LEC (1) CHEM 30A Sep 30th

(1) WHO/WHEN/WHERE/HOW?
(2) WHAT?

HMK: READ 1-1.4
PROBLEMS 1.1-1.5, 1.19-1.22

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(1) ME
- 3077D YOUNG HALL
- WEBSITE
  - Lecture notes
  - Announcements
  - Handouts
  - Exams & Keys
  - Policy

- 8AM SUCKS, but I strongly recommend you come to class
- QUESTIONS OK

- ENGLISH ENGLISH
26th letter, 13th element, football etc

- MODEL KITS, not required, but useful

TAs: Cari, Heather, Kaushik, Ryan

- Discussion sections
(be consistent, exams returned there)

- office hours (v. useful)
times posted on website / syllabus
MINE are M 4-6, R 12-2

- TEXTBOOK
Brown & Foote 4th Ed (3rd ok)
↳ reading & hmk assignments

- EXAMS

3 QUIZZES 100 (3 x 35)
2 MIDTERMS 200 (2 x 115)
1 FINAL 200 (1 x 230)
500 (565)

FINAL is COMPREHENSIVE
Rules: SEE SYLLABUS + WEBSITE

- CHEATING, don't even think about it

- SYLLABUS - read it, things may change
(like FRI Nov 11th)

- WAITLIST (not my decision)
- IMPACTED CLASS....

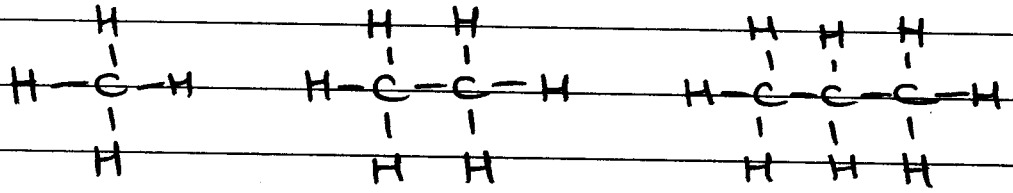
(2) WHAT? – ORGANIC CHEMISTRY

ORGANIC ⇒ compounds from living things (as opposed to inorganic)

↳ study of compounds containing carbon.

SIMPLEST ⇒ HYDROCARBONS

contain H and C ONLY



CH_4 methane

C_2H_6 ethane

C_3H_8 propane

FRAMEWORK ⇒ dangle FUNCTIONAL GROUPS

⇒ specific combinations of atoms in precise arrangements

WHY (i) CLASSIFY organic compounds

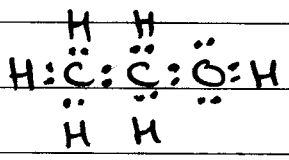
(ii) BASIS for NAMING

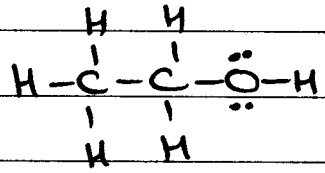
(iii) PREDICTABLE CHARACTERISTIC REACTIVITY

for example: ALCOHOLS

e.g. CH_3-CH_2-OH ethanol

DRAWING MOLECULES

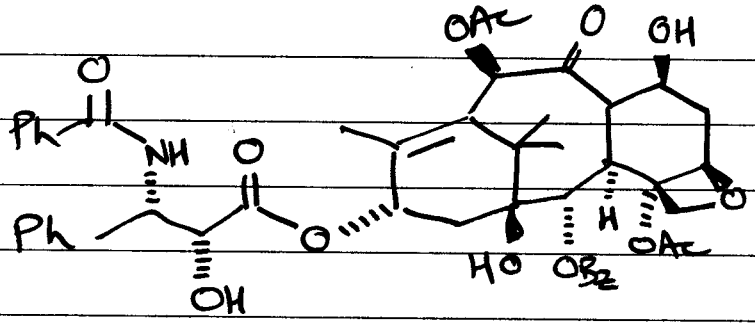
(i) 

(ii) 

(iii) CH_3CH_2OH (iv) C_2H_5OH

(v) EtOH (vi)  LINE FORMULA (get used to it!)

Atoms other than C, H => HETEROATOMS
e.g. O, N, S, P, F, Cl, Br, I



TAXOL

- FUNCTIONAL GROUPS - STEREOCHEMISTRY
- ABBREVIATIONS - LINE FORMULAE

most promising ANTI-TUMOR agent developed in 3 DECADES => 1998 sales $1.2 BILLION

- Where do we get it? Not like it grows on trees...

- Well... YES.... it does PACIFIC YEW BARK but six x100 yr old trees → 1 PATIENT

- SYNTHESIS (making molecules)

⇓

REACTIONS ($A + B \xrightarrow{C} D$)

⇓

MECHANISMS (how it works)

⇓

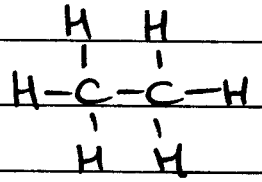
STRUCTURE & BONDING (electrons & orbitals)

THINGS YOU NEED TO KNOW

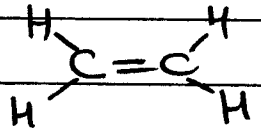
H forms 1 BOND
C forms 4 BONDS (neutral species)

not absolute, but good 99% of the time.

e.g.



(ALKANE)
ethane

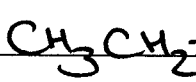


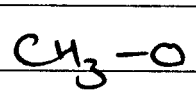
(ALKENE)
ethylene

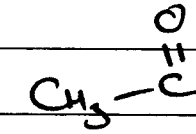
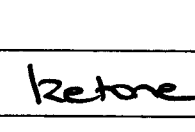
(ALKYNE)
acetylene

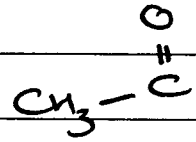
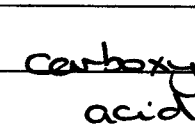
O forms 2 BONDS

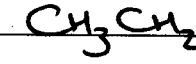
Hal (F, Cl, Br, I) form 1 BOND

 alcohol (R–O–H)

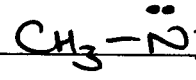
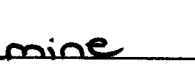
 ether (R–O–R)

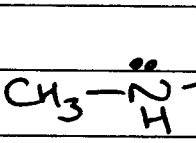
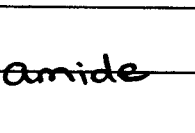
 ketone 

 carboxylic acid 

 alkyl chloride (R–Cl)

N forms 3 BONDS

 amine 

 amide 

S, P variable

R GROUPS – whatever you want them to be...

LEC (2) CHEM 30A Oct 3rd

(1) CHEMICAL BONDING
(2) LEWIS STRUCTURES
(3) FORMAL CHARGE
(4) SHAPES of MOLECULES

HMK: READ 1.3–1.4
PROBLEMS 1.6–1.13, 1.23–1.47
+ MOLECULAR SHAPE PROB SETS ON WEB

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(1) CHEMICAL BONDING

Valence electrons (outer shell electrons)
⇒ BOND FORMATION

# VALENCE e⁻	1	2		3	4	5	6	7	8
	H								He
	Li	Be	d	B	C	N	O	F	Ne
	Na	Mg	BLOCK	Al	Si	P	S	Cl	Ar

ELECTRONEGATIVITY (EN)
- AN ATOM'S ATTRACTION FOR ELECTRONS IT SHARES IN A CHEMICAL BOND WITH ANOTHER ATOM

F HAS HIGHEST VALUE ⇒ 4.0

← F
decreases
↓ decreases

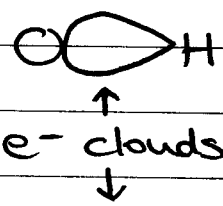
PAULING SCALE
(Linus Pauling 1901 - 1994) CHEM 1954 PEACE 1962

ORGANIC CHEMISTRY ⟹ COVALENT BONDS ⟹ EN DIFFERENCES < 2

SO, Consider:

Na F (3.1) NaF ($Na^+ F^-$) IONIC SALT
0.9 4.0

O H (1.4) $\delta-$ $\delta+$ O—H POLAR COVALENT
3.5 2.1



C C (ϕ) C—C NON POLAR COVALENT
2.5 2.5

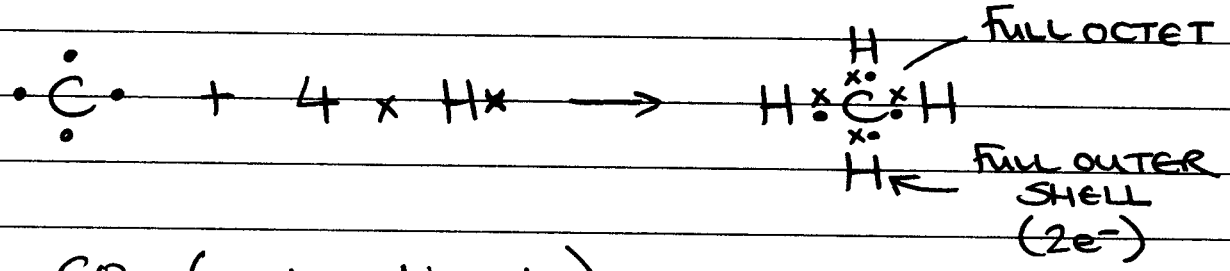
EN difference < 0.5 ≃ NON POLAR

C—H Table 1.5 Page 7
2.5 2.1 Know values for common elements & Know TRENDS

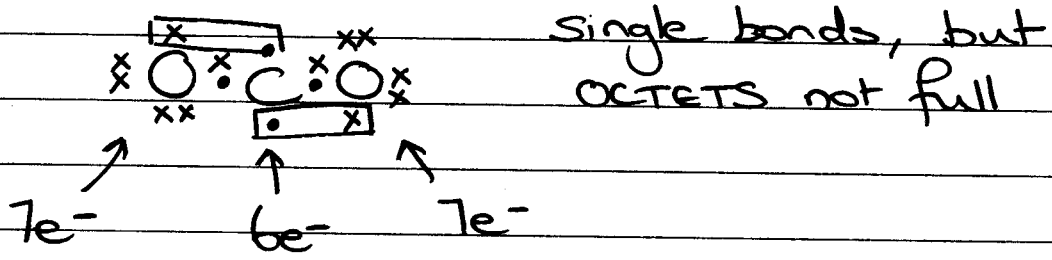
② LEWIS STRUCTURES

- # of valence e^- on each atom
- least EN element in center (not H)
- form SINGLE BONDS
- fill octets (multiple bonds / charges)

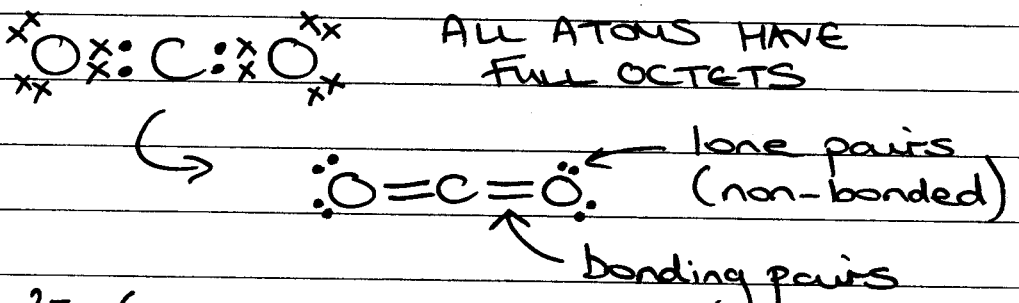
a) CH_4 (methane)



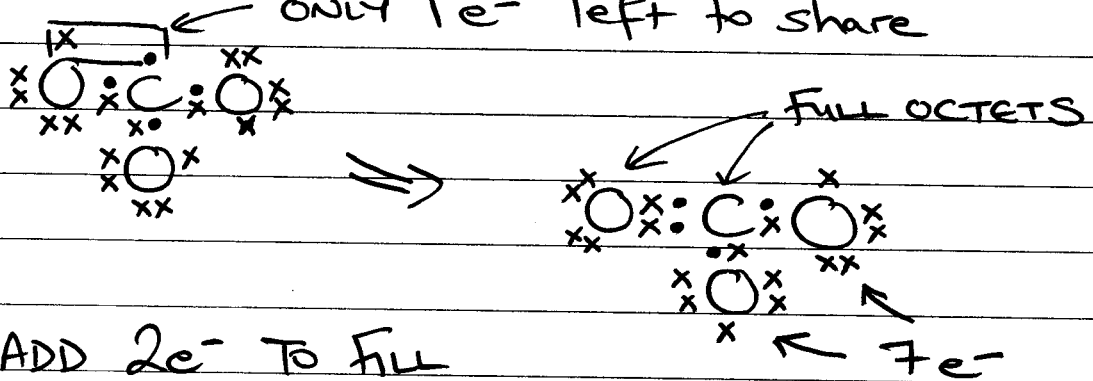
b) CO_2 (carbon dioxide)



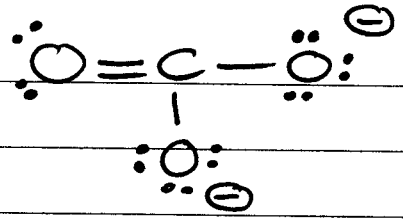
- share more electrons (MULTIPLE BONDS)
  ⟹ REDRAW



c) CO_3^{2-} (CARBONATE ANION)

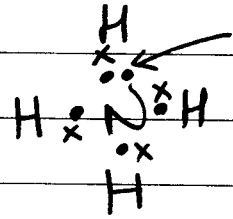


So, ADD 2e⁻ TO FILL OCTETS (DRAW THEM IN) →



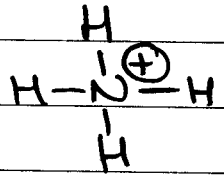
CO_3^{2-}

d) $NH_4^{\oplus}$ - AMMONIUM CATION



9 e^- in VALENCE shell

VIOLATES OCTET RULE

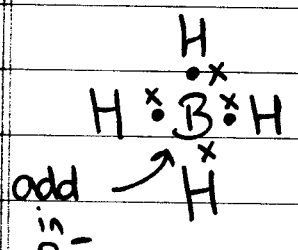
So, get rid of it $\Rightarrow$ 

③ FORMAL CHARGE

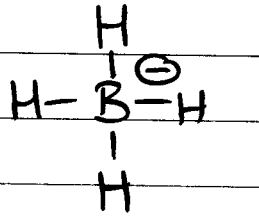
- Draw LEWIS structure for each atom:

FORMAL CHARGE = # VALENCE e^- IN ISOLATED NEUTRAL ATOM $-$ (# of NONBONDING e^- + $1/2$ # BONDING e^-)

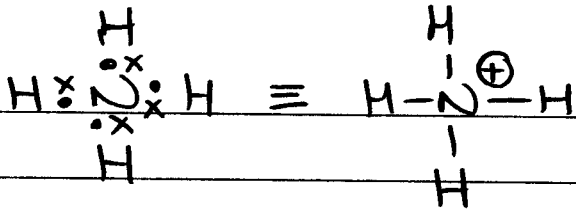
a) $BH_4^{\ominus}$



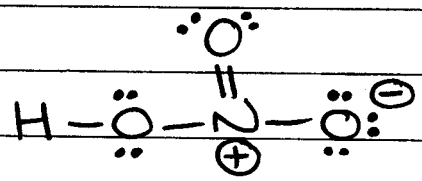
odd e^-

$\equiv$ 

$(3 - 8/2) = -1$

b) $NH_4^{\oplus}$  $(5 - 8/4) = +1$

c) HNO_3 (nitric acid)

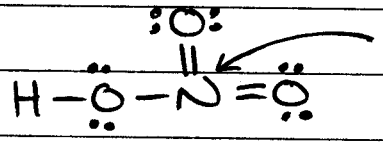


show how we get this.

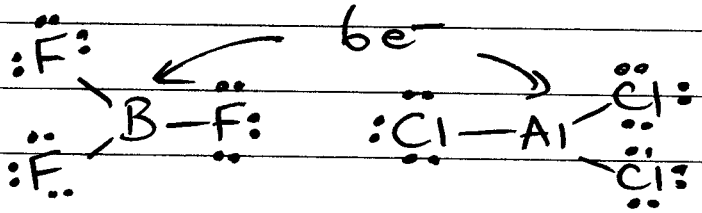
N $(5 - 8/2) = +1$

O $(6 - (6 + 2/2)) = -1$

other Os $(6 - (4 + 4/2)) = \emptyset$

note: not  10e⁻ violates OCTET rule

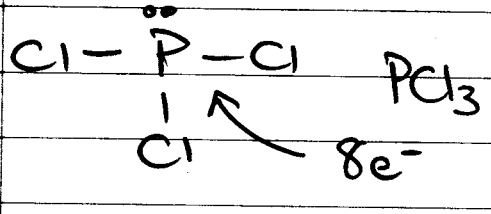
Note: there are exceptions to the OCTET rule

GROUP 3 

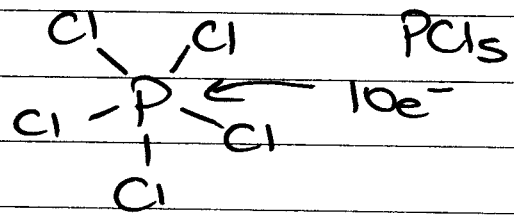
usually quite reactive species

3RD ROW ELEMENTS (P & S)

d orbitals ⇒ EXPAND octet



PCl_3

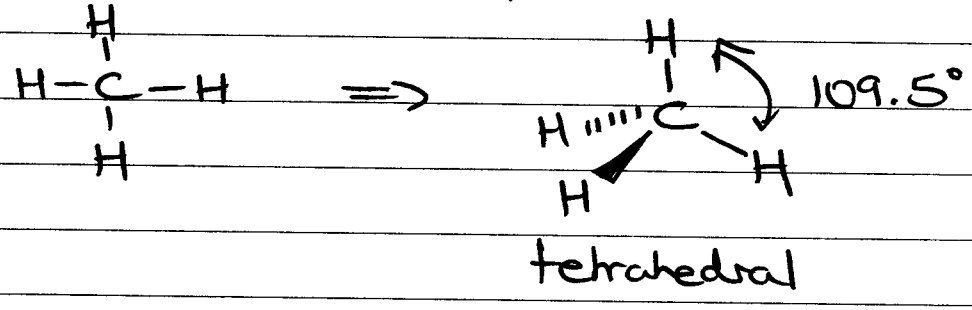


PCl_5

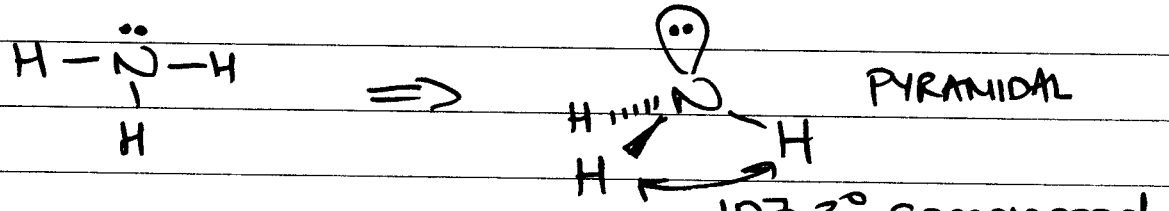
(4) SHAPES OF MOLECULES

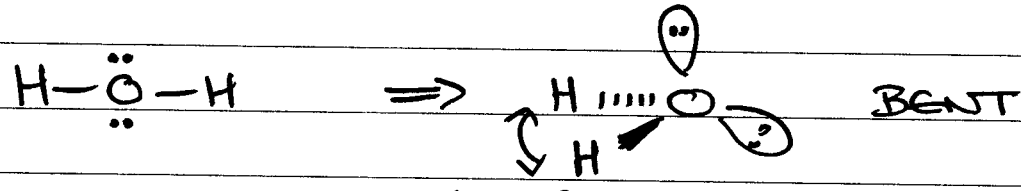
Valence Shell Electron Pair Repulsion Theory (VSEPR) – Simplified model

Geometry determined by valence shell e^- PAIRS both BONDED & NON BONDED arranging to minimize electrostatic repulsion

eg. 

tetrahedral





104.5° more compressed

WHY? lone pair/lone pair > lone pair/bond pair > bond pair/bond pair REPULSION

Also: $A \equiv B > A = B > A - B$

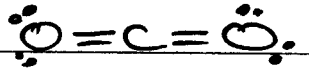
DISTINGUISH BETWEEN "SHAPE OF MOLECULE" VERSUS GEOMETRY AROUND AN ATOM.

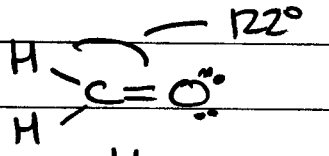
BASIC GEOMETRIES

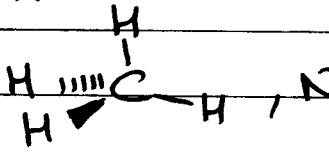
- for the sake of geometry, treat MULTIPLE BONDS as SINGLE BONDS

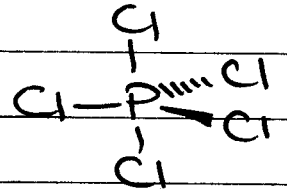
When considering geometry around a given atom, add # of ATOMS bonded to it to the # of LONE PAIRS.

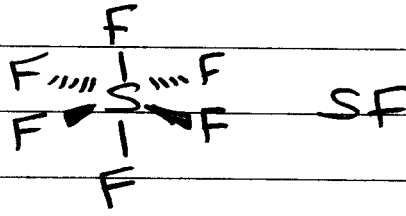
2 => LINEAR
3 => TRIGONAL PLANAR
4 => TETRAHEDRAL
5 => TRIGONAL BIPYRAMIDAL
6 => OCTAHEDRAL

2 → LINEAR 

3 → TRIGONAL PLANAR 

4 → TETRAHEDRAL  , NH_3, H_2O

5 → TRIGONAL PLANAR  PCl_5

6 → OCTAHEDRAL  SF_6

LEC 3 CHEM 30A Oct 5th

1. SHAPES OF MOLECULES
2. DRAWING ORGANIC STRUCTURES
3. RESONANCE

GRUBBS Pg 963

Hmk: READ rest of Ch 1
Problems: 1.14-1.17, 1.48-1.54 + molecular structure worksheets

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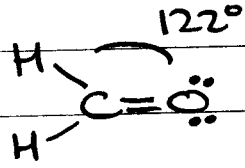
1. SHAPES OF MOLECULES

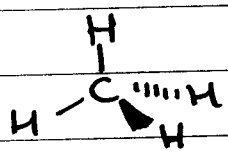
(PAIRS OF e^- IN VALENCE SHELL)
- BONDED & NONBONDED

BUT TREAT MULTIPLE BONDS AS SINGLE

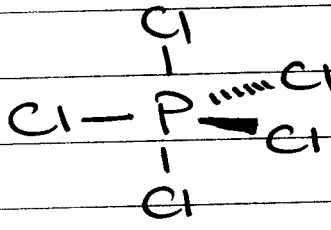
ADD #BP (or # atoms) to #LP

2 → LINEAR 

3 → TRIGONAL PLANAR 

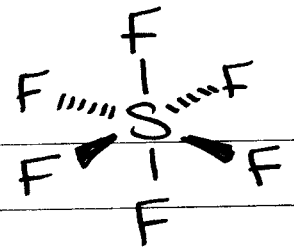
4 → TETRAHEDRAL 

, NH_3, H_2O

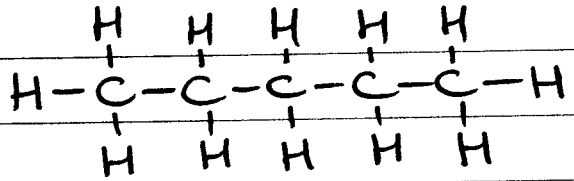
5 → TRIGONAL BIPYRAMIDAL 

PCl_5

6 → OCTAHEDRAL



(2) DRAWING ORGANIC MOLECULES

a) 

PENTANE (structural formula)

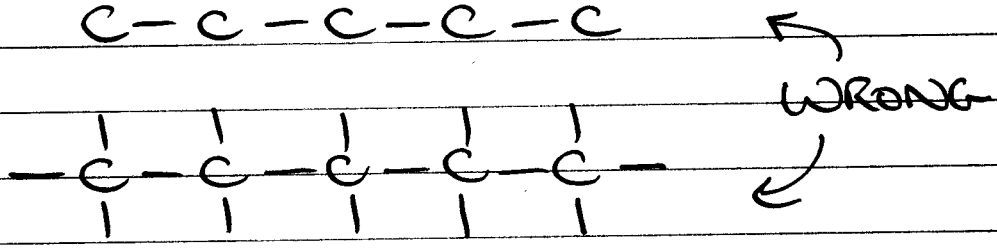
- condensed formula

$CH_3CH_2CH_2CH_2CH_3$ or $CH_3(CH_2)_3CH_3$

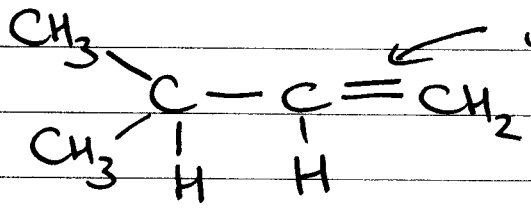
- line formula

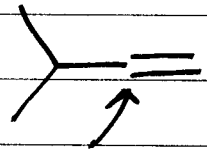
  - draw chains as ZIG-ZAGS
  - leave out any H attached to C
  - draw nonbonded electrons (lone pairs)

DO NOT WRITE

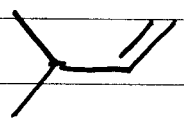


b) $(CH_3)_2CHCHCH_2$?



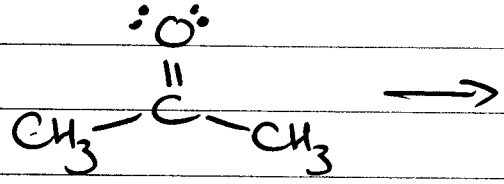
maybe you would draw 

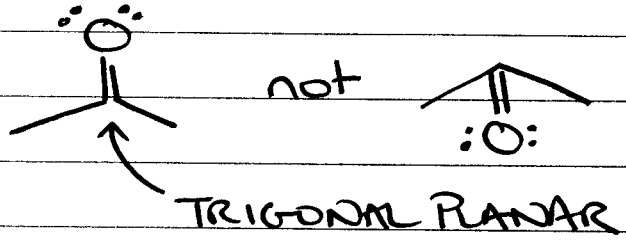
geometry of C atom
⇒ TRIGONAL PLANAR

So 

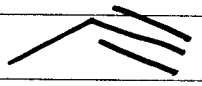
TRY to be as true to molecular shape as possible.

c) $CH_3(CO)CH_3$

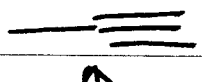




d) $CH_3CCH \Rightarrow CH_3-C\equiv C-H$

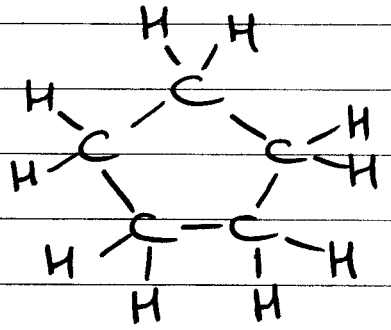


NO



LINEAR

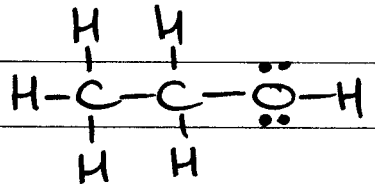
- RINGS



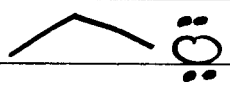
≡

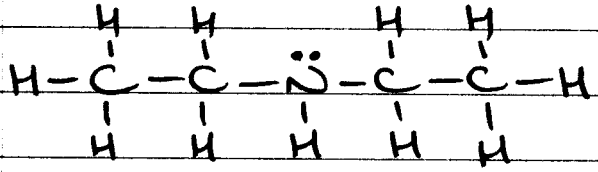
each of these is a CH_2

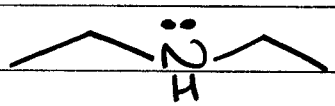
- HETEROATOMS (draw Hs & LONE PAIRS)



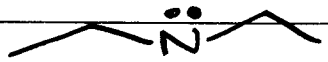
not



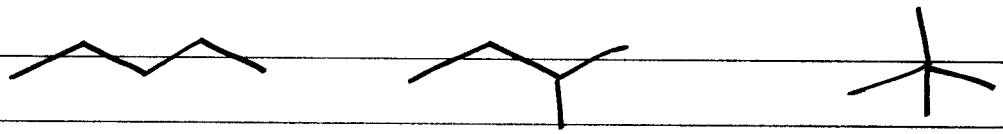




not



- example C_5H_{12}

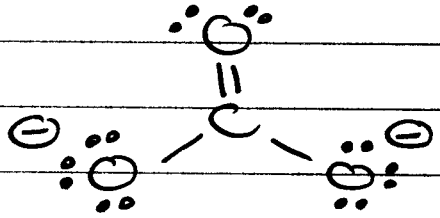


CONSTITUTIONAL ISOMERS

-same formula, different arrangements of atoms

(13) RESONANCE

consider CO_3^{2-}

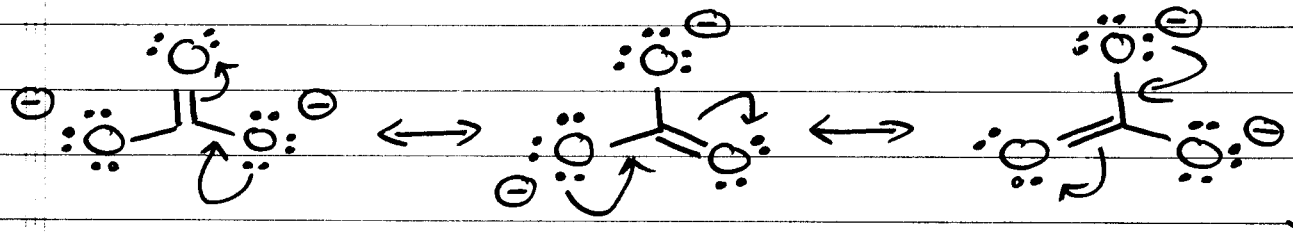


one C=O bond

two C-O bonds

C=O shorter/stronger bond than C–O

In CO_3^{2-} however, all CO bonds are identical & all angles 120° ⟹ WHY?



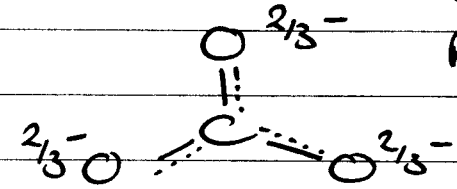
RESONANCE CONTRIBUTORS (all equivalent in this case

ARROWS ⟷ Separates resonance contributors

↷ CURLY ARROW: movement of a pair of ELECTRONS

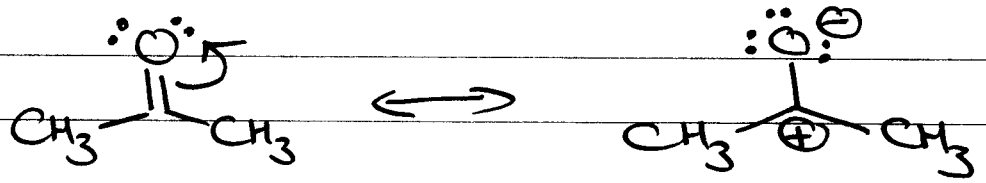
BUT NONE of these contributors actually EXIST!

actual structure is



RESONANCE HYBRID

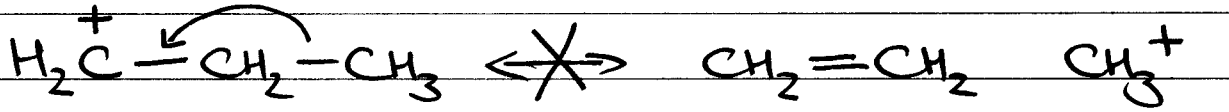
Not all resonance contributors are necessarily equivalent, e.g.



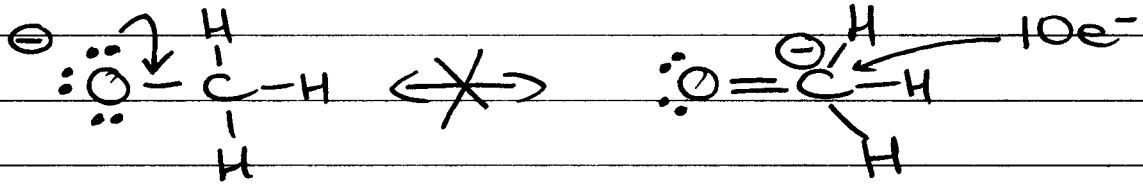
which of these is most stable?

- RULES FOR DRAWING RESONANCE STRUCTURES
- DO NOT

① Break any single bonds



② Violate the octet rule

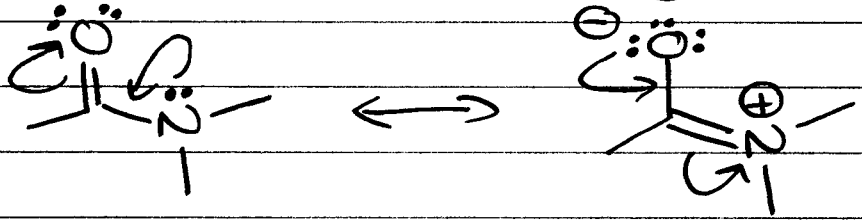


③ Move atoms (framework must stay same)

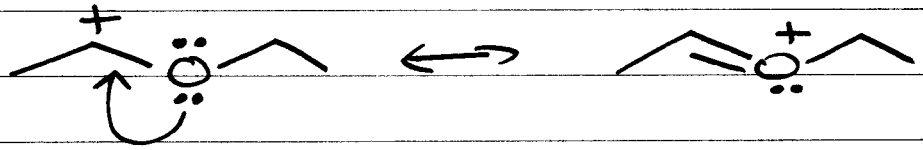
DRAWING RESONANCE STRUCTURES
- cannot break single bonds, so we can only move electrons from double (or triple) bonds and lone pairs.

PATTERNS

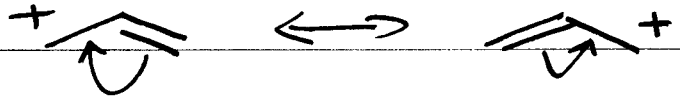
① LONE PAIR NEXT TO π BOND
double | triple
"next to" means one single bond away



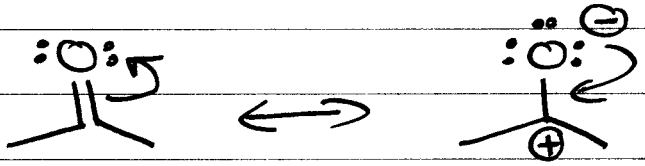
② LONE PAIR NEXT TO +VE CHARGE



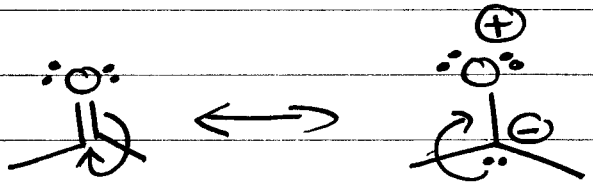
③ π BOND / +VE CHARGE



④ π BOND / TWO EN ATOMS

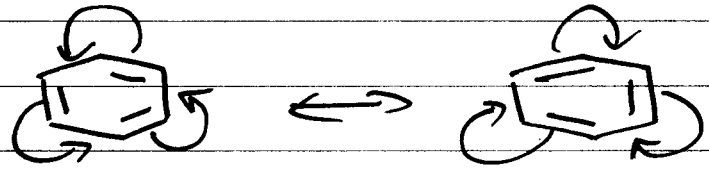


NOT



O is more EN than C

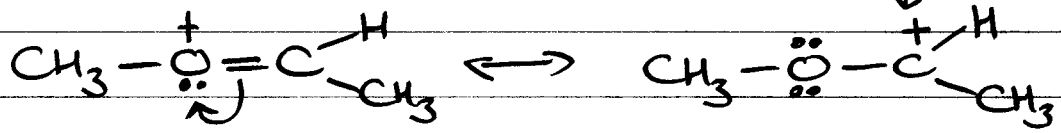
⑤ π BONDS in a RING



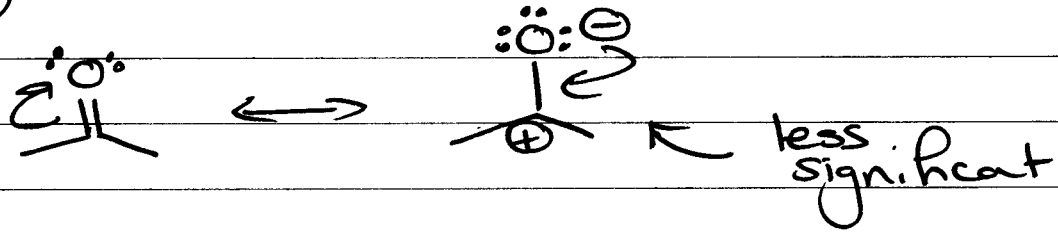
– RELATIVE IMPORTANCE OF CONTRIBUTORS

a) MAXIMISE OCTETS

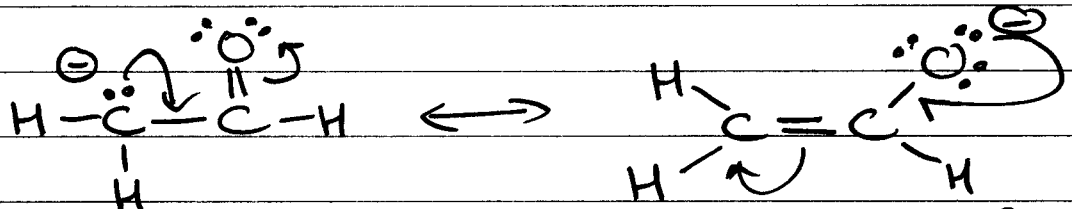
more significant



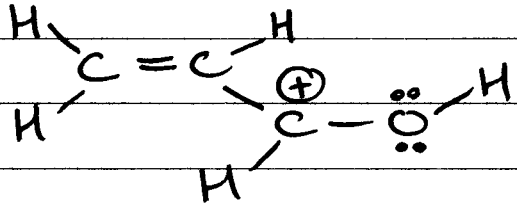
b) MINIMISE CHARGES



c) PUT -VE CHARGE ON MORE EN ELEMENT



HMK



DRAW TWO MORE RESONANCE FORMS

- which is most significant?
- structure of HYBRID?

LEC (4) CHEM 30A Oct 7th

1. RESONANCE
2. ATOMIC ORBITALS
3. MOLECULAR ORBITALS
4. HYBRIDISATION

HMK 1.18, 1.55–1.71 + RESONANCE PROBLEMS ON WEB

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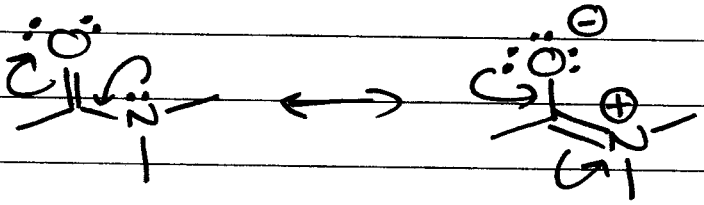
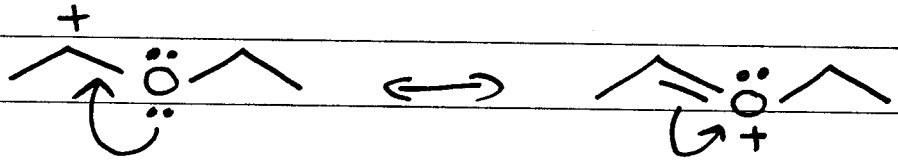
(1) RESONANCE

- Patterns

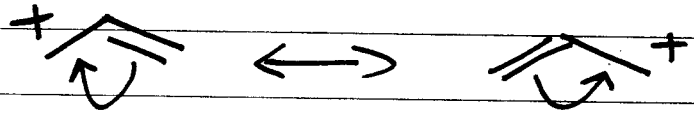
a) LONE PAIR / π BOND



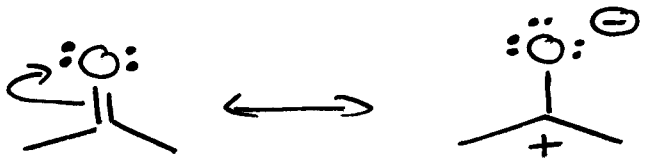
b) LONE PAIR / +ve CHARGE



c) π BOND / +ve CHARGE



d) π BOND / TWO EN ATOMS



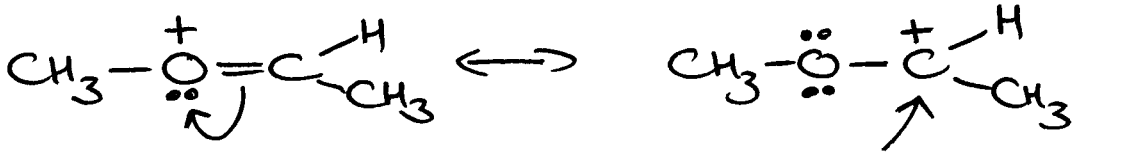
NOT

O is more EN than C

e) π BONDS in a RING

— RELATIVE IMPORTANCE OF CONTRIBUTING STRUCTURES

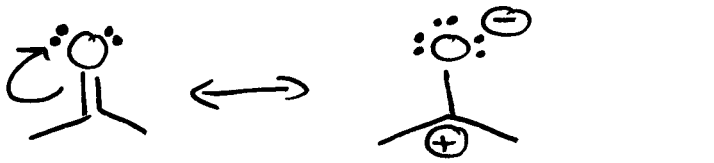
a) MAXIMISE OCTETS



more significant

not a full octet

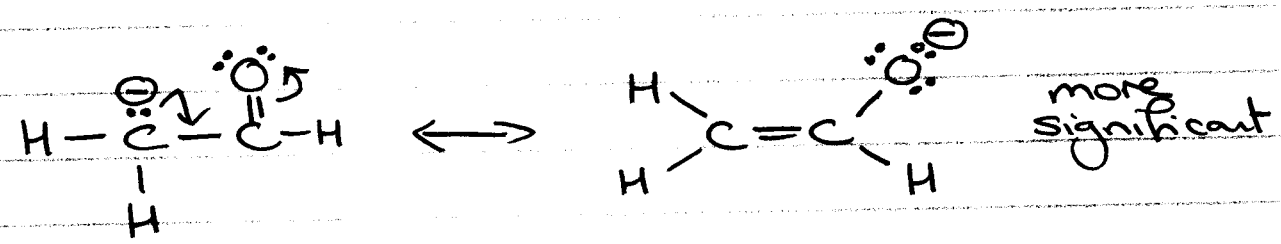
b) MINIMISE CHARGES



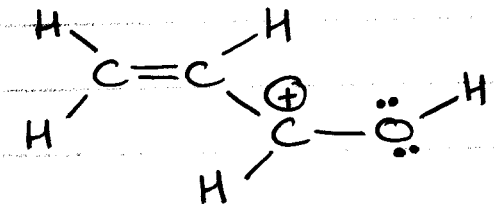
more significant

less significant

c) PUT -ve CHARGE ON MORE EN ELEMENT



HMK



DRAW OTHER TWO RESONANCE FORMS

- which is most significant?
- structure of hybrid?

(2) ATOMIC ORBITALS

Schrödinger equation

⇓

Probability distributions of electron density

⇓

Orbitals (shapes) s, p, d, f

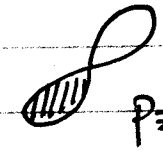
this class

sharp
principal
diffuse
fundamental

1s 

2s 

2p ORBITALS



(3) MOLECULAR ORBITALS

molecules => many atoms => many atomic orbitals

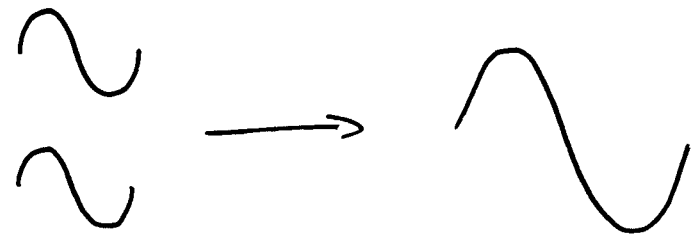
(LCAO - linear combination of atomic orbitals)

nAOs $\longrightarrow$ nMOs

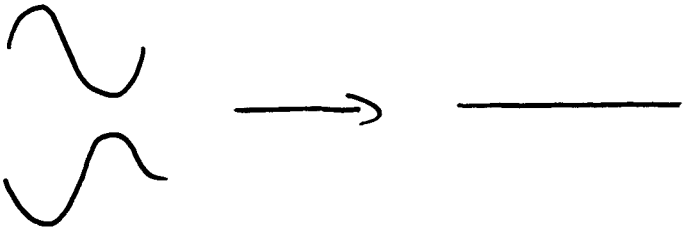
- same filling rules

AUFBAU PRINCIPLE (lowest energy first)
PAULI EXCLUSION PRINCIPLE (two e^-, opp spin)
HUND'S RULE (don't pair until you have to)

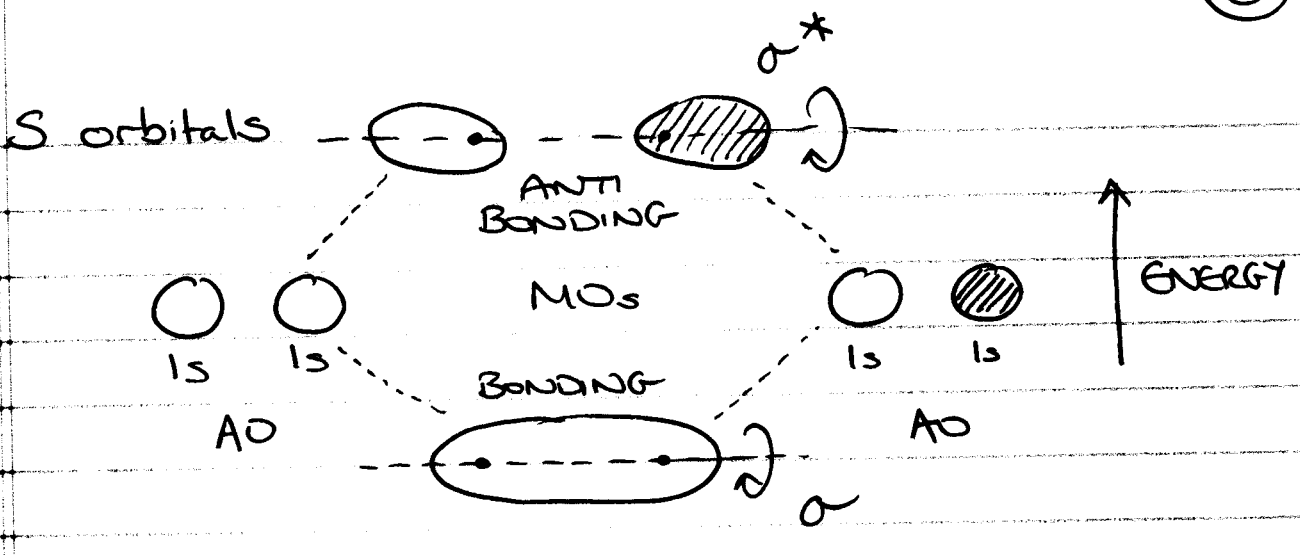
Orbitals → wavefunctions - combine like waves



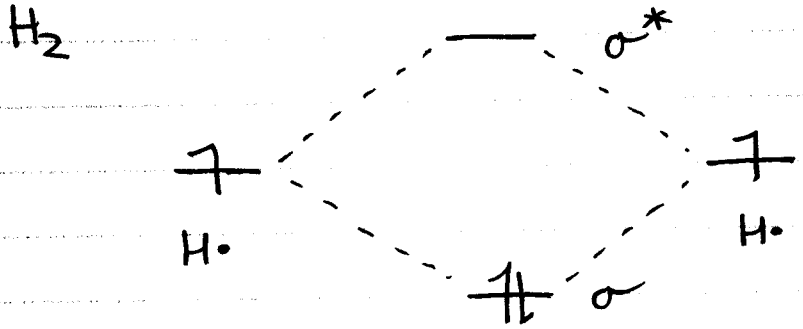
in phase
(constructive)



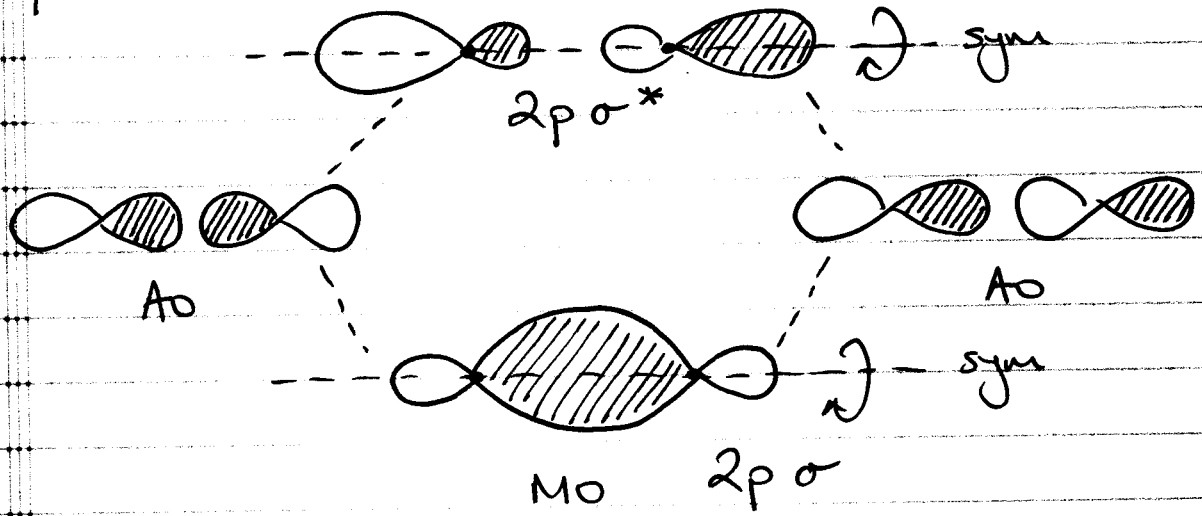
out of phase
(destructive)



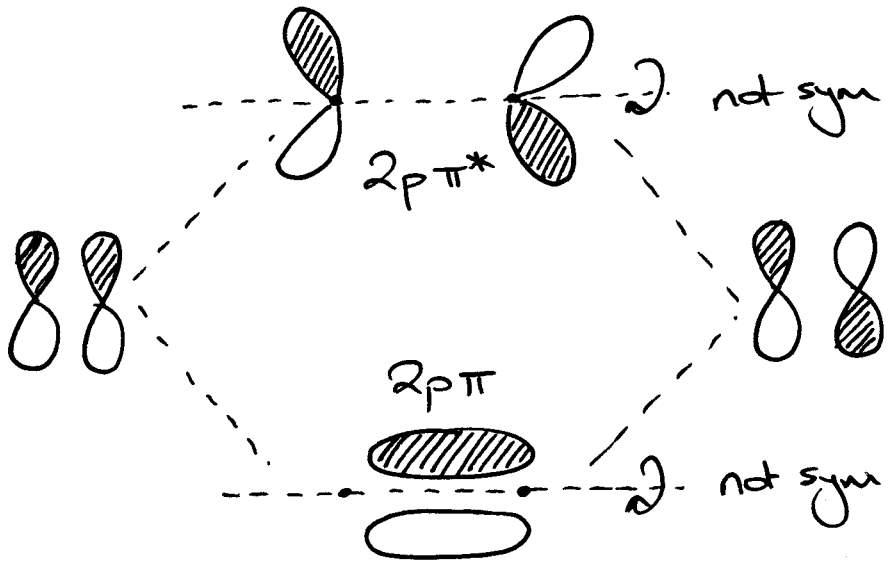
Symmetrical about axis ⇒ σ



p orbitals



p ORBITALS can also overlap side on...

