

## Lecture 2 - Bonding in Organic Compounds

Hybridization occurs when there are overlapping s & p bonds

In Alkanes (e.g. in CH<sub>4</sub> with a Tetrahedral shape)

Alkanes are held together by weak dispersion forces hence the boiling point is lower than any other type of compounds.

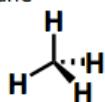
The melting points of alkanes increases with the molar mass.

Based on the characteristics of C, a very large number of constitutional isomers can be formed with a small number of Carbon and Hydrogen atoms

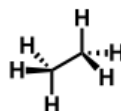
### sp<sup>3</sup> Hybridisation: Alkanes

- If the 2s orbital mixes with all **three** 2p orbitals ...
  - $1 \times s + 3 \times p \Rightarrow 4 \times sp^3$
  - i.e. 4 x identical orbitals  $\Rightarrow$  forms 4 x single bonds

Methane



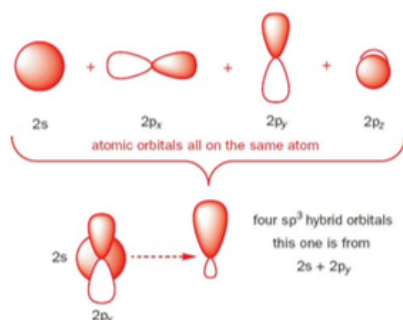
Ethane



The total number of s + p = the number of atoms surrounding the Central Atom (C in this example)

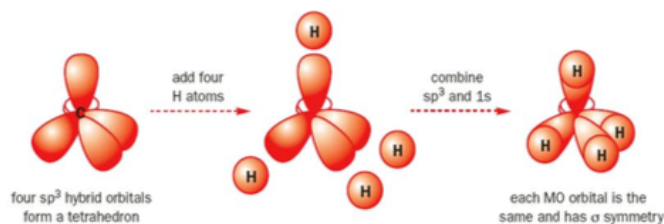
The Hybridization of orbitals start with:

from *Clayden et al.* – p105a



This results in a hybridized orbital that looks like:

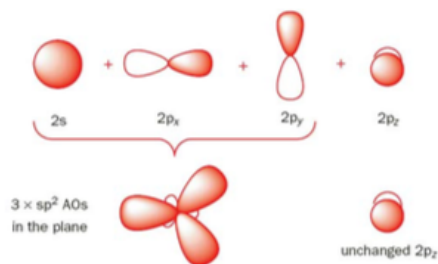
from *Clayden et al.* – p105b



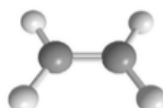
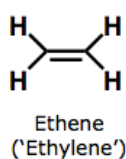
In the Alkenes, the C=C double bonds will result in only 3 bonds around the central C atom (1 C=C bond and 2 H-C bonds) hence the hybridized orbital will be  **$sp^2$**

## $sp^2$ Hybridisation: Alkenes

from *Clayden et al.* – p106a



- If the 2s orbital mixes with only **two** 2p orbitals ...
  - $1 \times s + 2 \times p \Rightarrow 3 \times sp^2$  (+ 1 x p unhybridised)
  - i.e. 3 x identical orbitals + one different one  
 $\Rightarrow$  forms 3 x single bonds + 1 x double bond



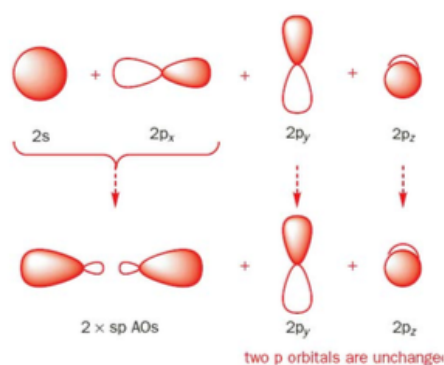
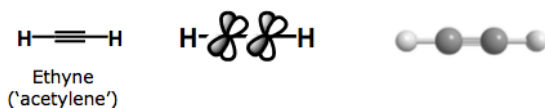
The Resulting Hybridized Orbital will look like:



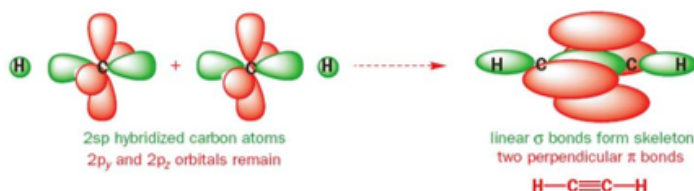
In Alkynes (where there are triple bonds), the hybridized orbital is  **$sp$**  (one C $\equiv$ C bond and one H-C bond)

## sp Hybridisation: Alkynes

- If the 2s orbital mixes with only **one** 2p orbitals ...
  - $1 \times s + 1 \times p \Rightarrow 2 \times sp$  (+ 2 x p unhybridised)
  - i.e. 2 x identical orbitals + two different ones  
 $\Rightarrow$  forms 2 x single bonds + 2 x double bond



The Hybridized Orbital will look like this



### Summary on Hybridization




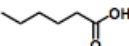
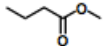

- Hybridization will always involve S & P.
- There will only be one S in the hybridized orbital since S is the same in all three planes
- The maximum # of P is 3 since there are 3 planes (X, Y and Z)
- The shape of the molecule / around the central atom impacts the hybridisation e.g. **the lone pairs should be considered** hence if its a **tetrahedral shape, the hybridized orbital will be sp<sup>3</sup>.**
- Single bonds are sigma (S)
- Double Bonds are Pi (P)
- Triple Bonds are Sigma & Pi (S & P)
- Alkenes and Alkynes are called unsaturated hydrocarbons (presence of double or triple bonds)
- They are non polar compounds and the only attractive forces are dispersion forces.

Functional Groups – usually are the interesting bits of the molecule

**List of Functional Groups include:**









For Reference ...

### Overview of Functional Groups (I)

	Alcohol	-ol	Propanol
	Ketone	-one	Butanone
	Aldehyde	-al	Ethanal
	Carboxylic Acid	-oic acid	Hexanoic acid
	Ester	-oate	Methyl butanoate
	Amide	-amide	Butanamide

For Reference ...

### Overview of Functional Groups (II)

	Ether	ether	Diethyl ether
	Sulfide	sulfide (thioether)	Diethyl sulfide
	Thiol	-thiol	Ethanethiol
	Amine	Amino- or -amine	Ethyl amine
	Fluoride	Fluoro- or fluoride	Fluoroethane
	Chloride	Chloro- or -chloride	2-Chlorobutane
	Bromide	Bromo- or -bromide	2-Bromobut-2-ene
	Iodide	Iodo- or -iodide	Iodobenzene

- Alkanes are usually joined together by Van der Waals forces, which increase when the size of the alkane increases.
- Their melting and boiling point also increases with size.
- Alkanes are generally inert and liberate a lot of energy in combustion. (reaction with oxygen)
- They are commonly used in fuels (short chain alkanes combust efficiently, long chain alkanes do not)
- Amides have a double bond to oxygen but Amines don't have oxygen

## Lecture 3 – Isomerism

Isomers are molecules with the same formula but different structures

The 3 C types of Isomerism are:

- **Constitutional Isomers** – different atom to atom bonding (different nature / sequence of bonds)
  - Stereoisomers – different arrangement of groups in space but same nature & sequence in bonding
- **Configurational Isomers** – Conversion of Isomers requires the breaking of bonds and remaking of bonds
  - Diastereoisomers – Not Mirror images
  - Enantiomers – Non-superimposable mirror images
  - Does not occur at room temperature as a lot of energy is required.
- **Conformational Isomers** – Differences in Isomers are based on a rotation of a single bond. (these tend to be hard to spot esp. where there are a lot of bond rotations)
  - Not normally separated at room temperature

In the example of  $C_2H_2BrClO$  – There are 16 possible different compounds

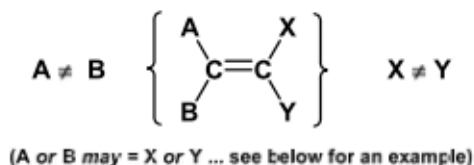
Isomers would have different properties and behaviours when they form different functional groups.

