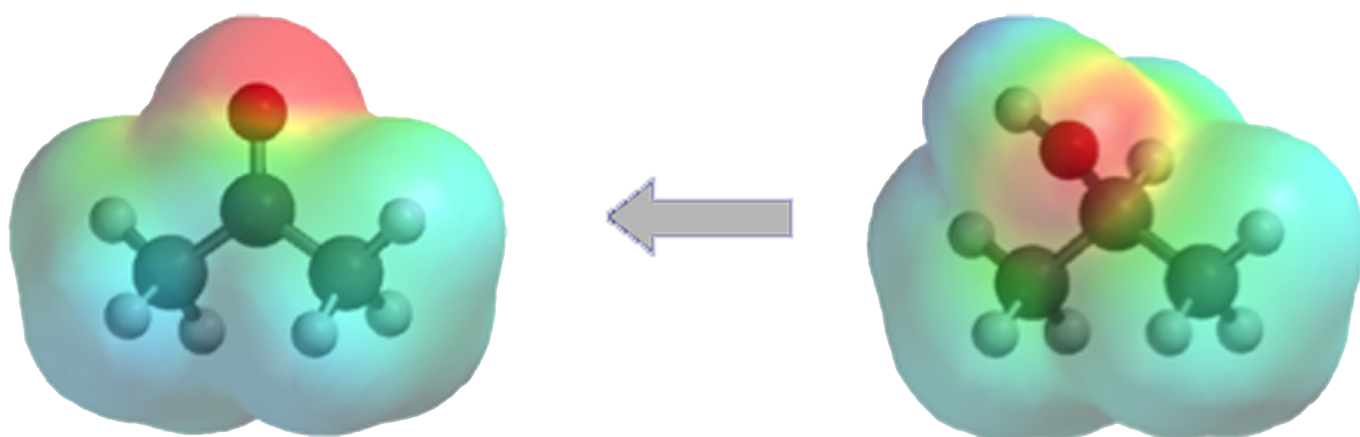


3.2

Organic Synthesis (Reaction Pathways)



Pupil Notes
Learning Outcomes
Questions
& Answers

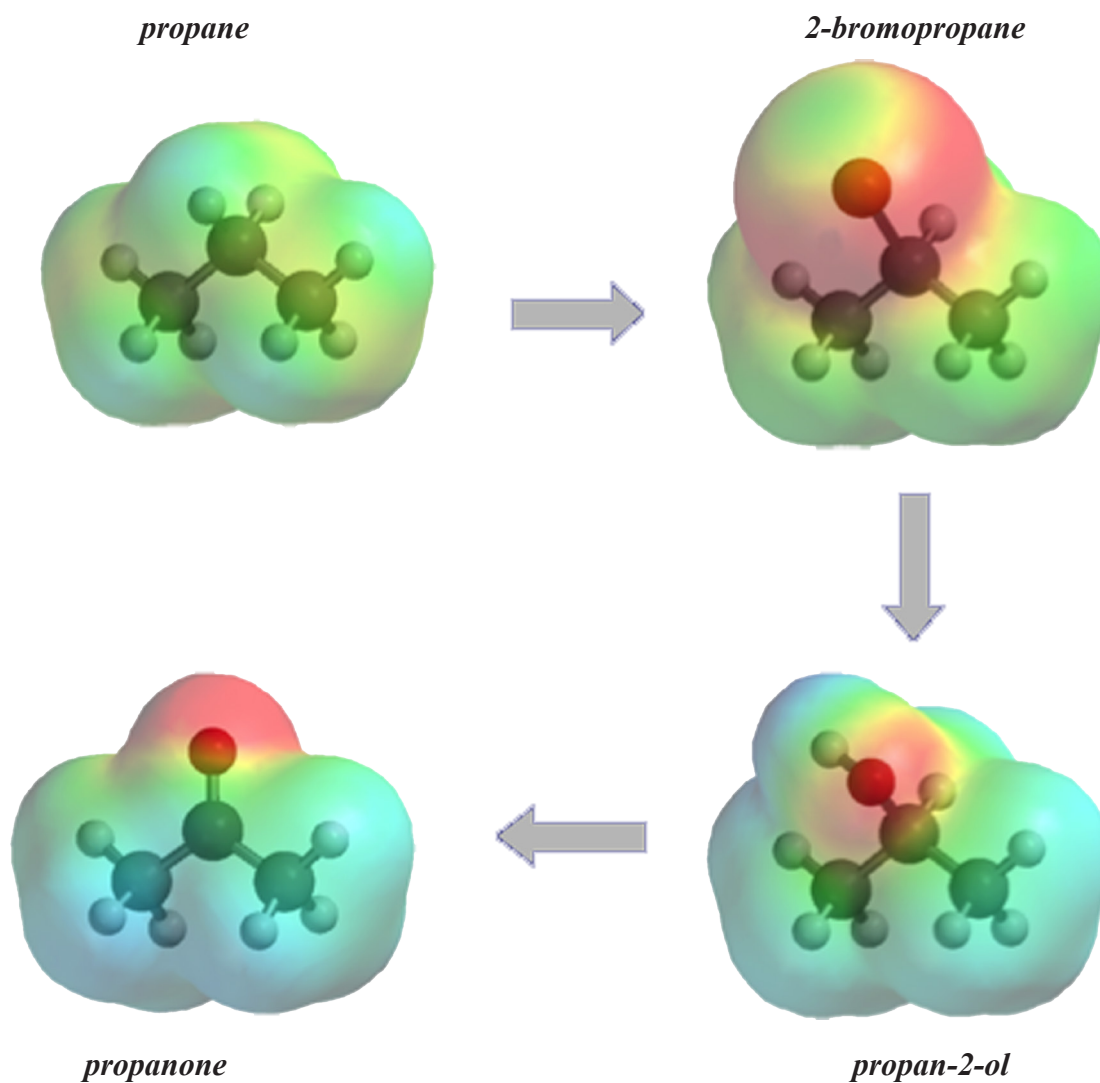
An Introduction to Organic Synthesis

- Organic synthesis creates molecules by design
- Synthesis can produce new molecules that are needed as drugs or materials
- Different syntheses for established chemicals can be designed and tested to improve efficiency
- Highly advanced synthesis is used to test new ideas and methods

In order to propose a synthesis you must be familiar with (*Named*) reactions

- What they begin with (*Reactant*)
- What they lead to (*Product*)
- How they are accomplished (*Reagent, Mechanism etc*)
- What the limitations are (*e.g. conditions, multiple products, isomeric products, solvents etc*)

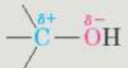
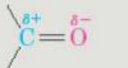

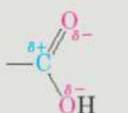
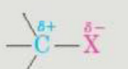
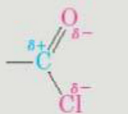
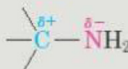
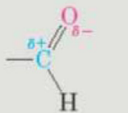

A synthesis combines a series of proposed steps to go from a defined set of reactants to a specified product. You will be expected to devise synthetic routes with up to 3 steps from a given reactant to a final product.

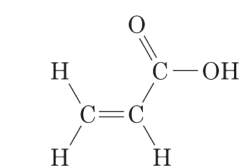


There are a series of animations that can be used in conjunction with these notes. They can be found at <http://www.new.chemistry-teaching-resources.com/Mechanisms.html>

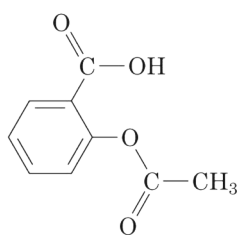
Functional Groups

The study of organic chemistry is made easier by knowledge of the various functional groups found in molecules. Some of the main functional groups are shown in the table below.

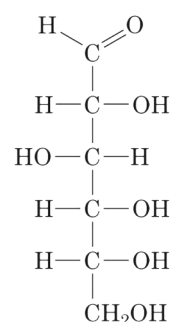
Compound type	Functional group structure	Compound type	Functional group structure
Alcohol		Carbonyl	
Alkene	 Symmetrical, nonpolar	Carboxylic acid	
Alkyl halide		Carboxylic acid chloride	
Amine		Aldehyde	
Ether			



Acrylic acid
(2 functional groups)

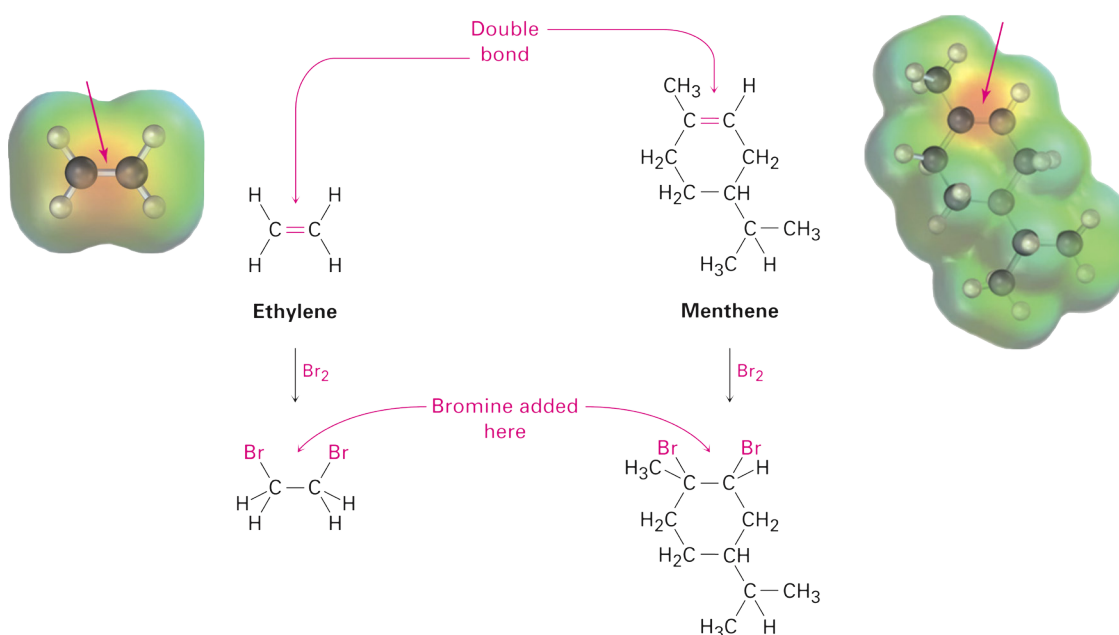


Aspirin
(3 functional groups)



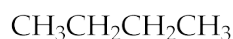
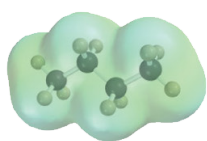
Glucose
(6 functional groups)

Reactions learnt in the context of simple families can be applied to more complex molecules.

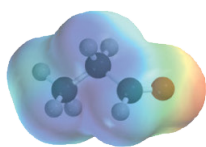


Intermolecular Attractions

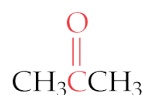
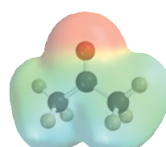
Intermolecular attractions are largely determined by the extent of polarity within a molecule.



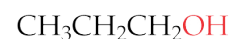
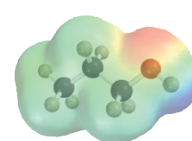
Butane, bp 0°C



Propanal, bp 50°C



Acetone, bp 56°C



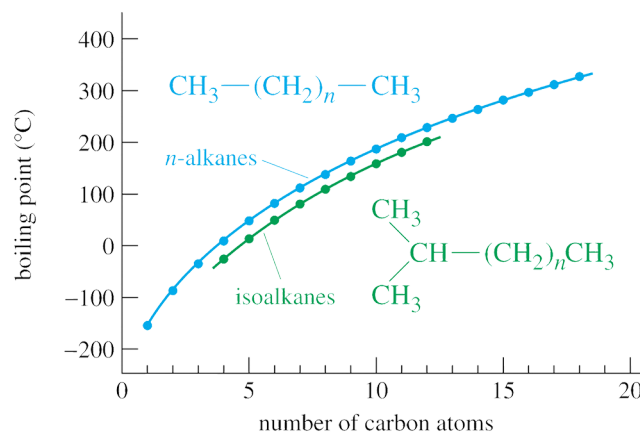
Propanol, bp 97°C

Non-polar molecules like *butane* rely on **London Dispersion forces**, while *propanal* and *acetone* will have **polar-polar attractions** between molecules. *Propanol* will benefit from the stronger **Hydrogen bonds** set up.

Boiling Points

Most organic molecules have a mainly *hydrocarbon* portion to their structures, and as the *hydrocarbon* chain increases in length the **number** of *London Dispersion forces* will increase.


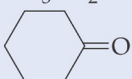
As a result, more energy is needed to move the molecules further apart. Branched molecules tend to be more compact and have **fewer** attractions so they tend to have slightly lower Boiling Points than the equivalent chain only molecule.



The elevated boiling points of the polar molecules reflect the extra energy needed to overcome the stronger attractions between their molecules.

Solubility

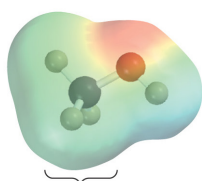
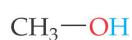
The increasing influence of the hydrocarbon chain in polar molecules has an effect on solubility as well as boiling points.

Structure	Name	Boiling Point (°C)	Water Solubility (g/100 mL H ₂ O)
HCHO	Formaldehyde	-21	55
CH ₃ CHO	Acetaldehyde	21	Soluble
CH ₃ CH ₂ CHO	Propanal	49	16
CH ₃ CH ₂ CH ₂ CHO	Butanal	76	7
CH ₃ CH ₂ CH ₂ CH ₂ CHO	Pentanal	103	1
 -CHO	Benzaldehyde	178	0.3
CH ₃ COCH ₃	Acetone	56	Soluble
CH ₃ CH ₂ COCH ₃	2-Butanone	80	26
CH ₃ CH ₂ CH ₂ COCH ₃	2-Pentanone	102	6
	Cyclohexanone	156	2

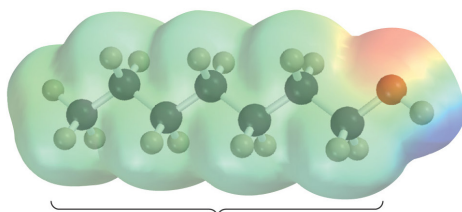
Solubility (in water) is also largely dependant on the polarity of the molecule. To dissolve in water a molecule would need to be able to establish attractions similar in strength to the *hydrogen bonding* that already exists between water molecules.

Alcohols and *acids* are amongst the most soluble because they also have *hydrogen bonding* between their molecules.

However, in larger *alcohols*, the non-polar carbon chain will begin to dominate the properties of the molecule and solubility will be much less than for the smaller *alcohols*.



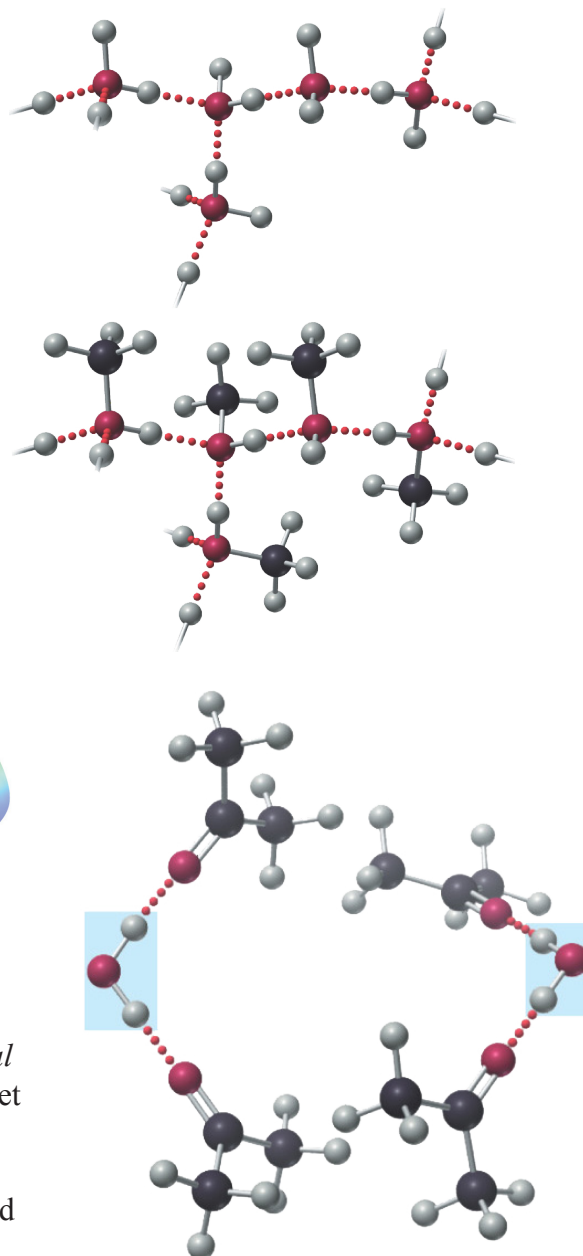
Methanol: has a small organic part and is therefore water-like.



1-Heptanol: has a large organic part and is therefore alkane-like.

Though only able to set up polar-polar attractions between their own molecules, *carbonyl* compounds such as *propanal* and *propanone* can be quite soluble due to their ability to get involved in *hydrogen bonding* with water.

Again, solubility will be greatly decreased in longer chained molecules as the '*hydrophobic*' hydrocarbon tails begin to dominate properties.



1. Which of the following has nucleophilic properties?

- A Na
 B Br⁺
 C CH₃⁺
 D NH₃

2. In the homologous series of amines, increase in chain length from CH₃NH₂ to C₄H₉NH₂ is accompanied by

	Volatility	Solubility in water
A	increased	increased
B	decreased	decreased
C	increased	decreased
D	decreased	increased

3. A compound, X, has the formula C₆H₁₂. X must be

- A a hydrocarbon
 B an alkene
 C a cycloalkane
 D hexene.

4. In the homologous series of alkanols, increase in chain length from CH₃OH to C₁₀H₂₁OH is accompanied by

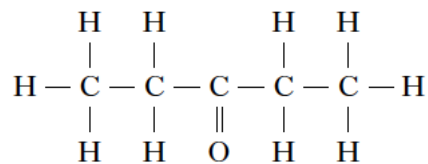
- A increased volatility and increased solubility in water
 B increased volatility and decreased solubility in water
 C decreased volatility and decreased solubility in water
 D decreased volatility and increased solubility in water.

5. Which of the following is not caused by hydrogen bonding?

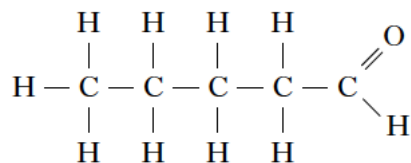
- A The low density of ice compared to water
 B The solubility of methoxymethane in water
 C The higher boiling point of methanol compared to ethane
 D The higher melting point of hydrogen compared to helium

6. Which of the following compounds is likely to be the most soluble in water?

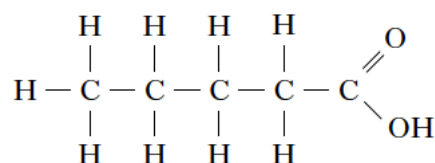
A



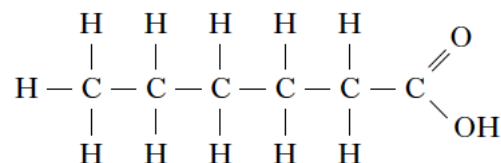
B



C



D



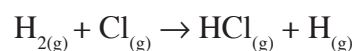
7. Which of the following is most reactive as a nucleophile?

- A Br₂
 B CH₃I
 C NH₄⁺
 D NH₃

8. Hydrogen bonding occurs in

- A CH₃I
 B CH₃OH
 C CH₃OCH₃
 D CH₃CH₂CHO.

9. In the presence of bright light, hydrogen and chlorine react explosively. One step in the reaction is shown below.



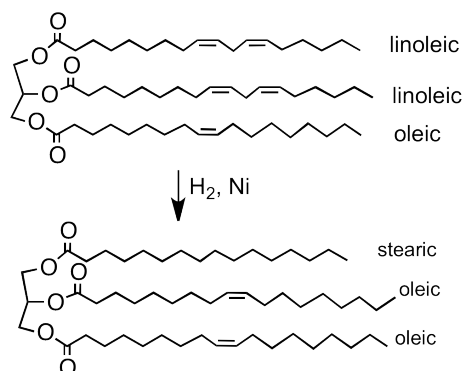
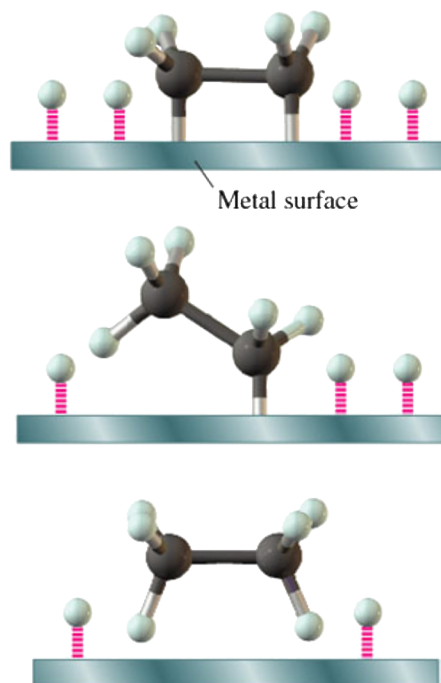
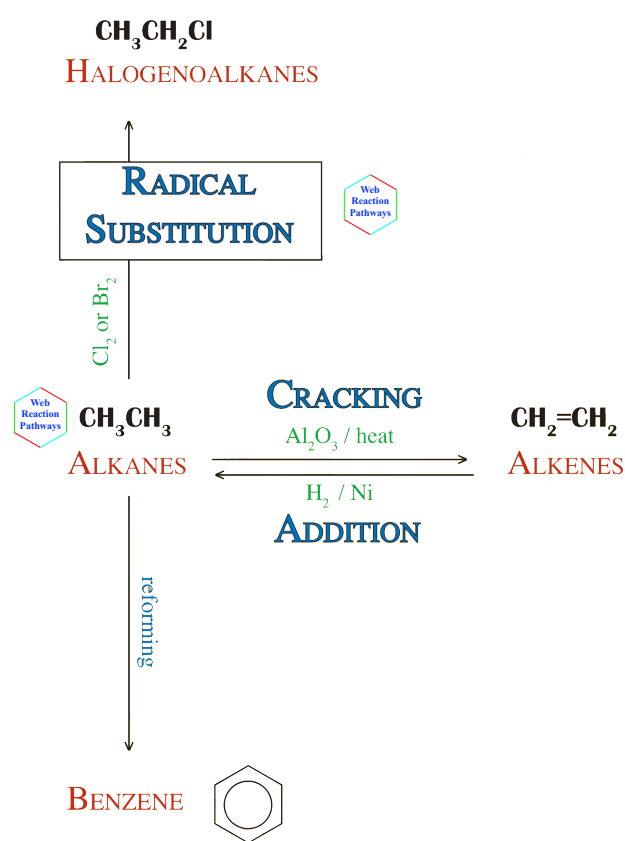
The enthalpy change for this step can be represented as the bond enthalpy of

- A (H—H) + (Cl—Cl)
 B (H—H) – (Cl—Cl)
 C (H—H) + (H—Cl)
 D (H—H) – (H—Cl).

ALKANES (& Cycloalkanes)

Just about everything you need to know about *alkanes* will have been covered in earlier courses.

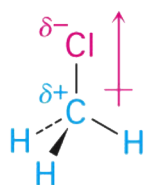
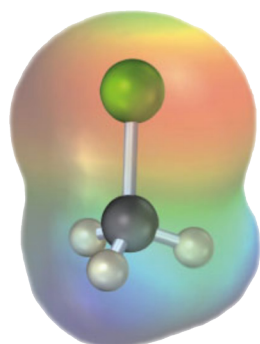
Though *alkanes* can be made by the **catalytic addition** of *hydrogen* to an *alkene* (**hydrogenation**), this would never be an economical way of making an *alkane*.



The conversion of unsaturated fatty acids into saturated fatty acids in the 'hardening' of vegetable oils is an example of **catalytic hydrogenation** that you will have met previously.

Alkanes tend to be extracted directly from the various fractions produced from the **fractional distillation** of crude oil.

Other processes such as **cracking** (to form *alkenes*) and **reforming** (to form ring molecules such as *benzene*) also take place during the refining process. Neither of these processes give us the specificity we would want in a Synthesis - too many different molecules would be produced.



Chloromethane

In the context of *Organic Synthesis*, the significant reaction is the **Radical Substitution** of an *alkane* using *halogens* such as *bromine* and *chlorine*.

This produces a polar molecule which can easily go on to produce a *carbonium ion* as a *reaction intermediate*.

