CHEM 2311
E4 Practice-iii (answers *not* provided)

1. (32 points) Circle the letter *on the right* which corresponds to the answer to each question. There is only one correct answer for each question.

(i) Which of the following reactions of alkenes is stereospecific?

A. Markovnikov addition of HBr **A**
B. acid-catalyzed hydration (treatment with aqueous H_2SO_4) **B**
C. hydrogenation (treatment with H_2/Pt) **C**
D. anti-Markovnikov addition of HBr to alkenes (treatment with HBr, peroxides) **D**

(ii) What is the mechanism by which the major product is formed upon treatment of 1-bromoethane and sodium *tert*-butoxide?

E. S_N1 **F.** S_N2 **G.** E1 **H.** E2 **E F G H**

(iii) What is the mechanism by which the major product is formed upon treatment of 1-bromoethane and sodium methoxide?

I. S_N1 **J.** S_N2 **K.** E1 **L.** E2 **I J K L**

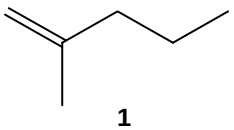
(iv) What is the mechanism by which the major product is formed upon treatment of 2-bromopropane and sodium iodide?

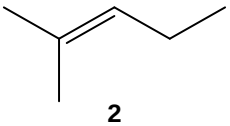
M. S_N1 **N.** S_N2 **O.** E1 **P.** E2 **M N O P**

(v) What type of reactive intermediate is formed in the reaction of an alkene with HBr and peroxides to give a bromoalkane?

Q. Carbocation **R.** Cyclic bromonium ion **S.** Carbanion **T.** Radical **Q R S T**

(vi) Which of the following alkenes undergoes the least exothermic hydrogenation upon treatment with H_2/Pd?


1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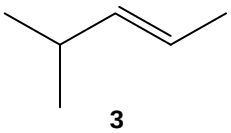
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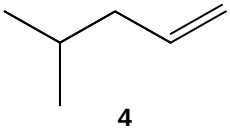
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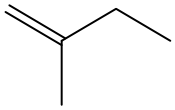
U. 1 **V. 2** **W. 3** **X. 4** **U V W X**

(vii) Rank the following alkenes in order of decreasing exothermicity for their combustion (more exothermic > less exothermic)

1


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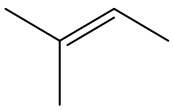

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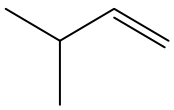
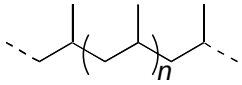


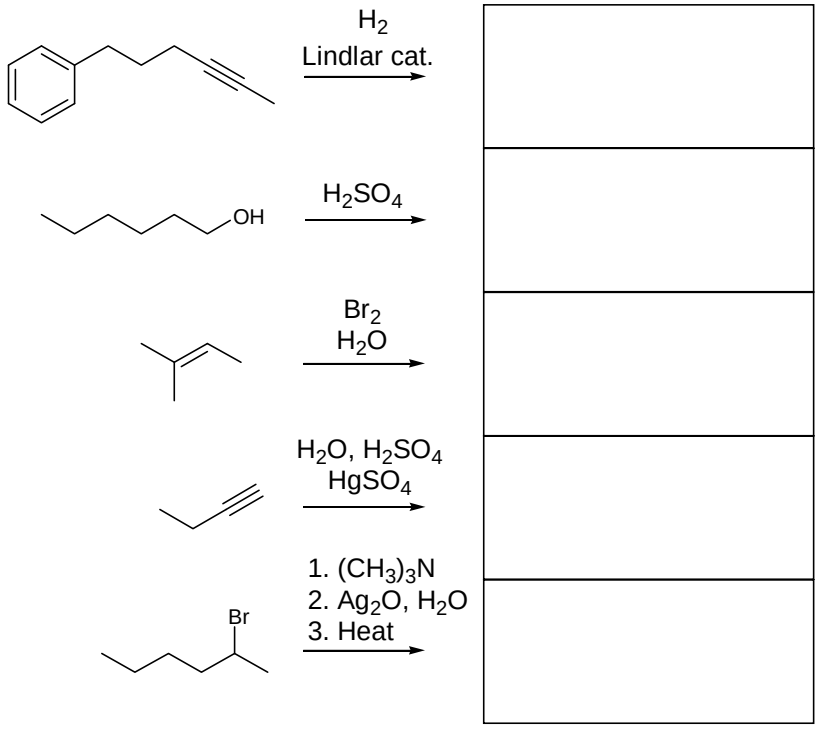
Y. 1 > 2 > 3 **Z. 3 > 1 > 2** **AA. 3 > 2 > 1** **BB. 2 > 1 > 3** **Y Z AA BB**

