Practice Tests Answer Keys, Organic Chemistry I

Online Organic Chemistry I, Chem 350, Dr. Craig P. Jasperse, Minnesota State University Moorhead For full class website, see

https://collaborate.mnstate.edu/public/blogs/jasperse/online-organic-chemistry-courses/online-organic-chemistry-i-350-fall-spring/

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JASPERSE CHEM 350 TEST 1

VERSION 1 Organic Chemistry I - Jasperse

Intro and Review

Structure and Properties of Organic Molecules

Structure, Nomenclature, and Conformation/Stereochemistry of Alkanes

1. Draw the correct <u>Lewis structure</u> of <u>CH₃CN</u>. (Needn't show 3-D geometry) (3pt)

1. Want normal bonding for all

. C=O (or C=C in other cases) may help

3. If you have any formal charges (not here), they must sum

to net charge of molecule (zero, in this case)

4. Organization must match condensed formula sequence

Metal >> formal chape

2. Draw the correct <u>Lewis structure</u> for HOClf₂CHO. (Needn't show 3-D geometry). (3pt)

3. Draw a 3-dimensional picture for the atoms in CH₃CO₂CH₂NHCH₃, using the hash-wedge convention. (You needn't specify lone pairs, and orbitals need not be shown). (5pt)

1. The Nitrogen is tetrahedral, so the N-H hydrogen must

convention. (You needn't specify lone pairs, and or

1. The Nitrogen is tetrahedral, so the N-H hydrogen must either be wedged or hashed. (The lone pair doesn't need to be drawn in, but it impacts the shape of the nitrogen)

2. Drawing the correct Lewis structure is essential! Do first!

Fine if N-H is hashed instead of wedged

4. For the structure shown, what is the <u>hybridization</u>, electron-pair geometry, and approximate <u>bond angle</u> (90, 109, 120, or 180) relative to: (6pt)

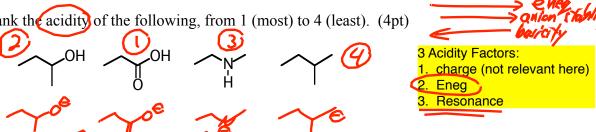
sp ²		electron-pa		H H		electron-pair	bond
<u> </u>	hybridizati	on geometry	angle		hybridizatio	n geometry	angle
O-1	sp3	tetvahedwl	~1090	C-5	5/2	trig planar	120
C-2	243	tet	109	N-7	s/3	tet	109
C-3	sp2	trigonal planor	120	O-9	592	trig planar	120

5. Assign any <u>formal charges</u> to any apropriate atoms for proline, given the structure shown (one of the body's 20 monomers from which protein and enzyme biopolymers are constructed). (3pt)

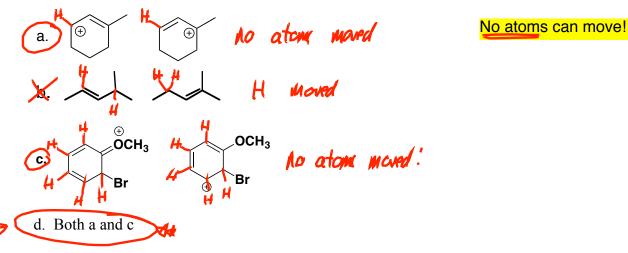


Ox 3 bands
$$\Rightarrow +$$
 V 4

6. Rank the acidity of the following, from 1 (most) to 4 (least). (4pt)



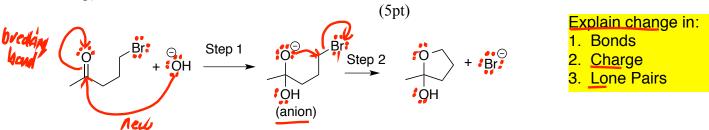
7. Which of the following represent pairs of resonance structures? (4pt)



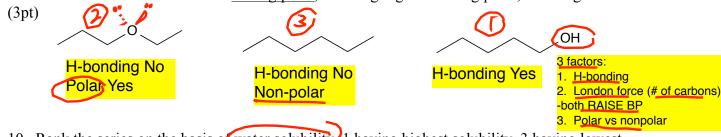
e. a, b, and c are all resonance structures.

6

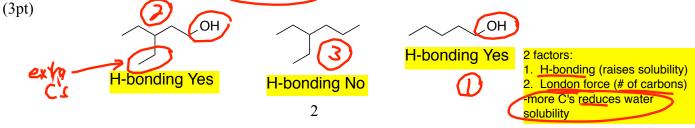
8. Draw arrows to show electron-movement in the following two steps (draw arrows for each step).



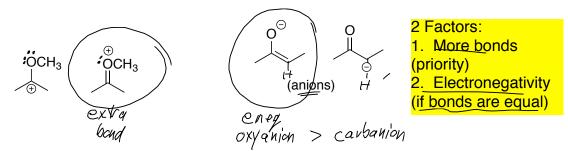
9. Rank the series on the basis of boiling point, 1 having highest boiling point, 3 having lowest.



10. Rank the series on the basis of water solubility. I having highest solubility, 3 having lowest.



11. For each of the following pairs of resonance structures, circle the one that would make a greater contribution to the actual resonance hybrid. (4pt)



12. Cyclopropane is much more "strained" than cyclopentane. Why? (Short!) (3pt)

Angle strain. Bonds are forced to be 60°, far from the ideal ~109° angle.

Note: angle strain only appears in certain rings;

For acyclics, steric and torsional are the only strains available.



- 13. For the following acid-base reaction,
- a. put a box around the weakest base in the reaction
- b. put a circle around the weakest acid
- c. draw an arrow to show whether the equilbrium goes to the right or left. (4pt)

Base Stability factors:

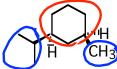
- 1. charge
- 2. eneg
- 3. resonance
- 1. Equilibrium favors the more stable base
- 2. More stable base is "weaker" base
- 3. "Weaker" acid + base on same side
- 14. Classify the relationship between the pairs of molecules as either: (8pt)

same compound geometric isomers

structural isomers resonance structures not isomers (different molecular formulas)



15. Give the name for the following. (7pt)



1. cis/trans for di-subbed rings 2. Alphabetize substituents

- 3. Numbering
- 4. Know isopropyl and t-butyl



1. Longest chain

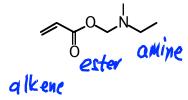
2. Alphabetize substituents

3. Number from end near substituent

cis-1-isopropyl-3-methylcyclohexane

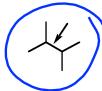
4-ethyl-3-methylheptane

16. Identify all the funtional groups in the following molecules. (Do not include "alkane", since that isn't "functional".) (6pt)



Letone ether aldehyde

17. Which of the following pair will have the larger rotation barrier, relative to the bonds indicated? (3pt)





steric reasons in totally eclipsed

18. For the following Newman projections, rank them in stability from 1 to 4, 1 being most stable. Identify the "anti" conformation, the "gauche" conformation, and the "totally eclipsed" conformation. (6pt)

19. Draw the Newman projection for the most stable conformation of 1,2-dichloroethane. (3pt)



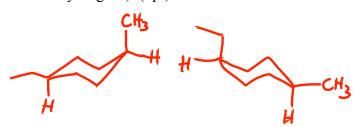


Best: staggered and "anti"

Worst: Totally eclipsed

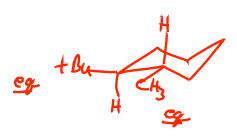


20. Draw the two chair conformations of cis-lethyl-4-methylcyclohexane. (You don't have to draw all the hydrogens). (5pt)



- 1. Make sure you've really drawn "flipped" chairs
- 2. What's "ax" in one chair flip is "eq" in the other.
- 3. Process cis-trans
- 4. Draw in H's on substituted carbons (easier to see ax/eq).

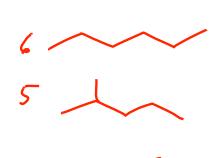
21. Which is more stable, cis- or trans-1-t-butyl-2-methylcyclohexane? Draw the best conformation of the more stable isomer. (4pt)



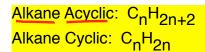
- More stable chair has both substituents equatorial
- 2. Process cis-trans



22. Draw as many structural isomers as you can for C_6H_{14} . Be careful not to draw the same isomer twice! I will take off points for duplicating! (6pt)









Beware of drawing same thing twice!





JASPERSE CHEM Intro and Review

CHEM 350 TEST 1

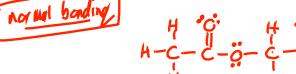
VERSION 2

VERSION 2 Organic Chemistry I - Jasperse

Structure and Properties of Organic Molecules

Structure, Nomenclature, and Conformation/Stereochemistry of Alkanes

1. Draw the correct Lewis structure of CH₃CO₂CH₂COCH₃. (Needn't show 3-D geometry) (3pt)



Want normal bonding for al

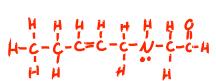
2. C=O (or C=C in other cases) may help

3. If you have any formal charges (not here), they must sum

to net charge of molecule (zero, in this case)

4. Organization must match condensed formula sequence

2. Draw a 3-dimensional picture for the atoms in CH3CH2CHCH2NHCH2CHO, using the hashwedge convention. (You needn't specify lone pairs, and orbitals need not be shown). (5pt)





The Nitrogen is tetrahedral, so the N-H hydrogen must either be wedged or hashed.
 (The lone pair doesn't need to be drawn in, but it impacts the shape of the nitrogen)
 Drawing the correct Lewis structure is essential! Do first!

3. For the structure shown, what is the <u>hybridization</u>, electron-pair geometry, and approximate bond <u>angle</u> (90, 109, 120, or 180) relative to: (7pt, 2 points off for each error)

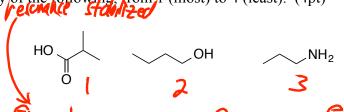
	1 1 11 11	electron-pair b	ond		1 1 11	electron-pair	bond
	hybridization geometry angle			hybridization geometry			angle
C-1	sp3	tetrahedial	M09°	C-4	sp2	trig planar	120
O-2	513	tetrahedral	1090	N-5	SP3	tet	109
C-3	sp2	trigonal planer	120	C-6	3/2	trig	120

4. Assign any formal charges to any appropriate atoms for the structure shown below. (4pt)





5. Rank the acidity of the following, from 1 (most) to 4 (least). (4pt)

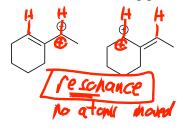


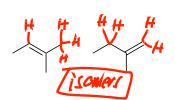
3 Acidity Factors:

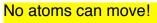
- 1. charge (not relevant here)
- 2. Eneg
- 3. Resonance

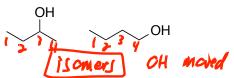


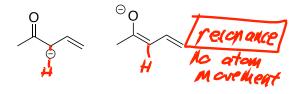
6. For the following pairs, identify as "isomers" ("I") or "resonance structures" ("R"). (6pt)



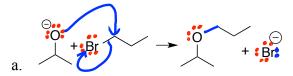


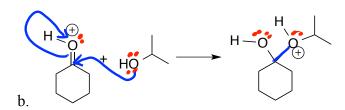






7. Draw arrows to show electron-movement in the following reactions. (These are reactions, not resonance.) (5pt)





Explain change in:

- 1. Bonds
- 2. Charge
- 3. Lone Pairs

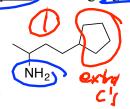
8. Rank the series on the basis of boiling point, I having highest boiling point, 3 having lowest. (3pt)



1. H-bonding

2. London force (# of carbons) both RAISE BP

NΗ₂ H-bonding

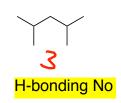




9. Rank the series on the basis of water solubility, 1 having highest solubility, 3 having lowest. (3pt)

2 factors:

- 1. H-bonding (raises solubility) 2. London force (# of carbons) -more C's reduces water solubility
- OH ÓН H-bonding

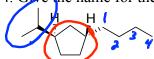


Extra C's reduce solubility

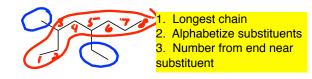


Alkane Acyclic: C_nH_{2n+2} Alkane Cyclic: C_nH_{2n} Alkene: C_nH_{2n} (not expected to remember, but evident if you count) Counting H's can always double-check on this! 10. Circle whichever of the following could fit the formula C_5H_{10} ? (3pt) 11. For the following acid-base reaction, a. put a box around the weakest base in the reaction b. put circle around the weakest acid c. draw an arrow to show whether the equilibrium goes to the right or left. (4pt) ONa + Base Stability factors: charge eneg resonance Equilibrium favors the more stable base 2. More stable base is "weaker" base "Weaker" acid + base on same side 12. Classify the relationship between each pair of molecules as either: (10 pt) same compound structural isomers resonance structures stereoisomers t our sterec structura

14. Give the name for the following. (7pt)



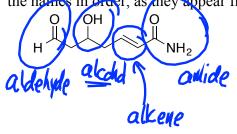
- 1. cis/trans for di-subbed rings
- 2. Alphabetize substituents
- 3. Numbering
- Know isopropyl and t-butyl

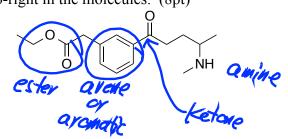


trans-1-butyl-3-isopropylcyclopentane

X

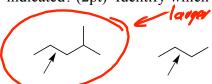
16. Identify and write down the names for each of the functional groups in each of the following molecules. (Do not include "alkane", since that isn't "functional".) For each molecule, try to write the names in order, as they appear from left-to-right in the molecules. (8pt)





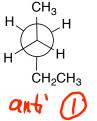
5-ethyl-3-methyloctane

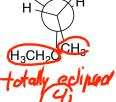
17. Circle which of the following pair will have the larger rotation barrier, relative to the bonds indicated? (2pt) Identify which reason explains why: steric strain, torsional strain, or angle strain?

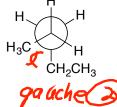


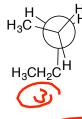
Greater steric strain when totally eclipsed. (Both will have equal torsional strain when totally eclipsed.)

