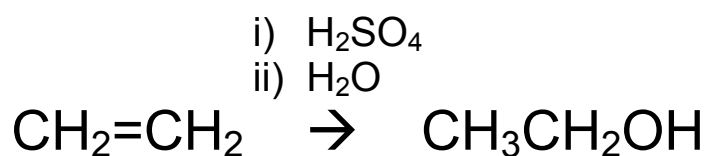


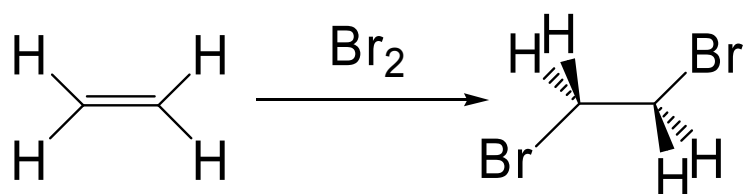
N.b. A catalyst is a species which speeds up a chemical reaction but which remains chemically unchanged.

Hydration (Addition)

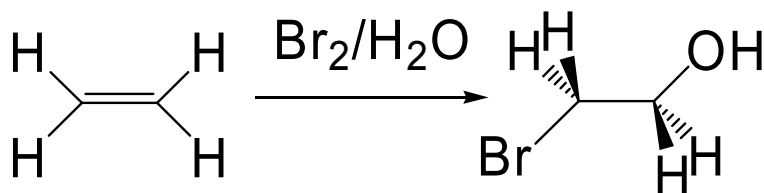
Reverse process of dehydration of an alcohol



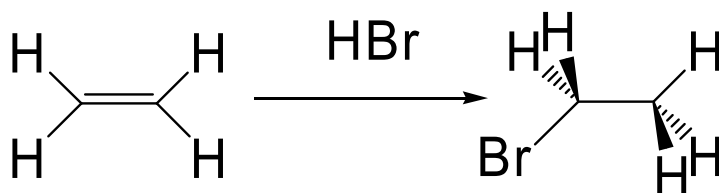
Reaction with Halogens (Addition)



BUT if Br₂ is dissolved in H₂O (bromine water) the following occurs:-

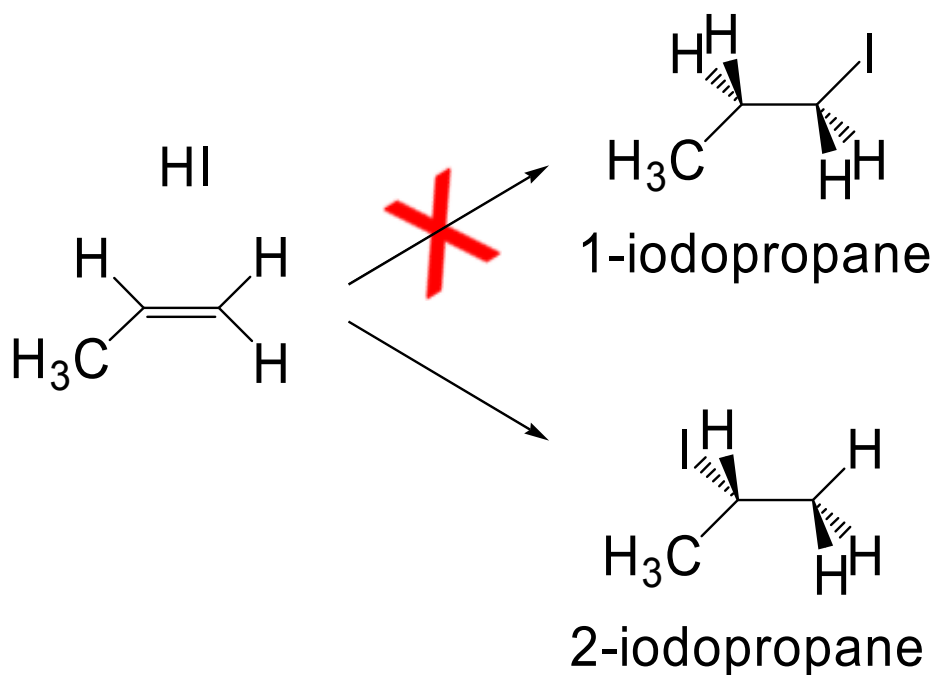


Reaction with Hydrogen Halides (Addition)



The product of this reaction is called a **haloalkane** or an **alkylhalide**.

But



Why is 1-iodopropane not formed?

The intermediate in the reaction which forms 1-iodopropane is too unstable. This is called a **regioselective** reaction as only one of the possible products is formed.

This is also a special named reaction: **Markovnikov addition**.

