

CHAPTER 8 LECTURE NOTES FOR ORGANIC CHEMISTRY ©MM 2011

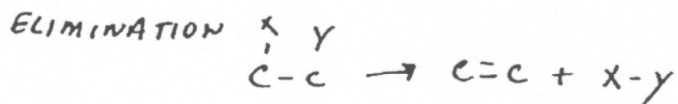
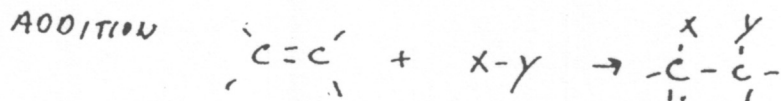
REACTIONS OF ALKENES AND ALKYNES

IN A WORD, ADDITION

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

THE FORMATION OF 2 NEW σ BONDS IS EXOTHERMIC

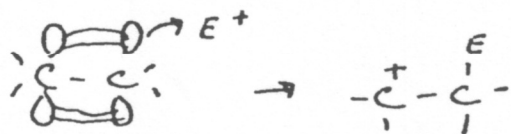
IN MANY WAYS ADDITION IS THE REVERSE OF ELIMINATION



ELECTROPHILIC ADDITION TO ALKENES

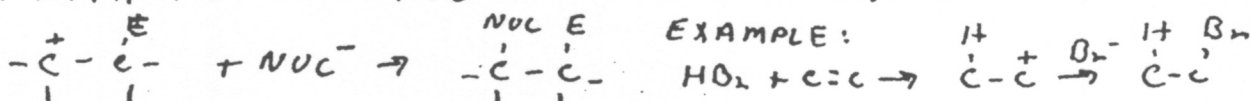
1) STRONG ELECTROPHILES PULL THE ELECTRONS OUT OF A π BOND TO FORM A NEW σ BOND

A CARBOCATION RESULTS



2) THE CARBOCATION THEN DOES WHAT CARBOCATIONS DO

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



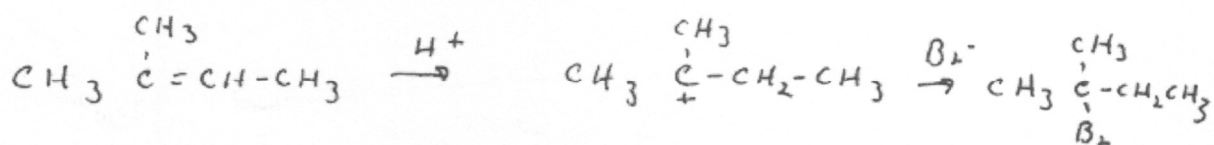
	Type of Addition [Elements Added] ^a	Product
hydration [H ₂ O]	$\begin{array}{c} \text{H} \quad \text{OH} \\ \quad \\ -\text{C}-\text{C}- \\ \quad \end{array}$	halogenation [X ₂], an oxidation
hydrogenation [H ₂], a reduction	$\begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ -\text{C}-\text{C}- \\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

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

ADDITION OF HYDROGEN HALIDES

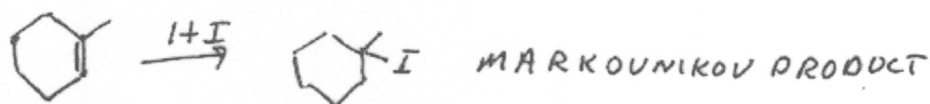
HYDROGEN HALIDES ADD TO DOUBLE BONDS REGIOSPECIFICALLY

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

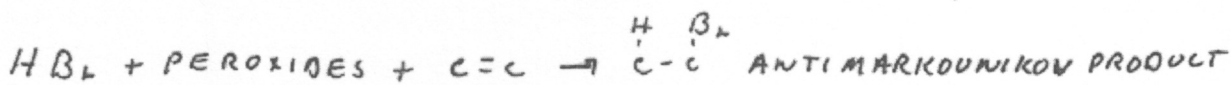
HCl AND HI REACT THE SAME WAY



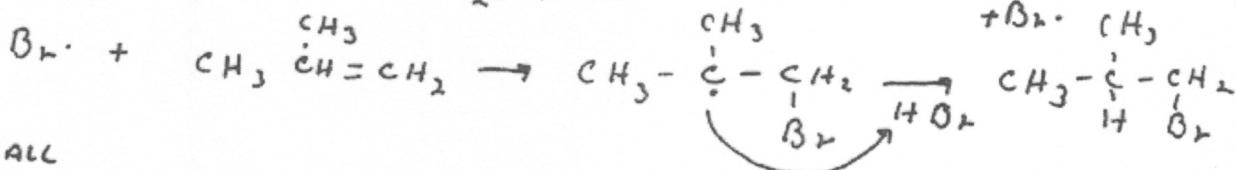
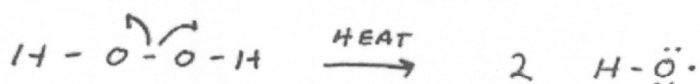
FREE RADICAL ADDITION

WITH FREE RADICAL ADDITION OF HBr THE ELECTROPHILE IS Br^\cdot IT ADDS THE SAME WAY, BUT IT ADDS FIRST, A H^\cdot SECOND

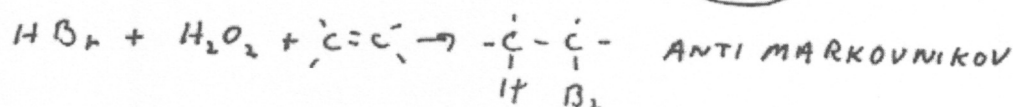
THIS RESULTS IN THE ANTI-MARKOVNIKOV PRODUCT (ONLY HBr DOES THIS)



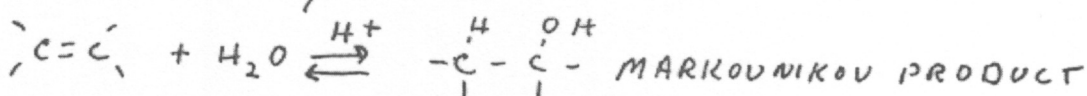
PEROXIDES ARE OFTEN USED AS FREE RADICAL INITIATORS



