



Organic Chemistry Revision Sheets

Alkenes | Electrophilic Addition (with Br₂)

Reaction

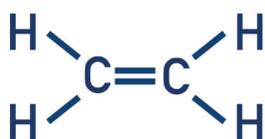
REACTANTS: Alkene and Bromine (Br₂)

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

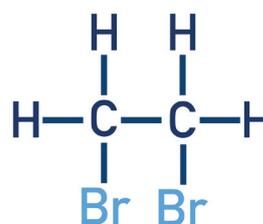
PRODUCT: Dibromoalkane

REACTION TYPE: Electrophilic Addition

REACTION:
(example of
ethene)



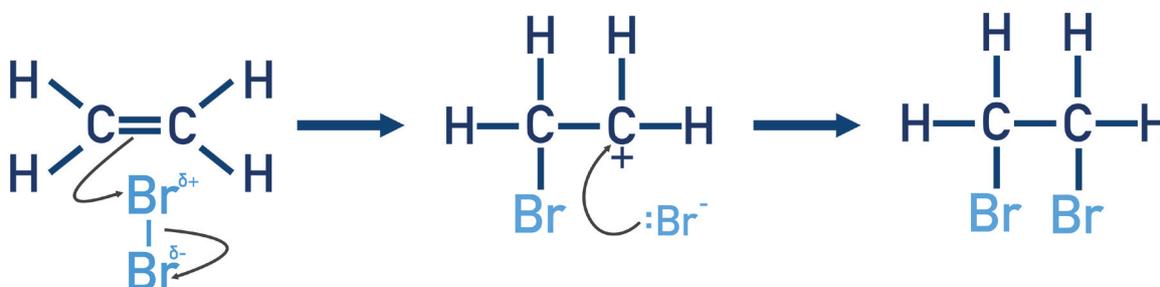
Alkene



Dibromoalkane

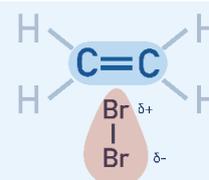
Mechanism

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)

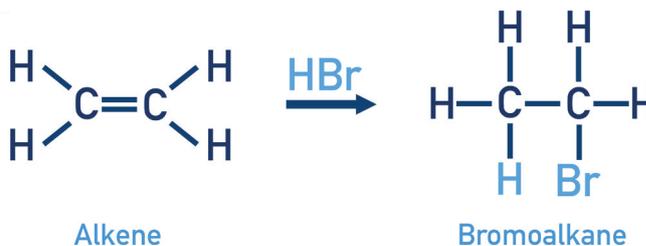
Reaction

REACTANTS: Alkene and HBr (Hydrogen Bromide)

PRODUCT(S): Bromoalkane

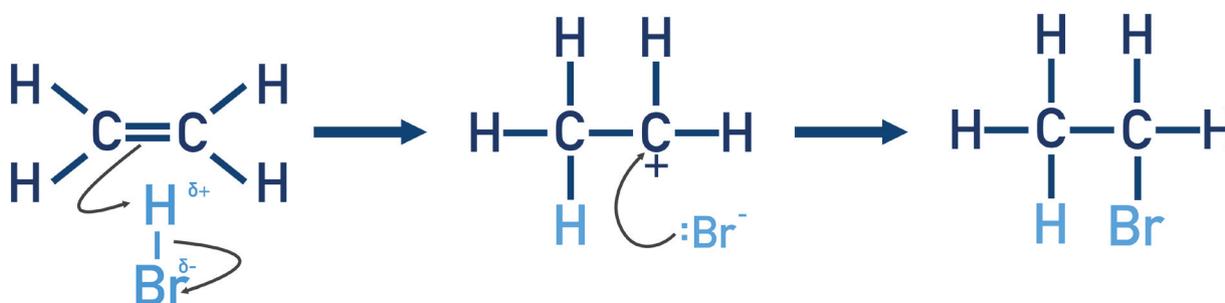
REACTION TYPE: Electrophilic Addition

REACTION:
(example of ethene)



