conc \cdot\ H_2SO_4, \Delta]\ CH_3CH{=}CH_2.$$

Step 2. (ii) **Benzoic acid → Benzaldehyde**.
$C_6H_5COOH -[SOCl_2]\ C_6H_5COCl -[H_2, Pd{-}BaSO_4]\ C_6H_5CHO$ (Rosenmund).

Step 3. (iii) **Ethanol → 3-Hydroxybutanal**.
$CH_3CH_2OH -[K_2Cr_2O_{7/}H^+]\ CH_3CHO -[dil \cdot\ NaOH]\ CH_3CH(OH)CH_2CHO$ (self-aldol).

Step 4. (iv) **Benzene → m-Nitroacetophenone**. Friedel-Crafts first (acetophenone), then nitrate (acetyl is meta directing): $C_6H_6 + CH_3COCl -[AlCl_3]\ C_6H_5COCH_3 -[HNO_{3/}H_2SO_4]\ m\text{-}O_2N{-}C_6H_4{-}COCH_3$.

Step 5. (v) **Benzaldehyde → Benzophenone**. Add PhMgBr to benzaldehyde, then oxidise:
$C_6H_5CHO + C_6H_5MgBr -[H_3O^+]\ (C_6H_5)_2CHOH -[K_2Cr_2O_7]\ (C_6H_5)_2C{=}O$.

Step 6. (vi) **Bromobenzene → 1-Phenylethanol**. Make Grignard, add to ethanal:
$C_6H_5Br -[Mg/Et_2O]\ C_6H_5MgBr -[CH_3CHO, \text{then}\ H_3O^+]\ C_6H_5CH(OH)CH_3$.

Step 7. (vii) **Benzaldehyde → 3-Phenylpropan-1-ol**. Cross-aldol with ethanal then reduce: $C_6H_5CHO + CH_3CHO -[dil \cdot\ NaOH]\ C_6H_5CH{=}CHCHO -[H_{2/}Pd]\ C_6H_5CH_2CH_2CH_2OH$.

Step 8. (viii) **Benzaldehyde → a-Hydroxyphenylacetic acid** (mandelic acid). Cyanohydrin then acid hydrolysis: $C_6H_5CHO + HCN \longrightarrow C_6H_5CH(OH)CN \xrightarrow{H_3O^+,\ \Delta} C_6H_5CH(OH)COOH$.

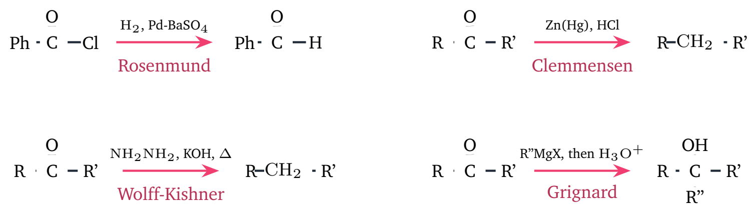
Step 9. (ix) **Benzoic acid → m-Nitrobenzyl alcohol**. Nitrate first (benzoic acid is meta directing), then reduce $-COOH$ with $LiAlH_4$: Nitrate ($HNO_{3/}H_2SO_4$):

$$C_6H_5COOH \longrightarrow m\text{-}O_2N{-}C_6H_4{-}COOH$$

Reduce with $LiAlH_4$:

$$m\text{-}O_2N{-}C_6H_4{-}COOH \longrightarrow m\text{-}O_2N{-}C_6H_4{-}CH_2OH.$$

Key named reductions illustrated:



$$Ph-\overset{O}{C}-Cl \xrightarrow[\text{Rosenmund}]{H_2,\ Pd\text{-}BaSO_4} Ph-\overset{O}{C}-H \qquad R-\overset{O}{C}-R' \xrightarrow[\text{Clemmensen}]{Zn(Hg),\ HCl} R-CH_2-R'$$

$$R-\overset{O}{C}-R' \xrightarrow[\text{Wolff-Kishner}]{NH_2NH_2,\ KOH,\ \Delta} R-CH_2-R' \qquad R-\overset{O}{C}-R' \xrightarrow[\text{Grignard}]{R''MgX,\ \text{then}\ H_3O^+} R-\underset{R''}{\overset{OH}{C}}-R'$$

Final Answer: Nine two-step conversions as written above.

☞ Why two steps

The skill being tested is to spot the *shortest* route by recognising one named operation per step. If you find yourself writing three or four steps, look for a Grignard, an aldol, a Rosenmund or a Clemmensen that compresses the route.

♥ Rosenmund and the stop-at-aldehyde problem

A common synthesis need is to convert $R-COOH$ to $R-CHO$. Catalytic hydrogenation usually goes all the way to $R-CH_2OH$. Rosenmund stops at the aldehyde because (i) the $R-COCl$ is much more reactive than $R-CHO$, so H_2 adds selectively to the acid chloride first; (ii) Pd-$BaSO_4$ is "poisoned" (S, quinoline) to slow it down enough that the aldehyde doesn't get reduced further. This is the classical selective-poisoning idea in catalysis.

EXPERT'S SOLUTION *: Meera Pillai, M.Sc Chemistry, IIT Kanpur*

Quick reading. Group the conversions by the central operation.

- Reductions: (i), (ii), (ix).
- Aldols: (iii), (vii).
- Grignards: (v), (vi).
- Cyanohydrin: (viii).
- Aromatic sequence: (iv).

