

KEY

1

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

**Student Number:**

---

---

**CHEMISTRY 3371**  
**SECOND MIDTERM EXAMINATION**

Josef Michl  
March 12, 2009

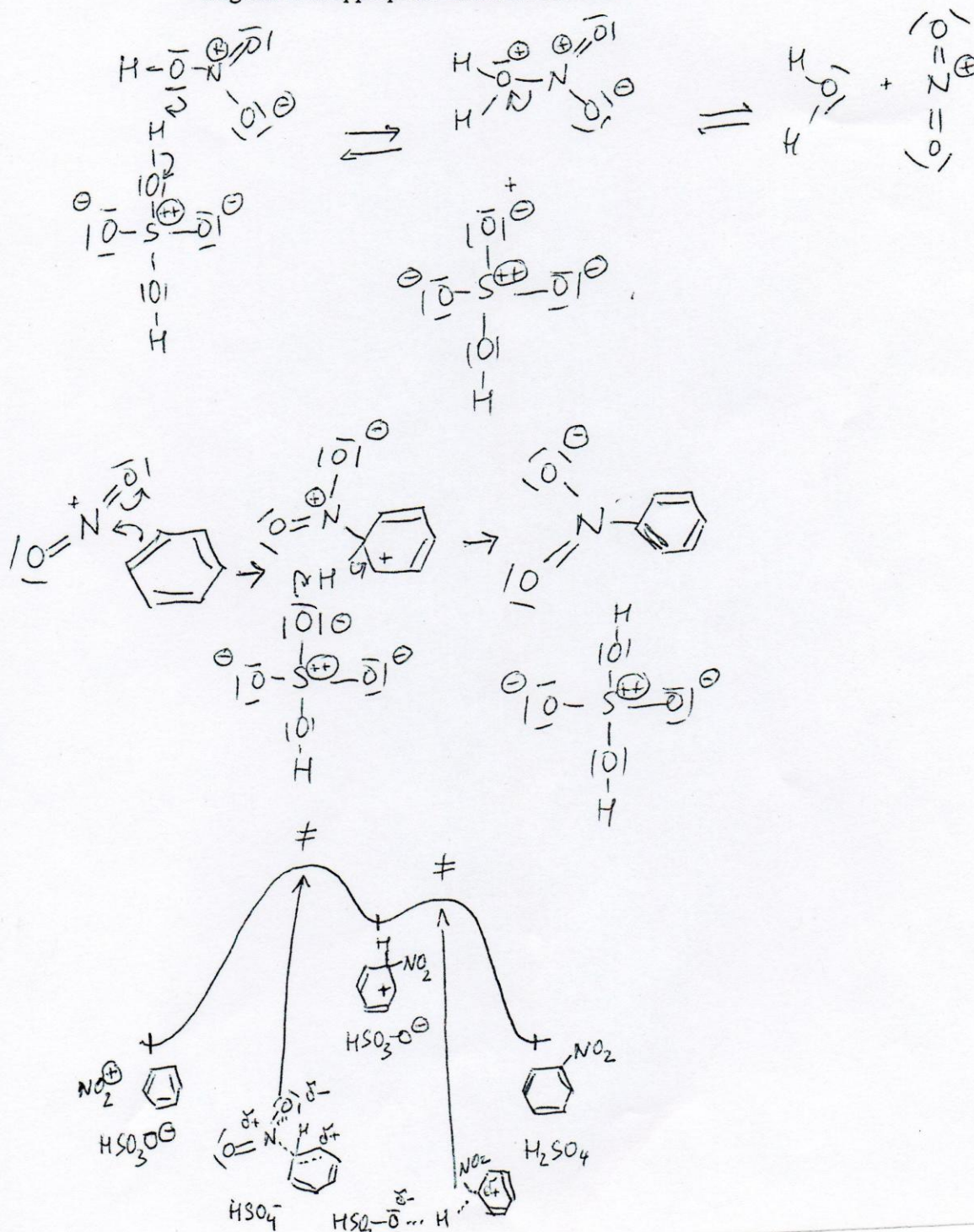
---

1. (20 points) Check the correct statements only (make no other marks):

