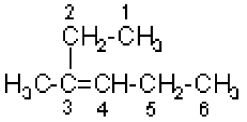
CHEM 3311
Fall 2001
Exam II (October 25)
ANSWER KEY

1. (25 points) Multiple Choice: Circle the **best** possible answer.

(i) Select the correct IUPAC name for the compound incorrectly labeled as 2-ethyl-2-pentene.

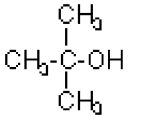
(A) 3-Methyl-3-pentene (B) 4-Methyl-3-pentene
(C) 3-Methyl-3-hexene (D) 3-Heptene



Correct name: 3-Methyl-3-hexene
Correct Answer: C

(ii) What is the slow, rate-determining step in the acid-catalyzed dehydration of 2-methyl-2-propanol

(A) The simultaneous loss of a b-hydrogen and water from the oxonium ion.
(B) Protonation of the alcohol to form an oxonium ion.
(C) Loss of water from the oxonium ion to form a carbocation.
(D) Loss of a beta-hydrogen from the carbocation to form an alkene.



is a tertiary alcohol; acid-catalyzed dehydration follows an E1 mechanism.
Correct Answer: C

(iii) Select the alkene that is thermodynamically the most stable.

(A) trans-3-hexene (B) cis-3-hexene
(C) 1-hexene (D) 2-methyl-2-pentene

In general, alkenes with more highly substituted double bonds are more stable than isomers with less substituted double bonds.
Correct Answer: D

(iv) The reaction of 1-butene with bromine, Br_2, in aqueous solution gives primarily 1-bromo-2-butanol. The nucleophilic species that leads to the above product is:

(A) Br_2 (B) Br^-
(C) H_2O (D) OH^-

1-butene forms the cyclic bromonium ion, which is captured by the nucleophile, H_2O, producing the bromohydrin after the loss of H^+. Correct Answer: C

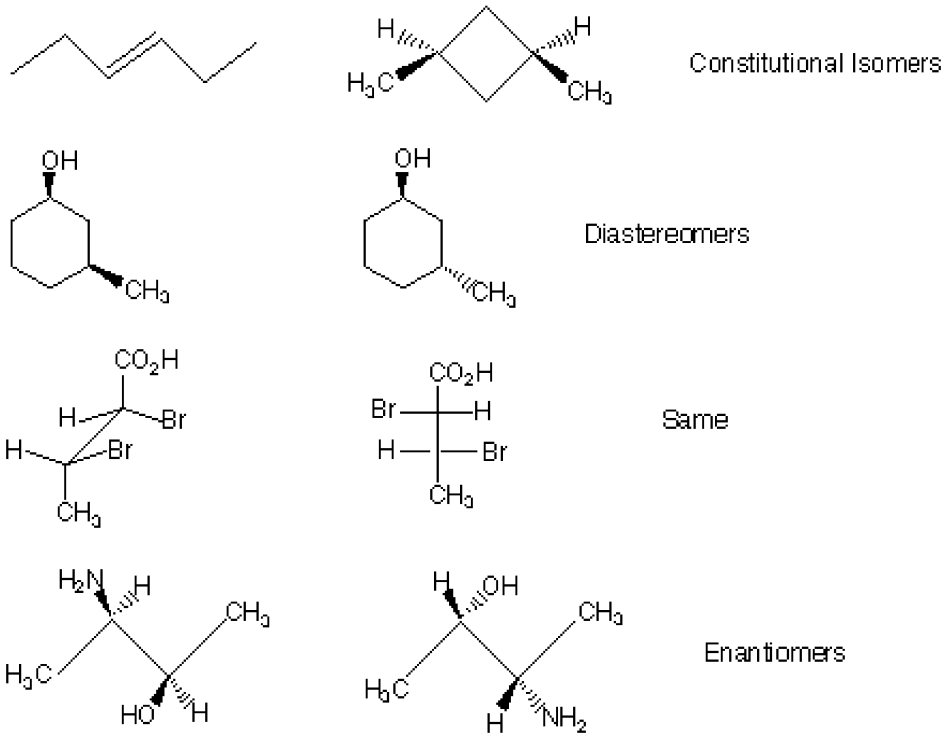
(v) Compound X, $C_5H_{10}O$, is optically active. The compound consumes one equivalent of H_2 to form $C_5H_{12}O$. The hydrogenation product is also optically active. The structure of compound X is most likely to be:

(A) $H_2C{=}CHCH_2CH_2CH_2OH$ (B) *trans*-$CH_3CH{=}CHCH_2CH_2OH$
(C) $CH_3CH_2CH(OH)CH{=}CH_2$ (D) $CH_3CH(OH)CH_2CH{=}CH_2$

Neither (A) nor (B) represents an optically active compound, while both (C) and (D) represent compounds with chiral centers. However, on hydrogenation, (C) is converted to $CH_3CH_2CH(OH)CH_2CH_3$ which is optically inactive.

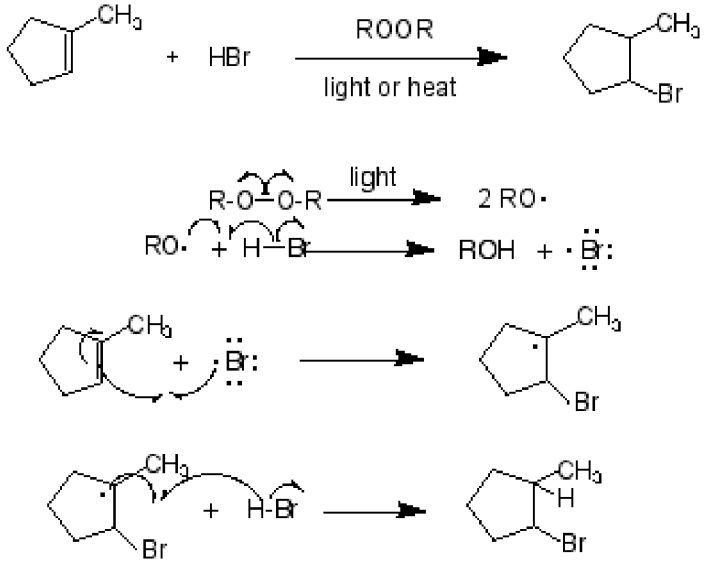
Hydrogenation of (D) produces an optically active product. Correct Answer: D

2. (20 points) Label each of the following pairs of structures as conformers, constitutional (or structural) isomers, diastereomers, enantiomers, or the same.

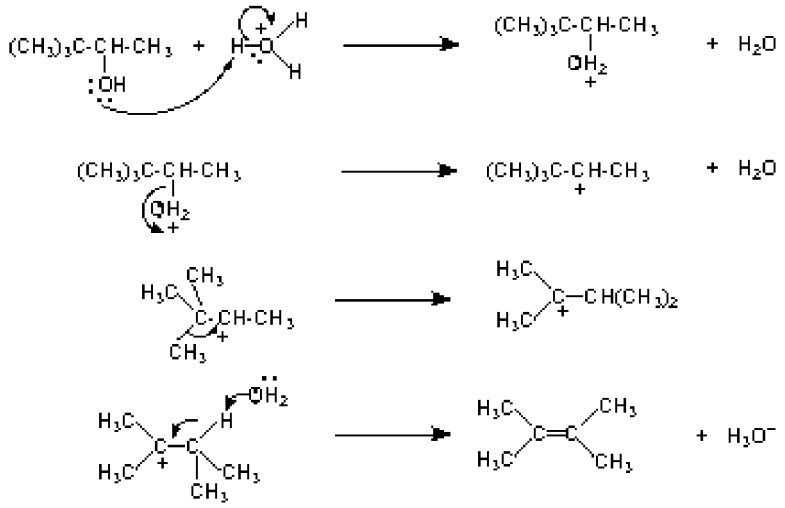


3. (20 points) Write an arrow pushing mechanism for **ANY TWO** of the following transformations. Be sure to show all intermediates in the pathway from starting material to product, but do not show transition states. All structures should have proper valence bond structures with correct formal charges and lone pairs as necessary. If you attempt all three, be sure to CROSS OUT the one that SHOULD NOT BE GRADED. If you do not follow the guidelines, only the first two mechanisms will be graded.

