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)	Solutions
Student Signature	N/A

Instructions & Scoring

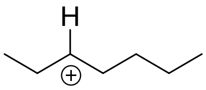
- Please write your answers on the official answer sheet. No answers marked in this booklet will be graded.
- Please write your name on the front *and* back of the answer sheet.
- You may use one letter-sized sheet of handwritten notes (on official paper) and your plastic model kit. No electronic resources 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

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.

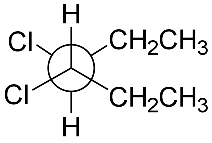
(1) C Which of the following statements most completely and correctly describes carbocation **A**?



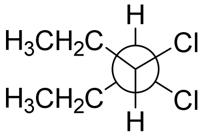
A

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



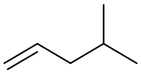
B



C

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

(3) A 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)?

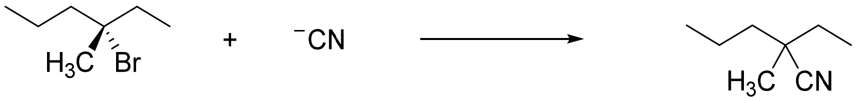


D

(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

Note that compound (a) is the best starting material because the only possible product of E2 elimination is **D**. A leaving group at the 2 position will generate a product mixture of 4-methyl-1-pentene and 4-methyl-2-pentene (both *cis* and *trans*).

(4) B Which of the following statements is not true of the reaction below?

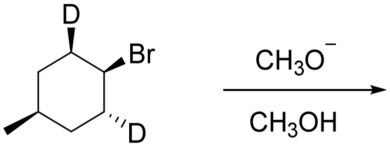


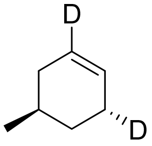
(a) the mechanism for this reaction is S$_N$1
(b) the product mixture will have an ee of roughly 50%
(c) the reaction would proceed slower if Br were replaced with F
(d) doubling the concentration of cyanide ($^-$CN) would not have a significant effect on the rate of the reaction
(e) none of the above (i.e., all of the above statements are true)

Note that an ee of 50% corresponds to a 75:25 product ratio. A 50:50 ratio, which is what we generally expect from S$_N$1 reactions, corresponds to an ee of 0% (as there is no enantiomeric excess).

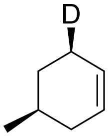
(5) E

Which of the following compounds is the <u>least</u> likely product of the following reaction?

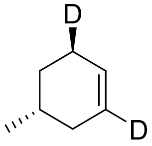




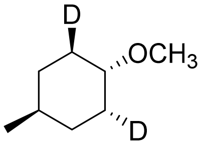
(a)



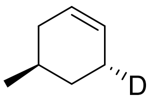
(b)



(c)



(d)

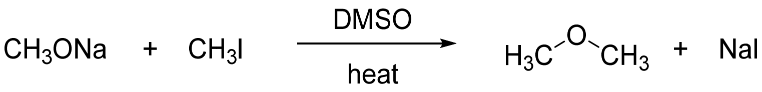


(e)

Note that choices (a) and (c) are identical—the product of the E2 elimination of the H at the "top" carbon of the structure, as drawn above. Choice (d) would form from an S_N2 reaction. Choice (e) will not form from this reaction because the starting material cannot adopt a conformation where the corresponding deuterium atom is anti-periplanar to the bromine leaving group.

(6) D

In the following reaction, what orbital does the nucleophile attack?



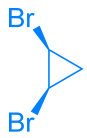
$$CH_3ONa + CH_3I \xrightarrow[\text{heat}]{\text{DMSO}} H_3C^{\diagup O \diagdown}CH_3 + NaI$$

(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) D 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)?

