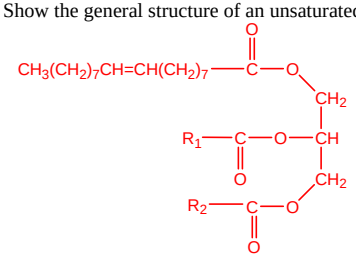
CHEM164/261, A2 **Final Practice Questions, Answers** 2010 11 27
HT

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^-

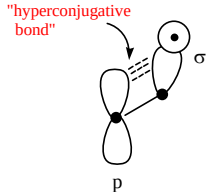
1. i. Show the general structure of an unsaturated fat.



has long side chain (16 - 18 C's normal); alkene function; triester of glycerol

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

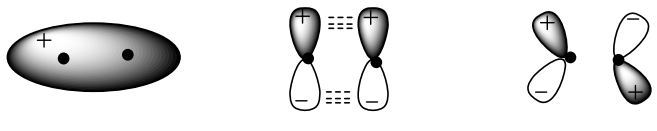
a.



sideways overlap between an empty p orbital and a σ MO between an adjacent C atom and another atom one more position removed

b. *rapid movement of an H atom from one of a molecule to another; esp., "enol → keto" conversion*

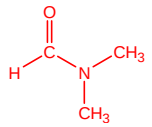
iii. Sketch the shapes of σ, π and π* orbitals, incl. phase designation.

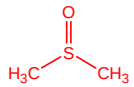


σ π π*

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

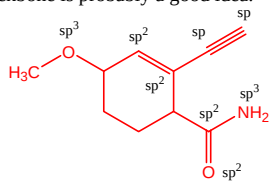
dimethylformamide, DMF dimethylsulfoxide, DMSO



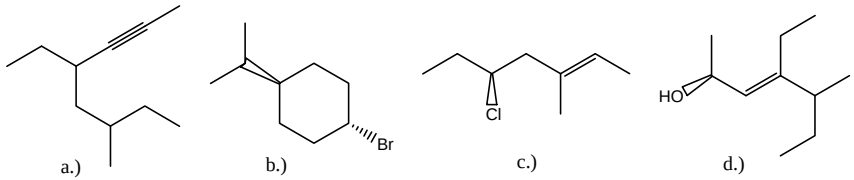


of course, there are many others

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.



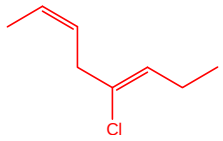
a.) 4-ethyl-6-methyl-2-octyne (unspecified stereochem. at C4 andC6)

b.) trans-1-bromo-4-isopropylcyclohexane (note: it is achiral)

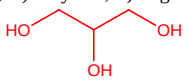
c.) (2E, 5S)-5-chloro-3-methyl-2-heptene

d.) (2S,3E)-4-ethyl-5-methyl-3-hepten-2-ol , (unspecified stereochem. at C7)

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



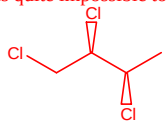
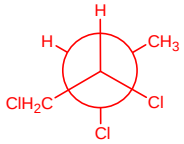
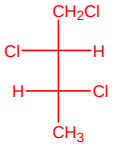
6. Provide structures for the substances with the following common names:
a.) methyl hydrate, b.)“ alcohol”, c.) formaldehyde, d.)glycerol, e.)acetylene, f.) D-glucose (approx.)

a.) CH_3OH b.) CH_3CH_2OH c.)  d.) 

e.) $HC{\equiv}CH$ f.) $C_6H_{12}O_6$, has linear chain of 6 C's, 1 aldehyde function & 5 OH functions

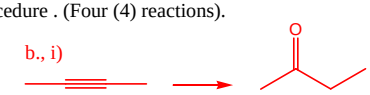
7. For (2R,3R)–1,2,3–trichlorobutane provide
a. molecular formula, b. “wedge & dash” structure,
c. Newman projection, viewing from C2 to C3 with H on C2 and Cl on C3 antiperiplanar,
d. Fischer projection with C1 high on the paper.

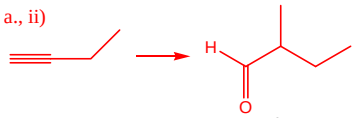
This problem is quite impossible to do without models!

$C_4H_7Cl_3$   

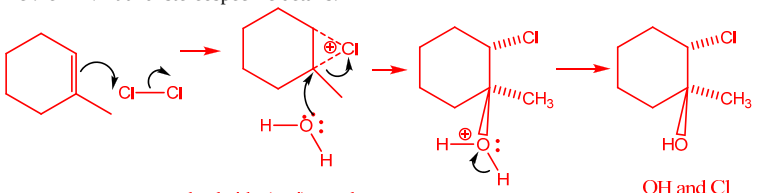
a.) b.) c.) d.)

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).

a., i)  b., i) 

a., ii)  b., ii) 

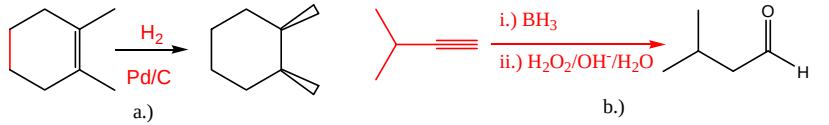
9. Give the detailed reaction mechanism for the chlorohydrin formation of 1-methylcyclohexene, incl. e^- mvmt and stereospecific details.



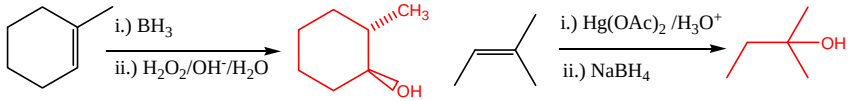
backside (anti) attack
at the more substituted C atom

OH and Cl
added *trans;*
racemic!

10. Complete the following reaction schemes:



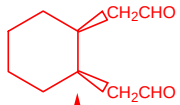
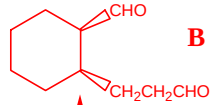
a.) b.)

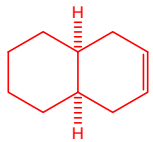
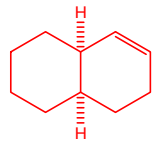


racemic

c.) 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?

B could be  or  **B**

derived from  

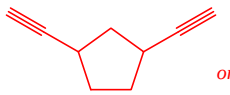
achiral = optically inactive chiral = optically active

This must be A

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?
2 moles H_2 over Lindlar → 2 triple bonds

4 moles of H_2 over active cat. → 2 triple bonds; no double bonds

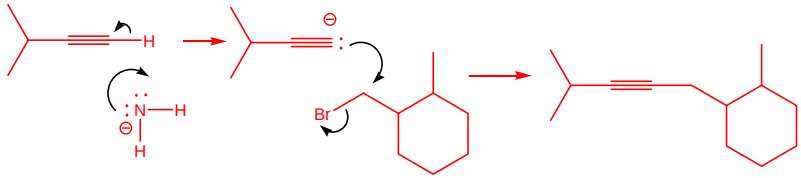
D of U = 5 → must have 1 ring; therefore the unknown is:



or similar; no triple bond in ring, though!

13. For the following H_2 addn reaction, what reagent would you use?
    a. alkyne → cis alkene *Lindlar catalyst/ H_2*
    b. alkyne → trans alkene *Na/ NH_3*

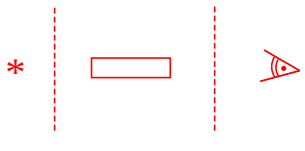
14. You want to produce the following by "alkynide rxn". Show the required steps . Indicate e^- flow by curved arrows.



15. Indicate two bases that will form alkynide ions from alkynes (hint: use the data table).
    In general, conjugate bases of acids with $pK_a > 25$;
    therefore: NH_2- ,derived from NH_3, or
    conjugate bases derived from hydrocarbons; R^- from RH; in practice this would be organometallics such as Grignard reagents

16. Describe the term specific rotation,$[\alpha]_D$, i.e. what do α, [α], and D mean.
    α, angle of rotation as observed in a polarimeter;
    [α] a divided by concentration & tube length to cancel the influence of these two factors;
    D, the sodium-D line (689 nm) was used as light source.

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



a. light source; normally "random" light

b. polarizing filter; produces plane-polarized light

c. tube containing (presumably) optically active substance

d. analyzing filter; must be turned to allow max. passsage of light; α can be read here

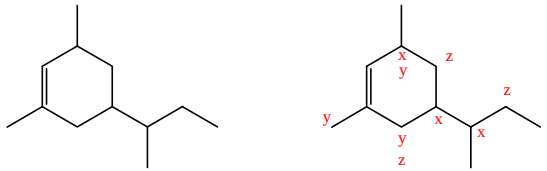
e. detection system; measures intensity of transmitted radiation; provides feedback for function d.

18. When can α_D of a substance be 0 (zero)? Describe 2 possibilities.
    i. achiral substance
    ii. racemic mixture of chiral substance
    (iii. also, in practice, α_D might be very low as to be below detection limit , i.e. unobservable)

19. Briefly describe the general process of racemate resolution.

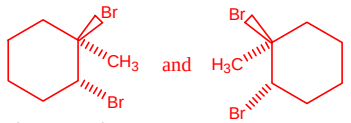
- *react the racemate w/ a chiral reagent in order to get a diastereomeric mixture*
- *separate the 2 diastereomers, e.g., by a chromatographic technique*
- *reverse the initial reaction for each diastereomer*
- *in each case, separate the substrate and reagent and obtain enantiomerically pure substances*

20. Consider

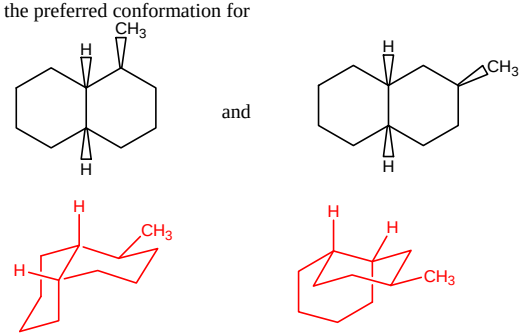


Indicate stereogenic centers by x , allylic carbons by y , and secondary carbons by z .

21. What product forms if 1-methylcyclohexene is reacted with Br_2/CCl_4? Also address chirality issues.
    The trans product will be formed. It will be chiral, but, of course a racemic mixture since the starting material is achiral.



22. Show the preferred conformation for



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

A good nucleophile speeds up an S_N2 reaction; but has no influence on the speed of an S_N1 reaction

Note, however, that if there is a choice between S_N1 and S_N2 a good nucleophile will favor S_N2.

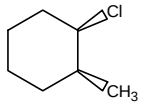
24. How can solvent choice be used to favor S_N2 reactions over S_N1 reactions.

*A polar **aprotic** solvent (such as DMSO) favors S_N2 since the nucleophile is not "solvated", therefore not deactivated and made more aggressive. Formation of the carbocation intermediate necessary for the S_N1 reaction becomes more unlikely.*

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

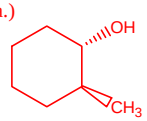
If the base involved is rather weak (such as H_2O) then the carbocation (required for E1) has a better chance to form.. If the base is strong(such as OH^- or OR^-) then the removal of the β hydrogen is faster and the concerted mechanism for E2 is more feasible.

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.



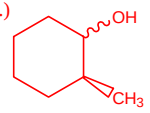
starting material

a.)



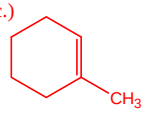
inversion of config.!

b.)



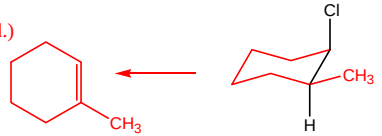
mixture of enantiomers , not necessarily 50:50

c.)



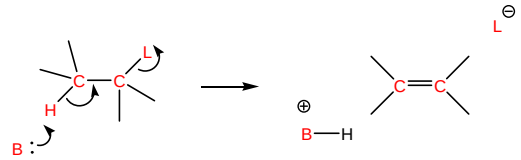
Zaitsev product tends to be favored in E1

d.)



Zaitsev is also formed in E2 if the required antiperiplanar conformation can be attained; which is possible in this case.

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.



all red atoms in same plane

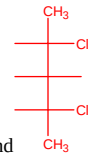
formed in a "concerted" mechanism

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

A carbocation is formed as an intermediate which is sp^2, planar , achiral at the reacting center. The nucleophile can attack from either side of the plane giving products w/ opposite configuration at the reacting center (= racemate).

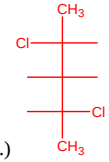
Note, however, this is absolutely true only if there is no other stereogenic center in the molecule.

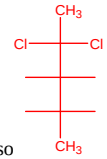
29. Radical halogenation of pentane can give a wide variety of products, including several dichloropentanes. Indicate a dichloropentane that is



a.) a meso compound

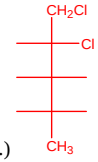
b.) a chiral diastereomer of a.)





c.) achiral, but not meso

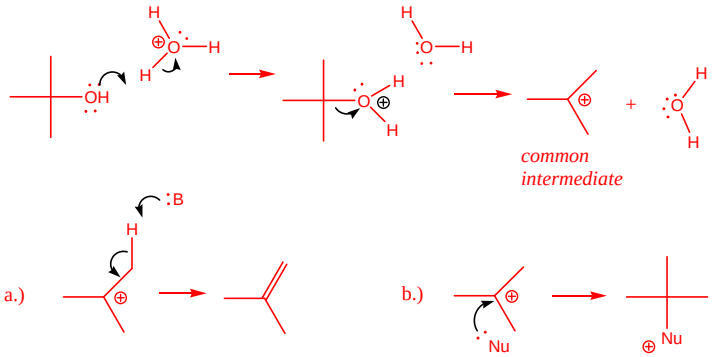
d.) chiral other than (but not enantiomeric to) b.)



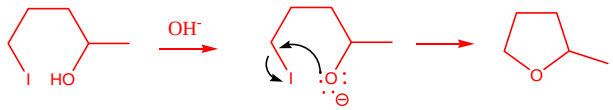
Note: H atoms have been omitted for clarity

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.*

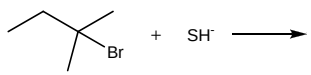
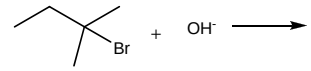
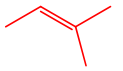
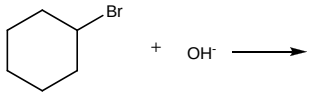
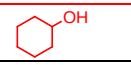
30. Show the mechanism for reactions of tertiary alcohols under acidic conditions.
a. elimination, b. substitution.



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)

		S_N1
		E2 a.)
		E2
		S_N2 b.)
CH_3CH_2Br + OH^- →	$H_2C{=}CH_2$	E2
CH_3CH_2Br + SH^- →	CH_3CH_2SH	S_N2
		S_N1 c.)
		E2

a.) probably some S_N1 product also: 

b.) E1 and S_N1 cannot be totally excluded either

c.) two S_N1 products can form due to the resonance stabilized carbocation