CHAPTER 5:

1) Developing a reaction mechanism:

- design experiments to reveal details
- propose a set or sets of steps that might account for the overall transformation - test for results
- this does not mean that the mechanism is correct, only that it is the best explanation we are able to devise

2) Alkenes undergo electrophilic addition reactions primarily:

***Some types of electrophilic additions:***

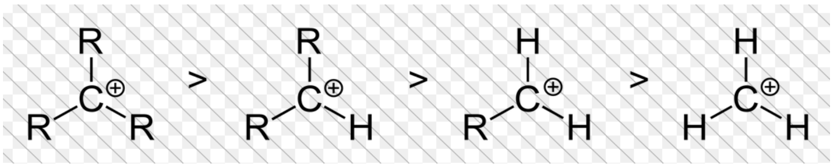
- hydrohalogenation using HCl, HBr, HI
- hydration using water in the presence of $H_2SO_4$
- halogenation using $Cl_2$, $Br_2$

## Carbocations and role in reactions:

- a species in which a carbon atom has only six electrons in its valence shell, bears a (+) charge
- are classified as $1^o$, $2^o$, or $3^o$ depending on the number of carbons bearing the positive charge.
- alkyl groups bonded to the positively charged carbon are electron releasing and thereby delocalize the positive charge of the cation.

Stability of Carbocations:

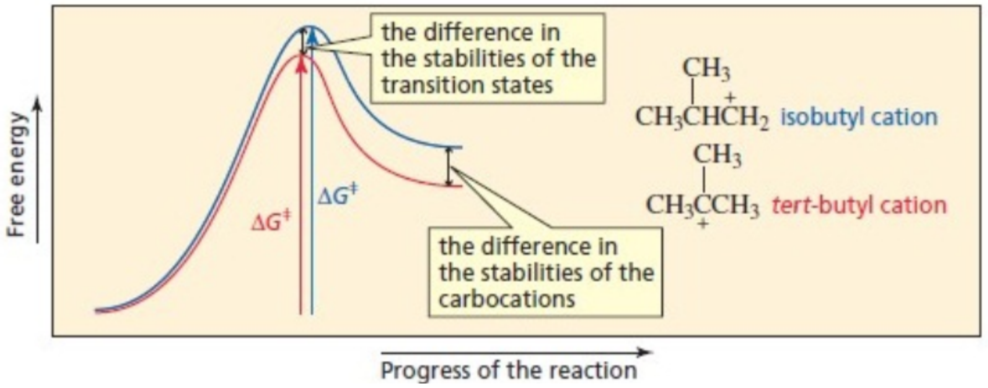
- $3^o > 2^o > 1^o >$ methyl cation



## How carbocations effect addition reactions:

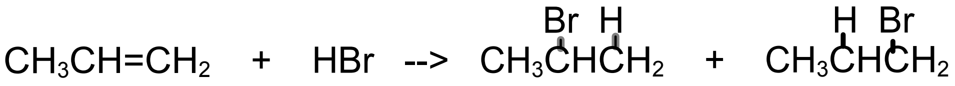
A) Addition will add to the area that will give a more stable cation

EX: React Propene + HCl (Which do you think will be preferred?)



**Addition reaction of a halide to an alkene:**

- carried out with pure reagents or in a polar solvent such as acetic acid



$$CH_3CH{=}CH_2 \;+\; HBr \;\text{-->}\; CH_3\overset{Br}{C}H\overset{H}{C}H_2 \;+\; CH_3\overset{H}{C}H\overset{Br}{C}H_2$$

propene 2-bromopropane 1-bromopropane

A) - **Addition is regioselective**

- this means one of two or more possible products is formed in preference to all others (Due to carbocation stability)

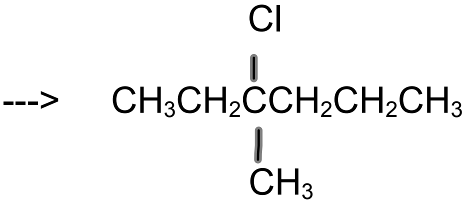
** If 50% of each isomer is produced, the C+s had the same stability

EX: 2-pentene + HBr ---> 2-bromopropane + 3-bromopropane (equally produced)

- **Markovnikov's Rule:** in the addition of HX, $H_2O$, or ROH to an alkene, H adds to the carbon of the double bond having the greater number of hydrogens, other "anion" adds to C that is more stable.

- The products are called regioisomers.
  - a.) If a reaction of this type gives ONLY ONE of the 2 possible regioisomers, it is said to be regiospecific.
  - b.) If it gives MAINLY one product, it is said to be regioselective.

Give all the possible alkenes you would start with to prepare the following alkyl halide:



$$\text{--->}\quad CH_3CH_2\overset{Cl}{\underset{CH_3}{C}}CH_2CH_2CH_3$$

## Evidence for the Mechanism of Electrophilic Additions: Carbocation Rearrangements

ex. 3-methylbut-1-ene reacting with HCl produced 2 products instead of the projected one product. The expected product is 2-chloro-3-methylbutane. However, there was an equal amount of 2-chloro-2-methylbutane.

HYDRIDE SHIFT: the shift of a hydrogen atom and its electron pair (a hydride ion, ($:H^{-1}$) between neighboring carbons

Carbocation rearrangement can also occur by the shift of an alkyl group with its electron pair.

ex. 3,3-dimethylbut-1-ene with HCl leads to (give the mechanism, name the products - give which is expected and which is unexpected)

a mixture of

3-chloro-2,2-dimethylbutane(unrearranged) and
2-chloro-2,3-dimethylbutane(rearranged)

## Addition of $H_20$ to an alkene = alchohol

A) Must add acid to alkene/$H_2O$ solution (without acid there is no electrophile to start rxn)

- Acid provides the H+ electrophile to start rxn
- Acid also acts as a catalyst
- $H_2SO_4$ is most commonly used

EX: Propene + $H_2O$ $\xrightarrow{H2SO4}$

Points to notice about rxn:

A) Which C does the H+ electrophile add to?

B) Which C does the -OH nucleophile add to?

C) What happens to the $H_3O^+$ at the end of the reaction?

## Addition reaction of an alchohol to an alkene = ether:

A) Need $H_2SO_4$ as a catalyst

B) Remember carbocation stability and Markovnikov's rule

EX: Propene + Methanol $\xrightarrow{H2SO4}$

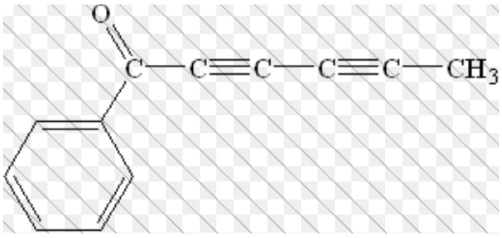
## Alkynes - naming and reactions:

A) Formula of an alkyne $C_nH_{2n-2}$

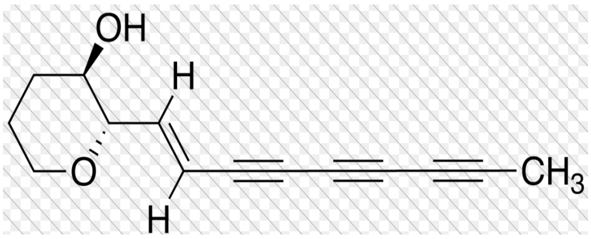
B) Contains at least 1 ≡

C) Most alkynes are man-made pharmaceuticals

D) Only a few ***natural*** alkynes exist



**Capillin -** natural antifungal



**Ichthyothereol-** convulsant used on

## Alkynes - naming, structure, and physical properties:

A) **Naming -**

- replace -ane with -yne ending
- # so the chain with the ≡ has he lowest #
- If numbering a chain with substituents gives alkyne same lowest #, # so the substituents get lower #'s too
- terminal alkynes vs internal alkynes (Ex: 1-butyne vs 2-butyne)

B) **Structure-**

- each C involved in ≡ bond has sp hybridization
- 2 Pi bonds + 1 sigma bond = a "cylinder" of e-

C) **Physical Properties-**

*- in general, alkynes have same trends as alkenes and alkanes*

Such as:

1) Insoluble in water (Because they are non-polar)
2) Soluble in other NP solvents
3) Less dense than water
4) Trend of increasing boiling points with increase in molec. wt.

**Differences to note:**

**Alkynes are more linear than alkanes

- this causes an increase in VDW forces (per alkyne)

Remember: laying pencils vs tennis balls, who has more surface area touching?

- There for, if comparing Alkyne vs alkene of same C chain length

the alkyne has a higher boiling point

Chapter 5: p120-21:

**Addition of HX to an Alkyne:**

$CH_3C{\equiv}CCH_3 \quad + \quad H\text{-}Cl \quad \text{-->}$

$CH_3C{\equiv}CCH_3 \quad + \quad \underset{\text{excess}}{\overset{\text{excess}}{H\text{--}Cl}} \quad \text{-->}$

ex. $CH_3CH_2C{\equiv}CH \quad + \quad \underset{\text{excess}}{HCl} \quad \text{-->}$

ex. $CH_3CH_2C{\equiv}CCH_3 \quad + \quad \underset{\text{excess}}{HCl} \quad \text{-->}$

## Addition of $H_2O$ to an Alkyne (hydration):

*enol* : compound with a C=C and an $OH^{-1}$ group bonded to one of the sp$^2$ group

en ol

double bond — alcohol group

$$CH_3C\equiv CCH_3 \xrightarrow{H_2O,\ H_2SO_4}$$

**enol:** is an intermediate in the reaction but immediately rearranges to a ketone by a process called ***keto/enol tautomerism***

keto and enol forms are said to be ***tautomers***

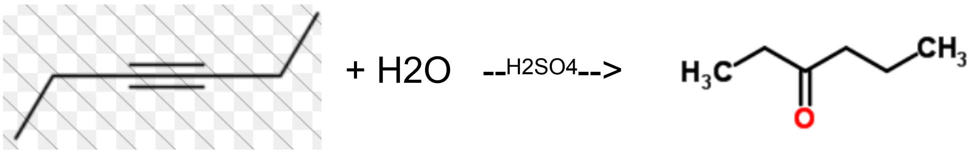
***Tautomomers- isomers in rapid equilibrium***

Keto tautomer Enol tautomer

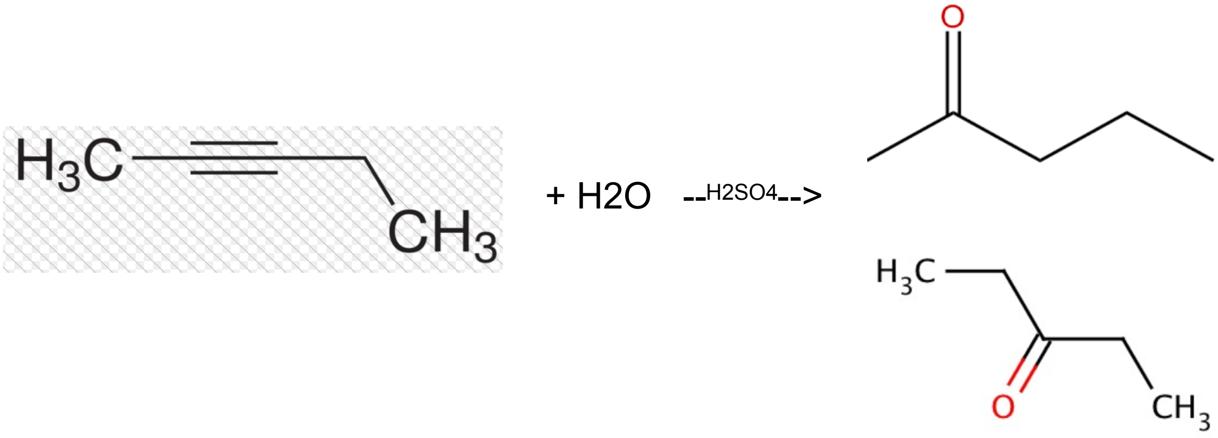
More details on alkyne + $H_2O$ addition:

**Internal alkynes + $H_2O$**

A) Addition of water to an internal alkyne RIGHT IN THE MIDDLE of carbon chain yields only one product (# R ---> L or L ---> R = same name)



B) If internal alkyne is offset - ketone formed will be 2 different products



**Terminal alkynes reacting with $H_2O$**

A) Terminal alkynes are less reactive to $H_2O$ than internal alkynes

B) To get them to react with water, $Hg^{+2}$ ion is needed also

Ex: $CH_3CH_2C \equiv CH + H_2O \xrightarrow{H_2SO_4 \text{ and } HgSO_4}$ (Show enol and ketone) enol - keto mechanism:

## Addition of hydrogen to alkenes and alkynes:

A) hydrogenation usually occurs with ***syn*** stereochemistry

↓

both hydrogens add to the
double bond from the same face

B) Must use Pt or Pd catalyst (these break the H-H bond initially)
-without this catalyst the bond of H-H is to strong ($E_a$ too high)

C) Pt and Pd are used in "a finely divided state, adsorbed on charcoal"
(Pt/C or Pd/C)

D) Some vocab:
<u>Hydrogenation:</u> addition of H
<u>Catalytic hydrogenation:</u> need/use a catalyst to add H
<u>Reduction Reaction:</u> reaction that INCREASES # of C-H bonds

E) For alkynes: final product is still an alkane (process doesn't stop until
all = and ≡ bonds are hydrogenated)

ex: 1,2 - dimethylcyclohexene + $H_2$

Hydrogenation:

reduction - a reaction that results in the gain of electron density by carbon either by bond formation between carbon and a less electronegative atom or by bond-breaking between carbon and a more electronegative atom.

- increases the electron density on carbon

forming this: C-H
breaking one of these: C-O C-N C-X

oxidation - reaction that results in a loss of electron density by carbon, caused either by bond formation between carbon and a more electronegative atom - usually oxygen, nitrogen, or a halogen - or by bond-breaking between carbon and a less electronegative atom - usually hydrogen

- decreases electron density on carbon

forming this: C-O C-N C-X
breaking one of these: C-H

How to stop a hydrogenation rxn at an alkene?

A) If left to go alkynes will always hydrogenate to alkanes

B) To stop at an alkene:

  1) Use a "poisoned metal catalyst" - it is partially deactivated

  2) Common poisoned catalyst = Lindlar Catalyst

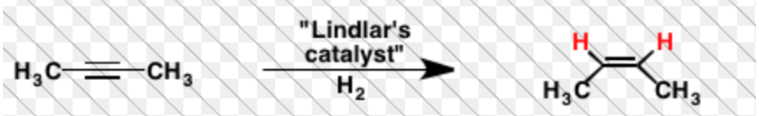
Ex: 2-pentene + $H_2$ ---Lindlar catalyst--->

Special Note:

  A) The alkyne sits on surface of catalyst as rxn progresses

  B) This will always cause a cis-alkene because H can only bond to the one side (top or bottom) of the bond

**Partial hydrogenation via the Lindlar catalyst gives the *cis* alkene**



*Lindlar's catalyst:* a mixture of Pd, $CaCO_3$, Pb salts, and quinoline

*Reduces alkynes but not alkenes*

## Chapter 5: p125-28

### 5.13 : Hybridization level of C causes acidity

- electronegativity: sp C > $sp^2$ C > $sp^3$ C

- the most acidic compound is the one with the hydrogen attached to the most electronegative atom (when the atoms are the same size)

- ethyne is a stronger acid than ethene which is a stronger acid than ethane

| | | | | | | |
|---|---|---|---|---|---|---|
| Most acidic | $H\text{-}C\equiv C\text{-}H$ | > | $H_2C=CH_2$ | > | $H_3CCH_3$ | Least acidic |
| | pKa=25 | | pKa=44 | | pKa>60 | |

- For a reaction to go in the forward direction, the base that removes the proton must be stronger than the base (CB) that is generated from H+ removal

- methane and ethane are very weak acids and do not react with any of the common bases

- acetylene is acidic enough that it will react with any base whose conjugate acid has a pKa > 25

  - $^-NH_2$, the amide ion, is the conjugate base of $NH_3$ (pKa = 35) and is often used to deprotonate terminal alkynes.

$$R\text{-}C\equiv C\text{-}H \;+\; :\overset{-}{N}H_2 \;\longrightarrow\; R\text{-}C\equiv \overset{-}{C}: \;+\; :NH_3$$

acid( pKa = 25) base base acid (pKa =36)

Thus: $NH_3$ is the weaker acid, so $NH_2^-$ is a stronger base than *carbanion*

***Carbanion*** - "acetylide ion" - ion formed when H is removed from a terminal alkyne

The ***Amide ion*** can remove the H+ from the alkyne BUT IT CANNOT remove a H+ from alkane (H - $sp^3$ C ) or alkene (H - $sp^2$ C)

## 5.14: Synthesis using acetylide ions

REACTION: acetylide ion + alkyl halide ( 1°)

↓

iodides
bromides

ex. $CH_3CH_2C\equiv\overset{\boxed{-}}{C}:$ + $CH_3CH_2\overset{\delta+}{C}H_2 - \overset{\delta-}{Br}$ -->

Alkylation: limited to primary alkyl bromides and iodides

**Note: This type of synthesis:

- A) Links a chain of terminal alkyne with a chain of a 1° alkyl halide
- B) The terminal alkyne must 1st be reacted with $NaNH_2$ to make it an acetylide ion
- C) Mechanism:
  - 1) acetylide ion acts as nucloeophile
  - 2) Donates e- to the $\delta^+$ C of the alkyl halide

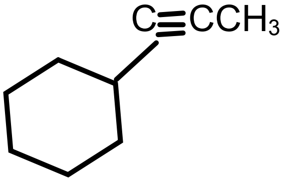
Practice:

Show the terminal alkyne and alkyl halide from which the following products can be obtained - if two routes look feasible, list both.

1) $CH_3CH_2CH_2C\equiv CCH_3$

2) $(CH_3)_2CHC\equiv CCH_2CH_3$

3)

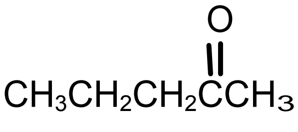


**Multistep synthesis:** Want route with fewest steps, work backward from

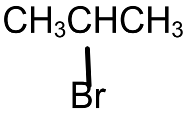
Starting with acetylene, show how you would prepare each of the following:

Ex: Starting with 1-butyne, make 3-hexanone

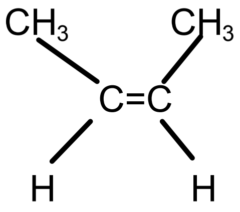
a) $CH_3CH_2CH_2C\equiv CH$

b) 
$CH_3CH_2CH_2\overset{\overset{O}{\|}}{C}CH_3$

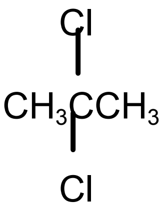
c) $CH_3CH{=}CH_2$

d) 
$\mathrm{CH_3\underset{\underset{Br}{|}}{C}HCH_3}$

e)



f)



$CH_3\overset{\displaystyle Cl}{\underset{\displaystyle Cl}{C}}CH_3$

**Some extra reactions:**

Addition of Halogens:

1) Alkynes:

2) Alkenes:

ethene + $Br_2$ -->

Cyclopentene + $Br_2$ -->

## Electrophilic Additions to Conjugated Dienes:

ex. Add HCl to buta-1,3-diene

PROB:

Give the structures of the likely products from the reaction of 1 equivalent of HCl with 2-methylcyclohexa-1,3-diene

Write an Equation for the reaction of $CH_2=CHCH_2CH_3$ with Each of the Following Reagents:

a) HCl

b) bromine

c) Hydrogen (Pt catalyst)

d) $H_2O$, $H^+$

e) ozone, followed by $H^+$

f) $KMnO_4$, $OH^{-1}$

g) $BH_3$ followed by $H_2O_2$, $OH^{-1}$

h) oxygen (combustion)

i) $KMnO_4$, $H^+$

$CH_2=CHCH_2CH_3$

$CH_2=CHCH_2CH_3$

$CH_2=CHCH_2CH_3$

$CH_2=CHCH_2CH_3$

$CH_2=CHCH_2CH_3$

$CH_2=CHCH_2CH_3$

$CH_2=CHCH_2CH_3$

$CH_2=CHCH_2CH_3$

$CH_2=CHCH_2CH_3$