LEC (1) CHEM 30A Apr 4th

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

HMK: READ 1-1.4
PROBLEMS 1.1-1.5, 1.19-1.22 (Same for 3rd/4th ED)

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(1) me

- 3077D YOUNG HALL

- www.chem.ucla.edu/~cantill/teaching.htm
  ↳
  Lecture notes (mine)
  Announcements
  Handouts
  Exams & keys
  Policy

- Recommend that you come to LECTURES (questions OK in class)

- ENGLISH ENGLISH
  26th LETTER, 13th ELEMENT, FOOTBALL

- MODEL KITS not required, may be useful

- TAs
Linh, Susan, Heather

- Discussion Sections
(be consistent as to which one you attend, quizzes & midterms returned there)

- Office Hours (YH 3077F)
Times posted on website

- TEXTBOOK
Brown & Foote 4th Edition
(Homework / Reading assignments)

- EXAMS

3 QUIZZES 100 (3x35)
2 MIDTERMS 200 (2x115)
1 FINAL 200 (1 x 230)
500 (565)

FINAL COMPREHENSIVE
RULES: SEE SYLLABUS AND WEBSITE

- CHEATING - Don't ever think about it...

- SYLLABUS - Tentative, but READ IT

- WAITLIST
  - not my decision (chem & biochem undergrad office)

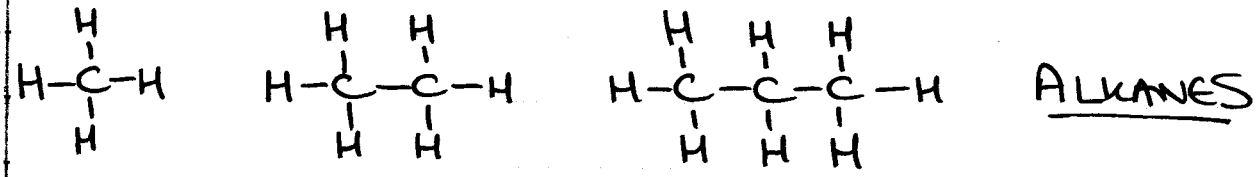
- IMPACTED CLASS...

(2) WHAT? - ORGANIC CHEMISTRY

ORGANIC ⇒ Chemistry of compounds from living things, as opposed to inorganic cmpds.

↳ study of compounds containing CARBON

SIMPLEST COMPOUNDS CONTAIN CARBON AND HYDROGEN ONLY ⇒ HYDROCARBONS



ALKANES

CH_4 methane

C_2H_6 ethane

C_3H_8 propane

- hydrocarbons serve as a framework from which to dangle FUNCTIONAL GROUPS.

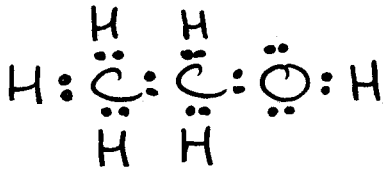
⇒ Specific combinations of atoms in precise arrangements

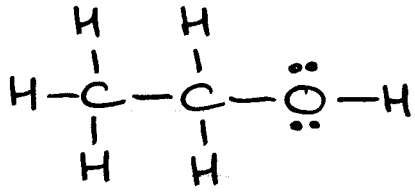
(i) CLASSIFY ORGANIC COMPOUNDS
(ii) BASIS FOR NAMING
(iii) PREDICTABLE CHARACTERISTIC REACTIVITY

For example : ALCOHOLS

e.g. CH_3CH_2OH ethanol

DRAWING MOLECULES

(i) 

(ii) 

(iii) CH_3CH_2OH

(iv) C_2H_5OH

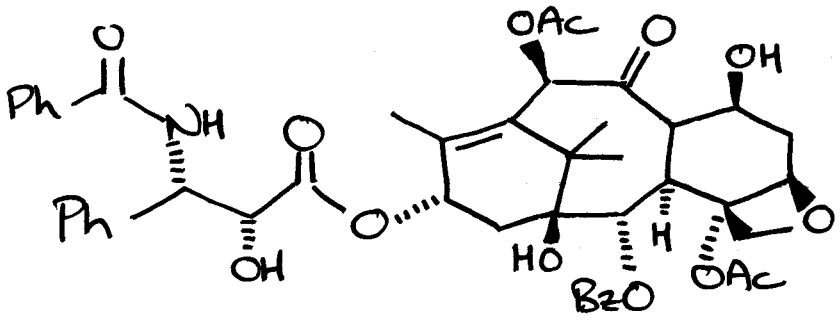
(v) EtOH

(vi) 

LINE FORMULA
(more on this later)

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-TUMOUR AGENT developed in three decades

1998 SALES $1.2 BILLION

- where do we get it - NOT like it grows on trees

- Well, yes it does... BARK OF PACIFIC YEW TREE

BUT six 100yr old trees → 1 patient (kills trees)

- SYNTHESIS (making molecules)

⇓

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

⇓

MECHANISMS (how it all works)

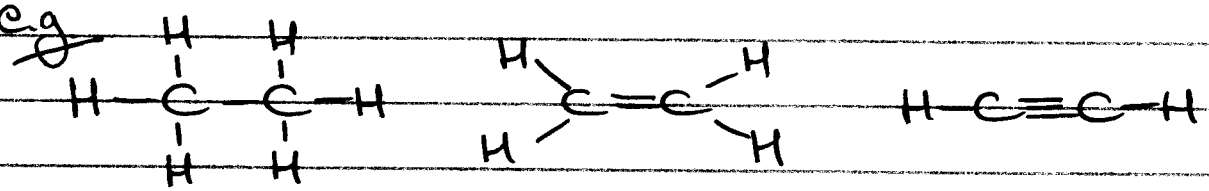
⇓

STRUCTURE & BONDING (electrons & orbitals)

THINGS YOU NEED TO KNOW

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

not absolute, but good 99% of the time

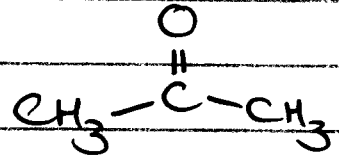
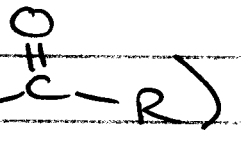
e.g. 

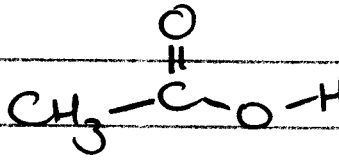
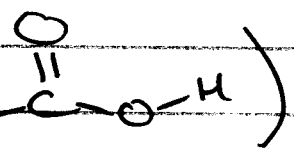
ethane — ALKANE
ethylene — ALKENE
acetylene — ALKYNE

O forms 2 BONDS
Hal (F, Cl, Br, I) form 1 BOND

CH_3CH_2-O-H alcohol $(R-O-H)$

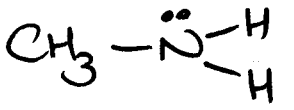
CH_3-O-CH_3 ether $(R-O-R)$

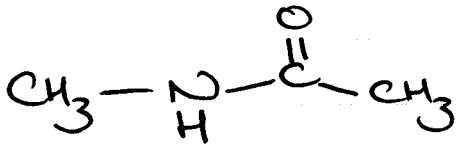
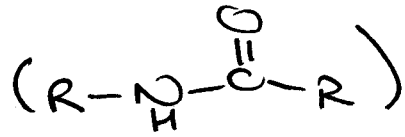
 ketone 

 carboxylic acid 

CH_3CH_2-Cl alkyl chloride $(R-Cl)$

N forms 3 BONDS

 amine $(R-\ddot{N}(H)(H))$

 amide 

S, P $\Rightarrow$ variable.

LEC (2) CHEM 30A Apr 6th

1. CHEMICAL BONDING
2. LEWIS STRUCTURES
3. FORMAL CHARGE
4. SHAPES of MOLECULES
5. DRAWING ORGANIC STRUCTURES

HMK READ 1.3–1.4

PROBLEMS: 1.6–1.13, 1.23–1.47 (3/4 Ed)
* 2 EXTRA PROBLEM SETS ON WEBSITE

(1) CHEMICAL BONDING

Valence electrons (outer shell electrons)
=> these involved in BOND FORMATION

# VALENCE e⁻	1	2		3	4	5	6	7	8
	H								He
	Li	Be	d-block	B	C	N	O	F	Ne
	Na	Mg		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

← decreases

F

↓ decreases

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

ORGANIC CHEMISTRY ⇒ COVALENT BONDS ⇒ EN DIFFERENCES < 2

so, consider:

Na F (3.1)
0.9 4.0 ⟶ NaF (Na^+F^-) IONIC Salt

O H (1.4) δ- δ+
3.5 2.1 ⟶ O—H  polar covalent

e⁻ clouds

C C (0)
2.5 2.5 ⟶ C—C  non polar covalent

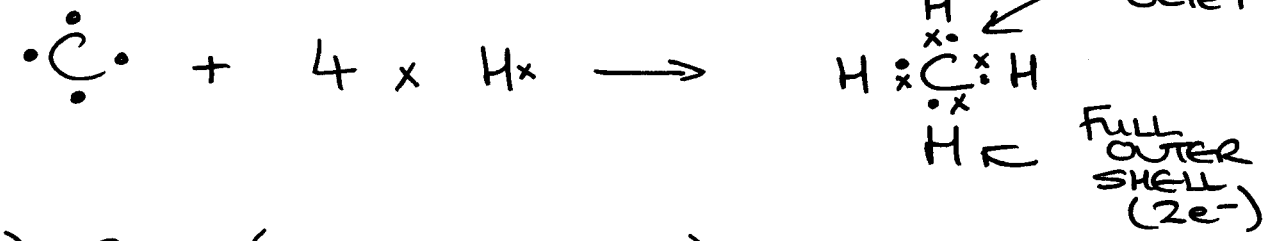
EN difference < 0.5 ≅ NONPOLAR

C—H check out Table 1.5 Page 7
2.5 2.1 know values for common elements & know TRENDS

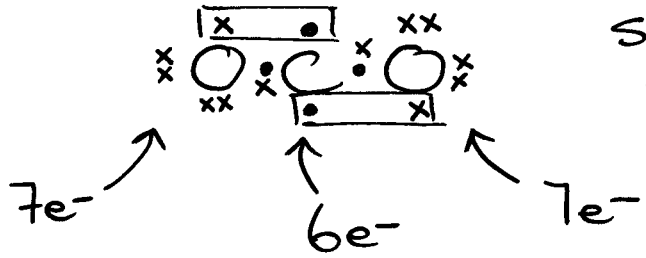
② LEWIS STRUCTURES

- # 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)

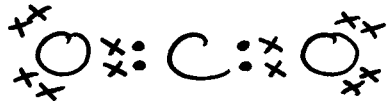


b) CO_2 (carbon dioxide)

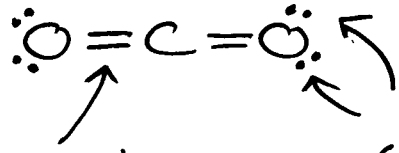


Single bonds, but OCTETS not full

- share more electrons (MULTIPLE BONDS)
  ⇒ redraw



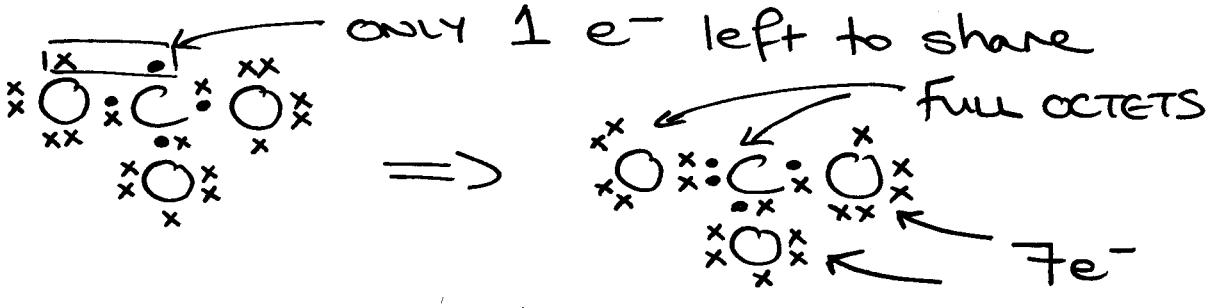
ALL ATOMS HAVE FULL OCTETS



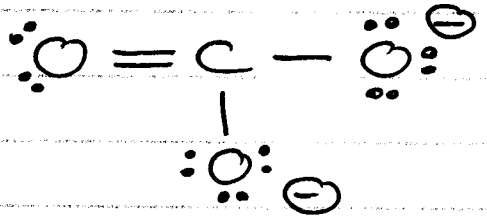
bonding pairs

lone pairs (non-bonded)

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

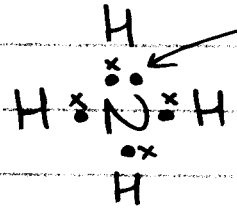


So, add in 2 electrons to fill octets (DRAW THEM IN ABOVE)



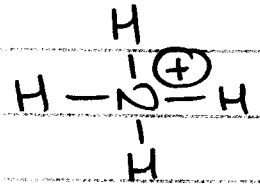
CO_3^{2-}

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



$9e^-$ in VALENCE SHELL
- violates OCTET rule

So, get rid of it ⟹



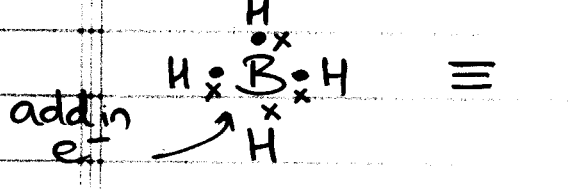
(3) FORMAL CHARGES

- Draw LEWIS structure

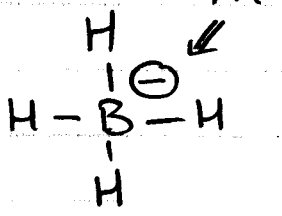
For each atom:

$$\text{FORMAL CHARGE} = \#\text{ VALENCE ELECTRONS IN ISOLATED NEUTRAL ATOM} - \left(\#\text{ OF NON-BONDING } e^- + \tfrac{1}{2}\#\text{ BONDING } e^-\right)$$

a) $BH_4^{\ominus}$ ⟸ ADD CHARGES AT END

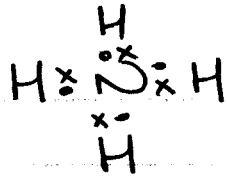


$\equiv$

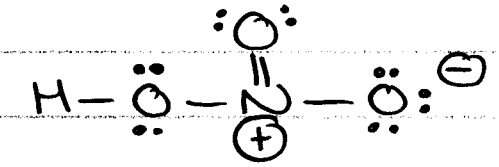


$(3 - 8/2) = -1$

ADD CHARGES AT END

b) NH_4^+  $(5 - 8/4) = +1$

c) HNO_3 (nitric acid)

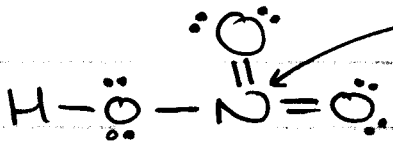


FILL OCTETS (ADD CHARGES AT END)

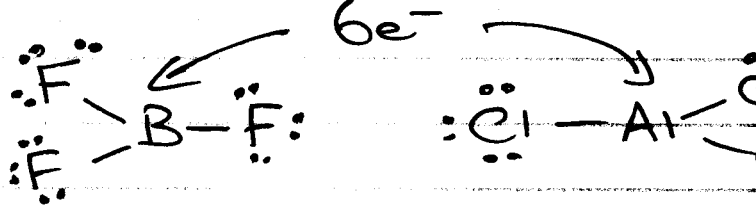
N $(5 - 8/2) = +1$

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

other O's $(6 - (4 + 4/2)) = 0$

Note: not  10e⁻ violates OCTET rule.

- Note There are exceptions to the octet rule

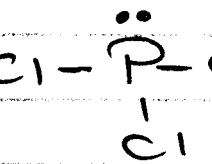
GROUP (3) 

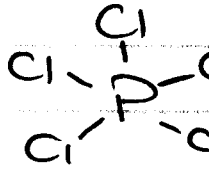
6e⁻

usually quite reactive species

3RD ROW ELEMENTS (P, S)

d orbitals ⇒ EXPAND OCTET

 PCl_3 8e⁻

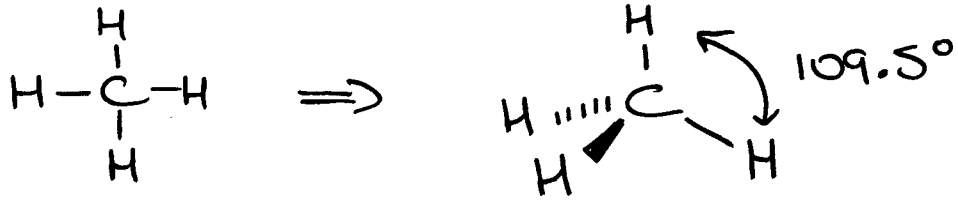
 PCl_5 10e⁻

(4) SHAPES of MOLECULES

Valence Shell Electron Pair Repulsion Theory (VSEPR) – SIMPLIFIED MODEL

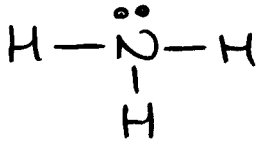
Geometry determined by valence shell electron pairs (BONDED & NONBONDED) arranging to minimise electrostatic repulsion

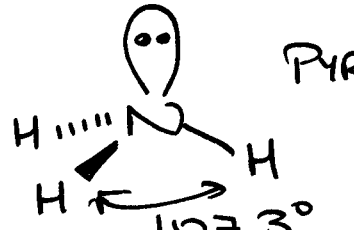
e.g.



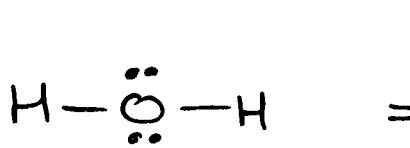
tetrahedral

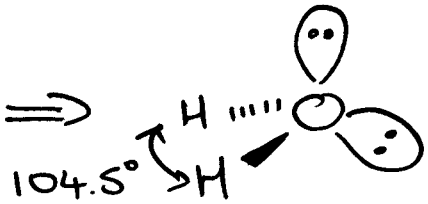
DISTINGUISH BETWEEN "SHAPE of MOLECULE" VERSUS GEOMETRY AROUND AN ATOM





PYRAMIDAL (compressed)





BENT (more compressed)

closer to nucleus ⇑

WHY? lonepair/lonepair > lone pair/bond.ng pair > bonding pair / bonding pair

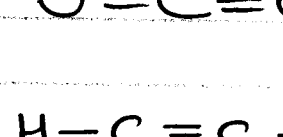
Also, $A \equiv B > A = B > A - B$

BASIC GEOMETRIES

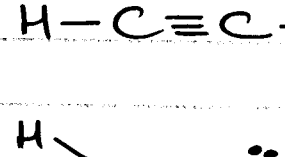
- for sake of geometry, treat multiple bonds as single bonds

- when considering the geometry of a given atom, add the number of other atoms bonded to it, to the number of lone pairs it has ⇒

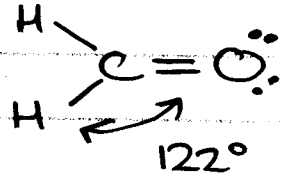
2 LINEAR
3 TRIGONAL PLANAR
4 TETRAHEDRAL
5 TRIGONAL BIPYRAMIDAL
6 OCTAHEDRAL



O=C=O LINEAR

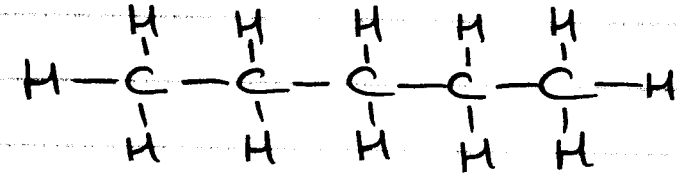


H−C≡C−H LINEAR



TRIGONAL PLANAR (BASICALLY)

(5) DRAWING ORGANIC STRUCTURES



PENTANE

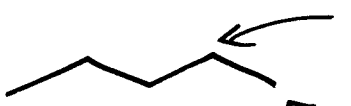
STRUCTURAL FORMULA

CONDENSED FORMULA

$CH_3CH_2CH_2CH_2CH_3$ or $CH_3(CH_2)_3CH_3$

LINE FORMULA

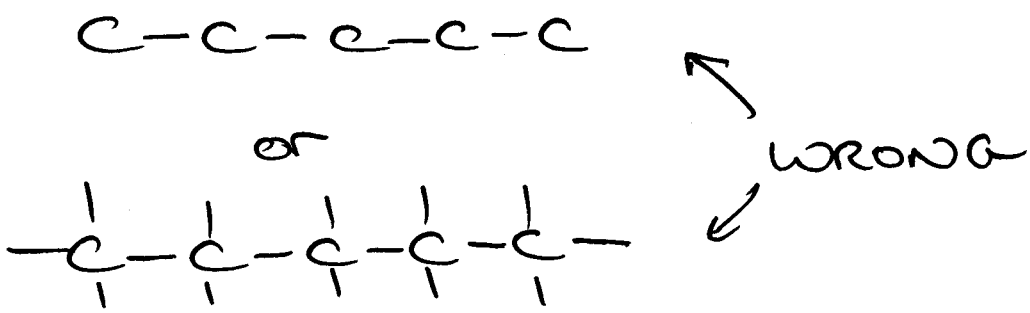
- draw CHAINS as ZIGZAGS
- leave out any H attached to C
- draw nonbonded electrons (lone pairs)



this is a C atom with 2 Hs on it

This is a C atom with 3 Hs on it

Do <u>NOT</u> WRITE



LEC (3) CHEM 30A Apr 8th

(1) SHAPES OF MOLECULES
(2) DRAWING ORGANIC STRUCTURES
(3) RESONANCE

Hmk: READ rest of Ch1
Problems 1.14-1.17, 1.48-1.54 + MOLECULAR STRUCTURES WORKSHEETS

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(1) SHAPES of MOLECULES

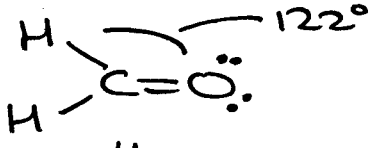
(PAIRS OF ELECTRONS IN VALENCE SHELL)
- BONDED & NONBONDED (lone pairs)

BUT TREAT MULTIPLE BONDS AS SINGLE

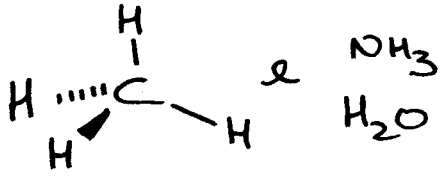
ADD #BP to LP
(or #atoms)

2 → LINEAR

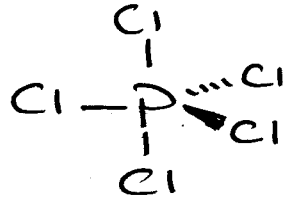
3 → TRIGONAL PLANAR



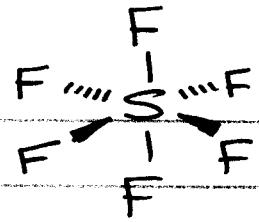
4 → TETRAHEDRAL



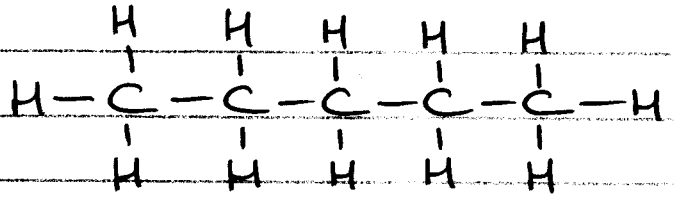
5 → TRIGONAL BIPYRAMIDAL



PCl5

6 → OCTAHEDRAL  SF_6

(2) DRAWING ORGANIC STRUCTURES

a)  ~~PENTANE~~ (structural formula)

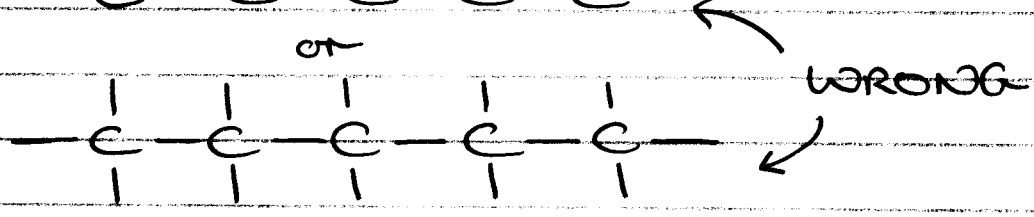
= condensed formula

$CH_3CH_2CH_2CH_2CH_3$ or $CH_3(CH_2)_3CH_3$

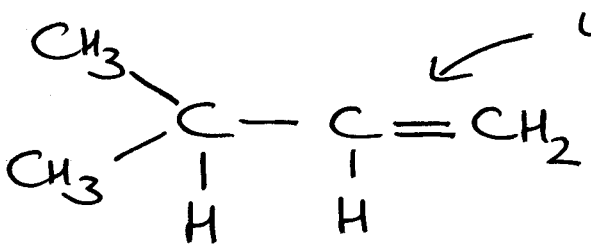
= line formula

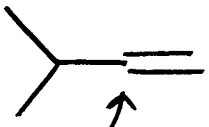
- draw CHAINS as ZIG-ZAGS
- leave out ANY H attached to C
- draw NONBONDED electrons (lone pairs)

DO NOT WRITE

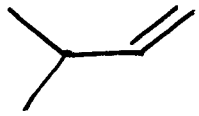


b) $(CH_3)_2CHCHCH_2$?

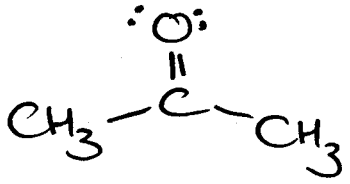


maybe you would draw 

geometry of C atom?
=> TRIGONAL PLANAR

So  TRY to be as true to molecular shape as possible

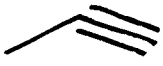
c) $CH_3(CO)CH_3$



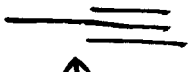
not 

TRIGONAL PLANAR

d) CH_3CCH => $CH_3-C\equiv C-H$

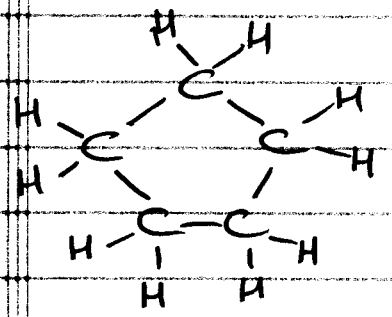
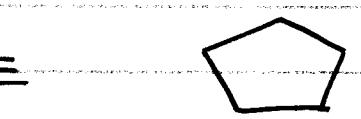


NO!



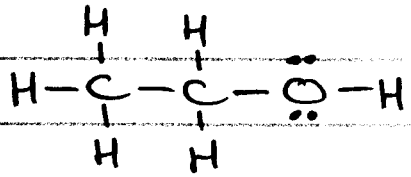
↑
Linear

- RINGS

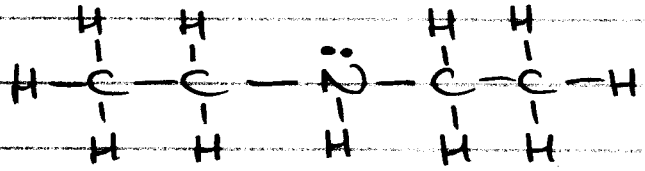



each of these is a CH_2

- HETEROATOMS (draw Hs and lone pairs)




not




not

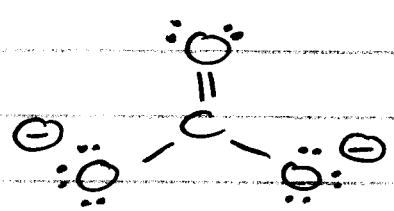
- example C_5H_{12}

CONSTITUTIONAL ISOMERS

- same formula, different arrangements of atoms

(3) RESONANCE

Consider CO_3^{2-}

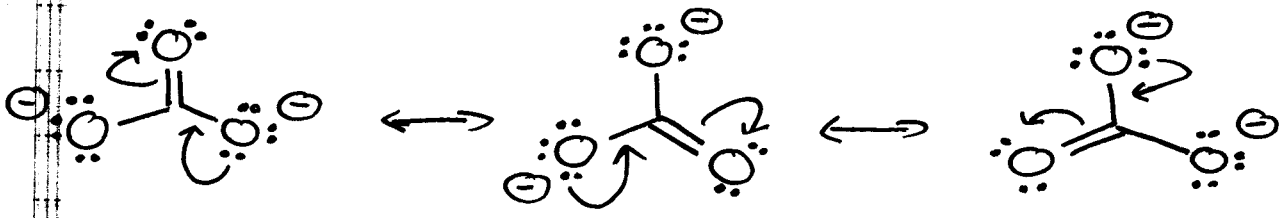


one C=O

two C–O bonds

C=O shorter/stronger bond than C–O

In CO_3^{2-} however, all carbon/oxygen bonds are identical ⇒ WHY?



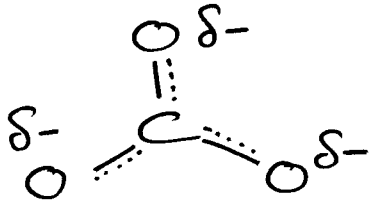
RESONANCE CONTRIBUTORS (ALL EQUIVALENT)

ARROWS ⟷ Separates resonance contributors

↷ CURLY ARROW movement of a pair of electrons

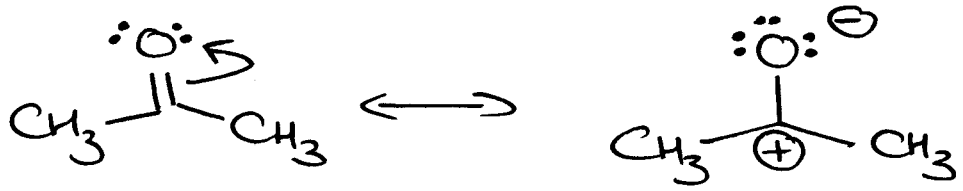
NONE of these contributors actually EXIST!

actual structure is



RESONANCE HYBRID

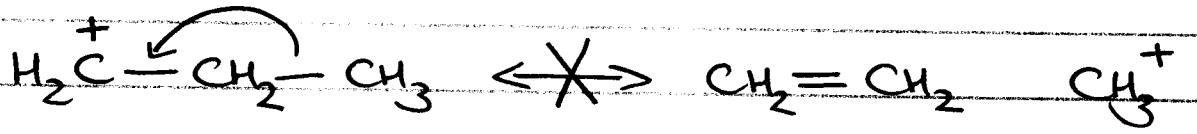
NOT all resonance contributors are necessarily equivalent, for example



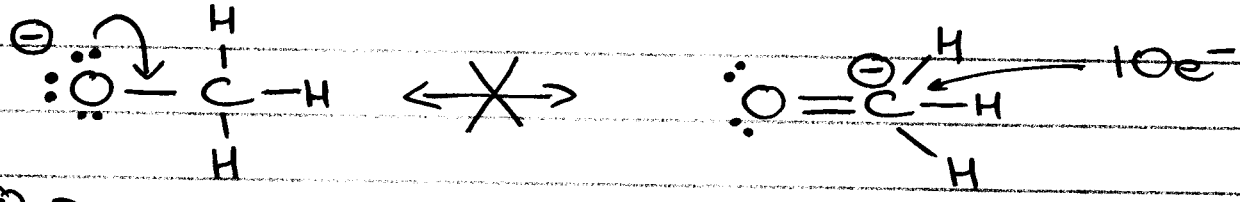
Which one of these is most stable?

- RULES for writing RESONANCE STRUCTURES
- DO NOT

① BREAK ANY SINGLE BONDS



② VIOLATE THE OCTET RULE



③ DO NOT MOVE ATOMS

- DRAWING RESONANCE STRUCTURES

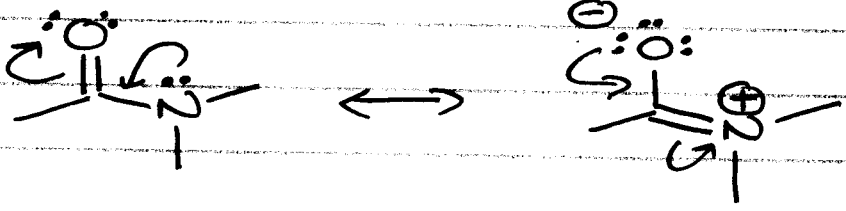
Cannot break single bonds, so we can only move electrons from double (or triple) bonds and lone pairs

PATTERNS

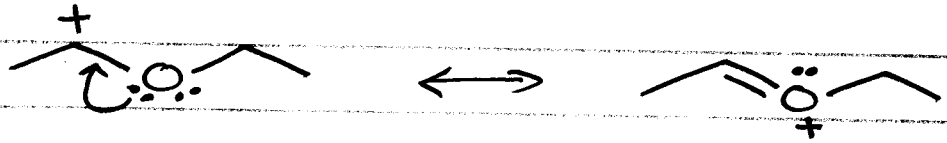
① LONE PAIR NEXT TO π BOND

double or triple bond

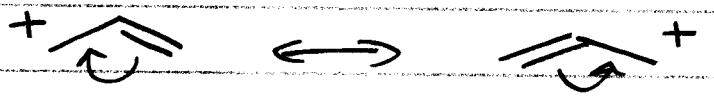
"next to" means one single bond away



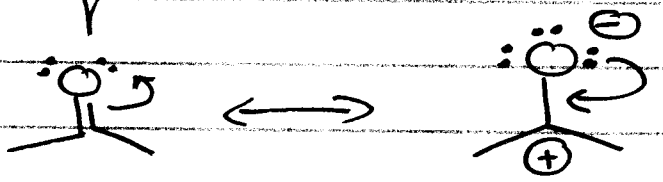
② LONE PAIR NEXT TO +ve CHARGE

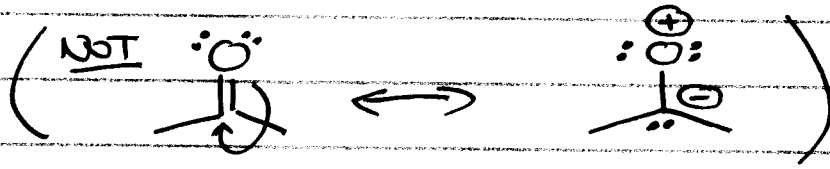


③ π BOND next to +ve CHARGE



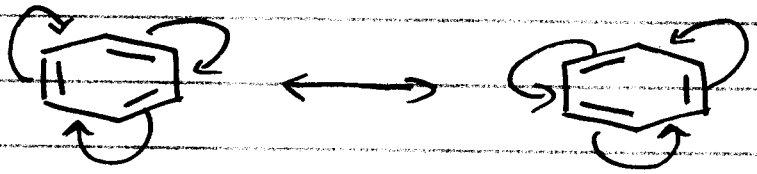
④ π BOND between two atoms where one is quite EN





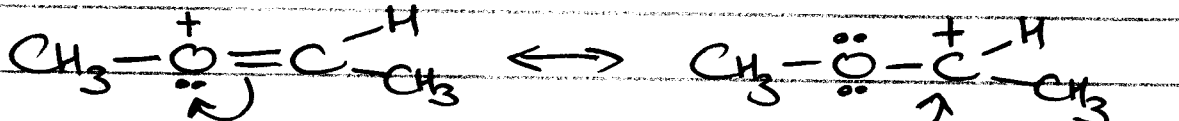
O is more EN than C

⑤ ALTERNATING π BONDS



– RELATIVE IMPORTANCE of CONTRIBUTING STRUCTURES

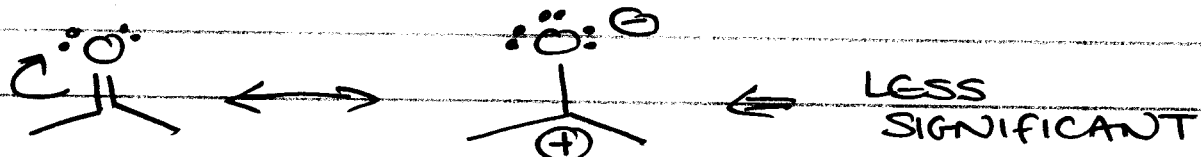
① MAXIMISE OCTETS



more significant

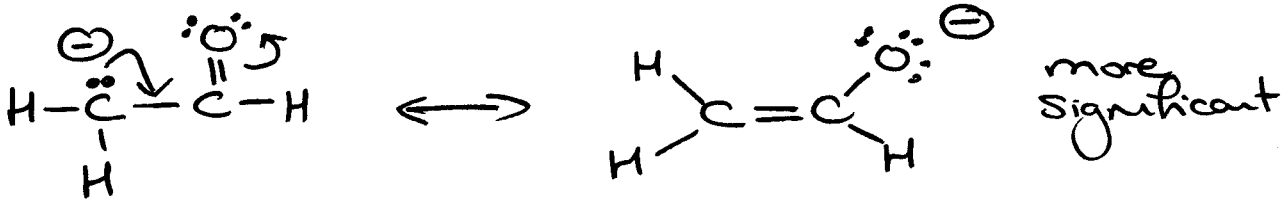
not a full octet

② MINIMISE CHARGES

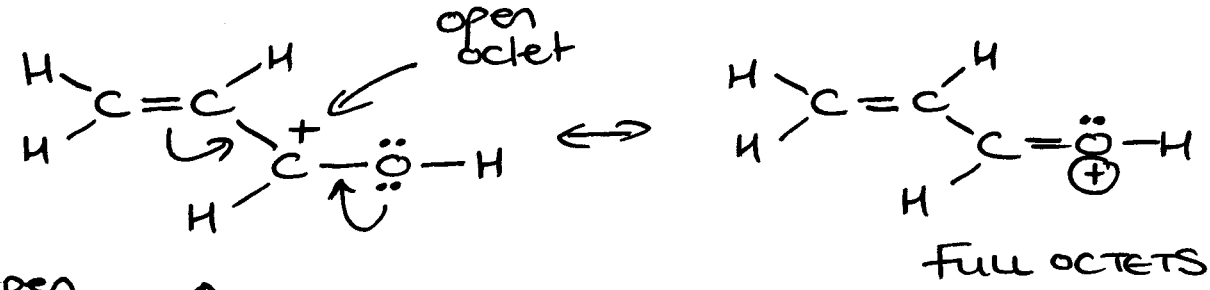


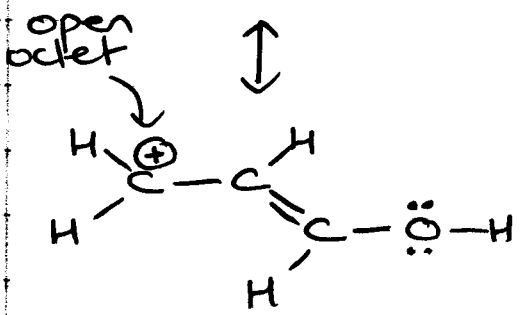
LESS SIGNIFICANT

(3) PUT -ve CHARGE ON MORE EN ELEMENT

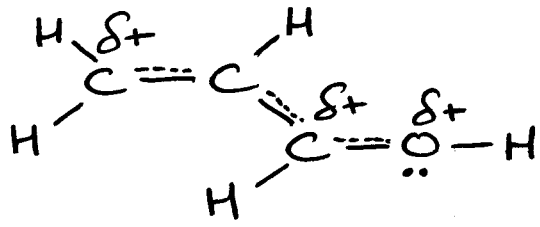


e.g.





HYBRID



next up: ATOMIC ORBITALS

LEC 4 CHEM 30A Apr 11th

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

HMK 1.18, 1.55 – 1.71 (1.70 3rd ed) + RESONANCE PROBLEMS ON WEB

QUIZ IN CLASS ON WEDNESDAY

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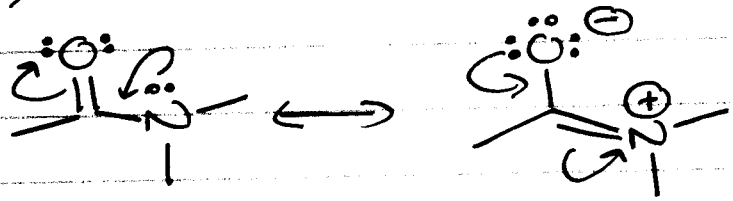
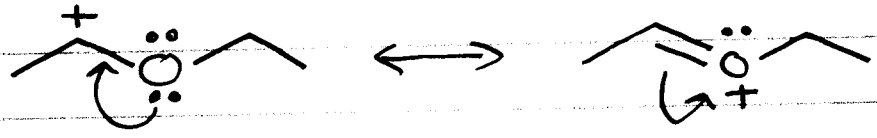
1. RESONANCE

– Patterns

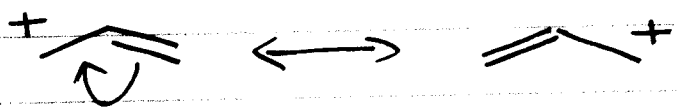
a) LONE PAIR / π-BOND



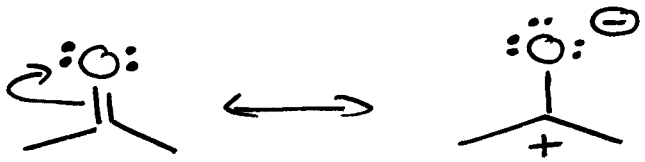
b) LONE PAIR / +ve CHARGE



c) π BOND / +ve CHARGE



d) π BOND / TWO EN ATOMS



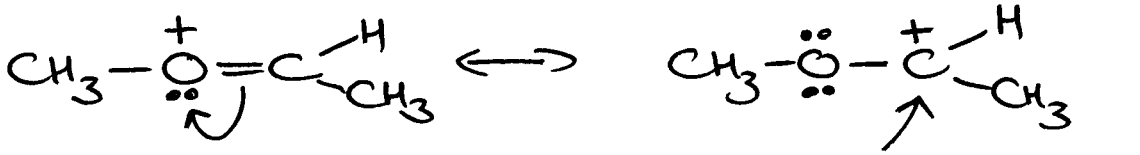
NOT

O is more EN than C

e) π BONDS in a RING

— RELATIVE IMPORTANCE OF CONTRIBUTING STRUCTURES

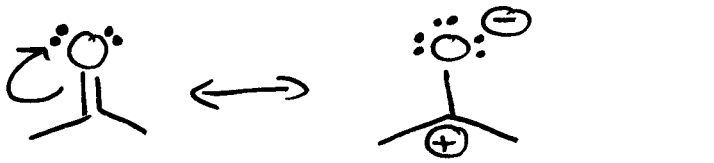
a) MAXIMISE OCTETS



more significant

not a full octet

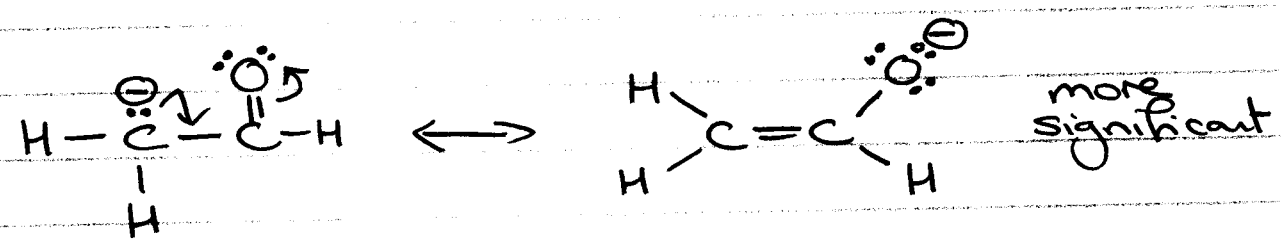
b) MINIMISE CHARGES



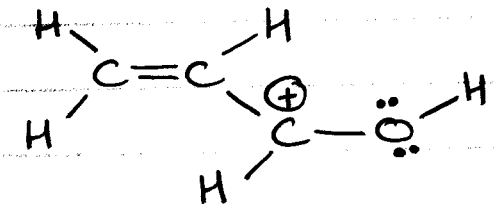
more significant

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

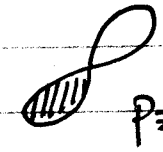
this class

sharp
principal
diffuse
fundamental

1s 

2s 

2p ORBITALS



(3) MOLECULAR ORBITALS

molecules => many atoms => many atomic orbitals

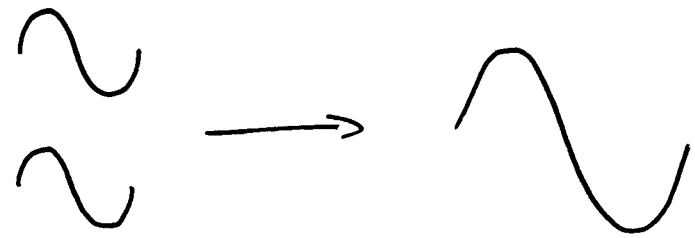
(LCAO - linear combination of atomic orbitals)

nAOs $\longrightarrow$ nMOs

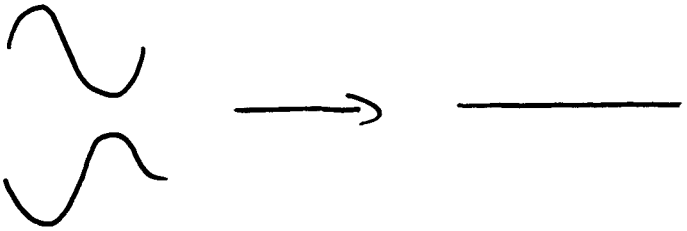
- same filling rules

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

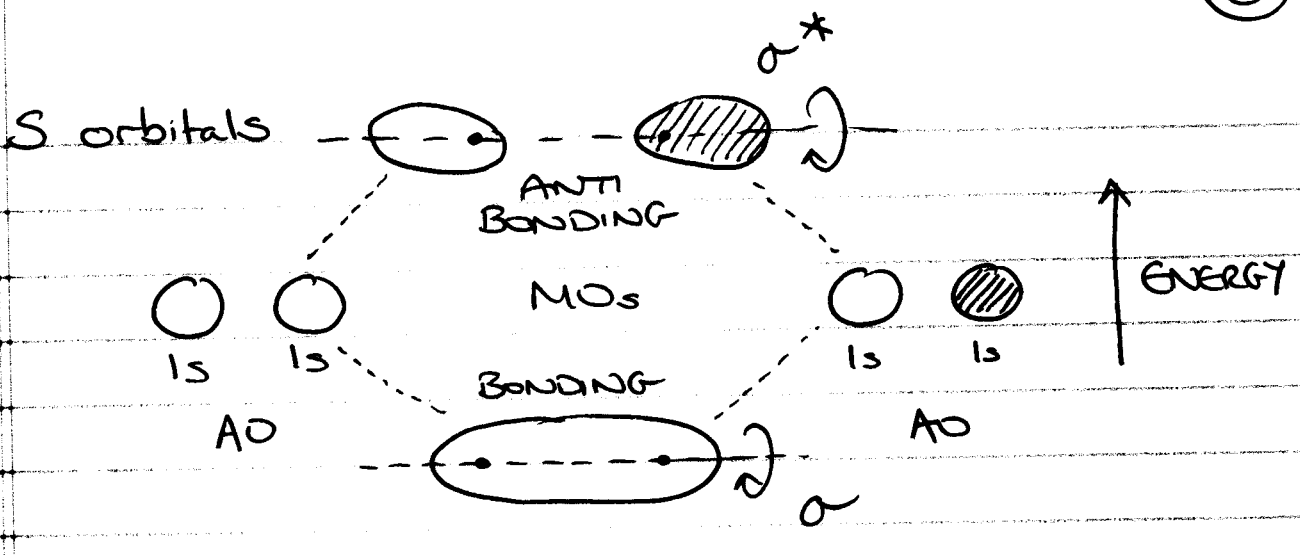
Orbitals → wavefunctions - combine like waves



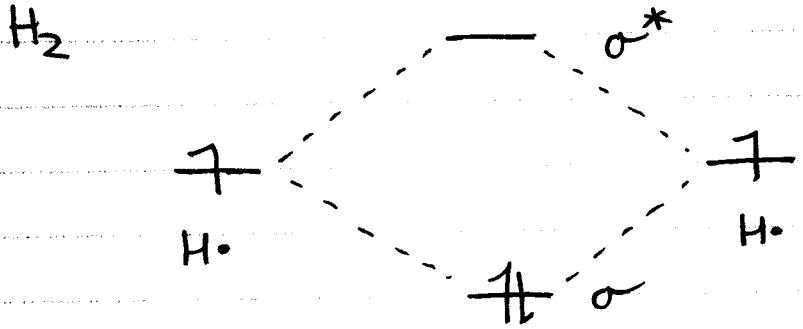
in phase
(constructive)



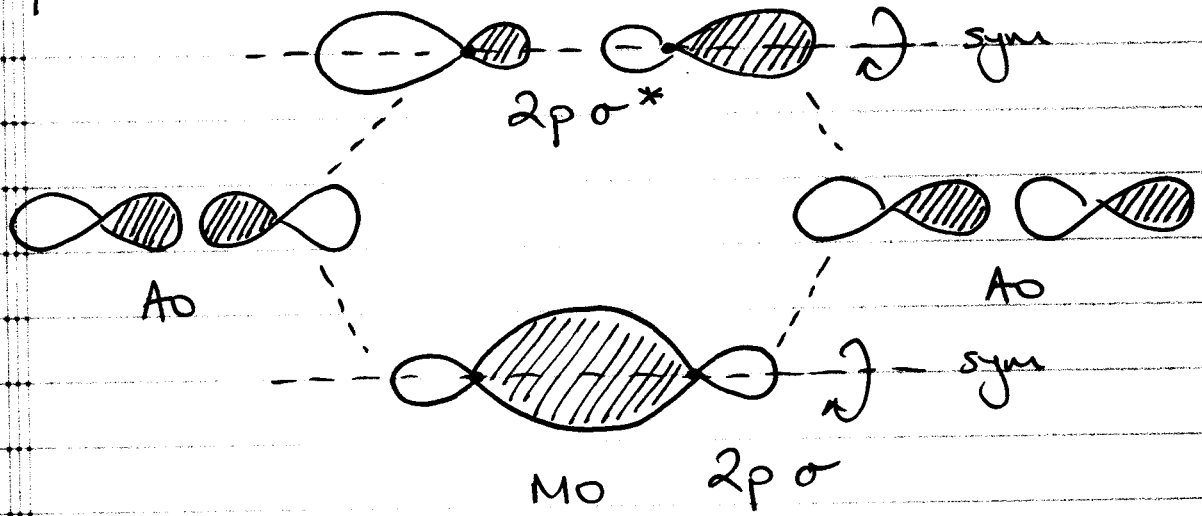
out of phase
(destructive)



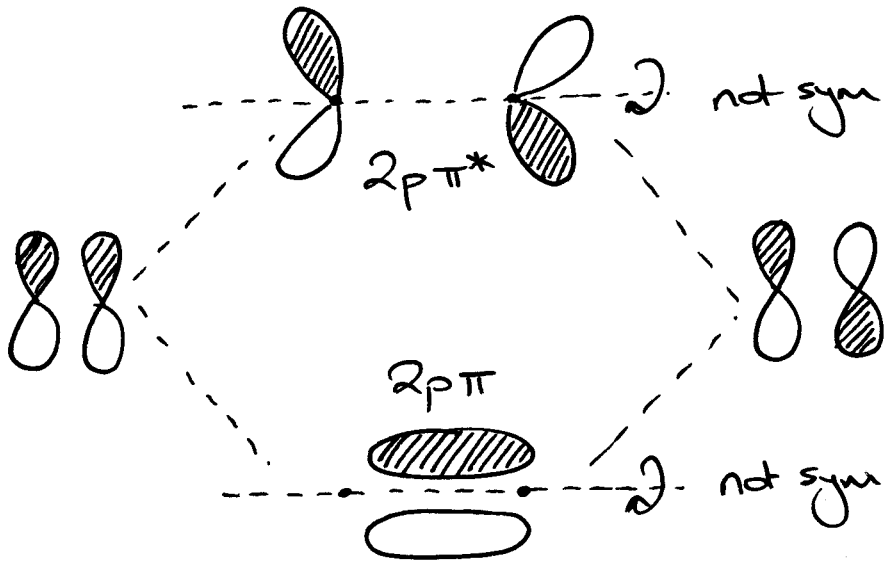
Symmetrical about axis ⇒ σ



p orbitals



p ORBITALS can also overlap side on...

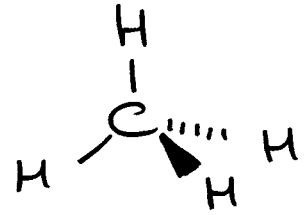


σ BONDS stronger than π BONDS ⇒ More overlap

④ HYBRIDISATION

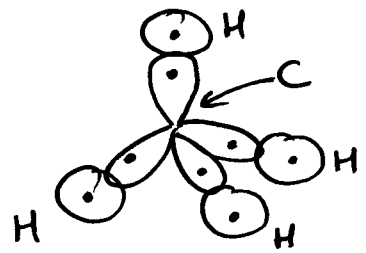
C $1s^2\ 2s^2\ 2p^2$
$1s^2\ 2s^2\ 2p_x^1\ 2p_y^1\ 2p_z^0$

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

So, how do we explain  ?

