

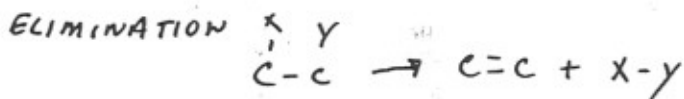
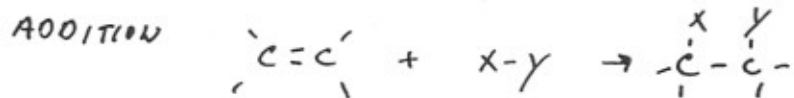
REACTIONS OF ALKENES

IN A WORD, ADDITION

ELECTROPHILES WILL ADD TO THE DOUBLE BOND TO FORM ADDITION PRODUCTS.

THE FORMATION OF 2 NEW σ BONDS IS EXOTHERMIC

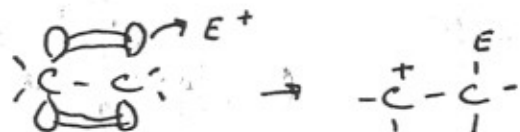
IN MANY WAYS ADDITION IS THE REVERSE OF ELIMINATION



ELECTROPHILIC ADDITION TO ALKENES

1) STRONG ELECTROPHILES PULL THE ELECTRONS OUT OF A π BOND TO FORM A NEW σ BOND

A CARBOCATION RESULTS



2) THE CARBOCATION THEN DOES WHAT CARBOCATIONS DO

REACT WITH A NUCLEOPHILE AS IN A $\text{S}_{\text{N}}1$ REACTION

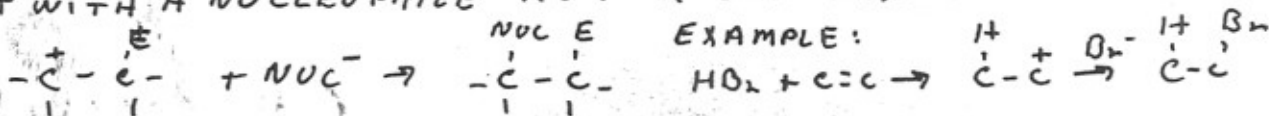


TABLE 8-1 Types of Additions to Alkenes

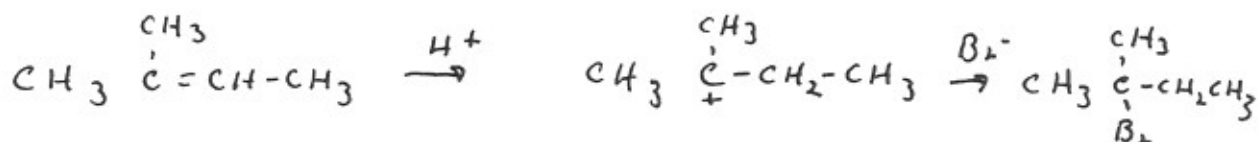
| | $\text{C}=\text{C}$ | Type of Addition [Elements Added] ^a | Product |
|---|---|---|---|
| hydration [H ₂ O] | $\begin{array}{c} \text{H} \quad \text{OH} \\ \quad \\ -\text{C}-\text{C}- \\ \quad \end{array}$ | | halogenation [X ₂], an oxidation |
| hydrogenation [H ₂], a reduction | $\begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ -\text{C}-\text{C}- \\ \quad \end{array}$ | | halohydrin formation [HOX], an oxidation |
| hydroxylation [HOOH], an oxidation | $\begin{array}{c} \text{OH} \quad \text{OH} \\ \quad \\ -\text{C}-\text{C}- \\ \quad \end{array}$ | | HX addition [HX] |
| oxidative cleavage [O ₂], an oxidation | $\begin{array}{c} \text{C}=\text{O} \quad \text{O}=\text{C} \\ \diagdown \quad \diagup \\ \text{O} \end{array}$ | | cyclopropanation [CH ₂] |
| epoxidation [O], an oxidation | $\begin{array}{c} \text{O} \\ \diagdown \quad \diagup \\ -\text{C}-\text{C}- \\ \quad \end{array}$ | | |

^aThese are not the reagents used but simply the groups that appear in the product.

