Chapter 3 Organic Chem: Alkenes & Alkynes

Don't need to know the following reactions found on summary pages 110-112:

1. Hydroboration-Oxidation
2. Cycloaddition to Conjugated Dienes
3. Alkyne reaction with the combination of H_2O, Hg^{2+}, H+
4. Formation of Acetylide Anions

Chapter 3 Alkenes & Alkynes Read Chap 3 (Not Sections11-13, 15b, 17c, 21) & p.153-154 & 157-158:

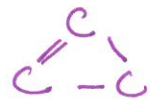
1. Differentiate between alkene, alkyne and diene; molecular formula comparisons, conjugated, cumulated, and isolated multiple bonds; polymer and monomer
2. Use IUPAC nomenclature to name and draw alkenes and alkynes including:
   a. Old names: ethylene & acetylene
   b. Cis/trans, E/Z & substituent priorities
   c. En-yne & priorities
3. Determine whether given compounds can display cis-trans and/or (E)-(Z) isomerism.
4. Describe the characteristics of alkanes, alkenes, & alkynes: relative bond length, geometry, rotation, relative reactivity of all 3 & why..
5. Know the meaning of: trigonal carbon, sigma (σ) and pi (π) bonds, sp^3 & sp^2 & sp hybridization, %s & %p in hybrids, type of bonds & orbitals between carbons.
6. Describe methods to obtain hydrocarbons of desired length- fractional distillation, cracking and alkylation.
7. Write equations for addition reactions of alkenes and alkynes including the reactants, catalysts and products for halogenation, hydration, hydrogenation, acids (HX & H_2SO_4).
   a. Given an alkyne or conjugated diene, write the structures of products obtained by adding 1 or 2 moles of a particular reagent.
   b. Given the structure or name of a compound that can be prepared by an addition reaction, deduce what unsaturated compound and what reagent reacted to form it.
   c. Write the steps of electrophilic addition reaction mechanisms involving the following terms: Markovnikov's rule, , name & drawing of 1,2-addition & 1,4-addition, polymerization, carbocation (Formation, classification, stability & resonance, type formed as intermediary in reaction. Example: what type of carbocation is formed when HBr is added to 3,3-dimethly-1-butene?).
8. Write equations for the reactions of ozonolysis and oxidation with $KMnO_4$.
   a. Given the structures of ozonolysis products, deduce the structure of the unsaturated hydrocarbon that produced them.
9. Describe 2 simple chemical tests that can distinguish an alkane from an alkene or alkyne.
10. Draw structures, with arrow formalism, for the contributors to the resonance hybrid of an allylic cation.
11. Know the steps in the mechanism of ethylene polymerization caused by a free radical chain mechanism.

Alkenes: C=C C_nH_{2n} IF only 1 dble bond is present.

Alkynes: C≡C C_nH_{2n-2} IF only 1 triple bond is present

Example: What are all the structural possibilities for C_3H_4?

C=C=C C≡C-C



Unsaturated hydrocarbons: Have ≥ 1 multiple bond

Bonding Patterns of Multiple Bonds

1. **Cumulated:** Double bonds next to one another.
2. **Conjugated:** Multiple bonds separated by only one C-C single bond.
   C=C-C=C C=C
3. **Non-conjugated/Isolated:** Separated by > 1 single bond

C≡C-C-C=C-C

Sec 3.2 IUPAC Names =International Union of Pure & Applied Chemistry

1. "ene" ending for C=C (diene, triene = 2 or 3 double bonds)
2. "yne" ending for C ≡ C (diyne, triyne = 2 or 3 triple bonds)
3. "enynes" ending if both double & triple bonds present

See p 73-74 Nomenclature AND Common Errors

Quick Summary/Overview

1. Select longest chain that includes ***both*** carbons of double or triple bond
2. Number from end **nearest multiple bond.** If multiple bond is equidistant from both ends, THEN number from 1st substituent.
3. Indicate the position of multiple bond w/# of lowest C of that bond
4. More than 1 multiple bond? # from end nearest the 1st multi-bond. Double bonds receive lowest # if equidistant w/triple bond.
5. Cyclic: Start numbering w/ both C's (#1 & 2) of the multiple bond, and add "cyclo" prefix.

Examples:

1-pentene

$CH_2{=}CHCH_2CH_2CH_3$

1 2 3 4 5

3-heptene

$CH_3CH_2CH_2CH{=}CHCH_2CH_3$

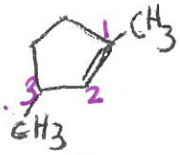
3 2 1

1 butene

C-C-C=C

1

1,3 dimethyl 1 cyclopentene.



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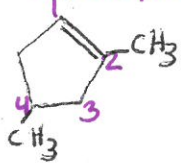
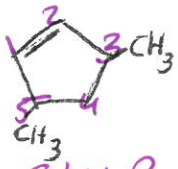
1,4 dimethyl 1-cyclopentene





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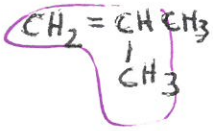
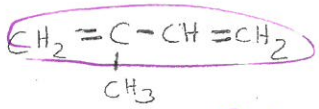
3,5 dimethyl 1 cyclopentene

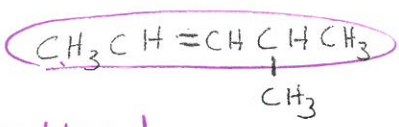


2 methyl 1 propene

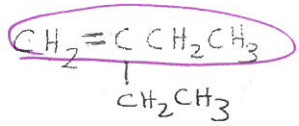


2 methyl 1,3 butadiene.

2 =

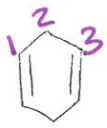


4 methyl 2 pentene



2 ethyl 1 butene

1,3 cyclohexadiene

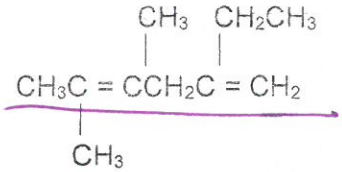


3 methyl 1 cyclopentene

1,3 cyclohexadiene

****See p.74 common mistakes****

Example: Name the following molecule:

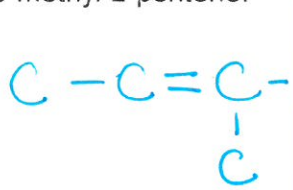


hexadiene

1. Longest chain with the double bonds: 6 = hex /ene = dble
2. How many double bonds? Prefix? 2 di-
3. Number for lowest sum of double bonds? 2, 5 vs 1, 5
4. Number & name substituent groups:

2 ethyl 4,5 dimethyl 1,4 hexadiene

2nd Example: Write the structural formula for 3-methyl-2-pentene:



Students need to get out their notes and complete problems #6 (pg 3) + #7 + 8 (pg 4).
* This is the key so if students get

