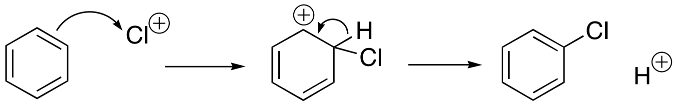
UNIT 16 – PRACTICE PROBLEMS KEY

16A.1

a)



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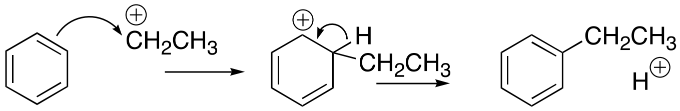

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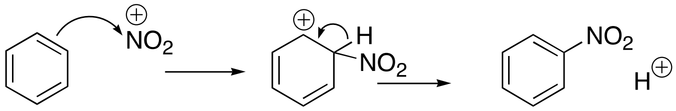

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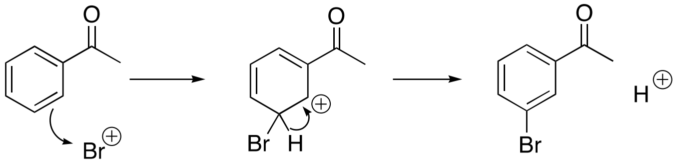

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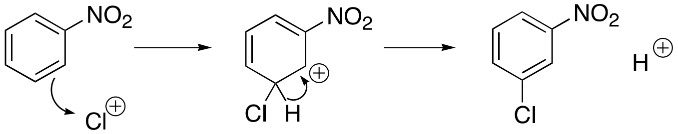

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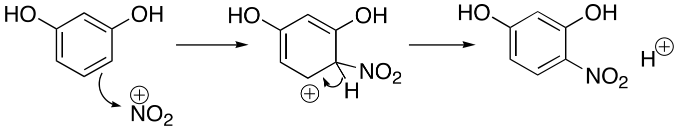
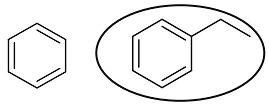


16B.1

a)



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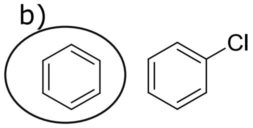

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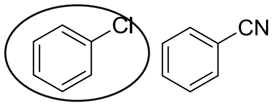

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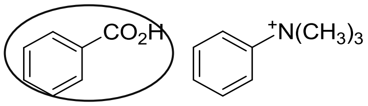

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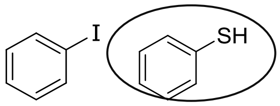

16B.2

a)

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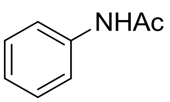

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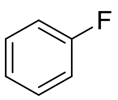

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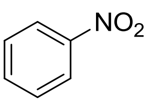

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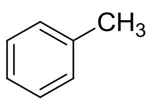

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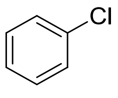

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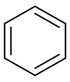

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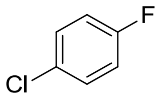

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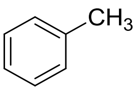

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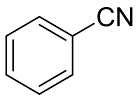

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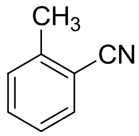

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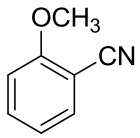

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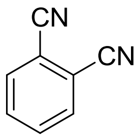

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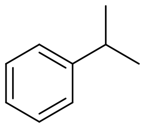

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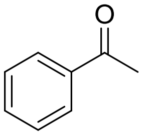

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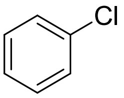
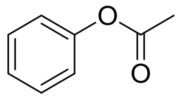
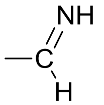


1

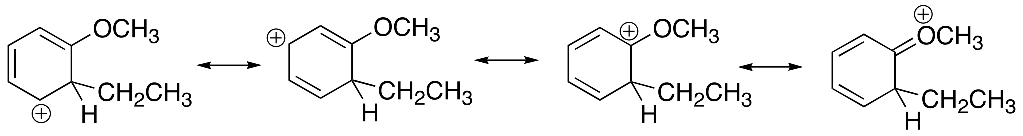


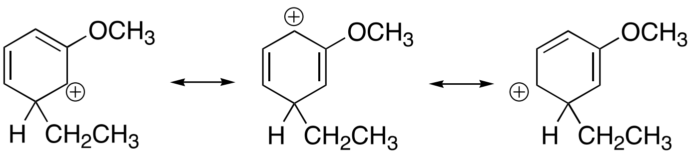
16B.3

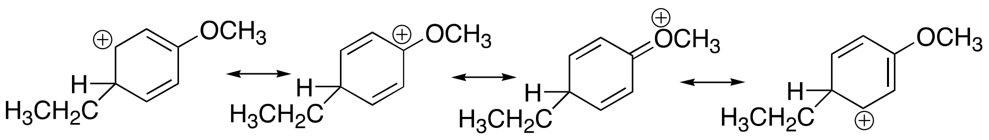
	$-OCH_3$	$-CH_3$	$-SCH_3$	
Inductive Effect	withdrawing	donating	withdrawing	withdrawing
Resonance Effect	donating	neither	donating	withdrawing

16B.4 Compound A is more inductively withdrawing than B due to oxygen's greater electronegativity. However, A also has a stronger resonance donating effect because sulfur's 3 shell lone pairs do not overlap as well with the 2p orbitals on benzene. If A is more reactive than B, the resonance effect must be more important than the inductive effect.