ADDITION OF HYDROGEN HALIDES

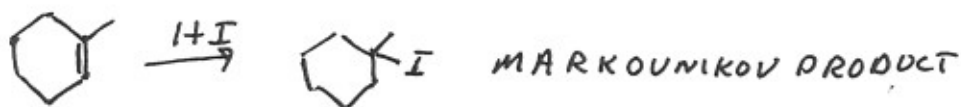
HYDROGEN HALIDES ADD TO DOUBLE BONDS REGIOSPECIFICALLY

A PROTON ADDS FIRST AND FORMS THE MOST STABLE CATION



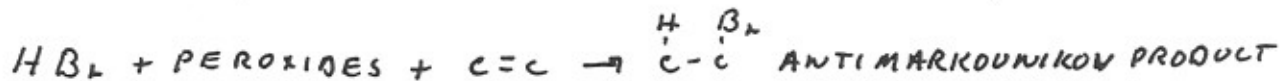
MARKOVNIKOV'S RULE SAYS THAT THE PROTON WILL ADD TO THE CARBON THAT ALREADY HAS THE MOST HYDROGENS - THIS LEAVES THE CATION ON THE CARBON WITH THE MOST CARBONS WHICH IS THE MOST STABLE CATION

HCl AND HI REACT THE SAME WAY

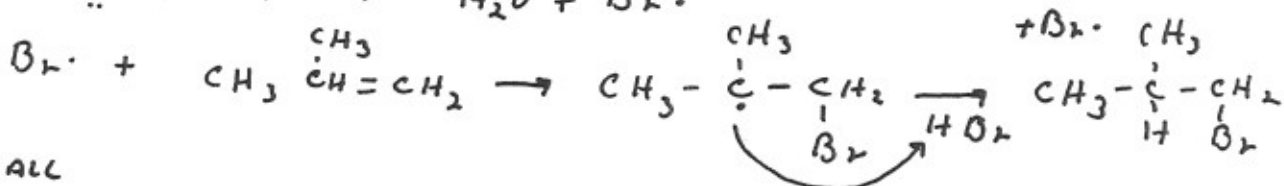


FREE RADICAL ADDITION

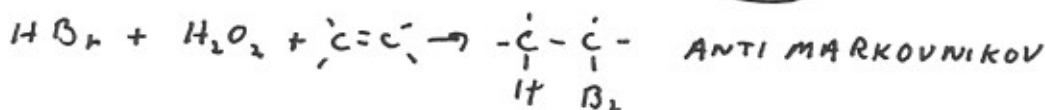
WITH FREE RADICAL ADDITION OF HBr THE ELECTROPHILE IS Br^\cdot IT ADDS THE SAME WAY, BUT IT ADDS FIRST, A H^\cdot SECOND THIS RESULTS IN THE ANTI-MARKOVNIKOV PRODUCT (ONLY HBr DOES THIS)



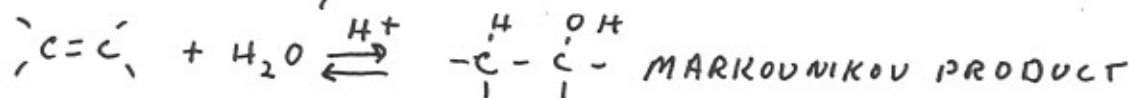
PEROXIDES ARE OFTEN USED AS FREE RADICAL INITIATORS



OVERALL



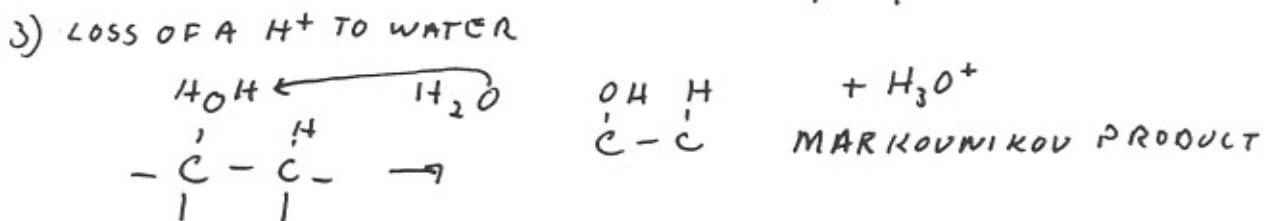
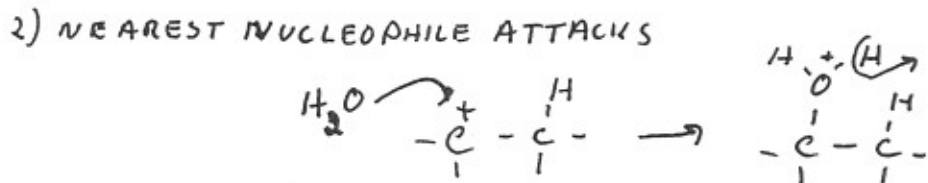
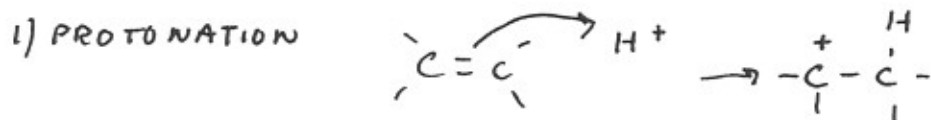
ADDITION OF WATER: HYDRATION



