CHEM 2430 – Organic Chemistry I – Fall 2015

Instructor: Paul Bracher

Hour Examination #2

Wednesday, October 14th, 2015

6:00–8:00 p.m. in Macelwane Hall 334

Student Name (Printed)	
Student Signature	

Instructions & Scoring

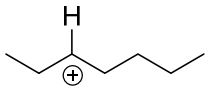
- Please write your answers on the official answer sheet. No answers marked in this booklet will be graded.
- Please write your name on the front *and* back of the answer sheet.
- You may use one letter-sized sheet of handwritten notes (on official paper) and your plastic model kit. No electronic resources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

Problem	Points Earned	Points Available
I		35
II		22
III		9
IV		20
V		14
TOTAL		100

Yay, midterms…

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.

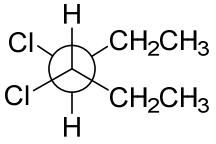
(1) _____ Which of the following statements most completely and correctly describes carbocation **A**?



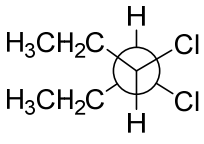
A

(a) **A** can be formed by homolytic cleavage of the C–Br bond in 3-bromoheptane
(b) **A** is a tertiary carbocation
(c) **A** is stabilized by the overlap of filled C–H and C–C σ bonding orbitals with the empty unhybridized p orbital on carbon
(d) both (b) and (c) are true
(e) (a), (b), and (c) are all true

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



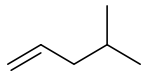
B



C

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

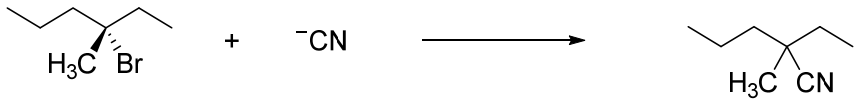
(3) _____ Which of the following choices is the best alkyl halide from which to prepare compound **D** by reaction with potassium *tert*-butoxide in *tert*-butanol (*t*-BuO$^-$/*t*-BuOH)?



D

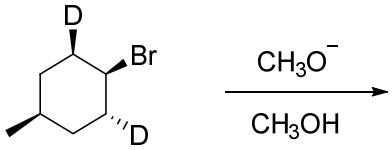
(a) 1-bromo-4-methylpentane
(b) 2-bromo-4-methylpentane
(c) 2-chloro-4-methylpentane
(d) 2-fluoro-4-methylpentane
(e) none of the above alkyl halides will yield compound **D** upon treatment with *t*-BuO$^-$/*t*-BuOH

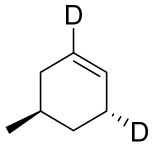
(4) _____ Which of the following statements is <u>not</u> true of the reaction below?



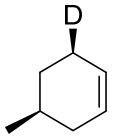
(a) the mechanism for this reaction is S_N1
(b) the product mixture will have an ee of roughly 50%
(c) the reaction would proceed slower if Br were replaced with F
(d) doubling the concentration of cyanide ($^-$CN) would not have a significant effect on the rate of the reaction
(e) none of the above (i.e., all of the above statements are true)

(5) _____ Which of the following compounds is the <u>least</u> likely product of the following reaction?

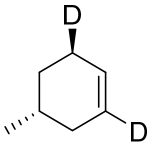




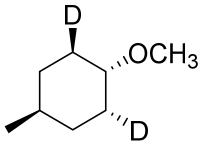
(a)



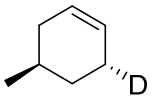
(b)



(c)

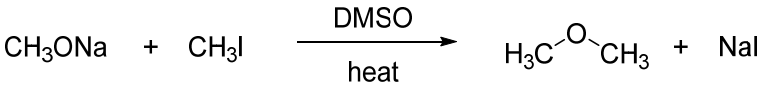


(d)



(e)

(6) _____ In the following reaction, what orbital does the nucleophile attack?

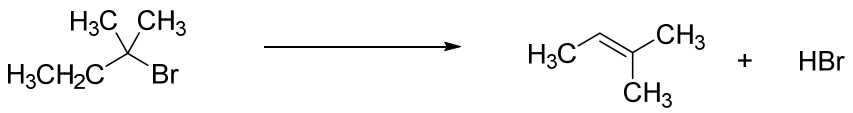


(a) the empty π bonding orbital of the C–I bond
(b) an unhybridized p orbital on carbon
(c) the σ* antibonding orbital of the C–O bond
(d) the σ* antibonding orbital of the C–I bond
(e) a lone pair on the negatively charged oxygen

(7) _____ What is the molecular formula of the smallest (by mass) alkyl halide that contains only ^{1}H, ^{12}C, and ^{79}Br atoms, is a meso compound, and is acyclic (contains no rings)?

(a) $C_3H_4Br_2$
(b) $C_5H_{10}Br_2$
(c) $C_7H_{15}Br$
(d) $C_9H_{11}Br$
(e) $C_9H_{19}Br$

Problem II. Reaction Diagram and Calculation (22 points). Consider the following reaction, for which the rate law is rate = k[**E**].



E **F**

(1) (10 points) Estimate the ΔH° for the reaction using the bond dissociation energies listed below. Show your work in the box on your answer sheet if you desire partial credit in the event of an incorrect answer.

Average Bond Dissociation Energies, D (kJ/mol)[a]									
H—H	436[a]	C—H	410	N—H	390	O—H	460	F—F	159[a]
H—C	410	C—C	350	N—C	300	O—C	350	Cl—Cl	243[a]
H—F	570[a]	C—F	450	N—F	270	O—F	180	Br—Br	193[a]
H—Cl	432[a]	C—Cl	330	N—Cl	200	O—Cl	200	I—I	151[a]
H—Br	366[a]	C—Br	270	N—Br	240	O—Br	210	S—F	310
H—I	298[a]	C—I	240	N—I	—	O—I	220	S—Cl	250
H—N	390	C—N	300	N—N	240	O—N	200	S—Br	210
H—O	460	C—O	350	N—O	200	O—O	180	S—S	225
H—S	340	C—S	260	N—S	—	O—S	—		
Multiple covalent bonds									
C=C	611	C≡C	835	C=O	732	O=O	498[a]	N≡N	945[a]

[a] Exact value

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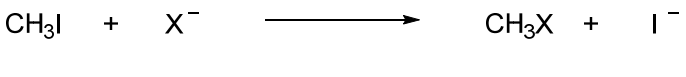
(2) (12 points) Draw a reaction diagram of ΔH° (enthalpy) versus the progress of the reaction on the set of axes found on your answer sheet. Label the positions of **E**, **F**, and any transition state(s) on your plot. Draw the Lewis structure of any intermediates.

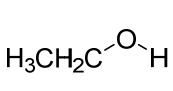
Problem III. Alkyl Halides (9 points). Provide the systematic IUPAC name of compound **G**.

G

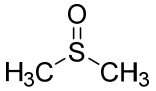
Problem IV. Explanations (20 points). Provide explanations for the observations noted below.

(1) (10 points) Explain why the following reaction proceeds slower for fluoride (F^-) than bromide (Br^-) in ethanol but faster for fluoride than bromide in dimethylsulfoxide.



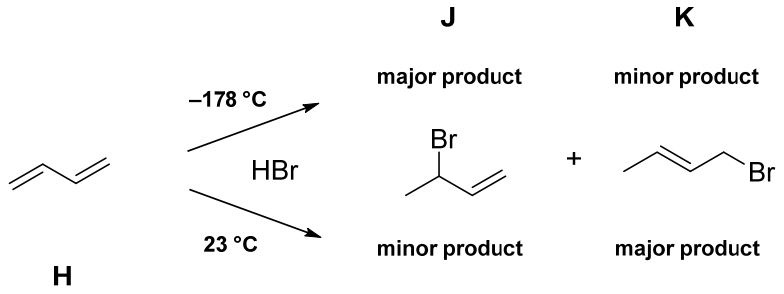


ethanol



dimethylsulfoxide

(2) (10 points) The addition of HBr to diene **H** forms two products, the relative ratio of which varies with temperature. Explain why product **K** is favored at higher temperature.



Problem V. Synthesis (14 points). Outline a synthesis—i.e, a sequence of reactions—to prepare compound **M** from compound **L** using any other reagents you wish.