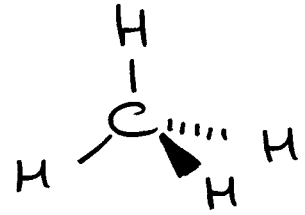


σ BONDS stronger than π BONDS ⇒ More overlap

④ HYBRIDISATION

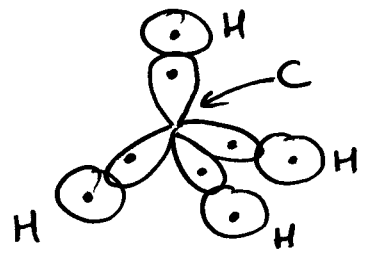
C $1s^2\ 2s^2\ 2p^2$
$1s^2\ 2s^2\ 2p_x^1\ 2p_y^1\ 2p_z^0$

ONLY 2 UNPAIRED e^- AND
p ORBITALS are 90° apart

So, how do we explain  ?

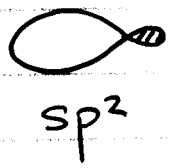
HYBRID ORBITALS (PAULING)

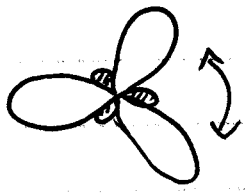
sp^3 (1 x 2s, 3 x 2p) ⇒ 4 sp^3 orbitals

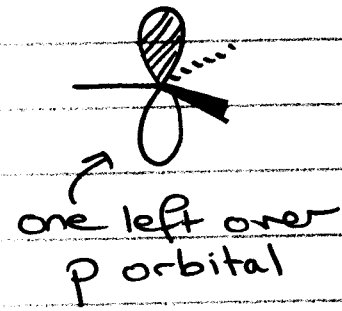


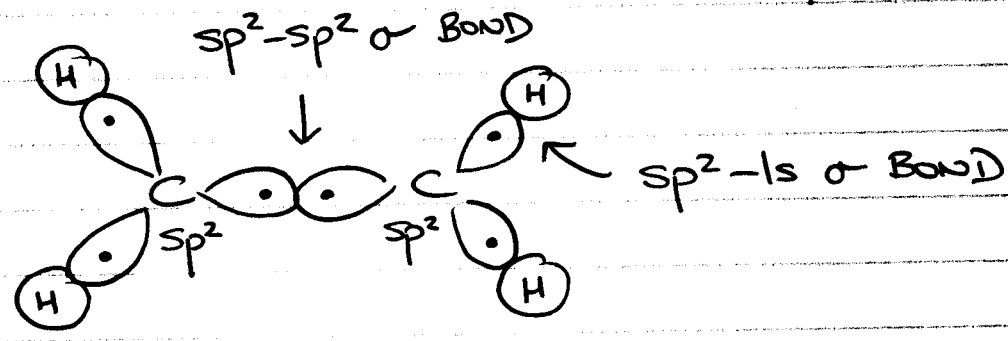
1s - $2sp^3$ σ BONDS

sp^2 $(1 \times 2s, 2 \times 2p) \Rightarrow 3\,sp^2$ orbitals

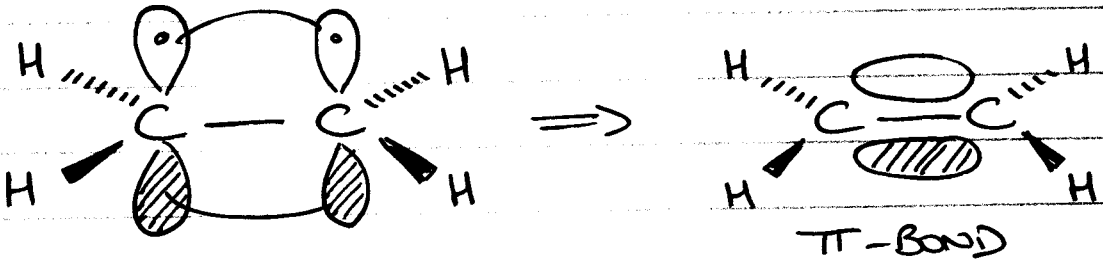




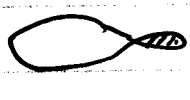


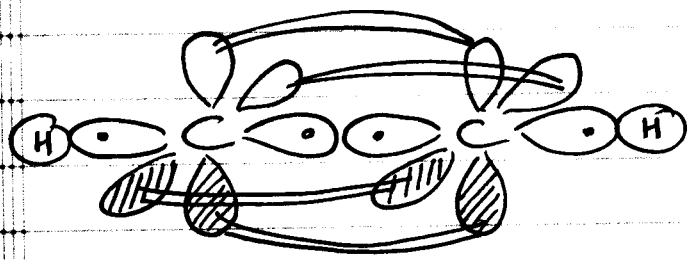


σ BOND FRAMEWORK



sp $(1 \times 2s, 1 \times 2p) \Rightarrow 2\,sp$ orbitals



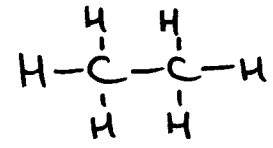


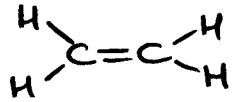
$H-C \equiv C-H$

$1 \times sp\text{-}sp\ \sigma$

$2 \times 2p\text{-}2p\ \pi$

CONSIDER





H–C≡C–H

C–C	C=C	C≡C
1.53 Å	1.34 Å	1.21 Å
88 kcal/mol	146 kcal/mol	200 kcal/mol

not ×2

not ×3

C–H	C–H	C–H
sp^3–1s σ 1.11 Å	sp^2–1s σ 1.10 Å	sp–1s σ 1.09 Å
98 kcal/mol	104 kcal/mol	125 kcal/mol

$\text{Å} = 10^{-10}\ m$

more s character
→ electrons closer to nucleus
→ stronger/shorter bonds

To determine HYBRIDIZATION of an ATOM

ADD # BONDED ATOMS to # LONE PAIRS

4 → sp^3
3 → $3 \times sp^2 + 1 \times p$
2 → $2 \times sp + 2 \times p$

LEC ⑤ CHEM 30A Oct 10th

① HYBRIDISATION
ALKANES
② STRUCTURE
③ ISOMERS
④ NOMENCLATURE

OFFICE HOURS Tues 11-1 pm
READ 2-2.6
PROBLEMS
2.1, 2.2, 2.7, 2.16-2.31

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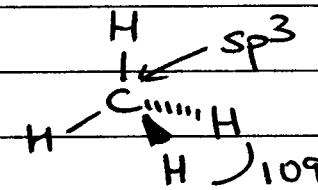
① HYBRIDISATION
pages 7 & 8 of LEC ④

ALKANES
② STRUCTURE

alkanes → saturated hydrocarbons
⇓ each C has max H's
⇓ only C & H

general formula C_nH_{2n+2} (no rings)



METHANE CH_4

CH_3-CH_3 ETHANE C_2H_6

PROPANE C_3H_8

BUTANE C_4H_{10}

PENTANE C_5H_{12}

and so on...
hex, hept, oct, non, dec

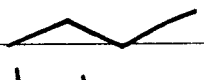
$CH_3(CH_2)_ACH_3$ UNBRANCHED

(3) ISOMERS

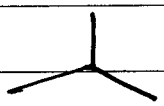
- same molecular formula, different arrangement of atoms => CONSTITUTIONAL ISOMERS

CH_4, C_2H_6, C_3H_8 only one possible arrangement

How about C_4H_{10}



butane



2 methylpropane

Do C_6H_{14} for HMK (5)

(4) NOMENCLATURE

International Union of Pure & Applied Chemistry

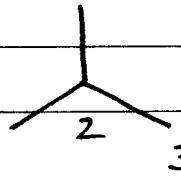
IUPAC => SYSTEMATIC NAMING

- straight chains (done)

- BRANCHED STRUCTURES

(i) identify longest chain

(ii) each substituent gets a name & number

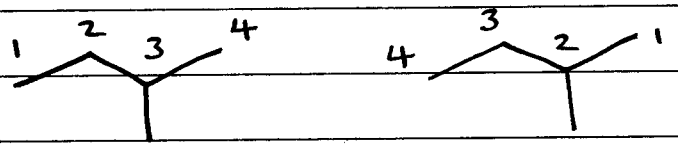


2-METHYL PROPANE

ALKYL GROUPS

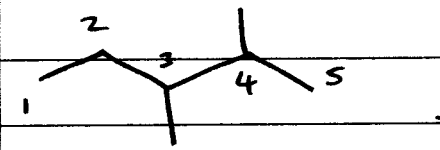
CH_3- methyl
CH_3CH_2- ethyl
$CH_3CH_2CH_2-$ propyl
$CH_3CH_2CH_2CH_2-$ butyl etc, etc

(iii) Minimise substituent number



~~3-methyl~~ butane 2-methyl butane ✓

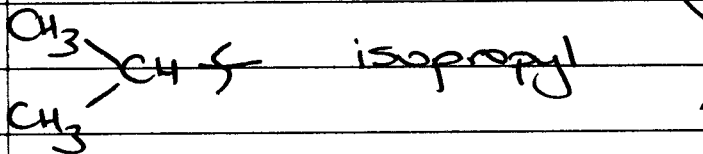
(iv) Same substituent more than once

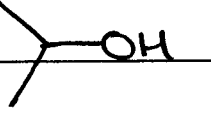


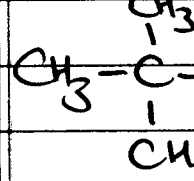
2,3-dimethyl pentane

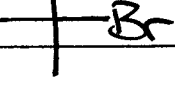
~~-~~ after this, it gets silly!

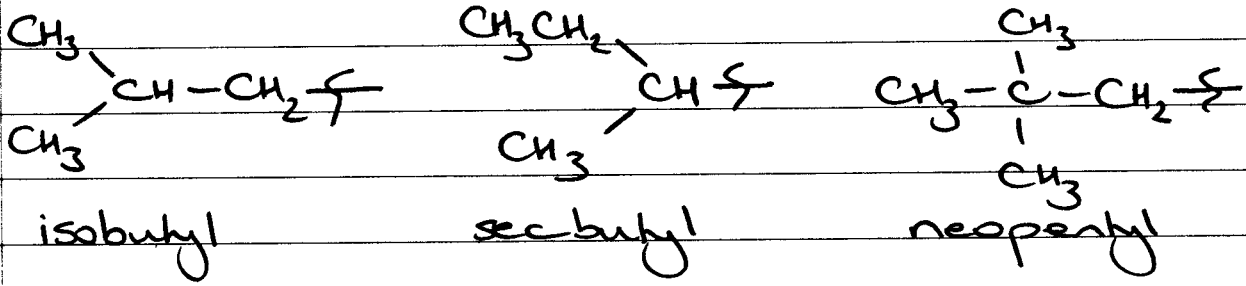
COMMON NAMES



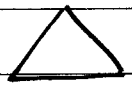
isopropyl  isopropyl alcohol



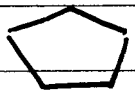
tertiary butyl (tert or t-butyl)  t-butyl bromide

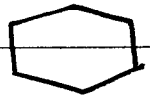


- CYCLOALKANES (C_nH_{2n})

 CYCLOPROPANE C_3H_6

 CYCLOBUTANE C_4H_8

 CYCLOPENTANE C_5H_{10}

 CYCLOHEXANE C_6H_{12}

BICYCLOALKANES — FORGET IT !!

General rules : PREFIX – INFIX – SUFFIX

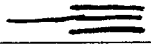
PROP AN E

3Cs single bonds hydrocarbon

PROPENE

-EN-

double bonds



PROPYNE

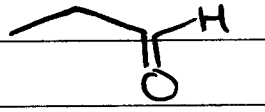
-YN-

triple bonds

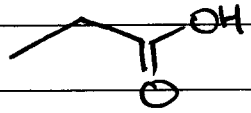
SUFFIXES → FUNCTIONAL GROUPS

-E  PROPANE

-OL  PROPANOL

-AL  PROPANAL

-ONE  PROPANONE

-OIC ACID  PROPANOIC ACID

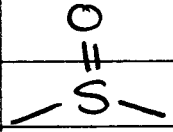
(-AMINE)  PROPYL AMINE
(not PROPANAMINE)

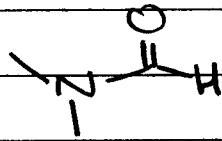
Common names / Structures / Acronyms
(keep a notebook)

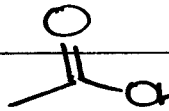

acetone


pyridine

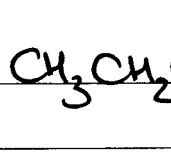
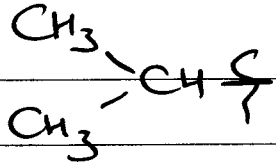

tetrahydrofuran (THF)

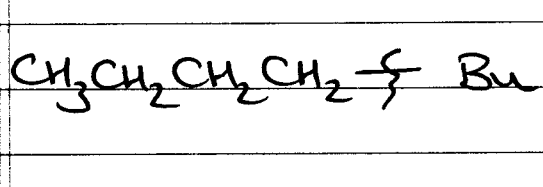

(DMSO)
dimethyl sulfoxide

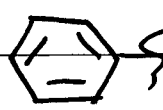

(DMF)
dimethylformamide

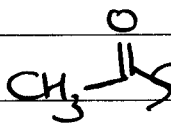
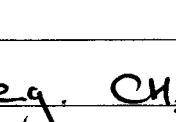

(AcOH)
acetic acid

Other common abbreviations CH_3– Me CH_3CH_2– Et

 Pr  ^{i}Pr

 ^{t}Bu

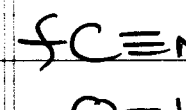
 Ph (PHENYL) e.g.  ≡ PhBr

 Ac (ACETYL) e.g.  ≡ AcCl

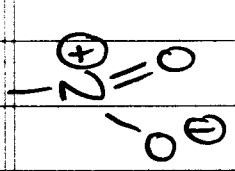
R GROUPS - stuff dangling off the area of interest in a molecule

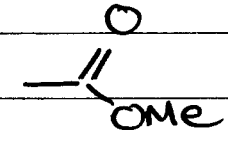
e.g. R–Cl chloride R–OH alcohol R–CO_2H carboxylic acid

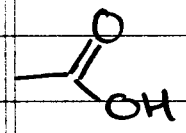
FUNCTIONAL GROUPS

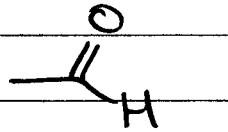
 –CN

 –OH

 $-NO_2$

 $-CO_2Me$

 $-CO_2H$

 –CHO

LEC (6) CHEM 30A Oct 12th

(1) NOMENCLATURE (Common names)
(2) CONFORMATIONAL ANALYSIS

READ 2.6-2.8 PROBLEMS 2.8, 2.32-2.35

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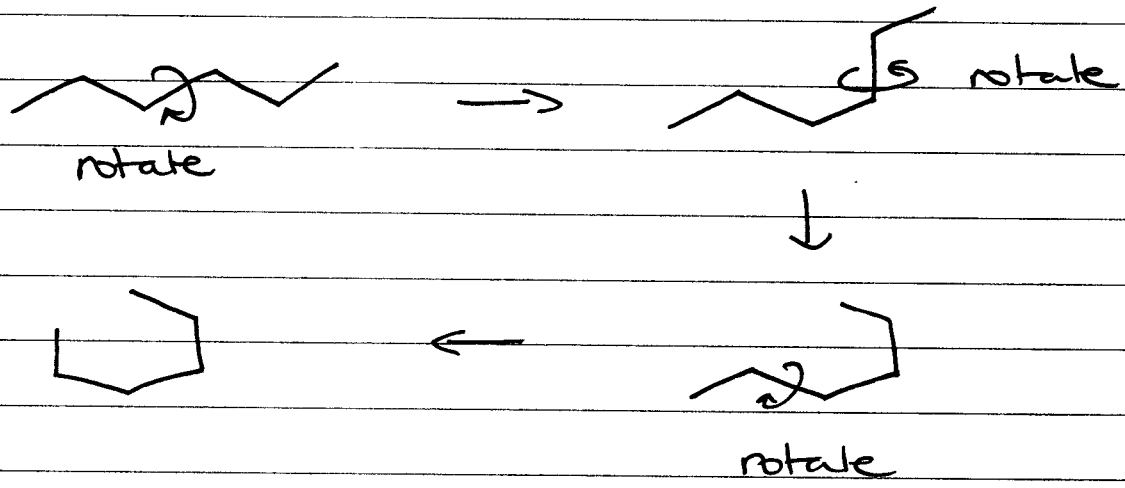
(1) Common NAMES
Pages (5)+(6) from Lec 5

(2) CONFORMATIONAL ANALYSIS

- Consider HEXANE

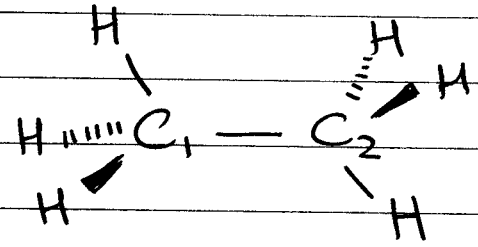


THESE ARE ALL THE SAME MOLECULE...

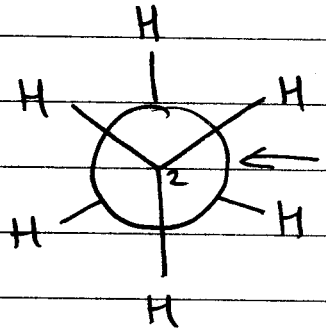
Different arrangements of atoms that result ONLY from single bond rotations are called CONFORMATIONS.

At room temperature, all single bonds are constantly rotating

- consider C_2H_6



← look from here

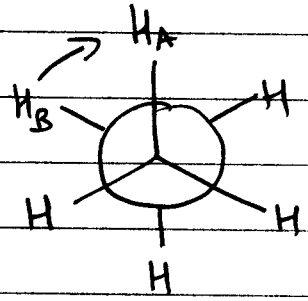


← C_1 is at back

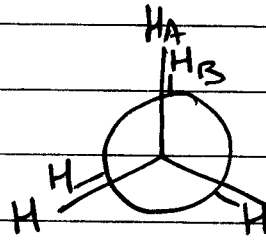
Look down C–C bond => NEWMAN PROJECTION

- TWO METHYL GROUPS CAN ROTATE WRT ONE ANOTHER (0 - 360°)
=> infinite number of conformations

At rt, rate of rotation is ~ 10 BILLION s^{-1}
but ROTATION is not completely UNHINDERED



rotate → 60°

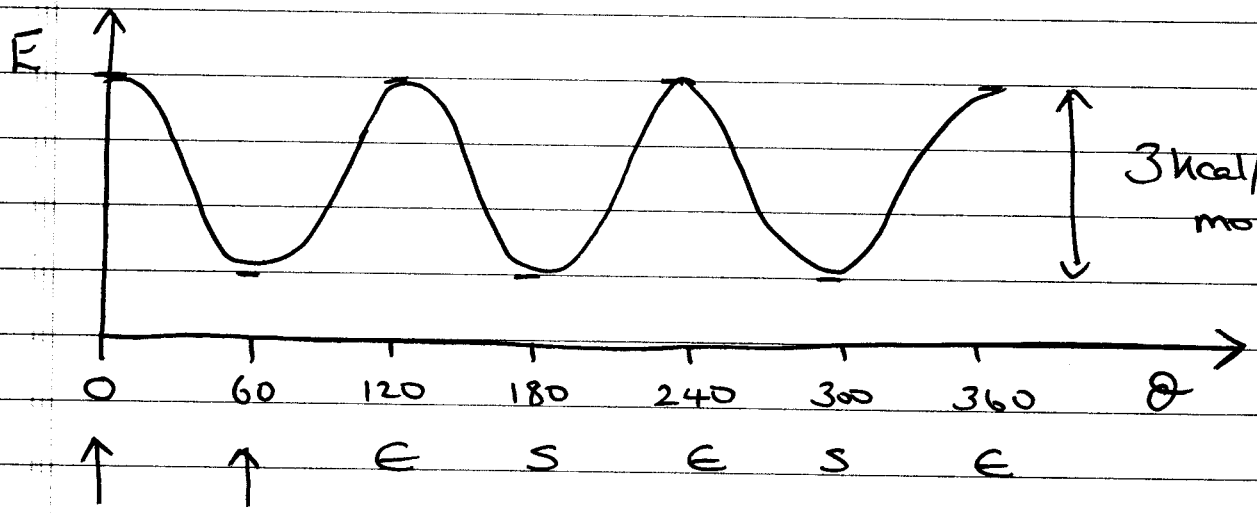


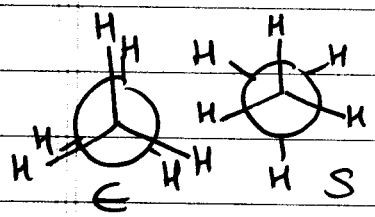
Higher in energy by 3 kcal/mol

STAGGERED ($\theta = 60°$)

ECLIPSED ($\theta = 0°$)

θ (DIHEDRAL ANGLE) – angle between 2 intersecting planes $H_A C_2 C_1$ & $H_B C_1 C_2$

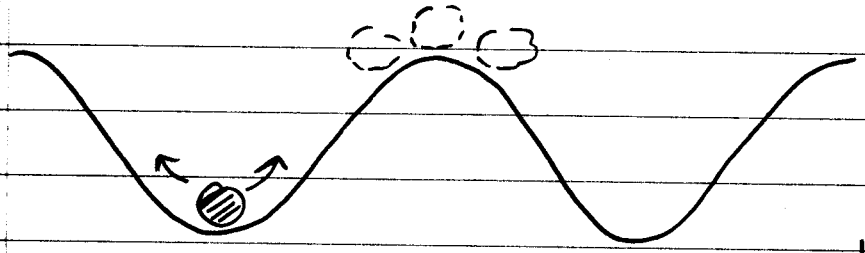




ENERGY BARRIER also REFERRED TO AS TORSIONAL STRAIN

Any given molecule will spend most of its time in a staggered or nearly staggered conformation (LOWEST ENERGY) and will only briefly pass through the eclipsed conformation on its way to the next staggered conformation.

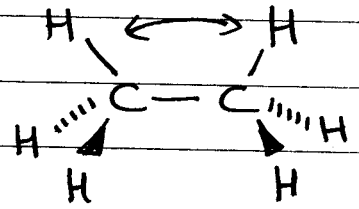
EQUILIBRIUM



enough energy and it will pass over the barrier, but won't spend a lot of time here.

WHY IS THERE A BARRIER?

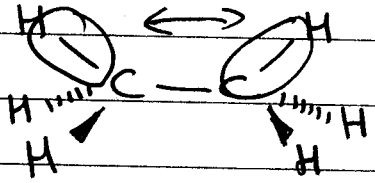
(i) STERIC INTERACTION?



BUT H ATOMS are VERY SMALL

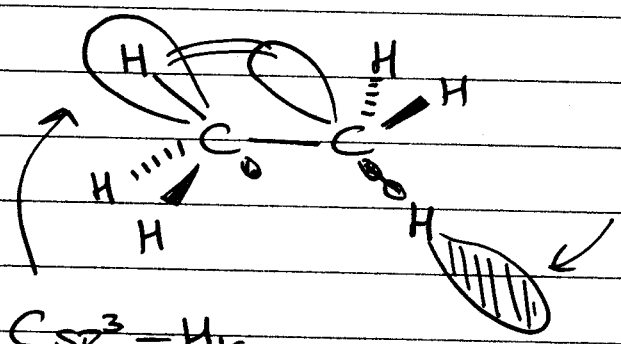
sterics account for ~10% of BARRIER

(ii) ELECTRON PAIR REPULSION



BIGGEST FACTOR

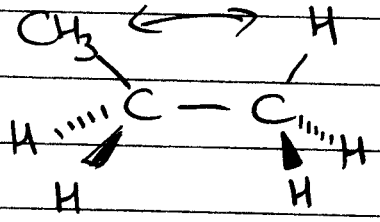
(iii) ATTRACTIVE INTERACTIONS



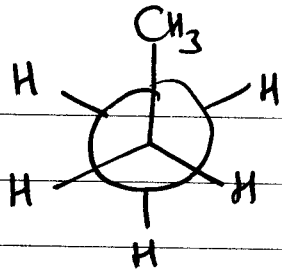
$Csp^3 - H_{1s}$ σ^* empty antibonding orbital

$Csp^3 - H_{1s}$ σ filled bonding orbital

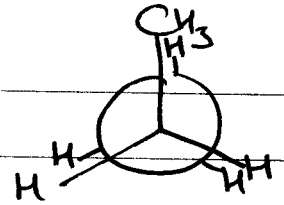
CONFORMATIONS OF PROPANE?



Bigger repulsive interaction than C–H/C–H



rotate ↻

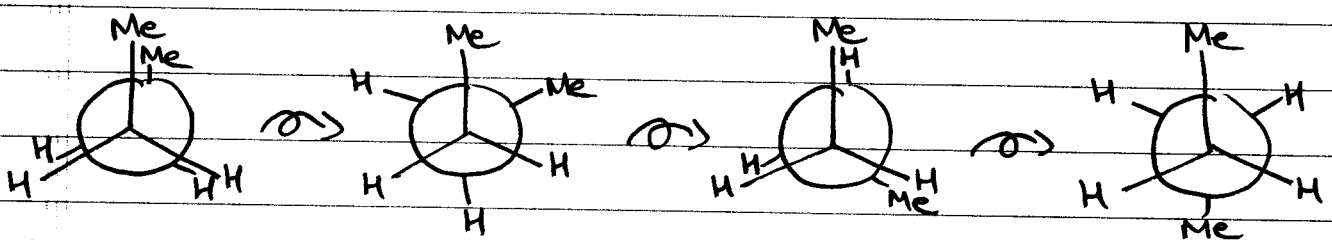


Same profile as ETHANE, but higher barrier (3.4 kcal/mol)

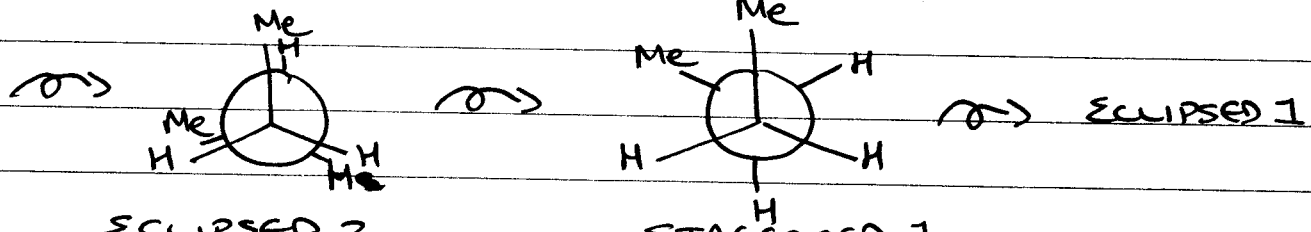
Staggered

Eclipsed

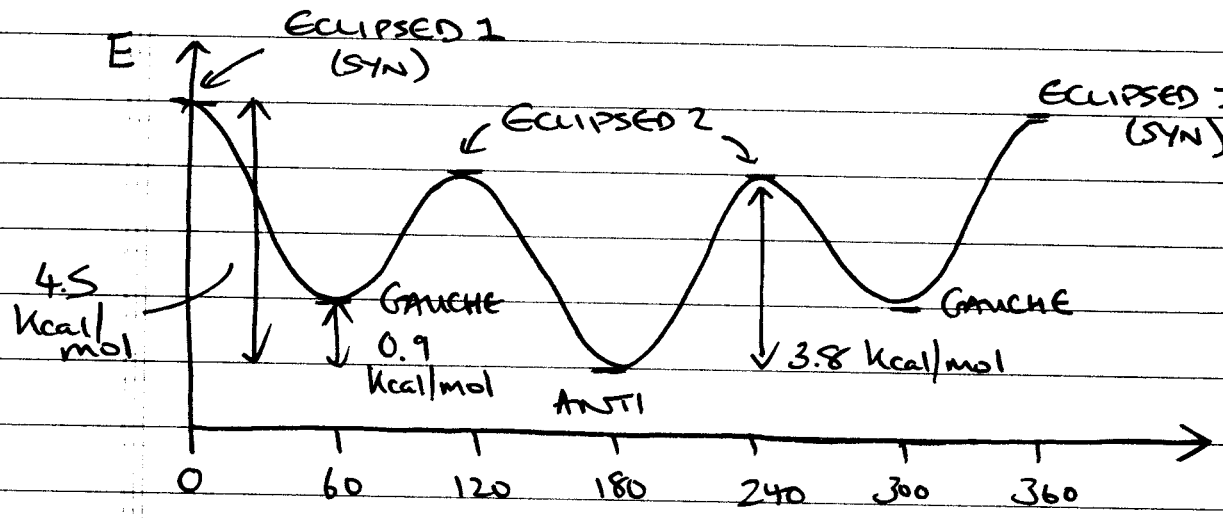
– CONFORMATIONS OF BUTANE



ECLIPSED 1 → STAGGERED 1 (GAUCHE) → ECLIPSED 2 → STAGGERED 2 (ANTI)

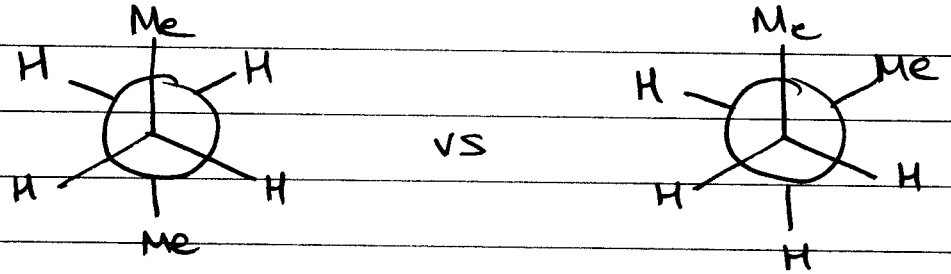


→ ECLIPSED 2 (mirror image of E1) → STAGGERED 1 (GAUCHE) (mirror image of other one) → ECLIPSED 1



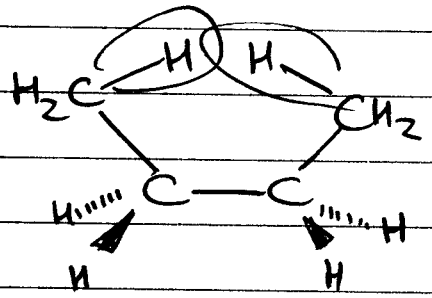
Each ECLIPSED conformer is a MINIMA
Each STAGGERED conformer is a MAXIMA

BUT different MINIMA/MAXIMA energies



ANTI (180°) GAUCHE (60°)

Neither is ECLIPSED, but ANTI is more stable than GAUCHE - difference in energy due to STERIC STRAIN



forcing atoms closer together than atomic radii will allow

At room temp, BUTANE is rapidly equilibrating between CONFORMERS

~80:20 anti/gauche

LEC (7) CHEM 30A Oct 14th

(1) CONFORMATIONAL ANALYSIS
(2) CYCLOALKANES

Read: rest of Ch2 Problems 2.9-2.11, 2.36, 2.37
Quiz low 0, high 36, mean 14

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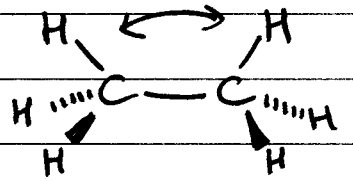
(1) CONFORMATIONAL ANALYSIS

- ETHANE, why is there a barrier to rotation (TORSIONAL STRAIN)

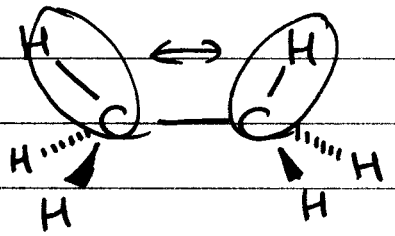
(i) STERIC INTERACTION? (STERIC => forcing atoms closer than atomic radii allow)



BUT H, very small

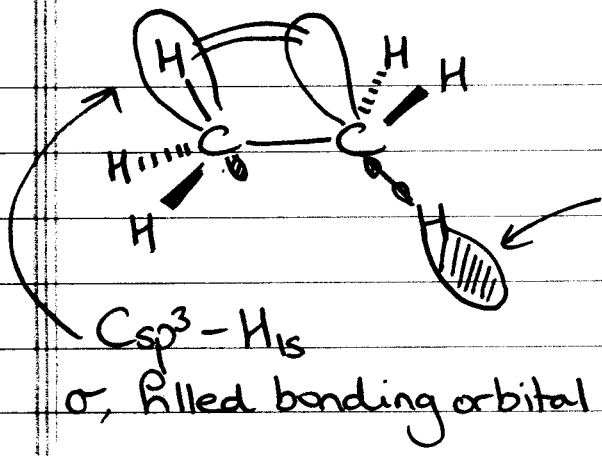
sterics account for ~10% of BARRIER

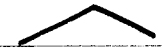
(ii) ELECTRON PAIR REPULSION

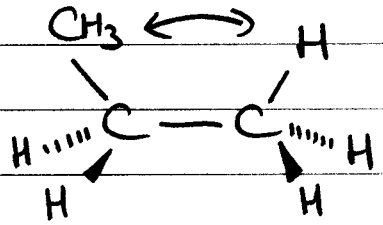


BIGGEST FACTOR

(iii) ATTRACTIVE INTERACTION

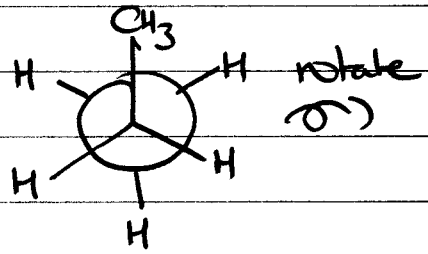


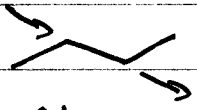
- PROPANE 

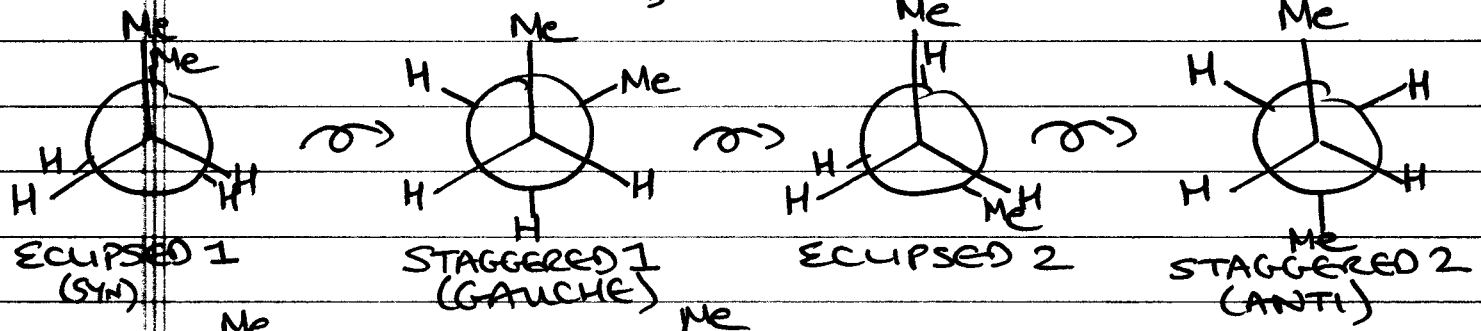


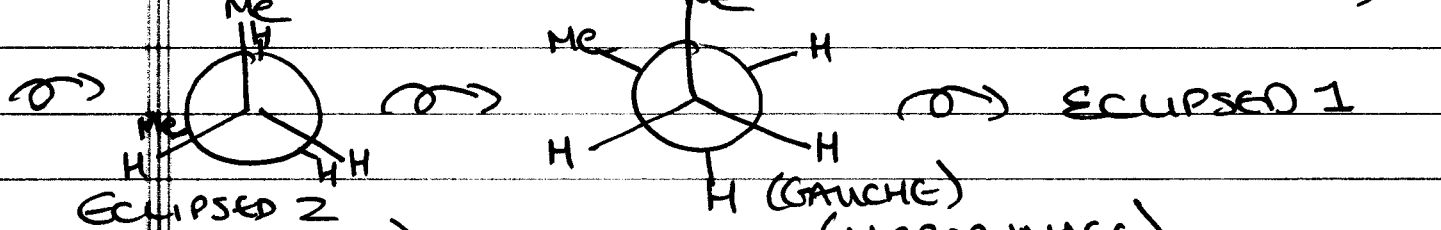
Bigger repulsive interaction than C–H/C–H

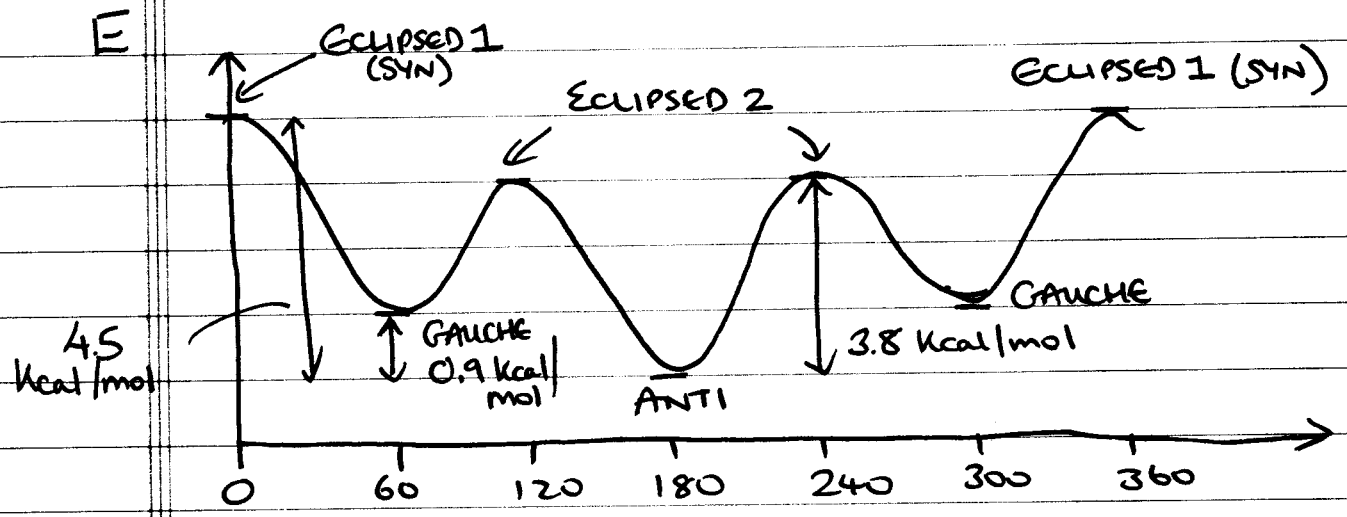
Same profile as ETHANE, but higher barrier (3.4 kcal/mol)



- BUTANE 

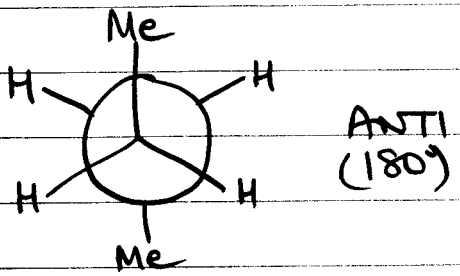




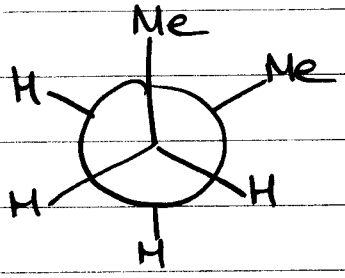


EACH ECLIPSED CONFORMER → MAXIMA
EACH STAGGERED CONFORMER → MINIMA

BUT DIFFERENT MAXIMA/MINIMA ENERGIES

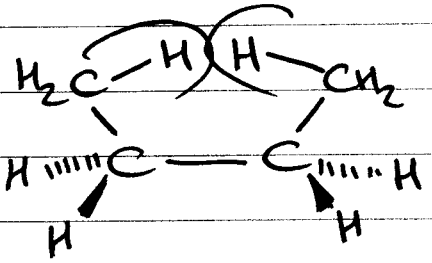


ANTI (180°)



GAUCHE (60°)

Neither is ECLIPSED, but ANTI more stable than GAUCHE – difference is due to STERIC STRAIN

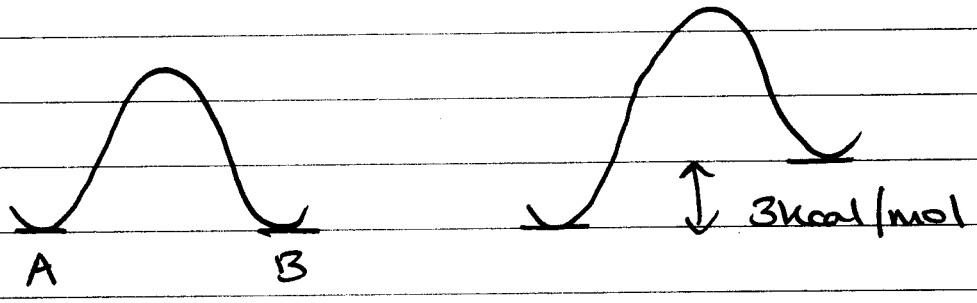


← STERIC STRAIN – forcing atoms closer together than atomic radii will allow

AT RT, butane is an 80:20 MIXTURE (anti/gauche) of rapidly equilibrating CONFORMERS

Note: very small differences in energy result in very different ratios of conformational isomers.

At room temperature:



50:50 99:1

$K \leftarrow$ equilibrium constant

$A \rightleftharpoons B$

↑ equilibrium arrows

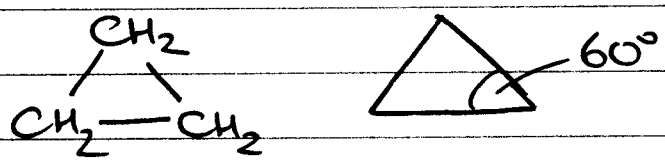
$$K = \frac{[B]}{[A]}$$

$\Delta G^{\circ} = -RT \ln K$

↑ difference in free energy

(2) CYCLOALKANES

(i) CYCLOPROPANE

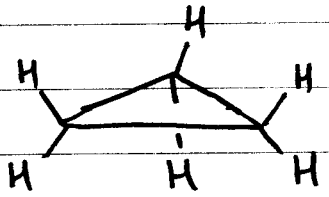


60° very different to 109.5° (sp^3 tetrahedral)

$\Longrightarrow$ ANGLE STRAIN

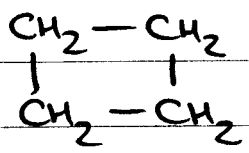
Total ring strain ~ 28 kcal/mol

- most of this is angle strain, but also ALL C—H bonds are eclipsed
  ⇒ TORSIONAL STRAIN

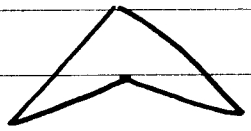


ALL ECLIPSED

(ii) CYCLOBUTANE



If PLANAR, all C-Hs would be ECLIPSED, so ring puckers to AVOID TORSIONAL STRAIN

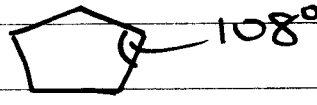


C-C-C angles ~88°
(worse than 90°, more angle strain)

Total ring strain is ~26 kcal/mol

IN ALL CYCLOALKANES LARGER THAN CYCLOPROPANE, NON-PLANAR CONFORMATIONS ARE FAVORED

(iii) CYCLOPENTANE



If it were PLANAR 108° ≃ 109.5°, there would be little angle strain.

BUT all C–H bonds would be ECLIPSED
⇒ TORSIONAL STRAIN

ENVELOPE CONFORMATION (105° ANGLES)

⇒ REDUCES TORSIONAL STRAIN

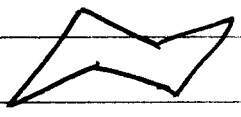
4Cs in PLANE, 1C OUT (EQUILIBRIUM)

Total ring strain ~7 kcal/mol

(iv) CYCLOHEXANE

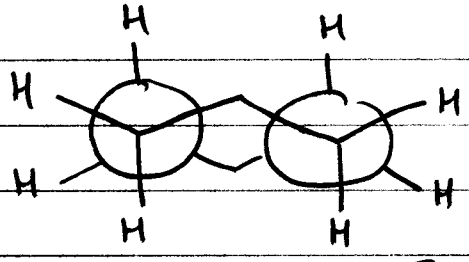
PLANAR STRUCTURE
⇒ angle & torsional strain

BUT cyclohexane is virtually STRAIN FREE



CHAIR CONFORMATION

C–C–C angles ~ 109.5°
no angle strain

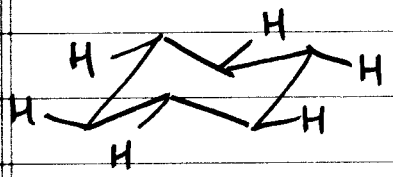


NO TORSIONAL STRAIN,
Hs are STAGGERED

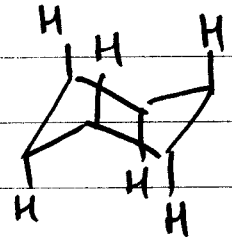
← NEWMAN PROJECTION

– ALSO, NO STERIC STRAIN

Two different orientations for C–H bonds

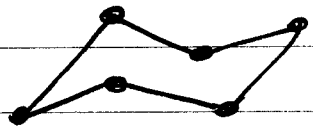


EQUATORIAL

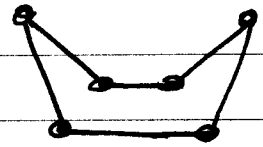


AXIAL

- other conformations

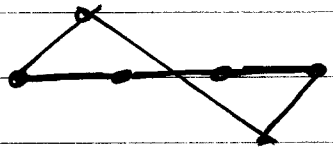


CHAIR

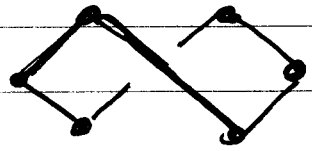


BOAT

⇐ KNOW THESE TWO



HALF-CHAIR



TWIST BOAT

LEC (8) CHEM 30A Oct 17th

READ
2.9, 2.10, 3.1, 3.2

PROBLEMS
2.12 - 2.15,
2.38 - 2.61

+ web worksheets

(1) CYCLOHEXANE
(2) PROPERTIES of ALKANES
(3) REACTIONS / SOURCES / IMPORTANCE
(4) STEREOCHEMISTRY

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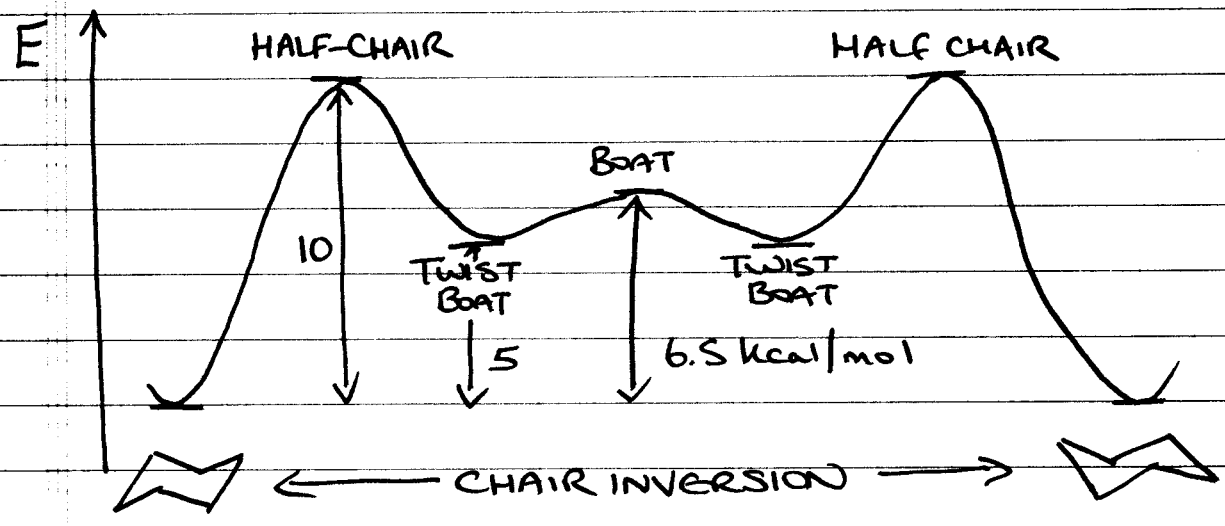
(1) CYCLOHEXANE

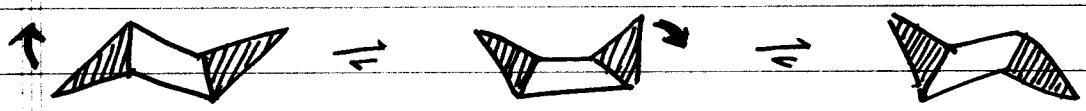
- conformations

CHAIR BOAT TWIST CHAIR TWIST BOAT

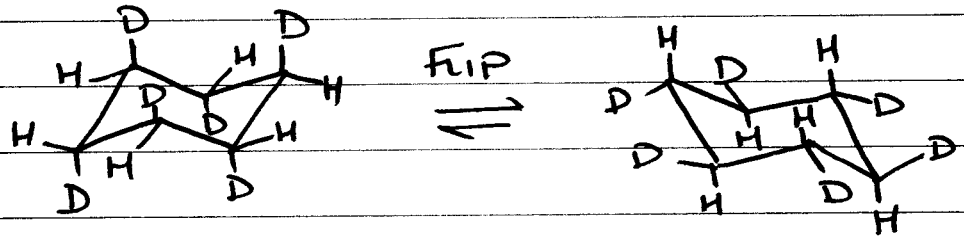


AT RT, CHAIR > 99.99% of EQUILIBRIUM MIXTURE

CHAIR FLIP



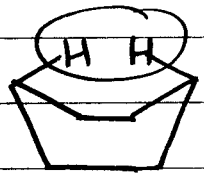
SWITCHES AXIAL & EQUATORIAL POSITIONS



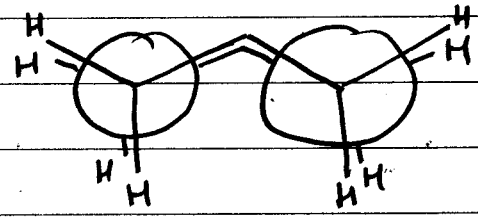
D AXIAL
H EQUATORIAL

H AXIAL
D EQUATORIAL

A CLOSER LOOK AT THE BOAT CONFORMATION



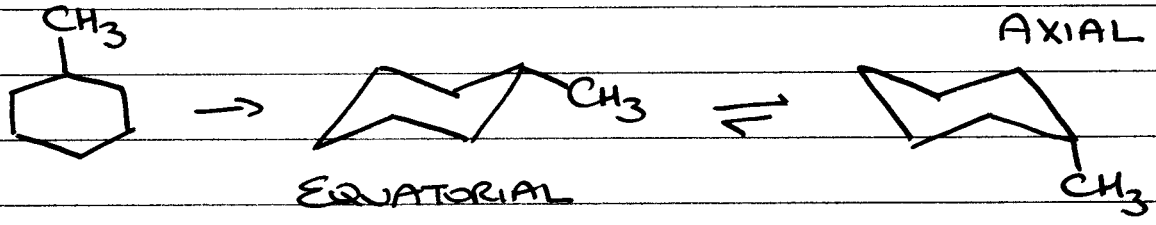
NONBONDED (STERIC) INTERACTIONS



ECLIPSED C—Hs too!

- SUBSTITUTED CYCLOHEXANES

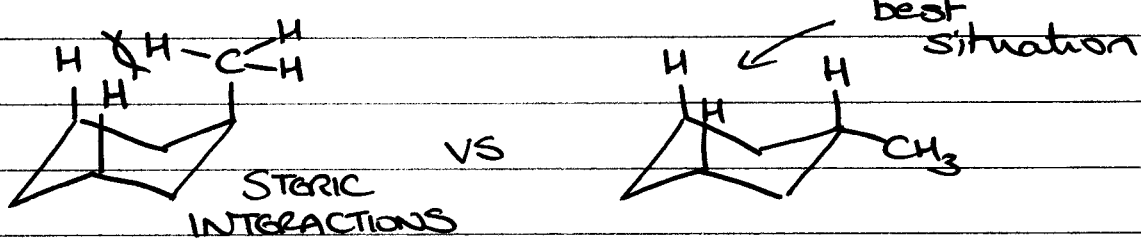
Consider methylcyclohexane



EQUATORIAL

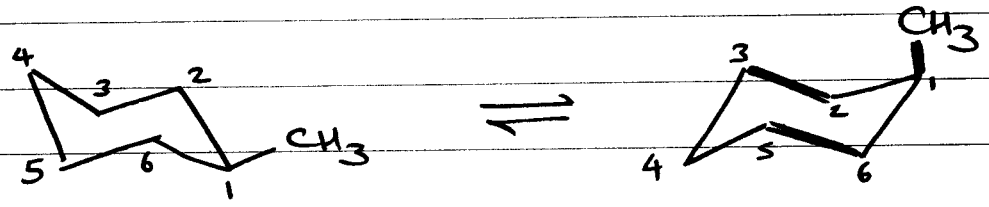
Which is more stable?

(i) 1,3 - DIAXIAL INTERACTIONS

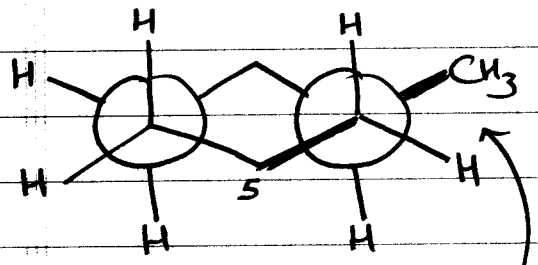


STERIC INTERACTIONS

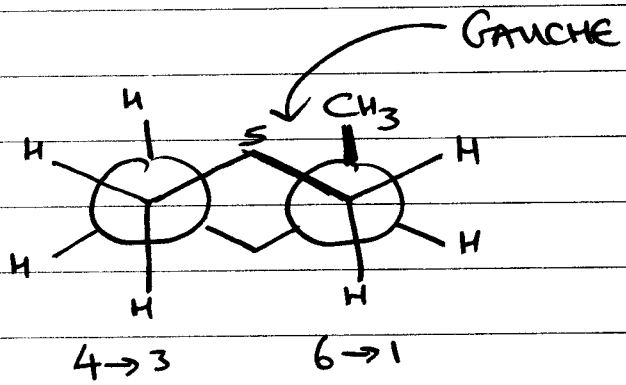
(ii) GAUCHE INTERACTIONS



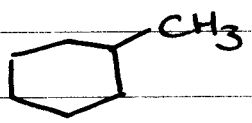
(mention naming)



ANTI PERIPLANAR

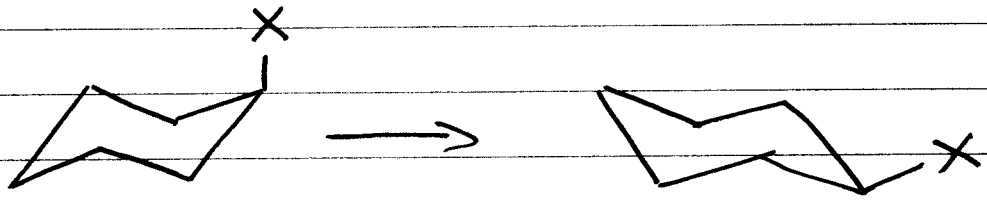


In general, conformer in which largest substituent is equatorial will be the most stable.

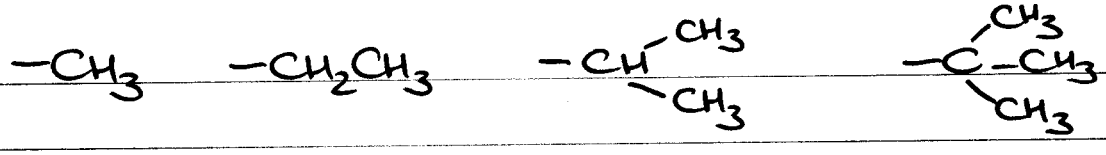
FOR 

CH_3– equatorial conformer more stable by 1.74 kcal/mol

A VALUES → measure of thermodynamic preference for equatorial position.

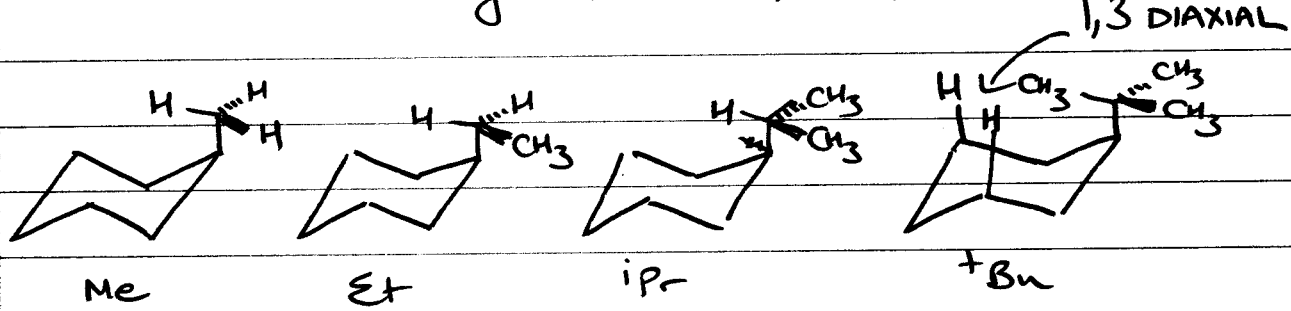


NEGATIVE of ΔG change for AXIAL → EQUATORIAL, so A values are usually positive



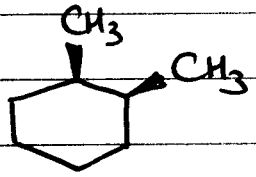
$-CH_3$	$-CH_2CH_3$	$-CH(CH_3)_2$	$-C(CH_3)_3$
1.74	1.75	2.15	>5

note small changes for Me, Et, iPr

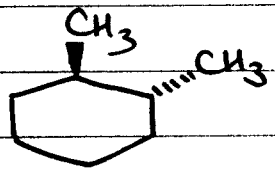


tBu ⇒ LOCKING GROUP
overwhelming pref for equatorial position

- DISUBSTITUTED CYCLOHEXANES



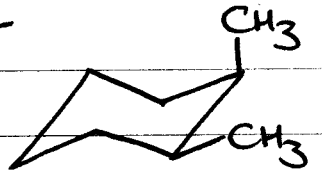
same side <u>cis</u>
cis-1,2-dimethylcyclohexane



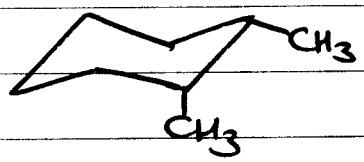
opposite side <u>trans</u>
trans-1,2-dimethylcyclohexane

<u>NOTE</u>: when converting to CHAIR form 1 & 2 have nothing to do with AXIAL/EQUATORIAL or UP/DOWN

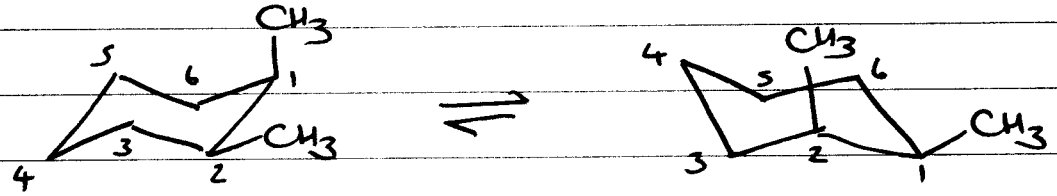
cis



same as



RING-FLIP

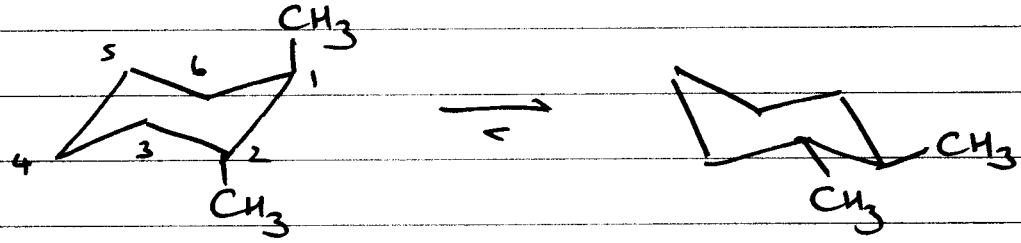


What is ΔG for this equilibrium?

C1 ax CH_3 → eq CH_3 −1.74
C2 eq CH_3 → ax CH_3 +1.74
0 kcal/mol

So, 50:50 mixture.

trans



What is ΔG for this equilibrium?

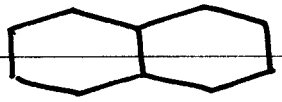
C1 ax CH_3 → eq CH_3 −1.74
C2 ax CH_3 → eq CH_3 −1.74
−3.5 kcal/mol
(actually −2.6 kcal/mol)

(A values generally ADDITIVE)

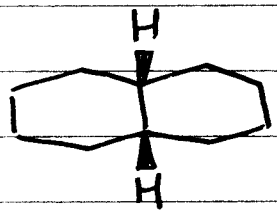
So, conformer with two equatorial methyls is favored.

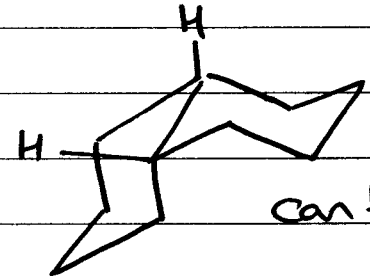
Do same for 1,3- and 1,4- cis & trans dimethylcyclohexanes

- DECALINS

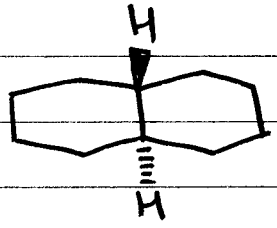


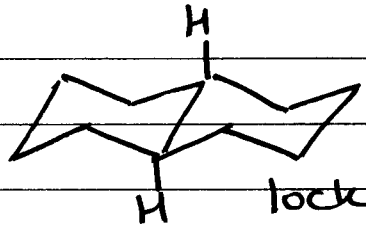
cis-decalin





trans-decalin





(2) PROPERTIES OF ALKANES

as MW increases, mp & bp increases

INTERMOLECULAR INTERACTIONS

- ionic
- hydrogen bonding
- dipole-dipole
- dipole-induced dipole
- induced dipole-induced dipole

↓ decreasing strength

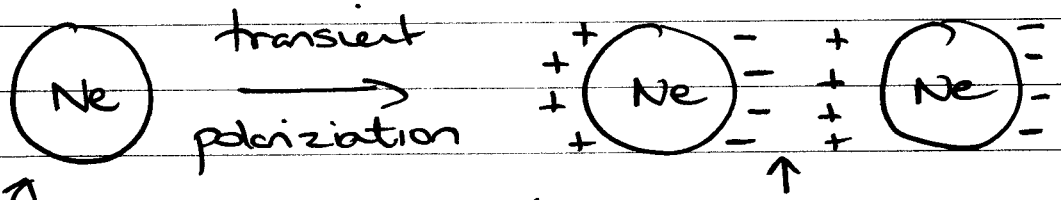
also called DISPERSION / LONDON forces

↓

reason why low MW non-polar substances can be liquified.

He 4K , Ne 27K

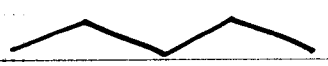
Bigger e⁻ clouds, stronger forces



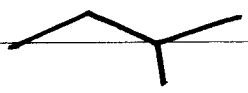
↑ symmetrical e⁻ density distribution

↑ temporary electrostatic interaction

consider:



bp 36°C



28°C

10°C

constitutional isomers

↓

more branching

↓

more compact shape

↓

less surface area

↓

less molecule / molecule contact

(3) Reactions / Sources / Importance

↳ read sections 2.9, 2.10
(and look over associated questions)

(4) STEREOCHEMISTRY

next time....

LEC (9) CHEM 30A Oct 19th

(1) CYCLOHEXANES READ 3-3.5
(2) PROPERTIES OF ALKANES
(3) REACTIONS / SOURCES / IMPORTANCE
— CH_3
(4) STEREOCHEMISTRY
(5) CHIRALITY / CHIRAL CENTERS

---

(1)-(3) Lec 8 notes

(4) STEREOCHEMISTRY

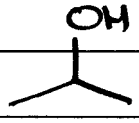
ISOMERS - different compounds with the same molecular formula.

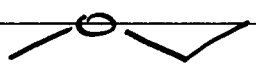
CONSTITUTIONAL ISOMERS or STEREOISOMERS (configurational isomers)

⇓ ⇓

Different connectivity

e.g. 





Same connectivity of atoms, BUT different geometries in 3D space

⇓

more categories

STEREOISOMERS → ENANTIOMERS (non superimposable mirror images)

↓

DIASTEREOISOMERS (non mirror image stereoisomers) → Configurational diastereoisomers

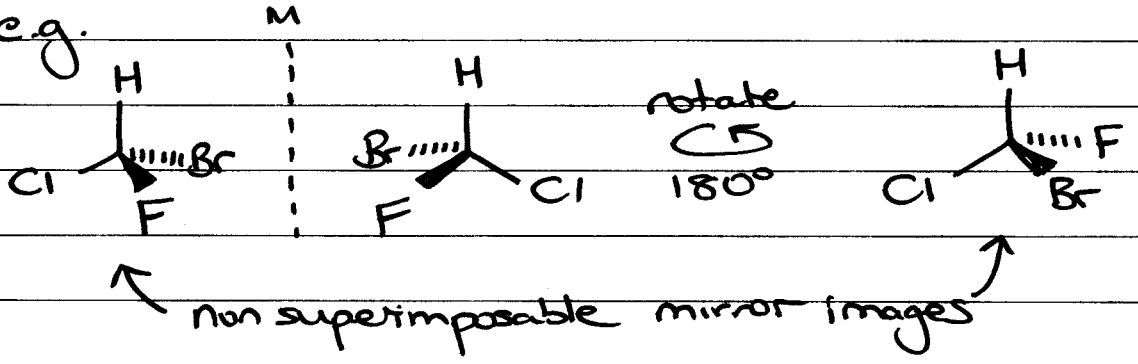
→ cis/trans diastereoisomers

A MAJOR part of STEREOCHEMISTRY is being able to recognise mirror images.

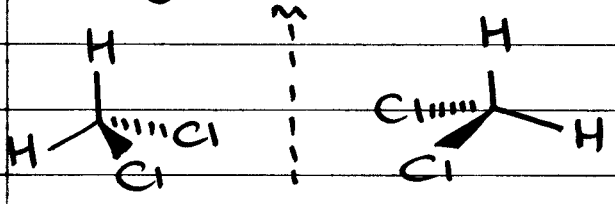
(5) CHIRALITY

An object (molecule) that is NOT superimposable on its mirror image is said to be CHIRAL (Greek 'cheir')

e.g.



So each of these molecules is CHIRAL, and they are ENANTIOMERS

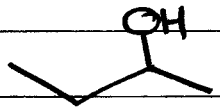


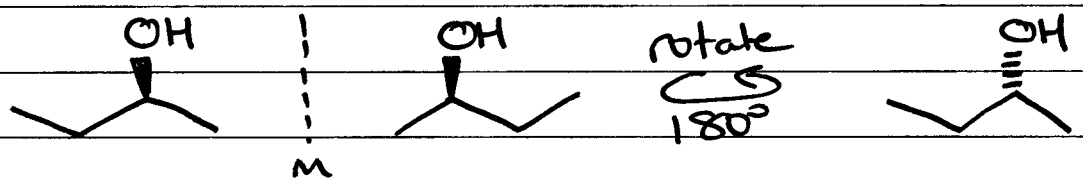
if an object (molecule) is not CHIRAL, it is ACHIRAL

One of the most common causes of chirality in organic molecules is a TETRAHEDRAL ATOM (usually C) bonded to four different groups

* THIS DOES NOT DEFINE "CHIRAL"

consider:





ENANTIOMERS COME IN PAIRS

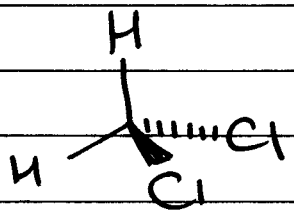
- Identifying CHIRAL objects

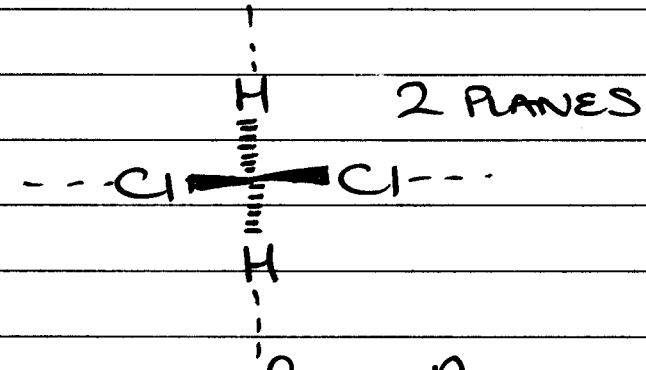
If a molecule can be drawn with:
(i) a PLANE OF SYMMETRY or
(ii) an INVERSION CENTER

it is ACHIRAL

e.g.

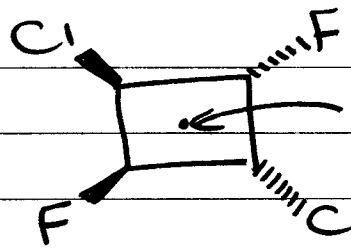
(i)





you will see this more often than:

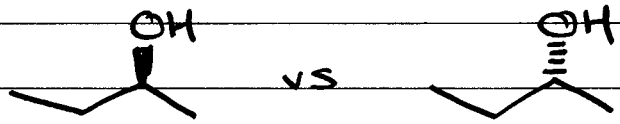
(ii)



center of inversion (NO PLANE)

centre of inversion => identical groups lie equidistant of a point, on opposite sides of that point.

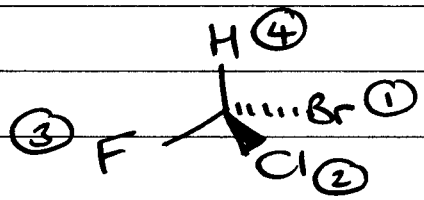
- DISTINGUISHING ENANTIOMERS



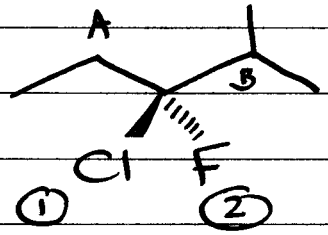
? R,S designation

- assign prority to 4 groups

(i) ATOMIC WEIGHT



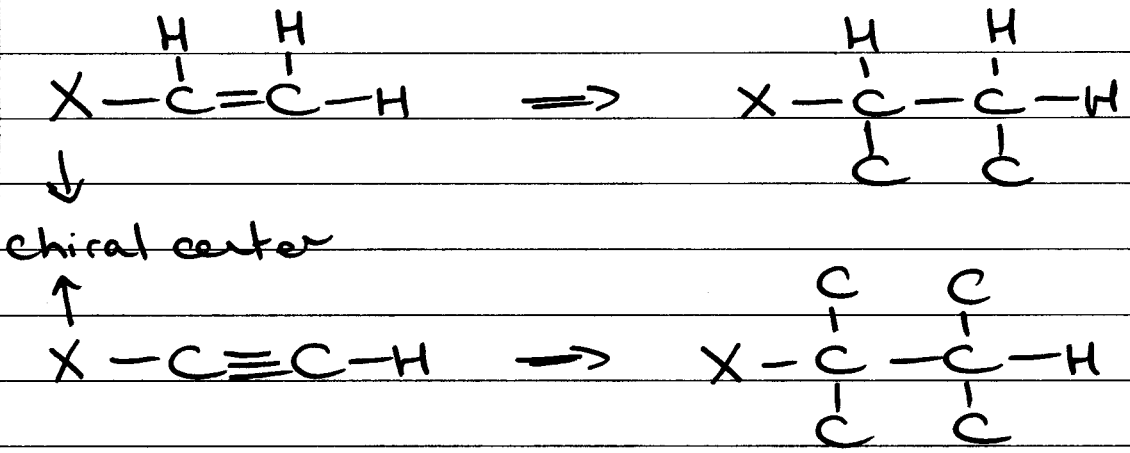
(ii) FIRST POINT of DIFFERENCE



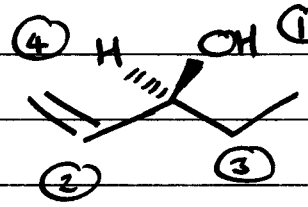
C_A => C, H, H ④

C_B => C, C, H ③

(iii) MULTIPLY BONDED ATOMS – count as the equivalent number of singly bonded atoms



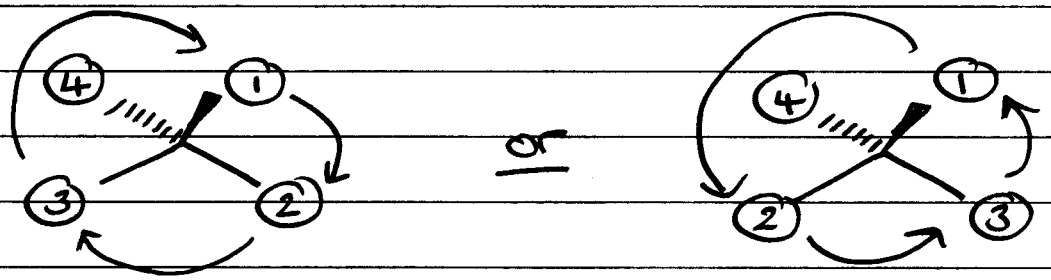
So, consider



use 1, 2, 3, 4 to set R/S

Rotate whole molecule in space to put the lowest priority group in the back =>

TWO POSSIBLE ORIENTATIONS



CLOCKWISE (R) COUNTERCLOCKWISE (S)

LEC (10) CHEM 30A Oct 21st

(1) R/S DESIGNATION
(2) FISCHER PROJECTIONS
(3) CIS/TRANS DIASTEREOISOMERS + WEB PROBLEMS

READ 3.4-3.5, PROBLEMS 3.1-3.8, 3.14-3.33
MIDTERM, WEDS, A-J CS76, K-Z CS5Φ
- ID, MODEL KITS etc

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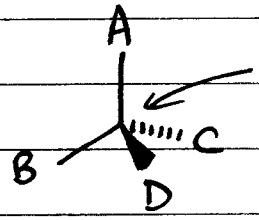
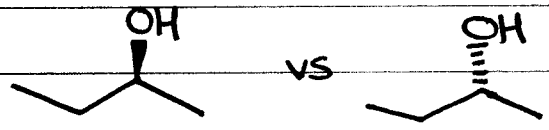
(1) R/S DESIGNATION



chiral center
stereocenter
stereogenic center

Tetrahedral atom
4 Different groups

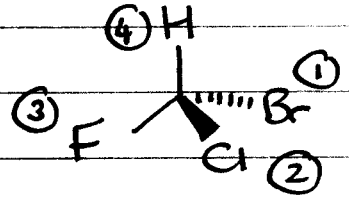
- DISTINGUISHING ENANTIOMERS



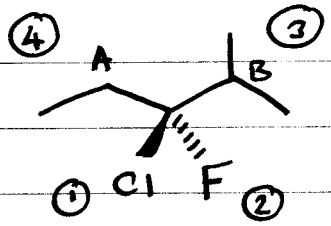
? R/S

- assign priority

(i) ATOMIC WEIGHT of atoms on STEREOCENTER



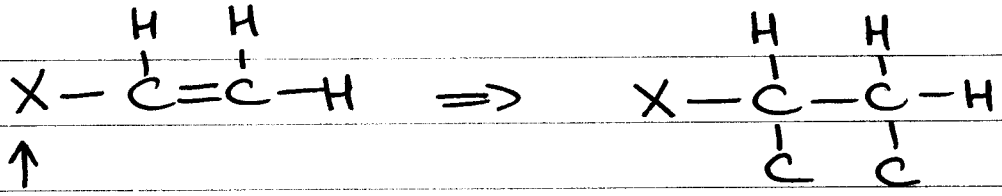
(ii) FIRST POINT of DIFFERENCE



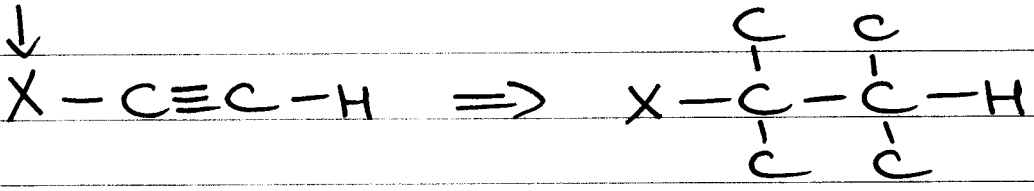
C_A attached to C, H, H ④
C_B attached to C, C, H ③

(HOW MANY CHIRAL CENTERS)

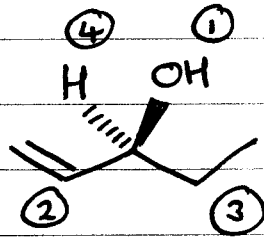
(iii) MULTIPLY BONDED ATOMS - count as the equivalent number of singly bonded atoms



↑
chiral center
↓



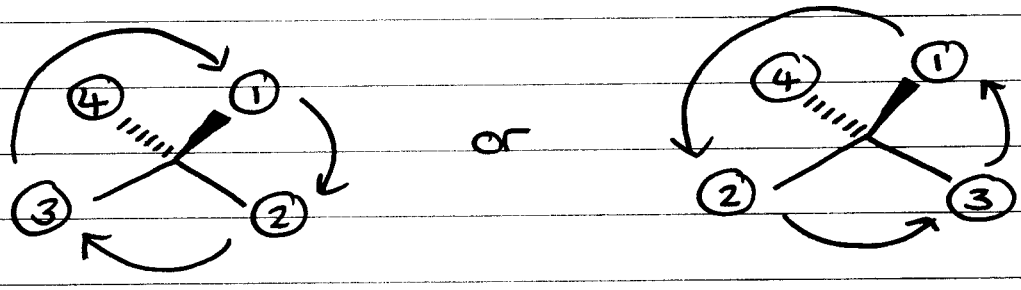
So consider:



use 1, 2, 3, 4 to set R/S

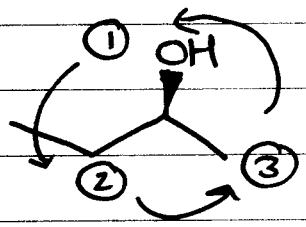
Rotate whole molecule in space to put the lowest priority group ④ in the back.

TWO POSSIBLE ORIENTATIONS

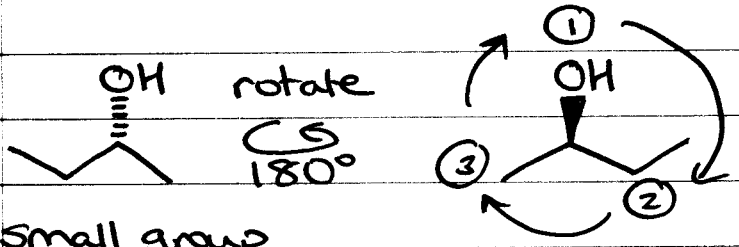


CLOCKWISE (R) COUNTERCLOCKWISE (S)

So,



(S)-2-BUTANOL



(R)-2-BUTANOL

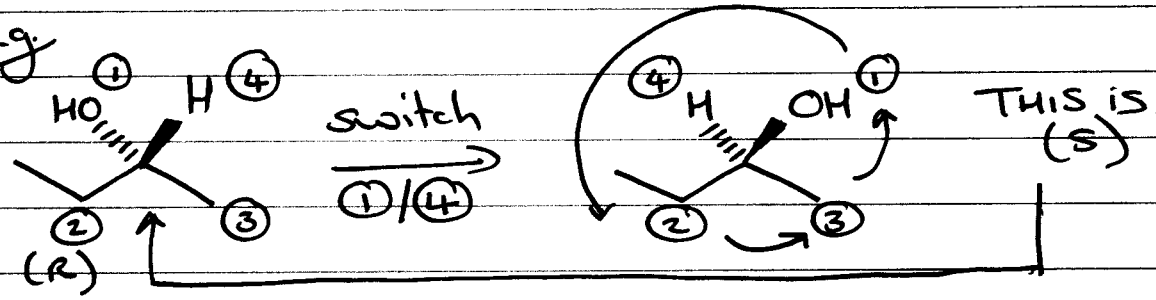
Small group
NOT in the back

or if you have trouble rotating molecules

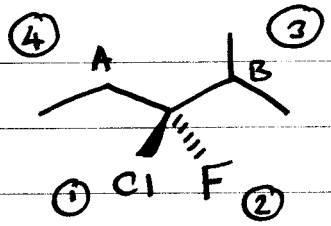
TRICK

- switch lowest priority group (4) with the group that is in the back
- assign R/S, then switch

e.g.



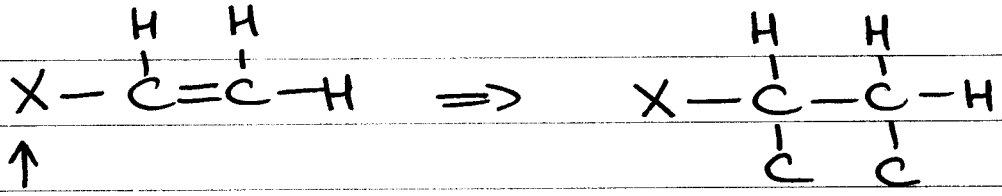
(ii) FIRST POINT of DIFFERENCE



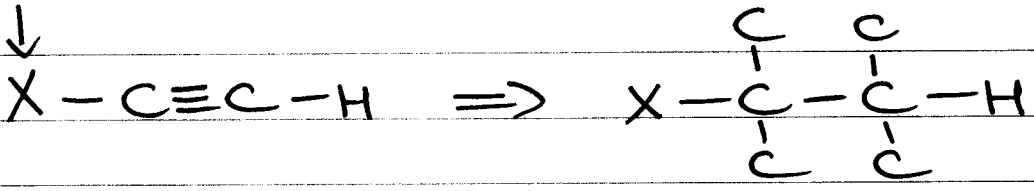
C_A attached to C, H, H ④
C_B attached to C, C, H ③

(HOW MANY CHIRAL CENTERS)

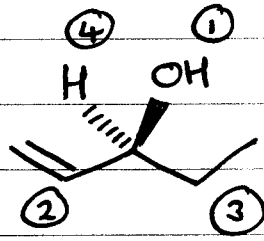
(iii) MULTIPLY BONDED ATOMS - count as the equivalent number of singly bonded atoms



↑
chiral center
↓

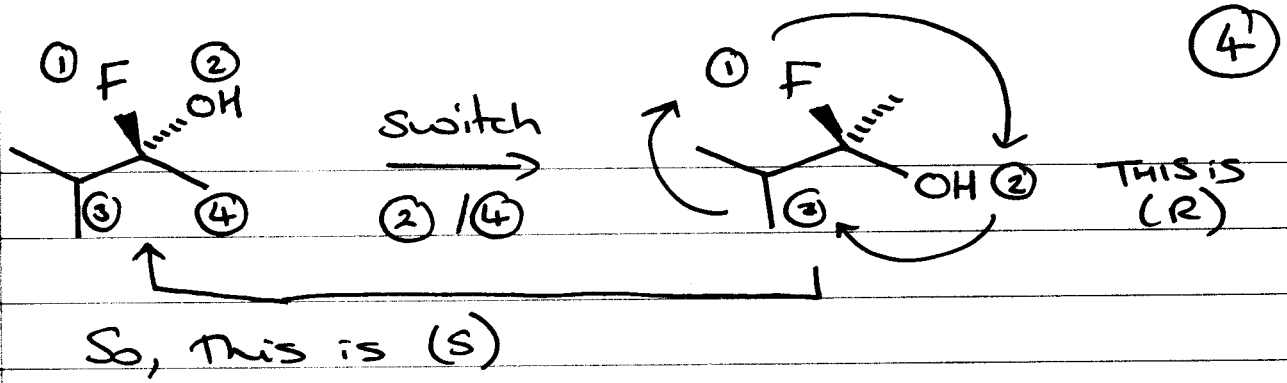


So consider:



use 1, 2, 3, 4 to set R/S

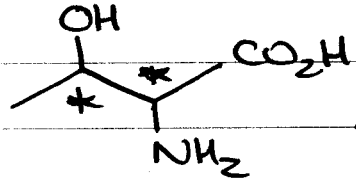
Rotate whole molecule in space to put the lowest priority group ④ in the back.



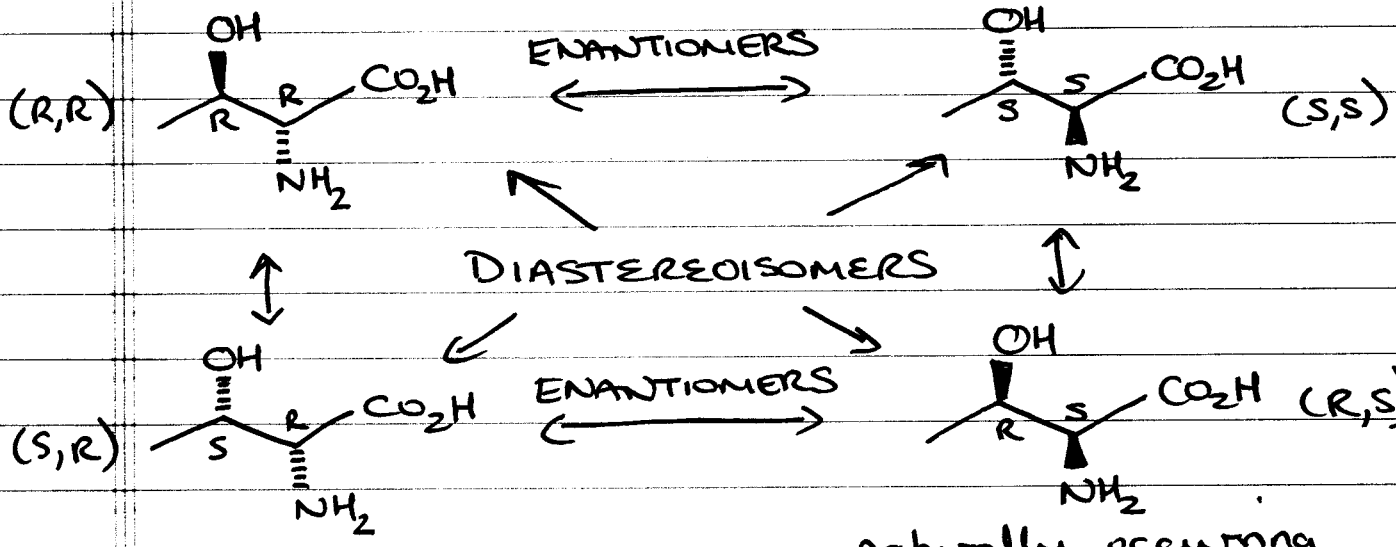
So, this is (S)

- compounds with more than one STEREOCENTER

THREONINE (amino acid)

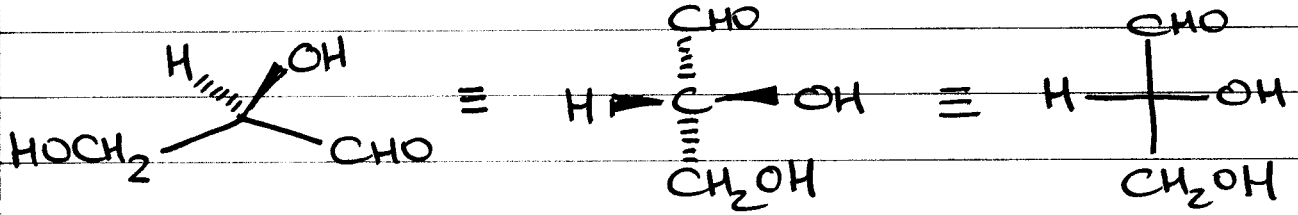


2 chiral centers



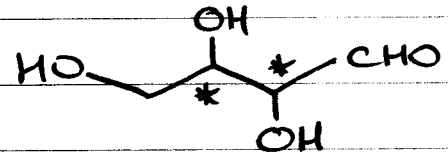
DIASTEREOISOMERS - non mirror image STEREOISOMERS

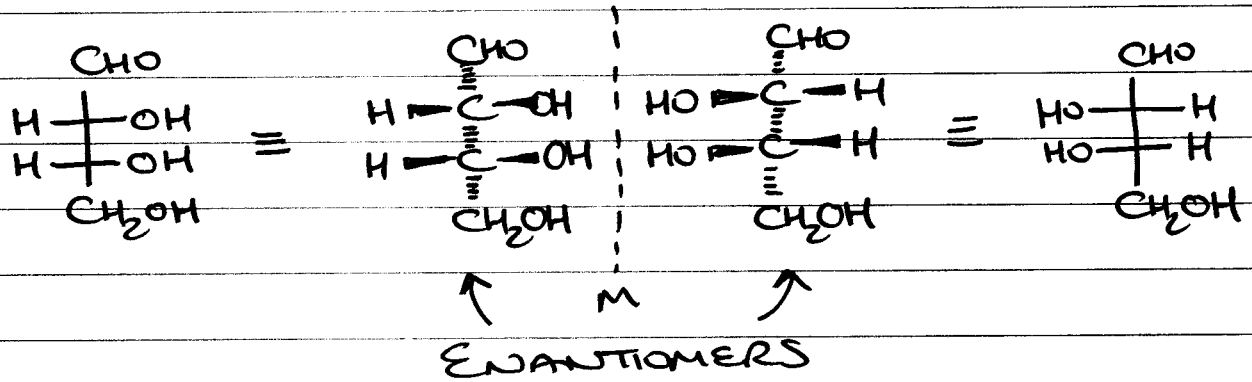
② FISCHER PROJECTIONS



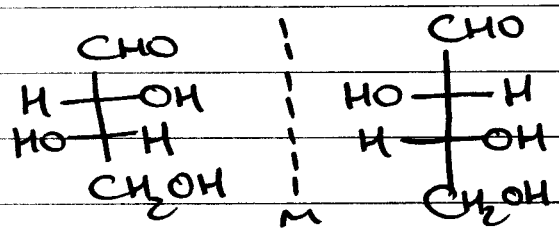
useful for compounds w/ continuous STEREOCENTERS

2,3,4-trihydroxybutanal

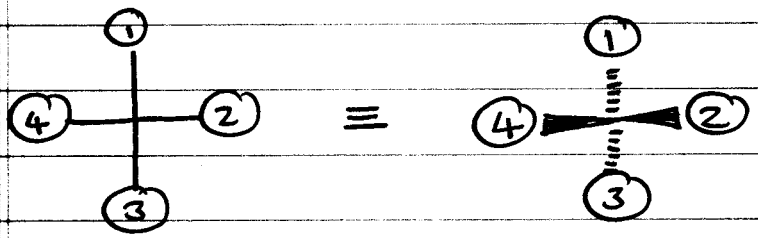




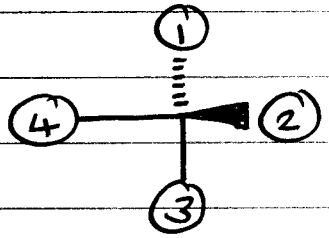
Another pair of ENANTIOMERS



Determining R/S for FISCHER PROJECTIONS



switch one wedge and one dash for straight lines



⇐ assign R/S

THIS ONE IS (S)

GO BACK and determine R/S for 2,3,4-trihydroxybutanal

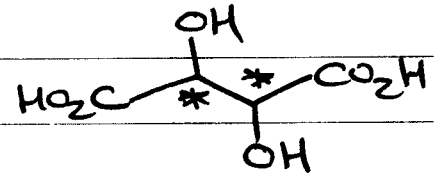
A molecule with n CHIRAL CENTERS can have a maximum number of STEREOISOMERS

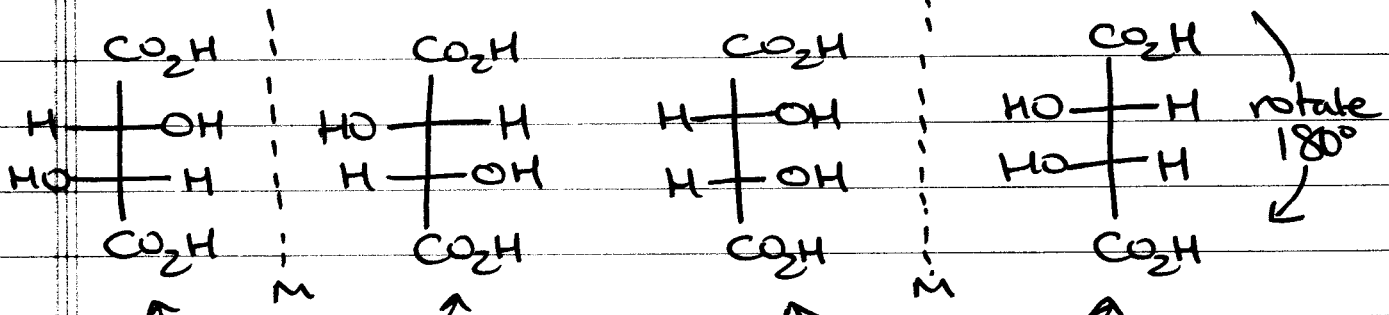
$= 2^n$

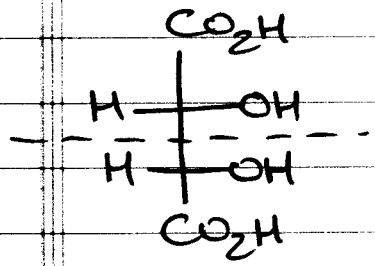
2,3,4 trihydroxybutanal has 2 stereocenters

$2^2 = 4$ stereocenters

Consider TARTARIC ACID







COMPOUND w/ CHIRAL CENTERS, but is ACHIRAL ⇒ MESO

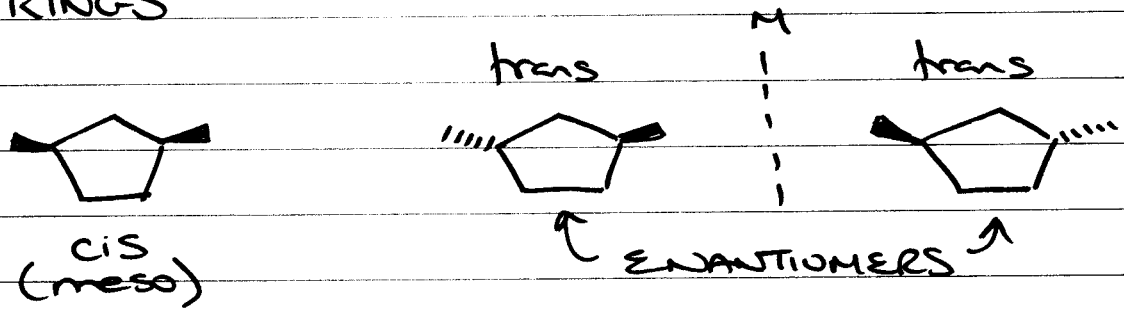
ENANTIOMERS ✓

③ DIASTEREOISOMERS → CONFIGURATIONAL

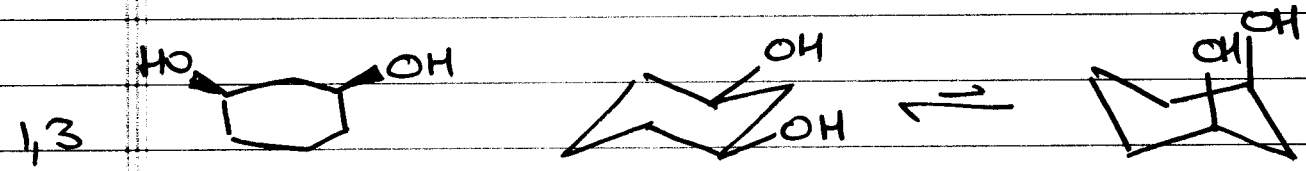
→ CIS/TRANS

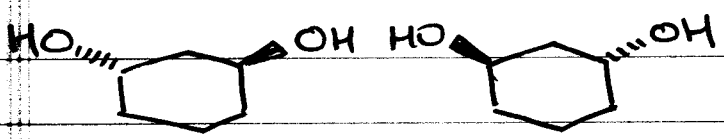
↳ RINGS/ALKENES

- RINGS

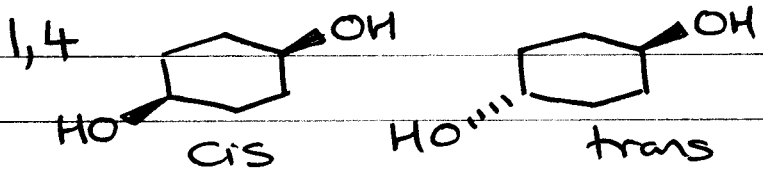


consider CYCLOHEXANES

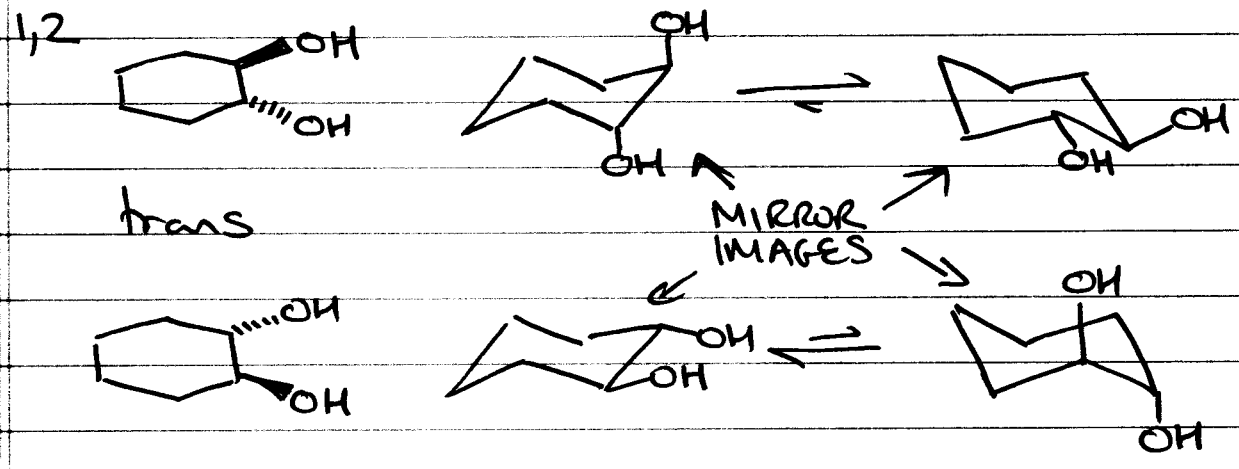


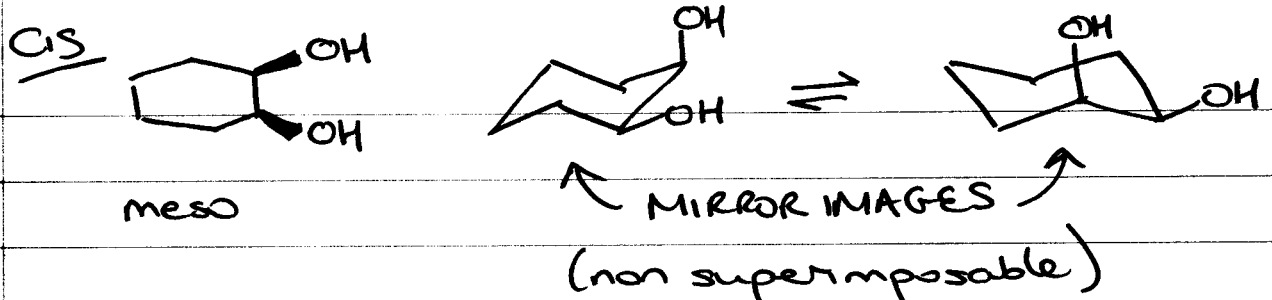


DRAW CHAIR FOR EACH AND DO A RING FLIP FOR EACH ENANTIOMER
(IN each case, chairs are identical)

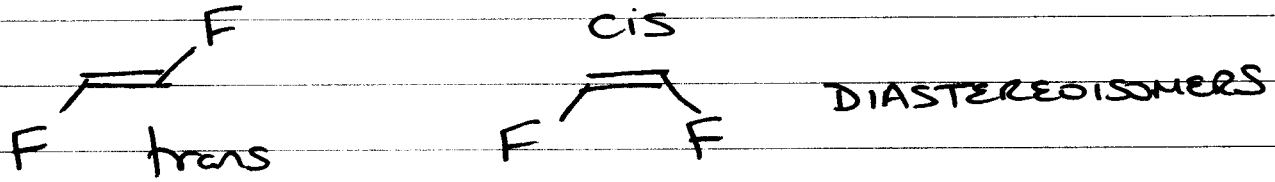


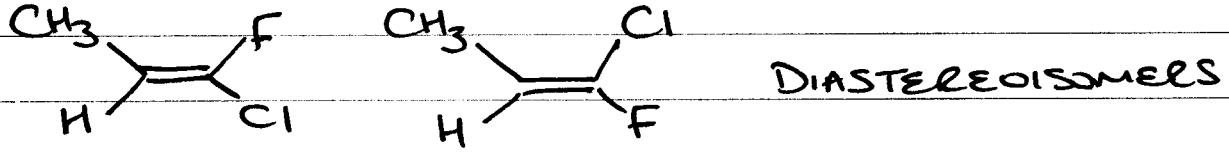
BOTH ACHIRAL





ALKENES

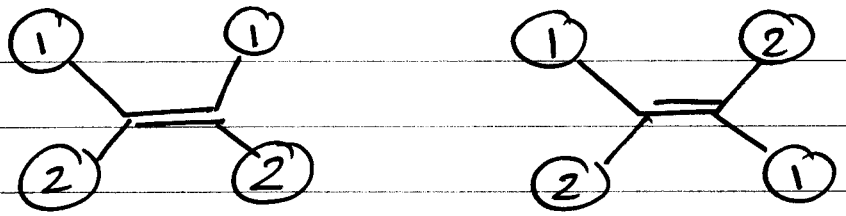




cis / trans

(E) (Z)

Use same priority rules as for R/S on each C of double bond.



Z E

LEC (11) CHEM 30A Oct 24th

(1) CIS/TRANS DIASTEREOISOMERS
(2) CONSEQUENCES of CHIRALITY
(3) RESOLUTION
(4) ACIDS/BASES

MIDTERM WEDS
A-J CS76
K-Z CS50

READ 3.6-3.9
PROBLEMS 3.8, 3.9, 3.34-3.40

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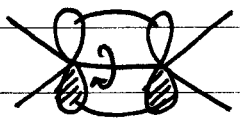
(1) CIS/TRANS DIASTEREOISOMERS

LEC (10) pages 7, 8

Why no rotation about double bonds?



would remove overlap & break the π BOND (doesn't happen under normal conditions)

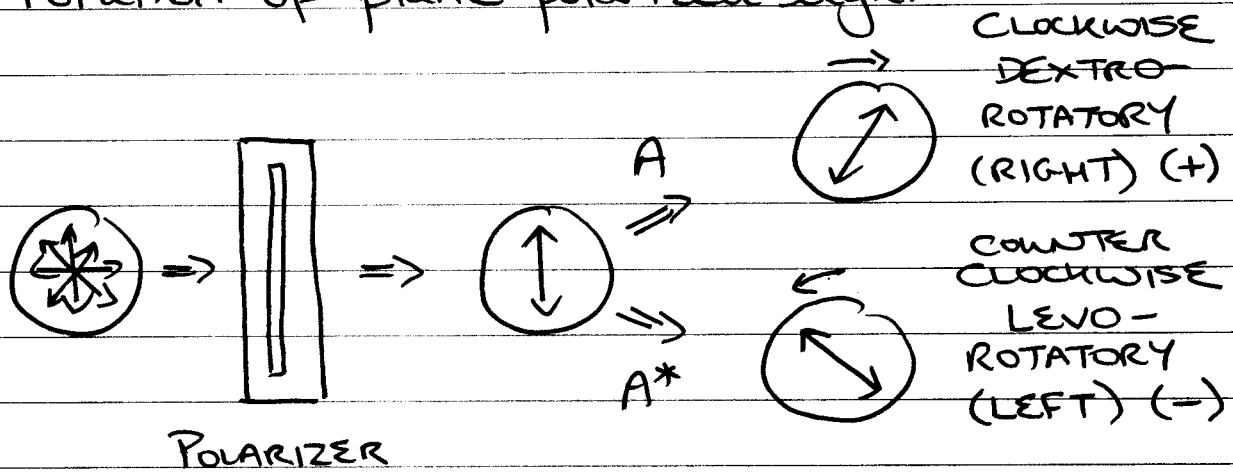
(2) CONSEQUENCES of CHIRALITY

Properties of enantiomers =>
IDENTICAL PHYSICAL & CHEMICAL PROPERTIES
(in an achiral environment)
e.g. mp, bp, solubility in water etc...

DIASTEREOISOMERS - different....

OPTICAL ACTIVITY

- rotation of plane polarized light



Specific Rotation $[\alpha]_\lambda^T = \dfrac{\text{Obs rotation (°)}}{\text{Length (dm)} \times \text{conc (g/mL)}}$

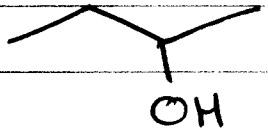
T = temperature λ = wavelength of light

(R)-2-BUTANOL (S)-2-BUTANOL

$[\alpha]_D^{25}$ −13.52° $[\alpha]_D^{25}$ +13.52°

1:1 mixture ⇒ RACEMIC MIXTURE

specific rotation = ϕ



(±)

NO relationship between R/S and +/-

enantiomeric excess (ee)

$$ee = \frac{[R] - [S]}{[R] + [S]} \times 100$$

$$= \%R - \%S$$

3 : 1

75% 25%

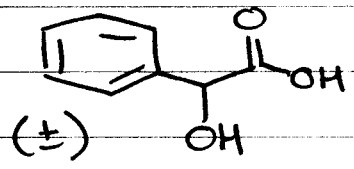
$[\alpha]_D^{25} = ?$ (-6.76°)

$ee = 50\%$

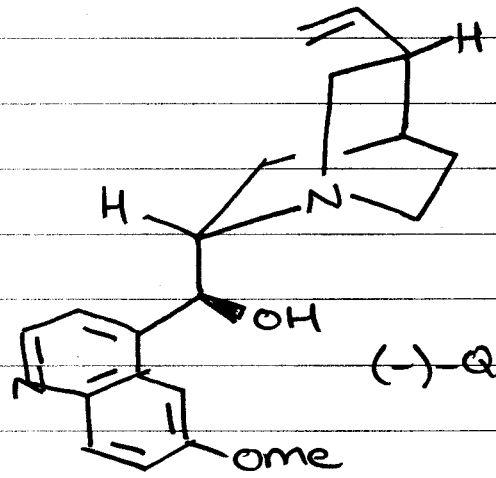
(3) RESOLUTION (separation of enantiomers)

(i) Natural products

$RCO_2H + R_3N \longrightarrow RCO_2^{\ominus}\ R_3\overset{\oplus}{N}-H$ (acid/base)



mandelic acid

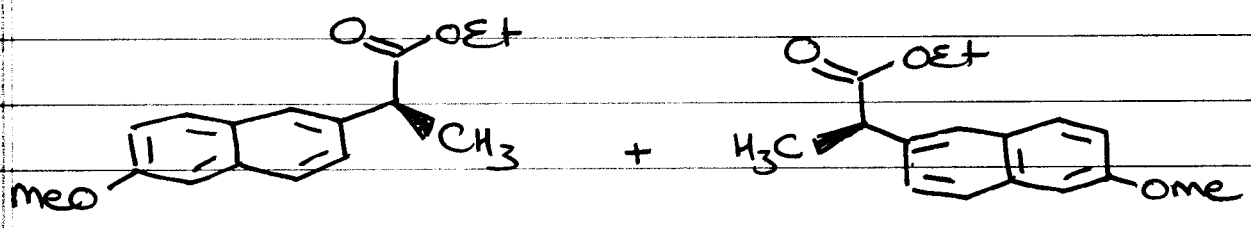


(-)-QUININE

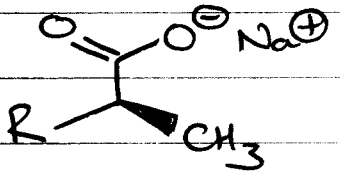
form 2 salts

(−)-QUININE-H^+ • (R)-MANDALATE$^-$
(−)-QUININE-H^+ • (S)-MANDALATE$^-$
} DIASTEREO-ISOMERS

(ii) ENZYMES



esterase / NaOH / H_2O



no reaction

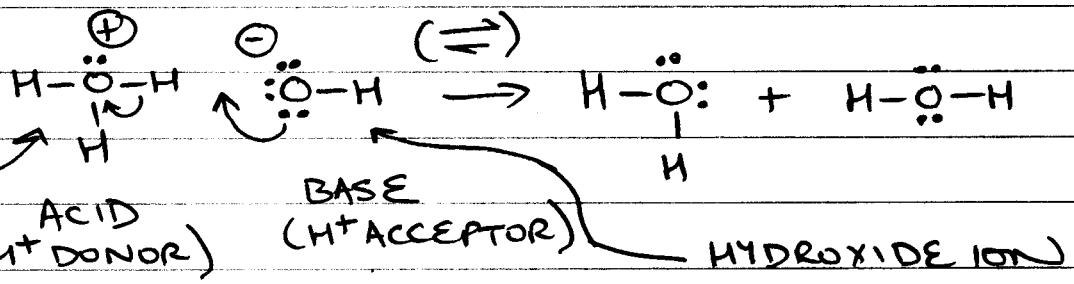
(iii) CHROMATOGRAPHY ⇒ read.

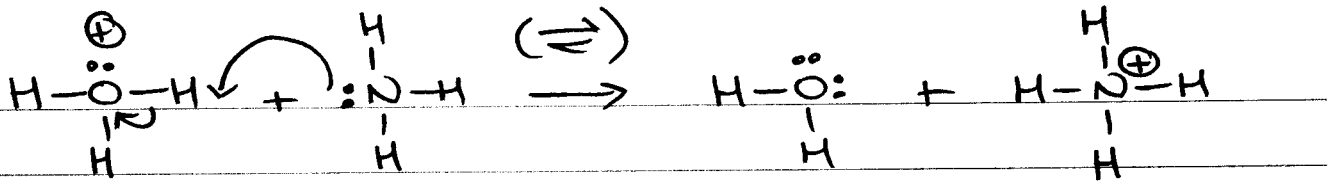
READ 3.9 CHIRALITY in BIOLOGICAL WORLD

(4) ACIDS & BASES

BRONSTED/LOWRY ⇒ ACID H^+ DONOR
BASE H^+ ACCEPTOR

e.g.





ACID BASE CONJUGATE BASE CONJUGATE ACID

— next:

Protonating organic structures.

LEC (12) CHEM 30A Oct 28th

ACIDS & BASES

(1) INTRO

(2) PROTONATING ORGANIC STRUCTURES

(3) ACID/BASE EQUILIBRIA

(4) STRUCTURE & ACIDITY

Read Ch4, Problems 4.1-4.47

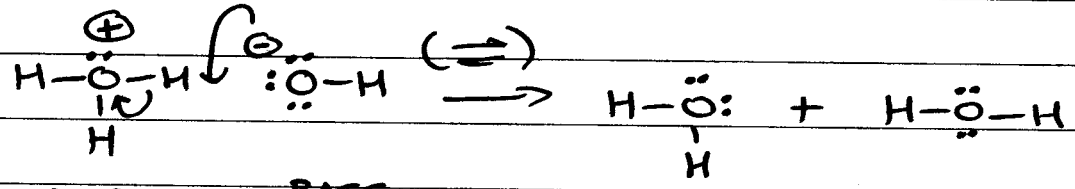
MIDTERM: LOW 5 HIGH 98, MEAN = 55

---

(1) INTRO

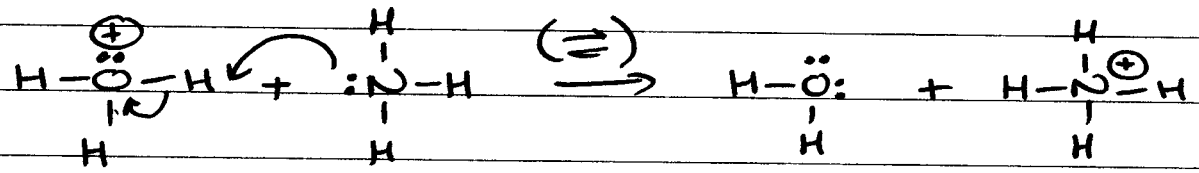
BRONSTED/LOWRY → ACID ⇒ H^+ DONOR
BASE ⇒ H^+ ACCEPTOR

e.g.



ACID (H^+ DONOR) BASE (H^+ ACCEPTOR)

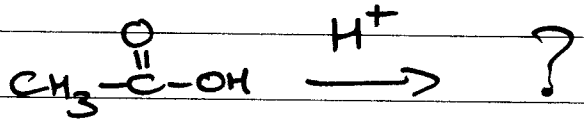
hydronium ion hydroxide ion

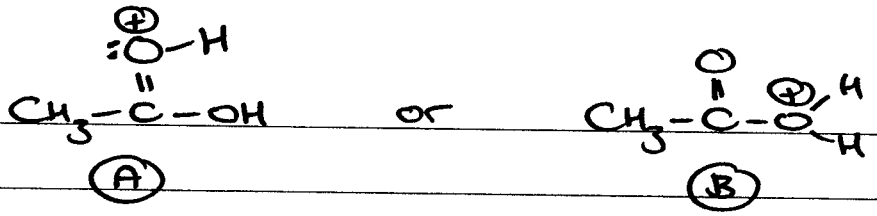


ACID BASE CONJUGATE BASE CONJUGATE ACID

(2) PROTONATING ORGANIC STRUCTURES

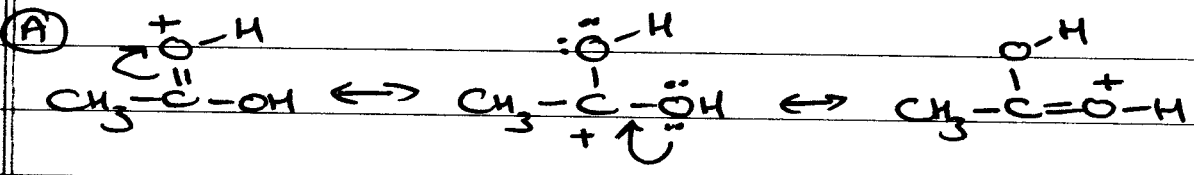
(i)

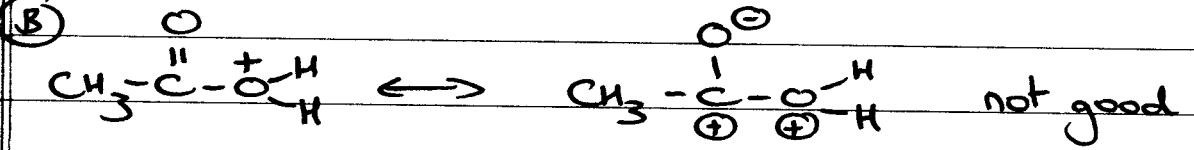




(A) or (B)

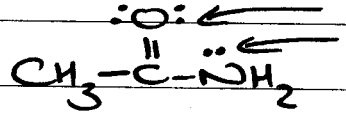
consider RESONANCE

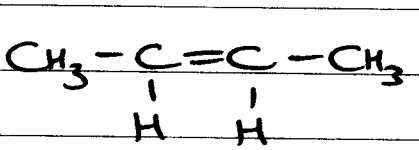


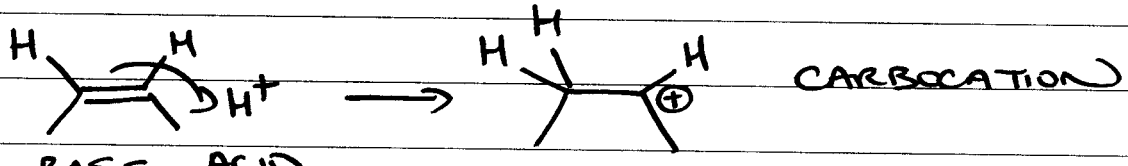


not good!

more basic than C–OH in

HMK  which is more basic?

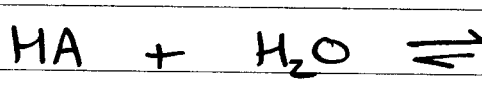
(ii) 



BASE ACID CARBOCATION

(3) ACID/BASE EQUILIBRIA

(quantify acid strength → acid dissociation constants)



$$K_{eq} = \frac{[H_3O^+][A^-]}{[HA][H_2O]}$$ ← changes very little (huge xs)

$$K_a = K_{eq}[H_2O] = \frac{[H_3O^+][A^-]}{[HA]}$$

e.g. acetic acid CH_3COOH

$K_a = 1.74 \times 10^{-5}$

Most organic acids have a K_a with a -ve exponent → hard to compare

$pK_a = -\log_{10} K_a$ pK_a (acetic acid) = 4.76

LARGER pK_a ⟶ WEAKER ACID

STRONG ACID ⇒ WEAK CONJUGATE BASE
WEAK ACID ⇒ STRONG CONJUGATE BASE

Scan through pK_a table in the book.

+ POSITION of EQUILIBRIUM

$$HA + B^\ominus \rightleftharpoons A^\ominus + HB$$

Competition between $B^\ominus$ and $A^\ominus$ for $H^\oplus$

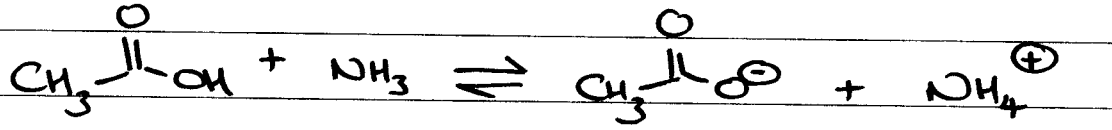
$$K_{eq} = \frac{[A^-][HB]}{[HA][B^-]} \quad \text{multiply by} \quad \frac{[H_3O^+]}{[H_3O^+]}$$

$$K_{eq} = \frac{[A^-][H_3O^+]}{[HA]} \times \frac{[HB]}{[B^-][H_3O^+]}$$

$$K_{eq} = \frac{K_{HA} \text{ (acid)}}{K_{HB} \text{ (conjugate acid)}}$$

$$pK_{eq} = pK_{HA} - pK_{HB}$$

e.g.



	ACID	BASE	CONJUGATE BASE	CONJUGATE ACID
pKa	4.76			9.24

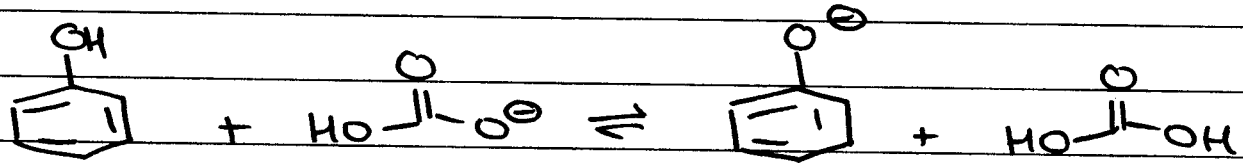
So $pK_{eq} = 4.76 - 9.24$
$= -4.48$

$$K_{eq} = 10^{-pK_{eq}} = 3 \times 10^4$$

STRONGER ACID and STRONGER BASE react to give WEAKER ACID and WEAKER BASE

If stronger acid on left, $K_{eq} > 1$
If stronger acid on right, $K_{eq} < 1$

for example:



pka ~ 10 — pka ~ 6.4 STRONGER ACID

$K_{eq} = 10^{-3.6}$

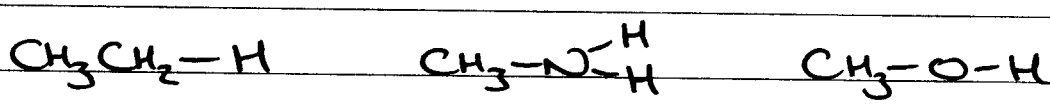
(4) STRUCTURE AND ACIDITY

$HA \rightleftharpoons H^+ + A^-$ all about A^-

The more stable A^-, the more acidic HA

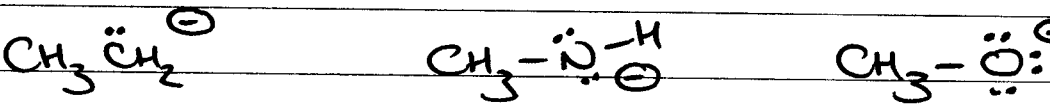
a) ELECTRONEGATIVITY (within a row)

consider:



51 38 16 pka

⟶ INCREASING ACIDITY



conjugate bases

⟵ INCREASING BASICITY

C 2.5 N 3.0 O 3.5 EN

Greater EN, electrons held more tightly, A^- more stable

b) ATOM SIZE

consider:

CH_3-S-H vs CH_3-O-H

7 16 pka

$CH_3-S^{\ominus}$ ← more stable $CH_3O^{\ominus}$

Negative charge spread over a larger volume (lower charge density)

So, for HALOGEN acids:

$HI > HBr > HCl > HF$ acidity.

because $I^- > Br^- > Cl^- > F^-$ size.

next up...

RESONANCE & the INDUCTIVE EFFECT.

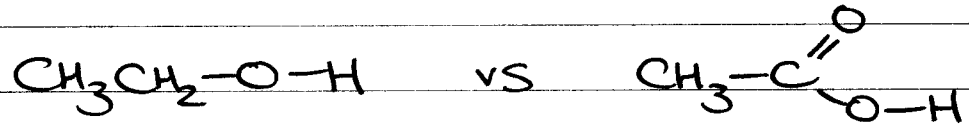
LEC (13) CHEM 30A Halloween

(1) STRUCTURE & ACIDITY	Finish Ch4 problems
(2) LEWIS ACIDS & BASES	Read Ch5 + problems
(3) ALKENES INTRO	Acid/base WEB
organic reactions	
(4) TYPES	Read 6.1-6.3
(6) MECHANISMS	

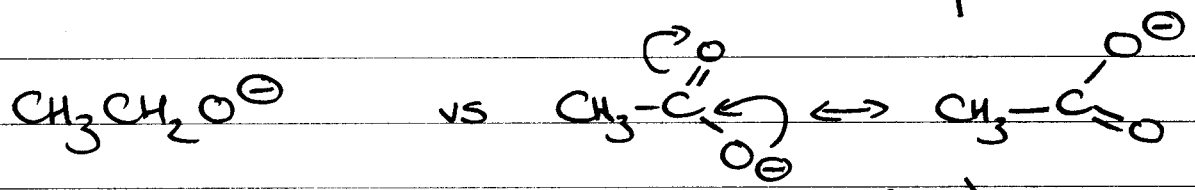
(1) STRUCTURE & ACIDITY cont...

c) RESONANCE

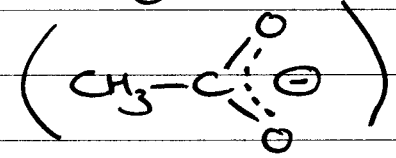
consider:



16 5 pka



charge localized on one atom



charge delocalized

DELOCALIZATION ≡ STABILITY (HOT POTATO)

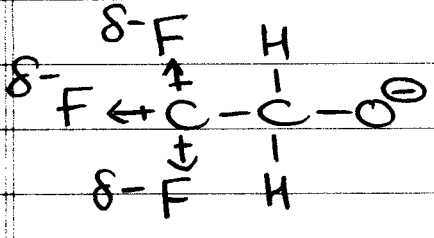
d) INDUCTIVE EFFECT

Consider

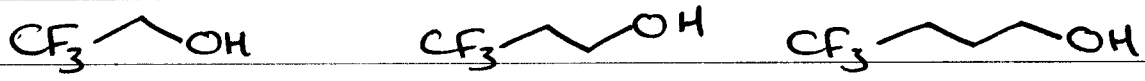
CH_3CH_2-O-H vs CF_3CH_2O-H

15.9 12.4 pKa

$CF_3CH_2O^{\ominus}$ is more stable than $CH_3CH_2O^{\ominus}$

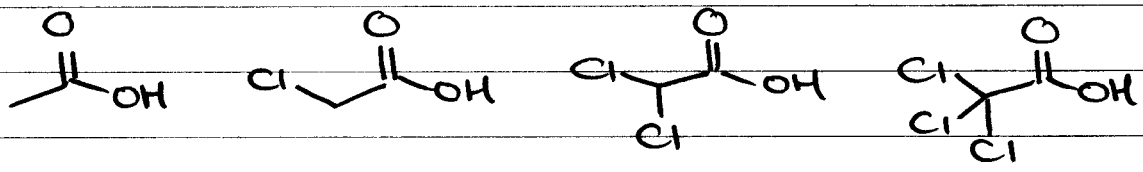


THROUGH BOND EFFECT, falls off rapidly with distance



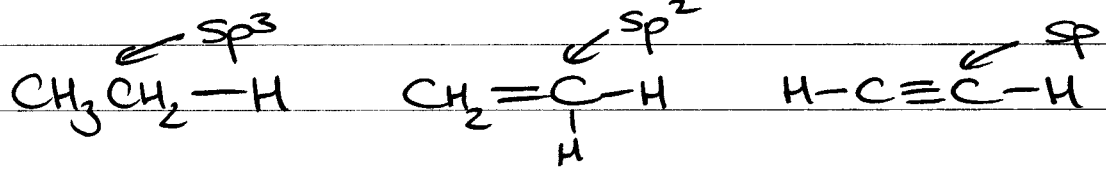
pKa 12.4 14.6 15.4

same effect w/ CARBOXYLIC ACIDS



4.75 2.85 1.48 0.64

e) HYBRIDISATION



51 44 25 pKa

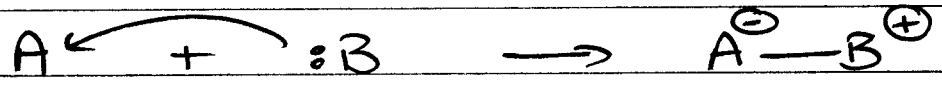
⟶ ACIDITY INCREASES as S character of orbital increases 25% → 33% → 50%

e^- closer to nucleus, A^- more stable, HA more acidic

② LEWIS ACIDS/BASES

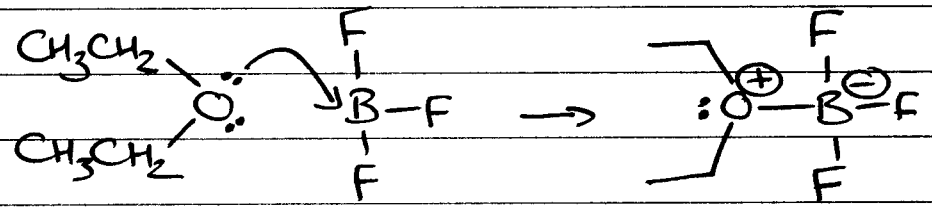
about e^- pairs, not H^+

LEWIS ACID accepts an e^- pair
LEWIS BASE donates an e^- pair



LEWIS ACID — LEWIS BASE

e.g.



LEWIS BASE — LEWIS ACID

③ Chapter 5 – Intro to Alkenes

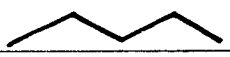
Structure / Cis/trans E/Z / Naming / Natural C=C

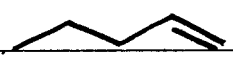
- Index of Hydrogen Deficiency (degrees of unsaturation)
1 per ring / π BOND

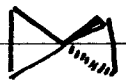
- max Hs in a structure C_nH_{2n+2}

$$\text{Deg Unsat} = \frac{\text{max H} - \text{actual H}}{2}$$

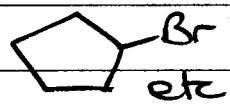
(i) C & H ONLY

C_5H_{12} $(12-12)/2 = 0$  no rings or π BONDS

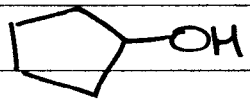
C_5H_{10} $(12-10)/2 = 1$  or 

C_5H_8 $(12-8)/2 = 2$   

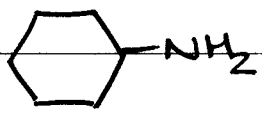
(ii) F, Cl, Br, I → replace for H

$C_5H_9Br \Rightarrow C_5H_{10}$ $(12-10)/2 = 1$ 

(iii) O, S → IGNORE

$C_5H_{10}O \Rightarrow C_5H_{10}$ 

(iv) N, P add a C & a H

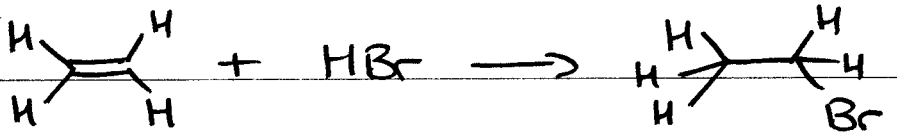


$C_6H_{13}N \Rightarrow C_7H_{14}$ $(16-14)/2 = 1$

ORGANIC REACTIONS

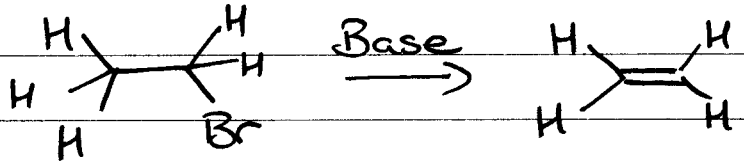
(4) TYPES

a) ADDITION (A + B → C)

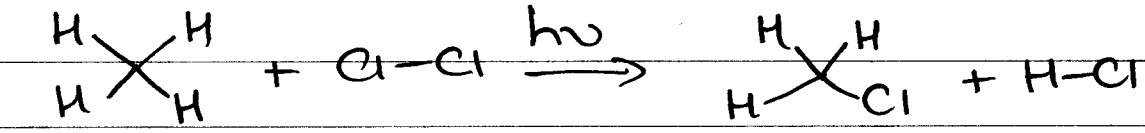
e.g.  + HBr ⟶

alkene alkyl bromide

b) ELIMINATION (A ⟶ B + C)

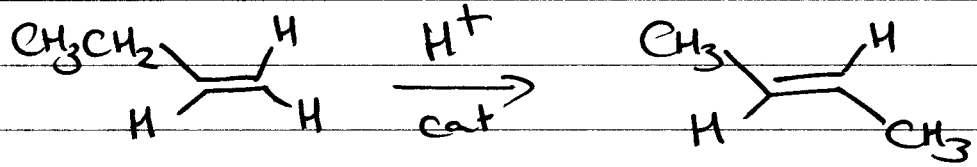
e.g. 

c) SUBSTITUTION (A-B + C-D ⟶ A-C + B-D)

e.g. 

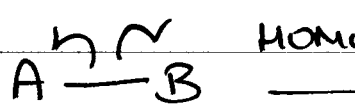
alkane alkyl halide

d) REARRANGEMENT



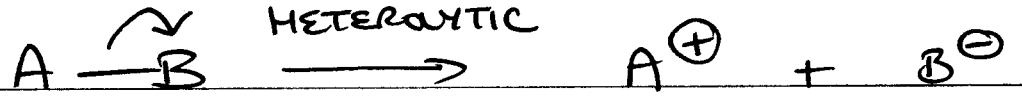
(5) MECHANISMS
(Bond making / bond breaking)

- BREAKING

 HOMOLYTIC ⟶ A• + B•

(↷ 1e⁻ arrow)

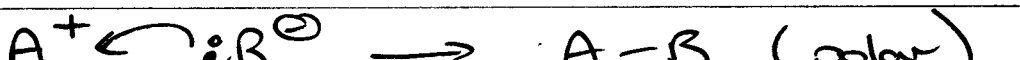
radical rxns (radicals → species containing unpaired e⁻)



POLAR REACTIONS

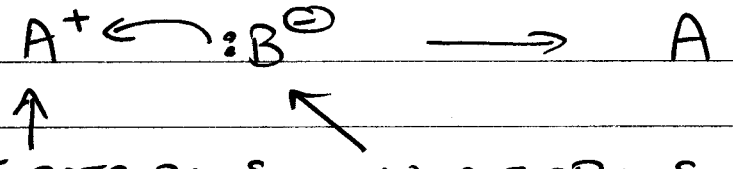
(↷ 2e⁻ arrow)

- MAKING



- POLAR RXNS (radicals in WK 9/10)

e⁻ RICH sites in one molecule react with e⁻ POOR sites in another molecule

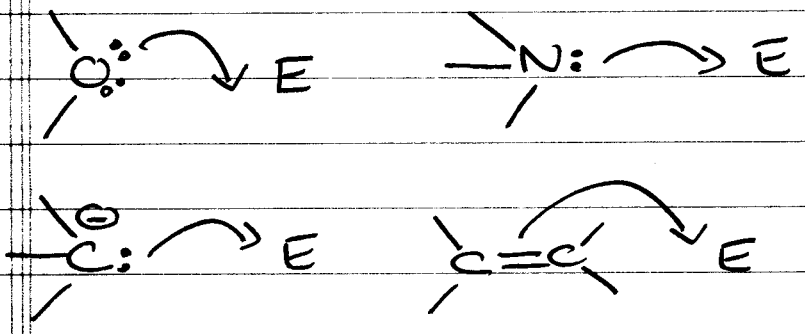


- NUCLEOPHILES
have an e⁻ RICH atom and are neutral or -vely charged

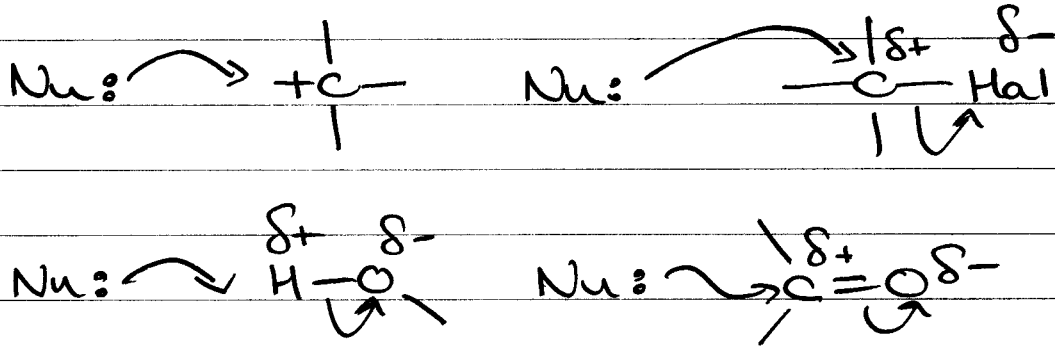
- ELECTROPHILES
have an e⁻ POOR atom and are neutral or +vely charged

PATTERNS

Electrons flow <u>from</u> nucleophiles

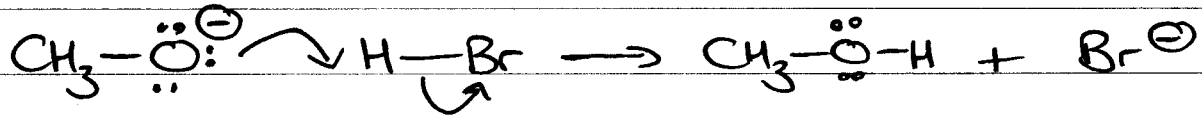


Electrons flow <u>to</u> electrophiles

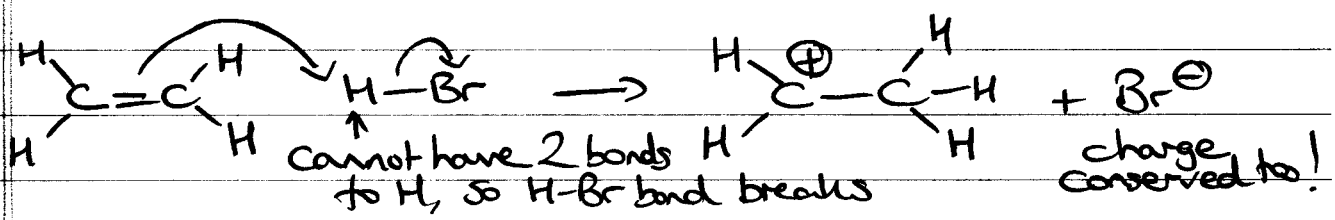


RULES

(i) CONSERVE CHARGE



(ii) OCTET RULE OBEYED



LEC (14) CHEM 30A NOV 2

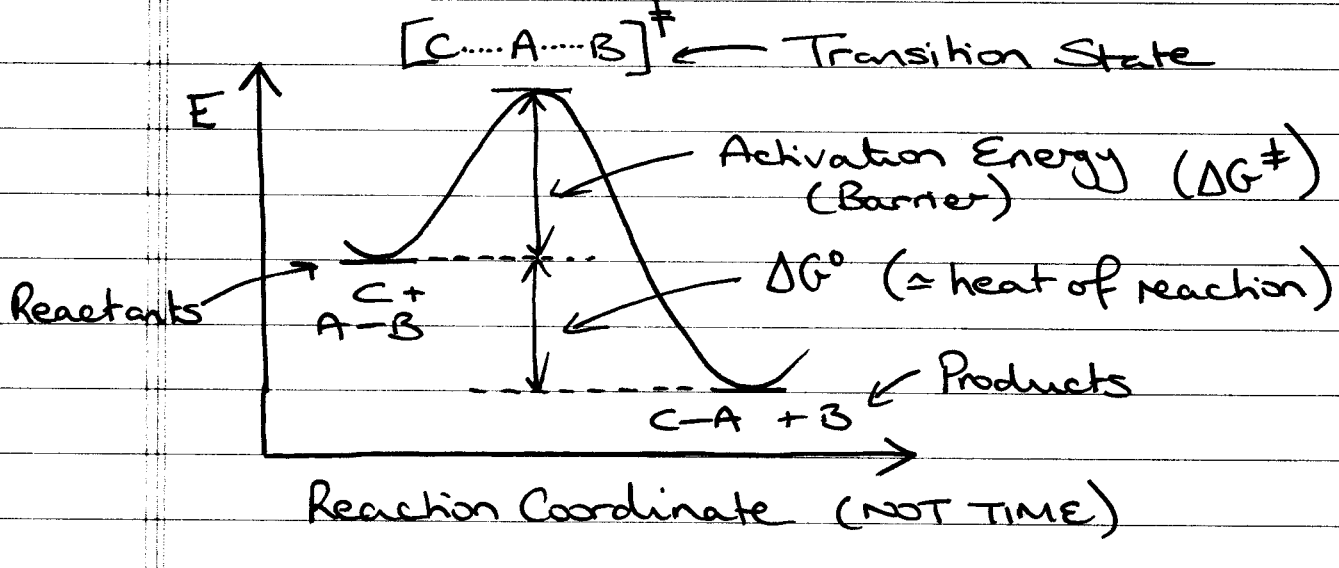
(1) ENERGY DIAGRAMS
(2) KINETICS vs THERMODYNAMICS
(3) ADDITION TO ALKENES
(4) CARBOCATIONS

READ 6.3–6.6 Q 6.1–6.3, 6.13–6.15

(1) ENERGY DIAGRAMS

– one step reaction

$$C + A-B \longrightarrow C-A + B$$



For a reaction to occur as written
$\Delta G^\circ < 0$ (proceeds spontaneously)

if $\Delta G^\circ > 0$ reaction does not proceed.

HEAT OF REACTION

$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ ← change in entropy (more significant at higher T)

↑ change in enthalpy (can be measured directly)

ΔH° −ve EXOTHERMIC rxn

ΔH° +ve ENDOTHERMIC rxn

TRANSITION STATE

energy maximum along reaction coordinate

⇒ definite GEOMETRY of atoms, but CANNOT be isolated, structure cannot be determined experimentally (COMPUTATION)

ACTIVATION ENERGY

difference in energy between starting materials and the transition state

$\Delta G^\ddagger$ or E_A

Arrhenius equation

$k = Ae^{(-E_A/RT)}$

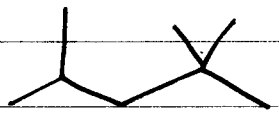
↑ rate constant for reaction

↖ pre-exponential factor

(2) KINETICS vs THERMODYNAMICS

↓ how fast will it happen?

↓ will it happen?

eg.  + $O_2 \rightleftharpoons 8CO_2 + 9H_2O$

isooctane

$\Delta G^\circ = -1000 kJ/mol$

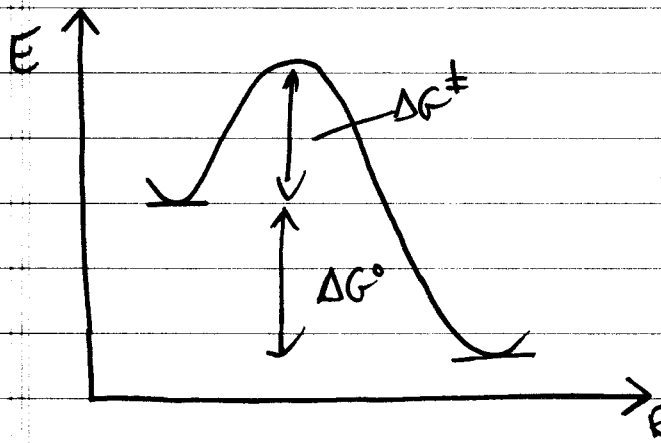
$K_{eq} = 10^{175}$ at 298k

(only 10^{86} atoms in observable universe)

<u>BUT</u> isooctane is stable

(you put it in your car)

- Energy required to start the reaction
  ⇒ ACTIVATION ENERGY (spark plug)

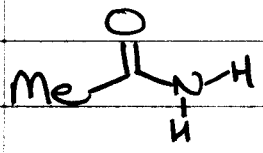
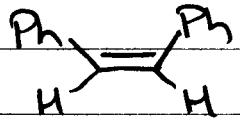


Isooctane + O_2 THERMODYNAMICALLY UNSTABLE, BUT KINETICALLY STABLE

However, apply a burst of energy to H_2O/CO_2 mixture you will not reconvert to octane + oxygen

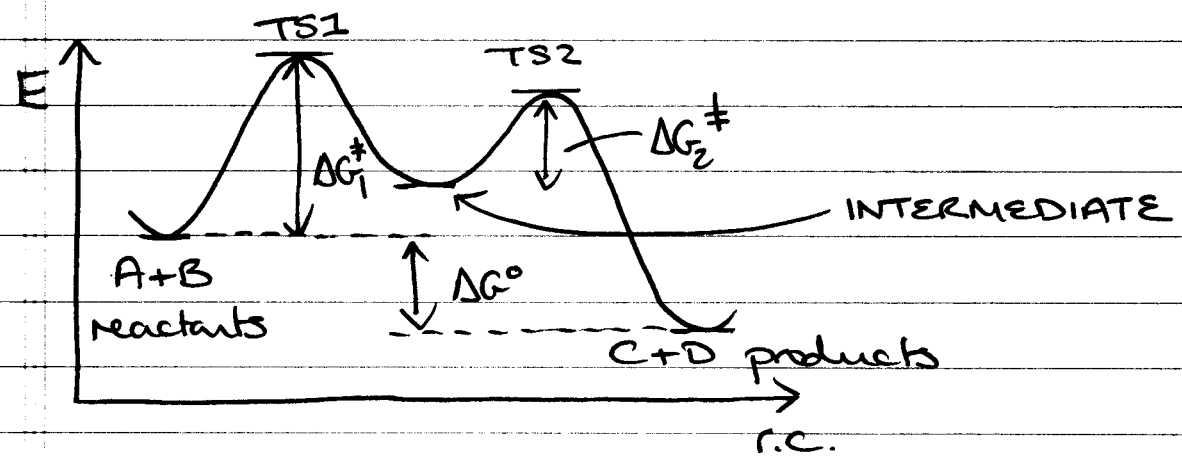
(MENTION GRAPHITE / DIAMOND)

Energy barriers and rate (consider BOND rotations → same principle as reactions)

	E_A (kcal/mol)	$k\ (s^{-1})$ (298K)	$t_{1/2}$
H_3C-CH_3	3	5×10^{10}	0.02 ns
Cl_3C-CCl_3	11	8×10^{4}	10 ps
	17	3	0.2 s
	45	2×10^{-19}	~10^{11} yrs

(age of the earth ~ 4.6×10^{9} yrs)

– ENERGY PROFILE (2 step rxn)

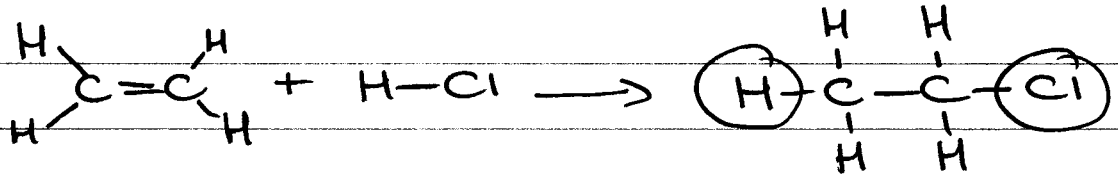


REACTION INTERMEDIATE ⇒ localized energy minimum between TWO TRANSITION STATES (sometimes possible to isolate)

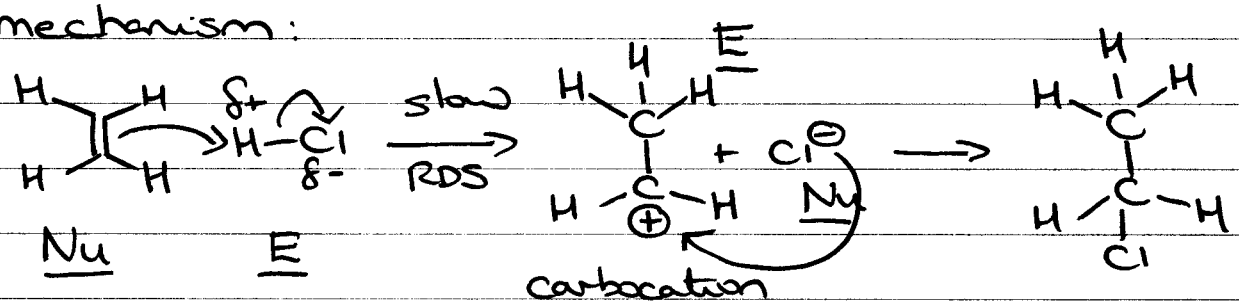
SLOWEST STEP in a multistep process (one w/ highest barrier) is called the RATE DETERMINING STEP (RDS)

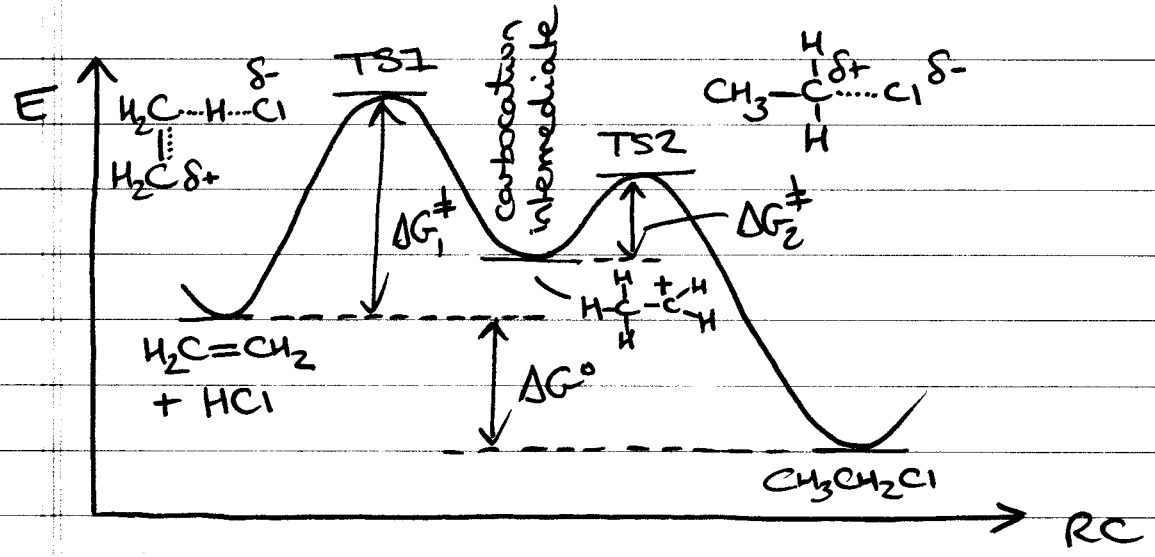
- Fill in RDS on graph above.

(3) ELECTROPHILIC ADDITION TO ALLENES

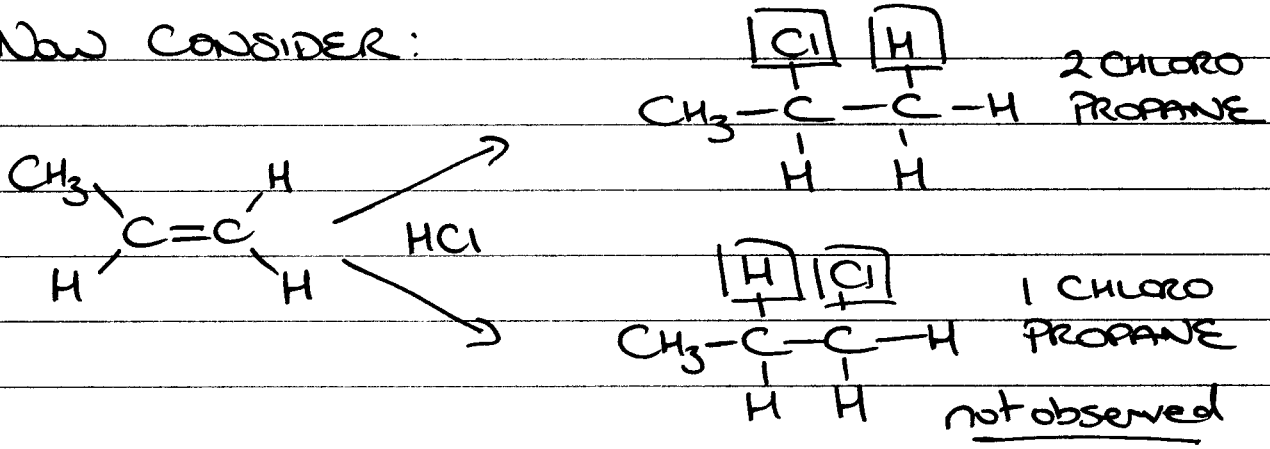


mechanism:





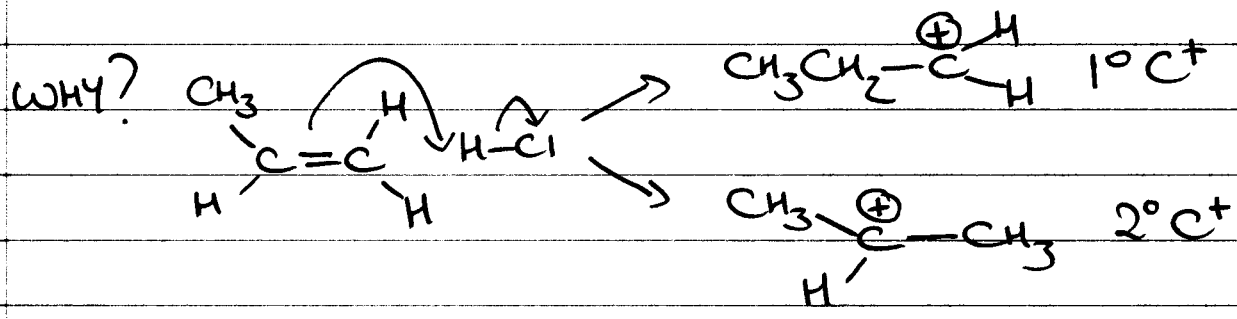
NOW CONSIDER:



REGIOSELECTIVE REACTION

⟹ MARKOVNIKOV'S RULE

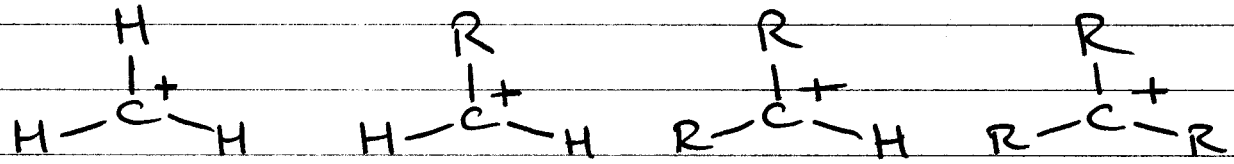
H ADDS TO DOUBLE-BONDED C WITH MOST Hs ALREADY ATTACHED



(4) CARBOCATIONS

(stability)

R = alkyl

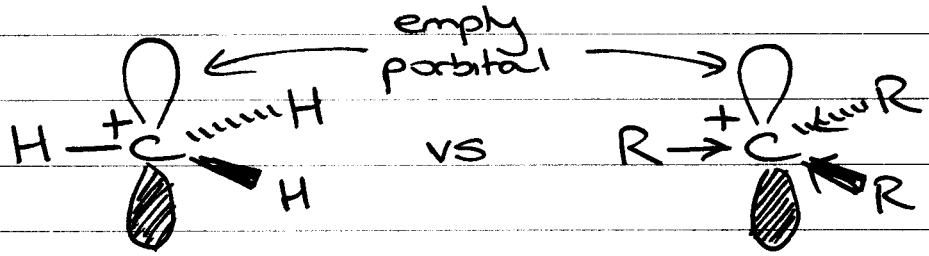


methyl 1° 2° 3°

INCREASING STABILITY ⟶

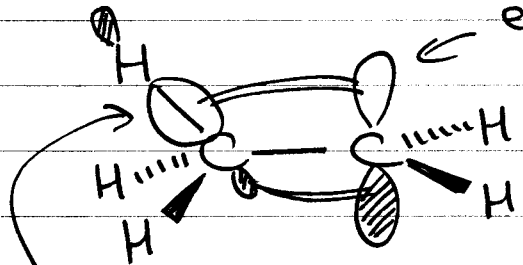
Two factors

(i) Inductive Effect



ALKYL GROUPS ARE INDUCTIVELY DONATING.

(ii) Hyperconjugation

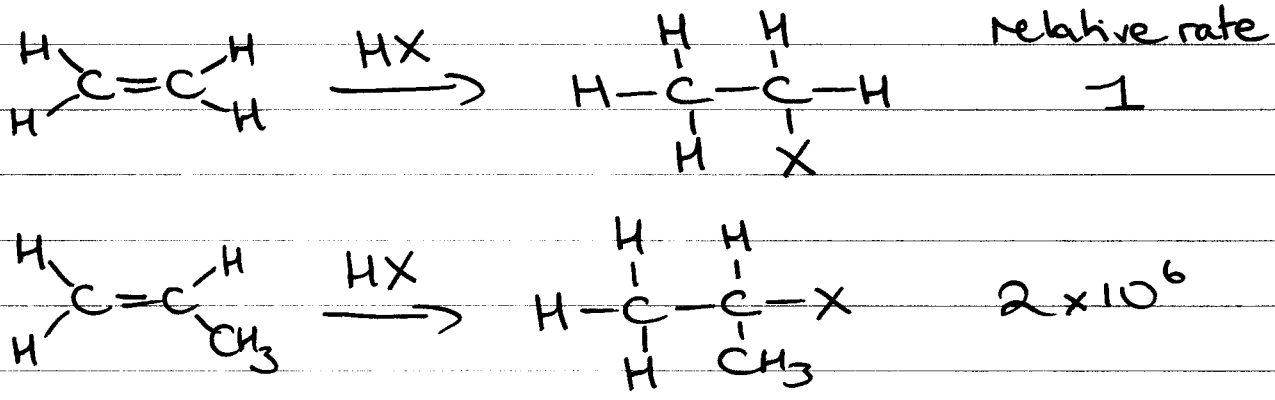


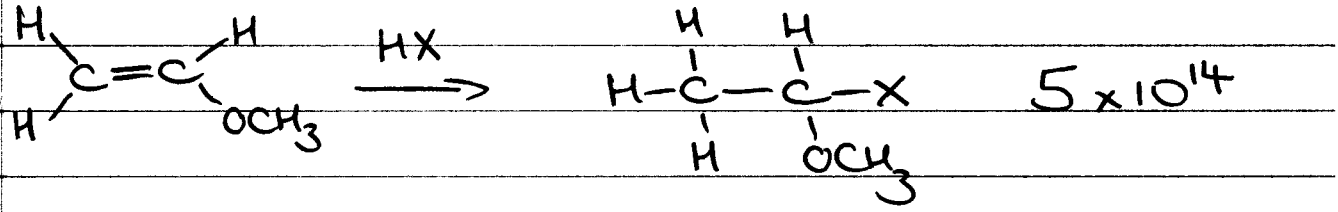
DELOCALIZATION of adjacent σ BONDS

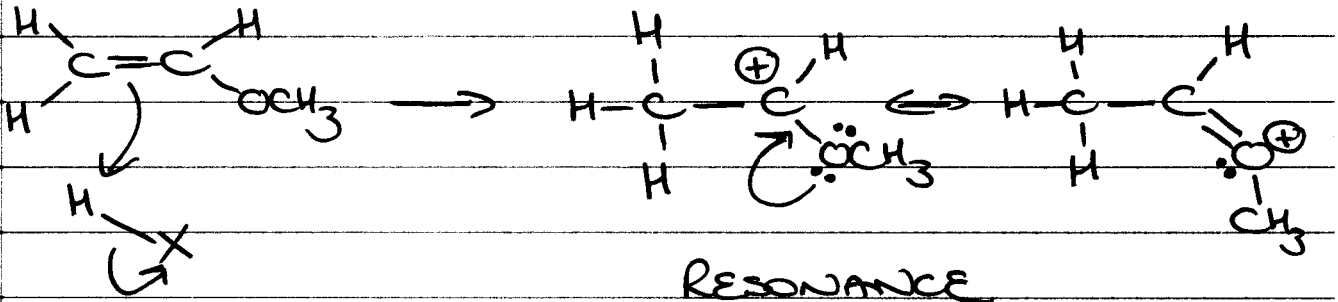
filled $C_{sp^3}-H_{1s}$ σ orbital

The more C–H or C–C bonds, the more significant the stabilization, so $Me^+ < 1° < 2° < 3°$

..... and other FACTORS (RESONANCE)







RESONANCE STABILIZED

LEC (15) CHEM 30A Nov 4th

(1) CARBOCATIONS READ 6.3-6.5
(2) REARRANGEMENT PROBLEMS 6.4-6.7
(3) ADDITION of H_2O
(4) ADDITION of Br_2/Cl_2

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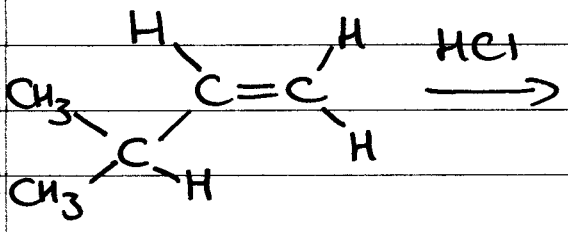
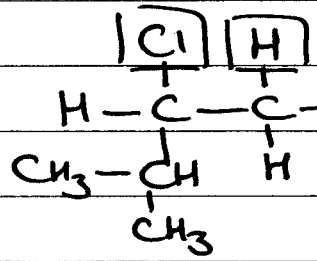
(1) CARBOCATIONS

Page 6-8 from LEC (14)

(2) REARRANGEMENT

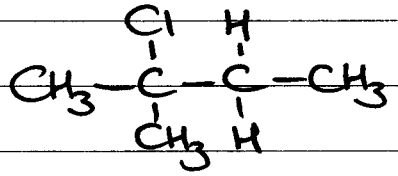




~40% expected product

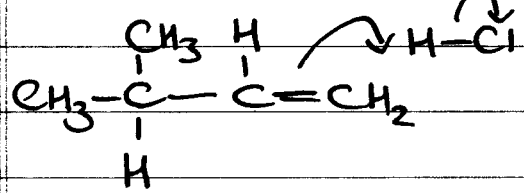
2 chloro 3 methyl butane

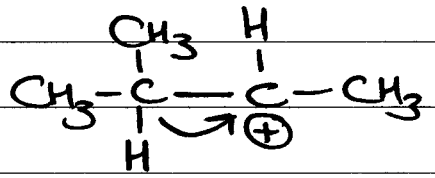
-other 60%



2 chloro-2-methyl butane

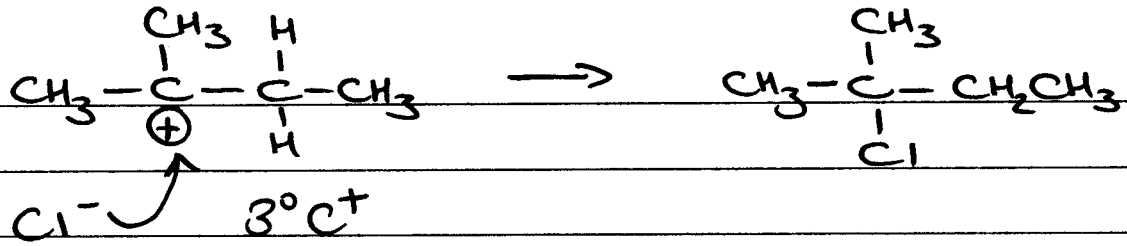
WHY?





$2°C^+$

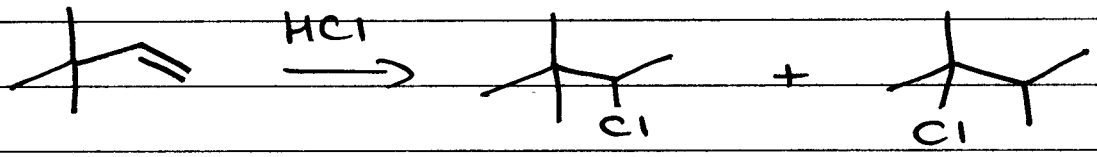
1,2 hydride shift (H^-)



Cl^- 3° C^+ (more stable)

Rearrangement is possible whenever a carbocation is formed.

consider:



MINOR (20%) MAJOR (80%)

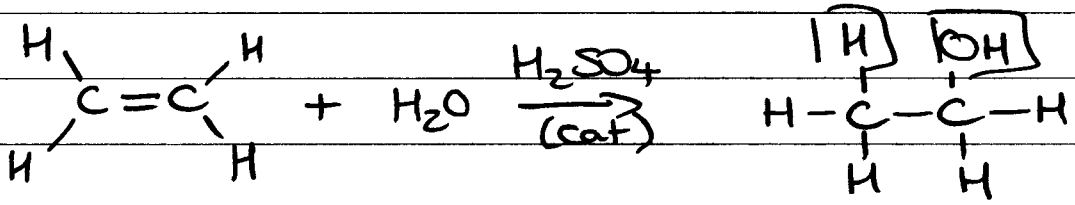
WHY? not 1,2 H^- shift, but 1,2 methyl shift

2° C^+ → 3° C^+

(rarely reverse, but is possible - ring strain)

[1° C^+ in reality do not really form during reactions in solution] UNSTABLE

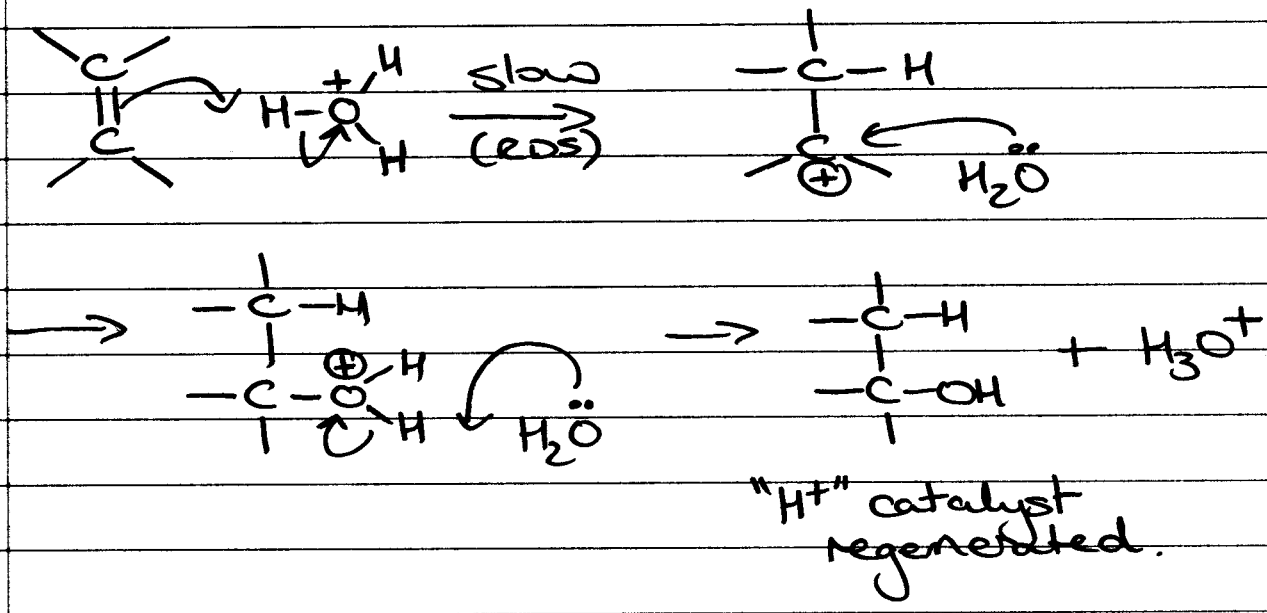
(3) ADDITION of H_2O (acid catalysed hydration)



H_2O alone not ACIDIC enough to protonate C=C

$H_2SO_4 + H_2O \rightleftharpoons H_3O^+ + HSO_4^-$

mechanism:

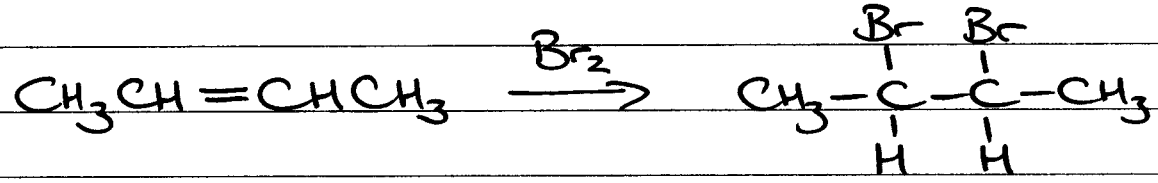


mechanism involves a CARBOCATION, so:

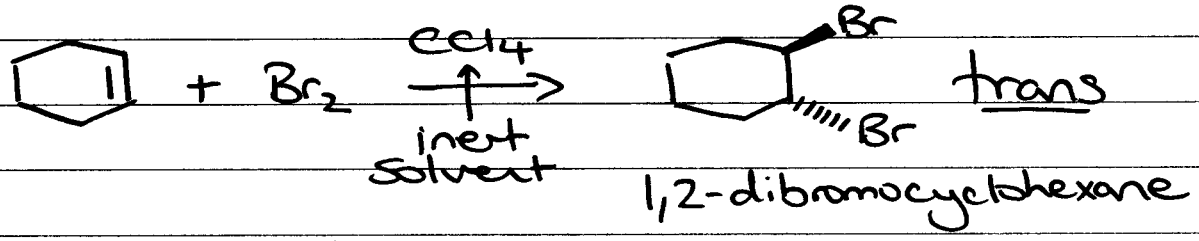
(i) rearrangement is possible

(ii) MARKOVNIKOV selectivity is observed.

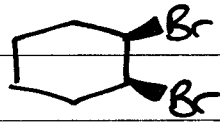
(4) ADDITION of Br_2/Cl_2



note:



STEREOSPECIFIC REACTION



cis isomer is NOT formed.

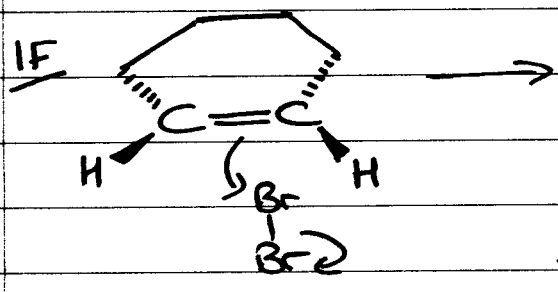
Note:

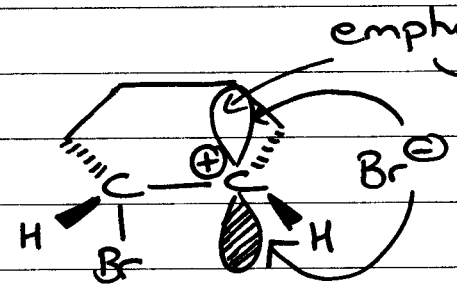
STEREOSPECIFIC (exclusion)
STEREOSELECTIVE (preference)

same for REGIO...

- consider mechanism

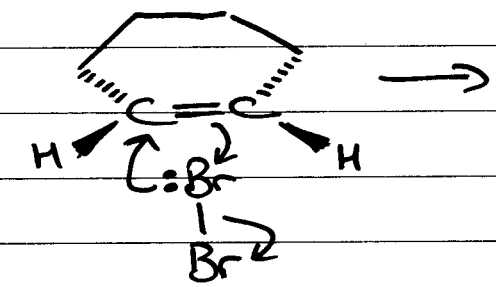
IF

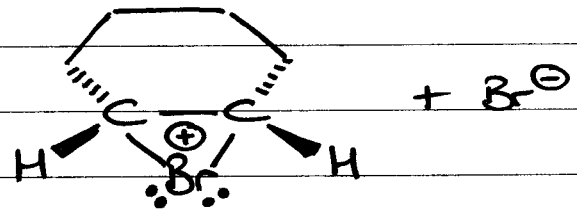




- could give cis & trans
- rearrangement is possible

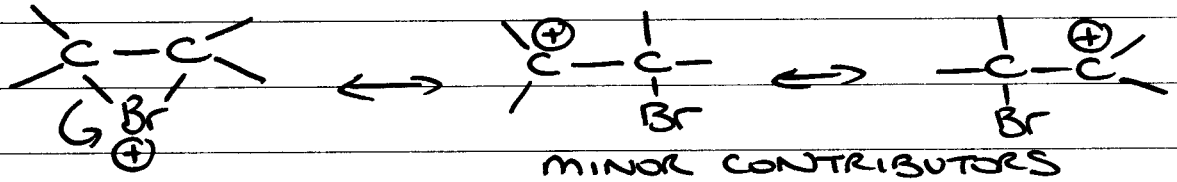
mechanism is:



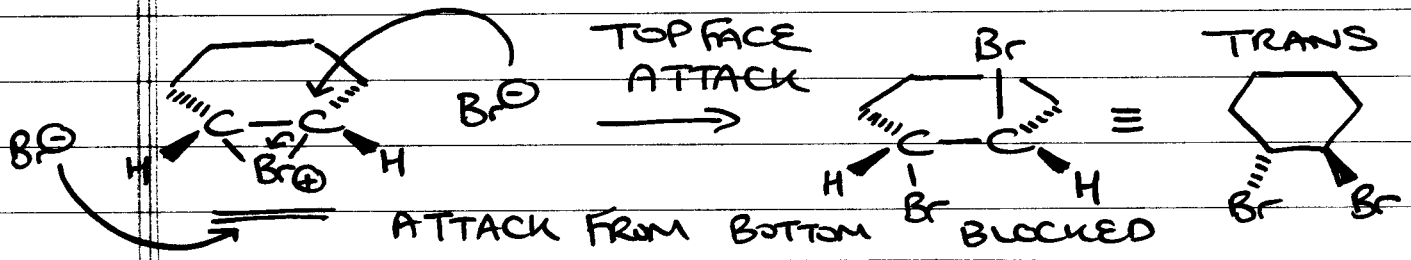


CYCLIC BROMONIUM ION

CONTRIBUTING "RESONANCE" STRUCTURES



MINOR CONTRIBUTORS



REACTION PROCEEDS W/ ANTISTEREOSPECIFICITY

- if $Br^{\ominus}$ had attached at other C atom, it would lead to the ENANTIOMER

LEC (16) CHEM 30A Nov 7th

(1) ADDITION of HOCl/HOBr
(2) OXYMERCURATION
(3) HYDROBORATION
(4) OXIDATION

Office hrs start at 5:30 pm
Quiz on WEDS
NO CLASS FRIDAY

- mechanism summarys

READ rest of Ch6

PROBLEMS 6.8, 6.9, 6.12, 6.16–6.40

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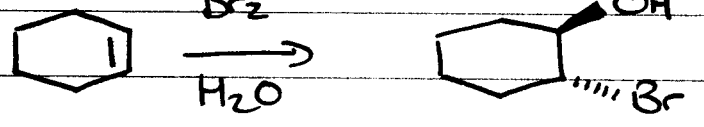
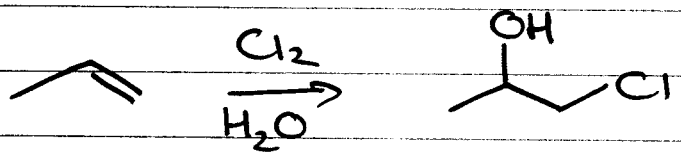
(1) ADDITION of HOCl/HOBr



ANTI STEREOSPECIFIC & (REGIOSELECTIVE)

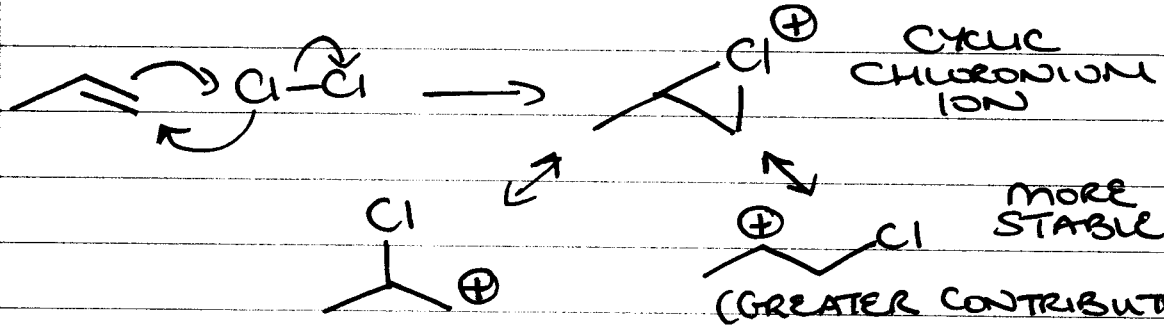
not an inert solvent

BROMOHYDRIN (halohydrin)

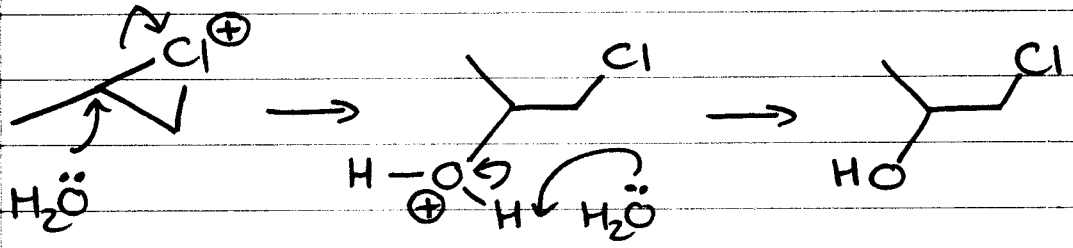


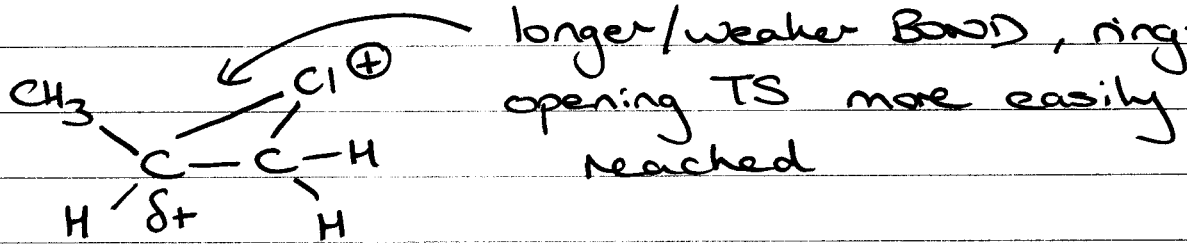
-OH adds to more SUBSTITUTED C atom

mechanism:

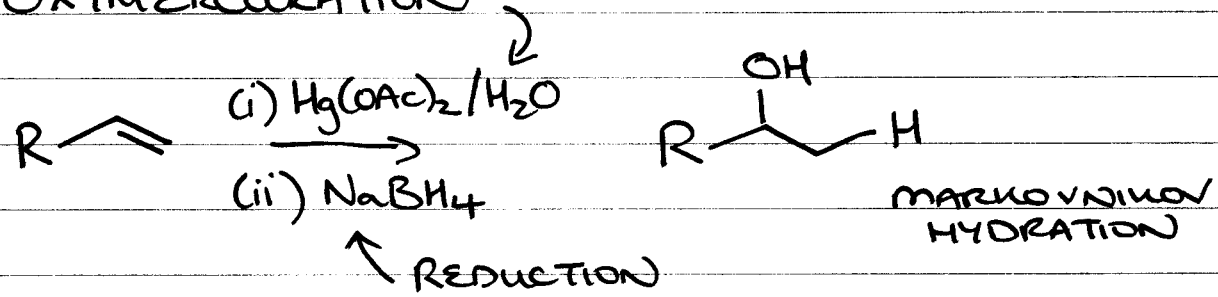


OPENS VIA MORE STABLE C^+

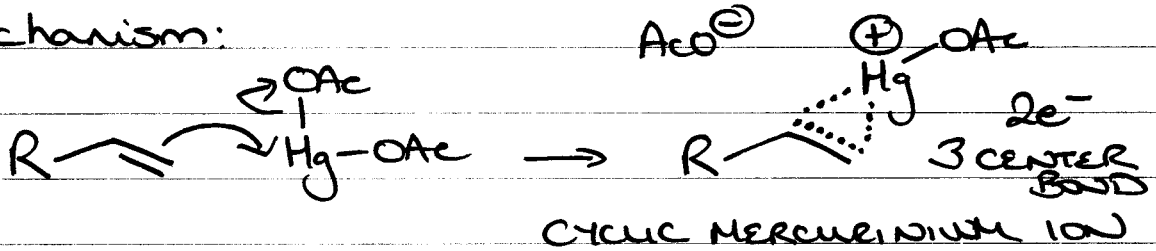




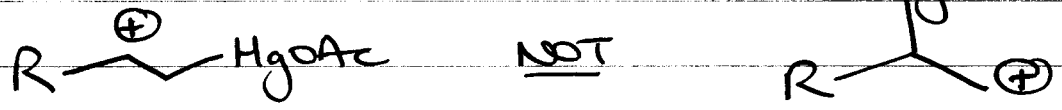
(2) OXYMERCURATION



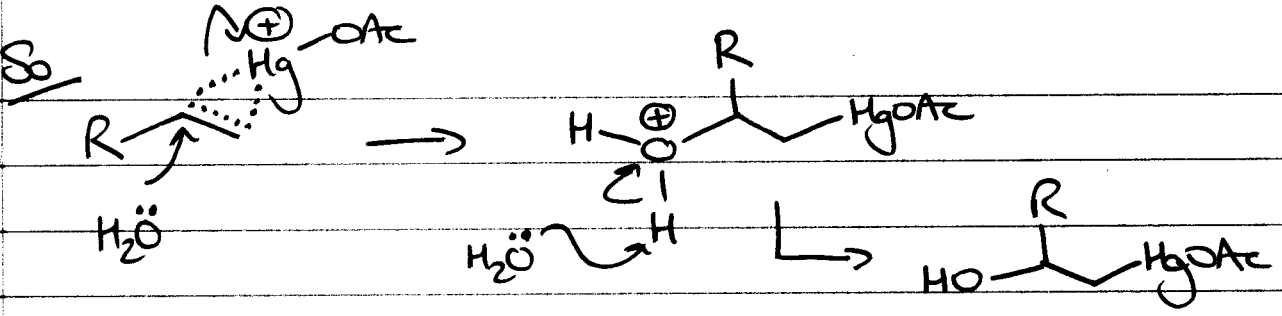
mechanism:



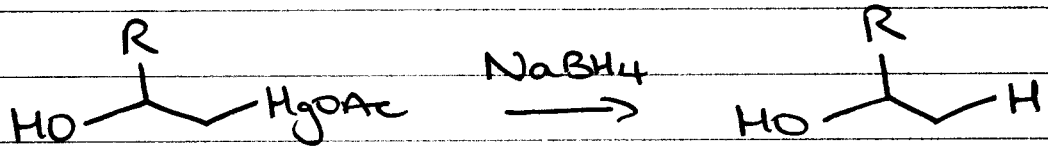
Opens via more stable C^+



So

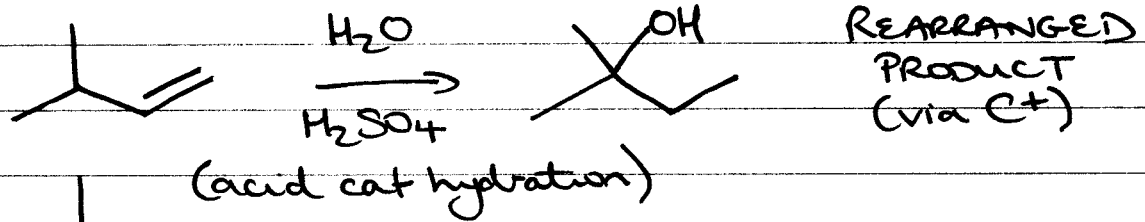


organomercury compound reduced w/ $NaBH_4$



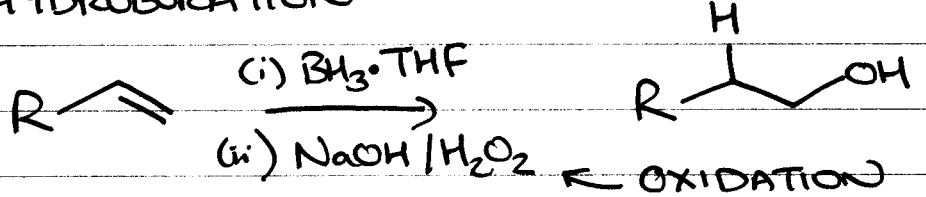
replaces HgOAc for H
(don't need to know mechanism for this)

WHY IS THIS USEFUL?
consider:

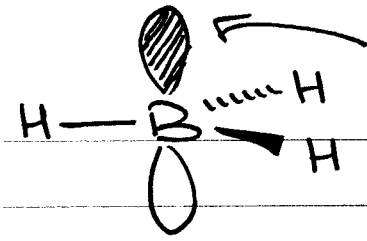


REGIOSELECTIVE, w/ ANTISTEREOSPECIFICITY (HOBr/HOCl)

③ HYDROBORATION

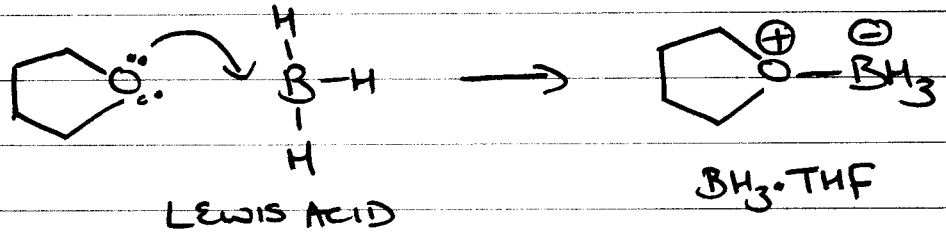


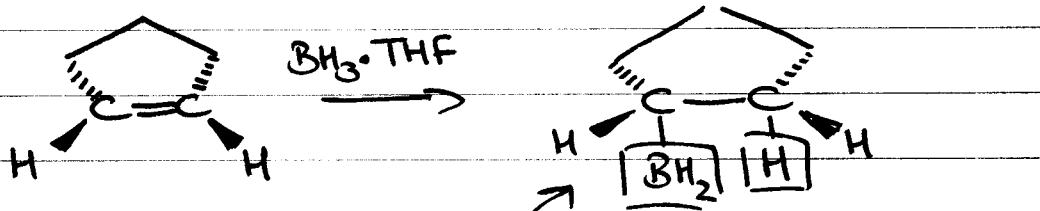
Borane (BH_3)



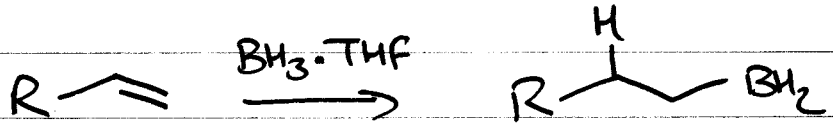
(actually exists as B_2H_6 – structure?)

LEWIS BASE



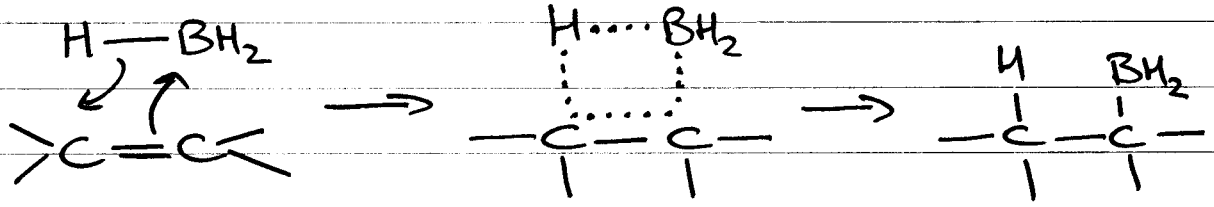


- SYN STEREOSPECIFIC

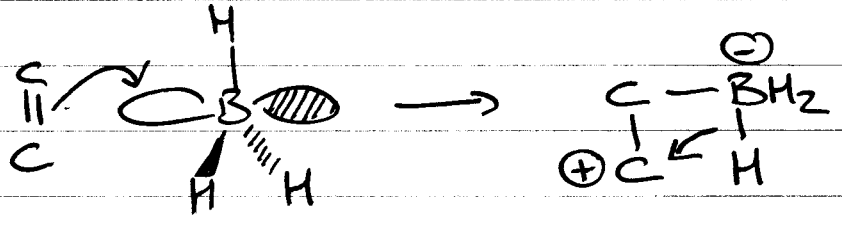


BORON ADDS TO LESS SUBSTITUTED C ATOM

mechanism:



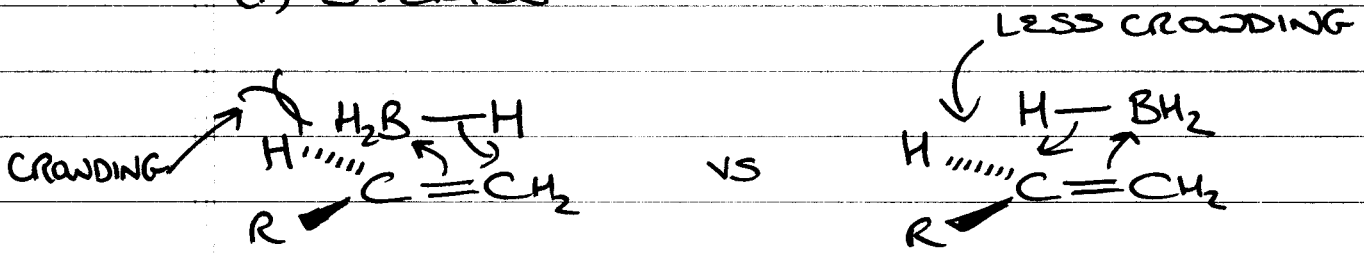
i.e



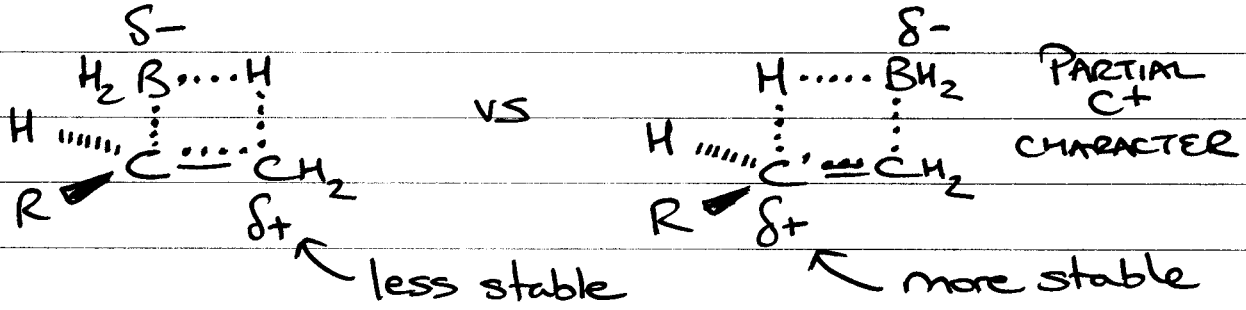
- BUT, NO REARRANGEMENTS (concerted mechanism)

WHY REGIOSELECTIVE?

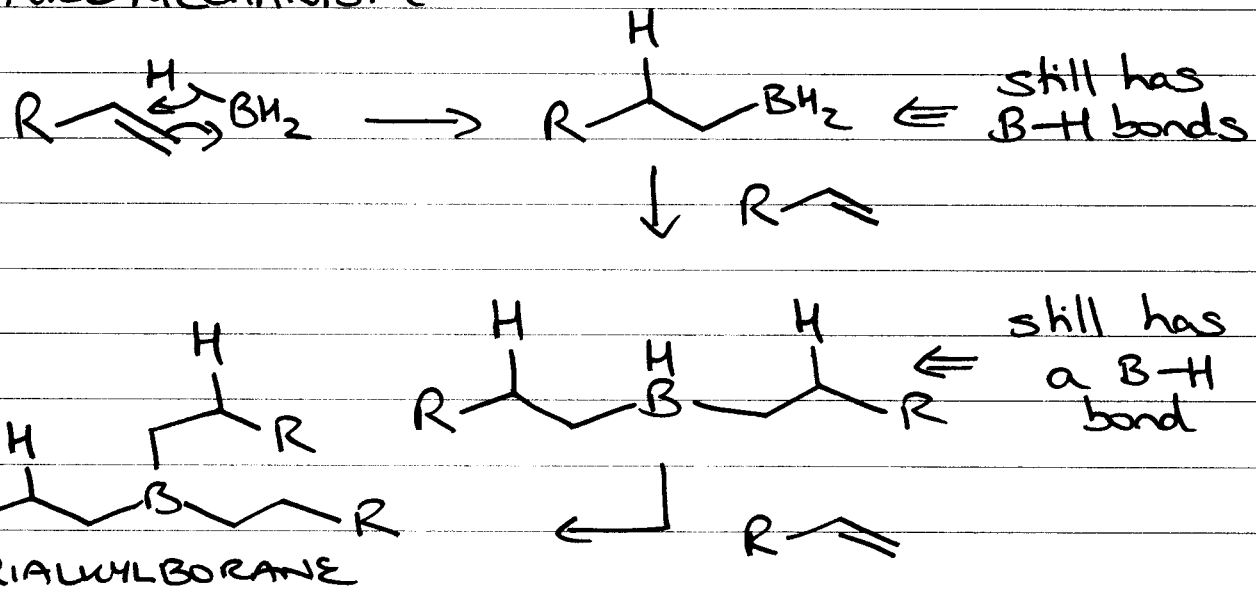
(i) STERICS



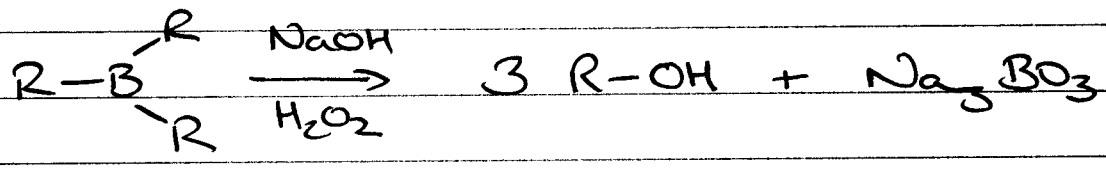
(ii) ELECTRONICS

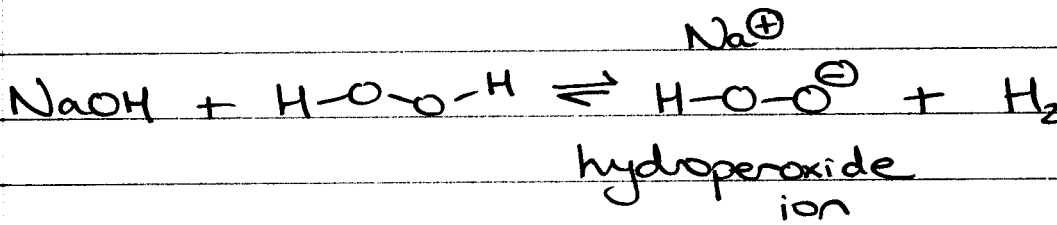


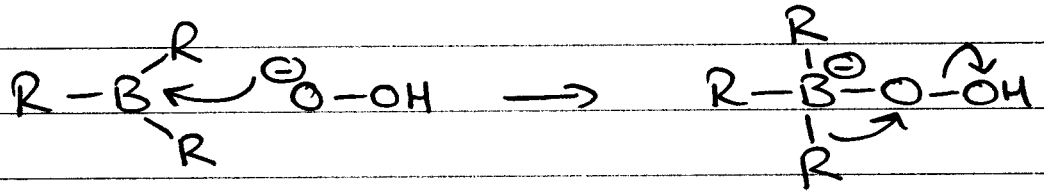
FULL MECHANISM

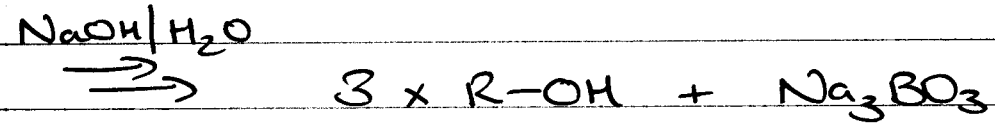


SECOND STEP



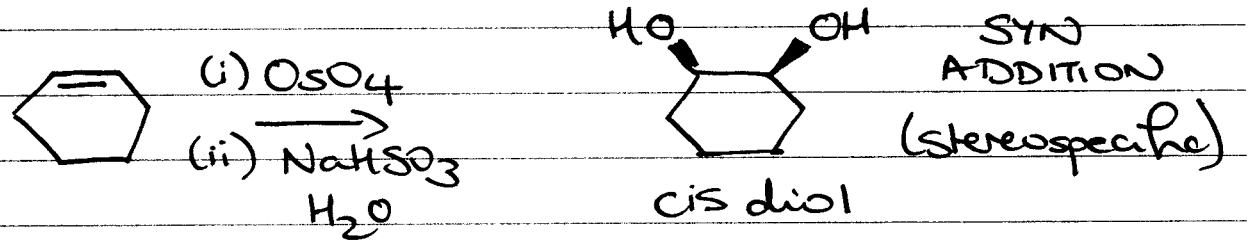


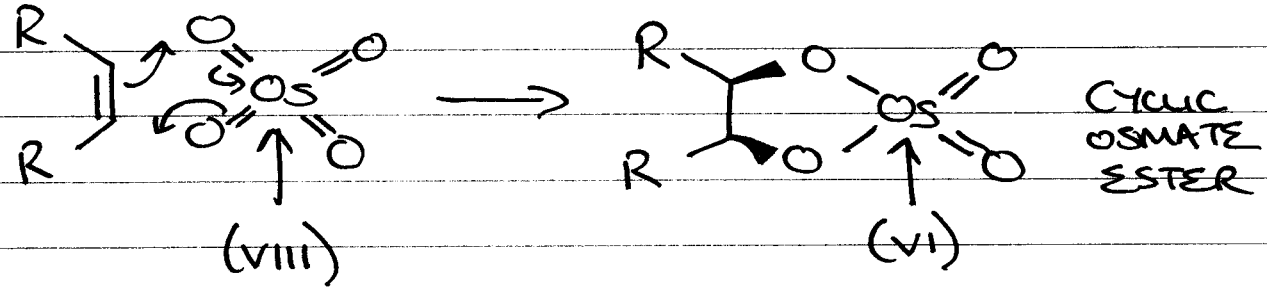


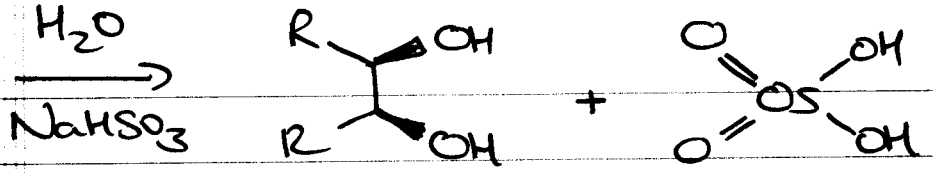


④ OXIDATION

(i) OSO_4 osmium tetroxide



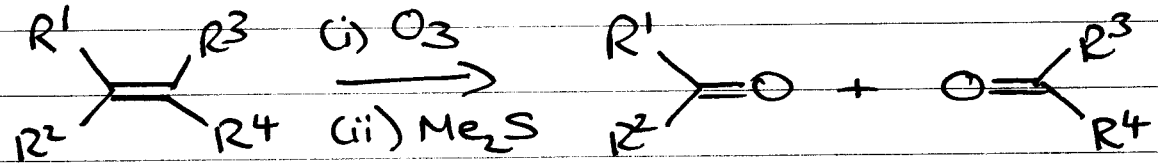


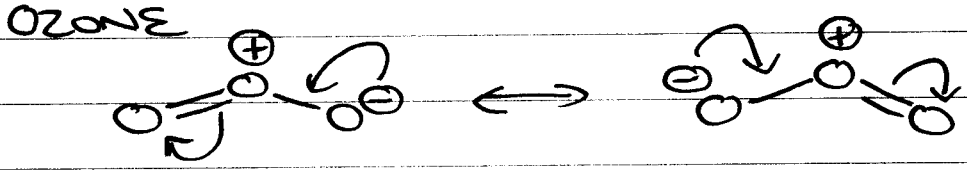


needs to be re-oxidised
- expensive
- toxic

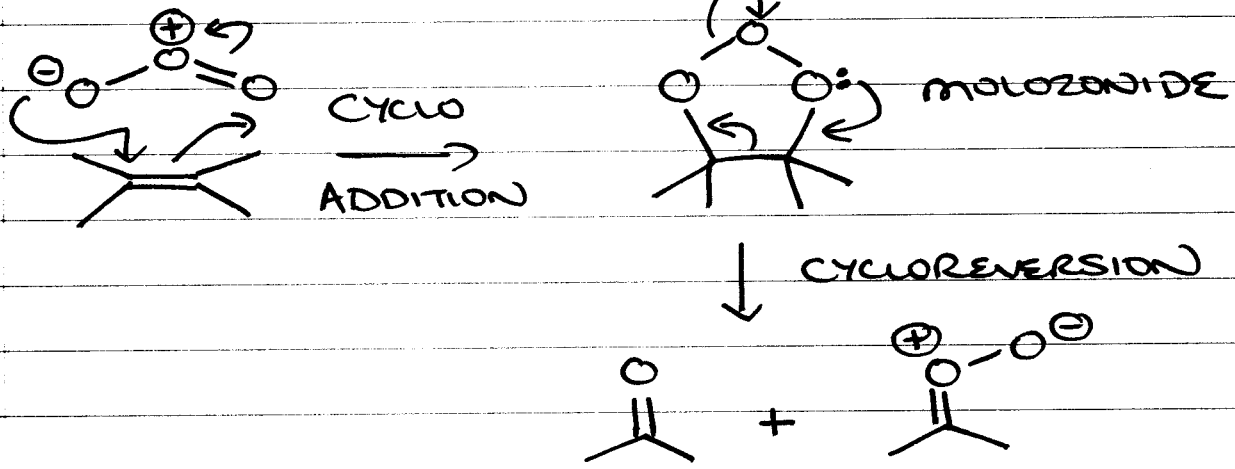
OS REDUCED (VIII → VI), ALKENE OXIDISED

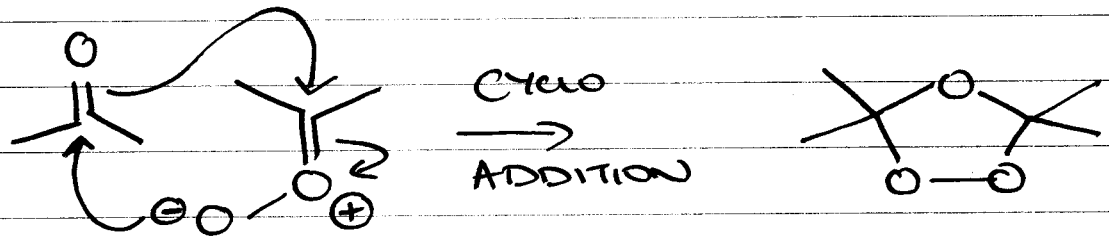
(ii) OZONOLYSIS



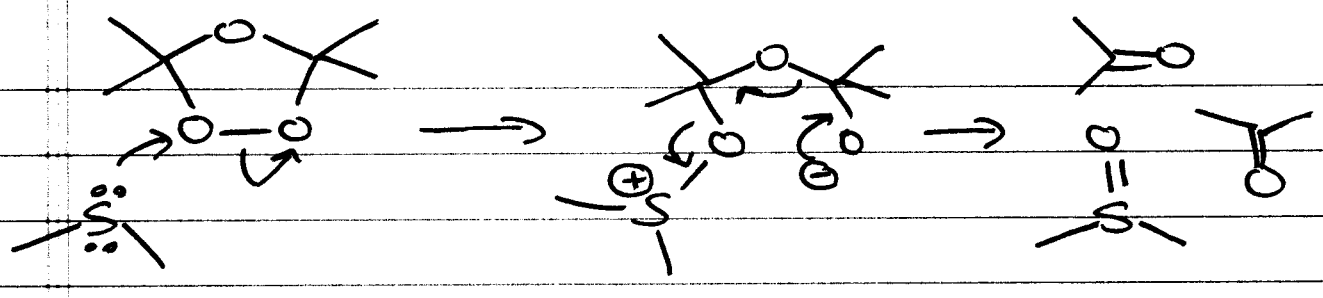


mechanism:





OZONIDE



next up... REDUCTION

LEC (17) CHEM 30A Nov 9th

(1) OXIDATION READ 6.5-6.7, 7.6
(2) REDUCTION PROBLEMS 6.41-6.52
(3) STEREOCHEMISTRY

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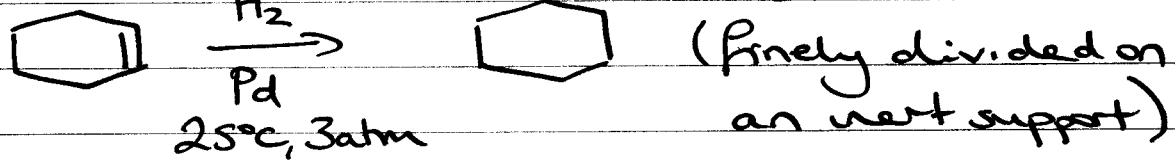
(1) See page 6-8 Lec (16)

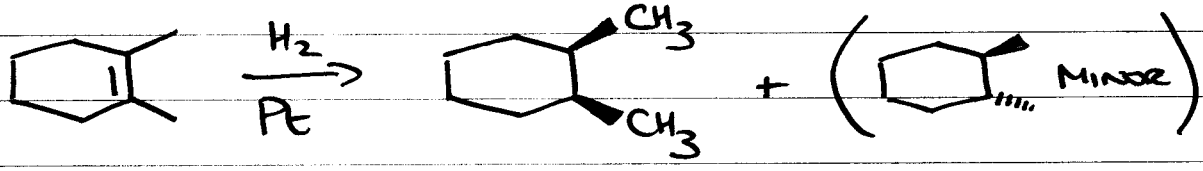
(2) REDUCTION



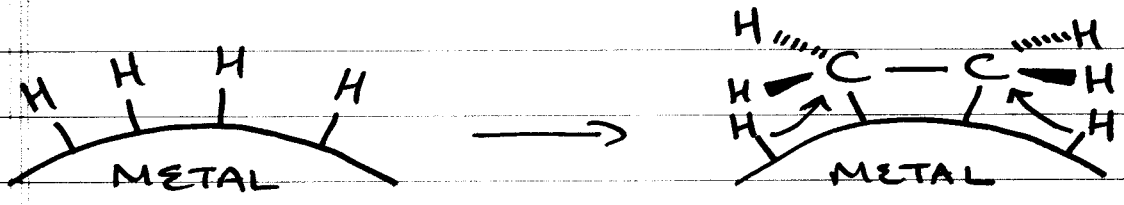
Transition metal catalyst Pt, Pd, Ru, Ni

CATALYTIC REDUCTION / HYDROGENATION

- Stereoselective

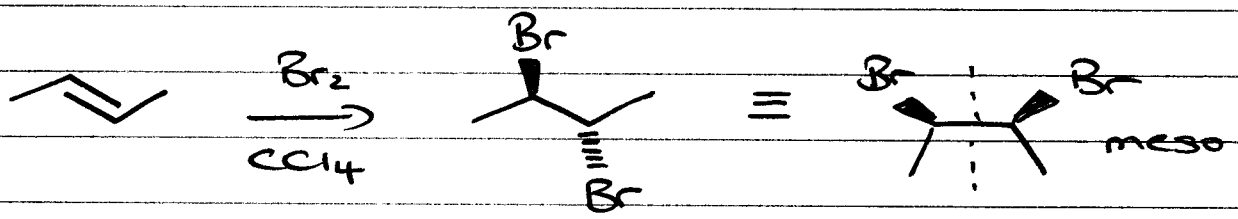


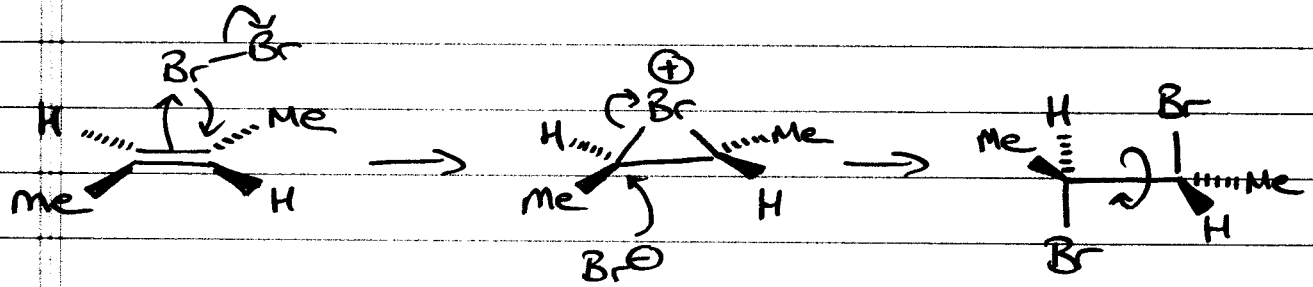
mechanism

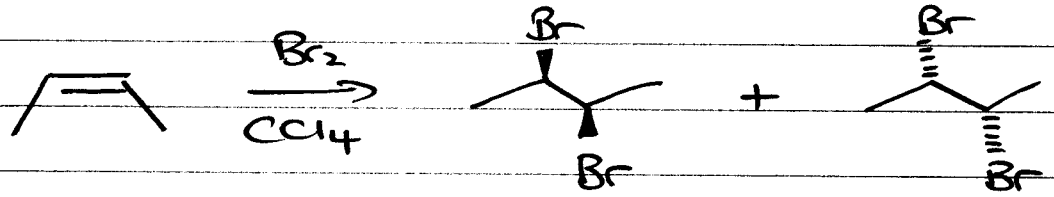


MINOR PRODUCTS result from isomerisation of the alkene on the metal catalyst

(3) STEREOCHEMISTRY (again)

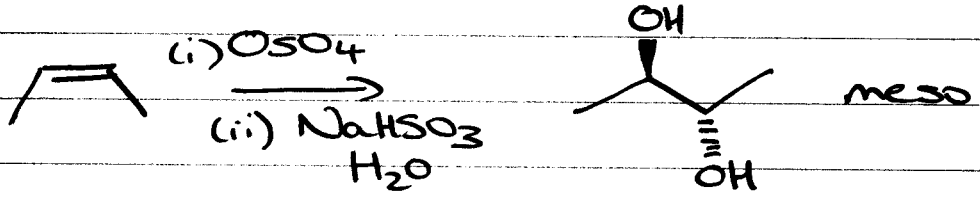


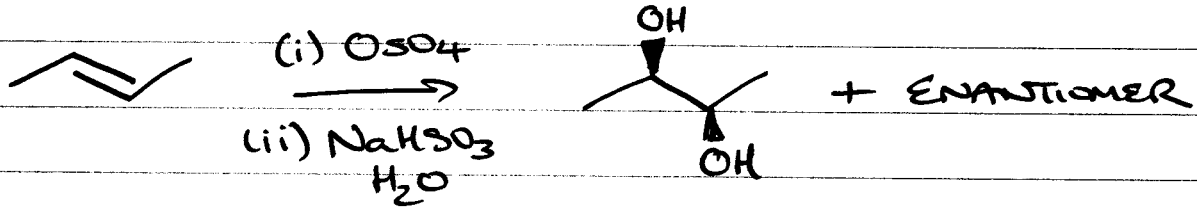




ENANTIOMERS

WORK THRU MECHANISM





Again, work through the mechanisms and show how you get to each product.

LEC (18) CHEM 30A Nov 14th

REACTIONS of ALKYNES READ 7.6-7.9, 9.1, 9.2

(1) ADDITION of X_2 PROBLEMS 7.4, 7.5

(2) ADDITION of HX 7.10-7.12, 7.16-7.18

(3) OXYMERCURATION ALKENE PROB SET

(4) HYDROBORATION

(5) REDUCTION

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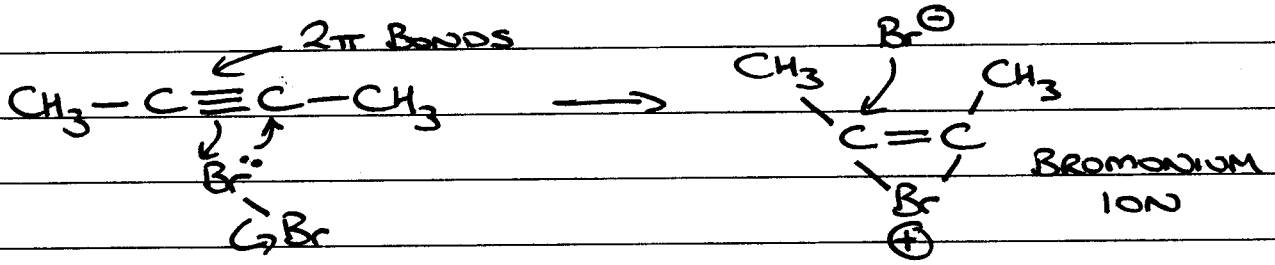
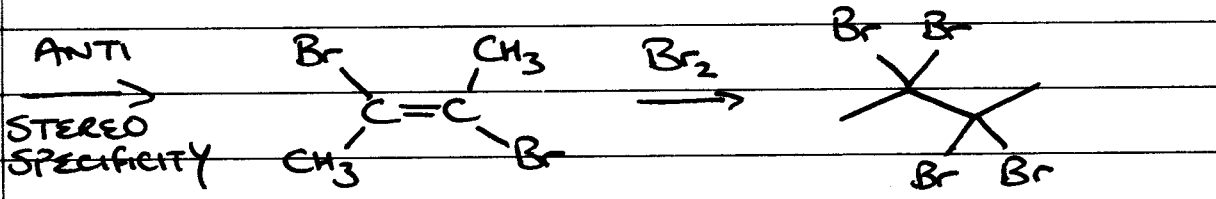
(1) ADDITION of X_2 (Br_2/Cl_2)

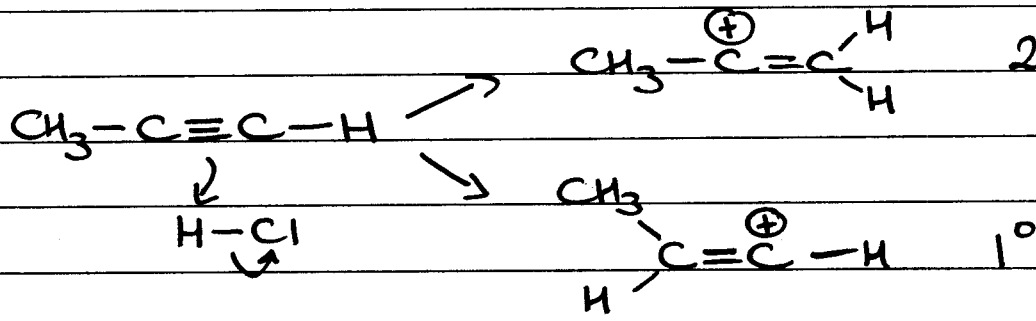




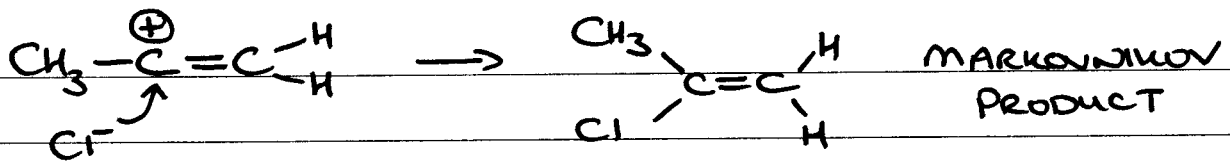
trans dibromide (DIFFICULT TO STOP HERE)

tetrabromoalkane

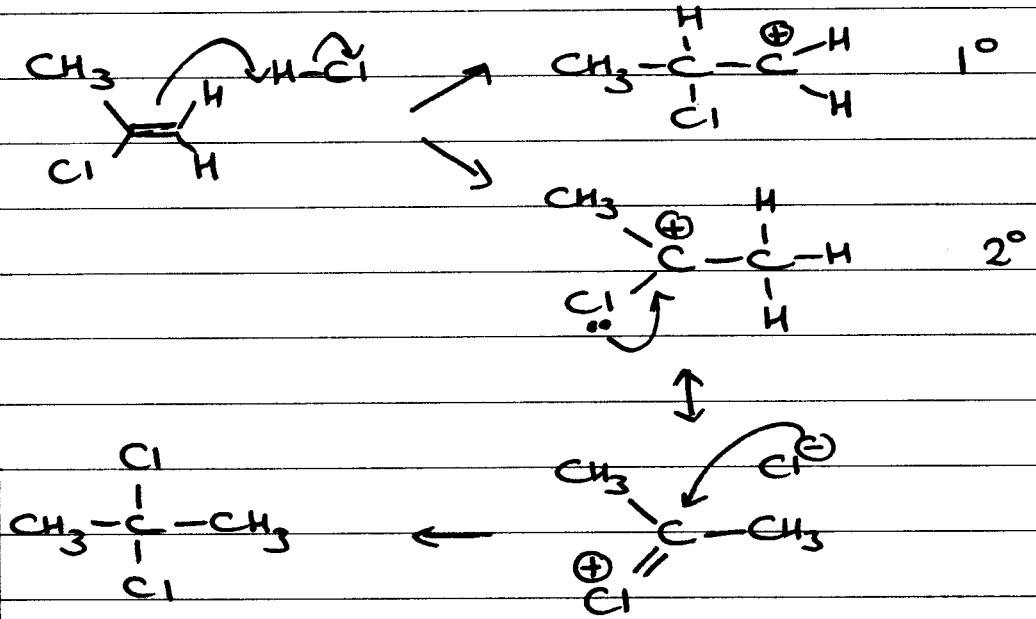
(2) HX (HCl, HBr, HI)



VINYL CARBOCATIONS (not very stable)



ALKENE PRODUCT COMPETES WITH ALKYNE FOR H-Cl IN THE REACTION (ALKENES MORE REACTIVE)

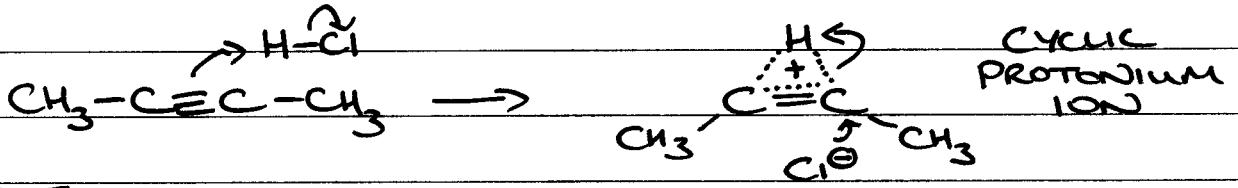


mechanisms actually more complicated, but this is not a bad model.

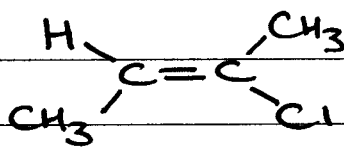
VINYLIC C^+ quite unstable

$2°$ VINYLIC $C^+ \cong 1° C^+$ not a viable reaction intermediate

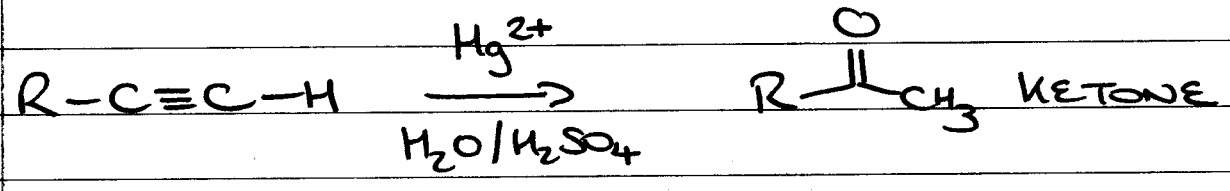
ALTERNATIVE:



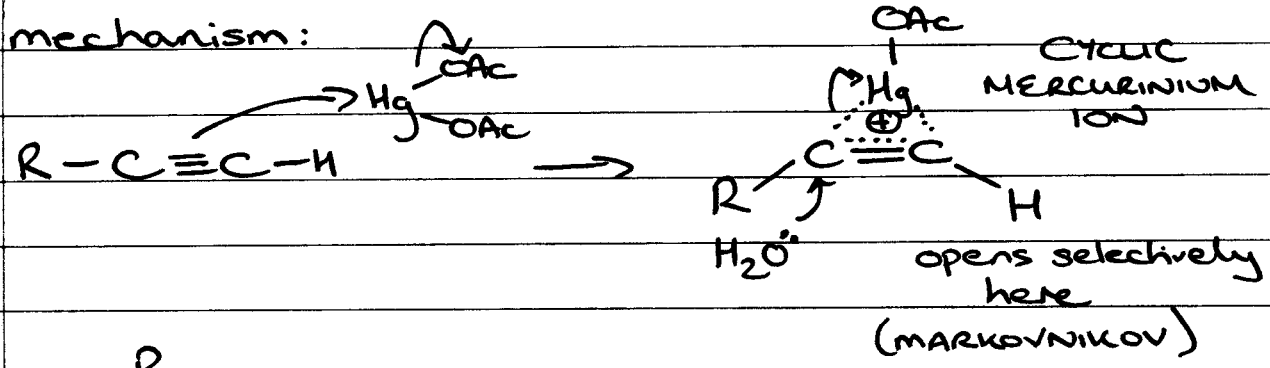
ACCOUNTS FOR OBSERVED TRANS SELECTIVITY

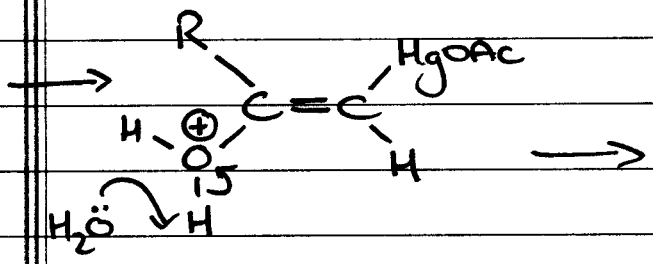


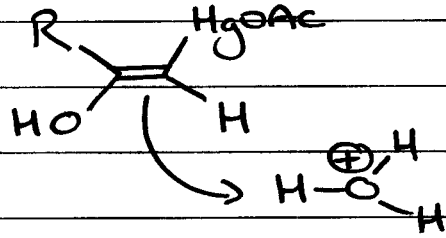
(3) OXYMERCURATION

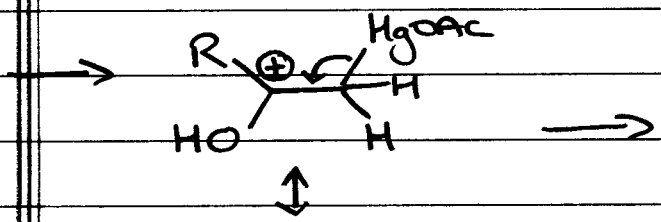


mechanism:

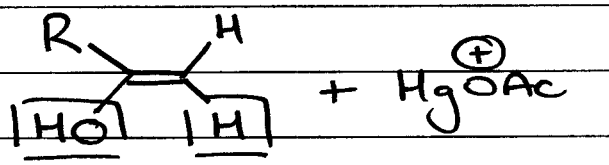






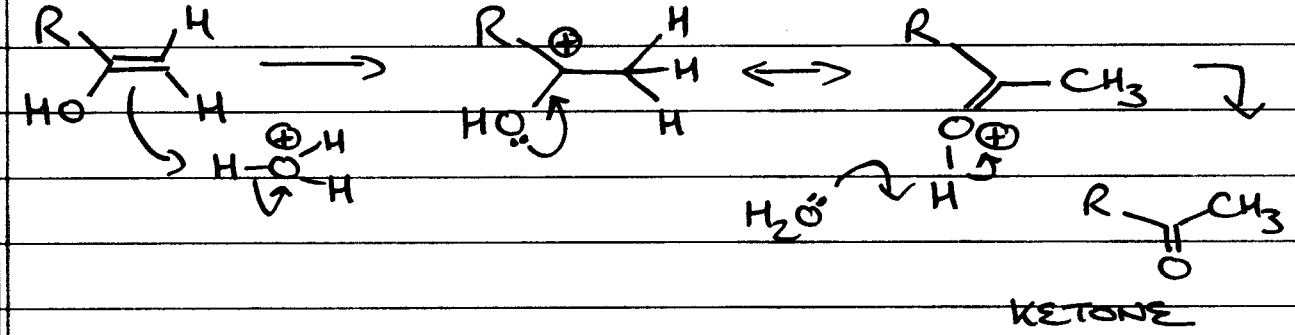


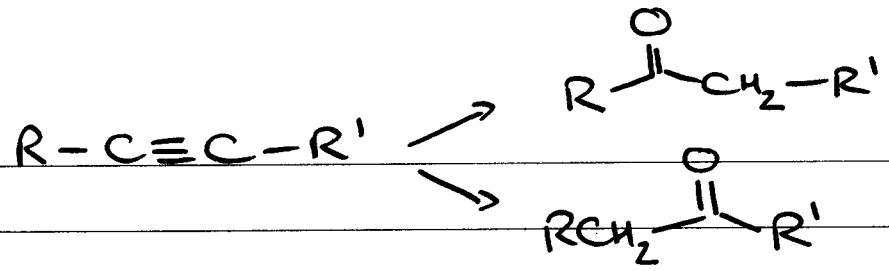
RESONANCE STABILIZED



ADDED H_2O ⇒ ENOL ACROSS C=C

KETO-ENOL TAUTOMERISATION

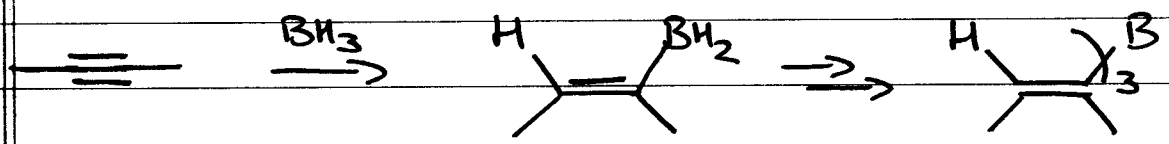




(4) HYDROBORATION

(R–C≡C–H, R–C≡C–R)

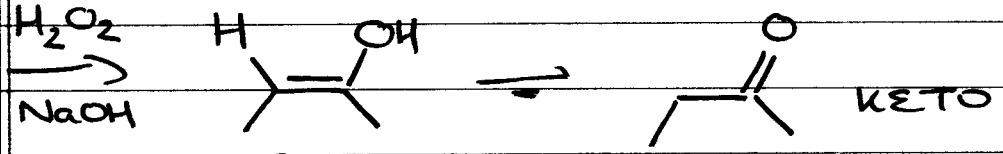
terminal non-terminal



cis

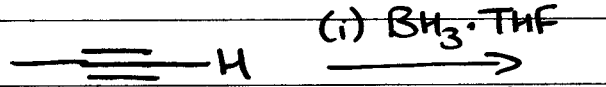
TRIALKENYL BORANE

(same mechanism as for alkenes)

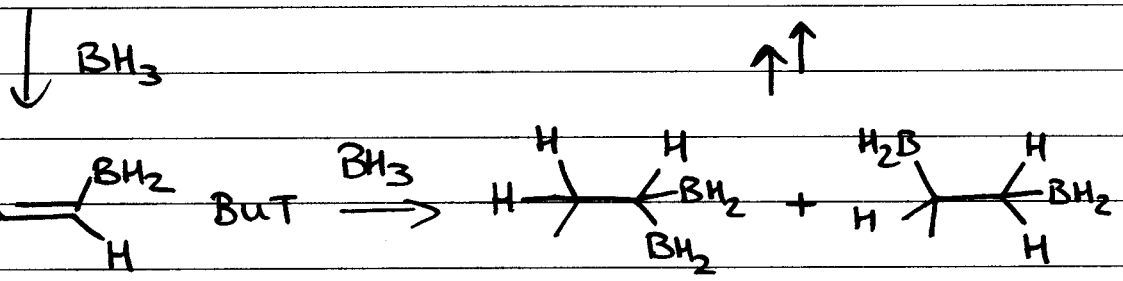


ENOL KETO

TERMINAL ALKYNES



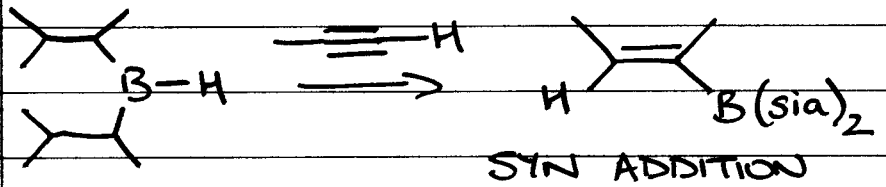
mixture of products



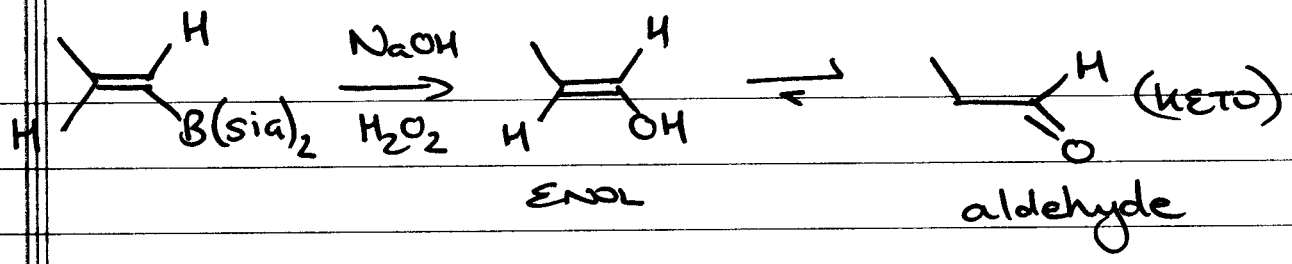
ANTI MARKOVNIKOV

STOPS HERE – ONLY ONE B–H ADDITION (STERICS)

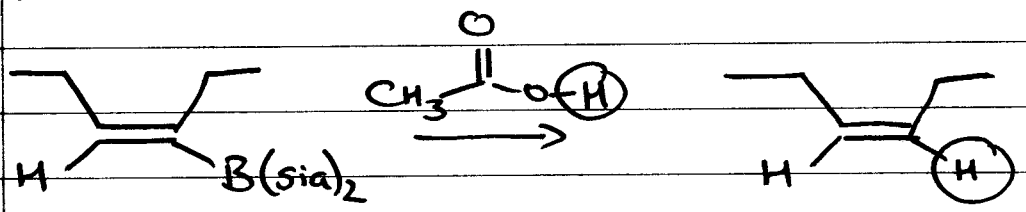
DISIAMYL BORANE $(sia)_2BH$



SYN ADDITION

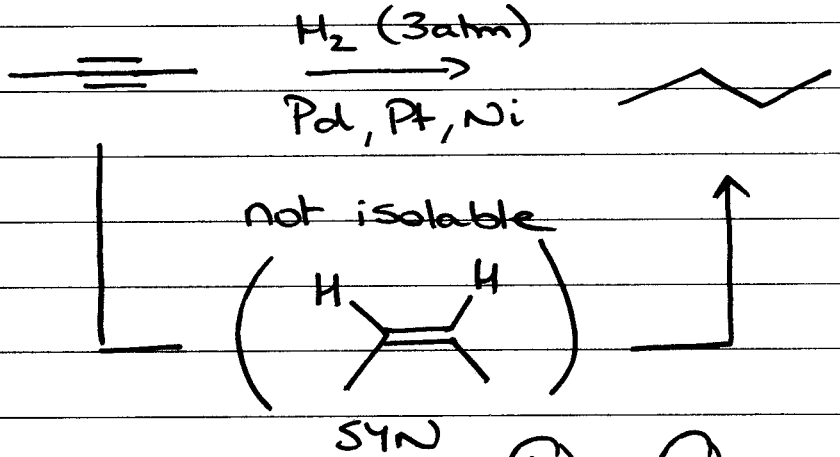


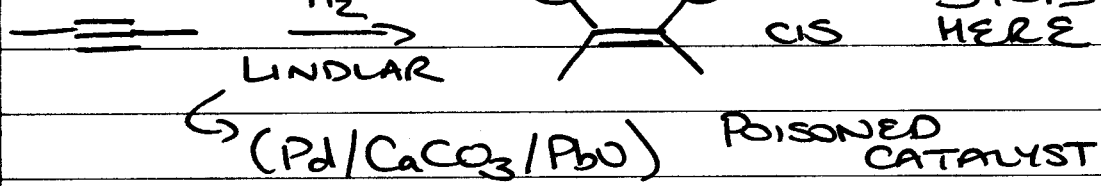
NOTE: RXN W/ ACETIC ACID

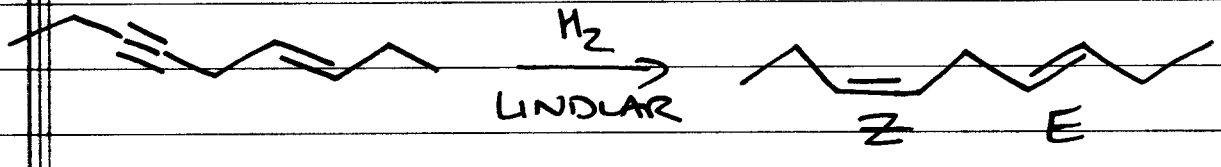


(5) REDUCTION

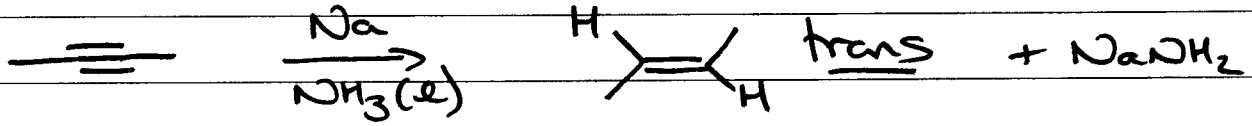
ALKYNE ⟶ [ALKENE] ⟶ ALKANE

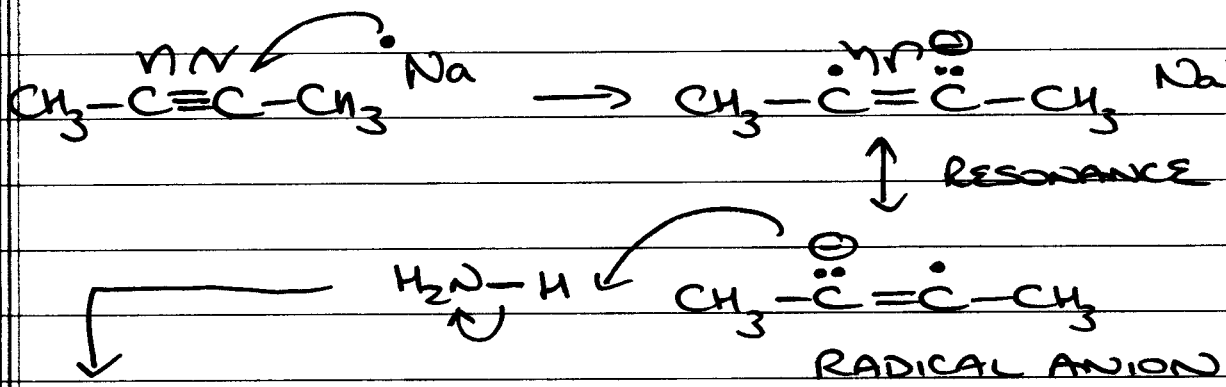
(i) 

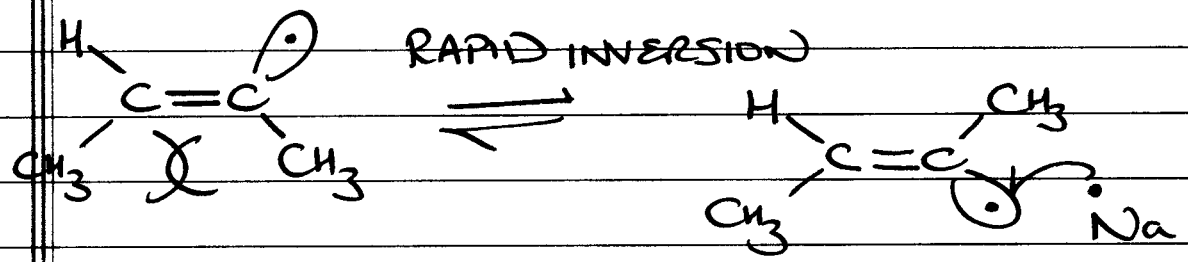
(ii) 

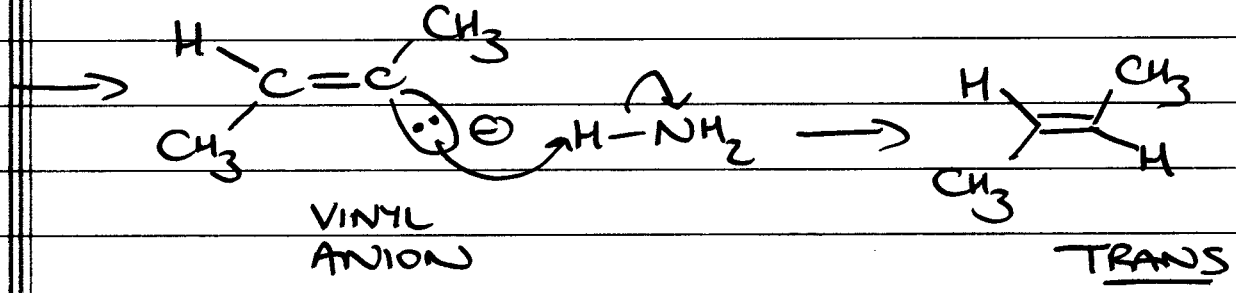


(iii) DISSOLVING METAL REDUCTION

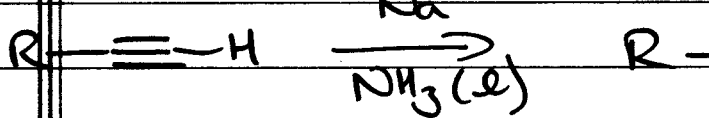








DOES NOT WORK FOR TERMINAL ALKYNES



LEC (19) CHEM 30A NOV 16th

(1) ALKYNES cont... READ 9.1-9.5

– NUCLEOPHILIC SUBSTITUTION PROBLEMS 9.1-9.30

(1) INTRODUCTION

(2) MECHANISMS MIDTERM on MONDAY

(3) ELECTROPHILE LAST NAME A-J CS76 K-Z CS50

(4) NUCLEOPHILE

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(1) ALKYNES - DISSOLVING METAL REDUCTION

See last page of LEC (18)

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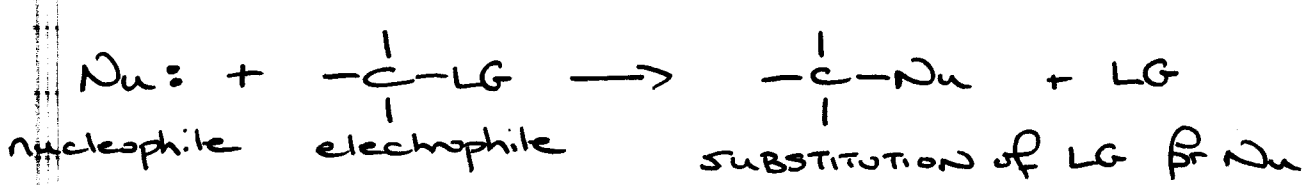
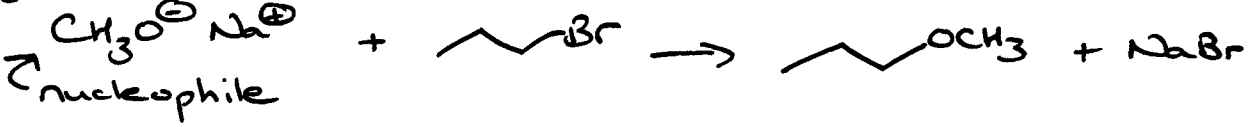
(1) INTRODUCTION TO NUCLEOPHILIC SUBSTITUTION

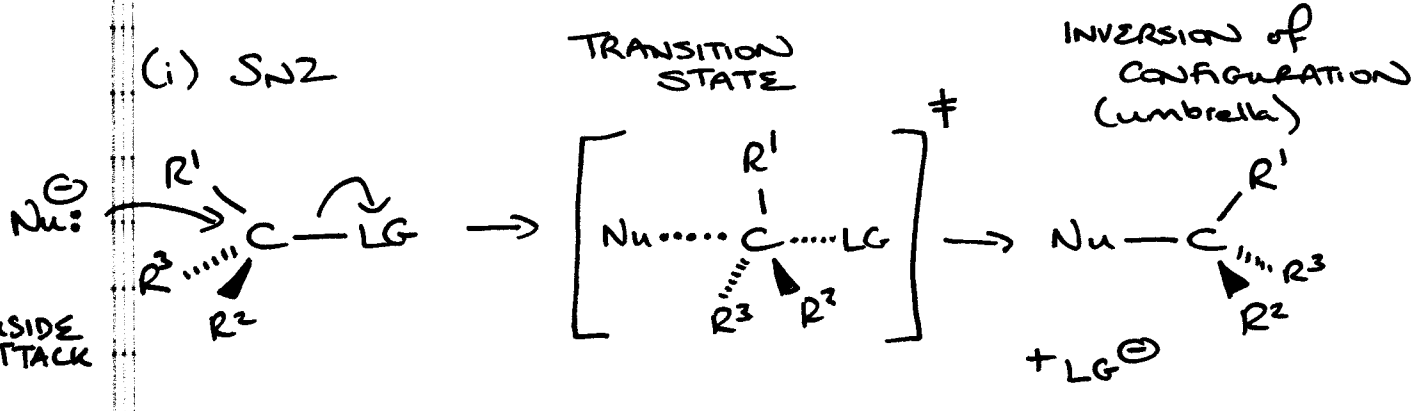


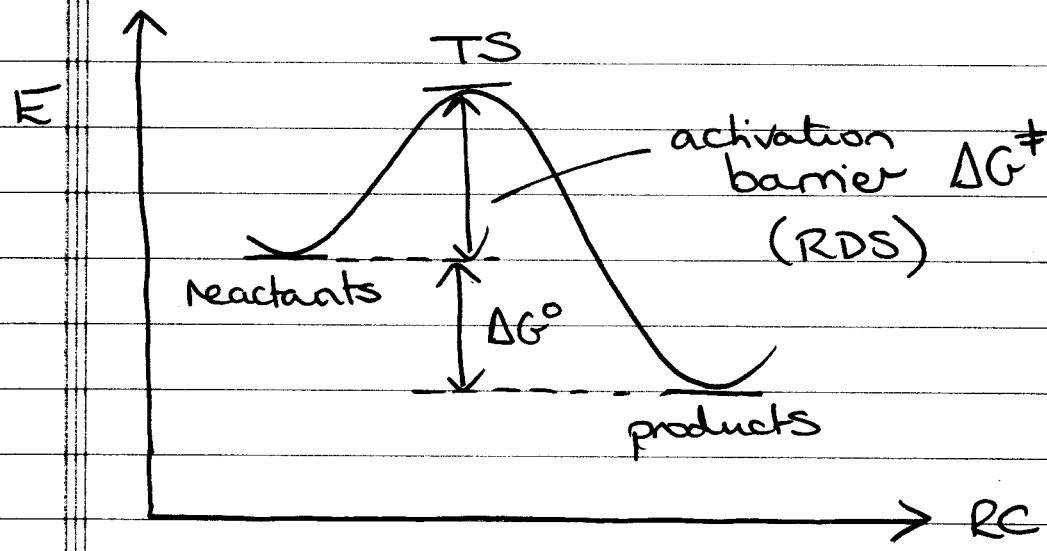
e.g.



(2) MECHANISMS (TWO LIMITING ONES)

(i) SN2





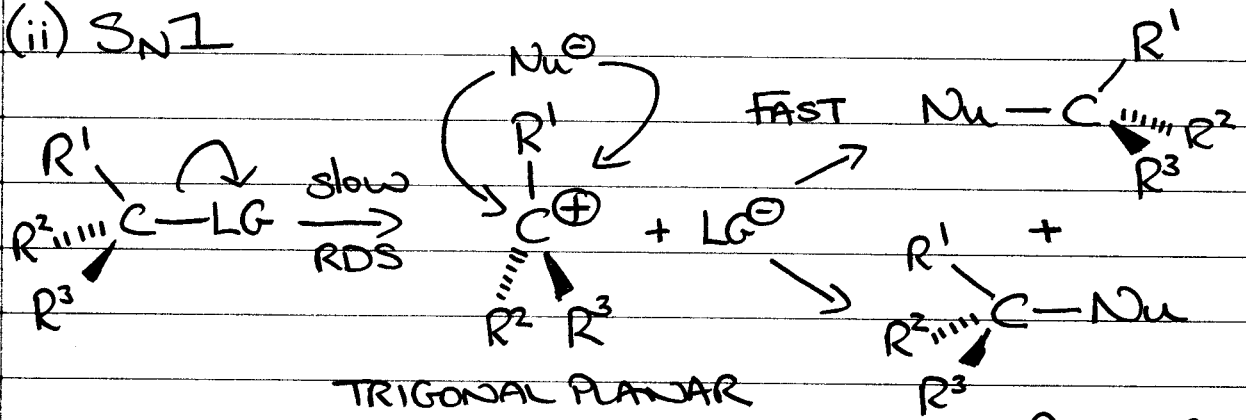
S_N2 = SUBSTITUTION, NUCLEOPHILIC, BIMOLECULAR

BIMOLECULAR – Rate of reaction is dependant upon the concentrations of <u>both</u> the NUCLEOPHILE and the ELECTROPHILE

$$\text{rate} = k_2[Nu][E]$$

k_2 ← 2nd order rate constant

(ii) S_N1



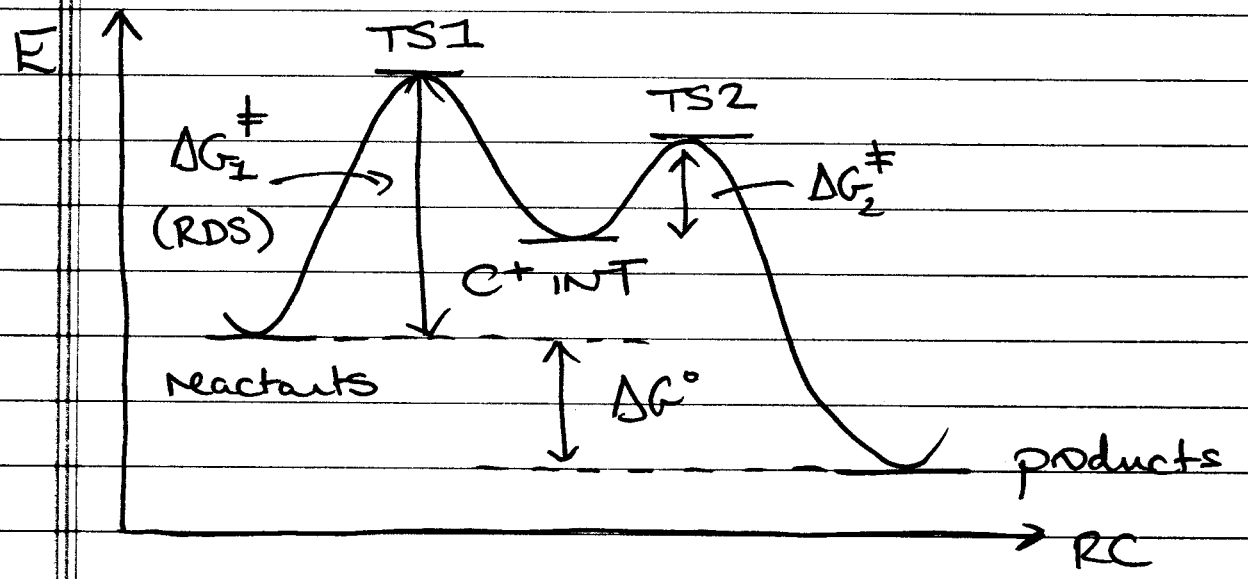
REARRANGEMENT ⇐

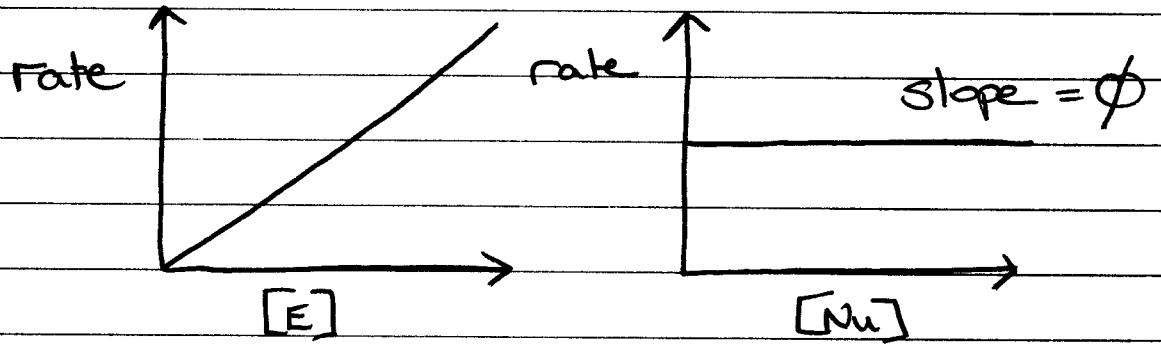
ANY STEREOCHEMICAL INFORMATION IN THE STARTING MATERIAL IS LOST

S_N1 - SUBSTITUTION, NUCLEOPHILIC, UNIMOLECULAR

Rate depends only on [E] rate = k_1[E]

first order rate constant

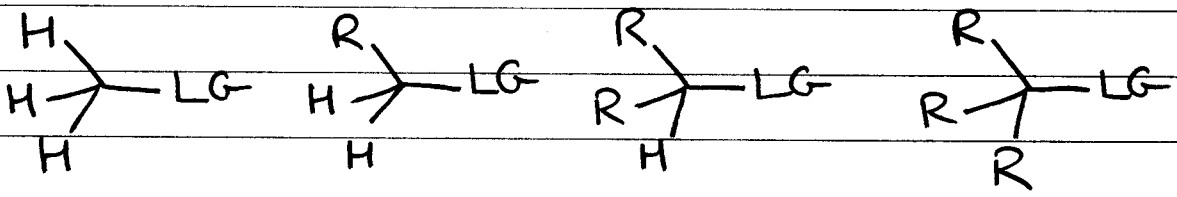




RDS does NOT involve the nucleophile, so adding more of it to the reaction does not alter the rate ⇒ Also, reactivity of the NUCLEOPHILE does not matter

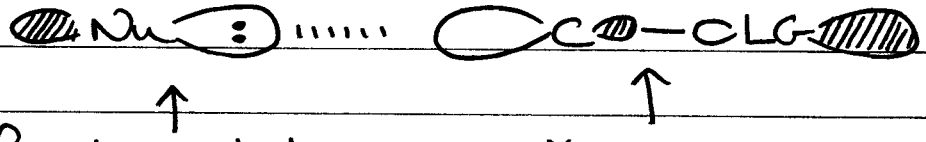
What decides S_N1 vs S_N2 ?

(3) THE ELECTROPHILE



methyl primary secondary tertiary

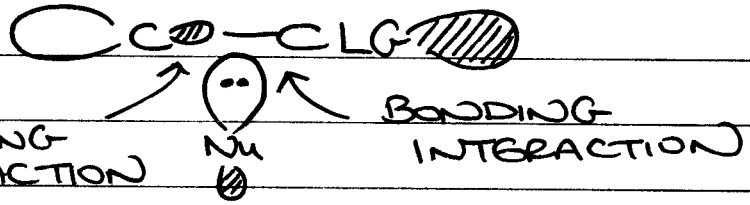
S_N2 — BACKSIDE ATTACK



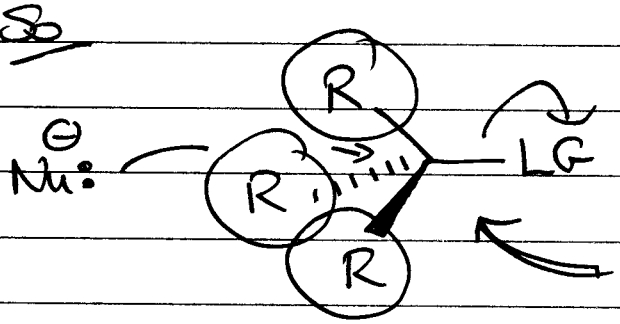
filled orbital in nucleophile

σ^* - empty antibonding orbital

FRONTSIDE ATTACK?



So



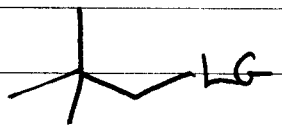
more R GROUPS, more STERIC CROWDING

Relative rates of S_N2 reactions

CH_3-LG	1
CH_3CH_2-LG	0.03
$(CH_3)_2CH-LG$	8×10^{-4}
$(CH_3)_3C-LG$	~0

DECREASING RATE ↓

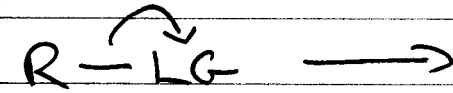
Some 1° groups also slow things down:



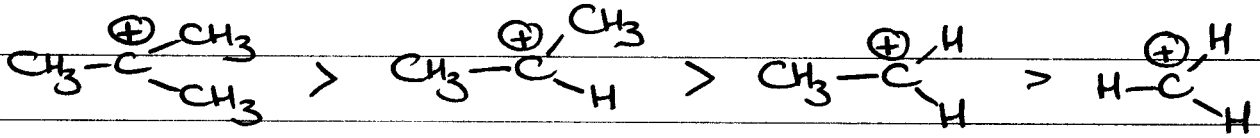
2×10^{-7}

neo-pentyl

CONSIDER S_N1 REACTIONS : OPPOSITE



C^+ STABILITY

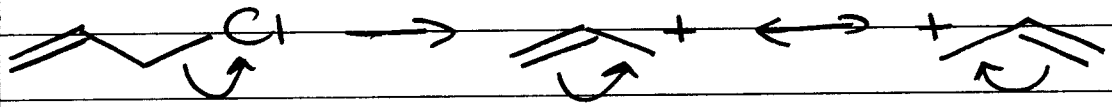


So, 1° and CH_3 electrophiles S_N2

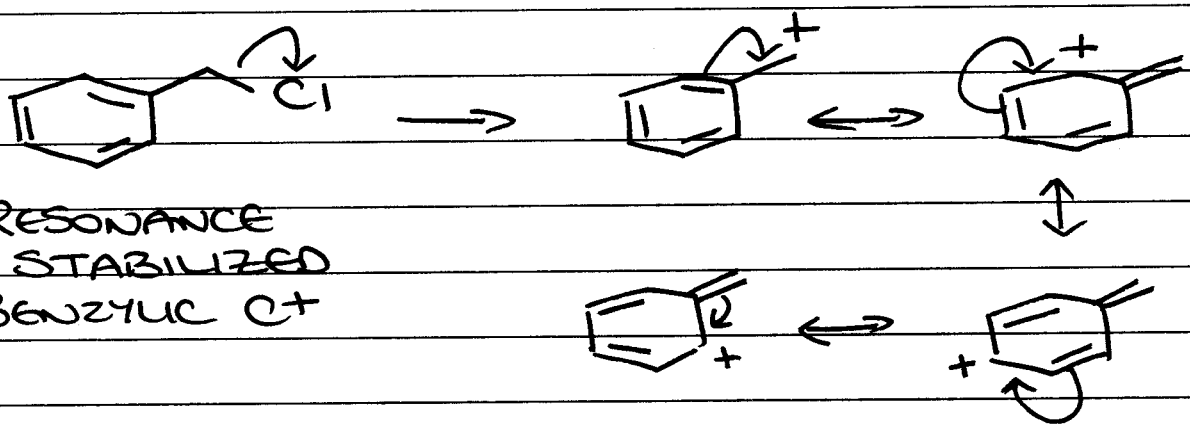
3° electrophiles S_N1 (WHAT ABOUT SECONDARY?)

2° C+ can react either way – depending on other factors

- other types of C+



RESONANCE STABILIZED
1° ALLYLIC



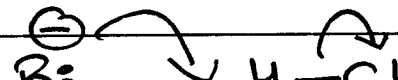
RESONANCE
STABILIZED
BENZYLIC C+

1° ALLYLIC / BENZYLIC electrophiles
SN1 vs SN2 (other factors, Nu, LG, solvent)
STERICS favors SN2 ELECTRONICS favors SN1

2°/3° ALLYLIC / BENZYLIC electrophiles
almost exclusively SN1

(4) NUCLEOPHILE

Consider BASICITY



LEC (20) CHEM 30A Nov 18th

NUCLEOPHILIC SUBSTITUTION

MIDTERM MONDAY
A-J CS76
K-Z CS50

(1) ELECTROPHILE
(2) NUCLEOPHILE
(3) LEAVING GROUP
(4) SOLVENT

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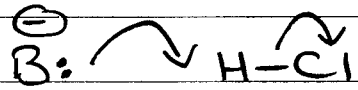
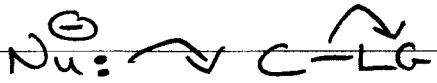
(1) ELECTROPHILE
Page 6 from LEC (19)

(2) NUCLEOPHILE

consider BASICITY 

NUCLEOPHILICITY is similar 

- affinity for a CARBON atom
- KINETIC rather than THERMODYNAMIC effect

IMPRECISE QUANTITY - for any given species can vary depending upon other factors (SOLVENT / ELECTROPHILE)

- General trends

(i) same nucleophilic atom
PARALLELS BASICITY

$HO^{\ominus}$ > $CH_3C(=O)-O^{\ominus}$ > H_2O: X

16 5 −2 pka of HX

consider CHARGE | RESONANCE

(ii) nucleophiles in same row
PARALLELS BASICITY

$CH_3^{\ominus}$ > $NH_2^{\ominus}$ > $HO^{\ominus}$ > $F^{\ominus}$

consider ELECTRONEGATIVITY

(iii) nucleophiles in the same group
(COMPLICATED)
SIZE MATTERS

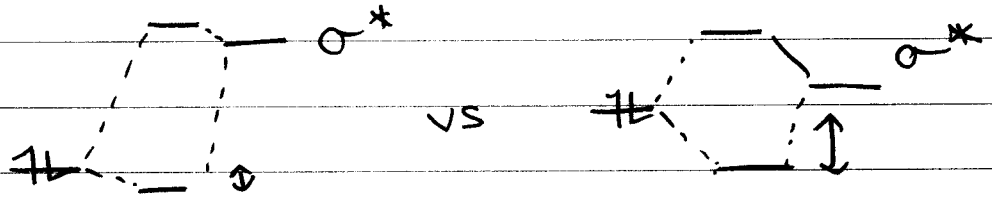
In general nucleophilicity increases going down a group...

$HS^{\ominus}$ > $HO^{\ominus}$

$I^{\ominus}$ > $Br^{\ominus}$ > $Cl^{\ominus}$ > $F^{\ominus}$

- opposite to BASICITY - why?

a) ENERGY LEVELS
- higher energy of lp electrons as you go down the periodic table → better overlap with σ^*



(b) POLARISABILITY

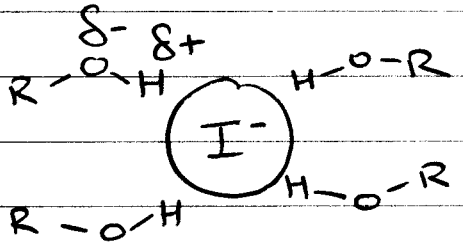
Larger atoms => more diffuse e^- clouds => GREATER POLARISABILITY, and bonds can begin to form at greater INTERATOMIC DISTANCES.

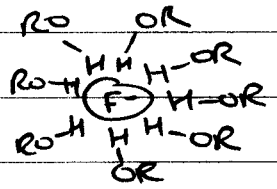
(c) SOLVENT (large effect – more later)

– POLAR PROTIC (H_2O, MeOH, EtOH, $H-\overset{\ominus}{\underset{|}{\perp}}OH$)
– POLAR APROTIC (DMSO, DMF, MeCN, Acetone)

POLAR PROTIC SOLVENTS

$I^\ominus > Br^\ominus > Cl^\ominus > F^\ominus$





LOW CHARGE DENSITY
(weak solvent cage)

HIGH CHARGE DENSITY
(strong solvent cage)

HYDROGEN BONDING

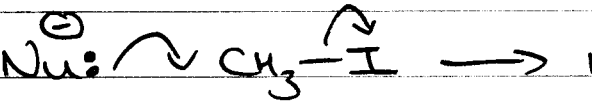
$X^{\delta-}—H^{\delta+} \cdots\cdots Y^\ominus$

↑ EN element

So, smaller Nu = higher charge DENSITY => more SOLVATED => less nucleophilic

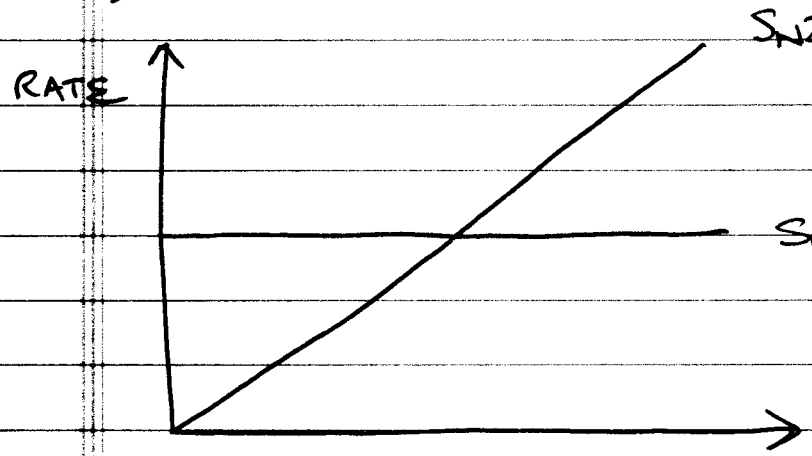
BUT

IN POLAR APROTIC SOLVENTS, anions only weakly solvated & trend is reversed (for halogens) and correlates w/ BASICITY

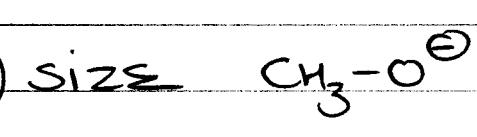


Nu	pKa	MeOH (time to complete RXN)	DMF	equivalent polarities
I^-	−10	17 min	8.7 s	overall message
Br^-	−8	12 h	8.7 s	POLAR APROTIC SOLVENTS GOOD
Cl^-	−6	13 d	1.4 s	
F^-	3	2 yrs	< 1.2 s	

So SN1 vs SN2



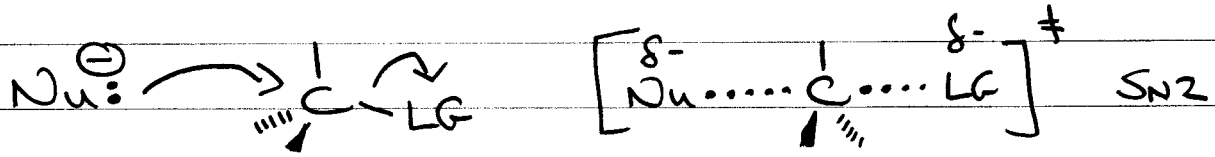
↳ no effect on SN1, but stronger Nuc favors SN2

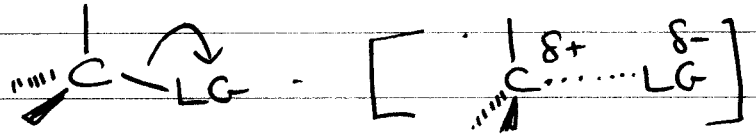
d) SIZE  VS

methoxide pKa 15.5 t-butoxide pKa ~18

tBuO$^{\ominus}$ more basic than MeO$^{\ominus}$, but less nucleophilic due to BAD STERICS

(3) LEAVING GROUP





LG develops -ve CHARGE in TS, so better charge stabilization, lower energy TS, faster RXN.

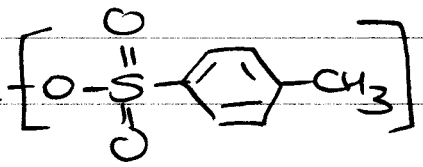
<u>THUS</u> more ACIDIC H–LG, more stable LG$^{\ominus}$

GOOD/BAD LG

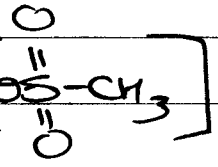
- relative reactivity

$NH_2^{\ominus}$	$OH^{\ominus}$	$OR^{\ominus}$	$F^{\ominus}$	$Cl^{\ominus}$	$Br^{\ominus}$	$I^{\ominus}$
$<<1$			1	200	10000	30000

other good LG

tosylate 

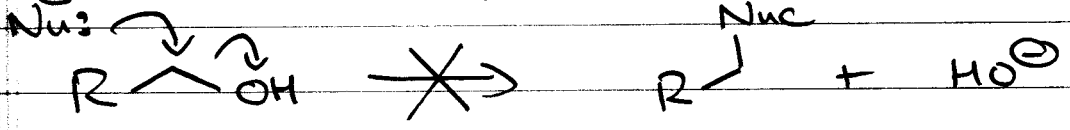
~60,000



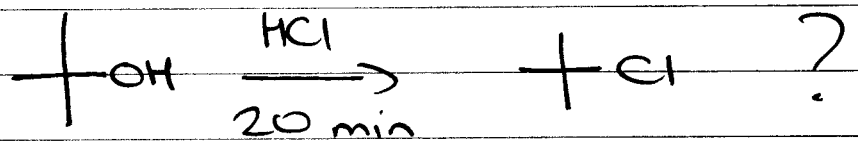
mesylate

So, R-F, R-OH, R-OR', $R-NH_2$

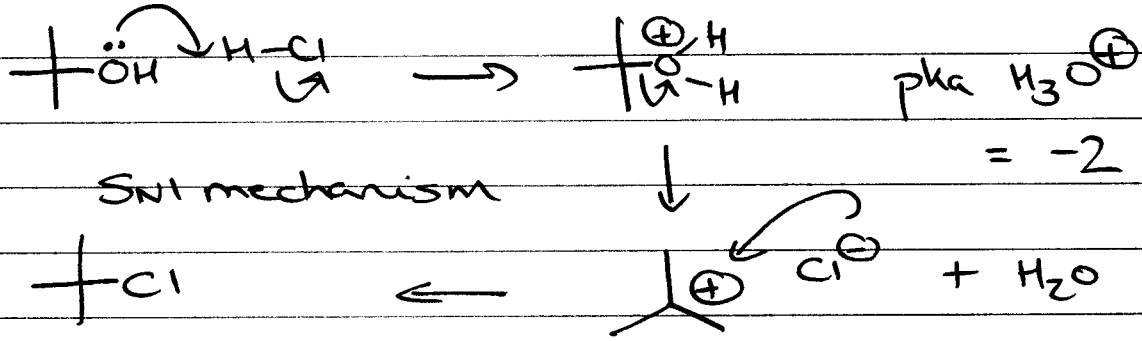
do NOT undergo S_N2 reactions



BUT



-OH converted into good leaving group



IN S_N2, as long as $LG^⊖$ more stable than $Nu^⊖$, reaction can proceed.

BUT LG ABILITY ALONE cannot determine S_N1 vs S_N2

LEC (21) CHEM 30A Nov 28th

Nucleophilic substitution

(1) LEAVING GROUP — READ 9.1-9.8

(2) SOLVENT — PROBLEMS 9.1-9.36

(3) REARRANGEMENT — MY OH POSTPONED

(4) S_N SUMMARY

(5) NEIGHBORING GROUP PARTICIPATION

(6) PHASE TRANSFER CATALYSIS

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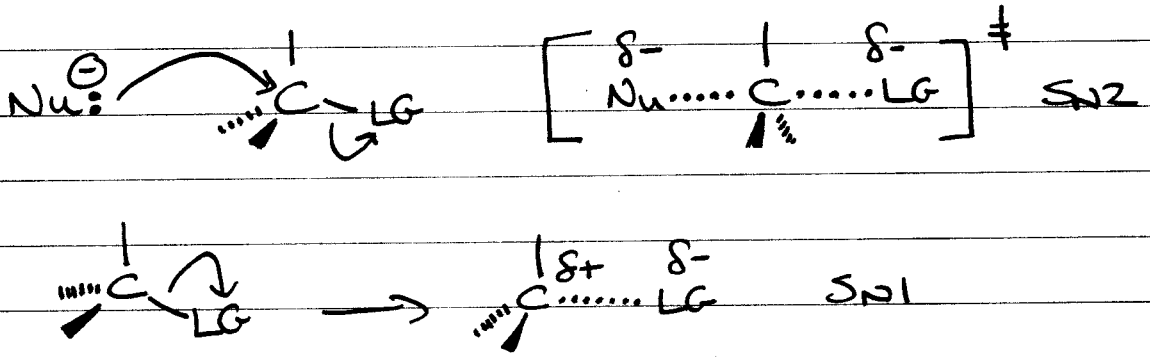
(1) LEAVING GROUP



LG develops -ve charge in TS, so better charge stabilization, lower energy TS, faster RXN.

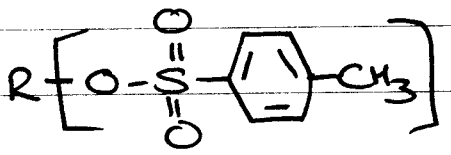
THUS more acidic H-LG, more stable $LG^{\ominus}$

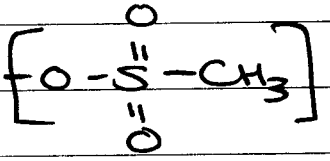
GOOD/BAD LEAVING GROUPS

- relative reactivity

$NH_2^{\ominus}$	$OH^{\ominus}$	$OR^{\ominus}$	$F^{\ominus}$	$Cl^{\ominus}$	$Br^{\ominus}$	$I^{\ominus}$
$\ll 1$			1	200	10000	30000

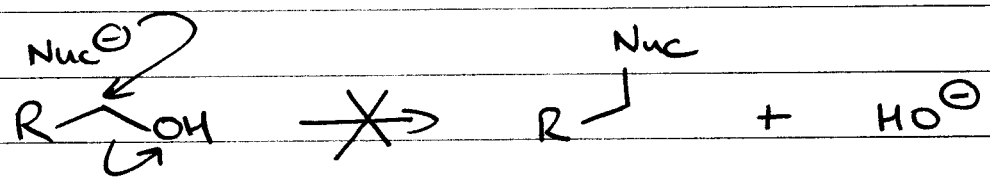
other good LG

tosylate  ~60,000

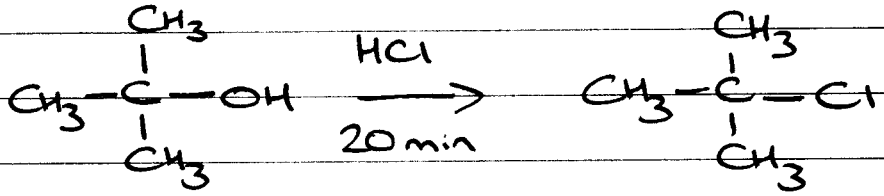
 mesylate

So R–F, R–OH, R–OR', R–NH$_2$

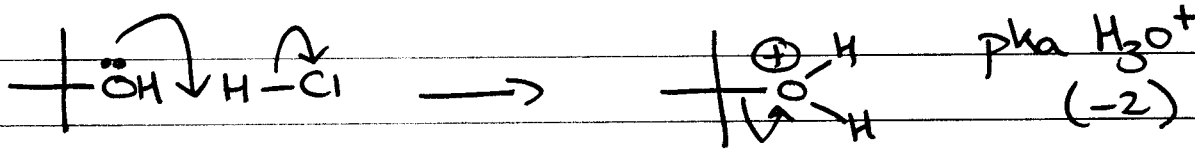
do NOT undergo S_N2 reactions



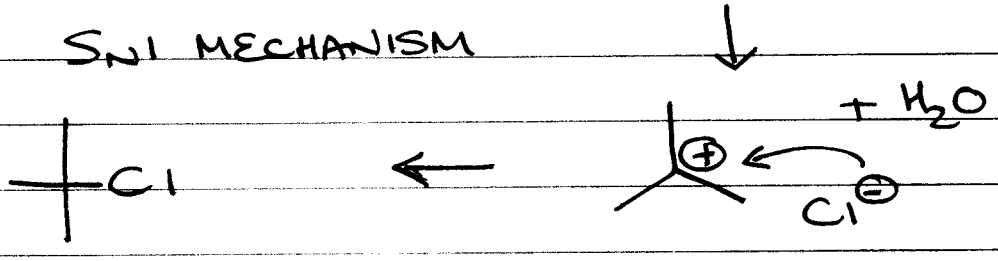
But

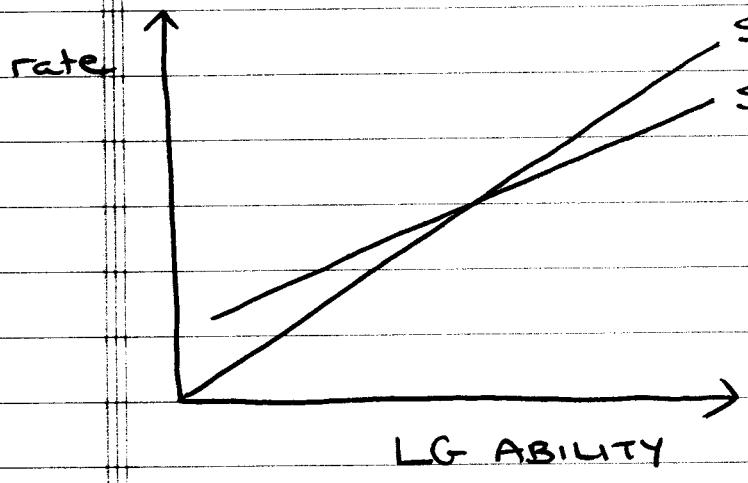


–OH converted into good LG



S_N1 MECHANISM





SN1 more sensitive to LG-ABILITY

$R\text{-}\overset{\curvearrowright}{LG} \rightarrow R^+ + LG^\ominus$

In SN2, as long as $LG^\ominus$ more stable than $Nu^\ominus$, reaction can proceed BUT LG ABILITY alone cannot determine SN1 vs SN2

(2) SOLVENT

- SN2 POLAR APROTIC solvents
  (solvate cations well, but not anions)

e.g. $NaBr \xrightarrow{\text{solvent}}$ Na^+ (solvated) + $Br^\ominus$ (solvated)

- SN1 $R\text{-}\overset{\curvearrowright}{LG} \rightarrow R^\oplus + LG^\ominus$
  creation & separation of charge

⟹ more POLAR the solvent, the better

$\text{-Cl} + R\text{-OH} \xrightarrow{\text{Solvolysis}} \text{-OH} + HCl$

Water/EtOH	rel. rate
100 / 0	100,000
80 / 20	14,000
40/60	100
0/100	1

So

SN2 reactions

DISFAVORED IN PROTIC SOLVENTS

(ground state energy lowered by SOLVATION)

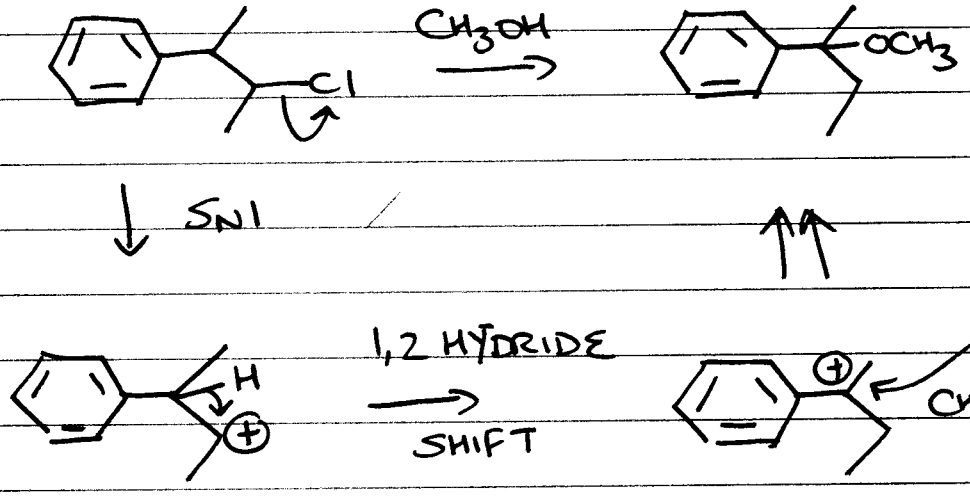
SN1 reactions

FAVORED IN PROTIC SOLVENTS

(transition state energy lowered by SOLVATION)

(3) REARRANGEMENT (SN1/C+)

e.g.



2° C+

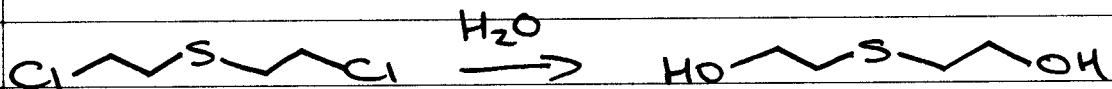
3°/BENZYLIC C+

(4) S_N Summary

Electrophile	S_N2	S_N1
Me / 1°	✓	X
2°	Good Nuc Polar Aprotic	Poor Nuc Polar Protic (Good LG)
3°	X	✓

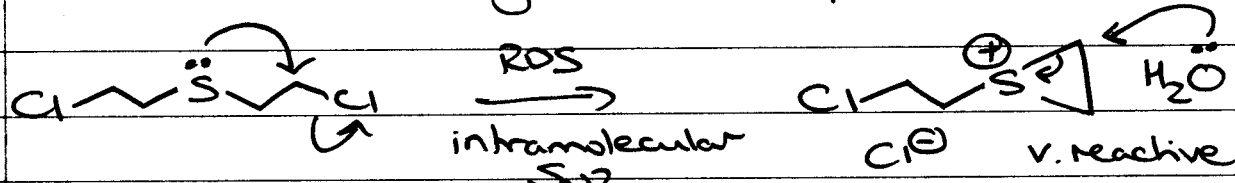
- gets complicated => elimination

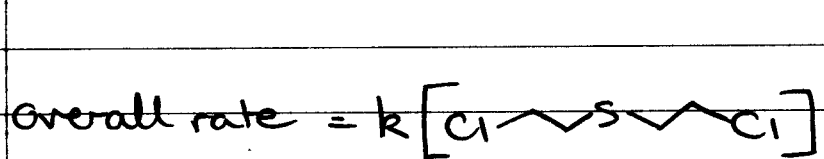
(5) Neighboring Group Participation

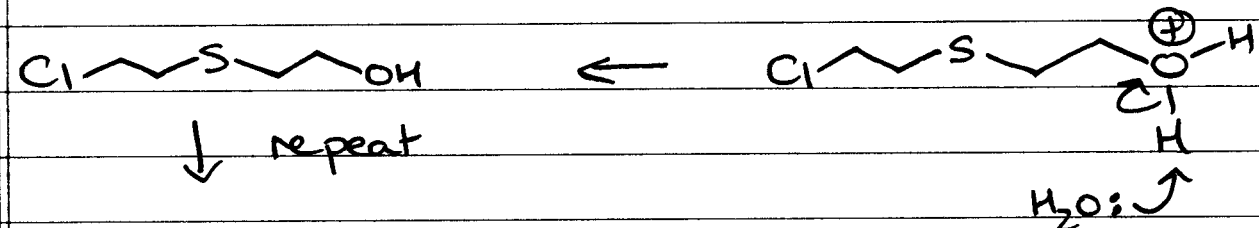


mustard gas

V. RAPID, even though H_2O is a poor Nucleophile





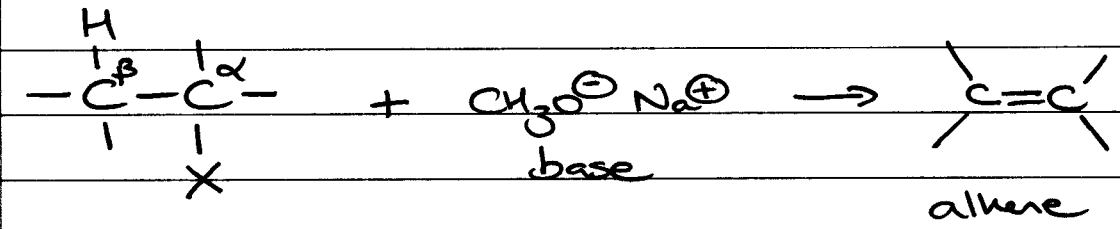


INDEPENDENT of [Nuc]

Two consecutive SN2 reactions with SN1 kinetics

(6) PHASE TRANSFER CATALYSIS
(read section in the book)

(7) INTRO TO β-ELIMINATION
- dehydrohalogenation (one example)

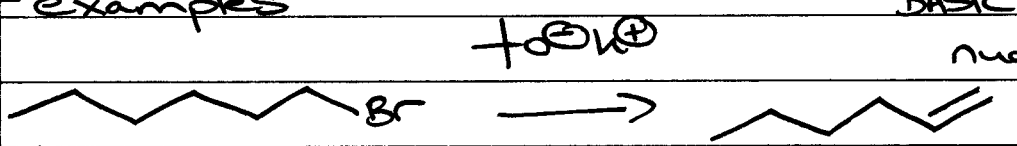


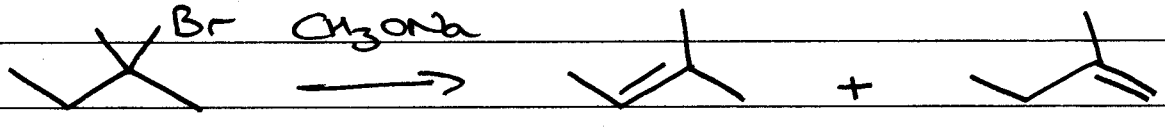
β-elimination

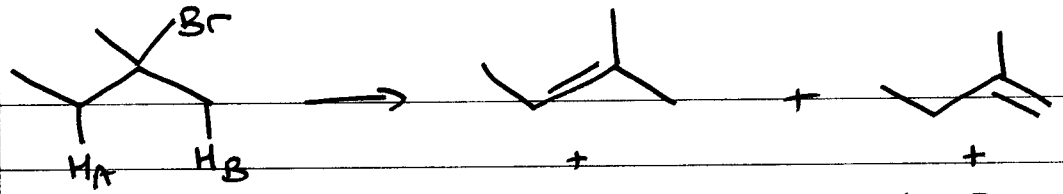
$CH_3OH + Na^{\oplus}X^{\ominus}$

ELIMINATION competes w/ SUBSTITUTION

- examples







β-PROTONS

ZAITSEV'S RULE → major product is the most substituted alkene (more stable)

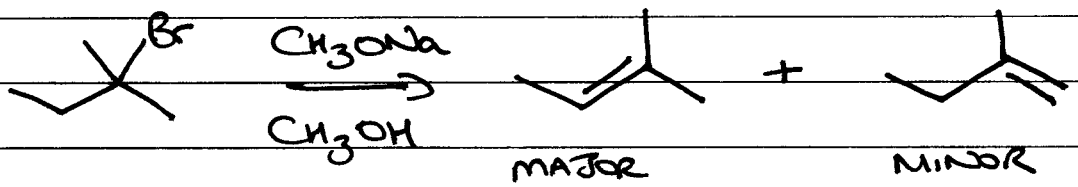
... and there are exceptions to this rule

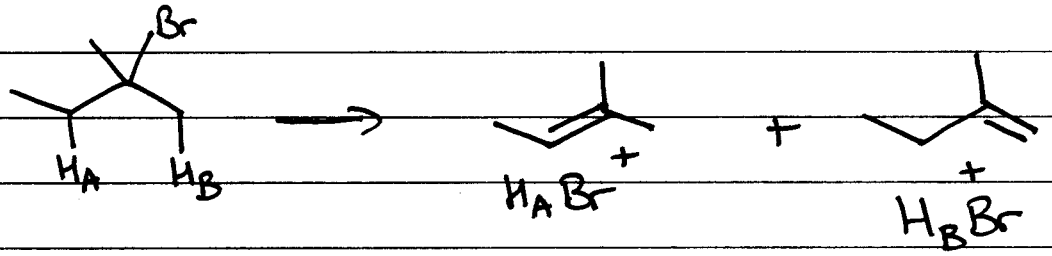
LEC (22) CHEM 30A Nov 30th

(1) INTRO TO β-ELIMINATION
(2) MECHANISMS
(3) STEREOCHEMISTRY
(4) SUMMARY

READ 9.5 - 9.11, PROBLEMS 9.37 - 9.42

(1) β-ELIMINATION

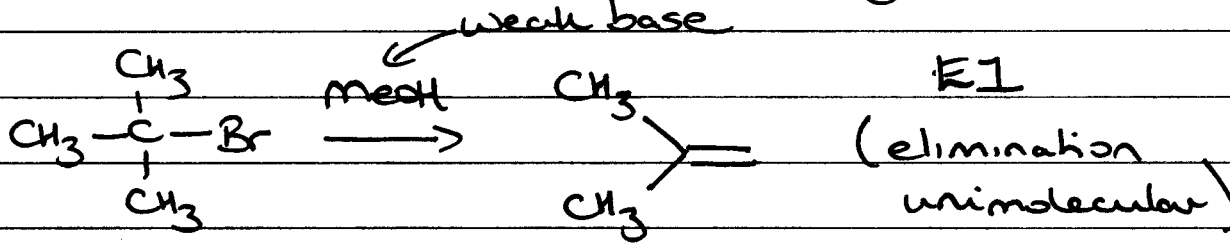




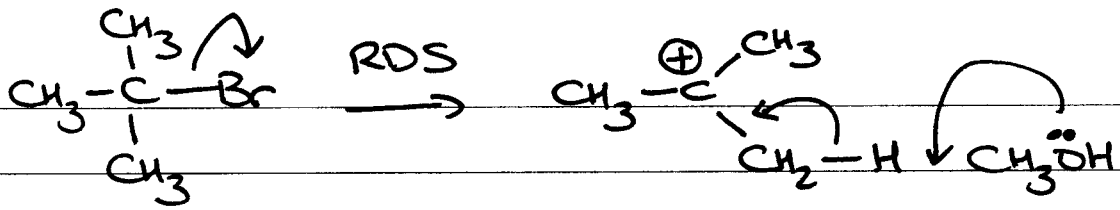
ZAITSEV'S RULE → major product is the most substituted alkene (more STABLE)

(2) MECHANISMS

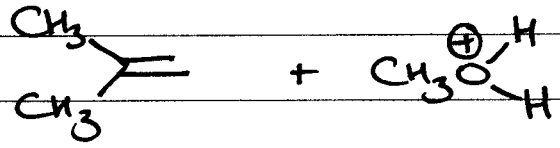
(like S_N reactions, two limiting ones)



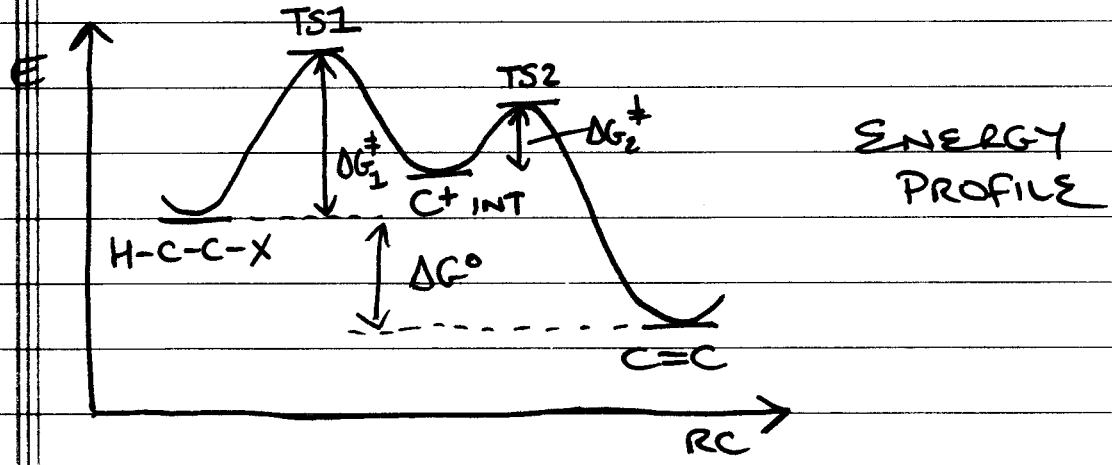
E1
(elimination unimolecular)



Competes with S_N1 reaction

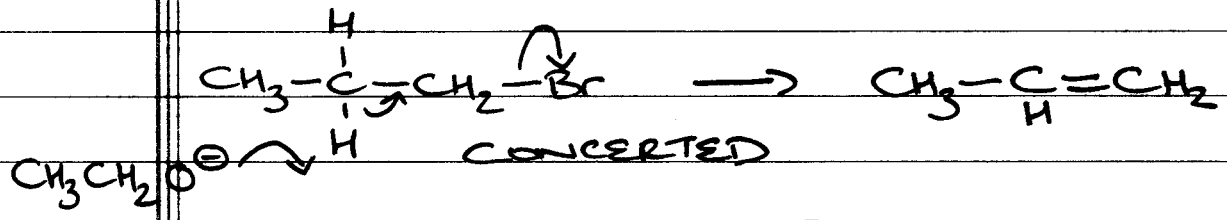


rate = $k_1[(CH_3)_3C-Br]$

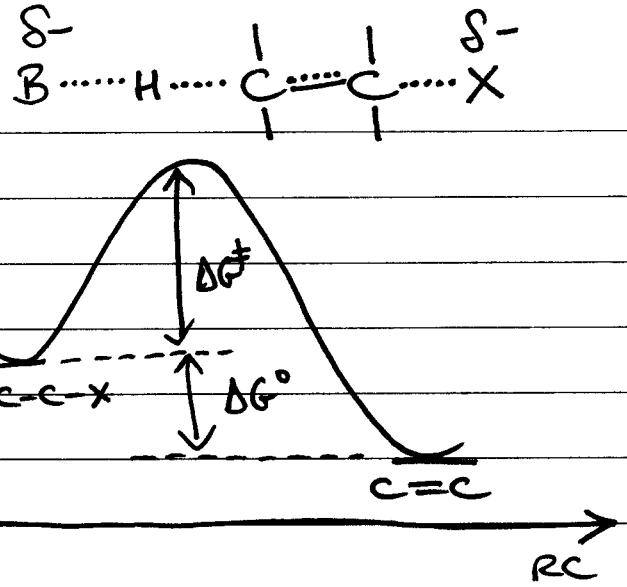


E2 (ELIMINATION BIMOLECULAR)

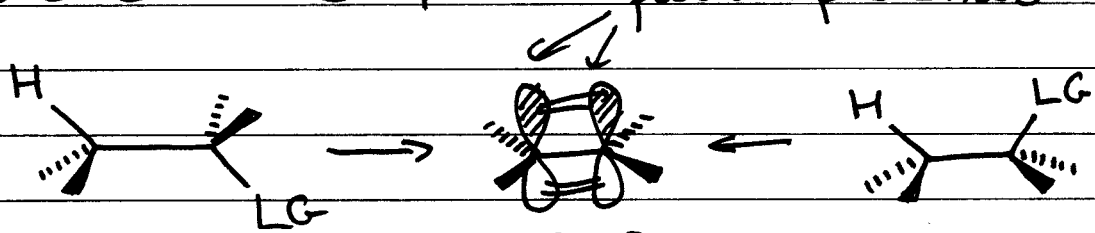
(competes with S_N2)

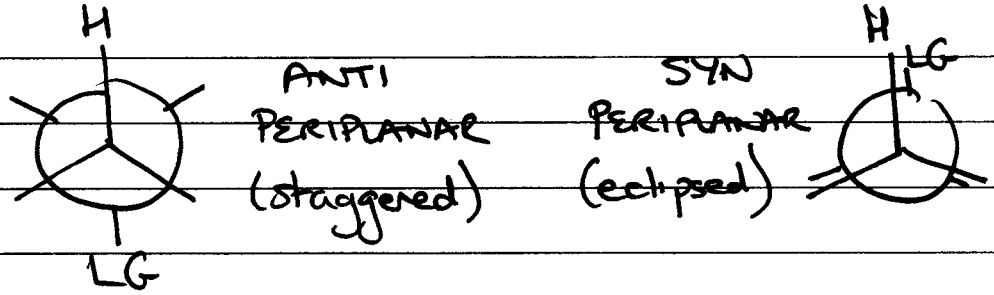


rate = k_2[~Br][Base]

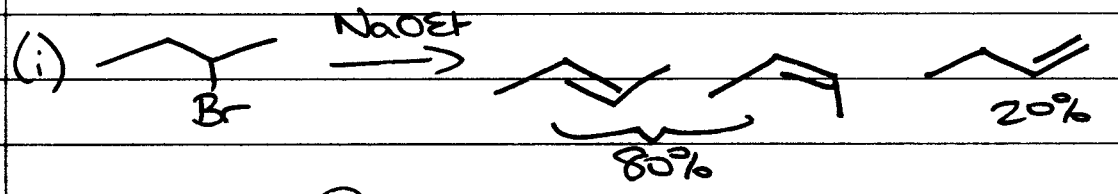


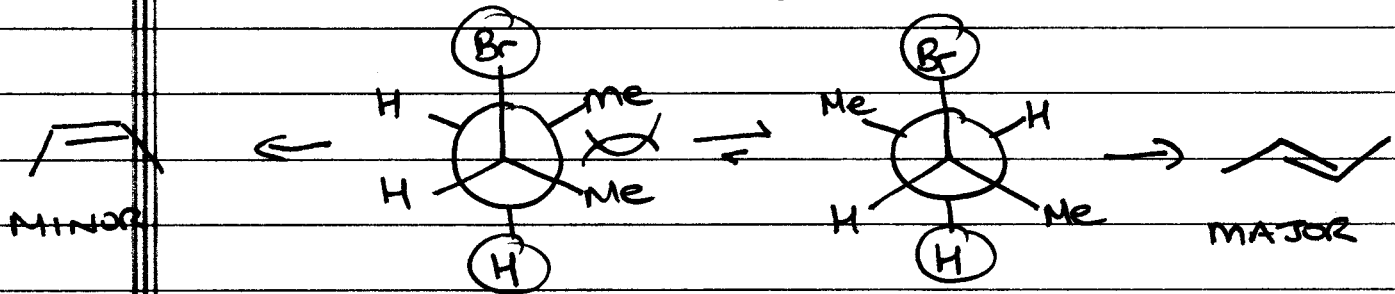
(3) STEREOCHEMISTRY

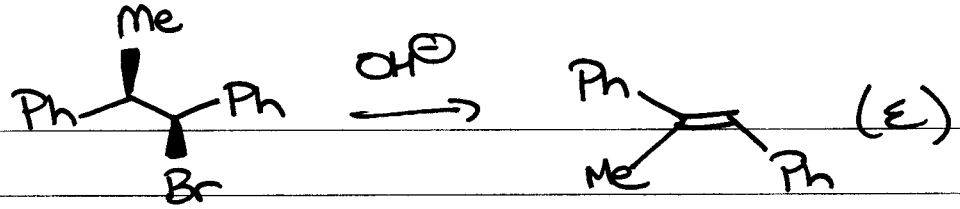


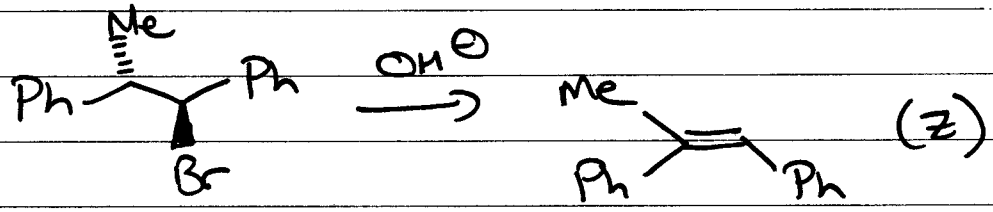


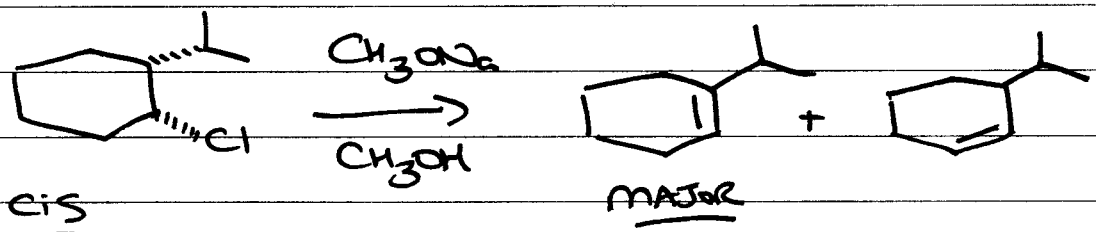
Generally, antiperiplanar geometry is preferred in an E2 reaction (exceptions)





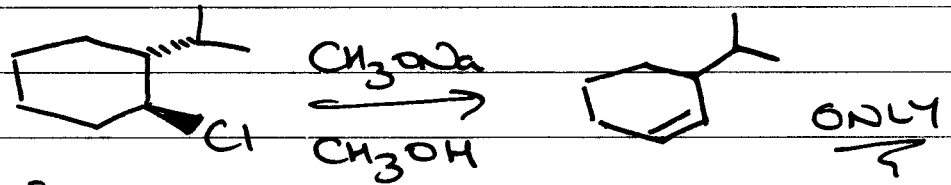
(ii) 

BUT 

(iii) 

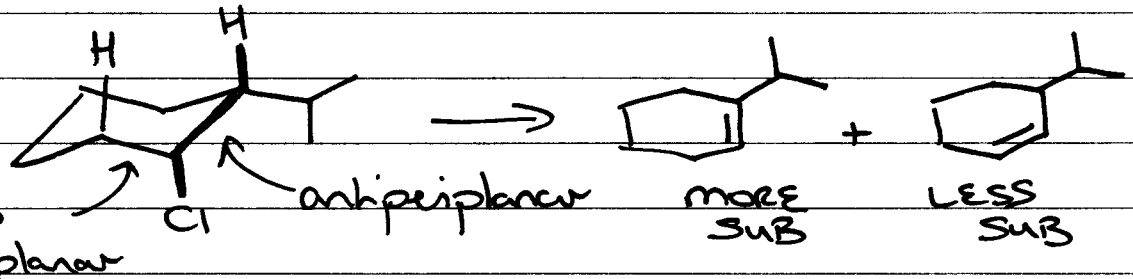
cis

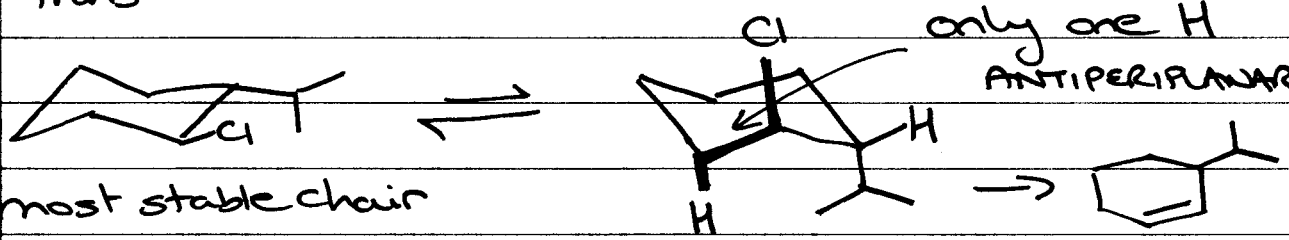
MAJOR

BUT 

trans

also, cis reacts faster => WHY?

-cis 

-trans 

most stable chair (NO Hs ANTIPERIPLANAR to Cl)

SLOWER because reacts THRU less stable CHAIR.

LEC 23 CHEM 30A Dec 2nd

1. STEREOCHEMISTRY — REVIEW Ch9
2. REGIOSELECTIVITY — PROBLEMS 9.43-9.53
3. SYN ELIMINATION — except 9.47g,h
4. E1 vs E2
5. S_N vs E

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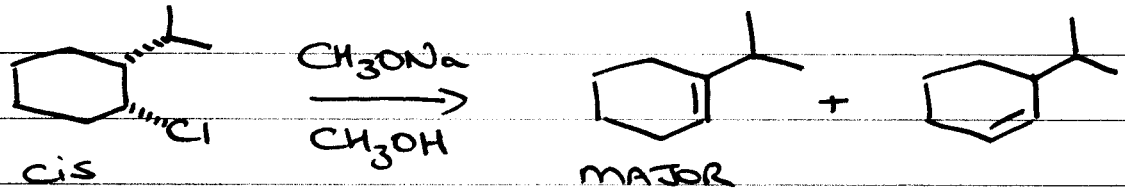
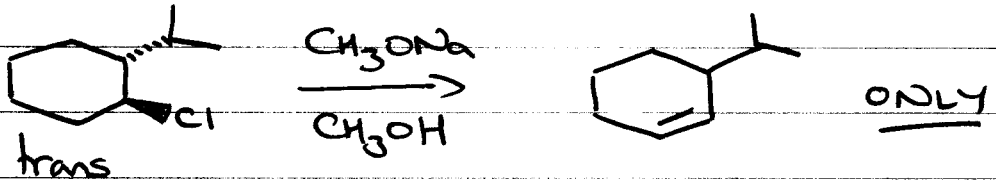
1) STEREOCHEMISTRY cont...

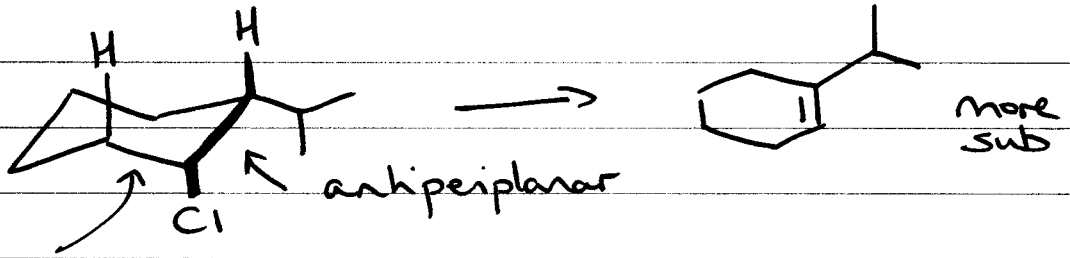


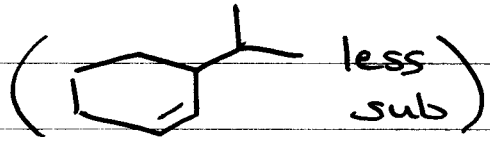
BUT



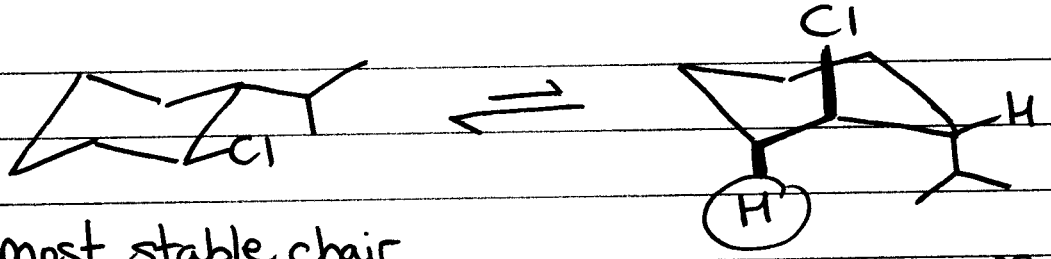
also, cis reaction FASTER than trans - WHY?

- cis



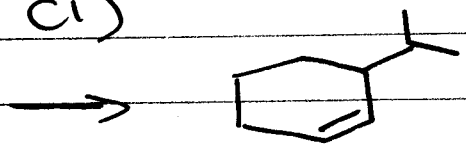
also antiperiplanar → → →  (less sub)

- trans



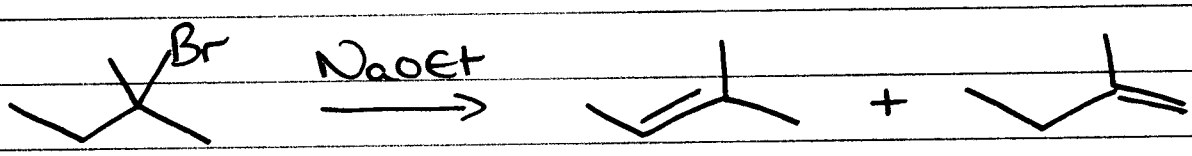
most stable chair
(no Hs ANTIPERIPLANAR to Cl)

ONLY ONE H IS ANTIPERIPLANAR



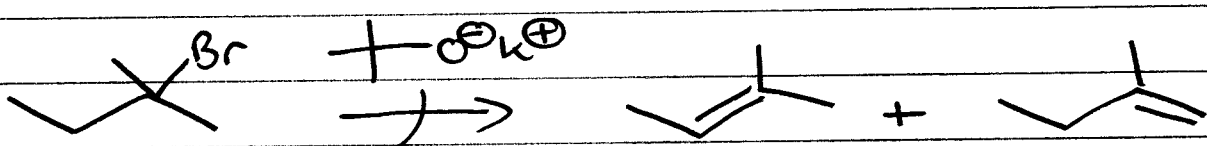
slower because reacts through less stable chair

(2) REGIOSELECTIVITY



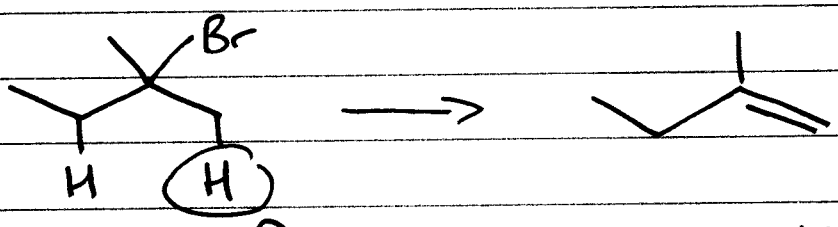
MAJOR (70%) MINOR (30%)

ZAITSEV SELECTIVITY → more sub, more stable alkene



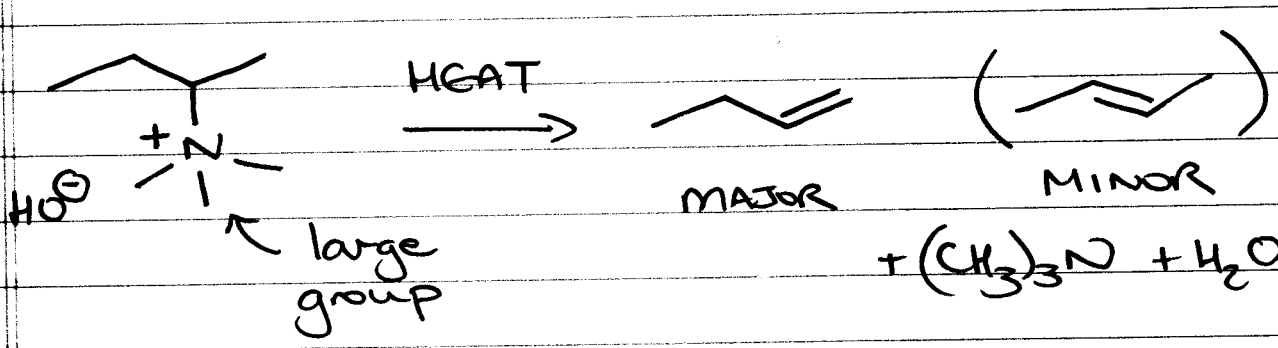
bulky base MINOR (30%) MAJOR (70%)

HOFMANN SELECTIVITY → least sub alkene preferred

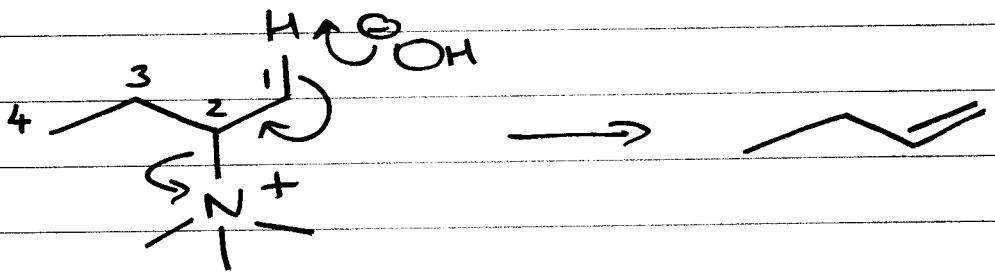


↑ more accesible β-H

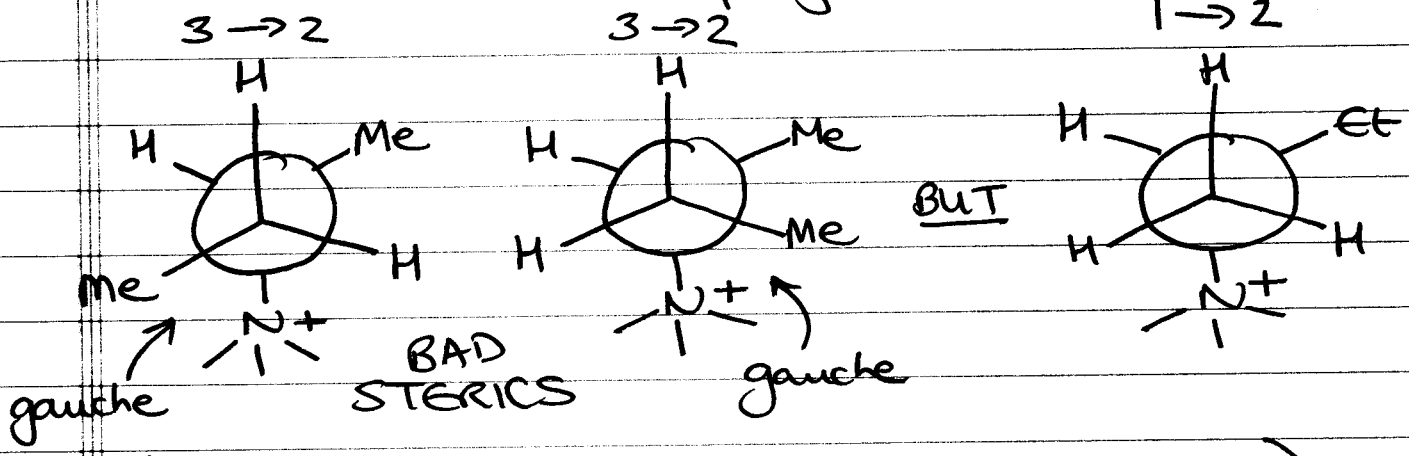
Common reaction w/
QUATERNARY AMMONIUM SALTS



PROCEEDS w/ ANTISTEREOSPECIFICITY

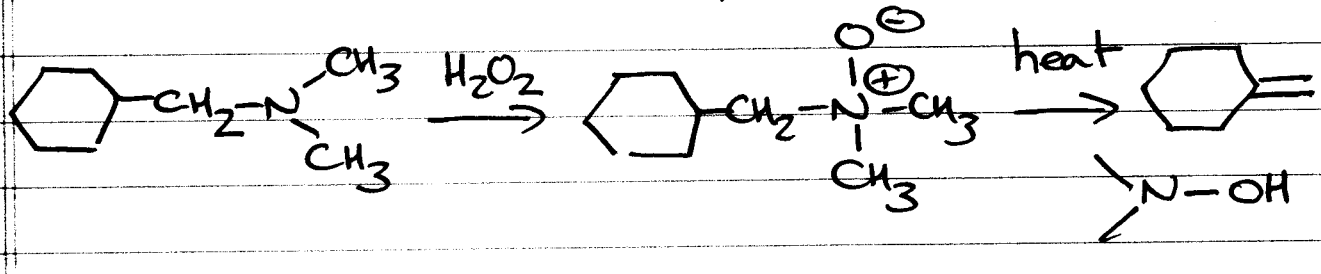


consider NEWMAN projections

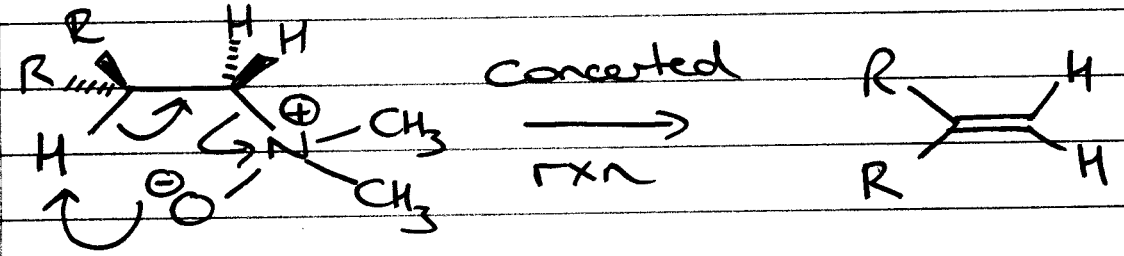


(also electronic effects.... don't worry)

(3) SYN ELIMINATION (cope elimination)

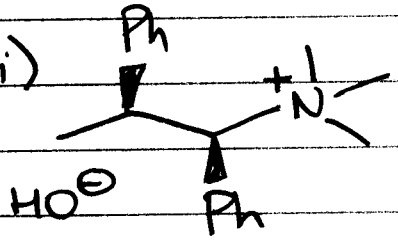


mechanism

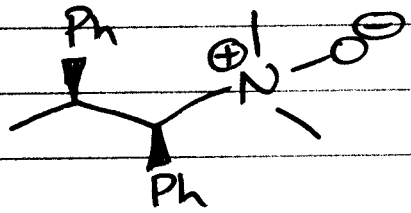


SYN

- figure out the products of these reactions

(i) 

heat → ?

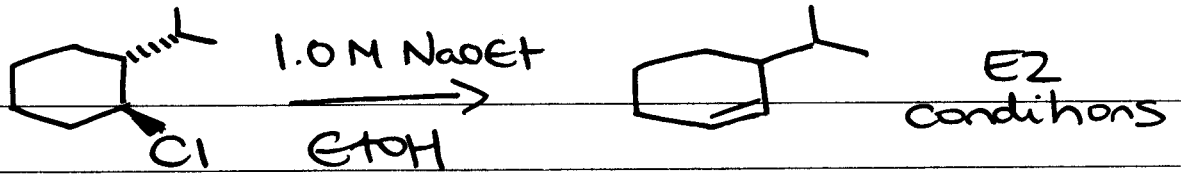
(ii) 

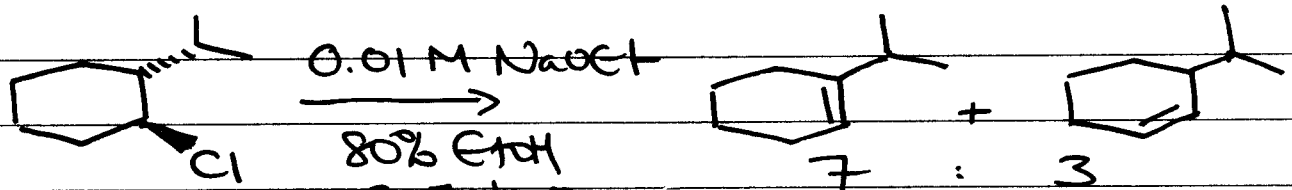
heat → ?

(4) E1 vs E2

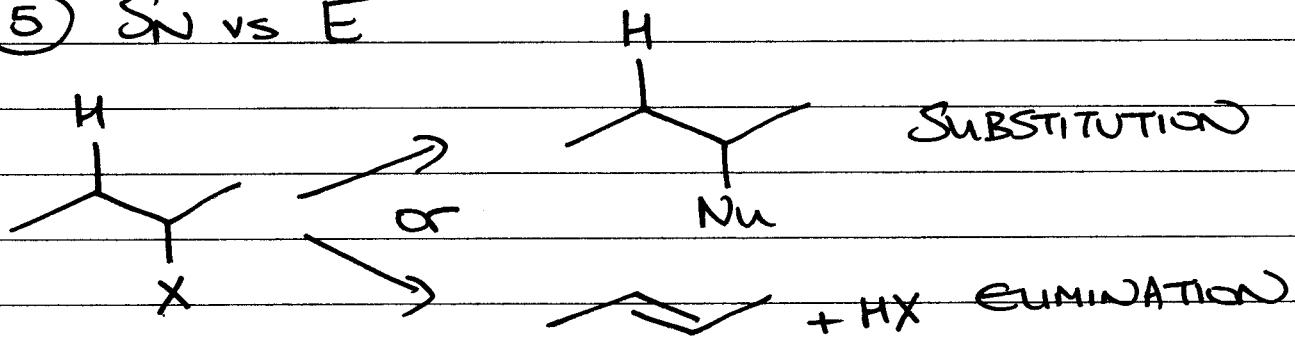
ALKYL HALIDE	E1	E2
methyl	— ELIMINATION IMPOSSIBLE —	
1° (RCH_2X)	DOES NOT HAPPEN (1°C+)	FAVORED ELIMINATION MODE
2° (R_2CHX)	H_2O/ROH (weak bases) ALLYLIC/BENZYLIC	STRONG BASES ($RO^\ominus$ / $HO^\ominus$)
3° (R_3CX)	WEAK BASES	STRONG BASES

- can also depend upon reaction conditions



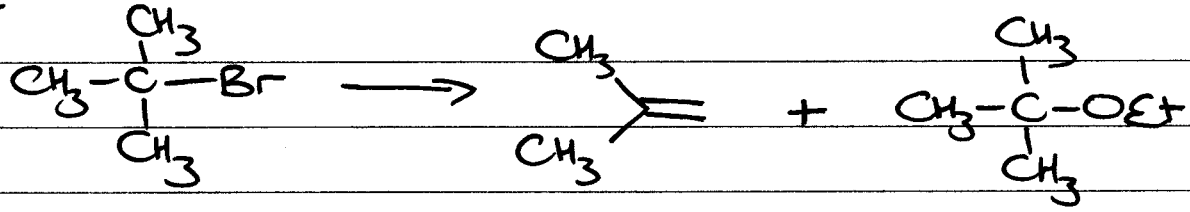


(5) S_N vs E



(i) S_N1 vs E1

e.g.



affinity for proton vs carbon ⇒ stronger base

EtOH/EtONa → 90%** (↳ E2 mechanism) 10%

Generally S_N1 is favored over E1 except at higher temperatures (more later)

LEC (24) CHEM 30A Dec 5th

1. S_N2 vs E2 — WEDS: QUIZ/EVALS
2. SYNTHESIS — READ Ch 8
3. HALOALKANES — QUESTIONS: 8.2-8.4, 8.9-8.28
4. PREPARATION

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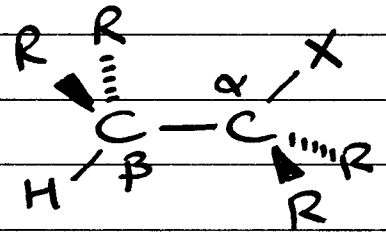
(1) S_N2 vs E2

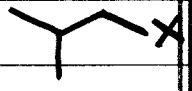
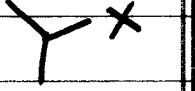
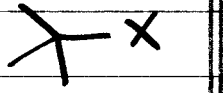
- structure of substrate



BRANCHING at α/β
slows S_N2 (STERICS)
speeds up E2 (MORE STABLE ALKENE)

- nucleophile

as nucleophilicity ↑ ratio $S_N2/E2$ ↑
as basicity ↑ ratio $E2/S_N2$ ↑

SUMMARY	POOR NUC (H_2O/ROH)	Weakly basic Nuc (I^-, RS^-, RCO_2^-)	Strongly basic Nuc (RO^-/HO^-) unhindered	Strongly basic Nuc (tO^-) hindered
CH_3X	NR	S_N2	S_N2	S_N2
	NR	S_N2	S_N2	E2
	NR	S_N2	E2	E2
	$S_N1/E1$ (slow)	S_N2	E2	E2
	$S_N1/E1$	$S_N1/E1$	E2	E2

2° SUBSTRATES

attacking Nuc → pka conjugate acid ≥ 11 ELIMINATION

attacking Nuc → pka conjugate acid < 11 SUBSTITUTION

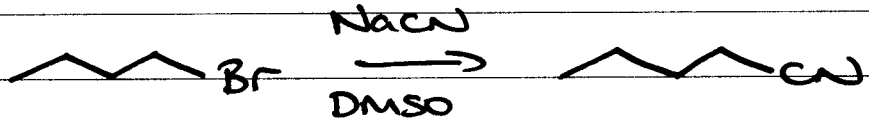
Also higher temp favors ELIMINATION

$\Delta G = \Delta H - T\Delta S$

S_N 2 molecules → 2 molecules

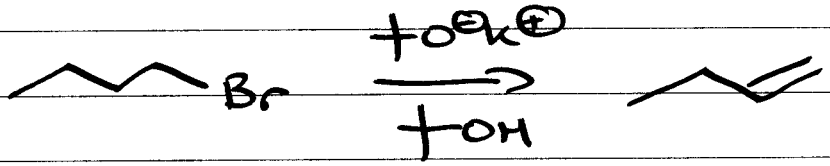
E 2 molecules → 3 molecules $+\Delta S$

examples

1° 

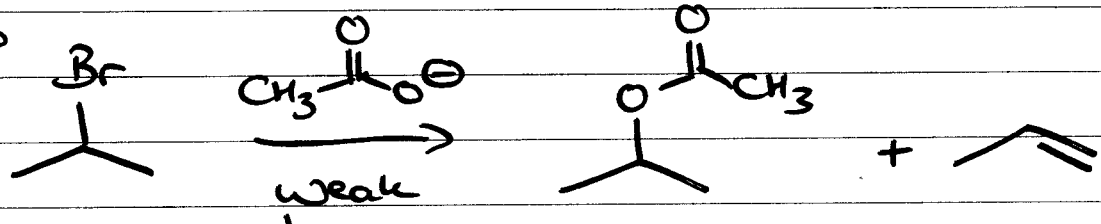
S_N2

($CN^\ominus$, $RS^\ominus$, $N_3^\ominus$, NH_3, $Br^\ominus$, $I^\ominus$) GOOD NUC

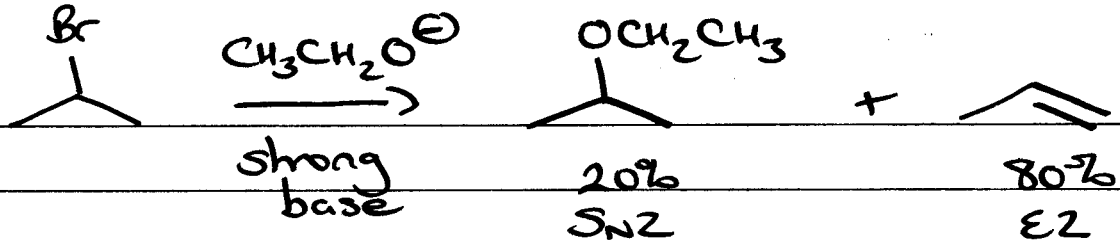


E2

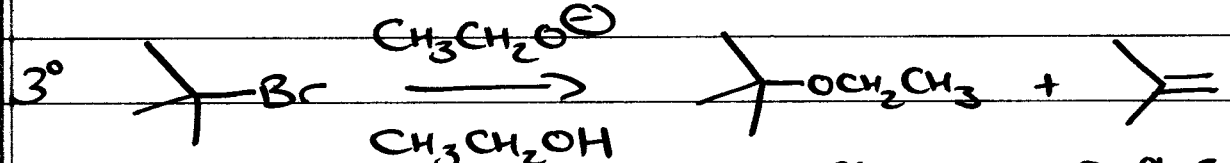
strongly hindered bases

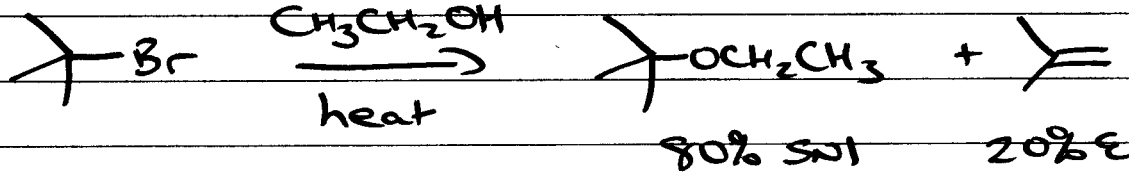
2° 

S_N2 100% E2 0%

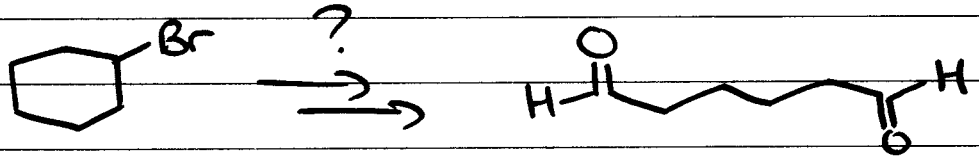


2° BENZYLIC/ALLYLIC substrates can do E1/SN1 with weakly basic NUC in polar protic solvents.





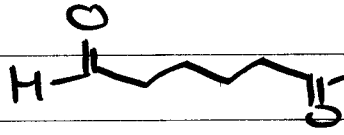
(2) SYNTHESIS - making molecules

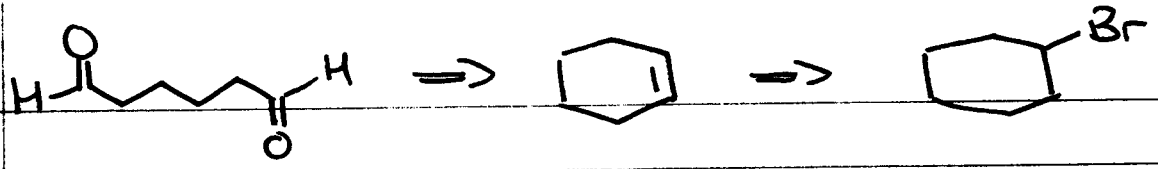


A → B → C → D → → → Z ?

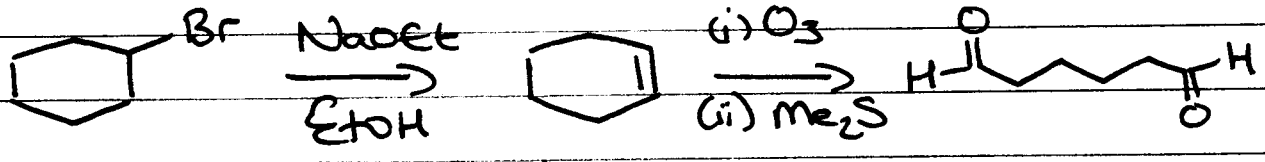
RETROSYNTHESIS (work backwards)

Z → Y → X → W → → → ...

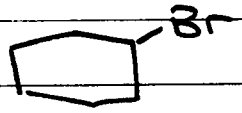
So, what can we make  from?



So, forward synthesis:

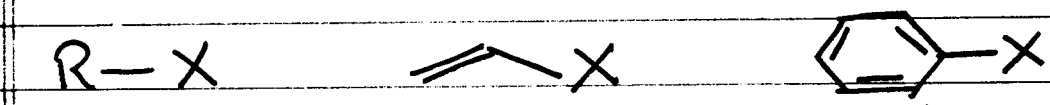


(E2 elimination) (OZONOLYSIS)

.... and, how do we make 

– we use chloro/bromoalkanes a lot.

(3) HALOALKANES
(halogens F, Cl, Br, I)



alkyl halide vinyl halide aryl halide

(read through naming rules – not so hard)

POLARITY $\overset{\delta+}{C} \longleftrightarrow \overset{\delta-}{X}$ ← POLARISABILITY

charges / distance

	EN of X	C–X (pm)	DIPOLE MOMENT (D)
CH_3F	4.0 ↑	139	1.85 D
CH_3Cl	3.0	178	1.87 D
CH_3Br	2.8 N	193 N	1.81 D
CH_3I	2.5	214 ↓	1.62 D

BOILING POINTS

R–X	H	< F	< Cl	< Br	< I
eg CH_3CH_2–	−89	−37	13	38	72 °C

POLARISABILITY ↑ DISPERSION FORCES ↑

BOND LENGTHS/STRENGTHS

⇓

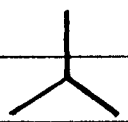
BOND DISSOCIATION ENERGY (BDE)

$A—B \xrightarrow[\text{cleavage}]{\text{Homolytic}} A\cdot + B\cdot$ (RADICALS)

	LENGTH (pm)	BDE (kcal/mol)
C–H	109	90–100
C–F	142	105
C–Cl	178	80
C–Br	193	65
C–I	214	50

(4) PREPARATION

ALKANE + X_2 (Br_2 or Cl_2) $\xrightarrow{\text{HEAT/LIGHT}}$ HALOALKANE + HX (substitution reaction)

eg  + Br_2 $\xrightarrow{\text{heat}}$  + HBr

LEC (25) CHEM 30A Dec 9th

HALOALKANES → ENERGETICS of RADICAL RXNS (not covered)

1. PREPARATION
2. REGIOSELECTIVITY
3. MECHANISMS
4. RADICAL STRUCTURE
5. ALLYLIC HALOGENATION

FINAL
WED 14th DEC
11:30 - 2:30 ACKERMAN
GRAND BALLROOM
- STAMPS

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(1) PREPARATION

$$\text{ALKANE} + X_2 \xrightarrow{\text{heat/light}} \text{HALOALKANE} + HX$$

(X_2 = Br_2 or Cl_2) (substitution reaction)

e.g.  + Br_2 $\xrightarrow{\text{heat}}$  + HBr

$$CH_4 + Cl_2 \xrightarrow[\text{rt}]{\text{dark}} \text{NO REACTION}$$

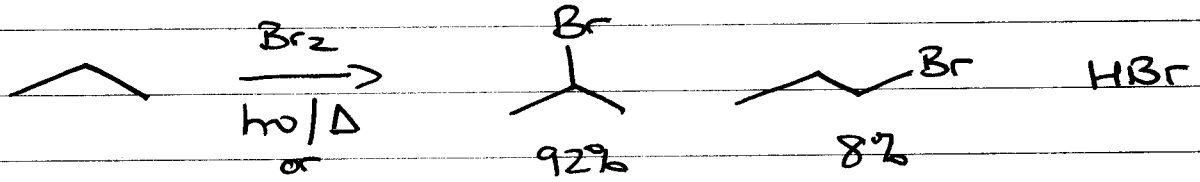
$$CH_4 + Cl_2 \xrightarrow{\text{heat}} CH_3Cl + HCl$$

$\Delta H = -24$ kcal/mol

Reaction continues:

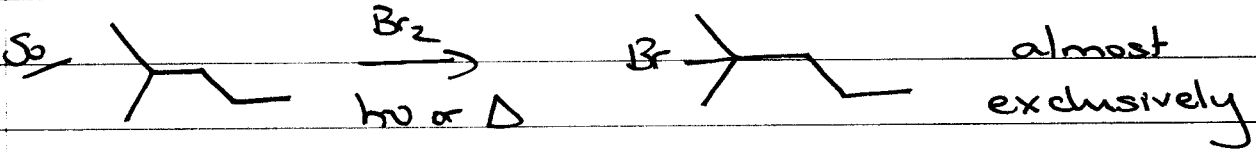
$$CH_3Cl \xrightarrow[\text{heat}]{Cl_2} CH_2Cl_2 \xrightarrow[\text{heat}]{Cl_2} CHCl_3 \xrightarrow[\text{heat}]{Cl_2} CCl_4$$

(2) REGIOSELECTIVITY

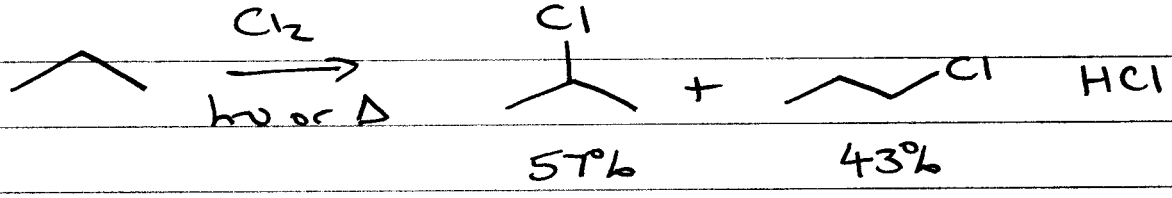


statistics 25 : 75

2° favored over 1° (also 3° favored over 2°)



REGIOSELECTIVITY less for Cl_2



	3°	2°	1°
Br_2	1600	80	1
Cl_2	5	4	1

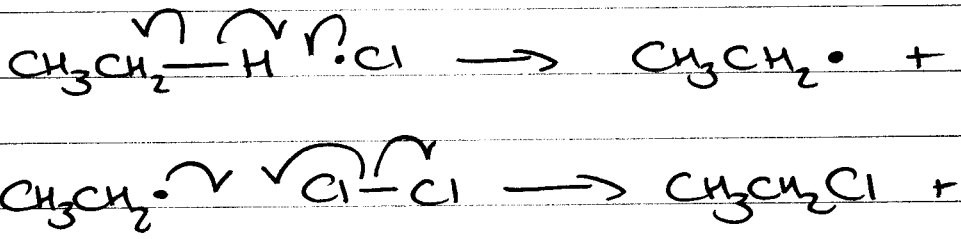
(3) MECHANISMS

3 steps : INITIATION / PROPAGATION / TERMINATION

e.g. $CH_3-CH_3 \xrightarrow{Cl_2} CH_3CH_2Cl + HCl$

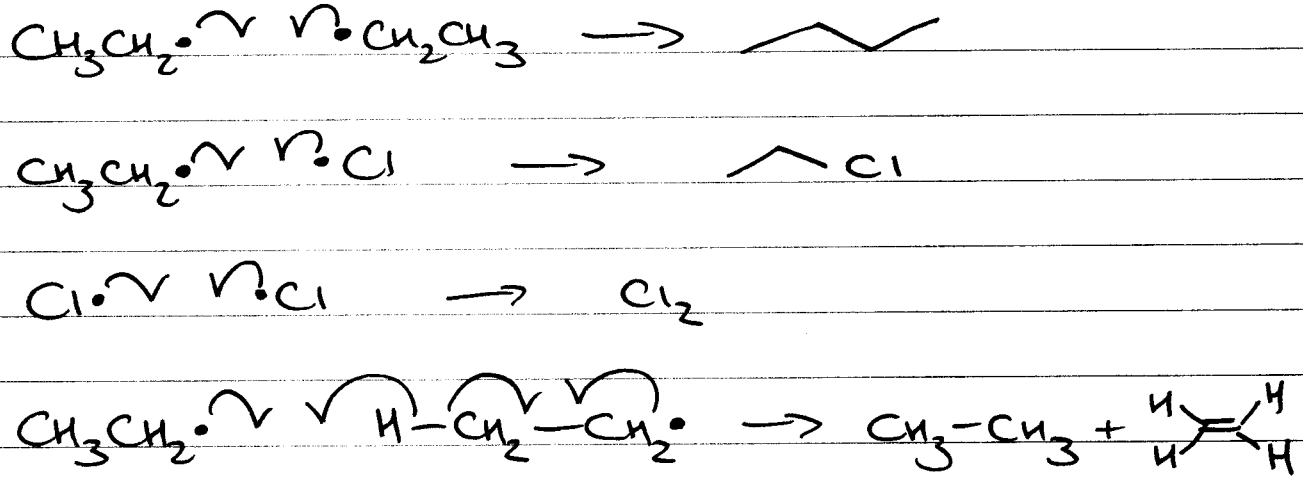
(i) CHAIN INITIATION

(ii) CHAIN PROPAGATION



PROPAGATES RADICALS

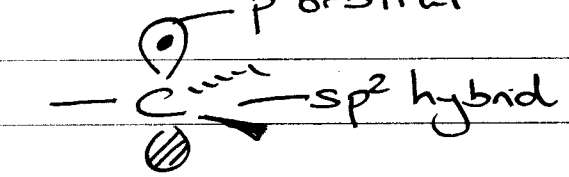
(iii) CHAIN TERMINATION

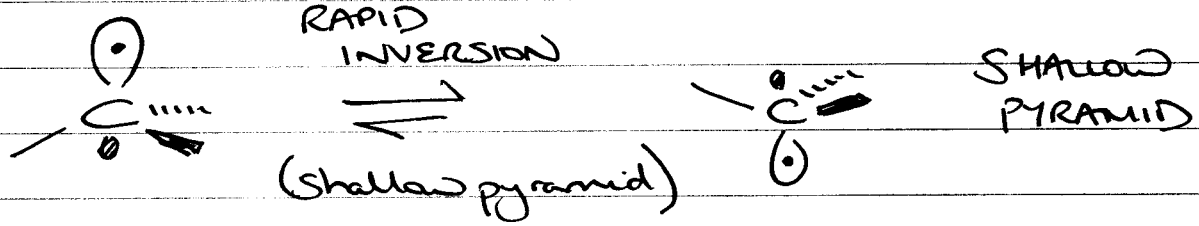


CONSUMES RADICALS

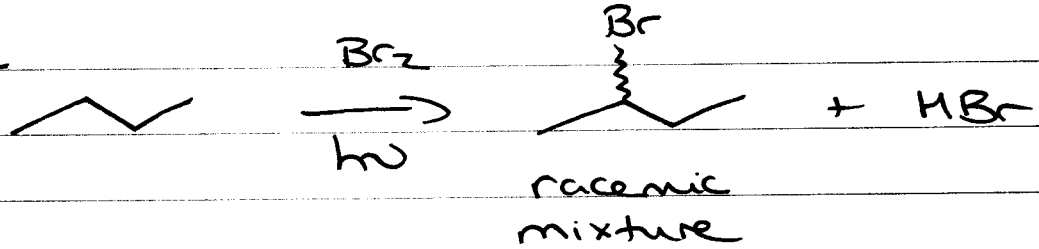
CHAIN PROPAGATION happens many times before termination → number of cycles is called the CHAIN LENGTH.

④ RADICAL STRUCTURE





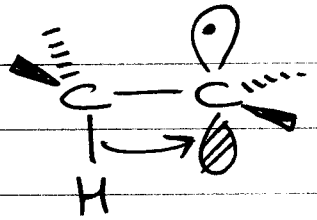
So



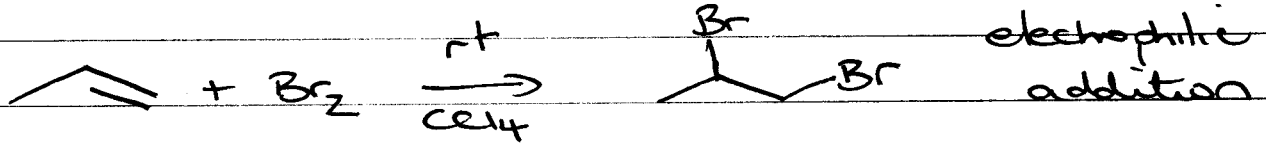
STABILITY (same trend as C+)

resonance

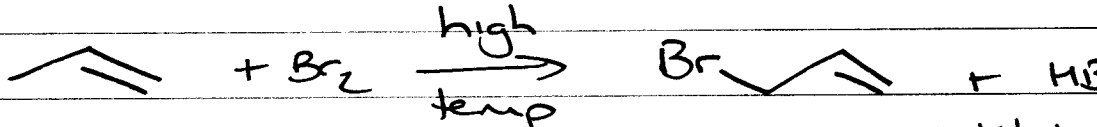
hyperconjugation



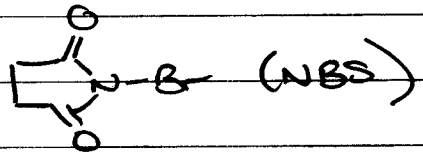
(5) ALLYLIC HALOGENATION



electrophilic addition



allylic substitution

- more convenient reagent 

(NBS)

reaction can be done at RT