

## Esterification

Subject & topics: Chemistry | Organic | Reactions Stage & difficulty: A Level P2

Part A  Banana
An ester with an odour of banana has the following formula.
$\mathrm{CH_{3}COOCH_{2}CH(CH_{3})CH_{2}CH_{3}}$
In which of the following will the substances react together to produce this ester?
${\color{blue} \textbf{CH}_3\textbf{CH}_2\textbf{CH}(\textbf{CH}_3)\textbf{CH}_2\textbf{COOH} + \textbf{CH}_3\textbf{OH}}$
$\qquad \qquad \mathrm{CH_{3}CH_{2}CH(CH_{3})CH_{2}COCl} + \mathrm{CH_{3}OH}$
$\bigcirc  \mathrm{CH_{3}COCl} + \mathrm{CH_{3}CH_{2}CH}(\mathrm{CH_{3}})\mathrm{CH_{2}OH}$
${\color{blue} \textbf{CH}_{3}\textbf{COOH} + \textbf{CH}_{3}\textbf{CH}_{2}\textbf{CH}(\textbf{CH}_{3})\textbf{CH}_{2}\textbf{Cl}}$
${\color{blue} \textbf{CH}_{3}\textbf{COONa} + \textbf{CH}_{3}\textbf{CH}_{2}\textbf{CH}(\textbf{CH}_{3})\textbf{CH}_{2}\textbf{Cl}}$

#### Part B

## Oil of wintergreen

A manufacturer wishes to make methyl salicylate, the aromatic liniment of oil of wintergreen, from salicylic acid.

salicylic acid methyl salicylate

Figure 1: Methyl salicylate from salicylic acid

How is this esterification of salicylic acid best achieved?

- mixing it with cold ethanoyl chloride
- warming it with anhydrous methanol
- heating it under reflux with aqueous methanol
- heating it under reflux with methanol and a little concentrated sulfuric acid
- heating it under reflux with ethanoic acid and a little concentrated sulfuric acid

Part A adapted with permission from UCLES, A-Level Chemistry, June 1990, Paper 1, Question 30; Part B adapted with permission from UCLES, A-Level Chemistry, June 1993, Paper 4, Question 28



## Esters with Aqueous Acid

Subject & topics: Chemistry | Organic | Reactions Stage & difficulty: A Level P2

Part A  Rate of hydrolysis
An experiment is set up to measure the rate of hydrolysis of methyl ethanoate.
$\mathrm{CH_{3}COOCH_{3}+H_{2}O} \Longrightarrow \mathrm{CH_{3}COOH} + \mathrm{CH_{3}OH}$
The hydrolysis is found to be slow in neutral aqueous solution but it proceeds at a measurable rate when the solution is acidified with hydrochloric acid.
What is the function of the hydrochloric acid in the reaction mixture?
to increase the reaction rate by catalytic action
to ensure that the reaction reaches equilibrium
$igcup$ to maintain a constant $\mathrm{pH}$ during the reaction
to suppress ionisation of the ethanoic acid formed
to dissolve the methyl ethanoate

Part B Ester P
An ester <b>P</b> with a fruity odour has the following structural formula:
CH <sub>3</sub> C OCH <sub>2</sub> CH <sub>2</sub> CH(CH <sub>3</sub> ) <sub>2</sub>
Figure 1: Structure of ester P
What compounds are produced when <b>P</b> is hydrolysed using aqueous hydrochloric acid?
$ ho$ CH $_3$ COCl and (CH $_3$ ) $_2$ CHCH $_2$ CH $_2$ OH
$ ho$ CH $_3$ CHO and (CH $_3$ ) $_2$ CHCH $_2$ CH $_2$ OH
$ ho$ CH $_3$ COOH and (CH $_3$ ) $_2$ CHCH $_2$ CHO
$ ho$ CH $_3$ COOH and (CH $_3$ ) $_2$ CHCH $_2$ CH $_2$ OH

Part A adapted with permission from UCLES, A-Level Chemistry, June 1992, Paper 4, Question 13; Part B adapted with permission from UCLES, A-Level Chemistry, November 1994, Paper 4, Question 27

Question deck:



## **Painkillers**

Subject & topics: Chemistry | Organic | Reactions Stage & difficulty: A Level P2

## Part A

### Benzocaine

Benzocaine is a local anaesthetic, often used to relieve pain from sunburn.

