

Rogers

CHEM 222 - ORGANIC CHEMISTRY II MIDTERM EXAMINATION

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

This test paper includes 4 pages (both sides) including a periodic table with electronegativities and a page of potentially useful information. Check that your paper is complete. You can remove the last page if you wish. Model kits and calculators are permitted; cell phones and electronic dictionaries are not allowed. You have 70 minutes to complete the test. Read through the whole test quickly before starting. **GOOD LUCK.**

LAST NAME: marking scheme FIRST NAME: _____

STUDENT NUMBER: _____

Mark breakdown:

	<u>Averages</u>	<u>90</u>
Page 2.	8.3 / 13	63.6
Page 3.	6.7 / 12	55.6
⊗ Page 4.	3.3 / 6	55.4
Page 5.	6.4 / 10	64.1

— Please practice mechanisms!
Review section 3.6...

TOTAL: 24.7 / 40 (maximum grade ⁴¹/40)

PERCENT: 61.7 %

EARNED toward
FINAL GRADE: 9.3 / 15

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

T F If a substance appears green, it likely absorbs in the orange region of the spectrum. red

T F If a carbonyl absorption band appears in a substance's IR spectrum at $< 1700 \text{ cm}^{-1}$, it suggests that the C=O bond in the substance is somewhat stronger than the C=O in a typical ketone. should have higher frequency absorption

T / F Thiols are more acidic than alcohols because sulfur atoms are larger than oxygen atoms. yes

T / F Mass spectrometry allows us to determine the molecular weight and the mass of some fragments of a compound.

T F The stronger the NMR spectrometer's magnet, the lower the energy of radio waves needed to cause protons to "flip" their spins. higher

T F Grignard reagents are best prepared using a protic solvent such as ethanol. !? no: require DRY ether
 $\text{RMgBr} = \text{"R}^\ominus \text{" strong base}$

2. (2 marks) Which of the following reagents would be best to convert ethanol to chloroethane in one step?

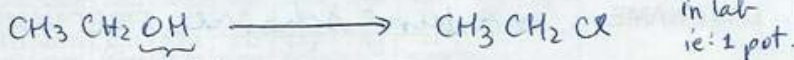
a) PCC oxidant

b) NaCl Cl^- Nu only...

c) TsCl makes tosylate

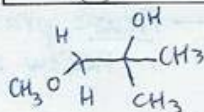
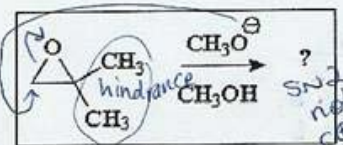
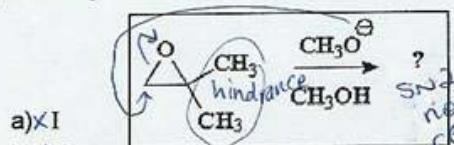
d) SOCl_2

e) $\text{Cl}_2/h\nu$ for halogenating alkanes



can't do $\text{S}_\text{N}2$
not good LG

3. (2 marks) What is the product of the following reaction?

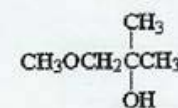
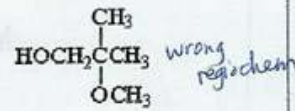


I $\text{CH}_3\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$

II $\text{HOCH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{OCH}_3$ rearranged?

III

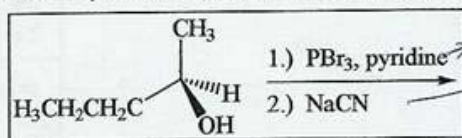
IV.



V.

NO ACID PRESENT!
 $\ominus + \text{IFSO}, \text{OCH}_3 \text{MeO}^\ominus$
 WOULD GET PROTONATED...

4. (3 marks) What is (are) the major product(s) from the following reaction sequence?



makes bromide via key $\text{S}_\text{N}2$ step \therefore inverts
displaces Br via $\text{S}_\text{N}2$ step \therefore inverts again \rightarrow back to original stereo.

