

HIGH SCORE 188  
LOW SCORE 30  
AVERAGE 135

1

Student Name (first, last):

ANSWER KEY

Student Number:

CHEMISTRY 3311  
FINAL EXAMINATION

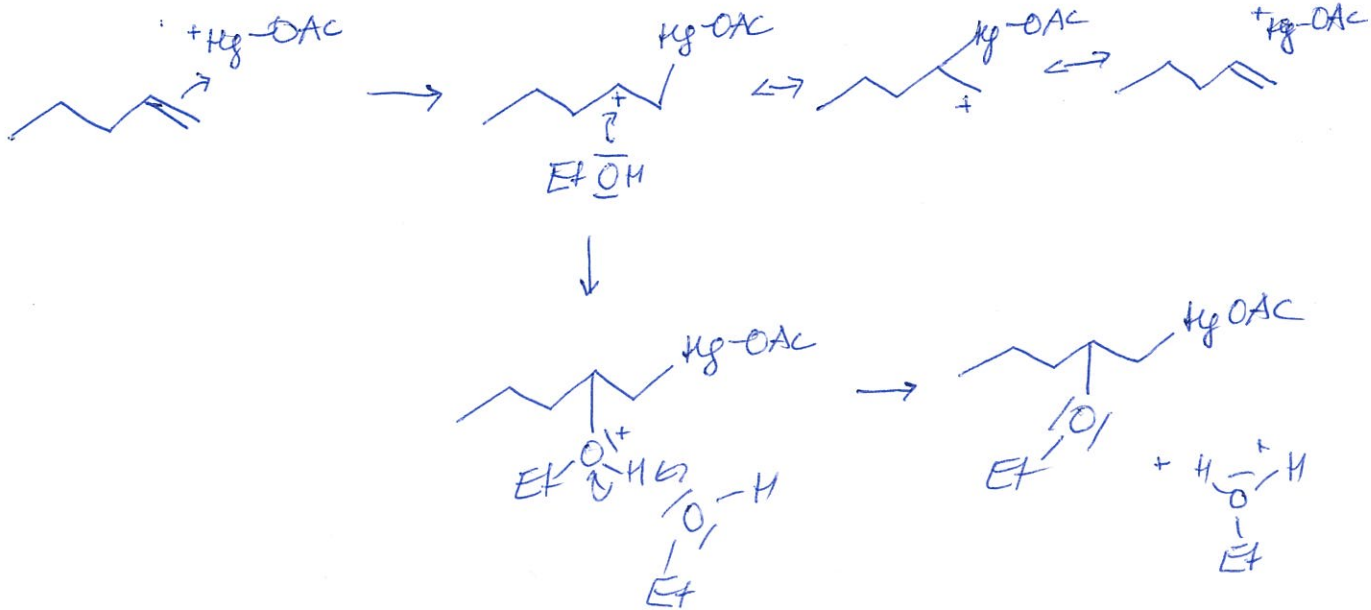
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1. (40 points) Check the correct statements only (make no other marks):

