CHEMISTRY 314-02

MIDTERM # 1 – answer key

February 10, 2005

Statistics:

- Average: 77 pts (77%);
- Highest: 99 pts (99%); Lowest: 40 pts (40%)
- Number of students performing at or above average: 25 (54%)

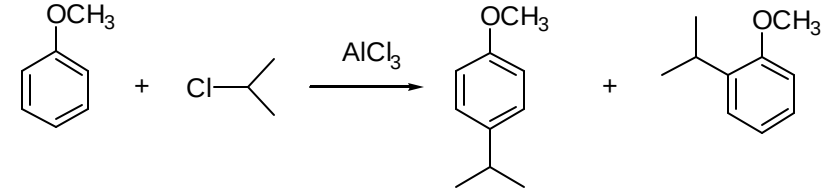
1. (8 pts) Mark as true (**T**) or false (**F**) the following statements. Do not explain!
   - (**F**) All π-donor substituents are activating;
   - (**F**) The *Wolf-Kishner* reduction transforms a ketone to an alcohol;
   - (**T**) The chemical shift is independent of the operating frequency of the NMR;
   - (**T**) The gyromagnetic ratio is independent of the operating frequency of the NMR;
   - (**T**) Only charged species are observed by MS;
   - (**T**) Organometallic compounds are strong bases;
   - (**T**) Organometallic compounds are strong nucleophiles;
   - (**T**) Carbenes are electron-deficient;

2. Circle ALL that apply:
   A. (3 pts) The following reactions are not possible:
      a. Benzene + bromine in the presence of $FeBr_3$;
      b. Nitrobenzene + butyl chloride, in the presence of $AlCl_3$;
      c. Benzaldehyde + acetyl chloride, in the presence of $AlCl_3$;
      d. Toluene + nitric/sulfuric acid mixture, upon heating;

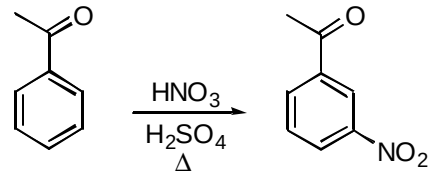
   B. (3 pts) In NMR, one observes nuclei that have:
      a. Odd atomic number but even mass number;
      b. Even atomic number but odd mass number;
      c. Odd atomic number and odd mass number;
      d. Even atomic number and even mass number;

   C. (3 pts) The following reactions are used to prepare tertiary alcohols:
      a. Reaction of aldehyde with an organolithium compound, followed by acid;
      b. Reaction of ketone with an organolithium compound, followed by acid;
      c. Reaction of a *Grignard* reagent with an ester, followed by acid;
      d. Acid-catalyzed hydration of alkynes;

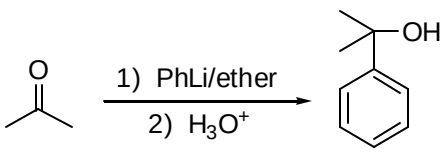
3. Write and complete a chemical equation for each of the following reactions:
   A. (3 pts) Anisole + isopropyl chloride, in the presence of $AlCl_3$;



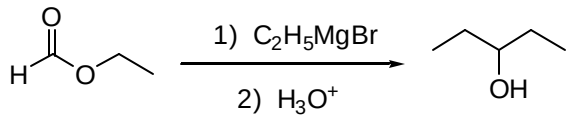
   B. (3 pts) Acetophenone + nitric acid/sulfuric acid, upon heating;



