Unit 8 · Haloalkanes

ANSWER KEY · FOR TEACHERS

Full marks 33

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** — K · 4

ii. ✗ **False**: In a geminal dihalide both halogens are on the same carbon; on neighboring carbons they make a vicinal dihalide.

iii. ✓ **True**

iv. ✗ **False**: C–I is the easiest to break (R–I > R–Br > R–Cl > R–F); C–F is the strongest.

v. ✓ **True**

vi. ✗ **False**: Alcoholic KOH gives alkenes, by elimination; aqueous KOH gives alcohols.

vii. ✓ **True**

viii. ✗ **False**: Chloroform is denser than water (1.48 g/mL) and sinks under it.

Each carries 0.5 mark.

2 Label the diagram

K · 2

1. bleaching powder paste + ethanol
2. cold water in
3. sand bath
4. condenser

Each carries 0.5 mark.

3 Multiple choice

i. **b.** 2-bromobutane — K · 1

The longest chain has four carbons, numbered from the end nearer the bromine: **2-bromobutane**. Sec-butyl bromide is its common name, not its IUPAC name.

ii. **b.** ethyl isocyanide, $CH_3CH_2–N{\equiv}C$ — U · 1

Silver cyanide is largely covalent, so it attacks through **nitrogen**, giving the **isocyanide**. Potassium cyanide, ionic, attacks through carbon and gives the nitrile.

iii. **a.** CH_3Br — U · 1

In SN2 the nucleophile attacks the carbon from behind, so the fewer groups crowding it the faster: methyl > 1° > 2° > 3°. **CH_3Br** is fastest.

iv. **b.** but-2-ene — A · 1

By **Saytzeff's rule**, the more substituted alkene forms more: hydrogen is taken from C-3, which has fewer hydrogens than C-1, giving **but-2-ene**, $CH_3CH{=}CHCH_3$.

v. **a.** primary amines — K · 1

Only a **primary** amine, $R–NH_2$, has the two hydrogens on nitrogen that the reaction needs: $R–NH_2 + CHCl_3 + 3\,KOH \rightarrow R–NC + 3\,KCl + 3\,H_2O$.

4 Short answers

a. MARKING SCHEME — U · 2

✓ The balanced equation.

✓ SO_2 and HCl are gases that leave, so the product is left pure.

b. MARKING SCHEME — U · 2

✓ Vicinal: halogens on neighboring carbons (an example).

✓ Geminal: both on one carbon (an example).

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c. MARKING SCHEME A · 3

- ✓ Ethanol (equation).
- ✓ Propanenitrile (equation).
- ✓ Nitroethane (equation).

5 Long answer

ANSWER U · 4

Acetone is warmed with a paste of bleaching powder in water and the chloroform distilled off.
Bleaching powder gives chlorine and calcium hydroxide: $CaOCl_2 + H_2O \rightarrow Ca(OH)_2 + Cl_2$.
Chlorination: $CH_3COCH_3 + 3\,Cl_2 \rightarrow CCl_3COCH_3 + 3\,HCl$
Hydrolysis: $2\,CCl_3COCH_3 + Ca(OH)_2 \rightarrow 2\,CHCl_3 + (CH_3COO)_2Ca$
In air and light, chloroform is slowly oxidized to poisonous phosgene:
$2\,CHCl_3 + O_2 \xrightarrow{h\nu} 2\,COCl_2 + 2\,HCl$. Dark bottles keep out the light, and filling them to the brim leaves no air.

MARKING SCHEME

- ✓ Bleaching powder gives Cl_2 and $Ca(OH)_2$ (equation).
- ✓ Chlorination of acetone to trichloroacetone (equation).
- ✓ Hydrolysis by $Ca(OH)_2$ to chloroform (equation).
- ✓ Stored dark and full, as light and air oxidize it to phosgene (equation).

6 Numerical problems

a. ANSWER A · 4

i. C: 29.3/12 = 2.44; H: 5.7/1 = 5.7; Br: 65.0/80 = 0.813. Dividing by 0.813: C 3, H 7, Br 1: **C_3H_7Br**.
ii. Molar mass = 2 × 61.5 = 123; C_3H_7Br = 36 + 7 + 80 = 123, so the molecular formula is **C_3H_7Br**.
iii. $CH_3CH_2CH_2Br$, **1-bromopropane** (primary); $CH_3CHBrCH_3$, **2-bromopropane** (secondary).
iv. **Propene**: $CH_3CHBrCH_3 + KOH(alc) \rightarrow CH_3CH{=}CH_2 + KBr + H_2O$.

MARKING SCHEME

- ✓ Empirical formula C_3H_7Br.
- ✓ Molecular formula C_3H_7Br (molar mass 123).
- ✓ 1-bromopropane (1°) and 2-bromopropane (2°).
- ✓ Propene, with a balanced equation.

b. ANSWER A · 4

i. $M(C_2H_5Br) = 24 + 5 + 80 = 109$ g/mol: 10.9/109 = **0.100 mol**.
ii. $2\,C_2H_5Br + 2\,Na \xrightarrow{\text{dry ether}} C_4H_{10} + 2\,NaBr$: 0.100 mol gives 0.0500 mol butane × 58 g/mol = **2.90 g**.
iii. 2.90 × 0.60 = **1.74 g**.
iv. $C_2H_5Br + 2\,[H] \rightarrow C_2H_6 + HBr$: 0.100 mol of ethane × 22.4 L = **2.24 L**.

MARKING SCHEME

- ✓ 0.100 mol.
- ✓ The Wurtz equation and 2.90 g of butane.
- ✓ 1.74 g at 60%.
- ✓ 2.24 L of ethane.

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7 Think

ANSWER HA · 3

In CH_3CH_2–Br the carbon is bonded to bromine, more electronegative than carbon, so it is $\delta+$ and an electrophile. In CH_3CH_2–MgBr it is bonded to magnesium, much less electronegative (Mg 1.31, C 2.55), so it is $\delta-$, almost a carbanion, and acts as a nucleophile: the polarity is reversed.
It attacks the $\delta+$ carbon of ethanal, forming a new C–C bond, and water gives butan-2-ol:
$CH_3CHO + C_2H_5MgBr \rightarrow CH_3CH(OMgBr)C_2H_5 \xrightarrow{H_2O} CH_3CH(OH)C_2H_5 + Mg(OH)Br$, a secondary alcohol.

MARKING SCHEME

- ✓ In bromoethane the carbon is $\delta+$ because bromine is more electronegative.
- ✓ In the Grignard reagent it is $\delta-$ because magnesium is less electronegative, so it acts as a nucleophile.
- ✓ Butan-2-ol (a secondary alcohol), with the equation.

8 Activity: Which halide comes off fastest?

(not marked)

WHAT STUDENTS SHOULD FIND

1-iodobutane gives a yellow precipitate (AgI) first, then 1-bromobutane a cream one (AgBr), and 1-chlorobutane a white one (AgCl) last and slowly. Reactivity R–I > R–Br > R–Cl: the C–I bond is the longest and weakest, so iodide leaves most easily; the C–Cl bond is the strongest of the three.

Marks by level	Knowledge	Understanding	Application	Higher ability	Total
Marks	8	10	12	3	**33**

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