Alternative approach (named reactions as one-step compressors). Each line below is a one-step name that compresses what otherwise would take 3-4 elementary steps:

- Rosenmund = $R-COCl + H_2 \rightarrow R-CHO$ (stops at aldehyde because Pd-$BaSO_4$ is poisoned).
- Clemmensen = $R_2C{=}O \rightarrow R_2CH_2$ in acidic conditions.
- Wolff–Kishner = same in basic conditions.
- Aldol = build $C-C$ bond between α-C and carbonyl-C.
- Friedel–Crafts = install acyl/alkyl on benzene ring.
- Grignard = make secondary/tertiary alcohol from aldehyde or ketone + $RMgX$.

- Cyanohydrin → acid = HCN adds, then hydrolyse $-CN$ to $-COOH$; raises carbon count by 1.

☞ Why aldol + catalytic H_2 gives a fully-saturated alcohol

After cross-aldol $PhCHO + CH_3CHO$, the β-hydroxy aldehyde dehydrates to $PhCH{=}CHCHO$ (cinnamaldehyde). H_2/Ni then adds across *both* $C{=}C$ and $C{=}O$, giving the primary alcohol $PhCH_2CH_2CH_2OH$ (3-phenylpropan-1-ol). Mild $NaBH_4$ would have reduced only the $C{=}O$, leaving cinnamyl alcohol.

Concept linkage — the reduction selectivity ladder. Strength order: $LiAlH_4 > NaBH_4 \gg H_2/Pd{-}BaSO_4 > NaBH_4/CeCl_3 >$ Rosenmund (poisoned). The stronger the reductant, the less selective. For multi-functional substrates pick the gentlest reductant that still does the job.

Step 1. (i) $(CH_3)_2CO -[NaBH_4]\, (CH_3)_2CHOH -[H^+, \Delta]\, CH_3CH{=}CH_2$.

Step 2. (ii) $PhCOOH -[SOCl_2]\, PhCOCl -[H_2/Pd{-}BaSO_4]\, PhCHO$. (Rosenmund.)

Step 3. (iii) $EtOH \xrightarrow{Cr_2O_7{}^{2-}/H^+} CH_3CHO \xrightarrow{OH^-} CH_3CH(OH)CH_2CHO$. (Self-aldol of acetaldehyde.)

Step 4. (iv)
$C_6H_6 -[CH_3COCl/AlCl_3]\, PhCOCH_3 -[HNO_3/H_2SO_4]\, m\text{-}O_2N{-}C_6H_4{-}COCH_3$.
The $-COCH_3$ is meta-directing, fixing nitration position.

Step 5. (v) $PhCHO + PhMgBr -[H_3O^+]\, Ph_2CHOH -[K_2Cr_2O_7]\, Ph_2C{=}O$. Grignard + oxidation.

Step 6. (vi) $PhBr -[Mg]\, PhMgBr -[CH_3CHO, H_3O^+]\, PhCH(OH)CH_3$. Grignard route to a secondary alcohol.

Step 7. (vii) $PhCHO + CH_3CHO -[OH^-]\, PhCH{=}CHCHO -[H_2/Ni]\, PhCH_2CH_2CH_2OH$. Cross-aldol + reduction.

Step 8. (viii) $PhCHO -[HCN]\, PhCH(OH)CN -[H_3O^+]\, PhCH(OH)COOH$. Cyanohydrin route to mandelic acid.

Step 9. (ix)
$PhCOOH -[HNO_3/H_2SO_4]\, m\text{-}O_2N{-}PhCOOH -[LiAlH_4]\, m\text{-}O_2N{-}PhCH_2OH$.
Nitrate first, then reduce the acid.

Exam relevance. The CBSE pattern: 1 mark per conversion (reagents + product), bonus 1-2 marks for naming the reaction (“Rosenmund”, “Clemmensen”, etc.). Always label.

Why this matters. Routine syntheses use a tiny toolbox: Rosenmund, Clemmensen, aldol, Grignard, cyanohydrin, Friedel-Crafts. Knowing what each step does and what it leaves alone makes 2-step problems easy.

Final Answer: Same nine sequences as in the main solution.

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

SOLUTION

Concept used. Four named reactions of carbonyls and carboxylic acids:

Step 1. (i) **Acetylation**: introduction of an acetyl group (CH_3CO^-) by reaction with acetic anhydride ($(CH_3CO)_2O$) or acetyl chloride (CH_3COCl), usually catalysed by pyridine. Targets alcohols, phenols and amines.

$$R{-}OH + (CH_3CO)_2O -[\text{pyridine}]\, R{-}O{-}COCH_3 + CH_3COOH.$$

$$Ar{-}NH_2 + CH_3COCl -[\text{pyridine}]\, Ar{-}NH{-}COCH_3 + HCl.$$

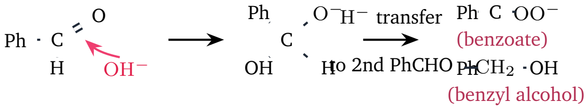
Acetylation protects $-OH$ and $-NH_2$ as the much less reactive acetate and amide.

Step 2. (ii) **Cannizzaro reaction**: disproportionation of an aldehyde with no α-H by concentrated $NaOH$. One molecule is oxidised to a carboxylate, the other reduced to an alcohol:

$$2\,HCHO -[\text{conc}\cdot\ NaOH]\, CH_3OH + HCOO^-Na^+,$$

$$2\,C_6H_5CHO -[\text{conc}\cdot\ NaOH]\, C_6H_5CH_2OH + C_6H_5COO^-Na^+.$$

Mechanism: OH^- adds to one $C{=}O$, then the tetrahedral intermediate transfers H^- (hydride) to a second aldehyde.



