

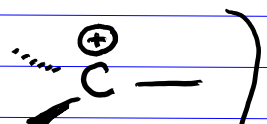
ORGANIC CHEMISTRY

- CHEMISTRY WHERE CENTRAL ELEMENT IS CARBON
- ALMOST ALWAYS H ATOMS
OFTEN O ATOMS, N ATOMS, HALOGENS.
SOMETIMES S ATOMS, P ATOM(S)

#1 RULE - CARBON MAKES 4 BONDS WHEN NEUTRAL & STABLE

CARBONS WITH 3 BONDS

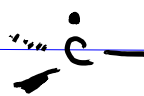
CARBOCATIONS



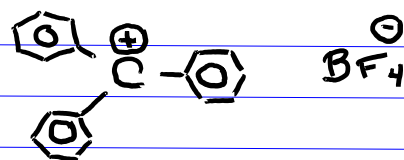
CARBANIONS



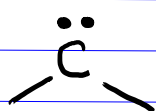
FREE RADICALS



REACTIVE INTERMEDIATES,
EXIST FOR A SHORT PERIOD
OF TIME



CARBONS WITH TWO BONDS RARER STILL, BUT ARE KNOWN
- TRANSIENT, REACTIVE INTERMEDIATES



CARBENES

BONDING

OGILVIE C-H 1 (1.6-1.7)
KARTY C-H 3

ORGANIC CHEMISTRY - ALMOST COVALENT OR
POLAR COVALENT BONDING

C $E_N \approx 2.5$

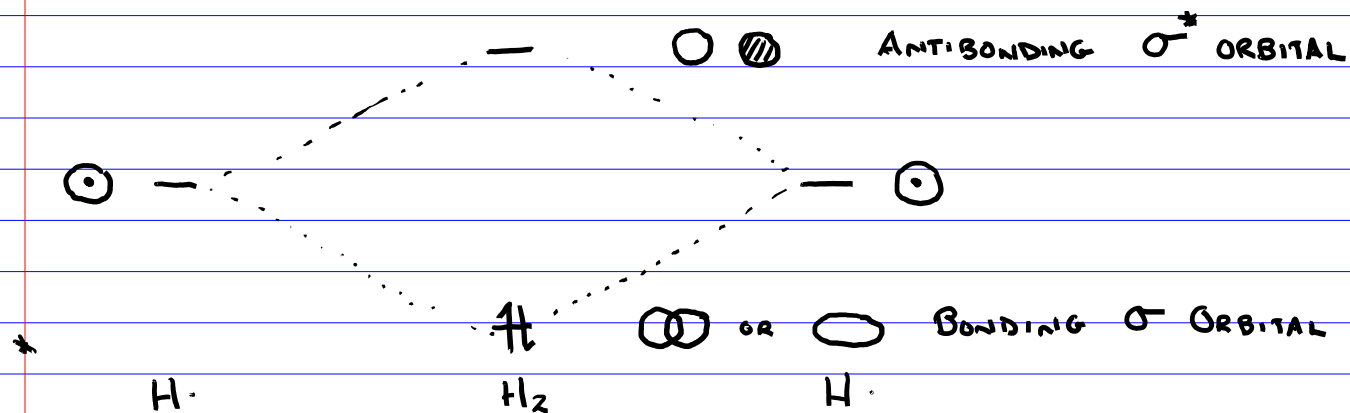
OTHER ATOMS H ($E_N \approx 2.2$); O ($E_N \approx 3.5$), N, Cl ($E_N \approx 3.0$)

IF POLAR COVALENT BONDING HAS DIFF'S IN E_N OF
 $0.5 > \Delta E_N < 1.7$

WE'RE ALWAYS COVALENT OR POLAR COVALENT.

- SINCE WE'RE COVALENT OR POLAR COVALENT, BONDING IS BEST DESCRIBED USING ORBITAL OVERLAP.

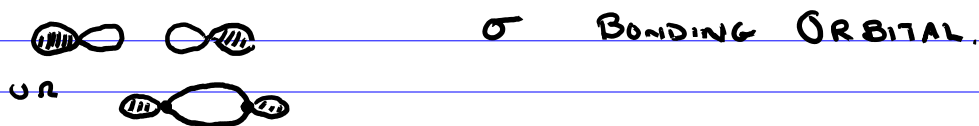
LCAO / MO APPROACH



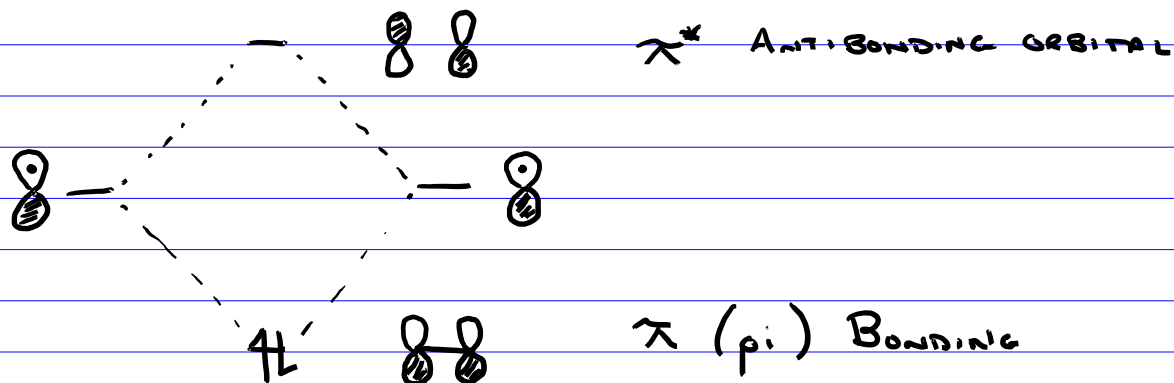
IF LOOKED DOWN BOND

AS YOU ROTATE 360° ,
PHASE NEVER CHANGES
" σ " IS USED.

AND FOR p-ORBITALS



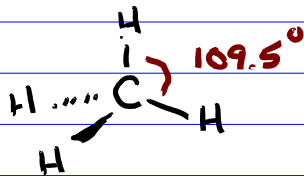
- ANOTHER ALTERNATE, WHERE THE p-ORBITALS INTERACT IN A SIDE ON FASHION.



π BOND - USUALLY NOT AS STRONG AS THE ANALOGOUS σ BOND - BUT STILL PRETTY STRONG

d ORBITALS? CAN ALSO HAVE δ BONDS
- BUT THIS IS IN CHEM 2500, NOT US.

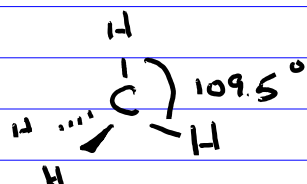
METHANE CH_4



- HOW DO WE USE AN s ORBITAL AND 3(?) p - ORBITALS TO GET 4 IDENTICAL BONDS AT 109.5° ?

SIMPLEST MODEL - HYBRIDIZATION
 sp^3 , sp^2 , sp HYBRIDIZATION

HYBRIDIZATION

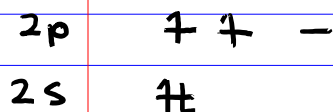


HOW DO WE GET THIS OUT ON A
S ORBITAL AND 3 p ORBITALS.

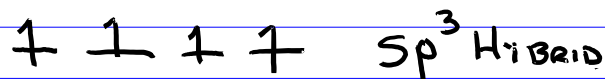
3 Common

FOR METHANE

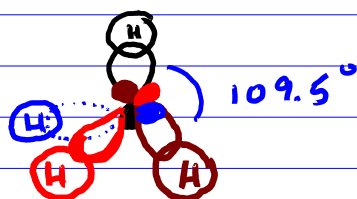
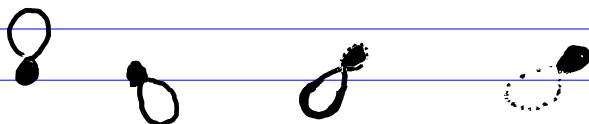
CREATE



A
HYBRID



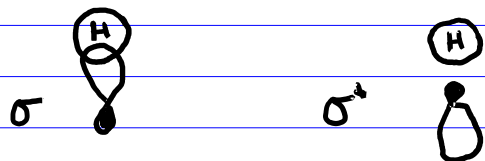
Look



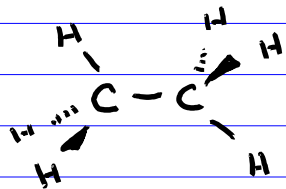
WE GET 4 σ BONDS AT 109.5°
ANGLES FROM EACH OTHER

75% p CHARACTER, 25% s CHARACTER

DON'T FORGET THERE ARE ALSO σ^* (ANTIBONDING ORBITALS)
WHICH ARE EMPTY.



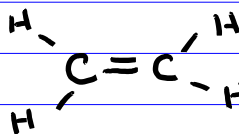
WORKS FOR ETHANE, PROPANE, BUTANE ETC.



ETHANE, C_2H_6

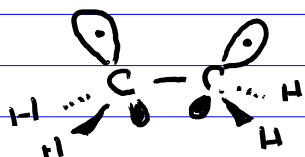
- ALL C'S ARE sp^3 HYBRIDIZED
- ALL BONDS ARE APPROX. 109.5°

CONSIDER C_2H_4 - ETHENE

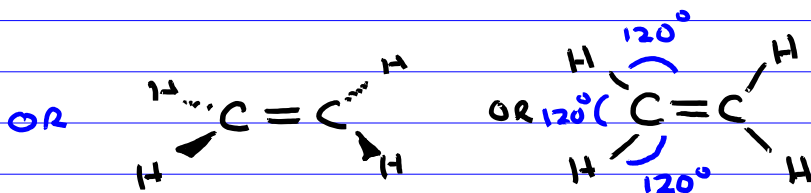
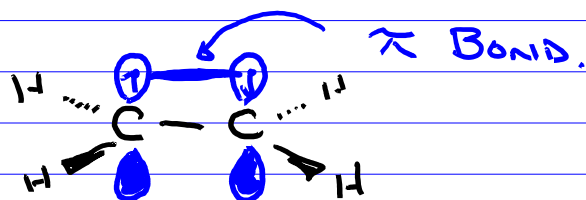
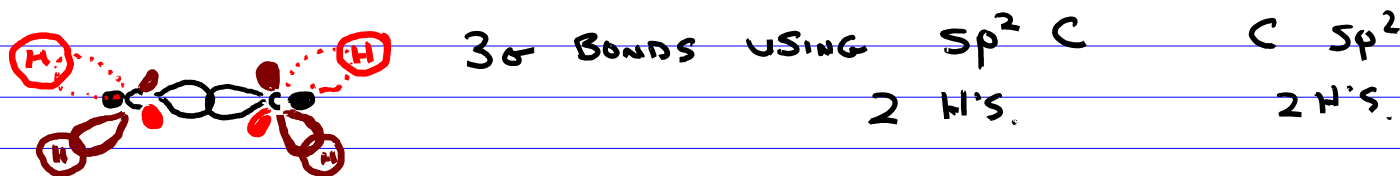
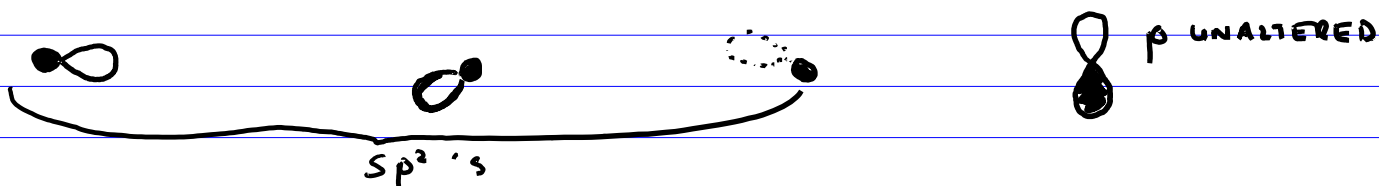
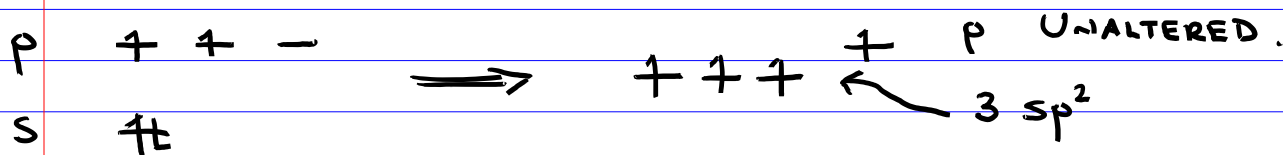


- IF WE TRY sp^3 HYBRIDIZATION

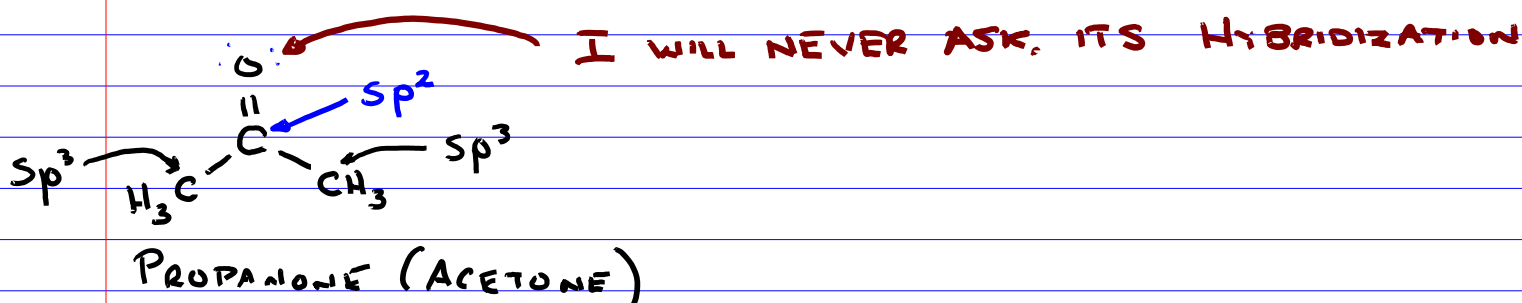
NOT VERY STABLE



- MOLECULE ADOPTS sp^2 HYBRIDIZATION TO BE MORE STABLE

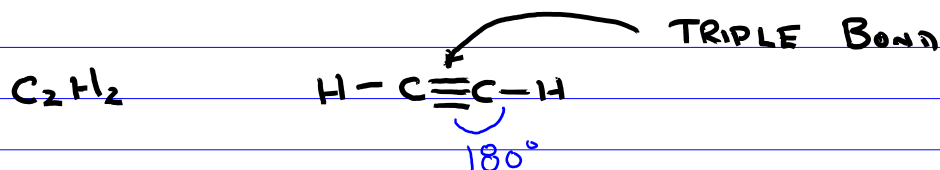
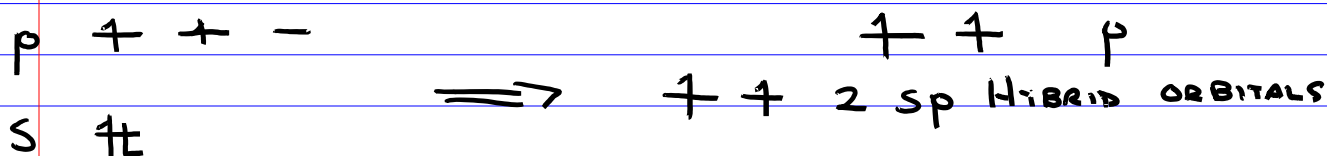


TYPICAL IN ALMOST C=ANYTHING SYSTEMS.

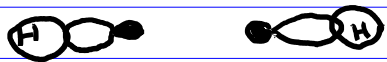


sp HYBRIDIZATION

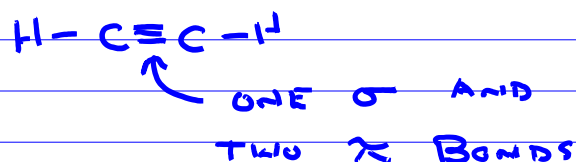
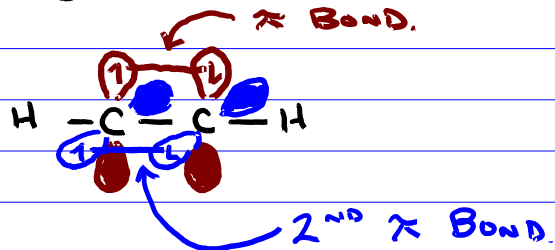
- USUALLY RESERVED FOR TRIPLE BONDED SYSTEMS.



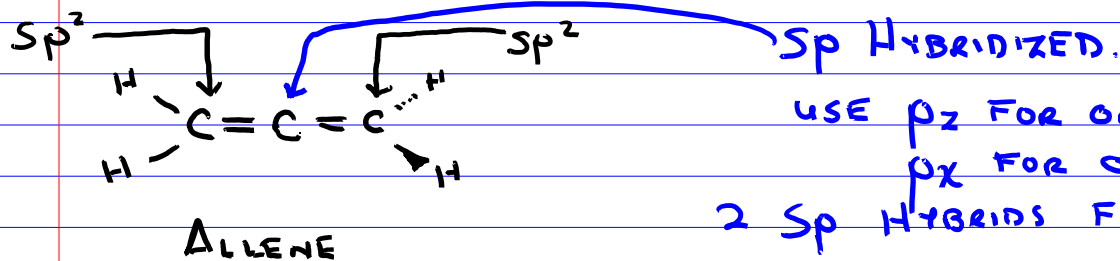
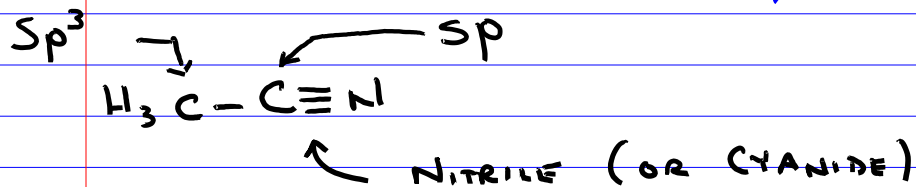
sp



180° RELATION



OTHER COMPOUNDS WITH sp HYBRID CARBONS

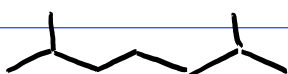
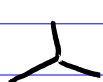
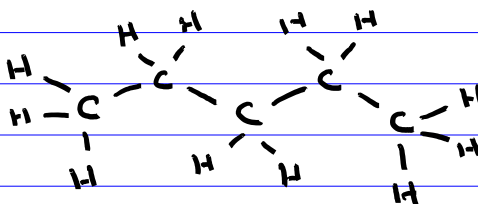
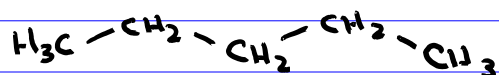


LECTURE 3 - THE HYDROCARBONS

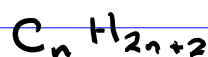
- SIMPLEST GROUP OF ORGANIC COMPOUNDS.
- ONLY C AND H ATOMS.

1) ALKANES

- COMPOUNDS WITH ONLY SINGLE BONDS



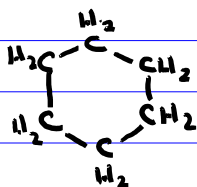
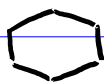
MOLECULAR FORMULA



EVERY CARBON ATOM IS sp^3 $\therefore$ ALL BOND ANGLES $\approx 109.5^\circ$

C-C BOND STRENGTH 350 KJ/mol (84 kcal/mol)
(C-H BONDS $\approx$ 420 KJ/mol)

- MANY, MANY CYCLIC VERSIONS.



CYCLOHEXANE
(FORMULA BECOMES $\text{C}_n \text{H}_{2n}$)

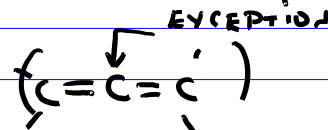
2) ALKENES

- AT LEAST ONE $\text{C}=\text{C}$ DOUBLE BOND PRESENT
- ALSO POSSIBLE TO HAVE > 1 DOUBLE
- MANY, MANY CYCLIC VERSIONS ARE KNOWN
- COMMON ONE 1 DOUBLE BOND, NO RING
FORMULA $\text{C}_n \text{H}_{2n}$



sp^2 HYBRIDIZED C'S.

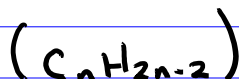
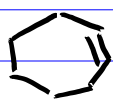
- OTHER C ATOMS ARE sp^3



- BOND STRENGTH	$C=C$	620 kJ/mol (148 kcal/mol)
	$\sigma C-C$	350 kJ/mol
	$\pi C-C$	270 kJ/mol
	BOND.	

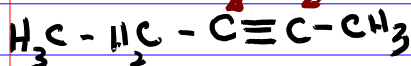
GOOD TO ASSUME THAT π BOND OF ALKENES WILL REACT FIRST

CYCLIC ONE
MANY
EXAMPLES

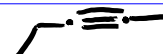
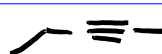


3) ALKYNES

sp HYBRIDIZED



(THE OTHER 3 ARE sp^3)



$C \equiv C$	BOND STRENGTH	835 kJ/mol (200 kcal/mol)
	$\sigma C-C$	350 kJ/mol
	2 π BONDS	$(485 \text{ kJ/mol}) \div 2$
		$\approx 243 \text{ kJ/mol PER } \pi \text{ BOND.}$

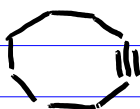
π BONDS WEAKER

MOST OF REACTIVITY INVOLVES
BREAKING A π BOND.

FORMULA C_nH_{2n-2}

MUCH FEWER CYCLIC ALKYNES

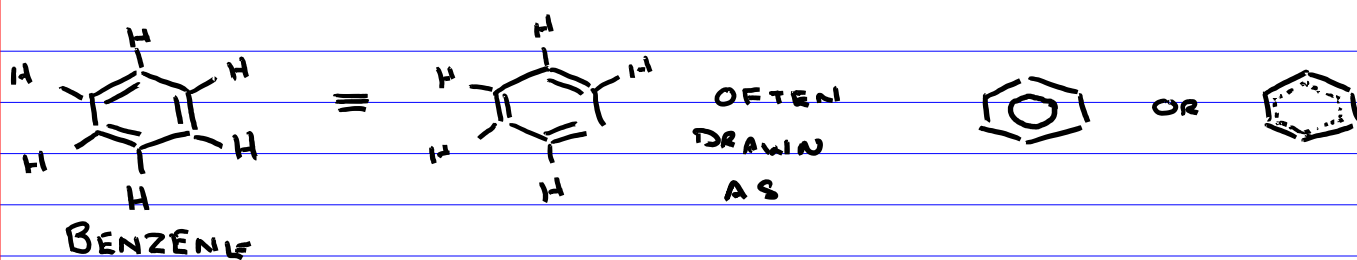
- SMALLEST THAT IS STABLE IS CYCLOOCTYNE (8)



- ANY SMALLER - NOT STABLE

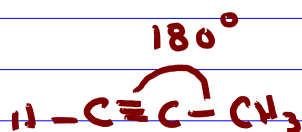
SMALL RING INCOMPATIBLE WITH A
180° BOND ANGLE AT sp C.

4) ARENES (OR BENZENES)



- EVERY C-C BOND IS A 1.5 BOND ORDER.
- MORE STABLE THAN ALKENES
- NOT ALTERNATING SINGLE / DOUBLE BOND
- ALL C ATOMS ARE sp^2

CHEM - 2310



ISOMERISM AND NOMENCLATURE

OGILVIE 2.5, 4.2, 4.8 (4.3, 4.4 LATER)

KARTY n_1, n_2, n_3, n_4 .

ISOMERISM

ISOMERS ARE COMPOUNDS WITH THE SAME MOLECULAR FORMULA, BUT WHICH ARE DIFFERENT CPDS.

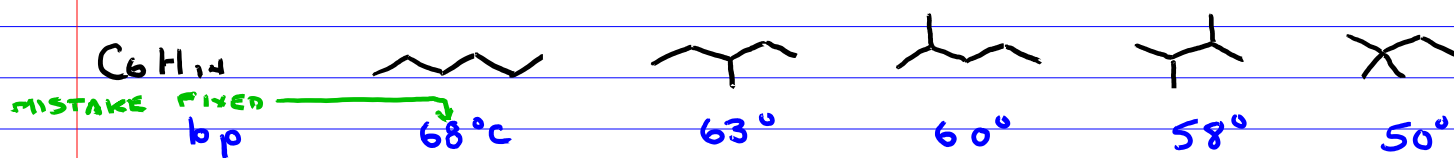
TYPES

- CONSTITUTIONAL
- CONFORMATIONAL *
- cis/trans
- ENANTIOMERS
- DIASTEREOMERS

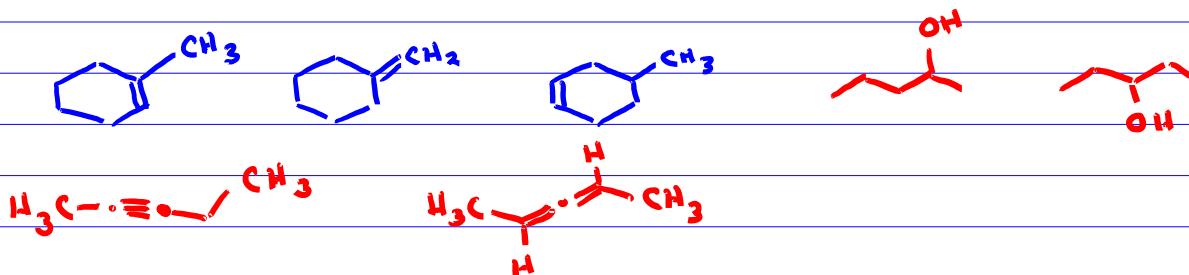
(STRUCTURAL, POSITIONAL) ISOMERS

STEREOMERS

CONSTITUTIONAL



- ISOMERS IN WHICH ATOMS ARE CONNECTED IN DIFFERENT POSITIONS
- DIFFERING PROPERTIES - bp, mp, IR, NMR SPECTRA



NAMING ORGANIC COMPOUNDS

- RULES DEVISED OVER TIME BY IUPAC TO NAME ORGANIC COMPOUND RIGOROUSLY

CONSTRUCTED FROM

$$\text{NAME} = \text{PREFIX} + \text{ROOT} + \text{SUFFIX}$$

ROOT $\Rightarrow$ REFERS TO # OF C ATOMS IN THE LONGEST CONTINUAL CHAIN

LENGTH OF CONTINUAL CHAIN

C	ROOT	C	ROOT
1	METH	7	HEPT
2	ETH	8	OCT
3	PROP	9	NON
4	BUT	10	DEC
5	PENT	11	UNDEC
6	HEX	12	DODEC

SUFFIX - IDENTIFIES WHAT KIND OF FUNCTIONAL GROUP IS PRESENT

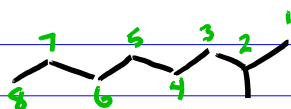
SUFFIX

- ALKANE	ANE
- ALKENE	ENE
- ALKYNE	YNE



NONANE

How ABOUT



NAMED DIFFERENTLY

- WE'LL USE THE PREFIX TO IDENTIFY WHERE THE SUBSTITUENT IS ON THE MAIN CHAIN

- THIS HAS 8C MAIN CHAIN $\therefore$ NAME AS TYPE OF OCTANE

- ONE CARBON SUBSTITUENT - CALLED 'METHYL'

- INCLUDE ITS LOCATION AS THE START OF NAME

- CHOOSE LOWEST # POSSIBLE

2-METHYLOCTANE

- MOST FUNCTIONAL GROUPS ARE PART OF SUFFIX

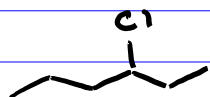
- TWO TYPES ARE CONSIDERED SUBSTITUENTS AND ARE IN THE PREFIX - HALIDES (& NITRO GROUPS)

F - FLUORO

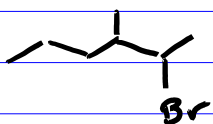
Br - BROMO

Cl - CHLORO

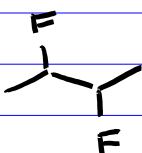
I - IODO



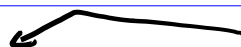
3 - CHLOROHYXANE



2 - BROMO - 3 - METHYL HEXANE



2,3 - DIFLUORO BUTANE



MISTAKE
FIXED

SPACING - WORDS NORMALLY RUN TOGETHER

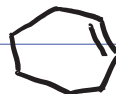
- NUMBERS SEPARATED FROM WORDS BY HYPHENS
- NUMBERS SEPARATED FROM NUMBERS BY COMMAS

LECTURE 5.

CYCLIC COMPOUND - ADD 'CYCLO' TO THE FRONT PART OF THE ROOT

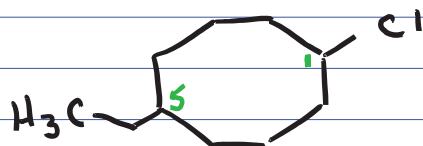


CYCLOPENTANE



CYCLOHEPTENE

- APPEND ANY SUBSTITUENTS IN ALPHABETICAL ORDER, WITH THE LOWEST POSSIBLE NUMBERS



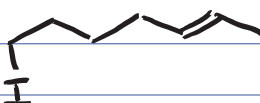
1-CHLORO-5-ETHYLCYCLOOCTANE

- ALKENES OR ALKYNES

- GIVE THE DOUBLE OR TRIPLE BOND THE LOWEST # POSSIBLE, SUBSTITUENTS FALL WHEREVER THEY FALL



2-HEPTENE

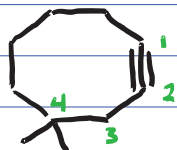


7-IODO-2-HEPTENE
(7-IODOHEPT-2-ENE)

- IF > 1 ALKENE, CALLED DIENE, TRIENE, TETRAENE



6-METHYL-1,3-OCTADIENE

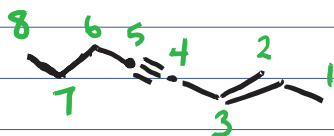


4,4-DIMETHYL-1-CYCLOOCTYNE - OVERKILL
4,4-DIMETHYLCYCLOOCTYNE

NOT NECESSARY

(SIMILAR APPROACH FOR DIENES, TRIENES AS DIENES, TRIENES)

IF BOTH AN ALKENE & ALKYNE PRESENT,
IT'S CALLED AN ENYNE



2-OCTEN-4-YNE
(OR OCT-2-EN-4-YNE)

NAMING FUNCTIONAL GROUPS.

- ALL OTHER FUNCTIONAL GROUPS ARE CONSIDERED HIGHER PRIORITY THAN ALKANES, ALKENES, ALKYNES.

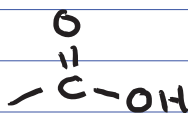
FROM HIGHEST TO LOWEST PRIORITY

NAME OF
GROUP

GROUP

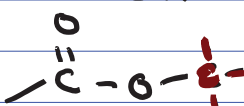
SUFFIX

ACID



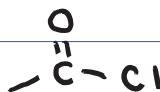
-OIC ACID

ESTER



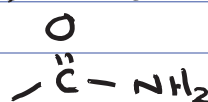
ALKYL -OATE

ACID CHLORIDE



-OYL CHLORIDE

AMIDE



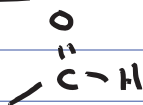
-AMIDE

NITRILE



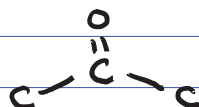
-NITRILE

-ALDEHYDE



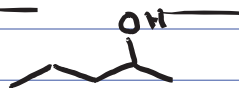
-AL

-KETONE



-ONE

ALCOHOL



-OL

AMINE



-AMINE

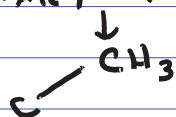
ETHER



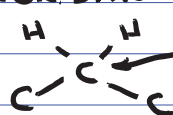
ALKYL ALKYL ETHER

OTHER TERMINOLOGY TO BE FAMILIAR WITH

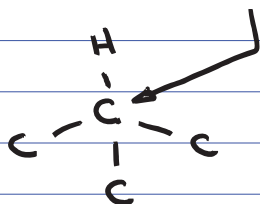
PRIMARY (1°)



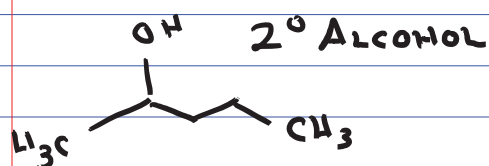
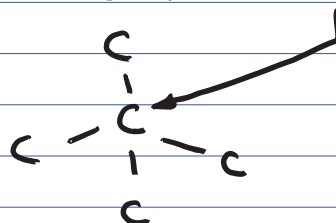
SECONDARY (2°)



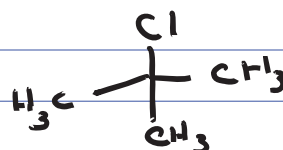
TERTIARY (3°)



QUATERNARY (4°)



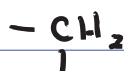
3° ALKYL CHLORIDE



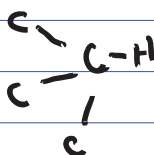
METHYL



METHYLENE



METHINE



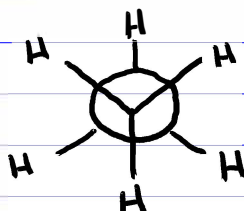
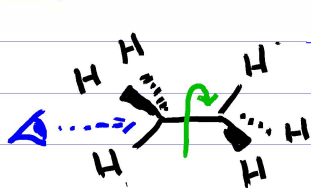
LECTURE 6

Ch 3 Ogilvie (1st and 2nd Eds; Ch 4 Karty)

CONFORMATIONS (CONFORMATIONAL ISOMERISM)

- DIFFERENCES IN ATOM ARRANGEMENTS DUE TO THE ROTATION OF SINGLE BONDS (C-C BONDS USUALLY)

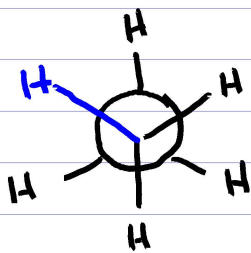
- THERE IS A BARRIER FOR THIS TO OCCUR, BUT IT'S SO SMALL IN ENERGY THAT THE MOLECULE CAN GET OVER THIS MANY TIMES PER SECOND.



