

## Nucleophiles and Electrophiles



- **Nucleophiles** are the atoms that donate the electron pairs and is added to the molecules (In the example above this is the CN)
- **Electrophiles** are the atoms that seek electron pairs and is removed from the molecule (In the example above it is the Br)
- We can name a reaction based on what the non-organic part of a molecule does. In the above case the CN is non-organic so we could call it **Nucleophilic substitution**

## pKa

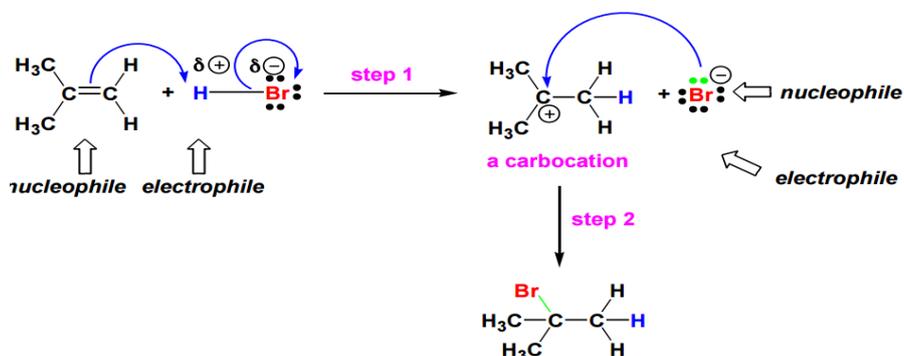
- Can help predict if acid base reactions will occur
- **pKa = -logKa**
- Ka is in relation to the equilibrium constant (concentration of products over concentration of reactants with H<sub>2</sub>O omitted because it stays relatively constant)
- The lower the pKa, the stronger an acid
  - HCl is -7, H<sub>2</sub>O is 15.74, CH<sub>4</sub> is 48

**HIGH pKa means more disassociation, means lower Ka = stronger acid!!!!**

**High pKb means lower Kb = stronger base!!!!**

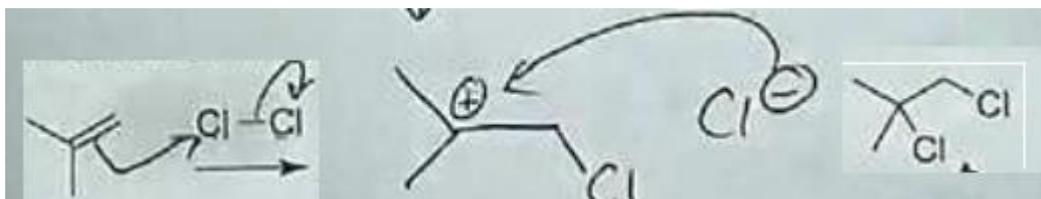
## Addition

- Electrophiles are attracted to the  $\pi$  bond
- Addition sees a  $\pi$  bond replaced with a  $\sigma$  bond
- There are many different types of addition reactions:
  - Hydrogenation:
    - The addition of hydrogen
    - Occurs in stages with **the positively charged substance first**
  - Hydrohalogenation:
    - Addition of a hydrogen halide (HBr)



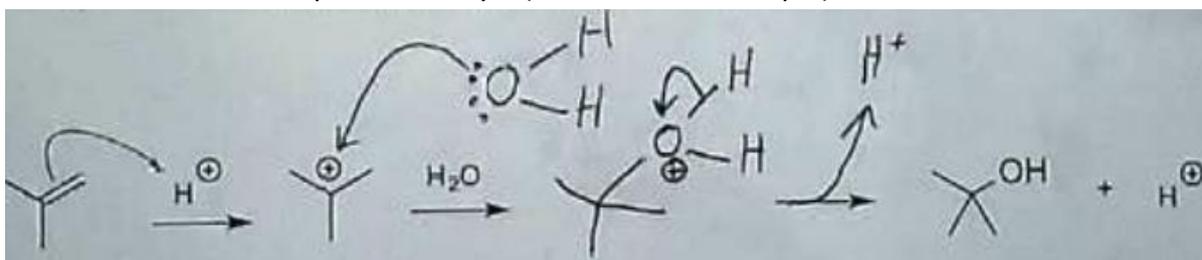
○ Halogenation:

- The addition of a halogen (Group 17 on periodic table, Cl, Br, etc)



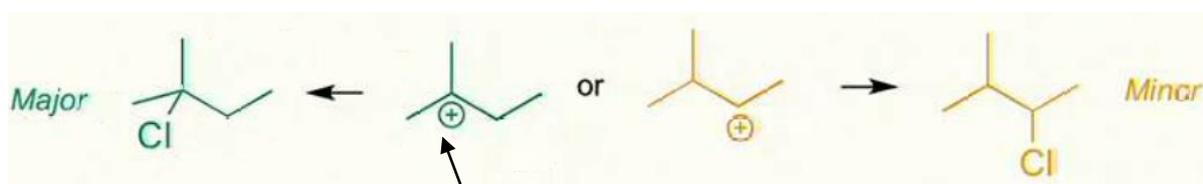
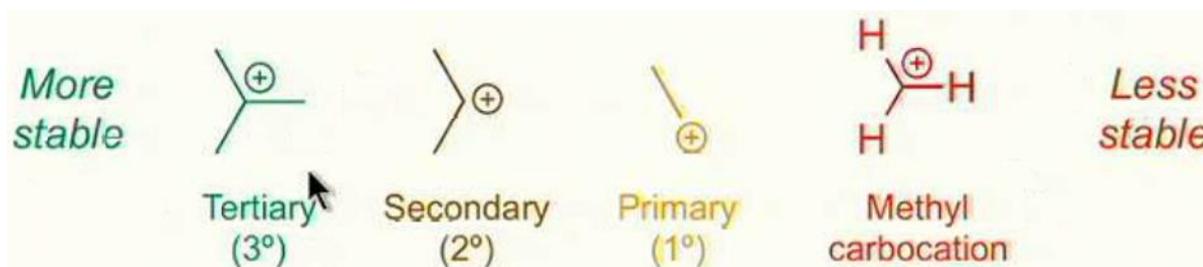
○ Hydration:

- Addition of water
- Requires a catalyst (dil.  $\text{H}_2\text{SO}_4$  for example)



**Carbocation stability**

- The more non-hydrogens a carbon has attached, the more stable it is
  - The other carbons around donate some of their electron density to create greater stability
  - Trying to spread the positive charge over the greatest distance possible through **induction**
  - **Hyperconjugation** is where the C-H bonds donate partial amounts of their electron densities
    - With more carbons present, there are more spare pi orbitals to accept these densities and therefore a greater stability

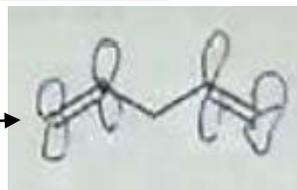


The one on the left is more stable and common because there are more carbons surrounding the positive charge than the one on the right has

## Conjugation

- This is the transfer of electrons between  $\pi$  bonds
- **Occurs when there is an uninterrupted sequence of  $\pi$  orbitals**

This alkane does have  $\pi$  orbitals but they are interrupted in the middle and not continuous. Therefore it is not conjugated.



- In substances like that seen to the right, electrons do not always stick to one place and instead form an electron "cloud" around the bonds

- This allows the electrons to move around



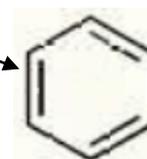
- **For something to be cyclic, it has to be conjugated**

- Must also follow Huckel's rule ( $4n+2$   $\pi$  electrons)

- Can be 2,6,10, etc...