Step 3. (iii) **Cross aldol condensation**: aldol between two *different* carbonyls. Useful only when one carbonyl has no α-H (e.g. HCHO, PhCHO) so it acts only as the electrophile; the other provides the enolate. Example:

$$C_6H_5CHO + CH_3CHO -[\text{dil}\cdot\ NaOH]\, C_6H_5CH{=}CH{-}CHO + H_2O,$$

producing cinnamaldehyde after dehydration.

Step 4. (iv) **Decarboxylation**: loss of CO_2 from a carboxylic acid. The classical preparation heats the sodium salt with soda lime ($NaOH/CaO$):

$$R{-}COONa + NaOH -[CaO, \Delta]\, R{-}H + Na_2CO_3.$$

Aromatic example: $C_6H_5COONa + NaOH -[CaO, \Delta]\, C_6H_6 + Na_2CO_3$. β-Keto acids and malonic-acid derivatives lose CO_2 on mild heating without soda lime.

Final Answer: Acetylation: install CH_3CO^-. Cannizzaro: disproportionation of α-Hless aldehydes. Cross aldol: aldol between two different carbonyls. Decarboxylation: $-COOH \rightarrow -H + CO_2$.

☞ Disproportionation in Cannizzaro — both products are correct

A common 2-mark trap: students write only the alcohol or only the carboxylate. Cannizzaro is a *disproportionation*, so *both* products must be shown in the same equation, with the 1:1 stoichiometry. Mark scheme: 1 mark for each product.

EXPERT'S SOLUTION : *Ananya Desai, Ph.D Organic Chemistry, IISc Bangalore*

Quick reading. Four small ideas with a shared theme: building or breaking $C-C$ and $C-O$ bonds at the carbonyl carbon.

Alternative approach (functional-group matrix). Sort each "describe" by what bond changes and where:

- Acetylation: new $C(O)-O$ or $C(O)-N$ bond on a nucleophile (OH/NH_2); no change at the carbonyl carbon of the acetyl group.
- Cannizzaro: new $C-H$ bond (hydride transfer to carbonyl) and new $C-O$ (in carboxylate); breaks the $C-H$ of the donor's $-CHO$.
- Cross aldol: new $C-C$ bond between α-C of one and carbonyl-C of the other; can be followed by β-elimination.
- Decarboxylation: breaks $C-C$ between the carboxylate carbon and the next.

☞ Why pyridine in acetylation

Pyridine has two jobs: (i) it neutralises the HCl or CH_3COOH produced (otherwise the by-product would protonate the amine and stop the reaction); (ii) it acts as a nucleophilic catalyst, forming a transient pyridinium acyl cation that is a better acetylating agent than acetyl chloride itself. Without pyridine, amines and phenols are slow to acetylate.

☞ Cannizzaro mechanism in three steps

Step 1: OH^- adds to a $C{=}O$, forming a tetrahedral alkoxide. Step 2: this alkoxide transfers its $C-H$ hydride to a second aldehyde's carbonyl carbon. Step 3: deprotonate the oxidised molecule (now a carboxylic acid) by base, giving the carboxylate + the alcohol from step 2. The disproportionation is intermolecular, and the slow step is hydride transfer.

Concept linkage — acetylation and amide/ester chemistry. Acetylation of an alcohol gives an ester, of an amine gives an amide. Both are protective: an amide doesn't react with electrophiles the way an amine does; an ester doesn't react with bases the way an alcohol does. This protective use links into the synthesis strategy in Q 8.14–8.17.

Step 1. Phenol → phenyl acetate by acetic anhydride/pyridine. Aniline → acetanilide. Acetanilide deactivates the ring enough to allow controlled mono-bromination.

Step 2. HCHO disproportionates to $CH_3OH + HCOO^-$. Industrial source of sodium formate.

Step 3. Benzaldehyde + ethanal → cinnamaldehyde (clean cross aldol because PhCHO has no α-H, so only ethanal can be the nucleophile).

Step 4. Sodium benzoate + soda lime → benzene + Na_2CO_3. The classical lab prep of benzene from benzoic acid.

Exam relevance. Definition-style questions are 4 marks (1×4). Marks split: 1 mark per definition with 1 example each. Definitions without examples score only half marks.

Why this matters. Each of these is a one-step transformation that you can drop into a multi-step synthesis. Acetylation protects; Cannizzaro makes both an alcohol and an acid at once; cross aldol builds a $C-C$ bond; decarboxylation strips an acid group.

> **Final Answer:** Definitions plus one example each, as above.

Q 8.17 **Complete each of the following syntheses by giving the missing starting material, reagent or product.**

(A) $C_6H_5CHO + (CH_3CO)_2O - [CH_3COONa]$ (E) $- C_6H_5CH=CH-COOH$ (Perkin reaction)

(B) $C_6H_5-CH=CH-COCH_3 \overset{?}{\rightarrow} C_6H_5CH_2CH_2COCH_3$

(C) $CH_3CH(OH)CN \xrightarrow{H_3O^+,\ \Delta} CH_3CH(OH)COOH$

SOLUTION

Concept used. Three named reactions are missing from the syntheses; we fill each in.

- **Perkin condensation**: an aromatic aldehyde with an anhydride and the sodium salt of the corresponding acid gives an α, β-unsaturated acid (here cinnamic acid).
- **Selective reduction of an α, β-unsaturated ketone**: $C=C$ is reduced to $C-C$ while the $C=O$ remains. Use $H_{2/}Pd$ at controlled pressure.
- **Cyanohydrin hydrolysis**: the cyano group is hydrolysed to $-COOH$ by aqueous mineral acid on warming.

