Concordia University CHEM 221

Fall 2008, Dr. C. Rogers, Section 01

LAST NAME: Rogers

FIRST NAME: marking scheme

STUDENT ID:

CHEM 221 - ORGANIC CHEMISTRY I
MIDTERM EXAMINATION

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

- Check that your paper is complete: 4 pages (both sides).
- Note the (removable) reference data page: table of pK_as, periodic table, electronegativities.
- Model kits and calculators are permitted. Cell phones & electronic dictionaries are not allowed.
- Read through the whole test quickly before starting.
- Please ask for clarification if you do not understand what a question is asking.
- You have 70 minutes to complete the test.

Mark breakdown:

Averages

Page 2.	8.7	/ ~~14~~ 13 oops	= 66.9%
Page 3.	6.8	/ ~~14~~ 12 oops	= 56.6%
Page 4.	4.8	/ 9	= 53.2%
Page 5.	2.8	/ 9	= 31.6%
TOTAL:	23.1	/ ~~45~~ 42 (maximum ~~46~~/~~45~~ 43/42)	

⇒ BUT, marked out of 40.

PERCENT: 57.8 % (out of 40)

EARNED toward FINAL GRADE: / 15

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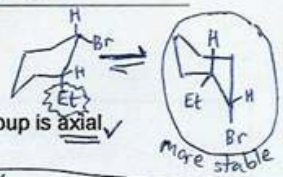
 # 1. (6 marks) TRUE or FALSE? Circle T *or* F to describe the following statements.

1 (T) / F In the most stable conformation of *cis*-1-bromo-2-ethylcyclohexane, the bromo group is axial. ✓
(same side; smaller; larger)

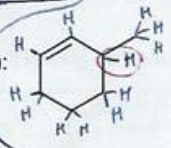


1 T / (F) Any molecule or atom described as a *Lewis base* can also be described as an *electrophile*. ✗
(lone pair donor; attracted TO e⁻s)

1 (T) / F The carbon-carbon bond in ethene (H_2CCH_2) is longer than the one in ethyne (HCCH). ✓
$H_2C=CH_2$ ⇒ sp^2-sp^2 (σ), p-p (π) H-C≡C-H ⇒ sp-sp (σ), p-p (π_1), p-p (π_2)

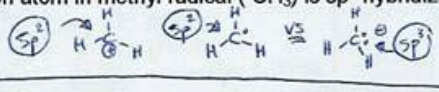
1 T / (F) When an electron pair enters a bond's σ* orbital, the bond becomes stronger. ✗
(breaks!; ↑ cancels energetic advantage of the σ bond!)

1 (T) / F The molecule shown here (at the right) contains one tertiary hydrogen: ✓



1° : 3
2° : 6
3° : 1
vinyl : 2

1 (T) / F The carbon atom in methyl radical (·CH_3) is sp^2 hybridized. ✓

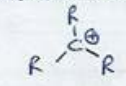


section 1.10

 # 2. (1 mark) What is the geometry around a carbon atom that has positive formal charge?

a) trigonal pyramidal
1 (b) trigonal planar
c) tetrahedral
d) linear

carbocation.



3 e⁻ pairs (σ bonds) ⇒ trigonal planar (sp^2)

 # 3. (2 marks) Which common base below would be strong enough to deprotonate $(CH_3)_2CHOH$? ← "substrate"

a) sodium acetate: weak B
b) potassium carbonate: weak B
2 (c) calcium hydride: strong B
d) ammonia: weak B

Conj. base	Conj. acid	pKa
$NaCH_3COO^-$	CH_3COOH	4.7
K_2CO_3 $2K^+$, CO_3^{2-}	HCO_3^-	10.2
CaH_2 Ca^{2+}, $2H^-$	H_2	35
NH_3	NH_4^+	9.4

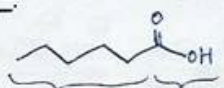
pKa of ~18 ?

CH_3OH pKa	15.5
CH_3CH_2OH	17
$(CH_3)_3COH$	19

Base's conj. acid must have pKa larger than our substrate.

 # 4. (2 marks) When a small amount of hexanoic acid [$CH_3(CH_2)_4CO_2H$, pK_a~4.8] is added to a separatory funnel which contains the organic solvent diethyl ether [$(CH_3CH_2)_2O$] and water at a pH of 2.0, it is found mainly in the _____ phase as _____.

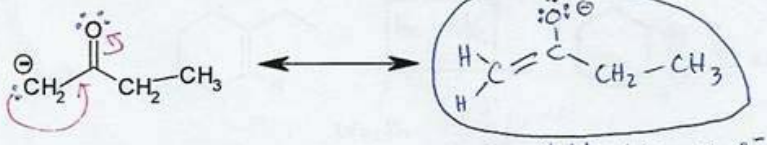
0 a) ether; $CH_3(CH_2)_4CO_2^-$ ✗
1 b) water; $CH_3(CH_2)_4CO_2^-$ ✗
2 (c) ether; $CH_3(CH_2)_4CO_2H$
1 d) water; $CH_3(CH_2)_4CO_2H$



large 5C nonpolar region; limited H-bonding region } not H_2O-soluble.

acidic, pH < pKa of hexanoic acid 4.8 ⇒ hexanoic acid in its acidic form ∴ not a, b.

 # 5. (2 marks) Draw the other major resonance contributor for the species shown below, then circle the structure that contributes more to the resonance hybrid. Briefly justify your choice (keywords only...).



structure 1 (0.75 if missing F.C.)
choice + explanation 1
(no points for choice only)

more stable because e⁻s on more electronegative atom
∴ contributes more to true structure (resonance hybrid)

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#ring on parent: 0.5

if mixed, lose 0.25.

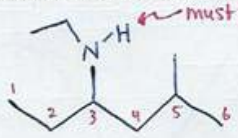
 # 6. (3 marks) Draw a line (skeletal) structure for the following compounds:

a) *trans*-1-methoxy-3-methylcyclopentane

1.5

b) *N*-ethyl-5-methylhexan-3-amine

must show H (on heteroatom) or lose 0.5 (since no points for geometry)



1.5

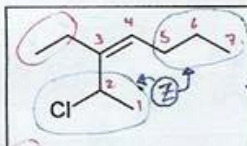
1.5
1.5

 # 7. (3 marks) Provide a systematic name (with E/Z/cis/trans if applicable) for the following compounds:

alkenes

NOTE: 2 CH_3 on C5 ∴ redundant to specify cis/trans relative to a CH_3 here!

a)



-hept-3-ene
3-ethyl-
2-chloro-
Z geometry alkene
(cis is too vague here)

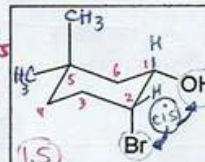
ring substituents or simple alkenes

1.5

(Z)-2-chloro-3-ethylhept-3-ene

3 for "ene" position could be here instead

b)



molecule is an alcohol... -1-ol

2-bromo...
5,5-dimethyl

all on cyclohexane frame.

1.5

cis-2-bromo-5,5-dimethylcyclohexanol

not Z (alkenes only)

can put -1- here but not essential

1.5
1.5

 # 8. (6 marks) Fill in the boxes: draw the missing reactant or major product (OR) list the missing conditions: reagent, catalyst, solvent (if critical for reaction)

a)

slightly more e⁻ rich due to Et vs. Me groups

1st step: E^+

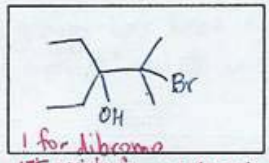
$Br-Br$

via bromonium ion...

Br_2

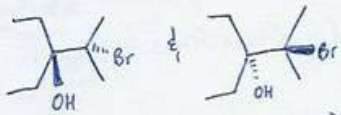
2nd step: Nu

H_2O



1 for dibromo
1.5 points for opposite regio. Br/OH

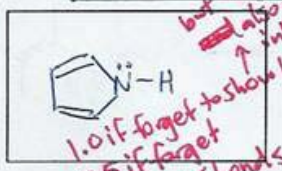
- should visualize in 3D...
- actually, both of these are same:



(verify this after doing Ch.5)

2

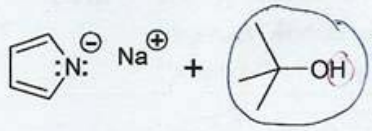
b)



but only if also add in Hdo.

1.0 if forget to show H
0.5 if forget the π bonds

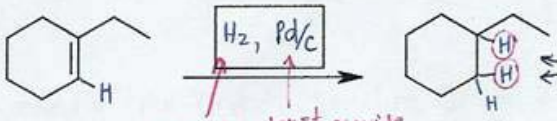
$(CH_3)_3CO^{\ominus}\ Na^{\oplus}$



protonated version of $(CH_3)_3CO^{\ominus}$....
ie. its conjugate acid...
∴ acid-base rxn!

2

c)



H_2, Pd/C

worth 1 only

must provide a catalyst

e.g. Pt/C
Pd/C
Ni

added 2H atoms (to the sp^2 C atoms...)
∴ hydrogenation!

2

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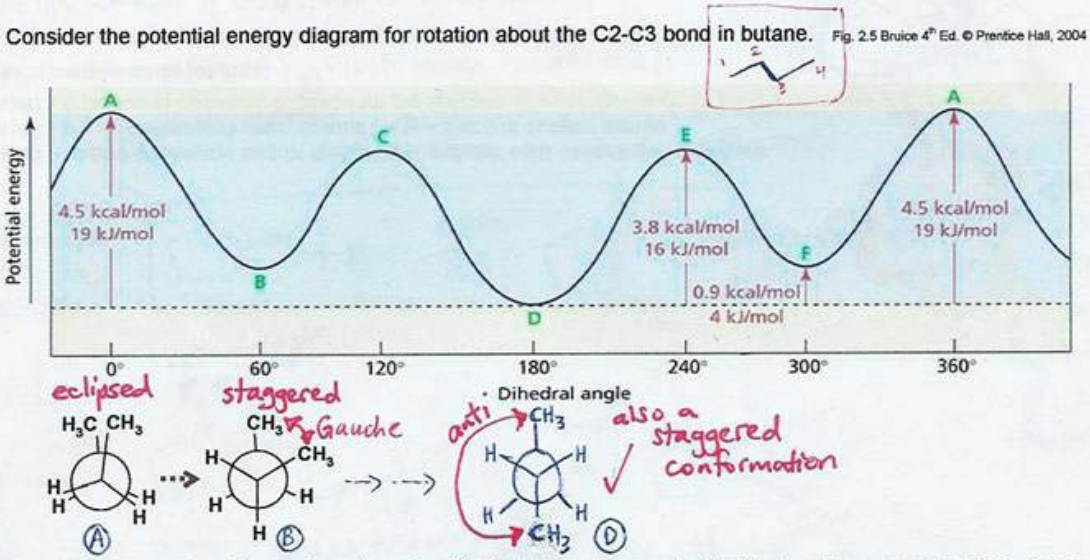
 # 9. Consider the potential energy diagram for rotation about the C2-C3 bond in butane. Fig. 2.5 Bruice 4th Ed. © Prentice Hall, 2004



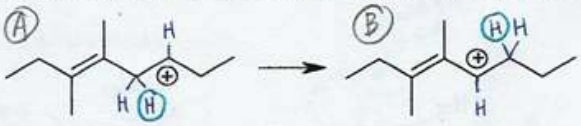
eclipsed staggered ✓ Gauche anti also a staggered conformation ✓

a) **(2 marks)** The molecule's conformation at points A & B are represented by the two Newman projections above.
What type(s) of strain is/are relieved by this 60° rotation about the C2-C3 bond? torsional ✓ AND steric ✓
What is the name of the relative orientation of the CH_3 groups in conformer B? Gauche ✓
→ not staggered, because that refers to the bonds, not the groups

b) **(3 marks)** Draw the Newman projection for the molecule's conformation at point D *(draw it up near the others)*.
What is the name of the relative orientation of the CH_3 groups in conformer D? anti ✓
What causes conformer D to be more stable than conformer B? *(keywords only)*
The steric strain ✓ between the CH_3 groups ✓ has been relieved ✓.
(No torsional strain difference ... both (B) and (D) are staggered conformations.) (✓)

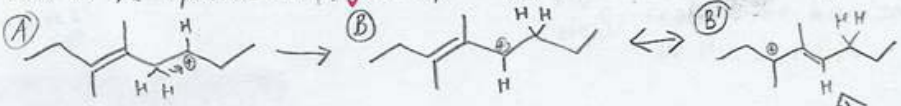
5

 # 10. (4 marks) Explain, in detail, both HOW and WHY the following carbocation rearrangement occurs:



NOTE: an H atom DID move... clear evidence of rearrangement. (they are not simply resonance structures.)

How it happened: (2) Via a 1,2-hydride shift ✓ (i.e. hyperconjugation turned into atom migration)



Why it happened: (2) the first carbocation, (A), is a 2° carbocation ... BUT.. the new carbocation (B) is both 2° and allylic ✓ ∴ more stable because of ✓ resonance.
...and the new resonance contributor (B') is even more stable (3° allylic!)

max 1 if don't notice resonance but give inductive reasoning

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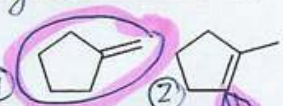
(*) Like example in class... worked on board.

 # 11. Which alkene shown undergoes acid-catalyzed hydrolysis more quickly? Why?



Your explanation must include: most people ignored this!

(2 marks) • a balanced chemical equation for the reaction of each alkene (*e.g.*, for reaction with H_2SO_4 / H_2O)

(4 marks) • full arrow-pushing mechanisms for the reaction of each alkene

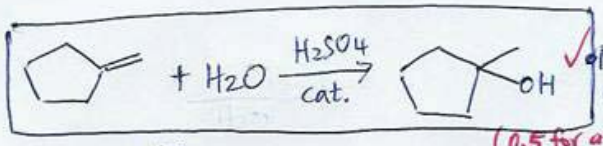
(3 marks) • written comments and/or diagrams to explain what causes the difference

less stable alkene

more stable alkene since more highly substituted

• Alkene ①

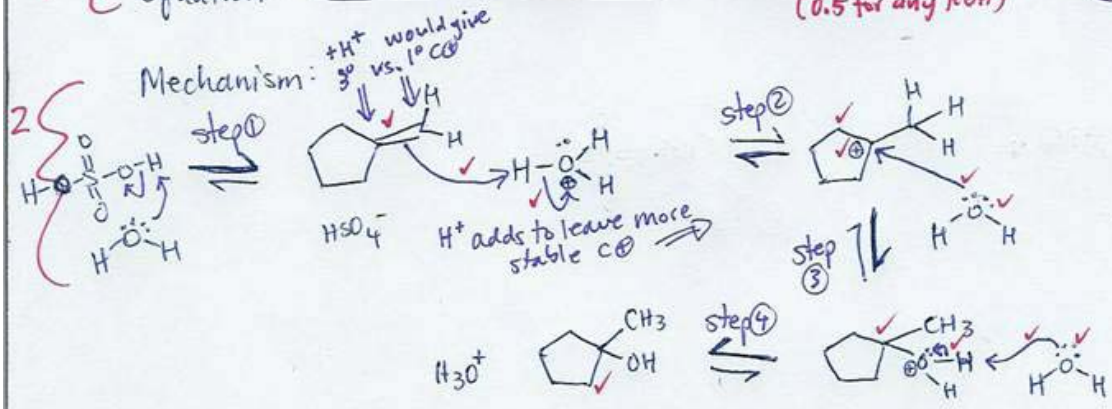
1 Reaction equation:



• Markovnikov addition

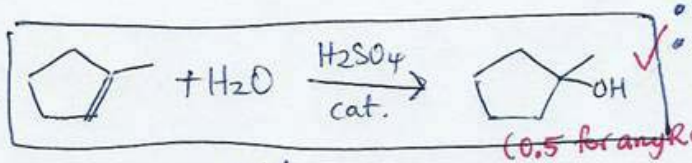
(0.5 for any ROH)

2 Mechanism:



• Alkene ②

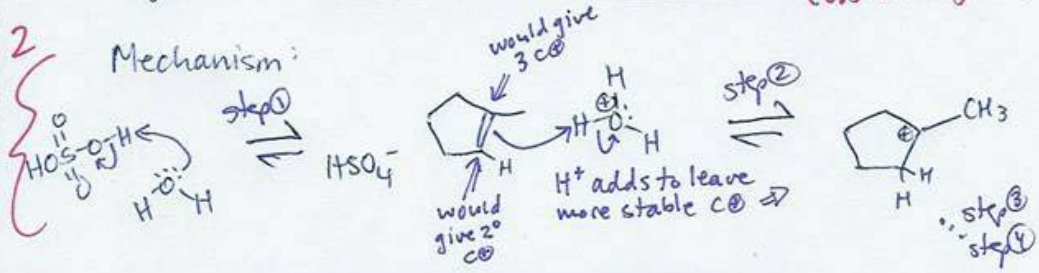
1 Reaction equation



• Markovnikov addition
• same final product as for alkene ①

(0.5 for any ROH)

2 Mechanism:

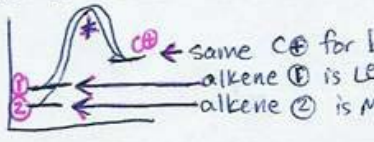


same carbocation intermediate as for alkene ①, so rest of mechanism is the same!

3 • **Explanation of rate difference:**

• the RLS is step ②, formation of carbocation from alkene attacking "H+"

• whatever decreases the E_a of C⊕ formation will make the rxn faster.



⇒ less energy required to reach the C⊕-like transition state (‡)

∴ FASTER rxn for alkene ①.

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