



Organic Chemistry Revision Sheets

Alkenes | Electrophilic Addition (with Br₂)

Reaction

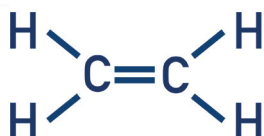
REACTANTS: Alkene and Bromine (Br₂)

CONDITIONS: Non-polar organic solvent (or pure liquid bromine)

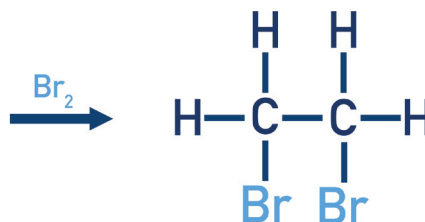
PRODUCT: Dibromoalkane

REACTION TYPE: Electrophilic Addition

REACTION:
(example of
ethene)



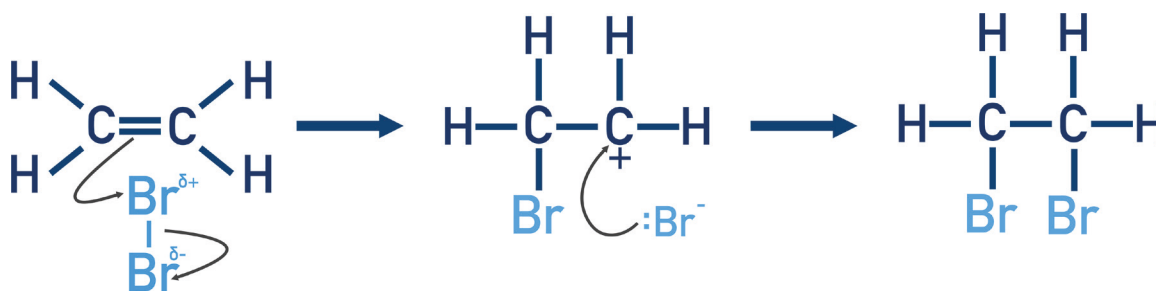
Alkene



Dibromoalkane

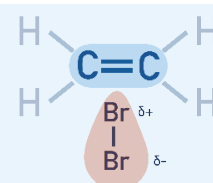
Mechanism

Br₂ 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 positively charged carbon (carbocation). The negatively charged bromide ion bonds with the carbocation. Br₂ 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^{δ+} 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 | Electrophilic Addition (with HBr)

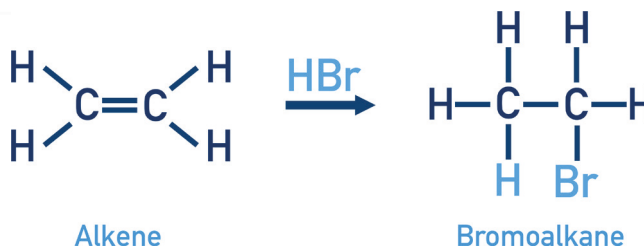
Reaction

REACTANTS: Alkene and HBr (Hydrogen Bromide)

PRODUCT(S): Bromoalkane

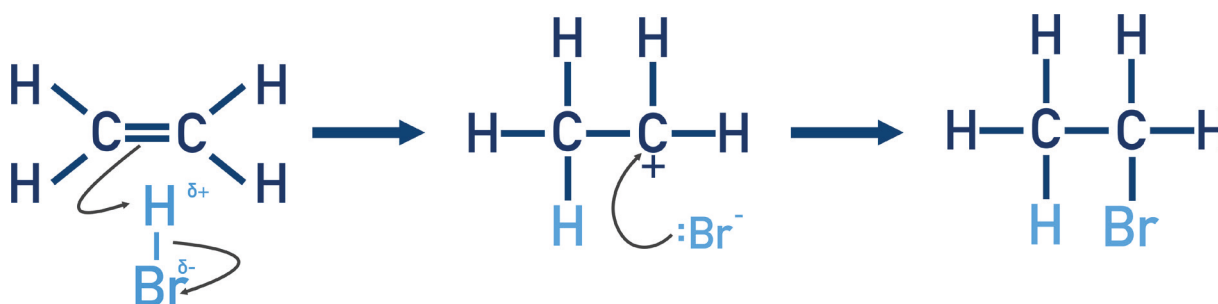
REACTION TYPE: Electrophilic Addition

REACTION:
(example of
ethene)



