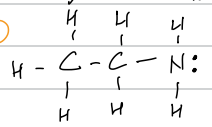
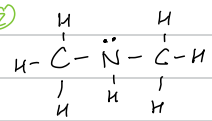
Exam 1 Material

Trevor Swan

Ch1 HW - 1-34 c, 1-39, 1-41i, d, c, k, l, 1-42 b, h, i, 1-44, 1-46, h, j, 1-52 a, f, 1-54d, 1-55d, e. 1-58 a, b, f, 1-59 c, f

1-34 c) two lewis for C_2H_7N

① 

② 

C: F.C = 4 − ½(6) = 0 N: F.C = 5 − ½(6) − 2 = 0

Is there a reliable way to predict EN differences?

1-39 a) C−Cl large (2.5) b) C−H small

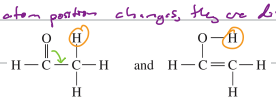
c) C−Li large d) C−N small

e) C−O large f) C−B large

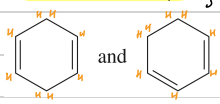
g) C−Mg large h) N−H large

i) O−H large j) C−Br small

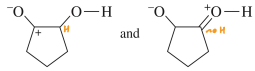
if atom position changes, they are different compounds!

1-41 i) 

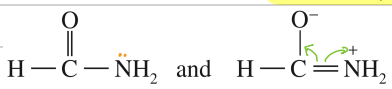
Different Compounds, H moved position

d) 

H changed position, different compounds

c) 

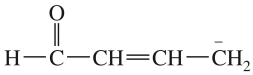
Missing H on a Carbon, different compounds

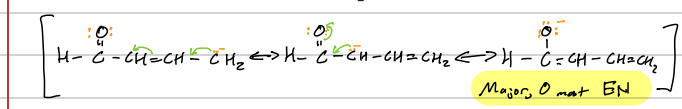
k) 

Resonance, e^- position changed only

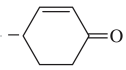
l)

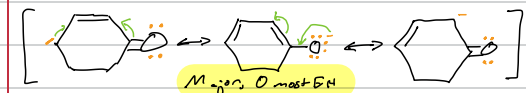
Resonance, e^- position changed only

1-42 b) 



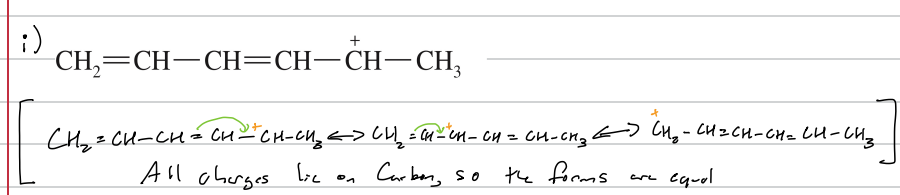
Major, O most EN

h) 

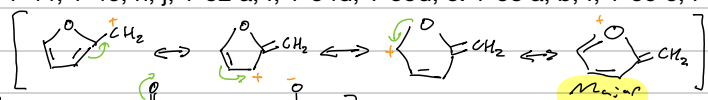


Major, O most EN

i) $CH_2{=}CH{-}CH{=}CH{-}\overset{+}{C}H{-}CH_3$



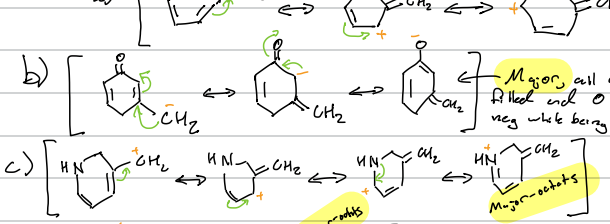
All charges lie on Carbon, so the forms are equal

1-44 a) 

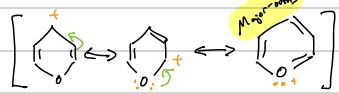
Major

b)

Major, all octets filled and O has neg while being most EN

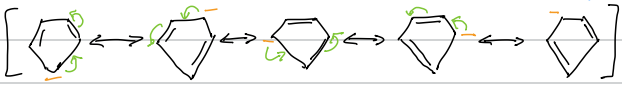
c) 

Major octets

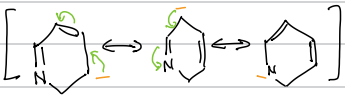
d) 

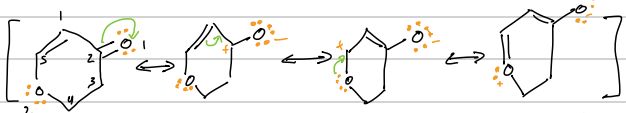
Major octets

The first and second resonance forms can be mirrored, should they be written

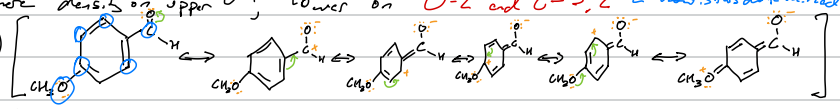
e) 

All equal

f) 

1-46 h) 

higher − density on upper O-1, lower on O-2 and C-5, 2 ← how is this determined

j) 

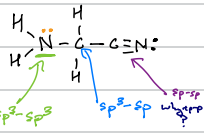
blue circles indicate areas of lower electron density

1-52 a) $[NH_2]^-$

i) H−N̈−H

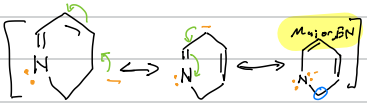
ii) N is sp^3 hybridized

iii) < 109°

f) $H_2N{-}CH_2{-}CN$:) 

ii) sp^3−sp^3 sp^3−sp sp−sp

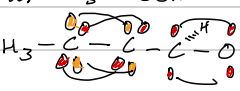
iii) N and C: 109° C and N: 180°

1-54 d) 

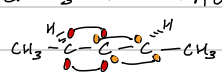
Major EN

Carbon is sp^3, but all other atoms are sp^2

1-55 d) $CH_3C{\equiv}CCHO$

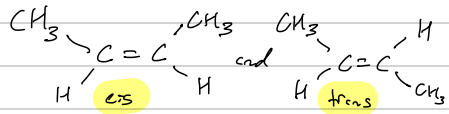


e) $CH_3CH{=}C{=}CHCH_3$



P: bond overlap, bonded orbitals are color coded

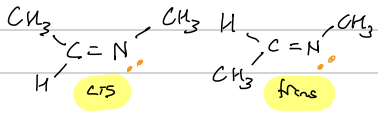
1-58 a) $CH_3CH=CHCH_3$



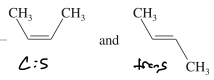
b) $CH_3-C\equiv C-CH_3$ no cis/trans

cannot occur around a triple bond!

f) $CH_3-CH=N-CH_3$

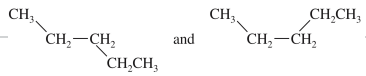


1-59 c)

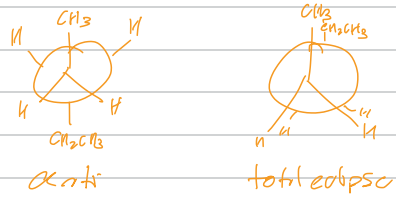


These are cis/trans isomers

f)

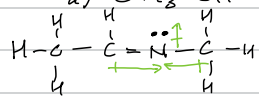


Same exact compound, free rotation



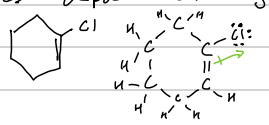
Ch2 HW - 2-29a, g, f part 2 and 3; 2-31a, d, j, i; 2-34; 2-35c, f; 2-36; 2-37; 2-42 g, h; 2-45; 2-48; 2-50 a, d, g; 2-52a, f; 2-56

2-29 a) $CH_3-CH=N-CH_3$



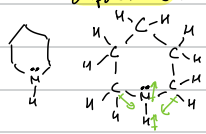
Yes dipole moment large

g)



Yes dipole moment moderate why

f)



Yes dipole moment not large? moderate

2-31) a) $(CH_3CH_2)_2NH$

This compound can H-bond with itself due to the δ^+ on Hydrogen and δ^- on Nitrogen. This also allows it to H-bond with water, increasing solubility.

d) $(CH_3CH_2CH_2)_2O$

The lone pair on the Oxygen allows it to H-bond with water, but no δ^+ on Hydrogen prevents H-bonding w/ itself. It will be soluble in water.

j)

can H-bond with water, but not itself. It is soluble.

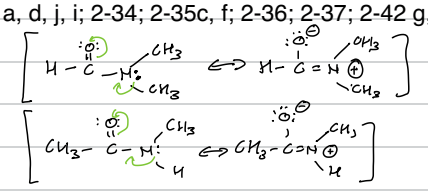
i) CH_3CH_2CHO

This can't H-bond with itself due to no δ^+ on the Hydrogen. Thus compound is an aldehyde so it ends with $\overset{O}{\overset{\|}{C}}-H$. It can H-bond with water due to Oxygen lone pairs. Thus means it is soluble in water too.

2-34) a) Piperidine has a higher bp because it can H-bond with itself, while N-methylpyrrolidine has no H-bonding so it is easier and requires less energy to separate it self.

b) Cyclopentanol has a higher bp than tetrahydropyran for a similar reason as (a). The OH H-bond is very strong and takes much more energy to separate molecules bonded this way. That also accounts for differences between the N-H molecule and O-H molecule.

2-34 c)



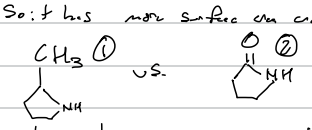
The nitrogen containing isomers have much higher bp differences because of the more linear structure. why compared to ether? These two are much more stable bc of resonance

Resonance forms → inc. stability → higher bp.

2-35c) $CH_3CH_2CH_2CH_2CH_3$ ① vs. $(CH_3)_2CHCH_2CH_3$ ②

Compound 1 will have higher bp because it is a straight chain. So it has more surface area and thus stronger LDFs than compound 2.

f)



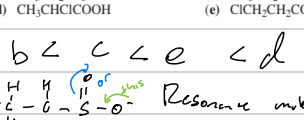
Comp 1 < Comp 2 bc it can H-bond with itself more effectively bc of the lone pairs on the oxygen.

2-36) All of the following compounds can react as acids. Without using a table of acidities, rank them in order of increasing acidity. Explain your ranking.

(a) $CH_3CH_2SO_3H$ (b) CH_3CH_2OH (c) CH_3CH_2COOH
(d) $CH_3CHClCOOH$ (e) $ClCH_2CH_2COOH$

b < c < e < d < a

for c



Resonance makes this conj. base super stable as illustrated roughly above.

c has resonance in its conj base but d and e are stabilized due to the inductive effect of Cl groups closer to -COOH than e, so it is more stabilized by

2-37) Rank the following species in order of increasing acidity. Explain your reasons for ordering them as you do.

~~HF~~ ~~NH_3~~ ~~H_2SO_4~~ CH_3OH CH_3COOH ~~H_3O^+~~ ~~H_2O~~

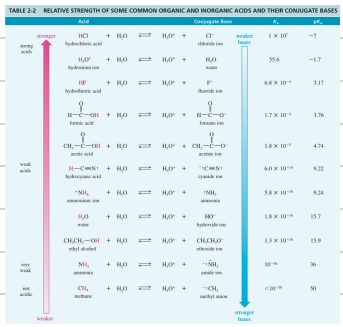


TABLE 2-2 RELATIVE STRENGTH OF SOME COMMON ORGANIC AND INORGANIC ACIDS AND THEIR CONJUGATE BASES

Acid		Conjugate Base	K_a	pK_a
strongest acid	$HCl + H_2O \rightleftharpoons H_3O^+ + Cl^-$	hydrochloric acid / chloride ion	1×10^7	−7
	$H_2O^+ + H_2O \rightleftharpoons H_3O^+ + H_2O$	hydronium ion / water	55.6	−1.7
	$HF + H_2O \rightleftharpoons H_3O^+ + F^-$	hydrofluoric acid / fluoride ion	6.8×10^{-4}	3.17
	$H-C(=O)-OH + H_2O \rightleftharpoons H_3O^+ + H-C(=O)-O^-$	formic acid / formate ion	1.7×10^{-4}	3.76
	$CH_3-C(=O)-OH + H_2O \rightleftharpoons H_3O^+ + CH_3-C(=O)-O^-$	acetic acid / acetate ion	1.8×10^{-5}	4.74
weak acids	$H-C\equiv N: + H_2O \rightleftharpoons H_3O^+ + :C\equiv N:^-$	hydrocyanic acid / cyanide ion	6.0×10^{-10}	9.22
	$^+NH_4 + H_2O \rightleftharpoons H_3O^+ + :NH_3$	ammonium ion / ammonia	5.8×10^{-10}	9.24
	$H_2O + H_2O \rightleftharpoons H_3O^+ + HO^-$	water / hydroxide ion	1.8×10^{-16}	15.7
	$CH_3CH_2-OH + H_2O \rightleftharpoons H_3O^+ + CH_3CH_2O^-$	ethyl alcohol / ethoxide ion	1.3×10^{-16}	15.9
very weak	$NH_3 + H_2O \rightleftharpoons H_3O^+ + :^-NH_2$	ammonia / amide ion	10^{-36}	36
not acids	$CH_4 + H_2O \rightleftharpoons H_3O^+ + :^-CH_3$	methane / methyl anion	$<10^{-50}$	50
		weakest base		strongest base

A lower pKa correlates to a stronger acid, as it is the -log of Ka. Using that knowledge along with the table to the right:

$NH_3 < H_2O < CH_3OH < CH_3COOH < HF < H_3O^+ < H_2SO_4$
36 15.7 15.5 4.74 3.17 -1.7

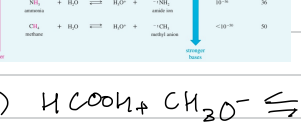
CH_3OH had to be looked up, but it is obvious that H_2SO_4 is the strongest acid

2-42 g) $HCOOH + CH_3O^- \rightleftharpoons HCOO^- + CH_3OH$
acid Base Conj base conj acid

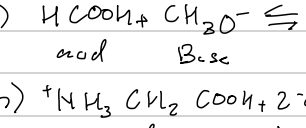
h) $^+NH_3CH_2COOH + 2^-OH \rightleftharpoons NH_2CH_2COO^- + 2H_2O$
acid base Conj. base Conj. acid

2-45)

① $CH_3-C(=O)-OH \rightarrow$



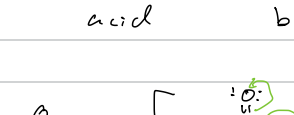
② $CF_3-C(=O)-OH \rightarrow$



Inductive effect Stabilizes bc F is EN

③ $CH_3-C(=O)-OOH \rightarrow CH_3-C(=O)-O-O^-$ No resonance !! electron-donates

④ $CF_3CH_2-C(=O)-OH \rightarrow$



electron inductive effect as F is far

⑤ $CH_3CH_2OH \rightarrow CH_3CH_2O^-$ no resonance !!

Rank conj. base stability: 2 > 4 ≥ 1 > 3 > 5

Rank acid strength: 2 > 4 > 1 > 3 > 5

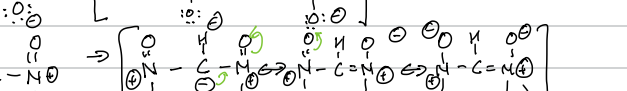
most → least

2-48) Consider the following compounds that vary from nearly nonacidic to strongly acidic. Draw the conjugate bases of these compounds, and explain why the acidity increases so dramatically with substitution by nitro groups.

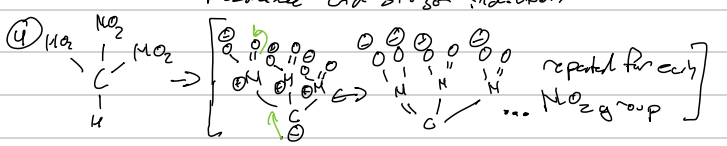
CH_4	CH_3NO_2	$CH_2(NO_2)_2$	$CH(NO_2)_3$
$pK_a = 50$	$pK_a = 10.2$	$pK_a = 3.6$	$pK_a = 0.17$
1	2	3	4

The NO_2 group is so strong because it opens the door to induction and strong resonance stabilization.

