

Chem 0310
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March 30, 2009
Exam 3

NAME _____

SIGNATURE _____

Answer all questions on this exam. If you need more space than that provided, use the back of any page.

1. _____ (20 points)

2. _____ (20 points)

3. _____ (30 points)

4. _____ (10 points)

5. _____ (20 points)

Total _____ (100 points)

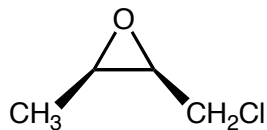
The test has **8** pages (including this cover page and the spectra Table at the end) and **5** questions
The exam ends at 10:55 am sharp.

Good Luck !!!

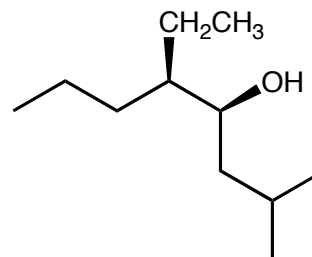
1) Structures and Names (20 points)

a-c) Provide IUPAC names for the following compounds. Be sure to include *cis/trans*, *R/S*, if needed.

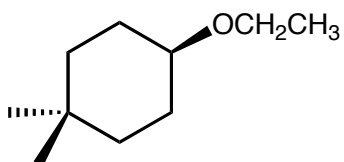
a)



b)



c)



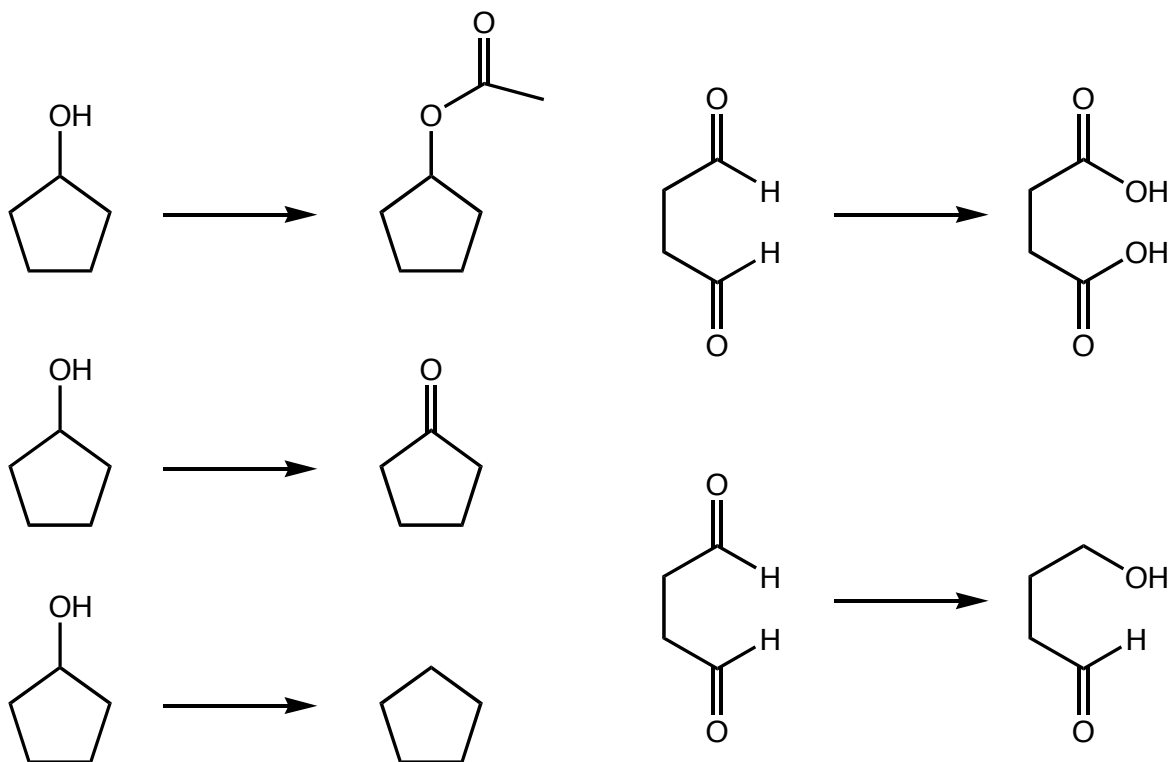
d-e) Provide clear structures for the following names. Be sure to show stereochemistry if relevant.

d) isobutyl ethyl ether

e) (1*S*,3*S*)-3-fluoro-2,2-dimethylcyclohexan-1-ol

2) Short Answer Questions (20 points)

a) Indicate whether each of the following transformations is an **oxidation**, a **reduction**, or **neither**.