- 18. For the following Newman projections: (6pt total)
 - a. rank them in stability from 1 to 4, 1 being most stable
 - b. identify the "anti", "gauche", and the "totally eclipsed" conformations.



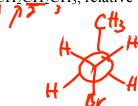




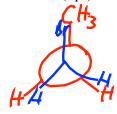


- c. Is the energy difference between the gauche and the anti conformation based on steric strain, torsional strain, or angle strain?
- d. In the case of ethane (not shown), staggered conformations are better than eclipsed conformations. Is the difference based on steric strain torsional strain, or angle strain?

19. Draw both the most stable and the least stable Newman projections for 1-bromopropane, BrCH₂CH₂CH₃, relative to C1-C2 bond. - (3pt)



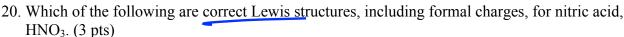
Best: staggered and "anti"

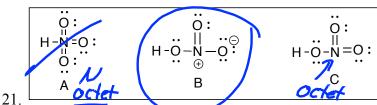


Worst: Totally eclipsed



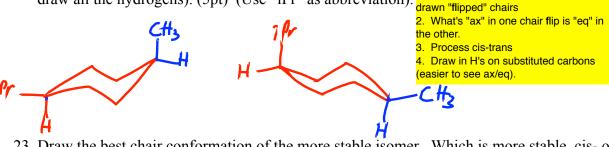
acyclic 🥥





- a. A only
- b. B only
- c. Conly
- d. Both A and C
- e. All of the above
- 1. Do not exceed octet
- 2. If formal charges, must sum to net charge
- 3. As much "normal bonding" as possible, given the above constraints.

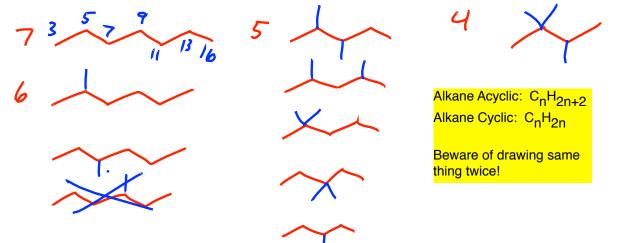
22. Draw the **two chair conformations** of cis 1-isopropyl-4-methylcyclohexane. (You don't have to draw all the hydrogens). (5pt) (Use "iPr" as abbreviation). 1. Make sure you've really draws. If the hydrogens is a substantial of the hydrogens in the hydrogens.



23. Draw the best chair conformation of the more stable isomer. Which is more stable, cis- or trans-1-butyl-2-methylcyclohexane? (4pt)



24. Draw any 6 of the 9 possible structural isomers for **alkanes** with formula C₇H₁₆. When deciding whether to draw cyclic or acyclic alkanes, make sure that you fit the formula! Be careful not to draw the same isomer twice! I will take off points for duplicating! (You can try to show off by getting more than 6, but if you do still be sure you don't duplicate!) (6pt)



JASPERSE CHEM 350 TEST 1 VERSION 3 Organic Chemistry I - Jasperse

Intro and Review

Structure and Properties of Organic Molecules

Structure, Nomenclature, and Conformation/Stereochemistry of Alkanes

1. (12 points) Give the relationship between the following pairs of structures. The possible relationships are the following:

same compound stereo isomers

structural isomers resonance structures not isomers (different molecular formula)

a.

Structural. 1,2-dibromo vs 1,3-dibromo.

1. Resonance: No atoms can move! 2. Stereo: same condensed formula 3. Structural: different condensed formula

H 🚱

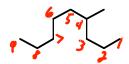
ΗН BrBr

Same. **Bond rotation around** single bonds is allowed.

Structural CH3CHCHBr vs CH2CHCH2Br

CH CH CH CH,

Stereo Trans-cis. Double bond can't rotate.



Same. Both are 4-methylnonane

Resonance. Electrons and charge is repositioned, but no atoms moved.

(8 points) Draw line-angle structures and names for 4 of the 5 structural isomers of C₆H₁₄.

3-methylpentane

Alkane Acyclic: C_nH_{2n+2} Alkane Cyclic C_nH_{2n}

Beware of drawing same

2,3-dimethylbutane





- 3. (10 Points)
- a. For the above structure, what is the hybridization and approximate bond angles (109, 120, or 180) about:
- C-2 C-4 109 C-6 $sp3, \sim 109$ 0-8
- b. In the above structure, N-1 is actually found to have 120° bond angles (This may seem unexpected to you at this point, but we'll learn why later in the course.) What must be the hybridization of the nitrogen?
- Hybridization, bond angle, and electron geometry are all interlocked. To know any one of them is to know the others.
- (2 Points) Bond rotation around <u>C6-C7 in the</u> above structure has a 7 kcal/mo barrier, while rotation around the C4-C5 bond has a 70 kcal/mol barrier. Explain very briefly why it is so much harder to rotate the latter bond?

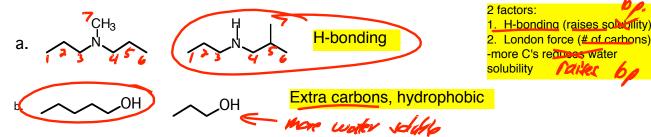
Single bond versus double bond.

A double bond has overlapping p-orbitals.

To rotate a double bond, the p-p overlap would be lost. The full pi-bond would need

By contrast, no bonds are broken when you rotate around a single bond.

5. (4 points) For each of the pairs listed, circle the one with the higher boiling point.



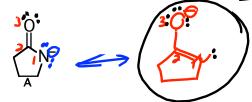
6. (6 points) Write a Lewis structure and assign any non-zero formal charges.

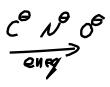
2

- a. [CH₃NH₃] b. CH₃CO₂Na c. CH₃CHO
- Want normal bonding for all: in absence of metal ions
- C=O (or C=C in other cases) may help
- If you have any formal charges (to net charge of molecule (zero, in this case)
- Organization must match condensed formula sequence



7. (5 points) a) Draw the best resonance structure for anion A, and circle the resonance structure that would make the greater contribution to the resonance hybrid.

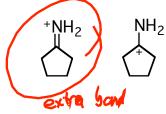




2 Factors:

- More bonds (priority)
- 2. Electronegativity (if bonds are equal)

b. For the two resonance structures shown below, <u>circle</u> the resonance structure that would make the greater contribution to the resonance hybrid.



(6 points) Rank the acidity of the following molecules, 1 being most acidic, 4 being least acidic. Hint: draw the anions!





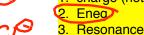


resonance



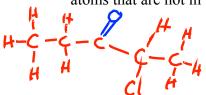
3 Acidity Factors:

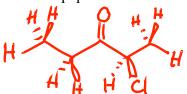
1 charge (not relevant here)

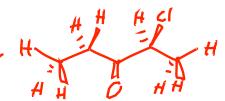




Draw a line-angle picture for all of the atoms in the molecule 9. (6 points) CH₃CH₂COCHClCH₃, including the hydrogens. Use the hash-wedge convention to indicate atoms that are not in the plane of the paper.







CI could equally well be drawn in the hashed spot

10. (5 points) Rank the ring strain in the following, from 1(most) to 3 (least). Explain very briefly the differences in strain.

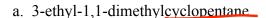




- A: has large angle strain (60° angles, not 109° angles)
- B: By taking on chair conformation, there is zero angle strain, and zero torsional (no eclipsing)
- C: If it has ideal angles, then some eclipsing and torsional strain destabilizes it

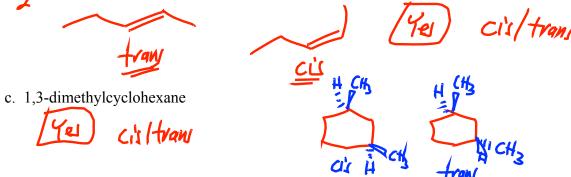


11. (6 points) Which of the following are capable of cis-trans stereoisomerism? (Yes/No).

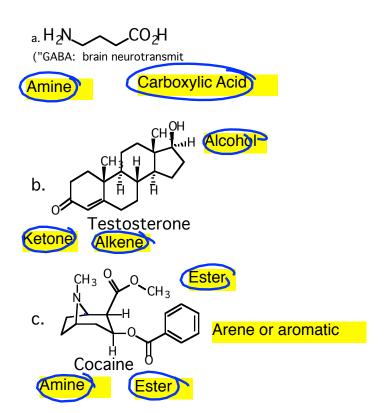




b. Expentene (name means a double bond is between carbons 3 and 4)

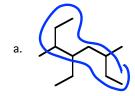


12. (9 points) Identify the functional groups in the following molecules. (Do not include "alkane", since that is not "functional". And do not specify "cyclic".)

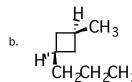




13. (5 points) Give the **IUPAC** name for the following compounds.



- 1. Longest chain
- Alphabetize substituents
 Number from end near
- substituent



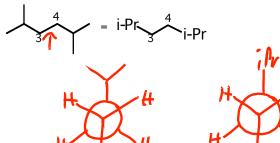
- 1. cis/trans for di-subbed rings
- 2. Alphabetize substituents
- 3. Numbering
- 4. Know isopropyl and t-butyl

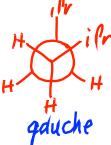
4-ethyl-3,6-dimethyloctane

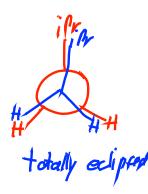
cis-3-methyl-1-propylcyclobutane

- 14. (8 points) a. Draw Newman projections for the totally eclipsed, the gauch, and the anti conformations of 2,5-dimethylhexane, relative to the C3-C4 bond. You may abbreviate the isopropyl groups attached to C3 and C4 as "i-Pr" for convenience.
- b. Explain very briefly why the rotation barrier around the C3-C4 bond of 2,5-dimethylhexane is greater than the rotation barrier in butane.





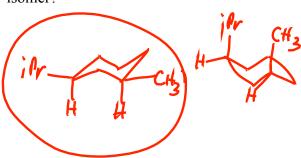




b. Steric Strain. Larger rotation barrier because greater steric strain in total eclipse between two larger isopropyl groups compared to steric strain between two methyl groups. Torsional stain is common to both, to the difference is the difference in steric strain.

- 15. (8 points) a.) Draw the two chair conformations of cis-1-isopropyl-3-methylcyclohexane. (You don't need to show the H's on carbons other than 1 and 3). For convenience, you may abbreviate methyl as "Me" and isopropyl as "iPr"
- b.) Circle the more stable conformation.
- c) Would trans-1-isopropyl-3-methylcyclohexane be more stable or less stable than the cis isomer?





- 1. Make sure you've really drawn "flipped" chairs
- 2. What's "ax" in one chair flip is "eq" in the other.
- 3. Process cis-trans
- 4. Draw in H's on substituted carbons (easier to see ax/eq).





TEST

VERSION 4 Organic Chemistry I - Jasperse

Intro and Review

Structure and Properties of Organic Molecules

Structure, Nomenclature, and Conformation/Stereochemistry of Alkanes

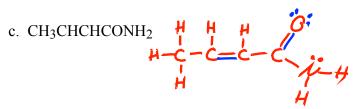


1. Order the following according to increasing electronegativity, 1 being highest, 4 lowest. (2pts)

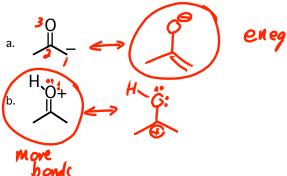
F C 4

2. Write Lewis structures and assign any non-zero formal charges. (3pts each)

- 1. Want normal bonding for all: in absence of metal ions or overall charge
- 2. C=O (or C=C in other cases) may help
- 3. If you have any formal charges, they must sum to net charge of molecule (zero, in this case)
- 4. Organization must match condensed formula sequence

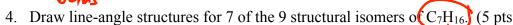


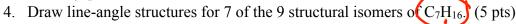
3. For each of the following, a) draw its resonance structure, and for each pair b) circle the structure that would make the greater contribution to the resonance hybrid. (2 pts each)

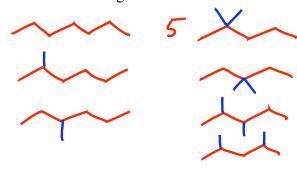


2 Factors:

- More bonds (priority)
- 2. Electronegativity (if bonds are equal)





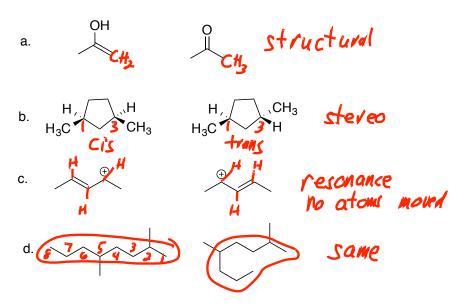




Alkane Acyclic: C_nH_{2n+2} Alkane Cyclic: C_nH_{2n}

Beware of drawing same thing twice!