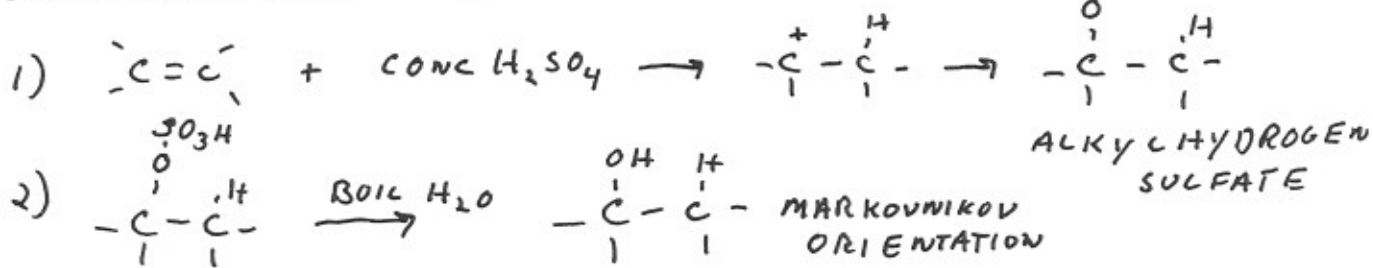
—————→ HYDRATION

DEHYDRATION ←————

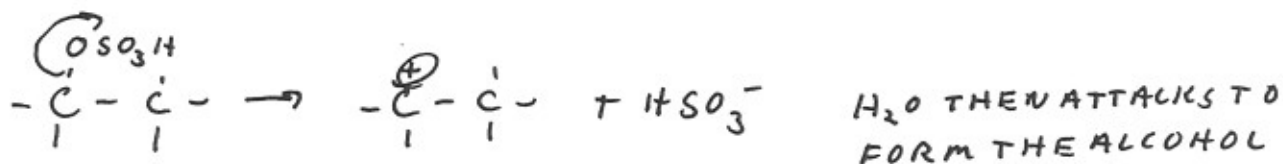
HYDRATION AND DEHYDRATION REALLY ARE REVERSIBLE
THE MECHANISM IS THE REVERSE OF CHAPTER 7



HOWEVER, MANY ALKENES ARE INSOLUBLE IN H_2O , OR THE
EQUILIBRIUM STRONGLY DISFAVORS THE ALCOHOL
SOME USE INDIRECT METHODS



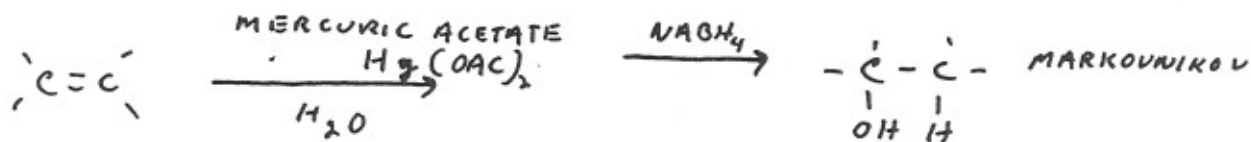
THIS STEP IS AN $\text{S}_{\text{N}}1$ REACTION, HSO_4^- IS THE LEAVING GROUP



MOST USEFUL OF ALL (HIGH YIELD, NO C^+ REARRANGEMENTS)

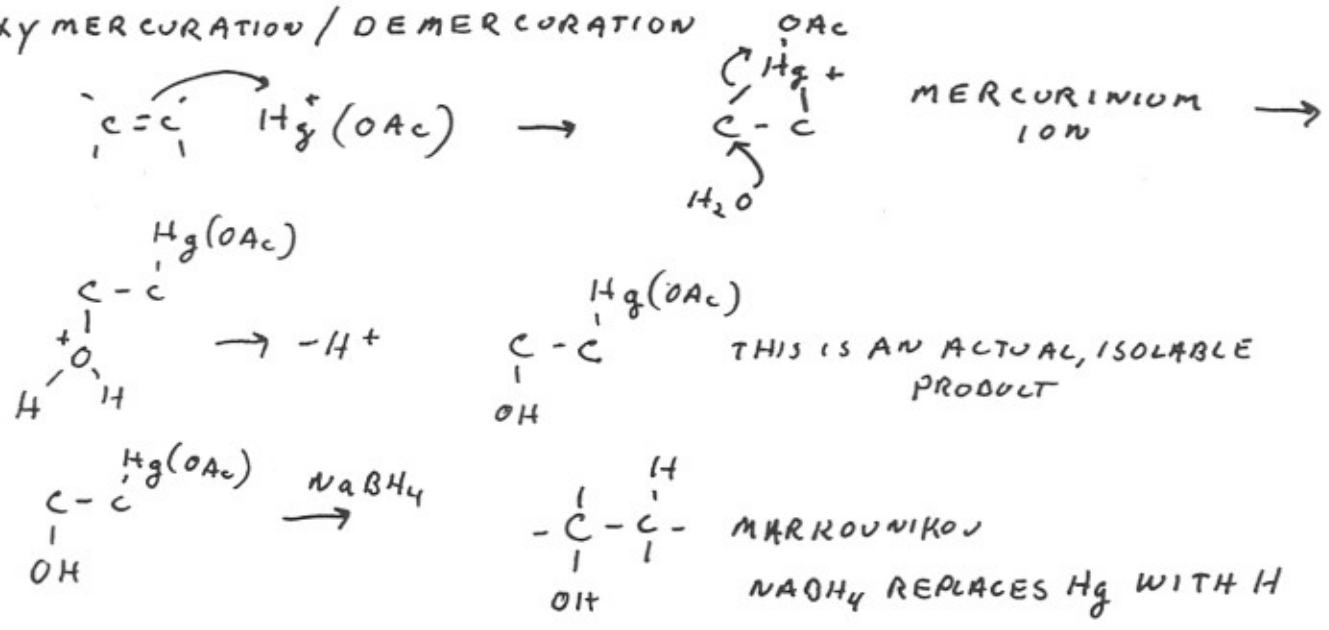
IS OXYMERCURATION/DEMERCURATION

ITS A TWO STEP REACTION WITH SOME EXOTIC REAGENTS, INTERMEDIATES
THAT PRODUCES A MARKOVNIKOV PRODUCT WITHOUT REARRANGEMENTS



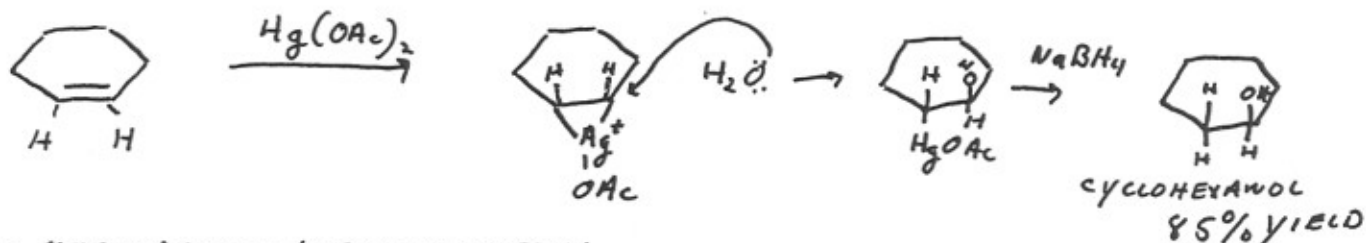
NaBH_4 IS SODIUM BOROHYDRIDE, A REDUCING AGENT

OXY MERCURATION / DEMERCURATION



THIS REACTION IS STEREO SPECIFIC

THE CYCLIC STRUCTURE OF THE MERCURY ADDUCT FORCES "ANTI" ADDITION OF OH

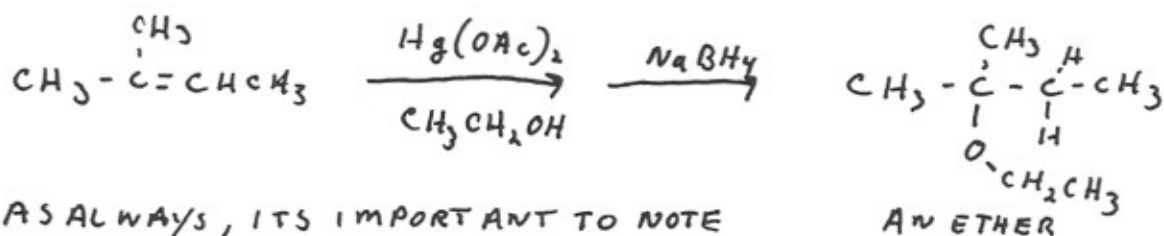


ALKOXY MERCURATION / DEMERCURATION

JUST PICTURE THE ABOVE REACTION IN AN ALCOHOL SOLVENT R-OH INSTEAD OF WATER

YOU GET THE SAME TYPE OF PRODUCT WITH A CARBON GROUP ATTACHED TO THE OXYGEN - AN ETHER

THIS IS ADDITION OF AN ALCOHOL TO THE DOUBLE BOND RO-H



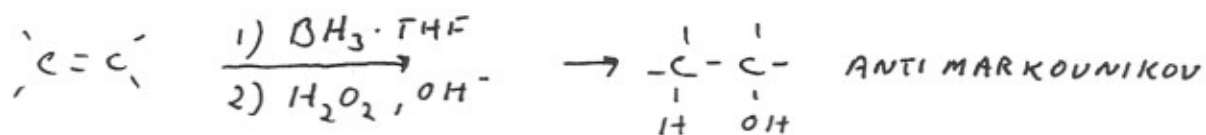
AS ALWAYS, ITS IMPORTANT TO NOTE THE DANGER FROM MERCURY TOXICITY

IN ALL ITS FORMS, METAL, ALKYL MERCURY ($\text{Hg}(\text{CH}_3)_2$) OR MERCURIC SALTS LIKE $\text{Hg}(\text{OAc})_2$, MERCURY IS DANGEROUSLY TOXIC

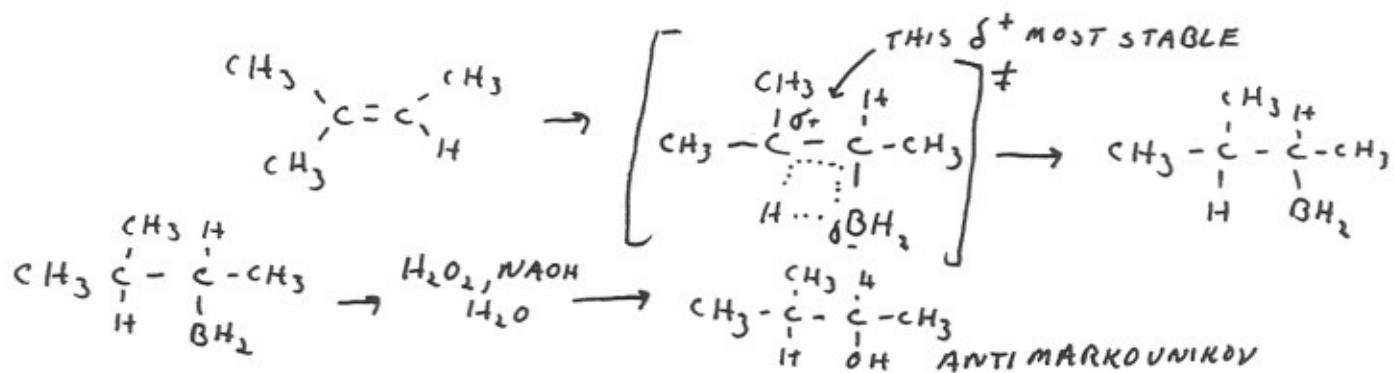
$\text{Hg}(\text{CH}_3)_2$ EVEN PENETRATES LATEX GLOVES!

HYDROBORATION / OXIDATION

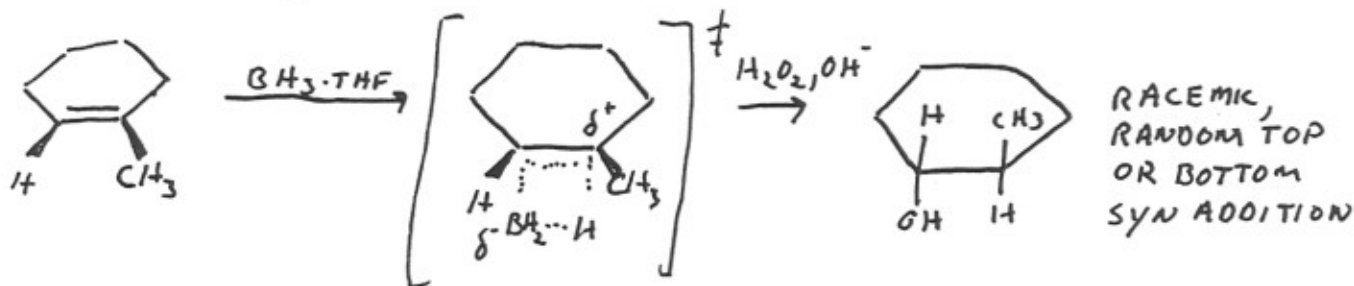
MAKE ANTI-MARKOVNIKOV ALCOHOLS FROM ALKENES



THIS REACTION INVOLVES A CYCLIC INTERMEDIATE:



THE STEREO SPECIFICITY OF THE REACTION IS SYN ADDITION



HYDROGENATION

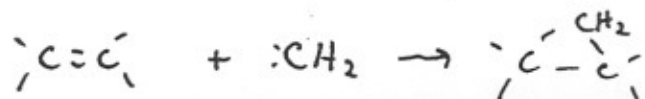
REDUCTION OF AN ALKENE (ALKYNE, C=O) WITH H_2 / CATALYST

HYDROGEN ADSORBED ON A METAL SURFACE ADDS TO ONE "FACE" OF THE DOUBLE BOND, USUALLY RANDOM "FACE", BUT OCCASIONALLY ONE FACE IS PREFERRED FIG 5-23

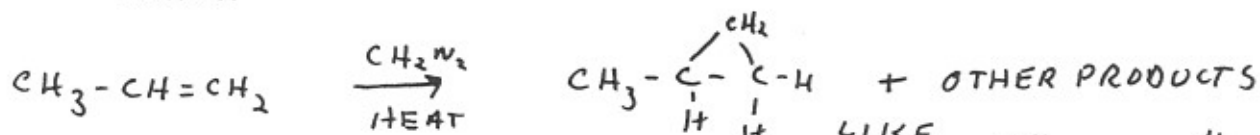
IT IS ALSO POSSIBLE TO USE CHIRAL CATALYSTS FOR ASYMMETRIC INDUCTION PG 219

CARBENES

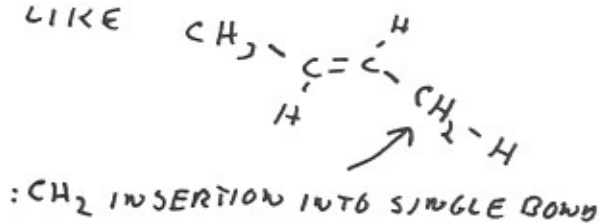
$:\text{CH}_2$ IS METHYLENE, THE SIMPLEST CARBENE. IT ADDS TO DOUBLE BONDS TO MAKE CYCLOPROPANES



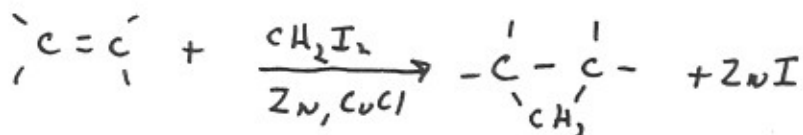
THE ORIGINAL CARBENE REACTION USES DIAZOMETHANE CH_2N_2



THIS, PLUS THE TOXIC, EXPLOSIVENESS OF CH_2N_2 LIMITS ITS USEFULNESS



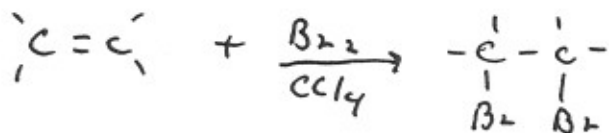
A BETTER REACTION IS THE SIMMONS-SMITH REACTION



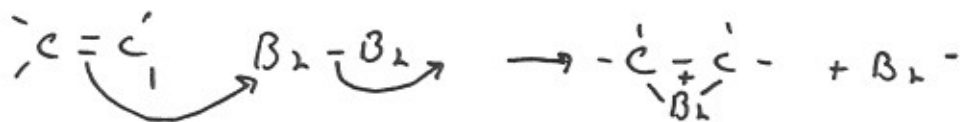
THIS IS THE PREFERRED METHOD FOR MAKING CYCLOPROPANES

ADDITION OF HALOGENS

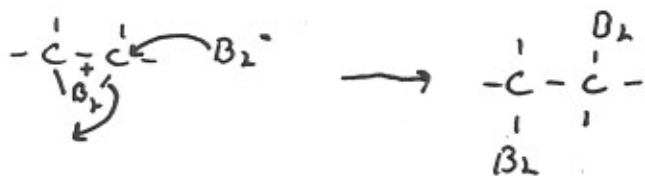
PG 355 SHOWS A PICTURE OF RED/BROWN BROMINE (Br_2) BEING "DECOLORIZED" BY AN ALKENE



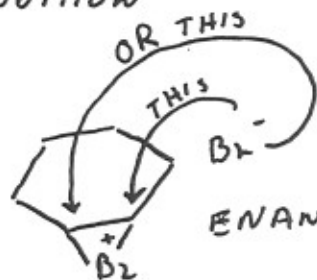
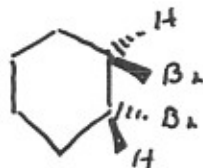
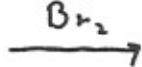
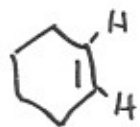
THE MECHANISM OF THIS REACTION INVOLVES A "CYCLIC BROMONIUM ION" OR CYCLIC "HALONIUM" ION IF Cl_2 OR I_2 ARE USED



THIS CYCLIC ION IS OPENED BY BROMIDE



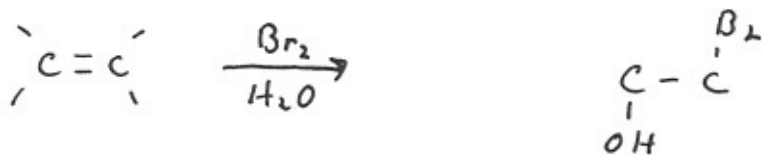
STEREOSPECIFIC ANTI ADDITION



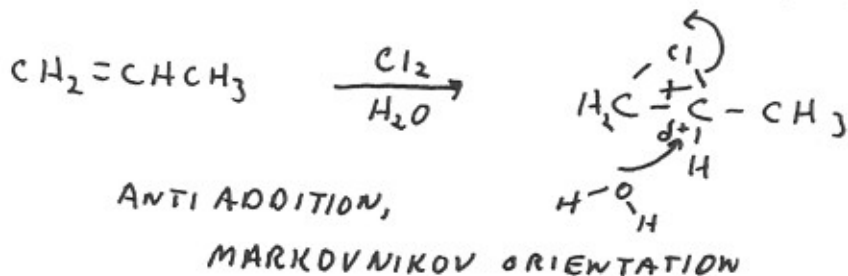
OR THIS ENANTIOMERS

HALOHYDRINS

HALOGENS PLUS WATER ADD TO ALKENES TO FORM HALOHYDRINS



A HALONIUM ION IS INVOLVED, SO STEREOCHEMISTRY IS ANTI MARKOVNIKOV ORIENTATION IS ALSO OBSERVED

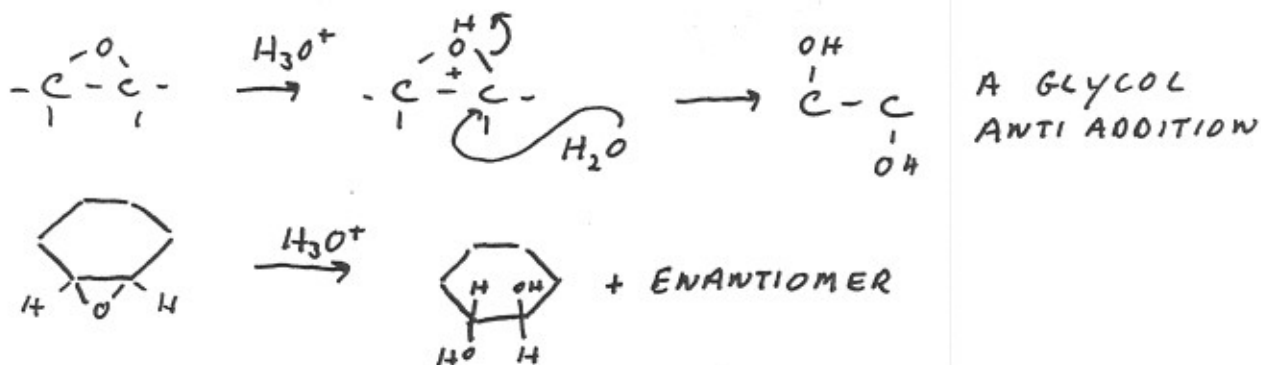


WHILE THE WHOLE RING BEARS A + CHARGE, MORE PARTIAL + IS ON THE MORE SUBSTITUTED CARBON

EPOXIDATION

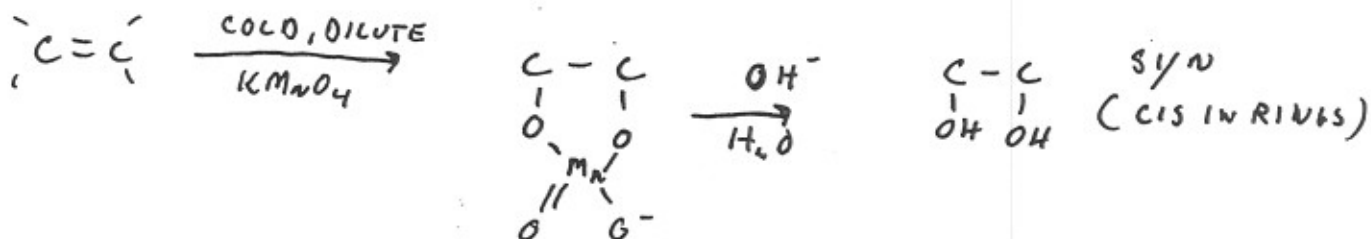


ACID CATALYSED OPENING OF EPOXIDES



WE CAN ALSO MAKE SYN GLYCOLS WITH O₃O₄, OSMIUM TETROXIDE OR KMnO₄ (COLD, DILUTE) POTASSIUM PERMANGANATE

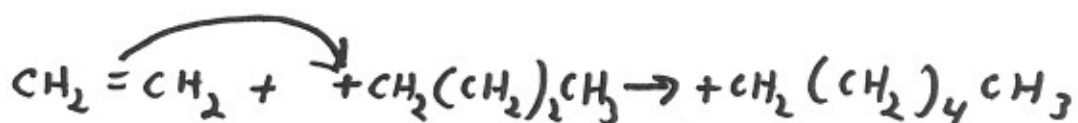
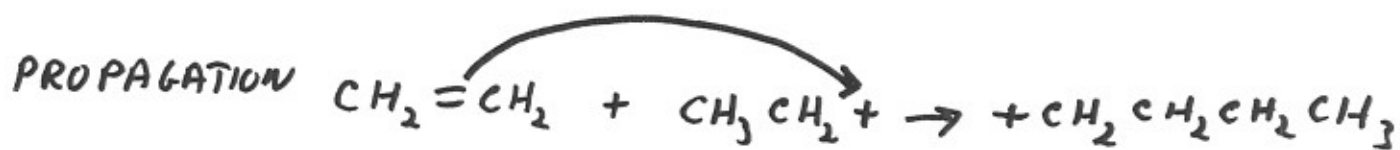
A CYCLIC INTERMEDIATE ENSURES SYN HYDROXYLATION



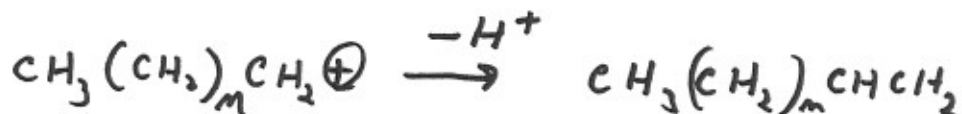
CATIONIC POLYMERIZATION

ACID CATALYSED, CATIONIC INTERMEDIATES

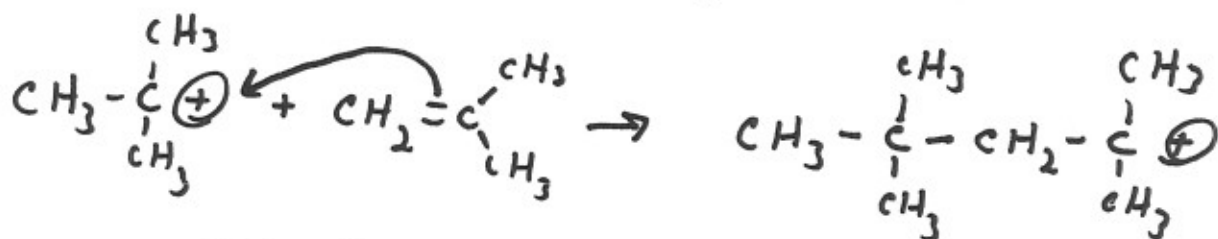
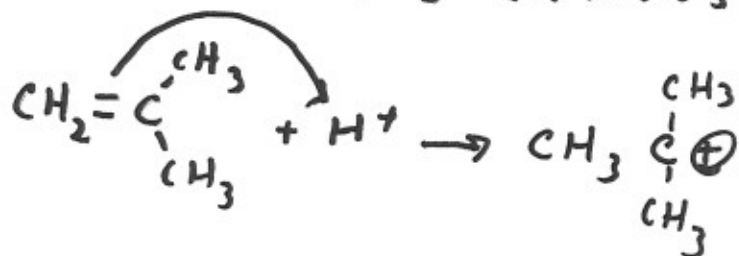
ANOTHER EXAMPLE OF ELECTROPHILIC ADDITION TO AN ALKENE:



THE GROWING CHAIN TERMINATES WHEN A CATION ELIMINATES A PROTON



WORKS BEST WITH 3° CATIONS



THIS POLYMER IS CALLED BUTYL RUBBER

CHAPTER 11

SHOW THE PRODUCTS
OF ADDITION REACTIONS
INC. STEREOCHEM & REGIOCHEM

30-35, 45, 56

WORK WITH ALKYNE REACTIONS

32, 33

MECHANISMS OF ELECTROPHILIC
ADDITION

36, ~~49~~ 39, 41, 42

WATCH FOR REARRANGEMENTS

32F, 33C

UNDERSTAND CONJUGATE ADDITION

33b

USE THESE REACTIONS FOR
SYNTHESIS

37, 38