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## Esterification

A Level

### Part A Banana

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

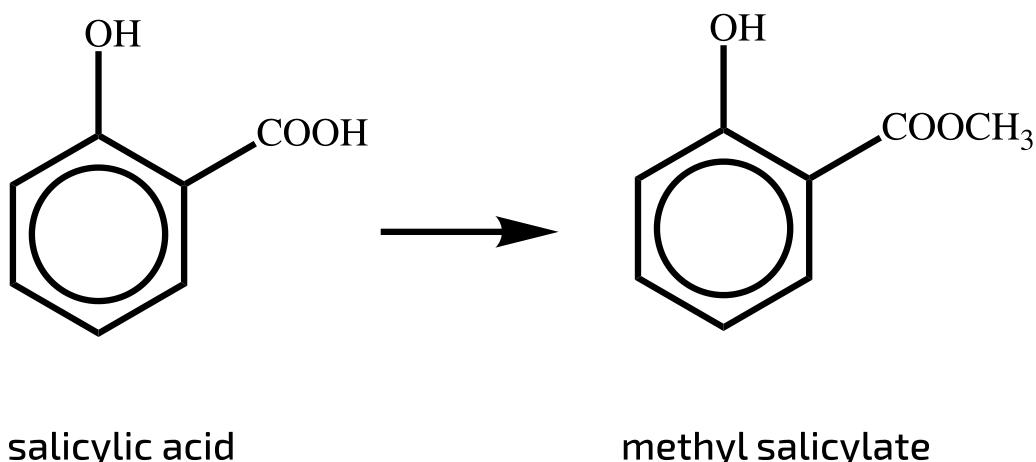


In which of the following will the substances react together to produce this ester?

- $\text{CH}_3\text{COCl} + \text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{OH}$
- $\text{CH}_3\text{COOH} + \text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{Cl}$
- $\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{COOH} + \text{CH}_3\text{OH}$
- $\text{CH}_3\text{COONa} + \text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{Cl}$
- $\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{COCl} + \text{CH}_3\text{OH}$

## Part B Oil of wintergreen

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



**Figure 1:** Methyl salicylate from salicylic acid

How is this esterification of salicylic acid best achieved?

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

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

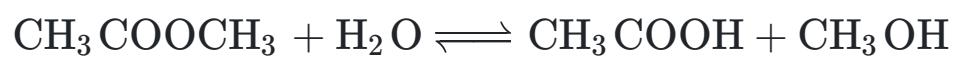


## Esters with Aqueous Acid

A Level

### Part A   Rate of hydrolysis

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



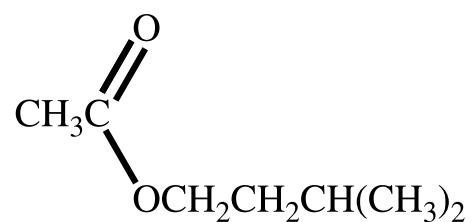
The hydrolysis is found to be slow in neutral aqueous solution but it proceeds at a measurable rate when the solution is acidified with hydrochloric acid.

What is the function of the hydrochloric acid in the reaction mixture?

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

## 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<sub>3</sub> COOH and (CH<sub>3</sub>)<sub>2</sub> CHCH<sub>2</sub> CHO
- CH<sub>3</sub> COCl and (CH<sub>3</sub>)<sub>2</sub> CHCH<sub>2</sub> CH<sub>2</sub> OH
- CH<sub>3</sub> CHO and (CH<sub>3</sub>)<sub>2</sub> CHCH<sub>2</sub> CH<sub>2</sub> OH
- CH<sub>3</sub> COOH and (CH<sub>3</sub>)<sub>2</sub> CHCH<sub>2</sub> CH<sub>2</sub> 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

