Esterification

A Level

Part A Banana

An ester with an odour of banana has the following formula.

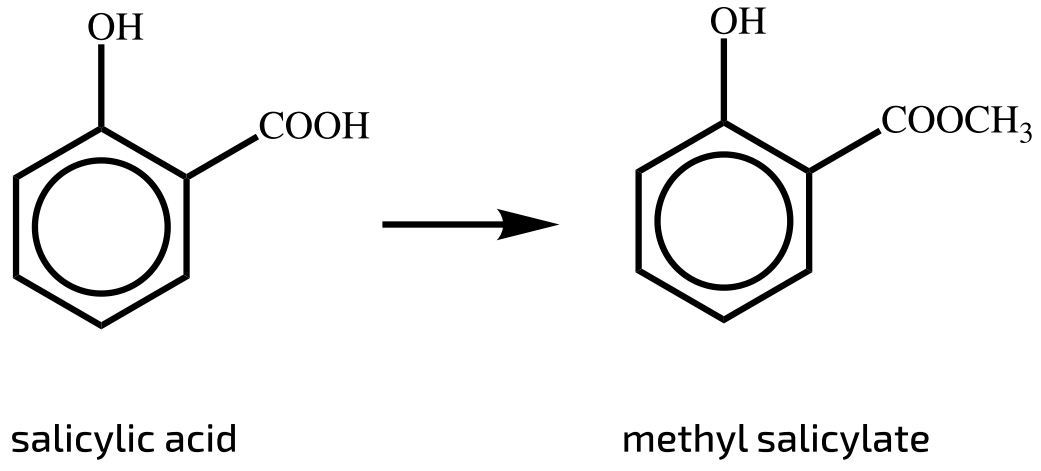
$$CH_3COOCH_2CH(CH_3)CH_2CH_3$$

In which of the following will the substances react together to produce this ester?

- $CH_3CH_2CH(CH_3)CH_2COOH + CH_3OH$
- $CH_3COCl + CH_3CH_2CH(CH_3)CH_2OH$
- $CH_3CH_2CH(CH_3)CH_2COCl + CH_3OH$
- $CH_3COOH + CH_3CH_2CH(CH_3)CH_2Cl$
- $CH_3COONa + CH_3CH_2CH(CH_3)CH_2Cl$

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?

[NB: The benzene ring is quite unreactive its reactions constitute a whole branch of organic chemistry we will be looking at in detail later. Until then, consider that **no reactions will be taking place at the benzene ring itself** in this or subsequent questions.]

- heating it under reflux with aqueous methanol
- mixing it with cold ethanoyl chloride
- warming it with anhydrous 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

A Level

Part A Rate of hydrolysis

An experiment is set up to measure the rate of hydrolysis of methyl ethanoate.

$$CH_3COOCH_3 + H_2O \rightleftharpoons CH_3COOH + CH_3OH$$

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 suppress ionisation of the ethanoic acid formed
- to dissolve the methyl ethanoate
- to increase the reaction rate by catalytic action
- to maintain a constant pH during the reaction
- to ensure that the reaction reaches equilibrium

Part B Ester P

An ester **P** with a fruity odour has the following structural formula:

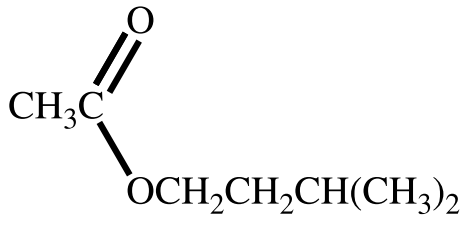


Figure 1: Structure of ester **P**

What compounds are produced when **P** is hydrolysed using aqueous hydrochloric acid?