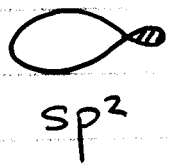
HYBRID ORBITALS (PAULING)

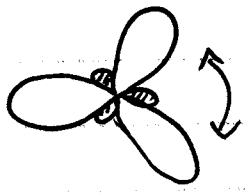
sp^3 (1 x 2s, 3 x 2p) ⇒ 4 sp^3 orbitals

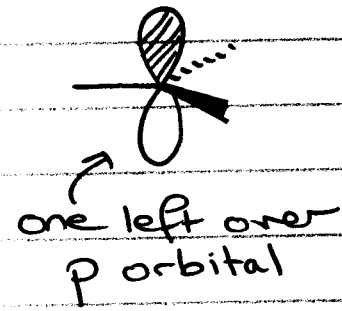


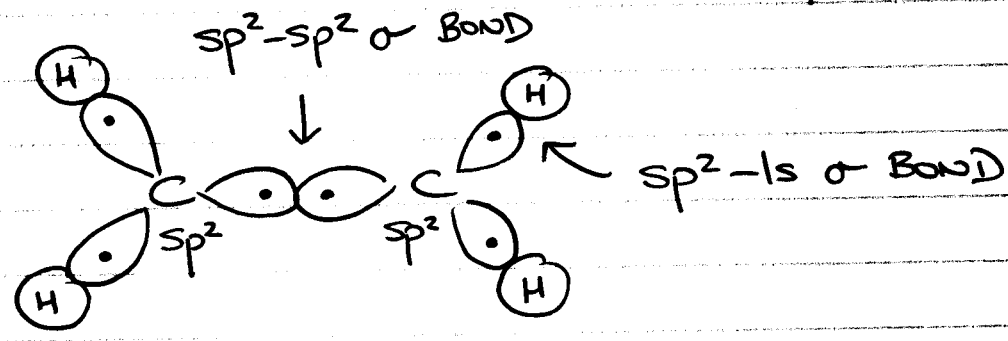
1s - $2sp^3$ σ BONDS

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

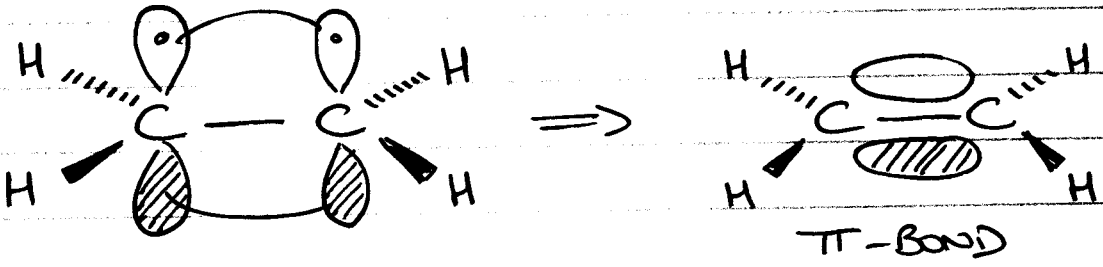




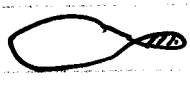


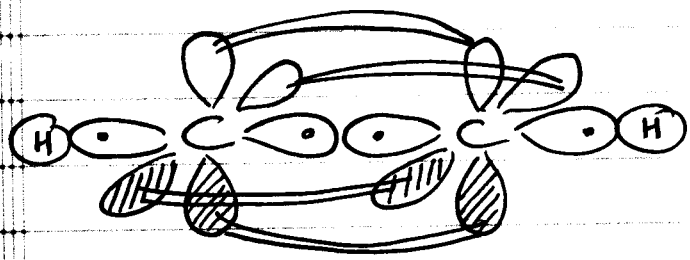


σ BOND FRAMEWORK



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



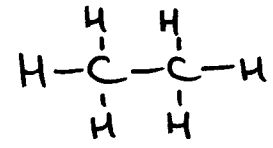


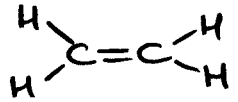
$H-C \equiv C-H$

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

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

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 Apr 13th

ALKANES

(1) STRUCTURE
(2) ISOMERS
(3) NOMENCLATURE

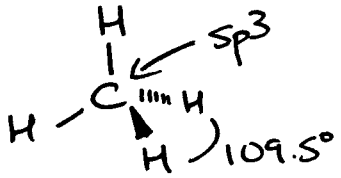
Read 2-2.6 PROBLEMS 2.1, 2.2 2.17-2.21 (3rd) 2.16-2.25 (4th)

---

(1) STRUCTURE

Alkanes → saturated HYDROCARBONS
⇓ each C has max # Hs
⇓ 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...

$CH_3(CH_2)_nCH_3$ UNBRANCHED

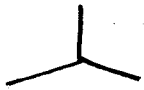
(2) ISOMERS

- same molecular formula, different arrangement of atoms
  ⇒ CONSTITUTIONAL ISOMERS

CH_4, C_2H_6, C_3H_8 ONLY ONE ARRANGEMENT POSSIBLE

How about C_4H_{10}

butane



2 methylpropane

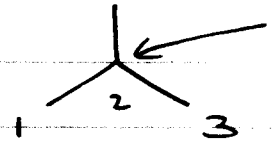
Do C_6H_{14} for HMK (5 structures)

(3) NOMENCLATURE

International Union of Pure and Applied Chemistry
IUPAC ⇒ SYSTEMATIC NAMING

- Straight chains (done)

- BRANCHED STRUCTURES
  (i) Identify longest chain
  (ii) Each substituent gets a name & number

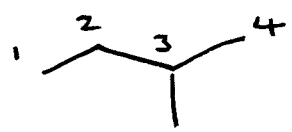


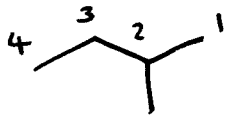
← 2 METHYL PROPANE

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

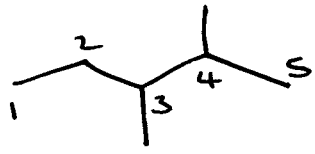


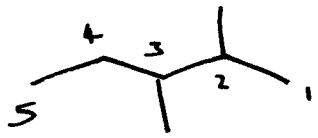


2-METHYL BUTANE ✓

~~3-METHYL BUTANE~~

(iv) SAME SUBSTITUENT MORE THAN ONCE

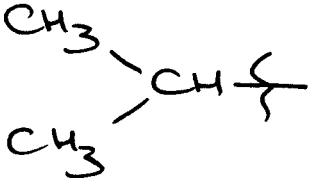




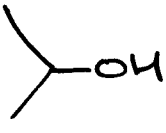
2,3-DIMETHYL PENTANE

- after this, it gets SILLY!

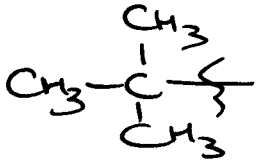
COMMON NAMES



isopropyl

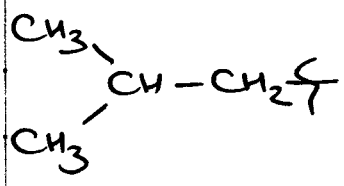


isopropyl alcohol

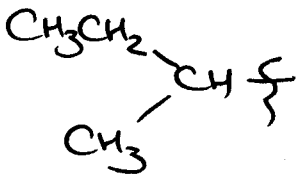


tertiary butyl (tert or t-butyl)

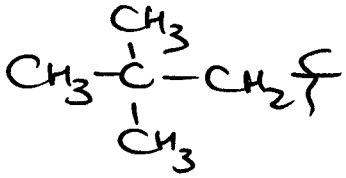
t-butyl bromide



isobutyl



secbutyl

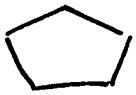


neopentyl

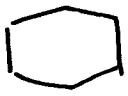
CYCLOALKANES (C_nH_{2n})

CYCLOPROPANE C_3H_6

CYCLOBUTANE C_4H_8



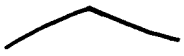
CYCLOPENTANE C_5H_{10}



CYCLOHEXANE C_6H_{12}

BICYCLOALKANES — FORGET IT!

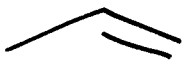
General rules: PREFIX - INFIX - SUFFIX



PROP — 3Cs

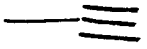
AN — Single Bonds

E — Hydrocarbon



PROPENE

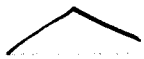
-EN- Double

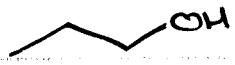


PROPYNE

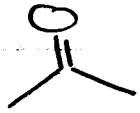
-YN- Triple

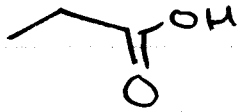
SUFFIXES - functional groups

-E  PROPANE

-OL  PROPANOL

-AL  PROPANAL

-ONE  PROPANONE

-OIC ACID  PROPANOIC ACID

(-AMINE)*  PROPYL AMINE

not PROPANAMINE!

- COMMON NAMES

LEC (6) CHEM 30 A Apr 15th

(1) NOMENCLATURE
(2) CONFORMATIONAL ANALYSIS
(3) CYCLOALKANES

QUIZ
Mean 18/30
Low 0
High 35

READ 2.6-2.8
HMK 2.8, 2.9, 2.24-2.30 (3rd)
2.7, 2.8, 2.28-2.37 (4th)

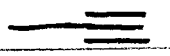
---

(1) NOMENCLATURE

General rules: PREFIX-INFIX-SUFFIX

PROP AN E
3Cs single bonds hydrocarbon

PROPENE -EN-
double bonds

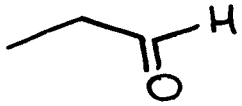


PROPYNE -YN-
triple bonds

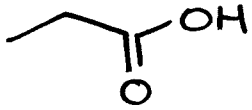
SUFFIXES → functional groups

- E  PROPANE

- OL  PROPANOL

- AL  PROPANAL

- ONE  PROPANONE

- OIC ACID  PROPANOIC ACID

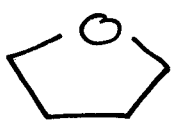
(- AMINE)  PROPYL AMINE
(not PROPANAMINE)

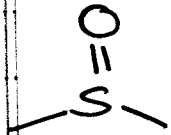
- CYCLOALKANES - easy
- BICYCLOALKANES - don't worry about it.

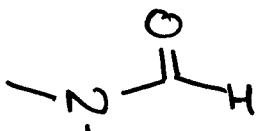
Common Names / Structures / Acronyms
(Keep a notebook)

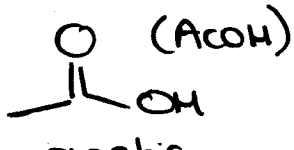

acetone


pyridine

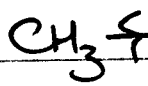

(THF)
tetrahydrofuran

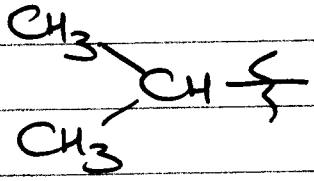

(DMSO)
dimethyl sulfoxide


(DMF)
dimethylformamide

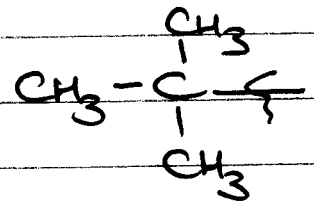

(AcOH)
acetic acid

- other common abbreviations

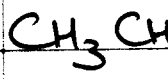
 Me

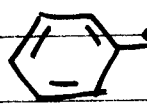
 ^{i}Pr

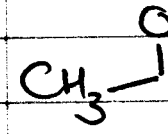
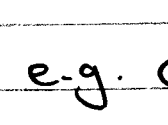
 Et

 ^{t}Bu

 Pr

 Bu

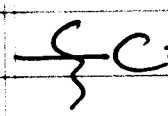
 Ph (PHENYL) e.g.  = PhBr

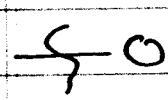
 Ac (ACETYL) e.g.  = AcCl

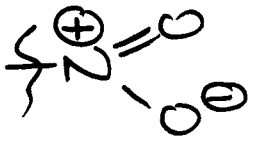
R GROUPS - stuff dangling off the area of interest in a molecule

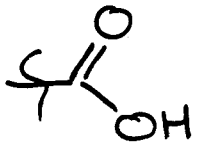
e.g. R-Cl, R-OH, $R-CO_2H$
chloride alcohol carboxylic acid

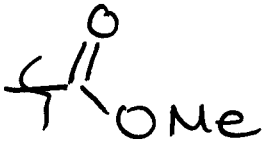
FUNCTIONAL GROUPS

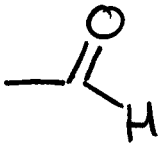
 —CN

 —OH



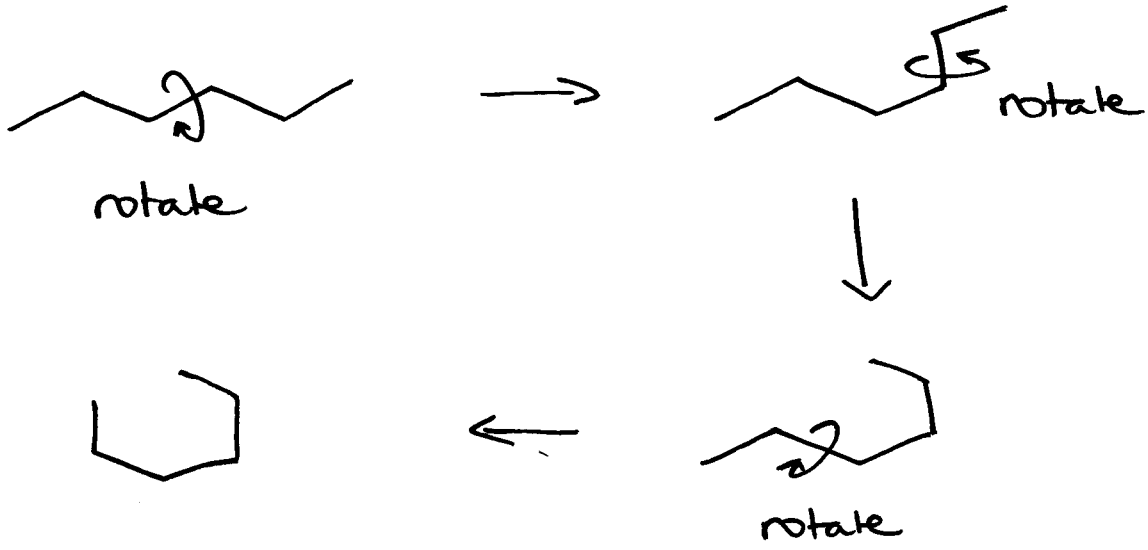






(2) CONFORMATIONAL ANALYSIS

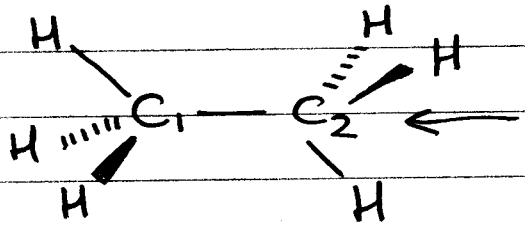
- consider HEXANE

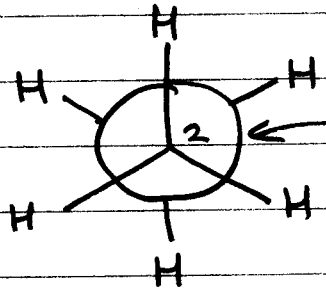


THESE ARE ALL THE SAME MOLECULE...
Different arrangements of atoms that result from ONLY single bond rotations are called CONFORMATIONS

At room temperature all single bonds are constantly rotating

- consider C_2H_6

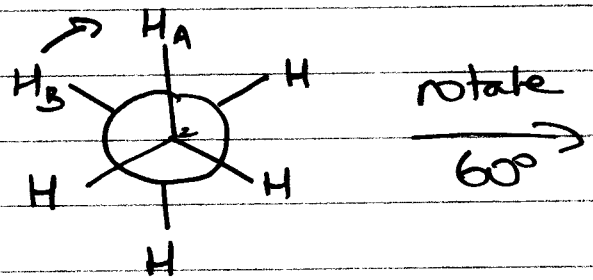


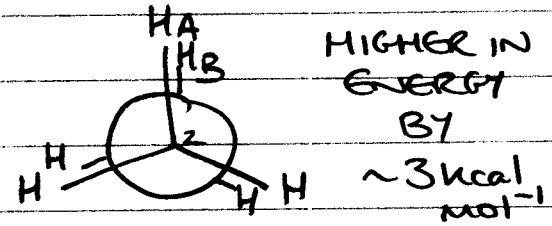


look down C–C bond
NEWMAN PROJECTION

- TWO METHYL GROUPS CAN ROTATE WRT ONE ANOTHER (0–360°)
  ⇒ INFINITE NUMBER of CONFORMATIONS

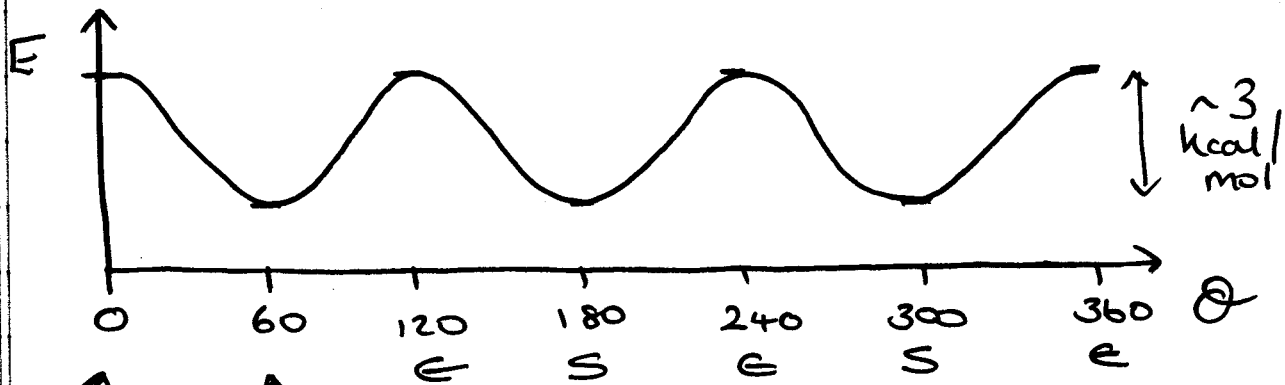
At rt, rate of rotation is ~ 10 BILLION s^{-1}
but rotation is not completely UNHINDERED

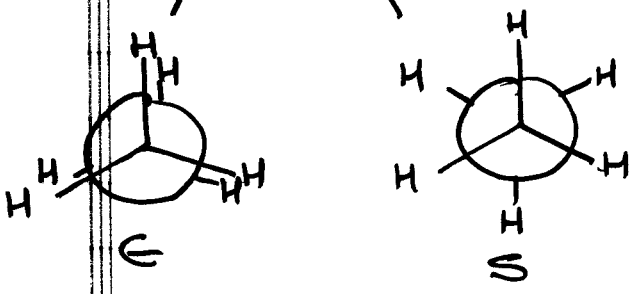




STAGGERED ($\theta = 60°$) ECLIPSED ($\theta = 0°$)

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

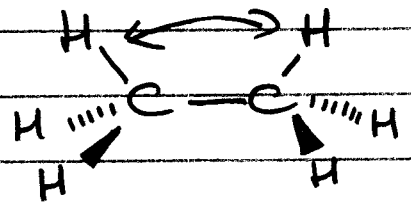
Any given molecule will spend most of its time in a staggered or nearly staggered conformation (LOWEST ENERGY) and will only briefly pass through the eclipsed conformation on its way to the next staggered conformation

EQUILIBRIUM

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

WHY IS THERE A BARRIER?

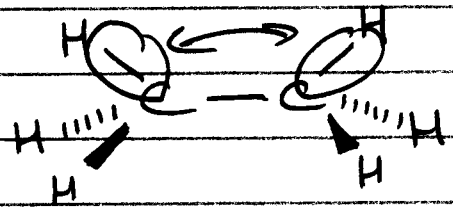
(i) STERIC INTERACTION?



BUT H ATOMS are VERY SMALL

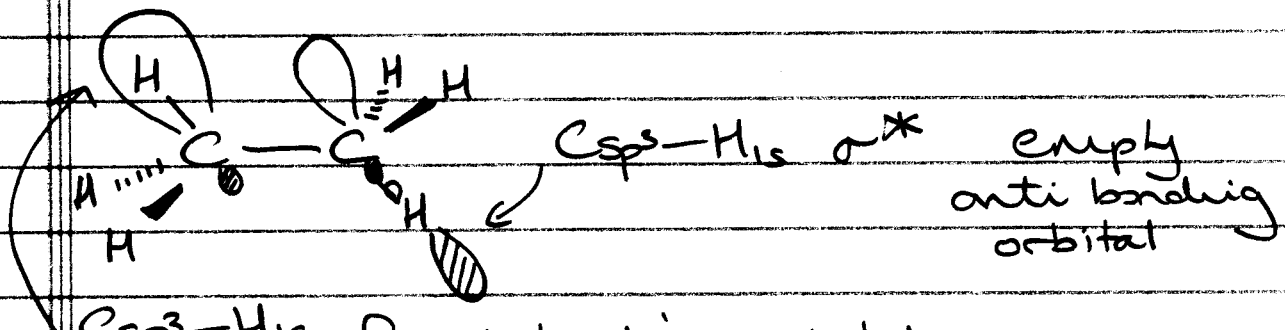
Sterics account for ~10% of BARRIER

(ii) ELECTRON PAIR REPULSION



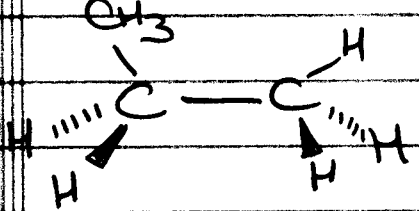
BIGGEST FACTOR

(iii) ATTRACTIVE INTERACTIONS

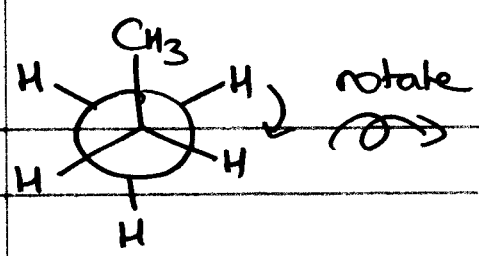


$C_{sp^3}-H_{1s}$ σ filled bonding orbital

CONFORMATIONS OF PROPANE?



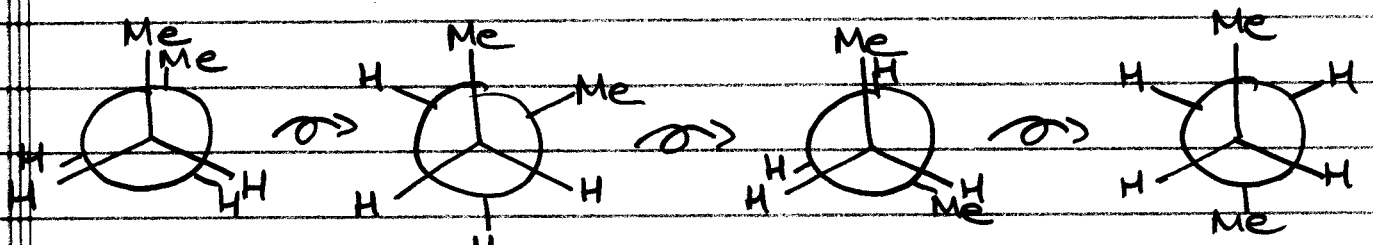
Bigger repulsive interaction Than C–H / C–H



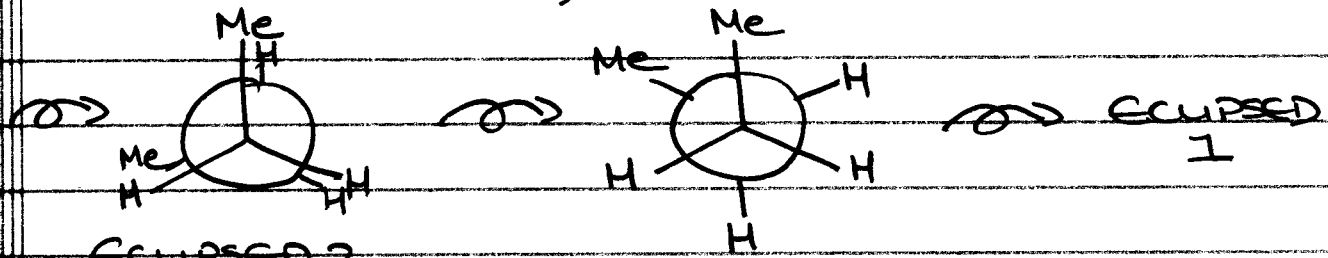
Same profile as ETHANE, but higher barrier (3.4 kcal/mol)

Staggered Eclipsed

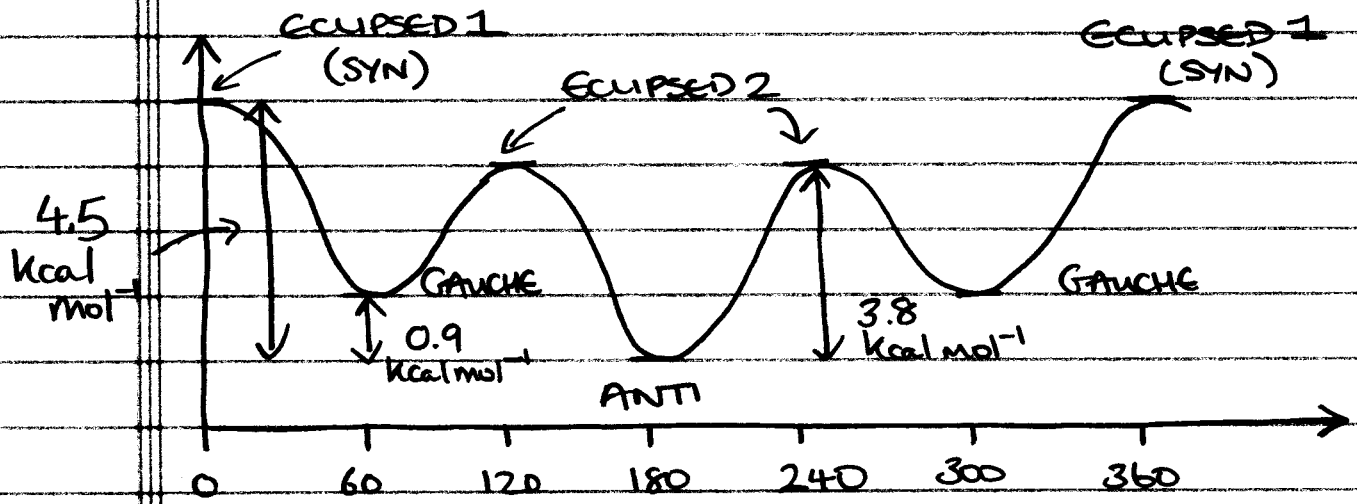
CONFORMATIONS OF BUTANE



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

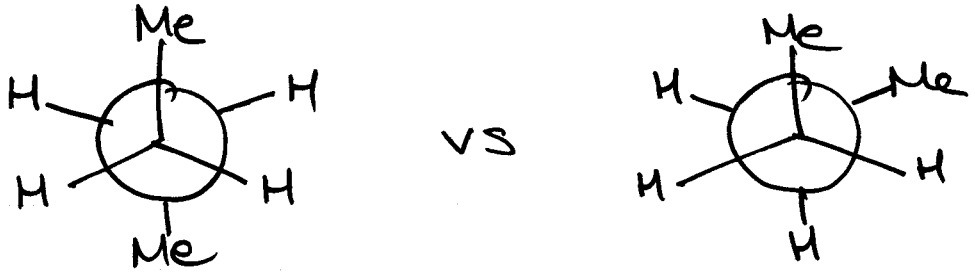


ECLIPSED 2 (mirror image of other one) — STAGGERED 1 (GAUCHE) mirror image of other one — ECLIPSED 1



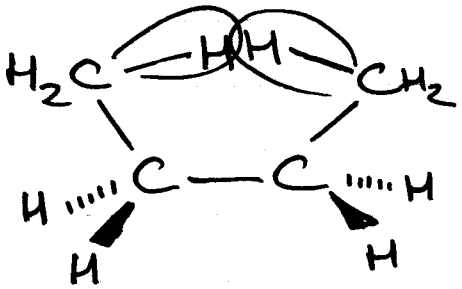
Each ECLIPSED conformer is a MINIMA
Each STAGGERED conformer is a MAXIMA

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



↓

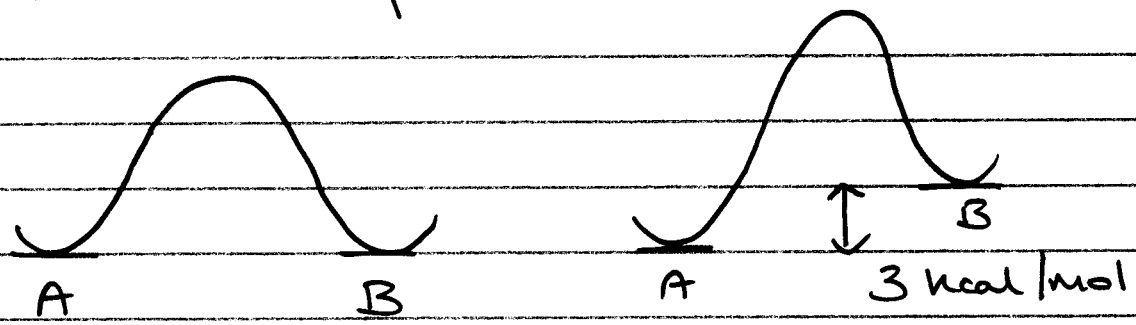
forcing atoms closer together than atomic radii allow

At room temperature, BUTANE is rapidly equilibrating between CONFORMERS

~80:20 anti / gauche

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

At room temperature:



50:50 99:1

K ← equilibrium constant

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

↑ equilibrium arrows

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

↑ difference in free energy

next up: CYCLOALKANES

LEC (7) CHEM 30A Apr 18th

(1) CONFORMATIONAL ANALYSIS
(2) CYCLOALKANES

Read: rest of Ch2
Problems: 2.10-2.12, 2.31-2.33 (3rd)
2.9-2.11, 2.36-2.37 (4th)

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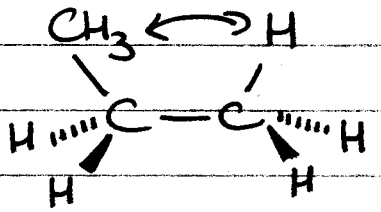
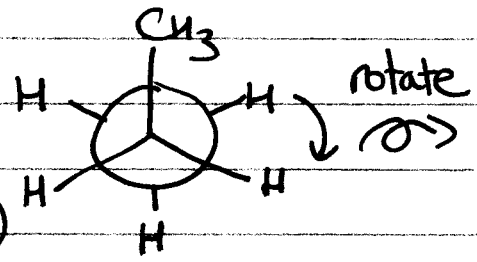
(1) CONFORMATIONAL ANALYSIS

– Propane

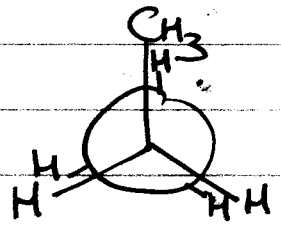


Bigger repulsive interaction
Me–H / C–H

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

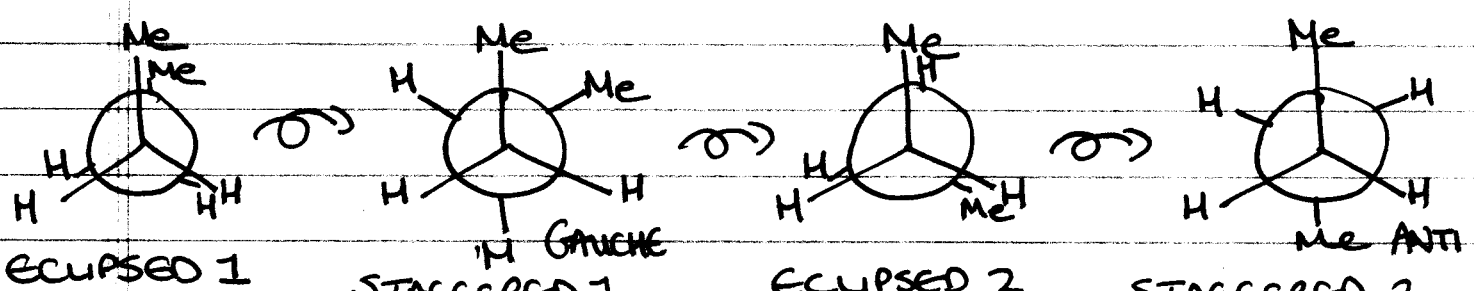


STAGGERED

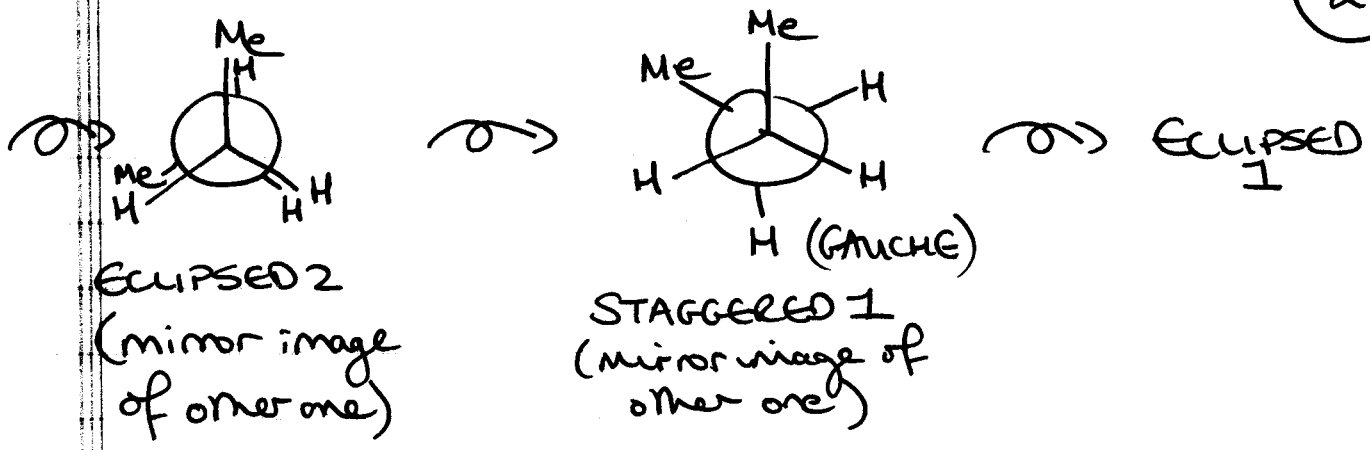


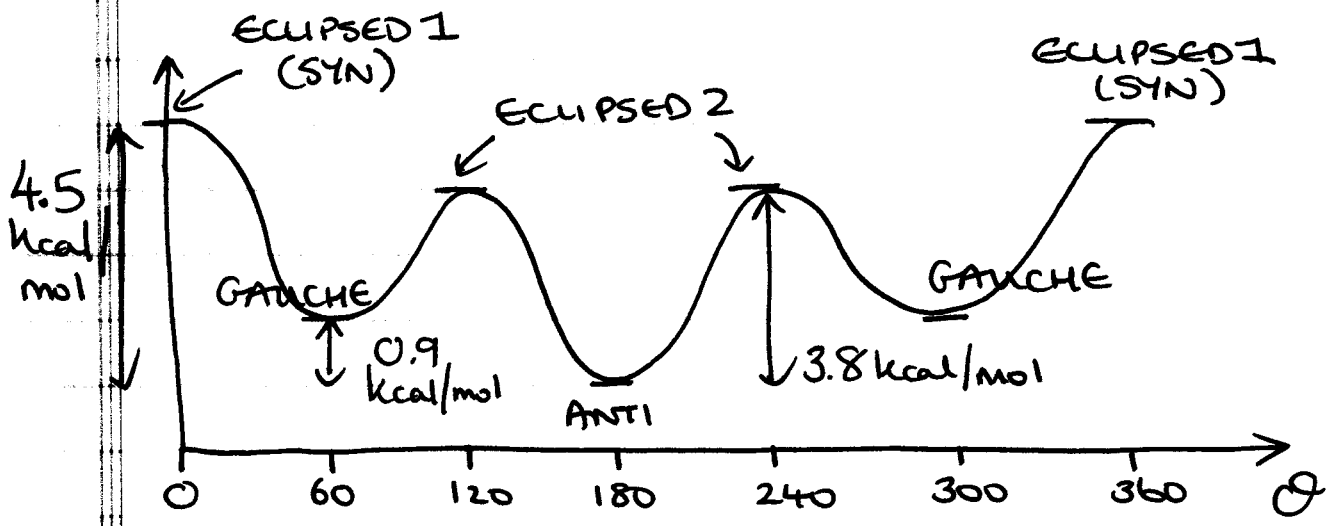
ECLIPSED

– CONFORMATIONS OF BUTANE



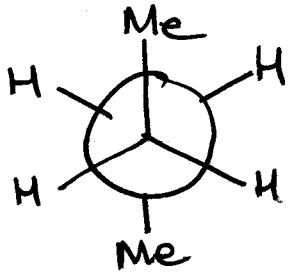
ECLIPSED 1 | STAGGERED 1 (H GAUCHE) | ECLIPSED 2 | STAGGERED 2



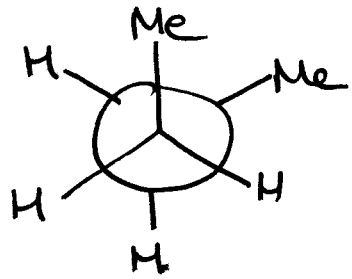


Each ECLIPSED conformer is a MAXIMA
each STAGGERED conformer is a MINIMA

<u>BUT</u> different MINIMA/MAXIMA energies

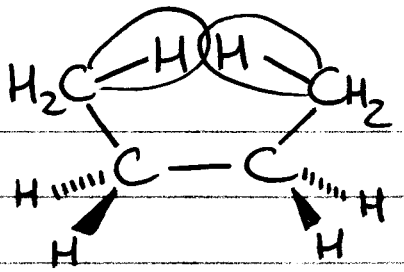


ANTI (180°)



GAUCHE (60°)

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



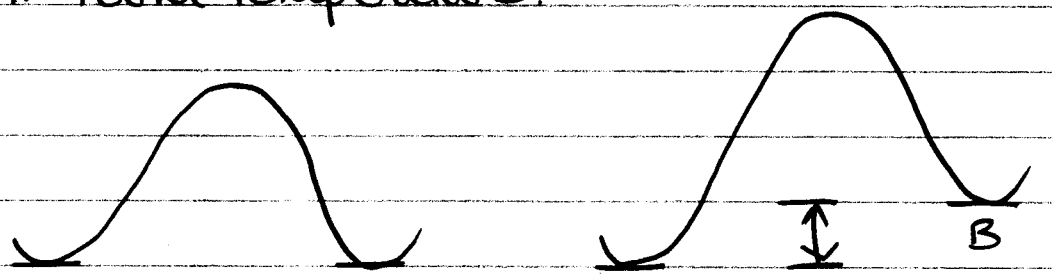
STERIC STRAIN — forcing atoms closer together than atomic radii will allow

At room temperature, BUTANE is rapidly equilibrating between CONFORMERS

~80:20 anti / gauche

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

At room temperature:



K ← equilibrium constant

$A \rightleftharpoons B$

↑ equilibrium arrows

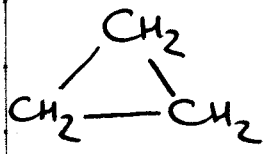
$$K = \frac{[B]}{[A]}$$

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

↑ difference in free energy

② CYCLOALKANES

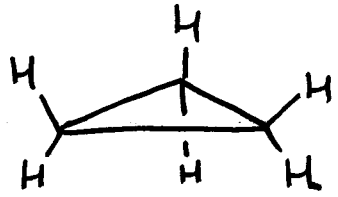
(i) CYCLOPROPANE



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

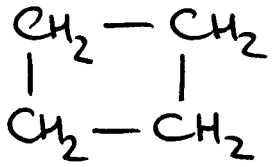
⇒ ANGLE STRAIN

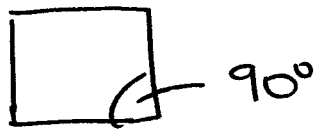
Total ring strain ~ 28 kcal/mol
– most of this is angle strain, but also ALL C–H bonds are ECLIPSED
⇒ TORSIONAL STRAIN



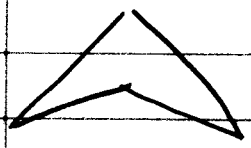
ALL ECLIPSED

(ii) CYCLOBUTANE





If PLANAR, all C–Hs would be eclipsed, so ring puckers to avoid TORSIONAL STRAIN

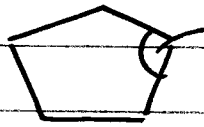


C-C-C angles ~ 88°
(so, worse than 90° => more angle STRAIN)

Total ring strain is ~ 26kcal/mol

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

(iii) CYCLOPENTANE



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

BUT all C-H bonds would be ECLIPSED
=> TORSIONAL STRAIN

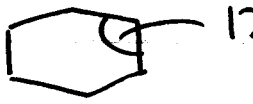
ENVELOPE CONFORMATION (105° ANGLES)

=> REDUCES TORSIONAL STRAIN

4 Cs in PLANE, 1 C OUT (EQUILIBRIUM)

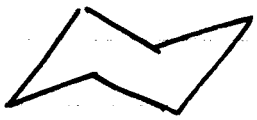
Total ring strain ~ 7 kcal/mol

(iv) CYCLOHEXANE



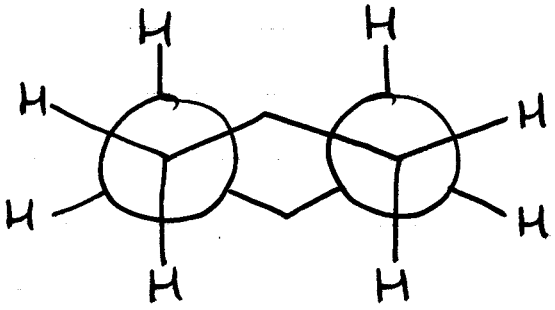
PLANAR STRUCTURE
⇒ angle & torsional strain

But cyclohexane is virtually STRAIN FREE



CHAIR CONFORMATION
C–C–C ANGLES 109.5°
no angle strain

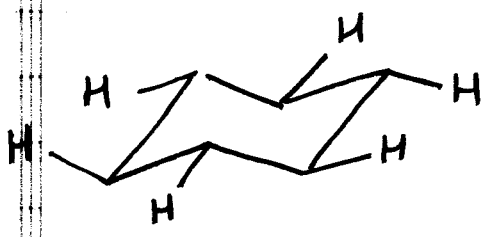
<u>ALSO</u> no torsional strain, Hs on adjacent carbon atoms are staggered.



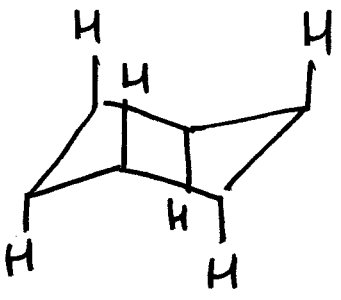
NEWMAN PROJECTION

also, no STERIC STRAIN

TWO DIFFERENT ORIENTATIONS for C–H BONDS

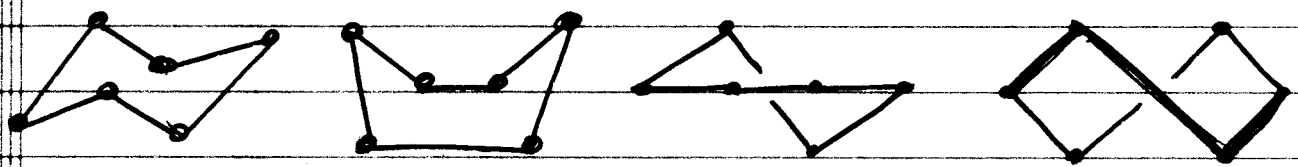


EQUATORIAL

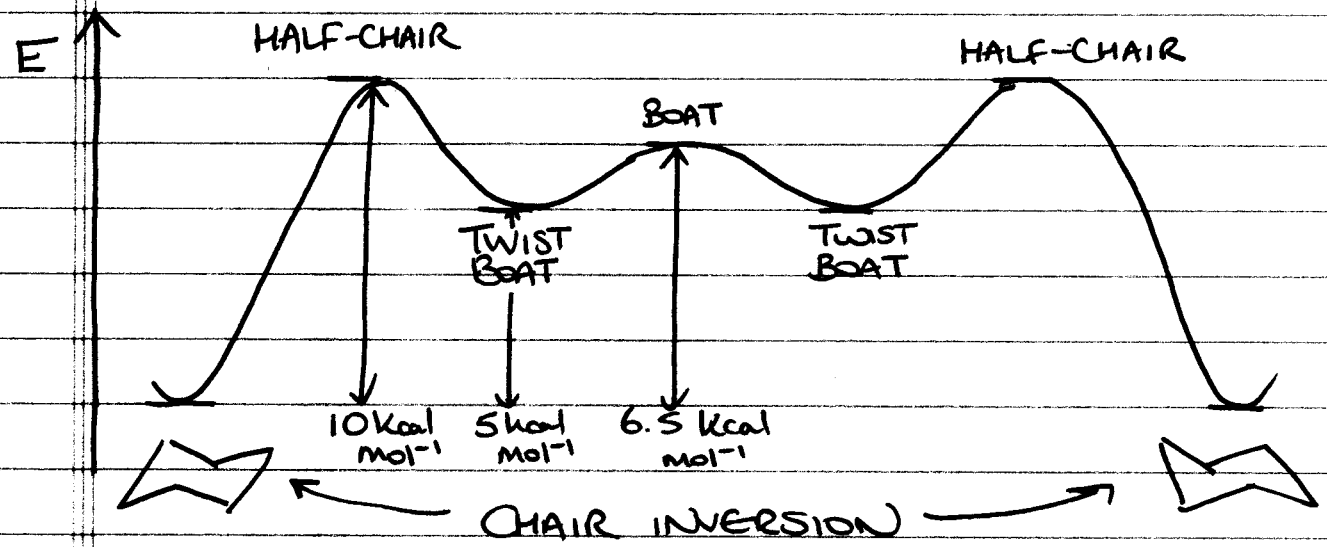


AXIAL

other conformations

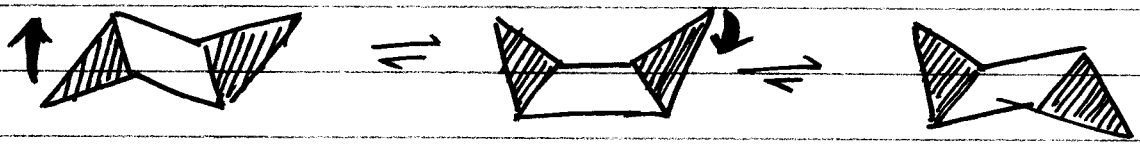


CHAIR BOAT HALF-CHAIR TWIST BOAT



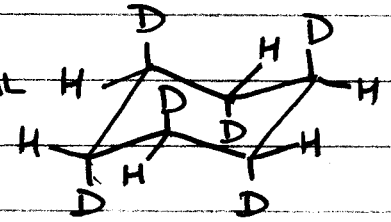
At RT, CHAIR > 99.99% of EQUILIBRIUM MIXTURE

CHAIR FLIP

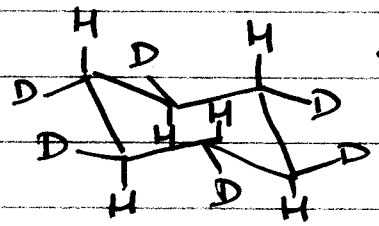


SWITCHES AXIAL & EQUATORIAL POSITIONS

D AXIAL
H EQUATORIAL

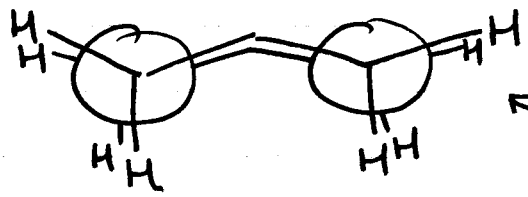


FLIP



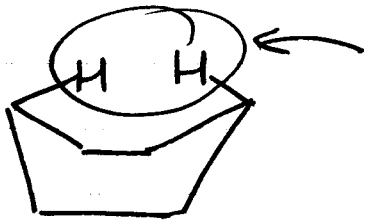
D EQUATORIAL
H AXIAL

BOAT CONFORMATION



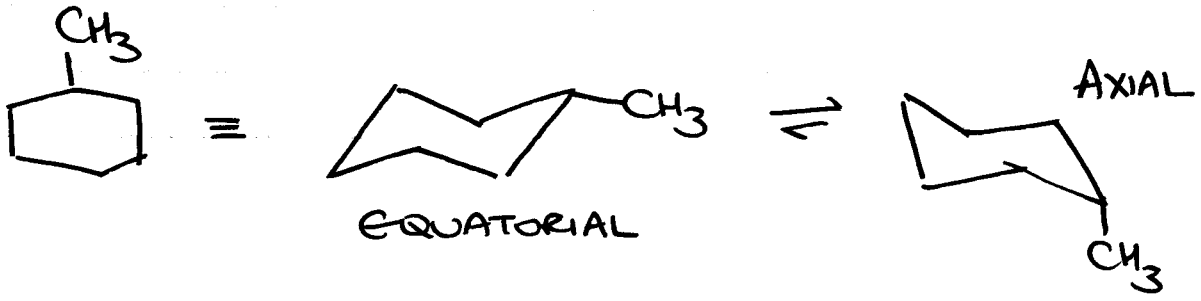
← ECLIPSED C–Hs

also



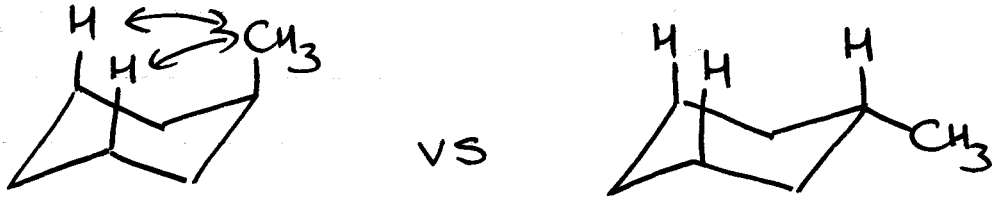
← NONBONDED – STERIC INTERACTIONS

consider METHYL CYCLOHEXANE



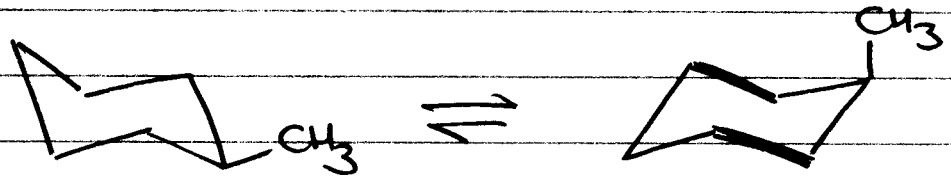
Which is more STABLE?

