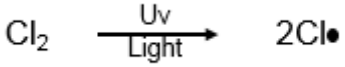
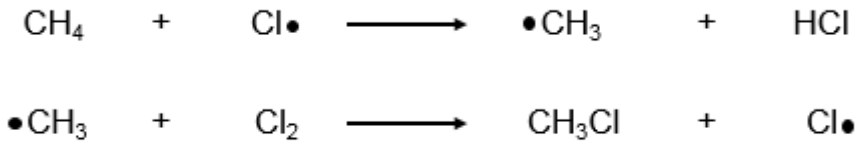
Mechanisms

1) Free radical substitution – Alkane → halogenoalkane

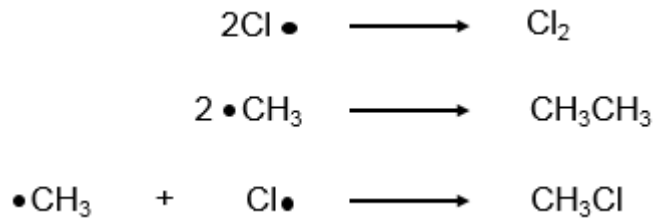
Initiation:



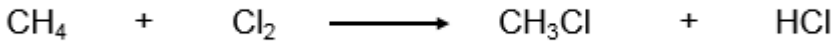
Propagation:



Termination:



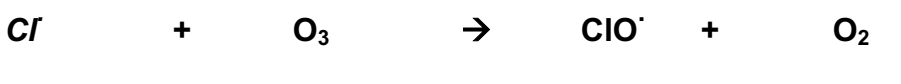
Overall:



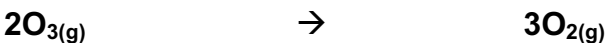
2) Ozone depletion

- UV light breaks the C – Cl bond releasing chlorine radical

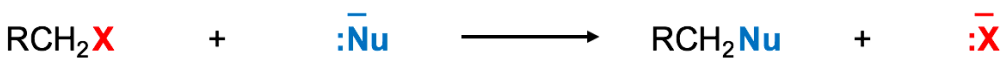
- This chlorine radical catalyses the decomposition of ozone with the chlorine radical coming out unchanged (and available for more ozone decomposition).



Overall

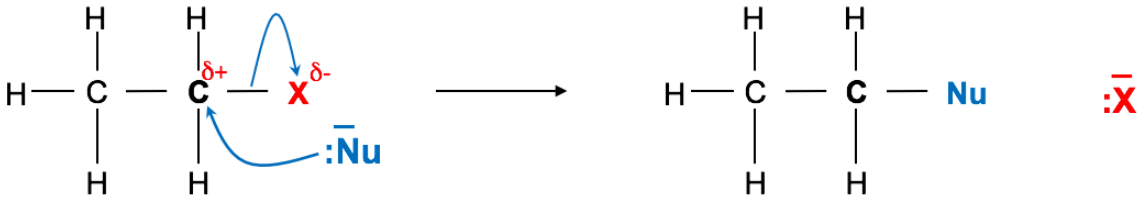


3) Nucleophilic substitution of halogenoalkanes



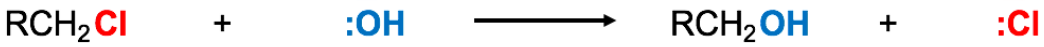
The mechanism:

X is a halogen



a) With aqueous hydroxide, OH^- Hydrolysis – forming alcohols

- This reaction converts a halogenoalkane to an alcohol

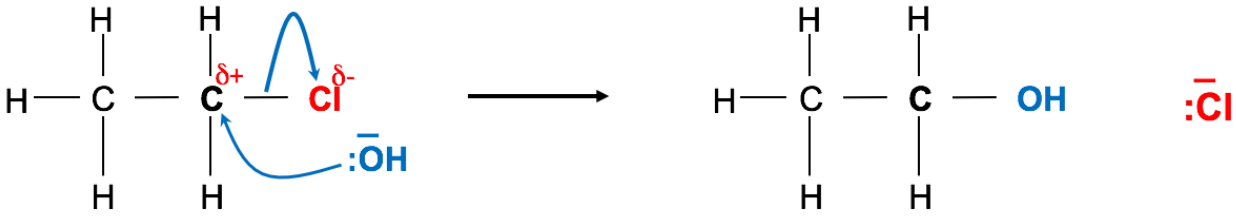


Reagents: Aqueous sodium hydroxide

Conditions: Reflux

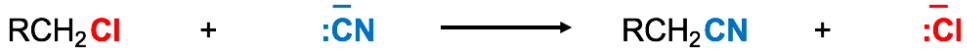
Hydrolysis: *Splitting a molecule apart by using water molecules*

The mechanism:



b) With ethanolic potassium cyanide, KCN – forming nitriles

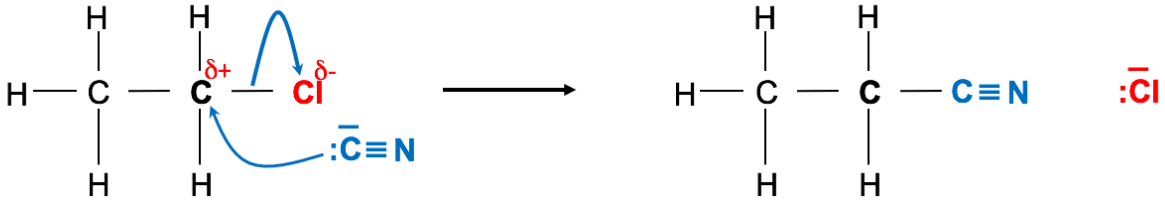
- This reaction converts a halogenoalkane to an alkyl nitrile
- This is a key reaction in chemical synthesis as the carbon chain length is increased



Reagents: Potassium cyanide dissolved in ethanol

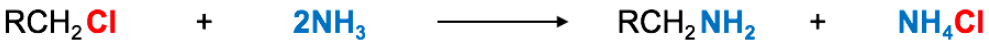
Conditions: Reflux

The mechanism:



c) With excess ethanolic ammonia, NH_3 – forming amines

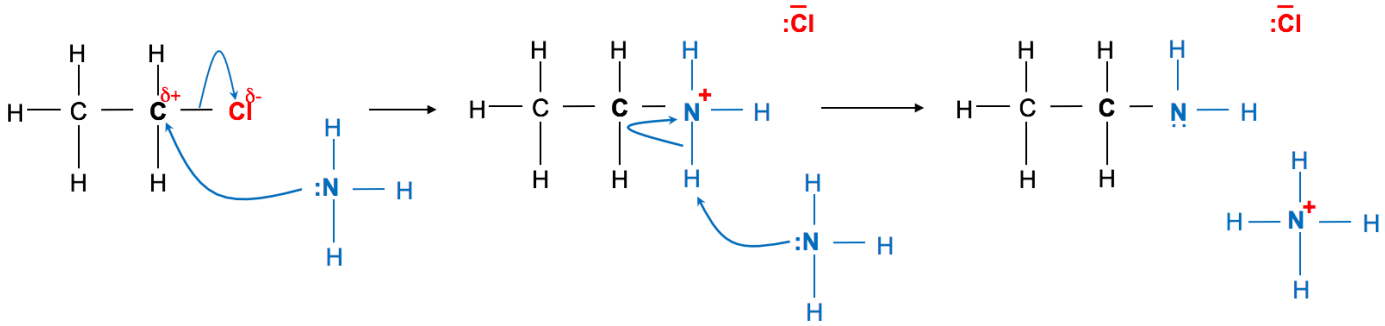
- This reaction converts a halogenoalkane to amines



