Unit 11 · Phenol

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
- **The paper:** 11 MCQs × 1 · 8 short × 5 · 3 long × 8; 3 hours; 1 mark per expected point
- **CDC's model paper:** short: a chain $C_6H_6 \rightarrow C_6H_5NO_2 \rightarrow C_6H_5NH_2 \rightarrow C_6H_5N_2Cl \rightarrow$ **p-hydroxyazobenzene** (coupling with phenol); short: monomers of Bakelite (phenol, methanal); long: methanal + phenol in acid
- **MCQ (1 mark)**
  - which structure is phenol; IUPAC name benzenol; Dow's process; diazonium salt + warm H_2O/H^+
  - acid order ethanol < water < phenol; why phenol doesn't fizz with $NaHCO_3$
  - products with Na, Zn dust, diazonium salt, CO_2 (Kolbe), $CHCl_3$ + KOH (Reimer–Tiemann), anhydride
  - dil. $HNO_3 \rightarrow$ o- and p-nitrophenol; Br_2 in $CS_2 \rightarrow$ o- and p-bromophenol; $FeCl_3$ violet; Liebermann's reagent; Bakelite
- **Short (5 marks, in parts)**
  - names of the cresols and benzenediols, with structures; phenol vs toluene polarity
  - solubility and b.p. against benzene and toluene; low b.p. of o-nitrophenol
  - phenoxide more stable than ethoxide; substituents and acidity (order four phenols)
  - –OH o, p directing and activating; Br_2 water vs Br_2 in CS_2; $FeCl_3$ test; phenol vs benzene with Br_2
- **Long (8 marks)**: complete a sequence from phenol (Zn dust, sulphonation, fusion); products with dil. and conc. HNO_3, CH_3COCl in pyridine

Key terms

Phenols: –OH joined **directly to a ring carbon** of an aromatic ring; **Ar–OH**; simplest C_6H_5OH, **phenol** (carbolic acid).

Mono-, di-, trihydric: by the number of **–OH groups** on the ring (phenol, catechol, pyrogallol).

Phenoxide ion: $C_6H_5O^-$; its charge spread over O and ring carbons 2, 4, 6 by **resonance**.

Coupling: phenoxide + benzenediazonium ion at the para carbon → azo dye (–N=N–).

Kolbe's reaction: sodium phenoxide + CO_2 (400 K, 4–7 atm) → salicylic acid.

Reimer–Tiemann reaction: phenol + $CHCl_3$ + NaOH (70 °C) → **salicylaldehyde** (–CHO at ortho); via dichlorocarbene $:CCl_2$.

O-acylation: acid chloride (pyridine) or anhydride acylates the –OH → **ester**; no $AlCl_3$.

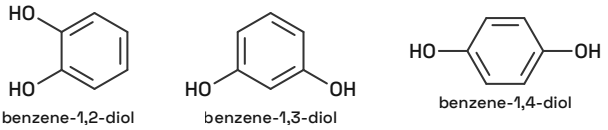
Fries rearrangement: ester + anhyd. $AlCl_3$, heat → acyl group moves to the ring (o- and p-hydroxyacetophenone).

Ortho effect (here): H bond **inside** 2-nitrophenol → lower b.p., less soluble, steam-volatile.

Naming

Common name	IUPAC name
phenol (carbolic acid)	phenol (benzenol)
o-, m-, p-cresol	2-, 3-, 4-methylphenol
catechol	benzene-1,2-diol
resorcinol	benzene-1,3-diol
quinol (hydroquinone)	benzene-1,4-diol
picric acid	2,4,6-trinitrophenol

- C bearing –OH is **C-1**; other groups as prefixes, lowest numbers; two or three –OH: **benzene-diol, -triol**



The three benzenediols, $C_6H_4(OH)_2$.

