Unit 11 · Phenol

ANSWER KEY · FOR TEACHERS

Full marks 37

Give the marks for the points in the marking scheme; an answer in other words that says the same is right.

1 Key words

1. cumene
2. phenoxide
3. salicylic acid
4. Kolbe's
5. Reimer–Tiemann
6. phenolphthalein
7. Bakelite
8. violet

K · 4

Each carries 0.5 mark.

2 Label the diagram

1. cumene
2. acetone
3. O2 (air)
4. cumene hydroperoxide

K · 2

Each carries 0.5 mark.

3 Multiple choice

i. **c.** phenol > water > ethanol — U · 1

pKa: phenol 10.0, water 15.7, ethanol 15.9. Phenoxide spreads its charge over the oxygen and three ring carbons.

ii. **d.** 4-nitrophenol — U · 1

A nitro group at the para position pulls electrons by both −R and −I and spreads the phenoxide's charge further: pKa 7.15, against 8.36 for 3-nitrophenol (−I only), 9.99 for phenol and 10.26 for 4-methylphenol.

iii. **a.** benzene — K · 1

The zinc takes phenol's oxygen and becomes zinc oxide: $C_6H_5OH + Zn \rightarrow C_6H_6 + ZnO$.

iv. **b.** has a hydrogen bond inside its own molecule, so its molecules hold each other less — U · 1

Its –OH and neighboring $–NO_2$ hydrogen-bond within one molecule, so it doesn't hydrogen-bond to other molecules or to water and is more volatile; 4-nitrophenol bonds between molecules and stays behind.

v. **b.** 4-bromophenol — A · 1

In a nonpolar solvent there is no phenoxide and the Br–Br bond is not polarized by water, so only one bromine goes in, mainly para.

4 Short answers

a. MARKING SCHEME — A · 2

- ✓ $C_6H_5SO_3H + 3\,NaOH \rightarrow C_6H_5ONa + Na_2SO_3 + 2\,H_2O$, then acid frees phenol: $C_6H_5ONa + HCl \rightarrow C_6H_5OH + NaCl$.
- ✓ $C_6H_5OCH_3 + HI \xrightarrow{\Delta} C_6H_5OH + CH_3I$

b. MARKING SCHEME — U · 2

- ✓ Phenol (pKa 10) is a much stronger acid than water (15.7), so OH^- takes its proton: sodium phenoxide forms and dissolves.
- ✓ It is weaker than carbonic acid (pKa 6.35), so it is too weak to set CO_2 free from hydrogencarbonate.

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c. MARKING SCHEME U · 2

- ✓ The ring's C–Cl bond is partly double, by resonance of chlorine's lone pair with the ring, so the chlorine is very hard to replace.
- ✓ Dow's process uses NaOH at about 623 K (350 °C) and 300 atm, then acid.

d. MARKING SCHEME A · 2

- ✓ Sodium phenoxide with CO_2 at about 400 K and 4–7 atm gives sodium salicylate; acid gives salicylic acid, 2-hydroxybenzoic acid.
- ✓ Its –OH group is acetylated with ethanoic anhydride: acetylsalicylic acid, aspirin.

e. MARKING SCHEME U · 3

- ✓ $FeCl_3$: violet with phenol.
- ✓ Bromine water: decolorized, white precipitate with phenol.
- ✓ NaOH (or Liebermann): phenol reacts, ethanol doesn't.

5 Long answer

ANSWER U · 4

In the phenoxide ion a lone pair of the oxygen joins the ring's π electrons, so the negative charge is spread over the oxygen and carbons 2, 4 and 6; every resonance structure carries the same single charge. The ion is stable, so phenol gives up its proton easily (pKa 10). In ethoxide the charge stays on one oxygen, and the ethyl group's +I effect makes it worse (pKa 15.9).

In phenol itself the oxygen's lone pair is pushed into the ring (+R, outweighing −I), so carbons 2, 4 and 6 carry extra electron density. Electrophiles, which seek electrons, attack faster and at those carbons.

