Concordia
UNIVERSITY

SOLUTIONS.

COURSE: ORGANIC CHEMISTRY I	NUMBER: CHEM 221	SECTION: f2 01	
EXAMINATION: FINAL EXAMINATION	DATE: DECEMBER 4, 2003	TIME: 9:30 am	
INSTRUCTOR: DR. CERRIE ROGERS			

NOTE: different textbook used
∴ topics covered NOT same!

MATERIALS ALLOWED:	☐ NO	☒ YES (PLEASE SPECIFY)	MOLECULAR MODEL KITS
CALCULATORS ALLOWED:	☐ NO	☒ YES	

LAST NAME: Rogers. FIRST NAME: _____

STUDENT NUMBER: _____ SIGNATURE: _____

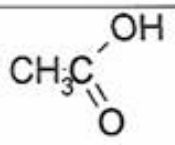
Instructions:

- ***Make sure your exam has 12 pages including this cover page and the periodic table.***
- ***Write your name on all pages.***
- ***Write all answers in the space provided.***
- ***You must answer ALL of the first 14 questions. The final question is an optional bonus question.***
- ***Read questions carefully before answering.***
- ***Molecular models and calculators are allowed.***
- ***A periodic table and table of pK_a values are provided.***

Mark breakdown:

---		Page 7.	/ 12
Page 3.	/ 17	Page 8.	/ 15
Page 4.	/ 9	Page 9.	/ 16
Page 5.	/ 15	Page 10.	/ 18
Page 6.	/ 10	Page 11.	/ 6 BONUS
		TOTAL:	/ 112 (MAXIMUM MARK = 120)

TABLE OF pKa VALUES

Compound	pK_a
$CH_3CH_2CH_2CH_3$	>51
CH_4	51
NH_3	38
HCCH	25
$(CH_3)_3COH$	19
CH_3CH_2OH	17
CH_3OH	15.5
H_2O	15.7
HCN	9
	4.7
HF	3.2
HN_3	3
$CH_3CH_2OH_2+$	-2.4
H_2SO_4	-5.2
HCl	-7
HI	-9

Rogers

Name: * = ambiguous question (would not ask this way again) CHEM 221 /2 01

#1. **(14 MARKS)** Circle TRUE or FALSE for the following statements.

H-bonding! no H-bonding

a) n-Butanol has a lower boiling point than diethyl ether. TRUE/(FALSE)

*b) According to IUPAC rules, an alcohol has priority over a halide. (TRUE)/FALSE
↳ for naming yes; for R/S nomenclature, no!

c) Stereoisomers are molecules that have the same connectivity of atoms, but different 3-dimensional arrangements of these atoms. (TRUE)/FALSE

d) If we know the R/S configurations of the stereocentres in a chiral molecule, we can predict the direction in which that molecule will rotate plane-polarized light. TRUE/(FALSE)

e) A racemic mixture can be "resolved" into pure enantiomers if we can convert the enantiomers into diastereomers using a chemical reaction that can later be reversed. (TRUE)/FALSE

f) An electron donating substituent on the carbon adjacent to the nitrogen atom increases the basicity of an amine. (TRUE)/FALSE

g) Markovnikov's rule is based on the fact that an electrophile will add to a π-bond to yield the more stable carbocation intermediate. (TRUE)/FALSE

h) In an elimination reaction, the thermodynamically favoured alkene product is known as the Saytzeff (or Zaitseff) product. (TRUE)/FALSE

i) Polar protic solvents stabilize carbocationic intermediates. (TRUE)/FALSE

j) Highly polarizable, or "soft", Lewis bases interact better with protons than with electrophilic carbon atoms. TRUE/(FALSE)
↳ Lewis base as base... ↳ as nucleophile

k) It is easier to deprotonate an sp^3 hybridized carbon than an sp hybridized carbon. TRUE/(FALSE)

l) $AlCl_3$ is a powerful nucleophile. TRUE/(FALSE)
electrophile!

m) A Lewis base can act both as a nucleophile and as a Brønsted base. (TRUE)/FALSE

n) When treated with sodium iodide in acetone solution, a tertiary alkyl halide will react faster than a primary alkyl halide. TRUE/(FALSE)
↑good Nu ↑aprotic ⇒ SN2

#2. **(3 MARKS)** Lithium diisopropyl amide $[(CH_3)_2CH]_2N^-$, known as "LDA", is commonly used as a base in organic transformations. Which of the following reagents could be used to completely deprotonate diisopropyl amine $[(CH_3)_2CH]_2NH$ in order to prepare this anion?

I LiF WEAK!
HF $pK_a = 3.2$

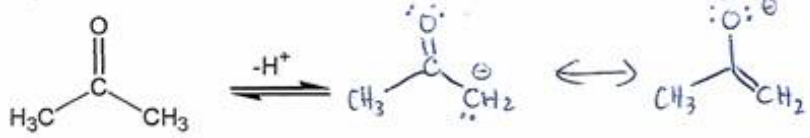
II CH_3CH_2OLi
CH_3CH_2OH $pK_a = 17$

no amine listed
but NH_3 $pK_a = 38$.

III $CH_3CH_2CH_2CH_2Li$
$CH_3CH_2CH_2CH_3$ $pK_a > 51$
↳ only base stronger than $NH_2^\ominus$ is $CH_3CH_2CH_2CH_2^\ominus$
↳ only one strong enough to deprotonate an amine.

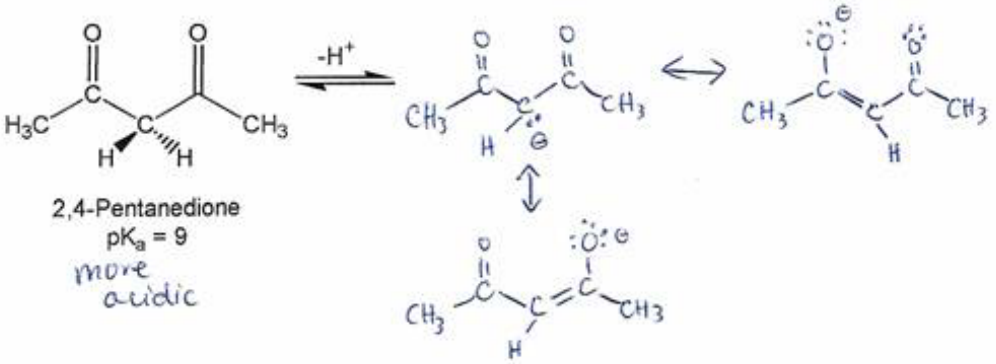
a) I, II, and III
b) I and II only
c) II and III only
d) I only
(e) III only

#3. (4 MARKS) 2,4-Pentanedione is considerably more acidic than propanone (acetone). Draw the structure of the conjugate base of each acid, and account for the greater stability of the conjugate base of 2,4-pentanedione.



2-Propanone
$pK_a = 22$

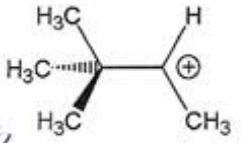
only 2 resonance structures



2,4-Pentanedione
$pK_a = 9$
more acidic

3 resonance structures
∴ the lone pair is more extensively delocalized
∴ more stable (less basic)

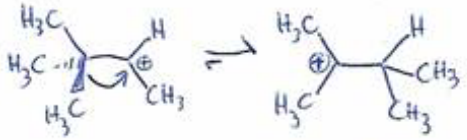
#4. (5 MARKS) Imagine that the following carbocation has formed:



a) Why is this species so reactive?

The carbocationic centre is a carbon with an open valence ($6e^-$'s in valence shell). It is highly electrophilic, because the charge of the nucleus has not been fully compensated by electrons!

b) What will this species do immediately after forming in order to increase its stability? Illustrate this process with curved arrows representing the movement of electrons, AND explain why this process increases the stability of the carbocation.



A 1,2-methyl shift will occur, where the CH_3-C bonding pair on an adjacent C moves into the empty p orbital.

The result: the C originally bearing the ⊕ charge now has a new bond to it & has a full valence. The C⊕ centre is now the adjacent 3° carbon. This new carbocation is more stable due to inductive electron donation by the 2 methyl groups + 1 isopropyl group. The original 2° carbocation was only stabilized by 2 e^--donating groups (EDG's).

c) Name a type of reaction that involves a carbocation intermediate.

SN1
E1
electrophilic addition (except for hydroboration + radical hydrohalogenation)

#5. **(3 MARKS)** Which reaction in each of the following pairs will take place more rapidly?

a) $CH_3Br + NH_3 \longrightarrow CH_3NH_3^+ + Br^-$ (stronger Nu) faster SN2 rxn

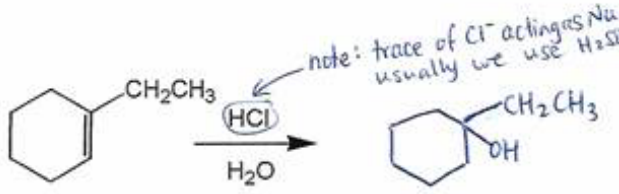
$CH_3Br + H_2O \longrightarrow CH_3OH_2^+ + Br^-$ (weaker Nu)

b) $(CH_3)_3CBr + CH_3O^- \xrightarrow{CH_3OH} (CH_3)_3COCH_3 + Br^-$ (protic solvent) faster SN1 rxn (via carbocation...)

$(CH_3)_3CBr$ (3°) + CH_3O^- $\xrightarrow[\text{aprotic solvent}]{H_3CCCH_3 (O)}$ $(CH_3)_3COCH_3 + Br^-$

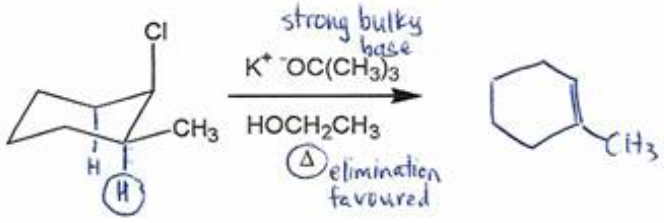
#6. **(12 MARKS)** The major product(s) of the following reactions would be:

a) $H_3C-C\equiv C-H \xrightarrow{NaNH_2} H_3C-C\equiv C:^{\ominus}\ Na^{\oplus} \xrightarrow{BrCH_2CH_3} H_3C-C\equiv C-CH_2CH_3$

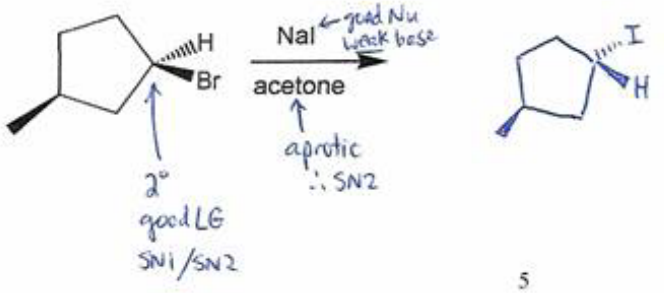
b) 

note: trace of Cl^- acting as Nu usually we use H_2SO_4 instead!

(achiral) Markovnikov addition of H_2O

c) 

Zaitsev product
base is bulky, but H is not terribly hindered so the more substituted alkene WILL be formed.