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## Painkillers

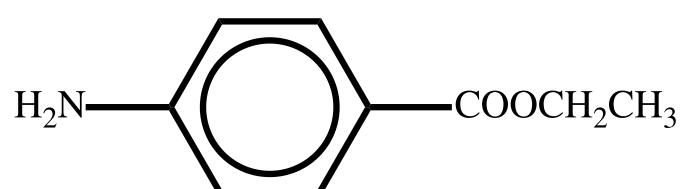
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A Level



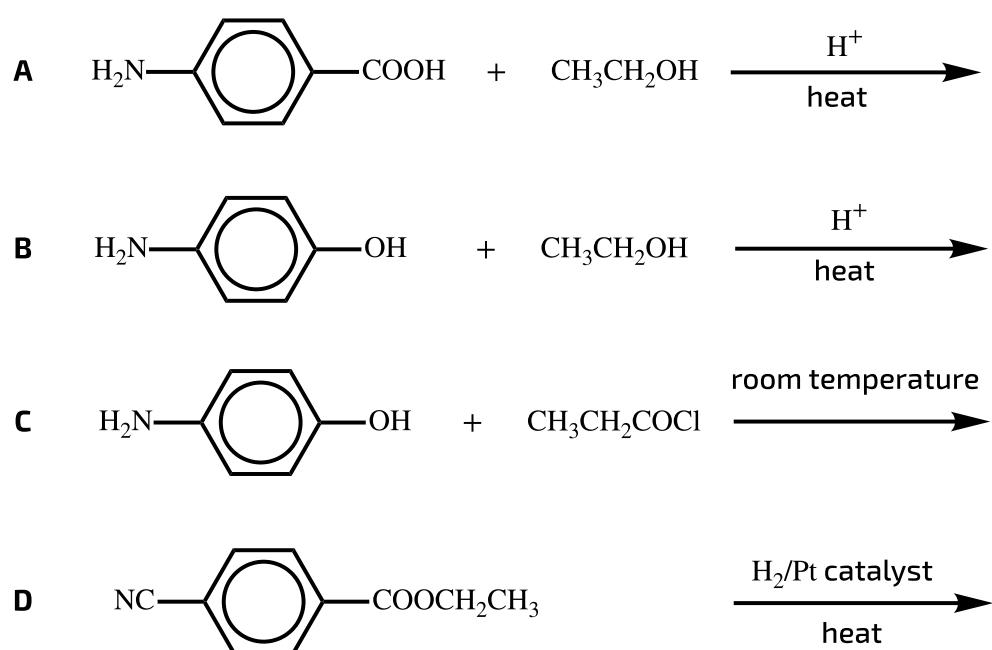
## Part A Benzocaine

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.

