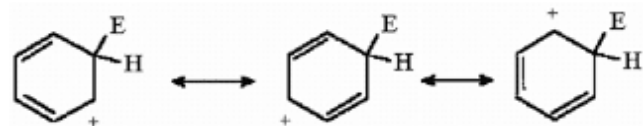


1) Provide the major resonance structures of the intermediate sigma complex in the reaction of benzene with the generic electrophile E^+ .

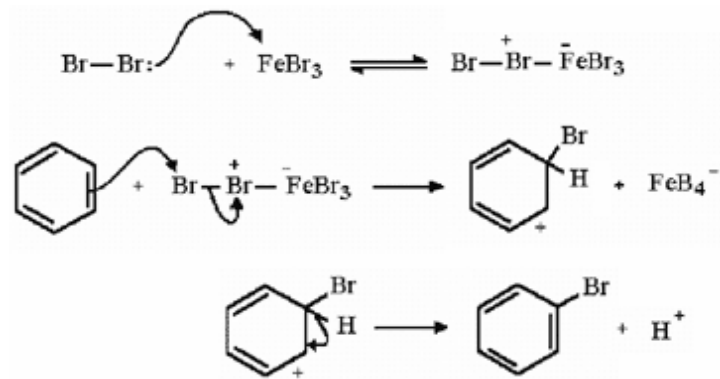
Answer:



Diff: 1

4) Provide a detailed, stepwise mechanism for the reaction of benzene with Br_2 and $FeBr_3$. Make sure to include the activating reaction between Br_2 and $FeBr_3$ in your mechanism.

Answer:



Diff: 3

6) Which of the following species is attacked by benzene in the electrophilic nitration reaction?

A) HNO_3

B) NO_2^+

C) NO_2

D) NO^+

E) N_3^-

Answer: B

Diff: 1

11) Which of the following is the strongest activating group in electrophilic aromatic substitution reactions?

A) $-\text{CH}_2\text{CH}_3$

B) $-\text{OCH}_3$

C) $-\text{CO}_2\text{CH}_3$

D) $-\text{NO}_2$

E) $-\text{N}(\text{CH}_3)_2$

Answer: E

Diff: 1

12) Rank the following groups in order of increasing activating power in electrophilic aromatic substitution reactions: $-\text{OCH}_3$, $-\text{OCOCH}_2\text{CH}_3$, $-\text{CH}_2\text{CH}_3$, $-\text{Br}$.

Answer: $-\text{Br} < -\text{CH}_2\text{CH}_3 < -\text{OCOCH}_2\text{CH}_3 < -\text{OCH}_3$

Diff: 2

13) In electrophilic aromatic substitution reactions a bromine substituent:

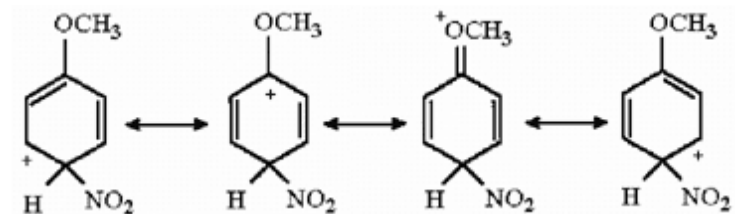
- A) is a deactivator and a m-director.
- B) is a deactivator and an o,p-director.
- C) is an activator and a m-director.
- D) is an activator and an o,p-director.
- E) none of the above

Answer: B

Diff: 2

14) Draw the four major resonance structures of the sigma complex intermediate in the reaction of anisole with $\text{HNO}_3/\text{H}_2\text{SO}_4$ to yield *p*-nitroanisole.

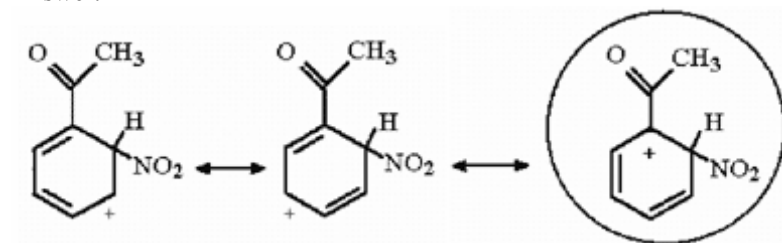
Answer:



Diff: 3

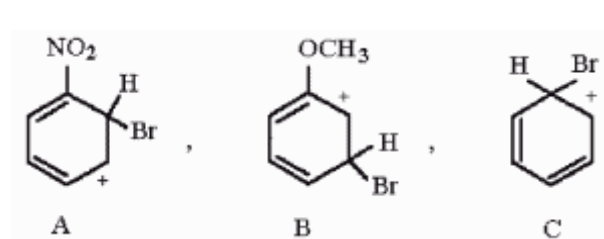
15) Draw the three major resonance structures of the sigma complex intermediate in the reaction of acetophenone with $\text{HNO}_3/\text{H}_2\text{SO}_4$ to yield *o*-nitroacetophenone. Circle the resonance form which is less stable than the other two.

Answer:



Diff: 3

16) Rank the following sigma complexes in order of increasing stability.



Answer: $A < B < C$

Diff: 2

17) Provide a series of synthetic steps by which 2-bromo-4-nitrobenzoic acid can be prepared from toluene.

Answer: 1. $\text{HNO}_3, \text{H}_2\text{SO}_4$

2. $\text{Br}_2, \text{FeBr}_3$

3. $\text{KMnO}_4, \text{OH}^-, \Delta$

4. H^+

Diff: 3

18) Provide a series of synthetic steps by which 3-bromoethylbenzene can be prepared from benzene.

Answer: 1. $\text{CH}_3\text{COCl}, \text{AlCl}_3$

2. $\text{Br}_2, \text{FeBr}_3$

3. $\text{Zn}(\text{Hg}), \text{HCl}$

Diff: 3

19) Provide a series of synthetic steps by which 4-*t*-butylbenzoic acid can be prepared from toluene.

