Unit 17 · Organometallic Compounds

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. organometallic
2. Grignard reagent
3. ether
4. Gilman reagent
5. transmetallation
6. back-bonding
7. ketones
8. Zeise's salt

K · 4

Each carries 0.5 mark.

2 Label the diagram

1. filled d orbital
2. carbon's lone pair goes into an empty orbital of the metal
3. electrons flow back to CO
4. empty π^* of CO

U · 2

Each carries 0.5 mark.

3 Multiple choice

i. **b.** $(CH_3)_2Cd$ — U · 1

Only dimethylcadmium has a metal bonded directly to carbon. In the other three the metal is attached to oxygen.

ii. **c.** CH_3Li — U · 1

Lithium (0.98) is the least electronegative of the four metals, so its difference from carbon (2.55) is largest and the C–Li bond the most polar.

iii. **c.** 2-methylbutan-2-ol — A · 1

A ketone gives a tertiary alcohol: the carbonyl carbon keeps its two CH_3 groups and gains the ethyl group, $(CH_3)_2C(OH)CH_2CH_3$.

iv. **c.** a carboxylic acid with one more carbon atom — K · 1

RMgX + CO_2 gives RCOOMgX, and acid turns it into RCOOH: the chain gains the carbon of CO_2.

v. **b.** side-on, with its C=C at right angles to the $PtCl_3$ plane — K · 1

The C=C bond is centered on one corner of the square and stands perpendicular to the plane of platinum and the three Cl atoms.

4 Short answers

a. MARKING SCHEME — U · 2

- ✓ Water, alcohols or anything with an O–H or N–H hydrogen destroys it, giving an alkane: RMgX + $H_2O \rightarrow RH + Mg(OH)X$.
- ✓ Ether is not just a solvent: its oxygen atoms bind to the magnesium and hold the reagent in solution.

b. MARKING SCHEME — A · 2

- ✓ $CH_3CH_2Cl + 2\,Li \xrightarrow{\text{dry ether}} CH_3CH_2Li + LiCl$
- ✓ $2\,CH_3MgBr + CdCl_2 \xrightarrow{\text{ether}} (CH_3)_2Cd + 2\,MgBrCl$

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c. MARKING SCHEME A · 2

- ✓ Propan-2-ol is a secondary alcohol, so an aldehyde other than methanal: ethanal with methylmagnesium bromide.
- ✓ $CH_3CHO + CH_3MgBr \xrightarrow{\text{dry ether}} CH_3CH(CH_3)OMgBr \xrightarrow{H_2O/H^+} CH_3CH(OH)CH_3 + Mg(OH)Br$

d. MARKING SCHEME U · 2

- ✓ HCN gives an aldehyde, RCHO, after hydrolysis; a nitrile gives a ketone, R′COR.
- ✓ HCN has an acidic hydrogen, which uses up Grignard reagent first; a nitrile has none (or: the new C=O carbon carries R and H, against R and R′).

e. MARKING SCHEME U · 3

- ✓ The C–Cd bond is less polar, so R_2Cd is less reactive.
- ✓ It doesn't attack the ketone, but a Grignard reagent would, giving a 3° alcohol.
- ✓ The balanced equation.

5 Long answer

ANSWER A · 4

i. With methanal, then acid:
$HCHO + CH_3MgBr \xrightarrow{\text{dry ether}} CH_3CH_2OMgBr \xrightarrow{H_2O/H^+} CH_3CH_2OH + Mg(OH)Br$

ii. With carbon dioxide, then acid:
$CH_3MgBr + CO_2 \xrightarrow{\text{dry ether}} CH_3COOMgBr \xrightarrow{H_2O/H^+} CH_3COOH + Mg(OH)Br$

iii. With propanone, then acid:
$CH_3COCH_3 + CH_3MgBr \xrightarrow{\text{dry ether}} (CH_3)_3COMgBr \xrightarrow{H_2O/H^+} (CH_3)_3COH + Mg(OH)Br$

iv. With water: $CH_3MgBr + H_2O \rightarrow CH_4 + Mg(OH)Br$

MARKING SCHEME

- ✓ Ethanol from methanal.
- ✓ Ethanoic acid from carbon dioxide.
- ✓ 2-Methylpropan-2-ol from propanone.
- ✓ Methane from water.

6 Numerical problems

a. ANSWER A · 4

i. $CH_3I + Mg \xrightarrow{\text{dry ether}} CH_3MgI$

ii. $CH_3I = 12 + 3 + 127 = 142$ g/mol; 2.84 g ÷ 142 = **0.0200 mol**, so 0.0200 mol of CH_3MgI.

iii. $CH_3MgI + H_2O \rightarrow CH_4 + Mg(OH)I$: 0.0200 mol $CH_4 \times 22.4$ L = 0.448 L = **448 mL**.

iv. $ROH + CH_3MgI \rightarrow CH_4 + ROMgI$: one mole of alcohol to one of methane, so 0.0200 mol of alcohol. M = 1.48 g ÷ 0.0200 mol = **74 g/mol**. For $C_nH_{2n+1}OH$, 14n + 18 = 74, so n = 4: **C_4H_9OH**, a butanol.

MARKING SCHEME

- ✓ The balanced equation.
- ✓ 0.0200 mol.
- ✓ 448 mL of methane.
- ✓ 74 g/mol, C_4H_9OH.

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b. **ANSWER** A · 4

i. $(CH_3)_2CuLi + CH_3CH_2Br \rightarrow CH_3CH_2CH_3 + CH_3Cu + LiBr$

ii. **Propane**.

iii. $C_2H_5Br = 24 + 5 + 80 = 109$ g/mol; 4.36 g ÷ 109 = 0.0400 mol, so 0.0400 mol of propane: 0.0400 × 44 = **1.76 g**, and 0.0400 × 22.4 L = **0.896 L** (896 mL).

iv. With two different haloalkanes the Wurtz reaction joins them at random, giving a mixture of ethane, propane and butane; the Gilman reagent joins its own methyl to the ethyl group only.

MARKING SCHEME

- ✓ The balanced equation.
- ✓ Propane.
- ✓ 1.76 g and 896 mL.
- ✓ Wurtz gives a mixture (ethane, propane, butane).

7 Think

ANSWER HA · 3

An ester takes two molecules of Grignard reagent: the first adds and the alkoxide leaves, giving an aldehyde or ketone; the second adds to that. The carbonyl carbon of a methanoate carries a hydrogen, so after two methyl groups have been added it holds H, CH_3 and CH_3: a secondary alcohol, propan-2-ol, $CH_3CH(OH)CH_3$. In methyl ethanoate the carbonyl carbon already carries a CH_3 group, so after two more it holds three: a tertiary alcohol, 2-methylpropan-2-ol, $(CH_3)_3COH$.

MARKING SCHEME

- ✓ Two molecules of RMgX add to an ester (the alkoxide leaves after the first).
- ✓ The methanoate's carbonyl carbon has an H, so it ends with H and two CH_3: propan-2-ol.
- ✓ The ethanoate's has a CH_3, so it ends with three CH_3: 2-methylpropan-2-ol.

8 Activity: Read the label

(not marked)

WHAT STUDENTS SHOULD FIND

Single-vitamin tablets usually contain methylcobalamin, in which a methyl group is bonded to cobalt through its carbon (Co–CH_3); multivitamins and injections usually have cyanocobalamin, with a cyanide group bonded through its carbon (Co–C≡N). Both have a direct cobalt–carbon bond, so vitamin B_{12} is organometallic; "methyl" and "cyano" name the carbon groups on the cobalt.

Marks by level	Knowledge	Understanding	Application	Higher ability	Total
Marks	6	11	17	3	**37**

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