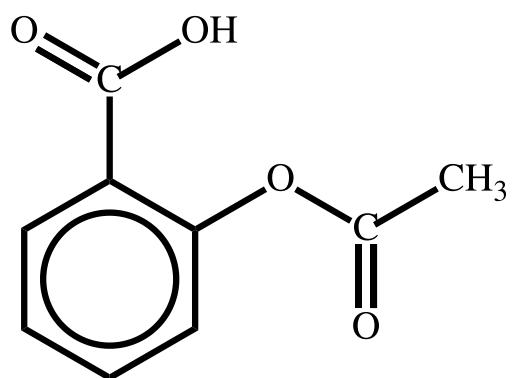


Figure 3: Structure of aspirin

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

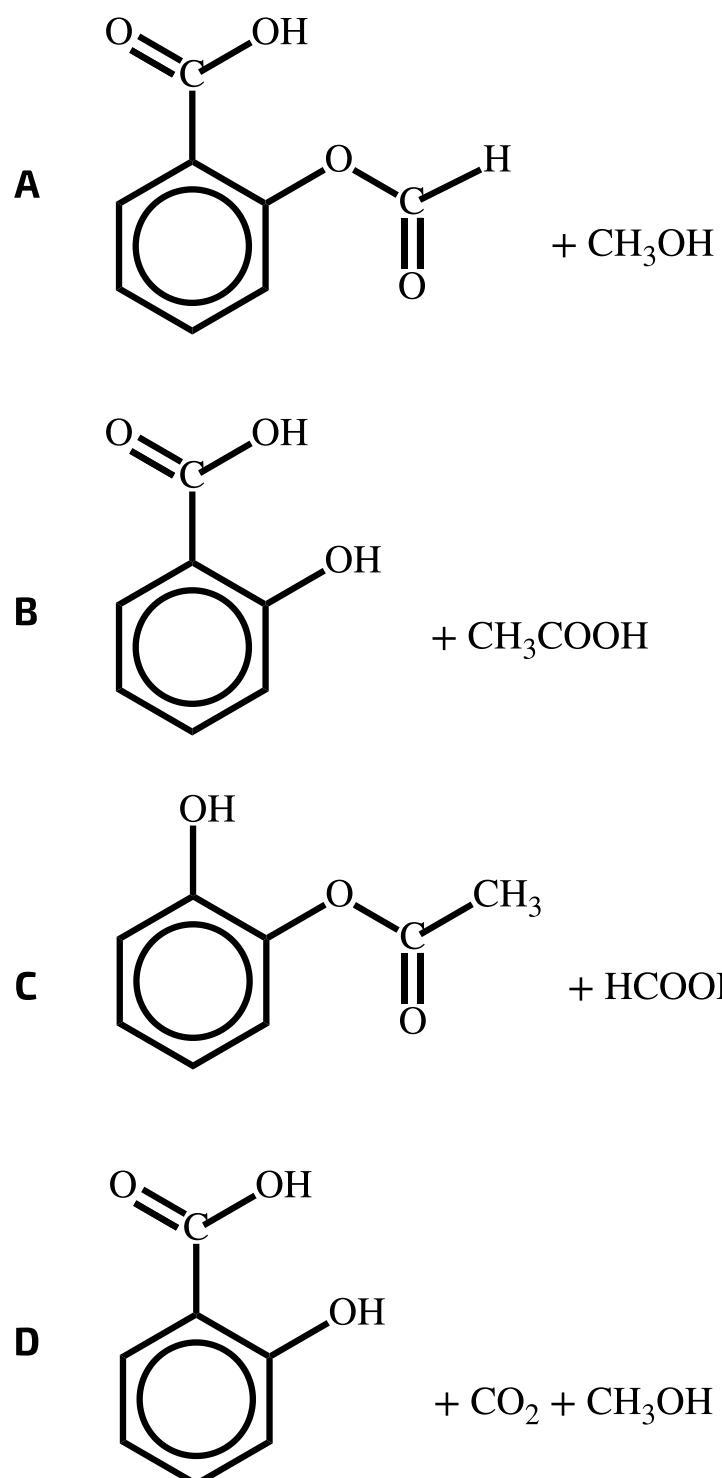


Figure 4: Possible products when aspirin is hydrolysed by acid

- A
- B

C

D

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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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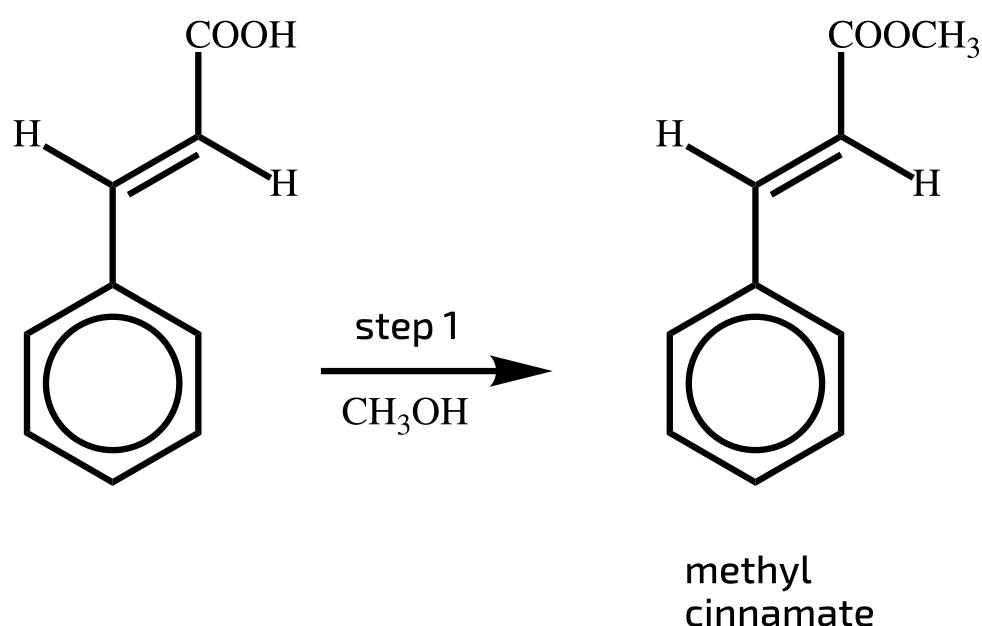
## Esters

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?

- conc. H<sub>2</sub>SO<sub>4</sub>, reflux