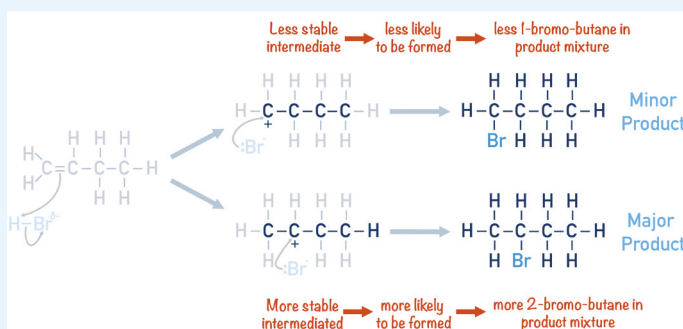
Mechanism

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 positively 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 Substitution (Halogenation, with Br₂)

Reaction

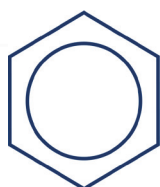
REACTANTS: Benzene and Halogen

CONDITIONS: Halogen carrier (AlCl₃, AlBr₃ or Fe)

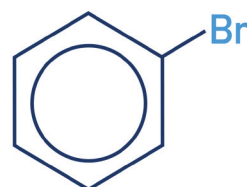
PRODUCT: Halogenated Arene (chloro-benzene, bromo-benzene)

REACTION TYPE: Electrophilic Substitution, *Halogenation*

REACTION:
(example of
benzene)



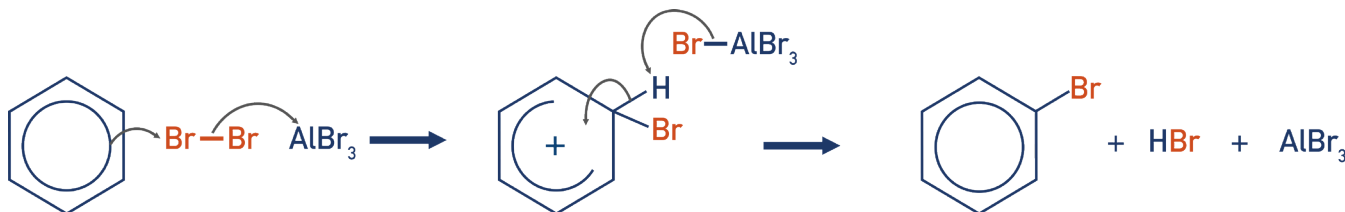
Benzene



Bromobenzene

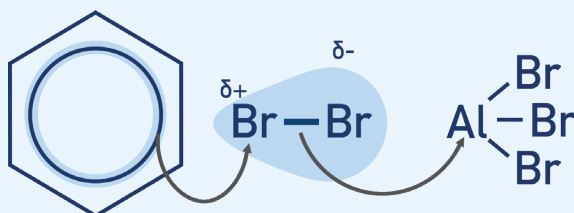
Mechanism

Bromine molecule **acts as an electrophile** because it is **polarised sufficiently by a halogen carrier (AlBr₃)** and accepts an electron pair from the delocalised ring of electrons in the benzene ring. A carbon-bromine bond forms. The carbon-hydrogen bond breaks to give the electron pair back to the delocalised ring of electrons. Br replaces H on the benzene ring. **Substitution reaction.**



Notes:

- Benzene is unable to undergo halogenation without a halogen carrier as the delocalised electron ring is unable to polarise the halogen molecule enough to form an electrophile.
- The halogen carrier polarises the halogen molecule to the point of enabling one of the halogen atoms (now with a partial positive charge) to act as an electrophile and accept a pair of electrons from benzene.





Organic Chemistry Revision Sheets

Benzene | Electrophilic Substitution, (Nitration, with HNO_3)

Reaction

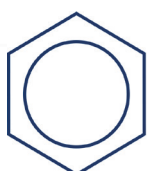
REACTANTS: Benzene and Nitric Acid

CONDITIONS: 55°C and conc. sulfuric acid (H_2SO_4)

PRODUCT: Nitrobenzene

REACTION TYPE: Electrophilic Substitution, *Nitration*

REACTION:
(example of
benzene)



Benzene

+

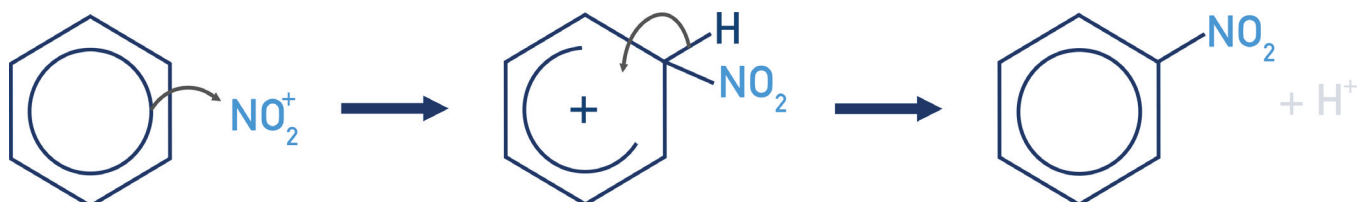
HNO_3



Nitrobenzene

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



Nitronium Ion

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





Organic Chemistry Revision Sheets

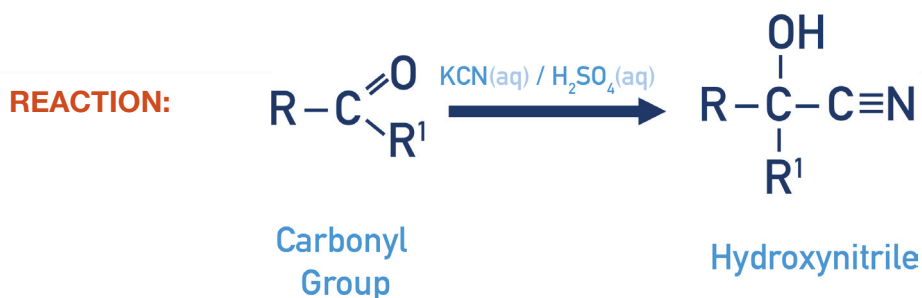
Carbonyl Compounds | Nucleophilic Addition (KCN, H⁺)

Reaction

REACTANTS: Carbonyl (aldehyde or ketone) and KCN (in acid)

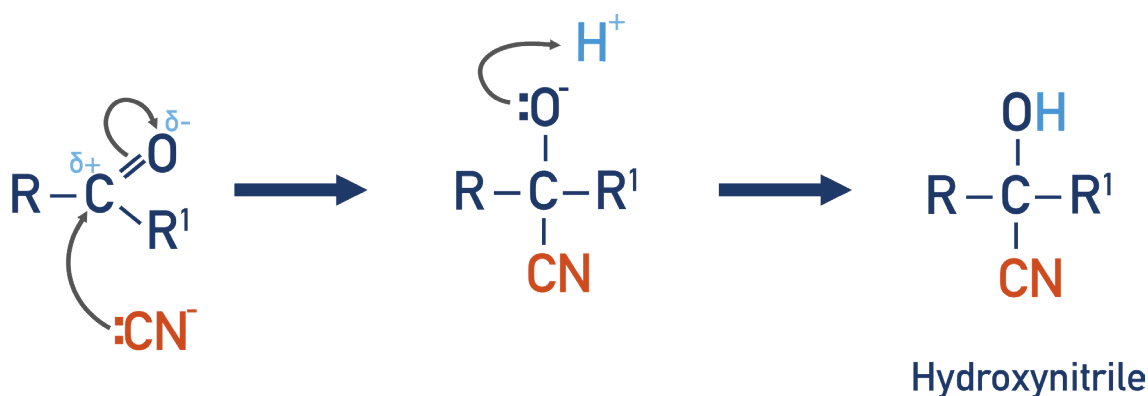
PRODUCT: Hydroxynitrile

REACTION TYPE: Nucleophilic Addition



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 (H₂SO₄), 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.



- 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

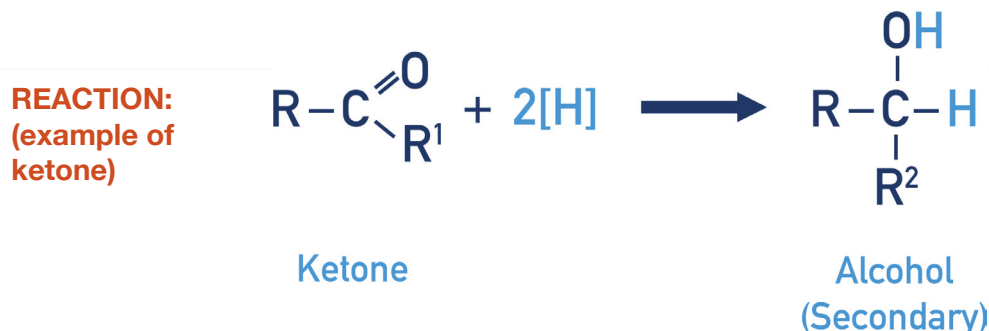
Carbonyl Compounds | Nucleophilic Addition (NaBH_4)

Reaction

REACTANTS: Carbonyl (aldehyde or ketone) and NaBH_4 or LiAlH_4

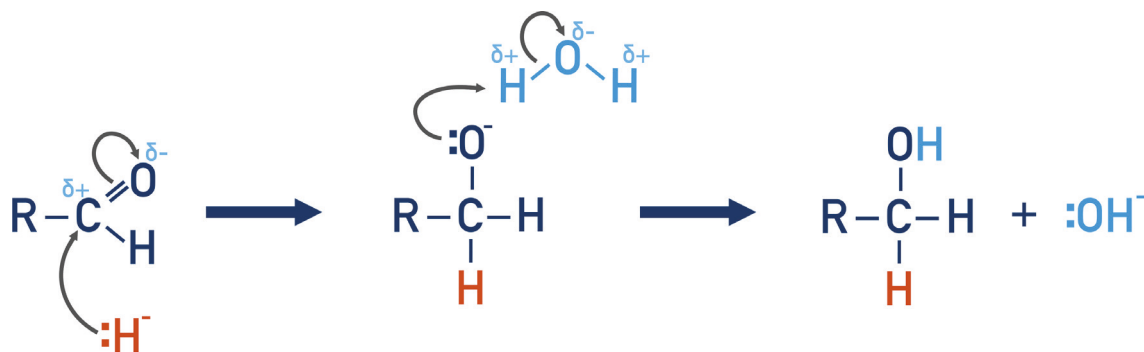
PRODUCT: Alcohol

REACTION TYPE: Nucleophilic Addition, *reduction*



Mechanism

Hydride ion ($:\text{H}^-$) 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 ($:\text{H}^-$) ions that are needed for the reduction of carbonyls.



Organic Chemistry Revision Sheets

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

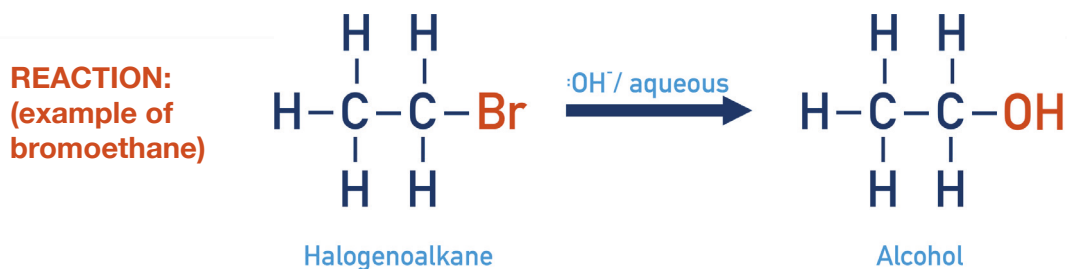
Reaction

REACTANTS: Halogenoalkane and Sodium Hydroxide, NaOH (for OH^- ions)

CONDITIONS: Aqueous ('aq' - water present)

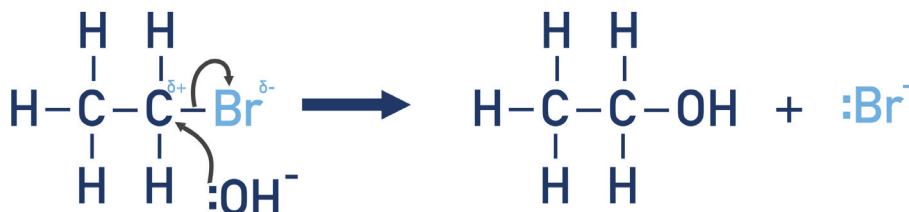
PRODUCT(S): Alcohol and Halide Ion (*sodium halide salt if sodium hydroxide used*)

REACTION TYPE: Nucleophilic Substitution



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

Alkanes | Free Radical Substitution

Reaction

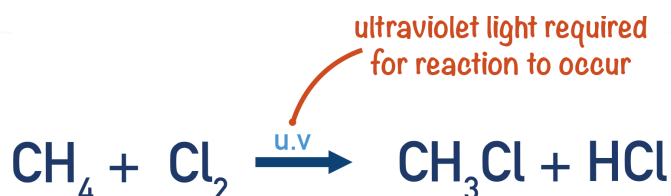
REACTANTS: Alkane and Halogen

CONDITIONS: U.V (ultraviolet) light

PRODUCT(S): Halogenoalkane and Hydrogen Halide

REACTION TYPE: Free Radical Substitution

REACTION:
(example of
methane and
chlorine)

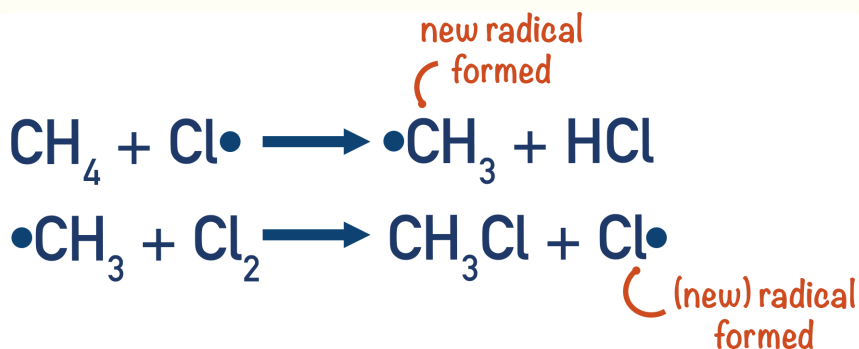


Mechanism

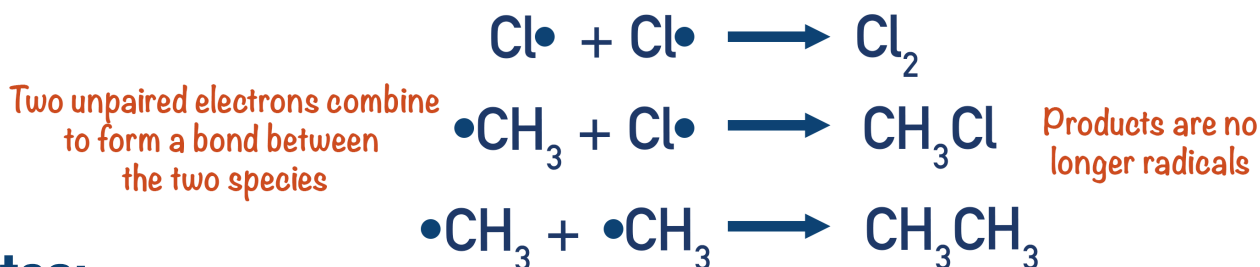
INITIATION STEP: Halogen molecule undergoes heterolytic fission to form radical species:



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**:



TERMINATION STEP: Radical species combine to end chain reaction:



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 heterolytic fission.
- Further substitution reactions can occur, eventually forming tetrachloromethane:
chloromethane to dichloromethane to trichloromethane to tetrachloromethane