CHEM 347 – Organic Chemistry II (for Majors)

Instructor: Paul J. Bracher

Hour Examination #1

Wednesday, February 12th, 2014

6:30–8:30 p.m.

Student Name (Printed)	Solutions
Student Signature	N/A

Instructions & Scoring

- Please write your answers on the official answer sheet. No answers marked in this booklet will be graded.
- If you wish, you may use two sheets (front-and-back) of handwritten notes and a plastic model kit.
- You may not use electronic devices or communicate with others for the duration of this exam.
- Your exam answer sheet may be photocopied.

Problem	Points Earned	Points Available
I		40
II		20
III		20
IV		20
TOTAL		100

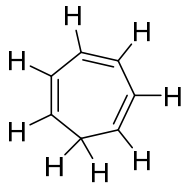
Questions, Required Information, Supplementary Information

Problem I. Multiple choice (40 points total; +4 points for a correct answer, +1 point for an answer intentionally left blank, and 0 points for an incorrect answer). For each question, select the best answer of the choices given. Write the answer, legibly, in the space provided on the answer sheet.

(1) A Which of the following methods represents the most straightforward technique for distinguishing a pure sample of *o*-dichlorobenzene from a pure sample of *m*-dichlorobenzene?

(a) nuclear magnetic resonance spectroscopy
(b) mass spectrometry
(c) infrared spectroscopy
(d) colonoscopy

(2) C Which of the following best describes the electronic structure of compound **A**?

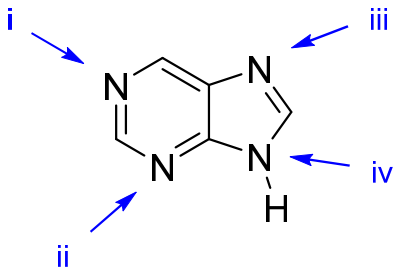


A

(a) aromatic
(b) antiaromatic
(c) nonaromatic
(d) pseudoaromatic
(e) aromatizzilistical

(3) E

Purine (**B**) is the parent compound of a class of heterocycles common in biochemistry. Which of the nitrogen atoms in purine is <u>not</u> sp^2 hybridized?

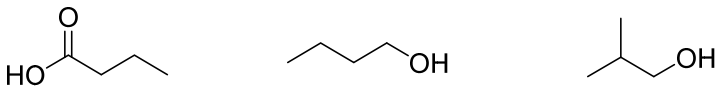


B

(a) i
(b) ii
(c) iii
(d) iv
(e) all four nitrogens are sp^2 hybridized

(4) B

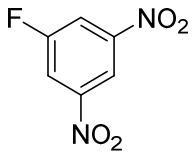
Which of the following compounds has four peaks in its ^{13}C NMR spectrum and a signal at δ 3.9 in its ^{1}H NMR spectrum that disappears upon addition of D_2O?



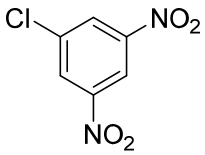
(a) (b) (c)

(d) (e)

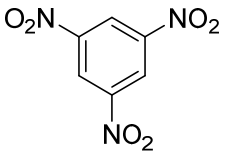
(5) E Which of the following compounds will react fastest with potassium hydroxide (KOH) in a nucleophilic aromatic substitution reaction?



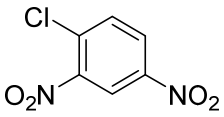
(a)



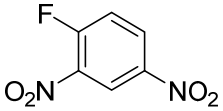
(b)



(c)

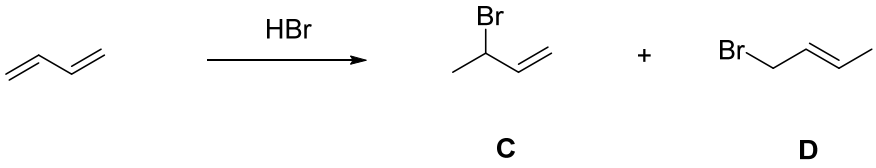


(d)



(e)

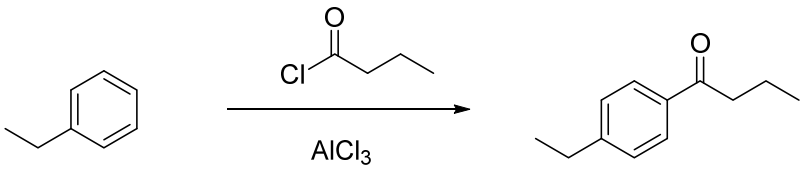
(6) B Which statement best describes the following reaction?



C **D**

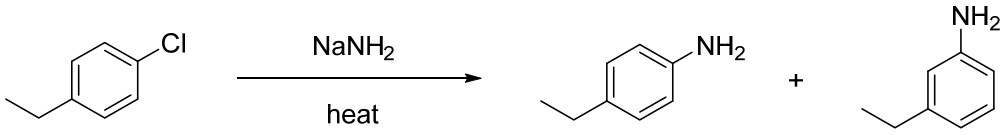
(a) the ratio of product **C** : **D** will increase at higher temperatures
(b) **C** forms from a resonance-stabilized carbocation intermediate
(c) **D** forms from a carbocation intermediate not stabilized by resonance
(d) all of the above

(7) E Which of the following is an appropriate solvent for the reaction shown below?



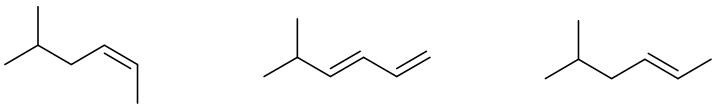
(a) methylene chloride (dichloromethane)
(b) toluene (methylbenzene)
(c) *p*-xylene (*p*-dimethylbenzene)
(d) water
(e) nitrobenzene

(8) D Which of the following best describes the role of NH_2^- in this reaction?



(a) a Brønsted–Lowry base
(b) a nucleophile
(c) a catalyst
(d) both (a) and (b) are correct
(e) both (b) and (c) are correct

(9) A Which of the following compounds will have the most exothermic reaction <u>per double bond</u> with H_2 in the presence of Pd-C? That is to say, which compound will have the most negative heat of hydrogenation <u>per double bond</u>?

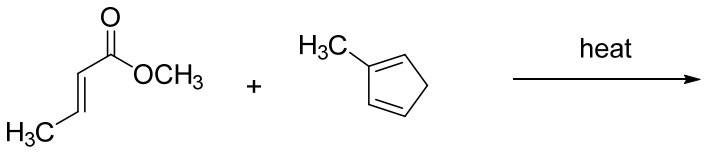


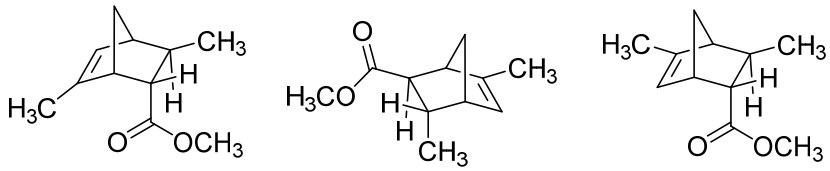
(a) (b) (c)

(d) (e)

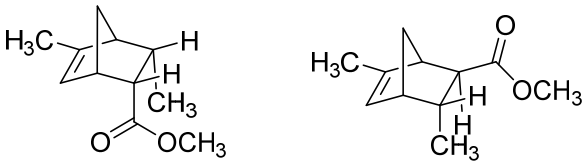
(10) D

Which of the following compounds would not be observed as the product of a Diels–Alder reaction between the diene and dienophile shown below? Note: this question is not asking what product(s) would you find little of in the reaction mixture; it is asking what product would you see none of.



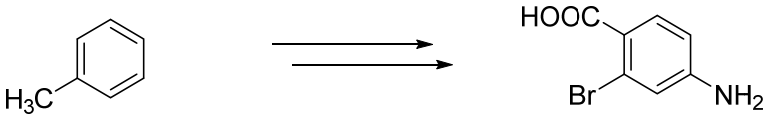


(a) (b) (c)

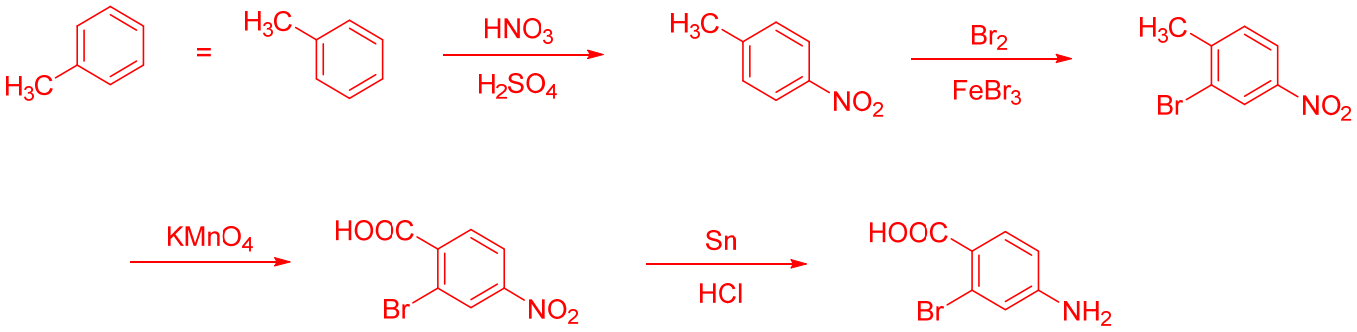


(d) (e)

Problem II. Synthesis (20 points). Design an efficient synthesis of compound **E** from toluene and any other reagents you wish that contain five atoms of carbon or fewer. Be careful in selecting the order of reactions you choose to use. This synthesis can be carried out in four steps.



E

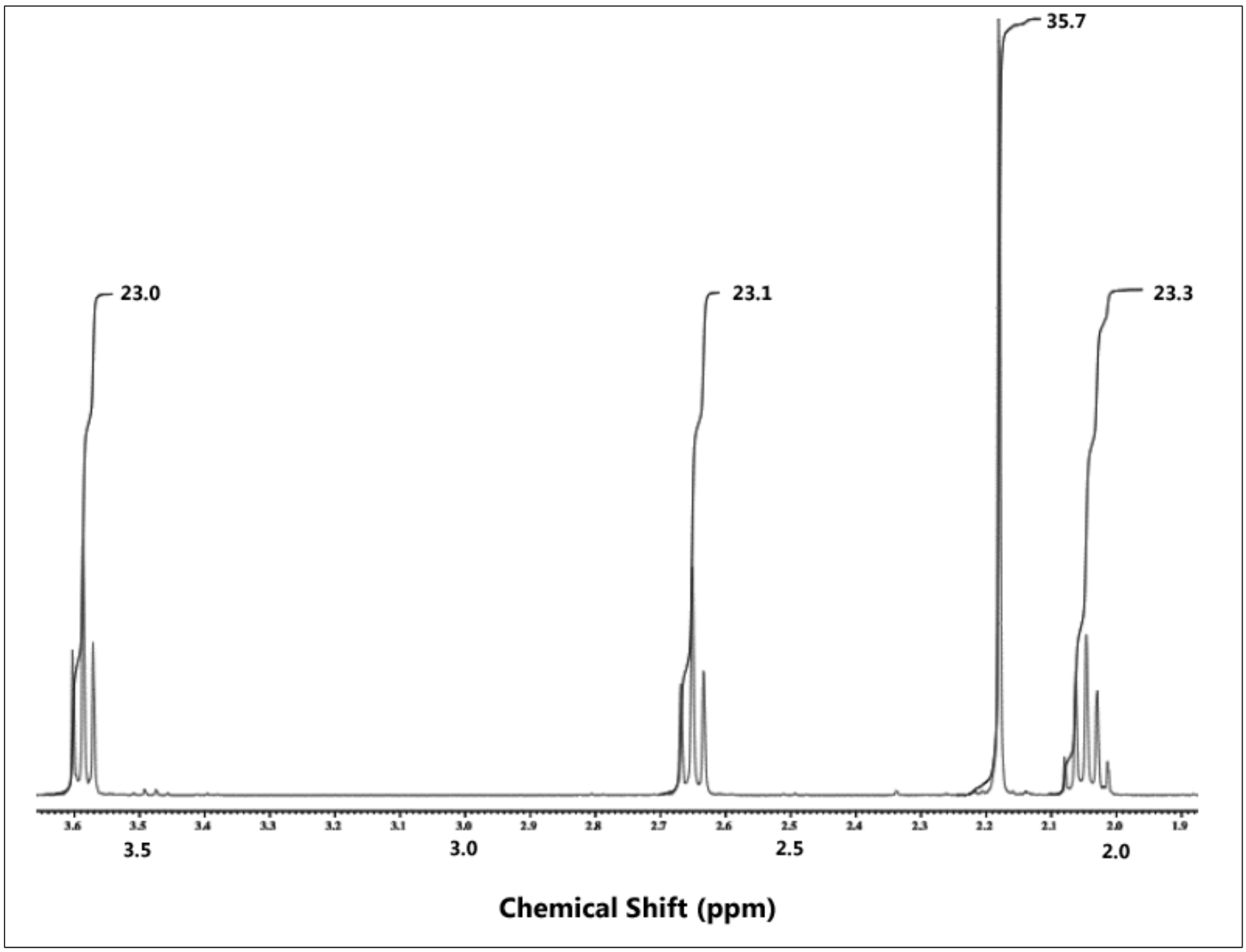


Notes:

- Performing the nitration first (instead of the bromination) is preferable because the methyl and nitro groups in the first intermediate both direct the next addition to occur at the same position. If the bromination were performed first, the methyl and bromo groups would direct to different positions on the ring, potentially leading to a mixture of products in the subsequent electrophilic aromatic substitution reaction.

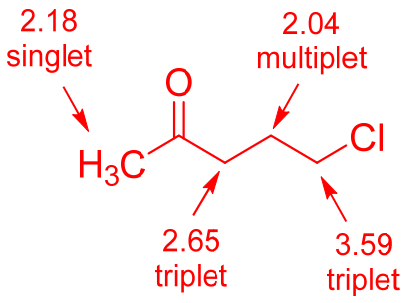
- The oxidation of the methyl group should be performed before the reduction of the nitro group because the amino group can be oxidized with $KMnO_4$, while the carboxylic acid cannot be reduced with Sn / HCl.

Problem III. Structure Determination (20 points). High resolution mass spectral analysis of a pure sample of compound **F** reveals it to have a molecular formula of C_5H_9OCl. ^1H NMR analysis of a sample dissolved in $CDCl_3$ yields the following spectrum. The numbers above each signal represent integration values for the area under the signal.

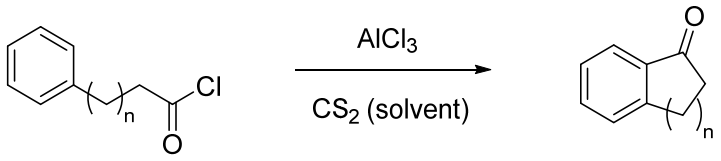


Source: Prof. John Hanson's Web site, University of Puget Sound
http://www2.ups.edu/faculty/hanson/c251.07.projects/frontalin/frontalin.htm

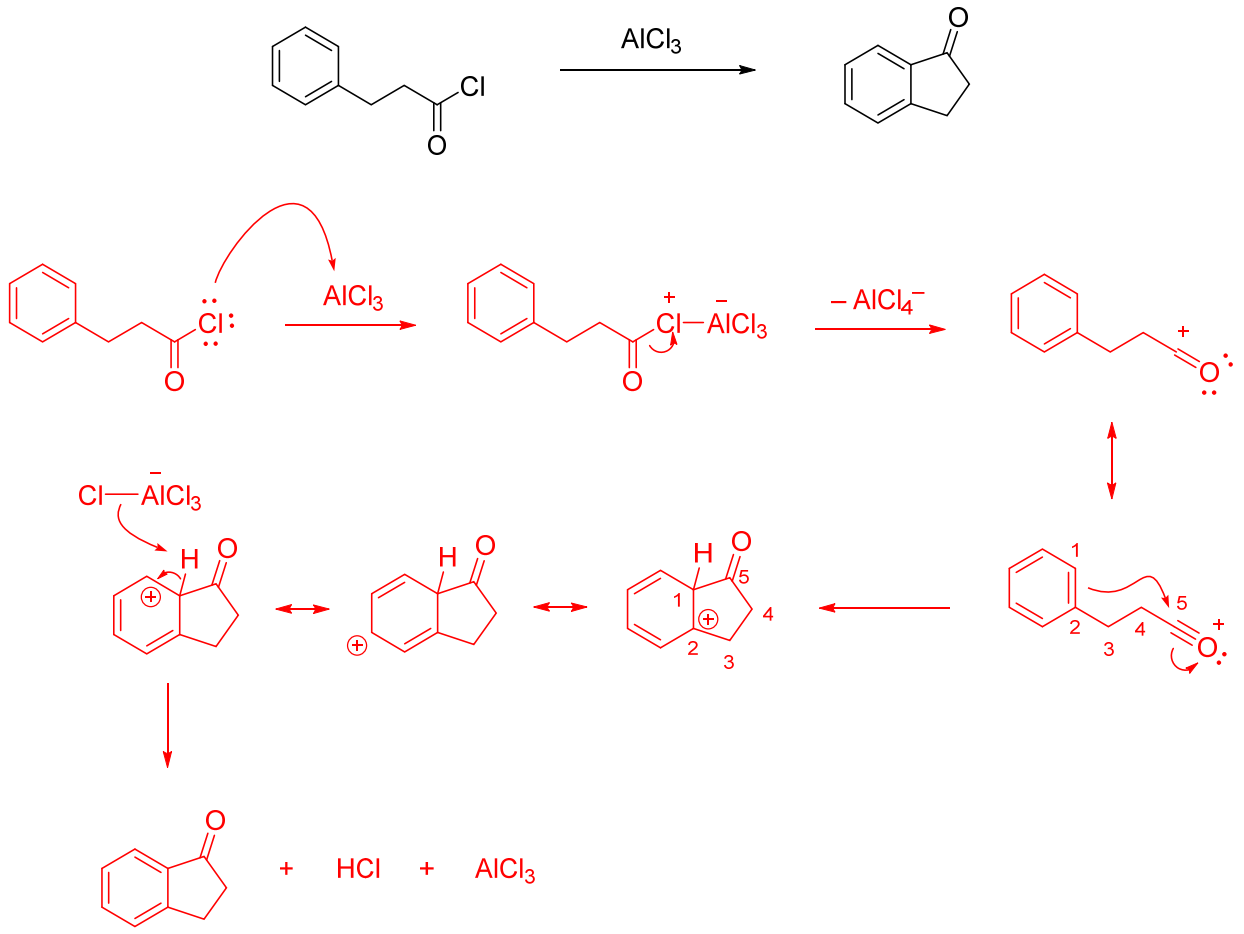
(i) Draw a Lewis structure for compound **F** consistent with the data provided above.
(ii) For each chemical shift, draw an arrow pointing to one of the hydrogens that gives rise to that signal.



Problem IV. Mechanism (20 points). In 1954, Schubert, et al., reported the synthesis of benzocyclanones by the following reaction:



(a) (15 points) Draw a sensible mechanism for the reaction where n = 1, shown below. Remember to use proper "curved arrow notation" to account for the movement of electrons in the making and breaking of bonds. Show all significant resonance forms that account for the stability of the intermediates in the reaction.



(b) (5 points) As the length of the chain grows, the yield of the reaction decreases until at n = 5, the general benzocyclanone product shown above is not observed. Instead, the authors observed the formation of a polymer. Draw one possible structure for this polymer (of the many possibilities). You do not need to draw a mechanism for its formation.

note that the substitution of the rings is para (or ortho) because alkyl group are o/p directors