

CHEMISTRY 314-02

MIDTERM # 1

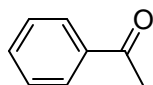
February 10, 2005

Name

The total number of points in this midterm is 100. The total exam time is 120 min (2 h). Good luck!

1. (8 pts) Mark as true (T) or false (F) the following statements. Do not explain!
- All π -donor substituents are activating;
 - The *Wolf-Kishner* reduction transforms a ketone to an alcohol;
 - The chemical shift is independent of the operating frequency of the NMR;
 - The gyromagnetic ratio is independent of the operating frequency of the NMR;
 - Only charged species are observed by MS;
 - Organometallic compounds are strong bases;
 - Organometallic compounds are strong nucleophiles;
 - Carbenes are electron-deficient;
2. Circle ALL that apply:
- A. (3 pts) The following reactions are not possible:
- Benzene + bromine in the presence of FeBr_3 ;
 - Nitrobenzene + butyl chloride, in the presence of AlCl_3 ;
 - Benzaldehyde + acetyl chloride, in the presence of AlCl_3 ;
 - Toluene + nitric/sulfuric acid mixture, upon heating;
- B. (3 pts) In NMR, one observes nuclei that have:
- Odd atomic number but even mass number;
 - Even atomic number but odd mass number;
 - Odd atomic number and odd mass number;
 - Even atomic number and even mass number;
- C. (3 pts) The following reactions are used to prepare tertiary alcohols:
- Reaction of aldehyde with an organolithium compound, followed by acid;
 - Reaction of ketone with an organolithium compound, followed by acid;
 - Reaction of a *Grignard* reagent with an ester, followed by acid;
 - 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;



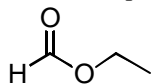
acetophenone

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



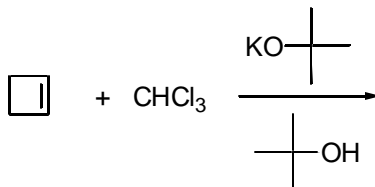
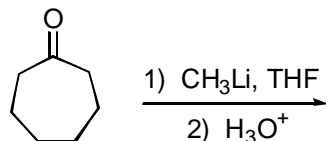
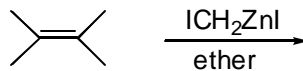
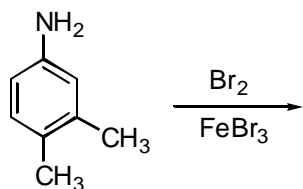
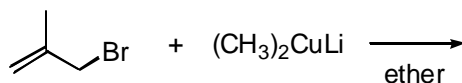
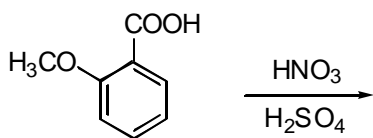
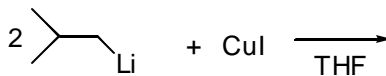
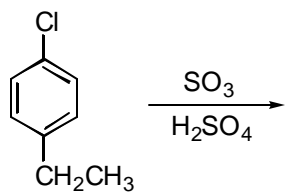
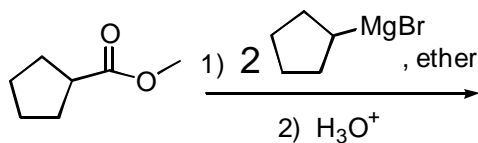
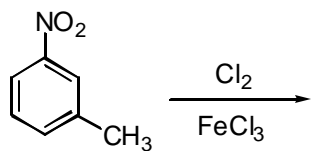
acetone

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

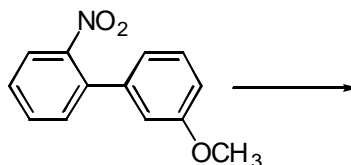
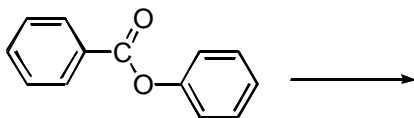


ethylformate

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 monobromination of the following compounds with $\text{Br}_2/\text{FeBr}_3$:

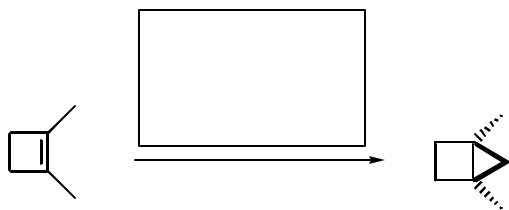
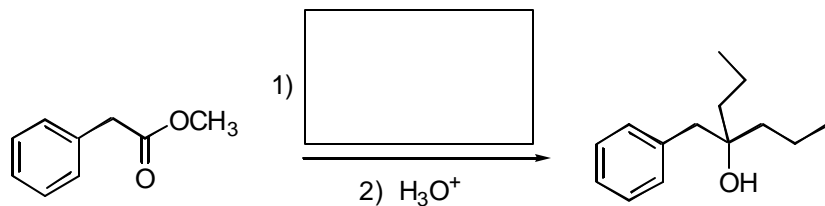
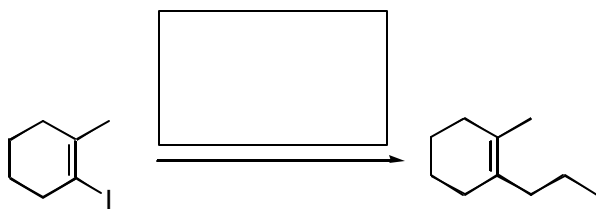


6. (8 pts) Suggest an appropriate combination of a **carbonyl compound (aldehyde or ketone) or ester** AND *an organolithium or organomagnesium compound* that can be used for the preparation of each of the compounds listed below. Write the complete chemical equation in each case.

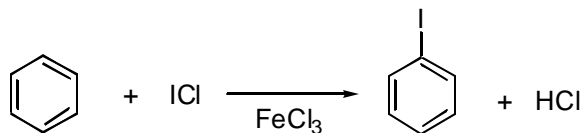
A. 3-Pentanol;

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.

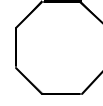
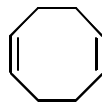
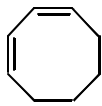
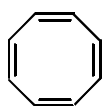
10. (5 pts) You are given three bottles containing *o*-dichlorobenzene, *m*-dichlorobenzene and *p*-difluorobenzene, along with three on-resonance decoupled ^{13}C NMR spectra. Assign each spectrum to a particular compound and briefly explain your reasoning.

A: δ 127.0, 128.9, 130.6, 135.1

B: δ 127.7, 130.5, 132.6

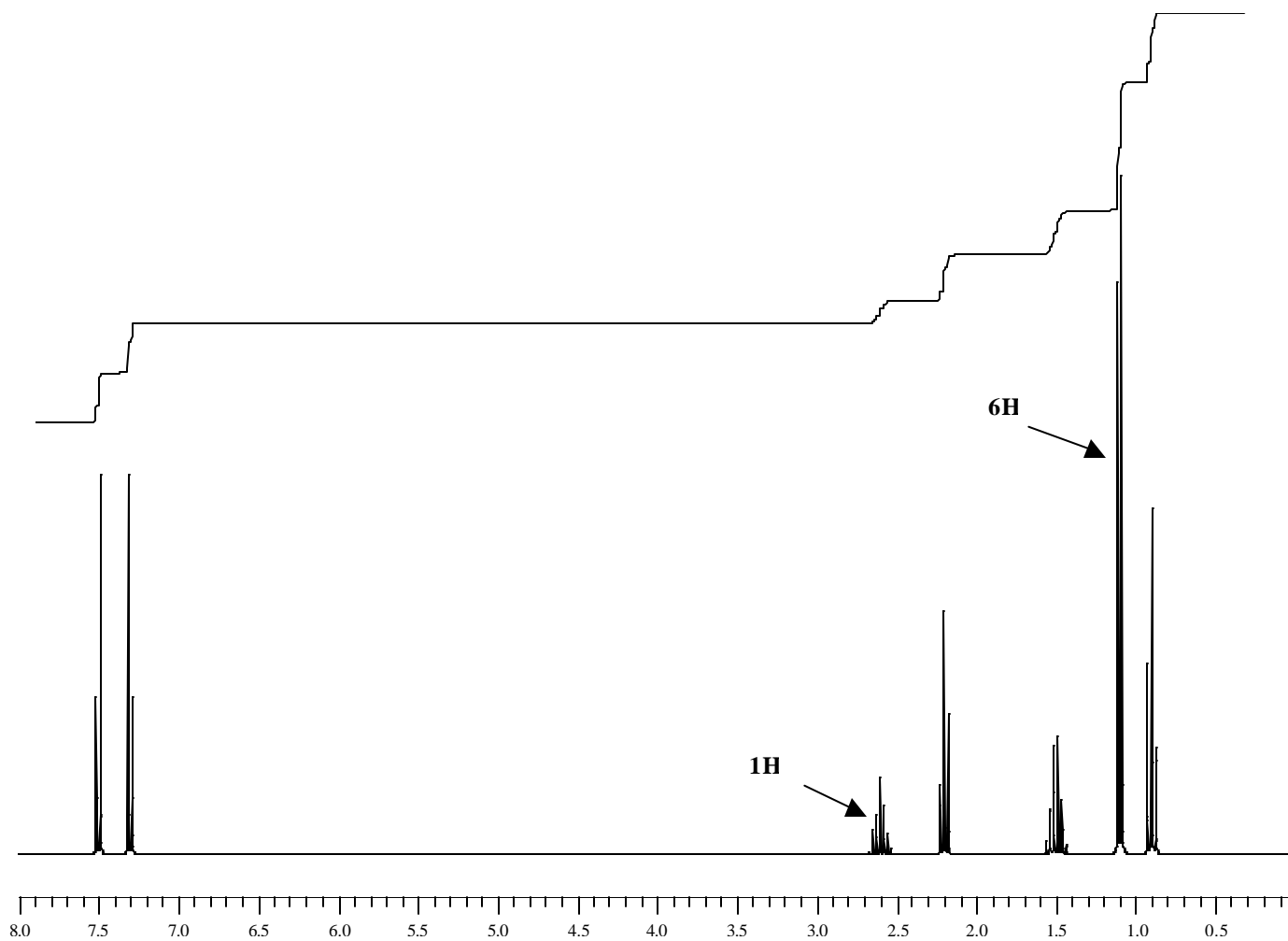
C: δ 116.5, 159.1

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



- 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, $\text{C}_{12}\text{H}_{18}$, whose ^1H NMR spectrum is shown below. Write the structural formula of $\text{C}_{12}\text{H}_{18}$. Write a structural formula for C_9H_{12} .



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:

