350 Organic Chemistry I
Exam #4B, December 9, 2013

Winona State University
Professor T. Nalli

Name_____

General Instructions: Write your name in the space provided above and on the provided Scan-tron form. ***Do not put your name anywhere else in this exam book***

Time limit is 2.0 h.

Grading: Grading will be on the basis of a highest possible score of 100 points.

I. Multiple Choice - 2 points each, 30 points total

II. Naming – 1.5 points each, 9 points total

III. Reaction Products - 3 points each, 30 points total

IV. Mechanism - 3 points each, 6 points total

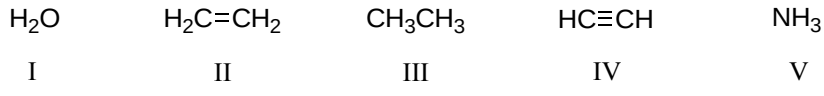
V. Synthesis – 3 points each, 6 points total

VI. Spectroscopy/Isomer Drawing – 19 points

VII. Extra Credit – 5 points

1. Rank the following acids according to *decreasing* acidity (from strongest acid to weakest).

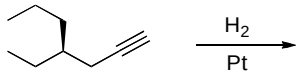
A. V > I > IV > II > III
B. III > IV > II > I > V
C. V > I > III > II > IV
D. I > IV > V > II > III
E. IV > I > V > II > III



2. Which of these bases can be used to deprotonate a terminal alkyne in excellent yield?

A. NH_3 B. BuLi C. NaOH D. $NaOCH_2CH_3$ E. *t*-BuOK

3. For the reaction shown at right, the stereochemistry of the product will be what?

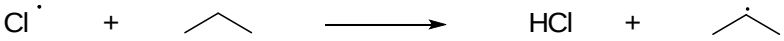


A. pure *S* enantiomer B. pure *R* enantiomer C. racemic D. *meso* E. achiral

4. Complete hydrogenation of a mixture of 1-octyne, 2-octyne, and 3-octyne, in the presence of a palladium catalyst, would produce how many distinct products?

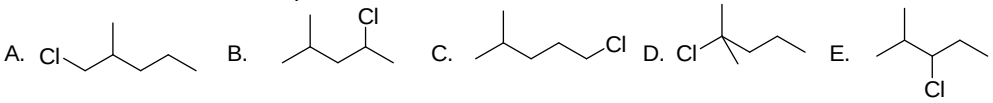
A. 1 B. 2 C. 3 D. 6 E.8

5. What term accurately describes the process shown below?



A. proton transfer B. halogen abstraction C. hydrogen abstraction D. radical coupling

6. Which of these alkyl halides can be expected to give the best yield of internal alkyne (with minimal side reactions) when reacted with an acetylide ion?



7. Why is ethanol never used as a solvent for the deprotonation of a terminal alkyne by $NaNH_2$?

A. Sodium amide in methanol reduces alkynes to alkenes.
B. Ethanol is a poor solvent for dissolving alkynes.
C. Ethanol will undergo an S_N2 reaction with the $NaNH_2$.
D. Ethanol is more acidic than the alkyne, and will be deprotonated instead of it.

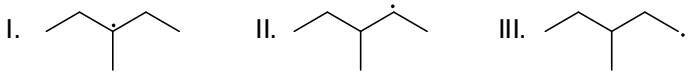
8. Which of the following is a compound often used for the hydration of terminal alkynes?

A. DBN B. 9-BBN C. AIBN D. NBS E. Ni_2B

9. Why is radical bromination selective whereas chlorination is not?

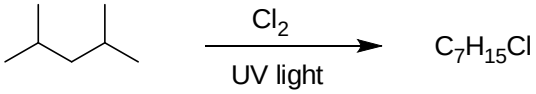
A. The TS for H abstraction by $Br^{\bullet}$ is more product-like than that for H abstraction by $Cl^{\bullet}$
B. The TS for H abstraction by $Br^{\bullet}$ is more reactant-like than that for H abstraction by $Cl^{\bullet}$
C. The Br-Br bond is weaker than the Cl-Cl bond so Br_2 is more reactive and more selective.
D. The Br-Br bond is stronger than the Cl-Cl bond so Br_2 is less reactive and more selective.

10. Rank the following radicals in order of decreasing stability (most stable to least stable).



A. I > II > III B. II > I > III C. III > II > I D. II > III > I E. III > I > II

11. How many total different constitutional isomers are formed as products in the monochlorination of 2,2-dimethylpentane as shown below? (Do not count enantiomers!)



A. 3 B. 5 C. 4 D. 2 E. 6

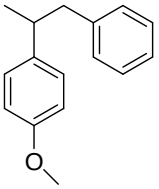
12. At room temperature, the relative reactivity of Cl• toward Hs on an organic molecule is 3° = 5.5, 2° = 3.8 and 1° = 1.0. What percentage of the most abundant product is formed in the room temperature chlorination of 2,2-dimethylpentane? (reaction shown in #11)

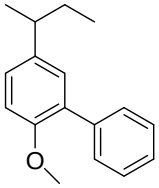
A. 33% B. 39% C. 56% D. 63% E. 92.5%

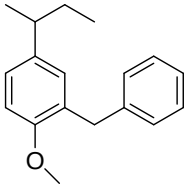
13. If pentane is subjected to radical chlorination and the monochlorinated products isolated and analyzed by ^{13}C NMR, how many total peaks would one expect to see?

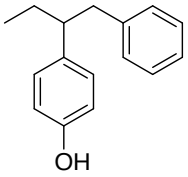
A. 5 B. 3 C. 13 D. 15 E. 11

14. Which of these compounds should be the most effective antioxidant?

A. 

B. 

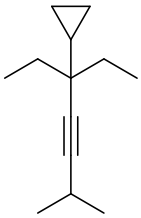
C. 

D. 

15. Which of these chemicals is **least** destructive to stratospheric ozone concentrations?

A. CF_2Cl_2 B. $CFCl_3$ C. CF_3CCl_3 D. Cl_2CHCF3 E. Cl_2CFCF3

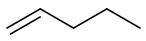
II. (a) Name each of the following.



II. (b) Give the structure of each of the following.

cis-hex-3-en-1,5-diyne NBS 9-BBN

III. Give the structure of the major organic product of each of the following reactions. (If the product can exist as more than one stereoisomer then be sure to show explicitly which stereoisomers are actually formed.)

1.  $\xrightarrow[\text{heat}]{\text{BPO}}$

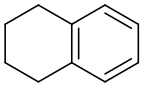
2.  $\xrightarrow[\text{2. } NaNH_2\text{(xs)}]{\text{1. } Br_2}$

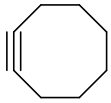
3. Ph—≡ $\xrightarrow{Br_2\text{ (1 equiv)}}$

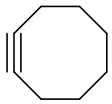
4. Ph—≡ $\xrightarrow[H_2SO_4]{HgSO_4,\ H_2O}$

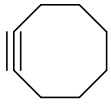
5. Ph—≡ $\xrightarrow{\text{HCl (xs)}}$

6. Ph—≡ $\xrightarrow[\text{2. } H_2O_2,\ OH^-]{\text{1. } Sia_2BH}$

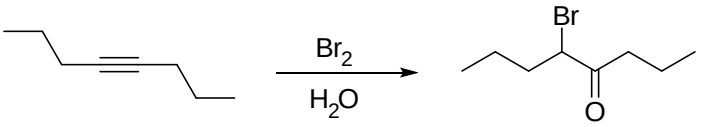
7.  $\xrightarrow[\text{heat}]{\text{NBS, h}\nu}$

8.  $\xrightarrow{Na,\ NH_3(l)}$

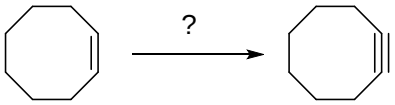
9.  $\xrightarrow[Pd/C]{H_2}$

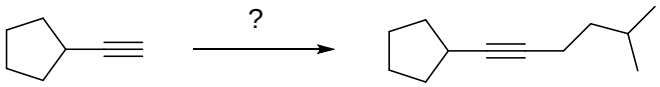
10.  $\xrightarrow[\text{Lindlar}]{H_2}$

IV. Write out the mechanism of each reaction shown. Used curved arrows to show the movement of electrons in each step.



V. Give a sequence of reactions, showing all necessary reagents, by which the following transformations can be accomplished. (In other words, replace the question marks with the reagents needed.) Explain how each part of the synthesis works by showing intermediate products of each synthetic step.





VI. There are 7 isomeric alkynes possible for molecular formula C_6H_{10} (4 terminal alkynes and 3 internal alkynes).
(1) Draw their structures. (5 pts)
(2) Tell how these could be differentiated by ^1H NMR spectroscopy (predict key peaks for each). (10 pts)
(3) Would there be any major differences in the functional group region of the IR spectrum for any of these? (1 pt)
(4) How many peaks does each compound show in its C-13 spectrum? (2 pts)
(5) Which compound most likely shows the strongest M-15 peak in the mass spectrum? (1 pt)