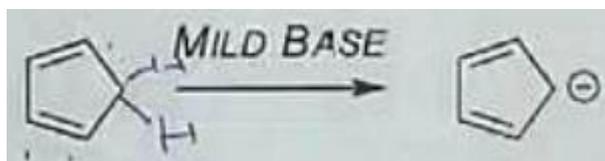
- If the number of  $\pi$  orbitals follows this rule above and it is cyclical then it is an aromatic system

There are 6  $\pi$  electrons in this molecule which fits in with Huckel's rule and therefore this is an aromatic ring



- In this example, originally there is no conjugation. However adding a base will remove one of the hydrogens.

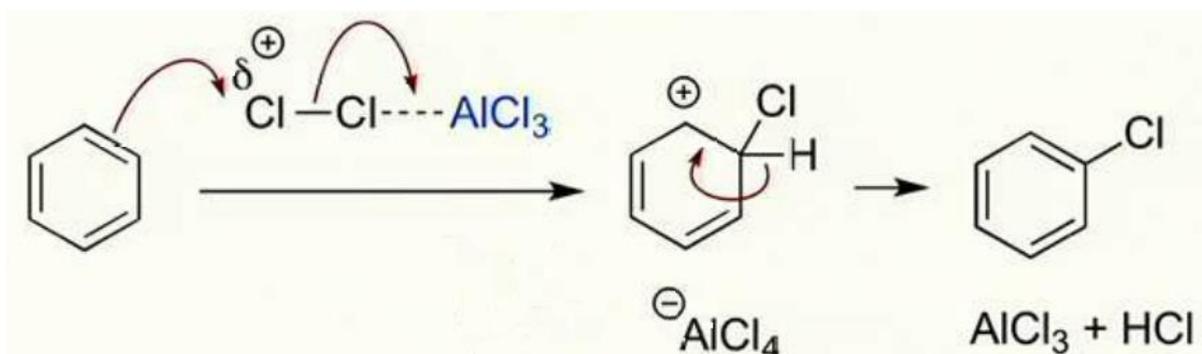
This will move the electrons that the H had, into the ring and create a  $\pi$  orbital. **This**



