CHEM 203

Midterm Exam 1
October 9, 2014

ANSWERS

Your name: _____

This a closed-notes, closed-book exam

You may use your set of molecular models

This exam contains 6 pages

Time: 1h 30 min

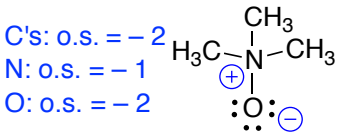
1. _____ / 15
2. _____ / 15
3. _____ / 15
4. _____ / 15
5. _____ / 20
6. _____ / 20

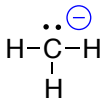
TOTAL _____ / 100

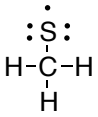
This exam counts for 18.75% of your CHEM 203 final grade

1. (10 pts) Indicate:

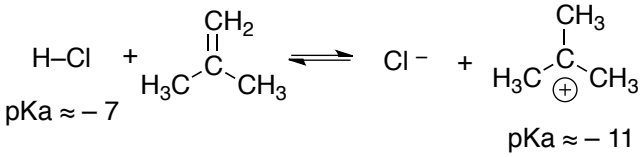
(i) the formal charge and the oxidation state of each atom other than H in the following molecules:





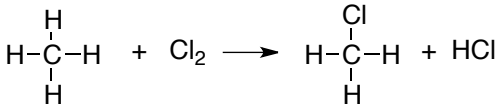


(ii) the approximate equilibrium constant for the following Bronsted acid-base equilibrium (write your answer in the box):



Keq ≈ 10^{-4}

(iii) whether the following reaction is enthalpically favorable or unfavorable (write your answer in the box):

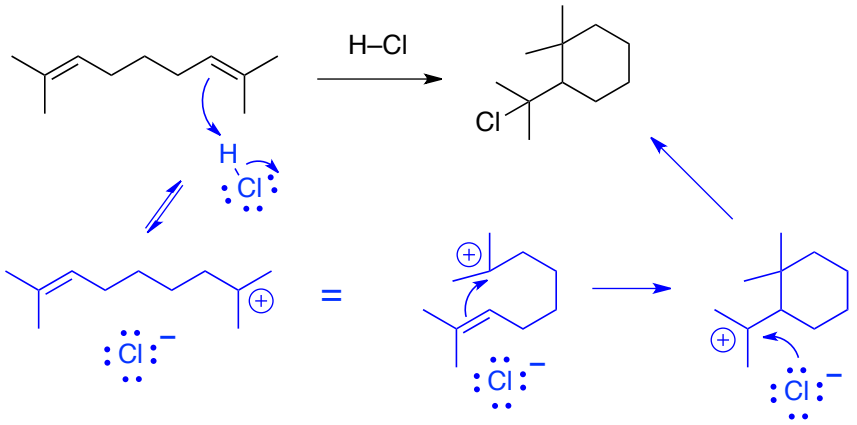


approximate bond dissociation energies (kcal/mol):

C–H ≈ 100; C–Cl ≈ 80; Cl–Cl ≈ 60; Cl–H ≈ 110

the reaction is **favorable**

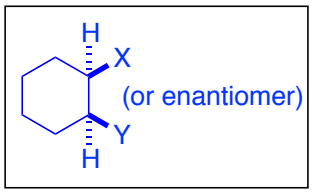
2. (15 pts.) Draw an accurate mechanism (curved arrows, formal charges, etc.) for the following known reaction:



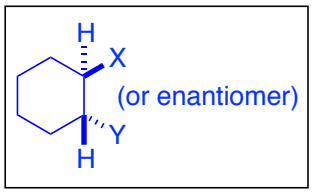
3. (15 pts.) Draw accurate structures of (write your answers in the appropriate boxes):

a. The product of *syn* addition of generic reagent X–Y to cyclohexene, and the product of *anti* addition of the same reagent, also to cyclohexene

product of *syn* addition

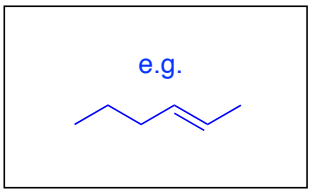


product of *anti* addition

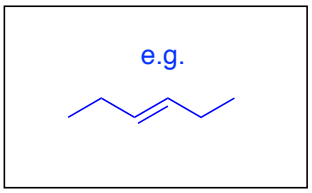


b. An alkene containing at least 4 carbon atoms that yields two distinct carbonyl products upon reaction with O_3 followed by Zn and H^+, and one that yields only one carbonyl product under the same conditions

yields two products

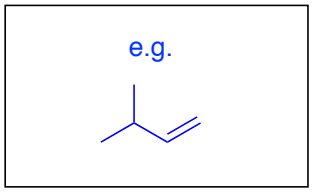


yields one product

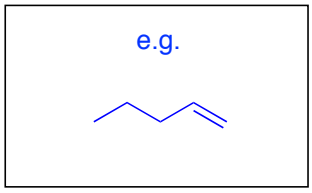


c. An alkene containing at least 4 carbon atoms that is likely to undergo rearrangement upon reaction with HBr, and one, also containing at least 4 carbon atoms, that is not likely to undergo rearrangement under the same conditions

rearrangement likely

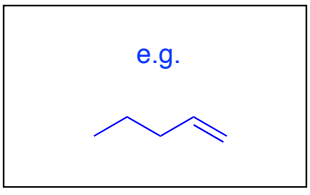


rearrangement unlikely



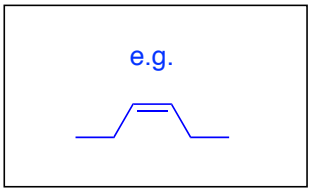
d An acyclic alkene containing at least 4 carbon atoms that yields a chiral product upon reaction with Br_2, but an achiral product upon reaction with BH_3 followed by H_2O_2 and aq. NaOH

structure of the alkene in question

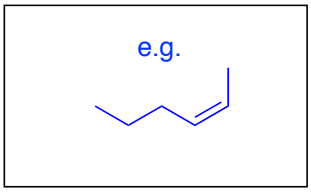


e. An acyclic alkene that contains at least 5 carbon atoms and that produces a *meso* diol upon reaction with OsO_4 followed by aq. $NaHSO_3$, and one, also containing at least 5 carbon atoms, that yields a chiral diol under the same conditions

produces a meso diol

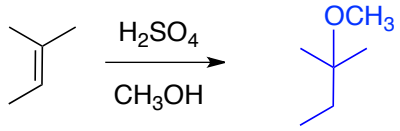


produces a chiral diol

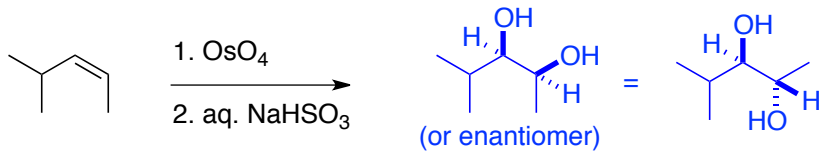


4. (15 pts.) Provide the structure of the major product(s) expected from the following reactions. If no reaction is expected, answer "NO REACTION". **Important**: compounds incorporating multiple stereogenic centers must be drawn with the correct relative configuration.

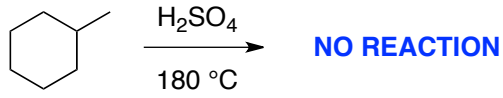
a.



b.

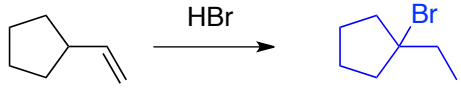


c.

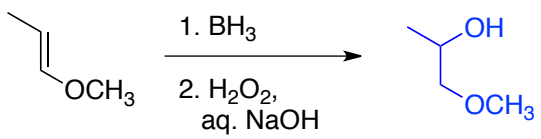


NO REACTION

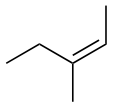
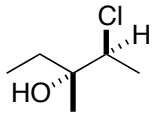
d.

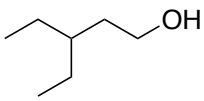


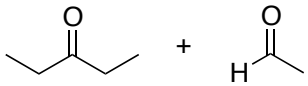
e.

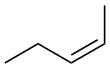
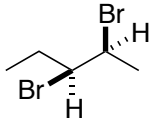


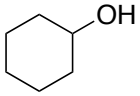
5. (20 pts.) Complete the following chemical equations by indicating all reagents / catalysts, in the correct order, that are required to convert the substrates into the products. More than one reaction may be needed to achieve the desired transformation. Provide your answer as a numbered list drawn above / below the reaction arrows. If you should conclude that a product cannot be obtained from the starting compound shown by any method known to you, write "INACCESSIBLE" on the reaction arrow.

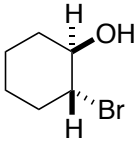
a.  **INACCESSIBLE** 

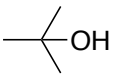
b. 

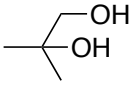
1. H_2SO_4, heat
2. O_3, then Zn, H^+


c.  **Br_2** 

d. 

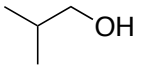
1. H_2SO_4, heat
2. Br_2, H_2O


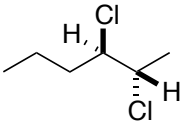
e. 

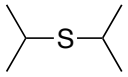
1. H_2SO_4, heat
2. OsO_4, then
aq. $NaHSO_3$


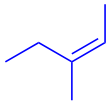
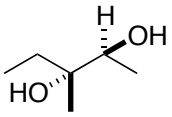
6. (20 pts.) Propose a method for the preparation of compounds a. – e. below starting from appropriate alkenes. Draw a clear structure of your proposed starting olefin on the left side of the reaction arrow. Above/below the reaction arrow, list all reagents / catalysts, in the correct order, that are required to induce the desired transformation. **Important**: the desired compound must be the major product of your reaction(s). If a product does not appear to be available by any reaction known to you, write "INACCESSIBLE" on the reaction arrow.

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

a.  BH_3, then; H_2O_2 and aq. NaOH → 

b.  Cl_2 → 

c.  1. H_2S, H_2SO_4; 2. Product of step 1. + more alkene + H_2SO_4; (or alkene, cat. H_2SO_4 + ≤ 0.5 equiv H_2S relative to alkene) → 

d.  OsO_4, then; aq. $NaHSO_3$ → 

e. INACCESSIBLE →