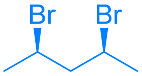
(a) $C_3H_4Br_2$
(b) $C_5H_{10}Br_2$
(c) $C_7H_{15}Br$
(d) $C_9H_{11}Br$
(e) $C_9H_{19}Br$

Compounds of interest:

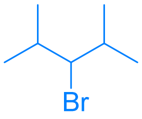


Chemical Formula: $C_3H_4Br_2$
Exact Mass: 197.87

(not acyclic)

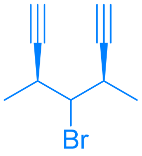


Chemical Formula: $C_5H_{10}Br_2$
Exact Mass: 227.91

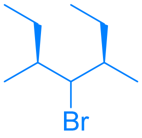


Chemical Formula: $C_7H_{15}Br$
Exact Mass: 178.04

(not meso)

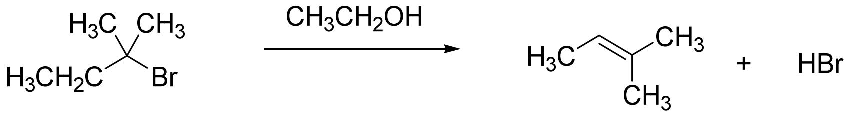


Chemical Formula: $C_9H_{11}Br$
Exact Mass: 198.00



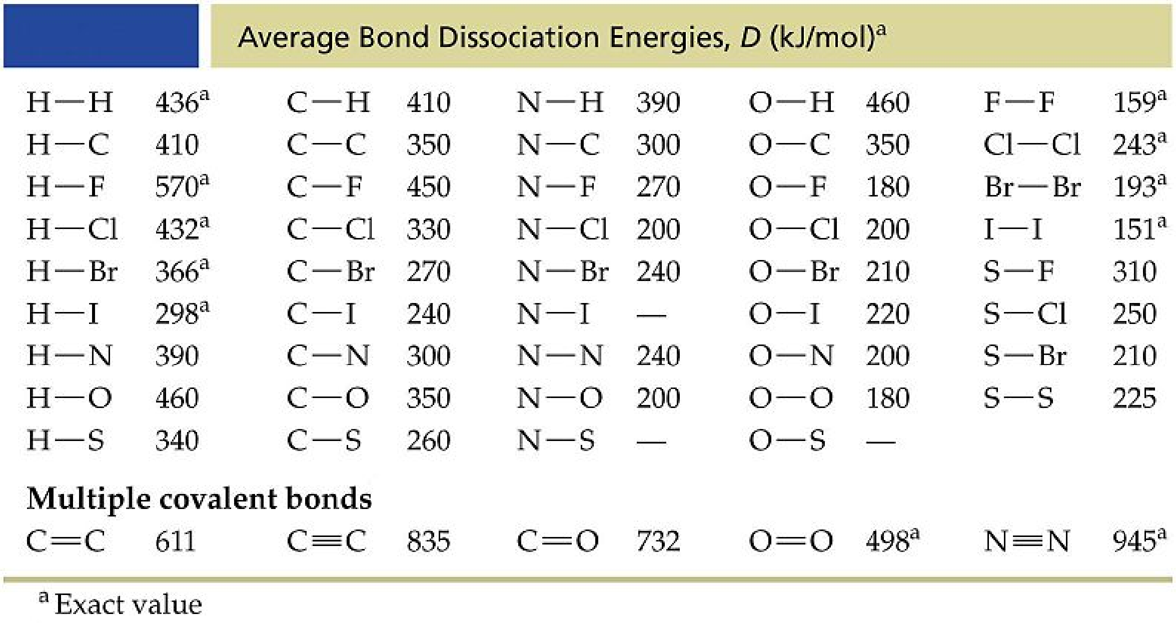
Chemical Formula: $C_9H_{19}Br$
Exact Mass: 206.07

