

Name: _____

Roll Number _____

“I was thrown out of N.Y.U. my freshman year for cheating on my metaphysics final. You know, I looked within the soul of the boy sitting next to me.” – Woody Allen

1. Write your roll number at the top of this page and in the box on the last page. If you need to verify your class roll number, you can do this at the front of the room when you turn in your exam paper.

2. The exam is divided into three parts.

Part A is Scantron scored (44 points, includes 4 extra points)

- a. **IMPORTANT** Bubble-in your GTID number correctly.
- b. **IMPORTANT** Bubble-in the TEST FORM, located at the top of the page.

Part B is free response (44 points)

Part C is free response (20 points)

Total (108 points available)

3. Materials: Turn off cell phones and wireless PDA devices. Place all other materials on the floor. You will only need a pencil. Molecular models are optional.
4. Show your Buzz Card when you turn in your completed exam.
5. You must work alone.
6. This is a closed book exam. Give or take no assistance from other students. Recall the Georgia Tech Honor Code.

"I have always worked better alone."-- Claude Monet

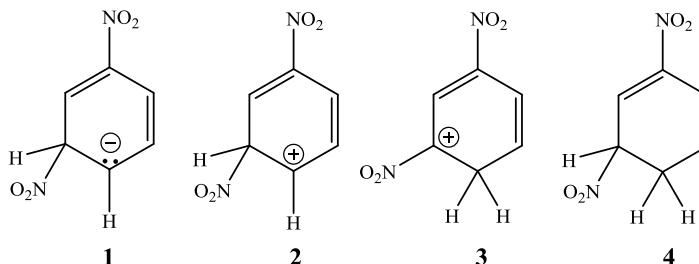
“I pledge my honor that I have not violated the Honor Code during this examination.”

Signed _____

7. **Note: A pKa table is provides on the last page of this exam.**

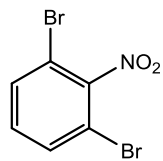
Part A Scantron scored (44 points, 4 points each) Circle the correct answer. There is only one correct answer.

1. Which of the following is the reactive intermediate formed in the electrophilic nitration of nitrobenzene with HNO_3 and H_2SO_4 ?

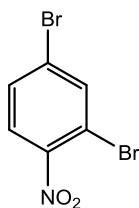


- A) 1
B) 2
C) 3
D) 4
2. Which of the following compounds reacts most rapidly with $\text{Br}_2/\text{FeBr}_3$?
- A) $\text{C}_6\text{H}_5\text{-CF}_3$
B) $\text{C}_6\text{H}_5\text{-CH}_2\text{CH}_3$
C) $\text{C}_6\text{H}_5\text{-COOH}$
D) $\text{C}_6\text{H}_5\text{-CN}$
E) $\text{C}_6\text{H}_5\text{-NO}_2$
3. Which of the following compounds reacts most rapidly with ethyl bromide and aluminum tribromide?
- A) Benzene (C_6H_6)
B) Nitrobenzene ($\text{C}_6\text{H}_5\text{NO}_2$)
C) Bromobenzene ($\text{C}_6\text{H}_5\text{Br}$)
D) Anisole ($\text{C}_6\text{H}_5\text{OCH}_3$)
E) Benzoic Acid ($\text{C}_6\text{H}_5\text{CO}_2\text{H}$)
4. What is the hybridization of the carbon atom that is attached to the electrophile in the arenium carbocation intermediate that is formed in an electrophilic aromatic substitution reaction?
- A) sp
B) sp^2
C) s
D) sp^3
E) p

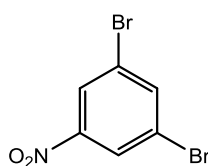
5. What would you expect to be the major product obtained from the mononitration of m-dibromobenzene?



I



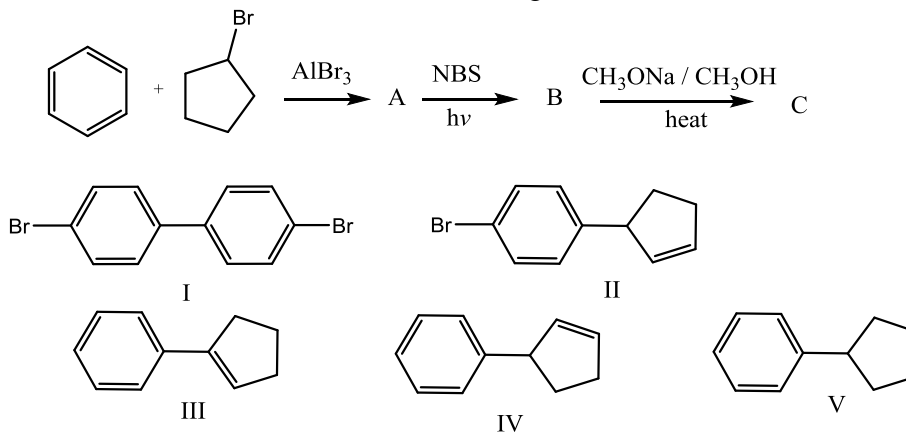
II



III

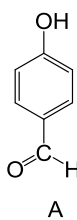
- A) I
B) II
 C) III
 D) Equal amounts of I and II
 E) Equal amounts of I, II, and III

6. The product, C, that would result from the following series of reactions,

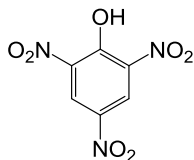


- A) I
 B) II
C) III
 D) IV
 E) V

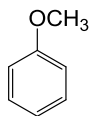
7. What is correct order of acidity of the following compounds (stronger acid > weaker acid)?



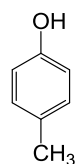
A



B



C



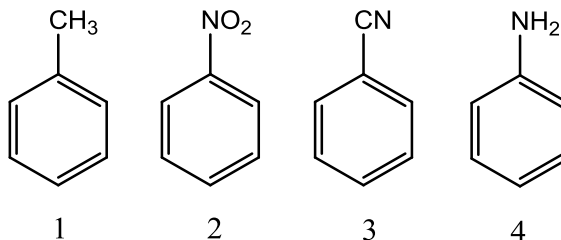
D

- A) A > B > D > C
B) B > A > D > C
 C) A > D > B > C
 D) D > C > A > B

8. For which set of conditions would a Friedel–Crafts alkylation of benzene not occur?

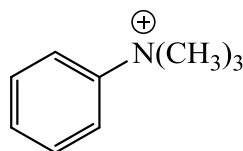
A) 1-chlorobutane + AlCl_3
B) propane + AlCl_3
C) 2-chloro-2-methylpropane + AlCl_3
D) propene + HF

9. Rank the following aromatics in order of decreasing reactivity toward electrophilic aromatic substitution (most reactive > least reactive).



A) $1 > 3 > 4 > 2$
B) $4 > 3 > 1 > 2$
C) $2 > 3 > 1 > 4$
D) $4 > 1 > 3 > 2$
E) $3 > 1 > 4 > 2$

10. Which of the ring carbons in the N, N, N-trimethylbenzeneaminium ion have a partial positive charge?



A) the carbon attached to the nitro group
B) the para carbon
C) the meta carbons
D) the ortho carbons
E) the ortho and para carbons

11. Using predominately electrophilic aromatic substitution reactions, how could you prepare 1,3-dichlorobenzene from benzene?

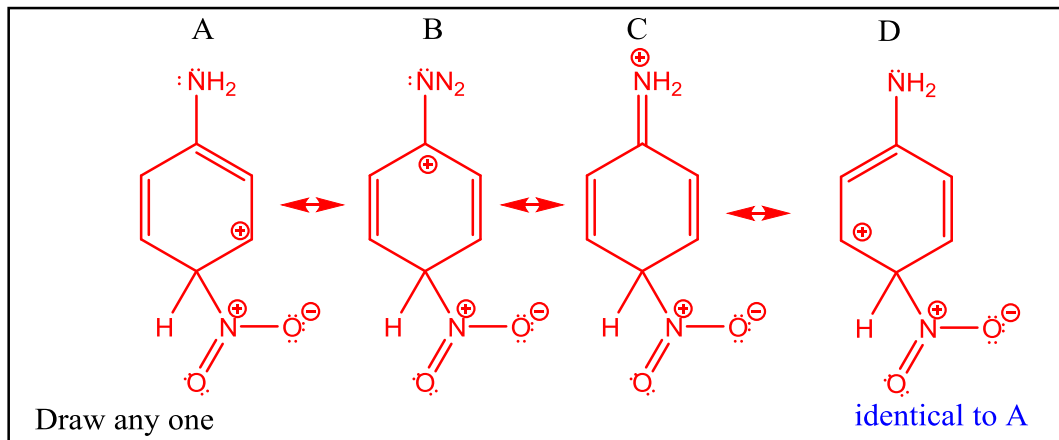
A) Chlorination of benzene (Cl_2 , FeCl_3); followed by a second chlorination (Cl_2 , FeCl_3).
B) Chlorination of benzene (Cl_2 , FeCl_3); followed by nitration (HNO_3 , H_2SO_4), reduction (Fe, HCl), diazotization (NaNO_2 , HCl) and reaction with CuCl.
C) Nitration of benzene (HNO_3 , H_2SO_4); followed by chlorination (Cl_2 , FeCl_3), reduction (Fe, HCl), diazotization (NaNO_2 , HCl) and reaction with CuCl.
D) Chlorination of benzene with excess Cl_2 .

End Part A

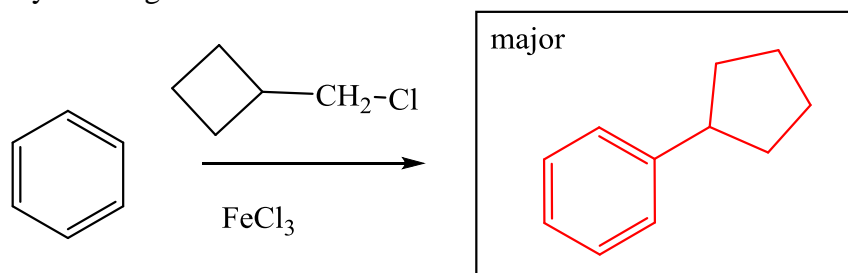
Part B (44 points, 4 points each) Provide the explanation or structure(s) of the major organic products(s), including stereochemistry.

12.

- a. Draw any **one** resonance structure for the arenium ion intermediates in the nitration of aniline (PhNH_2) when the electrophile attacks the *para* position. Show all lone pair electrons and charges.

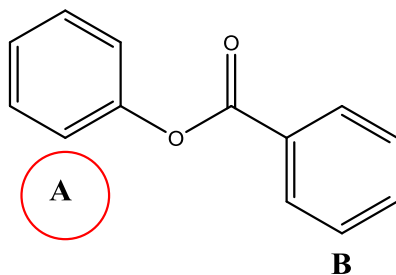


- b. Draw the major product for the following reaction. Hint: Consider carbocation stability and ring strain.



- c. One ring of phenyl benzoate undergoes electrophilic aromatic substitution much more readily than the other. Which ring is more activated? Explain your answer.

Circle: A or B (2 points)

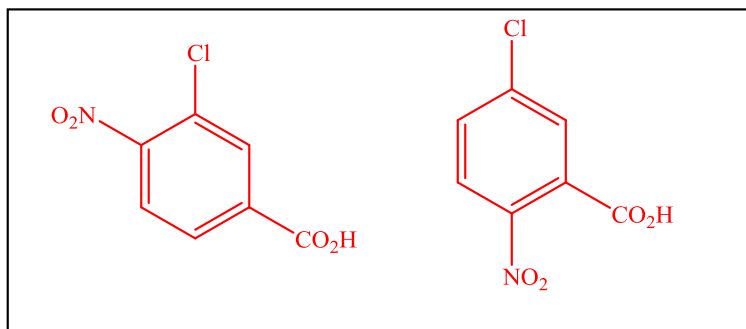


Explanation: (2 points)

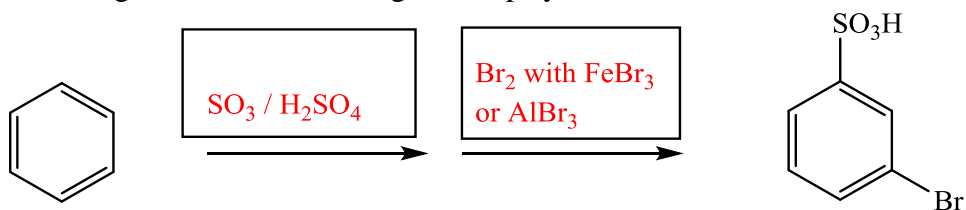
The ring attached to the methylene group, the A ring, is activated because the oxygen can donate unshared electron pair to it. This makes the ring more electron rich. The intermediate arenium ion is stabilized.

The B ring is deactivated due to the carbonyl group withdrawing electron density from the ring.

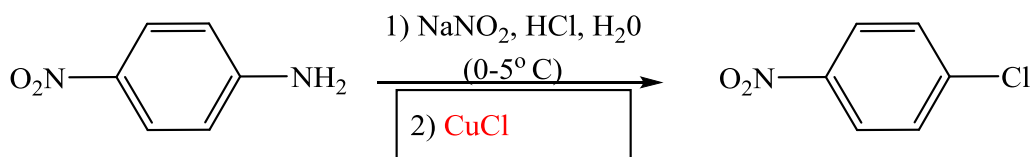
- d. Draw the major products for the reaction of HNO_3 and H_2SO_4 with 3-chlorobenzoic acid.



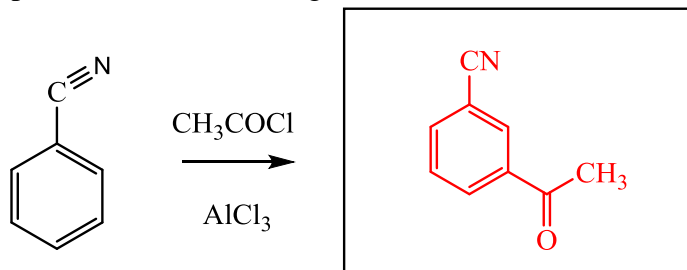
- e. The reagents for the following two step synthesis



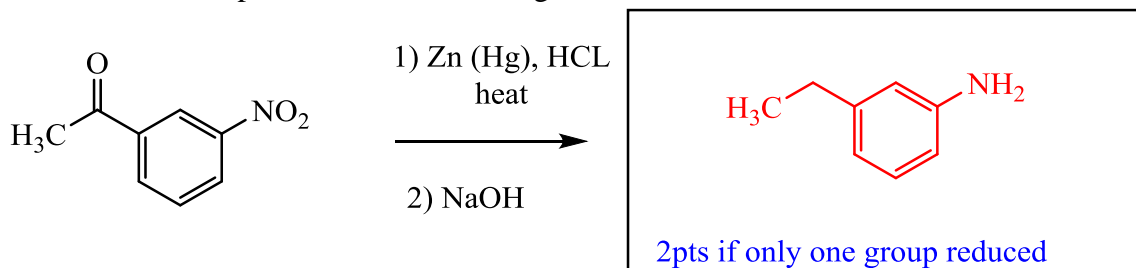
- f. What is the missing reagent?



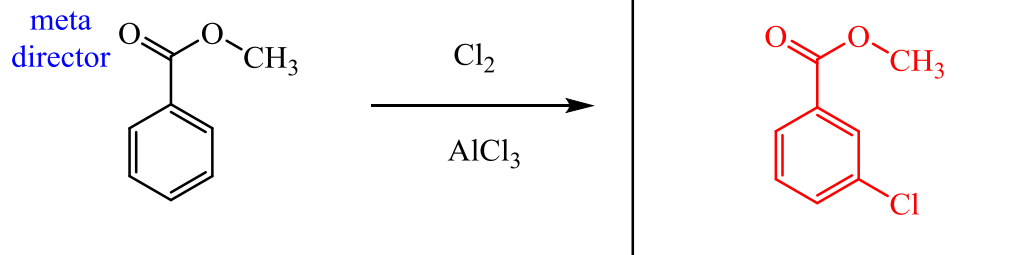
- g. Draw the product of the following reaction



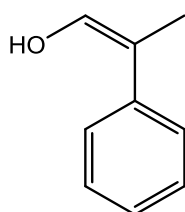
- h. Draw the product of the following reaction.



i. Draw the product for the following reaction



j.

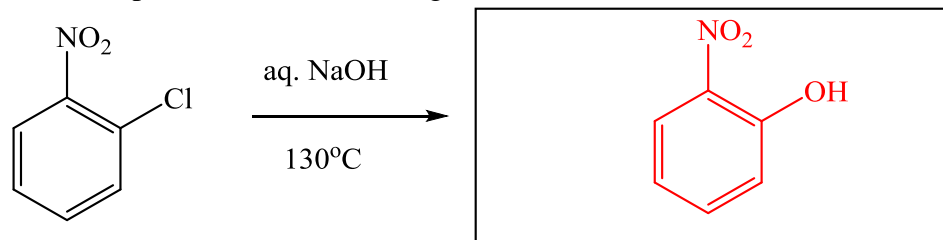


Using your knowledge of resonance theory, how would you expect the substrate on the left to react in an electrophilic aromatic substitution reaction?

Circle one (2 pts): activating or deactivating

Circle one (2 pts): ortho/para directing or meta directing

k. Draw the product of the following aromatic substitution reaction.

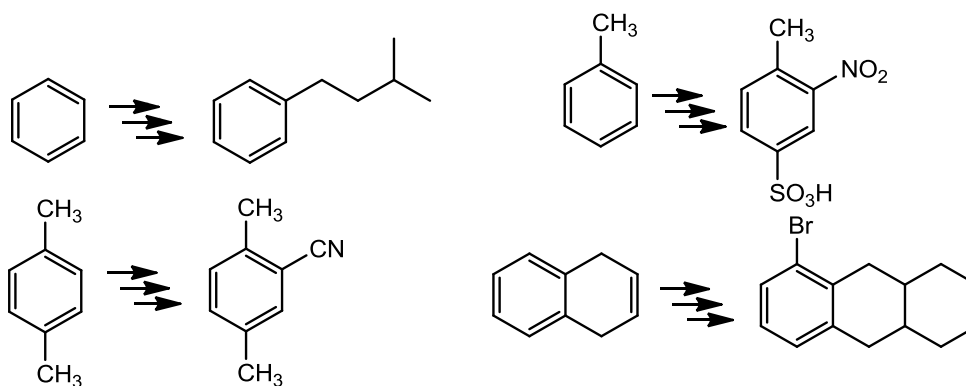


End Part B

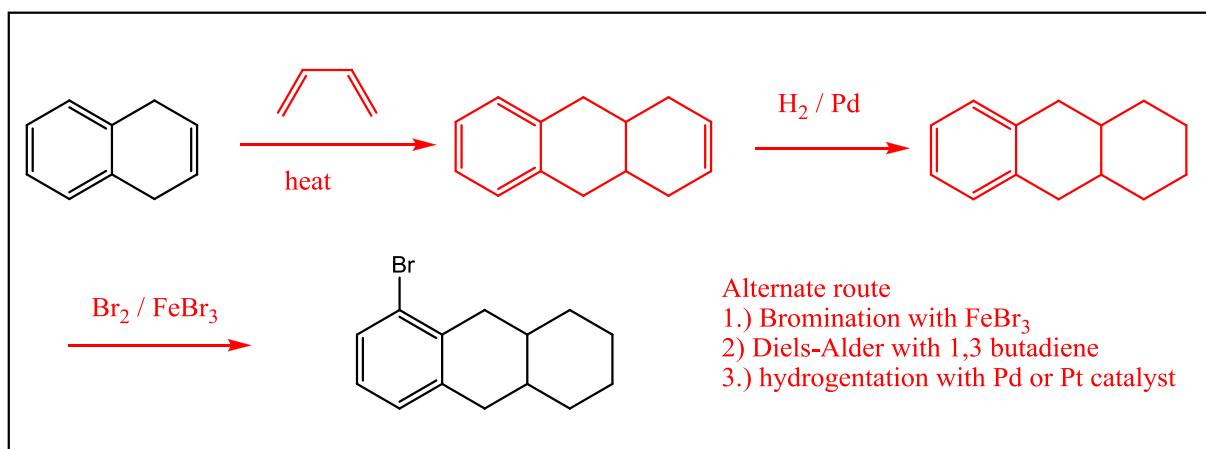
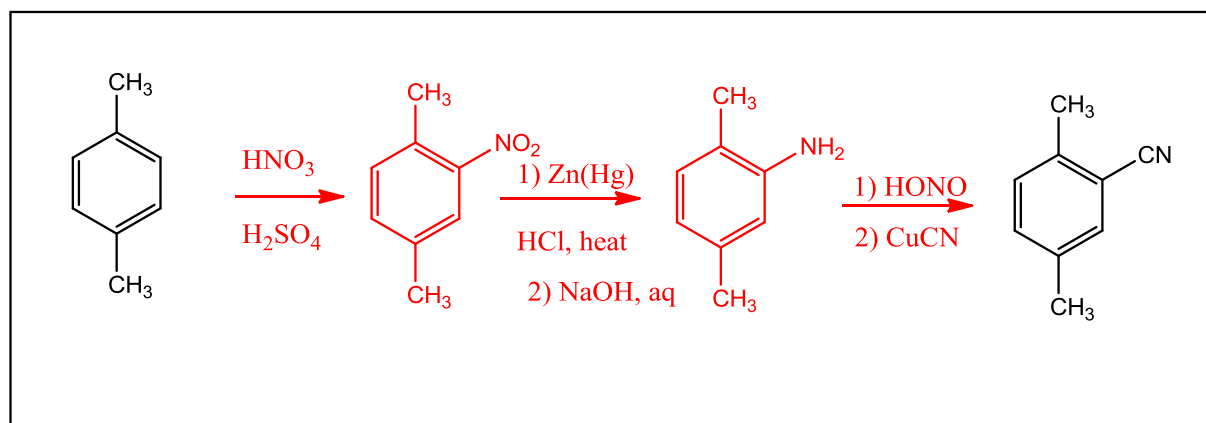
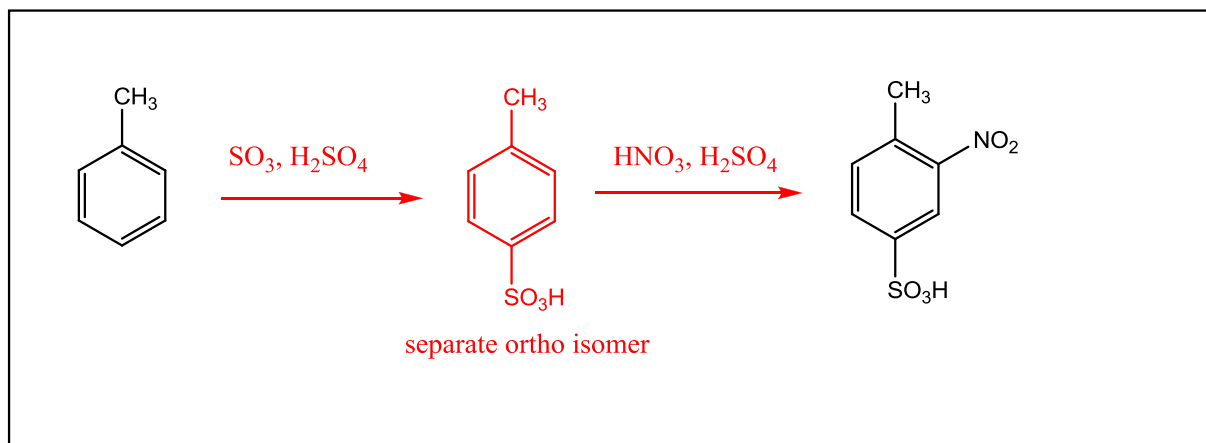
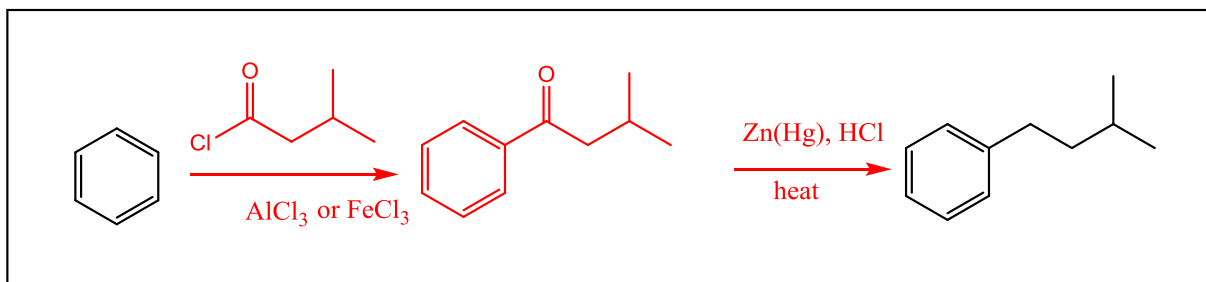
Part C continued on next page

Part C

13. (10 points) **Multi-step Synthesis:** Provide a sequence of reactions to perform the following transformations, showing the reagents and structures of all isolated synthetic intermediates. You may also use any other starting materials with 5 or fewer carbon atoms and any reagents. Inefficient sequences will lose credit. *You may select ANY ONE (1) of the following four (4) syntheses. Do not write the mechanism.*

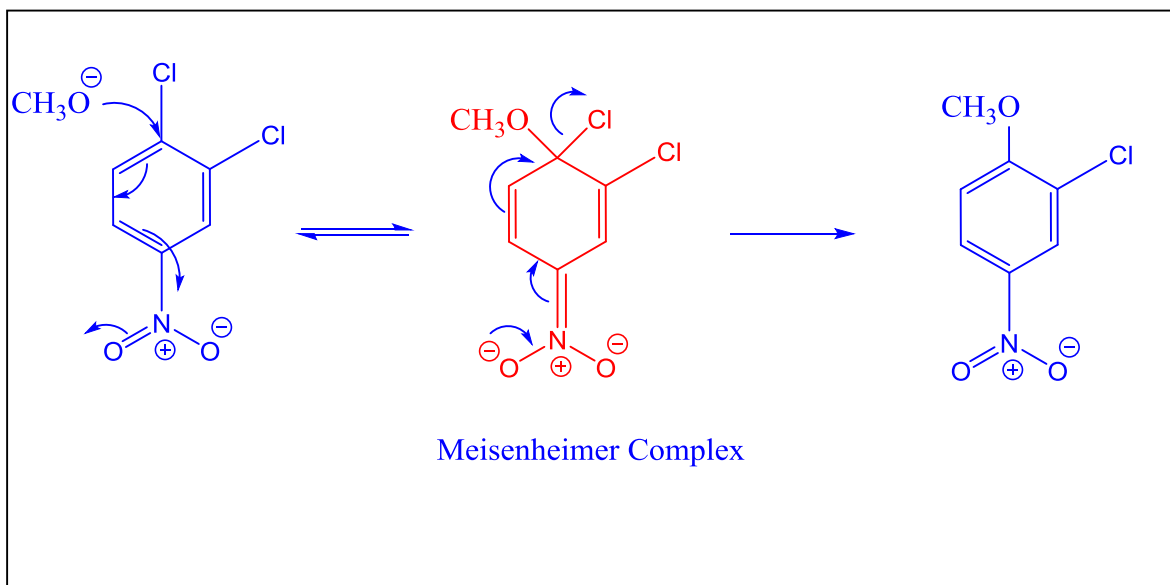
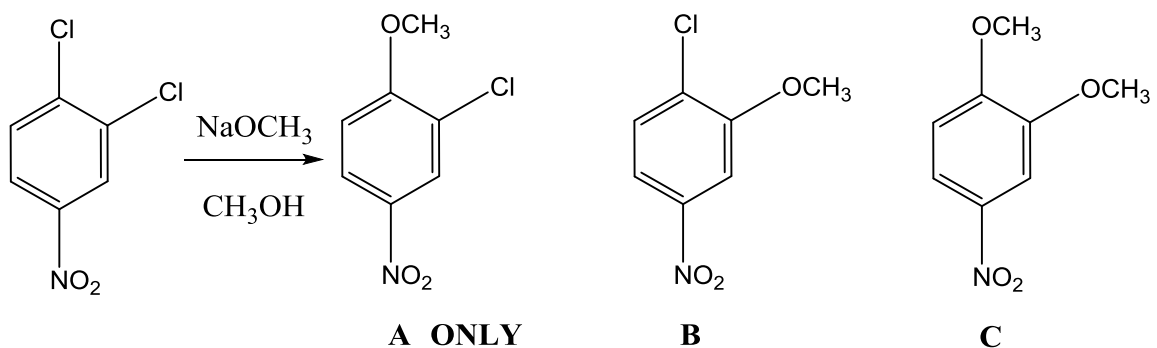


Select 1



14. (10 points) **Mechanistic Understanding:** When 1,2-dichloro-4-nitrobenzene is treated with an excess of sodium methoxide (NaOCH_3) in methanol solvent, three different substitution products could, in principle, be formed (two monosubstituted, one disubstituted). *In fact only product, A below, is obtained.*

Carefully analyze the mechanism for this nucleophilic aromatic substitution reaction. Provide a neatly drawn, detailed, arrow pushing mechanism for the key intermediate and indicate how this leads to the single product.



End of EXAM

Acid	Approximate pK_a	Conjugate Base
HSbF_6	< -12	SbF_6^-
HI	-10	I^-
H_2SO_4	-9	HSO_4^-
HBr	-9	Br^-
HCl	-7	Cl^-
$\text{C}_6\text{H}_5\text{SO}_3\text{H}$	-6.5	$\text{C}_6\text{H}_5\text{SO}_3^-$
$(\text{CH}_3)_2\text{OH}^+$	-3.8	$(\text{CH}_3)_2\text{O}$
$(\text{CH}_3)_2\text{C}=\text{OH}^+$	-2.9	$(\text{CH}_3)_2\text{C}=\text{O}$
CH_3OH_2^+	-2.5	CH_3OH
H_3O^+	-1.74	H_2O
HNO_3	-1.4	NO_3^-
$\text{CF}_3\text{CO}_2\text{H}$	0.18	CF_3CO_2^-
HF	3.2	F^-
$\text{CH}_3\text{CO}_2\text{H}$	4.75	CH_3CO_2^-
H_2CO_3	6.35	HCO_3^-
$\text{CH}_3\text{COCH}_2\text{COCH}_3$	9.0	$\text{CH}_3\text{COCH}^-\text{COCH}_3$
NH_4^+	9.2	NH_3
$\text{C}_6\text{H}_5\text{OH}$	9.9	$\text{C}_6\text{H}_5\text{O}^-$
HCO_3^-	10.2	CO_3^{2-}
CH_3NH_3^+	10.6	CH_3NH_2
H_2O	15.7	OH^-
$\text{CH}_3\text{CH}_2\text{OH}$	16	$\text{CH}_3\text{CH}_2\text{O}^-$
$(\text{CH}_3)_3\text{COH}$	18	$(\text{CH}_3)_3\text{CO}^-$
CH_3COCH_3	19.2	$^-\text{CH}_2\text{COCH}_3$
$\text{HC}\equiv\text{CH}$	25	$\text{HC}\equiv\text{C}^-$
H_2	35	H^-
NH_3	38	NH_2^-
$\text{CH}_2=\text{CH}_2$	44	$\text{CH}_2=\text{CH}^-$
CH_3CH_3	50	CH_3CH_2^-

NOTE: If you need to verify your class roll number, you can do this at the front of the room when you turn in your exam paper.

READ:

- ✓ **Write your class roll number on**
 (a) the top of the first page and
 (b) in the box to the right.
- ✓ **Verify that you have bubbled in the following on your Scantron card**
 (a) **Bubbled-In GTID number**
 (b) **Bubbled-In TEST FORM**
- ✓ **Show your Buzzcard when submitting exam and card.**

Class Roll number _____

Part A Scantron scored (44 points)
and will be posted on T-square

Part B & C Free Response

Page 5 (12) _____

Page 6 (20) _____

Page 7 (12) _____

Page 8 (10) _____

Page 9 (10) _____

Part B & C only _____ (64)