Unit 15 · Nitro Compounds

ANSWER KEY · FOR TEACHERS

Full marks 36

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

1 Key words

i. ✓ **True** — U · 3

ii. ✗ **False**: Nitroglycerin is an alkyl nitrate, R–O–NO_2, an ester; its nitrogen is bonded to oxygen, not carbon.

iii. ✓ **True**

iv. ✗ **False**: Alkanes are nitrated in the vapor phase with HNO_3 at about 420 °C, by free radicals; the nitrating mixture leaves them unchanged.

v. ✗ **False**: The nitro group directs meta: the product is mainly 3-bromonitrobenzene (m-bromonitrobenzene).

vi. ✓ **True**

Each carries 0.5 mark.

2 Label the diagram

K · 2

1. beaker
2. stopper
3. nitrobenzene 1.20 g/cm^3
4. stopcock

Each carries 0.5 mark.

3 Multiple choice

i. **b.** nitroethane — K · 1

The nitrite ion can attack with either end, but with silver nitrite the nitrogen end does most of the attacking: mainly nitroethane, with some ethyl nitrite.

ii. **b.** N-ethylhydroxylamine — K · 1

The neutral medium is a milder reducer and stops one step short of the amine: $C_2H_5NO_2 + 4[H] \rightarrow C_2H_5NHOH + H_2O$.

iii. **c.** azobenzene — U · 1

$2C_6H_5NO_2 + 8[H] \rightarrow C_6H_5N{=}NC_6H_5 + 4H_2O$. With aqueous NaOH and zinc it goes on to hydrazobenzene; with Na_3AsO_3 or glucose it stops at azoxybenzene.

iv. **c.** NO_2^+ — K · 1

Sulphuric acid protonates nitric acid, which loses water to leave the nitronium ion, NO_2^+.

v. **d.** less reactive, and directs to meta — U · 1

It pulls electrons out of the ring (−I and −R), so the ring is deactivated, and attack at ortho or para would put a positive charge beside N^+: meta is the least disfavored.

4 Short answers

a. MARKING SCHEME — A · 2

✓ i. 2-Nitropropane, secondary (–NO_2 on a carbon bonded to two others).

✓ ii. 2-Methyl-2-nitrobutane, tertiary (–NO_2 on a carbon bonded to three others).

b. MARKING SCHEME — U · 2

✓ The nitrite ion has lone pairs on its nitrogen and on both oxygens, so it can attack the carbon with either end (an ambident nucleophile).

✓ Bonding through nitrogen gives the nitroalkane, R–NO_2; through oxygen, the alkyl nitrite, R–O–N=O.

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c. MARKING SCHEME A · 2

✓ $C_6H_5NO_2 + 6[H] \xrightarrow{Sn,\ conc.\ HCl} C_6H_5NH_2 + 2H_2O$ (aniline).

✓ $C_6H_5NO_2 + 4[H] \xrightarrow{Zn,\ NH4Cl(aq)} C_6H_5NHOH + H_2O$ (N-phenylhydroxylamine).

d. MARKING SCHEME U · 2

✓ Above about 60 °C a second nitro group goes in.

✓ The product is then 1,3-dinitrobenzene, not nitrobenzene.

e. MARKING SCHEME U · 3

✓ Formation of NO_2^+ from HNO_3 and H_2SO_4.

✓ Slow attack by the ring, giving the arenium ion.

✓ Fast loss of H^+, restoring the ring.

5 Long answer

ANSWER U · 4

The positive nitrogen pulls electrons through the C–N bond (−I), and the ring's π electrons flow into the nitro group (−R): in three resonance structures of nitrobenzene there is a positive charge on carbons 2, 4 and 6. The whole ring is poorer in electrons, so it attracts an electrophile less and reacts far more slowly than benzene.

When an electrophile attacks ortho or para, one structure of the arenium ion puts the positive charge on carbon 1, beside N^+: two positive charges side by side, badly destabilized. Attack at meta keeps the charge on carbons 2, 4 and 6, never beside the nitro group, so meta is the least disfavored.