5. For the following pairs of structures, identify them as either: Resonance Structures, Structural Isomers, Stereoisomers, or Same. (2 pts each)



Resonance: No atoms can move!
 Stereo: same condensed formula
 Structural: different condensed formula

e. $CH_3CH_2CH_2CH_3$ $(CH_3)_2CHCH_2CH_3$ st fuctural

6. Rank the acidity of the following molecules, 1 being most acidic, 4 being least acidic. (3 pts)

Think CH₃NH₂ 3 CH₃OH 2 HCO₂H CH₃CH₃ 4

CH₃OH CH₃OH

CH₃OH

CH₃OH

CH₃OH

CH₃OH

CH₃OH

CH₃CH

CH₃CH

A A CH₃CH

CH₃CH

A A CH₃CH

A CH

- a) Put a box around the weakest base in the above reaction. (1pt)
- b) Put a circle around the weakest acid in the above reaction. (1pt)
- c) Draw an arrow to show whether at equilibrium the reaction will go left-to-right or right-to-left. (2pt)

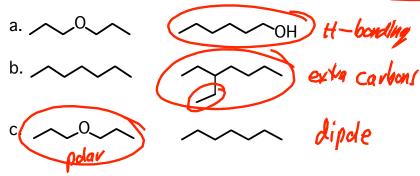
8. Draw the line-angle structure for the following condensed structural formula: (CH₃CH₂)₂CO (3pt)

a. For the above structure, what is the hybridization, electron-pair geometry, and approximate bond angles (109, 120, or 180) about: (6pt)

tetrahedral ~109 N-1 tetrahedral ~109
trigonal planar ~120
linear ~180 2 C-8

> b. Rank the length of the following bonds, 1 being shortest, 3 being longest. (2pt) C8-C9 C4-C5

10. For each of the pairs listed, circle the one with the higher boiling point (4pt)

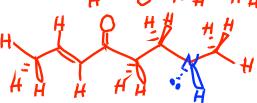


2 factors: 1. H-bonding (raises bp + solubility)

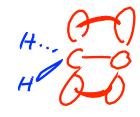
2. London force (# of carbons) -more C's raises bp but reduces water solubility

11. Draw a 3-dimensional picture for all of the atoms (hydrogens included) in the molecule CH3CHCHCOCH2CH2NHCH3. Your picture should use the hash-wedge convention to illustrate atoms that are not in the plane of the paper, and should reflect approximate bond

angles. (5pt)

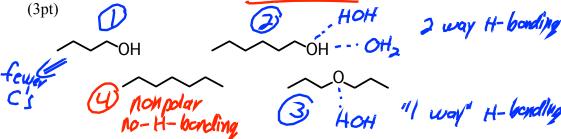


Note: N-H hydrogen is NOT in the plane. But it could be drawn hashed or wedged, either is fine.



p-orbitals used to make the pibond are perpendicular to the plane of the atoms. So if we draw the pi-bond in the plane, the attached H's must be out of plane.

13. For the following set, rank the solubility in water, from 1 (most soluble) to 4 (least soluble).

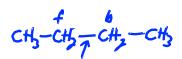


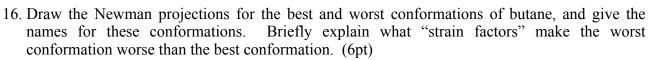
14. Identify the functional groups in the following molecules. (8pt)

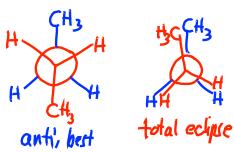
15. Give the IUPAC name for the following compounds. (6pt)

- 1. Longest chain
- 2. Alphabetize substituents
- 3. Number from end near substituent

- 1. cis/trans for di-subbed rings
- 2. Alphabetize substituents
- 3. Numbering
- 4. Know isopropyl and t-butyl



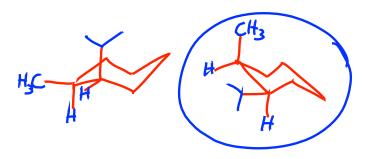




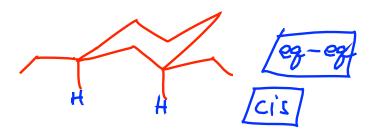
Torsional strain; any eclipsed conformation has torsional strain, repulsion beween bondpair electrons.

Steric strain: atom are unnecessarily close, and repel each other

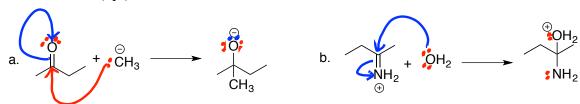
- 17. a.) Draw both chair conformations of cis-1-methyl-2-isopropylcyclohexane. substituents and H-atoms attached to carbons 1 and 2. (You don't need to show the H's on the other carbons). (4pt)
 - b.) Circle the more stable conformation. (1pt)



- 1. Make sure you've really drawn "flipped" chairs
- 2. What's "ax" in one chair flip is "eg" in the other.
- 3. Process cis-trans
- 4. Draw in H's on substituted carbons (easier to see ax/eq).
- 18. Draw the best chair conformation for 1,3-diethylcyclohexane, and identify whether it is "cis" or "trans". (3pt)



19. Use the arrow-pushing convention to show the electron-movement mechanisms for the follow two reactions. (5pt)



Good mechanism must explain changs in:

- 1. Bonds
- 2. Formal Charges
- Lone pairs



Ch. 4 The Study of Chemical Reactions; Ch. 5 Stereochemistry

Ch. 6 Alkyl Halides: Nucleophilic Substitution and Elimination

1. Predict the <u>major</u> organic product for each of the following. (3 points each)

2. Show an alkyl bromide and some nucleophile that you could use to make the following by

(3 points) \longrightarrow OCH_2CH_3 Correct

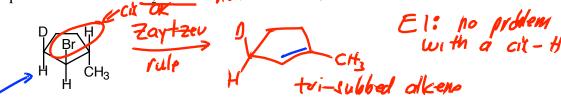
No Good:

3°, cairl do Sus (3 points each)

and do sus

3. For the structure shown,

a. Draw the major <u>elimination</u> product formed upon treatment with $H_2O/heat$. Neutral \Rightarrow SM /EI



b Draw the major <u>elimination</u> product formed upon treatment with CH₃CH₂ONa.

c. Draw the major <u>substitution</u> product formed upon treatment with CH₃CH₂ONa.

(3 points for each multiple choice question)

- 4. Which of the following is <u>true</u> regarding an $S_N 1$ reaction?
 - a. It would be faster at 25° than 50°

Solvent polarity factor, good for cations

b. It would be faster in ethanol than in pentane

c. Keeping the moles of reactants constant but doubling the quantity of solvent would Sul r= KLRXI decrease the rate by a factor of 4.

d. Stereochemical inversion occurs exclusively

suz not sul

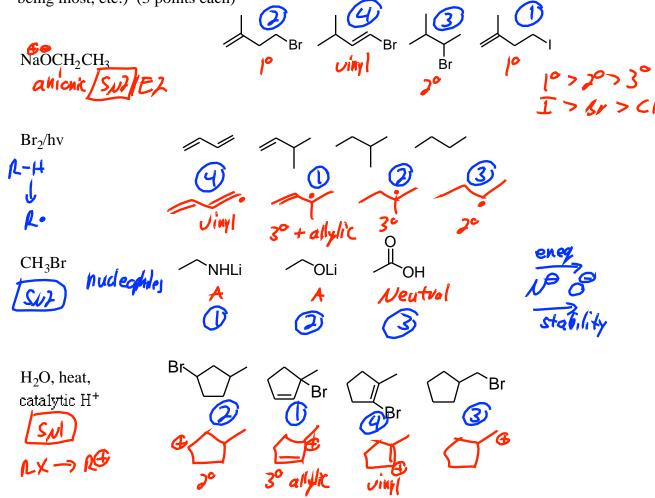
- 6. Which of the following statements is <u>true</u>?
 - a. The rate determining step is always the last step in a reaction mechanism.
 - b. The stability/reactivity principle says that the more stable of two chemicals will be more reactive
- c.) The reactivity/selectivity principle says that the more reactive of two chemicals will be less US. C.
 - d. The activation barrier for a reaction is the difference in energy between reactants and final products.
- 7. Which of the following statements is true about the chlorination of methane?
 - a. In each propagation step a radical is produced
 - b. 6.02×10^{23} initiation events are needed to make one mole of chloromethane
 - c. Most chloromethane is made by combination of a methyl radical with a chlorine radical \sqsubset
 - d. The overall chlorination of methane is strongly endothermic.
- 8. Which of the following statements is **FALSE**?
 - a. Optically active solutions solutions always contain chiral molecules.
 - b. Two diastereomers always have identical melting points F enant yes, digit. No
 - c. Optically inactive solutions are either racemic or else contain no chiral chemicals at all
 - d. A solution with 60% optical purity would have an 80/20 mix of enantiomers
- 9. When the reactants shown undergo substitution, which of the products A-D will form? (3 points)

a. A only

SN1, cationic, racemization results, two enantiomers form.

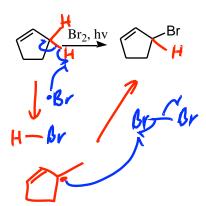
- b B only
- c. A and B
- d. A, B, and C
- e. A, B, C, and D

10. Rank the reactivity of the structures shown toward the reactant(s) indicated on the left (1 being most, etc.) (3 points each)



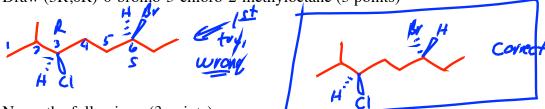
11. Draw the product(s) of the following reaction. Show substitution product(s) only. (There might be some some alkene products formed as well, but don't bother drawing those.). If two enantiomers form, draw them both. (3 points)

12. Draw the mechanism for the following reaction, propagation steps only. (4 points)

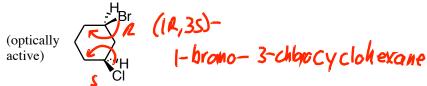




13. Draw (3R,6R)-6-bromo-3-chloro-2-methyloctane (3 points)



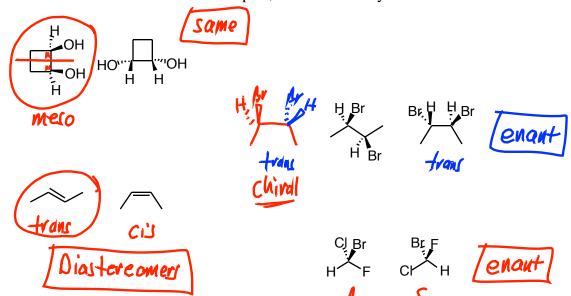
14. Name the following: (3 points)



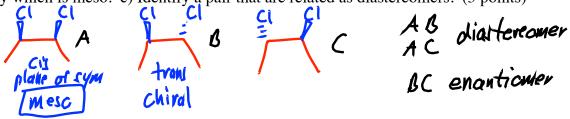
15. Classify each of the chiral carbons in the following structures as R or S (there may be more than one in a molecule). (10 points)



- 16. a. Classify each pair as diastereomers, enantiomers, or same. (12 points)
- b. For the first structure of each pair, circle it if it is **not** chiral
- c. For the first structure of each pair, write "meso" by it if it is meso



17a. a) Draw all the unique stereoisomers of 2,3-dichlorobutane. Cross out any duplicates. b) Identify which is meso. c) Identify a pair that are related as diastereomers. (5 points)



18. Draw the mechanisms for the following reactions, <u>using formal arrow pushing</u>. Note: in some case hydrogens that are not illustrated will be involved in bond changes. You would do well to write them in at the beginning. (12 points total, 3/3/6 distribution)



JASPERSE CHEM 350 TEST 2



Ch. 4 The Study of Chemical Reactions

Ch. 5 Sterochemistry

Ch. 6 Alkyl Halides: Nucleophilic Substitution and Elimination

1. Rank the reactivity of the following molecules toward Br₂/hv. (1 most, 4 least) (3 points)

Р-H Г вго Г

2. Rank the reactivity of the following molecules toward ethanol and AgNO3. (1 most, 4 least)

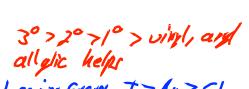
(3 points)







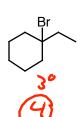


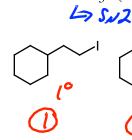


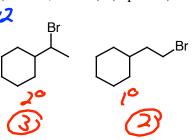
Jo jo aryl 20+allylic

3. Rank the reactivity of the following molecules toward NaOCH₃. (1 most, 4 least) (3 points)

1° > 2° > 3° I> Br > Cl







4. Rank the reactivity of the following toward 1-iodopropane. (1 most, 4 least) (3 points)

OF A (2)

CH₃CO₂H







Danion > neutral

D So > Obermon

0 Teneg

rei chance

5. What is the hybridization of a carbocation? (2 points)

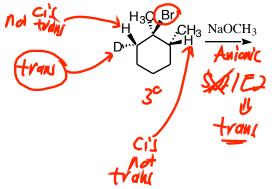
1

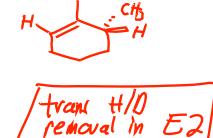


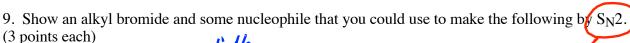
- 6. Predict the major organic product (1 major structure is all that is needed in each case) for each of the following reactions. (Minor products or inorganic side products need not be drawn.) (3 points each)

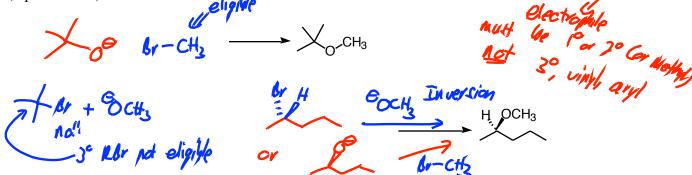
7. Draw the structures for intermediate \mathbf{A} and final product \mathbf{B} . (4 points)

8. Draw the product when the following substance undergoes E2 elimination. "D" is deuterium, basically just a labelled hydrogen). If the starting material is optically active, will the product by optically active? (4 points)

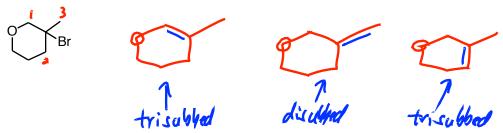








10. Draw all possible elimination products that could form from the following reactant. (5 points)



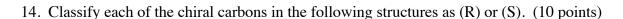
- 11. Which of the following would not increase the rate of an Ellreaction? (3 points)
 - a. an increase is temperature
 - ban increase in the "activation energy"
 - c. an increase in the concentration of the alkyl halide father
 - d. an increase in the stability of the carbocation intermediate
- 12. When comparing the reaction of 2-methylpropane with either Cl₂/hv or Br₂/hv, which of the following statements is true? (3 points)
 - a) bromine is less reactive and more selective
 - b. chlorine is less reactive and more selective
 - c. bromine is more reactive and more selective
 - d. chlorine is more reactive and more selective
- 13. Which of the following statements is true relative to reactions I-III: (3 points)