1) $CH_4 \rightarrow CH_3^-$ no stabilization

2) 

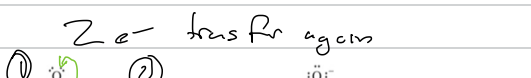
3)

4) 

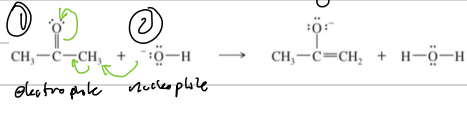
Tons of resonance stabilization and induction → most stabilization

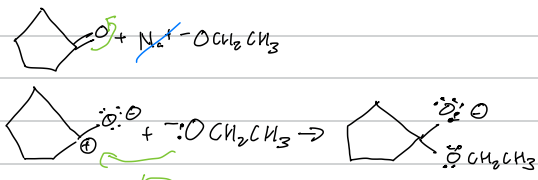
2-50 a)

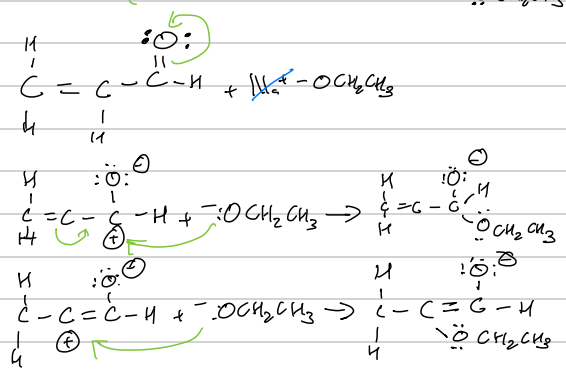
2 e⁻ transfers here

d) 

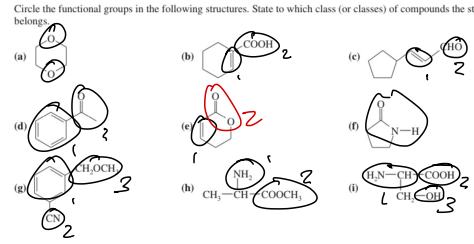
2 e⁻ transfer again

g) 

2-52a) 

f) 

2-56) Circle the functional groups in the following structures. State to which class (or classes) of compounds the structure belongs.



a) both ethers

b) 1 = alkene, 2 = carboxylic acid

c) 1 = alkene, 2 = aldehyde

are these other groups

d) 1 = benzene/phenol/aromatic, 2 = Ketone

e) 1 = alkene 2 = ester

f) amide

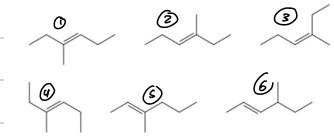
g) 1 = aromatic, 2 = nitrile, 3 = ether

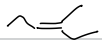
h) 1 = amine, 2 = ester

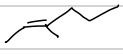
i) 1 = amine, 2 = carboxylic acid, 3 = alcohol

Ch3 HW - 3-34 d,e, f; 3-36 b, d, i, k; 3-40; 3-42; 3-44; 3-45; 3-46 c, f; 3-48 b, i; 3-49; 3-50, 3-52 a,

3-34 d)

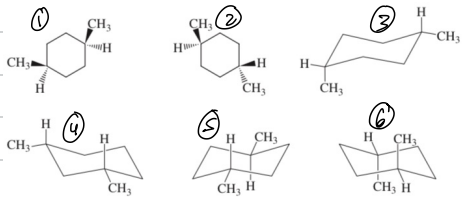


1: 2:  3:

4: 5:  6:

1, 2, and 4 are all identical. 3 is a cis- structure, so it is a geometric isomer of 1, 2, and 4. 5 and 6 are constitutional isomers, having same formula but diff. arrangements

e)



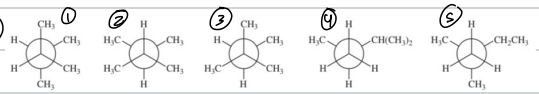
Methyl groups should point the same direction!

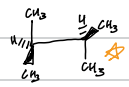
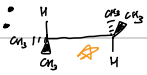
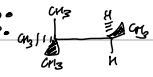
1 and 3 are identical compounds.

2, 5, and 6 are identical. They are trans, or geometric isomers of 1 and 3.

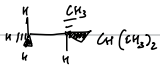
4 is a constitutional isomer. Methyls moved

f)



1:  2:  3: 

2,3-dimethyl 2,3 dimethyl 2,2-dimethyl

4:  5:

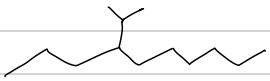
2,3-dimethyl 2,2-dimethyl

Constitutional

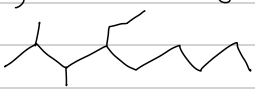
1 and 2 are conformers. 1, 2, and 4 are the same compound.

3 and 5 are the only non-identical

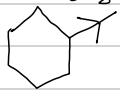
3-36 b) 4-isopropyl decane



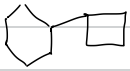
d) 2,3-dimethyl-4-propyl nonane



i) tert-butyl cyclohexane

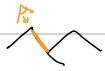


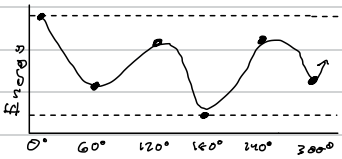
k) cyclobutylcyclobutane

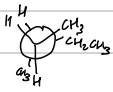
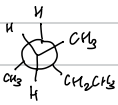


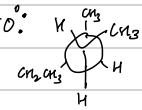
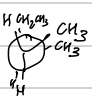
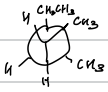
This is not dicyclobutyl

3-40) 3-methyl pentane





0°:  60°:  120°:

180°:  240°:  360°: 

Pattern repeats forever, 0° = 360°: omitted

3-42 Comparing boiling points

a) octane or 2,2,3-trimethyl pentane

Both have same formula look at surface area. Octane has more surface area and is less branched. This results in stronger London forces leading to increased boiling point.

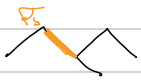
b) nonane or 2-methyl heptane

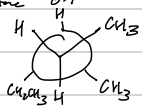
Nonane is a larger molecule and it has more surface area, so it has stronger LDFs ∴ Higher boiling point ← Can use molecular weight here

c) 2,2,5-trimethyl hexane or nonane

Same formula so look at surface area. Nonane is less branched → higher surface area → stronger LDFs → higher bp.

3-44 a) 3-methyl pentane on C2-C3 bond



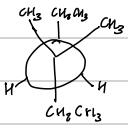


Most stable because low torsional strain as a result of staggered conformation.

anti

Bulky groups are furthest apart so lower steric hindrance from bulky overlap.

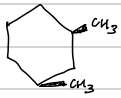
b) 3,3-dimethyl hexane on C3-C4 bond



anti

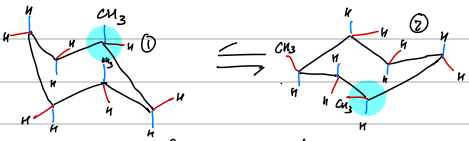
This is the most stable because the bulky methyl groups are far apart so there is low steric hindrance. Also, the conformation is staggered which reduces torsional strain.

3-45) cis-1,3-dimethyl cyclohexane



1 = equitorial, 1 = axial Carbon 1

a)

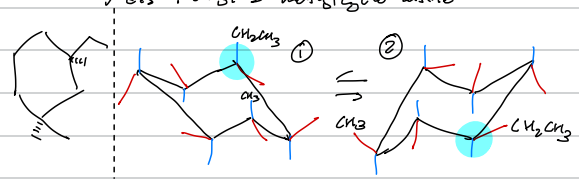


b) Higher energy (less stable) Lower energy (more stable)

c) Gauche is a result of torsional or angular strain. A lot of energy difference is likely due to these interactions

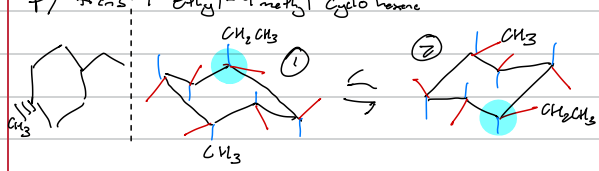
d) There is also most likely a large difference due to steric strain as the CH_3 groups are interacting. CH_3 isn't too bulky though, so its contribution is most likely not as large as torsional.

3-46 c) cis-1-ethyl-3-methyl cyclohexane



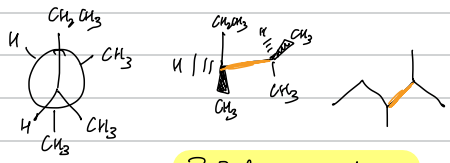
Structure 2 is more stable as the bulky groups are on the equitorial position, greatly reducing steric strain

f) trans-1-ethyl-4 methyl cyclohexane



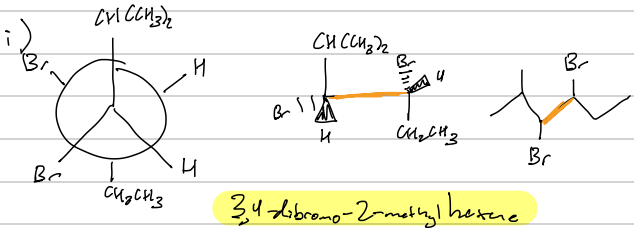
Structure 2 is more stable is more stable because both bulky groups are in the equitorial position, reducing steric strain / hindrance.

3-48 b)



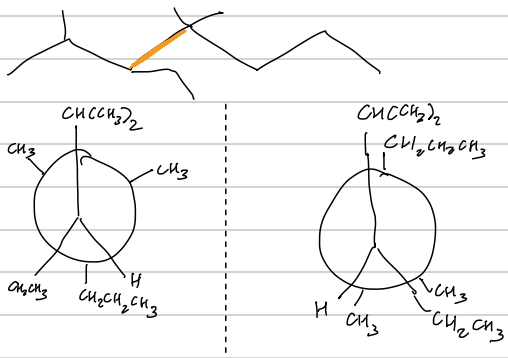
2,3-dimethyl pentane

i)



3,4 dibromo-2-methyl hexane

3-49) 3-ethyl-2,4,4-trimethyl heptane on C3-C4

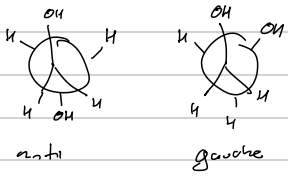


Most Stable — Least Stable

Staggered with bulky groups larger anti reduces torsional and steric strain the most. That makes it the most stable. Totally eclipsed places bulky groups very close to each other increasing torsional strain and steric hindrance

3-50) ethane-1,2-diol HO-CH_2-CH_2-OH

Gauche is a special type of staggered where the groups are close to each other

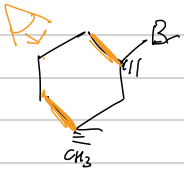


anti — gauche

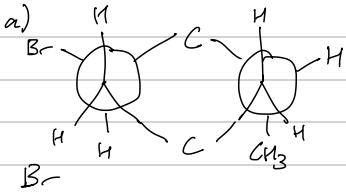
The gauche conformation is more stable because of the strong H-bond formed between the two -OH groups. This cannot happen in the stable anti conformation, but is allowed, and overcomes repulsion in the gauche conformation.

I changed this to challenge myself

3-52 Draw the (a) newman projection and (b) chair conformations along with cyclo depiction (c) for: trans-1-bromo-3-methyl cyclohexane

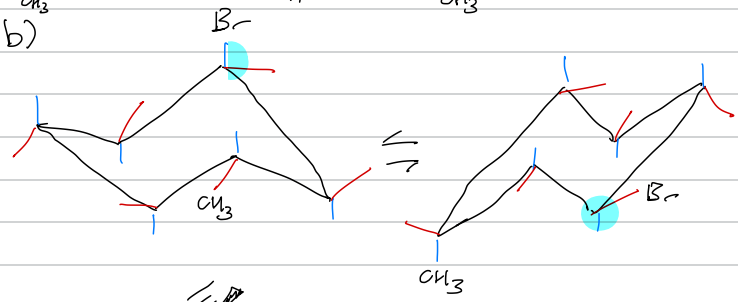


a)

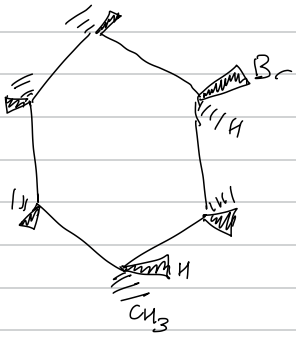


Clearly multiple ways to orientating specifics on exam?

b)

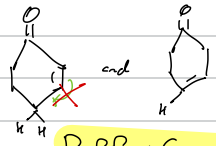


c)



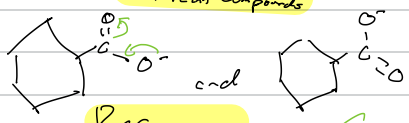
Chapter 1 Review

1-41 a)



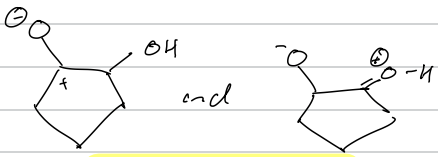
Different Compounds

b)



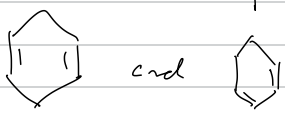
Resonance

c)



Different Compounds

d)



Different Compounds

e) $CH_2=C(=O)-H$ and $^{\ominus}CH_2-C(=O)-H$

Resonance

f) $CH_3-C(=NH_2^{\oplus})-NH_2$ and $CH_3-C(NH_2)=NH_2^{\oplus}$

Resonance

g) $CH_2=CH-CH_2^{\oplus}$ and $CH_2^{\oplus}-CH=CH_2$

Exact same compound Resonance

h) $CH_2=C=O$ and $H-C\equiv C-OH$

Different Compounds

i) $H-C(=O)-OH$ and $H-C\equiv C-OH$

Different Compounds

j) $H-C(:\ddot{O}-H)^{\oplus}-H$ and $H-C(=\overset{\oplus}{O}-H)-H$

Resonance

k) $H-C(=O)-NH_2$

c-d

$H-C(=O^{\ominus})-N^{\oplus}H_2$

Resonance

l) $CH_3-C(=O)-CH=CH_2$

and

$CH_3-C(=O^{\ominus})=CH-CH_2^{\oplus}$

Resonance

1-45 a) $CH_3-CH^{\oplus}-CH_3$ or $CH_3-CH^{\oplus}-OCH_3$

More stable bc resonance stabilized

c) $CH_2=CH-CH^{\oplus}-CH_3$ or $CH_2=CH-CH_2-CH_2^{\oplus}$

Good

Chapter 2 Review

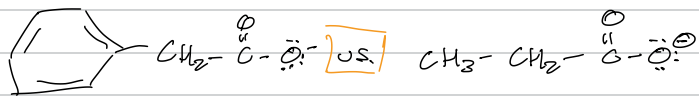
2-37)

	CB		CB
HF	$:\ddot{F}:^{\ominus}$ ✓	CH_3OH	$CH_3-\ddot{O}:^{\ominus}$
NH_3	$H-\ddot{N}H_2$	CH_3COOH	$CH_3-\overset{O}{\overset{\|\|}{C}}-\ddot{O}:^{\ominus}$ ✓
H_2SO_4	$HO-\overset{O}{\overset{\|\|}{S}}(=O)-\ddot{O}:$ ✓	H_3O^+	$H-\ddot{O}-H$ ✓
		H_2O	$OH^{\ominus}$

$H_2SO_4 > H_2O > HF > CH_3COOH > CH_3OH = H_2O > NH_3$

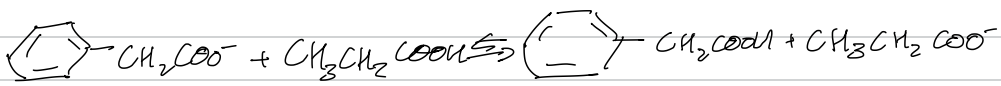
H_2SO_4 has a conj. base (CB) stabilized greatly by resonance and inductive effect from O^- and EN respectively. H_2O and F^- are invalidly stable. There is no resonance in CH_3O^-, but there is resonance in CH_3COO^- CB, accounts for that difference. OH^- is very unstable, but $:NH_2$ is less EN, so it donates its lone pair more easily. This leads to decreased stability.