- aq. H<sub>2</sub>SO<sub>4</sub>, reflux
- aq. NaOH, reflux
- conc. NaOH, 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**?

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

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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

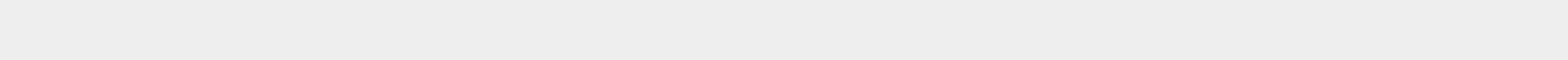
A Level



### Part A   Ethanamide hydrolysis

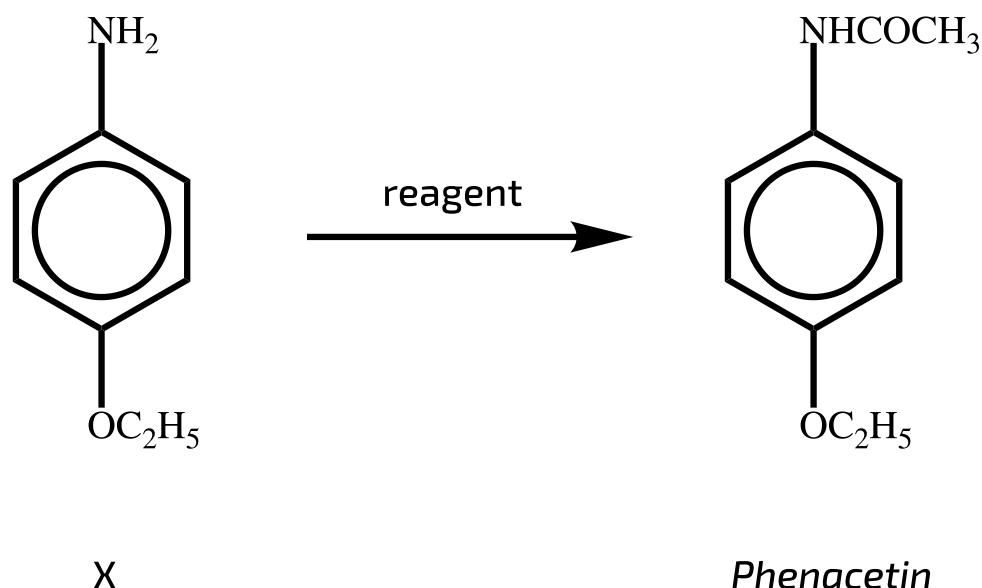
Ethanamide,  $\text{CH}_3\text{CONH}_2$ , is hydrolysed by warming with aqueous sodium hydroxide.

