

Rogers

## ORGANIC CHEMISTRY I MIDTERM TEST

**INSTRUCTIONS: PLEASE READ THIS PAGE WHILE WAITING TO START YOUR EXAM.**

This test paper includes 3 pages (both sides) plus a periodic table; some potentially useful information is given on the back of the periodic table. Check that your paper is complete. You can remove the periodic table if you wish. Calculators and model kits are permitted; cell phones and electronic dictionaries are not allowed. You have the whole class (75 minutes) to complete the test. Each page is worth 10 marks. Read through the whole test quickly before starting. **GOOD LUCK!**

LAST NAME: marking scheme FIRST NAME: \_\_\_\_\_  
STUDENT NUMBER: \_\_\_\_\_

Mark breakdown:

	AVG.	
Page 2.	7.2 / 10	
Page 3.	6.7 / 10	
Page 4.	5.2 / 10	
Page 5.	6.7 / 10	
TOTAL:	25.8 / 40	+0.5 ← to compensate for confusion about #2
PERCENT:	65.8 %	
EARNED toward		
FINAL GRADE:	9.9 / 15	



# 1. ( / 6 marks) TRUE or FALSE? Circle T or F to describe the following statements.

- (T) / F Propylamine is expected to have a higher boiling point than trimethylamine.  
 $\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$  can Hydrogen bond  
 N-H to :N  
 $\rightarrow$  higher bp  
 $(\text{CH}_3)_3\text{N}$ :  
 cannot hydrogen bond (NO NH)  
 with itself
- T / (F)  $(\text{CH}_3)_3\text{CBr}$  is an example of a secondary alkyl halide.  
 $\rightarrow$  connected to 3 carbons  $\therefore$  tertiary
- T / (F)  $\text{sp}^3$ -hybridized carbon atoms have an unhybridized p orbital and an overall tetrahedral geometry.  
 X ✓
- T / (F) Compounds with closed (full) valence shells are described as electrophiles or Lewis acids.  
 open valence  
 $\therefore$  can accept  $e^-$
- (T) / F Resonance can only occur in a molecule if p-orbitals on adjacent atoms are able to align parallel.  
 $\text{p}-\text{p}-\text{p}$  extended  $\pi$  systems  
 need a p orbital on every atom  
 involved in the delocalization.
- (T) / F Alkanes are unreactive under most conditions because they only contain C-C and C-H  $\sigma$ -bonds.  
 $\checkmark$  except halogenation and combustion...  $\checkmark$

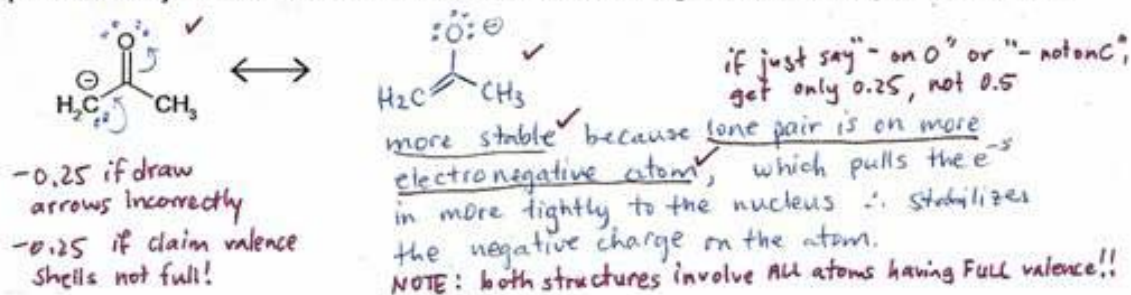
# 2. ( / 1 mark) Which of the following species contain(s) an  $\text{sp}^2$ -hybridized carbon? CHOOSE ONE. <sup>typo. Error in (a)'s choice!</sup>

- a)  $\text{:CH}_3$   $\text{sp}^3$   $\checkmark$     b)  $\cdot\text{CH}_3$   $\text{sp}^2$   $\checkmark$     c)  $\text{CH}_3^+$   $\text{sp}^2$   $\checkmark$     ~~both a & b~~    ~~all three~~

# 3. ( / 1 mark) What type of orbital results when orbitals overlap in each of the orientations shown below?

- a)  CIRCLE ONE:  
 $\sigma$ ,  $\sigma^*$ ,  $\pi$ ,  $\pi^*$   
 end-on, in-phase
- b)  CIRCLE ONE:  
 $\sigma$ ,  $\sigma^*$ ,  $\pi$ ,  $\pi^*$   
 side-on, out-of-phase

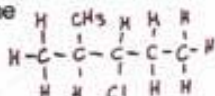
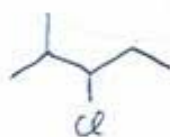
# 4. ( / 2 marks) Add lone pairs to the following Lewis structure, and draw another resonance contributor for this species. Identify which of the two structures is more stable, and give the reason why (just a few words).