- CH_3COCl and $(CH_3)_2CHCH_2CH_2OH$
- CH_3COOH and $(CH_3)_2CHCH_2CHO$
- CH_3COOH and $(CH_3)_2CHCH_2CH_2OH$
- CH_3CHO and $(CH_3)_2CHCH_2CH_2OH$

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

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Ester Hydrolysis

A Level

P P P

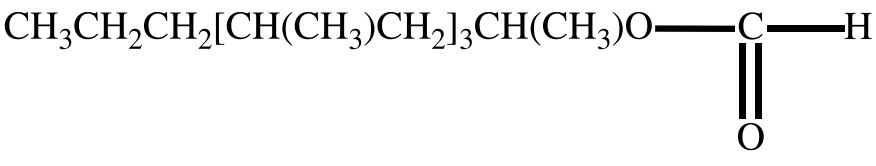
Part A Beeswax

One of the constituents of beeswax has the formula $\mathrm{CH_3(CH_2)_{24}COO(CH_2)_{29}CH_3}$. What are the products of its acid hydrolysis?

- $\mathrm{CH_3(CH_2)_{24}COOH}$ and $\mathrm{CH_3(CH_2)_{28}COOH}$
- $\mathrm{CH_3(CH_2)_{24}COOH}$ and $\mathrm{CH_3(CH_2)_{29}OH}$
- $\mathrm{CH_3(CH_2)_{24}OH}$, $\mathrm{CH_3(CH_2)_{29}OH}$ and $\mathrm{CO_2}$
- $\mathrm{CH_3(CH_2)_{29}COOH}$ and $\mathrm{CH_3(CH_2)_{24}OH}$
- $\mathrm{CH_3(CH_2)_{23}COOH}$ and $\mathrm{CH_3(CH_2)_{29}COOH}$

Part B Lardolure

The acarid mite releases *Lardolure** to attract other mites to a host: this chemical can be destroyed by hydrolysis with acid.



A simplified formula for *lardolure* may be written as

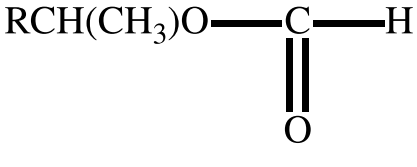


Figure 1: Structure of *Lardolure*

What are the products of its hydrolysis?

- $\mathrm{RCH(CH_3)OH + CO_2}$
- $\mathrm{RCH(CH_3)OH + HCOOH}$
- $\mathrm{RCH{=}CH_2 + HCOOH}$
- $\mathrm{RCH(CH_3)COOH + HCOOH}$
- $\mathrm{RCH_2CH_3 + CO_2}$

---

* *Lardolure* was isolated in 1982 by Y. Kuwahara as the aggregation pheromone of the acarid mite (*Lardoglyphus konoi*), a primary pest for stored products with high protein content such as dried meat and fish meal.

Part A adapted with permission from UCLES, A-Level Chemistry, June 1991, Paper 1, Question 29;
Part B adapted with permission from UCLES, A-Level Chemistry, June 1993, Paper 4, Question 27