Write an equation for this hydrolysis with the organic component in the form  $\text{CH}_3\text{C}\cdot\ldots$



## Part B Phenacetin

The painkiller *Phenacetin* can be made from compound **X**.



**Figure 1:** Preparation of *Phenacetin*

What would be the best reagent to use?

- CH<sub>3</sub>COCH<sub>3</sub>
- CH<sub>3</sub>COCl
- CH<sub>3</sub>CONH<sub>2</sub>
- CH<sub>3</sub>COOCH<sub>2</sub>CH<sub>3</sub>
- CH<sub>3</sub>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

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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](#)



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## Reactions of CH<sub>3</sub>COCl

A Level



Write equations (state symbols not required) for the reaction of CH<sub>3</sub>COCl with the following reagents:

Write the organic component in the form CH<sub>3</sub>C· . . .

**Part A**   H<sub>2</sub>O

H<sub>2</sub>O

**Part B**   NH<sub>3</sub>

NH<sub>3</sub>

**Part C**   C<sub>3</sub>H<sub>7</sub>OH

C<sub>3</sub>H<sub>7</sub>OH

**Part D Excess C<sub>4</sub>H<sub>9</sub>NH<sub>2</sub>**

C<sub>4</sub>H<sub>9</sub>NH<sub>2</sub>

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## 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 ( $\text{CH}_3\text{COONa}$ ) ?

- $\text{CH}_3\text{COCl}$
- $\text{CH}_3\text{COCH}_3$
- $\text{CH}_3\text{COOCOCH}_3$
- $\text{CH}_3\text{CN}$
- $\text{CH}_3\text{COOC}_2\text{H}_5$

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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**.

	<b>P</b>	<b>Q</b>
<b>A</b>	$\text{CH}_3\text{CH}_2\text{CN}$	$\text{CH}_3\text{CH}_2\text{OH}$
<b>B</b>	$(\text{CH}_3)_2\text{CHCN}$	$(\text{CH}_3)_3\text{COH}$
<b>C</b>	$\text{C}_6\text{H}_5\text{CH}(\text{CH}_3)\text{CN}$	$\text{C}_6\text{H}_5\text{CH}_2\text{CH}(\text{OH})\text{CH}_3$
<b>D</b>	$\text{C}_6\text{H}_5\text{CH}_2\text{CN}$	$\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{OH}$
<b>E</b>	$\text{C}_6\text{H}_5\text{CN}$	$\text{C}_6\text{H}_5\text{OH}$

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,  $\text{CH}_3\text{CH}_2\text{CN}$ , reacts with hydrogen using a palladium catalyst?

- $\text{CH}_3\text{CH}_2\text{NH}_2$
  - $\text{CH}_3\text{NH}_2$  and  $\text{CH}_4$
  - $\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$
  - $\text{CH}_3\text{CONH}_2$
- 

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

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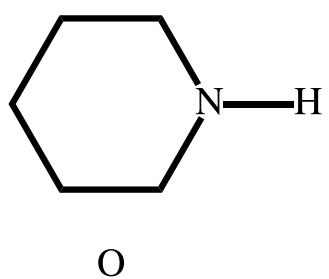
## Black Pepper

A Level

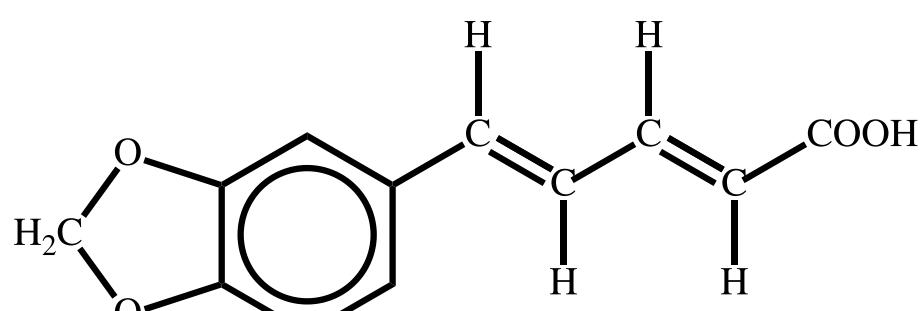
c c c

One of the constituents of black pepper is the neutral compound **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**.