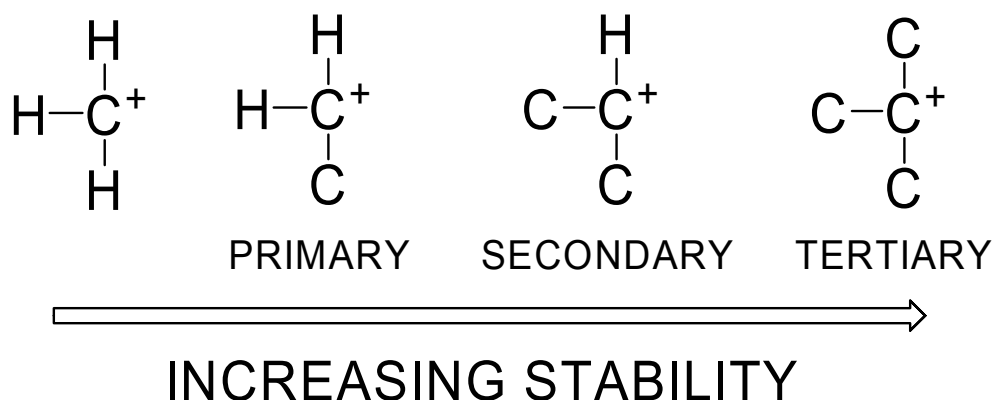
Markovnikov Rule

In the addition of an acid to a carbon-carbon double bond, the hydrogen of the acid attaches itself to the carbon atom of the double bond with the greater number of hydrogen atoms.



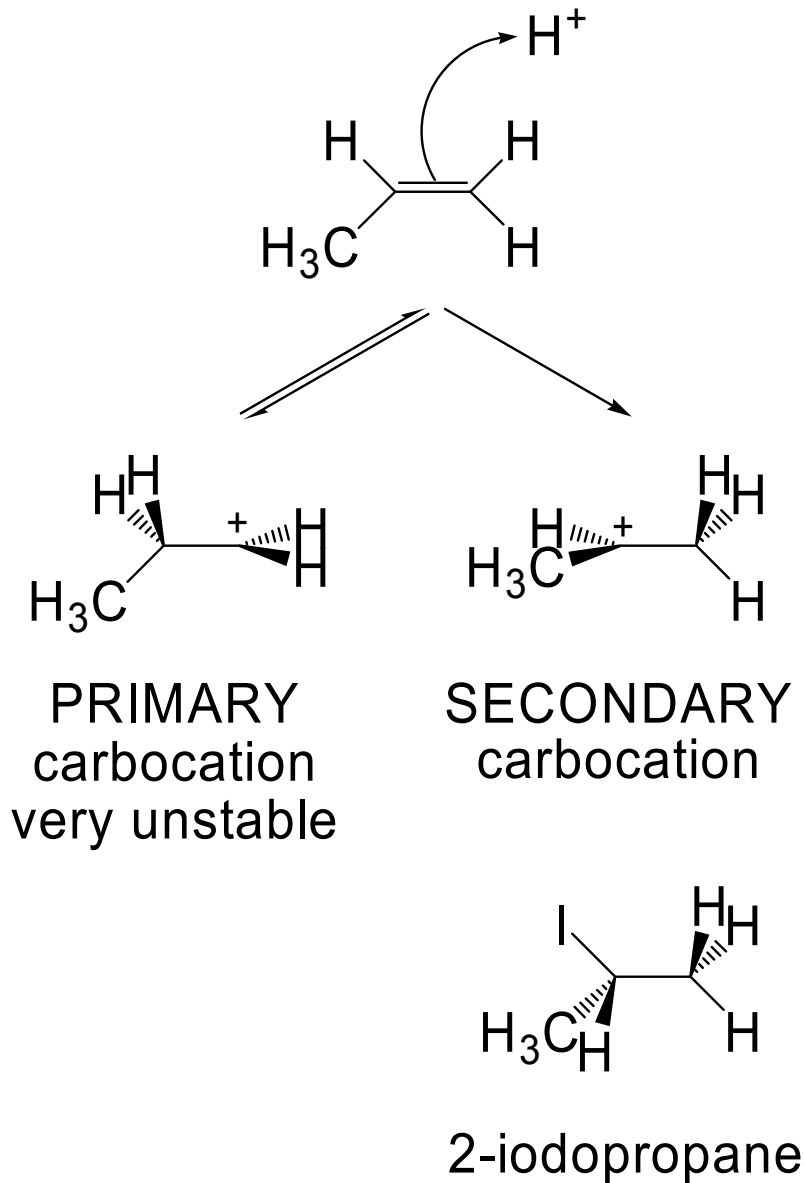
Why?

Due to the relative stability of the intermediate species in the reaction called carbocations.



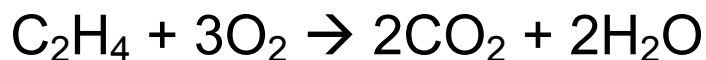
Consider the mechanism of the addition.