16C.1 a)

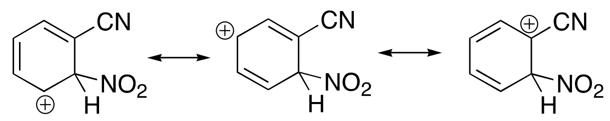


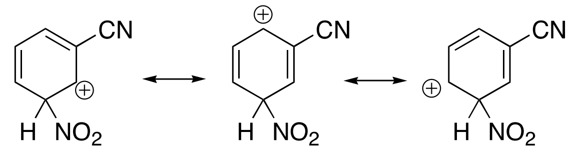


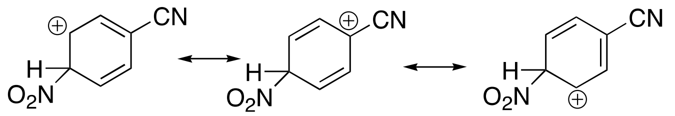


Ortho and para sigma complexes have a forth resonance structure making those intermediates more stable than meta. The more stable intermediates lead to the major products being ortho and para.

b)

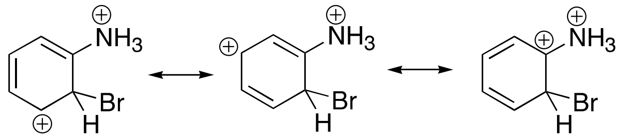


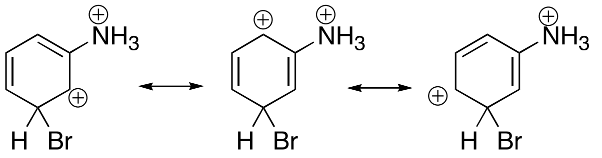


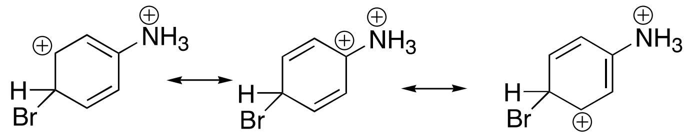


Ortho and para sigma complexes have an unstable resonance form with a cation next to a withdrawing group. These intermediates are unfavored so the major product is meta.

c)

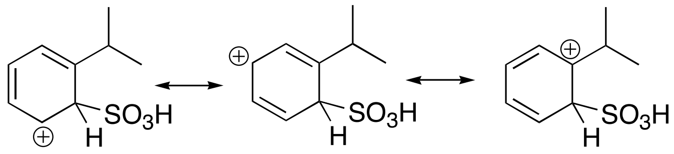


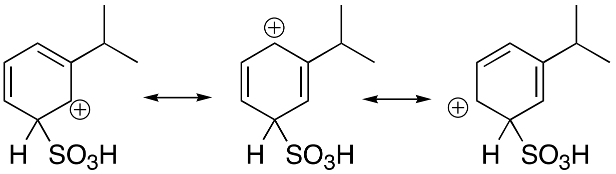


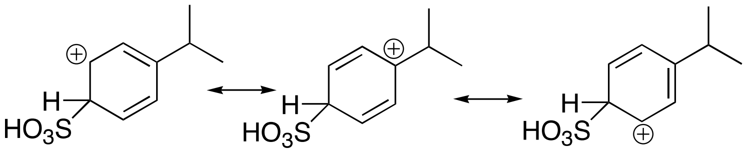


Ortho and para sigma complexes have an unstable resonance form with two adjacent cations. These intermediates are unfavored so the major product is meta.

d)

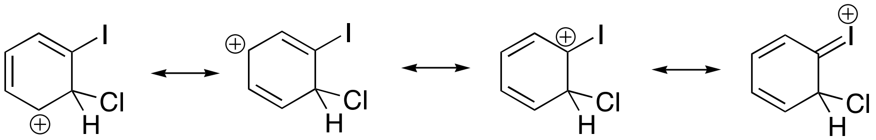


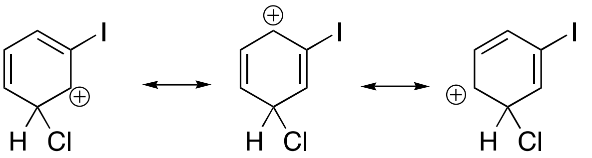


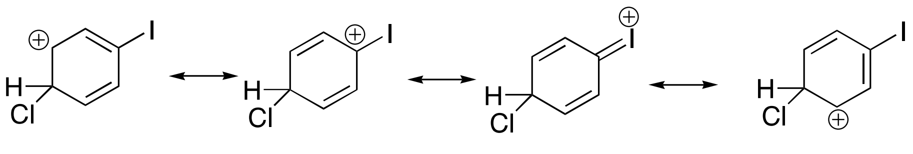


Ortho and para sigma complexes have a stable resonance structure with a cation next to an electron donating alkyl group. These intermediates are more stable than the meta leading the ortho and para as the major products.

e)



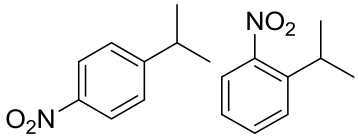




Ortho and para sigma complexes have a forth resonance structure making those intermediates more stable than meta. The more stable intermediates lead to the major products being ortho and para.