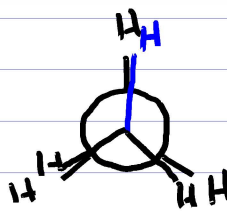
NEWMAN
PROJECTION

STAGGERED
CONFORMATION

LET'S DO ROTATION



ROTATE

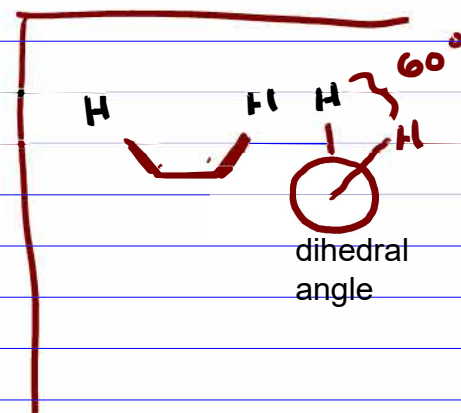
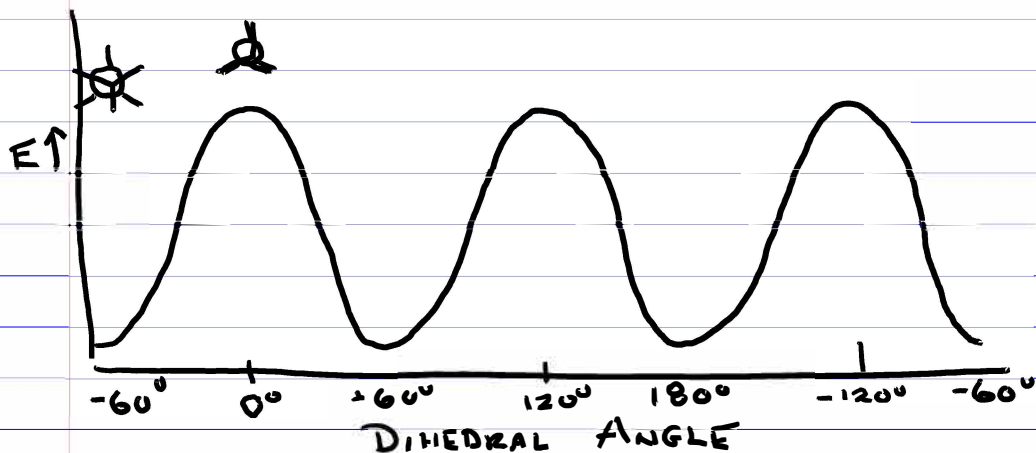
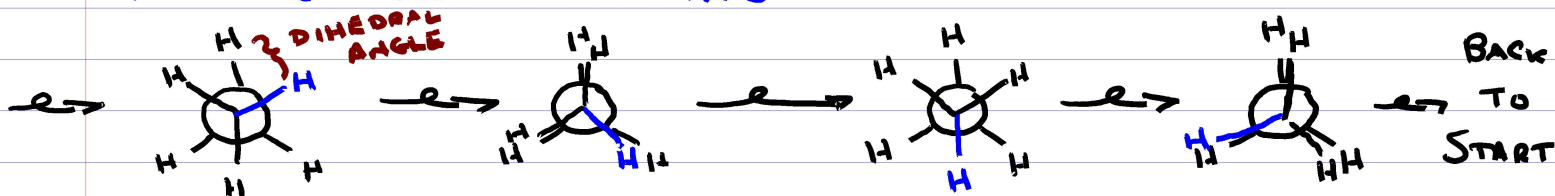


ECLIPSED CONFORMATION

POORER (HIGHER IN ENERGY)
B: 12 kJ/mol (3 kcal/mol)

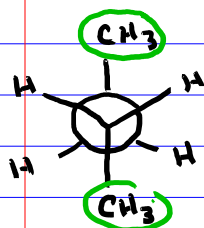
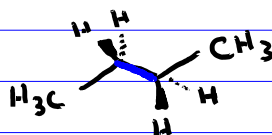
ECLIPSED IS HIGHER IN ENERGY BECAUSE THE ELECTRONS IN FILLED C-H σ BONDING ORBITALS REPEL EACH OTHER
= TORSIONAL STRAIN

IF WE KEEP ROTATING



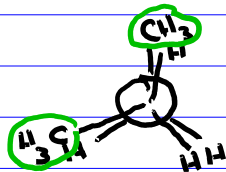
LET'S DO BUTANE

LET'S CONSIDER
C2-C3 BOND.



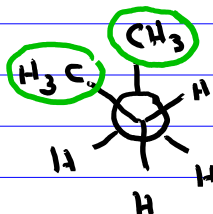
BEST
TWO BIGGEST
GROUPS ARE AS
FAR AWAY AS
POSSIBLE

ANTIPERIPPLANAR



ECLIPSED
FAIRLY BAD
- 2ND WORST

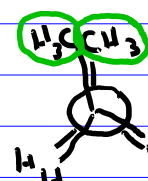
ANTICLINAL



STAGGERED,
BUT THERE IS
STERIC HINDRANCE
BETWEEN CH₃'S.

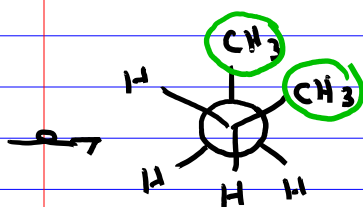
- 2ND BEST

SYNCLINAL
(GAUCHE)



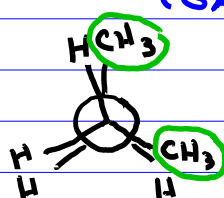
WORST ONE
- ECLIPSED AND
CH₃ GROUPS
HAVE STERIC
STRAIN

SYNPERIPLAR



SYNCLINAL

TIED FOR
2ND BEST



ANTICLINAL

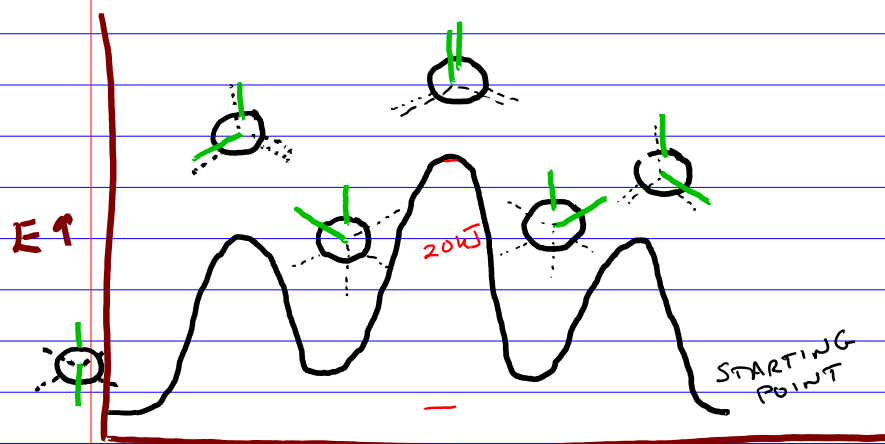
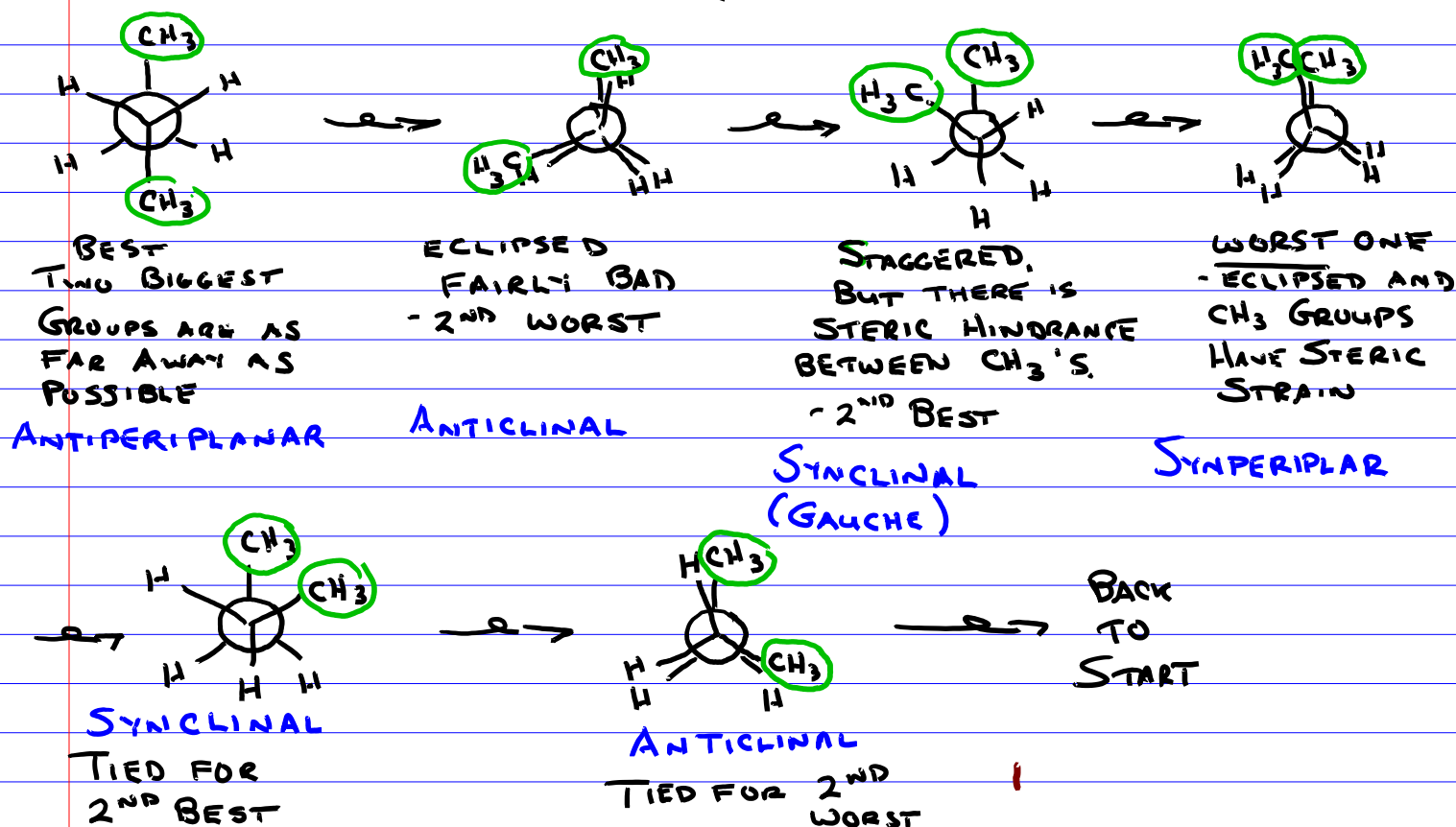
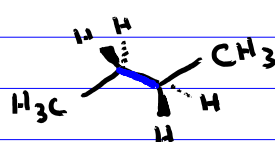
TIED FOR 2ND
WORST



BACK
TO
START

LECTURE 7 LET'S DO BUTANE

LET'S CONSIDER C2-C3 BOND



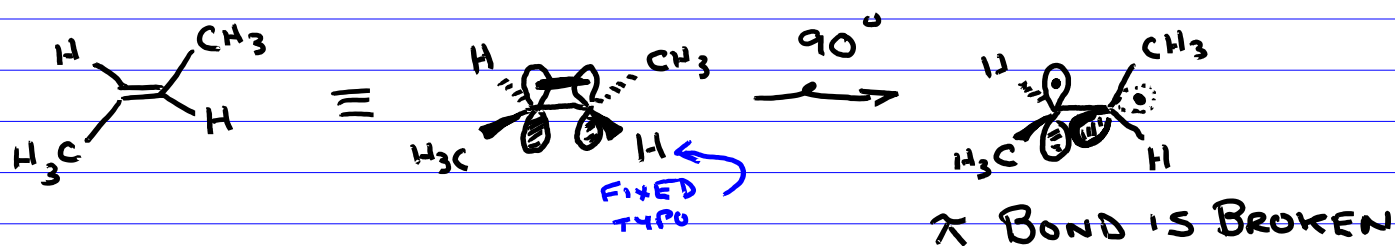
DIHEDRAL ANGLE

STERIC STRAIN (HINDRANCE) - REPULSION (ENERGETIC COST)
FROM ELECTRON CLOUDS AROUND ATOMS GETTING TOO CLOSE

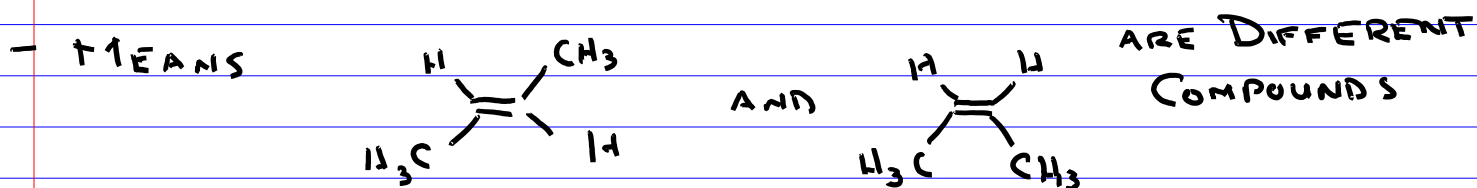
ONLY RARE INSTANCES ARE CONFORMATIONAL BARRIERS SO HIGH THAT THE MOLECULE CAN'T SURMOUNT THEM
= THESE CASES ARE CALLED
ATROPISOMERS

CONFIGURATIONS - PART I

- LET'S COMPARE THE CONFORMATIONAL ANALYSIS WE'VE JUST DONE WITH 2-BUTENE



COSTS 250 KJ/mol (65 kcal/mol) TO DO THIS - WAY TOO MUCH
- THIS DOESN'T HAPPEN

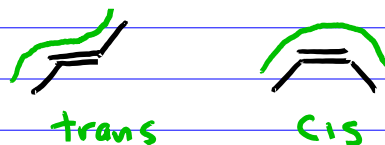


- DON'T INTERVERT
- HAVE DIFFERENT CONFIGURATIONS - THIS MEANS THAT THEY CAN'T BE INTERCONVERTED WITHOUT BREAKING A BOND(S).
- THESE TWO COMPOUNDS ARE TYPES OF STEREOISOMERS (SAME CONNECTIVITY, DIFFERENT ORIENTATION IN SPACE)
- THIS TYPE OF STEREOISOMERISM IS CALLED CIS/TRANS ISOMERISM (OR GEOMETRIC ISOMERISM)

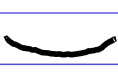
HOW DO WE NAME THEM?

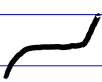
- OLD WAY?

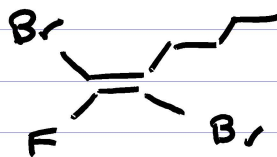
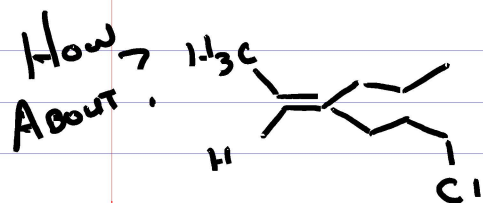
HOW TO ASSIGN



- a) FIND THE MAIN CHAIN AS IT RUNS THROUGH THE C=C OR C=X BOND.

- b) IF THAT CHAIN MAKES A  (C OR U) SHAPE, IT'S CALLED CIS-

- c) IF THAT CHAIN MAKES AN  (S) SHAPE, IT'S CALLED TRANS-



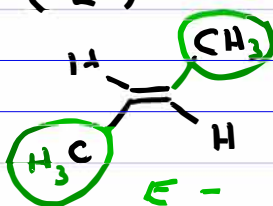
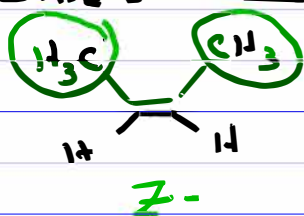
WHAT SERVES AS
MAIN CHAIN ISN'T
CLEAR ~~FEAR~~ HERE

OFFICIAL WAY - BI IUPAC HAVE COME UP WITH A
SERIES OF RIGOROUS RULES

- CREATE A SERIES OF GROUP PRIORITIES USING THE
CAHN - INGOLD - PRELOG (CIP) SEQUENCE RULES
- a) ASSIGN A HIGHEST PRIORITY GROUP FOR ATOMS ATTACHED
TO THE ALKENE CARBONS AT EACH END.

b) IF THE TWO HIGHEST PRIORITY GROUPS ARE BOTH ON THE
SAME SIDE $\Rightarrow$ (Z) - ISOMER

c) IF THE TWO HIGHEST PRIORITY GROUPS ARE ON OPPOSITE
SIDES $\Rightarrow$ (E) - ISOMER



HOW DO WE DECIDE ON CIP PRIORITY?

LECTURE 8

- ASSIGNING ALKENE STEREOCHEMISTRY RIGOROUSLY.

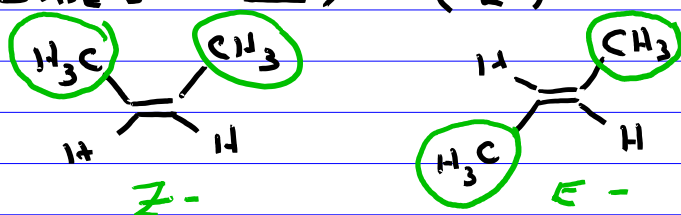
OFFICIAL WAY - IUPAC HAVE COME UP WITH A SERIES OF RIGOROUS RULES ^{GEOMETRIC} FOR NAMING ISOMERS

- CREATE A SERIES OF GROUP PRIORITIES USING THE CAHN - INGOLD - PRELOG (CIP) SEQUENCE RULES

a) ASSIGN A HIGHEST PRIORITY GROUP FOR ATOMS ATTACHED TO THE ALKENE CARBONS AT EACH END.

b) IF THE TWO HIGHEST PRIORITY GROUPS ARE BOTH ON THE SAME SIDE $\Rightarrow$ (Z) - ISOMER

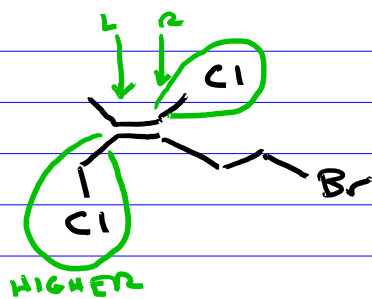
c) IF THE TWO HIGHEST PRIORITY GROUPS ARE ON OPPOSITE SIDES $\Rightarrow$ (E) - ISOMER



HOW DO WE DECIDE ON CIP PRIORITY?

- ATOM WITH THE HIGHER ATOMIC # HAS HIGHER PRIORITY
 - HIGHER ATOMIC MASS PRECEDES LOWER
 - H ATOM HAS HIGHER PRIORITY THAN A LONE PAIR.
- IF 1ST ATOM IS TIED, THEN MOVE DOWN THE CHAIN ATOM BY ATOM, UNTIL A POINT OF DIFFERENCE IS FOUND
- IF THERE'S A BRANCH POINT IN THE GROUP, YOU CHOOSE THE PATH LEADING TO THE EARLIEST POSSIBLE DISCRIMINATION

(E) - 5-BROMO-1,3-DICHLORO-2-METHYL-2-PENTENE

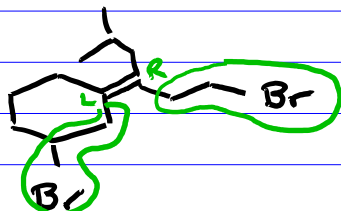


LEFT SIDE - C vs C TIE
ON THOSE
C → H, H, H
C → Cl, H, H
wins

RIGHT SIDE - Cl wins
vs
C

2-PENTENE

HIGHER PRIORITY GROUPS ON OPPOSITE SIDES ∴ (E) -



LEFT	TOP C	vs	BOT C	TIE
ON IT	C, H, H	vs	C, H, H	TIED
OT IT	C, H, H	vs	Br, C, H	wins

RIGHT	C	vs	C	TIE
ON IT	C, H, H	vs	C, H, H	TIE
ON IT	C, C, H		Br, H, H	wins

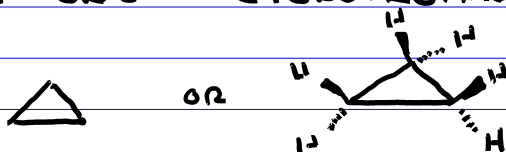
BOTH HIGHER PRIORITY GROUPS ARE DOWN

∴ (Z) - ISOMER

CYCLIC HYDROCARBONS - ALICYCLIC COMPOUNDS

MANY CASES WITH $sp^3 + sp^2$ CARBONS
MUCH SMALLER NUMBER WITH sp CARBONS

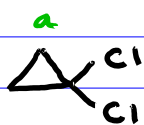
SMALLEST ONE - CYCLOPROPANE



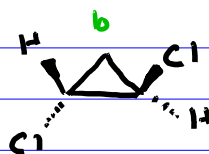
- HAS ANGLE STRAIN, SINCE
C-C-C ANGLES ARE 60° ,
BUT WOULD PREFER TO BE 109.5°
(sp^3 HYBRIDIZED)

THERE IS SOME TORSIONAL STRAIN ALSO

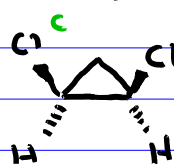
SUBSTITUTED CYCLOPROPANES - IF TWO SUBSTITUENTS PRESENT,
ISOMERS ARE POSSIBLE



1,1-DICHLORO



trans-1,2-DICHLORO



cis-1,2-DICHLORO

a IS A CONSTITUTIONAL ISOMER OF b AND c

b, c ARE STEREOISOMERS OF EACH OTHER
(cis/trans OR GEOMETRIC ISOMERS) IS FINE,
WE'LL SEE A BETTER NAME (DIASTEREOMERS) LATER

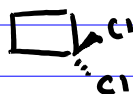
CYCLOBUTANE - SOME, BUT LESS ANGLE STRAIN



ACTUALLY



ACTUAL STRUCTURE IS
SLIGHT BUTTERFLY



1,1-DICHLORO



cis

1,2-DICHLORO



trans



cis

1,3-DICHLORO



trans

LECTURE 9

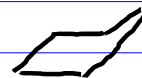
CYCLOPENTANE



C-C-C BOND ANGLES = 104.5°
- ALMOST NO ANGLE

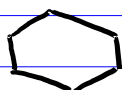
SEVERAL AVAILABLE
CONFORMATION

ENVELOPE CONFORMATION
IS LOWEST
ENERGY

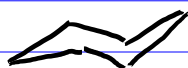


CYCLOHEXANE

- COMPLETELY LACKING IN ANGLE
STRAIN



- CONFORMATIONS VERY WELL UNDERSTOOD
- TWO LIMITING ONES WITH PERFECT C-C-C ANGLES

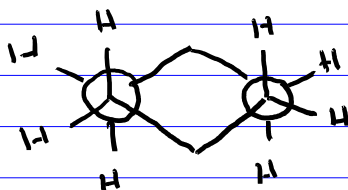


CHAIR

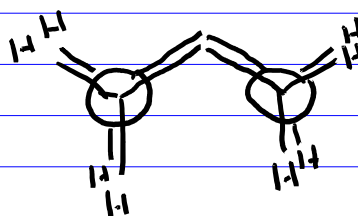


BOAT

CHAIR IS FAVOURED BY: 27 kJ/mol (6.5 kcal/mol)



CHAIR- RELATIONSHIPS
BETWEEN ADJACENT C'S
IS STAGGERED



BOAT- SEVERAL ECLIPSED
INTERACTIONS

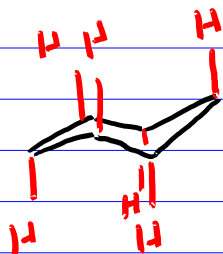
+



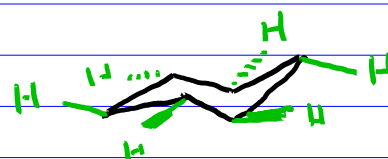
- A BIT OF STERIC
HINDRANCE
BETWEEN THE
FLAGPOLE H'S

- NOTE: THERE'S A TWIST BOAT
(OR TWIST) CONFORMATION THAT'S
A BIT BETTER THAN THE BOAT

- TWO TYPES OF SUBSTITUENTS ON THE CHAIR FORM OF CYCLOHEXANE

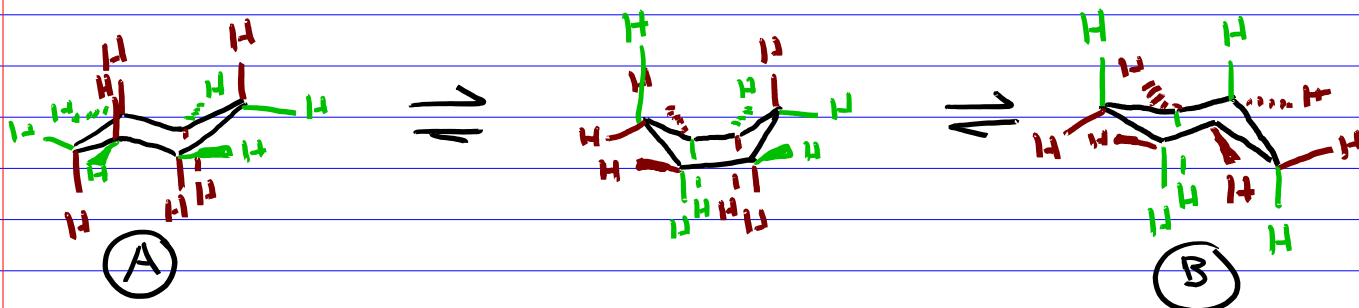


AXIAL SUBSTITUENTS



EQUATORIAL SUBSTITUENTS

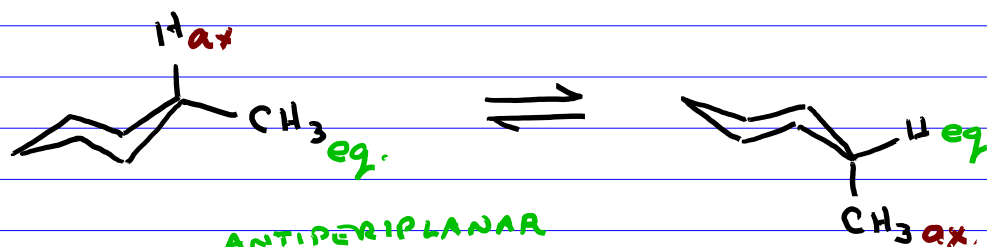
- EACH ALTERNATE AS TO WHETHER THEY ARE UP OR DOWN AND SWITCH WITH EACH CARBON



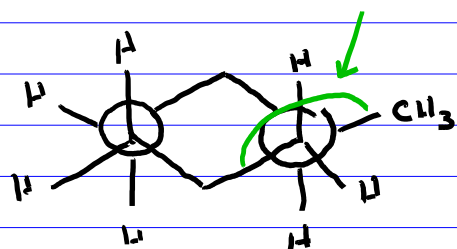
THE AXIAL AND EQUATORIAL SITES EXCHANGE BY A CHAIR-CHAIR INTERCONVERSION - BY A CONFORMATIONAL CHANGE BARRIER 45 kJ/mol (10.5 kcal/mol)

1:1 RATIO OF (A) : (B) IF ALL SUBSTITUENTS ARE H'S

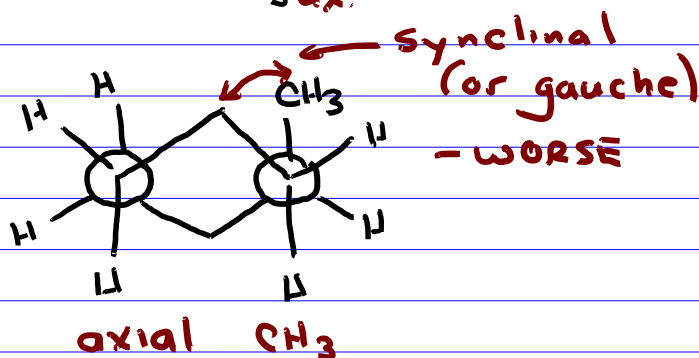
- BUT IF ONE GROUP ISN'T THE SAME



ANTIPERIPHERAL

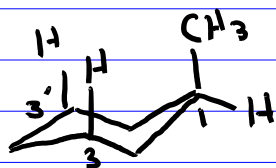


equatorial CH₃



axial CH₃

- SO, THE BIGGER GROUP (CH_3) PREFERENCES TO BE EQUATORIAL

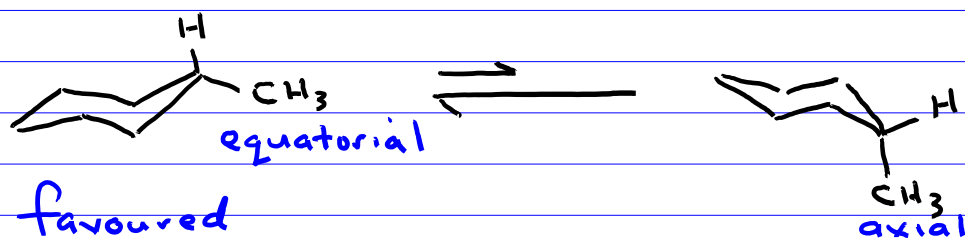


- ALSO 1,3-DIAXIAL INTERACTIONS (SLIGHT STERIC STRAIN) IN THE AXIAL CONFORMATION - THIS ALSO DISFAVOURS THE AXIAL

RULE:

FOR ANY NON-HYDROGEN SUBSTITUENT, THE EQUATORIAL ORIENTATION IS FAVOURED.

LECTURE 10



- THE DEGREE TO WHICH A GROUP IS FAVOURED IN AN EQUATORIAL ORIENTATION DEPENDS ON THE SIZE OF THAT GROUP

- CH₃ MEDIUM SIZED GROUP. 7 kJ/mol (1.7 kcal/mol) ^{eq.} FAVOURED

COMPARE

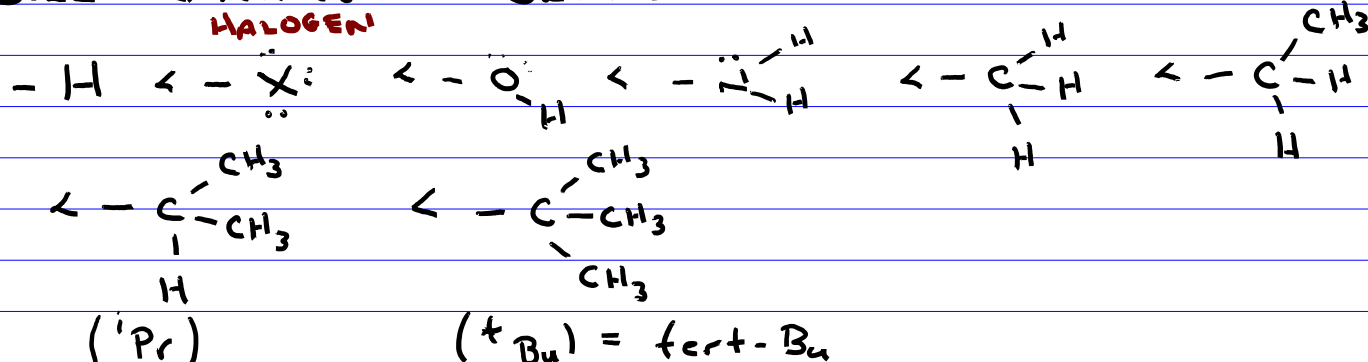
- OH 3.7 kJ/mol (0.9 kcal/mol) 4.5:1 eq/ax

- C(CH₃)₃ 19 kJ/mol (4.5 kcal/mol) 2600-2500:1 eq/ax

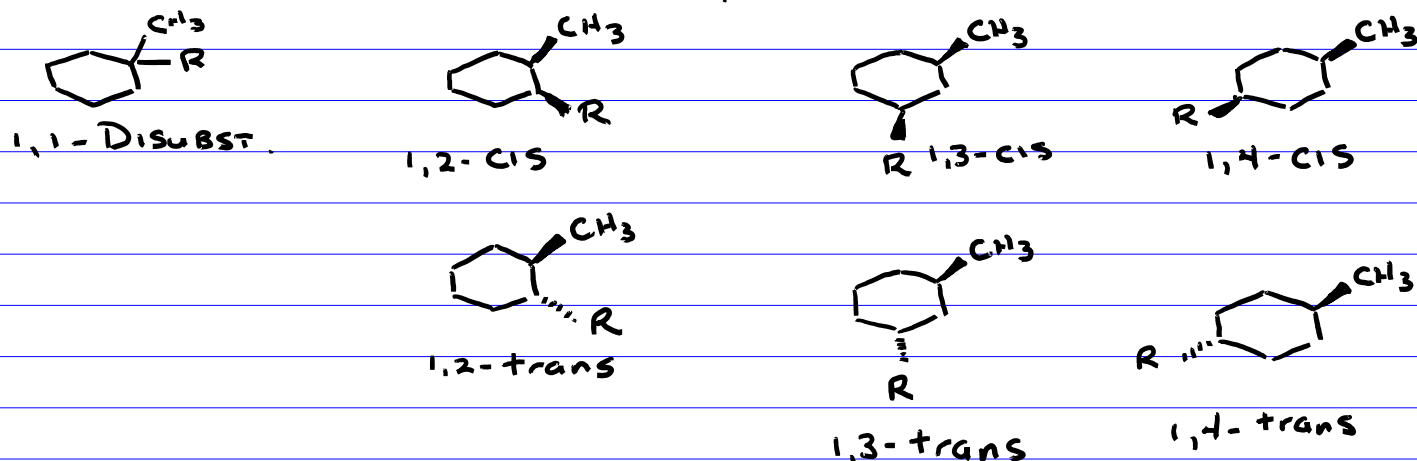
A VALUE : MOST COMMONLY USED MEASURE OF SIZE IN ORGANIC CHEMISTRY

SIZE RANKING OF GROUPS

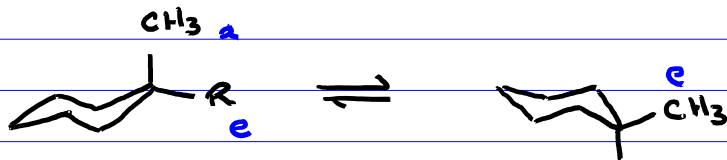
(E+)



DISUBSTITUTED CYCLOHEXANES



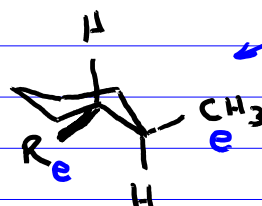
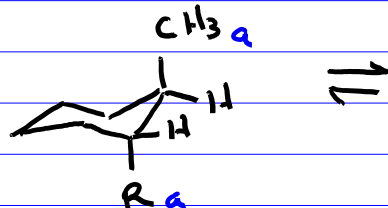
1,1-



THIS IS FAVOURED IF
R IS LARGER THAN
CH₃
(i.e. i-Pr)

THIS IS FAVOURED IF
R IS SMALLER THAN CH₃
(i.e. -Br)

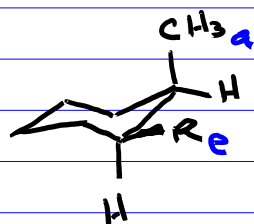
1,2-Trans



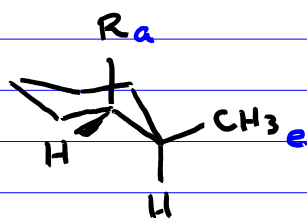
THIS ONE WINS
EASILY

BOTH LARGER THAN H
GROUPS GET TO BE
EQUATORIAL

1,2-cis

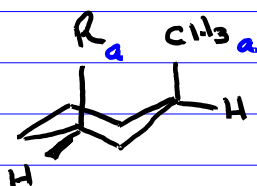


FAVOURED IF R IS
LARGER THAN CH₃



FAVOURED IF R IS
SMALLER THAN CH₃

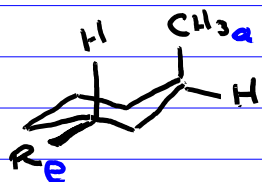
1,3-cis



THIS WINS
EASILY

R + CH₃ ARE
BOTH
EQUATORIAL

1,3-trans



FAVOURED IF R IS
LARGER THAN CH₃



FAVOURED IF R IS
SMALLER THAN CH₃

END OF FIRST MIDTERM MATERIAL

MON. OCT. 17

1:30 - 2:20 pm
(50 MINUTES)

