CHEM 2430 – Organic Chemistry I – Fall 2015

Instructor: Paul Bracher

Quiz #3

Due: Monday, October 12th, 2015

1:10 p.m. (in class)

Student Name (Printed)	Solutions
Student Signature	N/A

Instructions & Scoring

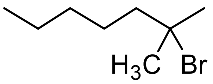
- Please write your answers on the official answer sheet. No answers marked in this booklet will be graded. Submissions submitted electronically will not be graded.
- You may use any resources you wish and collaborate with others.
- Any questions should be posted to the Blackboard discussion board so all students have equal access to the information.
- Your quiz answer sheet may be photocopied.

Problem	Points Earned	Points Available
I		35
II		20
III		10
IV		20
V		15
TOTAL		100

Questions, Required Information, Supplementary Information

Problem I. Multiple choice (35 points total; +5 points for a correct answer, +2 points for an answer intentionally left blank, 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.

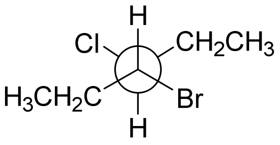
(1) B Which of the following statements is <u>not</u> true regarding compound **A**?



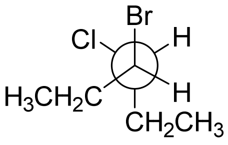
A

(a) compound **A** is achiral
(b) the rate of E1 reactions for **A** will be slower than for 1-bromoheptane
(c) the rate of S_N1 reactions for **A** will be faster than for 2-chloro-2-methylheptane
(d) heterolytic cleavage of the C–Br bond will generate a carbocation stabilized by hyperconjugation
(e) homolytic cleavage of the C–Br bond is less endothermic than homolytic cleavage of any of the C–H bonds

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



B

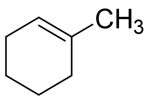


C

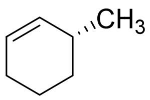
(a) enantiomers
(b) diastereomers
(c) identical compounds
(d) structural/constitutional isomers
(e) none of the above

(3) A

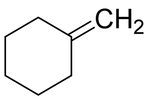
What is the major product when (1*R*,2*S*)-1-iodo-2-methylhexane is treated with 5 equivalents of sodium methoxide in methanol?



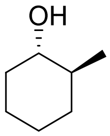
(a)



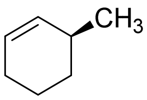
(b)



(c)



(d)



(e)

(4) B

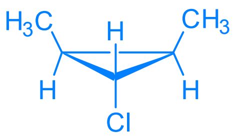
How many stereoisomers exist of 1,3-difluoro-5-methylcyclohexane? Assume the molecule is at room temperature so conformational isomers are not stereoisomers.

(a) 3
(b) 4
(c) 5
(d) 6
(e) 8

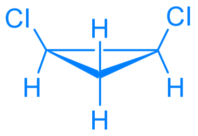
(5) E

What is the molecular formula of the smallest (by mass) alkyl halide that contains Only ^{1}H, ^{12}C, and ^{35}Cl atoms, is saturated (contains no π bonds), and is a meso compound?

(a) $C_3H_4Cl_2$
(b) C_3H_7Cl
(c) $C_4H_6Cl_2$
(d) $C_4H_8Cl_2$
(e) C_5H_9Cl



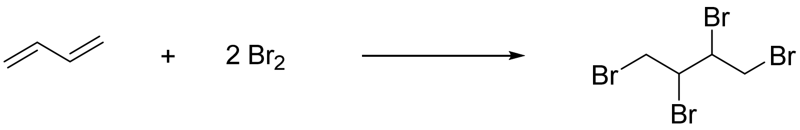
C_5H_9Cl
104 a.m.u.



$C_3H_4Cl_2$
110 a.m.u.

(6) B

Which of the following statements best describes the following reaction? Assume the bond dissociation energy of a carbon–carbon π bond is 264 kJ/mol.



(a) $\Delta H° > 0$
(b) $\Delta S° < 0$
(c) the product has four stereogenic centers
(d) the equilibrium constant, K, will quadruple if $[Br_2]$ is doubled
(e) two of the above statements are true

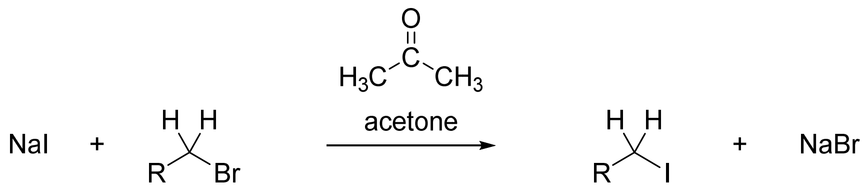
(7) E

Which change would <u>not</u> increase the rate of the following reaction?

$$CH_3Cl \quad + \quad {}^{-}CN \quad \xrightarrow{\text{tBuOH}} \quad CH_3CN \quad + \quad Cl^{-}$$

(a) raising the temperature
(b) changing the solvent from *tert*-butanol to dimethylsulfoxide (DMSO)
(c) increasing the concentration of cyanide ion
(d) changing the leaving group from chloride to bromide
(e) none of the above (i.e., all of the above changes would increase the rate of the reaction)

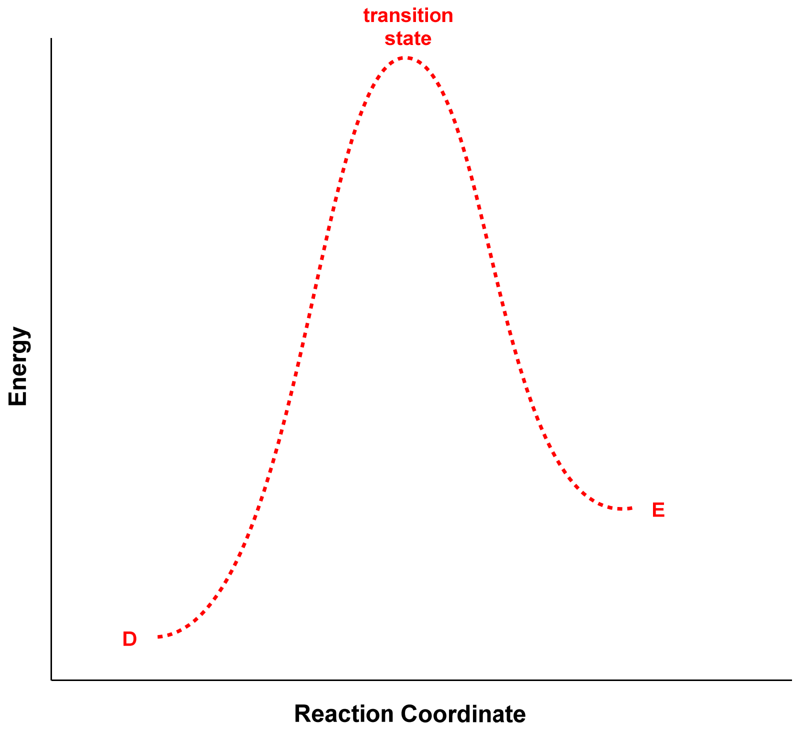
Problem II. Reaction Diagram (20 points). In the Finkelstein reaction, a primary alkyl bromide reacts with sodium iodide in acetone (as the solvent). While the equilibrium of this substitution reaction would usually[†] favor the reactants, in this case, the alkyl iodide can be produced in good yield because NaBr is not very soluble in acetone while NaI is soluble. This difference helps push the equilibrium to the right by Le Châtelier's principle.



D **E**

[†] consider "usually" to be in a solvent where both NaI and NaBr are soluble so the equilibrium mixture is homogeneous

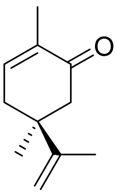
(1) (12 points) Draw a reaction diagram of Δ*H*° (enthalpy) versus the progress of the substitution reaction for the above reaction on the set of axes found on your answer sheet. You do not need to worry about drawing steps corresponding to the dissolution or precipitation of the salts—just the substitution reaction. Label the positions of **D**, **E**, and the transition state on your plot.



Note: The reaction is endothermic, and the reason you know is that if everything had remained dissolved in the solvent, the equilibrium would favor the reactants.

(2) (8 points) The chairman of the chemistry department at a pretentious local university hires you to design an air freshener to mask the foul smell of the lecture hall bathrooms immediately prior to their general chemistry exams. You decide that a mixture of (*R*)-carvone (which smells like spearmint) and (*S*)-carvone (which smells like caraway) would make an excellent fragrance, and you form a solution of these compounds that meets your olfactory satisfaction. After evaporating the solvent to leave just the solid, you find that a 1.0 g sample in 0.010 L of ethanol has an observed counterclockwise rotation of 4.2 degrees through a 10 cm polarimetry cell. What is the ratio of *R*:*S* enantiomers present in your solid sample? Express your answer with the lesser enantiomer having a value of 1 (e.g., 1:2.25 instead of 4:9).

(+)-carvone



$[\alpha] = +62.7° \, (\text{g/mL})^{-1} \, \text{dm}^{-1}$

Ref: Lambert, Compton, and Crawford. *J. Chem Phys.* **2012**, *136*, 114512.

From the structure given for (+)-carvone, we see it is the *S* enantiomer. Since the final sample is levorotatory (counterclockwise, −), we know that the opposite (*R*) enantiomer must be present in excess. We calculate the enantiomeric excess (e.e.) using the equation:

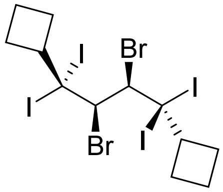
$$\text{e.e.} = \alpha_{\text{observed}} / ([\alpha] \cdot \text{pathlength} \cdot \text{total concentration})$$

$$= -4.2° / ((-62.7° \, (\text{g/mL})^{-1} \, \text{dm}^{-1}) \cdot 1 \text{ dm} \cdot (1 \text{ g}/10 \text{ mL})) = 67 \,\%$$

That means there must be 83.5% *R* and 16.5% *S* (as 83.5−16.5 = 67)

[*R*]:[*S*] = 83.5 : 16.5 = 5.1 : 1

Problem III. Alkyl Halides (10 points). Provide the systematic IUPAC name of compound **F**.

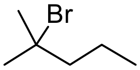


F

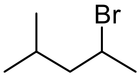
(*R*,*R*)-2,3-dibromo-1,4-dicyclobutyl-1,1,4,4-tetraiodobutane

Problem IV. Explanations (20 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.

(1) (10 points) Of compounds **G** and **H**, which will react faster with $NaOCH_3$ in methanol? It would be advisable for your explanation to include a drawing.



G

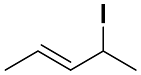


H

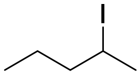
Compound **G**. The treatment of an alkyl halide that possesses β-hydrogen atoms with an alkoxide base usually results in an E2 reaction to generate an alkene. We generally judge the relative rates for two reactions by analyzing the relative stability of their transition states. In both of these reactions, the leaving group and the base are the same; the key difference is the substitution of the developing π bond. The transition state to produce **G** has a more substituted developing π bond than for H (tri- vs. di-), and thus, we expect the rate of the E2 reaction for **G** to be faster than for **H**.

(insert drawing of transition state)

(2) (10 points) Of compounds **J** and **K**, which would have a larger rate constant for its reaction with ethanol in an S_N1 reaction? Again, including drawings in your explanation would be advisable.

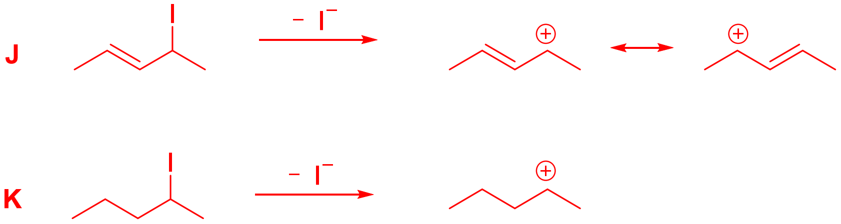


J



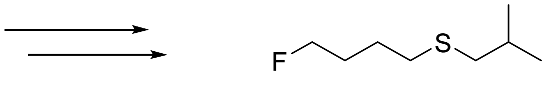
K

Compound **J**. The rate-determining step of an S_N1 reaction is the loss of halide to generate a carbocation. Since this step is endothermic, by the Hammond Postulate, effects that stabilize the carbocation will also tend to stabilize the transition state for this step, resulting in a faster reaction. Here, the carbocation produced from **J** is stabilized by a resonance effect, while that formed from **K** is not.



Problem V. Synthesis (15 points). Outline a synthesis—i.e, a sequence of reactions—to prepare compound **L** using any alkyl halides with four atoms of carbon or fewer and any inorganic reagents you wish as starting materials.

any alkyl halides with four or fewer
atoms of carbon and any inorganic
reagents you wish



L