16D.1

a)



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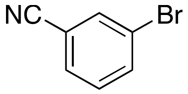

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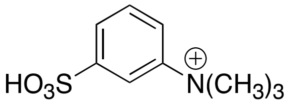

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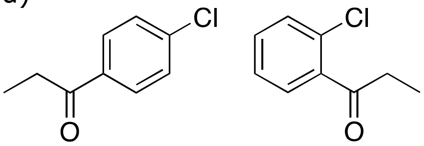

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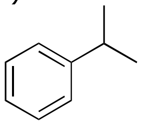

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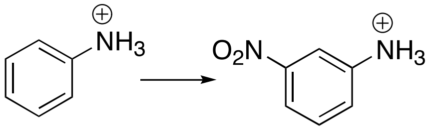
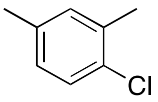


g)

NR

16D.2

a)



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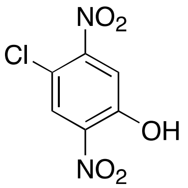

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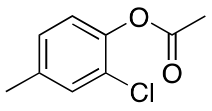

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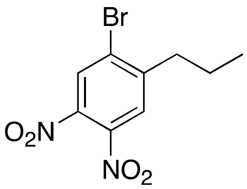

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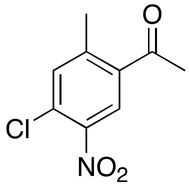

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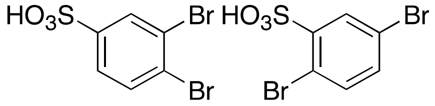

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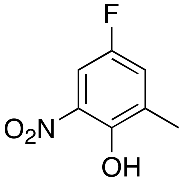

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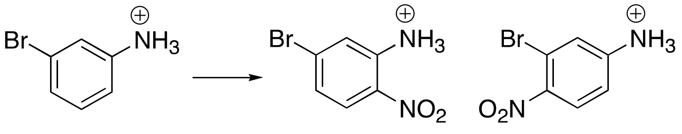

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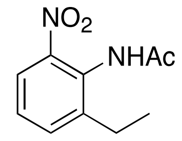

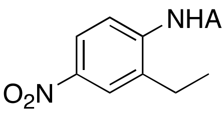

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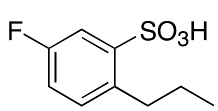

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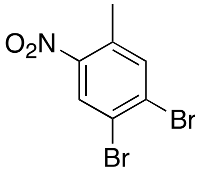
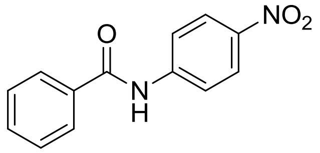


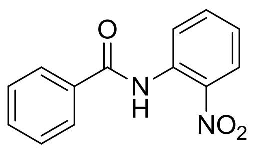
l)

NR

16D.3 Predict the major product(s) of the following reactions. If no reaction write "NR".

a)





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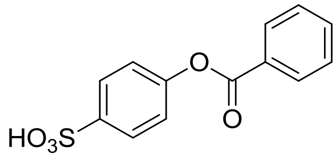

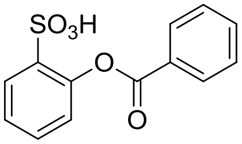

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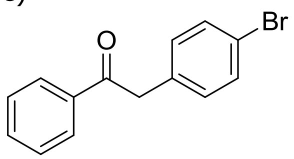

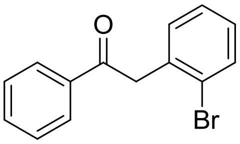

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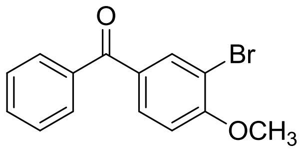

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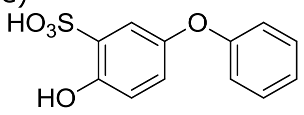
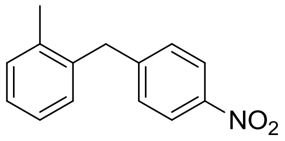
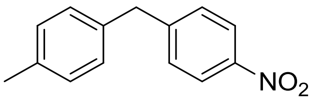


OH is more activated than OR, but I don't expect you to know that for the exam.

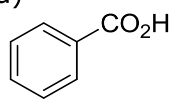
f)



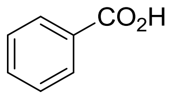


16D.4 Predict the major product of the following molecules reacted with $KMnO_4$.

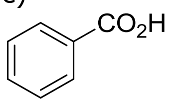
a)



b)

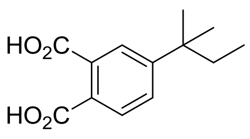


c)

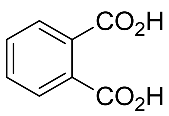


d)
NR

e)

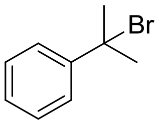


f)

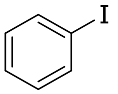


16D.5 Predict the major product(s) of the following reactions. If no reaction write "NR".

