EXAM PAPERS PRACTICE

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Detailed mark scheme

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Level: CIE AS and A Level (9701)
Subject: Chemistry
Topic: CIE Chemistry
Type: Mark Scheme

Chemistry CIE AS & A Level
To be used for all exam preparation for 2025+

CHEMISTRY AS and A

This to be used by all students studying CIE AS and A level Chemistry (9701) But students of other boards may find it useful

Mark Scheme

Answer 1.

a)

i) The carboxylic acid derivative in Fig 1.1 is:

- Butanoyl chloride; [1 mark]

[Total: 1 mark]

- Fig 1.1 is an acyl chloride / acid chloride
  - This means that you identify the longest carbon chain and add *-oyl chloride* to the chain name

b)

i) The other product formed in this reaction is:

- Hydrogen chloride / HCl; [1 mark]

ii) This reaction can also be described as a condensation reaction because:

- A small molecule / hydrogen chloride / HCl is eliminated; [1 mark]

[Total: 2 marks]

- Acyl chlorides can react with alcohols to form esters
- This is just like the reaction of carboxylic acids with alcohols
- The only difference is the other product
  - Carboxylic acids form esters and water
  - Acyl chlorides form esters and hydrogen chloride
- Some students mistake a condensation reaction as one in which water is produced, but it is one in which a small molecule is produced

c) The equation for this reaction is:

- $CH_3COCl + NH_3 \rightarrow CH_3CONH_2 + HCl$
  OR
- $CH_3COCl + 2NH_3 \rightarrow CH_3CONH_2 + NH_4Cl$; [1 mark]

[Total: 1 mark]

- When ethanoyl chloride and ammonia react, the amide and HCl are formed

$$CH_3COCl + NH_3 \rightarrow CH_3CONH_2 + HCl$$

- The ammonia is basic so will react with the HCl to form the ammonium salt NH_4Cl

$$CH_3COCl + 2NH_3 \rightarrow CH_3CONH_2 + NH_4Cl$$

- Either equation is accepted but the first equation would be the answer given by most students

d) The two reactants are:

- Propanoic acid;
  AND
  Sulfur dichloride oxide / $SOCl_2$; [1 mark]

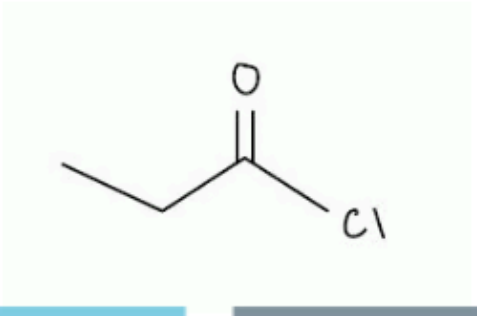
[Total: 1 mark]

- The equation for the reaction is:

$$CH_3CH_2COOH + SOCl_2 \rightarrow CH_3CH_2COCl + SO_2 + HCl$$

Answer 2.

a) The skeletal formula for propanoyl chloride is:



- Correct skeletal formula; [1 mark]

[Total: 1 mark]

- You must be able to draw the skeletal or displayed formulae for any given compound

b)

i) The two products formed when propanoyl chloride undergoes hydrolysis are:

- Propanoic acid; [1 mark]
- HCl; [1 mark]

ii) The mechanism by which hydrolysis occurs is:

- Addition-elimination; [1 mark]

[Total: 3 marks]

- The hydrolysis of an acyl chloride will form the corresponding carboxylic acid and HCl
- The water molecule acts as a nucleophile and attacks the carbonyl carbon atom
- The HCl molecule is then eliminated
- For harder questions, you must be able to draw the mechanism for this reaction

c) Propanoyl chloride will more readily undergo hydrolysis compared to 2-chloropropane because:

- It has a weaker C-Cl bond; [1 mark]
- Which can more easily break; [1 mark]

[Total: 2 marks]

- The question is only two marks so a detailed explanation is not required
- The strength of the C-Cl bond determines the tendency of these compounds to undergo hydrolysis
- 2-chloropropane is an alkyl chloride, propanoyl chloride is an acyl chloride
- The C-Cl bond is weaker in propanoyl chloride because the carbonyl carbon atom is bonded to oxygen - a very electronegative element which draws electron density away from the carbonyl carbon, leaving it with a slightly positive charge and therefore susceptible to attack by nucleophiles

Answer 3.

a) The correct equation is:

- $CH_3COCl + 2NH_3 \rightarrow CH_3CONH_2 + NH_4Cl$; [1 mark]
- The excess of ammonia means that a second ammonia molecule reacts with the HCl because it is basic