With bromine water all three are brominated at once, with no catalyst:

$C_6H_5OH + 3\,Br_2 \rightarrow C_6H_2Br_3OH + 3\,HBr$, a white precipitate of 2,4,6-tribromophenol.

MARKING SCHEME

- ✓ The phenoxide ion's charge is spread by resonance over O and three ring carbons.
- ✓ Ethoxide keeps its charge on one oxygen, made worse by +I: ethanol is weaker.
- ✓ +R of –OH puts extra electron density at carbons 2, 4 and 6: ring activated, ortho/para.
- ✓ Bromine water gives 2,4,6-tribromophenol, with the equation.

6 Numerical problems

a. ANSWER A · 4

i. $C_6H_5CH(CH_3)_2 + O_2 \rightarrow C_6H_5OH + CH_3COCH_3$ (through cumene hydroperoxide, split by dilute acid).

ii. Cumene $C_9H_{12} = 120$ g/mol: 1.00×10^6 g $\div$ 120 $= 8.33 \times 10^3$ mol. Phenol (94 g/mol): **783 kg**; acetone (58 g/mol): **483 kg**.

iii. One mole of O_2 per mole: $8.33 \times 10^3 \times 22.4$ L $= 1.87 \times 10^5$ L $=$ **187 m³**.

iv. 0.90×783 kg $=$ **705 kg**.

MARKING SCHEME

- ✓ The balanced overall equation.
- ✓ 783 kg of phenol and 483 kg of acetone.
- ✓ 187 m^3 of oxygen.
- ✓ 705 kg.

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b. ANSWER A · 4

i. $C_6H_5OH + 3\,Br_2 \rightarrow C_6H_2Br_3OH + 3\,HBr$

ii. Phenol 94 g/mol: $0.94 \div 94 = 0.0100$ mol. Br_2: $0.0300 \text{ mol} \times 160 =$ **4.80 g**; $C_6H_2Br_3OH = 72 + 3 + 240 + 16 = 331$ g/mol: **3.31 g**.

iii. $[H^+] = \sqrt{(1.0 \times 10^{-10} \times 0.010)} = 1.0 \times 10^{-6}$ M, **pH = 6.0**.

iv. $10\text{^}(9.99 - 7.15) = 10^{2.84} \approx$ **690 times**.

MARKING SCHEME

✓ The balanced equation.
✓ 4.80 g of Br_2 and 3.31 g of tribromophenol.
✓ pH 6.0.
✓ About 690 times.

7 Think

ANSWER HA · 3

$AlCl_3$ is a Lewis acid: it accepts a lone pair from phenol's oxygen. Then the oxygen can no longer push its lone pair into the ring, so the ring is deactivated, and the catalyst is used up. Phenol's oxygen is its most reactive site for an acid chloride or anhydride too, so acylation happens on the oxygen, giving an ester such as phenyl ethanoate. Heating the ester with anhydrous $AlCl_3$ moves the acyl group from the oxygen to the ortho and para carbons: the Fries rearrangement, giving hydroxyacetophenones.

MARKING SCHEME

✓ $AlCl_3$ takes the oxygen's lone pair, deactivating the ring and using up the catalyst.
✓ Acylation goes on the oxygen, giving an ester.
✓ The Fries rearrangement (anhydrous $AlCl_3$, heat) moves the acyl group to the ring.

8 Activity: Phenol bingo

(not marked)

WHAT STUDENTS SHOULD FIND

Bromine water: 2,4,6-tribromophenol (test); neutral $FeCl_3$: a violet complex (test); NaOH: sodium phenoxide; Na: sodium phenoxide and hydrogen; zinc dust: benzene; CO_2 under pressure (as phenoxide): salicylic acid (Kolbe's reaction); $CHCl_3$ + NaOH: salicylaldehyde (Reimer–Tiemann); phthalic anhydride: phenolphthalein; methanal: Bakelite. Everyday uses: salicylic acid gives aspirin, phenolphthalein is the titration indicator, Bakelite makes switches and handles.

Marks by level	Knowledge	Understanding	Application	Higher ability	Total
Marks	7	14	13	3	**37**

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