

high SE
910 67.5
low 42

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Student Name (first, last):

Student Number:

KEY

CHEMISTRY 3371
SECOND MIDTERM EXAMINATION

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March 15, 2007

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

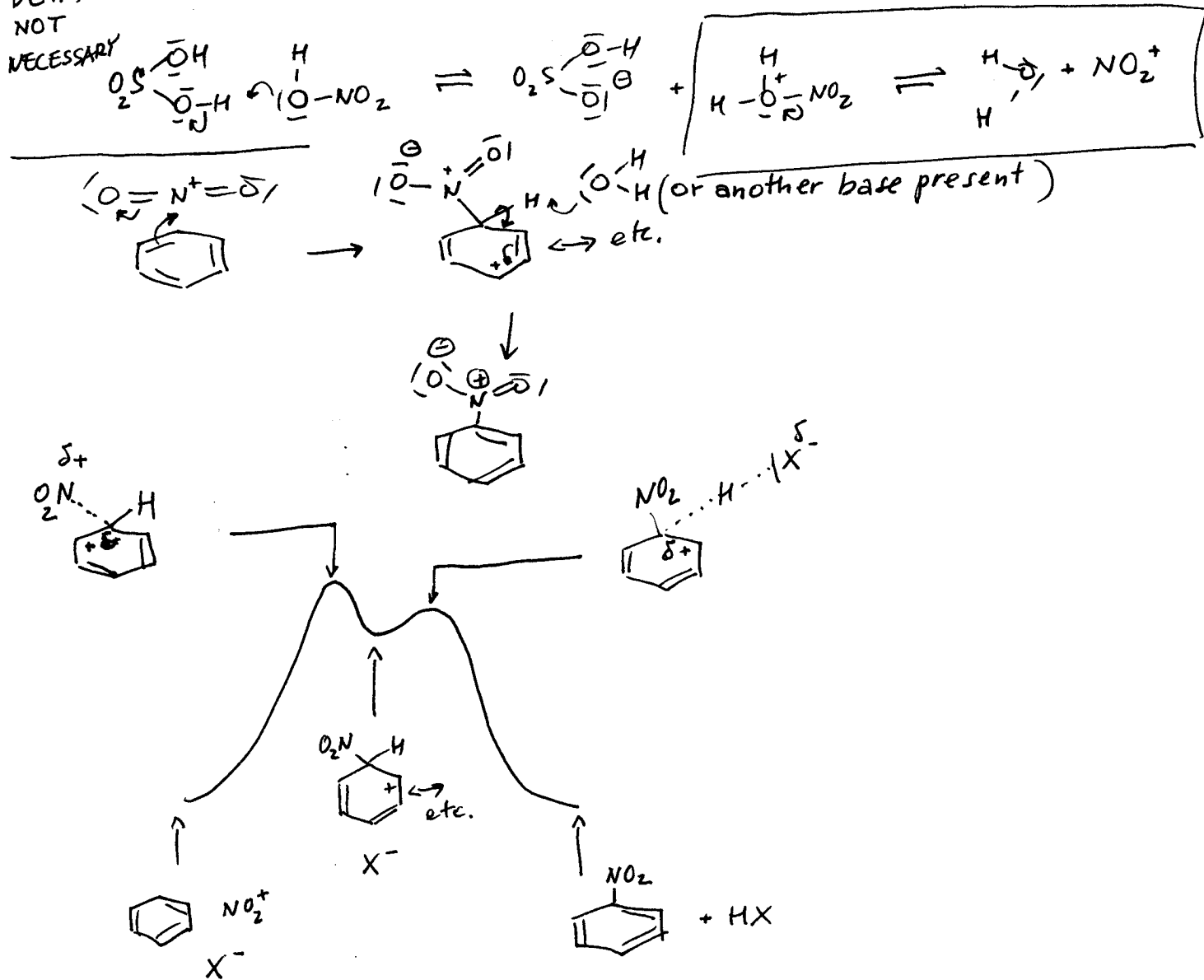
- An orbital is a region of space where an electron is likely to be found.
- The non-bonding pi molecular orbital of the allyl radical has the same amplitude on all three carbon atoms.
- The most antibonding of the six pi molecular orbitals of benzene has a node across each CC bond.
- Conrotatory ring opening of cyclobutene has an antiaromatic transition state and is forbidden.
- Cyclobutadiene is aromatic and not very reactive.
- As the length of a conjugated linear polyene increases, its longest-wavelength absorption peak in the ultraviolet-visible spectrum shifts to shorter wavelengths.
- The intensity I of light that passes through a solution is related to the incident intensity I_0 by Beer's law, $\log(I_0/I) = \epsilon cd$, where ϵ is the extinction coefficient (characteristic of the compound and the wavelength of the light), c is the molar concentration, and d is the density of the solution.
- The reaction of bromine with benzene to yield bromobenzene is normally performed with NaBr as a catalyst.
- Friedel-Crafts acylation of benzene with acetyl chloride and a catalytic amount of AlCl_3 will proceed to completion.
- Nitration of chlorobenzene proceeds primarily in the meta position.
- The aniline molecule is planar.
- The Gabriel synthesis is useful for converting an amino group on an aromatic ring to a fluoro substituent.
- p*-Nitroaniline is a stronger base than *p*-methoxyaniline.
- Secondary aliphatic amines react with nitrous acid to give carcinogenic nitrosamines.
- Low-molecular weight alkyl azides tend to be explosive and dangerous.
- Under anhydrous conditions, Curtius rearrangement of acyl azides leads to isocyanates.
- Hofmann rule for the direction of elimination quaternary ammonium salt states that the most stable alkene will be formed.
- Diazotization of an aromatic amine is best performed in a strongly basic solution.
- Benzidine rearrangement converts hydrazobenzene into 4,4'-diaminobiphenyl.
- Upon irradiation or heating, diazoalkenes lose N_2 and yield carbenes, which then react further.

2. (15 pts) Write a plausible mechanism for the nitration of benzene with a mixture of nitric and sulfuric acids (include all steps and intermediates and use curved arrows to indicate electron movement in each step).

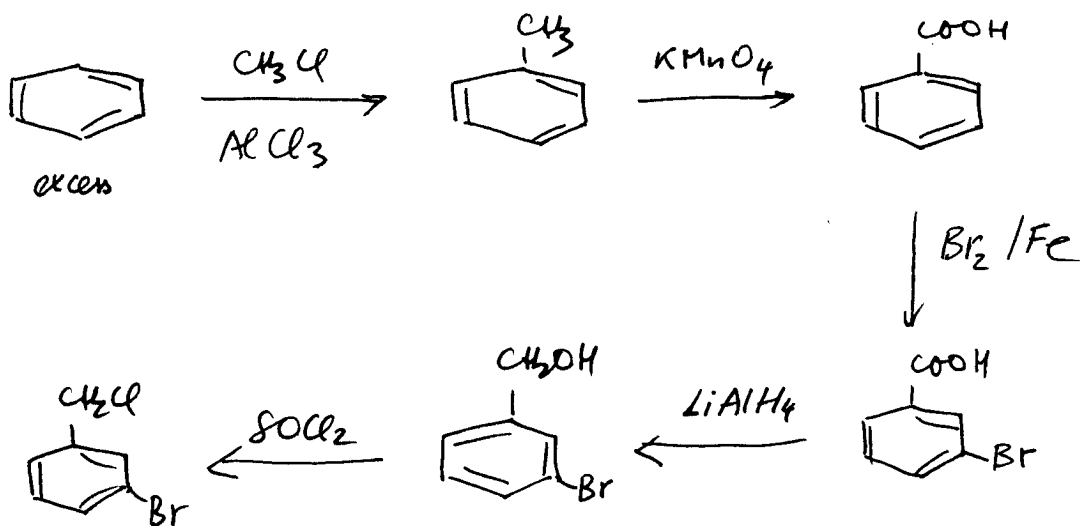
(5 pts)

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

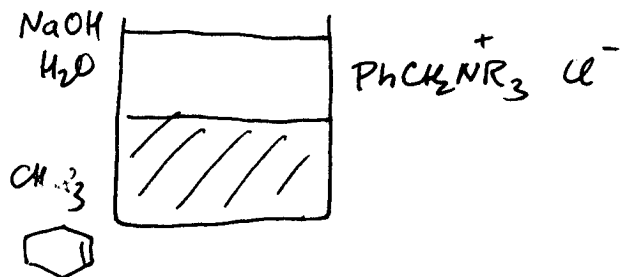
DETAIL
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3. (15 pts) Propose a reaction sequence for the synthesis of *m*-bromobenzyl chloride from benzene and reagents that contain no more than one carbon atoms in the molecule. Show all steps and all reagents (no mechanisms, no curved arrows, no solvents).



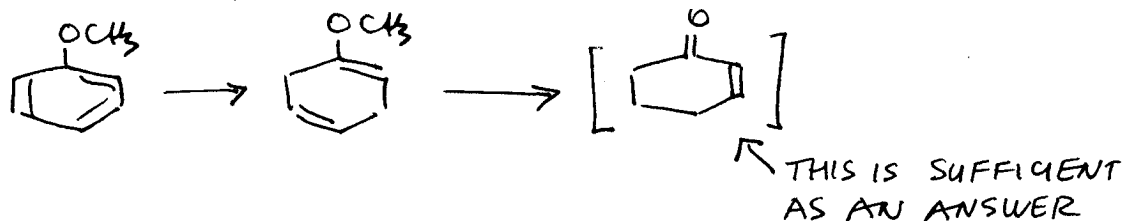
4. (15 pts) Explain how phase transfer catalysis works in the reaction of cyclohexene with dichlorocarbene (CCl_2), produced from chloroform and 50% aqueous NaOH.



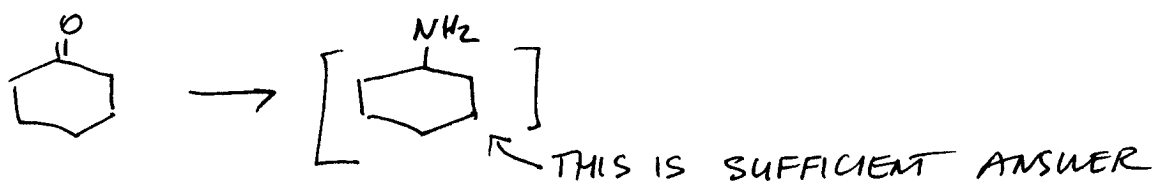
1. The ion pair $\text{PhCH}_2\text{NR}_3^+ \text{OH}^-$ is *(partitioned)* partially attracted from H₂O layer to CHCl₃ layer
2. $\text{OH}^- + \text{CHCl}_3 \rightleftharpoons \text{H}_2\text{O} + ^-\text{CCl}_3$
3. $^-\text{CCl}_3 \rightleftharpoons \text{Cl}^- + \text{CCl}_2$
4. $\text{CCl}_2 + \text{Cyclohexene} \rightarrow \text{Bicyclic product}$
5. $\text{PhCH}_2\text{NR}_3^+ \text{Cl}^-$ ion pair is partitioned from CHCl₃ to H₂O layer
6. Cycle continues

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.

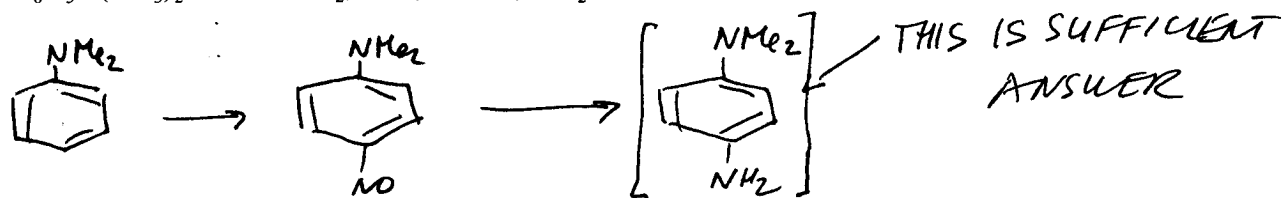
(a) $C_6H_5-OCH_3 + 1. Li, NH_3(liq), EtOH, isolate, 2. HCl/H_2O \rightarrow$



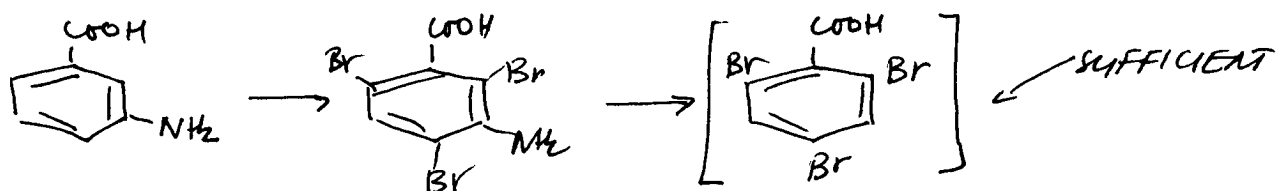
(b) cyclohexanone + NH_3 (excess), H_2 , Ni (cat.) \rightarrow



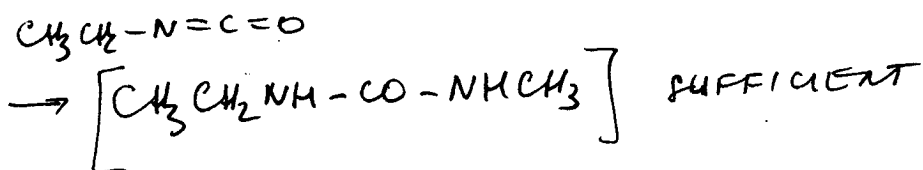
(c) $C_6H_5N(CH_3)_2 + 1. NaNO_2, HCl, isolate, 2. H_2/cat \rightarrow$



(d) $m-H_2N-C_6H_4-COOH + 1. Br_2$ (excess), isolate, 2. $NaNO_2, H_2SO_4, H_2O, 0^\circ C$, 3. $H_3PO_2 \rightarrow$



(e) $CH_3CH_2Br + 1. KNCO, 2. CH_3NH_2 \rightarrow$



6. (10 pts) Sketch a diagram showing the energies of six pi molecular orbitals of benzene and indicate the ground state electron occupancy.

