

## CHEM 3311-100

Exam 3 **KEY**

April 16, 2013

Time: 2 Hours

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

**PRINT YOUR FIRST & LAST NAME****PLEASE SIGN HERE**General Instructions

- 1) Please turn off your cell phone (contact me if you **MUST** have your cell phone on) and place it in your backpack.
- 2) This is a **CLOSED BOOK** exam; nothing is allowed except your student ID, a few pencils or pens, eraser, and **molecular models in a transparent/clear Ziploc bag** (quart size).
- 3) In the space below the double lines (for handwritten work), please copy the honor code (shown above) and sign your name.
- 4) Use the blank areas of the exam for scratch work; scratch paper will be provided as needed.
- 5) Your scantron **MUST INCLUDE** your (i) name, (ii) student ID #, and (iii) recitation section #. Please follow the detailed instructions provided below.
- 6) If suspected of/caught cheating, you will receive at best an F for the exam. The instructor reserves the right to proceed further in compliance with university policies on academic violations.
- 7) You may **NOT** leave the room after the exam has started to minimize disruptions to other students (contact a proctor if there are extenuating circumstances). When you finish the exam, **please return the completed scantron sheet to the exam proctors** at the front desk, and leave as quietly as possible. You are allowed to take the exam and scratch paper with you.

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 **5 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!

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> Value</u>
HI	-10.1
HCl	-3.9
$H_3O^+$	-1.7
$CH_3COOH$	4.7
$NH_4^+$	9.3
Phenol	10
$C_2H_5SH$	10.5

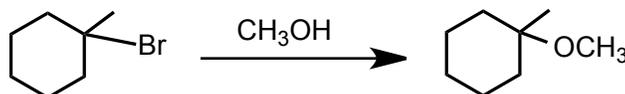
**Table of Acidities**

<u>Acid</u>	<u><math>pK_a</math> Value</u>	<u>Recitation Day/ Section #</u>	<u>TA's Name</u>
$H_2O$	15.7		
Alcohols	16-18	110	M 8 Greenberg
$HC\equiv CH$	26	113	M 12 Greenberg
$NH_3$	36	125	T 1 Chando
$H_2$	37	133	W 12 Carey
$H_2C=CH_2$	45	137	W 5 Carey
$CH_4$	60	143	R 12 Chando

1. Which compound would be *most soluble* in water?  
 (A) **Methanol** (B) Diethyl ether  
 (C) Carbon tetrachloride (D) 1-Octanol
2. Select the compound with the *higher* boiling point in each pair of compounds.  
 (I) Pentane or 2,2-dimethylpropane  
 (II) CH<sub>3</sub>CH<sub>2</sub>F or (CH<sub>3</sub>)<sub>2</sub>NH  
 (A) Pentane, CH<sub>3</sub>CH<sub>2</sub>F (B) **Pentane, (CH<sub>3</sub>)<sub>2</sub>NH**  
 (C) 2,2-dimethylpropane, CH<sub>3</sub>CH<sub>2</sub>F (D) 2,2-dimethylpropane, (CH<sub>3</sub>)<sub>2</sub>NH
3. Label each statement as true (T) or false (F). Then, select the correct combination with the answer for statement I followed by that for statement II.  
 (I) In C<sub>2</sub>H<sub>5</sub>OH, the ethoxide ion is a stronger base and a stronger nucleophile than the acetate ion.  
 (II) In CH<sub>3</sub>OH, the methoxide ion is a stronger base and a weaker nucleophile than F<sup>-</sup>.  
 (A) F, F (B) F, T (C) **T, F** (D) T, T
4. Which compound has the *best* leaving group?  
 (A) CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>OH (B) CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>Cl  
 (C) CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>Br (D) **CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>I**

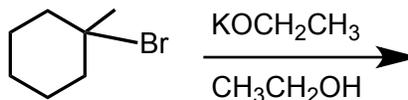
For questions 5-8, identify each reaction as S<sub>N</sub>1, S<sub>N</sub>2, E1, or E2.

5. Consider the reaction:



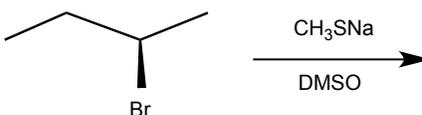
- (A) **S<sub>N</sub>1** (B) S<sub>N</sub>2 (C) E1 (D) E2

6. Consider the reaction:



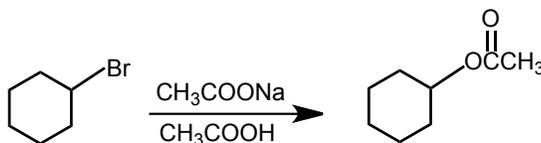
- (A) S<sub>N</sub>1 (B) S<sub>N</sub>2 (C) E1 (D) **E2**

7. Consider the reaction:



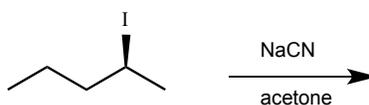
- (A)  $S_N1$       **(B)  $S_N2$**       (C) E1      (D) E2

8. Consider the reaction:



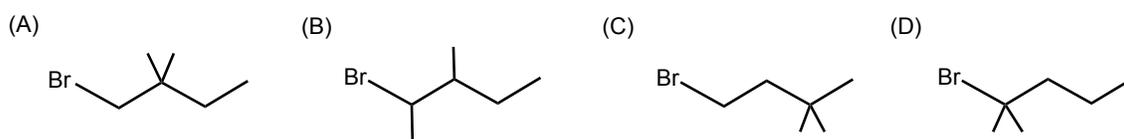
- (A)  $S_N1$**       (B)  $S_N2$       (C) E1      (D) E2

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



- (A) (R)-2-cyanopentane**      (B) (S)-2-cyanopentane  
(C) 1-Pentene      (D) 2-Pentene

10. Which alkyl bromide reacts fastest with NaCN in DMF?



**Correct Answer: C**

11. Which nucleophile reacts fastest with  $\text{CH}_3\text{I}$  in DMF?

- (A)  $\text{F}^-$**       (B)  $\text{Cl}^-$       (C)  $\text{Br}^-$       (D)  $\text{I}^-$

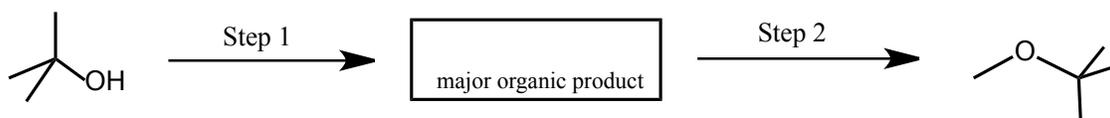
12. Select the best base for quantitative preparation of the ethane thiolate ion,  $\text{C}_2\text{H}_5\text{S}^-$ .

- (A)  $[(\text{CH}_3)_2\text{CH}]_2\text{NLi}$**       (B)  $\text{NH}_3$       (C)  $\text{CH}_3\text{COONa}$       (D)  $\text{H}_2\text{O}$

13. What is the stereochemical relationship between the products when (*E*)-3,4-dimethyl-2-pentene is treated with (1)  $\text{B}_2\text{H}_6$  in THF, and (2)  $\text{H}_2\text{O}_2$  in aqueous NaOH?

- (A) Diastereomers, equal amounts      (B) Diastereomers, unequal amounts  
**(C) Enantiomers, equal amounts**      (D) Enantiomers, unequal amounts

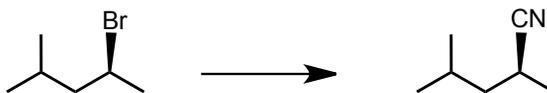
14. What is the stereochemistry of the product or the stereochemical relationship between the products formed when (*E*)-3-hexene reacts with Br<sub>2</sub> in CH<sub>2</sub>Cl<sub>2</sub>?
- (A) Constitutional isomers (B) Diastereomers  
(C) Enantiomers (D) **Meso**
15. Which reaction conditions will convert (*R*)-4-methyl-1-hexene to an optically pure alkyl bromide (not containing any other functional groups)?
- (A) Br<sub>2</sub>/H<sub>2</sub>O (B) Br<sub>2</sub>/CH<sub>3</sub>OH  
(C) HBr (D) **HBr, ROOR**
16. Cyclohexyl bromide is reacted with (1) Mg in ether, and (2) CH<sub>3</sub>OH. What is the final product of this reaction sequence?
- (A) Cyclohexanol (B) **Cyclohexane**  
(C) Cyclohexene (D) Cyclohexyl methyl ether
17. Select all the reactions for which free radical mechanisms are proposed.
- (I) Bromination of propane in the presence of light  
(II) Reaction of propene with Br<sub>2</sub> in CH<sub>2</sub>Cl<sub>2</sub>  
(III) Reaction of propene with HBr in the presence of ROOR
- (A) I and II (B) **I and III** (C) II and III (D) I, II, and III
18. When (*R*)-6-chloro-2,6-dimethyloctane undergoes solvolysis at 60°C in 80% aqueous acetone, the major substitution product contains 60.5% of the (*S*)-alcohol and 39.5% of the (*R*)-alcohol. Select the statement that **best explains** the relative experimental yields of the alcohol.
- (A) The reaction proceeds by an S<sub>N</sub>2 mechanism.  
(B) The first reactive intermediate is a fully solvated, achiral carbocation.  
(C) **The first reactive intermediate is an ion pair; the Cl<sup>-</sup> blocks solvent access to the front side of the carbocation.**  
(D) The first reactive intermediate is an ion pair; the Cl<sup>-</sup> blocks solvent access to the backside of the carbocation.
19. Consider the 2 steps in the transformation of (CH<sub>3</sub>)<sub>3</sub>COH to H<sub>3</sub>C-O-C(CH<sub>3</sub>)<sub>3</sub> shown below.



Which reagent must you use in **Step 1** to obtain the final product in high yield? Note: Each step is a single reaction and not a sequence of reactions.

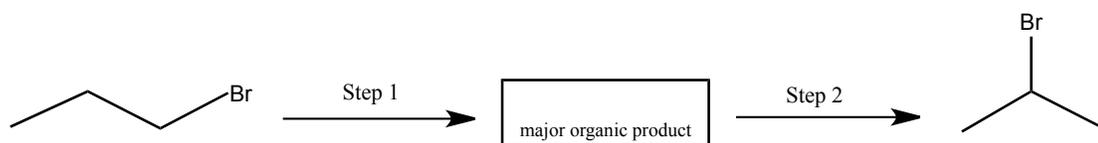
- (A) HI (B) CH<sub>3</sub>I (C) **NaH** (D) CH<sub>3</sub>COONa

20. Which reaction or reaction sequence would accomplish the transformation shown below?



- (A) HCN, acetone  
 (B) NaCN, DMSO  
**(C) (1) NaI, acetone, and (2) NaCN in DMSO**  
 (D) (1) NaOCH<sub>3</sub>, methanol, and (2) NaCN in DMSO

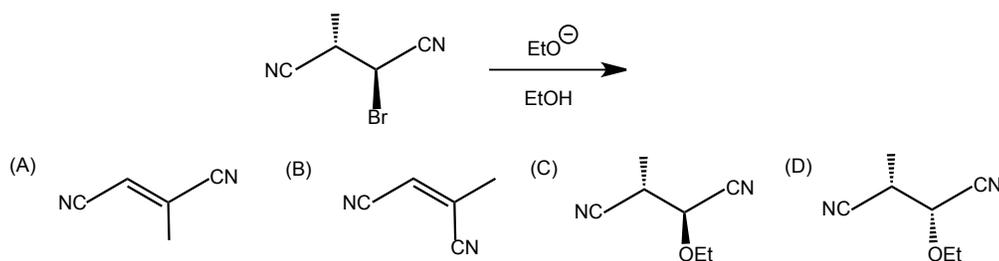
21. Consider the 2 steps in the transformation of 1-bromopropane to 2-bromopropane shown below.



Which reagent (including solvents where necessary) must you use in **Step 2**?

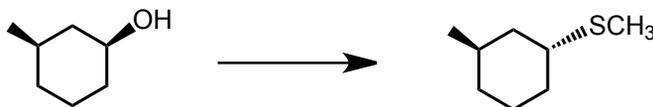
- (A) Br<sub>2</sub> in CH<sub>2</sub>Cl<sub>2</sub>                      (B) Br<sub>2</sub> in H<sub>2</sub>O  
**(C) HBr**                                      (D) HBr, ROOR

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



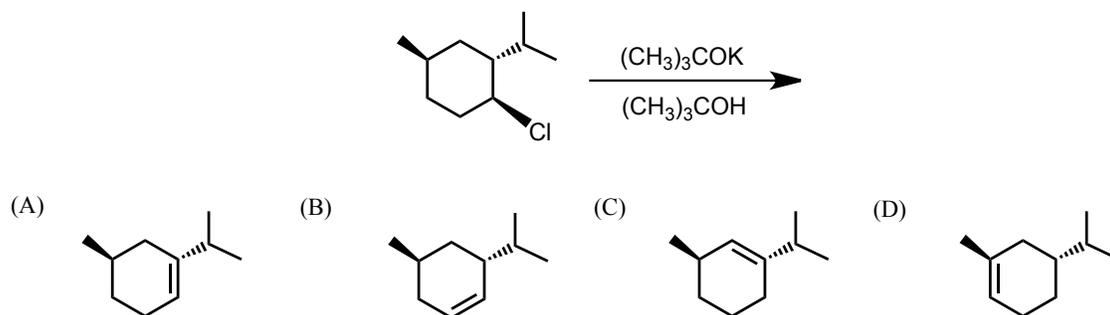
**Correct Answer: B**

23. Identify the reagent or reagents (including solvents where necessary) for accomplishing the following transformation. Your reaction(s) must be efficient (i.e. the target product should be the major product).



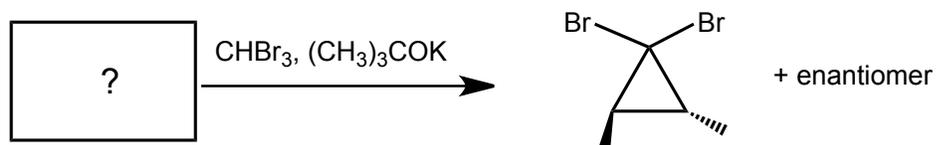
- (A) NaSCH<sub>3</sub>, DMSO  
 (B) (1) HI, and (2) NaSCH<sub>3</sub>, DMSO  
**(C) (1) p-TsCl, pyridine, and (2) NaSCH<sub>3</sub>, DMSO**  
 (D) (1) p-TsCl, pyridine, (2) NaI, acetone, and (3) NaSCH<sub>3</sub>, DMSO

24. Identify the major product of the reaction shown below.



**Correct Answer: B**

25. What is the starting compound in the reaction shown below?



(A) (*E*)-2-Butene

(B) (*Z*)-2-Butene

(C) (*E*)-2-Pentene

(D) (*Z*)-2-Pentene