
CHEM1201: Section 2

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1 Alkanes

1.1 Preamble

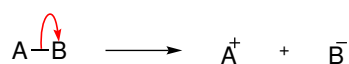
Rings, double bonds and other atoms in organic molecules introduce degrees of unsaturation or double bond equivalents. The formula for working out the degrees of unsaturation is:

$$DBE = \frac{(2 + (2 \times \#Carbons) + \#Nitrogens - \#Hydrogens - \#Halogens)}{2}$$

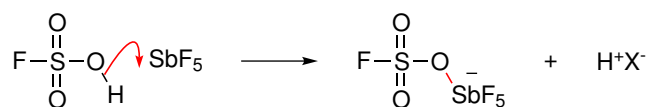
1.2 Reactions of Alkanes

The simplest saturated hydrocarbon is methane, CH_4 , which has bond angles of $109^\circ 28'$. Alkenes are made up of tetrahedral sp^3 hybridised carbon atoms covalently bonded with hydrogen. They undergo two elementary reactions:

1.2.1 Heterolytic Fission

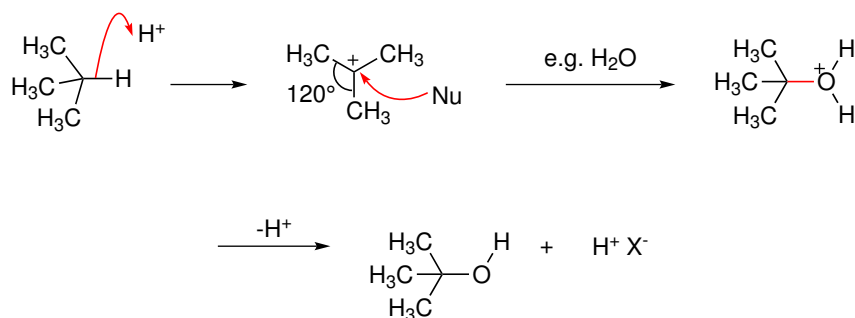


a)



"Superacid" mixture

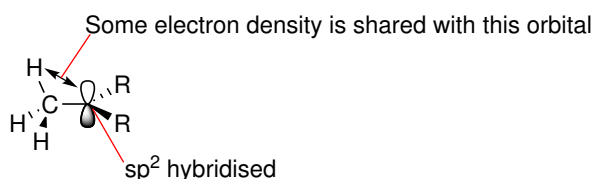
b)



A trigonal planar, carbocation is formed as the reactive intermediate

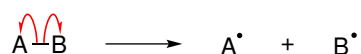
Note that charge is conserved and only the tertiary methane hydrogen is removed. This is because of the stabilisation effect from R groups. Primary carbocations ($\text{R}-\text{C}^+\text{H}_2$) are higher in energy than secondary ($\text{R}_2\text{C}^+\text{H}$) which are in turn higher than tertiary (R_3C^+) where R is an inductively

electron releasing alkyl group (e.g. $\text{CH}_3\text{CH}_2\text{CH}_3$ etc). This effect can be explained by hyperconjugation, as in a carbocation there will be a sp^2 hybridised vacant p orbital that can accept electrons coming out of the plane of the trigonal planar molecule. Electron donation occurs from the $\text{C}-\text{H}$ bond, in the same plane as the sp^2 orbital, into the empty p orbital.

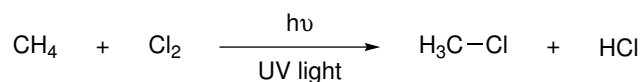


1.2.2 Homolytic Fission

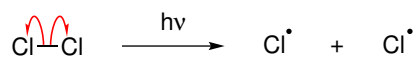
For example free radical chain reactions which are of preparative value.



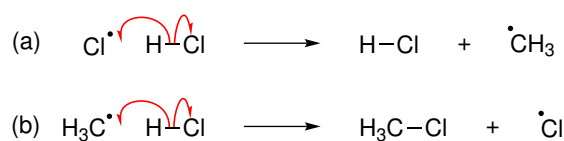
E.g. Free radical halogenation of methane:



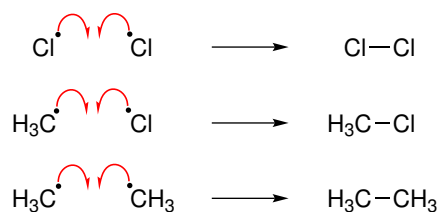
Initiation



Propagation



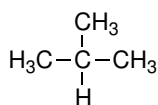
Termination



Termination reactions require another photon and account for less than 2% of the product.

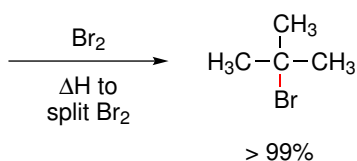
In the free radical halogenation of methane, the propagation steps take place 10^6 times for each initiation step. Additionally, other products are formed when more H's are replaced.

When using isobutane (2-methylpropane) we see interesting selectivity.