SHORT ANSWER

ROOMS FOR TEST

Room 1120 A - KOUAISSEM

TOLDU 100 KOVACEVICH - SAMMAN

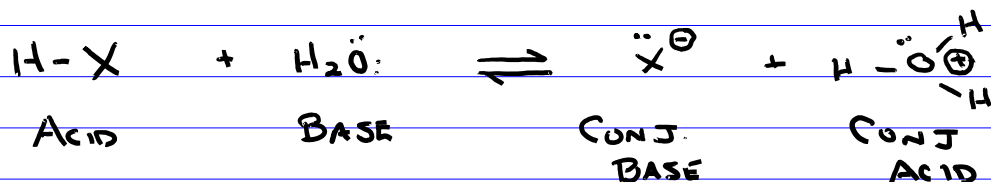
TOLDU 200 SANKARLAL - Z

FUNDAMENTAL OF ORGANIC CHEMISTRY

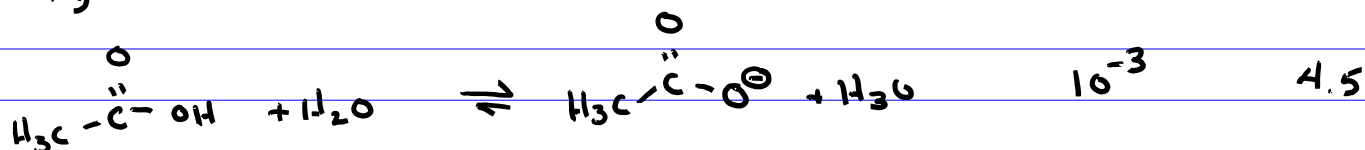
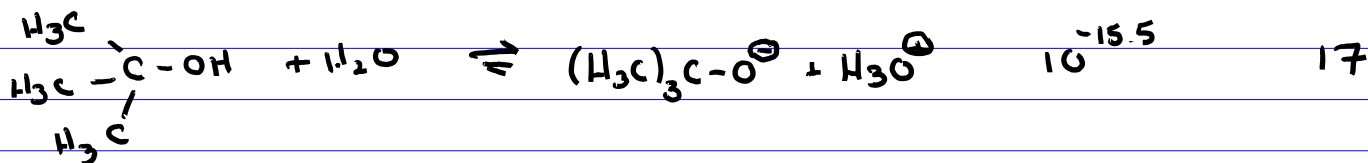
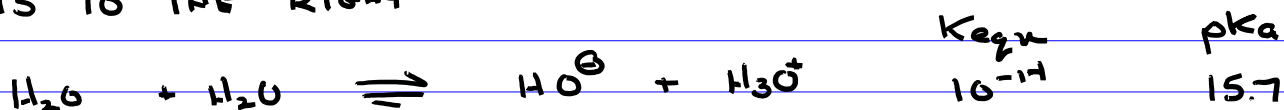
OGILVIE CH 5 + 6

KARTY 6, 7 & 1.10 - 1.11

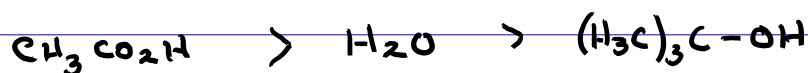
ACIDITY - BRONSTED



THE STRONGER THE ACID IS, THE FURTHER THE EQM. IS TO THE RIGHT

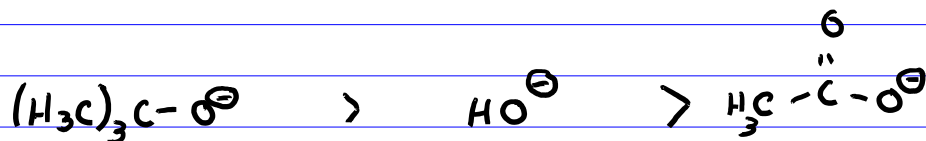


∴ STRENGTH ORDER IS:



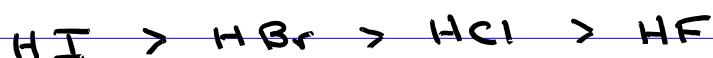
CONJUGATE BASE - IS EXACTLY IN REVERSE ORDER

∴ BASE STRENGTH IS



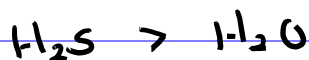
ACID STRENGTH VS THE PERIODIC TABLE

1) IN A GROUP (A COLUMN) IN THE PERIODIC TABLE, THE ACID STRENGTH INCREASES GOING DOWN THE GROUP

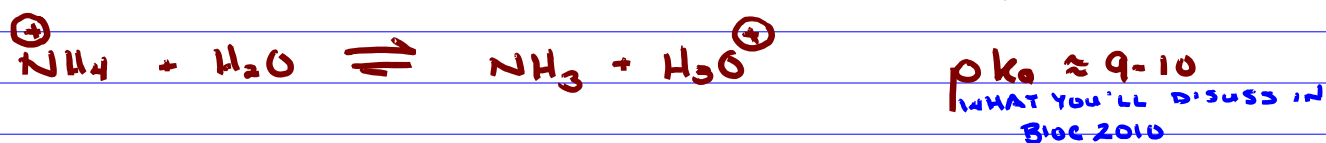
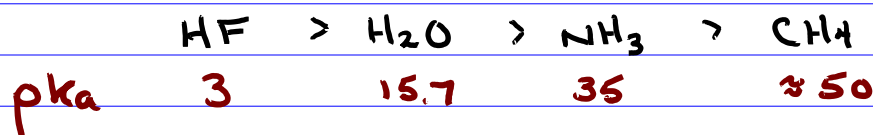


- REASONING - LARGER IONIC RADIUS (OR VOLUME) FOR I^- ,
 SO CHARGE SPREAD OUT OVER A GREATER VOLUME
 (LOWER CHARGE DENSITY) = GREATER STABILITY

SIMILARLY,

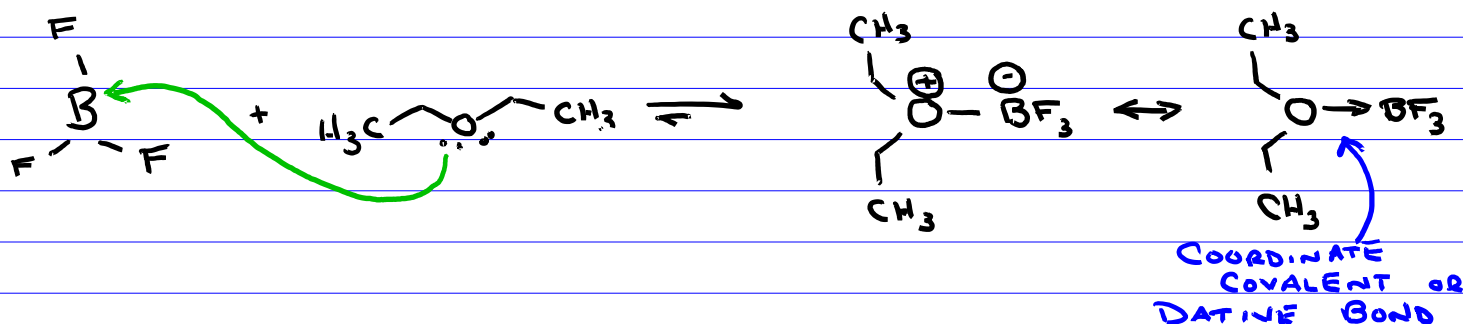


2) IN THE SAME ROW, ACIDITY GETS HIGHER AS WE GO
 RIGHT, FOLLOWING ELECTRONEGATIVITY



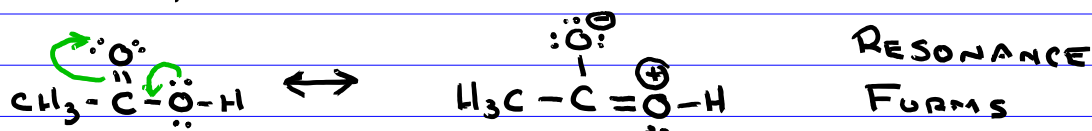
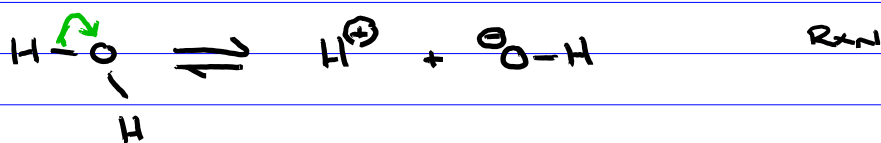
LEWIS ACIDITY

- SPECIES WILLING TO ACCEPT AN ELECTRON PAIR IN A RXN.
- LEWIS BASE DONATES AN ELECTRON PAIR IN A RXN

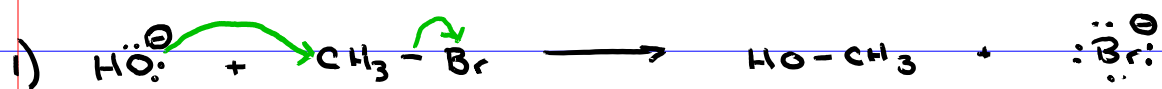


THE CURVED ARROW

- INDICATES THE MOVEMENT OF A PAIR (2) OF ELECTRONS FROM A REGION OF HIGH e^- DENSITY TO A REGION OF LOW e^- DENSITY

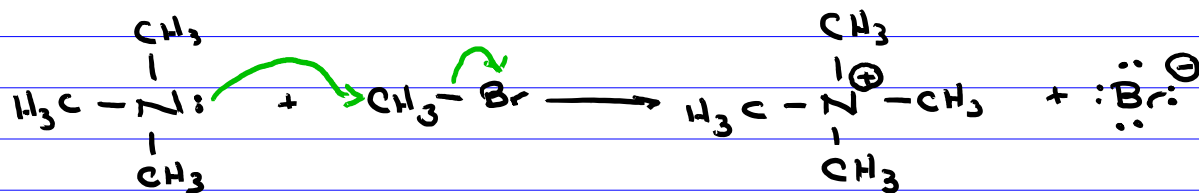


- SOME RULES

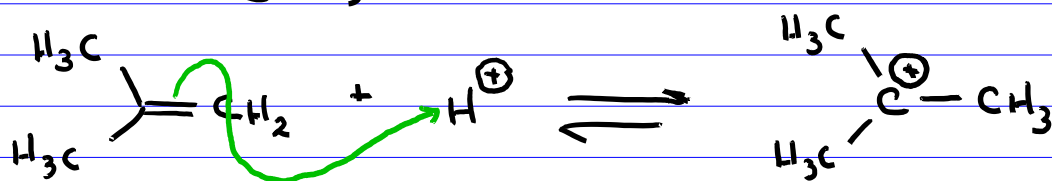


IF AN e^- PAIR MOVES FROM AN ATOM WITH A "-" CHARGE THAT ATOM BECOMES NEUTRAL

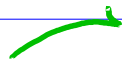
2) IF AN e^- PAIR MOVES FROM A NEUTRAL ATOM, IT WILL PICK UP A "+" CHARGE



3) IF THE e^- PAIR COMES FROM A BONDING PAIR, YOU BREAK THE BOND



SINGLE ELECTRON MOVEMENT ?

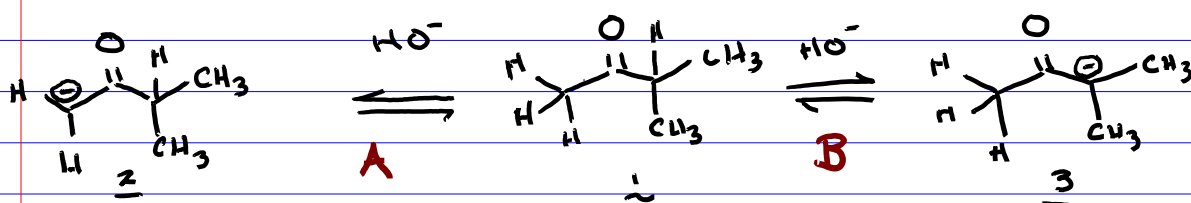
 HALF A HEAD ON ARROW MEANS 1 e^- MOVEMENT.

LECTURE 11

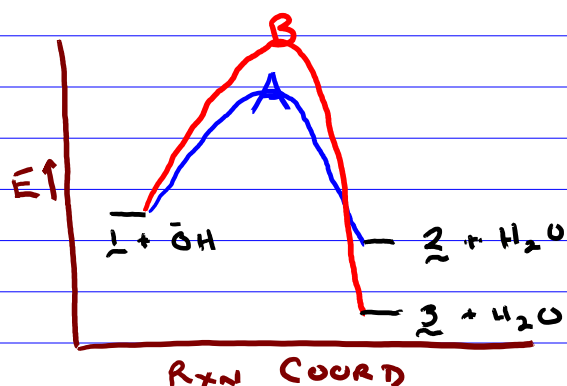
LECTURE 12

FUNDAMENTALS CONTD.

KINETIC VS. THERMODYNAMIC CONTROL



- ROUTE A TO CPD 2 IS FASTEST
- ROUTE B TO CPD 3 GIVES MORE STABLE PRODUCT



- IF YOU DO RXN UNDER MINIMUM CONDS - LOW TEMP, SHORT RXN TIMES - GET MOSTLY ROUTE A (CPD 2)
RXN IS UNDER KINETIC CONTROL
- IF YOU DO THE RXN UNDER MORE FORCING CONDITIONS - LONGER TIME; HIGHER TEMP - GET MOSTLY ROUTE B (CPD 3)
RXN IS UNDER THERMODYNAMIC CONTROL

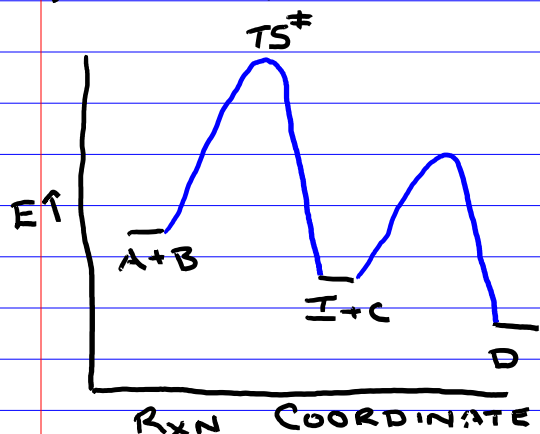
RATE DETERMINING STEP.

TAKE A 2 STEP RXN



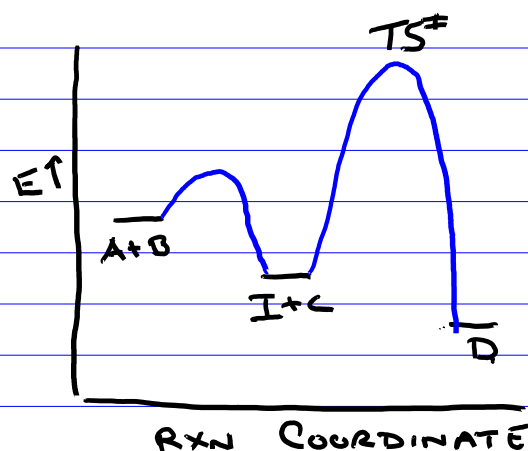
2 POSSIBILITIES FOR R_{XN} PROFILE

1) 1ST STEP IS SLOWEST



$$\text{RATE } v = k[A][B]$$

2) 2ND STEP IS SLOWEST (RDS)

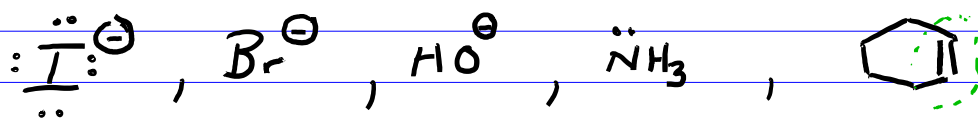


$$\text{RATE} = k'[A][B][C]$$

SO, ONLY THE CHEMICALS APPEARING IN OR BEFORE THE SLOW (RDS) STEP APPEAR IN THE RATE EQN

ELECTROPHILE & NUCLEOPHILES

NUCLEOPHILES (Nu^-) - ATOM, OR GROUP OF ATOMS, OR MOLECULE WILLING TO DONATE AN e^- PAIR IN A REACTION

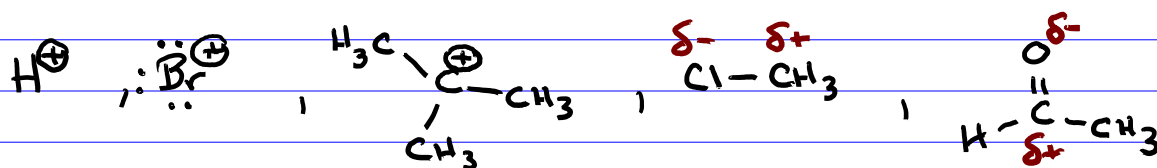


— OFTEN "—" CHARGED, BUT NOT ALWAYS.

DIFFERENCE FROM BASE

- NUCLEOPHILE REFERS TO KINETICS - I.E. HOW RAPIDLY IT ACTS
- BASE REFERS TO THERMODYNAMICS - I.E. POSITION OF EQUILIBRIUM.

ELECTROPHILE (E^+) - ATOM, GROUP OF ATOMS, OR MOLECULE WILLING TO ACCEPT e^- PAIR IN A RXN.



- IT'S A KINETIC TERM - GOOD ELECTROPHILES REACT V. RAPIDLY.

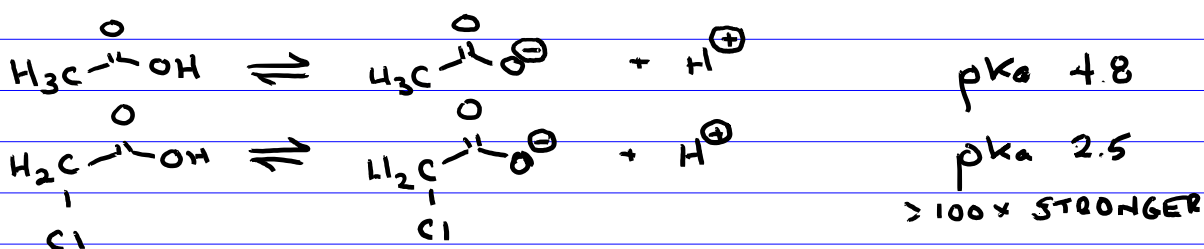
LECTURE 13

ELECTRONIC EFFECTS IN ORGANIC CHEMISTRY

- DIVIDED INTO INDUCTIVE EFFECTS, RESONANCE EFFECTS

INDUCTIVE EFFECTS (FIELD EFFECTS)

- BASED ON GROUPS WITHDRAWING e^- DENSITY ($-I$)
OR DONATING ELECTRON DENSITY ($+I$)
THROUGH σ BONDS



DUE TO FACT THAT Cl IS MORE E_N ELEMENT, PULLING SOME e^- DENSITY OFF THE O^-
 $\therefore$ SLIGHTLY MORE STABLE ANION

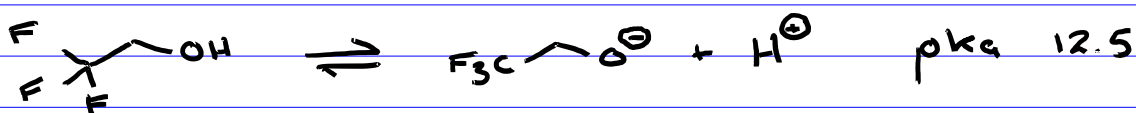
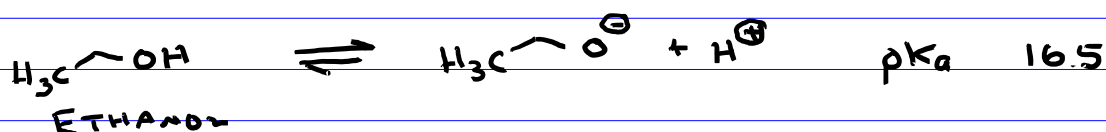
CONVERSELY, $-I$ GROUPS WOULD DESTABILIZE A CATION

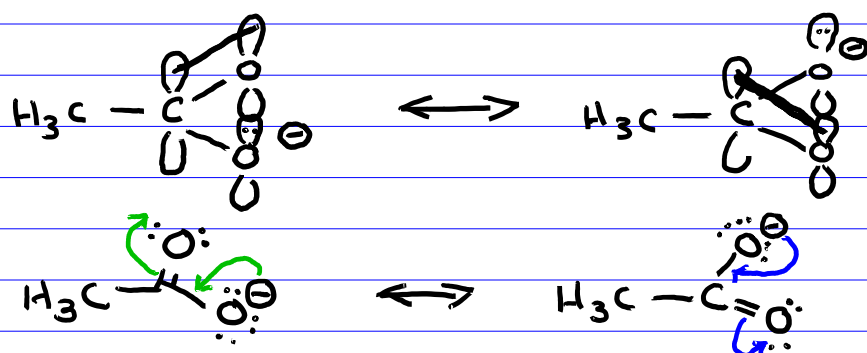
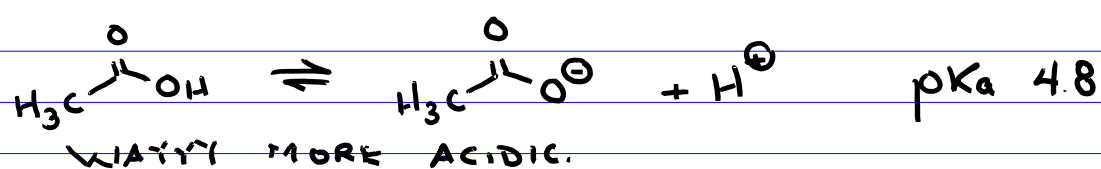
$-\text{Cl}, -\text{F}, -\text{Br}, -\text{OH}, -\text{NH}_2$ $-I$ GROUPS

- ALKYL GROUPS $-\text{CH}_3, -\text{CH}_2\text{CH}_3, -\underset{\text{CH}_3}{\overset{\text{CH}_3}{\text{C}}}$ ARE CONSIDERED $+I$ GROUPS

RESONANCE EFFECTS ($-M, +M$)

- VERY IMPORTANT, HAVE A MORE DRASTIC EFFECT
- NORMALLY OPERATE THROUGH π SYSTEM (p -ORBITALS)
- EXPLAIN STABILITY (OR LACK OF IT) IN REACTIVE INTERMEDIATES
- DEMONSTRATE REACTIVITY OF A NEUTRAL ORGANIC CPD.





BOTH REPRESENT
ELECTRONIC STRUCTURE
OF SPECIES

- EACH "O" ATOM IS
REALLY $-\frac{1}{2}$ CHARGE
- HUGE STABILIZATION

TYPES OF ARROWS - A MINI REVIEW

$\longrightarrow$ REACTION

$\rightleftharpoons$ OR $\longleftrightarrow$ REACTION SHOWING IT'S IN
EQUILIBRIUM

$\longleftrightarrow$ RESONANCE FORMS

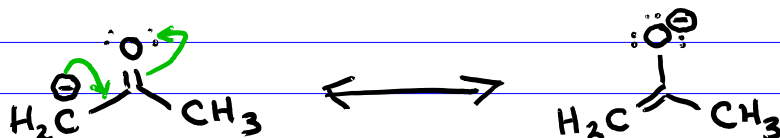
$\curvearrowright$ ELECTRON MOVEMENT

$\circ \longrightarrow$ NO OFFICIAL MEANING

GROUND RULES FOR RESONANCE FORMS.

1) NORMALLY IT INVOLVES THE π SYSTEM

2) IF YOU CAN PUT A "-" CHARGE ON AN EN ATOM, IT IS
A PARTICULARLY GOOD RESONANCE FORM



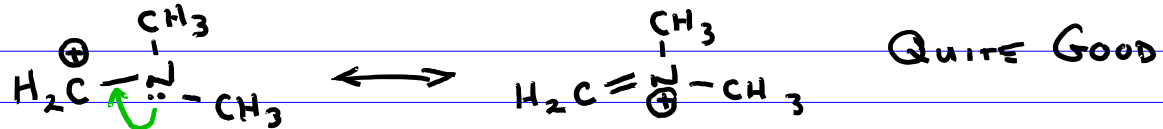
3) IF YOU PUT A "+" CHARGE ON AN EN ATOM

- 8 VALENCE e^-

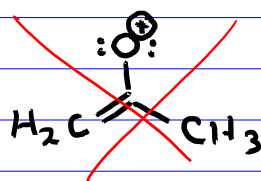
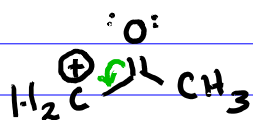
- OK

- 6 VALENCE e^-

- NO WAY - NOT STABLE IN
THE SLIGHTEST



Quite Good

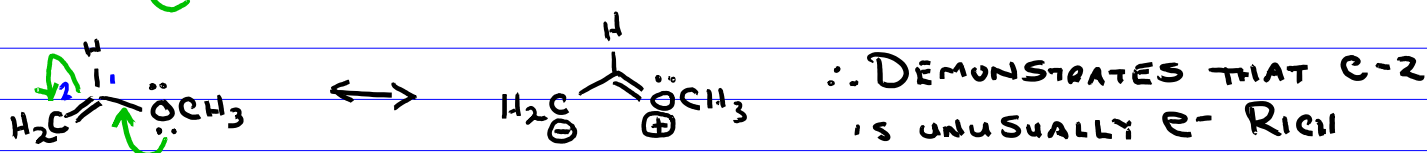
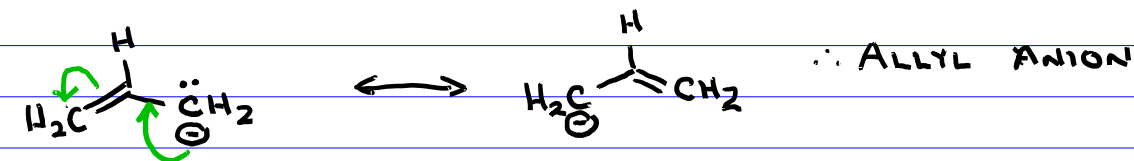


6 VALENCE e^-
No way
WAY UNSTABLE

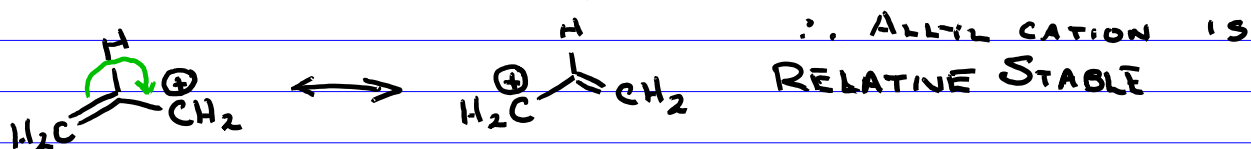
LECTURE 14

MOST COMMONLY ENCOUNTERED TYPES OF RESONANCE FORMS.

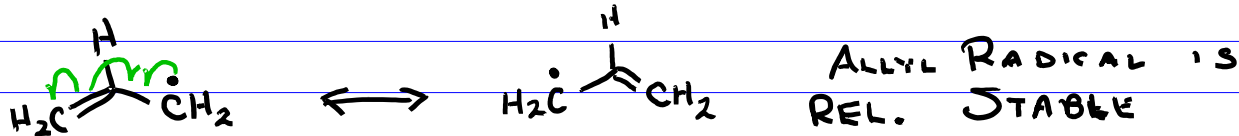
- 1) IF YOU HAVE A LONE PAIR OF e^- ON AN ATOM NEXT TO A MULTIPLE BOND



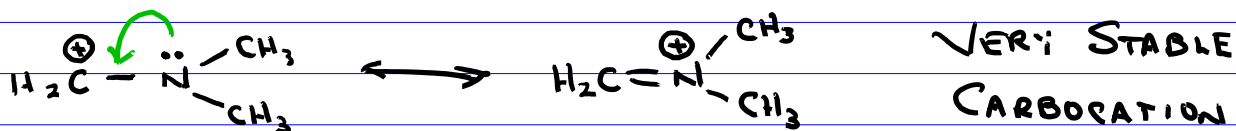
- 2) WHEN YOU HAVE AN EMPTY ORBITAL (USUALLY A p ORBITAL) NEXT TO A MULTIPLE BOND.



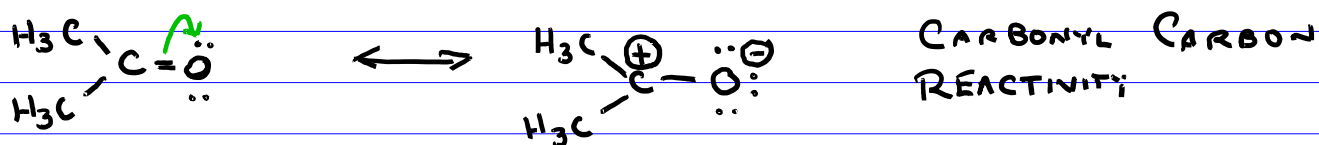
- 3) A FREE RADICAL NEXT TO A π BOND



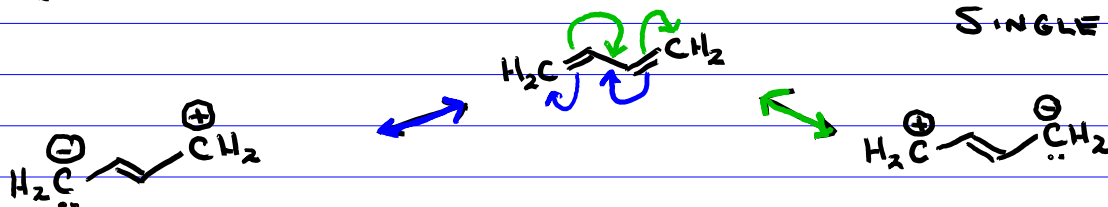
- 4) WHERE THERE'S A CATION NEXT TO AN ATOM WITH A LONE PAIR

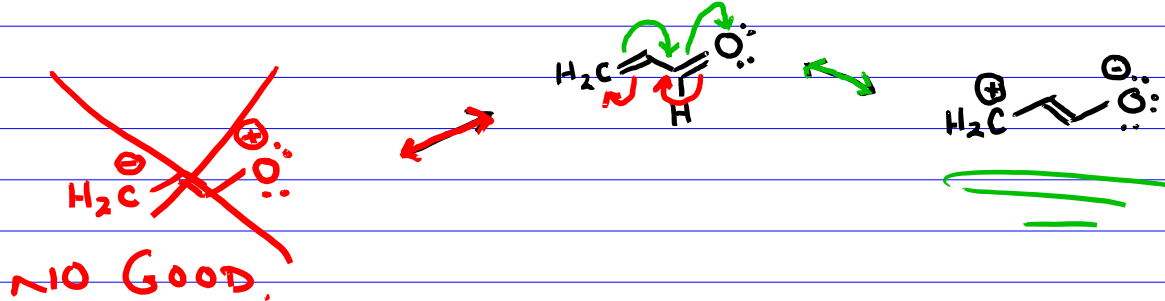


- 5) π BOND BETWEEN ATOMS OF DIFFERENT EN

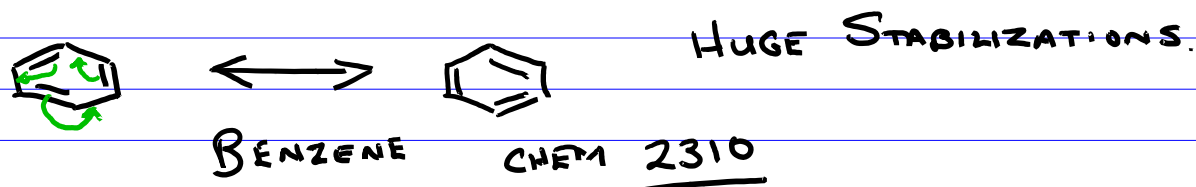


- 6) WHERE THERE ARE TWO MULTIPLE BONDS SEPARATE BY A SINGLE BOND





ULTIMATE CASE OF RESONANCE STABILIZATION OF A MOLECULE



CHEMISTRY OF ALKENES AND ALKYNES.

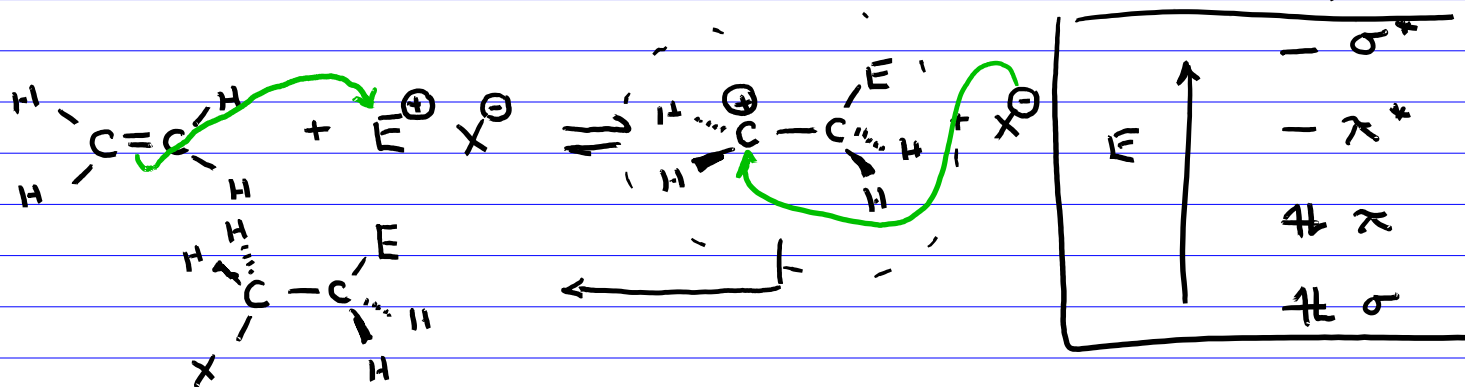
OGILVIE - CH 8

KARL CH 11 (+ A BIT OF CH 12)

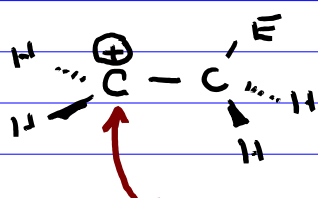
ALKENES

π BOND OF $C=C$ IS WEAKEST ONE
(250 KJ/mol)

- ALSO THE π BONDING ORBITAL IS HIGH LYING
- WILLING TO REACT WITH ELECTROPHILES EASILY.



