Name ___________________

Department of Chemistry
SUNY/Oneonta

Chem 221 - Organic Chemistry I

Examination #3 - November 9, 1998

INSTRUCTIONS ---

This examination has two parts. The first part is in multiple choice format; the questions are in this Exam Booklet and the answers should be placed on the "Test Scoring Answer Sheet" which must be turned in and will be machine graded.

The second part requires your responding to questions in the Exam Booklet by writing answers into the spaces provided. The Exam Booklet must be handed in and will be returned to you with a grade.

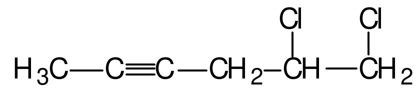
On the Test Scoring Answer Sheet, using a soft pencil, enter the following data (in the appropriate places): your name, instructor's name, your student (Social Security) number, course number (30022101) and the test number (03); darken the appropriate bubbles under the entries, making dark black marks which fill the bubbles.

You may use a set of molecular models, but no other aids, during the exam.

Answer all questions. The questions on Part I are worth 2.5 points each.

You have 90 minutes. Good luck!

1. Select the correct IUPAC name for the compound shown to the right.



(a) 1,2-dichloro-2-hexyne, (b) 1,2-dichloro-4-hexyne,
(c) 5,6-dichloro-2-hexyne, (d) 1,2-dichloro-2-acetylene,
(e) 1,2-dichloro-4-acetylene, (f) 5,6-dichloro-2-acetylene

2. Rank the following bonds in order of decreasing length (longest first).

I: carbon-carbon bond in ethane, II: carbon-carbon bond in ethene, III: carbon-carbon bond in ethyne, IV: carbon-hydrogen bond in methane.

(a) I>II>III>IV, (b) IV>III>II>I, (c) II>III>IV>I, (d) I>IV>III>II,
(e) None of the above answers is correct.

3. Select the answer which best describes the product(s) of the following reaction.

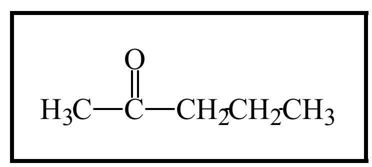
$H_3C{-}C{\equiv}C{-}CH_2CH_3 \quad + \quad HCl \longrightarrow$

(I) $H_3C{-}CH{=}CCl{-}CH_2CH_3$ (II) $H_3C{-}CCl{=}CH{-}CH_2CH_3$

(III) $H_3C{-}CCl{=}CCl{-}CH_2CH_3$

(a) I, (b) II, (c) III, (d) I & II, in approximately equal quantity,
(e) I & II, but considerably more I than II,
(f) I & II, but considerably more II than I,
(g) I, II, & III, but mostly III.

4. Which compound would you start with to prepare 2-pentanone?

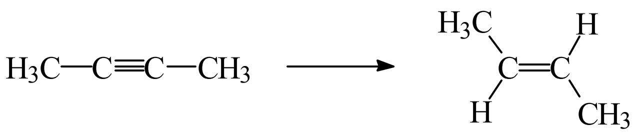


2-pentanone

(a) $HC{\equiv}C{-}CH_2CH_2CH_3$ (b) $H_3C{-}C{\equiv}C{-}CH_2CH_3$

(c) $H_2C{=}CH{-}CH_2CH_2CH_3$ (d) $H_3C{-}CH{=}CH{-}CH_2CH_3$

5. Select the appropriate reagents to carry out the following reaction.



(a) H_2, Lindlar catalyst, (b) H_2, Pt, (c) H_2O, H_2SO_4, $HgSO_4$, (d) Li, NH_3,
(e) $NaNH_2$ in NH_3