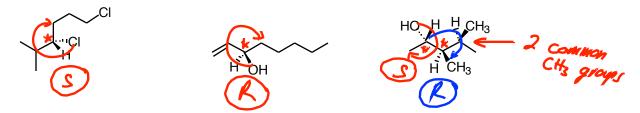
I
$$CH4 + Br \rightarrow CH3 \circ$$
 and HBr

II
$$CH_3CH_3 + Br^{\bullet} \rightarrow CH_3CH_2^{\bullet} + HBr$$

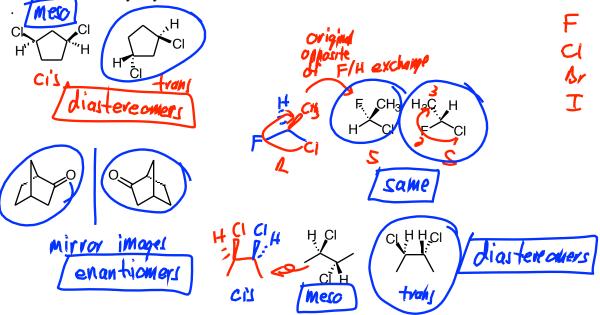
III
$$CH_3CH_2CH_3 + Br^{\bullet} \rightarrow (CH_3)_2CH^{\bullet} + HBr$$

- a. I has the smallest energy of activation and the highest energy transition state
- b. II has the smallest energy of activation and I has the lowest energy transition state
- c. III has the largest energy of activation and the highest energy transition state
- d. III has the smallest energy of activation and the lowest energy transition state

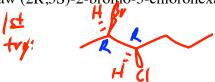


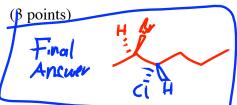


- 15. a. Classify each pair of molecules as diastereomers, enantiomers, or same. (12 points) b. Circle any molecules that are chiral
- c. Write "meso" by any structures that are meso

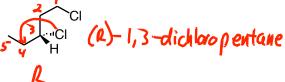


- 16. Which of the following statements is <u>true</u>? (3 points)
 - a. All solutions with chiral molecules are optically active F
- SOISO PACEMIC MIXTURE
- b. All molecules with chiral carbons are chiral
- c. A solution that has 50% optical purity has a 50/50 mixture of enantiomers d.) Two enantiomers always have identical boiling points
- 17. Draw (2R,3S)-2-bromo-3-chlorohexane (β points)



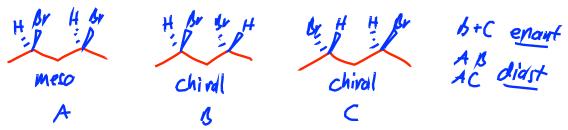


18. Name the following: (3 points)



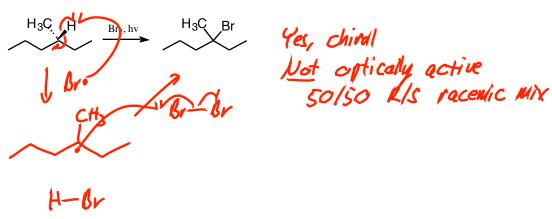


- 19. a) Draw all <u>unique</u> stereoisomers of <u>2,4-</u>dibromopentane. Label each with a letter, A, B, etc.. Cross out any duplicates. (8 points)
- b) Identify any that are chiral
- c) Identify any that are meso

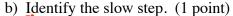


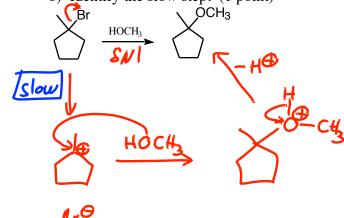
20. a) Draw the mechanism for the following reaction. (Draw the propagation steps only.) (4 points)

b) Is your product chiral, and if so is it optically active? (1 points)



21. a) Draw the mechanism for the following reaction. (4 points)







JASPERSE CHEM 350 TEST 2



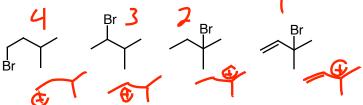
Ch. 4 The Study of Chemical Reactions Ch. 5 Sterochemistry

Ch. 6 Alkyl Halides: Nucleophilic Substitution and Elimination

1/4	6/9	<u>1</u> 1/6	16/4
2/4	7/4	12. Removed	<u>1</u> 7
			<u>1</u> 8/16
4/4	9/10	14	Total/100_
	10/6		

1. List the following radicals in order of increasing stability (from most stable 1 to least stable 4)

2. List the following alkyl halides in order of decreasing reactivity toward S_N1/E1 reactions (from most reactive 1 to least reactive 4).



3. List the following alkyl halides in order of decreasing reactivity toward S_N2 reactions (from most reactive 1 to least reactive 4). 10 > 20 > 30 > U/Myl

$$\frac{Br}{2}$$
 $\frac{Br}{3}$ $\frac{Br}{4}$ $\frac{Br}{1}$

4. Rank the bond strength of the following (from strongest 1 to weakest 4).

H-Br

H-Cl

H-F

H-I

5a. Put a 1 by the reaction for which $\Delta H^{\circ} = E_{act}$. $(E_{act} = activation energy)$

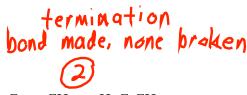
b. Put a **2** by the reaction for which $E_{act} = 0$.

c. Put a 3 by the reaction for which $E_{act} > \Delta H^{\circ}$.

 $Br-Br \rightarrow Br \bullet + Br \bullet$ initiation $H_3C-H + Br^{\bullet} \rightarrow H_3C^{\bullet} + H-Br$

hand breaks made





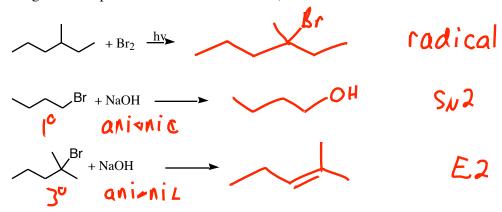
J > D1>C1

 $H_3C^{\bullet} + {}^{\bullet}CH_3 \rightarrow H_3C-CH_3$

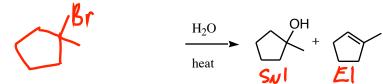




6. Predict the major organic product for each of the following reactions. (Minor products or inorganic side products need not be drawn.)



7. Show the Starting Alkyl Bromide which gave the following products.



8. Show an alkyl bromide and some nucleophile that you could use to make the following. (I don't care whether you specify a nucleophile just as the anion Z^- or as NaZ with a metal counterion.)

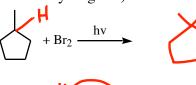
9. Optically active (R)-2-bromobutane can be converted to 2-butanol under either conditions A or conditions B. Describe the stereochemistry of the product solutions for the two different conditions.

- a. Alcohol is Chiral or Achiral?
- b. Optically Active or Not?
- c. (R), (S), or both?
- d. Reaction occured by Inversion, Retention, or Racemization?
- e. What happens to the rates if you double the concentrations of all reactants?



10. Draw the major product for the following reaction. Then draw the mechanism for its formation. (Draw the propagation steps only.) Is your product chiral? (You may need to add relevant hydrogens.)

relevant hydrogens.)



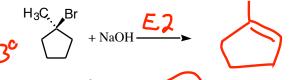




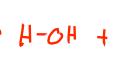




11. Draw the major product for the following reaction. Then draw the mechanism for its formation. (You may need to add relevant hydrogens.)









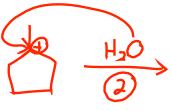
13. Draw the mechanism for the following reaction. (Don't worry about designating stereochem.) H_3C Br H_3C OH

SN

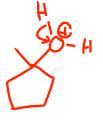


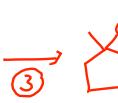
H₂O





+ H-Br



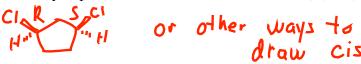




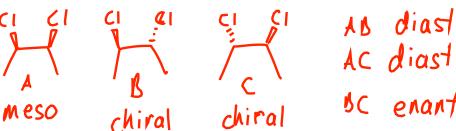
14. Classify each of the chiral carbons in the following structures as (R) or (S).



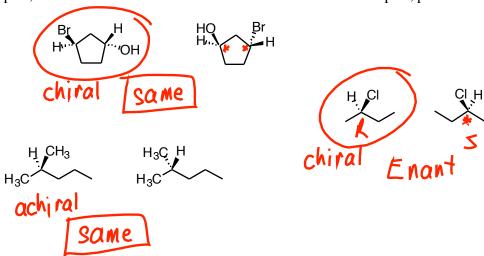
- 15. Draw (R)-2-bromopentane
- 16. Draw meso-1,3-dichlorocyclopentane, and mark the chiral C's as (R) or (S).



17. Draw all of the <u>different</u> isomers of 2,3-dichlorobutane, identify each as either chiral or meso, and classify the relationship between each two as enantiotopic or diastereotopic. (You may use Fischer projections or zig/zag/hash/wedge pictures, as you please. (If two are the same, cross one of them off your list.)



18. Classify the pairs of molecules as diastereomers, enantiomers, or same. For the first molecule in each pair, circle it if it is chiral. For the second molecule in each pair, put a * next to each chiral C.



JASPERSE CHEM 350 TEST 2

VERSION 4

Ch. 4 The Study of Chemical Reactions

Ch. 5 Alkyl Halides: Nucleophilic Substitution and Elimination

Ch. 6 Stereochemistry

1. Draw the mechanism for the following reaction, and <u>write "slow" next to the rate-determining step.</u> Be sure to draw all intermediates, and to correctly draw "electron-movement" arrows or half-arrows. (Show the propagation steps only.) (4 points)

2. Draw the mechanism for the following reaction, and <u>write "slow" above the rate-determing step.</u> Be sure to draw all intermediates, and to correctly draw "electron-movement" arrows. (5 points)

3. Predict the major products for the following reactions. (4 points each)

a)
$$\rightarrow$$
 Br + NaOCH₃ \rightarrow CH₃OH (solvent) \rightarrow OCH₃ \rightarrow S_N 2
b) \rightarrow + Br₂ \rightarrow Padical

4. Draw the <u>substitution products</u> for the following reactions. (Do not draw the accompanying elimination products). <u>Include stereochemistry in your answer, and if two substitution products are formed draw them both.</u> (4 points each)

a)
$$H_3C$$
 H H_2O H_3C H_3C H_4 H_2O H_4 H_4

5. Draw the <u>E2 elimination product(s)</u> [do not draw the substitution product(s)]. (4 points each)

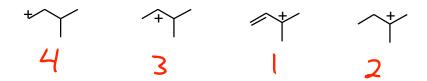
- 6. Of the following alkyl halides, (3 points)
- a) Circle the one that would be the most reactive toward $S_N 2$ substitution
- b) Put a box around the one that would be the least reactive toward $S_{\rm N}2$ substitution

45

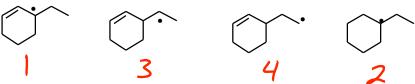
- 7. Of the following alkyl halides, (3 points)
- c) Circle the one that would be the most reactive toward $S_{\scriptscriptstyle N} 1$ substitution
- d) Put a box around the one that would be the least reactive toward $S_{\scriptscriptstyle N} 1$ substitution



8. Rank the stability of the following carbocations, from 1 (most stable) to 4 (least stable) (4 pts)



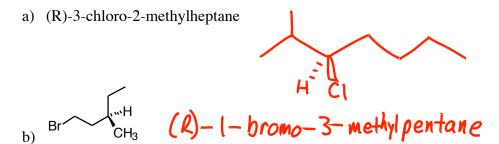
9. Rank the stability of the following radicals, from 1 (most stable) to 4 (least stable) (4 pts)



10. Classify as R or S (2 pts each)

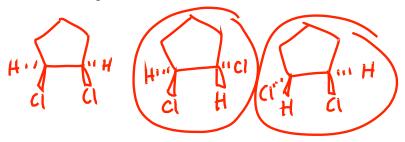
$$Bt$$
 H

11. Provide the structure and the IUPAC name for the following (3 pts each)



12. Classify the paris of molecules as <u>not isomers</u>, <u>structural isomers</u>, <u>diastereomers</u>, <u>enantiomers</u>, <u>or identical</u>, and circle any molecules that are <u>achiral</u>. (2 pts each)

- 13. For 1,2-dimethylcyclopentane, (8 pts)
- a) How many stereocenters are present 7
- b) Draw all the possible stereoisomers, and circle those that are chiral.



Each of the following multiple choice problems is worth 3 points.

14. For the reaction shown below, with bond dissociation energies listed below each key bond, the overall ΔH is:

(CH₃)₃C-H + Cl-Cl → (CH₃)₃C-Cl + H-Cl

$$\Delta$$
H (kcal/mol) 91 58 78 103

- a) +58 kcal/mol
- b) -32 kcal/mol
- c) +32 kcal/mol
- d) -57 kcal/mol
- e) +181 kcal/mol
- 15. Which factor would <u>not</u> increase the rate of an E1 reaction:
- a) Use of a more polar solvent
- b) Use of a 3° rather than a 2° alkyl halide
- (c) Doubling the concentration of the base
- d) Using iodide rather than bromide as leaving group
- 16. Consider the S_N 2 reaction shown below. Assuming no other changes, what effect on the rate would simultaneously doubling the concentrations of both 1-bromobutane and KOH have?

$$CH_3CH_2CH_2CH_2Br + KOH \rightarrow CH_3CH_2CH_2CH_2OH + KBr$$

- a) No effect
- b) It would double the rate
- c) It would triple the rate
- d) It would increase the rate by four times
- e) It would increase the rate six times
- 17. Of the $S_N 1/S_N 2/E 1/E 2$ reactions, rearrangements are likely to occur in:
- a) $S_N 1$ reactions only
- b) S_N^2 reactions only
- c) E1 reactions only
- d) Both $S_N 1$ and E1 reactions
- e) Both S_N2 and E2 reactions

1

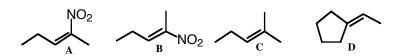
Ch. 7 Structure and Synthesis of Alkenes

Ch. 8 Reactions of Alkenes

1. How many elements of unsaturation are in the formula $C_6H_9NO_2$? (3 points)

(14+1)-q=6Hc. 2

2. For the three structures shown, which of the statements is true? (3 points)



a. A, C, and D are Z; B is E

b. A and B are the only Z compounds

c. A is the only Z compound; B is the only E compound

d. B, C, and D are Z; A is E

e. B is the only Z compound; A is the only E compound

3. Rank the reactivity of the following toward H_2SO_4/\hat{I} catalyzed dehydration. (3 points)

a. A is fastest; C is slowest

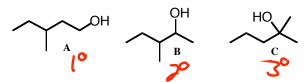
b. **B** is fastest; **C** is slowest

c. A is fastest; B is slowest

d. C is fastest; B is slowest

e. **B** is fastest; **A** is slowest

C is fastest; A is slowest



4. Which of the following reactants would give exaactly the same products from both (E)- and (Z)-2-butene? (3 points)

If two chiral centers are produced, then diastereomeric products are produced.

a. Br_2

b. PhCO₃H

(c.)1) BH_3 -THF 2) NaOH, H_2O_2

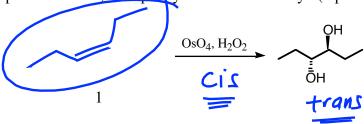
d. OsO_4 , H_2O_2

e. D_2 , Pt

But if only one (or zero) chiral centers are produced, then the two alkenes don't give different products. In this case, with H-OH being added, only the carbon to which OH is added ends up being chiral, so you get the same racemic mix of 2-butanol either way.