ELECTROPHILIC ADDN RXN TO ALKENES



CALLED A CARBOCATION OR A CARBENIUM ION

$E-X =$ $H-Cl$
($H^+ Cl^-$)

$H-Br$

Br_2

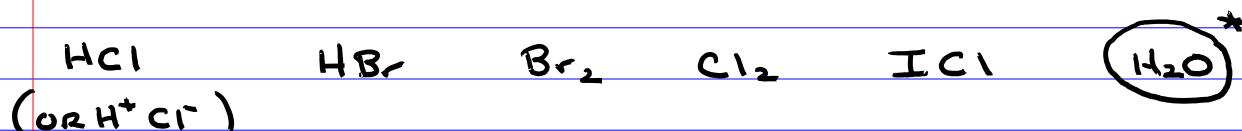
Cl_2

$I-Cl$

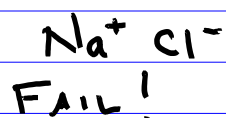
H_2O^*

LECTURE 15

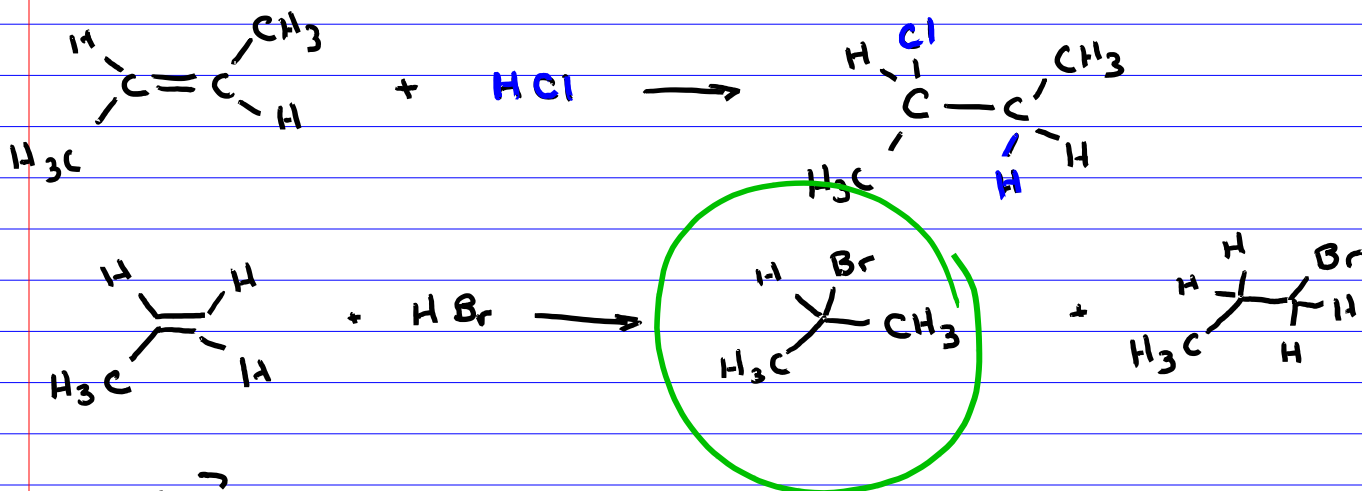
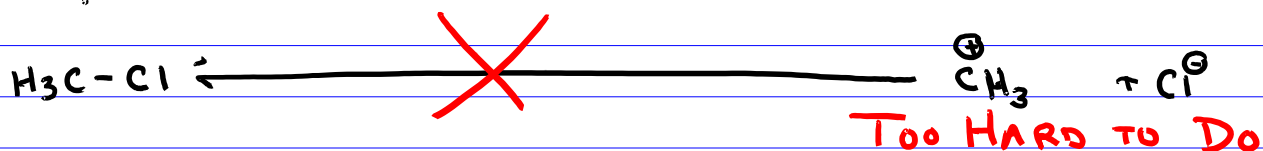
$E^+ X^-$ COMMON FOR ELECTROPHILIC ADDNS TO ALKENES



GOOD CANDIDATES - WE WANT AN E^+ THAT IS REACTIVE ENOUGH, BUT WHICH CAN BE GENERATED EASILY ENOUGH

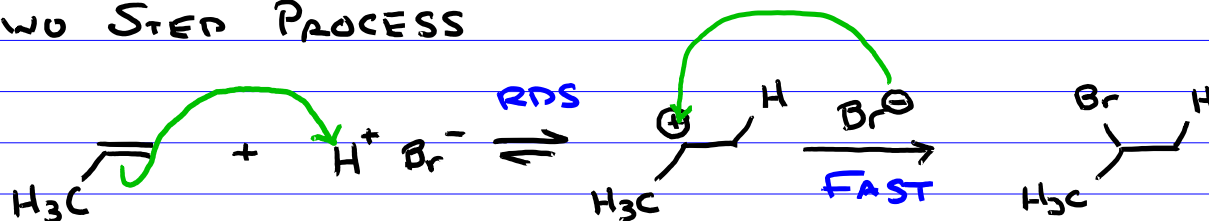


Na^+ IS JUST TOO STABLE



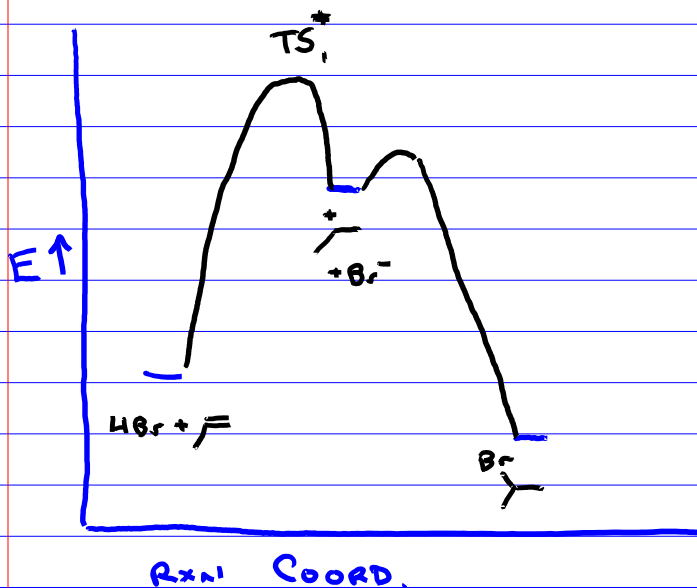
WHY?

TWO STEP PROCESS



TWO STEPS

- 1) GENERATING A REACTIVE CARBENIUM ION INTERMEDIATE FROM A NEUTRAL ORGANIC CPD. - SLOW OR RATE DETERMINING STEP
- 2) REACTION OF THAT CARBOCATION WITH A NUCLEOPHILE TO GIVE (USUALLY) A NEUTRAL ORGANIC - FAST



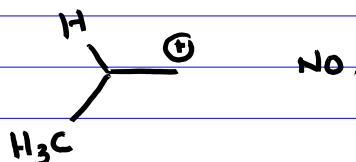
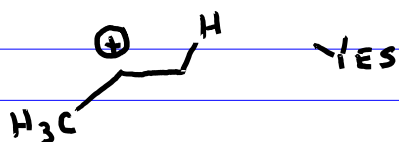
- TO TRULY PREDICT THE RXN'S OUTCOME, WE NEED TO UNDERSTAND TS_1^+

- THIS TAKES A WHILE TO CALCULATE A T.S.⁺

WE'LL MAKE AN APPROXIMATION

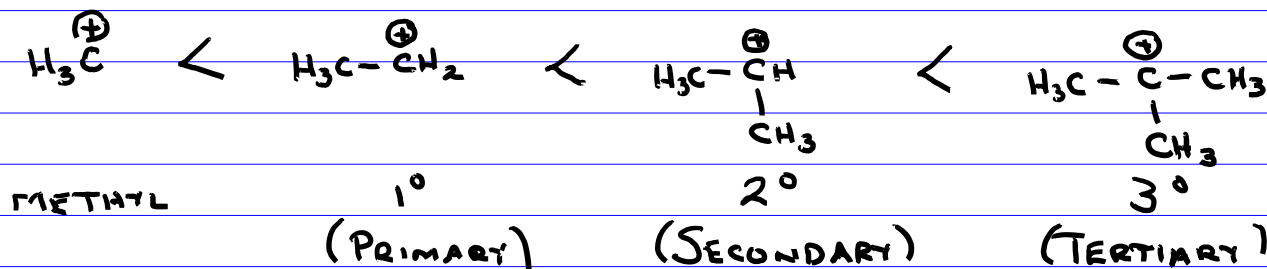
- ASSUME THAT THE SPECIES CLOSEST IN ENERGY TO THE TRANSITION STATE RESEMBLES IT BEST
- "HAMMOND POSTULATE"

- HERE, IT'S THE CARBOCATION



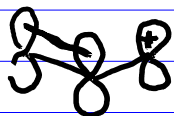
TWO REASONS

1) INDUCTIVE EFFECTS - ALKYL GROUPS ARE +I GROUPS (INDUCTIVELY e^- DONATING), STABILIZE CARBOCATIONS



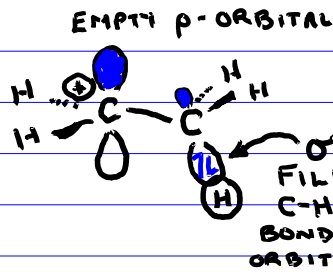
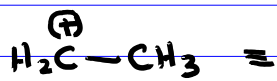
2) HYPERCONJUGATION

CONJUGATION - CONTINUOUS LINED UP p- ORBITAL OVER > 2 "CARBON" ATOMS

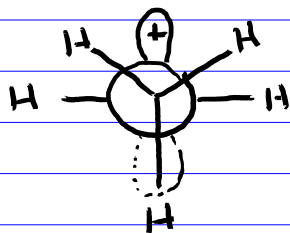


∴ STABLE

"NORMALLY" p- ORBITALS

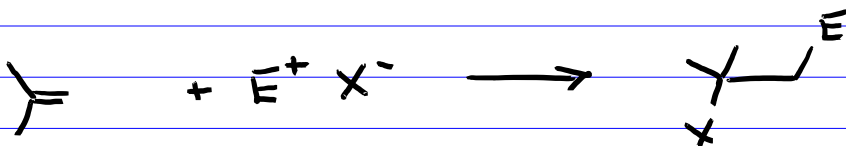
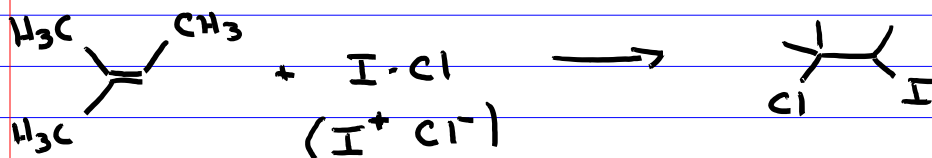
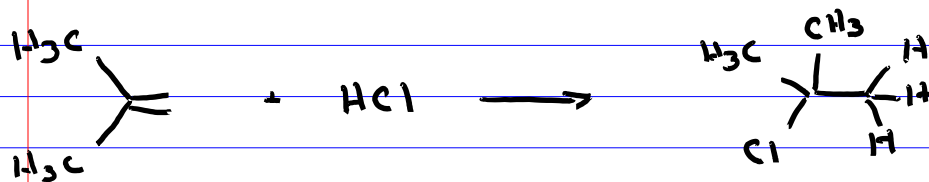


σ BONDING ORBITAL IS LINED UP TO DONATE / SHARE e^- DENSITY WITH EMPTY p-ORBITAL OF CARBOCATION $\therefore$ STABILIZATION



- BECAUSE IT'S OVERLAP OF σ SYSTEM WITH THE π SYSTEM, IT'S CALLED HYPERCONJUGATION.

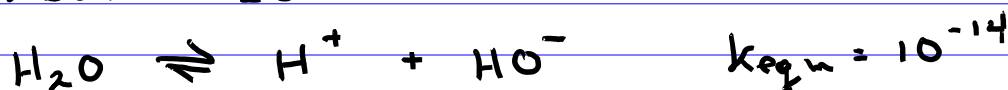
CH_3^+ DOESN'T HAVE THIS
 1° CARBOCATION HAS ONE OF THESE
 2° " HAS TWO OF THESE
 3° " HAS THREE OF THESE



GENERAL RULE - MARKOVNIKOV'S RULE

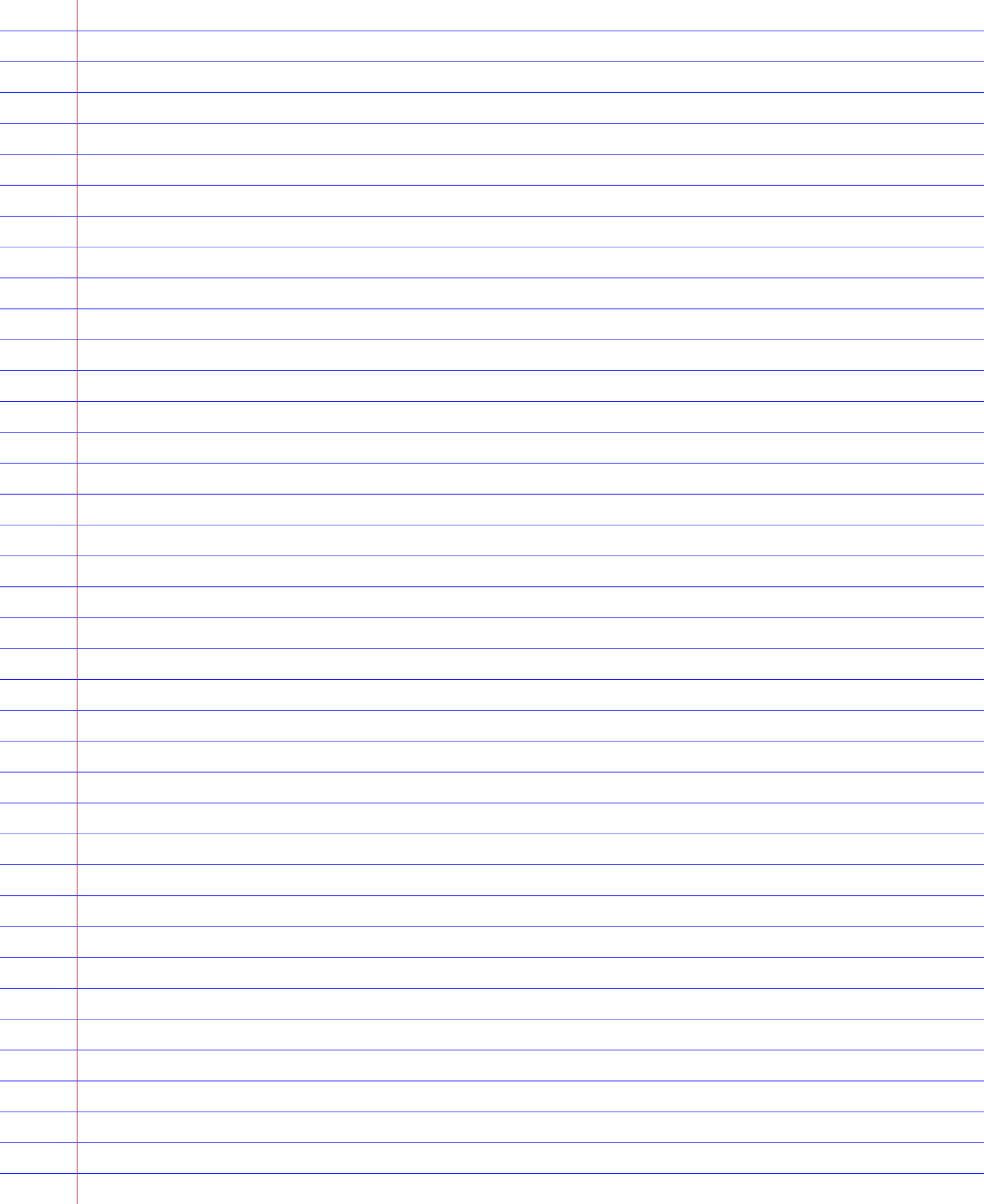
- ELECTROPHILIC ADDN TO ALKENE PROCEEDS BY GIVING THE MOST STABLE CARBOCATION INTERMEDIATE, WHICH IS NORMALLY THE ONE WITH THE MOST ALKYL OR ARYL GROUPS

WHAT ABOUT H_2O ?



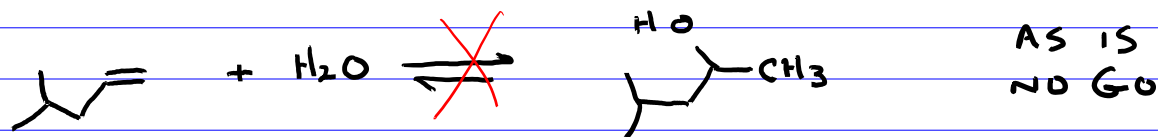
NOT ENOUGH TO REASONABLY REACT WITH AN ALKENE

SO WHAT DO WE DO?



LECTURE 16

ADDITION OF H_2O AND CATALYSIS

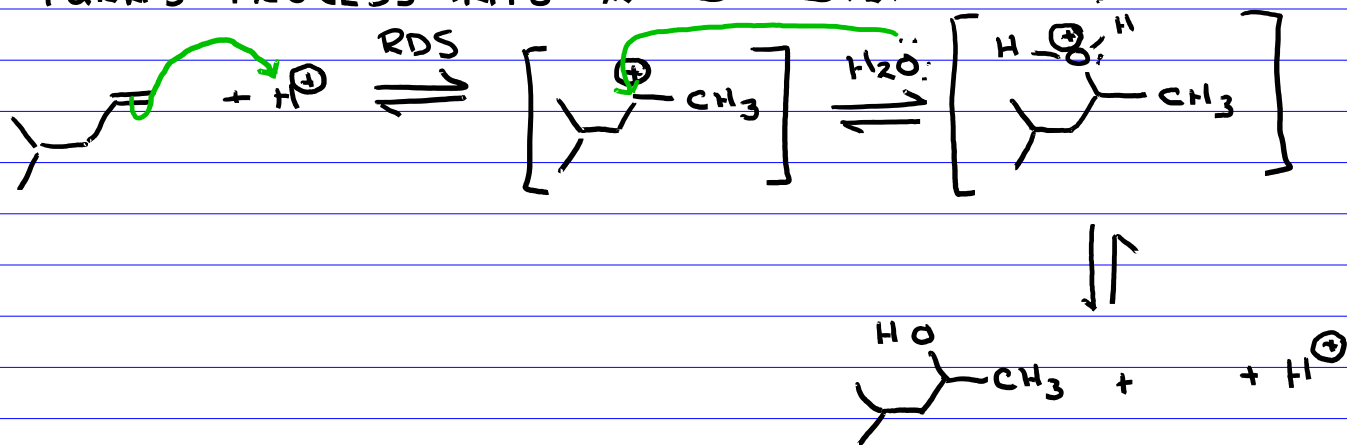


REASON $[H^+]$ IN H_2O IS $10^{-7} M$ TOO SMALL.
TO MAKE RXN WORK AT ANY REASONABLE RATE

SOLUTION: ADD SOME H^+ 10% H_2SO_4 (1.9M)
THAT'S ENOUGH TO GET RXN GOING
THAT MAKES $[OH^-]$ REALLY SMALL ($10^{-14} - 10^{-15} M$)

- NOT DEADLY, SINCE H_2O CAN ACT TO A NUCLEOPHILE

- TURNS PROCESS INTO A 3 STEP RXN.

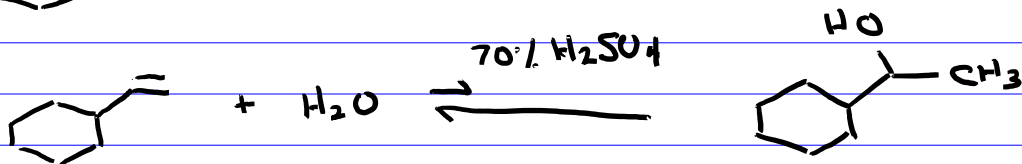
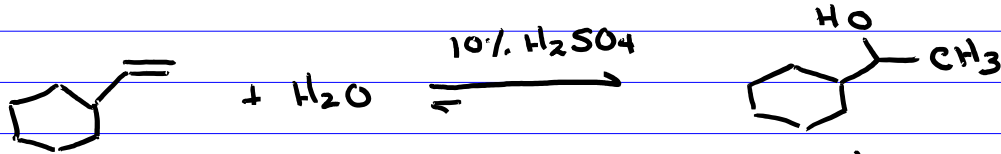


H^+ IS A TRUE CATALYST

- SPEEDS UP RXN BY CHANGING THE MECHANISM
- RECOVERED INTACT AT THE END OF THE RXN
- JUST NEED A MODEST AMOUNT TO GET RXN TO GO

NOTE:

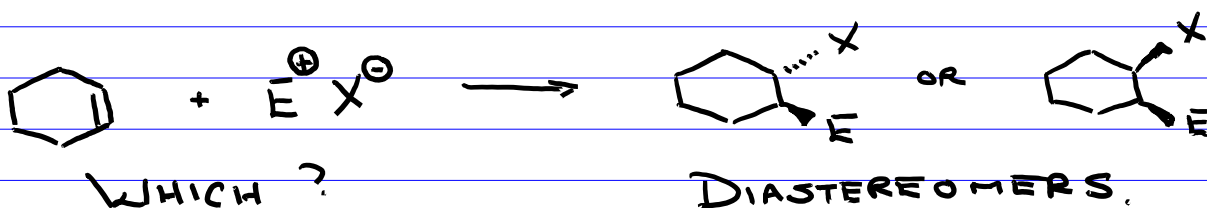
10% H_2SO_4 IS GOOD FOR GETTING THE RXN TO GO
70% H_2SO_4 IS BAD - RXN FAIL.



THIS CONTAINS
A LIE - WHAT
IS IT?

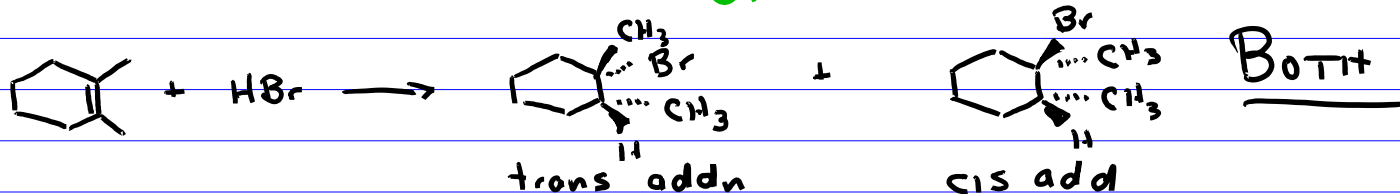
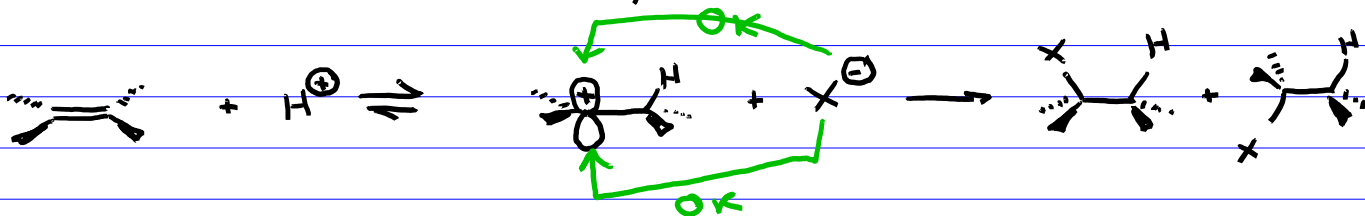
STEREOCHEMISTRY OF THE ADDITION

Q

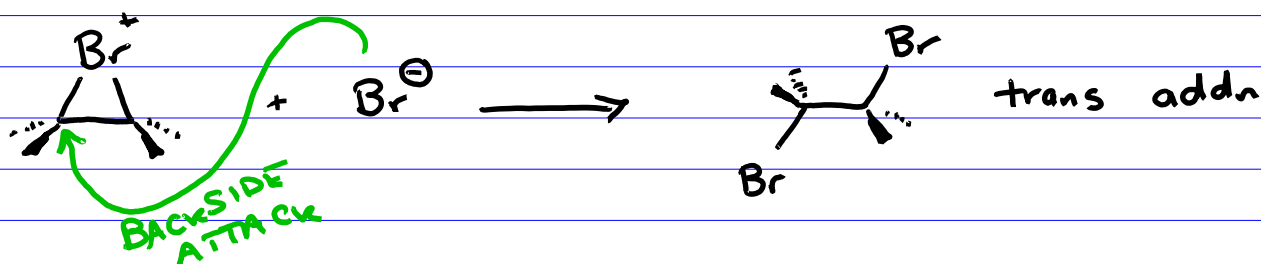
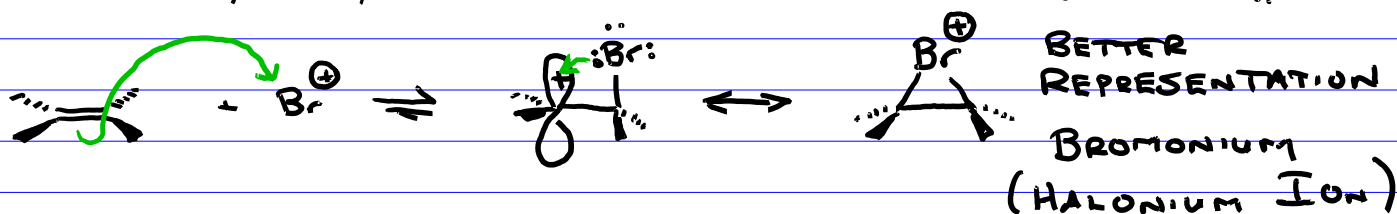


- ANSWER - IT DEPENDS.

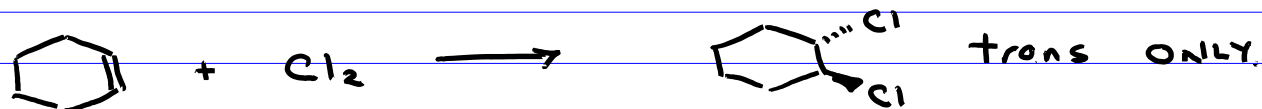
1) if E^+ is H^+ (HCl , HBr , H_2O)



2) in Br_2 , Cl_2 , ICl E^+ is :Br^+ or :Cl^+ or :I^+

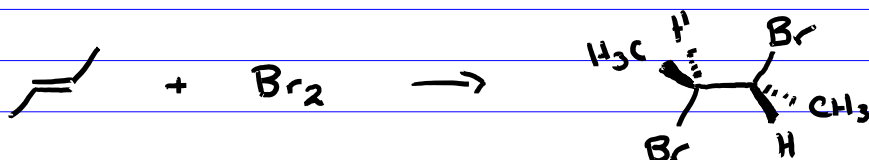
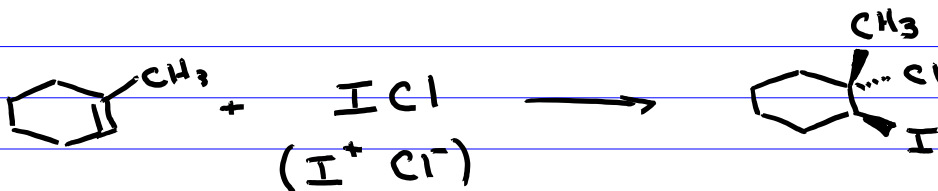


LOCATION OF
 σ^* ORBITAL IS
THERE

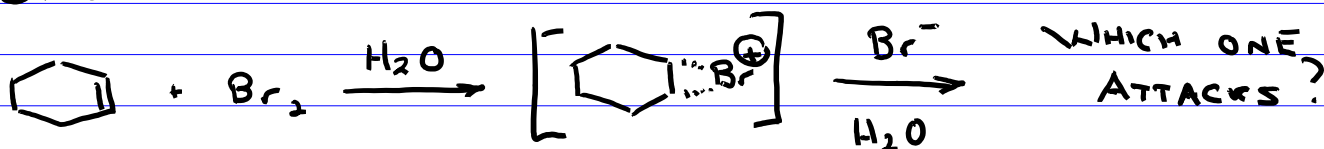


STEREOSPECIFIC REACTION

MARKOVNIKOV'S RULE DOES STILL HOLD



QUESTION

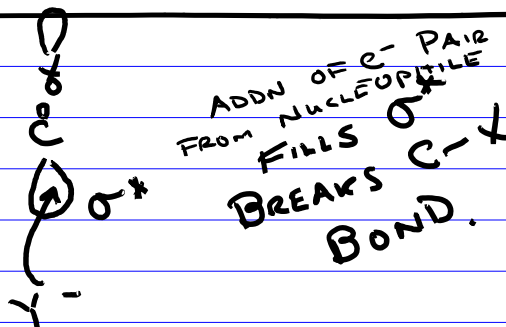


- MONDAY'S LECTURE

STUDENT Q

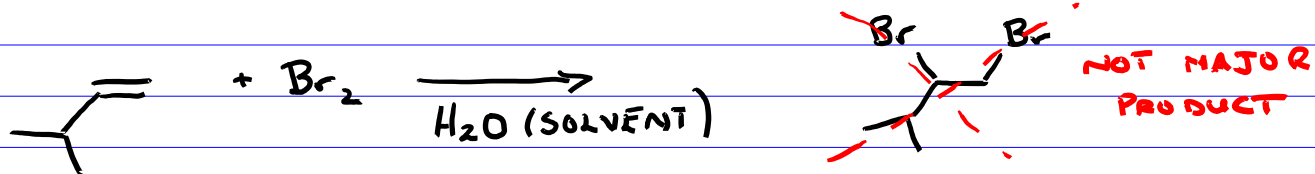
 σ BONDING ORBITAL OF C-X BOND

σ^* AND BACKSIDE ATTACK

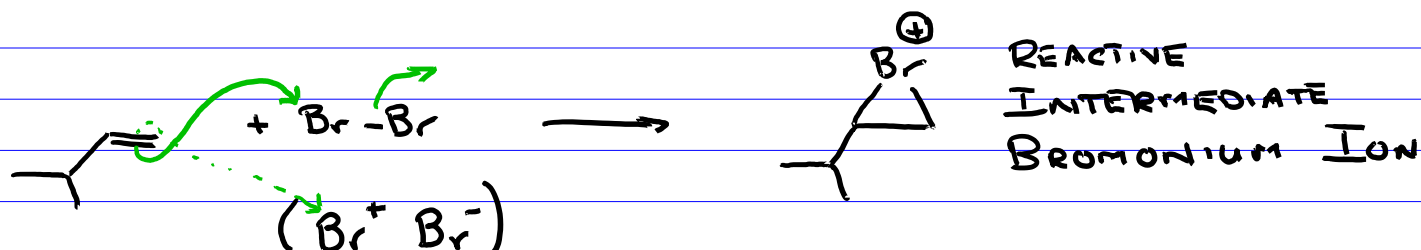


LECTURE 17.

INTERVENTION OF SOLVENT IN ELECTROPHILIC ADDN REACTIONS.



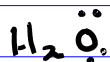
MECH



BUT, WE HAVE 2 NUCLEOPHILES PRESENT

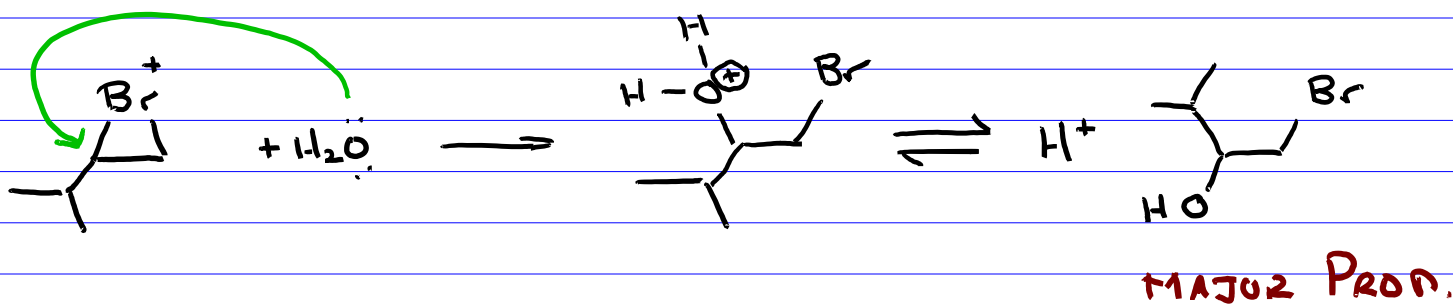


CONCENTRATION << 0.2 M

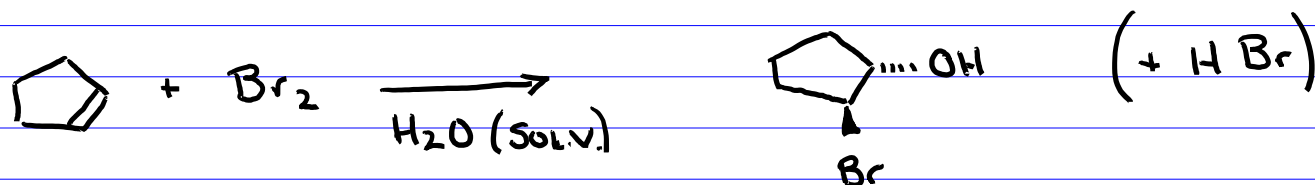


CONCENTRATION 55 M

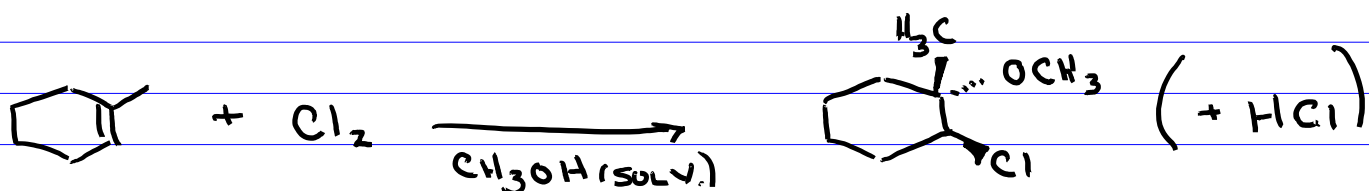
WINS



ADDITION IS STILL TRANS



ALSO OPERATES FOR SOLVENTS LIKE CH₃OH, H₃CCH₂OH,

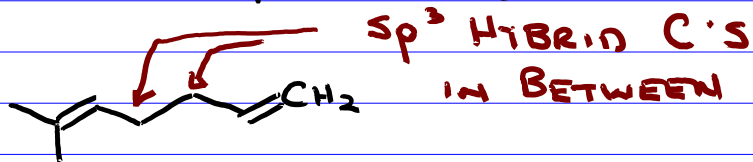
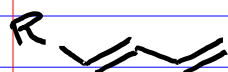


ELECTROPHILIC ADDITION AND DIENES.

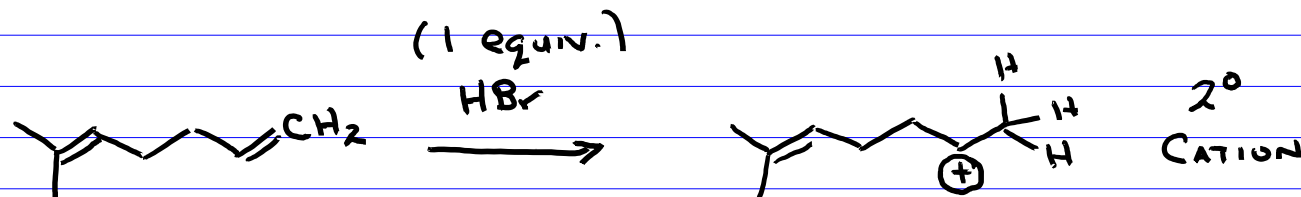
WE'LL CONSIDER TWO TYPES

CONJUGATED

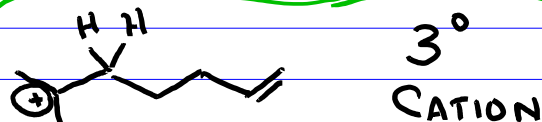
NON-CONJUGATED



WITH NON-CONJUGATED DIENES



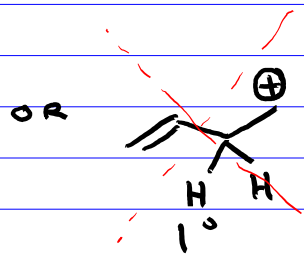
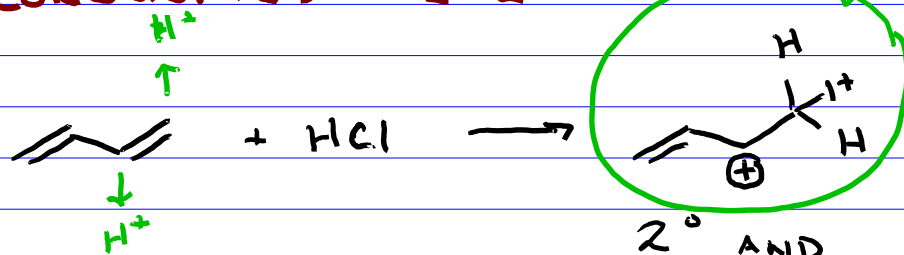
VERSUS



FORMED MORE RAPIDLY WINS

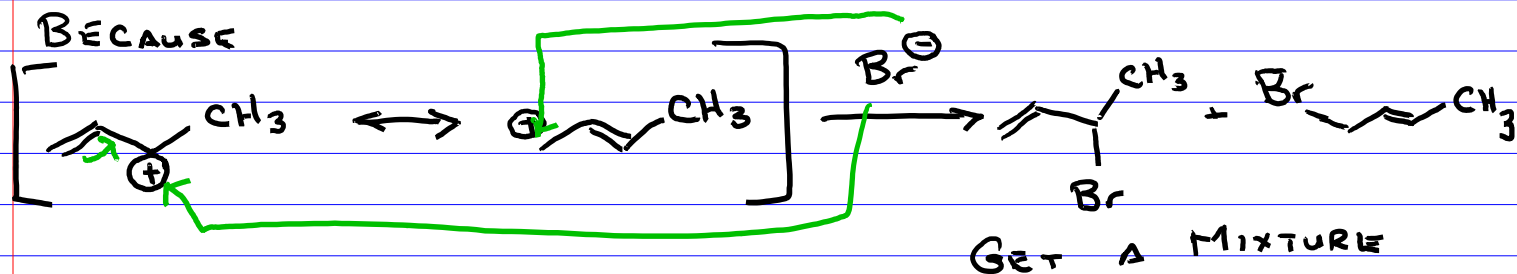
YES, IF WE ADD MORE HBr, THE OTHER ALKENE WILL REACT.

