CHEM 2410 – Principles of Organic Chemistry I – Summer 2016

Instructor: Paul Bracher

Quiz #2

Due: Sunday, June 5th, 2016

12:00 p.m. (online/Blackboard)

Student Name (Printed)	Solutions
Student Signature	N/A

Instructions & Scoring

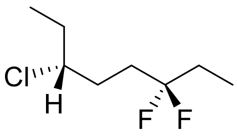
- Please post your answers to Blackboard. No answers marked in this booklet will be graded.
- You may use any resources you wish and collaborate with others.
- Any questions should be posted to the Blackboard discussion board so all students have equal access to the information.

Problem	Points Earned	Points Available
TOTAL		100

Questions, Required Information, Supplementary Information

Multiple choice (100 points total; +10 points for a correct answer, +3 points for answering with the letter “E”, and 0 points for an incorrect answer). For each question, select the best answer of the choices given.

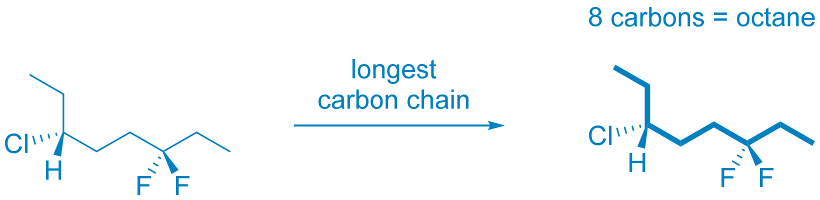
(1) D What is the systematic name of compound **A**?



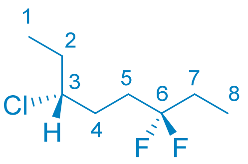
A

(A) (*S*)-3-chloro-6,6-difluorooctane
(B) (*R*)-3-chloro-6,6-difluorooctane
(C) (*S*)-6-chloro-3,3-difluorooctane
(D) (*R*)-6-chloro-3,3-difluorooctane

Begin by identifying the parent chain. Here, it is eight carbons long, so this compound is a substituted octane:

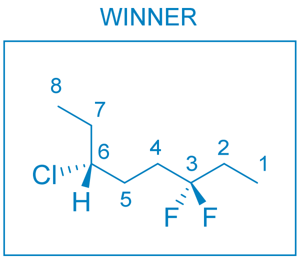


You should start numbering the parent octane chain from the right, based on locant minimization. Beginning from the left or right gives the same lower first locant (left: 3 for Cl vs. right: 3 for F), but numbering from the right end breaks the tie by giving a lower locant number to the second substituent (right: 3 for the second F vs. left: 6 for F):



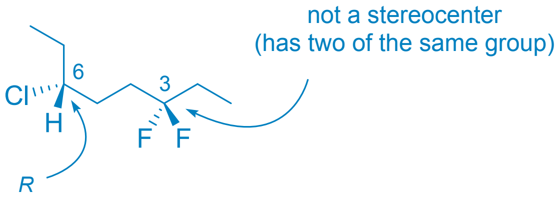
substituents at
locants 3,6,6

vs.

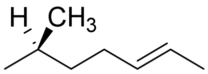


substituents at
locants 3,3,6

Note that the carbon with the fluorine atoms is <u>not</u> a stereocenter, since that carbon is not bonded to four different groups. Just because dashes and wedges are present doesn't necessitate the existence of a stereocenter.



(2) C What statement best describes compound **B**?

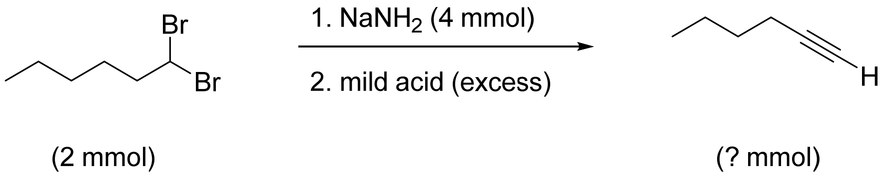


B

(A) compound **B** is chiral and has at least one stereoisomer
(B) compound **B** is chiral and has no stereoisomers
(C) compound **B** is achiral and has at least one stereoisomer
(D) compound **B** is achiral and has no stereoisomers

The compound is achiral—it is identical to its mirror image. The *sp*^{3} carbon with the wedge and dashed bonds is <u>not</u> a stereocenter because it has two methyl groups—the four groups bonded to that carbon are not all different. However, the compound <u>does</u> have a stereoisomer, because the *trans*-substituted alkene could be *cis*. Otherwise identical compounds that differ by a *cis*/*trans* relationship are diastereomers.

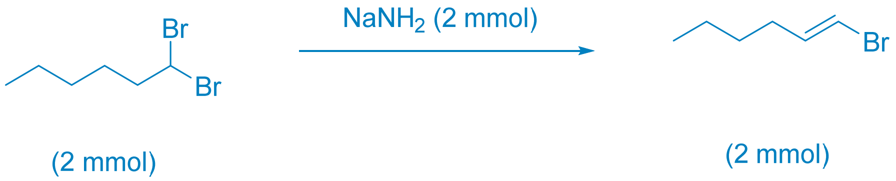
(3) ____A____ What is the theoretical yield of alkyne formed in the following reaction?



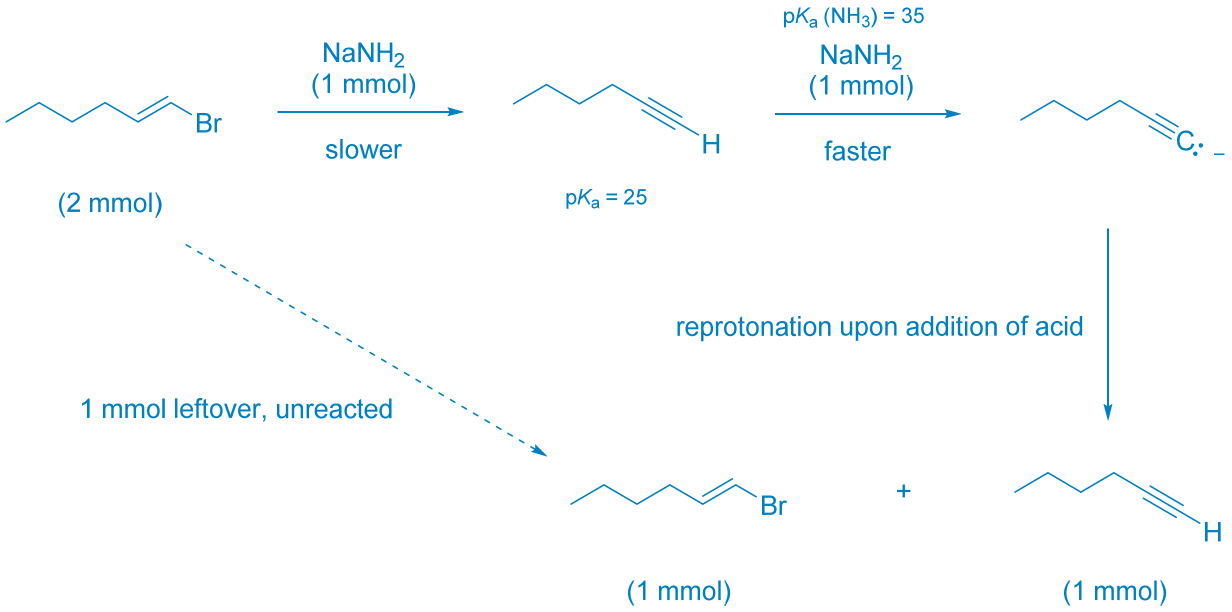
(A) 1 mmol
(B) 1.5 mmol
(C) 2 mmol
(D) 3 mmol

Once one molecule of terminal alkyne is formed upon the second elimination, it immediately consumes another equivalent of base because the acid–base reaction is much faster than (the fairly difficult) elimination of the vinyl bromide.

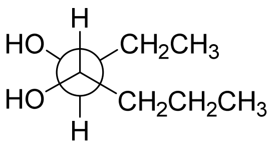
<u>consumption of the first equivalent of base</u>



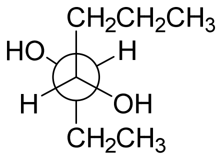
<u>consumption of the second equivalent of base</u>



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



C



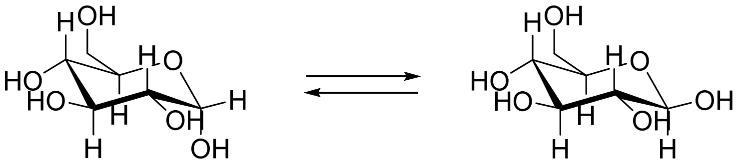
D

(A) enantiomers
(B) diastereomers
(C) identical compounds
(D) structural/constitutional isomers

I think that the easiest way to evaluate the relationship of these compounds is by naming them. Both of them are heptanes with hydroxyl groups at the 3 and 4 carbons. Next, we must determine *R* and *S* at these centers. Compound **C** is 3*S*,4*S* while **D** is 3*R*,4*S*. Thus, these compounds are diastereomers.

(5) C In water, glucose isomerizes between the two anomeric structures shown below. The specific rotation of a 10% (by mass) solution of the α-anomer in water at 20 °C is +112.2° per decimeter. The specific rotation of a 10% (by mass) solution of the β-anomer in water at 20 °C is +18.7° per decimeter. If a 10% (by mass) sample of glucose at equilibrium rotates light 52.7° clockwise over a 10 cm pathlength, which of the following values is closest to the ratio of the two isomers, α/β, at equilibrium?

(D)-glucose



α anomer

[α] = +112.2°

β anomer

[α] = +18.7°

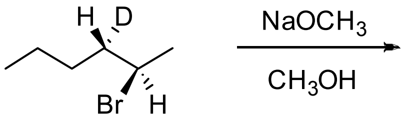
(A) 2.04
(B) 1.75
(C) 0.57
(D) 0.40

The answer can be obtained by algebra, letting x = the proportion of α-anomer and (1−x) = the proportion of β-anomer. This gives:

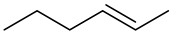
$$x(+112.2°) + (1-x)(+18.7°) = +52.7°$$
$$(112.2-18.7)x = (52.7-18.7)$$
$$x = 0.364$$

Therefore, at equilibrium, the ratio of α/β = 0.364/0.636 = 0.572.

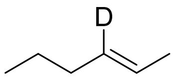
(6) A What is the major product when compound **E** is treated with sodium methoxide in methanol?



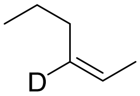
E



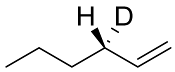
(A)



(B)



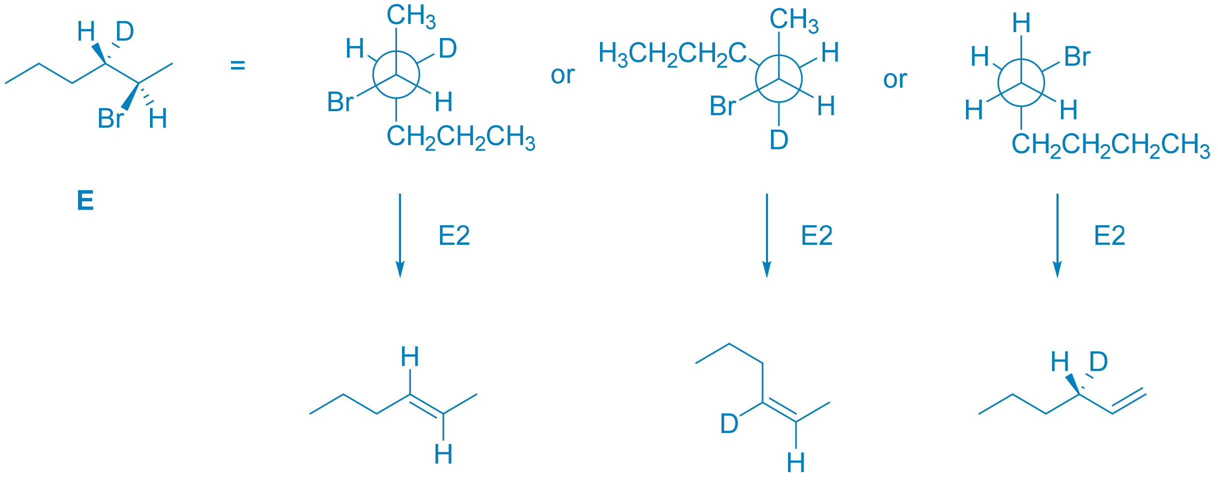
(C)



(D)

First off, remember that D = ^{2}H. It is an isotope of hydrogen. Both H and D will exhibit the same reactivity. Next, we should recognize that we have a strong base (methoxide) and a secondary alkyl halide with β-hydrogens. We expect the dominant reaction to be E2 elimination. As such, we are looking to preferentially eliminate: (i) the β-hydrogen that can be in a conformation that places it anti-periplanar to the halogen atom, (ii) that leads to the most substituted product, (iii) with a preference for *trans* or *cis* if all else is equal.

three different H/X anti-periplanar conformations

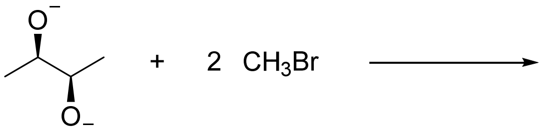


major

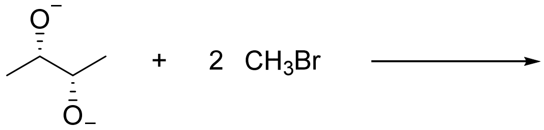
Here, the third possibility leads to a monosubstituted alkene product while the first two possibilities lead to disubstituted alkenes. The first possibility is preferred because there is less steric repulsion in the anti-periplanar conformation where the alkyl substituents are anti and there is less steric repulsion in the final product where the alkyl substituents of the alkene are *trans* instead of *cis*.

(7) B Which of the following pairs of nucleophiles and electrophiles is the best choice for synthesizing (*S*,*S*)-2,3-dimethoxybutane (**F**)?

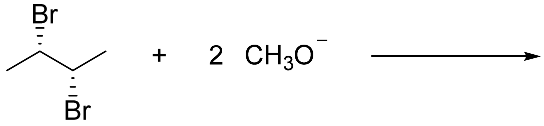
(A)



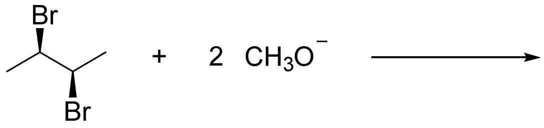
(B)

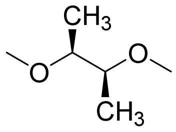


(C)



(D)



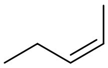


F

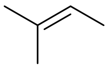
In reactions (C) and (D), E2 will compete with S_N2 and seriously erode the yield of substitution. Reactions (A) and (B) do not suffer from this limitation, since methyl bromide has no β-bydrogens that could be eliminated. But only reaction (B) gives the stereochemistry of the desired product.

(8) A

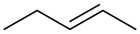
Which of the following isomers of C_5H_{10} will have the <u>most exothermic</u> heat of combustion? That is, if one mole of each compound is burned (completely) in an oxygen atmosphere, which will release the most heat?



(A)



(B)



(C)

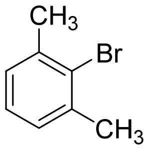
Since we are comparing isomers that will produce identical mixtures of products (5 CO_2 + 5 H_2O), the compound that will liberate the most energy upon combustion is the one that is least stable to begin with. For alkenes, stability is improved by increasing alkyl substitution of the π bond (thanks to hyperconjugation) and the placement of larger substituents farther away from each other (to avoid steric repulsion of their electron clouds). Here, compound (A) is disubstituted *cis*. Compound (B) is more stable by virtue of its higher substitution (tri- vs. di-), and compound (C) is more stable from its *trans* substitution despite also being disubstituted.

(9) A

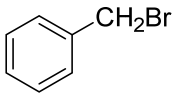
Which of the following compounds can participate in exactly one of the S_N1, S_N2, E1, or E2 mechanisms? That is, which substrate can react in one of these reactions but none of the other three?

CH_3Br

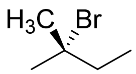
(A)



(B)



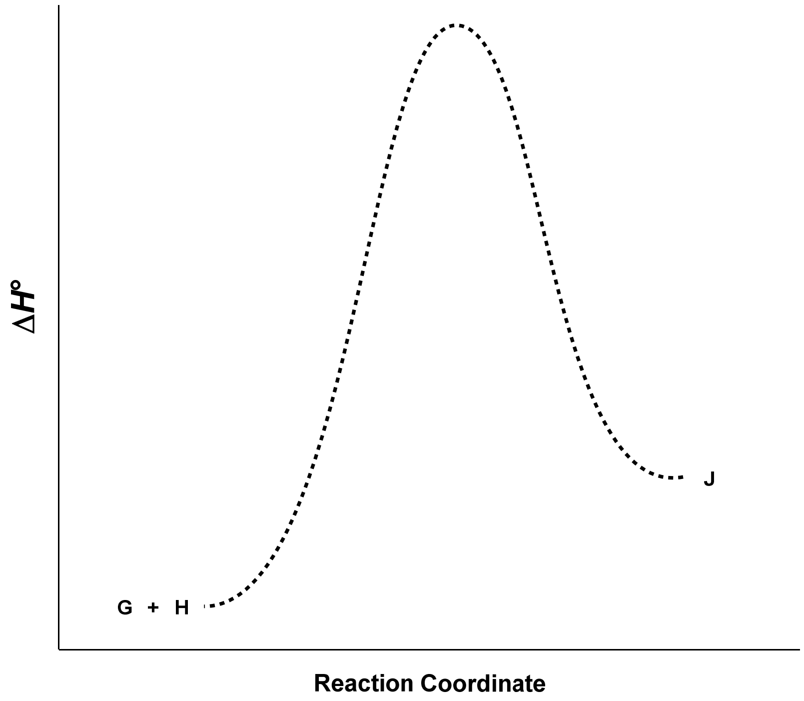
(C)



(D)

Compound (A) can undergo the S_N2 reaction, but not S_N1 (methyl carbocations are too unstable to form), E1 (methyl carbocations are too unstable to form), or E2 (it has no β-hydrogens). Compound (B) can't react through any of those four mechanisms (aryl halides are not easily substituted by nucleophiles). Compound (C) can react via S_N1 and S_N2, but not E1 or E2 (no β-hydrogens). Compound (D) can react by S_N1, E1, and E2, but not S_N2 (tertiary centers are too hindered).

(10) C Which of the following statements is <u>not</u> true of a reaction that corresponds to the following energy diagram?



(A) the reaction is endothermic
(B) the equilibrium will favor the reactants (**G** & **H**)
(C) the rate of the reaction will decrease at higher temperatures
(D) the reaction is concerted

The reaction is endothermic, because the products (**J**) have a higher potential energy than the starting materials (**G** + **H**). Correspondingly, at equilibrium, the reactants (which are lower in energy) will be favored. The reaction is concerted, because it proceeds through one transition state (a peak on the diagram) and has no intermediates. The rate of the reaction will not decrease at higher temperatures, it will increase. Rates increase with increasing temperature, because more molecules will have sufficient energy to get over the activation barrier. But here, the equilibrium may very well shift toward the products at higher temperature, if the rate of the reverse reaction does not keep pace with the increase in rate of the forward reaction.