CHEM 3331 Dr. Minger

## Please read and sign the Honor Code statement below:

I pledge that on my honor, as a University of Colorado at Boulder student, I have neither given nor received unauthorized assistance on this exam.

Signature

**General Instructions:** There are 25 questions. Be sure you have them all. Read each question carefully so that you know exactly what is being asked.

Each multiple choice question (1-25) is worth **4 points and has only one correct answer.** Bubble in your answers to these questions on the Scantron provided. Only the Scantron will be graded.

At the end of the exam, turn in your Scantron and this signed cover sheet. You may keep the rest of the exam to check your answers against the key later.

Good luck!

PERIODIC CHART OF THE ELEMENTS							INERT										
IA	IIA	IIIB	IYB	¥Β	¥ΙΒ	YIIB		YIII		IB	IIB	IIIA	IVA	YA	ΥIA	YIIA	GASES
1 H 1.00797																1 H 1.00797	2 He 4.0026
.3.	4											5	6	7	8	9	10
LI	Be											B	C	N.	0	<b> </b>	Ne
6.939	9.0122											10.811	12.0112	14.0067	15.9994	18.9984	20.183
	12												14	15	16	14	
Na 22.9898	Mg 24.312											AI 26.9815	<b>SI</b> 28.086	<b>۲</b> 30.9738	<b>5</b> 32.064	35.453	39.948
19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
39.102	40.08	44.956	47.90	50.942	51.996	54.9380	55.847	58.9332	58.71	63.54	65.37	69.72	72.59	74.9216	78.96	79.909	83.80
37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54
RÞ	Sr	Y	Zr	IND	Mo	IC	Ru	Rh	Pd	AQ	Cd	l In	Sn.	SD	lle		IXe∣
85.47	87.62	88.905	91.22	92.906	95.94	(99)	101.07	102.905	106.4	107.870	112.40	114.82	118.69	121.75	127.60	126.904	131.30
55	56	<del>*</del> 57	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86
	<b>Ba</b>		Hf	<b>Ta</b>	<b>W</b>	<b>Re</b>		<b>lr</b>	<b>Pt</b>	<b>Au</b>	Hg	204 37	<b>Pb</b>	<b>Bi</b>	Po		<b>Rn</b>
87	88	+ 89	104	105	106	107	108	102.2	110	111	112	201.01	201.10	1200.000	(210)	(210)	(222)
<b>Fr</b>	Ra	Ac	<b>Rf</b>	<b>Db</b>	Sg	<b>Bh</b>	Hs (265)	Mt (266)	<b>?</b>	<b>?</b>	? (277)						

1. Which of the following compounds could be used to make this target in one step (including any necessary workup)?



2. Select the enol from the structures shown.



- 3. Which of these hydride sources is non-nucleophilic?
  - a. NaBH<sub>4</sub>
  - b. LAH
  - c. NaH
  - d. All are nucleophilic
  - e. All are non-nucleophilic



4. Which of these structures is the product of the reaction?

5. You wish to make an epoxide from an alkene, but you have no mCPBA. However, you do have access to all the reagents listed below, plus all the materials necessary for appropriate aqueous workups. Can you make the epoxide?

Reagents available:

LDA	NaH
H <sub>2</sub> O	Hg(OAc) <sub>2</sub>
TBHP	HIO <sub>4</sub>
O <sub>3</sub>	
	LDA $H_2O$ TBHP $O_3$

- a. Yes! I can make the epoxide using some or all of the reagents above.
- b. No! An epoxide cannot be made from an alkene with the reagents shown above.
- 6. What are the best conditions to use to accomplish this transformation?



- a. H<sub>2</sub> and Lindlar's catalyst
- b. Na, NH<sub>3</sub>
- c. H<sub>2</sub> and Pd/C
- d. Either a or b
- e. a, b or c would all work



Select the reagent you would use to accomplish the following 8. transformation.



- LAH, then  $H_3O^+$  workup a.
- NaOH(aq) H<sub>3</sub>O⁺ b.
- C.
- d.
- NaH, then  $H_3O^+$  workup This transformation cannot be accomplished in one step. e.
- 9. Which of these is the *most* acidic hydrocarbon?



7. Which is the correct product of this reaction? 10. Which of the following is a mechanistic step in the dissolving metal reduction of an alkyne with sodium metal in liquid ammonia as the solvent?



11. What conditions could be used to accomplish this transformation?



- a. mCPBA, then  $H_3O^+$
- b. HIO<sub>4</sub> (periodic acid)
- c.  $OsO_4$ , TBHP, and  $H_2O$
- d.  $Hg(OAc)_2$ ,  $H_2O$ ; then NaBH<sub>4</sub>
- e. None of these conditions would work

12. Which of the following synthetic sequences produces the target molecule from the starting material? (Assume appropriate aqueous workups for all steps even if not explicitly written.)



- a. 1. H<sub>2</sub>, Pd 2. mCPBA
  - 3. CH<sub>3</sub>OH, H<sub>2</sub>SO<sub>4</sub>
- b. 1. Na, NH<sub>3</sub>
   2. mCPBA
   3. NaOCH<sub>3</sub>, CH<sub>3</sub>OH, then H<sub>3</sub>O<sup>+</sup>
- c. 1. H₂/Lindlar catalyst
  2. mCPBA
  3. NaOH, H₂O, then H₃O<sup>+</sup>
- d. 1. H<sub>2</sub>/Lindlar catalyst
  2. mCPBA
  3. CH<sub>3</sub>OH, H<sub>2</sub>SO<sub>4</sub>
- e. None of these syntheses will produce the target molecule
- 13. What is the major product of this reaction?



14. When a small amount of HBr is added to diethyl ether, there are various species present in solution. Which of the structures shown would you NOT expect to find in this solution?



15. Which statement about the final product of the sequence of reactions shown is *true*?



- a. The product contains at least one ketone
- b. The product contains at least one OH group
- c. The product contains at least one aldehyde
- d. The product contains an epoxide
- e. The product contains an alkene
- 16. Which of these  $C_5H_8$  dienes is least stable?



17. In aqueous acid, carbonyls are in equilibrium with their enol forms through a process called keto-enol tautomerization. In the example below, a ketone is placed in aqueous acid and allowed to come to equilibrium with its enol form. Which of these intermediates is observed in the tautomerization mechanism shown in class?



18. Which of the following statements is true about this reaction? (Note that if any part of a statement is not true, then you should reject the entire statement.)



- a. Product X is the thermodynamic product and could be formed using short reaction times and low temperatures.
- b. Product X is the thermodynamic product and could be formed using long reaction times and high temperatures.
- c. Product Y is the thermodynamic product and could be formed using short reaction times and low temperatures.
- d. Product Y is the thermodynamic product and could be formed using long reaction times and high temperatures.

19. Which of these mechanisms is the correct depiction of the reaction of a peroxycarboxylic acid (such as mCPBA or peracetic acid) with an alkene?



20. Consider this reaction:



Both kinetic and thermodynamic products can be formed in this reaction, depending on the conditions used. Which of these statements about this reaction is incorrect?

- a. The kinetic product forms fastest because the nucleophile is close to the new carbocation that forms when the diene is protonated.
- b. To form the thermodynamic product, the reaction mixture needs time to equilibrate.
- c. The thermodynamic product is more stable than the kinetic product.
- d. The path leading to the thermodynamic product has a lower activation energy than the path leading to the kinetic product.
- e. Both the kinetic product and the thermodynamic product share a common intermediate, which is a carbocation.

21. Given the following information, what is the resonance energy for 1,3butadiene? (The heats of hydrogenation in this table are experimentally determined.)

Compound	∆H <sub>hydrogenation</sub> ∣ (kcal/mol)				
1-butene	30				
1,3-butadiene	56.6				

- a. 56.6 30
- b. 56.6 + 30
- c. 60 56.6
- d. 60 (30 + 56.6)
- e. 56.6 + 60
- 22. Acetylide ions can be alkylated by treating them with a variety of electrophiles. One of these compounds would not be appropriate for an alkylation reaction with an acetylide ion. Which is it?



- 23. One version of the Lindlar catalyst includes Pd, CaCO<sub>3</sub> or BaSO<sub>4</sub>, a lead(II) (Pb<sup>2+</sup>) salt such as Pb(OAc)<sub>2</sub>, and a compound called quinoline. The Lindlar catalyst is called a "poisoned" catalyst. What is a poisoned catalyst?
  - a. It is a catalyst that has no effect on the reaction it is supposed to catalyze
  - b. It is a catalyst that is less effective than a catalyst that is not poisoned
  - c. It is a catalyst that accelerates the rate of the forward reaction, but slows the rate of the reverse reaction so that you get more product
  - d. It is a deadly, evil catalyst that goes around poisoning people

- 24. Which of the following reagents would you use to make a quantitative yield of an alkoxide ion from an alcohol?
  - a. H<sub>2</sub> (with or without a metal catalyst)
  - b. NaH
  - c. NaOH
  - d. Any alkoxide ion
  - e. None of the above
- 25. It's official -- Kim Kardashian and Kanye West are a couple! Even better, they're going to open a new business called "Kim 'n' Kanye's Ketone Korner". They want to produce ketones using alkynes as the starting material. Which of the following reagents should they order to make their ketones?
  - a. Catechol borane, hydrogen peroxide, and aqueous NaOH
  - b. Disiamylborane, hydrogen peroxide, and aqueous NaOH
  - c. Mercury (II) sulfate, sulfuric acid, water
  - d. Periodic acid, hydrogen peroxide, and water
  - e. The business will fail. Ketones cannot be produced from alkynes.