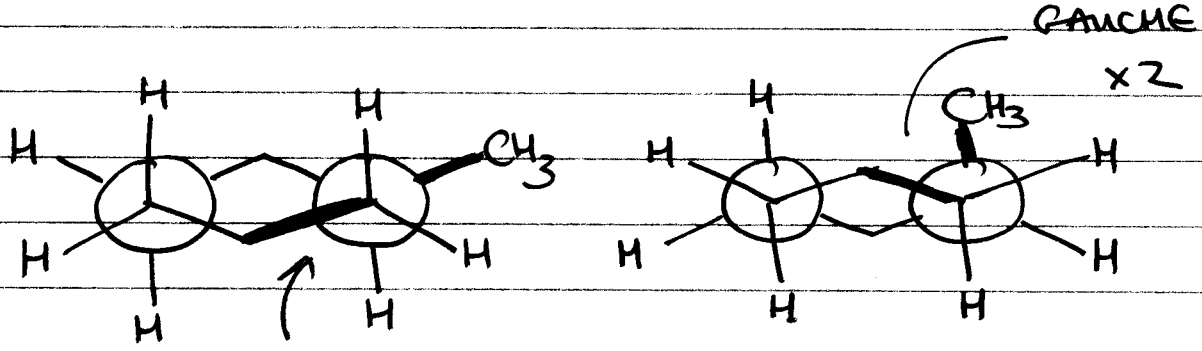
(i) 1,3 – DIAXIAL INTERACTIONS



NONBONDED INTERACTIONS (STERIC)

(ii) GAUCHE INTERACTIONS





ANTI PERIPLANAR

LEC (8) CHEM 30A Apr 20th

3rd 2.10-2.16, 2.34-2.53

4th 2.11-2.15, 2.36-2.61

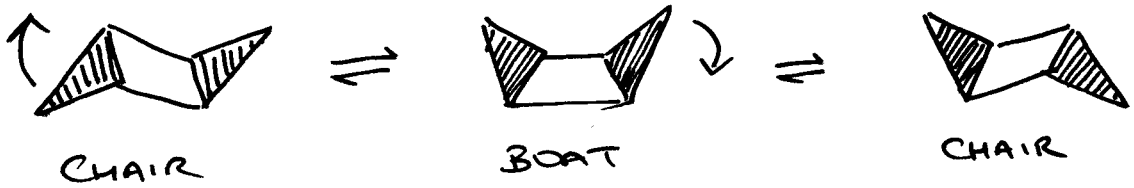
(1) CYCLOHEXANE
(2) PROPERTIES OF ALKANES
(3) REACTIONS / SOURCES / IMPORTANCE
(4) STEREOCHEMISTRY

READ: 2.9, 2.10, 3.1, 3.2

---

(1) CYCLOHEXANE

CHAIR FLIP

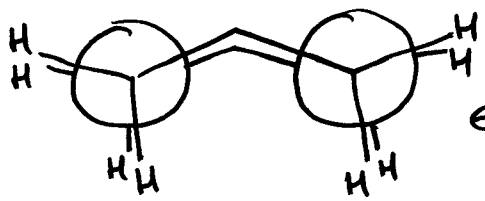


- switches AXIAL and EQUATORIAL POSITIONS

D AXIAL, H EQUATORIAL D EQUATORIAL, H AXIAL

A CLOSER LOOK AT THE <u>BOAT</u> CONFORMATION

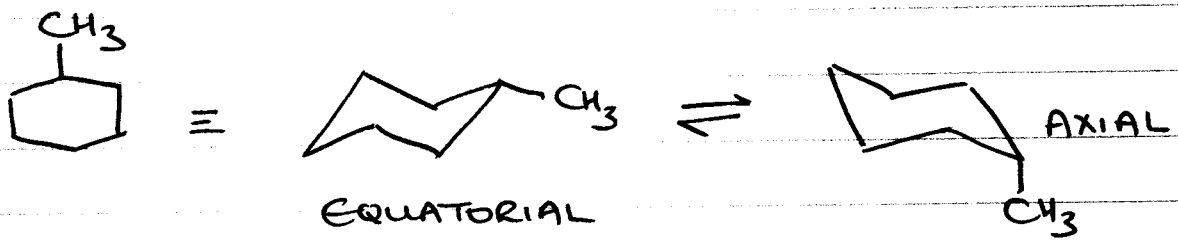
NONBONDED (STERIC) INTERACTIONS



ECLIPSED C–Hs

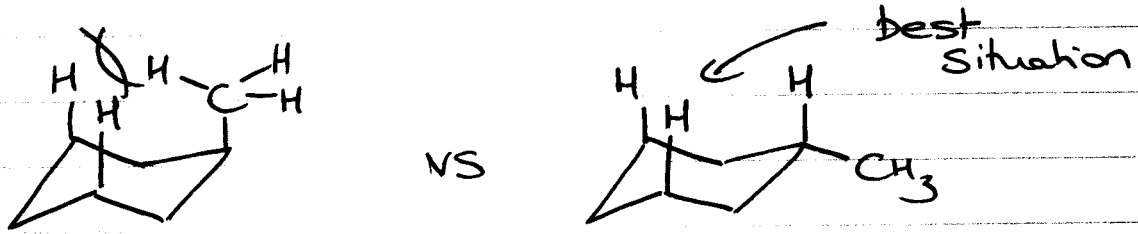
- SUBSTITUTED CYCLOHEXANES

Consider METHYL CYCLOHEXANE

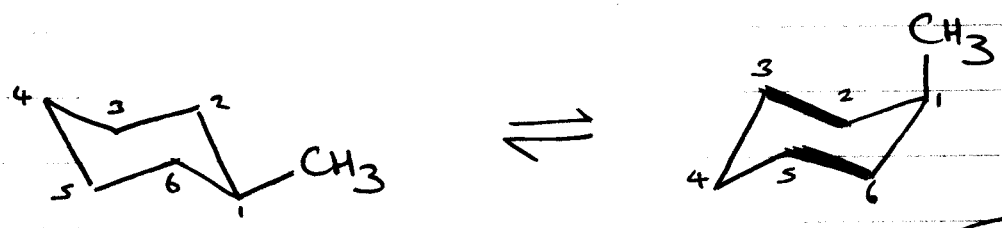


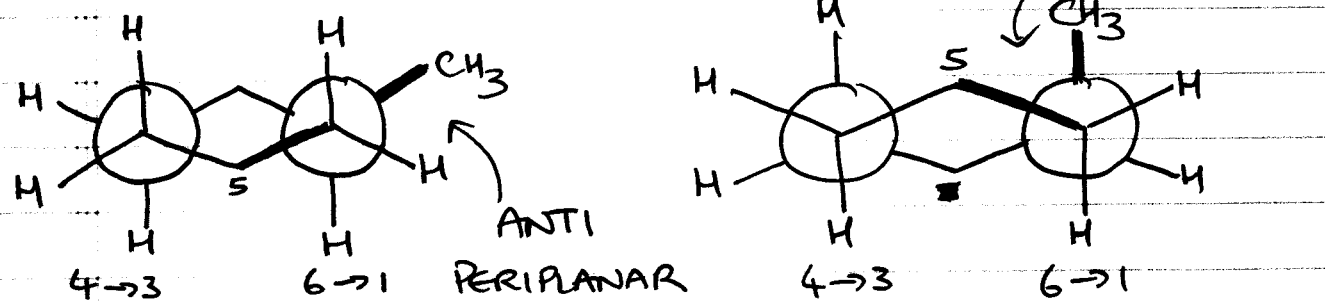
Which is more STABLE?

(i) 1,3- DIAXIAL INTERACTIONS

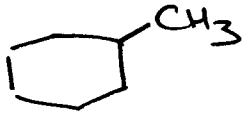


(ii) GAUCHE INTERACTIONS

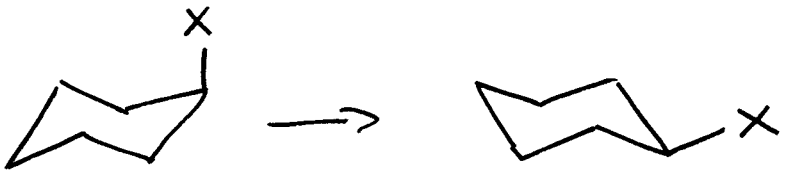




In general, conformer in which largest substituent is equatorial will be the most stable

For  CH_3 – equatorial more stable by ~1.74 kcal/mol

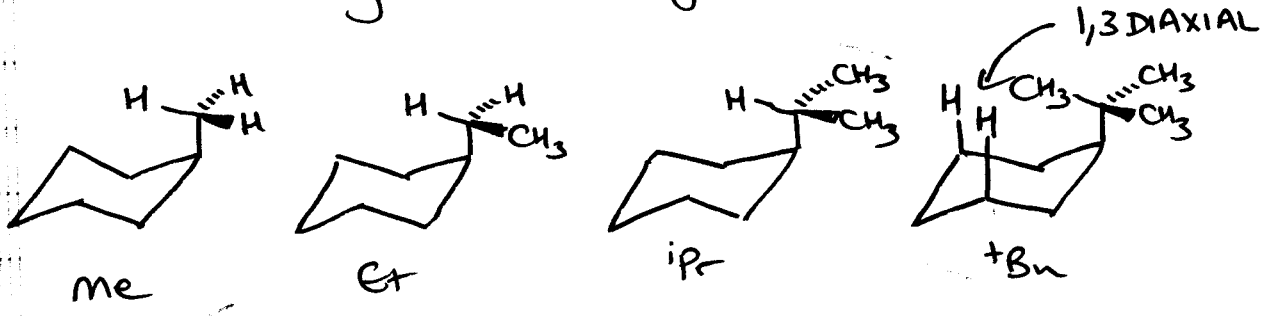
A VALUES → measure of preference for equatorial position



NEGATIVE OF ΔG FOR AXIAL → EQUATORIAL, SO, A values are usually positive.

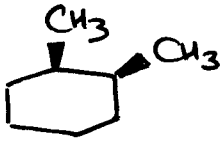
$-CH_3$	$-CH_2CH_3$	$-CH(CH_3)_2$	$-C(CH_3)_3$
1.74	1.75	2.15	> 5

Note relatively small changes for Me, Et, ^iPr

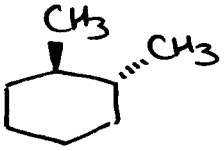


^tBu => LOCKING GROUP, OVERWHELMING PREF FOR EQUATORIAL POSITION

- DISUBSTITUTED CYCLOHEXANES



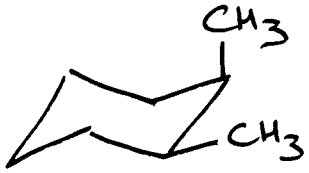
Same side CIS
cis-1,2-dimethyl cyclohexane



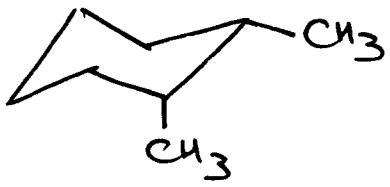
opposite side trans
trans-1,2-dimethylcyclohexane

Note when converting to CHAIR form, ▮ and ≡ have NOTHING to do with AXIAL/EQUATORIAL, or UP/DOWN

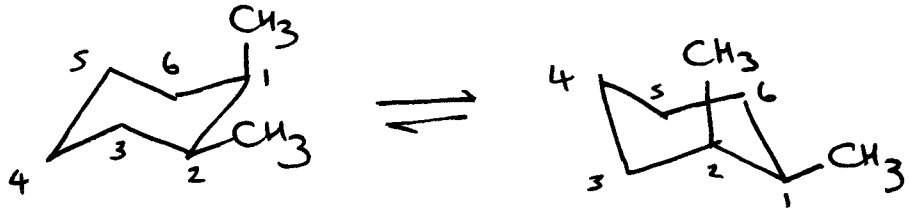
CIS



Same as



RING FLIP



What is ΔG for this equilibrium?

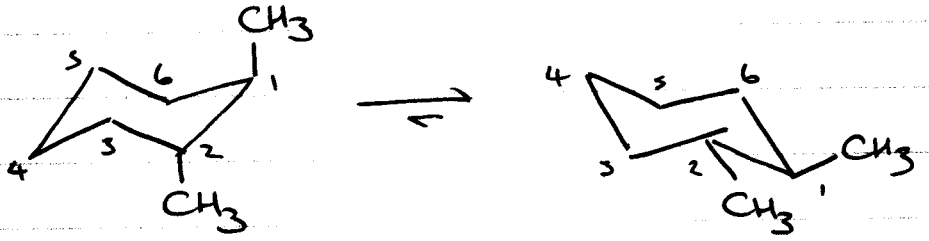
C1 Ax CH_3 → Eq CH_3 −1.74

C2 Eq CH_3 → Ax CH_3 +1.74

0 kcal/mol

So, 50:50 mixture

trans (opposite sides)



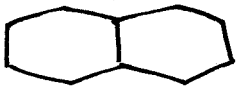
What is ΔG for this equilibrium?

C1	Ax CH_3 →	Eq CH_3	−1.74
C2	Ax CH_3 →	Eq CH_3	−1.74
			−3.5 kcal/mol *

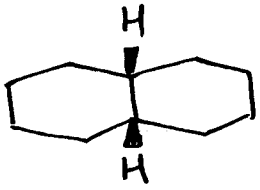
(actually ~2.6 kcal/mol)

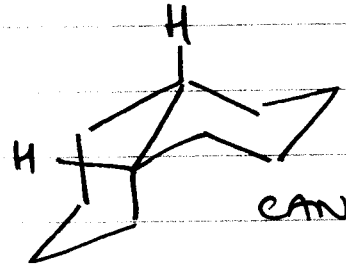
So, conformer w/ two equatorial methyls is favored.

— DECALINS



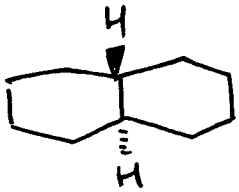
CIS DECALIN

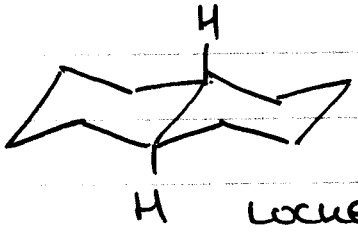




CAN FLIP

trans DECALIN





LOCKED.

② PROPERTIES OF ALKANES

as MW increases, mp & bp increase

INTERMOLECULAR INTERACTIONS

- IONIC
- HYDROGEN BONDING
- DIPOLE-DIPOLE
- DIPOLE-INDUCED DIPOLE
- INDUCED DIPOLE-INDUCED DIPOLE

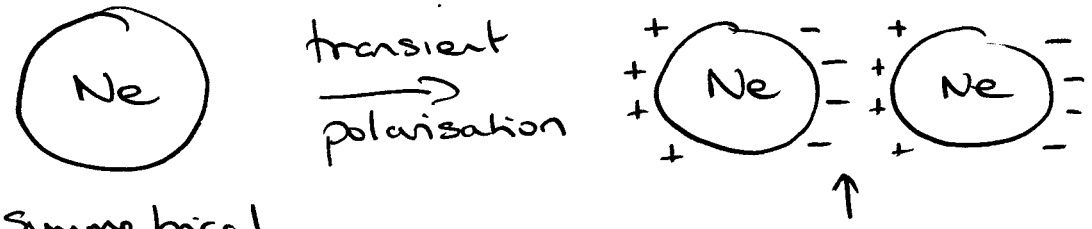
↓ Decreasing Strength

↳ Dispersion forces / LONDON forces

↳ Low MW non polar substances can be liquefied

He 4k Ne 27 K

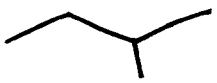
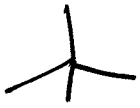
Bigger e⁻ clouds, stronger forces



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

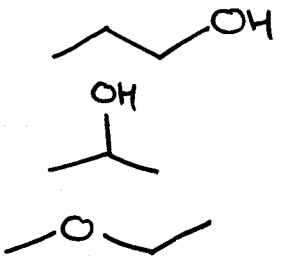
↳ Read Sections 2.9, 2.10

(and look over associated questions)

(4) STEREOCHEMISTRY

ISOMERS → different compounds with the same molecular formula.

CONSTITUTIONAL ISOMERS ⇓ Different connectivity

e.g 

or

STEREOISOMERS (configurational isomers) ⇓ Same connectivity of atoms, BUT different geometries

STEREOISOMERS → ENANTIOMERS (non superimposable mirror images)

↓

DIASTEREOISOMERS (non mirror image stereoisomers)

↗ CONFIGURATIONAL DIASTEREOISOMERS

↘ CIS/TRANS DIASTEREOISOMERS

LEC (9) CHEM 30A Apr 22nd

(1) PROPERTIES of ALKANES
(2) REACTIONS / SOURCES / IMPORTANCE
Ch3 (3) STEREOCHEMISTRY
(4) CHIRALITY / CHIRAL CENTERS
(5) R/S DESIGNATION

---

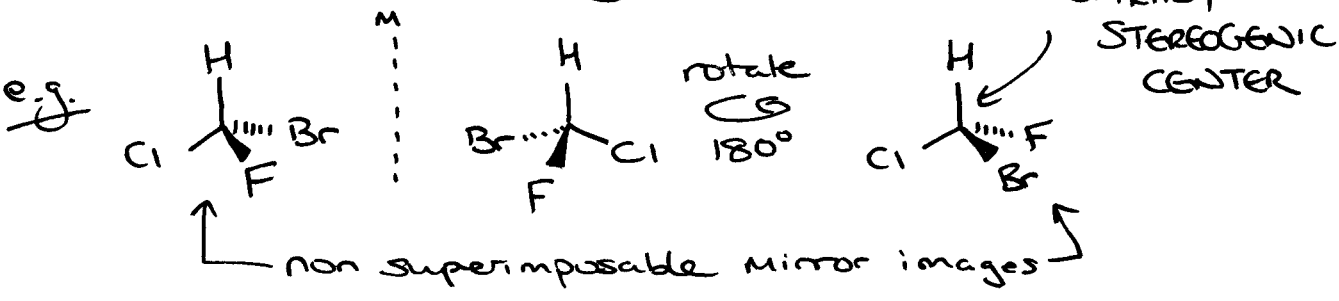
(1)-(3) Lec 9 notes

A major part of STEREOCHEMISTRY is being able to recognise mirror images

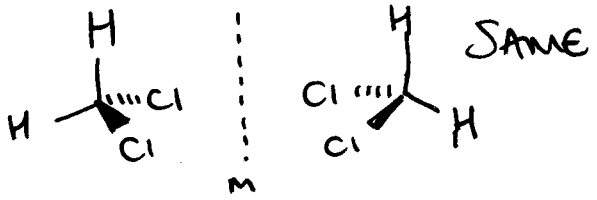
(4) CHIRALITY

An object (molecule) that is NOT superimposable on its mirror image is said to be chiral (GREEK 'cheir' meaning 'hand')

e.g.



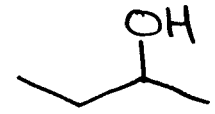
So each of these molecules is CHIRAL, and they are ENANTIOMERS

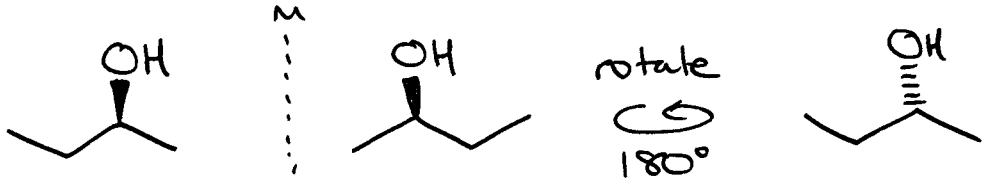


If an object (molecule) is not CHIRAL, it is ACHIRAL

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"

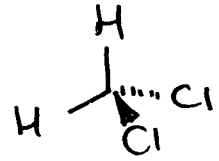
consider: 

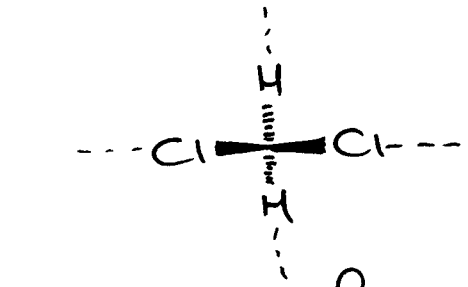


ENANTIOMERS COME IN PAIRS

– IDENTIFYING CHIRAL OBJECTS

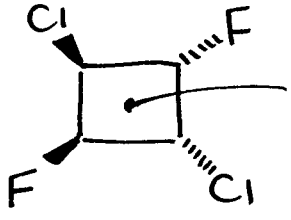
If a molecule can be drawn with:
(i) a PLANE of SYMMETRY or
(ii) an INVERSION CENTER
⇒ IT IS ACHIRAL

e.g. (i) 



2 PLANES

you will see this more often than:

(ii) 

center of inversion (NO PLANE)

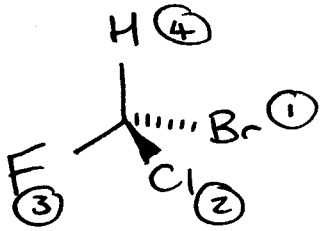
centre of inversion ⇒ identical groups lie equidistant of a point on opposite sides of mat point

- DISTINGUISHING ENANTIOMERS

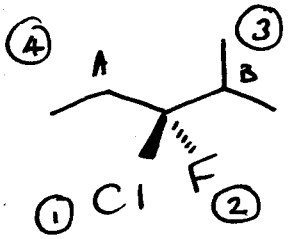
R,S designation

- assign priority

(i) ATOMIC WEIGHT of atoms on a Stereocentre



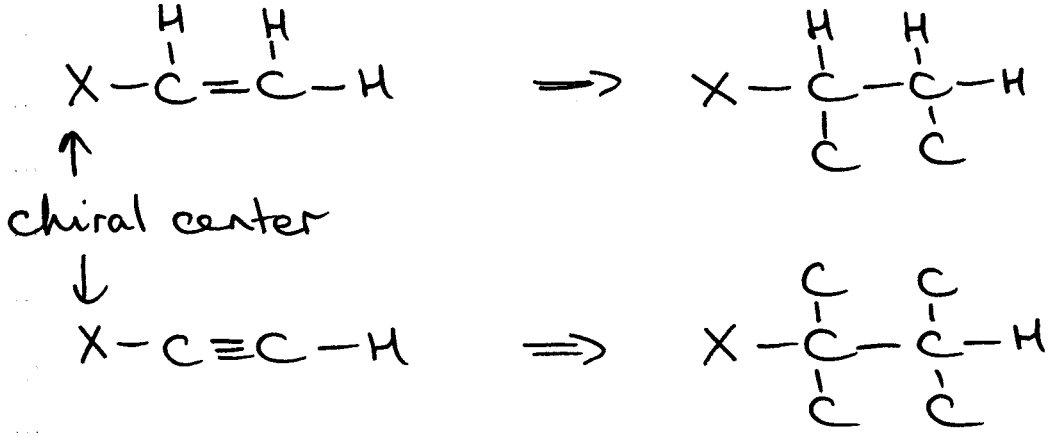
(ii) FIRST POINT of DIFFERENCE



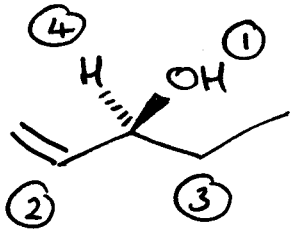
C_A attached to C, H, H (4)
C_B attached to C, C, H (3)

(HOW MANY CHIRAL CENTERS)

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



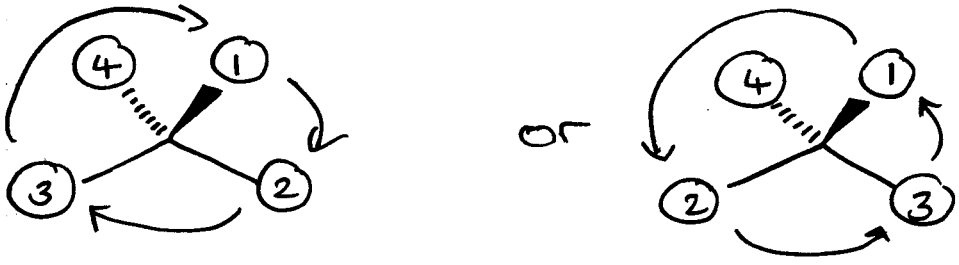
So, consider:



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

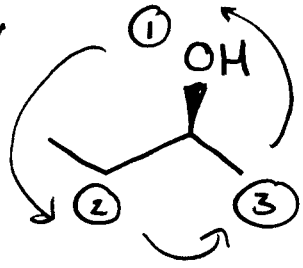
Rotate whole molecule in space to put the lowest priority group in the back ⇒

TWO POSSIBLE ORIENTATIONS:

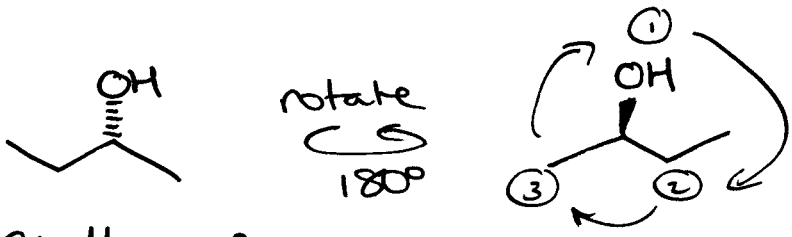


CLOCKWISE (R) COUNTERCLOCKWISE (S)

So/



(S)-2-BUTANOL



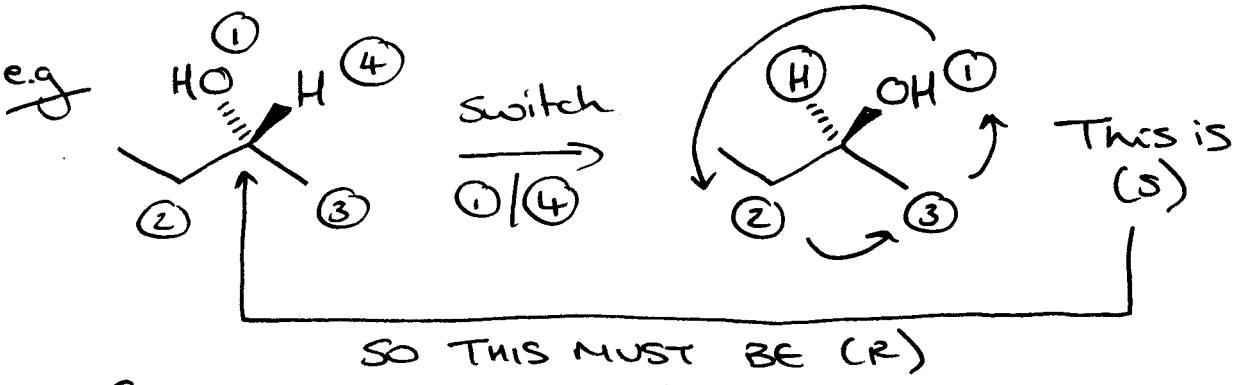
(R)-2-BUTANOL

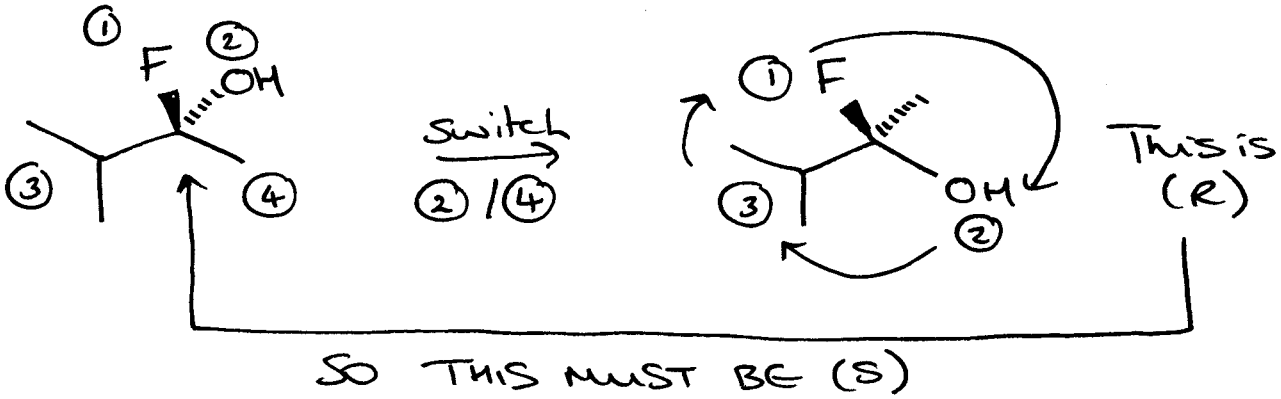
small group is NOT in the back

or if you have trouble rotating molecules

TRICK

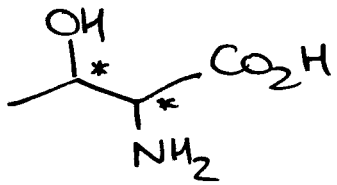
- switch lowest priority group (4) with the group that is in the back
- assign R/S, and switch



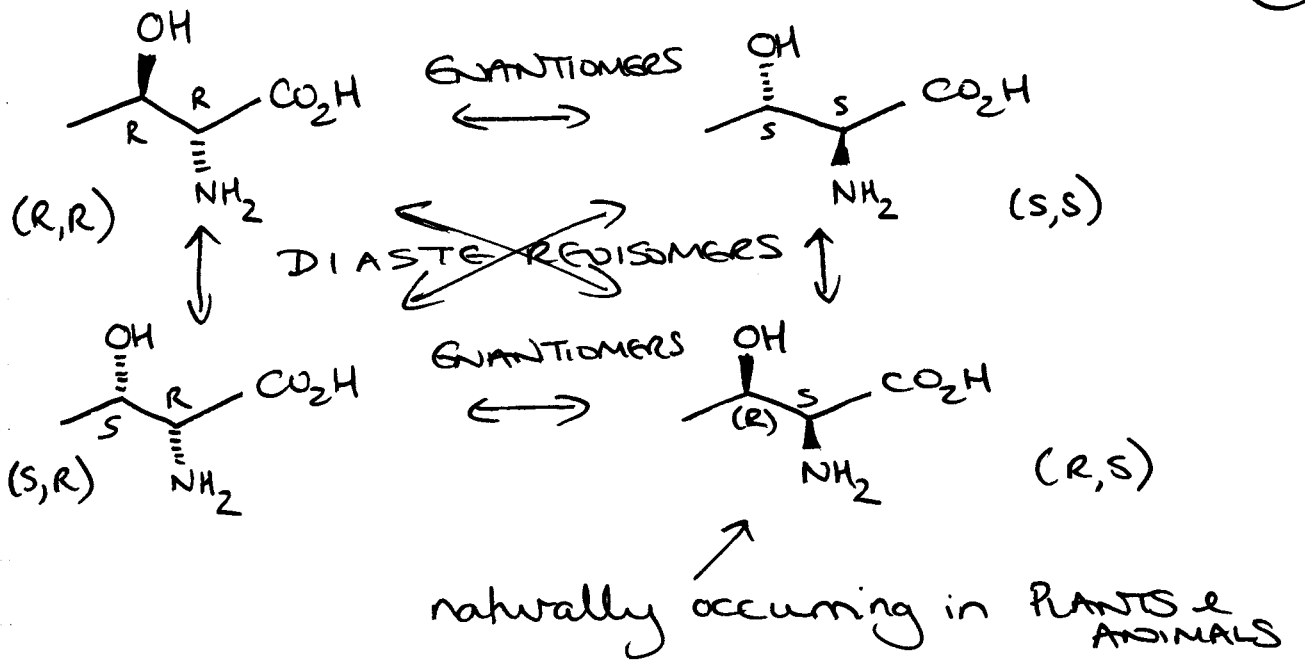


- compounds w/ more than one stereocenter

THREONINE (amino acid)



2 CHIRAL CENTERS



DIASTEREOISOMERS — NON MIRROR IMAGE STEREOISOMERS.

LEC (10) CHEM 30A Apr 25th

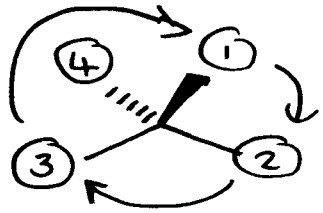
(1) R/S DESIGNATION
(2) FISCHER PROJECTIONS
(3) CIS/TRANS DIASTEREOISOMERS

PROBLEMS: 3.4-3.7, 3.24-3.32 (3rd)
3.4-3.8, 3.25-3.33 (4th)
READ: 3.4-3.5 (4th) & (3rd)

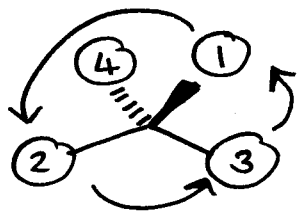
MIDTERM: ROOMS A-H ROYCE 190 I-Z CS50
ID, MODEL KITS

---

(1) R/S DESIGNATION

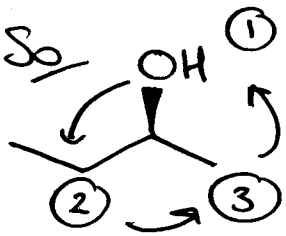


CLOCKWISE (R)

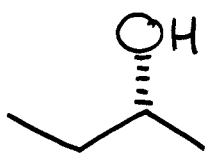


COUNTERCLOCKWISE (S)

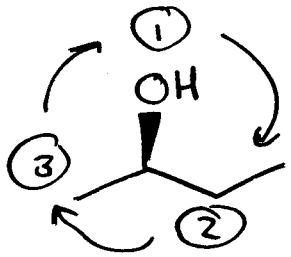
So



(S)-2-BUTANOL



rotate 180°

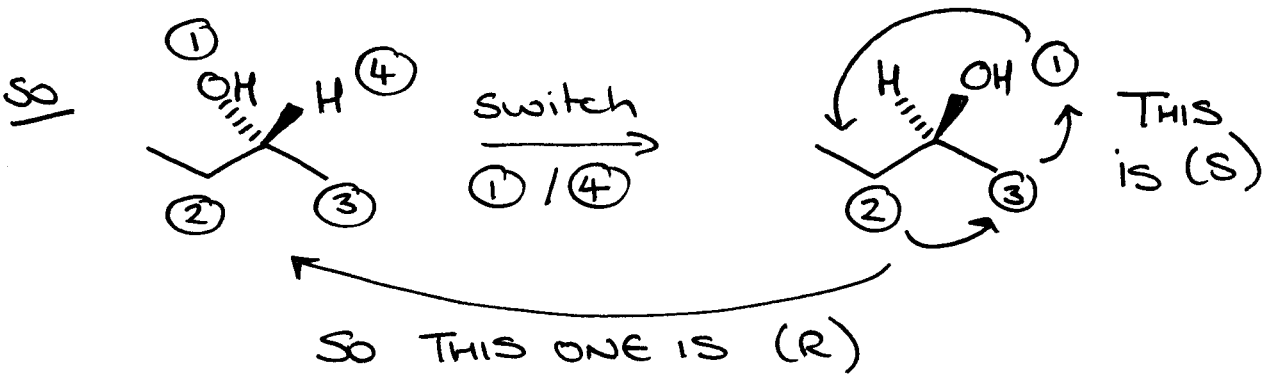


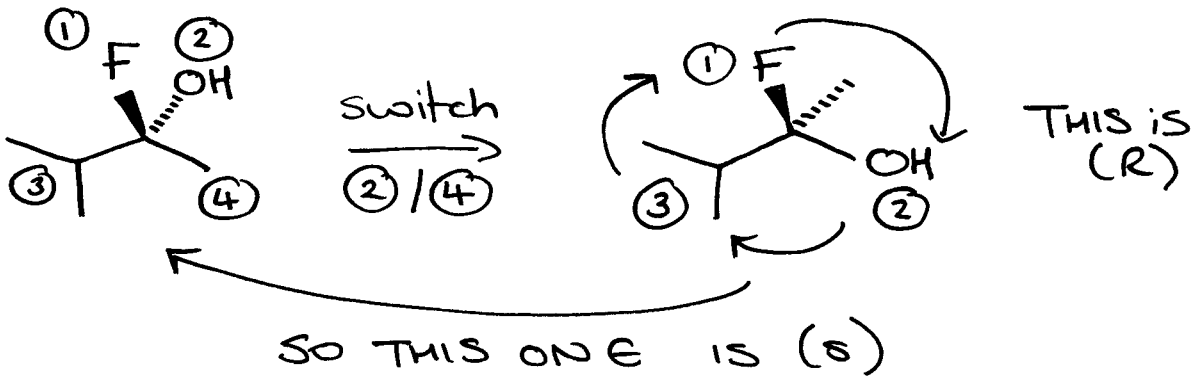
(R)-2-BUTANOL

Small group is NOT in the back

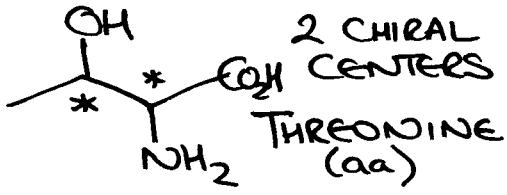
or if you have trouble rotating molecules

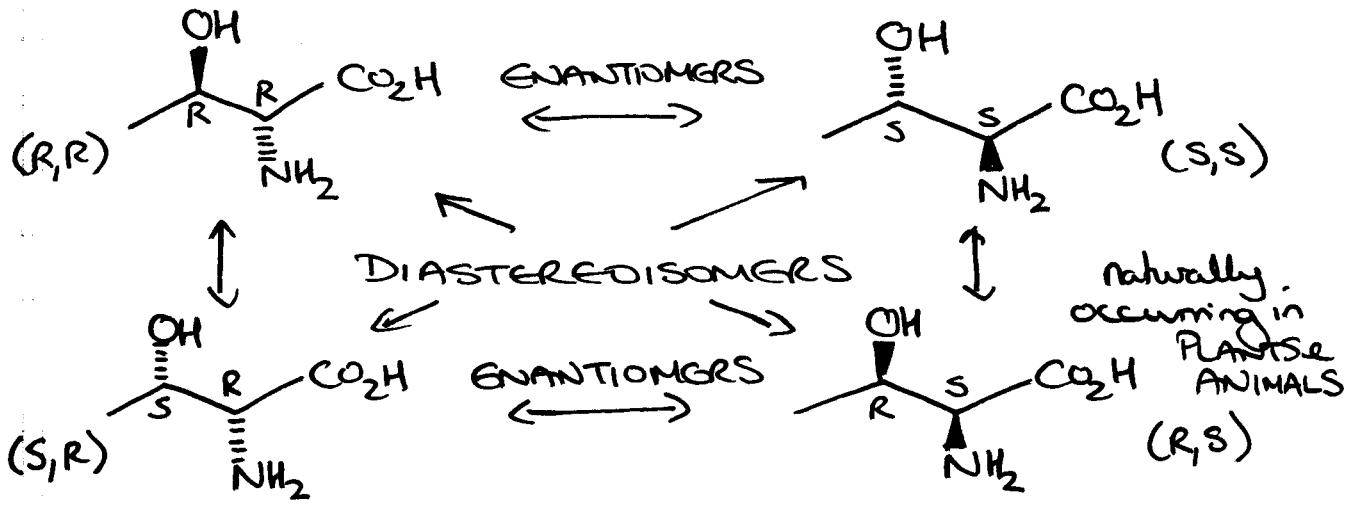
- SWITCH lowest priority group (4) with the group that is in the back
- ASSIGN R/S, and switch





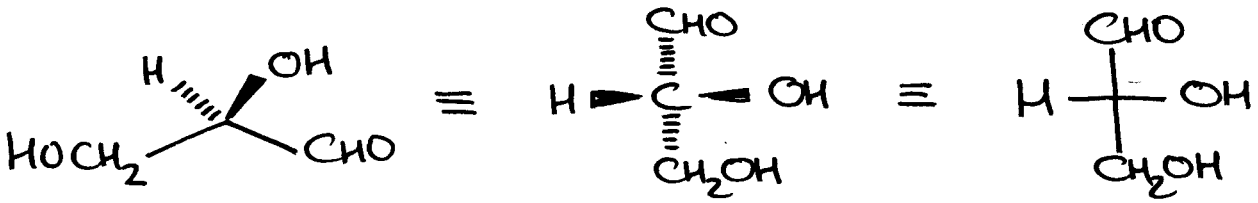
Compounds with more than one STEREOCENTER





DIASTEREOISOMERS – non mirror image STEREOISOMERS

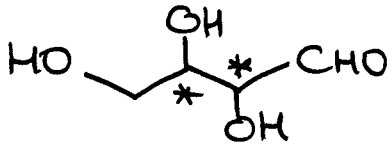
② FISCHER PROJECTIONS

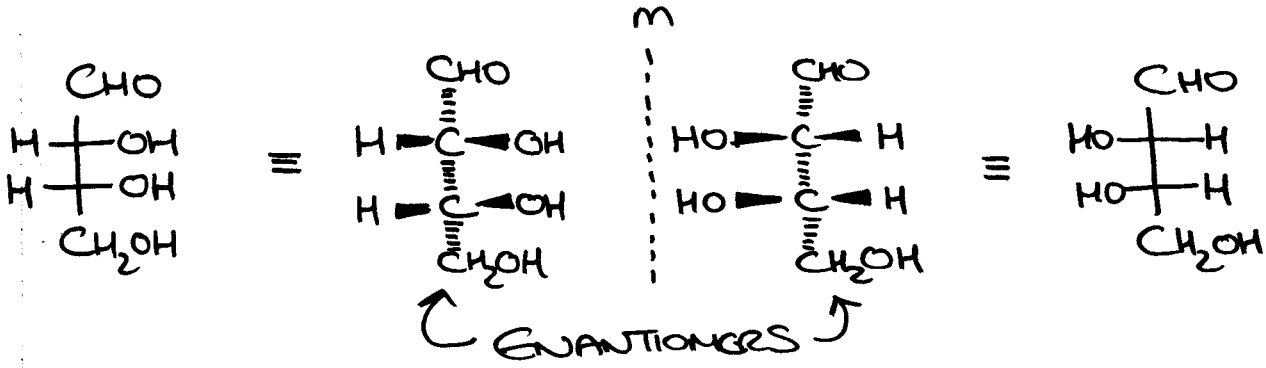


Glyceraldehyde

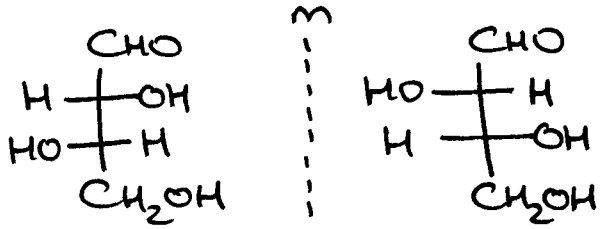
Useful for compounds with continuous STEREOCENTERS

2,3,4-trihydroxybutanal

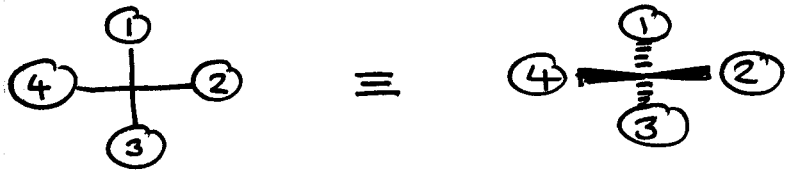




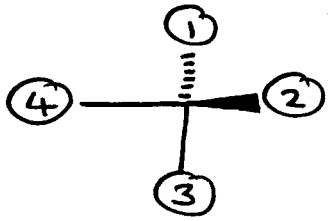
ANOTHER PAIR OF ENANTIOMERS



DETERMINING R/S FOR FISCHER PROJECTIONS



switch one wedge and one dash for STRAIGHT LINES



⇐ assign R/S

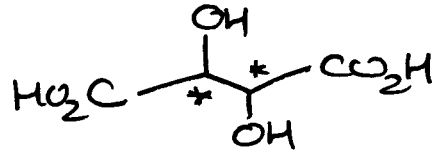
THIS ONE IS (S)

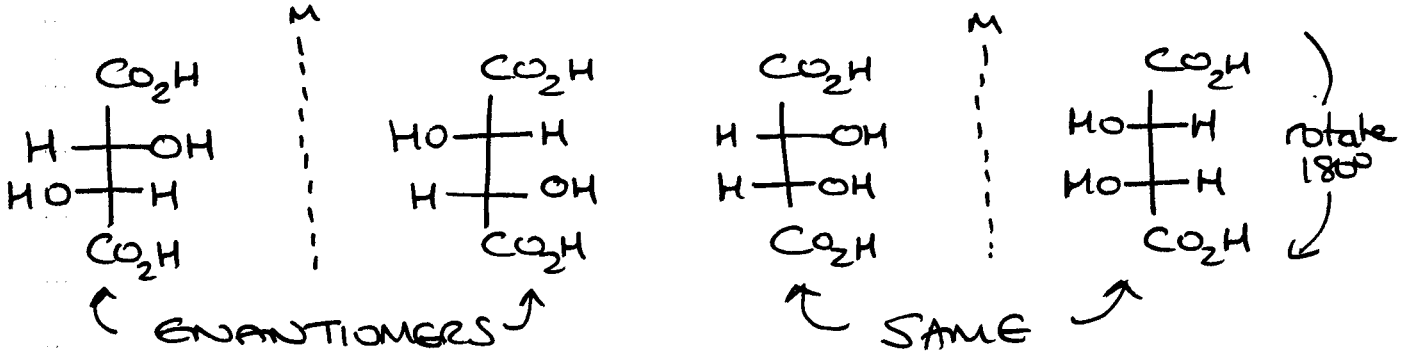
- Go BACK and DETERMINE R/S for 2,3,4-trihydroxybutanal

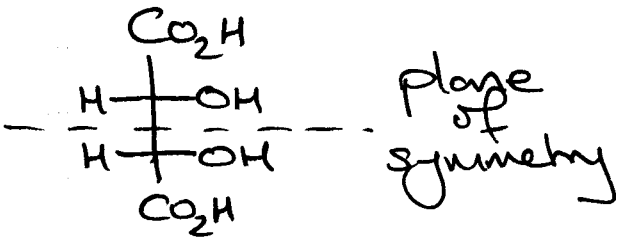
- A molecule with n chiral centers can have a maximum number of STEREOISOMERS = 2^n

2,3,4 trihydroxybutanal has 2 stereocenters

2^2 = 4 STEREOISOMERS

CONSIDER TARTARIC ACID 





COMPOUND w/ CHIRAL CENTERS, but is ACHIRAL

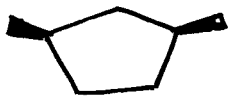
⇒ MESO

ENANTIOMERS ✓

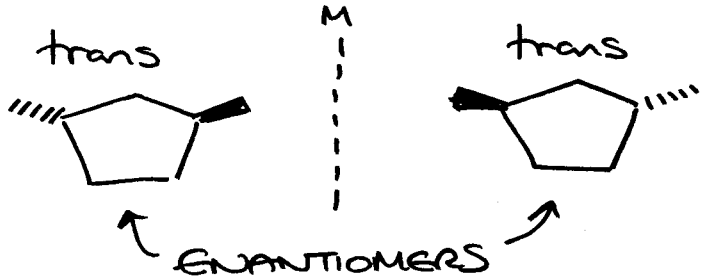
DIASTEREOISOMERS → CONFIGURATIONAL

DIASTEREOISOMERS → CIS/TRANS → RINGS, ALKENES

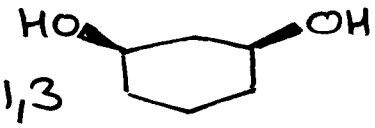
RINGS



cis
(meso)

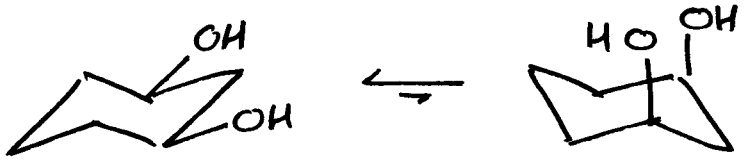


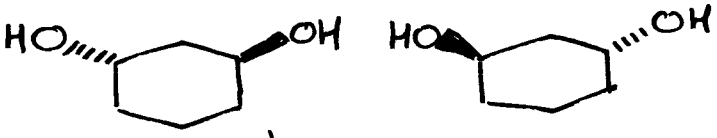
consider CYCLOHEXANES



1,3

cis
(meso)



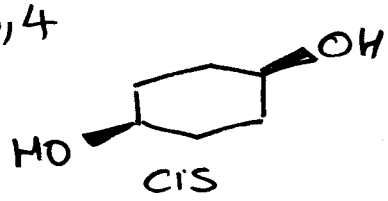


trans
ENANTIOMERS

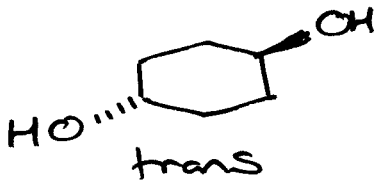
DRAW CHAIR FOR EACH AND DO A RING FLIP FOR EACH ENANTIOMER

(IN EACH CASE, CHAIRS ARE IDENTICAL)

1,4



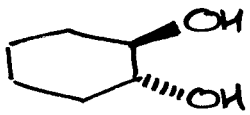
cis



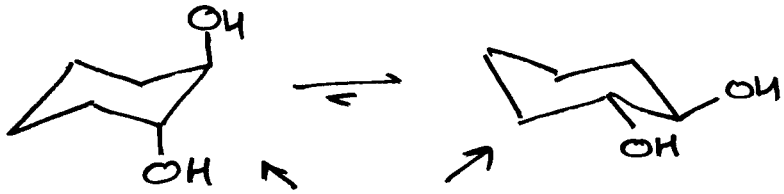
trans

BOTH ACHIRAL

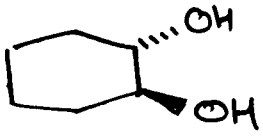
1,2

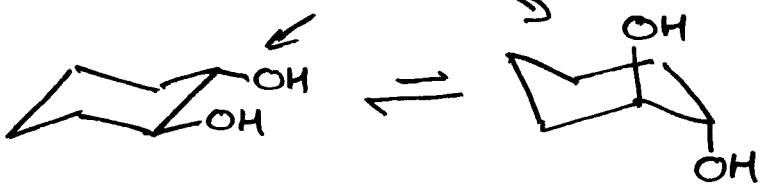


trans

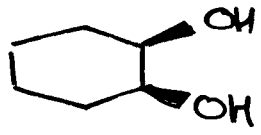


MIRROR IMAGES

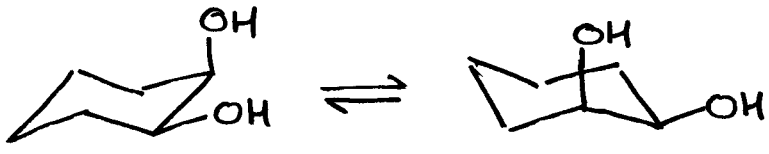




Cis

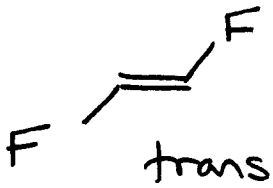


meso

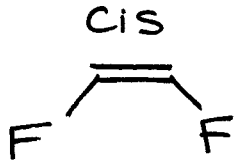


MIRROR IMAGES
(non superimposable)

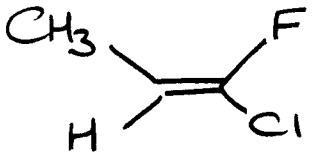
ALKENES

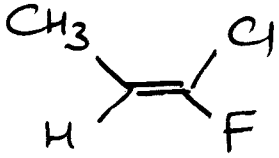


trans



DIASTEREOISOMERS



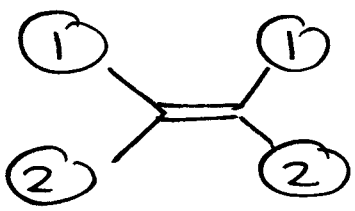


DIASTEREOISOMERS

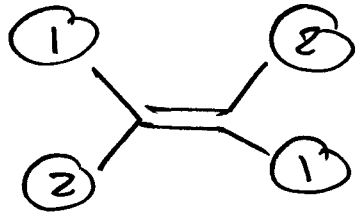
cis / trans?

(E) (Z)

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



Z



E

LEC (11) CHEM 30A Apr 29th

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

MIDTERM
LOW 10
HIGH 115
MEAN 66
(CHEATING...)

READ: 3.6 → 3.9 (3|4) Preview Ch4
PROBLEMS: 3.9, 3.10, 3.39, 3.40 (4) 3.8, 3.9, (+ MOLECULAR MODELING Q)

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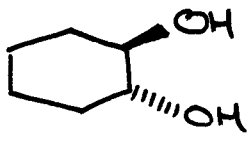
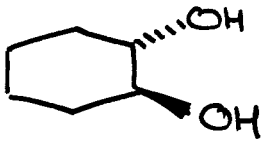
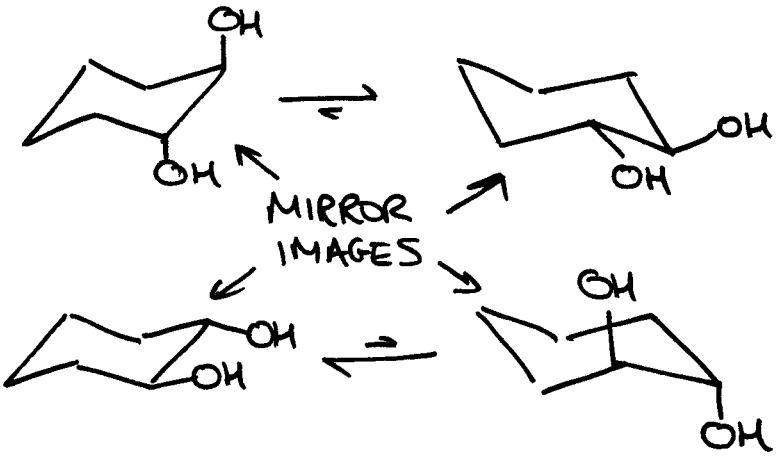
(1) CIS/TRANS

1,2

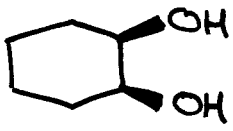


trans

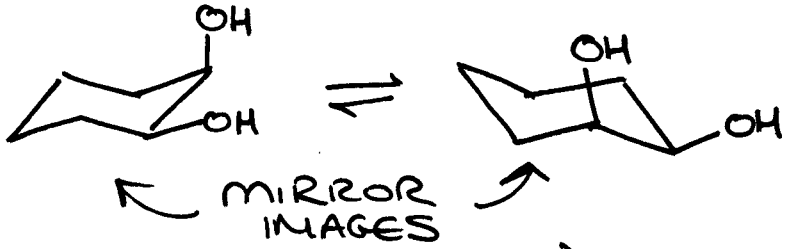




cis

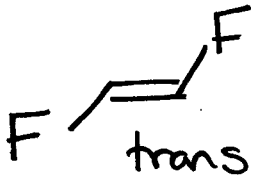


meso

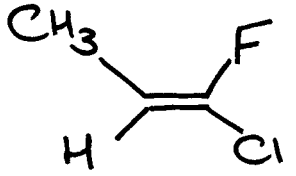


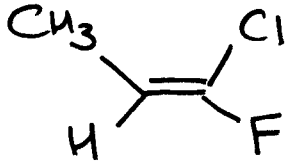
(non superimposable)

ALKENES



cis DIASTEREOISOMERS



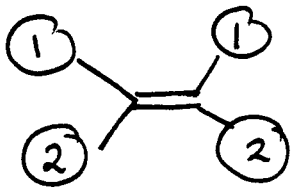


DIASTEREOISOMERS

cis / trans

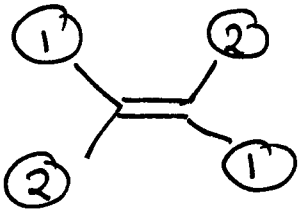
(E) (Z)

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



Z

and



E

WHY NO ROTATION ABOUT DOUBLE BONDS?