The first step of the reaction is proton addition:



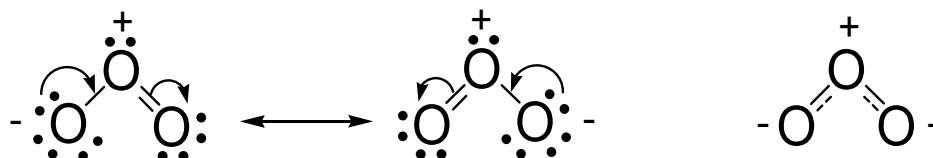
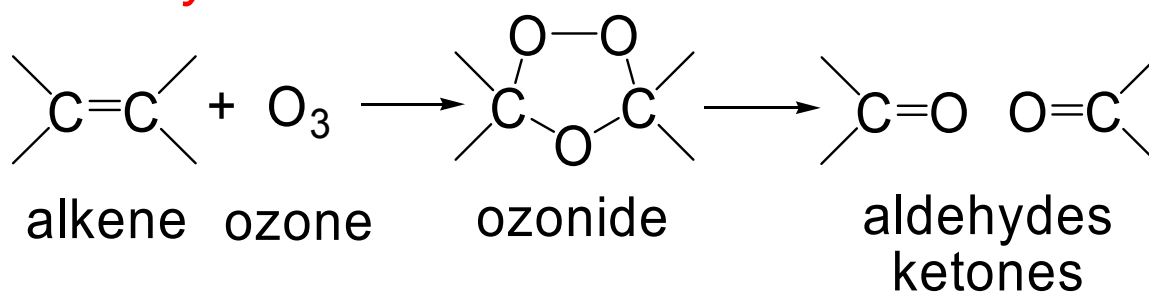
Oxidation

Like alkanes, alkenes can be burnt in the presence of oxygen



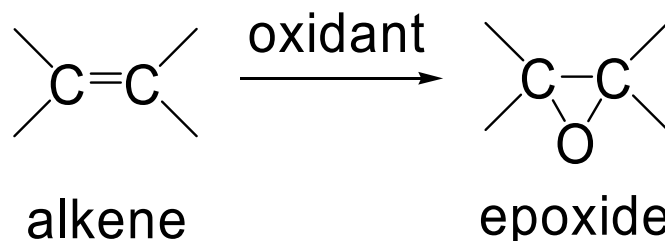
Of more synthetic use are processes such as ozonolysis and epoxidation.

Ozonolysis

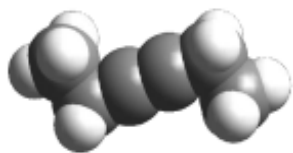


Resonance and canonical forms of ozone.

Epoxidation



The Alkynes



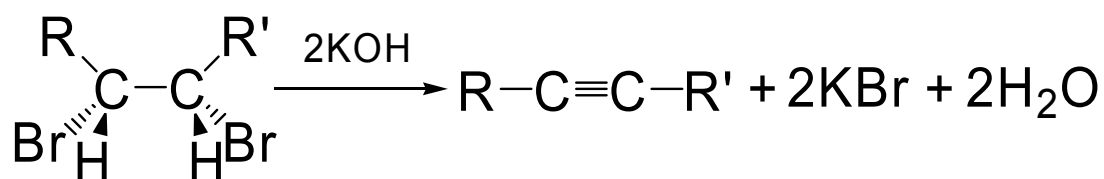
A homologous series of unsaturated compounds with general formula C_nH_{2n-2} (where n is an integer greater than 1) that contain a triple bond.

ethyne C_2H_2 , propyne C_3H_4 , butyne C_4H_6 , pentyne C_5H_8 , hexyne C_6H_{10} , heptyne C_7H_{12} , octyne C_8H_{14} , nonyne C_9H_{16} , decyne $C_{10}H_{18}$, etc.

Industrial Preparation of Ethyne (Acetylene)



Laboratory Preparation

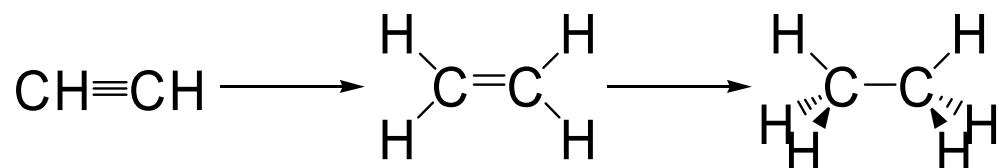


This process is called **dehydrohalogenation**.

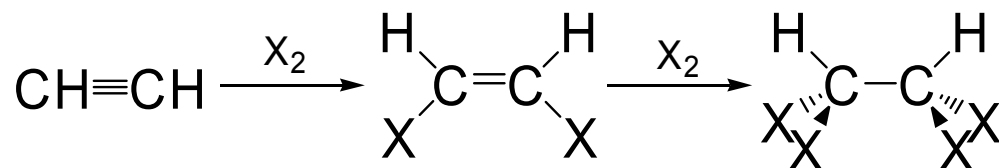
Chemistry

Catalytic Addition of Hydrogen (Hydrogenation)