Example: -en-yne naming:

1. C ≡ C – C – C = C

pentene

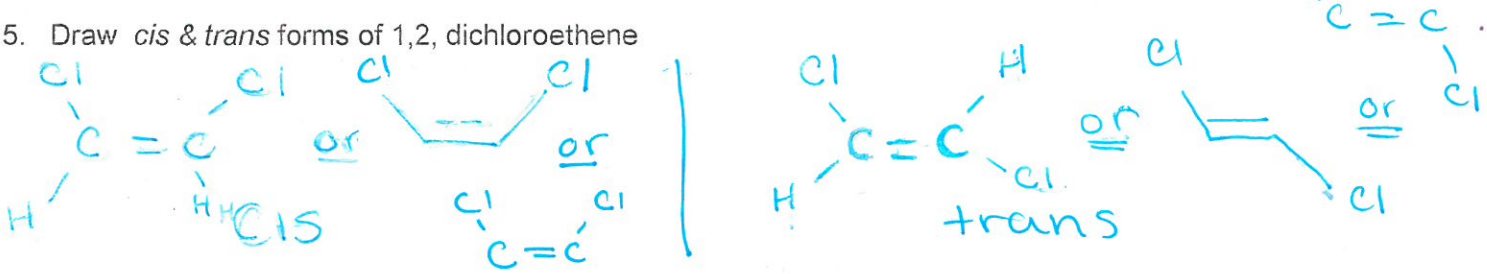
2. C ≡ C – C = C – C

pentene

Sec 3.5 *Cis-trans* Isomerism in Alkenes

1. Geometric (configurational): not interconvertible a
2. Each carbon must have 1 substituent + 1 H attached to it
3. "Cis"- form: substituents on same side of molecule top/top or bottom/bottom
4. "Trans" form: substituents on opposite sides top/ bottom

5. Draw *cis* & *trans* forms of 1,2, dichloroethene

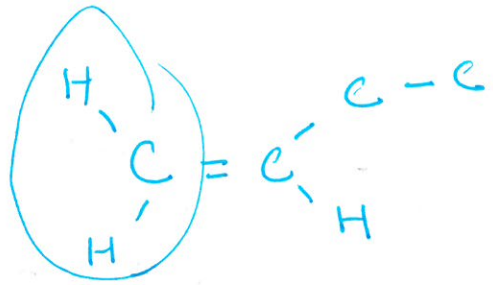


6. Cis/trans 2-butene:

7. Cis/trans 1-butene

C=C-C-C

not possible →



8. Name:

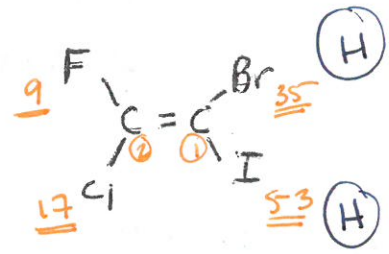
cis-2-pentene trans-2-pentene

<u>Sec 5.4 E-Z Isomerism in Alkenes, p. 157-158 and p. 153-155</u>

Is the following molecule cis or trans?

I > Br > Cl > F

(Z) 1-Bromo, 2-chloro
2-Fluoro, 1-iodo
1-ethene



When 2 different atoms, & neither are hydrogen, are attached to the carbons of a double bond, you are unable to use cis/trans. Instead, use the E-Z nomenclature.

1. Assign priority to the groups attached
2. Assign (E) vs. (Z)
   a. (Z) = High Priority on the same side OR "Ze Zame Zide"
   b. (E) = High priority on opposite sides

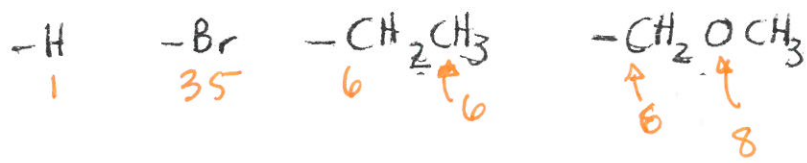
Priority:

1. Atoms directly attached to the carbons of the double bond are ranked according to atomic number.
   A. Higher atomic number = HIGHER priority
   B. Hydrogen always has lowest priority
   C. Example-rank the following atoms from highest to lowest priority: O, H, C, Cl

8 1 6 17

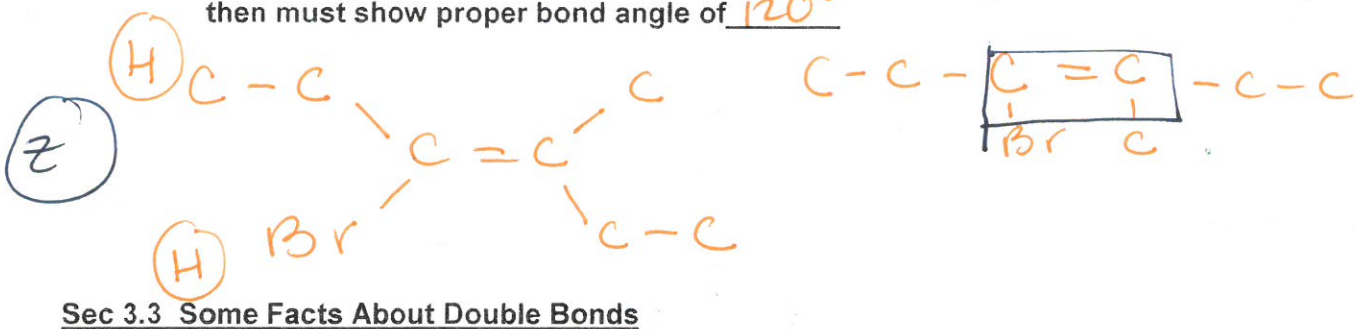
Cl > O > C > H

2. If attached atoms are the same element, work outward until reach unalike atoms, and assign priority. Example-rank the following groups from highest to lowest priority:



-Br > -CH2OCH3 > -CH2CH3 > -H

3. **Example: Draw (Z)-3-bromo-4-methyl-3-hexene**
   A. **NOTE: May draw out "straight" first and then place on opposite sides if that helps! But then must show proper bond angle of** 120°



Sec 3.3 Some Facts About Double Bonds

Property	C – C	C = C	C ≡ C
Rotation	Free	Restricted	None
Geometry	• Tetrahedral • staggered preferred – many possible	Trigonal Planar	LINEAR
Bond angle	109.5°	120°	180°
Bond length	Longest	medium	Shortest
Current / Old names for 2-C chain	C – C Ethane	C = C Ethene/ Ethylene	C ≡ C Ethyne/ Acetylene

Sec 3.4 Orbital Model of a Double Bond; the Pi Bond
Sec 3.18 – 3.19 The Orbital Model of a Triple Bond

