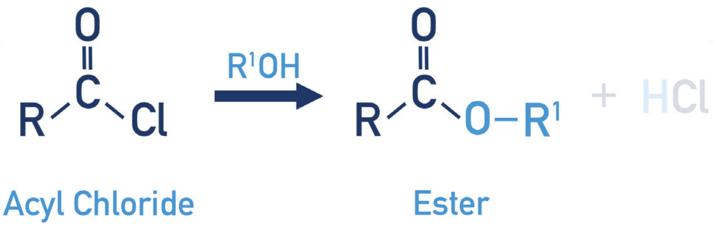
Organic Chemistry Revision Sheets
Acyl Chlorides | Nucleophilic Addition-Elimination (with alcohol)

Reaction

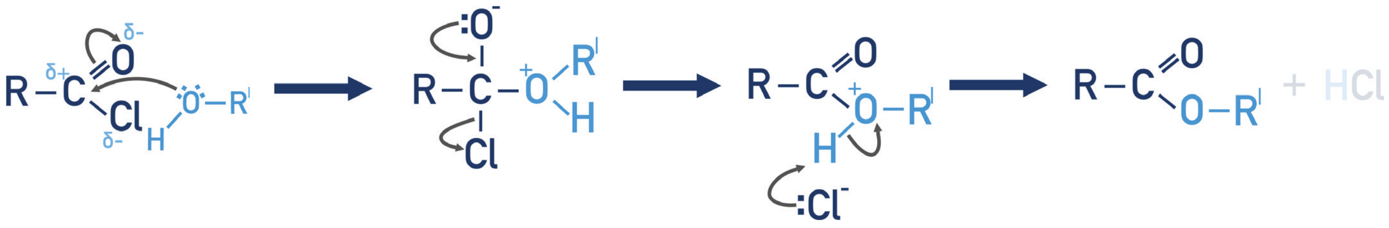
REACTANTS: Acyl Chloride and Alcohol
PRODUCT: Ester and HCl
REACTION TYPE: Nucleophilic Addition-Elimination, *Esterification*

REACTION:



Mechanism

The alcohol acts as a **nucleophile** due to the lone pair of electrons on the oxygen atom attacking the carbon (with a partial positive charge) in the acyl chloride group. A new carbon-oxygen bond forms between the acyl group and the alcohol. The carbon-oxygen double bond breaks to a single bond, giving the oxygen a negative charge. The carbon-oxygen double bond reforms, the carbon-chlorine bond breaks and a chloride ion is removed. Chloride ion removes H^+ ion from $-RCOOH^+R^1$ group, forming $RCOOR^1$. ***Addition-elimination reaction.***



Notes:

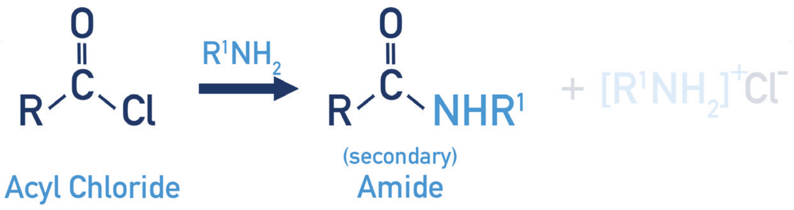
- As an ester is formed, this is an example of an esterification reaction

Organic Chemistry Revision Sheets
Acyl Chlorides | Nucleophilic Addition-Elimination (with amines)

Reaction

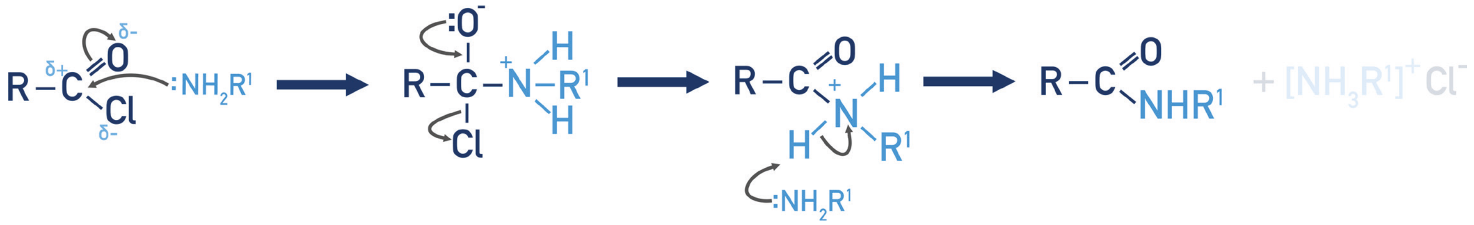
REACTANTS: Acyl Chloride and Amine (primary)
PRODUCT: (Secondary) Amide and Alkyl Ammonium Chloride
REACTION TYPE: Nucleophilic Addition-Elimination

REACTION:



Mechanism

The amine acts as a **nucleophile** due to the lone pair of electrons on the nitrogen atom attacking the carbon (with a partial positive charge) in the acyl chloride. A new carbon-nitrogen bond forms between the acyl group and the ammonia. The carbon-oxygen double bond breaks to a single bond, giving the oxygen a negative charge. The carbon-oxygen double bond reforms, carbon-chlorine bond breaks and a chloride ion is removed. Amine present removes H^+ ion from $-RCON^+HR^1$ group. ***Addition-elimination reaction.***



Notes:

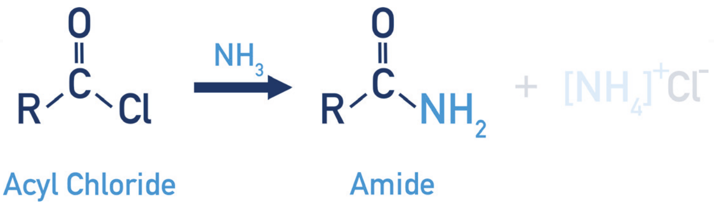
- Ammonia produces a **primary amide** and **ammonium chloride salt** when reacted with acyl chlorides.
- Primary amines produce a **secondary amide** and **an alkyl ammonium chloride salt** when reacted with acyl chlorides.
- Secondary amines produce a **tertiary amide** and **an alkyl ammonium chloride salt** when reacted with acyl chlorides.

