CHEMISTRY 313-01

MIDTERM # 2 – answer key

October 27, 2005

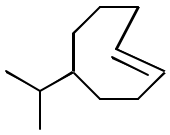
Statistics:

- Average: **72 pts (72%)**;
- Highest: **99 pts (99%)**; Lowest: **34 pts (34%)**
- Number of students performing at or above average: **27 (57%)**
- Number of students performing at or below 55%: **7 (15%)**

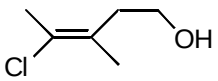
1. (7 pts) Mark as true (**T**) or false (**F**) the following statements. Do not explain!
   - (**F**) Reactions occurring according to the *E2* mechanism involve formation of carbocations;
   - (**T**) More stable alkenes have lower heats of hydrogenation;
   - (**T**) More stable radicals are generated faster;
   - (**T**) Free radicals are electron-deficient species;
   - (**T**) Polar addition reactions follow the *Markovnikov* rule;
   - (**T**) Epoxidation is a stereospecific process;
   - (**F**) Halogenation of cycloalkenes is a *syn*-addition process;

2. Circle ALL that apply:
   A. (3 pts) Free-radical chlorination:
      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 C – H and C – X bonds;
   D. (3 pts) The *Zaitsev* rule:
      a. Determines regioselectivity in reactions of alkene formation;
      b. Determines stereoselectivity in reactions of alkene formation;
      c. Accounts for the alkene stability order;
      d. Explains the Hammond postulate;

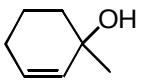
3. (3 pts) Provide an acceptable name for each of the following molecules. Specify stereochemistry wherever applicable:



5-isopropyl-*trans*-cyclooctene

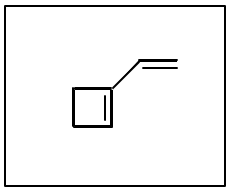


(E)-4-chloro-3-methyl-3-penten-1-ol

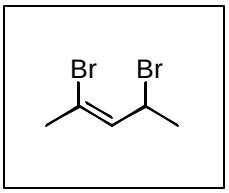


1-methyl-2-cyclohexenol

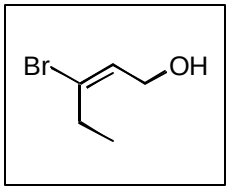
4. (5 pts) Provide structural formula for each of the following molecules:



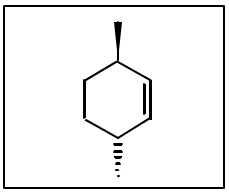
1-vinylcyclobutene



(Z)-2,4-dibromo-2-pentene

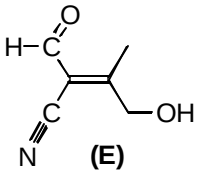


(E)-3-bromo-2-penten-1-ol

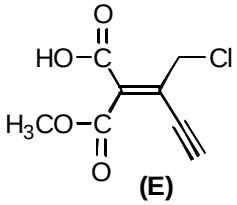


trans-3,6-dimethylcyclohexene

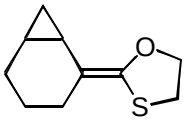
5. (4 pts) Assign *E* or *Z* configuration to each of the following alkenes. Do not explain!



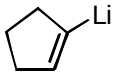
(E)



(E)

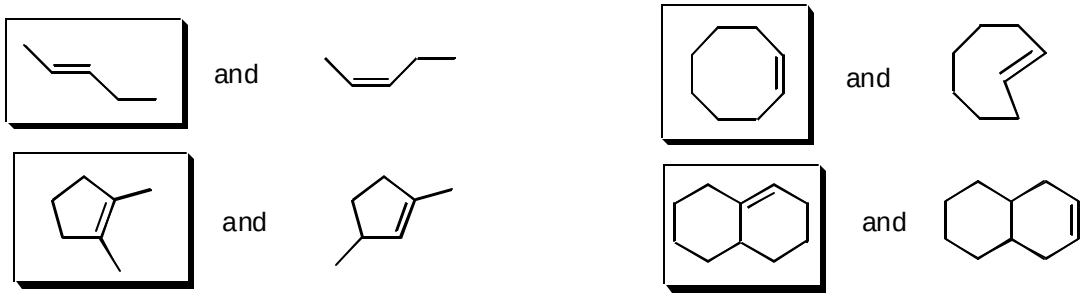


(E)

