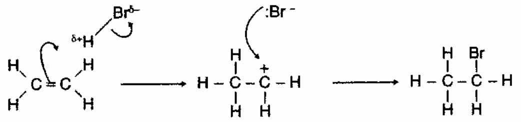
Electrophilic addition reactions (1)

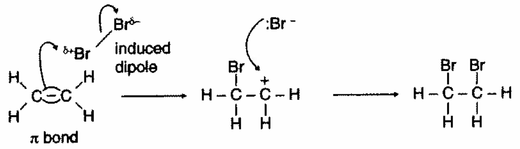
ELECTROPHILIC ADDITION TO SYMMETRIC ALKENES

Ethene readily undergoes addition reactions. With hydrogen bromide it forms bromoethane.

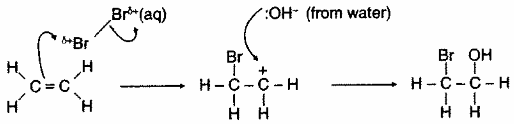
The reaction can occur in the dark which suggests that a free radical mechanism is not involved. The double bond in the ethene molecule has a region of high electron density above and below the plane of the molecule. Hydrogen bromide is a polar molecule due to the greater electronegativity of bromine compared with hydrogen. The hydrogen atom (which contains a charge of δ+) from the H–Br is attracted to the double bond and the H–Br bond breaks, forming a bromide ion. At the same time the hydrogen atom adds to one of the ethene carbon atoms leaving the other carbon atom with a positive charge. A carbon atom with a positive charge is known as a **carbocation**. The carbocation then combines with the bromide ion to form bromoethane. Because the hydrogen bromide molecule is attracted to a region of electron density it is described as an **electrophile** and the mechanism is described as **electrophilic addition**.



Electrophilic addition also takes place when bromine adds to ethene in a non-polar solvent to give 1,2-dibromoethane. Bromine itself is non-polar but as it approaches the double bond of the ethene an induced dipole is formed by the electron cloud.



Evidence for this mechanism is that when bromine water is reacted with ethene the main product is 2-bromoethanol not 1,2-dibromoethane. This suggests that hydroxide ions from the water add to the carbocation in preference to bromide ions.

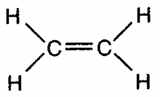


SYMMETRIC AND ASYMMETRIC ALKENES

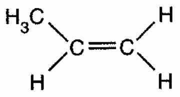
Asymmetric alkenes contain different groups attached to the carbon atoms of the C=C bond.

Symmetric alkenes

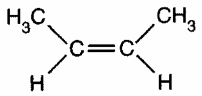
Asymmetric alkenes



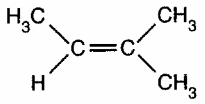
ethene



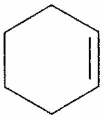
propene



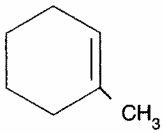
but-2-ene



2-methylbut-2-ene



cyclohexene

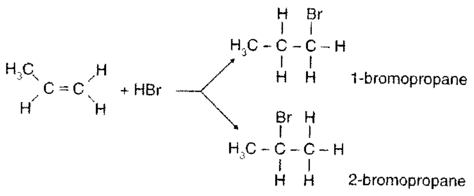


1-methylcyclohexene

Electrophilic addition reactions (2)

MARKOVNIKOV'S RULE

When hydrogen halides add to asymmetric alkenes two products are possible depending upon which carbon atom the hydrogen atom bonds to. For example, the addition of hydrogen bromide to propene could produce 1-bromopropane or 2-bromopropane.

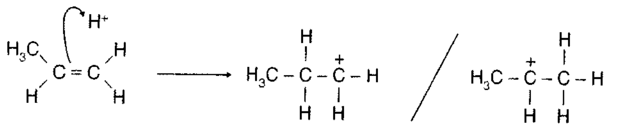


Markovnikov's rule enables you to predict which isomer will be the major product. It states that the hydrogen halide will add to the carbon atom that already contains the most hydrogen atoms bonded to it. Thus in the above example 2-bromopropane will be the major product.

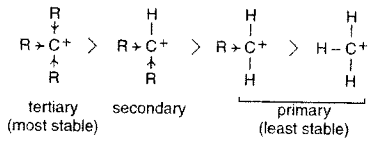
EXPLANATION OF MARKOVNIKOV'S RULE

Markovnikov's rule enables the product to be predicted but it does not explain why. It can be explained by considering the nature of the possible intermediate carbocations formed during the reaction.

When hydrogen ions react with propene two different carbocation intermediates can be formed.


primary carbocation / secondary carbocation

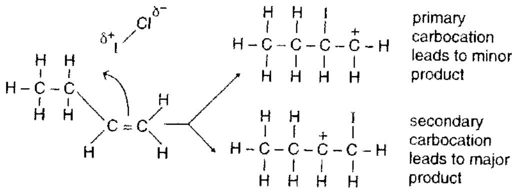
The first one has the general formula RCH_2^+ and is known as a **primary carbocation**. The second one has two R– groups attached to the positive carbon ion R_2CH^+ and is known as a **secondary carbocation**. A **tertiary carbocation** has the general formula R_3C^+. The R-groups (alkyl groups) tend to push electrons towards the carbon atom they are attached to which tends to stabilize the positive charge on the carbocation. This is known as a **positive inductive effect**. This effect will be greatest with tertiary carbocations and smallest with primary carbocations.



→ represents the pair of electrons being 'pushed' towards the carbon ion

Thus in the above reaction the secondary carbocation will be preferred as it is more stable than the primary carbocation. This secondary carbocation intermediate leads to the major product, 2-bromopropane.

Understanding this mechanism enables you to predict what will happen when an interhalogen adds to an asymmetric alkene even though no hydrogen atoms are involved. Consider the reaction of iodine chloride ICl with but-1-ene. Since iodine is less electronegative than chlorine the iodine atom will act as the electrophile and add first to the alkene.