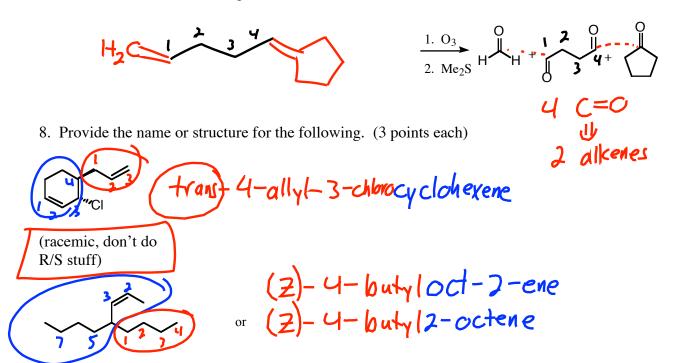
5. Draw the alkene that gives the product shown, and specify its stereochemistry. (2 points)

The normal "E" alkene would have given the wrong product stereochemistry. If the cis/ trans sense of the addition and the cis/trans appearance of the product match, then "E" alkene would have worked.



6. Draw the **major** product for each of the following reactions or reaction sequences. You needn't bother to show side products or minor products. For chiral molecules that are racemic, you needn't draw both enantiomers. BE CAREFUL TO SHOW THE CORRECT ORIENTATION, AND THE CORRECT STEREOCHEMISTRY IN CASES WHERE

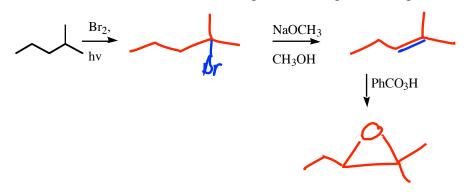
7. A single unknown reacts with O_3/Me_2S to give the following three products. What is the structure for the unknown? (3 points)



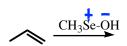
9. Provide a possible structure for a compound with formula C_5H_8 , given that it reacts with excess H_2/Pt to give C_5H_{10} . (3 points)



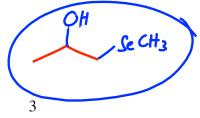
10. Fill in the blanks for the following reaction sequence: (6 points)



11. Consider how the Se-O bond would be polarized and predict the product which would result when CH₃SeOH adds to propene: (Selenium is located two rows directly below oxygen on the periodic table). (3 points)

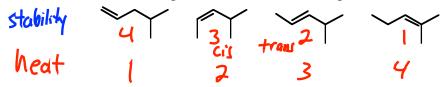


Markovnikov's rule. Electronegativity/periodic table shows Oyxgen more electronegative than selenium, so the oxygen adds to the more substituted end of the alkene.

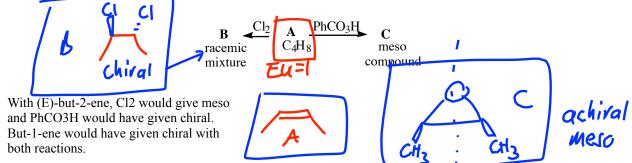




12. When the following isomeric alkenes are fully burned, rank the amount of heat produced in the combustions, from most heat produced (1) to least heat produced (4). (3 points)



13. Provide structures for starting material **A** and reactions products **B** and **C**, given the formula of starting material **A** and the stereochemical status of products **B** and **C**. (5 points)



14. Draw mechanisms for the following reactions, using formal arrow-pushing. Each intermediate along the mechanism pathway must be shown. (6 points, 3 points, 6 points)

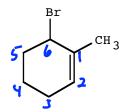
15. Provide reagents for the following transformations. (5 points each)

JASPERSE **CHEM 350** TEST 3

VERSION 2

(18+1)-9=10H

- Ch. 7 Structure and Synthesis of Alkenes
- Ch. 8 Reactions of Alkenes
- 1. How many elements of unsaturation are in the formula C_8H_9N ?
 - a. 0
 - b. 1
 - c. 2
 - d. 3
- 2. Provide the proper IUPAC name for the alkene shown below.



3. Provide the proper IUPAC name for the alkene shown below.

or
$$(2)$$
-5-chloro-2-pentene

4. Draw an acceptable structure for 4-phenyl-1-butene.

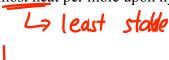


5. Draw the alkene of formula C₄H₈ which evolves the most heat per mole upon hydrogenation





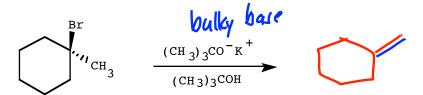




6. Choose the most stable alkene among the following.

- a. 1-hexene
 - b.) (E)-2-hexene
 - c. (Z)-2-hexene
 - d. They are all of equal stability according to Saytzeff's rule.

7. Draw the major product of the following reaction.

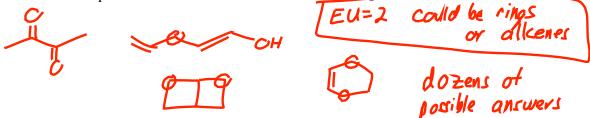


8. Draw the major product and the mechanism.

9. Which of the following best describes the geometry about the carbon-carbon double bond in the alkene below?

a. Eb. Zc. Neither E nor Z

10. Draw 3 examples of molecules with the formula C₄H₆O₂



11. Draw the major product.

12. Draw the major product.

13. Draw the major product.

14. Draw the major product.

15. Draw the major product.

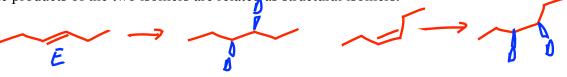
16. Draw the major product.

17. Complete the following reaction and provide a detailed, step-by-step mechanism for the process.

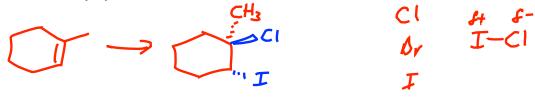
18. Suggest a reasonable detailed, step-by-step mechanism for the reaction shown below.

19. Provide the reagents necessary to complete the following transformation. (2 steps minimum).

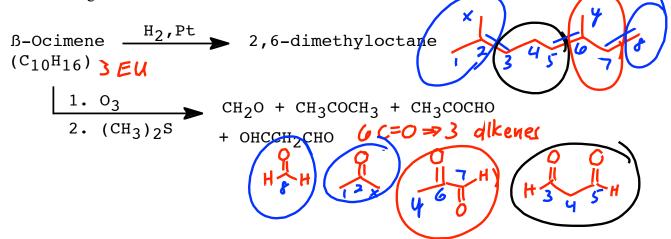
- 20. Both (E)- and (Z)-3-hexene can be treated with D_2 in the presence of a platinum catalyst. How are the products from these two reactions related to each other?
 - a. The (E)- and (Z)-isomers generate the same products in exactly the same amounts.
 - b. The (E)- and (Z)-isomers generate the same products but in differing amounts.
 - The products of the two isomers are related as diastereomers.
 - d. The products of the two isomers are related as enantiomers.
 - e. The products of the two isomers are related as structural isomers.



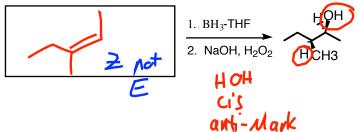
21. Consider how the I-Cl bond is polarized and predict the product which results when this mixed halogen adds to 1-methylcyclohexene.



22. β -Ocimene is a perfume. Suggest a possible structure for β -ocimene that is consistent with the following information.



23. Fill in the starting reactant.



24. Fill in the blanks for the following reaction sequence.

25. Provide reagents to carry out the following transformation: (3 steps minimum)

JASPERSE CHEM 350 TEST 3

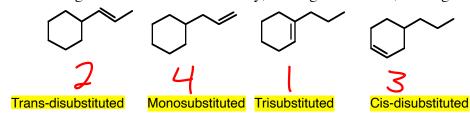
VERSION 3

Answers

Ch. 7 Structure and Synthesis of Alkenes Ch. 8 Reactions of Alkene

The number of points per problem is indicated in parentheses following each problem.

1. Rank the following alkenes in order of stability, 1 being most stable, 4 being least stable. (4)



2. Determine the number of elements of unsaturation for C₅H₇ClO. (3)

Eu=2

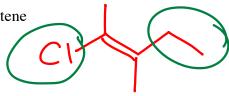
Theory: 12 H+halogen
Actual: 8 H+Cl

Halogen is equivalent to a hydrogen, both use up one singlebond.

3. Give the proper IUPAC name or the structure for the following compounds. (4 points each)

a. (E)-2-chloro-3-methyl-2-pentene

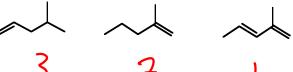
CI > CH3 on left alkene carbon



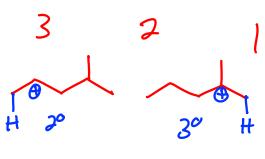
b.

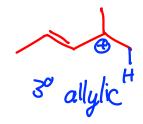
(Z)-5-methyloct-2-ene

4. Rank the reactivity of the following alcohols towards HBr, 1 being the fastest reactant, 3 being the slowest reactant. (3 points)

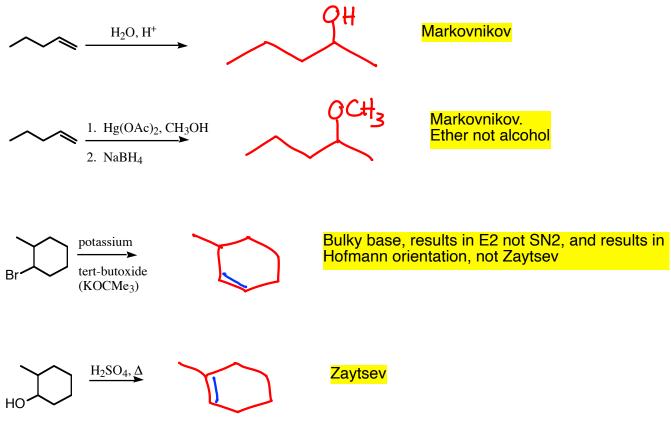


Cation stability following protonation (such that the best possible cation can form.)

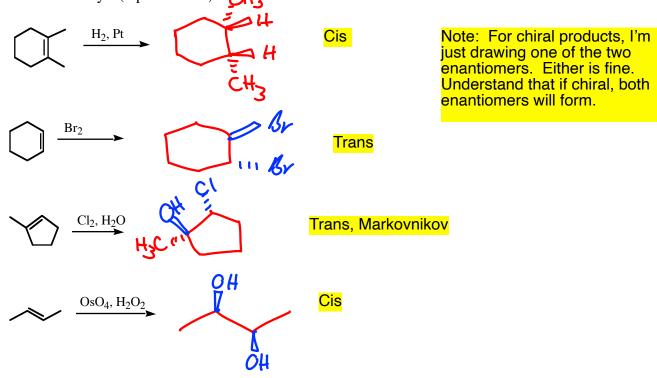




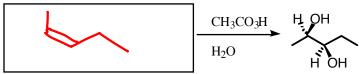
5. Predict the <u>major</u> product for the following reactions. You needn't bother to show any side products or minor products. Pay careful attention to orientation. (3 points each)



6. Predict the <u>major</u> product in each of the following reactions. Pay careful attention to stereochemistry! (3 points each)



7. Fill in the starting reactant. (4 points each)



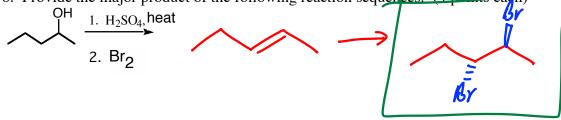
or

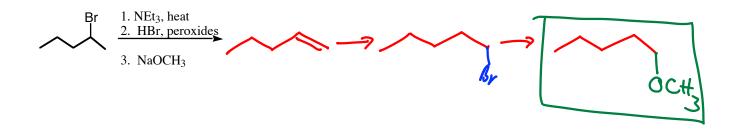
Z, not E alkene.

The mechanism of addition is trans, so to result in the "cis look" of the product as drawn, a bond rotation was required.

The product-look and the mechanism of addition are mismatched.

8. Provide the major product of the following reaction sequences. (4 points each)





- 9. What is a possible structure for a molecule A given the following: (6 points)
- a. is has the formula C_6H_{10}

EU=2

- b. it reacts with H_2/Pt to give a product with formula C_6H_{12} | Alkene
- c. upon ozonolysis (O₃; Me₂S) it gives two products, CH₂=O and a product C₅H₈O.