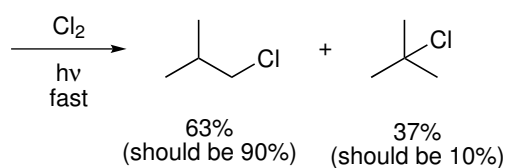


Isobutane

With Br_2 the reaction is regiospecific - a single regioisomer is formed.



With Cl_2 the reaction is regioselective meaning that there is a preference for one regioisomer rather than the others.



These regio effects occur because the chlorine is much more reactive and hence less discriminating in hydrogen abstraction than the bromine atom (more electronegative). One $\text{H}-\text{Cl}$ bond formed for Cl is -431 kJmol^{-1} and for Br is -366 kJmol^{-1} and the tertiary $\text{C}-\text{H}$ bond requires $+397 \text{ kJmol}^{-1}$ to break. Hence with Cl the reaction is exothermic and with Br it is endothermic meaning the bromine reaction requires energy, this in turn makes the reaction more discriminating.

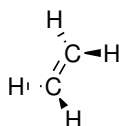
Breaking one primary bond needs $+423 \text{ kJmol}^{-1}$ and therefore, as reactions follow the path of least energy and the order of radical stability is $3^\circ > 2^\circ > 1^\circ$, the reaction proceeds above.

2 Alkenes

2.1 General

General formula: C_nH_{2n}

Ethene has a planar framework of atoms



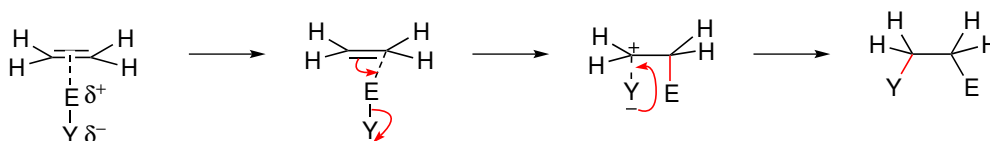
Each carbon atom has 3 sp^2 hybrid atomic orbitals (using the 2s and only 2 of the 2p orbitals) which lie in the xy plane orientated at 120° relative to each other. The C–H σ bonds are formed by overlap of the sp^2 hybrids on carbon and the 1s on hydrogen, the C–C σ bond is then constructed using the remaining sp^2 orbitals. The weaker π bond is constructed using sideways overlap of the remaining 2p_z on each carbon atom.



The chemistry of alkenes is dominated by the ability of the 2π electrons to donate themselves, i.e. function as a nucleophile. Geometrical isomerism occurs due to restricted rotation about the C=C. The Z isomer is when the larger products are on the same side (cis) and E is when they are on opposite sides (trans).

2.2 Reactions of Alkenes

Due to the ability of the π cloud to donate 2 electrons, electrophilic addition to alkenes is a wide ranging and general series of reactions. For a reagent of the form $E^{\delta+}-Y^{\delta-}$ the following mechanism can be written.



First there is complex formation with the polarization and lengthening of the E–Y bond followed by the formation of the C–E bond and breakage of the E–Y bond. Finally nucleophilic capture occurs with the reactive carbocation intermediate.

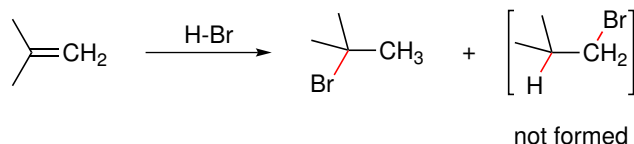
Some useful reagents are:

- Br_2
- $H-Cl$, $H-Br$, $H-X$ etc.
- H_3O^+ - acid

- $\text{Br}-\text{OH}$ - hypobromous acid (or from formation of borohydrin via $\text{H}_2\text{O}/\text{Br}_2$)
- $\text{Ph}-\text{S}^{\delta+}-\text{Cl}^{\delta-}$ - sulfenylation

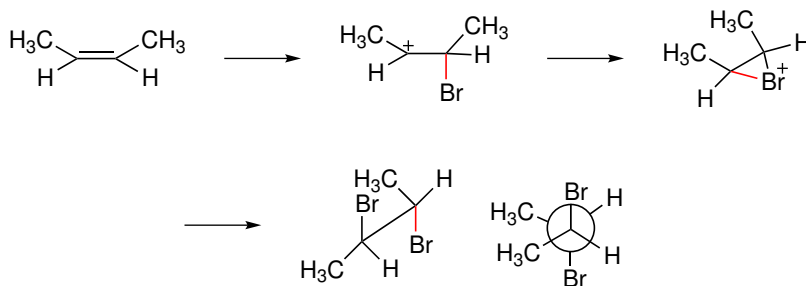
Electrophilic additions to unsymmetrical alkenes are regiospecific (only one regioisomer formed). This method of addition was first noted in 1870 by Markovnikov and is stated as an empirical rule – Markovnikov's rule. This is because addition always occurs via the lower energy carbocation.

E.g.



When the component E of the reagent $\text{E}^{\delta+}-\text{Y}^{\delta-}$ possesses lone pairs of electrons, reactions are also stereospecific (only one stereoisomer formed).

E.g. Addition of bromine to Z and E-but-2-ene.