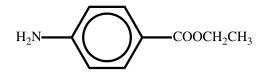


Figure 1: Structure of benzocaine

Which of the following is a possible means of its preparation?

**A** 
$$H_2N$$
  $\longrightarrow$   $COOH$  +  $CH_3CH_2OH$   $\xrightarrow{H^+}$  heat  $\longrightarrow$  **B**  $H_2N$   $\longrightarrow$   $OH$  +  $CH_3CH_2OH$   $\xrightarrow{H^+}$  heat



Figure 2: Possible preparations of benzocaine

Α
В
С

Aspirin has the following structure.

$$\begin{array}{c|c} OH & \\ \hline \\ O & \\ \hline \\ O & \\ \hline \\ O & \\ \end{array}$$

Figure 3: Structure of aspirin

When aspirin is hydrolysed by acid present in the stomach, what products are produced?

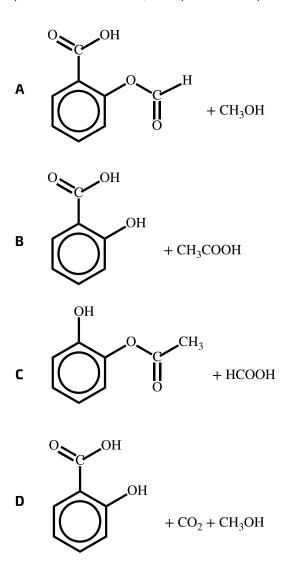


Figure 4: Possible products when aspirin is hydrolysed by acid

В			
c			
D			

Part A adapted with permission from UCLES, A-Level Chemistry, June 1996, Paper 3, Question 23; Part B adapted with permission from UCLES, A-Level Chemistry, November 1995, Paper 4, Question 25

Question deck:



### **Esters**

Subject & topics: Chemistry | Organic | Reactions Stage & difficulty: A Level P2

#### Part A

## Methyl cinnamate

The *matsutake* mushroom is a delicacy added to many Japanese foods. The spicy aroma of this mushroom is due to methyl cinnamate, which can be prepared in the laboratory according to the following reaction sequence.

Figure 1: Preparation of methyl cinnamate

What are the conditions required for step 1?

onc.	$H_2SO_4$ ,	reflux
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aq.  $\mathrm{H}_2\mathrm{SO}_4$ , reflux

conc. NaOH, reflux

aq. NaOH, reflux

Part B  Hydrolysis of compound Q
A compound ${\bf Q}$ of formula $C_5H_{10}O_2$ is boiled with aqueous sulfuric acid to give a carboxylic acid and an alcohol. This alcohol can be oxidised with sodium dichromate (VI) to give a compound of formula $C_3H_6O$ which does not give a silver mirror on addition of Tollens' reagent.
What is compound <b>Q</b> ?
$\bigcirc  \mathrm{CH_{3}CH_{2}COOCH_{2}CH_{3}}$
ho CH <sub>3</sub> COOCH(CH <sub>3</sub> ) <sub>2</sub>
$\bigcirc  \mathrm{CH_{3}COOCH_{2}CH_{2}CH_{3}}$
$(CH_3)_2CHCOOCH_3$

Part A adapted with permission from UCLES, A-Level Chemistry, June 1995, Paper 4, Question 24; Part B created for isaacphysics.org by R. Less

Question deck:



## **Amides**

### Part A

## Ethanamide hydrolysis

Ethanamide,  $CH_3CONH_2$ , is hydrolysed by warming with aqueous sodium hydroxide.

