***CHEMISTRY 313-02***
MIDTERM # 2 – answer key
October 27, 2009

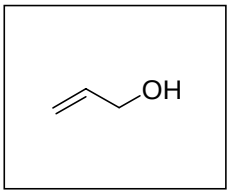
**Statistics:**

- Average: **71 pts (71%)**;
- Highest: **95 pts (95%)**; Lowest: **33 pts (33%)**
- Number of students performing at or above average: **19 (56%)**
- Number of students performing at or below 55%: **8 (24%)**
- Number of students performing at or above 90%: **7 (21%)**

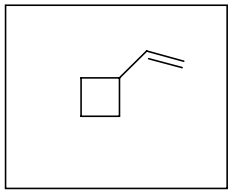
1. (7 pts) Mark as true (**T**) or false (**F**) the following statements. Do not explain!
   - (**T**) Reactions occurring according to the *E1* mechanism involve formation of carbocations;
   - (**T**) More stable alkenes have lower heats of hydrogenation;
   - (**T**) More stable carbocations are generated faster;
   - (**T**) Free radicals are electron-deficient species;
   - (**T**) Electrophilic addition reactions of alkenes follow the *Markovnikov* rule;
   - (**T**) Epoxidation is a stereospecific process;
   - (**T**) Hydrogenation of alkenes is a *syn*-addition process;

2. Circle ALL that apply:
   A. (3 pts) Free-radical bromination:
      a. Involves the formation of electron-deficient species;
      b. Is a chain reaction;
      c. Requires an initiation step;
      d. Occurs fastest at primary positions;
   B. (3 pts) $S_N1$ reactions:
      a. Occur *via* carbocation intermediates;
      b. Have a bimolecular rate-determining step;
      c. Are stepwise;
      d. Can yield rearranged products;
   C. (3 pts) *E1* reactions:
      a. Are concerted;
      b. Require strong bases;
      c. Occur *via* carbocations;
      d. Require coplanar arrangement of the C – H and C – X bonds;

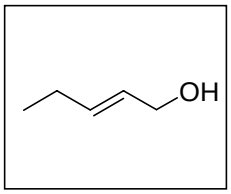
3. (4 pts) Provide structural formula for each of the following molecules:



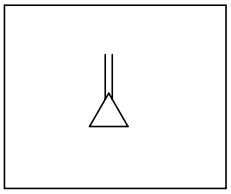

**allyl alcohol**



**vinylcyclobutane**

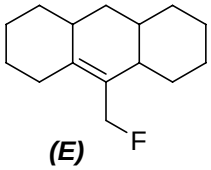



***(E)*-2-penten-1-ol**

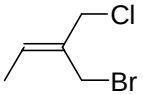


**methylenecyclopropane**

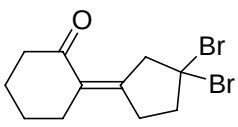
4. (4 pts) Assign *E* or *Z* configuration to each of the following alkenes. Do not explain!



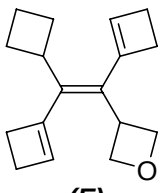

***(E)***




***(Z)***

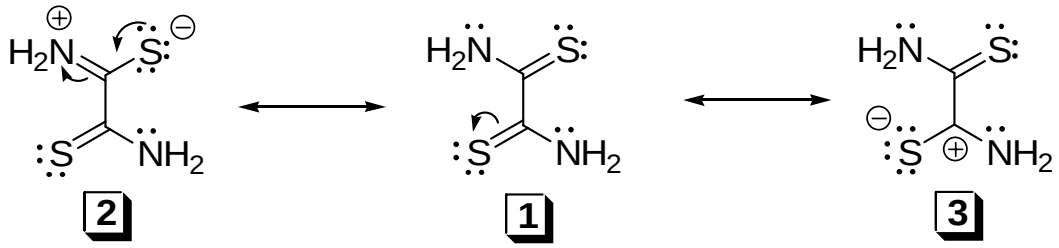



***(Z)***




***(E)***

5. (4 pts) Complete the given Lewis structure and draw <u>two more</u> valid resonance structures. Clearly show, using the curved arrow notation, the shift of electron pairs. Rank all three resonance structures.



**2** **1** **3**

charge separation

fewer bonds and charge separation

6. (4 pts) For each of the following pairs, draw the structures, indicate the more stable alkene and <u>briefly</u> account for your choice.

A. *Cis*-cycolpentene and *trans*-cyclopentene.

cis-cyclopentene trans-cyclopentene

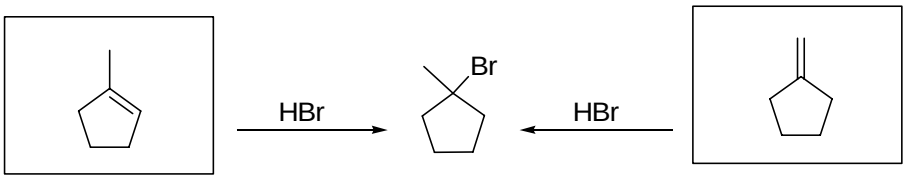
The cis-isomer is more stable. The presence of the trans-double bond introduces severe ring strain. Trans cycloalkenes with fewer than 7 carbons have never been isolated.

B. *(E)*-2-hexene and *(Z)*-2-hexene.

(E)-2-hexene (Z)-2-hexene

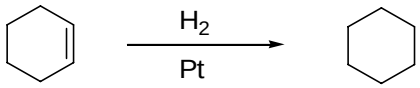
The E-isomer is more stable. The Z-isomer has van der Waals strain because of the cis-arrangement of the alkyl groups at the C = C bond

7. (2 pts) The following compound can be prepared by addition of HBr to either of two alkenes. Provide their structures.

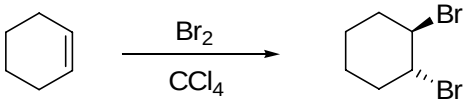



8. (8 pts) Write the equations for conversion of <u>cyclohexene</u> to each of the following, and in every case indicate the appropriate reagents/conditions:

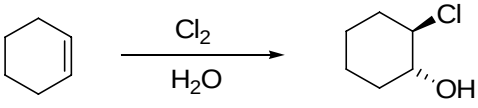
A. Cyclohexane.



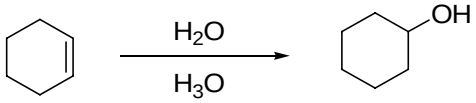

B. *Trans*-1,2-dibromocyclohexane.



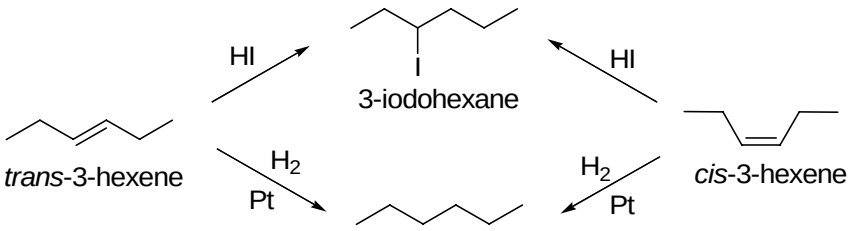

C. *Trans*-2-chlorocyclohexanol.




D. Cyclohexanol.

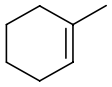


9. (3 pts) Give the structures of two stereoisomeric alkenes with molecular formula $C_6H_{12}$, which react with HI to give the same *single* product and undergo catalytic hydrogenation to produce hexane.

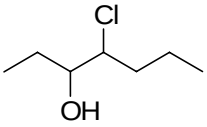



10. (3 pts) Provide one specific structure of each of the following:

A. A trisubstituted alkene;

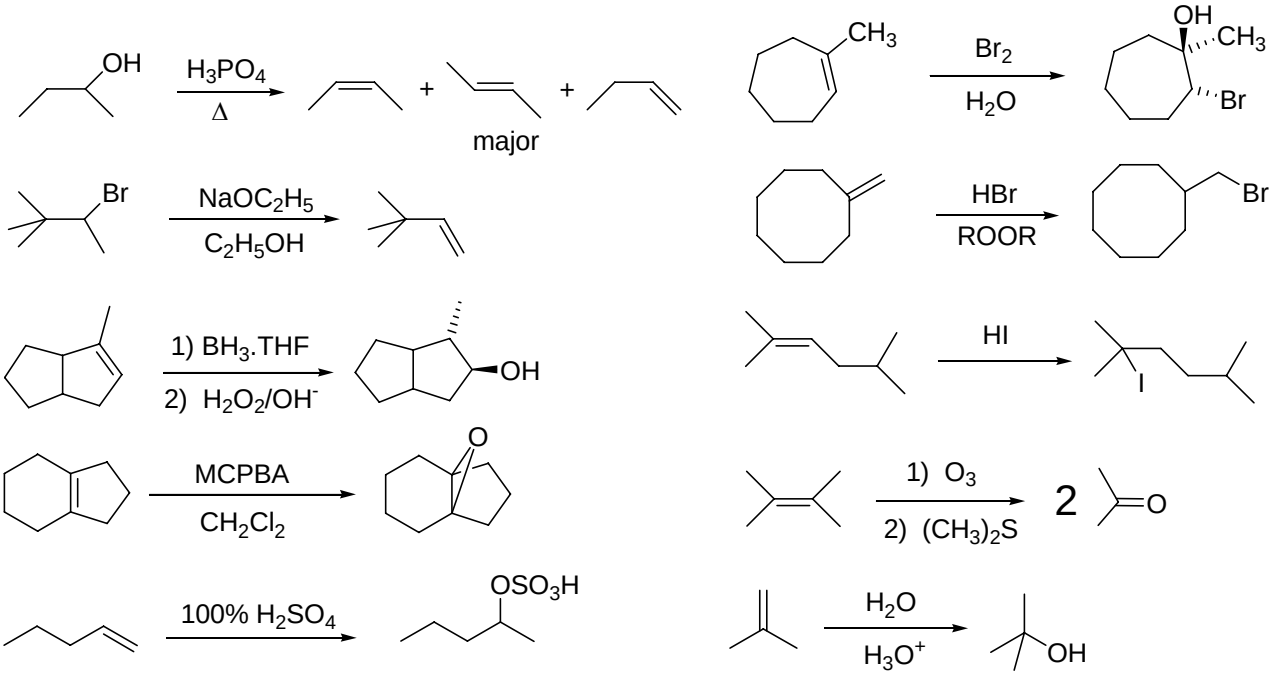


B. A vicinal halohydrin;

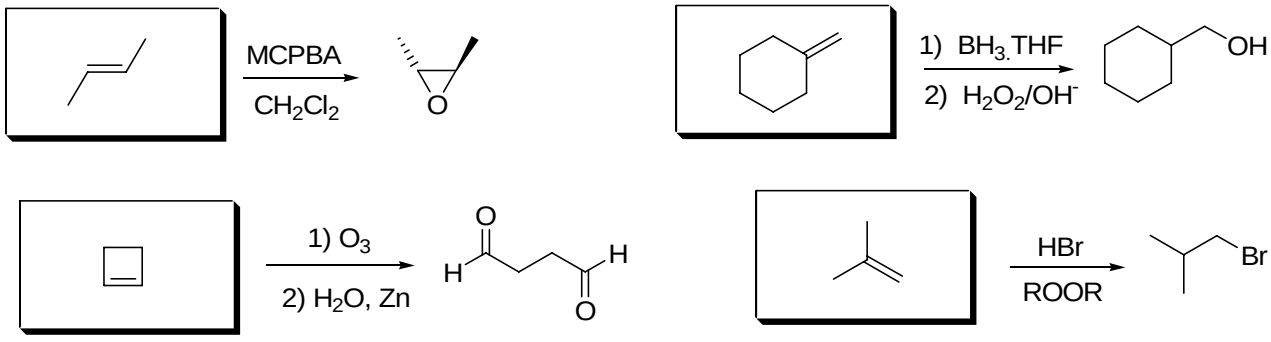



C. An ozonide;

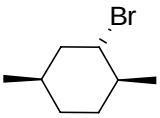

11. (10 pts) Predict the organic product in each of the following reactions, <u>including precise stereochemistry</u>, wherever applicable. If more than one product is formed, <u>indicate the major</u> component.



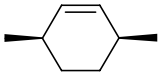

12. (8 pts) Suggest the structure of the alkene that would give the indicated product.

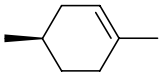


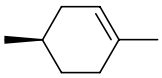
13. (4 pts) Consider the following structure:



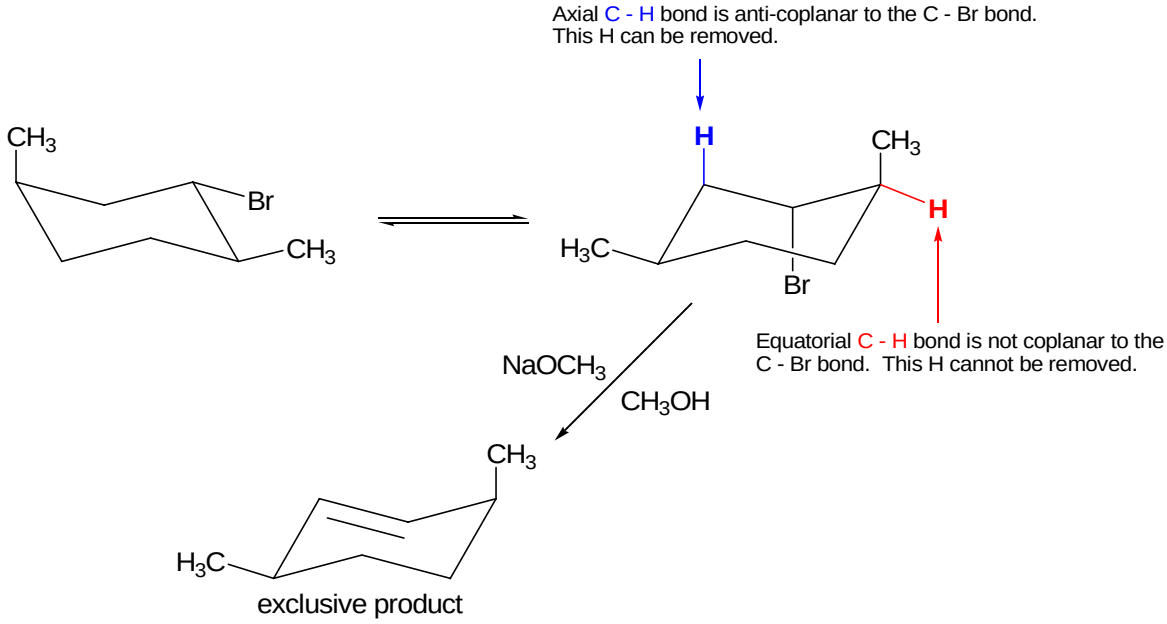

Select the correct outcome of its reaction with $NaOCH_3/CH_3OH$. Provide a structural rationalization for your choice (Less text, more structures and equations, please!).

A. The reaction produces only 

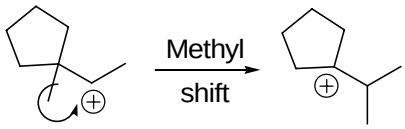
B. The reaction produces only 

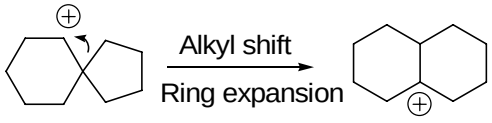
C. The reaction produces both  and 

**Solution:** The indicated conditions correspond to an E2 process (Presence of strong base!!). Thus, one has to identify C – H bonds, adjacent to the C – Br bond and coplanar with it. Only those H can be removed in an E2 process. First, represent the structure of the starting material with the appropriate chair conformations. Second, identify the conformation with axial C – Br bond. Third, in the same conformation identify adjacent C – H bonds, which are coplanar with the C – Br bond. Removal of each such H, together with Br, produces a product of elimination. As evident from the scheme below, only one H atom satisfies the condition (colored in blue). Therefore, only one elimination product is possible. The correct answer is (A).



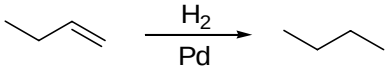

14. (4 pts) Each of the following carbocations can rearrange to a more stable ion. Propose structures for the likely rearranged species.



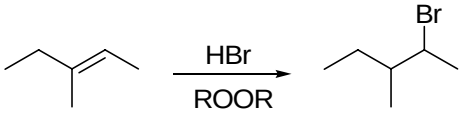




15. (6 pts) Suggest one specific example of each of the following:

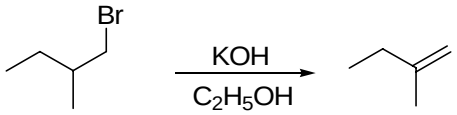
A. A *syn*-addition reaction;



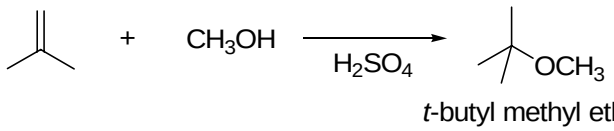

B. A reaction that produces an anti-*Markovnikov* alkyl bromide;



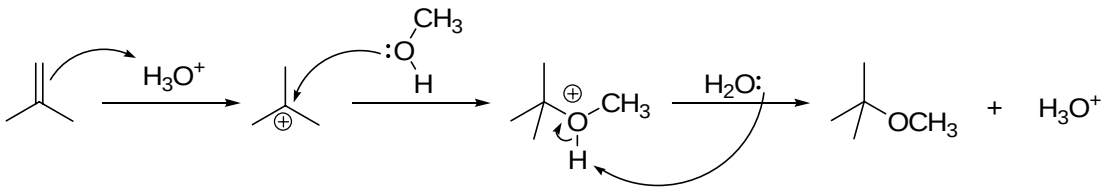
C. A β-elimination reaction;




16. (4 pts) The industrial synthesis of *t*-butyl methyl ether (see below!) involves treatment of methylpropene with methanol in the presence of acid catalyst, and is another example of an electrophilic addition reaction to an alkene. *t*-Butyl methyl ether is produced in large quantities and used as an antiknock gasoline additive. Suggest a reasonable mechanism for its formation. Use curved arrows to show the transfer of electron pairs.

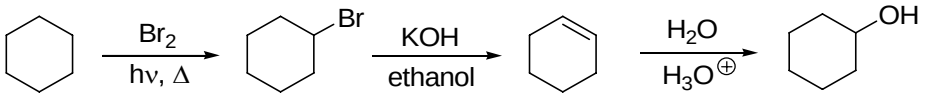



*t*-butyl methyl ether

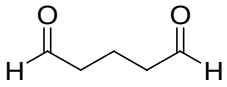


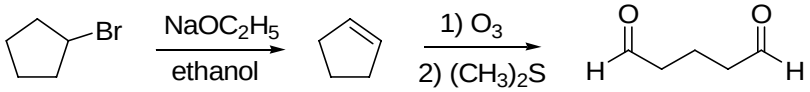

17. (8 pts) A sequence of two or more reactions is needed to realize each of the following transformations. Suggest the appropriate sequence in each case, clearly indicating the reagents/conditions and the compounds generated as products of each reaction.

A. cyclohexane $\xrightarrow{???}$ cyclohexanol



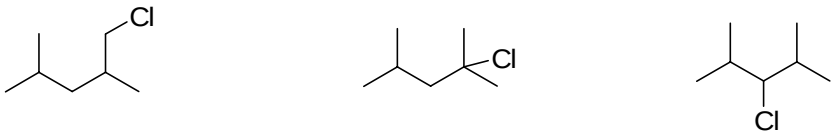

B. bromocyclopentane $\xrightarrow{??}$



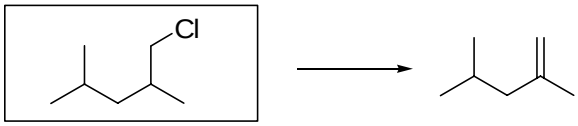




18. Consider the photochemical chlorination of 2,4-dimethylpentane.

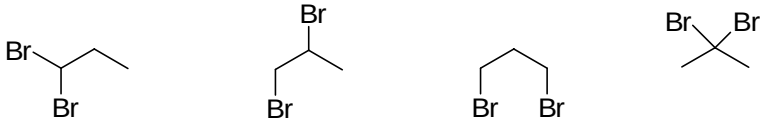
A. (3 pts) Write the structures of all possible monochlorinated products.




B. (2 pts) Indicate the monochloride that yields the alkene below as the exclusive product of E2 elimination.




19. (3 pts) Write the structures of all dibrominated derivatives of propane.



20. **(2 pts) BONUS PROBLEM (In order to receive credit for this problem, it has to be solved entirely!!).** Using the curved arrow notation, provide a plausible mechanism for the following reaction (*Hint:* First step is protonation. Think in terms of the most stable carbocation to be produced!!).