

**Student Name (first, last):**

**Student Number:**

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**CHEMISTRY 3311**  
**FINAL EXAMINATION**

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

- Carbene,  $\text{CH}_2$ , 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.
- 1-Pentene and cyclopentane have the same unsaturation number.
- The fastest step in a multistep reaction sequence is called the rate determining step.
- The bond dissociation energy of the H-S bond is higher than that of the H-O bond.
- Cyclooctatetraene is aromatic and extremely unreactive.
- An electrostatic potential map (EPM) is a picture of the total electron density in a molecule, usually colored to show areas of negative charge in red and areas of positive charge in blue.
- Zaitsev rule for the direction of base-induced elimination in alkyl halides states that the least substituted alkene will be formed.
- According to the Hammond postulate, energies of transition states for reactions involving unstable intermediates resemble the energies of the intermediates themselves.
- In general, primary carbocations are more stable than secondary carbocations.
- The central carbon of allene and both carbons of acetylene are  $sp$  hybridized.
- 2,3-Dimethyl-2-butene has a more negative heat of formation than 2-ethyl-1-butene.
- Thiols react with iodine in water to yield sulfoxides.
- A molecule that contains at least one asymmetric carbon must be chiral.
- Specific rotation of a compound will increase by a factor of two if its concentration is doubled.
- (2*S*, 3*S*)-pentanediol and (2*S*, 3*R*)-pentanediol are diastereomers.
- (*E*)-2-pentene and (*Z*)-2-pentene are enantiomers.
- The two chair conformations of methylcyclohexane are enantiomers of each other.
- Hepta-3,4-diene is chiral.
- The chair-chair interconversion in *cis*-decalin (bicyclo[4.4.0]decane) is facile.
- Hydroboration is an anti addition reaction.
- Both *cis*-cyclohexene and *trans*-cyclohexene are stable at room temperature.
- The  $\text{S}_{\text{N}}2$  substitution reaction occurs with inversion of stereochemistry at the carbon atom on which the substitution takes place.
- Tertiary alkyl halides are particularly reactive in  $\text{S}_{\text{N}}2$  substitution reactions.
- Since the acetate anion and the azide anion have similar basicity, they also have similar nucleophilicity.

- ( ) In water, fluoride is a stronger nucleophile than iodide, but in dimethylformamide, the opposite is true.
- ( ) The  $pK_a$  of 2,2,2-trichloroethanol is higher than the  $pK_a$  of ethanol.
- ( ) A sulfur atom can accommodate twelve valence electrons in its valence shell.
- ( ) Neopentyl halides are particularly unreactive in  $S_N2$  substitution reactions.
- ( ) Sharpless epoxidation uses achiral reagents 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 enantiotopic.
- ( ) Secondary alcohols are oxidized to ketones with  $CrO_3$ .
- ( )  $Me_3S^+$  is a weaker methylating agent than  $Me_3O^+$ .
- ( ) The extinction coefficient  $\epsilon$  of benzene at 270 nm will double if the concentration of benzene in the solution is doubled.
- ( ) The transition state of a pericyclic reaction contains a cyclic array of interacting (overlapping) orbitals.
- ( ) The allyl cation is stabilized by electron delocalization.
- ( )  $CH_3CH_2CH_2CH_2CH_2Cl$  reacts with water much more slowly than  $CH_3CH_2SCH_2CH_2Cl$ .
- ( ) The cyclic sulfide, thiophene  $(CH)_4S$ , is not aromatic.
- ( ) The Diels-Alder reaction of cyclopentadiene with another molecule of cyclopentadiene (dimerization) is reversible.
- ( ) The most stable occupied  $\pi$  molecular orbital of benzene has one node cutting across two CC bonds.

2. (20 pts) Write a plausible mechanism for the methoxymercuration of 1-butene by reaction with  $\text{Hg}(\text{OAc})_2$  in a methanol solution. 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. (20 pts) Draw the Newman projection of all stable conformers of *n*-butane (view along the C(2)-C(3) axis). Write down the names of these conformations and show the stereochemical relationships between each pair (enantiomers, diastereomers).

4. (30 pts) Propose efficient preparations of the racemic forms of (a) cis and (b) trans isomer of 1,1-dichloro-2-ethyl-3-methylcyclopropane 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 all enantiomers of both cis and trans products and label their asymmetric centers R or S as appropriate.

5. (40 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) cyclohexylacetylene +  $\text{H}_2\text{SO}_4, \text{H}_2\text{O}, \text{Hg}^{2+} \rightarrow$

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

(c)  $(\text{CH}_3)_2\text{C}=\text{CH}_2$  + 1. *m*-chloroperbenzoic acid 2.  $\text{MeONa}, \text{MeOH} \rightarrow$

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

(e) 1-butyl bromide + 1. *t*-BuOK, *t*-BuOH 2. O<sub>3</sub> 3. dimethyl sulfide →

(f) cyclopentene + 1. OsO<sub>4</sub>, (CH<sub>3</sub>)<sub>3</sub>NO 2. H<sub>5</sub>IO<sub>6</sub> →

(g) 1-heptene + 1. B<sub>2</sub>H<sub>6</sub> 2. H<sub>2</sub>O<sub>2</sub>, OH<sup>-</sup> 3. Na<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>, H<sub>2</sub>SO<sub>4</sub>, H<sub>2</sub>O →

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

6. (30 pts) Propose efficient preparations of (a) the cis and (b) the trans isomer of 1,2-cyclohexanediol (racemic where applicable) from cyclohexanol 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 the most stable conformer of the cis and of the trans product (if a product is racemic, draw both enantiomers and label their asymmetric centers R or S as appropriate).

7. (20 pts) Write the structures of all major products and show the mechanism of the addition of HBr to 1,3-butadiene in the absence of radicals. Include all steps and intermediates and use curved arrows to indicate electron movement in each step. If appropriate, label kinetic control products and thermodynamic control products. If an intermediate is described by more than one resonance structure, draw them all.