a) I

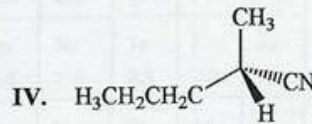
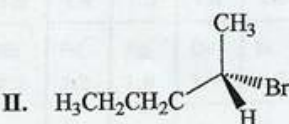
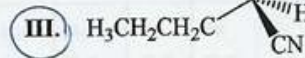
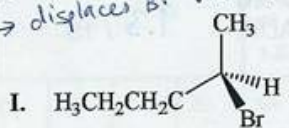
b) II

c) III

d) IV stereo. wrong in rxn 1

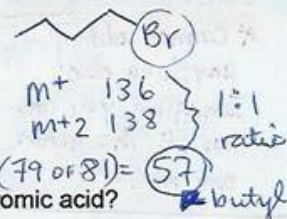
e) I and II

f) III and IV stereo. wrong in rxn 2



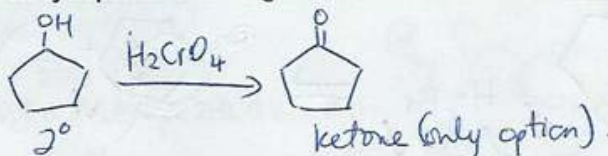
5. (2 marks) Which of the following is/are true about the mass spectrum of 1-bromobutane?

- a) Peaks of approximately equal intensity are observed at m/z 136 and 138.
- b) The major fragmentation occurs by cleavage of the C-Br bond.
- c) The most intense peak occurs at m/z 43. *X = propyl*
- d) both a and b
- e) both a and c
- f) all of the above (a, b and c)



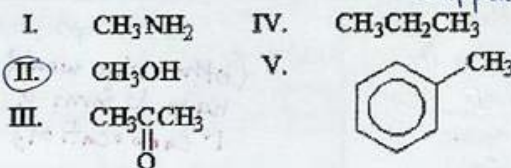
6. (2 marks) What compound results when cyclopentanol undergoes oxidation with chromic acid?

- a) cyclopentanone
- b) cyclopentanal
- c) cyclopentanoic acid
- d) cyclopentene
- e) 1,2-cyclopentanediol



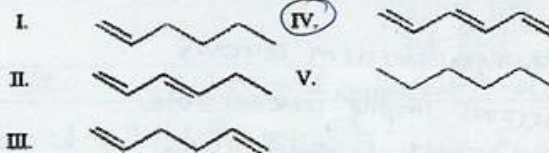
7. (2 marks) Which of the following methyl groups would be most deshielded in a 1H NMR experiment?

- a) I
- b) II
- c) III
- d) IV
- e) V



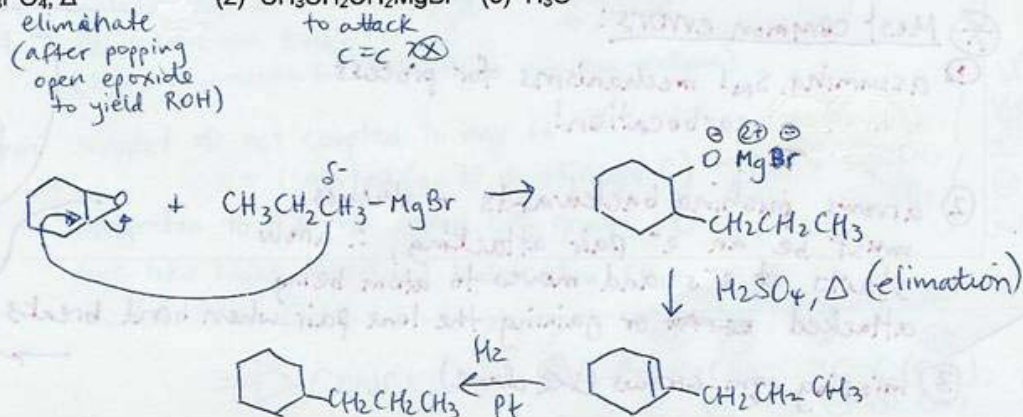
8. (2 marks) Which of the following compounds absorbs the longest wavelengths in the UV/Vis region?

- a) I
- b) II
- c) III
- d) IV
- e) V



9. (4 marks) Which of the following sequences of reactions would work best to convert cyclohexene oxide (shown at right) into propylcyclohexane?