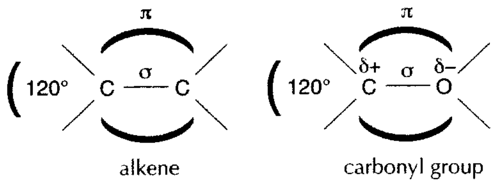


The major product will thus be 2-chloro-1-iodobutane.

Nucleophilic addition reactions and elimination reactions

ADDITION OF HYDROGEN CYANIDE TO ALDEHYDES AND KETONES

Aldehydes and ketones are both carbonyl compounds as they contain the $>C=O$ group. The double bond in carbonyl compounds is similar to the $C=C$ double bond in alkenes and the region around the bond is planar with bond angles of 120°.

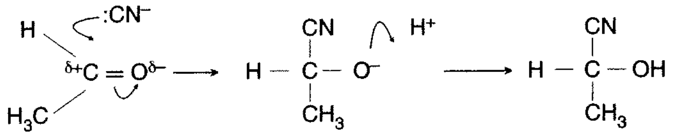


alkene

carbonyl group

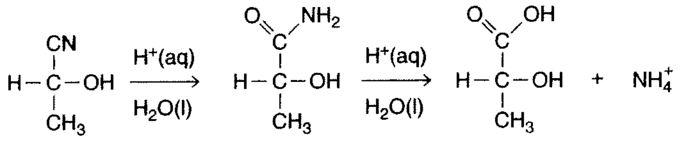
The essential difference is that oxygen is much more electronegative than carbon so that the bond is polar. Whereas alkenes undergo electrophilic addition, carbonyl compounds undergo **nucleophilic addition reactions.**

A typical example is the reaction of ethanal with hydrogen cyanide. Hydrogen cyanide is weakly acidic and dissociates to form the cyanide ion which acts as the nucleophile. The intermediate anion is then protonated to form the product, 2-hydroxypropanenitrile. Hydroxynitriles are also known as cyanohydrins.



2-hydroxypropanenitrile

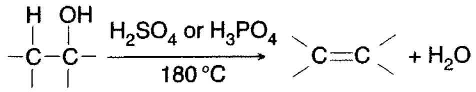
This reaction is useful in synthesis as it is a method by which an extra carbon atom can be introduced into a carbon chain. Nitriles can be hydrolysed in the presence of acid to form carboxylic acids so this product can easily be converted into 2-hydroxypropanoic acid (lactic acid).



2-hydroxypropanoic acid

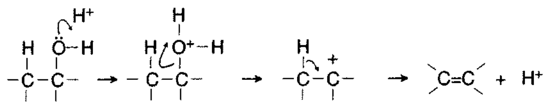
ELIMINATION REACTIONS OF ALCOHOLS

Alcohols can be dehydrated (elimination of water) by heating with concentrated sulfuric acid at 180 °C. In practice phosphoric acid is often used in place of sulfuric acid as fewer side reactions take place.



$$-\overset{H}{\underset{|}{\overset{|}{C}}}-\overset{OH}{\underset{|}{\overset{|}{C}}}- \xrightarrow[180\,°C]{H_2SO_4 \text{ or } H_3PO_4} >C=C< + H_2O$$

The strong acid acts as a catalyst by protonating the oxygen atom in the alcohol. Water is then lost to form a carbocation. The carbocation then donates a proton to form the double bond and regenerate the catalyst.

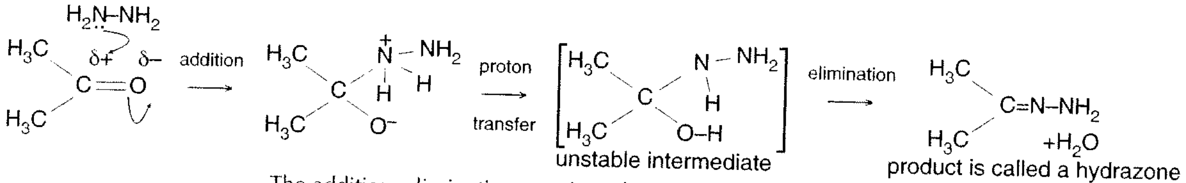


Tertiary alcohols are more readily dehydrated than primary and secondary alcohols because the intermediate tertiary carbocation is more stable.

Addition–elimination reactions

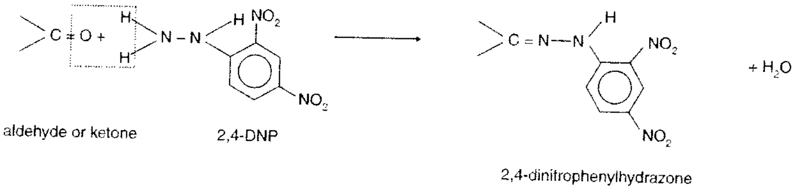
REACTION OF 2,4-DINITROPHENYLHYDRAZINE WITH ALDEHYDES AND KETONES

With nucleophiles containing the $-NH_2$ group add to aldehydes and ketones the addition can be followed by the elimination of water. For example, the reaction of hydrazine with propanone. The initial mode of attack is still nucleophilic addition but then the carbon atom forms a double bond with the nitrogen atom and a molecule of water is lost. The overall reaction is known either as an **addition–elimination reaction** or more simply as a **condensation reaction**.



The addition–elimination reaction of propanone and hydrazine

If 2,4-dintritrophenylhydrazine (2,4-DNP) is used instead of hydrazine the product is known as a 2,4-dinitrophenylhydrazone.



All aldehydes and ketones form red or orange crystalline solid 2,4-dinitrophenylhydrazones each of which has a characteristic melting point. These derivatives of 2,4-DNP are easy to make and purify so provide a convenient way of distinguishing between different aldehydes and ketones, although in a well-equipped laboratory chemists are now more likely to use a combination of spectroscopic techniques (e.g. ^1H NMR and mass spectrometry).

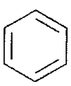
Melting points of 2, 4-dinitrophenylhydrazones of aldehydes and ketones

M. pt / °C		M. pt / °C	
methanal	166	propanone	126
ethanal	168	butanone	116
propanal	155	pentan-3-one	156
butanal	126	pentan-2-one	144
benzaldehyde	237	cyclohexanone	162

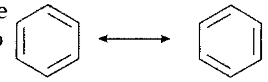
Arenes

STRUCTURE OF BENZENE

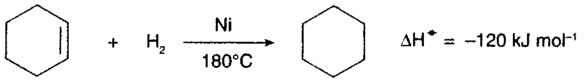
The simplest arene is benzene, C_6H_6. The Kekulé structure of benzene (cyclohexa-1,3,5-triene) consists of three double bonds.



There is both physical and chemical evidence to support the fact that benzene does not contain three separate double bonds but exists as a resonance hybrid structure with delocalized electrons. The two resonance hybrid forms are shown (right).

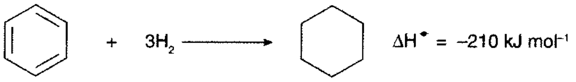


1. The C–C bond lengths are all the same and have a value of 0.139 nm which lies between the values for C–C (0.154 nm) and C=C (0.134 nm).
2. The enthalpy of hydrogenation of cyclohexene is -120 kJ mol^{-1}.



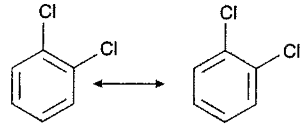
If benzene simply had the cyclohexa-1,3,5-triene structure with three double bonds the enthalpy change of hydrogenation of benzene would be expected to be equal to 3 times the enthalpy change of hydrogenation of cyclohexane, i.e. -360 kJ mol^{-1}.

However the experimentally determined value for benzene is -210 kJ mol^{-1}.



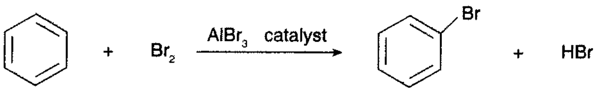
The difference of 150 kJ mol^{-1} is the extra energy associated with the delocalisation energy.

3. Only one isomer exists for 1,2- disubstituted benzene compounds. If there were simply alternate double bonds then two isomers would exist.



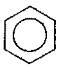
The two isomers of 1,2- dichlorobenzene which would be expected if benzene has the cyclohexa-1,3,5-triene structure

4. If benzene had three normal double bonds it would be expected to readily undergo addition reactions. In fact it will only undergo addition reactions with difficulty and more commonly undergoes substitution reactions. For example, with bromine it forms bromobenzene and hydrogen bromide rather than 1,2-dibromobenzene.



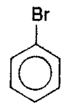
5. For those who are also studying Option A – Modern analytical chemistry one more piece of evidence is that the high resolution ^1H NMR spectrum of benzene shows a single peak. This would not be the case if benzene had three alternate double bonds as the hydrogen atoms would be in different chemical environments.

The actual bonding in benzene is best described by the delocalization of electrons. For this reason benzene is often represented by a hexagonal ring with a circle in the middle of it.

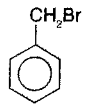


HYDROLYSIS OF HALOGENATED ARENES

The hydrolysis of halogenated alkanes and arenes proceeds by a nucleophilic substitiution reaction. Halogenated arenes can either contain the halogen atom substituted directly on the benzene ring, e.g. bromobenzene, C_6H_5Br, or on to a side chain e.g. bromomethylbenzene, $C_6H_5CH_2Br$.

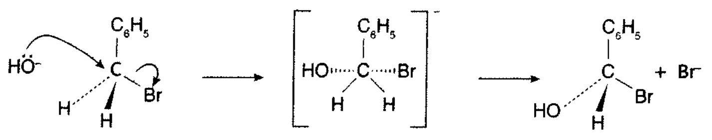


bromobenzene



bromomethylbenzene

If the halogen atom is on the side chain then the compound behaves like a normal halogenoalkane and readily undergoes nucleophilic substitution with aqueous sodium hydroxide solution. For example, bromomethylbenzene is a primary halogenoalkane and so the substitution proceeds by an S_N2 mechanism to produce phenylmethanol.



However if the halogen atom is directly attached to the benzene ring then nucleophilic substitution only occurs very slowly or not at all. There are two reasons for this. The nucleophile is unable to 'attack' the carbon atom bonded to the bromine atom as it is repelled by the dense cloud of electrons surrounding the arene ring. Secondly the C-Br bond is stronger in bromobenzene than the C-Br bond in halogenoalkanes. This is because one of the non-bonding pairs of electrons on the bromine atom is able to interact with the electrons in the benzene ring which makes the bond shorter and stronger and consequently the carbon to bromine bond stronger and more difficult to break.

Organometallic chemistry and reaction pathways

FORMATION OF GRIGNARD REAGENTS

Organometallic compounds contain a carbon atom covalently bonded directly to a metal. One important group of organometallic compounds which are used in organic synthesis is known as Grignard reagents. They consist of an alkyl group bonded directly to magnesium. They are usually prepared *in situ* by reacting magnesium metal with a halogenoalkane using dry ethoxyethane (ether) as the solvent. Sometimes a small amount of iodine is added to initiate the reaction.

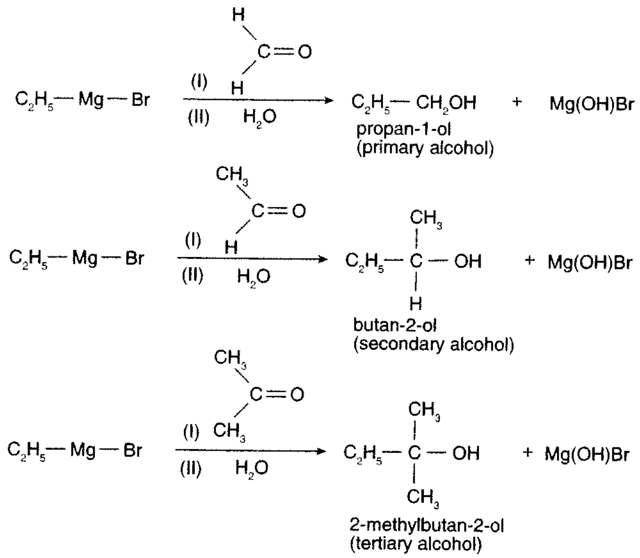
$$RX + Mg \longrightarrow R{-}Mg{-}X$$

They must be prepared in a non-polar solvent such as ether as Grignard reagents react with water to form alkanes, e.g.

$$C_2H_5{-}Mg{-}Br \xrightarrow{H_2O} \underset{\text{ethane}}{C_2H_6} + Mg(OH)Br$$

REACTIONS OF GRIGNARD REAGENTS

The magnesium to carbon bond is polar with the negative part of the dipole on the carbon atom as carbon is more electronegative than magnesium. This enables the carbon atom to act as a good nucleophile. Grignard reagents can add to the partially positive carbon atom in aldehydes and ketones and then be hydrolyzed in acid solution to form alcohols with a longer carbon chain. For example with methanal they form a primary alcohol, with other aldehydes they form secondary alcohols and with ketones they form tertiary alcohols.

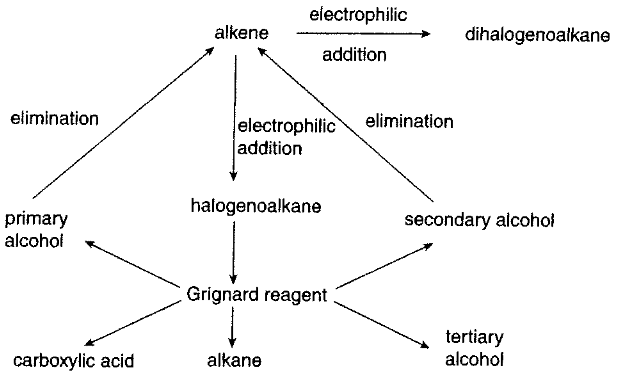


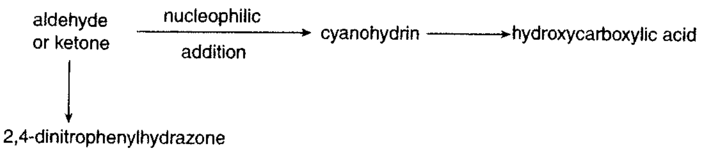
Grignard reagents can also react with carbon dioxide in a similar way to form carboxylic acids, e.g.

$$C_2H_5{-}Mg{-}Br \xrightarrow[\text{(II) } H_2O]{\text{(I) } CO_2} \underset{\text{propanoic acid}}{C_2H_5COOH} + Mg(OH)Br$$

REACTION PATHWAYS

The reactions studied in this part of the option can be summarized in the following two diagrams which include the required mechanisms.





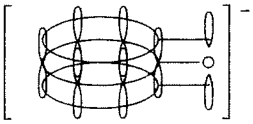
Acid–base reactions

STRENGTHS OF ORGANIC ACIDS AND BASES

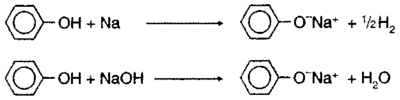
The acid strength of organic acids can be compared using pK_a values. These are the values given in the IB data booklet They work in a similar way to pH in that the lower the pKa value the stronger the acid. For organic bases pK_b values are used – the lower the pK_b value the stronger the base.

ACIDIC PROPERTIES OF PHENOLS

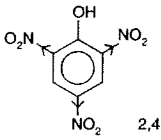
Phenol is weakly acidic because the negative charge in the conjugate phenoxide ion can be delocalized over the benzene ring. This makes it less likely to attract a proton than the ethoxide ion or hydroxide ion where delocalization cannot occur.



Phenol has a pK_a value of 10.00 making it a weaker acid than carboxylic acids. It is too weak to react with carbonates to give carbon dioxide but it will react with sodium to give hydrogen and form salts with sodium hydroxide.



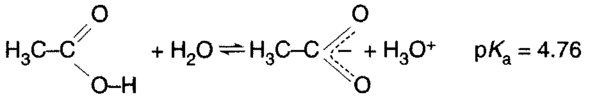
Substituted phenols containing electron withdrawing groups are much more acidic as the negative charge can be further delocalized. For example, 2-nitrophenol has a pK_a value of 7.21. In 2,4,6-trinitrophenol the effect is so great that the substituted phenol is nearly a strong acid with a pK_a value of 0.42.



2,4,6-trinitrophenol

ACIDIC PROPERTIES OF SUBSTITUTED CARBOXYLIC ACIDS

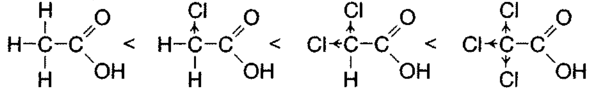
Although alcohols and carboxylic acids both contain an –OH group carboxylic acids are weak acids whereas alcohols are not. The electron withdrawing carbonyl group >C=O adjacent to the –OH group weakens the normally strong O–H bond so that the carboxyl group can lose a proton.



The acidity of carboxylic acids can also be explained by considering the conjugate base formed. In the carboxylate anion the negative charge is delocalized over three atoms as both C–O bond lengths are identical. This stabilizes the ion and makes it less likely to attract a proton as the charge density of the negative charge is reduced. Compare this with the strongly basic ethoxide ion where the negative charge is localized on the oxygen atom.