Double Bond Isomers would be **configurational isomers**. They have Pi bonds hence **the C=C bond rotation will break the pi bond.**

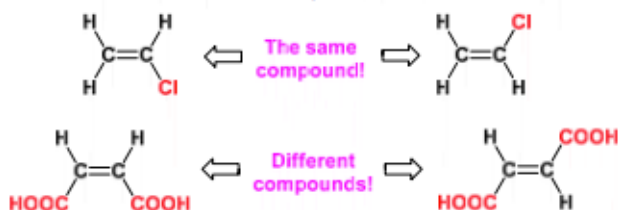
- This would require 10X more energy than breaking the sigma bond.

They would be known as Diastereoisomers if both end of the C=C bonds have different groups

- **Both ends of the C=C bond must have two different groups**



- If these conditions are met, two *diastereoisomers* result



Priority is assigned based on the place of the Periodic table of the atom --> atomic #

Called **diastereoisomers** and labeled *Z* or *E*

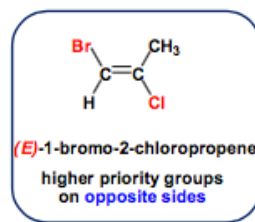
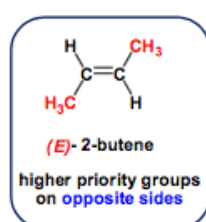
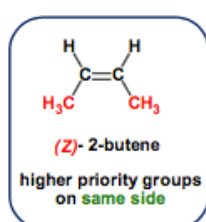
**Rules:**

- Assign **priority** to each group on each carbon of C=C
  - The **higher the atomic number** of the atom attached, the higher the priority
  - If identical atoms attached, work along the chain until the first point of difference, then go by atomic number
- If high priority groups on same side of C=C  
 $\Rightarrow$  *Z* double bond (German: *zusammen*, together)
- If high priority groups on opposite sides of C=C  
 $\Rightarrow$  *E* double bond (German: *entgegen*, opposite)

Note: '**diastereoisomer**' is often condensed to '**diastereomer**'

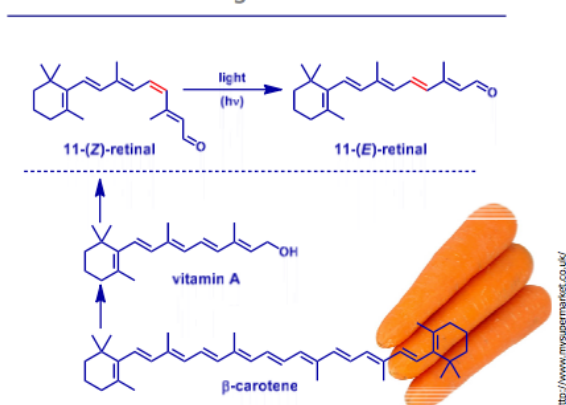
If it is **ZE ZAME** it is a Z diastereomer, since the bonds are on the same side.

The E double bonds are on different sides



Seeing isomers – light creates a change in the shape of the isomers

**Seeing Isomers**

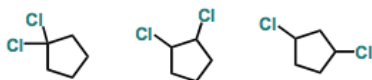


Cycloalkanes

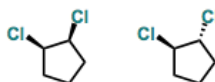
## Disubstituted Cycloalkanes

Various isomers are possible

- Constitutional:



- Configurational:



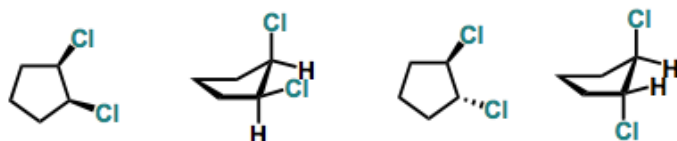
Note - Don't need to have double bonds to have configurational isomerism!

They are considered configurational since you need to break the aromatic ring to change the Cl bonding.

