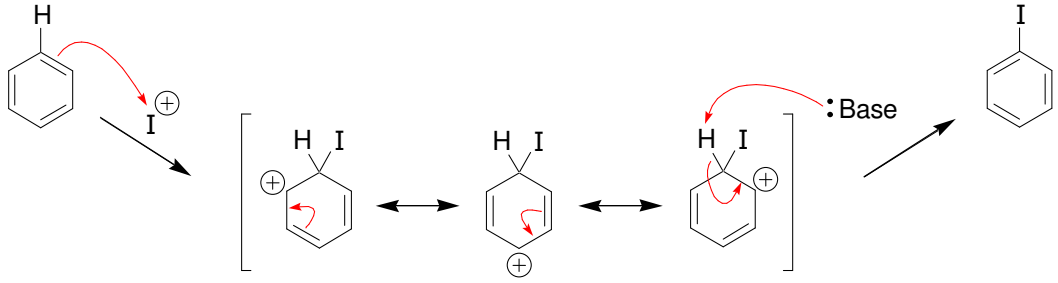
Solutions

19.1.



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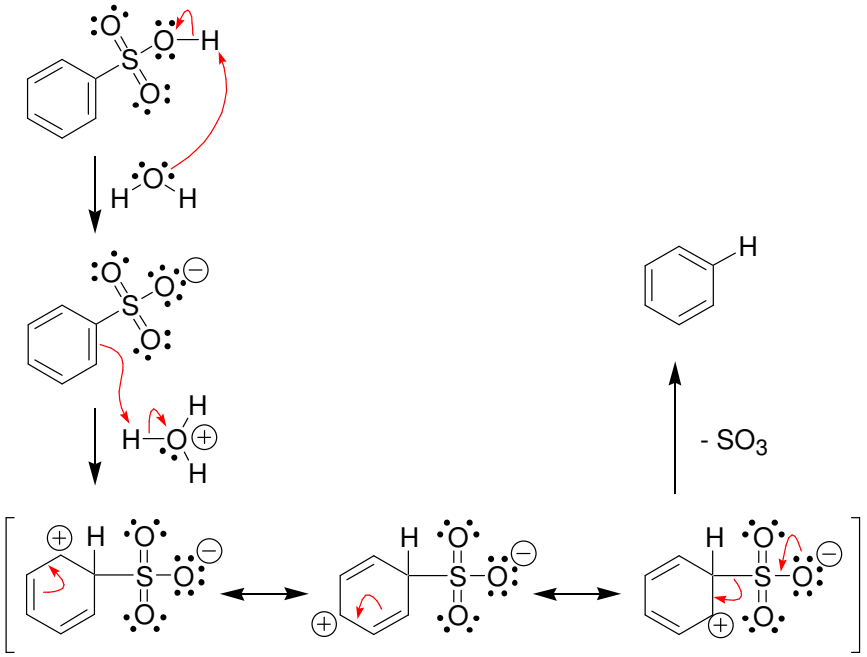

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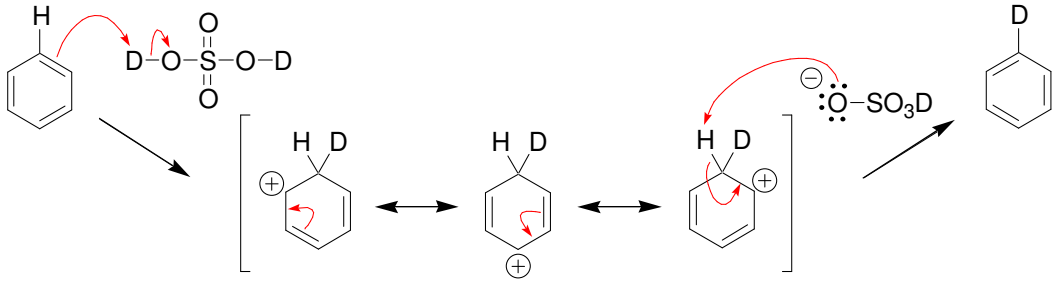

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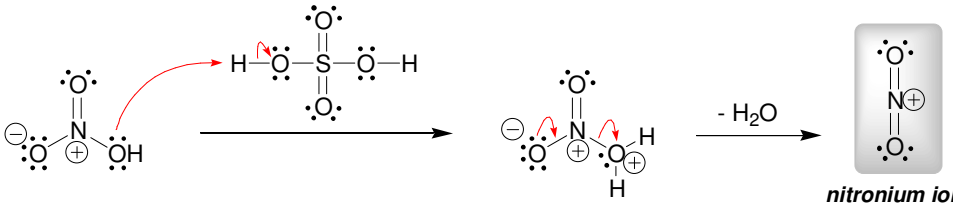
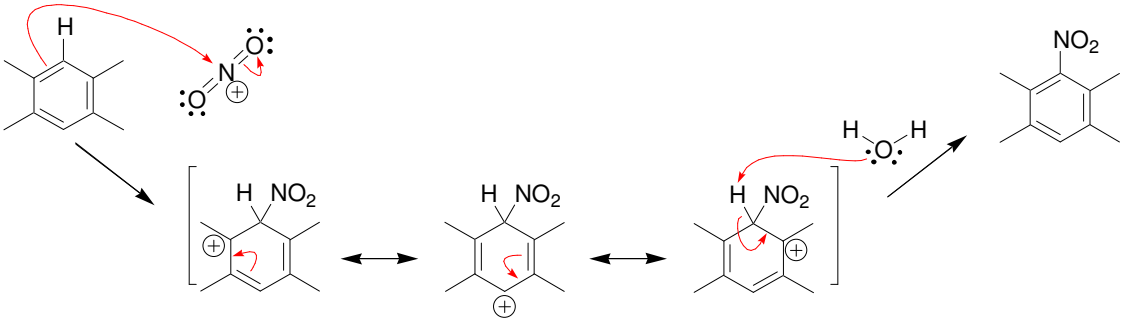
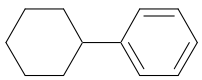
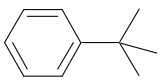
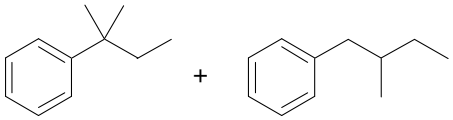




19.5.

a) 

b) 

c) 

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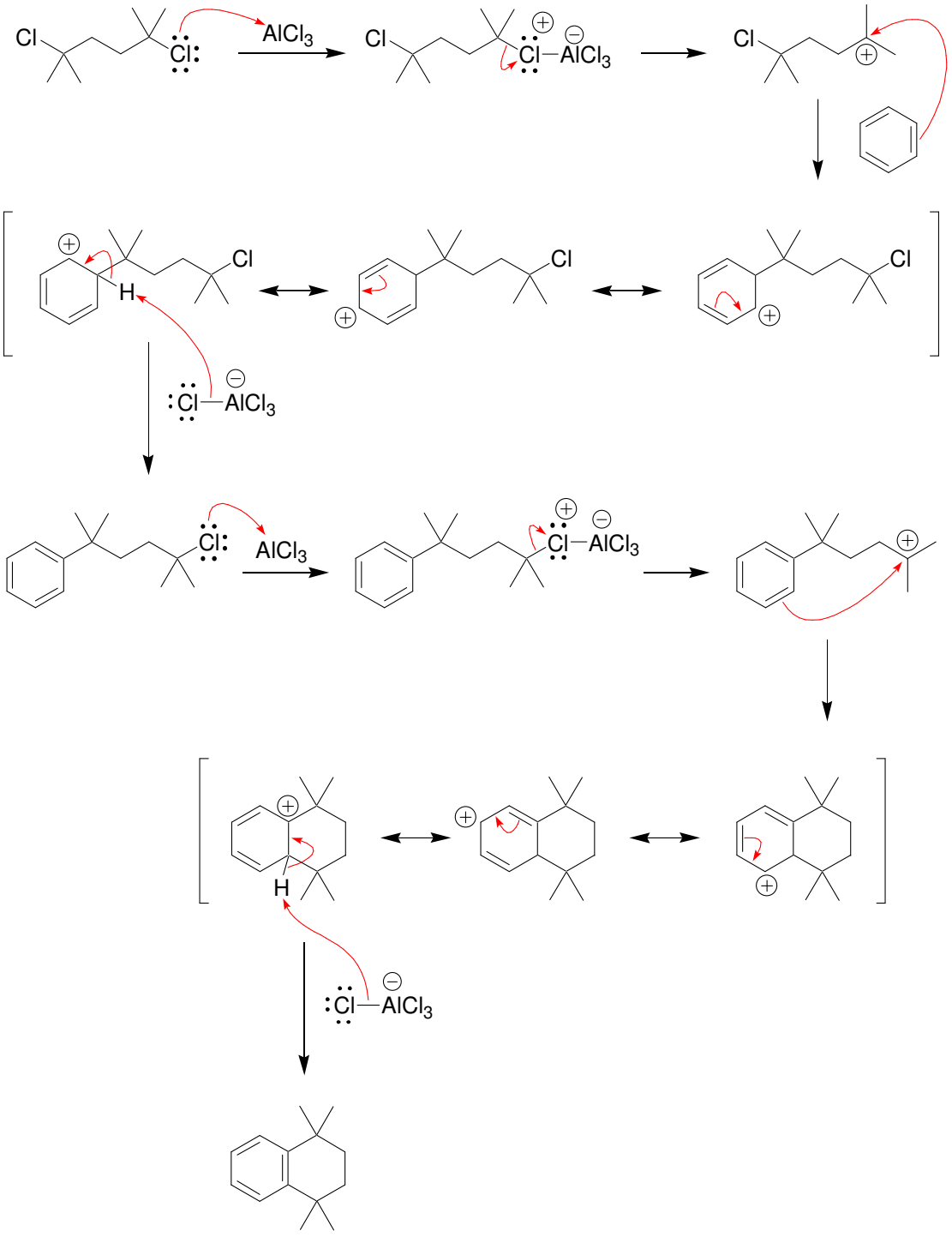
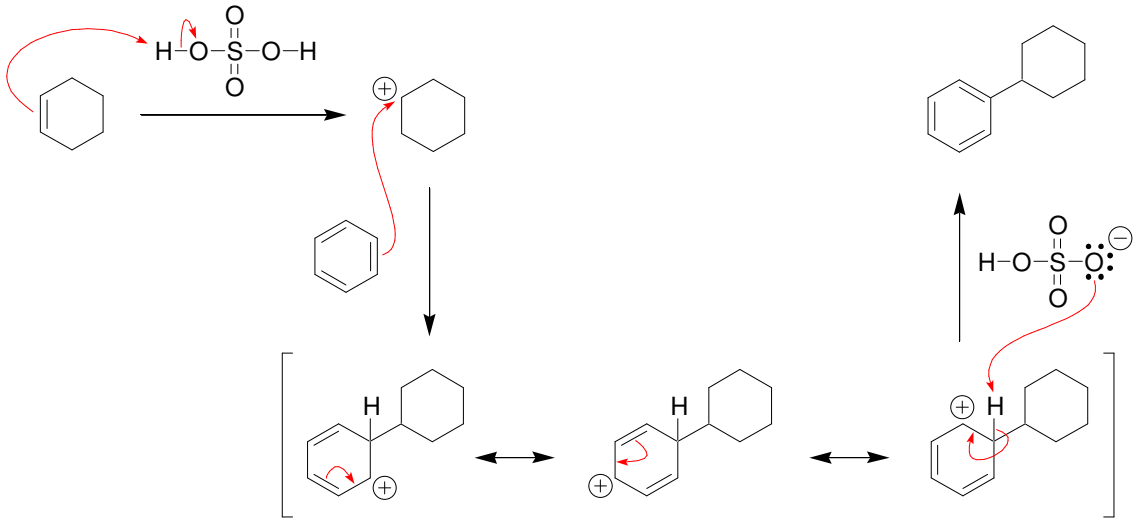

Cl
Cl
AlCl3
Cl
Cl
AlCl3
Cl
Cl
H
Cl
Cl
Cl
AlCl3
Cl
Cl
AlCl3
AlCl3
H
Cl
AlCl3

19.7.



19.8.

a) It is necessary to perform an acylation followed by a Clemmensen reduction to avoid carbocation rearrangements.

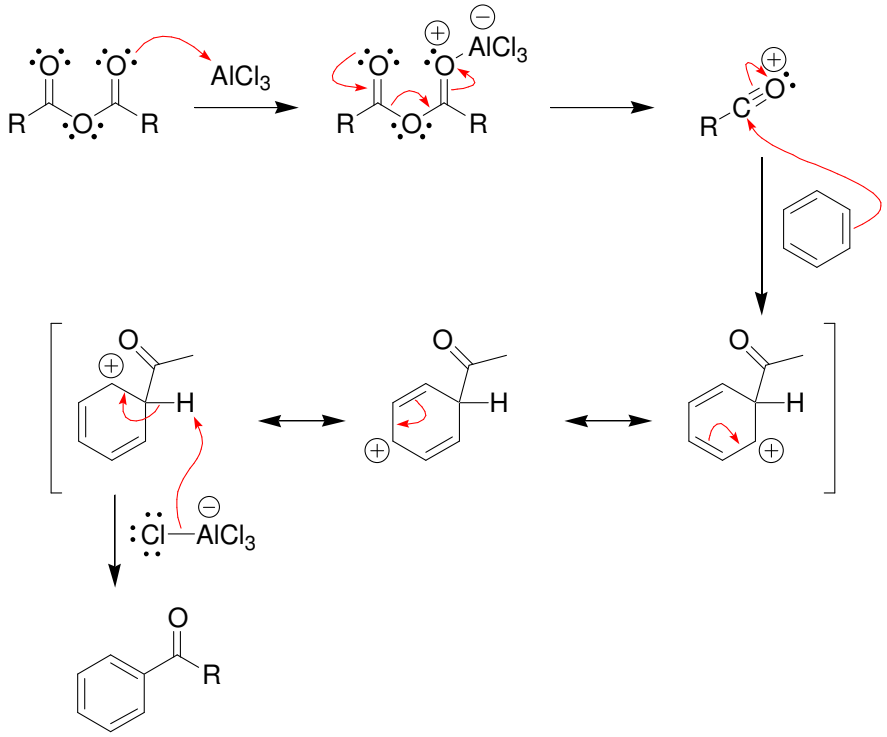
b) It is necessary to perform an acylation followed by a Clemmensen reduction to avoid carbocation rearrangements.

c) It is necessary to perform an acylation followed by a Clemmensen reduction to avoid carbocation rearrangements.