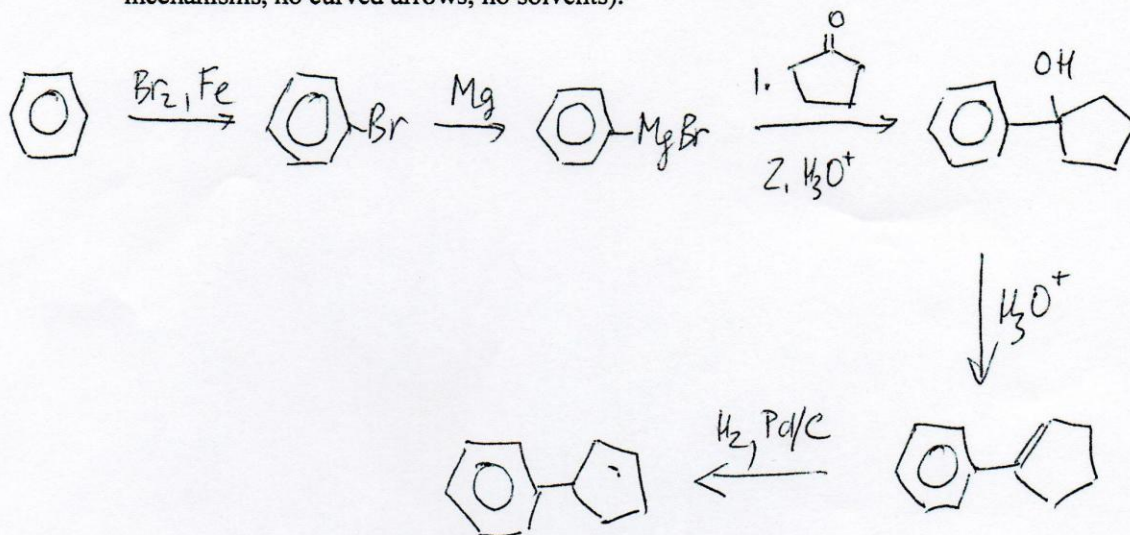
- Nitration of bromobenzene proceeds primarily in the meta position.
- Diazotization of *p*-nitroaniline followed by treatment with CuCN yields *p*-nitrobenzotrile.
- The Sandmeyer reaction is useful for converting an amino group on an aromatic ring to a chloro substituent.
- p*-Nitroaniline is a stronger base than aniline.
- Aromatic diazonium salts undergo azo coupling with arylamines and phenols to yield azo dyes.
- Disrotatory ring opening of cyclobutene to 1,3-butadiene has an antiaromatic transition state and is forbidden as a thermal process.
- The reduction of nitriles with lithium aluminum hydride yields primary amines after workup.
- Benzidine rearrangement is induced by heating with acid and converts 4,4'-diaminobiphenyl (benzidine) into hydrazobenzene, C<sub>6</sub>H<sub>5</sub>-NH-NH-C<sub>6</sub>H<sub>5</sub>.
- Upon reduction, alkyl azides yield primary alkylamines.
- Secondary aliphatic amines react with nitrous acid to give carcinogenic nitrosamines.
- Diazomethane is an explosive gas and is normally used in diethyl ether solution.
- An atomic orbital (AO) is a region of space where an electron is likely to be found.
- The reaction of bromine with benzene to yield bromobenzene proceeds well in the presence of a Lewis acid catalyst such as ferric bromide.
- As the length of a conjugated linear polyene increases, its longest-wavelength absorption peak in the ultraviolet-visible spectrum shifts to shorter wavelengths.
- The non-bonding pi molecular orbital (MO) of the allyl radical has a large amplitude at the two terminal carbon atoms, and zero amplitude (a node) at the central carbon atom.
- Gabriel synthesis is a method for preparing primary alkylamines.
- Friedel-Crafts acylation of benzene with acetyl chloride and a catalytic amount of AlCl<sub>3</sub> will not proceed to completion.
- In a Möbius cyclic pi system, there is an odd number of negative overlaps between AOs.
- Birch reduction of benzoic acid, followed by acid hydrolysis, yields 2,5-cyclohexadiene-1-carboxylic acid.
- Cyclobutadiene is aromatic and exceedingly stable.

2. (12 pts) Write a plausible mechanism for the nitration of benzene with a mixture of nitric and sulfuric acids all steps and intermediates and use curved arrows to indicate electron movement in each step).

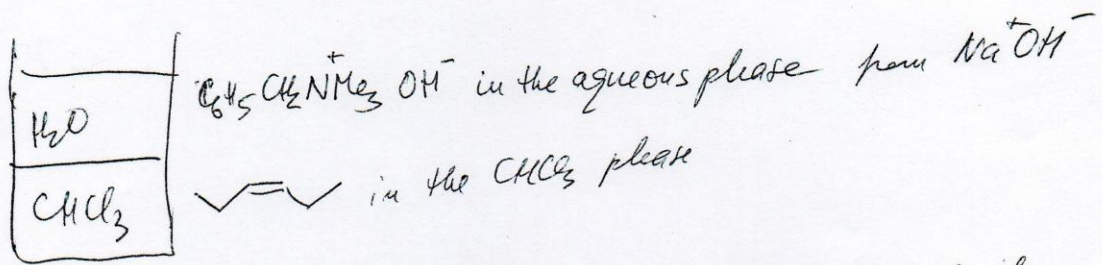
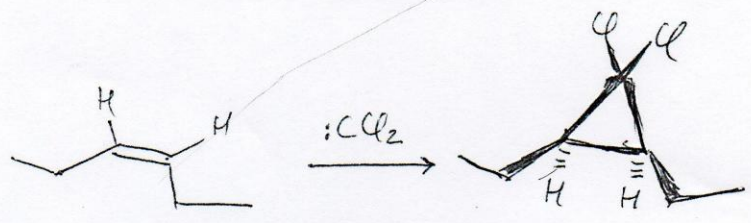
(5 pts) Draw a potential energy profile for this reaction and label all important points on the diagram with appropriate chemical structures.



3. (12 pts) Propose a reaction sequence for the synthesis of phenylcyclopentane from benzene and cyclopentanone, using inorganic reagents. Show all steps and all reagents (no mechanisms, no curved arrows, no solvents).

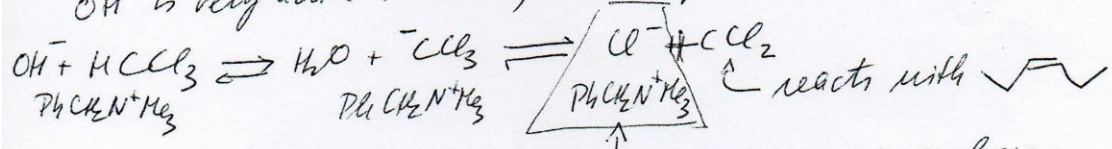


4. (15 pts) Show product structure and stereochemistry in the reaction of *cis*-3-hexene with dichlorocarbene ( $\text{CCl}_2$ ), produced from chloroform and 50% aqueous NaOH, and explain how phase transfer catalysis works.



Some  $\text{C}_6\text{H}_5\text{CH}_2\text{N}^+\text{Me}_3 \text{OH}^-$  dissolves in  $\text{CHCl}_3$  (the cation is lipophilic because of the benzyl part)

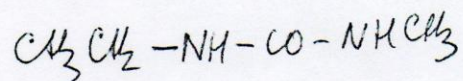
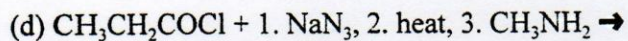
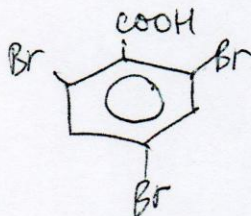
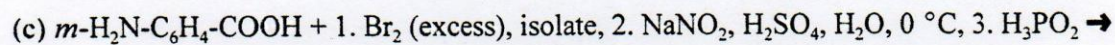
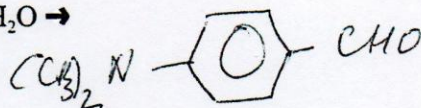
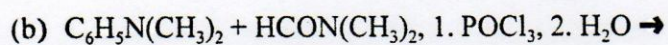
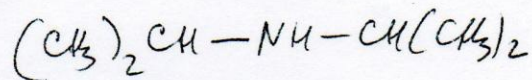
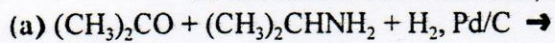
$\text{OH}^-$  is very active ("naked") in chloroform



↑ travels back to  $\text{H}_2\text{O}$  phase

$\text{PhCH}_2\text{N}^+\text{Me}_3 \text{Cl}^-$  returns to aqueous phase and equilibrates with  $\text{PhCH}_2\text{N}^+\text{Me}_3 \text{OH}^-$  (NaOH is in excess)  
Process is repeated

5. (20 pts) Write the structures of all principal organic products of the following reactions. You do not need to show solvents, mechanisms, or curved arrows.



6. (16 pts) Sketch a diagram showing the energies and nodal structure of the five pi molecular orbitals of the cyclopentadienyl anion  $C_5H_5^-$  and indicate the ground state electron occupancy.