$C_6H_5NO_2 + HNO_3 \xrightarrow[\text{about 100 °C}]{\text{conc. } H_2SO_4} C_6H_4(NO_2)_2 + H_2O$, 1,3-dinitrobenzene.

MARKING SCHEME

✓ −I and −R effects pull electrons from the ring, leaving + on carbons 2, 4, 6: deactivated.

✓ Ortho/para attack puts the ring's + beside N^+.

✓ Meta attack avoids it, so meta is favored (least disfavored).

✓ The equation, giving 1,3-dinitrobenzene.

6 Numerical problems

a. ANSWER A · 4

i. $C_6H_6 + HNO_3 \xrightarrow[50–60\ °C]{\text{conc. } H_2SO_4} C_6H_5NO_2 + H_2O$

ii. Benzene 78 g/mol: 15.6 ÷ 78 = 0.200 mol. Nitrobenzene, $C_6H_5NO_2$ = 72 + 5 + 14 + 32 = 123 g/mol: 0.200 × 123 = **24.6 g**.

iii. 0.85 × 24.6 = **20.9 g**; volume = 20.9 g ÷ 1.20 g/cm^3 = **17.4 cm^3**.

iv. The **lower** layer: it is almost insoluble in water and denser (1.20 against 1.00 g/cm^3).

MARKING SCHEME

✓ The balanced equation.

✓ 24.6 g.

✓ 20.9 g and 17.4 cm^3.

✓ The lower layer, being insoluble and denser.

b. ANSWER A · 4

i. $C_2H_5Br + AgNO_2 \xrightarrow{\text{ethanol, heat}} C_2H_5NO_2 + AgBr\downarrow$

ii. C_2H_5Br = 109 g/mol: 5.45 ÷ 109 = 0.0500 mol. $AgNO_2$ = 108 + 14 + 32 = 154 g/mol: **7.70 g**; AgBr = 188 g/mol: **9.40 g**.

iii. Nitroethane, $C_2H_5NO_2$ = 75 g/mol: 0.0500 × 0.70 × 75 = **2.63 g**.

iv. Some **ethyl nitrite**, C_2H_5–O–N=O, formed when the nitrite ion bonds through an oxygen instead of its nitrogen.

MARKING SCHEME

✓ The balanced equation.

✓ 7.70 g of $AgNO_2$ and 9.40 g of AgBr.

✓ 2.63 g of nitroethane.

✓ Ethyl nitrite, by attack through oxygen.

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7 Think

ANSWER HA · 3

They are functional isomers: in nitromethane the nitrogen is bonded to carbon and carries a positive charge, with both oxygens sharing a negative charge, so the molecule is very polar (about 3.5 D) and held by strong dipole–dipole forces. In methyl nitrite, CH_3–O–N=O, the nitrogen is bonded to oxygen and carries no such charges, so the molecule is much less polar and the forces between molecules weaker. Methyl nitrite should boil much lower.

MARKING SCHEME

- ✓ Functional isomerism (nitro and nitrite).
- ✓ Nitromethane's charged N and O make it very polar, with strong dipole–dipole forces.
- ✓ The nitrite has no such charges, so weaker forces and a much lower boiling point.

8 Activity: From nitrobenzene to five products

(not marked)

WHAT STUDENTS SHOULD FIND

Aniline, $C_6H_5NH_2$, 12[H]; N-phenylhydroxylamine, C_6H_5NHOH, 8[H]; azoxybenzene, $C_6H_5N(O)=NC_6H_5$, 6[H]; azobenzene, $C_6H_5N=NC_6H_5$, 8[H]; hydrazobenzene, $C_6H_5NH–NHC_6H_5$, 10[H]. The three products of the alkaline medium join two rings through two nitrogen atoms bonded to each other; aniline has one ring and one nitrogen.

Marks by level	Knowledge	Understanding	Application	Higher ability	Total
Marks	5	16	12	3	**36**

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