CHEM 203

Midterm Exam 2
November 15, 2012

ANSWERS

Your name: _____

This a closed-notes, closed-book exam

You may use your set of molecular models

This document contains 8 pages

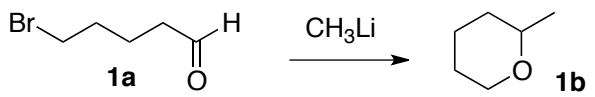
Time: 1h 30 min

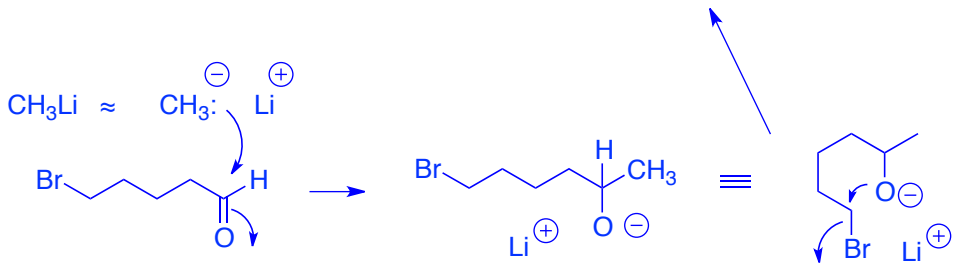
1. _____ / 10
2. _____ / 15
3. _____ / 15
4. _____ / 20
5. _____ / 20
6. _____ / 20

TOTAL _____ / 100

This exam counts for 25% of the CHEM 203 lecture grade

1. (10 pts.) Write an accurate electronic mechanism to account for the fact that the reaction of aldehyde **1a** with methyllithium yields compound **1b** as one of the products.

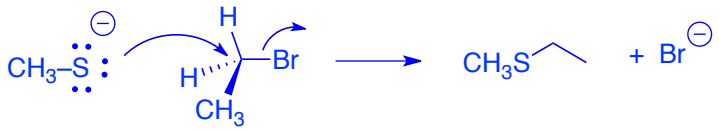




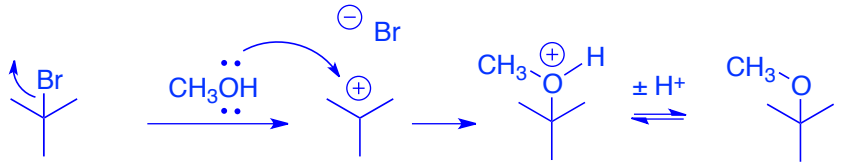
2. (15 pts.) Draw:

a. Accurate mechanisms for an example of S_N2 reaction and an example of S_N1 reaction:

S_N2 reaction:



S_N1 reaction:

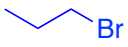


b. The structure of an alkyl chloride that is likely to dissociate readily when dissolved in CH_3OH and that of an alkyl chloride that is likely to dissociate with difficulty when dissolved in CH_3OH.

dissociates readily

e.g.

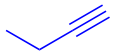
dissociates with difficulty

e.g. 

c. The structure of an alkyne that yields the same product when treated either with H_2 in the presence of Lindlar catalyst, followed by reaction with Br_2, or with Na in liquid NH_3, followed by reaction with Br_2 (write your answer in the box).

structure of the alkyne in question

any terminal alkyne,

e.g. 

d. The structure of an alkene that yields only one product when treated with O_3, followed by Zn / H^+, and that of an alkene that yields two products when treated also with O_3, followed by Zn / H^+.

yields one product

any alkene that is symmetrical around the π system, e.g.

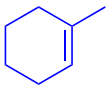
; **etc.**

yields two products

an unsymmetrical acyclic alkene, e.g.

e. The structure of an achiral cyclic alkene that yields a chiral product when treated with OsO_4, followed by aq. $NaHSO_3$, and that an achiral cyclic alkene that yields an achiral product when treated under the same conditions:

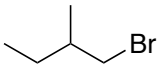
yields a chiral product

e.g. 

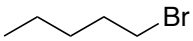
yields an achiral product

e.g.

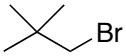
3. (15 pts.) Among the four isomeric, primary alkyl bromides **3a-3d** shown below, two undergo S_N2 reaction with NaN_3 at a rapid, and approximately equal, rate; one reacts at a less rapid rate, and one at an extremely slow rate.



