

CHEMISTRY 314-01
MIDTERM # 1 – answer key
September 29, 2009

Statistics:

- Average: 70 pts (70%);
- Highest: 96 pts (96%); Lowest: 37 pts (37%)
- Number of students performing at or above average: **16 (57%)**
- Number of students performing below 55%: **4 (14%)**

1. (10 pts) Mark as true (T) or false (F) the following statements. Do not explain!

- (T) Halogens are deactivating and *ortho/para*-directing groups;
- (T) All π -acceptor substituents are deactivating;
- (F) All π -donor substituents are activating;
- (F) All deactivating substituents are *meta*-directing;
- (F) The *Wolf-Kishner* reduction transforms a ketone to an alcohol;
- (F) The base peak in mass spectra is the peak with highest *m/z* ratio;
- (F) All electron-deficient species are observed in mass spectrometry;
- (T) Only charged species are observed in mass spectrometry;
- (T) Carbenes can serve as nucleophiles;
- (T) Carbenes are electron-deficient;

2. Circle ALL that apply:

A. (3 pts) The following structures are organometallic compounds:

a. Phenylsodium;

b. Sodium methoxide;

c. Trimethylaluminum;

d. Potassium acetylide;

B. (3 pts) The following values are independent of the operating frequency of the NMR:

a. Coupling constant;

b. Gyromagnetic ratio;

c. Chemical shift;

d. Integral intensity;

C. (3 pts) The following reactions lead to the conversion of a carbonyl group to a methylene group:

a. Clemmensen reduction;

b. Hydroboration - oxidation;

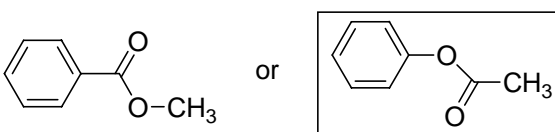
c. Wolff-Kishner reduction;

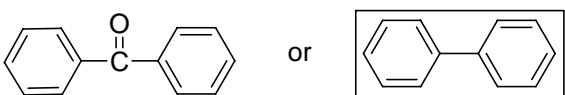
d. *Friedel-Crafts* acylation;

3. (8 pts) In each of the following pairs of compounds, indicate (circle) the compound, which will react faster with the indicated reagent. Do not explain!

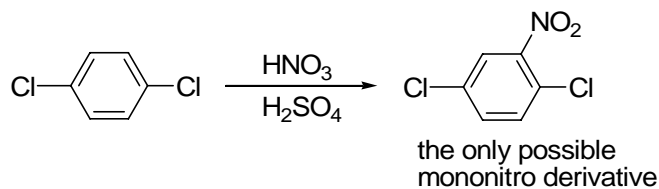
A. Ethylbenzene or benzaldehyde, with a mixture of nitric and sulfuric acid;

B. Anisole or trifluoromethylbenzene, with isopropyl chloride and aluminum trichloride;

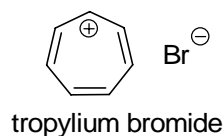
C.  , with bromine and iron tribromide;

D.  , with fuming sulfuric acid;

4. (2 pts) Suggest the correct structure of the isomer of dichlorobenzene that gives only a single product of mononitration.



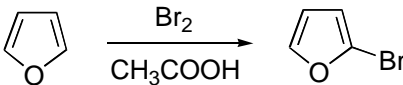
5. (2 pts) Although tropylium bromide is aromatic, it does not undergo any *Friedel – Crafts* reactions. Suggest a brief explanation.



