CHEM 346 – Organic Chemistry I – Fall 2014

Instructor: Paul Bracher

Quiz #3

Due: Monday, October 13th, 2014

6:00 p.m. (in Monsanto Hall 103)

Student Name (Printed)	Solutions
Student Signature	N/A

Instructions & Scoring

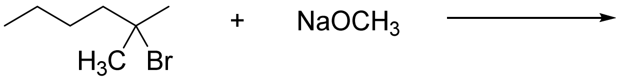
- Please write your answers on the official answer sheet. No answers marked in this booklet will be graded. You must submit a hard copy of your answer sheet. Answer sheets submitted electronically will not be graded.
- You may use any resources you wish and collaborate with others.
- Any questions should 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		26
III		27
IV		12
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.

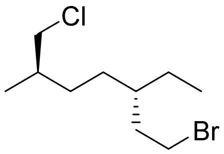
(1) B Which of the following types of reactions is <u>least</u> likely to occur when compound **A** is treated with sodium methoxide ($Na^{+-}OCH_3$)?



A

(a) S_N1
(b) S_N2
(c) E1
(d) E2

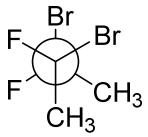
(2) B What is the best name for compound **B**?



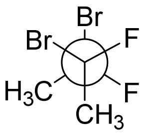
B

(a) (2*S*,5*S*)-5-bromoethyl-2-chloromethylheptane
(b) (2*R*,5*S*)-7-bromo-1-chloro-5-ethyl-2-methylheptane
(c) (2*R*,5*R*)-7-bromo-1-chloro-5-ethyl-2-methylheptane
(d) (3*S*,6*R*)-1-bromo-7-chloro-3-ethyl-6-methylheptane
(e) (3*R*,6*R*)-1-bromo-7-chloro-3-ethyl-6-methylheptane

(3) C What term best describes the relationship of the molecules drawn below as Newman projections **C** and **D**?



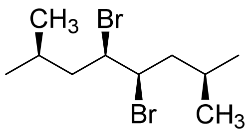
C



D

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

(4) A How many stereoisomers exist of compound **E** (including **E** itself)?

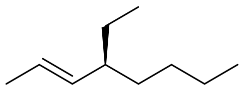


E

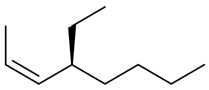
(a) 3
(b) 4
(c) 14
(d) 15
(e) 16

(5) E

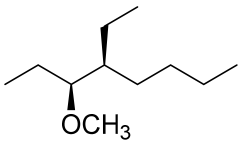
What is the major product when (3*R*,4*S*)-4-ethyl-3-iodooctane is treated with sodium methoxide ($NaOCH_3$) in methanol (CH_3OH)?



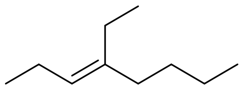
(a)



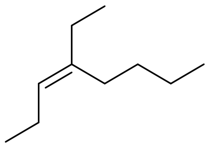
(b)



(c)



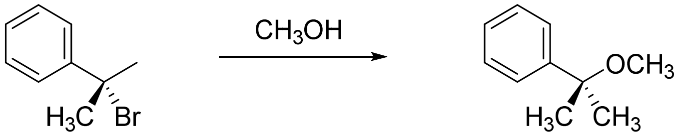
(d)



(e)

(6) D

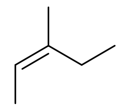
How many steps (i.e., transition states) appear in the mechanism for the following transformation?



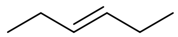
(a) 0
(b) 1
(c) 2
(d) 3
(e) 4

(7) C

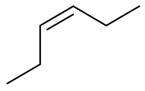
Which of the following isomers of C_6H_{12} would release the <u>most</u> heat when subjected to complete combustion in an oxygen atmosphere to produce 6 equivalents of CO_2 and 6 equivalents of H_2O?



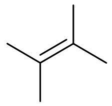
(a)



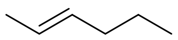
(b)



(c)



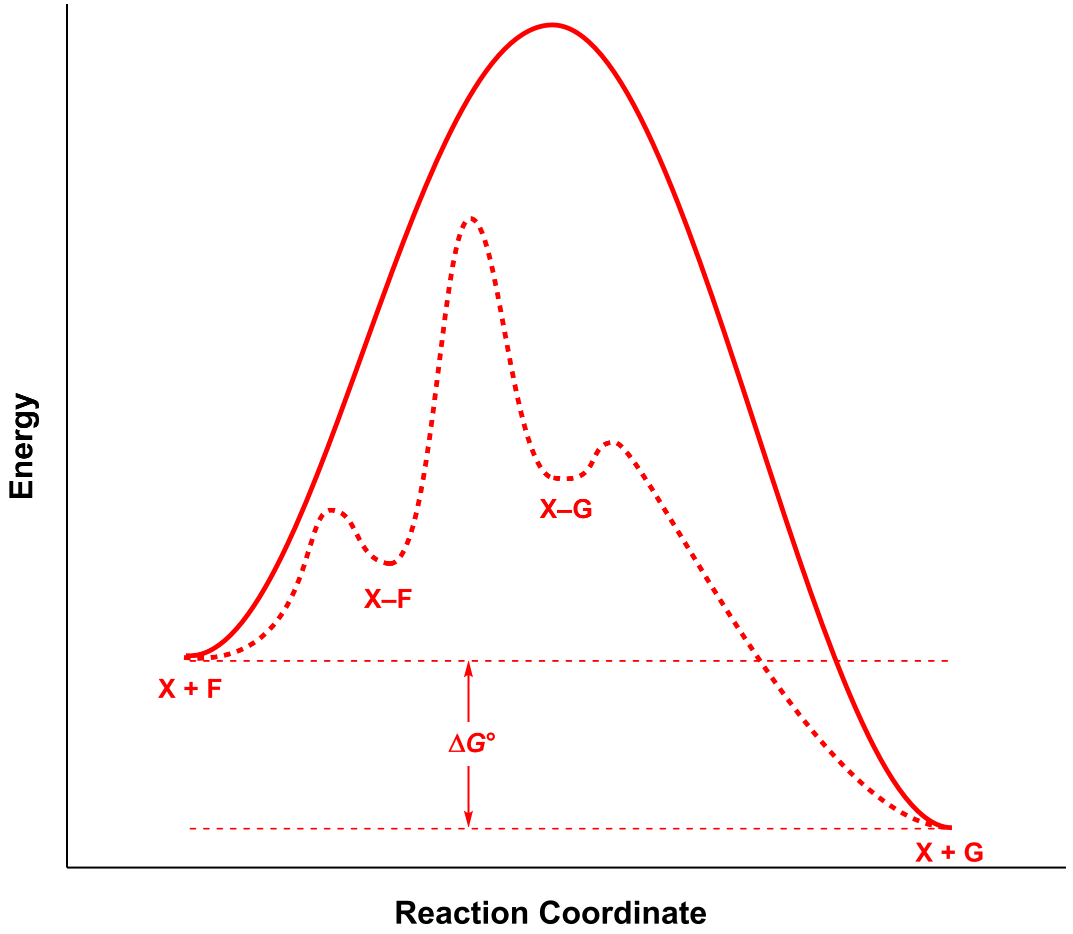
(d)



(e)

Problem II. Reaction Diagram (26 points).

(1) (18 points) Draw two superimposed reaction diagrams on the (same) set of axes found on your answer sheet. First, plot the one-step conversion of molecule **F** to molecule **G** in an exothermic process. On the same figure, plot a reaction diagram for the conversion of **F** to **G** when catalyzed by **X**. The catalyzed process proceeds via two intermediates: first, **X–F** and then, **X–G**. The formation of **X–G** from **X–F** is the rate-determining step of the catalyzed reaction. Label **F**, **G**, **X–F**, **X–G**, and Δ*G* on your plot.



(2) (8 points) A sample reaction mixture at equilibrium contains 2.8 mmol of **G** and 0.40 mmol of **F**. What is the value of Δ*G*° for the reaction in kJ/mol? Show your work for this calculation.

$$\begin{aligned}
\Delta G^\circ = -RT \ln K = -RT \ln([\mathbf{G}]/[\mathbf{F}]) &= -(8.315 \times 10^{-3}\ \text{kJ}\cdot\text{K}^{-1}\cdot\text{mol}^{-1})(298\ \text{K}) \ln(2.8\ \text{mmol}/0.40\ \text{mmol}) \\
&= -(8.315 \times 10^{-3}\ \text{kJ}\cdot\text{K}^{-1}\cdot\text{mol}^{-1})(298\ \text{K}) \ln(2.8\ \text{mmol}/0.40\ \text{mmol}) \\
&= -(2.4779\ \text{kJ}\cdot\text{mol}^{-1}) \ln(7) \\
&= -(2.4779\ \text{kJ}\cdot\text{mol}^{-1}) \ln(7) \\
\Delta G^\circ &= -4.8\ \text{kJ}\cdot\text{mol}^{-1}
\end{aligned}$$

Problem III. Explanations (27 points). For each question posed below, write the letter of your answer in the box on the answer sheet and provide a brief explanation (of no more than four sentences) for your choice. You should draw out any relevant structures or diagrams in your explanation.

(1) (9 points) Of compounds **H** and **J**, which reacts faster with potassium thiomethoxide ($K^{+-}SCH_3$) in DMSO?

CH_3CH_2I

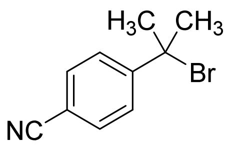
H

CH_3CH_2Br

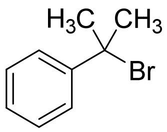
J

Compound **H** will react faster than **J**. This is an S_N2 reaction, and iodide is a better leaving group than bromide. Weaker bases typically make better leaving groups, and the pK_a of HI = −10 while the pK_a of HBr = −9.

(2) (9 points) Of compounds **K** and **L**, which reacts faster with methanol?

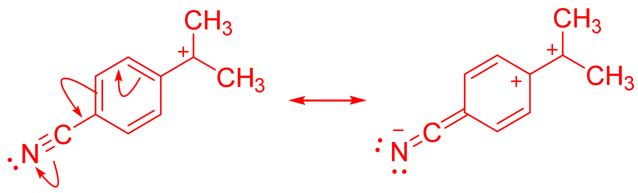


K



L

Compound **L** will react faster than **K**. This system will be a competition between S_N1 and E1 processes, which both have formation of the carbocation as the rate-determining step. Since formation of the carbocation in an endothermic step, by the Hammond Postulate, features that stabilize carbocations will stabilize the transition state for this step, and thus, speed the reaction. The key difference between **K** and **L** is the cyano group on the phenyl ring, which is electron-withdrawing by a resonance effect. This effect destabilizes the positive formal charge of the benzyllic carbocation:

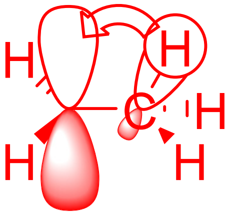


(3) (9 points) Of carbocations **M** and **N**, which is more stable? (Note: I want to see some sort of drawing or diagram in your explanation.)

$^{+}CH_3$ $^{+}CH_2CH_3$

M **N**

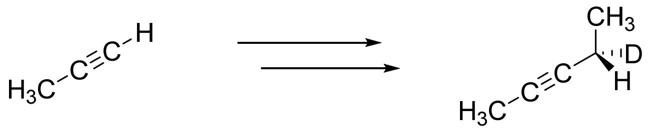
Carbocation **N** is more stable than carbocation **M**. Carbocations substituted with more R groups are more stable due to hyperconjugation, where filled $\sigma_{C\text{–}H}$ orbitals can align with, overlap with, and donate electron density into with the vacant unhybridized *p* orbital of the carbocation. These interactions help stabilize the cation, and are not possible for **M**, which has no bonds with orbitals capable of overlapping with the *p* orbital of the cation.



$^{+}CH_2CH_3$

N

Problem IV. Synthesis (12 points). Provide a synthetic route—i.e, a sequence of reactions—to produce compound **Q** using propyne (**P**) as the starting material and any other reagents you wish that contain two carbons or fewer.



P **Q**