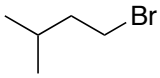
3a



3b



3c



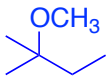
3d

i. Use the boxes below to indicate which substrates are the fast-reacting ones, which one reacts at an intermediate rate, and which one is the slow-reacting one.

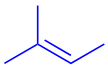
fast-reacting			intermediate rate	slow-reacting
3b	and	**3d**	**3a**	**3c**

ii. Prolonged heating of a solution of the slow-reacting bromide above in CH_3OH results in formation of an ether and of an alkene. Draw the structures of these products in the boxes below.

ether product



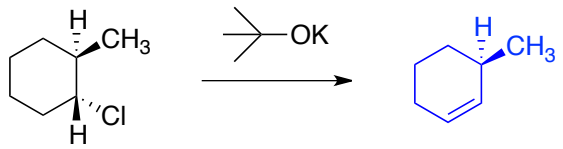
alkene product



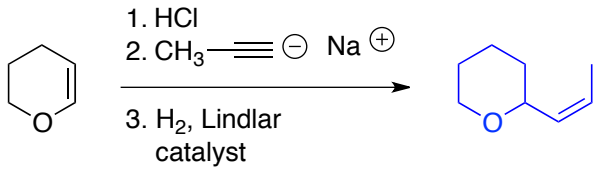
4. (20 pts.) Provide the structure of the major product expected from the following reaction sequences. If no overall change is expected, answer "NO REACTION." **Important**: compounds incorporating multiple stereogenic centers must be drawn with the correct relative configuration.

Note: it is understood that chiral compounds will be obtained as racemic mixtures.

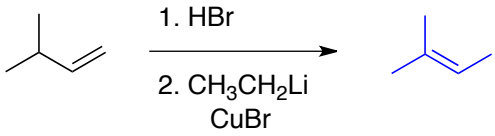
a.



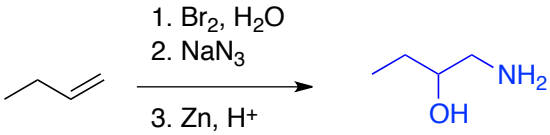
b.



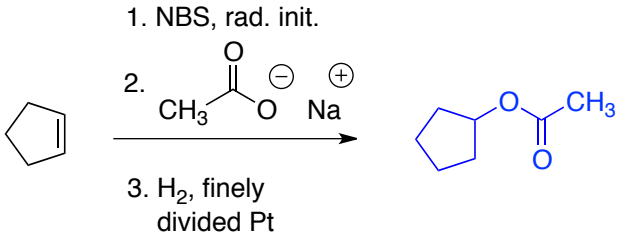
c.



d.



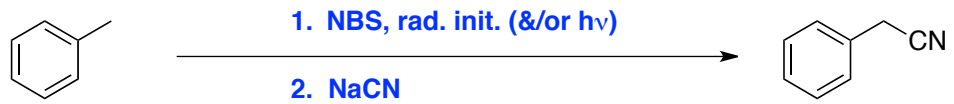
e.



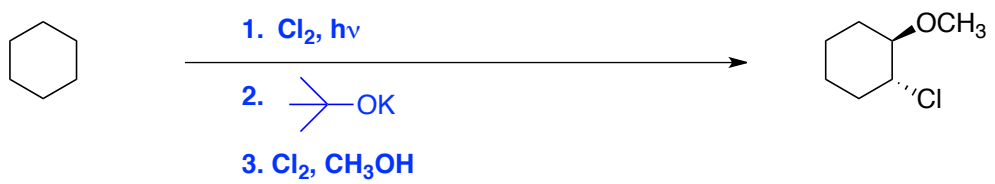
5. (20 pts.) Propose a method to achieve the transformations shown below. Indicate all the reagents, in the correct order, that are required to induce each transformation. Present your answer as a numbered list displayed above / below each reaction arrow. If a product appears to be unavailable from the indicated starting material by any method known to you, write "INACCESSIBLE" on the reaction arrow

Note: it is understood that chiral compounds will be obtained as racemic mixtures.

