CHEM 2410 – Principles of Organic Chemistry I – Summer 2016

Instructor: Paul Bracher

Hour Examination #2

Monday, June 6th, 2016

9:00–10:30 a.m. in Macelwane Hall 342

Student Name (Printed)	Solutions
Student Signature	N/A

Instructions & Scoring

- Please write your answers on the official answer sheet. No answers marked in this booklet will be graded.
- You may use one letter-sized sheet of handwritten notes (on "official" paper) and your plastic model kit. No electronic resources are permitted and you may not communicate with others.
- Your exam answer sheet may be photocopied.

Problem	Points Earned	Points Available
I		60
II		10
III		12
IV		18
TOTAL		100

Questions, Required Information, Supplementary Information

Special Instructions

Please Make Sure to Do the Following Before Starting Your Exam

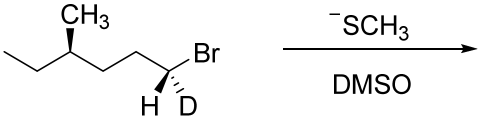
1. Both print your name and sign the front of the answer sheet in the appropriate boxes.
2. Also print your name at the top of the back of the answer sheet.
3. Enter your SLU Banner ID on the front of the answer sheet and bubble the corresponding numbers.
4. Do not check the "Hold for Pick-Up" box on the back of the answer sheet unless you want your graded sheet withheld from the distribution pile and handed back to you privately.

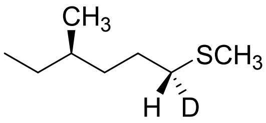
Please Make Sure to Do the Following After Completing Your Exam

1. Ensure that all of your selected circles are darkened completely.
2. Turn in your note sheet with your name and this exam number ($^{\#}$2) in the appropriate space.

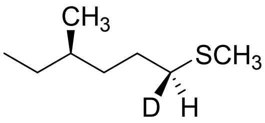
Problem I. Multiple choice (60 points total; +5 points for a correct answer, +2 points for answering with the letter "E", and 0 points for an incorrect answer). For each question, select the best answer of the choices given. Write the answer, legibly, in the space provided on the answer sheet.

(1) B What is the major product of the following reaction?

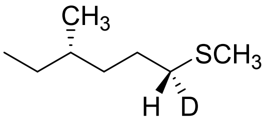




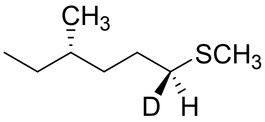
(A)



(B)



(C)



(D)

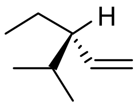
This is an S_N2 reaction. There is inversion of stereochemistry at the carbon atom where substitution occurs, but not at the distant stereocenter (where nothing is happening).

(2) C Which of the following is <u>not</u> true of a catalyst for a reaction?

(A) a catalyst lowers the overall activation barrier for the reaction
(B) a catalyst increases the rate of the reaction
(C) a catalyst shifts the equilibrium for the reaction towards the products
(D) none of the above (i.e., all of the above statements are true)

A catalyst speeds reactions, typically by providing a new route to the product that has a lower overall activation barrier. A catalyst does not shift the equilibrium for a reaction, since it does not change the relative energies of the reactants and products. The catalyst simply increases the speed at which equilibrium is reached. Also, remember that a catalyst is not consumed in a reaction.

(3) B Which of the following stereochemical designations appears in the name of compound **A**?

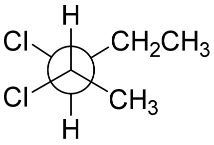


A

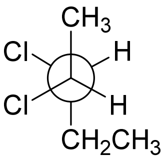
(A) *R*
(B) *S*
(C) *cis*
(D) *trans*

The order of priorities of the groups at the stereocenter is: (1) vinyl, (2) isopropyl, (3) ethyl, and (4) hydrogen.

(4) A What term best describes the relationship of the molecules represented below as Newman projections **B** and **C**?



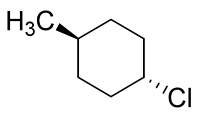
B



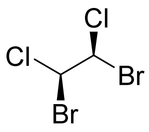
C

(A) enantiomers
(B) diastereomers
(C) identical compounds
(D) structural/constitutional isomers

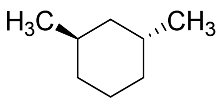
(5) B How many of the following three compounds (**D**, **E**, and **F**) are chiral?