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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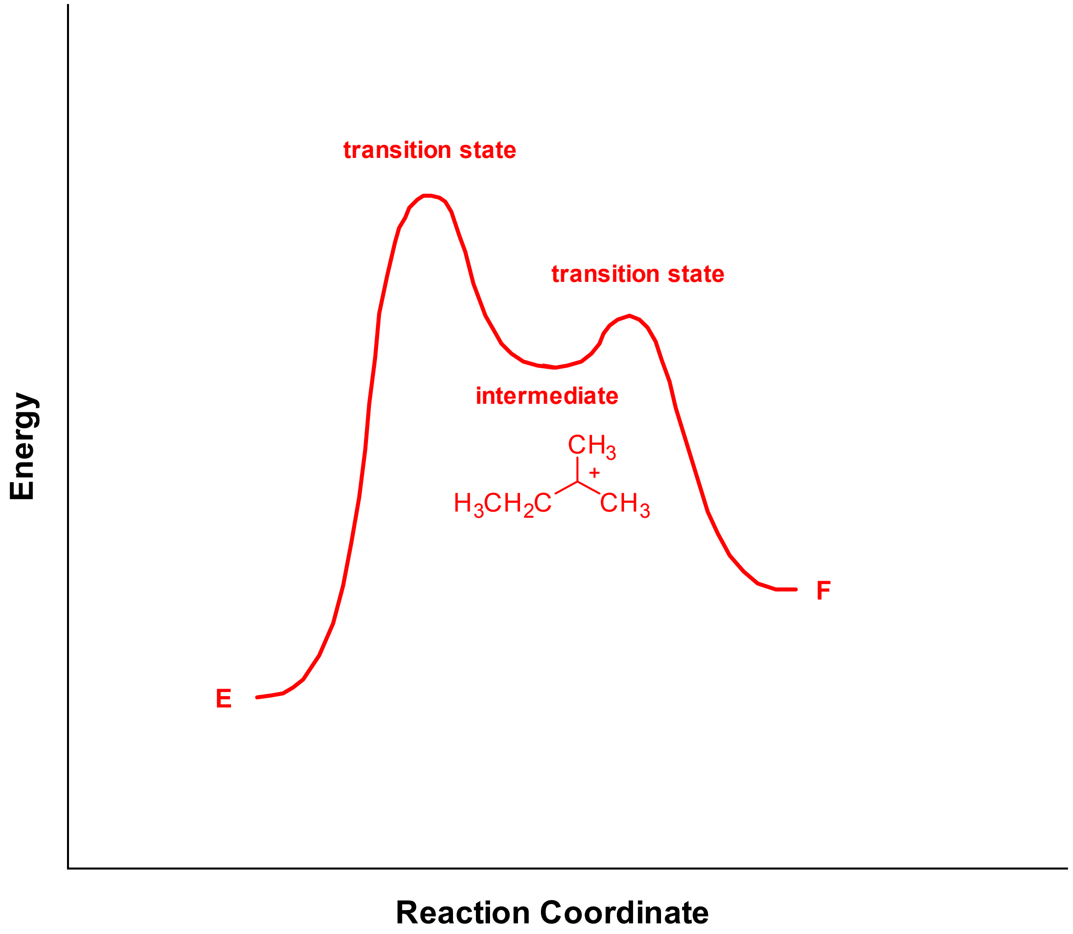
Bonds broken:	C–Br	(270 kJ/mol)	Bonds formed:	C=C (π only)	(611−350 = 261 kJ/mol)
	C–H	(410 kJ/mol)		H–Br	(366 kJ/mol)

$$\Delta H^\circ = \Sigma \text{ (BDEs for bonds broken)} - \Sigma \text{ (BDEs for bonds formed)}$$
$$= +(270+410) - (261 + 366) = 680 - 627 = +53 \text{ kJ/mol}$$

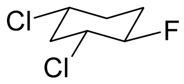
The BDE given for the C=C bond includes the energy required to break *both* the σ and π bonds. You can tell because the BDE for C–C is lower despite the fact that σ bonds are stronger than π bonds. In order to get the BDE for just the C=C π bond, we must subtract the BDE of the C–C σ bond. This was, by far, the most common error on the exam.

(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.



Given the fact we're dealing with elimination of a 3° alkyl halide and the rate law is unimolecular, we know the mechanism to be E1. Thus, we show the reaction to proceed in two steps, with the first step as rate-determining and a carbocation intermediate. Note that the diagram reflects the calculation in part (1) that the reaction is endothermic—the products lie higher in energy than the reactants.

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



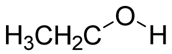
G

(1*R*,2*R*,4*R*)-2,4-dichloro-1-fluorocyclohexane

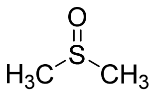
Problem IV. Explanations (20 points). Provide explanations for the observations noted below.

