CHEM 346 – Organic Chemistry I – Fall 2014

Instructor: Paul Bracher

Hour Examination #2

Wednesday, October 15th, 2014

6:00–8:00 p.m. in Macelwane Hall 334

Student Name (Printed)	Solutions
Student Signature	N/A

Instructions & Scoring

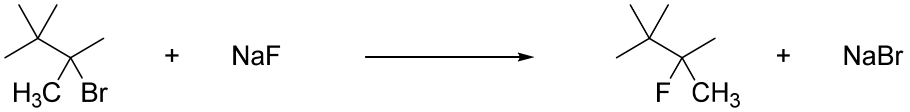
- Please write your answers on the official answer sheet. No answers marked in this booklet will be graded.
- Please write your name on the front *and* back of the answer sheet.
- You may use one letter-sized sheet of handwritten notes and your plastic model kit. No electronic resources are permitted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

Problem	Points Earned	Points Available
I		25
II		27
III		28
IV		20
TOTAL		100

Questions, Required Information, Supplementary Information

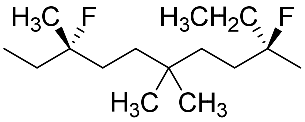
Problem I. Multiple choice (25 points total; +5 points for a correct answer, +2 points for an answer intentionally left blank, and 0 points for an incorrect answer). For each question, select the best answer of the choices given. Write the answer, legibly, in the space provided on the answer sheet.

(1) C For the reaction drawn below, how will the rate change if the concentration of NaF dissolved in the reaction mixture is doubled?



(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
(e) the new rate will be approximately quadruple the previous rate

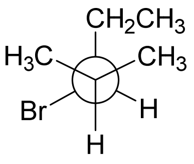
(2) A What is the best name for compound **A**?



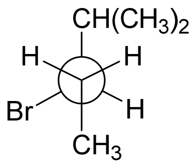
A

(a) *meso*-3,9-difluoro-3,6,6,9-tetramethylundecane
(b) (2*R*,8*S*)-2-ethyl-2,8-difluoro-5,5,8-trimethyldecane
(c) (3*S*,9*R*)-9-ethyl-3,9-difluoro-3,6,6-trimethyldecane
(d) (3*S*,9*R*)-3,9-difluoro-3,6,6,9-tetramethylundecane
(e) (3*R*,9*S*)-3,9-difluoro-3,6,6,9-tetramethylundecane

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



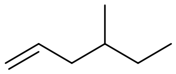
B



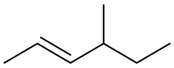
C

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

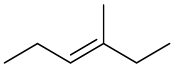
(4) ____C____ Which of the following isomers of C_7H_{14} would release the <u>least</u> heat upon hydrogenation with one equivalent of H_2 to produce 3-methylhexane? Note: all of these starting materials produce the identical product.



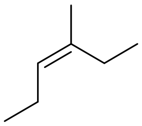
(a)



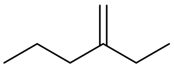
(b)



(c)



(d)



(e)

(5) E

Given the data provided in Problem II (below), which of the following groups is most consistent with the identity of the mystery R group in that problem?

$-CH_3$

(a)

$-CF_3$

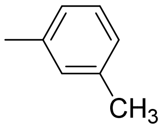
(b)

$-CH_2CH_3$

(c)

$-C(CH_3)_3$

(d)



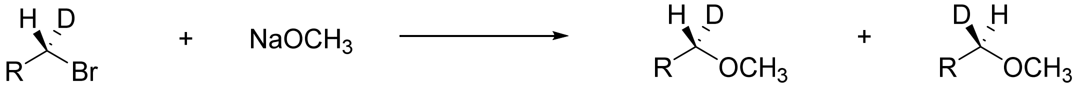
(e)

"(6)" D

Which of the following titles would make the most intriguing movie about organic chemistry?