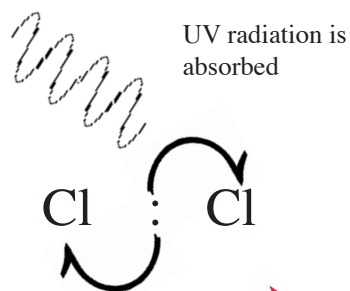


FREE RADICAL SUBSTITUTION

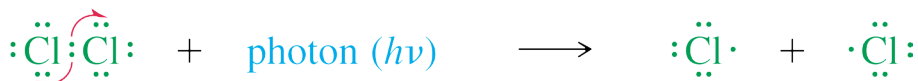
Though this reaction is due to become part of the Higher course, I would still expect aspects of the Mechanism to be tested at Advanced Higher.

INITIATION

'half arrows' are used to show the movements of single electrons

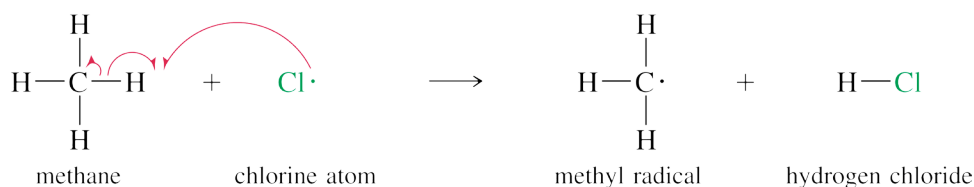


Homolytic fission results in the formation of two chlorine *free radicals*

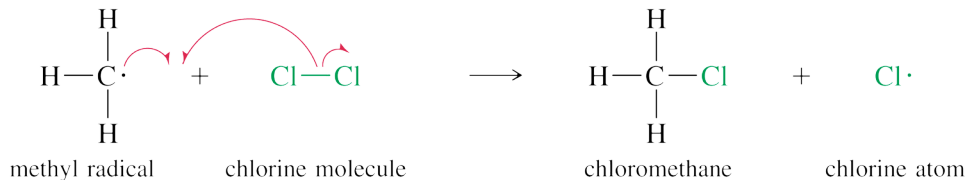


PROPAGATION

First propagation step



Second propagation step



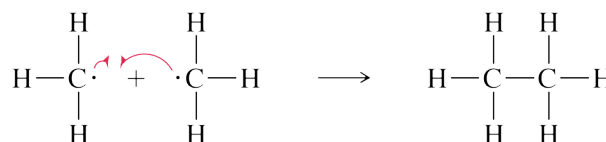
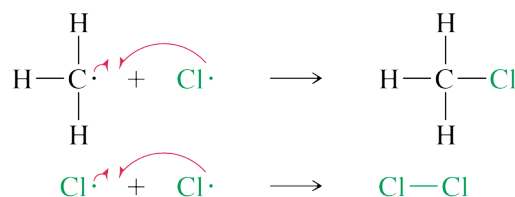
A series of reactions between a *free radical* and a molecule keep the reaction going.

Because each step makes another *free radical*, the reaction is a *chain reaction*.

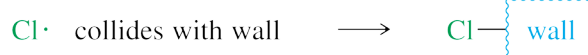
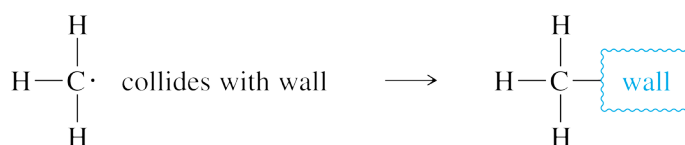
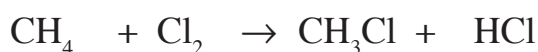
TERMINATION



Any collisions between two *free radicals* will stop a chain.



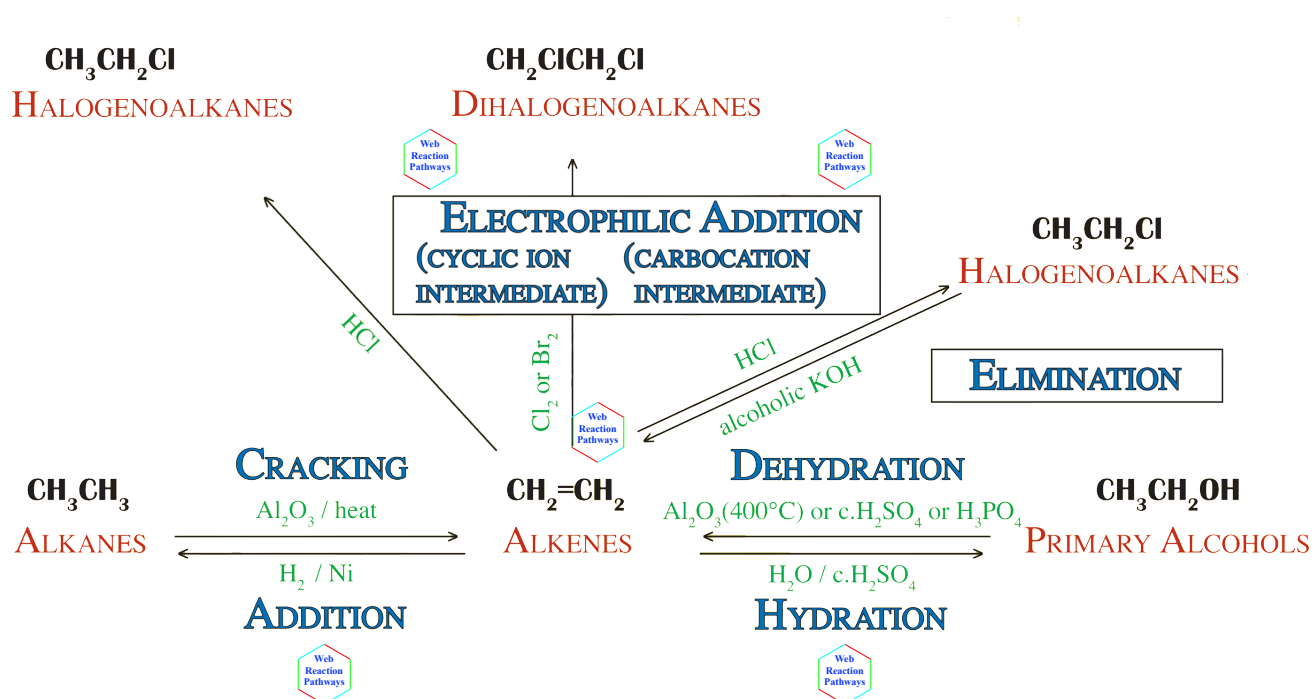
A mixture of haloalkanes will be produced but the first stage can be represented by the equation:



SUBSTITUTION

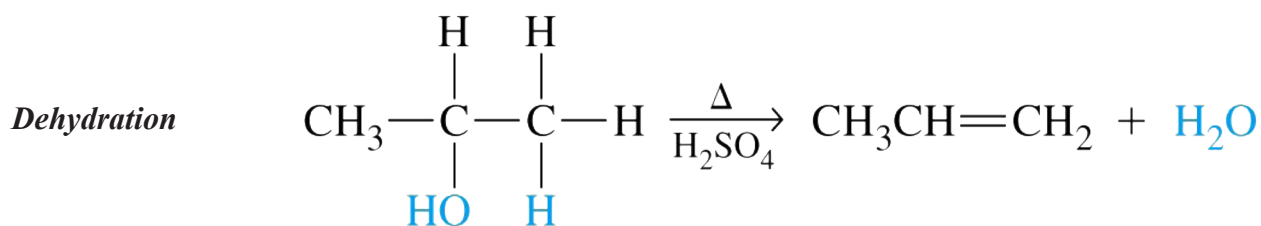
ALKENES (& Cycloalkenes, Alkynes)

Again, all of these reactions will have been met in earlier courses, so the emphasis shifts to **Mechanisms** and how these reactions would fit into **Synthesis Pathways**. In particular, the significance of *halogenoalkanes (alkylhalides)* cannot be overstressed.

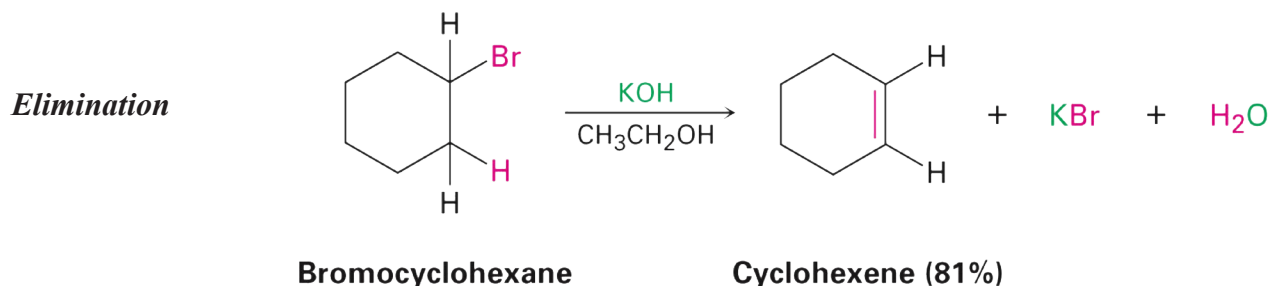


Synthesis of Alkene - Elimination

Though *alkenes* can be made by the **cracking** of *alkanes* (can be called *dehydrogenation*), this would only be used on a **specific alkane** (e.g. *propane*) to produce a **specific alkene** (e.g. *propene*) when part of a **Synthesis**. The other option would be to perform an **Elimination** reaction on either an *alcohol* (also called *dehydration*) or on an *alkylhalide* (rarely called *dehydrohalogenation* !)



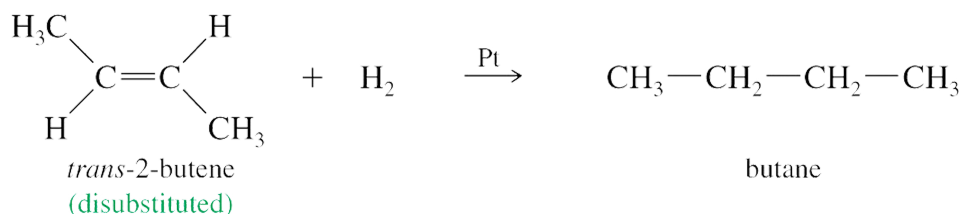
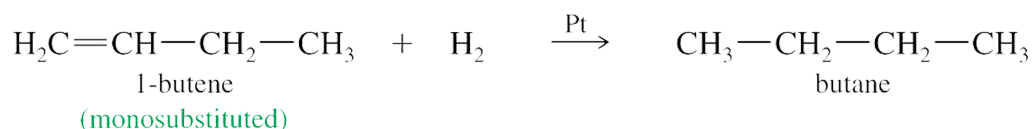
There is no requirement to know the mechanism of this reaction. The **concentrated** H₂SO₄ can be considered as a *dehydrating agent* in this reaction.



Again, there is no requirement to know the mechanism of this reaction. However, be aware that the **solvent used** is crucial. **Elimination** when *solvent* is **alcohol**, *substitution* if *solvent* is **water**.

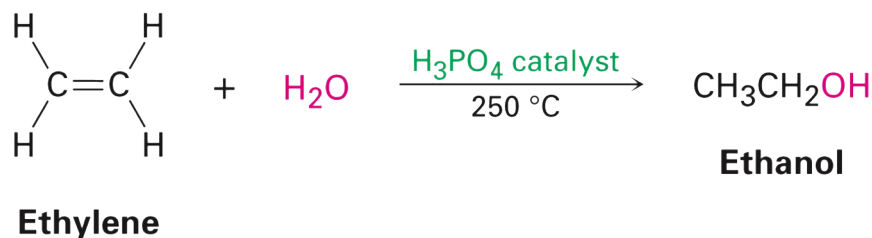
Reaction of Alkene - Radical Addition - Hydrogenation

Covered in Higher Chemistry and revised briefly in section on *Alkanes* (page 10).



Reaction of Alkene - Electrophilic Addition - Hydration

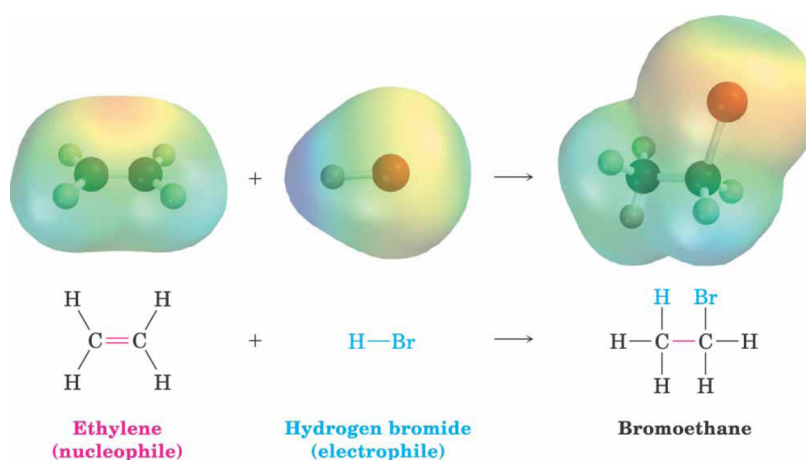
Also covered in Higher Chemistry and the production of an *alcohol* can be a significant step in **Synthesis** as it opens up the route to the oxygen containing molecules - *aldehydes, ketones, acids, esters etc.*



This is one of the main mechanisms that you will be expected to learn and a detailed description of the mechanism can be found on the next page.

Reaction of Alkene - Electrophilic Addition - Hydrohalogenation

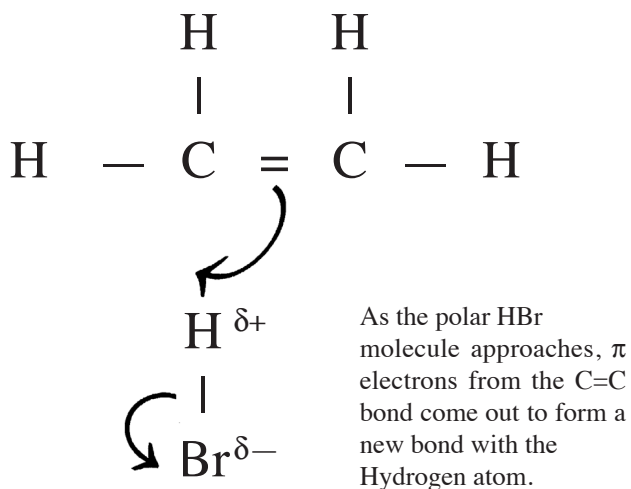
Also covered in Higher Chemistry and the production of an *alkylhalide* can be a significant step in **Synthesis** as it opens up the route to a variety of other molecules - *ethers, alcohols, amines, acids etc.*



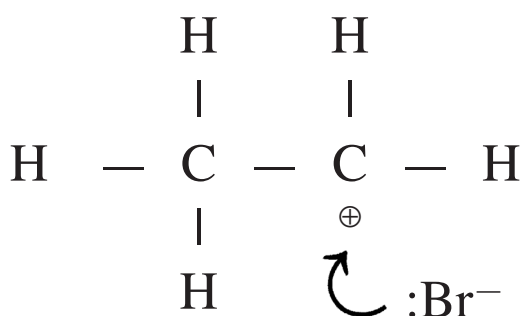
This is one of the main mechanisms that you will be expected to learn and a detailed description of the mechanism can be found on the next page.



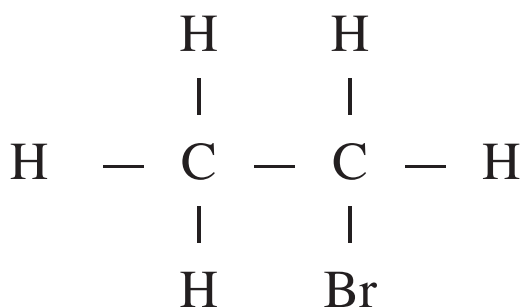
ELECTROPHILIC ADDITION (CARBOCATION INTERMEDIATE)



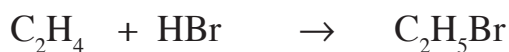
The electrons of the H—Br bond move onto the bromine to form a bromide ion, Br⁻.



The *carbocation* is then attacked by the lone pair of the bromide ion, a *nucleophile*.



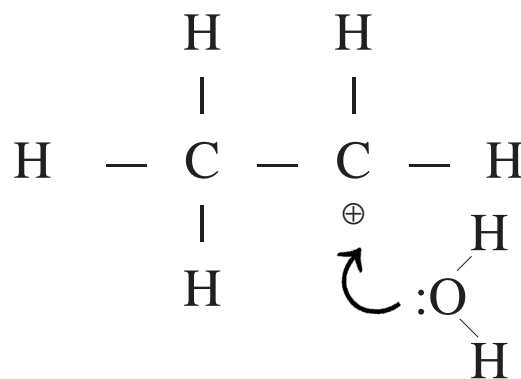
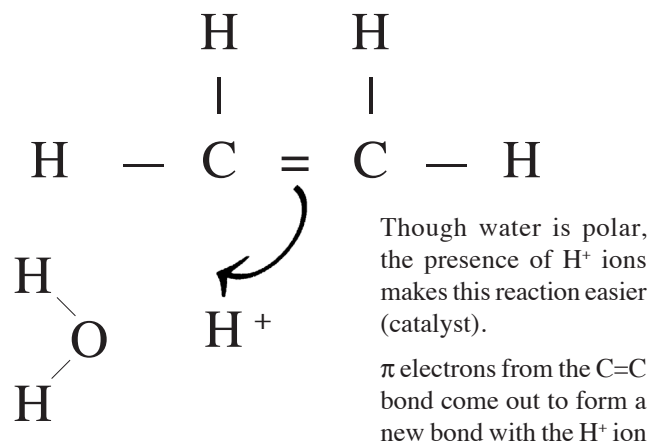
A monohaloalkane is produced and overall the reaction can be represented by the equation:



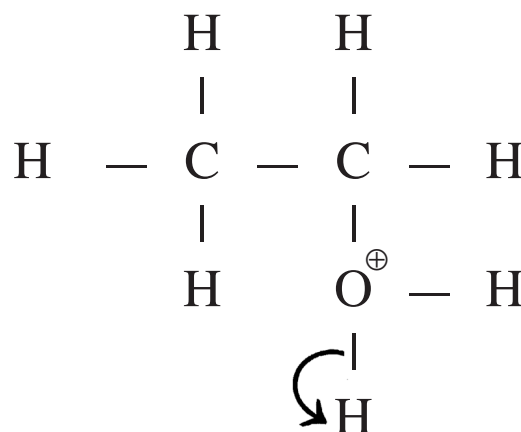
ADDITION



ELECTROPHILIC ADDITION (CARBOCATION INTERMEDIATE)



The *carbocation* is now attacked by a lone pair on the oxygen atom



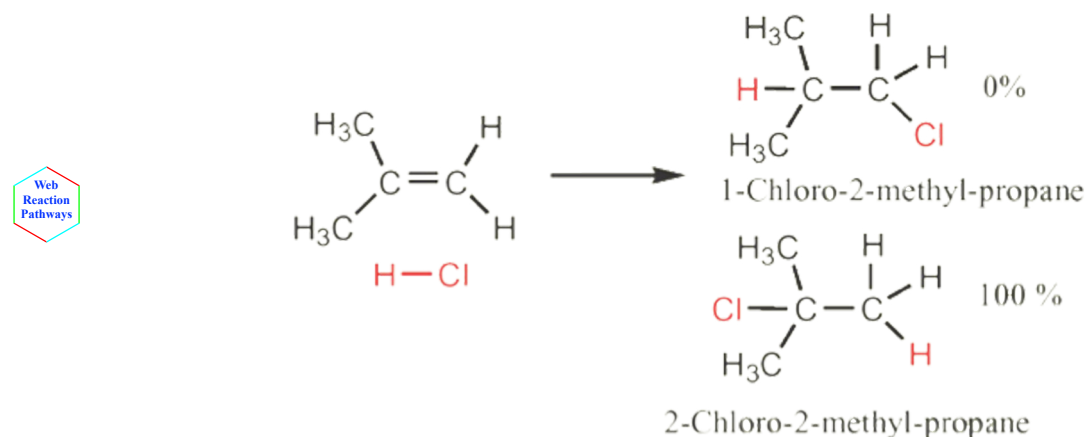
A hydrogen ion is reformed (catalyst) and an alkanol is produced. Overall the reaction can be represented by the equation:



ADDITION, HYDRATION

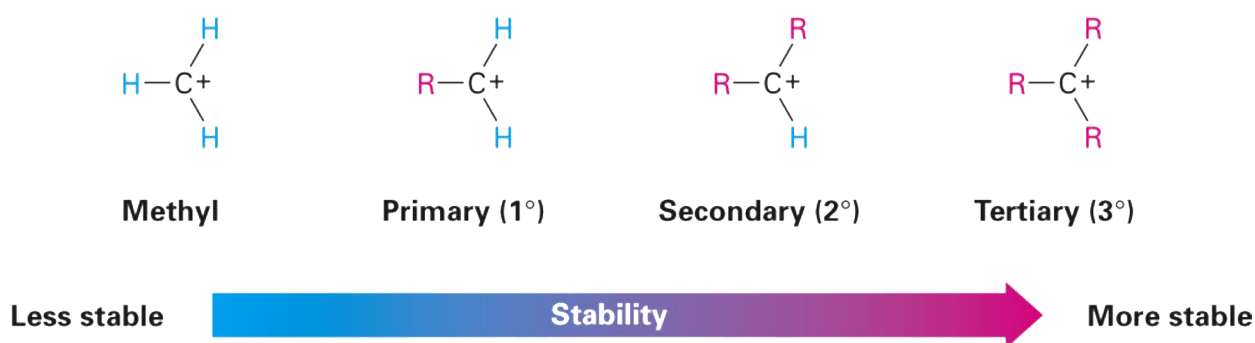
Markovnikov Rule

In the previous two addition reactions, there were the possibilities of two isomeric products forming depending on which of the carbon atoms in the C = C was attacked first by the electrophile (H⁺).

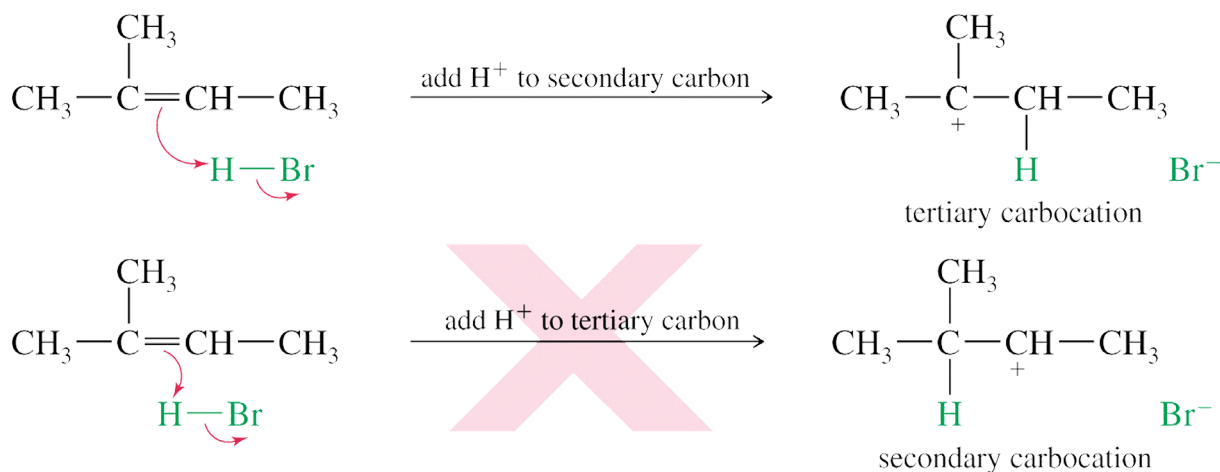


To understand (and therefore predict) which isomer is the more likely product, you need to learn about the **Inductive Effect**. In essence, when a positive charge forms on a carbon (*carbocation intermediate*) it can be stabilised by drawing in negative charge from any **alkyl groups** attached to the carbon.

The more alkyl groups attached, the greater the stability.



In forming two possible isomeric products, one of the *carbocation intermediates* will be more stable than the other and that isomer will be the main product formed - sometimes, the only product formed.

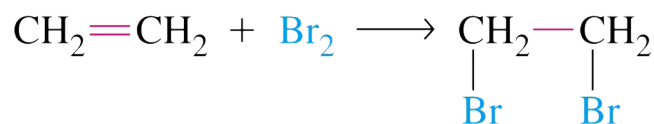


Quick 'Rule of Thumb' -

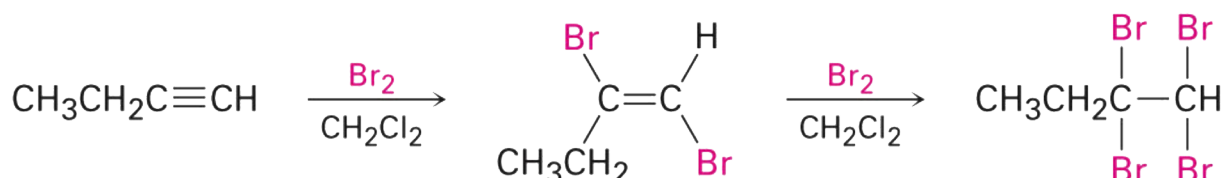
the hydrogen will always add to the carbon atom that already has the most hydrogen atoms attached.

