Electrophilic Addition

Example equations

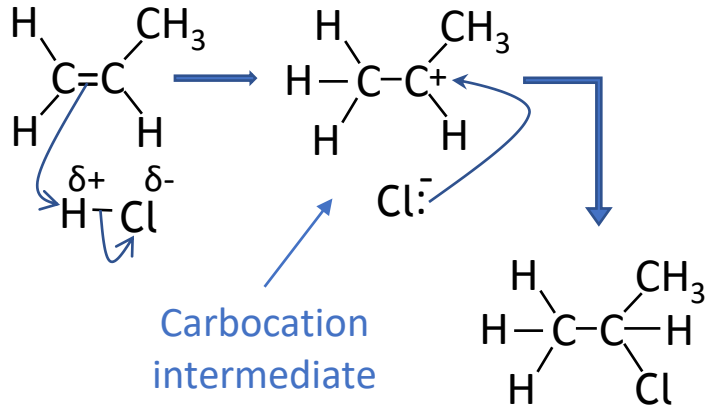
$CH_2CH_2 + Br_2 \rightarrow CH_2BrCH_2Br$

$CH_3CHCH_2 + HBr \rightarrow CH_3CHBrCH_3$

Which functional groups?

Alkenes:
Electrophiles accept a pair of electrons from the electron-rich π bond and add across the C=C bond

Mechanism



Important notes

Observations:
Bromine turns from orange to colourless – test for alkenes

Markovnikov's rule:
Secondary or tertiary carbocations are more stable so secondary/tertiary haloalkanes are the major product

Reagents/conditions

Halogen or hydrogen halide: room temperature

Hydrogen: Ni catalyst, 150°

Products of the reaction

+ halogen → dihaloalkane
+ hydrogen halide → haloalkane
+ hydrogen → alkane

Products can be position isomers or can contain chiral carbons

Nucleophilic Substitution

Example equations

$CH_3CH_2Br + NaOH \rightarrow CH_3CH_2OH + NaBr$

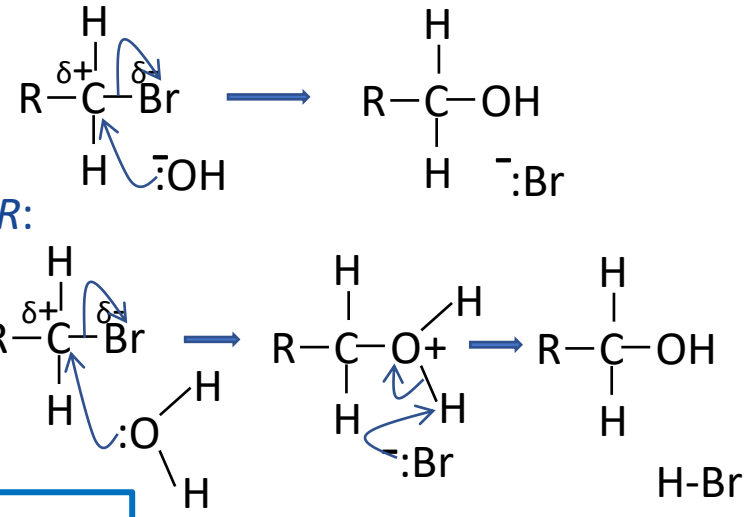
$CH_3CH_2Br + NH_3 \rightarrow CH_3CH_2NH_2 + HBr$

$CH_3CH_2Br + H_2O \rightarrow CH_3CH_2OH + HBr$

Which functional groups?

Haloalkanes or alcohols:
Nucleophiles donate a lone pair of electrons to the δ+ carbon atom

Mechanism



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Important notes

Observations:
Reaction can happen with aqueous silver nitrate and haloalkanes – you see the silver halide precipitates form

Rate of reaction:
Iodoalkanes react fastest as the C-I bond is the weakest

Reagents/conditions

Aqueous NaOH or NaCN, heated

NH_3 in ethanol, heated (under pressure)

Products of the reaction

+ $NaOH/H_2O$ → alcohol
+ hydrogen halide → haloalkane
+ NH_3 → amine

Products can contain <u>chiral carbons</u>
With NH_3 the product can be a salt
e.g. $CH_3CH_2NH_3^+Br^-$

Free Radical Substitution

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Example equations

$CH_4 + Cl_2 \rightarrow CH_3Cl + HCl$

$CH_3CH_3 + Cl_2 \rightarrow CH_3CH_2Cl + HCl$

Which functional groups?

Alkanes:
No π bond to attract electrophiles, no δ+ carbon to attract nucleophiles

Mechanism

Initiation:

$Cl_2 \rightarrow 2Cl\cdot$

Propagation:

$CH_4 + Cl\cdot \rightarrow CH_3\cdot + HCl$

$CH_3\cdot + Cl_2 \rightarrow CH_3Cl + Cl\cdot$

Termination:

$CH_3\cdot + Cl\cdot \rightarrow CH_3Cl$

$CH_3\cdot + CH_3\cdot \rightarrow CH_3CH_3$

Important notes

Radical:
A species with an unpaired electron

Overall reaction:
Usually you can add the two propagation steps together to get the overall reaction:

$CH_4 + \cancel{Cl\cdot} \rightarrow \cancel{CH_3\cdot} + HCl$

$\cancel{CH_3\cdot} + Cl_2 \rightarrow CH_3Cl + \cancel{Cl\cdot}$

$CH_4 + Cl_2 \rightarrow CH_3Cl + HCl$

Reagents/conditions

Halogen in the presence of UV light

UV light causes homolytic fission of the halogen bond to form halogen radicals

Products of the reaction

Multiple substitutions can occur as more hydrogens can be removed e.g.

$CH_3CH_3 + 3Cl_2 \rightarrow CH_2ClCHCl_2 + 3HCl$

Longer alkanes can be formed if two alkyl radicals react together:

$2CH_3CH_2\cdot \rightarrow CH_3CH_2CH_2CH_3$

Nucleophilic Addition

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Example equations

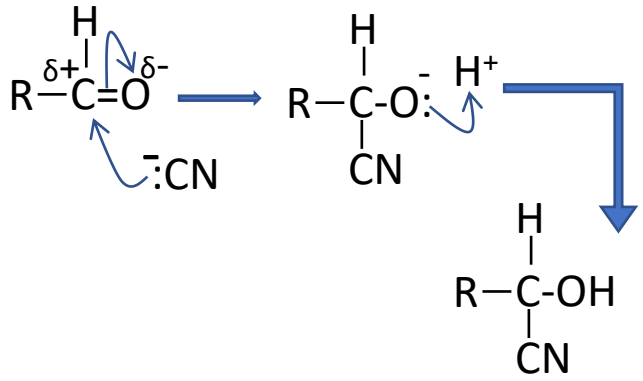
$CH_3CHO + HCN \rightarrow CH_3CH(OH)CN$

$CH_3COCH_3 + HCN \rightarrow CH_3CH(OH)CNCH_3$

Which functional groups?

Aldehydes and ketones:
Nucleophiles donate a lone pair of electrons to the δ+ carbon atom and add across the C=O bond

Mechanism



Important notes

Extending the carbon chain
This reaction is useful in synthesis because it is a way of joining carbon atoms together

Further reactions
The CN group can be turned into COOH or CH_2NH_2

Reagents/conditions

Hydrogen cyanide:
HCN is a weak acid which dissociates to form H^+ and CN^-
The negative charge is on the **carbon**

HCN made by combining NaCN and H_2SO_4: makes CN^- ions and H^+ ions separately

Products of the reaction

The product from an **aldehyde** is always **chiral** – carbon has H, OH, CN and R group attached
The product from a **ketone** can be chiral – depends on whether R groups are the same

The product is called a **hydroxynitrile**

Oxidation

Example equations

$CH_3CH_2OH + [O] \rightarrow CH_3CHO + H_2O$

$CH_3CH_2OH + 2[O] \rightarrow CH_3COOH + H_2O$

$CH_3CHOHCH_3 + [O] \rightarrow CH_3COCH_3 + H_2O$

Which functional groups?

Alcohols or aldehydes:
2 H atoms removed from alcohols to form a C=O bond
1 O atom added to aldehyde to form COOH

Tertiary alcohols are not oxidised by dichromate

Other examples

Aldehydes can also be easily oxidised by other oxidising agents – this can be used to test for aldehydes.

Tollen's: Produces a silver mirror
Brady's: Produces an orange precipitate
Benedict's: Produces a red precipitate

Important notes

Colour change: orange to green ($Cr_2O_7^{2-}$ is reduced to Cr^{3+})

Acid used: We use H_2SO_4 – if HCl used the Cl^- could act as a nucleophile, or could be oxidised to form Cl_2

Reagents/conditions

Acidified potassium dichromate $Cr_2O_7^{2-}$ / H^+

Heat under reflux to obtain carboxylic acid (primary alcohol/aldehyde) or ketone (secondary alcohol)

To make an **aldehyde** from a primary alcohol - **distillation** to remove the product as it forms

Products of the reaction

The product from an **aldehyde** is always **chiral** – carbon has H, OH, CN and R group attached
The product from a **ketone** can be chiral – depends on whether R groups are the same

The product is called a **hydroxynitrile**