Organic Chemistry Revision Sheets
Acyl Chlorides | Nucleophilic Addition-Elimination (with NH_3)

Reaction

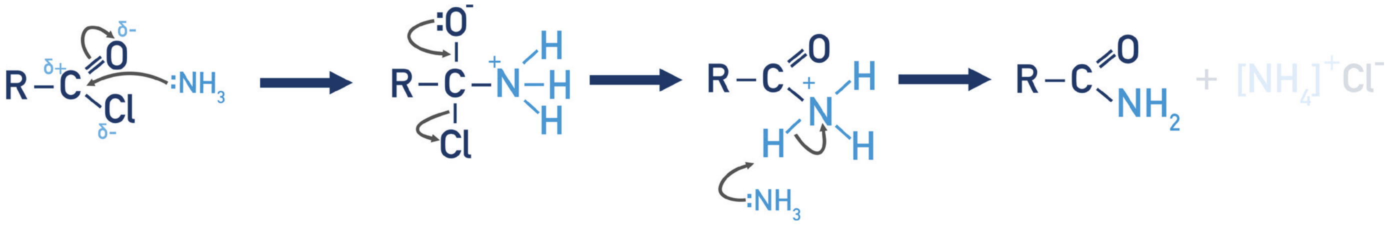
REACTANTS: Acyl Chloride and Ammonia
PRODUCT: Amide and Ammonium Chloride (salt)
REACTION TYPE: Nucleophilic Addition-Elimination

REACTION:



Mechanism

The ammonia acts as a **nucleophile** due to the lone pair of electrons on the nitrogen atom attacking the carbon (with a partial positive charge) in the acyl chloride. A new carbon-nitrogen bond forms between the acyl group and the ammonia. The carbon-oxygen double bond breaks to a single bond, giving the oxygen a negative charge. The carbon-oxygen double bond reforms, the carbon-chlorine bond breaks and a chloride ion is removed. The ammonia present removes H^+ ion from -$RCONH_3^+$ group. ***Addition-elimination reaction.***



Notes:

- Ammonia produces a **primary amide** and ammonium chloride salt when reacted with acyl chlorides.
- Primary amines produce a **secondary amide** and an alkyl ammonium chloride salt when reacted with acyl chlorides.
- Secondary amines produce a **tertiary amide** and an alkyl ammonium chloride salt when reacted with acyl chlorides.

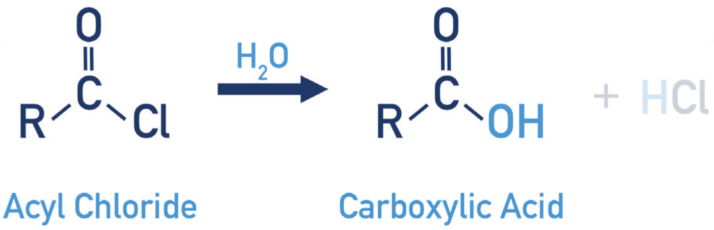
Organic Chemistry Revision Sheets

Acyl Chlorides | Nucleophilic Addition-Elimination (with water)

Reaction

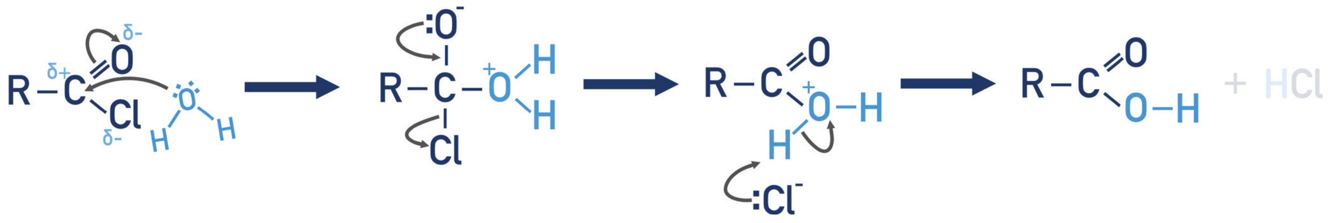
REACTANTS: Acyl Chloride and H_2O
PRODUCT: Carboxylic Acid and HCl
REACTION TYPE: Nucleophilic Addition-Elimination, *Hydrolysis of acyl chloride*

REACTION:



Mechanism

H_2O acts as a **nucleophile** due to the lone pair of electrons on the oxygen atom attacking the carbon (with a partial positive charge) in the acyl chloride. A new carbon-oxygen bond forms and the carbon-oxygen double bond breaks to a single bond, giving the oxygen a negative charge. The carbon-oxygen double bond reforms, the carbon-chlorine bond breaks and a chloride ion is removed. The chloride ion removes a H^+ ion from $-OH_2^+$ group, forming RCOOH. ***Addition-elimination reaction.***



Notes:

- Acyl chlorides are highly reactive and the reaction is vigorous, with heat given off (exothermic) and fumes of HCl released.

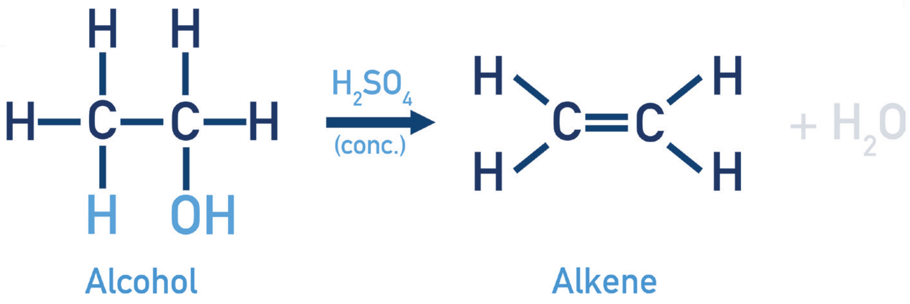
Organic Chemistry Revision Sheets

Alcohols | Elimination to form alkene (dehydration)

Reaction

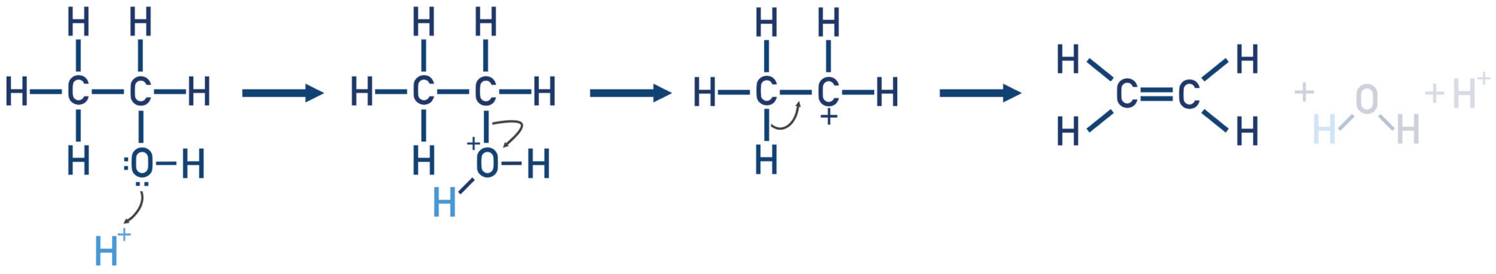
REACTANTS: Alcohol
CONDITIONS: Heat, Acid Catalyst (concentrated H_2SO_4 or concentrated H_3PO_4)
PRODUCT: Alkene
REACTION TYPE: Elimination Reaction, *dehydration*

REACTION: (example of ethanol)



Mechanism (simplified)

-OH group on alcohol accepts a H^+ ion from acid*, becoming $-OH_2^+$ (alcohol is 'protonated'). The carbon-oxygen bond breaks, forming a water molecule and a positively charged carbon atom (carbocation). A neighbouring carbon-hydrogen breaks, giving an electron pair to the carboncation, forming a carbon-carbon double bond. H^+ is released. H_2O is 'removed' from the alcohol - dehydration. ***Elimination reaction.***



Notes:

- The mechanism shown is a simplification as it is highly unlikely a primary carbocation would form (due to its instability as an intermediate).
- **It must be noted the H^+ ion comes from the concentrated acid (not shown in the mechanism), either H_2SO_4 or H_3PO_4.*
- The removal of a water molecule makes this a **dehydration** reaction.

