

Student Name (first, last):

Student Number:

CHEMISTRY 3371
FIRST MIDTERM EXAMINATION

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1. (15 points) Check the correct statements only and make no other marks:

- In the ground electronic state, the π orbitals of cyclobutadiene contain six electrons.
- An orbital is a region of space where an electron is likely to be found.
- Diels-Alder reactions are often performed at elevated temperature in order to shift the equilibrium to the product side.
- Internal acetylenes can be reduced to trans alkenes using sodium in liquid ammonia.
- An electrostatic potential map (EPM) is a picture of the total electron density on a surface surrounding a molecule, color coded to show areas of negative charge in red and areas of positive charge in blue.
- Under kinetic control, 1,3-dienes add hydrogen halides to yield the product of 1,4 addition.
- An electrostatic potential map (EPM) is a picture of the ease with which a positive point charge can be brought from infinity to various locations on an isodensity surface surrounding a molecule (red, easier, and blue, harder).
- Penta-2,3-diene is chiral.
- Cyclooctatetra-1,3,5,7-ene is aromatic.
- Pyridine is not aromatic.
- A molecule of an allene contains two cumulated C=C bonds with three sp^2 hybridized carbon atoms.
- Nitration of benzene followed by bromination produces *m*-bromonitrobenzene.
- Under radical bromination conditions, toluene is converted to benzyl bromide.
- Friedel-Crafts acylation requires the use of an equivalent of $AlCl_3$, while for Friedel-Crafts alkylation a catalytic amount is sufficient.
- Halogen substituents retard electrophilic aromatic substitution.

2. (30 pts) Write a plausible mechanism for the Hg^{2+} -catalyzed hydration of propyne (include all steps and intermediates and use curved arrows to indicate electron movement in each step). Be sure to remember how many valence electrons an Hg atom has.

3. (20 pts) Propose a reaction sequence for the synthesis of (*E*)-4-hexenal from acetylene and reagents containing at most five carbon atoms in the molecule. Show all steps and all reagents (no mechanisms, no curved arrows, no solvents).

4. (20 pts) Write the structures of the principal organic product in the following reactions. You do not need to show solvents, mechanisms, or curved arrows.

(a) *o*-chlorotoluene + KMnO_4 , $100\text{ }^\circ\text{C}$, 4 h \rightarrow

(b) benzyl chloride + NaI in acetone, heat \rightarrow

5. (15 points) Sketch the form of the four π and π^* molecular orbitals of 1,3-butadiene and indicate their relative energies on a vertical scale.