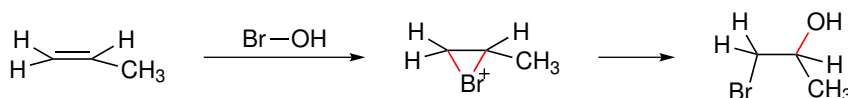


The opening of the bromonium cation occurs by nucleophilic attack from the least hindered opposite face (antiperiplanar position). Overall the reaction is a trans (or anti) electrophilic addition. Similarly the reaction of E-but-2-ene gives a different diastereoisomer.

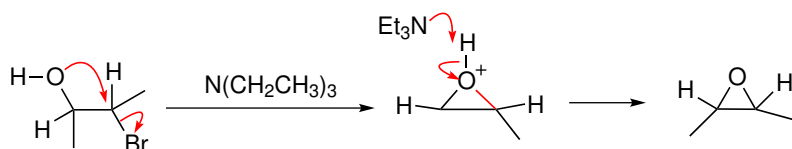
Other examples of bridged intermediates that form stereospecific compounds are:



Some reactions are both regio and stereospecific. E.g. BrOH



Bromohydrins are used in the preparation of epoxides. E.g.

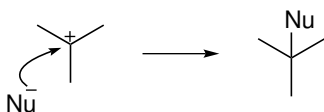


Hydration can also occur via acetomercuration to form an alcohol (see section 1) and either NaBH_4 or NaOH can be used as bases to remove the final $\text{Hg}-\text{OAc}$.

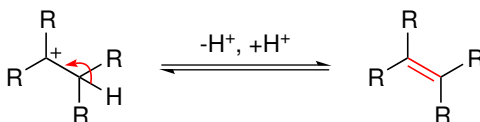
2.2.1 Reactions of Carbocations

Carbocations undergo 3 types of reaction:

- a) Capture by a nucleophile

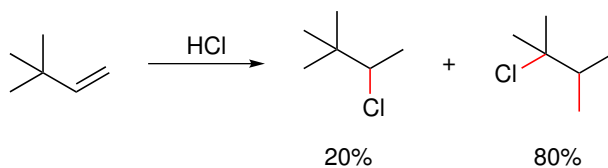


- b) Proton loss to give an alkene

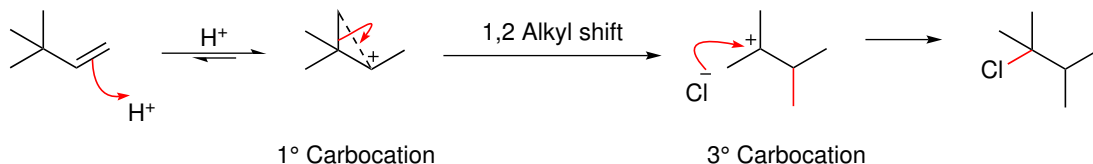


- c) Carbocation Rearrangement Rearrangement will always occur to give a lower energy carbocation. Examples of rearrangement during electrophilic addition to an alkene are:

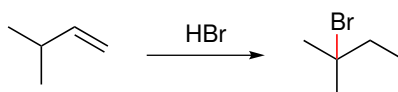
- i) Wagner–Meerwein rearrangement involving a 1,2-Alkyl shift



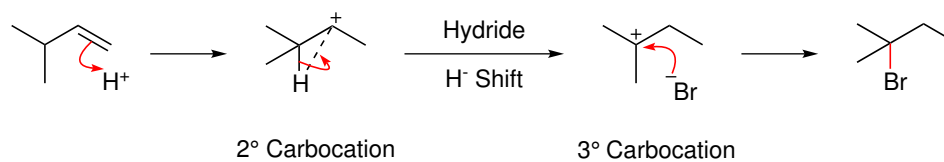
Mechanism



ii) Hydride Shift

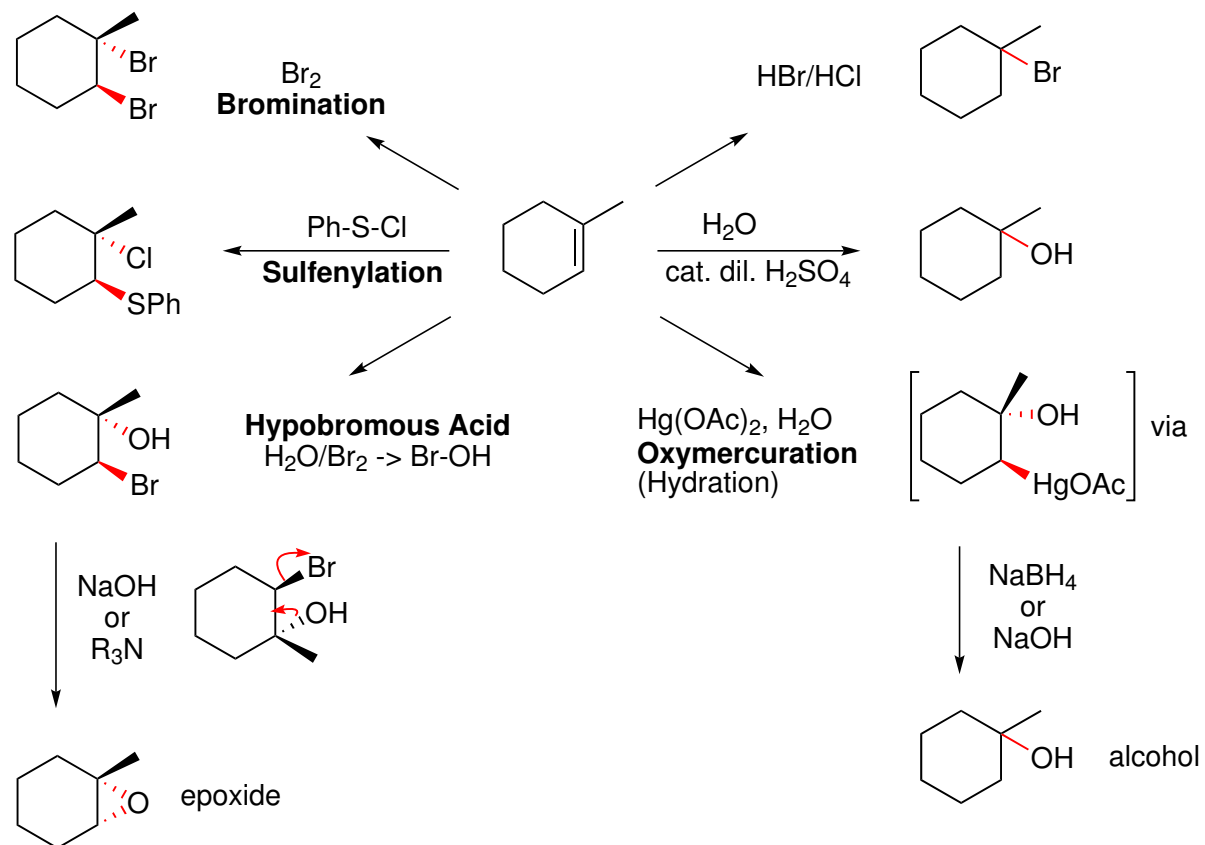


Mechanism



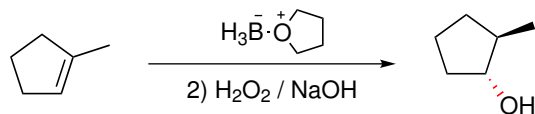
The 1,2 alkyl shift would give the same 2° carbocation and therefore would not be lower in energy.

2.2.2 Summary of all Electrophilic Additions to Alkenes



2.2.3 Other Alkene Reactions

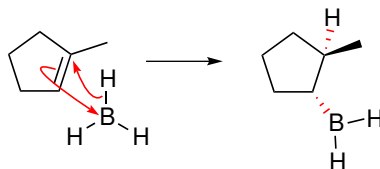
a) Hydroboration (followed by oxidation) - useful for anti-markovnikov hydration.



Mechanism

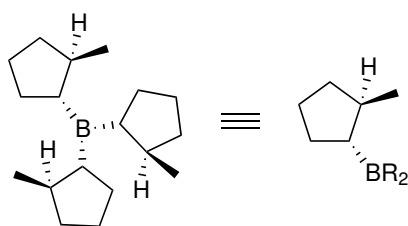


Is electron deficient but commercially available as a complex with the ether THF.

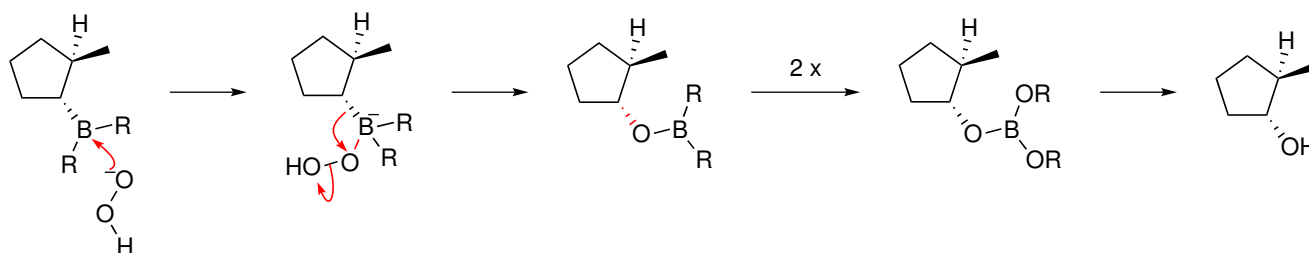


This takes place in a syn addition in a concerted way (both bonds are made in the same step). The bond to B is made slightly faster since it is the electrophilic center and the electron deficient atom. This results in the observed regiochemistry.

Each of the remaining B-H bonds also adds across an alkene to give

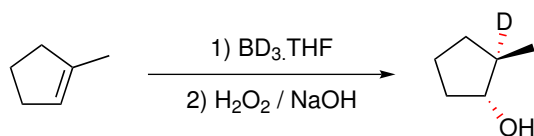


The carbon–boron bond is then replaced by a hydroxyl group with retention of configuration.

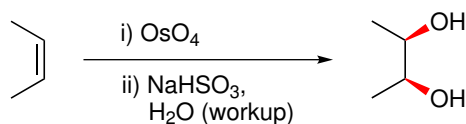


The final step occurs via borate ester hydrolysis

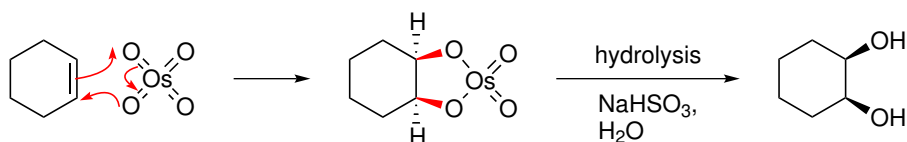
The proof of the hydroboration mechanism can be shown using deuterium labelling



b) Vicinal cis dihydroxylation



Mechanism via a concerted cycloaddition reaction.



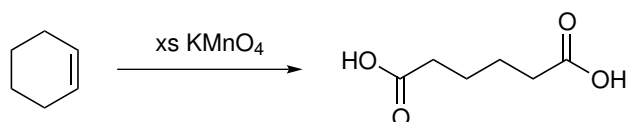
Osmate ester formed

Both the oxygen atoms are delivered from the same side (i.e. syn addition).

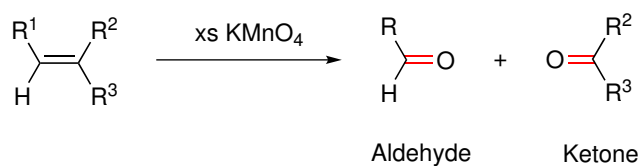
Similarly for K^+MnO_4^- under basic conditions using the ion



With excess KMnO_4 over oxidation can occur.

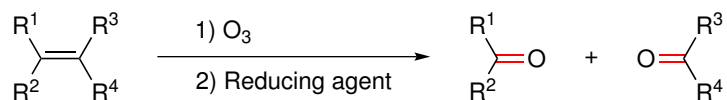


and in general for acyclic alkenes



c) Ozonolysis of alkenes

This is a milder method for oxidative cleavage of $\text{C}=\text{C}$ than KMnO_4



Common reducing agents are:

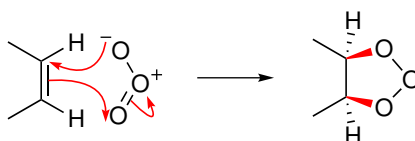
- Me_2S - Dimethyl sulfoxide
- Ph_3P - Triphenylphosphine
- $\text{Zn}/\text{H}_3\text{CCO}_2\text{H}$ - Zinc/acetic acid

Mechanism:

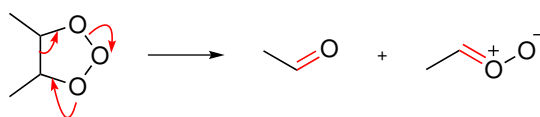
a) Formation of ozone electrophile



b) Concerted cycloaddition

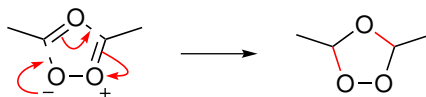


c) Fragmentation

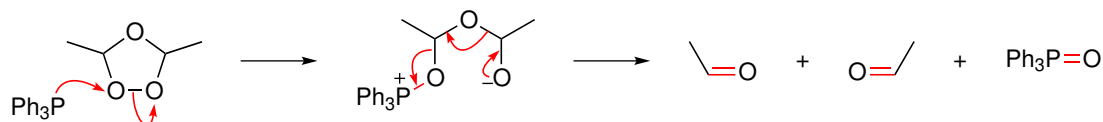


Carbonyl oxide intermediate

d) Recombination via a second cycloaddition

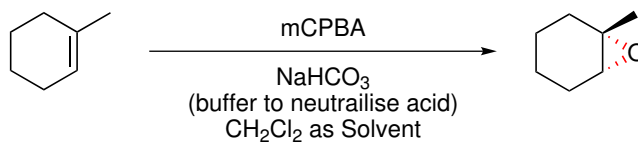


e) Reductive workup (e.g. Ph_3P)

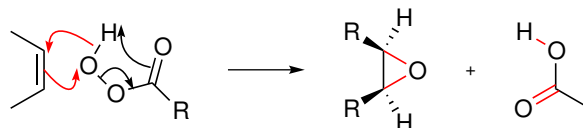


d) Preparation of epoxides using a peracid

This reaction preserves stereochemistry and preserves alkene geometry, it is stereospecific. The oxygen is delivered from the least hindered side - steric approach control.

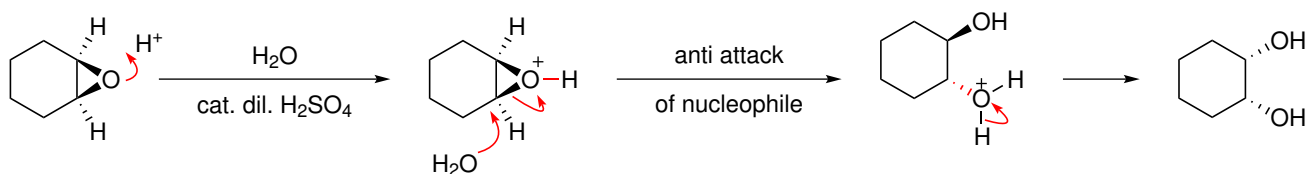


Mechanism

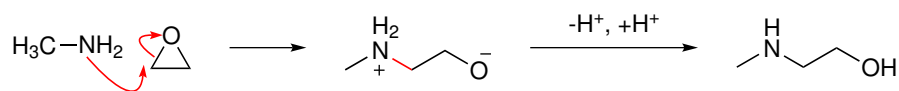


Epoxides are useful synthetic intermediates as they undergo ring opening reactions with nucleophiles and can easily be stored unlike bromium cations.

Example 1. Ring opening under acidic conditions with H_2O as a nucleophile



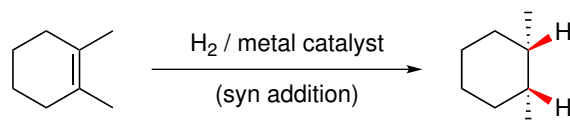
Example 2. Amines used as nucleophiles



Many other nucleophiles can be used including:

- $\text{RO}-\text{Na}^+$
- $\text{RS}-\text{Na}^+$
- R^- from RMgI

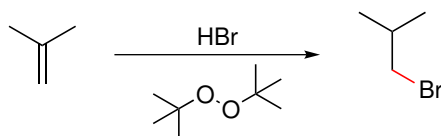
e) Catalytic hydrogenation - Synthetic route to alkanes



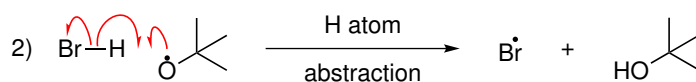
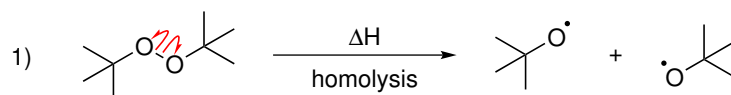
Typical metal catalysts are Pd, Pt, Ni and both hydrogen atoms are always delivered to the same side of the alkene.

f) Addition of hydrogen bromide in the presence of peroxides

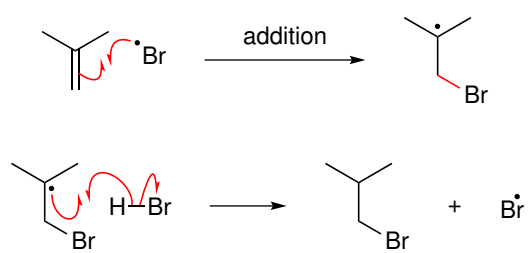
This is a free radical chain reaction that gives the anti-markovnikov product.



Initiation:



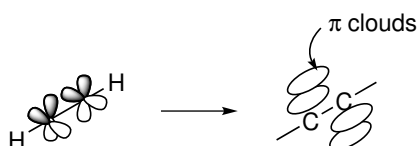
Propagation



Tertiary radical is favoured

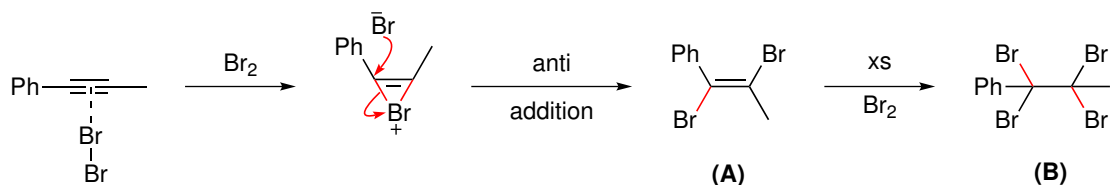
3 Alkynes

Alkynes have a single carbon-carbon triple bond and have the general formula C_nH_{2n-2} . Ethyne has a linear arrangement of the four atoms. The hybrid atomic orbitals in each carbon are constructed using the 2s orbital and only one of the 2p orbitals to give two sp hybrid atomic orbitals leaving the 2p_y and 2p_z orbitals. The two hybrid sp orbitals are constructed at 180° to each other. Each remaining p orbital contains a single electron, sideways overlap of each of these on the neighbouring carbon atoms forms two π bonds.



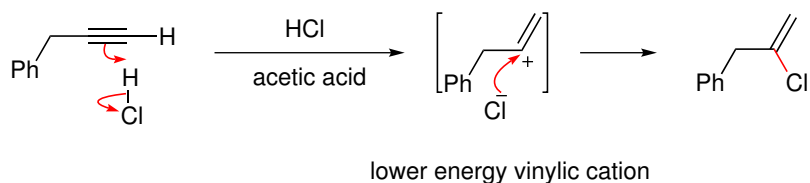
3.1 Reactions of Alkynes

a) Bromination



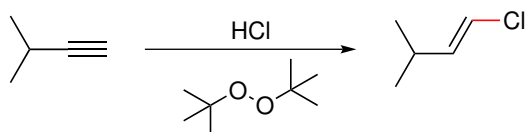
The reaction can be controlled to stop to give **(A)**. Xs reagent is needed to give **(B)**. The first anti addition is highly stereoselective to give the E (trans) isomer but it is not stereospecific.

b) Addition of Hydrogen Chloride.



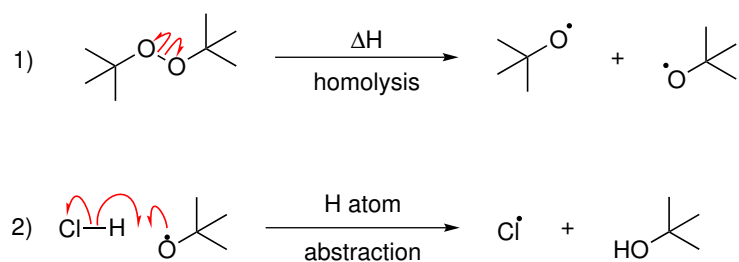
The reaction can be controlled to stop after this stage as further addition of HCl is slower. The addition is normally anti, resulting in the E (trans) isomer.

c) Addition of HCl in the presence of peroxides

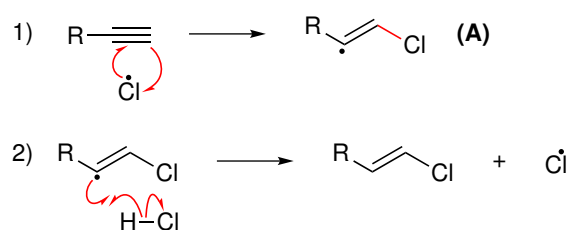


This reaction occurs by a free radical chain reaction process.

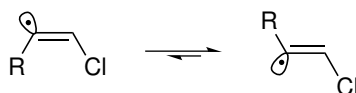
Initiation:



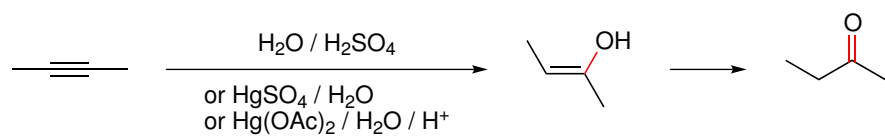
Propagation:



This reaction gives the anti-markovnikov addition as syn addition occurs to give the E isomer since the reaction occurs via the less hindered, trans form of vinylic radical. (A).

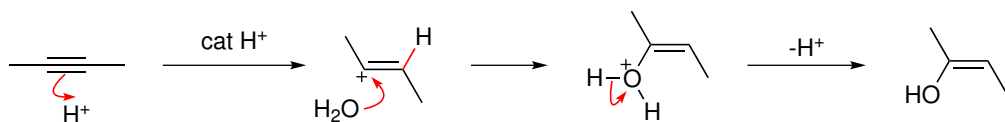


d) Hydration of alkynes by electrophilic addition of water - useful synthesis of ketones.

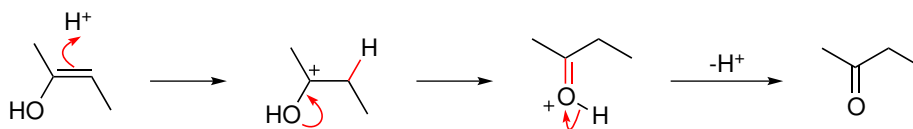


Mechanism:

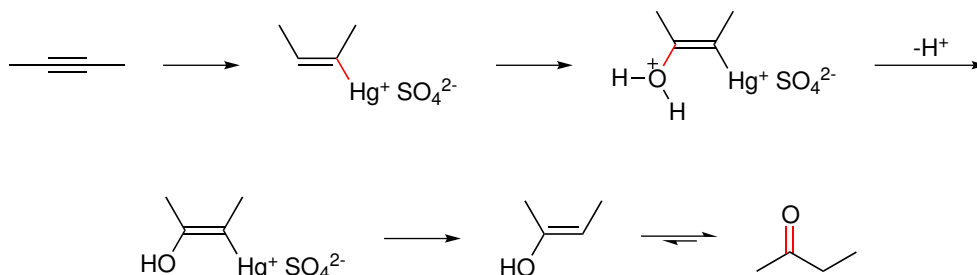
Formation of Enol:



Tautomerisation of the enol to the keto form

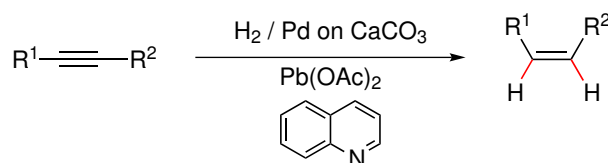


An alternate mechanism can be drawn using $\text{HgSO}_4/\text{H}_2\text{O}$:



Reduction of alkynes to alkenes takes place via 2 important reactions.

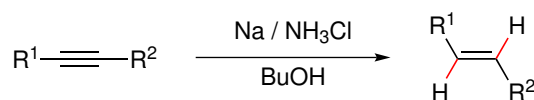
e) Catalytic hydrogenation using a Lindlar Catalyst - Forms the Z (cis) alkene



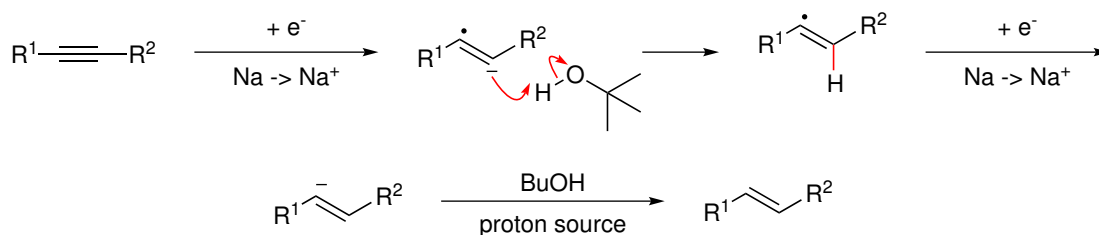
The Lindlar catalyst is a poisoned palladium catalyst, it allows syn addition. $\text{C}=\text{C}$ is not further reduced. Another variant of the catalyst is: $\text{Pd}/\text{BaSO}_4/\text{quinoline}$. An industrial use of the catalyst is in making "cis" jasmine which is used in perfumery.

f) Reduction of the $\text{C} \equiv \text{C}$ using dissolving metal reduction (Birch Reduction)

Forms the E (trans) alkene.



Mechanism: Sodium in liquid ammonia is a source of solvated electrons.

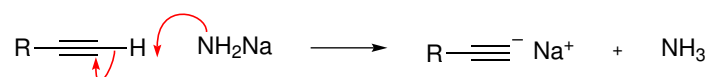


g) The deprotonation of terminal alkynes - Acetylide anions as carbon nucleophiles.

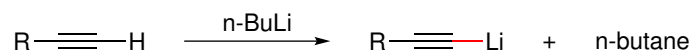
The acidity of a hydrogen atom attached to carbon varies with the degree of s character of the C atom. sp^3 (s character 25 %) < sp^2 (s character 33.3 %) < sp (s character 50 %) and consequently terminal alkynes can be deprotonated by a strong base such as:

- $Na^+NH_2^-$ - sodium amide
- $nBuLi$ - n-butyl lithium
- $R-MgX$ - grignard reagent

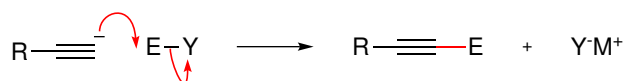
Therefore:



Or for synthesis:

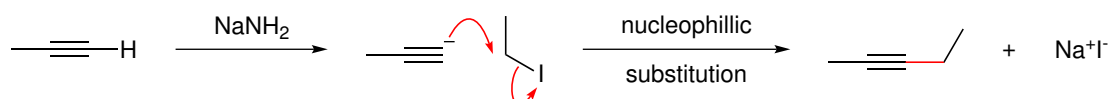


Acetylide anions are useful for making C–C bonds with electrophilic reagents.

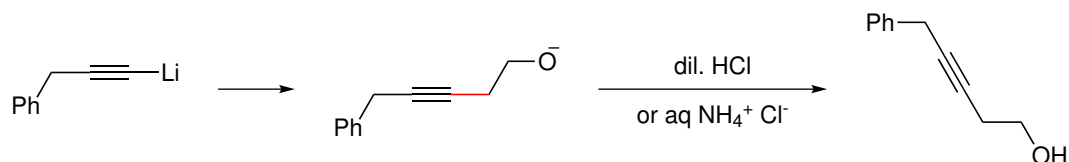


Examples of reagents:

i) Alkyl Halides

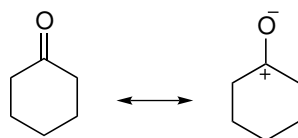


ii) Epoxide ring opening

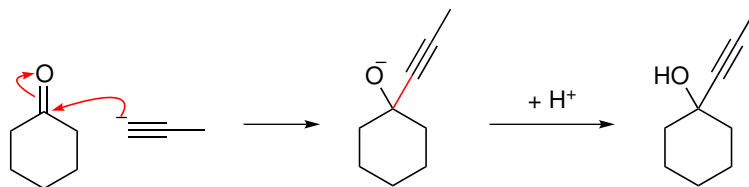


The deprotonated alkyne can then perform nucleophilic attack on the carbonyl groups of aldehydes and ketones.

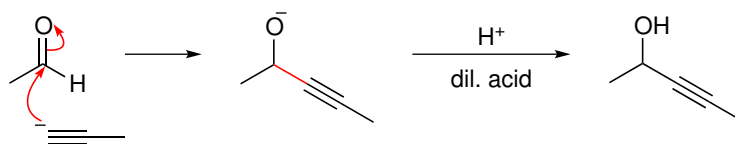
On ketones:



Therefore:



On aldehydes:



$\text{Me}_3\text{Si}-\text{C}\equiv\text{H}$ - Trimethylsilylacetylene

This is a useful compound as it allows addition on each C atom of the alkyne unit in turn.