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

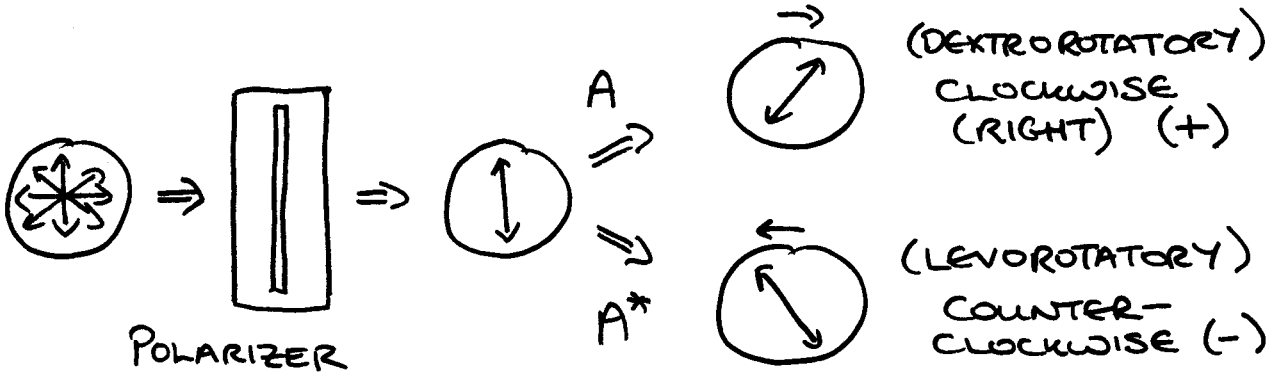
(2) CONSEQUENCES OF CHIRALITY

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

DIASTEREOISOMERS – different...

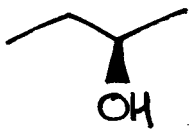
OPTICAL ACTIVITY

– rotation of plane polarized light



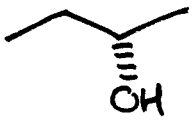
Specific Rotation $[\alpha]^T_\lambda = \dfrac{\text{Obs rotation (°)}}{\text{Length (dm)} \times \text{Conc (g/mL)}}$

T = temperature λ = wavelength of light



(R)-2-BUTANOL

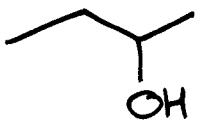
$[\alpha]_D^{25}$ −13.52°



(S)-2-BUTANOL

$[\alpha]_D^{25}$ +13.52°

1:1 mixture ⇒ RACEMIC MIXTURE,
specific rotation = ∅



(±)

NO RELATIONSHIP b/w R/S and +/-

enantiomeric excess (ee)

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

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

3 : 1

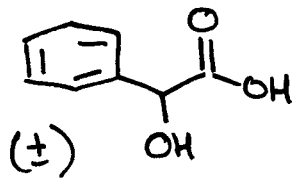
75% 25%

$[\alpha]_D^{25} = ? \quad -6.76°$

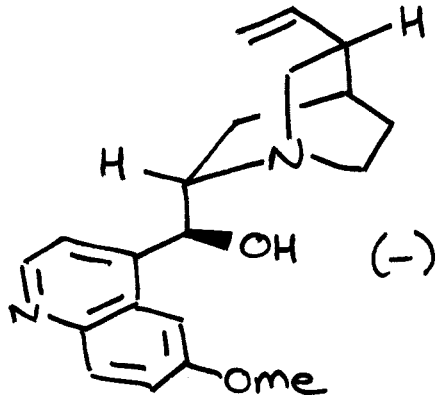
ee = 50%

(3) RESOLUTION (i) Natural products

$$RCO_2H + R_3N \longrightarrow RCO_2^{\ominus}\ R_3\overset{\oplus}{N}\text{-}H \quad (\text{ACID BASE})$$



(±) mandelic acid



(-)-QUININE

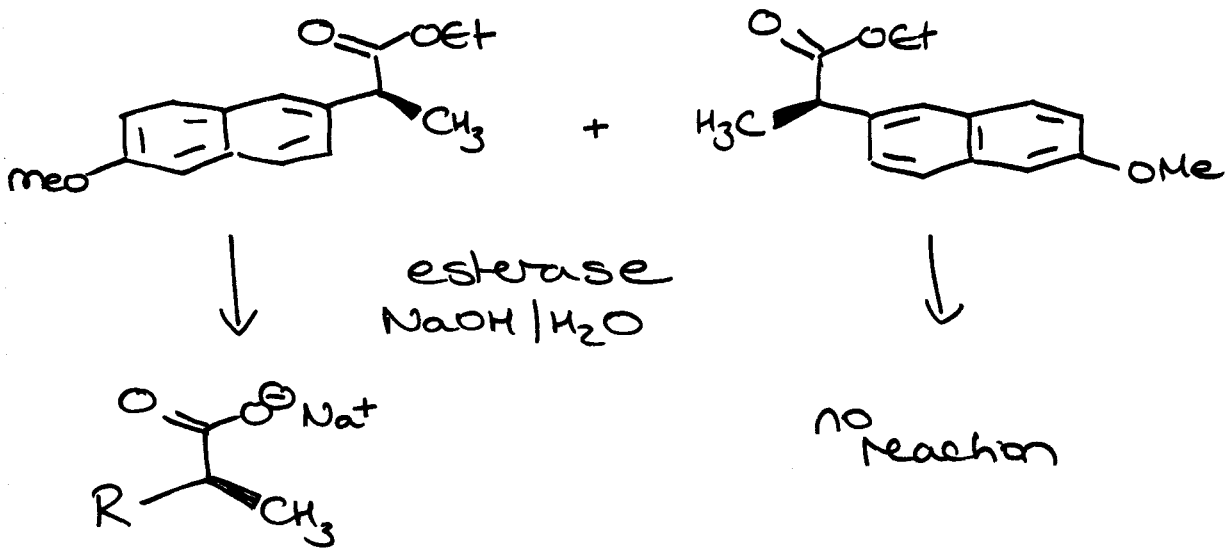
FORMS 2 SALTS

(-)-QUININE-H^+ · (R)-MANDALATE$^-$

(-)-QUININE-H^+ · (S)-MANDALATE$^-$

} DIASTEREOISOMERS

(ii) ENZYMES



READ 3.9 – CHIRALITY IN BIOLOGICAL WORLD

(4) ACIDS & BASES

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

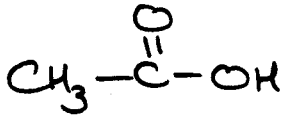
e.g.

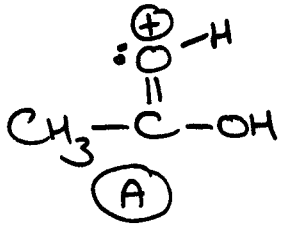
ACID (H+ DONOR) — BASE (H+ ACCEPTOR)

hydronium ion — hydroxide ion

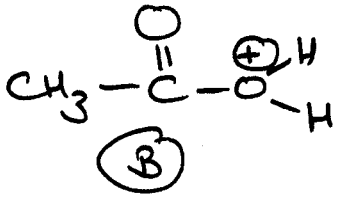
ACID — BASE — CONJUGATE BASE — CONJUGATE ACID

(i) ORGANIC STRUCTURES



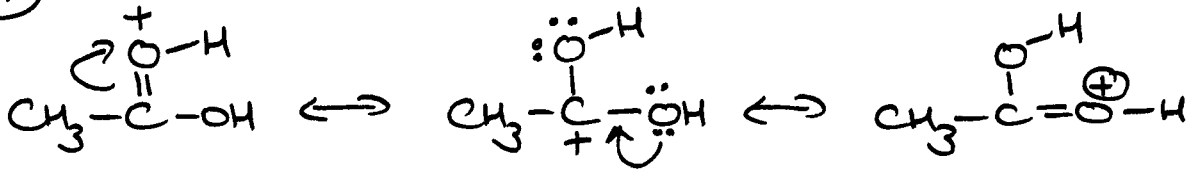


or

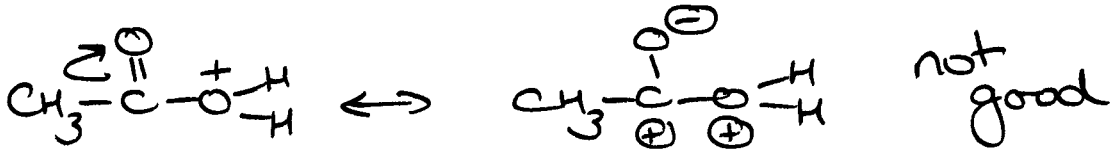


consider resonance

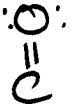
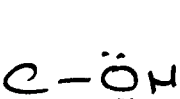
(A)



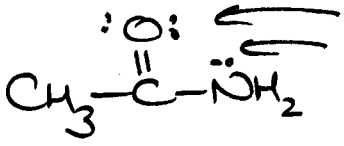
(B)



not good

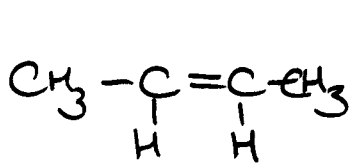
In  more basic than  is 

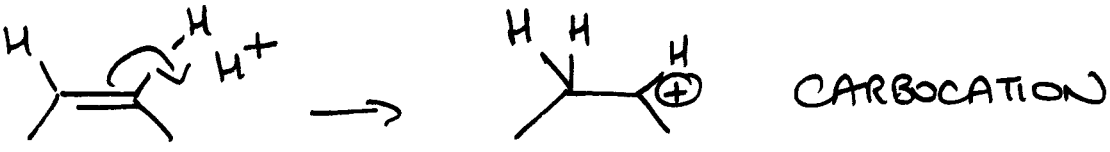
HMK



which is more basic?

(ii)





CARBOCATION

LEC (12) CHEM 30A May 2nd

(1) PROTONATING ORGANIC STRUCTURES
(2) ACID/BASE EQUILIBRIA
(3) STRUCTURE & ACIDITY
(4) LEWIS ACIDS/BASES

MIDTERMS back in DISCUSSION

Read Ch4 Problems 4.1 → 4.45 (3rd)
(4.47) 4th

---

(1) PROTONATING ORGANIC STRUCTURES

see last page Lec (11)

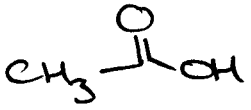
(2) ACID/BASE EQUILIBRIA

Quantify acid strength → acid dissociation constants

$$HA + H_2O \rightleftharpoons A^- + H_3O^+$$

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

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

e.g. acetic acid 

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

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

$pK_a = -\log_{10} K_a$ $\quad pK_a(CH_3CO_2H) = 4.76$

LARGER pK_a → WEAKER ACID

STRONG ACID = WEAK CONJUGATE BASE
WEAK ACID = STRONG CONJUGATE BASE

Scan through table Pg 141 (3)

– POSITION of EQUILIBRIUM

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

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

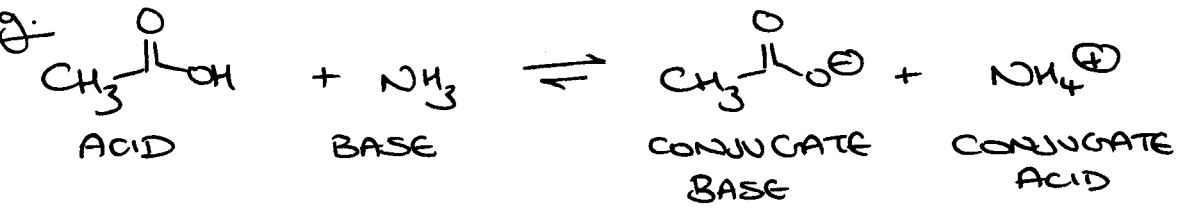
$$K_{eq} = \frac{[A^-][HB]}{[HA][B^-]}$$ multiply by $\frac{[H_3O^+]}{[H_3O^+]}$

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

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

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

eg.



pka 4.76 pka 9.24

So $pK_{eq} = 4.76 - 9.24$

$= -4.48$

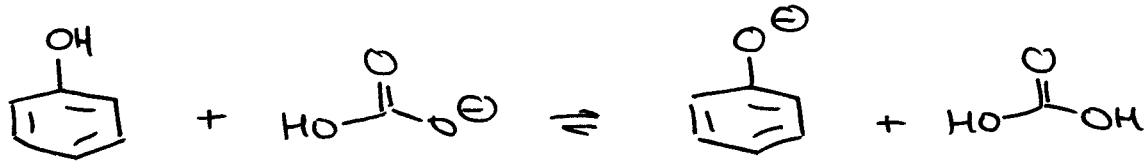
$K_{eq} = 10^{-pK_{eq}}$

$= 3 \times 10^{4}$

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

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

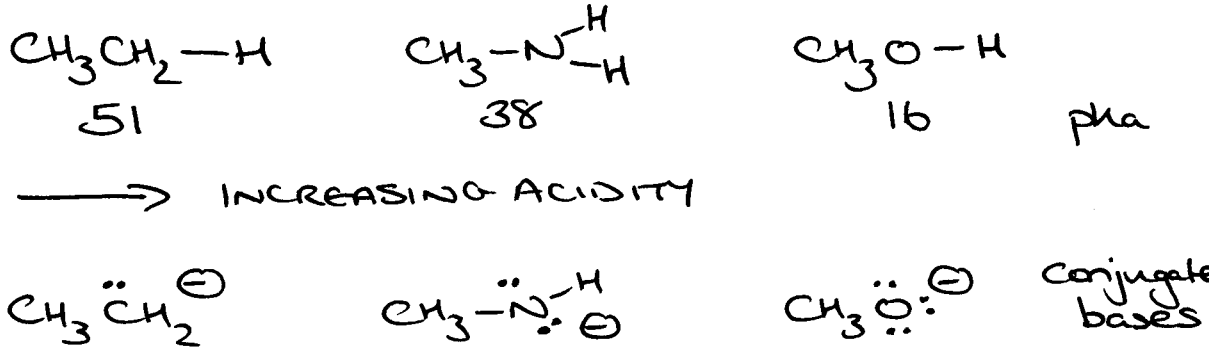
③ STRUCTURE AND ACIDITY

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

The more stable A^-, the more acidic HA

a) ELECTRONEGATIVITY (within a row)

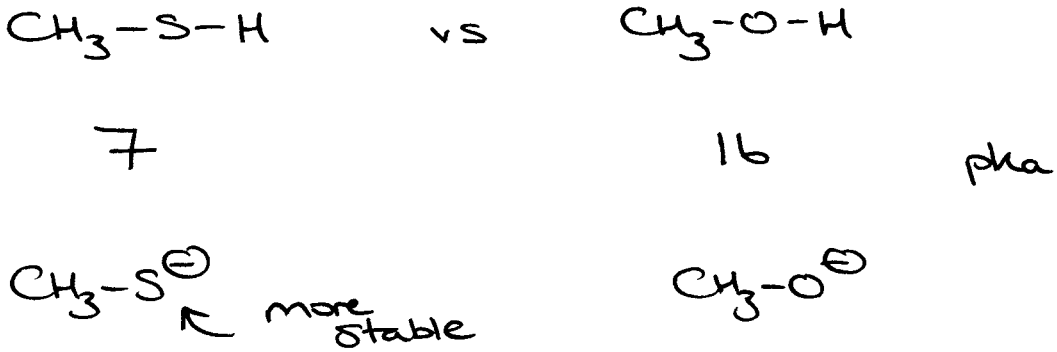
consider:



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

b) ATOM SIZE

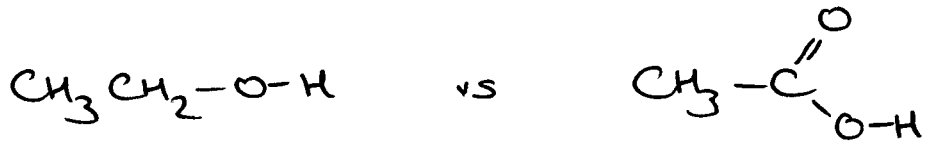
consider



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

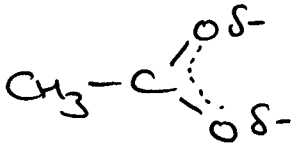
So, for HALOGEN ACIDS, $HI > HBr > HCl > HF$

c) RESONANCE
consider



16 5 pka

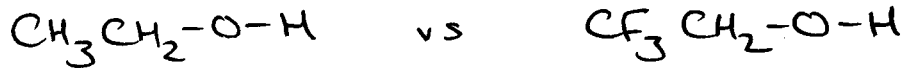
charge localized on one atom



charge delocalized

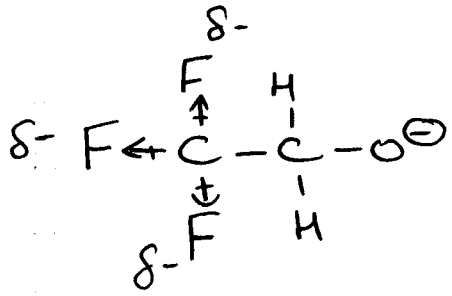
DELOCALIZATION ≡ STABILITY (HOT POTATO)

d) INDUCTIVE EFFECT
consider:



15.9 12.4 pka

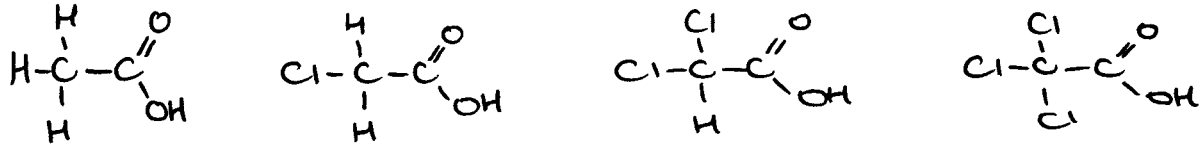
$CF_3CH_2O^{\ominus}$ is more stable than $CH_3CH_2O^{\ominus}$



Through BOND effect, falls off rapidly with distance.

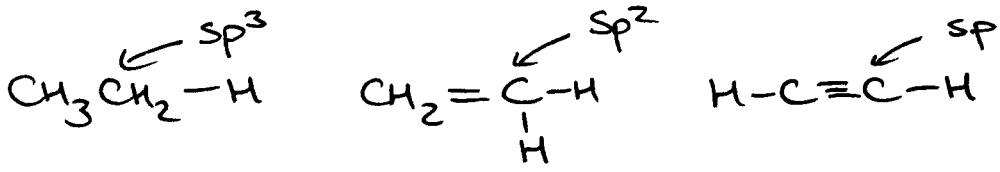
	CF_3CH_2OH	$CF_3CH_2CH_2OH$	$CF_3CH_2CH_2CH_2OH$
pka	12.4	14.6	15.4

Same effect w/ CARBOXYLIC ACIDS



4.75	2.85	1.48	0.64

e) HYBRIDIZATION



51	44	25	pka

⟶ ACIDITY INCREASES

s character of orbital 25% → 33% → 50%

- electrons held closer to the nucleus
  - more stable anion
  - more acidic

LEC (13) CHEM 30A May 4th

① STRUCTURE & ACIDITY — no OH Thursday (Fri?)
② LEWIS ACIDS/BASES
③ ALKENES INTRO
organic rxns

Finish Ch4 problems + acid/base WEB worksheet

④ TYPES
⑤ MECHANISMS
⑥ ENERGY DIAGRAMS

Read Ch5 and do problems (Don't worry too much about naming)

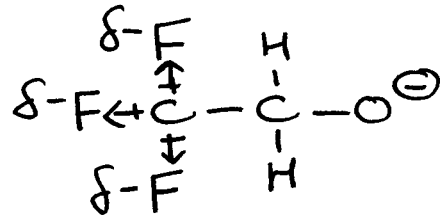
Read 6.1-6.3

① STRUCTURE & ACIDITY
inductive effect

CH_3CH_2-O-H vs CF_3CH_2-O-H

15.9 12.4 pka

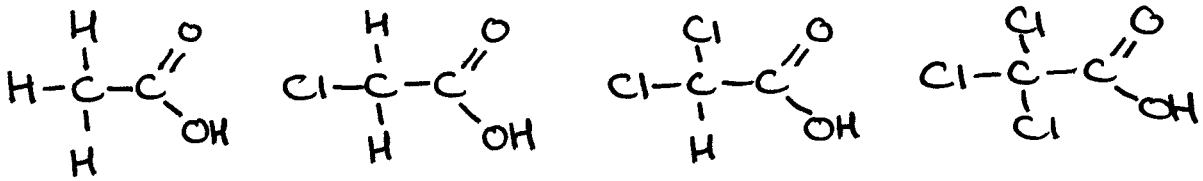
$CF_3CH_2O^{\ominus}$ is more stable than $CH_3CH_2O^{\ominus}$



THROUGH BOND EFFECT falls off rapidly with distance

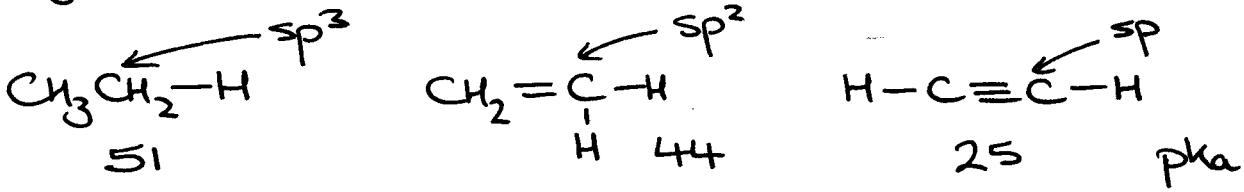
CF_3CH_2OH	$CF_3CH_2CH_2OH$	$CF_3CH_2CH_2CH_2OH$
pka 12.4	14.6	15.4

Same effect w/ CARBOXYLIC ACIDS



4.75 2.85 1.48 0.64

hybridization



⟶ ACIDITY INCREASES

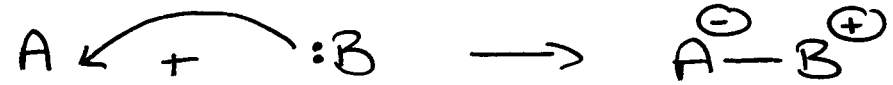
s character of orbital 25% → 33% → 50%

- electrons held closer to the nucleus
  more stable anion
  more acidic

(2) LEWIS ACIDS/BASES

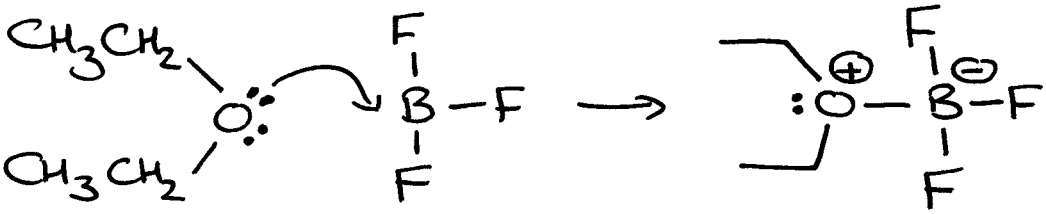
about e⁻ pairs, not H^+

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

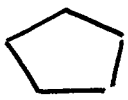
- Index of Hydrogen Deficiency
(Degrees of Unsaturation)
1 per rng / π BOND

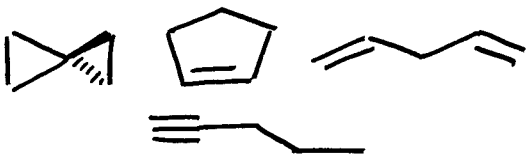
- max Hs in a structure C_nH_{2n+2}

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

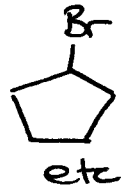
(i) C and H only

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

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

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

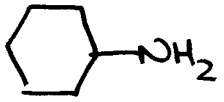
(ii) F, Cl, Br, I → replace for H

C_5H_9Br ⇒ C_5H_{10} $(12-10)/2 = 1$  etc

(iii) O, S → IGNORE

$C_5H_{10}O$ ⇒ C_5H_{10} 

(iv) for N, P add a C and H



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

- ORGANIC REACTIONS

(4) TYPES

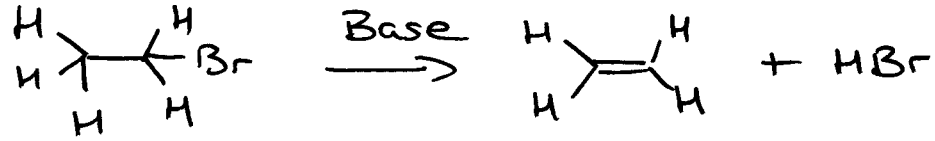
a) ADDITION (A + B → C)

e.g.

alkene alkyl halide

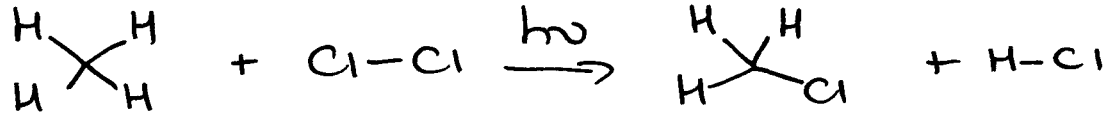
b) ELIMINATION (A → B + C)

e.g.



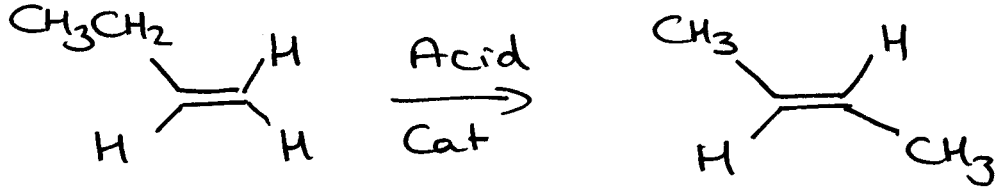
c) SUBSTITUTION (A–B + C–D → A–C + B–D)

e.g.



alkane alkyl halide

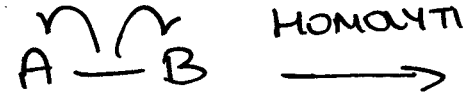
d) REARRANGEMENT



⑤ MECHANISMS

(Bond making / bond breaking)

-BREAKING



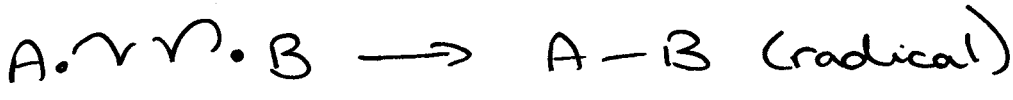
(↶ 1e⁻ arrow)

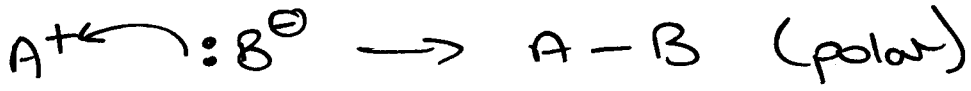
Radical reactions
(radicals → species containing unpaired electrons)

POLAR REACTIONS

(↷ 2e⁻ arrow)

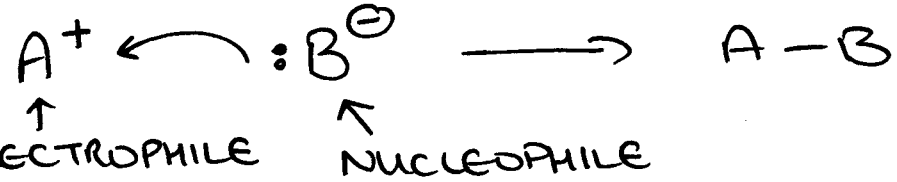
-MAKING





- POLAR RXNS (RADICALS in WK9/10)

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



NUCLEOPHILES

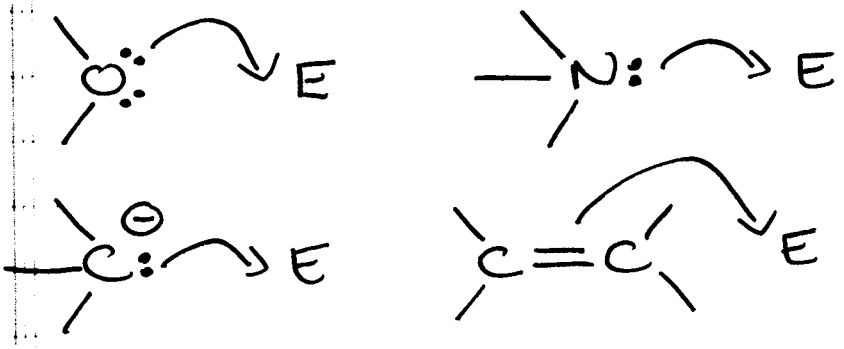
have an e^- RICH atom and are NEUTRAL or -VELY charged

ELECTROPHILES

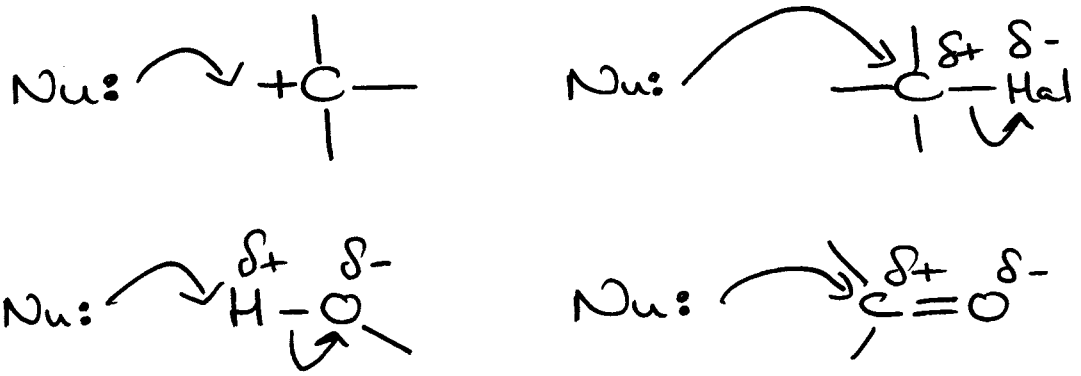
have an e^- POOR atom and are NEUTRAL or +VELY charged

PATTERNS

Electrons flow <u>from</u> nucleophiles

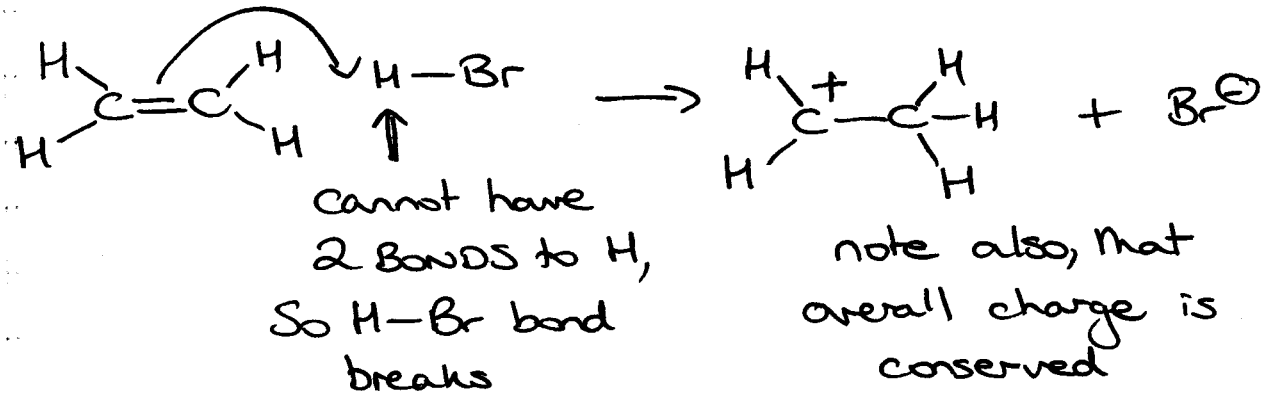


Electrons flow <u>to</u> electrophiles



- RULES (i) CONSERVE CHARGE

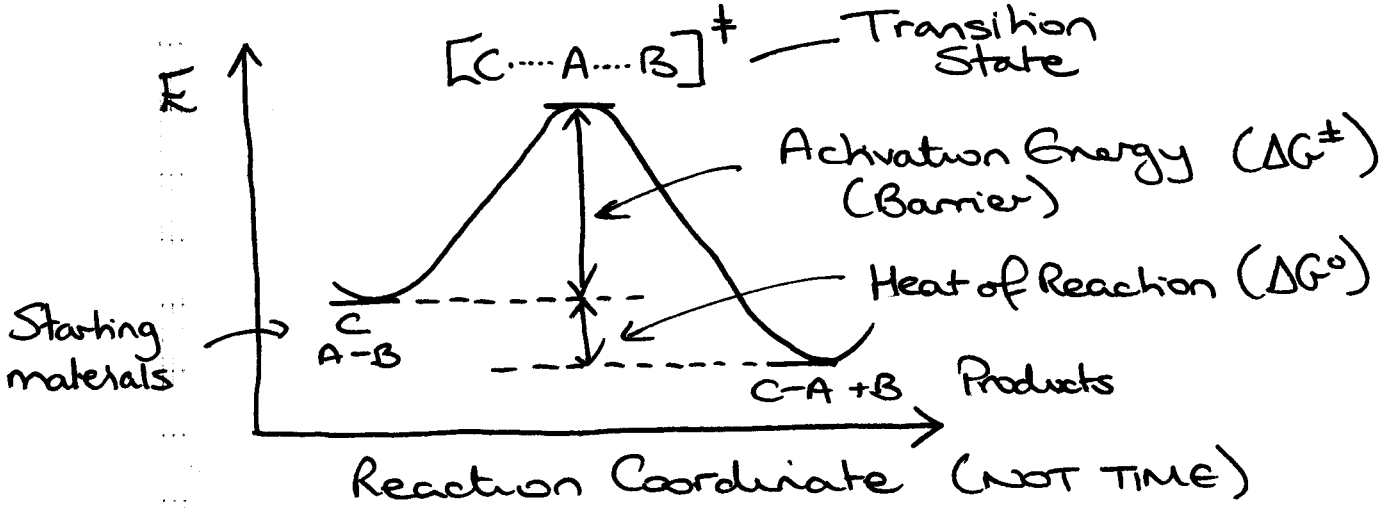
– octet rule must be obeyed (if necessary)



⑥ 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 on 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

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

↑ rate constant of reaction

↖ pre-exponential factor.

Lec (14) CHEM 30A May 6th

1. MECHANISMS
2. ENERGY DIAGRAMS
3. KINETICS vs THERMODYNAMICS
4. ADDITION ALKENES

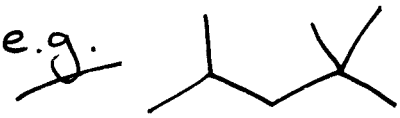
READ 6.1–6.3 PROBLEMS 6.1, 6.2 (3rd)

(1)+(2) Pages 6–8 from LEC 13

(3) KINETICS vs THERMODYNAMICS

how fast will it happen

will it happen

e.g.  + $O_2 \rightleftharpoons 8CO_2 + 9H_2O$

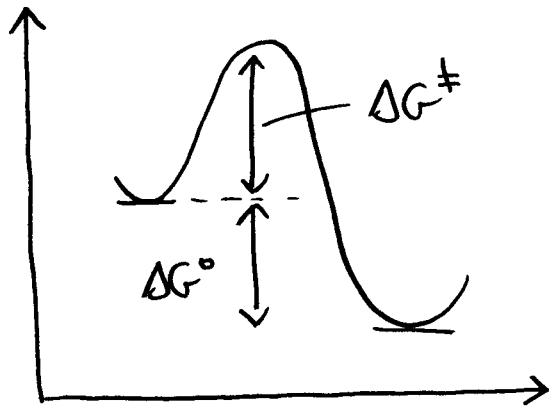
isooctane

$\Delta G^\circ = -1000\ kJ\,mol^{-1}$

$K_{eq} = 10^{175}$ at 298K
(only 10^{86} atoms in observable universe!)

<u>BUT</u> isooctane is stable
(you put it in your car)

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



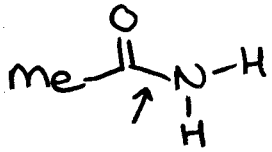
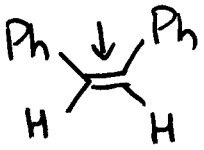
Isooctane + O_2

THERMODYNAMICALLY UNSTABLE, BUT KINETICALLY STABLE

However, apply a burst of energy to a mixture of H_2O & CO_2 will NOT reconvert to octane and oxygen

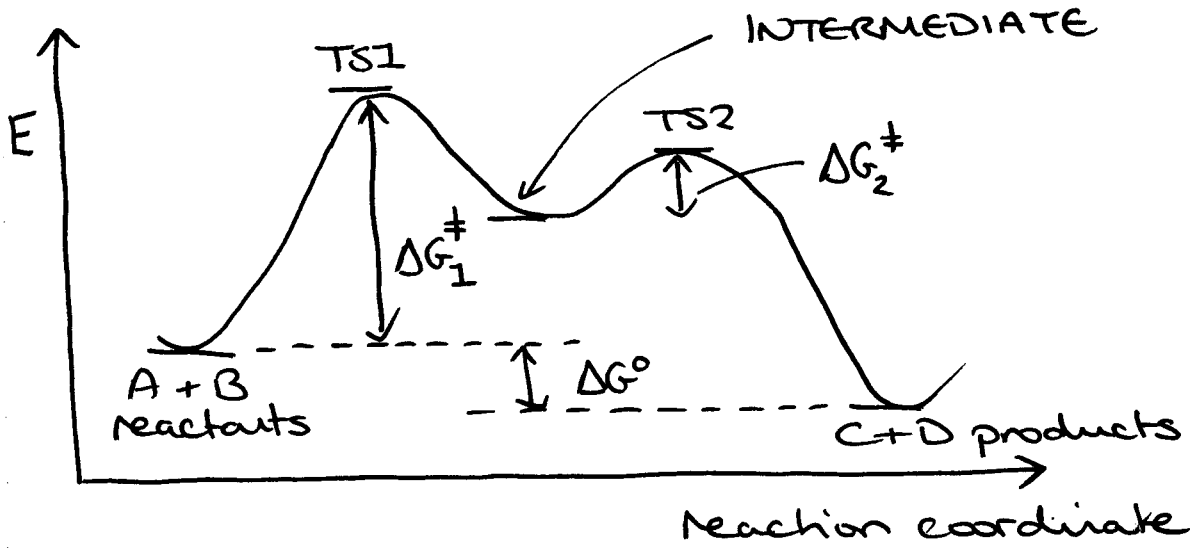
(MENTION GRAPHITE/DIAMOND)

Energy barries and rate (consider BOND ROTATIONS → some principles as reactions)

	E_A (kcal/mol)	k (s^{-1}) (298 k)	$t_{1/2}$
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} years

(Age of the earth ~ 4.6×10^9 YEARS)

- energy profiles ⇒ 2 STEP RXN

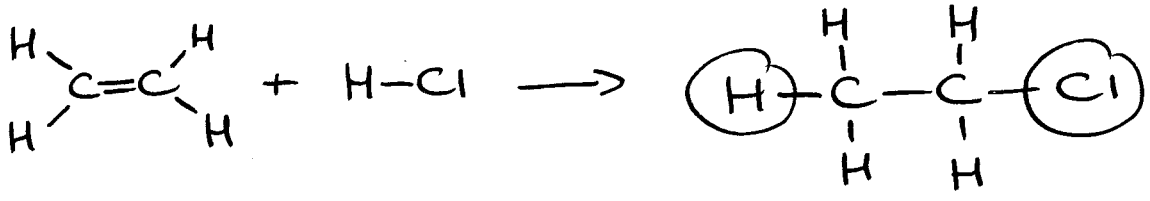


REACTION INTERMEDIATE ⇒ localized energy minimum between two TRANSITION STATES (sometimes possible to isolate)

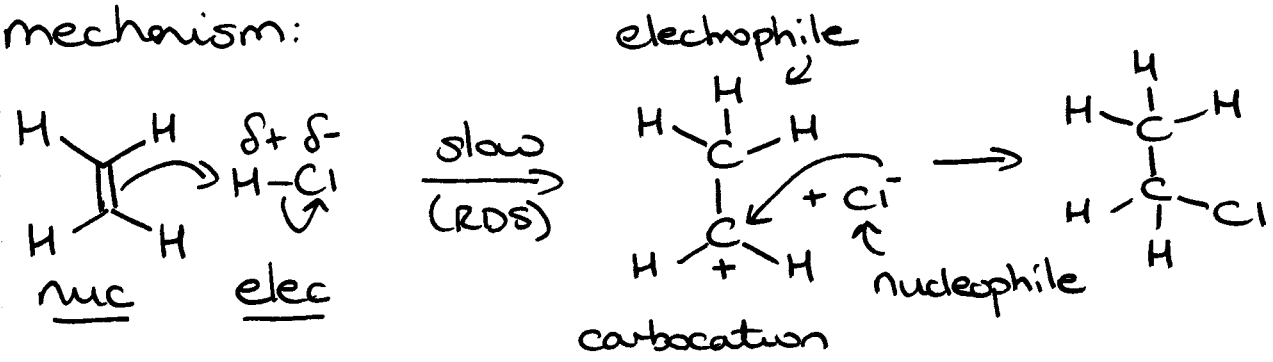
SLOWEST STEP in a multistep process (one w/ highest barrier) is called the RATE DETERMINING STEP (RDS)

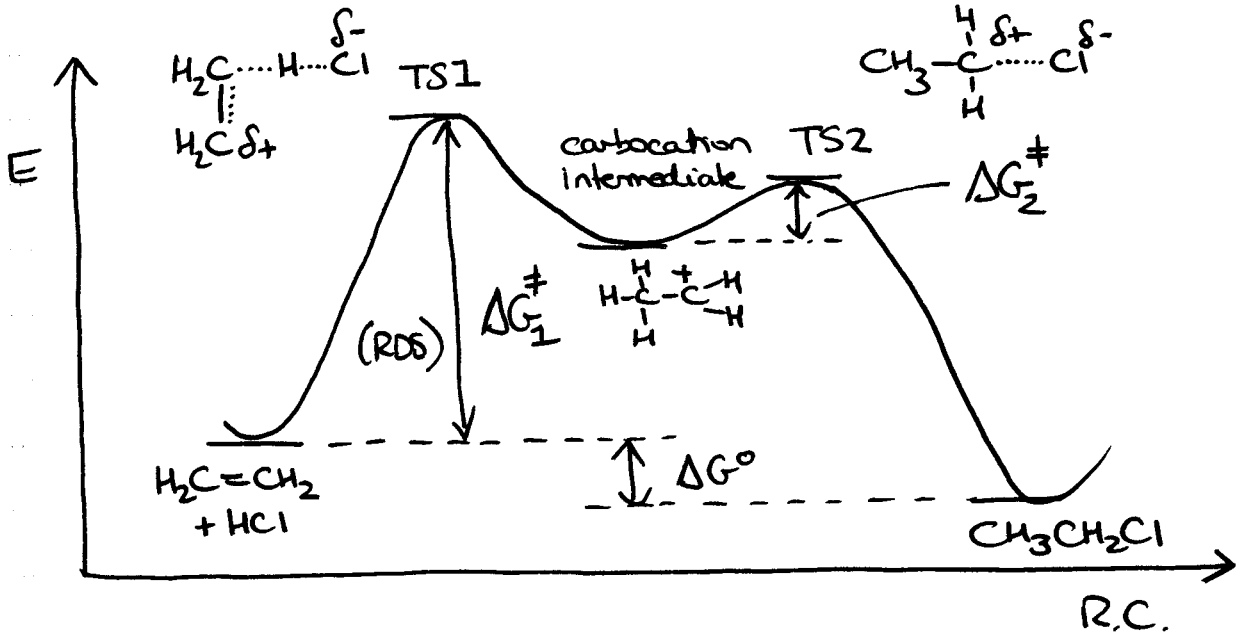
- fill RDS in on graph above

④ ELECTROPHILIC ADDITION TO ALLENES



mechanism:


δ+ δ-
H–Cl
slow
(RDS)
nuc
elec
electrophile
+ Cl⁻
nucleophile
carbocation


E
TS1
carbocation intermediate
TS2
(RDS)
ΔG₁‡
ΔG₂‡
ΔG°
H₂C=CH₂ + HCl
CH₃CH₂Cl
R.C.

LEC (15) CHEM 30A May 9th

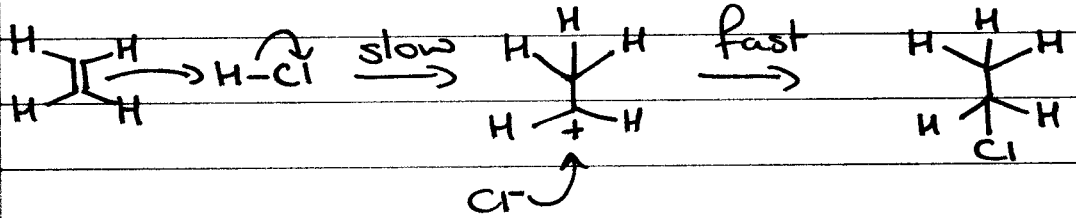
1. ADDITION TO ALKENES — QUIZ IN CLASS WEDS
2. CARBOCATIONS
3. REARRANGEMENT
4. ADDITION of H_2O
5. ADDITION of Br_2/Cl_2

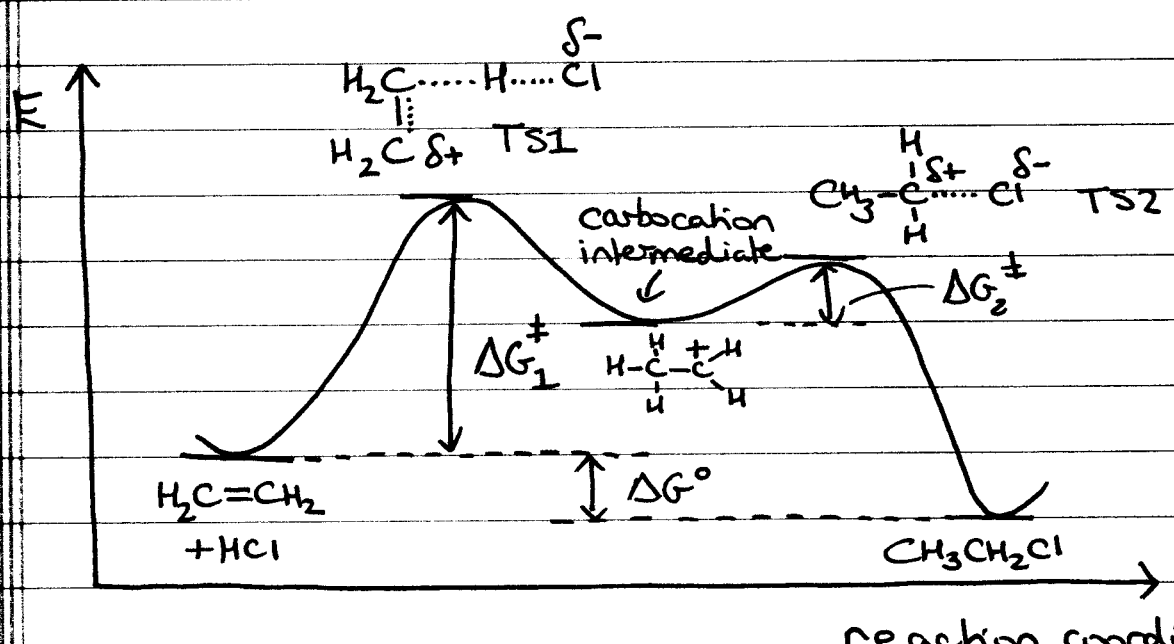
(3/4)

Read 6.3–6.5 Prob: 6.3–6.8, 6.14–6.16 (3rd)
6.1–6.6, 6.13–6.15 (4th)

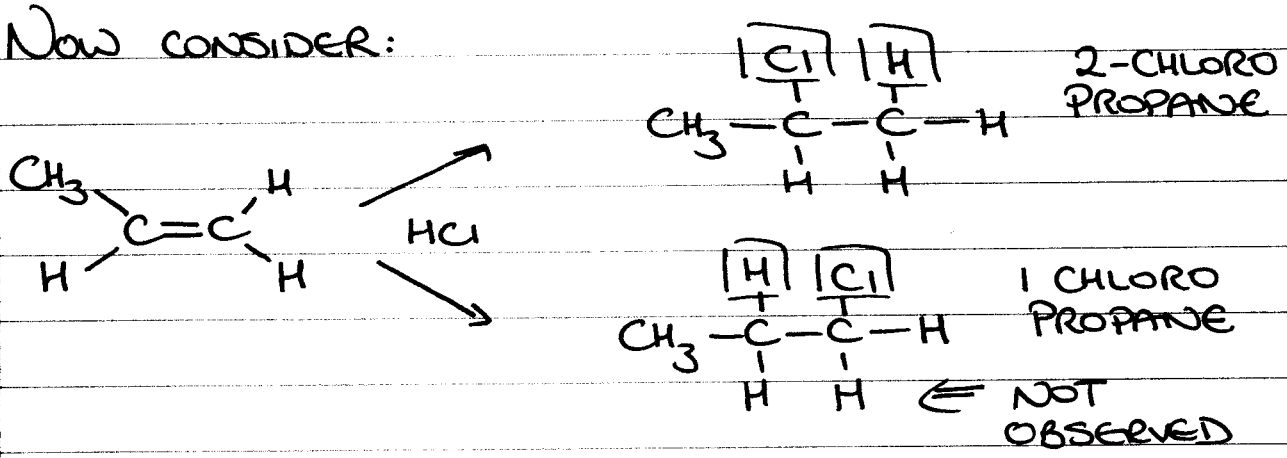
---

(1) ADDITION TO ALKENES (HCl, HBr, HI)





NOW CONSIDER:

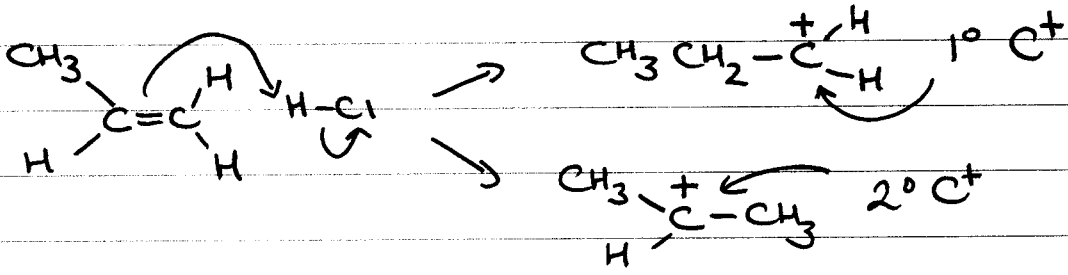


REGIOSELECTIVE REACTION

⇒ MARKOVNIKOV'S RULE

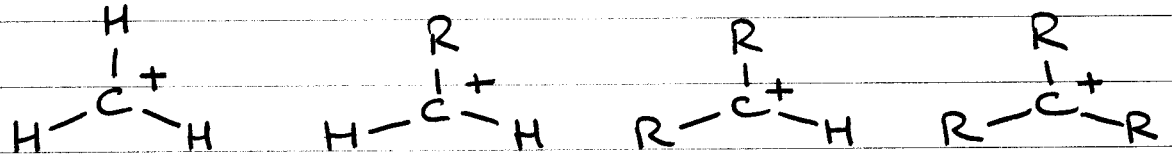
H ADDS TO DOUBLE BONDED C WITH MOST Hs ALREADY ATTACHED

WHY?



(2) CARBOCATIONS

(Stability R = ALKYL)

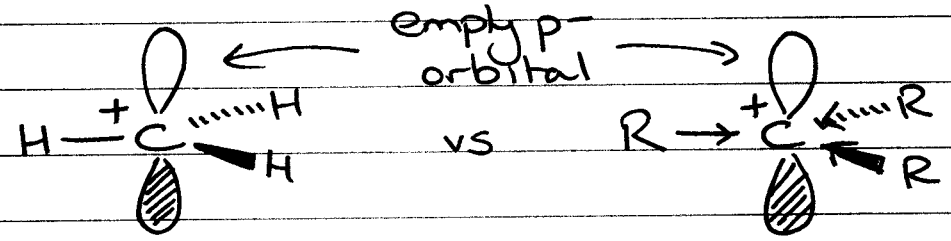


methyl 1° 2° 3°

INCREASING STABILITY →

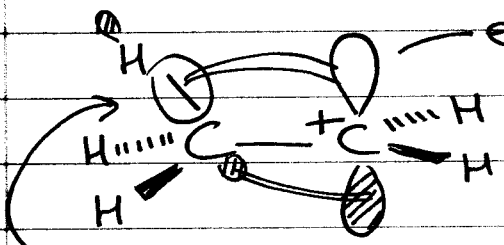
TWO FACTORS

(i) Inductive Effect



ALKYL GROUPS ARE INDUCTIVELY DONATING

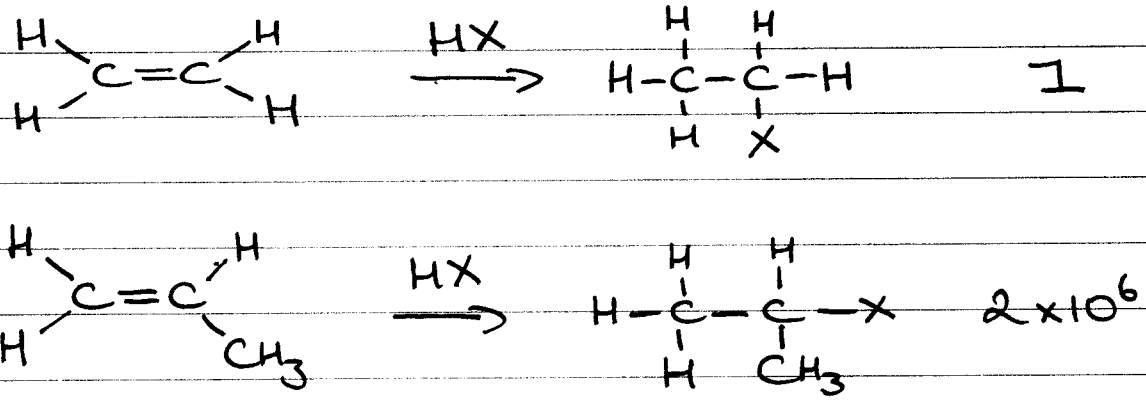
(ii) Hyperconjugation

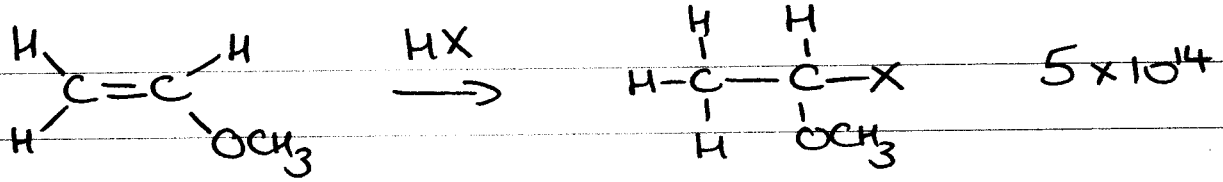


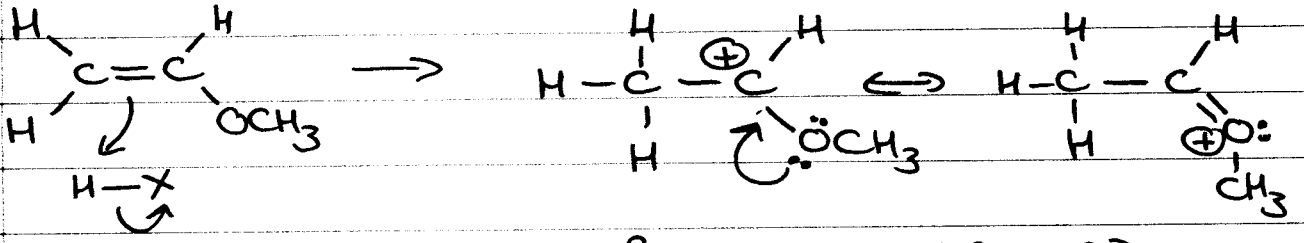
DELOCALIZATION of ADJACENT σ BONDS

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

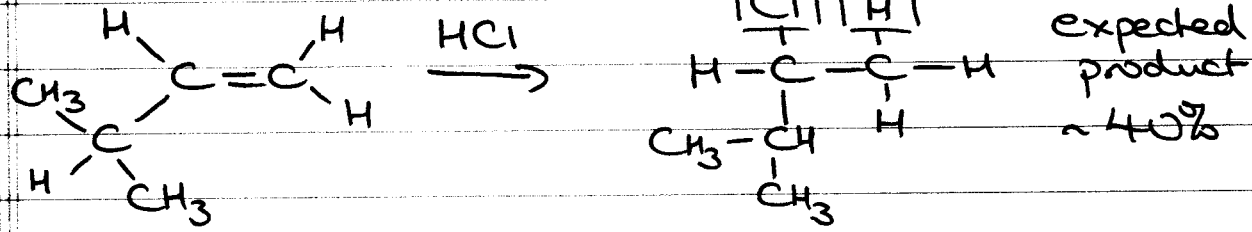
.... and other factors (RESONANCE)



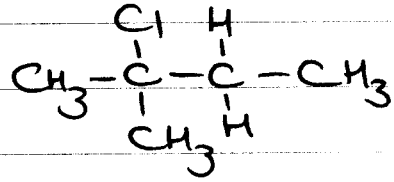




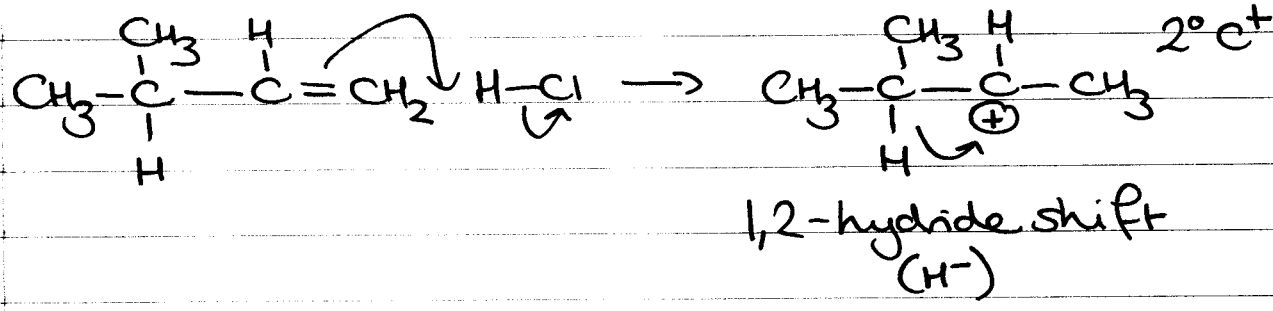
(3) REARRANGEMENT

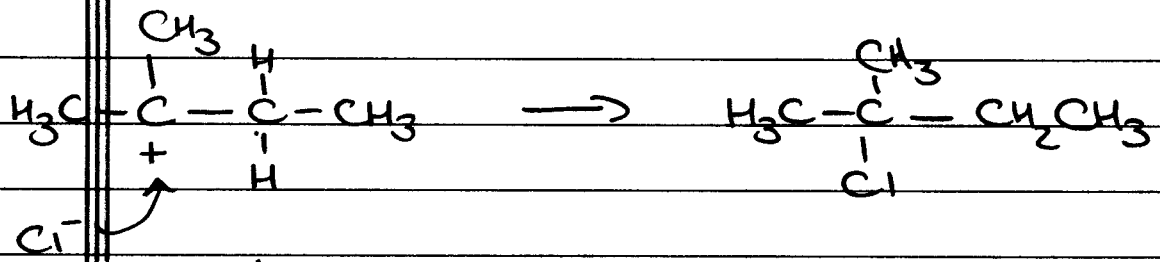


- other 60%



WHY?

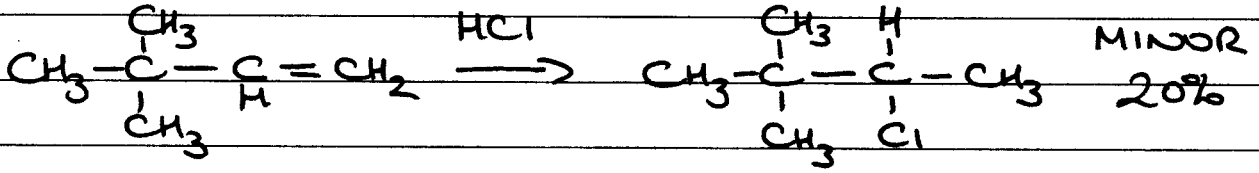




3° C⁺
(more stable)

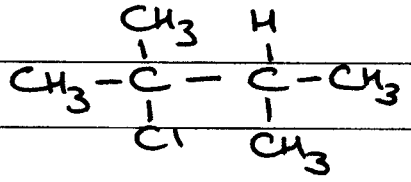
Rearrangement possible wherever a carbocation is formed.

Consider:



MINOR 20%

SHOW WHY THIS HAPPENS? ⇒



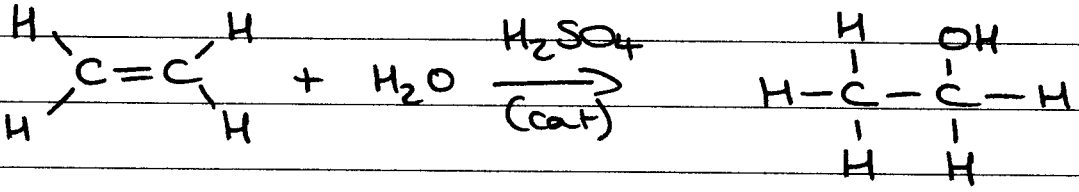
MAJOR 80%

not 1,2 H^- shift,
but 1,2 METHYL shift

2° CARBOCATIONS ⟲ 3° CARBOCATIONS
(rarely rearrange in reverse direction, but is possible ~ ring strain)

In reality, 1° C⁺ do not form during reactions in solution, as they are so unstable.

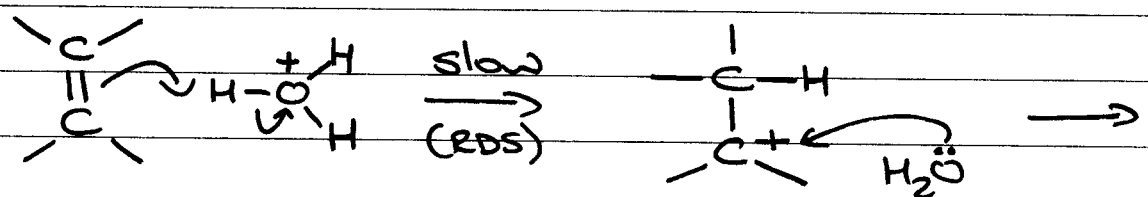
(4) ADDITION of H_2O (acid catalysed hydration)

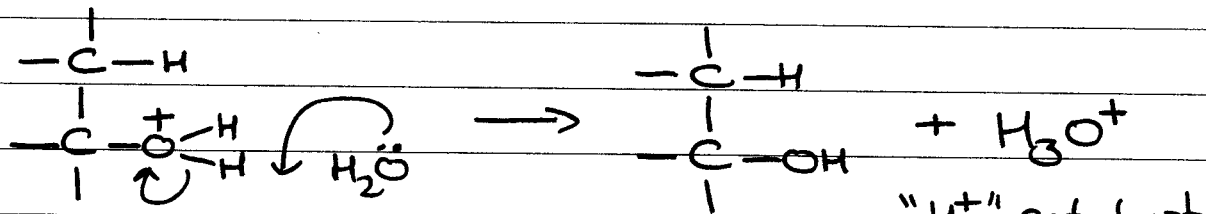


H_2O alone is not acidic enough to protonate C=C, so need an acid catalyst

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

mechanism:



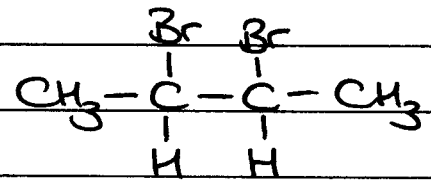


mechanism involves a CARBOCATION, so:

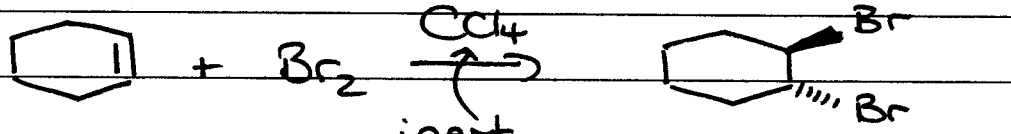
(i) Rearrangement is possible in ACID cat hydration

(ii) MARKOVNIKOV selectivity is observed

(5) ADDITION of Br_2/Cl_2

$CH_3CH=CHCH_3 \xrightarrow{Br_2}$ 

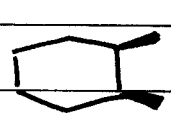
note:



TRANS

1,2-dibromo cyclohexane

STEREOSPECIFIC reaction

cis isomer () IS NOT formed

note:

STEREOSPECIFIC (exclusion)

STEREOSELECTIVE (preference)

Same goes for (REGIO)

LEC (16) CHEM 30A May 11th

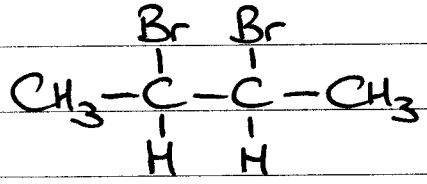
(1) ADDITION of H_2O
(2) ADDITION of Br_2/Cl_2
(3) ADDITION of HOCl/HOBr

PROBLEMS 6.7, 6.8 (4th) 6.9, 6.10 (3rd)
READ 6.3 – 6.6.

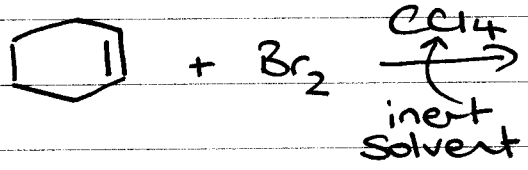
---

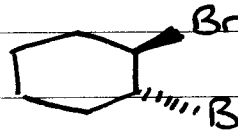
(1) ADDITION of H_2O
see page 6 of Lec 15

(2) ADDITION of Br_2/Cl_2

$CH_3CH=CHCH_3 \xrightarrow{Br_2}$ 

note:

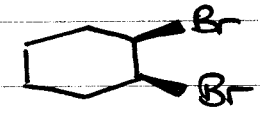




trans

1,2-dibromo-cyclohexane

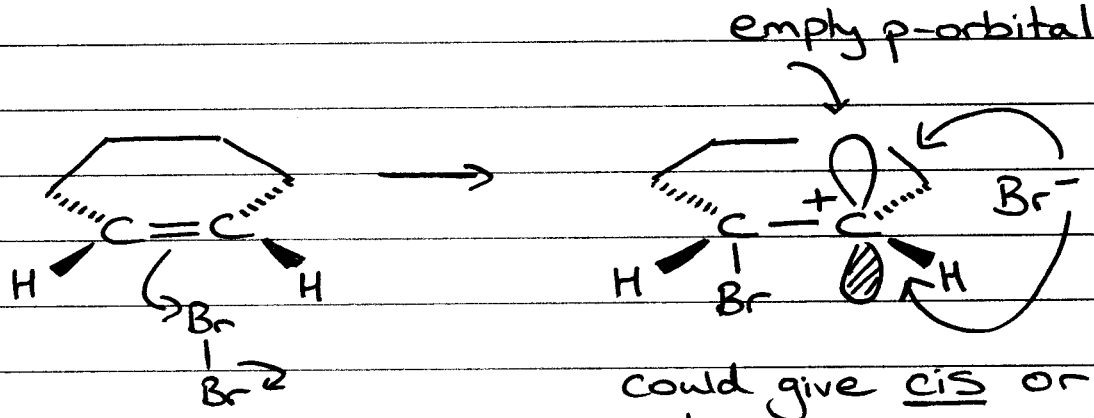
STEREOSPECIFIC REACTION

cis isomer  is NOT formed

note:
STEREOSPECIFIC (exclusion) (REGIO)
STEREOSELECTIVE (preference)

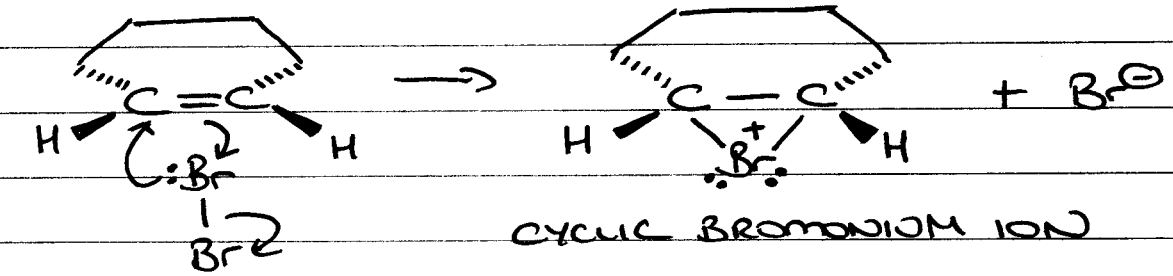
- consider the mechanism

IF



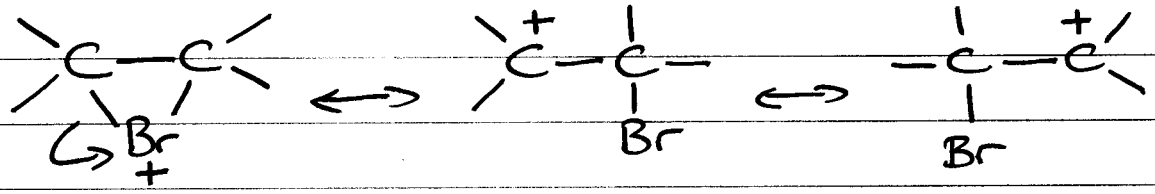
could give cis or trans (possibility Br rearrangement)

mechanism is:

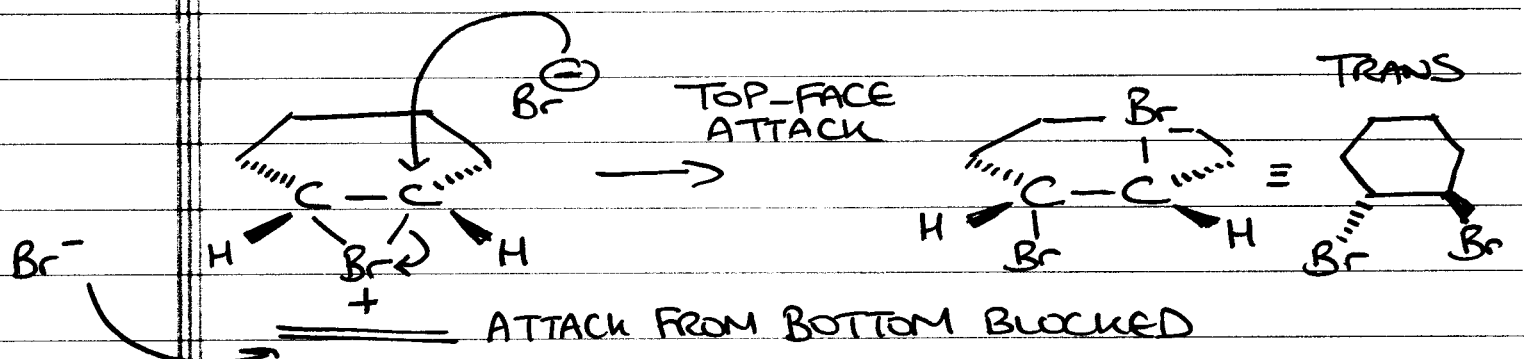


CYCLIC BROMONIUM ION

CONTRIBUTING RESONANCE STRUCTURES



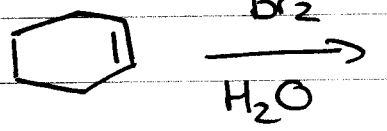
MINOR CONTRIBUTORS



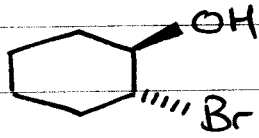
REACTION PROCEEDS w/ ANTISTEREOSPECIFICITY

- If Br^- had attacked at other C atom
  ⇒ ENANTIOMER

(3) ADDITION of HOCl | HOBr

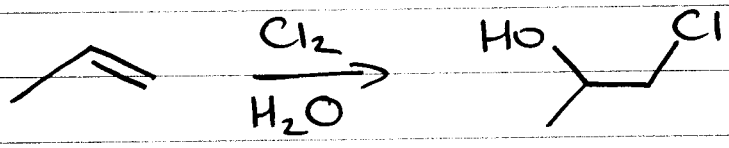


not an INERT solvent



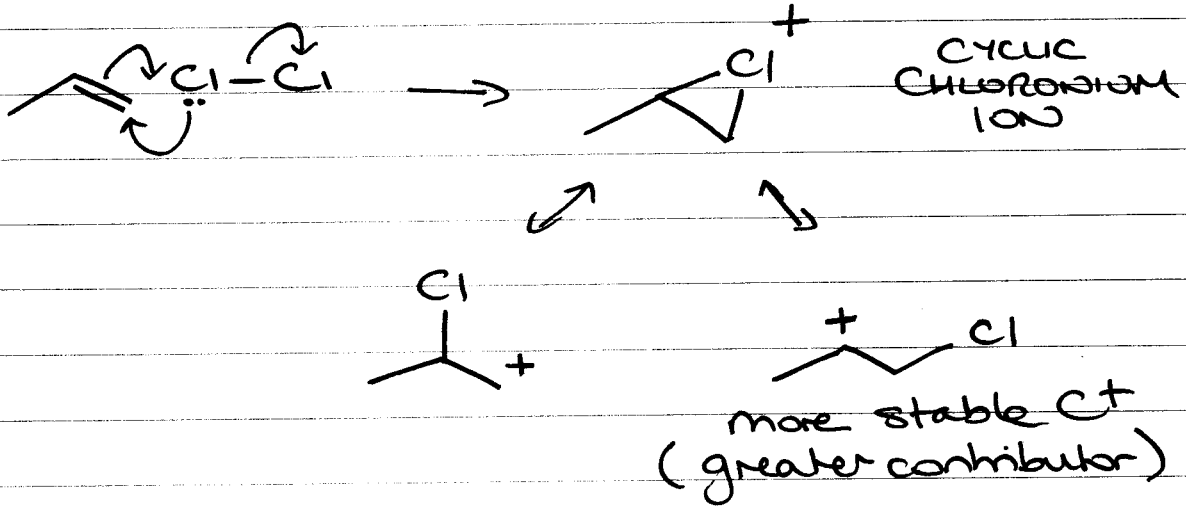
BROMOHYDRIN (HALOHYDRIN)

ANTI STEREOSPECIFIC & (REGIO SELECTIVE)



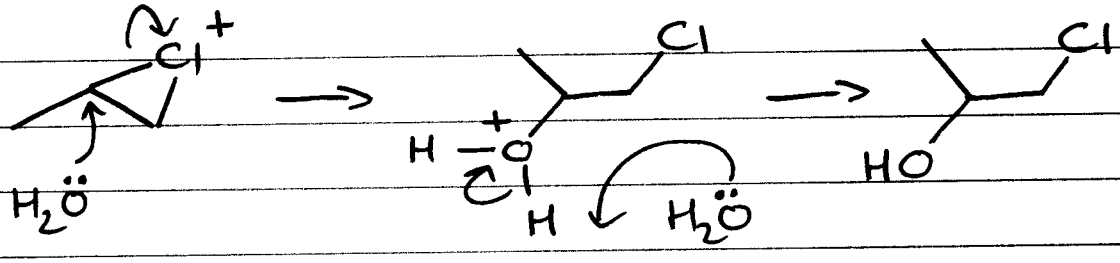
- OH adds to more substituted C ATOM of the alkene

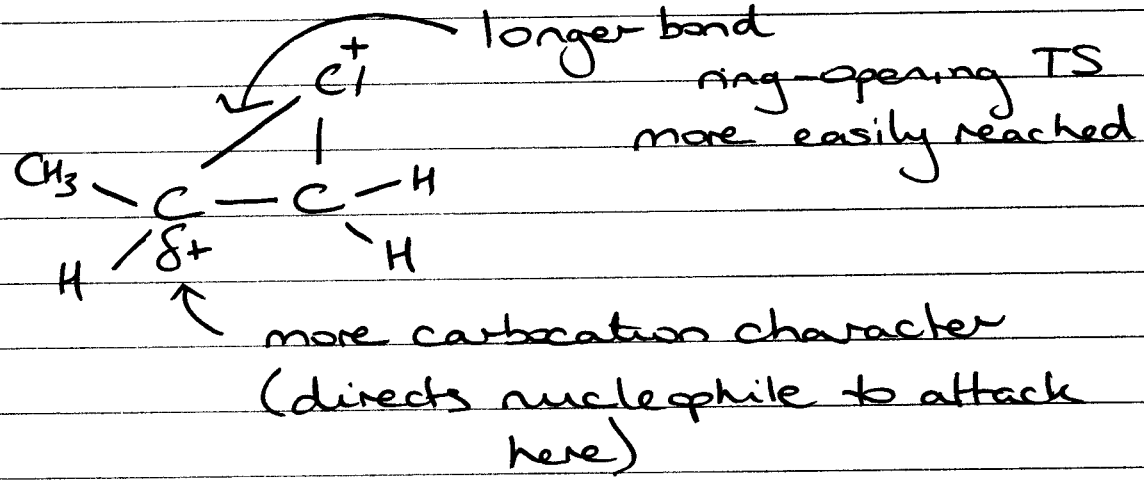
mechanism:



more stable C+ (greater contributor)

OPENS VIA MORE STABLE C^+





LEC (17) CHEM 30A May 13th

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

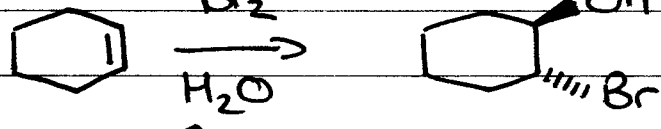
QUIZ LOW = 3
HIGH = 33
MEAN = 19

- mechanism worksheets

READ rest of Ch6

(3rd) 6.9-6.11, 6.13, 6.17-6.42
(4th) 6.7-6.9, 6.12, 6.16-6.40

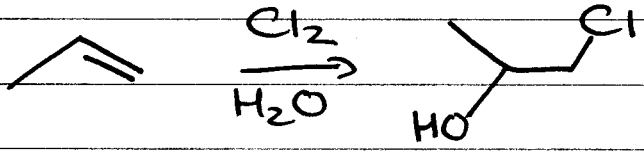
(1) ADDITION of HOCl/HOBr



ANTI
STEREOSPECIFIC
&
(REGIOSELECTIVE)

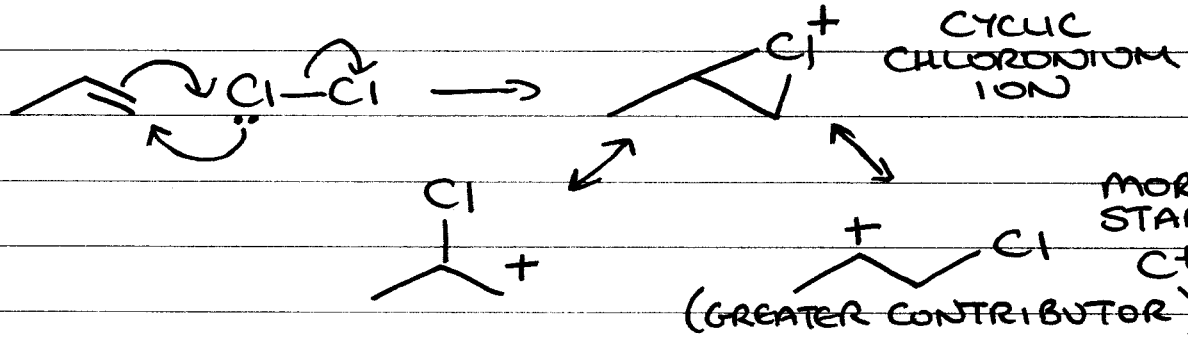
not an inert solvent

BROMOHYDRIN
(Halohydrin)

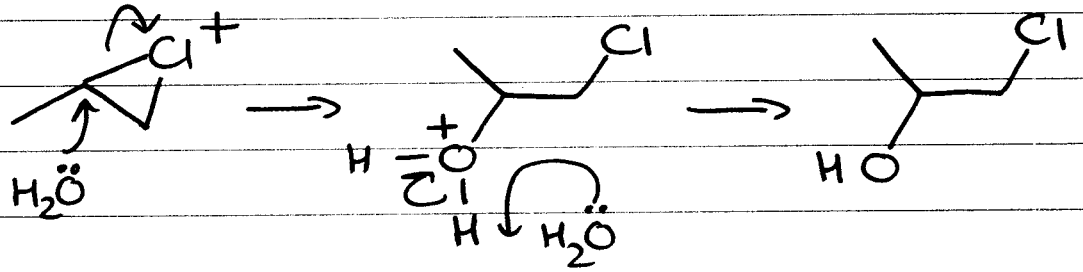


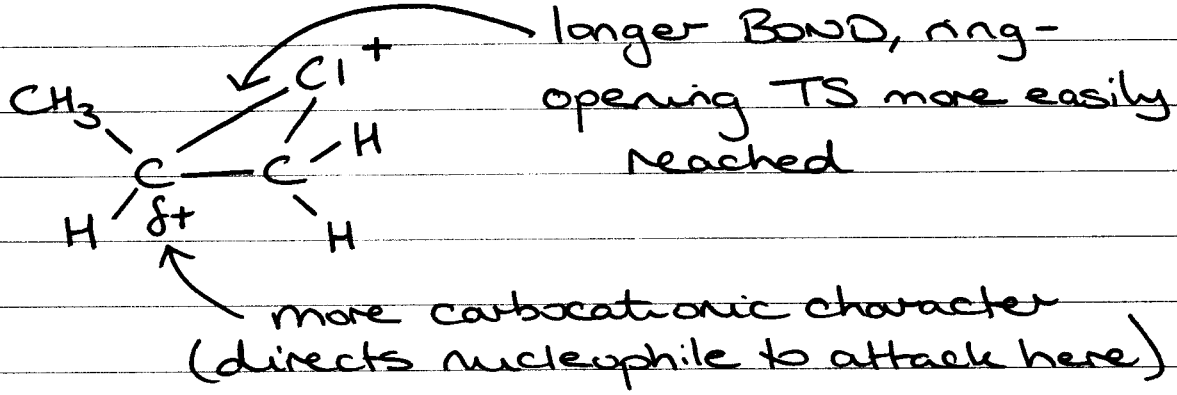
-OH adds to more SUBSTITUTED C atom

mechanism

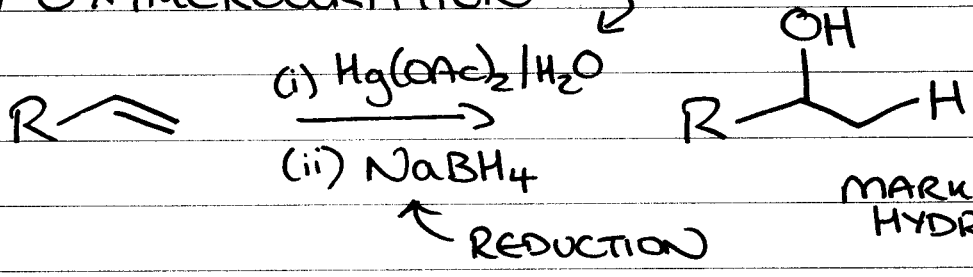


OPENS VIA MORE STABLE C^+

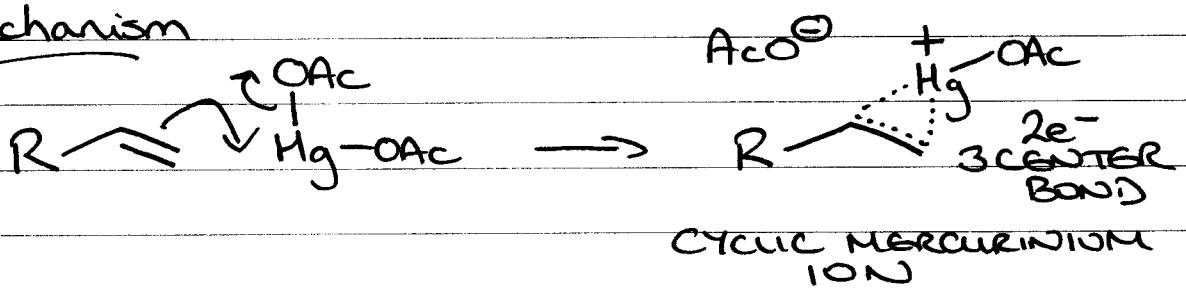




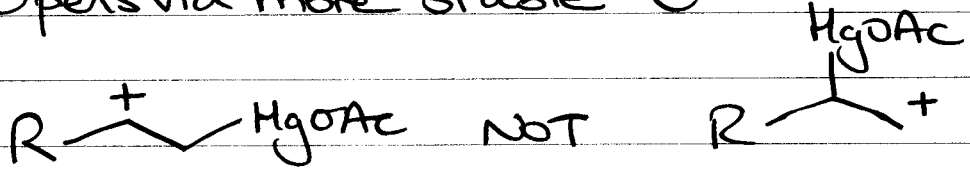
(2) OXYMERCURATION



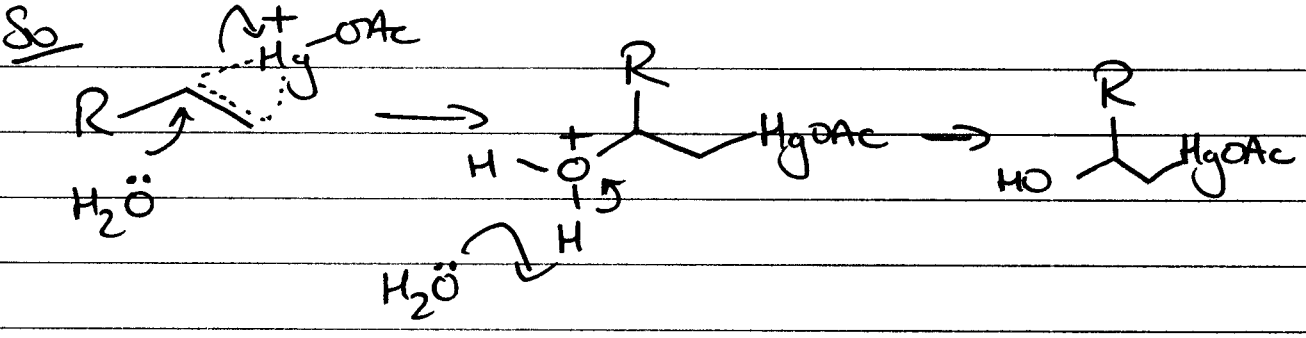
mechanism



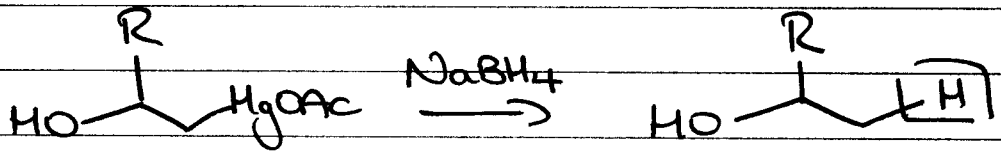
Opens via more stable C^+



So



organomercury cmpd reduced w/ $NaBH_4$

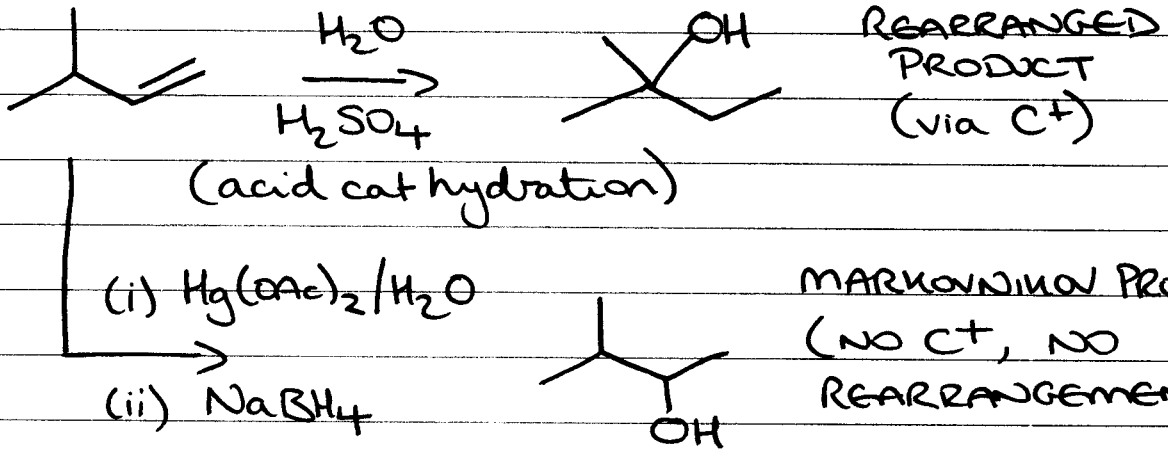


replaces HgOAc for H

(Don't need to know mechanism for this)

WHY IS THIS USEFUL?

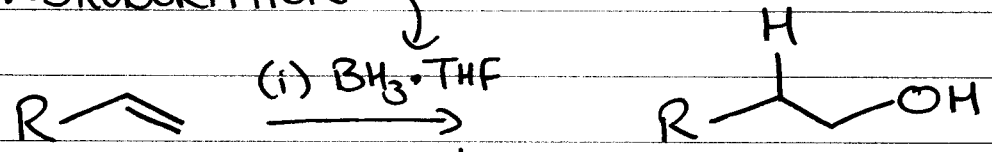
Consider:



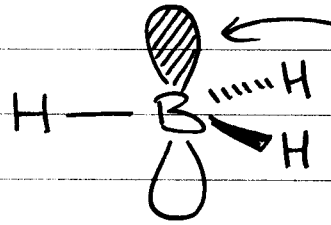
REGIOSELECTIVE, W/ ANTISTEREOSPECIFICITY

(similar to addition of HOCl/HOBr)

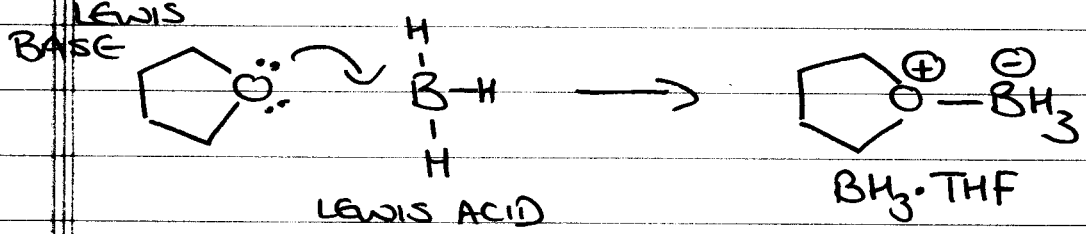
(3) HYDROBORATION

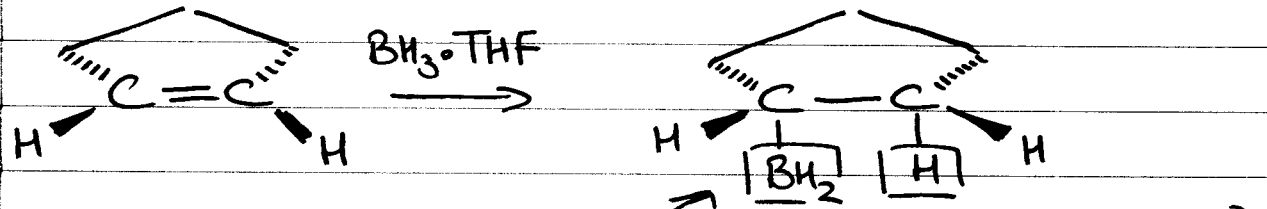


Borane (BH_3)

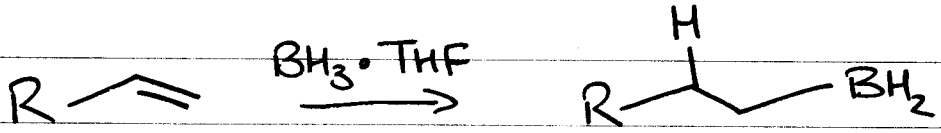


(actually exists as B_2H_6 - structure?)



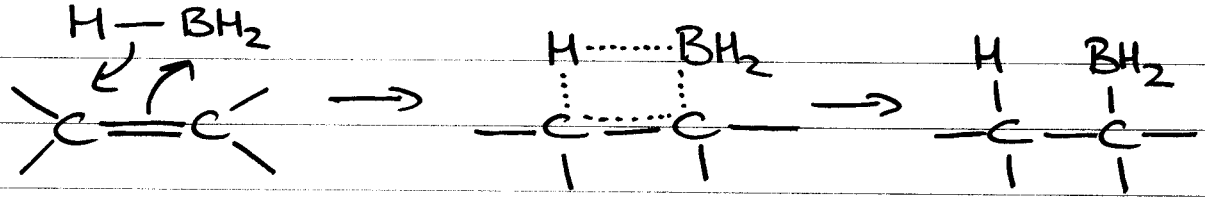


SYN STEREOSPECIFIC

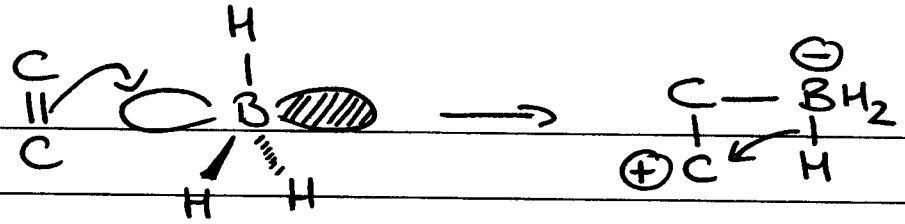


BORON ADDS TO LESS SUBSTITUTED C ATOM

Mechanism



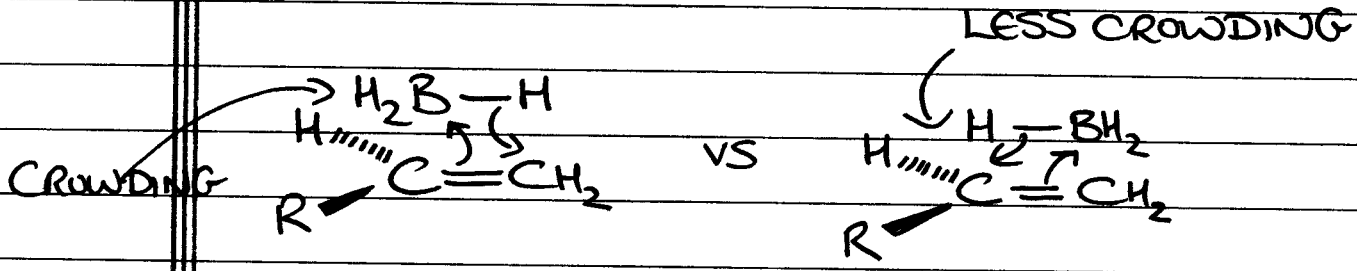
i.e.



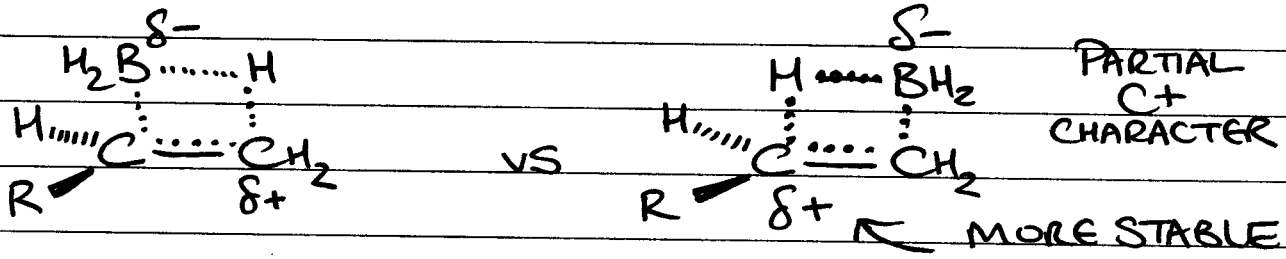
— NO REARRANGEMENTS

Why REGIOSELECTIVE?

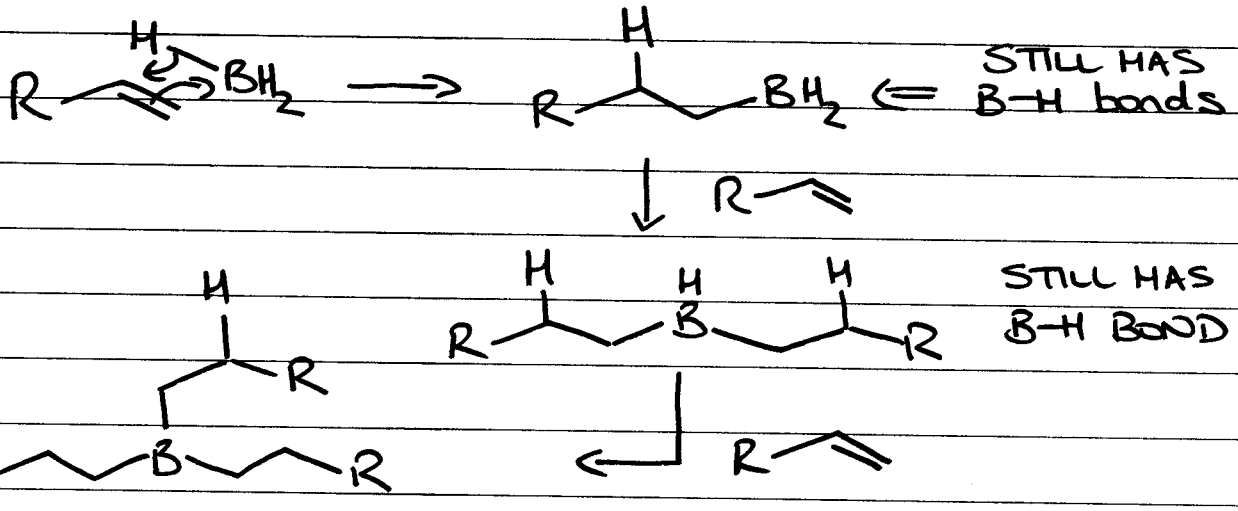
(i) STERICS



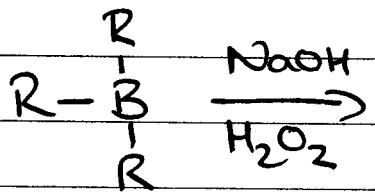
(ii) ELECTRONICS

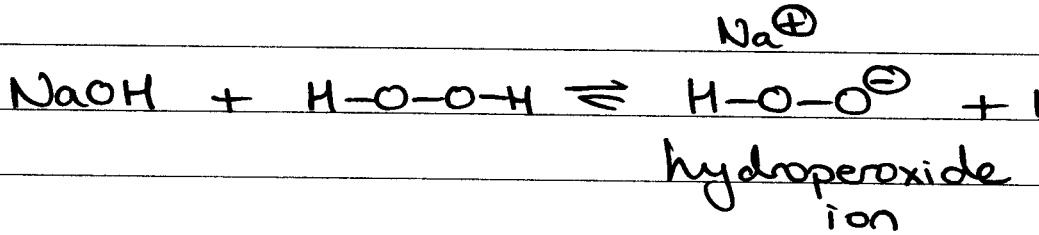


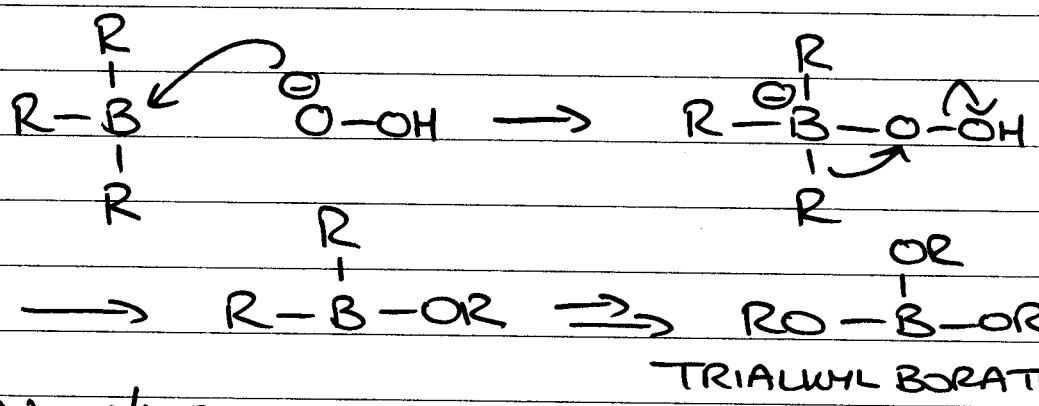
FULL MECHANISM:



SECOND STEP

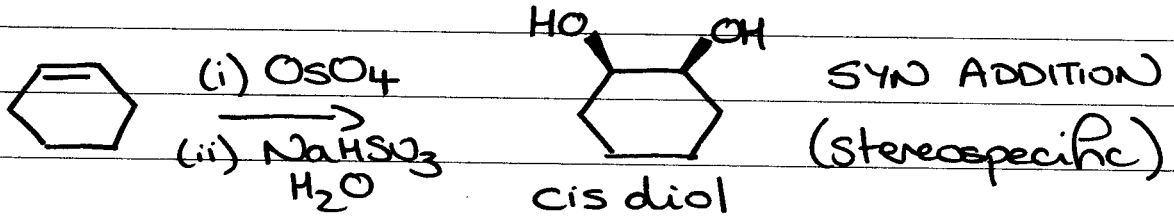


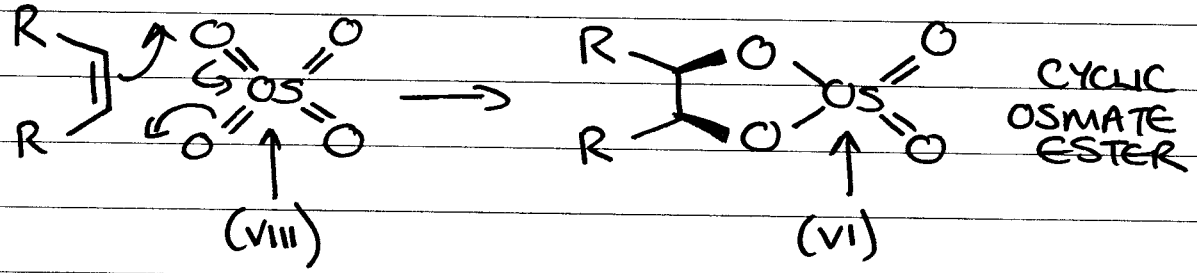


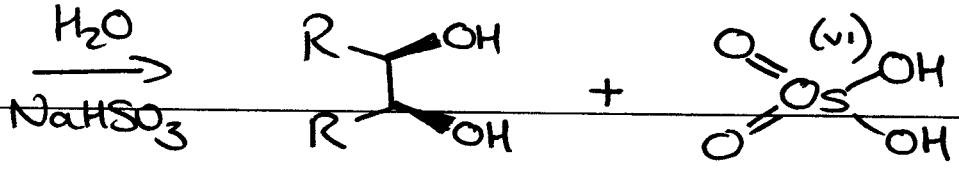


(4) OXIDATION

(i) OsO_4 osmium tetroxide



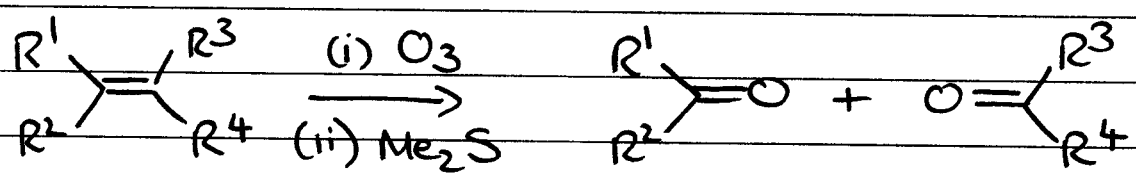




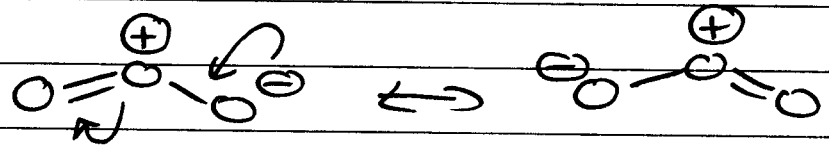
(needs to be re-oxidised)
expensive / toxic

OS REDUCED (VIII → VI), ALKENE OXIDISED

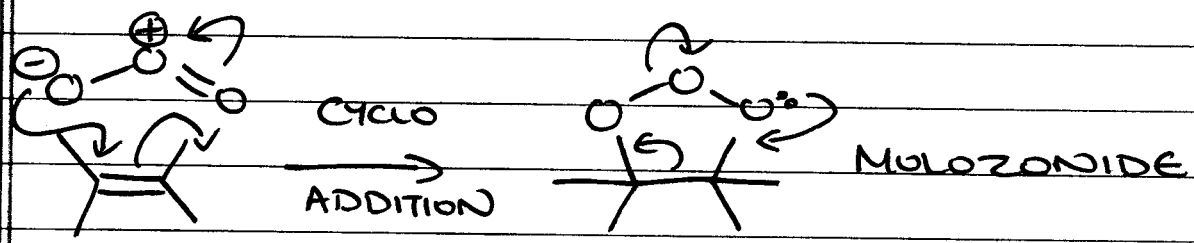
(ii) OZONOLYSIS

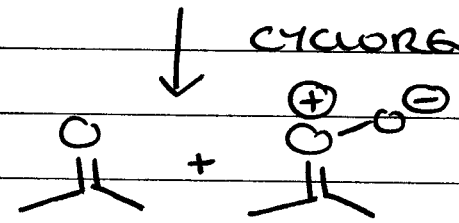


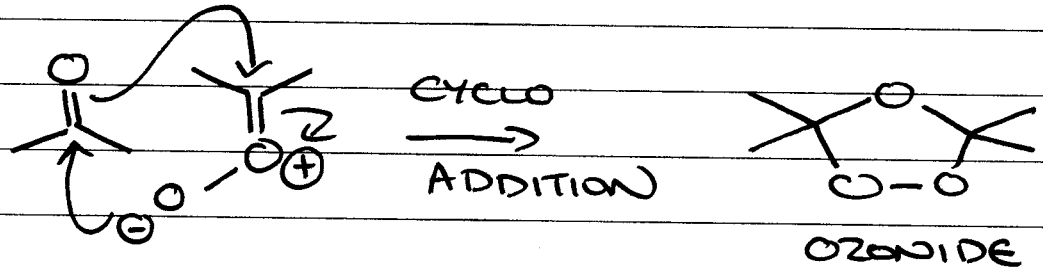
OZONE



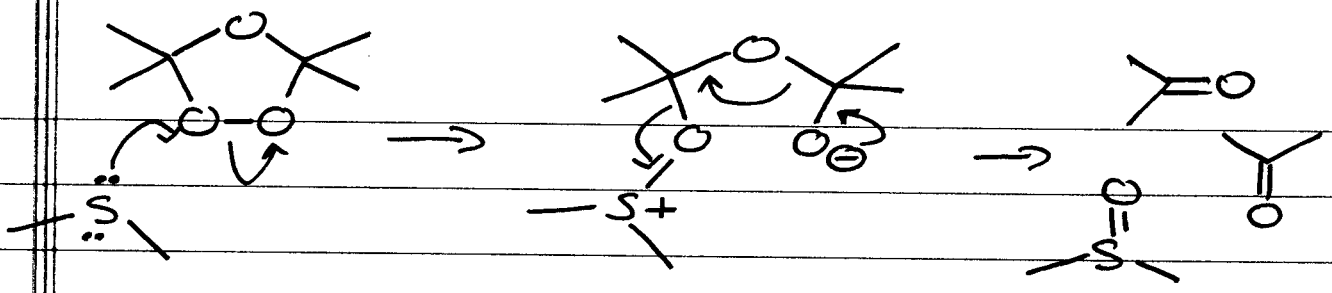
MECHANISM







OZONIDE



next up... reduction

LEC (18) CHEM 30A May 16th

(1) HYDROBORATION cont...
(2) OXIDATION — Read 6.5 - 6.7, 10.9 (3rd)
(3) REDUCTION — 6.5 - 6.7, 7.6 (4th)
(4) STEREOCHEMISTRY
(5) ALKYNES — 6.43-6.49 (3rd)
6.41 - 6.52 (4th)

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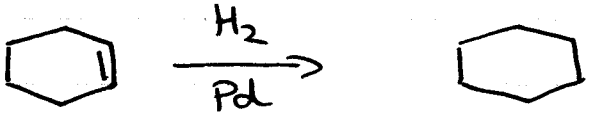
(1) & (2) See pages 6-8 Lec (17)

(3) REDUCTION

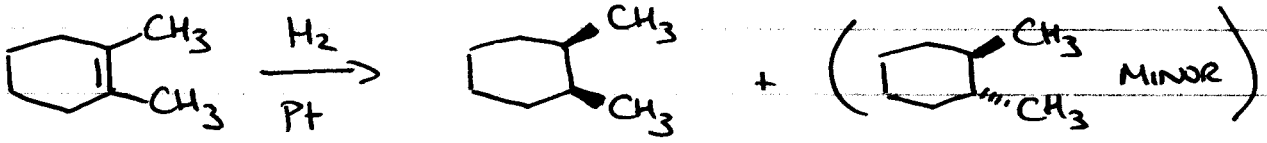


METAL CATALYST
(finely divided on an inert support → charcoal)

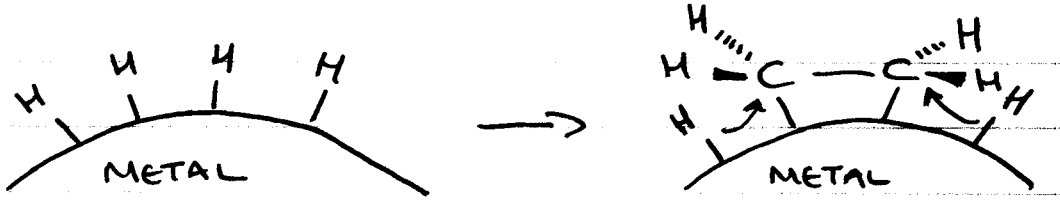
Transition metal catalyst Pt, Pd, Ru, Ni

- CATALYTIC REDUCTION / HYDROGENATION

- Stereoselective

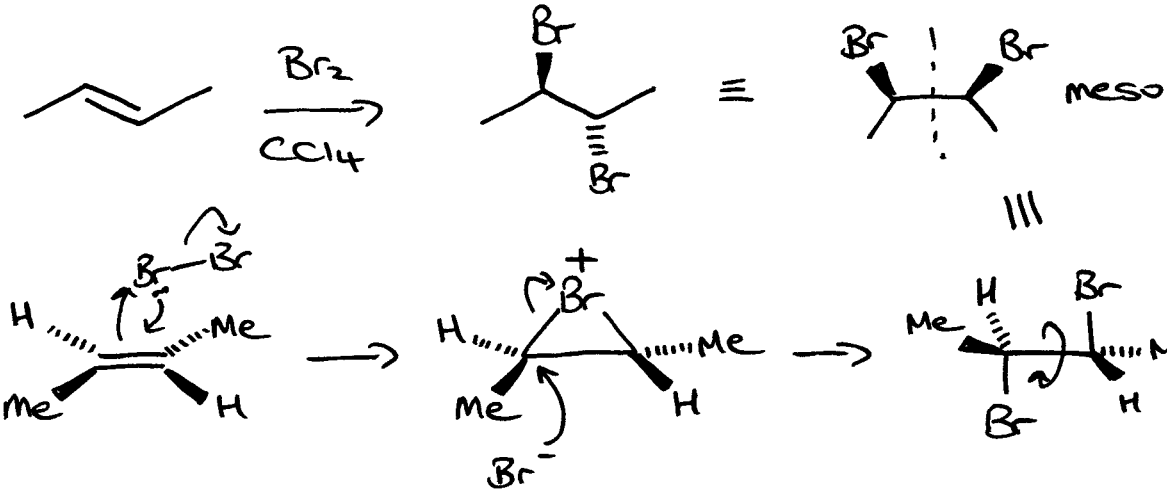


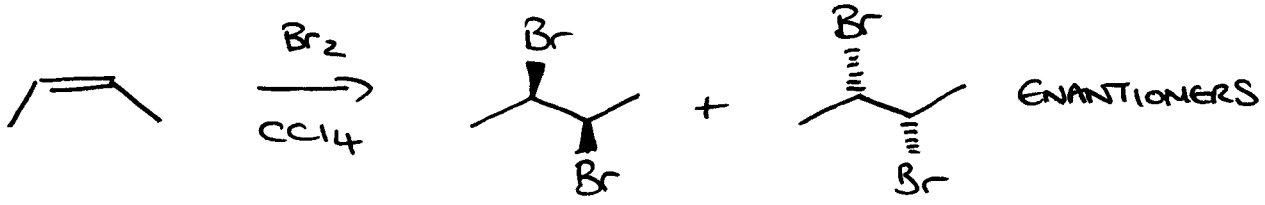
mechanism:



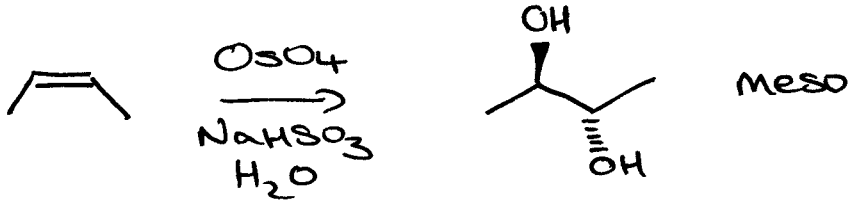
MINOR PRODUCTS result from isomerisation of the alkene on the metal catalyst.

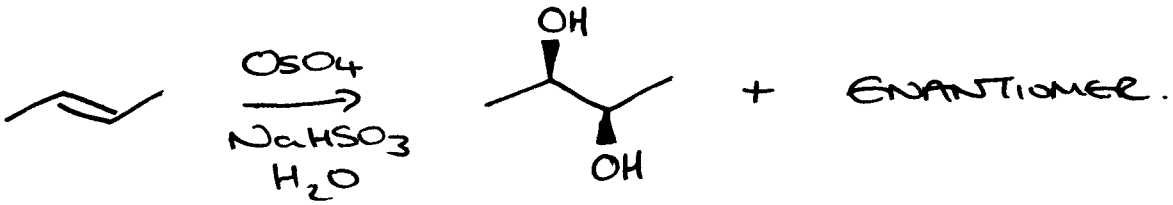
(4) STEREOCHEMISTRY (again)





WORK THROUGH THE MECHANISM

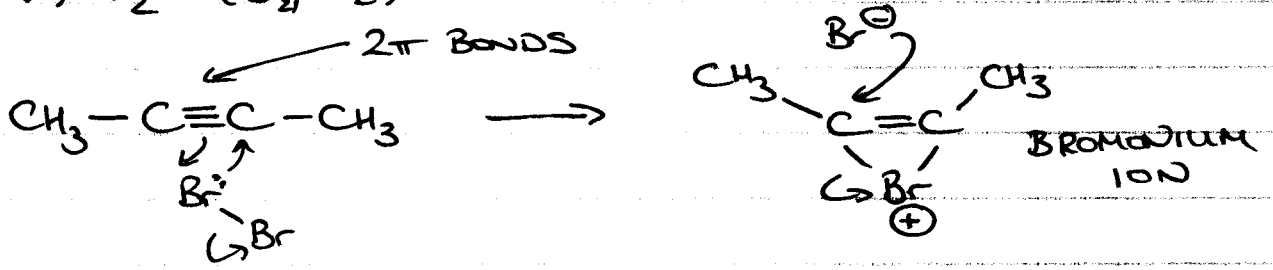




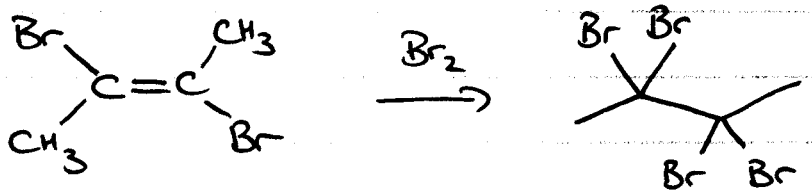
Again, work through the mechanisms and show how to get each product

(5) ALKYNES

(i) X_2 (Br_2, Cl_2)



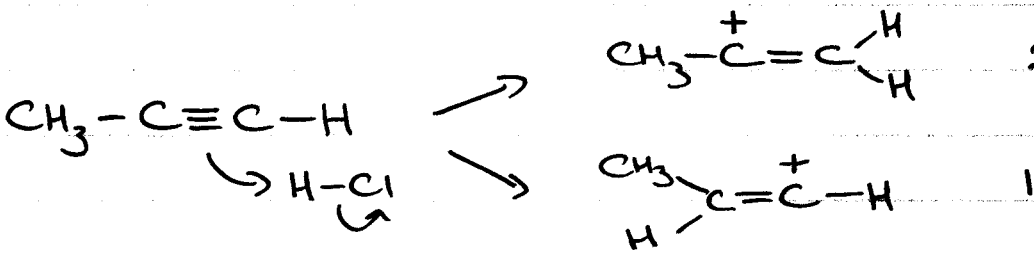
ANTI STEREOSPECIFICITY



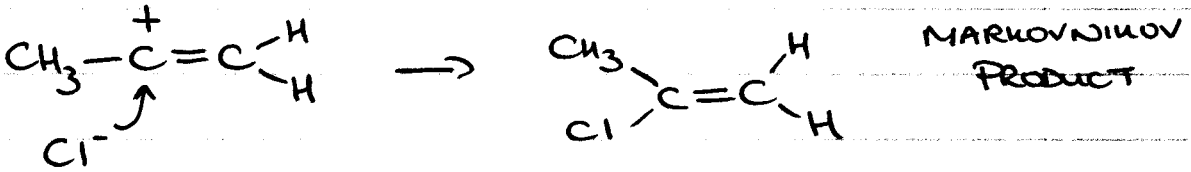
trans dibromide (difficult to stop here)

tetrabromoalkane

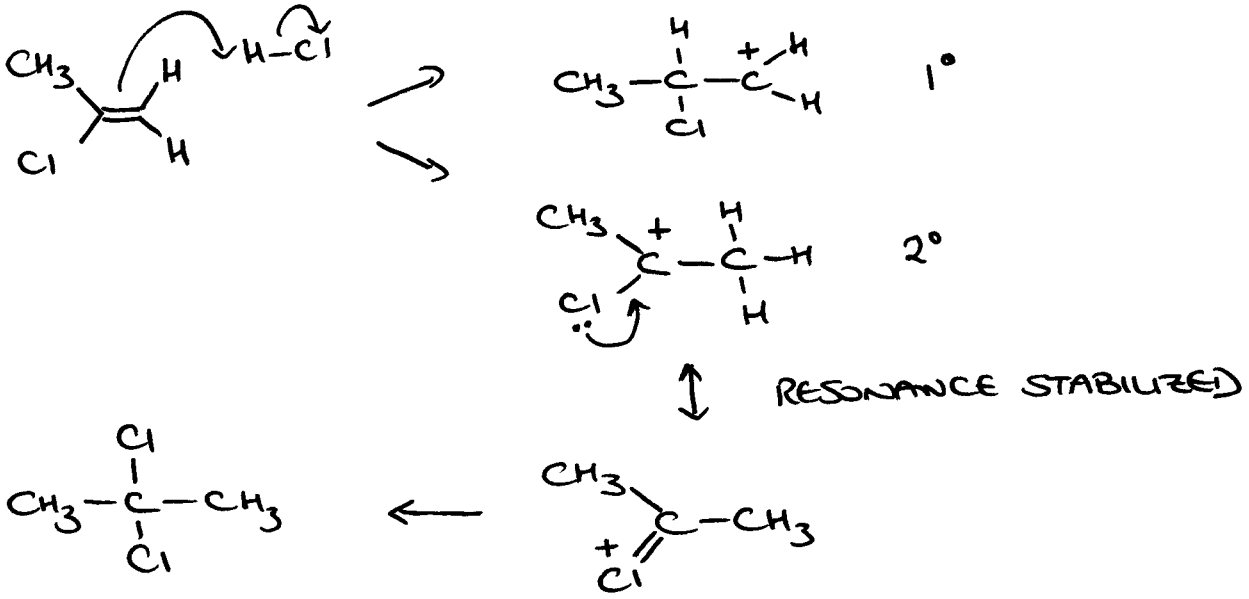
(ii) HX (HCl, HBr, HI)



VINYL CARBOCATIONS (not very stable)



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

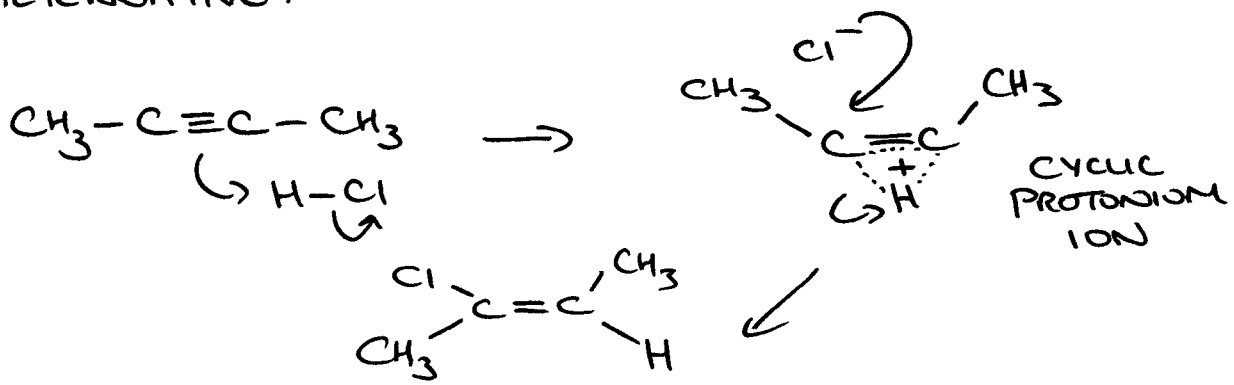


mechanisms may be more complicated, but this is not a bad model

VINYLIC C^+ quite unstable

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

ALTERNATIVE:



ACCOUNTS FOR OBSERVED TRANS SELECTIVITY.

LEC (19) CHEM 30A May 18th

ALKYNES

READ 10.7–10.9 (3)
8.1–8.2
7.8–7.9
9.1–9.2 (4)

(1) HX ADDITION
(2) OXYMERCURATION
(3) HYDROBORATION
(4) REDUCTION

NUCLEOPHILIC SUBSTITUTION
(5) INTRO

PROBLEMS
(3) 10.4, 10.15–10.17, 10.21–10.23
(4) 7.4, 7.5, 7.10–7.12
7.16–7.18

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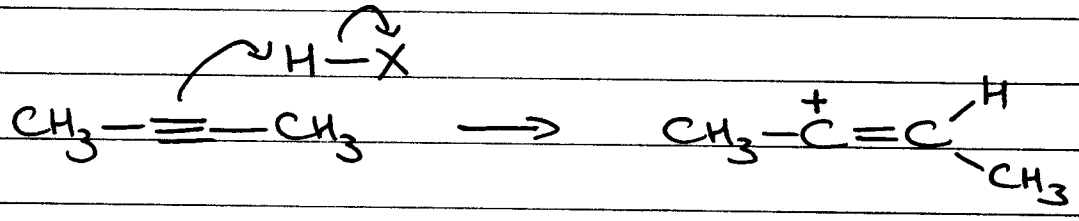
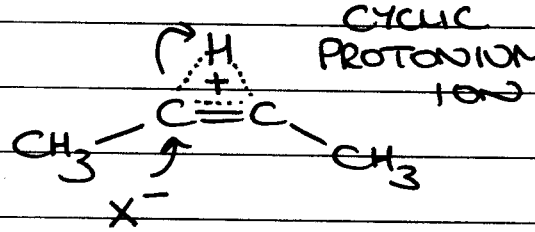
(1) HX ADDITION

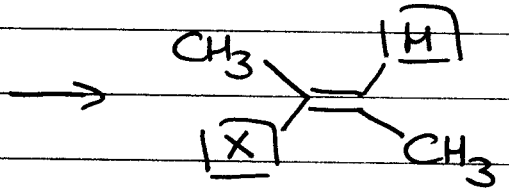


VINYLIC C+ UNSTABLE, 2° C+ VINYLIC ≈ 1° C+
(1° C+ not viable rxn intermediate)

PROPOSED INTERMEDIATE:

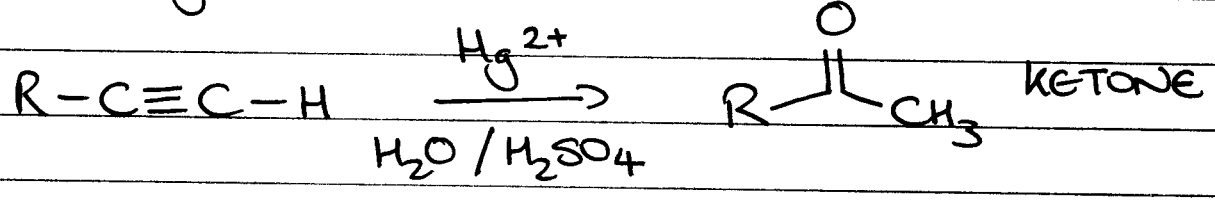


CYCLIC PROTONIUM ION



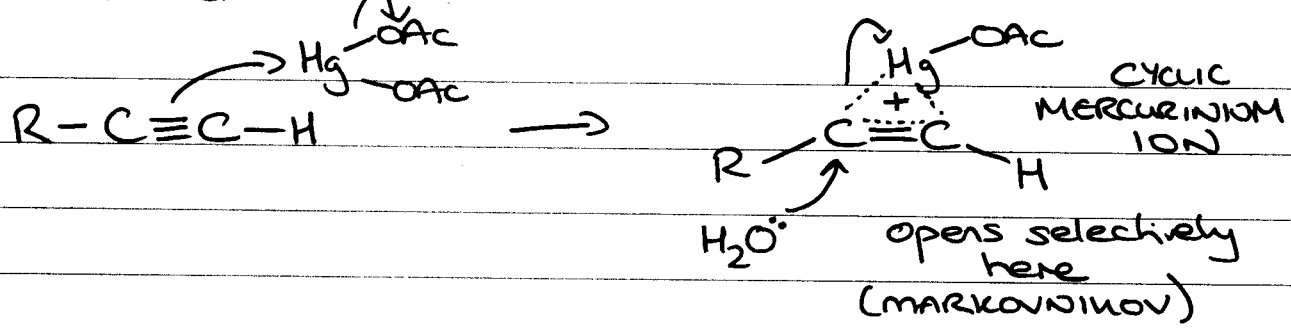
ACCOUNTS FOR TRANS SELECTIVITY

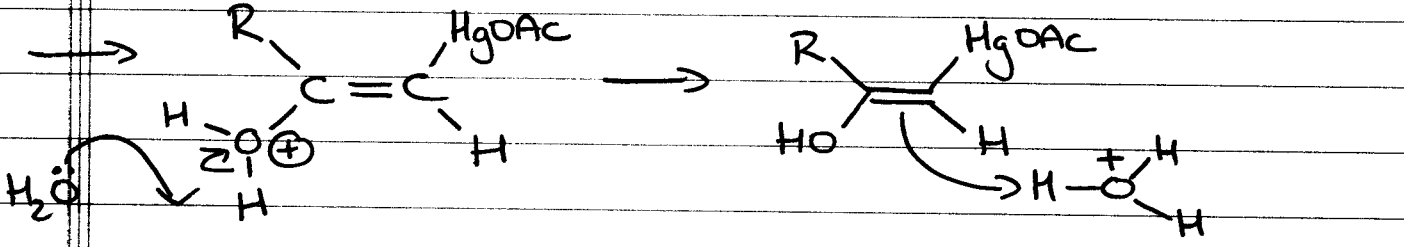
(2) Oxymercuration

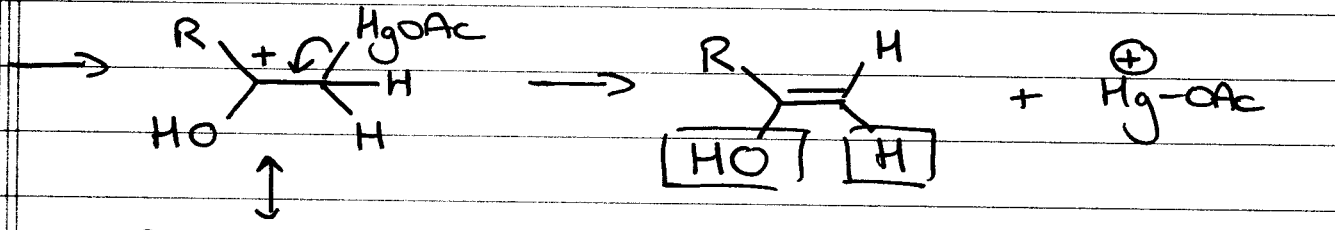


KETONE

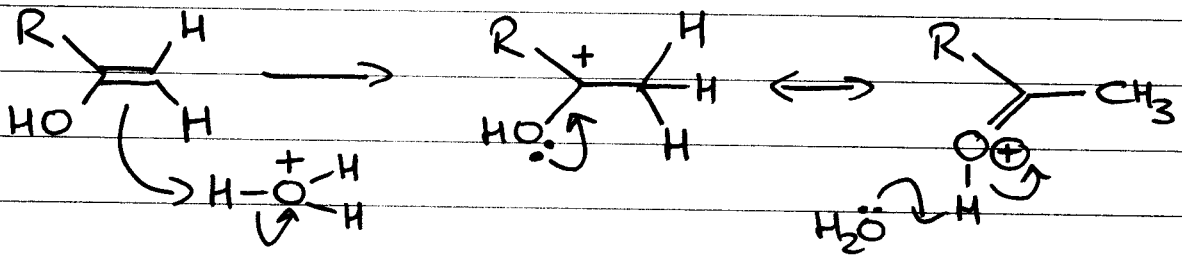
mechanism

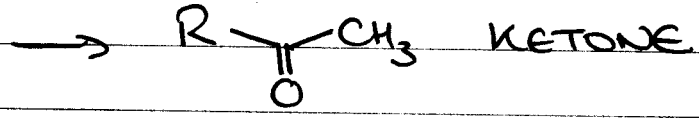


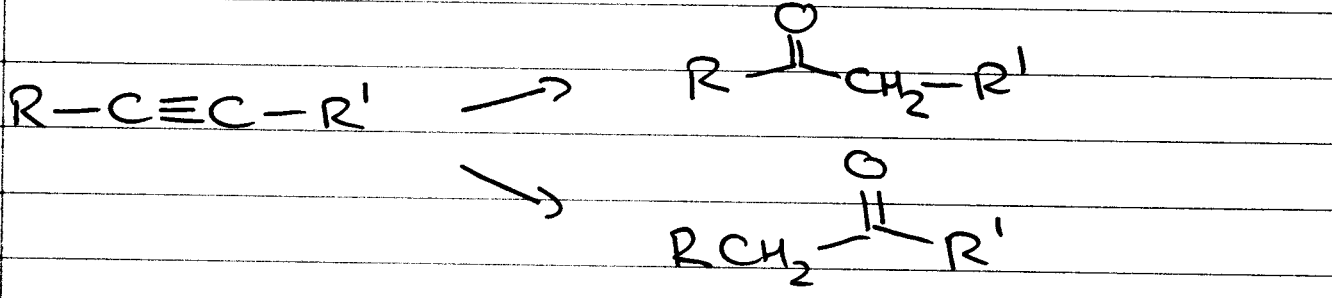




KETO-ENOL TAUTOMERIZATION



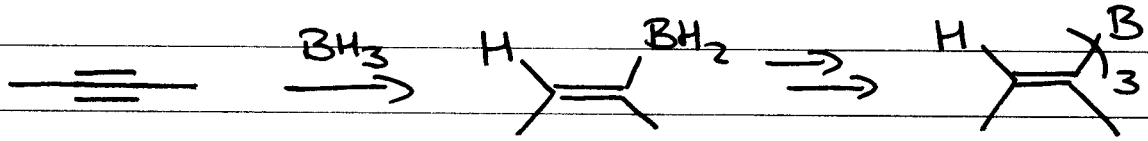




(3) HYDROBORATION

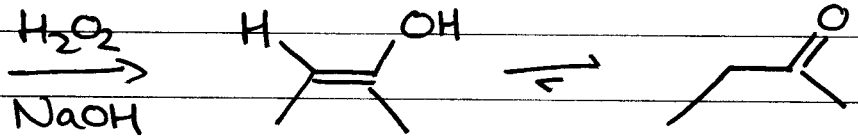
(R—≡—H, R—≡—R)

terminal non-terminal



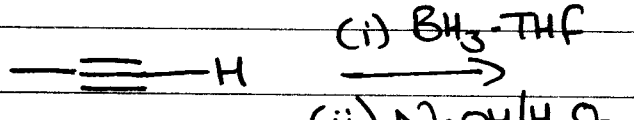
TRIALKENYL BORANE

⇑ same mechanism as B alkenes

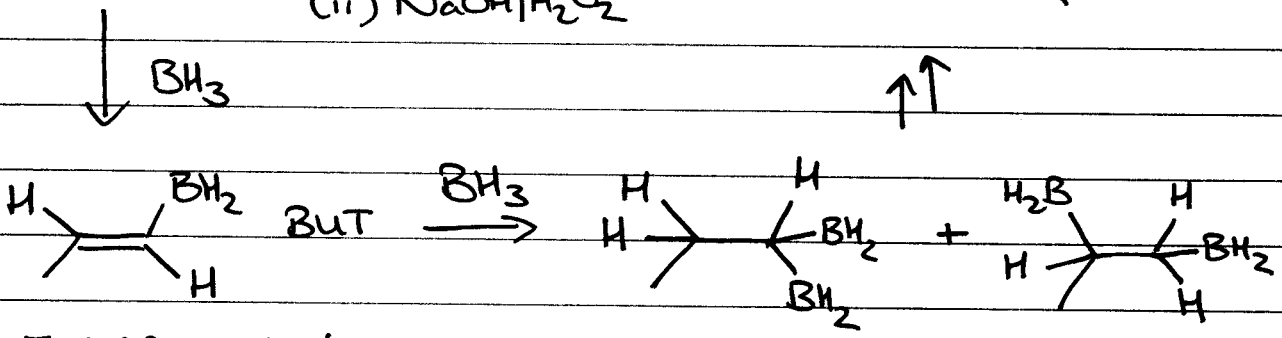


ENOL ⇌ KETO

Terminal Alkynes

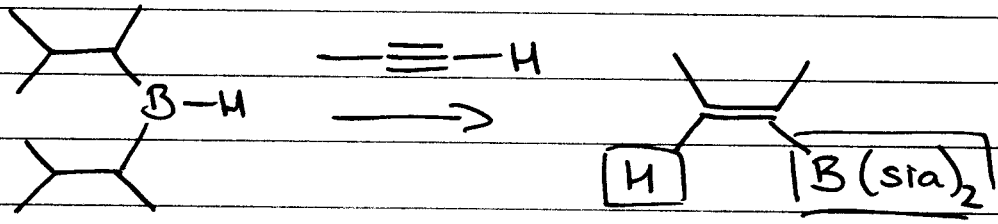


mixture of products



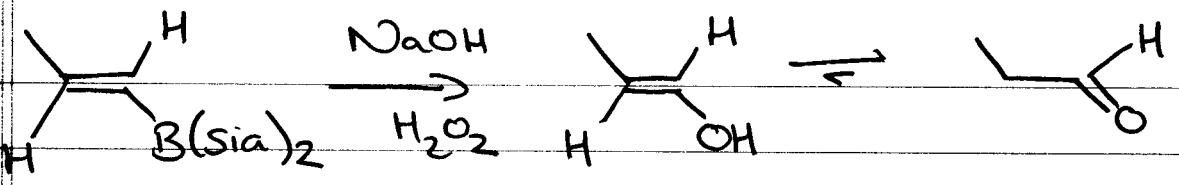
ANTI MARKOVNIKOV

DISIAMYL BORANE $(sia)_2BH$

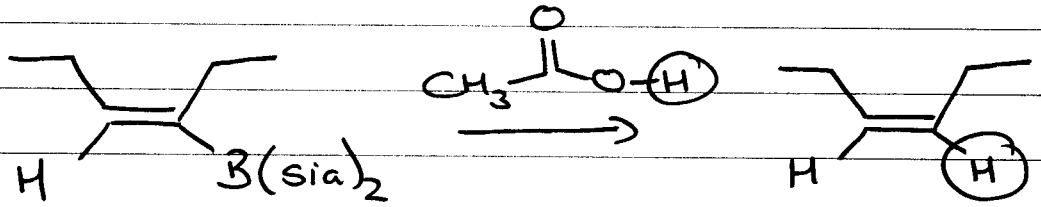


SYN ADDITION

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



NOTE: RXN w/ ACETIC ACID

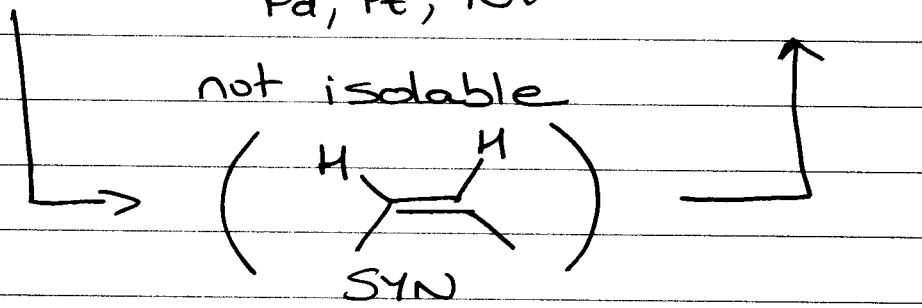


STEREOSPECIFIC
(HYDROBORATION | PROTONOLYSIS)

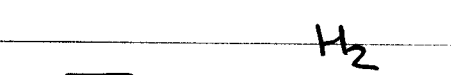
(4) REDUCTION

ALKYNE ⟶ [ALKENE] ⟶ ALKANE

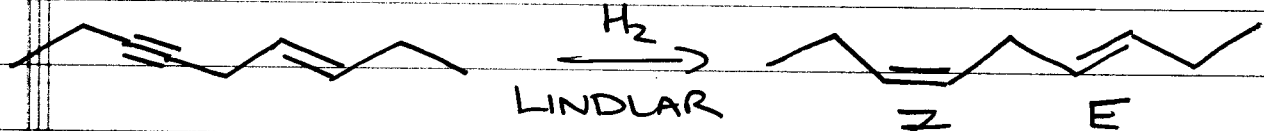
(i) H_2 (3 atm), Pd, Pt, Ni



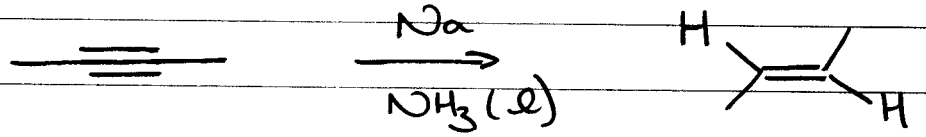
(ii) H_2, LINDLAR ↳ ($Pd/CaCO_3/PbO$) POISONED CATALYST

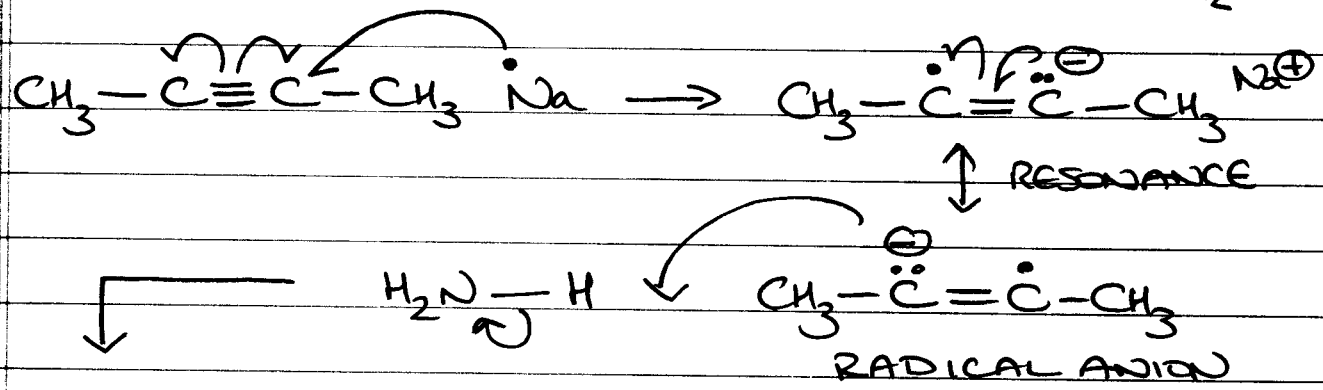


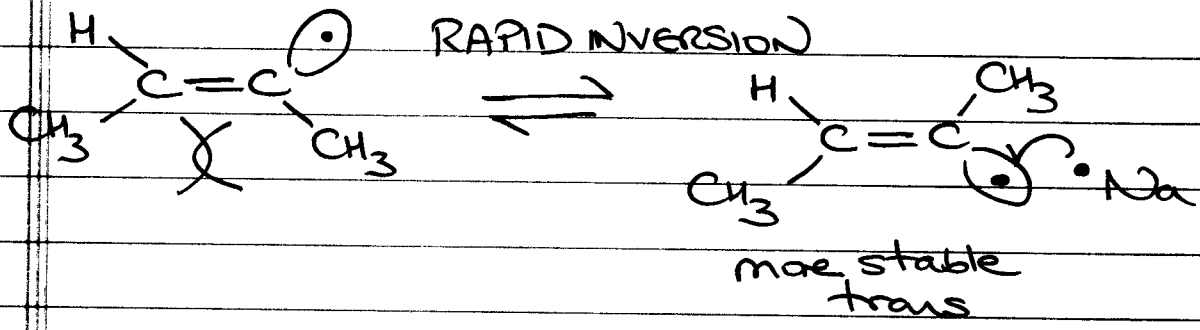
CIS — STOPS HERE

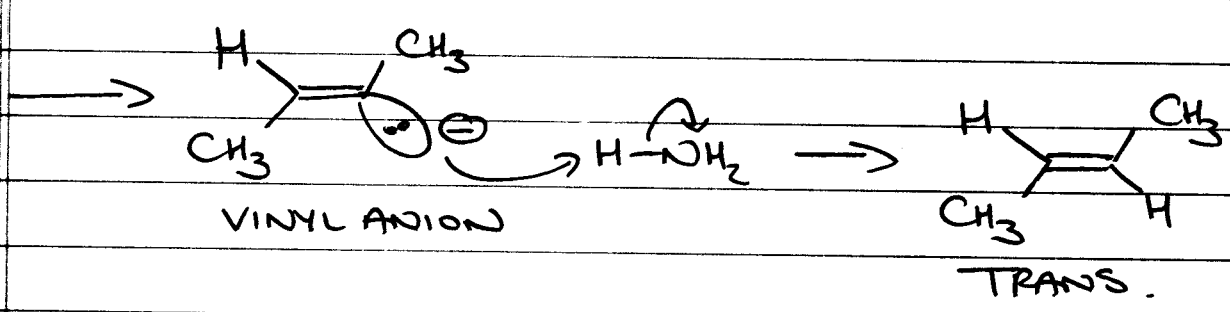


(iii) DISSOLVING METAL REDUCTION

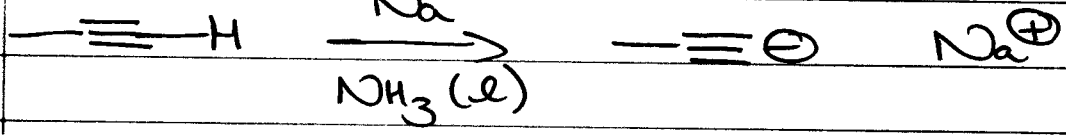




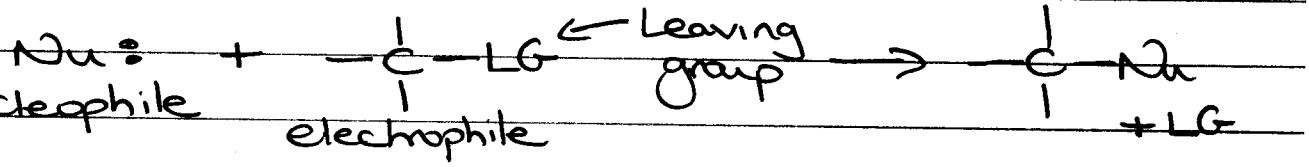




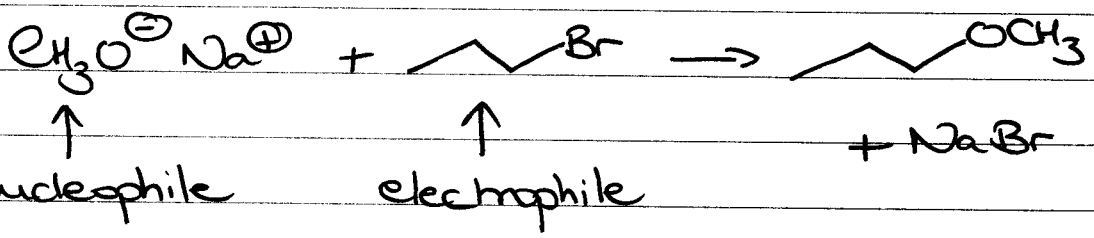
DOES NOT WORK FOR TERMINAL ALKYNES



(5) NUCLEOPHILIC SUBSTITUTION



Substitution of Nu for LG

e.g. 

nucleophile — electrophile

LEC (20) CHEM 30A May 20th

- NUCLEOPHILIC SUBSTITUTION

(1) INTRODUCTION — READ 8.1 – 8.6

(2) MECHANISMS — 8.1 – 8.29 (3rd)

(3) ELECTROPHILE — READ 9.1 – 9.5

(4) NUCLEOPHILE — 9.1 – 9.30 (4th)

- MIDTERM ON WEDS (usual rules)

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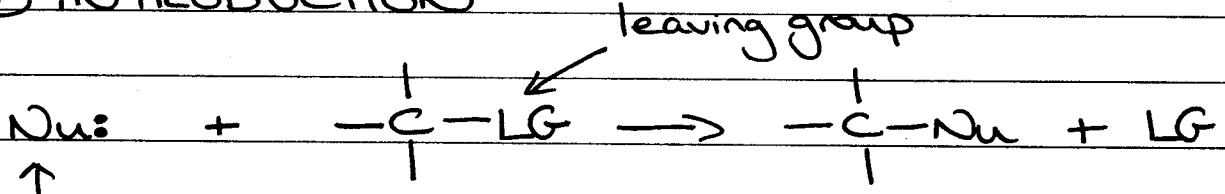
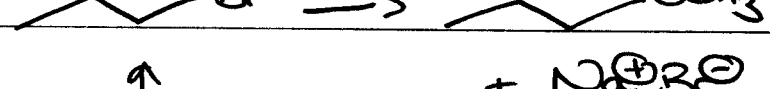
(1) INTRODUCTION



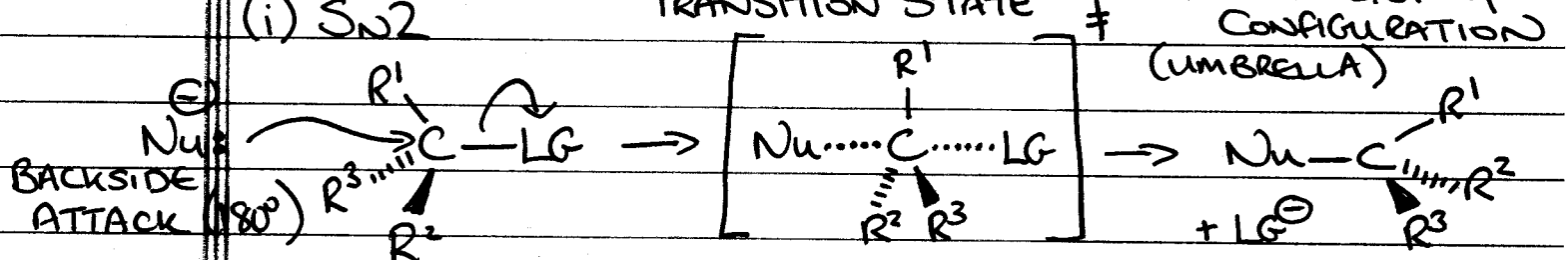
SUBSTITUTION of LG for Nu

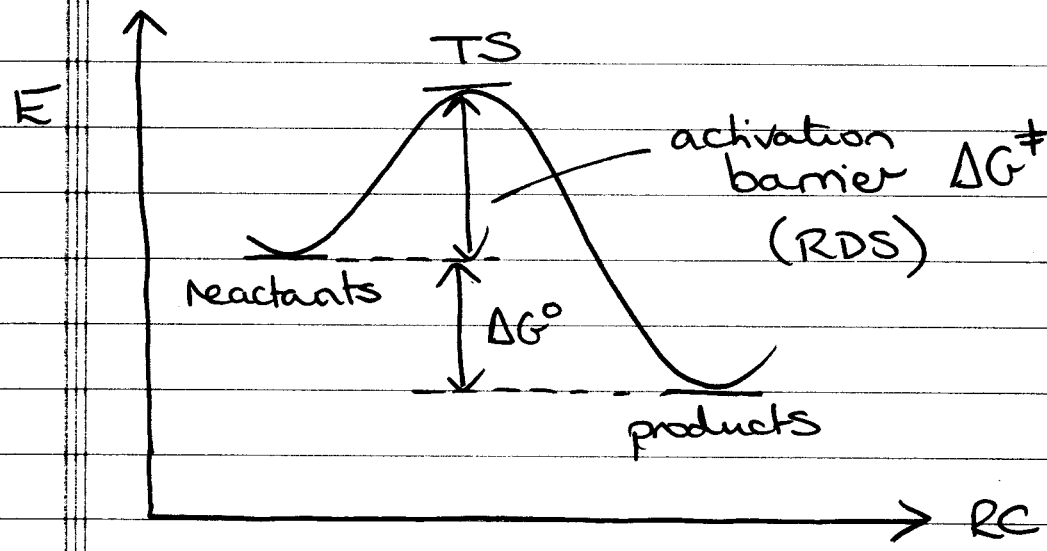
e.g. $CH_3O^{\ominus}Na^{\oplus}$ +  → + $NaBr$

nucleophile — electrophile

(2) MECHANISMS (TWO LIMITING ONES)

(i) S_N2





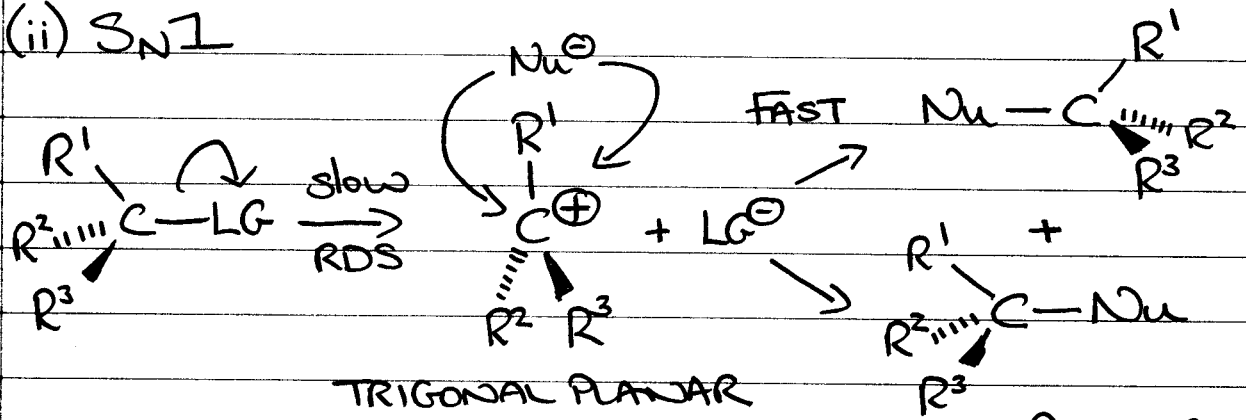
S_N2 = SUBSTITUTION, NUCLEOPHILIC, BIMOLECULAR

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



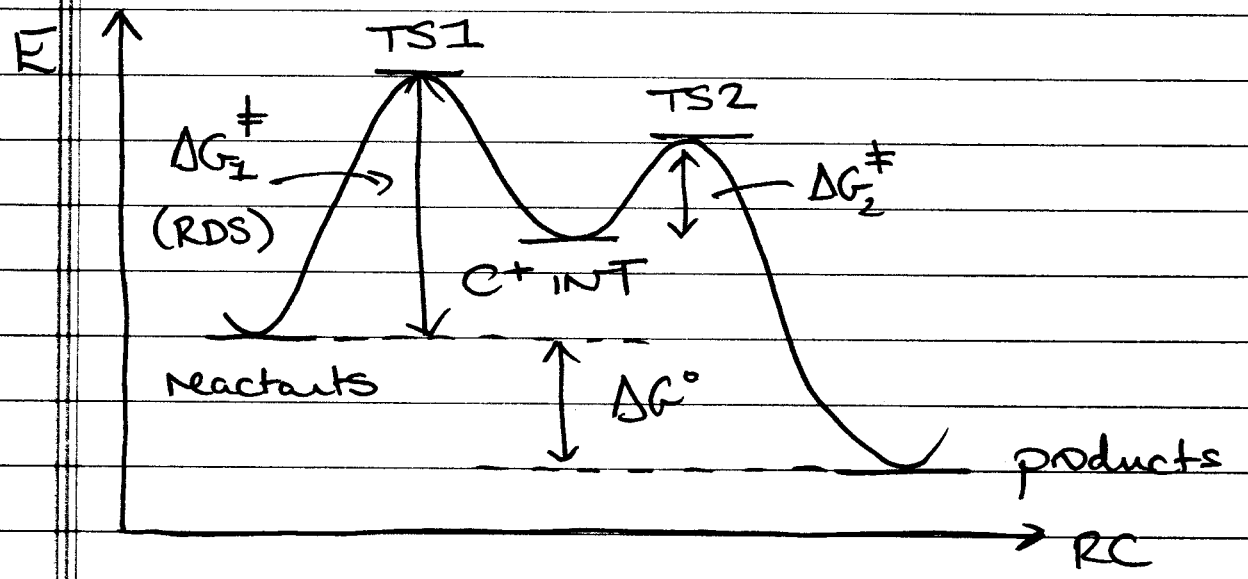
REARRANGEMENT ⇐

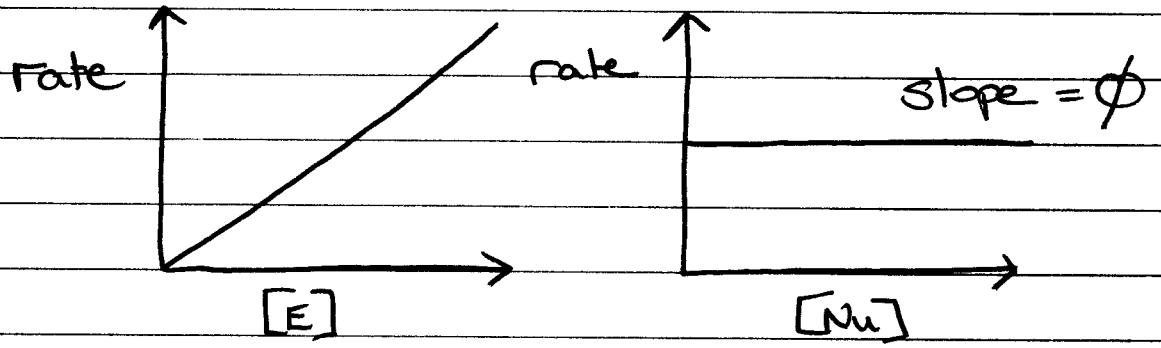
ANY STEREOCHEMICAL INFORMATION IN THE STARTING MATERIAL IS LOST

S_N1 - SUBSTITUTION, NUCLEOPHILIC, UNIMOLECULAR

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

first order rate constant

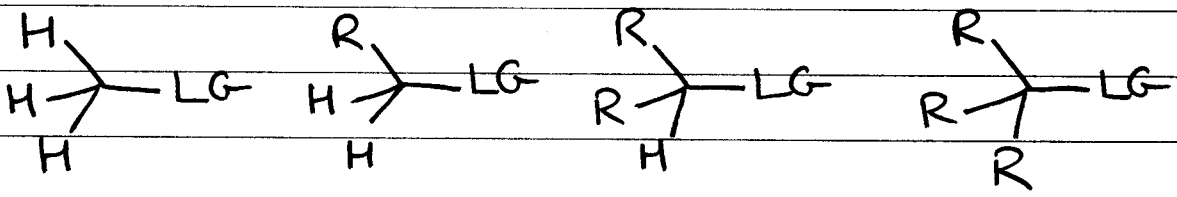




RDS does NOT involve the nucleophile, so adding more of it to the reaction does not alter the rate ⇒ Also, reactivity of the NUCLEOPHILE does not matter

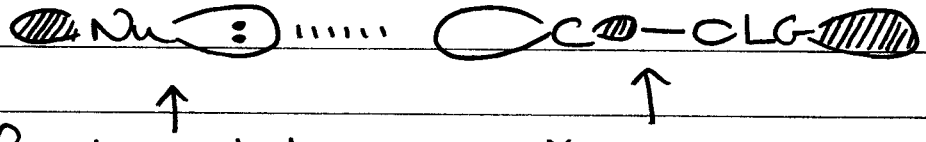
What decides S_N1 vs S_N2 ?

(3) THE ELECTROPHILE



methyl primary secondary tertiary

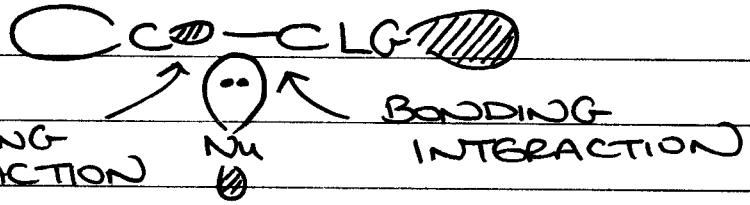
S_N2 — BACKSIDE ATTACK



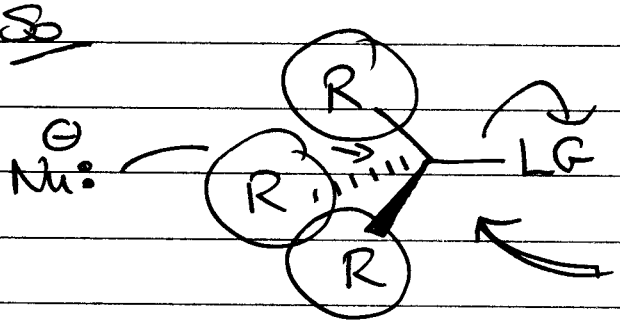
filled orbital in nucleophile

σ^* - empty antibonding orbital

FRONTSIDE ATTACK?



So



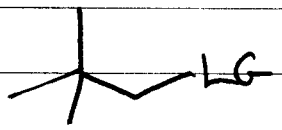
more R GROUPS, more STERIC CROWDING

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 ↓

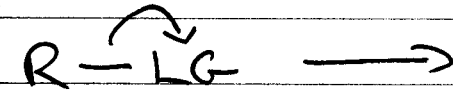
Some 1° groups also slow things down:



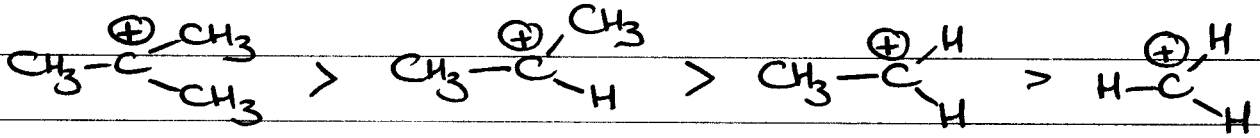
2×10^{-7}

neo-pentyl

CONSIDER S_N1 REACTIONS : OPPOSITE



C^+ STABILITY

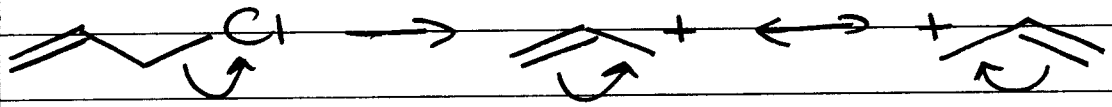


So, 1° and CH_3 electrophiles S_N2

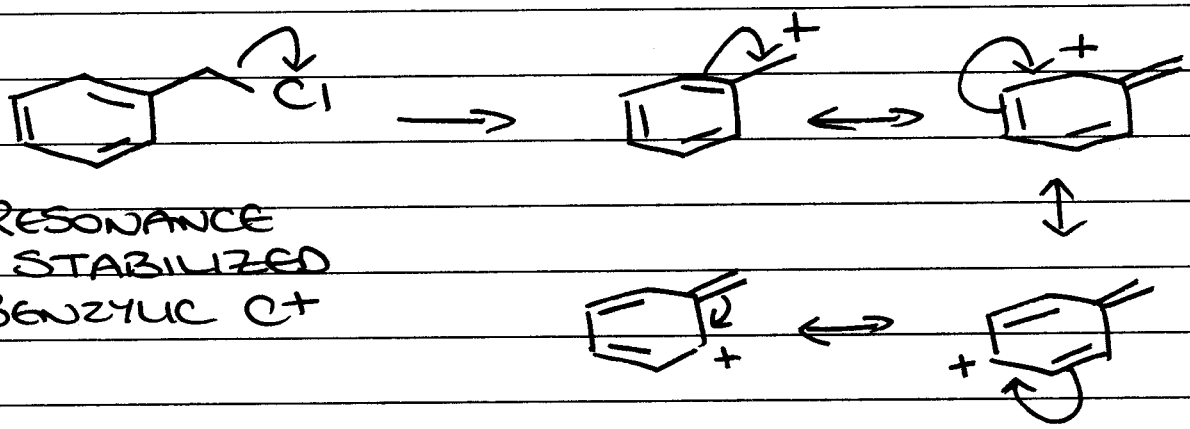
3° electrophiles S_N1 (WHAT ABOUT SECONDARY?)

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

- other types of C+



RESONANCE STABILIZED
1° ALLYLIC



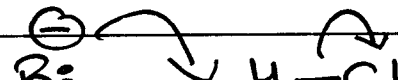
RESONANCE
STABILIZED
BENZYLIC C+

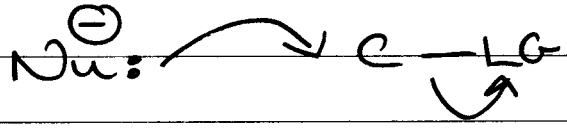
1° ALLYLIC / BENZYLIC electrophiles
SN1 vs SN2 (other factors, Nu, LG, solvent)
STERICS favors SN2 ELECTRONICS favors SN1

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

(4) NUCLEOPHILE

Consider BASICITY



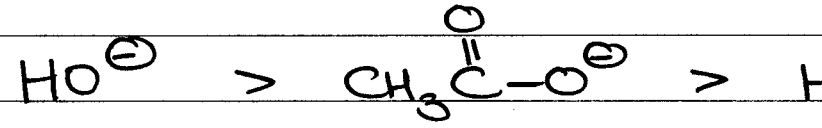
NUCLEOPHILICITY is similar 

- affinity for C atom
- KINETIC rather than THERMODYNAMIC effect

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

- General trends

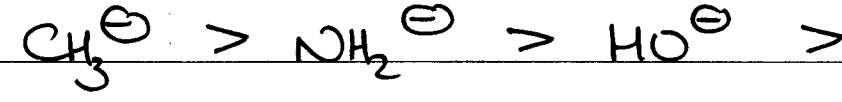
(i) Same NUCLEOPHILIC atom (parallels BASICITY)



16 5 -2 pKa of HX

consider CHARGE & RESONANCE

(ii) NUCLEOPHILES IN THE SAME ROW (parallels basicity)



consider ELECTRONEGATIVITY

(iii) NUCLEOPHILES IN THE SAME GROUP (COMPLICATED)

All comes down to size.

In general nucleophilicity increases going down a group...

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

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

- opposite to BASICITY - why?

(i) ENERGY LEVELS

- higher energy of lone pair electrons as you go down the periodic table → better overlap w/ σ^*

(ii) POLARISABILITY

Larger atoms, more diffuse electron clouds → greater polarisability → BONDS can begin to form at greater INTERATOMIC DISTANCES.

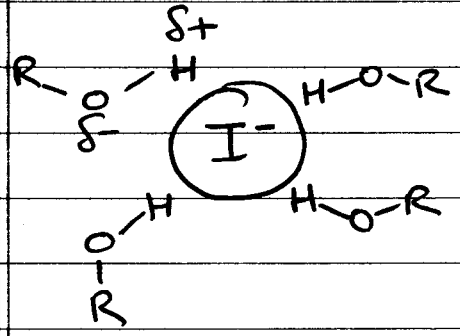
(iii) SOLVENT (large effect)

- POLAR PROTIC (H_2O, MeOH, EtOH, $H-\overset{O}{\overset{\|}{C}}-OH$)

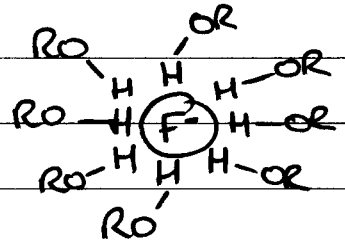
- POLAR APROTIC (DMSO, DMF, MeCN, Acetone)

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 – noncovalent interaction

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

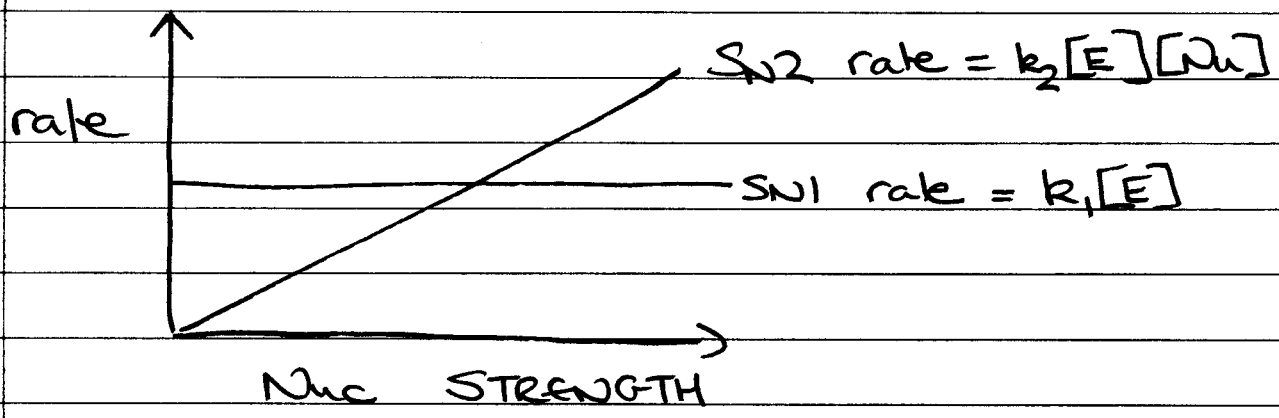
So, smaller Nu = higher charge density
⇒ more solvated LESS NUCLEOPHILIC

BUT IN POLAR APROTIC SOLVENTS
⇒ ANIONS WEAKLY SOLVATED, trend is reversed and correlates w/ BASICITY

$$Nu^{\ominus}: \rightarrow CH_3-I \longrightarrow Nu-CH_3 + I^{\ominus}$$

Nu	pka	MeOH (time to complete reaction)	DMF → equiv	Polarizibes
I^-	−10	17 min	8.7s	OVERALL MESSAGE
Br^-	−8	12h	8.7s	
Cl^-	−6	13d	1.4s	POLAR PROTIC SOLVENTS ARE GOOD
F^-	3	>2yrs	<1.2s	

S_N1 vs S_N2



No effect on S_N1, but stronger Nu favors S_N2 reactions.

LEC (21) CHEM 30A May 23rd

- NUCLEOPHILIC SUBSTITUTION

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

MIDTERM (Weds) LAST NAME A–O (CSSϕ)
P–Z (Royce 19ϕ)

---

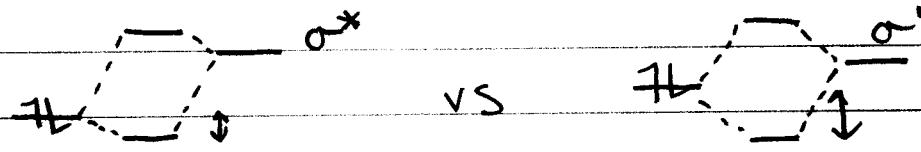
(1) NUCLEOPHILES
(same group)

GENERAL TREND: increases down a group

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

opposite to BASICITY – why?

(i) ENERGY LEVELS
- higher energy of lone pair electrons as you go down the periodic table → better overlap with σ^*



(ii) POLARISABILITY

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

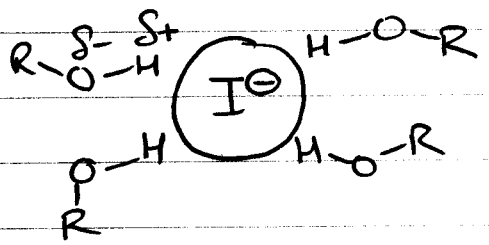
(iii) SOLVENT (large effect - more later)

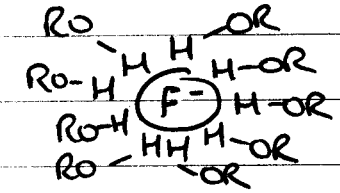
- POLAR PROTIC (H_2O, MeOH, EtOH, $H-\overset{\ominus}{\underset{\|}{C}}=O-H$)

- 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)

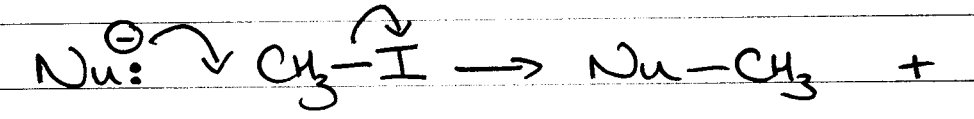
HYDROGEN BONDING - noncovalent interaction

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

So, SMALLER Nu = higher charge DENSITY
=> more SOLVATED, LESS nucleophilic

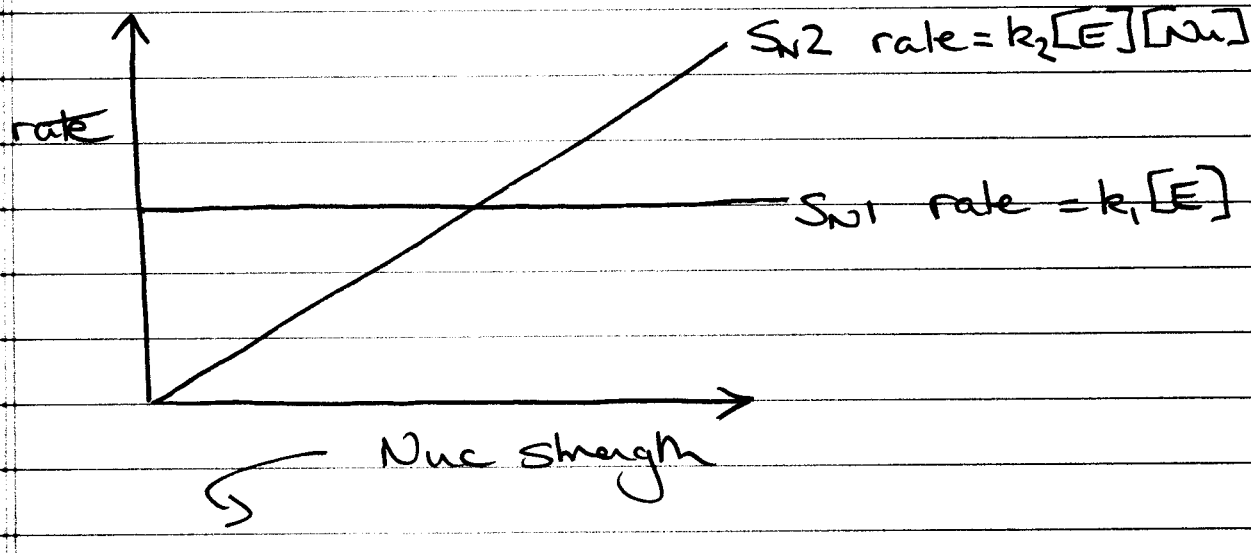
BUT

IN POLAR APROTIC SOLVENTS, ANIONS are weakly solvated, trend is reversed (for halogens) and correlates w/ BASICITY

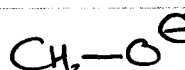
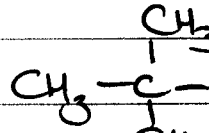


Nu	pka	MeOH (time to complete rxn)	DMF (time to complete rxn)	equiv polarities
I^-	−10	17 min	8.7 s	Overall message
Br^-	−8	12 h	8.7 s	POLAR APROTIC SOLVENTS GOOD
Cl^-	−6	13 d	1.4 s	
F^-	3	> 2 yrs	< 1.2 s	

So SN1 vs SN2



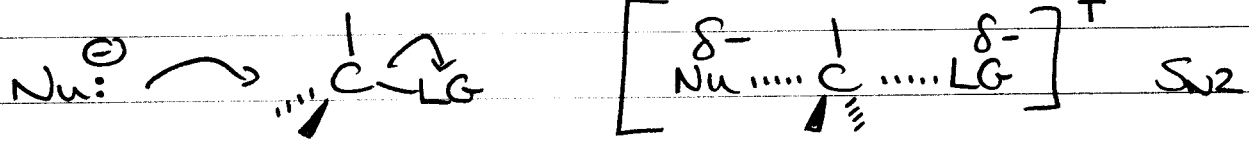
NO EFFECT on SN1, but Stronger Nuc favors SN2 reactions

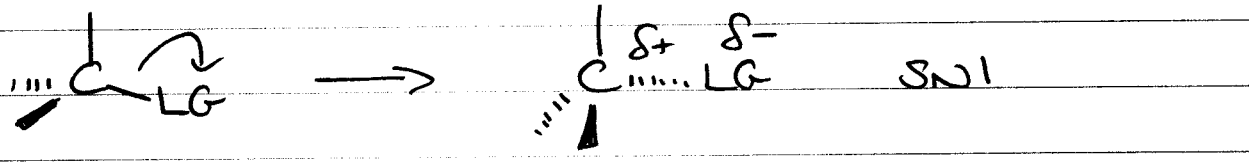
(iv) SIZE  vs 

methoxide pka 15.5 t-butoxide pka ~ 18

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

② LEAVING GROUP





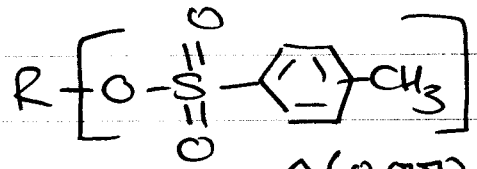
LG develops -ve charge in TS, so, better charge stabilization, lower energy TS, faster rxn.

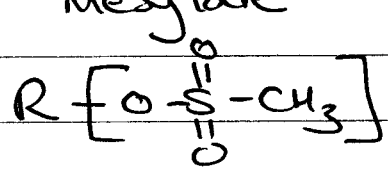
<u>Thus</u> MORE ACIDIC H–LG, more stable $LG^{\ominus}$

GOOD/BAD LEAVING GROUPS
– relative reactivity

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

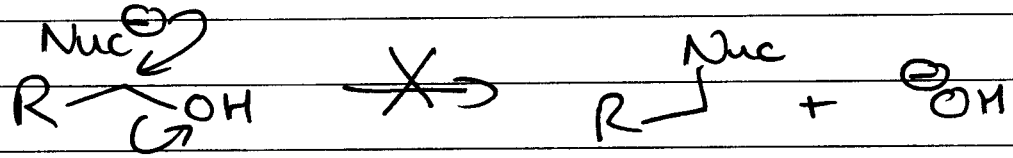
other good LG

tosylate  ~60,000

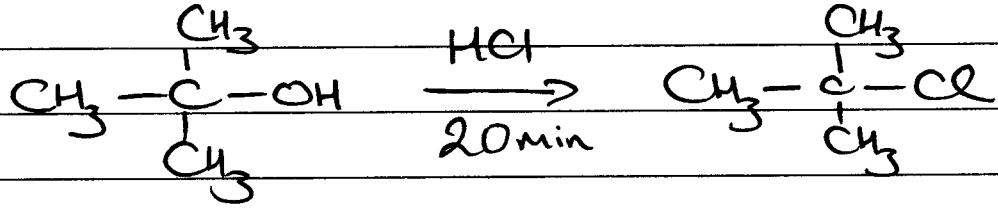
mesylate 

So R-F, R-OH, R-OR', R-NH$_2$

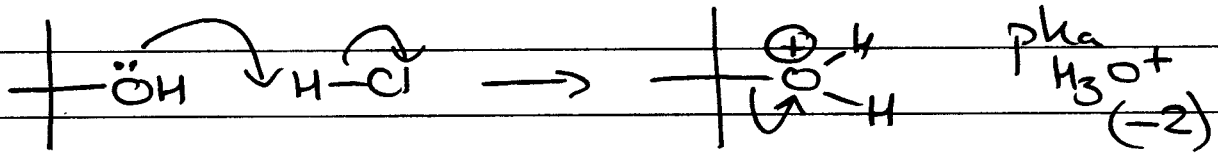
do NOT undergo SN2 reactions



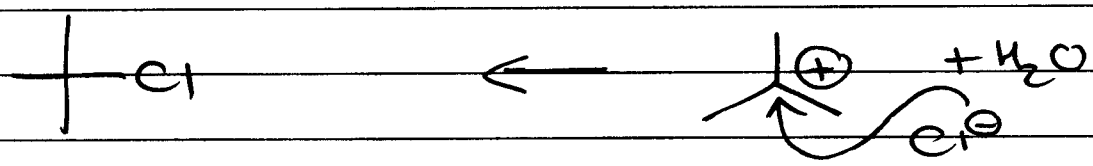
BUT

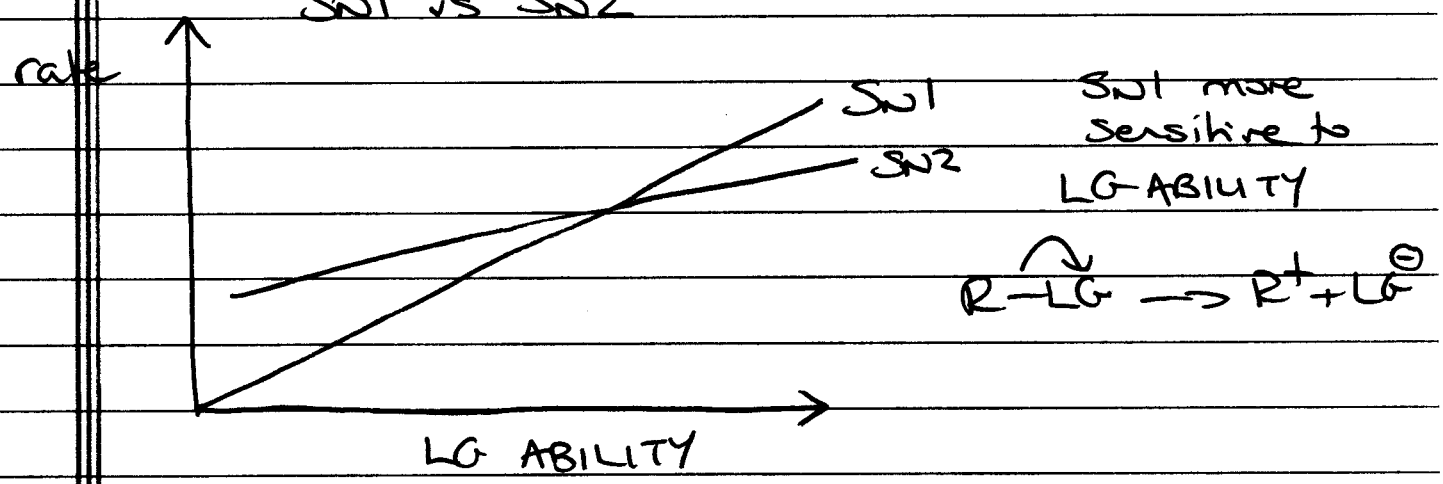


-OH converted into good LG



SN1 MECHANISM





In S_N2 reaction, as long as $LG^{\ominus}$ is more stable than $Nuc^{\ominus}$, reaction can proceed.

But cannot determine S_N1 vs S_N2 on LG ability alone

(3) SOLVENT

S_N2 POLAR APROTIC solvents
(solvate cations well, but not anions)

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

S_N1 $R-LG \longrightarrow R^{\oplus} + LG^{\ominus}$
creation & separation of charge

⇒ more polar the solvent, the better

$\rangle\!-Cl + R-OH \xrightarrow{\text{solvolysis}} \rangle\!-OH + HCl$

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

8/

S_N2 reactions

DISFAVORED IN PROTIC SOLVENTS

(ground state energy lowered by SOLVATION)

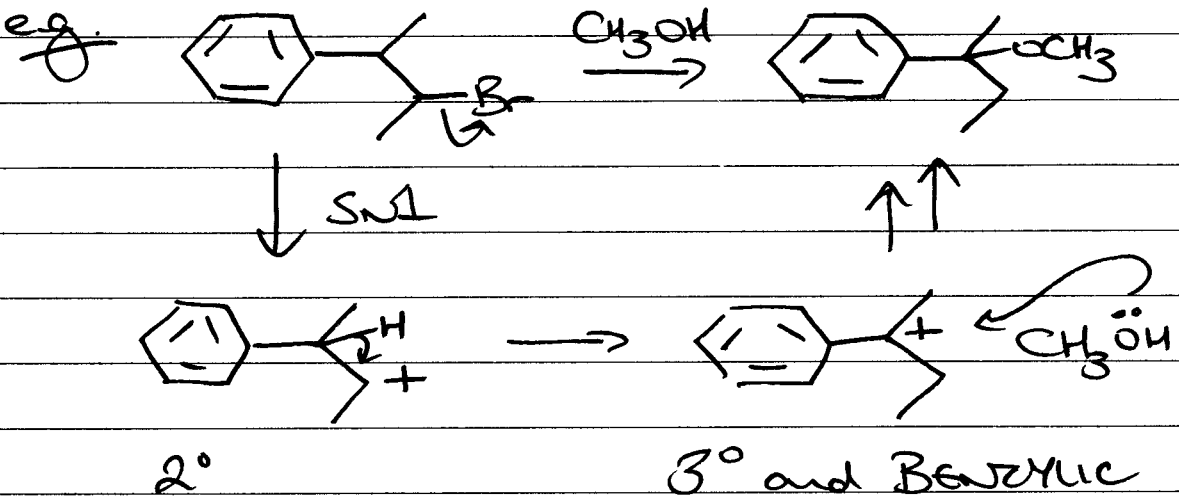
S_N1 reactions

FAVORED IN PROTIC SOLVENTS

(transition state energy lowered by SOLVATION)

Note about S_N1

- goes thru C^+, so look for rearrangement



+ SUMMARY of S_N RXNS

ELECTROPHILE	S_N2	S_N1
Me / 1°	✓	X
2°	FAVORED GOOD Nuc POLAR APROTIC Solvents	FAVORED POOR Nuc PROTIC SOLVENTS V. GOOD LG, BENZYLIC/ALLYLIC
3°	X	✓

– <u>but</u> it gets COMPLICATED

⇒ COMPETING ELIMINATION RXNS...

LEC (22) CHEM 30A Jun 1st

(1) SOLVENT
(2) REARRANGEMENT
(3) NEIGHBORING GROUP PARTICIPATION
(4) PHASE TRANSFER CATALYSIS
(5) INTRO TO β ELIMINATION
(6) MECHANISMS
(7) STEREOCHEMISTRY
(8) SUMMARY

3RD READ 8.6-8.10, Q 8.30-8.41
4th READ 9.5-9.11, Q 9.31-9.42

---

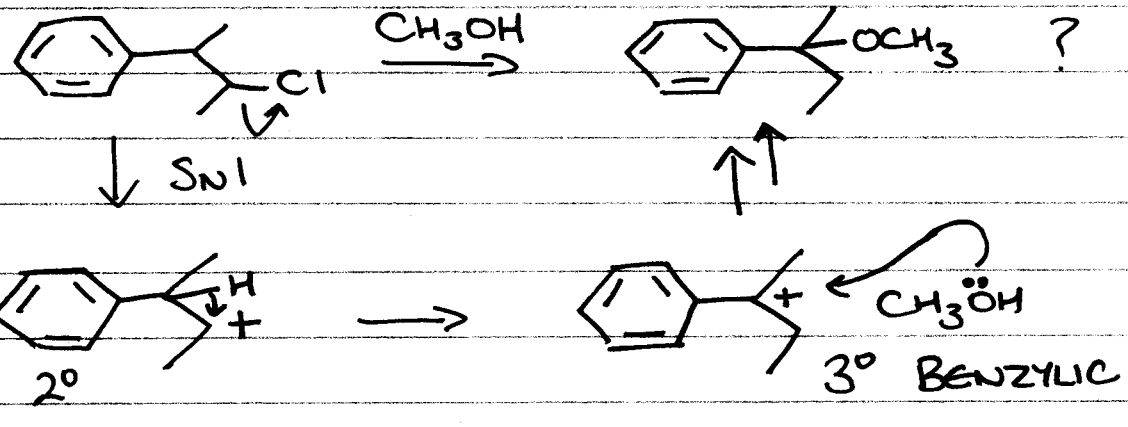
(1) SOLVENT

S_N2 DISFAVORED in PROTIC SOLVENTS
(ground state energy $Nuc^{\ominus}$ lowered by solvation)

S_N1 FAVORED IN PROTIC SOLVENTS
(transition state energy lowered by solvation)

(2) REARRANGEMENT (S_N1 / C^+)

e.g.



Summary

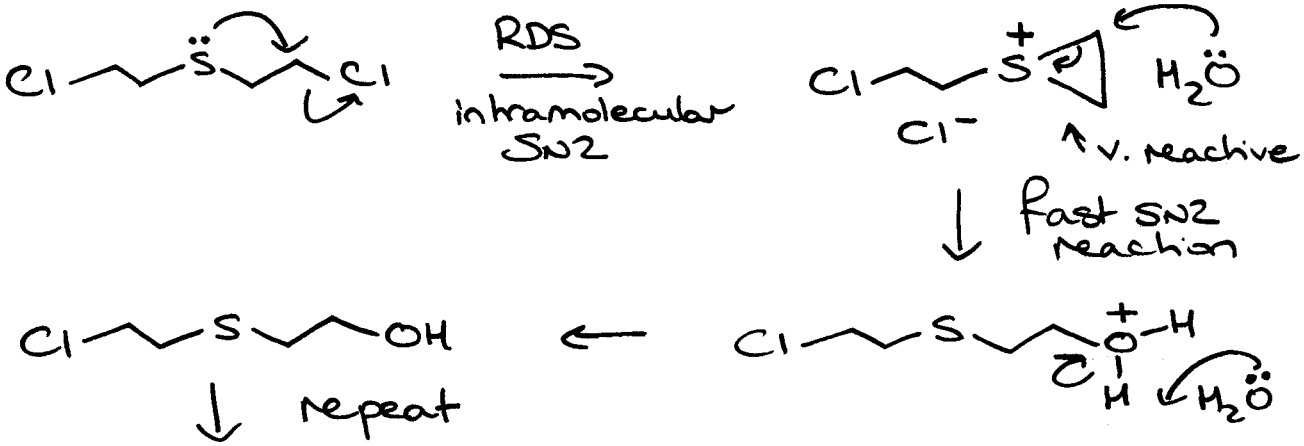
ELECTROPHILE	SN2	SN1
Me / 1°	✓	×
2°	GOOD NUC POLAR APROTIC	POOR NUC POLAR PROTIC (GOOD LG)
3°	×	✓

– gets COMPLICATED => ELIMINATION

(3) NEIGHBORING GROUP PARTICIPATION

(mustard gas)

V. RAPID, even though H_2O is very poor Nuc



overall rate = $k[\text{Cl}\sim\text{S}\sim\text{Cl}]$

INDEPENDENT of [Nuc]

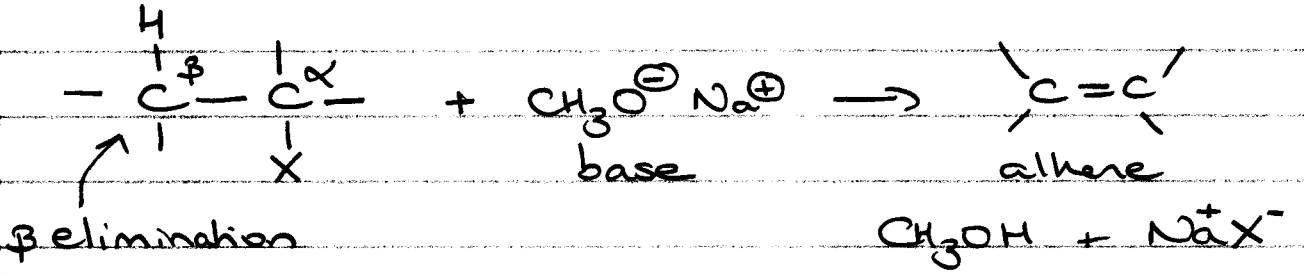
Two consecutive SN2 reactions with SN1 KINETICS

(4) PHASE TRANSFER CATALYSIS

(read section in the book)

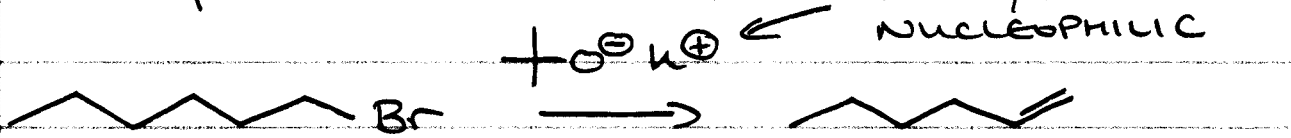
(5) INTRO TO β-ELIMINATION

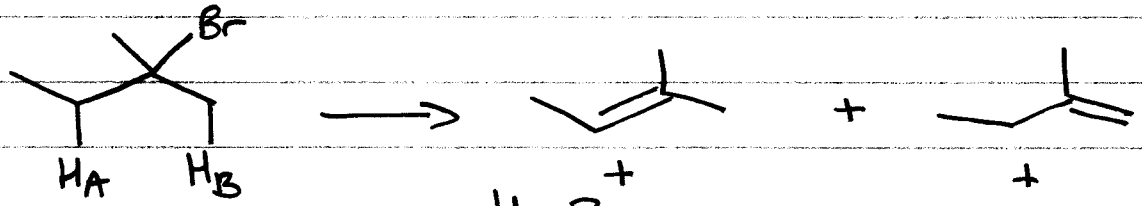
- dehydrohalogenation (one example)



- ELIMINATION competes w/ SUBSTITUTION

- examples





β PROTONS

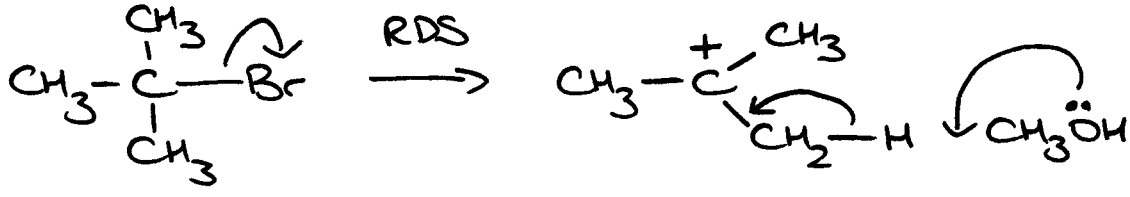
ZAITSEV'S RULE → major product is the most SUBSTITUTED ALKENE (more stable)

.... and there are EXCEPTIONS to this rule.

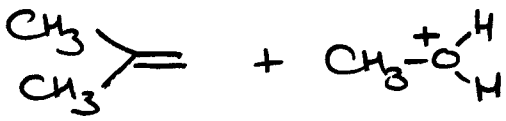
(6) MECHANISMS

(like SN reactions, two limiting ones)

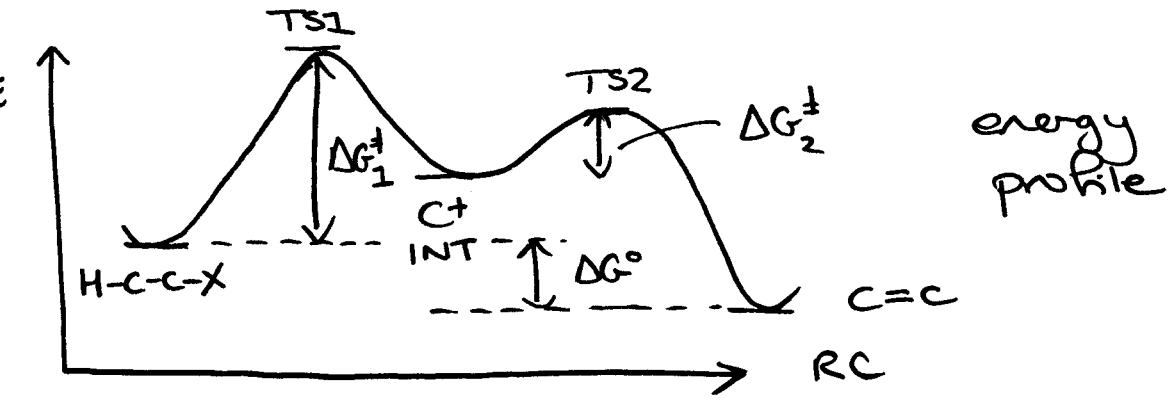
E1 (elimination unimolecular)



COMPETES with SN1 REACTION



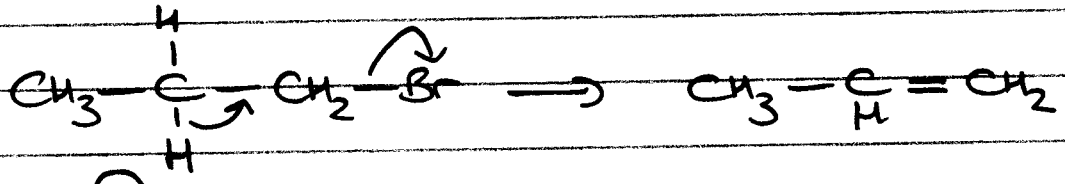
rate = $k_1[(CH_3)_3C-Br]$

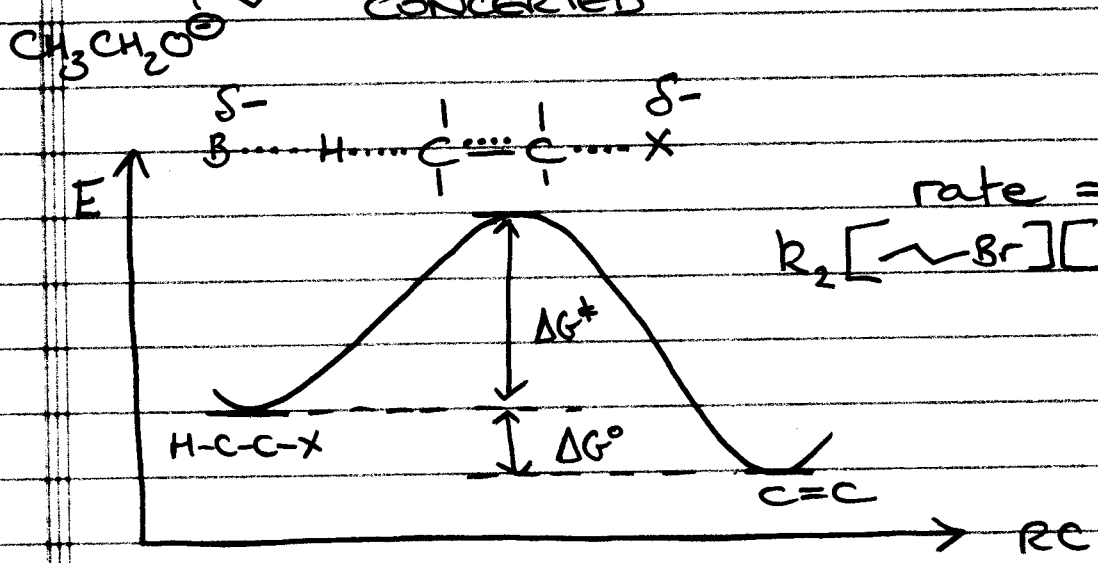


energy profile

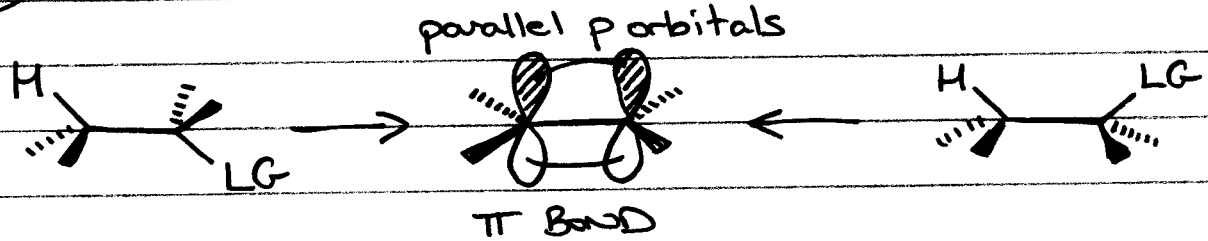
E2 (ELIMINATION BIMOLECULAR)

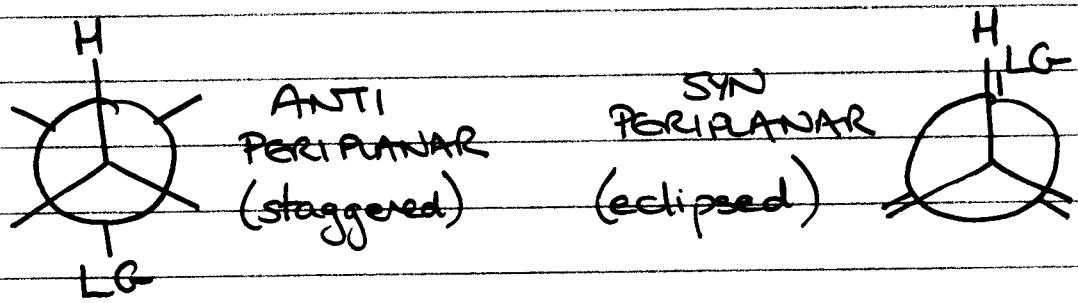
(competes with SN2)



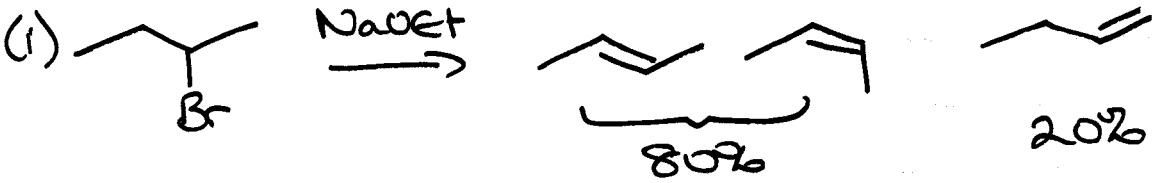


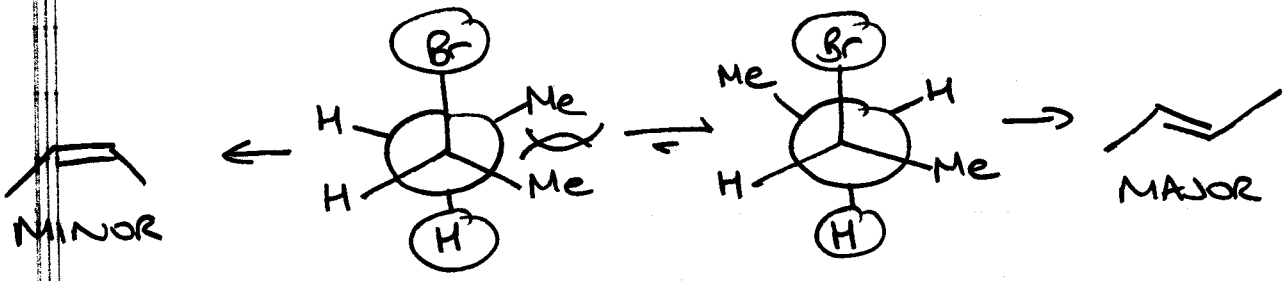
(7) STEREOCHEMISTRY





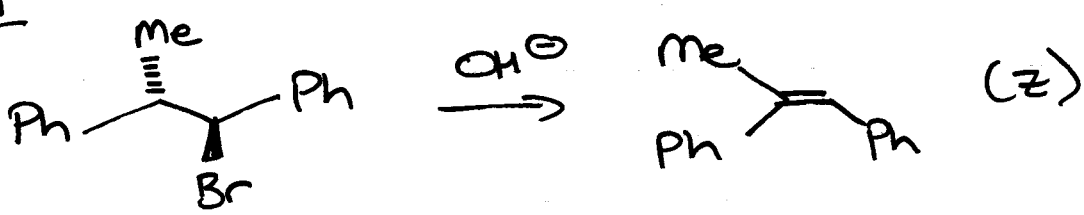
Generally, antiperiplanar geometry is preffered in an E2 reaction (excephons)

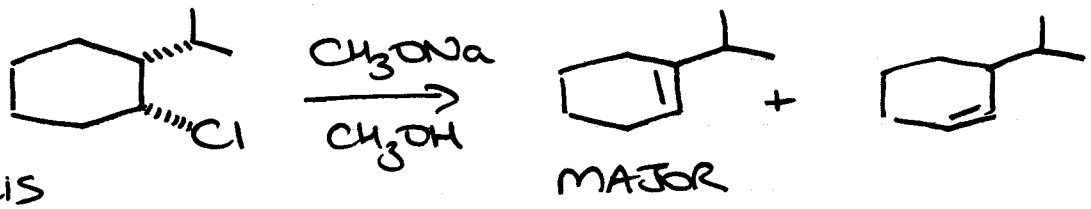
(i) 



(ii) 

BUT

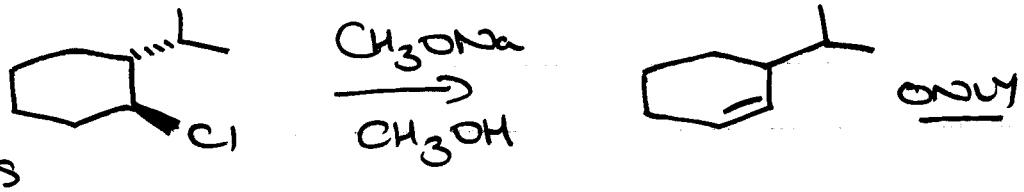


(iii) 

CIS

MAJOR

BUT

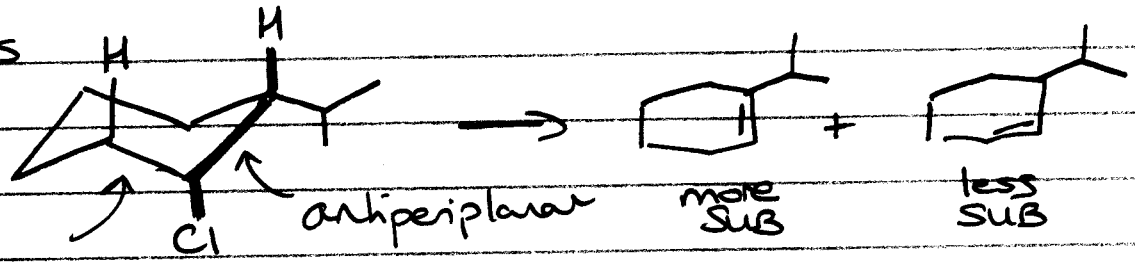


trans

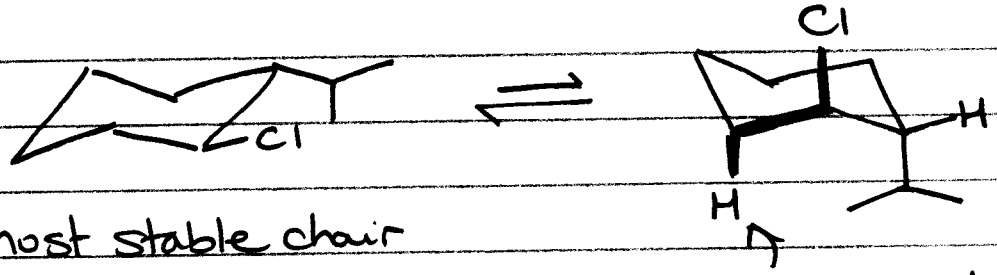
ONLY

also, cis reacts faster ⇒ WHY?

- cis



- trans



most stable chair (NO Hs ANTI-PERIPLANAR to Cl)

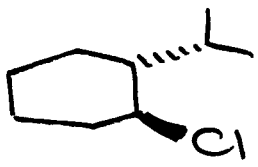
only one H is antiperiplanar

→ SLOWER because reacts through less stable chair

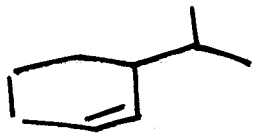
(8) SUMMARY E1/E2

alkyl halide	E1	E2
METHYL	– ELIMINATION IMPOSSIBLE –	
1° (RCH_2X)	DOES NOT HAPPEN	Favored Elim MODE
2° (R_2CHX)	H_2O/ROH weak bases (allylic/benzylic sub)	Strong $RO^{\ominus}$ bases $HO^{\ominus}$
3° (R_3C-X)	weak bases	strong bases

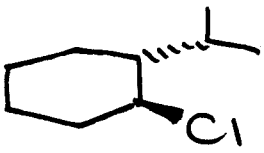
Reaction Conditions



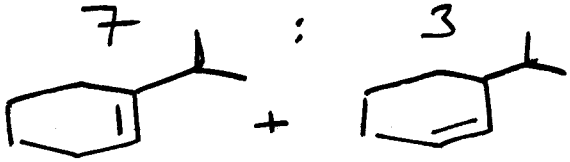
1.0 M NaOEt
EtOH



E2 conditions

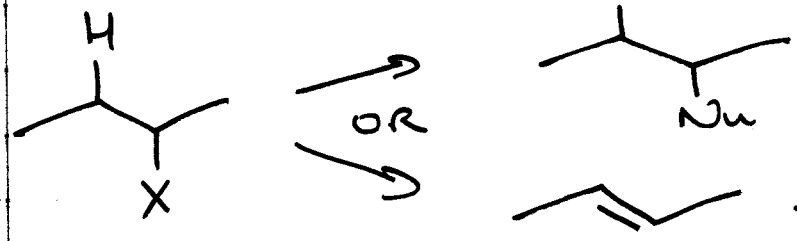


0.01 M NaOEt
80% EtOH
20% H_2O



E1 conditions

UP NEXT — Sub vs E



SUBSTITUTION

ELIMINATION

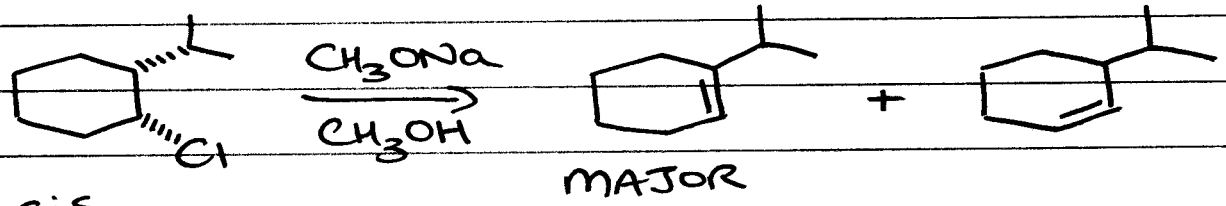
LEC (23) CHEM 30A Jun 3rd

1. STEREOCHEMISTRY
2. REGIOSELECTIVITY
3. SYN ELIMINATION
4. E1 vs E2
5. S_N vs E
6. SYNTHESIS

3rd Ed
Review Ch 8
Q 8.42 – 8.50
(except 8.46g,h)

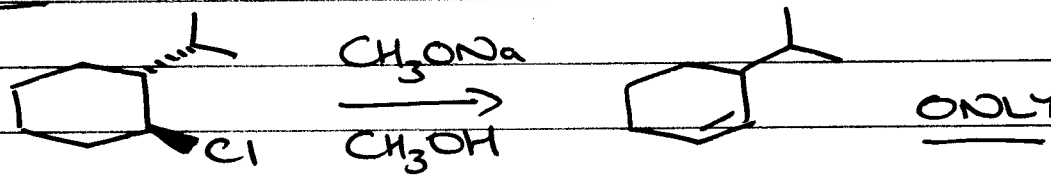
4th Ed
Review Ch 9
Q 9.43 – 9.53
(except 9.47g,h)

(1) STEREOCHEMISTRY cont



cis

BUT

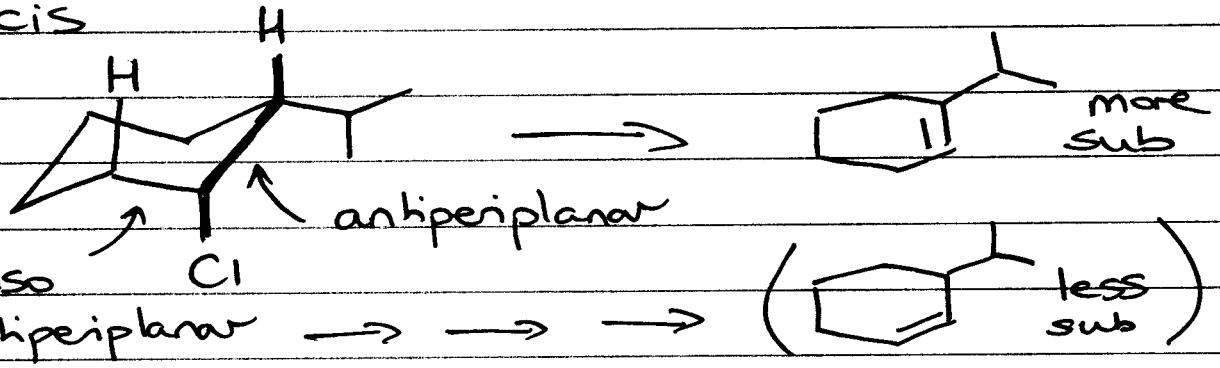


ONLY

trans

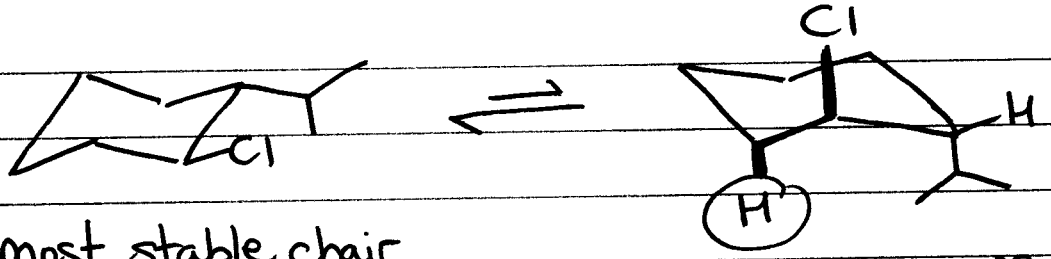
also: cis reaction FASTER than trans – WHY?