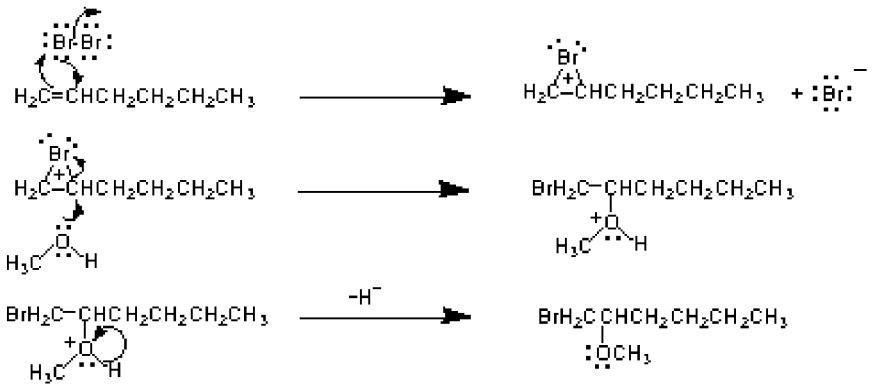
A)



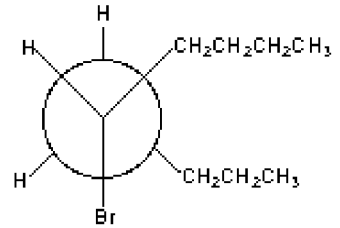
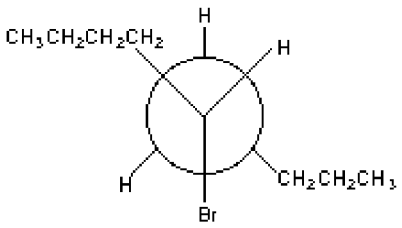
B) $(CH_3)_3C\text{-}CH(OH)\text{-}CH_3 \xrightarrow[\text{heat}]{H_3PO_4}$ 2,3-Dimethyl-2-butene



3C) $H_2C{=}CHCH_2CH_2CH_2CH_3 \xrightarrow[CH_3OH]{Br_2} BrCH_2CH(OCH_3)CH_2CH_2CH_2CH_3$



4. (10 points) 5-Bromononane on treatment with potassium ethoxide in ethanol produces a mixture of *cis*-4-nonene (23%) and *trans*-4-nonene (77%). Draw Newman projections of 5-bromononane, **looking down the C5-C6 bond**, showing the conformations that lead to *cis*-4-nonene and *trans*-4-nonene, respectively. Assume that C5 is closest to you and C6 is pointing away from you.

Conformation leading to *cis*-4-nonene	Conformation leading to *trans*-4-nonene
	

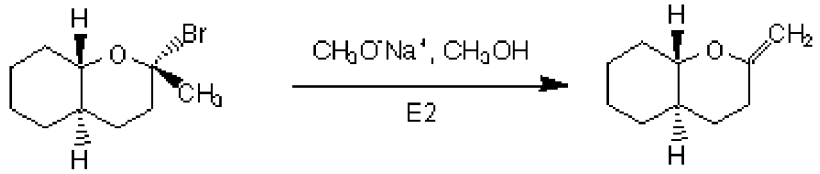
Based on your conformations, explain in one or two sentences, why the *trans*-alkene is the major product.

The staggered conformation leading to the trans-alkene is the anti conformation where the alkyl substitutents are separated by a dihedral angle of 180°, while the gauche conformation (dihedral angle of 60°) leads to the relatively less stable cis-alkene. More molecules are present in the anti

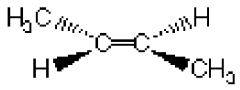
conformation and the reaction is faster; hence, the trans-alkene is the major product.

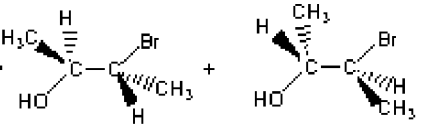
5. (25 points) Write the structure of the single major product of each of the following reactions. If two or more major products are formed, write the structures of both. Show the stereochemistry, where appropriate, using wedges and dashes.

A)

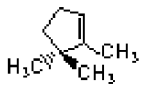


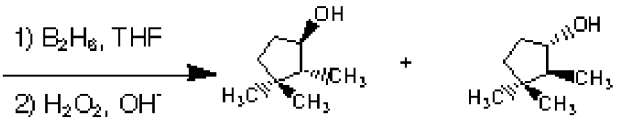
B) (E)-2-butene
(Draw structure)



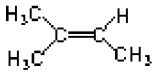


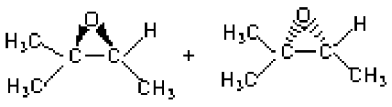
C) 1,5,5-Trimethylcyclopentene
(Draw structure)





D) 2-methyl-2-butene + CH_3COOH
(Draw structure)





E) $HOH_2C\text{-}CH_2\text{-}CH{=}CH_2$
(Write correct name for 3 bonus points)
3-Buten-1-ol