(a) The Cation in the Hat
(b) Yield of Dreams
(c) The Dukes of Hazardous Waste
(d) The Texas Carbon Massacre
(e) Star Wars: The Empire Strikes the Back Side

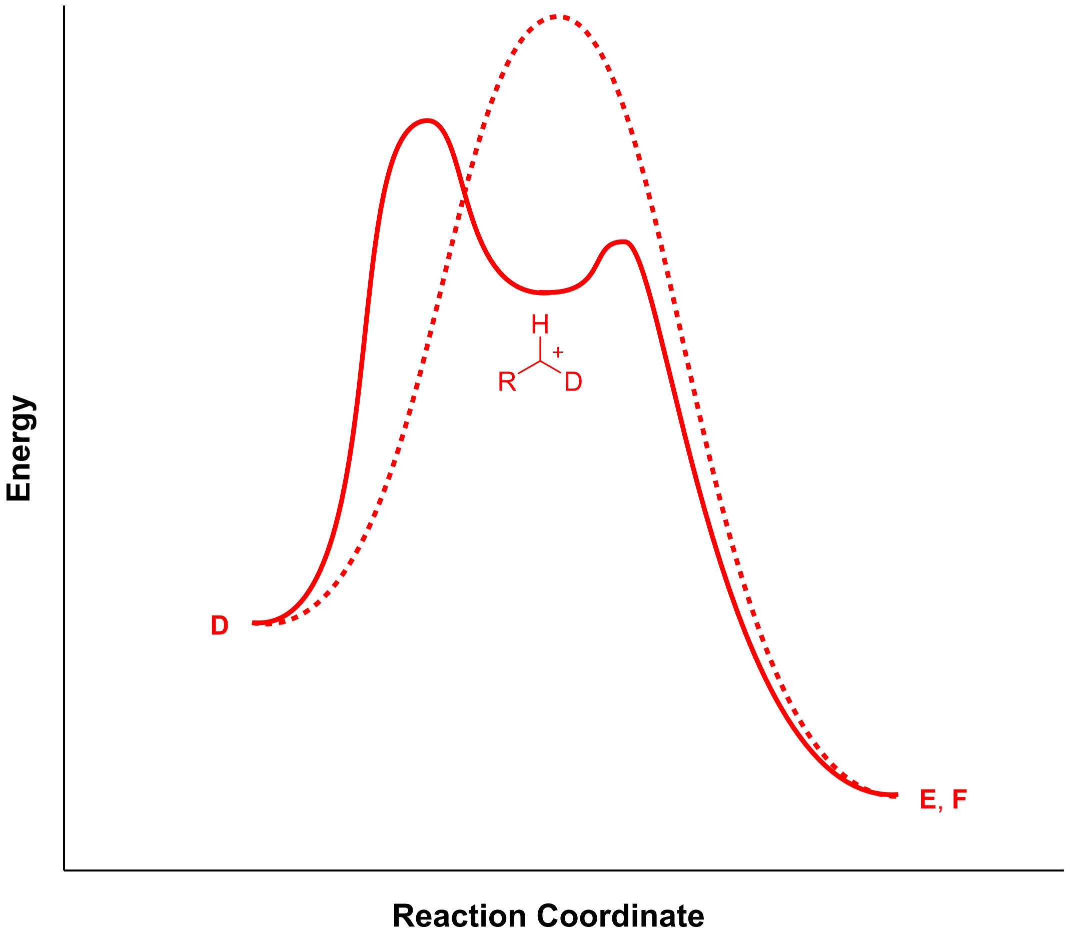
Problem II. Reaction Diagram (27 points). Consider the reaction of alkyl bromide **D** with sodium methoxide to form compounds **E** and **F**. R is an achiral mystery group that is bonded to the structure by a carbon atom.



D **E** **F**

$[\alpha] = -10° \text{ mM}^{-1} \text{ dm}^{-1}$ $[\alpha] = -30° \text{ mM}^{-1} \text{ dm}^{-1}$

(1) (17 points) Draw two superimposed diagrams for the above reaction on the (same) set of axes found on your answer sheet. First, with a solid line, plot the reaction diagram for an S_N1 mechanism. Second, with a dashed line, plot the reaction diagram for an S_N2 mechanism. Assume the reaction is exothermic. Draw the Lewis structure of any intermediates. Label the position of **D**, **E**, and **F** on your plot.