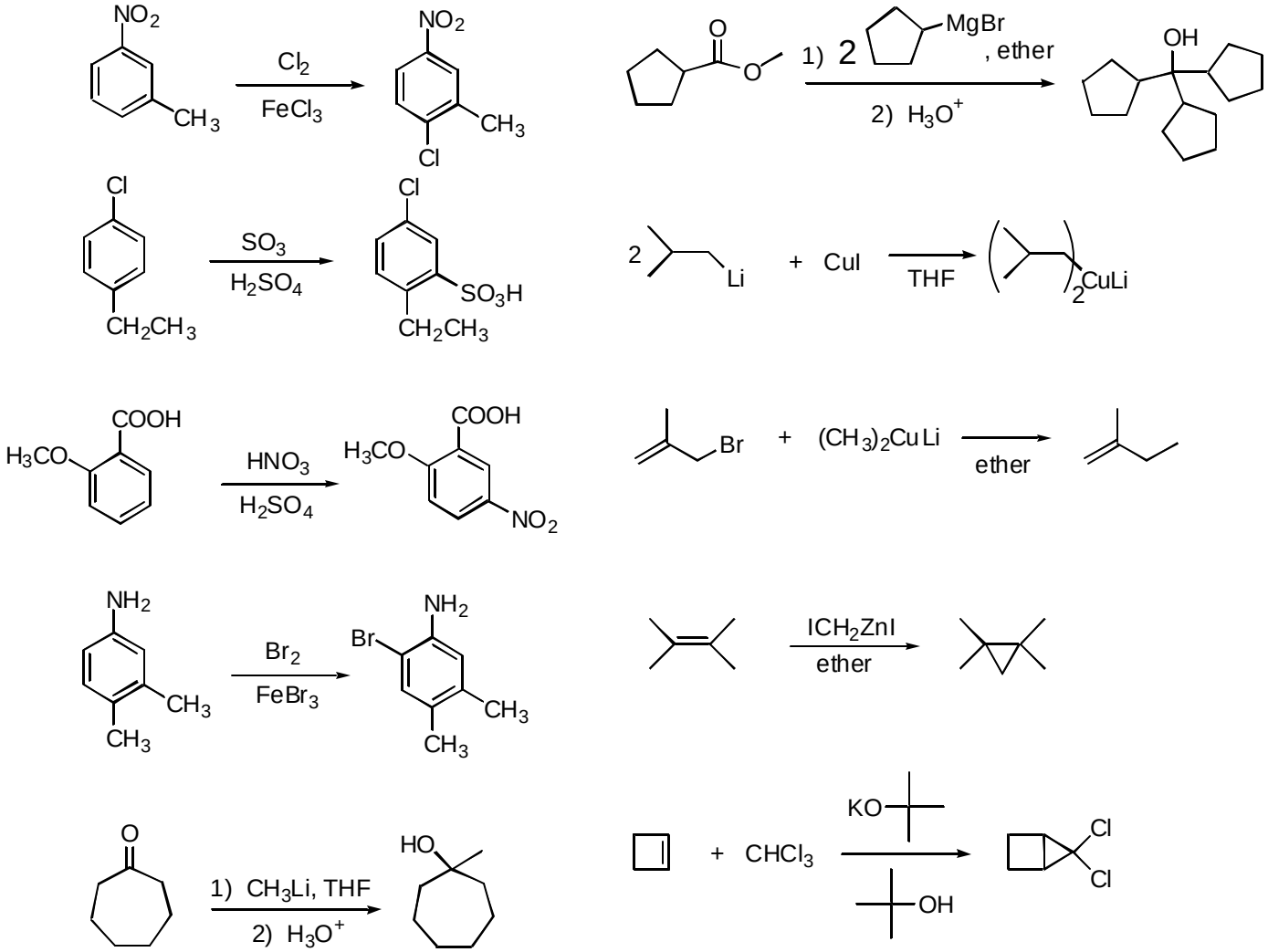
   C. (3 pts) Acetone + phenyllithium, followed by acid;



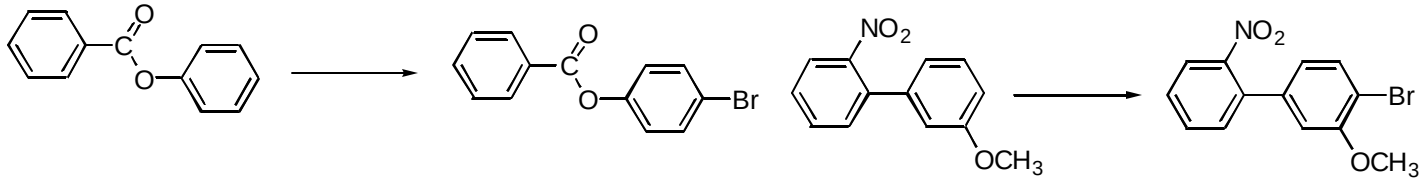
D. (3 pts) Ethyl formate + 2 equivalents of ethylmagnesium bromide, followed by acid;



4. (25 pts) Indicate the principal organic product of each of the following reactions. If *o*-,*p*-mixture is expected, write both products.

