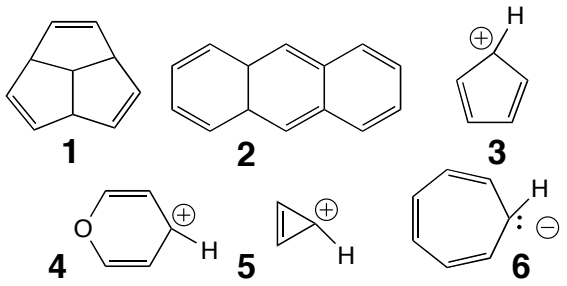
Organic Synthesis (Chem-2260) **Examination #2**

Alan Cutler, Spring 2009 Wednesday, March 18

Name _____

Part A. Short Answers

1. Which of the following compounds are aromatic? Assume that each compound is planar.



A. 1 & 3
B. 2 & 6
C. 4 & 5
D. 1 & 2
E. 3 & 6

2. Which of the following statements about the π molecular orbital description of cyclobutadiene is not correct?

A Cyclobutadiene has two degenerate nonbonding π molecular orbitals

B Cyclobutadiene has a single bonding π molecular orbital

C Cyclobutadiene has two electrons in nonbonding π molecular orbitals

D Cyclobutadiene has electrons in an antibonding π* molecular orbital, which makes it antiaromatic

E none of the above

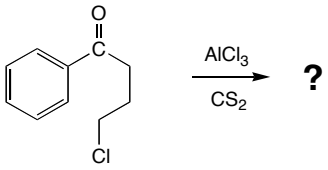
A.
B.
C.
D.
E.

3. Cycloheptatriene (C_7H_8) has a **(A.)** **higher**/**lower** pKa than cyclopentadiene (C_5H_6); its conjugate base carbanion thus is much **(B.)** **more**/**less** stable than the cyclopentadienyl carbanion. This is consistent with the cycloheptatrienyl conjugate base having **(C.)** **aromatic**/**antiaromatic** character. Circle each of your three choices in the answer box.

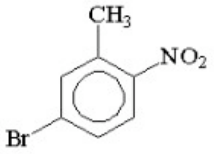
A. higher or lower
B. more or less
C. aromatic or antiaromatic

4. Acetic anhydride (below) in the presence of aluminum chloride also acetylates benzene. Draw the Lewis structure for the reactive electrophile intermediate responsible for acetylating benzene. Transfer your structure to the answer box on the answer sheet. Hint: Use the interaction of acetic anhydride with $AlCl_3$, with arrow pushing, to generate the required electrophile.

5. Transfer the structure for the following reaction product to the answer box on the answer sheet.

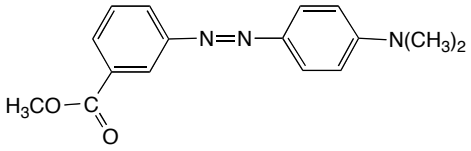


6. What is the name of the following compound?

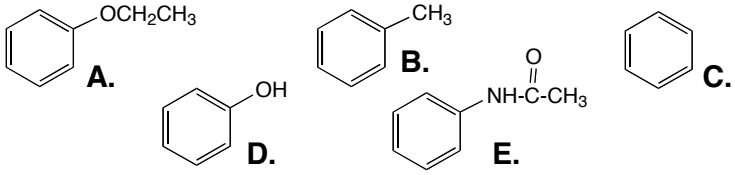


A. *o*-nitro-*m*-bromotoluene
B. 3-bromo-6-nitrotoluene
C. *m*-bromo-*o*-nitrotoluene
D. 5-bromo-2-nitrotoluene
E. 2-nitro-5-bromotoluene

7. What two organic compounds react to yield the following diazo product? Draw both structures as Lewis structures in the answer box on the answer sheet.



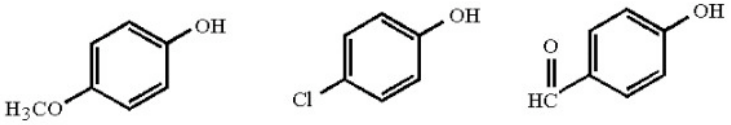
8. Which of the following compounds reacts most slowly during nitration?



9. How many ^{13}C NMR spectral absorptions appear for the *o*-, *m*-, and *p*-substituted xylenes?

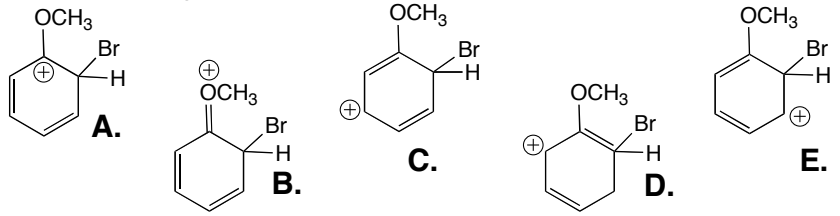
	ortho	meta	para
A.	3	4	2
B.	4	5	3
C.	3	6	3
D.	4	5	4
E.	5	6	4

10. List the following compounds in order of decreasing acidity.

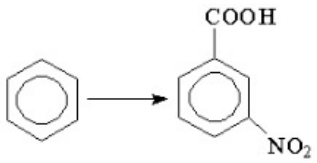


A. I > II > III
B. II > I > III
C. III > II > I
D. II > III > I
E. I > III > II

11. Which of the following structures is the most important contributor to the resonance hybrid formed when anisole undergoes o-bromination?



12. Which is the best method for carrying out the following preparation?



A. +COOH // HNO_3, H_2SO_4

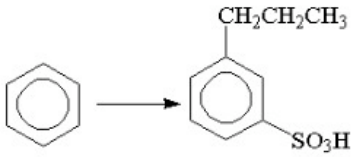
B. CH_3Cl, $AlCl_3$ // HNO_3, H_2SO_4 // $KMnO_4$, H^+, heat

C. $CH_3Cl/AlCl_3$ // $KMnO_4/H^+$, heat // HNO_3, H_2SO_4

D. HNO_3, H_2SO_4 // CH_3Cl, $AlCl_3$ // $KMnO_4$, H^+, heat

E. HNO_3, H_2SO_4 // +COOH

13. Which is the best method for carrying out the following preparation?



A. H_2SO_4 // $CH_3CH_2CH_2Cl$, $AlCl_3$

B. $CH_3CH_2CH_2Cl$, $AlCl_3$ // H_2SO_4

C. $CH_3CH_2(C{=}O)Cl$, $AlCl_3$ // H_2SO_4

D. $CH_3CH_2(C{=}O)Cl$, $AlCl_3$ // Zn(Hg), HCl(heat)

E. $CH_3CH_2(C{=}O)Cl$, $AlCl_3$ // H_2SO_4 // Zn(Hg), HCl(heat)

14. What is the <u>best</u> method for the preparation of *p*-chlorotoluene in high yield?

A. start with benzene; CH_3Cl, $AlCl_3$ // Cl_2, $FeCl_3$

B. start with benzene; Cl_2, $FeCl_3$ // CH_3Cl, $AlCl_3$

C. start with toluene; Cl_2, $FeCl_3$

D. start with chorobenzene; CH_3Cl, $AlCl_3$

E. start with *p*-aminotoluene; $NaNO_2$, HCl, 0° C // CuCl

15. What is the <u>best</u> method for the preparation of *m*-dibromobenzene from benzene?

A. HNO_3, H_2SO_4 // Pd(C), H_2 // $NaNO_2$, HCl, 0°C // Br_2, $FeBr_3$ twice

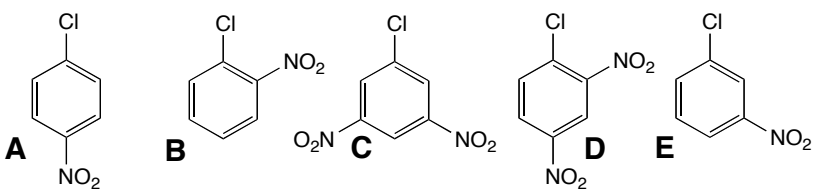
B. HNO_3, H_2SO_4 // Pd(C), H_2 // $NaNO_2$, HCl, 0°C // Br_2, $FeBr_3$ twice // H_3PO_2

C. HNO_3, H_2SO_4 // Pd(C), H_2 // $NaNO_2$, HCl, 0°C // H_3PO_2 // Br_2, $FeBr_3$ twice

D. HNO_3, H_2SO_4 // Br_2, $FeBr_3$ // Pd(C), H_2 // $NaNO_2$, HCl, 0°C // CuBr

E. Br_2, $FeBr_3$ twice

16. Which of the following is <u>most</u> reactive toward nucleophilic aromatic substitution?



17. Provide a series of synthetic steps by which *p*-bromoanisole can be prepared from benzene.

A. HNO_3, H_2SO_4 // Cl_2, $FeCl_3$ // Sn, HCl // $NaOCH_3$, heat // $NaNO_2$, HCl, 0°C // CuBr

B. HNO_3, H_2SO_4 // Cl_2, $FeCl_3$ // $NaOCH_3$, heat // Sn, HCl // $NaNO_2$, HCl, 0°C // CuBr

C. Cl_2, $FeCl_3$ // HNO_3/H_2SO_4 // $NaOCH_3$, heat // Sn, HCl // $NaNO_2$, HCl, 0°C // CuBr

D. Cl_2, $FeCl_3$ // HNO_3/H_2SO_4 // Sn, HCl // $NaOCH_3$, heat // $NaNO_2$, HCl, 0°C // CuBr

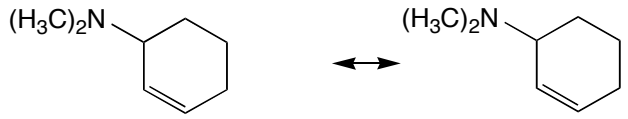
E. HNO_3, H_2SO_4 // Cl_2, $FeCl_3$ // Sn, HCl // $NaNO_2$, HCl, 0°C // CuBr // $NaOCH_3$, heat

(Note: the Sn, HCl reaction requires OH^- treatment in its workup)

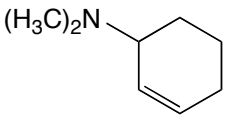
<u>Part B. All work and answers must be recorded on this sheet</u>.

1. Consider dimethylaniline, Ph-$N(CH_3)_2$ (or $C_6H_5N(CH_3)_2$), with the dimethylamine group on benzene.

(a) Decide whether the dimethylamine group is a <u>net</u> electron donor group (edg) or withdrawal group (ewg) with benzene. Explain, using Lewis structures and resonance forms (maximum two) as appropriate. (All Lewis structures must show all lone pairs, multiple bonds and formal charges.) An unsubstantiated answer will not be graded.

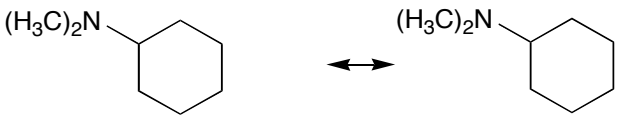


(b) Dimethylaniline undergoes electrophilic aromatic substitution with bromine under unspecified conditions (but in the absence of $FeBr_3$) to yield a monobromination product. This product could be either the meta- or para-substituted bromodimethylaniline, $C_6H_4(Br)N(CH_3)_2$). What is the <u>rate-determining step</u> for this reaction? Use <u>arrow pushing</u> to illustrate your answer.

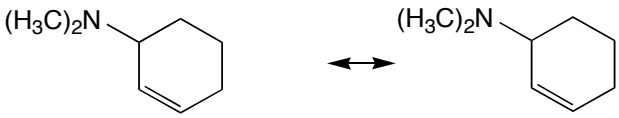


(c) Explain whether dimethylaniline is a p- or m- director when it undergoes monobromination under these conditions. Provide one set of just two resonance forms for <u>both</u> the meta- and para-substituted product <u>with arrow pushing</u> to justify your answer.

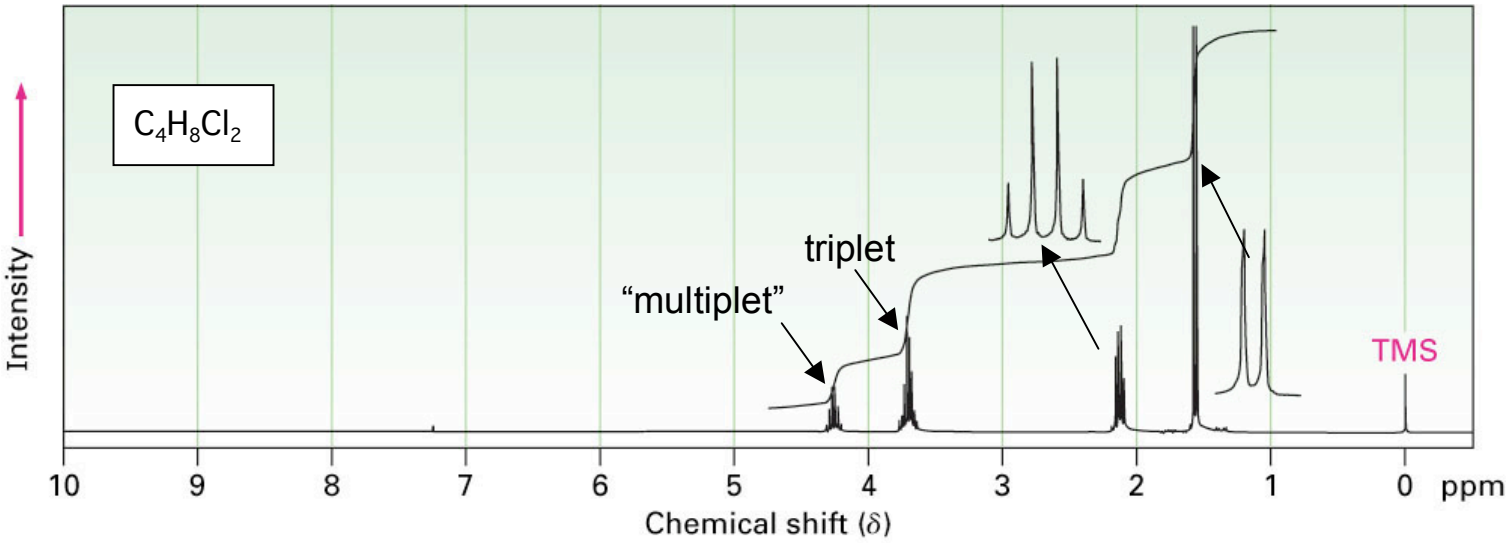
meta



para



2. (a) Assign the structure that is consistent with the following ^{1}H NMR spectrum of a compound with the empirical structure, $C_4H_8Cl_2$. All H's are accounted for by the integration of 1 : 2 : 2 : 3, going downfield to upfield. Make sure that you assign each multiplet to its H's.



(b) The apparent 1:3:3:1 quartet at δ 2.2 is intriguing in that it does not "fit" the usual assignment for three equivalent hydrogens undergoing spin-spin interactions with the hydrogens absorbing at δ 2.2. Identify these interacting hydrogens and do a splitting tree that replicates this apparent quartet. Then come up with the correct symbol, e.g., 'dd' for doublet of doublets.

1.

A. 1 & 3
B. 2 & 6
C. 4 & 5
D. 1 & 2
E. 3 & 6

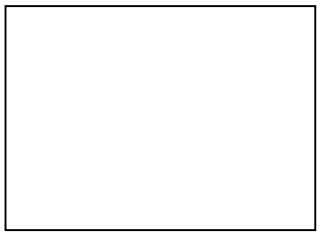
2.

A.
B.
C.
D.
E.

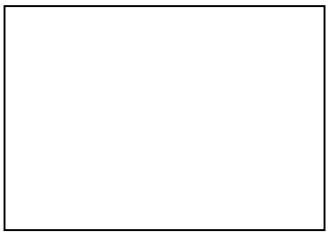
3.

A. higher or lower
B. more or less
C. aromatic or antiaromatic

4.



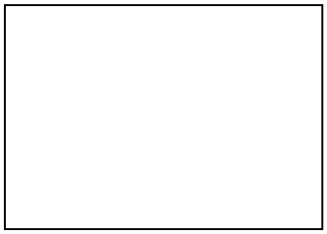
5.



6.

A.
B.
C.
D.
E.

7.



8.

A.
B.
C.
D.
E.

9.

A.
B.
C.
D.
E.

10.

A. I > II > III
B. II > I > III
C. III > II > I
D. II > III > I
E. I > III > II

11.

A.
B.
C.
D.
E.

12.

A.
B.
C.
D.
E.

13.

A.
B.
C.
D.
E.

14.

A.
B.
C.
D.
E.

15.

A.
B.
C.
D.
E.

16.

A.
B.
C.
D.
E.

17.

A.
B.
C.
D.
E.

Name _____