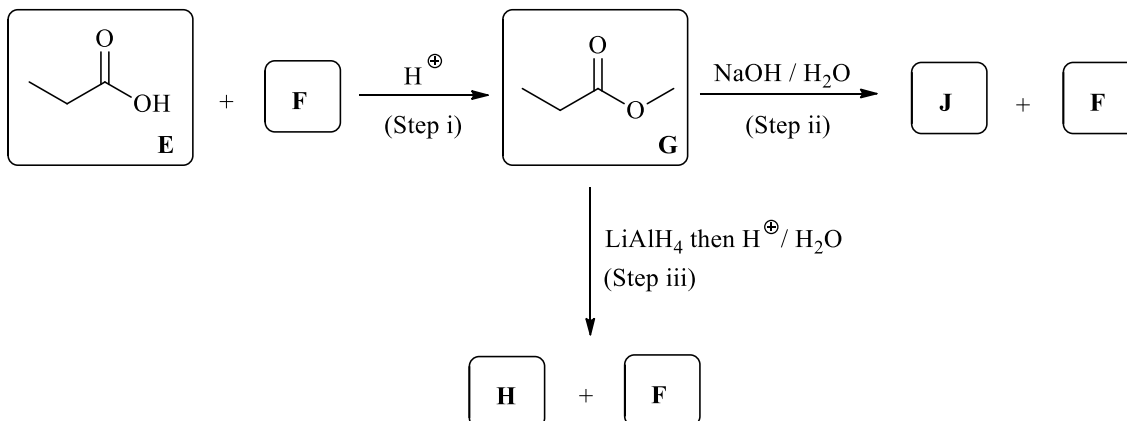
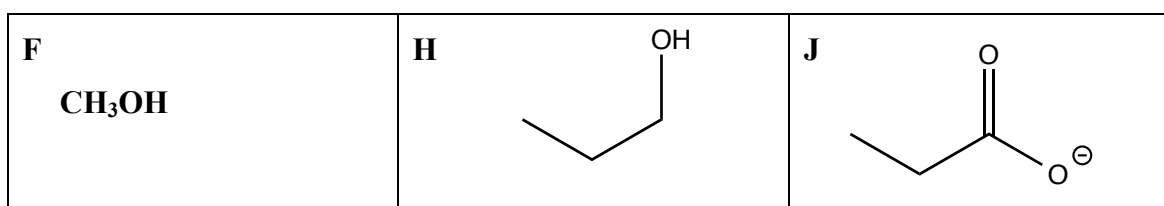
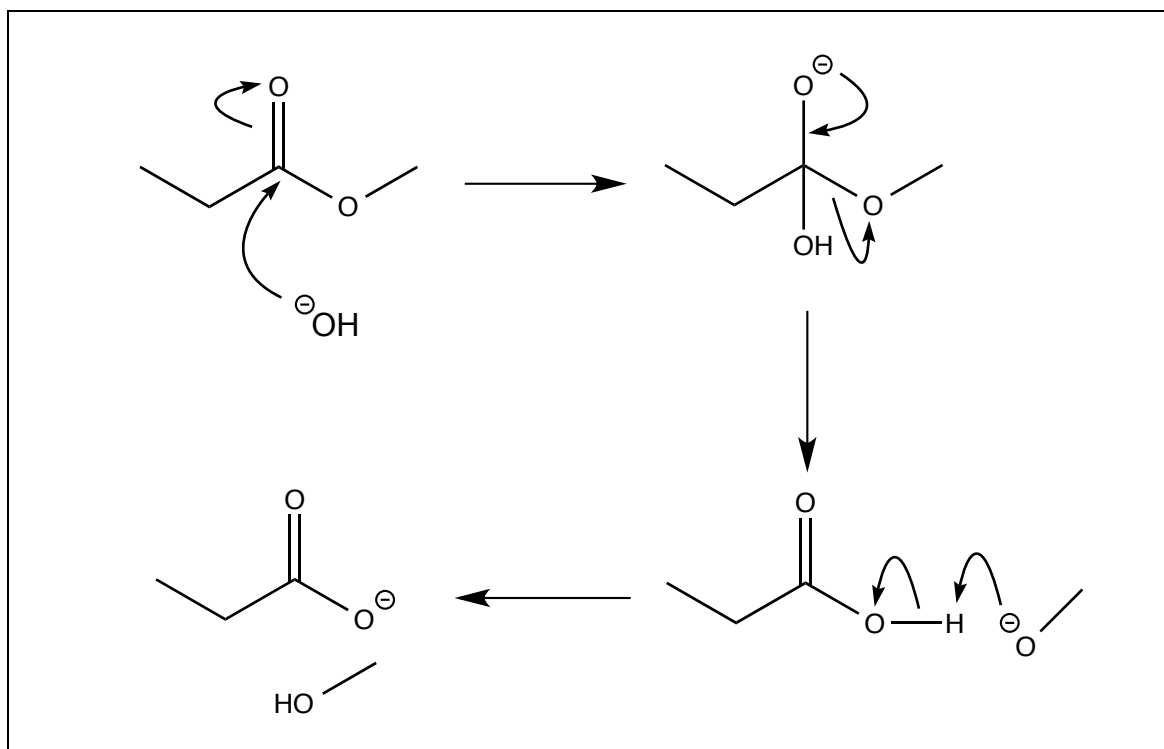


Marks
6

- Consider the following reaction sequences beginning with the carboxylic acid, **E**.

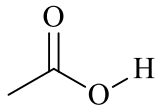
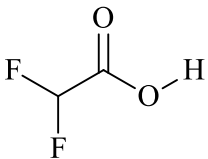
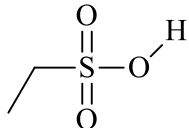
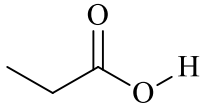
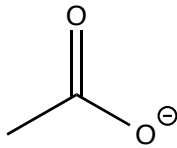
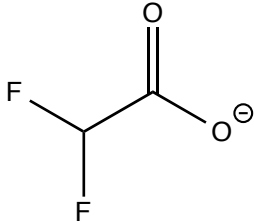
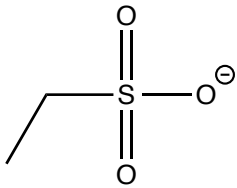
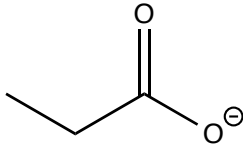
Name compounds **E** and **G**.**E: propionic acid****G: methyl propionate**Propose structures for compounds **F**, **H** and **J**.

Propose a mechanism for step (ii).



Marks
5

- Draw the conjugate bases for the following acids.