2-39 b)



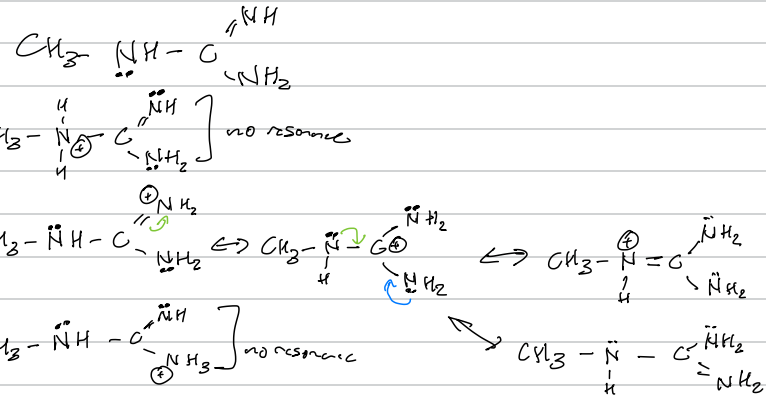
The CB with a phenol group will have the stronger acids as the delocalized electrons on the ring increase stability

c)



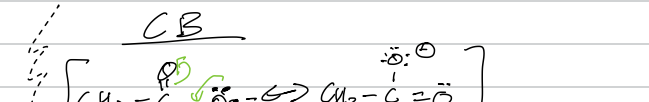
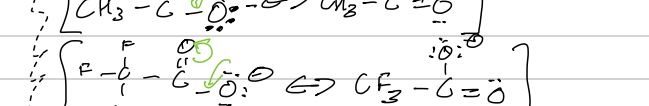
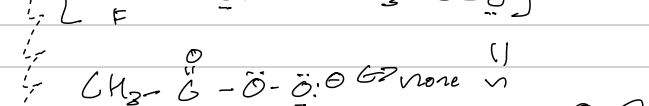
Equilibrium always favors the side with weaker acids/bases. In this case, reactants will be favored because CH_3CH_2COOH is weaker than the phenol acid and the phenol base is so stable meaning it is a weaker base.

2-40)



b) The second protonation will be more basic because its conjugate acid is more stable. It is stabilized by the delocalization of electrons through resonance.

2-45 a)

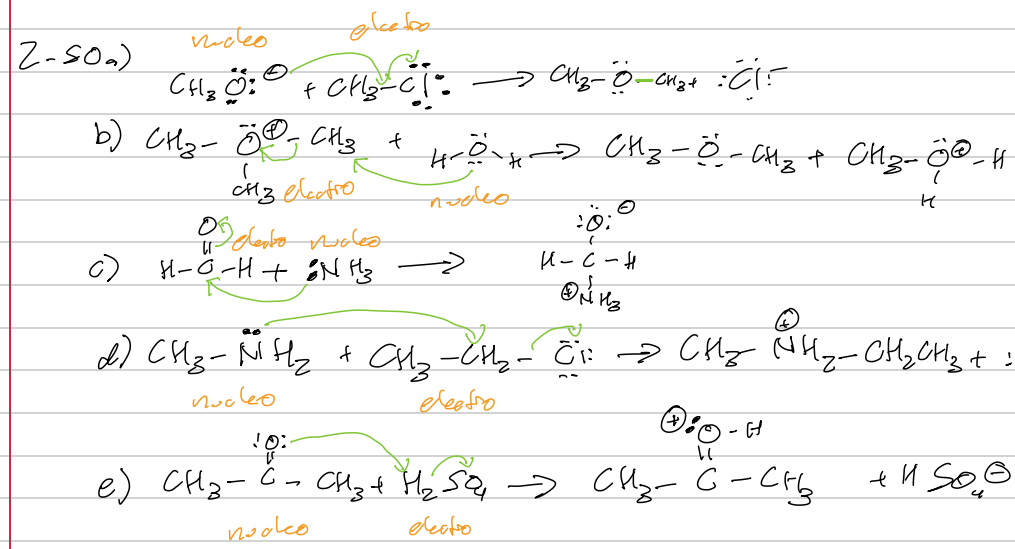
		CB
①	$CH_3-\overset{O}{\overset{\|\|}{C}}-OH$	
②	$CF_3-\overset{O}{\overset{\|\|}{C}}-OH$	
③	$CH_3-\overset{O}{\overset{\|\|}{C}}-OH$	$CH_3-\overset{O}{\overset{\|\|}{C}}-\ddot{O}-\ddot{O}:^{\ominus} \leftrightarrow$ none !!
④	$CF_3CH_2-\overset{O}{\overset{\|\|}{C}}-OH$	
⑤	CH_3CH_2-OH	$CH_3CH_2-\ddot{O}:^{\ominus} \leftrightarrow$ none !!

b) 2 > 4 > 1 > 3 > 5

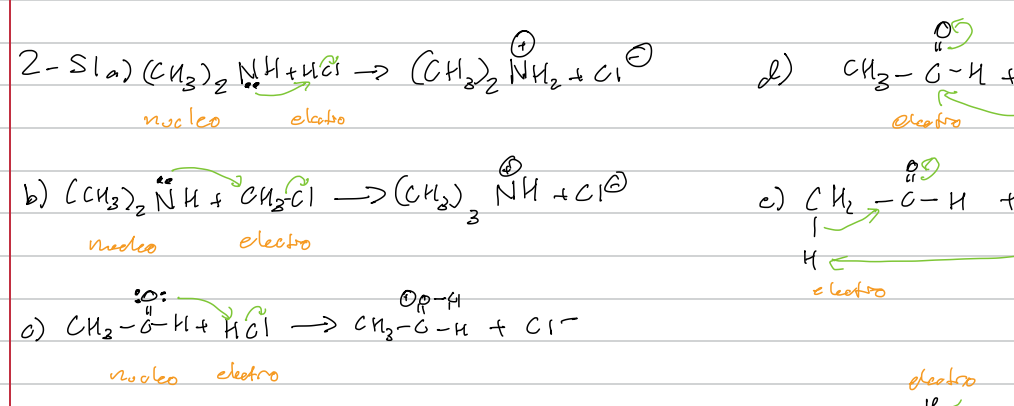
2 is stronger than 4 because 2 has the EN fluorine closer to the negative charge, amplifying the inductive effect. 1 shows resonance but has weaker induction. There is weak induction in 3, and none in 5 with neither having resonance forms.

c) Acids ranked same as bases as more stable conj. base = stronger acid.

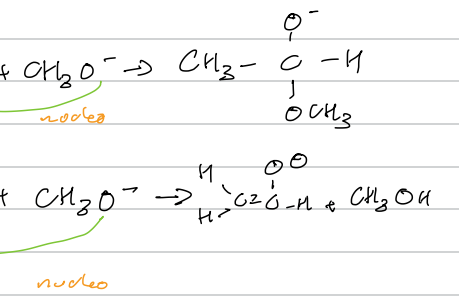
2-S0 a)



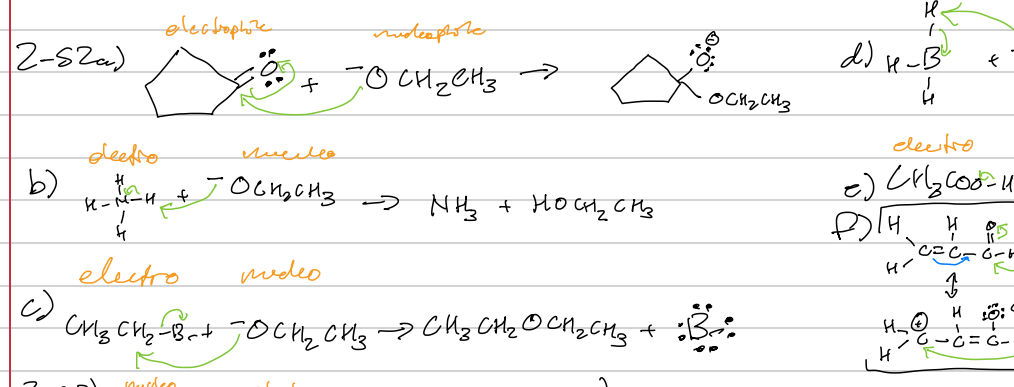
2-S1 a)



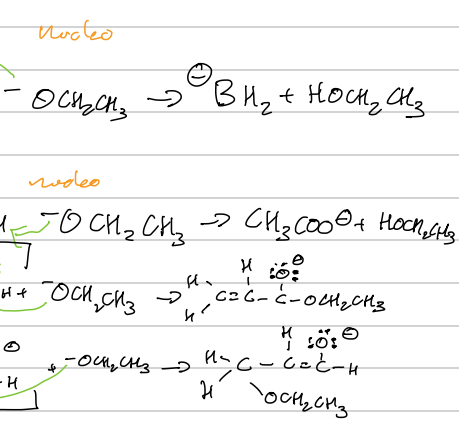
d)



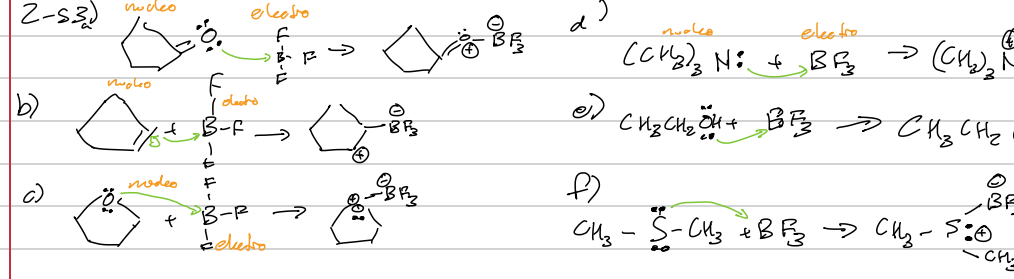
2-S2 a)



d)

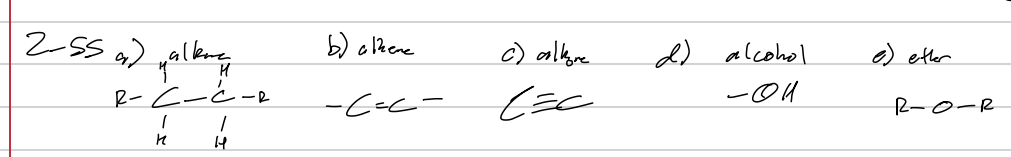


2-S3 a)



d)

2-S5 a) alkane



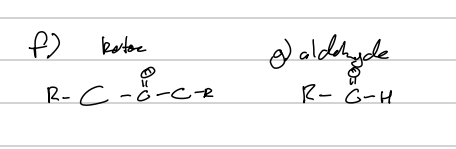
b) alkene $-C=C-$

c) alkyne $C\equiv C$

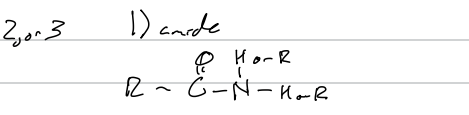
d) alcohol $-OH$

e) ether $R-O-R$

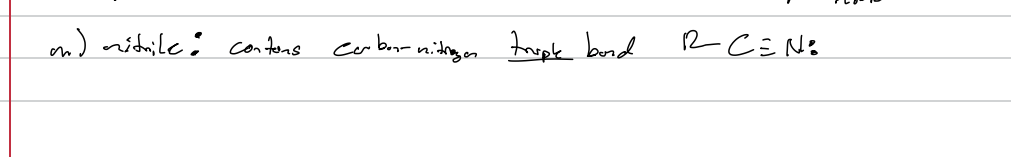
f) ketone



g) aldehyde



h) aromatic



i) carboxylic acid

j) ester

k) amine

nitrogen to 1, 2, or 3 carbons

l) amide

m) nitrile: contains carbon-nitrogen triple bond $R-C\equiv N:$

Chapter 3 Review

3-41 a) 2-ethyl pentane

not longest chain

3-methyl hexane

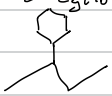
c) 5-chloro-4-methyl hexane

started counting C

2-chloro-3-methyl hexane

e) 2-cyclohexyl butane

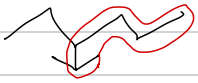
bro...



(1-methyl propyl) cyclohexane

b) 3-isopropyl hexane

common name!!



3-ethyl-2-methyl hexane

d) 2-dimethyl butane

skipped here 2 substituents

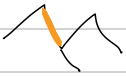
2,2-dimethyl butane

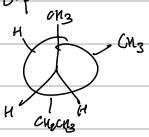
f) 2,3-diethyl cyclopentane

start at 1 for cyclo

1,2-dimethyl pentane

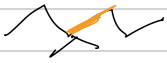
3-44 a) 3-methyl pentane on C2-C3

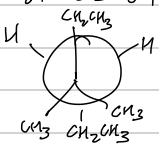




Staggered conformation is always more stable to reduce torsional. The anti conformation of bulky groups reduces steric strain as the groups don't interfere

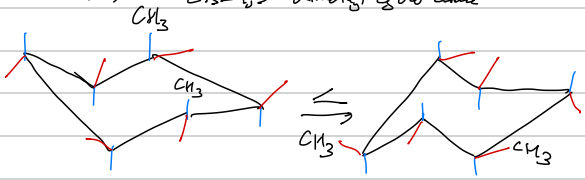
b) 3,3-dimethyl hexane on C3-C4





The bulky groups are in the anti conformation, reducing steric strain. Staggered = less torsional strain.

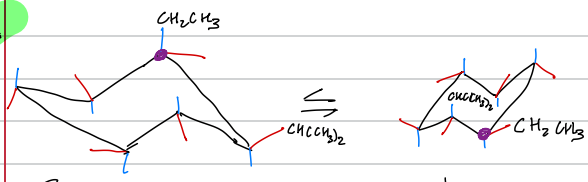
3-45 a/b) cis-1,3-dimethyl cyclohexane



The structure is more stable because the methyl groups are in the equitorial position. These conformations place the groups further from the ring, decreasing energy and increasing stability.

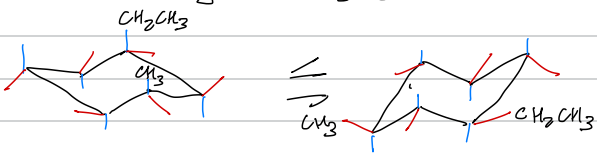
3-46 a) cis-1-ethyl-2-isopropyl cyclohexane

correct eq. positions here!



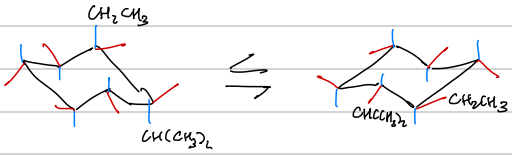
Struct. One more stable as it has the bulkier group in the further away → reduced steric effects

c) cis-1-ethyl-3-methyl cyclohexane



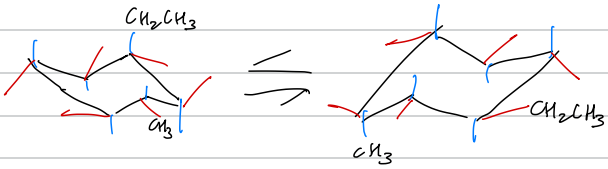
Structure 2 is more stable as the bulkier ethyl and methyl groups are equitorial, reducing steric strain.

b) trans-1-ethyl-2-isopropyl cyclohexane



Structure 2 is more stable because both bulky groups are equitorial

d) trans-1-ethyl-3-methyl cyclohexane

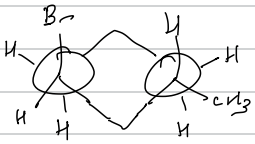


Structure 2 is more stable as bulkier ethyl group is in the equitorial position reducing steric strain.