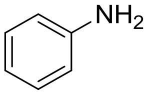
a)



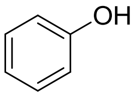
b)



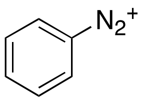
c)



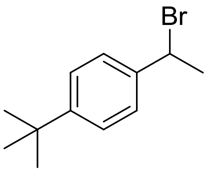
d)



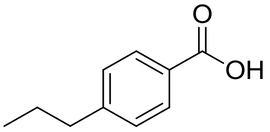
e)



f)

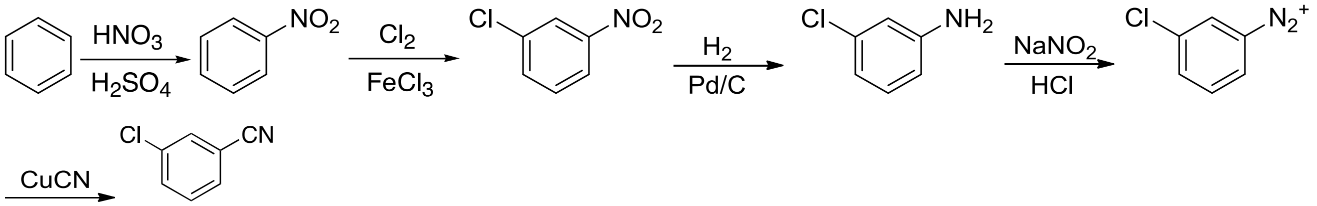


g)

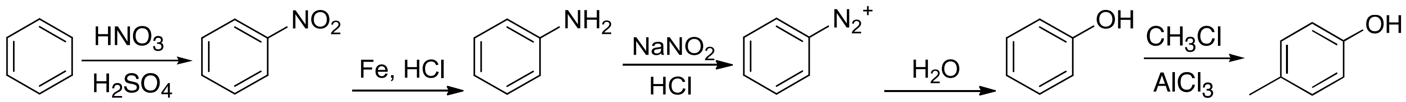


16E.1.

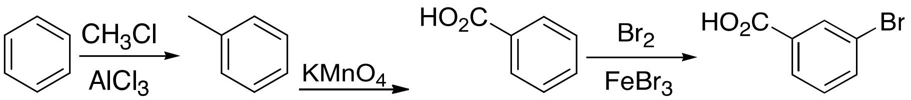
a)



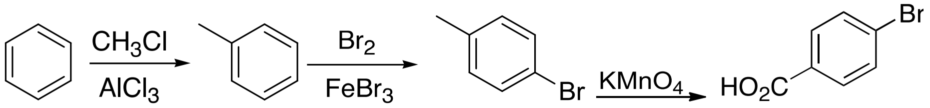
b)



c)

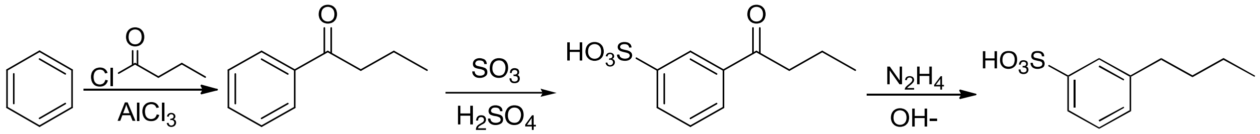


d)



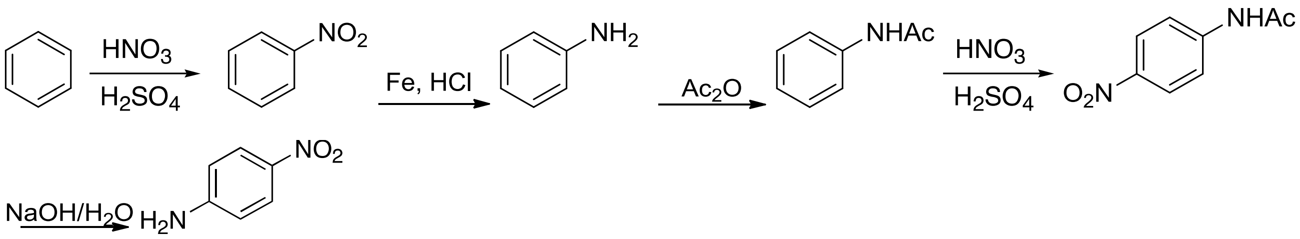
CH_3Cl
$AlCl_3$
Br_2
$FeBr_3$
Br
$KMnO_4$
HO_2C
Br

e)



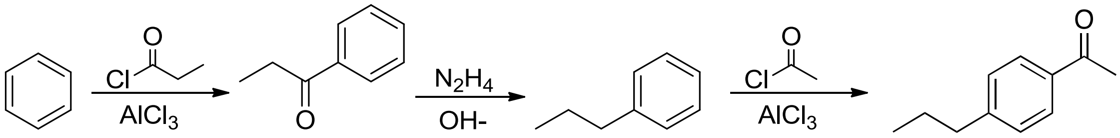
O
Cl
$AlCl_3$
O
SO_3
H_2SO_4
HO_3S
O
N_2H_4
OH-
HO_3S

f)