Write an equation for this hydrolysis with the organic component in the form  $\mathrm{CH_3C} \cdot \ldots$ 

# Part B Phenacetin The painkiller *Phenacetin* can be made from compound **X**. $NH_2$ NHCOCH<sub>3</sub> reagent Х Phenacetin Figure 1: Preparation of Phenacetin What would be the best reagent to use? $\mathrm{CH_{3}COCH_{3}}$ $\mathrm{CH_{3}COCl}$ $\mathrm{CH_{3}CONH_{2}}$ $\mathrm{CH_{3}COOCH_{2}CH_{3}}$ $\mathrm{CH_{3}COOH}$

Part A adapted with permission from UCLES, A-Level Chemistry, June 1991, Paper 2, Question 5; Part B adapted with permission from UCLES, A-Level Chemistry, June 1992, Paper 4, Question 40

Question deck:



## **Acyl Chlorides**

Subject & topics: Chemistry | Organic | Reactions Stage & difficulty: A Level P2

Part A With alcohols
What is the product of the reaction between phenylmethanol, $ m C_6H_5CH_2OH$ , and ethanoyl chloride, $ m CH_3COCl$ ?
$ ho_6 ext{H}_5 ext{CH}_2 ext{Cl}$
${ m C_6H_5CH_2COCl}$
${ m C_6H_5CH_2OCOCH_3}$
$ ho_6 ext{H}_5 ext{COCH}_3$
$ ho_6 ext{H}_5 ext{OCOCH}_3$
Part B With amines
What is the product of the reaction between propionyl chloride, ${ m CH_3CH_2COCl}$ and ethanamine ${ m CH_3CH_2NH_2?}$
Draw the product in the <u>structure editor</u> and give your answer as a SMILES string.
In the editor, after drawing your structure, click on the round, yellow smiley face to generate a SMILES string.  Copy the SMILES string and paste it in the answer box.
<u>Using the structure editor</u>

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Question deck:



## Reactions of $CH_{3}COCl \\$

Subject & topics: Chemistry | Organic | Reactions

Write equations (state symbols not required) for the reaction of $ m CH_3COCl$ with the following reagents:
Write the organic component in the form $\mathrm{CH_3C} \cdot \ldots$
Part A
$ m H_2O$
$ m H_2O$
Part B $\mathrm{NH}_3$
$\mathrm{NH_{3}}$
Part C
$\mathrm{C_{3}H_{7}OH}$
$\mathrm{C_{3}H_{7}OH}$

Stage & difficulty: A Level P2

Part D			
$ m C_4H_9NH_2$			

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Question deck:



## Hydrolysis of Functional Groups

Subject & topics: Chemistry	Organic   Reactions	Stage & difficulty: A Level P1

e compounds below were treated with prolonged heating with aqueous sodium hydroxide under reflux. of the compounds would not give sodium ethanoate $(\mathrm{CH_3COONa})$ ?
$ m CH_3COCl$
CH <sub>3</sub> COOCOCH <sub>3</sub>
$ m CH_3CN$
$\mathrm{CH_{3}COOC_{2}H_{5}}$
$\mathrm{CH_{3}COCH_{3}}$

Adapted with permission from OCSEB, A-Level Chemistry, June 1994, Paper 1, Question 27

Question deck:



## Nitrile Reactions

Subject & topics: Chemistry | Organic | Reactions Stage & difficulty: A Level P3

e same carboxylic acid is obtained either by the hydrolysis of a nitrile <b>P</b> or by the oxidation of an alcohol <b>Q</b> .			
	P	Q	
Α	$\mathrm{CH_{3}CH_{2}CN}$	$\mathrm{CH_{3}CH_{2}OH}$	
В	$(\mathrm{CH_3})_2\mathrm{CHCN}$	$(\mathrm{CH_3})_3\mathrm{COH}$	
С	$\mathrm{C_6H_5CH(CH_3)CN}$	$\mathrm{C_6H_5CH_2CH(OH)CH_3}$	
D	$\mathrm{C_6H_5CH_2CN}$	$\mathrm{C_6H_5CH_2CH_2OH}$	
E	$\mathrm{C_6H_5CN}$	$\mathrm{C_6H_5OH}$	
) A В С	lowing pairs could be <b>P</b> and <b>Q</b> ?		

Part B  Hydrogenation of nitriles		
What is produced when propanenitrile, $\mathrm{CH_3CH_2CN}$ , reacts with hydrogen using a palladium catalyst?		
ho $ ho$		
$\bigcirc$ CH $_3$ CONH $_2$		
ho CH <sub>3</sub> CH <sub>2</sub> NH <sub>2</sub>		
$\bigcirc  \mathrm{CH_{3}CH_{2}CH_{2}NH_{2}}$		

Part A adapted with permission from UCLES, A-Level Chemistry, June 1990, Paper 1, Question 28; Part B adapted with permission from UCLES, A-Level Chemistry, November 1995, Paper 4, Question 28

Question deck:



## **Black Pepper**

Subject & topics: Chemistry | Organic | Reactions Stage & difficulty: A Level C2

One of the constituents of black pepper is the neutral compound  ${\bf N}$  with molecular formula  $C_{17}H_{19}NO_3$ .

When heated with dilute acid under reflux, **N** produces two components: piperidine, **O** and an unsaturated carboxylic acid **P**, of formula  $C_{12}H_{10}O_4$ . **P** adds two molecules of  $Br_2$  when treated with bromine in 1,1,1-trichloroethane to give compound **Q**.

Figure 1: Structures of O and P

## Part A Compound N

Draw the compound N. Use the structure editor to generate a SMILES string.

In the editor, after drawing your structure, click on the round, yellow smiley face to generate a SMILES string. Copy the SMILES string and paste it in the answer box.

Using the structure editor

Part B  Compound Q
Draw the compound <b>Q</b> . Use the <u>structure editor</u> to generate a SMILES string.
In the editor, after drawing your structure, click on the round, yellow smiley face to generate a SMILES string. Copy the SMILES string and paste it in the answer box.
Part C O with ethanoyl chloride
Suggest how piperidine ${\bf O}$ would react with ethanoyl chloride (CH $_3$ COCl). Draw the structure of the resulting compound formed.
Use the <u>structure editor</u> to generate a SMILES string as your answer.
In the editor, after drawing your structure, click on the round, yellow smiley face to generate a SMILES string. Copy the SMILES string and paste it in the answer box.
Part D O with dilute $\mathrm{HCl}$
Suggest how piperidine would react with dilute hydrochloric acid.

### Part E

## **Compound R**

When piperidine is treated with one equivalent of iodomethane, compound  ${\bf R}$  is formed.

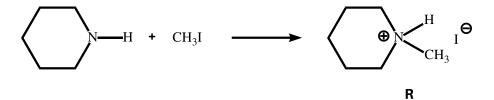


Figure 2: Compound R

Mechanistically, what type of reaction is occurring?

#### Part F

## **Compound T**

Further reaction of  $\mathbf{R}$  with more iodomethane gives compound  $\mathbf{S}$ , which on heating with alcoholic potassium hydroxide, reacts to form compound  $\mathbf{T}$  in the following scheme.

Figure 3: Compound S reacting to form compound T.

What type of reaction is occurring here?

### Part G

### T with iodomethane

What might be formed if compound **T** were treated with more iodomethane, followed by alcoholic potassium hydroxide?

Use the <u>structure editor</u> to generate a SMILES string as your answer.

In the editor, after drawing your structure, click on the round, yellow smiley face to generate a SMILES string. Copy the SMILES string and paste it in the answer box.

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