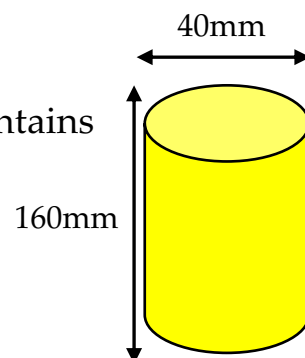


Questions

1. Devise a synthetic route from methane (CH_4) to ethane (CH_3CH_3). For each step, outline how the reaction proceeds, giving relevant mechanisms where possible. The yield and the number of steps used are not important.

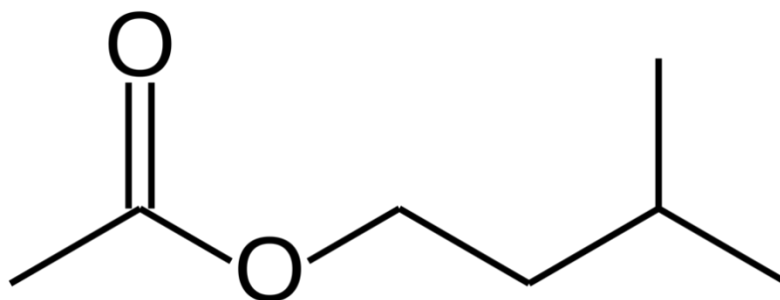
2. As part of my breakfast, I eat a 200g banana which contains 390mg of potassium.

Assume that the banana is cylindrically shaped and has dimensions of 160mm by 40mm, as shown in the diagram.



Giving answers to 1 significant figure and stating any other assumptions you make, calculate:

- a) How many potassium ions are contained within the banana?
- b) What is the concentration of potassium in the banana, expressed in units of ions cm^{-3} ?



The molecule shown above, isoamyl acetate, is largely responsible for giving bananas their characteristic scent and taste. It can be made artificially in an acid-catalysed esterification reaction, by reacting 3-methylbutan-1-ol with acetic (ethanoic acid).

- c) Provide a mechanism for this reaction.

Hints

Question 1

- 1) Alkanes are fairly unreactive molecules. Can you think of a way of converting methane to another family of organic molecules?
- 2) How can we extend the carbon chain?
- 3) A carboxylic acid can be converted to a primary alcohol using borane (BH_3).
- 4) Only 2 steps are required from ethanol to ethane.

Question 2

- a) Use Avogadro's constant (N_A) – $6.02 \times 10^{23} \text{ mol}^{-1}$.
- b) Use $\pi \approx 3.14$.
- c)
 - 1) The reaction is occurring under acidic conditions, what may be protonated?
 - 2) Start with the carbonyl oxygen becoming protonated.
 - 3) A lone pair of electrons on the oxygen of the alcohol acts a nucleophile and attacks the $\text{C}=\text{O}$ of the carboxylic acid.

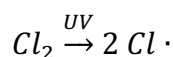
Suggested answers

Question 1

Creating a haloalkane

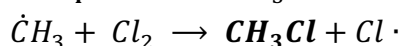
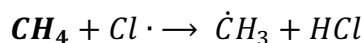
- CH₄ can be converted to CH₃Cl via a free-radical substitution reaction:
 - This mechanism consists of 3 steps – initiation, propagation (2) and termination.

- Initiation:



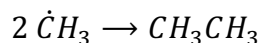
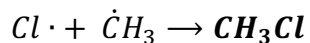
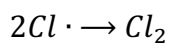
UV light causes homolytic bond fission of the Cl-Cl bond, forming 2 chlorine radicals.

- Propagation:



- Since the desired product, CH₃Cl, can undergo further substitution, it is important to have an extremely high concentration of CH₄ and a very low concentration of Cl₂ to favour the production of chloromethane.
 - A very high [CH₄] means that the likelihood of a Cl· colliding with a CH₄ is far higher than with a CH₃Cl, favouring the monosubstituted product.

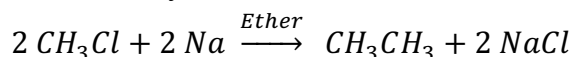
- Termination:



You may notice that this termination step actually results in the formation of our target molecule – ethane.

- Interestingly, if considerations about yield are not important, the required synthetic route can be achieved in one step.
- Having obtained CH₃Cl, there are multiple synthetic pathways which could be taken.
 - CH₃Cl can be directly converted into CH₃CH₃ using the Wurtz reaction:

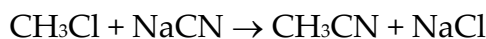
It's *highly* unlikely that you will have encountered this reaction. I have just included it for completeness.