O



P

**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 **Q**. 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.

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## **Part C    O with ethanoyl chloride**

Suggest how piperidine **O** would react with ethanoyl chloride ( $\text{CH}_3\text{COCl}$ ). Draw the structure of the resulting compound formed.

Use the [structure editor](#) 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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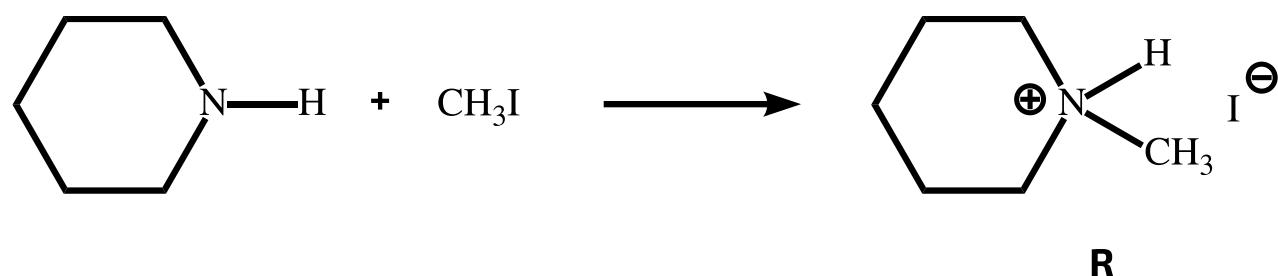
## **Part D    O with dilute HCl**

Suggest how piperidine would react with dilute hydrochloric acid.

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## Part E Compound R

When piperidine is treated with one equivalent of iodomethane, compound **R** is formed.

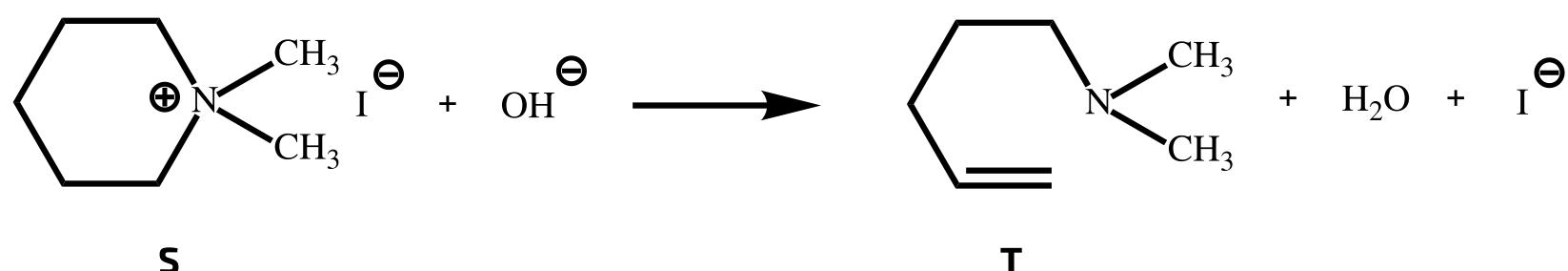


**Figure 2:** Compound **R**

Mechanistically, what type of reaction is occurring?

## Part F Compound T

Further reaction of **R** with more iodomethane gives compound **S**, which on heating with alcoholic potassium hydroxide, reacts to form compound **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 [structure editor](#) 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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