D



E

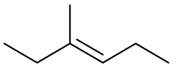


F

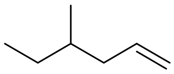
(A) none
(B) one
(C) two
(D) three

F is chiral. **D** and **E** are achiral. **D** has no stereocenters and **E** is a meso compound.

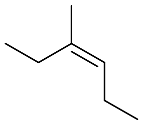
(6) D Rank the following three alkenes in descending order of stability (i.e., most stable to least stable).



G



H

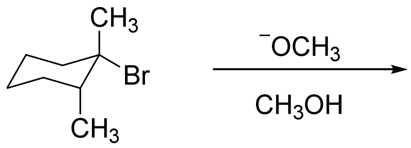


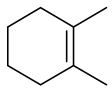
J

(A) **J** > **G** > **H**
(B) **H** > **G** > **J**
(C) **H** > **J** > **G**
(D) **G** > **J** > **H**

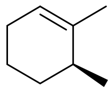
H is the least stable alkene since it has the fewest alkyl substituents. **G** and **J** are both trisubstituted, but **J** is less stable from a steric effect—the larger ethyl groups are in closer proximity.

(7) A What is the major product of the following reaction?

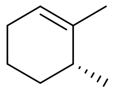




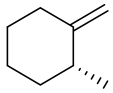
(A)



(B)



(C)



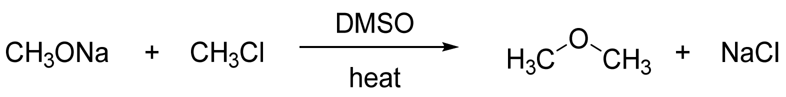
(D)

The elimination reaction will occur after the ring has flipped chair conformations to place the Br leaving group in an axial position, where it is anti-periplanar to two β-hydrogens. The preferred β-hydrogen to eliminate is the one that leads to the most substituted alkene (Zaitsev's Rule).

(8) C Compound **K** has a specific rotation of $[\alpha] = -10° \, (g/mL)^{-1} \, dm^{-1}$. If a mixture of **K** and its enantiomer, **L**, gives an observed rotation of $+2° \, (g/mL)^{-1}$ over a 10 cm path-length, what is the ratio of **K**:**L** in the solution?

(A) 4:1
(B) 3:2
(C) 2:3
(D) 1:4

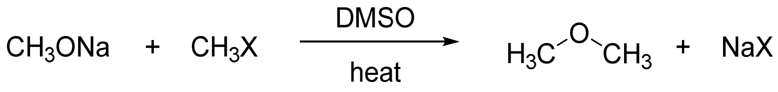
(9) C For the following reaction, what description most accurately describes the reactive orbital on the nucleophile?



$$CH_3ONa + CH_3Cl \xrightarrow[\text{heat}]{\text{DMSO}} H_3C{-}O{-}CH_3 + NaCl$$

(A) the empty π bonding orbital of the C–Cl bond
(B) an unhybridized p orbital on carbon
(C) a filled sp^3-hybridized orbital on oxygen
(D) the σ* antibonding orbital of the C–Cl bond

(10) D Which of the following alkyl halides reacts fastest when DMSO is the solvent?

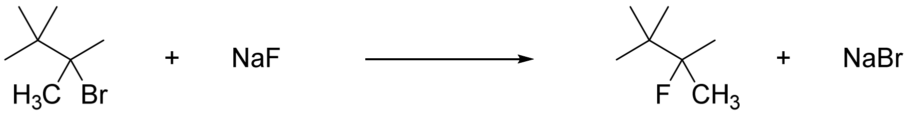


$$CH_3ONa + CH_3X \xrightarrow[\text{heat}]{\text{DMSO}} H_3C{-}O{-}CH_3 + NaX$$

(A) CH_3F
(B) CH_3Cl
(C) CH_3Br
(D) CH_3I

The choice of solvent is irrelevant. Iodide is always a better leaving group than bromide… chloride… fluoride.