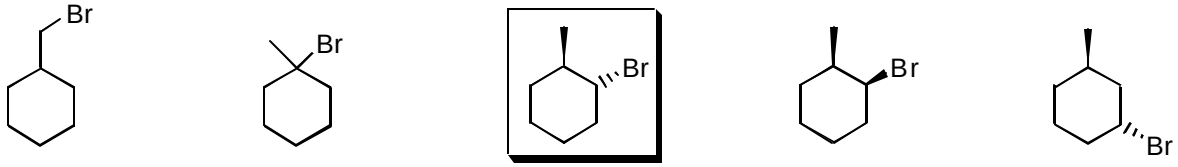


(Z)

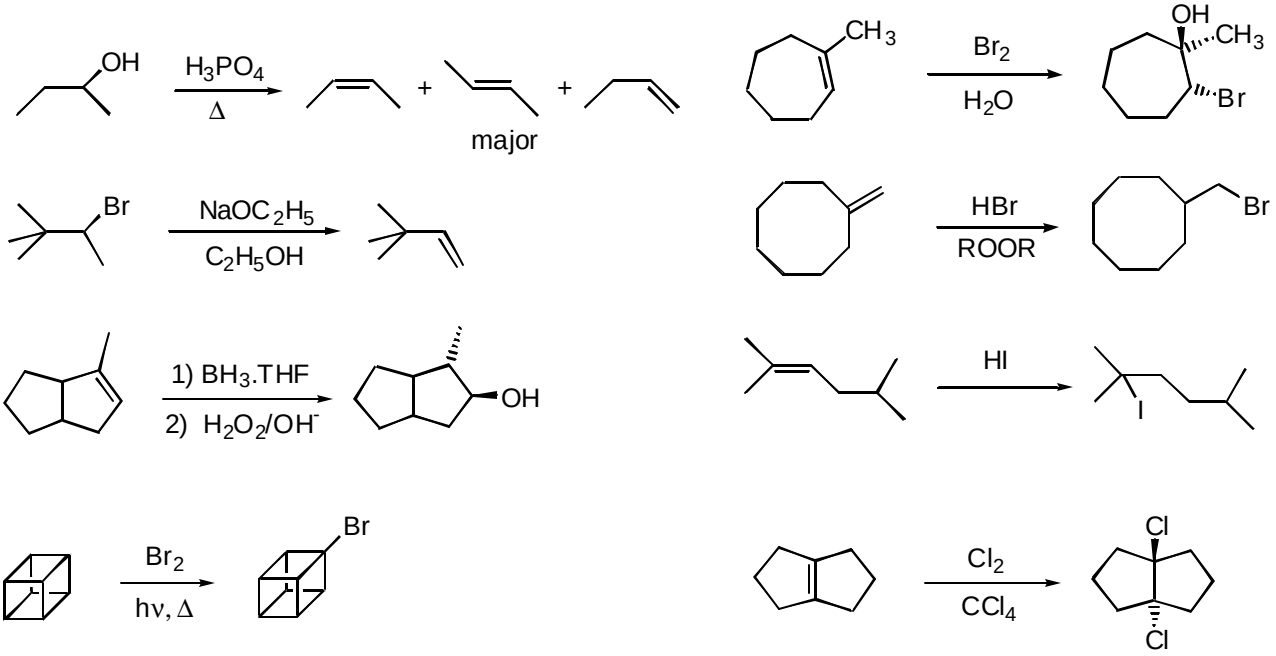
6. (4 pts) In each of the following pairs, indicate the more stable alkene. Do not explain!