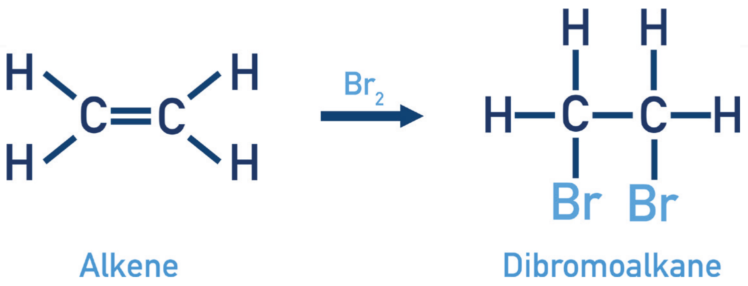
Organic Chemistry Revision Sheets

Alkenes | Electrophilic Addition (with Br_2)

Reaction

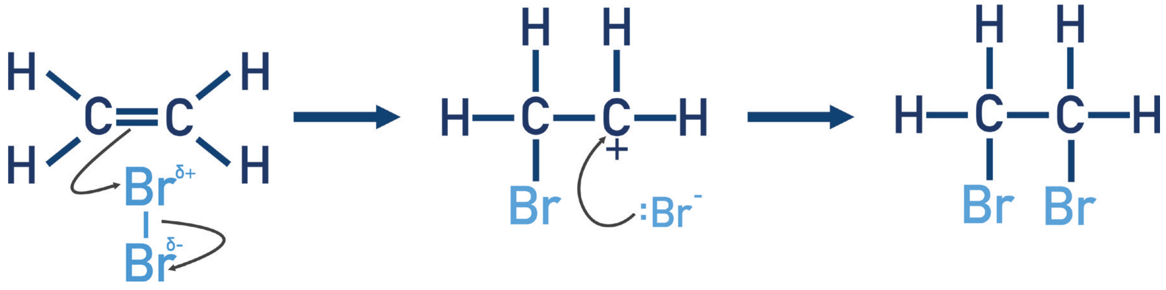
REACTANTS: Alkene and Bromine (Br_2)
CONDITIONS: Non-polar organic solvent (or pure liquid bromine)
PRODUCT: Dibromoalkane
REACTION TYPE: Electrophilic Addition

REACTION: (example of ethene)



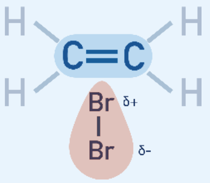
Mechanism

Br_2 acts as an electrophile so the bromine-bromine bond is polarised by the carbon-carbon double bond so the bromine atom with a partial positive charge accepts an electron pair from the carbon-carbon double bond. During the reaction the carbon-carbon double bond breaks, forming a postively charged carbon (carbocation). The negatively charged bromide ion bonds with the carbocation. Br_2 is 'added' across the double carbon-carbon bond. ***Addition reaction.***



Notes:

- The high electron density in the carbon-carbon double bond (pi-bond) polarises the bromine molecule to create the $Br^{\delta+}$ electrophile.
- *This reaction is often used to identify an alkene as the colour of bromine water changes from orange / brown to colourless when mixed with an alkene (due to the above reaction).*



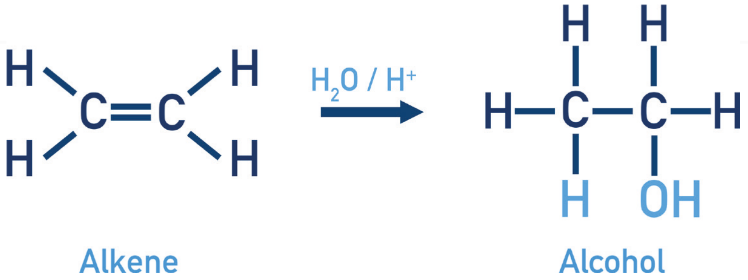
Organic Chemistry Revision Sheets

Alkenes | Hydration (with H_2O in presence of acid, H^+)

Reaction

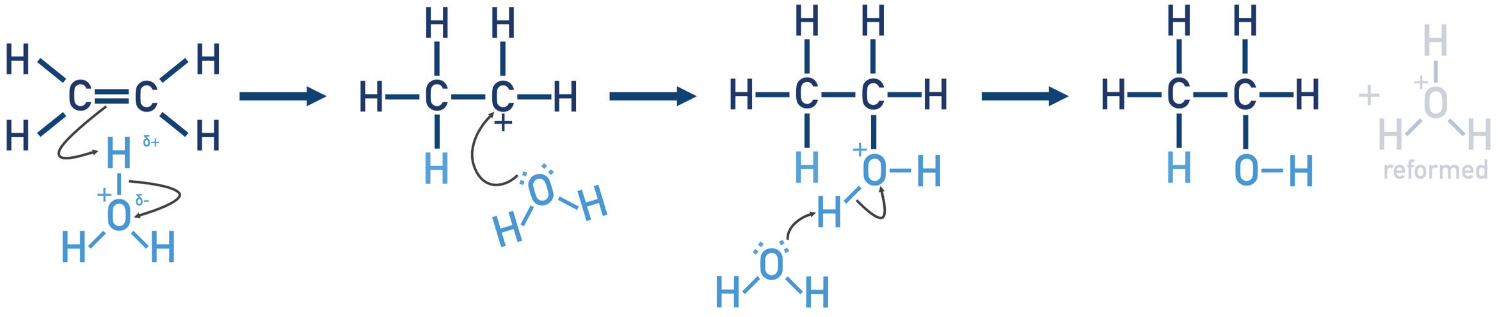
REACTANTS: Alkene and H_2O
CONDITIONS: Acid Catalyst
PRODUCT: Alcohol
REACTION TYPE: Electrophilic Addition, *Acid Catalysed Hydration*

REACTION: (example of ethene)



Mechanism

H_3O^+ acts as an electrophile because one of its $H^{\delta+}$ atoms accepts an electron pair from the carbon-carbon double bond, causing H_2O to form from the H_3O^+. The carbon-carbon double bond breaks, forming a postively charged carbon (carbocation). The lone pair of electrons on an oxygen atom in H_2O form a bond with the carbocation. Another water molecule removes a H^+ from the $-OH_2^+$ group and H_3O^+ is reformed. H_2O is 'added' across the carbon-carbon double bond - hydration. ***Addition reaction.***



Notes:

- The reaction must be carried out in acidic conditions to form a H_3O^+ (hydroxonium) ion.