Step 1. (A) Perkin condensation. Full equation:

$$C_6H_5CHO+(CH_3CO)_2O-[CH_3COONa, \Delta]\ C_6H_5CH=CH-COOH+CH_3COOH.$$

Product: **cinnamic acid (*trans*)**.

Step 2. (B) The substrate $C_6H_5CH{=}CH{-}COCH_3$ (benzalacetone) has a $C{=}C$ and a $C{=}O$. To leave the ketone intact and reduce only the $C{=}C$, use $H_{2/}Pd$:

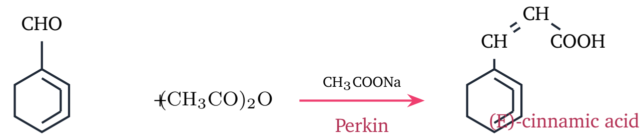
$$C_6H_5CH{=}CHCOCH_3 -[H_2, Pd{-}C]\, C_6H_5CH_2CH_2COCH_3.$$

Step 3. (C) Cyanohydrin hydrolysis. $-CN \to -COOH$ via an amide intermediate; mineral acid suffices:

$$CH_3CH(OH)CN + 2\,H_2O \xrightarrow{H_3O^+,\ \Delta} CH_3CH(OH)COOH + NH_3.$$

Product: **2-hydroxypropanoic acid (lactic acid)**.

Perkin reaction structures (E-cinnamic acid):



Final Answer: (A) Cinnamic acid via Perkin; (B) $H_{2/}Pd$ reduces $C{=}C$ keeping $C{=}O$ intact; (C) cyanohydrin hydrolysis gives lactic acid.

✗ Don't reduce $C{=}O$ along with $C{=}C$

For (B) one common error is to write "$H_{2/}Ni$" or "$LiAlH_4$". Both would reduce the $C{=}O$ along with the $C{=}C$. The correct chemoselective reagent here is H_2 over Pd/C at *controlled* pressure (1 atm, room temperature): Pd preferentially adsorbs the $C{=}C$ and reduces it, but does not touch the $C{=}O$ until the conditions are forced.

♥ Perkin gives *trans* cinnamic acid

The Perkin reaction is the standard route to cinnamic acid. It uses an acid anhydride as both the α-H source (the methyl of $(CH_3CO)_2O$ is the nucleophile) and the acylating agent. Acetate ion CH_3COO^- deprotonates the anhydride to give an enolate, which then attacks the aromatic aldehyde, followed by dehydration to the conjugated α,β-unsaturated acid in the more-stable *trans* geometry. Industrial flavour and fragrance chemistry uses this exact reaction.

EXPERT'S SOLUTION : *Dev Rao, M.Sc Physical Chemistry, IIT Madras*

Strategic angle. Identify the named transformation behind each blank: (A) Perkin synthesis of cinnamic acids; (B) chemoselective hydrogenation of $C{=}C$ over $C{=}O$; (C) nitrile-to-acid hydrolysis.

Alternative approach (functional-group bookkeeping). For each blank, write down the starting functional groups and the ending functional groups; the reagent must accomplish exactly the difference and no more.

- (A) Start: $ArCHO$ + anhydride. End: $ArCH{=}CH{-}COOH$. So we built a $C{-}C$ bond (aldol-like) and lost water — that's Perkin.
- (B) Start: $ArCH{=}CH{-}CO{-}CH_3$. End: $ArCH_2CH_2{-}CO{-}CH_3$. So we reduced $C{=}C$ but *not* $C{=}O$. Choose mild H_2/Pd-C.
- (C) Start: $R{-}CH(OH)CN$. End: $R{-}CH(OH)COOH$. So we hydrolysed $-CN$ to $-COOH$; aqueous mineral acid or aqueous NaOH/heat works.

☞ Cyanide hydrolysis goes through an amide

$R{-}CN -[H_2O, H^+]\, R{-}C(=NH)OH -[H_2O, H^+]\, R{-}CONH_2 -[H_2O, H^+]\, R{-}COOH + NH_3$.
The intermediate primary amide is sometimes isolable if you stop the reaction; full hydrolysis requires either strong acid + heat or strong base. The amide stage is more stable than the imino-acid stage because of partial double-bond character of the C–N bond.

Concept linkage — condensation + chemoselective reduction + hydrolysis. The three blanks span three of the most-asked exam reaction types. Recognising each as a single named transformation is the trick.

Step 1. Perkin: PhCHO + Ac_2O / NaOAc → *E*-cinnamic acid + acetic acid by-product.

Step 2. $H_{2/}Pd{-}C$ adds across $C{=}C$ first; ketone is untouched.

Step 3. Aqueous mineral acid converts $-CN$ to $-COOH$ through an amide intermediate; the product here is 2-hydroxypropanoic acid (lactic acid).

Exam relevance. CBSE 2019 and 2024 set fill-in-the-blank synthesis questions modelled on this. Marking: 1 mark for the correct reagent/product, 1 mark for naming the named reaction.
Why this matters. The three transformations span condensation, chemoselective reduction and hydrolysis, three of the most often tested classes of carbonyl chemistry.

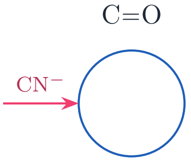
Final Answer: Three blanks filled as above.

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

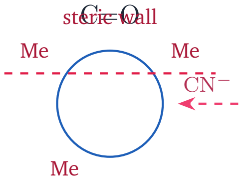
SOLUTION

Concept used. Three short conceptual points:

- Cyanohydrin formation is a nucleophilic addition to a carbonyl; its rate depends on (a) electrophilicity of the carbonyl carbon and (b) steric crowding at that carbon.
- Resonance can withdraw lone pairs from a nitrogen and remove its nucleophilicity.
- Esterification (Fischer) is reversible: $R{-}COOH + ROH \rightleftharpoons R{-}COOR + H_2O$. Le Chatelier's principle sets the forward yield.



Cyclohexanone (open)



2,2,6-Trimethylcyclohexanone

Step 1. (i) In cyclohexanone the $C{=}O$ is accessible, so CN^- attacks easily to give a high yield of cyanohydrin. In 2,2,6-trimethylcyclohexanone three methyl groups crowd the α-positions on both sides; the approaching CN^- cannot reach the carbonyl carbon, so the reaction stalls.

Step 2. (ii) In semicarbazide $H_2N{-}NH{-}CO{-}NH_2$ the right-hand $-NH_2$ (the one attached to CO) loses its lone pair to the $C{=}O$ by resonance:

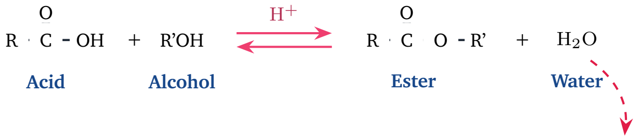
$$H_2N{-}NH{-}CO{-}NH_2 \longleftrightarrow H_2N{-}NH{-}C(O^-){=}NH_2{}^+.$$

That delocalisation makes it a poor nucleophile. The left-hand $-NH_2$ (attached to $-NH-$, not in resonance with the $C{=}O$) keeps its lone pair and acts as the nucleophile in the carbonyl condensation.

Step 3. (iii) Fischer esterification is reversible:

$R{-}COOH + R{-}OH \overset{H^+}{\rightleftharpoons} R{-}COO{-}R + H_2O$. By Le Chatelier's principle, removing one of the products (water by azeotropic distillation with benzene/toluene, or ester as a low-boiling distillate) drives the equilibrium forward and increases the yield. If neither is removed, the equilibrium constant is only ~ 4 and conversion stops around 65–70%.

Fischer esterification equilibrium (structures):



Remove H_2O (or distil ester) ⇒ shift forward (Le Chatelier).

> **Final Answer:** (i) Steric block in the trimethyl ketone; (ii) only the non-conjugated $-NH_2$ is nucleophilic; (iii) remove a product to drive a reversible esterification forward.

☞ State the principle by name in your answer

“Plausible explanation” questions reward you for naming the principle (steric hindrance, resonance, Le Chatelier) before explaining. CBSE marking: 0.5 mark for naming, 1 mark for the explanation. Always lead with the principle.

EXPERT’S SOLUTION *: Siddharth Sharma, M.Sc Chemistry, IIT Kanpur*

Strategic angle. Three problems, three different principles: steric hindrance, resonance donation, and equilibrium control.

Alternative approach (apply the electrophilicity–steric–resonance trio). For each item, decide which member of the trio explains the observation:

- (i) Steric dominates: methyls at C-2, C-2, C-6 cage the $C{=}O$ from both diastereotopic faces. Electronically the $C{=}O$ is unchanged from cyclohexanone, but kinetics fail.
- (ii) Resonance dominates: the carbonyl-adjacent $-NH_2$ is conjugated into the amide π system, losing its lone-pair availability. Inductive effects play a minor role.
- (iii) Neither steric nor resonance — a thermodynamic equilibrium control (Le Chatelier).

☞ Why amide nitrogen is not nucleophilic

In an amide $R{-}C({=}O){-}NH_2$, the nitrogen lone pair is delocalised into the carbonyl π system (the molecule is best drawn as a resonance hybrid of $R{-}C({=}O){-}NH_2 \leftrightarrow R{-}C(O^-){=}NH_2{}^+$). The nitrogen acts as a π-donor, not a σ-nucleophile: it cannot attack a new electrophile because its lone pair is already busy. This is why amides are much less basic than amines.

☞ Esterification equilibrium constant is small

For ethanol + acetic acid $\rightarrow$ ethyl acetate + water at $298\,K$, $K \approx 4$. That is small enough that at equilibrium only $\sim 67\%$ of the acid has been esterified. Removing water (Dean–Stark) or removing the lower-boiling ester (distill it off) pushes conversion to $> 95\%$. The reaction is “yield-controlled by separation”, not by kinetics.

Step 1. (i) Steric: methyls at C-2, C-2, C-6 wall off the $C{=}O$ face; CN^- cannot get within bonding distance. The electronic environment is similar to cyclohexanone but the approach trajectory is blocked. This is the same idea that makes acetone > pinacolone > di-t-butyl ketone in HCN reactivity (Q 8.12).

Step 2. (ii) Resonance: the $-NH_2$ next to $C{=}O$ in semicarbazide donates into the amide π system and is no longer nucleophilic; only the $-NH_2$ on the hydrazine nitrogen (the one bonded to $-NH-$) reacts with a carbonyl. Drawing the resonance structure helps make this clear.

Step 3. (iii) Le Chatelier: pull out water (or ester) and the equilibrium shifts toward more ester. This is the basis of azeotropic esterification (Dean–Stark trap) and the reason molecular sieves are used in modern Fischer esterification.

Concept linkage with carbonyl reactivity. Every nucleophilic addition to a carbonyl is gated by exactly these three factors (electrophilicity of C, steric access, resonance donation by substituents). Knowing the trio lets you predict every related reactivity ordering in this chapter.

Exam relevance. CBSE 2017, 2021 and 2024 set very similar “explanation” questions. Marking is consistent: name the principle, then explain with a structural sketch where possible.

Why this matters. Each item is a model problem: “steric vs electronic” (i), “resonance switches off nucleophilicity” (ii), “shift the equilibrium by removing a product” (iii). These three ideas recur all over organic chemistry.

> **Final Answer:** Three explanations as in the main solution.

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

SOLUTION

Concept used. We combine percent-composition arithmetic with functional-group tests:

- Percentage composition $\rightarrow$ empirical formula $\rightarrow$ molecular formula using the molar mass.
- Reaction tests fix the functional group: $\mathrm{NaHSO_3}$ *addition* happens with methyl ketones and aldehydes; *no Tollens’* rules out aldehyde; *iodoform* fires for methyl ketones $\mathrm{CH_3{-}CO{-}R}$; *vigorous oxidation cleaving the* $\mathrm{C{-}CO{-}C}$ *bond* gives two carboxylic acids whose chain lengths reveal the carbon skeleton.

Step 1. Empirical formula. Mass of O $= 100 - 69.77 - 11.63 = 18.60\%$. Convert to moles per 100 g:

$$n_\mathrm{C} = \frac{69.77}{12} = 5.81\,\mathrm{mol}, \quad n_\mathrm{H} = \frac{11.63}{1} = 11.63\,\mathrm{mol}, \quad n_\mathrm{O} = \frac{18.60}{16} = 1.16\,\mathrm{mol}.$$

Divide each by the smallest, 1.16:

$$\mathrm{C} : \frac{5.81}{1.16} = 5.0, \quad \mathrm{H} : \frac{11.63}{1.16} = 10.0, \quad \mathrm{O} : \frac{1.16}{1.16} = 1.0.$$

Empirical formula $= \mathrm{C_5H_{10}O}$, empirical mass $= 5(12) + 10(1) + 16 = 86$ g/mol.

Step 2. Molecular formula. Given $M_w = 86 \approx$ empirical mass; molecular formula $= \mathrm{C_5H_{10}O}$. Degree of unsaturation $= (2(5) + 2 - 10)/2 = 1$, consistent with one $\mathrm{C{=}O}$.

Step 3. **Functional group.** $NaHSO_3$ + iodoform but no Tollens' ⇒ methyl ketone $CH_3{-}CO{-}R$ where $R = C_3H_7$.

Step 4. **Locate methyl: oxidative cleavage.** Vigorous oxidation cleaves a methyl ketone at the $C{-}CO^-$ bonds either side of the $C{=}O$. The two acids are **ethanoic acid** (CH_3COOH) and **propanoic acid** (CH_3CH_2COOH). So one side of the ketone is a single carbon (CH_3CO^-) and the other side has 2 carbons ($-CH_2CH_2CH_3$ converted to propanoic acid). That makes the compound $CH_3{-}CO{-}CH_2{-}CH_2{-}CH_3$ (pentan-2-one).

Step 5. **Check formula.** $CH_3COCH_2CH_2CH_3 = C_5H_{10}O$, $M_w = 86$. ✓

> **Final Answer:** The compound is **pentan-2-one**, $CH_3COCH_2CH_2CH_3$.

♥ Why oxidation cleaves a methyl ketone here

Vigorous oxidation of a methyl ketone (e.g. with hot acidic $KMnO_4$) breaks the $C{-}C$ bonds either side of the $C{=}O$; the smaller fragment ends up as CH_3COOH (from the methyl side) and the longer side ends up as the corresponding carboxylic acid. So the two acids tell you exactly where the carbonyl sat.

☞ Don't shortcut the arithmetic

Always carry the percent-composition arithmetic to one decimal place before rounding to integer ratios. A C:H:O ratio that "looks like" 2:5:1 may actually be 2.00:5.00:0.50 (which doubles to 4:10:1, not 2:5:1). CBSE awards 1 mark for the correct empirical formula *and* 1 mark for showing the arithmetic. Skip the arithmetic and you lose half the question.

EXPERT'S SOLUTION *: Priya Joshi, B.Tech Chemical Engineering, IIT Bombay*

Strategic angle. Run the arithmetic, then read the clues.
Alternative approach (combine tests before arithmetic). A faster strategy: read the tests first.

- "Forms $NaHSO_3$ adduct" ⇒ methyl ketone or aldehyde with limited steric bulk.
- "No Tollens" ⇒ not an aldehyde ⇒ methyl ketone.
- "Iodoform positive" ⇒ $CH_3CO{-}R$ confirmed.
- "Vigorous oxidation gives $CH_3COOH + CH_3CH_2COOH$" ⇒ structure is $CH_3{-}CO{-}CH_2CH_2CH_3$ (the methyl-side gives CH_3COOH, the C_3 side gives CH_3CH_2COOH).

Now use the molecular formula as a verification, not as the starting point.

☞ **Why $NaHSO_3$ tests methyl ketones**

Bisulphite addition $R_2C{=}O + NaHSO_3 \rightarrow R_2C(OH)SO_3Na$ requires the carbonyl to be unhindered. Aldehydes (RCHO) and small methyl ketones (CH_3COR with R small) form the white crystalline adduct; bulky ketones (di-*t*-butyl ketone) and aromatic ketones (acetophenone with bulky R) don't react cleanly. So a positive $NaHSO_3$ test narrows the substrate to aldehyde-or-methyl-ketone.

Concept linkage with iodoform and oxidative cleavage. The methyl-ketone signature recurs through this chapter: iodoform (§8.13), $NaHSO_3$ adduct (§8.19), α-bromination via HVZ-like or direct Br_2/H^+ (more in Q 8.20), and oxidative cleavage (this Q). Recognising it on first sight saves you 5 minutes per problem.

Step 1. %O = 18.60. Ratio C:H:O = 5.81:11.63:1.16 = 5:10:1. Empirical $C_5H_{10}O$, mass 86 = given M_w. Molecular formula $C_5H_{10}O$.

Step 2. DoU $= (2 \times 5 + 2 - 10)/2 = 1$; one $C{=}O$, consistent with all tests.

Step 3. Tests ⇒ methyl ketone (iodoform $+$; $NaHSO_3$ $+$; Tollens' $-$).

Step 4. Cleavage to ethanoic + propanoic acid pins the methyl on a C_2 neighbour: $CH_3{-}CO{-}CH_2{-}CH_2{-}CH_3$ (pentan-2-one). Other $C_5H_{10}O$ isomers (e.g. 3-pentanone, $C_2H_5COC_2H_5$, gives propanoic acid only) are ruled out.

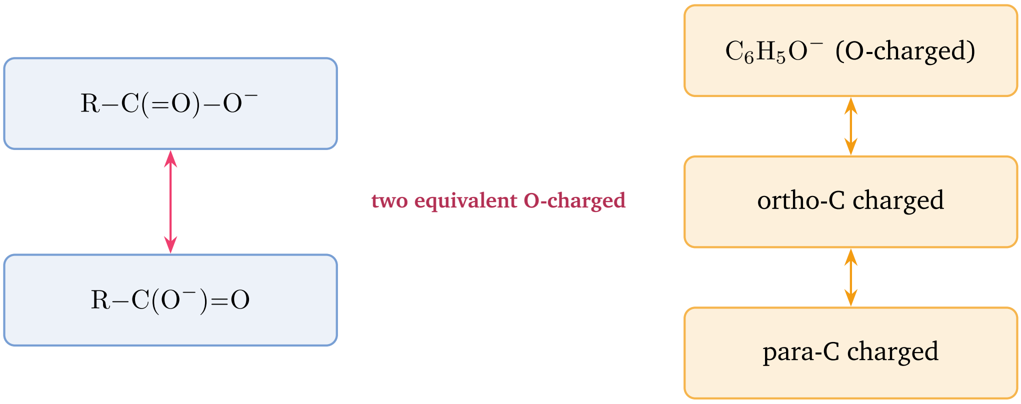
Exam relevance. 5-mark CBSE structure-elucidation problems follow this exact template. Marking: 1 for empirical, 1 for molecular, 1 for DoU and tests, 1 for the structure, 1 for ruling out isomers. Always write out the structural isomer rule-out.
Why this matters. Mixed quantitative-and-qualitative problems are a CBSE staple. The algorithm is always: empirical from %, molecular from M_w, then layer the tests to fix the isomer.

Final Answer: Pentan-2-one, $CH_3COC_3H_7$, $M_w = 86$.

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

SOLUTION

Concept used. Acidity depends on the stability of the conjugate base. Stability of an anion depends on (i) how many resonance structures it has, but more importantly on (ii) *the quality* of those structures, in particular whether the negative charge sits on the more electronegative atom (oxygen) and whether the contributing structures are equivalent.



Step 1. In carboxylate $R{-}COO^-$ the two resonance structures are *equivalent* and place the negative charge on the more electronegative oxygen in both. The actual structure is a symmetrical anion with each $C{-}O$ bond order ≈ 1.5 and the charge split equally over both oxygens. This is very effective stabilisation.

Step 2. In phenoxide $C_6H_5O^-$ the negative charge can be drawn on oxygen and on the *ortho* and *para* carbons of the ring. The carbon-charged structures are *less stable* than the oxygen-charged one because carbon is less electronegative than oxygen. They also break the aromatic sextet partially.

Step 3. So although phenoxide *has more* contributing structures (4) than carboxylate (2), the carboxylate's two structures are both "best-quality" (charge on O, both equivalent), whereas only one of phenoxide's structures has charge on O. The carboxylate is therefore the more stable conjugate base, and the parent carboxylic acid ($pK_a \approx 4.7$) is a stronger acid than phenol ($pK_a \approx 10$).

Step 4. Inductive effects reinforce: in $R{-}COO^-$ the adjacent $C{=}O$ pulls electron density and stabilises the anion; in $C_6H_5O^-$ the ring is overall electron-rich.

> **Final Answer:** Number of resonance structures is not enough; what counts is whether the charge ends up on the more electronegative atom and whether the structures are equivalent. Carboxylate scores on both counts, so $RCOOH$ ($pK_a \approx 4.7$) is more acidic than phenol ($pK_a \approx 10$).

★ Quality vs quantity of resonance

A single resonance structure with charge on the most electronegative atom often outranks several structures with charge on carbon. This is why guanidine is so basic: the conjugate acid $C(NH_2)_3{}^+$ has three equivalent resonance structures, each with positive charge delocalised over three nitrogens.

✗ Don't just count resonance structures

A frequent CBSE wrong answer is "Phenoxide has more resonance structures than carboxylate, so phenol is more acidic." This counts but does not weigh. The right answer says: phenoxide has *more structures but they are mostly low-quality* (C-charged); carboxylate has *fewer but high-quality* (O-charged, equivalent). Net effective stabilisation is higher in carboxylate.

♥ Quantitative comparison with pK_a values

RCOOH: $pK_a \approx 4.7$ (acetic acid 4.76, benzoic acid 4.20). Phenol: $pK_a \approx 10.0$. Difference of ~ 5 units $=$ factor of $\sim 10^5$ in K_a. Carboxylic acid is about $100\,000$ times more acidic than phenol. This is large enough that $\mathrm{NaHCO_3}$ (a mild base) protonates only carboxylic acids; phenols stay un-ionised. That is why $\mathrm{NaHCO_3}$ test distinguishes the two functional groups (Q 8.13 iii).

EXPERT'S SOLUTION *: Ankit Kumar, Ph.D Organic Chemistry, IIT Madras*

Picture-first. Count resonance structures, but weigh them. Carboxylate's two structures place the charge symmetrically on the two oxygens; phenoxide's four structures spread the charge over O, ortho-C, para-C, with the C-charged structures dominating numerically but contributing weakly.

Alternative approach (charge-on-oxygen weighting). Two factors determine resonance quality:

- *Electronegativity of the atom carrying the negative charge*: O ($\chi = 3.5$) is much better than C ($\chi = 2.5$). A structure with negative charge on O is about 10^4 times more stable than one on C.
- *Equivalence*: two equivalent structures (like the two C-O bonds of carboxylate) give complete delocalisation; non-equivalent structures contribute unequally.

Carboxylate scores on both counts; phenoxide scores on only one (the O-charged structure is good, but the three C-charged ones drag the average down).

Concept linkage with the pK_a map. Acidity scales:

- Strong acids ($pK_a < 0$): HCl, HNO_3, RSO_3H.
- Carboxylic acids (pK_a 3-5): RCOOH, ArCOOH.
- Phenols (pK_a 9-11): ArOH.
- Alcohols (pK_a 15-19): ROH.
- α-H of carbonyls (pK_a 18-25).
- Hydrocarbons ($pK_a > 40$).

The 5-unit gap between carboxylic acids and phenols is the largest on this scale at biological pH.

Step 1. Carboxylate ($\mathrm{RCOO^-}$): two equivalent structures, both $\mathrm{O^-}$. High-quality stabilisation. The C-O bond order is 1.5, charges $-1/2$ on each oxygen.

Step 2. Phenoxide ($\mathrm{PhO^-}$): four structures, only one with $\mathrm{O^-}$; three put the negative on a ring carbon, which is less stable. Also, the C-charged structures break the aromatic sextet partially.

Step 3. Effective stabilisation: carboxylate $>$ phenoxide. Therefore RCOOH ($pK_a \approx 4.7$) is more acidic than PhOH ($pK_a \approx 10$).

Step 4. Inductive support: the carboxylate's $\mathrm{C{=}O}$ also inductively withdraws electron density (the σ^* of C-O is $-I$), reinforcing resonance stabilisation. Phenoxide sits on an electron-rich benzene ring with no such reinforcement.

Exam relevance. The carboxylic-acid-vs-phenol question is asked in some form almost every CBSE year (1-mark to 3-mark variants). Key phrases for full marks: "equivalent resonance structures", "charge on electronegative oxygen", "inductive reinforcement".
Why this matters. Acid-strength explanations in organic chemistry almost always boil down to "stability of the conjugate base". Do not count resonance forms blindly; ask whether the charge sits on the better atom.

> **Final Answer:** Carboxylic acid is stronger because its conjugate base puts the charge on equivalent, electronegative oxygens; phenoxide's extra resonance structures place the charge on less stable ring carbons.

Key Takeaways

- The carbonyl carbon ($\mathrm{C^{\delta+}{=}O^{\delta-}}$) is the site of nucleophilic addition. Nucleophiles (HCN, $NaHSO_3$, ROH, $\mathrm{NH_2{-}X}$) attack carbon; the oxygen becomes an $-\mathrm{OH}$ after protonation.
- Aldol condensation requires an α-H; Cannizzaro requires its absence. The same test (α-H availability) sorts every aldehyde/ketone into one camp or the other.
- IUPAC naming: principal group ($-\mathrm{COOH}\ -\mathrm{CHO}\ \mathrm{C{=}O}$) gets the lowest locant; the chain is numbered from the end nearer this group; substituents are listed alphabetically.
- Acidity is governed by conjugate-base stability. Electron withdrawal ($-\mathrm{I}, -\mathrm{M}$) increases acidity; electron donation ($+\mathrm{I}, +\mathrm{M}$) decreases it. Carboxylates are more stable than phenoxides because both equivalent resonance structures place the charge on oxygen.
- Carbonyls are protected as acetals/ketals (stable to base, cleaved by dilute acid). Carbonyls are reduced fully by Clemmensen ($\mathrm{Zn(Hg)/HCl}$) or Wolff-Kishner ($\mathrm{NH_2NH_2/KOH/\Delta}$); to alcohol by $\mathrm{NaBH_4}$ / $\mathrm{LiAlH_4}$; to aldehyde from acid chloride by Rosenmund ($\mathrm{H_2/Pd{-}BaSO_4}$).
- Directing effects rule aromatic carbonyl/acid syntheses: $-\mathrm{CH_3}$ is o/p directing, $-\mathrm{COOH}$ is meta directing. Sequencing decides the substitution pattern.

End of Chapter 8 Exercises