OVERALL



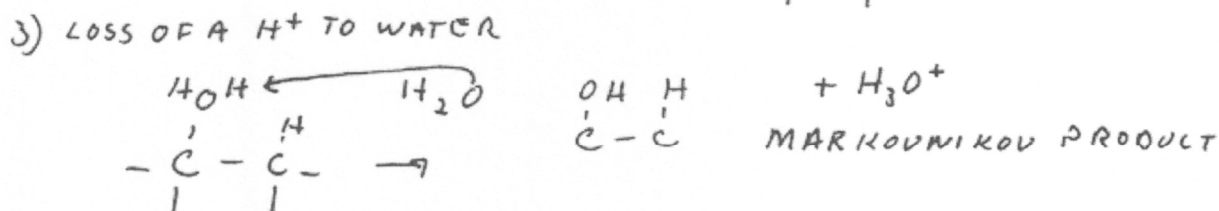
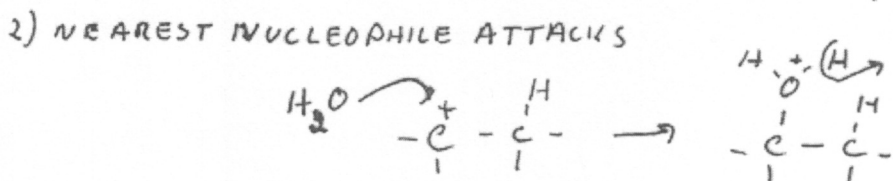
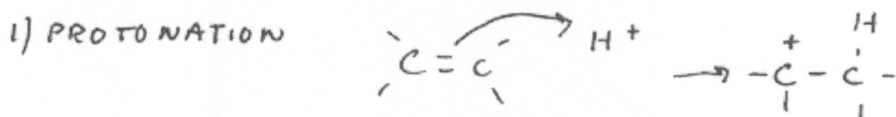
ADDITION OF WATER: HYDRATION



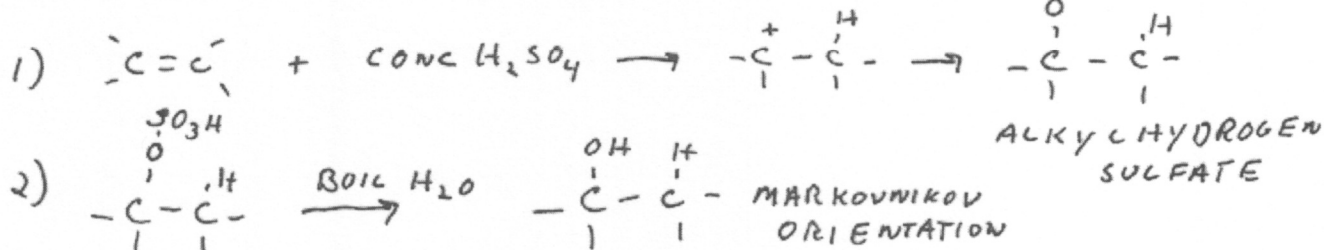
—————→ HYDRATION

DEHYDRATION ←————

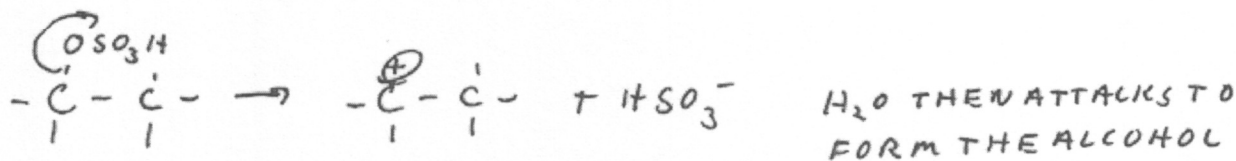
HYDRATION AND DEHYDRATION REALLY ARE REVERSIBLE
THE MECHANISM IS THE REVERSE OF CHAPTER 7



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



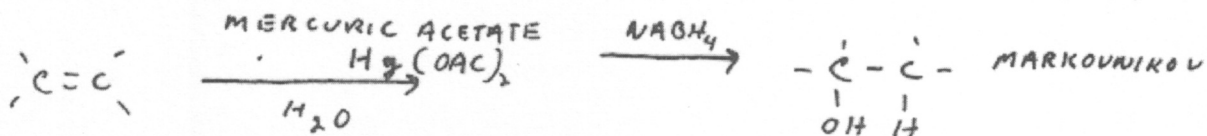
THIS STEP IS AN $\text{S}_{\text{N}}1$ REACTION, HSO_4^- IS THE LEAVING GROUP



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

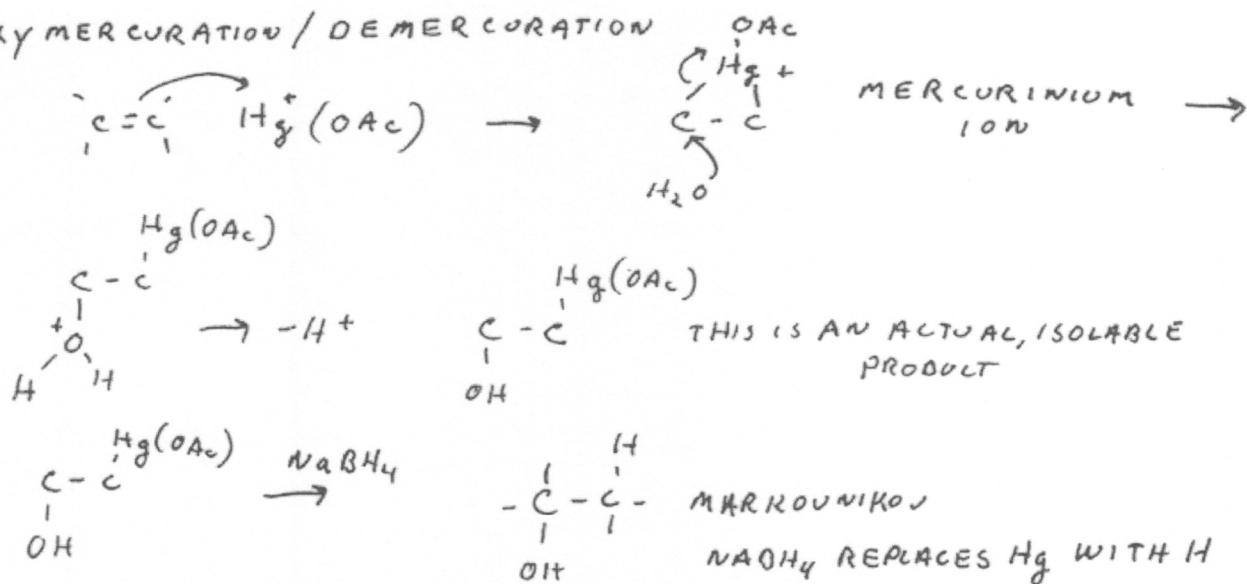
IS OXYMERCURATION/DEMERCURATION

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



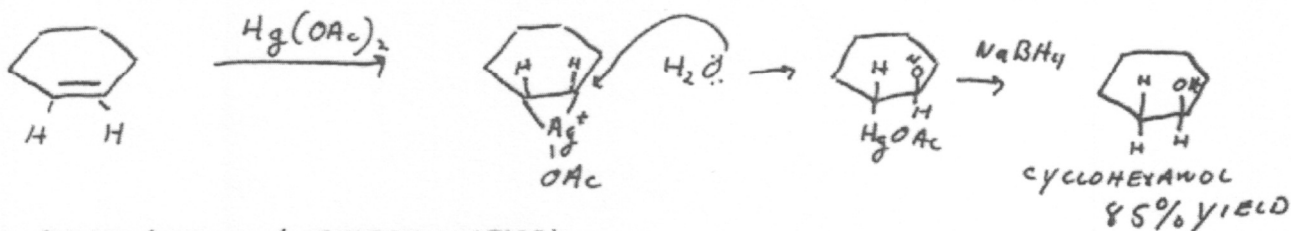
NaBH_4 IS SODIUM BOROHYDRIDE, A REDUCING AGENT

OXYMERCURATION / DEMERCURATION



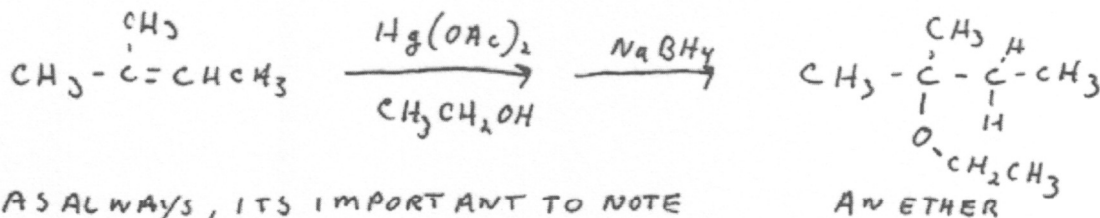
THIS REACTION IS STEREO SPECIFIC

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



ALKOXY MERCURATION / DEMERCURATION

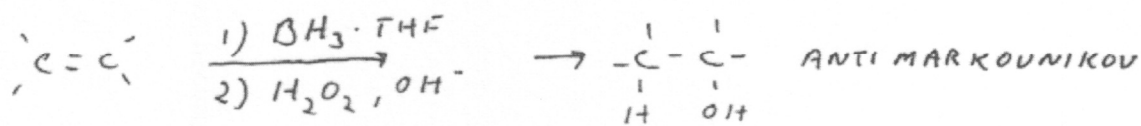
JUST PICTURE THE ABOVE REACTION IN AN ALCOHOL SOLVENT R-OH INSTEAD OF WATER
 YOU GET THE SAME TYPE OF PRODUCT WITH A CARBON GROUP ATTACHED TO THE OXYGEN - AN ETHER
 THIS IS ADDITION OF AN ALCOHOL TO THE DOUBLE BOND RO-H



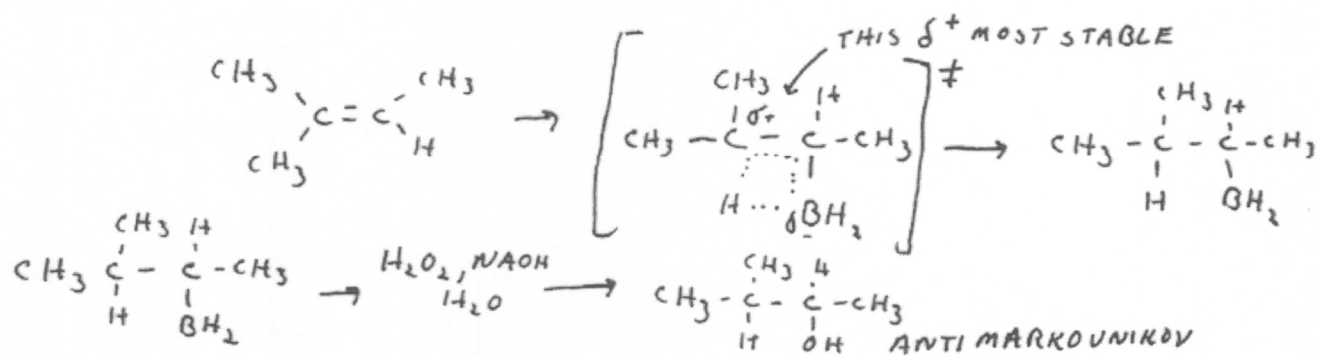
AS ALWAYS, ITS IMPORTANT TO NOTE THE DANGER FROM MERCURY TOXICITY IN ALL ITS FORMS, METAL, ALKYL MERCURY (Hg(CH₃)₂) OR MERCURIC SALTS LIKE Hg(OAc)₂, MERCURY IS DANGEROUSLY TOXIC Hg(CH₃)₂ EVEN PENETRATES LATEX GLOVES!

