JEE MAIN · PAPER 1 · CHEMISTRY

17 Organic Compounds Containing Oxygen

Formula & concept sheet

Alcohols, phenols, ethers, aldehydes, ketones and carboxylic acids with every NCERT preparation and reaction drawn as a scheme: oxidation ladders, dehydration, Lucas test, Kolbe and Reimer-Tiemann, Williamson and ether cleavage, nucleophilic addition, aldol, Cannizzaro, haloform, HVZ, esterification, and the tests that tell them apart. Each idea is explained first, then the reactions and the traps.

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READ ALONGSIDE NCERT XII · Alcohols, Phenols and Ethers

NCERT XII · Aldehydes, Ketones and Carboxylic Acids

HOW TO USE THIS SHEET

1. **Skim** — Read the Key ideas, then the formula cards.
2. **Memorise** — Learn the formulas and check every Trap box.
3. **Test** — Do the worked examples, then this chapter's PYQs.
4. **Revise** — Use the last-minute checklist before the exam.

CHAPTER 17

Organic Compounds Containing Oxygen

NCERT XII · Alcohols, Phenols and Ethers | NCERT XII · Aldehydes, Ketones and Carboxylic Acids

Covers: classification, nomenclature, structure and physical properties · preparation and reactions of alcohols, phenols (acidity, electrophilic substitution, Kolbe, Reimer-Tiemann), ethers (Williamson, cleavage) · aldehydes and ketones (Rosenmund, Stephen, Etard, Gattermann-Koch; addition, condensation, reduction, oxidation tests, aldol, Cannizzaro, haloform) · carboxylic acids (acidity, reactions, HVZ, derivatives) · distinguishing tests.

1 Structure, properties and acidity

- **Alcohols** $\mathrm{R-OH}$ (1°, 2°, 3° by the carbon bearing OH); **phenols** have OH on an aromatic ring; **ethers** $\mathrm{R-O-R'}$ (the C−O−C angle is a little above tetrahedral, about 111.7°, because the alkyl groups repel; methanol C−O−H about 108.9°); **aldehydes** $\mathrm{R-CHO}$ and **ketones** $\mathrm{R-CO-R'}$ have a planar sp^2 carbonyl carbon; **carboxylic acids** $\mathrm{R-COOH}$.
- **Boiling point** (similar molar mass): carboxylic acid (hydrogen-bonded dimers) > alcohol (H bonds) > aldehyde/ketone (dipole-dipole) > ether > alkane. Lower members dissolve in water by H bonding; solubility falls as the chain lengthens. *o*-Nitrophenol and salicylaldehyde (intramolecular H bond) are volatile in steam; the para isomers (intermolecular H bonds) are not.

ACIDITY: VALUES AND REASONS

COMPOUND	pK_a	REASON
HCOOH	3.75	no +I group; stronger than any alkyl acid
$\mathrm{C_6H_5COOH}$	4.20	sp^2 ring (–I of aryl) stabilises the carboxylate; stronger than acetic acid
$\mathrm{CH_3COOH}$	4.76	carboxylate: two equivalent resonance forms
phenol	10.0	phenoxide delocalised into the ring (not equivalent forms): weaker than acids, stronger than alcohols
water	15.7	
ethanol	about 16	alkoxide destabilised by +I; acidity $\mathrm{CH_3OH} > 1^\circ > 2^\circ > 3^\circ$

WHAT CHANGES ACIDITY

FACTOR	RULE
carboxylic acids	–I/–M groups raise acidity, +I lowers it; the effect falls with distance; more halogens means stronger: $\mathrm{Cl_3CCOOH} > \mathrm{Cl_2CHCOOH} > \mathrm{ClCH_2COOH} > \mathrm{CH_3COOH}$; $\mathrm{FCH_2COOH} > \mathrm{ClCH_2COOH} > \mathrm{BrCH_2COOH} > \mathrm{ICH_2COOH}$; $\mathrm{HCOOH} > \mathrm{C_6H_5COOH} > \mathrm{CH_3COOH} > \mathrm{CH_3CH_2COOH}$
substituted benzoic acids	*p*-nitro > *m*-nitro > benzoic > *p*-methyl > *p*-methoxy; ortho effect makes nearly any *o*-substituted benzoic acid stronger
substituted phenols	picric acid ≫ 2,4-dinitrophenol > *p*-nitrophenol > *o*-nitrophenol (intramolecular H bond) > *m*-nitrophenol > phenol > cresols; the nitro group helps most at o/p by resonance
reaction with bases	phenol reacts with Na and NaOH, **not** with $\mathrm{NaHCO_3}$; carboxylic acids (and picric acid) liberate $\mathrm{CO_2}$ from $\mathrm{NaHCO_3}$

KEY IDEA

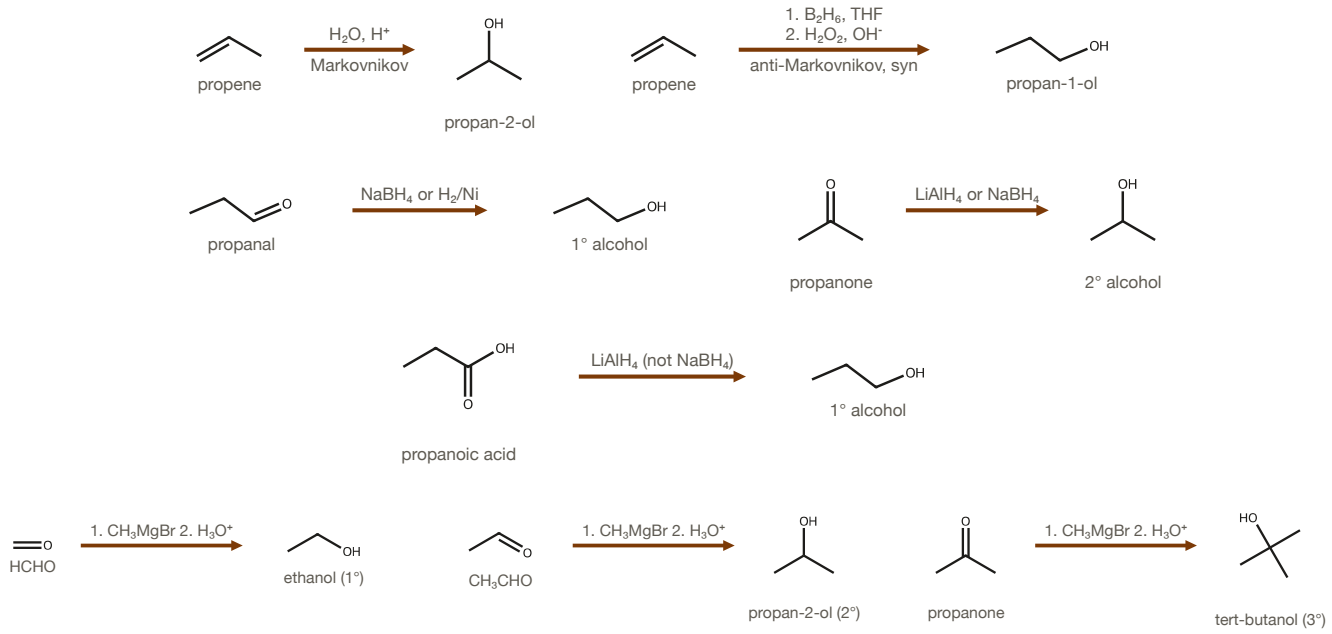
Acidity is the stability of the conjugate base. In carboxylate the charge is shared equally by two oxygens (two equivalent forms); in phenoxide it spreads onto ring carbons (less stable); in alkoxide it stays on one oxygen and is pushed up by alkyl groups. So acid > phenol > water > alcohol.

QUICK CHECK

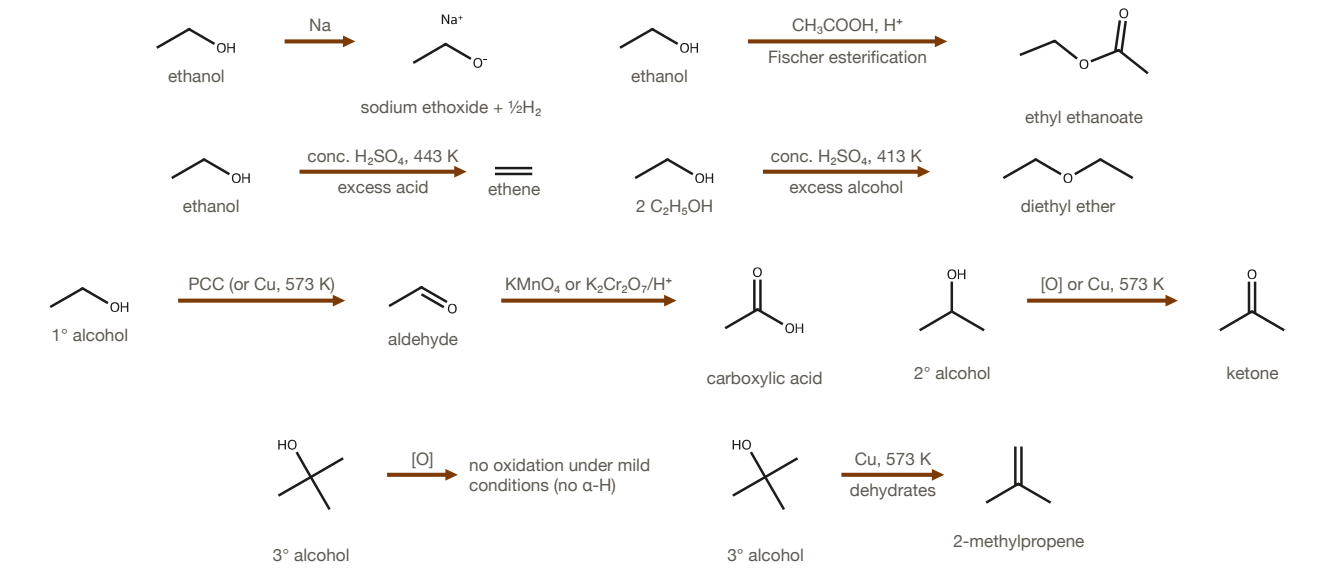
Rank by acidity: ethanol, phenol, *p*-nitrophenol, acetic acid, trichloroacetic acid.

Answer: $Cl_3CCOOH > CH_3COOH >$ *p*-nitrophenol > phenol > C_2H_5OH.

2 Alcohols: preparation and reactions



preparation of alcohols: hydration (Markovnikov), hydroboration-oxidation (anti-Markovnikov), reduction of carbonyl compounds and acids, and the Grignard routes to 1°, 2° and 3° alcohols



reactions of alcohols: O–H cleavage (Na, esterification), C–O cleavage (dehydration, halides), oxidation ladder (1° to aldehyde to acid, 2° to ketone, 3° resists) and dehydrogenation over Cu

REACTIONS OF ALCOHOLS: CONDITIONS AND FACTS

REACTION	DETAIL
with sodium	$2\,\mathrm{ROH} + 2\,\mathrm{Na} \longrightarrow 2\,\mathrm{RONa} + \mathrm{H_2}$; acidity $1^\circ > 2^\circ > 3^\circ$; reaction with Grignard and NaH also shows the acidic H
esterification	$\mathrm{ROH} + \mathrm{R'COOH} \overset{\mathrm{H^+}}{\rightleftharpoons} \mathrm{R'COOR} + \mathrm{H_2O}$ (acyl-oxygen cleavage: the ester's OR oxygen comes from the alcohol); faster and complete with $(\mathrm{R'CO})_2\mathrm{O}$ or $\mathrm{R'COCl}$ (pyridine); aspirin is made this way from salicylic acid
to alkyl halides	$\mathrm{HX}/\mathrm{ZnCl_2}$, $\mathrm{PCl_3}$, $\mathrm{PCl_5}$, $\mathrm{SOCl_2}$ (see Haloalkanes)
Lucas test (conc. HCl + anhyd. $\mathrm{ZnCl_2}$)	3° turbid **immediately**; 2° in about 5 min; 1° no turbidity at room temperature (only on heating): the rate follows carbocation stability
dehydration	1°: conc. $\mathrm{H_2SO_4}$, 443 K; 2°: 85% $\mathrm{H_3PO_4}$, 440 K; 3°: 20% $\mathrm{H_3PO_4}$, 358 K; ease $3^\circ > 2^\circ > 1^\circ$. Mechanism: (1) protonation of OH; (2) loss of $\mathrm{H_2O}$ to give a carbocation (slow); (3) loss of a β-$\mathrm{H^+}$ (Saytzeff alkene; rearrangement possible). At 413 K with excess alcohol, ethanol gives diethyl ether (S_N2 of a second ROH on the protonated alcohol)
oxidation	$1^\circ \rightarrow$ aldehyde (PCC, anhydrous $\mathrm{CrO_3}$) $\rightarrow$ acid ($\mathrm{KMnO_4}$, acidified $\mathrm{K_2Cr_2O_7}$); $2^\circ \rightarrow$ ketone; 3° resist (strong conditions break C$-$C)
dehydrogenation	over Cu at 573 K: $1^\circ \rightarrow$ aldehyde, $2^\circ \rightarrow$ ketone, $3^\circ \rightarrow$ alkene

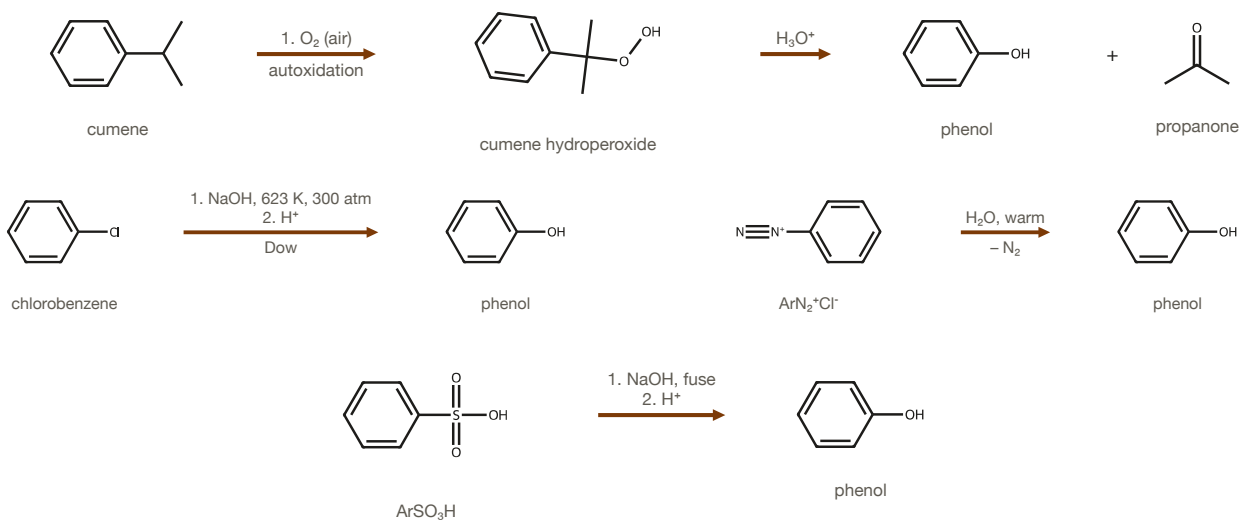
REMEMBER

- Hydroboration gives the anti-Markovnikov alcohol without rearrangement; acid hydration gives Markovnikov and may rearrange.
- $\mathrm{LiAlH_4}$ reduces acids and esters; $\mathrm{NaBH_4}$ does not (aldehydes and ketones only).
- Grignard + HCHO $\rightarrow 1^\circ$; + other RCHO $\rightarrow 2^\circ$; + ketone $\rightarrow 3^\circ$; + ester (2 equivalents) $\rightarrow 3^\circ$; + $\mathrm{CO_2} \rightarrow$ acid.

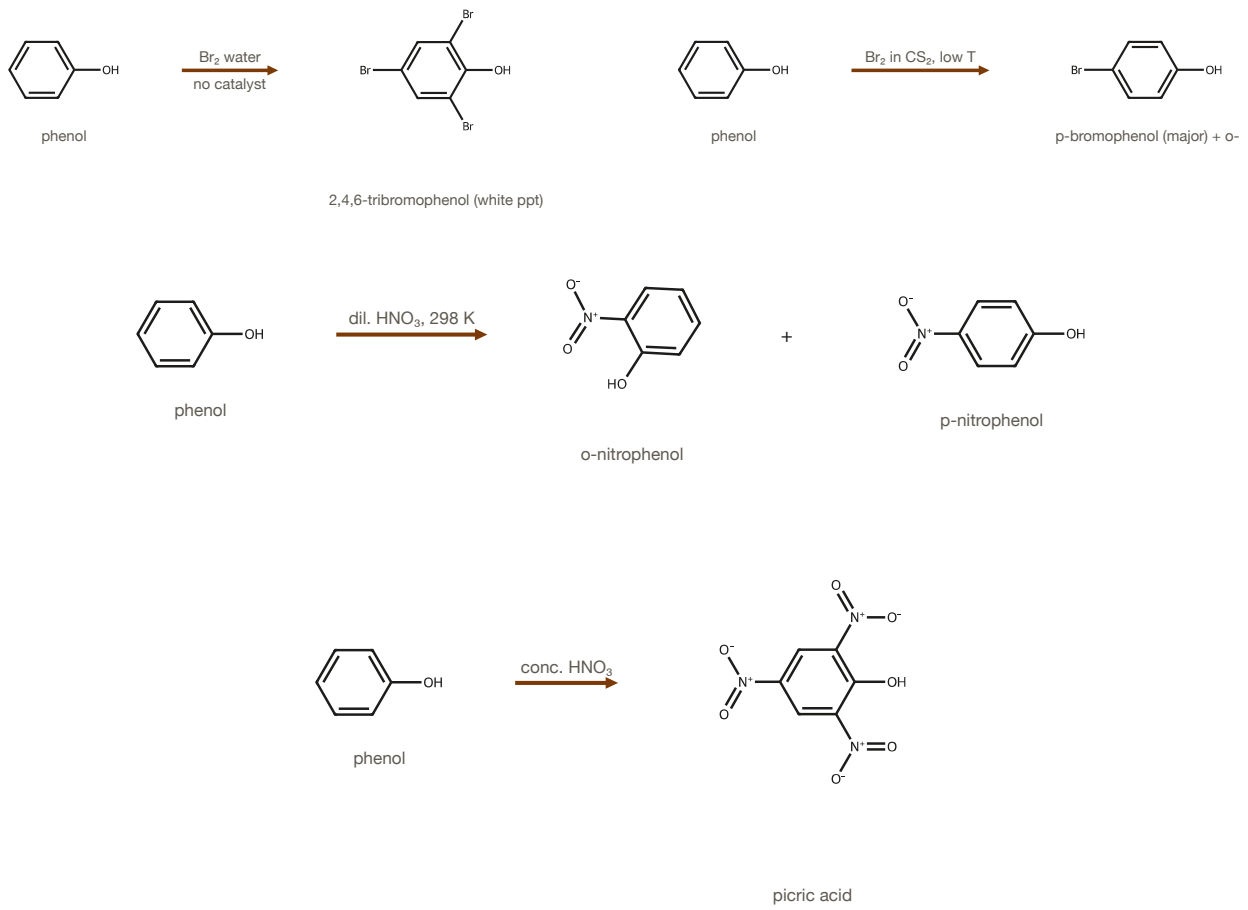
TRAP

Ethanol (1°) gives no immediate turbidity with Lucas reagent. $\mathrm{NaBH_4}$ does not reduce RCOOH. Dehydration needs heat and excess acid for the alkene but excess alcohol and lower temperature for the ether.

3 Phenols



preparation of phenol: cumene process (industrial, also gives acetone), Dow process, hydrolysis of benzenediazonium salt, fusion of benzenesulphonic acid with NaOH



reactions of phenol (1): bromination and nitration (OH activates the ring, o/p directing)

FACTS ABOUT PHENOL

ITEM	DETAIL
acidity	phenoxide is resonance stabilised, so phenol dissolves in NaOH but not $\mathrm{NaHCO_3}$; $-NO_2$ at o/p raises acidity, alkyl groups lower it
nitration	dilute $\mathrm{HNO_3}$ at 298 K gives o- and p-nitrophenol (separated by steam distillation: the ortho isomer is volatile); concentrated gives picric acid (better by sulphonation first, then nitration)
halogenation	$\mathrm{Br_2}$ water: white precipitate of 2,4,6-tribromophenol (no Lewis acid needed, OH strongly activates); $\mathrm{Br_2}$ in $\mathrm{CS_2}$ or $\mathrm{CHCl_3}$ at low T: mono-bromophenols (para major)
sulphonation	conc. $\mathrm{H_2SO_4}$: o-hydroxybenzenesulphonic acid at room T (kinetic), p- at 373 K (thermodynamic)
Kolbe reaction	sodium phenoxide + $\mathrm{CO_2}$ (4 to 7 atm, about 400 K), then $\mathrm{H^+}$: salicylic acid; the electrophile is $\mathrm{CO_2}$
Reimer-Tiemann	$\mathrm{CHCl_3}$ + aq. NaOH (about 340 K) then $\mathrm{H^+}$: salicylaldehyde; electrophile dichlorocarbene : $\mathrm{CCl_2}$ (with $\mathrm{CCl_4}$ the product is salicylic acid)
other	Zn dust, heat: benzene; oxidation to p-benzoquinone; neutral $\mathrm{FeCl_3}$: violet colour (also enols)

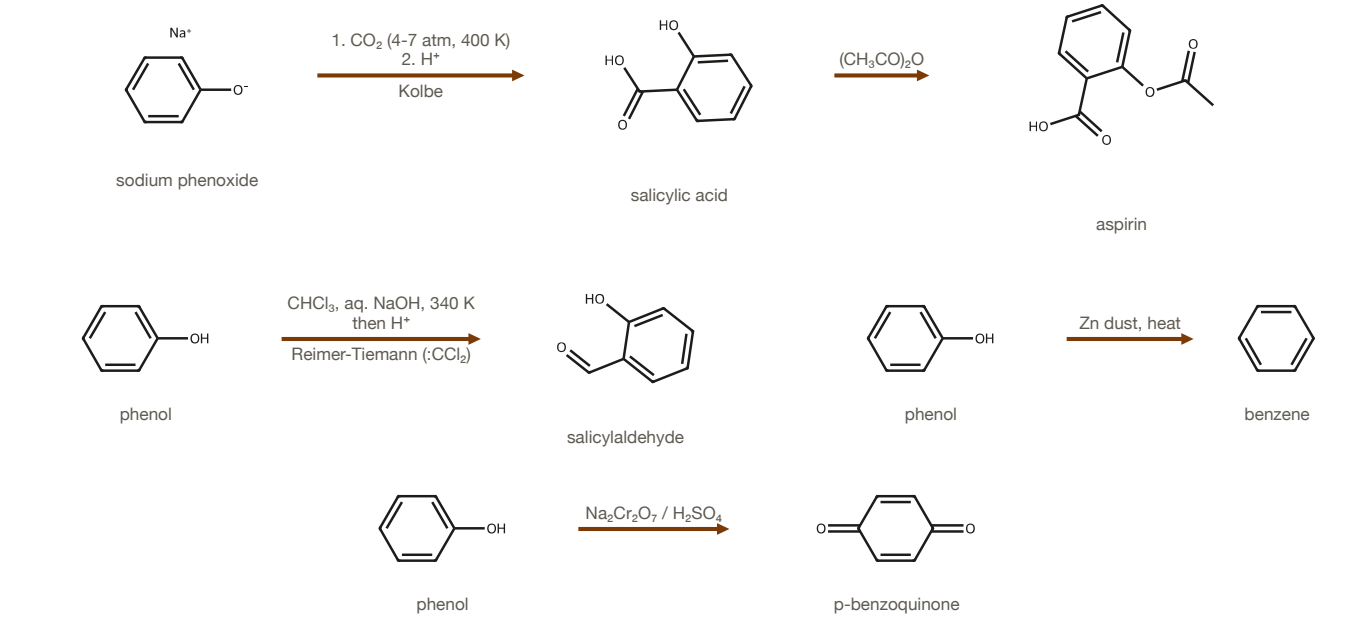
WHY IT WORKS

The lone pair of O delocalises into the ring ($+M$), so OH is a strong ortho/para activator (bromine water goes to the tri-bromide at once) and the C$-$O bond has partial double-bond character (phenol does not give aryl halides with HX). Intramolecular H bonding in the ortho isomers lowers their boiling point and acidity.

QUICK CHECK

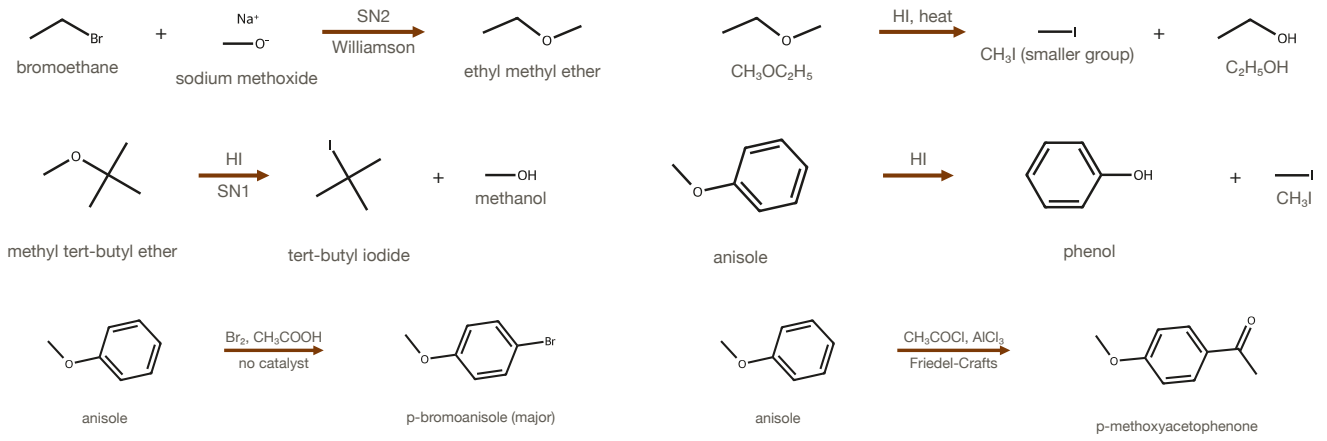
How can o- and p-nitrophenol be separated, and which is more acidic?

Answer: Steam distillation: o-nitrophenol (intramolecular H bond) distils over. p-Nitrophenol is the stronger acid.



reactions of phenol (2): Kolbe, Reimer-Tiemann, zinc dust, oxidation

4 Ethers



ethers: Williamson synthesis (SN2: 1° halide + alkoxide), cleavage with HI (SN2 at the smaller group, SN1 for a tertiary group; an aryl alkyl ether always gives phenol + alkyl halide), electrophilic substitution of anisole

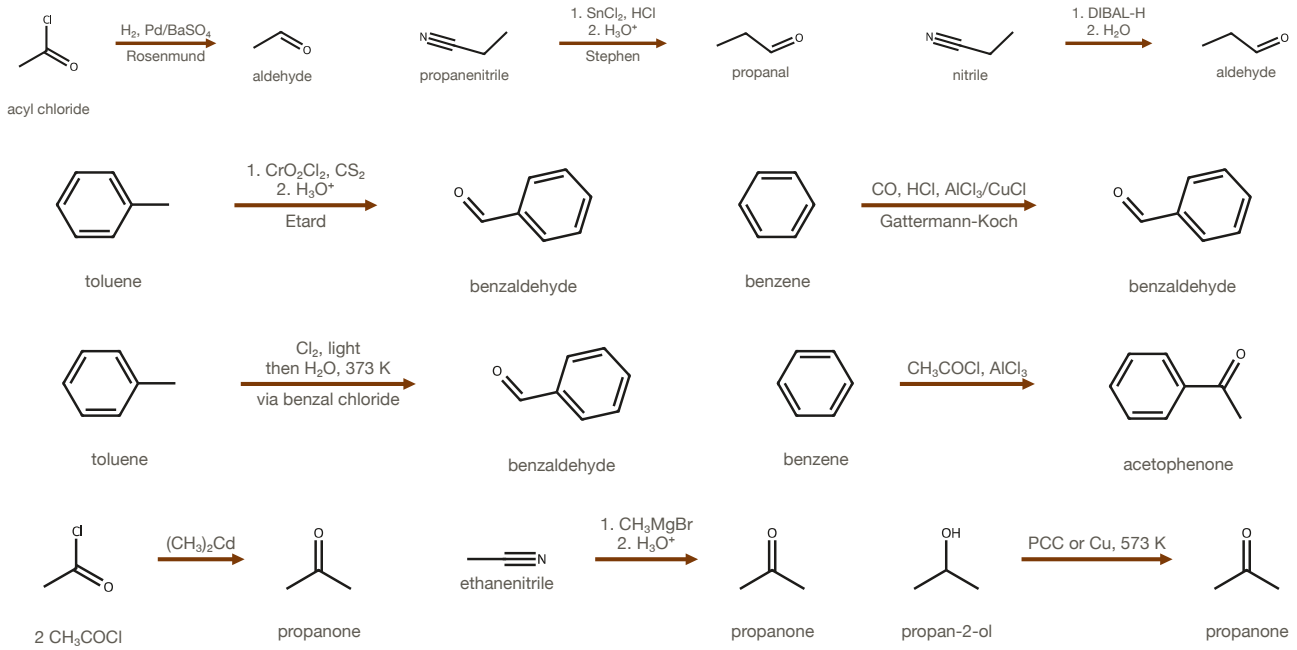
WILLIAMSON SYNTHESIS AND ITS LIMITS

- $\mathrm{R{-}X + R'O^{-}Na^{+} \longrightarrow R{-}O{-}R' + NaX}$ (S_N2). Use the **primary** (or methyl) halide with the bulkier alkoxide: a 3° halide gives an alkene by E2.
- Aryl ethers: phenoxide + alkyl halide, never aryl halide + alkoxide (ArX does not do S_N2).
- Other routes: dehydration of alcohols with excess alcohol at 413 K (symmetrical ethers only).

CLEAVAGE AND SUBSTITUTION

- $\mathrm{R{-}O{-}R' + HI \longrightarrow ROH + R'I}$ (HI > HBr > HCl). Methyl with $1^\circ/2^\circ$ alkyl: $\mathrm{I^-}$ attacks the smaller group (S_N2): $\mathrm{CH_3I}$ + the other alcohol. A 3° group: S_N1, the tertiary iodide.
- **Alkyl aryl ethers** always give **phenol** + alkyl halide (the $\mathrm{Ar{-}O}$ bond is stronger).
- Anisole: $-\mathrm{OCH_3}$ is an o/p activator: bromination (in ethanoic acid, no catalyst) gives mainly p-bromoanisole; Friedel-Crafts and nitration go o/p.

5 Aldehydes and ketones: preparation



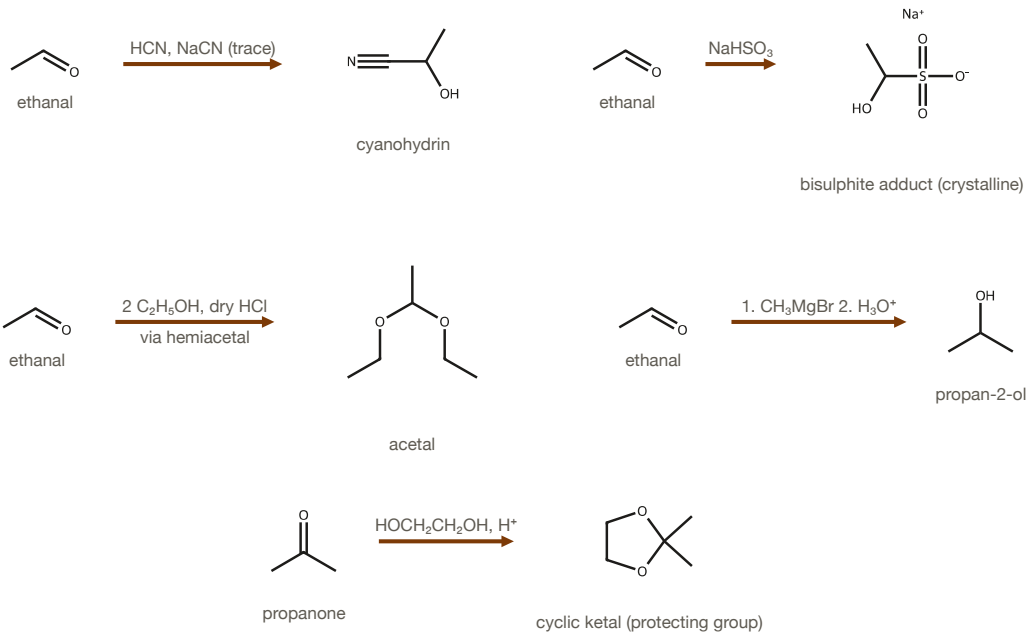
preparation of aldehydes and ketones: Rosenmund, Stephen, DIBAL-H, Etard, Gattermann-Koch, side-chain chlorination, Friedel-Crafts acylation, dialkylcadmium and nitrile + Grignard

PREPARATION: SUMMARY OF NAMED METHODS

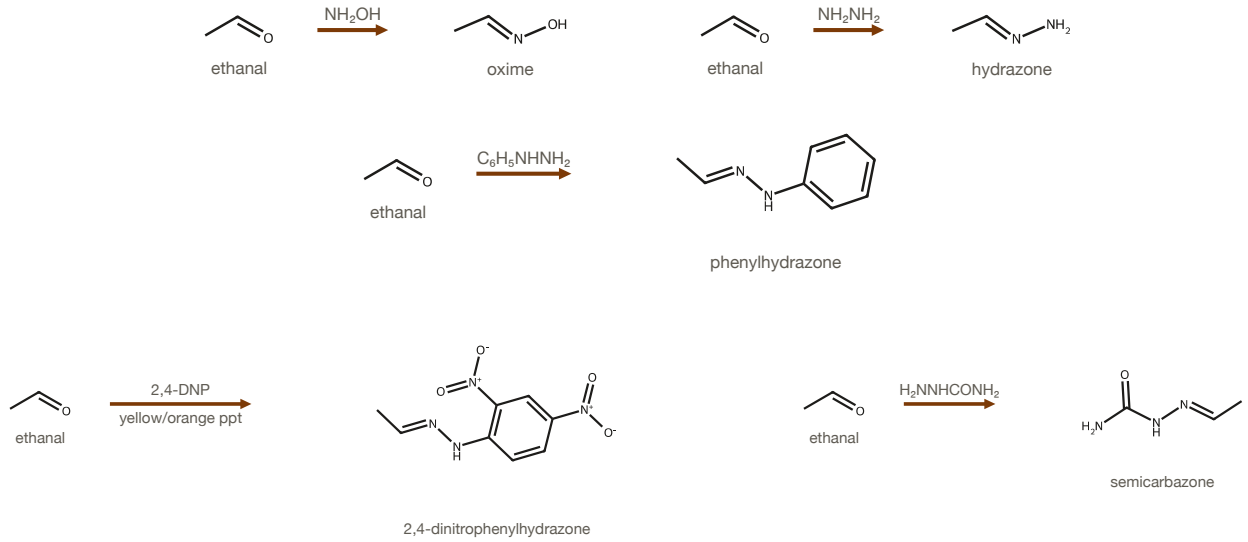
NAME	REACTION
Rosenmund	$\mathrm{RCOCl} + \mathrm{H_2} \xrightarrow{\mathrm{Pd/BaSO_4}} \mathrm{RCHO} + \mathrm{HCl}$ ($\mathrm{BaSO_4}$ poisons the catalyst so reduction stops at the aldehyde)
Stephen	$\mathrm{RCN} + \mathrm{SnCl_2} + \mathrm{HCl} \longrightarrow \mathrm{RCH{=}NH \cdot HCl} \xrightarrow{\mathrm{H_3O^+}} \mathrm{RCHO}$
DIBAL-H	nitrile or ester, then $\mathrm{H_2O}$: aldehyde
Etard	toluene + $\mathrm{CrO_2Cl_2}$ in $\mathrm{CS_2}$, then $\mathrm{H_3O^+}$: benzaldehyde (chromium complex); with $\mathrm{CrO_3}$/acetic anhydride the benzylidene diacetate hydrolyses to benzaldehyde
Gattermann-Koch	benzene + CO + HCl, anhyd. $\mathrm{AlCl_3}$/CuCl: benzaldehyde (formyl chloride, HCOCl)
ketones	Friedel-Crafts acylation; $2\,\mathrm{RCOCl} + \mathrm{R'_2Cd} \longrightarrow 2\,\mathrm{RCOR'} + \mathrm{CdCl_2}$; nitrile + Grignard then $\mathrm{H_3O^+}$; oxidation or dehydrogenation of 2° alcohols; hydration of alkynes (Markovnikov)
aldehydes (others)	oxidation or dehydrogenation of 1° alcohols (PCC, Cu, 573 K); ozonolysis of alkenes; hydration of ethyne (ethanal)

6 Aldehydes and ketones: reactions

The carbonyl carbon is sp^2, planar and $\delta+$, so the characteristic reaction is **nucleophilic addition**: the nucleophile attacks from either face, the oxygen takes the electrons (tetrahedral alkoxide), then protonation. If a new chiral centre forms the product is racemic. **Reactivity**: $\mathrm{HCHO} > \mathrm{CH_3CHO} >$ other RCHO $> \mathrm{CH_3COCH_3} >$ other ketones (sterics plus $+I$ of two alkyl groups); aromatic carbonyls are less reactive than aliphatic (resonance with the ring); electron-withdrawing groups raise reactivity (p-nitrobenzaldehyde $>$ benzaldehyde $>$ p-tolualdehyde).



nucleophilic addition to ethanal: HCN (cyanohydrin), $NaHSO_3$, alcohols and dry HCl (hemiacetal then acetal), Grignard reagent



condensation with ammonia derivatives $H_2N–Z$ (weakly acidic medium) gives C=N–Z; 2,4-DNP is the test for any carbonyl; semicarbazide reacts through the NH_2 next to NH

ADDITION AND CONDENSATION PRODUCTS

REAGENT	PRODUCT	NOTES
HCN (with base)	cyanohydrin $R_2C(OH)CN$	extends the chain by one carbon; hydrolysis gives a hydroxy acid
$NaHSO_3$	crystalline bisulphite adduct	aldehydes and methyl ketones; used to separate and purify, regenerated by acid or base
ROH / dry HCl	hemiacetal then acetal	ketone + ethylene glycol: cyclic ketal (protecting group)
H_2N-Z in weak acid	$R_2C{=}N-Z$	NH_2OH oxime; NH_2NH_2 hydrazone; $C_6H_5NHNH_2$ phenylhydrazone; 2,4-DNP orange precipitate (test for C=O); semicarbazide: semicarbazone $R_2C{=}N-NH-CO-NH_2$
Grignard reagent	alcohol	HCHO 1°, RCHO 2°, ketone 3°

REDUCTIONS AND OXIDATION TESTS

REACTION	DETAIL
to alcohols	$NaBH_4$, $LiAlH_4$, H_2/Ni
Clemmensen	$C{=}O \longrightarrow CH_2$ with Zn-Hg and conc. HCl (acid-stable substrates)
Wolff-Kishner	$C{=}O \longrightarrow CH_2$ with NH_2NH_2 then KOH in ethylene glycol, heat (N_2 lost; base-stable substrates)
Tollens' reagent	$RCHO + 2\,[Ag(NH_3)_2]^+ + 3\,OH^- \longrightarrow RCOO^- + 2\,Ag + 2\,H_2O + 4\,NH_3$: silver mirror (aldehydes, also HCOOH); ketones negative
Fehling's, Benedict's	$RCHO + 2\,Cu^{2+} + 5\,OH^- \longrightarrow RCOO^- + Cu_2O + 3\,H_2O$: red-brown precipitate; **aromatic aldehydes negative**, ketones negative (except α-hydroxy ketones such as fructose)
Schiff's reagent	magenta colour restored (pink) by aldehydes
strong oxidants	ketones with hot HNO_3 or $KMnO_4/H_2SO_4$ cleave next to C=O to a mixture of acids; benzaldehyde is a meta director

TRAP

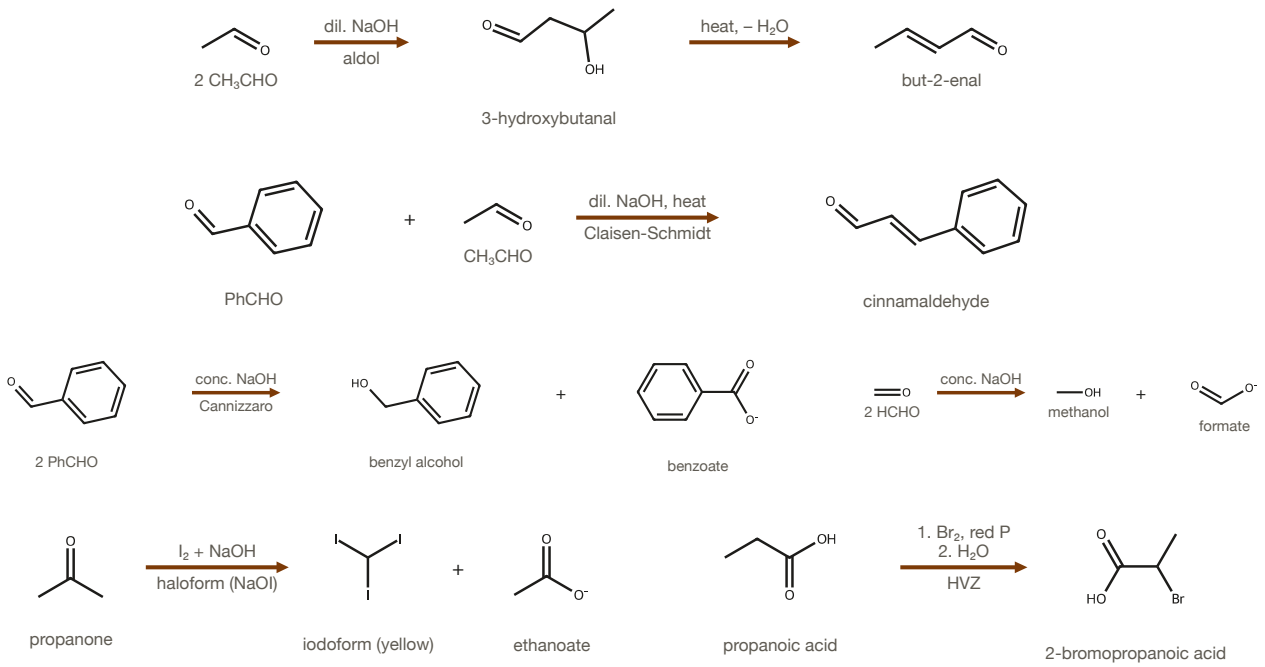
The semicarbazone forms through the NH_2 that is attached to NH, not the amide NH_2. Benzaldehyde: Tollens' positive, Fehling's negative. KOI (hypoiodite) is an **oxidising** agent. Formaldehyde with excess Tollens' can give more than 2 Ag: use the $2:1$ ratio for RCHO only.

QUICK CHECK

Which of ethanal, propanal, benzaldehyde, propanone give (a) Tollens', (b) Fehling's, (c) iodoform?

Answer: (a) first three; (b) ethanal and propanal; (c) ethanal and propanone (CH_3CO- group).