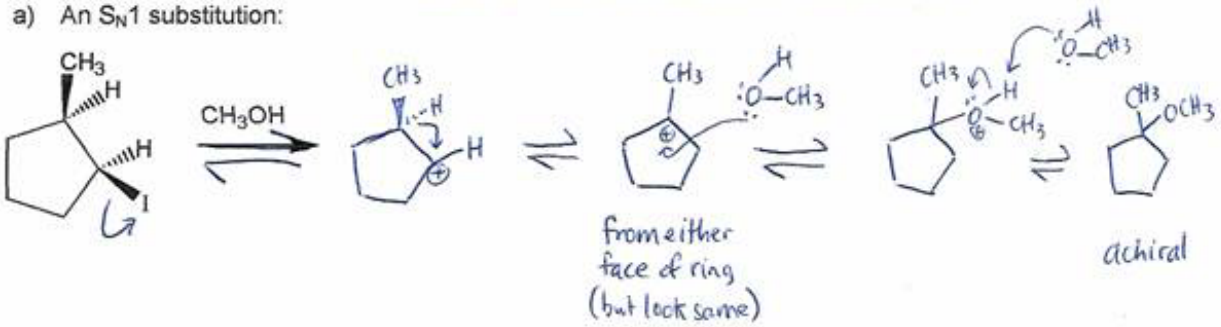
d) 

inverted stereochem. dominates (SN2)

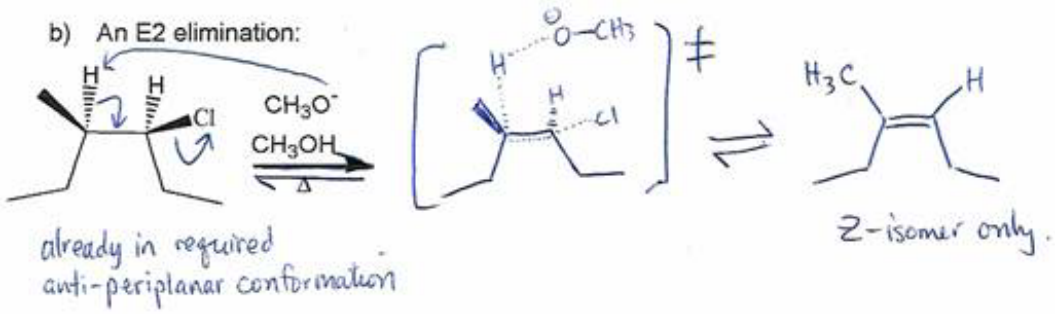
#7. (10 MARKS) Write mechanisms for ***TWO*** of the following reactions. Show full, detailed mechanisms that illustrate step-by-step how the reaction occurs: use curved arrows for "electron pushing", include the transition state and all intermediates (show rearrangements where appropriate), and clearly indicate the stereochemistry of the products.

ONLY IF RXN IS ONE-STEP (CONCERTED)

a) An S_N1 substitution:

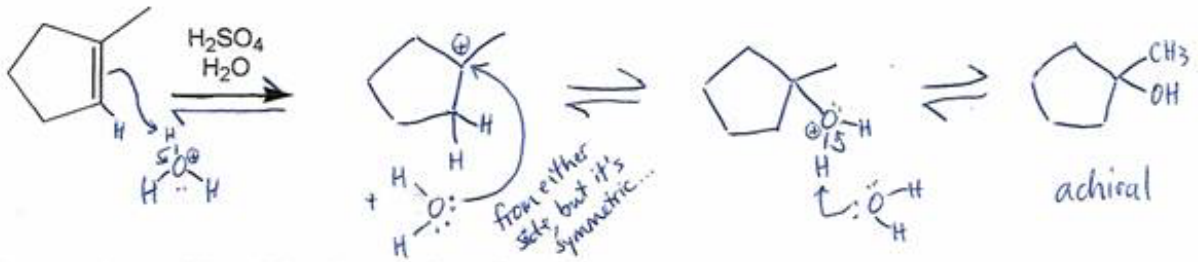


b) An E2 elimination:

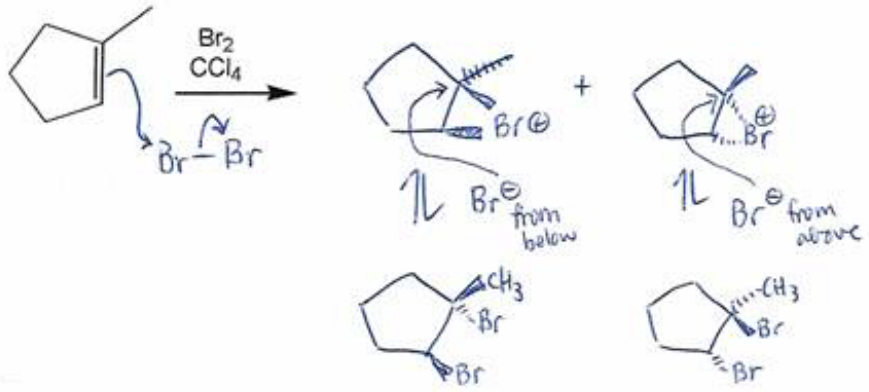


already in required anti-periplanar conformation

c) An electrophilic addition: hydration of an alkene:



d) An electrophilic addition: bromination of an alkene:



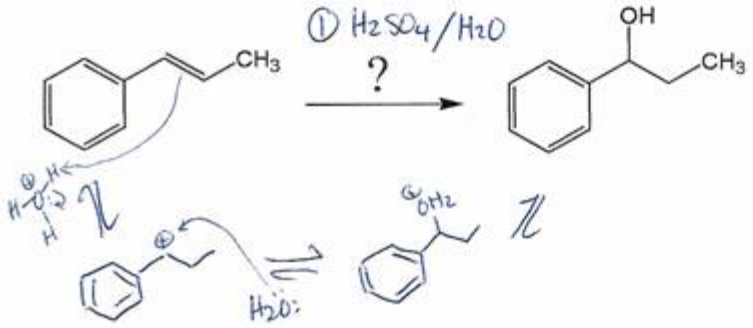
Name: Rogers CHEM 221 /2 01

only required to show these (not mechanisms)

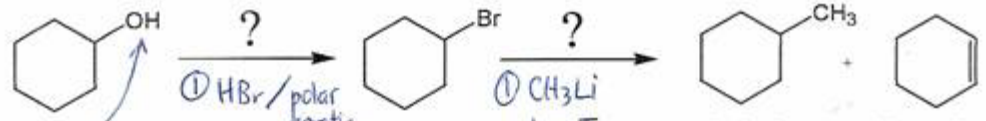
#8. **(12 MARKS)** Suggest reagents and solvents for each of the following synthetic transformations.

Note that these transformations may require more than one step.

a)



b)

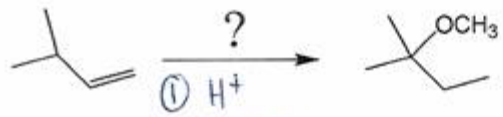


poor LG must be converted to good LG by protonating it!
then gets displaced by the Br^-

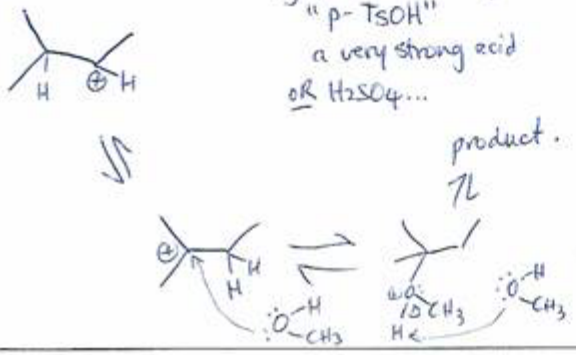
($CH_3^\ominus$ is a STRONG base!)

minimize elimination by lowering temp.

c)



eg. protonated tosylate
"p-TsOH"
a very strong acid
OR H_2SO_4...



