

CHEM 3311
Fall 2001
Exam III (November 15)

Name: _____

Your Recitation TA's name: _____

Please write your name on each exam page.

Please check to see that you have all 4 questions. Read the questions very carefully and underline keywords that may help to focus your answer.

Question #	Points Earned
1 (25 points)	_____
2 (24 points)	_____
3 (24 points)	_____
4 (27 points)	_____
Max: 100	Total _____

Special Instructions

This is a "Closed Book" exam. You are permitted to use molecular models. Answers should be written clearly to receive partial credit. Additional scratch paper will not be graded or collected. You have two hours to complete the exam.

Nucleophilicity of Some Common Nucleophiles

Very good nucleophiles: I^- , HS^- , RS^-

Good nucleophiles: Br^- , HO^- , RO^- , CN^- , N_3^-

Fair nucleophiles: NH_3 , Cl^- , F^- , RCO_2^-

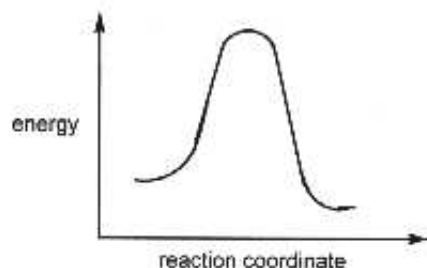
Weak nucleophiles: H_2O , ROH

Very weak nucleophiles: RCO_2H

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1. (25 points) **Multiple Choice:** Circle the **best** possible answer.

- (i) Considering the S_N1 , S_N2 , E1 and E2 mechanisms, carefully examine the energy diagram shown below. Which mechanism(s) is(are) best illustrated by the energy diagram

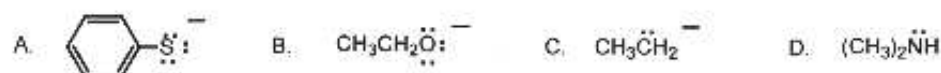


shown?

- (A) only the S_N1 mechanism
(B) only the S_N2 mechanism
(C) both the S_N1 and E1 mechanisms
(D) both the S_N2 and E2 mechanisms
- (ii) Consider the reaction of 1-bromopentane with each of the following reagents in the solvents shown at the specified temperatures. Which reaction would have the highest elimination/substitution ratio?
- (A) $\text{NaOCH}_2\text{CH}_3$, ethanol, 55°C
(B) $\text{KOC}(\text{CH}_3)_3$, $(\text{CH}_3)_3\text{COH}$, 55°C
(C) NaSH , ethanol-water, 25°C
(D) KCN , DMSO, 40°C
- (iii) Compound X is reacted with excess NaNH_2 in liquid ammonia. Upon completion of the reaction, water or acid is added to the reaction mixture. The product is identified as hexa-1,5-diyne. The correct structure of X must be:
- (A) $\text{BrCH}_2\text{CH}(\text{Br})\text{CH}_2\text{CH}_2\text{CH}=\text{CH}_2$
(B) $\text{Br}_2\text{CHCH}_2\text{CH}_2\text{CH}_2\text{CH}=\text{CH}_2$
(C) $\text{BrCH}_2\text{CH}(\text{Br})\text{CH}_2\text{CH}_2\text{CH}_2\text{CHBr}_2$
(D) $\text{Br}_2\text{CHCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Br}$

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(iv) Rank the following nucleophiles in order of increasing basicity.



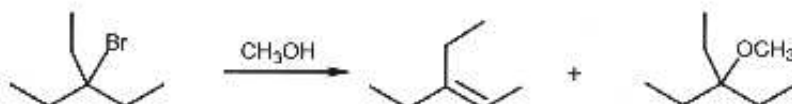
(A) $\text{D} < \text{B} < \text{A} < \text{C}$

(B) $\text{A} < \text{D} < \text{B} < \text{C}$

(C) $\text{C} < \text{B} < \text{D} < \text{A}$

(D) $\text{D} < \text{A} < \text{B} < \text{C}$

(v) Identify the mechanistic pathways, respectively, for the products in the following reaction:



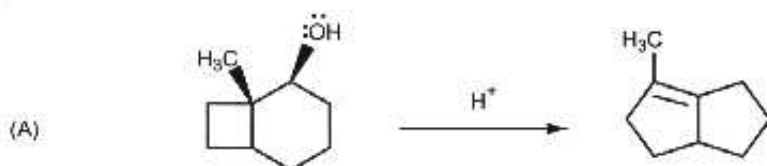
(A) $\text{E}1, \text{S}_{\text{N}}1$

(B) $\text{E}1, \text{S}_{\text{N}}2$

(C) $\text{E}2, \text{S}_{\text{N}}1$

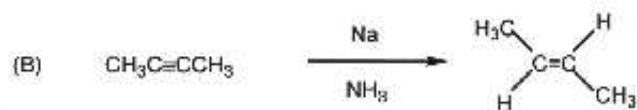
(D) $\text{E}2, \text{S}_{\text{N}}2$

2. (24 points) Write an arrow pushing mechanism for the following transformations. Be sure to show all intermediates in the pathway from starting material to product, but do not show transition states. All structures should have proper valence bond structures with correct formal charges and lone pairs as necessary



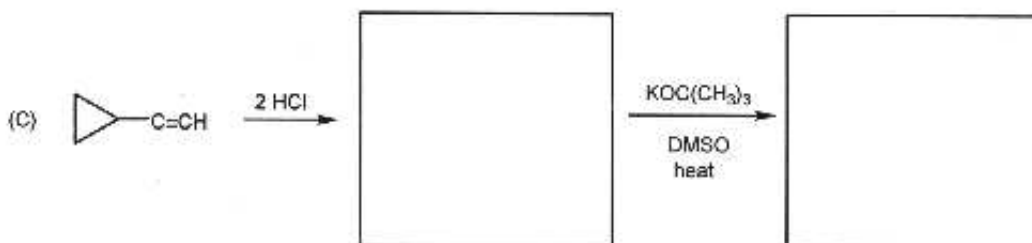
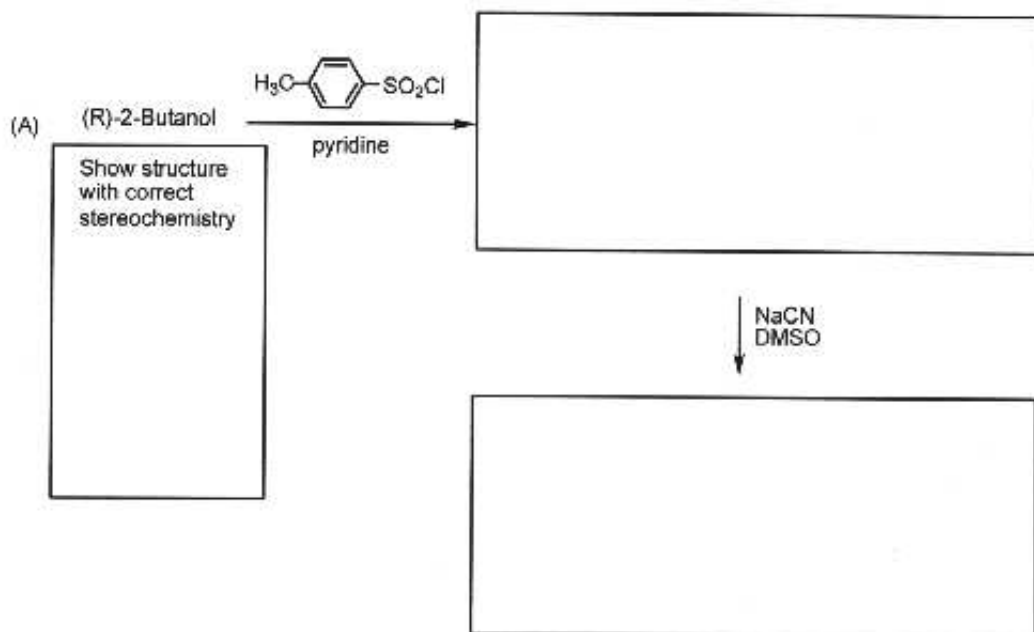
Name: _____

Write an arrow pushing mechanism for the following transformations. Be sure to show all intermediates in the pathway from starting material to product, but do not show transition states. All structures should have proper valence bond structures with correct formal charges and lone pairs as necessary



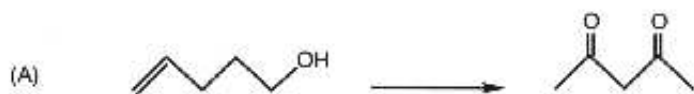
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3. (24 points) Write the structure of the missing reactant, reagents, or products as necessary. Show the **correct stereochemistry** where appropriate.



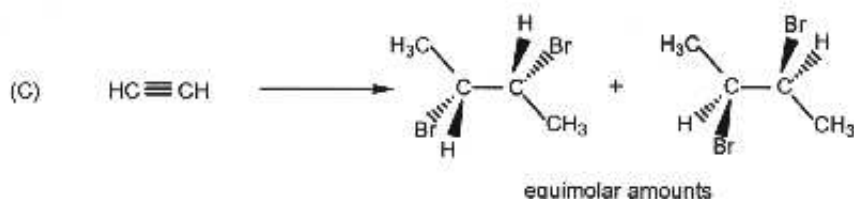
Name: _____

4. (27 points) Propose an efficient synthesis of the product shown starting with the given reactant. Note: More than one step may be required. You may use any other organic or inorganic reagent as necessary. In an efficient synthesis, the desired product should be the major product. Pay attention to stereochemistry where applicable.



Name: _____

Propose an efficient synthesis of the product(s) shown starting with the given reactant. Note: More than one step may be required. You may use any other organic or inorganic reagent as necessary. In an efficient synthesis, the desired product should be the major product. Pay attention to stereochemistry where applicable.



- (i) Assign the correct absolute configuration to each stereogenic center in the products shown above. Write your answer next to the stereogenic carbon center(s).
- (ii) Identify the mixture of products shown above as constitutional isomers, conformational isomers, diastereomers, racemic mixture or meso compound.

Answer: _____

- (ii) Using the conclusion arrived at in (ii), propose an efficient synthetic route.