

average

111

low score 40

high score 195

Student Name (first, last):

KEY

1

Social Security Number:

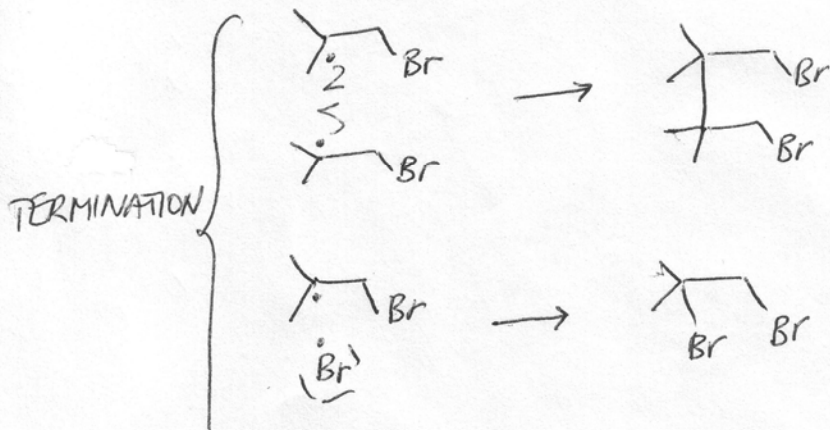
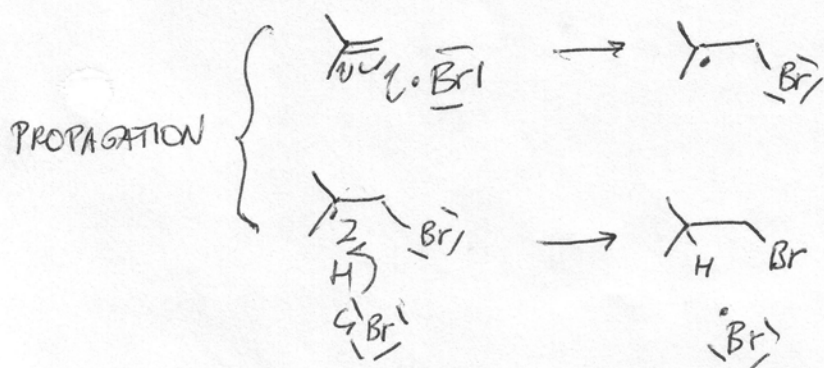
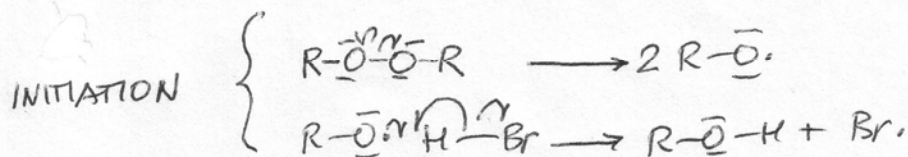
TA Name:

CHEMISTRY 3311 (100)
FINAL EXAMINATION

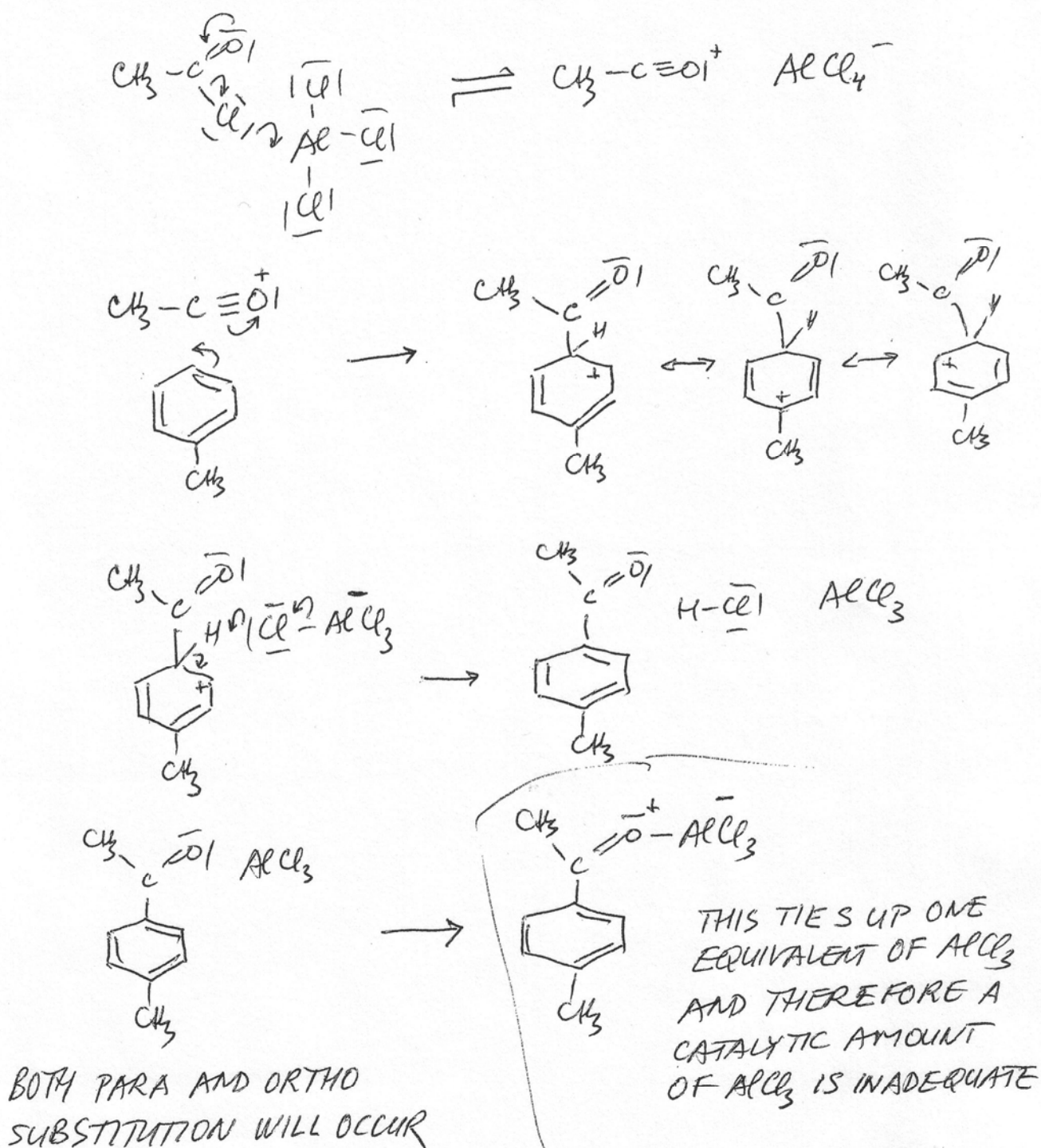
Josef Michl
December 11, 2004

1. (50 points) Check the correct statements only and **make no marks at the incorrect statements:**
- The S_N1 mechanism is favored for substitution on primary carbons and disfavored at tertiary carbons.
 - The S_N2 mechanism is favored for substitution on tertiary carbons and disfavored at primary carbons.
 - The E1 mechanism of elimination requires a strong base.
 - The rate of an E2 reaction is inversely proportional to the concentration of base used.
 - Disulfides are often prepared by oxidation of thiols.
 - The conversion of an alkyl halide to a primary amine via an *N*-alkylphthalimide is the Gabriel synthesis.
 - The ^1H NMR spectrum of benzene contains seven lines.
 - 2 g of ethylcyclopropane generates more heat upon complete combustion than 2 g of cyclopentane.
 - The chair is the most stable conformation of cyclohexane.
 - At room temperature, *cis*-1,3-dimethylcyclohexane exists mostly as the axial,axial conformer.
 - A meso compound is not chiral although it contains centers of chirality (stereogenic centers).
 - In a sample that is a 80:20 mixture of enantiomers, the enantiomeric excess is 20%.
 - The rate of a thermoneutral reaction with $\Delta S^\ddagger = 0$ is always the same in forward and reverse directions.
 - Ethylamine is a weaker acid than ethanol.
 - Ethylamine is a weaker base than ethanol.
 - 2-Aminohexane is a secondary amine.
 - An orbital is a region of space where an electron is likely to be found.
 - Reaction with hypophosphorous acid, H_3PO_2 , replaces a diazonium group with a hydrogen atom.
 - The heterolytic cleavage of the carbon-halogen bond is easier in allyl bromide than in methyl bromide.
 - The sulfur atom can have more than eight electrons in its valence shell.
 - Molecular orbitals are mathematical surfaces that describe the likely positions of electron density.
 - Homolytic cleavage of a single bond produces a pair of radicals.
 - 1-Butene has a more negative heat of hydrogenation than 2-butene.
 - Cyclobutadiene is aromatic.
 - Thiophene has eight electrons in its pi orbitals.

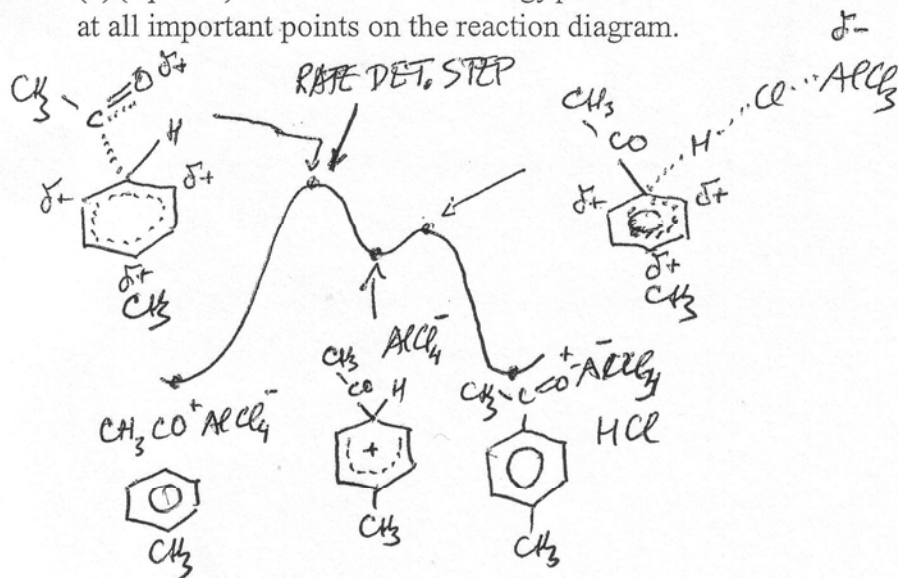
2. (20 pts) Write the mechanism of free-radical induced addition of HBr to isobutene in the presence of peroxides. Show all reaction steps and structure of the main organic product and of all intermediates, if any. Use curved arrows to indicate how electrons move in the individual elementary reaction steps. Label reaction steps or groups of reaction steps with names, if they have any.



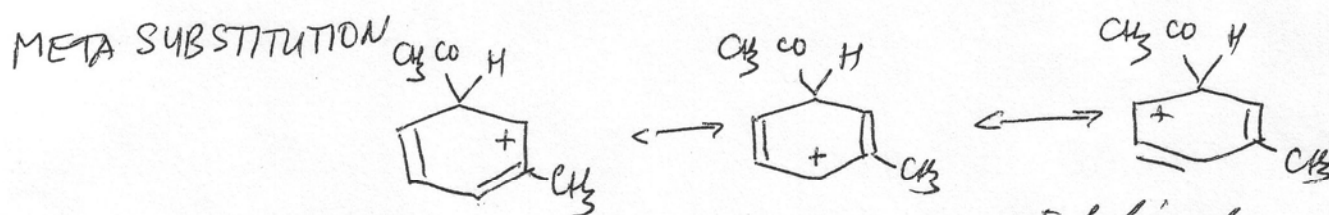
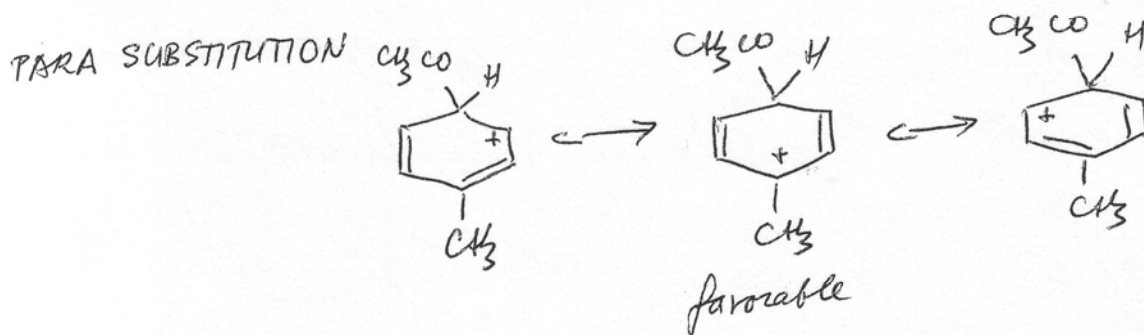
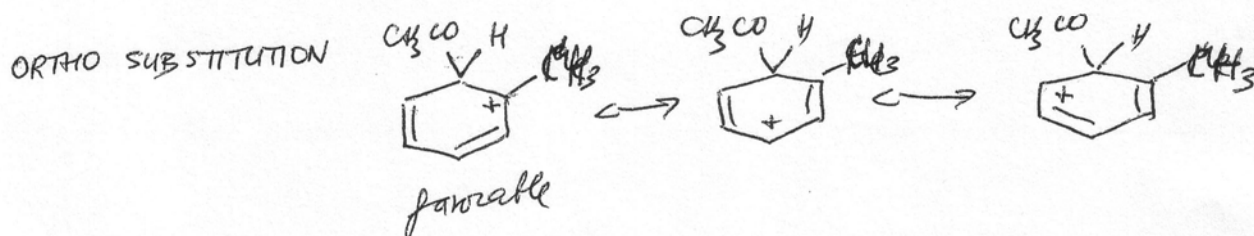
3. (25 pts) (a) (15 points) Write the mechanism of the Friedel-Crafts reaction of acetyl chloride with toluene, using any additional reagent needed (specify whether a catalytic amount of any such reagent is sufficient or if an equivalent is needed). Show all reaction steps and structure of the main organic product and of all intermediates, if any. Use curved arrows to indicate how electrons move in the individual elementary reaction steps.



(b) (5 points) Draw the reaction energy profile and mark the rate determining step. Show the structures at all important points on the reaction diagram.



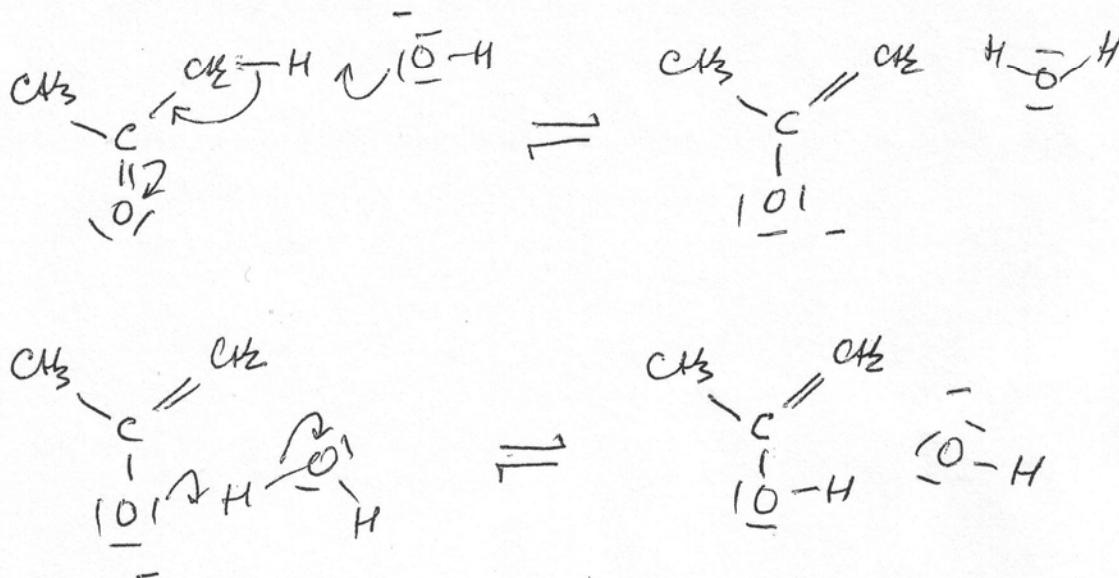
(c) (5 points) Use resonance structures appropriate to the rate determining step to explain why the position of substitution is the one you have shown. Specify which other positions are also likely to react, if any.



ortho and para attack leads to a more stabilized intermediate, and a more stabilized transition state (which is close in structure)

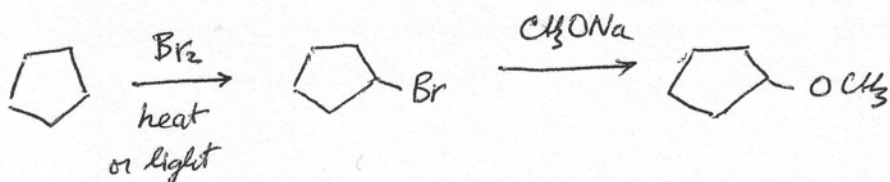
4. (10 pts)

Write the mechanism of base-catalyzed keto-enol tautomerization of acetone in aqueous solution. Show all reaction steps and structures of all intermediates, if any. Use curved arrows to indicate how electrons move in the individual elementary reaction steps.

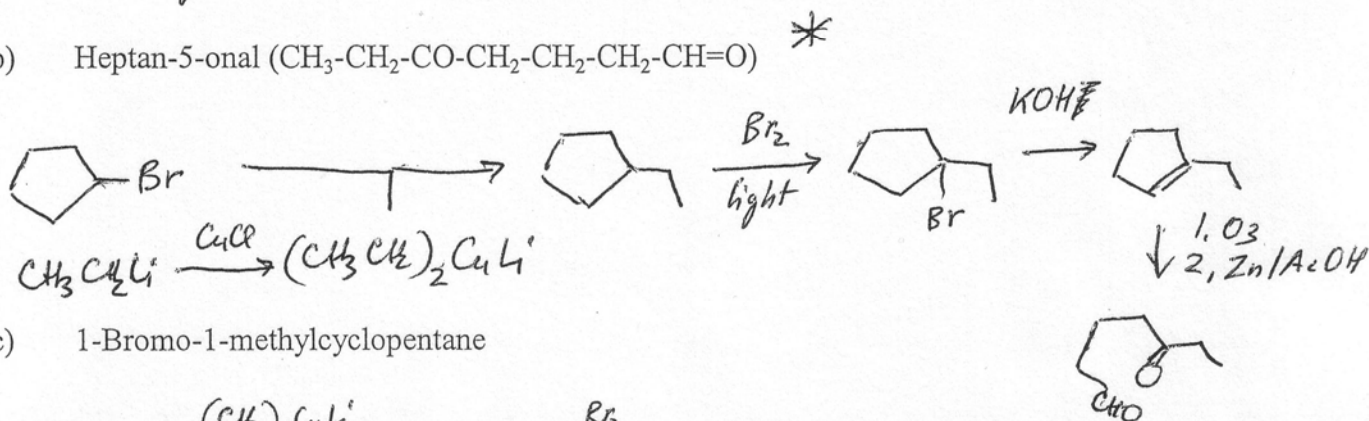


5. (30 pts) Propose an efficient synthesis of each of the following compounds, starting with cyclopentane and any reagents whose molecule contains no more than two carbon atoms. Specify all reagents used, but do not specify mechanisms. If you have already described the synthesis of compound and use it again later, you do not need to describe its preparation again.

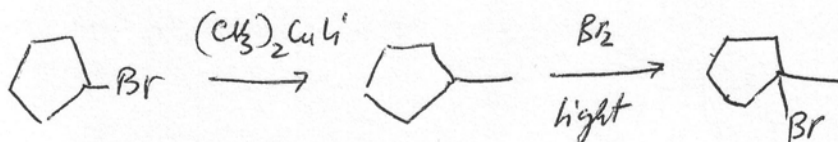
(a) Cyclopentyl methyl ether



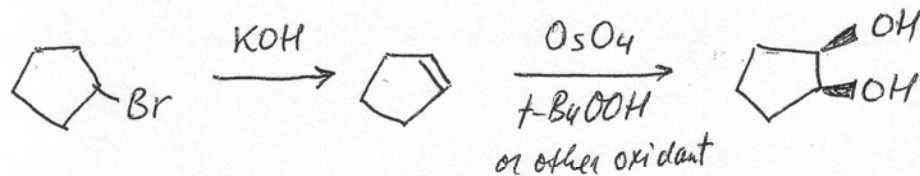
(b) Heptan-5-onal ($\text{CH}_3\text{-CH}_2\text{-CO-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH=O}$) *



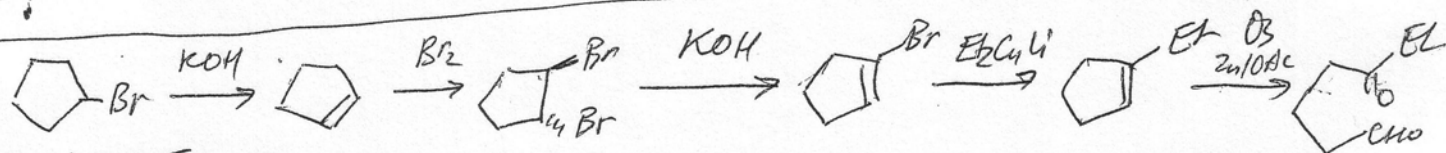
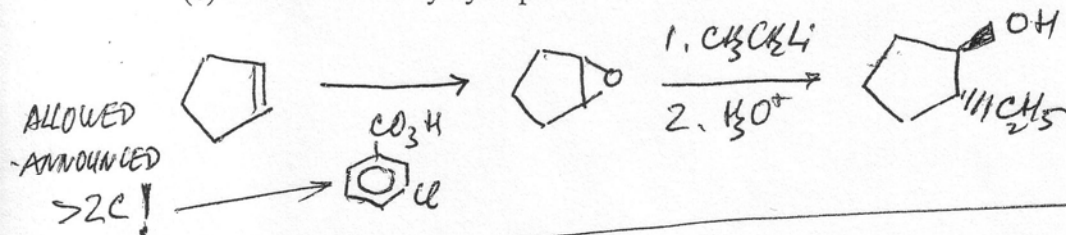
(c) 1-Bromo-1-methylcyclopentane



(d) *cis*-1,2-Dihydroxycyclopentane

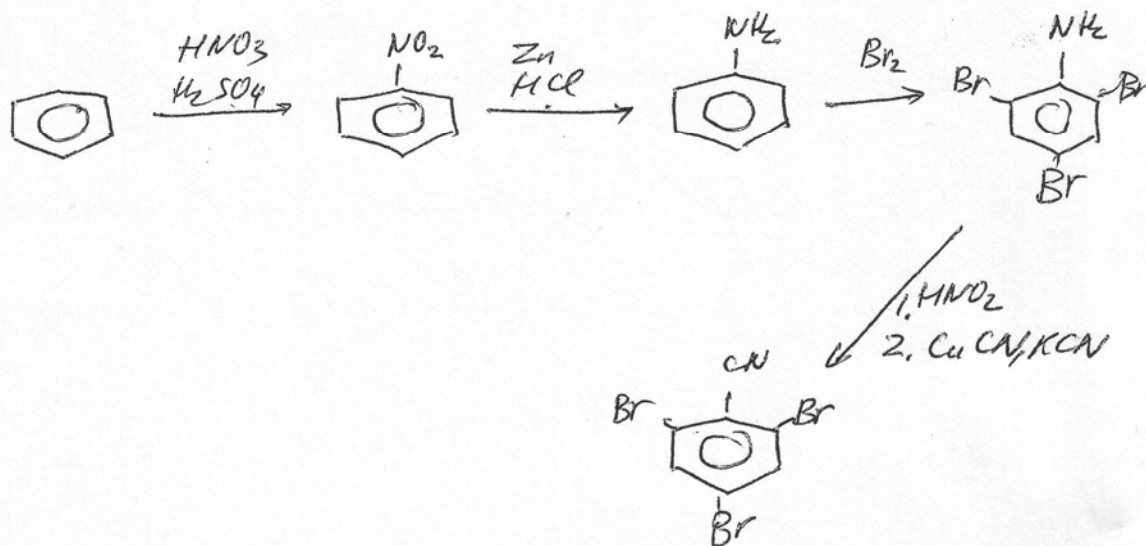


(e) *trans*-2-Ethylcyclopentanol



* ALTERNATIVE

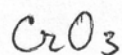
6. (12 pts) Propose an efficient synthesis of 2,4,6-tribromobenzonitrile, starting with benzene and any reagents whose molecule contains no more than two carbon atoms. Specify all reagents used, but do not specify mechanisms.



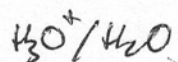
7. (21 pts) Write the reagents you would use to convert the starting materials given into the products shown in a single step. Specify the solvent only if its use is critical since other solvents would not work. You do not need to specify mechanisms.

Cyclohexanol into:

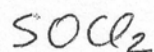
- (a) Cyclohexanone



- (b) Cyclohexene

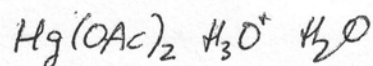


- (c) Cyclohexyl chloride

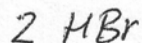


2-Butyne into

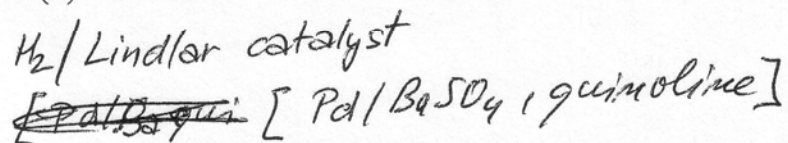
- (d) Methyl ethyl ketone



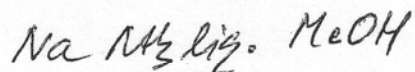
- (e) 2,2-Dibromobutane



- (f) (Z)-2-butene

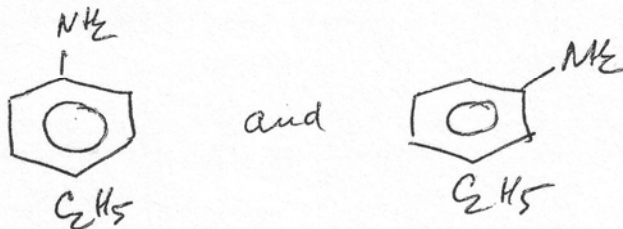


- (g) (E)-2-butene

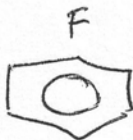


8. (16 pts) Fully specify all the principal organic products of the following reactions (do not write the mechanism).

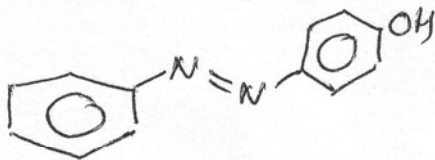
(a) *p*-Bromoethylbenzene and NaNH_2 in liquid ammonia solvent



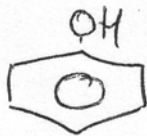
(b) Benzenediazonium tetrafluoroborate and heat



(c) Benzenediazonium chloride and phenol in basic solution

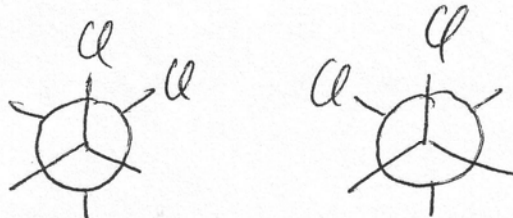


(d) Benzenediazonium chloride heated in aqueous solution

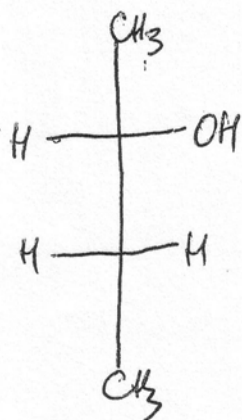


9. (16 points)

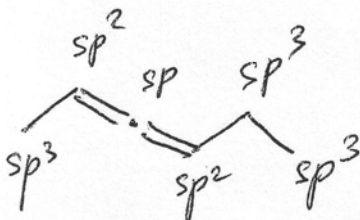
(a) (4 points) Draw Newman projections of both enantiomers of the gauche conformer of 1,2-dichloroethane.



(b) (5 points) Draw the Fischer projection of (*S*)-2-butanol.



(c) (4 points) Draw the structure of 2,3-hexadiene and indicate the hybridization state of each carbon atom.



(3 points) Is it chiral?

yes