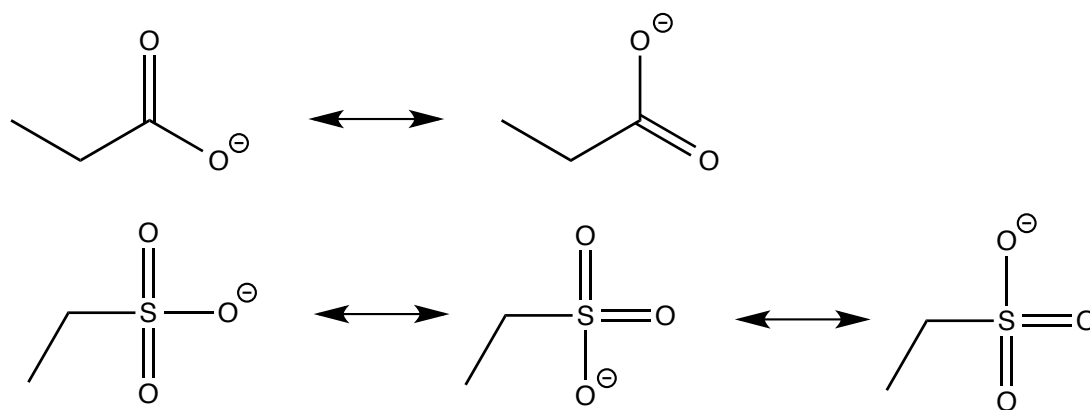
S	T	U	V
			
Conjugate base of S	Conjugate base of T	Conjugate base of U	Conjugate base of V
			

Which of **S** and **T** is the stronger acid? Give a reason for your answer.

T will be a stronger acid. In acting as an acid, the conjugate base will be formed. The conjugate base of T is more stable than that of S as the electronegative fluorine atoms will withdraw electron density from the negatively charged O atom.

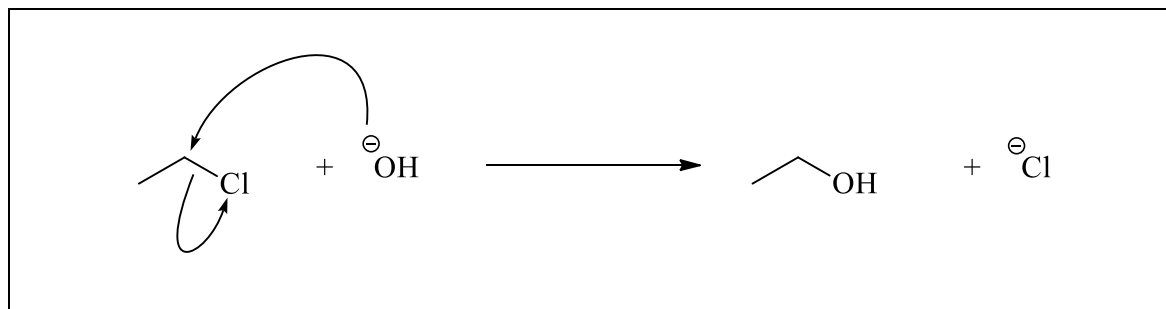
Which of **U** and **V** is the stronger acid? Give a reason for your answer.

U is a stronger acid than V because the conjugate base is more stable. Both are stabilised by resonance which acts to delocalise the negative charge over the electronegative O atoms present:



For the conjugate base of U, the negative charge is delocalised over 3 O atoms. For the conjugate base of V, the negative charge is only delocalised over 2 O atoms

- The hydroxide anion can react with chloroethane via a mechanism that is abbreviated S_N2 , as shown below. Add curly arrows to the reaction scheme to complete a mechanism for this reaction.



Explain what each part of the abbreviation S_N2 means.

S = **substitution**

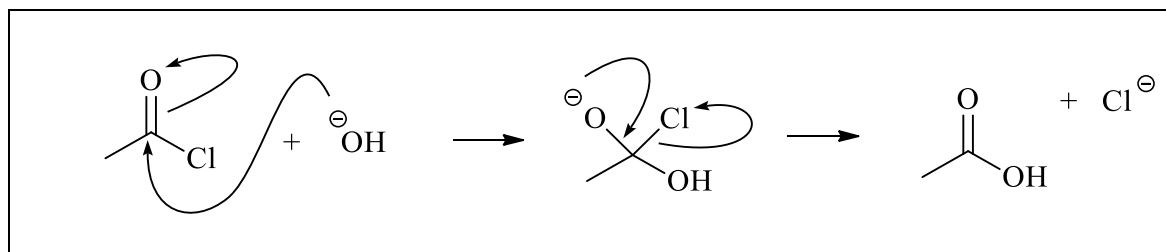
N = **nucleophilic**

2 = **bimolecular**

The hydroxide anion undergoes an apparently similar reaction with ethanoyl chloride:



Draw a mechanism (using curly arrows) for this reaction, thereby demonstrating how it is fundamentally different to the reaction of chloroethane above.



In each of these reactions, a full molecular orbital of the hydroxide anion (the HOMO) interacts with an empty molecular orbital of the organic halogen compound (the LUMO).

Which orbital is the LUMO in chloroethane?

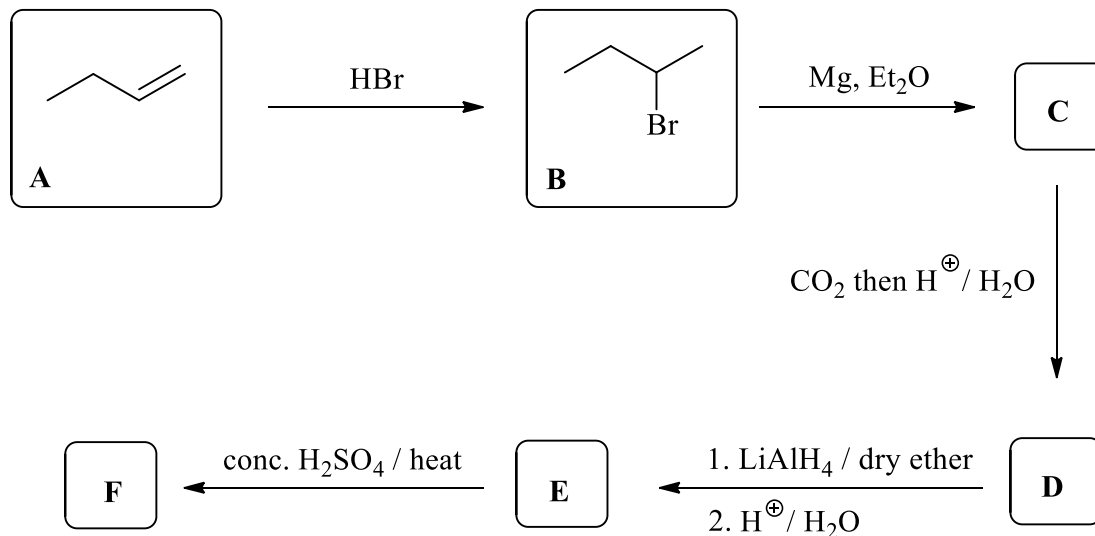
σ^*_{C-Cl}

Which orbital is the LUMO in ethanoyl chloride?

$\pi^*_{C=O}$

Marks
6

- Consider the following reaction sequence beginning with the alkene **A**.



Suggest structures for compounds **C** – **F** in the reaction sequence above.

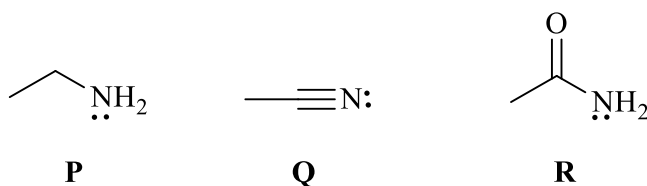
C 	D
E 	F

Describe the selectivity observed, and briefly explain the reasons for it, in the conversion of alkene **A** to compound **B**.