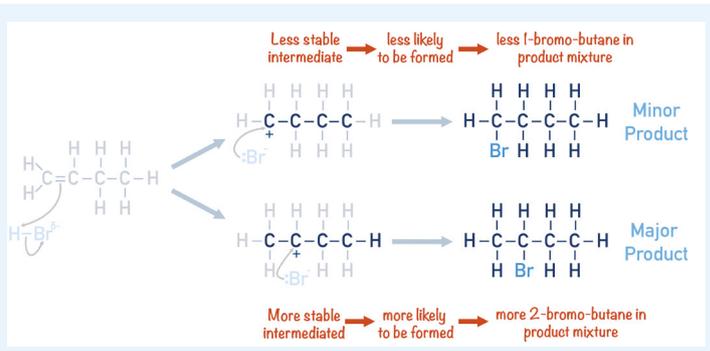
Mechanism

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

Alkanes | Free Radical Substitution

Reaction

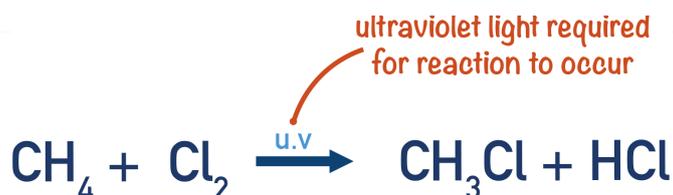
REACTANTS: Alkane and Halogen

CONDITIONS: U.V (ultraviolet) light

PRODUCT(S): Halogenoalkane and Hydrogen Halide

REACTION TYPE: Free Radical Substitution

REACTION:
(example of
methane and
chlorine)

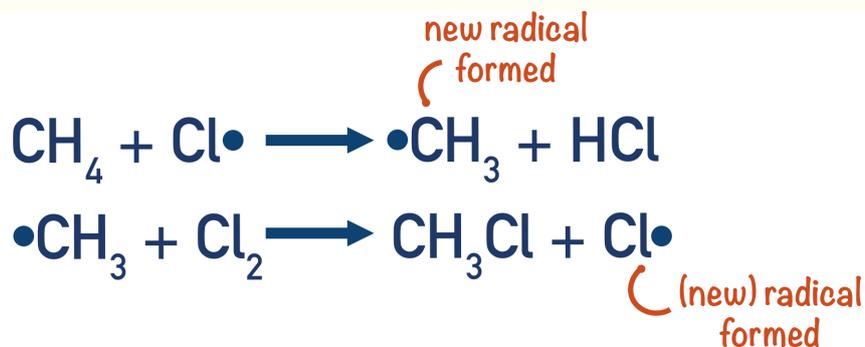


Mechanism

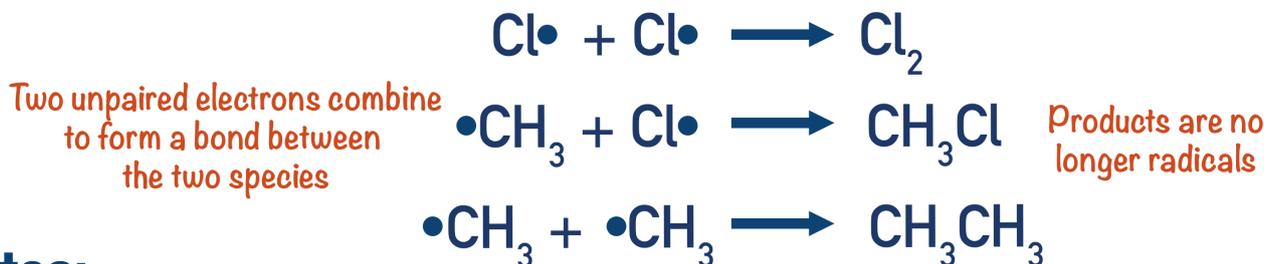
INITIATION STEP: Halogen molecule undergoes heterolytic fission to form radical species:



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



Organic Chemistry Revision Sheets

Halogenoalkanes | Nucleophilic Substitution (S_N1)

