CHEM 203

Midterm Exam 2
November 12, 2013

ANSWERS

Your name: _____

This a closed-notes, closed-book exam

You may use your set of molecular models

This document contains 7 pages

Time: 1h 30 min

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

TOTAL _____ / 100

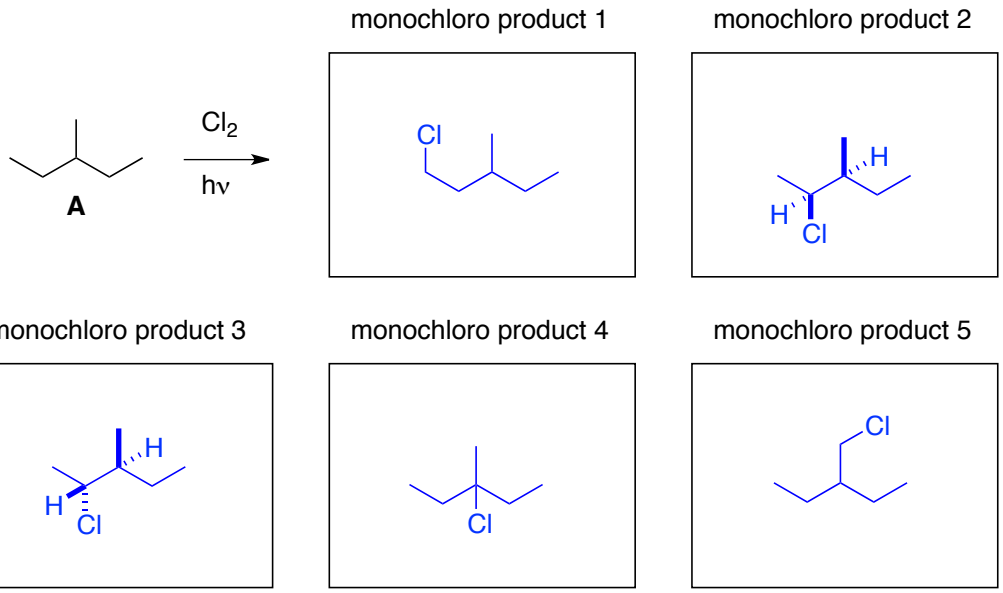
This exam counts for 18.75% of your CHEM 203 final grade

1. (10 pts.) Indicate the approximate pKa for the dissociation of the protons in boldface in the following molecules (write your answers in the appropriate boxes):

H–CH_3	**H**–OSO_2CF_3	**H**–O-CH_2CH_3	**H**–$CH{=}CH_2$	**H**-$\overset{\oplus}{O}H_2$
50	–10	17	40	–2

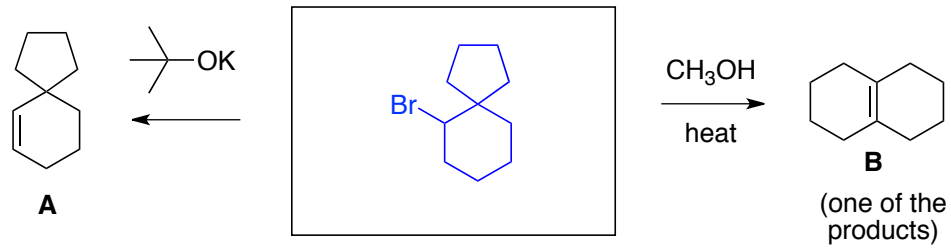
H–C≡C–CH_3	**H**–H	**H**–Br	**H**–OH	**H**-NH_2
25	40	–8	16	33

2. (15 pts.) The radical chlorination of compound **A** afforded a mixture of products, from which five distinct mono-chlorinated derivatives were isolated. Draw the structures of the five monochloro products in the boxes below.



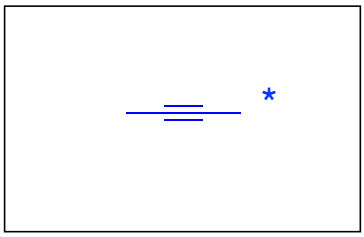
3. (15 pts.) Inside the appropriate boxes, draw:

   a. The structure of an alkyl bromide that furnishes alkene **A** when treated with potassium *tert*-butoxide, but alkene **B** as one of the products obtained upon heating in CH_3OH:



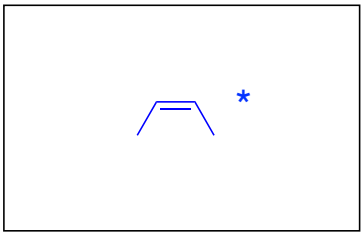
b. The structure of an alkyne that yields one product when treated with H_2 in the presence of Lindlar catalyst, and then with OsO_4 followed by aqueous $NaHSO_3$ solution, but a different product when treated with Na in liquid NH_3, and then with OsO_4 followed by aqueous $NaHSO_3$ solution.

structure of the alkyne in question

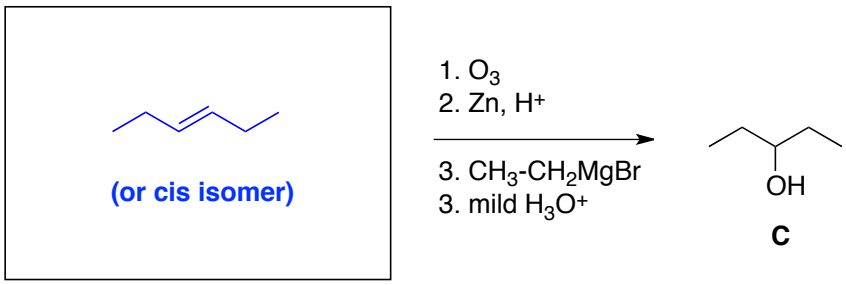


c. The structure of an alkene that yields a chiral product when treated with Br_2, but an achiral product when treated with OsO_4 followed by aqueous $NaHSO_3$ solution:

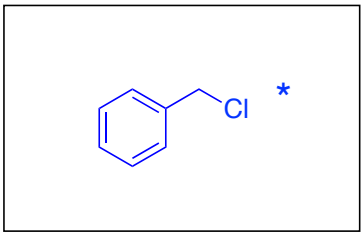
structure of the alkene in question



d. The structure of an alkene that yields only product **C** when treated with O_3 and then with Zn / H^+, followed by CH_3CH_2MgBr and then mild H_3O^+:



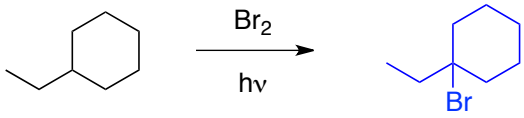
e. The structure of an alkyl halide that cannot undergo E2 reaction

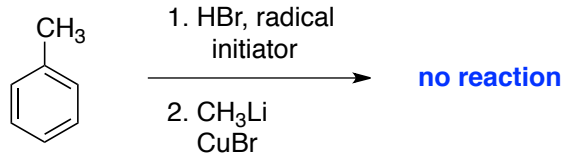


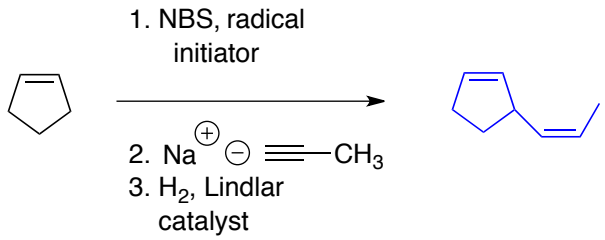
*** other answers are possible**

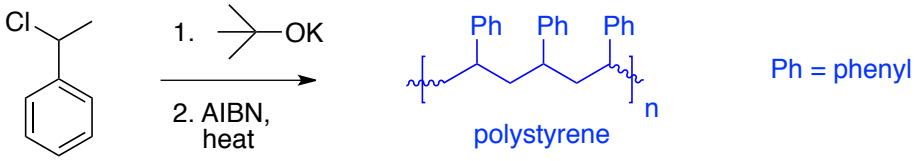
4. (20 pts.) Provide the structure of the major product expected from the following reaction sequences. If no overall change is expected, answer "NO REACTION." **Important**: compounds incorporating multiple stereogenic centers must be drawn with the correct relative configuration.

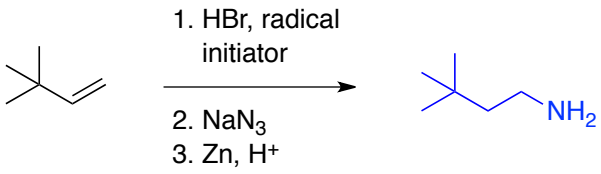
Note: it is understood that chiral compounds will be obtained as racemic mixtures.

a. 

b. 

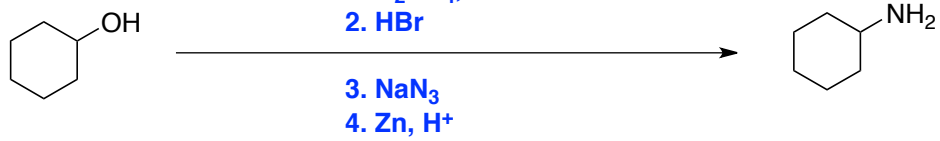
c. 

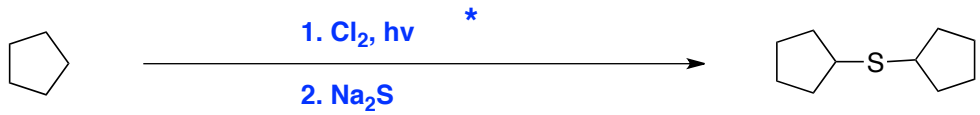
d. 

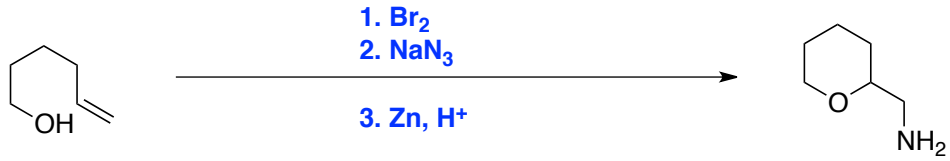
e. 

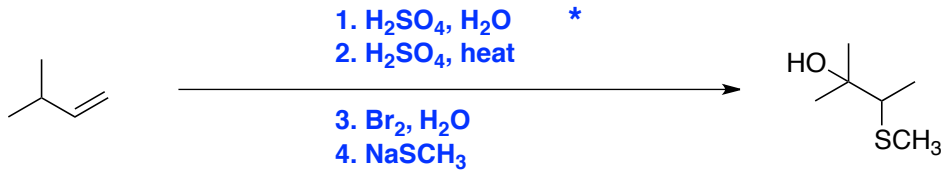
5. (20 pts.) Propose a method to achieve the transformations shown below. Indicate all the reagents, in the correct order, that are required to induce each transformation. Present your answer as a numbered list displayed above / below each reaction arrow. If a product appears to be unavailable from the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

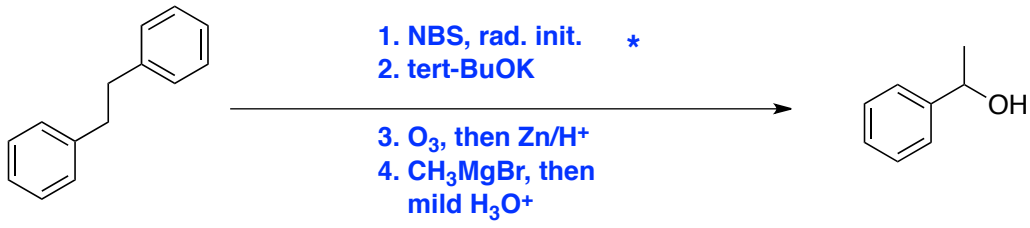
Note: it is understood that chiral compounds will be obtained as racemic mixtures.

a. 

b. 

c. 

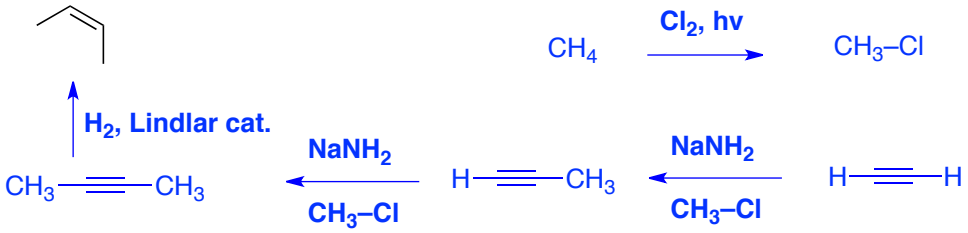
d. 

e. 

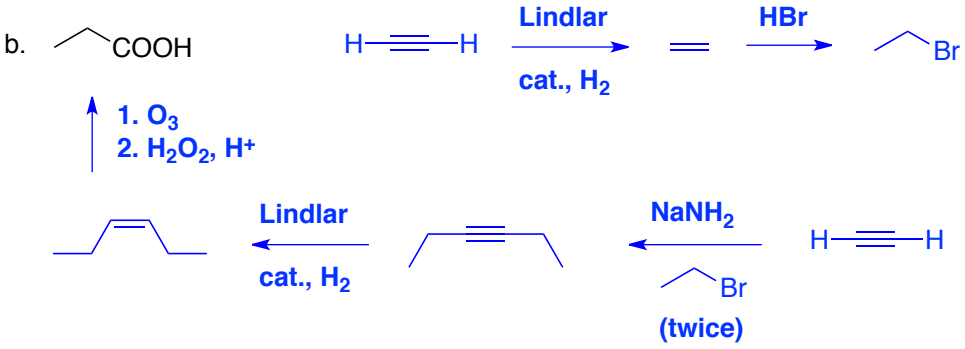
* other answers are possible

6. (20 pts.) Propose a method for the preparation of compounds a. – e. below starting ONLY with methane (CH_4) and acetylene (H–C≡C–H) 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**

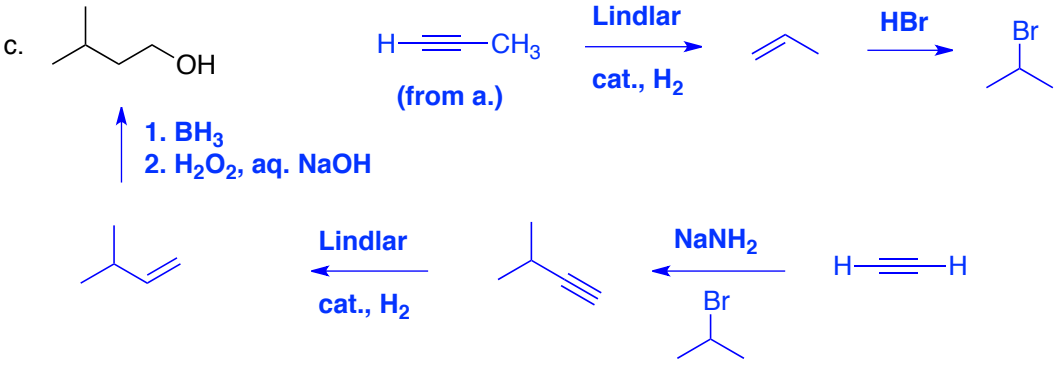
a.



b.

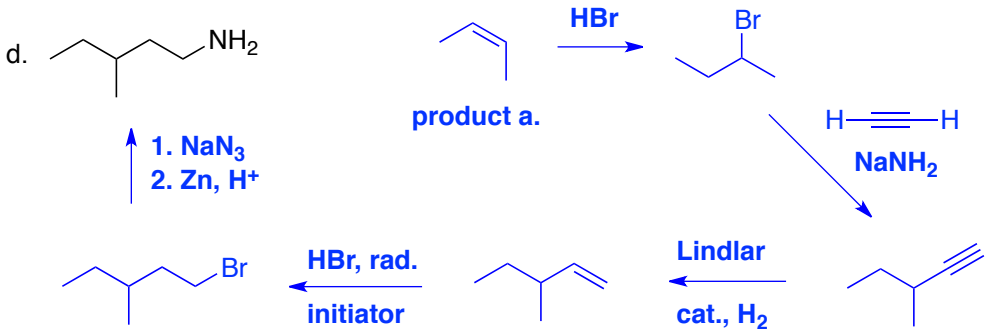


c.

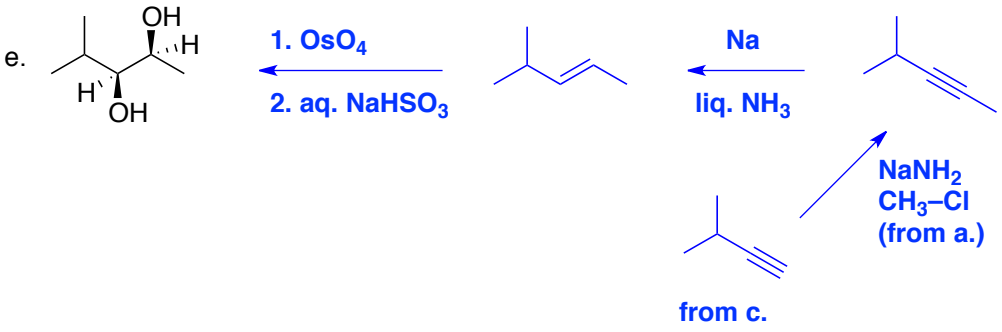


$Na/NH_{3\ (liq)}$ instead of H_2/Lindlar would be OK in the above cases

d.



e.



alternative answers may be OK