Reaction of Alkene - Electrophilic Addition - Bromination

Also covered in Higher Chemistry, the production of an *alkylhalide* can be a significant step in *Synthesis* as it opens up the route to a variety of other molecules
- *ethers, alcohols, amines, acids etc.*



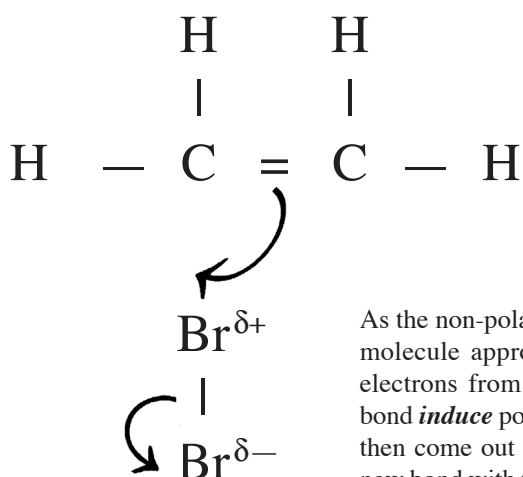
Alkynes will have a similar addition reaction but will be able to react with 2 moles of halogen.



1-Butyne

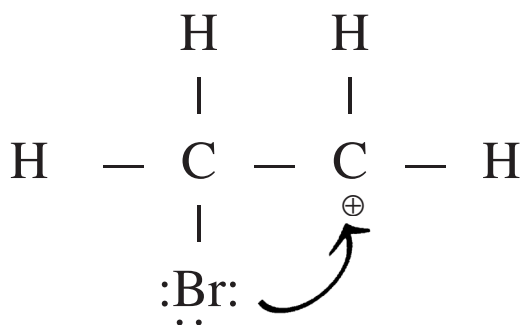
(E)-1,2-Dibromo-1-butene

1,1,2,2-Tetrabromobutane

ELECTROPHILIC ADDITION
(CYCLIC ION INTERMEDIATE)

As the non-polar Br_2 molecule approaches, π electrons from the $\text{C}=\text{C}$ bond *induce* polarity and then come out to form a new bond with the nearer Bromine atom.

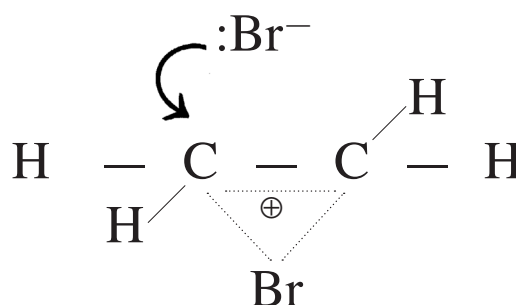
The electrons of the $\text{Br}-\text{Br}$ bond move onto the further bromine to form a bromide ion, Br^- .



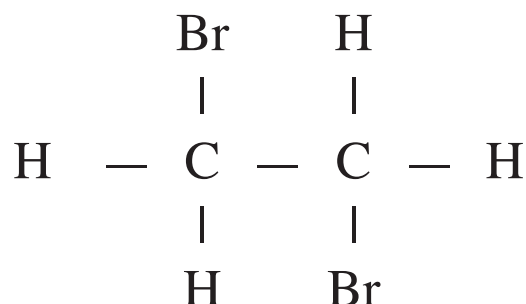
Unlike the previous mechanism, where the H^+ ion was effectively the electrophile, the bromine has lone pairs of electrons. One of these will be attracted to the charge on the *carbocation*. The bromine forms two bonds.

From the normal equation there is no obvious sign that this addition is any different from the previous additions.

However, it has a totally different mechanism and is also one of those you will be expected to learn.



The positive charge is shared between the 2 carbon atoms and the bromine atom. The Bromide ion will then attack *from the other side*. A *TRANS* arrangement.



A dihaloalkane is produced and overall the reaction can be represented by the equation:



ADDITION

10. Which of the following is a propagation step in the chlorination of methane?

- A $\text{Cl}_2 \rightarrow \text{Cl}\cdot + \text{Cl}\cdot$
 B $\text{CH}_3\cdot + \text{Cl}\cdot \rightarrow \text{CH}_3\text{Cl}$
 C $\text{CH}_3\cdot + \text{Cl}_2 \rightarrow \text{CH}_3\text{Cl} + \text{Cl}\cdot$
 D $\text{CH}_4 + \text{Cl}\cdot \rightarrow \text{CH}_3\text{Cl} + \text{H}\cdot$

11. Which of the following does not occur in the reaction between methane and chlorine?

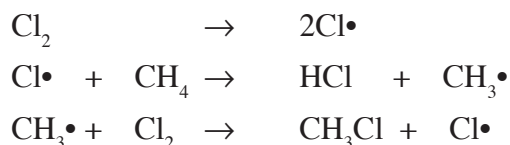
- A A chain reaction
 B Homolytic fission
 C Free radical formation
 D An addition reaction

12. Propene can be produced by heating 1-bromopropane with ethanolic potassium hydroxide.

This reaction is an example of

- A reduction
 B hydrolysis
 C elimination
 D condensation.

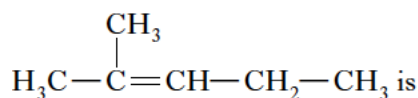
13. Part of a possible chain reaction mechanism for chlorine reacting with methane is:



Which of the following will not be a termination step in this reaction?

- A $\text{H}\cdot + \text{Cl}\cdot \rightarrow \text{HCl}$
 B $\text{Cl}\cdot + \text{Cl}\cdot \rightarrow \text{Cl}_2$
 C $\text{CH}_3\cdot + \text{CH}_3\cdot \rightarrow \text{C}_2\text{H}_6$
 D $\text{CH}_3\cdot + \text{Cl}\cdot \rightarrow \text{CH}_3\text{Cl}$

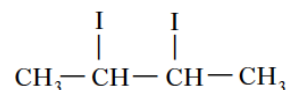
14. The major product in the reaction of HCl with 2-methylpent-2-ene,



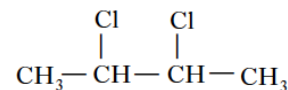
- A 2-chloro-2-methylpentane
 B 3-chloro-2-methylpentane
 C 2,3-dichloro-2-methylpentane
 D 4-chloro-4-methylpentane.

15. When but-2-ene is shaken with an aqueous solution of chlorine in potassium iodide, the structural formula(e) of the product(s) is/are

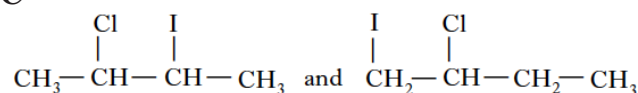
A



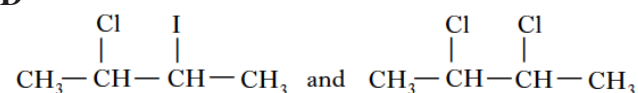
B



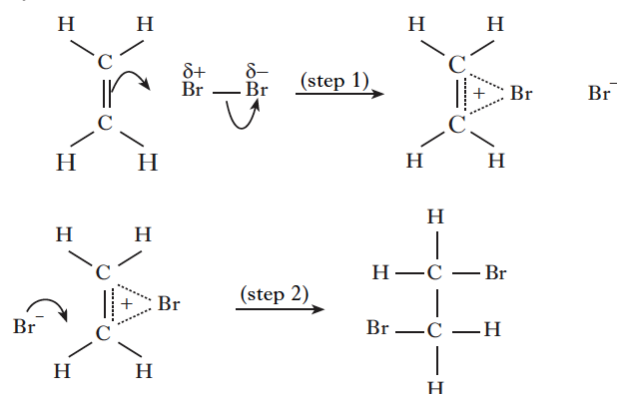
C



D



16.



The two steps in the reaction mechanism shown can be described as

- A ethene acting as a nucleophile and Br_2 acting as a nucleophile
 B ethene acting as a nucleophile and Br_2 acting as an electrophile
 C ethene acting as an electrophile and Br_2 acting as a nucleophile
 D ethene acting as an electrophile and Br_2 acting as an electrophile.

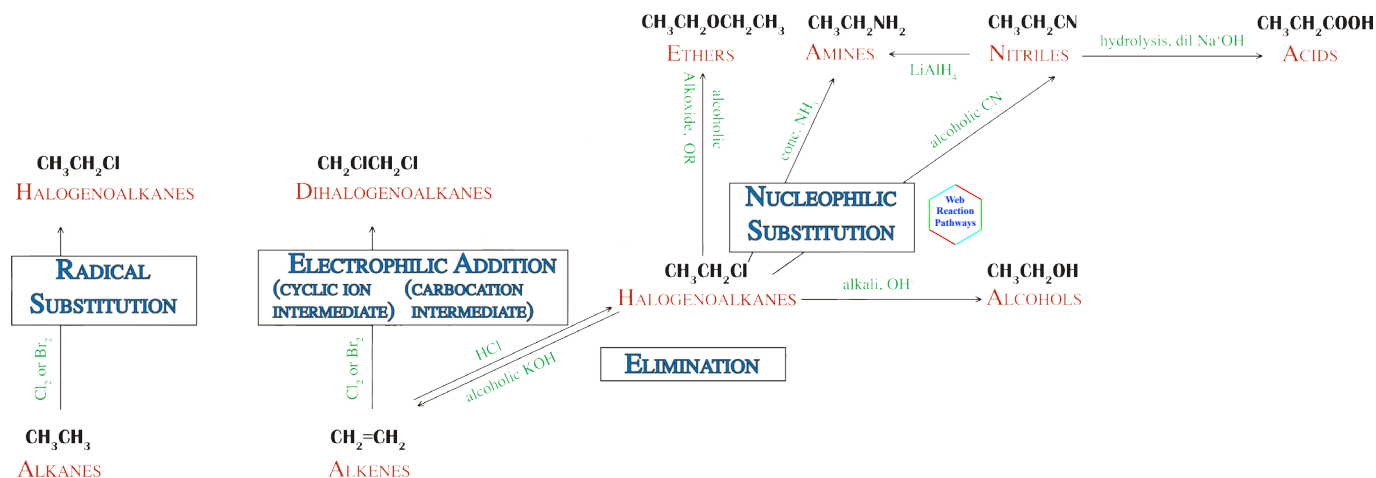
17. $\text{OH}^- + \text{CO}_2 \rightarrow \text{HCO}_3^-$
 $\text{C}_2\text{H}_4 + \text{Br}_2 \rightarrow \text{C}_2\text{H}_4\text{Br}^+ + \text{Br}^-$

Which substances act as electrophiles in the above reactions?

- A OH^- and Br_2
 B OH^- and C_2H_4
 C CO_2 and Br_2
 D CO_2 and C_2H_4

HALOGENOALKANES (Alkylhalides)

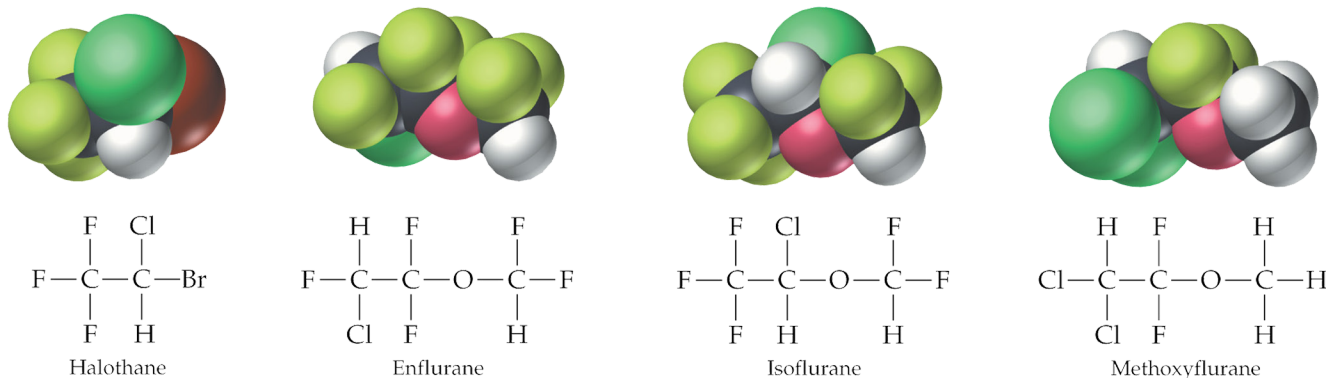
In Higher Chemistry the *alkylhalides* were not particularly important chemicals. In Advanced Higher, however, the significance of *halogenoalkanes (alkylhalides)* cannot be overstressed. They can be a very important step in many **Synthesis Pathways**.



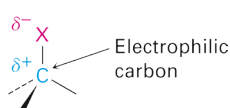
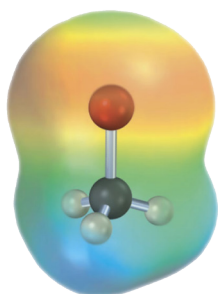
Introduction to Halogenoalkanes

Organic compounds containing halogen substituents are comparatively rare in the natural world. Consequently, most have to be synthesised in laboratories. They are widely used in the modern world.

For example, they are important in medicine, agriculture and in the manufacture of plastics. In medicine, one of the first examples of their use was in 1847 by James Young Simpson of Bathgate, who was the first to use chloroform (trichloromethane) as a general anaesthetic.



More recently, safer *halogenoalkanes* and *halothanes* have been devised for use as anaesthetics.

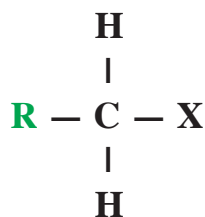
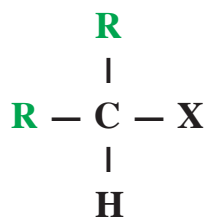
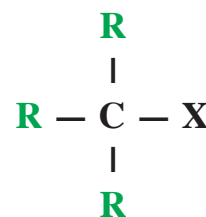


In this course, the most significant feature of a *halogenoalkane* is the production of a *dipole* and, in particular, a *positively charged carbon*.

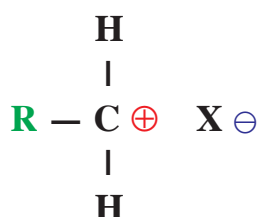
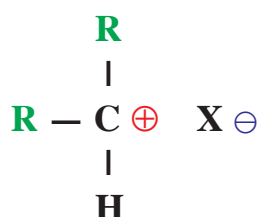
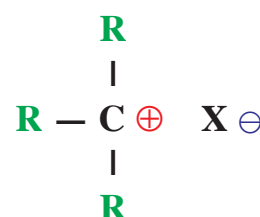
This carbon is now vulnerable to attack by a number of different *nucleophiles* leading to:

Nucleophilic Substitution

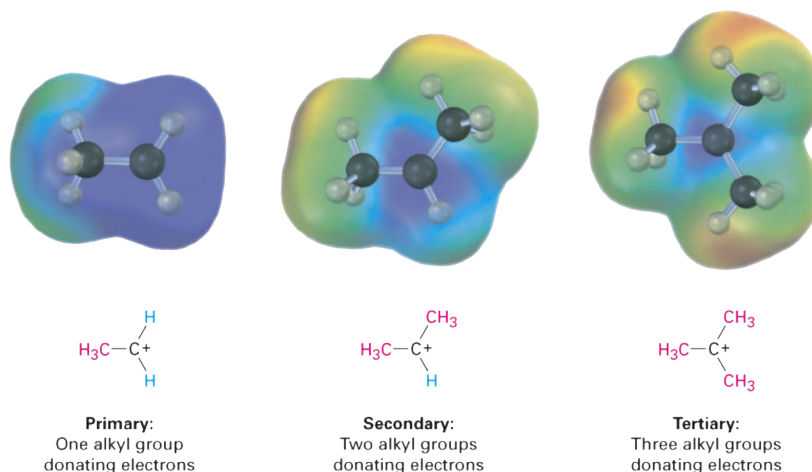
The other significant feature in a *halogenoalkane* can be the **number of alkyl groups** attached to the carbon with the halogen atom - whether it is a *primary*, *secondary* or *tertiary* alkylhalide.

*primary alkylhalide**secondary alkylhalide**tertiary alkylhalide*

One possible mechanism for **nucleophilic substitution** involves the formation of a **carbonium ion** after the halogen atom leaves as a halide ion.

*primary carbonium**secondary carbonium**tertiary carbonium*

As in the explanation for the **Markovnikov Rule**, the inductive effect of the *alkyl groups* helps stabilise the carbonium ion making this mechanism **more likely** with *tertiary alkylhalides* and **less likely** with *primary alkylhalides*.



The other factor that can have a major effect, is the nature of the halogen present. Fluorine is the most *electronegative* and will result in the most polar molecule.

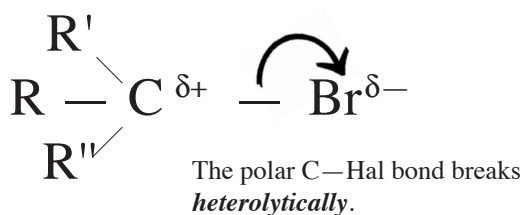
However, the C — F bond is also the *strongest* and will therefore be the *hardest to break*.

Halomethane	Bond length (pm)	Bond strength		Dipole moment (D)
		(kJ/mol)	(kcal/mol)	
CH ₃ F	139	452	108	1.85
CH ₃ Cl	178	351	84	1.87
CH ₃ Br	193	293	70	1.81
CH ₃ I	214	234	56	1.62

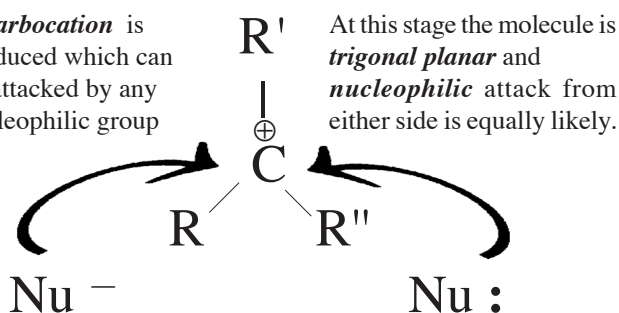
Overall, the most reactive *halogenoalkanes* are the **iodo-** and **bromo-alkanes** and they tend to be used almost exclusively for **nucleophilic substitution**.



NUCLEOPHILIC SUBSTITUTION

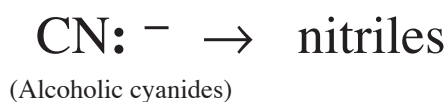
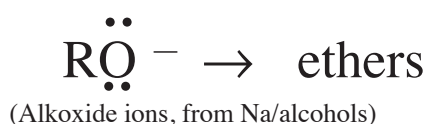
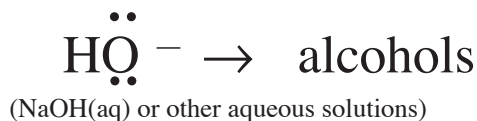
(S_N1)

A *carbocation* is produced which can be attacked by any nucleophilic group



If R , R' and R'' are all different (assymmetric carbon), then a mixture of *optical isomers* will be produced.

Nucleophiles include:



A variety of products can be made by this reaction but overall the reaction can be represented by the equation:



SUBSTITUTION

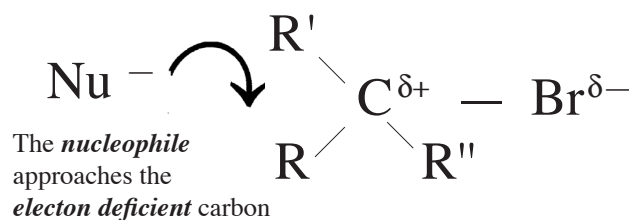
The first step is the *rate determining step* and, since it only involves one substance, the reaction is *first order*

S_N1 or S_N2 ?

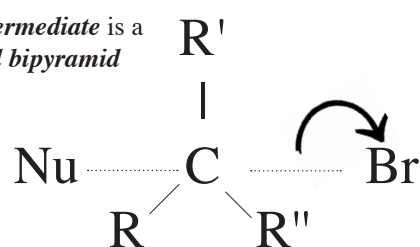
Can depend on the polarity of the C—Hal bond. Can depend on the polarity of the solvent used. Can depend on the size of the R , R' and R'' groups. No easy answer. Just need to be aware of the the two possibilities.



NUCLEOPHILIC SUBSTITUTION

(S_N2)

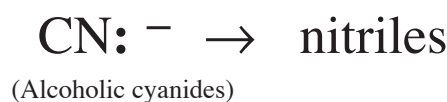
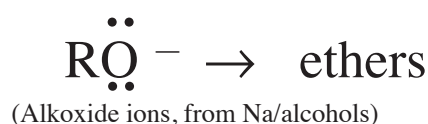
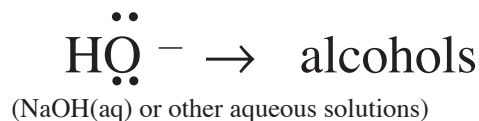
The *intermediate* is a *trigonal bipyramid* shape



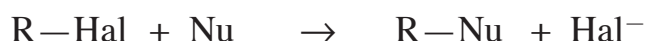
As the *nucleophiles'* electron pair moves in, the electrons of the C—Br bond move onto the bromine

Even if R , R' and R'' are all different (assymmetric carbon), only *one possible isomer* can be produced.

Nucleophiles include:



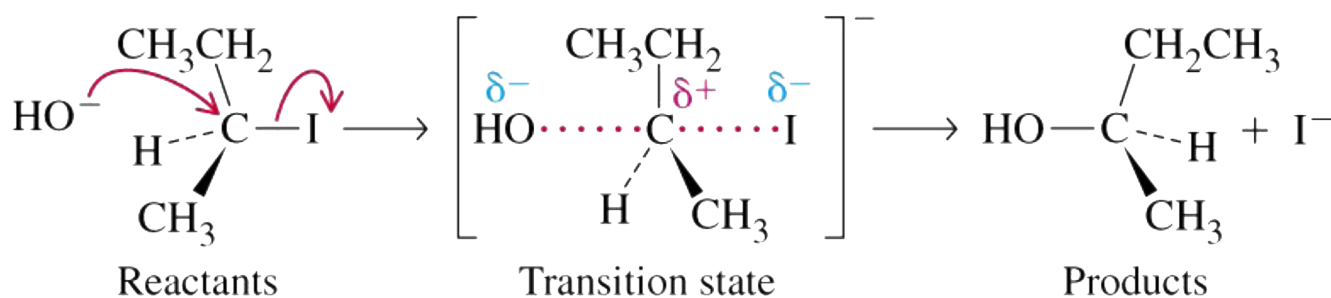
A variety of products can be made by this reaction but overall the reaction can be represented by the equation:



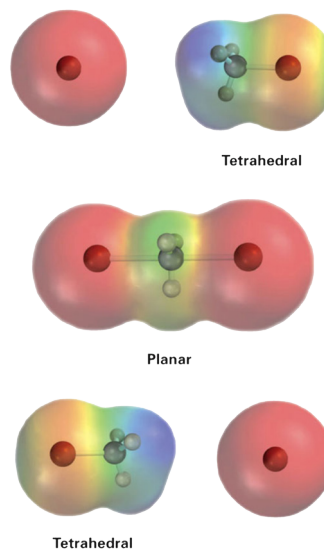
SUBSTITUTION

The *rate determining step* involves both chemicals so the reaction is *second order*

Summary of SN2 Mechanism

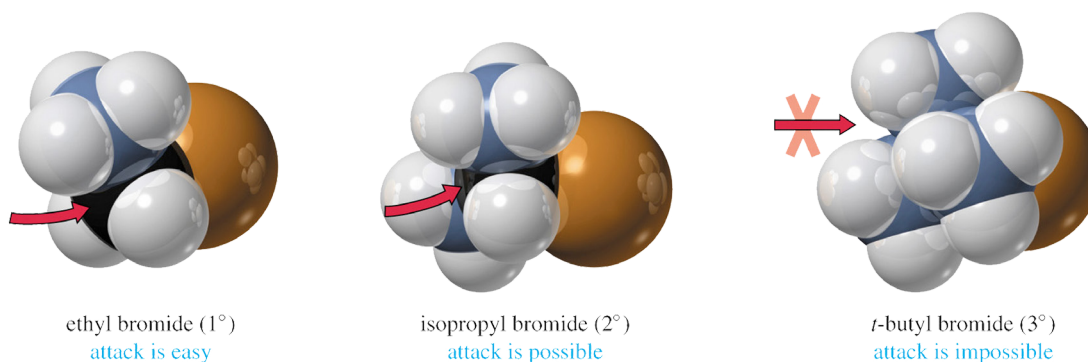


- **2 molecules** involved in *rate determining step*
- Transition state is **trigonal bipyramidal** - 5 groups arranged around carbon atom
- **No isomeric products** though *inversion* of the molecule will take place
- **Nucleophile** has to attach from **opposite side** to the departing halogen
- **Most likely for primary alkylhalide**, least likely for tertiary alkylhalide - **steric hindrance** is 'best' explanation.



