Chemistry 112B: Midterm 2, Tuesday April 15, 2008

Name: Key

UCSID: ____________________ *GSI:*____________________

Question 1 ________________ (18 points)

Question 2 ________________ (25 points)

Question 3 ________________ (25 points)

Question 4 ________________ (8 points)

Question 5 ________________ (33 points)

Question 6 ________________ (10 points)

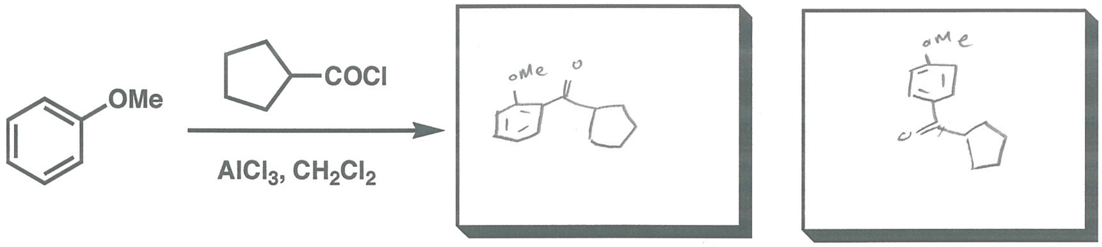
Question 7 ________________ (36 points)

Question 8 ________________ (20 points)

Total ——————————————/175 points

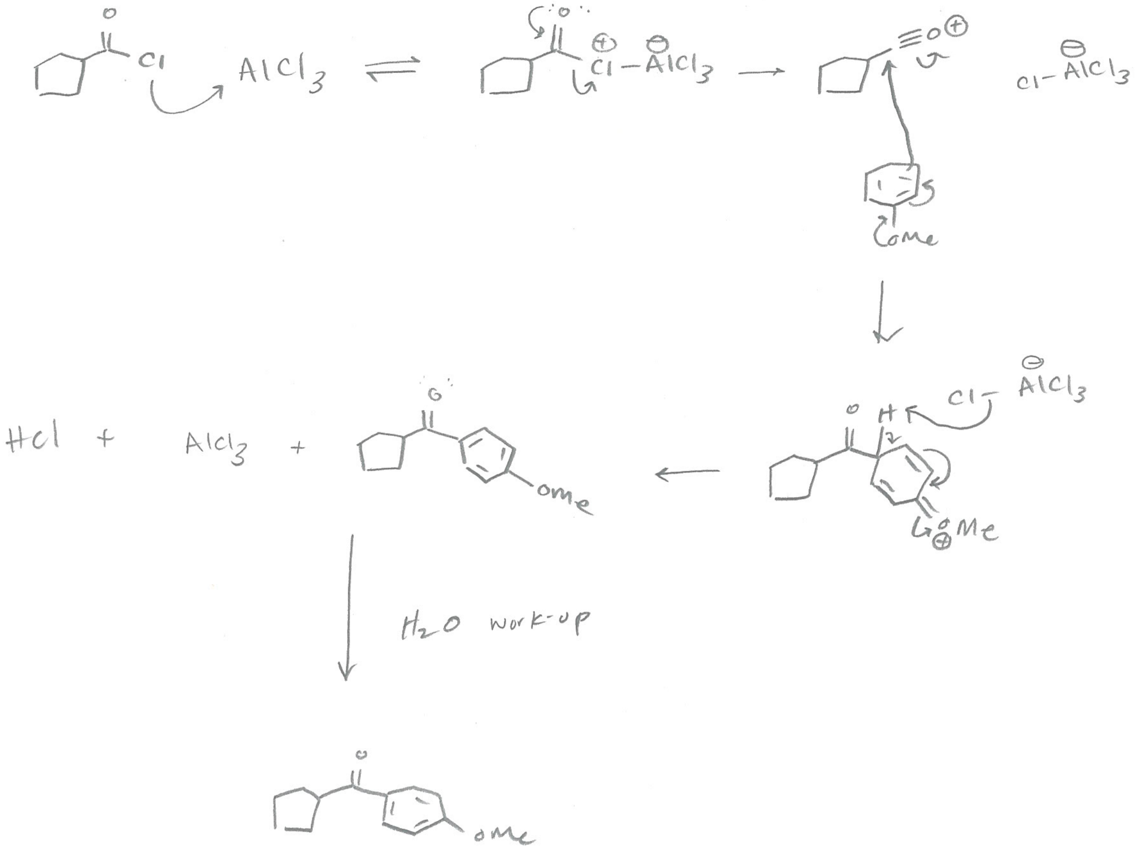
Question 1

(a) Predict 2 possible products of the following reaction (6 points).