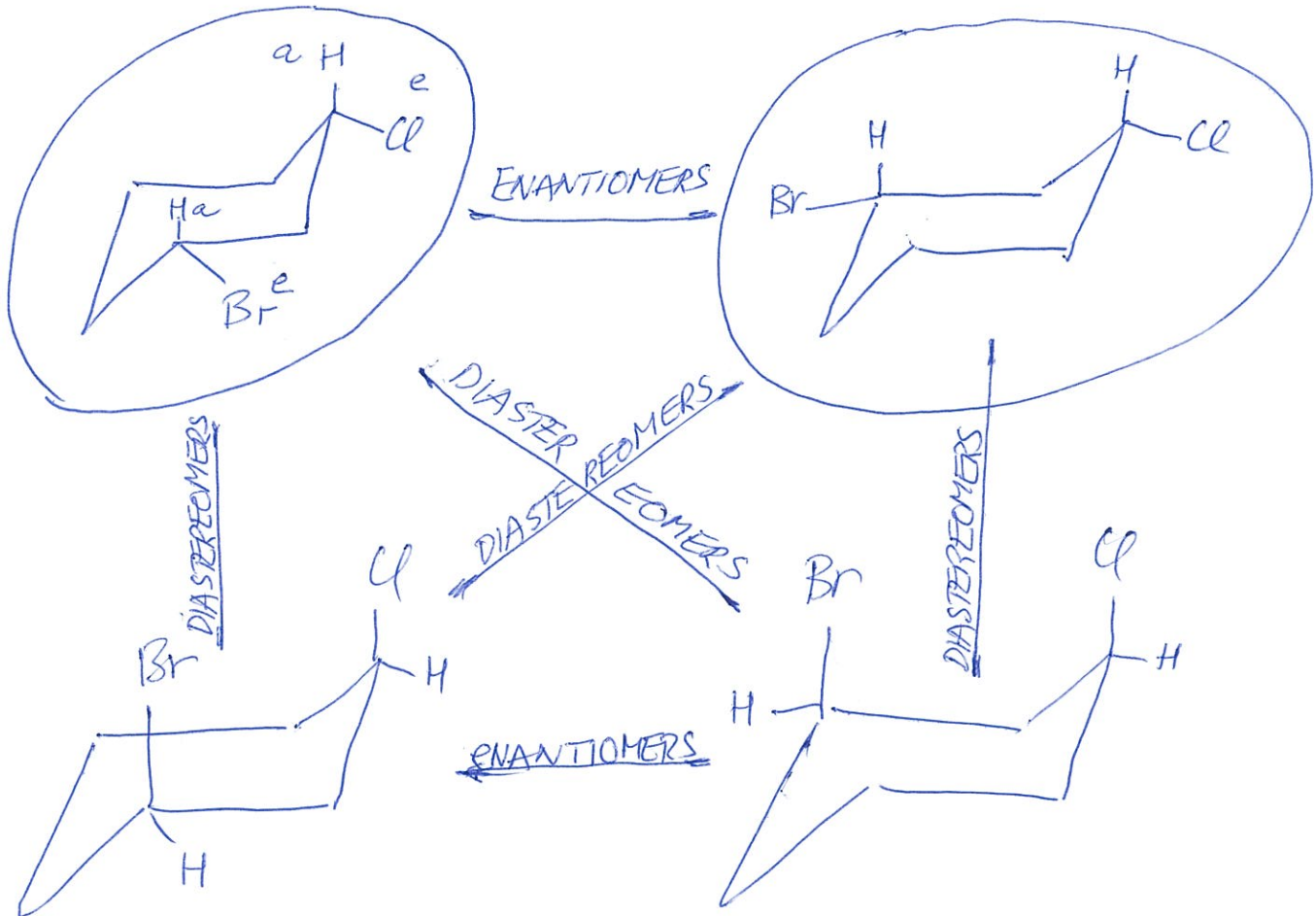
- The dipole moment of  $\text{CO}_2$  is smaller than that of  $\text{H}_2\text{O}$ .
- The molecule of ammonia,  $\text{NH}_3$ , is not planar.
- In the ground electronic state, the  $\sigma$  bonding orbitals of ethane contain 14 valence electrons..
- The transition state of a pericyclic reaction contains a linear array of interacting orbitals.
- The 1-cyclopropen-3-yl cation is stabilized by electron delocalization.
- $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl}$  reacts with water much more slowly than  $\text{CH}_3\text{CH}_2\text{SCH}_2\text{CH}_2\text{Cl}$ .
- Pyridine,  $\text{C}_5\text{NH}_5$ , is not aromatic.
- Both *cis*-cyclooctene and *trans*-cyclooctene are stable at room temperature.
- The  $\text{S}_{\text{N}}2$  substitution reaction occurs with retention of stereochemistry at the carbon atom on which the substitution takes place.
- Neopentyl halides are particularly reactive in  $\text{S}_{\text{N}}2$  substitution reactions.
- Sulfoxides can be oxidized to sulfones with hydrogen peroxide.
- A molecule that contains one asymmetric carbon is chiral.
- Specific rotation of a compound will decrease by a factor of two if its concentration is doubled.
- The central carbon of allene is  $\text{sp}^2$  hybridized.
- 1-Butene has a more negative heat of formation than 2-butene.
- (2*S*, 3*S*)-pentane-2,3-diol and (2*S*, 3*R*)-pentane-2,3-diol are enantiomers.
- Penta-2,3-diene is chiral.
- The chair-chair interconversion in *trans*-decalin (bicyclo[4.4.0]decane) is facile.
- Hydroboration of an alkene is a pericyclic reaction.
- Dichlorocarbene,  $\text{CCl}_2$ , has an octet of valence electrons on the carbon atom.
- An orbital is a region of space where an electron is likely to be found.
- Benzene and 1,3,5-cycloheptatriene have the same unsaturation number.
- The slowest step in a multistep reaction sequence is called the rate determining step.
- The bond dissociation energy of the H-C bond is higher than that of the H-Si bond.
- 1,3-Cyclobutadiene is aromatic and extremely unreactive.
- An electrostatic potential map (EPM) is a picture of the total electron density in a molecule.
- Base-induced elimination in an alkyl halide yields the most substituted alkene (Zaitsev rule).
- Transition state energies of reactions producing high-energy intermediates resemble the energies of the intermediates themselves (Hammond postulate).
- Fluoride is a weaker nucleophile than iodide in water, but not in dimethylformamide.

- (X) The Diels-Alder reaction of a diene with an alkene yields a cyclic product.
- (X) The most stable occupied  $\pi$  molecular orbital of benzene has no nodes cutting across CC bonds.
- (X) The  $pK_a$  of 2,2,2-trifluoroethanol is lower than the  $pK_a$  of ethanol.
- ( ) A sulfur atom can accommodate twelve electrons in its valence shell.
- (X) Tertiary alkyl halides are particularly unreactive in  $S_N2$  substitution reactions.
- (X) Sharpless epoxidation uses a chiral reagent to convert an achiral allylic alcohol almost entirely to only one of the two possible enantiomers of an epoxide.
- ( ) The two protons of the  $CH_2$  group in ethanol are diastereotopic.
- ( ) In the absence of water, secondary alcohols are oxidized to aldehydes with  $CrO_3$ .
- ( ) The two chair conformations of *tert*-butylcyclohexane have the same heat of formation.
- (X) In general, tertiary carbocations are more stable than secondary carbocations.
- ( )  $Me_3S^+$  is a stronger methylating agent than  $Me_3O^+$ .

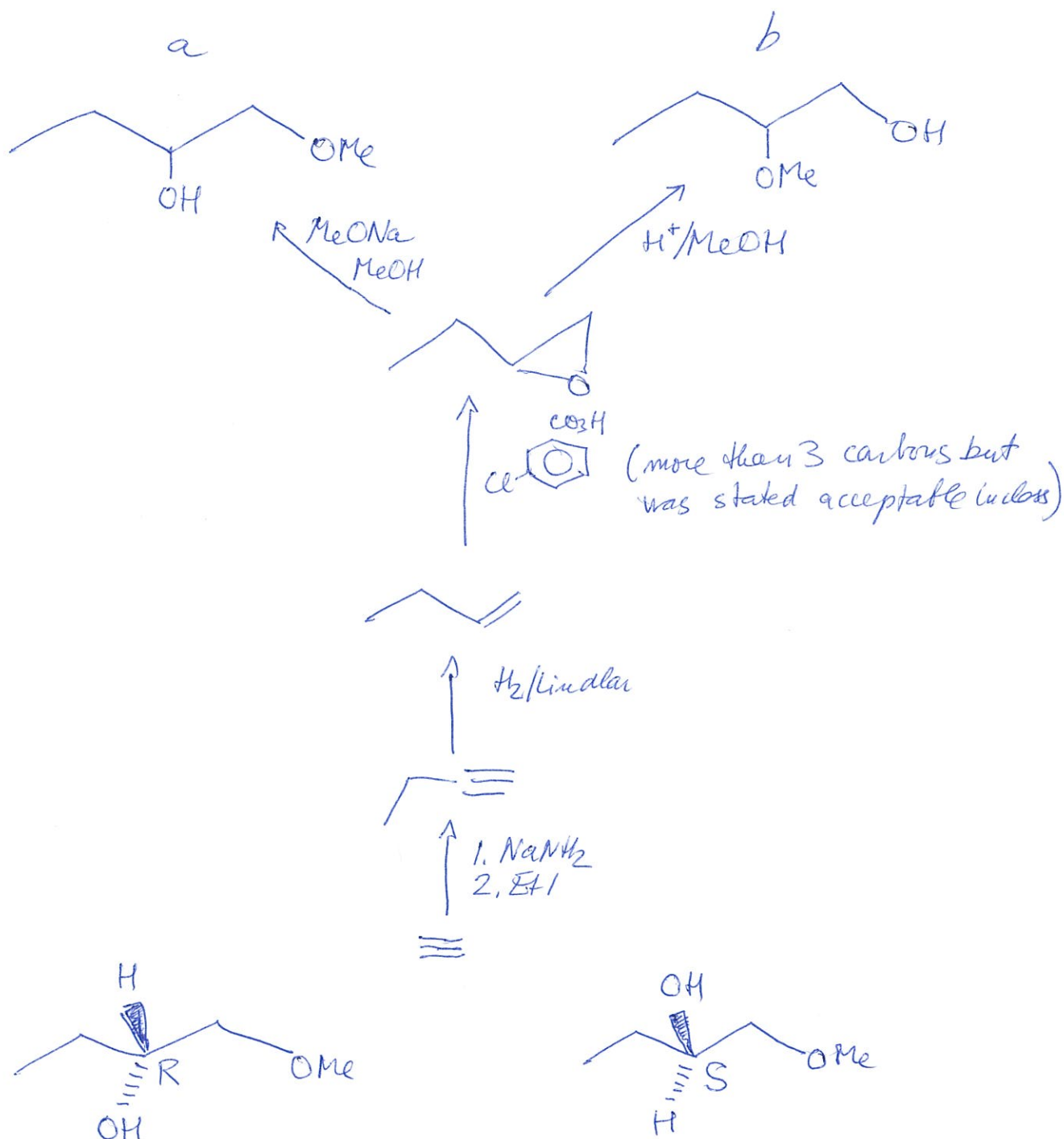
2. (20 pts) Write a plausible mechanism for the ethoxymercuration of 1-pentene by reaction with  $\text{Hg}(\text{OAc})_2$  in an ethanol solution (you do not need to show the reduction step that is usually performed subsequently). Include all steps and intermediates and use curved arrows to indicate electron movement in each step. If you need more than one resonance structure to show the structure of an intermediate correctly, draw all of them. Hint: remember how many valence electrons Hg has.



