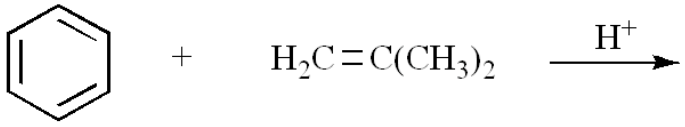
Chapter 12: Reactions of Arenes - Electrophilic Aromatic Substitution

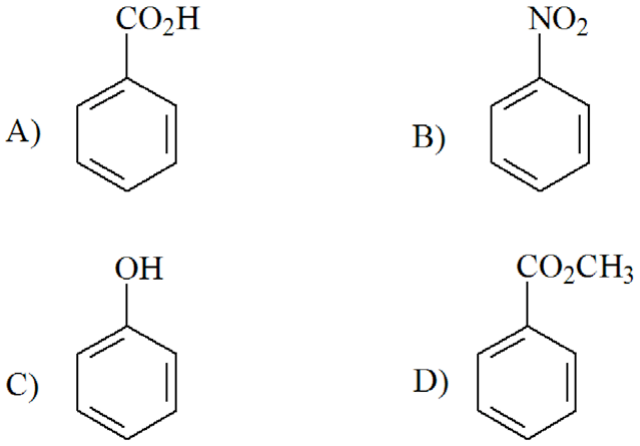
1. What is the product of the following reaction?



A) isobutylbenzene
B) 2-methyl-1-phenylpropene
C) *sec*-butylbenzene
D) *tert*-butylbenzene
Ans: D

2. The major product(s) in the nitration of benzoic acid is(are)
A) mixture of *ortho* and *para*-nitrobenzoic acid.
B) nitrobenzene.
C) *meta*-nitrobenzoic acid.
D) nitrobenzene and *para*-nitrobenzoic acid.
Ans: C

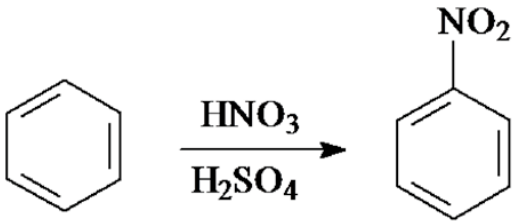
3. Which of the following aromatic compounds reacts faster than benzene in electrophilic aromatic bromination?



A) A B) B C) C D) D
Ans: C

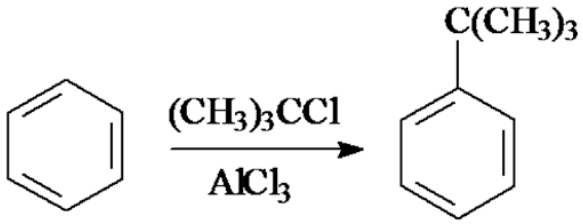
4. Nitration of benzoic acid has a reaction rate which is _____ than the nitration rate of benzene and gives primarily the _____ product(s).
A) slower, *meta*
B) slower, *ortho,para*
C) faster, *ortho,para*
D) faster, *meta*
Ans: A

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



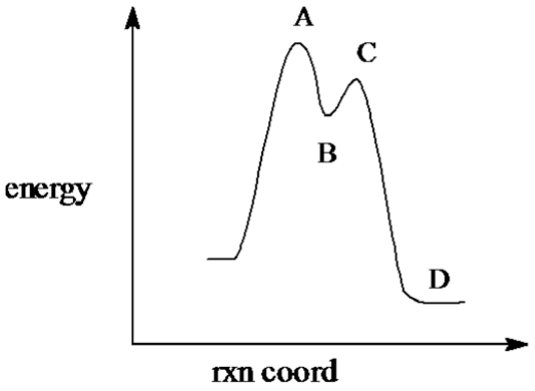
A) benzene B) NO_3^- C) NO_2^+ D) H_2SO_4
Ans: C

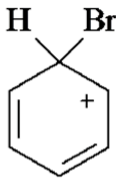
6. What is the electrophile in the Friedel-Crafts alkylation reaction below?



A) $AlCl_3$ B) Cl^- C) benzene D) $(CH_3)_3C^+$
Ans: D

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





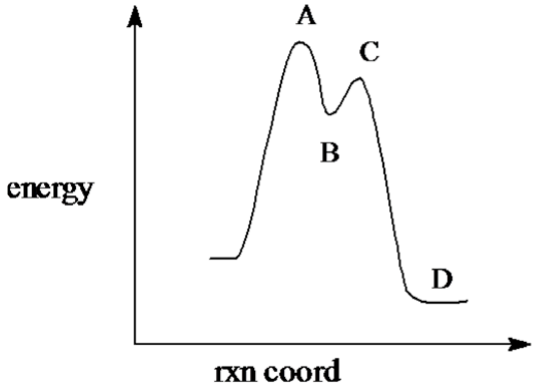
A) A B) B C) C D) D
Ans: B

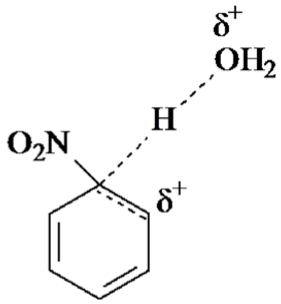
8. Which species below best depicts the electrophile in the $FeBr_3$-catalyzed bromination of benzene?

A) Br_2 B) $FeBr_4^-$ C) $\overset{\delta^+}{Br}\text{--}\overset{\delta^-}{Br}\text{--}FeBr_3$ D) $FeBr_3$
Ans: C

9. 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 + $(CH_3)_3COH/H_2SO_4$
   Ans: C

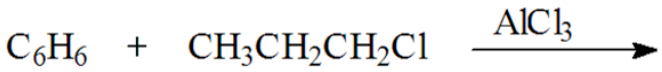
10. Which point on the potential energy diagram corresponds to the species shown to the right for the electrophilic nitration of benzene with HNO_3/H_2SO_4?





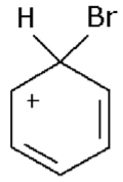
   A) A B) B C) C D) D
   Ans: C

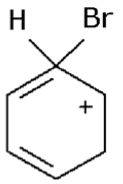
11. What is(are) the product(s) of the following reaction?