(2) (10 points) A reaction mixture containing pure **D**, sodium methoxide, and an achiral solvent is placed in a polarimetry cell. Using a polarimeter, you observe the sample rotates light counterclockwise by 50 degrees. At the end of the experiment, the rotation is 30 degrees clockwise. If you assume the conversion of **D** to **E** and **F** is clean and complete (i.e., no **D** remains and it is all converted to either **E** or **F**), what is ratio of the rates of the reactions? Express your answer as the relative rate of S_N1:S_N2. Assume both reactions are irreversible under the conditions of the experiment (i.e., once you make **E** or **F**, the reverse reaction to re-form **D** does not take place). Specific rotation data for **D** and **E** are given in the figure above. I suggest working your answer on scratch paper and then transferring it to your answer form.

To simplify the calculation, let's assume a cell pathlength of 1 dm. (You could pick any value; it doesn't matter.) At the start of the experiment, **D** is the only molecule present that is optically active. Since you have the observed rotation at the start and the specific rotation of **D**, the concentration of **D** at the start of the experiment is given by:

$$[\mathbf{D}]_0 = \alpha_{\text{observed}} / ([\alpha] \cdot \text{pathlength}) = -50° / ((-10° \text{ mM}^{-1} \text{ dm}^{-1}) \cdot 1 \text{ dm}) = 5.0 \text{ mM}$$

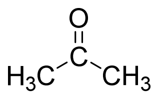
The prompt of the problem tells us that **D** reacts to produce **E** and **F** by competing S_N1 and S_N2 mechanisms. We know that S_N1 reactions give racemic mixtures while S_N2 reactions are stereospecific, producing only the product with inversion at the stereocenter. Thus, any optical activity in the product mixture must be the result of the S_N2 reaction. Here, that is the conversion of **D** to **F**. The excess of **F** in the product mixture is given by:

$$[\mathbf{F}]_0 = \alpha_{\text{observed}} / ([\alpha] \cdot \text{pathlength}) = +30° / ((+30° \text{ mM}^{-1} \text{ dm}^{-1}) \cdot 1 \text{ dm}) = 1.0 \text{ mM}$$

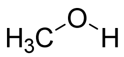
Note that the specific rotation of **F** is equal and opposite to the specific rotation of **E**, its enantiomer. If 1 mM of **D** reacted by the S_N2 mechanism, the other 4 mM must have reacted by the S_N1 mechanism, so the rate of S_N1:S_N2 = 4:1. Note that the final concentration of **E** = 2 mM and **F** = 3 mM, since the S_N1 reaction produces 2 mM of each from the 4 mM of **D** that reacted by this mechanism.

Problem III. Explanations (28 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 six 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 is the better choice of solvent for the reaction between bromomethane (CH_3Br) and potassium thiomethoxide ($K^{+-}SCH_3$)?



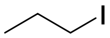
H



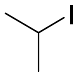
J

Compound **H** is the better solvent. Given that thiomethoxide is a strong nucleophile, methyl carbocations are too unstable, and elimination is impossible from bromomethane, the reaction between bromomethane and thiomethoxide will be substitution by the S_N2 mechanism. This reaction favors polar, aprotic solvents like **H**, where the anionic nucleophile will be less solvated and more available to react. Polar, protic solvents like **J** will solvate anions more strongly, making them less available to react as nucleophiles. Finally, there is a chance that **J** could react (as a nucleophile) with bromomethane, whereas **H** will not.

(2) (9 points) Of compounds **K** and **L**, which reacts faster with potassium cyanide (KCN) in DMSO to form a nitrile compound (R–CN)? (Note: Your explanation should include discussion touching on the subject of orbitals.)



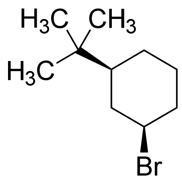
K



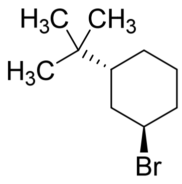
L

Compound **K** will react faster than **L**. The strong nucleophile (cyanide) and polar, aprotic solvent (DMSO) suggest an S_N2 reaction. While the leaving groups are the same for both compounds, the iodide is attached to a less substituted carbon on **K** than **L**. The extra alkyl substituent on **L** creates a bulkier electron cloud that hinders access of the nucleophile to the back side of the $\sigma^*_{C\text{–}I}$ bond, thereby slowing the reaction for **L** relative to **K** by a steric effect.

(3) (10 points) Of isomers **M** and **N**, which will react faster with sodium methoxide to produce an alkene? (Note: I want to see some sort of drawing or diagram in your explanation.)



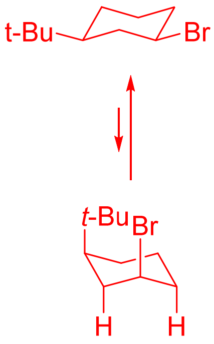
M



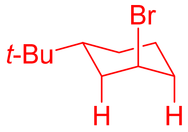
N

Compound **N** will react faster than **M**. The conversion of an alkyl halide to an alkene in the presence of strong base typically proceeds by the E2 mechanism. This reaction requires the departing halide and proton to be positioned antiperiplanar with respect to each other. The most stable chair conformation of **M** and **N** will place the bulky *tert*-butyl groups in equatorial positions to minimize steric repulsion:

M



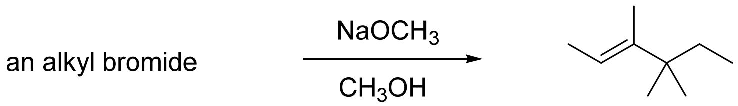
N



The H and Br in compound **N** have the necessary antiperiplanar geometry for E2 when the *t*-butyl group preferentially occupies an equatorial position. In order for **M** to have the required geometry, the chair must flip conformations to unfavorably place the bulky *t*-butyl group in an axial position. Thus, at any given time, more of **N** is in a conformation capable of E2 elimination than **M**, so the reaction will proceed faster for **N**.

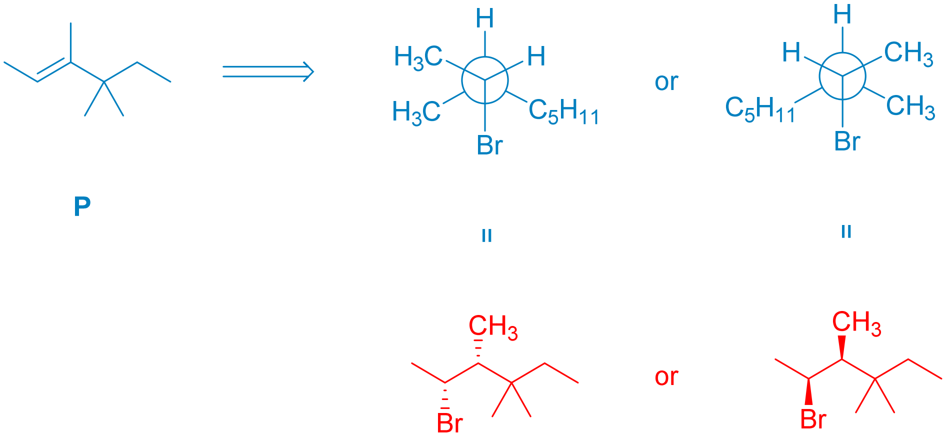
Problem IV. Synthesis (20 points).

(1) (10 points) Propose the alkyl halide that will react with sodium methoxide to synthesize compound **P** in highest yield, with the least amount of alkene side product(s).



P

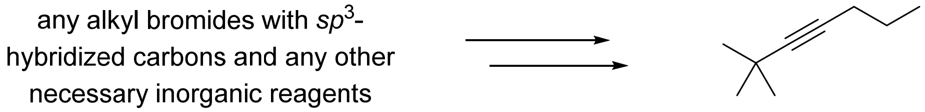
We should place the bromide such that the product can be generated with as few side reactions as possible. Note that the conformation in which the departing bromide and proton have an antiperiplanar relationship will determine which diastereomer of the alkene is produced.



Note that use of the tertiary alkyl bromide is less preferable as it opens up the possibility for two trisubstituted alkene products:

Use of either the secondary or tertiary alkyl halide comes with roughly the same probability of elimination to generate a terminal alkene as a side product, so there is no preference from that standpoint.

(2) (10 points) Plan a synthesis of compound **Q** starting from any inorganic reagents you wish and any alkyl bromides that contain six or fewer *sp*^{3}-hybridized carbon atoms.



Q