3-51)

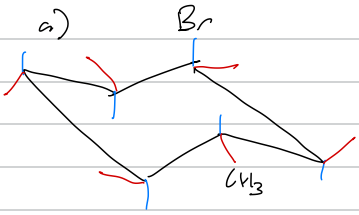
Very clearly the most stable conformation as all groups are equitorial

3-52)



c) 1-bromo-3-methyl cyclohexane

a)

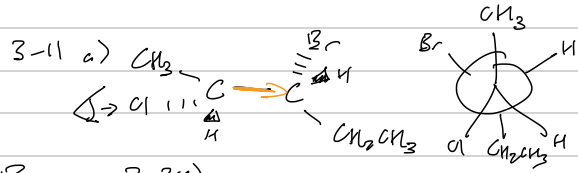


The restare H's

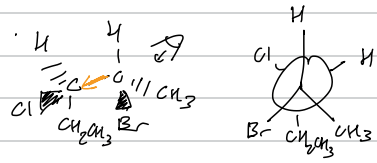
3-6 a) C_6H_{14}

$CH_3CH_2CH_2CH_2CH_2CH_3$ $\quad CH_3CH(CH_3)CH_2CH_2CH_3$ $\quad CH_3C(CH_3)_2CH_2CH_2CH_3$ $\quad CH_3CH_2CH(CH_3)CH_2CH_3$ $\quad CH_3CH_2C(CH_3)_2CH_2CH_3$

3-11 a)



b)



c)

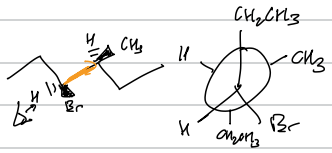
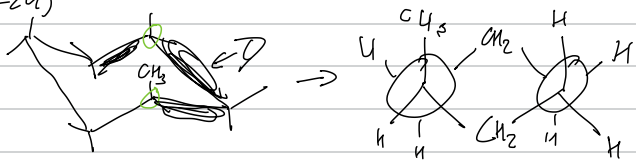
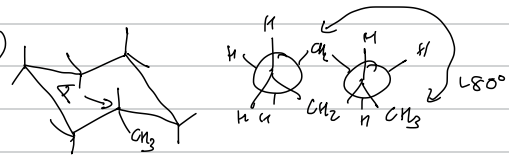


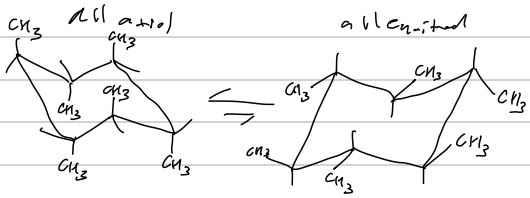
Figure 3-24)



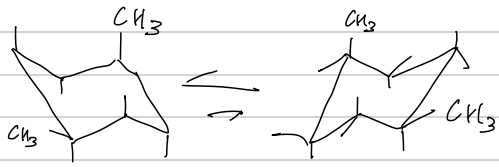
3-23)



3-22) 1,2,3,4,5,6-hexamethylcyclohexane

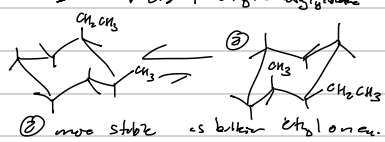


3-27 a) cis-1,4-dimethylcyclohexane



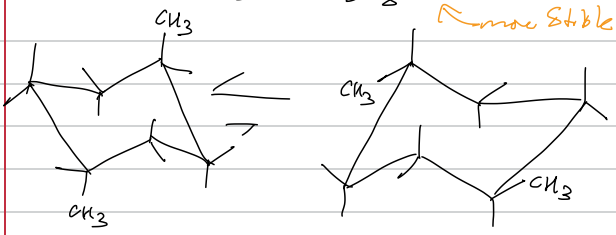
Equally as stable

3-29 a) cis-1-ethyl-2methylcyclohexane



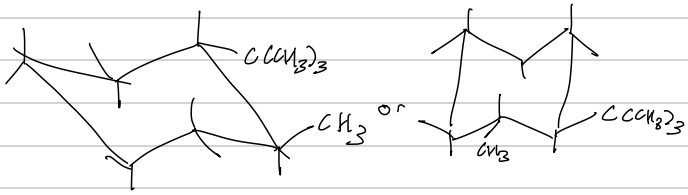
③ more stable as bulkier CH_3 on eq. position which reduced steric hindrance

3-27 b) trans-1,4-dimethylcyclohexane



more Stable

3-30 b) trans-1-t-butyl-2methylcyclohexane



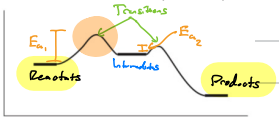
Second is more stable as bulky group are equatorial

Exam 2 Material

Ch4 HW - 4-35; 4-40; 4-41c; 4.42; 4.46; 4.47b, f; 4.52

4-35 a)

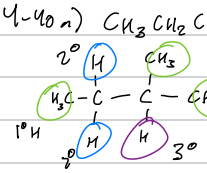
c)



b) The reactants have higher energy than the products, so the reaction is exothermic, which a $-\Delta H$.

d) The transition state of the rate limiting step is highlighted in orange. It resembles the intermediate because it is closest in energy.

4-40 a) $CH_3CH_2CH(CH_3)_2$



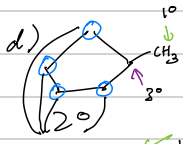
b) $(CH_3)_3CCH_2CH_3$

1° 2° 1°

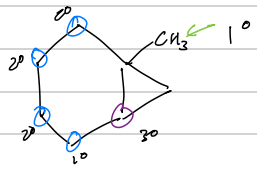
c) $(CH_3)_2CHCH(CH_3)CH_2CH_3$

1° 3° 3° 1° 2° 1°

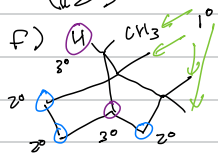
d)



e)



f)

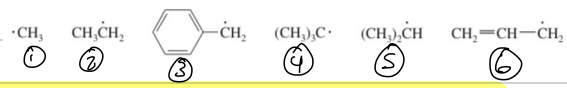


4-41c) $(CH_3)_3C-OH + HCl \rightarrow (CH_3)_3C-Cl + H_2O$

$\Delta H = \Sigma$ reactants $- \Sigma$ products

$\Delta H = (432 + 401) - (447 + 355) = -19$ kJ/mol

4-42)

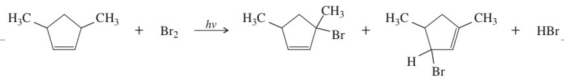


3 > 6 > 4 > 5 > 2 > 1

most stable — least stable

Stability decreases as non-hydrogen substituents

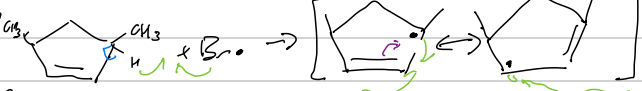
4-46



a) Mechanism

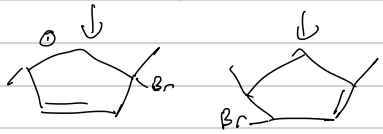
Initiation: $Br-Br \xrightarrow{h\nu} 2\,Br\cdot$

Propogation:



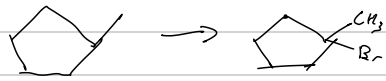
Second Propogation Step: $Br-Br$ + $Br-Br$

b) The 3° hydrogen is removed in this case, which creates a more stable radical. The hydrogen removed in compound 1 is also allylic.



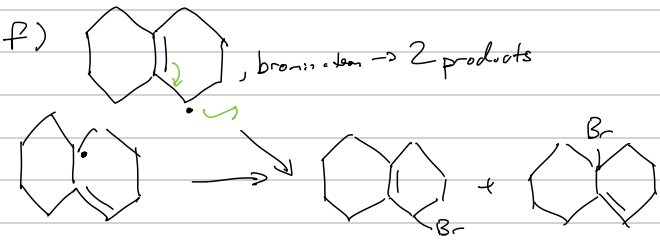
+ HBr

4-47 b) methylcyclopentane, bromination

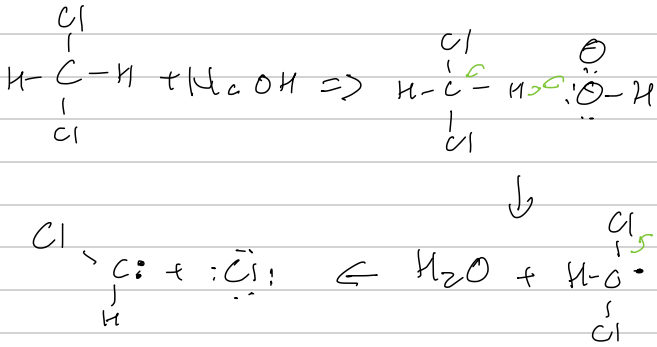


3° is attached

f)



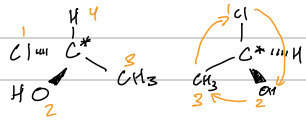
4-52) Dichloromethane treated with NaOH.



Review Mechanisms!

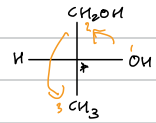
Ch5 HW - 5-26; 5-28a,c; 5-29, a, d; 5-30 b, d, e, h, i; 5-31c; 5-36

S-26 a)



R and chiral

b)



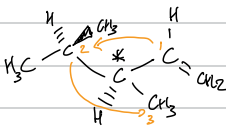
R and Chiral

Bookmarks ↓ configuration rules

c)

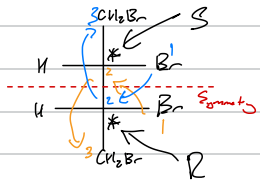
S and S Both Chiral

d)



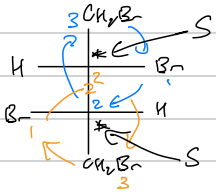
S and Chiral

e)



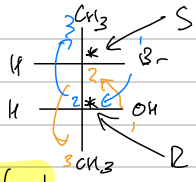
mesoⓐ chiral

f)



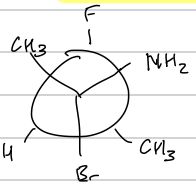
Chiral

g)

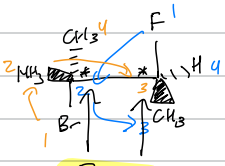


Chiral

h)

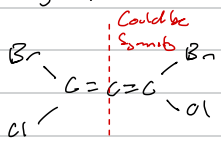


Chiral



R and S

i)

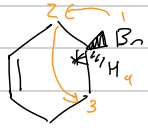


Could be Symmetry

Cannot establish Symmetry or meso

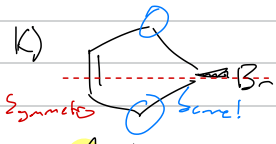
No chiral Carbon, Chiral Struct.

j)



S and Chiral

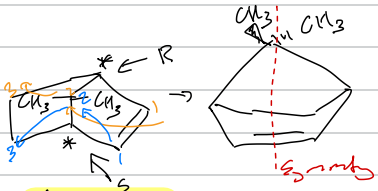
K)



Symmetry Same!

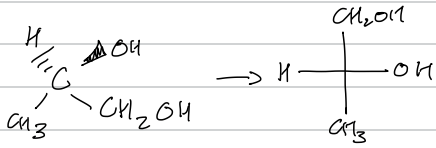
Achiral

l.

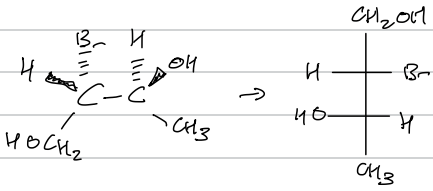


Achiral, meso

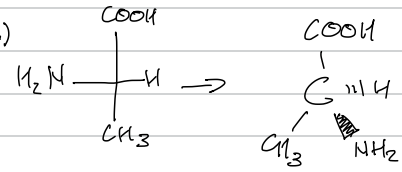
S-28 a)



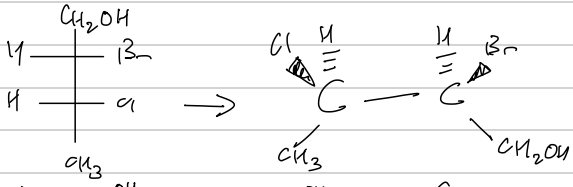
c)



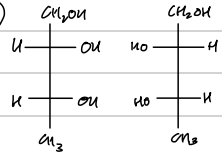
S-29 a)



d)

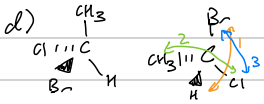


S-30 b)



enantiomers be mirror images

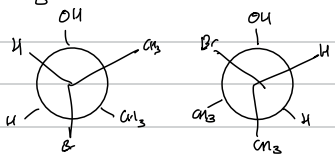
d)



Enantiomers, not superimposable

3 measurements/observations → Enantiomers

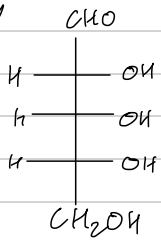
e)



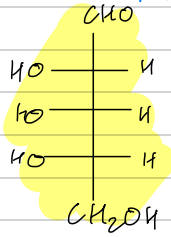
Diastereomers, two chiral carbons, non superimposable

Can be separated by distillation or recrystallization

S-31 c)

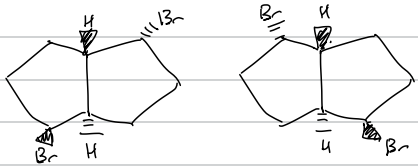


Just draw Mirror



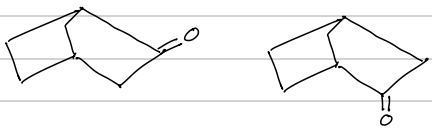
Hydrogen bonds → reverse?

h)



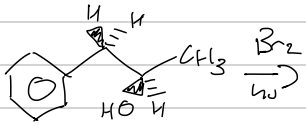
180° rotation (Vogel) shows same compound

i)



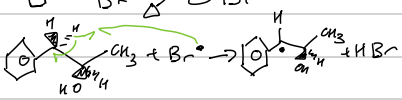
Enantiomers, non-superimposable Mirrors

S-36)

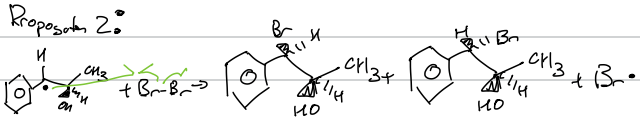


a) Initiation: $Br-Br \xrightarrow[\Delta]{h\nu} 2Br\cdot$

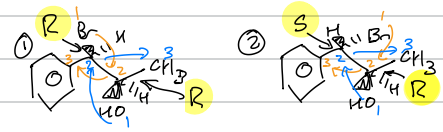
Proposed 1:



Proposed 2:



b and c)



d) Diastereomers, two chiral centers → non-superimposible

One S and One R vs. Both R

not as abundant

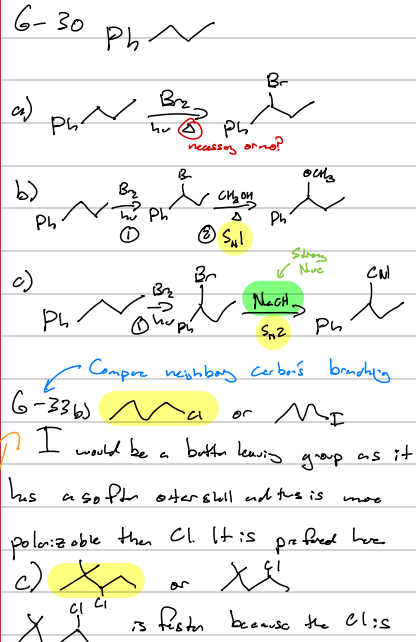
e) No, Diastereomers aren't always a 50:50 split

f) Diastereomers, unlike enantiomers, have different properties, so they can be separated w/ lab techniques.

Ph = ⬡ for my own sake

Ch6 HW - 6-30; 6-33b, c, f; 6-34 a, d, f; 6-37; 6-41, 6-42; 6-43; 6-45c, d, h; ; 6-46e; 6-49, 6-50

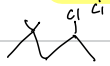
6-30

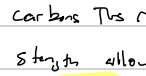


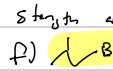
6-33b) or

I would be a better leaving group as it has a soft, outer shell and this is more polarizable than Cl. It is preferred here.

c) or

 is faster because the Cl is further from the rest of the carbons. This reduces the inductive effects strengthen allowing Cl to leave more easily.

f)  or

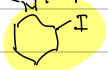
 is faster as the neighboring carbon is less substituted.

Solvolysis in ethanol = SN1

6-34 a) $(CH_3CH_2)_2CH-Cl$

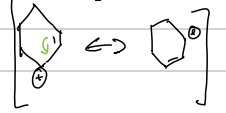
or $(CH_3)_3C-Cl$

will be faster as the mechanism creates a 3° carbocation which SN1 favors.

d) or 

I is a better leaving group so its molecule undergoes SN1 more rapidly.

f) or



Carbocation stabilized by resonance as shown to the left. Possible as compound is allylic.

