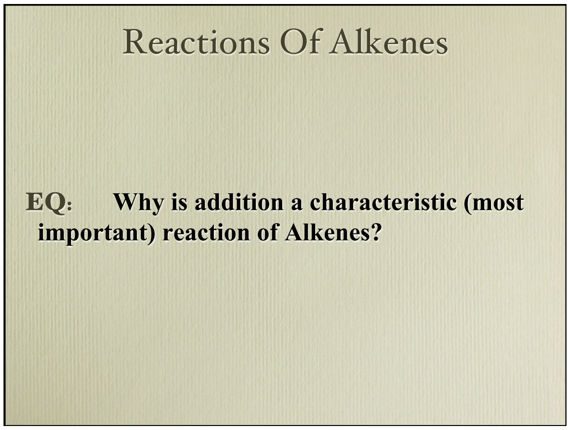
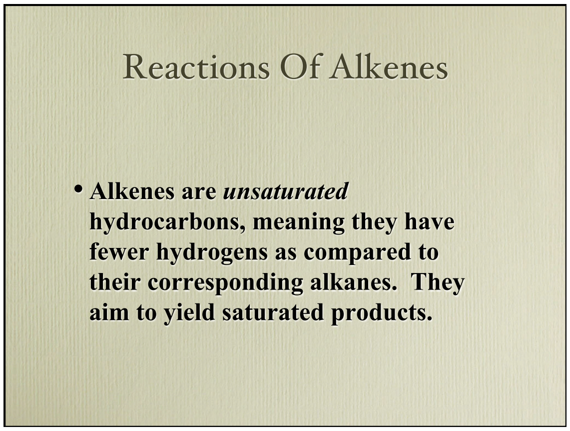


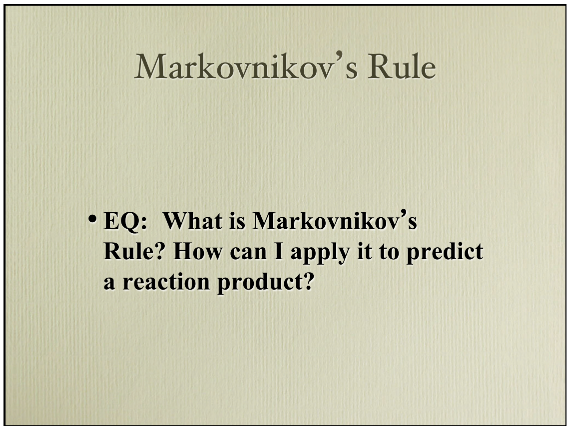
Reactions Of Alkenes

EQ: **Why is addition a characteristic (most important) reaction of Alkenes?**



Reactions Of Alkenes

- **Alkenes are *unsaturated* hydrocarbons, meaning they have fewer hydrogens as compared to their corresponding alkanes. They aim to yield saturated products.**



Markovnikov’s Rule

- **EQ: What is Markovnikov’s Rule? How can I apply it to predict a reaction product?**

EQ: What is Markovnikov's Rule? How can I apply it to predict a reaction product?

Reaction between Ethylene and HCl

Ethylene + HCl →

carbocation intermediate → chloraethane

EQ: What is Markovnikov's Rule? How can I apply it to predict a reaction product?

2. Addition of HI to 1-Pentene

1-Pentene + HI →

carbocation intermediate →

____

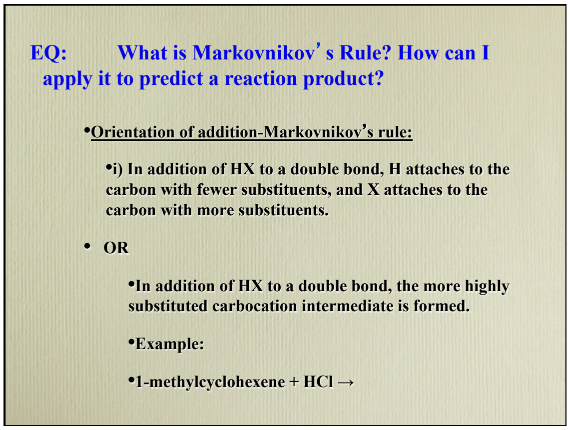
There are 2 possible products. Which one will be formed?

EQ: What is Markovnikov's Rule? How can I apply it to predict a reaction product?

- 2. Addition of HI to 1-Pentene

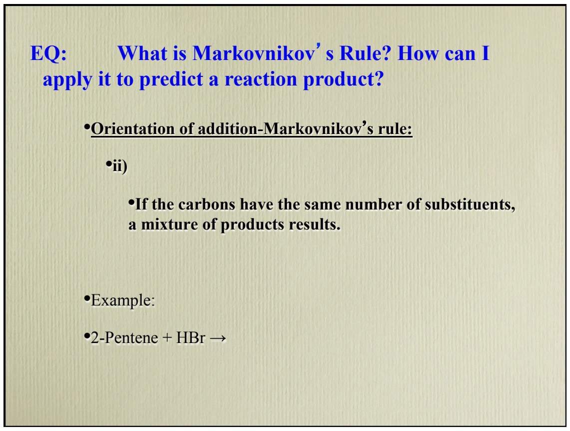
1-Pentene + HI → carbocation intermediate → 2-Iodopentane

- Regiospecific Reaction: Reactions are regiospecific when only one of the two directions of addition occur.



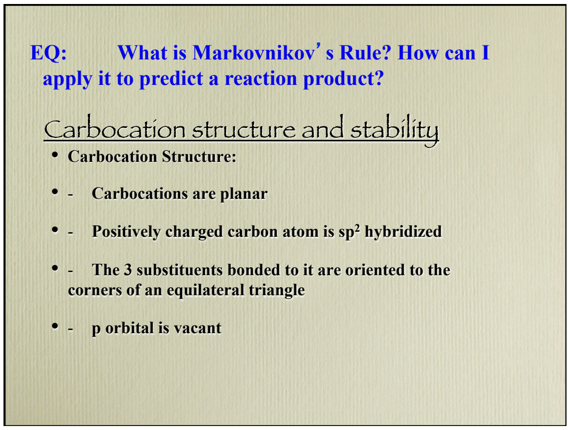
EQ: What is Markovnikov's Rule? How can I apply it to predict a reaction product?

- **Orientation of addition-Markovnikov's rule:**
  - **i) In addition of HX to a double bond, H attaches to the carbon with fewer substituents, and X attaches to the carbon with more substituents.**
- **OR**
  - **In addition of HX to a double bond, the more highly substituted carbocation intermediate is formed.**
  - **Example:**
  - **1-methylcyclohexene + HCl →**



EQ: What is Markovnikov's Rule? How can I apply it to predict a reaction product?

- **Orientation of addition-Markovnikov's rule:**
  - **ii)**
    - **If the carbons have the same number of substituents, a mixture of products results.**
- Example:
- 2-Pentene + HBr →



EQ: What is Markovnikov's Rule? How can I apply it to predict a reaction product?