$$H_2O + H^+ \rightarrow H_3O^+$$

- If a primary or secondary carbocation can be formed during the reaction, **the secondary carbocation will form more readily than the primary carbocation** - creating 'major' and 'minor' products*.
- The secondary carbocation is more stable due to an increased positive inductive effect from neighbouring alkyl chains.
- **The product mixture will contain more of the major than the minor product.*

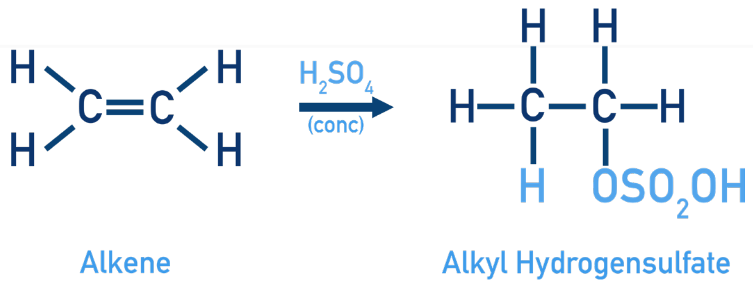
Organic Chemistry Revision Sheets

Alkenes | Electrophilic Addition (with H_2SO_4)

Reaction

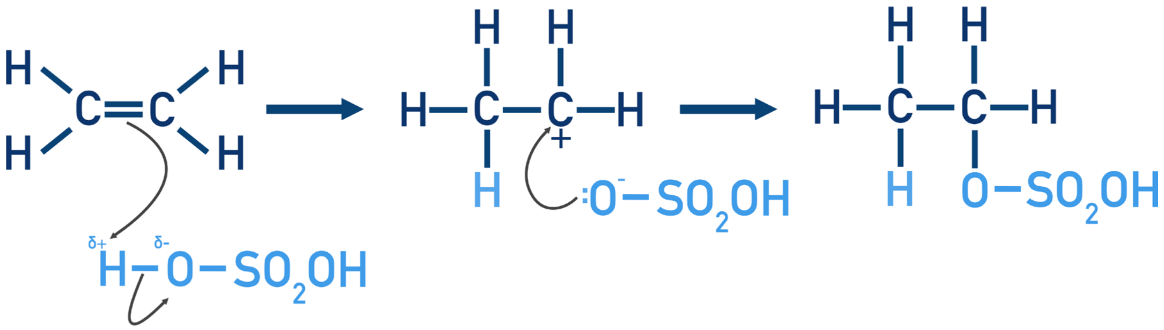
REACTANTS: Alkene and H_2SO_4 (*Concentrated Sulfuric Acid*)
CONDITIONS: Concentrated H_2SO_4
PRODUCT: Alkyl Hydrogensulfate
REACTION TYPE: Electrophilic Addition

REACTION: (example of ethene)



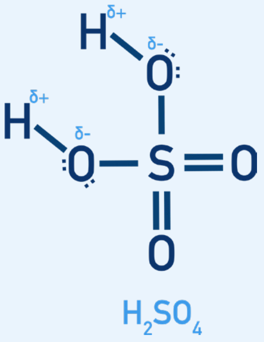
Mechanism

H_2SO_4 acts as an electrophile because its hydrogen atoms have a large partial positive charge, so one of them accepts an electron pair from the carbon-carbon double bond. During the reaction the carbon-carbon double bond breaks, forming a postively charged carbon (carbocation). The negatively charged hydrogensulfate ion bonds with the carbocation. H and HSO_4 is 'added' across the carbon-carbon double bond. ***Addition reaction.***



Notes:

- If a primary or secondary carbocation can be formed during the reaction, **the secondary carbocation will form more readily than the primary carbocation** - creating 'major' and 'minor' products*.
- The secondary carbocation is more stable due to increased positive inductive effect from neighbouring alkyl chains.
- Oxygen atoms in the sulfuric acid have lone pairs of electrons (not shown in the mechanism above).
- **The product mixture will contain more of the major product than the minor product.*



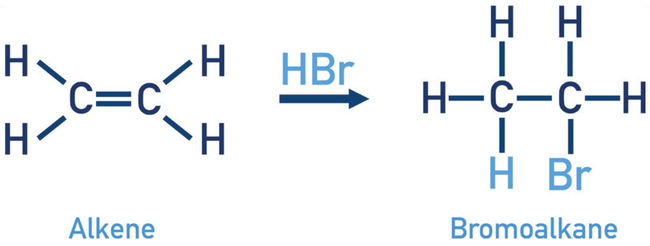
Organic Chemistry Revision Sheets

Alkenes | Electrophilic Addition (with HBr)

Reaction

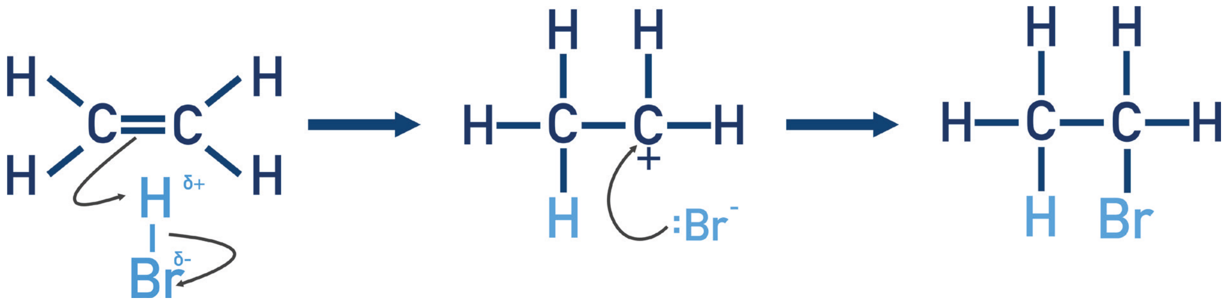
REACTANTS: Alkene and HBr (Hydrogen Bromide)
PRODUCT(S): Bromoalkane
REACTION TYPE: Electrophilic Addition

REACTION:
(example of ethene)



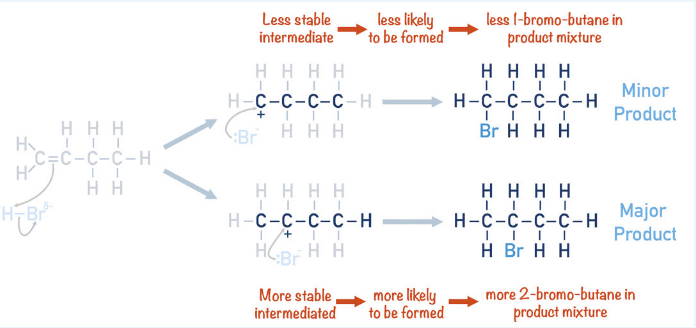
Mechanism

HBr acts as an electrophile because its hydrogen atom (with a partial positive charge) accepts an electron pair from the carbon-carbon double bond. During the reaction the carbon-carbon double bond breaks, forming a postively charged carbon ion (carbocation). The negatively charged bromide ion bonds with the carbocation. HBr is 'added' across the carbon-carbon double bond. ***Addition reaction.***



Notes:

- If a primary or secondary carbocation can be formed during the reaction, **the secondary carbocation will form more readily than the primary carbocation** - creating 'major' and 'minor' products*.
- The secondary carbocation is more stable due to increased positive inductive effect from neighbouring alkyl chains.
- **The product mixture will contain more of the major product than the minor product.*



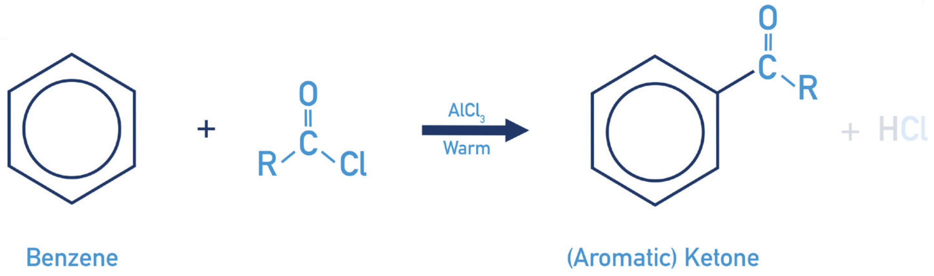
Organic Chemistry Revision Sheets

Benzene | Electrophilic Subsititution, Friedel-Crafts (Acylation)

Reaction

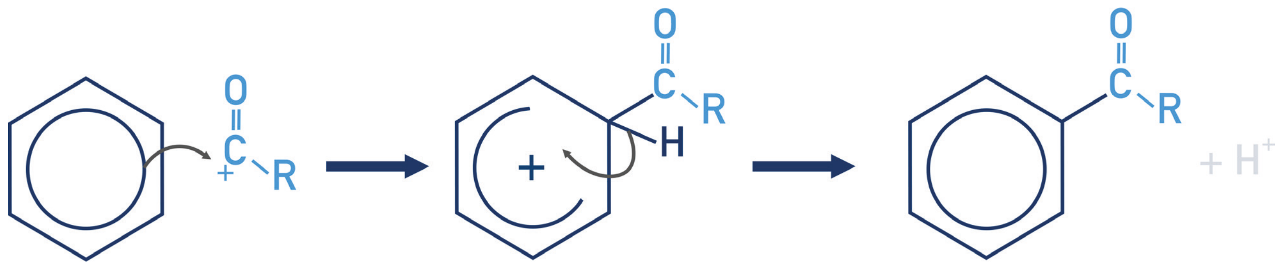
REACTANTS: Benzene and Acyl Chloride
CONDITIONS: Warm and $AlCl_3$ catalyst
PRODUCT: (Aromatic) Ketone
REACTION TYPE: Electrophilic Substitution, *Acylation*

REACTION: (example of benzene)



Mechanism

Acylium (RCO^+) ion **acts as an electrophile due to its carbocation accepting an electron pair** from the delocalised ring of electrons in the benzene ring. A carbon-carbon bond forms. The carbon-hydrogen bond breaks to give the electron pair back to the ring of delocalised electrons. RCO^+ ion replaces H on benzene ring. ***Substitution reaction***.



Notes:

- Acylium (RCO^+) ion is formed by reacting an acyl chloride with a halogen carrier ($AlCl_3$)

$$RCOCl + \underset{\text{Halogen Carrier}}{AlCl_3} \longrightarrow \underset{\text{Acylium ion}}{R\overset{+}{C}O} + [AlCl_4]^-$$

- H^+ ion removed from benzene ring combines with $[AlCl_4]^-$ to reform $AlCl_3$ catalyst and HCl is formed:

$$H^+ + Cl{-}AlCl_3^- \longrightarrow HCl + \underset{\text{Halogen Carrier}}{AlCl_3}$$

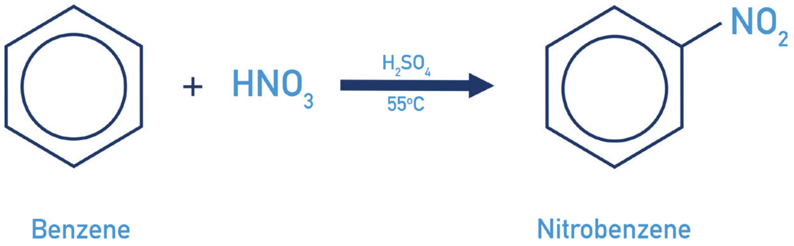
Organic Chemistry Revision Sheets

Benzene | Electrophilic Subsititution, (Nitration, with HNO_3)

Reaction

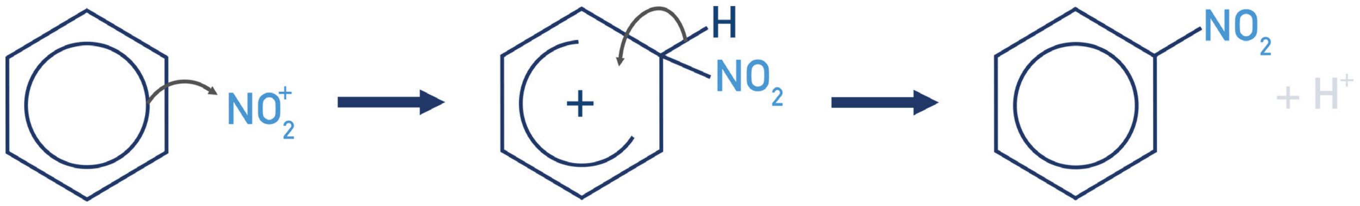
REACTANTS: Benzene and Nitric Acid
CONDITIONS: 55°C and conc. sulfuric acid (H_2SO_4)
PRODUCT: Nitrobenzene
REACTION TYPE: Electrophilic Substitution, *Nitration*

REACTION: (example of benzene)



Mechanism

Nitronium (NO_2^+) ion **acts as an electrophile due to its positively charged nitrogen atom accepting an electron pair** from the delocalised ring of electrons in the benzene ring. A Carbon-nitrogen bond forms. The carbon-hydrogen bond breaks to give electron pair back to delocalised ring of electrons. NO_2^+ ion replaces H on benzene ring - ***substitution reaction***.