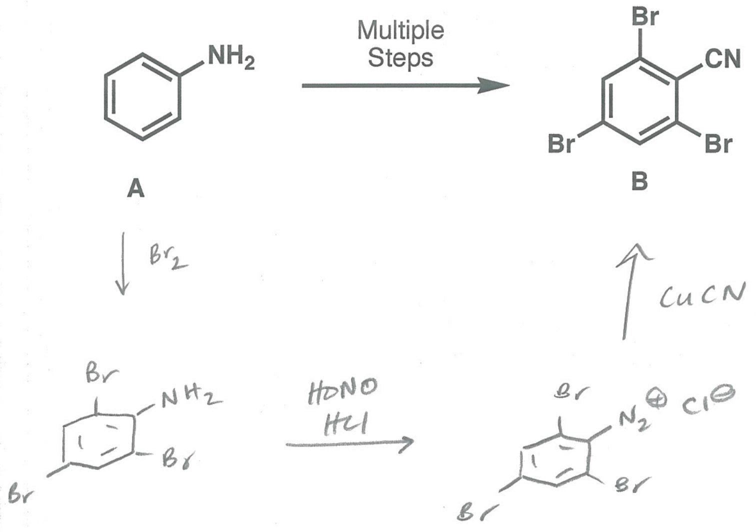
(b) Provide a name for this type of reaction (2 points) : Friedel-Crafts acylation

(c) Provide a mechanism for the formation of *one* of the products from Part (a) (10 points).

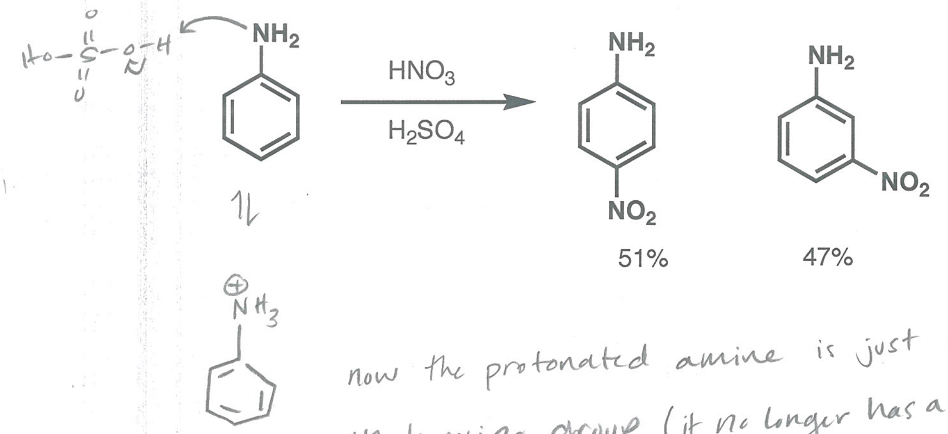


Question 2

(a) Provide a synthesis of **B** from **A**. (Hint: the sequence involves a diazotization reaction) (15 points)



(b) The amino group is *normally* an ortho/para director. However, in the following nitration reaction, a significant amount of meta product is formed, why? (10 points)

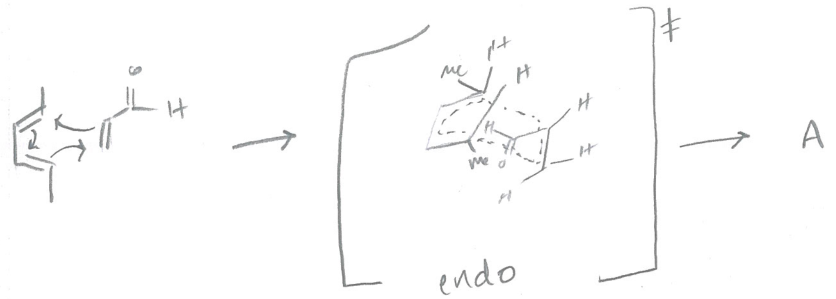


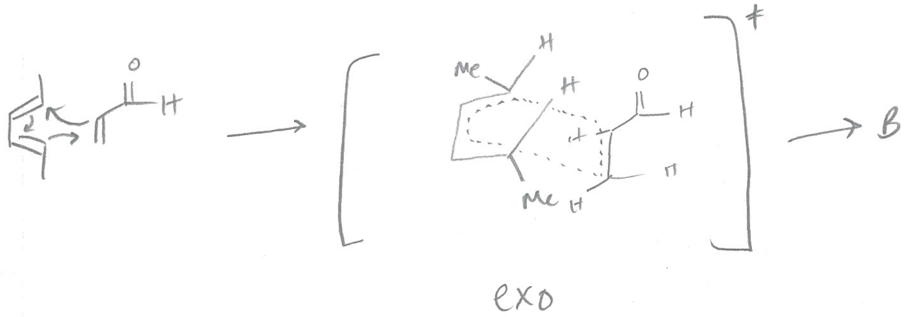
now the protonated amine is just an electron-withdrawing group (it no longer has a lone pair to donate into the ring), & it's a meta-director

Question 3

(a) Provide a mechanism and transition states that rationalize the stereochemical outcome in the formation of **A** and **B**. Label the transition states *endo* or *exo* (20 points).

A **B**





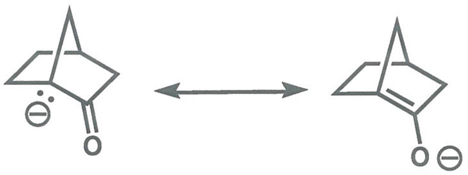
(b) Which is the major product (**A** or **B**)? (5 points)

A

Question 4

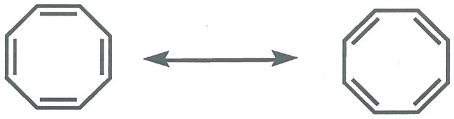
Explain with appropriate figures why the following resonance structures are **not** possible (8 points).

(a)



lone pair in an sp^3 orbital is orthogonal to the p-orbitals of the π- bond

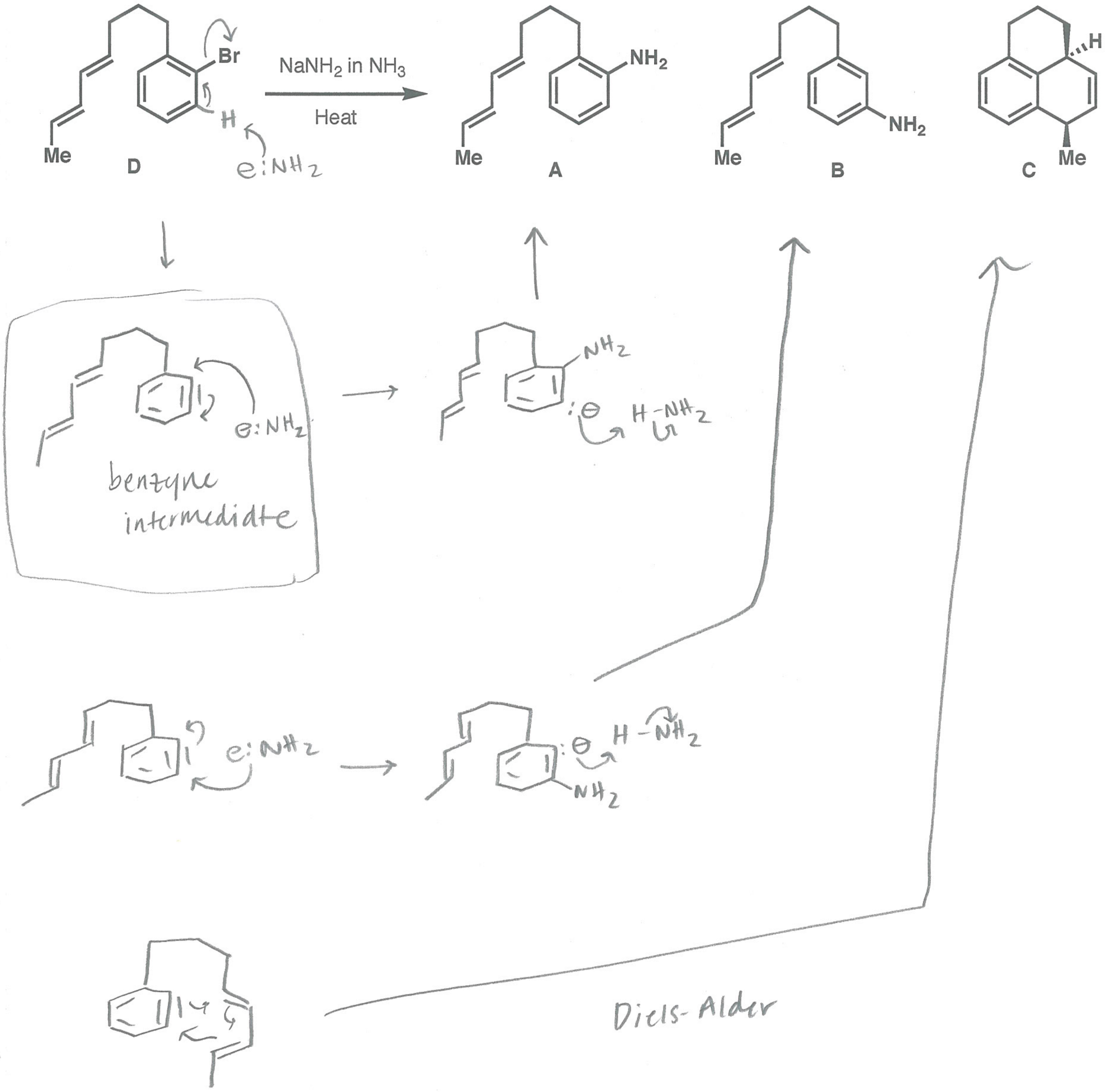
(b)



if planar, it is antiaromatic, so it adopts a tub shape where there is no p-orbital overlap

Question 5

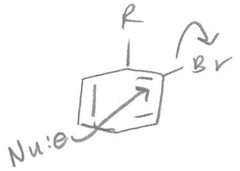
(a) Provide mechanisms to explain the formation of **A**, **B** and **C** from **D** (25 points).



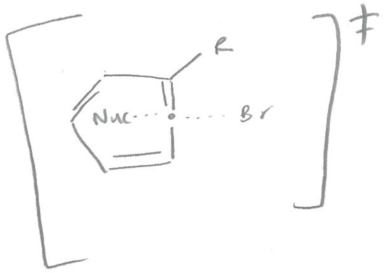
(b) Give *two* reasons why an S_N2 reaction is *unlikely* to explain the formation of **A** in part (a). (8 points).

Possible answers include:

① it's impossible for the nucleophile to approach through the ring



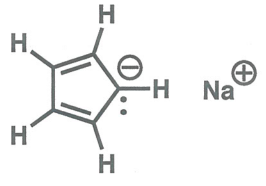
② sp-hybridized carbon in TS‡ is highly strained + very high energy



Question 6

(From Loudon; Problem 16.36)

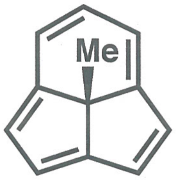
(a) The ^{1}H NMR spectrum of the sodium salt of cyclopentadiene (**A**) consists of a singlet, why? (5 points)



A

A is aromatic + all resonance structures are equivalent, ∴ all ^{1}H resonances equivalent

(b) The methyl group in the following compound (**B**) has an unusual ^{1}H chemical shift of δ (-1.67), about 4 ppm lower than the chemical shift of a typical allylic methyl group, why? (5 points)

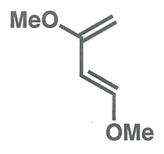


B

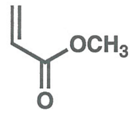
The methyl group is in the shielded region of the aromatic system.

Question 7

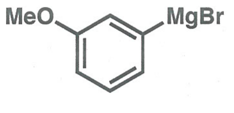
Provide a synthesis for **E** given that it begins with a Diels Alder reaction of **A** and **B**. Other steps could include an acid-catalyzed enol hydrolysis of the Diels Alder product (i.e., loss of two equivalents of methanol), a conjugate addition (with a cuprate formed from **C**) and other steps. Provide reagents and a complete synthesis using additional reactions of carbonyl and aromatic compounds that you have learned. Alternatively, you may also propose a synthesis of **E** from any starting material six carbons or less. (36 points)



A



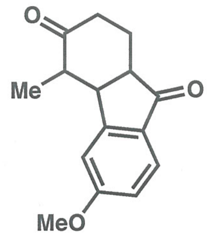
B



C

MeI

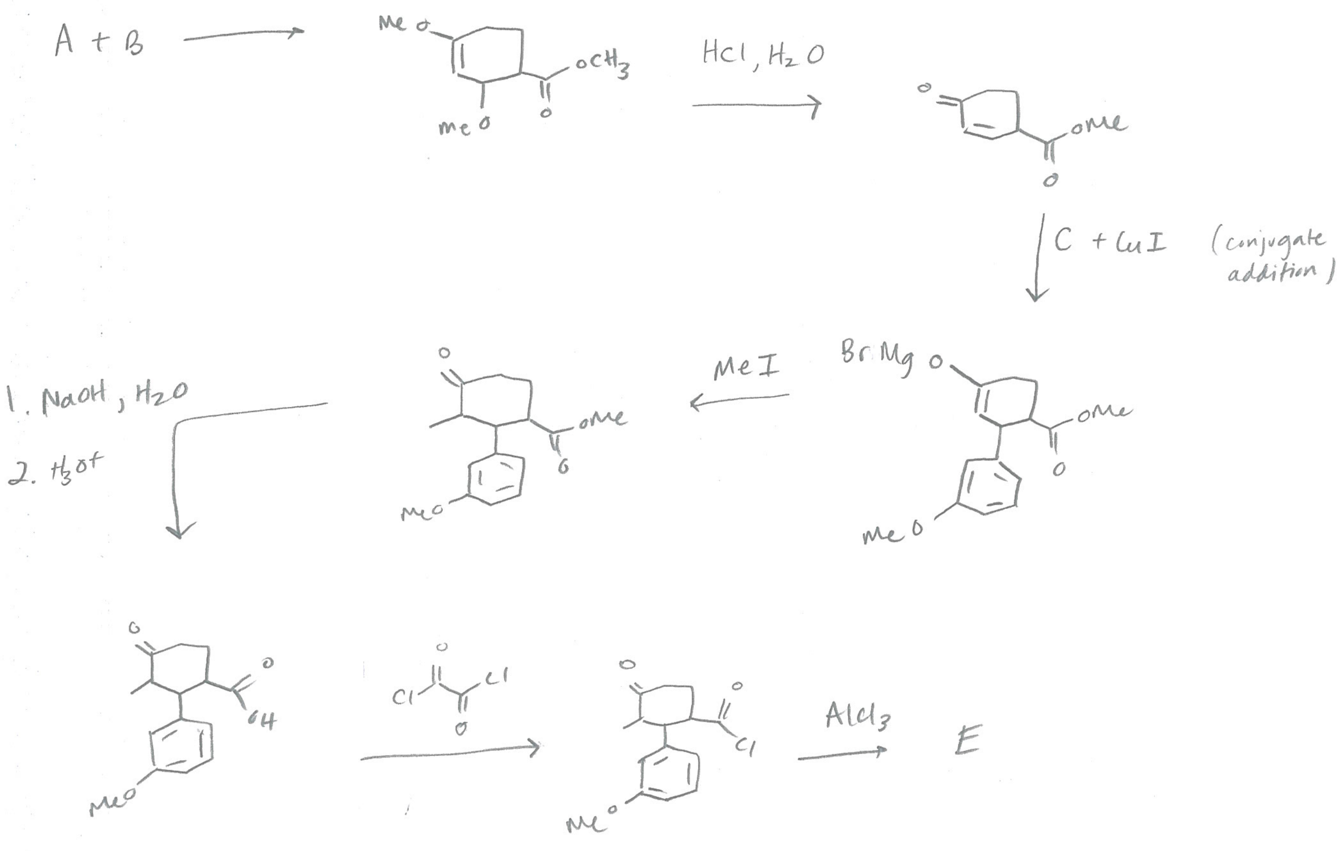
D



E

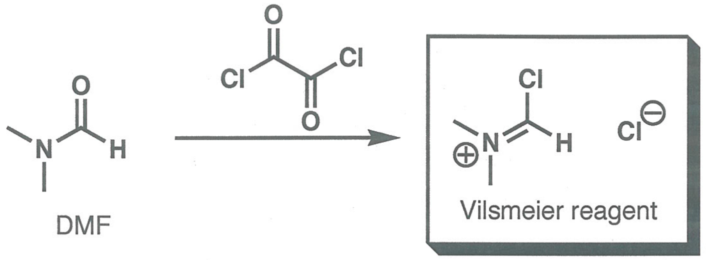
(Diels-Alder)

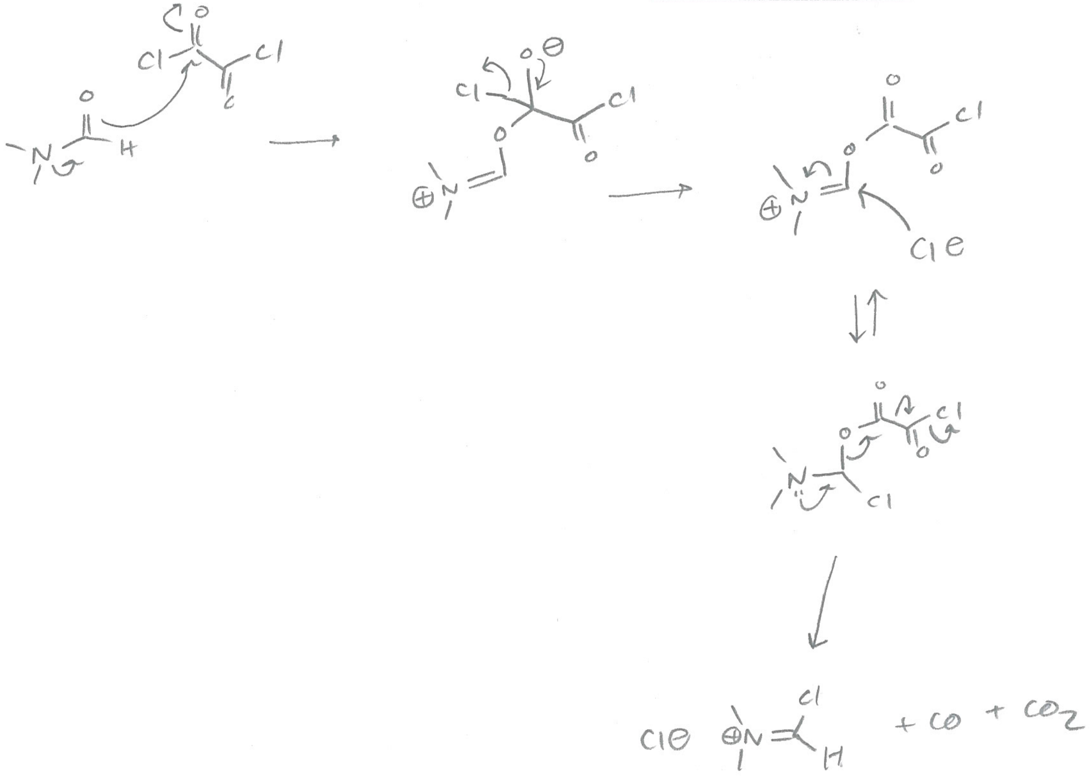
(acid-catalyzed enol hydrolysis)



Question 8

(a) The Vilsmeier reagent can be formed from dimethylformamide (DMF) and oxalyl chloride. Draw a detailed mechanism for the formation of the Vilsmeier reagent (10 points). (Hint: this relies on a lot of the same mechanistic steps as acid chloride formation).





(b) Formylations (the addition of an aldehyde) of benzene are not possible using the reactions we have learned so far. Instead the Vilsmeier-Haack reaction (using the Vilsmeier reagent as the electrophile) is employed. Using this information, draw a detailed mechanims for the following formylation (10 points).