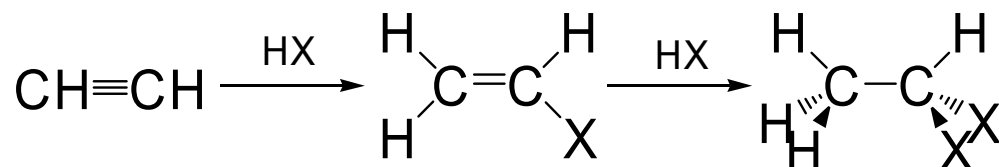
Compare with the hydrogenation of alkanes



Addition of halogens

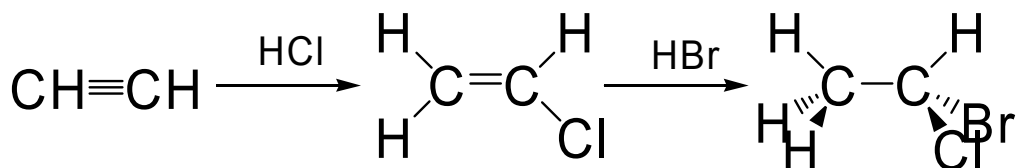


Addition of hydrogen halides

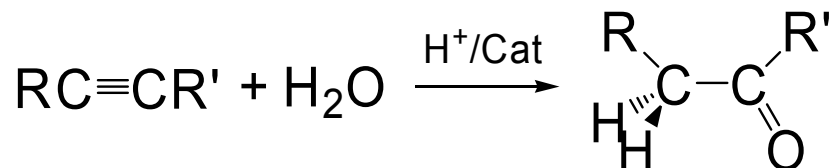


The addition follows the Markovnikov rule.

It is also possible to add different halogens

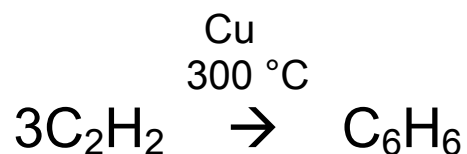


Hydration



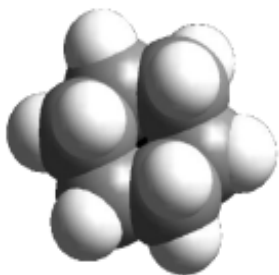
The catalyst is usually mercury(II) or iron(III)

Conversion to Benzene



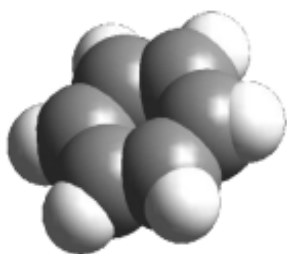
Cyclic Hydrocarbons

Cycloalkanes



General formula C_nH_{2n} due to closing the ring but chemistry is typical of alkanes not alkenes.

Aromatic Hydrocarbons



The most important one is benzene C_6H_6 .

A planar ring of six carbon atoms in which all the carbon-carbon bonds are equal in length.

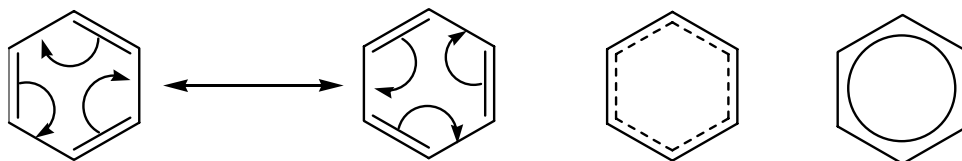
C-C	0.154 nm
C=C	0.132 nm
C-C _{benzene}	0.139 nm

Therefore the C-C bonds in benzene are intermediate between single and double bonds...



How might this be explained?

Kekulé approach



Canonical or resonance forms (or in the case of benzene Kekulé forms)

ii) Molecular orbital approach

Each C is sp^2 hybridised with a surplus electron in the p_z orbital. These p electrons

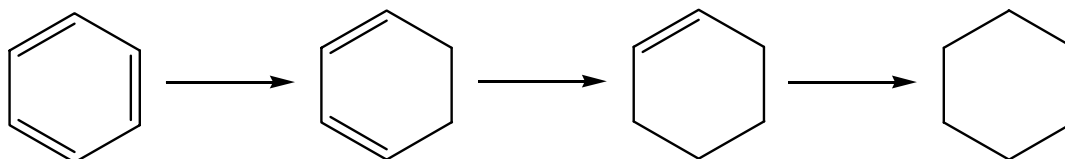


The **delocalised ring** or **aromatic** system is very stable.