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Painkillers

A Level

Part A Benzocaine

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

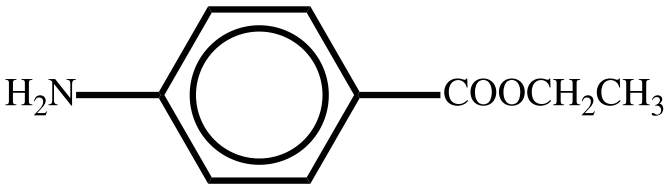


Figure 1: Structure of *Benzocaine*

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

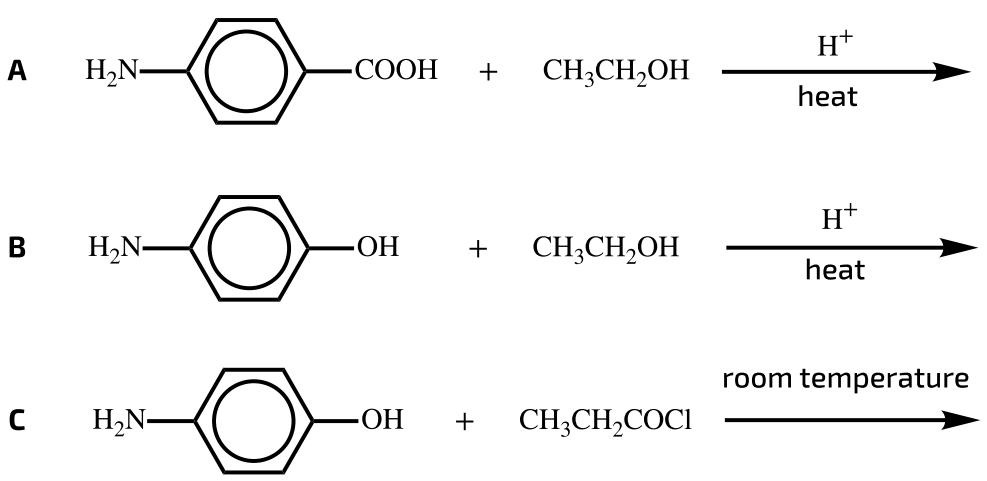


Figure 2: Possible preparations of *benzocaine*

- A
- B
- C
- D

Part B Aspirin

Aspirin has the following structure.

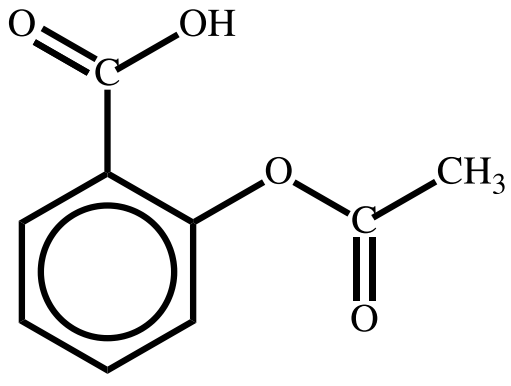
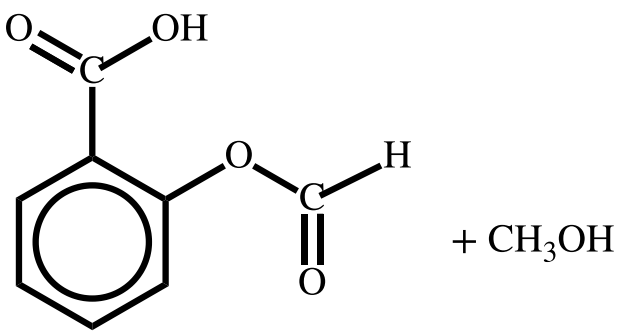