Steric Hindrance

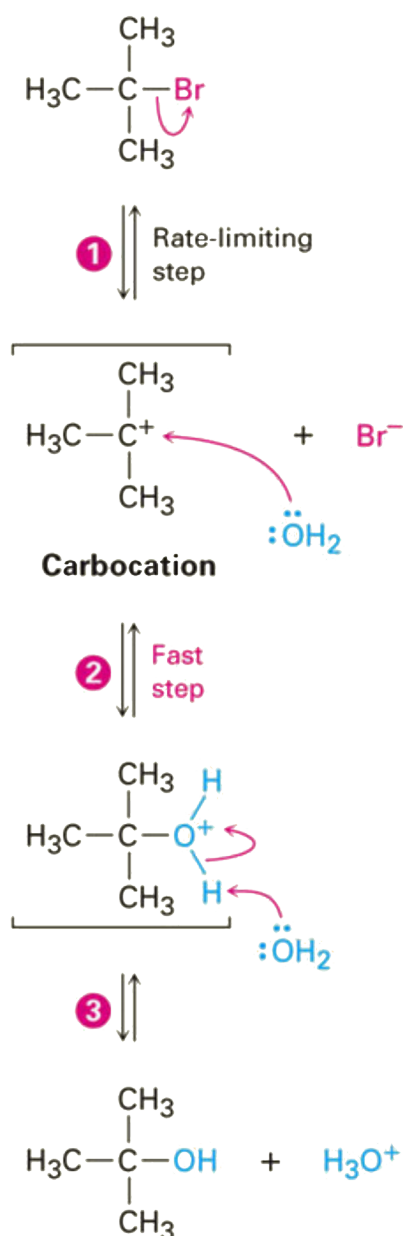
Steric Hindrance refers to the effect that larger groups can have on the formation of a bond to a new group.



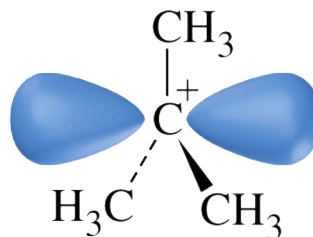
with one methyl and two hydrogen atoms, there is **still room** for the **nucleophile** to attach to the **carbonium ion**

with three methyl groups and no hydrogen atoms, there is **no room** for the **nucleophile** to attach to the **carbonium ion**

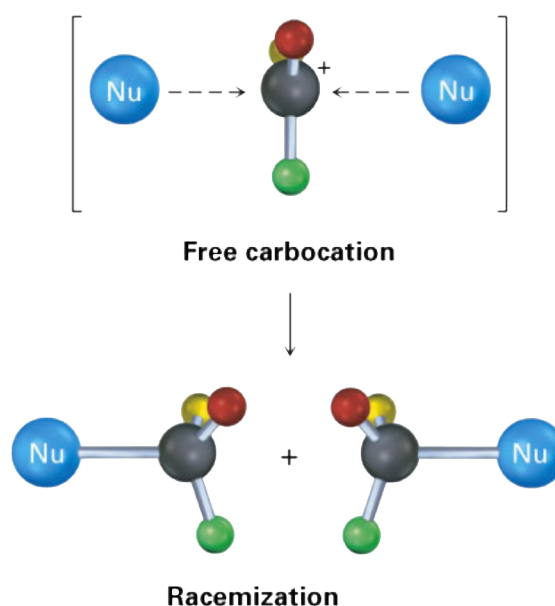
Summary of SN1 Mechanism



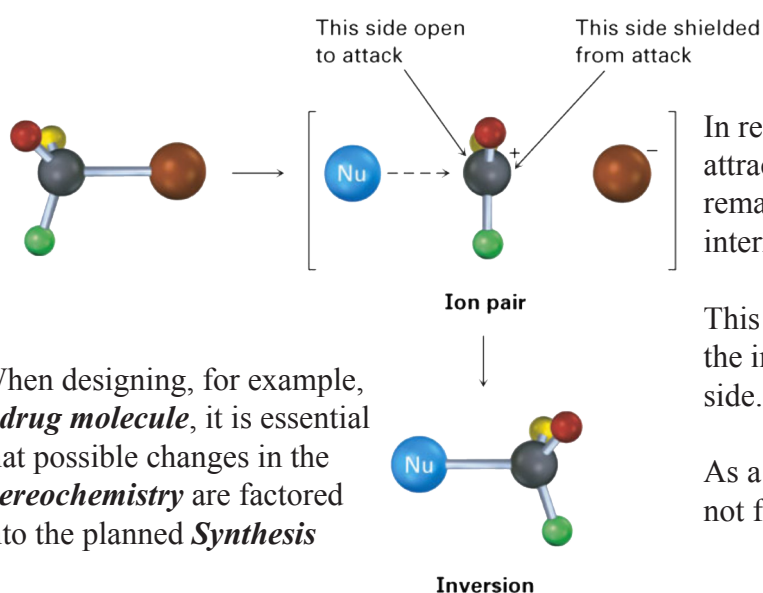
- **Only 1 molecule** involved in *rate determining step*
- Transition state is **planar trigonal** - 3 groups arranged around **carbonium ion**



- **Isomeric products** possible if *alkylhalide* was **chiral**
- **Nucleophile** can attach from **either side**



- Least likely for primary alkylhalide, *most likely for tertiary alkylhalide* - **inductive effect** is 'best' explanation.



When designing, for example, a **drug molecule**, it is essential that possible changes in the **stereochemistry** are factored into the planned **Synthesis**

In reality, the departing halide ion is likely to be attracted by the carbocation formed and may remain in close proximity to the reaction intermediate.

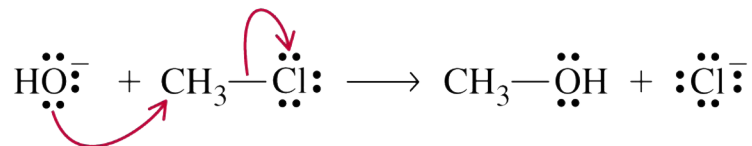
This may make it very difficult or impossible for the incoming nucleophile to approach from that side.

As a result, one of the possible isomers may not form or will be the minority product only.

Reaction of Alkylhalide - Nucleophilic Substitution - to Alcohol

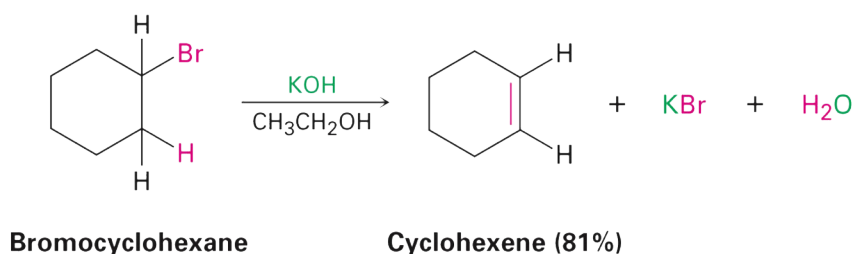
The production of an *alcohol* can be a significant step in **Synthesis** as it opens up the route to the oxygen containing molecules - *aldehydes, ketones, acids, esters etc.*

Traditionally, the 'easiest' reagent given for this reaction is $\text{NaOH}_{(aq)}$ and it is perfectly acceptable to assume that the *hydroxide ion* is the attacking *nucleophile*:



In reality, just about any *aqueous* solution can be used as the attacking *nucleophile* is actually a **water molecule**, but the final step requires the **elimination of a H^+** and the *hydroxide ion* can play an important part here.

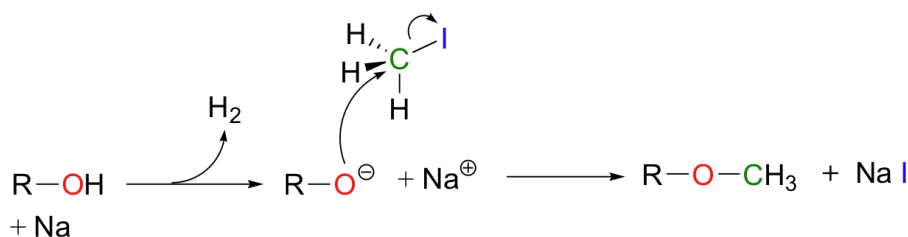
What is much more important is that careful attention is paid to the **solvent** used as *hydroxides dissolved in ethanol*, e.g. $\text{NaOH}_{(\text{ethanol})}$, can lead to an **Elimination** reaction instead



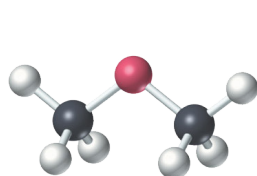
Reaction of Alkylhalide - Nucleophilic Substitution - to Ether

Ethers are introduced in Advanced Higher and generally would be the final product in a Synthesis.

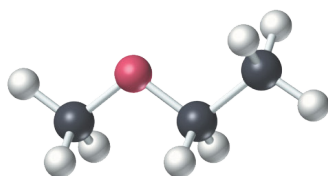
Traditionally, there would appear to be two different reagents given for this reaction but, in reality, it is the same reagent both times. The key to this reaction is the production of an **alkoxide ion** ($\text{R} - \text{O}^-$) which can be conveniently made by reacting an *alkali metal*, e.g. Na, with the equivalent alcohol ($\text{R} - \text{OH}$).



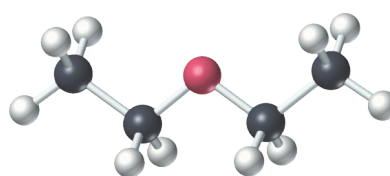
Reagent: $\text{Na} / \text{alcohol}$ or $\text{Na}^+ \text{alkoxide}^-$ - both will lead to formation of *ether*



$\text{CH}_3\text{---O---CH}_3$
Dimethyl ether
(bp = -24.5°C)



$\text{CH}_3\text{---O---CH}_2\text{CH}_3$
Ethyl methyl ether
(bp = -10.8°C)



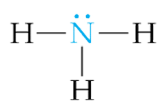
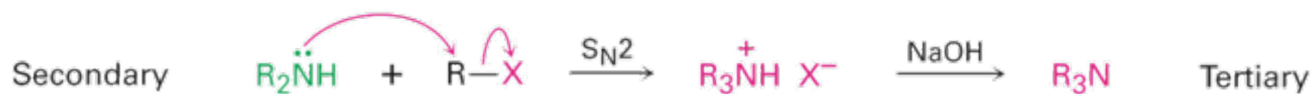
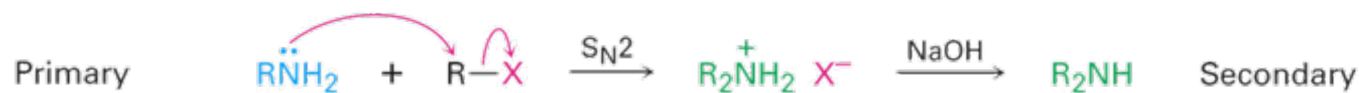
$\text{CH}_3\text{CH}_2\text{---O---CH}_2\text{CH}_3$
Diethyl ether
(bp = 34.5°C)

Reaction of Alkylhalide - Nucleophilic Substitution - to Amines

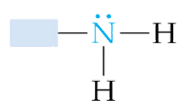
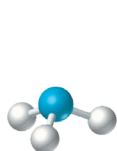
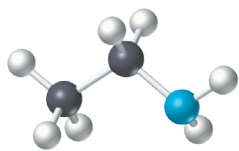
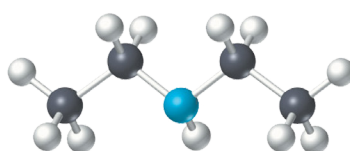
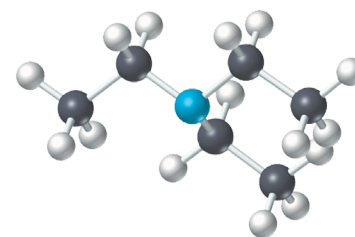
The production of an *amine* group can be an important step in the synthesis of complex molecules but in Advanced Higher it will usually be the final product.



Normally, it will be enough to know the reaction above but be aware that *amines* can themselves act as the *nucleophile* which would lead to the production of *secondary* and *tertiary amines*.



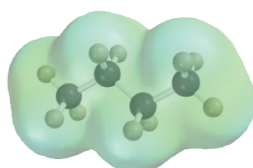
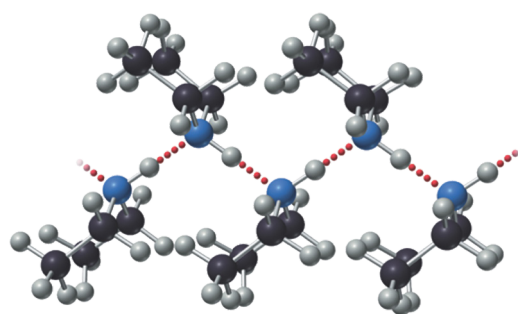
Ammonia

A primary amine
(RNH₂)A secondary amine
(R₂NH)A tertiary amine
(R₃N)NH₃CH₃CH₂NH₂(CH₃CH₂)₂NH(CH₃CH₂)₃N

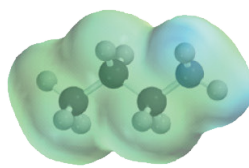
Like *ammonia*, *primary* and *secondary amines* can do *hydrogen bonding* which makes the smaller molecules **very soluble in water**.

Tertiary amines have **no hydrogen bonding**.

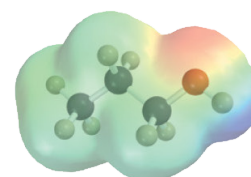
Another effect of this *hydrogen bonding* is that *amines* have **higher than expected boiling points**.

CH₃CH₂CH₂CH₃

Butane, bp 0°C

CH₃CH₂CH₂NH₂

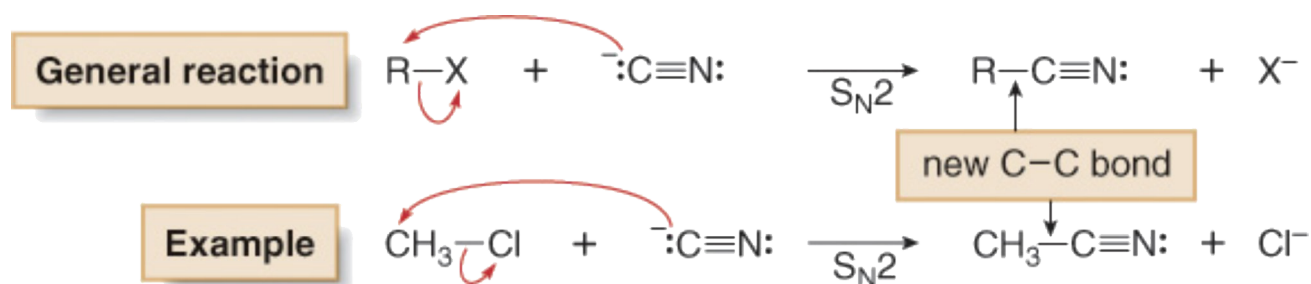
Propylamine, bp 48°C

CH₃CH₂CH₂OH

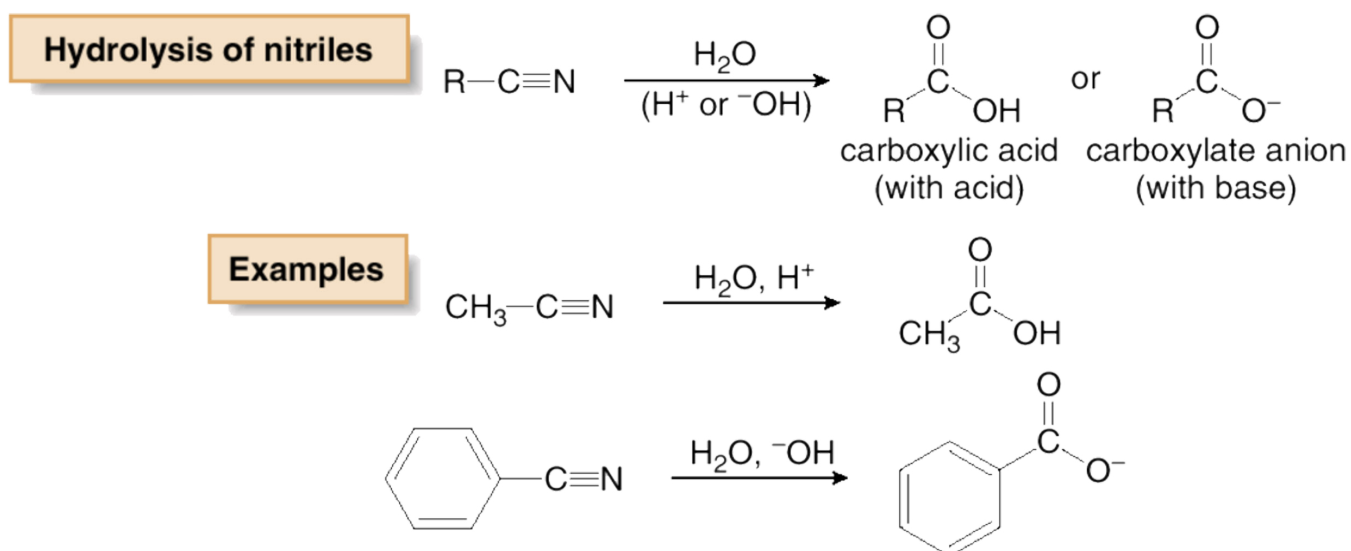
Propanol, bp 97°C

Reaction of Alkylhalide - Nucleophilic Substitution - to Nitrile

The production of a *nitrile* group can be an important step in the synthesis of complex molecules. At one level it can be a means of '*growing a chain*' as it results in an *extra carbon being added* to a molecule.

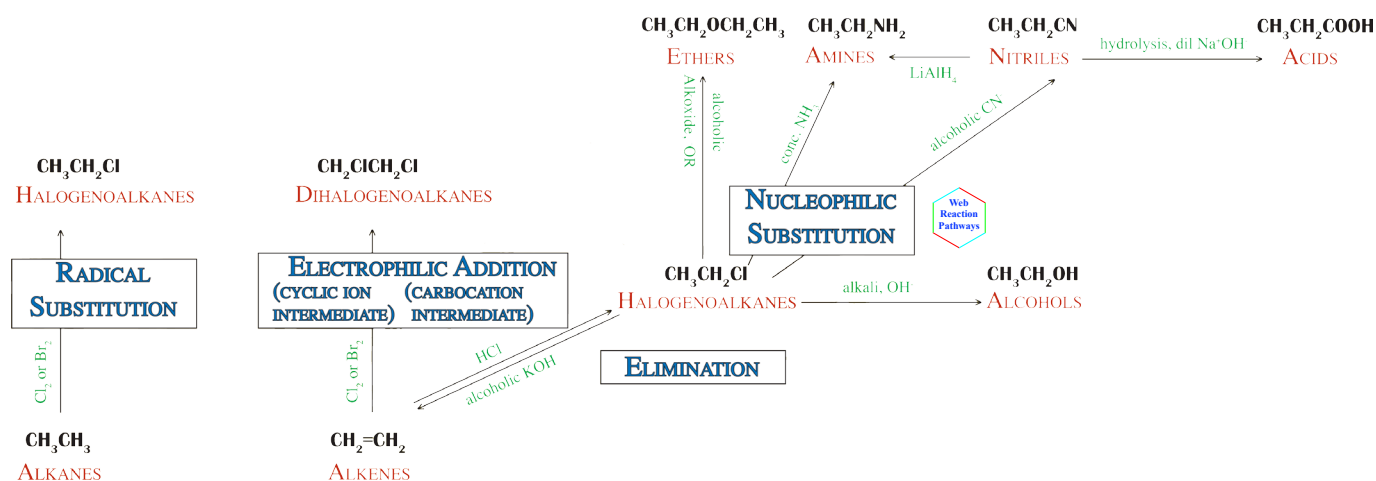


Having produced a *nitrile* group, the next step is usually *hydrolysis*, which results in the production of an *acid (carboxyl)* group.



Importance of Alkylhalides

As mentioned earlier, the importance of *alkylhalides*, and the *nucleophilic substitution* reaction in particular, cannot be stressed enough and they will feature in many of the reaction pathways met at Advanced Higher.



18. Which of the following amines has the lowest boiling point?

- A $C_4H_9NH_2$
 B $C_3H_7NHCH_3$
 C $C_2H_5NHC_2H_5$
 D $C_2H_5N(CH_3)_2$

19. Which of the following is the formula for a tertiary halogenoalkane?

- A $CHBr_3$
 B $(CH_3)_3CBr$
 C $(CH_2Br)_3CH$
 D $BrCH_2C(CH_3)_3$

20. Which of the following molecules is likely to produce the most stable carbocation intermediate in a substitution reaction?

- A CH_3CH_2I
 B $(CH_3)_3CCl$
 C CH_3CH_2Cl
 D $CH_3CHICH_2CH_3$

21. Which of the following bases is the strongest?

- A $C_2H_5NH_2$
 B $(C_2H_5)_2NH$
 C $C_6H_5NH_2$
 D $(C_6H_5)_2NH$

22. $C_3H_7Cl + C_2H_5O^- \rightarrow C_3H_7OC_2H_5 + Cl^-$

The above reaction is

- A an elimination reaction
 B a nucleophilic addition reaction
 C a nucleophilic substitution reaction
 D an electrophilic substitution reaction.

23. 2-Bromobutane reacts with KOH in ethanol to produce two unsaturated products.

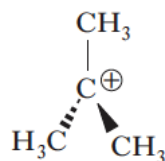
The type of reaction involved is

- A addition
 B elimination
 C oxidation
 D substitution.

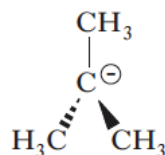
24. The hydrolysis of the halogenoalkane $(CH_3)_3CBr$ was found to take place by an SN_1 mechanism.

The rate-determining step involved the formation of

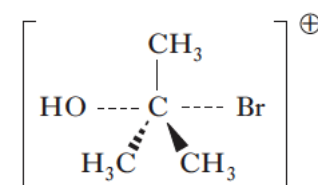
A



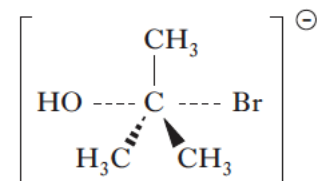
B



C



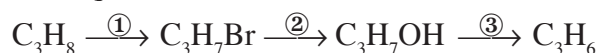
D



25. When 2-bromobutane is reacted with potassium cyanide and the compound formed is hydrolysed with dilute acid, the final product is

- A butanoic acid
 B pentanoic acid
 C 2-methylbutanoic acid
 D 2-methylpropanoic acid.

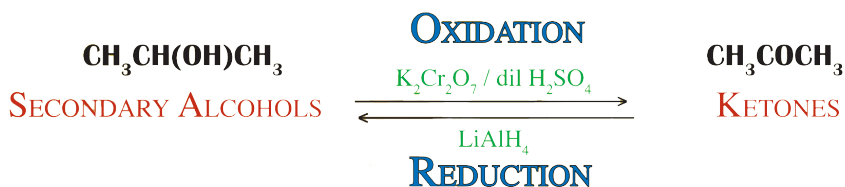
26. Which line in the table correctly describes the types of reaction in the following sequence?



- | | <i>Reaction 1</i> | <i>Reaction 2</i> | <i>Reaction 3</i> |
|---|-------------------|-------------------|-------------------|
| A | addition | substitution | elimination |
| B | addition | addition | condensation |
| C | substitution | substitution | dehydration |
| D | substitution | addition | condensation |

ALCOHOLS

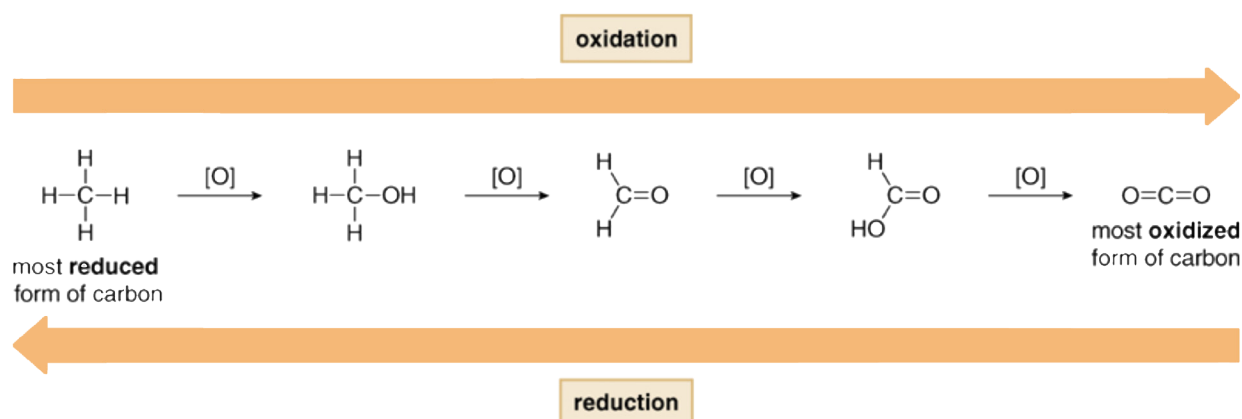
One of the most important reactions met in Higher Chemistry was the *oxidation* of *alcohols* and this remains a very useful step in many Synthesis Pathways. The production of an *alcohol* from *alkylhalide* is new but was covered in the previous section.



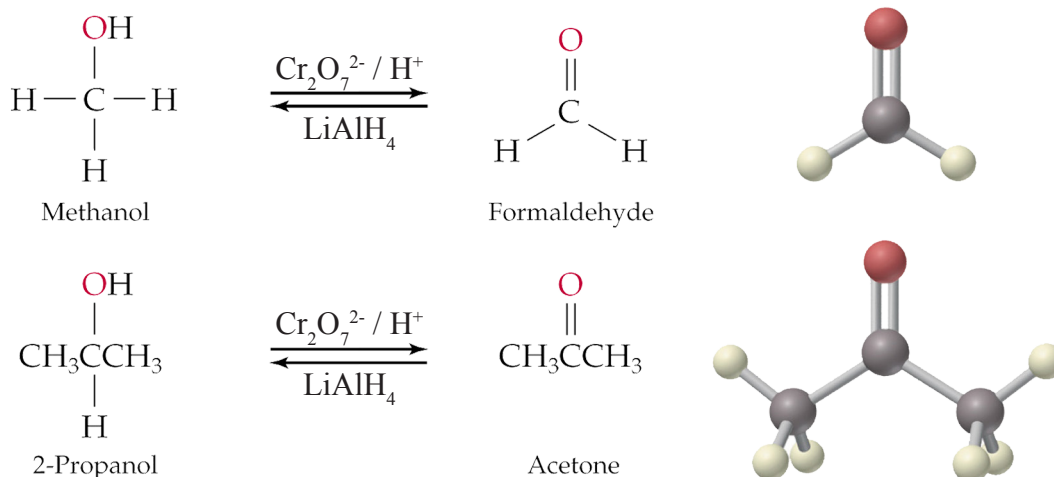
Absolutely new is the use of *hydrides* (H^-) to reduce *aldehydes* and *ketones* back to the corresponding *alcohol*.

Oxidation & Reduction

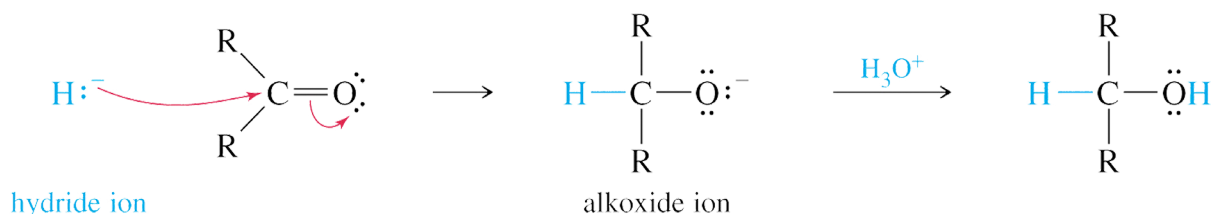
In general, **Oxidation** - increase in the **O:H ratio** (more **O** or less **H**)
Reduction - decrease in the **O:H ratio** (less **O** or more **H**)



As it was at Higher Chemistry, **acidified $K_2Cr_2O_7$** (*orange to green*) remains the **oxidising agent** of choice. There is no need to know how this reagent works.



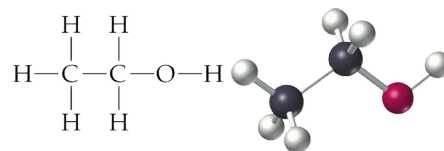
Hydrides are compounds containing the H^- ion. Again, there is no need to know how this reagent works but it is not a complicated reaction:



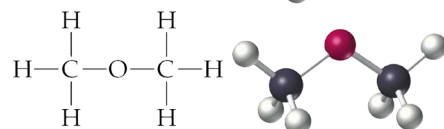
Comparison between Alcohols and Ethers

With *alcohols* and *ethers* being **isomeric**, there is much scope for 'confusion' but the two families have distinctly different properties and reactions so should be easy to distinguish between them.

ethanol $\text{C}_2\text{H}_6\text{O}$



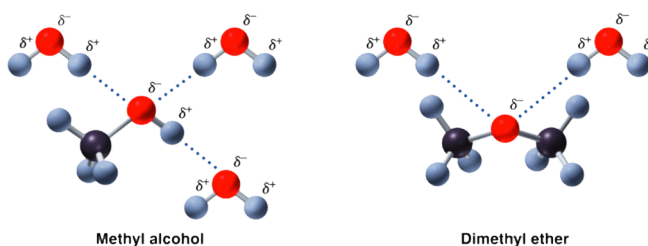
dimethylether $\text{C}_2\text{H}_6\text{O}$



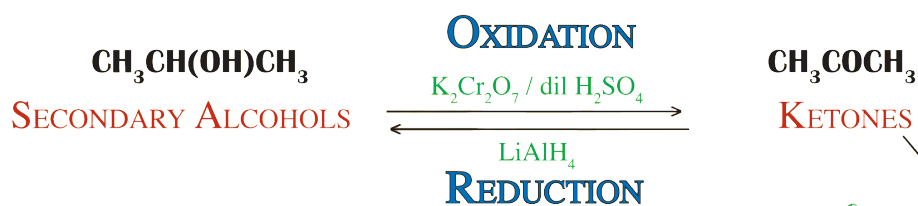
Unlike *alcohols*, *ethers* are **unable to do hydrogen bonding** between their molecules. They are only *slightly polar* so tend to be *very volatile*, *very flammable liquids*.

They can, however, set up *hydrogen bonds* with *water molecules* so the smaller members of the family can be *reasonably soluble*.

	Compound	Molar Mass	Boiling Point (°C)	Soluble in Water?
Alkane	$\text{CH}_3-\text{CH}_2-\text{CH}_3$	44	-42	No
Ether	$\text{CH}_3-\text{O}-\text{CH}_3$	46	-23	Yes
Alcohol	$\text{CH}_3-\text{CH}_2-\text{OH}$	46	78	Yes

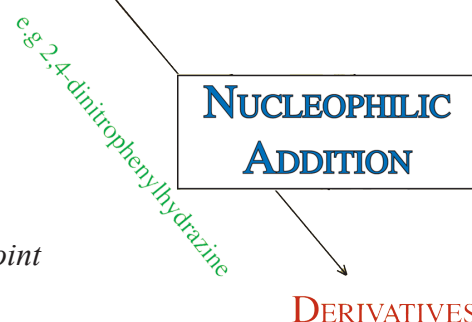


KETONES

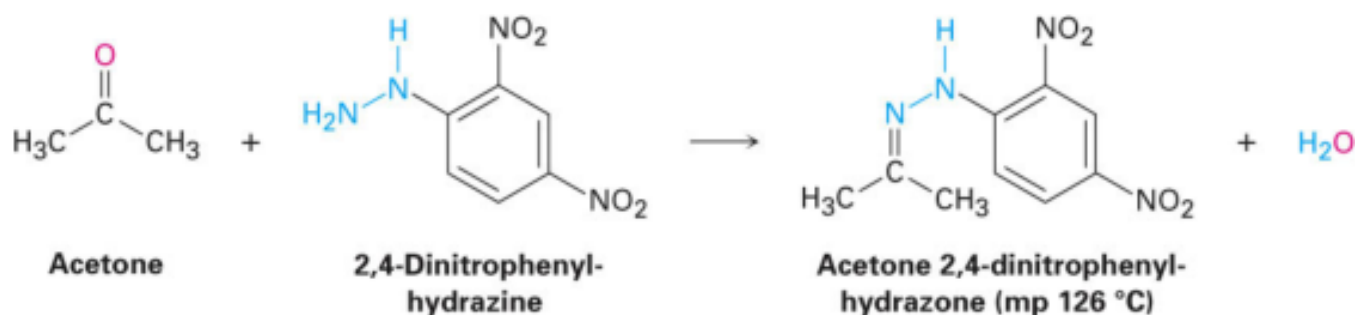


Again, **Oxidation** was covered in Higher chemistry and **Reduction** in the previous section.

A better way of identifying individual *aldehydes* and *ketones* is to produce a **solid derivative** and determine accurately its *Melting Point* which can be compared with DataBook values.

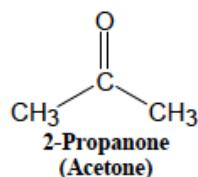


Nucleophilic Addition - Derivative Formation

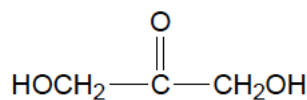


Important Ketones

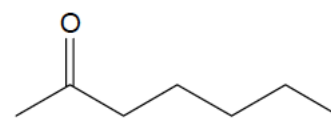
Due to their susceptibility to **oxidation**, *aldehydes* are fairly rare in the natural world whereas *ketones* are found everywhere including many steroids and medicinal drugs.



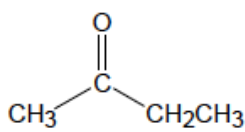
1 billion pounds used annually in U.S.; good solvent for most organic compounds, and is also soluble in water; solvent for coatings such as fingernail polish and enamel paints, etc.

**Dihydroxyacetone**

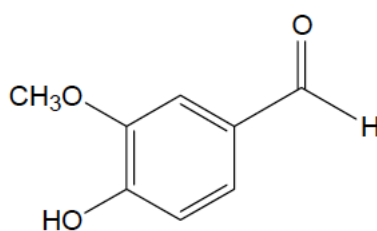
Active ingredient in "bronzers" that provide fake suntan coloration; reacts with dead, outer skin cells to produce a darker color; fades as the dead skin cells slough off.

**2-Heptanone**

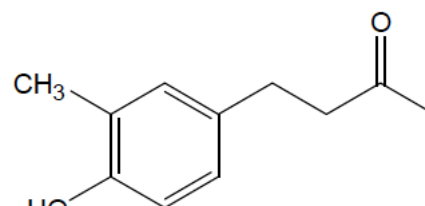
Found in oil of clove; also present in the odor of many fruits and dairy products, and is also responsible for the odor of blue cheese.



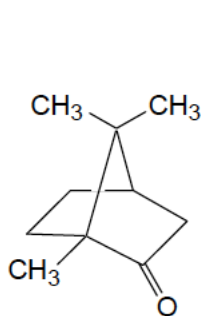
2-Butanone
(Methyl ethyl ketone, MEK)
Common industrial solvent



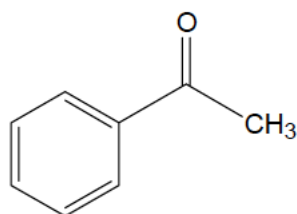
Vanillin
flavoring in Vanilla beans



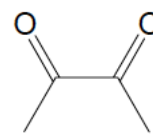
Zingerone
The pungent, hot component of ginger

**Camphor**

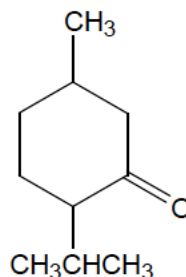
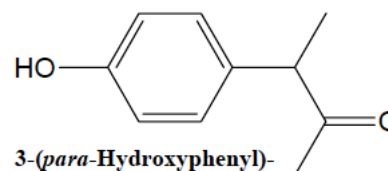
Isolated by steam distillation from the camphor tree of China and Japan. Camphor is a counter-irritant (produces a superficial inflammation to reduce deeper inflammation) and antipruritic (anti-itching) medication; it appears to selectively stimulate cold sensors. It also stimulates the respiratory systems and inspires deep breathing, but can cause convulsions and respiratory collapse in larger doses.

**Acetophenone**

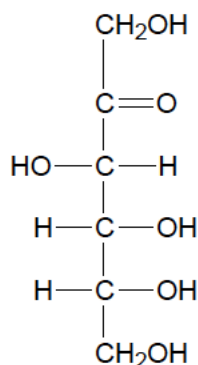
Used in perfumery, and as an organic solvent; also used in the synthesis of some pharmaceuticals

**Butanedione**

A volatile yellow liquid compound with the odor of cheese; gives butter its characteristic flavor. It also contributes to the odor of armpits and unwashed feet by the action of bacteria which ferment the compounds in perspiration.

**Menthone****3-(para-Hydroxyphenyl)-2-butanone**

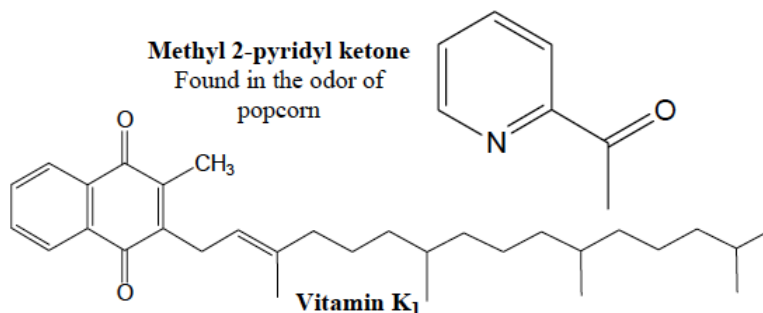
Responsible for the odor of ripe raspberries.

**Fructose**

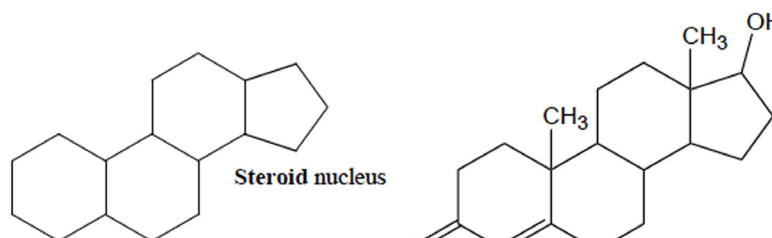
Another important carbohydrate; a major component of corn syrup; found in honey, syrups, and preserves; in combination with glucose it forms the disaccharide **sucrose**.

Methyl 2-pyridyl ketone

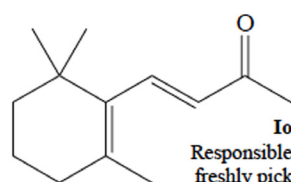
Found in the odor of popcorn

**Vitamin K₁**

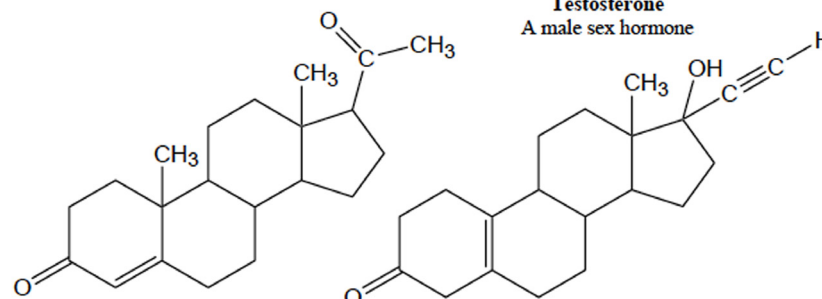
A fat soluble vitamin obtained from green leafy vegetables, cabbage, cauliflower, kale, spinach, pork liver; also made by intestinal bacteria. Essential for blood clotting.

**Steroid nucleus****Testosterone**

A male sex hormone

**Ionone**

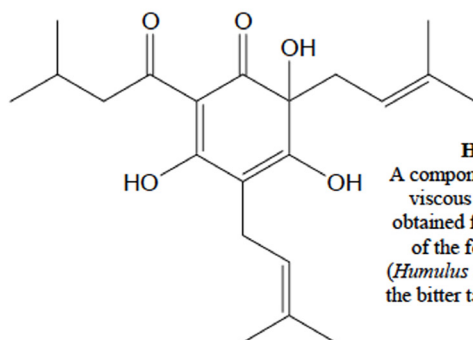
Responsible for the odor of freshly picked raspberries, violets (and the extract, oil of violets), and sun-dried hay.

**Progesterone**

A female sex hormone

Norethynodrel

Active ingredient in birth-control pills

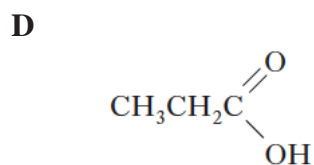
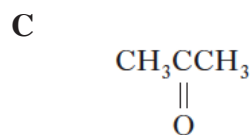
**Humulone**

A component of hop resin, a viscous yellow material obtained from the blossoms of the female hop plant (*Humulus lupulus*); it adds to the bitter taste of some beers.

27. A substance, X, is readily oxidised by acidified potassium dichromate solution to give a product which does not react with sodium carbonate, nor with Tollens' reagent.

Which of the following could represent the structure of X?

- A $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$
 B $\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$



28. Which of the following compounds would liberate one mole of hydrogen gas if one mole of it reacts with two moles of sodium?

- A $\text{C}_2\text{H}_5\text{OH}$
 B $\text{HOCH}_2\text{CH}_2\text{OH}$
 C CH_3COOH
 D CH_3CHO

29. Which of the following compounds would liberate one mole of hydrogen gas if one mole of it reacts with excess sodium?

- A $\text{C}_2\text{H}_5\text{OH}$
 B CH_3CHO
 C CH_3COOH
 D $\text{HOCH}_2\text{CH}_2\text{OH}$

30. Which of the following reacts with ethanol to form the ethoxide ion?

- A $\text{Na}_{(s)}$
 B $\text{Na}_2\text{O}_{(s)}$
 C $\text{NaCl}_{(aq)}$
 D $\text{NaOH}_{(aq)}$

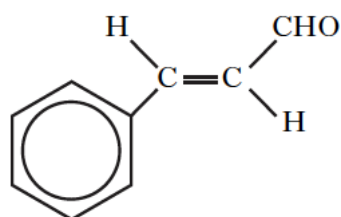
31. Which of the following compounds could not be oxidised by acidified $\text{K}_2\text{Cr}_2\text{O}_7$ solution?

- A $\text{CH}_3\text{CH}_2\text{CHO}$
 B $\text{CH}_3\text{CH}_2\text{COOH}$
 C $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$
 D $\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$

32. Which of the following is not a correct statement about ethoxyethane?

- A It burns readily in air.
 B It is isomeric with butan-2-ol.
 C It has a higher boiling point than butan-2-ol.
 D It is a very good solvent for many organic compounds.

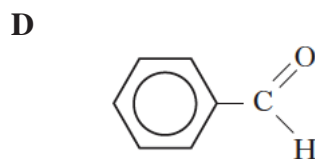
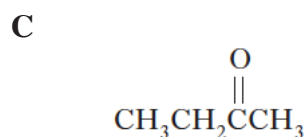
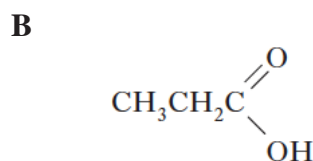
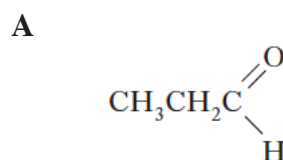
33. Cinnamaldehyde, which can be extracted from cinnamon, has the structure:



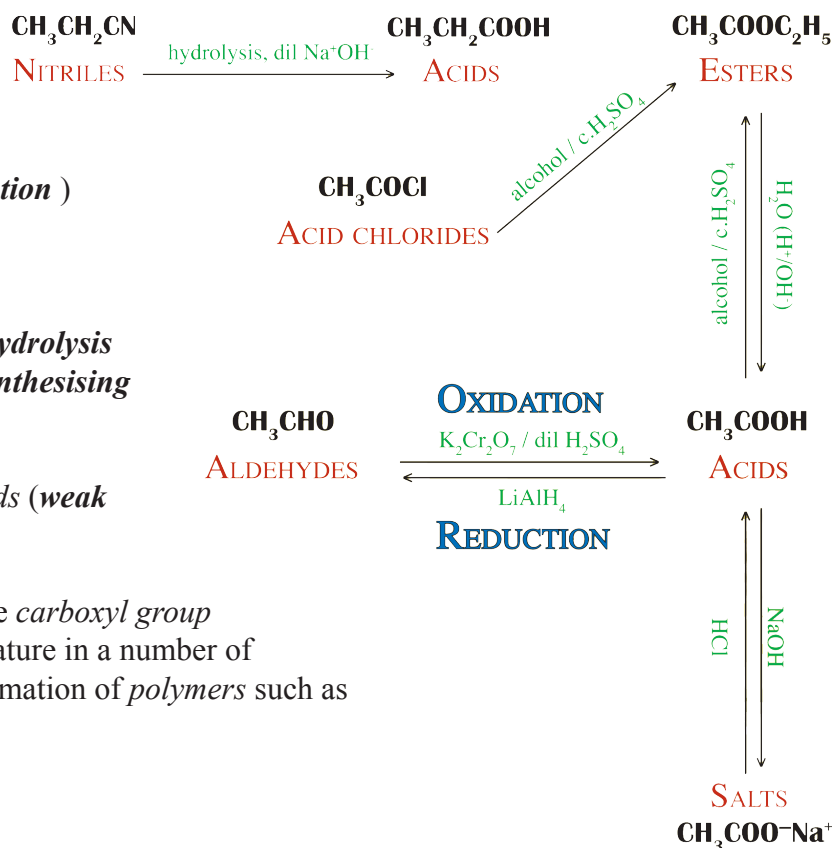
Cinnamaldehyde will not react with

- A sodium metal
 B bromine solution
 C lithium aluminium hydride
 D acidified potassium dichromate.

34. Which of the following will not form a derivative with 2,4-dinitrophenylhydrazine?



ACIDS & ESTERS



Oxidation and **Esterification (Condensation)** were covered in Higher chemistry and **Reduction** in the previous section.

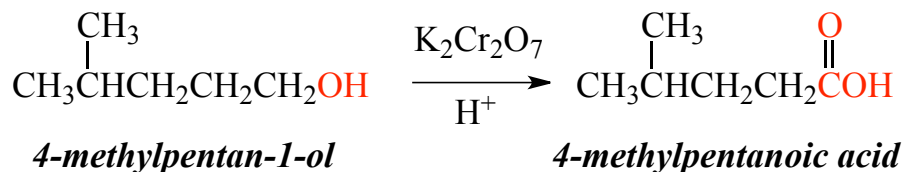
Also met in a previous section was the **Hydrolysis** of a *nitrile* as an alternative method of **synthesising** an *acid*.

The production of *salts* from *organic acids (weak acids)* is covered in Unit 2.

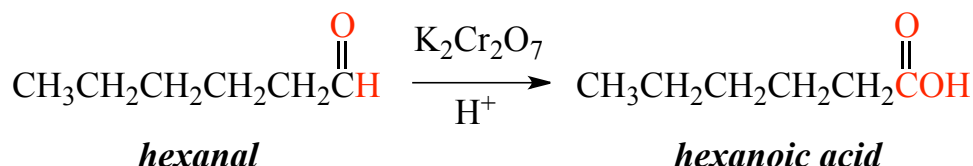
The *carboxyl group* and *derivatives* of the *carboxyl group* such as *acid chlorides* and *amides* can feature in a number of **condensation** reactions leading to the formation of *polymers* such as *polyesters*, *polyamides* and *proteins*.

Synthesis of Acids - Recap

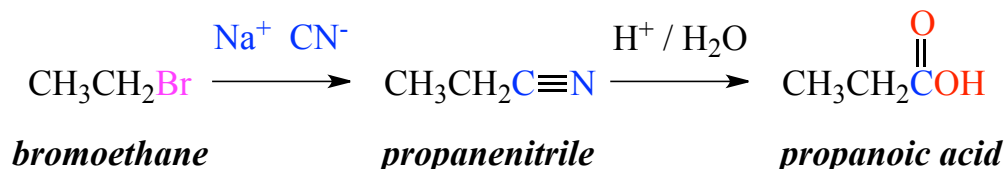
Oxidation of a *primary alcohol*



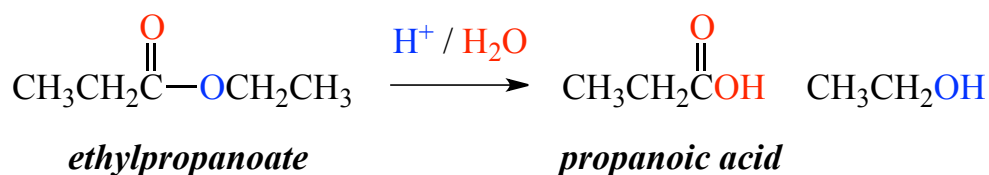
Oxidation of an *aldehyde*



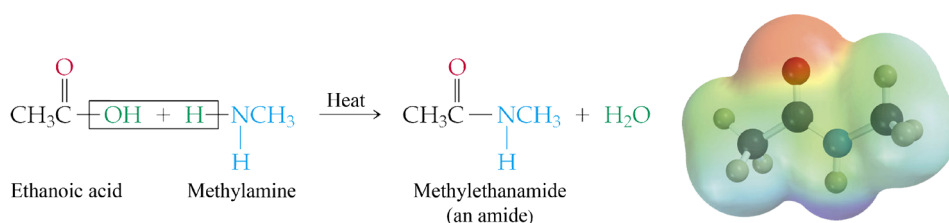
Hydrolysis of a *nitrile* (after **nucleophilic substitution** of an *alkylhalide*) - **grows the carbon chain**



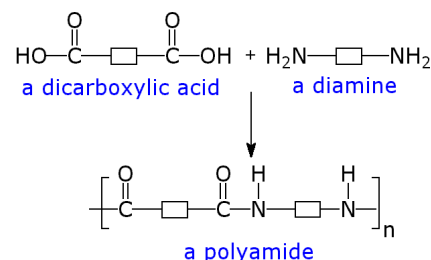
Hydrolysis of an *ester*



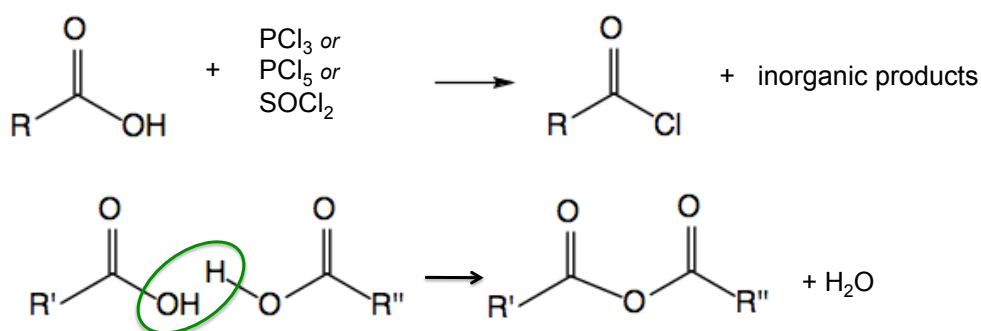
Another previously met reaction of *carboxylic acids* involves the formation of an *amide* (a **condensation** reaction in which an *acid* and an *amine* join together with the elimination of a small stable molecule, usually *water*). An *amide* can also be considered as a **derivative** of an *acid*.



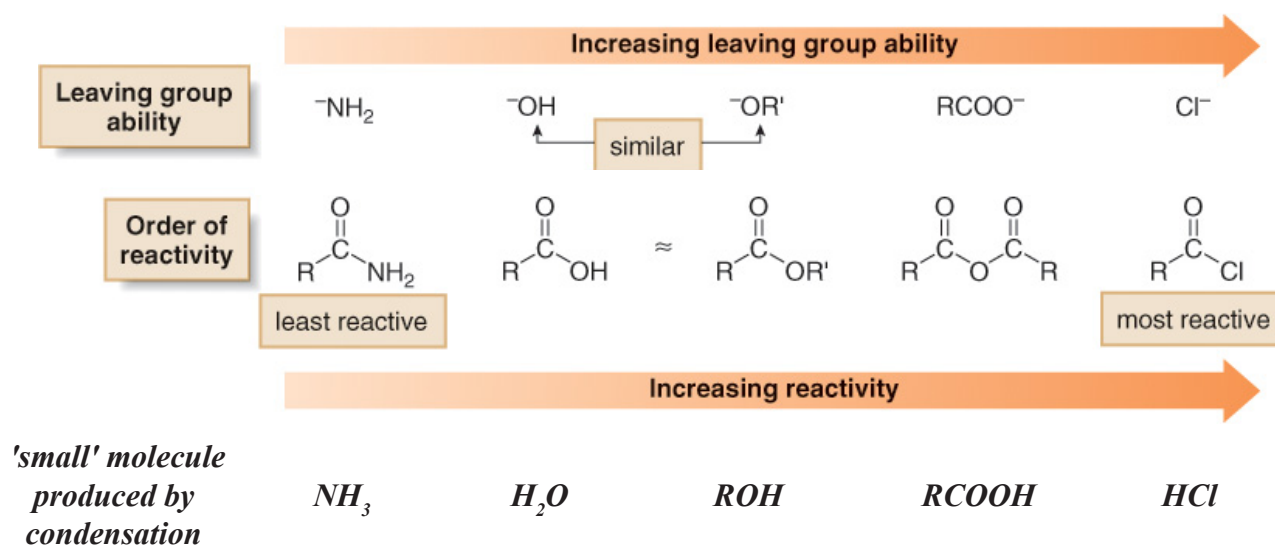
The **amide link** is much used in the manufacture of polymers, whilst the same **condensation** reaction is used to join together *amino acids* in the production of *proteins*, though in this context it is more normally referred to as the **peptide link**.

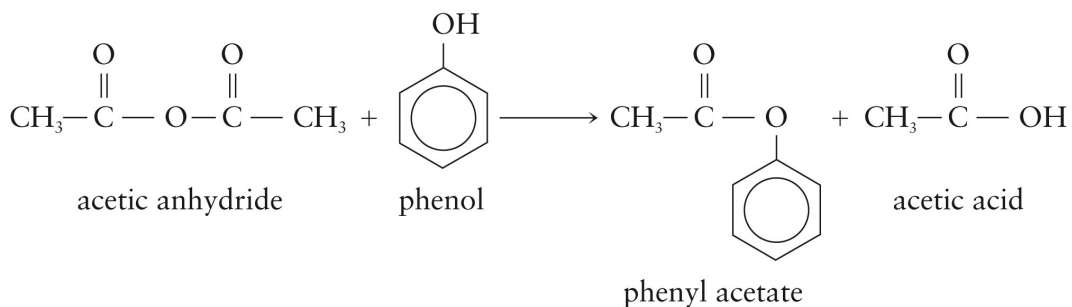
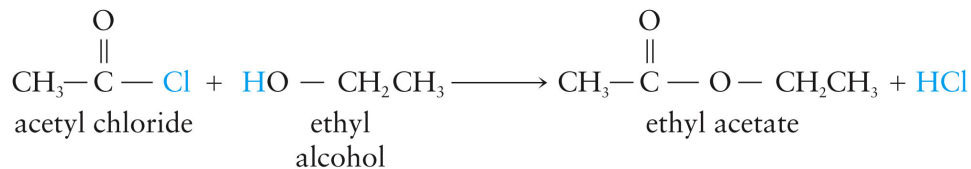


Two less familiar **condensation** reactions lead to unfamiliar products - an *acid chloride* and an *anhydride*.

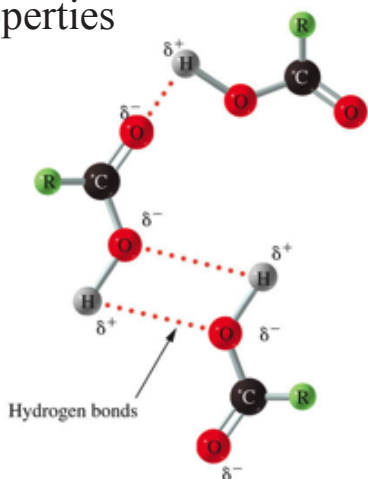


Unusually, the significance of these **derivatives** is less as products and more as **alternative reactants**. All of these **derivatives**, including *esters and amides*, are themselves capable of doing the **same condensation** reactions as the *acid* molecules themselves. However, they can be **more reactive** which can make them the preferred option in many **synthesis pathways** as **alternatives to acids** - particularly the *acid chlorides*.





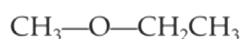
Properties



The properties of *acids* are strongly influenced by the ability of the molecules to set up **hydrogen bonding**. This can be seen clearly by comparing molecules of *similar size and mass*.



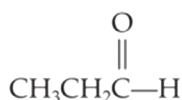
Butane
(butane)
M.W. = 58
b.p. -0.5°C



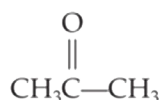
Methoxyethane
(ethyl methyl ether)
M.W. = 60
b.p. 7.0°C



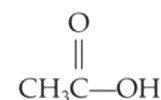
1-Propanol
(propyl alcohol)
M.W. = 60
b.p. 97.2°C



Propanal
(propionaldehyde)
M.W. = 58
b.p. 49°C

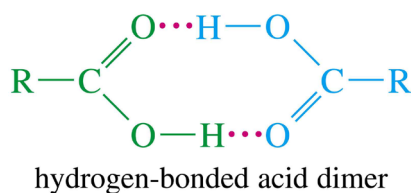


Propanone
(acetone)
M.W. = 58
b.p. 56°C

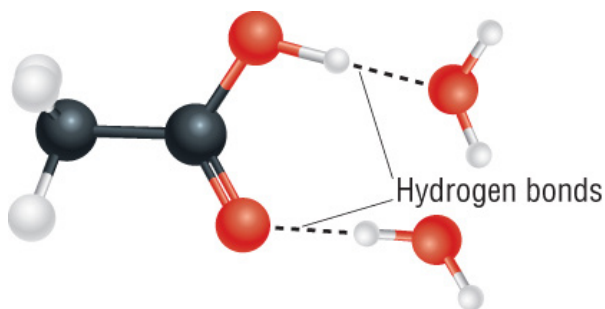


Ethanoic acid
(acetic acid)
M.W. = 60
b.p. 118°C

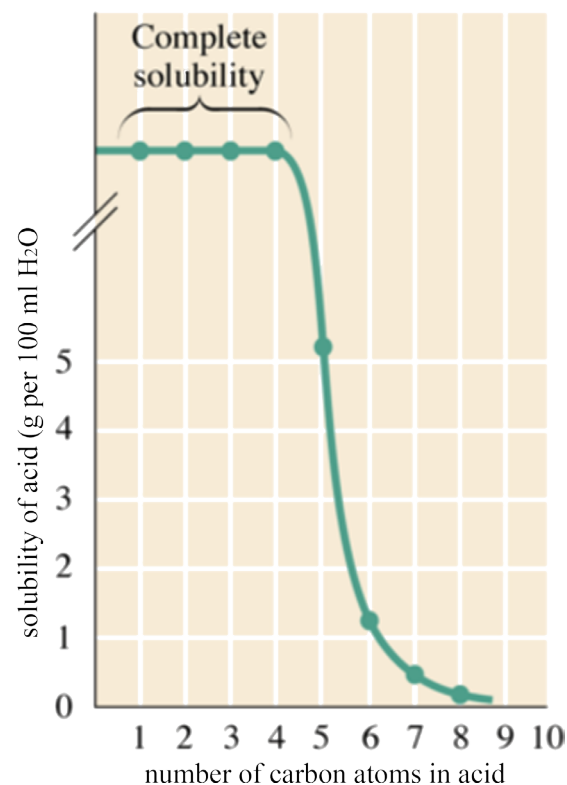
Acids can often form *two hydrogen bonds* which lock two molecules together to form a **dimer**.



The ability to *hydrogen bond* with water molecules ensures that the smaller carboxylic acids are **very soluble in water**.



However, the solubility falls off quite quickly as the length of the carbon chain increases.



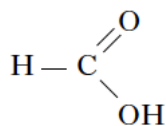
35. A compound C_3H_8O does not react with sodium and is not reduced by lithium aluminium hydride. It is likely to be an

- A acid
- B ether
- C alcohol
- D aldehyde.

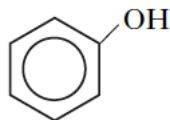
36. Which of the following is least acidic?

A CH_3OH

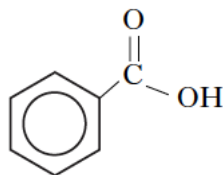
B



C



D



37. Two isomeric esters, X and Y, have the molecular formula $C_4H_8O_2$. Ester X on hydrolysis with sodium hydroxide solution gives CH_3CH_2COONa , and ester Y on similar treatment gives CH_3CH_2OH .

Which line in the table shows the correct names of X and Y?

	X	Y
A	propyl methanoate	ethyl ethanoate
B	methyl propanoate	ethyl ethanoate
C	methyl propanoate	ethyl methanoate
D	propyl methanoate	methyl propanoate

38. A white crystalline compound, soluble in water, was found to react with both dilute hydrochloric acid and sodium hydroxide solution.

Which of the following might it have been?

A C_6H_5OH

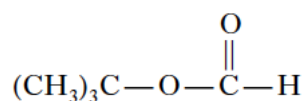
B $C_6H_5NH_2$

C C_6H_5COOH

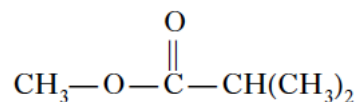
D H_2NCH_2COOH

39. Which of the following esters gives a secondary alcohol when hydrolysed?

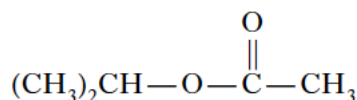
A



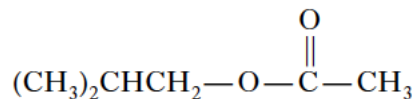
B



C



D



40. Which of the following will react with dilute sodium hydroxide solution?

A $CH_3CHOHCH_3$

B $CH_3CH=CH_2$

C CH_3COOCH_3

D $CH_3CH_2OCH_3$

41. Which of the following compounds would be produced by passing ammonia gas into dilute ethanoic acid?

A CH_3CONH_2

B $CH_3COO-NH_4^+$

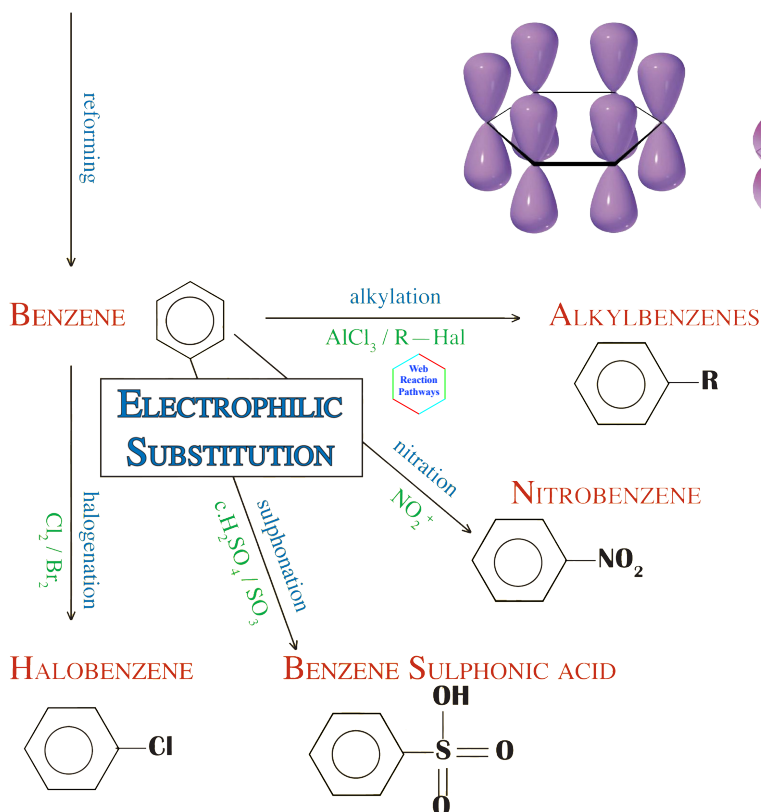
C NH_2CH_2COOH

D $CH_3CH_2NH_3^+Cl^-$

AROMATICS

CH_3CH_3
ALKANES

Aromatics are an enormous group of chemicals based on the *benzene* ring. The ring gives distinctive properties to any molecule that contains it.

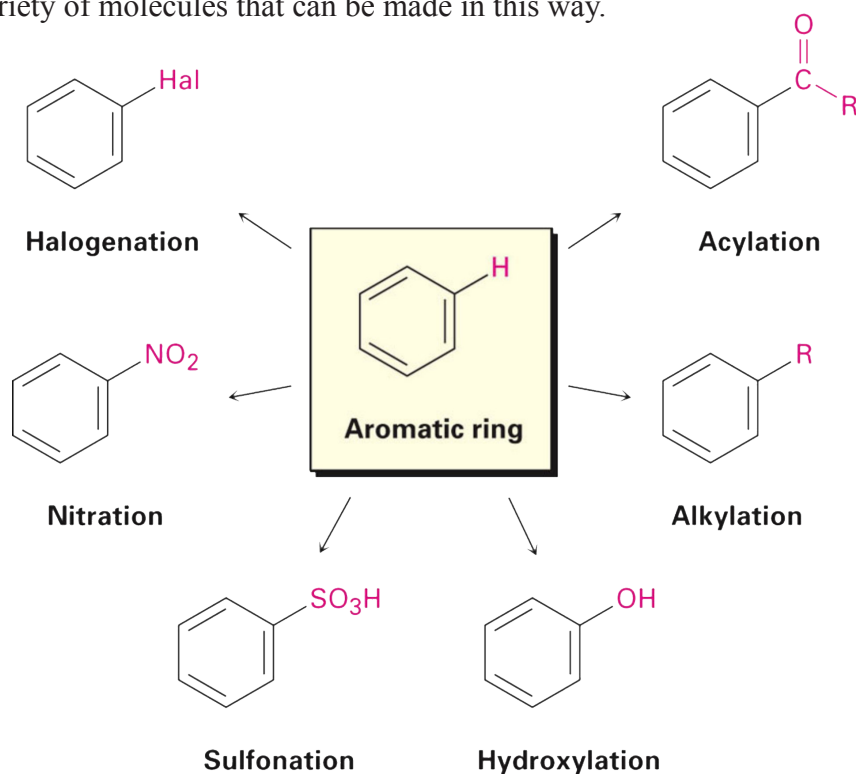


Despite the *unsaturated* nature of a *benzene*, it does not readily undergo *addition* reactions as this would destroy the *delocalised π cloud* which is responsible for the *great stability of this ring structure*.

Most functional groups are introduced into the *benzene* ring by means of a *substitution* reaction. Though the *delocalised π cloud* of electrons will be disturbed during the reaction, it will be re-established in the final product molecule.

Electrophilic Substitution

Though only four *electrophilic substitution* reactions need to be learnt in detail for Advanced Higher, there are a wide variety of molecules that can be made in this way.

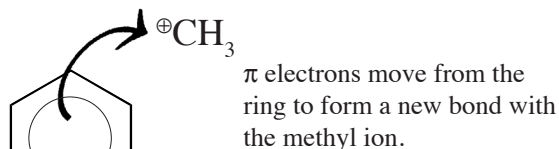
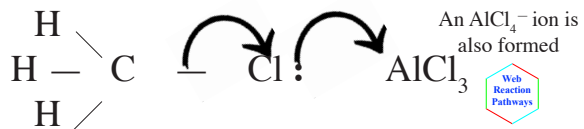


ELECTROPHILIC SUBSTITUTION

This is the main reaction of benzene rings. Though they have even more π electrons than the $C=C$ bond in alkenes, they **resist addition** because the loss of the **delocalised ring** is too destabilising.

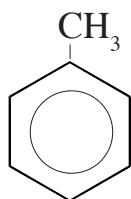
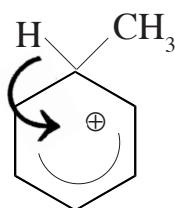
ALKYLATION - USING ALKYL HALIDES/ $AlCl_3$

The production of the **electrophile** requires the presence of $AlCl_3$. (The Al make use of its empty 4th orbital).



The positive charge is shared over the whole ring.

Electrons move from the $C-H$ bond, a H^+ ion is **eliminated**.

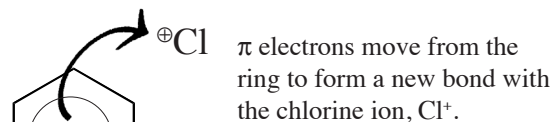


Overall, an alkyl group takes the place of a hydrogen atom, **SUBSTITUTION**.

The H^+ ion reacts with the $AlCl_4^-$ to reform $AlCl_3$ and a molecule of HCl .

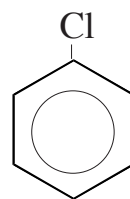
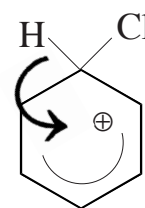
HALOGENATION - USING HALOGENS/ $AlCl_3$

The production of the **electrophile** is helped by the presence of $AlCl_3$. The reaction would be very slow otherwise.



The positive charge is shared over the whole ring.

Electrons move from the $C-H$ bond, a H^+ ion is **eliminated**.

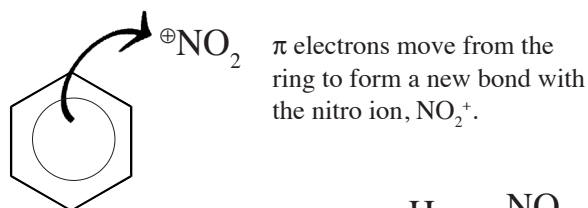


Overall, a halogen atom takes the place of a hydrogen atom, **SUBSTITUTION**.

The H^+ ion reacts with the $AlCl_4^-$ to reform $AlCl_3$ and a molecule of HCl .

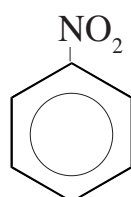
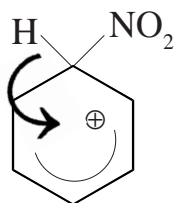
NITRATION - USING H_2SO_4/HNO_3

The production of the **electrophile**, NO_2^+ is a result of a reaction between these two strong acids.



The positive charge is shared over the whole ring.

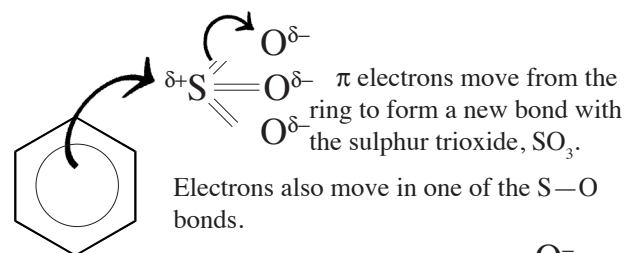
Electrons move from the $C-H$ bond, a H^+ ion is **eliminated**.



Overall, a nitro group takes the place of a hydrogen atom, **SUBSTITUTION**.

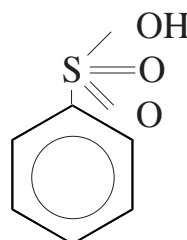
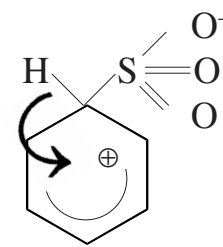
SULPHONATION - USING H_2SO_4/SO_3

The **electrophile** is a molecule of SO_3 . The 3 oxygen atoms are more electronegative; a large δ^+ forms on the sulphur.



The positive charge is shared over the whole ring.

Electrons move from the $C-H$ bond, a H^+ ion is **eliminated**.

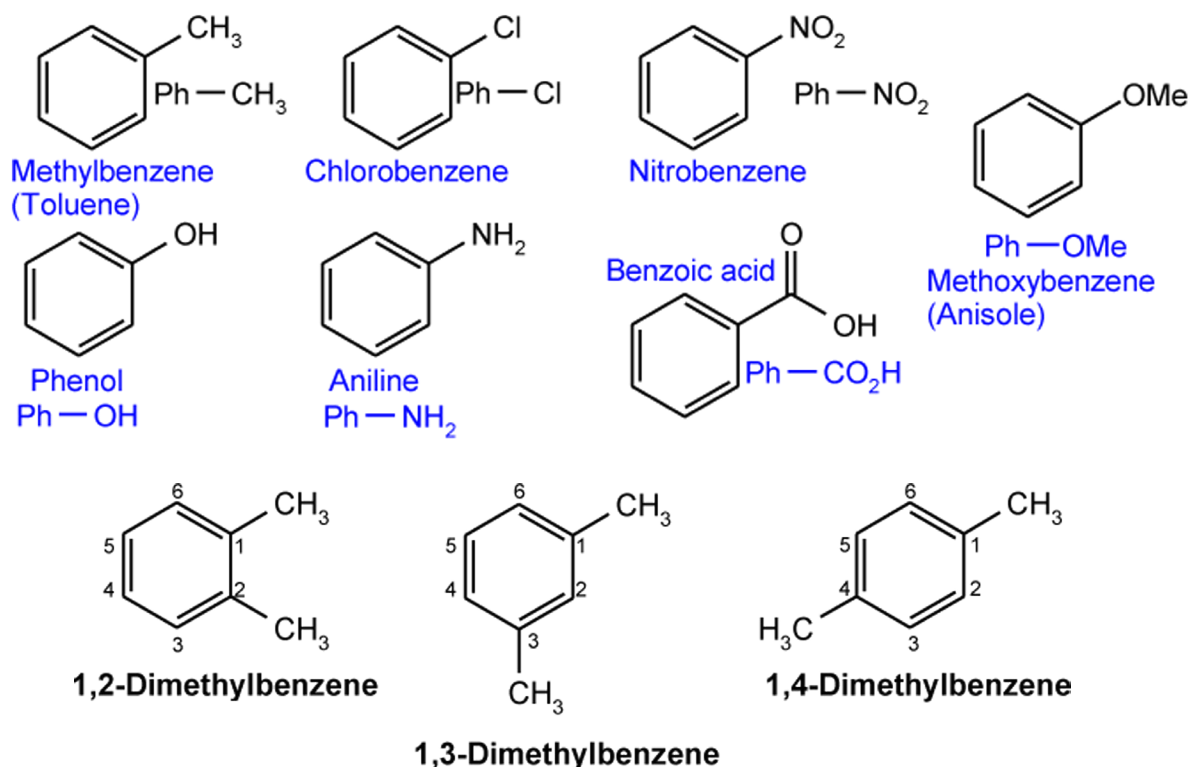


The H^+ ion that is eliminated from the benzene ring attaches itself to the oxygen ion.

Overall, a HSO_3 group takes the place of a hydrogen atom, **SUBSTITUTION**.

Common Aromatics

Most of the aromatics you will come across are *substituted benzene* rings and can be named accordingly with the substituent's name preceding *benzene* - *chlorobenzene*. Alternatively the label *phenyl* can be used for the *benzene* ring followed by the substituent - *phenylchloride*.

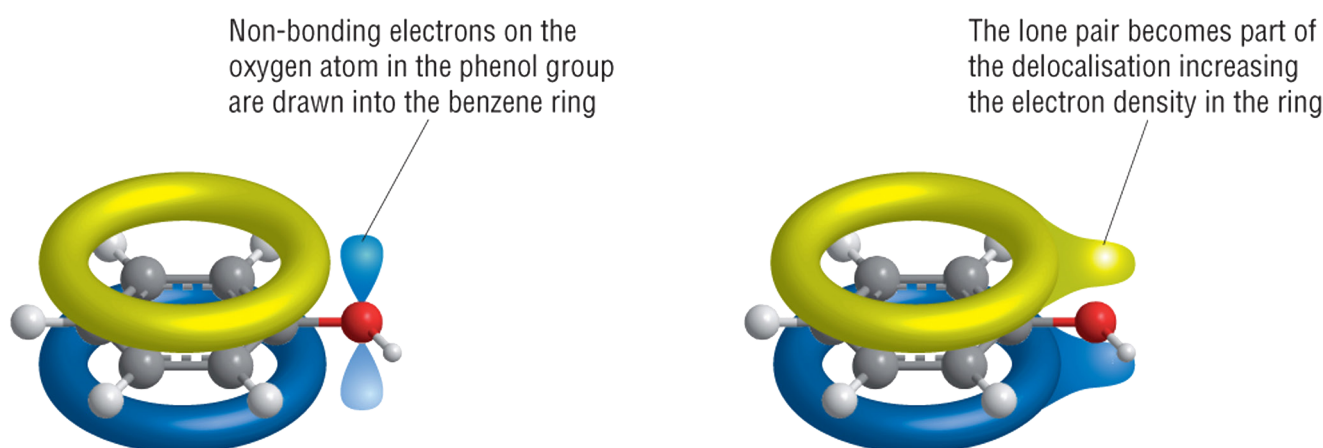


Conjugated Systems

In general, you can assume that a *functional group* attached to a *benzene* ring will continue to behave as normal. There are, however, two exceptions that you will be expected to be aware of.

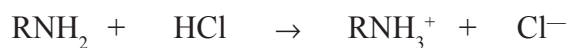
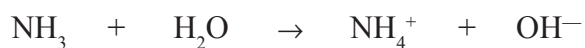
Alcohols all possess a *very polar* O — H bond, but have little to no ability to form H^+ ions (*acidity*) due to the instability of the *alkoxide ion* that would also have to form. *Phenol* is an exception. The **molecular orbital** of the *benzene* ring can extend to form a **conjugated system** with the orbitals containing the lone pairs on the *oxygen*. This draws electrons away from the *oxygen* to be shared between 7 atoms (1 *oxygen* plus 6 *carbons*).

This allows *phenol* (also called *carbolic acid*) to be **weakly acidic**.



A similar **conjugated system** can be set up in *aniline* (*aminobenzene* or *phenylamine*) with the lone pair of electrons on the nitrogen atom.

However, *amines* rely on the attraction of their lone pair for H^+ ions to give them their **basic** properties.

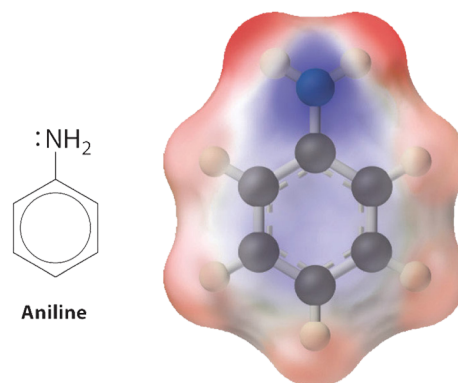
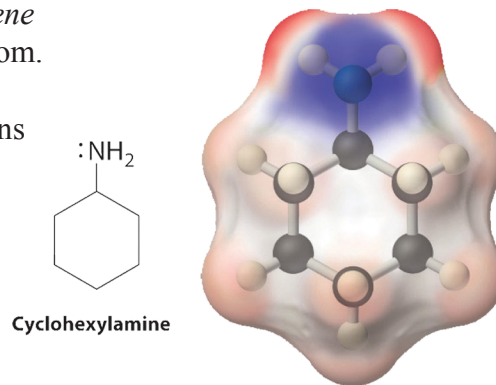


The formation of the **conjugated system** results in electrons being drawn away from the *amine* group which explains why *aniline* is a **much weaker base** than would be expected.

The strengths of weak bases are measured on the pK_b scale. The smaller the number on this scale, the stronger the base is.

<i>ammonia</i>	pK_b	4.75
<i>methylamine</i>	pK_b	3.36
<i>phenylamine</i>	pK_b	9.38

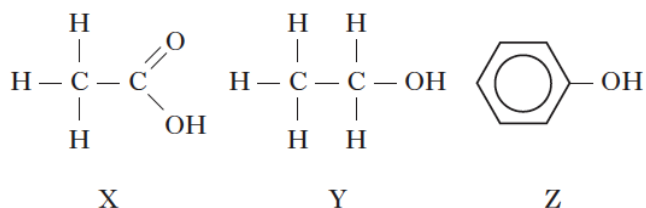
Methylamine is a stronger base than *ammonia* because alkyl chains are generally *electron donating* (the **inductive effect** met earlier) and so increase the electron density on the nitrogen atom.



42. Chlorobenzene, nitrobenzene and ethylbenzene can all be formed from benzene by

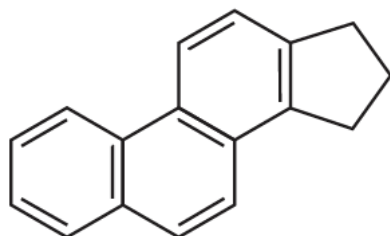
- A electrophilic substitution
 B electrophilic addition
 C nucleophilic substitution
 D nucleophilic addition.

43. Which of the following shows the above compounds in order of increasing acid strength?



- A X Y Z
 B Y Z X
 C Z X Y
 D X Z Y

44.



What is the molecular formula for the above structure?

- A $C_{17}H_{11}$
 B $C_{17}H_{14}$
 C $C_{17}H_{17}$
 D $C_{17}H_{20}$

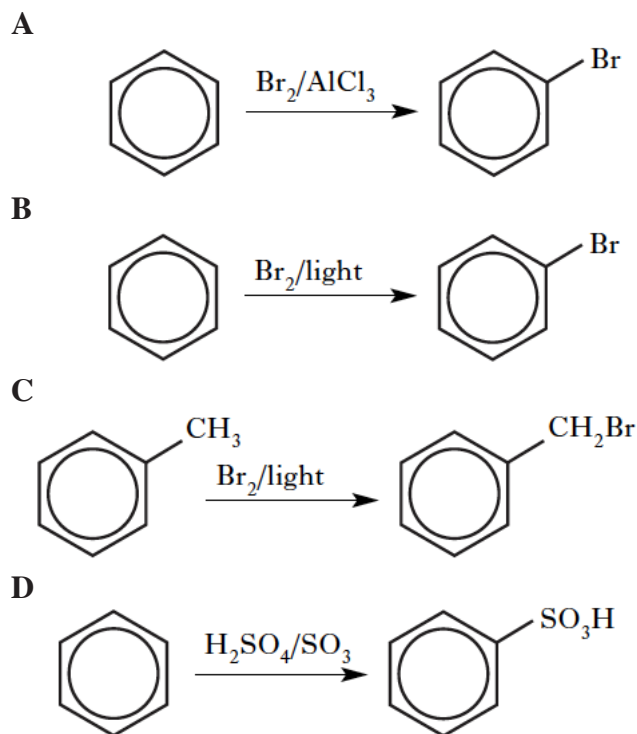
45. Which of the following compounds is soluble in water and reacts with both dilute hydrochloric acid and sodium hydroxide solution?

- A $C_2H_5NH_2$
 B $C_6H_5NH_2$
 C $C_2H_5NH_3Cl$
 D $HOOCCH_2NH_2$

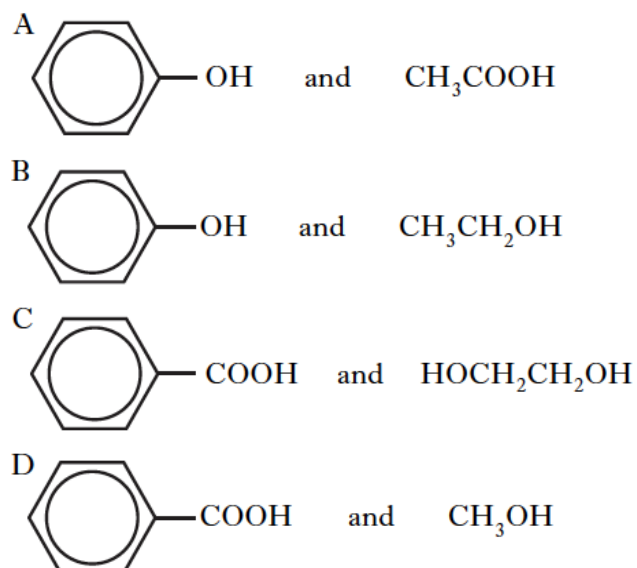
46. Which of the following molecules is planar?

- A Hexane
 B Cyclohexane
 C Chlorobenzene
 D Methylbenzene (toluene)

47. Which of the following reactions is least likely to take place?



48. In which of the following pairs does an aqueous solution of the first compound have a higher pH than an aqueous solution of the second?



3.2. ORGANIC SYNTHESIS

Hydrocarbons & Haloalkanes

- 3.2.1** *Bonding in alkanes can be described in terms of sp^3 hybridisation and sigma bonds.*
- 3.2.2** *Hybridisation is the process of mixing atomic orbitals in an atom to generate a set of new atomic orbitals called hybrid orbitals.*
- 3.2.3** *A sigma (σ) bond is a covalent bond formed by end on overlap of two atomic orbitals lying along the axis of the bond*
- 3.2.4** *Alkanes undergo substitution reactions with chlorine and bromine by a chain reaction mechanism.*
- 3.2.5** *The chain reaction includes the following steps*
- (i) initiation by homolytic fission to produce radicals*
 - (ii) propagation*
 - (iii) termination*
- 3.2.6** *Bonding in ethene can be described in terms of sp^2 hybridisation, sigma and pi bonds.*
- 3.2.7** *Alkenes can be prepared in the laboratory by*
- (i) dehydration of alcohols using aluminium oxide, concentrated sulphuric acid or orthophosphoric acid*
 - (ii) base-induced elimination of hydrogen halides from monohalogenoalkanes.*
- 3.2.8** *Alkenes undergo:*
- (i) catalytic addition with hydrogen to form alkanes*
 - (ii) addition with halogens to form dihalogenoalkanes*
 - (iii) addition with hydrogen halides according to Markovnikov's rule to form monohalogenoalkanes*
 - (iv) acid-catalysed addition with water according to Markovnikov's rule to form alcohols.*
- 3.2.9** *The mechanisms of the above reactions involve*
- (i) for halogenation cyclic ion intermediate*
 - (ii) for hydrohalogenation carbocation intermediate*
 - (iii) for acid catalysed hydration carbocation intermediate*
- 3.2.10** *Halogenoalkanes are named according to IUPAC rules.*
- 3.2.11** *Monohalogenoalkanes can be classified as primary, secondary or tertiary.*
- 3.2.12** *Monohalogenoalkanes undergo nucleophilic substitution reactions.*
- 3.2.13** *Monohalogenoalkanes undergo elimination reactions to form alkenes.*

3.2.14 Monohalogenoalkanes react with:

- (i) alkalis to form alcohols
- (ii) alcoholic alkoxides to form ethers
- (iii) ethanolic cyanide to form nitriles which can be hydrolysed to carboxylic acids(chain length increased by one carbon atom)
- (iv) ammonia to form amines via alkyl ammonium salts.

Alcohols and ethers

3.2.15 Alcohols exhibit hydrogen bonding and as a result have higher boiling points than other organic compounds of comparable relative formula mass and shape.

3.2.16 The lower alcohols are miscible with water but as their chain length increases their solubility in water decreases.

3.2.17 Alcohols can be prepared from

- (i) alkenes by hydration
- (ii) halogenoalkanes by substitution.

3.2.18 In industry, alcohols (except methanol) can be manufactured by the acid-catalysed hydration of alkenes.

3.2.19 Alcohols react with some reactive metals to form alkoxides .

3.2.20 Alcohols can be dehydrated to alkenes.

3.2.21 Alcohols undergo condensation reactions slowly with carboxylic acids and more vigorously with acid chlorides to form esters.

3.2.22 Ethers have the general formula R^1-O-R^2 where R^1 and R^2 are alkyl groups.

3.2.23 Ethers are named according to IUPAC rules.

3.2.24 Due to the lack of hydrogen bonding, ethers have lower boiling points than the corresponding isomeric alcohols.

3.2.25 Ether molecules can hydrogen bond with water molecules thus explaining the solubility in water of some ethers of low relative formula mass.

3.2.26 Ethers are highly flammable and on exposure to air may form explosive peroxides.

3.2.27 Ethers can be prepared by the reaction of halogenoalkanes with alkoxides.

3.2.28 Ethers are useful solvents for many organic compounds due to

- (i) relative stability with respect to oxidation and reduction
- (ii) polarity

Aldehydes, ketones & carboxylic acids

- 3.2.29** *The following physical properties can be explained in terms of dipole-dipole attractions and/or hydrogen bonding*
- (i) *higher boiling points than corresponding alkanes*
 - (ii) *lower boiling points than corresponding alcohols*
 - (iii) *miscibility of lower members with water*
- 3.2.30** *Tollens' reagent or Benedict's solution can be used to distinguish between aldehydes and ketones. Aldehydes reduce the complexed silver(I) ion and the complexed copper(II) ion to silver and copper(I), respectively.*
- 3.2.31** *Aldehydes and ketones can be reduced to primary and secondary alcohols, respectively, by reaction with lithium aluminium hydride in ether.*
- 3.2.32** *Aldehydes and ketones undergo*
- (i) *addition reactions in which the carbon atom in the polar carbonyl group submits to nucleophilic attack.*
 - (ii) *condensation reactions with derivatives of ammonia (XNH_2) which proceed by nucleophilic addition of XNH_2 followed by elimination of a water molecule.*
- 3.2.33** *The reaction with 2,4-dinitrophenylhydrazine to form a 2,4-dinitrophenylhydrazone is an example of a condensation reaction.*
- 3.2.34** *The melting points of the resulting 2,4-dinitrophenylhydrazones are used to identify carbonyl compounds.*
- 3.2.35** *Aldehydes are generally more reactive than ketones because the presence of two alkyl groups in ketones hinders nucleophilic attack and reduces the partial positive charge on the carbonyl carbon atom.*
- 3.2.36** *In pure carboxylic acids hydrogen bonding produces dimers thus explaining the relatively high boiling points. Dimerisation does not occur in aqueous solution.*
- 3.2.37** *Carboxylic acid molecules also form hydrogen bonds with water molecules thus explaining the appreciable solubility of the lower carboxylic acids in water. As the chain length increases water solubility decreases.*
- 3.2.38** *Carboxylic acids are weak acids. Their slight dissociation in water can be explained by the stability of the carboxylate ion caused by electron delocalisation.*
- 3.2.39** *Carboxylic acids can be prepared by:*
- (i) *oxidising primary alcohols and aldehydes*
 - (ii) *hydrolysing nitriles, esters or amides*

3.2.40 *Reactions of carboxylic acids include:*

- (i) *formation of salts by reactions with metals, carbonates and alkalis*
- (ii) *condensation reactions with alcohols to form esters*
- (iii) *reaction with ammonia or amines and subsequent heating of the ammonium salt to form amides*
- (iv) *reduction with lithium aluminium hydride to form primary alcohols.*

Amines

3.2.41 *Amines are named according to IUPAC rules.*

3.2.42 *Amines are organic derivatives of ammonia and can be classified as primary, secondary or tertiary.*

3.2.43 *Primary and secondary amines, but not tertiary amines, associate by hydrogen bonding and as a result have higher boiling points than isomeric tertiary amines and alkanes with comparable relative formula masses.*

3.2.44 *Amine molecules can hydrogen bond with water molecules thus explaining the appreciable solubility of the lower amines in water.*

3.2.45 *The nitrogen atom in amines has a lone pair of electrons which can accept a proton from water, producing hydroxide ions. Amines are weak bases.*

3.2.46 *Amines react with aqueous mineral or carboxylic acids to form salts.*

Aromatics

3.2.47 *Bonding in benzene can be described in terms of sp^2 hybridisation, sigma and pi bonds and electron delocalisation.*

3.2.48 *Benzene is the simplest aromatic hydrocarbon and its unexpected stability can be attributed to the presence of delocalised electrons.*

3.2.49 *Most reactions of benzene involve attack of an electrophile on the cloud of delocalised electrons, that is electrophilic substitution.*

3.2.50 *Benzene resists addition reactions but undergoes electrophilic substitution reactions. These include:*

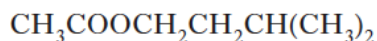
- (i) *chlorination and bromination to produce chlorobenzene and bromobenzene*
- (ii) *nitration to produce nitrobenzene*
- (iii) *sulphonation to produce benzene sulphonic acid*
- (iv) *alkylation to produce alkylbenzenes.*

3.2.51 *The presence of delocalised electrons in the phenyl group can be used to explain:*

- (i) *the stronger acidic nature of phenol compared to aliphatic alcohols*
- (ii) *the weaker basic nature of the aromatic amine, aniline compared with aliphatic amines.*

Exam Practice

1. Isoamyl acetate is found naturally as the flavour and scent of bananas.
Its shortened structural formula is

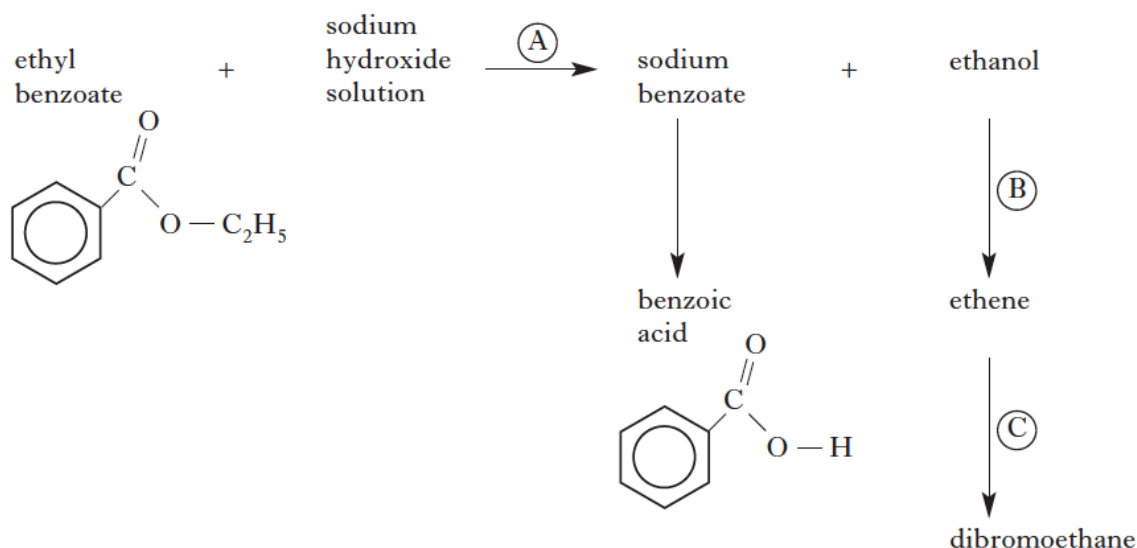


- (a) (i) To which class of organic compounds does isoamyl acetate belong? 1
(ii) Apart from flavouring agents, suggest another common use for this class of organic compound. 1

Isoamyl acetate can be made in the laboratory by reacting ethanoic acid with another substance, **X**.

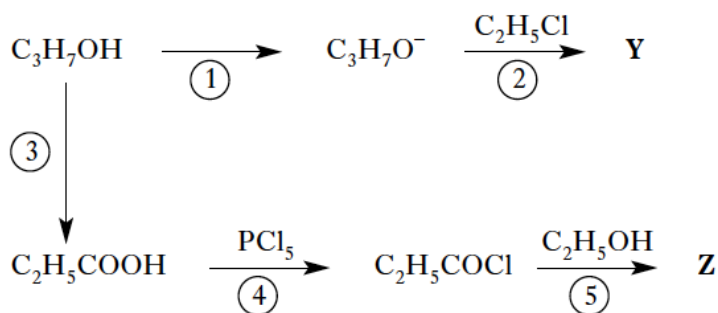
- (b) (i) Write the systematic name of substance **X**. 1
(ii) Name the type of reaction which takes place. 1
(4)

2. A student designed the following reaction scheme starting from ethyl benzoate.



- (a) In a PPA, benzoic acid was prepared from ethyl benzoate.
(i) Name the type of reaction occurring in step (A). 1
(ii) What is added to sodium benzoate solution to precipitate out benzoic acid? 1
(iii) Name the procedure used to purify the benzoic acid. 1
(iv) Assuming the percentage yield is 70%, what is the minimum mass of ethyl benzoate required to produce at least 4.0 g of benzoic acid? 2
- (b) (i) Name the type of reaction occurring in step (B). 1
(ii) Using structural formulae, outline the mechanism for the reaction occurring in step (C). 2
(8)

3. A student devised the following reaction sequence starting from propan-1-ol, C_3H_7OH .



- (a) Name a suitable reagent to carry out
- Step $\textcircled{1}$
 - Step $\textcircled{3}$.
- (b) Name Y.
- (c) Draw a structural formula for Z.

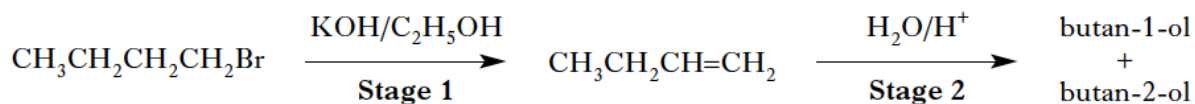
2

1

1

(4)

4. A mixture of butan-1-ol and butan-2-ol can be synthesised from 1-bromobutane in a two stage process.



- (a) What type of reaction is taking place in **Stage 1**?
- (b) The bonding in but-1-ene can be described in terms of sp^2 and sp^3 hybridisation and sigma and pi bonds.
- What is meant by sp^2 hybridisation?
 - What is the difference in the way atomic orbitals overlap to form sigma and pi bonds?
- (c) Draw a structural formula for the major product of **Stage 2**.
- (d) 1-Bromobutane reacts with hydroxide ions in a nucleophilic substitution reaction to produce butan-1-ol. The following results were obtained for this reaction.

1

1

1

1

Experiment	[1-Bromobutane]/mol l ⁻¹	[OH ⁻]/mol l ⁻¹	Initial rate/mol l ⁻¹ s ⁻¹
1	0.25	0.10	3.3×10^{-6}
2	0.50	0.10	6.6×10^{-6}
3	0.50	0.20	1.3×10^{-5}

- What is the overall order of this reaction?
- Calculate a value for the rate constant of this reaction, giving the appropriate units.
- Outline the mechanism for this nucleophilic substitution reaction using structural formulae.

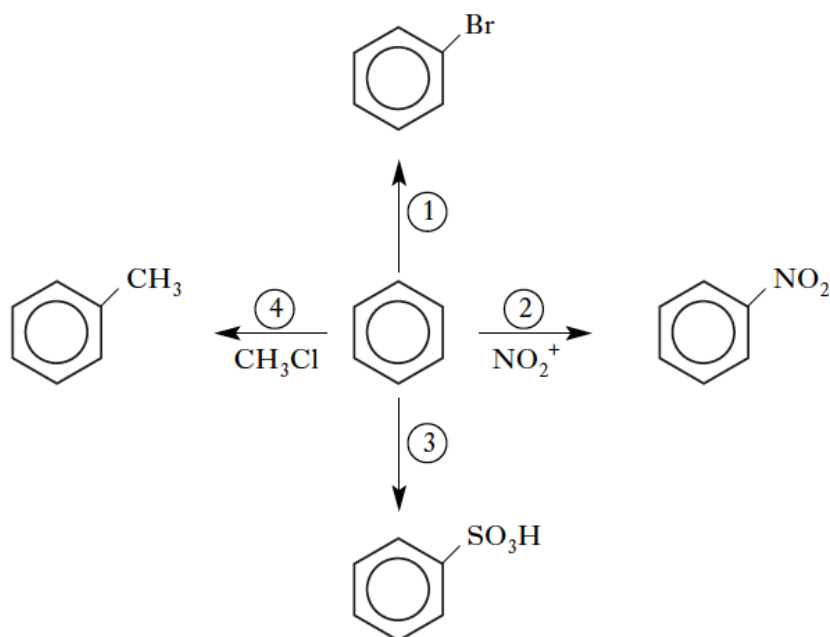
1

2

2

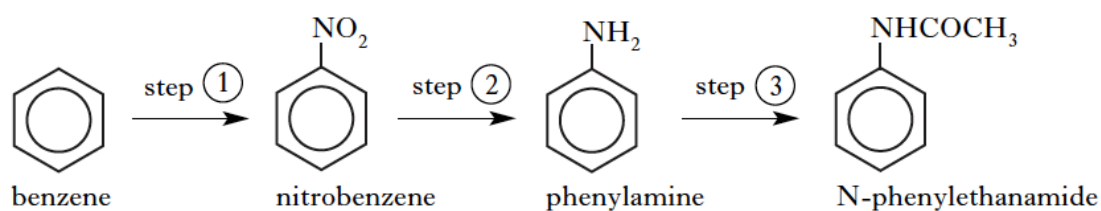
(9)

7. A student devised the following reaction scheme starting with benzene.



- (a) What type of reaction does benzene undergo in reactions (1) – (4)? 1
- (b) Name a suitable reagent and catalyst for reaction (1). 1
- (c) Reaction (2) involves nitration of benzene.
Which reagents are used to produce the NO₂⁺ ion? 1
- (d) What is the molecular formula for the product of reaction (3)? 1
- (e) The product of reaction (4) was reacted with bromine in the presence of light.
Draw a structural formula for an organic product of this reaction. 1
- (5)**

8. N-Phenylethanamide can be prepared from benzene in three steps.



- (a) What chemicals are required to react with benzene to bring about step (1)? 1
- (b) What type of reaction occurs in step (2)? 1
- (c) Suggest a reagent which could be used to bring about step (3). 1
- (3)**

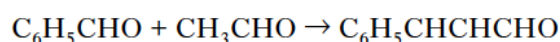
9. Alkenes can be prepared from alcohols.

In a PPA, 22.56 g of cyclohexanol was dehydrated using an excess of concentrated phosphoric acid. The reaction mixture was then distilled. The crude cyclohexene was added to a separating funnel containing a solution which was used to wash the cyclohexene and improve the separation of the aqueous and organic layers. The organic layer was separated and treated with anhydrous calcium chloride before it was distilled to yield 6.52 g of pure cyclohexene.

- (a) Why was concentrated phosphoric acid used as the dehydrating agent rather than concentrated sulphuric acid? 1
- (b) Name the solution that the crude cyclohexene was added to in the separating funnel. 1
- (c) What was the function of the anhydrous calcium chloride? 1
- (d) The relative formula masses of cyclohexanol and cyclohexene are 100 and 82 respectively. Calculate the percentage yield of cyclohexene. 2

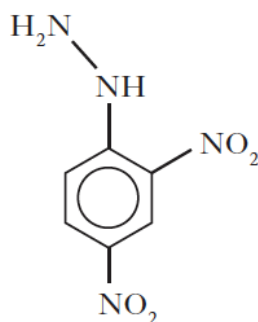
(5)

10. Cinnamaldehyde is an aromatic compound found in cinnamon. It can also be prepared by the reaction of benzaldehyde and ethanal.



- (a) What type of reaction is this? 1
- (b) Draw a full structural formula for cinnamaldehyde. 1
- (c) All three of the carbonyl compounds shown above react with 2,4-dinitrophenylhydrazine, (Brady's reagent), forming solid derivatives.

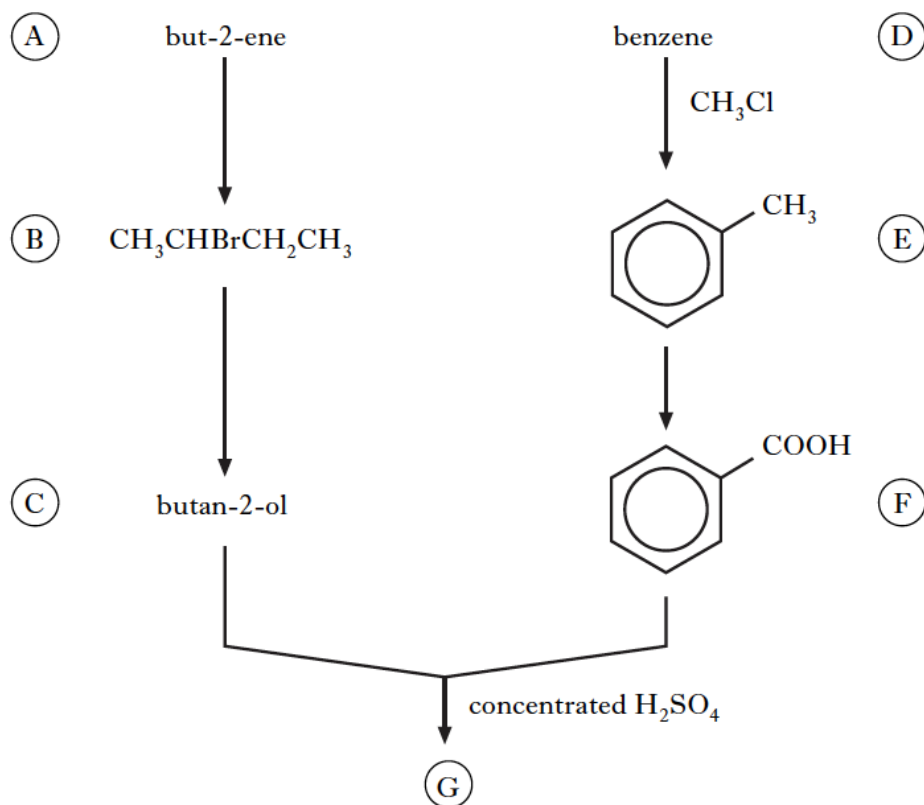
The structure of 2,4-dinitrophenylhydrazine is



- (i) Draw a structural formula of the compound formed when ethanal reacts with 2,4-dinitrophenylhydrazine. 1
- (ii) The compound formed is impure. How would this compound be purified? 1
- (iii) How would the purified compound be used to show that the original carbonyl compound was ethanal? 1
- (iv) 2,4-Dinitrophenylhydrazone derivatives have distinctive colours. What colour is the 2,4-dinitrophenylhydrazone derivative of propanone? 1

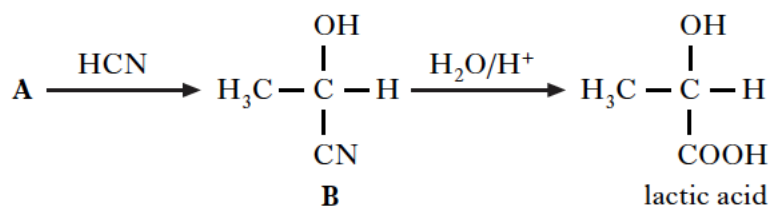
(6)

11. Consider the following reaction scheme.



- (a) Explain why but-2-ene exhibits geometric isomerism yet its structural isomer but-1-ene does not. 1
- (b) But-2-ene undergoes electrophilic addition to form (B).
Draw a structure for the carbocation intermediate formed in this electrophilic addition reaction. 1
- (c) Name a reagent used to convert (B) to (C). 1
- (d) Name a catalyst required in converting (D) to (E). 1
- (e) Draw a structural formula for ester (G). 1
- (5)**

12. Consider the following reaction sequence.

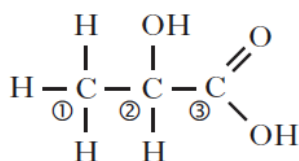


- (a) Name compound A. 1
- (b) To which class of organic compounds does compound B belong? 1
- (c) Name the type of reaction taking place in converting compound B into lactic acid. 1

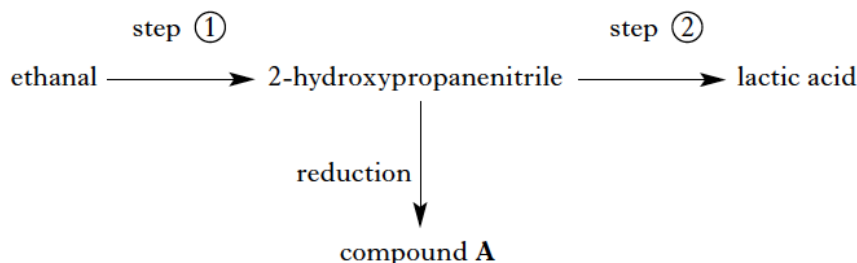
13. When sodium hydroxide solution was added to 2-bromomethylpropane an S_N1 reaction took place producing methylpropan-2-ol and hydrobromic acid.

- (a) (i) What is meant by an S_N1 reaction? 2
- (ii) Draw the structure of the carbocation intermediate formed in this reaction. 1
- (b) Chloromethane reacts with sodium ethoxide in an S_N2 reaction.
- (i) How is sodium ethoxide prepared in the laboratory? 1
- (ii) Name the organic product of this S_N2 reaction. 1
- (5)**

14. The structure of lactic acid is



- (a) What is the systematic name of lactic acid? 1
- (b) Lactic acid contains an asymmetric carbon atom.
Identify, and **explain**, which one of the numbered carbon atoms is asymmetric. 1
- (c) Lactic acid can be produced from ethanal by the reaction sequence below.



- (i) Which reagent could be used in step ①? 1
- (ii) What type of reaction takes place in step ②? 1
- (iii) Draw a structure for compound A. 1
- (5)**

Multiple Choice Answers

Page 7:

1.	D	2.	B	3.	A	4.	C	5.	D	6.	C	7.	D	8.	B	9.	D
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Page 15:

10.	C	11.	D	12.	C	13.	A	14.	A	15.	D	16.	A	17.	C
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Page 24:

18.	D	19.	B	20.	B	21.	B	22.	C	23.	B	24.	A	25.	C	26.	C
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Page 30:

27.	B	28.	B	29.	D	30.	A	31.	B	32.	C	33.	A	34.	B
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Page 35:

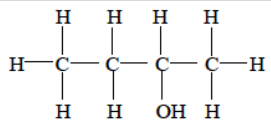
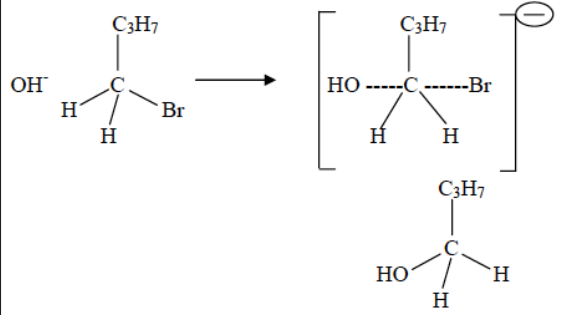
35.	B	36.	A	37.	B	38.	D	39.	C	40.	C	41.	B
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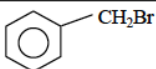
Page 40:

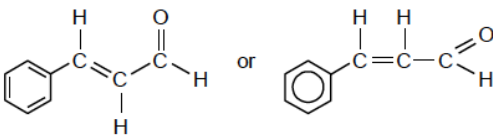
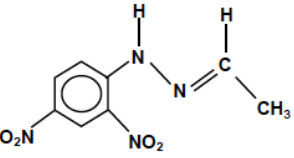
42.	A	43.	B	44.	B	45.	D	46.	C	47.	B	48.	A
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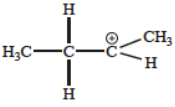
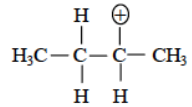
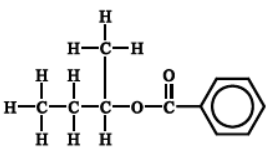
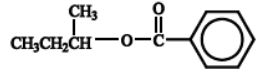

Exam Practice Answers

Question	Acceptable Answer	Mark	Unacceptable Answer
1. (a)	(i) Esters	1	
	(ii) Solvents, perfumes etc	1	To make things smell good
(b)	(i) 3-methylbutan-1-ol	1	3-methylbut-1-ol
	(ii) Condensation/esterification	1	
Question	Acceptable Answer	Mark	Unacceptable Answer
2. (a)	(i) Hydrolysis/Alkaline hydrolysis	1	Acid hydrolysis/substitution
	(ii) Hydrochloric acid/HCl/Conc HCl	1	Weak acid/acids
	(iii) Recrystallisation	1	
	(iv) 7.02 g/7.03 g/7.0g	1	
	Method 1 theoretical mass of benzoic acid = $\frac{4.0 \times 100}{70}$ = 5.71 g	(1)	
	122 \longleftrightarrow 150 5.71 \longleftrightarrow $\frac{150 \times 5.71}{122}$ = 7.02 g (- 1 mark if no units)	(1)	
	Method 2 150 g \longleftrightarrow 122 g $\frac{150 \times 4.0}{122} \longleftrightarrow$ 4.0 = 4.92 mass required = $\frac{4.92 \times 100}{70}$ = 7.03 g (- 1 mark if no units)	(1)	
	Other methods acceptable but deduct 1 mark if wrong GFM which may give correct final answer	(1)	
Question	Acceptable Answer	Mark	Unacceptable Answer
3. (a)	(i) Sodium metal or any reactive metal Any Gp 1 metal and Ba	1	Mg NaOH Ca
	(ii) (Hot) copper (II) oxide or acidified dichromate or acidified permanganate or correct formulae H^+/MnO_4^- $H^+/Cr_2O_7^{2-}$ Copper oxide Acidified chromate	1	Tollens Benedict's/Fehlings } reagents H^+/MnO_4^- $H^+/Cr_2O_7^{2-}$
(b)	Ethoxypropane or ethylpropylether	1	Propoxyethane Propylethylether Do not accept formulae
(c)	$CH_3CH_2 - \overset{O}{\parallel} C - O - CH_2CH_3$ $CH_3CH_2COOCH_2CH_3$ $C_2H_5COOC_2H_5$	1	

Question	Acceptable Answer	Mark	Unacceptable Answer															
4. (a)	Elimination	1	Nucleophilic elimination															
(b) (i)	sp^2 hybridisation is a mixing of one s orbital and two p orbitals, (hybridising of one s orbital and two p orbitals)	1	A 1s orbital...															
(ii)	Sigma bonds – end on overlap of (atomic) orbitals Pi bonds – sideways overlap of (atomic) orbitals 2 correct diagrams	1	Overlap between 2 carbons															
(c)	 or $CH_3CH_2CHOHCH_3$	1																
(d) (i)	2 nd order	1																
(ii)	Rate = $k[OH^-][1\text{-bromobutane}]$ $k = \frac{3.3 \times 10^{-6}}{0.1 \times 0.25} = 1.32 \times 10^{-4}$ or 1.3×10^{-4} Units = $l \text{ mol}^{-1} \text{ s}^{-1}$ Correct units = 1 mark Accept correct follow through from (d) (i) (see below for follow through) <table border="1" data-bbox="287 1209 861 1332"> <thead> <tr> <th>[1 bromobutane]</th> <th>[OH⁻]</th> <th>k</th> </tr> </thead> <tbody> <tr> <td>0.25</td> <td>0.10</td> <td>$1.32 \times 10^{-4} \text{ l mol}^{-1} \text{ s}^{-1}$</td> </tr> <tr> <td>$(0.25)^2$</td> <td>0.10</td> <td>$5.28 \times 10^{-4} \text{ l}^2 \text{ mol}^{-2} \text{ s}^{-1}$</td> </tr> <tr> <td>0.25</td> <td>$(0.10)^2$</td> <td>$1.32 \times 10^{-3} \text{ l}^2 \text{ mol}^{-2} \text{ s}^{-1}$</td> </tr> <tr> <td>$(0.25)^2$</td> <td>$(0.10)^2$</td> <td>$5.28 \times 10^{-3} \text{ l}^3 \text{ mol}^{-3} \text{ s}^{-1}$</td> </tr> </tbody> </table>	[1 bromobutane]	[OH ⁻]	k	0.25	0.10	$1.32 \times 10^{-4} \text{ l mol}^{-1} \text{ s}^{-1}$	$(0.25)^2$	0.10	$5.28 \times 10^{-4} \text{ l}^2 \text{ mol}^{-2} \text{ s}^{-1}$	0.25	$(0.10)^2$	$1.32 \times 10^{-3} \text{ l}^2 \text{ mol}^{-2} \text{ s}^{-1}$	$(0.25)^2$	$(0.10)^2$	$5.28 \times 10^{-3} \text{ l}^3 \text{ mol}^{-3} \text{ s}^{-1}$	1 1	
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$(0.25)^2$	$(0.10)^2$	$5.28 \times 10^{-3} \text{ l}^3 \text{ mol}^{-3} \text{ s}^{-1}$																
(iii)	 – ve charge must be given outside the brackets or on the C (in the transition state)	1 1	C_4H_9Br C_4H_9OH															

Question	Acceptable Answer	Mark	Unacceptable Answer
5. (a)	Condensation or addition + elimination	1	
(b) (i)	By recrystallisation/crystallisation	1	Evaporate off the water
(ii)	Measure melting point of derivative and compare with literature values/expected value/data book value/known value	1	Boiling point instead of MP Measure melting point
(c) (i)	Fehling's solution and blue to orange/brown with the isomer (propanal) or Benedict's → orange/red/green Tollens' reagent and silver mirror with the isomer Acidified dichromate and orange to green with the isomer Acidified permanganate and purple to colourless with the isomer (Hot) copper (II) oxide and black to brown with the isomer 3 points – Aldehyde/reagent/result (final) or – Ketone/reagent/result	1	Cancelling errors eg propanone instead of propanal
Question	Acceptable Answer	Mark	Unacceptable Answer
6. (a)	$ \begin{array}{cccc} \text{H} & \text{H} & \text{O} & \text{H} \\ & & & \\ \text{H}-\text{C} & -\text{C} & -\text{C} & -\text{C}-\text{H} \\ & & & \\ \text{H} & \text{H} & & \text{H} \end{array} $ <p>OR CH₃CH₂COCH₃ OR butanone</p>	1	
(b)	(nucleophilic) substitution	1	not electrophilic
(c)	Find its melting point and check with literature values	1	Boiling point OR Melting point and compare with melting point of Y
(d)	$ \begin{array}{ccc} \text{H} & & \text{CH}_3 \\ & \diagdown & / \\ & \text{C} = \text{C} & \\ & / & \diagdown \\ \text{H}_3\text{C} & & \text{H} \end{array} \qquad \begin{array}{ccc} \text{H} & & \text{H} \\ & \diagdown & / \\ & \text{C} = \text{C} & \\ & / & \diagdown \\ \text{H}_3\text{C} & & \text{CH}_3 \end{array} $ <p><i>trans</i>-but-2-ene <i>cis</i>-but-2-ene</p>	2	
Question	Acceptable Answer	Mark	Unacceptable Answer
7. (a)	Electrophilic substitution	1	Nucleophilic substitution
(b)	Br ₂ and FeBr ₃ /FeCl ₃ /AlBr ₃ /Fe/AlCl ₃ Correct answers in words rather than formulae	1	
(c)	Sulphuric acid and nitric acid H ₂ SO ₄ and HNO ₃ Concentrated/fuming H ₂ SO ₄ + HNO ₃	1	Dilute H ₂ SO ₄ and HNO ₃
(d)	C ₆ H ₆ SO ₃ Any order	1	C ₆ H ₅ SO ₃ H
(e)	 <p>or – CHBr₂ or – CBr₃</p>	1	

Question	Acceptable Answer	Mark	Unacceptable Answer
8. (a)	H ₂ SO ₄ and HNO ₃ or H ₂ SO ₄ and NaNO ₃	1	Acids in dilute form
(b)	reduction	1	
(c)	Ethanoic acid/CH ₃ COOH or Ethanoyl chloride/CH ₃ COCl or Ethanoic anhydride/(CH ₃ CO) ₂ O	1	
Question	Acceptable Answer	Mark	Unacceptable Answer
9 (a)	to give a higher yield or to reduce side reactions or to prevent charring	1	H ₃ PO ₄ is a better dehydrating agent Faster reaction
(b)	sodium chloride (solution)/brine/salt water	1	
(c)	to dry the cyclohexene/dry the organic layer/drying agent/ absorbs water/removes water	1	removes impurities dehydrating agent
(d)	Theoretical mass of cyclohexene = $\frac{82 \times 22.56}{100} = 18.5 \text{ g}$ % yield = $\frac{6.52 \times 100}{18.5} = 35 \%$ or Moles cyclohexanol = 22.56/100 = 0.2256 mol Moles cyclohexane = 6.52/82 = 0.0795 mol % yield = $\frac{0.0795}{0.2256} \times 100 = 35.2 \%$ or 35%	1 1 1 1	
Question	Acceptable Answer	Mark	Unacceptable Answer
10 (a)	Condensation	1	elimination
(b)	 Accept either cis/trans isomer	1	
(c) (i)		1	
(ii)	Crystallisation/recrystallisation	1	
(iii)	Measure melting point and compare to known data/value	1	Measure melting point (on its own)
(iv)	Accept yellow/orange/gold	1	

Question	Acceptable Answer	Mark	Unacceptable Answer
11. (a)	because but-2-ene has two different groups attached to each of the carbon atoms of the double bond or because in but-1-ene one of the carbon atoms of the double bond has identical groups (H) attached 3 H atoms around the C=C in but-1-ene Structures with explanation	1	But-1-ene, double bond at end of chain But-2-ene, double bond in middle of chain But-2-ene, symmetrical 3 H atoms at end of chain
(b)	 $\text{CH}_3\text{CH}_2^+\text{CHCH}_3$	1	$\text{CH}_3\text{CH}_2\overset{+}{\text{C}}\text{HCH}_3$ 
(c)	aqueous potassium (or sodium) hydroxide $\text{KOH}_{(\text{aq})}$ or $\text{NaOH}_{(\text{aq})}$ or potassium (or sodium) hydroxide solution or aqueous alkali or alkali solution or water/ H_2O	1	OH^- or $\text{OH}^-_{(\text{aq})}$ LiOH NaOH KOH ethanolic KOH
(d)	aluminium chloride or AlCl_3 or iron(III) chloride or FeCl_3 or iron(III) bromide or FeBr_3 or aluminium bromide or AlBr_3	1	FeCl_2 or iron(II) chloride
(e)	 or  Use of C_6H_5 in place of 	1	
12 (a)	ethanal/acetaldehyde/correct structural formula	1	$\text{C}_2\text{H}_4\text{O}$
(b)	cyanohydrin or hydroxynitrile or cyanoalcohol	1	nitrile
(c)	hydrolysis/acid hydrolysis	1	alkaline hydrolysis

Question	Acceptable Answer	Mark	Unacceptable Answer
13. (a) (i)	Nucleophilic substitution/replacement by a nucleophile First order unimolecular	1 1	
(ii)	$\begin{array}{c} \text{CH}_3 \\ \\ \text{H}_3\text{C}-\text{C}^+ \\ \\ \text{CH}_3 \end{array} \quad (\text{CH}_3)_3\text{C}^+$		
(b) (i)	Na in ethanol	1	
(ii)	Methoxyethane Accept methyl ethyl ether or ethylmethylether	1	
Question	Acceptable Answer	Mark	Unacceptable Answer
14. (a)	2-hydroxypropanoic acid (spelling must be correct)	1	
(b)	Carbon atom ② because it has 4 different groups attached	1	Carbon atom ② with no explanation
(c) (i)	KCN or NaCN or HCN or any cyanide compound that would work or correct names	1	
(ii)	Hydrolysis/acid hydrolysis	1	
(iii)	$\begin{array}{ccccccc} & \text{H} & \text{OH} & \text{H} & & & \\ & & & & & & \\ \text{H} & -\text{C} & -\text{C} & -\text{C} & -\text{N} & & \\ & & & & / \quad \backslash & & \\ & \text{H} & \text{H} & \text{H} & \text{H} & & \text{H} \end{array}$ or $\text{CH}_3\text{CHOHCH}_2\text{NH}_2$	1	