Notes:

- Nitronium ion is formed by the reaction of concentrated nitric acid with concentrated sulfuric acid

$$HNO_3 + H_2SO_4 \longrightarrow H_2NO_3^+ + HSO_4^-$$

$$H_2NO_3^+ \longrightarrow NO_2^+ + H_2O$$

Nitronium Ion

- H^+ ion removed from benzene ring combines with hydrogen sulfate (HSO_4^-) ion to reform catalyst H_2SO_4:

$$\mathbf{H^+ + HSO_4^- \rightarrow H_2SO_4}$$

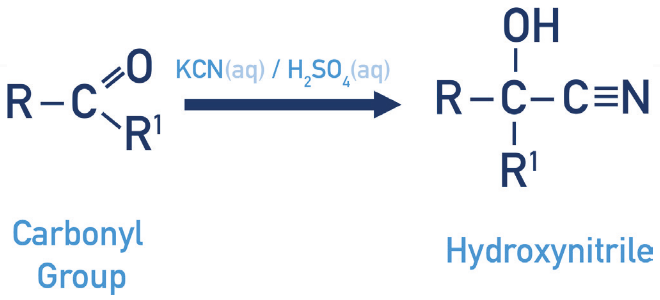
Organic Chemistry Revision Sheets

Carbonyl Compounds | Nucleophilic Addition (KCN, H^+)

Reaction

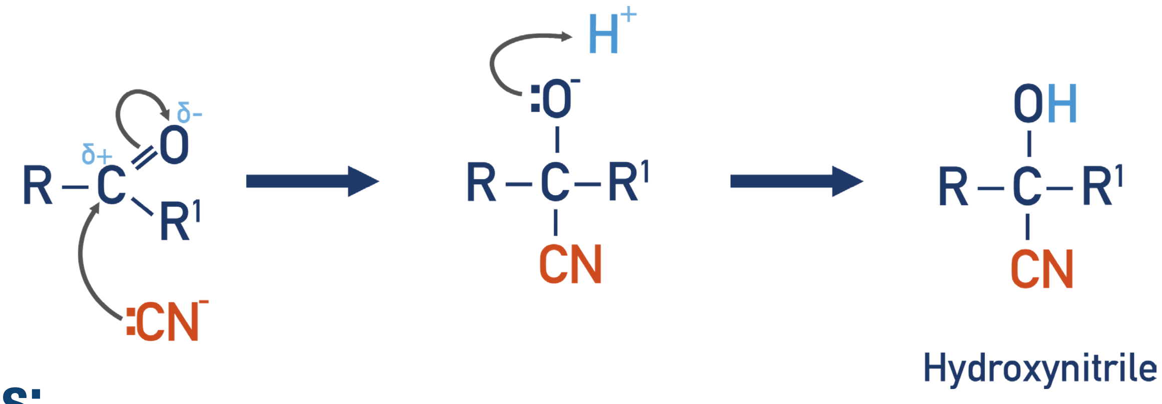
REACTANTS: Carbonyl (aldehyde or ketone) and KCN (in acid)
PRODUCT: Hydroxynitrile
REACTION TYPE: Nucleophilic Addition

REACTION:



Mechanism

Cyanide ion (:CN^-) comes from KCN(aq) and **acts as a nucleophile due to its lone pair of electrons, attacking the carbon (with partial positive charge) in the carbonyl group.** Carbon-carbon bond forms. The carbon-oxygen double bond breaks to a single bond, giving the oxygen a negative charge. The negative oxygen is protonated in dilute acid (H_2SO_4), forming a hydroxyl group. Hydroxynitrile is formed. CN and H are added to the carbonyl. ***Addition reaction.***



Notes:

- HCN is sometimes written as the reactant, but HCN is very reactive and dangerous however. By using KCN in dilute acid, the same product can be formed as with HCN.

  $$\mathrm{HCN + RR'CO \rightarrow RR'C(OH)CN}$$

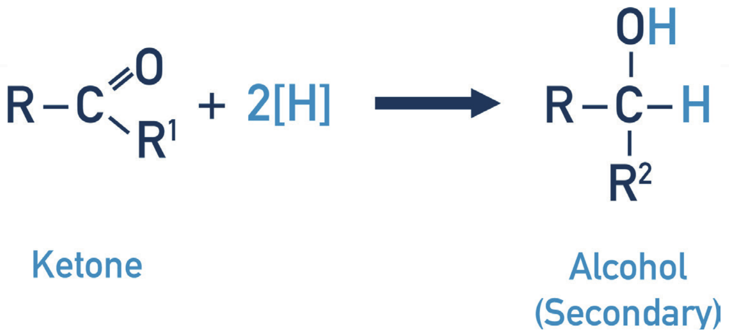
- If a chiral carbon centre is formed in the product, the final product mixture will be **racemic** containing both enantiomers in a 50:50 ratio. This is because carbonyl groups are planar and there is equal chance of the :CN^- nucleophile attacking the carbonyl group from above or below the plane - producing two possible enantiomers in equal amounts.

Organic Chemistry Revision Sheets
Carbonyl Compounds | Nucleophilic Addition ($NaBH_4$)

Reaction

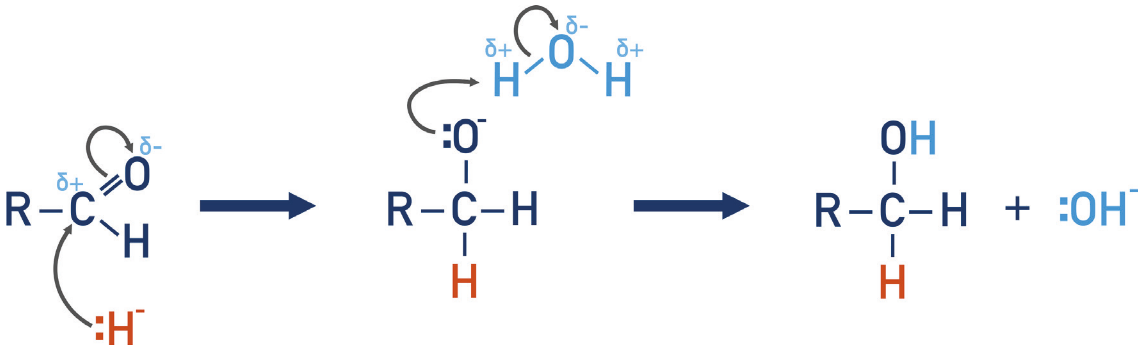
REACTANTS: Carbonyl (aldehyde or ketone) and $NaBH_4$ or $LiAlH_4$
PRODUCT: Alcohol
REACTION TYPE: Nucleophilic Addition, *reduction*

REACTION:
(example of ketone)



Mechanism

Hydride ion (:H$^-$) comes from reducing agent ($NaBH_4$ or $LiAlH_4$*) and **acts as a nucleophile due to its lone pair of electrons attacking the carbon (with partial positive charge) in the carbonyl group**. A carbon-hydrogen bond forms. The carbon-oxygen double bond breaks to a single bond, giving the oxygen a negative charge. The negative oxygen is protonated by water, forming a hydroxyl group and a hydroxide ion. Alcohol is formed, H is added to the carbonyl.***Addition reaction.***



Notes:

- Aldehydes form **primary alcohols** when reduced.
- Ketones form **secondary alcohols** when reduced.
- *$NaBH_4$ and $LiAlH_4$ are reducing agents, they are able to provide hydride (:H$^-$) ions that are needed for the reduction of carbonyls.