Answer: 1. $(\text{CH}_3)_3\text{CCl}, \text{AlCl}_3$

2. $\text{KMnO}_4, \text{OH}^-, \Delta$

3. H^+

Diff: 3

20) Provide a series of synthetic steps by which *p*-nitrobutylbenzene can be prepared from benzene.

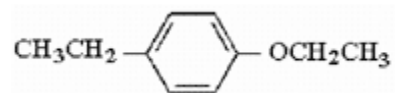
Answer: 1. $\text{CH}_3\text{CH}_2\text{CH}_2\text{COCl}, \text{AlCl}_3$

2. $\text{Zn}(\text{Hg}), \text{HCl}$

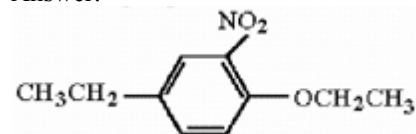
3. $\text{HNO}_3, \text{H}_2\text{SO}_4$

Diff: 3

21) Provide the structure of the major mononitration product of the compound below.

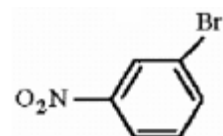


Answer:

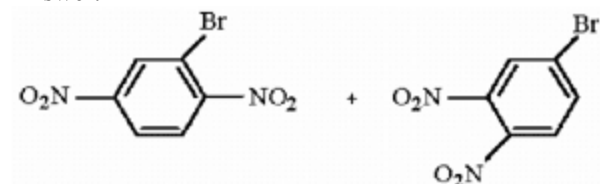


Diff: 2

22) Provide the structure of the major mononitration product(s) of the compound below.

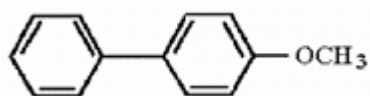


Answer:

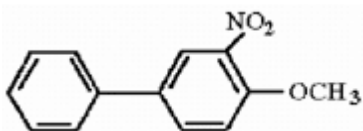


Diff: 2

23) Provide the structure of the major mononitration product of the compound below.

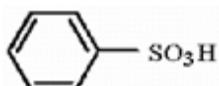


Answer:

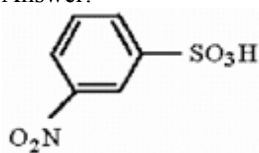


Diff: 2

24) Provide the structure of the major mononitration product of the compound below.



Answer:



Diff: 2

25) Which of the following compounds will undergo bromination most rapidly using Br₂, FeBr₃?

- A) *p*-methylacetanilide
- B) bromobenzene
- C) acetanilide
- D) benzenesulfonic acid
- E) dibromobenzene

Answer: A

Diff: 2

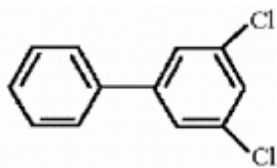
26) In the addition of an electrophile to acetophenone, which of the following best describes the expected mode of reaction?

- A) The *o,p*-positions are most activated to attack by the electrophile.
- B) The *m*-positions are most activated to attack by the electrophile.
- C) The *o,p*-positions are most deactivated to attack by the electrophile.
- D) The *m*-positions are most deactivated to attack by the electrophile.
- E) All positions (*o*, *m*, and *p*) are equally activated to attack by the electrophile.

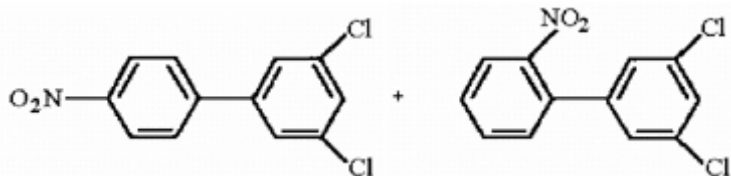
Answer: C

Diff: 2

27) Provide the structure of the major mononitration product(s) of the compound below.

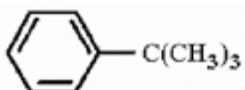


Answer:

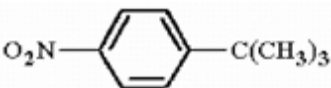


Diff: 2

28) Provide the structure of the major mononitration product of the compound below.

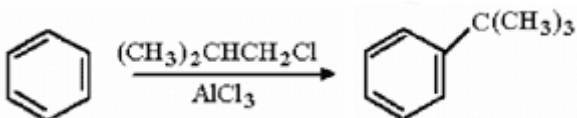


Answer:

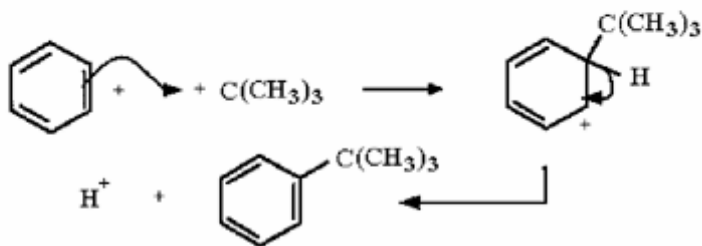
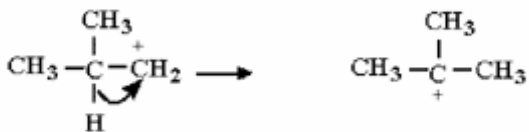
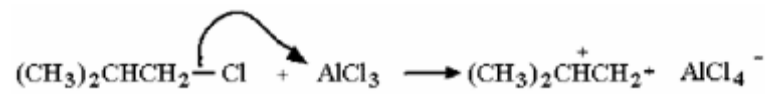


Diff: 1

29) Provide a detailed, stepwise mechanism for the following reactions.

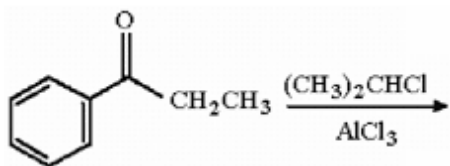


Answer:



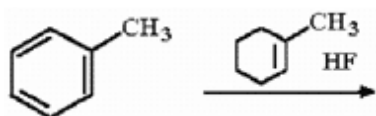
Diff: 3

31) Provide the structure of the major organic product of the following reaction.

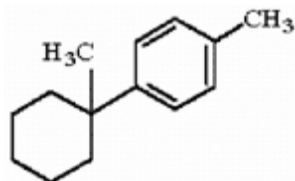


Answer: No reaction. The ring is too deactivated by the acyl substituent to undergo Friedel-Crafts alkylation.
Diff: 3

32) Provide the structure of the major organic product of the following reaction.



Answer:



Diff: 2

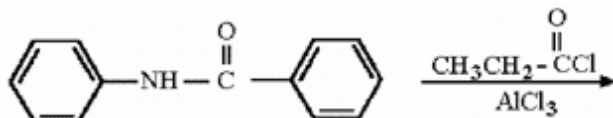
33) Which of the following compounds would most likely be used in the preparation of isobutylbenzene from benzene?

- A) (CH₃)₂CHCOCl
- B) (CH₃)₂CHCH₂Cl
- C) (CH₃)₂CHCH₂Br
- D) CH₃CH₂CH₂CH₂Cl
- E) CH₃CH₂CH₂COCl

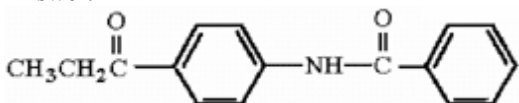
Answer: A

Diff: 2

34) Provide the structure of the major organic product of the following reaction.



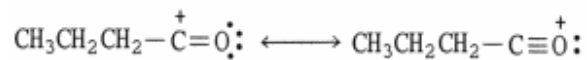
Answer:



Diff: 2

35) Draw the two major resonance structures of the acylium ion which results when butanoyl chloride [CH₃CH₂CH₂COCl] is treated with AlCl₃.

Answer:



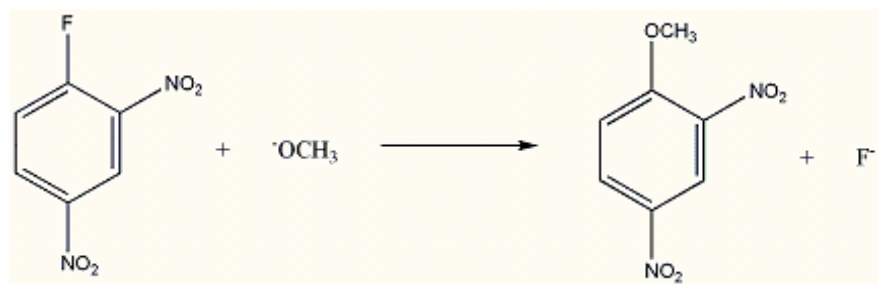
Diff: 2

36) Why are Friedel-Crafts acylation reactions not prone to polyacylation?

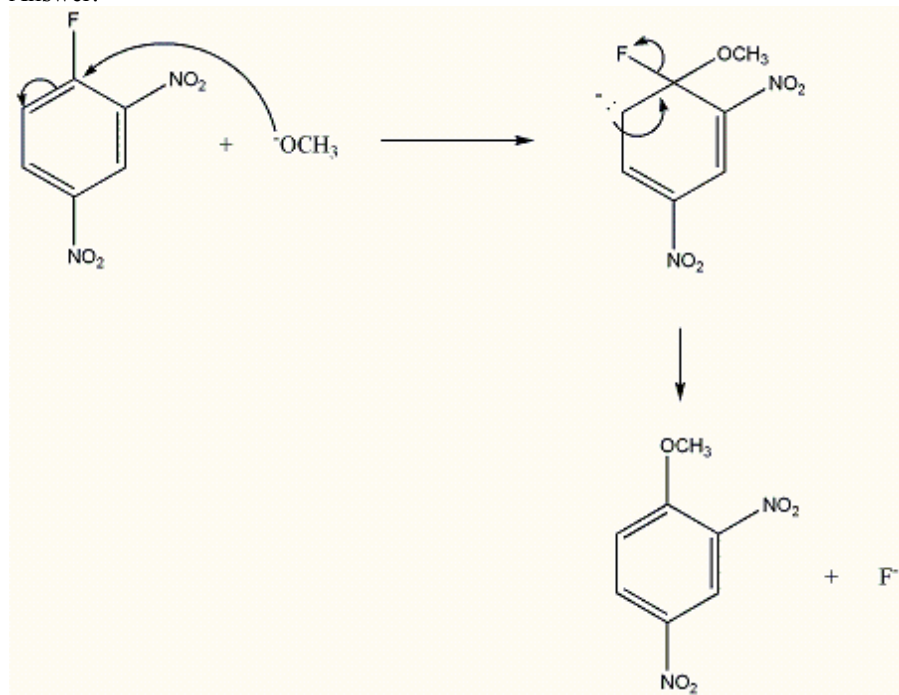
Answer: Once the ring is acylated, it is deactivated to further electrophilic attack since the acyl group is electron withdrawing.

Diff: 2

37) Provide a detailed, stepwise mechanism for the following reaction.