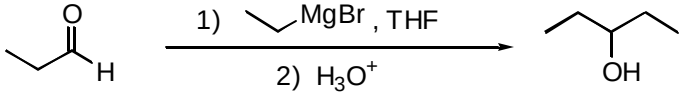


5. (6 pts) Predict the major product of <u>monobromination</u> of the following compounds with $Br_2/FeBr_3$:

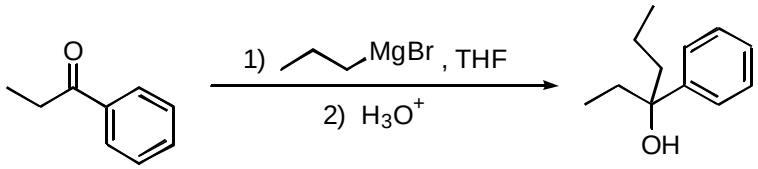


6. (8 pts) Suggest an appropriate combination of a **carbonyl compound (aldehyde or ketone) or ester** AND *an organolithium or organomagnesium compound* that can be used for the preparation of each of the compounds listed below. Write the complete chemical equation in each case.

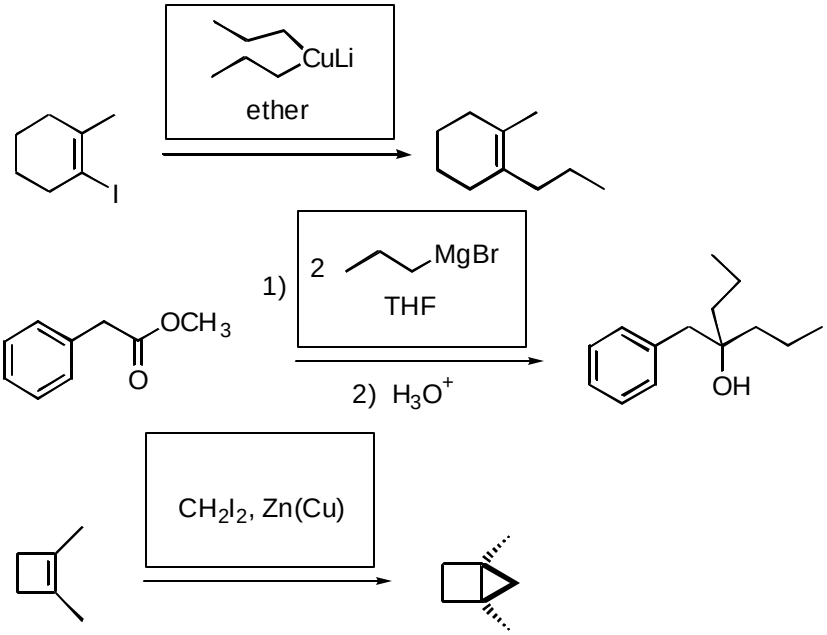
A. 3-Pentanol;



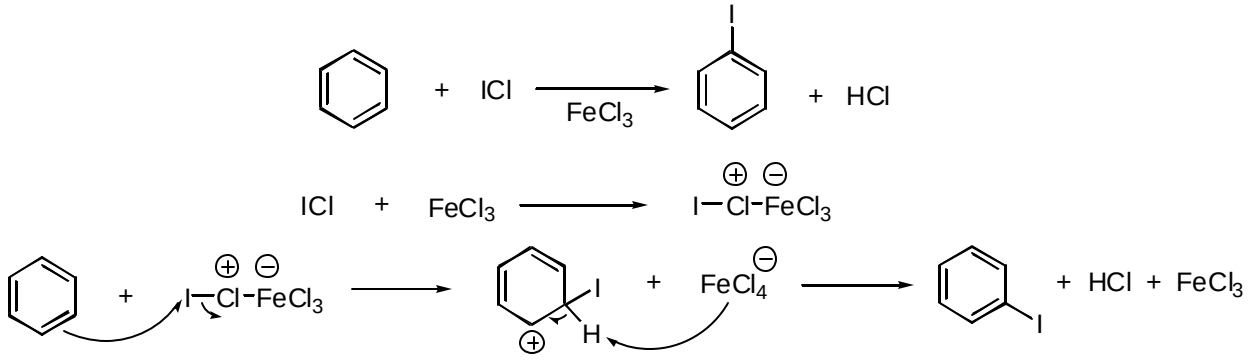
B. 3-Phenyl-3-hexanol;



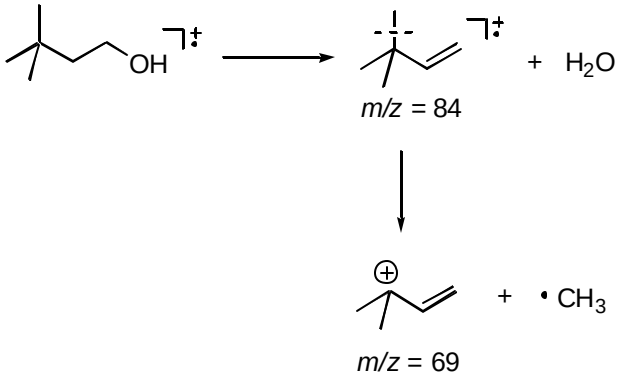
7. (6 pts) Give the structure of the organometallic reagent necessary to carry out each of the following reactions.



8. (5 pts) While chlorination and bromination of benzene are easily accomplished with Br_2 or Cl_2 as reagents, iodination cannot be conducted with I_2, because it is not reactive enough. Instead, the compound iodine monochloride (ICl) is used. Write a detailed mechanism for the reaction below.



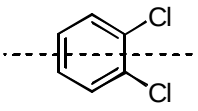
9. (5 pts) Predict TWO likely MS fragmentations for 3,3-dimethyl-1-butanol.



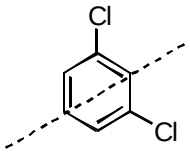
10. (5 pts) You are given three bottles containing *o*-dichlorobenzene, *m*-dichlorobenzene and *p*-difluorobenzene, along with three on-resonance decoupled ^{13}C NMR spectra. Assign each spectrum to a particular compound and briefly explain your reasoning.

A: δ 127.0, 128.9, 130.6, 135.1
B: δ 127.7, 130.5, 132.6
C: δ 116.5, 159.1

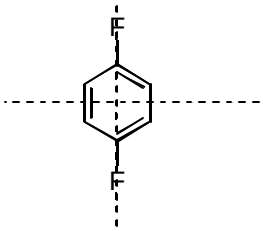
The dashed lines represent internal planes of symmetry:



three types of unequivalent C-atoms, 3 signals in ^{13}C NMR, spectrum **B**

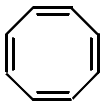


four types of unequivalent C-atoms, 4 signals in ^{13}C NMR, spectrum **A**

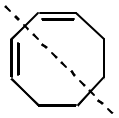


two types of unequivalent C-atoms, 2 signals in ^{13}C NMR, spectrum **C**

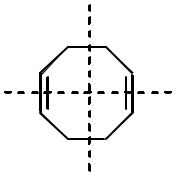
11. (5 pts) Shown below are four eight-membered ring compounds and four ^{1}H NMR spectra. Assign the appropriate spectrum to each compound and briefly explain your reasoning.



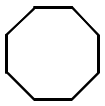
All H-atoms are equivalent, hence 1 signal in ^{1}H NMR. H-atoms are attached to C=C bonds: Spectrum **B**



Four types of H-atoms, hence 4 signals in ^{1}H NMR: Spectrum **D**



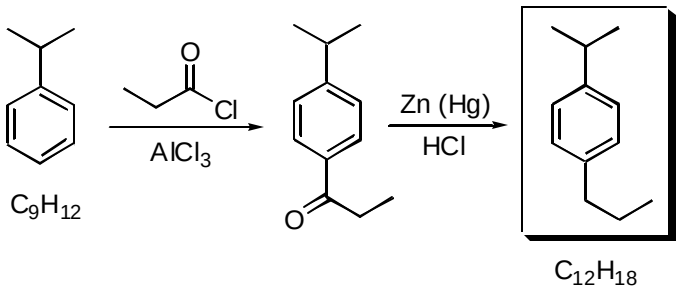
Two types of H-atoms, hence 2 signals in ^{1}H NMR: Spectrum **C**



All H-atoms are equivalent, hence 1 signal in ^{1}H NMR. H-atoms are attached to C-C bonds: Spectrum **A**

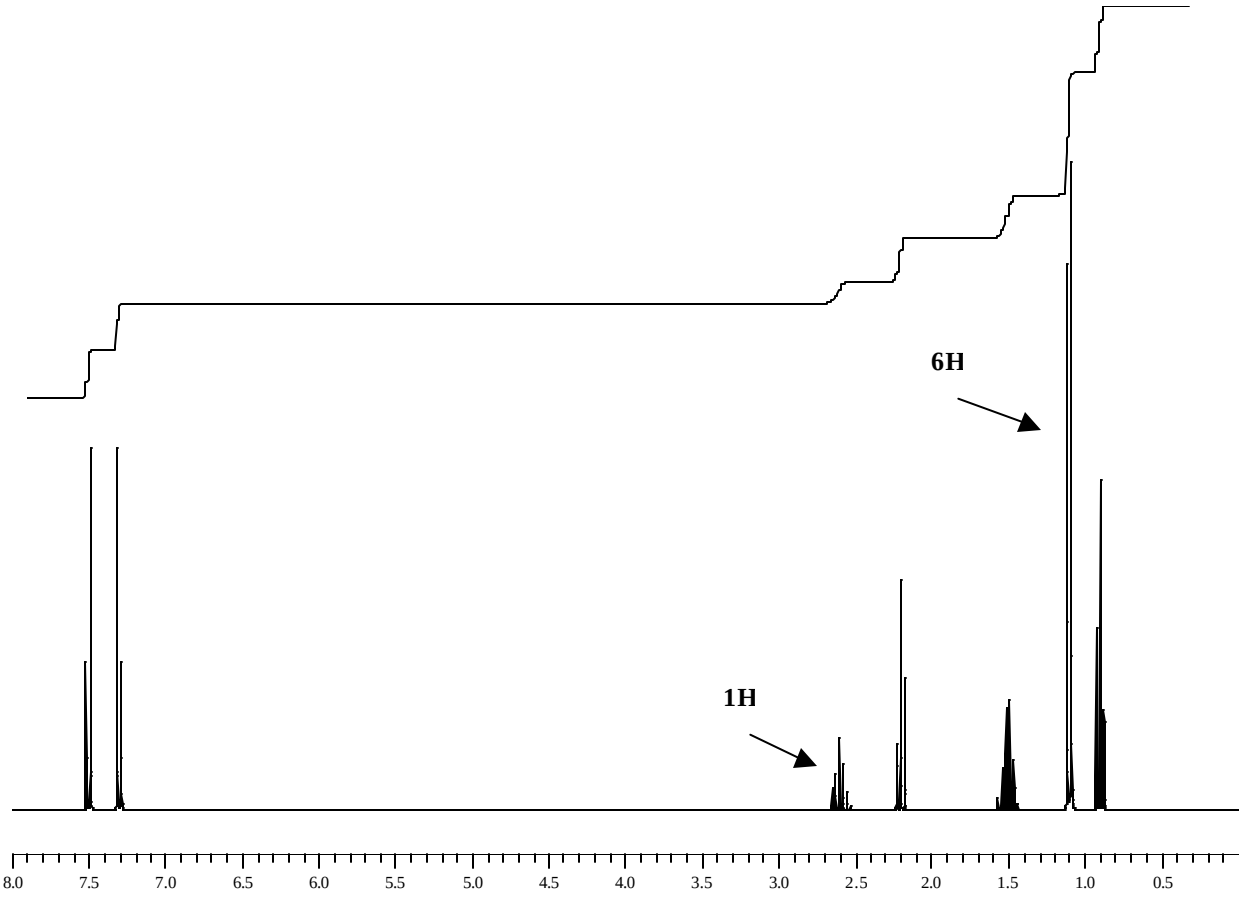
A: δ 1.54 (singlet)
B: δ 5.74 (singlet)
C: δ 2.39 (multiplet, 8H), 5.60 (multiplet, 4H)
D: δ 1.45 (multiplet, 4H), 2.20 (multiplet, 4H), 5.43 (multiplet, 2H), 5.78 (multiplet, 2H)

12. (6 pts) Compound C_9H_{12} is an alkylbenzene. It is subjected to a *Friedel-Crafts* acylation, followed by a *Clemmensen* reduction, giving a product, $C_{12}H_{18}$, whose ^{1}H NMR spectrum is shown below. Write the structural formula of $C_{12}H_{18}$. Write a structural formula for C_9H_{12}.



C_9H_{12} $C_{12}H_{18}$

There are two types of propyl groups (a propyl and an isopropyl) with their characteristic NMR patterns. The downfield region shows the characteristic pattern for a p-disubstituted benzene ring.



13. (3 pts) **BONUS PROBLEM (In order to receive credit for this problem, it has to be solved entirely!!).** When aromatic compounds are treated with formaldehyde, CH_2O, and HCl, the CH_2Cl group is introduced onto the aromatic ring. The reaction is known as chloromethylation. Propose a detailed mechanism for the following chloromethylation reaction: