**Potentially useful data**

Electronegativity: H 2.1, C 2.5, N 3.0, O 3.5, F 4.0, Cl 3.0

Strain energy for a 1,3-diaxial interaction in cyclohexanes:

$CN < F < Cl < OH < CH_3 < CH_2CH_3 < C(CH_3)_3$

$pK_a$ trends: $CH_3CO_2H$, $H_2O$, $CH_3CH_2OH$, alkyne, $NH_3$, alkene, alkane

Nucleophilicity trends: $H_2O$, $CH_3CO_2^-$,$Cl^-$,$OH^-$, $OCH_3^-$, $I^-$, $CN^-$, $SH^-$

Leaving group trends: ( $OH^-$, $NH_2^-$, $OR^-$), $F^-$, $Cl^-$, $Br^-$, $I^-$, $OTs^-$

1. i. Show the general structure of an unsaturated fat.

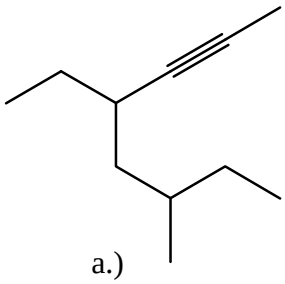
   ii. Explain the terms: a. hyperconjugation, b. tautomerizaton.

   iii. Sketch the shapes of σ, π and π* orbitals, incl. phase designation.

2. Give the name ( acronym is OK) of 2 polar aprotic solvents. For one of them give the structural and molecular formula.

3. Write a structure containing an alkyne, alkene, ether **and** amide functional group. Indicate the hybridization of all atoms that are part of the functional groups. Using a cyclic structure for a backbone is probably a good idea.

4. Provide names for the following, incl. E, Z, R, S as required.



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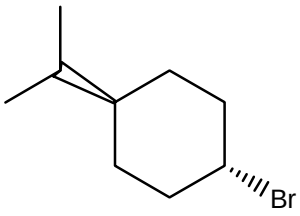


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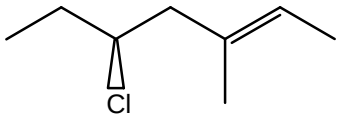


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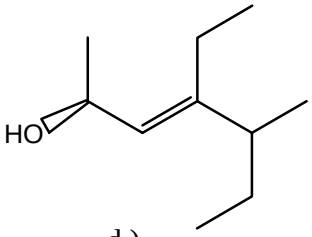



d.)

5. Give the bond-line structure for (2Z,5Z)-5-chloro-2,5-octadiene.

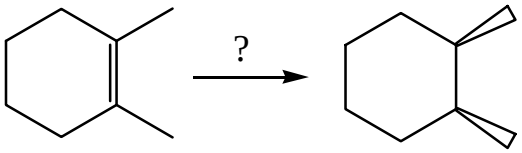
6. Provide structures for the substances with the following common names:
   methyl hydrate, " alcohol", formaldehyde, glycerol, acetylene, D-glucose (approx.)

7. For (2R,3R)–1,2,3–trichlorobutane provide
   a. molecular formula, b. "wedge & dash" structure,
   c. Newman projection, viewing from C2 to C3 with H on C2 and Cl on C3 antiperiplanar,
   d. Fischer projection with C1 high on the paper.

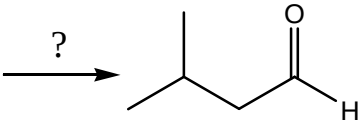
8. What are the products if a) 1-butyne and b) 2-butyne are subjected to
   i.) the oxymercuration, ii.) the hydroboration procedure . (Four (4) reactions).

9. Give the detailed reaction mechanism for the chlorohydrin formation of 1-methylcyclohexene, incl. $e^-$ mvmt and stereospecific details.

10. Complete the following reaction schemes:




a.)

(alkyne?) 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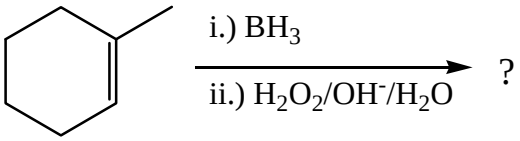


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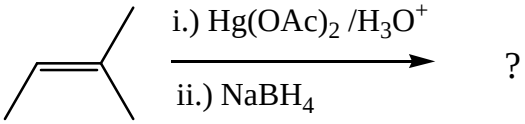


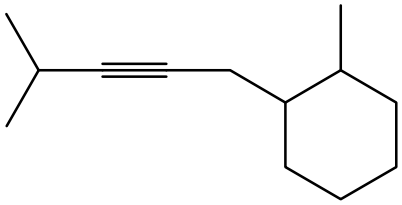

d.)

11. An optically active compound A produces only B when subjected to "ozonolysis". Formula of B = $C_{10}H_{16}O_2$. Other evidence indicates that B has a 6-membered ring with cis oriented substituents. What are the structures of A and B , incl. stereochemistry?

12. An unsaturated compound, $C_9H_{10}$, picks up 2 moles of $H_2$ when hydrogenated in the presence of Lindlar catalyst and 4 moles of $H_2$ in the presence of a Pd/C catalyst. What is the structure of the unknown?

13. For the following $H_2$ addn reaction, what reagent would you use?
    a. alkyne $\rightarrow$ cis alkene
    b. alkyne $\rightarrow$ trans alkene

14. You want to produce the following by "alkynide rxn". Show the required steps . Indicate $e^-$ flow by curved arrows.



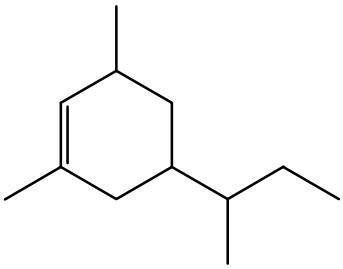
15. Indicate two bases that will form alkynide ions from alkynes ( hint: use the data table)

16. Describe the term specific rotation,$[\alpha]_D$, i.e. what do $\alpha$, $[\alpha]$, and D mean.

17. Provide a functional block diagram of a polarimeter. Describe the purpose and function of each component.

18. When can $\alpha_D$ of a substance be 0 (zero)? Describe 2 possibilities.

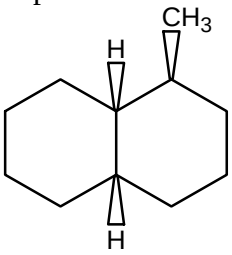
19. Briefly describe the general process of racemate resolution.

20. Consider 

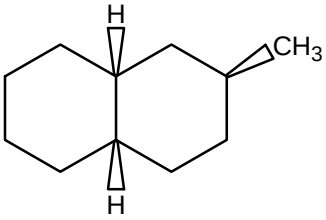
Indicate stereogenic centers by x , allylic carbons by y , and secondary carbons by z .

21. What product forms if 1-methylcyclohexene is reacted with $Br_2/CCl_4$? Also address chirality issues.

22. Show the preferred conformation for




and




23. How does nucleophilicity of a reactant influence a. $S_N2$ reactions ? b. $S_N1$ reactions ?

24. How can solvent choice be used to favor $S_N2$ reactions over $S_N1$ reactions.

25. What factors have an influence on whether a reaction will go E2 or E1 ?

26. Assume you can control reaction conditions to force clean substitution or elimination reactions.
What product is formed if cis –1 –chloro-2-methylcyclohexane is reacted $OH^-$ acc. to the:
a.) $S_N2$ b.) $S_N1$ c.) E1 d.) E2 mechanism?
Include stereochemical configurations/descriptions.

27. Sketch the transition state of the rate limiting step of the general E2 reaction. Include curved arrows for electron flow that show formation of the product from the transition state.

28. Explain why racemization of optically active substances can occur during $S_N1$ reactions.

29. Radical halogenation of pentane can give a wide variety of products, including several dichloropentanes. Indicate a dichloropentane that is

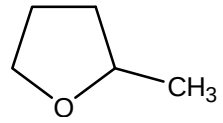
a.) a meso compound b.) a chiral diastereomer of a.)

c.) achiral, but not meso d.) chiral other than (but not enantiomeric to) b.)

**Notes:** *Be sure to show clear stereochemistry. It is possible that several answers exist.*
***Use Fischer projections**., i. e., all carbon atoms in a vertical line.*

30. Show the mechanism for reactions of tertiary alcohols under acidic conditions.
a. elimination, b. substitution.

31. Show the optimal method for the synthesis of the following compound by the Williamson reaction.




32. For the following reactions,
show the most likely product **and** the most likely mechanism ($S_N2$, $S_N1$, E2 or E1)

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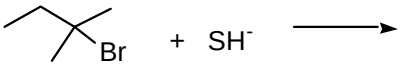
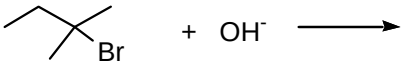
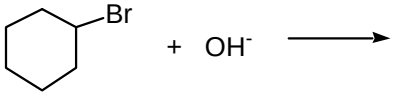
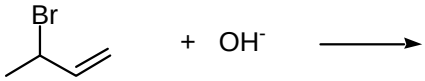
|---|---|---|
|   | | |
|   | | |
|   | | |
| $CH_3CH_2Br$ + $OH^-$ → | | |
| $CH_3CH_2Br$ + $SH^-$ → | | |
|   | | |