Many other possibilities (less efficient)

A { ① H_2SO_4/H_2O ② KOH/CH_3OH ③ CH_3Br/CH_3OH

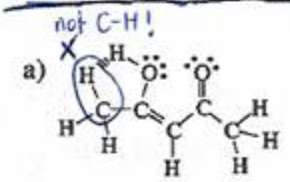
B { ① H_2SO_4/H_2O ② CH_3OH / cat. H^+

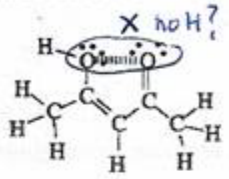
etc...

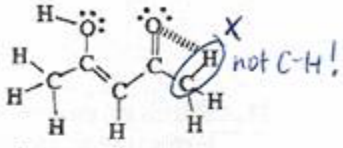
Name: Rogers CHEM 221 /2 01

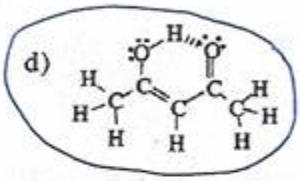
PART B

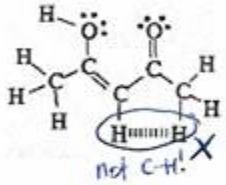
#9. **(3 MARKS)** CIRCLE YOUR CHOICE. The "enol" form of acetylacetone is stabilized by an intramolecular hydrogen bond. Which of these structures best represents this enol form?

a) 

b) 

c) 

d) 

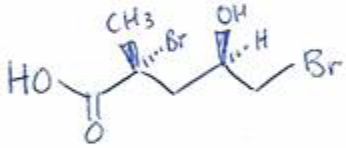
e) 

Requires:
① H bonded to N, O or F only
② lone pair on N, O, or F to interact with δ+ H from ①

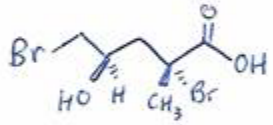
#10. **(8 MARKS)** Draw 3-dimensional representations of the following compounds, showing the stereochemistry of the stereocenters.

we did not cover these this term. (W2005)

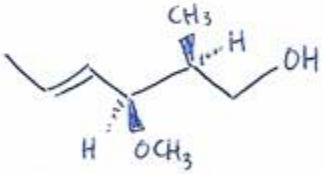
(a) (*2R,4R*)-4-hydroxy-2,5-dibromo-2-methylpentanoic acid



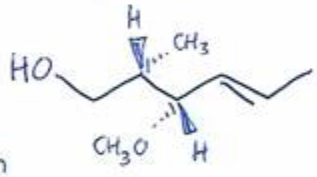
or in other orientation



(b) (*4E*)-(*2S,3R*)-3-methoxy-2-methylhex-4-en-1-ol

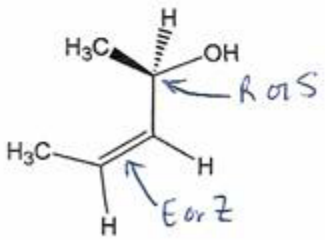


or in other orientation



#11. **(4 MARKS)** CIRCLE ONE. How many optically active stereoisomers does this substance have?

a) 0
b) 1
c) 2
d) 3
e) 4



both chiral carbon & double bond can have 2 configurations

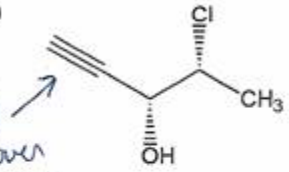
E, R
E, S
Z, R
Z, S

none is meso ∴ all chiral ∴ all optically active

Name: Rogers CHEM 221 /2 01

#12. (8 MARKS) Give the IUPAC names for the following compounds, including stereochemistry.

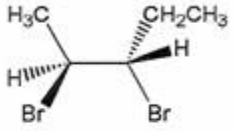
a)



NOTE: we did not cover alkynes in W2005

(3R, 4R)-4-chloropentyn-3-ol

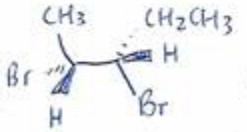
b)



(2S, 3S)-2,3-dibromopentane

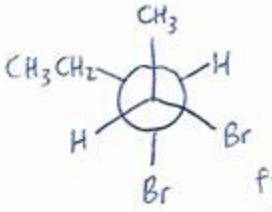
#13. (8 MARKS TOTAL) Consider the compound in #12(b).

a) (2 marks) Draw and name a diastereomer of this compound. ~ possibilities: (2R, 3S)-... (2S, 3R)-...



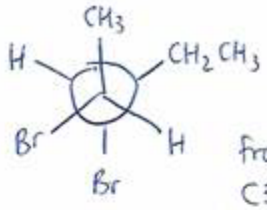
(2R, 3S)-2,3-dibromopentane

b) (3 marks) Draw a Newman projection that represents the conformation shown in #12(b), looking down the bond between the bromine-substituted carbon atoms.



from left C2→C3

OR

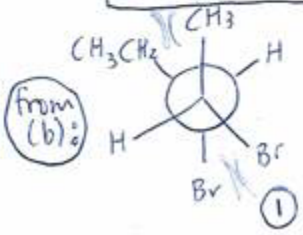


from right C3→C2

c) (3 marks) Is this the most stable conformation for this molecule? Why or why not? Explain in terms of electrostatic (*i.e.*, gauche vs. eclipsed bonds) and steric interactions.

Yes, this is the most stable conformation. The most stable conformation will be the conformation with the minimum number of eclipsed bonds and the minimam number of Gauché interactions, because BOTH electrostatic repulsion between bonding electrons (torsional strain) AND steric repulsion between non-H groups will be minimized. Staggered confo. ① (from b) is therefore the most stable.

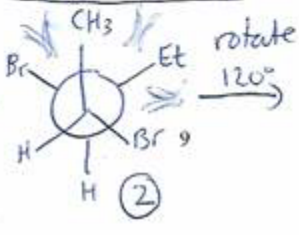
2 Gauche interactions



from (b)

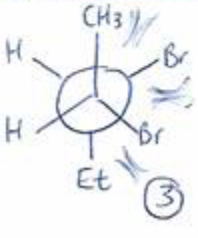
rotate 120°

3 Gauche interactions



rotate 120°

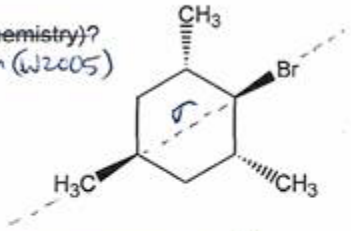
3 Gauche interactions



Note: all (not shown) eclipsed confo's have ↑ torsional strain ∴ even less stable.

Name: Rogers CHEM 221 /2 01

#14. **(18 MARKS TOTAL)** The questions on this page deal with the following substituted cyclohexane:



a) (4 marks) ~~What is the IUPAC name of this compound (including stereochemistry)?~~ too much stereochem – beyond scope this term (W2005)
(trans, cis, trans) - 2-bromo-1,3,5-trimethylcyclohexane

b) (1 mark) Is this compound chiral? Circle one: YES / (NO)

c) (2 marks) If you think it is chiral: draw its enantiomer.
If you think it is achiral: what makes it achiral?

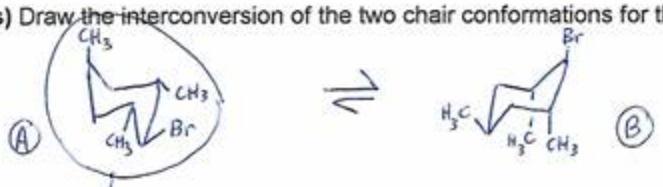
Plane of symmetry down $CH_3-C\cdots C-Br$ (shown as "σ")

c) (1 mark) Is this compound optically active? Circle one: YES / (NO) since achiral

d) (2 marks) Pick the solvent in which you expect this compound to be most soluble:

(i) ethanol very polar (ii) hexane nonpolar (iii) THF very slightly polar

e) (2 marks) Draw the interconversion of the two chair conformations for this substituted cyclohexane.



f) (2 marks) Circle the preferred conformation from part (e). Why is that conformation is more stable?

This is more stable because more substituents are in equatorial positions ∴ 1,3-diaxial interactions are minimized (only the 1 axial methyl experiences 1,3-diaxial steric interactions, compared to both CH_3s + the Br).

NOT TRUE

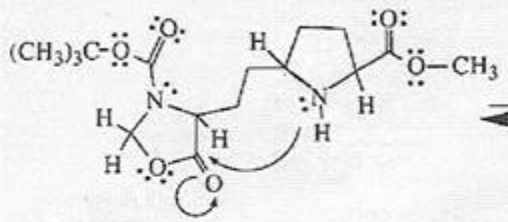
g) (5 marks) This compound can undergo an E2 elimination if it is heated in a solution containing KOH. Which conformation is the one that participates in this reaction? Why? You may wish to support your argument with Newman projections and a discussion of the orbitals involved in the reaction.

To undergo E2 elimination: requires a conformation in which a hydrogen on a β-carbon can be oriented anti-periplanar with respect to the Br. That allows the C-H bonding pair to attack the C-Br σ* orbital (backside).

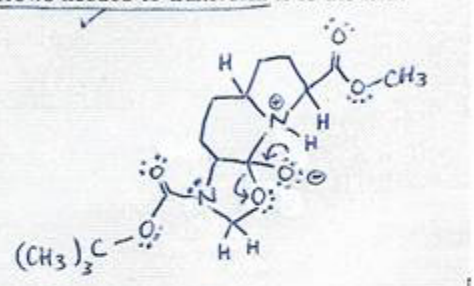
Thus, we would require the Br to be axial, and a hydrogen on an adjacent carbon to be axial as well. In confo. (B), where the Br is axial, we can see that there are only methyls in axial positions on the β-carbons. For this reason, this compound CANNOT undergo E2 elimination. Any elimination product seen after heating the compound in a solution containing KOH would therefore have formed via an E1 mechanism (reasonable since has a 2° Br ....).

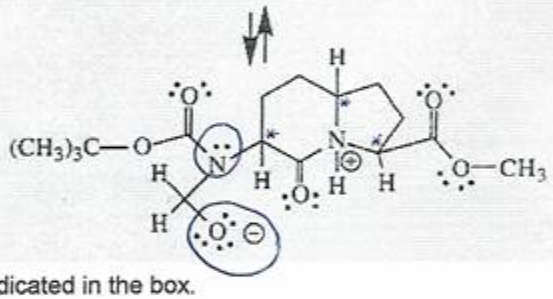
OPTIONAL BONUS QUESTION (8 marks)

Chemists in the pharmaceutical (drug/medicine) industry have targeted molecules that mimic the action of amino acids as being important to prepare. The preparation of one such compound was reported recently (*Tetrahedron Lett.* **1997**, *37*, 6483). Following the implications for bonding changes of the curved-arrow convention, draw the single intermediate structure that follows from the starting compound, and then add the set of arrows to the structure you have drawn that would explain the formation of the next intermediate, as shown.



Draw: the structure implied by the curved arrows AND the curved arrows needed to transform it to the next structure.





B1: Draw the structure and 'arrow pushing' steps as indicated in the box.

B2: How many chiral carbons are there in the final product?

3

B3: Circle the functional groups in the final product that would be protonated in acidic solution.

① $-\ddot{O}:^{\ominus}$ is the most basic atom present $\Rightarrow$ $-OH$ ($pK_a \sim 15$)

② $-\ddot{N}R_a$ is next $\Rightarrow$ $-\overset{\oplus}{N}HR_a$ ($pK_a \sim 10$)

NOTE: would have to become strongly acid ($pH < 1$) to protonate the ester $-\overset{O}{\overset{\|}{C}}-\ddot{O}-R$ oxygens and the carbonyl $>C=\ddot{O}:$ oxygens

plus, will get more + more ⊕ charge building up on atom, making it even less likely that they will get protonated.

HAPPY HOLIDAYS!