6-37) $CH_3CH_2-Br + (CH_3)_3C-O^{\ominus}\ K^{\oplus} \rightarrow (CH_3)_3C-O-CH_2CH_3$

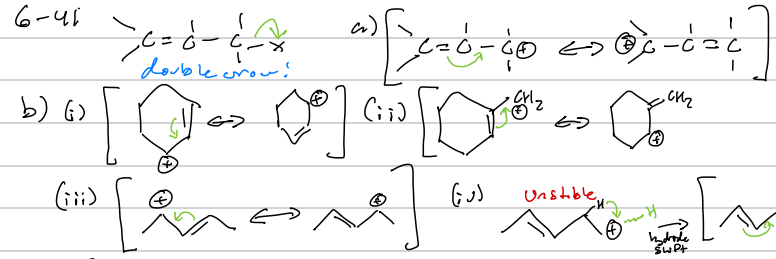
a) CH_3CH_2-Br creates a 1° carbocation which is formed by SN2. This is second order, and the reaction rate doubles if CH_3CH_2-Br doubles.

b) Rate = $k_r[CH_3CH_2Br][(CH_3)_3CO^-]$

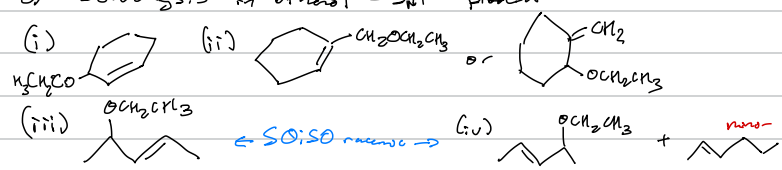
3×2=6 so rate is increased by a factor of 6.

c) Increasing temperature increases overall reaction rate.

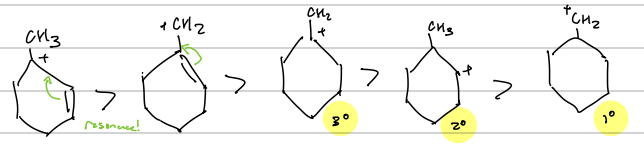
6-41



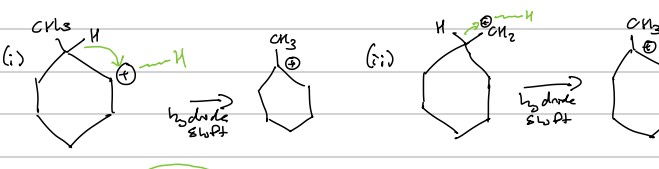
c) Solvolysis in ethanol – SN1 product



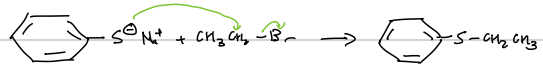
6-42)



6-43)



6-45c)

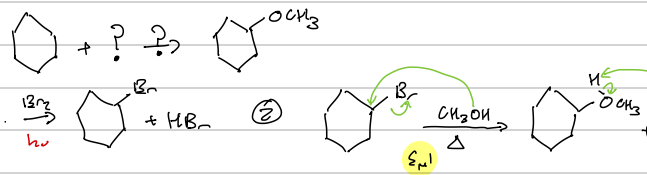


d) $CH_3(CH_2)_8CH_2Cl + Na^+ {}^-{:}C\equiv CH \rightarrow CH_3(CH_2)_8CH_2C\equiv CH$

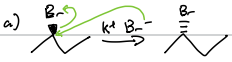
h)

SN2 leads to inversion

6-46e)



6-49 a)

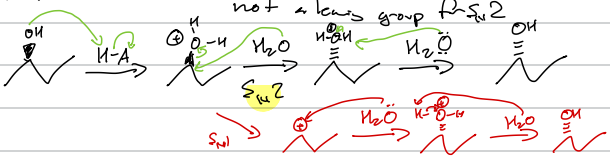


Back side Attack causes inversion on chiral center ← SN2 rxn.

b)

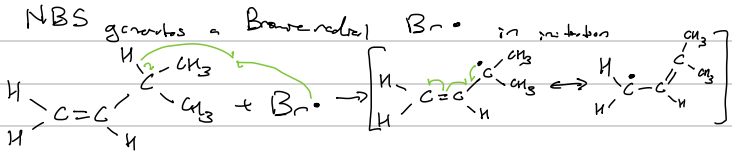
cannot occur because OH is not a leaving group for SN2

c)

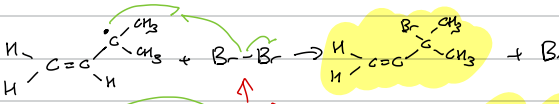


Racemic mixture created as OH was inverted

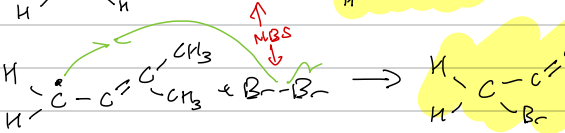
6-50) NBS generates a Br• radical in initiation



(i)



(ii)



Chapter 4 Review

4-2) Dichloromethane from Chloromethane

a) (I) $Cl-Cl \xrightarrow{h\nu} 2\,Cl\cdot$

(PI) $Cl-C(H)_2-H + Cl\cdot \rightarrow Cl-C(H)_2\cdot + HCl$

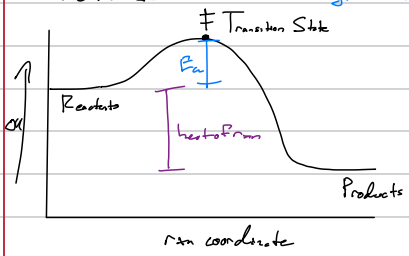
(PII) $Cl-C(H)_2\cdot + Cl-Cl \rightarrow Cl-C(H)_2-Cl + Cl\cdot$

b) The remaining hydrogens on CH_2Cl_2 can react continuously until all hydrogens are used up. Also varying degrees of hydrogens can change products

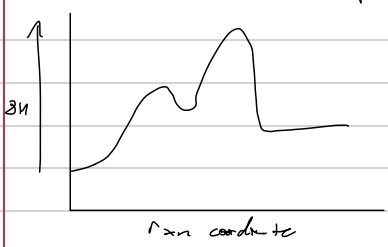
c) Use excess of either reactants

4-36) One-Step Exothermic Rxn

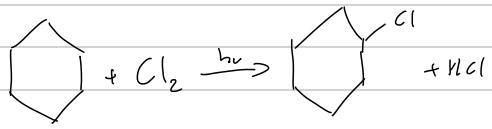
Exothermic = $-\Delta H$ ← given offhand



4-37) Endothermic 2-step with rate limiting second step

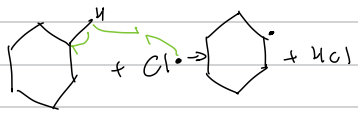


4-44)

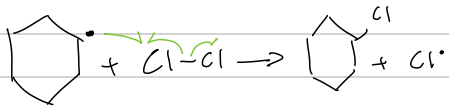


(I) $Cl-Cl \xrightarrow{h\nu} 2\,Cl\cdot$

(Pi)



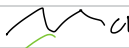
(Pii)



4-46)

Chapter 5 Review

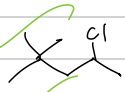
Chapter 6 Review

6-33a) 

faster; Steric effect

b)

faster; I more polarizable

c) 

faster; less branching

d)

; 1° best bc steric

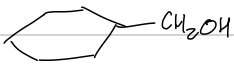
e)

; tertiary > 2°

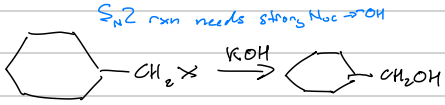
f)

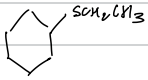
; less steric

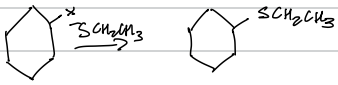
6-34a) $(CH_3)_3C-Cl$; 3° C^+ better

6-35a) 

S_N2 rxn needs strong Nuc → OH



b) 

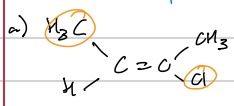


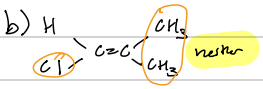
c)

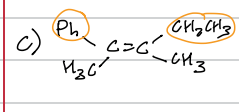
Exam 3 Material

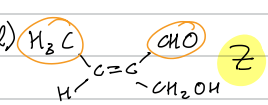
Ch7 HW - 7-41; 7-42a, e, f; 7-47; 7-49a; 7-50c, e; 7-51e; 7-52c, d; 7-54c; 7-55a, d, f; 7-58; 7-61b; 7-62b; 7-65; 7-68

7-41 High priority on Same = Z, different = E

a) 

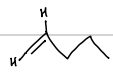
b) 

c) 

d) 

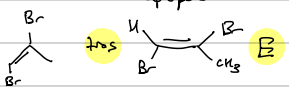
match for multiple double bonds

7-42a) pent-1-ene

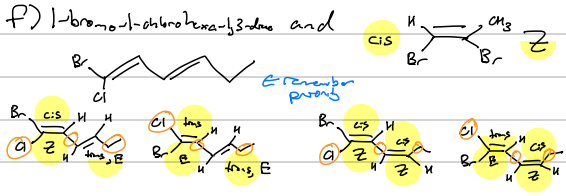


No Isomers

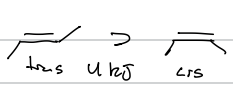
e) 1,2-dibromopropene



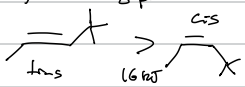
f) 1-bromo-1-chlorohexa-1,3-diene and



7-47 but-2-ene

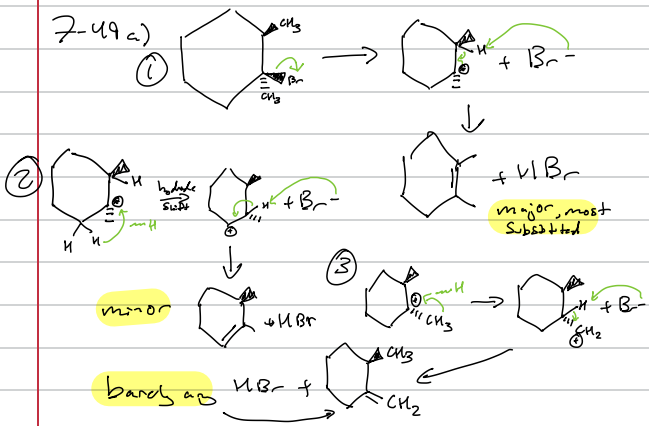


4,4-dimethylpent-2-ene

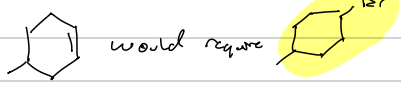


In 4,4-dimethylpent-2-ene, the t-butyl group causes a strong steric effect which greatly decreases stability. The trans config places this group further from the methyl so stability is drastically increased and energy lowered

7-49 a)



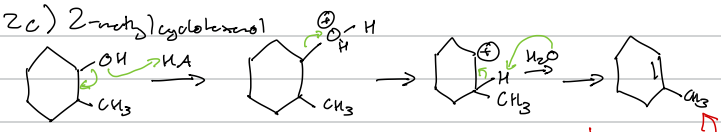
7-50 e) 4-methylcyclohexene



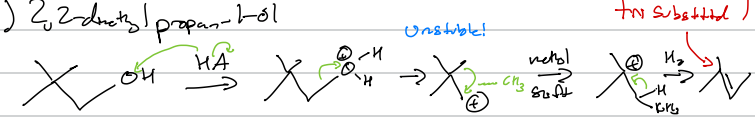
would require

Polar up on B2 vs. B1, then look at comparison with S_N1 and S_N2.

7-52 c) 2-methylcyclohexanol

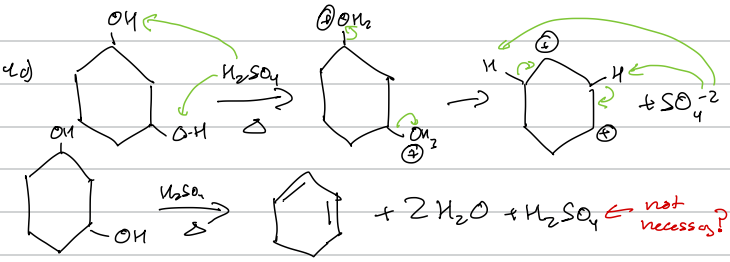


d) 2,2-dimethylpropan-1-ol



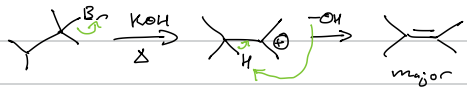
tri substituted

7-54 d)

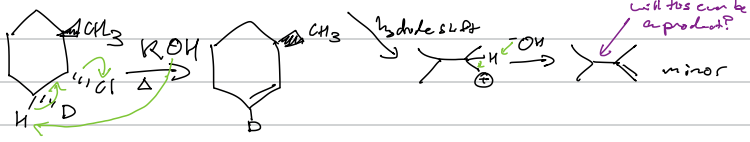


not necessary?

7-55 a)

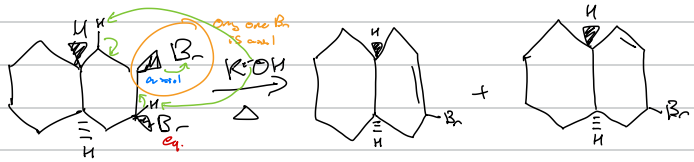


d)



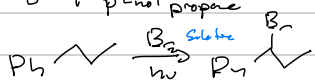
Will this can be a product?

f)



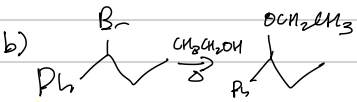
7-58 1-phenylpropene

a)



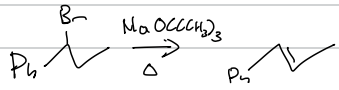
Too much Br_2 may result in dibromination

b)



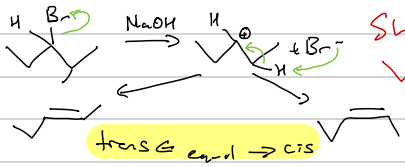
CH_3CH_2OH is weak Nuc, so too much heat may lead to some E1 product

c)



Exclusive Rxn, as KOH is not used → S_N2

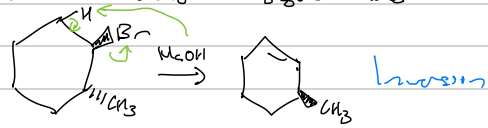
7-60 e) 3-bromopentane



Should be one step

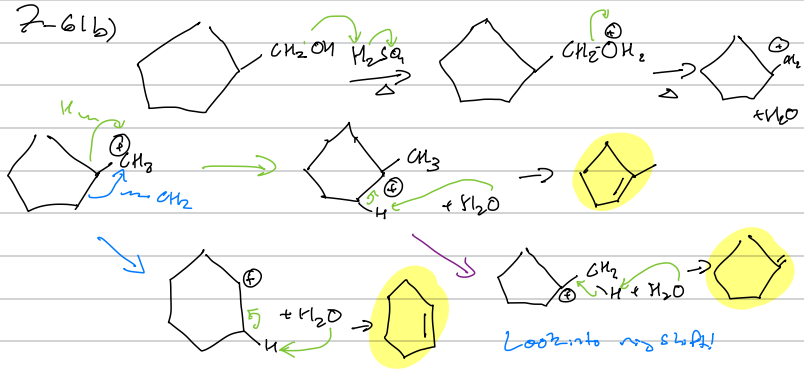
trans ⇌ equil → cis

e) trans-1-bromo-2-methylcyclohexane



Inversion

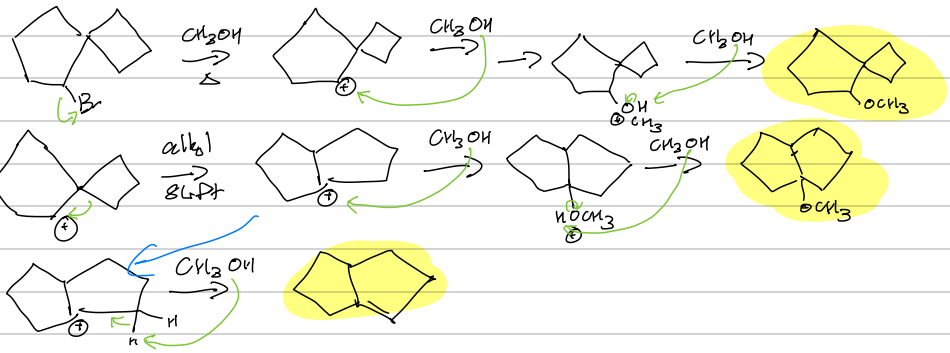
7-61 b)



Look into ring shift!