Reagents: Excess ethanolic ammonia

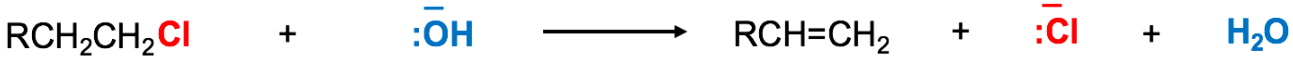
Conditions: Reflux

The Mechanism



4) Elimination of halogenoalkanes

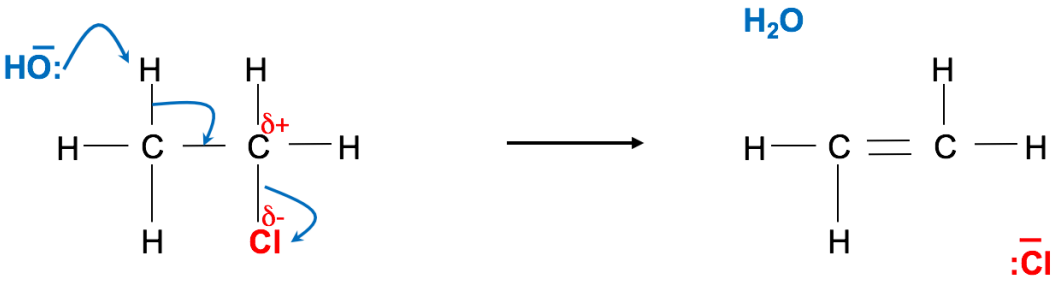
With ethanolic potassium hydroxide, reflux – forming alkenes



Reagents: KOH dissolved in ethanol

Conditions: Reflux

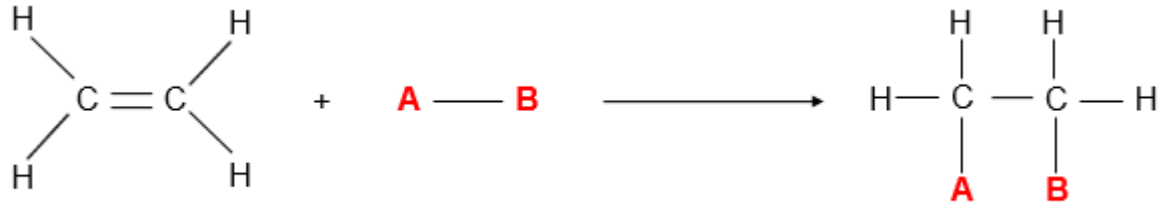
The mechanism:



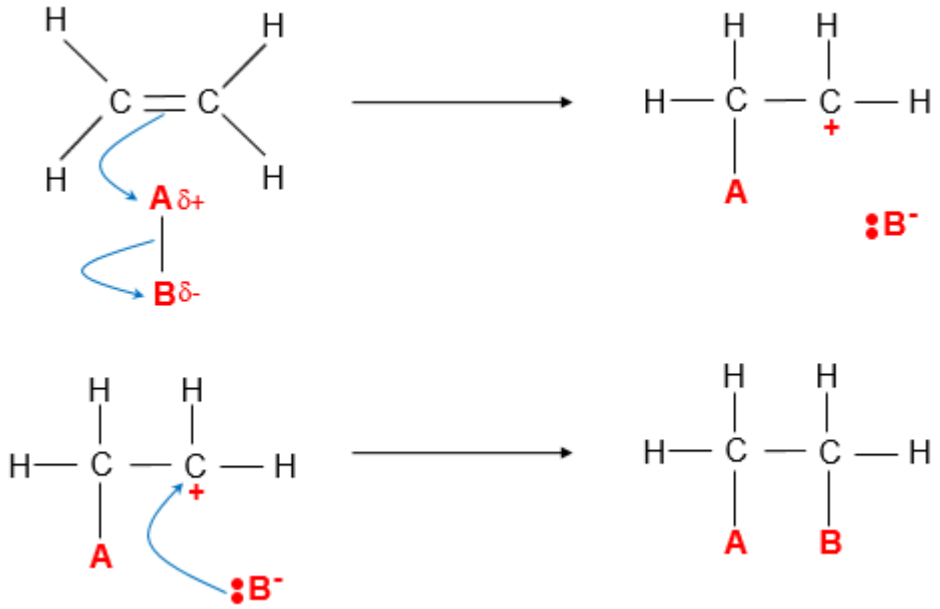
Substitution vs elimination

Substitution	Elimination
Aqueous conditions – **substitution** predominates	**Ethanolic** conditions – **Elimination** predominates
OH^- behaves as a **nucleophile**	OH^- behaves as a **base** (accepting a proton)
50 : 50 mixture of water : ethanol means substitution : elimination equally likely	

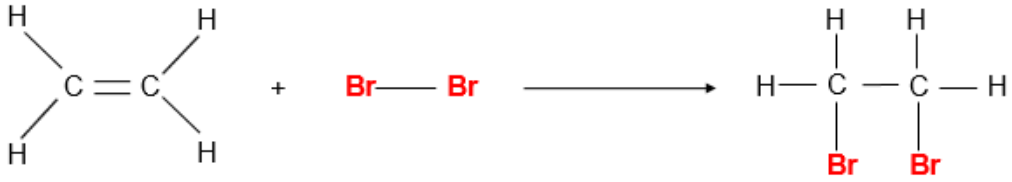
5) Electrophilic addition mechanism of the alkenes:



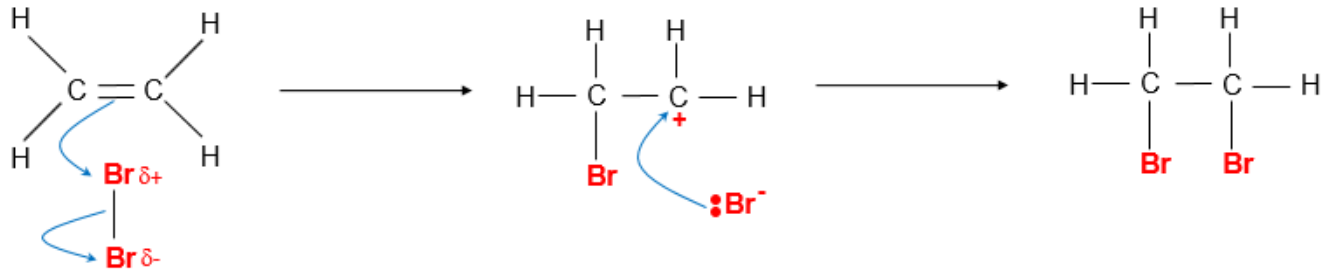
The mechanism



a) Addition of halogens - Br_2: *Forming a dihalogenoalkane*



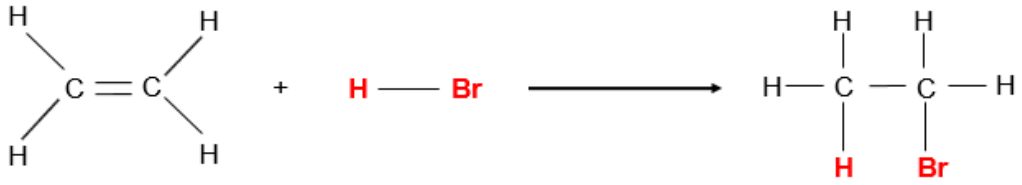
The mechanism:



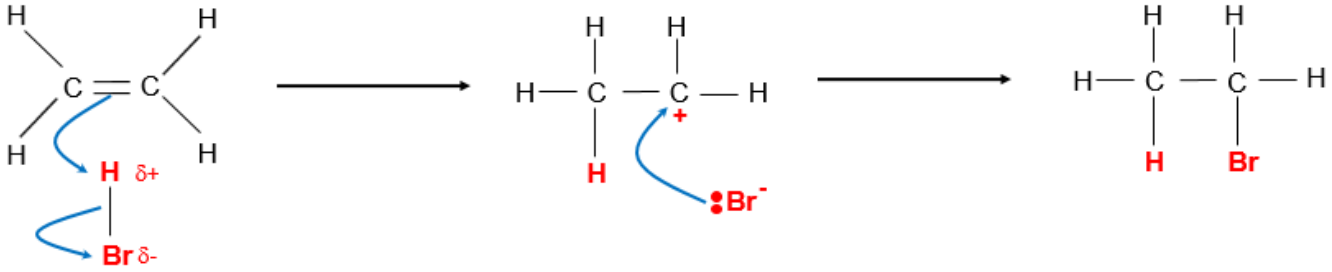
Chemical test for C=C / unsaturation:

- Bromine water
- Orange to clear and colourless

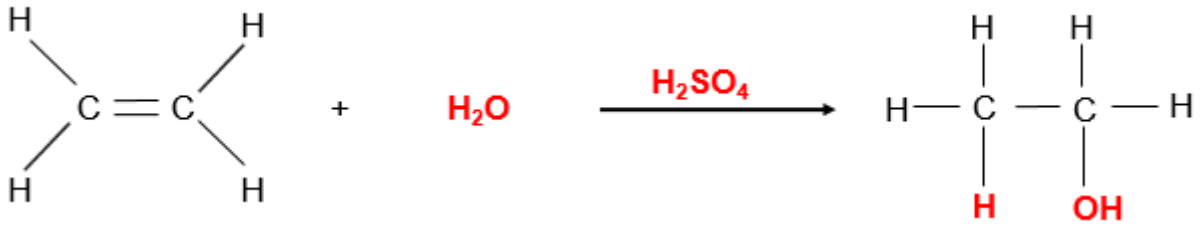
b) **Addition of hydrogen halides - HBr:** ***Forming a halogenoalkane***



The mechanism:

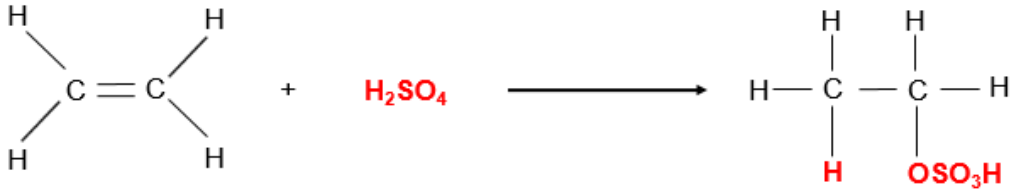


c) Heating with H_2O / H_2SO_4: ***Forming an alcohol (in 2 steps)***

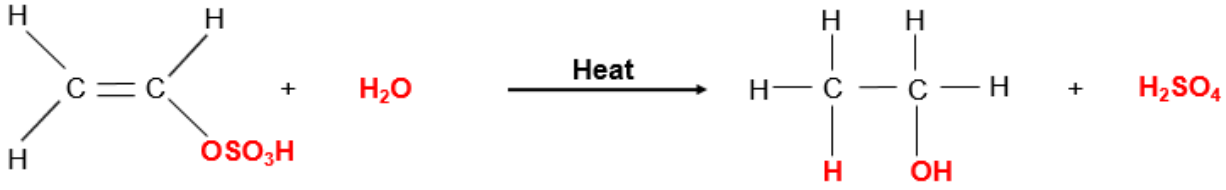


- However this happens in 2 stages with the sulphuric acid behaving as a **catalyst:**

Step 1:

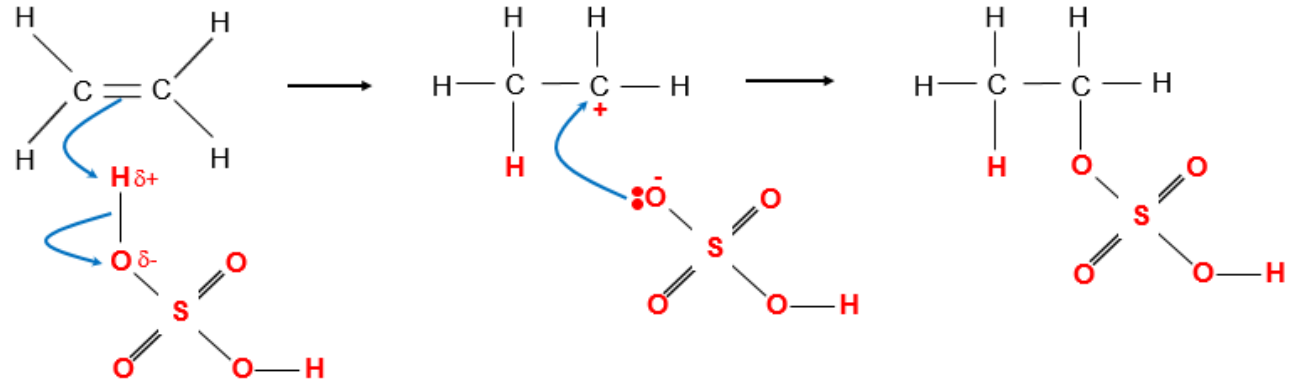


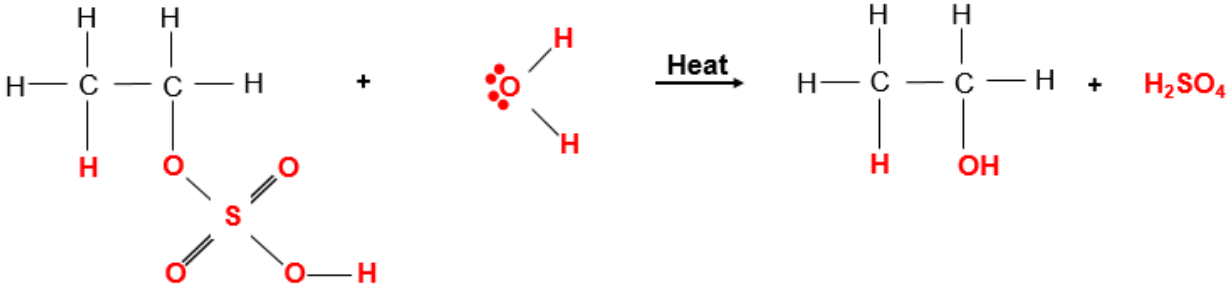
Step 2:



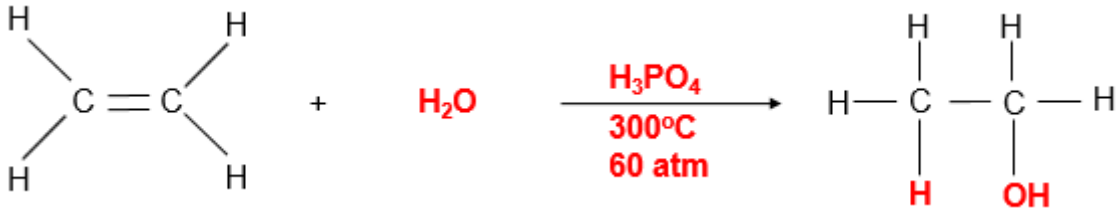
- The sulphuric acid is used up in step 1 but regenerated in step 2

The mechanism:

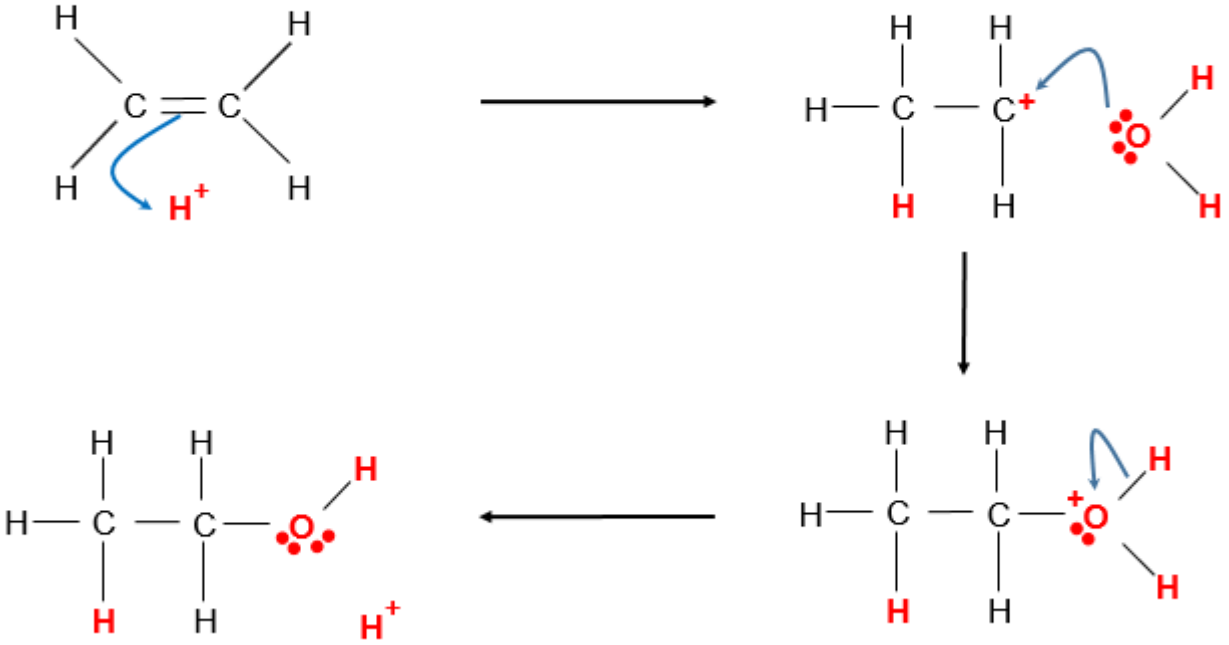




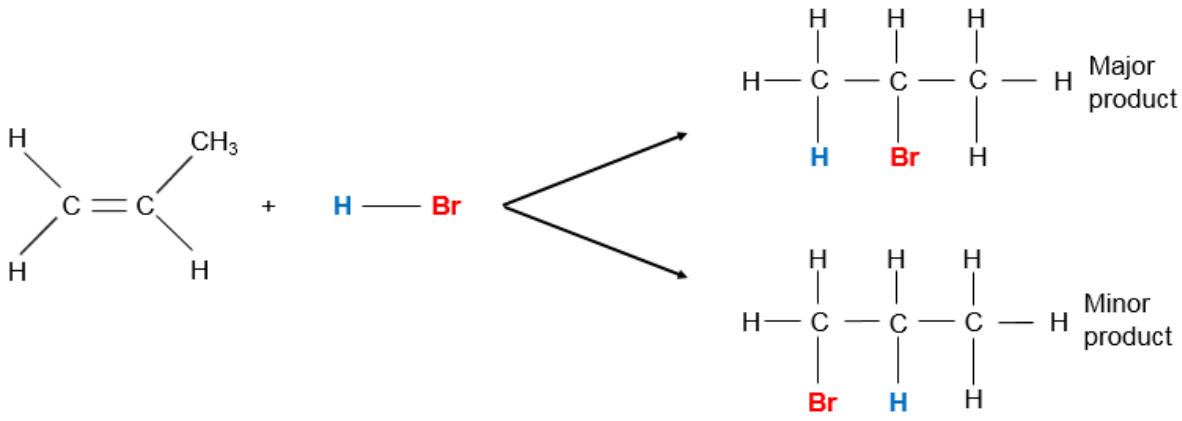
d) Hydration of alkenes with H_2O / H_3PO_4 catalyst / 300°C / 60atm: ***Forming an alcohol***