6. How would you prepare 2-butyne from 2-butene?

$$H_3C{-}CH{=}CH{-}CH_3 \xrightarrow{?} H_3C{-}C{\equiv}C{-}CH_3$$

(a) 1. HBr, 2. $NaNH_2$ (b) H_2, Pt, (c) 1. Br_2, 2. $NaNH_2$, (d) 1. $NaNH_2$, 2. HBr,
(e) H_2SO_4

7. In the following reaction, where R is an alkyl group,

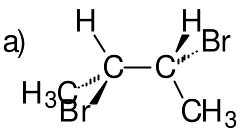
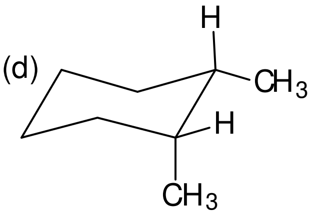
$CH_3C{\equiv}C{:}^- \, Na^+ \;+\; R\text{-}Cl \;\rightarrow\; CH_3C{\equiv}C\text{-}R \;+\; Na^+Cl^-$,

(a) tertiary chlorides may be used and give good yields of the alkyne product.
(b) tertiary chlorides may not be used because they are too reactive.
(c) tertiary chlorides may not be used because they are not reactive enough.
(d) tertiary chlorides may not be used because they largely undergo elimination under the reaction conditions.
(e) Bogus question! The reaction does not proceed with any alkyl chloride.

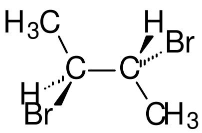
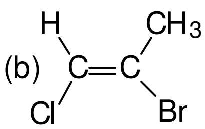
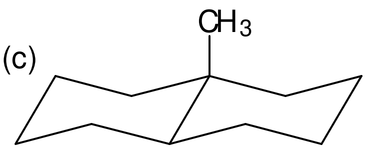
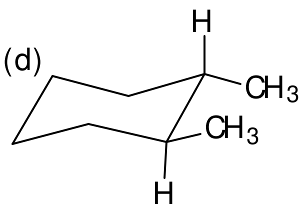
8. Your first assignment as junior chemist at the Carbonaceous Chemical Corporation is to make *meso*-3,4-dibromohexane from 3-hexyne. Which of the following routes would be most successful?

(a) 1. H_2, Lindlar catalyst, 2. Br_2 in CCl_4, (b) 1. 1 equivalent Br_2 in CCl_4,
2. BH_3, 3. H_2O_2, KOH, (c) 1. Li, NH_3, 2. Br_2 in CCl_4, (d) 2 equivalents HBr.

9. Which of the following molecules is **achiral** ?

(a)  (b) $CH_3CHBrCl$ (c) $CH_3CHBrCH_2Br$ (d) 

10. Which of the following molecules is **chiral** ?

(a)  (b)  (c)  (d) 

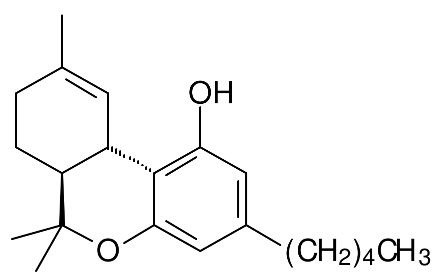
11. A meso structure is one which

(a) has stereogenic (chiral) centers and is chiral.
(b) has stereogenic centers and is achiral.
(c) has no stereogenic centers and is chiral.
(d) has no stereogenic centers and is achiral.

12. If a molecule has a plane of symmetry

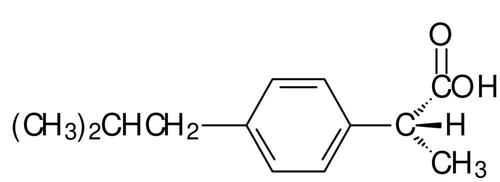
(a) it is chiral. (b) it is achiral.
(c) it has stereogenic centers. (d) it has no stereogenic centers.

13. The structure of Δ^1-3,4-trans-tetrahydrocannabinol, a psychoactive constituent of marijuana, is shown to the right. How many stereogenic centers does it have?