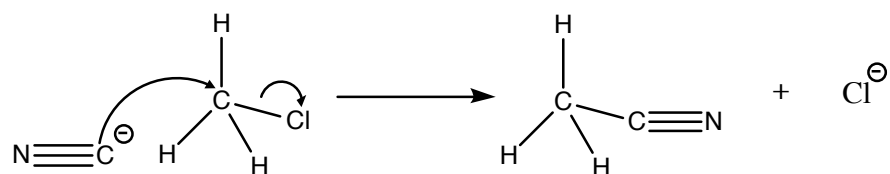
Creating a nitrile

- Having obtained chloromethane, the molecule can be heated under reflux with a solution of sodium cyanide (NaCN) in ethanol to produce acetonitrile (CH₃CN).

- Overall equation:



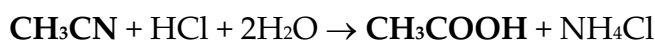
- Mechanism:



- The reaction proceeds through a nucleophilic substitution (S_N2).
 - Note – there are two main types of nucleophilic substitution: S_N1 and S_N2; the number refers to how many species are in the rate determining step.

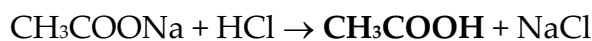
Acidic/Alkaline hydrolysis of acetonitrile (CH₃CN) to ethanoic acid:

Acidic



- Acetonitrile can be converted into ethanoic acid (CH₃COOH) when it is heated under reflux with dilute aqueous acid.

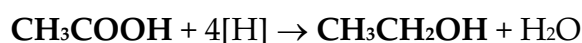
Alkaline



- Acetonitrile can also be converted into ethanoic acid by heating under reflux with NaOH before a separate protonation stage involving a strong acid.

Reducing a carboxylic acid to an alcohol

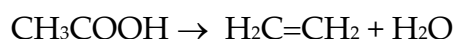
- A powerful reducing agent is required to carry out the reduction of ethanoic acid to ethanol.
 - Lithium aluminium hydride (LiAlH₄) can be used.
 - Sodium borohydride (NaBH₄) is not strong enough and so is unsuitable.
 - Borane (BH₃) is another reagent that can be used to reduce carboxylic acids.
- Overall equation using LiAlH₄:



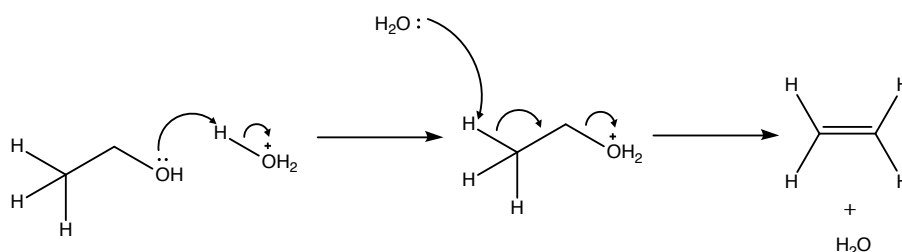
The [H] represents a hydrogen from the reducing agent and is used to simplify the equation.

Dehydrating the alcohol to an alkene

- Ethanol can be heated with a strong acid (H₃PO₄ or H₂SO₄) to form ethene in an elimination (E2) reaction.
 - Overall equation:

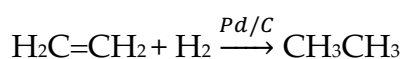


- Mechanism:

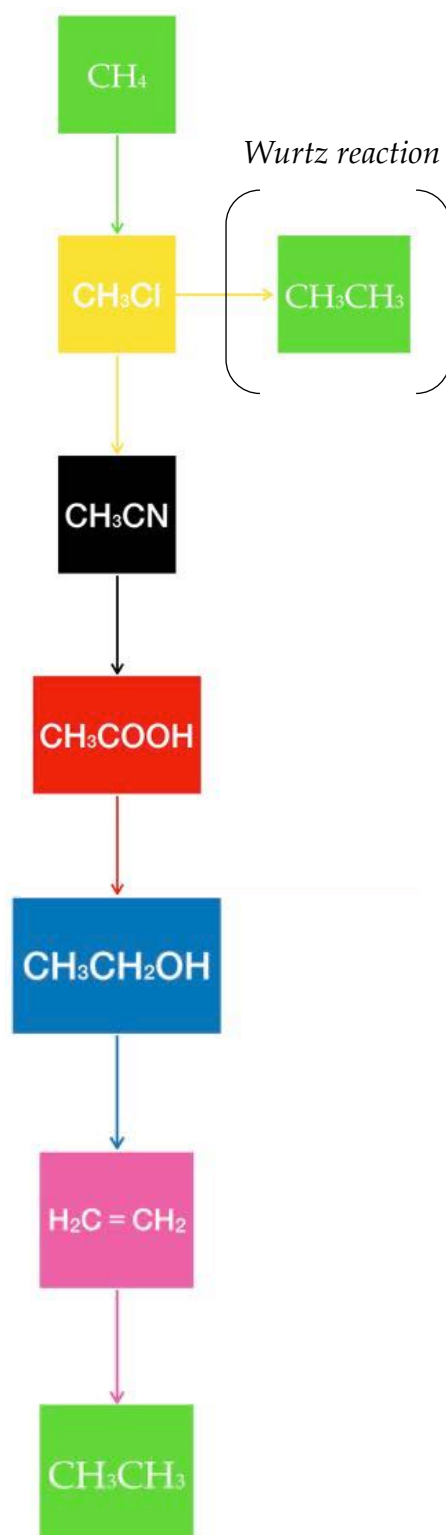


Reduction of an alkene to an alkane

- Ethene undergoes an addition reaction with H₂ to form ethane.
 - The reaction requires the presence of a metal catalyst such as:
 - Palladium on charcoal (Pd/C)
 - Raney nickel (Ni)
 - Overall equation:



Overall process



Question 2

a)

- There are 390mg of potassium within the banana and so there must be 0.39g of K^+ ions.

Therefore, the total number of moles of potassium ions within the banana:

$$\text{Number of moles} = \frac{\text{Mass}}{\text{Mass of 1 mole}}$$

$$n = \frac{0.39}{39.1} \approx \frac{1}{100} = 0.01 \text{ mol}$$

To find the number of potassium ions, multiply the number of moles by Avogadro's constant (N_A), which is equal to $6.02 \times 10^{23} \text{ mol}^{-1}$:

$$\text{Number of potassium ions} = 0.01 \times 6.02 \times 10^{23}$$

$$= 1 \times 10^{-2} \times 6.02 \times 10^{23} = 6.02 \times 10^{21}$$

- Therefore, the banana contains 6.02×10^{21} potassium ions.

b)

- The question asks for the concentration of potassium ions per cm^3 , and so we need to calculate the volume of the banana in cm^3 .
 - The banana has a length of 16cm and a width of 4cm.

Using the fact that the volume of a cylinder, V , is given by:

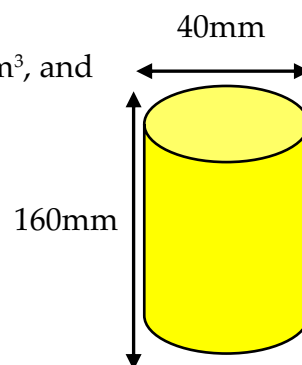
$$V = \pi r^2 h$$

The volume of the banana is equal to:

$$V = \pi \times 2^2 \times 16 = 64\pi \approx 200.96 \approx 200\text{cm}^3$$

Use column multiplication to obtain this result if you cannot do it in your head.

This assumes π is equal to 3.14.



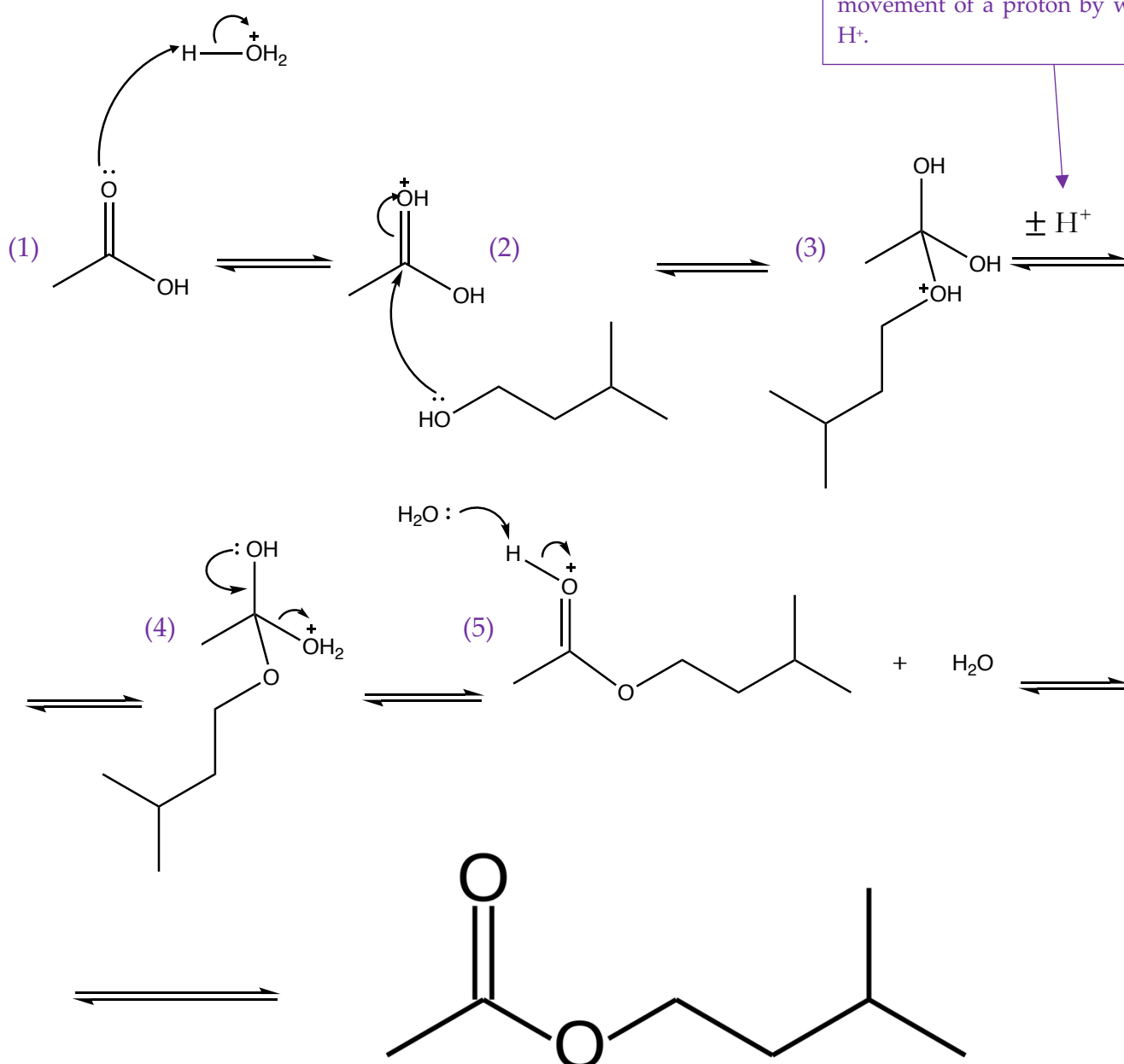
To calculate the concentration of potassium ions within the banana in units of ions cm^{-3} , we need to find the number of K^+ ions within 1cm^3 of banana:

$$\frac{6.02 \times 10^{21}}{200} \approx \frac{6 \times 10^{21}}{2 \times 10^2} = 3 \times 10^{19} \text{ ions cm}^{-3}$$

- Therefore, the concentration of potassium is 3×10^{19} ions cm^{-3} .

c) The mechanism is that of an esterification reaction:

The proton transfer could be intermolecular or intramolecular, and so you can represent the movement of a proton by writing $\pm \text{H}^+$.



- (1) Since the process is being carried out under acidic conditions – sulfuric acid is commonly used as a catalyst – the carbonyl oxygen becomes protonated. This protonation draws electron density away from the C=O bond, towards the oxygen, making the carbon more electron deficient. This makes the C=O group more reactive, as the carbon is a better electrophile.
- (2) The nucleophile, a lone pair of electrons on the oxygen of the alcohol group, now attacks the more reactive carbonyl.
- (3) A proton is transferred to one of the hydroxyl groups, making it a better leaving group; H₂O is more stable than an OH⁻ ion.
- (4) A lone pair of electrons from the carbonyl oxygen reforms the C = O and pushes out the H₂O group, forming water.
- (5) The carbonyl oxygen becomes deprotonated, reforming the acid catalyst.