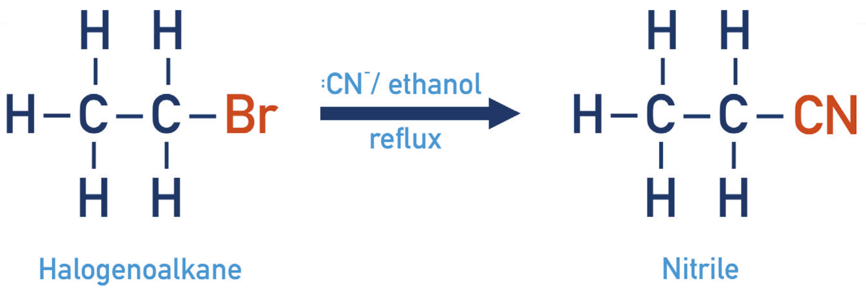
Organic Chemistry Revision Sheets

Halogenoalkanes | Nucleophilic Substitution (with :CN^-)

Reaction

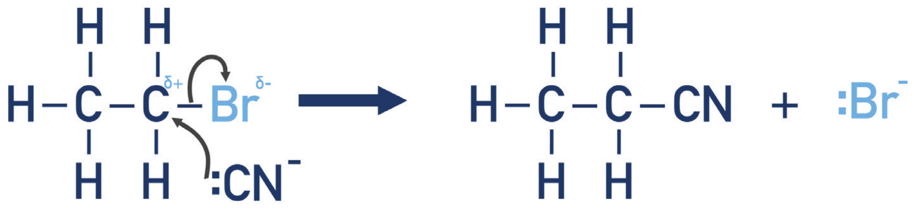
REACTANTS: Halogenoalkane and Sodium *or Potassium* Cyanide (NaCN *or KCN*)
CONDITIONS: Heat under reflux, Ethanolic (ethanol as the solvent, **no water present**)
PRODUCT(S): Nitrile and Halide Ion (*forms salt with Na^+ or K^+*)
REACTION TYPE: Nucleophilic Substitution

REACTION: (example of bromoethane)



Mechanism

Cyanide ion (CN^-) acts as a nucleophile and attacks the partially positive carbon atom in the carbon-halogen bond. The carbon-halogen breaks, forming a nitrile and a halide ion. CN group is **substituted** for the halogen group.



Notes:

- Reaction must be carried out in **ethanolic conditions (in ethanol, no water present), otherwise an alcohol is likely to form** rather than the nitrile.
- Reaction is heated under reflux to ensure no volatile substances are lost.
- The strength of the carbon-halogen bond (bond enthalpy) determines the speed of the reaction. The stronger the bond, the slower the nucleophilic substitution reaction. *C-F bond is strongest, giving the slowest reaction; the C-I bond is weakest, giving the fastest reaction.*

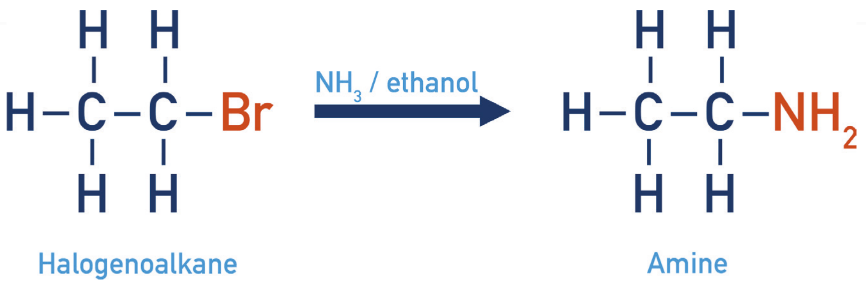
Organic Chemistry Revision Sheets

Halogenoalkanes | Nucleophilic Substitution (with NH_3)

Reaction

REACTANTS: Halogenoalkane and Ammonia (NH_3)
CONDITIONS: Heat*, Ethanolic conditions
PRODUCT(S): Amine and Ammonium Halide Salt
REACTION TYPE: Nucleophilic Substitution

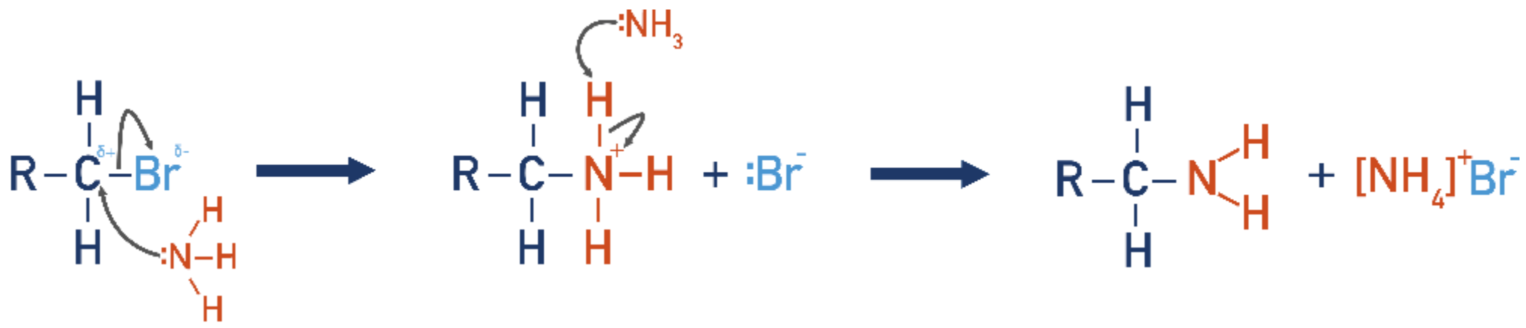
REACTION:
(example of bromoethane)



$$CH_3CH_2Br \xrightarrow{NH_3\ /\ \text{ethanol}} CH_3CH_2NH_2$$

Mechanism

Ammonia (NH_3) acts as a nucleophile, due to its lone pair of electrons on the nitrogen atom and attacks the partially positive carbon atom in the carbon-halogen bond. The carbon-halogen bond breaks, forming an (aliphatic) amine and ammonium halide salt. NH_2 group is **substituted** for the halogen group.



Notes:

- Reaction must be carried out in **ethanolic conditions (in ethanol, no water present), otherwise an alcohol is likely to form** rather than the nitrile.
- *A sealed container containing reactants is heated (otherwise ammonia would escape due its high volatility).
- The amine formed in the reaction is actually a stronger base than ammonia, so an ammonium-alkyl salt may be formed. The amine can be obtained by adding sodium hydroxide to the mixture - forcing the amine group to 'release' a H^+ ion and become a neutral molecule.
- The strength of the carbon-halogen bond (bond enthalpy) determines the speed of the reaction. The stronger the bond, the slower the nucleophilic substitution reaction. *C-F bond is strongest, giving the slowest reaction; C-I bond is weakest, giving the fastest reaction.*

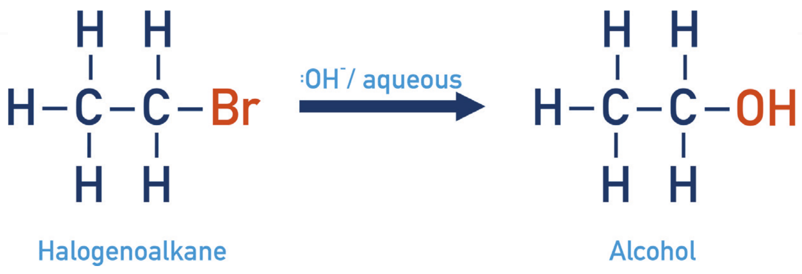
Organic Chemistry Revision Sheets

Halogenoalkanes | Nucleophilic Substitution (with $OH^-_{(aq)}$)