Markovnikov's rule: the H^+ of HBr adds to C1 leading to a secondary carbocation rather than to C2 which leads to a primary carbocation. The more substituted carbocation is more stable due to hyperconjugation.

- Consider the three nitrogen-containing compounds **P**, **Q** and **R**.

**Mark
s**
5



What is the hybridisation at *N* in compound **P**?

sp^3

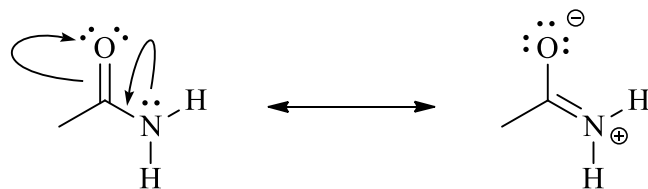
What is the hybridisation at *N* in compound **Q**?

sp

Use this information to decide which of **P** or **Q** is more basic. Explain your reasoning.

P is more basic. The sp^3 hybridised N has more *p* orbital character (75%) compared to sp (50%). P therefore has a more diffuse lone pair that is more available for protonation. Conversely, the lone pair in Q is more tightly bound and Q is therefore a weaker base.

Show curly arrows and another structure to show how compound **R** is stabilised by resonance.



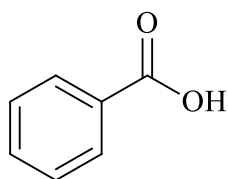
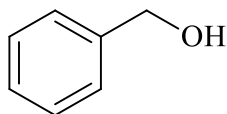
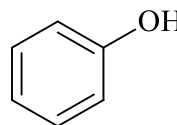
Which is more basic, compound **P** or compound **R**? Why?

P is more basic.

The 'lone pair' in R contributes to the resonance structure and is partially delocalised into the carbonyl group and is therefore unavailable for protonation.

- Benzoic acid **H**, benzyl alcohol **I** and phenol **J** are shown below. The pK_a values of these three compounds are 15.2, 9.9 and 4.2, but not in that order.

**Mark
s**
6

**H****I****J**

Assign the correct pK_a to each of these three compounds.

pK_a values:

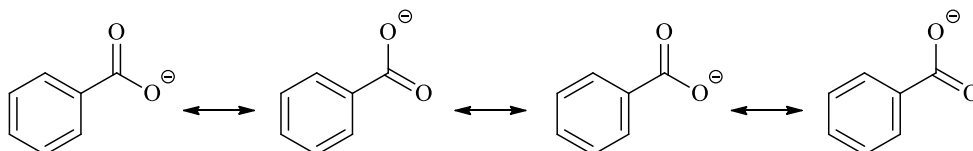
H = 4.2

I = 15.2

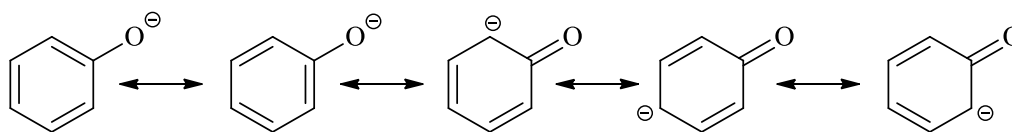
J = 9.9

Draw resonance structures to explain your answer.

The conjugate base of H is stabilised by delocalisation of the negative charge over two electronegative O atoms and over the ring:



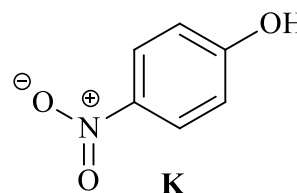
The conjugate base of J is stabilised by delocalisation of the negative charge over an O atom and the ring:



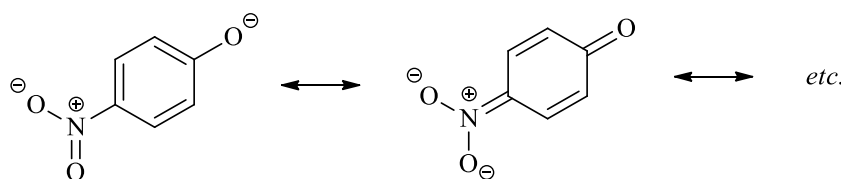
As the delocalisation places negative charge over C as well as O, the stabilisation is smaller than for H.

By resonance stabilisation is possible for the conjugate base of I.

Would you expect 4-nitrophenol, **K**, to be more or less acidic than phenol, **J**? Explain your answer.

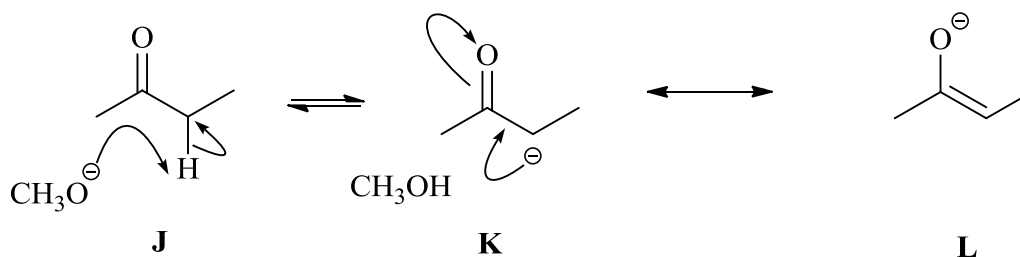


K will be more acidic than J as the negative charge of the phenoxide ion can be delocalised into the nitro group, increasing the resonance stabilisation.



Marks
6

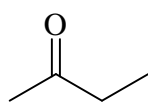
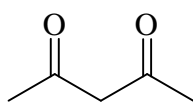
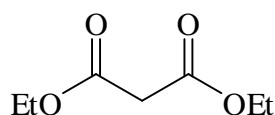
- Protons next to a carbonyl group can be removed by alkoxide bases as shown below.



Apply your understanding of resonance to propose a structure **L** that explains how the carbonyl group increases the acidity of these hydrogens.

Add curly arrows to the reaction scheme above to complete a mechanism for the deprotonation of **J** to give **K**, and the stabilisation of **K** by resonance.

The $\text{p}K_{\text{a}}$ values of compounds **J**, **M** and **N** are 9, 13 and 19, but not in that order. Match each compound with the correct $\text{p}K_{\text{a}}$, and explain your answer.

**J****M****N**
 $\text{p}K_{\text{a}}$ values:
J = 19**M = 9****N = 13**

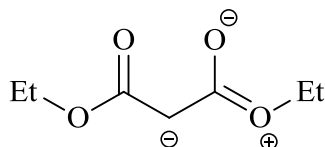
Reasoning for above assignments

M and N are stronger acids than J as the charge on the carbanion can be delocalised onto 2 carbonyl groups rather than 1 (i.e. there are more resonance structures).

Enolate anions are stabilised by electron withdrawing groups which help reduce the negative charge on the carbon atom.