**leaves the chain uninterrupted and creates an aromatic ring**

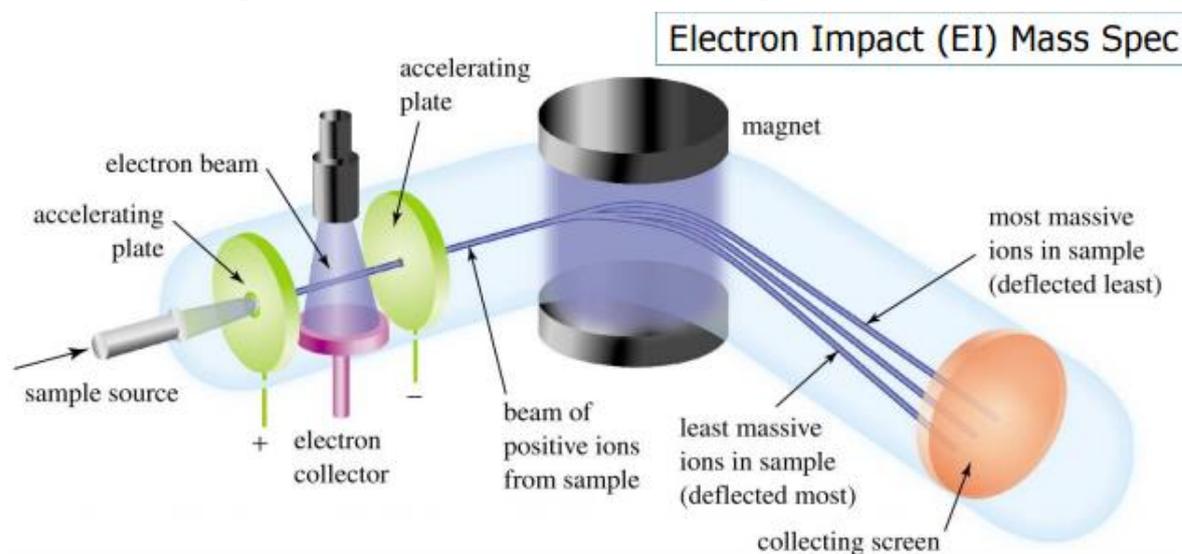
## Substitution on aromatic rings

- We never see nucleophilic substitution in aromatic rings because the nucleophile cannot get through the electron cloud and substitute
- We can get however, get electrophilic substitution in aromatic rings
  - The aromatic ring "attacks" the electrophile with its electron cloud
  - Usually need a catalyst to make the electrophile more reactive



## Structure Identification

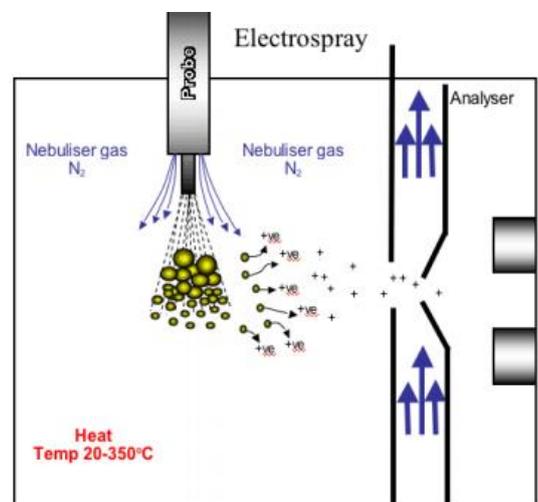
- Steps:
  - Isolate and purify it (precipitation, distillation, chromatography)
  - Determine molecular mass (atomic spectrometry)
  - Identify functional groups and conjugations (infrared and UV/VIS spectroscopies)
  - Assemble structural formula (MMR spectroscopy)
- Using molecular formula
  - We can react a species with oxygen to produce  $\text{CO}_2$  and  $\text{H}_2\text{O}$
  - We can then work out the percentage compositions (**Empirical formula**)
  - However, an empirical formula can mean many different forms so we must look at **molecular formula**
  - We can use **mass spectrometry** to determine molecular mass
- Mass Spectrometry
  - First a source is ionized and then shot out of a source
  - The accelerator plates and electron beam give the source a charge which allows them to bend around the magnet
  - **Heavier substances will take longer to bend around while lighter substances will bend around faster**
  - Ion fragments that come off are known as **daughter ions**



- The most intense signal is called the **base peak**

- Detection without smashing the substance apart

- Most common technique is known as **electrospray**
- Very gentle so can be used to analyse proteins



- Isotopes

- The mass spectrum registers **the specific isotopes of the elements present in that individual ion**
- The numbers we use to calculate mass numbers are approximations of the weights of the isotopes

- Spectroscopy

- Absorption of part of the electromagnetic spectrum
- The energy absorbed gives a signal in the spectrum which gives structural information

- Nuclear Magnetic Resonance

- Uses energy in the radio frequency region
- Involves “flipping” the spin of a nucleus in a magnetic field
- Used for analysis and structural connectivity determination (NMR) and imaging soft tissue in animals (MRI)
- Some nuclei can spin and other cannot
  - Each resonates at a particular frequency in a given magnetic field

- **Nuclear Spin**

- In NMR atomic nuclei act as if they are “mini-magnets”
- They will align parallel or anti-parallel to an external magnetic field
  - Parallel spin is connected with low energy and anti parallel spin is connected with high energy

- **<sup>13</sup>C NMR Spectroscopy**

- Depends on the environment around an atomic nucleus
  - The proximity of a Carbon to an oxygen changes where it will appear on the spectrum
  - Nuclei with similar environments (similar locations) will be found similarly on the spectrum
  - Carbons that are less involved and less proximal to Oxygen will appear further upfield (towards 0)