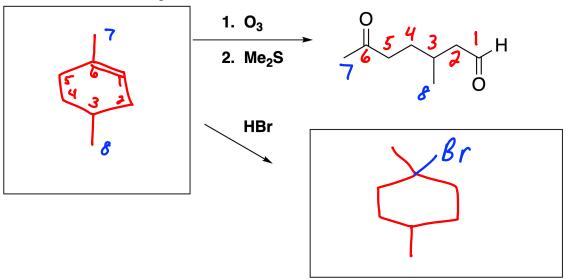
Must have an alkene with =CH on end



Many answers possible.
But, must have the following:

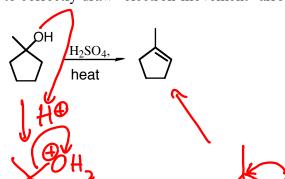
- 1. One alkene
- 2. One ring
- 3. An alkene with CH2 on end

10. Fill in the boxes. (6 points total)



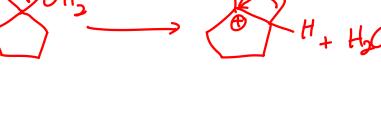
11. Provide reagents to accomplish the following transformations. (6 points each)

12. Draw the mechanisms for the following reactions. Be sure to draw all intermediates, and try to correctly draw "electron-movement" arrows. (8 points for the first, 6 points for the second)

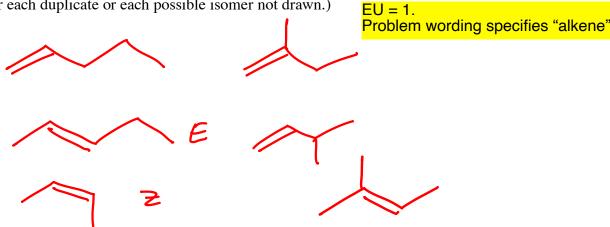


- 3 steps:
- 1. Protonation
- Loss of neutral water
 Deprotonation

Note: identify of agent who grabs the H in step 3 Could be water or HSO4-anion. I don't need that to be specified.



13. Draw as many isomers as you can for alkenes with formula C_5H_{10} . (8 points. 2 points off for each duplicate or each possible isomer not drawn.)



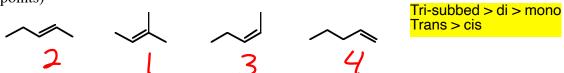
JASPERSE CHEM 350 TEST 3

VERSION 4



Ch. 7 Structure and Synthesis of AlkenesCh. 8 Reactions of Alkenes

1. Rank the following alkenes in order of stability, 1 being most stable, 4 being least stable. (3 points)

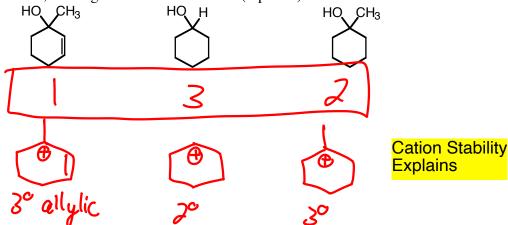


2. Determine the number of elements of unsaturation for C₅H₈O. (2 points)

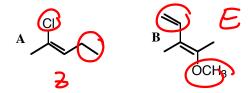


- 3. Give the proper IUPAC name or the structure for the following compounds. (3 points each)
- a. 4-vinylcyclopentene
- b. (E)-5-propyloct-2-ene Or trans-
- 4. Rank the reactivity of the following alcohols towards H_2SO_4/Δ catalyzed dehydration, 1 being

the fastest reactant, 3 being the slowest reactant. (3 points)



- 5. Which of the following statements is true for the structures shown: (3 points)
 - a. \mathbf{A} is \mathbf{Z} and \mathbf{B} is \mathbf{Z}
 - b. A is Z and B is E c. A is E and B is Z
 - d. **A** is E and **B** is E



6. Predict the <u>major</u> product for the following reactions. You needn't bother to show any side products or minor products. Pay careful attention to orientation, which is important in many of these problems. (3 points each)

b.
$$\frac{1. \text{ Hg(OAc)}_2, \text{H}_2\text{O}}{2. \text{ NaBH}_4}$$

7. Predict the <u>major</u> product in each of the following reactions. Pay careful attention to stereochemistry: stereochemistry is involved in each of these problems! (3 points each)

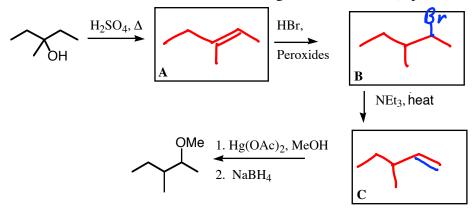
a.
$$\frac{\text{Br}_2, \text{H}_2\text{O}}{\text{CH}_3}$$
b. $\frac{\text{OsO}_4}{\text{H}_2\text{O}_2}$

Note: For chiral products I just drew one of the two enantiomers. Either is fine. You should be aware that both form, but as time-saver we usually only draw one

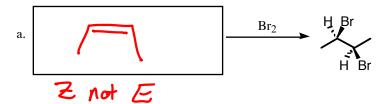
c.
$$\frac{1. \text{ BH}_3\text{-THF}}{2. \text{ H}_2\text{O}_2, \text{ NaOH}}$$

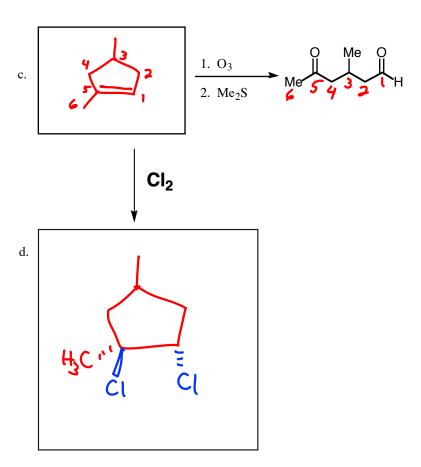
d. $\frac{\text{CH}_3\text{CO}_3\text{H}, \text{H}_2\text{O}}{\text{CH}}$

8. Fill in the intermediates in the following transformation. (3 points each)

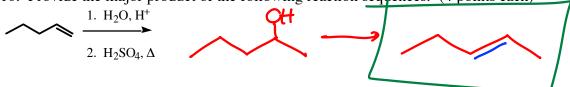


9. For the following reactions, fill in the missing <u>starting materials</u>, <u>reagents</u>, <u>or products</u>. (3 points each)

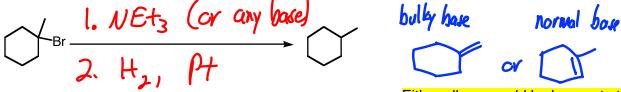




10. Provide the major product of the following reaction sequences. (4 points each)



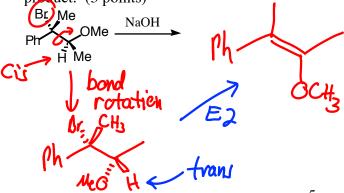
11. Provide reagents to accomplish the following transformations. (4 points each)



OH 1. Hascy, heat CH3 OH OH HAC2

Either alkene could hydrogenate to the product shown. So, whether you use a bulky base or a normal base, doesn't really matter.

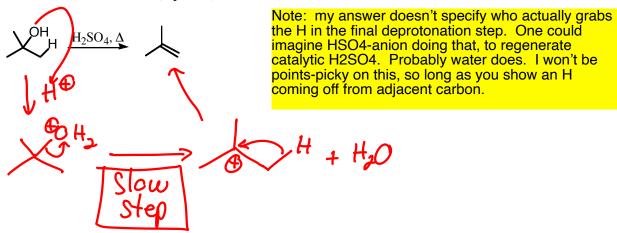
12. Provide the product for the following reaction. Be sure to show the stereochemistry of the product. (3 points)



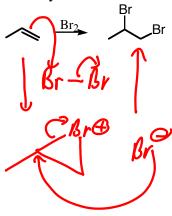
Very trick one! Notes:

- 1. 3° R-Br required E2, not SN2.
- 2. But, E2 requires a trans H.
- 3. In the original figure, the H is cis, not trans.
- 4. Bond rotation can happen to spin the H into the trans position, enabling E2 elimination and leading to the resulting stereochemistry.

13. Draw the mechanism for the following reaction, and <u>write "slow" next to the rate determining step.</u> Be sure to draw all intermediates, and to correctly draw "electron-movement" arrows or half-arrows. (4 points)



14. Draw the mechanism for the following reaction. Be sure to draw all intermediates, and to correctly draw "electron-movement" arrows or half-arrows. (4 points)



In practice, the bromide does attack the more substituted carbon of the bromonium ion ring, because the more substituted carbon has more partial-positive charge on it.

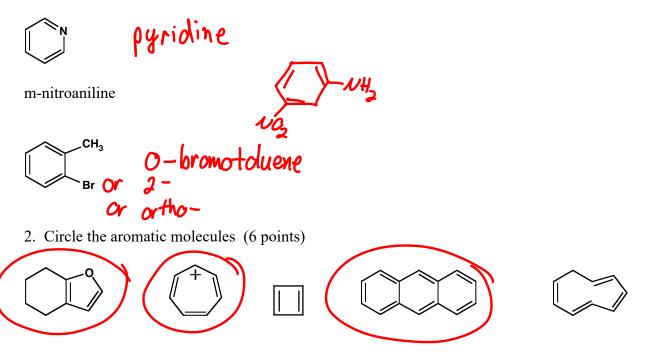
15. Formula: C₄H₈ | EU | Q| Lene, no rings Reactivity: reacts with H₂/Pt to give C₄H₁₀ | Q| Lene, no rings DRAW ALL POSSIBLE ISOMERS, INCLUDING STEREOISOMERS. (4)

DRAW ALL POSSIBLE ISOMERS, INCLUDING STEREOISOMERS. (4 isomers are possible!) (5 points)



JASPERSE CHEM 350 TEST 4 VERSION 1 Conjugation, Diels-Alder, Aromaticity, Aromatic Reactions

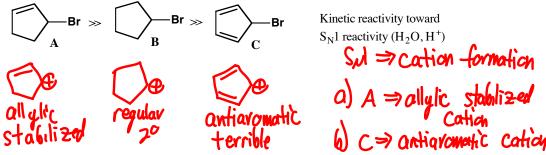
1. Provide the Name or Structure for the Following (7 points)



3. For each nitrogen in the molecule, classify the hybridization of the nitrogen atom, the hybridization of the nitrogen lone pair, and classify whether the basicity of the nitrogen is "normal" or "low". (5 points)

	Nitrogen	Lone-Pair	Nitrogen	
	Hybridization	Hybridization	Basicity	
N_a	sp ²	حم ی	nor mal	
N_{b}	Sp ²	P	low	H
N_{c}	Sp ²	P	low	a N C NH_2
N_{d}	2h3	Sp3	nor Mal	h h

4. Bromide **B** has normal reactivity (for a 2° bromide) toward S_N1 substitution, but **A** has much higher reactivity and **C** has much lower reactivity. a) Why is **A** more reactive toward S_N1 ? b) Why is **C** much less reactive toward S_N1 ? (4 points)



5. Synthesis Reactions. Draw the feature product of the following reactions (need not show any byproducts). (21 points, 3 points each)

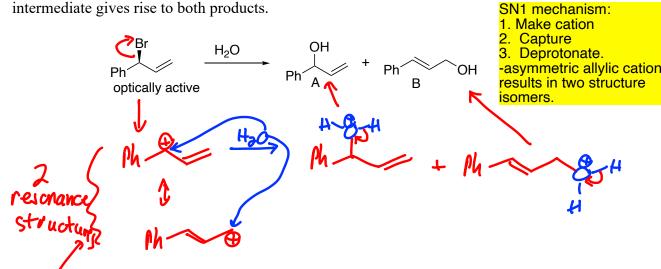
6. Design sequences for the designated conversions. (5 points each)

7. Design a synthesis for the following molecule beginning with toluene. (6 points)

8. Draw the Reactants for the following (3 points)

9. a) Draw the major product for the following reaction, and b) draw the mechanism for its formation. c) Identify the slow step. d) Draw all the resonance structures for the cation intermediate. (7 points)

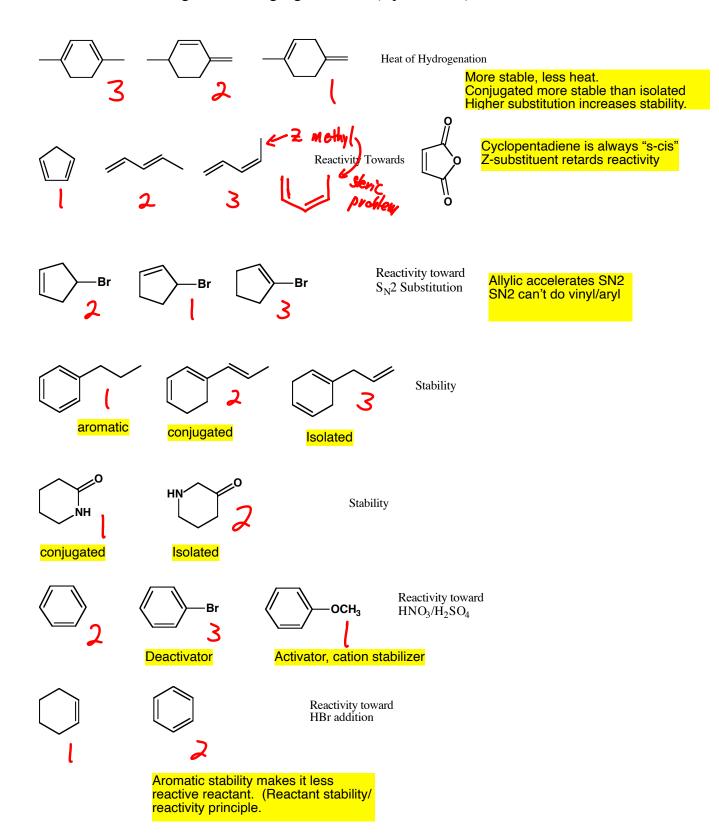
10. (9 points total) a) Draw the mechanism for the following reaction, in which a common



- b) In the above reaction, is product A chiral or achiral? A is chiral (but would be racemic)
- c) Which is the "thermodynamic" product (more stable, which builds up under equilibrating conditions)?

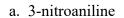
 B is the thermodynamic product, due to both higher substitution (di-substituted versus mono-substituted) and also due to conjugation with the phenyl
- d) You probably already did this, but either re-draw or identify the two key resonance structures for the intermediate in the mechanism above. (You can just circle the two of them, assuming you already sketched them above.).

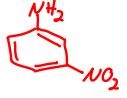
11. Rank the following, with 1 being highest/most. (2 points each)



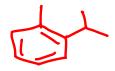
JASPERSE CHEM 350 TEST 4 VERSION 2 Conjugation, Aromatic Compounds, Reactions of Aromatic Compounds

1. Provide the Name of Structure for the following. (7 points)



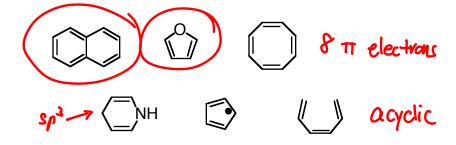


b. o-isopropyltoluene



Pyrrole

2. Circle the aromatic molecules. (7 points)



3. The molecule has 3 different nitrogens. For each of them, classify the hybridization of the nitrogen atom, the hybridization of the nitrogen lone pair, and whether the basicity of the nitrogen is "normal" or "low". (6 points)

	Nitrogen	Lone-Pair	Nitrogen
	Hybridization	Hybridization	Basicity
Na	sp2	ρ	low
Nb	5p3	5p3	nor mal
Nc	s p 2	Sp2	normal

4. Draw the major products of the following reaction (4 points).

5. Draw the Major Product of the Following Reactions. Note: I want one major product in each

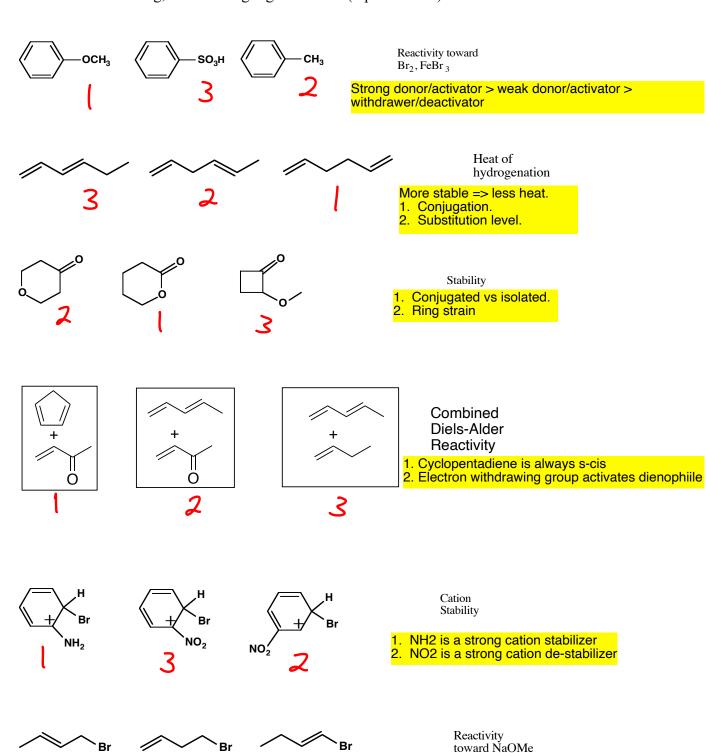
Note: This answer key is showing intermediates along the pathway for multi-step reactions, so it's easier for students to see how the final product was formed. But for test grading, all I would need is the final product.

$$\frac{1. \text{ Br}_2, \text{hv}}{2. \text{ NaOH}}$$

Radical bromination on allylic spot
 Hydroxide does SN2 >>> E2.
 Small nucleophile, and SN2 is greatly accelerated by being allylic

Note: Either of two structural isomers is acceptable as answer. First actually predominates, but that wasn't covered in class.

6. Rank the following, with 1 being highest/most. (2 points each)



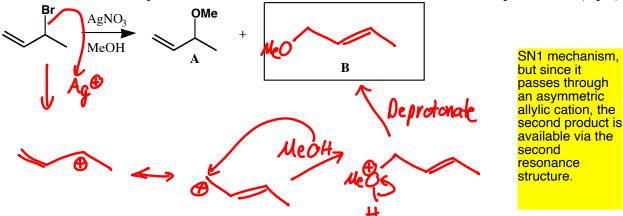
For SN2,

vinyl/aryl is bad.
 Allylic accelerates

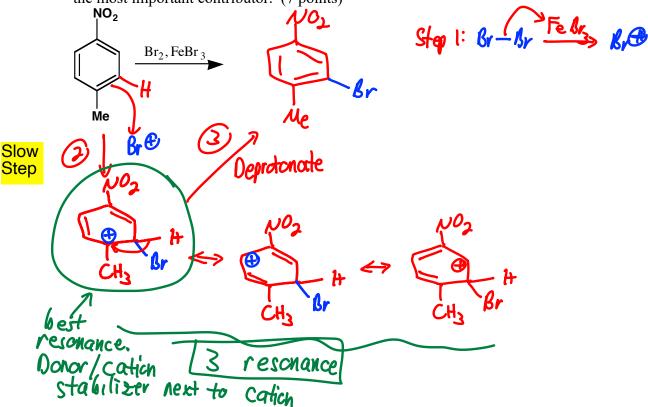
8. Treatment of an alkyl halide with methanolic AgNO₃ often promotes ionization, via the following:

$$R - X$$
 Ag^+ $R^+ + AgX$

When 3-bromo-1-butene undergoes this reaction, two isomeric products **A** and **B** are formed. Draw the structure for product **B** and the detailed mechanism for formation of product **B**. (7 pts)



9. Draw the product for the following reaction and draw the mechanism for its formation. Identify the slow step. Draw all the resonance structures for the cation intermediate and circle the most important contributor. (7 points)

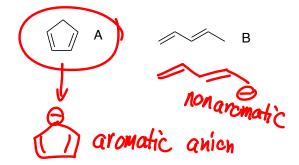


mostly go para not

ortho.

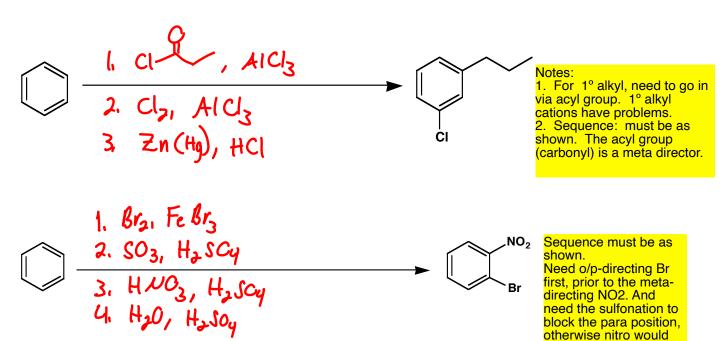
10. (3 pt) When comparing cyclopentadiene (**A**) versus 1,3-pentadiene (CH₂=CH-CH=CH-CH₃, **B**), one is much more acidic. Circle the more acidic chemical, and explain why it is much more acidic.

Since acidity involves donating a proton and getting one charge unit more negative, any neutral acid will create an anion.
The cyclopentadiene anion is aromatic.



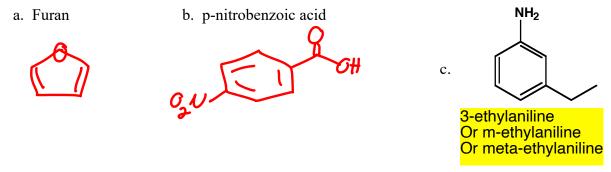
11. Draw the Reactants for the Following Reactions (6 points)

12. Provide reagents for the following transformations. (5 points each)



JASPERSE CHEM 350 TEST 4 VERSION 3 Conjugation, Aromaticity, Electrophilic Aromatic Substitution

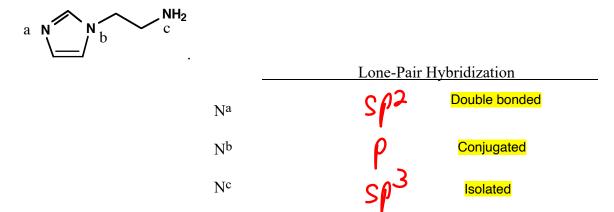
1. Provide Either the Name or the Structure for the Following Chemicals. (6 points) (3 minutes)



2. For the following substituents, classify each as 1) electron-donating or electron-withdrawing ["D" or "W"], 2) as activating or deactivating ["Act" or "Deact"], and as 3) ortho-para directing or meta directing ["o/p" or "m"]. (6 points) (2 minutes)

	-OCH ₃	O ∥ -CCH₂CH₃	-CH ₃	-Cl
1. D or W	D	ω	D	ω
2. Act or Deact	Act	Deact	Act	Deact
3. o/p or m	Olp	M	dp	de

3. The molecule below has 3 different nitrogens. For each of the nitrogens, classify the hybridization of the nitrogen atom, the hybridization of the nitrogen's lone pair, and whether the basicity of the nitrogen is "normal" or "low". (6 points, 2 min)



4. Rank the reactivity (rates!) of the following sets of molecules toward the reagents shown, 1 being most reactive, 2 being middle, and 3 being least reactive. (10 points) (6 minutes)

Molecules Being Compared Reagent H_2, Pt a. Isolated, Conjugated Aromatic, least stable most stable Br Br b. H^+, H_2O ($S_N1/E1$) Carbocation is key Br Allylic cation best 2° cation 1° cation worst c. Never s-cis Always s-cis NO_2 CH₃ d. HNO₃, H₂SO₄ deactivator **Activator** Br f. NaOMe Br Br (S_N2 reactivity) $1^{\circ} > 2^{\circ}$ for SN2 Allylic, fast

5. Draw the major product for each of the following reactions. (3 points each, 21 total, 7 minutes)

a.
$$\frac{\text{Cl}_2, \text{AlCl}_3}{\text{Cl}_2, \text{AlCl}_3}$$
b. $\frac{1. \text{SO}_3, \text{H}_2 \text{SO}_4}{2. \text{HNO}_3, \text{H}_2 \text{SO}_4}$
3. $\text{H}_2 \text{O}, \text{H}_2 \text{SO}_4$

c.
$$\frac{1, \text{HNO}_3, \text{H}_2\text{SO}_4}{2. \text{ Fe}, \text{HCl}}$$

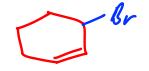
While both substituents are o/p directors, the oxygen group is much strong activator and dictates position.

d.
$$\frac{1. \text{ Br}_2, \text{hv}}{2. \text{ NaOMe}}$$

Br2 with Lewis acid adds to the ring. But under radical conditions, radical bromination occurs on the benzylic site. SN2 beats E2 because being allylic/benzylic greatly activates SN2, plus methoxide is pretty small.

e.
$$O_2N$$
 — CH_3 Cl_2 , $FeCl_3$ CH_3 CH_3

Nitro deactivates the left ring, so the methyl-activated right ring wins.



Many allylic brominations give isomers. In this case, both allylic positions are symmetry equivalent, and the allylic radical is also symmetric.

6. Provide reagents for the following transformations. (5 points each, 10 total, 6 minutes)

Note: Methyl is an o/p director, carboxylic acid is a meta director. So, you wanted to install the CI ortho prior to converting the methyl to carboxyl. But direct chlorination would have come in predominantly para, *IF* the para position was not blocked. Thus the use of sulfonation to block the para position.

Notes: Direct install of 1° alkyl is problem, due to both instability of 1° carbocations and carbocation rearrangement. So, you need to install the carbon as the carbonyl, and convert it later. When the second group gets added, the first must be a meta director. Nitro could have gone in first.

7. Daw the diene and dienophile from which the following Diels-Alder products would have come. (3 points each, 6 total, 2 minutes)

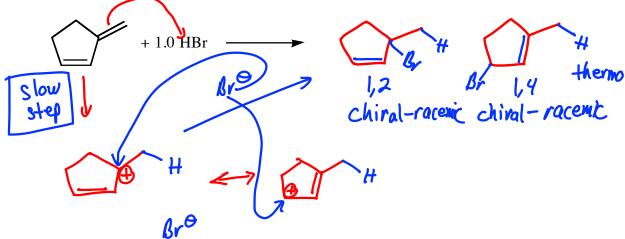
8. a. Draw the mechanism for the formation of the major product shown, and identify the "slow" step in the reaction. (6 points, 5 minutes).

b. Also draw all 4 resonance structures for the cation intermediate in the reaction. (4 points)

10. Circle the aromatic molecules: (6 points) (3 minutes)

90

9. Draw the major product or products that would result from the following reaction, and write either "chiral" or "achiral" and "optically active" or "racemic" by each product. Draw a mechanism for the reaction, and identify the "slow" step in the reaction. (8 points, 5 min)



9. Provide a synthesis for the following molecule, starting from benzene and anything else you like. (7 points, 5 min)

JASPERSE CHEM 350 FINAL EXAM 150 points total

VERSION 1

1. Provide names or structures for the following. 2 points each. Specify stereochemistry when appropriate!

$$Cl$$
— CH_3

trans-1-chloro-4methylcyclohexane Note: Version 1 is relatively representative in terms of length. Version 2 is longer than the real test will be. But provides lots more practice.