AND

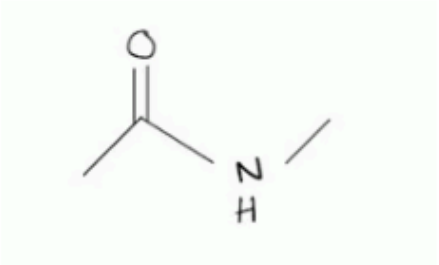
Ammonium chloride is formed as the second product (not hydrogen chloride); [1 mark]

[Total: 2 marks]

- The student's equation would have been correct if **excess** ammonia had not been used

b)

i) The skeletal formula of *N*-methylethanamide is:



- Correct skeletal formula; [1 mark]

ii) An equation for the formation of *N*-methylethanamide from ethanoyl chloride is:

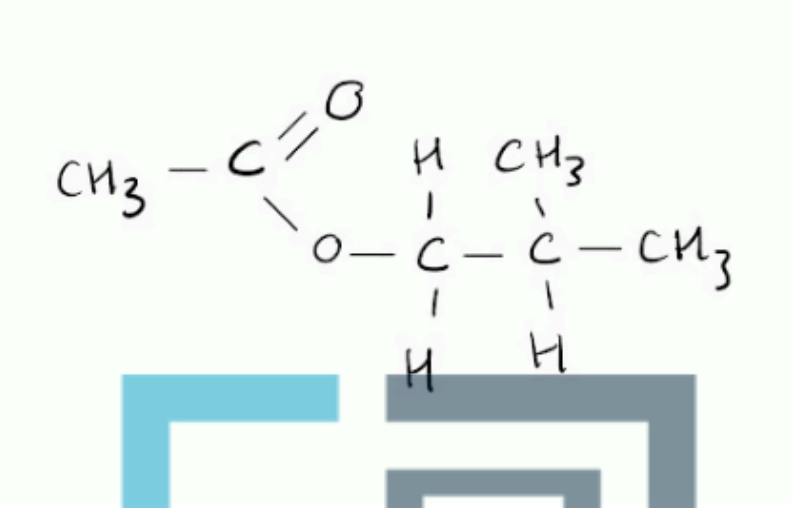
$$CH_3COCl + 2CH_3NH_2 \rightarrow CH_3CONHCH_3 + CH_3NH_3Cl$$

- Correct reactants; [1 mark]
- Correct products and balancing; [1 mark]

[Total: 3 marks]

- **Remember:** The name having the *N* at the beginning indicates that the methyl group is attached to the nitrogen rather than a carbon atom in the main carbon chain
- Once you have drawn your amide you can tell it is a secondary amide as the nitrogen atom is attached to two carbon atoms
- Secondary amides are formed from the reaction between ethanoyl chloride and a primary amine

c) The structure of the ester is:



- Correct displayed formula; [1 mark]

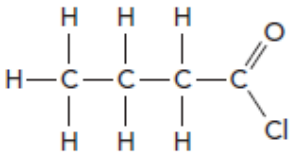
[Total: 1 mark]

- You should be able to draw the structures of esters for any combination of alcohol and carboxylic acid / acyl chloride / acid anhydride

Answer 4.

a)

i) The displayed formula of butanoyl chloride is:



- Correct displayed formula; [1 mark]

ii) The name and formula of a reagent that produces butanoic acid from butanoyl chloride is:

Alternative 1:

- PCl_5
  AND
  phosphorus(V) chloride; [1 mark]

Alternative 2:

- PCl_3
  AND
  phosphorus(III) chloride; [1 mark]

Alternative 3:

- $SOCl_2$
  AND
  sulfur dichloride oxide; [1 mark]

[Total: 2 marks]

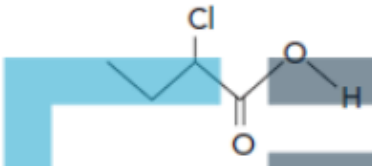
- Acyl chlorides have the functional group -COCl
- Butanoyl chloride has four carbon atoms, the fourth being that in the -COCl group
- You might have to write equations for the reaction between a carboxylic acid and a specific reagent so you must learn the names and formulas for all three

b)

i) Butanoic acid is a weaker acid than 2-chlorobutanoic acid because:

- Chlorine atom withdraws electrons from the -COOH group; [1 mark]
- Weakening the -OH bond so it is easier for 2-chlorobutanoic acid to lose an H^+ ion; [1 mark]

ii) The skeletal formula for 2-chlorobutanoic acid is:



- Correct skeletal formula; [1 mark]

[Total: 3 marks]

