

CHEM 3311-200**Exam 3****November 13, 2012****Time: 2 Hours****ANSWER KEY**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!

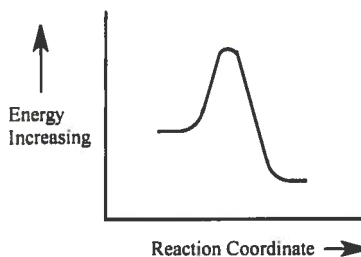
Please return the completed scantron sheet to the exam proctors. You may take the exam and scratch paper with you.

1 H						2 He
3 Li	4 Be					
11 Na	12 Mg	5 B	6 C	7 N	8 O	9 F
		13 Al	14 Si	15 P	16 S	17 Cl
						18 Ar

Table of Acidities

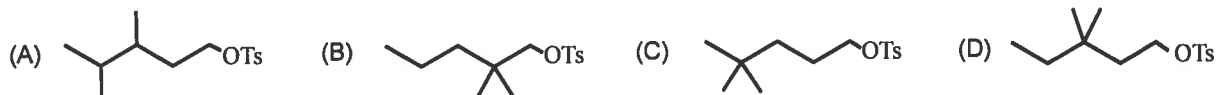
<u>Acid</u>	<u>pK_a Values</u>	<u>Recitation Section #</u>	<u>Recitation TA's name</u>
HI	-10.1	210 (Mon, 8 AM)	Ryan Michael
HCl	-3.9	212 (Mon, 8 AM)	Katelyn Chando
H_3O^+	-1.7	216 (Mon, 2 PM)	Katelyn Chando
CH_3COOH	4.7	217 (Mon, 5 PM)	Ryan Michael
NH_4^+	9.3	220 (Tues, 8 AM)	Katelyn Chando
Phenol	10	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:



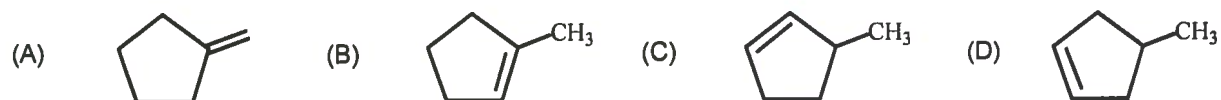
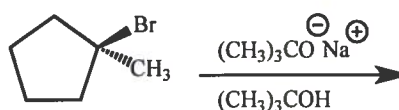
- (A) only the S_N1 mechanism.
 (B) only the S_N2 mechanism.
 (C) both the S_N1 and E1 mechanisms.
(D) both the S_N2 and E2 mechanisms.

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



Correct Answer: B

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



Correct Answer: A

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.

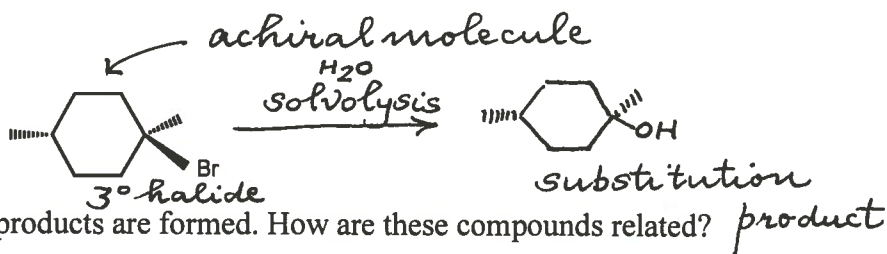
- (I) Both ethoxide and *t*-butoxide are strong bases; ethoxide is a good nucleophile whereas *t*-butoxide is a poor nucleophile.
 (II) In methanol, the methoxide ion is a better nucleophile than the methane thiolate ion.
 (III) Cyanide and azide ions are good nucleophiles in DMSO.

- (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_N1 **(B) S_N2** (C) E1 (D) E2

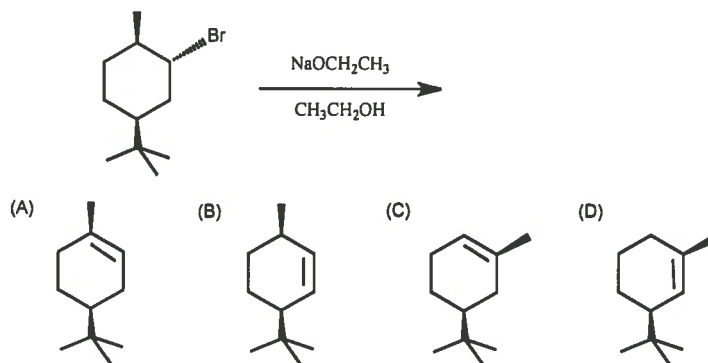
7. When the compound shown below
Bad Question; all answers receive credit



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

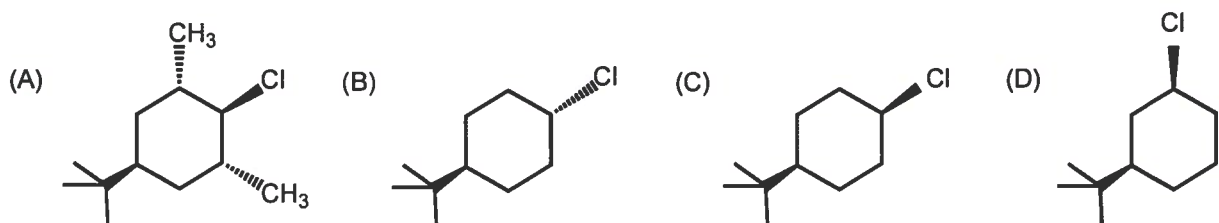
- (A) Constitutional isomers
 (B) Diastereomers
 (C) Enantiomers
 (D) Meso compounds

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



Correct Answer: B

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



Correct Answer: C

10. Compound X is treated with Na metal, followed by reaction with CH_3I ; 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 CH_3OH .

- (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 + Br_2 using heat or light, followed by (2) reaction with NaCN in DMSO

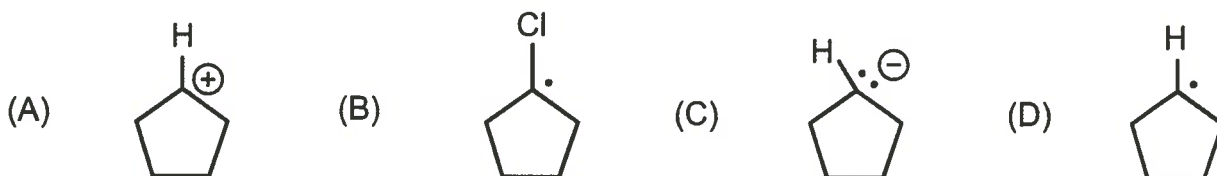
13. Which reaction or sequence of reactions would produce the best yield of isobutyl alcohol starting with *t*-butyl chloride?

- (A) Reaction with NaOH
 (B) Reaction with CH₃OH
 (C) (1) Reaction with NaOCH₃, followed by (2) oxymercuration and reduction with NaBH₄/NaOH
(D) (1) Reaction with NaOCH₃, followed by (2) hydroboration & oxidation

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

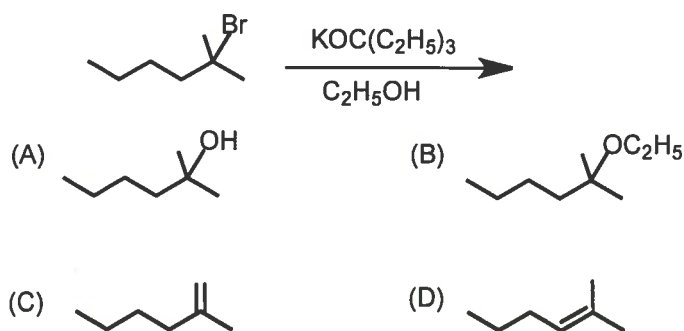
- (A) React (R)-2-chlorobutane with HCN in DMSO
 (B) React (R)-2-chlorobutane with NaCN in DMSO
 (C) React (R)-2-chlorobutane with NaOC₂H₅ in ethanol, followed by addition of HCN
(D) React (R)-2-chlorobutane with NaI in acetone, followed by reaction with NaCN in DMSO

15. Which of the following is an intermediate in the reaction of cyclopentyl chloride in CH₃COOH?



Correct Answer: A

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



Correct Answer: C

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 CH_3OH , 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 HBr ?

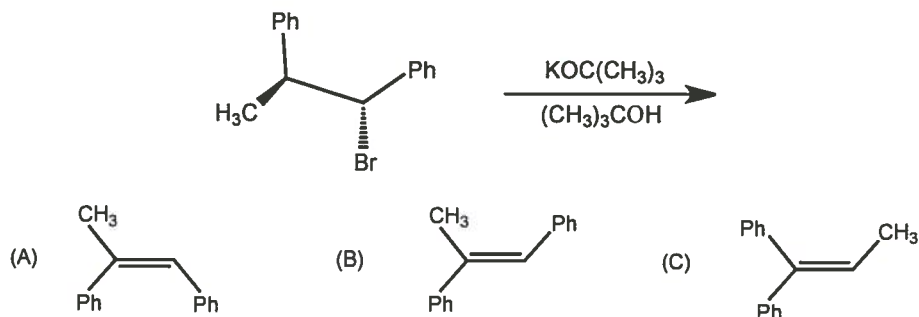
(A) Constitutional isomers

(B) Diastereomers

(C) Enantiomers

(D) Meso compound

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



(D) There is no reaction.

Correct Answer: B

20. When 2-chlorobutane is reacted with H_2O , a substitution product is 2-butanol. Which mechanism best explains the formation of this product?

(A) $\text{S}_{\text{N}}2$ mechanism with H_2O acting as the nucleophile.

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

(C) $\text{S}_{\text{N}}1$ mechanism with H_2O acting as the nucleophile.

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

21. What is the stereochemical relationship between the products formed when (Z)-3-hexene is reacted with CH_2I_2 and Zn/Cu couple?

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

22. Calculate the ΔH° 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
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 Br_2 in CH_2Cl_2
(II) Reaction of (Z)-2-butene with CH_2I_2 in the presence of Zn/Cu
(III) Reaction of (E)-2-butene with 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, 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) $\text{HC}\equiv\text{C}^- < \text{CH}_3\text{O}^- < \text{CH}_3\text{COO}^- < \text{I}^-$