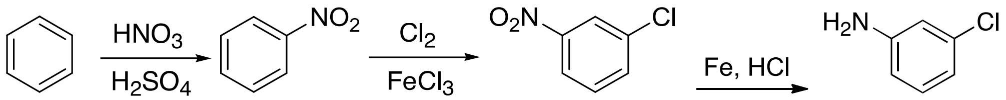
HNO_3
H_2SO_4
NO_2
Fe, HCl
NH_2
Ac_2O
NHAc
HNO_3
H_2SO_4
O_2N
NHAc
$NaOH/H_2O$
H_2N
NO_2

g)



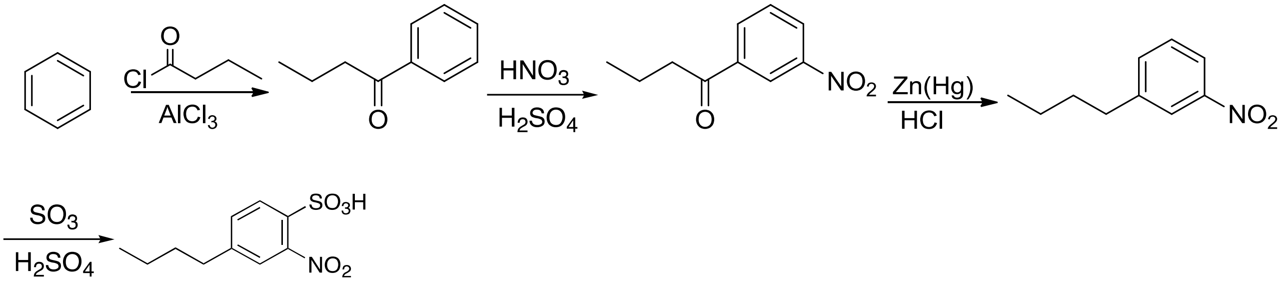
O
Cl
$AlCl_3$
O
N_2H_4
OH-
O
Cl
$AlCl_3$
O

h)



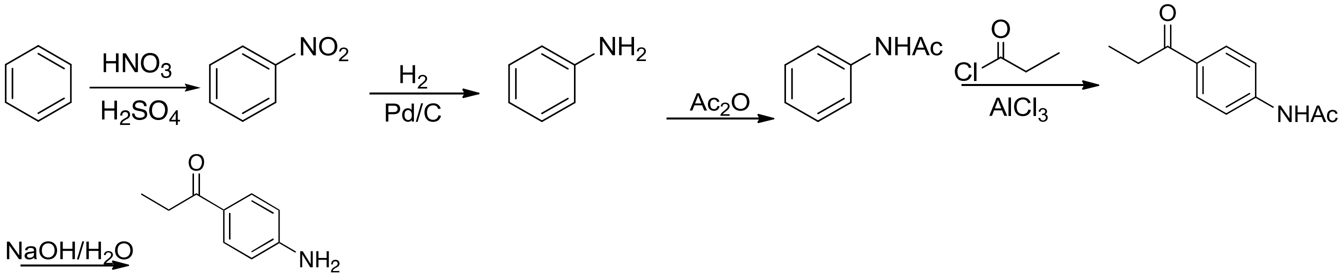
HNO_3
H_2SO_4
NO_2
Cl_2
$FeCl_3$
O_2N
Cl
Fe, HCl
H_2N
Cl

i)



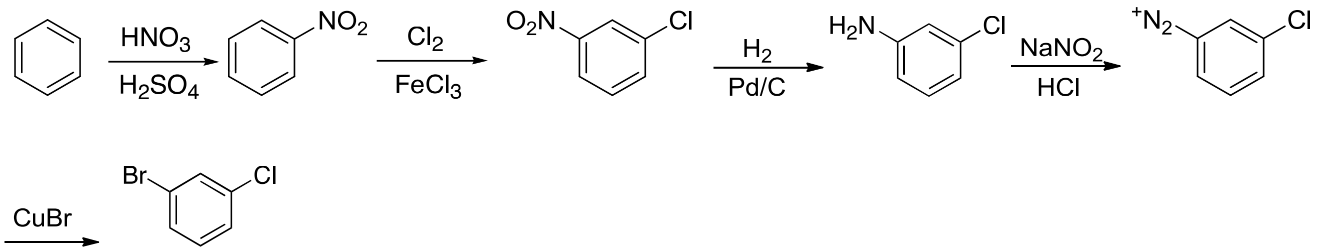
O
Cl
$AlCl_3$
O
HNO_3
H_2SO_4
O
NO_2
Zn(Hg)
HCl
NO_2
SO_3
H_2SO_4
SO_3H
NO_2

j)