(a) 0, (b) 1, (c) 2, (d) 3, (e) 4
(f) Like wow! THC! It must have billions of stereogenic centers. There goes one now.

14. Indicate the absolute configuration of the stereogenic center in the ibuprofen, shown to the right.



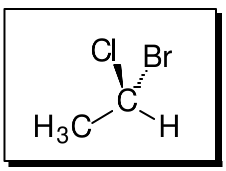
(a) R, (b) S, (c) E, (d) Z.

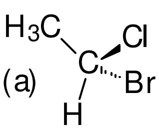
15. Which of the following is (are) always true about a compound which has two stereogenic centers, one R, the other S.

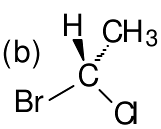
I: It is dextrorotatory (+ rotation of light). II: It is levorotatory (- rotation of light).
III: It is optically inactive. IV: It must have an enantiomer in which the configurations of the stereogenic centers are reversed from the original.

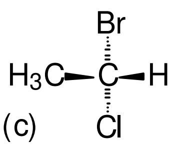
(a) I, (b) II, (c) III, (d) IV, (e) III&IV, (f) None of the previous answers is correct.

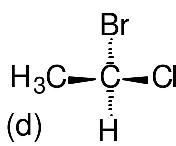
16. Which of the molecules shown below is the enantiomer of the boxed structure?

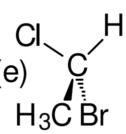


(a)


(b)


(c)


(d)


(e)


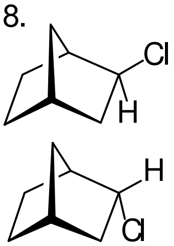
17. Which of the following is **not** true of enantiomers?

(a) They have the same boiling point. (b) They have the same melting point.
(c) They have the same specific rotation. (d) They have the same density.
(e) They have the same chemical reactivity toward achiral reagents.

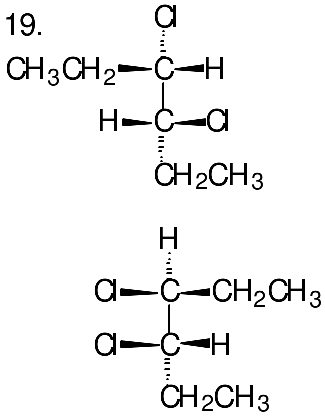
In each of questions 18-20 classify the pair of compounds shown as:

(a) constitutional isomers
(b) superimposable without rotation around single bonds.
(c) conformational isomers.
(d) enantiomers.
(e) diastereomers

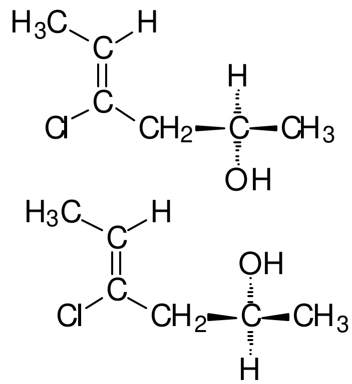
18.



19.



20.



21. What is (are) the principal product(s) of the following reaction?

$$CH_3CH_2CH{=}CH_2 \xrightarrow[H_2O]{H_3O^+}$$

(a) $CH_3CH_2CH_2CH_2OH$

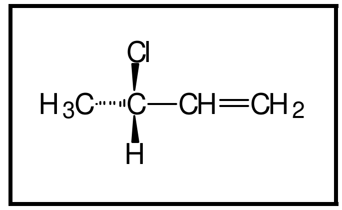
(b) (R-isomer only)
$CH_3CH_2CHCH_3$
OH

(c) (S-isomer only)
$CH_3CH_2CHCH_3$
OH

(d) (unequal amounts of R&S isomers)
$CH_3CH_2CHCH_3$
OH

(e) (equal amounts of R&S isomers)
$CH_3CH_2CHCH_3$
OH

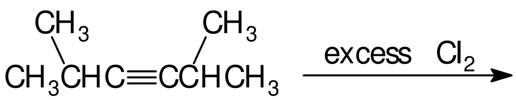
22. (S)-3-chloro-1-butene reacts with HCl by Markovnikov addition. Two stereoisomers are produced. Which of the following statements about these stereoisomers is true?