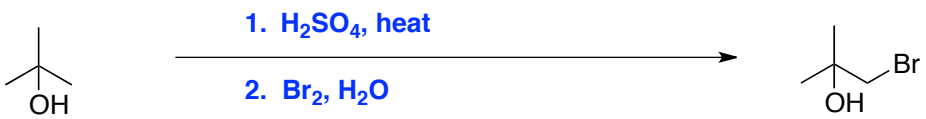
a.



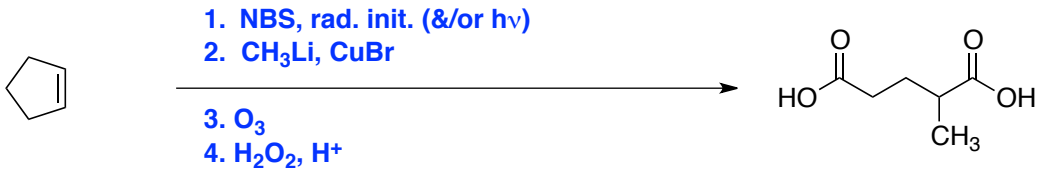
b.



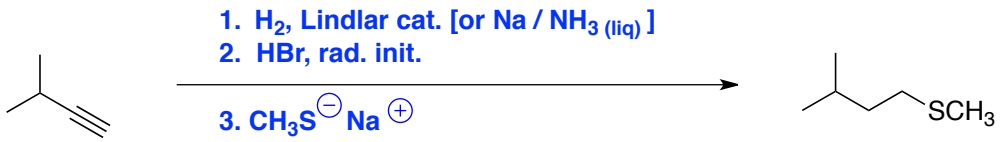
c.



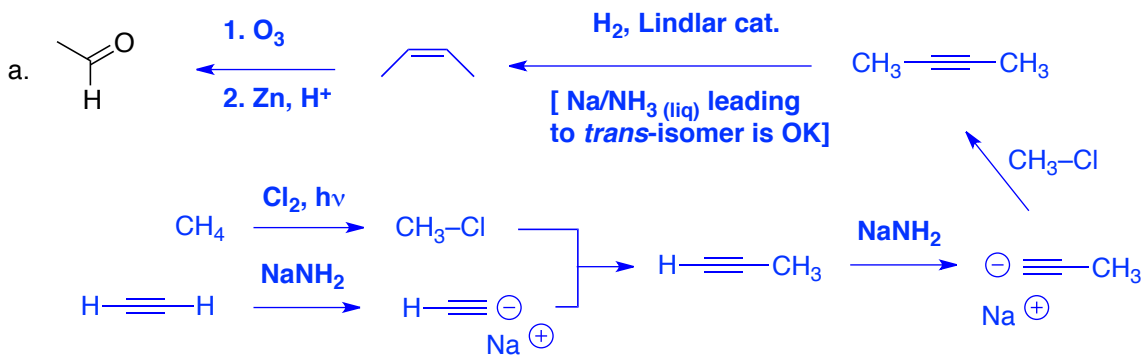
d.

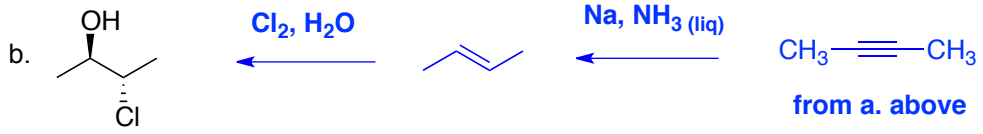


e.