Reaction

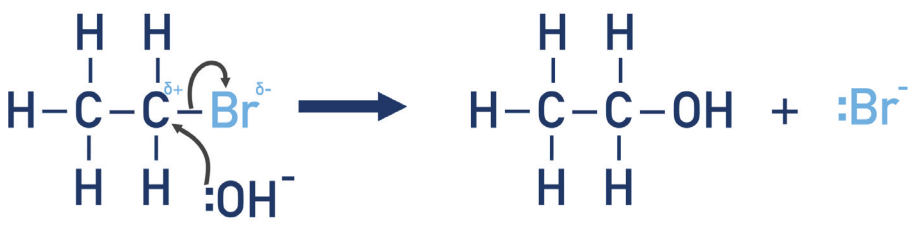
REACTANTS: Halogenoalkane and Sodium Hydroxide, *NaOH* (for OH^- ions)
CONDITIONS: Aqueous ('aq' - water present)
PRODUCT(S): Alcohol and Halide Ion (*sodium halide salt if sodium hydroxide used*)
REACTION TYPE: Nucleophilic Substitution

REACTION:
(example of bromoethane)



Mechanism

Hydroxide ion (OH^-) acts as a nucleophile and attacks the partially positive carbon atom in the carbon-halogen bond. The carbon-halogen breaks, forming alcohol and halide ion. OH group is **substituted** for the halogen group.



Notes:

- Reaction **must be carried out in aqueous conditions (in water), otherwise an elimination reaction will occur and an alkene will be formed.**
- The strength of the carbon-halogen bond (bond enthalpy) determines the speed of the reaction. The stronger the bond, the slower the nucleophilic substitution reaction. *C-F bond is strongest, giving the slowest reaction; C-I bond is weakest, giving the fastest reaction.*

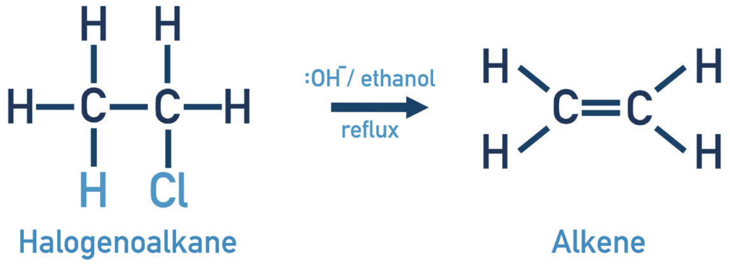
Organic Chemistry Revision Sheets

Halogenoalkanes | Elimination (with OH^-)

Reaction

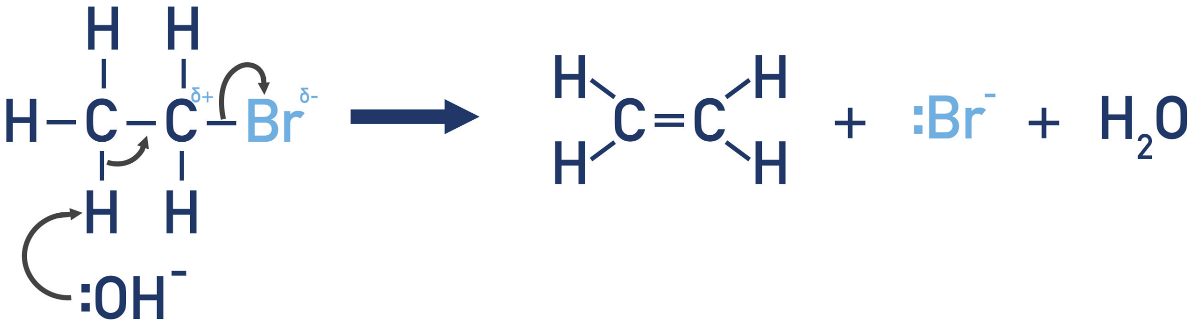
REACTANTS: Halogenoalkane and Sodium (*or Potassium*) Hydroxide, $NaOH$
CONDITIONS: Heat under reflux, Ethanolic conditions (in ethanol, no water present)
PRODUCT(S): Alkene and Halide Ion (and water)
REACTION TYPE: Elimination

REACTION:
(example of chloroethane)



Mechanism

Hydroxide ion ($:OH^-$) acts as a base due to the lone pair of electrons on the oxygen atom allowing it to remove a H^+ ion from the carbon atom next to the carbon-halogen bond. The carbon-halogen bond breaks, forming a double bond between carbon atoms. The halogen group is **eliminated** from the halogenoalkane.



Notes:

- Reaction must be carried out in **ethanolic conditions (in ethanol, no water present), otherwise an alcohol is likely to form** rather than the alkene.
- Unlike in nucleophilic substitution reactions of halogenoalkanes, the **hydroxide ion is acting as a base**.
- The strength of the carbon-halogen bond (bond enthalpy) determines the speed of the reaction. The stronger the bond, the slower the nucleophilic substitution reaction. *C-F bond is strongest, giving slowest reaction; C-I bond is weakest, giving fastest reaction.*

Organic Chemistry Revision Sheets

Alkanes | Free Radical Substitution

Reaction

REACTANTS: Alkane and Halogen
CONDITIONS: U.V (ultraviolet) light
PRODUCT(S): Halogenoalkane and Hydrogen Halide
REACTION TYPE: Free Radical Substitution

REACTION: (example of methane and chlorine)

ultraviolet light required for reaction to occur

$$CH_4 + Cl_2 \xrightarrow{u.v} CH_3Cl + HCl$$

Mechanism

INITIATION STEP: Halogen molecule undergoes heterolytic fission to form radical species:

$$Cl_2 \xrightarrow{u.v} 2Cl\bullet$$

PROPAGATION STEP: Radical species reacts with alkane to form alkyl radical and HCl. Alkyl radical then reacts with halogen molecule, reforming another halogen radical, creating a **chain reaction**:

new radical formed

$$CH_4 + Cl\bullet \longrightarrow \bullet CH_3 + HCl$$

$$\bullet CH_3 + Cl_2 \longrightarrow CH_3Cl + Cl\bullet$$

(new) radical formed

TERMINATION STEP: Radical species combine to end chain reaction:

$$Cl\bullet + Cl\bullet \longrightarrow Cl_2$$

$$\bullet CH_3 + Cl\bullet \longrightarrow CH_3Cl$$

$$\bullet CH_3 + \bullet CH_3 \longrightarrow CH_3CH_3$$

Two unpaired electrons combine to form a bond between the two species

Products are no longer radicals

Notes:

- Heterolytic fission is the even breaking of a covalent bond (each bonded atom gets an electron and becomes a radical species).
- UV light provides the energy required for hetereolytic fission.
- Further substitution reactions can occur, eventually forming tetrachloromethane:
  chloromethane to dichloromethane to trichloromethane to tetrachloromethane