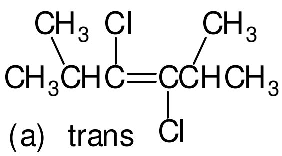


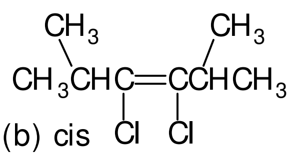
(S)-3-chloro-1-butene

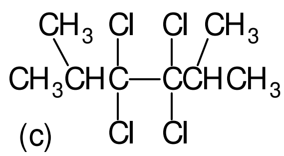
(a) Both stereoisomers are chiral and they are produced in equal amounts.
(b) One of the stereoisomers is chiral and the two stereoisomers are produced in equal amounts.
(c) Neither of the stereoisomers is chiral and they are produced in equal amounts.
(d) Both of the stereoisomers are chiral and they are produced in unequal amounts.
(e) One of the stereoisomers is chiral and the two stereoisomers are produced in unequal amounts.
(f) Neither of the stereoisomers is chiral and they are produced in unequal amounts.

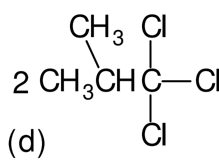
23. Select the principal product of the following reaction.




(a) trans


(b) cis


(c)


(d)

24. Tautomers are

(a) constitutional isomers that are in equilibrium with each other.
(b) stereoisomers that are in equilibrium with each other.
(c) conformational isomers that are in equilibrium with each other.
(d) the individual structures we draw when indicating resonance.

25. In keto-enol tautomerism,

(a) the keto form is usually favored. (b) the enol form is usually favored.
(c) the equilibrium constant is usually about 1.
(d) Bogus question! There is no such thing as keto-enol tautomerism.

26. Which of the following best represents the polarity of methyl magnesium bromide?

(a) $\overset{\delta+}{H_3C}-\overset{\delta-}{Mg}-\overset{\delta+}{Br}$ (b) $\overset{\delta-}{H_3C}-\overset{\delta+}{Mg}-\overset{\delta-}{Br}$ (c) $\overset{\delta+}{H_3C}-\overset{\delta+}{Mg}-\overset{\delta-}{Br}$ (d) $\overset{\delta-}{H_3C}-\overset{\delta+}{Mg}-\overset{\delta+}{Br}$

27. At room temperature the reactivity per hydrogen in free radical chlorination of alkanes is tertiary : secondary : primary = 5.0 : 3.5 : 1.0. If one chlorinates propane under these conditions, the product mixture will contain approximately ______% 1-chloropropane and ______% 2-chloropropane.

(a) 75, 25, (b) 60, 40, (c) 22, 78, (d) 46, 54, (e) None of the preceding answers is correct.

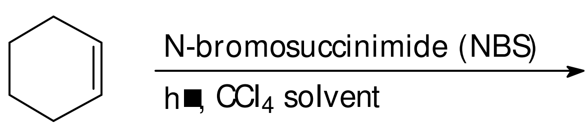
28. Which of the following compounds will **not** react with a Grignard reagent?