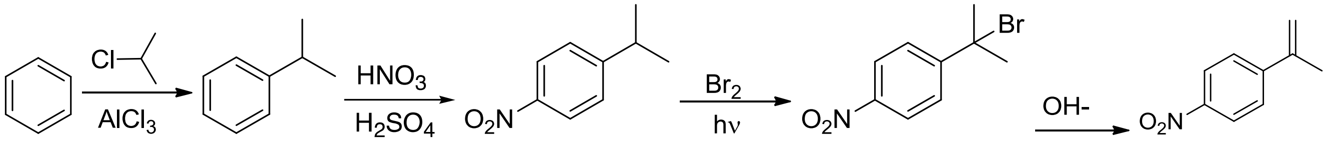
HNO3
H2SO4
NO2
H2
Pd/C
NH2
Ac2O
NHAc
O
Cl
AlCl3
O
NHAc
NaOH/H2O
O
NH2

k)



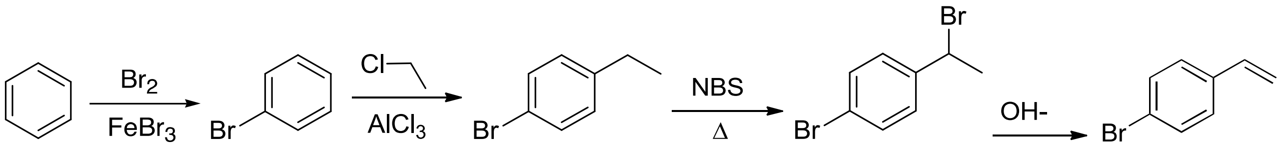
HNO3
H2SO4
NO2
Cl2
FeCl3
O2N
Cl
H2
Pd/C
H2N
Cl
NaNO2
HCl
+N2
Cl
CuBr
Br
Cl

l)



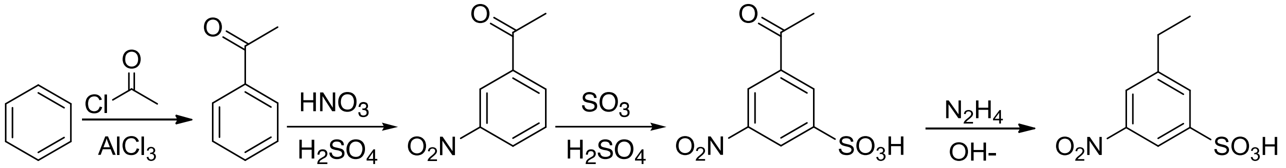
Cl
AlCl3
HNO3
H2SO4
O2N
Br2
hν
Br
O2N
OH-
O2N

m)



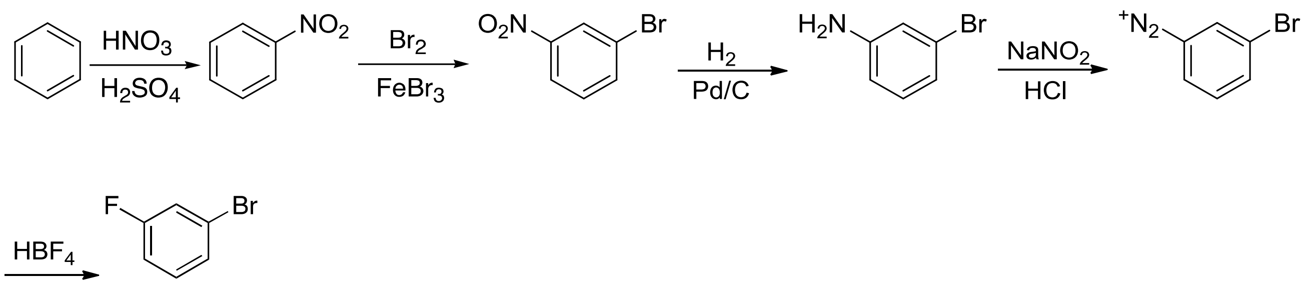
Br2
FeBr3
Br
Cl
AlCl3
Br
NBS
Δ
Br
Br
OH-
Br

n)



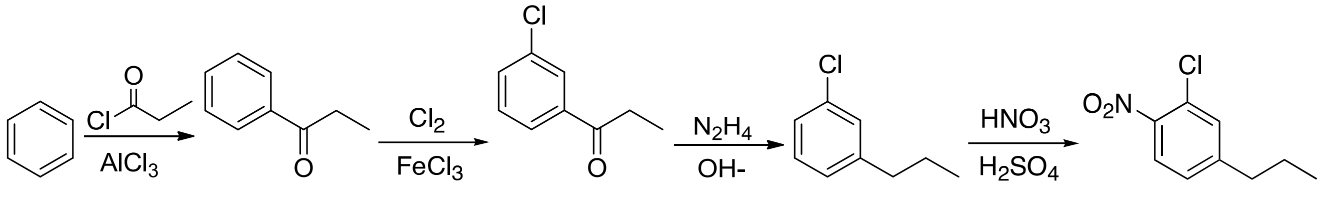
O
Cl
AlCl3
O
HNO3
H2SO4
O
O2N
SO3
H2SO4
O
O2N
SO3H
N2H4
OH-
O2N
SO3H

o)

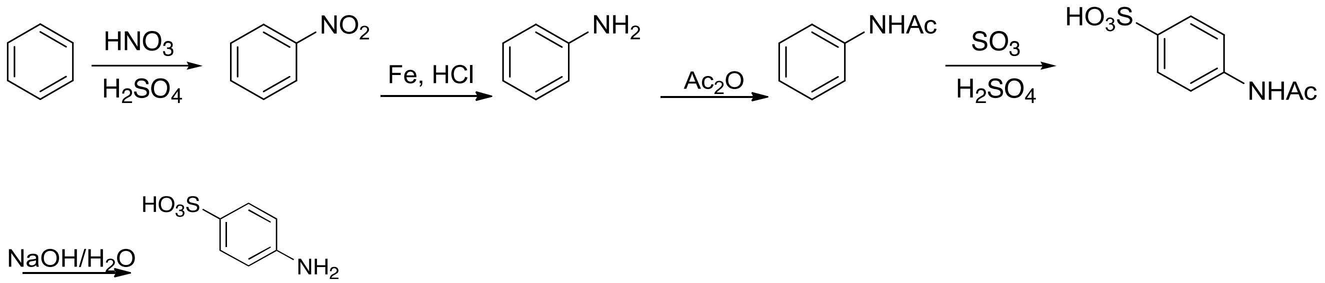


HNO3
H2SO4
NO2
Br2
FeBr3
O2N
Br
H2
Pd/C
H2N
Br
NaNO2
HCl
+N2
Br
HBF4
F
Br

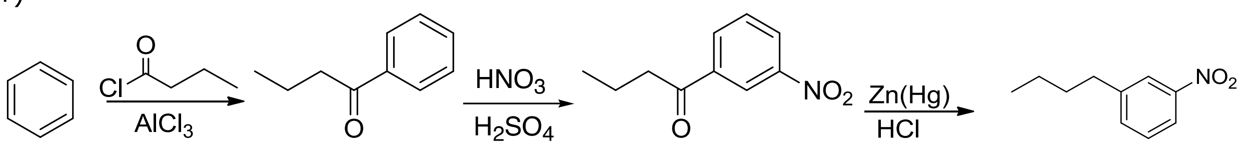
p)


Cl
O
Cl
AlCl3
O
Cl2
FeCl3
Cl
O
N2H4
OH-
Cl
HNO3
H2SO4
Cl
O2N

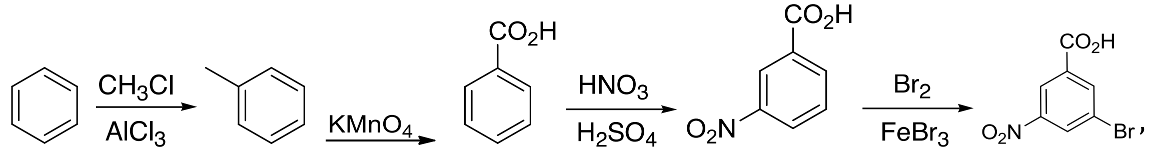
q)


HNO3
H2SO4
NO2
Fe, HCl
NH2
Ac2O
NHAc
SO3
H2SO4
HO3S
NHAc
NaOH/H2O
HO3S
NH2

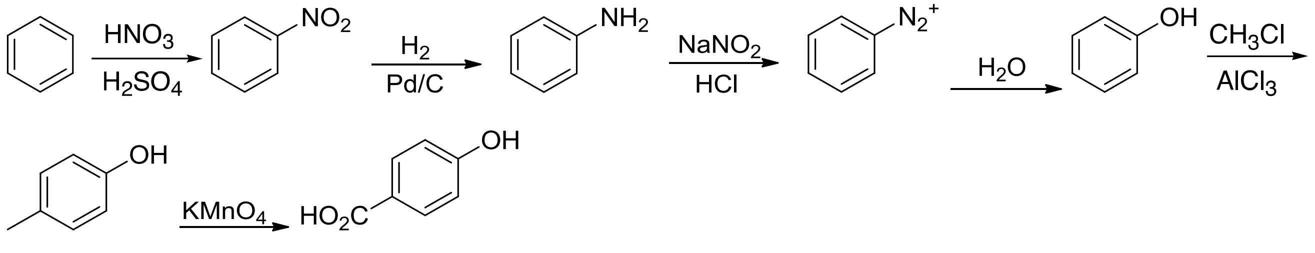
r)


O
Cl
AlCl3
O
HNO3
H2SO4
O
NO2
Zn(Hg)
HCl
NO2

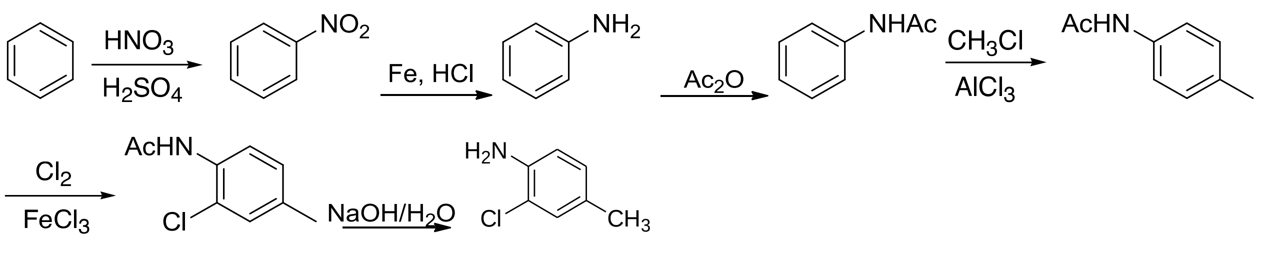
s)


CH3Cl
AlCl3
KMnO4
CO2H
HNO3
H2SO4
CO2H
O2N
Br2
FeBr3
CO2H
O2N
Br

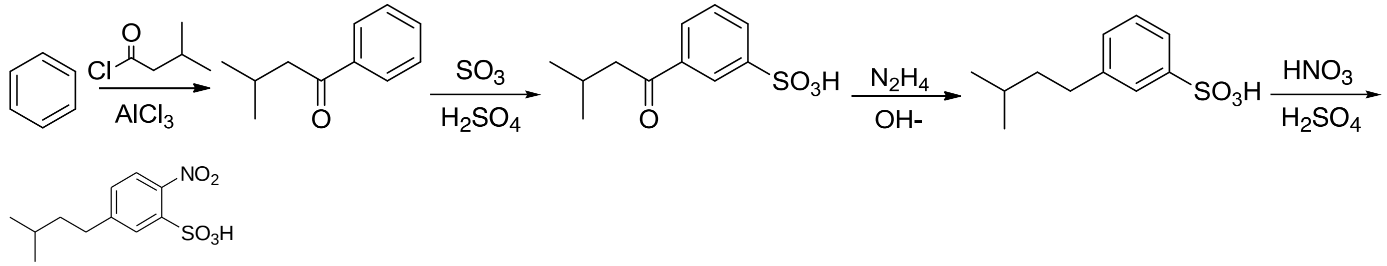
t)


HNO3
H2SO4
NO2
H2
Pd/C
NH2
NaNO2
HCl
N2+
H2O
OH
CH3Cl
AlCl3
OH
KMnO4
OH
HO2C

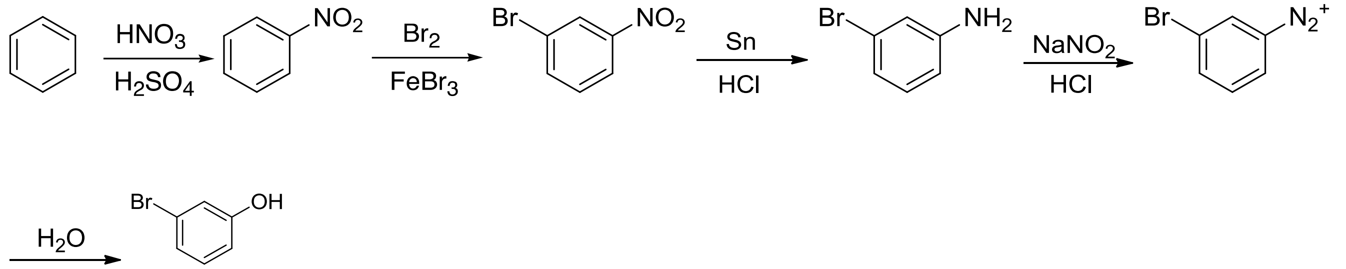
u)


HNO3
H2SO4
NO2
Fe, HCl
NH2
Ac2O
NHAc
CH3Cl
AlCl3
AcHN
Cl2
FeCl3
AcHN
Cl
NaOH/H2O
H2N
Cl
CH3

v)



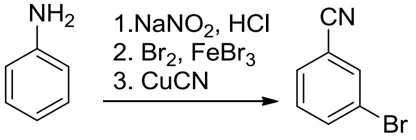
w)



x) see l

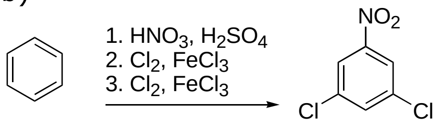
16E.2 The following syntheses are flawed. Explain what is wrong with each.

a)



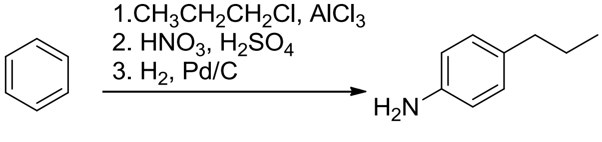
Diazos must be used immediately after formation. It will not survive the bromination step.

b)



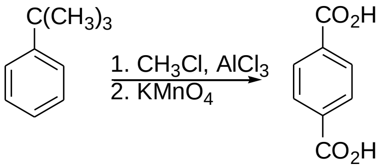
Once the first chlorine is on the ring, it becomes the most activated group, so the second chlorine will add o/p to the first chlorine, not meta to nitro.

c)



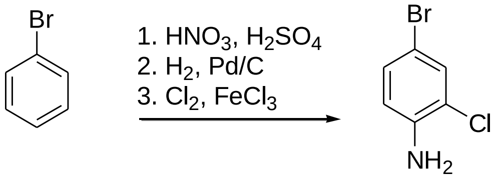
The propyl cation will rearrange leading to addition of an isopropyl group.

d)



The methyl will oxidize to a carboxylic acid, the t-butyl group will not.

e)



Iron chloride is a lewis acid – it reacts with the amino group making it positive and a meta deactivator. When the chlorine adds it is directed o/p to the bromine.