HYDROBORATION / OXIDATION

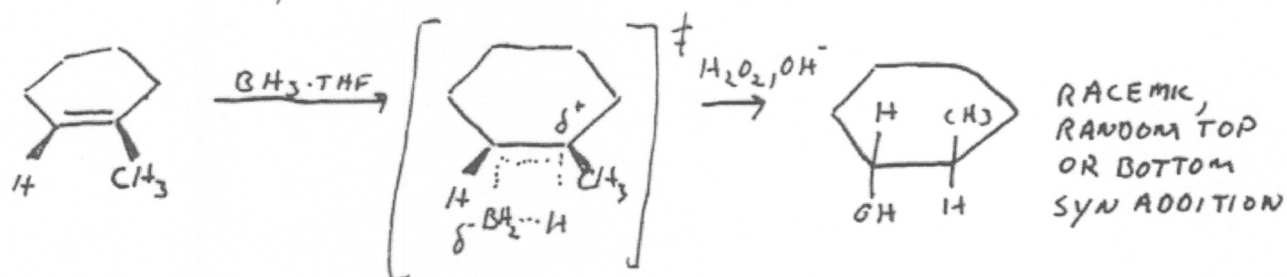
MAKE ANTI-MARKOVNIKOV ALCOHOLS FROM ALKENES



THIS REACTION INVOLVES A CYCLIC INTERMEDIATE:



THE STEREO SPECIFICITY OF THE REACTION IS syn ADDITION



HYDROGENATION

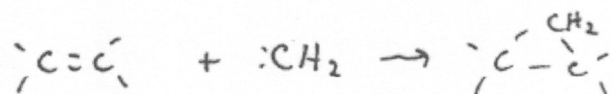
REDUCTION OF AN ALKENE (ALKYNE, C=O) WITH H_2 / CATALYST

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

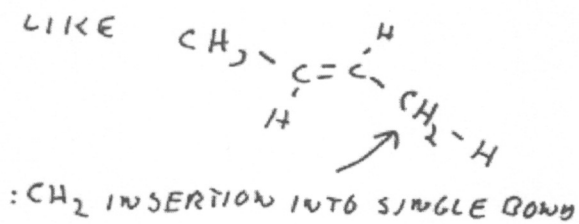
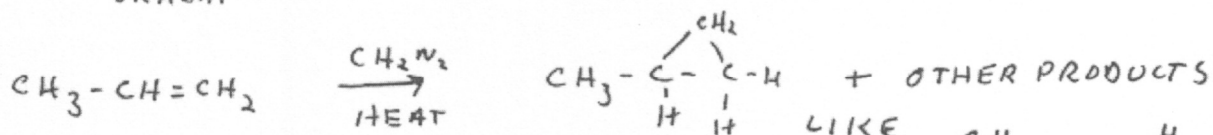
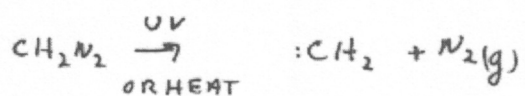
IT IS ALSO POSSIBLE TO USE CHIRAL CATALYSTS FOR ASYMMETRIC INDUCTION PG 219

CARBENES

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

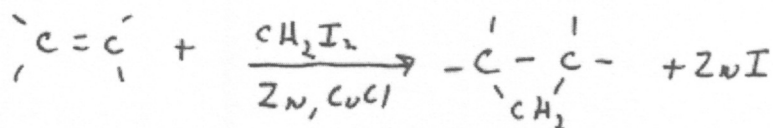


THE ORIGINAL CARBENE REACTION USES DIAZOMETHANE CH_2N_2



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

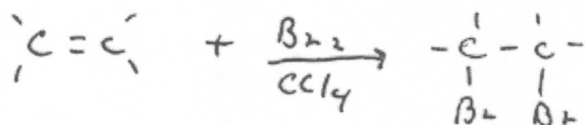
A BETTER REACTION IS THE SIMMONS-SMITH REACTION



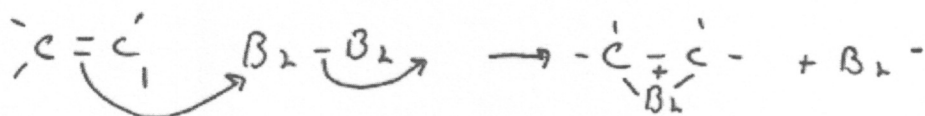
THIS IS THE PREFERRED METHOD FOR MAKING CYCLOPROPANES

ADDITION OF HALOGENS

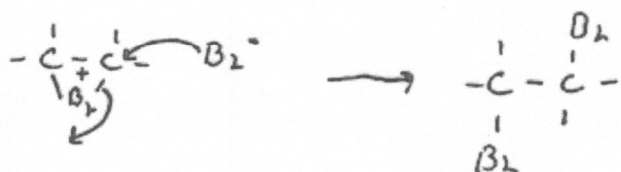
Br_2 BEING "DECOLORIZED" BY AN ALKENE



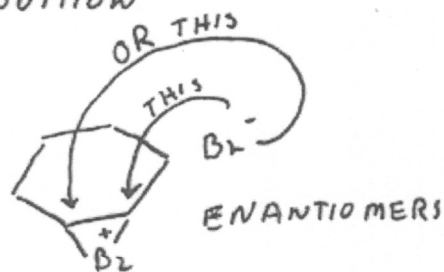
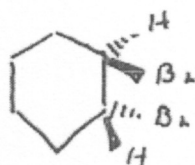
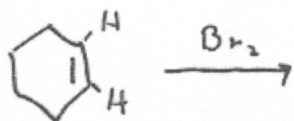
THE MECHANISM OF THIS REACTION INVOLVES A "CYCLIC BROMONIUM ION" OR CYCLIC "HALONIUM" ION IF Cl_2 OR I_2 ARE USED



THIS CYCLIC ION IS OPENED BY Br^- ION

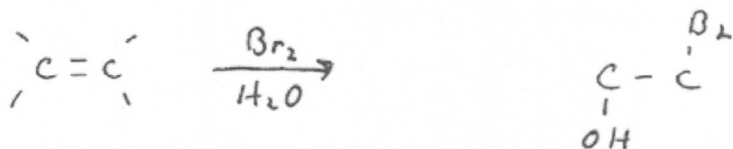


STEREOSPECIFIC ANTI ADDITION

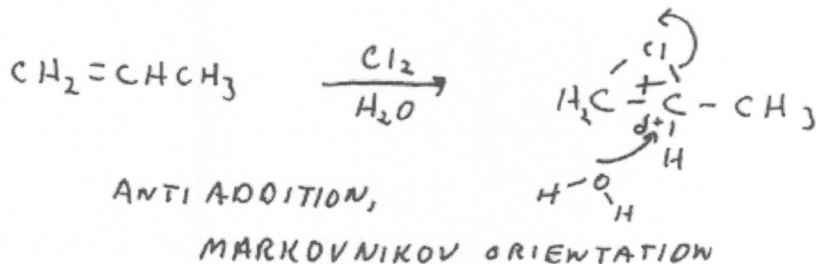


HALOHYDRINS

HALOGENS PLUS WATER ADD TO ALKENES TO FORM HALOHYDRINS



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

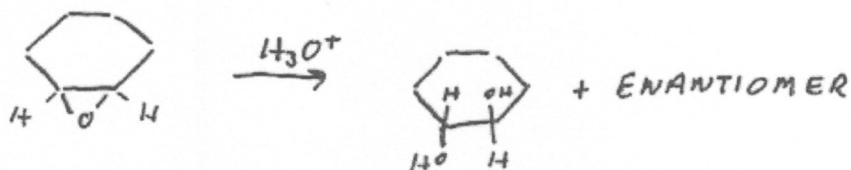
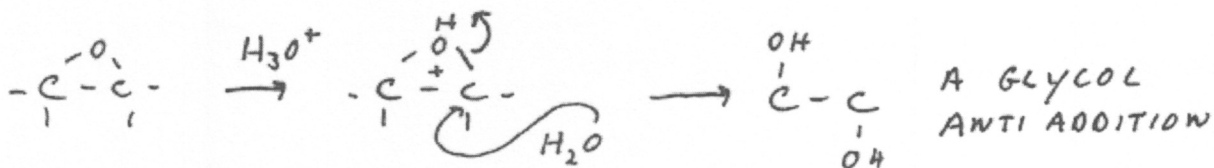


WHILE THE WHOLE RING
BEARS A + CHARGE,
MORE PARTIAL + IS
ON THE MORE
SUBSTITUTED CARBON

EPOXIDATION

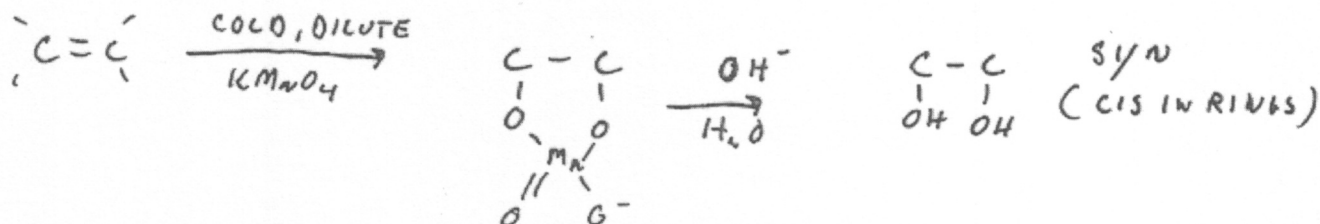


ACID CATALYSED OPENING OF EPOXIDES

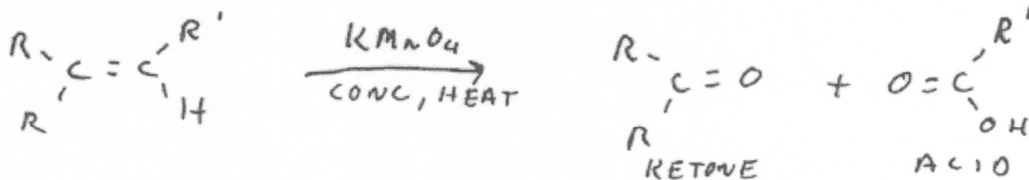


WE CAN ALSO MAKE SYN GLYCOLS WITH OsO_4 OSMIUM TETROXIDE
OR KMnO_4 (COLD, DILUTE) POTASSIUM PERMANGANATE

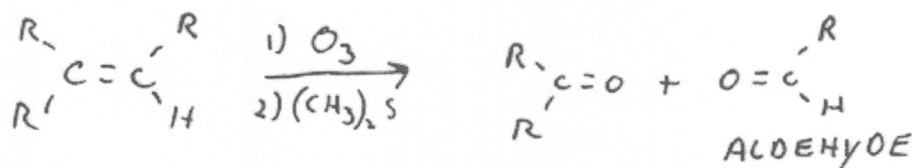
A CYCLIC INTERMEDIATE ENSURES SYN HYDROXYLATION



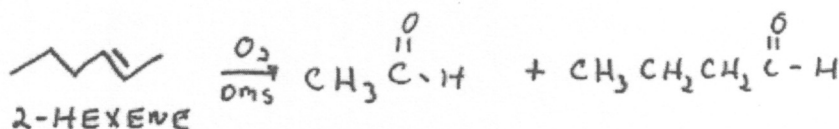
OXIDATIVE CLEAVAGE



OR OZONOLYSIS (MILDER)

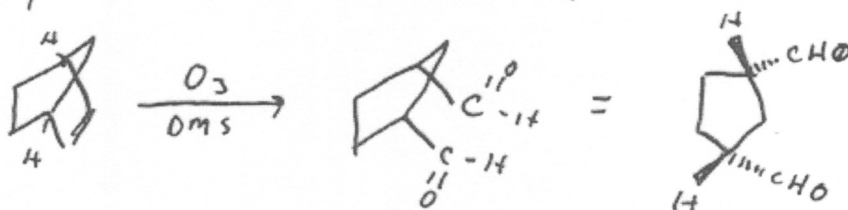


EXAMPLES



ANY C=C IS REPLACED BY C=O AND C=O

THE OZONOLYSIS INTERMEDIATE IS CYCLIC, SYN PRODUCTS RESULT

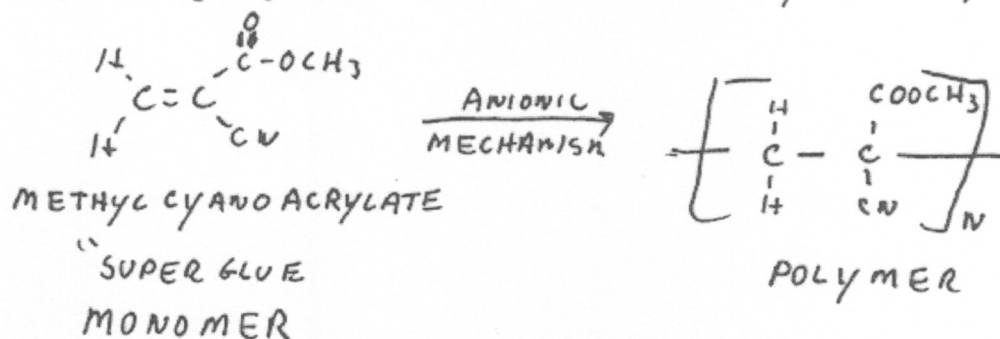


POLYMERIZATION

ITS ARGUABLY THE MOST IMPORTANT REACTION OF ALKENES / EPOXIDES

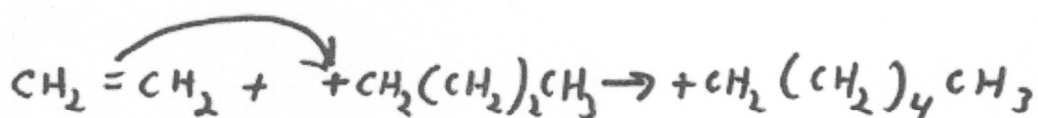
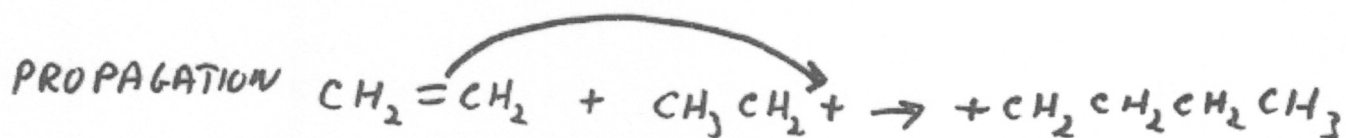
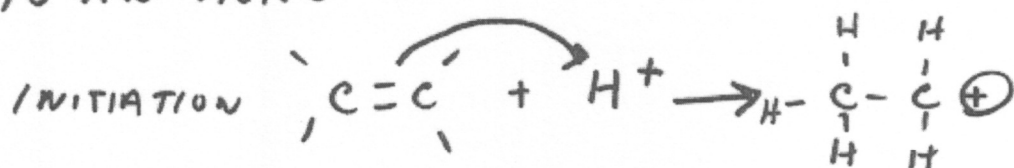
POLYMERS ARE LARGE (MW 10,000 → >1,000,000) MOLECULES MADE FROM REPEATING UNITS (MONOMERS)

MECHANISMS ARE CHAIN REACTIONS, ANIONIC, CATIONIC, FREE RADICAL

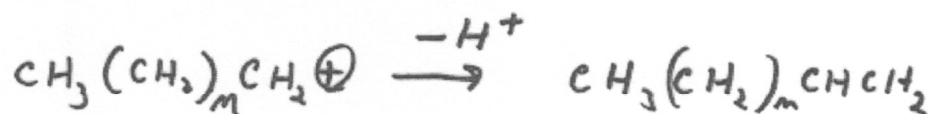


CATIONIC POLYMERIZATION

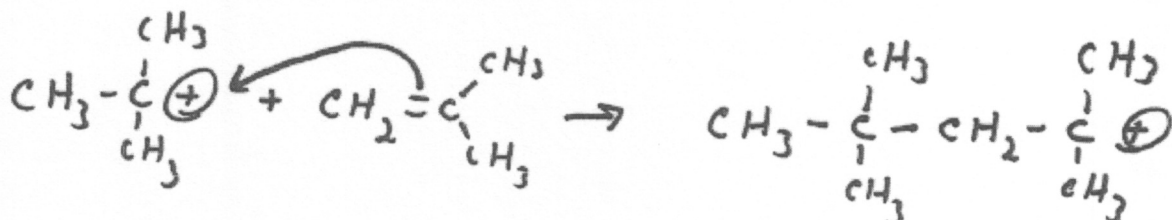
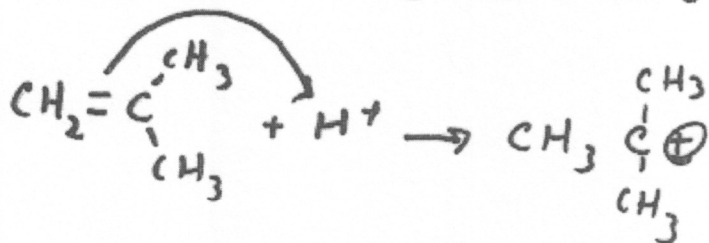
ACID CATALYSED, CATIONIC INTERMEDIATES
ANOTHER EXAMPLE OF ELECTROPHILIC ADDITION
TO AN ALKENE:



THE GROWING CHAIN TERMINATES WHEN A CATION
ELIMINATES A PROTON



WORKS BEST WITH 3° CATIONS



THIS POLYMER IS CALLED BUTYL RUBBER

ALKYNES

ALKYNES CONTAIN THE TRIPLE BOND $-C\equiv C-$ 2^o UNSATURATION
OFTEN NAMED AS ACETYLENES (COMMON NAMES)