Reaction

REACTANTS: Halogenoalkane and Nucleophile

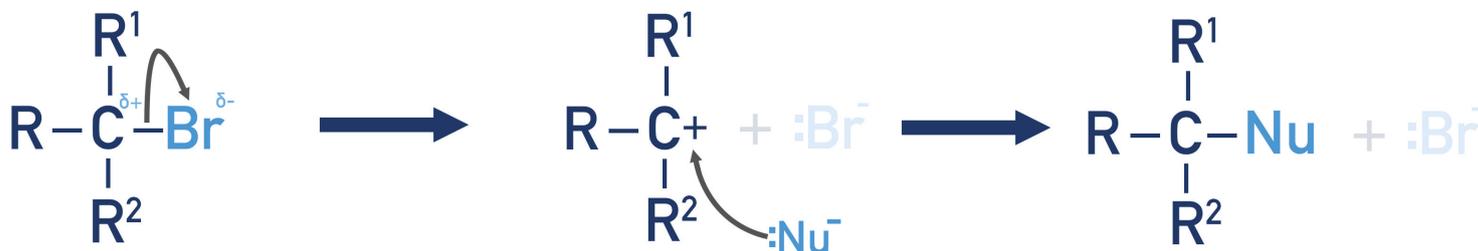
REACTION TYPE: Nucleophilic Substitution, S_N1

REACTION:
(example of
2-bromo-2-meth-
ylpropane)



Mechanism

The first step of the S_N1 mechanism is the breaking of the carbon-halogen bond in the halogenoalkane, forming a carbocation. The nucleophile is then able to form a bond with the carbocation.



Notes:

- The S_N1 reaction occurs (usually) with tertiary halogenoalkanes and only slightly with secondary halogenoalkanes. This is because the carbon-halogen bond is too 'crowded' by alkyl groups for the nucleophile to attack the partially positive carbon directly.
- S_N1 reaction is **slower** than S_N2 reaction.
- S_N2 reaction occurs mainly with primary halogenoalkanes (and, to a lesser extent, secondary halogenoalkanes).



Organic Chemistry Revision Sheets

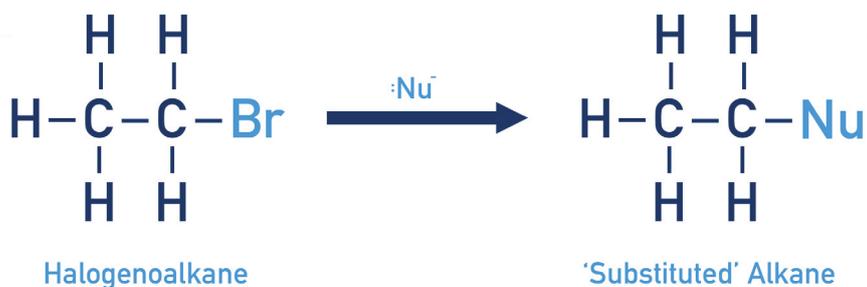
Halogenoalkanes | Nucleophilic Substitution (S_N2)

Reaction

REACTANTS: Halogenoalkane and Nucleophile

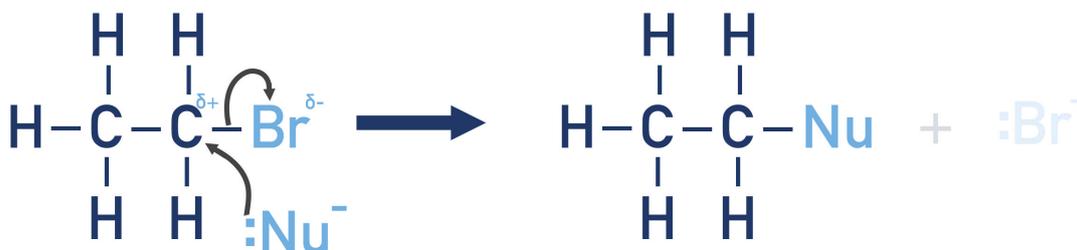
REACTION TYPE: Nucleophilic Substitution, S_N2

REACTION:
(example of
bromoethane)



Mechanism

S_N2 reaction mechanisms have only one step. The nucleophile attacks the carbon-halogen bond directly, forming a new carbon-nucleophile bond as the carbon-halogen bond breaks.



Notes:

- The **S_N2 reaction occurs (usually) with primary halogenoalkanes** and only slightly with secondary halogenoalkanes. This is because the carbon-halogen bond in the primary halogenoalkane is more available for the nucleophile to attack than the partially positive carbon directly.
- S_N2 reaction is **faster** than S_N1 reaction.
- S_N1 reaction occurs mainly with tertiary halogenoalkanes (and, to a lesser extent, secondary halogenoalkanes).