CONJUGATED DIENES



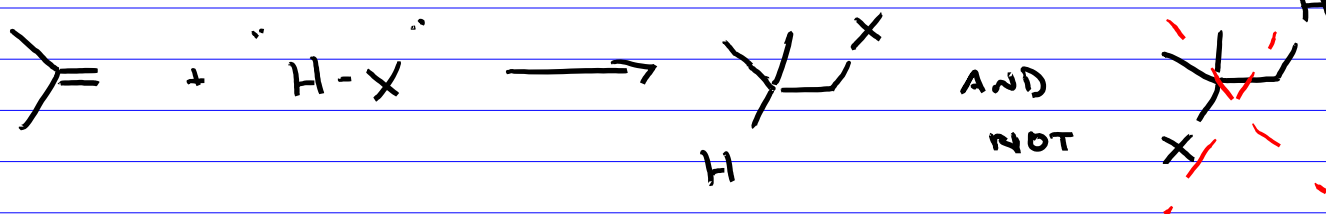
FAVOURABLE

BECAUSE

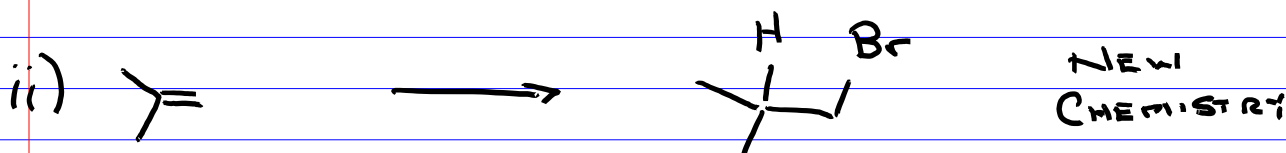
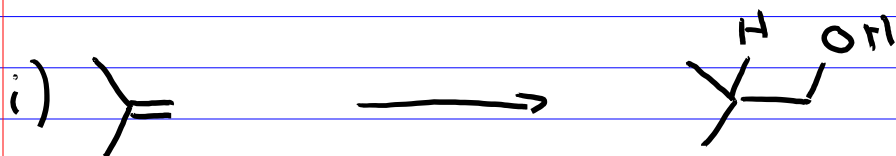


MARKOVNIKOV ADDN. HAS BEEN A RULE

HOW CAN WE DO ANTI-MARKOVNIKOV ADDITION

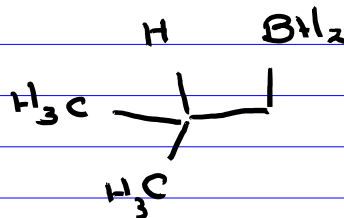
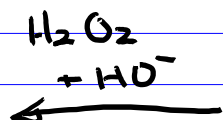
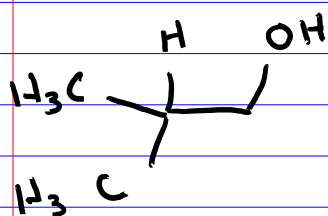
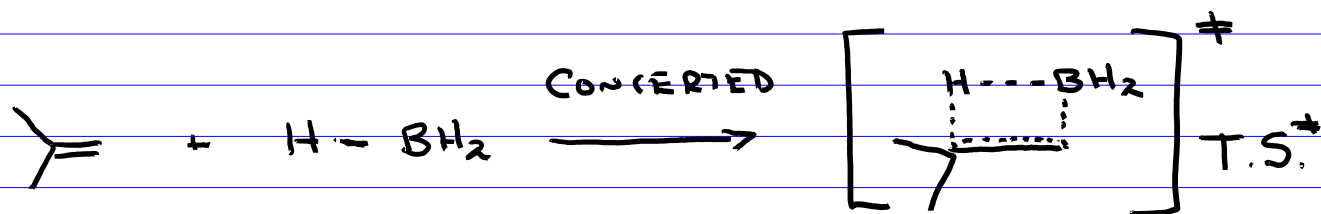
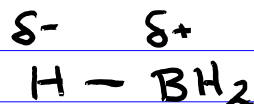


2 EXAMPLES - MUST LEAVE TRADITIONAL ELECTROPHILIC ADDN MECHANISM BEHIND



i) HYDROBORATION / OXIDATION

BORANE BH_3

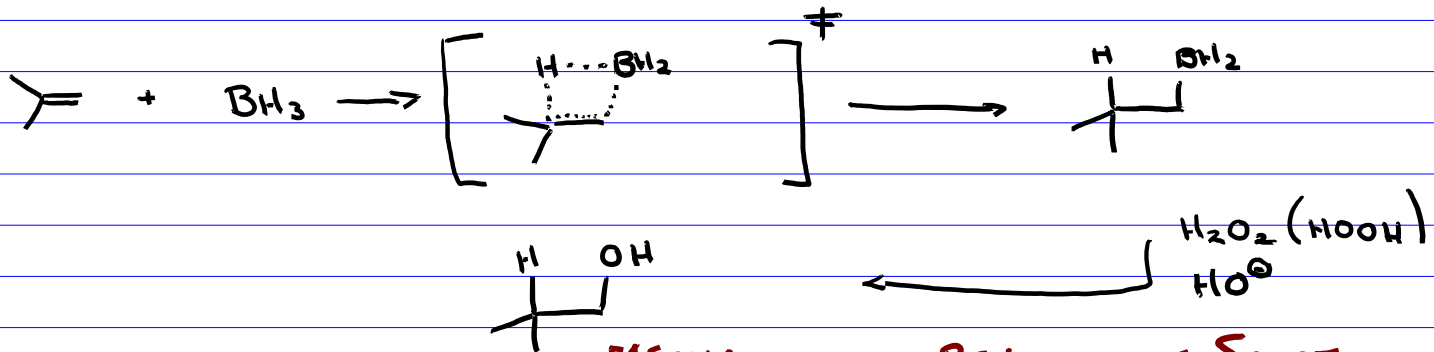
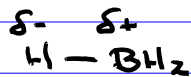


WE'LL REVISIT NEXT LECTURE

LECTURE 18

i) ANTI-MARKOVNIKOV ADDITION

HYDROBORATION - OXIDATION



MECHANISM IS BEYOND THE SCOPE OF THIS COURSE

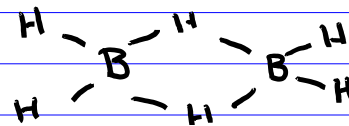
POINTS:

1) IT'S REALLY MOSTLY STERIC - H GOES TO MOST STERICALLY HINDERED END OF THE ALKENE BECAUSE IT'S SMALL - AND BH₂ IS LARGER

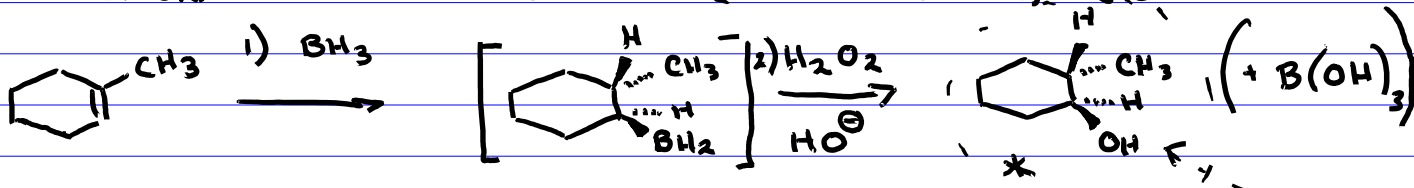
2) "BH₃" ACTUAL STRUCTURE IS A DIMER B₂H₆

REASON?

- ASK PROF. DROWER (CHEM 2510)

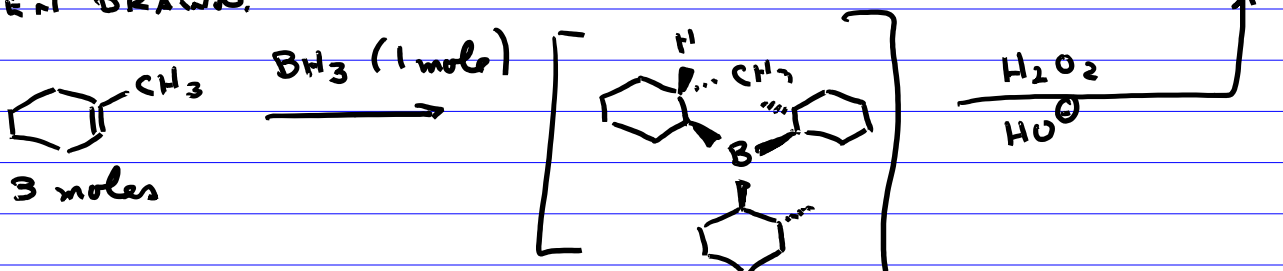


3) ADDITION REACTION IS STEREOSPECIFIC AND CIS-

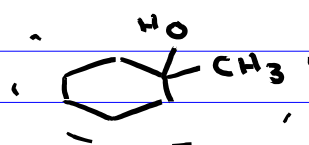
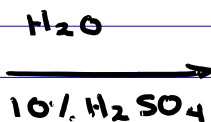
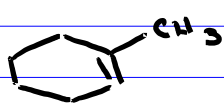


4) BECAUSE ALL 3 B-H BONDS CAN REACT

OFTEN DRAWN.



COMPARE
TO



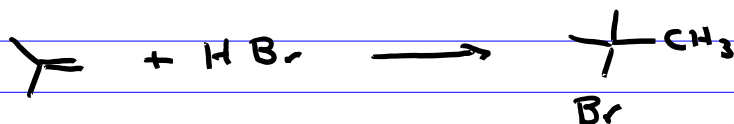
ii) RADICAL ADDITION OF HBr

OGILVIE CH 19.7

KARTY CH 25.5

CONTRAST TO

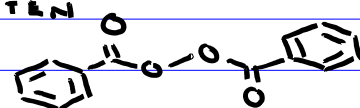
VIA H^+ AND A
CARBOCATION



IF WE WANT TO REVERSE WHERE H AND Br GO, JUST
ADD A PEROXIDE

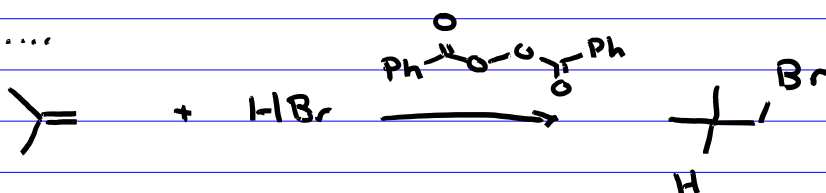
RO-OR
V. WEAK BOND

OFTEN



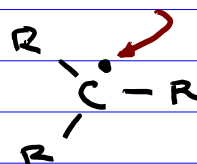
BENZOYL PEROXIDE

SO.....



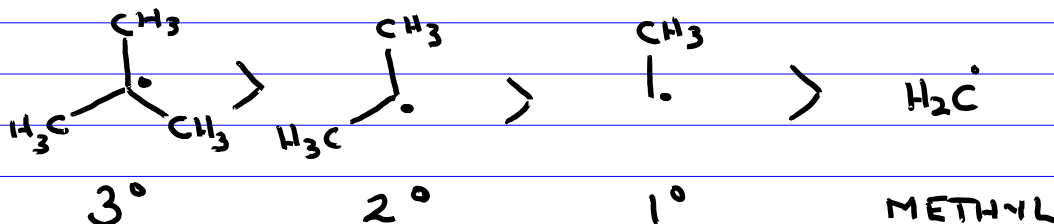
MAJOR PROD

SINGLE e^-

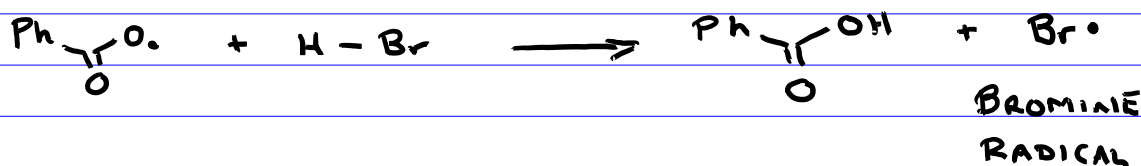
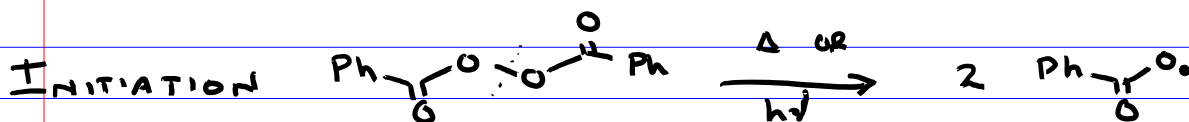


BIGGEST CHANGE - NO CARBOCATION
- INVOLVES A (FREE) RADICAL

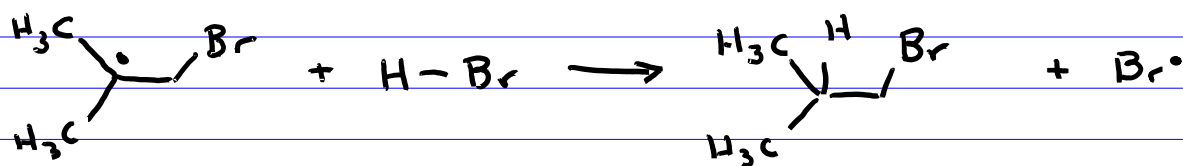
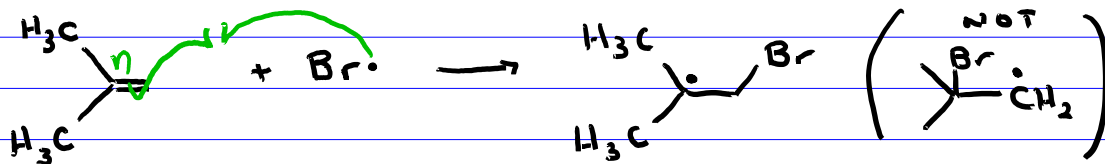
STABILITY ORDER IS SAME AS CARBOCATIONS



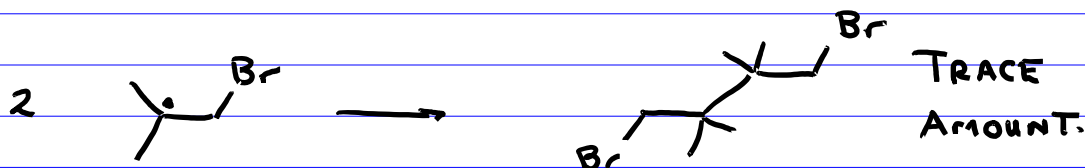
RADICAL CHAIN MECHANISM.



PROPAGATION

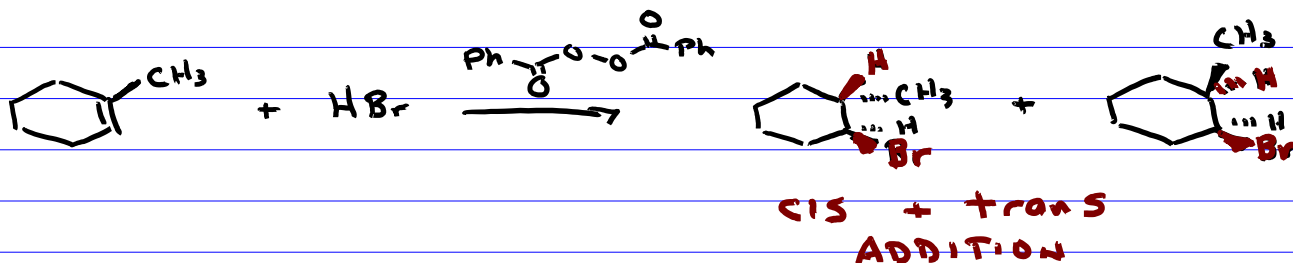


TERMINATION



STEREOCHEMISTRY - MIXTURE

RADICAL IS sp^2 HYBRIDIZED - SO ADDITION ON BOTH TOP OR BOTTOM IS OK

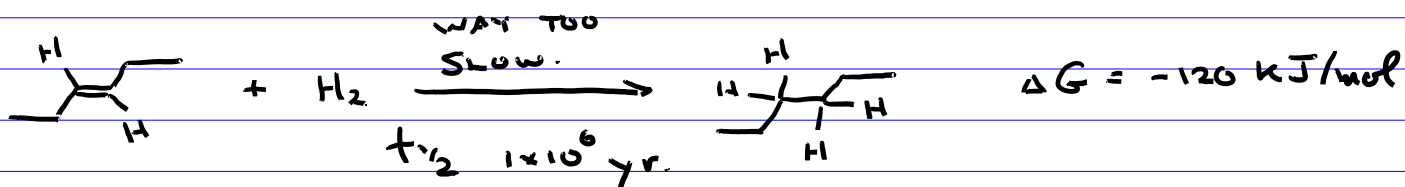


ONLY FOR HBr - NOT HCl, HI or HF

LECTURE 18

LECTURE 19

CATALYTIC HYDROGENATION (OF ALKENES)



- RATE BECOMES REASONABLE (MINUTES TO HOURS) WITH A CATALYST

- FINELY DIVIDED METAL

$\text{Pd} \geq \text{Ni} > \text{Pt} \gg \text{ALL OTHERS}$

OFTEN WRITTEN

Pd^0

OR

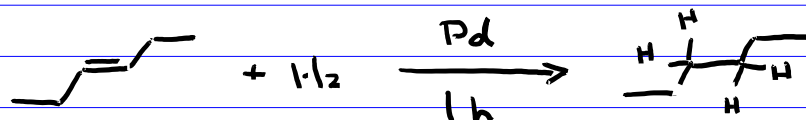
Pd/C

Ni^0

OR

$\text{R}_\text{N}\text{Ni}$

(RANEY NICKEL)

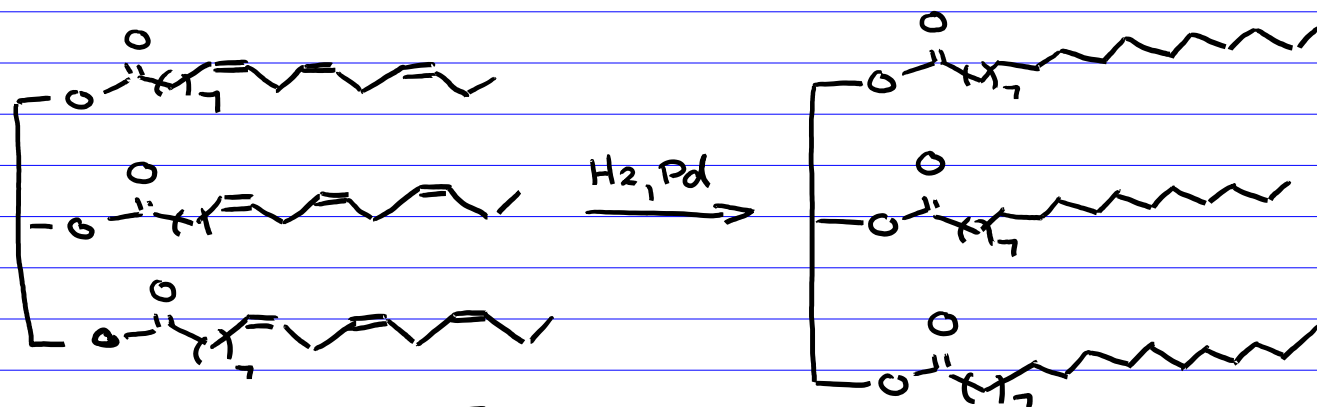


THIS REACTION IS A TYPE OF REDUCTION

ORGANIC DEFINITION - ADDITION OF 'H' ATOMS OR REMOVAL OF 'O' ATOMS

MECHANISM - COMPLEX, DON'T NEED TO KNOW FOR CHEM 2300

- SEE BLACKBOARD FOR MECHANISM.

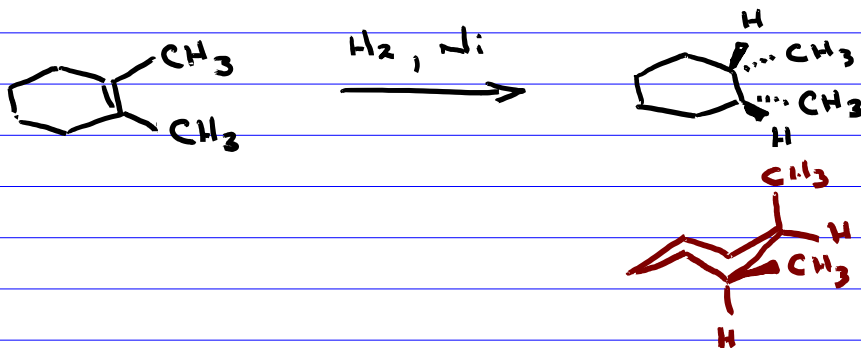


POLYUNSATURATED FAT

SATURATED FAT

STEREOCHEMISTRY OF HYDROGENATION

- THE TWO H ATOMS ADD CIS ACROSS THE ALKENE



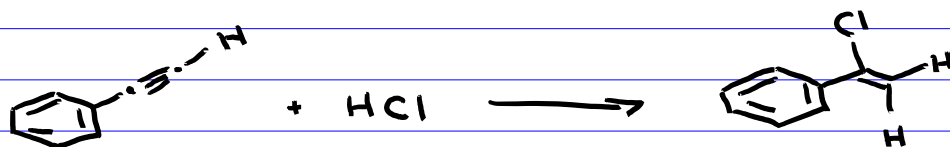
BOTH H ATOMS
ON SAME SIDE

REACTIONS OF ALKYNES

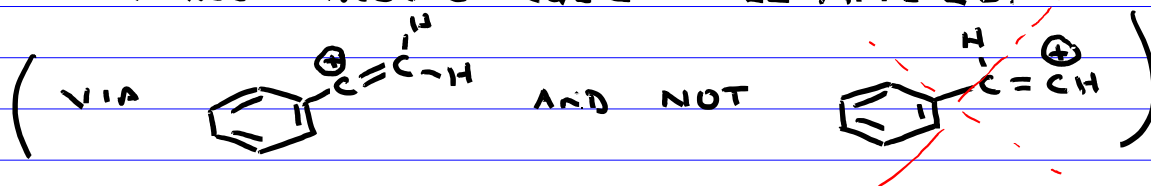
- DO THEY DO THE SAME THINGS

ELECTROPHILIC ADDITION

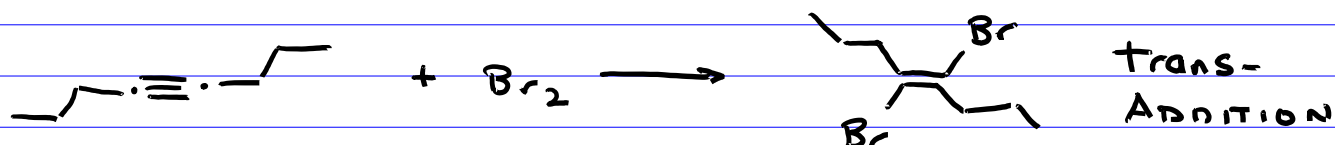
- YES, ALKYNES DO THESE REACTIONS



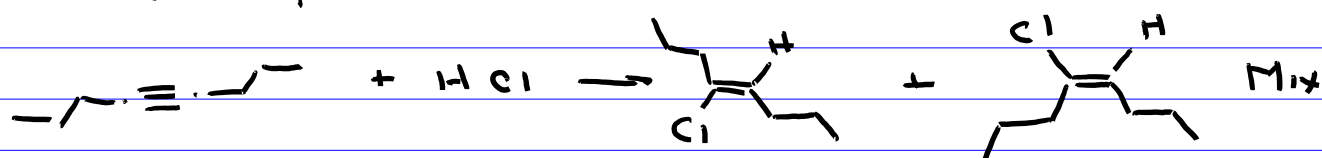
- MARKOVNIKOV'S RULE STILL APPLIES.



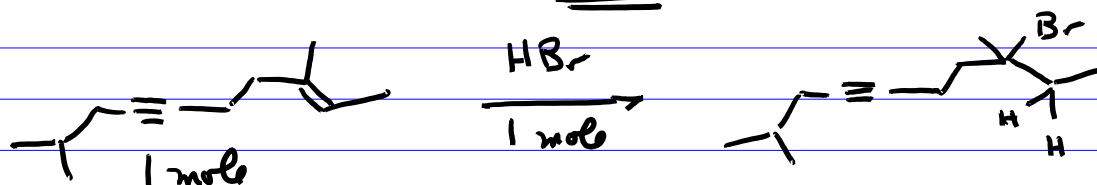
Br2, Cl2 AND ICl STILL ADD TRANS



BUT HCl, HBr, H2O $\neq$

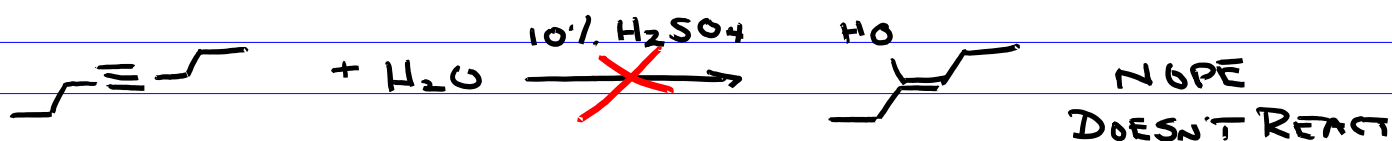


NOTE: ALKYNES ARE LESS REACTIVE THAN ALKENES.

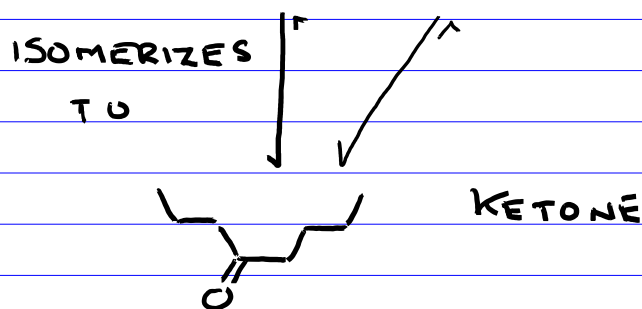
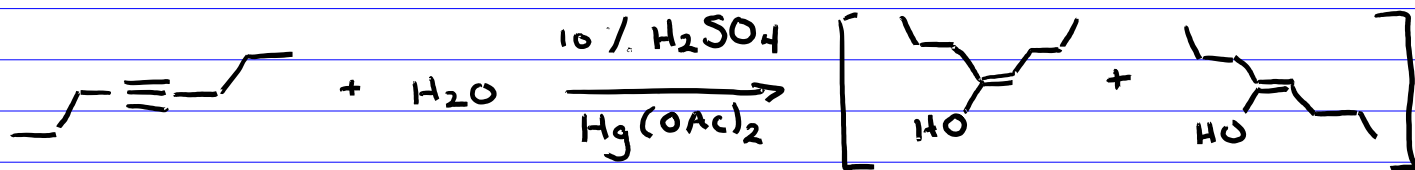


IF WE ADDED MORE HBr, THE C#C
WOULD REACT.

ADDITION OF H_2O



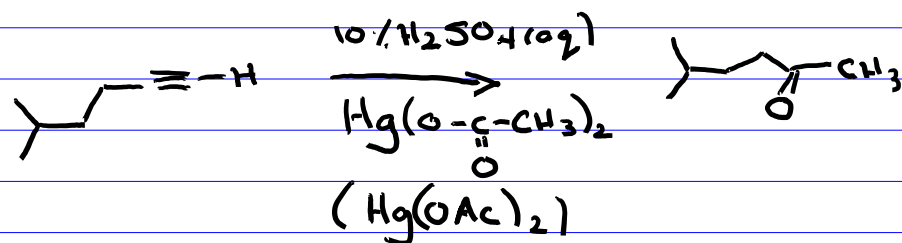
SOLUTION: ADD Hg^{2+} CC(=O)O[Hg]OC(=O)C ($Hg(OAc)_2$)



THIS TYPE OF ISOMERISM
 WHERE SINGLE & DOUBLE
 BOND POSITIONS SWITCH
 IS OFTEN CALLED TAUTOMERISM

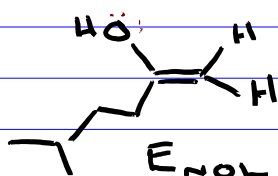
LECTURE 20

HYDRATION OF ALKYNES.

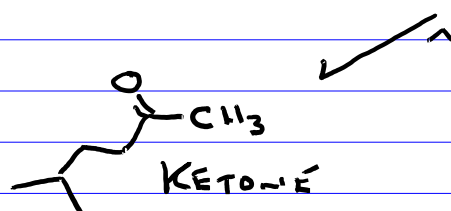


REASON:

ADDN: PROD. IS



FOLLOWS MARKOVNIKOV'S
RULE

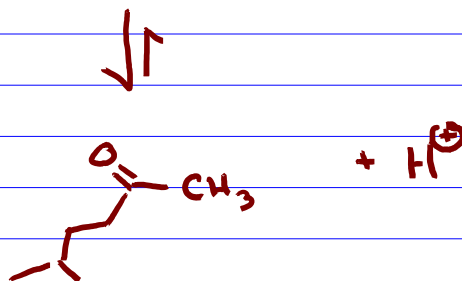
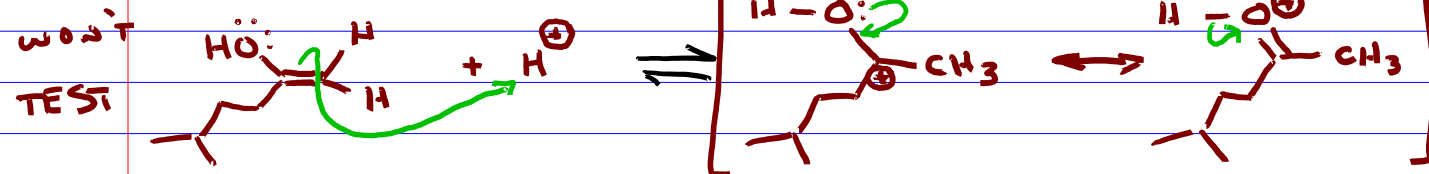


EQUILIBRIUM

$10^5 - 10^6 : 1$

IN FAVOUR OF THE
KETONE

MECH.



OXIDATION REACTIONS OF ALKENES.

OGILVIE 8.7, 20.3.6
KARTI 12.5, 24.7, 24.8

ORGANIC DEFINITION: - REACTION THAT ADD AN 'O' ATOM,
OR REMOVE H ATOMS.

1) EPOXIDATION OF ALKENES

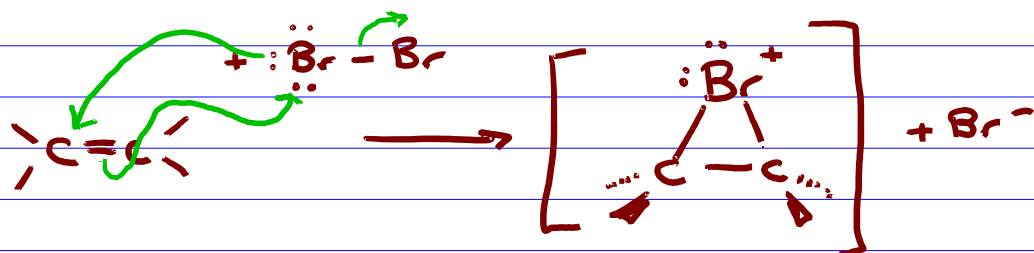


PROPER NAME OXIRANE

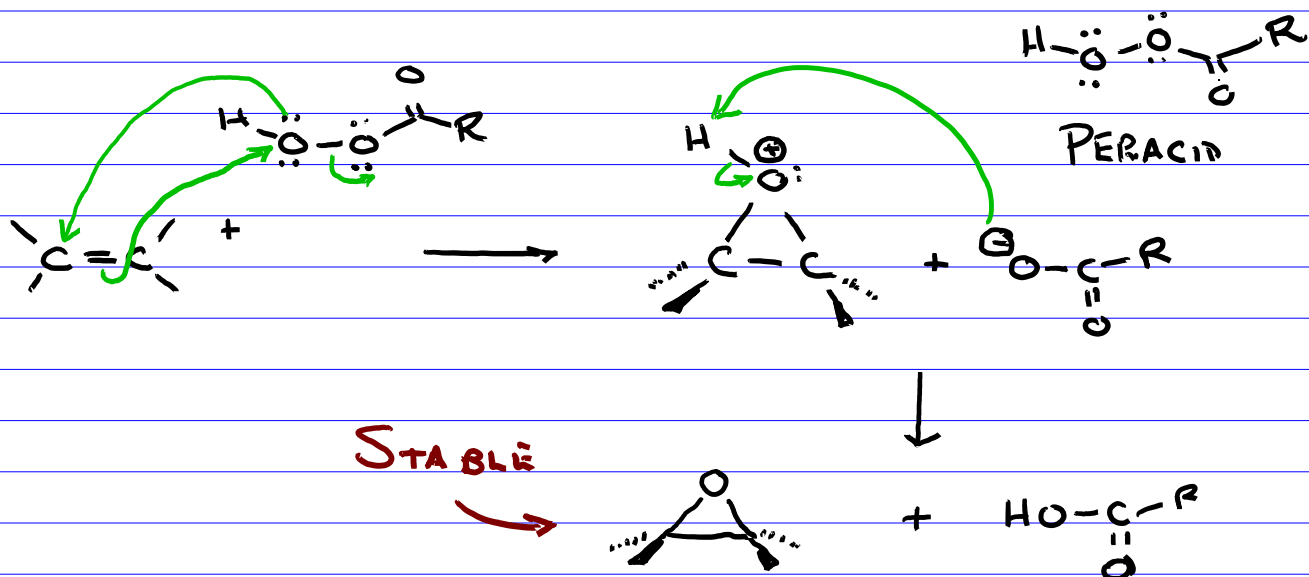
EVERYONE CALLS IT AN EPOXIDE

PREPN: OF EPOXIDES.

ANALOGY: BROMONIUM IONS

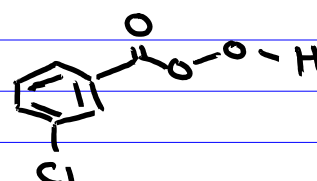


IF WE REACT AN ALKENE WITH A PERACID



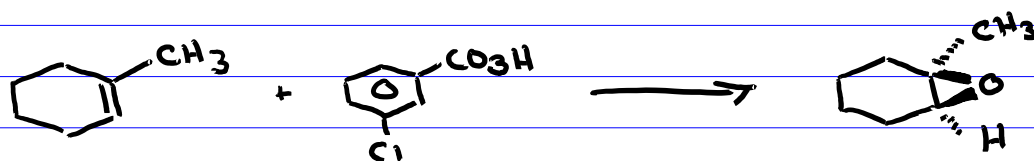
- EPOXIDES ARE STABLE ENOUGH TO ISOLATE; NOT HARD TO MAKE THEM REACT IF YOU WANT TO.

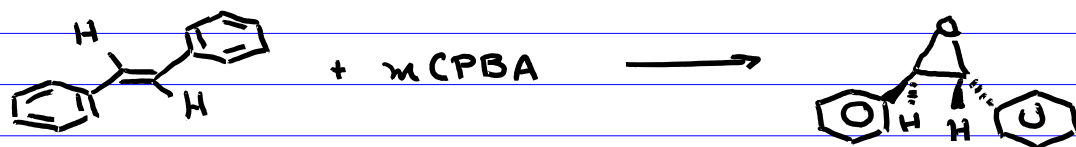
NOTES: 1) MOST COMMON PERACID



meta-CHLOROPEROBENZOIC ACID (MCPBA)

2) ADDITION IS CIS-



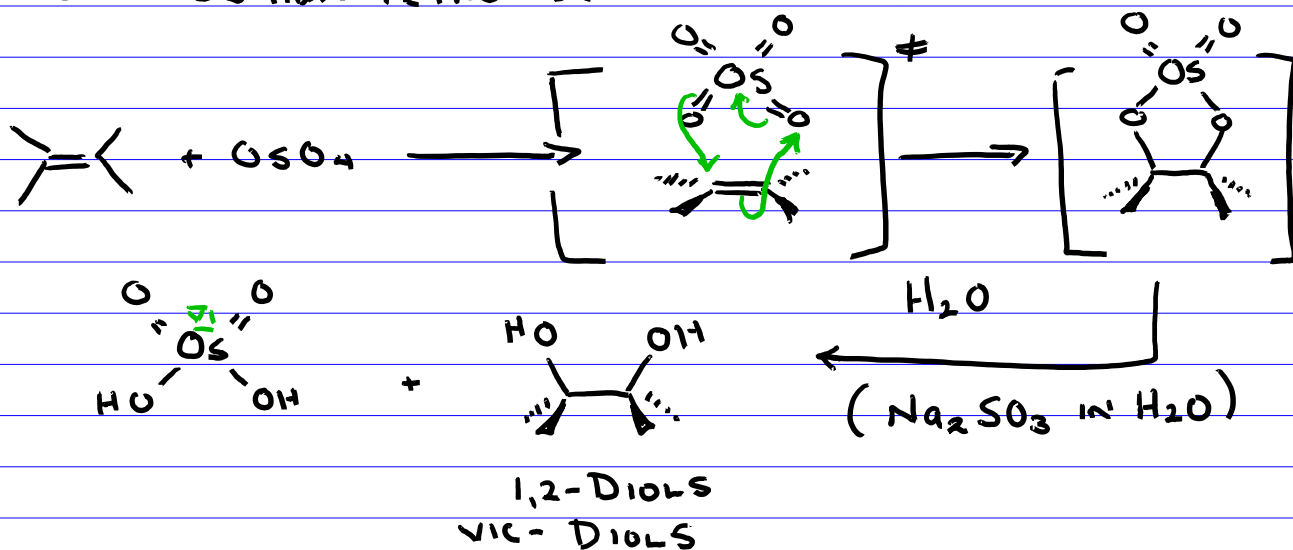


2) DIHYDROXYLATION OF ALKENES

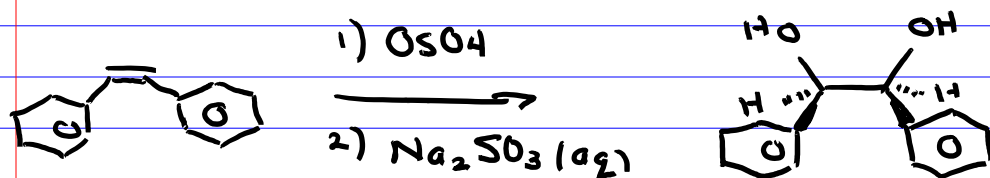
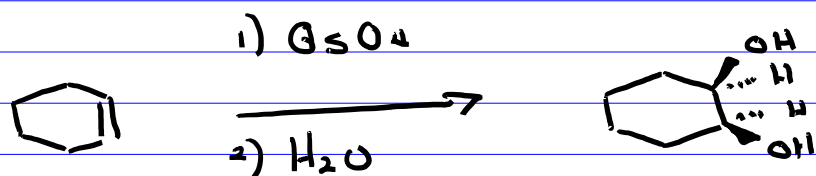


OsO_4 OSMIUM TETROXIDE

WON'T
TEST
MECH



NOTE: REACTION IS CIS- WITH RESPECT TO OH ADDITIONS



YOU CAN ALSO USE KMnO_4 , $\text{pH} > 7$ FOR SAME PURPOSE

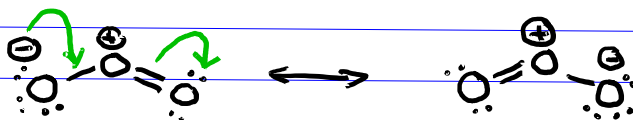
LECTURE 21

OXIDATIONS OF ALKENES, CONT'D

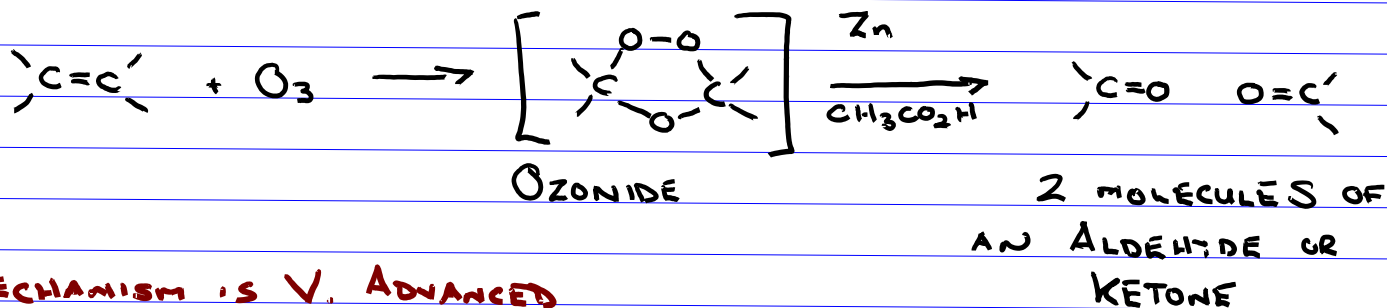
3) OZONOLYSIS

Note: There is a lone pair on the central O of ozone that I neglected to draw

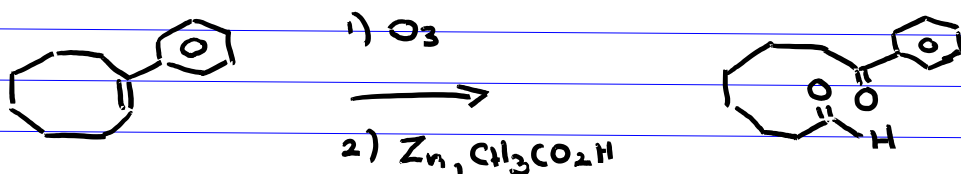
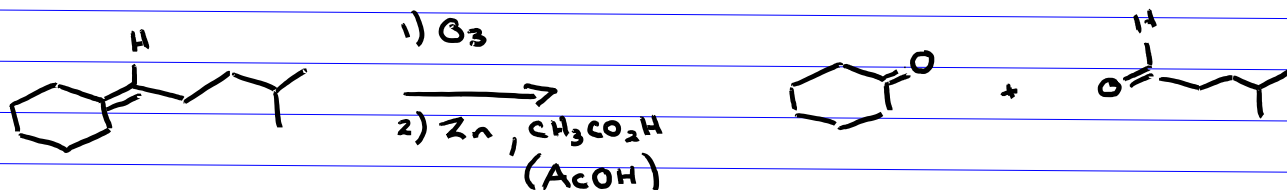
- USES OZONE



- WILL CLEAVE BOTH THE π AND σ BOND OF AN ALKENE



MECHANISM IS V. ADVANCED



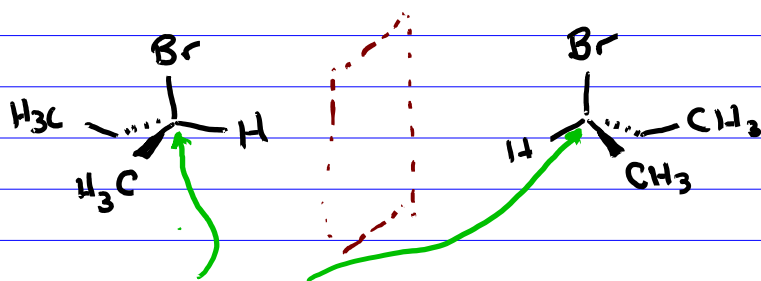
CHIRALITY AND NUCLEOPHILIC SUBSTITUTION

OGILVIE 4.3-4.9

KARTY CH 5

- WE HAVE MISSED AT LEAST ONE MORE TYPE OF STEREOISOMERS.
- SIMPLEST EXAMPLE - YOUR HANDS
 - THEY ARE MIRROR IMAGES OF EACH OTHER, BUT THEY ARE NOT SUPERIMPOSABLE
- $\therefore$ THEY ARE ENANTIOMERS OF EACH OTHER
 - CONSIDER TO BE CHIRAL OBJECTS
- VERY COMMON IN ORGANIC CHEMISTRY
 - MOST COMMON SITUATION

- A CARBON ATOM WITH 4 DIFFERENT GROUPS



- NON-SUPERIMPOSABLE MIRROR IMAGES OF EACH OTHER
- ENANTIOMERS

THESE CARBON ATOMS ARE CALLED

CHIRAL CENTRES
CHIRALITY CENTRES
STEROGENIC CENTRES

I'M OK WITH EACH OF THESE

THESE ENANTIOMERS

- SAME THE SAME PHYSICAL AND SPECTRAL PROPERTIES FOR THE MOST PART

mp, bp, SOLUBILITY, REFRACTIVE INDEX, R_f , NMR, IR

- THEY WILL ROTATE PLANE POLARIZED LIGHT TO THE SAME DEGREE, BUT IN OPPOSITE DIRECTIONS

- IF CLOCKWISE DIRECTION, d -ENANTIOMER

- IF COUNTERCLOCKWISE, l -ENANTIOMER

NOTE: THESE ARE NOT THE SAME AS THE D-AN L- (CAPITALIZED) THAT YOU MAY SEE IN BIOL 2010

- OFFICIAL MEASUREMENT OF THIS VALUE

$[\alpha]_D$ SPECIFIC ROTATION

$$[\alpha]_D^T = \frac{100 \alpha}{c \times l}$$

α = OBSERVATION

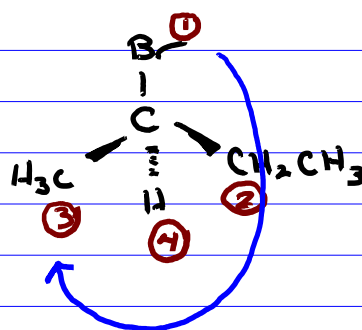
l = PATH LENGTH (1 dm)

c = CONCENTRATION IN g per 100 mL OF SOLUTION

CHIRAL MOLECULES OBTAINED AS A 50:50 MIXTURE OF THE TWO ENANTIOMERS HAVE AN $[\alpha]_D = 0$

- CALLED A RACEMIC MIXTURE (OR RACEMATE)

- HOW DO WE REFER TO



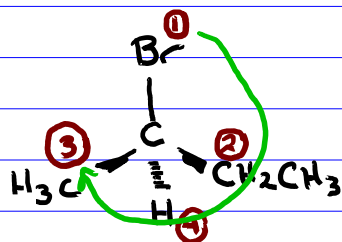
1 $\rightarrow$ 2 $\rightarrow$ 3
CLOCKWISE
WITH 4 AWAY
FROM US

(R)-ENANTIOMER

- IF COUNTERCLOCKWISE

(S)-ENANTIOMER

LECTURE 22



(R) -

1) RANK THE 4 GROUPS ON THE C OF INTEREST BY CIP PRIORITIES

① → ② → ③ → ④

2) ORIENT MOLECULE SUCH THAT ④ IS AWAY FROM THE VIEWER

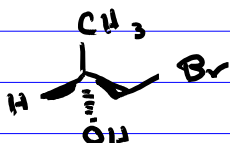
3) TRACE ① → ② → ③

4) IF THE TRACE IS CLOCKWISE, IT'S THE (R) - ENANTIOMER
IF THE TRACE IS COUNTERCLOCKWISE, IT'S THE (S) - ENANTIOMER

(R) - 2-BROMOBUTANE

NOTE: (R)- or (S)- IS NOT PREDICTABLY CORRELATED WITH d- AND l-

CONSIDER - WHAT IF H ISN'T BACK?

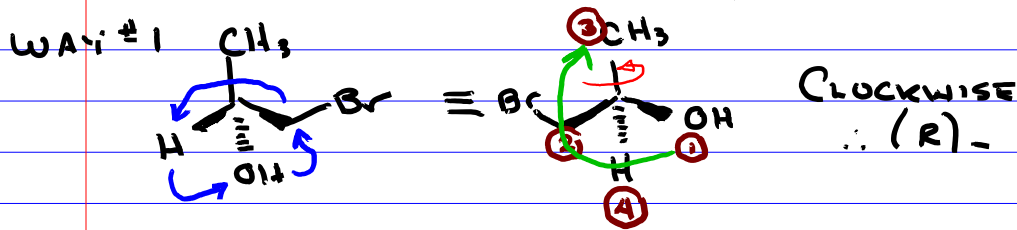


ROTATE .

TECHNOLOGICAL HICCUP - CONTINUED ON NEXT PAGE.

LECTURE 22 CONT'D

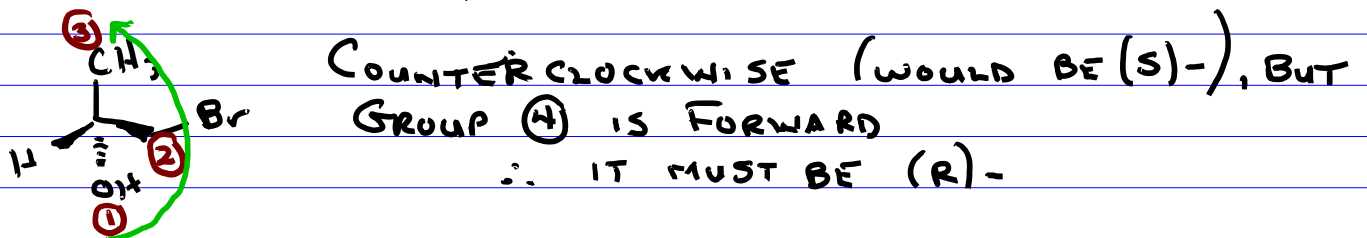
WHAT ABOUT - H (4) ISN'T BACK!



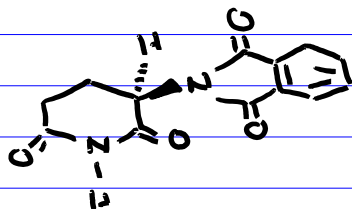
- DO A SEQUENTIAL MOVING OF THREE GROUPS IN THE SAME DIRECTION (TO GET (4) IN BACK)

WAY #2

- IF GROUP (4) IS OUT TOWARDS YOU, AND YOU SCAN ① → ② → ③, YOU'LL GET EXACTLY THE WRONG ANSWER

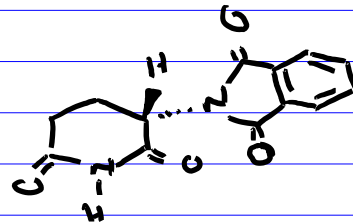


WHY DO WE CARE?



(R) - THALIDOMIDE

SEDATIVE, ANTI MORNING
SICKNESS

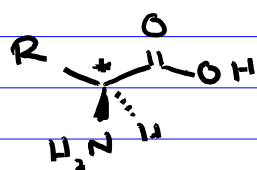


(S) - THALIDOMIDE

TERATOGEN (BIRTH DEFECTS)

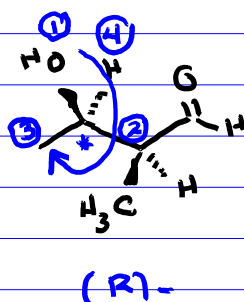
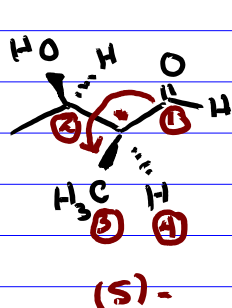
AMINO ACIDS

20 COMMON AMINO ACIDS



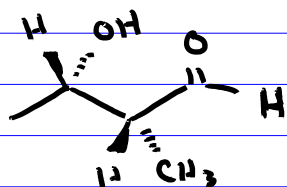
18 OF THEM (S)-

HOW ABOUT COMPOUNDS WITH > 1 CHIRAL CENTRES



(2S, 3R) -

AND

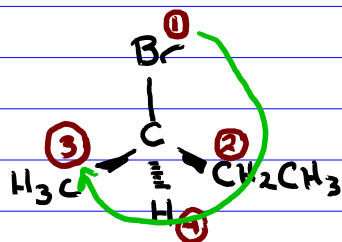


ENANTIOMER OF 1ST ONE
(2R,3S)-

WHAT IF 1 CHIRAL CENTRE IS THE SAME, AND
1 IS DIFFERENT?

- MONDAY.

LECTURE 22



(R) -

1) RANK THE 4 GROUPS ON THE C OF INTEREST BY CIP PRIORITIES

① → ② → ③ → ④

2) ORIENT MOLECULE SUCH THAT ④ IS AWAY FROM THE VIEWER

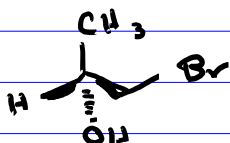
3) TRACE ① → ② → ③

4) IF THE TRACE IS CLOCKWISE, IT'S THE (R) - ENANTIOMER
IF THE TRACE IS COUNTERCLOCKWISE, IT'S THE (S) - ENANTIOMER

(R) - 2-BROMOBUTANE

NOTE: (R)- or (S)- IS NOT PREDICTABLY CORRELATED WITH d- AND l-

CONSIDER - WHAT IF H ISN'T BACK?

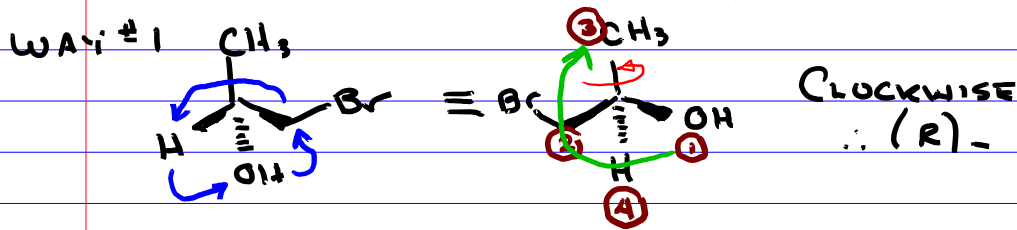


ROTATE .

TECHNOLOGICAL HICCUP - CONTINUED ON NEXT PAGE.

LECTURE 22 CONT'D

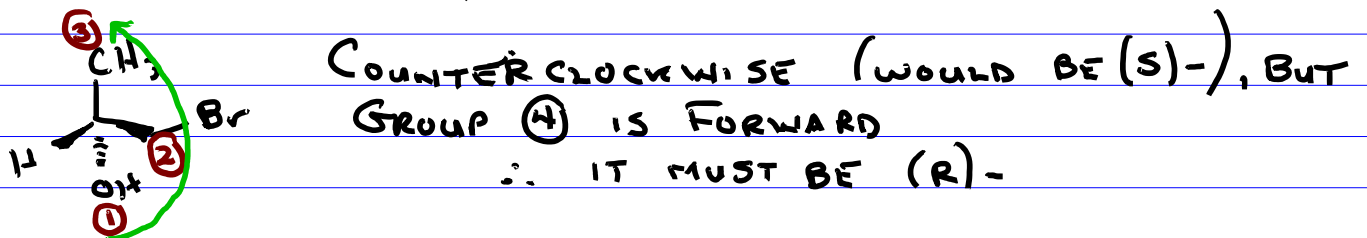
WHAT ABOUT - H (4) ISN'T BACK!



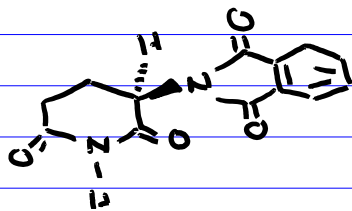
- DO A SEQUENTIAL MOVING OF THREE GROUPS IN THE SAME DIRECTION (TO GET (4) IN BACK)

WAY #2

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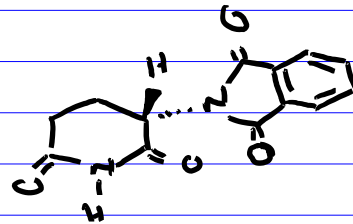


WHY DO WE CARE?



(R) - THALIDOMIDE

SEDATIVE, ANTI MORNING
SICKNESS

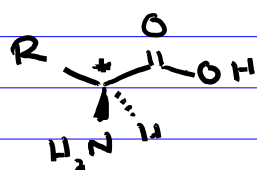


(S) - THALIDOMIDE

TERATOGEN (BIRTH DEFECTS)

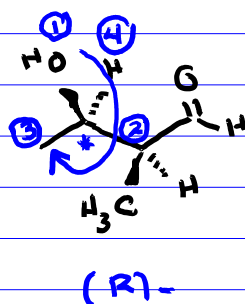
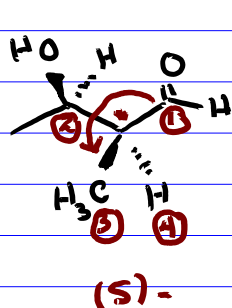
AMINO ACIDS

20 COMMON AMINO ACIDS



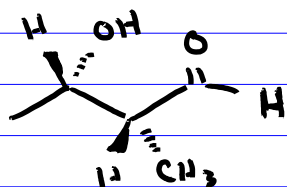
18 OF THEM (S)-

HOW ABOUT COMPOUNDS WITH > 1 CHIRAL CENTRES



(2S, 3R)-

AND



ENANTIOMER OF 1ST ONE
(2R,3S)-

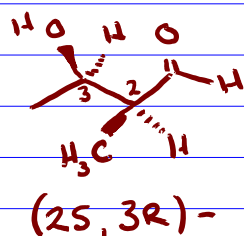
WHAT IF 1 CHIRAL CENTRE IS THE SAME, AND
1 IS DIFFERENT?

- MONDAY.

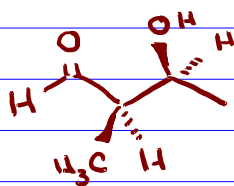
LECTURE 23

WHERE WE LEFT OFF.....

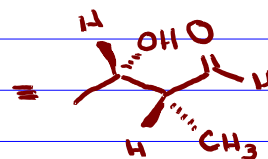
> 1 CHIRAL/STEREOGENIC CENTRE



AND

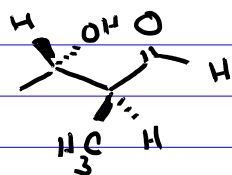


(2R,3S)-

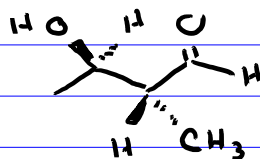


ARE ENANTIOMERS

SO HOW ABOUT (2S,3S)- AND (2R,3R)- ??



(2S,3S)-



(2R,3R)-

THESE TWO ARE
ENANTIOMERS OF
EACH OTHER

BUT THE RELATIONSHIP OF EITHER OF THESE TWO TO EITHER
OF THE TOP TWO IS CALLED DIASTEREOMERS

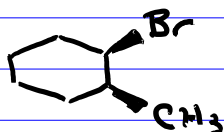
THIS IS WHERE YOU HAVE > 1 STEREOGENIC (CHIRAL) CENTRES
WHERE SOME CENTRE(S) HAVE IDENTICAL CHIRALITY AND OTHER(S)
ARE OPPOSITE

DIASTEREOMERS WILL HAVE DIFFERENT PHYSICAL PROPERTIES
(mp, bp, Rf, NMR OR IR SPECTRA, ETC).

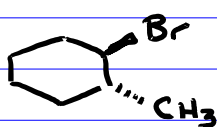
OFFICIAL DEFINITION OF DIASTEREOMERS

- ANY STEREOISOMERS THAT ARE NOT MIRROR IMAGES
(ENANTIOMERS)

SO, RECALL



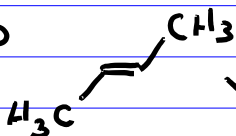
VS



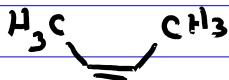
cis/trans

DIASTEREOMERS IS THE BETTER TERM FOR THESE

AND



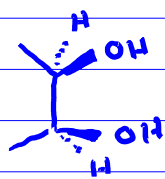
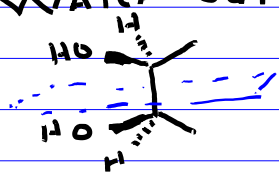
VS.



CAN BE CALLED DIASTEREOMERS TOO

(GEOMETRIC OR CIS/TRANS- ISOMERS IS
MORE COMMON)

WATCH OUT FOR



MIRROR IMAGE

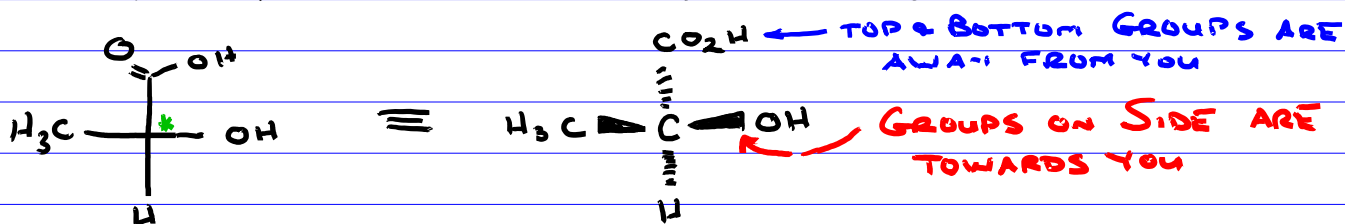
- IT IS SUPERIMPOSABLE

MESO FORM. - MOLECULE CONTAINS AN INTERNAL MIRROR PLANE

- IN THESE CASES, THE MOLECULE DOES NOT HAVE AN ENANTIOMER, MOLECULE AS A WHOLE IS NOT CHIRAL

FISCHER PROJECTION (S)

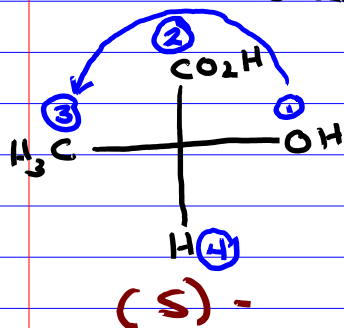
- ARTIFICIAL WAY OF DRAWING STEREOGENIC CENTRES



USED IN CARBOHYDRATES - A LOT

HOW TO TELL IN A FISCHER IF A CENTRE IS (R)- OR (S)-

- IF LOWEST PRIORITY GROUP IS AT UP OR DOWN POSITION



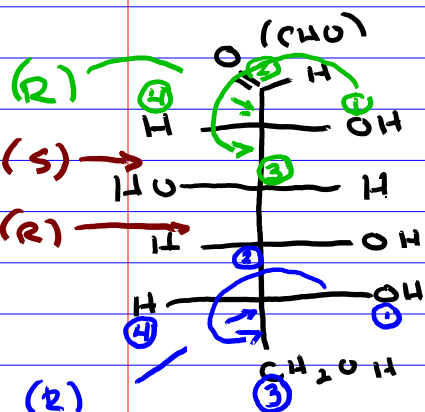
FOLLOW ① → ② → ③

CLOCKWISE ∴ (R)-

COUNTERCLOCKWISE ∴ (S)-

(S)-

BUT....



GLUCOSE

IF H IS ON THE SIDES, YOU HAVE TO REMEMBER THAT YOU GET THE BACKWARDS ANSWER

1 → 2 → 3 COUNTERCLOCKWISE, BUT H IS FORWARD ∴ (R)-

1 → 2 → 3 COUNTERCLOCKWISE, BUT H IS FORWARD ∴ (R)-

• NOTE: A FISCHER PROJECTION IS NOT A MAJOR CONFORMATION

NOTE #2 - IF YOU HAVE MULTIPLE CHIRAL CENTRES, YOU HAVE MANY POSSIBLE STEREOISOMERS

- ASSUMING NO MESO FORMS

1	CHIRALITY CENTRE	-	2	POSSIBLE STEREOISOMERS
2	"	-	4	"
3	"	-	8	"
4	"	-	16	"
n	"	-	2^n	POSSIBLE STEREOISOMERS

END OF TEST #2 MATERIAL.

LECTURE 24

MIDTERM #2

Mon. Nov. 21

1:30 - 2:20 PM (50 min)

A- KOUASSIEM
KOVACEVICH-SAMMAN
SANKARLAL - Z

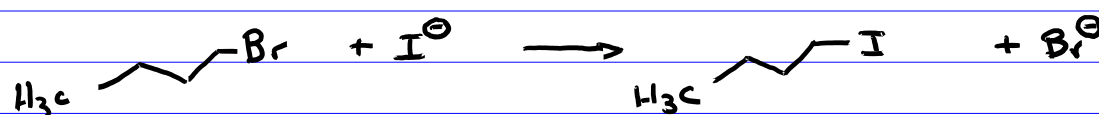
1120 ERIE HALL
100 TOLDO
200 TOLDO.

NUCLEOPHILIC SUBSTITUTION REACTION

OGILVIE - CH 11

KARTI - 8, 9, 10

CONSIDER



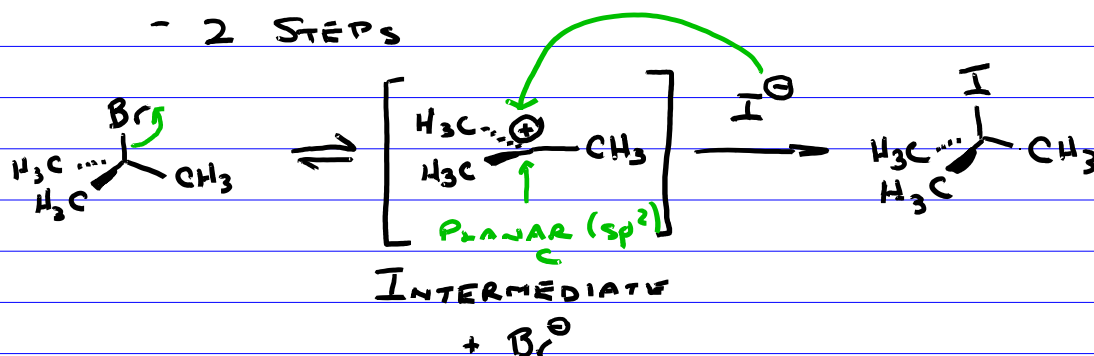
I^- IS A NUCLEOPHILE
 Br^- IS A LEAVING GROUP

$\text{CH}_3\text{CH}_2\text{CH}_2\text{Br}$ IS AN ELECTROPHILE

HOW? FOR sp^3 CARBONS, TWO MECHANISMS DOMINATE

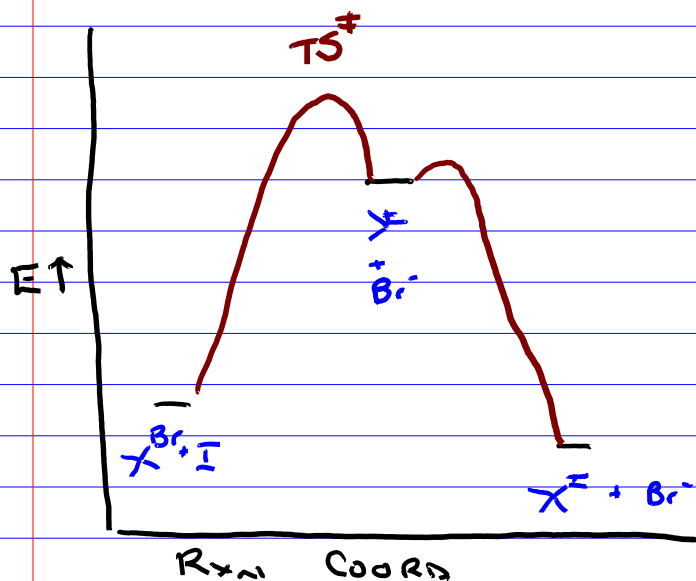
1) $\text{S}_{\text{N}}1$ MECHANISM

- INVOLVES A CARBOCATION INTERMEDIATE
- 2 STEPS



- TWO STEPS

- 1ST STEP IS TOUGHER - SLOW OR RATE DETERMINING STEP
- 2ND STEP IS V. FAST



RATE

$$v = k [X-Br]$$

1ST ORDER (UNIMOLECULAR)

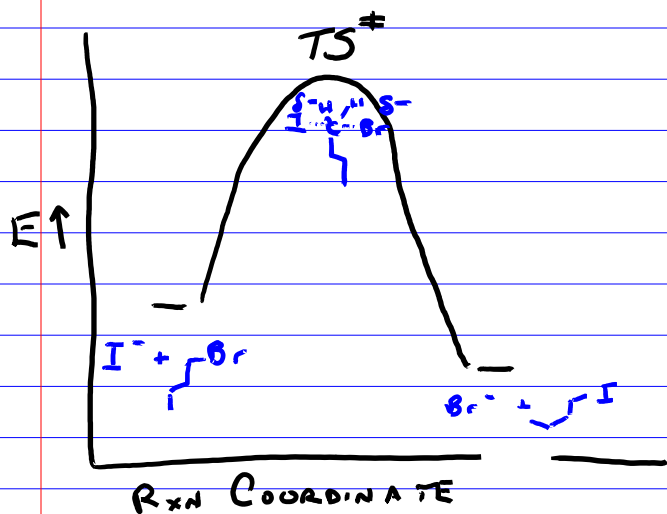
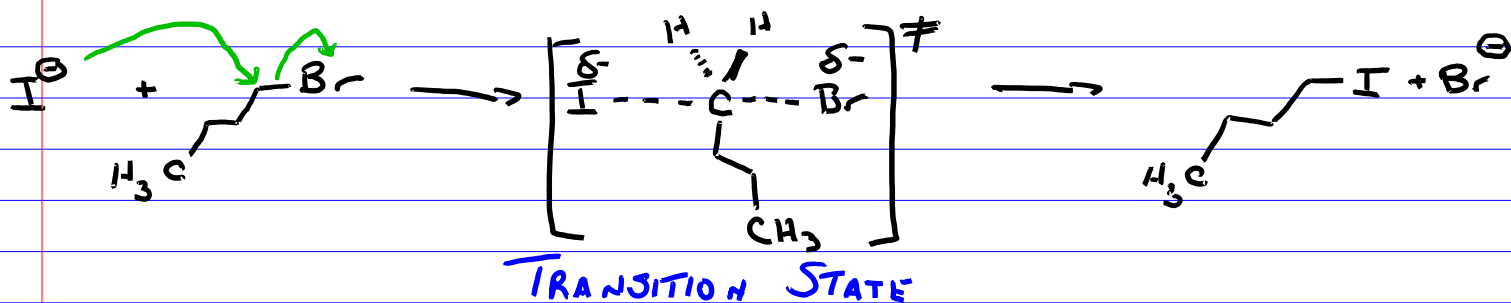
S - SUBSTITUTION

N - NUCLEOPHILIC

1 - 1ST ORDER

2) S_N2 MECHANISM

- 1 STEP ; CONCERTED BOND MAKING AND BOND BREAKING



RATE

$$v = k' [CH_3CH_2Br] [I^-]$$

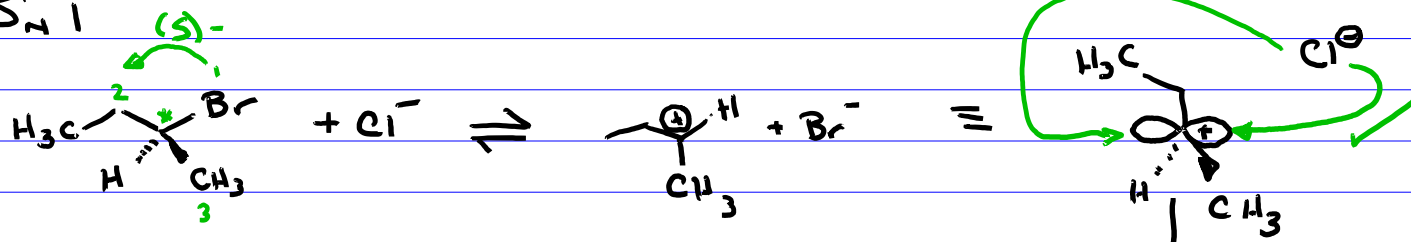
S SUBSTITUTION

N NUCLEOPHILIC

2 2ND ORDER / BIMOLECULAR

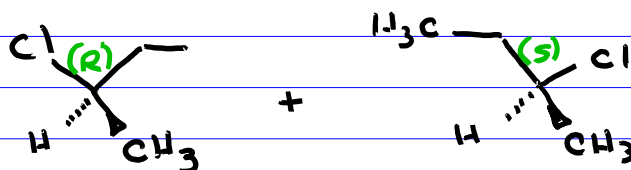
STEREOCHEMISTRY OF S_N1 AND S_N2

S_N1



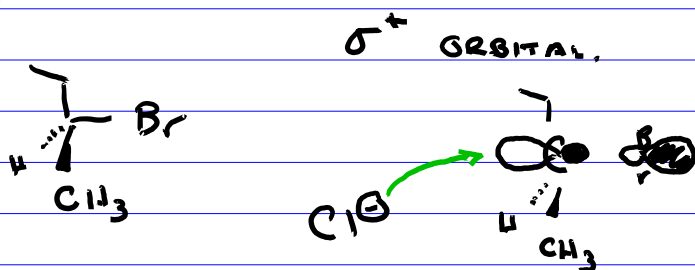
ATTACK FROM LEFT OR RIGHT IS EQUALLY SIMPLE, SINCE THE CARBOCATION IS PLANAR.

GET
RACEMIZATION
AT THE CHIRAL
CENTRE

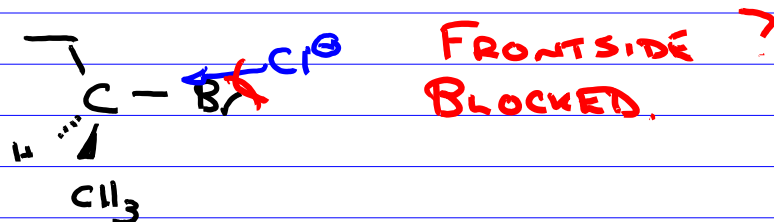


50 : 50 MIXTURE

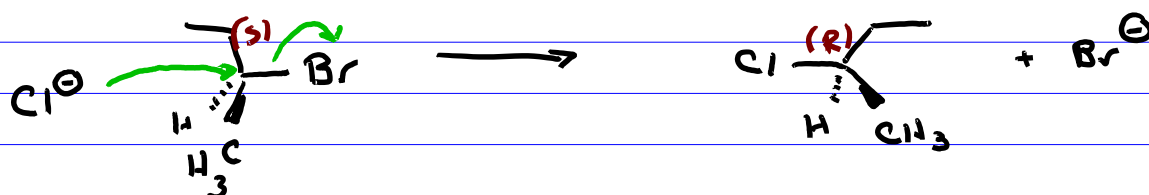
S_N2



BACKSIDE ATTACK
YES!



So.....

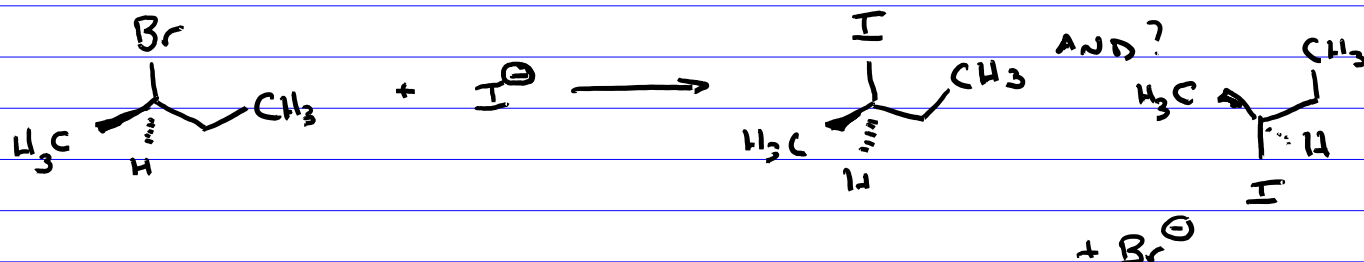


INVERSION OF CONFIGURATION

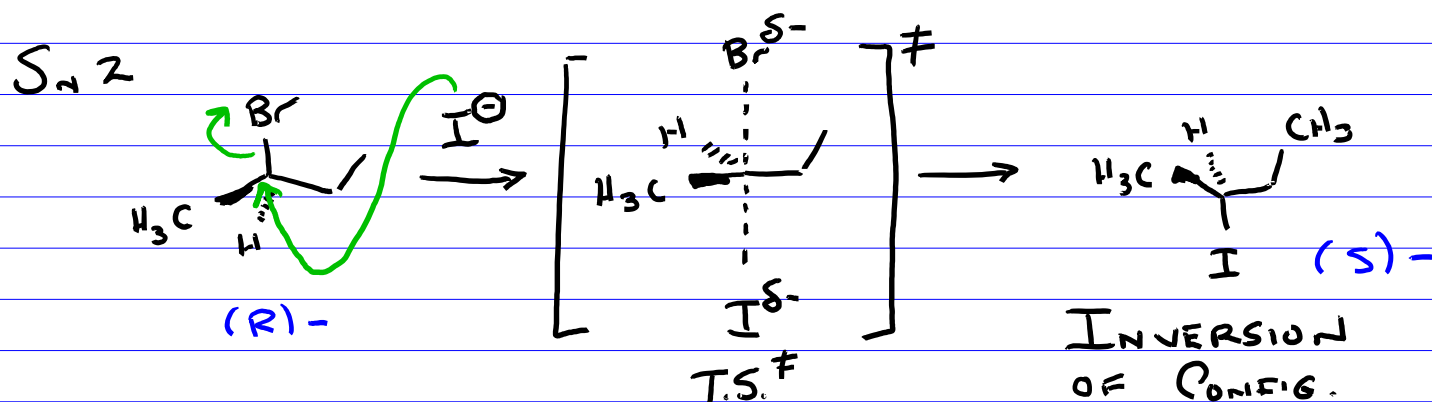
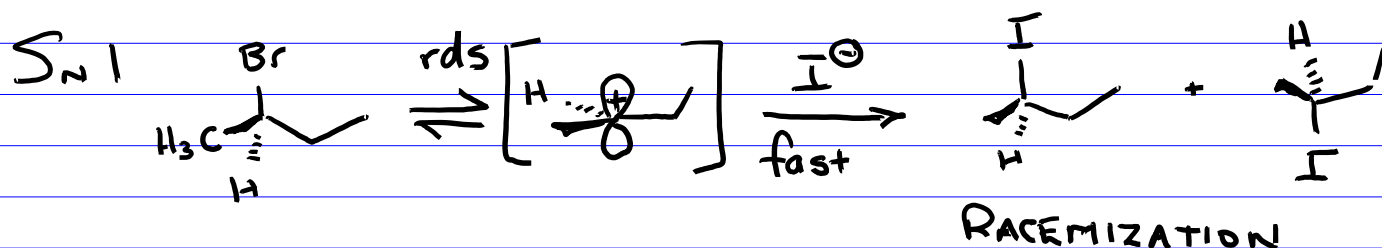
NOT ALWAYS (R) TO (S) OR (S) TO (R),
BUT USUALLY.

LECTURE 25

- RECALL: NUCLEOPHILIC SUBSTITUTION



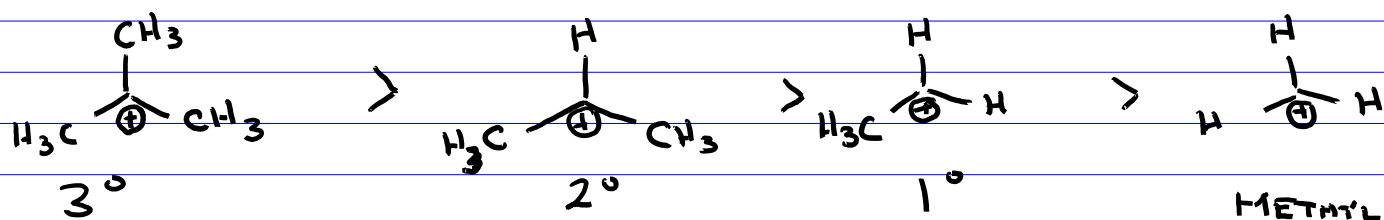
MECHANISMS S_N1 AND S_N2



HOW DO WE KNOW IF IT'S S_N1 OR S_N2 ?
 - SEVERAL CONSIDERATIONS

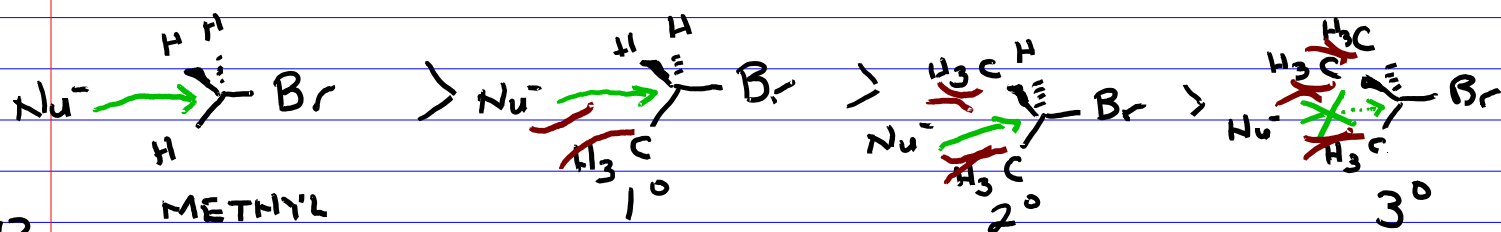
1) CENTRE BEING ATTACKED

S_N1 - DETERMINED BY EASE OF CARBOCATION FORMATION



S_N1 ABILITY: V. GOOD SO-SO PRETTY POOR FORGET IT

S_N2 - DOMINATED BY EASE OF BACKSIDE ATTACK



S_N2

ABILITY V.V. EASY PRETTY EASY SO-SO NO WAY

TAKEN TOGETHER

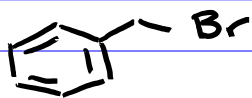
METHYL SUBSTRATE - ALWAYS S_N2

1° SUBSTRATE - NORMALLY S_N2

2° SUBSTRATE - COULD BE EITHER - DEPENDS ON OTHER FACTORS

3° SUBSTRATE - ALWAYS S_N1

SOME TYPES OF SUBSTRATES ARE GOOD AT BOTH S_N1 AND S_N2



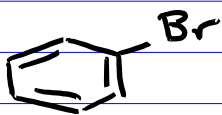
BENZYLIC



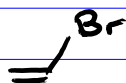
ALLYLIC

EXCELLENT AT BOTH
S_N1 AND S_N2

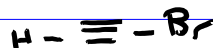
SOME TYPES OF SUBSTRATES ARE BAD AT BOTH S_N1 AND S_N2



ARYL



VINYL OR
ALKENYL



ALKYNYL

NO GOOD AT EITHER
S_N1 OR S_N2

2) NUCLEOPHILE Nu⁻ (I^o)

S_N1 - STRENGTH OF Nu⁻ NOT THAT IMPORTANT.

∴ MEDIOCRE / POOR-ISH NUCLEOPHILES ARE FINE

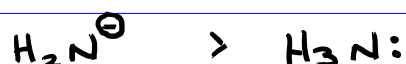
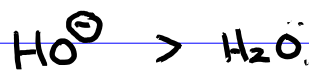
i.e. H₂O:

S_N2 - IT MATTERS A LOT, BETTER IF Nu^- IS A V. GOOD ONE

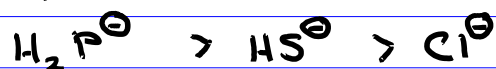
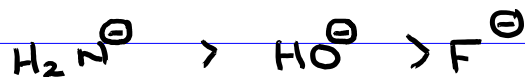
- PUSHING OUT THE LEAVING GROUP
- INVOLVED IN R.D.S.

- WHAT MAKES A GOOD Nu^-

i) A NEGATIVE CHARGED Nu^- IS BETTER THAN A COMPARABLE NEUTRAL ONE



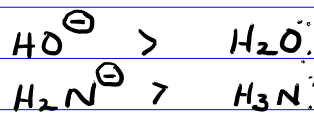
(ii) IN SAME ROW OF PERIODIC TABLE, NUCLEOPHILICITY PARALLELS BASICITY



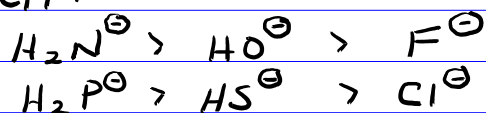
LECTURE 26

RECALL - WHAT MAKES A GOOD NUCLEOPHILE?

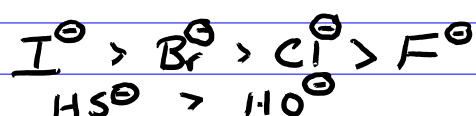
- 1) NEGATIVELY CHARGED Nu^- 's ARE BETTER THAN ANALOGOUS NEUTRAL ONES.



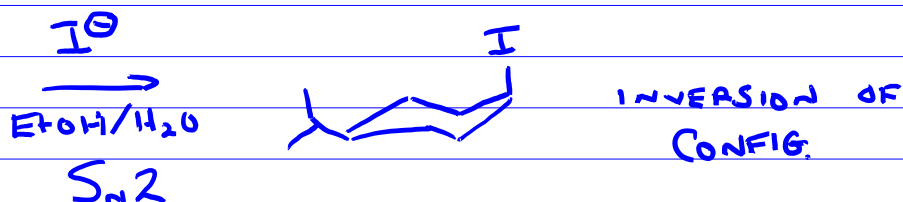
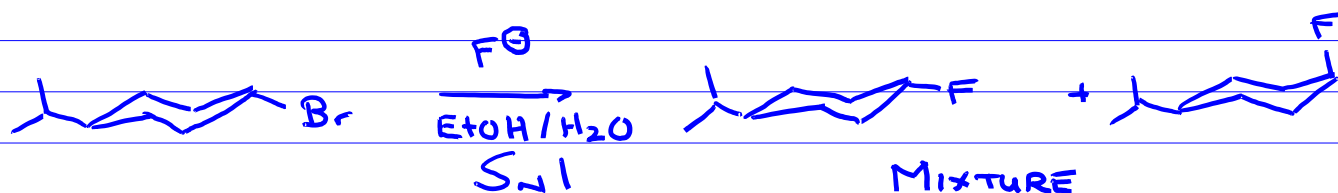
- 2) IN THE SAME ROW OF THE PERIODIC TABLE, NUCLEOPHILICITY PARALLELS BASICITY



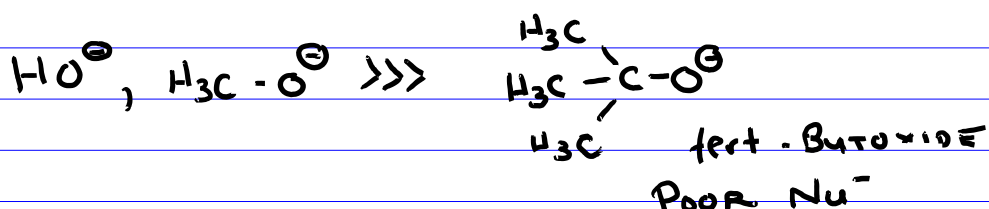
- 3) IN HYDROXYLIC SOLVENTS (H_2O or CH_3OH or EtOH)
- AS YOU GO DOWN A COLUMN IN PERIODIC TABLE,
THE Nu^- GETS BETTER



REASON FOR THIS - HYDROXYLIC SOLVENTS PACK TIGHTLY AROUND SMALLER IONS BY HYDROGEN BONDING; GETS IN THE WAY OF RXN.

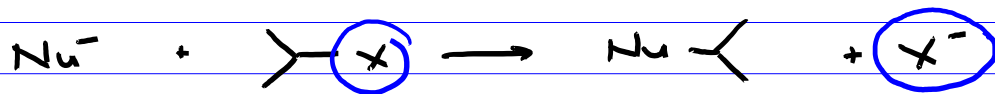


- iv) STERIC HINDRANCE AROUND Nu^- - HURTS NUCLEOPHILICITY

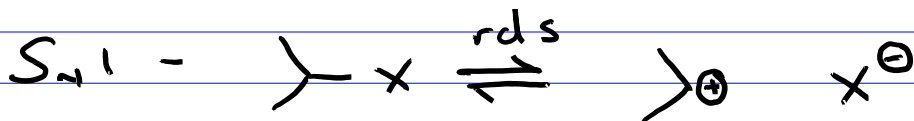




v) NATURE OF THE LEAVING GROUP (L.G.)



$\text{S}_\text{N}2$ - LEAVING GROUP IS BEING PUSHED OFF, SO IT HELPS IF IT'S BETTER - BUT IT'S NOT THE ONLY / CENTRAL THING



IT LEAVES ON ITS OWN IN R.D.S.
 $\therefore$ CRITICAL IMPORTANCE

HOW DO WE TELL IF A L.G. IS GOOD OR EXCELLENT?
 LOOK AT THE ACID STRENGTH OF CORRESPONDING CONJUGATE ACID

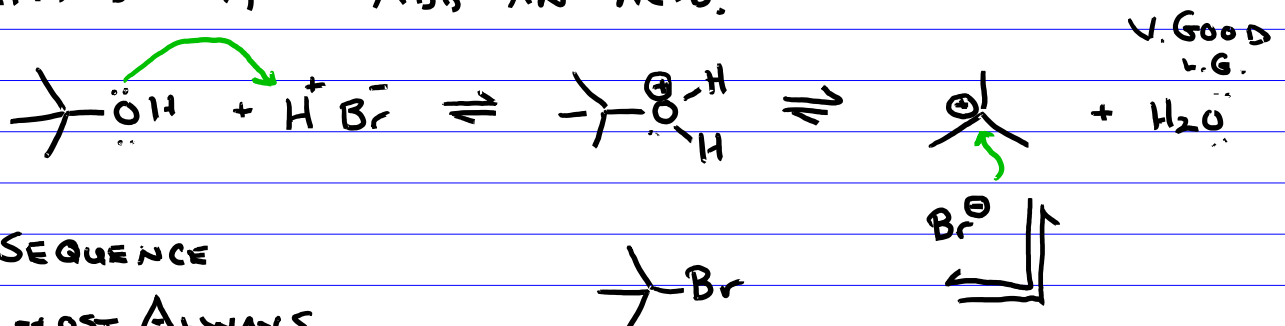


$\therefore$ L.G. ABILITIES



SO WHAT IF YOU WANT TO SUBSTITUTE AN ALCOHOL?

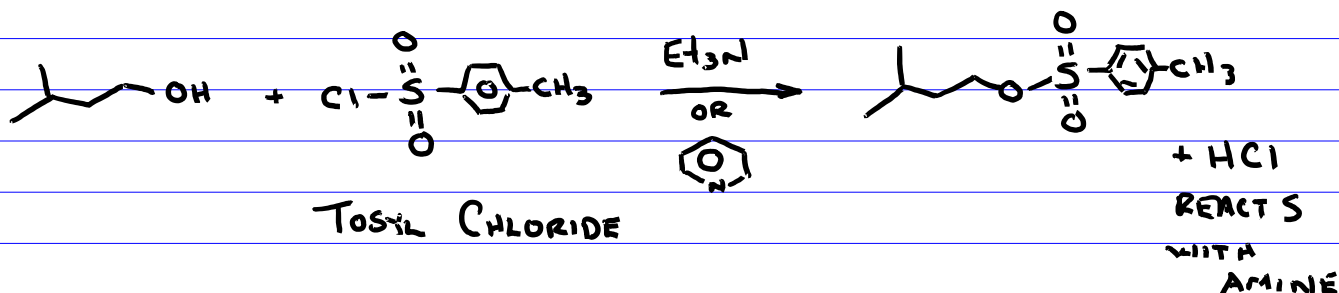
SOLUTIONS i) ADD AN ACID.



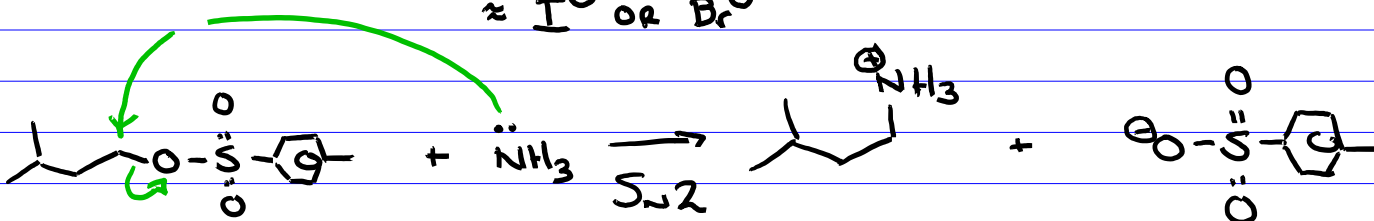
CONSEQUENCE

- ALMOST ALWAYS
 WILL BE $\text{S}_\text{N}1$
 MECH

ii) CONVERT TO A TOLUENESULFONATE (TOSYLATE) ESTER



TOSYLATES ARE EXCELLENT L.G.'S
 $\approx \text{I}^-$ OR Br^-

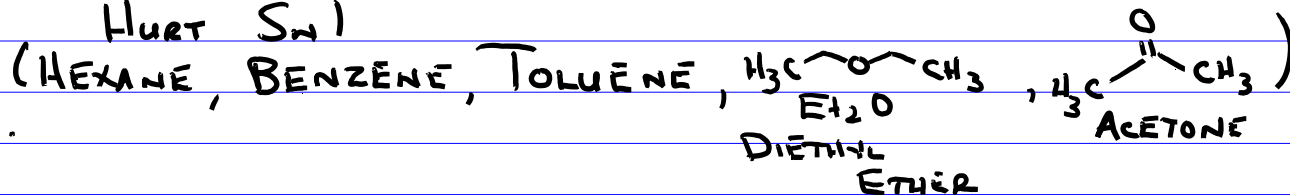


$\text{S}_\text{N}1$ IS ALSO POSSIBLE WITH TOSYLATE

vi) SOLVENT EFFECTS

- $\text{S}_\text{N}1$ RXNS PREFER POLAR SOLVENTS
(H_2O , CH_3OH , EtOH ($\text{CH}_3\text{CH}_2\text{OH}$), $\text{CH}_3\text{-C}\equiv\text{N}$)
HIGH DIELECTRIC CONSTANTS.
- STABILIZE THE CARBOCATION

- NON POLAR / LOW DIELECTRIC CONSTANT SOLVENTS
HURT $\text{S}_\text{N}1$



FOR $\text{S}_\text{N}2$ 'S - IN MANY CASES, LOWER POLARITY SOLVENTS ARE BETTER

LECTURE 27

RECALL:

SOLVENT EFFECTS

- S_N1 RATES ENHANCED BY POLAR SOLVENT (H_2O , ALCOHOLS, CH_3CN).

REASON: RATE DETERMINING FORMATION OF CARBOCATION

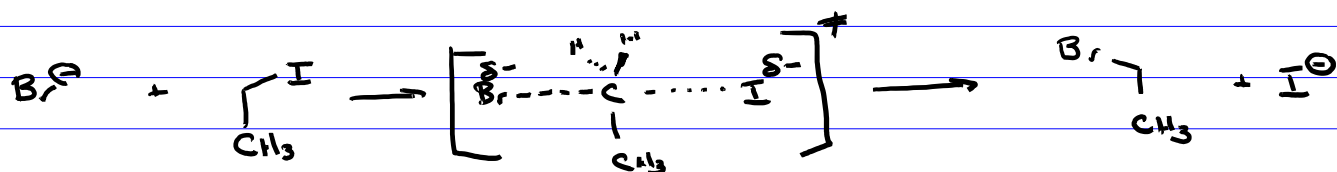


- ASSISTED / STABILIZED BY POLAR SOLVENT

- HURT / SLOWED BY NON-POLAR SOLVENTS (HEXANES, BENZENE, Et_2O , ACETONE)

AND S_N2 'S

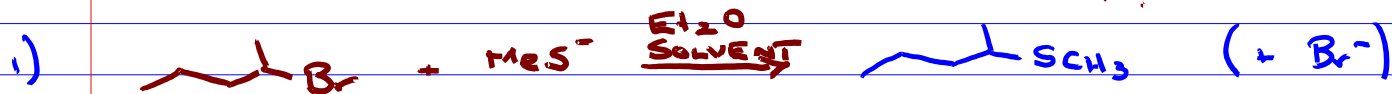
- IT VARIES, BUT...



- CHARGE TO VOLUME IS LOWER IN THE TRANSITION STATE
- ASSISTED (MODESTLY) BY NON-POLAR SOLVENTS
- DISCOURAGED (MODESTLY) BY POLAR SOLVENTS

REASONABLE TYPE OF QUESTION

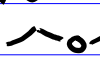
PRODUCTS?
 S_N1 VS S_N2 ORDER?
WHY?



#2 3° ALKYL HALIDE - FAVOURS S_N1
 CH₃OH NUCLEOPHILE (Nu⁻) - POOR Nu⁻ - FAVOURS S_N1
 SOLVENT CH₃OH - POLAR - FAVOURS S_N1
 ∴ MOST S_N1 CHARACTER

#4 2° ALKYL HALIDE - S_N1 OR S_N2 POSSIBLE
 CH₃OH Nu⁻ - POOR - FAVOURS S_N1
 SOLVENT CH₃OH - POLAR - FAVOURS S_N1
 ∴ 2ND MOST S_N1 CHARACTER

#3 2° ALKYL HALIDE - S_N1 OR S_N2 POSSIBLE
 CH₃S[⊖] Nu⁻ - REALLY GOOD - FAVOURS S_N2
 SOLVENT CH₃OH - POLAR - FAVOURS S_N1
 ∴ 2ND MOST S_N2 CHARACTER

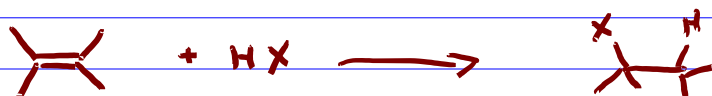
#1 2° ALKYL HALIDE - S_N1 OR S_N2 POSSIBLE
 CH₃S[⊖] Nu⁻ - REALLY GOOD - FAVOURS S_N2
 SOLVENT  - NOT POLAR - FAVOUR S_N2
 ∴ MOST S_N2 CHARACTER.

ABBREV. Me ≡ CH₃
 Et ≡ CH₃-CH₂-

ELIMINATION REACTIONS

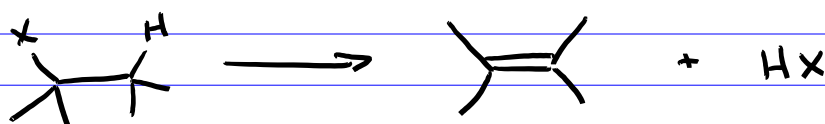
CH 12 OGILVIE
 CH 9 KARTY

RECALL



ADDITION
REACTION

ELIMINATION REACTION IS THE OPPOSITE

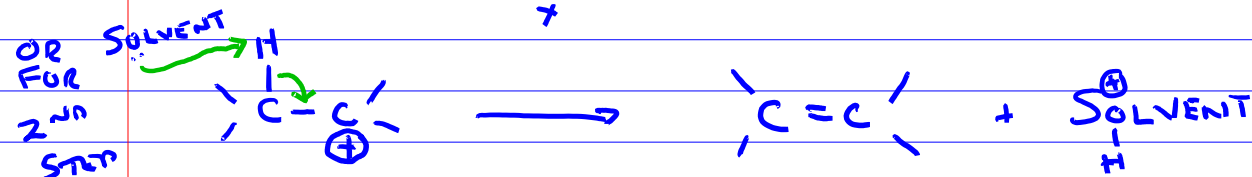
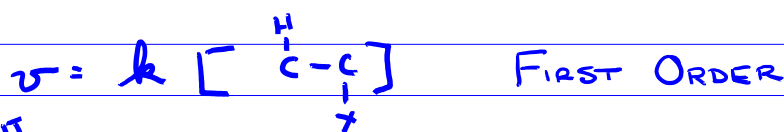
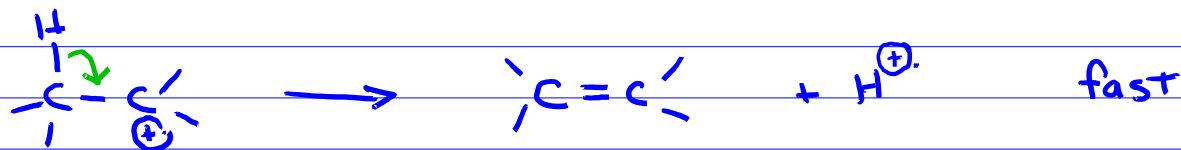
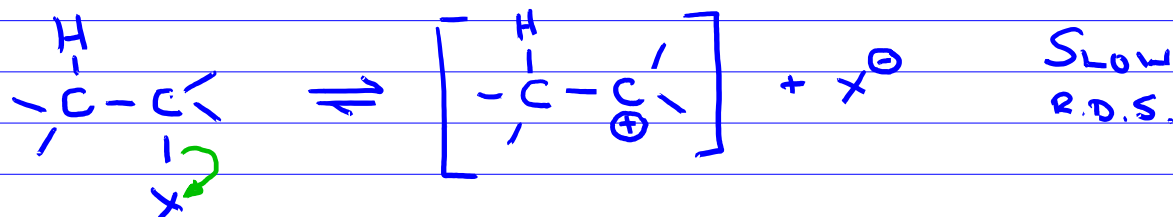


'H-X IS
ELIMINATED'

THREE MAIN ONES (BY MECHANISM)

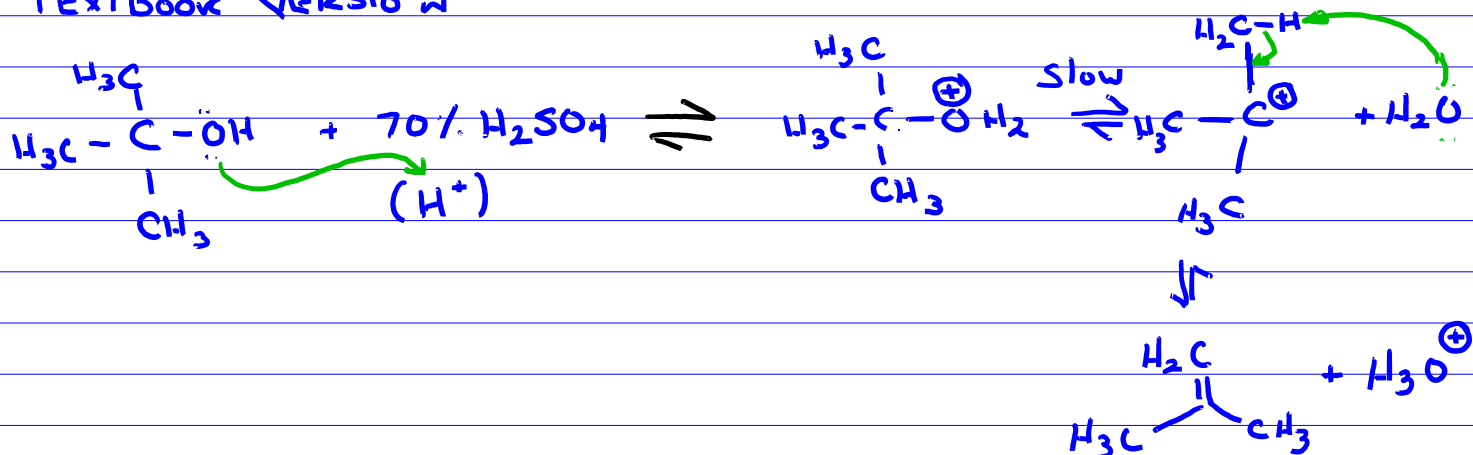
E1 E2 E1cb
 WE'LL LOOK AT THESE CLOSELY

E1 MECHANISM - TWO STEPS, INCLUDES CARBOCATION
 - FIRST ORDER KINETICS

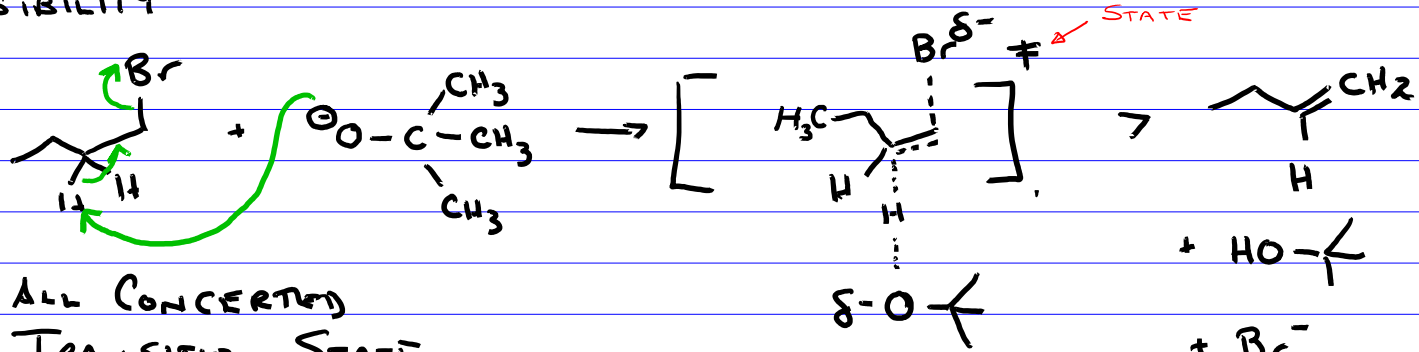


YOU CAN SHOW H⁺ JUST FALLING OFF, OR THE SOLVENT ABSTRACTING THAT H⁺

TEXTBOOK VERSION

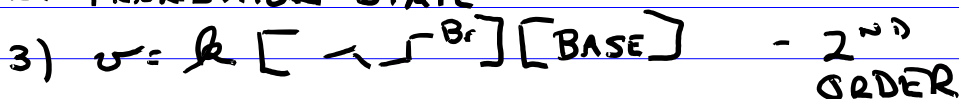


ALTERNATE - E2 - ALL STEPS AT ONCE



1) ALL CONCERTED

2) TRANSITION STATE



LECTURE 28

FINAL EXAM

MON. DEC. 12

8:30 AM - 11:30 AM

ERIE 1120

A - MAGDA

ERIE 2123

MALAKOTI - NEGAD - QUERBACH

ERIE 3123

QUIMBY - SZALAY

ERIE 1118

T - Z

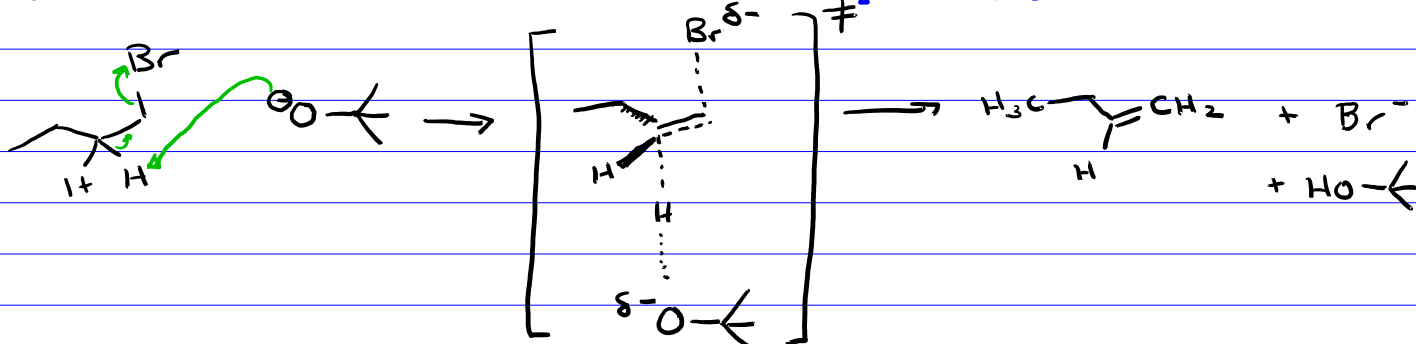
WHERE WE LEFT OFF

E1 ELIMINATION - INVOLVES CARBOCATION

- 1ST ORDER KINETICS

- NO BASE "OF NOTE" (TECHNICALLY, THE SOLVENT ACTS AS BASE)