## Disubstituted Cycloalkanes

### *cis* and *trans*

- These structures are diastereoisomers or diastereomers
- They have different physical and chemical properties
- The terms *cis* and *trans* are used to distinguish them



*cis*-1,2-dichlorocyclopentane    *trans*-1,2-dichlorocyclopentane

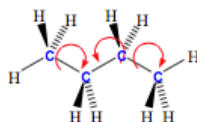
- Cis – Same Phase
- Trans – Different Phase

Conformational Isomers – rotate around the C-C bonds

## Conformational Isomers

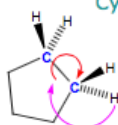
### Straight chain alkanes

- Rotation around each C-C bond readily occurs
- Conformational isomers result

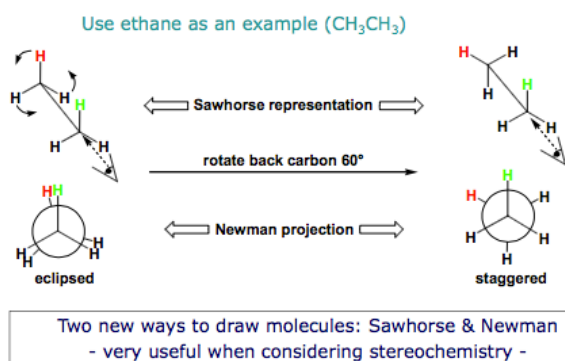


### Cyclic alkanes

- Rotation is restricted within a ring
- Since rotation would require atoms to pass through the ring – very high energy barrier



## Conformational Isomers

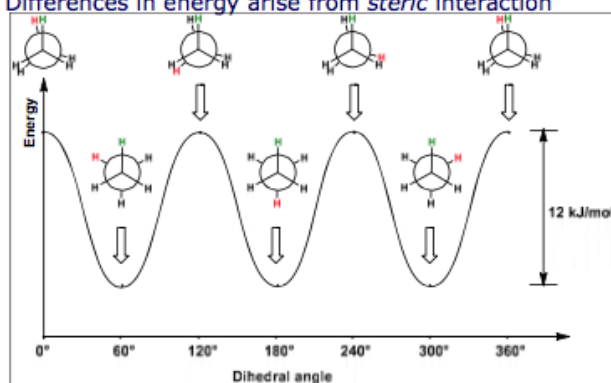


Staggered Newman projection means they are not blocked whereas Eclipsed they are blocked by a bit

The Newman projection is important

## Barriers to Rotation

- In 'straight chain' alkanes, rotation about C-C rapid at R.T.
- Differences in energy arise from *steric interaction*



Because the two H in the staggered form is directly opposite, they kinda cancel each other out hence the energy will be lower!



## Lecture 4 – Curly Arrows

1. Reaction Types
  - a. Acid – Base
  - b. Substitution
  - c. Addition
  - d. Elimination
  - e. Oxidation - Reduction
2. Nucleophiles & Electrophiles
3. Curly Arrows

### Acid – Base Reaction

Bronsted acids are proton donors

- electron pair acceptors

- Acid

-CH, -NH, -OH, -ClH (arranged in increasing electro negativity.)

The pKa scale (which is  $\log_{10} K_a$ ) indicates which is the easiest donor.

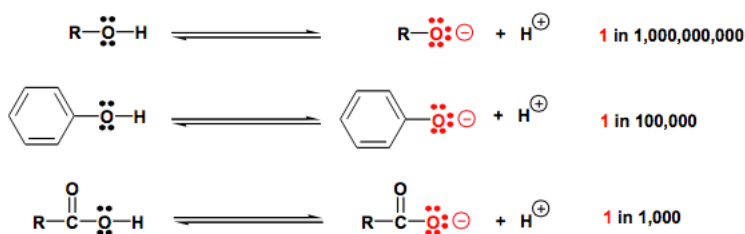
Organic acid compounds are identified by the – OH group.

The degree of acidity is related to the stability of the anion.

**For organic acids look for –OH group**

Carboxylic acids, phenols and alcohols all contain –OH

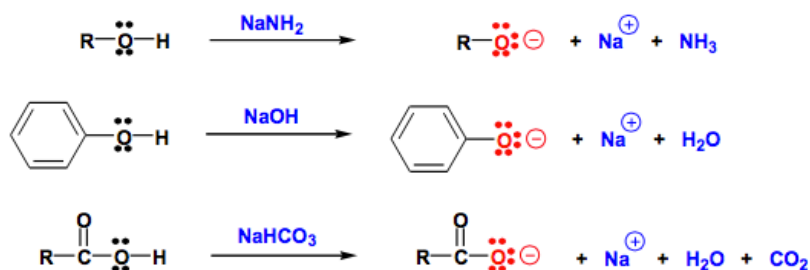
The degree of acidity is related to **the stability of the anion**



Note: R = 'rest of molecule'

**Organic compounds can have very different acidities.**

Reaction may occur in the presence of a strong enough base



	NaNH <sub>2</sub>	NaOH	NaHCO <sub>3</sub>
Alcohol	✓	X	X
Phenol	✓	✓	X
Carboxylic acid	✓	✓	✓

Very strong base is required to deprotonate the electron. Hence the  $\text{NaNH}_2$  is the only one that is able to deprotonate the electrons for alcohols, Phenols & Carboxylic Acid.

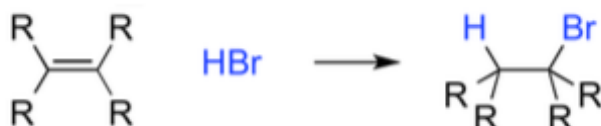
- In this list, the  $\text{NaNH}_2$  is the strongest base.
- $\text{NaOH}$  – Mid-strength
- $\text{NaHCO}_3$  – the weakest base (reacts only with the weak acids).
- This is due to how the electrons are distributed.

### Substitution Reaction



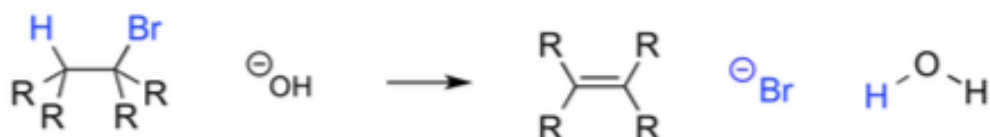
The OH is substituting the Cl

### Addition Reaction



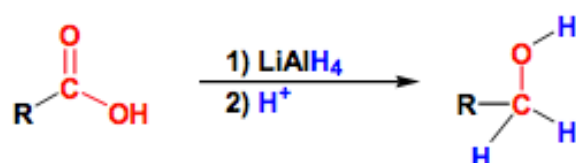
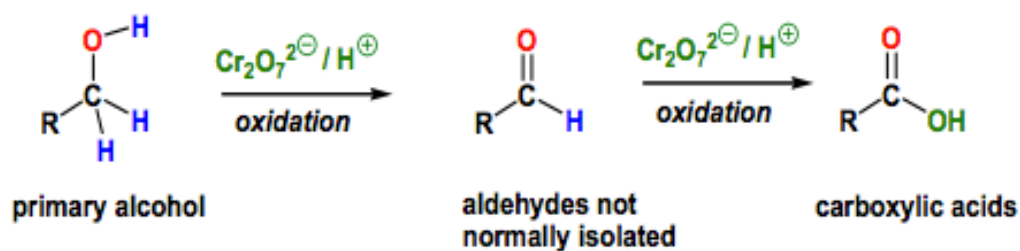
This occurs when you have a double bond  $\rightarrow$  compound is unsaturated.  
Saturated compounds max out the # of joints.

### Elimination Reaction



The Saturated compound becomes unsaturated

## Oxidative – Reduction Reaction



### Oxidation

- decrease in the number of C-H bonds (net increase)
- increase in the number of C-O bonds (increase the number of bonds with O)

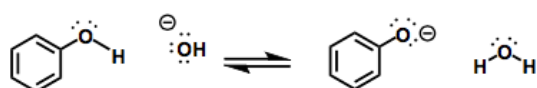
### Reduction

- Increase the number of bonds with H (increase the number of C-H bonds)
- Decrease the number of C-O bonds

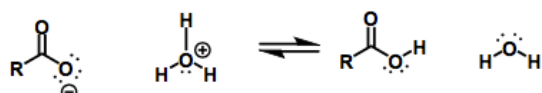
### Curly Arrows

#### A curly arrow indicates electron pair movement

- A curly arrow starts at the electron pair that moves and ends at the atom to which the electron pair has moved



- An arrow from a bond indicates breaking of that bond; an arrow between two species indicates a bond is formed between the species



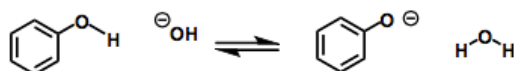
## Curly Arrow Drawing Conventions

It's important you **can** supply lone pairs on mechanisms to understand what's going on:



...but, we *tend not to draw them all in*, because we assume they're there (like H's on carbons on organic structures). Typically we:

1) Draw arrows coming from negative charges (if there are any)



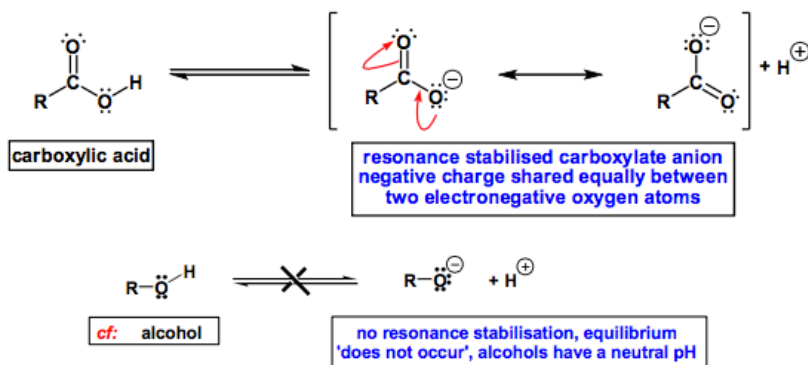
2) Temporarily supply one lone pair for the drawing



- This shows where the charge is moving or the moving electron pair.
- Always work in one direction
- Either FROM the lone pair or FROM the negative charge AND towards H<sup>+</sup>

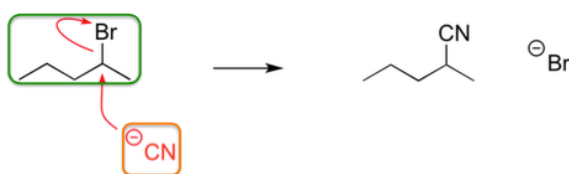
## Curly Arrows Help to Explain Acidity

Difference in acidity results from resonance stabilisation of the anion



The resonance structures are two extremes which the molecule could exist as, the real structure is somewhere in the middle of both resonance structures.

## Using Curly Arrows to describe Substitution



## The Nucleophile

- attracted to the nucleus which is positive
- are electrons rich hence it is negative
- donates its lone pair of electrons

## The Electrophile

- Wants to receive a lone pair of electrons
- Is positively charged/ polarized.

The **Curly Arrows** is drawn in the direction of nucleophile to electrophile.  $N \rightarrow E$

- The electrophile is the reagents that participate in the reactions.
- Name of the reaction is governed by what the organic substance is doing.
- All Nucleophile reaction will work with an electrophile – these are a pair reaction.

## Lecture 5 – Addition Reaction

In each reaction, there are two reagents that participate in the reactions.

### Two types of reagent that participate in reactions

- Electrophiles (seek electron pairs) eg  $H^+$ ,  $HCl$ ,  $NO_2^+$
- Nucleophiles (donate electron pairs) eg  $OH^-$ ,  $Br^-$ ,  $:NH_3$

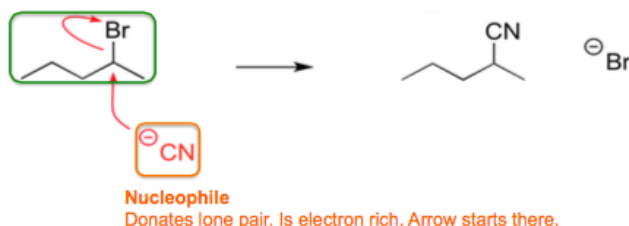
Name of reaction governed by **what the organic substrate is doing**:

- Use 'nucleophilic X' if being attacked by a nucleophile
- Use 'electrophilic X' if organic substrate is attacking an electrophile

The curly arrows move from where the electrons are (-) to where they are not (+)



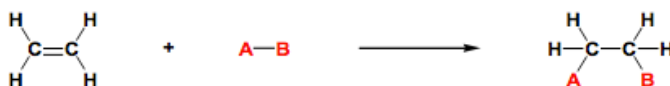
**Electrophile**  
Seeks a lone pair. Is electron deficient. Nucleophile's arrow goes there.



Addition reactions tend to occur to an alkene as it is unsaturated.

### Dominated by weak and accessible $\pi$ -bond

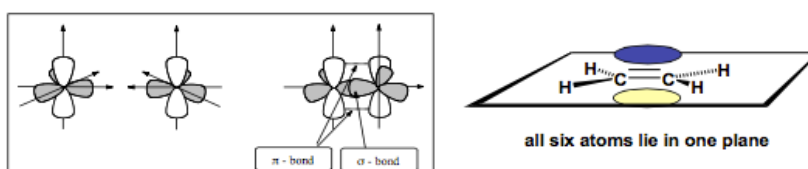
- Electrophiles attracted to the  $\pi$  bond
- **Addition** occurs with overall replacement of a  $\pi$  bond with a  $\sigma$  bond: *energetically favourable*



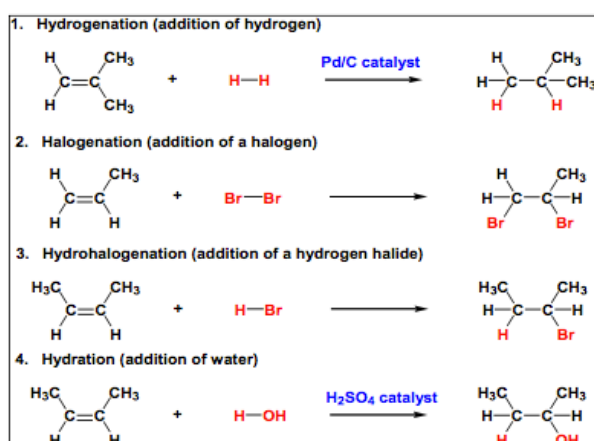
- A-B can be  $\text{H}_2$ ,  $\text{Cl}_2$ ,  $\text{Br}_2$ ,  $\text{HCl}$ ,  $\text{HBr}$ ,  $\text{HI}$ ,  $\text{H}_2\text{O}$

### Reminder:

- A double bond is composed of one  $\sigma$  and one  $\pi$  bond
- The electron density of a  $\pi$  bond is above and below the plane of the double bond
- Quite reactive towards electrophiles



## Alkene Reactions

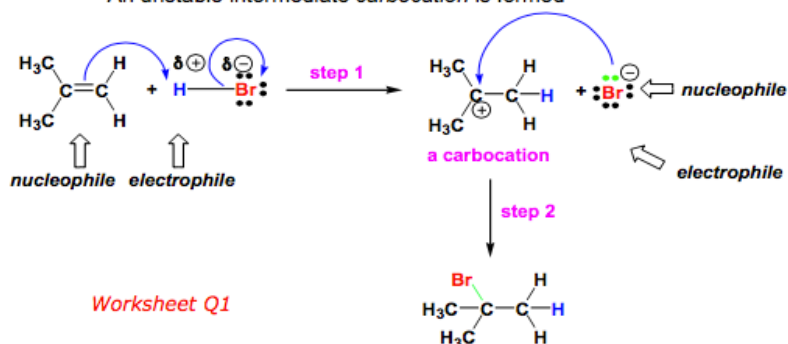


Note that based on the catalyst used, you can guess the kind of Alkene Reaction.

## Mechanism: Hydrohalogenation

### Two steps

- An unstable intermediate *carbocation* is formed



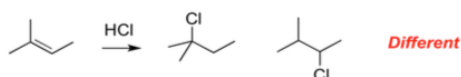
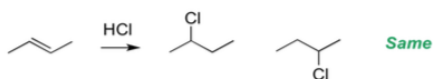
Worksheet Q1

Terminology: We say this is an **electrophilic addition** since the thing that is reacting with the organic starting material is an electrophile

The Carbocation (Carbo-cat-ion) stability is dependent on which C the H connects to in the reaction. The Carbocations are more stable if they have more C attached to it.

The electrophilic addition is more energetically favoured as it replaces the pi bond with a sigma bond.

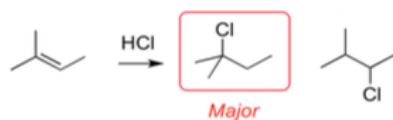
What if there's a Choice? Isomeric Products?



So ... do we get both these products?

### One Product is Favoured

There is *selectivity*



The rate limiting step is the generation of the carbocation, which is high in energy. If the carbocation is easier to form, the reaction goes faster.

There are differences in carbocation stability

- Alkyl groups help to spread the positive charge along the bonds
- More substituted cations are more stable

## Carbocation Stability

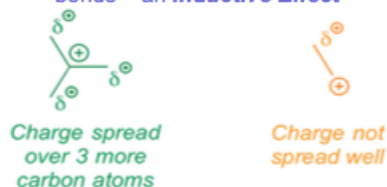
The intermediate in the reaction is a carbocation

- Carbocations have 6 electrons and a positive charge
- All carbocations are unstable but not all to the same extent

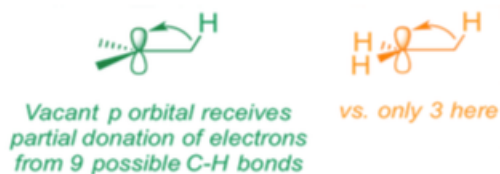


## Carbocation Stability – Why?

Alkyl groups help to spread the positive charge a little along the bonds – an **Inductive Effect**

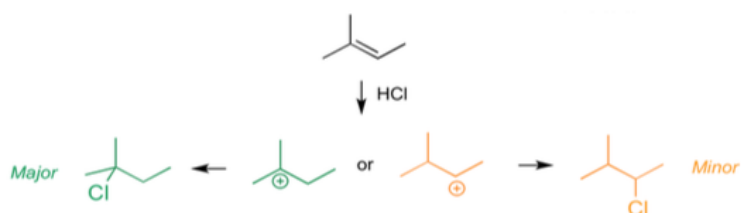


Adjacent C-H bonds donate a little electron density through space – **Hyperconjugation**



## Carbocation Stability Governs Major Product

The more stable carbocation forms preferentially. This defines which product is major



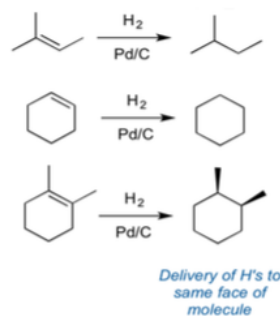
This product selectivity is sometimes referred to as **Markovnikov's Rule**

Markovnikov's Rule – shows that the more stable carbocation is the majority product between the two isomers



## Hydrogenation

Catalyst required (e.g. Pd on charcoal) to break strong H-H bond

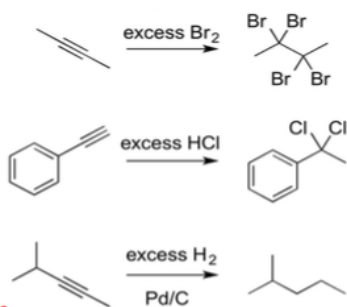


Mechanism different to electrophilic addition – don't need to know

## Alkyne Chemistry Similar

A triple bond is composed of two  $\pi$ - and one  $\sigma$ -bond

- Electrophilic addition occurs to both  $\pi$ -bonds
- Same selectivity rules for terminal alkynes



*Socratic Practice...*

Reaction with Alkynes is similar to Alkene