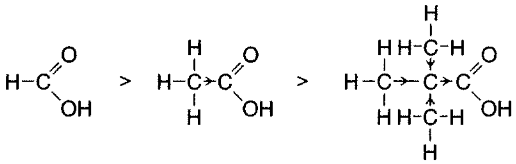
$C_2H_5{-}O{-}H + H_2O \rightleftharpoons C_2H_5{-}O^- + H_3O^+$ pK_a = approx. 16

Electron withdrawing atoms such as chlorine can further delocalize the negative charge on the anion increasing the acid strength.



ethanoic acid $pK_a = 4.76$
chloroethanoic acid $pK_a = 2.86$
dichloroethanoic acid $pK_a = 1.29$
trichloroethanoic acid $pK_a = 0.65$

Groups with a positive inductive effect such as alkyl groups will decrease the ability of the charge to delocalize and the acid will be weaker.



methanoic acid $pK_a = 3.75$
ethanoic acid $pK_a = 4.76$
trimethylethanoic acid $pK_a = 5.05$

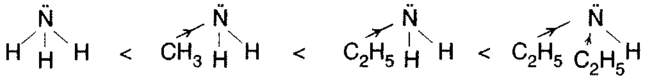
RELATIVE BASICITIES OF AMMONIA AND AMINES

Ammonia is a weak base with a pK_b of 4.75 and forms salts with strong acids.

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

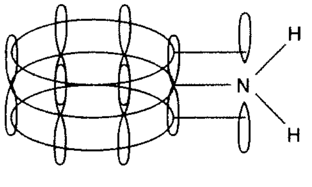
$$NH_3 + HCl \rightarrow NH_4^+Cl^-$$

Amines are more basic than ammonia because the positive inductive effect of the alkyl group 'pushes' electrons towards the nitrogen atom increasing the electron density of the non-bonding pair of electrons. Thus aminoethane (ethylamine) is more basic than aminomethane (methylamine) as the positive inductive effect of an ethyl group is greater than a methyl group. Secondary amines are more basic still, although tertiary amines are slightly less basic.



ammonia $pK_b = 4.75$
methylamine $pK_b = 3.36$
ethylamine $pK_b = 3.27$
diethylamine $pK_b = 3.08$

However, aminobenzene (phenylamine), although still basic with a pK_b of 9.48, is considerably less basic than ammonia. The non-bonding pair of electrons on the nitrogen atom is delocalized with the electrons in the ring and so is less available to donate to a proton.



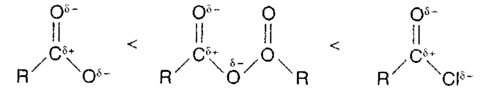
All amines can be obtained from their salts by reacting with sodium hydroxide.

$$RNH_3^+ + OH^- \rightarrow RNH_2 + H_2O$$

Addition–elimination reactions of acid anhydrides

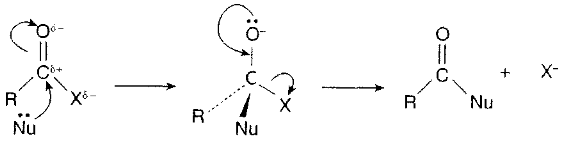
MECHANISM

When carboxylic acids react with alcohols to form esters the –OH group of the carboxylic acid is replaced by the –OR group of the alcohol. This is an example of an addition-elimination reaction as the alcohol acts as a nucleophile and the –OH group of the acid is eliminated as water. An acid anhydride is a carboxylic acid in which the hydroxyl group has been replaced by the -OCOR group from another molecule of the acid. Similarly in acyl chlorides the hydroxyl group has been replaced by a chlorine atom. Both -OCOR and -Cl are more easily replaced than -OH so acid anhydrides and acyl chlorides are much more reactive with nucleophiles than carboxylic acids.



carboxylic acid (least reactive)　acid anhydride　acyl chloride (most reactive)

The -OCOR and -Cl groups are more electron withdrawing than the -OH group. this increases the small positive charge, δ^+,on the carbon atom making them more reactive with nucleophiles.

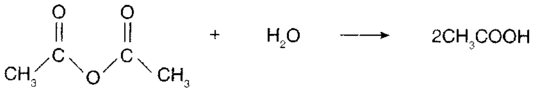


Nu represents a nucleophile e.g. H_2O, NH_3, ROH and amines

X represents Cl or OCOR

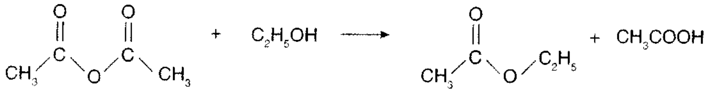
ACID ANHYDRIDES

1. **Water**. Acid anhydrides react with water to form carboxylic acids, e.g.



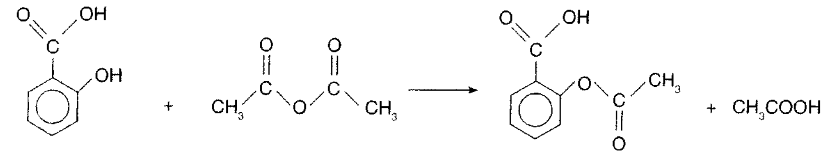
ethanoic anhydride　ethanoic acid

2. **Alcohols**. Acid anhydrides react with alcohols to form esters, e.g.



ethanoic anhydride　ethanol　ethylethanoate

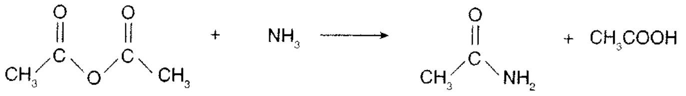
The reaction of ethanoic anhydride with 2-hydroxybenzoic acid (salicylic acid), is used to prepare aspirin. In this reaction it is the –OH group on the benzene ring which is functioning as the alcohol.



