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

Student Number:

CHEMISTRY 3371
SECOND MIDTERM EXAMINATION

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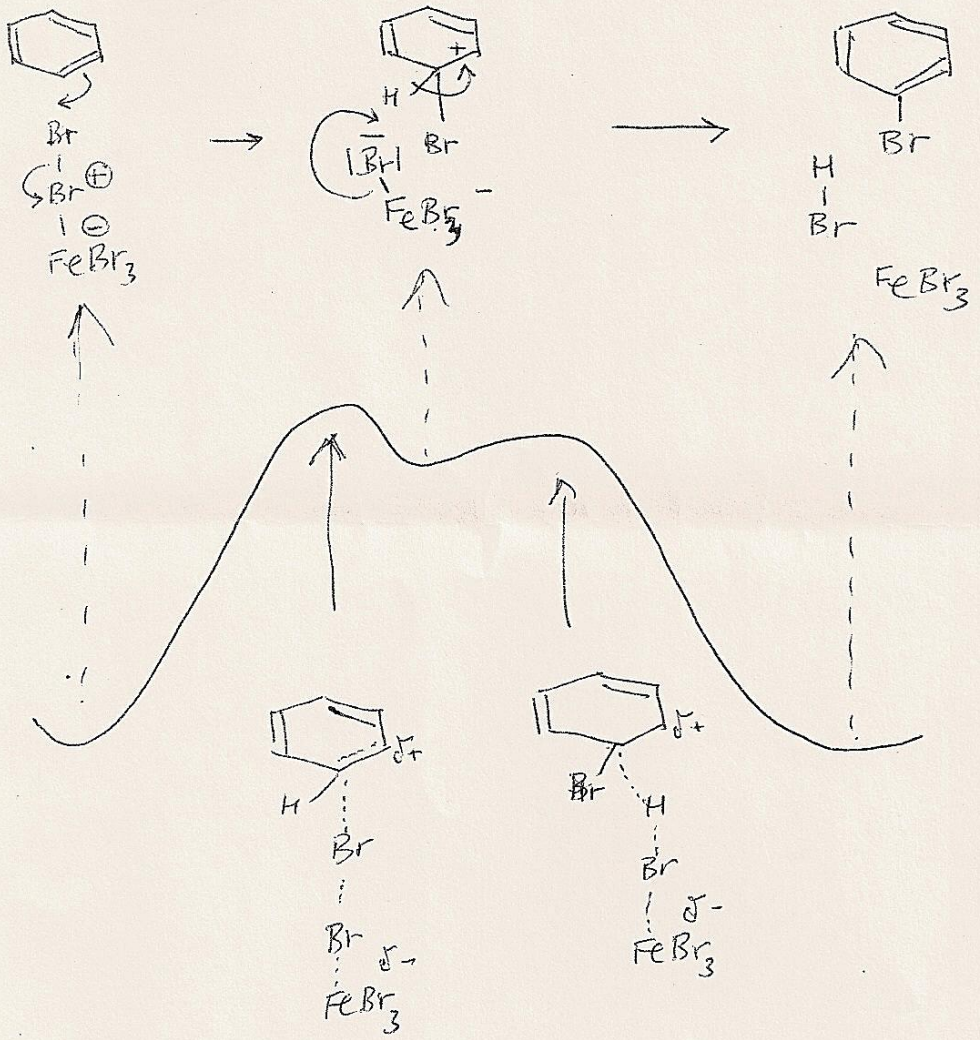
March 13, 2008