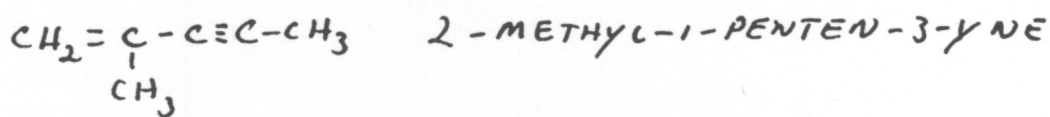
$R-C\equiv C-R \rightarrow$ A DIALKYL ACETYLENE

OR AS ALKYNES



NUMBERED AS BEFORE, FROM THE END OF THE CHAIN CLOSEST TO THE TRIPLE BOND

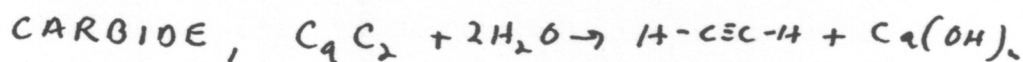
WHEN ADDITIONAL FUNCTIONAL GROUPS ARE PRESENT, SUFFIXES MAY BE COMBINED



ACETYLENE $H-C\equiv C-H$ IS THE MOST COMMON ALKYNE, USED IN OXYACETYLENE TORCHES

ITS MADE FROM NATURAL GAS: $CH_4 \xrightarrow[1500^\circ C]{}$ $H-C\equiv C-H + 3H_2$

IT ALSO COMES FROM CALCIUM



HYBRIDIZATION IS sp , LINEAR GEOMETRY AND A "CYLINDER" OF π ELECTRONS

MANY IMPORTANT REACTIONS OF ACETYLENES INVOLVE THE

ACIDITY OF ACETYLENIC HYDROGENS: $H-C\equiv C-H \rightarrow H-C\equiv C:^- + H^+$

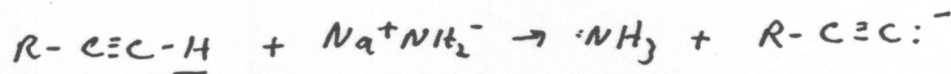
SO ITS A VERY WEAK ACID, BUT

$$pK_a \approx 25$$

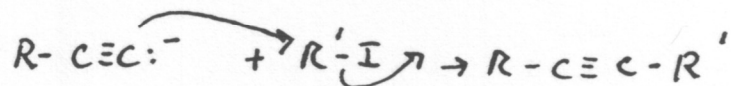
STILL STRONGER THAN OTHER

ALKANES OR ALKENES ($pK_a = 50, 40$ RESPECTIVELY)

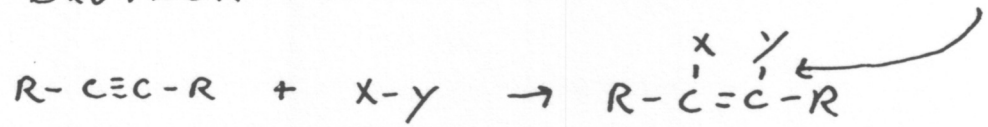
VERY STRONG BASES LIKE NH_2^- DEPROTONATE



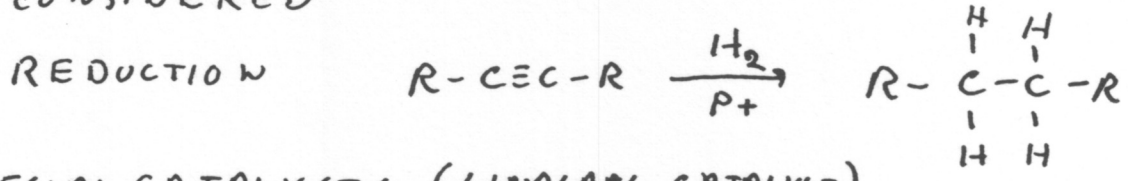
ACETYLIDES ARE STRONG NUCLEOPHILES



LIKE ALKENES, ALKYNES DO ADDITION REACTIONS
THIS EXOTHERMIC REACTION PRODUCES NEW σ BONDS

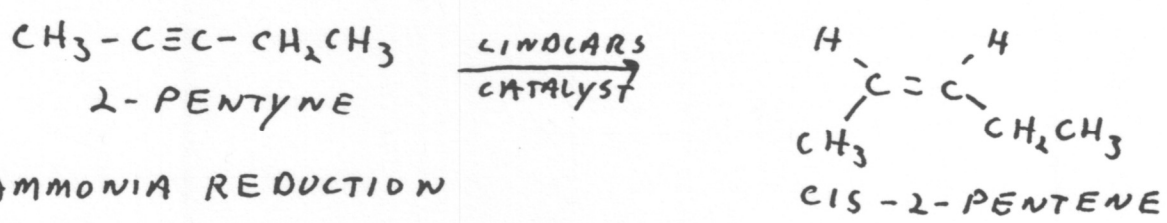
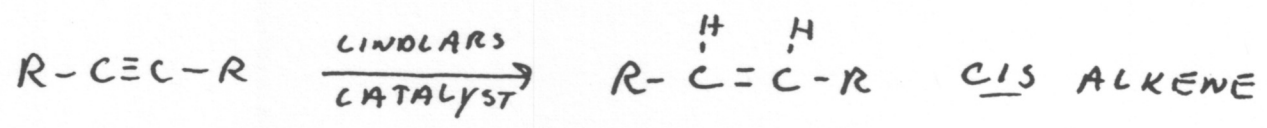


THE POSSIBILITY OF DOUBLE ADDITION REACTIONS MUST BE CONSIDERED



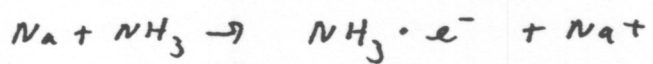
SPECIAL CATALYSTS (LINDLARS CATALYST)

ARE LESS EFFICIENT, STOP AT THE ALKENE



METAL-AMMONIA REDUCTION

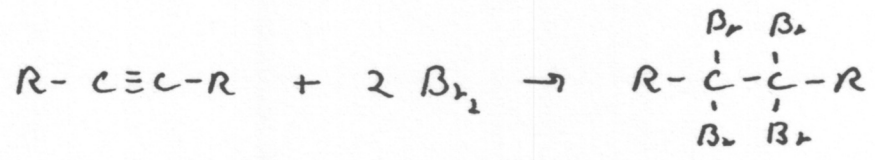
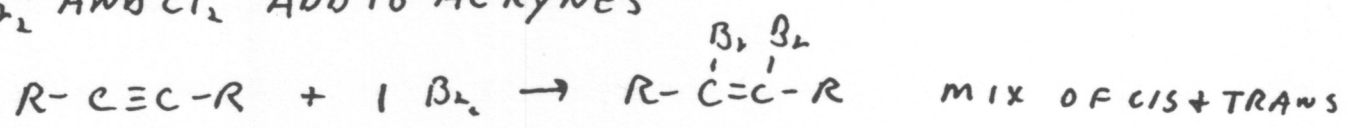
TRANS ALKENES ARE MADE WITH Na/NH_3



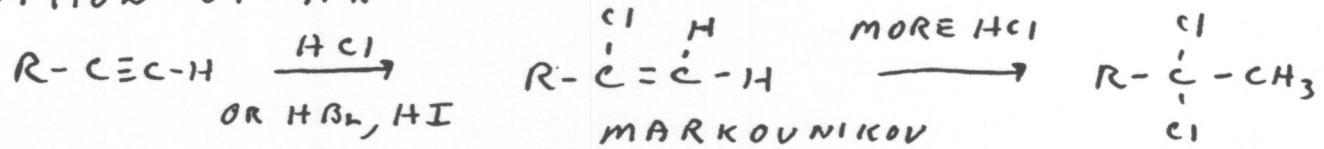
THE "SOLVATED ELECTRON", IT HAS A DEEP BLUE COLOR

ADDITION OF HALOGENS

Br_2 AND Cl_2 ADD TO ALKYNES



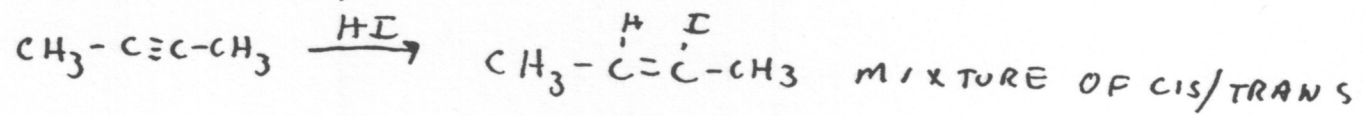
ADDITION OF HX



MARKOVNIKOV

IN BOTH CASES \rightarrow GEMINAL DIHALIDE

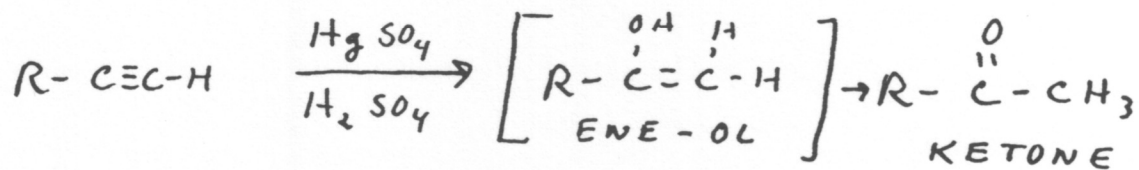
INTERNAL ALKYNES GIVE MIXTURES



HYDRATION OF ALKYNES

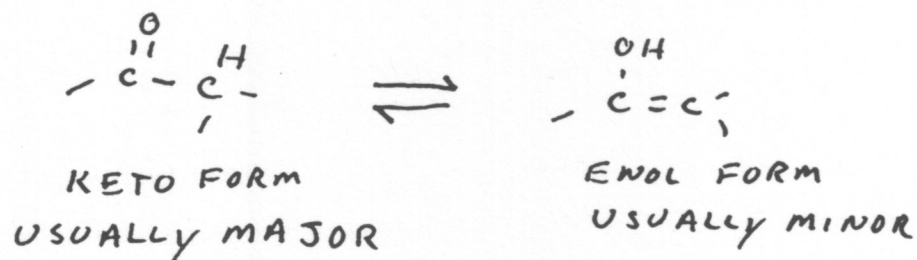
ACID CATALYSED ADDITION OF H-OH TO ALKYNES

MERCURIC ION IS USED AS A CATALYST

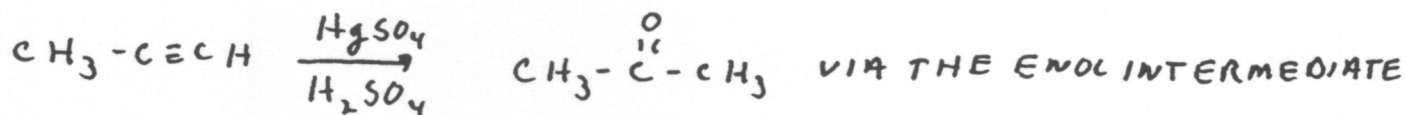


THIS IS KETO-ENOL TAUTOMERISM (CHAPTERS 18 AND 22)

TAUTOMERISM IS A REVERSIBLE EQUILIBRIUM BETWEEN TWO ISOMERS (CALLED TAUTOMERS)

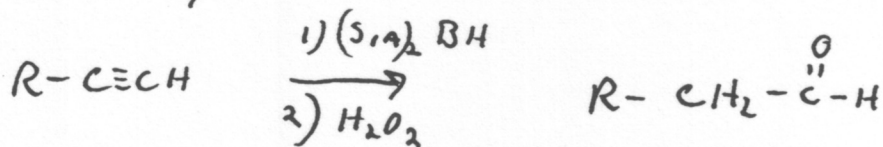


THE PRODUCTS OF ADDITION OF H₂O TO C≡C ARE KETONES



AS WITH ALKENES, HYDROBORATION/OXIDATION ADDS H-OH IN AN ANTI-MARKOVNIKOV SENSE

TERMINAL ALKYNES ARE CONVERTED TO ALDEHYDES USING (SIA)₂BH



OXIDATIONS

WITH ALKENES, KMnO₄ MAKES DIOLS

WITH ALKYNES, NEUTRAL KMnO₄ MAKES DIONES