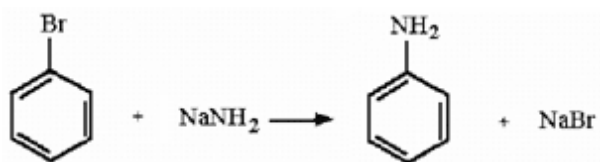


Answer:

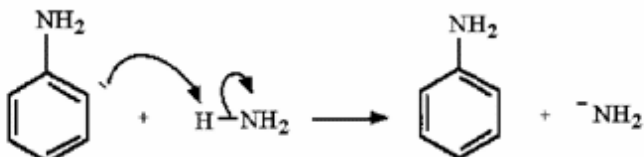
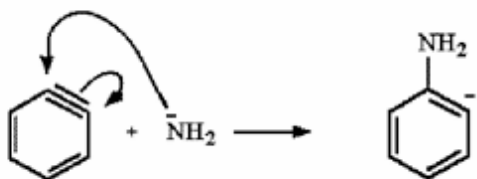
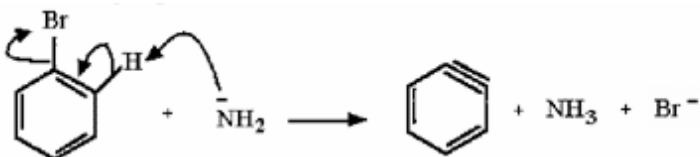


Diff: 3

38) Provide a detailed, stepwise mechanism for the following reaction.

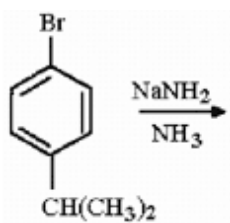


Answer:

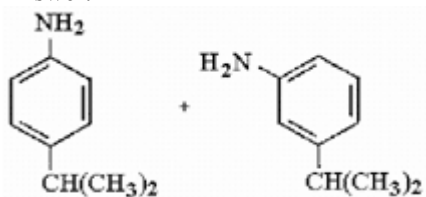


Diff: 3

42) Provide the structures of the major organic products of the following reaction.

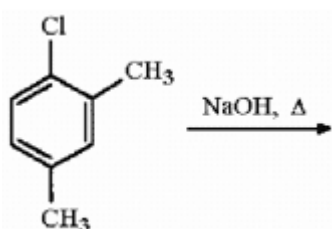


Answer:

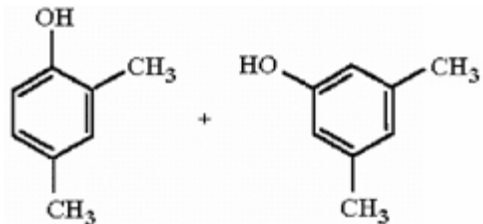


Diff: 2

43) Provide the structures of the major organic products of the following reaction.



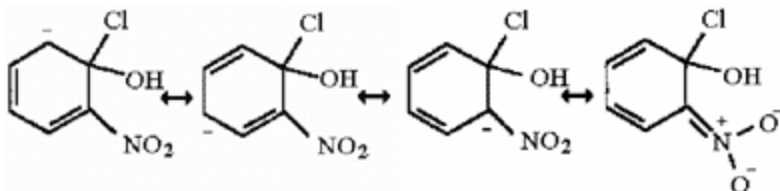
Answer:



Diff: 2

44) Draw the four major resonance structures of the intermediate which results when *o*-nitrochlorobenzene is treated with NaOH.

Answer:



Diff: 3

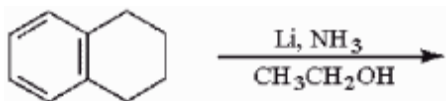
45) Which toluidine isomers are possible products when *m*-bromotoluene is treated with NaNH₂?

- A) ortho, meta, and para
- B) meta only
- C) para only
- D) ortho only
- E) meta and para only

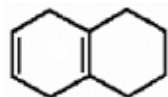
Answer: A

Diff: 2

46) Provide the structure of the major organic product in the following reaction.

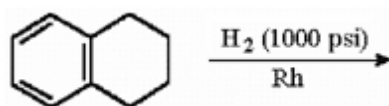


Answer:



Diff: 2

47) Provide the structures of the major organic products in the following reaction.

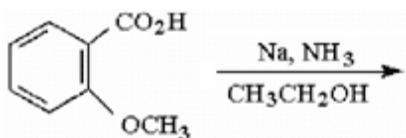


Answer:

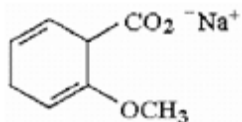


Diff: 2

48) Provide the structure of the major organic product in the following reaction.

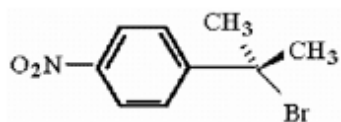


Answer:



Diff: 2

49) Provide a series of synthetic steps by which the compound below can be prepared from benzene.

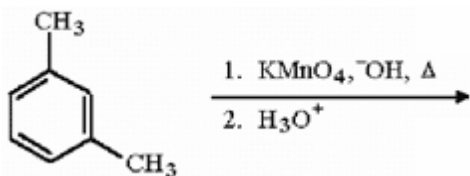


Answer: 1. $(\text{CH}_3)_2\text{CHCl}$, AlCl_3
2. HNO_3 , H_2SO_4
3. Br_2 , $h\nu$
Diff: 3

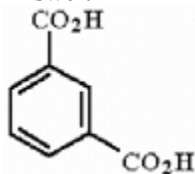
50) Provide a series of synthetic steps by which 4-phenylheptan-4-ol can be prepared from benzene.

Answer: 1. Br_2 , FeBr_3
2. Mg , ether
3. $\text{CH}_3\text{CH}_2\text{CH}_2\text{COCH}_2\text{CH}_2\text{CH}_3$
4. H_3O^+
Diff: 3

51) Provide the structure of the major organic product in the following reaction.

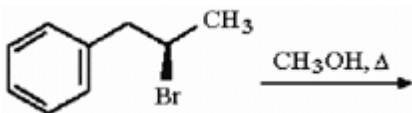


Answer:

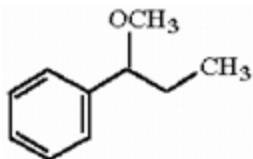


Diff: 2

52) Provide the structure of the major organic product in the following reaction.

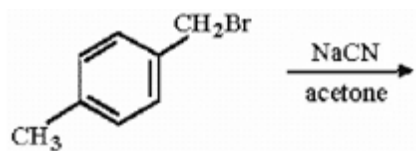


Answer:

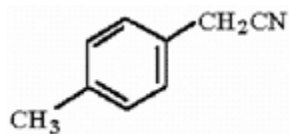


Diff: 3

53) Provide the structure of the major organic product in the following reaction.

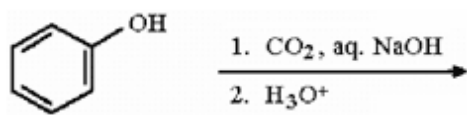


Answer:

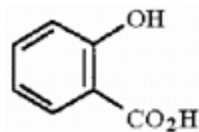


Diff: 1

54) Provide the structure of the major organic product in the following reaction.

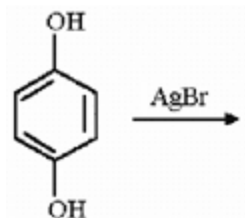


Answer:

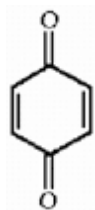


Diff: 3

55) Provide the structure of the major organic product in the following reaction.



Answer:



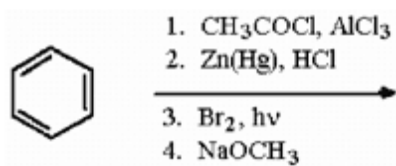
Diff: 2

56) Provide a series of synthetic steps by which *p*-methylanisole can be prepared from *p*-cresol.

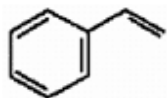
Answer: 1. NaOH
2. (CH₃O)₂SO₂ or CH₃I

Diff: 2

57) Provide the structure of the major organic product in the following reaction sequence.

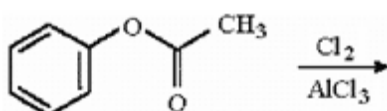


Answer:

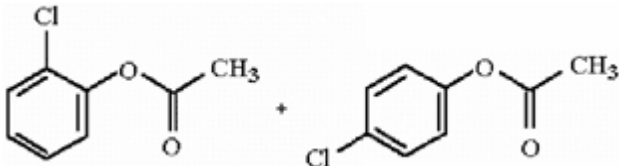


Diff: 2

58) Provide the structure of the major organic product(s) in the following reaction.

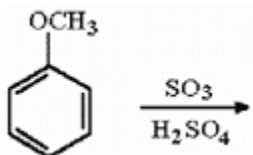


Answer:

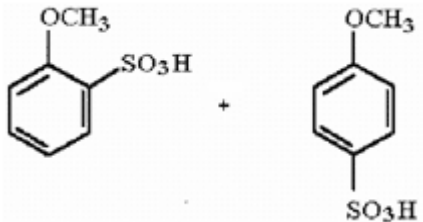


Diff: 1

59) Provide the structure of the major organic product(s) in the following reaction.

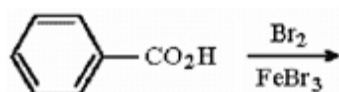


Answer:

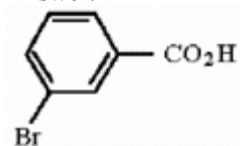


Diff: 1

60) Provide the structure of the major organic product(s) in the following reaction.

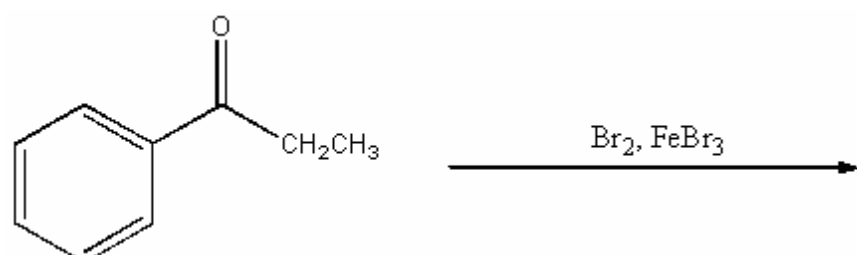


Answer:

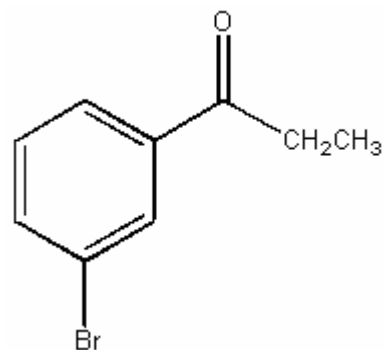


Diff: 1

71) Provide the major organic product of the following reaction.

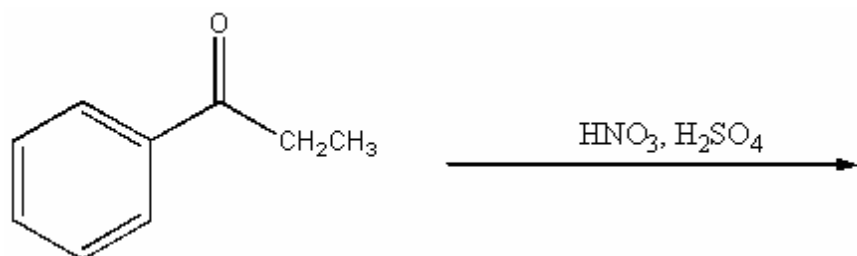


Answer:

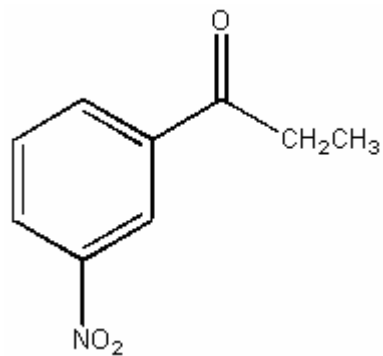


Diff: 2

72) Provide the major organic product of the following reaction.

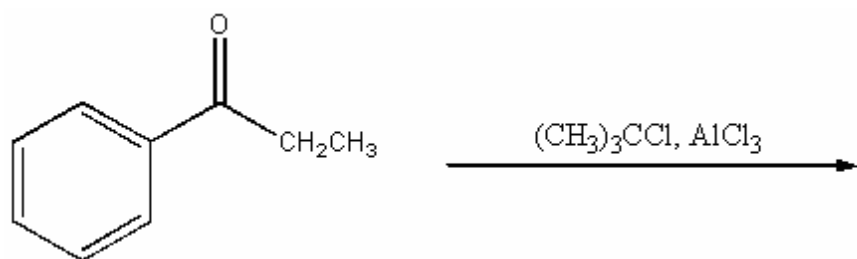


Answer:



Diff: 2

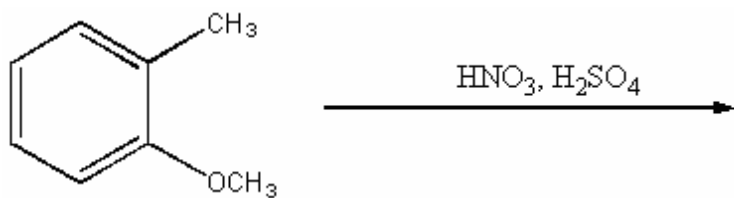
73) Provide the major organic product of the following reaction.



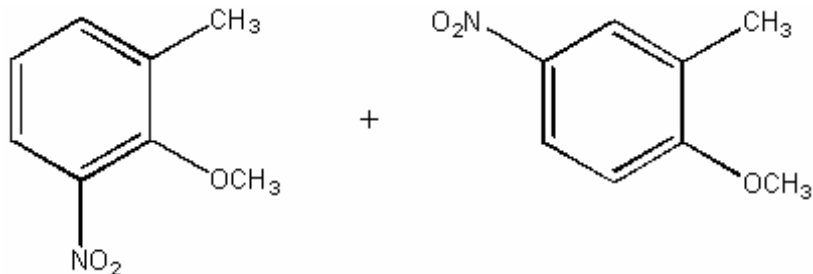
Answer: No reaction. Friedel-Crafts alkylation reactions will not proceed when the aromatic ring of the starting material is deactivated.

Diff: 3

74) Provide the major organic product of the following reaction.

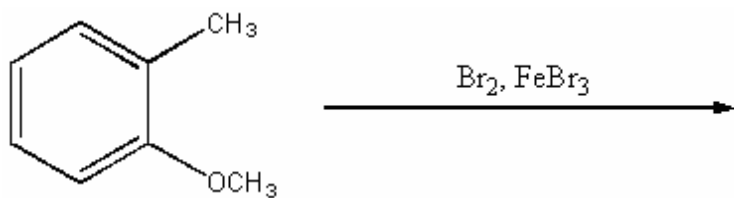


Answer:

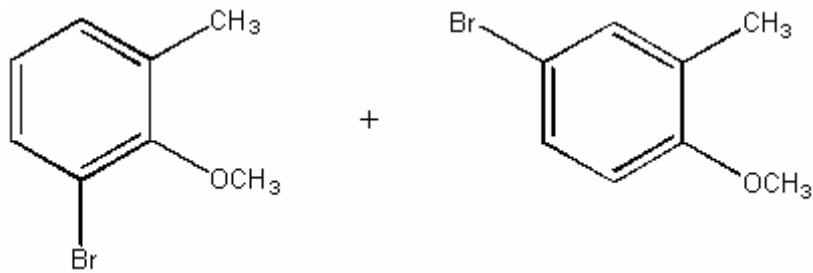


Diff: 2

75) Provide the major organic product of the following reaction.

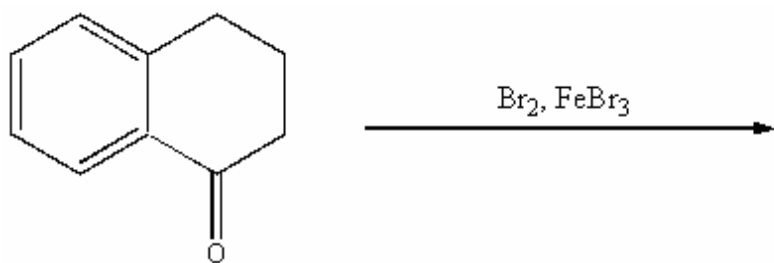


Answer:

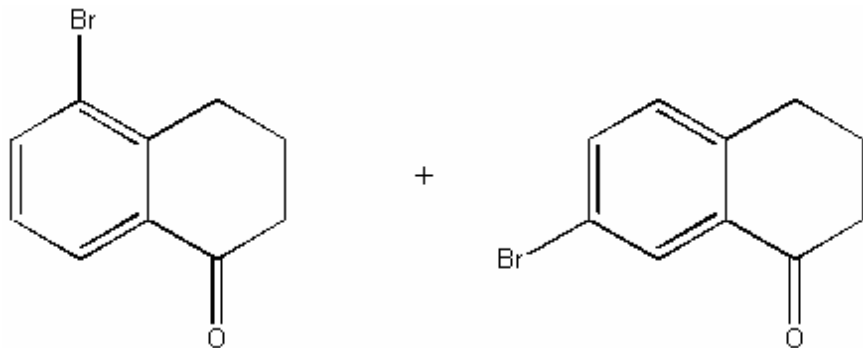


Diff: 2

76) Provide the major organic product of the following reaction.

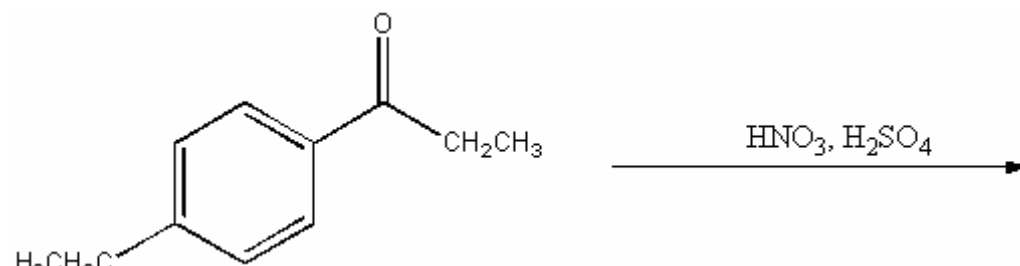


Answer:

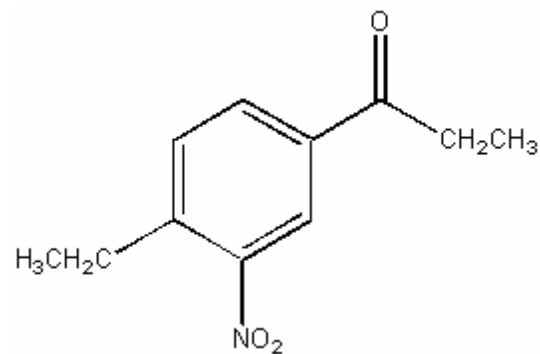


Diff: 2

77) Provide the major organic product of the following reaction.

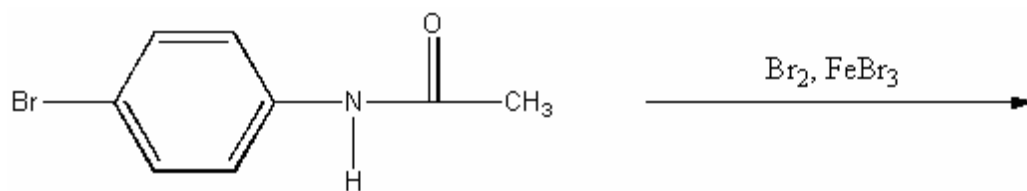


Answer:

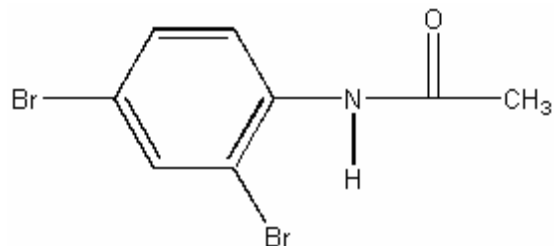


Diff: 2

78) Provide the major organic product of the following reaction.

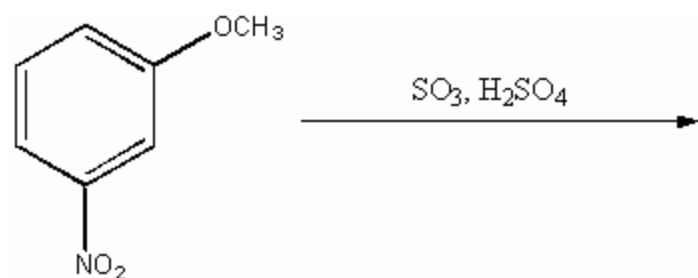


Answer:

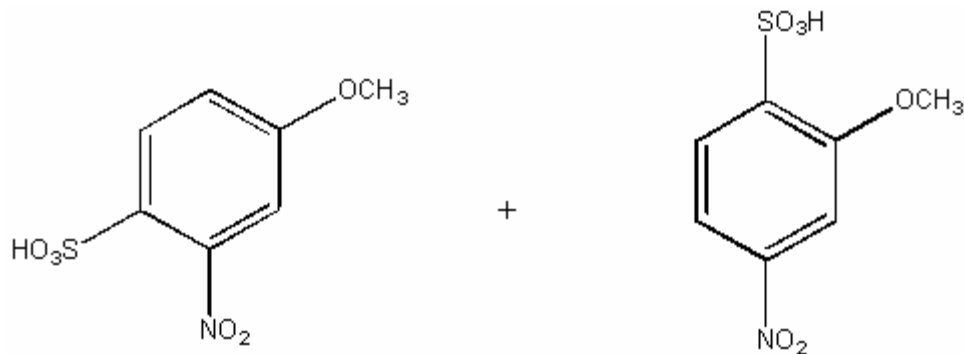


Diff: 2

79) Provide the major organic product of the following reaction.

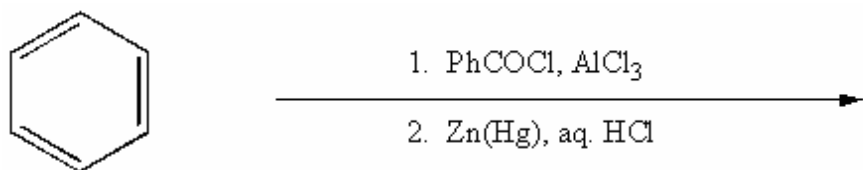


Answer:

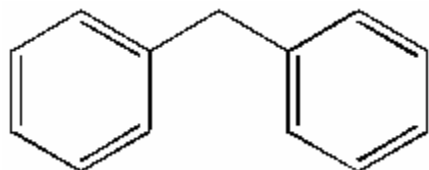


Diff: 2

80) Provide the major organic product of the following reaction sequence.



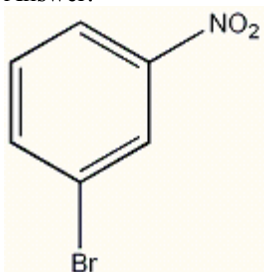
Answer:



Diff: 2

86) Provide the major organic product that results when benzene is treated with the following sequence of reagents:
1. HNO_3 , H_2SO_4 2. Br_2 , FeBr_3 .

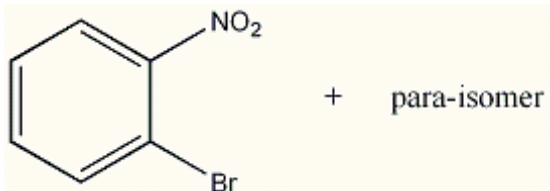
Answer:



Diff: 2

87) Provide the major organic product that results when benzene is treated with the following sequence of reagents:
1. Br_2 , FeBr_3 2. HNO_3 , H_2SO_4 .

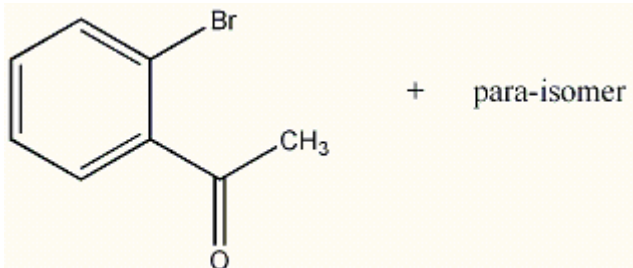
Answer:



Diff: 2

88) Provide the major organic product that results when benzene is treated with the following sequence of reagents:
1. Br_2 , FeBr_3 2. CH_3COCl , AlCl_3 .

Answer:

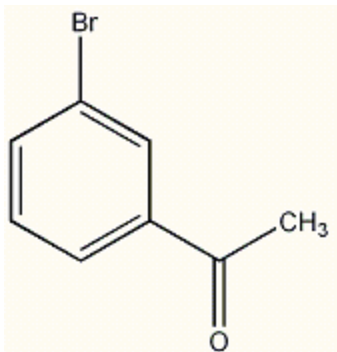


Diff: 2

89) Provide the major organic product that results when benzene is treated with the following sequence of reagents:

1. CH_3COCl , AlCl_3 2. Br_2 , FeBr_3 .

Answer:



Diff: 2

90) What sequence of reagents is needed to convert benzene into m-bromoethylbenzene?

Answer: 1. CH_3COCl , AlCl_3

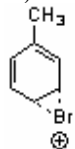
2. Br_2 , FeBr_3

3. $\text{Zn}(\text{Hg})$, HCl

Diff: 2

91) Which of the following is an intermediate in the bromination of toluene?

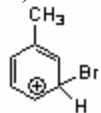
A)



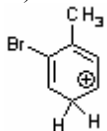
B)



C)



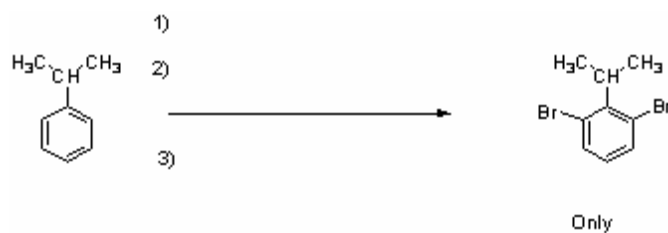
D)



Answer: B

Diff: 2

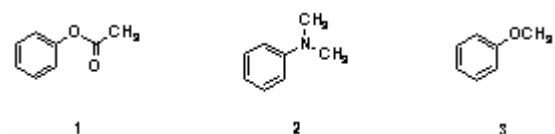
92) Provide the necessary reagents to accomplish the following transformation.



Answer: 1) $\text{SO}_3 / \text{H}_2\text{SO}_4$ 2) excess $\text{Br}_2 / \text{FeBr}_3$ 3) H^+ , H_2O , heat

Diff: 3

93) Which sequence correctly ranks the following aromatic rings in order of increasing rate of reactivity with chlorine and aluminum chloride?



A) $1 < 2 < 3$

B) $2 < 3 < 1$

C) $3 < 2 < 1$

D) $2 < 1 < 3$

E) $1 < 3 < 2$

Answer: E

Diff: 2

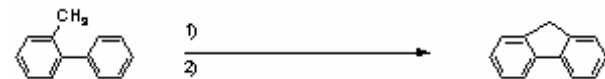
94) Show how the following product can be made from benzene.



Answer: 1) isobutyryl chloride / AlCl_3 2) $\text{I}_2 / \text{HNO}_3$ 3) Zn (Hg) / aq HCl

Diff: 3

95) Show what reagents are needed to complete the transformation below.

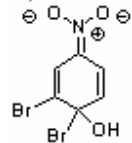


Answer: 1) $\text{Cl}_2 / h\nu$ 2) AlCl_3

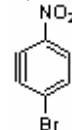
Diff: 3

96) Which of the following is an intermediate when 1,2-dibromo-4-nitrobenzene is heated with NaOH in a nucleophilic aromatic substitution reaction?

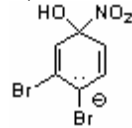
A)



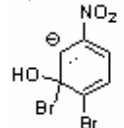
B)



C)



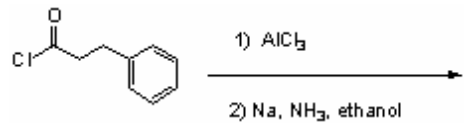
D)



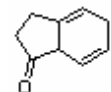
Answer: A

Diff: 3

97) Predict the major organic product resulting from the following sequence of reactions.

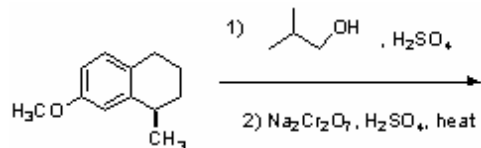


Answer:

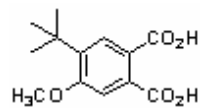


Diff: 3

98) Draw the major organic structure that results from the following sequence of reactions.



Answer:



Diff: 3