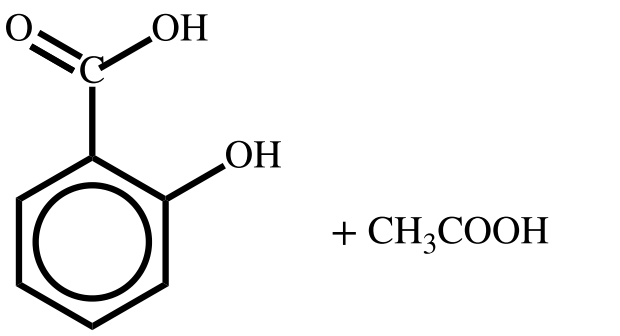
Figure 3: Structure of aspirin

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

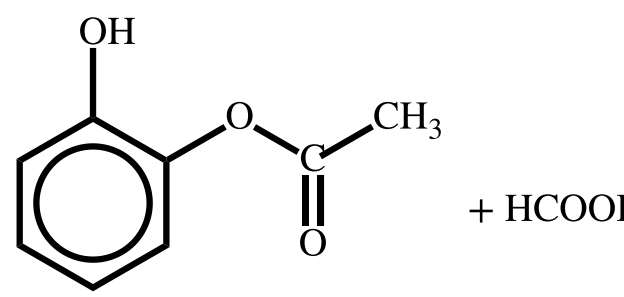
A



B



C



D

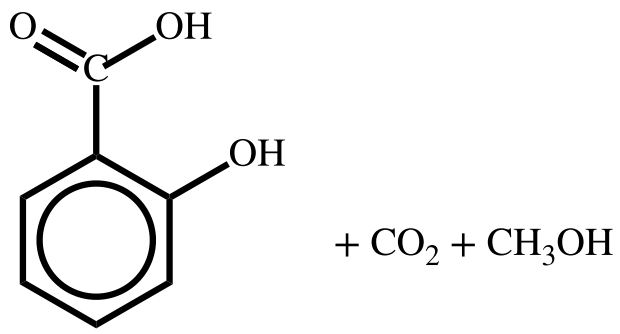


Figure 4: Possible products when aspirin is hydrolysed by acid

- A
- B
- 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

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Esters

A Level

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.

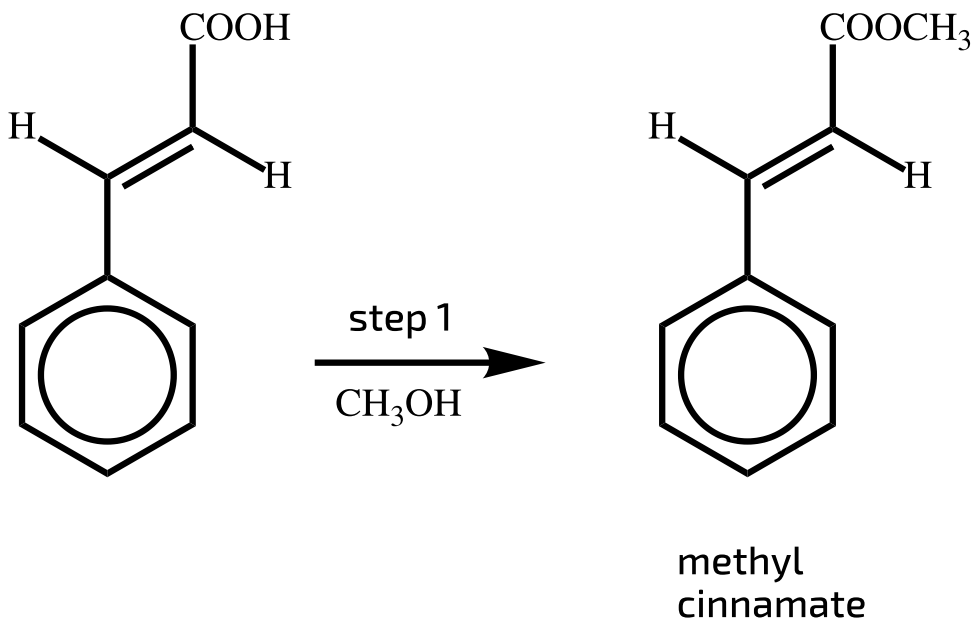

Figure 1: Preparation of methyl cinnamate

What are the conditions required for step 1?

- aq. $NaOH$, reflux
- conc. H_2SO_4, reflux
- conc. $NaOH$, reflux
- aq. H_2SO_4, reflux

Part B Hydrolysis of compound Q

A compound **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 **Q**?