Chemistry

Hydrogenation

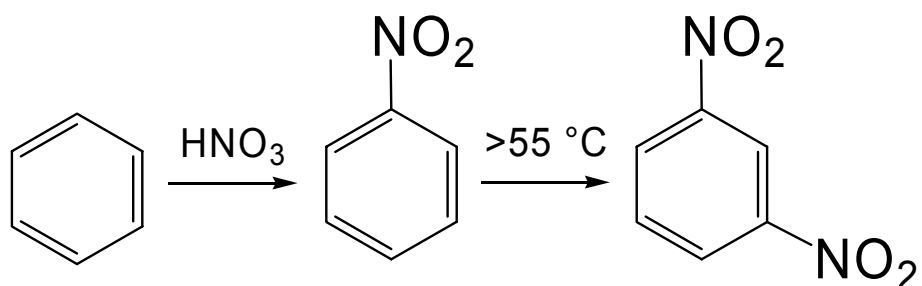
For aromatic systems we use:
150-200 °C / H_2 / Ni catalyst



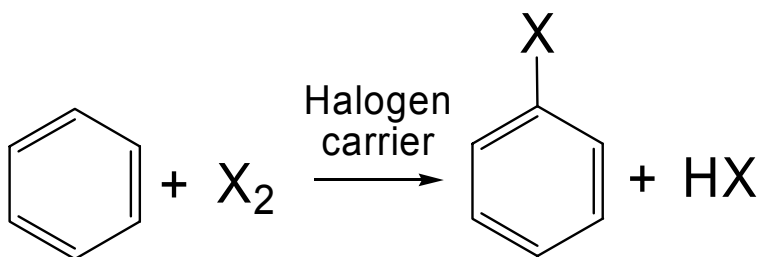
Of greater interest are substitution reactions. All of the examples given here are **electrophilic substitution** reactions.

An **electrophile** (E^+) is an electron deficient species which is capable of accepting a lone pair of electrons - “electron seeking”.

Nitration



Halogenation



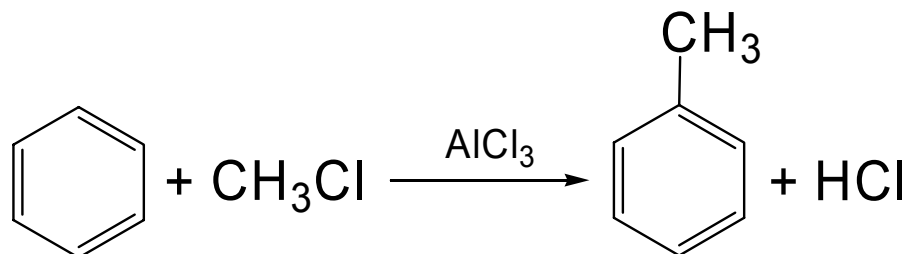
X_2 is chlorine or bromine

The halogen carrier is AlCl_3 , FeCl_3 or iodine.

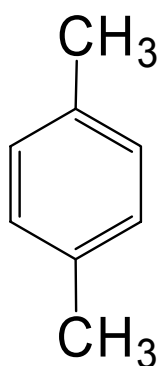
Friedel-Crafts Reactions

Very important in synthetic chemistry. There are two main types, both usually require a Lewis acid.

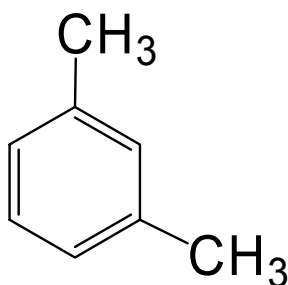
Alkylation



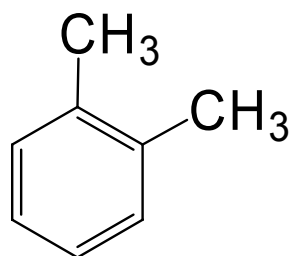
The reaction is difficult to stop at this point



31%



17%



52%

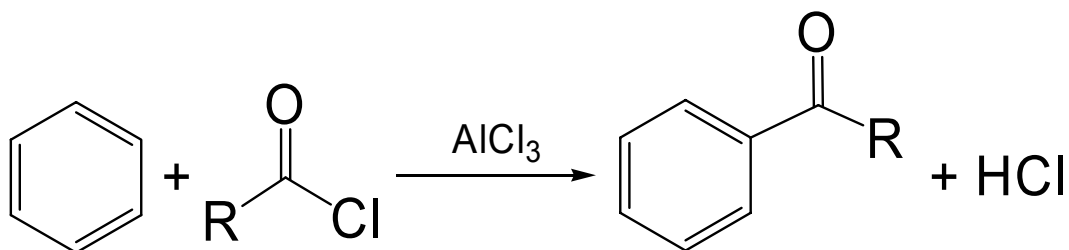
The products of the second Friedel-Crafts reaction show different substitution about the aromatic ring: **ortho**, **meta** and **para**.