Carbocation structure and stability

- **Carbocation Structure:**
- **- Carbocations are planar**
- **- Positively charged carbon atom is sp^2 hybridized**
- **- The 3 substituents bonded to it are oriented to the corners of an equilateral triangle**
- **- p orbital is vacant**

EQ: What is Markovnikov's Rule? How can I apply it to predict a reaction product?

- Stability: Stability increases with increasing alkyl substituents.

```
•     H          H              R              R
  • /          /              /              /
• H-C+       R-C+           R-C+           R-C+
•     \          \              \              \
•     H          H              H              R
• Methyl       (1°)           (2°)           (3°)

• Less Stable    ➠         More stable
```

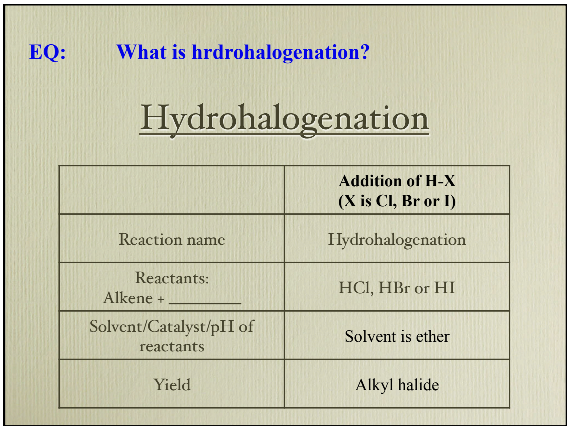
EQ: What is Markovnikov's Rule? How can I apply it to predict a reaction product?

Carbocation structure and stability

- This is because alkyl groups tend to donate electrons to the positively charged C atom.

EQ: What is Markovnikov's Rule? How can I apply it to predict a reaction product?

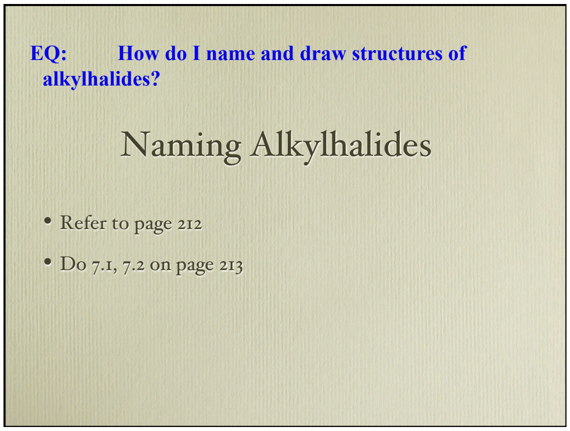
- **Try These …..**
- 4.1, 4.2, 4.3 (on pages 109- 110)



EQ: What is hrdrohalogenation?

Hydrohalogenation

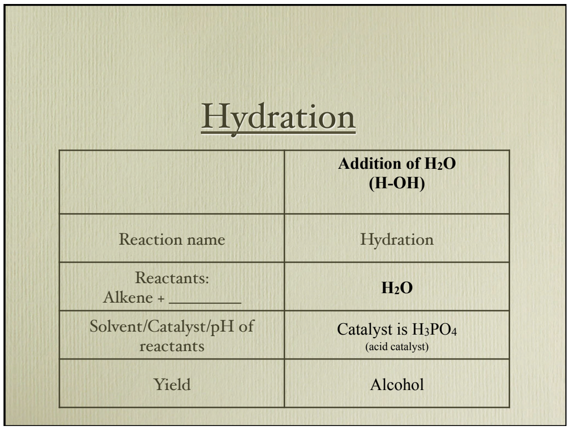
	Addition of H-X (X is Cl, Br or I)
Reaction name	Hydrohalogenation
Reactants: Alkene + ________	HCl, HBr or HI
Solvent/Catalyst/pH of reactants	Solvent is ether
Yield	Alkyl halide



EQ: How do I name and draw structures of alkylhalides?

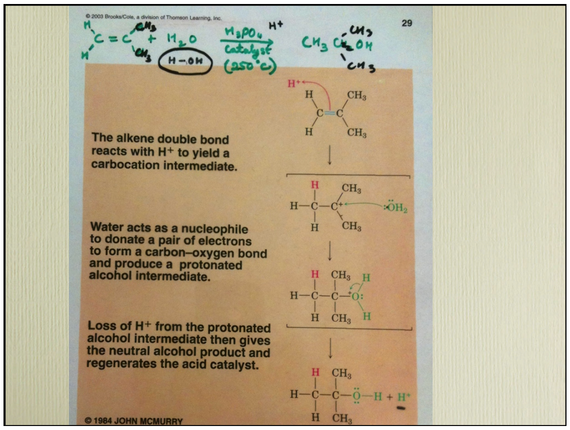
Naming Alkylhalides

- Refer to page 212
- Do 7.1, 7.2 on page 213



Hydration

	Addition of H_2O (H-OH)
Reaction name	Hydration
Reactants: Alkene + ________	H_2O
Solvent/Catalyst/pH of reactants	Catalyst is H_3PO_4 (acid catalyst)
Yield	Alcohol



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The alkene double bond reacts with H+ to yield a carbocation intermediate.

Water acts as a nucleophile to donate a pair of electrons to form a carbon–oxygen bond and produce a protonated alcohol intermediate.

Loss of H+ from the protonated alcohol intermediate then gives the neutral alcohol product and regenerates the acid catalyst.

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Hydration

- Examples:
- Ethylene + water
- methylenecyclopentane (C_5H_8=CH2) + water

EQ: How do I name and draw structures of alcohols?

Naming Alcohols

- Refer to page 244, 245
- Do 8.1 a, 8.3 a-d on page 246

Try these........

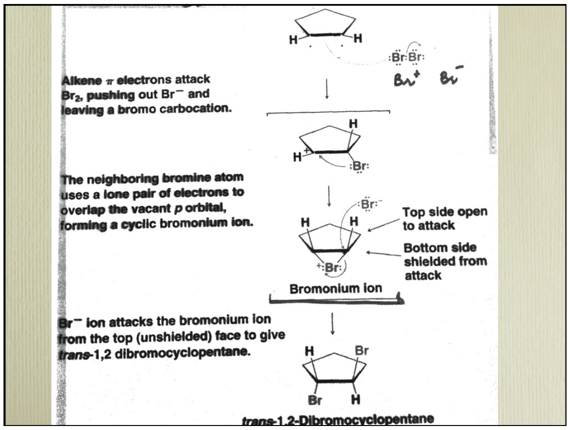
- Problems 4.4, 4.5 on page 112

Halogenation

	Addition of X_2 (X-X)
Reaction name	Halogenation
Reactants: Alkene + ________	**Cl_2, Br_2, I_2**
Solvent/Catalyst/pH of reactants	
Yield	dihaloalkane

Halogenation

- Examples:
- Ethylene + Cl_2
- cyclopentene + Br_2 (yields a trans product)
- This reaction occurs with anti-stereochemistry - the 2 Bromines come from opposite sides.



Alkene π electrons attack Br_2, pushing out Br^- and leaving a bromo carbocation.

The neighboring bromine atom uses a lone pair of electrons to overlap the vacant *p* orbital, forming a cyclic bromonium ion.