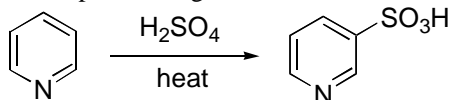
The tropylium cation has an overall positive charge, which would make very difficult any attachment of electrophile (which is itself positively charged). In other words, the aromatic ring is severely deactivated. And, as we know, *Friedel – Crafts* reactions do not occur with deactivated aromatic substances

6. Write and complete a chemical equation for each of the following reactions:

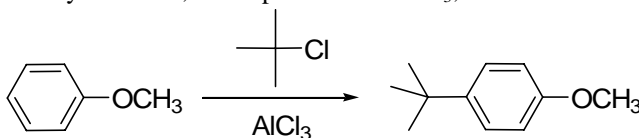
- A. (3 pts) Furan + bromine, in acetic acid;



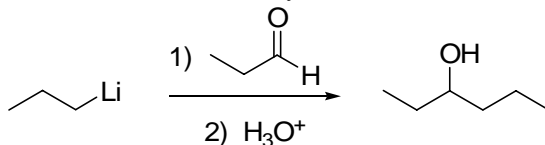
- B. (3 pts) Pyridine and sulfuric acid, upon heating;



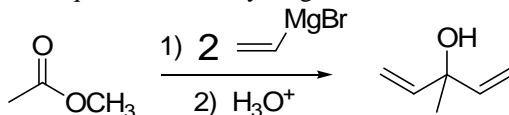
- C. (3 pts) Anisole with *t*-butyl chloride, in the presence of AlCl₃;



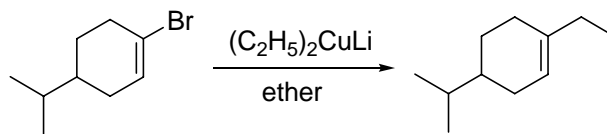
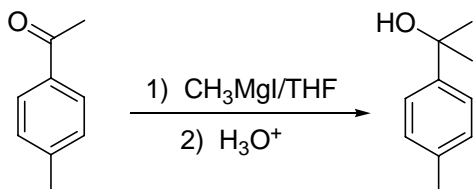
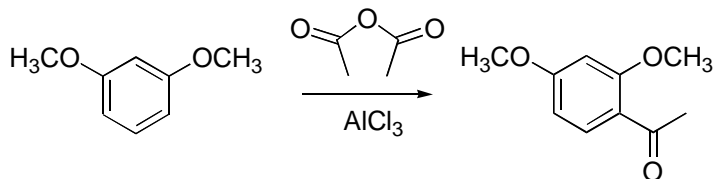
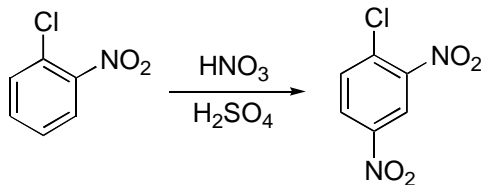
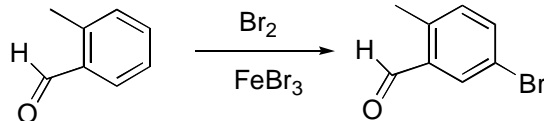
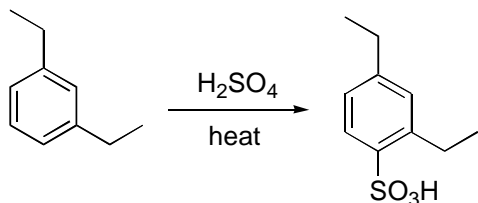
- D. (3 pts) Propyllithium with , followed by acidification;

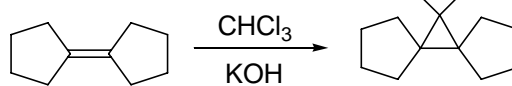
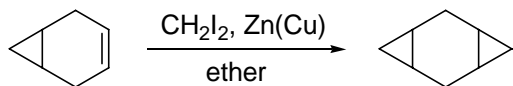
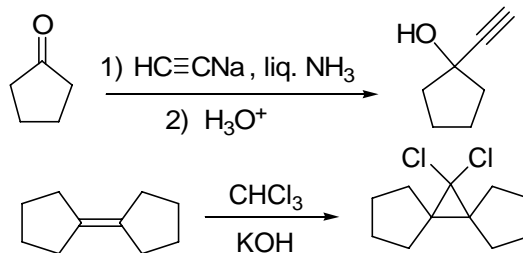
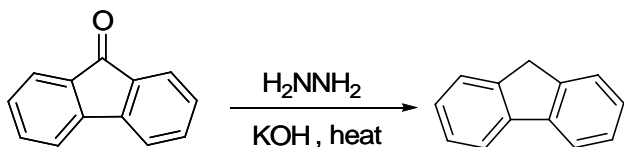


- E. (3 pts) with two equivalents of vinylmagnesium bromide, followed by acidification;

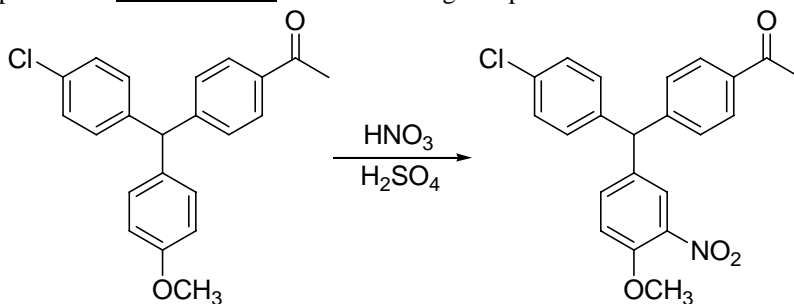


7. (14 pts) Indicate the principal organic product of each of the following reactions. If *o*-,*p*-mixture is expected, write both products.





8. (2 pts) Predict the major product of mono-nitration of the following compound:



9. (4 pts) Suggest one example of each of the following (formulas please!):

A. A *Grignard* reagent.



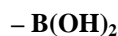
B. A metal carbonyl.



C. A carbene.

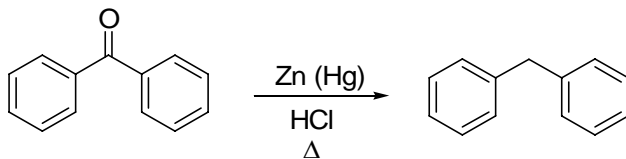


D. A σ -donor, π -acceptor group.

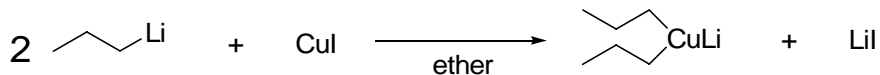


10. (4 pts) Using specific structures, suggest an example of each of the following:

A. A *Clemmensen* reduction.

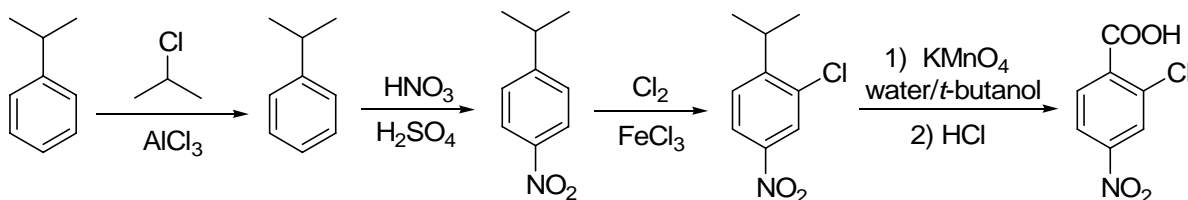


B. Preparation of a lithium dialkylcuprate.

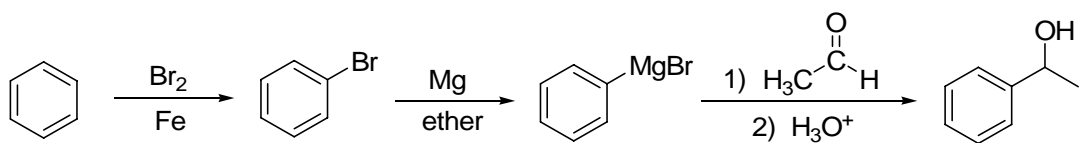


11. Suggest a detailed synthetic sequence for the preparation of each of the following molecules, starting from the indicated compound, and using any other necessary reagents.

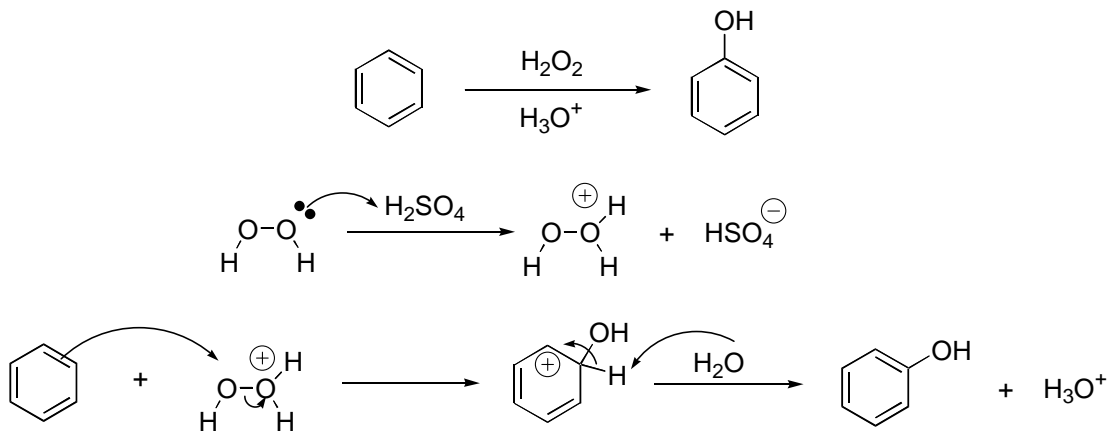
A. (5 pts) **2-Chloro-4-nitrobenzoic acid**, using benzene as a starting material (Assume you can separate *o*- and *p*-isomers);



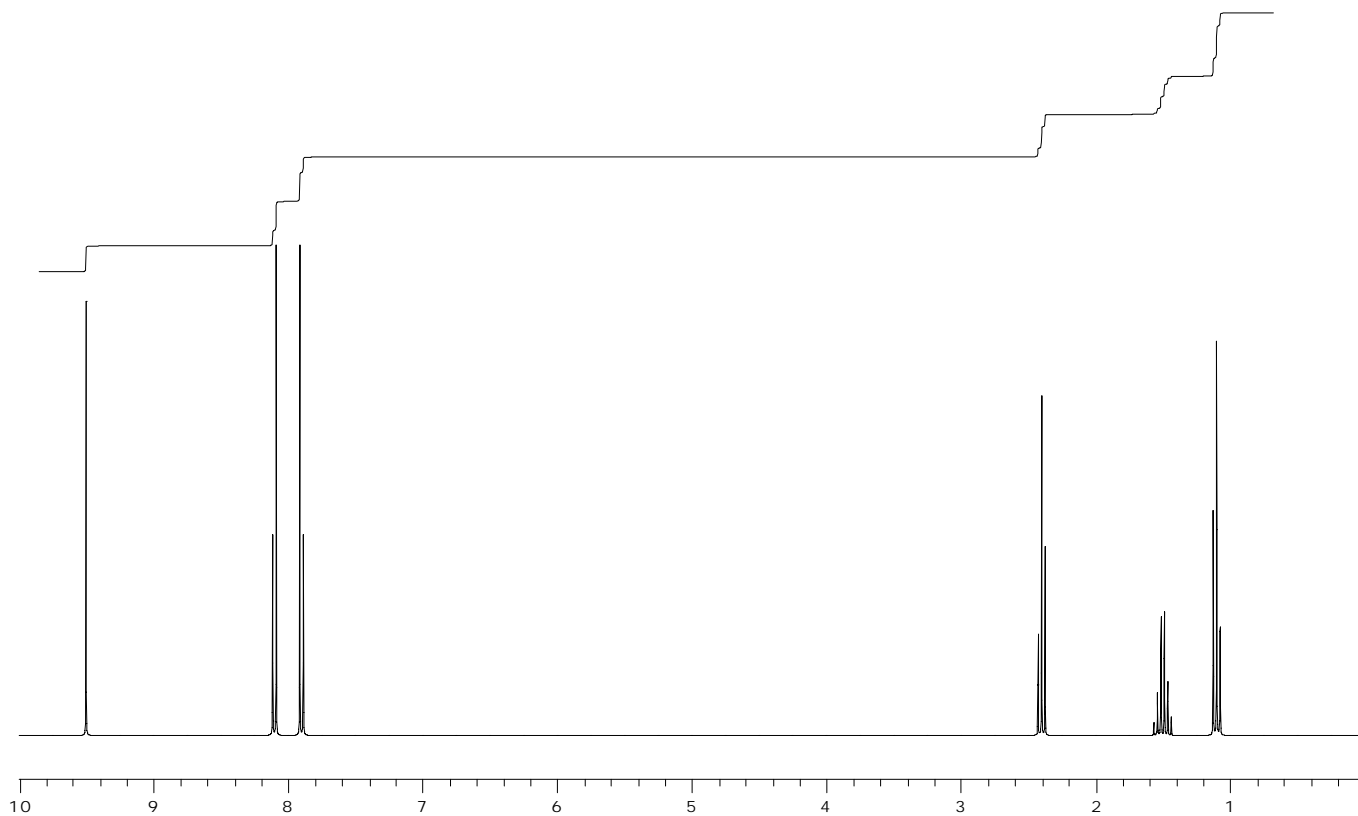
B. (5 pts) **1-phenyl-1-ethanol**, using benzene as a starting material;

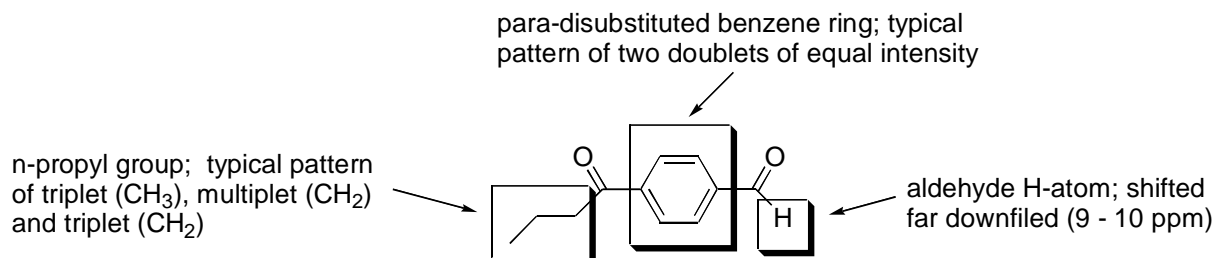
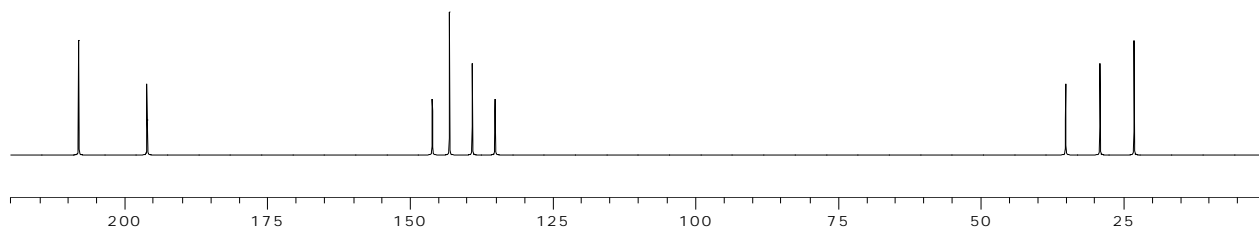


12. (4 pts) In presence of acid catalyst benzene undergoes an S_EAr reaction with H_2O_2 to form phenol. Suggest a detailed mechanism for this conversion.

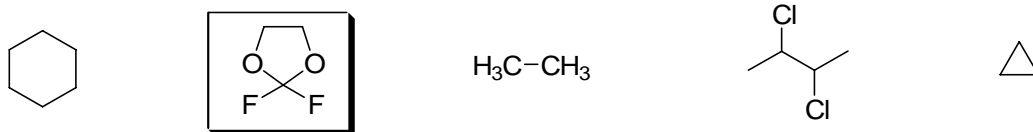


13. (5 pts) Certain compound has molecular formula $\text{C}_{11}\text{H}_{12}\text{O}_2$. Its ^1H and ^{13}C NMR spectra are shown below. Propose a structure for this molecule.





14. (2 pts) Among the following structures, circle the compound that has one signal in its ¹H NMR and two signals in its ¹³C NMR:

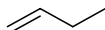


15. (2 pts) In class, our NMR discussion started with just the hydrogen nucleus, without any electrons. If you were able to run an ¹H NMR spectrum of a sample of H-nuclei (e.g. some H⁺ in the gas phase), where would you expect to find the signal:

- A. Far downfield, $\delta > 10$ ppm.
 B. Within the typical range for hydrogen, $10 > \delta > 0$ ppm.
 C. Far upfield, $\delta < 0$ ppm.

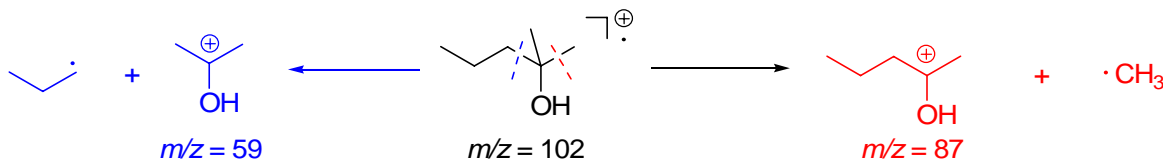
Briefly account for your choice: The H-nucleus is not shielded at all, since there isn't any electron density around it. When nuclei are not shielded (or, alternatively, heavily deshielded), then their signals experience considerable downfield shifts. Thus, one would expect the signal for the H-nucleus to be found far downfield, with chemical shift value $\delta > 10$ ppm.

16. (3 pts) Among the isomeric alkenes C₄H₈, suggest the structure that would exhibit 4 signals in its ¹H NMR spectrum.

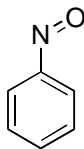


17. (4 pts) In the mass spectrum of 2-methyl-2-pentanol, among other signals, there are two prominent peaks at $m/z = 87$ and $m/z = 59$. Suggest structures for the species that are responsible for these signals and the fragmentation that leads to them from the molecular ion.

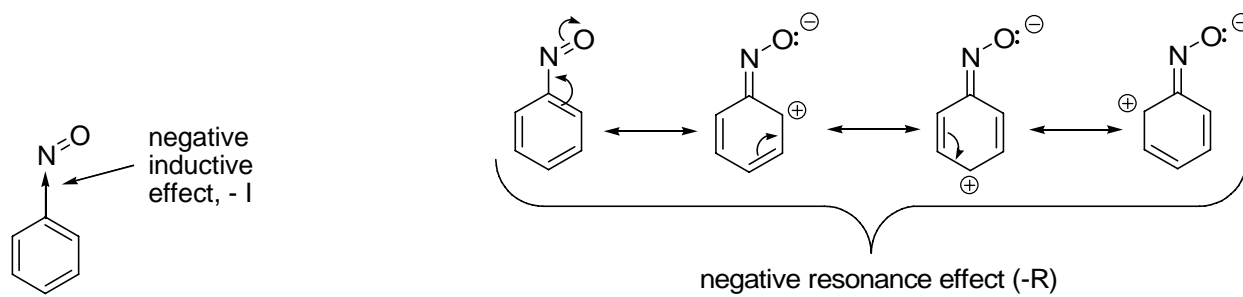
Solution: Since the signals are prominent, they must correspond to very typical alcohol fragmentations. It turns out that both signals in question are generated by the same type of fragmentation: **α -cleavage**.



18. (2 pts) **BONUS PROBLEM (In order to receive credit for this problem, it has to be solved entirely!!)**. The nitroso group ($-N=O$) has a directing and activating effect identical to that of halogens. Account for this by using appropriate resonance structure analysis.



In order to mimic a halogen, the NO group must have a deactivating, but o-,p-directing effect. The deactivation is a result of both an inductive and resonance effect:



The o-,p-orientation is a result of a positive resonance effect (conjugation of N-lone pair with the π -system of the ring):