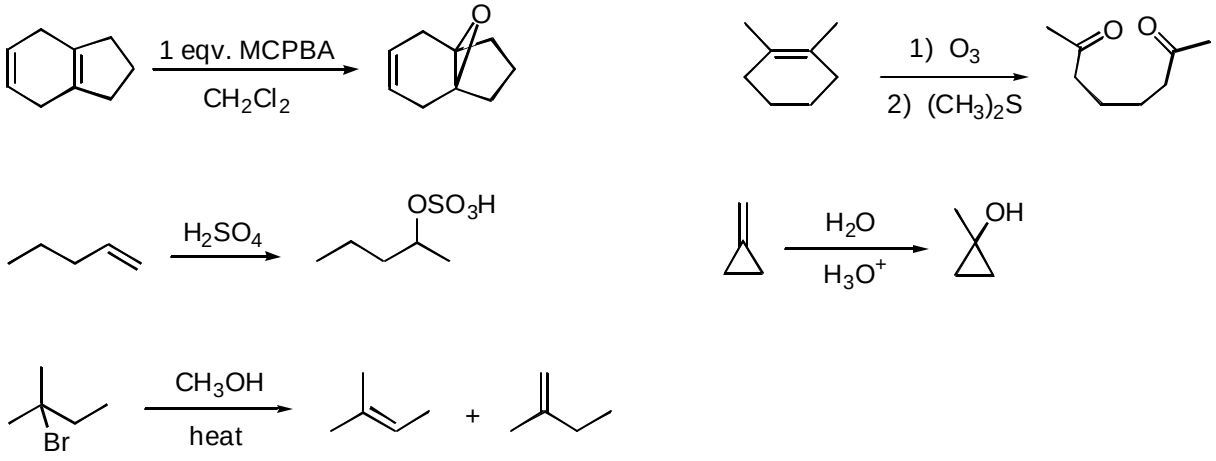


7. (4 pts) Several isomeric bromides are given below. Select the structure that will give you 3-methylcyclohexene as the sole product in *E2*-elimination conditions.

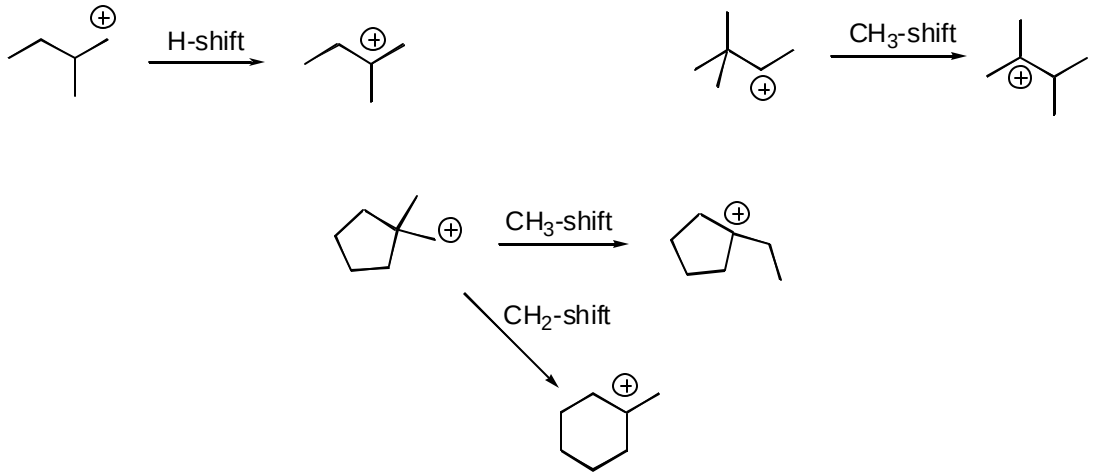


8. (29 pts) Predict the organic product in each of the following reactions, including precise stereochemistry, wherever applicable. If more than one product is formed, indicate the major component.

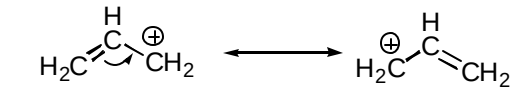




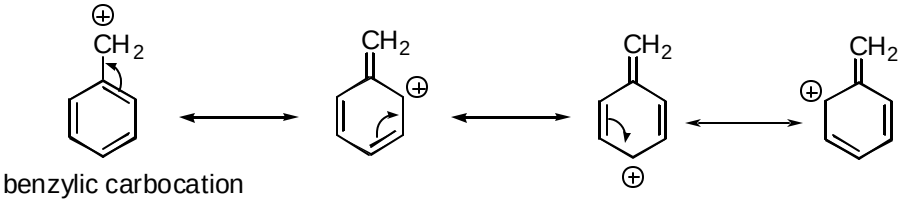
9. (5 pts) Each of the following carbocations can rearrange to a more stable ion. Propose structures for the likely rearranged species.



10. (4 pts) Although the general order of stability of carbocations is *tertiary* > *secondary* > *primary*, there are two important primary carbocations, which are exceptionally stable: the **allylic** and **benzylic** carbocations, shown below. For both of them, stability is due to very effective delocalization of the positive charge. For each one, draw other, equally important resonance structures to demonstrate the charge delocalization.