7 α-Hydrogen chemistry: aldol, Cannizzaro, haloform



α-hydrogen chemistry: aldol and its dehydration, Cannizzaro (no α-H, conc. alkali), haloform ($CH_3CO–$ or $CH_3CH(OH)–$), Claisen-Schmidt crossed aldol, HVZ α-halogenation

A-HYDROGEN REACTIONS

REACTION	REQUIREMENT AND FACTS
acidity of α-H	enolate resonance stabilises the carbanion; pK_a about 19 to 20 for simple ketones
aldol condensation	aldehyde or ketone with α-H + dilute NaOH: $2\,CH_3CHO \longrightarrow CH_3CH(OH)CH_2CHO$ (3-hydroxybutanal, aldol); heating dehydrates to but-2-enal; acetone gives 4-hydroxy-4-methylpentan-2-one, then 4-methylpent-3-en-2-one. Cross-aldol of two enolisable carbonyls gives 4 products
Claisen-Schmidt	C_6H_5CHO (no α-H) + CH_3CHO: cinnamaldehyde; + acetophenone: chalcone (benzalacetophenone)
Cannizzaro	aldehydes with **no** α-H ($HCHO$, C_6H_5CHO, $(CH_3)_3CCHO$) + **concentrated** NaOH: half oxidised to carboxylate, half reduced to alcohol ($2\,HCHO + NaOH \longrightarrow CH_3OH + HCOONa$; $2\,C_6H_5CHO + KOH \longrightarrow C_6H_5CH_2OH + C_6H_5COOK$); crossed Cannizzaro with HCHO: HCHO is oxidised, the other aldehyde reduced
haloform	CH_3CO^- (methyl ketones, ethanal) and $CH_3CH(OH)^-$ (ethanol, propan-2-ol, butan-2-ol) with $X_2/NaOH$: $RCOCH_3 + 3\,I_2 + 4\,NaOH \longrightarrow CHI_3 + RCOONa + 3\,NaI + 3\,H_2O$; iodoform is a yellow solid with a characteristic smell (M = 394). Methanol, propanal, pentan-3-one, benzophenone, propan-1-ol: negative

KEY IDEA

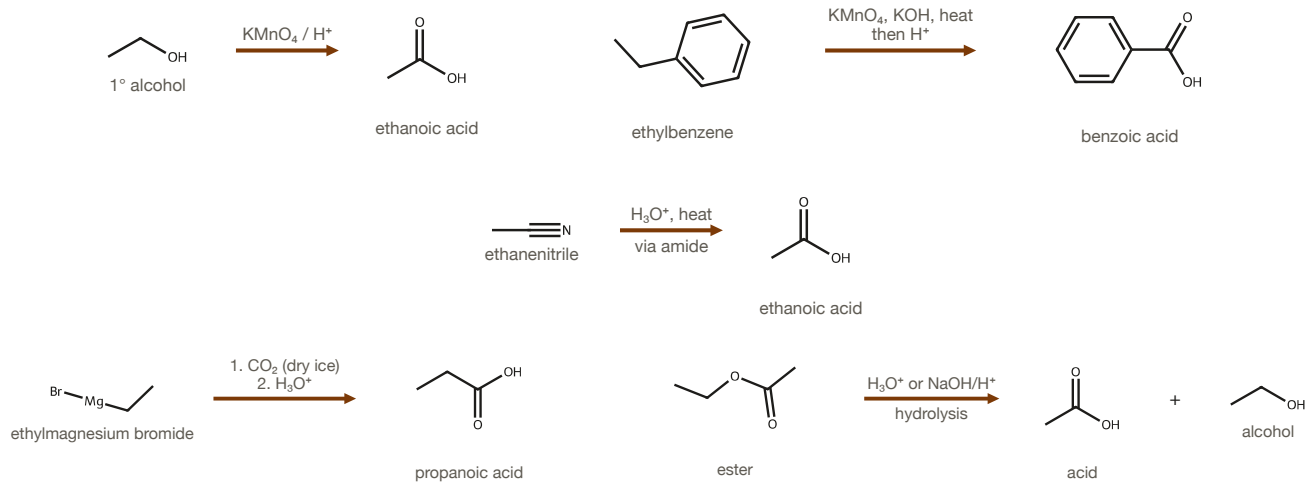
With α-H and **dilute** base, aldehydes and ketones undergo aldol (C−C bond formation). Without α-H and with **concentrated** base they undergo Cannizzaro (disproportionation by hydride transfer). Look for the methyl-carbonyl or methyl-carbinol group for iodoform.

QUICK CHECK

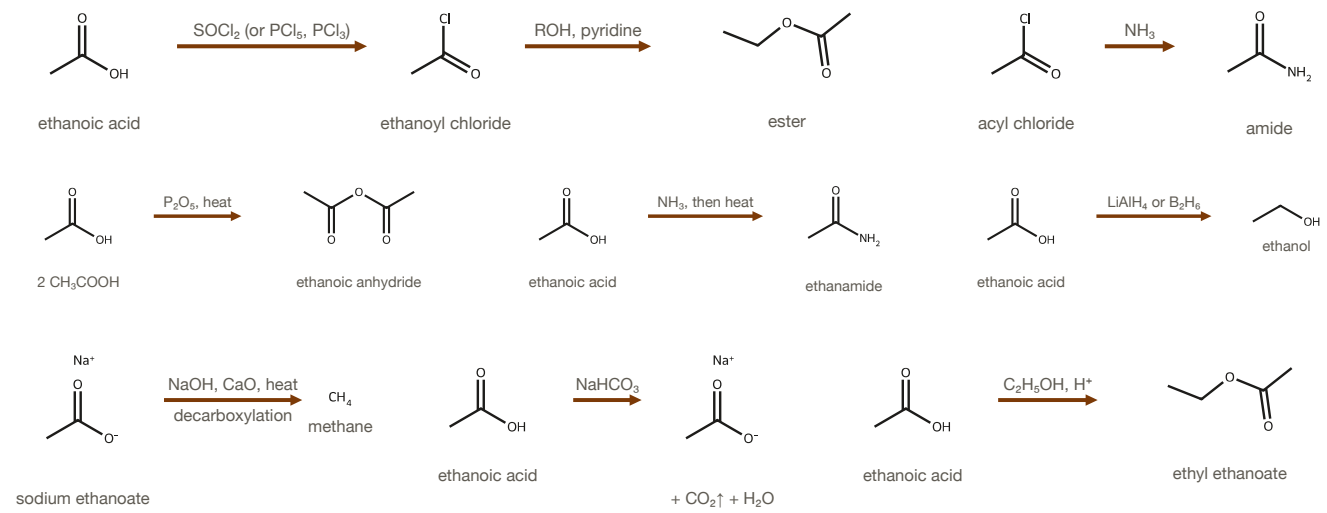
Products of cross-Cannizzaro of $HCHO$ with C_6H_5CHO and conc. NaOH.

Answer: $HCOONa$ (HCHO oxidised) and $C_6H_5CH_2OH$ (benzaldehyde reduced).

8 Carboxylic acids and their derivatives



preparation of carboxylic acids: oxidation, side-chain oxidation of arenes, hydrolysis of nitriles, Grignard + CO_2 (one carbon added), and hydrolysis of derivatives



reactions of ethanoic acid and its derivatives: acid chloride, anhydride, amide, ester; reduction, decarboxylation, $NaHCO_3$ test

REACTIONS OF CARBOXYLIC ACIDS

REACTION	DETAIL
with $NaHCO_3$	$RCOOH + NaHCO_3 \longrightarrow RCOONa + H_2O + CO_2$: brisk effervescence (test; phenols do not)
acid chloride	$RCOOH + PCl_5 \longrightarrow RCOCl + POCl_3 + HCl$; $3\,RCOOH + PCl_3 \longrightarrow 3\,RCOCl + H_3PO_3$; $RCOOH + SOCl_2 \longrightarrow RCOCl + SO_2 + HCl$
anhydride	heat with P_2O_5 or H_2SO_4 (two molecules, loss of water)
amide	$RCOOH + NH_3 \rightleftharpoons RCOO{-}NH_4^+ \xrightarrow{\text{heat}} RCONH_2 + H_2O$
ester	Fischer: $RCOOH + R'OH \overset{H^+}{\rightleftharpoons} RCOOR' + H_2O$, $K_c \approx 4$ for acetic acid with ethanol (use excess alcohol or remove water)
reduction	$LiAlH_4$ or B_2H_6 gives the 1° alcohol ($NaBH_4$ does not)
decarboxylation	$RCOONa + NaOH \xrightarrow{\text{CaO, heat}} RH + Na_2CO_3$; Kolbe electrolysis gives R−R
HVZ (Hell-Volhard-Zelinsky)	$RCH_2COOH \xrightarrow{1\cdot X_2/\text{red P } 2\cdot H_2O} RCHXCOOH$ (α-halogenation)
aromatic ring	$-COOH$ is a meta director and deactivating; benzoic acid does not undergo Friedel-Crafts
formic acid	also has a $-CHO$ group: reduces Tollens' and Fehling's reagents

REACTIVITY OF ACID DERIVATIVES AND DISTINGUISHING TESTS

ORDER OR TEST	RESULT
nucleophilic acyl substitution	$RCOCl > (RCO)_2O > RCOOR' > RCONH_2$ (better leaving group = more reactive)
alcohols 1°/2°/3°	Lucas test: 3° immediate, 2° in 5 min, 1° none at room T
phenol vs alcohol	neutral $FeCl_3$ violet; Br_2 water white precipitate; dissolves in NaOH
phenol vs carboxylic acid	$NaHCO_3$: only the acid gives CO_2
aldehyde vs ketone	Tollens\' silver mirror, Fehling\'s red Cu_2O (aliphatic aldehydes), Schiff\'s pink
any carbonyl	2,4-DNP: yellow-orange-red precipitate
methyl ketone, $CH_3CH(OH)^-$, ethanol	iodoform: yellow precipitate
benzaldehyde vs ethanal	Fehling's and iodoform positive only for ethanal
formic vs acetic acid	Tollens': only formic acid

TRAP

Fischer esterification: the alkoxy oxygen of the ester comes from the **alcohol**, the water's oxygen from the acid. $LiAlH_4$ on an α,β-unsaturated ester ($CH_3CH{=}CHCO_2CH_3$) usually reduces only the ester: $CH_3CH{=}CHCH_2OH + CH_3OH$. Aldehydes are oxidised easily (reducing agents); ketones are not.

QUICK CHECK

Order the acidity: $HCOOH$, CH_3COOH, C_6H_5COOH, CH_3CH_2COOH, $ClCH_2COOH$.

Answer: $ClCH_2COOH > HCOOH > C_6H_5COOH > CH_3COOH > CH_3CH_2COOH$.

9 Worked examples

GRIGNARD GAS VOLUME

1 g of an alcohol (active H, one OH) liberates 0.7 L of CH_4 at STP with CH_3MgI. Its molar mass?

$0.7\text{ L} = 0.03125\text{ mol } CH_4 = \text{mol of OH};\ M = \dfrac{1}{0.03125} = 32$: methanol (check: $CH_3OH = 32$)

IODOFORM STOICHIOMETRY

Mass of iodoform from 1.16 g of propanone ($M = 58$)?

$\dfrac{1.16}{58} = 0.02\text{ mol} \rightarrow 0.02\text{ mol } CHI_3\ (M = 394) = 7.88\text{ g}$

TOLLENS' SILVER

Mass of silver from 0.44 g ethanal ($M = 44$) with Tollens' reagent?

$0.01\text{ mol } CH_3CHO \rightarrow 2 \times 0.01 = 0.02\text{ mol Ag} = 2.16\text{ g}$

ROAD MAP

A (C_3H_6O) gives a 2,4-DNP precipitate and no silver mirror; with $I_2/NaOH$ it gives a yellow solid. Identify A, and its reaction with CH_3MgBr.

A is propanone (ketone, methyl ketone); with CH_3MgBr then H_3O^+: tert-butanol

ETHER CLEAVAGE

Products of heating $C_2H_5OCH_3$ with HI, and of $C_6H_5OC_2H_5$ with HI.

CH_3I + C_2H_5OH (I^- attacks the smaller methyl); phenol + C_2H_5I (aryl-O bond not cleaved)

CANNIZZARO OR ALDOL

Which of $HCHO$, C_6H_5CHO, CH_3CHO, $(CH_3)_2CHCHO$ undergo Cannizzaro?

those with no α-H: $HCHO$ and C_6H_5CHO; the others (with α-H) undergo aldol

PERCENT OXYGEN

%O in phenol (C_6H_6O, 94) and in *o*-nitrophenol ($C_6H_5NO_3$, 139)?

$\dfrac{16}{94} = 17.0\%$; $\dfrac{48}{139} = 34.5\%$

CONVERSION

Propene to propan-1-ol and to propan-2-ol; ethanal to 2-hydroxypropanoic acid.

1° via B_2H_6 then H_2O_2/OH^-; 2° via H_2O/H^+; ethanal $\xrightarrow{HCN}$ cyanohydrin $\xrightarrow{H_3O^+}$ lactic acid

KOLBE THEN ASPIRIN

Phenol to aspirin.

$$C_6H_5OH \xrightarrow{NaOH} C_6H_5ONa \xrightarrow[H^+]{CO_2,\ 400\text{ K}} \text{salicylic acid} \xrightarrow{(CH_3CO)_2O} \text{aspirin}$$

REAGENT FOR A STEP

$C_6H_5COCl \rightarrow C_6H_5CHO$ and $C_6H_5CN \rightarrow C_6H_5CHO$.

Rosenmund (H_2, $Pd/BaSO_4$); Stephen ($SnCl_2/HCl$, then H_3O^+) or DIBAL-H

10 Last-minute checklist

BEFORE YOU ANSWER

Which functional group, and is there an α-H? Mild or strong oxidant? Acid or base catalyst? For tests: which reagent is positive only for the aldehyde, the methyl ketone, the acid or the phenol?

- Alcohol prep: hydration (Markovnikov), hydroboration (anti), $\mathrm{NaBH_4/LiAlH_4}$, Grignard (1° HCHO, 2° RCHO, 3° ketone); reactions: Na, esterification, dehydration (443 K alkene, 413 K ether), oxidation ladder, Lucas (3° fast).
- Phenol: Dow, cumene, diazonium; acidity (not with $\mathrm{NaHCO_3}$); $\mathrm{Br_2}$ water tribromide; nitration o/p, picric; Kolbe (salicylic acid, aspirin); Reimer-Tiemann (salicylaldehyde, $:\mathrm{CCl_2}$); Zn gives benzene; $\mathrm{FeCl_3}$ violet.
- Ethers: Williamson (1° halide + bulky alkoxide), HI cleavage (smaller group, 3° by S_N1, aryl alkyl gives phenol), anisole o/p.
- Carbonyl prep: Rosenmund, Stephen, DIBAL-H, Etard, Gattermann-Koch, FC acylation, $\mathrm{R_2Cd}$; addition: HCN, $\mathrm{NaHSO_3}$, acetal, $\mathrm{H_2N-Z}$ (2,4-DNP, semicarbazide), Grignard; Clemmensen (acid), Wolff-Kishner (base); Tollens', Fehling's, Schiff's.
- Aldol (dilute, α-H), Cannizzaro (conc., no α-H), Claisen-Schmidt, haloform ($\mathrm{CH_3CO-}$ and $\mathrm{CH_3CH(OH)-}$); acids: HVZ, $\mathrm{SOCl_2}$, esterification, $\mathrm{NaHCO_3}$ test, $\mathrm{LiAlH_4}$; acidity: $\mathrm{HCOOH > C_6H_5COOH > CH_3COOH}$; reactivity $\mathrm{RCOCl > (RCO)_2O >}$ ester $>$ amide.

Now test it. Practise this chapter with past-paper and bank questions on Prep Vault. **Practice this chapter →**