- a) $(1) CH_3C\equiv CNa$ (2) $H_3O^+ \rightarrow$ leaves $-C\equiv CCH_3$, not Pr, substituent
- b) $(1) CH_3CH_2CH_2MgBr$ (2) H_2SO_4, Δ (3) H_2, Pt
- c) $(1) H_3O^+$ open epoxide (2) $CH_3C\equiv CNa$ - alcohol from (1) will protonate $C\equiv C-CH_3$, not substitute
- d) $(1) CH_3CH_2CH_2Li$ (2) $HBr \rightarrow$ leaves a bromide? (as well as desired Pr group)
- e) $(1) H_3PO_4, \Delta$ (2) $CH_3CH_2CH_2MgBr$ (3) H_3O^+



2 D

2 A

2 B

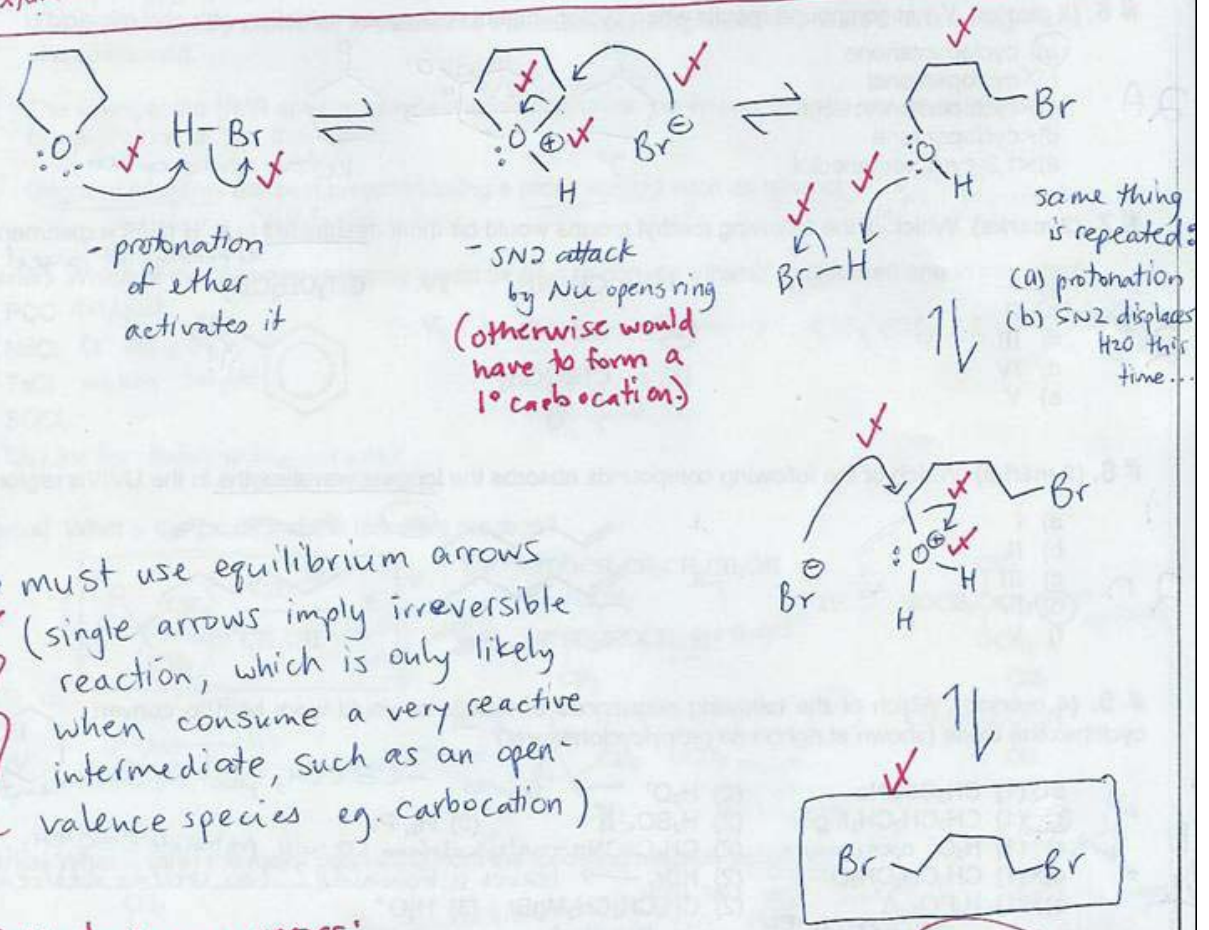
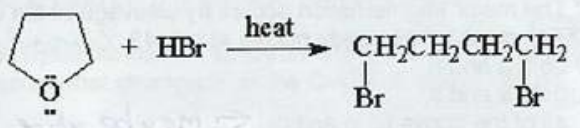
2 D

4 B

12

10. (6 Marks) Provide a step-by-step mechanism to explain how THF undergoes the following reaction in the presence of excess hydrogen bromide:

* cannot add anything else! requires 2 equivalents of HBr
Imagine you are INSIDE the given rxn mixture...



0.5 { must use equilibrium arrows (single arrows imply irreversible reaction, which is only likely when consume a very reactive intermediate, such as an open-valence species eg. carbocation)

* Most common errors:

1 assuming S_N1 mechanisms for process via a 1° carbocation!

2 arrows pushing backwards - always must be an e⁻ pair attacking, ∴ arrow starts at e⁻s and moves to atom being attacked ~~or~~ or gaining the lone pair when bond breaks

6 3 missing eqm arrows (see above)

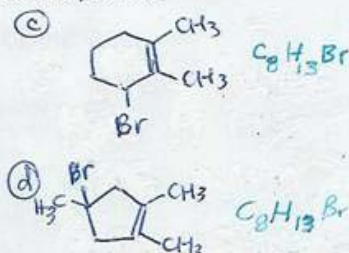
+ H₂O
-0.5 if absent.

see ch.3's intro. to arrow-pushing (Sect. 3.6)

11. (10 marks) Deduce the identity of the compound from the following experimental data. In the tables announced below, provide a point-form summary of the information you learned from each type of experimental data. on board + RATIONALIZE HOW YOUR CHOSEN STRUCTURE FITS THE DATA (DRAW + EXPLAIN).

The compound has molecular formula $C_8H_{13}Br$, and it is one of the following five compounds:

- a) $CH_3CHBrCCC(CH_3)_3$ **(a)** $CH_3-C(H)Br-C \equiv C-C(CH_3)_3$
 b) $XHCCCH_2C(CH_3)_2CH_2CH_2Br$ $HC \equiv C-CH_2-C(CH_3)_2-CH_2CH_2Br$ **(b)**
 c) \times 3-bromo-1,2-dimethylcyclohexene
 d) \times 4-bromo-1,2,4-trimethylcyclopentene
(e) $BrCH_2CH_2CCC(CH_3)_3$ $Br-CH_2CH_2-C \equiv C-C(CH_3)_3$



Data: IR (selected peak positions in cm^{-1}): 2950, 2150
 1H NMR (δ , multiplicity, integral): 3.5 (t, 2H), 1.8 (t, 2H), 0.9 (s, 9H)
 ^{13}C NMR: 6 signals

1	Formula $C_8H_{13}Br$	IR data	^{13}C NMR data
5/5	Units of unsaturation: $\frac{2(8)+2-(13+1)}{2} = 2$ \Rightarrow 2 π bonds and/or rings \Rightarrow Cannot rule any choice out (all have 2 units of unsaturation)	no $C=O$, no OH (but no $C \equiv N$!!) 2950 $cm^{-1} \Rightarrow$ CH stretches aliphatic 2150 $cm^{-1} \Rightarrow$ $C \equiv C$ unit... \Rightarrow must be (a), (b) or (e) \Rightarrow cannot be (c) or (d)	6 signals \Rightarrow six different types of carbon atom i.e. some C's must be in identical chemical environments. (a) 6 types of C environment (b) 7 types of C \leftarrow not this one (c) 6 types of C

(4) 1H NMR data can assign it all... (x) 3 types of equivalent H \rightarrow (matches a, d, e)

- (1)** 3.5 ppm triplet \Rightarrow coupled to 2H's \checkmark
 integrates to 2H \Rightarrow CH_2 group close to EWG (deshielded) \checkmark
 \Rightarrow $?-CH_2-\overset{EWG}{\underset{no H's}{CH_2}}$
- (2)** 1.8 ppm triplet \Rightarrow coupled to 2H's \checkmark
 integrates to 2H \Rightarrow CH_2 group farther from EWG (typical position for allylic-type position \rightarrow close)
 \Rightarrow $\overset{no H's}{CH_2}-CH_2-\overset{EWG}{\text{...}}$
- (3)** 0.9 ppm singlet \Rightarrow not coupled to any H's \checkmark
 = isolated (no H on adjacent C)
 integrates to 9H \Rightarrow three CH_3 groups \checkmark
 \Rightarrow $?-C(CH_3)_3$
- look like highly shielded hydrocarbon CH_3 's.
 i.e. far from EWG
- compound must be **(e)** because (a) has a CH coupled to CH_3 .
 \times would fit with (a) or (e) just fine.

(1) \checkmark **(4)** \checkmark \Rightarrow CONCLUSION **(e)**: $BrCH_2CH_2-C \equiv C-C(CH_3)_3$
 (1) (2) (3) (4) (5) (6)x3

10