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

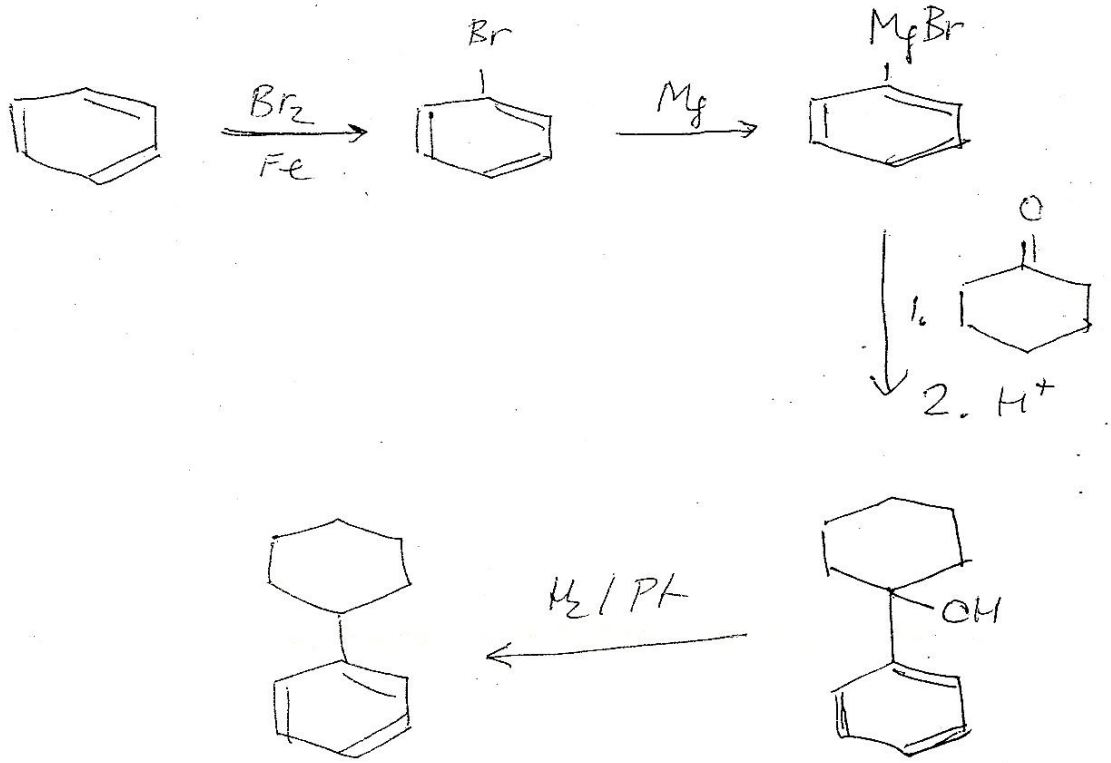
( ) An atomic orbital (AO) is a region of space near an atom where an electron is likely to be found.
(X) In a Möbius cyclic pi system, there is an odd number of negative overlaps between AOs.
(X) The non-bonding pi molecular orbital (MO) of the allyl radical has a large amplitude at the two terminal carbon atoms, and zero amplitude (a node) at the central carbon atom.
(X) Birch reduction of anisole, $C_6H_5OCH_3$, followed by acid hydrolysis, yields cyclohexen-3-one.
( ) Disrotatory ring opening of cyclohexa-1,3-diene to 1,3,5-hexatriene has an antiaromatic transition state and is forbidden as a thermal process.
(X) Cyclobutadiene is antiaromatic and exceedingly reactive.
( ) As the length of a conjugated linear polyene increases, its longest-wavelength absorption peak in the ultraviolet-visible spectrum shifts to longer wavelengths and acquires n-pi* character.
( ) The intensity I of light that passes through a solution is related to the incident intensity I_0 by Beer's law, $\log(I_0/I) = \varepsilon cl$, where ε is the absorption (extinction) coefficient, characteristic of the compound and the wavelength of the light, c is the speed of light in vacuum, and l is the optical path length through the solution.
( ) The reaction of chlorine with benzene to yield chlorobenzene is normally performed without catalyst and with UV irradiation.
(X) Friedel-Crafts acylation of benzene with acetyl chloride and a catalytic amount of $AlCl_3$ will not proceed to completion.
( ) Nitration of fluorobenzene proceeds primarily in the meta position.
( ) The aniline molecule is planar.
(X) The Schiemann reaction is useful for converting an amino group on an aromatic ring to a fluoro substituent.
(X) *p*-Nitroaniline is a weaker base than aniline.
( ) Tertiary aliphatic amines react with nitrous acid to give carcinogenic nitrosamines.
(X) Low-molecular weight diazoalkanes tend to be explosive and dangerous.
(X) Aromatic diazonium salts undergo azo coupling with arylamines and phenols to yield azo dyes.
(X) Nitrosoalkanes tend to be dimeric and colorless, whereas nitrosoarenes tend to be monomeric and colored.
( ) Benzidine rearrangement is induced by treatment with acid and converts 4,4'-diaminobiphenyl into hydrazobenzene.
(X) Upon irradiation or heating, alkyl azides lose N_2 and yield nitrenes, which then react further.