– cis



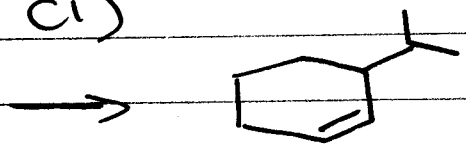
also antiperiplanar → → → ( )

- trans



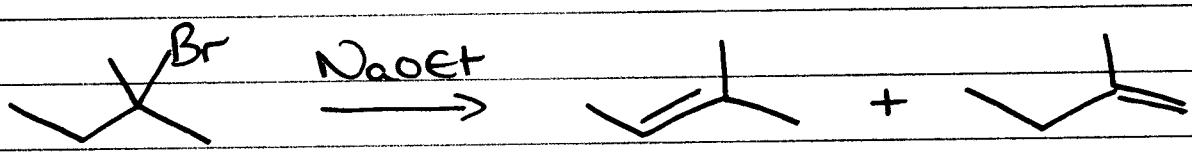
most stable chair
(no Hs ANTIPERIPLANAR to Cl)

ONLY ONE H IS ANTIPERIPLANAR



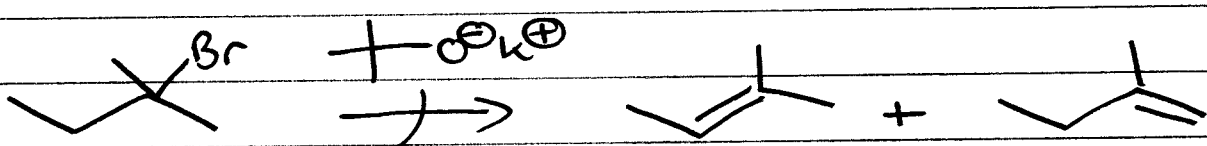
slower because reacts through less stable chair

(2) REGIOSELECTIVITY



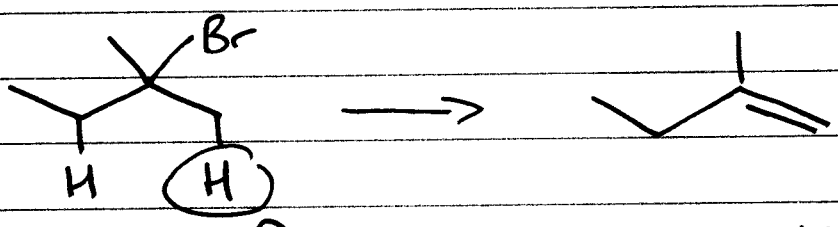
MAJOR (70%) MINOR (30%)

ZAITSEV SELECTIVITY → more sub, more stable alkene



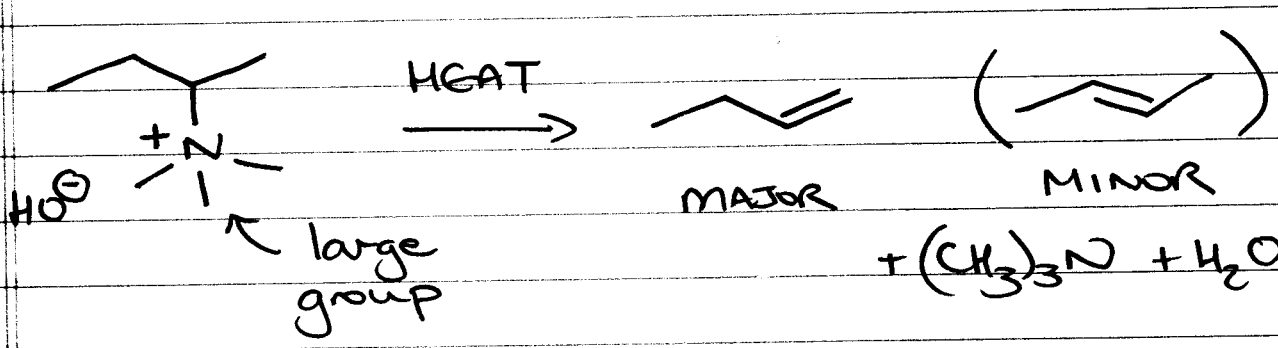
bulky base MINOR (30%) MAJOR (70%)

HOFMANN SELECTIVITY → least sub alkene preferred

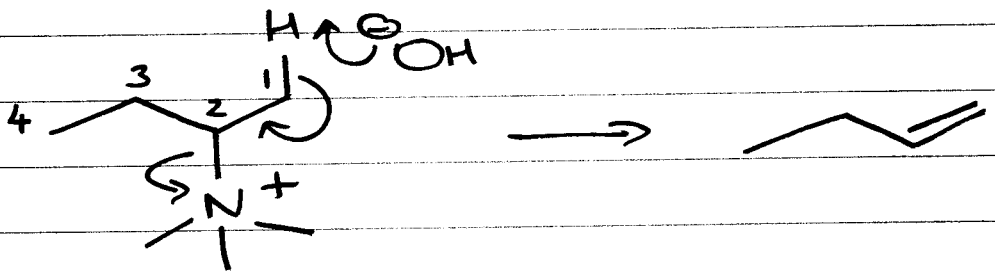


↑ more accesible β-H

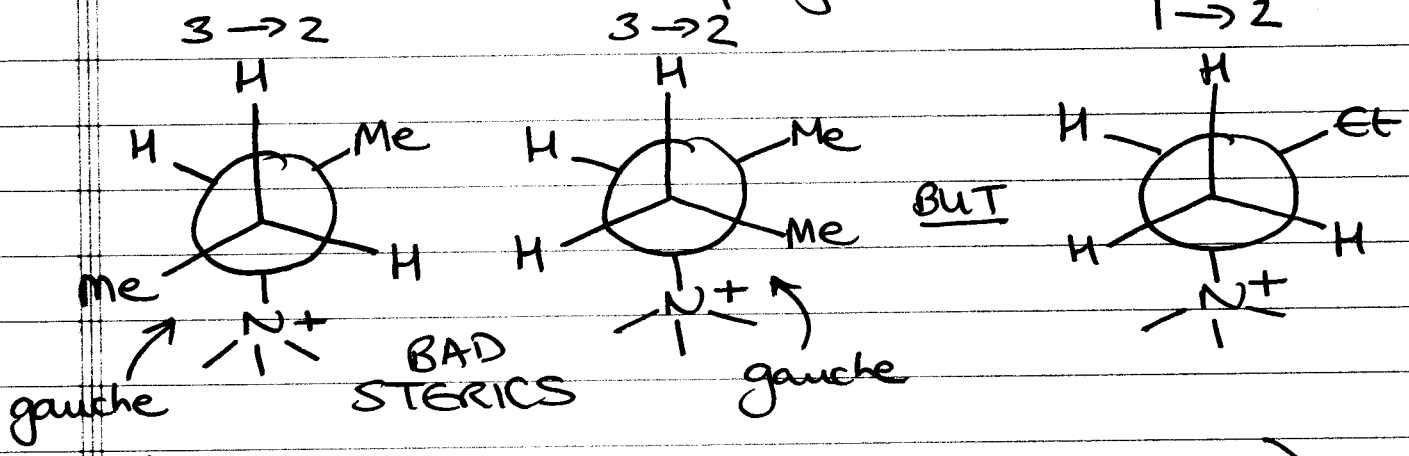
Common reaction w/
QUATERNARY AMMONIUM SALTS



PROCEEDS w/ ANTISTEREOSPECIFICITY

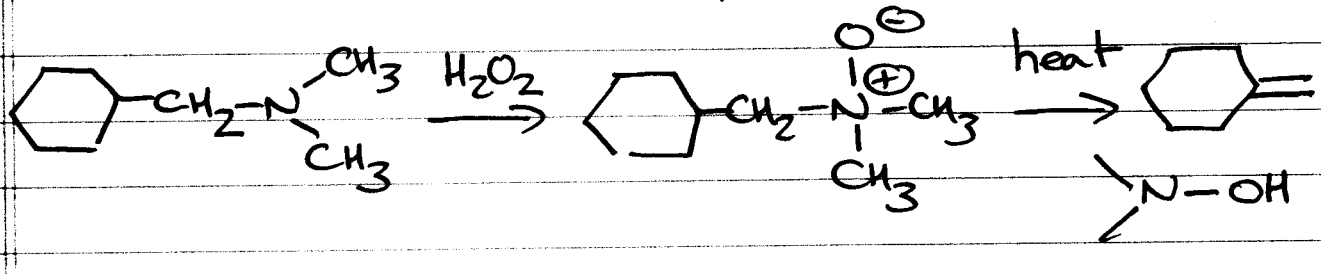


consider NEWMAN projections

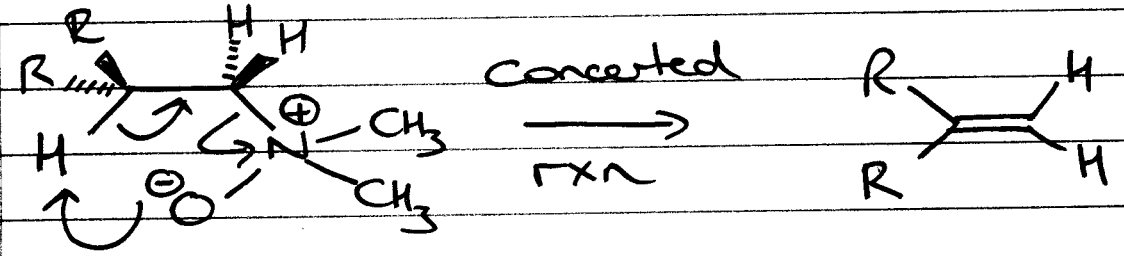


(also electronic effects.... don't worry)

(3) SYN ELIMINATION (cope elimination)

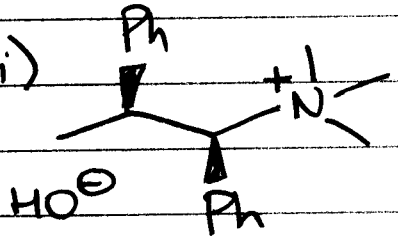


mechanism

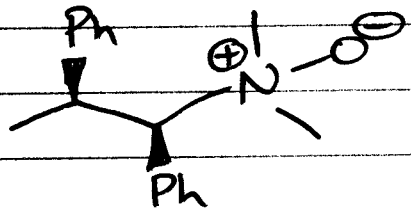


SYN

- figure out the products of these reactions

(i) 

heat → ?

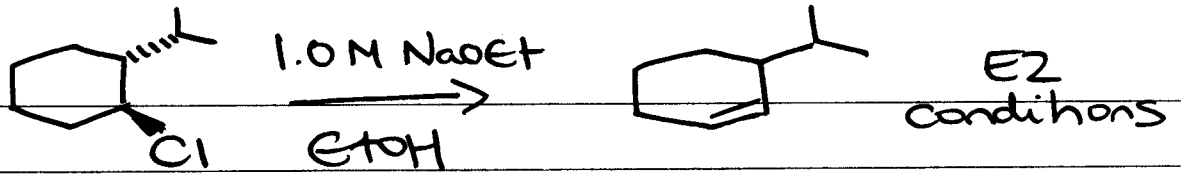
(ii) 

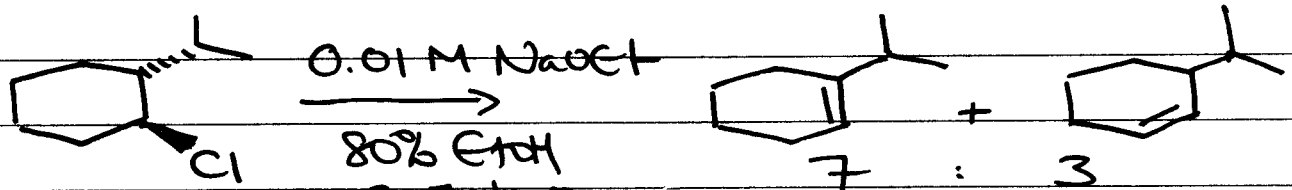
heat → ?

(4) E1 vs E2

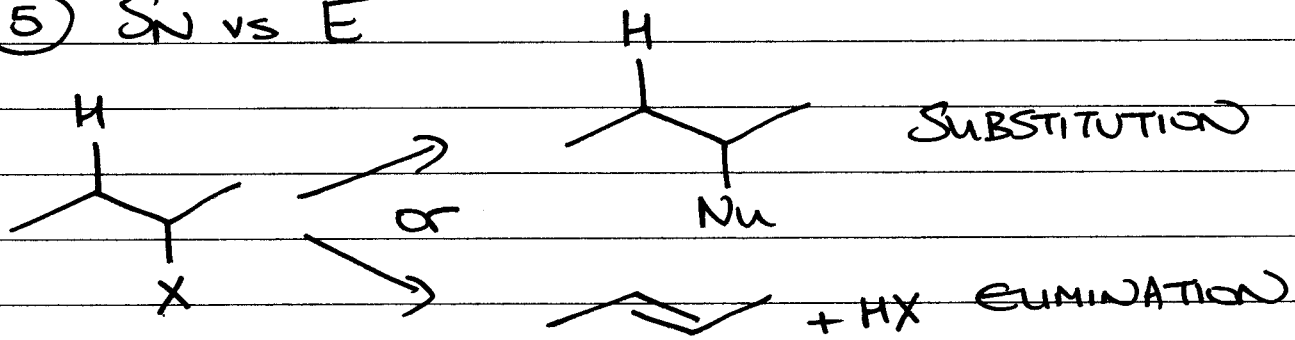
ALKYL HALIDE	E1	E2
methyl	— ELIMINATION IMPOSSIBLE —	
1° (RCH_2X)	DOES NOT HAPPEN (1°C+)	FAVORED ELIMINATION MODE
2° (R_2CHX)	H_2O/ROH (weak bases) ALLYLIC/BENZYLIC	STRONG BASES ($RO^\ominus$ / $HO^\ominus$)
3° (R_3CX)	WEAK BASES	STRONG BASES

- can also depend upon reaction conditions



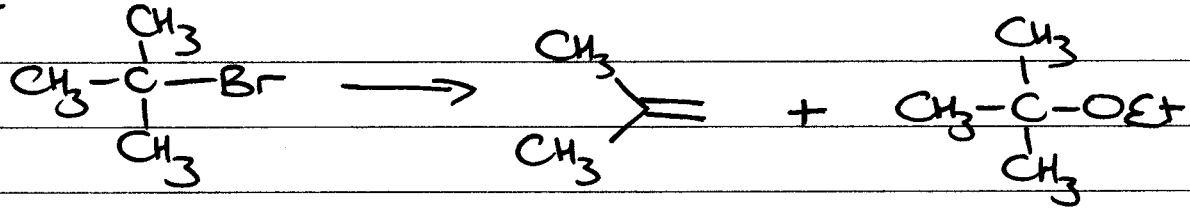


(5) S_N vs E



(i) S_N1 vs E1

e.g.



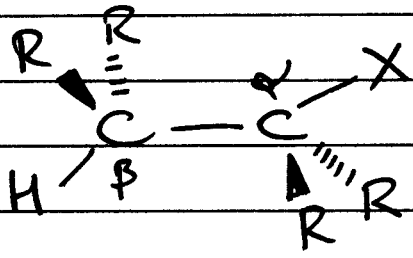
affinity for proton vs carbon ⇒ stronger base

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

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

(ii) S_N2 vs E2

- structure of substrate

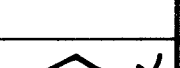
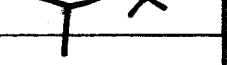
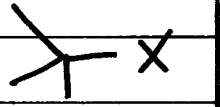


BRANCHING AT α / β
slows S_N2 (STERICS)
speeds up E2 (more stable alkene)

- 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^-)	(Unhindered) Strongly BASIC Nuc (RO^-/HO^-)	(Hindered) Strongly BASIC Nuc ($^+O^\ominus$)
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

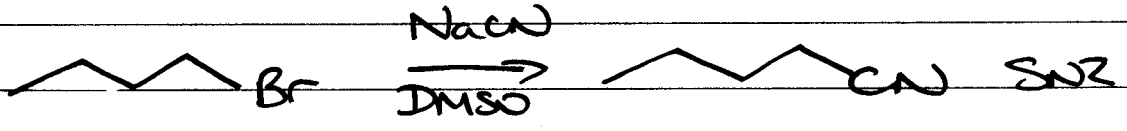
Also higher temp favors ELIMINATION

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

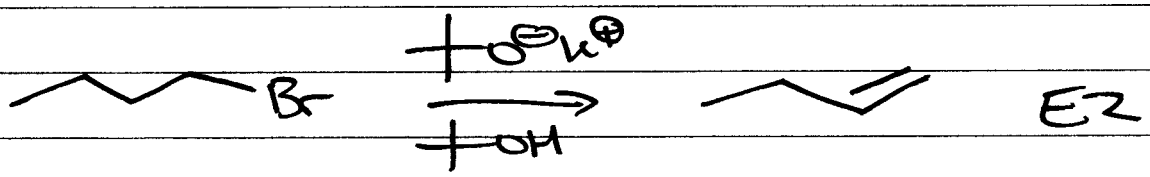
S_N2 2 molecules → 2 molecules

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

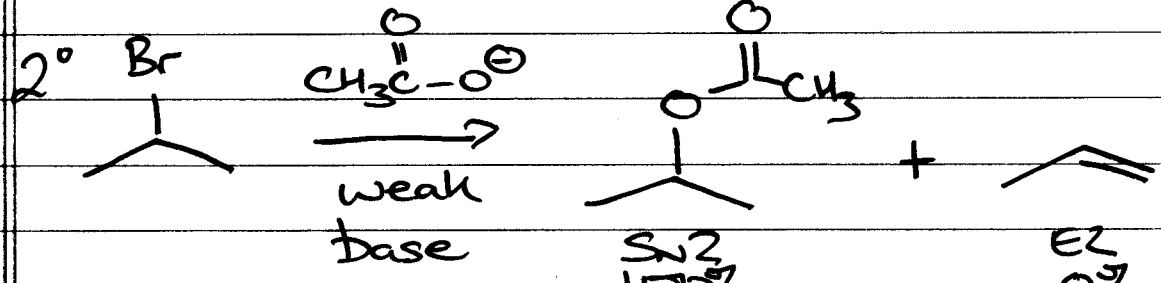
- examples

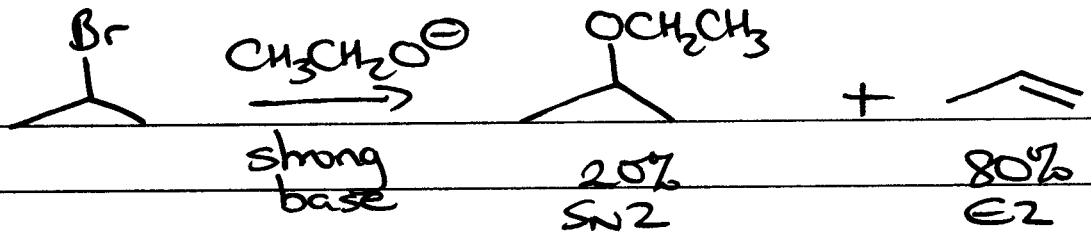
1° 

(CN^-, RS^-, N_3^-, NH_3, Br^-, I^-) GOOD NUC

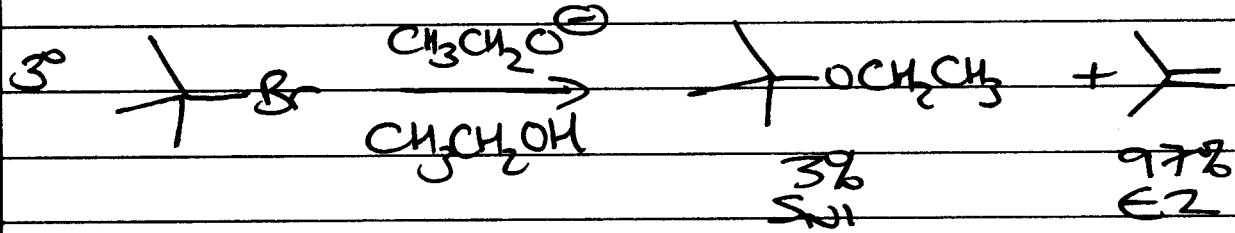


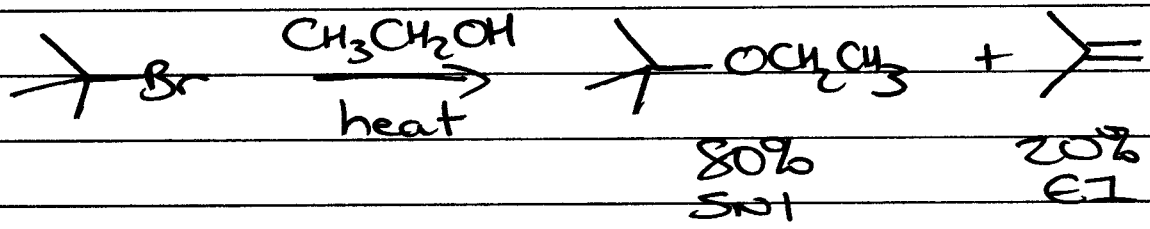
strong hindered bases

2° 



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





LEC 24 CHEM 30A Jun 6th

1. S_N vs E — FINAL (ROOM)
2. SYNTHESIS — REVIEW SESSION
3. HALOALKANES — QUIZ/EVALS
4. PREPARATION — READ Ch7 Q 7.3-7.27
   READ Ch8 Q 8.2-8.4, 8.9-8.28

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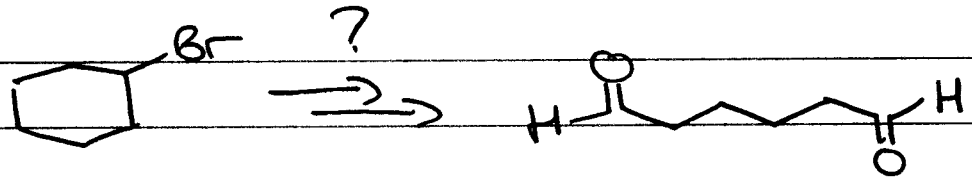
1. S_N vs E pages 6-8 LEC 23

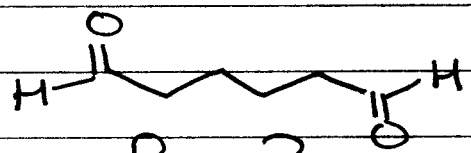
2. SYNTHESIS
- making molecules

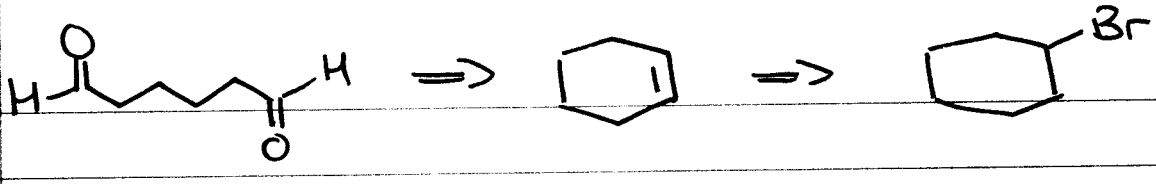


A → B → C → D → → → Z ?

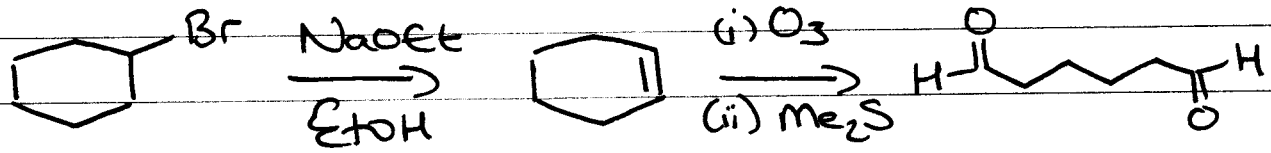
RETROSYNTHESIS
(work backwards)

Z → Y → X → W....

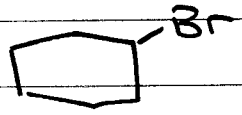
So, what can we make  from?



so, forward synthesis:

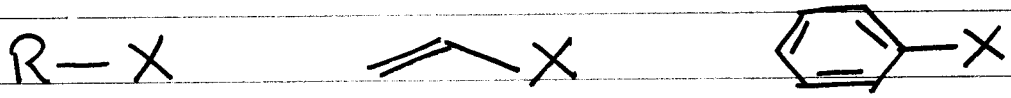


(E2 elimination) (OZONOLYSIS)

.... and, how do we make 

– we use chloro/bromoalkanes a lot.

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



R–X alkyl halide | vinyl halide | aryl halide

(read through naming rules – not so hard)

POLARITY $\delta+$ C ⟷ X $\delta-$ ← 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
e.g. 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)

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

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

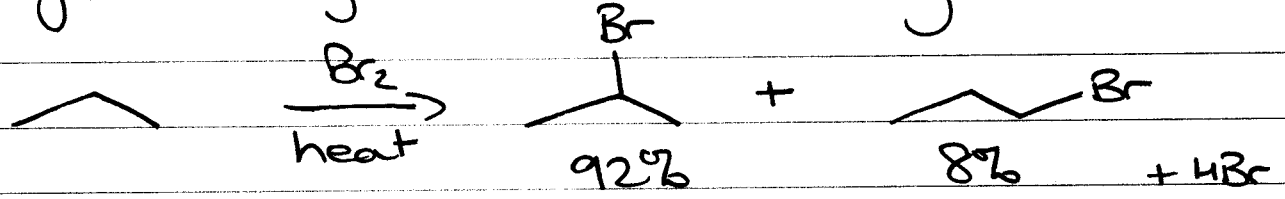
$CH_4 + Cl_2 \xrightarrow{HEAT} CH_3Cl + HCl$

$\Delta H = -24$ kcal/mol

Reaction continues:

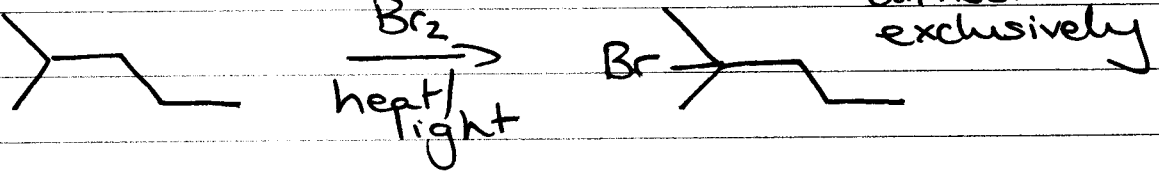
$CH_3Cl \xrightarrow[heat]{Cl_2} CH_2Cl_2 \xrightarrow[heat]{Cl_2} CHCl_3 \xrightarrow[heat]{Cl_2} CCl_4$

Regioselectivity: statistics say 25:75

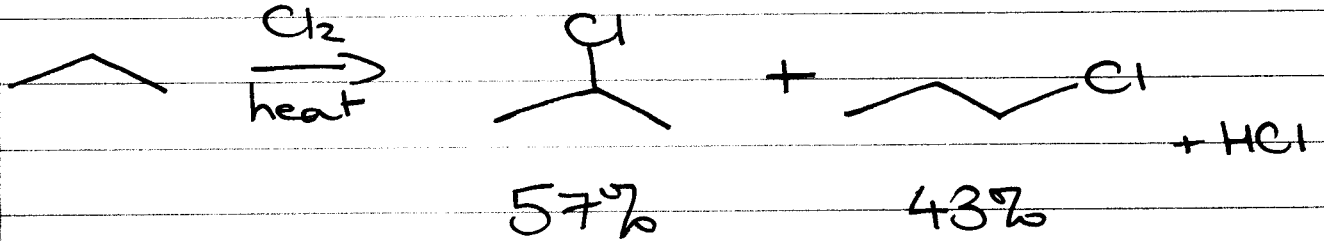


sub of 2° favored over 1°
(also 3° favored over 2°)

So,

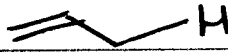
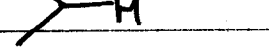
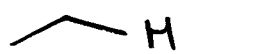


REGIOSELECTIVITY less pronounced for CHLORINATION



3°/2°/1° 1600 : 80 : 1 Br
5 : 4 : 1 Cl

ENERGETICS of RADICAL REACTIONS

C–H BOND		BDE (kcal/mol)
	(ALLYL)	86
	(BENZYL)	88
	(t BUTYL)	93
	(i PROPYL)	96
	(ETHYL)	100
CH_3–H	(METHYL)	105
	(VINYL)	106

RADICAL STABILITY INCREASES

So, Br

$$CH_4 + Cl_2 \longrightarrow CH_3Cl + H\text{–}Cl$$

BDE	105	59	−85	−103
	164		−188	

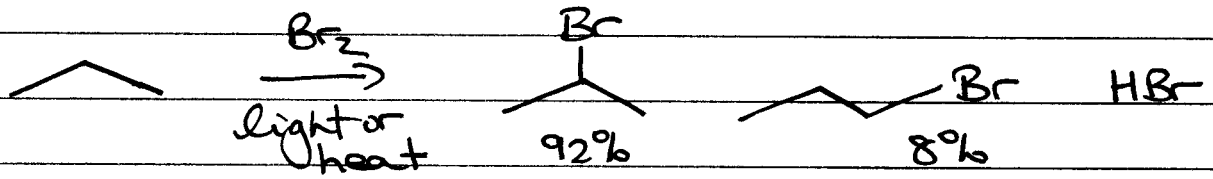
($\Delta H = -24$ kcal/mol) ⇒ EXOTHERMIC REACTION

LEC (25) CHEM 30A Jun 10th

1. REGIOSELECTIVITY
2. BOND ENERGETICS
3. MECHANISMS
4. HAMMOND POSTULATE
5. RADICAL STRUCTURE / STABILITY
6. ALLYLIC HALOGENATION

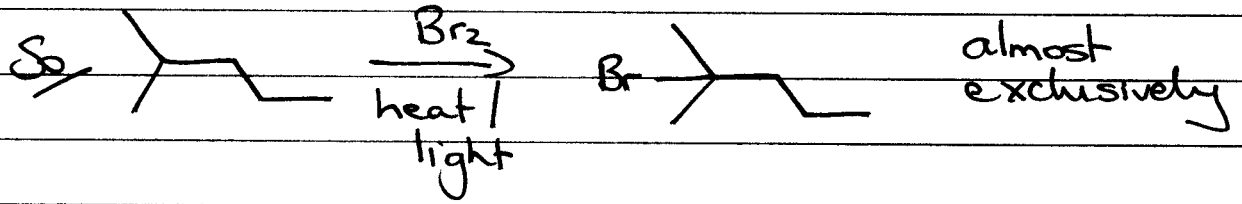
OH Mon
Reviews Tues/Wed
FINAL THURS
ROOM

(1) REGIOSELECTIVITY

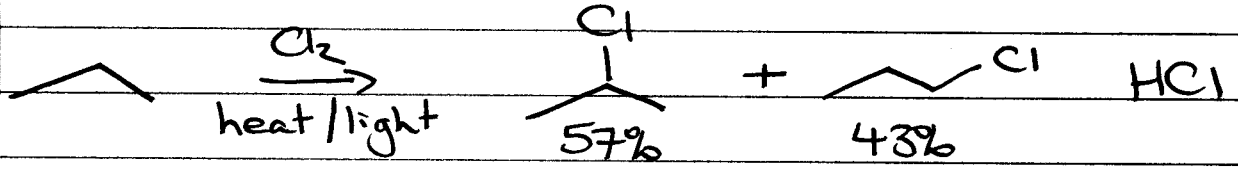


(statistics say 25:75)

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

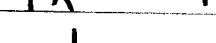
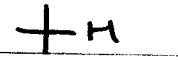
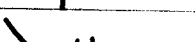


REGIOSELECTIVITY LESS FOR Cl_2



Br_2	3°/2°/1°	1600 / 80 / 1
Cl_2		5 / 4 / 1

(2) BOND ENERGETICS

C–H BOND		BDE (kcal/mol)
	(ALLYL)	86
	(BENZYL)	88
	(tBUTYL)	93
	(iPROPYL)	96
	(ETHYL)	100
CH_3-H	(METHYL)	105
	(VINYL)	106

So, consider:

	CH_4	+	Cl_2	⟶	CH_3Cl	+	H–Cl
BDE	105		59		−85		−103
	164				−188		

$\Delta H = -24$ kcal/mol (EXOTHERMIC RXN)

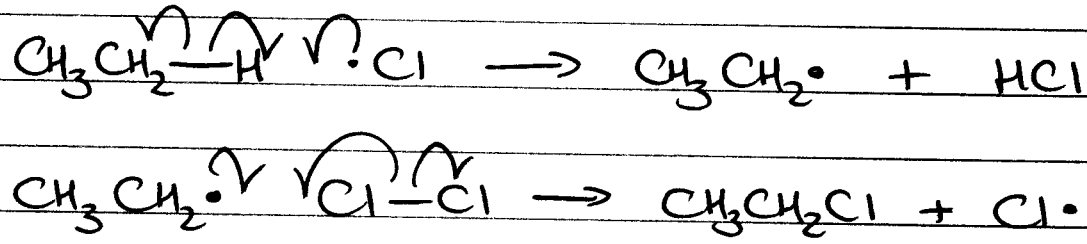
(3) MECHANISMS

3 steps: INITIATION / PROPAGATION / TERMINATION

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

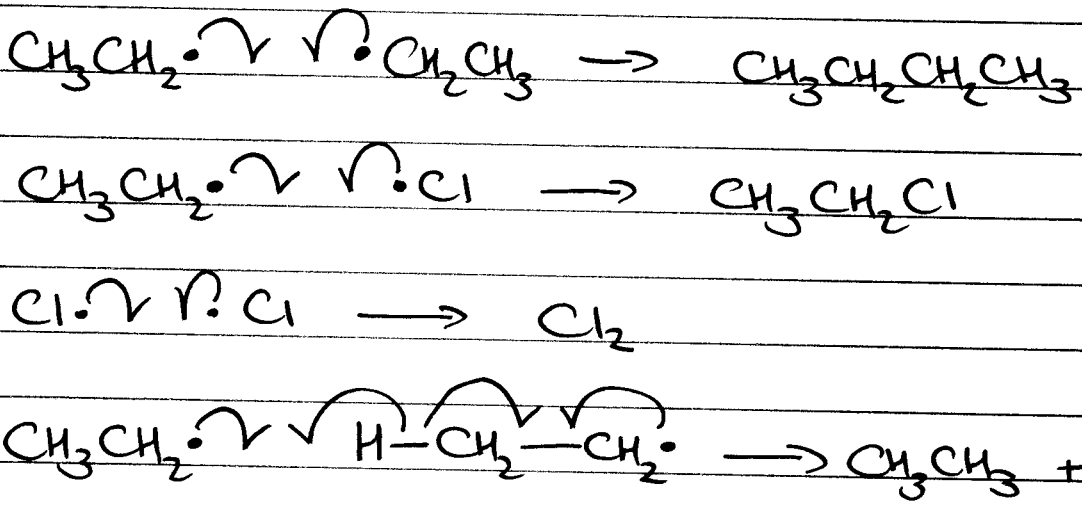
(i) CHAIN INITIATION

(ii) CHAIN PROPAGATION



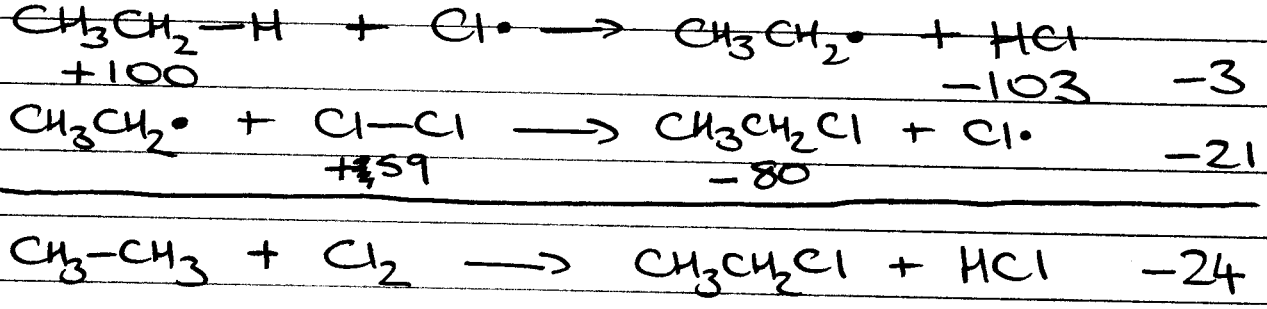
PROPAGATES RADICALS

(iii) CHAIN TERMINATION



CONSUMES RADICALS

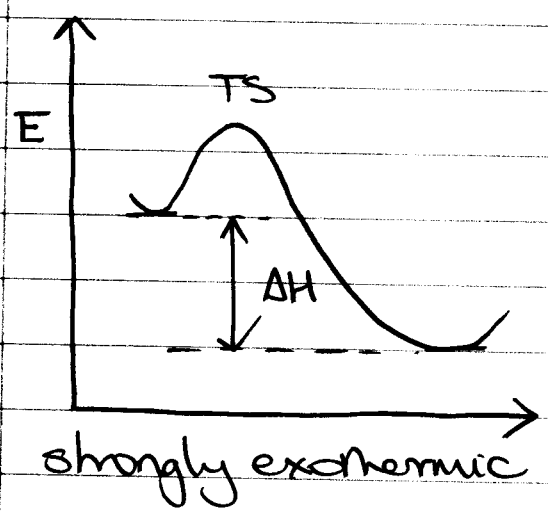
CHAIN PROPAGATION happens many times before termination → number of cycles is called the CHAIN LENGTH



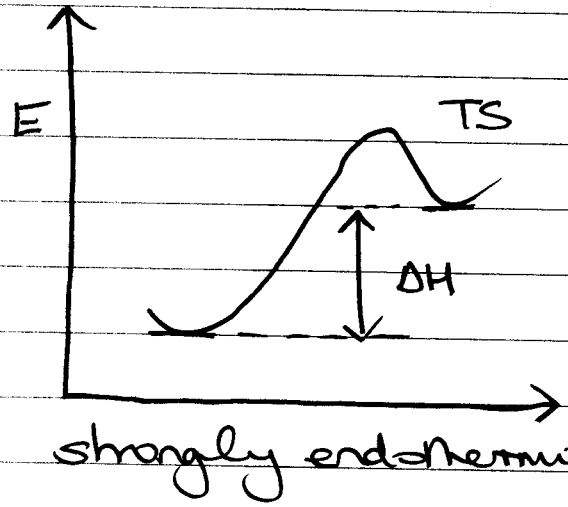
– gives: REACTION STOICHIOMETRY and ΔH for REACTION

(4) HAMMOND POSTULATE

– a transition state will be most like the reactant, the intermediate, or the product, if it is close in energy to one of those structures.



strongly exothermic

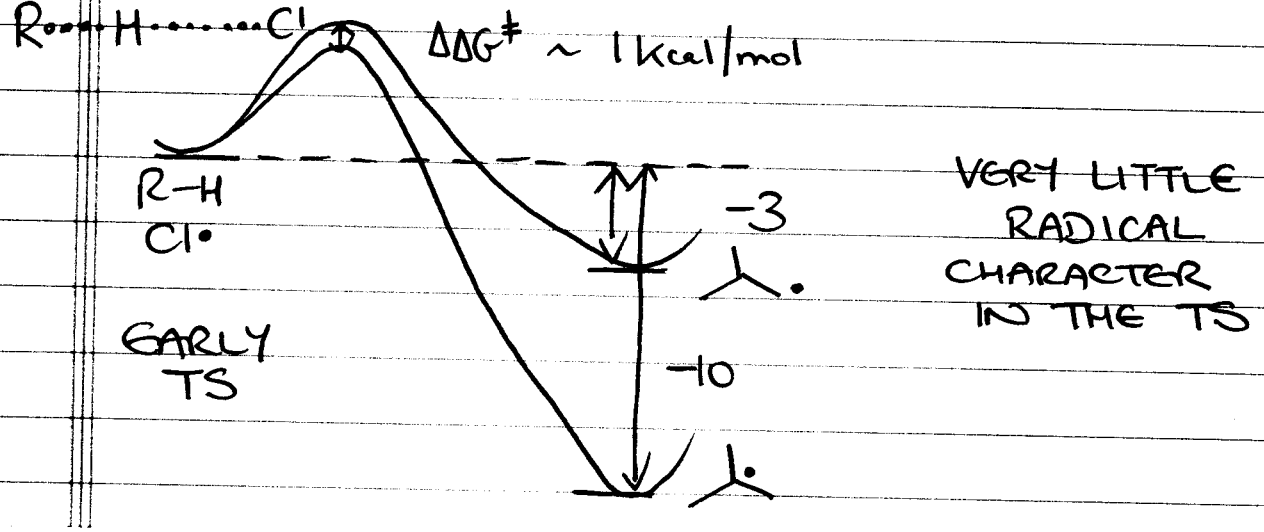


strongly endothermic

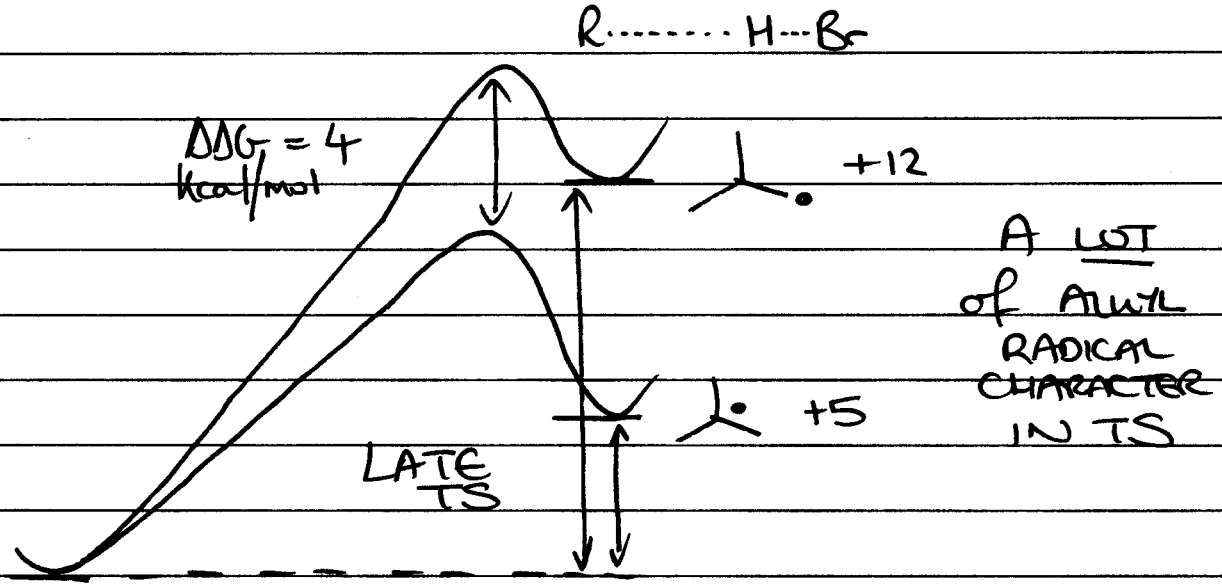
TS looks like reactant

TS looks like product

– Abstraction of H is RDS, consider CHLORINATION (exothermic RDS)

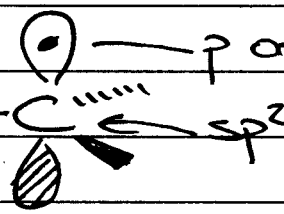


-BROMINATION (endothermic RDS)

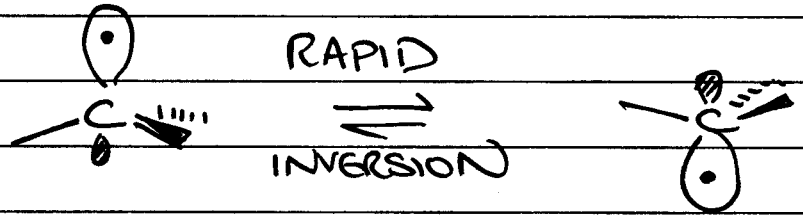


In Bromination, stability of radical is MUCH MORE reflected in TS than in CHLORINATION, so REGIOSELECTIVITY greater for bromination.

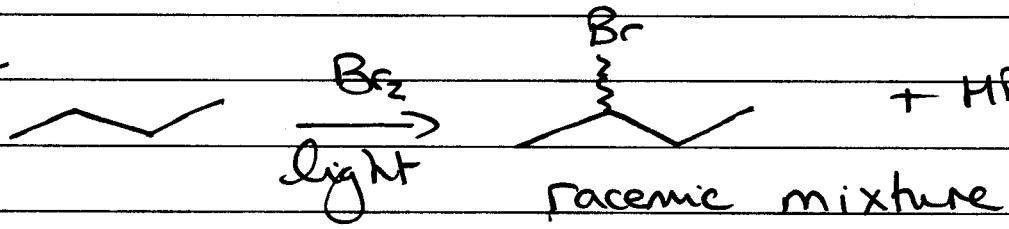
(5) RADICAL STRUCTURE



actually a SHALLOW PYRAMID

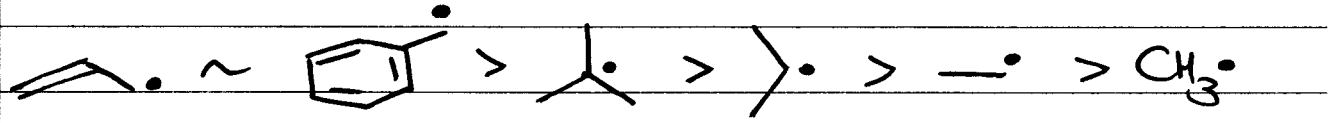


So

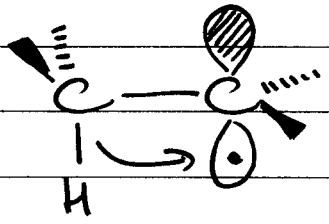


racemic mixture

- STABILITY
(reflected in BDE values)

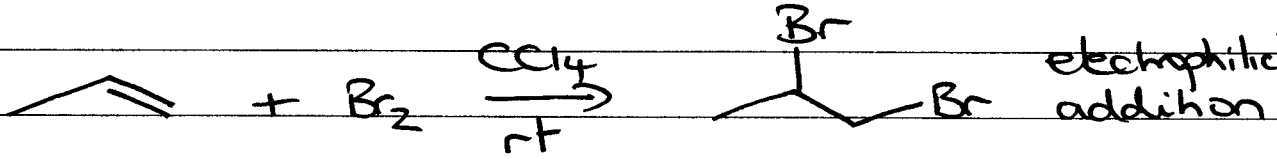


resonance hyperconjugation

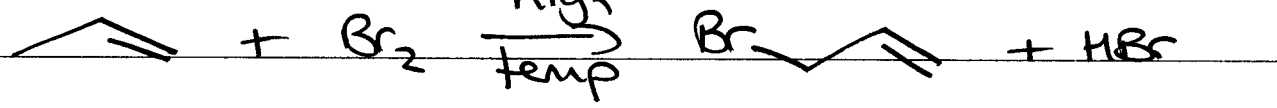


same effect as with CARBOCATIONS

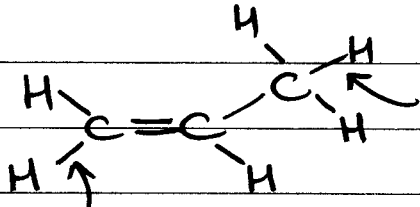
(6) ALLYLIC HALOGENATION



electrophilic addition

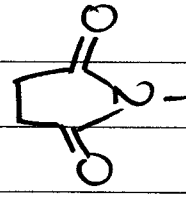


allylic substitution



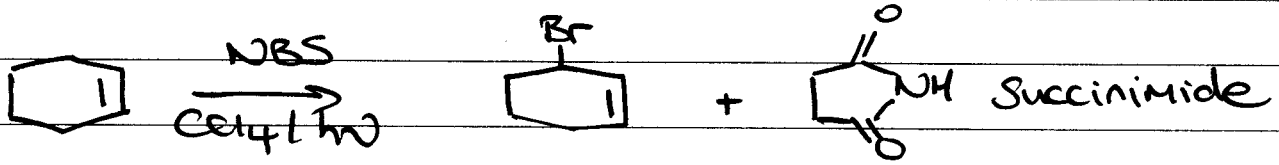
86 kcal/mol

BDE 106 kcal/mol

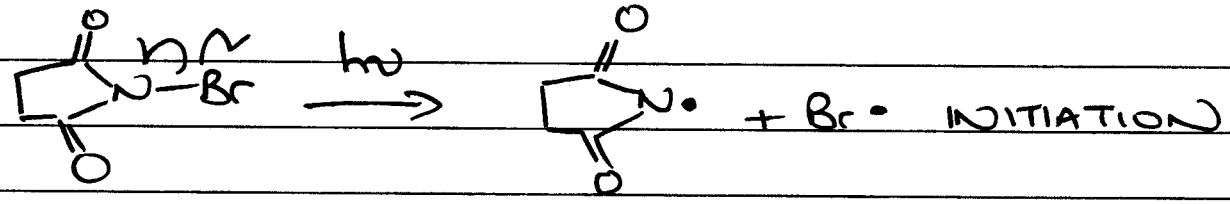
+ more convenient reagent  NBS

N-BROMOSUCCINIMIDE

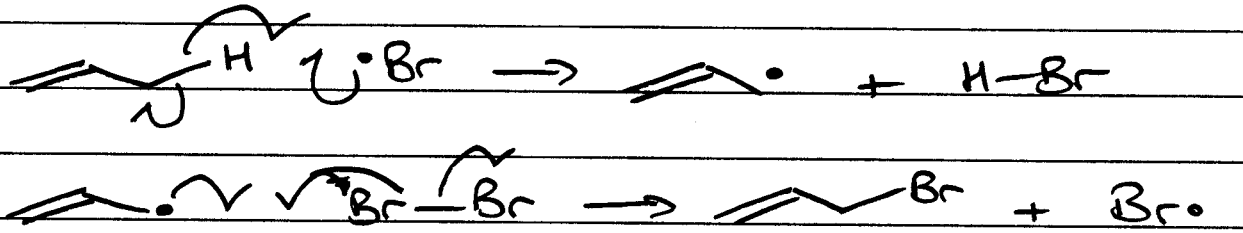
Reaction can be done at RT



Mechanism

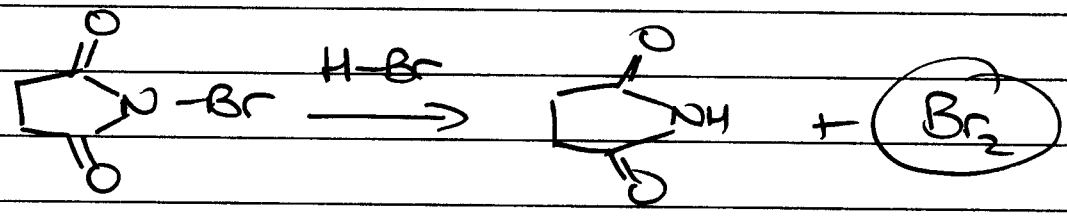


PROPAGATION



TERMINATION – combination of radicals to form non-radical species

BUT WHERE DID THE Br_2 come from?



Why does Br_2 not do electrophilic sub?

- low conc
- RADICAL RXNS ARE MUCH FASTER...