3. (30 pts) Draw a three-dimensional view of all possible stable chair conformers of *cis*-1,3-bromochlorocyclohexane. In one conformer, label the substituents *a* for axial and *e* for equatorial. Write the names of all stereochemical relationships between the conformers (enantiomers, diastereomers). Circle the most stable one (or ones).



4. (40 pts) Propose efficient preparation of the racemic form of (a) 1-methoxy-2-hydroxybutane and (b) 1-hydroxy-2-methoxybutane from acetylene using reagents that contain no more than two carbon atoms in the molecule. Show all steps and all reagents (no mechanisms, no curved arrows, no solvents). Draw a three-dimensional (perspective) view of both enantiomers of the product (a) and label their asymmetric centers R or S as appropriate.



5. (30 pts) Write the structures of all principal organic products of the following reactions after workup. You do not need to show solvents, mechanisms, or curved arrows. Reagents applied concurrently are separated with a comma. Reagents applied after isolation of the product of the preceding step are numbered 1. 2. ....

(a) 1-hexyne +  $\text{H}_2\text{SO}_4, \text{H}_2\text{O}, \text{Hg}^{2+} \rightarrow$



(b) 1-butanol + 1.  $\text{PBr}_3$  2.  $\text{Mg}$  3.  $\text{D}_2\text{O} \rightarrow$



(d) 1-hexyne + 1.  $(\text{isoamyl})_2\text{BH}$  2.  $\text{H}_2\text{O}_2, \text{OH}^- \rightarrow$



(e) 1-pentyl iodide + 1. *t*-BuOK, *t*-BuOH 2. diiodomethane, Zn/Cu →



(g) 1-pentene + 1.  $B_2H_6$  2.  $H_2O_2$ ,  $OH^-$  3.  $Na_2Cr_2O_7$ ,  $H_2SO_4$ ,  $H_2O$  →



(h) 2-bromo-3,3-dimethylbutane + ethanol, heat →



6. (40 pts) Propose efficient preparations of (a) racemic and (b) meso hexane-3,4-diol from 3-hexyne using reagents that contain no more than three carbon atoms in the molecule. Show all steps and all reagents (no mechanisms, no curved arrows, no solvents). Draw both enantiomers of the racemic product and label their asymmetric centers R or S as appropriate.