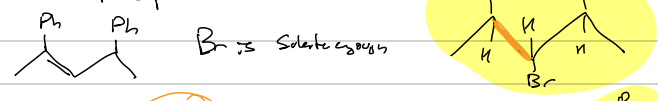
7-62b)

S_N1



E1

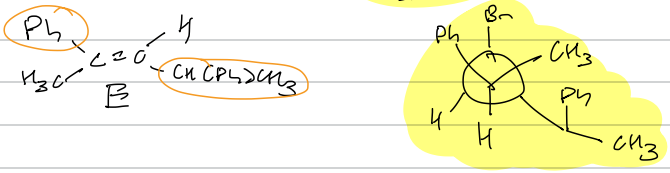
7-65 a) Form only 2,4-diphenylpent-2-ene



Rebuilt on "reverse synthesis" and stereochemistry of reagents/reactants

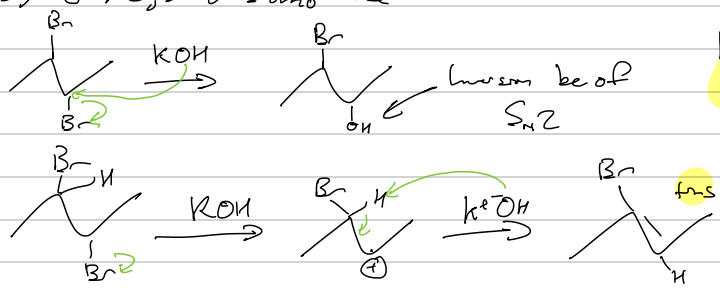
b) Stereochemistry Such that

Br and H must be anti-coplanar



7-68) (±)-2,3-dibromobutane

S_N2

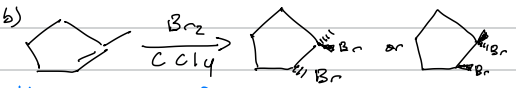


Inversion on chiral C results in trans

H and Br must be anti-coplanar so trans changes to product

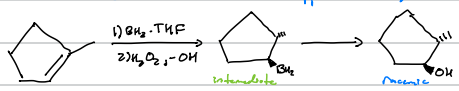
Ch8 HW - 8-46b, c, g, h, o; 8-48d; 8-49e; 8-50a, c, h; 8-51a, f, h; 8-52c; 8-55b; c; 8-56a, c, f; 8-61; 8-64; 8-67; 8-68

8-46b)

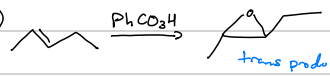


Halogen attacks from opposite sides, Chiral → racemic

c)

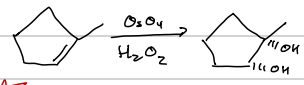


g)



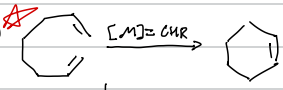
trans product

h)



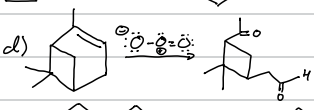
OsO_4 will be Syn Addition

o)



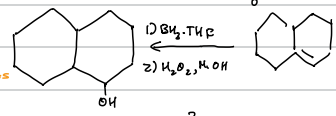
Olefin Metathesis

8-48d)



Ozonolysis

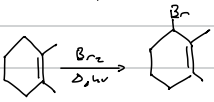
8-49e)



retro-synthesis

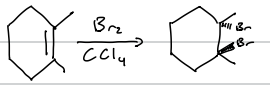
Hydroboration reactants

8-50a)



Free Radical, Br is selective. Position stabilized by Resonance. 2° radical > 1° radical

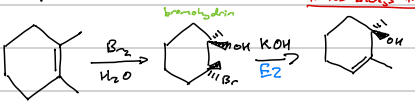
c)



Br_2 with CCl_4 produces anti-addition product

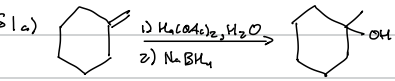
→ is always true?

h)



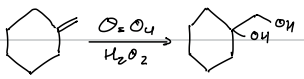
Stereochemistry lost @ Rxl Step. Production of bromohydrine

8-51a)



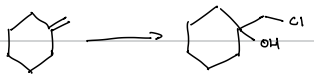
OH on more substituted source Oxymercuration

f)



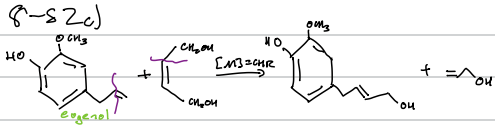
Syn addition, Racemic as well.

h)



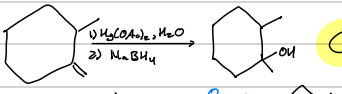
Halohydrin Formation

8-52c)

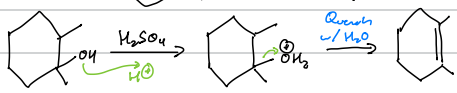


Double bond 'splits and rejoins' with other doublebond

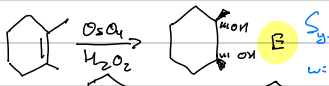
8-55b)



C



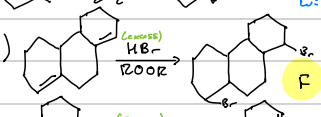
D



E

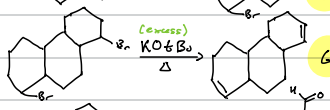
Syn hydrogenation with OsO_4!

c)



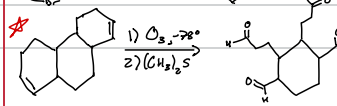
F

Anti-Markovnikov Addition here



G

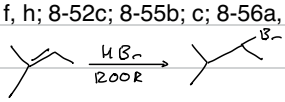
Bulky base leads to less substituted DZ



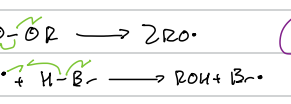
H

Ozonolysis: word of study up a lot more!

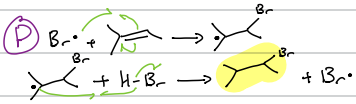
8-56a)



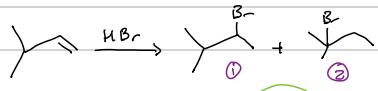
I

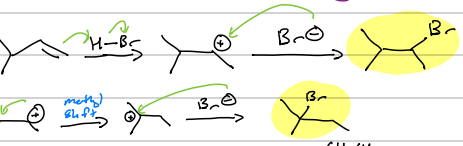


P

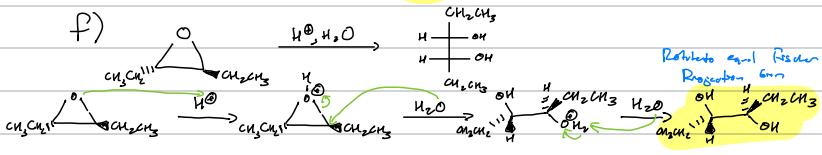


c)

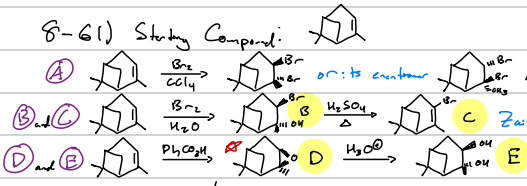




f)



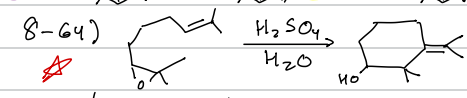
8-61) Starting Compound:



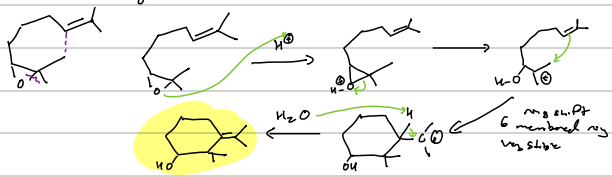
Zaitsev Product

Bredt's Rule: no Double bond @ bridge

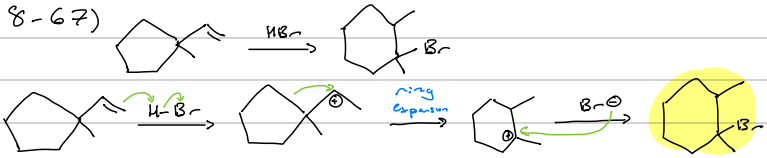
8-64)



Determining which end when carbon bonds are broken

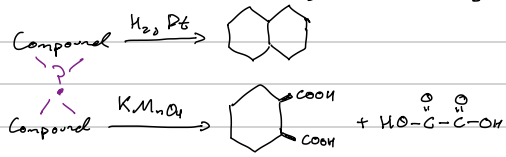


8-67)



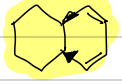
The Rearrangement occurs to have both a 3° Carbocation and a 6-membered ring which is much more stable due to reduced cycle strain on ring carbons.

8-68)



Ozonolysis must occur, so the single compound needs 2 double bonds

Unknown Compound:



Ch9 HW - 9-29; 9-32; 9-33; 9-34; 9-39; 9-43

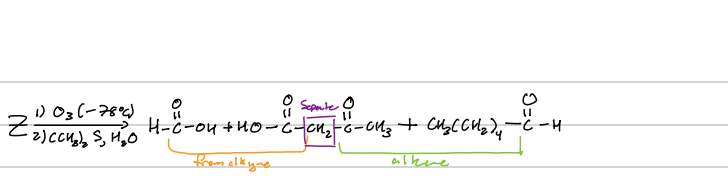
9-29) hexa-1-ene starting, synthesize

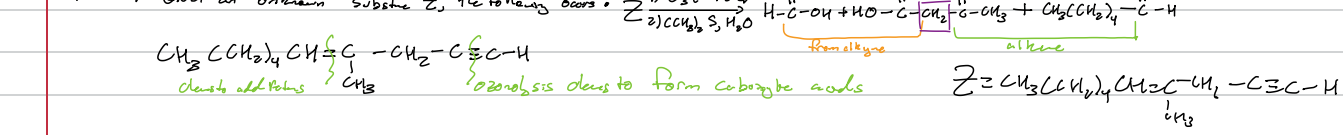
9-32) Synthesize cis-tricos-9-ene

9-33) Predict Products in rxn with pent-1-yne

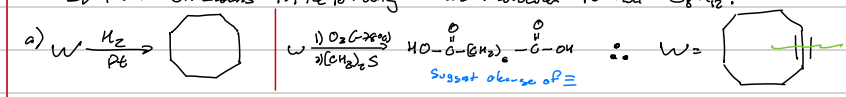
9-34) Show syntheses and reaction intermediates

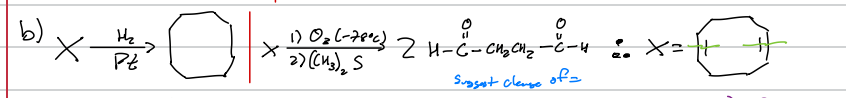
4-39) Given an unknown substrate Z, the following occurs:

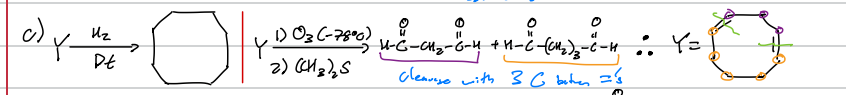


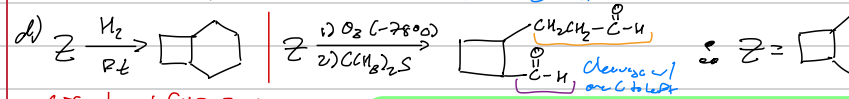


4-43) All unknowns in the following have molecular formula C_8H_{12}.

a) 

b) 

c) 

d) 

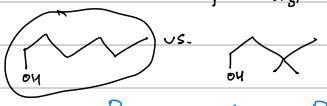
cis-bicyclo[4.2.0]octene

Cleavage lines in green above for unknowns

Ch10 HW - 10-33a; 10-34a; 10-35a; 10-36a, f, g, m, n; 10-37a, e, f; 10-39d, f; 10-40a, d, f; 10-42a, d; 10-49;10-52c; 10-58a

10-33e) Predict Higher BP

hexan-1-ol vs. 3,3-dimethylbutan-1-ol

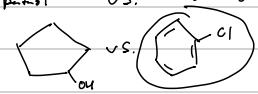


hexan-1-ol has higher BP as its less branched

Branching decreases BP and MP

10-34a) Predict More acidic molecule

Cyclopentanol vs. 3-chlorophenol

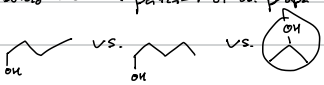


3-chlorophenol is much more acidic since they are considerably more stable as conjugate bases. M_2. charge is easily resonance stabilized.

Phenol groups have resonance

10-35a) Predict highest solubility in water

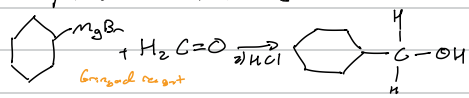
butan-1-ol vs. pentan-1-ol vs. propan-2-ol



propan-2-ol has lowest alkyl group size so it can dissolve in water much easier.

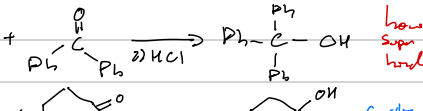
Solubility ↓ as alkyl group ↑ in size

10-36) Predict Rxn Products

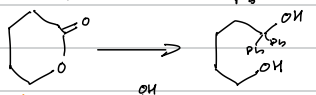
a) 

Grignard reagent

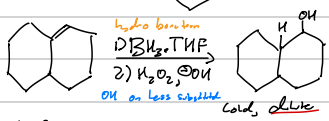
Grignard does substitution S_N2 here

f) 

how is this not super strongly hindered?

g) 

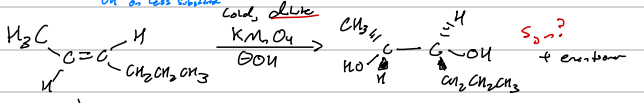
Cyclic ester opens. Olefin bond!

m) 

hydro boration

OH on less substituted

mixture of enantiomers. Hand OH added in syn addition. Both on orbitals trans

n) 

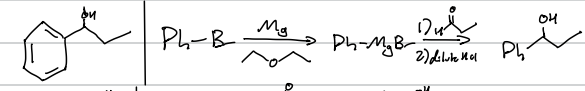
cold, dilute

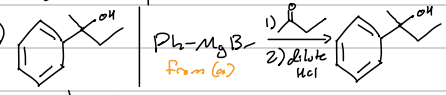
syn?

+ enantiomer

10-37) Synthesize starting with Ph-Br

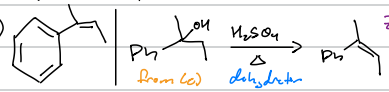
Know how to make Grignard

a) 

e) 

from (a)

typical grignard reaction here too

f) 

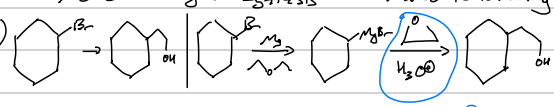
from (c)

dehydration

Zaitsev product

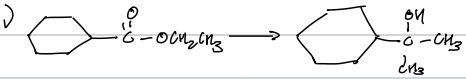
Rearrangements possible for this rxn, watch out!

10-39) Use Grignard synthesis to make the following

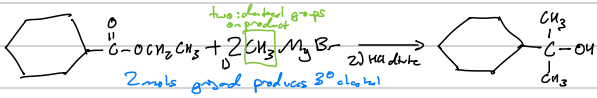
d) 

create grignard → react

Reference for this reaction?

f) 

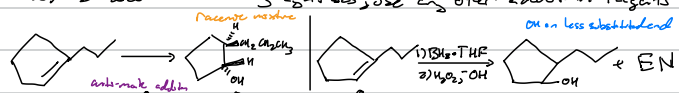
Have 2 mols grignard for tertiary alcohol product



two identical groups on product

2 mols grignard produces 3° alcohol

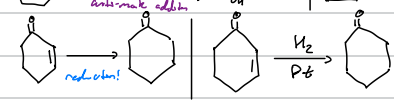
10-40) Show the following syntheses, use any other additional reagents

a) 

racemic mixture

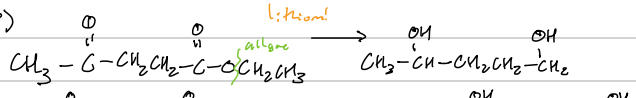
anti-markov addition

OH on less substituted end

d) 

reduction!