To

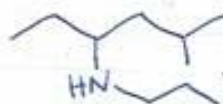
# 5. (4 Marks) Draw a line structure for each of the following compounds:

a) 3-chloro-2-methylpentane



is NOT a line structure!  
(only get 1/2)

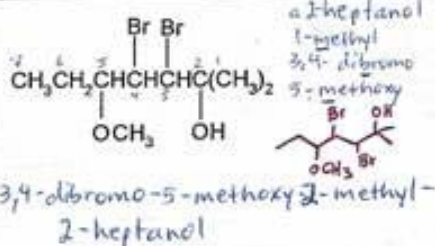
b) N-propyl-5-methyl-3-hexanamine



-1 if wrong alkyl on N.

# 6. (4 Marks) Provide a systematic IUPAC name for each of the following compounds:

a)



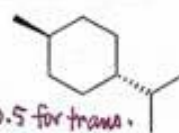
OR heptan-2-ol

• alpha error: -0.5

• position label error: -1

• wrong orders: -1

b)



0.5 for trans.

IUPAC:

trans-1-methyl-4-(1-methylethyl)cyclohexane

less correct: mix of IUPAC + common name  
trans-1-isopropyl-4-methylcyclohexane

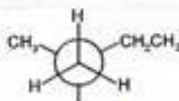
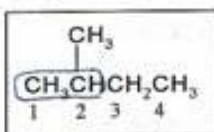
Specify relative stereochemistry only; ignore absolute configurations.

worth 2

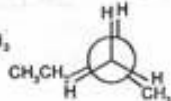
• alpha error -0.5

• if forgotten: -0.5

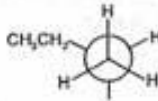
# 7. (1 mark) Which diagram (I-V) represents a Newman projection along the C1-C2 bond for a staggered conformation of the compound shown in the box? CIRCLE YOUR CHOICE.



I

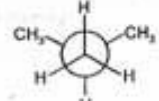


II  
eclipsed



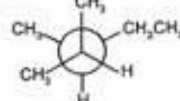
III

wrong compound



IV

wrong compound



V

wrong compound

# 8. (1 mark) The Newman projections below represent different conformations of butane. Which one of the following statements is true?

a) Both torsional and steric strain are lower in I than in II. X

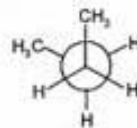
b) The methyl groups are gauche in conformer I. ✓

c) An intramolecular hydrogen bond stabilizes conformer I. X

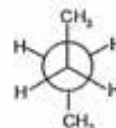
d) The C1-C4 dihedral angle in II is 60°. no, 180° X

e) More than one of these statements is true. X

f) All of these statements are false. X



I

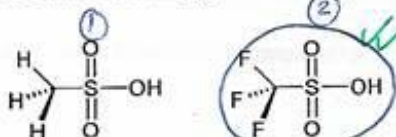


II

10

# 10. ( / 6 marks) Think about the acid-base properties of the following pairs of compounds.

- a) (1 mark) Which is the stronger acid?  
(weaker conjugate base)\*



(2 marks) Give a brief explanation:

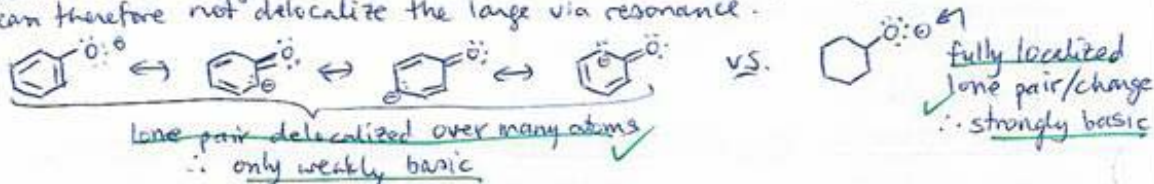
The 2 conjugate bases (deprotonated -OH group) are similar except for the fluorines in the conjugate base of ②. The electron-withdrawing nature of the fluorine atoms (due to their high electronegativity (large  $2^+$ )) provides inductive stabilization of the negatively charged conjugate base. (Hydrogen atoms are not able to provide this type of stabilization since their electronegativity is less than that of carbon). Note that both ① + ② are quite strong acids because of the resonance stabilization afforded by the adjacent  $S=O$   $\pi$  bonds.

- b) (1 mark) Which is the stronger base?  
(more localized attacking lone pair)



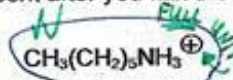
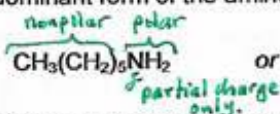
(2 marks) Give a brief explanation:

The phenyl-substituted anion is stabilized by resonance, making it a weaker base than the cyclohexyl-substituted anion, which lacks  $sp^2$ -hybridized atoms + can therefore not delocalize the lone pair via resonance.



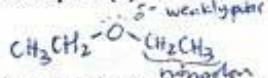
# 11. ( / 4 marks) Imagine you add a small amount of n-hexyl amine ( $CH_3(CH_2)_5NH_2$ ) to a separatory funnel that contains the organic solvent diethyl ether ( $CH_3CH_2OCH_2CH_3$ ) and water at a pH of 4.0.

- a) (1 mark) Circle the dominant form of the amine present after you mix the phases:



$pK_a = \text{approx. } 9$   
 $\therefore$  predominantly in "HA" form at  $pH \ll 9$ .

- b) (1 mark) After the layers separate (water and diethyl ether are immiscible liquids), will the species identified in part (a) be found in the organic phase or in the aqueous phase?



$Et_2O$  is largely non-polar

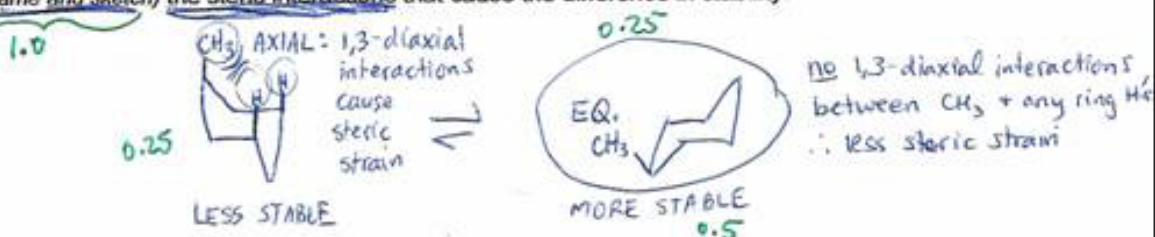


$H_2O$  is HIGHLY POLAR  $\rightarrow$  solvates ions + polar compounds well

- c) (2 marks) Briefly explain your choice in part (b) using a discussion of intermolecular forces.

The protonated form (conjugate acid) of the amine is cationic. The dipole moment of water is enormous compared to that of diethyl ether, therefore water will provide much stronger solvation via electrostatic dipole-cation interaction than ether will. To fully analyze the situation: ① The long nonpolar tail of the alkyl ammonium cation would certainly interact well with diethyl ether's ethyl groups via London dispersion (induced-dipole/induced-dipole) forces. ② The magnitude of the electrostatic (attractive) force between the  $H_2O$ 's  $\delta^-$  oxygen and the fully charged  $RNH_3^+$  cation is large, more than a hydrogen bond!, and more than sufficient to "pull" the nonpolar end of the molecule into the polar aqueous phase. It is the full unit of  $\oplus$  charge that is responsible; the neutral amine is ether-soluble. Hydrogen bonding is not enough to pull a 6-carbon chain into water. (see Bruice, P. 87).

# 12. ( / 2 marks) Draw the chair-chair interconversion (ring-flipping equilibrium) for methylcyclohexane. Label the substituent as axial ("ax") or equatorial ("eq") as appropriate. Circle the more stable conformer and identify (name and sketch) the steric interactions that cause the difference in stability.



# 13. ( / 3 marks) Which of the following compounds has two equatorial alkyl substituents in its most stable conformation? CIRCLE YOUR CHOICE(S).

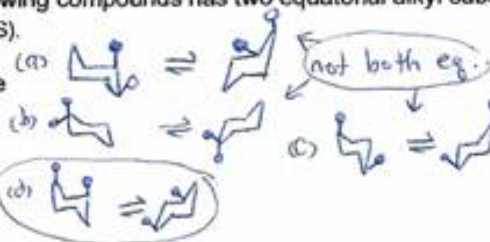
X a) cis-1,2-dimethylcyclohexane

X b) 1,1-dimethylcyclohexane

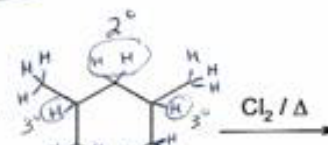
X c) cis-1,4-diethylcyclohexane

d) cis-1,3-diethylcyclohexane

X e) all of the above



# 14. ( / 5 marks) Consider the following reaction:



a) (1 mark) How many hydrogen atoms of each type are present in the alkane starting material?

→ 0.5 per error  
or 0.25 each correct.

Primary (1°):

12

Secondary (2°):

2

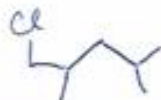
Tertiary (3°):

2

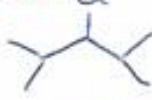
b) (2 marks) How many monochlorinated products (ignoring stereochemistry) can form? Draw them.

3

0.5 each structure  
0.5 for correct #



can draw 3 others  
but are identical molecules!



can draw 1  
other stereoisomer  
(its enantiomer)



can draw 1 other (identical)  
+ enantiomer

c) (2 marks) Bromination is a more convenient reaction to use in the lab than chlorination. Explain why.

Bromine atoms (Br• radicals) are larger + therefore less reactive than Cl•.

This makes Br• more selective with substitution occurring preferentially at

3° sites (3° H abstraction to yield 3° radical C•), and lower probability of reacting at 2° site and essentially no reaction at 1° sites. (More highly substituted (more R groups) radicals are easier to form, because the C• radical pulls slightly less strongly on the H• being abstracted. Thus, radical bromination is more useful because we can predict more

confidently what the products of the reaction will be, AND in general there will be predominantly 1 product in many cases rather than complex mixtures of products. Thus, it is easier to purify the desired product as it will be formed in higher yield.

10