Br^- ion attacks the bromonium ion from the top (unshielded) face to give *trans*-1,2 dibromocyclopentane.

trans-1,2-Dibromocyclopentane

Try these...

- Problems 4.6, 4.7 on page 114

Hydrogenation (Reduction)

	Addition of H_2 (H-H)
Reaction name	Hydrogenation
Reactants: Alkene + ________	**H_2**
Solvent/Catalyst/pH of reactants	Catalysts are Pd and PtO_2
Yield	alkane

Hydrogenation (Reduction)

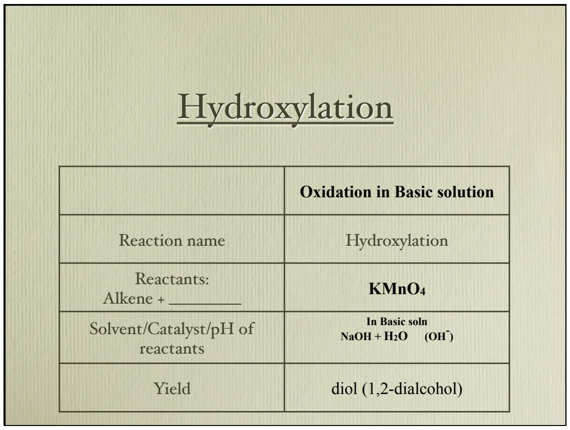
- Examples
- ethylene + H_2
- 1,2-dimethylcyclohexene + H_2
- This reaction occurs with syn stereochemistry - the 2 hydrogens add to the double bond from the same side.

try this ...

- problem 4.8 on page 116

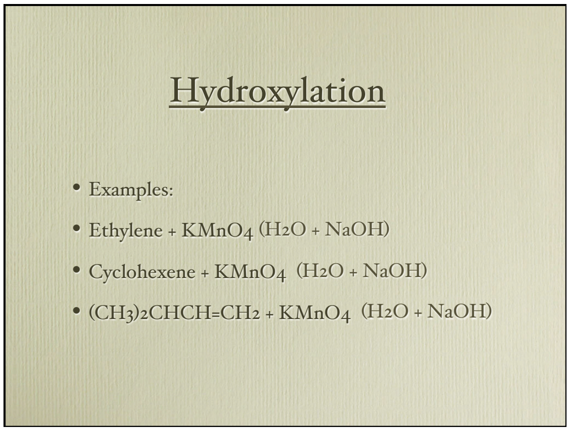
Oxidation Of Alkenes

- two types - depending on the pH of the solution
- In basic medium - Hydroxylation
- In acidic medium - Cleavage



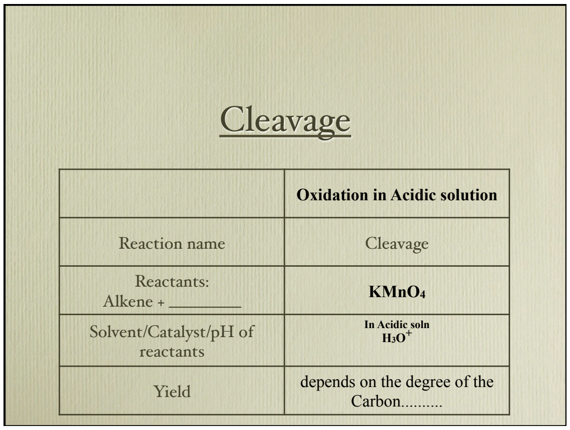
Hydroxylation

	Oxidation in Basic solution
Reaction name	Hydroxylation
Reactants: Alkene + _________	**$KMnO_4$**
Solvent/Catalyst/pH of reactants	**In Basic soln** **$NaOH + H_2O$ (OH^-)**
Yield	diol (1,2-dialcohol)



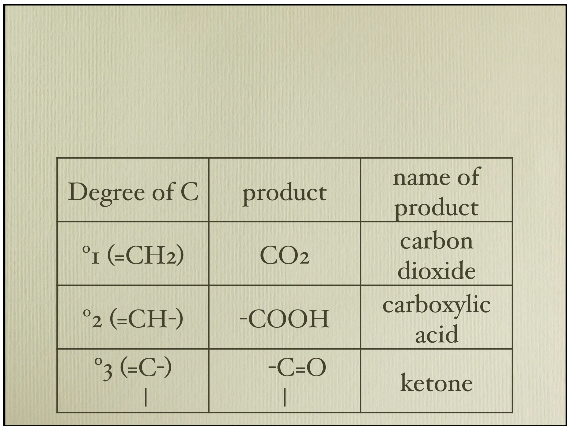
Hydroxylation

- Examples:
- Ethylene + $KMnO_4$ (H_2O + NaOH)
- Cyclohexene + $KMnO_4$ (H_2O + NaOH)
- $(CH_3)_2CHCH{=}CH_2$ + $KMnO_4$ (H_2O + NaOH)

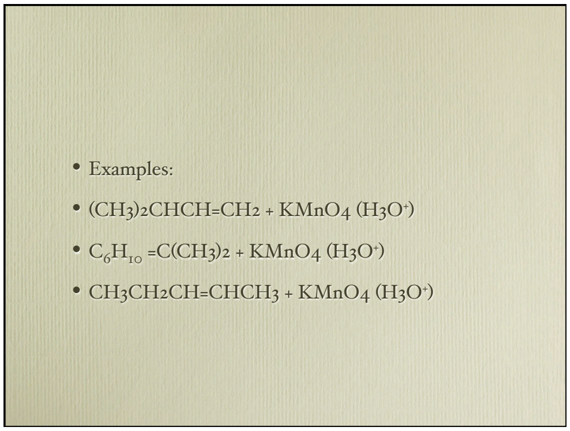


Cleavage

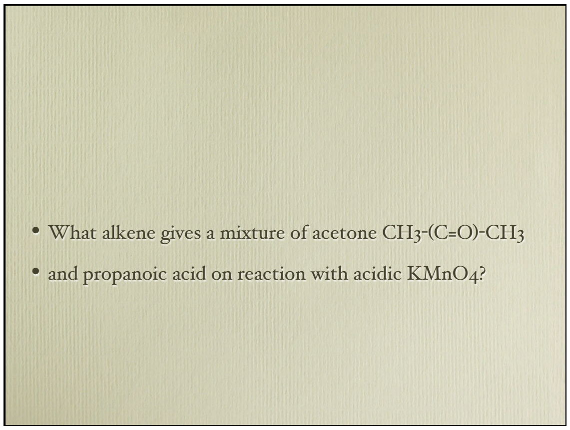
	Oxidation in Acidic solution
Reaction name	Cleavage
Reactants: Alkene + _________	**$KMnO_4$**
Solvent/Catalyst/pH of reactants	**In Acidic soln** **H_3O^+**
Yield	depends on the degree of the Carbon..........



Degree of C	product	name of product
°1 (=CH_2)	CO_2	carbon dioxide
°2 (=CH-)	-COOH	carboxylic acid
°3 (=C-) |	-C=O |	ketone



- Examples:
- $(CH_3)_2CHCH{=}CH_2 + KMnO_4\ (H_3O^+)$
- $C_6H_{10}{=}C(CH_3)_2 + KMnO_4\ (H_3O^+)$
- $CH_3CH_2CH{=}CHCH_3 + KMnO_4\ (H_3O^+)$



- What alkene gives a mixture of acetone $CH_3\text{-}(C{=}O)\text{-}CH_3$
- and propanoic acid on reaction with acidic $KMnO_4$?

- Try 4.9, 4.10 on page 118

Naming Aldehydes and Ketones

- Page 279-281
- 9.2 (a, c, d, e, f)
- 9.3 (a, b, c, e, f)

Naming Carboxylic Acids

- Page 306
- 10.1 (a-e)
- 10.2 (a, b, d)

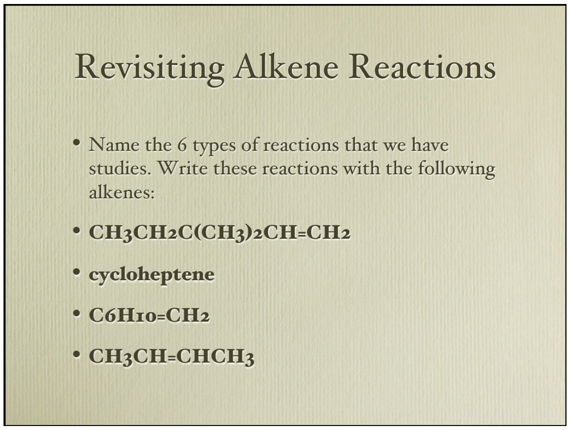
- Show the reaction of $CH_2{=}C(CH_3)CH_2CH_3$ with H_2, HCl, Cl_2, H_2O, $KMnO_4$(basic), $KMnO_4$(acidic)

Quiz

- Draw the reaction mechanism for a Hydration reaction.

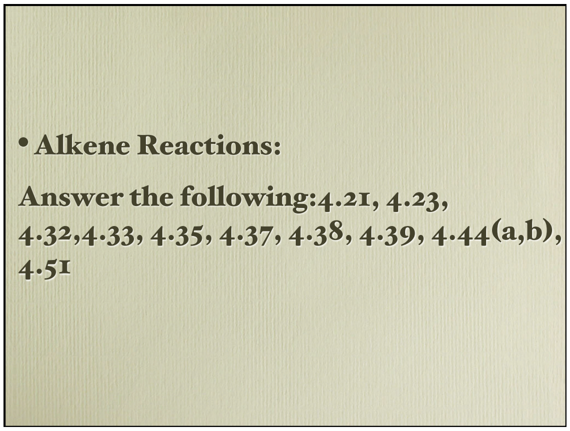
Naming Alcohols and Ethers

- Presentation
- EQ: How do I name alcohols and Ethers?
- Practice problems: page 246; #8.1 (a,c,d), 8.3(a-d), 8.4(a,b)



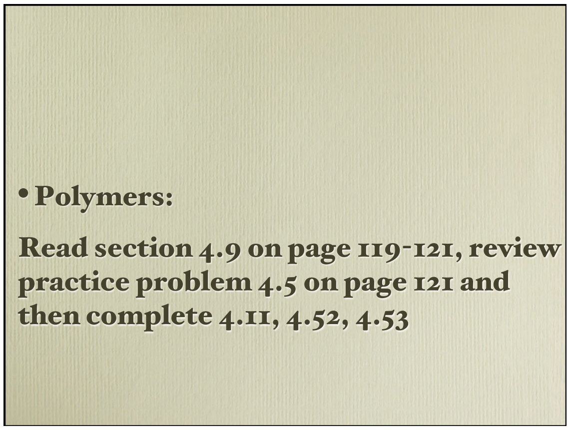
Revisiting Alkene Reactions

- Name the 6 types of reactions that we have studies. Write these reactions with the following alkenes:
- **$CH_3CH_2C(CH_3)_2CH=CH_2$**
- **cycloheptene**
- **$C_6H_{10}=CH_2$**
- **$CH_3CH=CHCH_3$**



- **Alkene Reactions:**

Answer the following:4.21, 4.23, 4.32,4.33, 4.35, 4.37, 4.38, 4.39, 4.44(a,b), 4.51



- **Polymers:**

Read section 4.9 on page 119-121, review practice problem 4.5 on page 121 and then complete 4.11, 4.52, 4.53

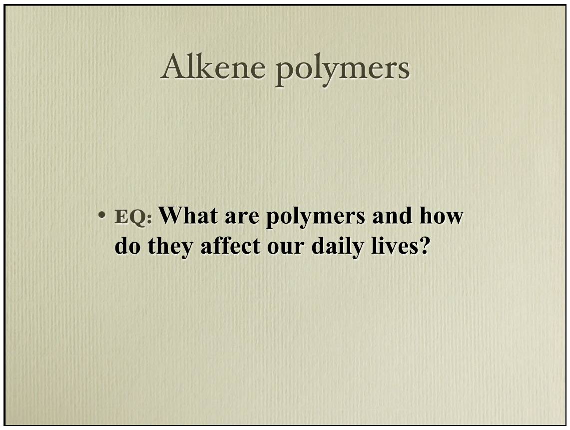
Biological addition reactions of alkenes

- EQ: What are enzymes?

Biological addition reactions of alkenes

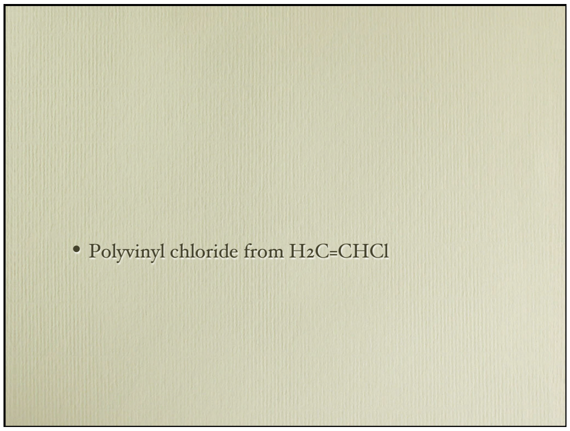
Biological organic chemistry takes place in an *aqueous medium* inside a cell rather than an *organic solvent* and it involves complex *catalysts* called *enzymes*.

I need a brave volunteer…

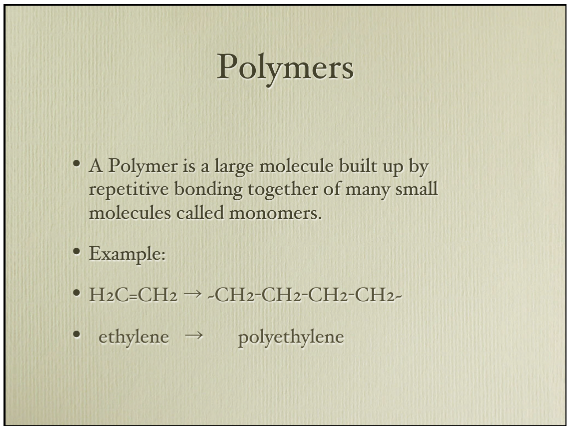


Alkene polymers

- **EQ: What are polymers and how do they affect our daily lives?**

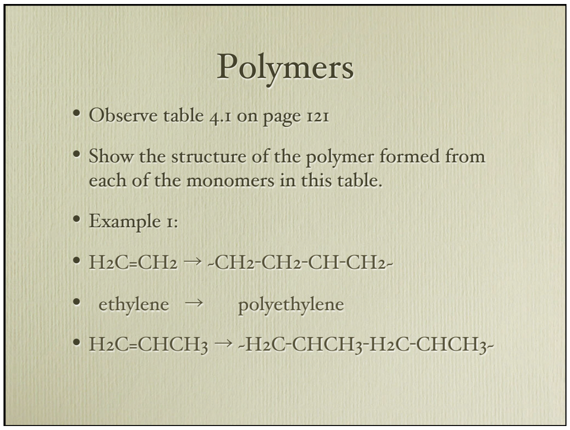


- Polyvinyl chloride from $H_2C{=}CHCl$



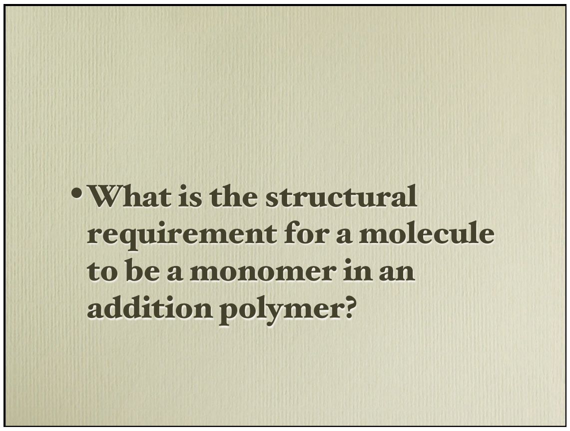
Polymers

- A Polymer is a large molecule built up by repetitive bonding together of many small molecules called monomers.
- Example:
- $H_2C{=}CH_2 \rightarrow -CH_2-CH_2-CH_2-CH_2-$
- ethylene → polyethylene

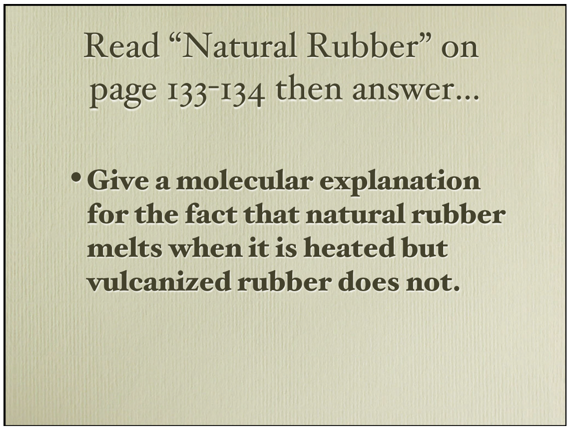


Polymers

- Observe table 4.1 on page 121
- Show the structure of the polymer formed from each of the monomers in this table.
- Example 1:
- $H_2C{=}CH_2 \rightarrow -CH_2\text{-}CH_2\text{-}CH\text{-}CH_2-$
- ethylene → polyethylene
- $H_2C{=}CHCH_3 \rightarrow -H_2C\text{-}CHCH_3\text{-}H_2C\text{-}CHCH_3-$



- **What is the structural requirement for a molecule to be a monomer in an addition polymer?**



Read “Natural Rubber” on page 133-134 then answer…

- **Give a molecular explanation for the fact that natural rubber melts when it is heated but vulcanized rubber does not.**

Quiz

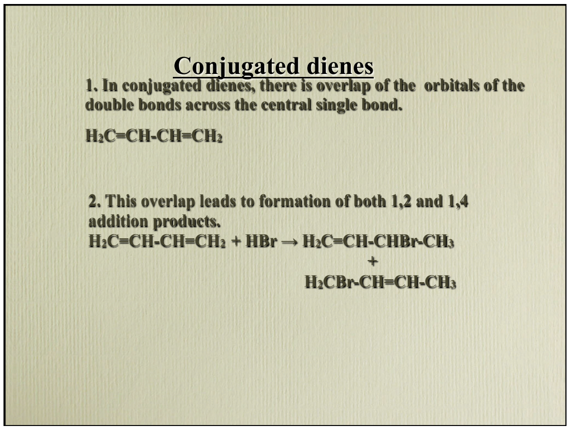
- Do 4.52 and 4.53 on page 141

Conjugated dienes and resonance

- EQ: **What are Conjugated dienes? What is the structural difference between conjugated and non-conjugated dienes?**

Conjugated dienes and resonance

- **Conjugated means multiple bonds alternating with single bonds.**
- **Conjugated diene: double bonds alternating with single bonds.**
- **1, 3 butadiene is a conjugated diene but 1, 4 pentadiene is not .... why? (draw the 2 structures and explain!)**



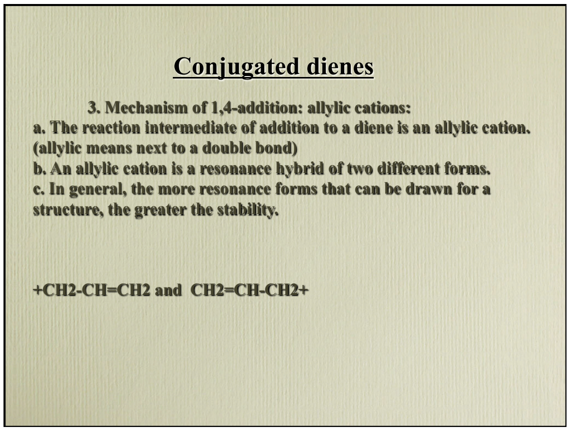
Conjugated dienes

1. In conjugated dienes, there is overlap of the orbitals of the double bonds across the central single bond.

$H_2C{=}CH{-}CH{=}CH_2$

2. This overlap leads to formation of both 1,2 and 1,4 addition products.

$$H_2C{=}CH{-}CH{=}CH_2 + HBr \rightarrow H_2C{=}CH{-}CHBr{-}CH_3 + H_2CBr{-}CH{=}CH{-}CH_3$$



Conjugated dienes

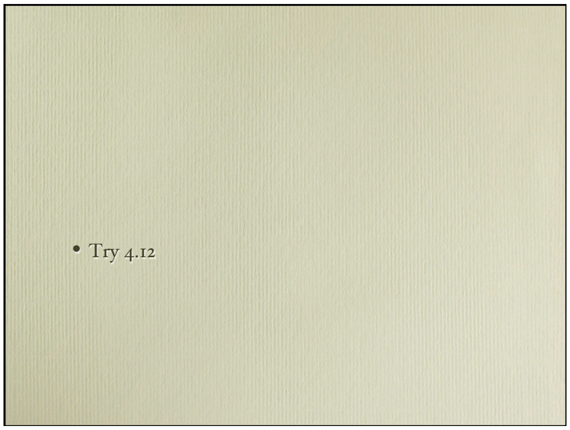
3. Mechanism of 1,4-addition: allylic cations:

a. The reaction intermediate of addition to a diene is an allylic cation. (allylic means next to a double bond)

b. An allylic cation is a resonance hybrid of two different forms.

c. In general, the more resonance forms that can be drawn for a structure, the greater the stability.

+CH2-CH=CH2 and CH2=CH-CH2+

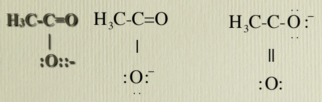


- Try 4.12

Drawing and interpreting resonance structures

1. Resonance forms are imaginary.
Example :
Benzene:

acetate ion



$$\begin{array}{c}H_3C\text{-}C\text{=}O\\ \;\;|\\ :O::^-\end{array}\quad \begin{array}{c}H_3C\text{-}C\text{=}O\\ \;\;|\\ :\ddot{O}:^-\end{array}\quad \begin{array}{c}H_3C\text{-}C\text{-}\ddot{O}:^-\\ \|\\ :O:\end{array}$$

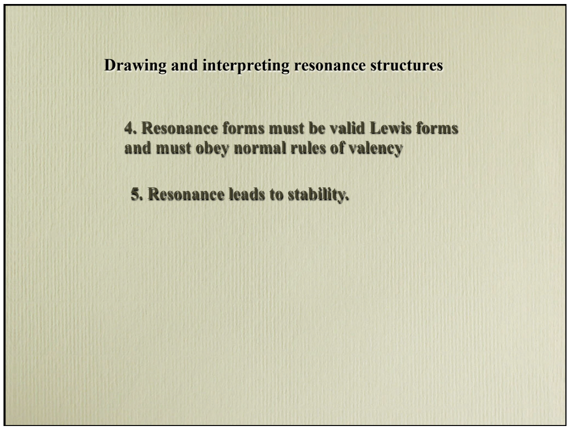
Drawing and interpreting resonance structures

2. Resonance forms differ only in the placement of their pi or nonbonding electrons.
Note: 1,3-cyclohexadiene and 1,4-cyclohexadiene are not resonance structures (They are constitutional isomers)

Drawing and interpreting resonance structures

3. Different resonance forms of a structure don't have to be equivalent.

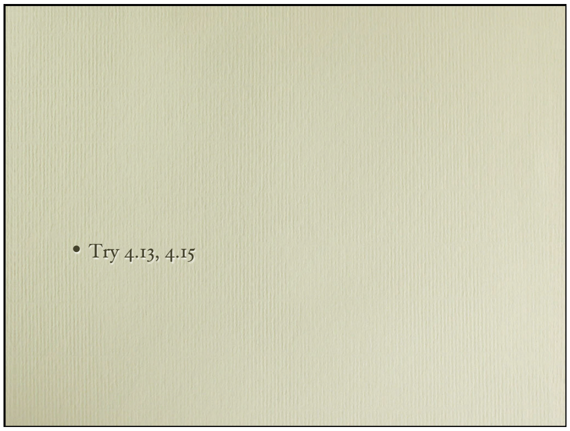
$CH_2\text{=}CH\text{-}\overset{+}{C}H\text{=}CH_3$ **and** $\overset{+}{C}H_2\text{-}CH\text{=}CH\text{-}CH_3$



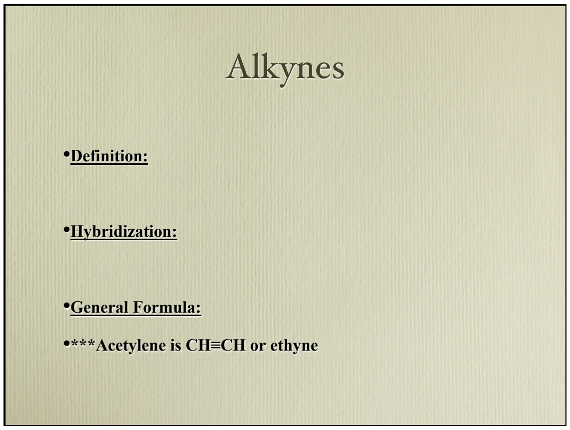
Drawing and interpreting resonance structures

4. Resonance forms must be valid Lewis forms and must obey normal rules of valency

5. Resonance leads to stability.

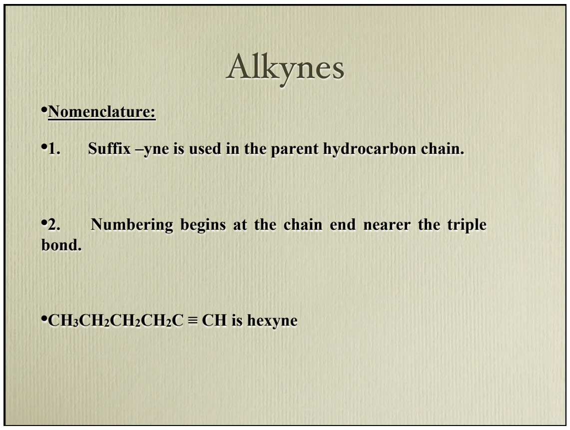


- Try 4.13, 4.15



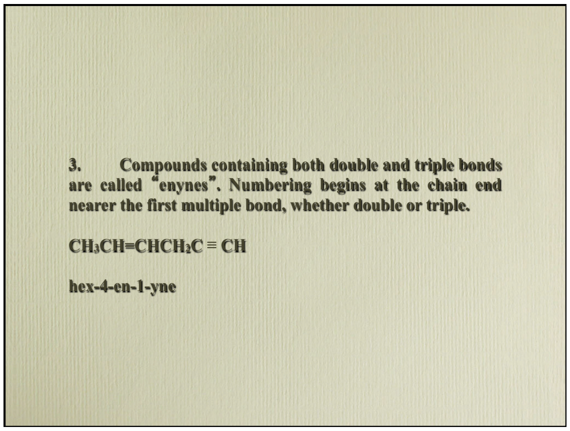
Alkynes

- **Definition:**
- **Hybridization:**
- **General Formula:**
- *****Acetylene is CH≡CH or ethyne**



Alkynes

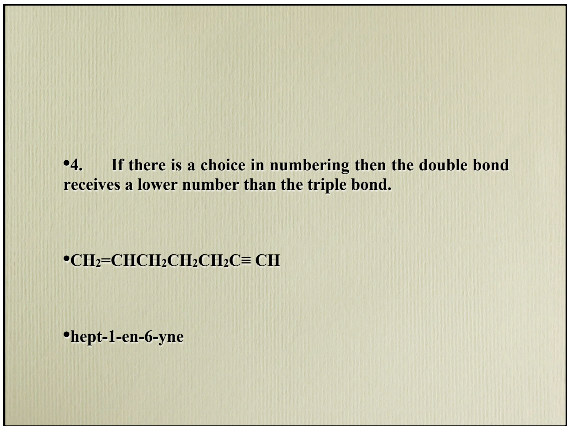
- **Nomenclature:**
- 1. Suffix –yne is used in the parent hydrocarbon chain.
- 2. Numbering begins at the chain end nearer the triple bond.
- $CH_3CH_2CH_2CH_2C \equiv CH$ is hexyne



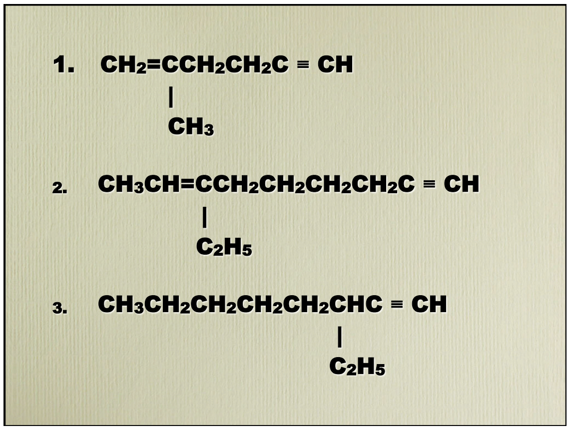
3. Compounds containing both double and triple bonds are called "enynes". Numbering begins at the chain end nearer the first multiple bond, whether double or triple.

$CH_3CH{=}CHCH_2C \equiv CH$

hex-4-en-1-yne



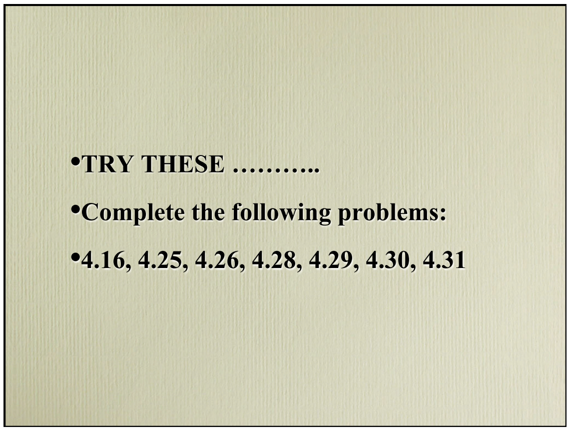
- 4. If there is a choice in numbering then the double bond receives a lower number than the triple bond.
- $CH_2{=}CHCH_2CH_2CH_2C \equiv CH$
- hept-1-en-6-yne



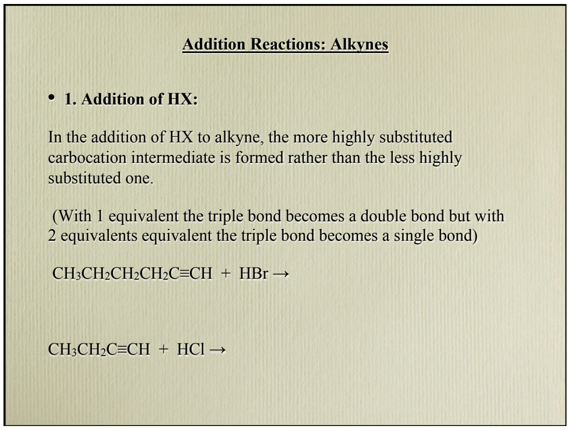
1. $CH_2{=}\underset{CH_3}{\underset{|}{C}}CH_2CH_2C \equiv CH$

2. $CH_3CH{=}\underset{C_2H_5}{\underset{|}{C}}CH_2CH_2CH_2CH_2C \equiv CH$

3. $CH_3CH_2CH_2CH_2CH_2\underset{C_2H_5}{\underset{|}{CH}}C \equiv CH$



- TRY THESE ………..
- Complete the following problems:
- 4.16, 4.25, 4.26, 4.28, 4.29, 4.30, 4.31



Addition Reactions: Alkynes

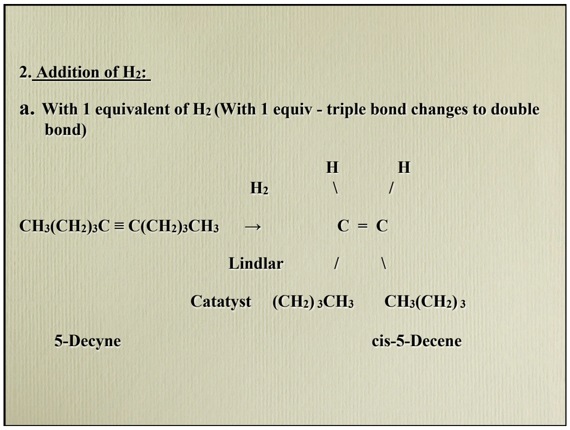
- **1. Addition of HX:**

In the addition of HX to alkyne, the more highly substituted carbocation intermediate is formed rather than the less highly substituted one.

(With 1 equivalent the triple bond becomes a double bond but with 2 equivalents equivalent the triple bond becomes a single bond)

$CH_3CH_2CH_2CH_2C{\equiv}CH + HBr \rightarrow$

$CH_3CH_2C{\equiv}CH + HCl \rightarrow$



2. **Addition of H_2:**

a. With 1 equivalent of H_2 (With 1 equiv - triple bond changes to double bond)

H H

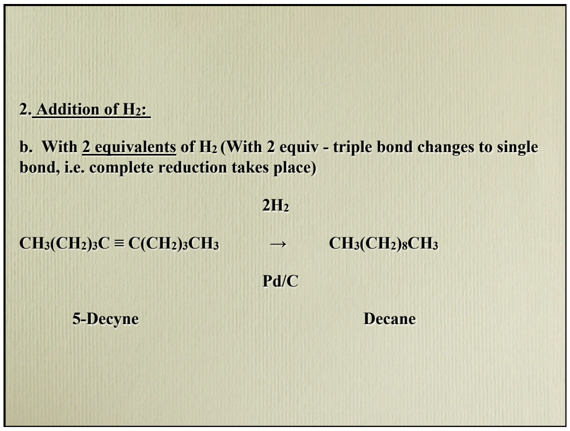
H_2 \ /

$CH_3(CH_2)_3C \equiv C(CH_2)_3CH_3$ → C = C

Lindlar / \

Catatyst $(CH_2)_3CH_3$ $CH_3(CH_2)_3$

5-Decyne cis-5-Decene

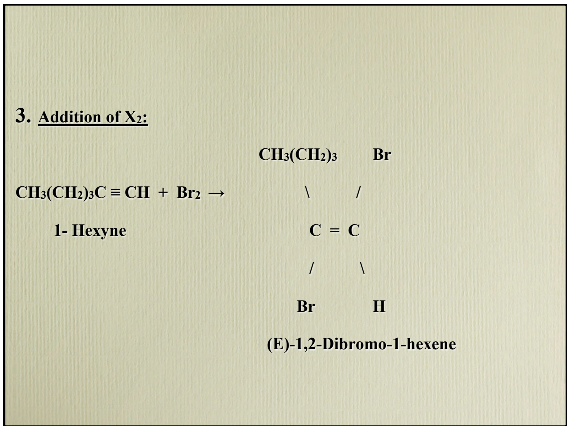


2. **Addition of H_2:**

b. With 2 equivalents of H_2 (With 2 equiv - triple bond changes to single bond, i.e. complete reduction takes place)

$$CH_3(CH_2)_3C \equiv C(CH_2)_3CH_3 \xrightarrow[Pd/C]{2H_2} CH_3(CH_2)_8CH_3$$

5-Decyne Decane



3. **Addition of X_2:**

$CH_3(CH_2)_3$ Br

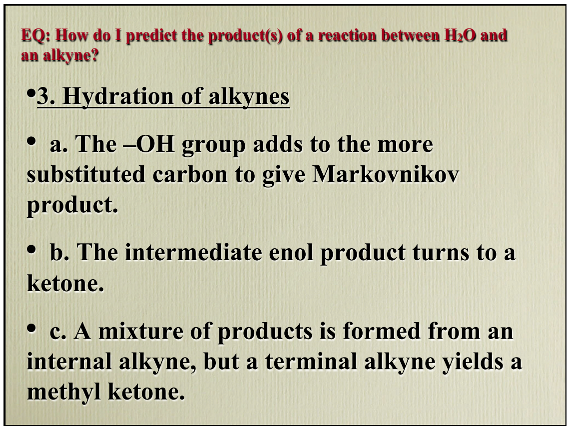
$CH_3(CH_2)_3C \equiv CH + Br_2$ → \ /

1- Hexyne C = C

/ \

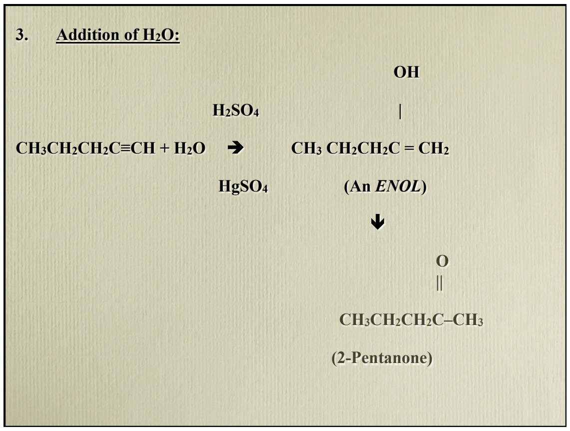
Br H

(E)-1,2-Dibromo-1-hexene



EQ: How do I predict the product(s) of a reaction between H_2O and an alkyne?

- **3. Hydration of alkynes**
- a. The –OH group adds to the more substituted carbon to give Markovnikov product.
- b. The intermediate enol product turns to a ketone.
- c. A mixture of products is formed from an internal alkyne, but a terminal alkyne yields a methyl ketone.



3. Addition of H_2O:

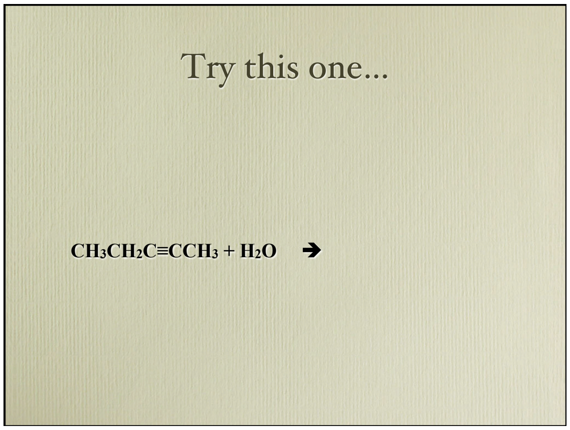
$$CH_3CH_2CH_2C{\equiv}CH + H_2O \xrightarrow[HgSO_4]{H_2SO_4} CH_3\,CH_2CH_2\overset{\overset{\displaystyle OH}{|}}{C} = CH_2$$

(An *ENOL*)

$$\downarrow$$

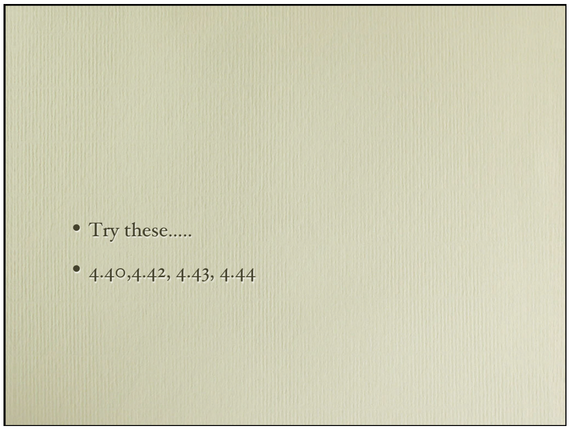
$$CH_3CH_2CH_2\overset{\overset{\displaystyle O}{\|}}{C}{-}CH_3$$

(2-Pentanone)

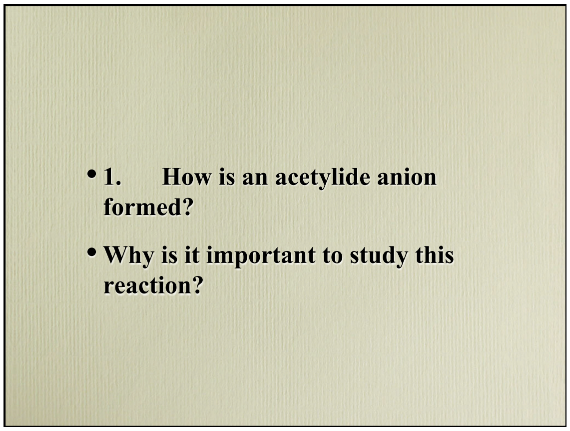


Try this one…

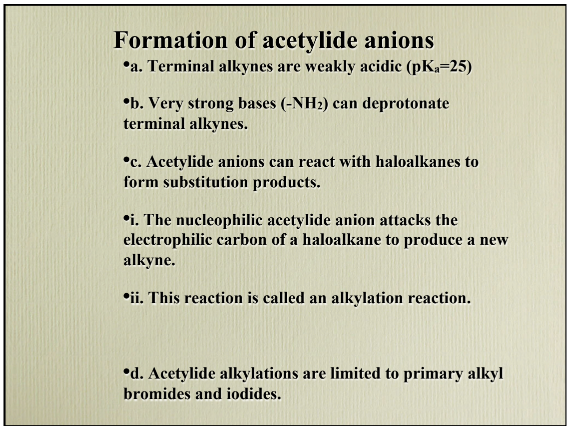
$CH_3CH_2C{\equiv}CCH_3 + H_2O$ →



- Try these.....
- 4.40,4.42, 4.43, 4.44



- 1. How is an acetylide anion formed?
- Why is it important to study this reaction?



Formation of acetylide anions

- a. Terminal alkynes are weakly acidic (pK_a=25)
- b. Very strong bases ($^-NH_2$) can deprotonate terminal alkynes.
- c. Acetylide anions can react with haloalkanes to form substitution products.
- i. The nucleophilic acetylide anion attacks the electrophilic carbon of a haloalkane to produce a new alkyne.
- ii. This reaction is called an alkylation reaction.
- d. Acetylide alkylations are limited to primary alkyl bromides and iodides.