2-hydroxybenzoic acid (salicylic acid)　ethanoic anhydride　2-ethanoyloxybenzenecarboxylic acid (aspirin or acetylsalicylate)

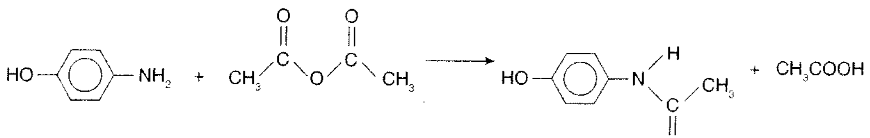
A similar reaction is used to turn morphine into heroin (see Option D – Medicines and drugs).

3. **Ammonia and amines**. Acid anhydrides react readily with concentrated aqueous ammonia to form amides, e.g.



ethanamide

Secondary amines also contain a non-bonded pair of electrons on the nitrogen atom so can also function as nucleophiles. When 4-aminophenol is reacted with ethanoic anhydride in the presence of water at room temperature the product is *N*-(4-hydroxylphenyl)ethanamide. This has the common name of paracetamol in the U.K and acetaminophen in the U.S.A. and like aspirin it is also a pain killer and fever reducer.



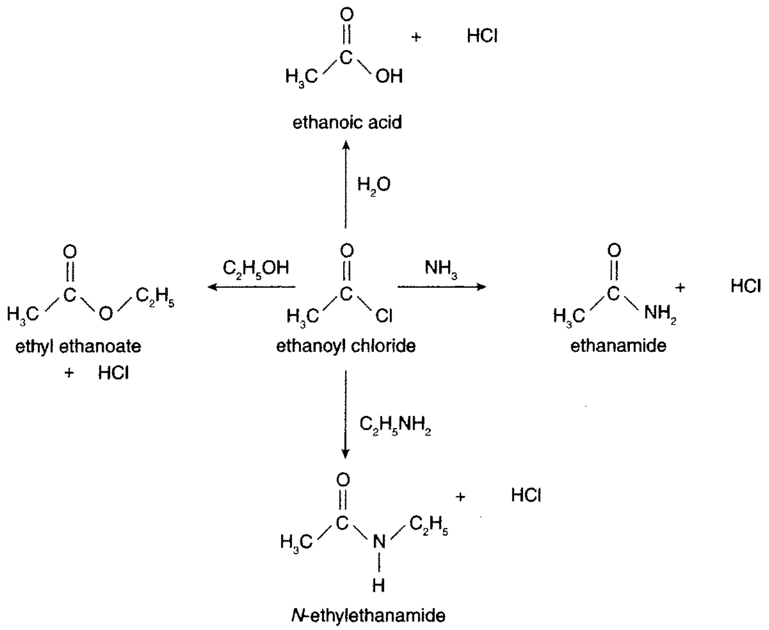
4-aminophenol　ethanoic anhydride　*N*-(4-hydroxyphenyl)ethamide (paracetamol or acetaminophen)

Addition–elimination reactions of acyl chlorides

ACYL CHLORIDES

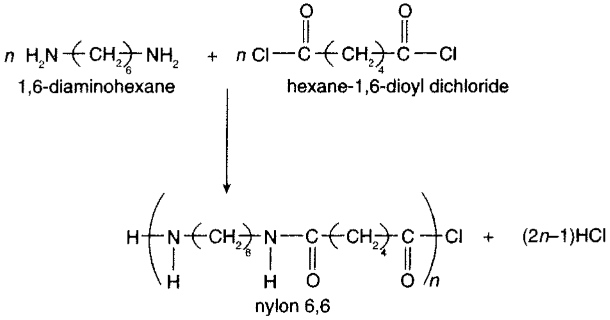
Acyl chlorides react in a very similar way to acid anhydrides except that now the other product is hydrochloric acid rather than the carboxylic acid. The reactions are more vigorous. This explains why acyl chlorides fume in moist air to form droplets of hydrochloric acid as soon as the stopper is taken off the bottle.

summary of reactions of ethanoyl chloride



The reaction of acyl chlorides with secondary amines is used to make nylon. For example nylon 6,6 can be prepared by reacting hexane-1,6-dioyl dichloride with 1,6-diaminohexane.

preparation of nylon 6,6

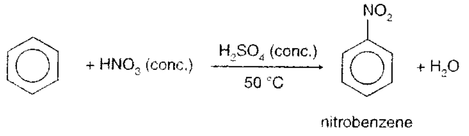


Electrophilic substitution reactions (1)

Benzene does not readily undergo addition reactions since an additional 150 kJ mol^{-1} of energy would be required to overcome the energy of delocalization. Instead it undergoes electrophilic substitution reactions. Electrophiles are attracted to the region of high electron density above and below the plane of the molecule due to the delocalized π bond.

NITRATION OF BENZENE

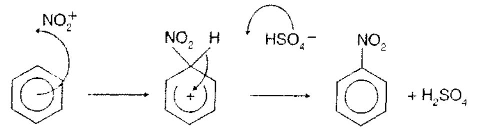
Benzene reacts with a mixture of concentrated nitric acid and concentrated sulfuric acid when warmed at 50 °C to give nitrobenzene and water. Note that the temperature should not be raised above 50 °C otherwise further nitration to dinitrobenzene will occur.



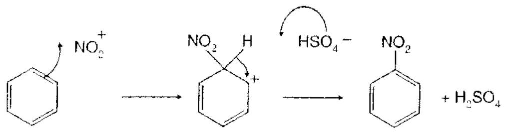
The electrophile is the **nitryl cation NO_2^+** (also called the nitronium ion). The concentrated sulfuric acid acts as a catalyst. Its function is to protonate the nitric acid which then loses water to form the electrophile. In this reaction nitric acid is acting as a base in the presence of the more acidic sulfuric acid.

$$H_2SO_4 + HNO_3 \rightleftharpoons H_2NO_3^+ + HSO_4^-$$
$$\downarrow$$
$$H_2O + NO_2^+$$

The NO_2^+ is attracted to the delocalized π bond and attaches to one of the carbon atoms. This requires considerable activation energy as the delocalized π bond is partially broken. The positive charge is distributed over the remains of the π bond in the intermediate. The intermediate then loses a proton and energy is evolved as the delocalized π bond is reformed. The proton can recombine with the hydrogensulfate ion to regenerate the catalyst.