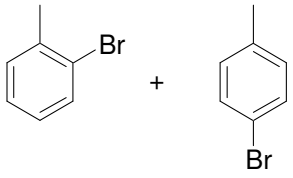
d) The compounds can be made using a direct Friedel–Crafts alkylation.

19.9. It cannot be made via alkylation because the carbocation required would undergo a methyl shift to give a tertiary carbocation. It cannot be made via acylation followed by a Clemmensen reduction, because the product of a Clemmensen reduction has two benzylic protons. This compound has only one benzylic proton, which means that it cannot be made via a Clemmensen reduction.

19.10.

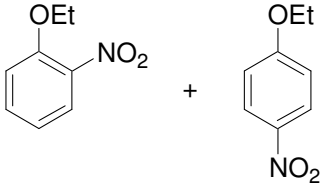


19.11.



19.12.

a)



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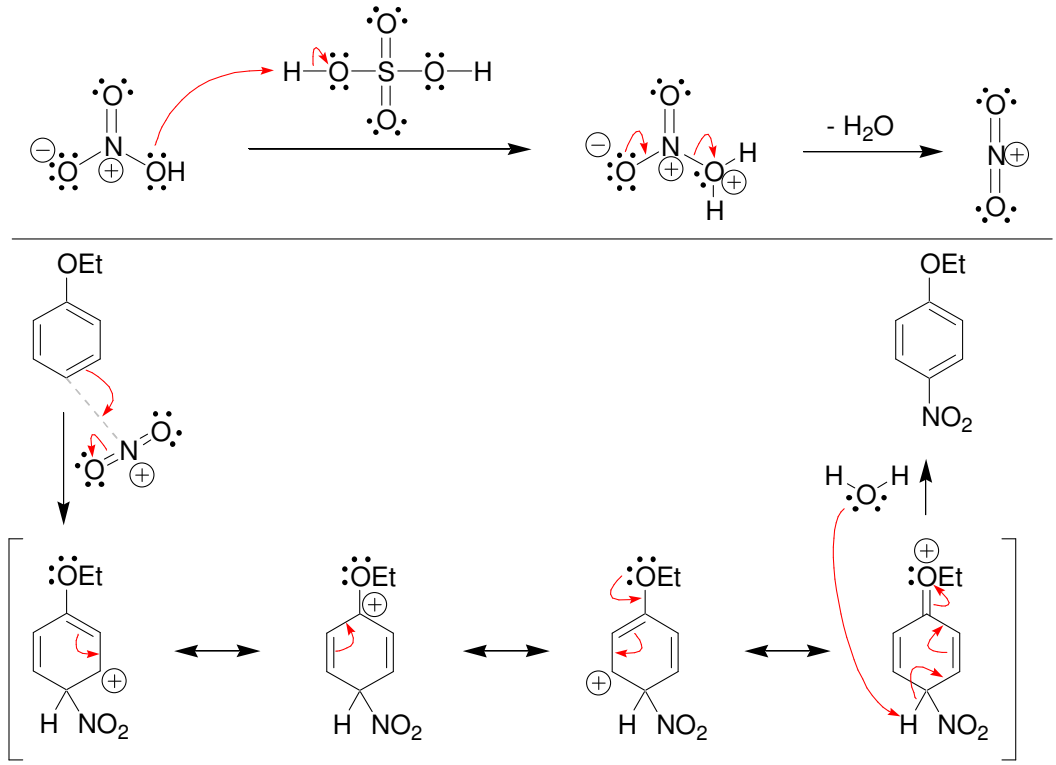
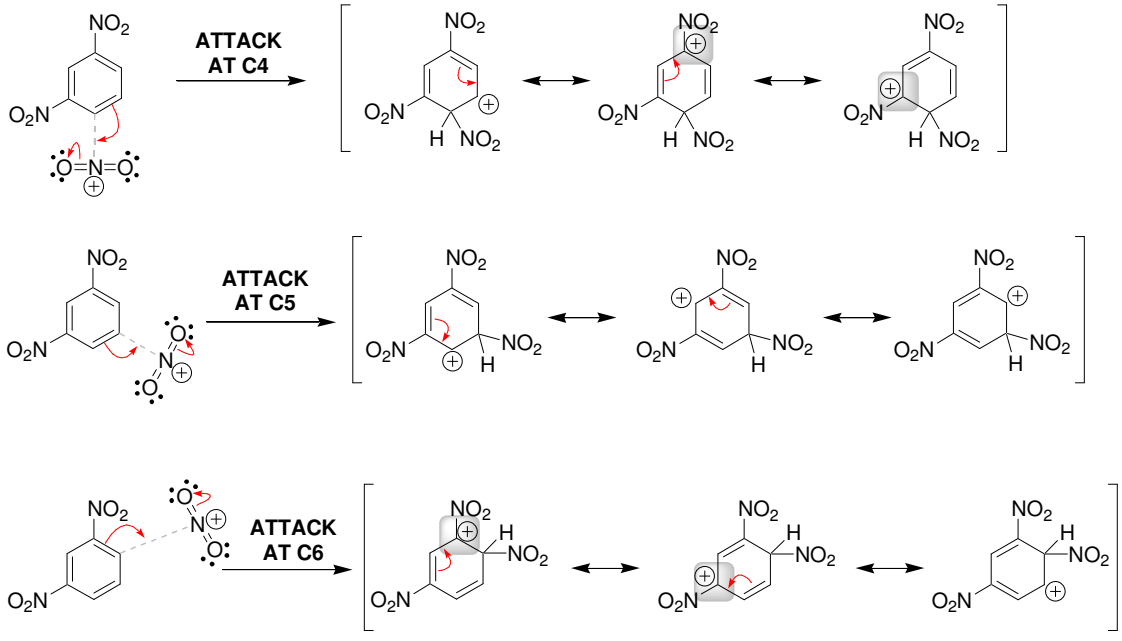
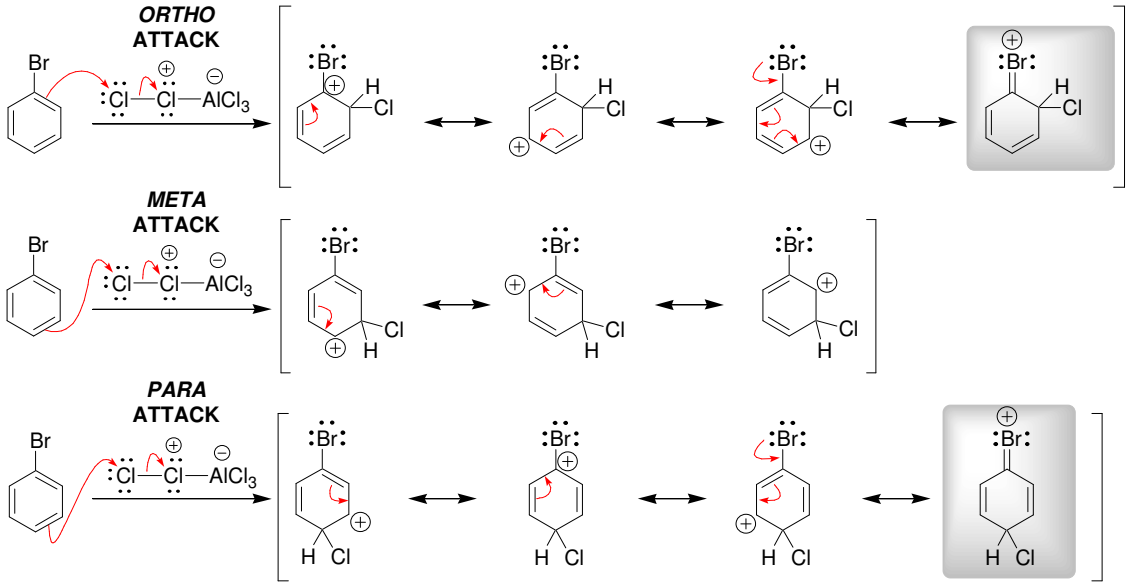


19.13. As show below, attack at C4 or C6 produces a sigma complex in which two of the resonance structures have a positive charge next to an electron-withdrawing group (NO_2). These resonance structures are less contributing to the resonance hybrid, thereby destabilizing the sigma complex. In contrast, attack at C5 produces a sigma complex for which none of the resonance structures have a positive charge next to a nitro group.



19.14. The chlorine atom in chlorobenzene deactivates the ring relative to benzene. If benzene requires a Lewis acid for chlorination, than chlorobenzene should certainly require a Lewis acid for chlorination.

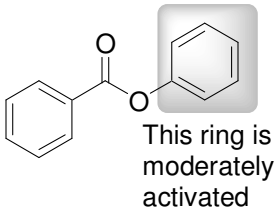
19.15. *Ortho* attack and *para* attack are preferred because each of these pathways involves a sigma complex with four resonance structures (shown below). Attack at the *meta* position involves formation of a sigma complex with only three resonance structures, which is not as stable as a sigma complex with four resonance structures. The reaction will proceed more rapidly via the lower energy sigma complex, so attack takes place at the *ortho* and *para* positions in preference to the *meta* position.



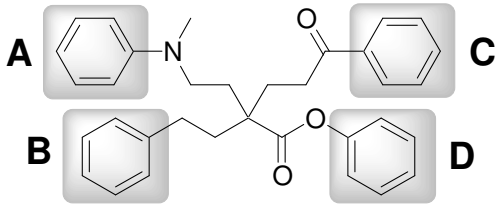
19.16.

a) The nitro is strongly deactivating and *meta*-directing.
b) An acyl group is moderately deactivating and *meta*-directing.
c) A bromine atom weakly deactivating and *ortho, para*-directing.
d) This group is moderately deactivating and *meta*-directing.
e) This group is moderately deactivating and *meta*-directing.
f) This group is moderately activating and *ortho, para* -directing.

19.17.



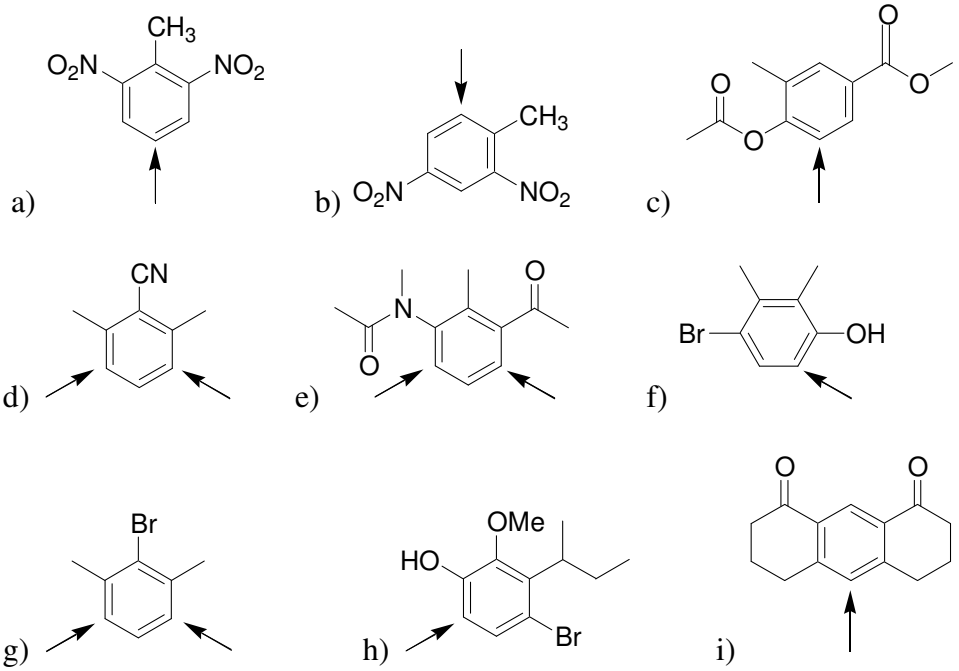
19.18.



Increasing reactivity toward electrophilic aromatic substitution

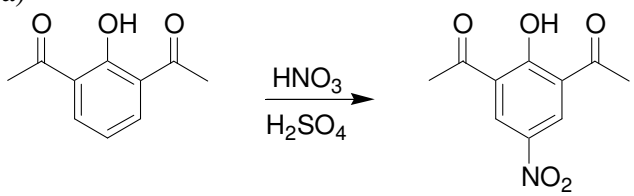
C B D A

19.19.