2. (12 pts) Write a plausible mechanism for the bromination of benzene with a mixture of elemental bromine and ferric bromide (include all steps and intermediates and use curved arrows to indicate electron movement in each step).

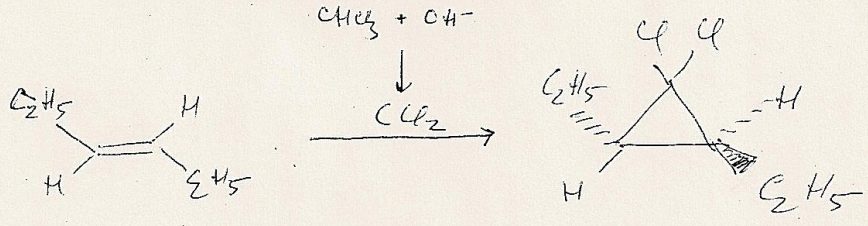
(5 pts) Draw a potential energy profile for this reaction and label all important points on the diagram with appropriate chemical structures.



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



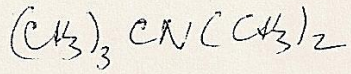
4. (15 pts) Show product structure and stereochemistry in the reaction of *trans*-3-hexene with dichlorocarbene (CCl_2), produced from chloroform and 50% aqueous NaOH, and explain how phase transfer catalysis works.



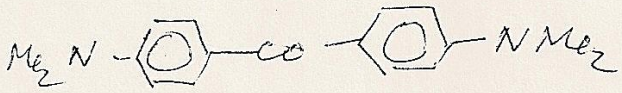
The phase transfer catalyst such as $C_6H_5CH_2\overset{+}{N}Me_3\ Cl^-$ is soluble in water but also in chloroform and ion pairs $C_6H_5CH_2\overset{+}{N}Me_3\ OH^-$ will enter chloroform. Since OH^- is poorly solvated there, it is very basic and will deprotonate $CHCl_3$ to CCl_3^-, which falls apart into CCl_2 and Cl^-. The pair $C_6H_5CH_2N^+Me_3\ Cl^-$ returns to water, where it can pick up another OH^-, etc.

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.

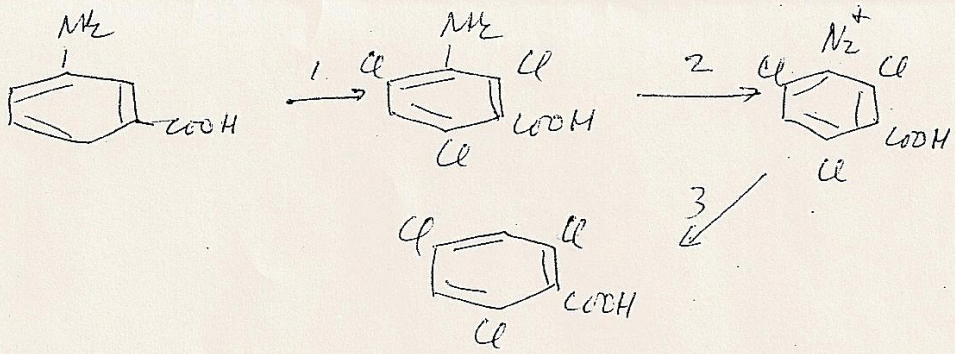
(a) CH_2O (excess) + $(CH_3)_3CNH_2$ + HCOOH, heat →



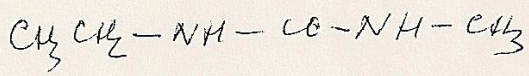
(b) $C_6H_5N(CH_3)_2$ (excess) + $COCl_2$, $ZnCl_2$, heat →



(c) *m*-H_2N-C_6H_4-COOH + 1. Cl_2 (excess), isolate, 2. $NaNO_2$, H_2SO_4, H_2O, 0 °C, 3. H_3PO_2 →



(d) CH_3CH_2COCl + 1. NaN_3, 2. heat, 3. CH_3NH_2 →



6. (16 pts) Sketch a diagram showing the energies and nodal structure of the eight pi molecular orbitals of cyclooctatetraene and indicate the ground state electron occupancy in the planar dianion, $C_8H_8(2-)$.