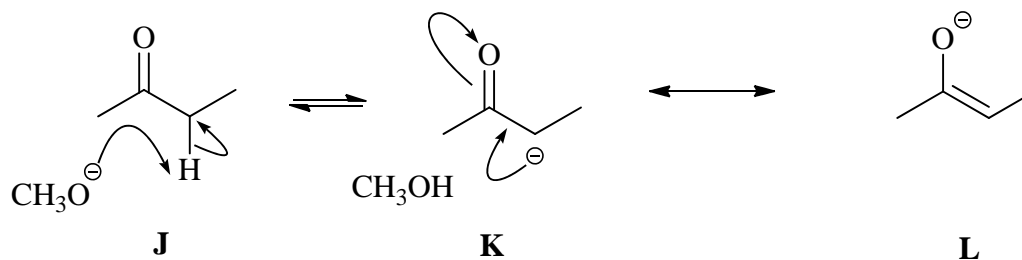
N is a weaker acid than M because the OEt group of the ester donates electron density towards the enolate anion, thus destabilising it.

Also the following resonance form of the ester would mean that the carbonyl group is less available to share the negative charge of the enolate anion.



Marks
6

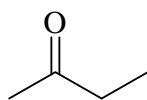
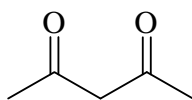
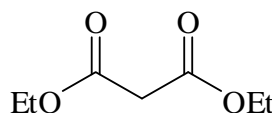
- Protons next to a carbonyl group can be removed by alkoxide bases as shown below.



Apply your understanding of resonance to propose a structure **L** that explains how the carbonyl group increases the acidity of these hydrogens.

Add curly arrows to the reaction scheme above to complete a mechanism for the deprotonation of **J** to give **K**, and the stabilisation of **K** by resonance.

The $\text{p}K_{\text{a}}$ values of compounds **J**, **M** and **N** are 9, 13 and 19, but not in that order. Match each compound with the correct $\text{p}K_{\text{a}}$, and explain your answer.

**J****M****N**

$\text{p}K_{\text{a}}$ values:

J = 19

M = 9

N = 13

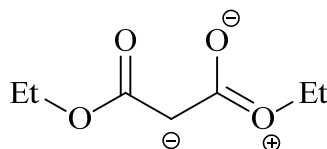
Reasoning for above assignments

M and **N** are stronger acids than **J** as the charge on the carbanion can be delocalised onto 2 carbonyl groups rather than 1 (*i.e.* there are more resonance structures).

Enolate anions are stabilised by electron withdrawing groups which help reduce the negative charge on the carbon atom.

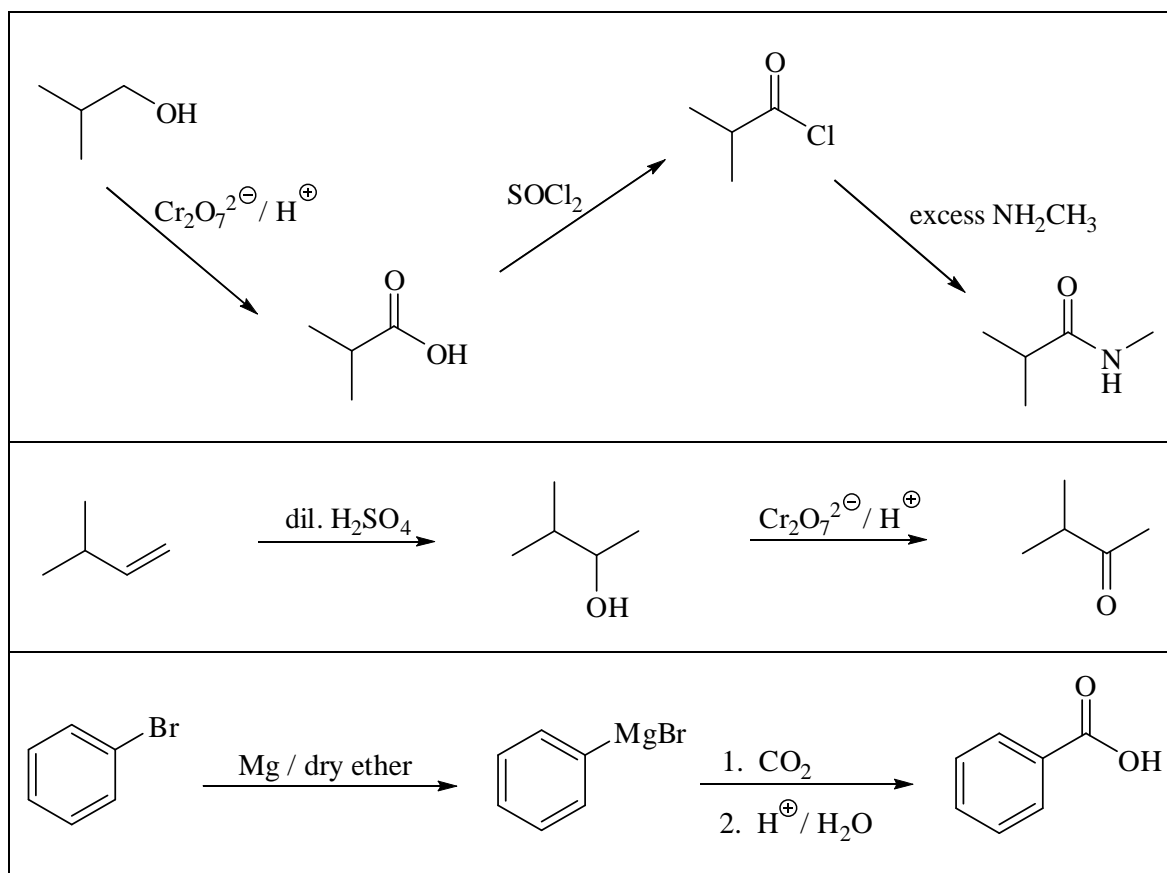
N is a weaker acid than **M** because the OEt group of the ester donates electron density towards the enolate anion, thus destabilising it.

Also the following resonance form of the ester would mean that the carbonyl group is less available to share the negative charge of the enolate anion.

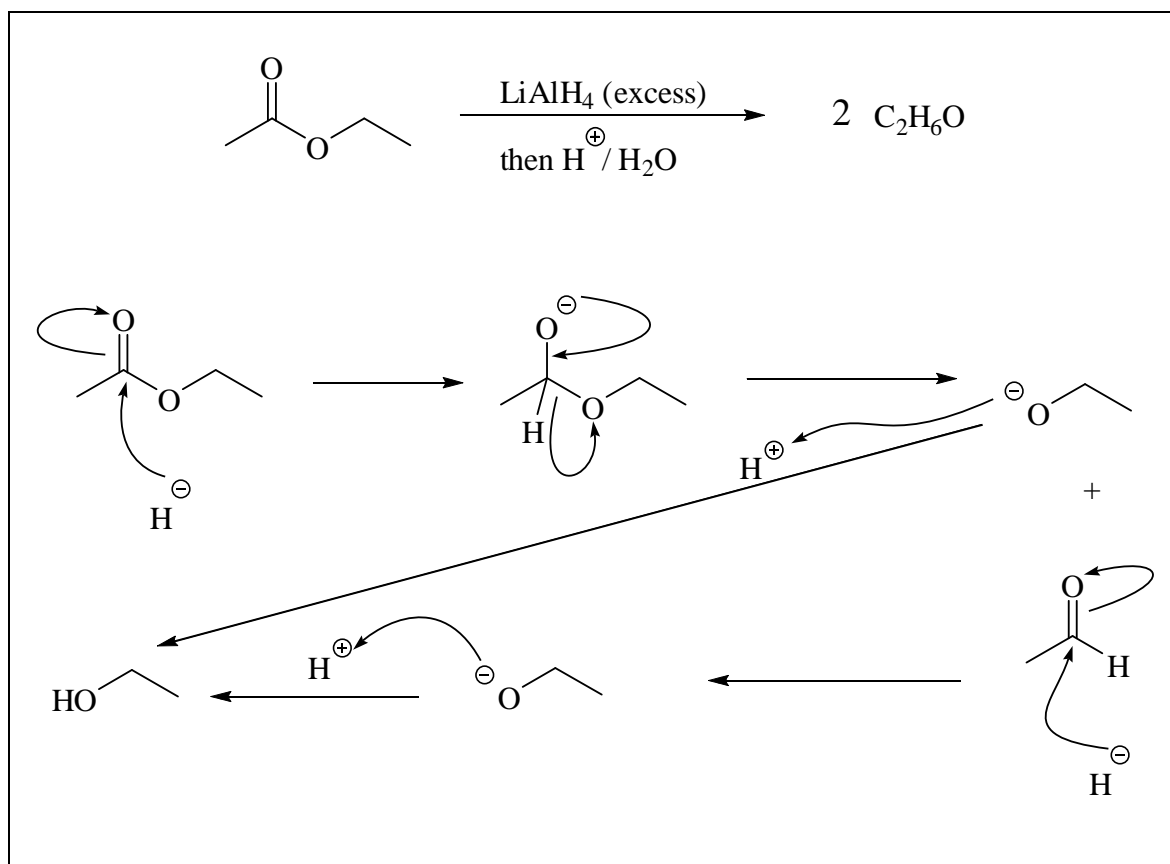


Marks
6

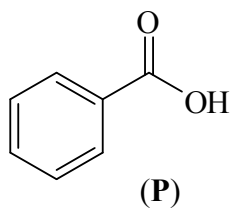
- Suggest reagents to accomplish the following transformations. More than one step is required in all cases.



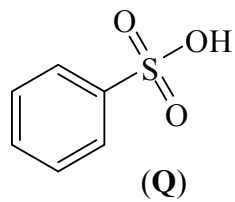
- Propose a structure for the product of the following reaction. Outline a mechanism for its formation. Show all curly arrows and any intermediates.

Marks
4

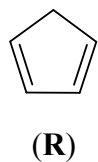
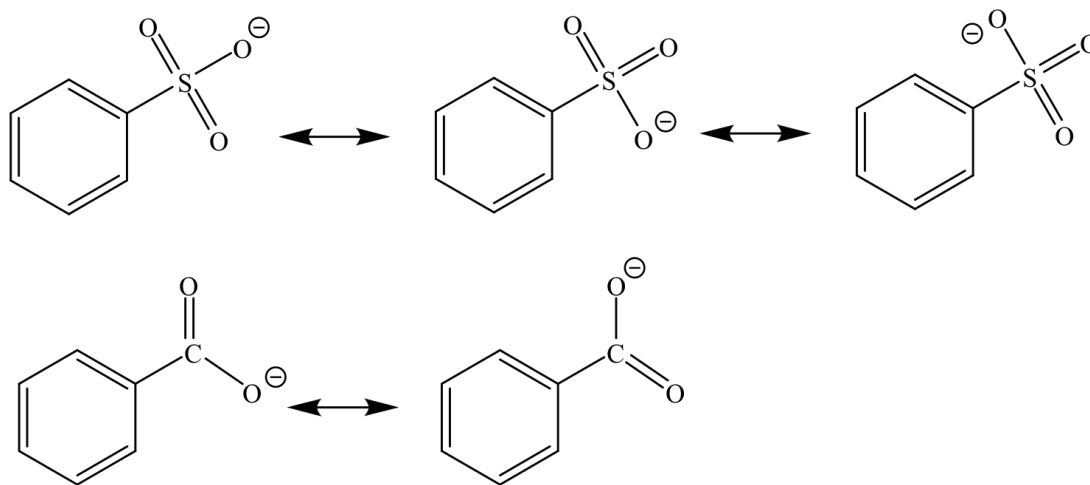
- For each of the following pairs of compounds, identify which is the stronger acid and give reasons for your choice.

Marks
3

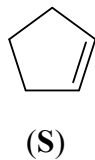
and



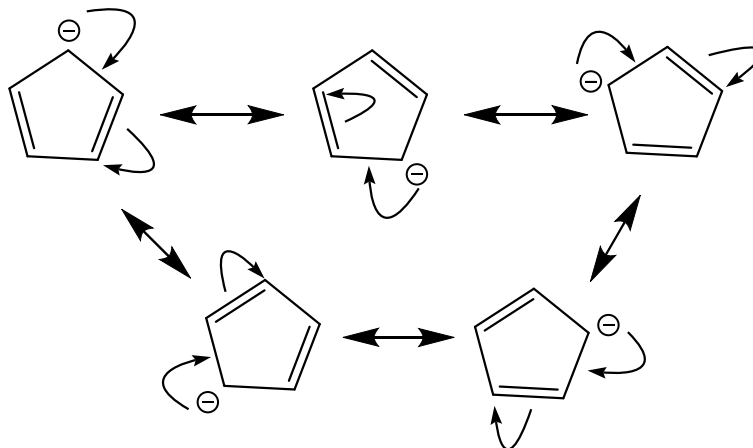
(Q) There is greater resonance stabilisation of the conjugate base (more canonical forms):



and



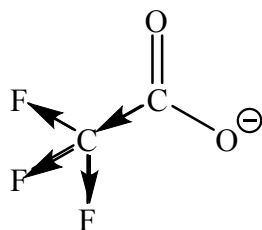
(R) There is greater resonance stabilisation of the conjugate base because it is aromatic.



ANSWER CONTINUES ON THE NEXT PAGE

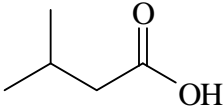
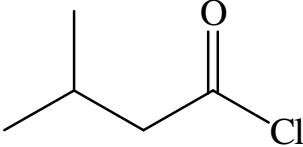
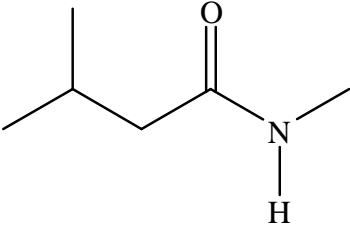
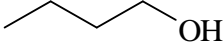
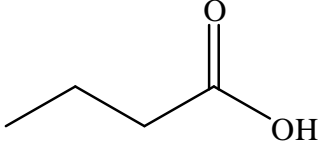
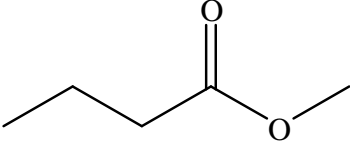
$\text{CF}_3\text{CO}_2\text{H}$ and $\text{CH}_3\text{CO}_2\text{H}$
(T) (U)

(T) There is greater resonance stabilisation of the conjugate base due to the inductive electron withdrawal of the very electronegative F atoms.



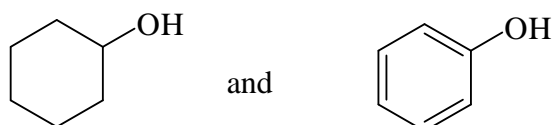
Marks
4

- Complete the following table by drawing the structures of the intermediate and final organic product(s) as required. The intermediate product is formed when the starting material is treated with Reagent 1. The final product is formed when the intermediate product is treated with Reagent 2.

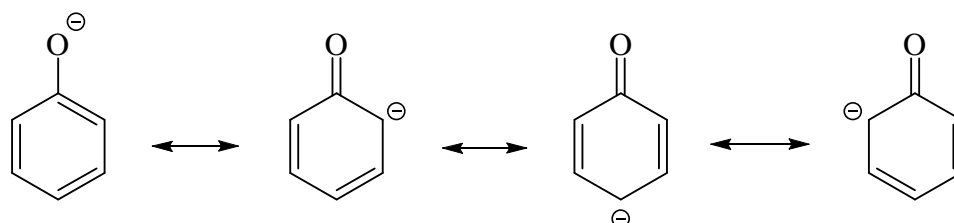
Starting material	Intermediate product	Final product
	Reagent 1: SOCl_2 	Reagent 2: CH_3NH_2  + $\text{CH}_3\text{NH}_2^+ \text{Cl}^-$
	Reagent 1: $\text{K}_2\text{Cr}_2\text{O}_7 / \text{H}^+$ 	Reagent 2: $\text{CH}_3\text{OH} / \text{H}^+$ 

Marks
4

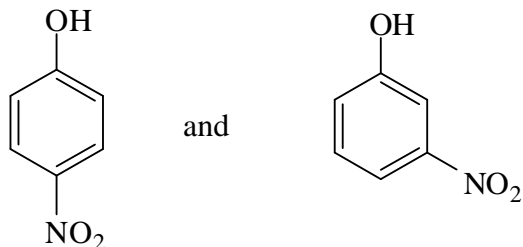
- For each of the following pairs of compounds, identify which is the stronger acid and give reasons for your choice.



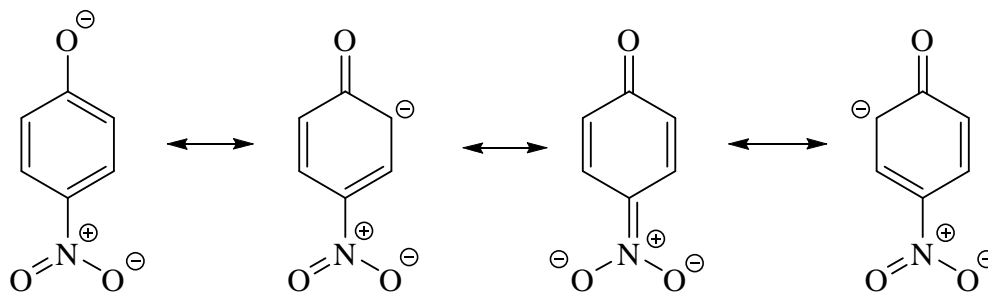
Phenol is more acidic as the phenoxide ion is resonance stabilised:



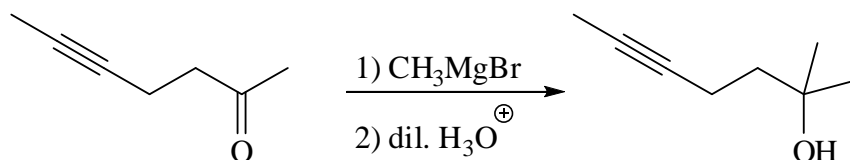
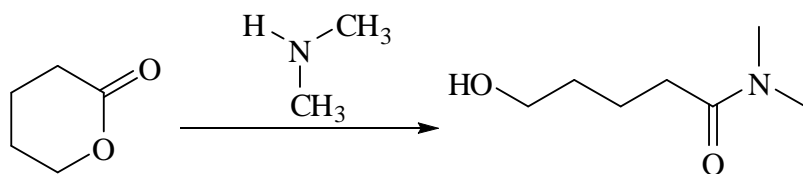
Chloroacetic acid is more acidic. The Cl atom is electronegative and pulls electrons from the carboxylic acid, thus weakening the O-H bond.



The *para* isomer is more acidic as the charge on the phenoxide ion can be delocalised into the nitro group. This is not possible with the *meta* isomer.

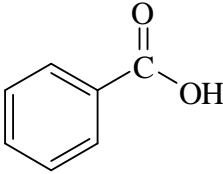
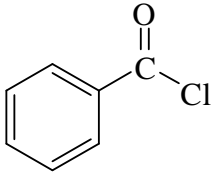
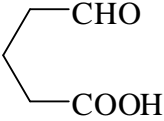
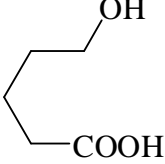
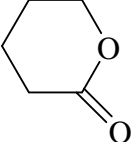


- Draw the structure(s) of the major organic product(s) formed in each of the following reactions. Give the names of the products where requested.

Marks
3**Name(s): 2-methylhept-5-yn-2-ol****THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.**

Marks
3

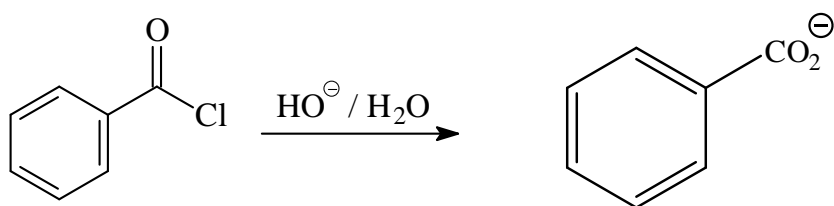
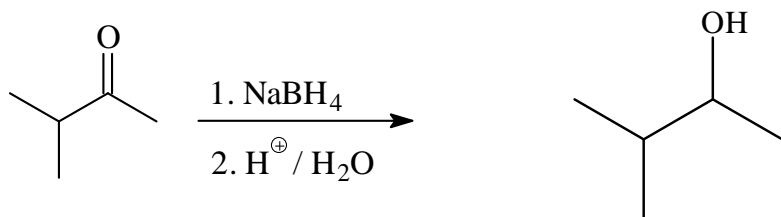
- Complete the following table.

Starting material	Reagents / Conditions	Major organic product(s)
	SOCl_2	
	1. NaBH_4 2. $\text{H}^+ / \text{H}_2\text{O}$	 or 

THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.

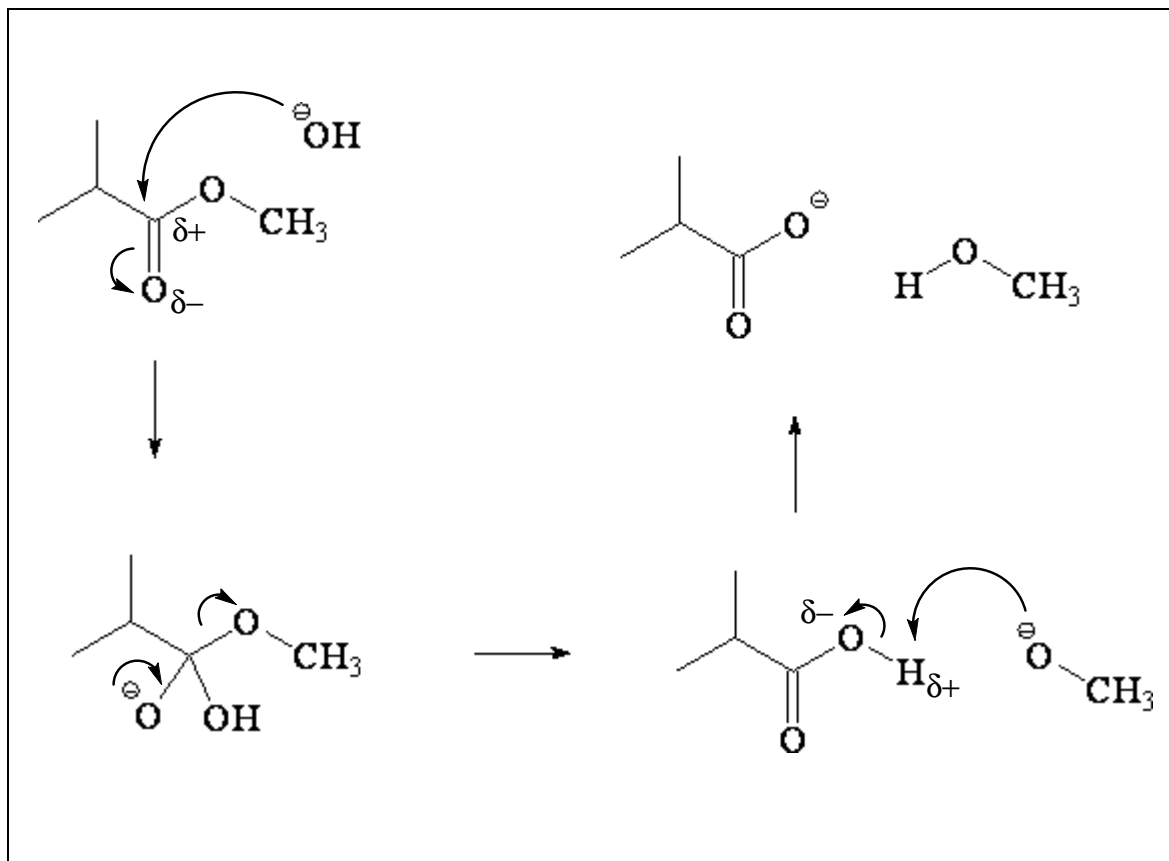
Marks
2

- Draw the structure(s) of the major organic product(s) formed in each of the following reactions. Give the names of the products where requested.



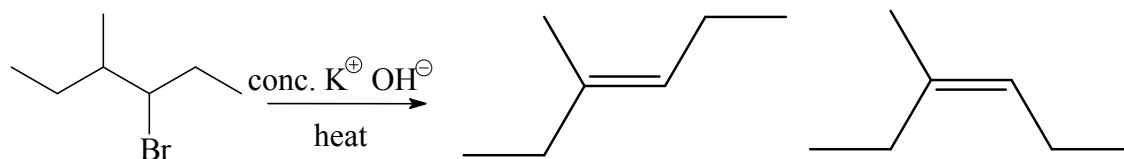
Marks
3

- Complete the mechanism for the reaction given below. Draw partial charges and curly arrows as appropriate to illustrate the bonding changes that take place.

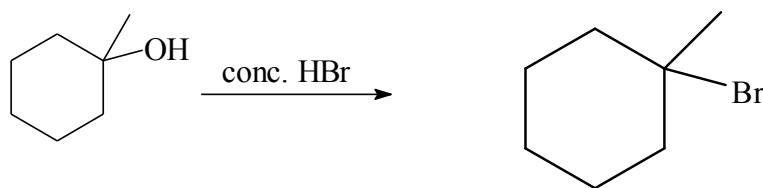
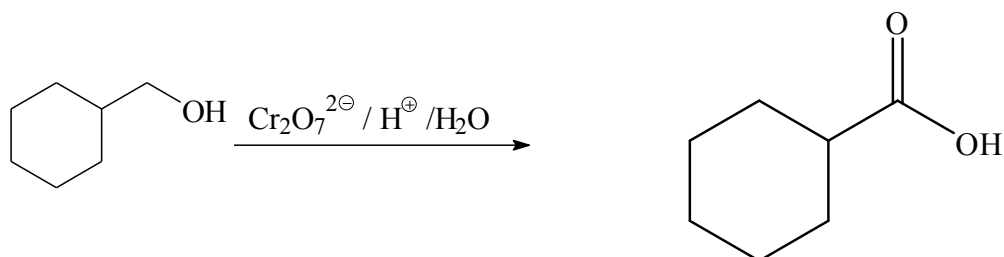


**Marks
5**

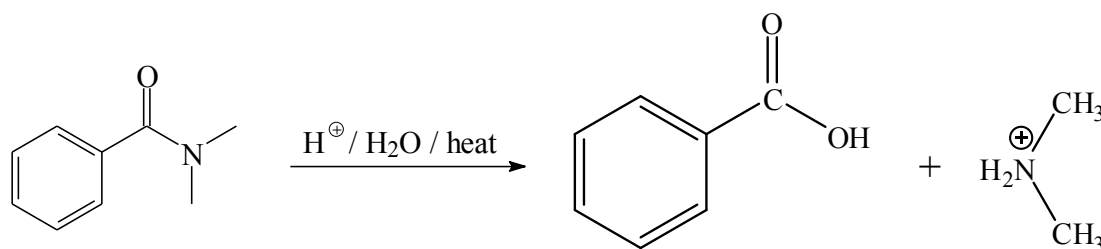
- Draw the structure(s) of the major organic product(s) formed in each of the following reactions. Give the names of the products where requested.



Name(s): (E)-3-methylhex-3-ene (Z)-3-methylhex-3-ene

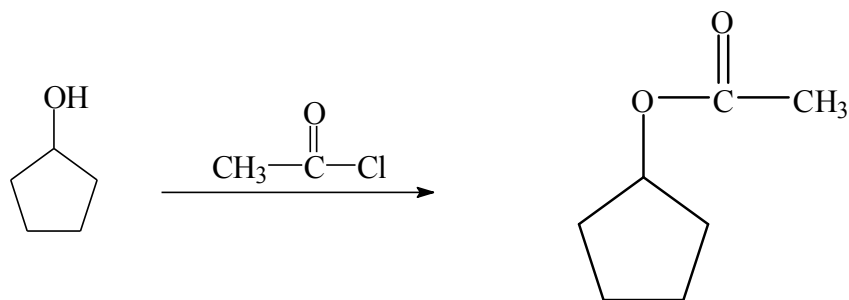


Name(s): 1-bromo-1-methylcyclohexane



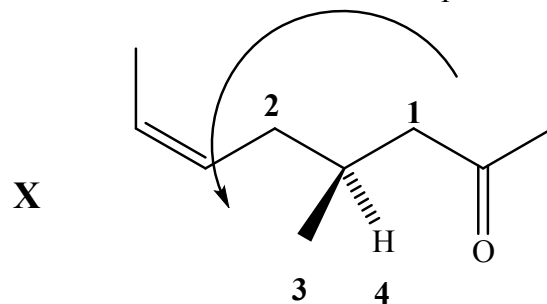
Marks
2

- Draw the constitutional formula(s) of the major organic product(s) formed in each of the following reactions.



Marks
6

- Compound **X** was isolated as a derivative of a natural product.