(R)-2-bromobutane

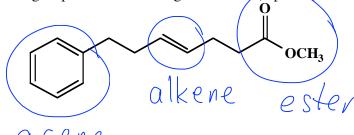
Optically active

m-isopropylphenol

Z-2-chloro-2-hexene

m-butylphenol or meta-butylphenol or 3-butylphenol

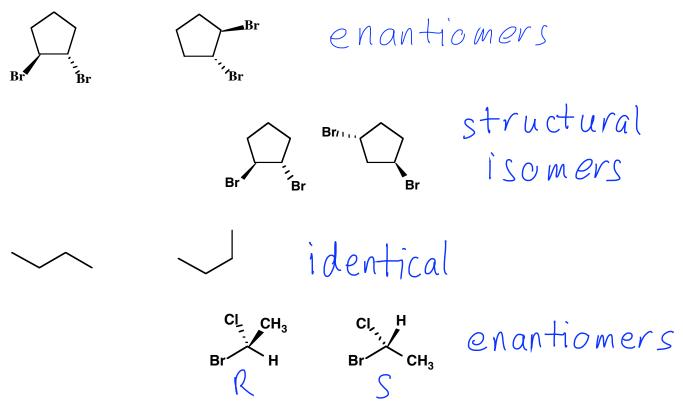
2. Identify the functional groups in the following molecule. (4 points)



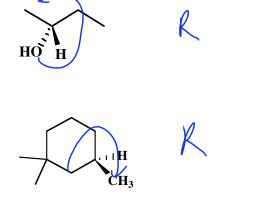
or aromatic

3. Predict the major products for the following reactions. Pay careful attention when orientation is a factor. Draw just one major product in each case. (3 points each)

4. Classify the pairs of molecules as totally different, identical, structural isomers, diastereomers, or enantiomers. (2 points each)



5. Classify each chiral carbon as R or S. (2 points each)



6. Classify the hybridization and bond angles (109, 120, or 180) at the labelled atoms. (5 points)

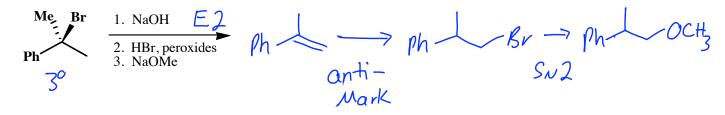
7. Draw the mechanisms for the following reactions. For any radical reactions, draw

propagation steps only. 5 points each.

OCH₃

$$Cl_2$$
 $AlCl_3$
 Cl_2
 $AlCl_3$
 Cl_2
 Cl_2
 Cl_2
 Cl_2
 Cl_3
 Cl_4
 $Cl_$

8. Draw the products of the following multi-step sequences. (4 points each)



OH
$$\frac{1. \text{ H}_2\text{SO}_4}{2. \text{ HBr, Peroxides}}$$

$$\frac{3. \text{ NEt}_3}{2. \text{ DU/Cy}}$$

9. Draw as many structural isomers as you can for C_6H_{14} . Circle any that are chiral. (Note: be careful! You will lose points for any repeats!) (6 points)

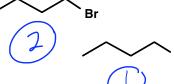


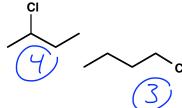
10. Rank the Following, from most to least. 2 points each.

a. Reactivity toward S_N2 T>Br>Cl

0720

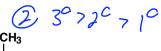
b. Stability

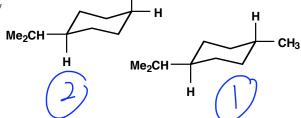


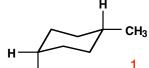




c. Stability







Me₂CH

- 1. Equatorial preferred
- 2. If forces to be axial, worse for big group than for smaller group

d. Acidity

PhCO₂H

(CH₃)₂NH

HC1

CH₃CH₂OH

- 1. Anion stability
- 2. HCl by memory is strong
- 3. Electronegativity factor
- 4. Resonance factor

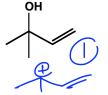
e. Stability



Ме

- staggered vs eclipsed
- 2. Anti > gauche
- 3. Eclipsed > total eclipsed

f. Reactivity toward H₂SO₄/Acatalyzed dehydration



ОН

Cation stability is key

g. Boiling Point

OH

3

OH 2

- 1. Hydrogen bonding
- 2. Molecular weight factor

11. Provide reagents for the following transformations. You may use anything you like. Each can be done within ≤ 3 steps. (4 points each)

12. Provide the appropriate reactant for the following transformation. (3 points)

Theory = Actual = 12 13. Suggest a structure for **X**, given the following info: (5 points) 18 Formula: C_8H_{12} It Reacts With excess H₂/Pt to produce C₈H₁₆ alkenes When it reacts with O₃/Me₂S, one of the products is CH₂=O. 14. Which of the following are aromatic Protonation gives

H Osymmetric allylic

cation, leading to

two isomers. Protonation

on left end would

have given an inferior 15. Draw the products and mechanism for the following reaction: 16. Rank the following: O Dienophile-wise better, two w groups (2) Diene-wite Combined Br S_N2 Reactivity ONa

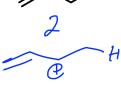
1

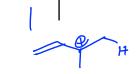
Note: Good for practice, but significantly longer than the real one will be.

1. Rank the Following, from most to least. 2 points each.

d. Acidity
$$CH_3OH$$
 $PhCO_2H$ NH_3 CH_3CH_3 \checkmark









g. Reactivity toward Br ₂/hv



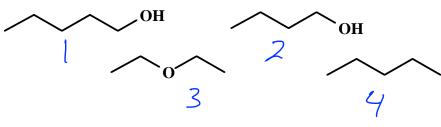


h. Reactivity toward S_N2

Ph'

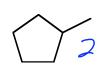


i. Boiling Point



j. Stability





2. Provide names or structures for the following. 3 points each. Note: don't forget to specify stereochemistry!

If optically active: (15,35)-1,3-dimethyloyclohexane

b.

allylcyclohexane or 3-cyclohexyl propene

c. optically active
$$S-2$$
—butanol

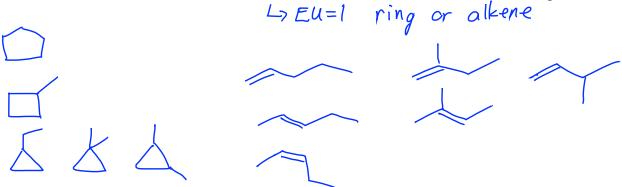
f. trans-1-bromo-3-isopropylcyclopentane

3. Classify the pairs of molecules as totally different, identical, structural isomers, diastereomers, or enantiomers. (2 points each)

3. (continued) Classify the pairs of molecules as totally different, identical, structural isomers, diastereomers, or enantiomers. (2 points each)



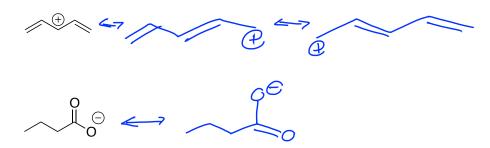
4. Draw at least four different isomers for C_5H_{10} . (There are lots more than four...) (6 points)



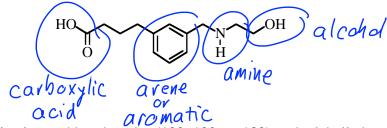
- 5. (a) Draw the appropriate number of lone pairs on the oxygen atom,
- (b) Assign a formal charge on oxygen if appropriate,
- (c) Draw an additional resonance structure for the following, and
- (d) Identify which of the two structures would make the greater contribution to the hybrid. (4 points)



6. Draw resonance structures for each of the following:.



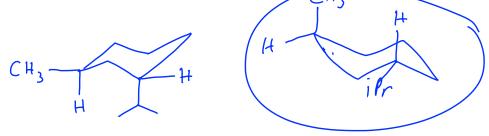
7. Identify the functional groups in the following molecule. (4 points)



8. Classify the hybridization and bond angles (109, 120, or 180) at the labelled atoms. (4 points)

$$rac{2}{10}$$
 $rac{3}{3}$ C-1 $rac{5}{7}$ $rac{3}{109}$ C-3 $rac{5}{7}$ 109

- 9. Draw both chair conformations of trans-1-methyl-3-isopropylcyclohexane, and circle the more stable one. (5 points.)
- Note 1: It will simplify things if you abbreviate the isopropyl group as "R".
- Note 2: Make sure that your second chair has the same "configuration" as the first, and is not an enantiomer.

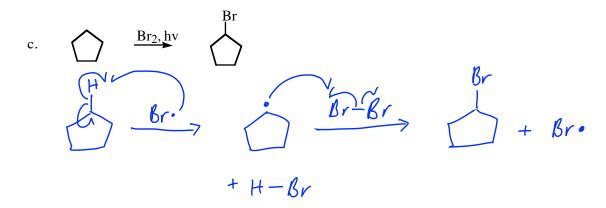


10. Classify each chiral carbon as R or S. (Some structures may have more than one chiral carbon!) (2 points each)



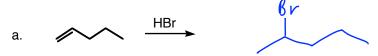
11. Mechanisms Problem. Draw the mechanism for the following reactions, and write "slow" next to the rate-determining step. Be sure to draw all intermediates, and to correctly draw "electron-movement" arrows or half-arrows. For radical reactions, draw propagation steps only. 4 points each.

a.
$$H_2O, H^+$$
 $H_2O \rightarrow H$
 $H_2O \rightarrow H$



d.
$$\frac{H}{Ph}$$
 $\frac{H}{H_{2}O}$ $\frac{H}{$

12. Predict the major products for the following reactions. In each case, pay careful attention to orientation and stereochemistry. Draw just one product in each case. (3 points each)



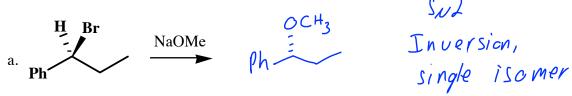
b.
$$H_2O, H^+$$

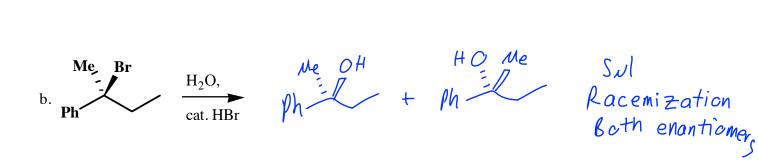
d.
$$\underbrace{\qquad \qquad }_{b. \text{ Me}_2S}$$

e.
$$\frac{Br_2, hv}{bv}$$

h.
$$\frac{1. \text{ NEt}_3}{2. \text{ Cl}_2}$$

13. Draw the <u>substitution</u> products for the following reactions. (Do not draw any accompanying elimination products.) Include stereochemistry in your answer, and if two substitution products are formed, draw them both. Assume the starting material is optically active as drawn. (3 points each)





14. Draw the products of the following multi-step sequences. (4 points each)

a.
$$\underbrace{\begin{array}{c} 1. \text{ H}_2\text{SO}_4 \\ 2. \text{ CH}_3\text{CO}_3\text{H}, \text{H}_2\text{O} \end{array}}_{\text{OH}}$$

a.
$$\frac{Br}{2, Br_2}$$
Br
Br
Br

b.
$$\frac{OH}{2} \frac{1}{PhCO_3H}$$

16. Provide the appropriate reactant for the following transformation. (3 points)

17. Suggest a structure for A that is consistent with the following information. (There is more than one possible solution, but you only need to provide one.) (5 points)

$$E U = 2 A \frac{1. O_3}{2. Me_2 S} C + C_2 H_4 O$$

$$C_7 H_{12}$$

$$C_5 H_8 O$$

$$C_5 H_8 O$$

$$C_7 H_{12}$$

$$C_7 H_{12}$$

$$C_7 H_{14}$$

$$C_7 H_{15}$$

18. Draw the products for the following reactions:

Flawed problem. Not clear which allylic cation you_a. should use. Protonation on the left gives allylic where both + carbons are 2°; protonation on the right gives a hybrid of a 3°/1° cation.

g.

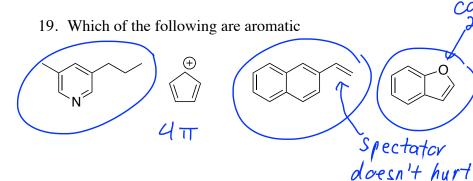
$$\frac{1}{3} + \frac{0}{4} + \frac{0}{3} + \frac{0}$$

$$\frac{H_2O}{\text{Draw substitution product(s) only}}$$

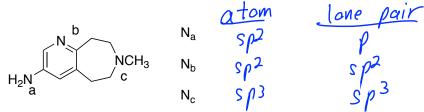
e.
$$\frac{1. \text{ Br}_2, \text{FeBr}_3}{2. \text{ HNO}_3, \text{H}_2\text{SO}_4}$$

$$\frac{1. \quad \text{Br} + \text{AlCl}_3}{2. \quad \text{KMnO}_4} \quad \text{Ho}$$

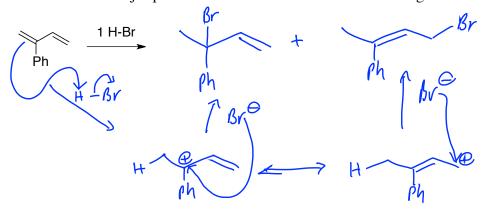
$$\begin{array}{c|c} & 1. \ \, \text{Br}_2, \, \text{hv} \\ \hline 2. \ \, \text{NaOCH}_3 \end{array}$$



20. Classify the lone pair hybridization on the three nitrogen atoms in the following molecule:



21. Draw the major products and mechanism for the following reaction:



Protonation occurs on the leftmost carbon, because that gives by far the best cation. 3° allylic and conjugated to the phenyl as well. The asymmetric allylic cation gives two different products (1,2 and 1,4 addition).

22. Draw the major product and mechanism for the following reaction. Draw all of the resonance structures for the key carbocationic intermediate

$$\frac{HNO_3}{H^2SO_4}$$

$$O_2N$$

$$\frac{H}{VO_2}$$

$$O_2N$$

$$\frac{H}{VO_3}$$

$$O_3N$$

$$\frac{H}{VO_3}$$

$$\frac{H}{VO_3$$

$$O_2N$$
 H
 NO_2
 O_2N
 H
 NO_2
 O_2N
 H
 NO_2

23. Design a synthesis for the following:

$$\frac{1. \text{ Cl} + \text{AlCl}_3}{2. \text{ Zn}(H_q), \text{ HCl}}$$
3. $H \times O_3$, $H_2 \times O_4$
 O_2N

24. Explain why **A** is more acidic than **B**, but **C** is less reactive than **D** towards $S_N 1$ reactivity

25. Rank the following