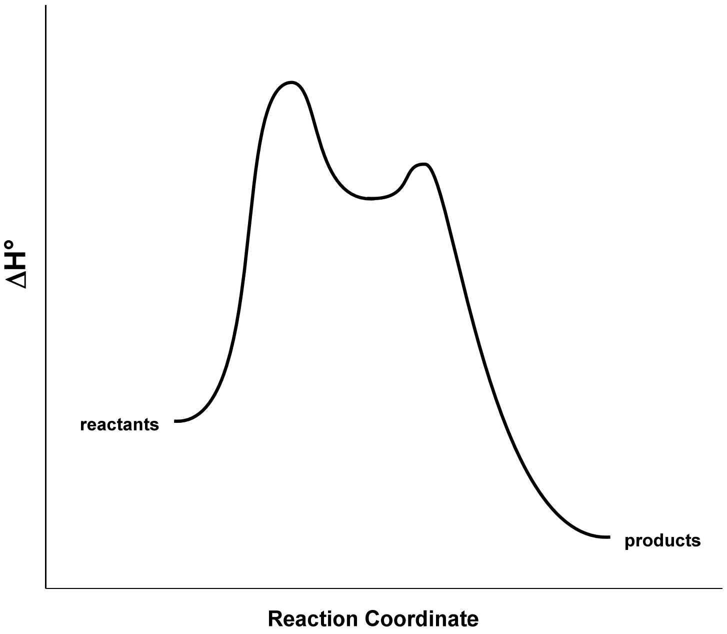
(11) B For the reaction drawn below, how will the rate change if the concentration of 2-bromo-2,3,3-trimethylbutane dissolved in the reaction mixture is halved (0.5x) and the concentration of sodium fluoride is doubled (2x)?



(A) the new rate will be approximately one-fourth of the previous rate
(B) the new rate will be approximately one-half of the previous rate
(C) the new rate will be approximately equal to the previous rate
(D) the new rate will be approximately double the previous rate

This is an S_N1 reaction (of a tertiary alkyl bromide). Thus, the rate is proportional to the concentration of alkyl halide and does not depend on the concentration of the nucleophile.

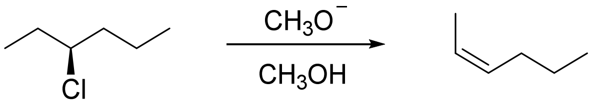
(12) ____D____ What statement is <u>true</u> of the following reaction diagram?

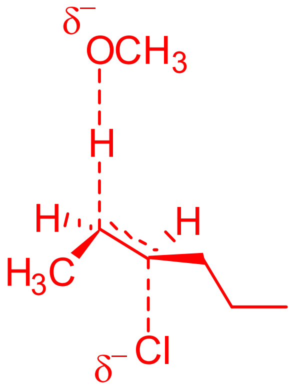


(A) the reaction is endothermic
(B) the diagram is consistent with that expected of an S_N2 reaction
(C) the reaction has two intermediates
(D) none of the above statements is true

This reaction is exothermic, as the products are more stable than the reactants. An S_N2 reaction, which is concerted, would have a reaction diagram with a single transition state and no intermediates. Here, the diagram has one intermediate—the “valley” between the two “peaks” (transition states).

Problem II. Transition States (10 points). Provide a 3-D drawing of the transition state of the rate-determining step for the following reaction. Used dashed lines to represent bonds that are being broken or formed. Indicate all formal charges and/or partial formal charges that are in the process of developing.

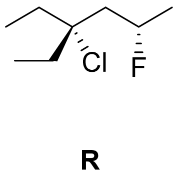




Note that the H being deprotonated and the Cl are antiperiplanar. The stereocenter should match the *S* designation when drawn in your structure. Also, for the formation of the product drawn (*cis*), the conformation of the transition state should have the alkyl groups positioned in a gauche relationship, not anti.

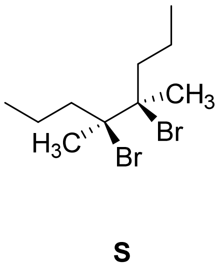
Problem III. Alkyl Halides (12 points). Provide the systematic IUPAC names of the following two compounds.

Part (1) (6 points).



(*S*)-4-chloro-4-ethyl-2-fluorohexane

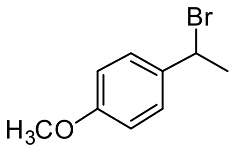
Part (2) (6 points).