Carbon 4 of X is a stereogenic centre. List the substituents attached to C4 in descending order of priority according to the sequence rules.

highest priority

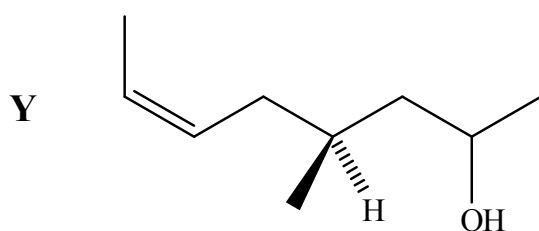
lowest priority

-CH₂COCH₃	CH₂CH=CHCH₃	-CH₃	-H
--	--	------------------------	-----------

What is the systematic name for compound **X**? Make sure you include all relevant stereochemical descriptors.

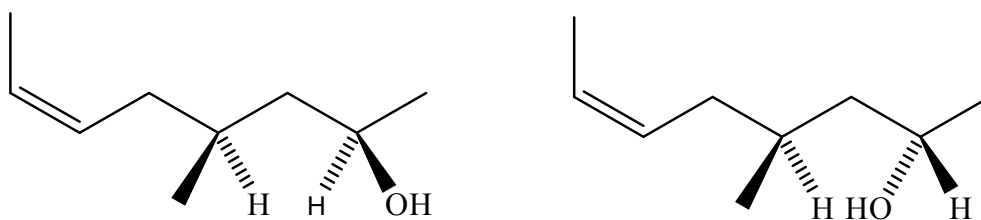
(4*S*,6*Z*)-4-methyloct-6-en-2-one. As shown above, the stereochemistry about carbon 4 is (*S*) (anticlockwise). The C=C bond has the two higher priority groups (-CH₃ and -CH₂CH(CH₃)CH₂COCH₃) on the same side so it has a (*Z*) configuration.

Reduction of **X** with sodium borohydride (NaBH₄) followed by quenching the reaction with dilute acid gives **Y**. Give the constitutional formula for **Y**.

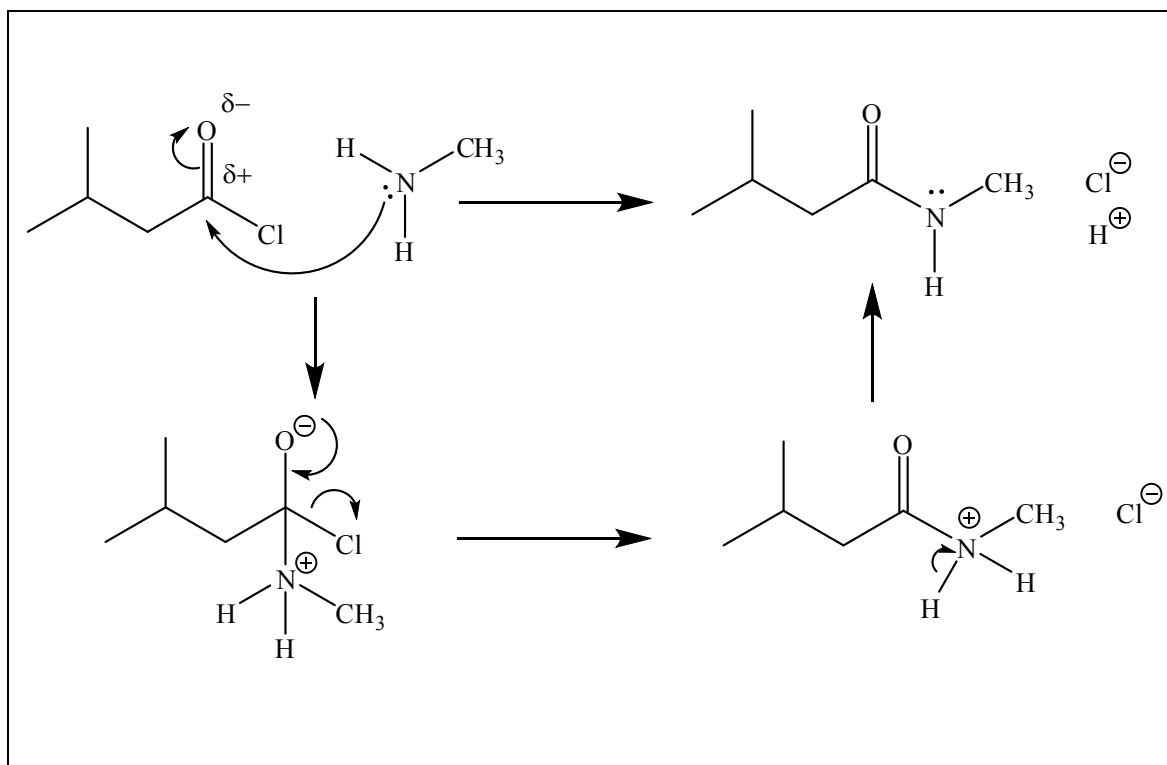


Product **Y** can be separated into two isomers. Explain.

The reduction introduces a second stereogenic centre into the molecule. The two products are diastereoisomers (not enantiomers) and hence have different chemical and physical properties and can be separated.

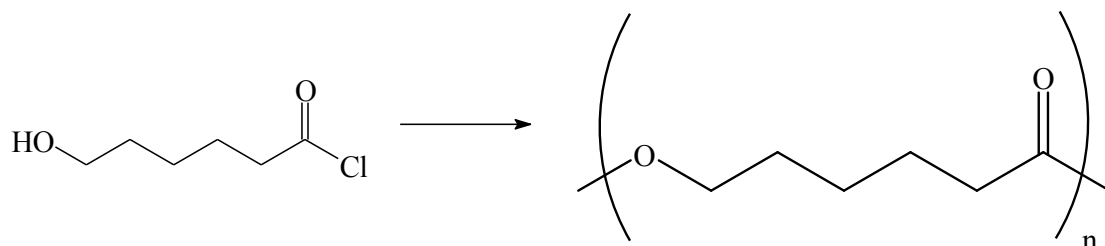
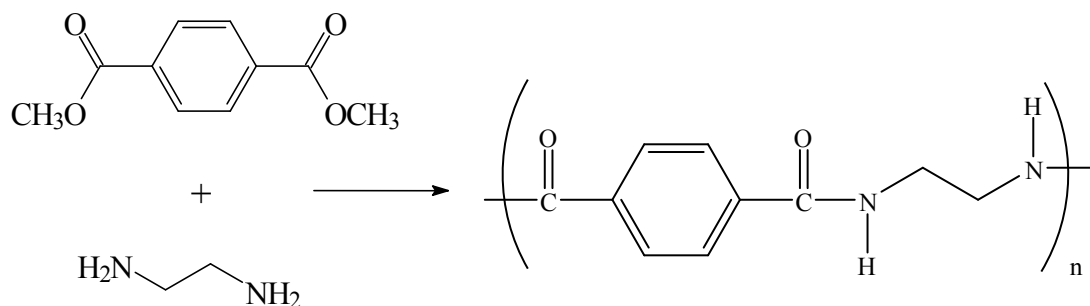


- Complete the three step mechanism for the reaction given below. Draw intermediate structures, curly arrows and partial charges as appropriate to illustrate the bonding changes that take place.



Marks
2

- Draw the repeating unit of the polymer formed in the following reactions.

**4**

- Show clearly the reagents you would use to carry out the following chemical conversion. Draw constitutional formulas for any intermediate compounds. NOTE: More than one step is necessary.