- $(CH_3)_2CHCOOCH_3$
- $CH_3CH_2COOCH_2CH_3$
- $CH_3COOCH(CH_3)_2$
- $CH_3COOCH_2CH_2CH_3$

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

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Amides

A Level

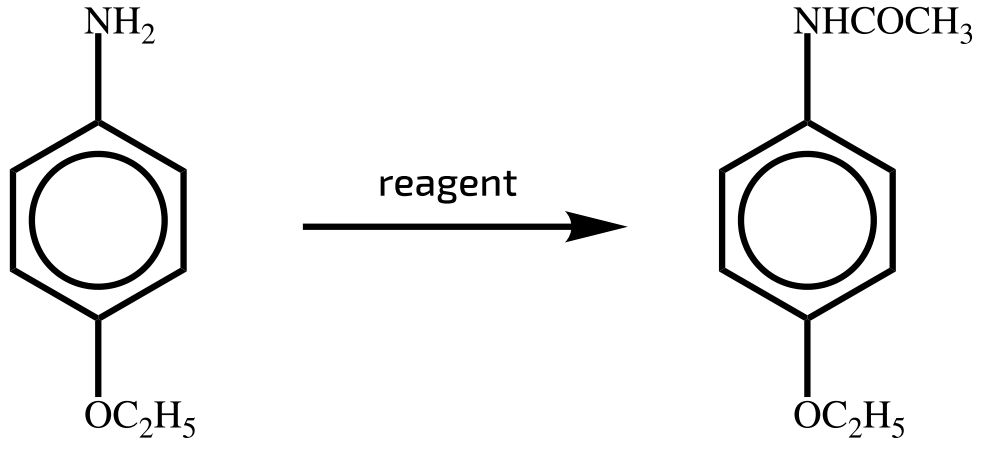
Part A Ethanamide hydrolysis

Ethanamide, $\mathrm{CH_3CONH_2}$, 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**.



X *Phenacetin*

Figure 1: Preparation of *Phenacetin*

What would be the best reagent to use?

- CH_3COCH_3
- CH_3COCl
- CH_3CONH_2
- $CH_3COOCH_2CH_3$
- CH_3COOH

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

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Acyl Chlorides

A Level

Part A With alcohols

What is the product of the reaction between phenylmethanol, $C_6H_5CH_2OH$, and ethanoyl chloride, CH_3COCl ?

- $C_6H_5CH_2Cl$
- $C_6H_5CH_2COCl$
- $C_6H_5CH_2OCOCH_3$
- $C_6H_5COCH_3$
- $C_6H_5OCOCH_3$

Part B With amines

What is the product of the reaction between propionyl chloride, CH_3CH_2COCl and ethanamine $CH_3CH_2NH_2$?

Draw the product in the structure editor 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.

Using the structure editor

Part A adapted with permission from UCLES, A-Level Chemistry, November 1992, Paper 4, Question 27;
Part B created for Isaac Physics by R. Less

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Reactions of CH_3COCl

A Level

Write equations (state symbols not required) for the reaction of CH_3COCl with the following reagents:

Write the organic component in the form $CH_3C\cdot\ldots$

Part A H_2O

H_2O

Part B NH_3

NH_3

Part C C_3H_7OH

C_3H_7OH

Part D **Excess** $C_4H_9NH_2$

$C_4H_9NH_2$

Hydrolysis of Functional Groups

A Level

The five compounds below were treated with prolonged heating with aqueous sodium hydroxide under reflux. Which of the compounds would not give sodium ethanoate (CH_3COONa) ?

- CH_3CN
- CH_3COCH_3
- $CH_3COOC_2H_5$
- $CH_3COOCOCH_3$
- CH_3COCl

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

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Nitrile Reactions

A Level

Part A Acids from nitriles

The same carboxylic acid is obtained either by the hydrolysis of a nitrile **P** or by the oxidation of an alcohol **Q**.

	P	Q
A	CH_3CH_2CN	CH_3CH_2OH
B	$(CH_3)_2CHCN$	$(CH_3)_3COH$
C	$C_6H_5CH(CH_3)CN$	$C_6H_5CH_2CH(OH)CH_3$
D	$C_6H_5CH_2CN$	$C_6H_5CH_2CH_2OH$
E	C_6H_5CN	C_6H_5OH

Which of the following pairs could be **P** and **Q**?

- **A**
- **B**
- **C**
- **D**
- **E**

Part B Hydrogenation of nitriles

What is produced when propanenitrile, CH_3CH_2CN, reacts with hydrogen using a palladium catalyst?

- CH_3NH_2 and CH_4
- $CH_3CH_2NH_2$
- CH_3CONH_2
- $CH_3CH_2CH_2NH_2$

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