1,2-dimethylbenzene (ortho-xylene)

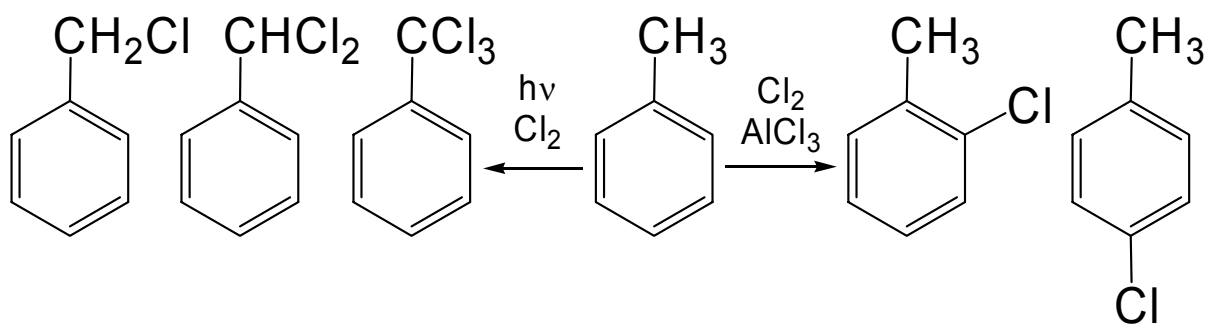
1,3-dimethylbenzene (metaxylene)

1,4-dimethylbenzene (paraxylene)

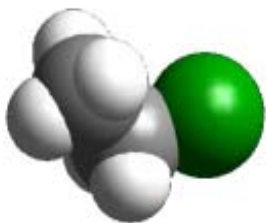
Acylation



N.B. If a molecule has multiple functional groups it can display the chemistry of both groups.



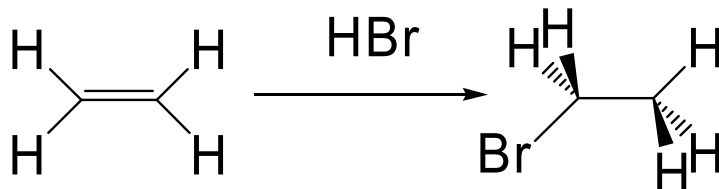
Organohalogen Compounds



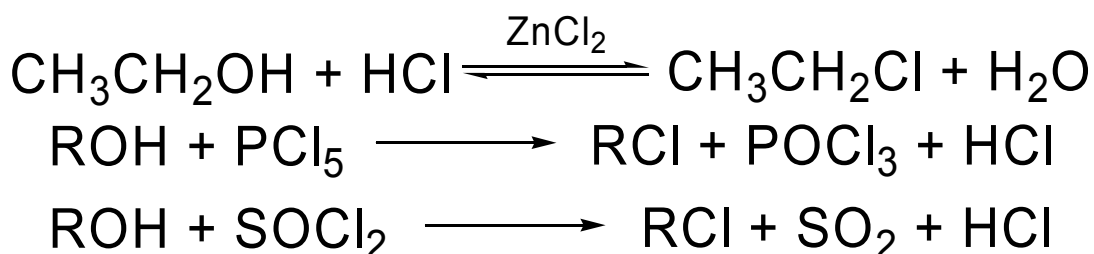
General formula R-X where X is a halogen. If R is an alkyl group then R-X is called an alkyl halide. Alkyl halides are useful reagents in synthesis as the halogen is easily replaced. If R is an aryl group (benzene) then R-X is called an aryl halide. The halogen of aryl halides is difficult to replace.

Preparation

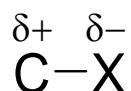
Via Markovnikov addition of HX to an alkene.



From alcohols.



Their reactivity arises from the polarity in the carbon-halogen bond

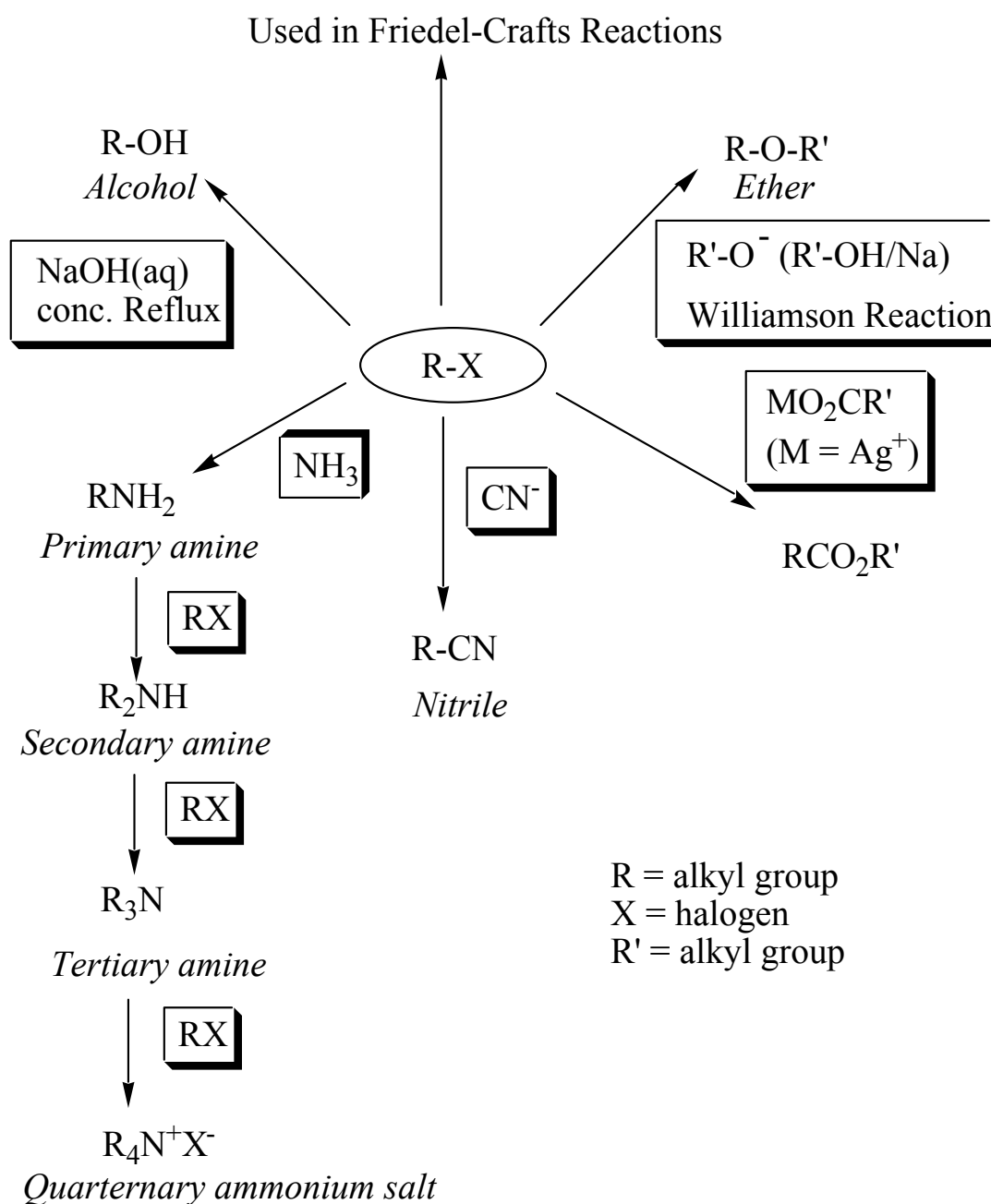


Alkyl halides react readily with nucleophiles.

A **nucleophile** is an electron rich species (Lewis base) which is capable of donating a lone pair of electrons.

Chemistry

Reaction scheme for alkyl halides



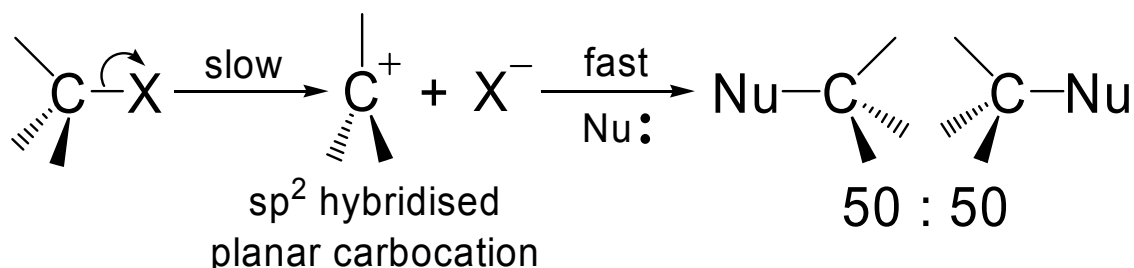
ALL the reactions shown (except the Friedel-Crafts reaction) are nucleophilic substitution reactions.



Do they all proceed via the same mechanism?

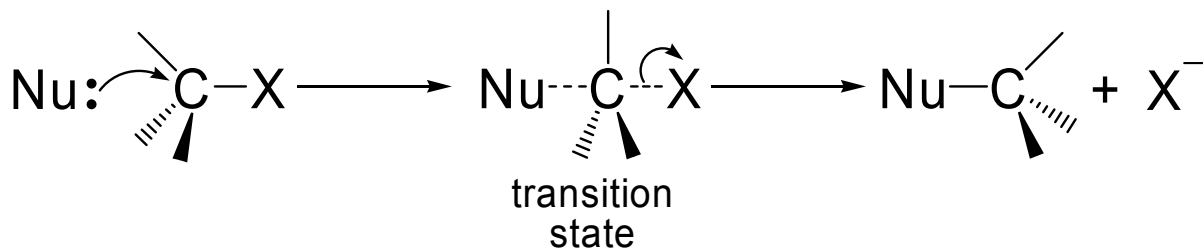
There are two possible routes:

S_N1 unimolecular nucleophilic substitution reaction proceeds in TWO steps – the slower first rate determining step (RDS) involves only ONE molecule.



Note there is no control over stereochemistry due to the planar intermediate – a racemic mixture is always produced.

S_N2 bimolecular nucleophilic substitution reaction proceeds in ONE step involving TWO molecules.

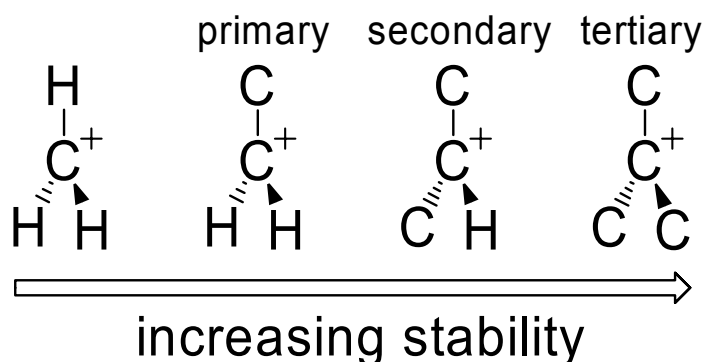


Note the inversion of stereochemistry.

How is one pathway favoured?

The **S_N1** pathway necessitates the formation of a **carbocation**. These are unstable species, but may be stabilised by:

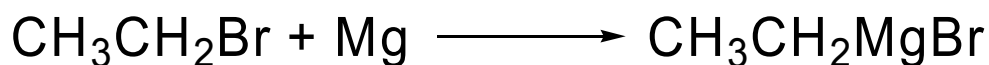
- i) **alkyl groups** – the **inductive effect** of such groups reduces the positive charge thus stabilising the carbocation.



- ii) solvent choice – polar solvents will better stabilise the carbocation.

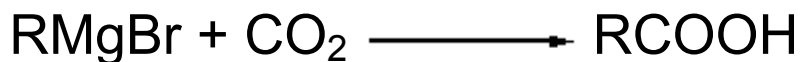
Grignard Reagents

Grignard reagents are very useful in synthesis. They are formed from the reaction of organohalogen compounds with magnesium e.g.



Formally CH_3CH_2^- i.e. nucleophilic carbon.

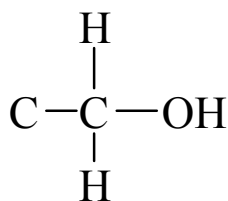
- i) React with aldehydes and ketones forming secondary and tertiary alcohols respectively.
- ii) React with carbon dioxide.



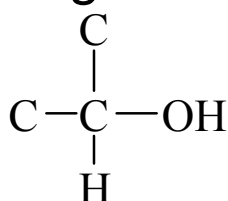
Alcohols



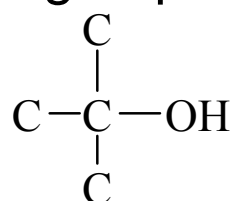
Compounds containing the -OH group.



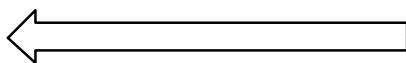
Primary



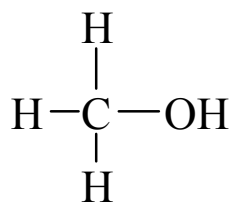
Secondary



Tertiary



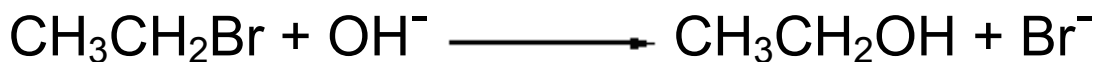
Increasing reactivity



methanol is also a primary alcohol

Preparation

i) From alkyl halides



ii) **Reduction** of aldehydes, ketones and carboxylic acids.



What is reduction?

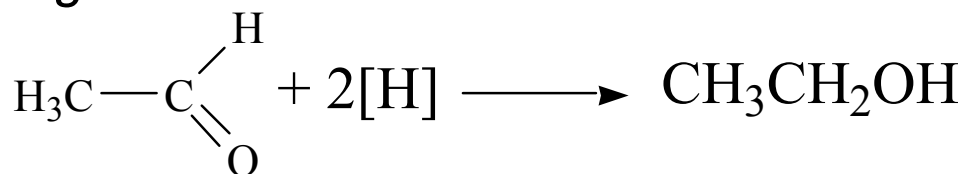
In organic chemistry, it can simply be considered as the addition of hydrogen and/or the lessening of oxygen content in a molecule. Conversely oxidation is the removal of hydrogen and/or addition of oxygen.

Common reducing agents are hydrides and sources of H^- (nucleophilic hydrogen) e.g. NaBH_4 and LiAlH_4 .

[H] symbolises **reducing agent**

[O] symbolises **oxidising agent**

e.g.



Chemistry

Oxidation

Primary alcohols are most reactive and susceptible to oxidation yielding aldehydes which in the presence of excess oxidant yield carboxylic acids. Secondary alcohols oxidise to ketones. Tertiary alcohols are very difficult to oxidise since they undergo cleavage.

Common oxidising agents [O] are typically metal based oxidants in which the metal is in a high oxidation state. e.g.

- i) Chromium(vi) in acid:
Chromium is reduced from Cr(vi) to Cr(iii).
- ii) Manganese (vii) in permanganate (MnO_4^-)
Manganese (vi) in manganate (MnO_4^{2-})
Manganese is typically reduced to Mn(iv) or Mn(ii)