C=O reduced much slower than C=C bond.

f) 

Lithium!

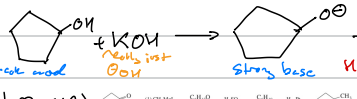
allyl

10-42) Complete rxns and determine equilibrium favor

a) $CH_3CH_2-O^\ominus + Ph-OH \rightleftharpoons CH_3CH_2-OH + Ph-O^\ominus$

weaker acid, weaker base, more stable base

Products favored, compounds more stable

d) 

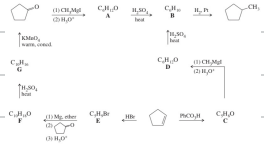
weak acid

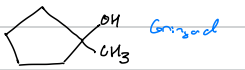
KOH reacts just $^\ominus OH$

strong base

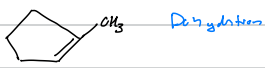
Reactants favored due to stability

H_2O vs. KOH pKa, but the same?

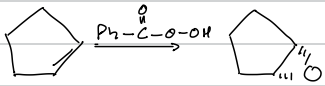
10-49) 

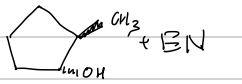
A) 

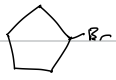
Grignard

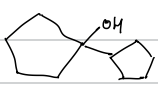
B) 

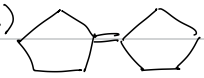
Dehydration

C) 

D) 

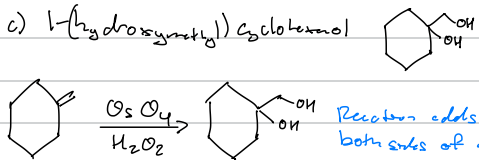
E) 

F) 

G) 

10-52) Synthesize starting with methylenecyclohexane

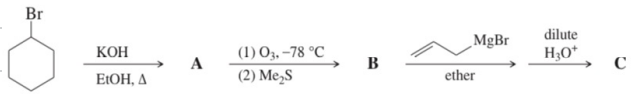
c) 1-(hydroxymethyl) cyclohexanol



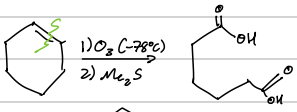
Reaction adds OH to both sides of double bond

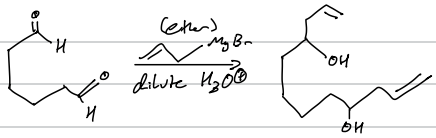
Syn stereochemistry with OsO_4

10-58) Predict Products For each synthesis step

a) 

A)

B) 

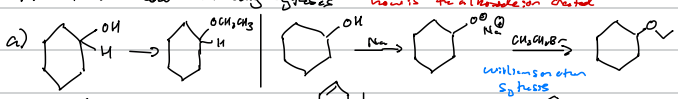
C) 

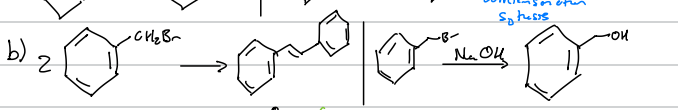
(ether)

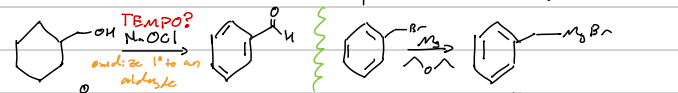
dilute $H_3O^\oplus$

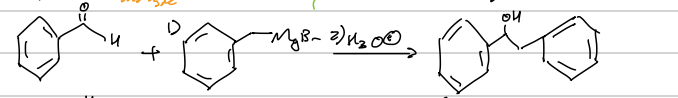
Ch11 HW - 11-42; 11-46; 11-47; 11-48c, e; 11-49b, e; 11-50; 11-52; 11-54; 11-55c, 11-56a, b

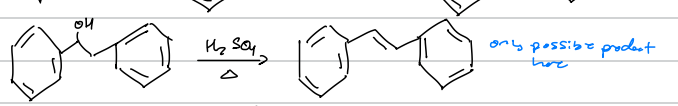
11-41) Show the following S_N2 rxns — how is the alkoxide ion created

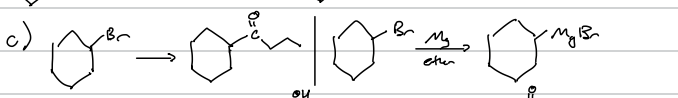
a) 

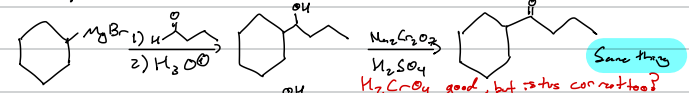
b) 

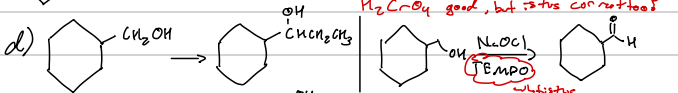


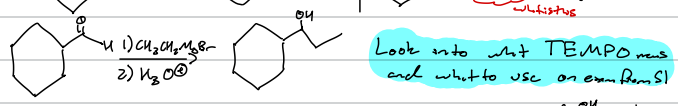




c) 



d) 



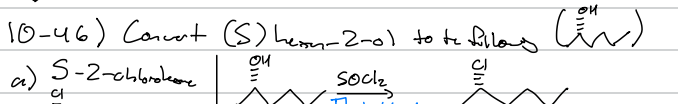
Look into what TEMPO means and what to use on exam Rem 51

Recall ch5
R = clockwise
S = counterclockwise

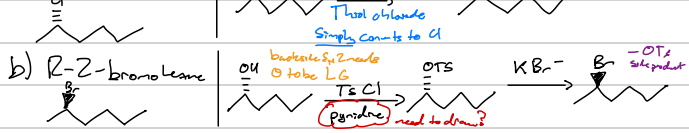
Pyridine

10-46) Convert (S)-hexan-2-ol to the following

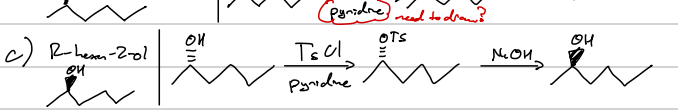
a) S-2-chlorohexane



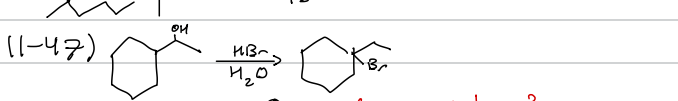
b) R-2-bromohexane

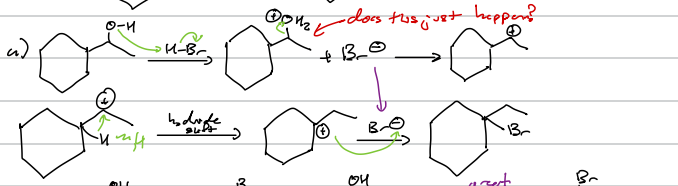


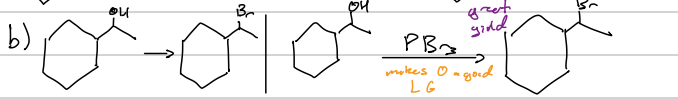
c) R-hexan-2-ol



11-47)

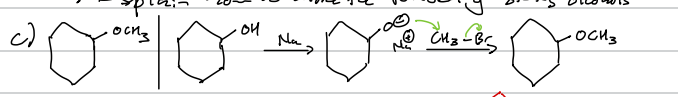


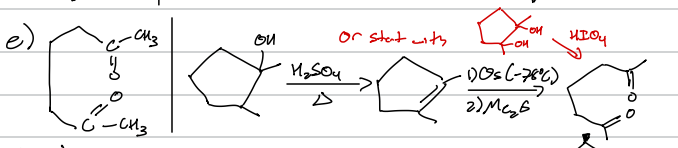
a) 

b) 

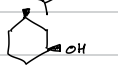
PBr_3 uses displacement and S_N2 to replace Br

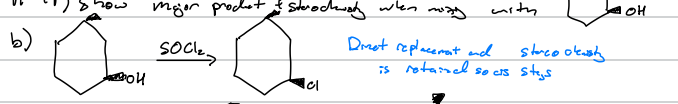
11-48) Explain how to make the following stereo alcohols

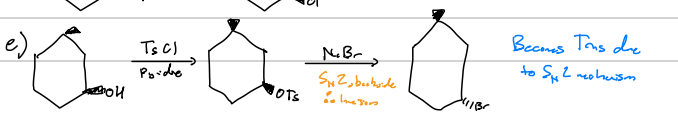
c) 

e) 

11-49) Show major product & stereochemistry when rxn with



b) 

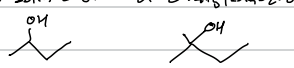
e) 

11-50) Show how to distinguish between these in each pair

a) butan-1-ol and butan-2-ol

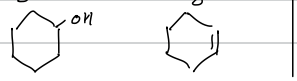
I will use the Lucas Test as 1° alcohols will not react at all with $ZnCl_2$ in HCl.

b) butan-2-ol and 2-methylbutan-2-ol



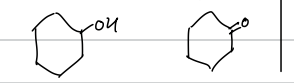
I will use the Lucas test. 3° react in around a min (quick), 2° react slower (1-5 min)

c) cyclohexanol and cyclohexene



I will use the Lucas test. 2° alcohol will react slowly (1-5 min) but alkene will not react at all.

d) Cyclohexanol and cyclohexanone

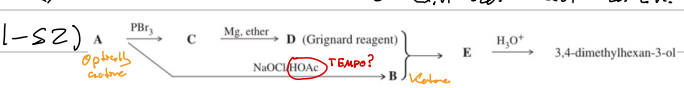


I will use the Lucas test. 2° alcohol will react slowly (1-5 min) but Ketone will not react at all.

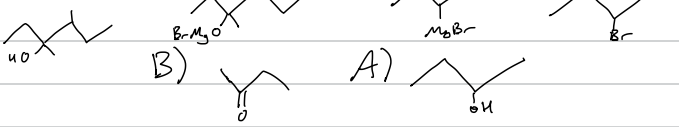
e) Cyclohexanone and 1-methylcyclohexanol

I will use the Lucas test. 3° alcohol will react quickly (1 min) but Ketone will not react at all.

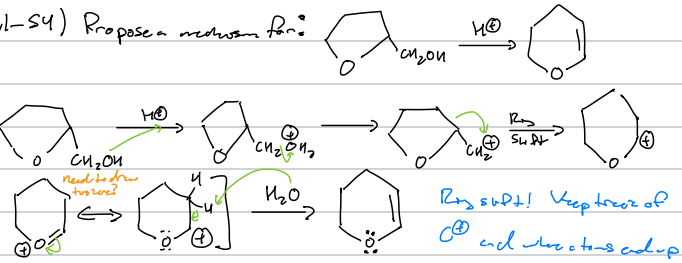
11-52)



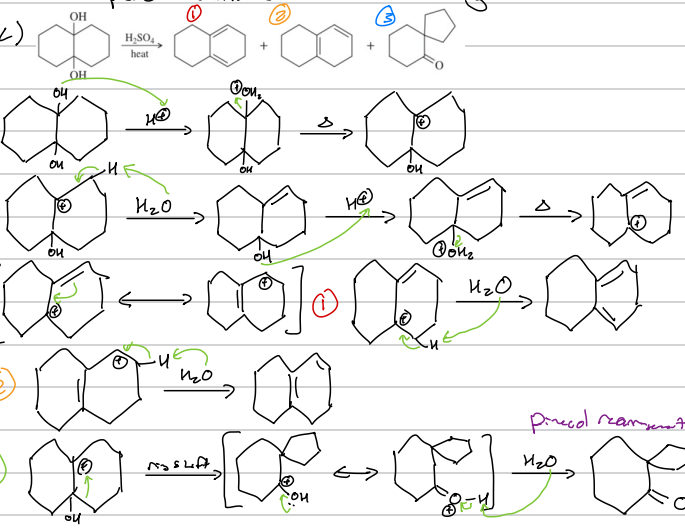
Desired Product



11-54) Propose a mechanism for:

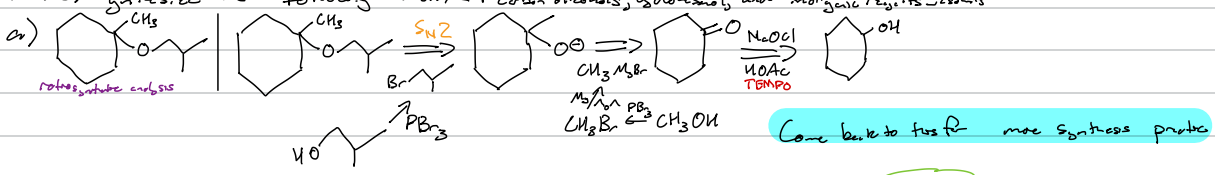


11-55) Propose mechanisms for the following

c) 

11-56) Synthesize the following from <4 carbon alcohols, cyclohexanol, and inorganic reagents/solvents

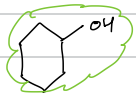
a)



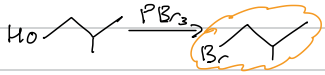
Come back to this for more synthesis practice

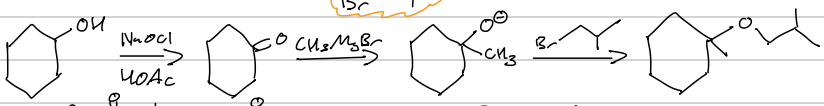
Reactant 1: $CH_3OH \xrightarrow{PBr_3} CH_3Br \xrightarrow[\text{Et}_2\text{O}]{Mg} CH_3MgBr$

Starting Material:

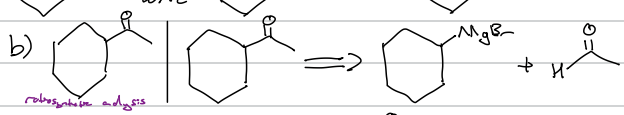


Reactant 2:

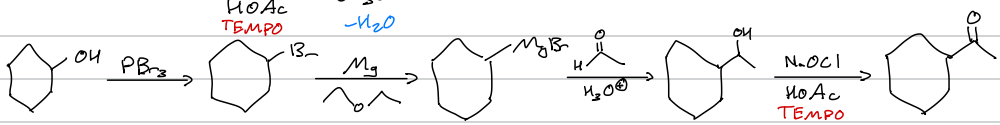




b)



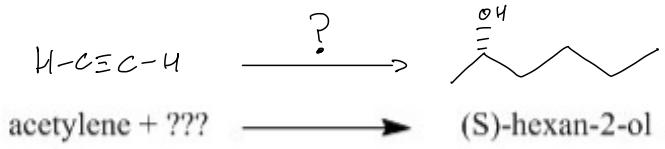
Reactant: $CH_3CH_2OH \xrightarrow[\text{HOAc, TEMPO}]{\text{NaOCl}} CH_3C(=O)-H$ ($-H_2O$)



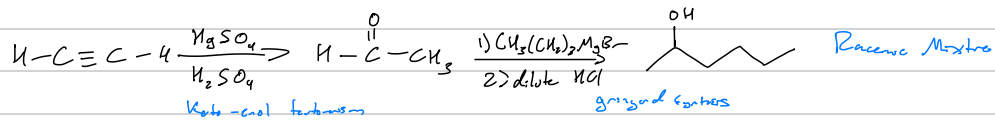
Trevor Swan
tcs94

Extra Credit Synthesis

Provide a synthetic strategy in four steps or less to complete the following chemical transformation in > 50% yield. You must using acetylene as one of the starting materials and additional reaagents that can be purchased from www.sigmaaldrich.com. You must provide the catalogue numbers of all the reagents in your answer. You do not need to provide any mechanism.