- Acids lose a proton, H^+ in aqueous solution
- The more easily the H^+ ion is lost the stronger the acid
- Butanoic acid contains a carbonyl group which draws electron density away from the O-H bond in the -COOH group making it relatively easy to lose a proton
- 2-chlorobutanoic acid contains a carbonyl group **AND** a chlorine atom (attached to the carbon atom which is bonded to the carbonyl group)
- Chlorine is also able to withdraw electron density away from the O-H in the -COOH group making the bond even weaker than that of butanoic acid and making it easier to lose the H^+

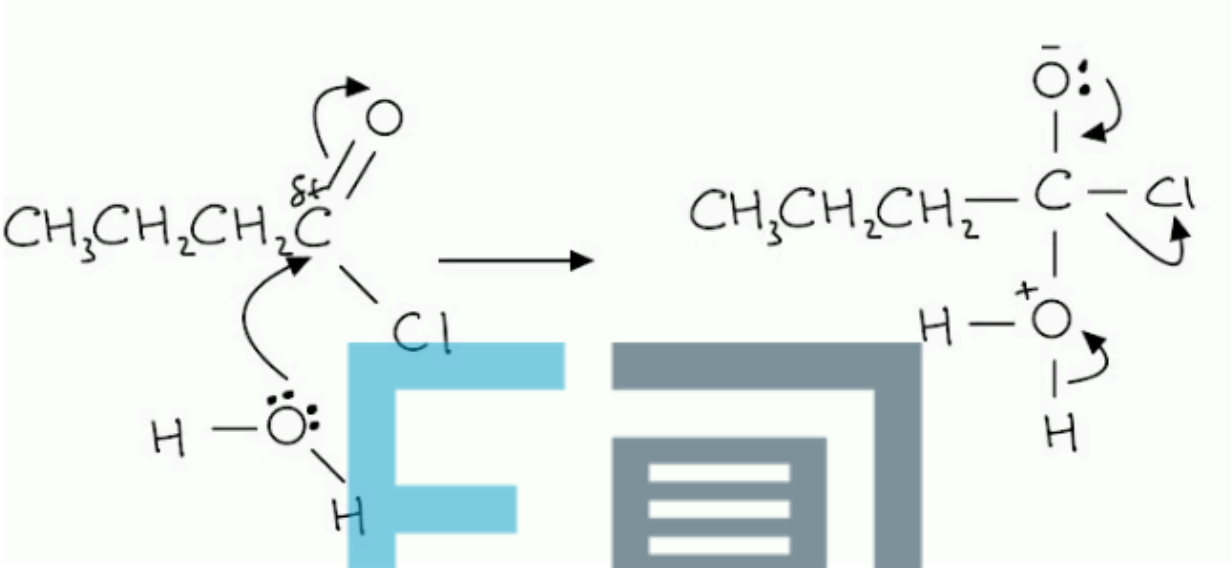
c) A chloro-substituted butanoic acid that is a strong acid than 2-chlorobutanoic acid is:

- 2,2-dichlorobutanic acid
  OR
  2,3-dichlorobutanoic acid; [1 mark]

[Total: 1 mark]

- The more chlorine atoms there are in the carboxylic acid, the stronger the acid is
- This is because they can draw more electron density away from the O-H bond, weakening it and causing it to more readily lose H^+

d) The mechanism for this reaction is:



- Curly arrow from the lone pair on the oxygen (of the H_2O) to carbon atom (of the C=O)
  AND
  δ+ on carbon atom; [1 mark]
- Curly arrow from C=O bond to the O of the C=O bond; [1 mark]
- Three arrows correct
  AND
  Lone pair on the O atom; [1 mark]
- Correct structure of ion including the two charges; [1 mark]

[Total: 5 marks]

- It is definitely worth learning this addition-elimination mechanism, as it crops up a lot
- Make sure your curly arrows are double headed and you have the δ+ on the carbon atom

e) Explain the relative ease of hydrolysis for butanoyl chloride, chlorobenzene and 1–chorobutane:

- The ease of hydrolysis with that most easily broken down is butanoyl chloride > 1–chlorobutane > chlorobenzene; [1 mark]

Explanation for order of butanoyl chloride and 1–chlorobutane:

- (Butanoyl chloride undergoes hydrolysis more easily than 1–chlorobutane because) butanoyl chloride has a carbon atom bonded to two electronegative atoms / oxygen as well as chlorine; [1 mark]
- So the carbon atom is more strongly δ+ than the carbon atom in 1–chlorobutane; [1 mark]

Explanation for chlorobenzene:

- A lone pair of electrons from the Cl atom overlaps with the delocalised p electrons in the benzene ring; [1 mark]
- Making the C-Cl bond stronger / harder to break; [1 mark]

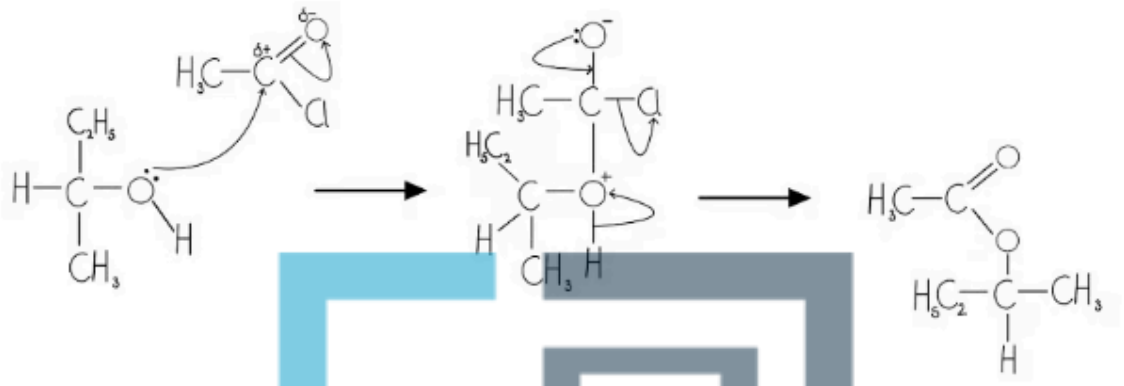
[Total: 5 marks]

- Acyl chlorides can be hydrolysed at room temperature using a neutral water molecule as a nucleophile
- Alkyl chlorides such as 1-chlorobutane, require a strong alkali to be refluxed with it to provide a source of $:OH^-$ ions
  - The OH^- ions are a stronger nucleophile than H_2O
- Aryl chlorides, like chlorobenzene, have the carbon atom bonded to the chlorine atom as part of the delocalised π bonding system of the benzene ring
  - One of the lone pairs of electrons of the Cl atom overlaps with this delocalised system
  - The C-Cl bond, therefore, has some double-bond character causing it to become stronger and harder to break

Answer 5.

The mechanism for the reaction of butan-2-ol with ethanoyl chloride is:

- Nucleophilic addition-elimination; [1 mark]



- Curly arrow from the lone pair on the O (of the OH) to the C (of the C=O); [1 mark]
- Curly arrow from the C=O bond to the O of the C=O bond; [1 mark]
- O has a lone pair and negative charge
  AND
  Arrow from the lone pair of the :O- to the C-O bond
  AND
  O has a positive charge
  AND
  Arrow from O-H bond to the O+ ; [1 mark]
- Correct final structure; [1 mark]

[Total: 5 marks]

- This mechanism is a standard nucleophilic addition-elimination mechanism - you must ensure that you know this mechanism
- You should learn how mechanisms work and what the arrows etc. represent, rather than trying to learn the exact mechanism for each reaction
  - If you understand what is happening, then you will be able to apply your knowledge and figure a mechanism out
  - You need to be able to apply your knowledge to ANY situation - this could be a reaction you have never seen before

The reactants required to make ethanamide are:

Alternative 1:

- Reactant = Ethanoyl chloride; [1 mark]
- Reactant = Ammonia; [1 mark]
- Product = Ammonium chloride; [1 mark]

OR

Alternative 2:

- Reactant = Ethanoic anhydride; [1 mark]
- Reactant = Ammonia; [1 mark]
- Product = Ammonium ethanoate; [1 mark]

[Total: 3 marks]

- One of the simplest ways to be sure of getting this mark is to draw out the product and identify the functional components and their origins

  - We can see a carbonyl group which would suggest a carboxylic acid, an acid anhydride or an acyl chloride
  - We can also see an amine group which suggests ammonia

i) Ethanoyl chloride is quicker to react with ethylamine than phenylamine because:

Alternative 1:

- Ethylamine is a stronger base; [1 mark]
- (Because) the alkyl group donates electron density making the N lone pair more available; [1 mark]

OR

Alternative 2:

- Phenylamine is a weaker base; [1 mark]
- (Because) the phenyl group withdraws electron density making the N lone pair more available
  OR
  (Because) the phenyl group delocalises electron density into the ring, making the N lone pair more available; [1 mark]

ii) The products of the reactions between ethanoyl chloride and ethylamine or phenylamine are:

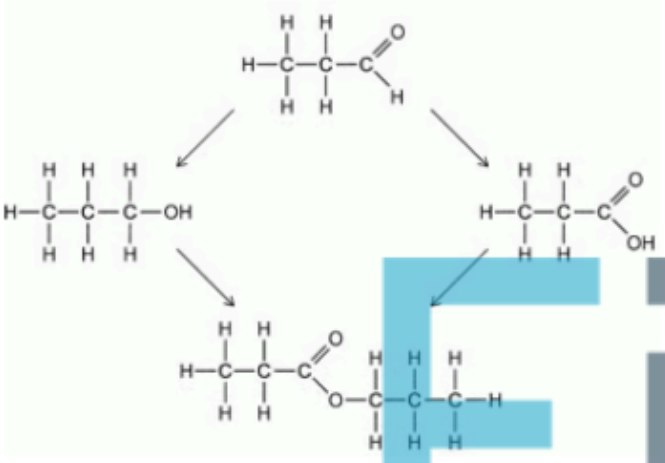
- N-ethylethanamide **AND** N-phenylethanamide; [1 mark]
- (The nitrogen in both amides can be classified as a) secondary / 2° / II° amine; [1 mark]

[Total: 4 marks]

- Naming amides is a tricky skill:
  - Name the chain attached to the N-group
  - Name the chain that includes the carbonyl group
  - Add amide to the end of the chemical name

Answer 6.

a) A reaction scheme, using displayed formulae, that could be used to prepare a sample of propyl propanoate is:



- Correct displayed formulae of propan-1-ol and propanoic acid; [1 mark]
- Correct displayed formula of propyl propanoate; [1 mark]

[Total: 2 marks]

- There are several ways the reaction scheme can be presented but it must show propanal being converted into propan-1-ol in one reaction and into propanoic acid in another reaction
  - These must then be shown to form the propyl ethanoate
- The question is unusual because you are typically given a reaction scheme to work with or asked to write the steps, not draw a reaction scheme but this can be asked as it as an application of your synthesis knowledge
- **Remember:** Esters are formed by the reaction of an acid and an alcohol
- Propyl propanoate will require propanoic acid and propan-1-ol
- This is another aspect that makes this question challenging as you may not think to split the propanal, reduce one portion and oxidise the other
- This means that you have to convert propanal into propanoic acid **and** propan-1-ol, then react them both together

b) The reagents and conditions required to form this intermediate are:

- (Acidified) potassium dichromate(VI) solution **AND** heated under reflux
  OR
  $K_2Cr_2O_7$/ H_2SO_4 **AND** heated under reflux; [1 mark]

[Total: 1 mark]

- From your reaction scheme in part **(a)**, you should be able to deduce that the intermediate with a molecular mass of 74.0 g mol^{-1} is propanoic acid
- This means that you are stating the reagents and conditions to convert propanal into propanoic acid

c) The chemical that will distil first is:

- Propanal; [1 mark]
- (Because) propan-1-ol has hydrogen bonding resulting in a higher boiling point
  OR
  (Because) propanal only has permanent dipole-dipole interaction, resulting in a lower boiling point; [1 mark]

[Total: 2 marks]

- As the propanal and propan-1-ol (intermediate with an M_r of 60.0) are being distilled, then you have to consider the intermolecular forces
- Propanal only has permanent dipole interactions
- Propan-1-ol has the strongest intermolecular force - hydrogen bonding
- This means that propan-1-ol will have a higher boiling point and propanal will have a lower boiling point
- Therefore, propanal will distil first

Answer 7.

a) To obtain $CH_3CH_2COOCH_2CH(CH_3)_2$ the reaction needs to involve:

- Propanoic acid; [1 mark]
- 2-methylpropan-1-ol; [1 mark]
- Heat; [1 mark]
- Concentrated H_2SO_4; [1 mark]

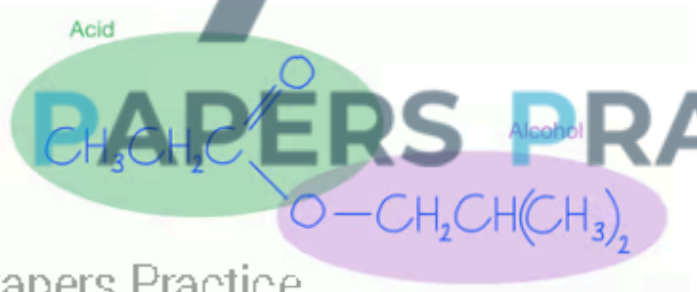
The equation is:

$$CH_3CH_2COOH + (CH_3)_2CHCH_2OH \rightarrow CH_3CH_2COOCH_2CH(CH_3)_2 + H_2O$$

- Correct reactants and products; [1 mark]

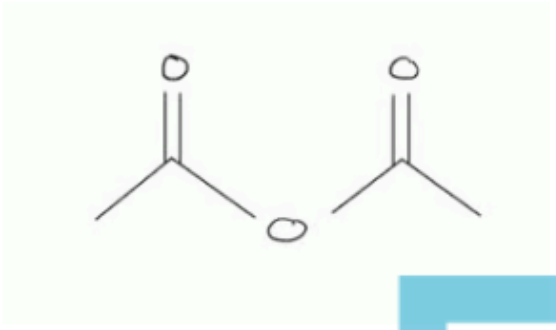
[Total: 5 marks]

- You should be able to write equations for the formation of any named ester you are given
- A good place to start is to draw the displayed formula of the ester so that you can deduce which alcohol and carboxylic acid (or derivative) it is formed from



b)

i) The structure of the acid anhydride used is:



- Correct skeletal formula of ethanoic anhydride; [1 mark]

ii) The equation for the reaction is:

$C_6H_5OH + (CH_3CO)_2O \rightarrow CH_3COOC_6H_5 + CH_3COOH$

- Correct reactants and products; [1 mark]

[Total: 2 marks]

- To deduce which anhydride has been used in the formation of an ester:
  - Look at the second part of the ester name, just like when you are working out which carboxylic acid is used
  - In this case, the ester name ends in ethanoate which means that ethanoic anhydride is required
- Acid anhydrides are formed when two carboxylic acid molecules join together and water is eliminated
  - **Careful:** When drawing their structures, make sure the number of carbon atoms on either side of the single 'bridging' -O- corresponds to the name of the anhydride
- **Remember:** The first part of the ester name indicates the alcohol that is required
  - In this case, the ester name starts with phenyl which means that phenol is required

c) The steps involved in forming phenyl ethanoate from ethanoyl chloride are:

- $CH_3COOH + SOCl_2 \rightarrow CH_3COCl + SO_2 + HCl$
  OR
  $CH_3COOH + PCl_5 \rightarrow CH_3COCl + POCl_3 + HCl$
  OR
  $CH_3COOH + PCl_3 \rightarrow CH_3COCl + H_3PO_3$; [1 mark]
- $CH_3COCl + C_6H_5OH \rightarrow CH_3COOC_6H_5 + HCl$; [1 mark]

Condition:

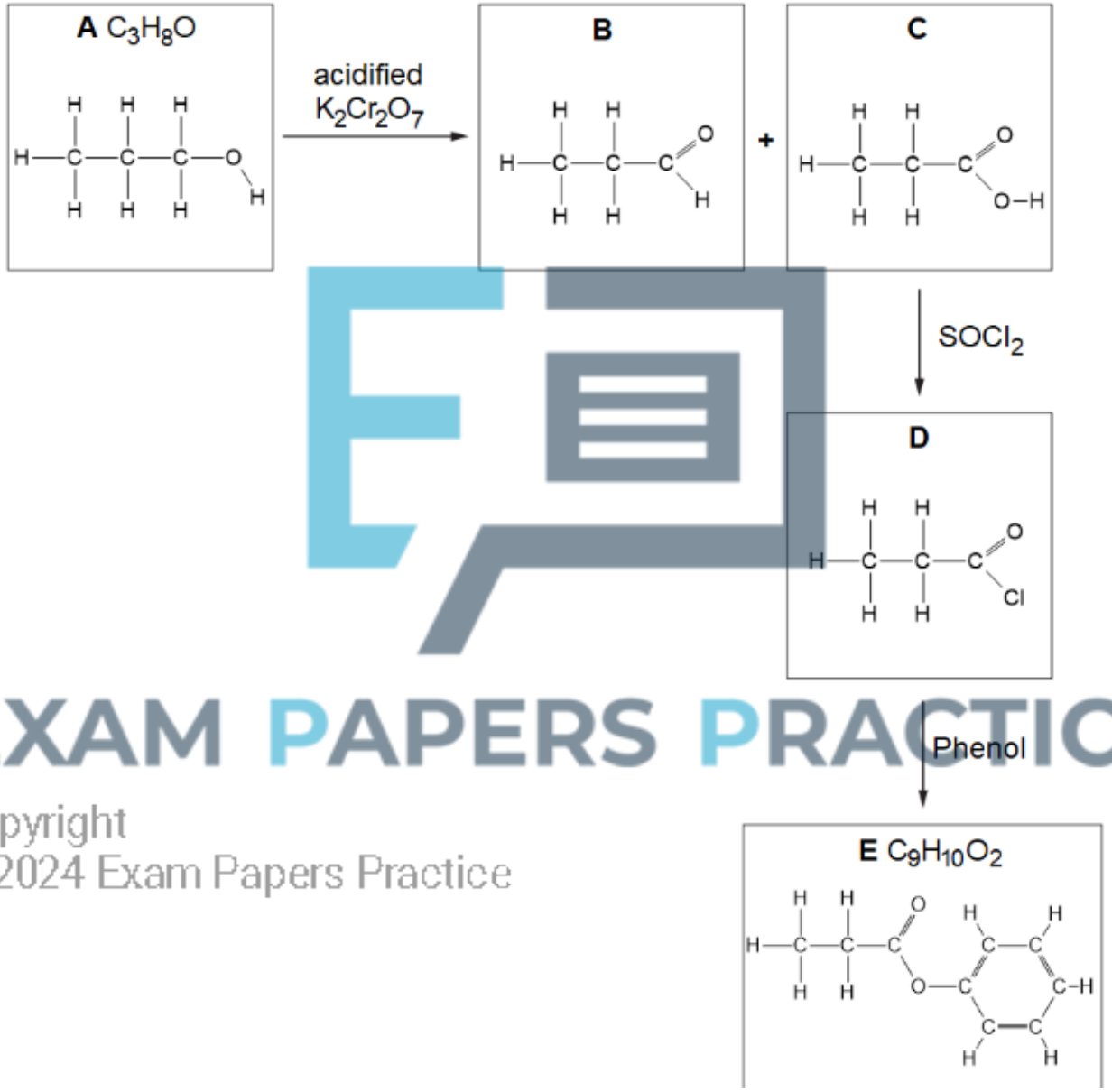
- NaOH
  OR
  Heat; [1 mark]

[Total: 3 marks]

- An acyl chloride must be formed from carboxylic acids using either
  - $SOCl_2$
  - PCl_3
  - PCl_5

Answer 8.

a) The structures of compounds **A**, **B**, **C**, **D** and **E** are:



- Correct structure of compound **A** / propan-1-ol; [1 mark]
- Correct structure of compound **B** / propanal; [1 mark]
- Correct structure of compound **C** / propanoic acid; [1 mark]
- Correct structure of compound **D** / propanoyl chloride; [1 mark]
- Correct structure of compound **E** / phenyl propanoate; [1 mark]

[Total: 5 marks]

- The reaction of **A** with acidified potassium dichromate should suggest that the compound could be a primary alcohol, secondary alcohol or aldehyde
  - Only a primary alcohol could react with acidified potassium dichromate to form two possible products
  - **Remember:** Primary alcohol → aldehyde → carboxylic acid
- The question gives the molecular formula of **A** and that its ^{13}C NMR spectrum contains 3 peaks
  - The NMR data suggests that **A** is a primary alcohol or an ether (which are not on the specification)
  - Therefore, **A** is propan-1-ol / $CH_3CH_2CH_2OH$
- Depending on the conditions, propan-1-ol will react with acidified potassium dichromate to form propanal or propanoic acid
  - **Careful:** Compound **C** has to be propanoic acid / CH_3CH_2COOH for the next step to be able to occur
  - Therefore, **B** is propanal / CH_3CH_2CHO
- $SOCl_2$ is a reagent that is used to convert carboxylic acids into acyl chlorides
  - Therefore, **D** is propanoyl chloride / CH_3CH_2COCl
- The subsequent reaction with phenol is an esterification reaction
  - **Careful:** Do not be put off by the ring inside phenol and automatically assume that it is an electrophilic substitution reaction
  - **Remember:** Alcohol + acyl chloride → ester + HCl
    - Phenol + propanoyl chloride → phenyl propanoate + HCl
    - Therefore, **E** is phenyl propanoate / $CH_3CH_2COOC_6H_5$
- Make sure that you draw the structures of all the compounds as instructed in the question

b)

i) The mixture can be separated into compounds **B** and **C** by:

- Distillation
  AND
  (Because,) **C** has a higher boiling point than **B**; [1 mark]
- Compound **C** can form hydrogen bonds which require more energy to overcome; [1 mark]

ii) An improvement to the reaction with acidified potassium dichromate to ensure the production of compound **C** only is to:

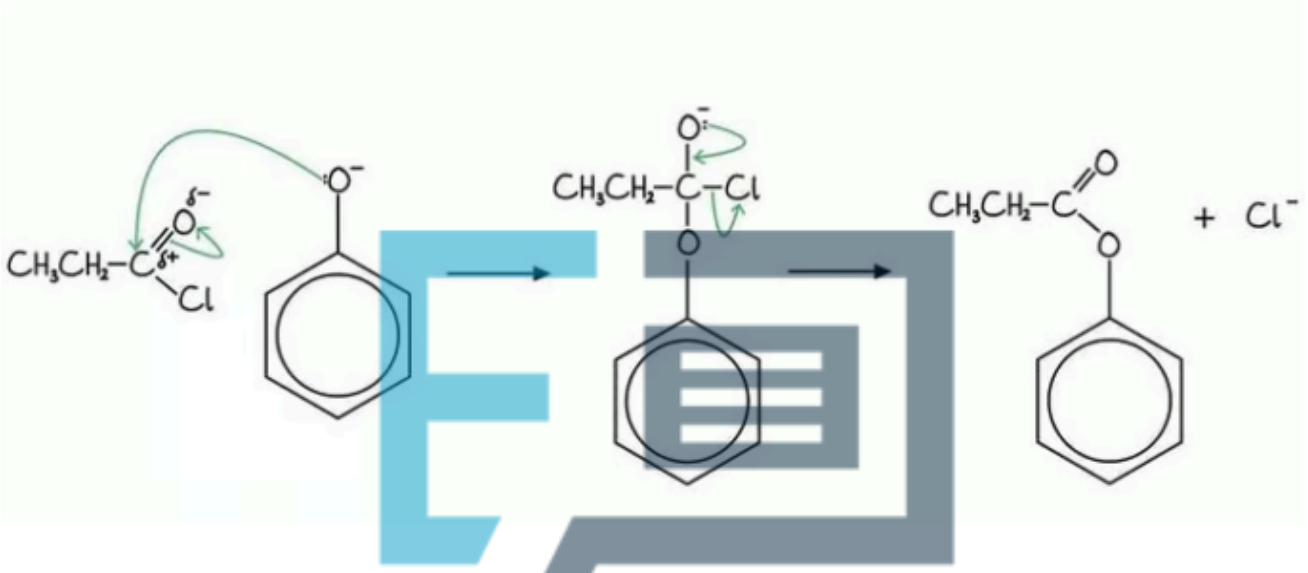
- Reflux (**A** with the acidified potassium dichromate); [1 mark]

[Total: 3 marks]

- From part (a), compound **B** is propanal and compound **C** is propanoic acid
  - Compound **C** has lone pairs on the oxygen atoms **AND** has a hydrogen atom attached to the electronegative oxygen atom
    - This means that it is able to hydrogen bond
    - Hydrogen bonding is the strongest intermolecular force and requires a large amount of energy to overcome, resulting in high boiling points
  - Compound **B** has a dipole on the carbonyl group
    - But, the energy required to overcome this is much less than the energy required to overcome hydrogen bonding
  - This means that compounds **B** and **C** have different boiling points and can be separated by distillation
    - It is not necessary to specify simple or fractional for the mark
- To ensure that all of the propan-1-ol / **A** is oxidised into propanoic acid / **C**, the reaction with acidified potassium dichromate should be performed under reflux

c)

i) The mechanism for the formation of compound **E** from compound **D** and an appropriate nucleophile is:



- Curly arrow from the lone pair on the oxygen atom of the nucleophile to the δ+ carbon
  AND
  Curly arrow from the carbonyl / C=O bond to the oxygen atom in propanoyl chloride; [1 mark]
- Correct intermediate structure; [1 mark]
- Curly arrow from the lone pair on the O^- on the intermediate to the C-O bond
  AND
  Curly arrow from the C-Cl bond to the chlorine atom; [1 mark]

ii) The reaction of compound **D** with phenol is faster because:

- The partial charge on the carbonyl carbon in compound **D** is more positive than compound **C**
  AND
  Which makes compound **D** more susceptible to attack from the nucleophile / phenoxide ion; [1 mark]

[Total: 4 marks]

- For part (i)
  - The mechanism for this reaction is a nucleophilic addition-elimination reaction
  - **Careful:** The question states that the mechanism should be drawn with an appropriate nucleophile
    - In this case, the nucleophile is the phenoxide ion / $C_6H_5O^-$
      - This is formed by sodium hydroxide deprotonating phenol : $C_6H_5OH + NaOH \rightarrow C_6H_5O^- + Na^+ + H_2O$
- For part (ii)
  - Compounds **C** and **D** will both react with the phenoxide ion
  - Therefore, any difference in the speed / rate of reaction must be due to the structure of compounds **C** and **D**
    - Both compounds have a carbonyl group
    - Compound **C** has the carbonyl / C=O group attached to an OH group
    - Compound **D** has the carbonyl / C=O group attached to a Cl atom
  - Oxygen and chlorine are both electronegative
    - For compound **D** to react faster, chlorine must be more electronegative than oxygen
    - This results in compound **D** have a larger partial positive charge on the carbonyl carbon, which makes it more attractive to a nucleophile