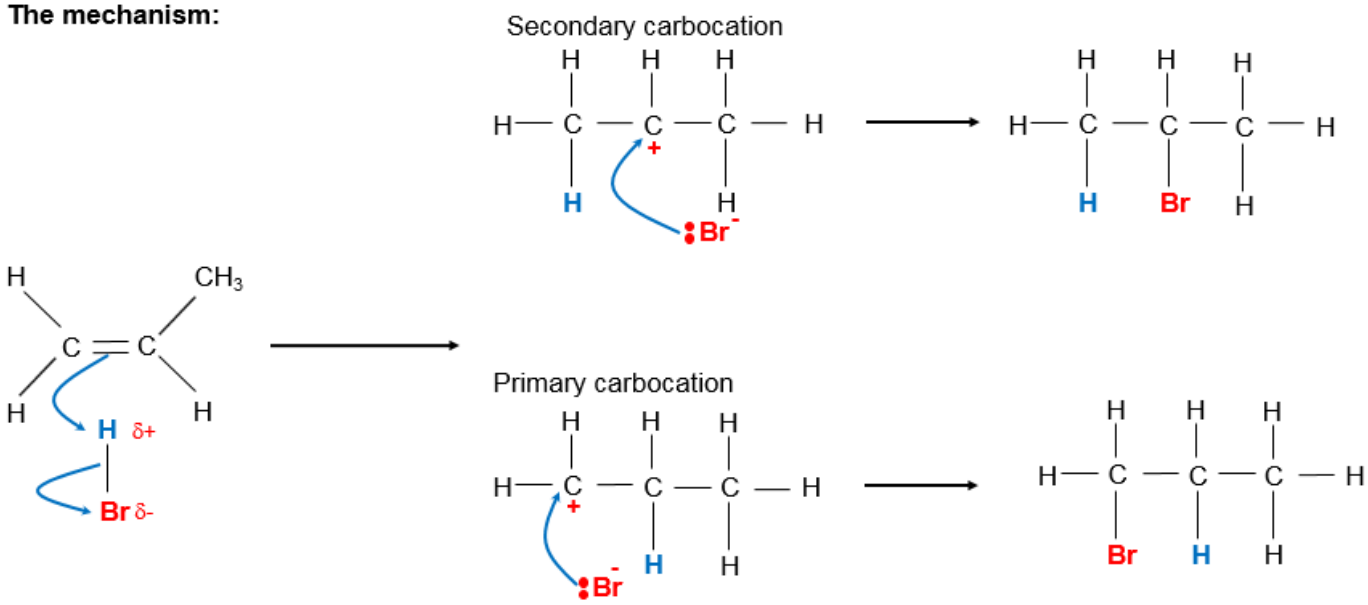
The mechanism:

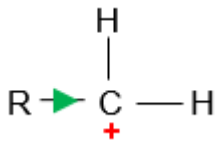
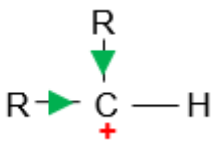
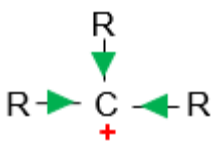


6) Addition to unsymmetrical alkenes: Markovnikov addition



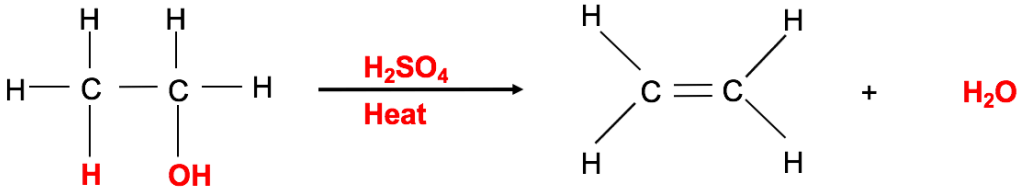
The mechanism:



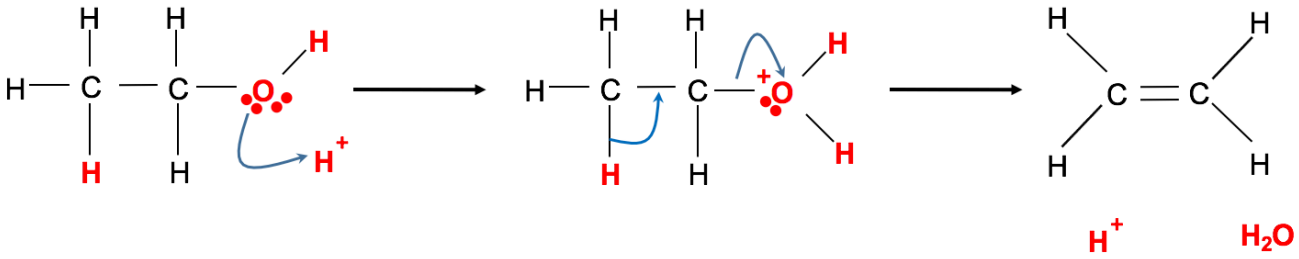
		
1° as it has 1 alkyl group attached	2° as it has 2 alkyl group attached	3° as it has 3 alkyl group attached
1° Primary carbocation	**2° Secondary carbocation**	**3° Tertiary carbocation**
1 alkyl group	**2 alkyl groups**	**3 alkyl groups**
Alkyl groups are slightly electron releasing		

- As the number of alkyl groups increase there is an increase in the negative electrons released to the positive charge
- This increases the stability of the carbocation

7) Dehydration of an alcohol – Elimination reaction



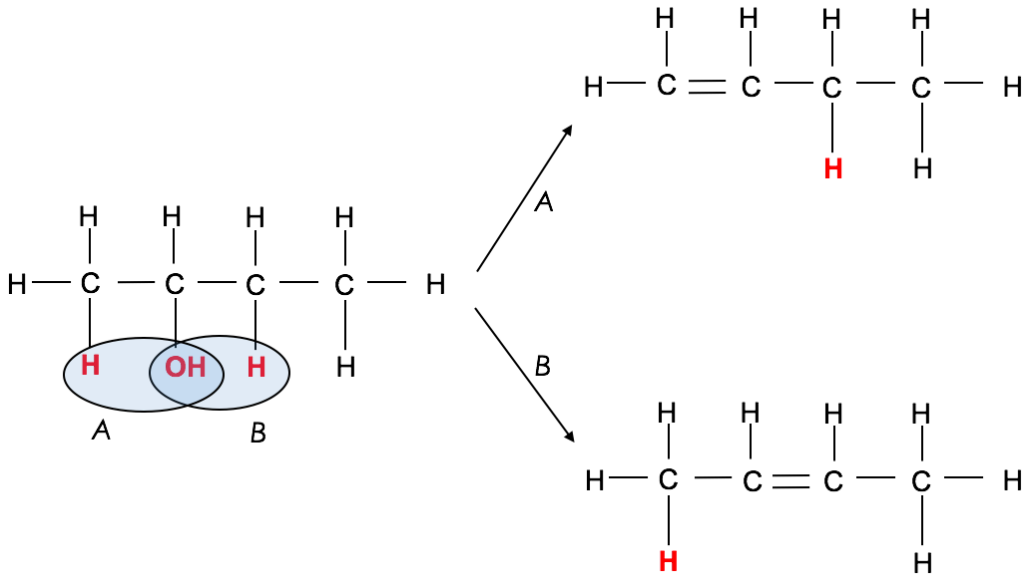
The mechanism:



- The catalyst is concentrated sulphuric acid, H_2SO_4
- The reaction requires heat

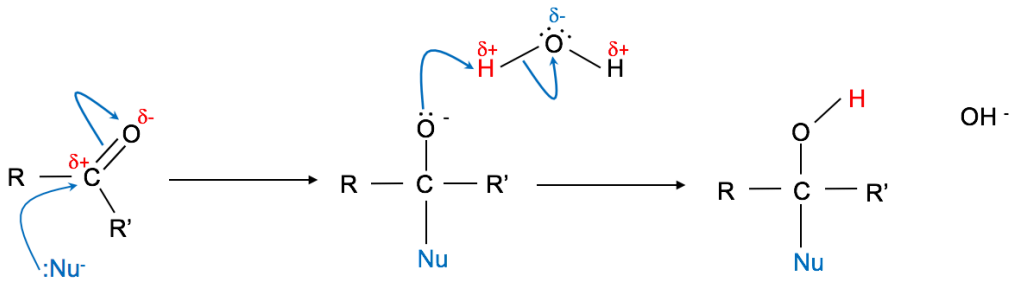
Unsymmetrical alcohols

- Dehydration of unsymmetrical alcohols gives rise to 2 alkenes, **position isomers**