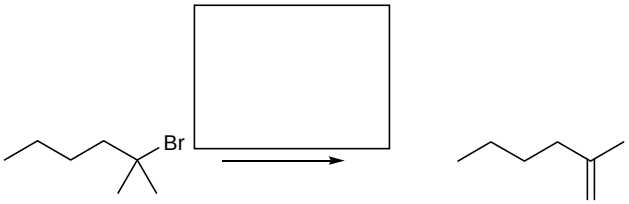
(viii) Which monomer is used to prepare the following polymer?

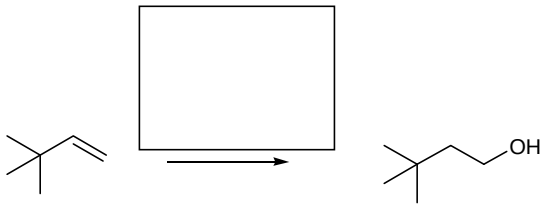


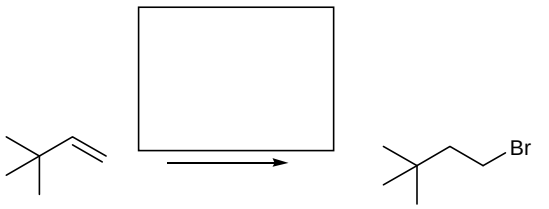
CC. ethene **DD.** propene **EE.** 1-butene **FF.** styrene **CC DD EE FF**

2. (32 points) Provide the structures (first five reactions) and reagents (last three reactions) to complete the following reaction schemes. Indicate the stereochemistry of the products wherever appropriate.

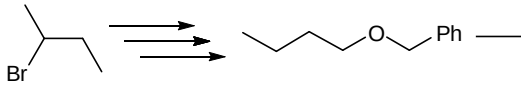


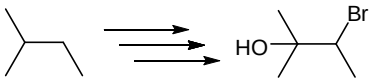


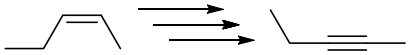




3. (20 points) The following transformations *cannot* be performed in a single step. Provide sequences of reactions, showing reagents and isolated synthetic intermediates, to achieve each transformation. *PROBLEM SOLVING HINTS: Each of these transformations requires 2-3 steps. Approach this type of problem by asking yourself what the final product can, in fact, be made from. Can this compound be prepared from the given starting material?*



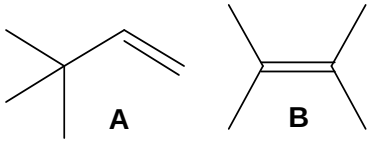




4. (12 points)

(a) Reaction of *cis*-2-butene with Br_2 provides *racemic* 2,3-dibromobutane. However, reaction with OsO_4 followed by $NaHSO_3$ gives *meso*-2,3-butanediol. Briefly explain the origin of the different stereochemical outcomes of these reactions.

(b) Treatment of alkene **A** with H_2SO_4 gives alkene **B**. (i) Provide the structure of the initially-formed carbocation, (ii) show the movement of electrons which takes place when this carbocation rearranges, and (iii) show the structure of the rearranged carbocation.



rearrangement

-structure of first-formed carbocation
-add curved arrows to show movement of electrons which takes place upon rearrangement

-structure of carbocation after rearrangement