Preparation

- **Dow's process** (623 K, 300 atm):
  $C_6H_5Cl + 2\,NaOH \longrightarrow C_6H_5ONa + NaCl + H_2O$, then
  $C_6H_5ONa + HCl \longrightarrow C_6H_5OH + NaCl$
- **diazotization** (0–5 °C):
  $C_6H_5NH_2 + NaNO_2 + 2\,HCl \longrightarrow C_6H_5N_2Cl + NaCl + 2\,H_2O$
- **diazonium salt warmed with water** (H^+; best lab method): $C_6H_5N_2Cl + H_2O \longrightarrow C_6H_5OH + N_2 + HCl$
- **benzenesulphonic acid** (first industrial route):
  $C_6H_6 \xrightarrow[\text{heat}]{\text{conc. } H_2SO_4} C_6H_5SO_3H$
  $\xrightarrow[\text{about 570 K}]{\text{NaOH, fuse}} C_6H_5ONa \xrightarrow{H^+} C_6H_5OH$
- **anisole + HI** (O–CH_3 bond breaks, not ring–O):
  $C_6H_5OCH_3 + HI \xrightarrow{\text{heat}} C_6H_5OH + CH_3I$
- **cumene process** (nearly all the world's phenol; acetone sells too):
  - $C_6H_6 + CH_3CH{=}CH_2 \xrightarrow[\text{about 520 K}]{H_3PO_4} C_6H_5CH(CH_3)_2$ (cumene)
  - $C_6H_5CH(CH_3)_2 + O_2 \longrightarrow C_6H_5C(CH_3)_2OOH$ (cumene hydroperoxide)
  - $C_6H_5C(CH_3)_2OOH \xrightarrow{\text{dil. } H_2SO_4} C_6H_5OH + CH_3COCH_3$

Physical properties

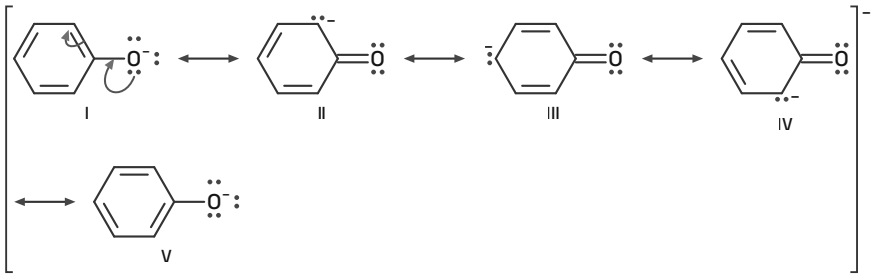
- colorless crystalline solid; m.p. about **41 °C**, b.p. **182 °C**; **hygroscopic**; turns **pink** in air and light
- moderately soluble in water (about 8 g/100 mL): –OH H-bonds to water; large non-polar ring → less soluble than ethanol
- H-bonds between phenol molecules → b.p. far above benzene and toluene

- b.p.: benzene (80 °C) < toluene (111) < phenol (182) < cresol (191–202)
- **corrosive, toxic**: white burn, numbs, absorbed through skin; wash 15 min with running water (PEG 300/400 better)

Acidic nature

$C_6H_5OH + H_2O \rightleftharpoons C_6H_5O^- + H_3O^+$; $K_a \approx 1.0 \times 10^{-10}$, **pKa 10.0**; 0.1 M: pH ≈ 5.5

- **phenoxide** stabilized by resonance: charge on O and C-2, 4, 6; no structure separates charges
- **phenol's** own resonance structures **separate charge** (O^+, C^-), add little → losing H^+ is downhill
- **ethoxide**: charge on one O, made worse by +I of C_2H_5; OH^-: on one O; no resonance



Resonance structures of the phenoxide ion: the negative charge on O and on carbons 2, 4 and 6.

Compound	pKa	Ion's charge held by
ethanol	15.9	one O (+I of C_2H_5)
water	15.7	one O
phenol	10.0	O + three ring C

- acid strength: **ethanol < water < phenol**
- $2\,C_6H_5OH + 2\,Na \longrightarrow 2\,C_6H_5ONa + H_2$; $C_6H_5OH + NaOH \longrightarrow C_6H_5ONa + H_2O$ (alcohols don't)
- **no CO_2 with $NaHCO_3$**: carbonic acid (pKa 6.35) stronger than phenol
- test: carboxylic acid fizzes with $NaHCO_3$; phenol dissolves in NaOH, no fizz; alcohol neither

Groups on the ring

- electron-pulling (–NO_2, –Cl, –CN) → **stronger** acid; pushing (–CH_3, –OCH_3) → **weaker**
- –NO_2 best at **o, p** (−R and −I); at meta −I only

Phenol	pKa
4-methylphenol	10.26 (+I)
4-methoxyphenol	10.21 (+R > −I)
phenol	9.99
4-chlorophenol	9.41 (−I > +R)
3-nitrophenol	8.36 (−I)
4-nitrophenol	7.15 (−R, −I)
2,4-dinitrophenol	4.07
2,4,6-trinitrophenol	0.42

Reactions of the –OH

- **NH_3**, anhyd. $ZnCl_2$, 673 K: $C_6H_5OH + NH_3 \longrightarrow C_6H_5NH_2 + H_2O$ (aniline; drastic: C–O partly double)
- **zinc dust** (reduction): $C_6H_5OH + Zn \xrightarrow{\text{heat}} C_6H_6 + ZnO$
- **coupling** (cold, slightly alkaline, para carbon): $C_6H_5OH + C_6H_5N_2Cl \longrightarrow HOC_6H_4N{=}NC_6H_5 + HCl$ (4-hydroxyazobenzene, **orange** azo dye)
- **phthalic anhydride** + conc. H_2SO_4, heat: $C_8H_4O_3 + 2\,C_6H_5OH \longrightarrow C_{20}H_{14}O_4 + H_2O$ (**phenolphthalein**: colorless in acid, pink in alkali, pH 8.2–10)
- **acylation** (on O): $C_6H_5OH + CH_3COCl \xrightarrow{\text{pyridine}} C_6H_5OCOCH_3 + HCl$; $C_6H_5OH + (CH_3CO)_2O \longrightarrow C_6H_5OCOCH_3 + CH_3COOH$ (phenyl ethanoate)
- **Schotten–Baumann**: $C_6H_5OH + C_6H_5COCl \xrightarrow{\text{NaOH (aq)}} C_6H_5OCOC_6H_5 + HCl$ (phenyl benzoate, white)

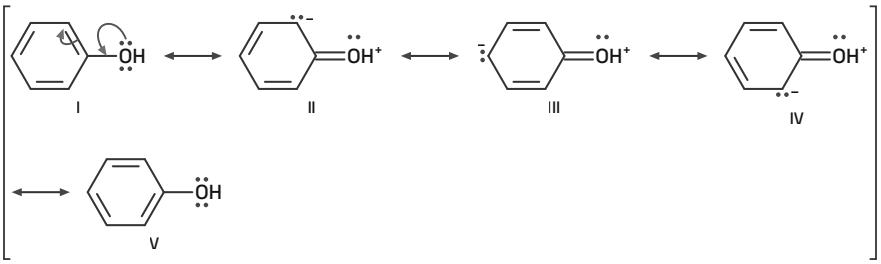
Kolbe's reaction

- $C_6H_5ONa + CO_2 \xrightarrow[4–7\text{ atm}]{400\text{ K}} C_6H_4(OH)COONa \xrightarrow{H^+} C_6H_4(OH)COOH$ (salicylic acid)
- aspirin (acetylsalicylic acid, $C_9H_8O_4$): $C_7H_6O_3 + (CH_3CO)_2O \longrightarrow C_9H_8O_4 + CH_3COOH$

Reimer–Tiemann: phenol + $CHCl_3$ + NaOH (aq), about 340 K → (:CCl_2 attacks the phenoxide ring; Cl hydrolyzed) → H^+ → **salicylaldehyde** (2-hydroxybenzaldehyde), some para

Ring: electrophilic substitution

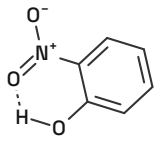
- –OH: −I through σ, but **+R** (lone pair into the ring) far larger → ring **activated**, faster than benzene
- extra electron density at C-2, 4, 6 → **ortho, para director**



Resonance structures of phenol: a lone pair of O moves into the ring, putting negative charge on carbons 2, 4 and 6.

Reagent	Product
dil. HNO_3, 293 K (no H_2SO_4)	2-nitrophenol (major) + 4-nitrophenol
conc. HNO_3 + conc. H_2SO_4	picric acid (poor yield: HNO_3 oxidizes phenol)
conc. H_2SO_4, room temp.	2-hydroxybenzenesulphonic acid
conc. H_2SO_4, 373 K	4-hydroxybenzenesulphonic acid (ortho → para on heating)
bromine water	**white ppt**, 2,4,6-tribromophenol
Br_2 in $\mathbf{CS_2}$ or CCl_4, 273 K	4-bromophenol (major) + 2-bromophenol
CH_3Cl, anhyd. $AlCl_3$	2- and 4-methylphenol (para major), poor yield

- $C_6H_5OH + 3\,HNO_3 \xrightarrow{\text{conc. } H_2SO_4} C_6H_2(NO_2)_3OH + 3\,H_2O$
- $C_6H_5OH + 3\,Br_2 \longrightarrow C_6H_2Br_3OH + 3\,HBr$; no catalyst (benzene: none with Br_2 water)
- **water**: some phenoxide (even more activated), Br–Br polarized → all three o, p; $\mathbf{CS_2}$ (low polarity): phenol un-ionized, Br_2 unpolarized → one Br
- **steam distillation** separates nitrophenols: 2-nitrophenol (b.p. 216 °C, intramolecular H bond) comes over; 4-nitrophenol (279 °C) H-bonds to other molecules, stays
- Friedel–Crafts poor: $AlCl_3$ (Lewis acid) bonds to O's lone pair, pulls electrons from the ring
- an electron-pulling group at meta: ring **less** reactive (–OH still directs o, p), phenol **more** acidic



2-nitrophenol: H-bond inside the molecule

2-nitrophenol: H bond inside the molecule.

Other reactions

- **hydrogenation**: $C_6H_5OH + 3\,H_2 \xrightarrow[423\,K]{Ni} C_6H_{11}OH$ (cyclohexanol → cyclohexanone → nylon)
- **air and light**: slowly → 1,4-benzoquinone (yellow) + phenol → colored (phenoquinone, red): crystals pink, red-brown; chromic acid → 1,4-benzoquinone
- **methanal** (H^+ or OH^-): $-CH_2OH$ at o, p (2- and 4-hydroxybenzyl alcohol) → $-CH_2-$ bridges, losing water → **novolac** (linear, soft) → more HCHO, heat → **Bakelite** (3-D network, **thermosetting**; insulator: switches, plugs, cooker handles, plywood glue)

Tests

- **neutral $FeCl_3$** → **violet** complex (alcohols none; fades in acid):
  $6\,C_6H_5OH + FeCl_3 \longrightarrow [Fe(OC_6H_5)_6]^{3-} + 3\,H^+ + 3\,HCl$
- **bromine water** → decolorized + **white ppt** (alkenes: no ppt)
- **Liebermann**: phenol + $NaNO_2$ + conc. H_2SO_4 → **deep green to blue**; in water **red**; with NaOH **deep blue**; 4-nitrosophenol + phenol → **indophenol** (rings joined by one N, C=N–C, not –N=N–)

Uses

- **plastics**: bisphenol A (+ acetone) → polycarbonates, epoxy resins; Bakelite; cyclohexanone → nylon
- **medicines**: salicylic acid, aspirin; paracetamol from 4-aminophenol
- **antiseptics**: chloroxylenol (Dettol), cresols; sore-throat sprays
- **dyes, indicators**: azo dyes, phenolphthalein
- **antioxidants**: BHT, vitamin E
- picric acid (explosive, dye); herbicides, pesticides

COMMON MISTAKES

✗ phenols classed by the number of aryl groups
✓ by the number of **–OH groups**.

✗ catechol = 2-hydroxyphenol
✓ **benzene-1,2-diol** (resorcinol 1,3-, quinol 1,4-).

✗ phenoxide stable because of greater charge separation
✓ **phenol's** structures separate charge; phenoxide's don't.

✗ acid order water < ethanol < phenol
✓ **ethanol < water < phenol**.

✗ $C_6H_5OH + Na \rightarrow C_6H_5ONa + H_2$
✓ $\mathbf{2}C_6H_5OH + \mathbf{2}Na \rightarrow \mathbf{2}C_6H_5ONa + H_2$.

✗ picric acid yield low from oxidation of benzene
✓ of **phenol**.

✗ phenol + CH_3COCl with $AlCl_3$ (Friedel–Crafts) gives the ester
✓ O-acylation needs **pyridine** or base, no $AlCl_3$; ring acylation by **Fries**.

✗ quinone pink
✓ 1,4-benzoquinone is **yellow**; pink from phenoquinone.

✗ indophenol drawn with –N=N–
✓ **one N**, C=N–C.

✗ 0.1 M phenol turns blue litmus red
✓ pH ≈ 5.5, at most a **faint** change.