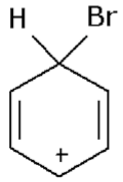


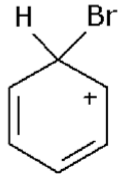
   A) $C_6H_5CH_2CH_2CH_3$
   B) $C_6H_5CH(CH_3)_2$
   C) $C_6H_5CH_2CH_2CH_2Cl$
   D) a mixture of $C_6H_5CH_2CH_2CH_3$ and $C_6H_5CH(CH_3)_2$
   Ans: D

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

A) 

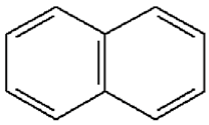
B) 

C) 

D) 

A) A B) B C) C D) D
Ans: B

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



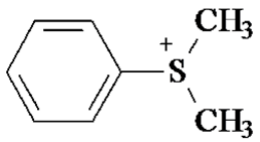
A) only 1 B) 2 C) 3 D) 4
Ans: B

14. 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
Ans: A

15. 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
Ans: C

Prof. Sivaguru Jayaraman

16. 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
Ans: D

17. 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.
Ans: A

18. Which of the following is the best method to make *n*-butylbenzene?

A) benzene + $CH_3CH_2CH_2CH_2Cl/AlCl_3$

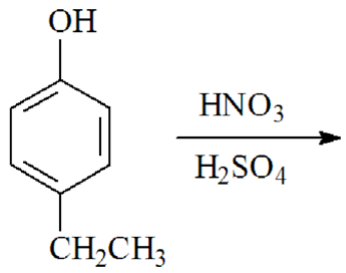
B) benzene + $CH_3CH_2CH{=}CH_2/H_2SO_4$

C) (1) benzene + $CH_3CH_2CH_2\overset{\overset{O}{\|}}{C}Cl/AlCl_3$ (2) H_2NNH_2/KOH, heat

D) (1) benzene + $CH_3CH_2CH_2CH_2OH/H_2SO_4$

A) A B) B C) C D) D
Ans: C

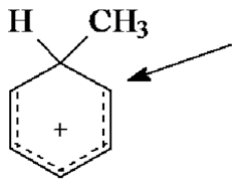
19. What is the major product of the following reaction?



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

Ans: A

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



A) +1 B) +0.50 C) +0.33 D) +0.20

Ans: C

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

A) ortho B) meta C) para D) none of them

Ans: C

22. Arrange the following compounds in order of increasing reaction rate with HNO_3/H_2SO_4.

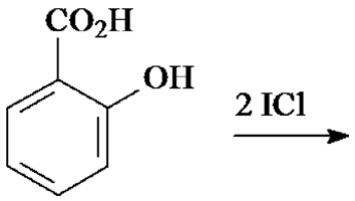
I. $C_6H_5CH{=}O$ II. $C_6H_5OCH_3$ III. C_6H_5Br IV. $C_6H_5CH_3$

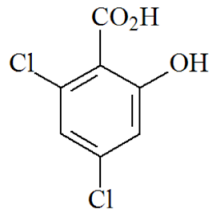
A) I < III < IV < II
B) I < IV < III < II
C) III < I < II < IV
D) III < I < IV < II

Ans: A

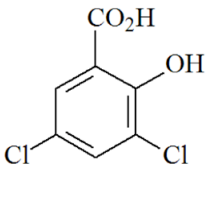
Prof. Sivaguru Jayaraman

23. 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.)

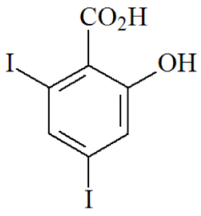




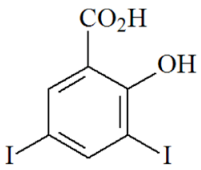
A)



B)



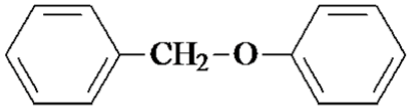
C)



D)

A) A B) B C) C D) D
Ans: D

24. 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

Ans: C

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

A) (1) benzene + $CH_3CH_2Cl/AlCl_3$ (2) $Br_2/FeBr_3$

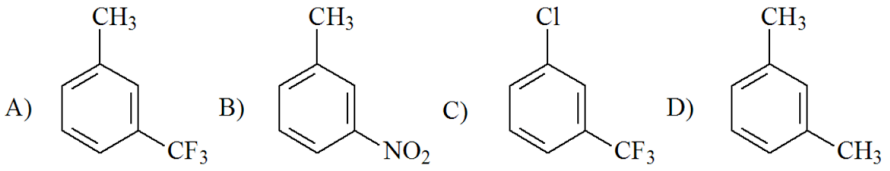
B) (1) benzene + $Br_2/FeBr_3$ (2) $CH_3CH_2Cl/AlCl_3$

C) (1) benzene + $CH_3\overset{O}{\overset{\|}{C}}Cl/AlCl_3$ (2) Zn(Hg), HCl (3) $Br_2/FeBr_3$

D) (1) benzene + $CH_3\overset{O}{\overset{\|}{C}}Cl/AlCl_3$ (2) $Br_2/FeBr_3$ (3) Zn(Hg), HCl

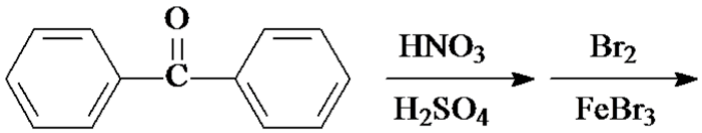
A) A B) B C) C D) D
Ans: D

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

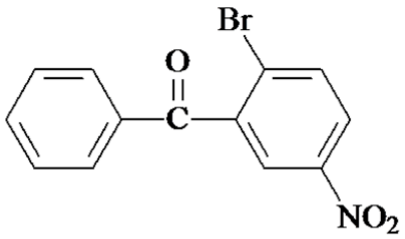


A) A B) B C) C D) D
Ans: D

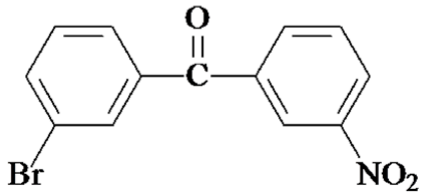
27. What is the product of the following series of reactions?



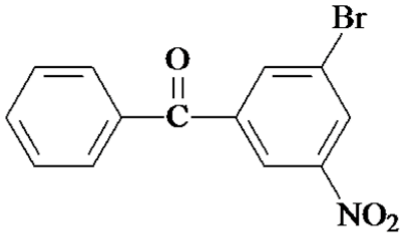
A)



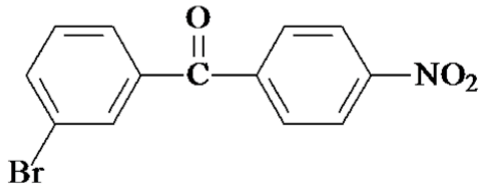
B)



C)



D)

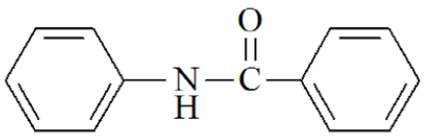


A) A B) B C) C D) D
Ans: B

28. 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
Ans: C

29. What is the major product of the Friedel-Crafts alkylation of benzene with $(CH_3)_2CHCH_2Cl$ and $AlCl_3$?
A) isobutylbenzene
B) *tert*-butylbenzene
C) *sec*-butylbenzene
D) butylbenzene
Ans: B

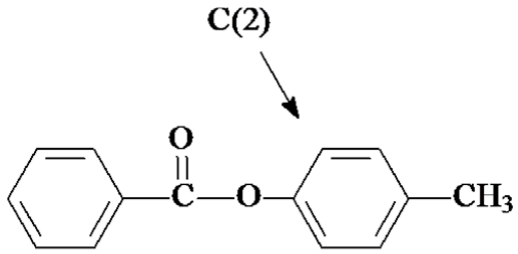
30. Where would the compound shown below undergo bromination with $Br_2/FeBr_3$?



ring 1 ring 2

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
Ans: A

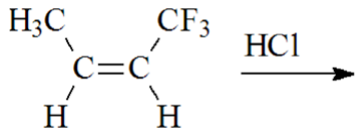
31. Where would the compound shown below undergo bromination with NBS and benzoyl peroxide?



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
Ans: D

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



A) $CH_3CH_2CHCF_3$ (Cl)

B) $CH_3CHCH_2CF_3$ (Cl)

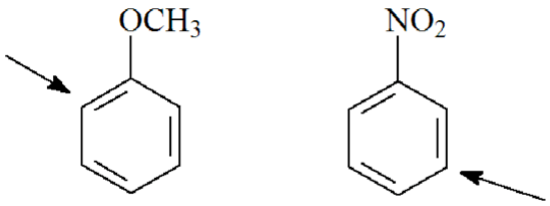
C) $CH_3CH_2CH_2CF_3$

D) $CH_3CHCHCF_3$ (Cl, Cl)

A) A B) B C) C D) D
Ans: B

33. Which one of the following substituents is deactivating and ortho-para directing in electrophilic aromatic substitution reactions?
A) –Cl B) $-N(CH_3)_2$ C) $-CO_2H$ D) $-CH=CH_2$
Ans: A

34. 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?



	anisole	nitrobenzene
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
Ans: B

35. 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)**

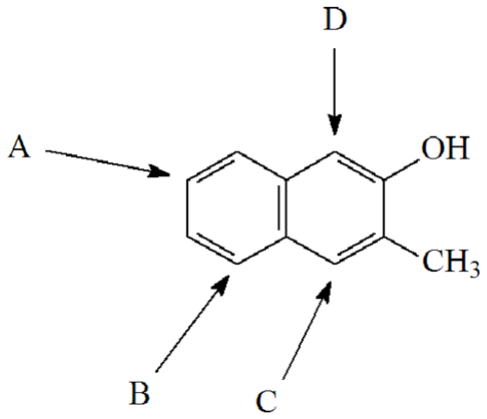
B) (1) Br_2, $h\nu$ **(2) $K_2Cr_2O_7$, H_2SO_4 (heat)**

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, $h\nu$**

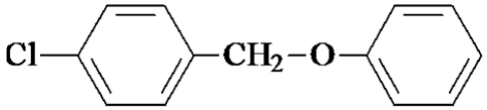
A) A B) B C) C D) D
Ans: C

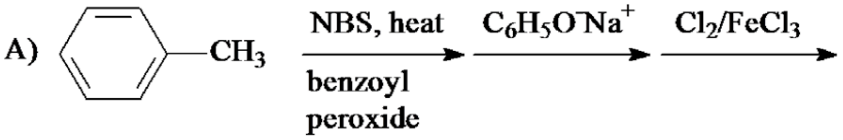
36. Predict which position of the naphthalene compound below is the most reactive with electrophiles in electrophilic aromatic substitution?

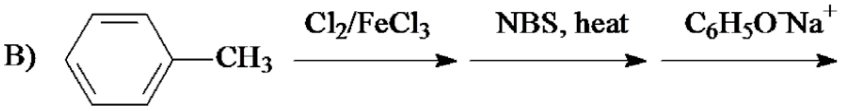


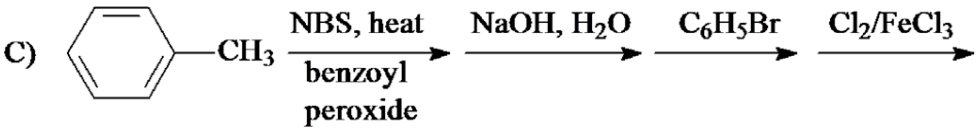
A) A B) B C) C D) D
Ans: D

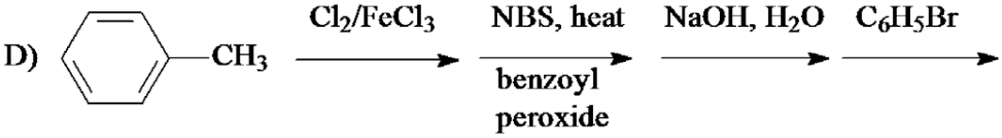
37. Starting with toluene, which of the following is the best method to make the ether shown below? (Assume you can separate ortho and para isomers.)



A) 

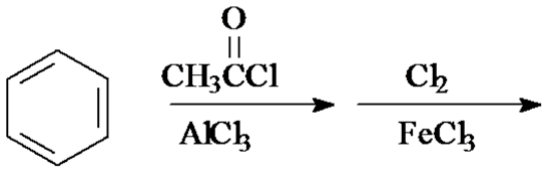
B) 

C) 

D) 

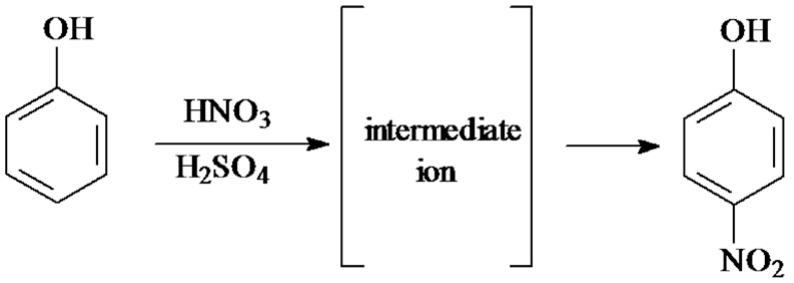
A) A B) B C) C D) D
Ans: B

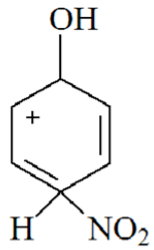
38. Identify the major product(s) of the reaction sequence shown below.

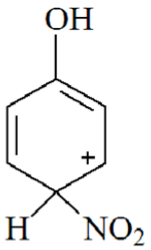


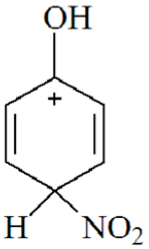
A) *ortho* and *para*-chloroacetophenone
B) *meta*-chloroacetophenone
C) *ortho* and *para*-chlorobenzaldehyde
D) *meta*-chlorobenzaldehyde
Ans: B

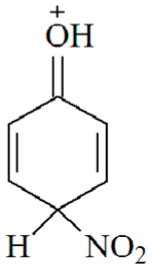
39. Which of the following is not a valid resonance form of the intermediate species in the reaction shown below?



A)


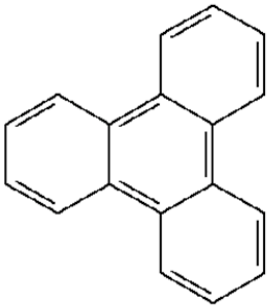
B)


C)


D)


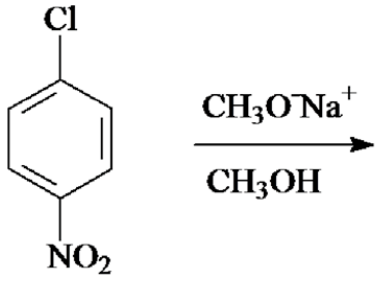
A) A B) B C) C D) D
Ans: A

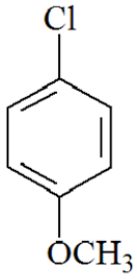
40. How many mononitration products are possible in the nitration of the compound shown below?

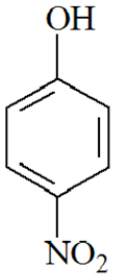


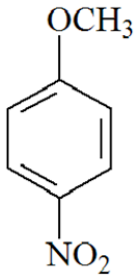
A) only 1 B) 2 C) 3 D) 4
Ans: B

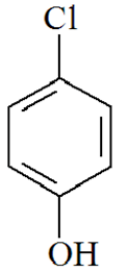
41. What is the product of the following reaction?



A) 

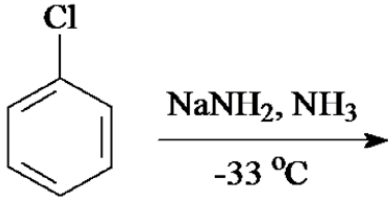
B) 

C) 

D) 

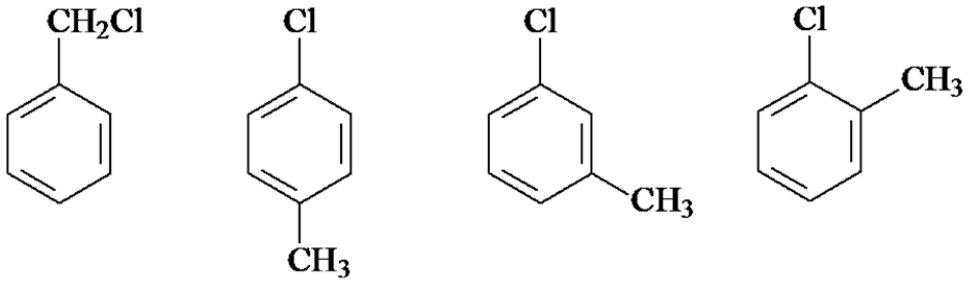
A) A B) B C) C D) D
Ans: C

42. What is the product of the following reaction?



A) benzene B) *ortho*-chloroaniline C) *meta*-chloroaniline D) aniline
Ans: D

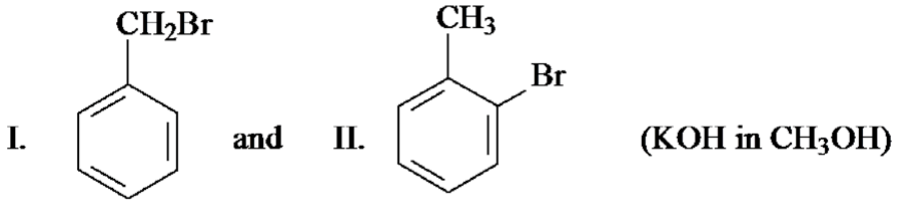
43. Which one of the following has the weakest carbon-chlorine bond?

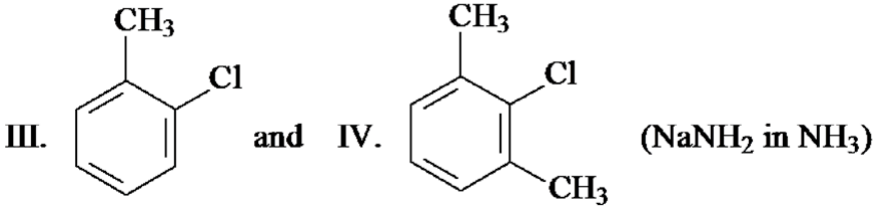


I II III IV

A) I B) II C) III D) IV
Ans: A

44. Which compound in each of the following pairs is the most reactive to the conditions indicated?





A) I and III B) I and IV C) II and III D) II and IV
Ans: A

45. Which of the following reacts at the fastest rate with potassium methoxide ($KOCH_3$) in methanol?

A) fluorobenzene
B) 4-nitrofluorobenzene
C) 2,4-dinitrofluorobenzene
D) 2,4,6-trinitrofluorobenzene

Ans: D

46. Which of the following reacts at the fastest rate with potassium methoxide ($KOCH_3$) in methanol?

A) fluorobenzene
B) *p*-nitrofluorobenzene
C) *p*-fluorotoluene
D) *p*-bromofluorobenzene

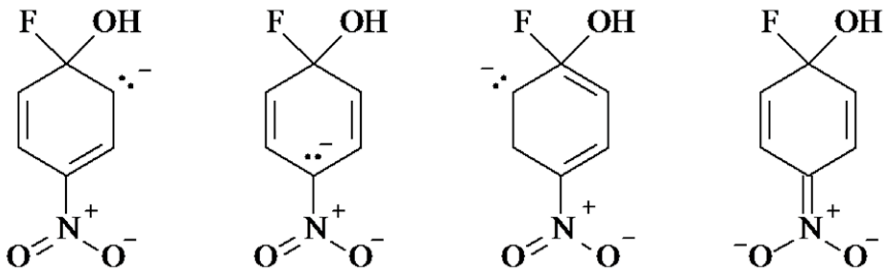
Ans: B

47. Which of the following is the kinetic rate equation for the addition-elimination mechanism of nucleophilic aromatic substitution?

A) rate = k[aryl halide]
B) rate = k[nucleophile]
C) rate = k[aryl halide][nucleophile]
D) rate = k[aryl halide][nucleophile]^2

Ans: C

48. Which of the following is <u>not</u> a resonance form of the intermediate in the nucleophilic addition of hydroxide ion to *para*-fluoronitrobenzene?

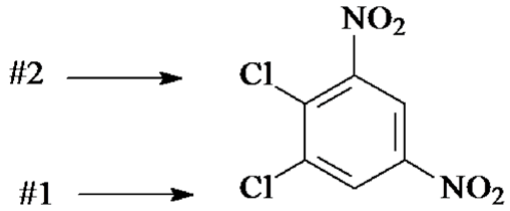


I II III IV

A) I B) II C) III D) IV

Ans: C

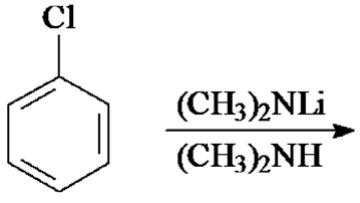
49. Which chlorine is most susceptible to nucleophilic substitution with $NaOCH_3$ in methanol?



A) #1
B) #2
C) #1 and #2 are equally susceptible.
D) No substitution is possible.

Ans: B

50. What is the product of the following reaction?

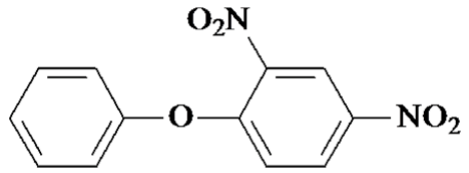


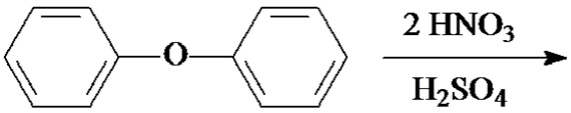
A) *N*,*N*-dimethylaniline
B) *para*-chloro-*N*,*N*-dimethylaniline
C) phenyllithium (C_6H_5Li)
D) *meta*-chloro-*N*,*N*-dimethylaniline

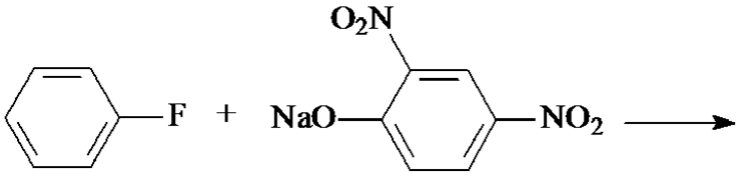
Ans: A

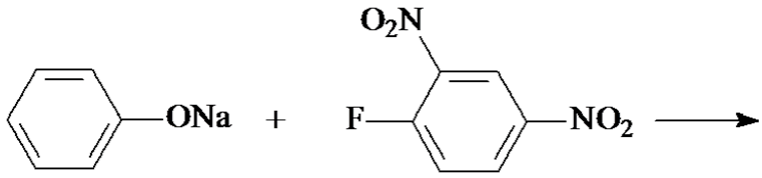
51. Which one of the reagents readily reacts with bromobenzene without heating?
A) $NaOCH_2CH_3$ B) NaCN/DMSO C) $NaNH_2/NH_3$ D) $(CH_3)_2NH$
Ans: C

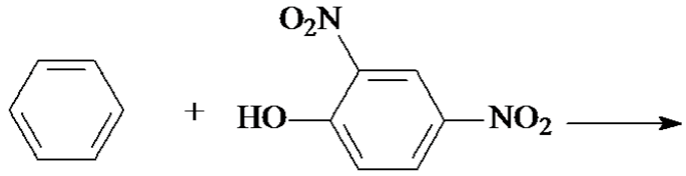
52. Which of the following would work best for the synthesis of the ether shown below?



A) 

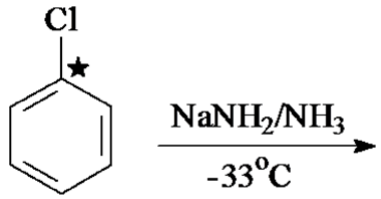
B) 

C) 

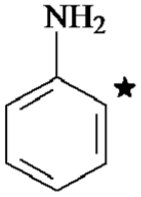
D) 

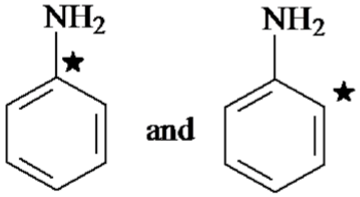
A) A B) B C) C D) D
Ans: C

53. Carbon-14 labelled chlorobenzene is reacted with sodium amide in ammonia as shown below. Which of the following depicts the carbon-14 labeled in the product(s)?

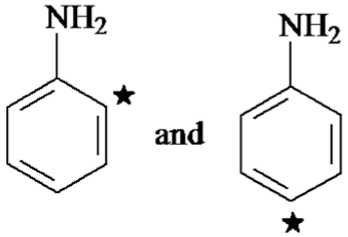


A) 

B) 

C) 

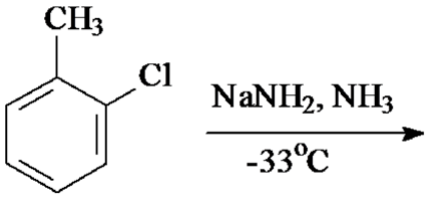
(about 50% each)

D) 

(about 50% each)

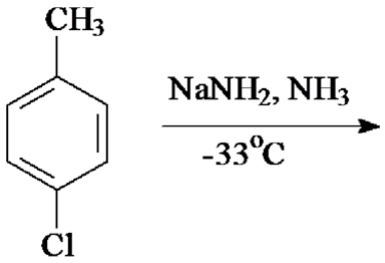
A) A B) B C) C D) D
Ans: C

54. Identify the product(s) of the following reaction.



A) only *ortho*-methylaniline
B) *ortho*-methylaniline and *meta*-methyaniline
C) *meta*-methylaniline and *para*-methyaniline
D) *ortho*-methylaniline and *para*-methyaniline
Ans: B

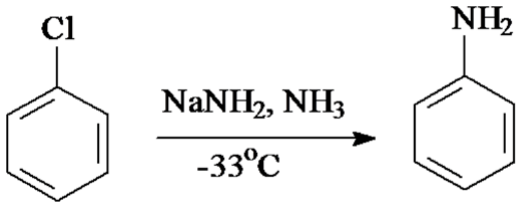
55. Which of the following best estimates the percentages of the three isomeric methylanilines from the reaction shown below?

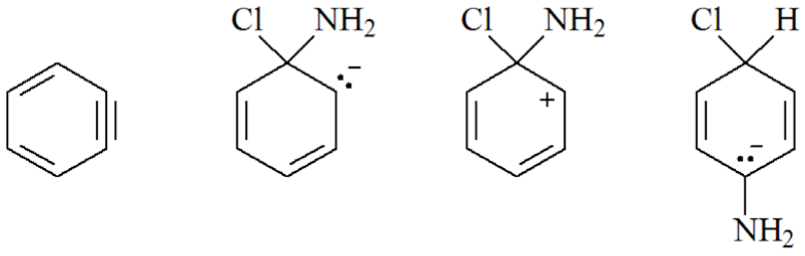


	ortho-methylaniline	*meta*-methyaniline	*para*-methyaniline
A)	33%	33%	33%
B)	40%	40%	20%
C)	0%	50%	50%
D)	0%	66%	33%

A) A B) B C) C D) D
Ans: C

56. Which of the following is a key intermediate in the reaction shown below?

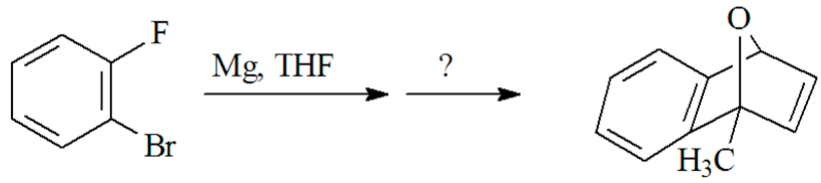


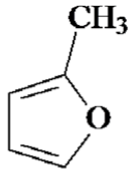


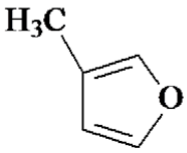
I II III IV

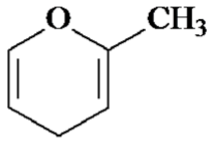
A) I B) II C) III D) IV
Ans: A

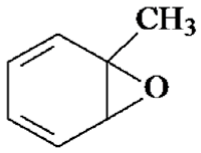
57. Identify the diene required for the synthesis shown below.



A) 

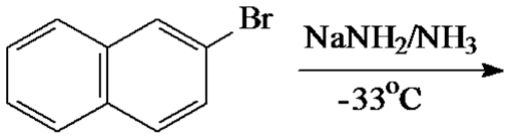
B) 

C) 

D) 

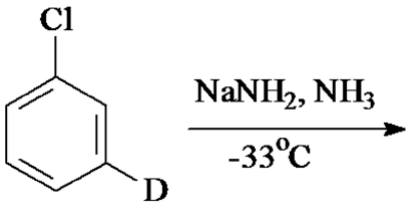
A) A B) B C) C D) D
Ans: A

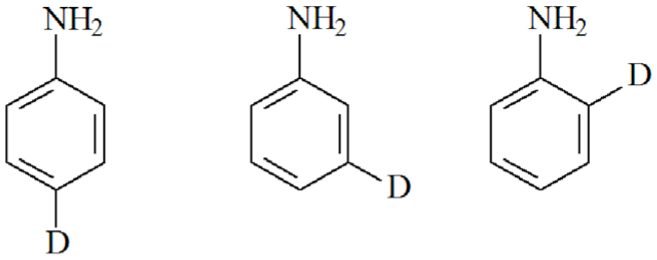
58. Assume that the following reaction goes by the elimination-addition mechanism for nucleophilic aromatic substitution. Based on that, how many isomeric naphthylamines are expected in the following reaction?



A) only a single product B) two C) three D) four
Ans: C

59. Which of the following best estimates the percentages of the three isomeric deuterated anilines from the reaction shown below?



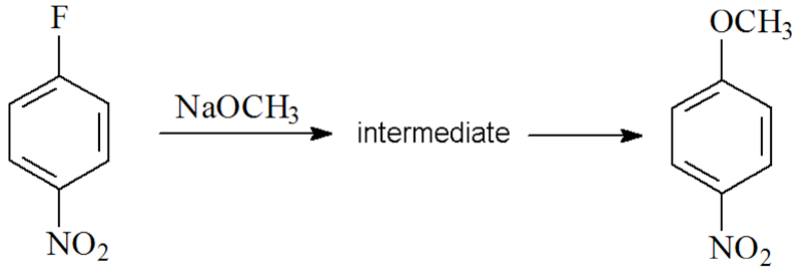


A)	25%	50%	25%
B)	33%	33%	33%
C)	50%	25%	25%
D)	66%	33%	0%

A) A B) B C) C D) D
Ans: A

60. Which of the following is(are) true concerning the intermediate benzyne?
I. Benzyne is aromatic.
II. All the hydrogens of benzyne are equivalent and indistinguishable.
III. The benzyne molecule has strain energy.
A) only I B) only III C) I and III D) II and III
Ans: C

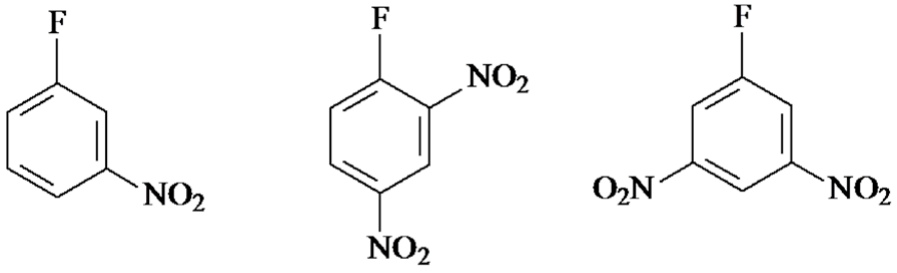
61. Which of the following is(are) true concerning the intermediate in the addition-elimination mechanism of the reaction below?



I. The intermediate is aromatic.
II. The intermediate is a resonance stabilized anion.
III. Electron withdrawing groups on the benzene ring stabilize the intermediate.
A) only I B) only II C) I and III D) II and III
Ans: D

62. Which one of the following has the fastest rate of reaction with sodium ethoxide, $NaOCH_2CH_3$, at 25°C?
A) *para*-fluoronitrobenzene
B) *para*-chloronitrobenzene
C) *para*-bromonitrobenzene
D) *para*-iodonitrobenzene
Ans: A

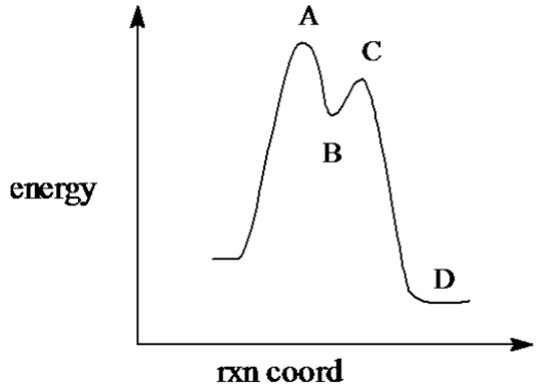
63. Arrange the following compounds in order of increasing reactivity with sodium methoxide, $NaOCH_3$?

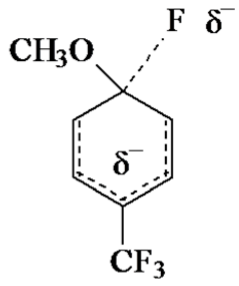


I **II** **III**

A) I < II < III B) I < III < II C) II < I < III D) III < II < I
Ans: B

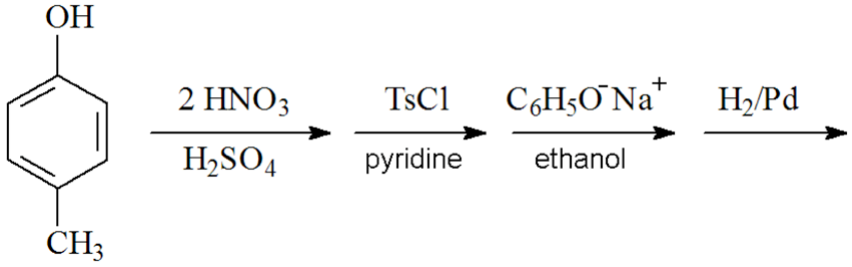
64. Which position on the potential energy diagram corresponds to the species shown for the reaction of *para*-fluoro (trifluoromethyl) benzene with sodium methoxide?

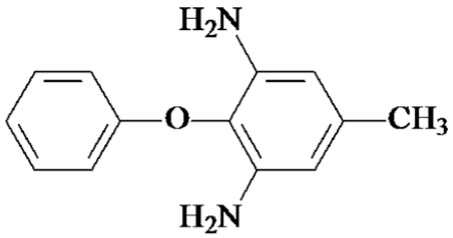


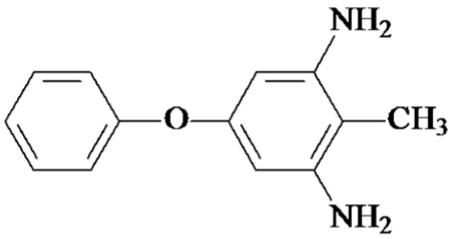


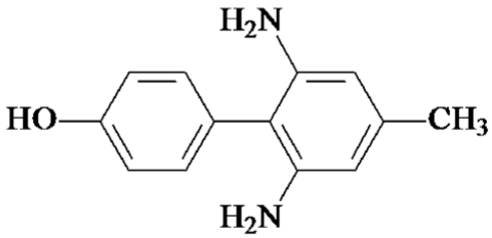
A) A B) B C) C D) D
Ans: C

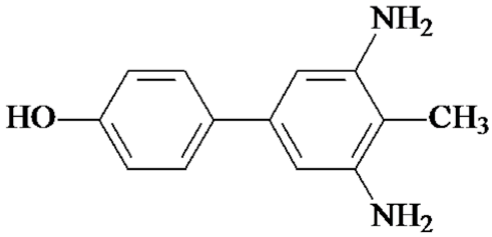
65. Which of the following is the product from the reaction sequence shown below?



A)


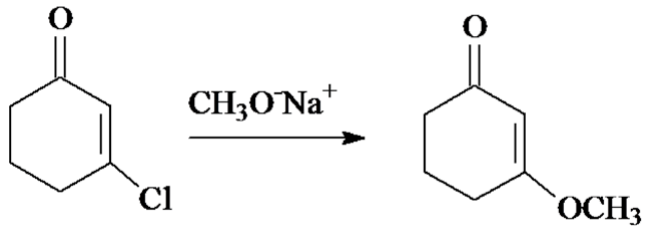
B)


C)


D)


A) A B) B C) C D) D
Ans: A

66. Identify the likely mechanism in the reaction shown below.



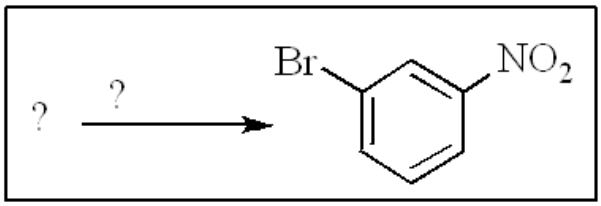
A) S_N2
B) S_N1
C) electrophilic addition-elimination
D) nucleophilic addition-elimination
Ans: D

67. Which of the following is NOT a common electrophile in electrophilic aromatic substitution reactions?
A) $^+SO_3H$ B) ^+Br C) ^+CN D) $^+NO_2$
Ans: C

68. Ranked in order of decreasing reactivity in electrophilic aromatic substitution reactions, the order would be (more reactive > less reactive)
A) chlorobenzene > toluene > acetophenone
B) chlorobenzene > acetophenone > toluene
C) toluene > chlorobenzene > acetophenone
D) toluene > acetophenone > chlorobenzene
Ans: C

69. Which statement is true in electrophilic aromatic substitution?
A) no meta directors have a nitrogen atom directly attached to the ring
B) all ortho/para directors make the ring more reactive than benzene
C) no meta directors have non-bonding electrons on the atom directly attached to the ring
D) all ortho/para directors have non-bonding electrons on the atom directly attached to the ring
Ans: C

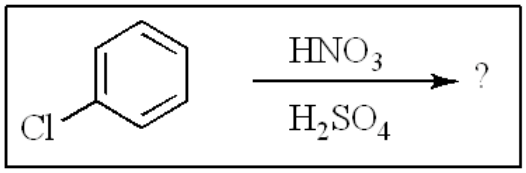
70. What would be the most efficient way to make meta-nitrobromobenzene?

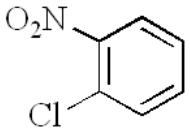


A) bromobenzene + HNO_3/H_2SO_4
B) nitrobenzene + $Br_2/FeBr_3$
C) either of these approaches would work
D) neither of these approaches would work
Ans: B

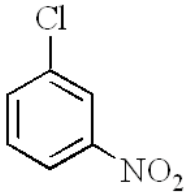
71. Which one of the common electrophilic aromatic substitution reactions puts an electron donating group on a benzene ring?
A) Br_2, $FeBr_3$ B) $SO_3 + H_2SO_4$ C) RCOCl + $AlCl_3$ D) RCl + $AlCl_3$
Ans: D

72. What major product do you expect?

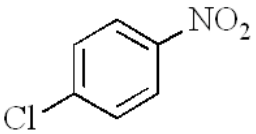




A



B

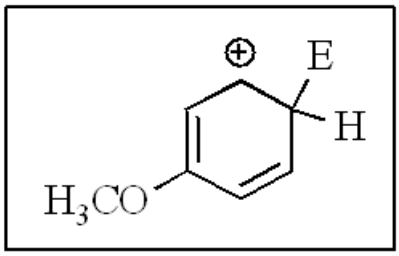


C

D: more than one of these

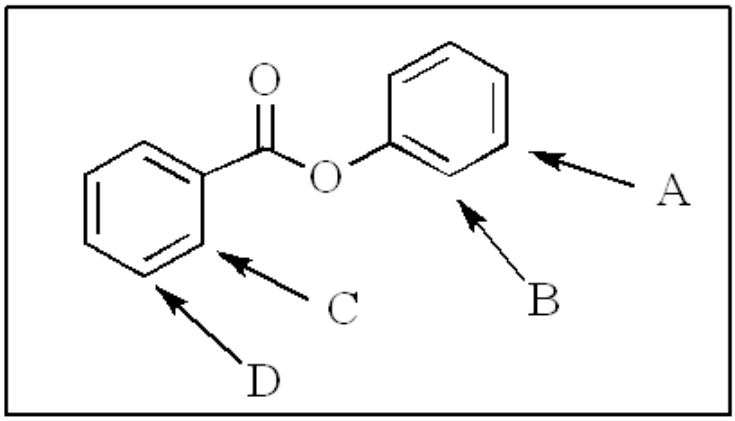
A) A B) B C) C D) D
Ans: D

73. How many TOTAL resonance structures can be drawn for this intermediate? (incl. this one)



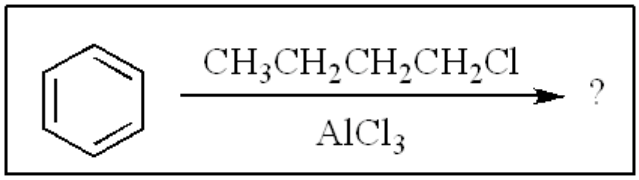
A) one B) two C) three D) four
Ans: D

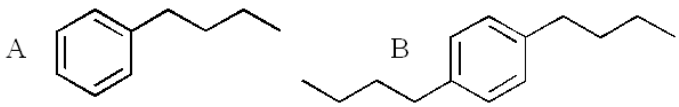
74. Of the choices given, where would an aromatic substitution occur on this molecule?

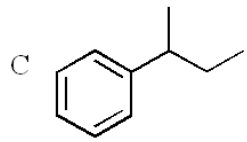


A) A B) B C) C D) D
Ans: B

75. What major product(s) would you expect from this reaction?



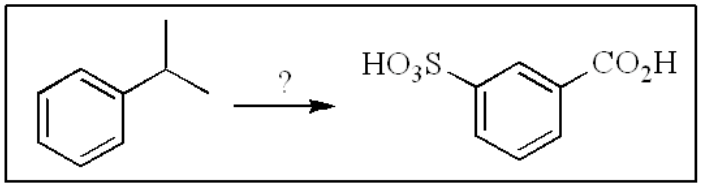




D. more than one of these

A) A B) B C) C D) D
Ans: C

76. How would you best accomplish this?



A) 1. SO_3, H_2SO_4, heat; 2. $K_2Cr_2O_7$, H_2SO_4
B) 1. $K_2Cr_2O_7$, H_2SO_4, heat; 2. SO_3, H_2SO_4
C) either of these would work.
D) neither of these would work.
Ans: B

Prof. Sivaguru Jayaraman