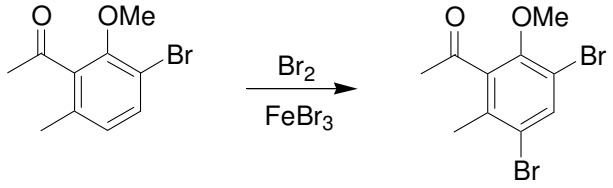


19.20.

a)



b)



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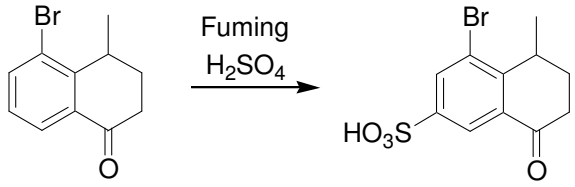
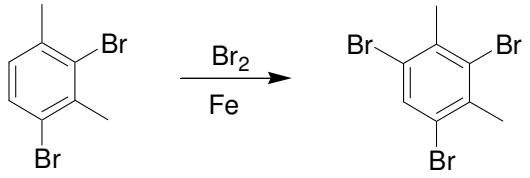


19.21.



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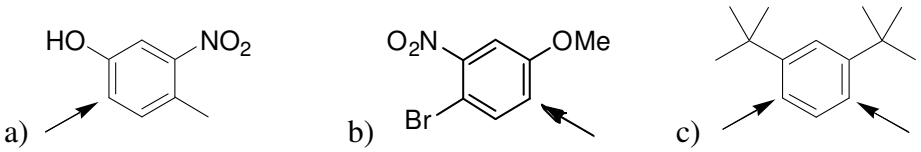
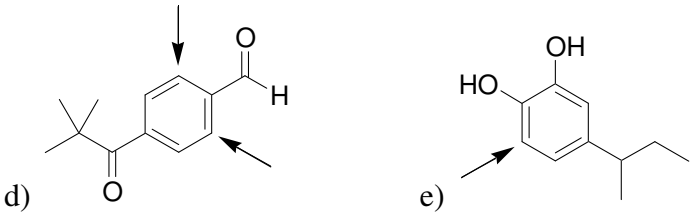
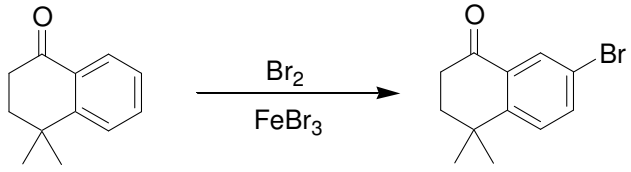




19.23. All three available positions are sterically hindered.

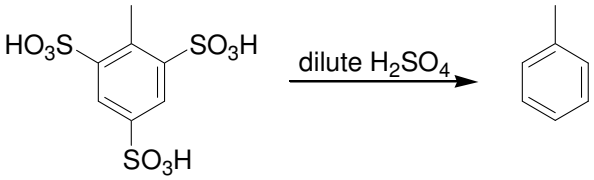
19.24.



19.25.

a) Yes b) No c) Yes d) No

19.26.



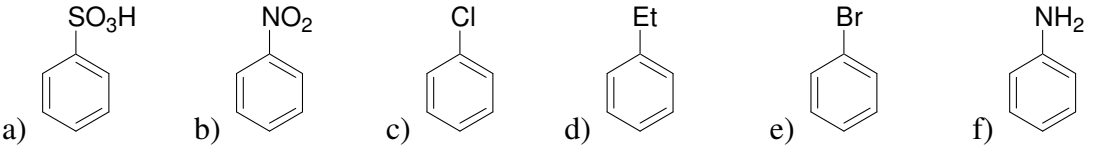
19.27.

a) The nitro group must be installed in a position that is *meta* to each of the OH groups. Even with a blocking group, *meta* attack cannot be achieved on a highly activated ring.
b) The position that must undergo bromination is too sterically hindered because of the presence of the *tert*-butyl groups.

19.28.

a) Cl_2, $AlCl_3$
b) HNO_3, H_2SO_4
c) Br_2, $FeBr_3$
d) CH_3CH_2Cl, $AlCl_3$
e) CH_3CH_2COCl, followed by HCl, Zn[Hg], heat
f) $(CH_3)_2CHCl$, $AlCl_3$
g) HNO_3, H_2SO_4, followed by followed by HCl, Zn
h) CH_3Cl, $AlCl_3$, followed by $KMnO_4$, NaOH, heat, followed by H_3O^+
i) CH_3Cl, $AlCl_3$

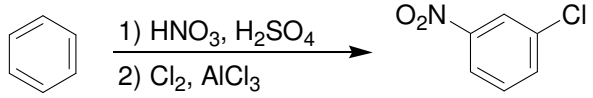
19.29.



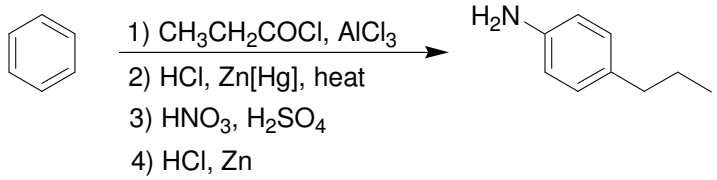
19.30.

a)

b)



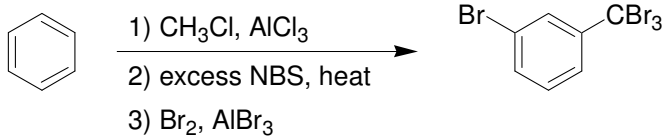
c)


1) CH_3CH_2COCl, $AlCl_3$
2) HCl, Zn[Hg], heat
3) HNO_3, H_2SO_4
4) HCl, Zn
H_2N

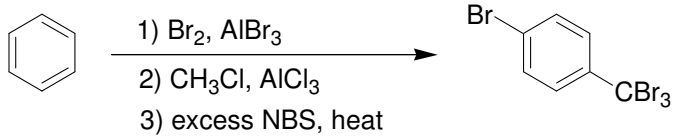
d)


1) HNO_3, H_2SO_4
2) Cl_2, $AlCl_3$
3) HCl, Zn
NH_2
Cl

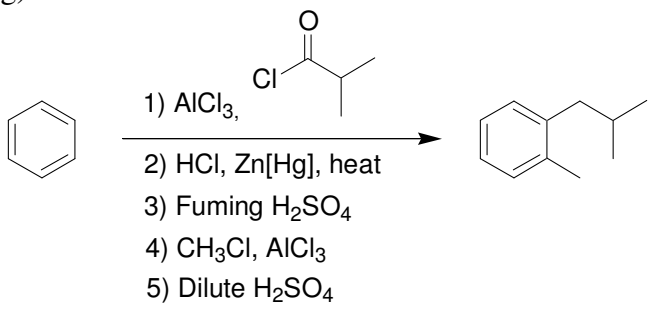
e)


1) CH_3Cl, $AlCl_3$
2) excess NBS, heat
3) Br_2, $AlBr_3$
Br
CBr_3

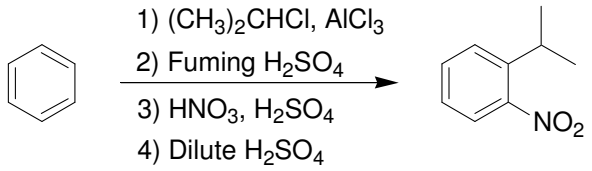
f)


1) Br_2, $AlBr_3$
2) CH_3Cl, $AlCl_3$
3) excess NBS, heat
Br
CBr_3

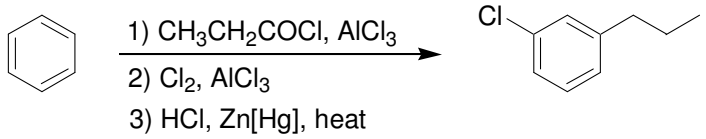
g)


1) $AlCl_3$,
O
Cl
2) HCl, Zn[Hg], heat
3) Fuming H_2SO_4
4) CH_3Cl, $AlCl_3$
5) Dilute H_2SO_4

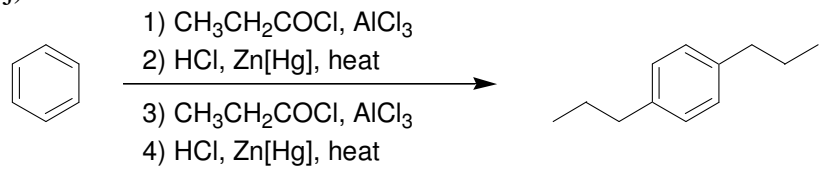
h)


1) $(CH_3)_2CHCl$, $AlCl_3$
2) Fuming H_2SO_4
3) HNO_3, H_2SO_4
4) Dilute H_2SO_4
NO_2

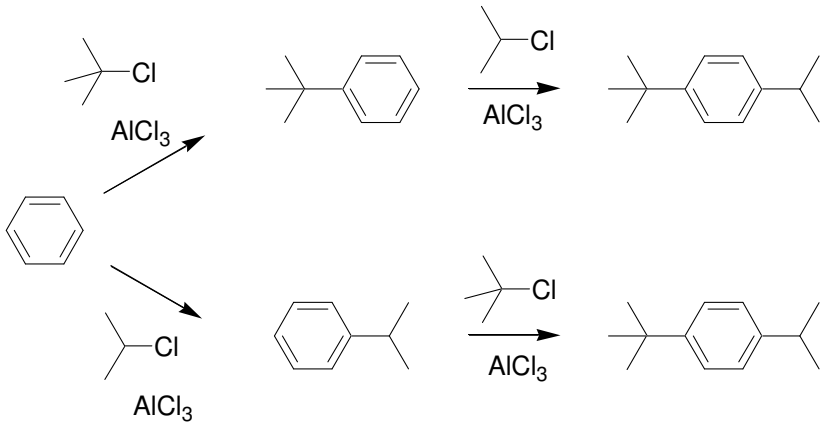
i)



j)



19.31. The *para* product will be more strongly favored over the *ortho* product if the *tert*-butyl group is installed first. The steric hindrance provided by a *tert*-butyl group is greater than the steric hindrance provided by an isopropyl group. Of the following two possible pathways, the first should provide a greater yield of the desired product.



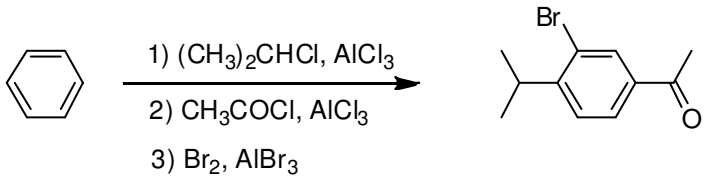
19.32.

a) Nitration cannot be achieved effectively in the presence of an amino group.

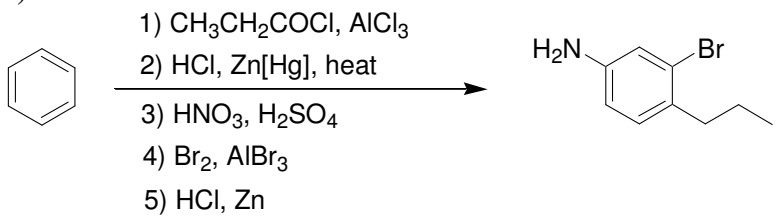
b) Each of the two alkyl groups is *ortho-para* directing, but the two groups are *meta* to each other. A Friedel-Crafts acylation will not work in this case (see solution to problem 19.9)

19.33.

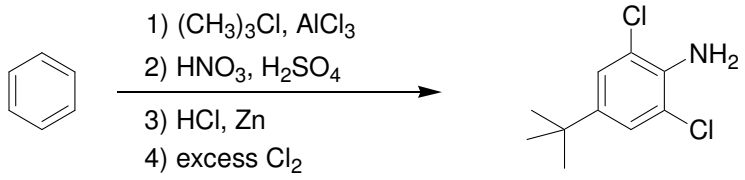
a)



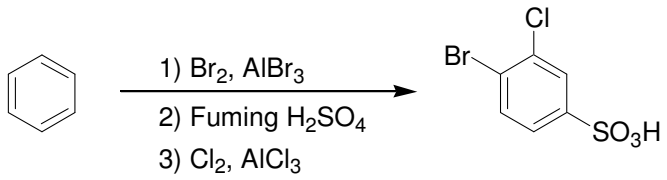
b)



c)



d)



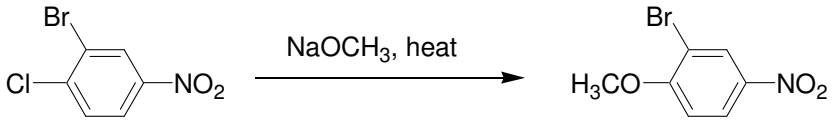
19.34.

a)

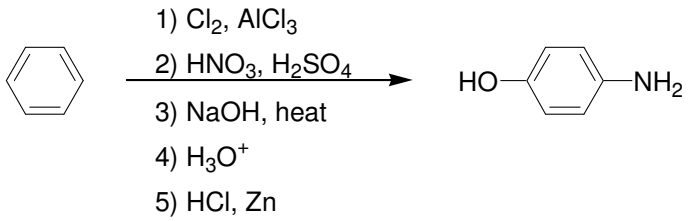
b) The sixth position is sterically hindered by the presence of the Cl atoms.

c) The ring is deactivated because all five groups are deactivators.

19.35.



19.36.

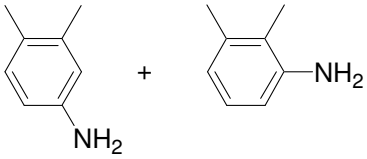


19.37.

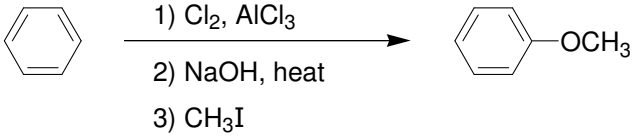
a) Each additional nitro group serves as a reservoir of electron density and provides for an additional resonance structure in the sigma complex, thereby stabilizing the sigma complex and lowering the energy of activation for the reaction.

b) No, a fourth nitro group would not be *ortho* or *para* to the leaving group, and therefore cannot function as a reservoir.

19.38.

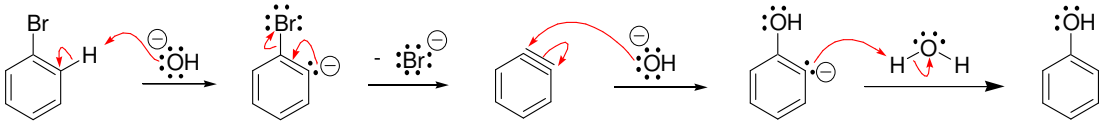


19.39.

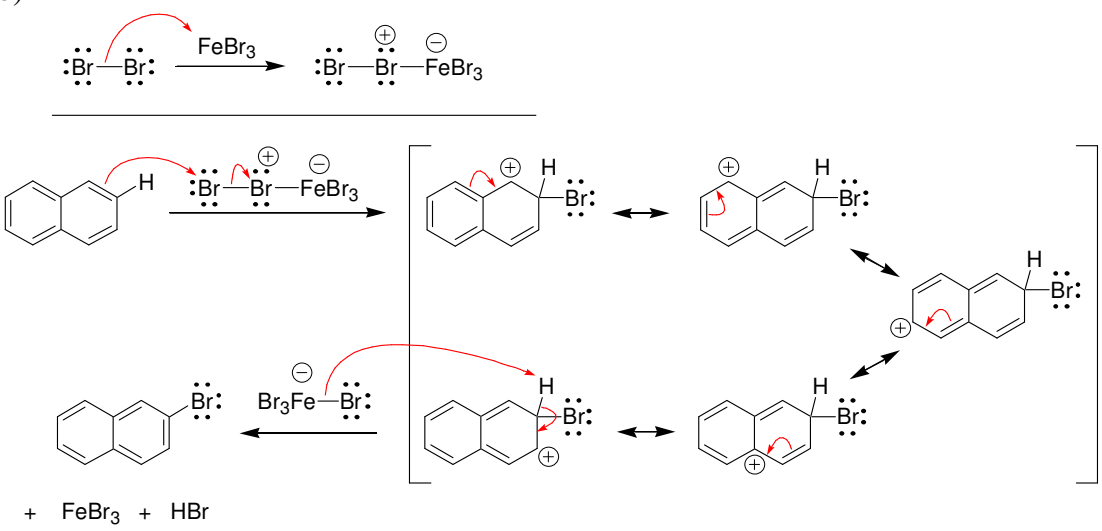


19.40.

a)



b)



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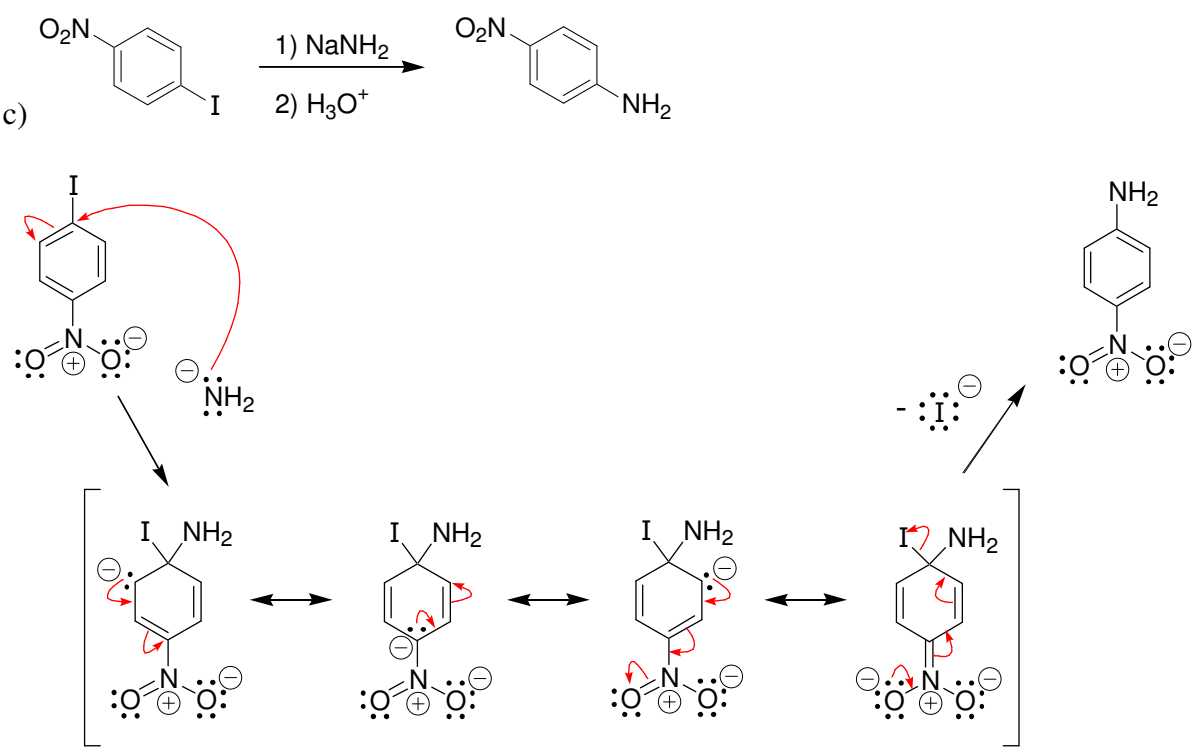
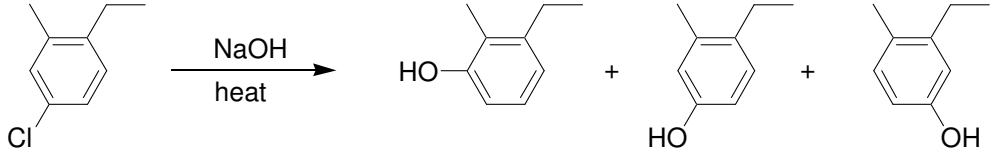
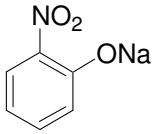


19.41.

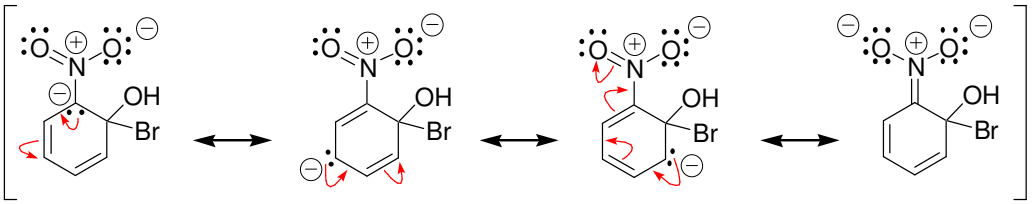


19.42.

a)



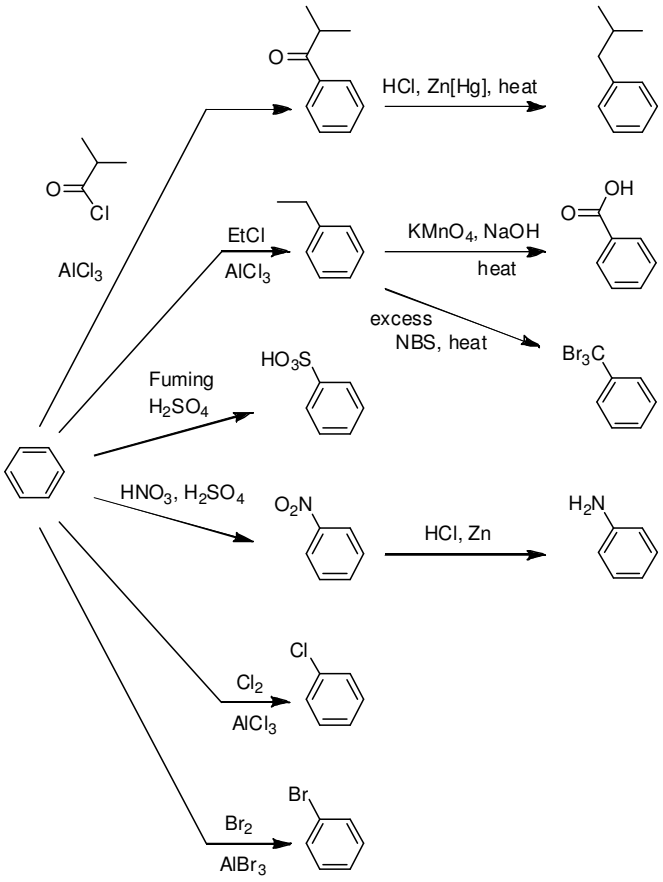
b)



c) No

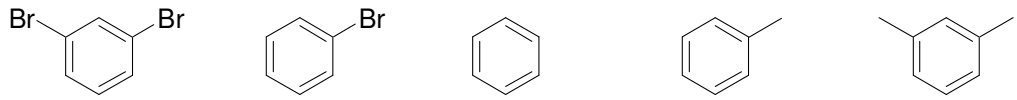
d) Yes

19.43.

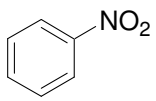


19.44.

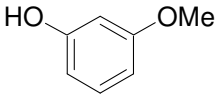
Increasing Reactivity toward Electrophilic Aromatic Substitution



19.45.



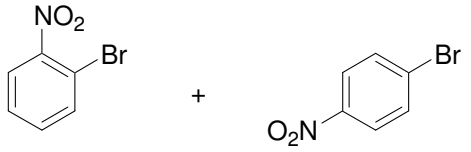
least activated



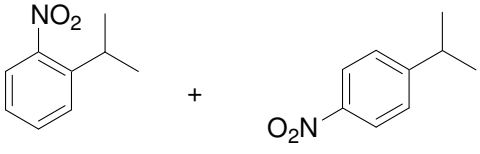
most activated

19.46.

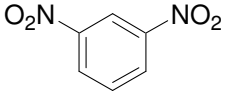
a)



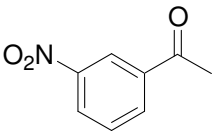
b)



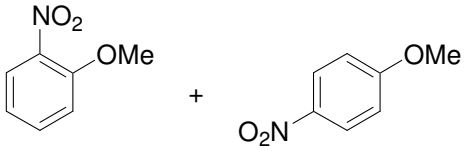
c)



d)

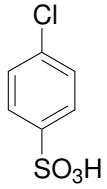


e)

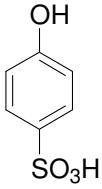


19.47.

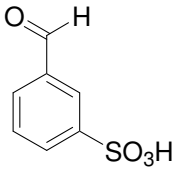
a)



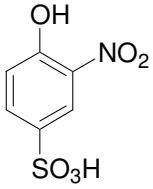
b)



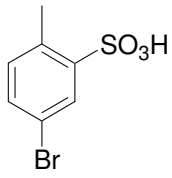
c)



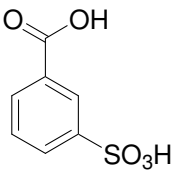
d)



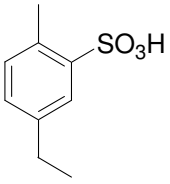
e)



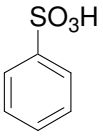
f)



g)



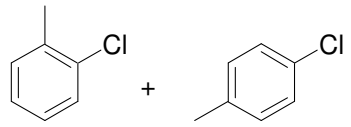
h)



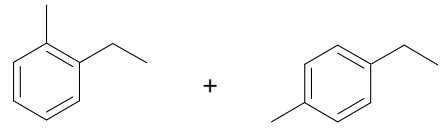
19.48.

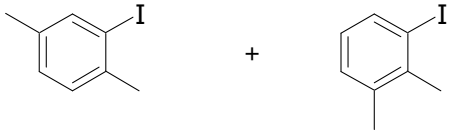
a) This group is an activator and an *ortho*,*para*-director.
b) This group is an activator and an *ortho*,*para*-director.
c) This group is an activator and an *ortho*,*para*-director.
d) This group is a deactivator and an *ortho*,*para*-director.
e) This group is a deactivator and a *meta*-director.
f) This group is a deactivator and a *meta*-director.
g) This group is a deactivator and a *meta*-director.
h) This group is a deactivator and a *meta*-director.
i) This group is a deactivator and an *ortho*,*para*-director.
j) This group is a deactivator and a *meta*-director.

19.49.

a) 

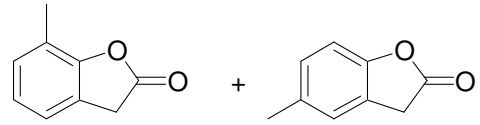
b) unreactive c) unreactive

d) 

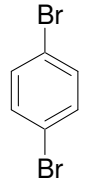
e) 

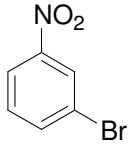
f) 

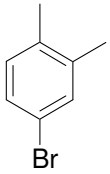
g) unreactive

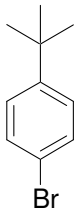
h) 

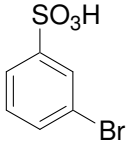
19.50.

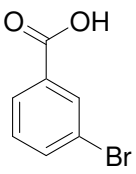
a) 

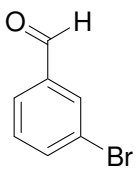
b) 

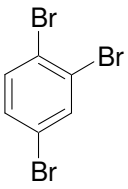
c) 

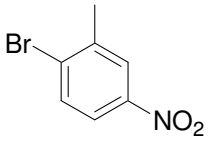
d) 

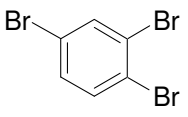
e) 

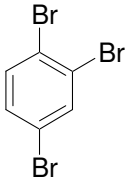
f) 

g) 

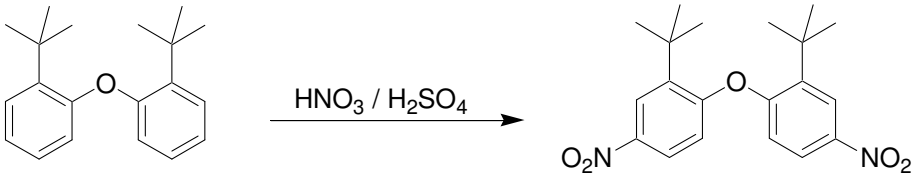
h) 

i) 

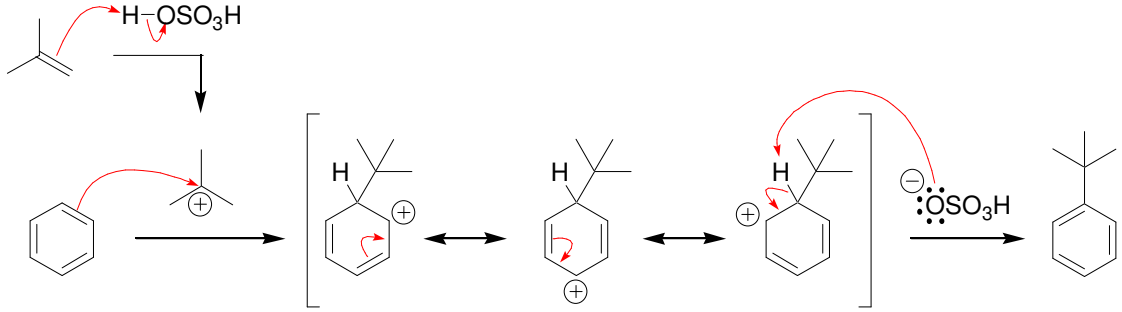
j) 

k) 

19.51.

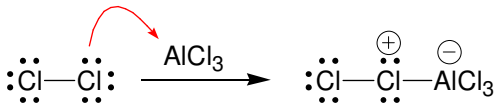


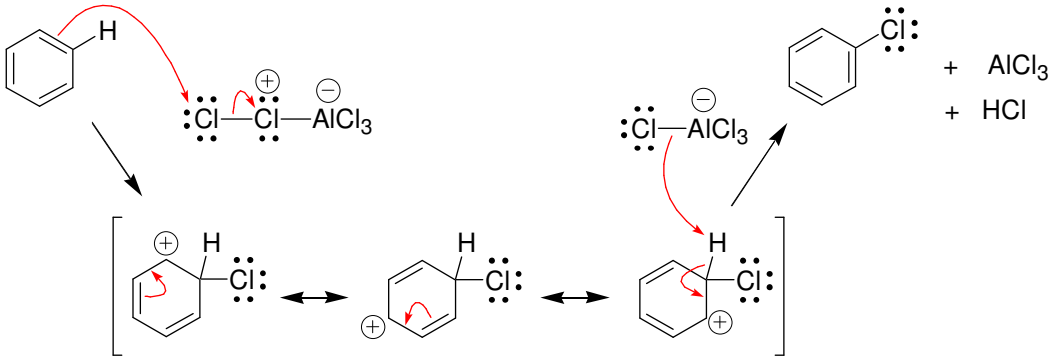
19.52.



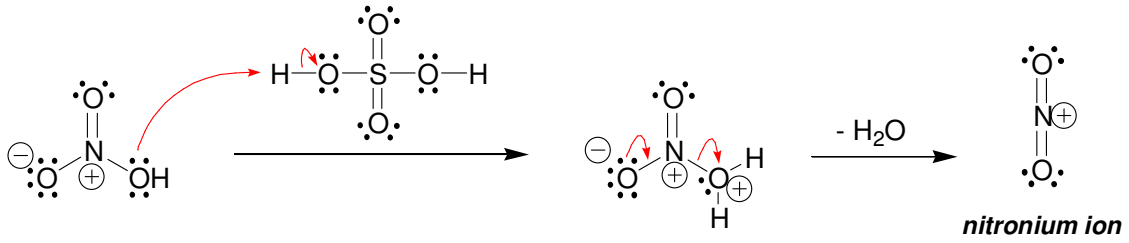
19.53.

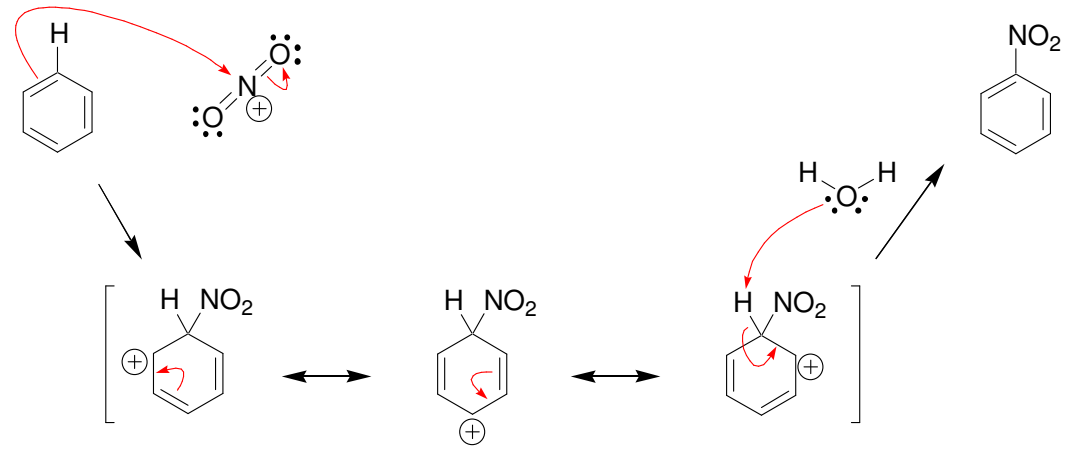
a)



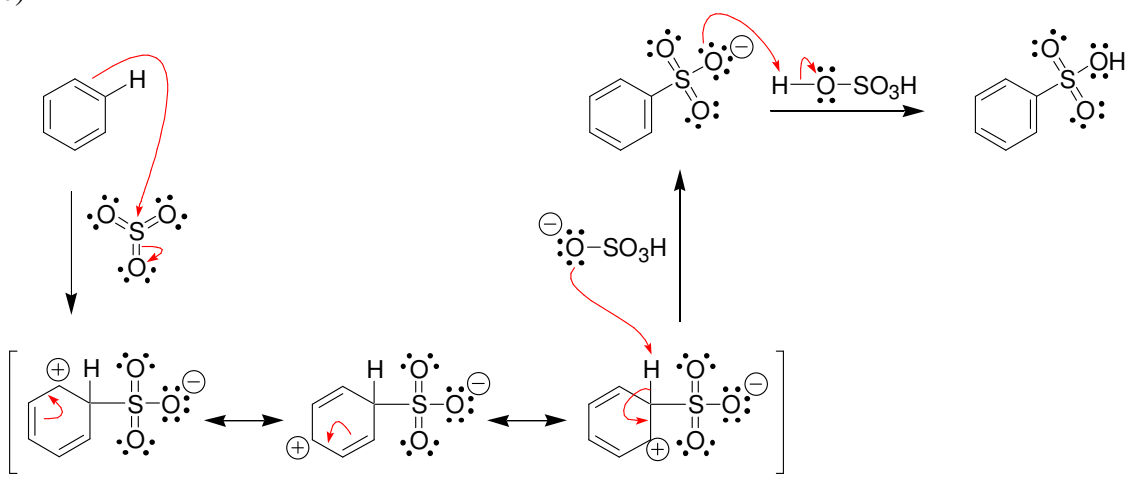


b)

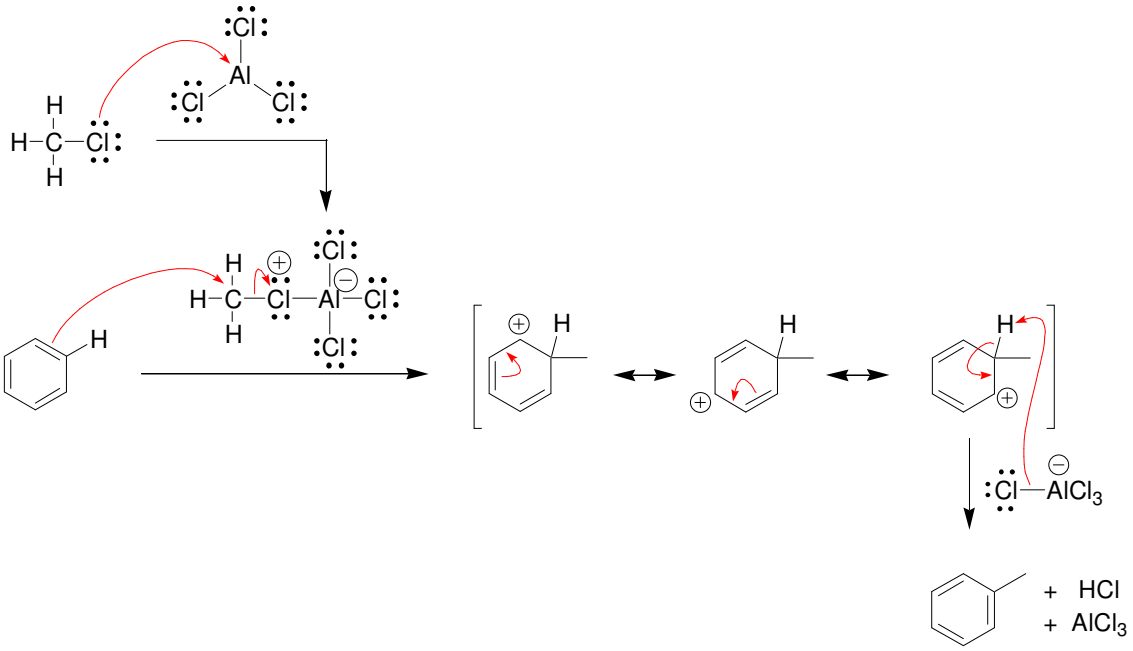




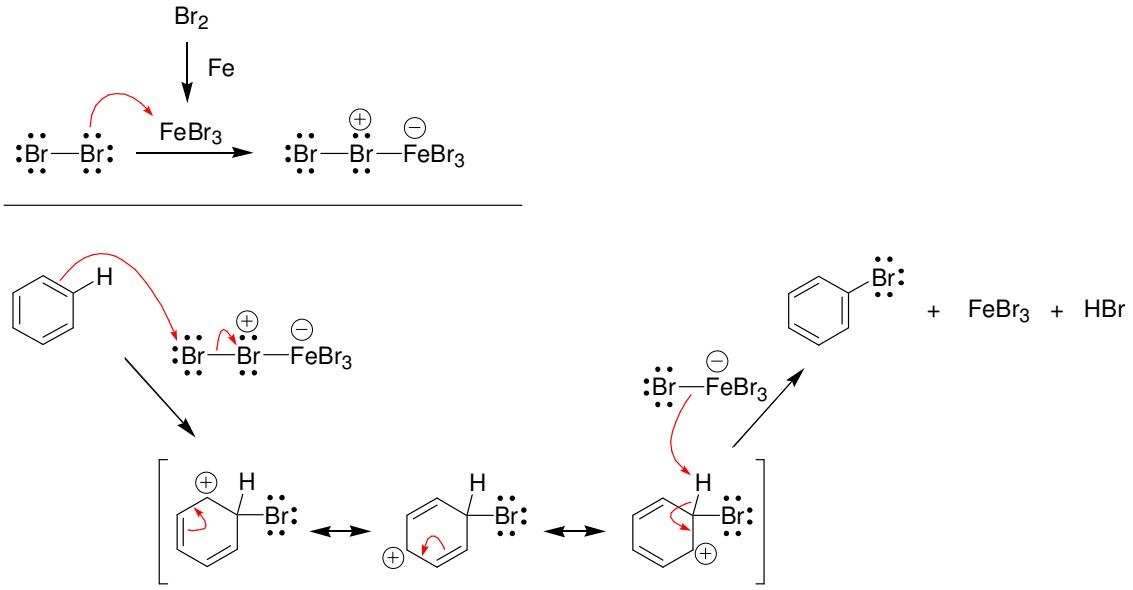
c)



d)

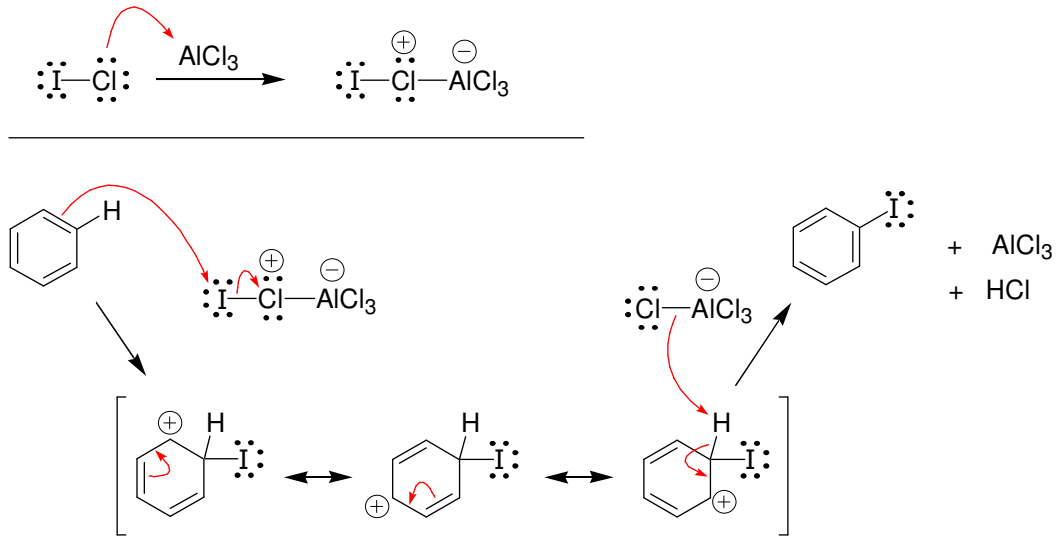

Cl
Al
Cl
Cl
H
H—C—Cl
H
H
H—C—Cl—Al—Cl
H
Cl
Cl
H
H
H
Cl—AlCl3
+ HCl
+ AlCl3

e)

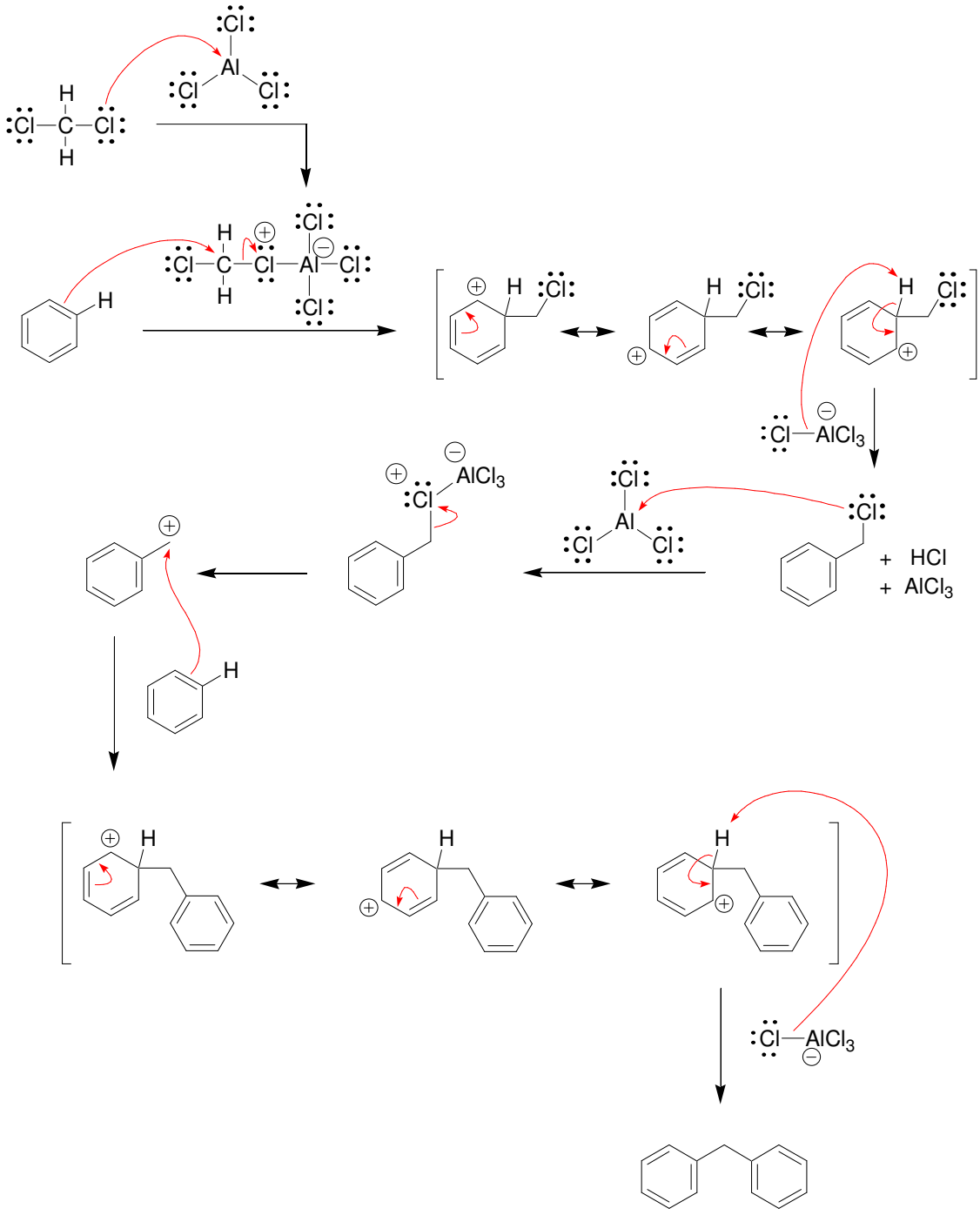

Br2
Fe
FeBr3
Br—Br
Br—Br—FeBr3
H
Br—Br—FeBr3
Br
+ FeBr3 + HBr
Br—FeBr3
H
Br
H
Br
H
Br

19.54.

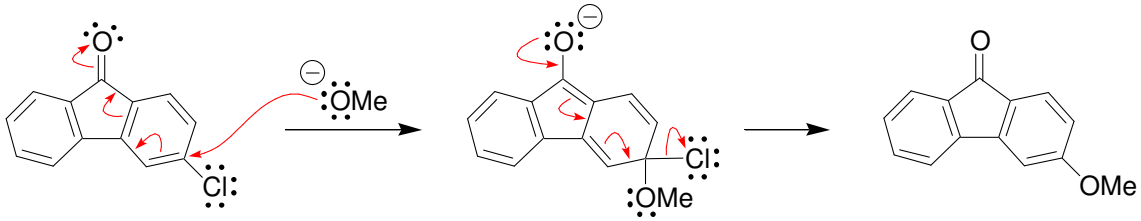
a)



b)

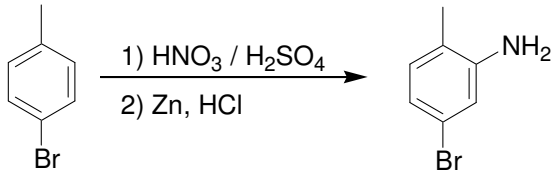

Cl
Al
Cl
Cl
H
C
Cl
H
H
Cl
Al
Cl
Cl
Cl
H
H
Cl
Cl
AlCl3
AlCl3
Cl
Al
Cl
Cl
+ HCl
+ AlCl3
H
H
H
H
Cl
AlCl3

19.55.

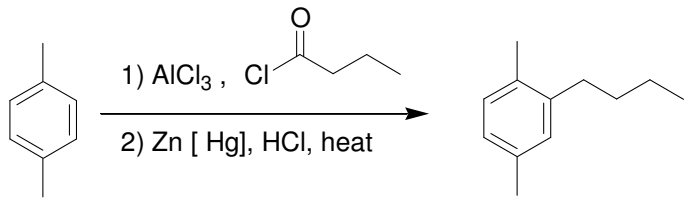


19.56.

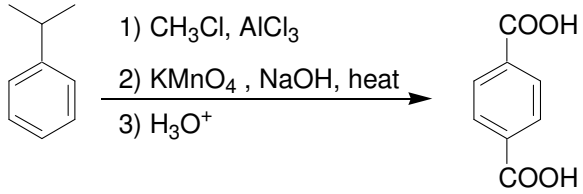
a)



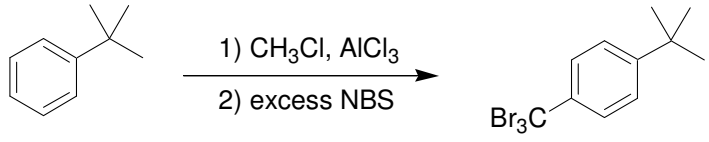
b)



c)

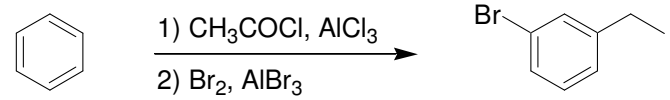


d)

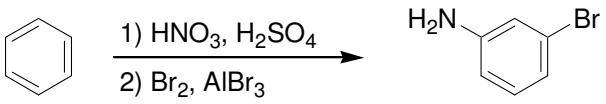


19.57.

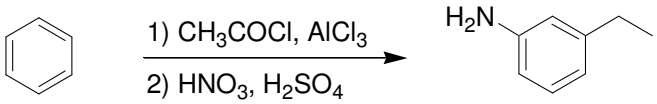
a)



b)



c)



19.58.

a) The second step of the synthesis will not work, because a strongly deactivated ring will not undergo a Friedel-Crafts alkylation. The product of the first step, nitrobenzene, will be unreactive in the second step.

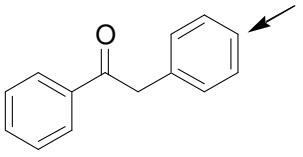
b) The second step of the synthesis will not efficiently install a propyl group, because a carbocation rearrangement can occur, which will result in the installation of an isopropyl group.

c) The second step of the synthesis will not install the acyl group in the *meta* position. It will be installed in a position that is either *ortho* or *para* to the bromine atom.

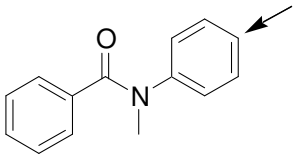
d) The second step of the synthesis will not install the bromine atom in the *ortho* position, because of steric hindrance from the *tert*-butyl group. Bromination will occur primarily at the *para* position.

19.59.

a)



b)



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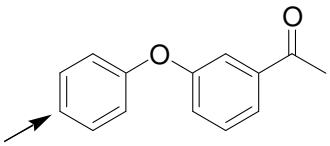
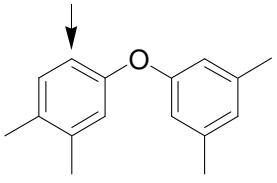
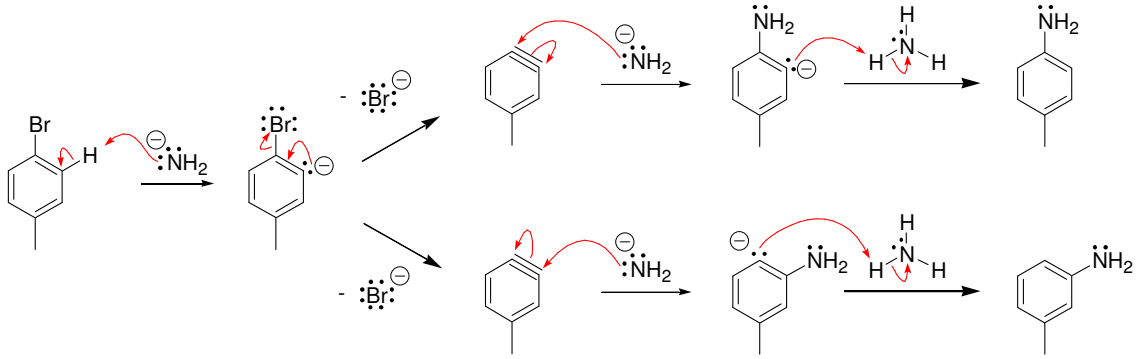


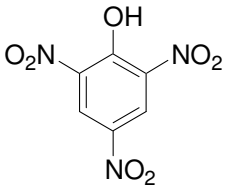
d)



19.60.

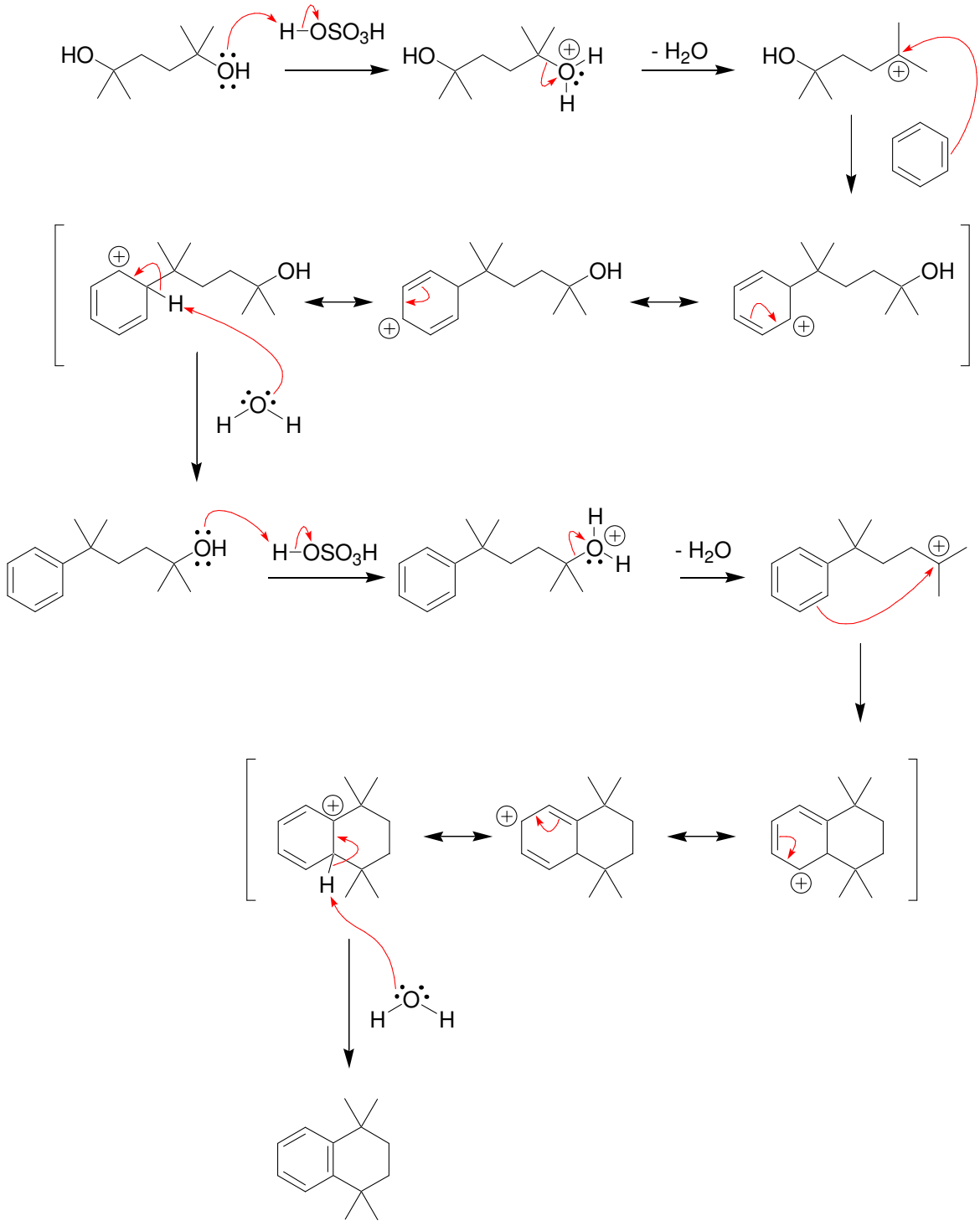


19.61.



2,4,6-trinitrophenol
(picric acid)

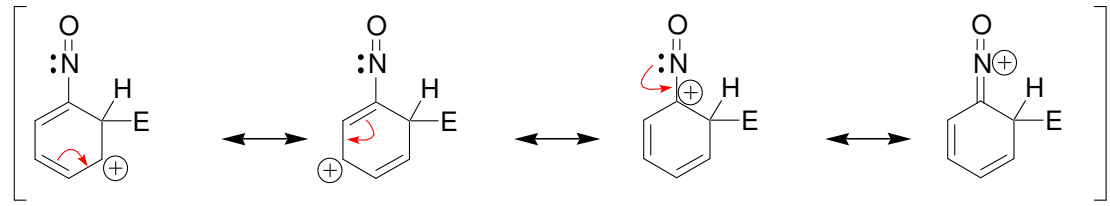
19.62.



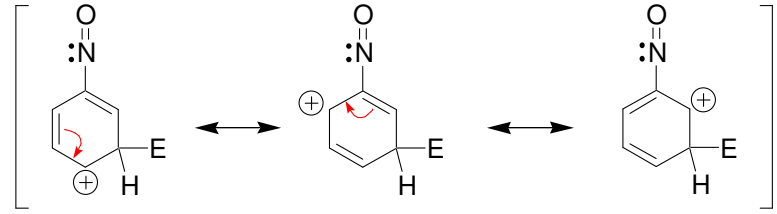
19.63.

19.64.

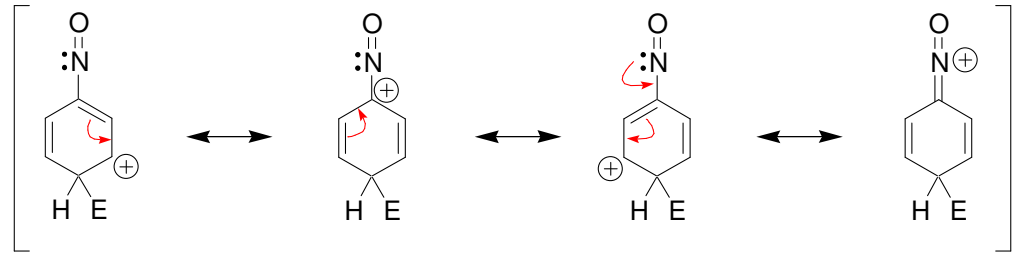
a)



b)



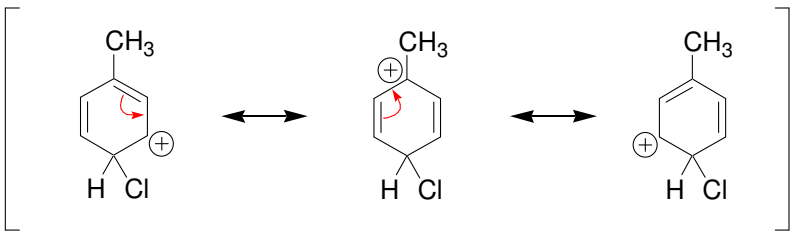
c)



d) The nitroso group should be *ortho-para* directing, because attack at the *ortho* or *para* position generates a sigma complex with an additional resonance structure.

e) The nitroso group is a deactivator, yet it is an *ortho-para* director, just like a chlorine atom.

19.65.

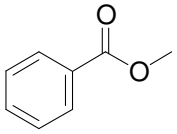


19.66.

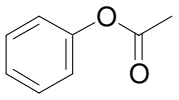
a) Toluene is the only compound containing an activated ring, and it is expected to undergo a Friedel-Crafts reaction most rapidly to give *ortho*-ethyltoluene and *para*-ethyltoluene.

b) Anisole is the most activated compound (among the three compounds), and is expected to undergo a Friedel-Crafts reaction most rapidly to give *ortho*-ethylanisole and *para*-ethylanisole.

19.67.



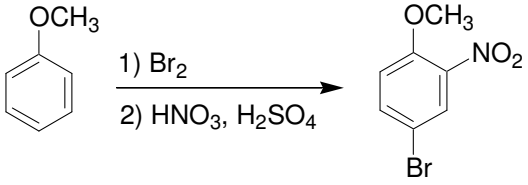
Compound A



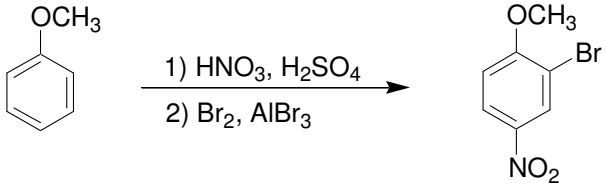
Compound B

19.68.

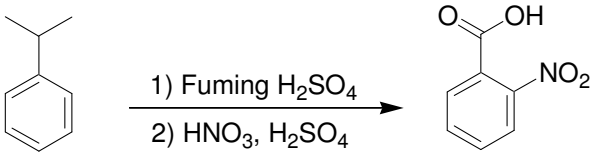
a)



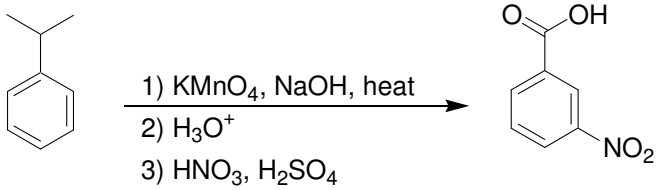
b)



c)

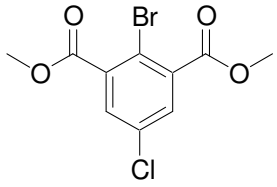


d)



19.69.

a)



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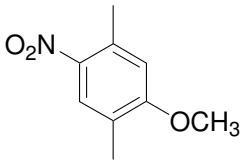
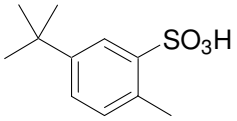
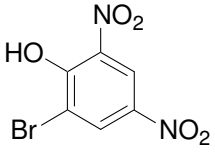


c)

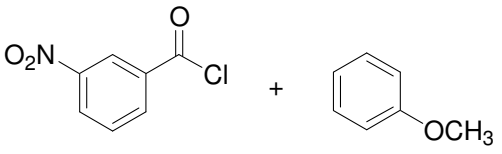


d)

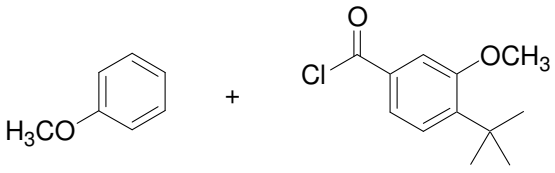


19.70.

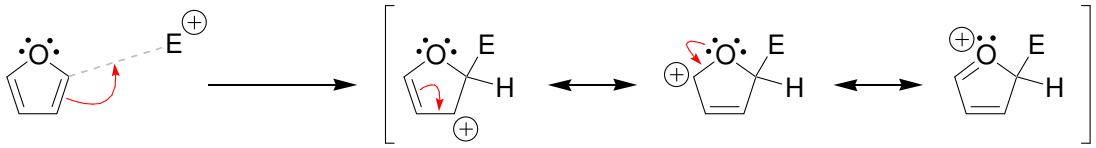
a)



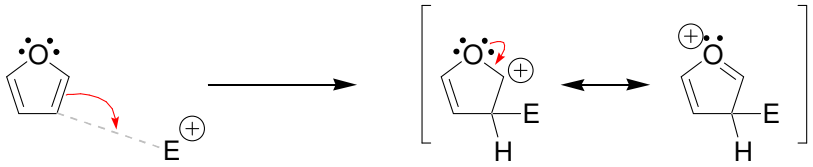
b)



19.71. Attack at the C2 position proceeds via an intermediate with three resonance structures:



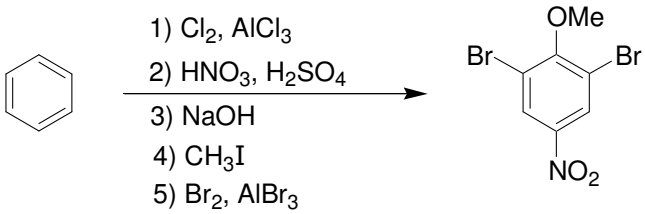
In contrast, attack at the C3 position proceeds via an intermediate with only two resonance structures:



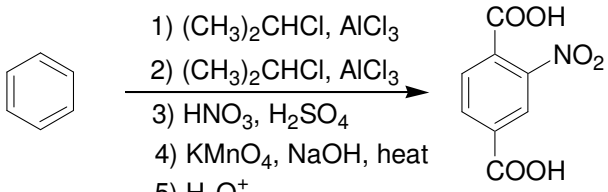
The intermediate for C2 attack is lower in energy than the intermediate for C3 attack. The transition state leading to the intermediate of C2 attack will therefore be lower in energy than the transition state leading to the intermediate of C3 attack. As a result, C2 attack occurs more rapidly.

19.72.

a)

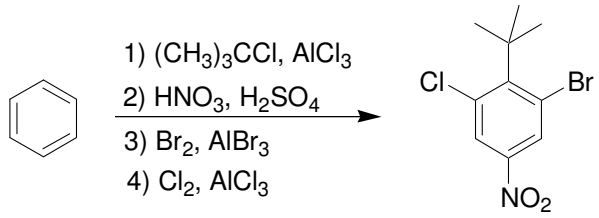


b)



c)

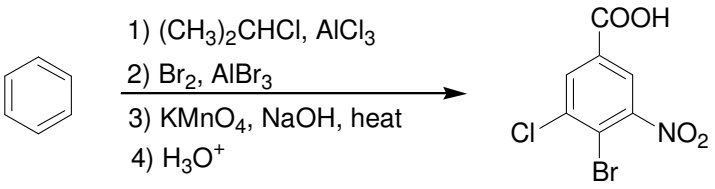
d)


1) $(CH_3)_3CCl$, $AlCl_3$
2) HNO_3, H_2SO_4
3) Br_2, $AlBr_3$
4) Cl_2, $AlCl_3$
Cl
Br
NO_2

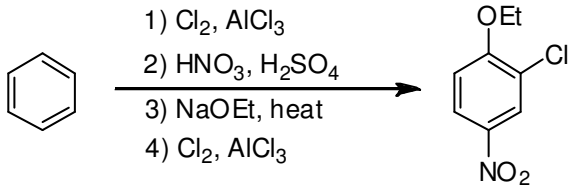
e)


1) CH_3CH_2COCl, $AlCl_3$
2) HNO_3, H_2SO_4
3) Cl_2, $AlCl_3$
O
NO_2
Cl

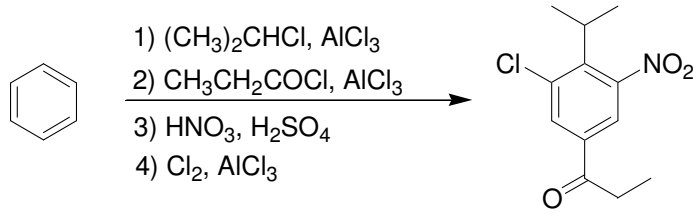
f)


1) $(CH_3)_2CHCl$, $AlCl_3$
2) Br_2, $AlBr_3$
3) $KMnO_4$, NaOH, heat
4) H_3O^+
4) HNO_3, H_2SO_4
5) Cl_2, $AlCl_3$
COOH
Cl
NO_2
Br

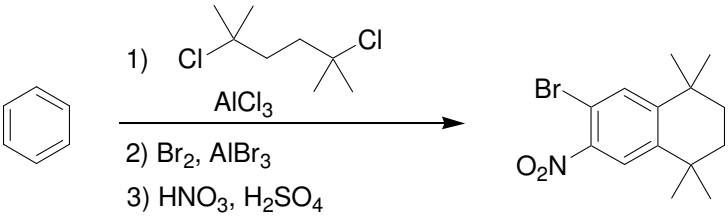
g)


1) Cl_2, $AlCl_3$
2) HNO_3, H_2SO_4
3) NaOEt, heat
4) Cl_2, $AlCl_3$
OEt
Cl
NO_2

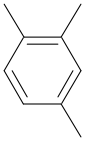
h)


1) $(CH_3)_2CHCl$, $AlCl_3$
2) CH_3CH_2COCl, $AlCl_3$
3) HNO_3, H_2SO_4
4) Cl_2, $AlCl_3$
Cl
NO_2
O

i)

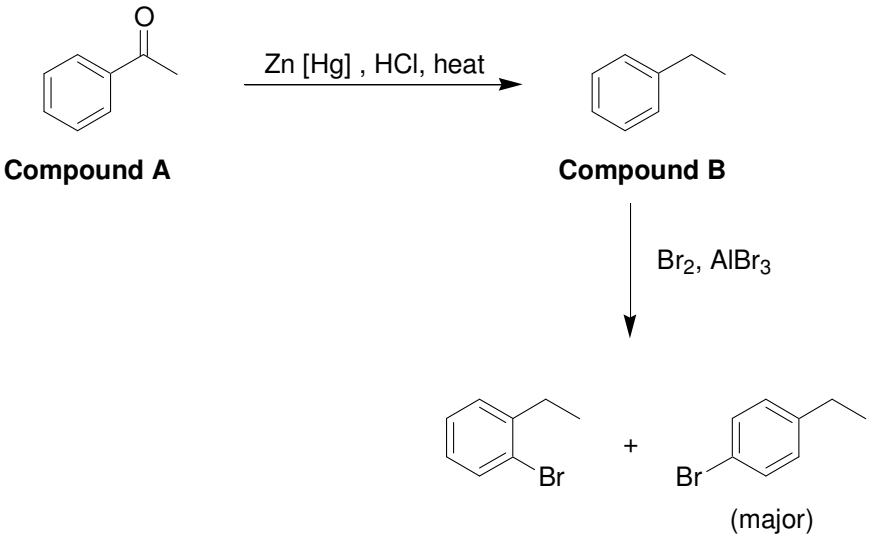

1)
Cl
Cl
$AlCl_3$
2) Br_2, $AlBr_3$
3) HNO_3, H_2SO_4
Br
O_2N

19.73.



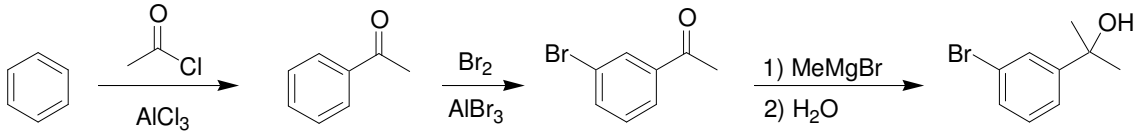
1,2,4-trimethylbenzene

19.74. Bromination at the para position occurs more rapidly because ortho attack is sterically hindered by the ethyl group:

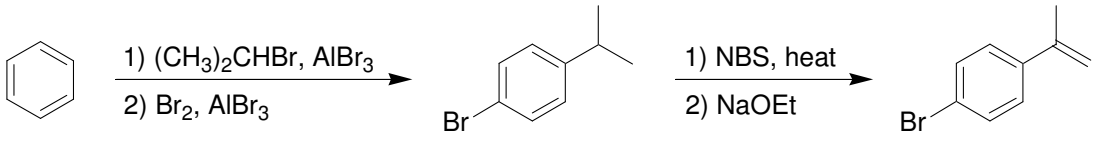


19.75.

a)

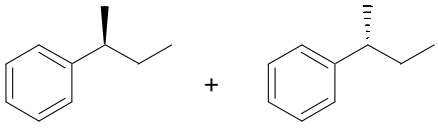


b)



19.76.

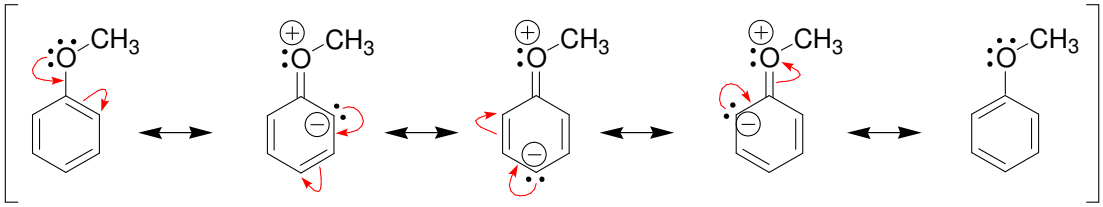
a)



b) The reaction proceeds via a carbocation intermediate, which can be attacked from either face, leading to a racemic mixture.

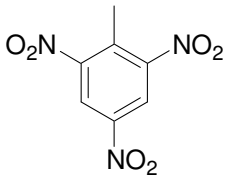
19.77.

The OH group activates the ring toward electrophilic aromatic substitution because the OH group donates electron density via resonance.



This effect gives electron density primarily to the *ortho* and *para* positions, as seen in the resonance structures above. These positions are shielded, and the protons at these positions are expected to produce signals farther upfield than protons at the *meta* position. According to this reasoning, the *meta* protons correspond with the signal at 7.2ppm.

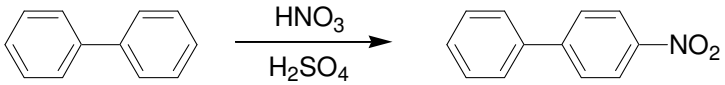
19.78.



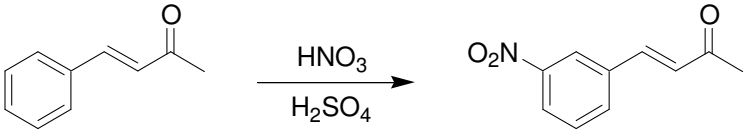
2,4,6-trinitrotoluene

19.79.

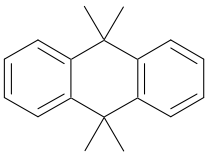
a) A phenyl group is an *ortho-para* director, because the sigma complex formed from *ortho* attack or *para* attack is highly stabilized by resonance (the positive charge is spread over both rings). The *ortho* position is sterically hindered while the *para* position is not, so we expect nitration to occur predominantly at the *para* position:



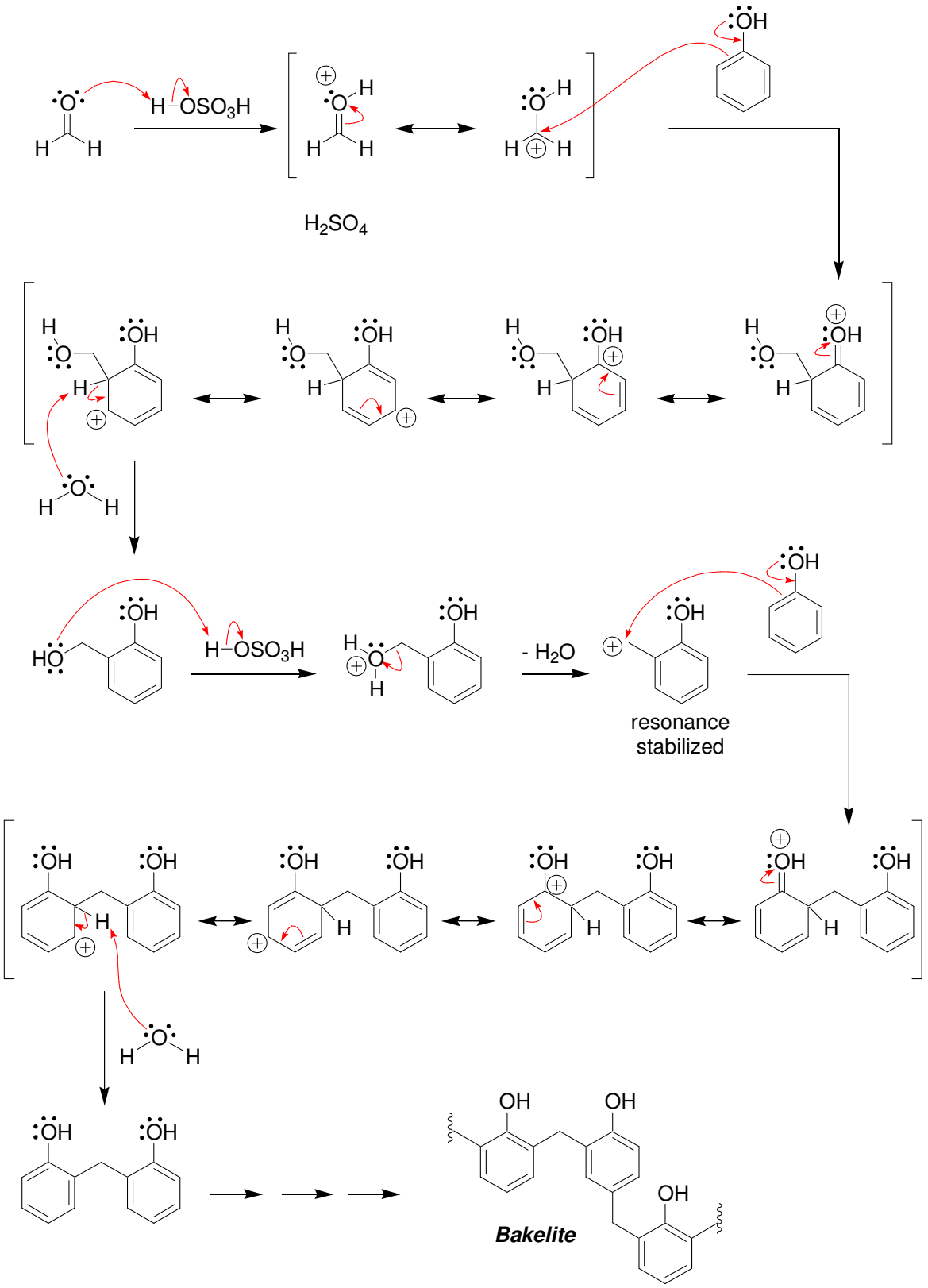
b) This group withdraws electron density form the ring via resonance (the resonance structures have a positive charge in the ring). As a result, this group is a moderate deactivator, and therefore a *meta*-director:



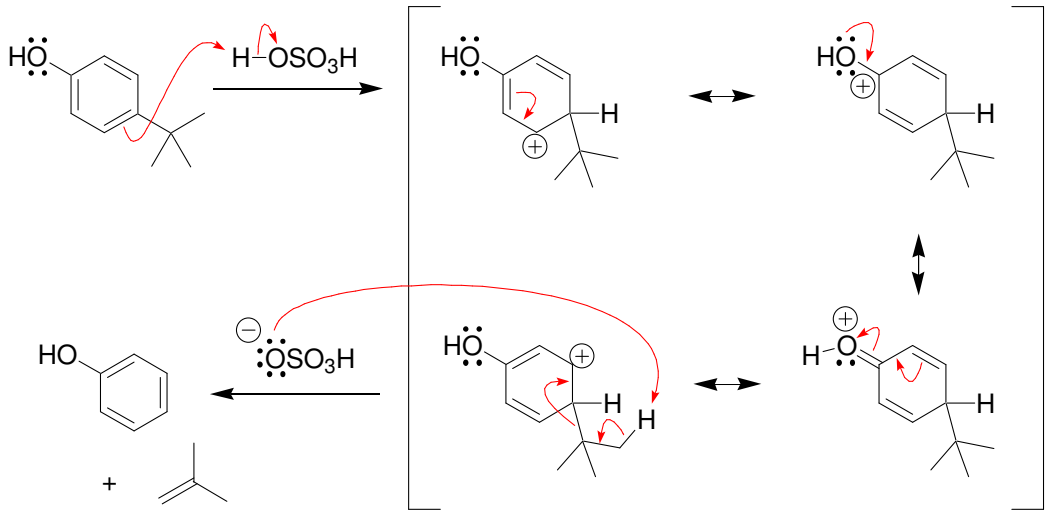
19.80.



19.81.



19.82.



19.83. The amino group in *N,N*-dimethylaniline is a strong activator, and therefore, an *ortho-para* director. For this reason, bromination occurs at the *ortho* and *para* positions. However, in acidic conditions, the amino group is protonated to give an ammonium ion. Unlike the amino group, an ammonium ion is a strong deactivator and a *meta* director. Under these conditions, nitration occurs primarily at the *meta* position.