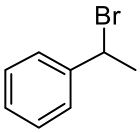
meso-4,5-dibromo-4,5-dimethyloctane

Problem IV. Explanations (18 points). For each question posed below, write the letter of your answer in the box on the answer sheet and provide a brief explanation for your choice. You should draw out any relevant resonance forms if the concept factors into your explanation.

(1) (9 points) Of compounds **T** and **U**, which reacts faster in hot methanol?

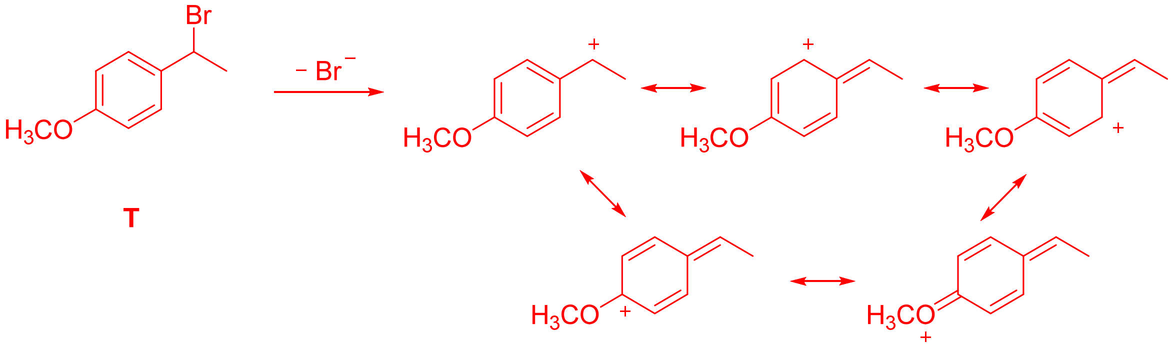


T

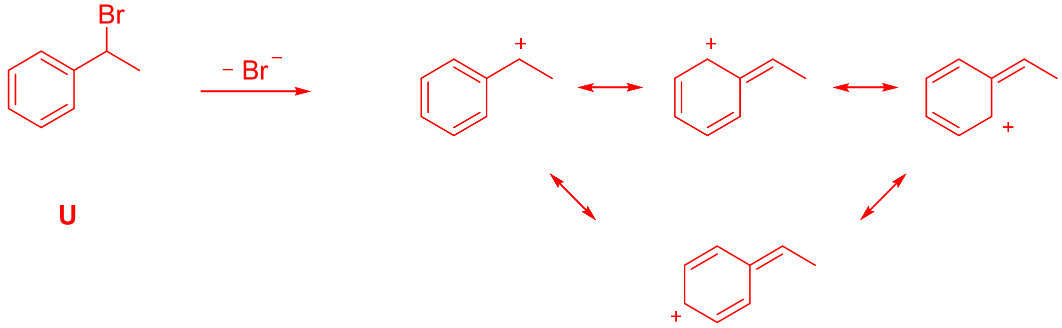


U

This is likely to be an S_N1 reaction, as (i) the substrate is a secondary alkyl halide, (ii) the leaving group is in a benzyl position, (iii) methanol is a weak nucleophile, and (iv) methanol is a polar, protic solvent. The faster reaction will be that with the lower activation barrier for the formation of the carbocation. From the Hammond Postulate, we expect the transition state to resemble the carbocation intermediate more than the starting material since that step is endothermic. The carbocation intermediates formed upon departure of Br^- are stabilized by a resonance effect for both **T** and **U**, but that of **T** is stabilized by an extra resonance form. This extra delocalization of the positive charge helps stabilize the intermediate formed from **T** relative to that formed from **U**.



T



U

(2) (9 points) Of methyl bromide (**X**) and ethyl bromide (**Y**), which reacts faster with potassium cyanide in DMSO? Your response should include a discussion of orbitals.

CH_3Br	CH_3CH_2Br
X	**Y**

Compound **X** reacts faster. These are both S_N2 reactions, as (i) cyanide is a strong nucleophile, (ii) DMSO is a polar, aprotic solvent, and (iii) methyl and primary carbocations are too unstable to form. The speed of the reaction will depend, in part, on the accessibility of the $\sigma^*_{C–Br}$ orbital's lobe behind the carbon atom. As alkyl substitution increases, the extra bulk of the alkyl group's electron cloud helps repel the electron-rich nucleophile and hinder access to the empty orbital.