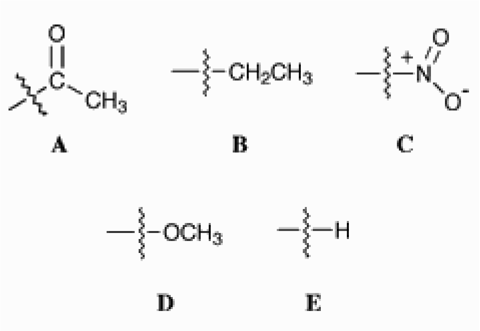
CHEM 242 **REACTIONS OF ARENES:** **CHAP 13 ASSIGN**

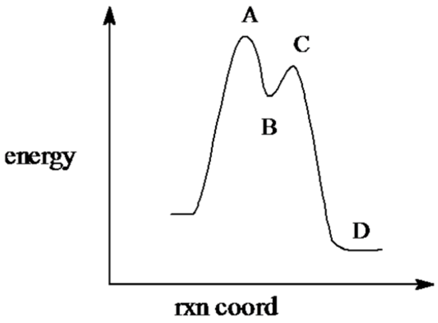
ELECTROPHILIC AROMATIC SUBSTITUTION

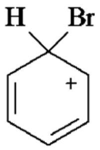
1. Rank the following functional groups in order of decreasing reactivity in electrophilic aromatic substitution (i.e., decreasing electron-donating ability to an aromatic ring). Rank them as most reactive > least reactive.

   A. **B** > **D** > **A** > **E** > **C**
   B. **C** > **A** > **E** > **B** > **D**
   C. **D** > **A** > **E** > **C** > **B**
   D. **E** > **C** > **A** > **B** > **D**
   E. **D** > **B** > **E** > **A** > **C**



2. Which point on the potential energy diagram corresponds to the species shown to the right for the electrophilic bromination of benzene with $Br_2/FeBr_3$?





3. Which species below best depicts the electrophile in the $FeBr_3$-catalyzed bromination of benzene?

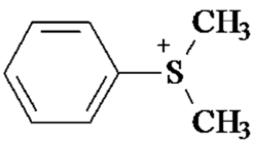
   A. Br_2 B. $FeBr_4^-$ C. $\overset{\delta^+}{\mathrm{Br}}\text{--}\overset{\delta^-}{\mathrm{Br}}\text{--}\mathrm{FeBr_3}$ D. $FeBr_3$

4. Which one of the following reactions does <u>not</u> give *tert*-butylbenzene?

   A. benzene + $(CH_3)_3CCl/AlCl_3$
   B. benzene + $(CH_3)_2C{=}CH_2/H_2SO_4$
   C. benzene + $(CH_3)_3CH/AlCl_3$
   D. benzene + $(CH_3)_3COH/H_2SO_4$

5. Predict the effect the substituent attached to the benzene ring below would have on electrophilic aromatic substitution reactions?

   A. *ortho*/*para* director, activator
   B. *ortho*/*para* director, deactivator
   C. *meta* director, activator
   D. *meta* director, deactivator



6. Which of the following groups are *ortho*/*para* directors?

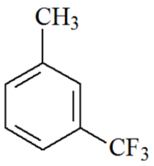
   I. $–NO_2$ II. $–OCH_3$ III. $–CO_2CH_3$ IV. $–CH_3$

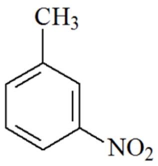
   A. I and III   B. II and III   C. II and IV   D. III and IV

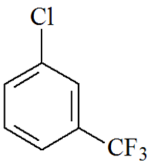
7. In the Friedel-Crafts alkylation of benzene, dialkylation is often a significant by-product. In the Friedel-Crafts acylation of benzene, diacylation is <u>not</u> a significant by-product. Which of the following is the primary reason for this difference?

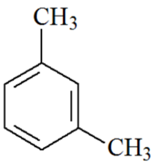
   A. Alkyl groups activate the ring to further substitution, acyl groups deactivate it.
   B. Alkyl groups are less sterically hindered than acyl groups.
   C. Acyl cations are more difficult to make with Lewis acids.
   D. Unlike acyl cations, carbocations can undergo rearrangements.

8. Which one of the following compounds undergoes electrophilic aromatic sulfonation at the fastest rate?

A) 

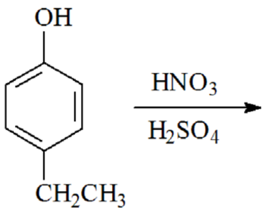
B) 

C) 

D) 

9. What is the major product of the following reaction?

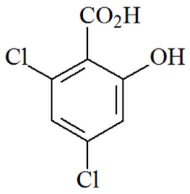
   A. 4-ethyl-2-nitrophenol
   B. 4-ethyl-3-nitrophenol
   C. 1-ethyl-4-nitrobenzene
   D. 4-nitrophenol



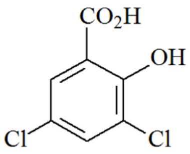
10. Which isomer of dichlorobenzene gives a single mononitration product?

   A. *ortho*   B. *meta*   C. *para*   D. none of them

11. Salicylic acid reacts with two equivalents of ICl to give one of the products below. Which one is it?



A)



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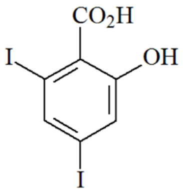

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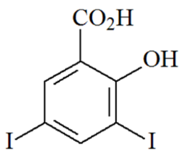

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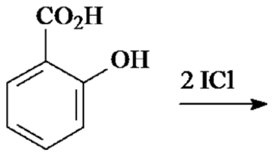
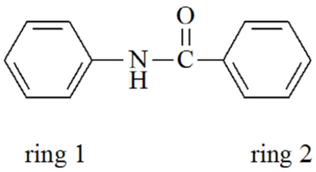
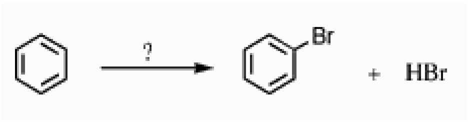


12. Where would the compound shown below undergo bromination with $Br_2/FeBr_3$?

   A. *ortho*/*para* position on ring 1
   B. *meta* position on ring 1
   C. *ortho*/*para* position on ring 2
   D. *meta* position on ring 2

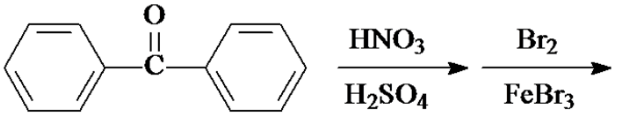


13. Which of the following combinations of reagents is appropriate to brominate the ring of benzene as shown below?

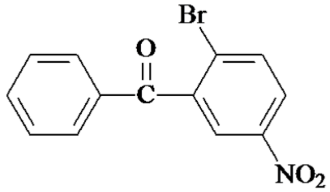


   A. Br_2, light   B. Br_2, H_2O C. Br_2, NaOH   D. Br_2, H_2SO_4 E. Br_2, $FeBr_3$

14. What is the product of the following series of reactions?



A)



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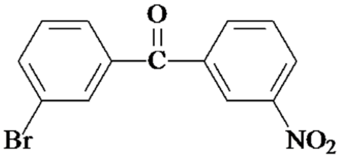

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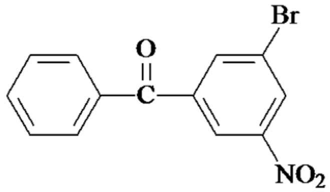

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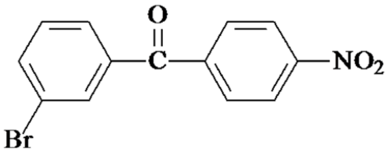
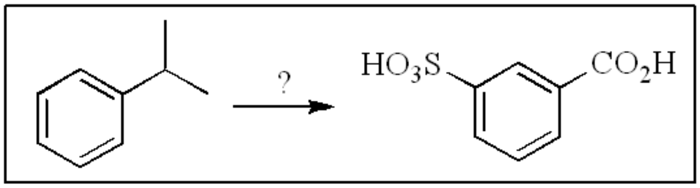


15. Which of the following is NOT a common electrophile in electrophilic aromatic substitution reactions?

A. $^+SO_3H$ B. ^+Br C. ^+CN D. $^+NO_2$

16. How would you best accomplish this?

A. 1. SO_3, H_2SO_4, heat; 2. $K_2Cr_2O_7$, H^+
B. 1. $K_2Cr_2O_7$, H^+, heat; 2. SO_3, H_2SO_4
C. either of these would work.
D. neither of these would work.



17. Starting with toluene, which of the following is the best synthesis of *meta*-bromobenzoic acid?

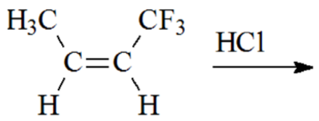
A) (1) Br_2, $FeBr_3$ (2) $K_2Cr_2O_7$, H_2SO_4 (heat)

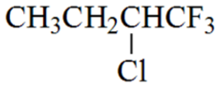
B) (1) Br_2, $h\nu$ (2) $K_2Cr_2O_7$, H_2SO_4 (heat)

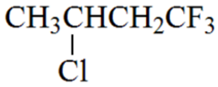
C) (1) $K_2Cr_2O_7$, H_2SO_4 (heat) (2) Br_2, $FeBr_3$

D) (1) $K_2Cr_2O_7$, H_2SO_4 (heat) (2) Br_2, $h\nu$

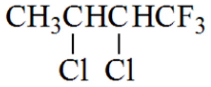
18. Based on directing effects in electrophilic aromatic substitution reactions, predict the major addition product of the following reaction.



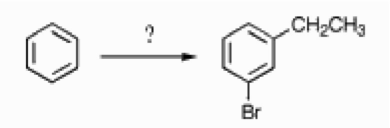
A) 
$CH_3CH_2\underset{\substack{|\\ Cl}}{C}HCF_3$

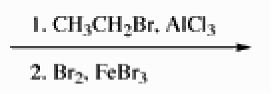
B) 
$CH_3\underset{\substack{|\\ Cl}}{C}HCH_2CF_3$

C) $CH_3CH_2CH_2CF_3$

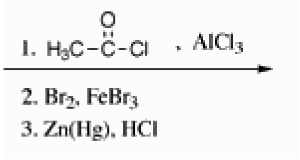
D) 
$CH_3\underset{\substack{|\\ Cl}}{C}H\underset{\substack{|\\ Cl}}{C}HCF_3$

19. What combination of reagents would be required to produce 3-bromoethylbenzene from benzene?

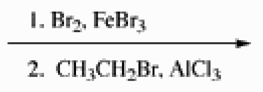


A. 

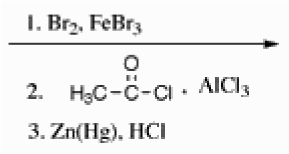
1. CH_3CH_2Br, $AlCl_3$
2. Br_2, $FeBr_3$

B. 

1. $H_3C-\overset{\substack{O\\ \|}}{C}-Cl$, $AlCl_3$
2. Br_2, $FeBr_3$
3. Zn(Hg), HCl

C. 

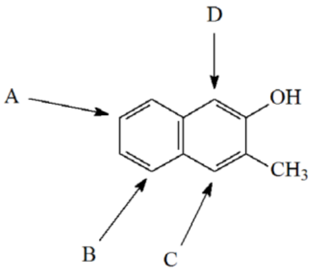
1. Br_2, $FeBr_3$
2. CH_3CH_2Br, $AlCl_3$

D. 

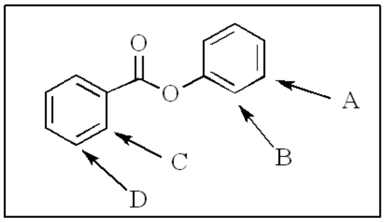
1. Br_2, $FeBr_3$
2. $H_3C-\overset{\substack{O\\ \|}}{C}-Cl$, $AlCl_3$
3. Zn(Hg), HCl

E. None of these would work.

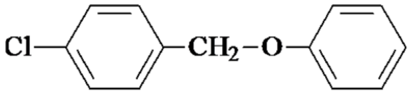
20. Predict which position of the naphthalene compound at the right is the most reactive with electrophiles in electrophilic aromatic substitution?



21. Of the choices given, where would an aromatic substitution occur on this molecule?



22. Starting with toluene, which of the following is the best method to make the ether shown below? (Assume you can separate *ortho* and *para* isomers.)



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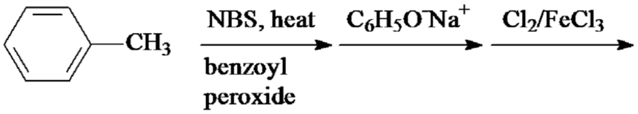

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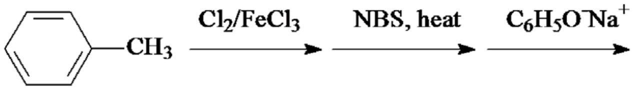

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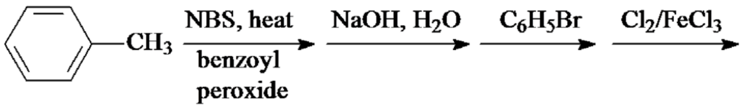

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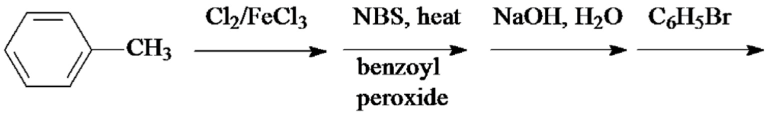

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ANSWER SHEET

CHEM 242 – CHAP 13 ASSIGN

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