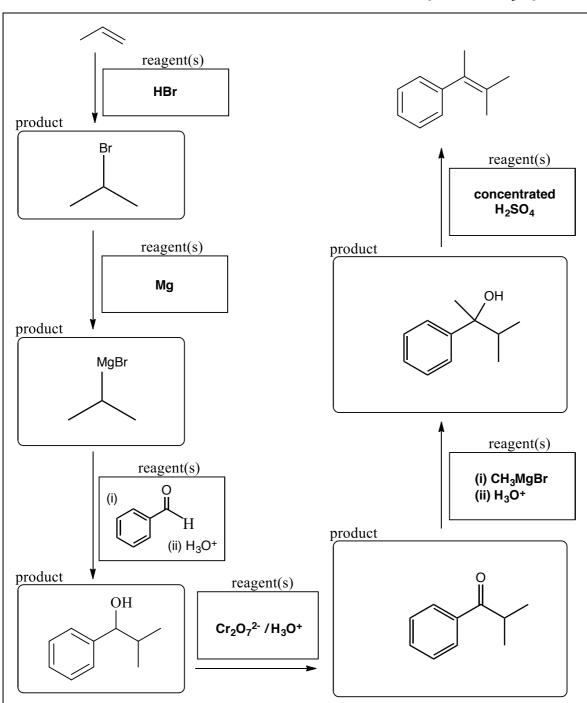
Marks 6

• Show clearly the reagents you would use to carry out the following chemical conversions. More than one step is required in each case. Give the structure of any intermediate compounds formed.

Marks 8

• Propene can be converted into 1,2-dimethyl-1-phenylpropene using a sequence of 6 reactions. Demonstrate your knowledge of Grignard reactions by suggesting a plausible sequence. Make sure you draw the correct structure for each intemediate product and clearly indicate the reagent(s) required for each reaction. The following list of suggested reagents is sufficient to accomplish all necessary reactions, but you may use other reagents if you wish. One of the intermediates is shown for you.



• Devise a synthesis of the alkene **M** using 2-bromobutane (**L**) and acetone (propanone) as starting materials. Show all relevant intermediates and reagents.

Marks 5

THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.

• Show clearly the reagents you would use to carry out the following chemical conversion. More than one step is required. Give the structures of any intermediate compounds formed.

• Devise a way to convert alkene **C** to alkene **D** using hydrogen bromide (HBr) as one of the reagents. Provide any other reagents you might need. If any of the steps you use could form two products, explain whether there is any selectivity and why.

Marks

Electrophilic addition follows Markovnikov's rule. There are two possible intermediates, a primary and a tertiary cabocation. The tertiary is more stable so is formed preferentially.

Base catalysed elimination of HBr follows Saytzev's rule - the more highly substituted product will predominate.

• Show clearly the reagents you would use to carry out the following chemical conversions. Note that more than one step is required and you should indicate all necessary steps and the constitutional formulas of any intermediate compounds.

O 1. 
$$CH_3MgBr$$

2.  $H^{\oplus}/H_2O$ 

conc.  $H_2SO_4/heat$ 

CI

Mg

(dry ether solvent)

$$\begin{array}{c} & & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & \\ & & & \\ & &$$

3

• Devise a synthesis of the following compound from the starting material indicated. Note that more than one step will be required. Indicate all necessary reagents and the constitutional formulas of any intermediate compounds.

Br OH OH 
$$\operatorname{Cr}_2\operatorname{O}_7^{2\Theta}/\operatorname{H}^{\oplus}$$
 heat

• Devise a synthesis of the following compounds from the starting materials indicated. Note that more than one step will be required. Indicate all necessary reagents and the constitutional formulas of any intermediate compounds.

$$\begin{array}{c} O \\ \\ \\ \\ \\ \\ \end{array}$$

$$\begin{array}{c} O \\ \\ \\ \\ \end{array}$$

• Devise a synthesis of the following compounds from the starting materials indicated. Note that more than one step will be required. Indicate all necessary reagents and the constitutional formulas of any intermediate compounds.

$$\begin{array}{c} Cl \\ MeO \end{array}$$

$$\begin{array}{c} MgCl \\ Mg/dry\ ether \\ MeO \end{array}$$

$$\begin{array}{c} MgCl \\ 1.\ CO_2 \\ \hline 2.\ H^{\oplus}/\ H_2O \end{array}$$

$$\begin{array}{c} MeO \end{array}$$

• Devise a synthesis of the following compounds from the starting materials indicated. Note that more than one step will be required. Indicate all necessary reagents and the constitutional formulas of any intermediate compounds.

$$\begin{array}{c|c}
OH & OH \\
\hline
H_2 / Pd catalyst
\end{array}$$

$$\begin{array}{c|c}
Cr_2O_7^{2\Theta} / H^{\oplus}
\end{array}$$

OH
$$\frac{1. \text{ CH}_3 \text{MgBr}}{2. \text{ H}^{\oplus}/\text{H}_2 \text{O}}$$

$$\frac{\text{conc. H}_2 \text{SO}_4}{\text{conc. H}_2 \text{SO}_4}$$

Marks 5

• The following is a nucleophilic addition-elimination reaction between ammonia and an acid anhydride. Provide curly arrows needed for the mechanism, and draw the structures of the two intermediates on this pathway.

Marks 5

• Devise a synthesis of 1-cyclohexyl-2-propanol (**D**) from cyclohexene (**C**). Provide reagents for each step, as well as the structures of any intermediate compounds generated as part of the route. You do not need to show any mechanisms. Hint: a number of steps is required.

• Devise a synthesis of the following compounds from the starting materials indicated. Note that more than one step will be required. Indicate all necessary steps and the constitutional formulas of any intermediate compounds.

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• Bromide **A** undergoes a reaction with hydroxide ions (OH<sup>-</sup>) to produce alcohol **C**. Complete the mechanism by adding curly arrows to illustrate the bonding changes that take place in the conversion of **A** to **B** and from **B** to **C**.

Marks 5

What is the name of the reaction taking place when A is converted to C via carbocation intermediate B?

## S<sub>N</sub>1 reaction (nucleophilic substitution, unimolecular)

What is the stereochemical outcome of this reaction? Give reasons for your answer.

The product is racemic because the intermediate carbocation (B) is planar. Attack by OH<sup>-</sup> is therefore equally likely from either top or bottom, leading to equimolar amounts of the two enantiomers.

Alcohol **C** can be further reacted with reagent **D** to generate ester **E**. Provide a structure of a suitable reagent **D** for the synthesis of ester **E** from alcohol **C**.

The acid chloride,  $CH_3CH_2COCl$ , or the acid anhydride,  $(CH_3CH_2CO)_2O$ , would be used.

• Consider the following reaction sequence.

Marks 6

Compound K below can be converted into two different intermediates, L and M, which can react together to give compound N and the inorganic byproduct HCl. Give the reagents A and B and draw the structure of the intermediates L and M.

A SOCl <sub>2</sub>	B 1. LiAlH <sub>4</sub> / dry ether 2. H <sup>+</sup> / H <sub>2</sub> O
L O CI	M HO

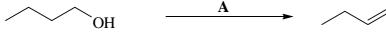
• Devise a synthesis of propylbenzene (V) using propanal (T) and bromobenzene (U) as starting materials. Provide any intermediate structures and reagents. (Hint: More than one step is required.)

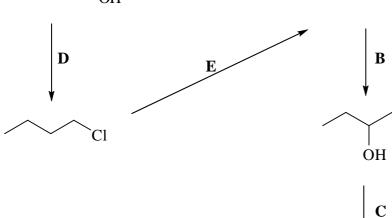
Br 
$$Mg/dry$$
 ether

 $MgBr$ 
 $M$ 

• Consider the following reaction sequence.

HO





Clearly state the reagents required (including conditions and solvent where appropriate) for each of the steps.

A: hot, concentration  $H_2SO_4(aq)$ (dehydration)

B: cold, dilute H<sub>2</sub>SO<sub>4</sub>(aq) (acid catalysed addition of H-OH)

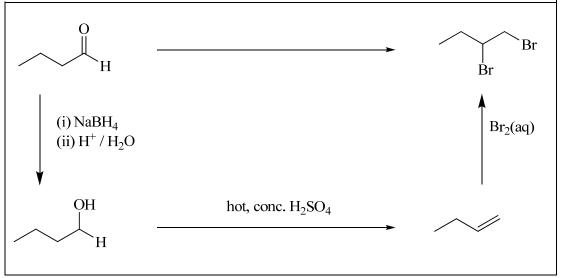
C:  $K_2Cr_2O_7(aq) / H_2SO_4(aq)$ (oxidation of secondary alcohol to ketone)

D: hot, concentrated HCl(aq) or SOCl (nucleophilic substitution of water soluble alcohol)

E: hot, concentrated KOH in ethanol (elimination – heat and solvent prevents substitution)

• Devise a synthesis of the following compounds from the starting materials indicated. Note that more than one step may be required and you should indicate all necessary steps and the constitutional formulas of any intermediate compounds.

• Devise a synthesis of 1,2-dibromobutane from butanal. Provide any intermediate structures and reagents. (Hint: More than one step is required.)



THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.

• Devise a synthesis of the product **Y**, starting from compound **X**. Note that more than one step may be required and you should indicate all necessary steps and the constitutional formulas of any intermediate compounds.

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 $NH_2$   $NH_2$   $Cr_2O_7^{2-}H^+$   $Cr_2O_7^{2-}H^+$   $Cr_2O_7^{2-}H^+$   $Cr_2O_7^{2-}H^+$   $Cr_2O_7^{2-}H^+$   $Cr_2O_7^{2-}H^+$ 

• Devise a synthesis of 3-methylheptan-3-ol using the two starting materials shown. Show the structures of any intermediate products involved, as well as the reagents required for each step. More than one step is required.

Marks 6

OH
$$Cr_2O_7^{2^{\odot}}/H^{\oplus}$$

$$Mg/dry \text{ ether}$$

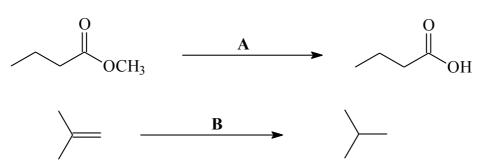
$$O$$

$$2. H^{\oplus}/H_2O$$
OH

Would the product be isolated as a racemic mixture or a single enantiomer or is the product achiral?

racemic mixture

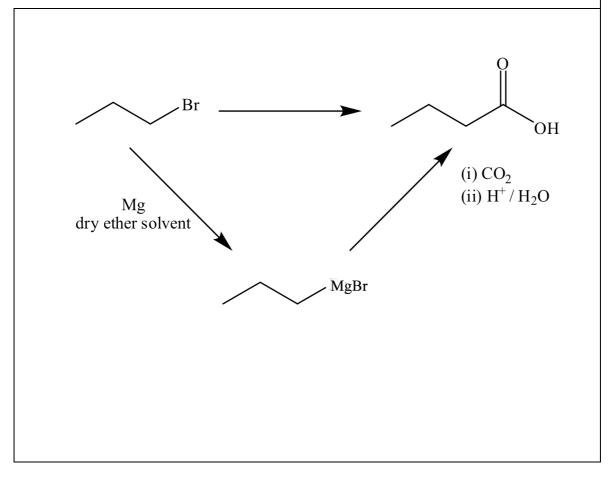
• Suggest reagents you could use to achieve the following transformations:



A: H<sup>+</sup> / H<sub>2</sub>O / heat

B: H<sub>2</sub> / Pd catalyst

• Clearly show the reagents you would use to carry out the following chemical conversion. Draw constitutional formulas for any intermediate compounds. Note that more than one step is required.



3

Marks

2

• Devise a synthesis of the product **Y**, starting from compound **X**. Note that more than one step may be required and you should indicate all necessary steps and the constitutional formulas of any intermediate compounds.

Marks 4

$$\begin{array}{c} \text{CH}_3\\ \text{OH} \\ \text{X (1-methylcyclohexanol)} \\ \text{Cr}_2\text{O}_7^{2-}/\text{H}^+\\ \text{(i) CH}_3\text{MgBr}\\ \text{(ii) H}^+/\text{H}_2\text{O} \\ \end{array}$$

What is the systematic name for compound  $\mathbf{Y}$ ?

## 1-methylcyclohexanol

• Devise a synthesis of 2-phenyl-2-propanol, starting from propene and bromobenzene. Note that your synthetic route will require more than one step from each starting material. Show clearly the reagents you would use and draw constitutional formulas for all intermediate compounds.

• Consider the following reaction sequences.

 $A \longrightarrow OH$   $B \longrightarrow B$ 

 $\mathbf{C}$ 

NH<sub>2</sub> O OH

D O N H

List the reagents A - E.

A NaOH

B hot, concentrated H<sub>2</sub>SO<sub>4</sub>

C NaNH<sub>2</sub>

D CH<sub>3</sub>COCl or (CH<sub>3</sub>CO)<sub>2</sub>O

E Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup>/H<sup>+</sup>

• Compare the acidity of a phenol to that of a carboxylic acid.

Phenols are less acidic than carboxylic acids. Phenols react with aqueous hydroxide solution to form the phenoxide ion; carboxylic acids react with either aqueous hydroxide or aqueous hydrogen carbonate to form the carboxylate ion.

The difference in stability arises from the relative stability of the conjugate base: there is delocalisation of the charge in the carboxylate ion over two electronegative oxygen atoms. The resonance stabilisation of the charge in the phenoxide ion is over the much less electronegative carbon atoms of the ring.

Marks 5

2