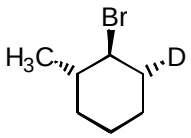


allylic carbocation

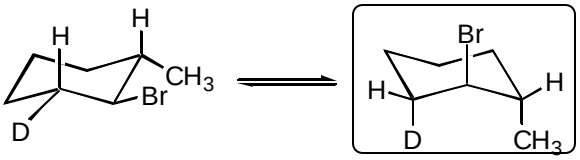


benzylic carbocation

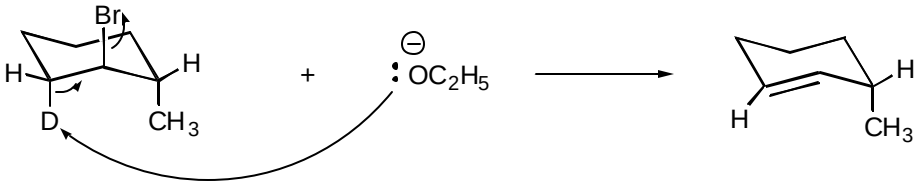
11. (5 pts) When the deuterium-labeled compound shown below is subjected to dehydrohalogenation, using $NaOC_2H_5$ in ethanol, the only alkene product is 3-methylcyclohexene, and it does not contain any deuterium. Provide a structural rationalization for these observations.



Solution: In the presence of NaOC2H5/ethanol, the process is E2. Therefore it is subject to stereoelectronic control:

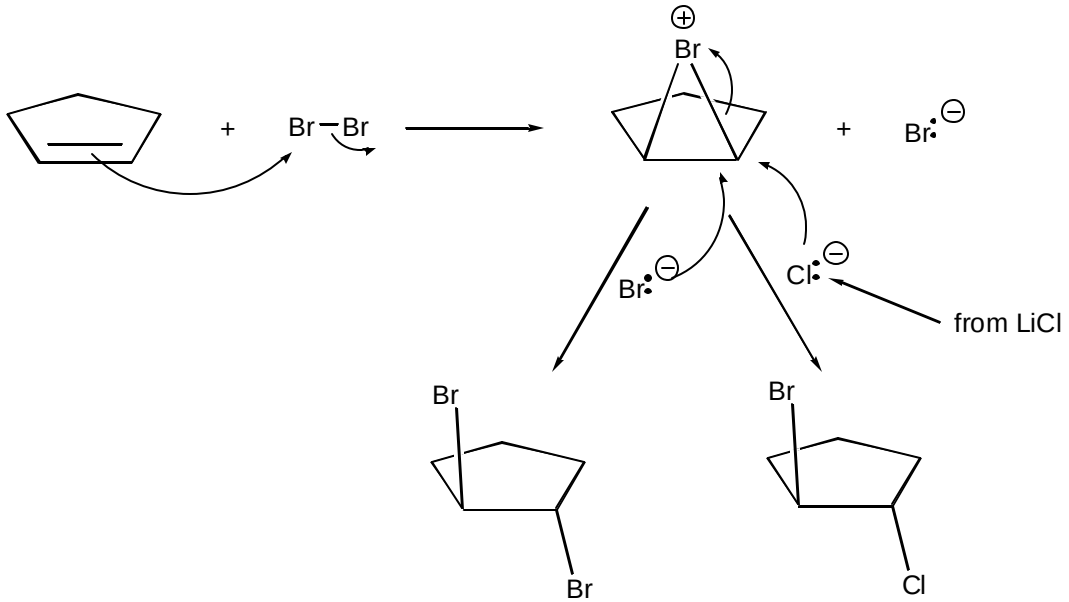


elimination can occur only from this chair conformation, since it has an axial C - Br bond. At the two adjacent carbons the C - H bonds are equatorial and these H-atoms cannot be eliminated (C - H bonds are nor co-planar to C - Br bond. However, the C - D bond is anti-coplanar to the C - Br bond. Thus, the only possible elimination is of D and Br, leading to 3-methylcyclohexene



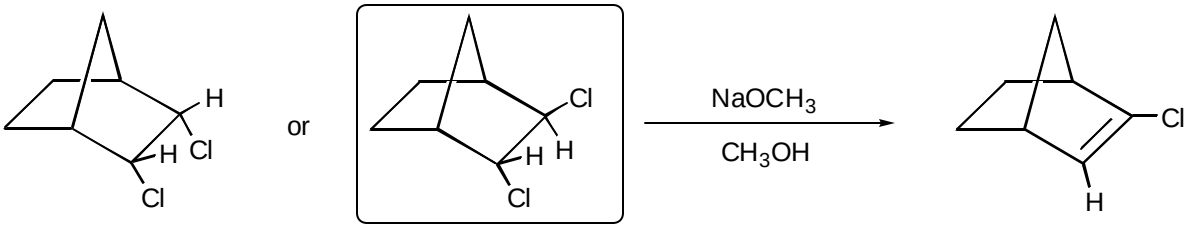
12. (5 pts) When cyclopentene is reacted with a solution of bromine in CCl_4 that also contains 1 equivalent of LiCl, then two products are isolated: *trans*-1,2-dibromocyclopentane and *trans*-1-bromo-2-chlorocyclopentane. Suggest a detailed mechanism to account for these observations (Structures and equations, please!!).