- The dehydration using ‘B’ would also give **E/Z isomerism**

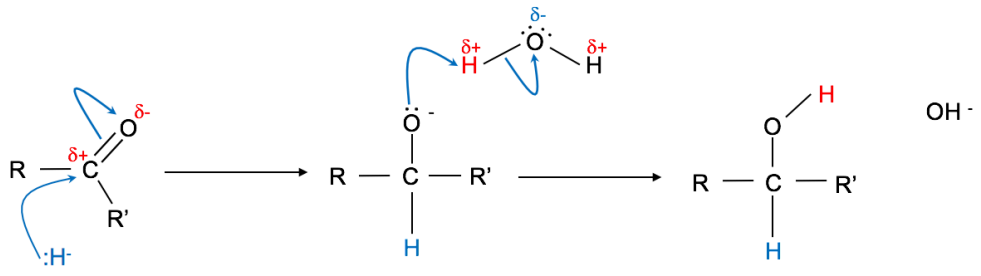
8) Nucleophilic addition reactions of Aldehydes / Ketones



Aldehyde / Ketone

a) Reduction to alcohols

Conditions: $NaBH_4$ - a source of hydride ions, H^-

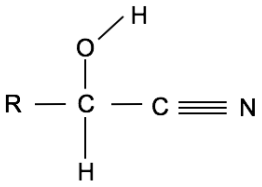


Aldehyde
or
Ketone

1º Alcohol
or
2º Alcohol

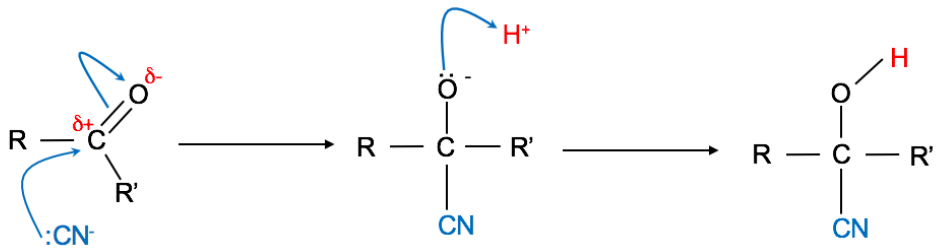
b) To form Hydroxynitriles

Conditions: KCN followed by dilute acid (HCl) – This produces HCN



$CH_3CHO_{(aq)}$ + $HCN_{(aq)}$ → $CH_3CH(OH)CN_{(aq)}$

- **CN^-** is the nucleophile and is attracted to the **δ+** carbon in the carbonyl group.

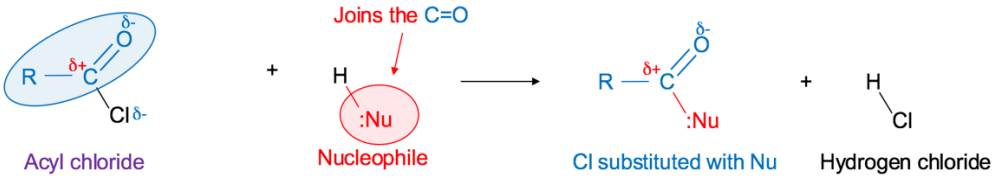


Aldehyde / Ketone

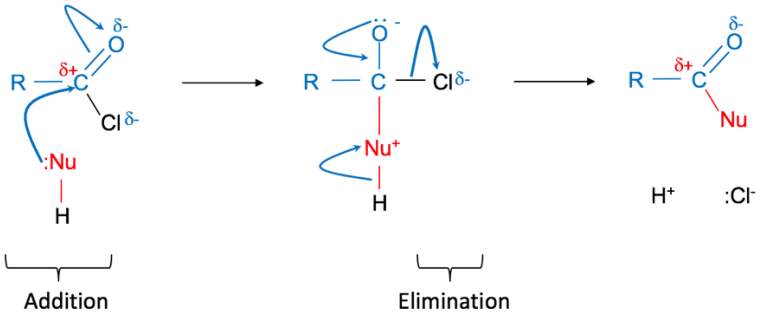
Hydroxynitrile

- In practise, KCN is added.
- This is because HCN is a weak acid (partially dissociates) giving a low $[CN^-]$
- Can produce optical isomers

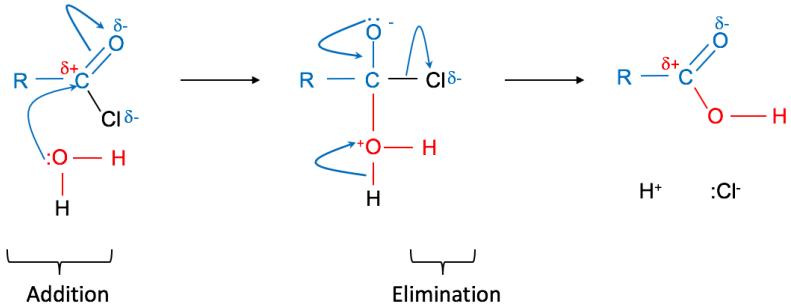
Nucleophilic addition – elimination reaction of the acyl chlorides



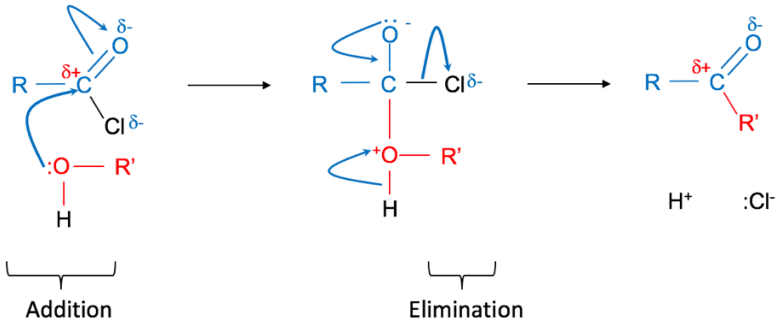
The mechanism:



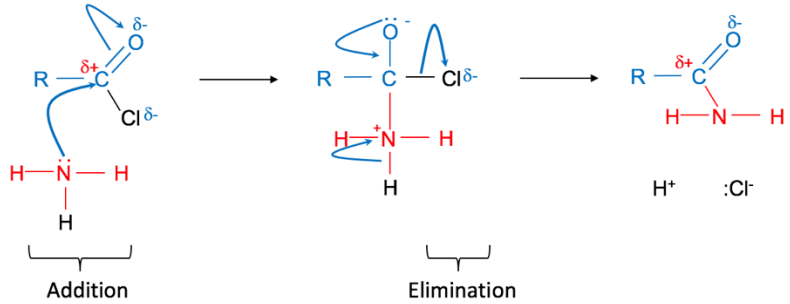
1) With water:



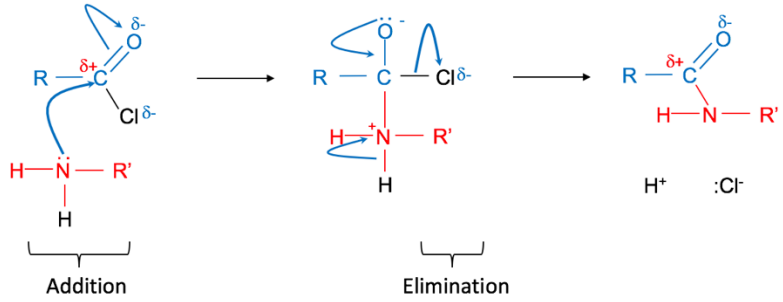
2) With alcohol:



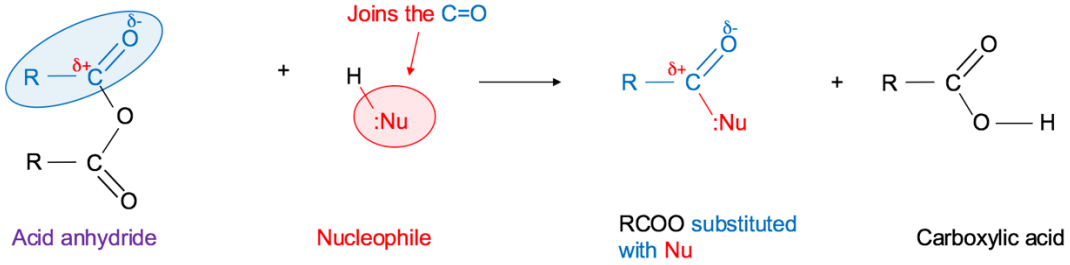
3) With ammonia:



4) With primary amines:

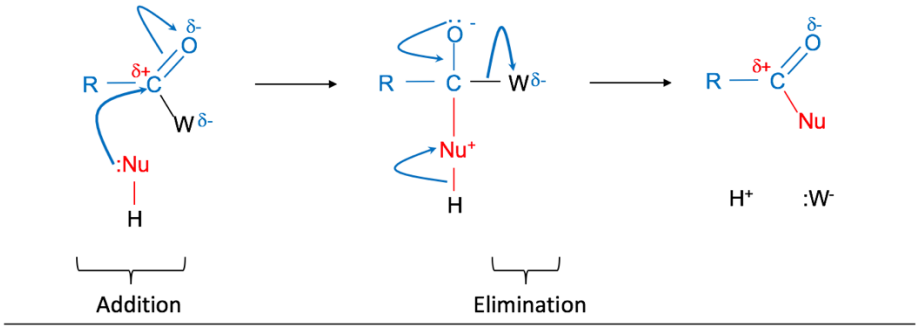


Nucleophilic addition – elimination reaction of the acid anhydrides



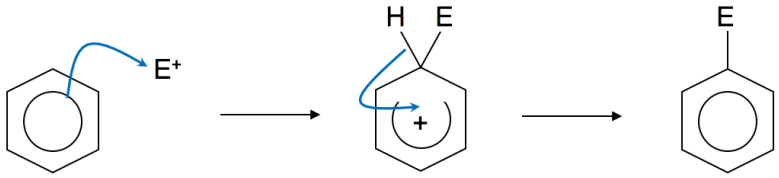
Summary – Carboxylic acid / derivative mechanisms

- The mechanism Is not required but they ***all*** follow the general mechanism:



Nucleophiles: Nu — H		Leaving groups: W
HO — H	H_2N — H	Cl
RO — H	RHN — H	RCOO

Reactions of benzene – Electrophilic substitution



1) Nitration:

Reagents and conditions:

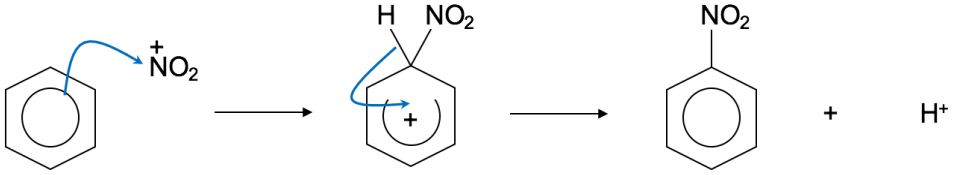
Concentrated nitric acid and concentrated sulphuric acid (catalyst) / Reflux at 55°C

Reaction:

a) Generation of the electrophile:

$$HNO_3 + H_2SO_4 \rightarrow NO_2^+ + HSO_4^- + H_2O$$

b) Electrophilic Substitution Steps



c) Regeneration of the catalyst

$$H^+ + HSO_4^- \rightarrow H_2SO_4$$

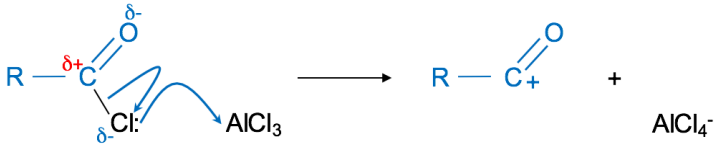
2) Fiedel – Crafts - Acylation:

Reagents and conditions:

Acyl chloride and $AlCl_3$ (**Halogen carrier** / catalyst) / Heat under reflux

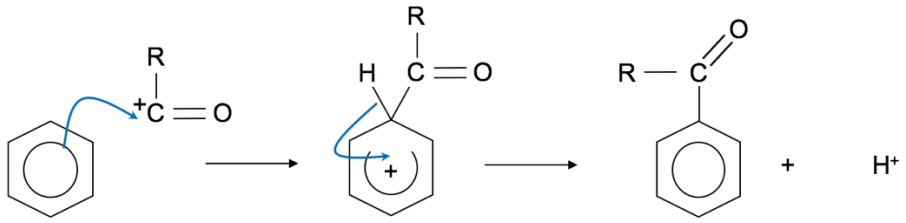
Reaction:

a) Generation of the electrophile:



Carbocation is the electrophile

b) Electrophilic Substitution Steps



c) Regeneration of the catalyst

$$H^+ + AlCl_4^- \rightarrow AlCl_3 + HCl$$

Extension – 3 and 4 are not in the specification.

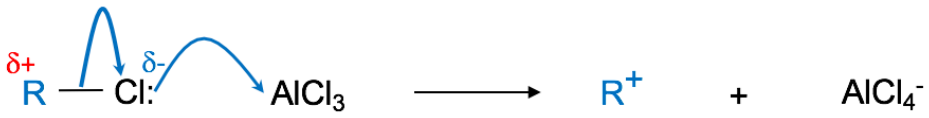
3) Fiedel – Crafts - Alkylation:

Reagents and conditions:

Halogenoalkane, RCl and $AlCl_3$ (**Halogen carrier** / catalyst) / Heat under reflux

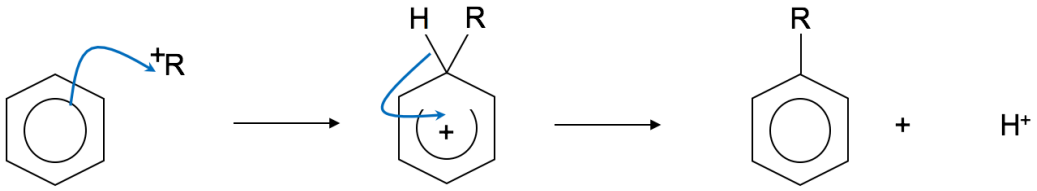
Reaction:

a) Generation of the electrophile:



Carbocation is the electrophile

b) Electrophilic Substitution Steps



c) Regeneration of the catalyst

$$H^+ + AlCl_4^- \rightarrow AlCl_3 + HCl$$

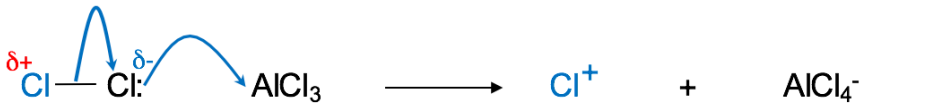
4) Halogenation:

Reagents and conditions:

Halogen, Cl_2 and $AlCl_3$ (**Halogen carrier** / catalyst) / Heat under reflux

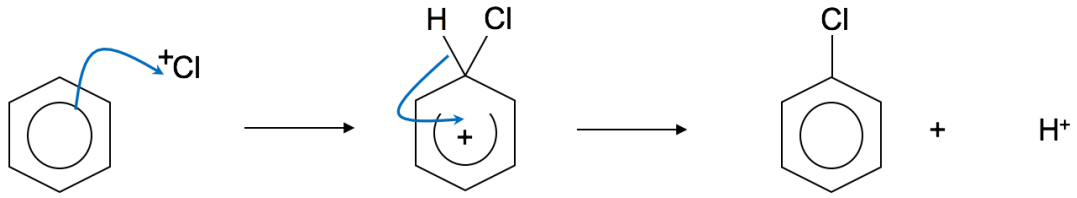
Reaction:

a) Generation of the electrophile:



Chloronium is the electrophile

b) Electrophilic Substitution Steps



c) Regeneration of the catalyst

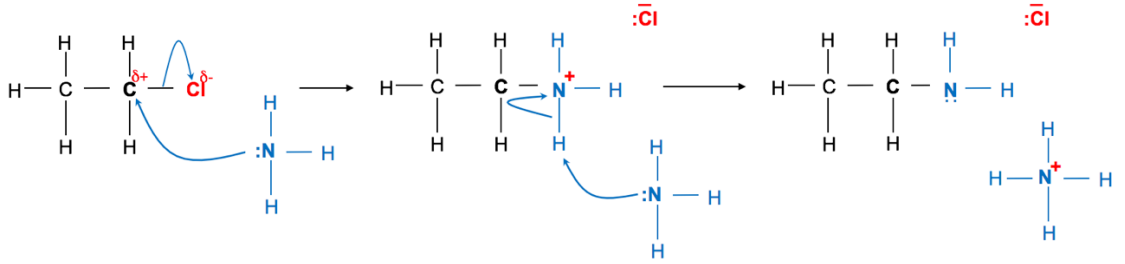
$$H^+ + AlCl_4^- \rightarrow AlCl_3 + HCl$$

Nucleophilic substitution reactions involving amines:

1) With ammonia, NH_3, to form 1° amines: Year 1, recap: The nucleophilic substitution

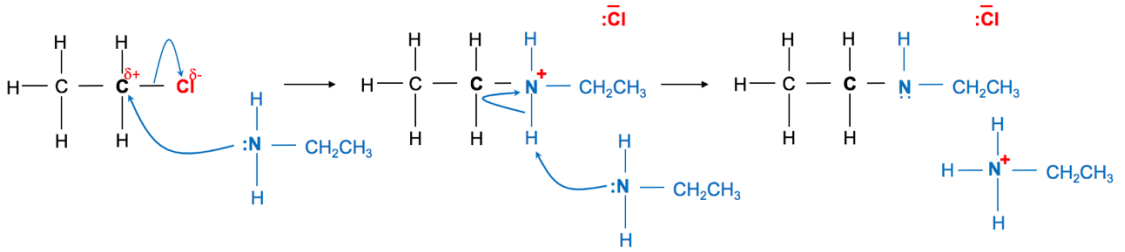
Reagents: Excess ethanolic ammonia

Conditions: Reflux



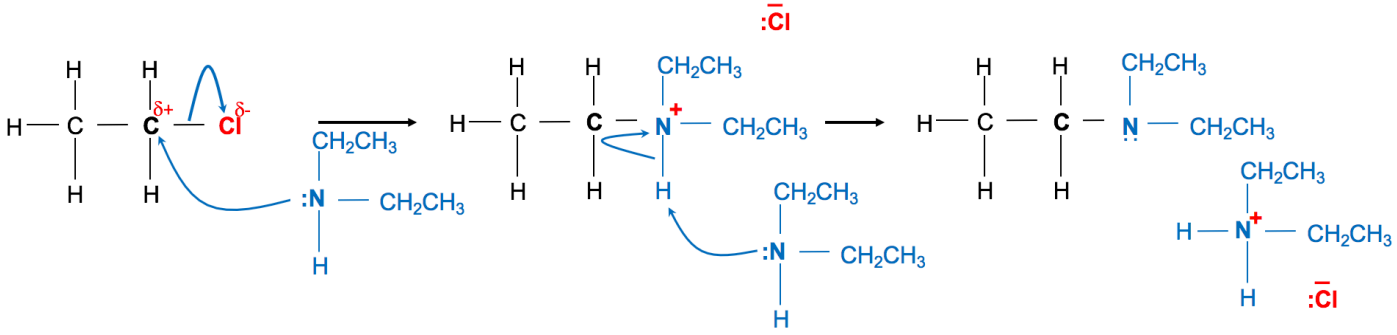
Ammonia 1° amine Quaternary ammonium salt

2) With 1° amines, RNH_2, to form 2° amines, R_2NH:



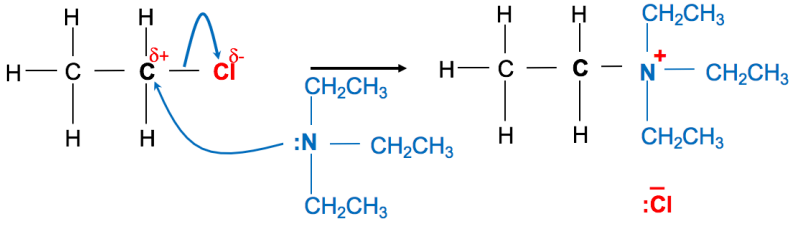
1° Amine 2° Amine Quaternary ammonium salt

3) With 2° amines, R_2NH, to form 3° amines, R_3N:



2° Amine ammonium salt 3° Amine quaternary

4) With 3° amines, R_3N, to form quartenary ammonium salt, R_4N^+:



3° Amine Quaternary ammonium salt

Summary:

Ammonia 1° Amine 2° Amine 3° Amine 4° Amine