E2 ELIMINATION - ONE STEP



POINTS

1) CONCERTED - ALL BOND MAKING, BOND BREAKING PROCESSES OCCUR AT SAME TIME

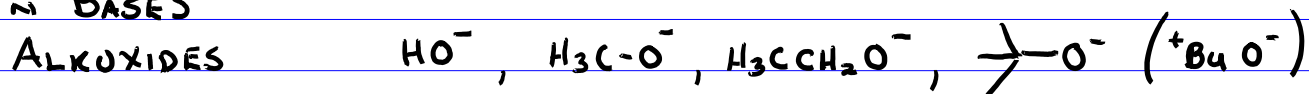
2) NO INTERMEDIATE, BUT RATHER A TRANSITION STATE

3) $v = k [\text{substrate}] [\text{BASE}]$ 2ND ORDER

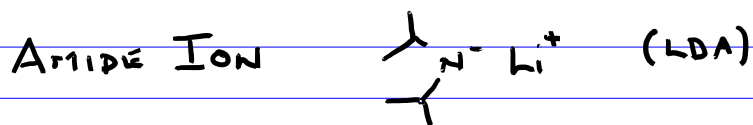
4) HERE WE HAVE A REAL BASE

COMMON BASES

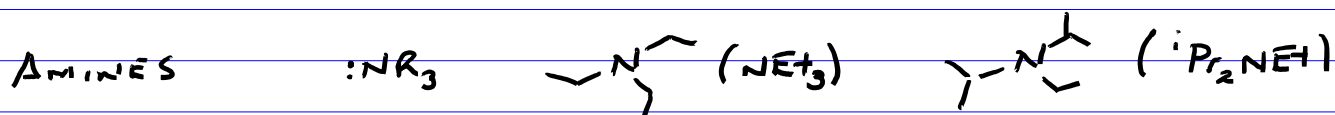
ALKOXIDES



AMIDE ION

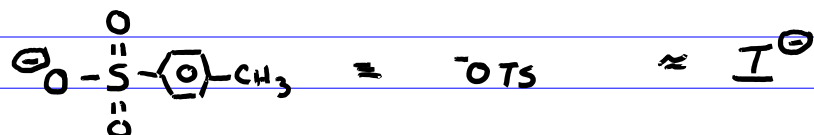


AMINES



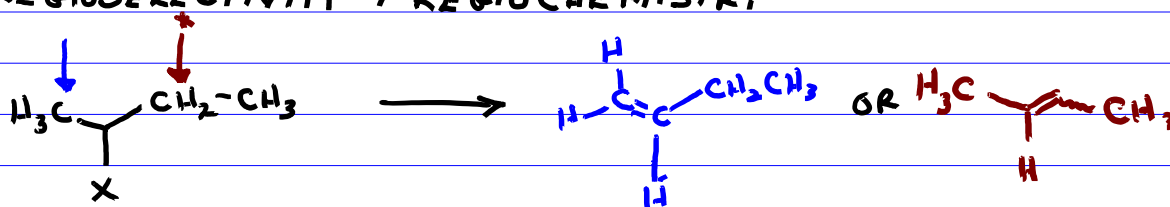
LEAVING GROUPS - THE GROUPS THAT COME OFF

HALIDES $I^- > Br^- > Cl^-$

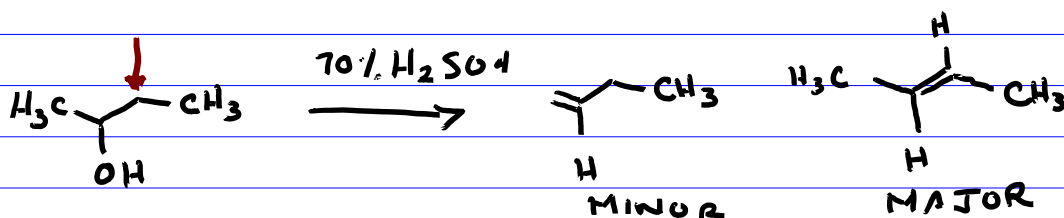


ISSUES TO ADDRESS:

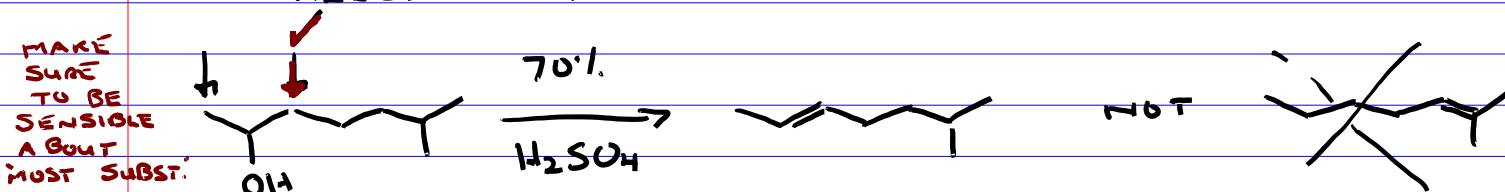
REGIOSELECTIVITY / REGIOCHEMISTRY



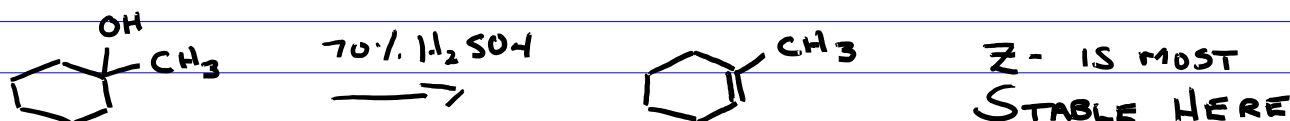
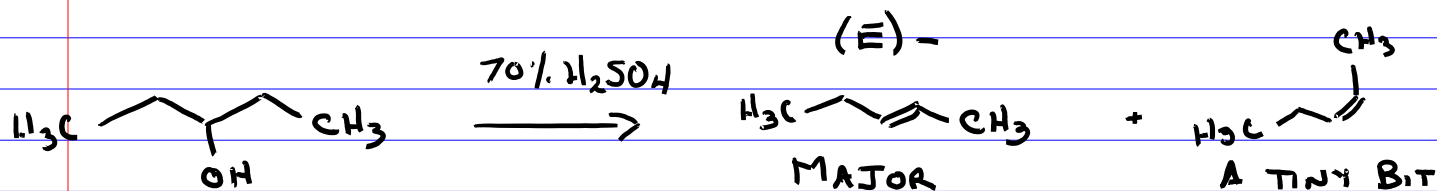
FOR E1 ELIMIN.

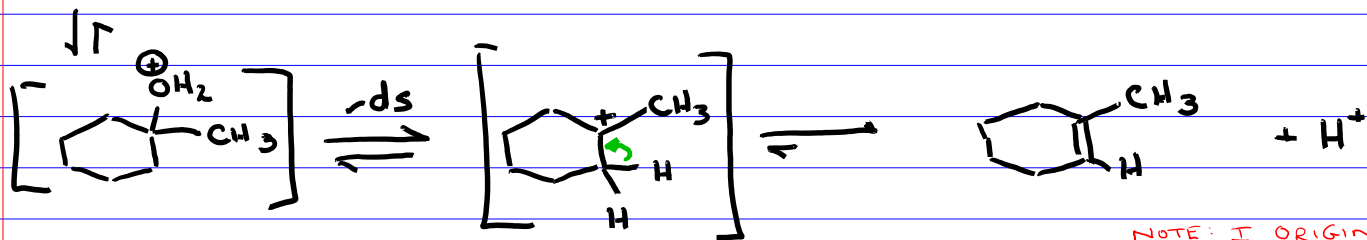


- NORMALLY GET THE MORE SUBSTITUTED ALKENE
- MORE STABLE ISOMER
- CALLED ZAITSEV RULE



- THIS IDEA (MOST STABLE ALKENE) ALSO GOVERNS WHICH GEOMETRIC ISOMER YOU GET
- IT WILL BE THE ONE WITH THE TWO BIGGEST GROUPS TRANS- TO EACH OTHER

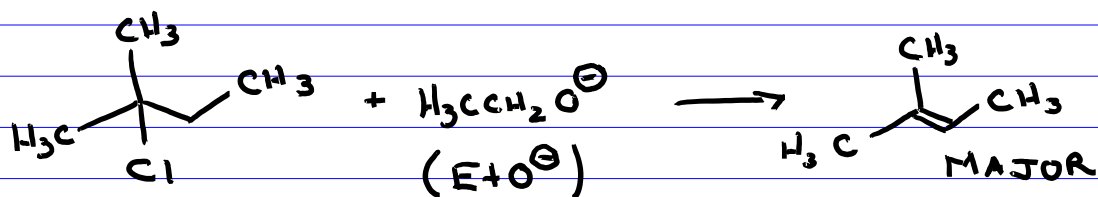




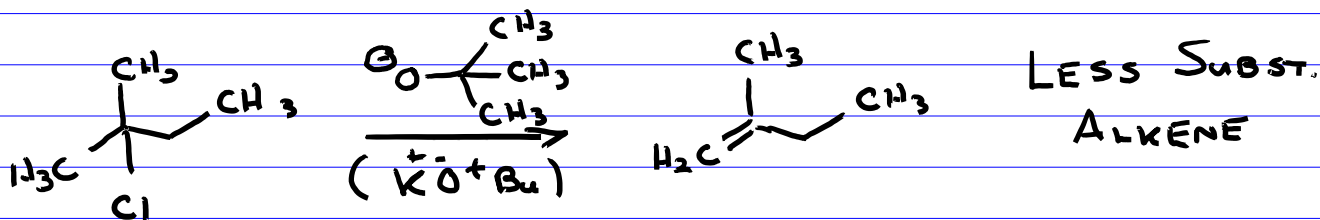
NOTE: I ORIGINALLY WROTE HOFMANN HERE - MISTAKE!

E2 - CAN BE MORE COMPLEX

- IN SIMPLE CASES, WITH MOST BASES, IT LOOKS SIMILAR (MUST SUBST. ALKENE - ZAITSEV RULE)



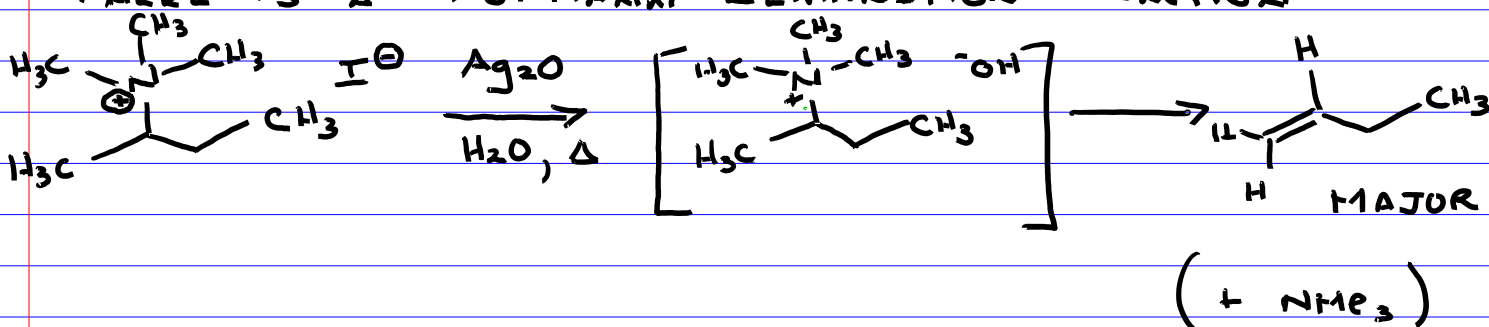
BUT - IF BASE IS STERICALLY HINDERED, ONE TENDS TO GET THE LESS SUBSTIT. ALKENE



USING O^- , N^- (LDA) STERICALLY HINDERED BASES.

- SAID TO BE FOLLOWING HOFMANN ORIENTATION

THERE IS A HOFMANN ELIMINATION REACTION



STEREOCHEMISTRY OF E2 ?

- ANTIPERIDPLANAR.

LECTURE 29

FINAL EXAM - MON. DEC. 12

8:30 - 11:30 AM

ERIE 1120

A - MAGDA

ERIE 2123

MALAKUTI-NEGAD - QUERBACH

ERIE 3123

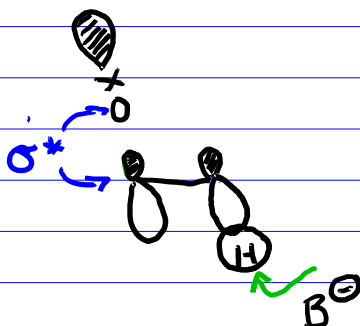
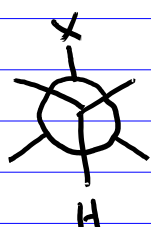
QUIMBY - SZALAY

ERIE 1118

T - Z

STEREOCHEMISTRY

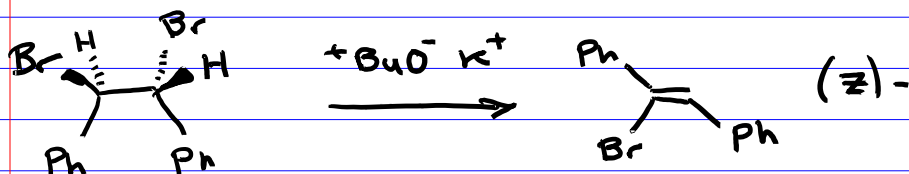
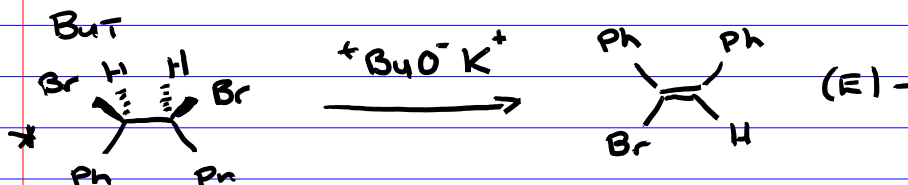
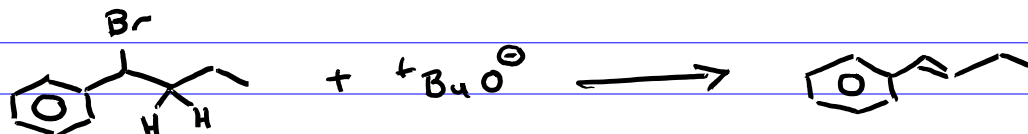
E2 ELIMINATION: THE H AND THE X⁻ ELIMINATED
MUST BE ANTIPERIPLANAR



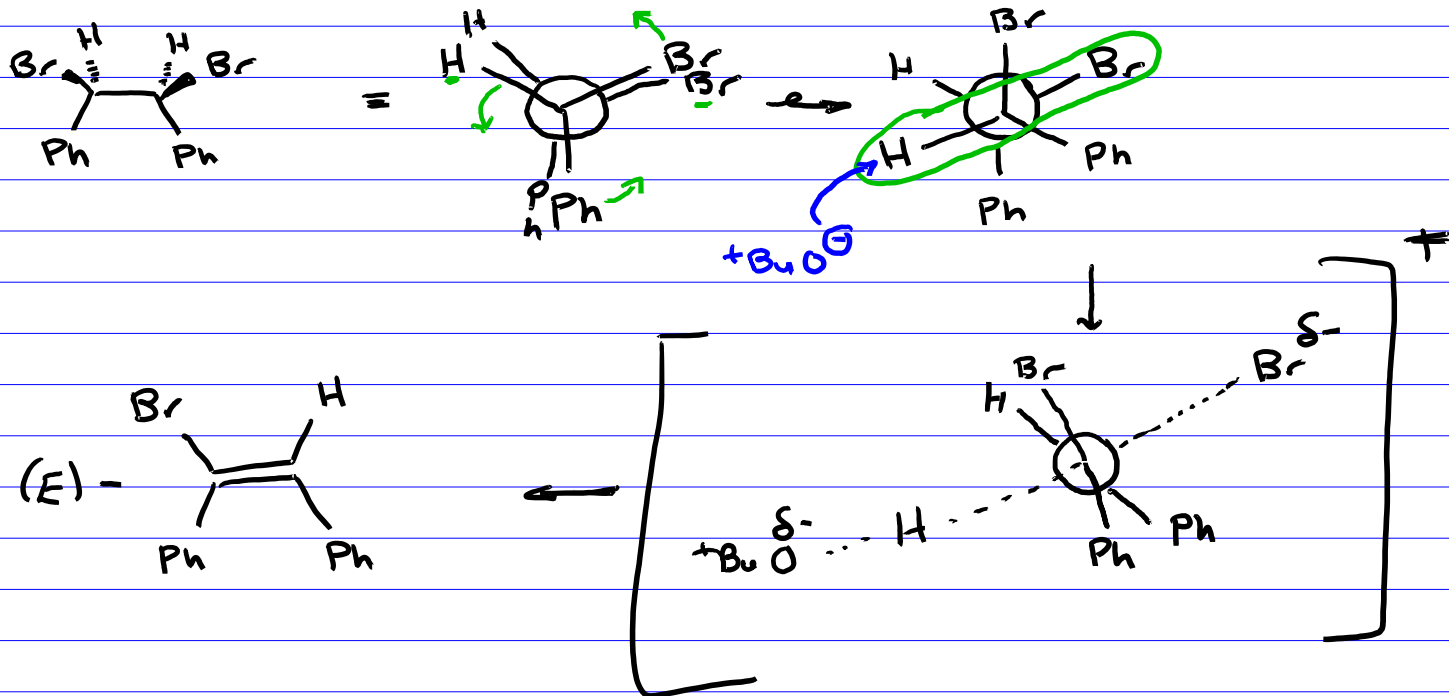
- AS C-H BOND IS ABSTRACTED,
THE e⁻ PAIR LEFT BEHIND
OVERLAPS WITH σ^* C-X
ORBITAL
- THIS BREAKS C-X BOND

CONSEQUENCES:

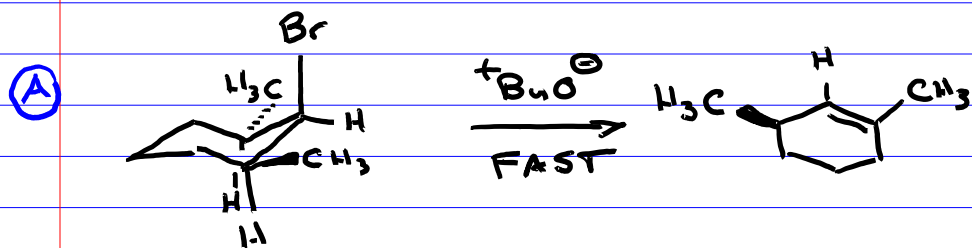
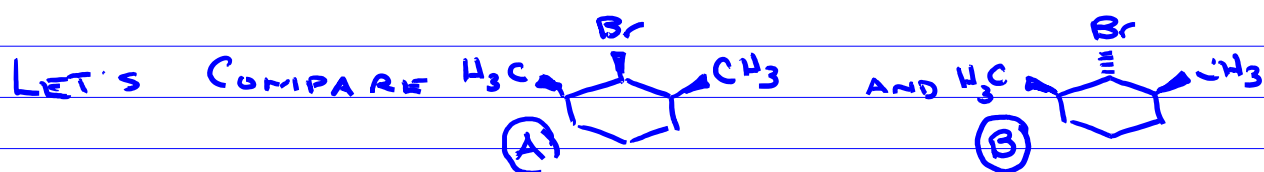
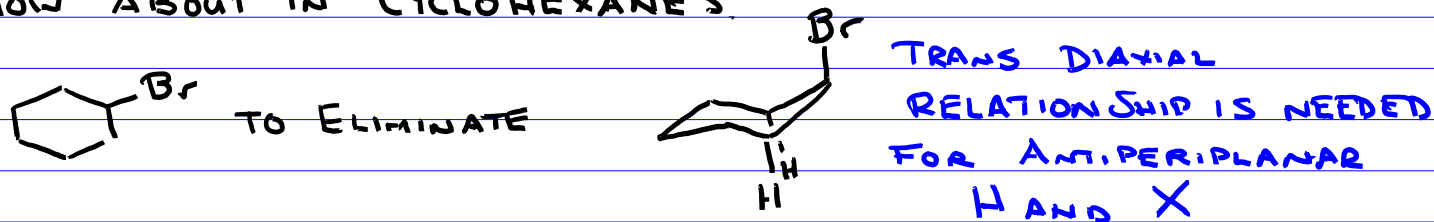
IN SIMPLE CASES, I.E. WHERE >1 IS AVAILABLE, YOU'LL
STILL GET THE MOST STABLE (I.E. TRANS) ALKENE



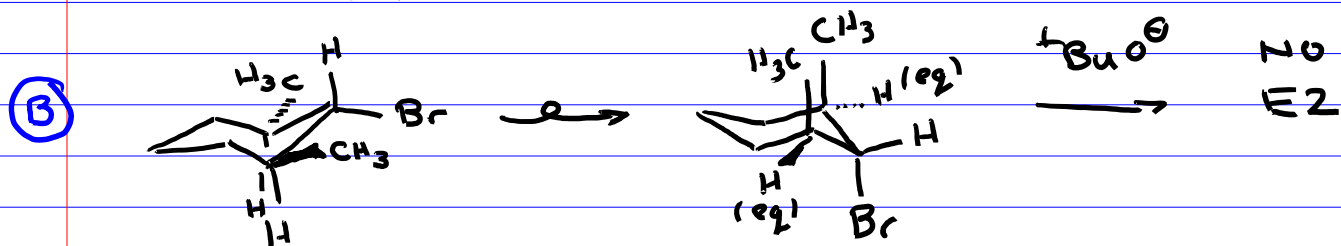
ONE ISOMER OF S.M. GIVES ONE ISOMER OF PROD.
OTHER ISOMER OF S.M. GIVES THE OTHER ISOMER OF PROD.
... STEREOSPECIFIC RXN.



HOW ABOUT IN CYCLOHEXANES.



H AND Br ARE
TRANS & DIAXIAL
IS BEST CONF.



E2 vs. E1 How do we know which it is?

A) LEAVING GROUP.

E1 - LEAVING GROUP MUST BE REALLY GOOD.

H_2O , I^- , Br^- , TsO^- MAYBE Cl^-

FOR E2 - CERTAINLY GOOD LEAVING GROUPS DON'T HURT
BUT NOT AS CRITICAL - FAIR L.G.'S OFTEN "PLAY"
IN E2'S

H_2O L.G. "NEVER" E2

B) BASE - FOR E2 WE NEED A REAL BASE

- FOR E1, NO "REAL" BASE - TECHNICALLY
SOLVENT AS A FORMAL BASE.

LECTURE 30

FINAL EXAM - MON. DEC. 12 8:30 - 11:30 AM

ERIE 1120

A - MAGDA

ERIE 2123

MALAKUTI-NEGAD - QUERBACH

ERIE 3123

QUIMBY - SZALAY

ERIE 1118

T - Z

E2 vs. E1 How do we know which it is?

A) LEAVING GROUP -

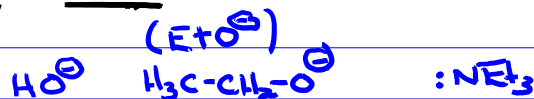
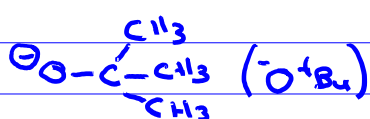
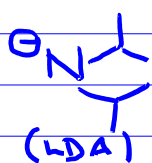
E1 - LEAVING GROUP MUST BE REALLY GOOD.

H_2O , I^- , Br^- , TSO^- MAYBE Cl^-

FOR E2 - CERTAINLY GOOD LEAVING GROUPS DON'T HURT
BUT NOT AS CRITICAL - FAIR L.G.'S OFTEN "PLAY"
IN E2'S

H_2O L.G. "NEVER" E2

B) BASE - FOR E2 WE NEED A REAL BASE



- FOR E1, NO REAL BASE
- TECHNICALLY SOLVENT AS A FORMAL

BASE.

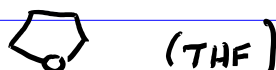
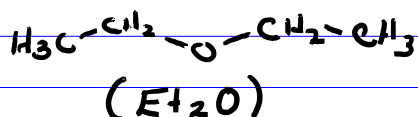
(H_2O , CH_3OH , $EtOH$)

C) SOLVENT

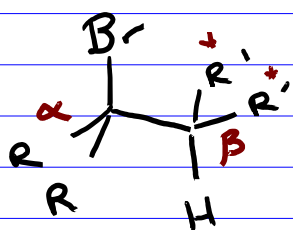
E1'S - A POLAR SOLVENT NORMAL - REALLY ENCOURAGES
THE CARBOCATION FORMATION

H_2O , CH_3OH , CH_3CH_2OH

E2'S - POLAR SOLVENT CERTAINLY TOLERATE E2'S
BUT V. COMMON TO HAVE LESS POLAR, APROTIC SOLVENTS



D) THE SUBSTRATE STRUCTURE



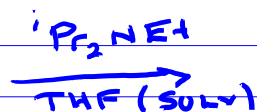
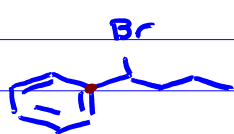
α -SITE
 - THE MORE SUBSTITUENTS AT α -SITE,
 THE MORE IT WILL TEND TO E1 ELIMIN.
 (MORE STABILIZED CARBOCATION)

β -SITE

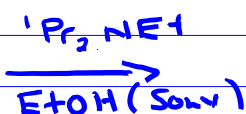
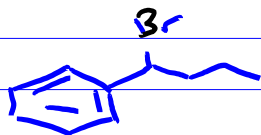
- MORE ALKYL R' 's, IT WILL TEND TO FAVOUR E1
 MORE - DUE TO SLOWING DOWN OF THE E2 MECH.

- MORE PHENYL R' 's (OR OTHER ARYLs) IT FAVOURS
 E2 - MAKES TO REMAINING H EASIER TO ABSTRACT
 (MORE ACIDIC)

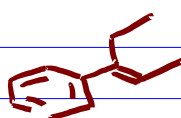
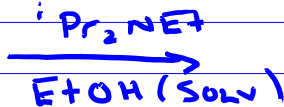
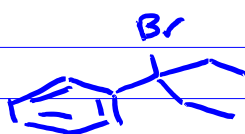
THE TYPE OF QUESTION YOU'RE LIKELY TO GET.



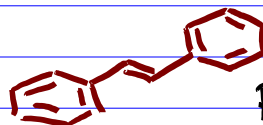
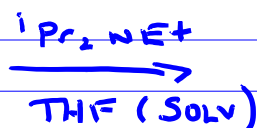
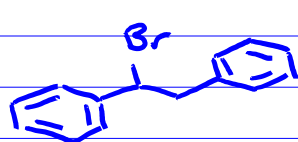
LOW POLARITY SOLV $\Rightarrow$ E2
 2° SUBST $\Rightarrow$ E1 OR E2
 β -ALKYL - MORE E1 THAN
 BOTTOM CASE $\Rightarrow$ 2ND MOST E2



POLAR SOLVENT $\Rightarrow$ E1
 2° SUBST $\Rightarrow$ E1 OR E2
 β -ALKYL CASE $\Rightarrow$ MORE E1
 THAN BOTTOM CASE
 2ND MOST E1

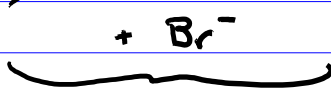
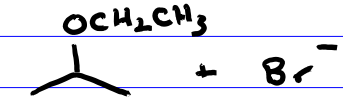
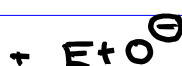
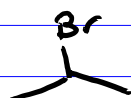


POLAR SOLVENT $\Rightarrow$ E1
 3° SUBSTRATE $\Rightarrow$ E1 } MOST E1



LOW POLARITY SOLV. $\Rightarrow$ E2
 β -SITE HAS ARYL GROUP $\Rightarrow$ E2
 MOST E2 OF THEM ALL

How DO YOU KNOW IF IT'S ELIMINATION OR SUBSTITUTION?



E2

S_N2

E2 vs S_N2

1. THE MORE YOU HEAT THE RXN, THE MORE THE ELIMINATION PRODUCTS ARE FAVOURED.

- DUE TO ENTROPY $\Delta S_{\text{ELIMIN}} > 0$ (2 PARTICLES $\Rightarrow$ 3)
 $\Delta S_{\text{SUBST}} \approx 0$ (2 PARTICLES $\Rightarrow$ 2)

2) BASE / NUCLEOPHILE

3) SUBSTRATE

LECTURE 31

FINAL EXAM - MON. DEC. 12 8:30 - 11:30 AM

ERIE 1120

A-MAGDA

ERIE 2123

MALAKUTI-NEGAD - GUERBACH

ERIE 3123

QUIMBY - SZALAI

ERIE 1118

T - Z

E2 vs S_N2

- HOW DO YOU KNOW WHETHER
SUBSTITUTION OR ELIMINATION
PREDOMINATES

1. THE MORE YOU HEAT THE REACTION, THE MORE THE
ELIMINATION PRODUCTS ARE FAVOURED.

- DUE TO ENTROPY $\Delta S_{\text{ELIMIN.}} > 0$ (2 PARTICLES $\rightarrow$ 3)
 $\Delta S_{\text{SUBSTIT.}} \approx 0$ (2 PARTICLES $\rightarrow$ 2)

2. SUBSTRATE

$\text{H}_3\text{C}-\text{I}$ METHYL	$\text{H}_3\text{C}-\text{CH}_2-\text{I}$ 1°	$\text{H}_3\text{C}-\text{CH}(\text{I})-\text{CH}_3$ 2°	$\text{H}_3\text{C}-\text{C}(\text{I})(\text{CH}_3)_2$ 3°
S _N 2 ONLY E2 IMPOSSIBLE	TENDS MORE TO S _N 2	RIGHT IN THE MIDDLE	E2 ONLY S _N 2 FORBIDDEN

3. BASE / NUCLEOPHILE QUALITY.

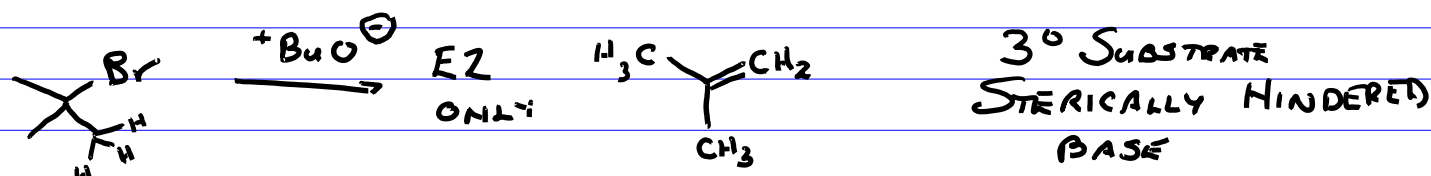
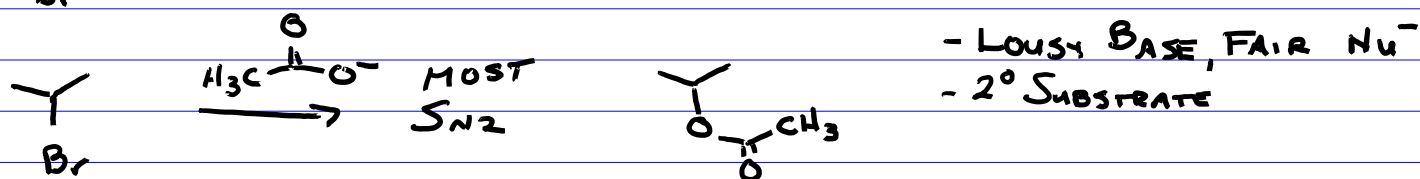
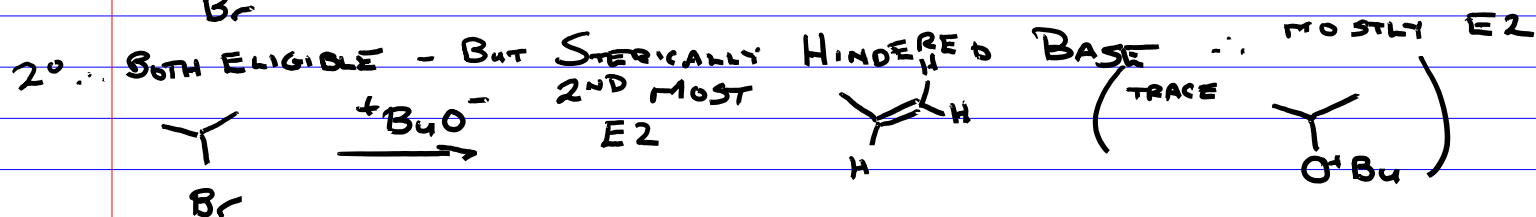
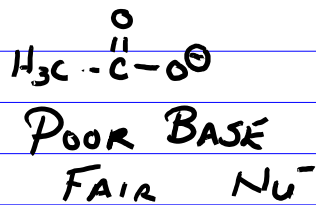
- THE BETTER THE BASE IS - MORE E2

- THE BETTER THE NUCLEOPHILE IS - MORE S_N2

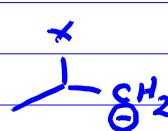
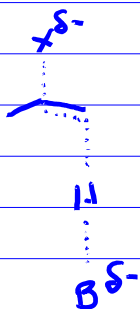
HO^- , $\text{H}_3\text{C}-\text{O}^-$, $\text{H}_3\text{C}-\text{CH}_2-\text{O}^-$ (E⁺O⁻)
✓. GOOD BASES
✓. GOOD NUCLEOPHILES

$(\text{H}_3\text{C})_3\text{C}-\text{O}^-$
✓. ✓. GOOD BASE
✓. POOR NU⁻ (STERICALLY
HINDERED)
E2

$\text{CH}_3\text{CH}_2\text{CH}_2\text{N}^-\text{Li}^+$ (LDA)
✓. OUTSTANDING BASE
POOR NU⁻



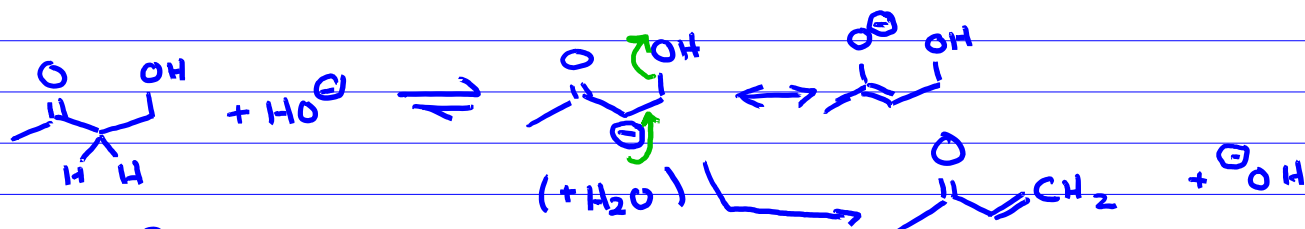
INTEREST ONLY. - WHAT ABOUT THAT Elcb ??



H IS ABSTRACTED
IN 1ST STEP

(cb = CONJUGATED BASE)

- TEND TO SEE IT WHEN THERE'S A GOOD ELECTRON WITH - DRAWING GROUP TO MAKE C-H ACID



ALDOL CONDENSATION (BENZYLNE FORMATION)