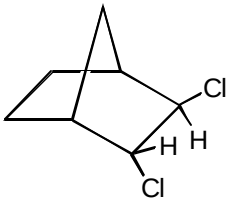
Solution: Bromination of alkenes occurs through a cyclic bromonium cation, which is further reacted with a nucleophile (or nucleophiles) present in the medium. In this particular case, there will be present two nucleophilic species: The bromide anion (a byproduct of the original formation of the bromonium cation) and the chloride anion (from the ionic LiCl). Thus two products are expected, both with an overall *anti*-addition (because they have the bromonium cation as a common intermediate).



trans-1,2-dibromocyclopentane *trans*-1-bromo-2-chlorocyclopentane

13. (5 pts) One of the following dichloronorbornanes undergoes elimination, while the other does not. Determine which one reacts and explain the difference in their reactivity.

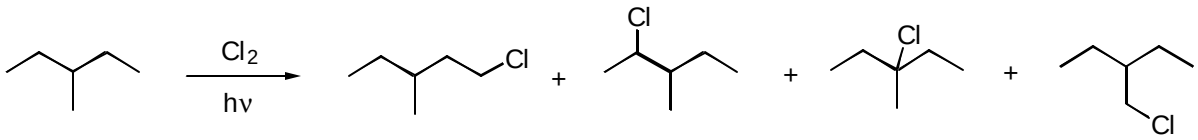




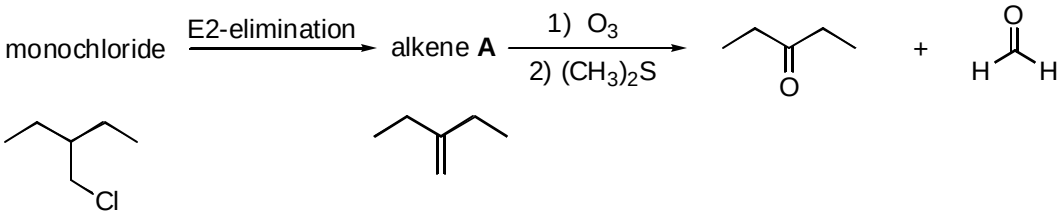
this isomer will undergo elimination since it has C - H and C - Cl bonds that are syncoplanar. The other compound does not have coplanar C - H and C - Cl bonds

14. The photochemical chlorination of 3-methylpentane leads to a mixture of monochlorides.

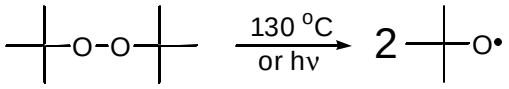
A. (4 pts) Write the equation of the reaction and indicate all possible different monochlorinated products.



B. (4 pts) One of the monochlorides yields a single alkene product **A** in E2-elimination conditions. Reaction of **A** with ozone, followed by treatment with $(CH_3)_2S$ leads to the generation of the products shown below. Propose structures for the monochloride and the alkene **A**.

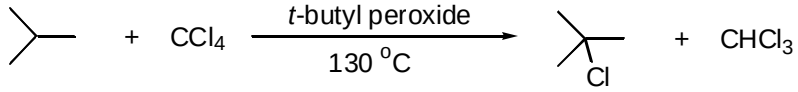


15. **(3 pts) BONUS PROBLEM (In order to receive credit for this problem, it has to be solved entirely!!).**) *tert*-Butyl peroxide is a stable, easy to handle liquid that serves as a convenient source of free radicals via thermal or light initiation:

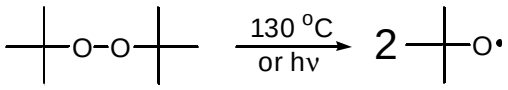


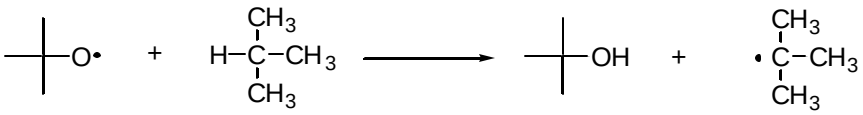
t-butyl peroxide *t*-butoxy radical

A mixture of isobutane and carbon tetrachloride (CCl_4) is quite stable at 130 °C, but if a small amount of *tert*-butyl peroxide is added, a reaction occurs, yielding *t*-butyl chloride and chloroform. Provide a <u>detailed, plausible</u> mechanism for the reaction.



Initiation steps:





Propagation steps: