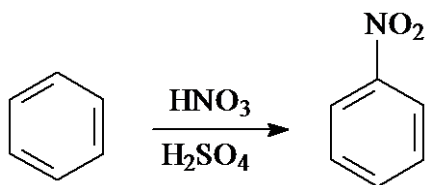
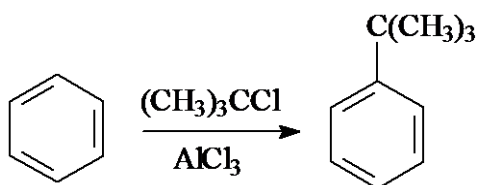


ACS Review Reactions of Arenes - Electrophilic Aromatic Substitution

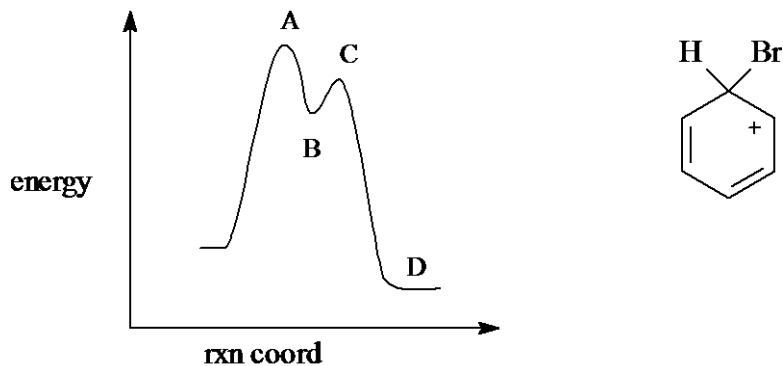
1. Which one of the following is the electrophile in the reaction shown below?



- A. benzene
 B. NO_3^-
 C. NO_2^+
 D. H_2SO_4
2. What is the electrophile in the Friedel-Crafts alkylation reaction below?



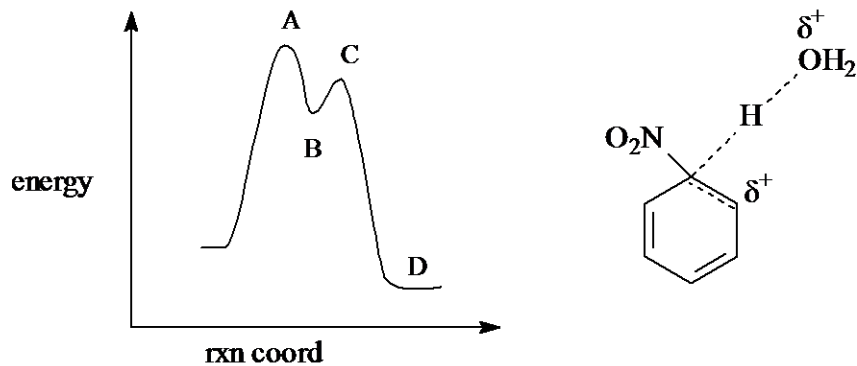
- A. AlCl_3
 B. Cl^-
 C. benzene
 D. $(\text{CH}_3)_3\text{C}^+$
3. Which point on the potential energy diagram corresponds to the species shown to the right for the electrophilic bromination of benzene with $\text{Br}_2/\text{FeBr}_3$?



- A. A
 B. B
 C. C
 D. D
4. Which species below best depicts the electrophile in the FeBr_3 -catalyzed bromination of benzene?
- A. Br_2
 B. FeBr_4^-
 C. $\delta^+ \delta^- \text{Br}-\text{Br}-\text{FeBr}_3$
 D. FeBr_3
5. Which one of the following reactions does not give *tert*-butylbenzene?

- A. benzene + $(\text{CH}_3)_3\text{CCl}/\text{AlCl}_3$
- B. benzene + $(\text{CH}_3)_2\text{C}=\text{CH}_2/\text{H}_2\text{SO}_4$
- C. benzene + $(\text{CH}_3)_3\text{CH}/\text{AlCl}_3$
- D. benzene + $(\text{CH}_3)_3\text{COH}/\text{H}_2\text{SO}_4$

6. Which point on the potential energy diagram corresponds to the species shown to the right for the electrophilic nitration of benzene with $\text{HNO}_3/\text{H}_2\text{SO}_4$?



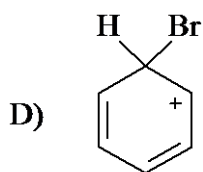
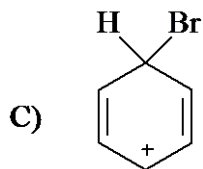
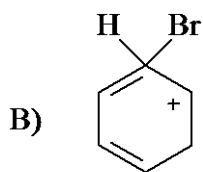
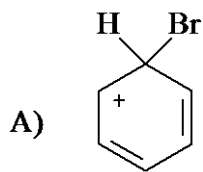
- A. A
- B. B
- C. C
- D. D

7. What is(are) the product(s) of the following reaction?



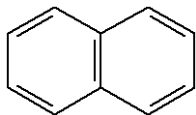
- A. $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{CH}_3$
- B. $\text{C}_6\text{H}_5\text{CH}(\text{CH}_3)_2$
- C. $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl}$
- D. a mixture of $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{CH}_3$ and $\text{C}_6\text{H}_5\text{CH}(\text{CH}_3)_2$

8. Which one of the following is not a resonance form of the cyclohexadienyl cation intermediate in the bromination of benzene?



- A. A
B. B
C. C
D. D

9. How many mononitration products are possible in the nitration of naphthalene, shown below?



- A. only 1
B. 2
C. 3
D. 4

10. Rank the following compounds in order of decreasing reactivity to aromatic electrophilic bromination.

I. benzene II. toluene III. benzoic acid IV. phenol

- A. IV > II > I > III
B. IV > III > II > I
C. II > I > IV > III
D. II > III > IV > I

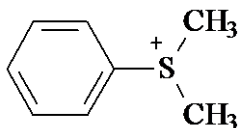
11. Which of the following groups are ortho/para directors?

I. -NO₂ II. -OCH₃ III. -CO₂CH₃ IV. -CH₃

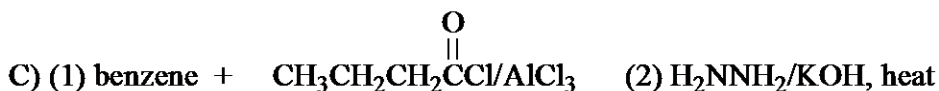
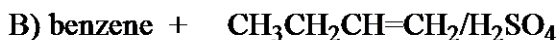
- A. I and III
B. II and III

- C. II and IV
D. III and IV

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

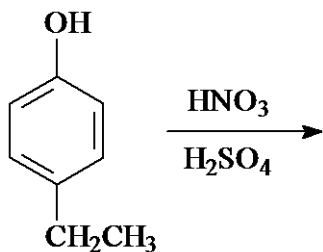


- A. ortho/para director, activator
B. ortho/para director, deactivator
C. meta director, activator
D. meta director, deactivator
13. In the Friedel-Crafts alkylation of benzene, dialkylation is often a significant by-product. In the Friedel-Crafts acylation of benzene, diacylation is not a significant 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.
14. Which of the following is the best method to make *n*-butylbenzene?



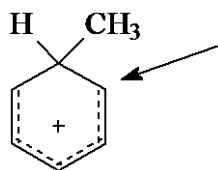
- A. A
B. B
C. C
D. D

15. 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

16. Based on resonance theory, what is the approximate charge on the indicated carbon?

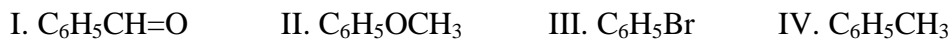


- A. +1
- B. +0.50
- C. +0.33
- D. +0.20

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

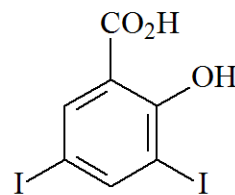
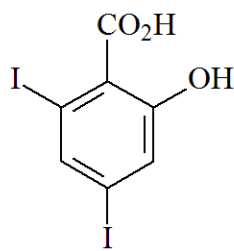
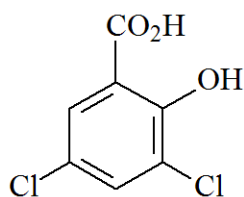
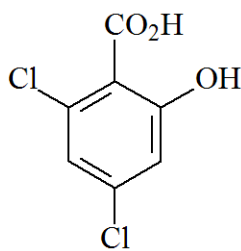
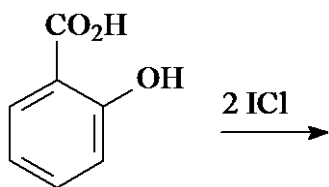
- A. ortho
- B. meta
- C. para
- D. none of them

18. Arrange the following compounds in order of increasing reaction rate with HNO₃/H₂SO₄.



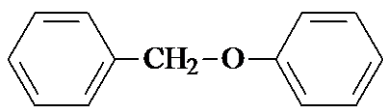
- A. I < III < IV < II
- B. I < IV < III < II
- C. III < I < II < IV
- D. III < I < IV < II

19. Salicylic acid reacts with two equivalents of ICl to give one of the products below. Which one is it? (Hint: Cl is more electronegative than I.)



- A. A
- B. B
- C. C
- D. D

20. Identify the preferred site(s) of electrophilic attack on the following compound.



ring 1

ring 2

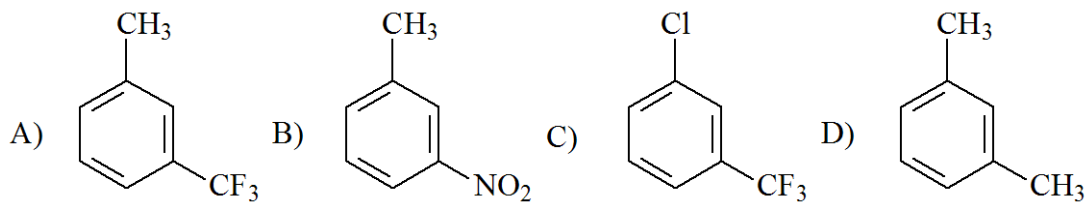
- A. ortho/para positions on ring 1
- B. meta position on ring 1
- C. ortho/para positions on ring 2
- D. meta position on ring 2

21. Which of the following is the best method to make *meta*-bromoethylbenzene from benzene?

- A) (1) benzene + $\text{CH}_3\text{CH}_2\text{Cl}/\text{AlCl}_3$ (2) $\text{Br}_2/\text{FeBr}_3$
- B) (1) benzene + $\text{Br}_2/\text{FeBr}_3$ (2) $\text{CH}_3\text{CH}_2\text{Cl}/\text{AlCl}_3$
- C) (1) benzene + $\text{CH}_3\text{COCl}/\text{AlCl}_3$ (2) $\text{Zn}(\text{Hg}), \text{HCl}$ (3) $\text{Br}_2/\text{FeBr}_3$
- D) (1) benzene + $\text{CH}_3\text{COCl}/\text{AlCl}_3$ (2) $\text{Br}_2/\text{FeBr}_3$ (3) $\text{Zn}(\text{Hg}), \text{HCl}$

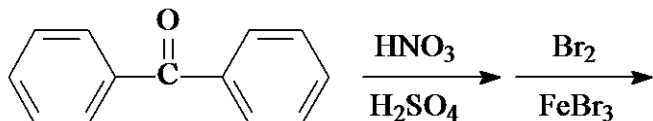
- A. A
- B. B
- C. C
- D. D

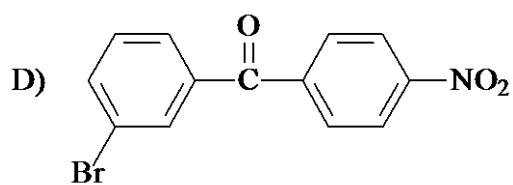
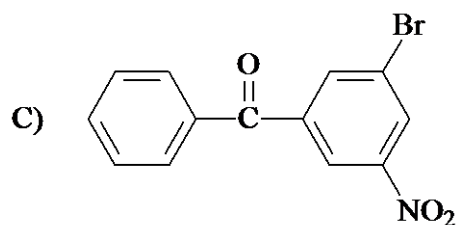
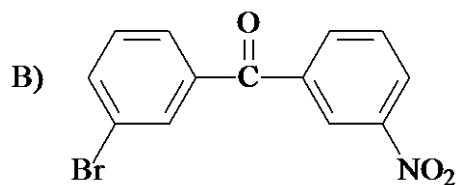
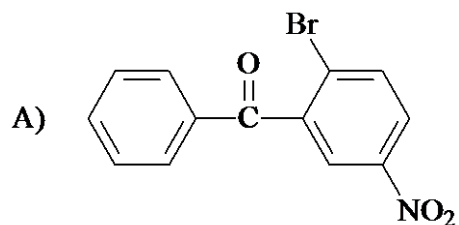
22. Which one of the following compounds undergoes electrophilic aromatic sulfonation at the fastest rate?



- A. A
- B. B
- C. C
- D. D

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





- A. A
B. B
C. C
D. D

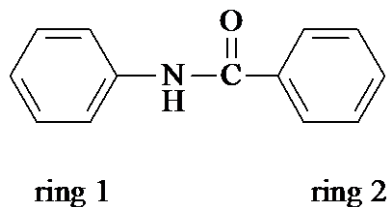
24. Nitration of chlorobenzene has a reaction rate which is _____ than the nitration rate of benzene and gives primarily the _____ product(s).

- A. faster, ortho/para
B. faster, meta
C. slower, ortho/para
D. slower, meta

25. What is the major product of the Friedel-Crafts alkylation of benzene with $(\text{CH}_3)_2\text{CHCH}_2\text{Cl}$ and AlCl_3 ?

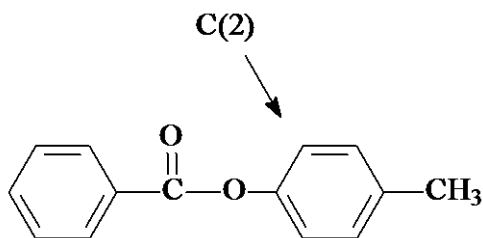
- A. isobutylbenzene
B. *tert*-butylbenzene
C. *sec*-butylbenzene
D. butylbenzene

26. Where would the compound shown below undergo bromination with $\text{Br}_2/\text{FeBr}_3$?



- 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

27. Where would the compound shown below undergo bromination with NBS and benzoyl peroxide?

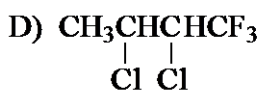
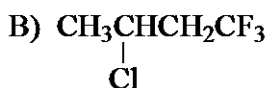
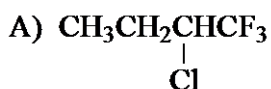
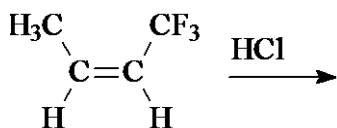


ring 1

ring 2

- A. ortho/para position on ring 1
- B. meta position on ring 1
- C. C(2) position on ring 2
- D. methyl group on ring 2

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

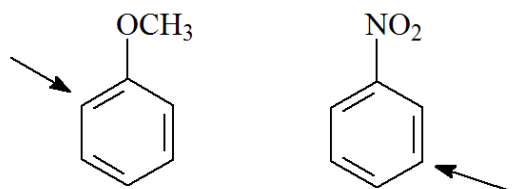


- A. A
- B. B
- C. C
- D. D

29. Which one of the following substituents is deactivating and ortho-para directing in electrophilic aromatic substitution reactions?

- A. -Cl
- B. -N(CH₃)₂
- C. -CO₂H
- D. -CH=CH₂

30. Consider the partial rate factors for electrophilic aromatic substitution at the indicated position of anisole and nitrobenzene. Which of the following correlates to these partial rate factors?



	<u>anisole</u>	<u>nitrobenzene</u>
A) partial rate factor	>1	>1
B) partial rate factor	>1	<1
C) partial rate factor	<1	>1
D) partial rate factor	<1	<1

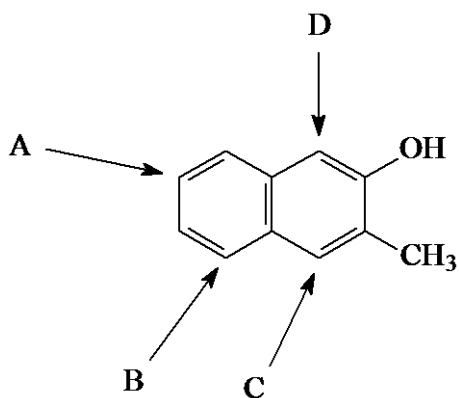
- A. A
 B. B
 C. C
 D. D

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

- A) (1) $\text{Br}_2, \text{FeBr}_3$ (2) $\text{K}_2\text{Cr}_2\text{O}_7, \text{H}_2\text{SO}_4$ (heat)
 B) (1) $\text{Br}_2, h\nu$ (2) $\text{K}_2\text{Cr}_2\text{O}_7, \text{H}_2\text{SO}_4$ (heat)
 C) (1) $\text{K}_2\text{Cr}_2\text{O}_7, \text{H}_2\text{SO}_4$ (heat) (2) $\text{Br}_2, \text{FeBr}_3$
 D) (1) $\text{K}_2\text{Cr}_2\text{O}_7, \text{H}_2\text{SO}_4$ (heat) (2) $\text{Br}_2, h\nu$

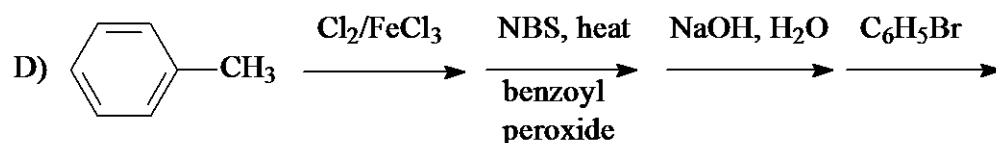
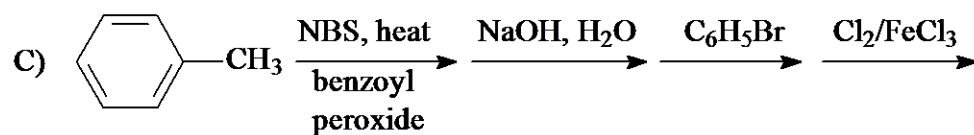
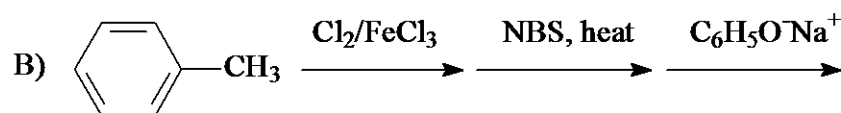
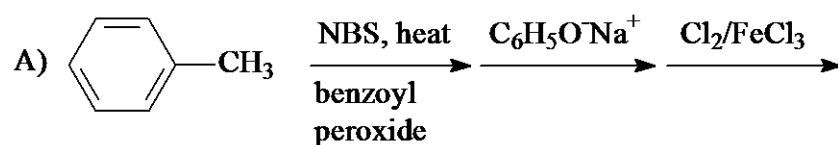
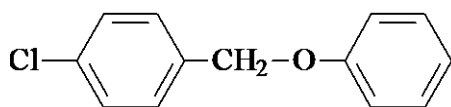
- A. A
 B. B
 C. C
 D. D

32. Predict which position of the naphthalene compound below is the most reactive with electrophiles in electrophilic aromatic substitution?



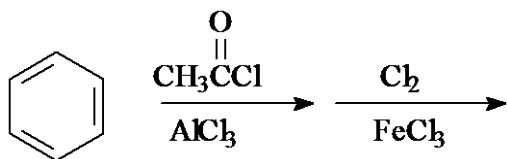
- A. A
 B. B
 C. C
 D. D

33. 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.)



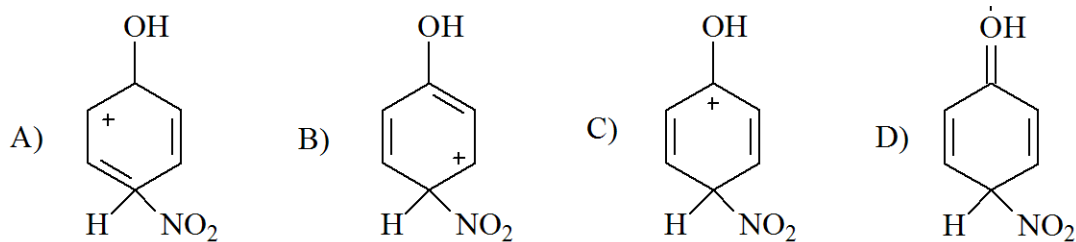
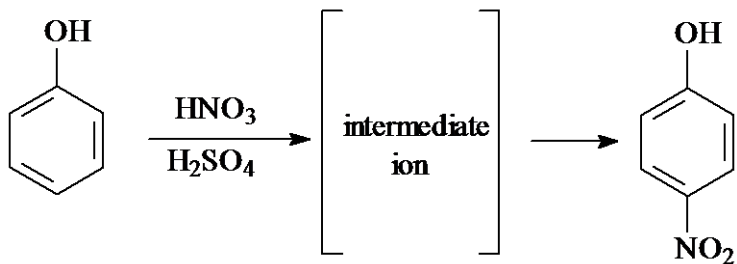
- A. A
 B. B
 C. C
 D. D

34. Identify the major product(s) of the reaction sequence shown below.



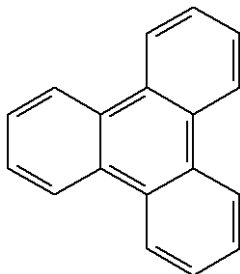
- A. *ortho* and *para*-chloroacetophenone
- B. *meta*-chloroacetophenone
- C. *ortho* and *para*-chlorobenzaldehyde
- D. *meta*-chlorobenzaldehyde

35. Which of the following is not a valid resonance form of the intermediate species in the reaction shown below?



- A. A
- B. B
- C. C
- D. D

36. How many mononitration products are possible in the nitration of the compound shown below?



- A. only 1
- B. 2
- C. 3
- D. 4

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1. C
2. D
3. B
4. C
5. C
6. C
7. D
8. B
9. B
10. A
11. C
12. D
13. A
14. C
15. A
16. C
17. C
18. A
19. D
20. C
21. D
22. D
23. B
24. C
25. B
26. A
27. D
28. B
29. A
30. B
31. C
32. D
33. B
34. B
35. A
36. B