Unit 13 · Aldehydes and Ketones

STUDY NOTES

WHAT NEB'S GRADE 12 EXAM ASKS

- **CDC's grid (2078):** Organic Chemistry (Units 8–17 together): 33 of 75 marks; 2 MCQs, 3 short and 2 long questions
- **CDC's model paper:** long: formalin (museum specimens): its Cannizzaro reaction, urotropine (urinary antiseptic) drawn, + phenol in acid (Bakelite), made from methanol; C_3H_6O with no silver mirror (propanone) + HCN (Y) → cyanohydrin (Z) → 2-hydroxy-2-methylpropanoic acid
- **The paper:** 11 MCQs × 1 · 8 short × 5 · 3 long × 8; 3 hours; 1 mark per expected point
- **MCQ (1 mark)**
  - Tollens' but not Fehling's (aromatic aldehyde); Cannizzaro needs no α-H; ozonolysis of 2-methylbut-2-ene
  - Clemmensen product; Rosenmund; aldol from dil. NaOH; chloretone; urotropine and the kidneys
  - pentan-2-one vs pentan-3-one (iodoform); iodoform and Fehling's both: ethanal; propyne + $HgSO_4$ → propanone
  - match Perkin, aldol, Claisen, benzoin with their products; reagent and reaction-name tables
- **Short (5 marks, in parts)**
  - aldehydes more reactive than ketones; C=O adds nucleophiles, C=C electrophiles
  - tell ethanal from propanone, propanal from propanone, aliphatic from aromatic aldehyde (tests, equations)
  - an example each: Tollens', Fehling's, aldol, Cannizzaro, Clemmensen; what happens with 2,4-DNP, NH_3, NH_2OH, HCN, alcoholic KCN
  - Étard, Rosenmund, benzoin equations; C_4H_8O or C_8H_8O from DNP, iodoform, Tollens' results
- **Long (8 marks)**: identify A–E from formulas, ozonolysis, oxidation and tests; benzene → toluene → benzaldehyde → cinnamic acid; a cycle from an aromatic aldehyde of 106 u

Key terms

Carbonyl group: >C=O; **aldehyde** R–CHO (C=O carbon has at least one H, at the chain's end); **ketone** R–CO–R′ (two carbon groups); open chain $C_nH_{2n}O$.

α-carbon, α-hydrogens: next to the C=O; slightly acidic (aldol, iodoform).

Nucleophilic addition: Nu^- bonds to the $\delta+$ C; π electrons go to O; then H^+ to O.

Addition–elimination (condensation): H_2N–Z adds, water lost → C=N–Z.

Aldol condensation: two molecules **with α-H**, cold dil. NaOH → β-hydroxy aldehyde/ketone.

Cannizzaro reaction: aldehyde **without α-H**, conc. NaOH, heat → alcohol + acid salt (disproportionation).

Tautomerism: one compound in two forms that interconvert by an H moving: keto ⇌ enol (needs α-H).

Formalin: 37–40% methanal in water, with about 10% methanol (stops paraformaldehyde forming).

Naming and isomers

- aldehyde **alkanal**: longest chain with the CHO carbon, which is **C-1** (never numbered): Cl–CH_2CH_2CHO **3-chloropropanal**; $CH_3CH_2CH(CH_3)$CHO 2-methylbutanal
- ketone **alkan-n-one**: number from the end **nearer C=O**: butan-2-one, pentan-3-one; propanone
- common: aldehydes from the acid (formaldehyde, acetaldehyde, propionaldehyde, butyraldehyde); ketones: two groups alphabetically + ketone

Formula	IUPAC	Common
HCHO	methanal	formaldehyde
CH_3CHO	ethanal	acetaldehyde
CH_3COCH_3	propanone	acetone, dimethyl ketone
$CH_3COC_2H_5$	butan-2-one	ethyl methyl ketone
$C_2H_5COC_2H_5$	pentan-3-one	diethyl ketone
C_6H_5CHO	benzaldehyde	benzaldehyde
$C_6H_5COCH_3$	1-phenylethanone	acetophenone

- **chain**: pentanal / 2-methylbutanal; **position**: pentan-2-one / pentan-3-one; **functional**: pentanal / pentan-2-one; **tautomerism**: CH_3COCH_3 ⇌ CH_2=C(OH)CH_3; CH_3CHO ⇌ CH_2=CHOH (ethenol)
- C_3H_6O: propanal, propanone, prop-2-en-1-ol, methoxyethene
- aliphatic or aromatic (ring on the C=O); ketones **simple** (propanone) or **mixed** (butan-2-one)

Preparation

Method	Example
dehydrogenation, Cu, 573 K	1° alcohol → aldehyde; 2° → ketone (+ H_2); 3°: alkene
$K_2Cr_2O_7/H^+$	1° → aldehyde (distill off, b.p. 20 °C) or PCC in CH_2Cl_2; 2° → ketone
ozonolysis (O_3, then Zn/H_2O)	C=C cut, =O on each end
Rosenmund	$RCOCl + H_2$ ($Pd–BaSO_4$, S, xylene) → RCHO; aldehydes only
gem dihalide + aq. alkali	end C → aldehyde; middle C → ketone
alkyne + H_2O ($HgSO_4$, dil. H_2SO_4, 333 K)	ethyne → ethanal; others → ketones

- $CH_3CH_2OH \xrightarrow[573\ K]{Cu} CH_3CHO + H_2$; $(CH_3)_2CHOH \xrightarrow[573\ K]{Cu} CH_3COCH_3 + H_2$
- $CH_3CH_2OH + [O] \xrightarrow{K_2Cr_2O_7/H^+} CH_3CHO + H_2O$; left in: $CH_3CHO + [O] \longrightarrow CH_3COOH$
- $CH_3COCl + H_2 \xrightarrow[S,\ xylene]{Pd-BaSO_4} CH_3CHO + HCl$ (catalyst poisoned so the aldehyde isn't reduced)
- $CH_3CHCl_2 + 2\,KOH \longrightarrow CH_3CH(OH)_2 + 2\,KCl$; $CH_3CH(OH)_2 \longrightarrow CH_3CHO + H_2O$
- $CH_3CCl_2CH_3 + 2\,NaOH \longrightarrow CH_3COCH_3 + 2\,NaCl + H_2O$
- $HC{\equiv}CH + H_2O \xrightarrow[dil.\ H_2SO_4]{HgSO_4} CH_3CHO$ (via ethenol); propyne → **propanone** (Markovnikov); but-2-yne → butan-2-one
- ozonolysis: ethene → 2 HCHO; propene → CH_3CHO + HCHO; 2-methylpropene → CH_3COCH_3 + HCHO; but-2-ene → 2 CH_3CHO; **2-methylbut-2-ene → CH_3COCH_3 + CH_3CHO**; 2,3-dimethylbut-2-ene → 2 CH_3COCH_3

Physical properties

- HCHO gas (b.p. −19 °C), CH_3CHO liquid (20 °C); aliphatic **less dense** than water; lower aldehydes sharp smell, ketones pleasant
- methanal, ethanal, propanone **mix with water** (H bonds from water to the C=O oxygen); pentan-3-one about 5 g/100 g
- b.p.: **alkanes < aldehydes, ketones < alcohols, acids**: dipole–dipole, but no H bonds between their own molecules

The carbonyl group

- C and O **sp^2**, flat, 120°; $\sigma + \pi$ bond; O's two lone pairs; O pulls the π electrons: **C δ+, O δ−**
- δ+ C attacked by **nucleophiles** (nucleophilic addition; alkenes' C=C by electrophiles); δ− O takes H^+
- **aldehydes more reactive than ketones**: ketone's two alkyl groups +I (C less positive) and bulky (steric); HCHO most reactive

Tests

Test	Aldehyde	Ketone
2,4-DNP (Brady's)	orange-yellow ppt	orange-yellow ppt
Tollens' (warm)	**silver mirror**	none
Fehling's (boil)	**brick-red** Cu_2O (aliphatic only)	stays blue
iodoform (I_2 + NaOH)	ethanal only	methyl ketones

- **2,4-DNP**: C=N formed, + H_2O; each hydrazone its own m.p. (identification)
- **Tollens'** made fresh: $2\,AgNO_3 + 2\,NaOH \longrightarrow Ag_2O + 2\,NaNO_3 + H_2O$; $Ag_2O + 4\,NH_3 + H_2O \longrightarrow 2\,[Ag(NH_3)_2]^+ + 2\,OH^-$
  - $RCHO + 2\,[Ag(NH_3)_2]^+ + 3\,OH^- \longrightarrow RCOO^- + 2\,Ag + 4\,NH_3 + 2\,H_2O$
  - aldehyde the **reducing** agent, reagent the oxidizing agent; aromatic aldehydes give it too; never store (explosive)
- **Fehling's**: A $CuSO_4$ + B Rochelle salt in NaOH (deep blue tartrate complex)
  - $RCHO + 2\,Cu^{2+} + 5\,OH^- \longrightarrow RCOO^- + Cu_2O + 3\,H_2O$ (also HCHO, glucose)
  - weaker than Tollens': **benzaldehyde doesn't** reduce it; Benedict's similar (citrate, Na_2CO_3)
- **iodoform**: **CH_3CO–** (and $CH_3CH(OH)$– alcohols: ethanol, propan-2-ol) → pale yellow CHI_3
  - $CH_3COCH_3 + 3\,I_2 + 4\,NaOH \longrightarrow CHI_3 + CH_3COONa + 3\,NaI + 3\,H_2O$
  - not methanal, propanal, pentan-3-one; tells pentan-2-one from pentan-3-one

Reactions

Nucleophilic addition

- **H_2** (Ni, Pt, Pd), or **$LiAlH_4$** then H_3O^+ ($NaBH_4$ milder): aldehyde → 1° alcohol, ketone → 2°: $CH_3COCH_3 + H_2 \longrightarrow CH_3CH(OH)CH_3$
- **HCN** (NaCN + acid, CN^- attacks) → cyanohydrin; H_3O^+, heat → **α-hydroxy acid** (one C more)
  - $CH_3CHO + HCN \longrightarrow CH_3CH(OH)CN \xrightarrow{H_3O^+} CH_3CH(OH)COOH$ (lactic acid, **racemic**)
  - $CH_3COCH_3 + HCN \longrightarrow (CH_3)_2C(OH)CN \xrightarrow{H_3O^+} (CH_3)_2C(OH)COOH$ (2-hydroxy-2-methylpropanoic acid, not chiral)
  - HCHO → hydroxyethanoic acid
- **$NaHSO_3$** (aldehydes, small methyl ketones): $CH_3CHO + NaHSO_3 \rightleftharpoons CH_3CH(OH)SO_3Na$; crystals; no by-product; acid or Na_2CO_3 gives it back: **purification**
- **chloretone**: $CH_3COCH_3 + CHCl_3 \xrightarrow{KOH} (CH_3)_2C(OH)CCl_3$ (sedative, preservative)

Ammonia derivatives

$>C{=}O + H_2N{-}Z \longrightarrow >C{=}N{-}Z + H_2O$, best at pH 4–5

- NH_2OH → **oxime**, $(CH_3)_2C{=}NOH$; NH_2NH_2 → hydrazone; $C_6H_5NHNH_2$ → phenylhydrazone; 2,4-DNP

→ 2,4-dinitrophenylhydrazone; $NH_2NHCONH_2$ → semicarbazone (the end NH_2 reacts)

Aldol condensation (α-H; cold dil. NaOH)

- $2\,CH_3CHO \xrightarrow{\text{dil. NaOH}} CH_3CH(OH)CH_2CHO$ (3-hydroxybutanal, aldol, β-hydroxy aldehyde)
- OH^- takes an α-H → carbanion (enolate) → attacks a second C=O → alkoxide takes H^+ (OH^- catalyst)
- $2\,CH_3COCH_3 \longrightarrow (CH_3)_2C(OH)CH_2COCH_3$ (4-hydroxy-4-methylpentan-2-one, diacetone alcohol)
- heat: $CH_3CH(OH)CH_2CHO \longrightarrow CH_3CH{=}CHCHO + H_2O$ (but-2-enal, α,β-unsaturated)

Cannizzaro (no α-H: HCHO, $(CH_3)_3CCHO$, C_6H_5CHO; conc. NaOH, heat)

- $2\,HCHO + NaOH \longrightarrow CH_3OH + HCOONa$
- $2\,C_6H_5CHO + NaOH \longrightarrow C_6H_5CH_2OH + C_6H_5COONa$
- OH^- adds to one; it passes a **hydride** (H^-) to the second; one oxidized, one reduced

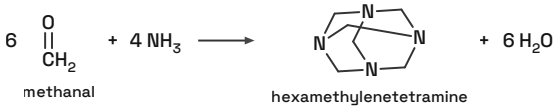
Reduction to CH_2 $>C{=}O + 4\,[H] \longrightarrow >CH_2 + H_2O$

- **Clemmensen** (Zn–Hg, conc. HCl; in acid): ethanal → ethane, propanone → propane, acetophenone → ethylbenzene
- **Wolff–Kishner** (NH_2NH_2, then KOH in ethane-1,2-diol, about 470 K; in base): hydrazone → alkane + N_2

PCl_5 → gem dihalide: $CH_3COCH_3 + PCl_5 \longrightarrow CH_3CCl_2CH_3 + POCl_3$; ethanal → 1,1-dichloroethane

Methanal

- **urotropine**: $6\,HCHO + 4\,NH_3 \longrightarrow (CH_2)_6N_4 + 6\,H_2O$ (hexamethylenetetramine; **urinary antiseptic**: gives back HCHO in acidic urine; fuel tablets; RDX)
- **phenol** (H^+ or OH^-): 2- and 4-hydroxybenzyl alcohol → –CH_2– bridges → **Bakelite** (thermosetting)
- from methanol: $CH_3OH \xrightarrow[573\,K]{Cu} HCHO + H_2$



Urotropine, $(CH_2)_6N_4$.

Formalin

- **preserves** specimens, bodies (–CH_2– links between proteins); **disinfectant**; paraformaldehyde fumigates rooms; **resins** (urea–, phenol–formaldehyde, Bakelite), tyre-cord adhesives
- **carcinogenic** (IARC Group 1, 2004: nasopharynx; leukemia 2009); about 30 mL can kill; **never in food**

Aromatic aldehydes and ketones

Benzaldehyde from toluene

- $C_6H_5CH_3 \xrightarrow[(CH_3CO)_2O]{CrO_3} C_6H_5CH(OCOCH_3)_2 \xrightarrow{H_3O^+} C_6H_5CHO$ (benzylidene diacetate traps it)
- **Étard**: $C_6H_5CH_3 \xrightarrow[H_3O^+]{CrO_2Cl_2,\ CS_2} C_6H_5CHO$
- $C_6H_5CH_3 + 2\,Cl_2 \xrightarrow{light} C_6H_5CHCl_2 + 2\,HCl$; $C_6H_5CHCl_2 + H_2O \xrightarrow{373\,K} C_6H_5CHO + 2\,HCl$
- $C_6H_5CH_3 + 2\,[O] \xrightarrow[\text{dil. } H_2SO_4]{CeO_2} C_6H_5CHO + H_2O$

Acetophenone (Friedel–Crafts acylation, anhyd. $AlCl_3$, CH_3CO^+)

- $C_6H_6 + CH_3COCl \longrightarrow C_6H_5COCH_3 + HCl$; $C_6H_6 + (CH_3CO)_2O \longrightarrow C_6H_5COCH_3 + CH_3COOH$

Benzaldehyde (no α-H: no aldol, no iodoform; Tollens' yes, Fehling's no)

- **Perkin**: $C_6H_5CHO + (CH_3CO)_2O \xrightarrow[450\,K]{CH_3COONa} C_6H_5CH{=}CHCOOH + CH_3COOH$ (cinnamic acid; anhydride a reactant)
- **benzoin**: $2\,C_6H_5CHO \xrightarrow{KCN,\ \text{ethanol}} C_6H_5CH(OH)COC_6H_5$ (CN^- catalyst)
- **Cannizzaro**: above
- ring: –CHO −I, −M, **deactivating, meta** (resonance puts + on ring C-2, 4, 6): 3-nitrobenzaldehyde, 3-formylbenzenesulphonic acid, 3-bromobenzaldehyde

Chains in the exercise

- $C_6H_5OH \xrightarrow{Zn} C_6H_6 \xrightarrow[AlCl_3]{CH_3Cl} C_6H_5CH_3 \xrightarrow{CeO_2/H^+} C_6H_5CHO \xrightarrow{Perkin} C_6H_5CH{=}CHCOOH$ (C_6H_5CHO 106 u)
- Claisen condensation: two **esters** + strong base → β-keto ester (a match option, not a test)

COMMON MISTAKES

✗ Cl–CH_2CH_2CHO 2-chloropropanal
✓ **3-chloropropanal** (CHO carbon is C-1).

✗ butan-2-one = methyl propyl ketone
✓ **ethyl methyl ketone** (methyl propyl ketone is pentan-2-one).

✗ ethanal's enol is ethanol
✓ **ethenol**, $CH_2{=}CHOH$.

✗ PCC is Collins reagent
✓ PCC is **pyridinium chlorochromate**; Collins is $CrO_3{\cdot}2C_5H_5N$.

✗ Tollens' reagent the reducing agent
✓ the **aldehyde** reduces it; ion is **diammine**silver(I).

✗ the products of HCN are optically active
✓ ethanal's is **racemic**; acetone's has **no** chiral C.

✗ $2HCHO \rightarrow CH_3OH + HCOONa$ (no NaOH)
✓ **2HCHO + NaOH** → $CH_3OH + HCOONa$.

✗ Wolff–Kishner in glycerine with aq. KOH
✓ KOH in **ethane-1,2-diol**, about 470 K.

✗ $POCl_3$ phosphonyl trichloride
✓ **phosphoryl chloride**.

✗ toluene + [O] → benzaldehyde
✓ **2[O]**; one leaves as H_2O.

✗ Perkin with CH_3COONa alone
✓ benzaldehyde + **$(CH_3CO)_2O$**, CH_3COONa as base.

✗ ozonolysis with O_2
✓ **O_3**.