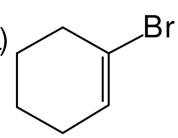
(I) CH_3CH_2OH (II) $CH_3(CH_2)_4CH_3$ (III) $CH_3CH_2OCH_2CH_3$

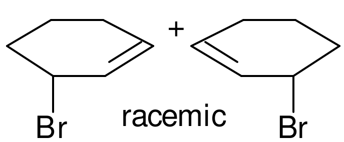
(IV) $CH_3C{\equiv}CH$ (V) $CH_3CH_2CH_2NH_2$

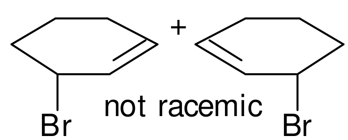
(a) I&II, (b) II&III, (c) III&IV, (d) IV&V, (e) I&IV

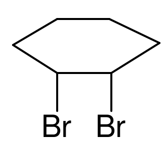
29. Select the principal product of the following reaction.

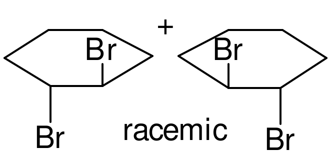


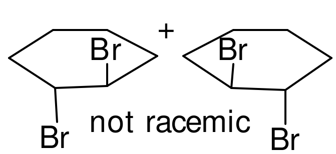
(a) 

(b) 

(c) 

(d) 

(e) 

(f) 

30. The two reactions shown to the right are the first and second propagation steps, respectively, in the free radical halogenation of an alkane. Which step is rate limiting?

$$X\cdot + RH \longrightarrow R\cdot + HX \quad \text{step 1}$$

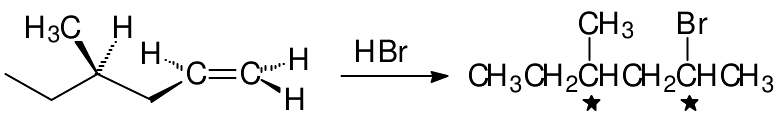
$$R\cdot + X_2 \longrightarrow RX + X\cdot \quad \text{step 2}$$

(a) Step 1 is rate limiting for chlorination and bromination.
(b) Step 1 is rate limiting for chlorination and step 2 is rate limiting for bromination.
(c) Step 1 is rate limiting for bromination and step 2 is rate limiting for chlorination.
(d) Step 2 is rate limiting for chlorination and bromination.

Directions for Part II --- Answer the questions in the space provided. If there is insufficient space continue your answer on the back of the sheet but clearly indicate on the front of the sheet that you have done this.

1. Mechanism. (a) (i) Show all steps in the mechanism for the following reaction (as discussed in McMurry, Sect. 9.17). Be certain to –

- ☞ show all intermediates and their stereo (3-dimensional) structure(s),
- ☞ show direction(s) of approach of reacting species if it has stereochemical consequences for the product(s), and
- ☞ show the configurations around the stereogenic (★) carbons in the product(s).



Clearly show all stereoisomers formed and mechanistic paths leading to them.

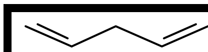
(ii) Is the product (or product mixture) of this reaction optically active?

(iii) Is the product (or products) of this reaction a meso structure, a racemate, or neither?

2. Synthesis. Outline syntheses which would produce each of the following compounds in good yield. You must start your synthesis with the indicated starting material, and may use any other materials you need to carry it out. More than one step may be required. [Note: In outlining a synthesis you should show explicitly what compounds you are using and any special conditions. You need not balance equations or show mechanisms; doing so correctly will gain you no additional credit, doing so incorrectly will cost you.]

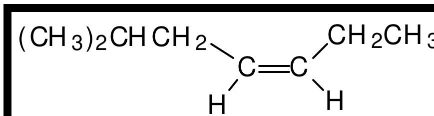
(a) Make 1,1,1,2,2,2-hexachloroethane, $Cl_3C\text{-}CCl_3$, from acetylene (ethyne).

(b) Make 1,4-pentadiene from acetylene (ethyne).



1,4-pentadiene

(c) Make (Z)-6-methyl-3-heptene from 4-methyl-1-pentyne.



(Z)-6-methyl-3-heptene

Part I (75)	________
Part II	
1. (10)	________
2. (15)	________
Total(100)	________