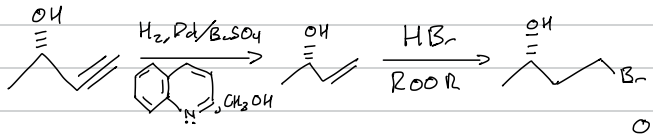
www.sigmaaldrich.com

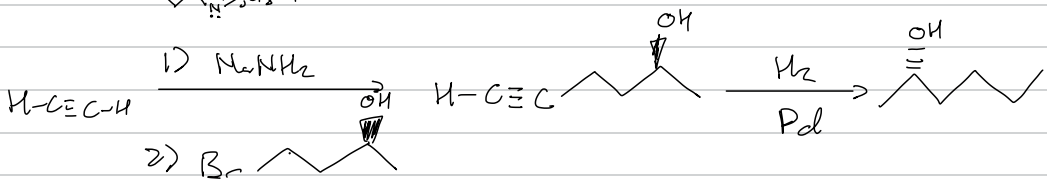


1

• Low yield of enantiomers due to lack of possible rearrangements. Reactions are not occurring in acidic/base conditions so equilibrium is not happening.

Would have to use advanced techniques to separate enantiomers.





2

Good Yield, but 5 steps which is bad

Reagent Links

Synthesis path one:

- HgSO4: Mercury(II) sulfate = 7783-35-9
- H2SO4: Sulfuric acid concentrate = 7664-93-9
- But-MgBr: Butylmagnesium chloride solution = 693-04-9
- HCl: Hydrochloric acid = 7647-01-0

4 reagents on aldrich to synthesize hexan-2-ol from acetylene. Should be (S)-hexan-2-ol, but a racemic mixture would be created here. Suspicious synthesis, though Oswin said it's ok?

Synthesis path two:

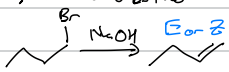
- (S)-Alcohol: (S)-(-)-3-Butyn-2-ol = 2914-69-4
- Lindlar: Barium Sulfate = 7727-43-7, Quinoline = 91-22-5, Methanol = 67-56-1
- HBr: Hydrobromic acid = 10035-10-6
- ROOR: tert-Butyl peroxide = 110-05-4
- NaNH2: Sodium amide = 7782-92-5
- H2: Hydrogen = 1334-74-0
- Pd: Palladium = 7440-05-3

While this synthesis produces a product with correct configuration, the issue lies within the fact that it is a 5 step process, while we are required to use 4 or less steps.

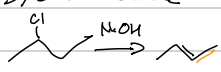
Chapter 7 Review

7-50) NaOH promoted dehydrohalogenation

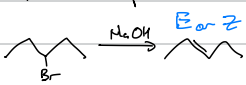
a) 1-bromobutane



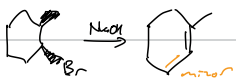
b) 2-chlorobutane



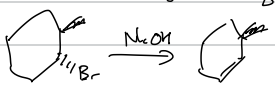
c) 3-bromopentane



d) cis-1-bromo-2-methylcyclohexane



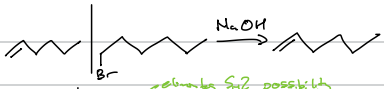
e) trans-1-bromo-2-methylcyclohexane



E2 needs anticoplanar, so H on methyl carbon cannot be abstracted!

7-51) Predict Reactant for E2 product

a)



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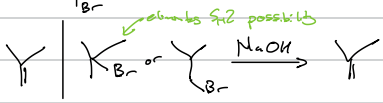
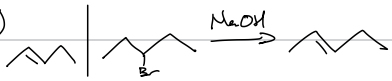
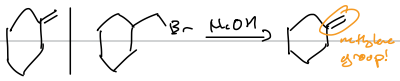


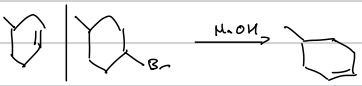
c)



d)

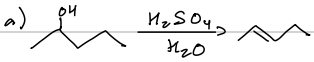


e)



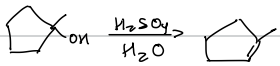
7-52) Predict Major Products from ACD

a)



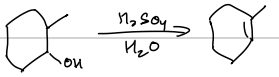
Zaitsev Product

b)



Zaitsev Product

c)

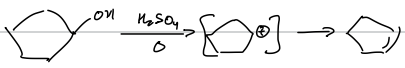


Zaitsev Product

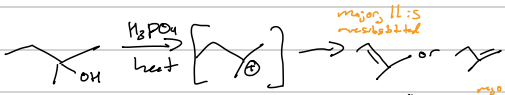
d)

7-53) Predict products from ACD

a)



b)



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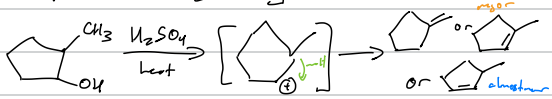
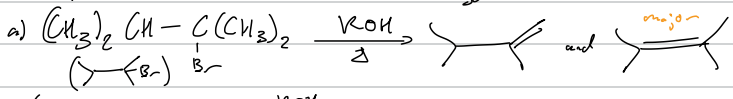
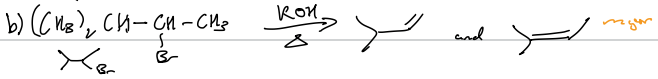


7-55) Predict Product from KOH dehydrohalogenation

a)

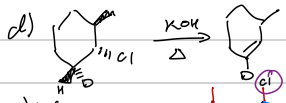


b)



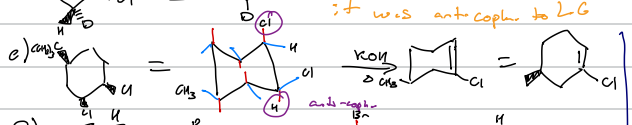
c)

d)

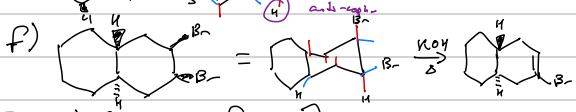


D could be abstracted if it was anticoplanar to LG

e)



f)



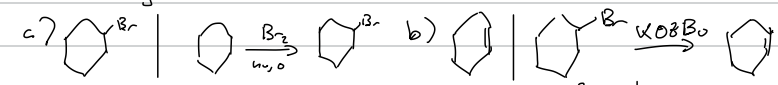
Must draw chair!

Draw other chair conformation to get full credit on conformations where H is axial

7-56) Synthesize from

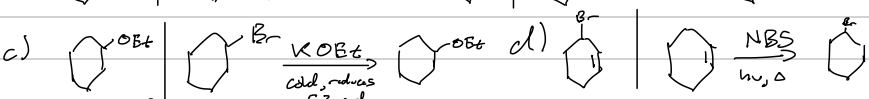
a)

b)



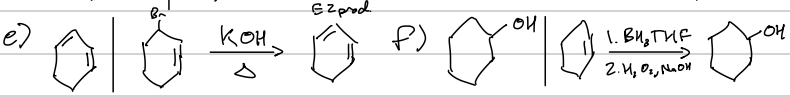
c)

d)



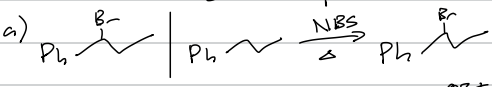
e)

f)



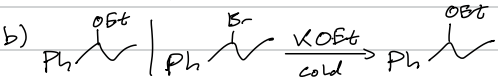
7-58) Provide Syntheses to produce the following from Ph ~ in 1/2 steps

a)



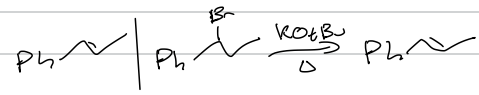
Br is

b)



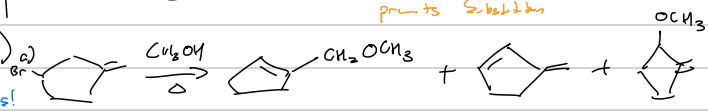
Keep cold so SN1 favorites over E1

c)

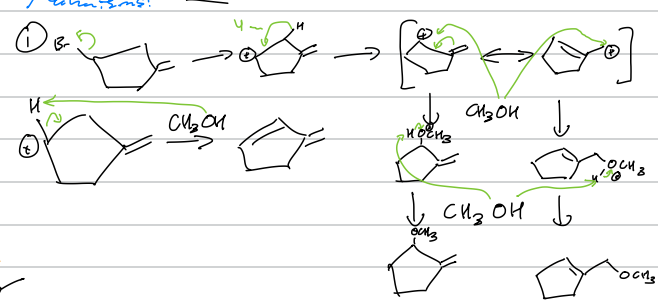


hindered base prevents substitution

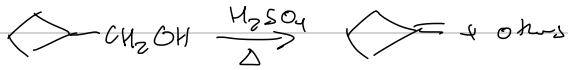
7-62) a)

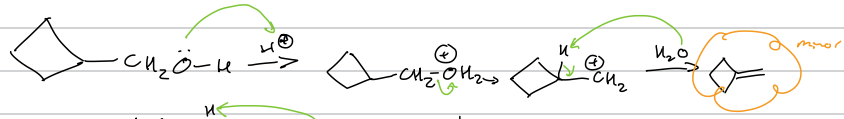


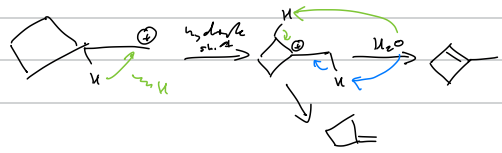
Mechanisms!



7-72)







Mac strike by the major product

HOW TO PREDICT S_N vs. E MECHANISMS

Is the base/nucleophile strong or weak?

STRONG (like HO^- or RO^-) — Second order: S_N2, E2

WEAK (like H_2O or ROH) — First order: S_N1, E1

Type of carbon with leaving group

- 1°, CH_3, esp. benzylic and allylic → S_N2 > E2; easy for nucleophile to attack electrophilic carbon; higher temperature and hindered base favor elimination
- 2° → S_N2 and E2; higher temperature and hindered base favor elimination
- 3° or hindered → E2 (S_N2 extremely slow)

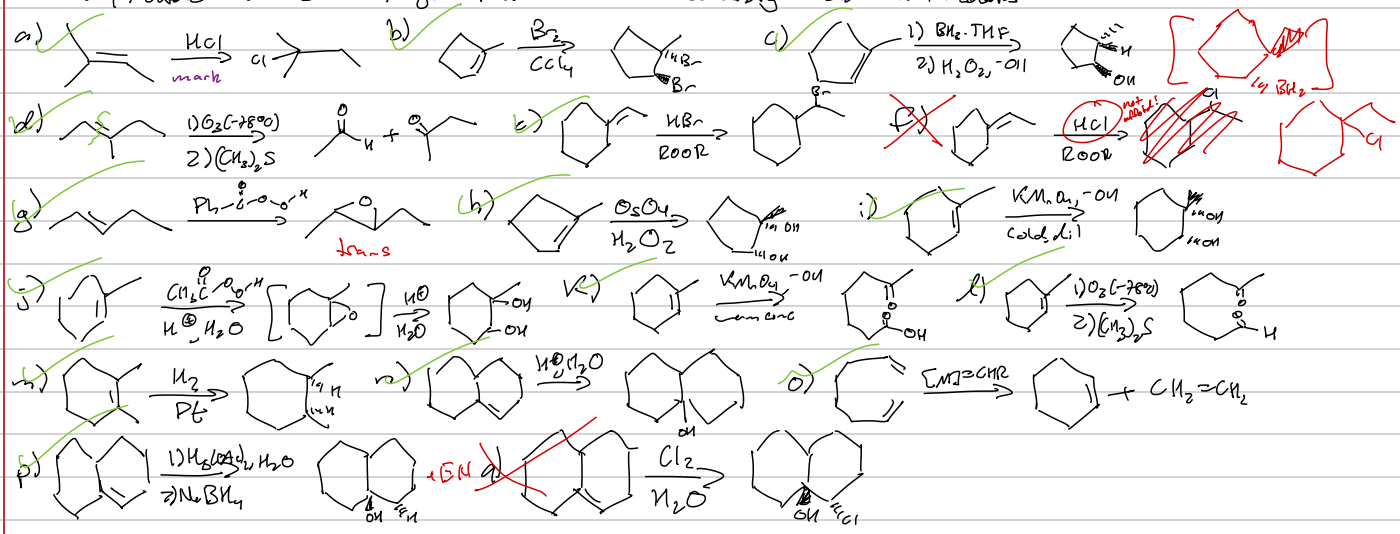
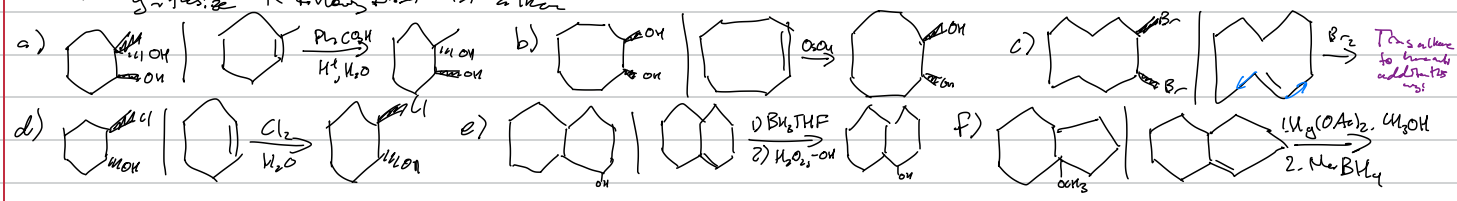
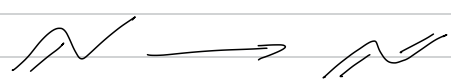
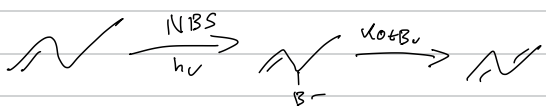
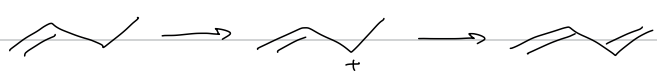
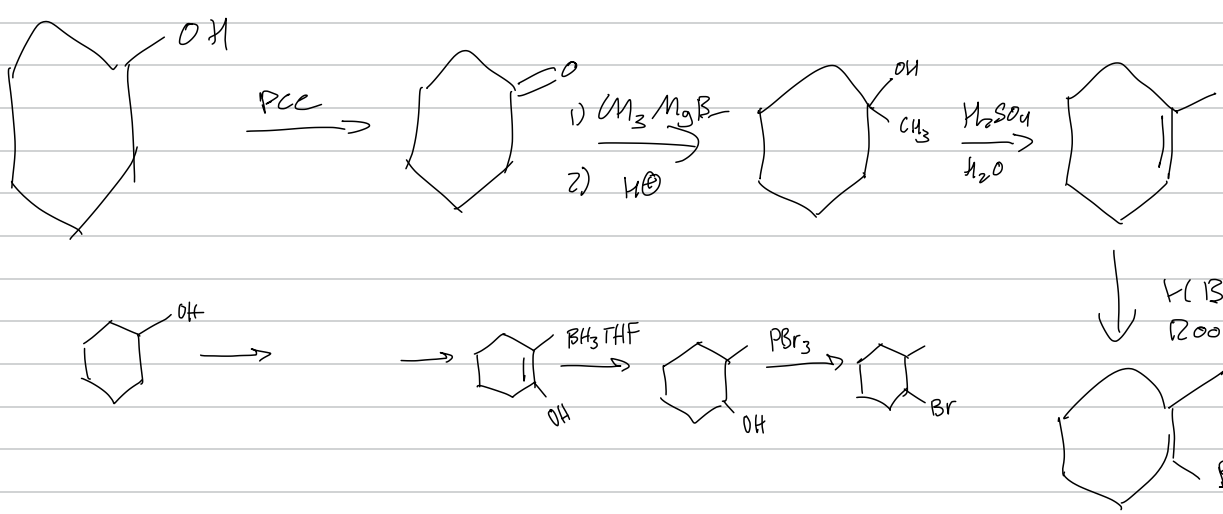
Note: a methyl halide cannot undergo elimination.

Type of carbon with leaving group

- 2°, 3°, allylic, benzylic → S_N1 and E1; higher temperature and hindered base favor elimination
- 1°, CH_3 → no appreciable reaction, very slow

Chapter 8 Review

8-46) Provide Structures of Major Products w/ Stereochemistry and intermediates



8-49) Synthesize the following from an alkene