(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.

$$CH_3I \quad + \quad X^- \longrightarrow CH_3X \quad + \quad I^-$$



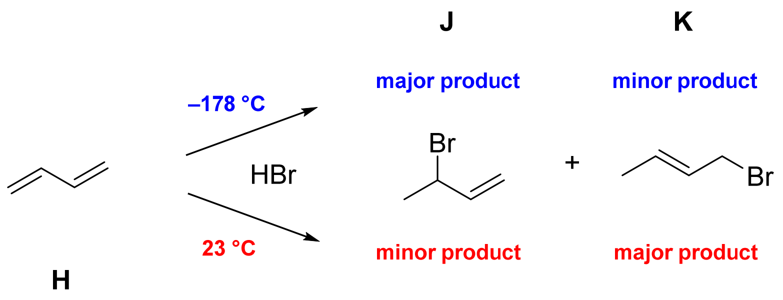
ethanol



dimethylsulfoxide

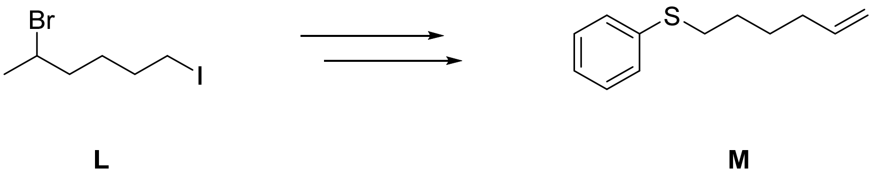
The general reaction can be classified as S_N2, so the strength of the nucleophile has a significant impact on the rate. In general, nucleophilicity parallels basicity—stronger bases are better nucleophiles. F^- (pK_a of conjugate acid = 3.2) is a stronger base than Br^- (pK_a of conjugate acid = −8), so we generally expect fluoride to be the better nucleophile. This is what we observe in DMSO, a polar, aprotic solvent that does not solvate anions well. Ethanol, on the other hand, is a polar, protic solvent that is capable of donating hydrogen bonds and solvating anions well with particularly strong ion–dipole interactions. The compact, charge-dense nature of F^- makes the solvation shell of ethanol molecules around the anion much tighter than for Br^-. This tighter solvation shell makes the fluoride anion less available to react, reducing its nucleophilicity to the point that bromide is more nucleophilic in ethanol.

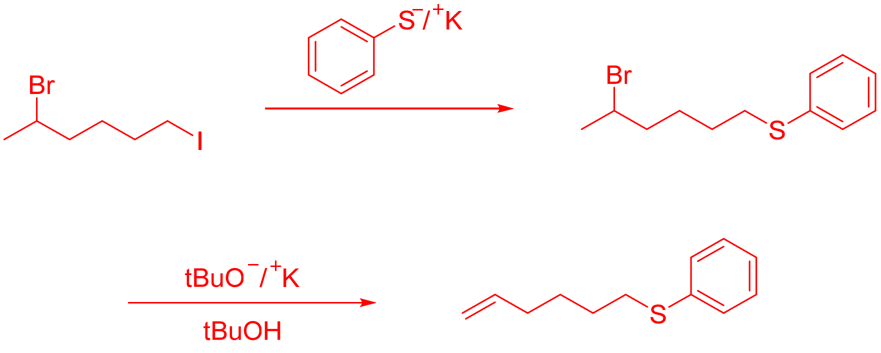
(2) (10 points) The addition of HBr to diene **H** forms two products, the relative ratio of which varies with temperature. Explain why product **K** is favored at higher temperature.



The dependence of the major product on temperature suggests this is a case of thermodynamic vs. kinetic control. The major product at low temperature forms faster (has a lower kinetic barrier) while the major product at high temperature is more stable (and favored when there is plenty of ambient energy to overcome the higher activation energy required for its formation). Why is **K** the more stable product? Because its double bond is more substituted than the double bond in **J**. The increased stability can be attributed to an increase in favorable hyperconjugation interactions (filled $\sigma_{C–H}$ orbitals donating into the empty $\pi^*_{C=C}$ orbital) in **K** relative to **J**.

Problem V. Synthesis (15 points). Outline a synthesis—i.e, a sequence of reactions—to prepare compound **M** from compound **L** using any other reagents you wish.





In looking at the starting material, it is important to note that there are two functional groups of interest. Generally, you will want to “use” the most reactive functional group first—here, the primary iodide instead of the secondary bromide—because you will have the most selectivity. That is, you expect one equivalent of a good nucleophile to target the primary iodide without “touching” the less reactive secondary bromide. If you had tried to conduct elimination of the bromide first, you would expect treatment of **L** with a strong base to generate a mixture of elimination products.

Once you get to the first intermediate—following an S_N2 reaction with potassium thiophenol—you want to eliminate HBr to generate the anti-Zaitsev product. This product is favored when the substrate is treated with a bulky base rather than a smaller base.