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ORGANIC

CH 08

Aldehydes & Ketones — Nucleophilic Addition & Named Reactions

Structure and physical properties, every preparation route, nucleophilic addition and its reactivity order, reactions with ammonia derivatives, reductions, oxidation tests, haloform, aldol, Cannizzaro and ring substitution — with conversions, an exam trap gallery, graded MCQs and a one-page revision sheet.

WHAT YOU WILL BE ABLE TO DO

- Prepare aldehydes and ketones by oxidation, ozonolysis, hydration of alkynes and the named reductions (Rosenmund, Stephen, Etard, Gattermann–Koch)
- Explain nucleophilic addition and rank carbonyl compounds by reactivity
- Predict products with HCN, $NaHSO_3$, Grignard reagents, alcohols and ammonia derivatives
- Use Tollens', Fehling's, iodoform and 2,4-DNP tests to distinguish carbonyl compounds
- Predict aldol, cross-aldol, Claisen–Schmidt and Cannizzaro products, and solve conversions

INSIDE

A The big picture
B Structure and physical properties

HOW TO USE THESE NOTES

IN ONE LINE The core idea of a section	**KEY IDEA** The concept to remember	**EXAM TRAP** Where marks are usually lost
SOLVED EXAMPLE Worked step by step	**CHECK YOURSELF** Quick self-test	**MEMORY HOOK** A line that sticks

SECTION A

The big picture

A

Three ideas run the whole chapter.

IN ONE LINE

The polar C=O makes the carbonyl carbon electrophilic (nucleophilic addition); the α-hydrogen is acidic (aldol, haloform); and aldehydes are easily oxidised while ketones are not (Tollens', Fehling's).

Idea	Reactions it explains
Nucleophile attacks C of C=O	HCN, $NaHSO_3$, Grignard, alcohols (acetals), ammonia derivatives, reductions
α-H is acidic	Aldol, cross-aldol, Claisen–Schmidt, haloform
No α-H + strong base	Cannizzaro
Aldehyde H is easily removed in oxidation	Tollens', Fehling's, Benedict's; aldehydes → acids
–CHO / –COR deactivates a benzene ring	meta substitution in benzaldehyde and acetophenone

THINK OF IT LIKE THIS

The carbonyl carbon is like a shop door with a bright "Open" sign (δ+): nucleophiles walk straight in. In a ketone, two alkyl "bouncers" stand at the door and make it harder to enter (steric hindrance), and they also dim the sign by pushing electrons in. That is why aldehydes react faster than ketones.

SECTION B

Structure and physical properties

B

A polar, planar group.

- The carbonyl carbon is **sp^2**; the C=O group and its two attached atoms are **trigonal planar** (bond angles about 120°). The C=O π bond is polarised: $C^{\delta+}=O^{\delta-}$.
- Resonance: C=O ↔ $C^+–O^-$ explains the large dipole moment (about 2.3–2.8 D).

- **Boiling points** lie between hydrocarbons/ethers and alcohols of similar mass: dipole–dipole attractions but no H bonding between molecules.
- **Lower members are water-soluble** (H bonding with water); solubility falls as the carbon chain grows. Methanal is a gas; its 40% solution is formalin.

Compound	Molar mass	b.p. / K
n-Butane	58	273
Methoxyethane	60	281
Propanal	58	322
Acetone	58	329
Propan-1-ol	60	370

SECTION C

C

Preparing aldehydes and ketones

The routes you must know.

Route	Reagent	Gives	Note
Oxidation of alcohols	PCC; $K_2Cr_2O_7/H^+$	1° → aldehyde; 2° → ketone	Strong oxidants take aldehydes on to acids; PCC stops at the aldehyde
Dehydrogenation	Cu or Ag, 573 K	1° → aldehyde; 2° → ketone	Industrial route; vapours over hot metal
Ozonolysis	O_3, then Zn/H_2O	Aldehydes and/or ketones	Cuts C=C into two C=O
Hydration of alkynes	dil. H_2SO_4 + $HgSO_4$	Ethyne → ethanal; other alkynes → ketones	Markovnikov; via the enol
Rosenmund reduction	RCOCl + H_2, $Pd/BaSO_4$	Aldehyde	$BaSO_4$ poisons Pd so it stops at the aldehyde
Stephen reaction	RCN + $SnCl_2$/HCl, then H_3O^+	Aldehyde	Via the imine
DIBAL-H	RCN or RCOOR′, then H_2O	Aldehyde	Selective partial reduction; C=C untouched
Grignard + nitrile	RCN + R′MgX, then H_3O^+	Ketone R–CO–R′	Via the imine

Route	Reagent	Gives	Note
Acyl chloride + dialkylcadmium	2RCOCl + R'_2Cd	Ketone	R'_2Cd from R'MgX + $CdCl_2$

Aromatic aldehydes and ketones

Reaction	Reagent	Product
Etard reaction	Toluene + CrO_2Cl_2 (in CS_2), then H_3O^+	Benzaldehyde
Chromic oxide method	Toluene + CrO_3 in acetic anhydride (gives benzylidene diacetate), then hydrolysis	Benzaldehyde
Side-chain chlorination	Toluene + Cl_2 (light) → $C_6H_5CHCl_2$; hydrolysis at 373 K	Benzaldehyde
Gattermann–Koch	Benzene + CO + HCl, anhydrous $AlCl_3$/CuCl	Benzaldehyde
Friedel–Crafts acylation	Benzene + RCOCl, anhydrous $AlCl_3$	Aryl ketone (e.g. acetophenone)

SOLVED EXAMPLE 01 — CHOOSING A ROUTE

Give a method to prepare (a) propanal from propanoyl chloride, (b) butan-2-one from propanenitrile.

SOLUTION

1. (a) Rosenmund: $CH_3CH_2COCl + H_2$ over $Pd/BaSO_4$ → CH_3CH_2CHO.
2. (b) $CH_3CH_2CN + CH_3MgBr$ → imine salt; H_3O^+ → $CH_3CH_2COCH_3$.

ANSWER (a) Rosenmund reduction. (b) Grignard addition to the nitrile, then hydrolysis.

SOLVED EXAMPLE 02 — OZONOLYSIS BACKWARDS

An alkene C_6H_{12} on ozonolysis gives only propanone. Identify it.

SOLUTION

1. Propanone is $(CH_3)_2C{=}O$; joining two at their carbonyl carbons gives $(CH_3)_2C{=}C(CH_3)_2$.

ANSWER 2,3-Dimethylbut-2-ene.

CHECK YOURSELF

C1 Why is $BaSO_4$ added to the catalyst in the Rosenmund reduction?

C2 Which alkyne gives an aldehyde on hydration?

Answers at the end of the chapter.

SECTION D

Nucleophilic addition

D

The core mechanism.

1. The nucleophile attacks the electrophilic carbonyl carbon from above or below the planar group.
2. The carbon changes from sp^2 (trigonal) to sp^3 (tetrahedral); the π electrons move onto oxygen, giving an alkoxide.
3. The alkoxide takes H^+ from the medium to give the neutral addition product.

KEY IDEA

Reactivity: HCHO > CH_3CHO > CH_3COCH_3; aldehydes > ketones; aliphatic > aromatic. Alkyl groups donate electrons (lowering δ+) and crowd the carbon. In benzaldehyde the ring's resonance with C=O lowers δ+ on the carbon, so it is less reactive than ethanal.

Reagent	Product	Note
HCN (trace base)	Cyanohydrin $R_2C(OH)CN$	Base generates CN^-, the real nucleophile; cyanohydrins → α-hydroxy acids
$NaHSO_3$ (saturated)	Bisulphite adduct (crystalline)	With aldehydes and methyl ketones; regenerated with dilute acid or alkali — used to separate them
RMgX, then H_3O^+	Alcohol	HCHO → 1°; RCHO → 2°; R_2CO → 3°
ROH, dry HCl	Hemiacetal, then acetal	Ketones with ethylene glycol give cyclic ketals — protects C=O during other steps
H_2O	Gem-diol (hydrate)	Mostly reversible; chloral hydrate is stable

SOLVED EXAMPLE 03 — RANKING REACTIVITY

Arrange HCHO, CH_3CHO, CH_3COCH_3 and C_6H_5CHO in decreasing reactivity toward HCN.

SOLUTION

1. HCHO: no alkyl groups — most electrophilic, least hindered.
2. CH_3CHO: one methyl donor.
3. C_6H_5CHO: ring resonance lowers δ+.
4. CH_3COCH_3: two methyls — electronic and steric effects.

ANSWER **HCHO > CH_3CHO > C_6H_5CHO > CH_3COCH_3 (benzaldehyde and acetone are close; acetone is usually placed last).**

SECTION E

Reactions with ammonia derivatives

E

Addition followed by loss of water.

$$R_2C{=}O + H_2N{-}Z \rightleftharpoons R_2C{=}N{-}Z + H_2O$$

Best at a weakly acidic pH (about 3.5): enough H^+ to activate C=O, not so much that the amine is fully protonated

Reagent H_2N-Z	Name	Product
$H_2N{-}OH$	Hydroxylamine	Oxime
$H_2N{-}NH_2$	Hydrazine	Hydrazone
$H_2N{-}NHC_6H_5$	Phenylhydrazine	Phenylhydrazone
$H_2N{-}NH{-}C_6H_3(NO_2)_2$	2,4-Dinitrophenylhydrazine (2,4-DNP, Brady's reagent)	2,4-DNP derivative — yellow/orange/red precipitate
$H_2N{-}NHCONH_2$	Semicarbazide	Semicarbazone
$H_2N{-}R$	Primary amine	Imine (Schiff base)

KEY IDEA

2,4-DNP gives a coloured precipitate with every aldehyde and ketone — the general test for a carbonyl group. Only one NH_2 of semicarbazide reacts: the other is part of an amide and its lone pair is delocalised onto C=O.

CHECK YOURSELF

C3 Why is the reaction with ammonia derivatives carried out at a weakly acidic pH?

C4 Name the product of acetone with hydroxylamine.

Answers at the end of the chapter.

SECTION F

Reduction

F

Three outcomes: alcohol, CH_2 or pinacol.

Reagent	Product	Note
$NaBH_4$ or $LiAlH_4$; H_2/Ni, Pt or Pd	Alcohol (aldehyde → 1°, ketone → 2°)	$NaBH_4$ does not reduce C=C
Clemmensen: Zn–Hg / conc. HCl	C=O → CH_2 (alkane)	For substrates stable to acid

Reagent	Product	Note
Wolff–Kishner: NH_2NH_2, then KOH in ethylene glycol, heat	C=O → CH_2 (alkane)	For substrates stable to base; via the hydrazone

SOLVED EXAMPLE 04 — CLEMMENSEN OR WOLFF-KISHNER?

Convert acetophenone to ethylbenzene.

SOLUTION

1. The C=O must become CH_2 without touching the ring.
2. Clemmensen: Zn–Hg / conc. HCl, heat (or Wolff–Kishner).

ANSWER $C_6H_5COCH_3 \rightarrow C_6H_5CH_2CH_3$.

SECTION G

Oxidation and the classic tests

Aldehydes are easily oxidised; ketones are not.

Test	Reagent	Positive result	Given by
Tollens'	$[Ag(NH_3)_2]^+$ (ammoniacal $AgNO_3$)	Silver mirror	All aldehydes (aliphatic and aromatic)
Fehling's	Cu^{2+} tartrate complex (Fehling A + B), alkaline	Red-brown Cu_2O precipitate	Aliphatic aldehydes (not benzaldehyde)
Benedict's	Cu^{2+} citrate complex	Red-brown Cu_2O	Aliphatic aldehydes, reducing sugars
Iodoform	I_2 + NaOH	Yellow CHI_3 (antiseptic smell)	$CH_3CO–$ compounds and $CH_3CH(OH)–$ alcohols (incl. ethanal, ethanol)
2,4-DNP	Brady's reagent	Yellow–red precipitate	All aldehydes and ketones
Schiff's reagent	Decolourised rosaniline	Pink colour restored	Aldehydes

- Aldehydes → carboxylic acids with HNO_3, $KMnO_4$, $K_2Cr_2O_7$ and even mild oxidants.
- Ketones are oxidised only by strong oxidants at high temperature, with C–C bond cleavage, giving a mixture of acids with fewer carbons.

Haloform reaction

$$R{-}CO{-}CH_3 + 3NaOI \rightarrow R{-}COONa + CHI_3\downarrow + 2NaOH$$

Methyl ketones (and ethanal) are converted to the acid with one carbon fewer; the CH_3 becomes CHX_3

- The α-H of the CH_3 group is replaced by halogen three times, then OH^- cleaves the $C{-}CX_3$ bond.
- Alcohols with $CH_3CH(OH)-$ give a positive test because NaOI first oxidises them to methyl ketones (or ethanal).
- The C=C of α,β-unsaturated methyl ketones is not attacked.

SOLVED EXAMPLE 05 — DISTINGUISHING PAIRS

Give one test to distinguish (a) propanal and propanone, (b) acetophenone and benzophenone, (c) pentan-2-one and pentan-3-one.

SOLUTION

1. (a) Tollens' (or Fehling's): propanal gives a silver mirror; propanone does not.
2. (b) Iodoform: acetophenone ($C_6H_5COCH_3$) gives yellow CHI_3; benzophenone does not.
3. (c) Iodoform: pentan-2-one (a methyl ketone) is positive; pentan-3-one is not.

ANSWER (a) Tollens' test. (b) and (c) Iodoform test.

SECTION H

H

Reactions at the α-carbon

The acidic α-hydrogen.

The α-hydrogen is acidic (pKa about 19–20 for acetone) because the anion left behind (the **enolate**) is stabilised by resonance with C=O.

Aldol condensation

$$2CH_3CHO \rightarrow CH_3CH(OH)CH_2CHO \rightarrow CH_3CH{=}CHCHO + H_2O$$

dil. NaOH: aldol (3-hydroxybutanal); heat: dehydration to but-2-enal (crotonaldehyde)

1. OH^- removes an α-H, giving the enolate ion.
2. The enolate attacks the carbonyl carbon of a second molecule.
3. The alkoxide takes H^+ from water: β-hydroxy aldehyde (aldol).
4. On heating, loss of water gives the α,β-unsaturated carbonyl compound (conjugated, so very favourable).

- Ketones give aldols too: acetone → 4-hydroxy-4-methylpentan-2-one → 4-methylpent-3-en-2-one (mesityl oxide).
- **Cross aldol** of two different compounds that both have α-H gives four products — not useful.
- **Claisen–Schmidt:** an aldehyde without α-H (benzaldehyde) + a ketone or aldehyde with α-H gives one main product: $C_6H_5CHO + CH_3COCH_3 \rightarrow C_6H_5CH{=}CHCOCH_3$ (benzalacetone); with acetophenone → $C_6H_5CH{=}CHCOC_6H_5$ (chalcone).

SOLVED EXAMPLE 06 — **COUNTING CROSS-ALDOL PRODUCTS**

How many aldol products (β-hydroxy aldehydes, ignoring stereoisomers) form from a mixture of ethanal and propanal with dilute NaOH?

SOLUTION

1. Both have α-H, so each can act as the enolate (donor) and as the acceptor.
2. Donor/acceptor pairs: ethanal/ethanal, propanal/propanal, ethanal enolate + propanal, propanal enolate + ethanal.

ANSWER **Four: 3-hydroxybutanal, 3-hydroxy-2-methylpentanal, 3-hydroxypentanal and 3-hydroxy-2-methylbutanal.**

SECTION I

Cannizzaro reaction

I

No α-H plus strong base: one molecule oxidised, one reduced.

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

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

Disproportionation by hydride transfer

- Only aldehydes **without α-H**: HCHO, C_6H_5CHO, $(CH_3)_3CCHO$, furfural.
- Mechanism: OH^- adds to C=O; the tetrahedral intermediate transfers a **hydride ion** to a second aldehyde molecule.
- **Crossed Cannizzaro:** with HCHO and another aldehyde without α-H, **HCHO is always oxidised** (to formate) and the other is reduced to the alcohol: $C_6H_5CHO + HCHO \rightarrow C_6H_5CH_2OH + HCOONa$.

SOLVED EXAMPLE 07 — CROSSED CANNIZZARO

Predict the products when benzaldehyde and formaldehyde are treated with conc. NaOH.

SOLUTION

1. Neither has α-H, so Cannizzaro occurs.
2. HCHO is the more reactive and is preferentially attacked by OH^-; it donates the hydride and is oxidised.
3. Benzaldehyde accepts the hydride and is reduced.

ANSWER Benzyl alcohol + sodium formate.

CHECK YOURSELF

C5 Which of these gives Cannizzaro: ethanal, benzaldehyde, acetone?

C6 What is the product of acetone with dilute NaOH on heating?

Answers at the end of the chapter.

SECTION J

Ring substitution

J

The carbonyl group is a meta director.

- –CHO and –COR withdraw electrons (–R, –I), deactivating the ring and directing electrophiles to the **meta** position.
- Benzaldehyde + conc. HNO_3/H_2SO_4 (273–283 K) → m-nitrobenzaldehyde.
- Friedel–Crafts reactions fail on these rings (deactivated, and $AlCl_3$ complexes with C=O).

SECTION K

Uses

K

Where these compounds turn up.

- Formalin (40% HCHO) preserves biological specimens; HCHO is used to make Bakelite and urea–formaldehyde resins.
- Acetaldehyde makes acetic acid, ethyl acetate and drugs; acetone is a common solvent.
- Benzaldehyde (bitter almond), vanillin (vanilla), cinnamaldehyde (cinnamon) and camphor are flavours and fragrances.

SECTION L

Conversions

L

Multi-step problems.

SOLVED EXAMPLE 08 — ETHANAL TO BUT-2-ENAL

Convert ethanal into but-2-enal.

SOLUTION

1. Aldol: $2CH_3CHO$ + dil. NaOH → $CH_3CH(OH)CH_2CHO$.
2. Heat: loss of water → $CH_3CH{=}CHCHO$.

ANSWER Aldol condensation followed by dehydration.

SOLVED EXAMPLE 09 — BENZENE TO M-NITROACETOPHENONE

Convert benzene into m-nitroacetophenone.

SOLUTION

1. Friedel–Crafts acylation: $C_6H_6 + CH_3COCl / AlCl_3 \rightarrow C_6H_5COCH_3$.
2. Nitration: the acetyl group directs meta → m-nitroacetophenone.

ANSWER Acylate first, then nitrate (the order matters: nitrobenzene will not undergo Friedel–Crafts).

SOLVED EXAMPLE 10 — PROPANONE TO PROPENE

Convert propanone into propene.

SOLUTION

1. Reduce: $CH_3COCH_3 + NaBH_4 \rightarrow CH_3CH(OH)CH_3$.
2. Dehydrate: conc. H_2SO_4, heat → $CH_3CH{=}CH_2$.

ANSWER Reduction to propan-2-ol, then dehydration.

SOLVED EXAMPLE 11 — ETHANOL TO 3-HYDROXYBUTANAL

Convert ethanol into 3-hydroxybutanal.

SOLUTION

1. Oxidise ethanol with PCC → ethanal.
2. Aldol with dilute NaOH (no heating) → 3-hydroxybutanal.

ANSWER PCC oxidation, then aldol addition.

SECTION M

Advanced problems

Identify the compound from its reactions.

SOLVED EXAMPLE 12 — IDENTIFY A

Compound A (C_3H_6O) gives a 2,4-DNP precipitate and a positive iodoform test, but does not reduce Tollens' reagent. Identify A.

SOLUTION

1. 2,4-DNP positive: A is an aldehyde or ketone.
2. Tollens' negative: a ketone.
3. Iodoform positive: a methyl ketone with three carbons.

ANSWER A is propanone, CH_3COCH_3.

SOLVED EXAMPLE 13 — IDENTIFY B AND ITS PRODUCTS

B (C_7H_6O) gives a silver mirror but no Fehling's test and no iodoform. With conc. NaOH it gives C_7H_8O and the sodium salt of $C_7H_6O_2$. Identify all three.

SOLUTION

1. Tollens' positive, Fehling's negative: an aromatic aldehyde.
2. C_7H_6O = C_6H_5CHO (benzaldehyde).
3. Conc. NaOH: Cannizzaro → $C_6H_5CH_2OH$ (C_7H_8O) + C_6H_5COONa.

ANSWER B = benzaldehyde; products = benzyl alcohol and sodium benzoate.

SOLVED EXAMPLE 14 — IDENTIFY C FROM OZONOLYSIS

An alkene C_5H_{10} on ozonolysis gives ethanal and propanone. Identify it.

SOLUTION

1. Join the carbonyl carbons: $CH_3CH=$ + $=C(CH_3)_2$.

ANSWER 2-Methylbut-2-ene, $CH_3CH=C(CH_3)_2$.

SECTION N

Exam trap gallery

Where marks are lost in this chapter.

✗ TRAP 01 · WHAT STUDENTS WRITE

Ketones are more reactive than aldehydes toward nucleophiles.

✓ WHAT IS ACTUALLY CORRECT

Aldehydes are more reactive.

WHY Ketones have two electron-donating, bulky alkyl groups.

✗ TRAP 02 · WHAT STUDENTS WRITE	✓ WHAT IS ACTUALLY CORRECT
Benzaldehyde gives Fehling's test.	It gives Tollens' but not Fehling's.

WHY Fehling's works for aliphatic aldehydes.

✗ TRAP 03 · WHAT STUDENTS WRITE	✓ WHAT IS ACTUALLY CORRECT
Acetone gives the Cannizzaro reaction.	It has α-H, so it gives aldol condensation.

WHY Cannizzaro needs an aldehyde without α-H.

✗ TRAP 04 · WHAT STUDENTS WRITE	✓ WHAT IS ACTUALLY CORRECT
In crossed Cannizzaro with HCHO, benzaldehyde is oxidised.	HCHO is oxidised (to formate); benzaldehyde is reduced to benzyl alcohol.

WHY HCHO is the better hydride donor once OH^- adds.

✗ TRAP 05 · WHAT STUDENTS WRITE	✓ WHAT IS ACTUALLY CORRECT
Pentan-3-one gives the iodoform test.	Only methyl ketones ($CH_3CO–$) do; pentan-3-one has two ethyl groups.

WHY The CH_3 next to C=O is needed.

✗ TRAP 06 · WHAT STUDENTS WRITE	✓ WHAT IS ACTUALLY CORRECT
Ethanol gives a negative iodoform test because it is an alcohol.	Ethanol is positive (oxidised to ethanal first).

WHY $CH_3CH(OH)–$ alcohols count.

✗ TRAP 07 · WHAT STUDENTS WRITE	✓ WHAT IS ACTUALLY CORRECT
Clemmensen and Wolff–Kishner give alcohols.	Both reduce C=O to CH_2.

WHY $NaBH_4$ or $LiAlH_4$ give alcohols.

✗ TRAP 08 · WHAT STUDENTS WRITE	✓ WHAT IS ACTUALLY CORRECT
Hydration of propyne gives propanal.	It gives propanone (Markovnikov).

WHY Only ethyne gives an aldehyde.

✗ TRAP 09 · WHAT STUDENTS WRITE	✓ WHAT IS ACTUALLY CORRECT
Both NH_2 groups of semicarbazide react with C=O.	Only the NH_2 attached to the other NH reacts.

WHY The amide NH_2 lone pair is delocalised.

✗ TRAP 10 · WHAT STUDENTS WRITE	✓ WHAT IS ACTUALLY CORRECT
Cross aldol of two enolisable aldehydes gives one product.	Four products.
WHY Each can be donor and acceptor.	

✗ TRAP 11 · WHAT STUDENTS WRITE	✓ WHAT IS ACTUALLY CORRECT
The carbonyl group directs ortho/para in electrophilic substitution.	It is a meta director and deactivates the ring.
WHY Electron-withdrawing by resonance.	

✗ TRAP 12 · WHAT STUDENTS WRITE	✓ WHAT IS ACTUALLY CORRECT
Rosenmund reduction goes all the way to the alcohol.	It stops at the aldehyde.
WHY $BaSO_4$ poisons the Pd catalyst.	

MEMORY HOOK

"**Nucleophile knocks, carbon opens**" — nucleophilic addition.

"**Tollens' for all aldehydes, Fehling's for aliphatic only.**"

"**No α-H, Cannizzaro; with α-H, aldol.**"

"**Methyl next to C=O → yellow iodoform.**"

SECTION 0

Practice MCQs

Levels: Easy, Moderate, Tough.

Q01 Hybridisation of the carbonyl carbon: [EASY]

(a) sp
(b) sp^2
(c) sp^3
(d) sp^3d

Q02 A general test for both aldehydes and ketones: [EASY]

(a) Tollens'
(b) Fehling's
(c) 2,4-DNP
(d) Schiff's

Q03 Tollens' reagent is: [EASY]

(a) alkaline Cu^{2+}
(b) ammoniacal $AgNO_3$
(c) I_2 + NaOH
(d) acidified $KMnO_4$

Q04 Hydration of ethyne with $HgSO_4/H_2SO_4$ gives: [EASY]

(a) ethanol
(b) ethanal
(c) acetone
(d) acetic acid

Q05 Most reactive toward nucleophilic addition: [EASY]

(a) HCHO
(b) CH_3CHO
(c) CH_3COCH_3
(d) $C_6H_5COCH_3$

Q06 Iodoform test is given by: [EASY]

(a) methanol
(b) propan-1-ol
(c) ethanal
(d) benzaldehyde

Q07 Cannizzaro reaction is given by: [EASY]

(a) CH_3CHO
(b) HCHO
(c) CH_3COCH_3
(d) CH_3CH_2CHO

Q08 Rosenmund reduction converts: [MODERATE]

(a) RCN → RCHO
(b) RCOCl → RCHO
(c) RCOOH → RCH_2OH
(d) RCHO → RCH_3

Q09 Toluene + CrO_2Cl_2, then hydrolysis, gives: [MODERATE]

(a) benzoic acid
(b) benzaldehyde
(c) benzyl alcohol
(d) phenol

Q10 Acetophenone → ethylbenzene uses: [MODERATE]

(a) $NaBH_4$
(b) Clemmensen reduction
(c) Tollens' reagent
(d) Cannizzaro

Q11 Benzaldehyde gives a negative test with: [MODERATE]

(a) Tollens'
(b) Fehling's
(c) 2,4-DNP
(d) Schiff's

Q12 Product of HCHO + CH_3MgBr, then H_3O^+: [MODERATE]

(a) methanol
(b) ethanol
(c) propan-2-ol
(d) ethanal

Q13 Acetone with hydroxylamine forms: [MODERATE]

(a) a hydrazone
(b) an oxime
(c) a semicarbazone
(d) an imine of ammonia

Q14 Ethanal with dil. NaOH gives: [MODERATE]

(a) ethanol + acetate
(b) 3-hydroxybutanal
(c) but-1-ene
(d) acetone

Q15 Benzaldehyde + acetone with dil. NaOH gives: [MODERATE]

(a) benzalacetone (b) benzoin
(c) benzyl alcohol (d) benzoic acid

Q16 Nitration of benzaldehyde gives mainly: [MODERATE]

(a) o-nitrobenzaldehyde (b) m-nitrobenzaldehyde
(c) p-nitrobenzaldehyde (d) nitrobenzene

Q17 Correct order of boiling points: [MODERATE]

(a) propanal > propan-1-ol > butane (b) propan-1-ol > propanal > butane
(c) butane > propanal > propan-1-ol (d) propanal > butane > propan-1-ol

Q18 Methyl ketones on haloform reaction give an acid with: [MODERATE]

(a) the same number of C (b) one C fewer
(c) one C more (d) two C fewer

Q19 Benzaldehyde + HCHO + conc. NaOH gives: [TOUGH]

(a) benzoic acid + methanol (b) benzyl alcohol + formate
(c) benzyl alcohol + methanol (d) benzoic acid + formate

Q20 Number of aldol products from ethanal + propanal (no stereoisomers): [TOUGH]

(a) 2 (b) 3
(c) 4 (d) 6

Q21 The best pH for oxime formation is about: [TOUGH]

(a) 1 (b) 3.5
(c) 7 (d) 12

Q22 Which gives both iodoform and Tollens' tests? [TOUGH]

(a) acetone (b) ethanal
(c) propanal (d) benzaldehyde

Q23 Ozonolysis of 2-methylbut-2-ene gives: [TOUGH]

(a) acetone + ethanal (b) two acetone
(c) propanal + methanal (d) butanone + methanal

Q24 DIBAL-H converts an ester into: [TOUGH]

(a) an alcohol only (b) an aldehyde
(c) an acid (d) an alkane

Q25 Pinacolone-type ketone $CH_3COC(CH_3)_3$ with NaOI gives: [TOUGH]

(a) CHI_3 + $(CH_3)_3CCOONa$ (b) no reaction
(c) CHI_3 + CH_3COONa (d) an aldol

Answer key with explanations

Q01 **(b) sp^2** — Trigonal planar.

Q02 **(c) 2,4-DNP** — Coloured precipitate.

Q03 **(b) ammoniacal $AgNO_3$** — $[Ag(NH_3)_2]^+$.

Q04 **(b) ethanal** — Via vinyl alcohol.

Q05 **(a) HCHO** — No alkyl groups.

Q06 **(c) ethanal** — $CH_3CO–$.

Q07 **(b) HCHO** — No α-H.

Q08 **(b) RCOCl → RCHO** — H_2, $Pd/BaSO_4$.

Q09 **(b) benzaldehyde** — Etard reaction.

Q10 **(b) Clemmensen reduction** — C=O → CH_2.

Q11 **(b) Fehling's** — Aromatic aldehyde.

Q12 **(b) ethanol** — 1° alcohol.

Q13 **(b) an oxime** — NH_2OH.

Q14 **(b) 3-hydroxybutanal** — Aldol.

Q15 **(a) benzalacetone** — Claisen–Schmidt.

Q16 **(b) m-nitrobenzaldehyde** — meta director.

Q17 **(b) propan-1-ol > propanal > butane** — H bonding > dipole > dispersion.

Q18 **(b) one C fewer** — CH_3 leaves as CHX_3.

Q19 **(b) benzyl alcohol + formate** — HCHO is oxidised.

Q20 **(c) 4** — Each acts as donor and acceptor.

Q21 **(b) 3.5** — Balance of activation and free amine.

Q22 **(b) ethanal** — CH_3CHO.

Q23 **(a) acetone + ethanal** — $(CH_3)_2C=$ + $=CHCH_3$.

Q24 **(b) an aldehyde** — Partial reduction at low temperature.

Q25 **(a) CHI_3 + $(CH_3)_3CCOONa$** — Methyl ketone → acid with one C fewer.

Check-yourself answers

C1 $BaSO_4$ poisons (partly deactivates) the palladium so reduction stops at the aldehyde instead of continuing to the alcohol.

C2 Ethyne (gives ethanal).

C3 In strong acid the nitrogen nucleophile is protonated and cannot attack; in neutral or basic solution the C=O is not activated. Around pH 3.5 both conditions are balanced.

C4 Acetone oxime, $(CH_3)_2C=NOH$.

C5 Benzaldehyde (no α-H).

C6 Mesityl oxide, 4-methylpent-3-en-2-one (via the aldol).

QUICK REVISION

One-page revision

Read this page the night before the exam.

Preparation

- 1° alcohol + PCC → aldehyde; 2° → ketone
- Ozonolysis; $HgSO_4$ hydration (only ethyne → aldehyde)
- Rosenmund RCOCl; Stephen / DIBAL-H RCN
- Etard, Gattermann–Koch, Friedel–Crafts acylation

Nucleophilic addition

- HCHO > RCHO > R_2CO; aliphatic > aromatic
- HCN → cyanohydrin; $NaHSO_3$ adduct
- RMgX: HCHO 1°, RCHO 2°, R_2CO 3°
- ROH/HCl → acetal; glycol protects C=O

Ammonia derivatives

- pH ≈ 3.5; addition then $-H_2O$
- NH_2OH oxime; NH_2NH_2 hydrazone
- 2,4-DNP: coloured ppt with all carbonyls
- Semicarbazide: one NH_2 reacts

Reduction and oxidation

- $NaBH_4$, $LiAlH_4$ → alcohols
- Clemmensen (acid), Wolff–Kishner (base) → CH_2
- Tollens' all aldehydes; Fehling's aliphatic
- Iodoform: CH_3CO- and $CH_3CH(OH)-$

α-H chemistry

- Aldol → β-hydroxy carbonyl → α,β-unsaturated
- Cross aldol: 4 products
- Claisen–Schmidt: PhCHO + ketone
- Acetone → mesityl oxide

No α-H and ring

- Cannizzaro: HCHO, PhCHO + conc. NaOH
- Crossed: HCHO oxidised
- –CHO, –COR: meta directors
- Order: acylate before nitrating

END OF NOTES · RAMGOVINDYADAV.COM