Bond Types 1.4 & 1.8 Figures

1. σ bond; end – on overlap of orbitals

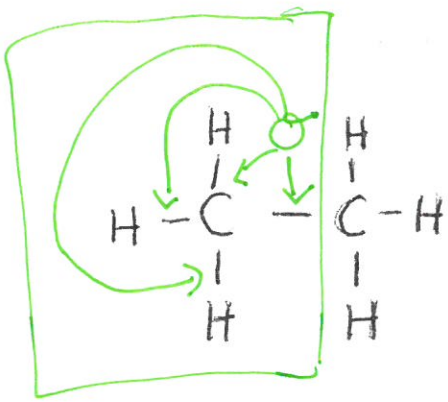
2. π bond; lateral overlap of both lobes of a p orbitals

   A. More exposed electrons (above & below)

   B. Will be attacked by electrophiles and are more reactive than alkanes

Carbon Bond & Orbital Types

1. Valence shells of all atoms contain 1 s & 3 p orbitals.
2. π bonds always are made from the lateral overlap of p orbitals.
   a. The p orbitals involved in the π bond, are the only original carbon orbitals that do not hybridize.
   b. π bonds are only present in multiple bonds (alkenes & alkynes)
3. All orbitals "left over" and NOT involved in π bonds will hybridize.

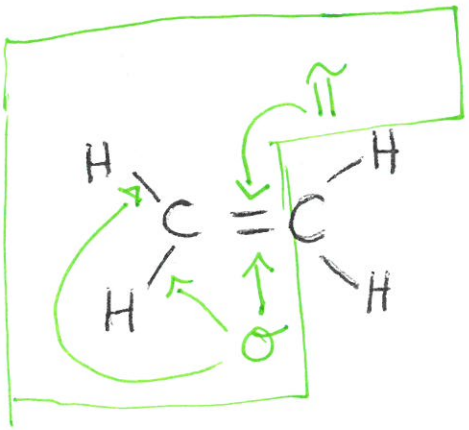


1s + 3p available to hybridize

Alkane

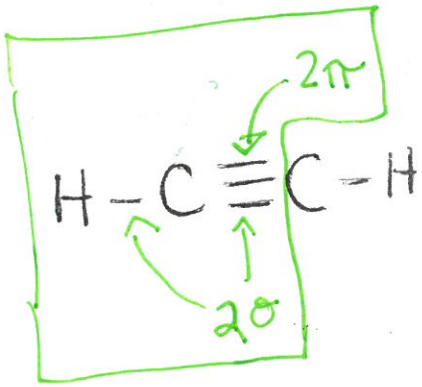
- 0 π bonds – 0 "p" orbitals used
- 4 σ ← sp^3 hybrid orbitals

add superscripts → 4



Alkene

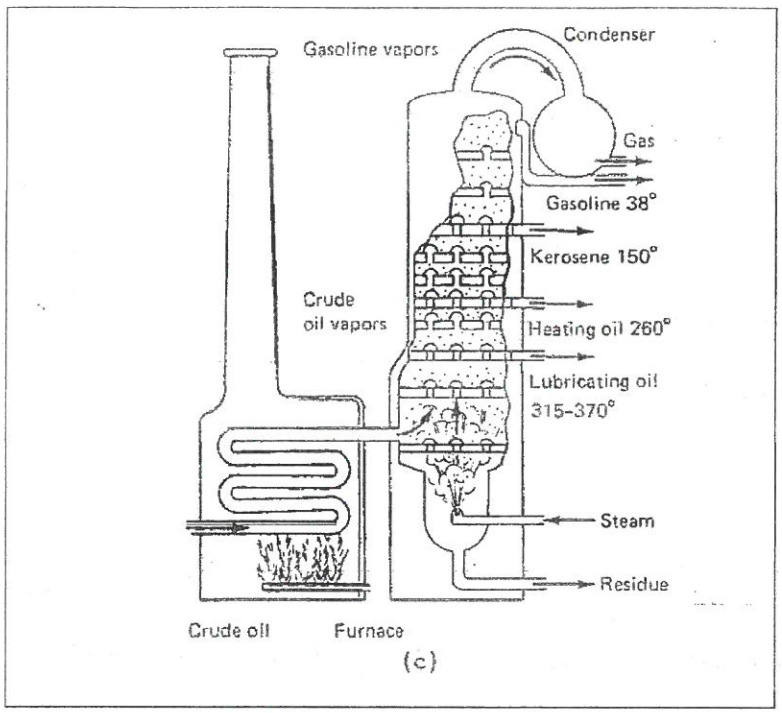
- 1 π bond → 1 "p" orbital used up
- 1s 2p left to hybridize
- 3 σ bonds ← sp^2 orbitals



Alkyne – 2 π bonds – 2 "p" orbitals are used up

2 σ bonds – sp orbital

Sec Production/Purification



Petroleum: Mixture of Hydrocarbons

1. **Fractional Distillation:** Separation of petroleum into "simpler & purer fractions" by condensation at different temps
   A. Low molecular weight compounds boil off 1st & rise to the top for collection (methane/ethane).
   B. Compounds w/high bp condense close to the bottom (oils, grease, tar, asphalt)
   C. Location and temp of condensation tube set to collect desired hydrocarbons
   D. See Table 3.3 p. 106 for uses of fractions

2. **Cracking:** Process that breaks alkanes into shorter alkanes & alkenes.
   A. "Cracked" alkane yields BOTH an alkane + alkene. Multiple combinations possible.
   B. Example: $C_{10}H_{22} \rightarrow C_4H_{10} + C_6H_{12}$
      Alkane C_nH_{2n+2} — Alkane C_nH_{2n+2} — Alkene C_nH_{2n}

3. **Alkylation:** Combination of an alkane with an alkene to form a longer alkane.

Read Chap 3 (Not Sections 11-13, 15b, 17c) and p.153-154 & 157-158:

Alkene Addition Reactions

- **Addition in alkenes, rather than substitution as in alkanes**

1. Addition of Halogens

a. No light or heat required as in alkanes (no radicals just bond breaking)

b. Iodine or Bromine used to test for unsaturation

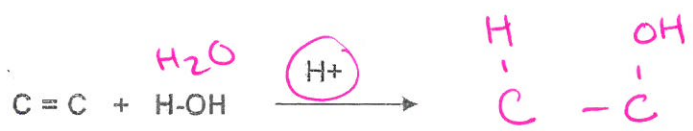
Brown

2. Polar Addition of Water (Hydration)

$H_2O \rightarrow H^+ + OH^-$

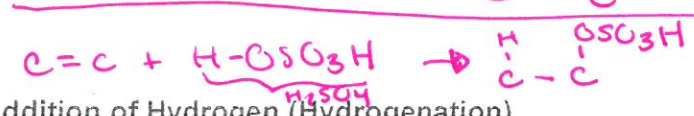
a. Requires Acid Catalyst (water ionizes to replace H^+ catal

b. Product is an alcohol



3. Polar Addition of Acids (HX & $H\text{-}OSO_3H$ which is another way to write H2SO4)

← Halogen (HCl / HBr)



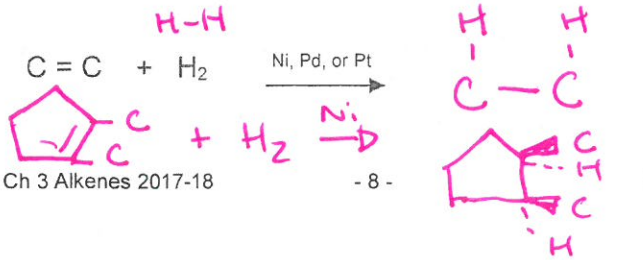
4. Addition of Hydrogen (Hydrogenation)

a. Requires appropriate catalyst-metal such as Ni, Pt, Pd.

i. H_2 sits on metal surface and adds to same side of double bond.

IMPORTANT- forms CIS if converting from:

1. cycloalkene to cycloalkane OR
2. alkyne to alkene (Requires Lindlar's catalyst, "poisoned" weakened Pd, to stop at alkene)



Miscellaneous Notes: Stop

1. If **either** the alkene or the reagent is symmetrical, only 1 product is possible.

2. If both are unsymmetrical 2 products are possible. But only 1 usually forms. The one that predominates is considered to be "regiospecific", and its formation follows Markovnikov's Rule.

* RICH get RICHER (C with more H get more H)

* POOR get poorer

3. Polar reactants can be classified as electrophiles or nucleophiles

   a. Electrophile has a partial + charge (electropositive): & is "e⁻ loving"

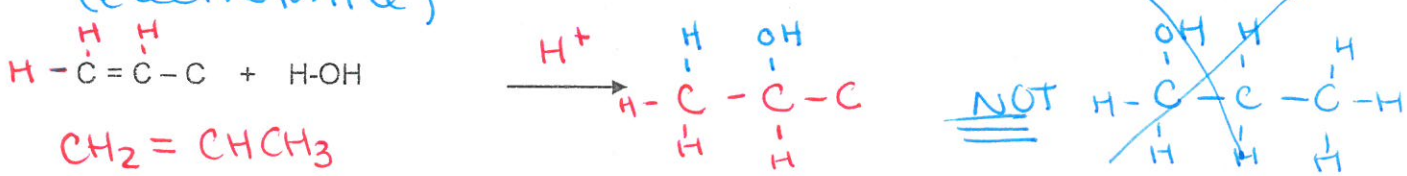
   b. Nucleophile: has a partial − charge (electronegative) & is "nucleus loving"

   c. Leads to **electrophilic additions to double bond site on alkenes.**

   d. The electrophile ALWAYS adds first. USUALLY, the electrophile is H^+ but it can be other things.

Markovnikoff's Rule: Addition of Unsymetric Reagents to Unsymmetric Alkenes

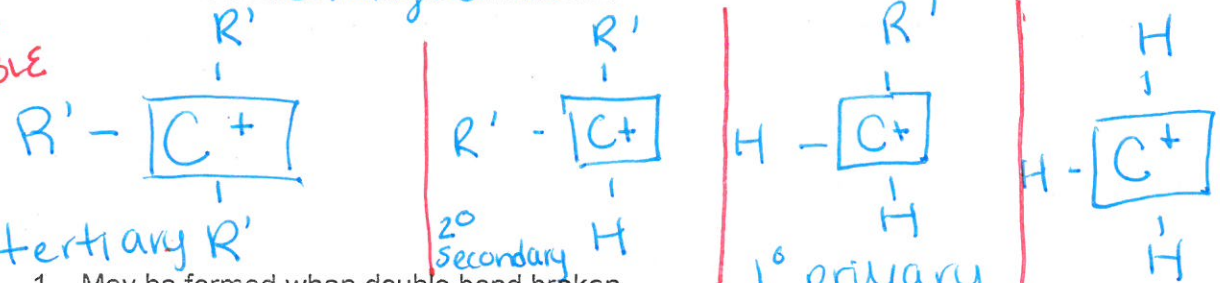
➢ Electropositive (electrophile) → usually H^+ part of the reagent bonds to the C with greater # H



Carbocation Stability

Carbocation: + charged C that is classified as:

MOST STABLE



1. May be formed when double bond broken
2. W/Markinov's rule, + part of reagent bonds 1st, to the C w/ greater # H, so that the most stable carbocation is produced.
3. Example:

$CH_2 = CHCH_3$ + H-OH $\xrightarrow{H^+}$??

1. Pos (H+) adds first: $H^+ + C=C-C \rightarrow C-\overset{+}{C}-C$ (H on the first C)
2. Possible cations: $C-\overset{+}{C}-C$ (2°) or $\overset{+}{C}-C-C$ (1°)
3. Which is more stable?
4. Follow Markovnikov?
5. Neg (OH-) adds 2nd $C-C(OH)-C$ (H, OH) NOT $C(OH)-C(H)-C$

4. Restated rule: Electro+ part adds in a way to produce/involve most stable carbocation.

$C-C=C + H-Cl \rightarrow$

Possible cations $C-C(H)-\overset{+}{C}$ (1°) or $C-\overset{+}{C}-C(H)$ (2°)

Classify

Cross off least stable

Final Product: $C-C(Cl)-C(H)$

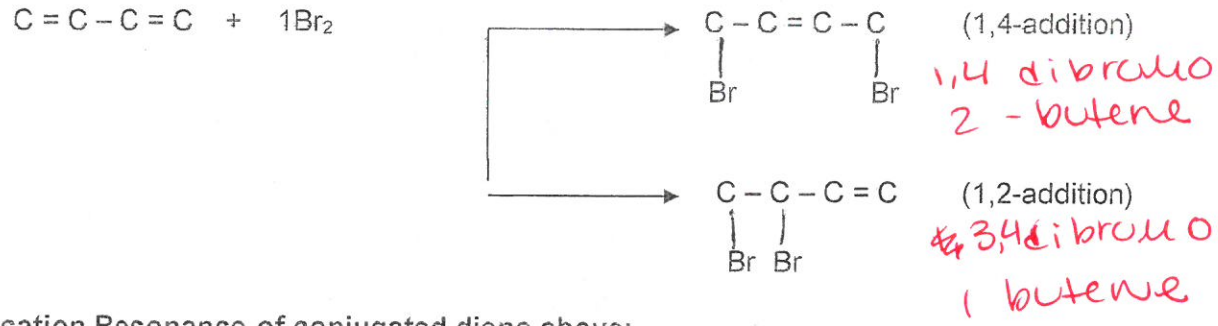
$C-C(C)=C-C-C$

→ ?

Conjugated alkene (diene) addition-– *Symmetrical* - 1 mole *of addition reagent* –

Obtain 2 products in equal portions

1. 1 mole of addition reactant will produce 2 products, each with 1 double bond
2. 2 moles of addition reactant will produce 1 product without any double bond.
3. Example w/1 mole Br_2:

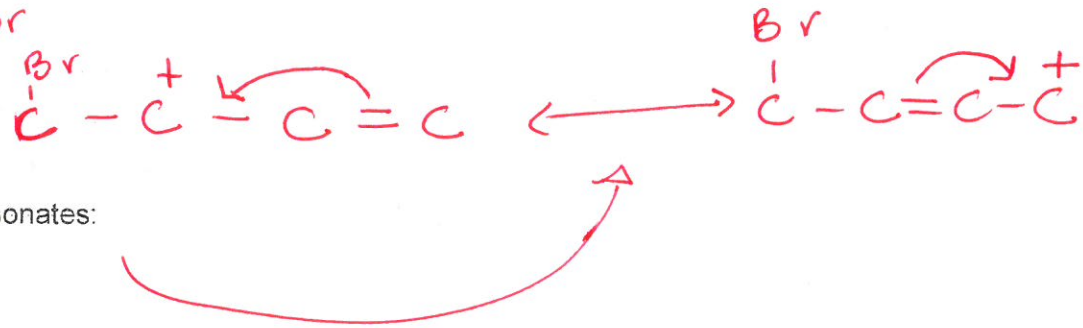


Carbocation Resonance of conjugated diene above:

C = C – C = C + 1 Br_2 →

Br-Br

1. Br+ adds:

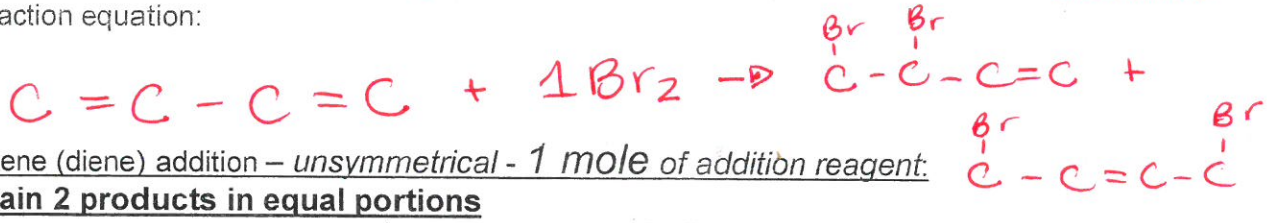


2. Double bond resonates:

3. 2nd Br adds to both carbocations:

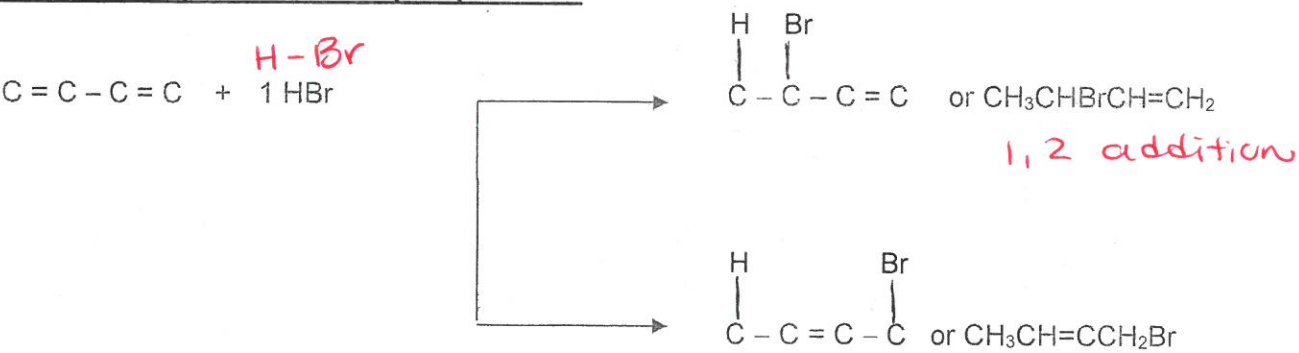
1,2 addition  1,4 addition

4. Overall reaction equation:



Conjugated alkene (diene) addition – *unsymmetrical* - 1 mole *of addition reagent*:

1. **Again obtain 2 products in equal portions**

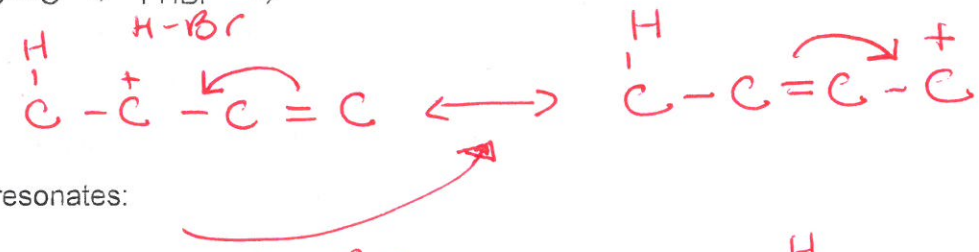


Carbocation Resonance of above conjugated diene:

C = C – C = C + 1 HBr →

H-Br

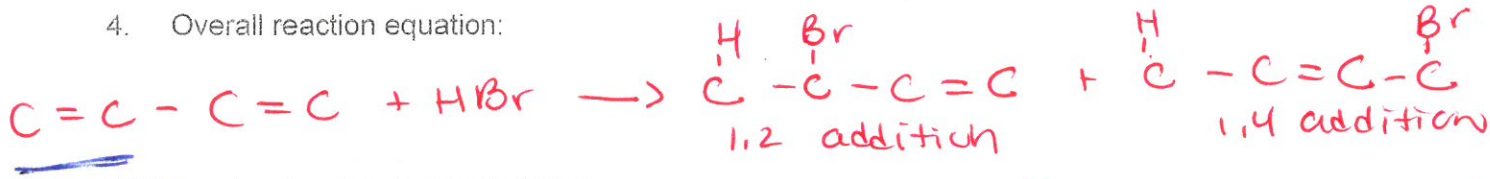
1. H+ adds:



2. Double bond resonates:

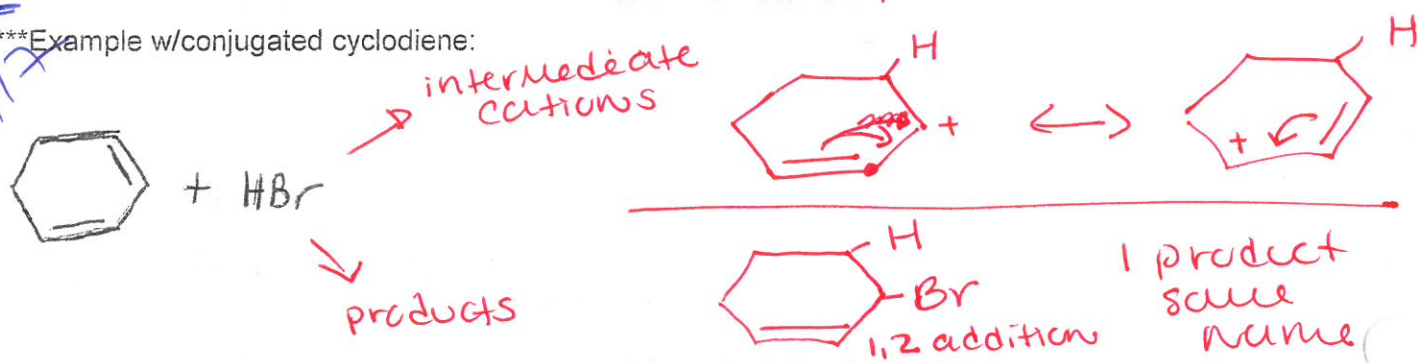
3. Br- adds to both carbocations:

4. Overall reaction equation:

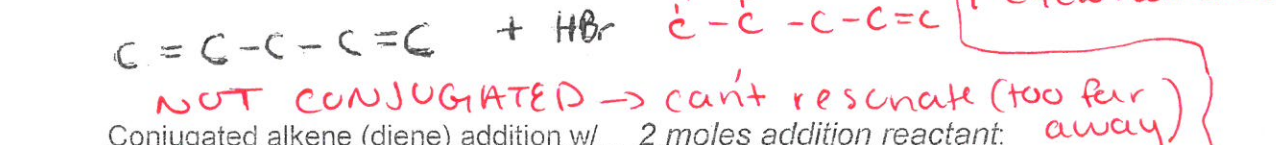


Start 10/19/17

***Example w/conjugated cyclodiene:



5. Show resonance forms for carbocation formed from the following:

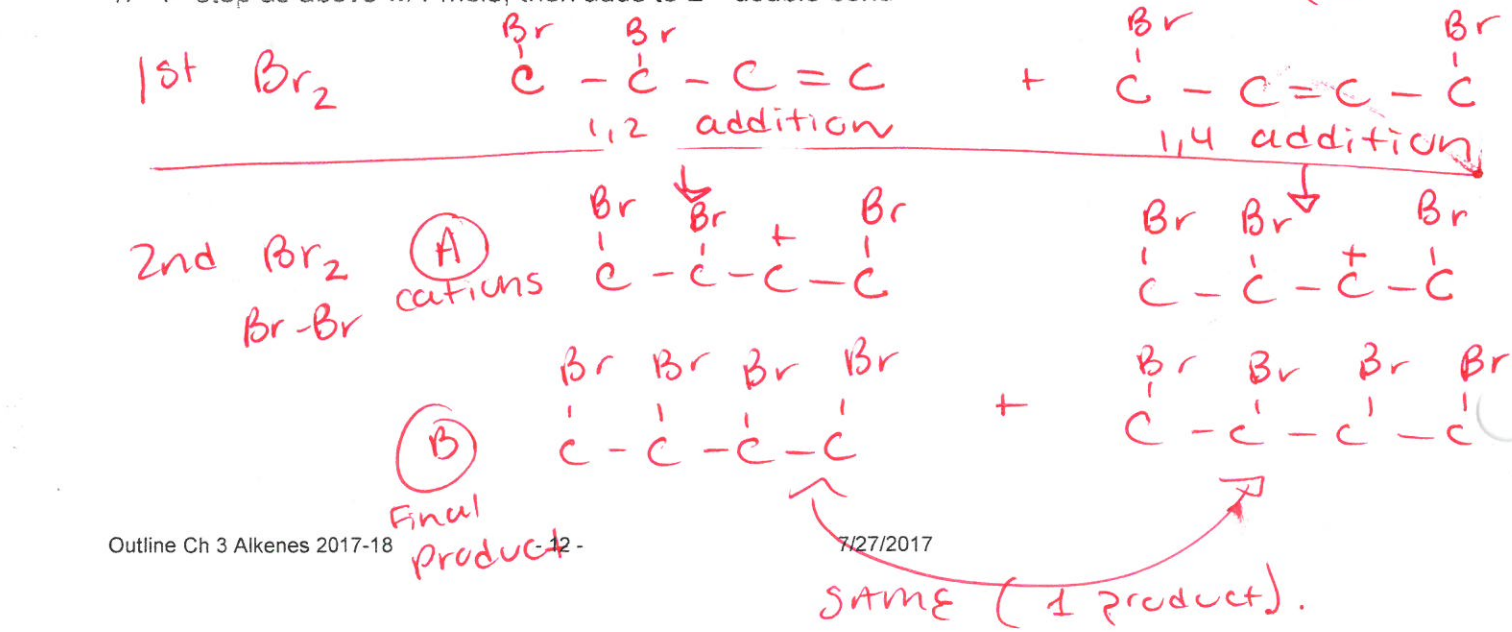


NOT CONJUGATED → can't resonate (too far away)

Conjugated alkene (diene) addition w/ *2 moles addition reactant*:

Overall Equation: C = C – C = C + 2 Br_2 → Br Br Br Br C – C – C – C

1. 1st step as above w/1 mole, then adds to 2nd double bond



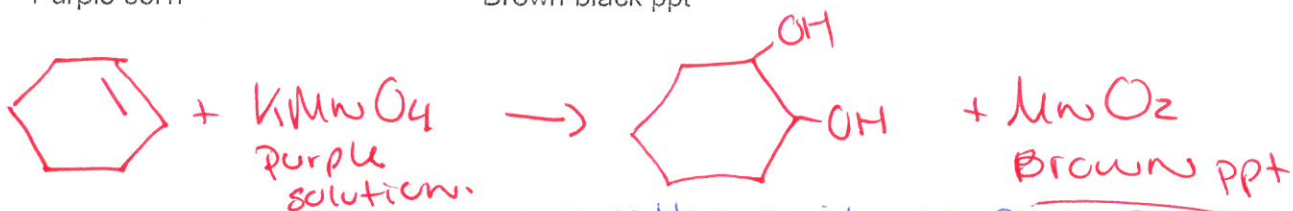
.40 .49

Oxidation w/$KMnO_4$

- Test to tell Alkenes from Alkanes (No reaction occurs with alkanes)
- Produces compound w/ 2 adjacent -OH groups
- If alkene, changes from purple sol'n to brown ppt

$$C=C + KMnO_4 + H_2O \rightarrow \underset{OH}{C} - \underset{OH}{C} + MnO_2 + KOH$$

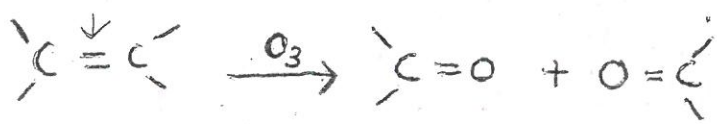
Purple sol'n → $KMnO_4$; Brown-black ppt → MnO_2



Ozonolysis: Oxidation of alkenes w/ ozone splitting it to give 2 carbonyl compounds

1. Used to determine location of double bond
2. Requires: O_3
3. Forms aldehydes $-\underset{H}{C}=O$, names end in "-al"
4. If only 1 aldehyde product formed, the original reactant was 1 of the following:
   a. Cycloalkene. Product will be a "dial".
   b. Symmetrical Acyclic Alkene

- Overall reaction summary:



- Example w/ 1-butene:

$$C=C-C-C \xrightarrow{O_3} C=O + O=C-C-C$$

- Example w/2-pentene

$$C-C=C-C-C \xrightarrow{O_3} C-C=O + O=C-C-C$$

- Other examples:

$$C-C \neq C-C \xrightarrow{O_3} C-C=O \overset{\text{SAME}}{+} \cancel{O=C-C}$$

Acyclic & Symmetric → 1 product

STOP

Alkyne Additions:

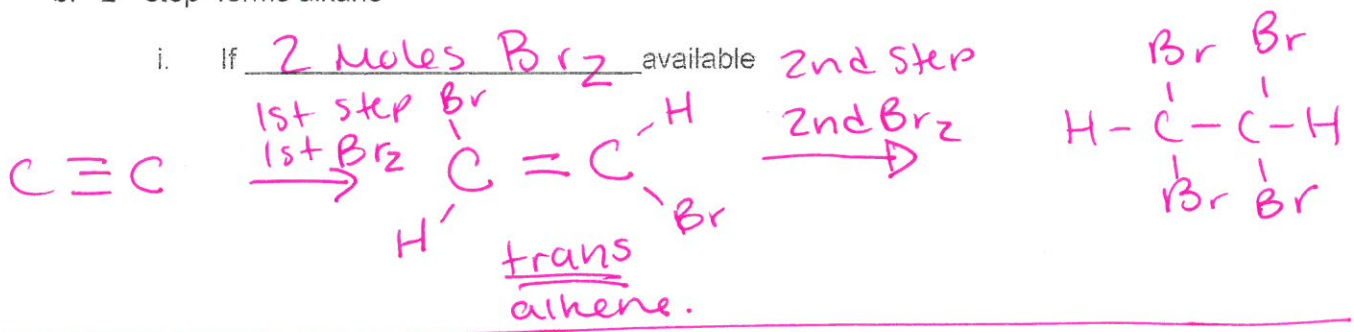
Similar to alkene reactions, with the following exceptions:

1. Needs 2 addition steps to go to alkane.
   a. Requires 2 moles of the addition reagent.
   b. Markovnikov's rule followed in each of the 2 steps.

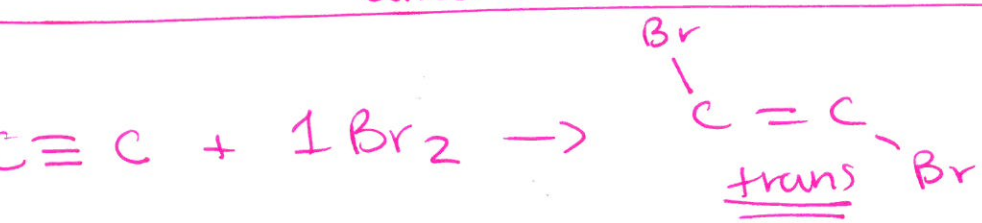
2. May stop at alkene
   a. If only 1 mole of the addition reagent is available
   b. Forms trans isomer, with 1 exception
   c. Exception: Hydrogenation
      i. Forms cis alkene
      ii. Use Lindlar's catalyst (Poisoned Pd) to stop at alkene.
      iii. Other metal catalysts (Ni, Pt, Pd) go 2 steps to alkane

3. **Symmetrical addition (not H_2) w/o catalyst (X_2):**
   a. 1st step forms trans-alkene (Trans favored).
      i. Stops here if only 1 mole Br available
   b. 2nd step forms alkane
      i. If 2 moles Br_2 available

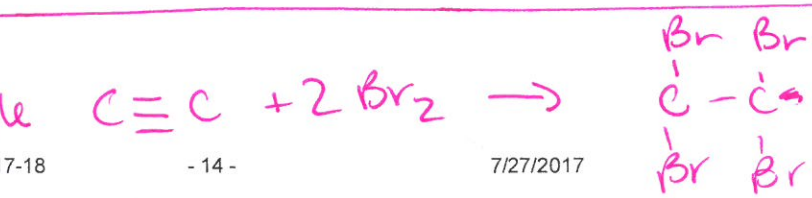
steps



Equation w/ 1 mole



Equation w/ 2 mole



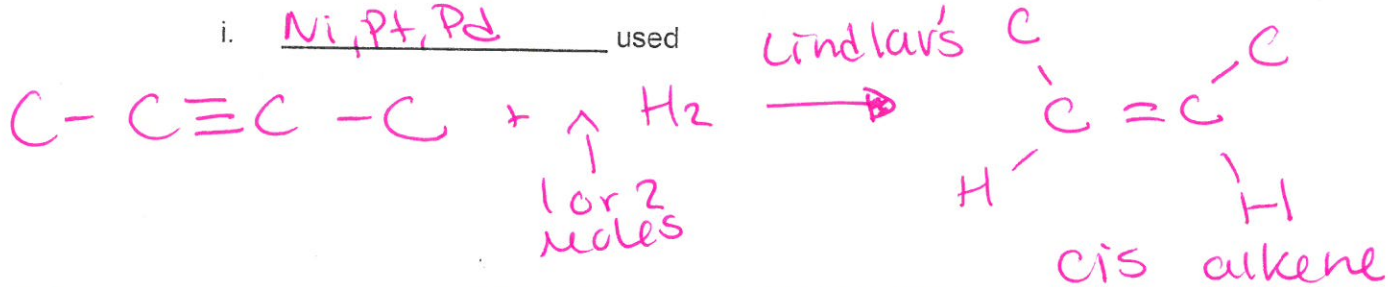
4. **Symmetrical addition of H_2 w/ catalyst:**

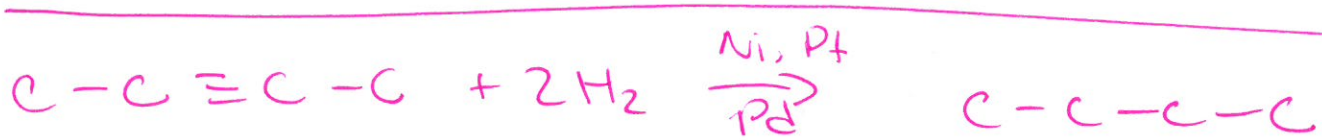
   a. 1st step forms Cis- Alkene.

      i. Stops here if Lindlar's catalyst, poisoned Pd used
      (DOESN'T matter the number of moles of H2)

   b. 2nd step forms alkane, if allowed

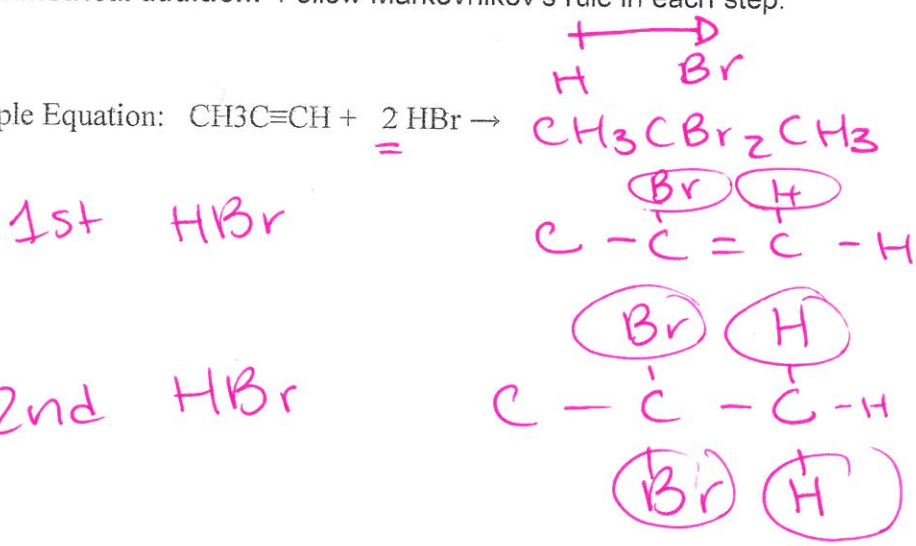
      i. Ni, Pt, Pd used





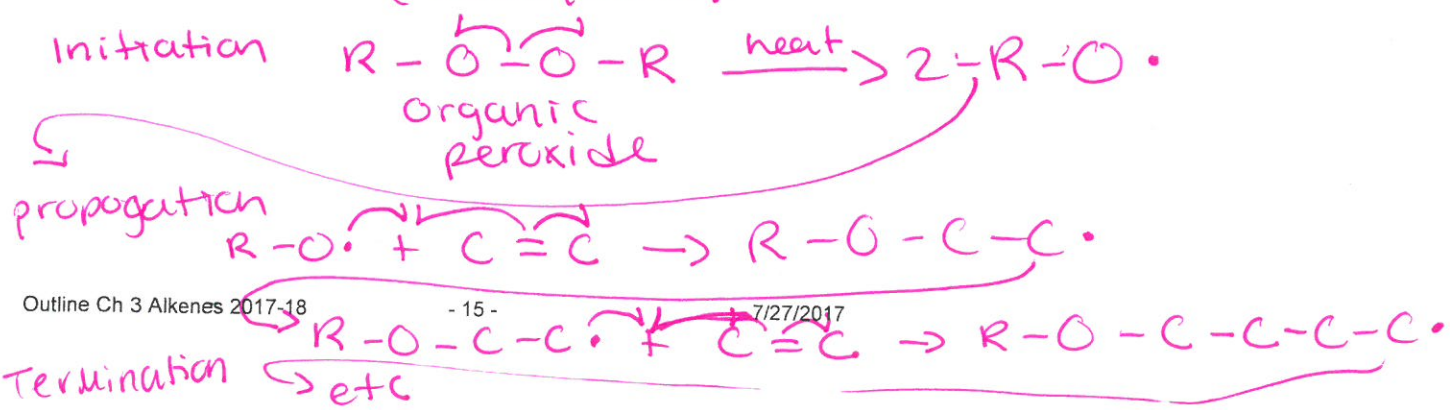
5. **Unsymmetrical addition:** Follow Markovnikov's rule in each step.

Example Equation: CH3C≡CH + 2 HBr → CH3CBr2CH3



Free –Radical Additions: Polymerization

- Polymer: Large Molecule made of repeating monomers.
- Radical mechanism of ethene (ethylene) to form polyethylene.



Chapter 3 Alkenes & Alkynes

Bellwork

Review #1 - Basics

How name if = ? ≡ ?

Is cis/trans possible with? (Show models)

A. Single bond?

B. Double bond?

C. Triple bond?

How does reactivity of alkenes & alkynes compare to that of alkanes?

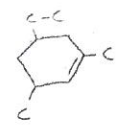
Where do reactions occur? Why?

Prior Knowledge – Prep for Lab #8 Ethyne

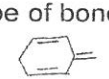
1. Double Replacement reactions in General Chemistry, what happens?
2. Example:
   A. $Na_3PO_4 + CaBr_2 \rightarrow$??
   B. How decide subscripts? Important to be able to balance.
3. Water breaks into what ions?
4. Indicators – what are they?
   A. Discuss phenolphthalein.

Review #2 Bond Arrangement & Names

1. Draw the abbreviated formula for 2,2-dimethyl-3-hexene:
2. Name



3. What is the type of bond arrangement in the following? Ⓐ



Ⓑ C≡C-C-C≡C

Ⓒ C≡C-C=C-C

Review #3 E-Z, Cis-Trans

1. Draw (Z)-3-methyl-2-pentene
2. Name

(A) 

(B) 

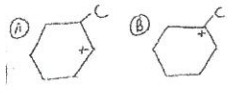
3. Quiz Overview:
   A. 8 Name & 8 Draw (any formula type)
   B. E-Z, Cis-Trans
   C. No boat/chair (use dash wedge)

Review #4 Halogenation & Carbocations

1. What 2 molecules combine to get:
   A. $CH_3CH_2CHBrCHBrCH_2CH_3$

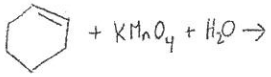
   B. $CH_3CH_2CH_2CHBrCH_2CH_3$

2. Classify:



Review #5 $KMnO_4$

1. Complete the following equation:



2. What observations would be made as reaction occurred?

3. What other tests could be used for the same purpose?

Quiz #2 Overview

1. Alkenes, NOT alkynes
2. All covered so far (not free radicals)
3. Equations-show all reactants, catalysts, products. Products must reflect cis-trans orientation.
4. Dienes: Watch for conjugation
   A. 1,2 & 1,4 addition
   B. 1 vs. 2 moles of reactant
5. Classify carbocations
6. Resonate-show structures
7. All will be skeletal or abbreviated
8. Review objectives #7, 8, 10 (Alkenes only)