

**CHEM 3311-200**  
**Exam 3**  
**November 13, 2012**

**Time: 2 Hours**

Please *copy* and *sign* the Honor Pledge on the scantron sheet in the space below the double lines.

I pledge that

“On my honor, as a University of Colorado-Boulder student, I have neither given nor received unauthorized assistance on this work.”

General Instructions

On the computer graded answer sheet (also known as a scantron), enter **your name** and **student identification number** in the appropriate boxes. Enter the number of your recitation section in the four columns at the upper left of the sheet. (Use a zero before the recitation section number - for example, section 237 is written as 0237.) Then **fill in the corresponding bubbles below your name, ID number, and recitation section.**

Answer all questions on the computer graded answer sheets by filling in the proper bubble with a No. 2 pencil. If you change an answer, erase the undesired mark thoroughly. Mark only the best answer to each question. Programmable calculators are not permitted during the exam.

A section of the Periodic Table with atomic numbers and masses is shown on this cover page. A Table of  $pK_a$  values is included here. Use the back of the exam pages as scratch paper. There are 6 exam pages (with 25 questions), a cover page, and two blank pages (scratch paper). When you are instructed to begin the exam, please check that you have all pages. Good luck!

**Please return the completed scantron sheet to the exam proctors.** You may take the exam and scratch paper with you.

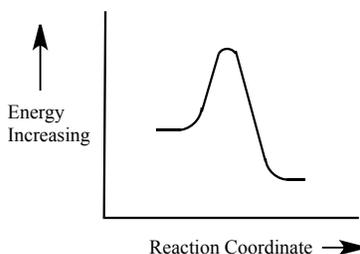
1 H	
3 Li	4 Be
11 Na	12 Mg

				2 He	
5 B	6 C	7 N	8 O	9 F	10 Ne
13 Al	14 Si	15 P	16 S	17 Cl	18 Ar

**Table of Acidities**

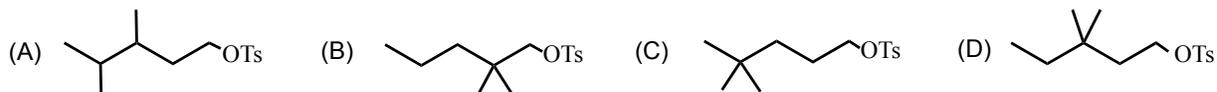
<u>Acid</u>	<u><math>pK_a</math> Values</u>	<u>Recitation Section #</u>	<u>Recitation TA's name</u>
HI	-10.1	210 (Mon, 8 AM)	Ryan Michael
HCl	-3.9	212 (Mon, 8 AM)	Katelyn Chando
$H_3O^+$	-1.7	216 (Mon, 2 PM)	Katelyn Chando
$CH_3COOH$	4.7	217 (Mon, 5 PM)	Ryan Michael
$NH_4^+$	9.3	220 (Tues, 8 AM)	Katelyn Chando
Phenol	10	227 (Tues, 5 PM)	Zhangxing Shi
$C_2H_5SH$	10.5	228 (Tues, 5 PM)	Katelyn Chando
$H_2O$	15.7	231 (Wed, 8AM)	Ryan Michael
Alcohols	16-18	233 (Wed, 12 PM)	Patrick Castro
$HC\equiv CH$	26	237 (Wed, 5 PM)	Katelyn Chando
$NH_3$	36	238 (Wed, 5 PM)	Will Hartwig
$H_2C=CH_2$	45	239 (Wed, 5 PM)	Josh Sloan
$CH_4$	60	250 (Fri, 8 AM)	Ryan Michael

1. Considering the  $S_N1$ ,  $S_N2$ , E1, and E2 mechanisms, the energy diagram shown below corresponds to:

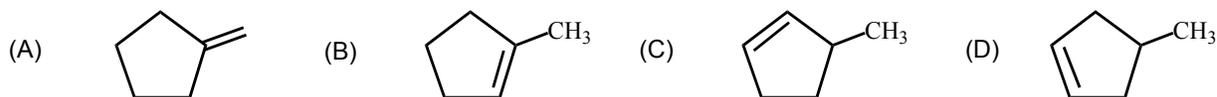
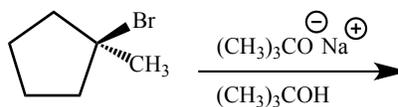


- (A) only the  $S_N1$  mechanism.  
 (B) only the  $S_N2$  mechanism.  
 (C) both the  $S_N1$  and E1 mechanisms.  
 (D) both the  $S_N2$  and E2 mechanisms.

2. Tosylate, represented as OTs, is an excellent leaving group. Which tosylate reacts slowest with sodium azide in acetone?



3. Predict the major product of the reaction shown below.



4. What is the mechanism that accounts for the major product in the reaction of 3-bromo-2,4-dimethylpentane with sodium ethoxide in ethanol?

- (A)  $S_N1$  (B)  $S_N2$  (C) E1 (D) E2

5. Select all the statements that *correctly* describe relative nucleophilicities under the conditions described in each.

(I) Both ethoxide and *t*-butoxide are strong bases; ethoxide is a good nucleophile whereas *t*-butoxide is a poor nucleophile.

(II) In methanol, the methoxide ion is a better nucleophile than the methane thiolate ion.

(III) Cyanide and azide ions are good nucleophiles in DMSO.

(A) I and II

(B) I and III

(C) II and III

(D) I, II and III

6. What is the mechanism that accounts for the major product in the reaction of 1-chlorobutane with methoxide ion in methanol?

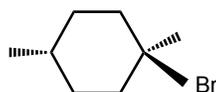
(A) S<sub>N</sub>1

(B) S<sub>N</sub>2

(C) E1

(D) E2

7. When the compound shown below



is dissolved in water, two substitution products are formed. How are these compounds related?

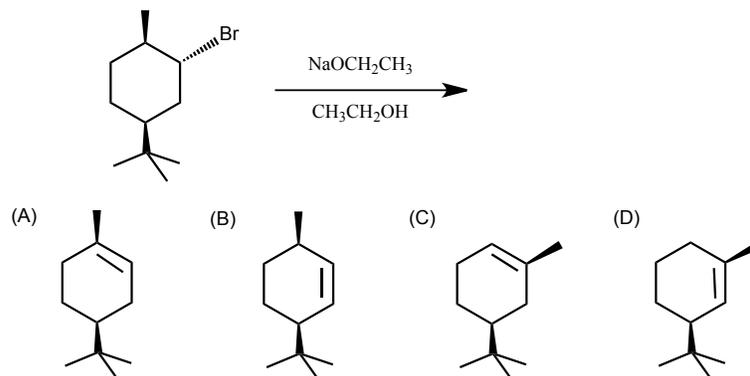
(A) Constitutional isomers

(B) Diastereomers

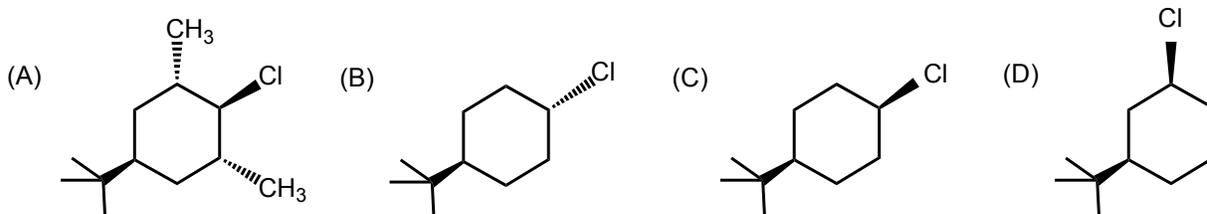
(C) Enantiomers

(D) Meso compounds

8. What is the major product in the reaction shown below?



9. Which cyclohexyl chloride will react at the fastest rate with *t*-butoxide in *t*-butanol?



10. Compound X is treated with Na metal, followed by reaction with  $\text{CH}_3\text{I}$ ; the final product is butyl methyl ether. What is the identity of compound X?

- (A)  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$  (B)  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{SH}$   
 (C)  $\text{CH}_3\text{CH}_2\text{CHOHCH}_3$  (D)  $\text{CH}_3\text{CH}_2\text{CHSHCH}_3$

11. Identify the compound in each pair that reacts at the faster rate in  $\text{CH}_3\text{OH}$ .

- (I) Isopropyl bromide or isobutyl bromide  
 (II) *t*-Butyl chloride or *t*-butyl iodide  
 (III) 1-Methylcyclopentyl iodide or cyclopentyl iodide

- (A) Isobutyl bromide, *t*-butyl chloride, cyclopentyl iodide  
 (B) Isobutyl bromide, *t*-butyl iodide, cyclopentyl iodide  
 (C) Isopropyl bromide, *t*-butyl iodide, 1-methylcyclopentyl iodide  
 (D) Isopropyl bromide, *t*-butyl chloride, 1-methylcyclopentyl iodide

12. Which sequence of reactions would you use to convert cyclopentane to cyclopentyl cyanide?

- (A) Cyclopentane + NaCN in acetone  
 (B) Cyclopentane + HCN  
 (C) (1) Cyclopentane + HBr, followed by (2) reaction with NaCN in DMSO  
 (D) (1) Cyclopentane +  $\text{Br}_2$  using heat or light, followed by (2) reaction with NaCN in DMSO

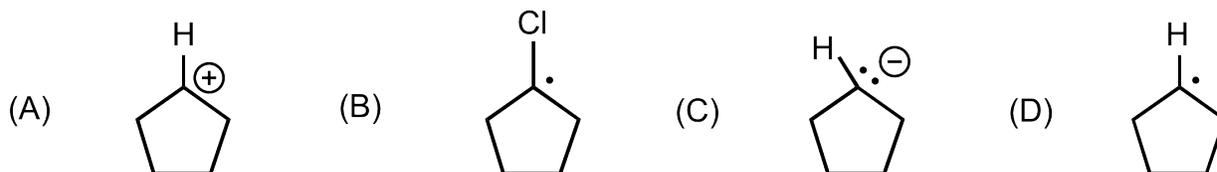
13. Which reaction or sequence of reactions would produce the best yield of isobutyl alcohol starting with *t*-butyl chloride?

- (A) Reaction with NaOH  
 (B) Reaction with CH<sub>3</sub>OH  
 (C) (1) Reaction with NaOCH<sub>3</sub>, followed by (2) oxymercuration and reduction with NaBH<sub>4</sub>/NaOH  
 (D) (1) Reaction with NaOCH<sub>3</sub>, followed by (2) hydroboration & oxidation

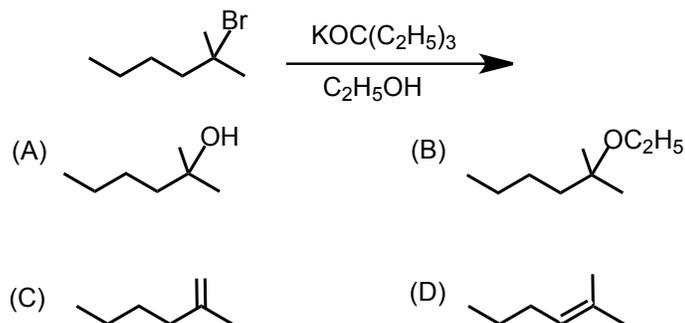
14. Select the best method for the synthesis of (R)-2-cyanobutane from (R)-2-chlorobutane.

- (A) React (R)-2-chlorobutane with HCN in DMSO  
 (B) React (R)-2-chlorobutane with NaCN in DMSO  
 (C) React (R)-2-chlorobutane with NaOC<sub>2</sub>H<sub>5</sub> in ethanol, followed by addition of HCN  
 (D) React (R)-2-chlorobutane with NaI in acetone, followed by reaction with NaCN in DMSO

15. Which of the following is an intermediate in the reaction of cyclopentyl chloride in CH<sub>3</sub>COOH?



16. Select the major product in the reaction shown below.



17. Select all the statements that *correctly* describe relative nucleophilicities under the conditions described in each.

(I) The acetate ion and the azide ion have similar basicities; however, the azide ion is a better nucleophile than the acetate ion.

(II) Acetate ion is a weaker nucleophile than trifluoroacetate in acetone.

(III) In  $\text{CH}_3\text{OH}$ , the iodide ion is a better nucleophile than fluoride.

(A) I and II

(B) I and III

(C) II and III

(D) I, II, and III

18. What is the relationship between the products formed when (S)-4-methyl-1-hexene is reacted with  $\text{HBr}$ ?

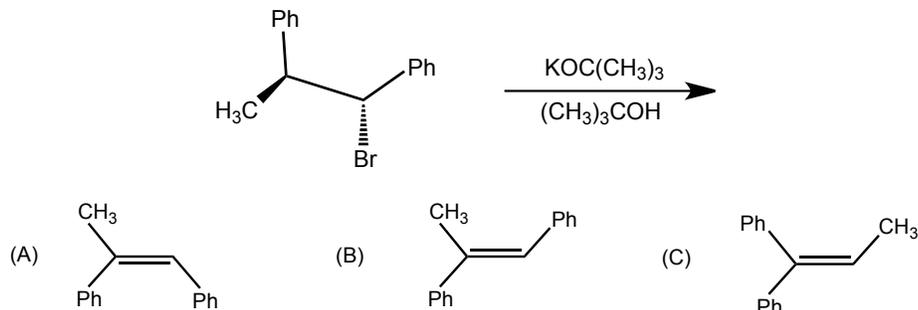
(A) Constitutional isomers

(B) Diastereomers

(C) Enantiomers

(D) Meso compound

19. Select the major product in the reaction shown below.



(D) There is no reaction.

20. When 2-chlorobutane is reacted with  $\text{H}_2\text{O}$ , a substitution product is 2-butanol. Which mechanism best explains the formation of this product?

(A)  $\text{S}_{\text{N}}2$  mechanism with  $\text{H}_2\text{O}$  acting as the nucleophile.

(B)  $\text{S}_{\text{N}}2$  mechanism with  $\text{OH}^-$  acting as the nucleophile.

(C)  $\text{S}_{\text{N}}1$  mechanism with  $\text{H}_2\text{O}$  acting as the nucleophile.

(D)  $\text{S}_{\text{N}}1$  mechanism with  $\text{OH}^-$  acting as the nucleophile.

21. What is the stereochemical relationship between the products formed when (Z)-3-hexene is reacted with  $\text{CH}_2\text{I}_2$  and Zn/Cu couple?

- (A) Constitutional isomers (B) Diastereomers  
(C) Enantiomers (D) Meso compound

22. Calculate the  $\Delta H^\circ$  for the second propagation step in the free radical bromination of cyclopentane to give bromocyclopentane.

Bond Type	Bond Dissociation Energy (kJ/mol)
C-H in cyclopentane	395
C-Br in bromocyclopentane	284
$\text{Br}_2$	192
HBr	366

- (A) -92 kJ/mol (B) -29 kJ/mol (C) +29 kJ/mol (D) +92 kJ/mol

23. Select all the reactions that involve carbocation mechanisms.

- (I) Reaction of (E)-2-butene with  $\text{Br}_2$  in  $\text{CH}_2\text{Cl}_2$   
(II) Reaction of (Z)-2-butene with  $\text{CH}_2\text{I}_2$  in the presence of Zn/Cu  
(III) Reaction of (E)-2-butene with  $\text{Br}_2$  in the presence of ROOR and heat

- (A) I and II (B) I and III (C) All of these (D) None of these

24. Select the order of **decreasing reactivity** of the alkyl chlorides, 1-chlorohexane, 2-chlorohexane, and 2-chloro-2-methylpentane, when reacted in formic acid,  $\text{HCOOH}$ .

- (A) 1-chlorohexane > 2-chlorohexane > 2-chloro-2-methylpentane  
(B) 1-chlorohexane > 2-chloro-2-methylpentane > 2-chlorohexane  
(C) 2-chloro-2-methylpentane > 2-chlorohexane > 1-chlorohexane  
(D) 2-chlorohexane > 1-chlorohexane > 2-chloro-2-methylpentane

25. Select the order of **increasing** basicity of the nucleophiles listed.

- (A)  $\text{I}^- < \text{CH}_3\text{COO}^- < \text{CH}_3\text{O}^- < \text{HC}\equiv\text{C}^-$   
(B)  $\text{CH}_3\text{O}^- < \text{I}^- < \text{HC}\equiv\text{C}^- < \text{CH}_3\text{COO}^-$   
(C)  $\text{CH}_3\text{COO}^- < \text{HC}\equiv\text{C}^- < \text{I}^- < \text{CH}_3\text{O}^-$   
(D)  $\text{HC}\equiv\text{C}^- < \text{CH}_3\text{O}^- < \text{CH}_3\text{COO}^- < \text{I}^-$