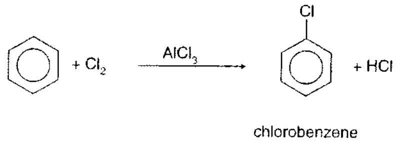


Although it is more correct to draw the intermediate as a partially delocalized π bond it can sometimes be convenient to show benzene as if it does contain alternate single and double carbon to carbon bonds. In this model the positive charge is located on a particular carbon atom.

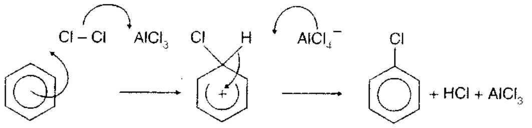


CHLORINATION, ALKYLATION AND ACYLATION OF BENZENE

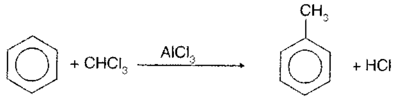
Benzene can also undergo electrophilic substitution with chlorine. This only happens in the presence of a **halogen carrier**, such as anhydrous aluminium chloride or iron.



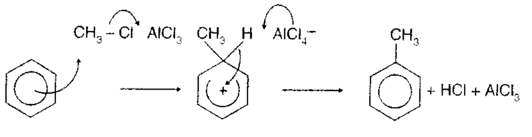
The halogen carrier is a catalyst (sometimes known as a Friedel–Crafts catalyst after its discoverers). It functions as a Lewis acid by accepting a pair of electrons from the chlorine. The electrophile is the resulting chlorine ion, Cl$^+$.



Halogen carriers can also be used to attract the electron pair in the C–Cl bond in halogenoalkanes R–Cl. The resulting electrophile will now be the positive alkyl ion R$^+$. The resulting substituted product will be an alkylbenzene. For example, methylbenzene can be prepared by warming benzene with chloromethane in the presence of anhydrous aluminium chloride.



Mechanism:



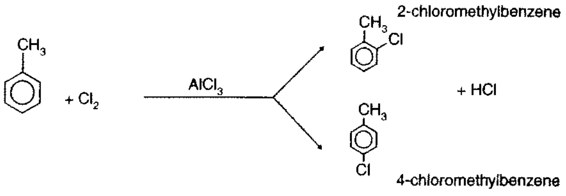
A similar reaction can occur with acyl chlorides to produce ketones – this is known as acylation. For example, benzene can react with ethanoyl chloride in the presence of a halogen carrier to form 1-phenylethanone (acetophenone). The electrophile is CH$_3$CO$^+$.

$$C_6H_6 + CH_3COCl \xrightarrow{AlCl_3} C_6H_5COCH_3 + HCl$$

HL Electrophilic substitution reactions (2)

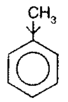
SUBSTITUTION REACTIONS OF METHYLBENZENE

The reaction between methylbenzene and chlorine provides a good example of how altering the conditions can completely alter the products. In the presence of ultraviolet light the reaction proceeds by a free radical substitution mechanism and chloromethylbenzene is formed. In this reaction methylbenzene is behaving as a substituted alkane. In the presence of a halogen carrier it behaves as a substituted arene and the substitution takes place on the aromatic ring. The organic products are a mixture of 2-chloromethylbenzene and 4-chloromethylbenzene.

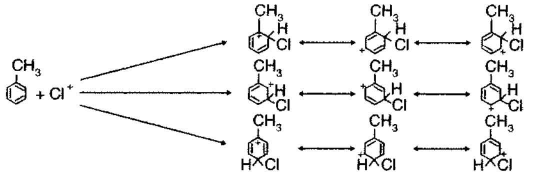


There are two important features about this reaction.

1. **The reaction is faster than the chlorination of benzene**
   This is due to the positive inductive effect of the CH_3 group. Electrons are 'pushed' towards the ring increasing the electron density of the delocalized π bond. This results in a stronger attraction towards electrophiles.



2. **The products are the 2- and 4- substituted isomers**
   Virtually none of the 3- isomer is obtained. This can be explained by considering the position of the positive charge in the possible intermediates. Each of the three possible intermediates is a resonance hybrid of three structures.



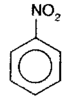
Only the 2-substituted and the 4-substituted intermediate have the positive charge adjacent to the methyl group. This will make them more stable due to the positive inductive effect of the methyl group and thus more likely to be formed.

DIRECTING EFFECTS OF SUBSTITUENTS IN SUBSTITUTED BENZENE COMPOUNDS

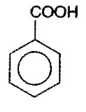
The methyl group has a positive inductive effect and this both increases the rate of substitution and directs towards the 2- and 4- positions. Many other groups are electron withdrawing and these can be sub-divided into two groups depending on whether the atom bonded to the benzene ring contains a non-bonding pair of electrons or not.

Electron withdrawing with no non-bonded pair

Examples include:



and



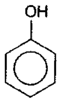
nitrobenzene

benzoic acid

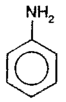
Because the electron density on the ring is reduced the substitution reaction will be slower relative to benzene, hence these substituents are known as **deactivating**. The substitution will direct towards the 3-position since none of the intermediate structures will be destabilized by having the positive charge adjacent to the electron withdrawing group. For example, the nitration of nitrobenzene requires the nitrating mixture of the two concentrated acids to be refluxed with nitrobenzene rather than just heated to 50 °C to produce 1,3-dinitrobenzene.

Electron withdrawing with a non-bonded pair

Examples include:



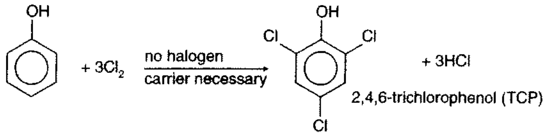
and



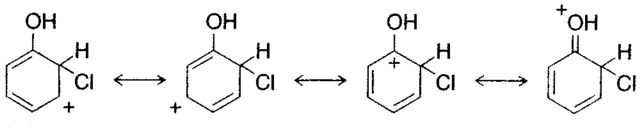
phenol

aminobenzene

These **activating** substituents make the compound much more reactive (faster) towards electrophilic substitution than benzene. The delocalization in the ring is now able to include the non-bonding pair of electrons on the substituent. Whereas six electrons are delocalized over six atoms in benzene eight electrons are delocalized over seven atoms in phenol and phenylamine. This increases the electron density and makes them much more attracted to electrophiles. This can be exemplified by the reaction of phenol with chlorine. The reaction is so fast that no halogen carrier is necessary and the trisubstituted product is formed immediately.



These substituents are 2- and 4-directing as the intermediate can now be considered as a resonance hybrid of four structures thus increasing its stability. In the 3-position the positive charge cannot be positioned on the substituent.



The four possible locations of the positive charge in the 2-substituted intermediate of phenol.

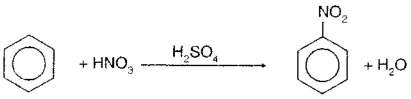
Summary of reaction mechanisms

To assist in devising reaction pathways a summary of all the mechanisms covered in IB organic chemistry, with one example for each, is provided.

ELECTROPHILIC SUBSTITUTION

Occurs when electrophiles, such as NO_2^+ or Cl^+ (from Cl_2 in the presence of a halogen carrier), substitute for hydrogen on one of the carbon atoms in a benzene ring. Addition does not occur as this would require extra energy to overcome the delocalization energy of the ring.

Example: nitration of benzene



NUCLEOPHILIC SUBSTITUTION

Occurs when nucleophiles such as CN^-, OH^-, NH_3, and H_2O are attracted to the δ^+ carbon atom and substitute the halogen atom in halogenoalkanes.

S_N2 example: reaction of dilute aqueous sodium hydroxide solution with bromoethane

$$CH_3CH_2Br + NaOH \rightarrow CH_3CH_2OH + NaBr$$

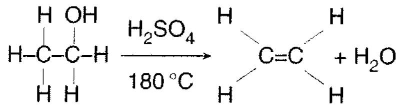
S_N1 example: reaction of dilute aqueous sodium hydroxide with 2-bromo-2-methlypropane

$$(CH_3)_3CBr + NaOH \rightarrow C(CH_3)_3OH + NaBr$$

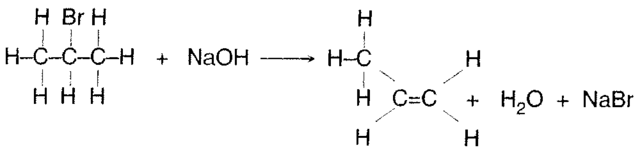
ELIMINATION

Occurs when concentrated sulfuric acid catalyses the elimination of water from alcohols and when hydroxide ions act as a base with halogenoalkanes.

Example for alcohols: dehydration of ethanol with concentrated sulphuric acid



Example for halogenoalkanes: reaction of hot alcoholic sodium hydroxide with 2-bromopropane



FREE RADICAL SUBSTITUTION

Occurs when ultraviolet light breaks a Cl–Cl bond homolytically and the chlorine radicals react with compounds containing C–H bonds.

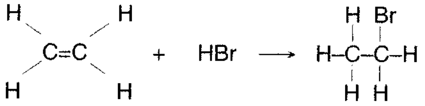
Example: methane and chlorine

$$CH_4 + Cl_2 \xrightarrow{UV} CH_3Cl + HCl$$

ELECTROPHILIC ADDITION

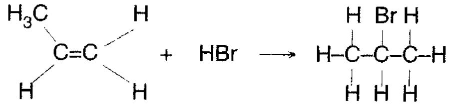
Occurs when hydrogen halides, halogens or interhalogens add across the double bond of alkenes. The electrophile is attracted to the electron rich π bond of the alkene forming a carbocation intermediate.

Example: reaction of ethene with hydrogen bromide



Note that for asymmetric alkenes Markovnikov addition occurs due to the stability of the intermediate carbocation.

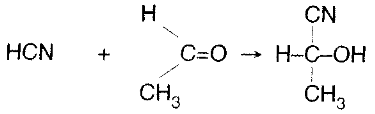
Example: reaction of propene with hydrogen bromide



NUCLEOPHILIC ADDITION

Occurs when nucleophiles add initially to the δ^+ carbon atom attached to oxygen in carbonyl compounds (aldehydes and ketones).

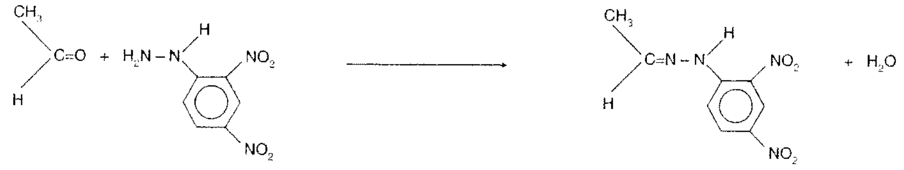
Example: addition of hydrogen cyanide to ethanal



ADDITION-ELIMINATION (CONDENSATION)

Occurs when nucleophiles containing the $-NH_2$ group react with aldehydes or ketones. The initial step is nucleophilic addition then elimination of water occurs.

Example: reaction of 2,4-dinitrophenylhydrazine with ethanal



Addition-elimination also occurs when acid anhydrides and acyl chlorides react with H_2O, ROH, NH_3 and amines.