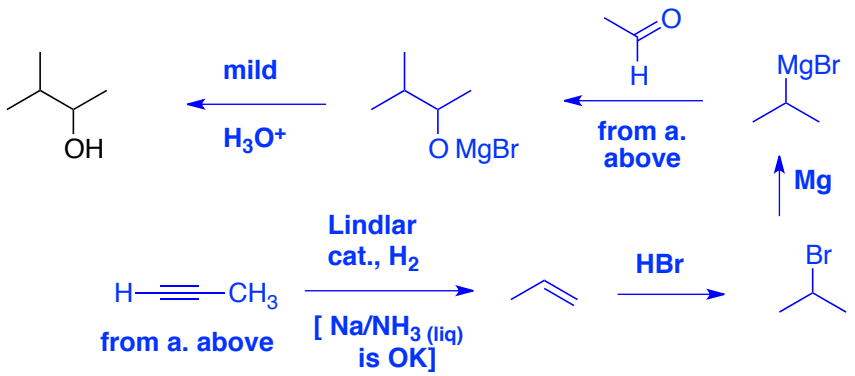


6. (20 pts.) Propose a method for the preparation of compounds a. – e. below starting ONLY with methane and acetylene as the source of carbon atoms. You may use any additional reagent that might be needed (e.g., borane, HCl, Mg, H_2O_2, potassium tert-butoxide, etc.). Present your answer as a clear flowchart that shows all intermediate steps and products. Substances obtained in a prior sequence may be used in later sequences. **It is not necessary to draw mechanisms**

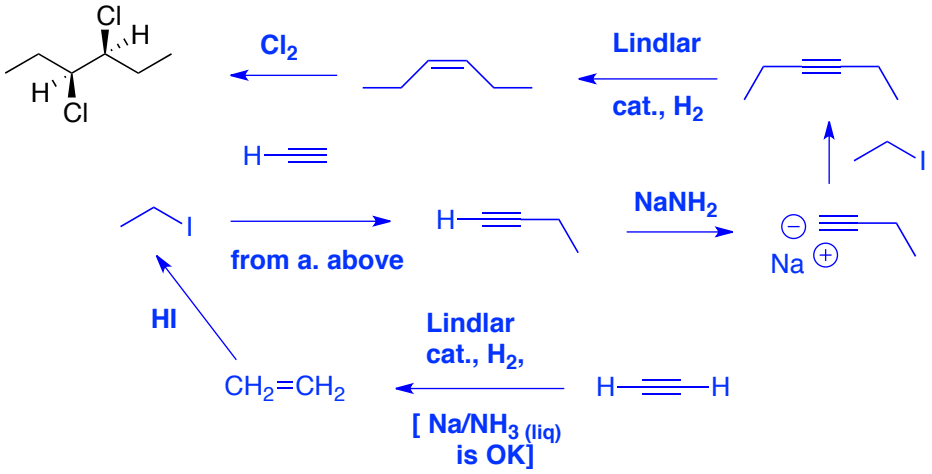




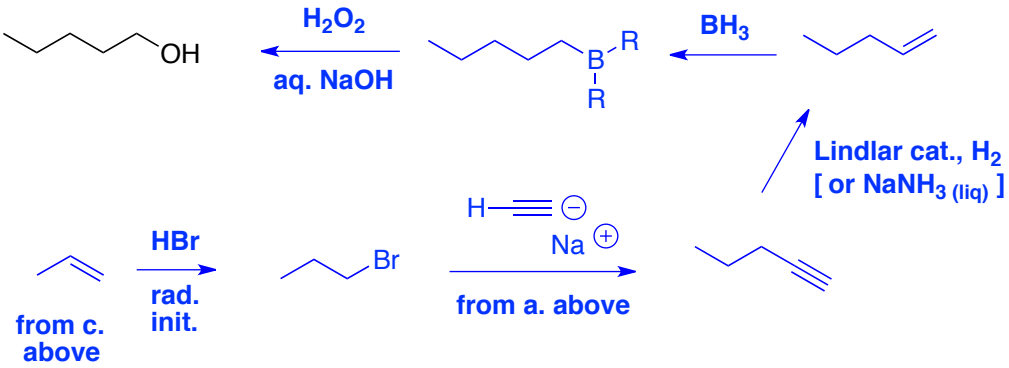
c.


OH
mild
H_3O^+
O MgBr
O
H
from a. above
MgBr
Mg
Lindlar
cat., H_2
H—≡—CH_3
from a. above
[Na/NH_3 (liq) is OK]
HBr
Br

d.


Cl
H
H
Cl
Cl_2
Lindlar
cat., H_2
H—≡
I
from a. above
H—≡
$NaNH_2$
Na
HI
$CH_2=CH_2$
Lindlar
cat., H_2,
[Na/NH_3 (liq) is OK]
H—≡—H

e.


OH
H_2O_2
aq. NaOH
B
R
R
BH_3
Lindlar cat., H_2
[or $NaNH_3$ (liq)]
from c. above
HBr
rad. init.
Br
H—≡
Na
from a. above