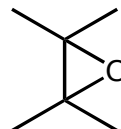
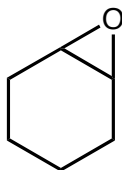
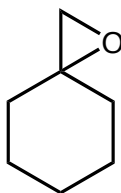
b) Provide a specific example of an oxidation of an alcohol to a carboxylic acid. Show the starting material, the reagents and the product.

c) Draw Lewis structures of the following two reagents.

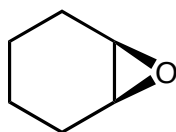
i. thionyl chloride (SOCl_2)

ii. Ethyl magnesium bromide complexed to two molecules of diethyl ether

d) Rank the following oxiranes in order of *decreasing* reactivity towards sodium cyanide (NaCN) in DMF (most reactive first).



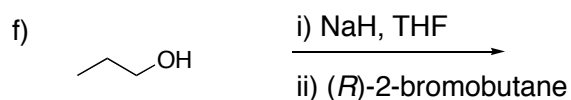
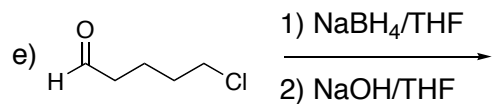
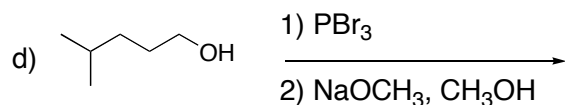
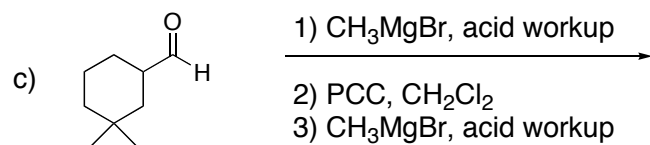
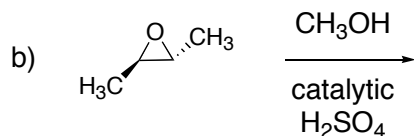
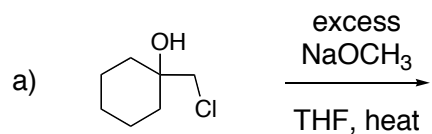
e) Grignard reagents react with oxiranes to provide two types of products, a product in which the Grignard reagent functions as a nucleophile (usually minor) and a product in which the Grignard reagent functions as a base (usually major). Based on that information, predict the products of the following reaction.



1) MeMgBr , THF
→
2) mild acid workup

major product
+
minor product

3) Reaction products. (30 points). Show all expected products of the following reactions. Be sure to indicate stereochemistry, if relevant. NOTE: numbers "1), 2)" mean two separate reactions with workup in between. Letters "i), ii)" mean two parts of the same reaction with no workup in between.

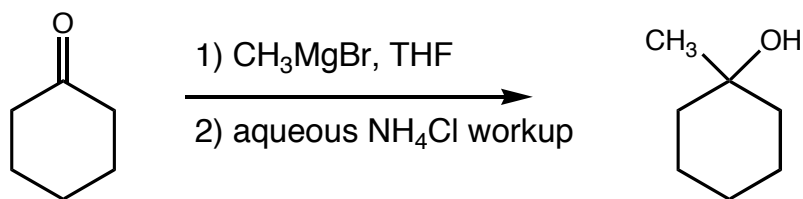


4) Mechanisms (10 points)

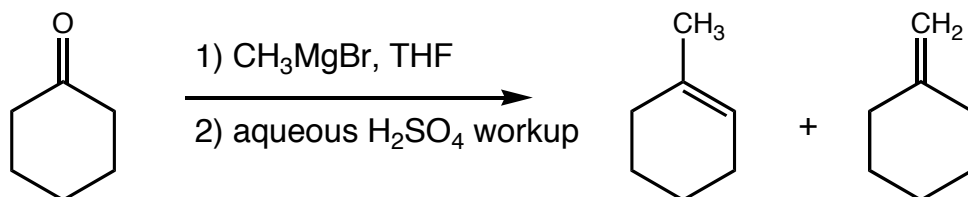
Show detailed mechanisms for each of the following two reactions. Show all individual steps, including acid/base reactions. Use arrows to track electron flow.

The products of Grignard reactions with ketones depend on the strength of the acid used in the workup:

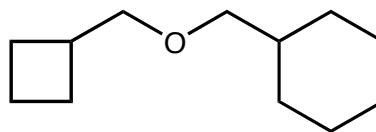
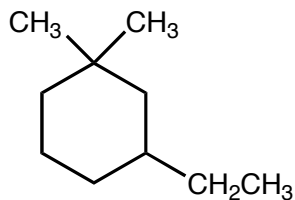
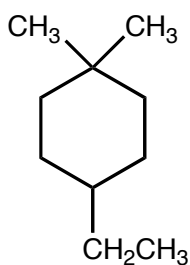
a) **Mild acid**, show the mechanisms for **both** steps



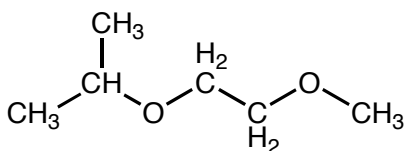
b) **Strong acid**, show the mechanism for step 2 only



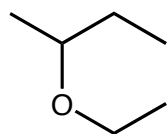
- 5) NMR (20 points) Spectroscopy, see the chemical shift Tables on the next page.
 a) Indicate the number of resonances (peaks) expected in the broadband (proton) decoupled ^{13}C NMR spectra of the following compounds (6 points).



- b) Indicate the expected multiplicities (splittings) for all the protons in the following bis-ether (6 points).



- c) Below are listed the ^1H NMR spectral data for *sec*-butyl ethyl ether (2-ethoxybutane). Assign each resonance to the relevant proton atoms (6 points).



sec-butyl ethyl ether
(2-ethoxybutane)

^1H NMR, δ 3.7 (1H, sextet), 3.5 (2H, quartet), 1.6 (2H, quintet), 1.3 (6H, two overlapping triplets), 1.0 (3H, doublet)

- d) In the ^{13}C NMR spectrum of *sec*-butyl ethyl ether (above), how many resonances will be above 50 ppm and how many resonances will be below 50 ppm? (2 points)

^1H , ^{13}C Chemical Shift Summary

TYPE OF ATOMS		^1H CHEMICAL SHIFT (δ , ppm)	^{13}C CHEMICAL SHIFT (δ , ppm)
1°-Alkyl	RCH_3	0.8–1.0	5–20
2°-Alkyl	RCH_2R	1.2–1.4	20–30
3°-Alkyl	R_3CH	1.4–1.7	30–45
allylic	$\begin{array}{c} \text{CH}_3 \\ \diagup \\ \text{R}_2\text{C}=\text{C} \\ \diagdown \\ \text{R} \end{array}$	1.6–1.9	20–40
α -ketone	$\begin{array}{c} \text{O} \\ \parallel \\ \text{RC}^{\text{b}}\text{C}^{\text{a}}\text{H}_3 \end{array}$	2.5–3.0	a, 25–40 b, 190–210
alkyne	$\text{R}-\text{C}\equiv\text{C}-\text{H}$	2.1–2.6	65–95
alkyl bromide	RCH_2Br	3.4–3.6	~20
alkyl chloride	RCH_2Cl	3.6–4.0	~35
alcohol or ether	RCH_2OH RCH_2OR	3.5–4.0	60–70
vinylic	$\text{R}_2\text{C}=\text{CH}_2$	4.6 – 5.0	100–160
	$\begin{array}{c} \text{R}_2\text{C}=\text{C}-\text{H} \\ \\ \text{R} \end{array}$	5.2 – 5.7	