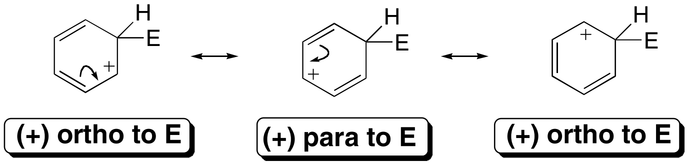
Chapter 18: Electrophilic Aromatic Substitution

◆ Mechanism of electrophilic aromatic substitution (18.2)

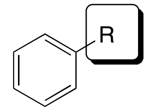
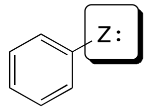
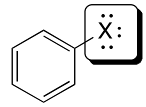
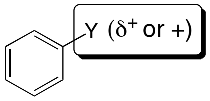
- Electrophilic aromatic substitution follows a two-step mechanism. Reaction of the aromatic ring with an electrophile forms a carbocation, and loss of a proton regenerates the aromatic ring.
- The first step is rate-determining.
- The intermediate carbocation is stabilized by resonance; a minimum of three resonance structures can be drawn. The positive charge is always located ortho or para to the new C–E bond.



◆ Three rules describing the reactivity and directing effects of common substituents (18.7–18.9)

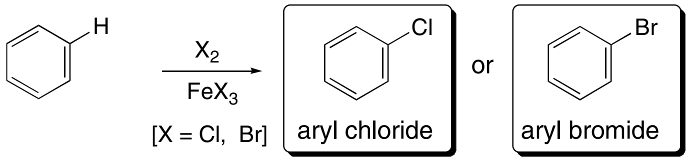
[1] All ortho, para directors except the halogens activate the benzene ring.
[2] All meta directors deactivate the benzene ring.
[3] The halogens deactivate the benzene ring.

◆ Summary of substituent effects in electrophilic aromatic substitution (18.6–18.9)

	Substituent	Inductive effect	Resonance effect	Reactivity	Directing effect
[1]	 R = alkyl	**donating**	**none**	**activating**	**ortho, para**
[2]	 Z = N or O	**withdrawing**	**donating**	**activating**	**ortho, para**
[3]	 X = halogen	**withdrawing**	**donating**	**deactivating**	**ortho, para**
[4]		**withdrawing**	**withdrawing**	**deactivating**	**meta**

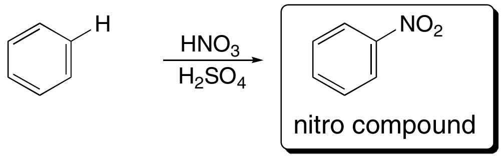
♦ Five examples of electrophilic aromatic substitution

[1] Halogenation–Replacement of H by Cl or Br (18.3)

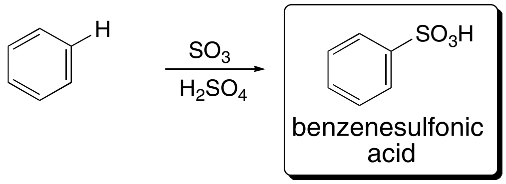


- Polyhalogenation occurs on benzene rings substituted by OH and NH_2 (and related substituents) (18.10A).

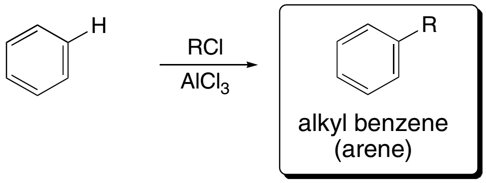
[2] Nitration–Replacement of H by NO_2 (18.4)



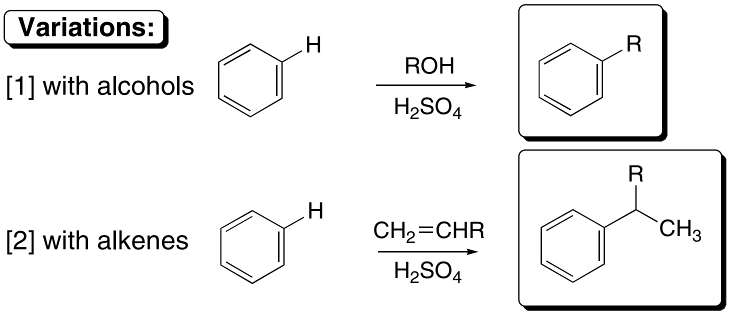
[3] Sulfonation–Replacement of H by SO_3H (18.4)



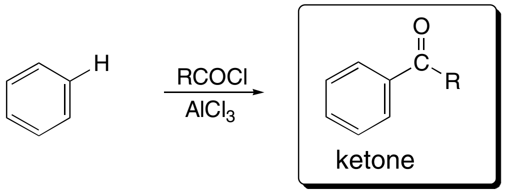
[4] Friedel–Crafts alkylation–Replacement of H by R (18.5)



- Rearrangements can occur.
- Vinyl halides and aryl halides are unreactive.
- The reaction does not occur on benzene rings substituted by meta deactivating groups or NH_2 groups (18.10B).
- Polyalkylation can occur.



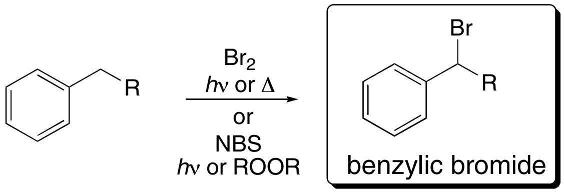
[5] Friedel–Crafts acylation–Replacement of H by RCO (18.5)



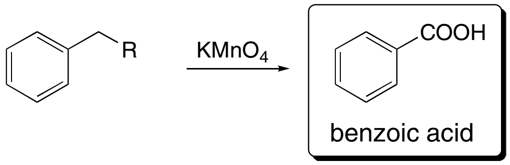
- The reaction does not occur on benzene rings substituted by meta deactivating groups or NH_2 groups (18.10B).

◆ Other reactions of benzene derivatives

[1] Benzylic halogenation (18.13)

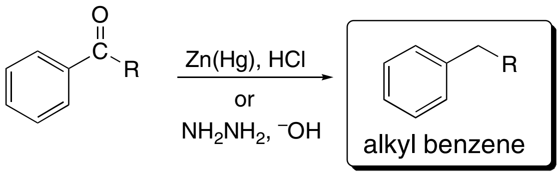


[2] Oxidation of alkyl benzenes (18.14A)

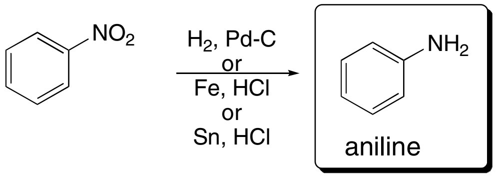


- A benzylic C–H bond is needed for reaction.

[3] Reduction of ketones to alkyl benzenes (18.14B)



[4] Reduction of nitro groups to amino groups (18.14C)

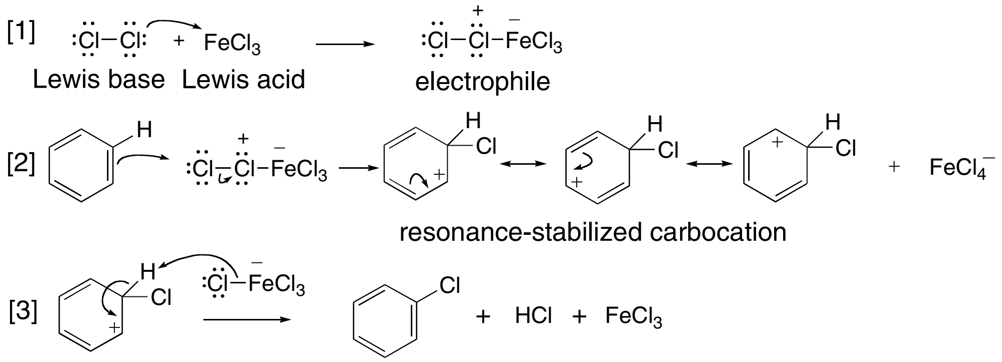


Chapter 18: Answers to Problems

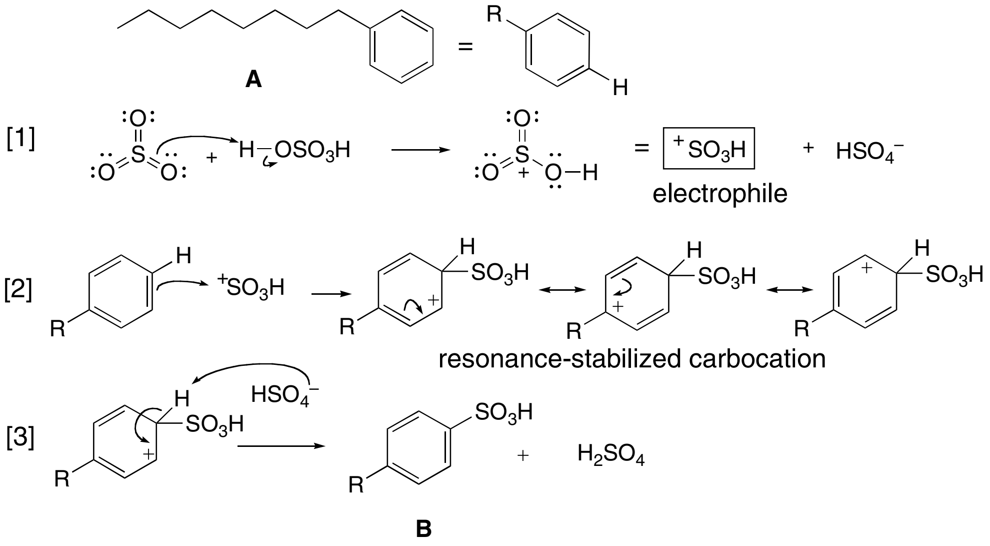
18.1 The π electrons of benzene are delocalized over the six atoms of the ring, increasing benzene's stability and making them less available for electron donation. With an alkene, the two π electrons are localized between the two C's making them more nucleophilic and thus more reactive with an electrophile than the delocalized electrons in benzene.

18.2

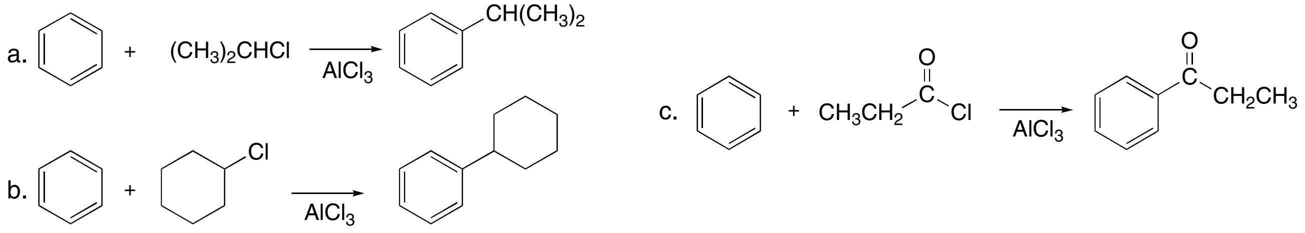
18.3 Reaction with Cl_2 and $FeCl_3$ as the catalyst occurs in two parts. First is the formation of an electrophile, followed by a two-step substitution reaction.



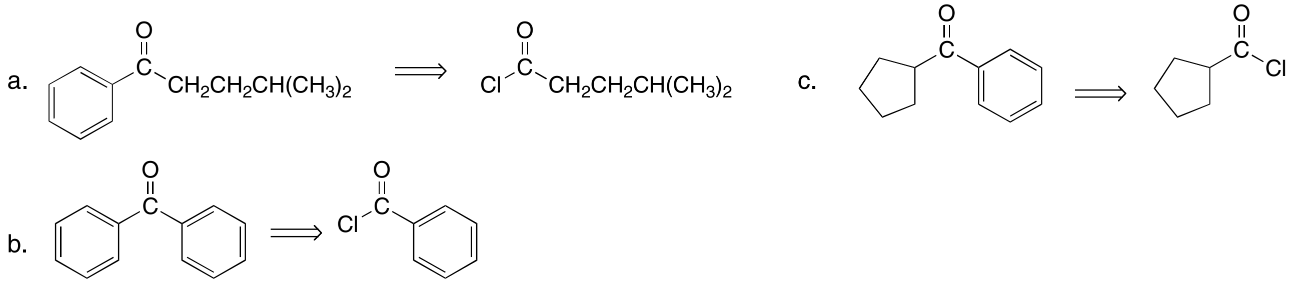
18.4 There are two parts in the mechanism. The first part is formation of an electrophile. The second part is a two-step substitution reaction.



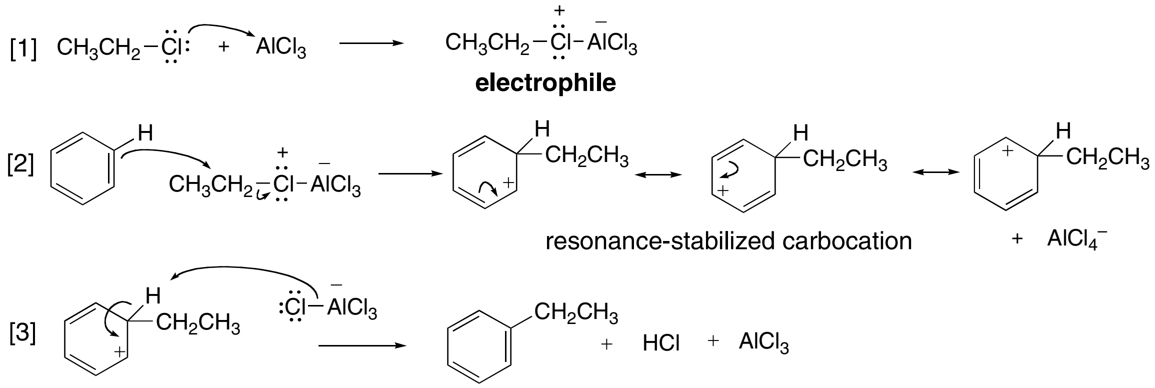
18.5 Friedel–Crafts alkylation results in the transfer of an alkyl group from a halogen to a benzene ring. In Friedel–Crafts acylation an acyl group is transferred from a halogen to a benzene ring.



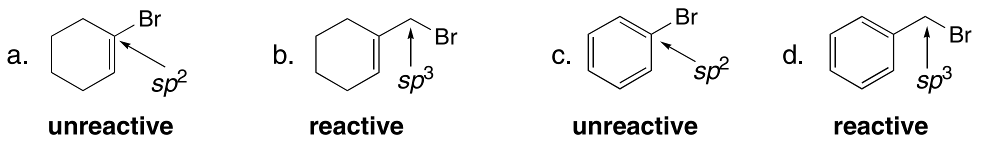
18.6 Remember that an acyl group is transferred from a Cl atom to a benzene ring. To draw the acid chloride, substitute a Cl for the benzene ring.



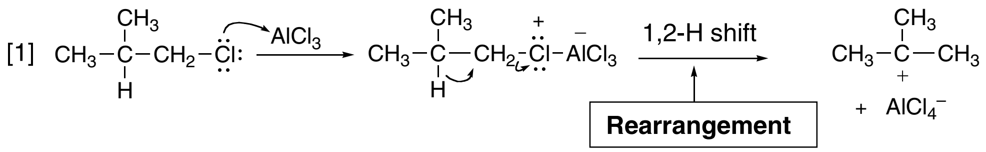
18.7

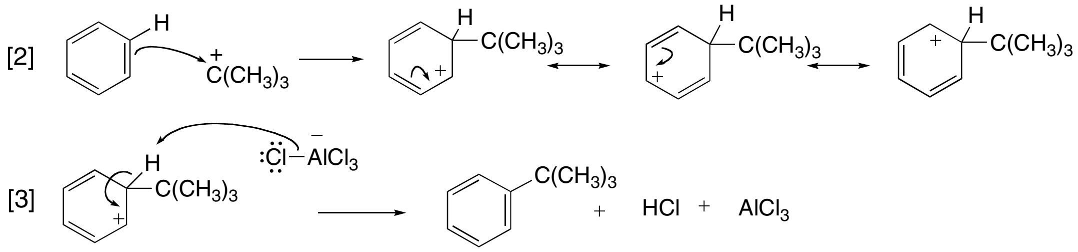


18.8 To be reactive in a Friedel–Crafts alkylation reaction, the X must be bonded to an sp^3 hybridized carbon atom.

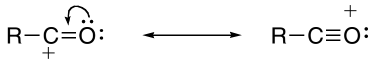


18.9 The product has an "unexpected" carbon skeleton, so rearrangement must have occurred.



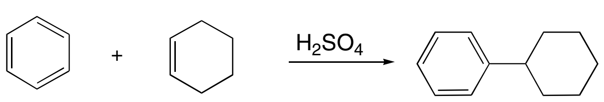


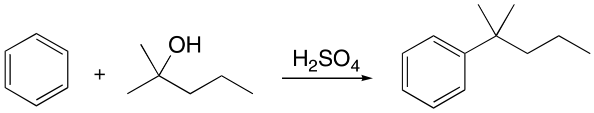
18.10 Rearrangements do not occur with acylium ions formed in a Friedel–Craft acylation because the acylium ion is resonance stabilized.

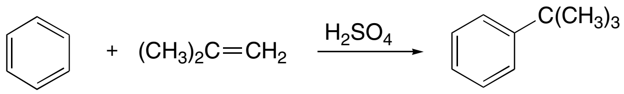


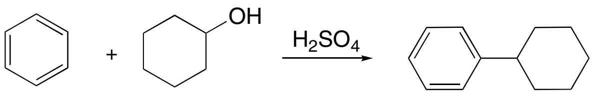
$$\mathrm{R{-}\underset{+}{C}{=}\ddot{O}\colon} \longleftrightarrow \mathrm{R{-}C{\equiv}\overset{+}{O}\colon}$$

18.11 Both alkenes and alcohols can form carbocations for Friedel–Crafts alkylation reactions.

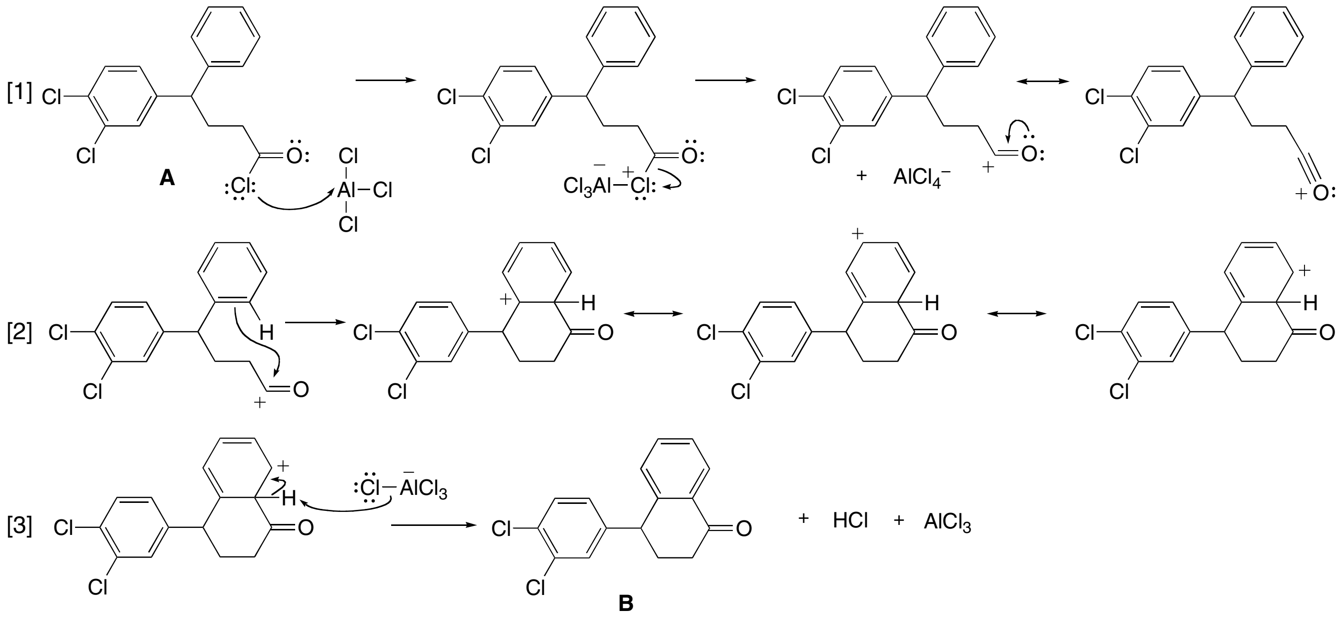
a. 

c. 

b. 

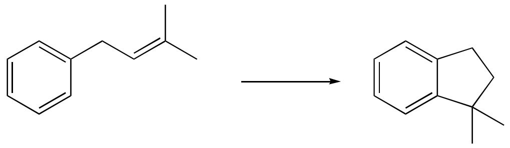
d. 

18.12

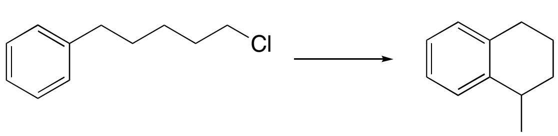


18.13 In parts (b) and (c), a 1,2-shift occurs to afford a rearrangement product.

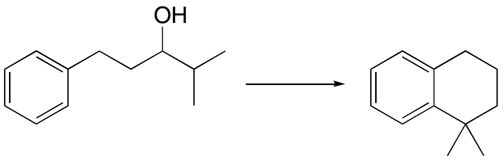
a.



c.



b.

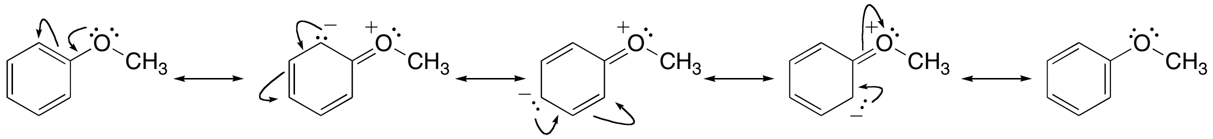


18.14

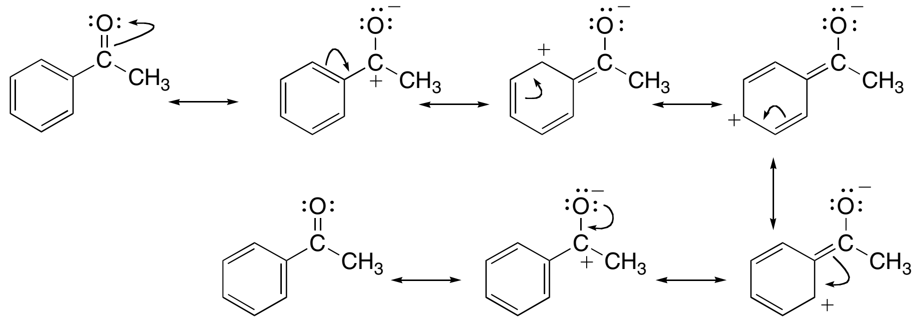
a. $-CH_2CH_2CH_2CH_3$	b. $-Br$	c. $-OCH_2CH_3$
alkyl group	halide	electronegative O
electron donating	**electron withdrawing**	**electron withdrawing**

18.15 Electron-donating groups place a negative charge in the benzene ring. Draw the resonance structures to show how –OCH$_3$ puts a negative charge in the ring. Electron-withdrawing groups place a positive charge in the benzene ring. Draw the resonance structures to show how –COCH$_3$ puts a positive charge in the ring.

a.

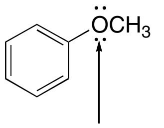


b.



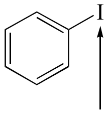
18.16 To classify each substituent, look at the atom bonded directly to the benzene ring. All R groups and Z groups (except halogens) are electron donating. All groups with a positive charge, δ$^+$, or halogens are electron withdrawing.

a.



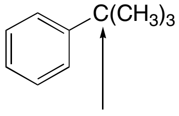
lone pair on O
electron donating

b.



halogen
electron withdrawing

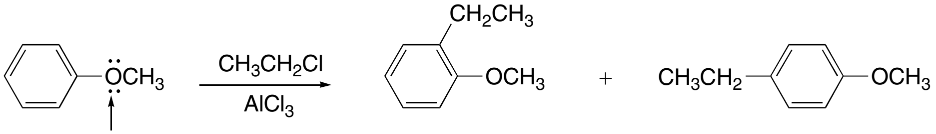
c.



R group
electron donating

18.17 First classify the substituents in the starting material as: ortho, para activating, ortho, para deactivating, or meta deactivating. Then draw the products.

a.

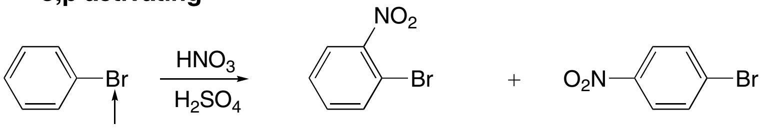


lone pair on O
o,p activating

ortho product

para product

b.

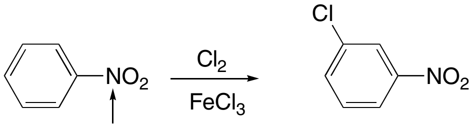


halogen
o,p deactivating

ortho product

para product

c.

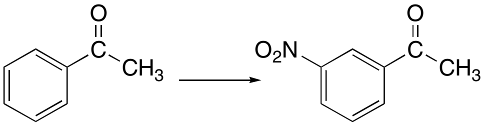


meta deactivating

meta product

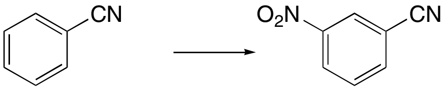
18.18 **Electron-donating groups** make the compound ***react faster*** than benzene in electrophilic aromatic substitution. **Electron-withdrawing groups** make the compound ***react more slowly*** than benzene in electrophilic aromatic substitution.

a.



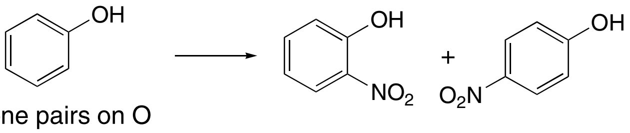
electron withdrawing
reacts slower

b.



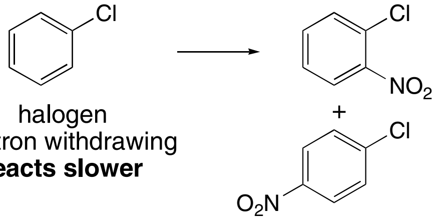
electron withdrawing
reacts slower

c.



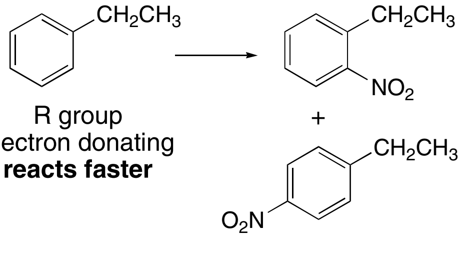
lone pairs on O
electron donating
reacts faster

d.



halogen
electron withdrawing
reacts slower

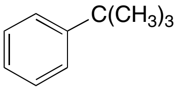
e.



R group
electron donating
reacts faster

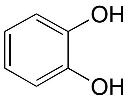
18.19 **Electron-donating groups** make the compound ***more reactive*** than benzene in electrophilic aromatic substitution. **Electron-withdrawing groups** make the compound ***less reactive*** than benzene in electrophilic aromatic substitution.

a.



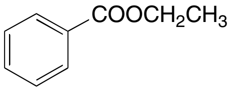
R group
electron donating
more reactive

b.



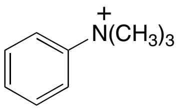
two OH's
electron donating
more reactive

c.



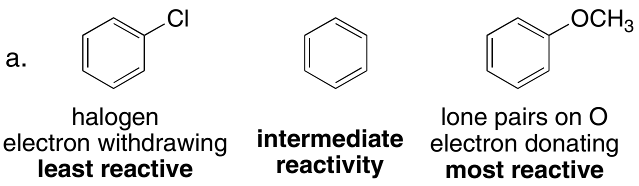
C with 2 electronegative O's
electron withdrawing
less reactive

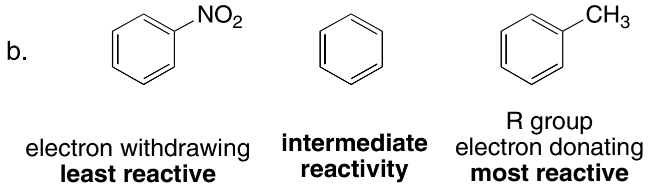
d.



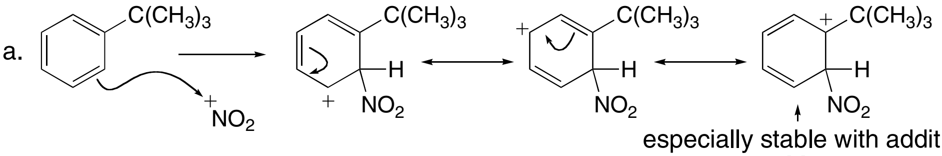
electron withdrawing
less reactive

18.20

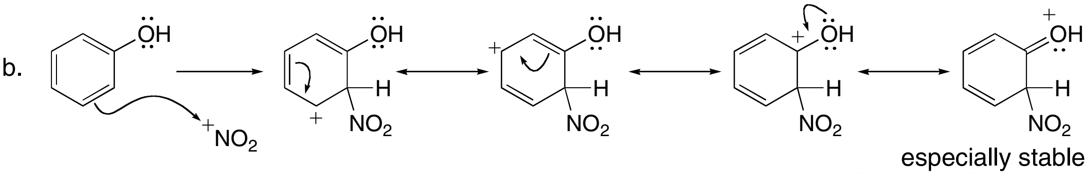




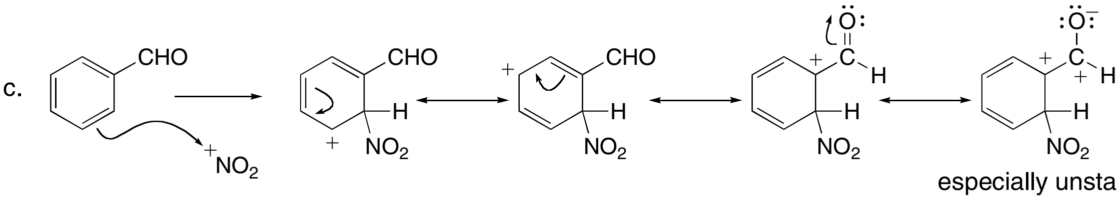
18.21 Especially stable resonance structures have all atoms with an octet. Carbocations with additional electron donor R groups are also more stable structures. Especially unstable resonance structures have adjacent like charges.



especially stable with additional R group
stabilized carbocation



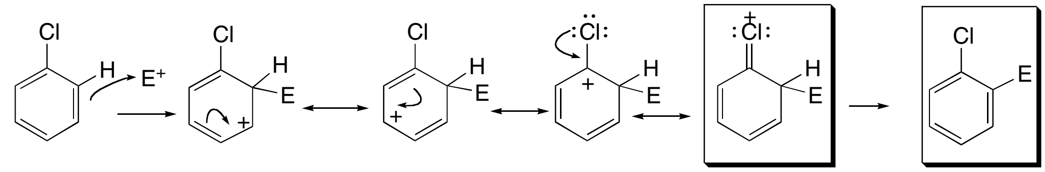
especially stable
All atoms have an octet.



especially unstable
2 adjacent (+) charges

18.22

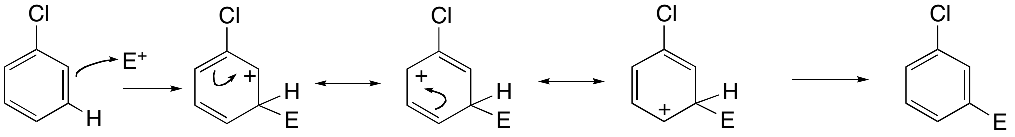
ortho attack

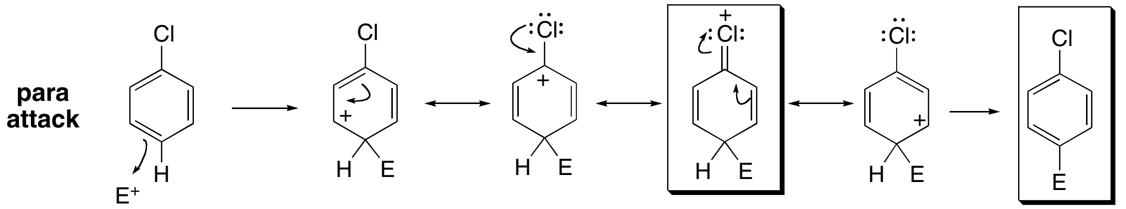


especially good
All atoms have an octet.

preferred product

meta attack

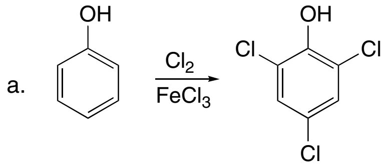


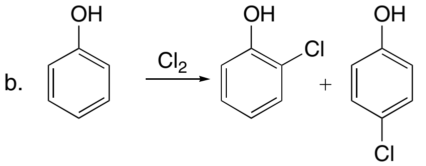


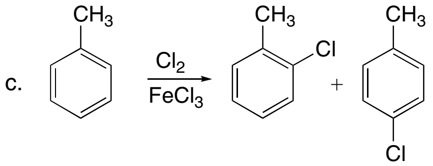
especially good
All atoms have an octet.

preferred product

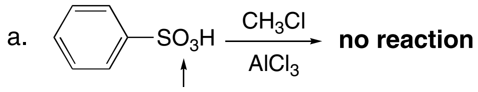
18.23 Polyhalogenation occurs with highly activated benzene rings containing OH, NH_2, and related groups with a catalyst.





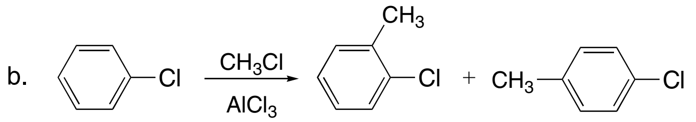


18.24 Friedel–Crafts reactions do not occur with strongly deactivating substituents including NO_2, or with NH_2, NR_2, or NHR groups.

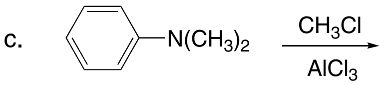


no reaction

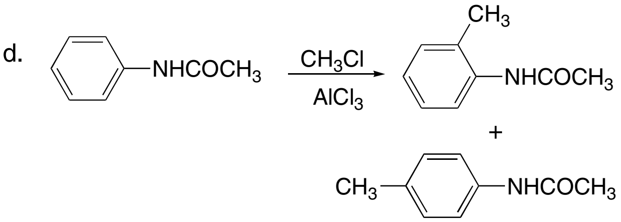
strongly deactivating



Cl is an o,p director.



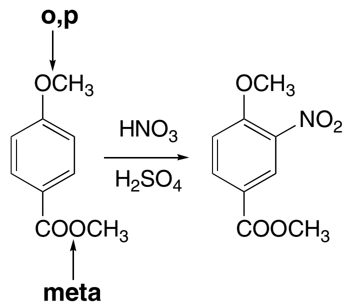
no Friedel–Crafts reaction



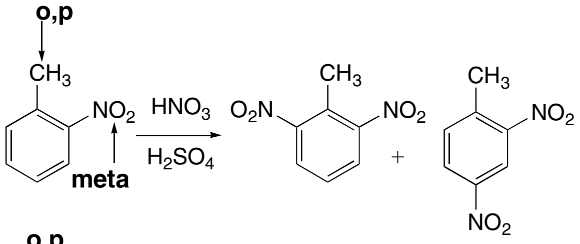
18.25 To draw the product of reaction with these disubstituted benzene derivatives and HNO_3, H_2SO_4 remember:

- If the two directing effects reinforce each other, the new substituent will be on the position reinforced by both.
- If the directing effects oppose each other, the stronger activator wins.
- No substitution occurs between two meta substituents.

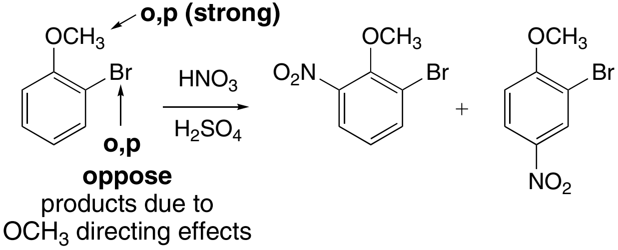
a.



c.



b.



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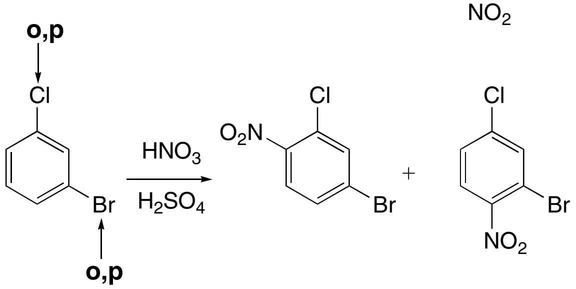
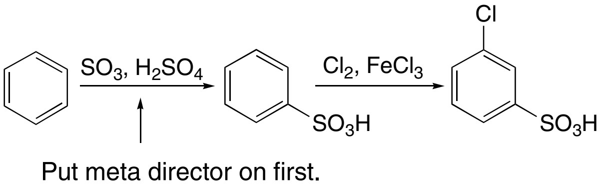


18.26

a.



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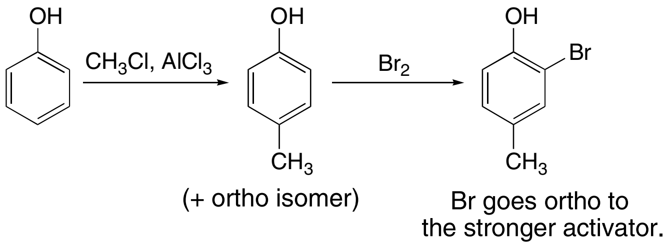

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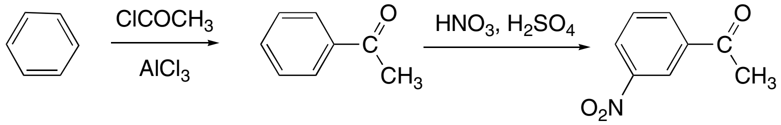
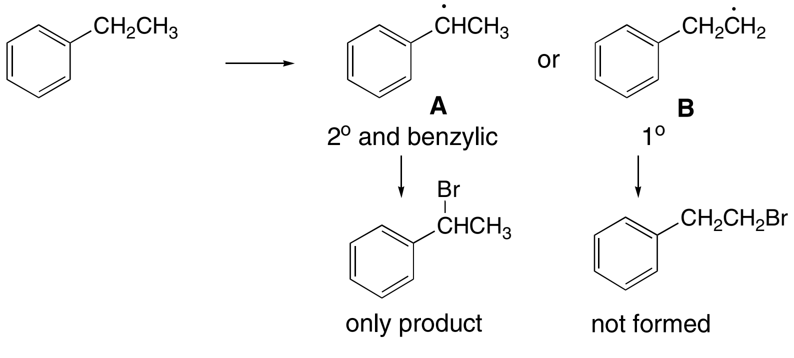
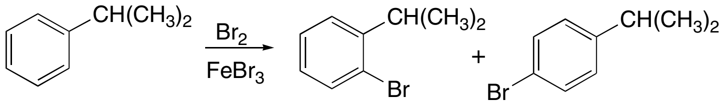


18.27 This reaction proceeds via a radical bromination mechanism and two radicals are possible: **A** (2° and benzylic) and **B** (1°). Since **B** (which leads to $C_6H_5CH_2CH_2Br$) is much less stable, this radical is not formed so only $C_6H_5CH(Br)CH_3$ is formed as product.



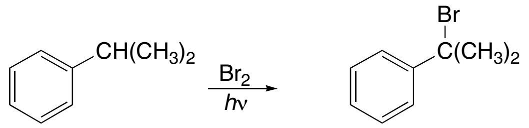
18.28 **Radical substitution** occurs at the carbon adjacent to the benzene ring (at the **benzylic position**).

a.



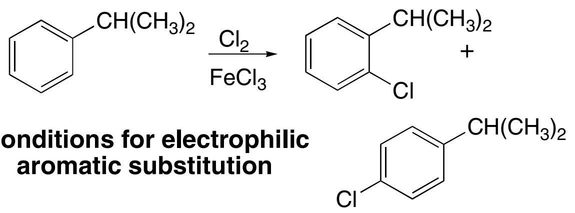
conditions for electrophilic aromatic substitution

b.



conditions for radical substitution

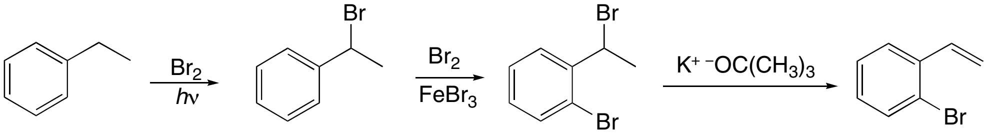
c.



conditions for electrophilic aromatic substitution

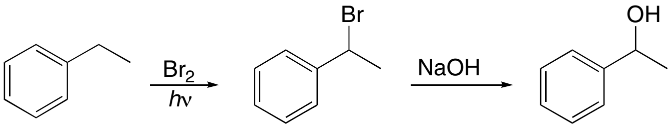
18.29

a.



(+ para isomer)

b.



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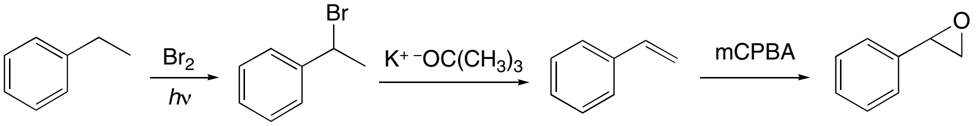
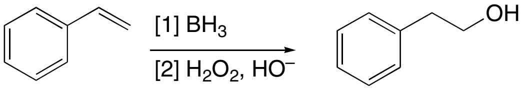


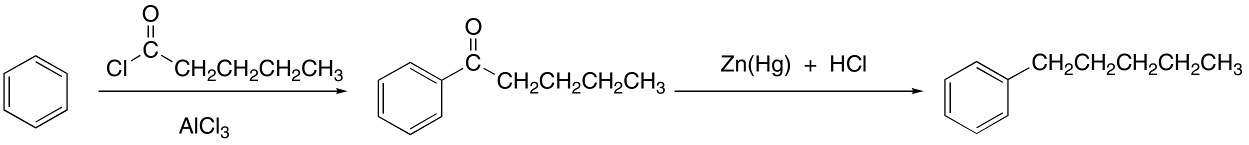
d.



(from c.)

18.30 First use an acylation reaction, and then reduce the carbonyl group to form the alkyl benzenes.

a.



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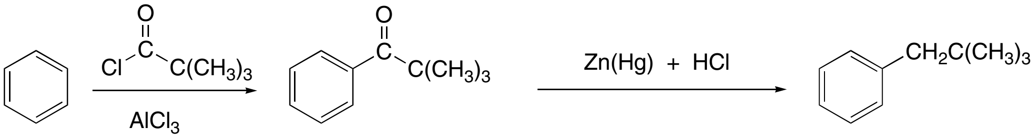
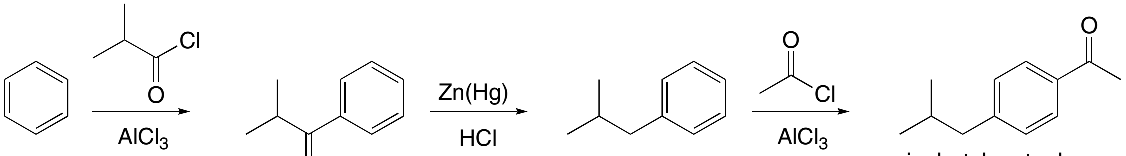
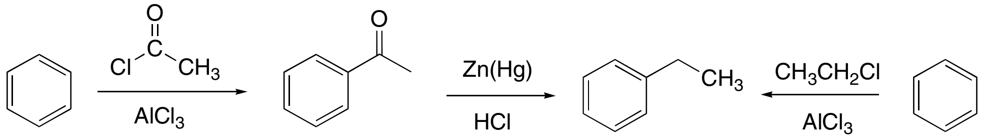


18.31



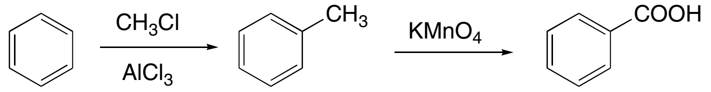
p-isobutylacetophenone
(+ ortho isomer)

18.32 When R = CH_3 in $C_6H_5CH_2R$, the product can be made by two different Friedel–Crafts reactions.



18.33

a.



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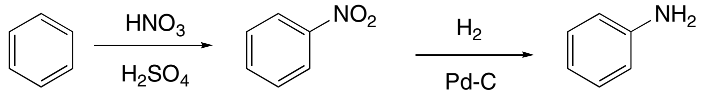

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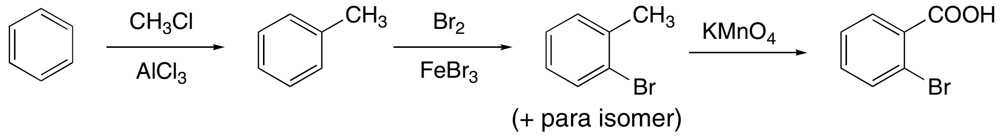
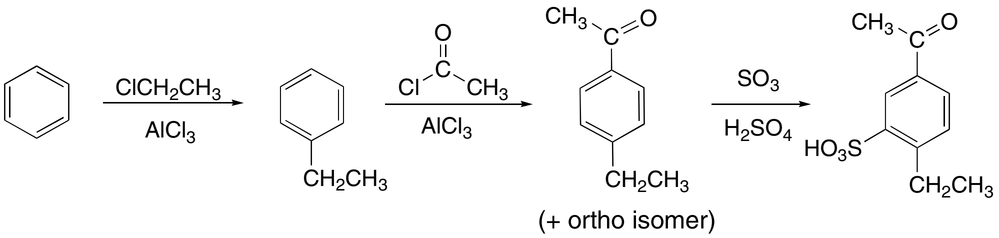


18.34

a.



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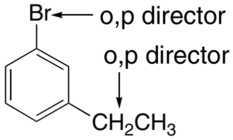
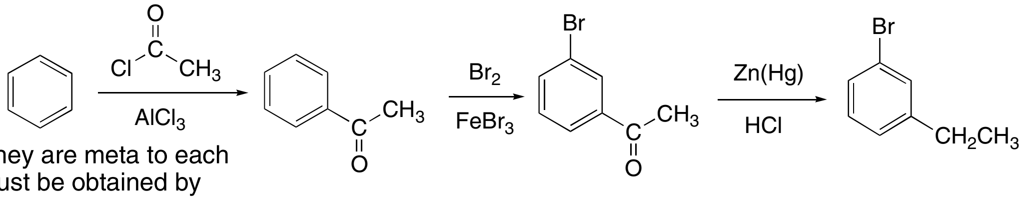


Both are o,p directors, but they are meta to each other. The alkyl group must be obtained by reduction of a carbonyl.



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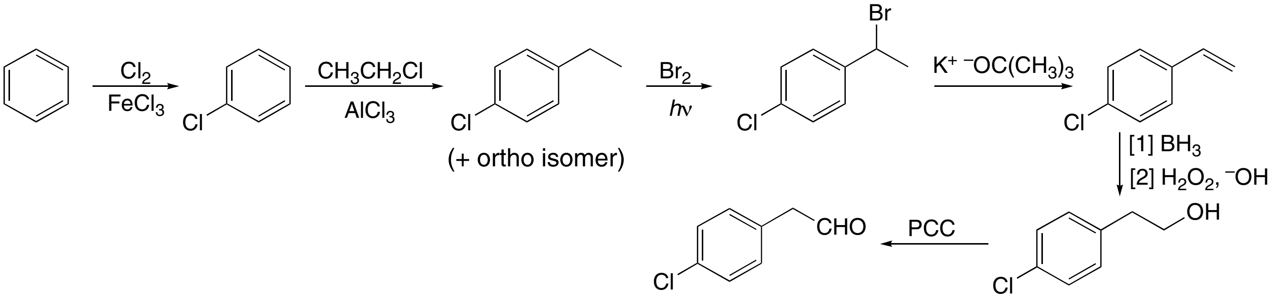
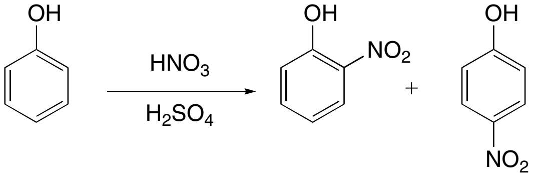


18.35 OH is an ortho, para director.

a.


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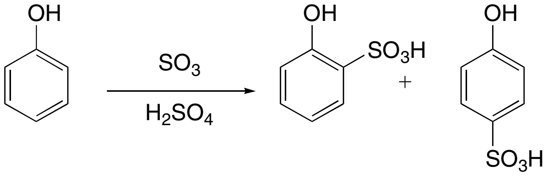

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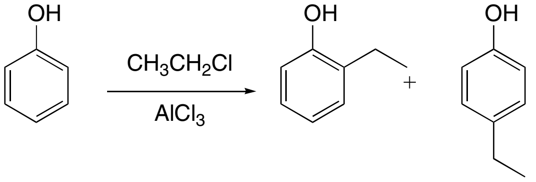

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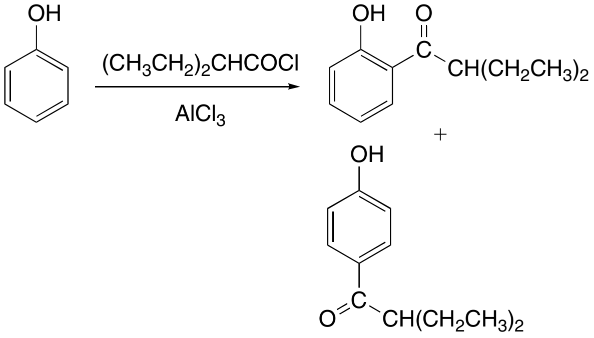
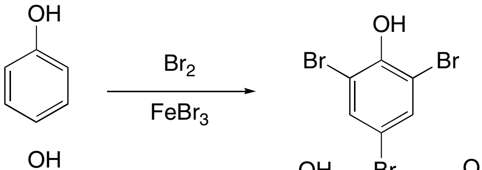


e.


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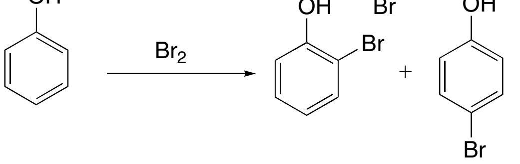

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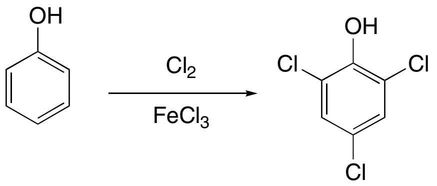

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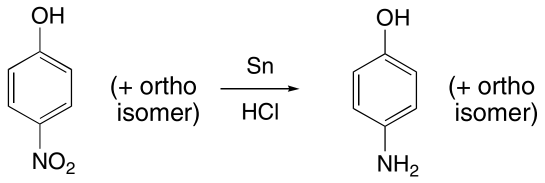

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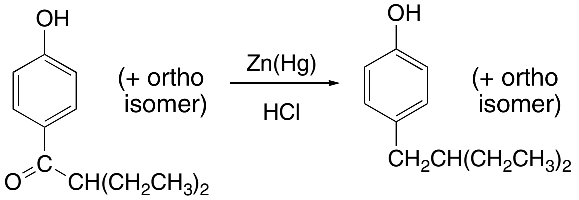

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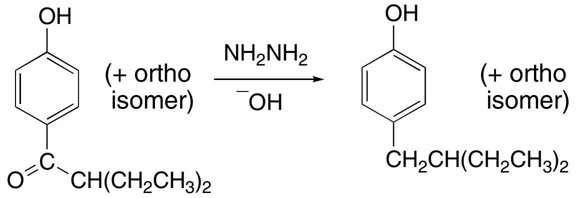
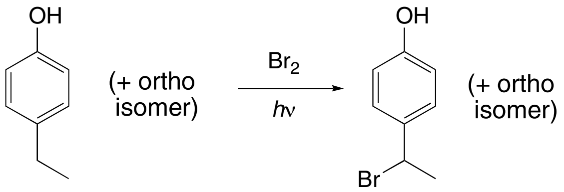
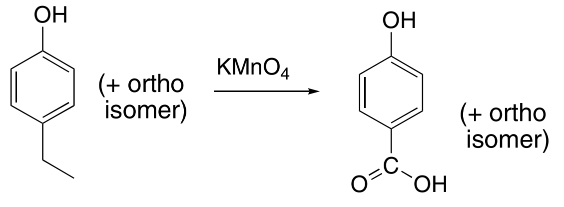
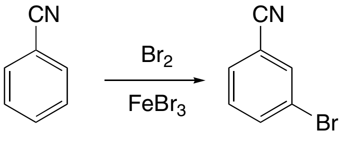


k.


l.


18.36 CN is a meta director that deactivates the benzene ring.

a.


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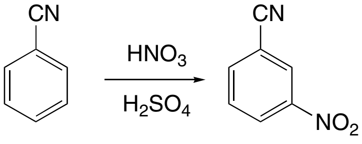

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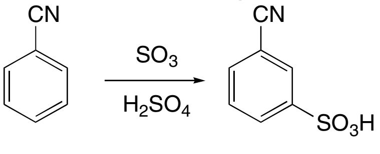

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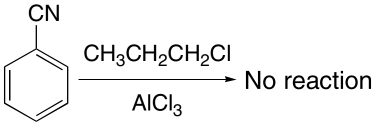

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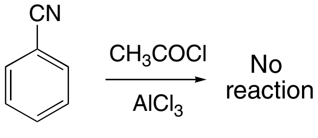
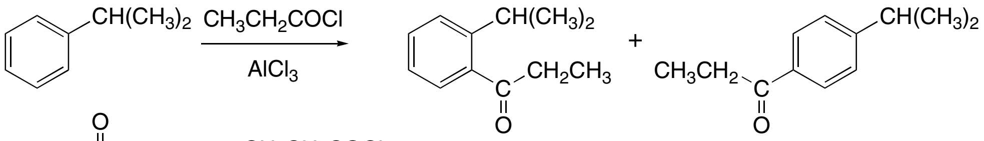


18.37

a.



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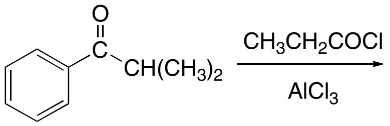
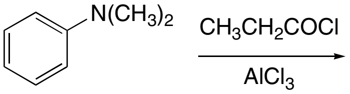


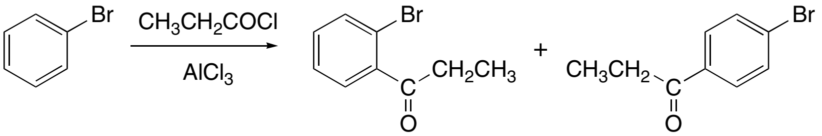
No reaction

c.



No Friedel–Crafts reaction

d.



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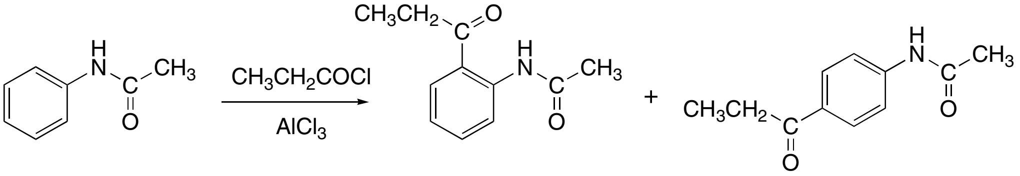
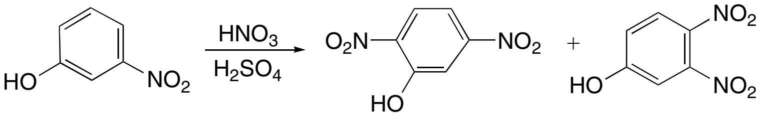


18.38

a.



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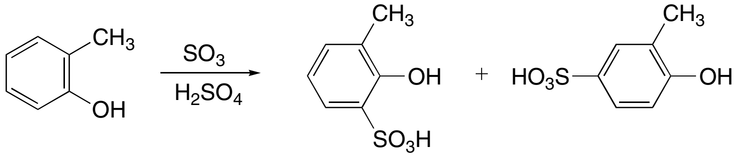

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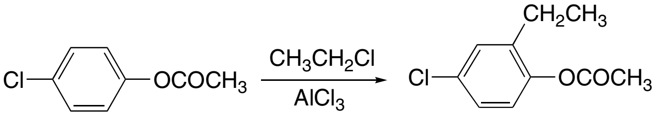

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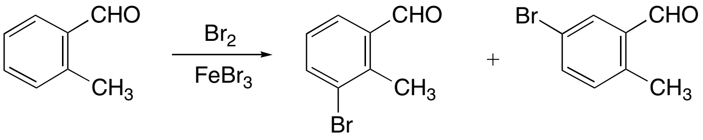

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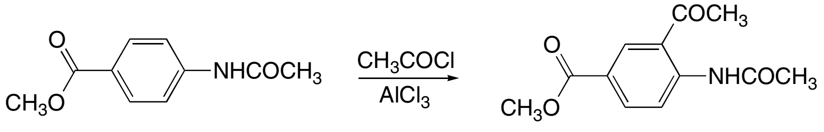

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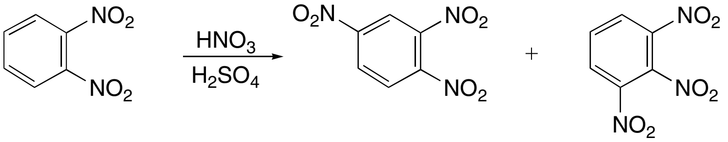

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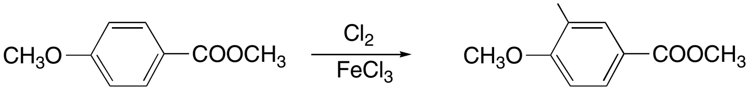

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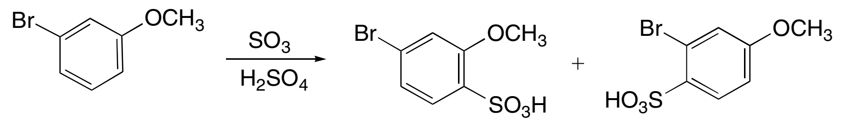
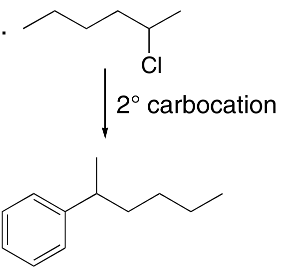


18.39 Watch out for rearrangements.

a.



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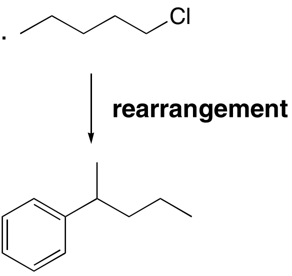

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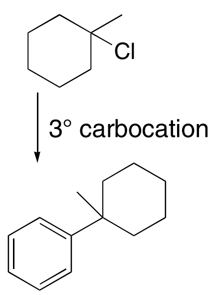

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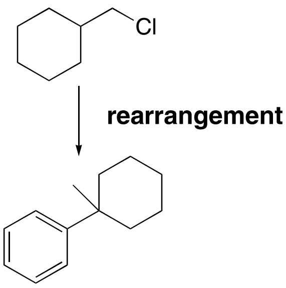
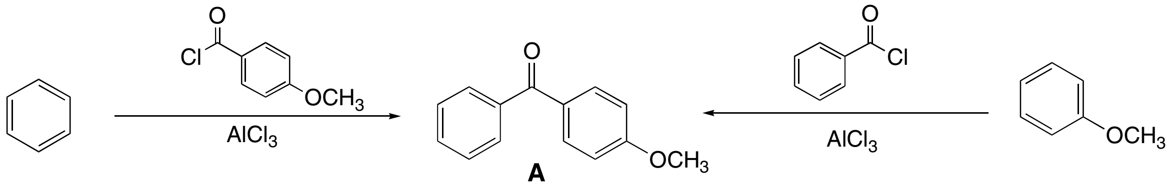
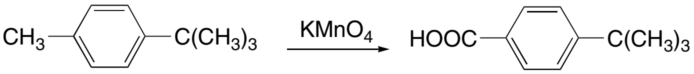


18.40

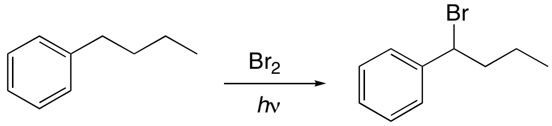


18.41

a.



b.



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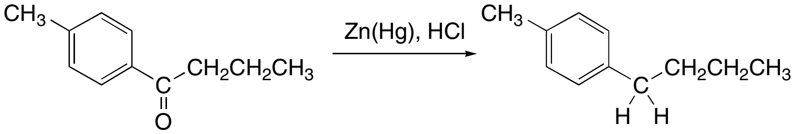

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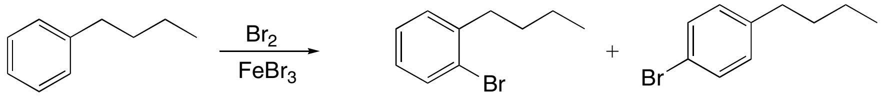
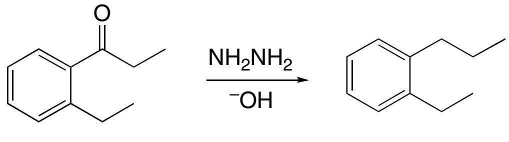
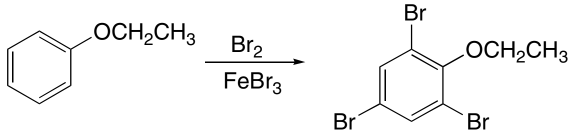


e.



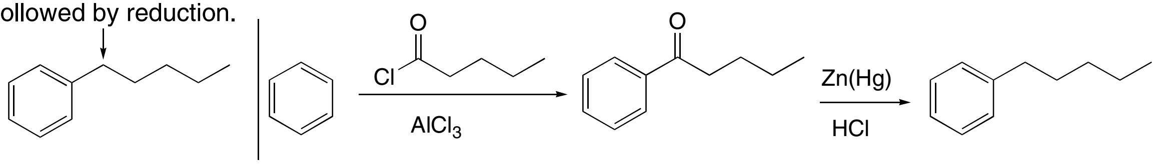
f.



18.42

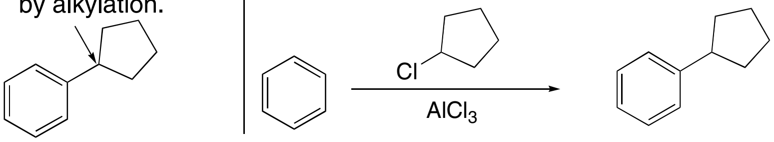
C bonded to 2 H's must use acylation followed by reduction.

a.

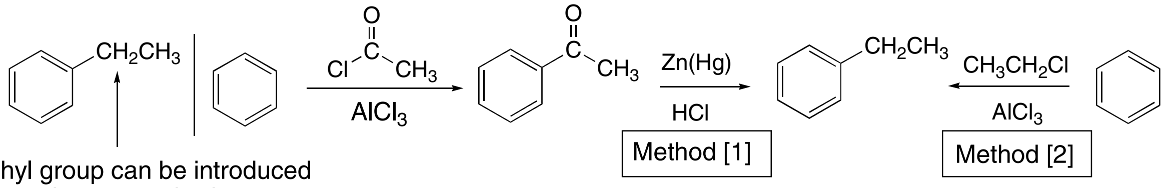


C bonded to 1 H can be added directly by alkylation.

b.

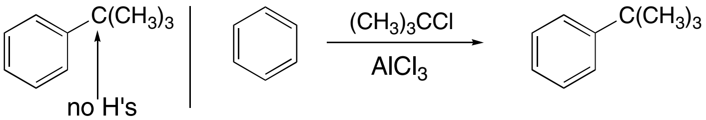


c.



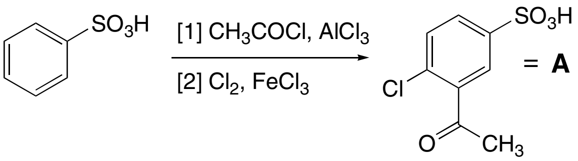
Ethyl group can be introduced by two methods.

d.



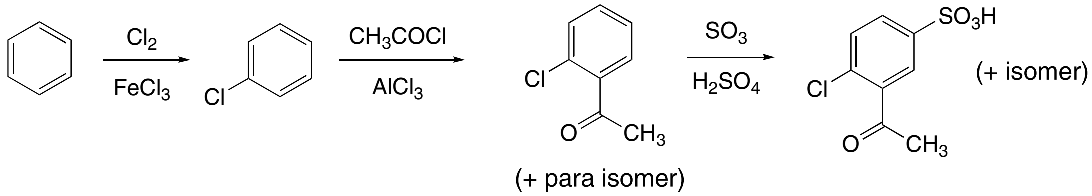
18.43

a.

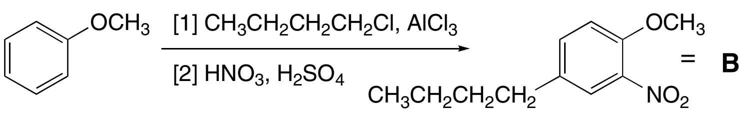


Step [1] won't work because a Friedel–Crafts reaction can't be done on a deactivated benzene ring, as is the case with the SO_3H substituent. Even if Step [1] did work, the second step would introduce Cl meta to SO_3H, not para as drawn.

Alternate synthesis:

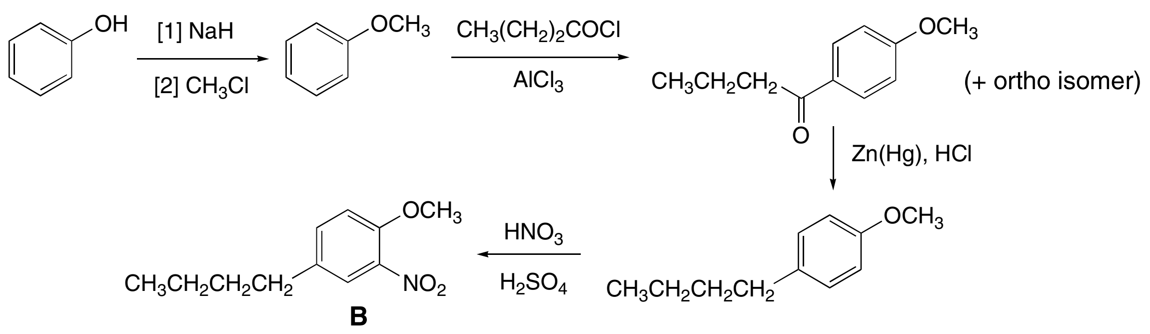


b.



Step [1] involves a Friedel–Crafts alkylation using a 1° alkyl halide that will undergo rearrangement, so that a butyl group will not be introduced as a side chain.

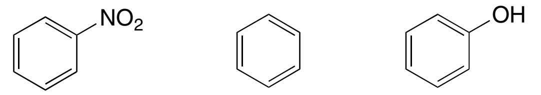
Alternate synthesis:



(+ ortho isomer)

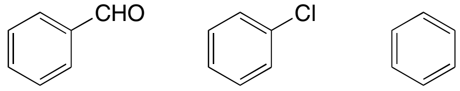
18.44 Use the directions from Answer 18.19 to rank the compounds.

a.



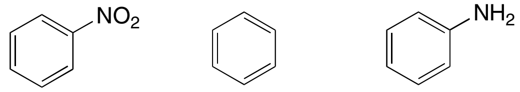
least reactive **intermediate reactivity** **most reactive**

b.



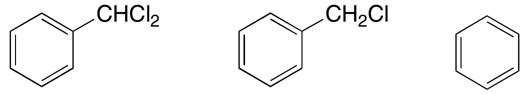
least reactive **intermediate reactivity** **most reactive**

c.



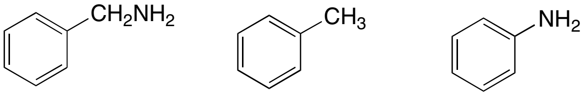
least reactive **intermediate reactivity** **most reactive**

d.



least reactive **intermediate reactivity** **most reactive**

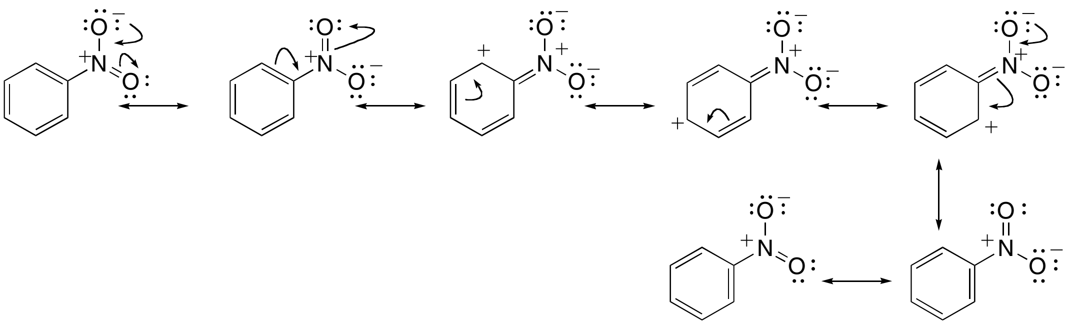
e.

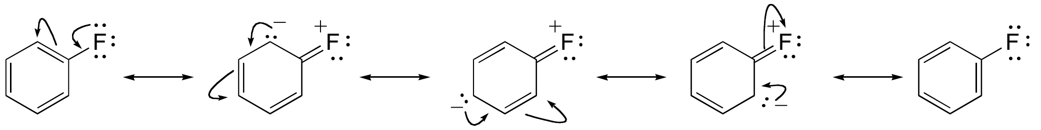


least reactive **intermediate reactivity** **most reactive**

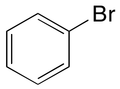
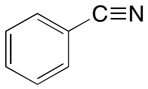
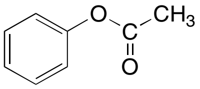
18.45 Electron-withdrawing groups place a positive charge in the benzene ring. Draw the resonance structures to show how NO_2 puts a positive charge in the ring, giving it an electron-withdrawing resonance effect. Electron-donating groups place a negative charge in the benzene ring. Draw the resonance structures to show how F puts a negative charge in the ring, giving it an electron-donating resonance effect.

a.

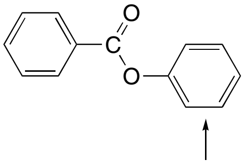


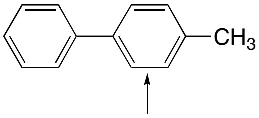
b.


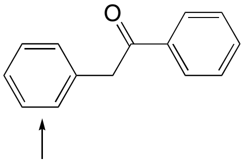
18.46

[1] 	[2] 	[3] 
a. withdraw	a. withdraw	a. withdraw
b. donate	b. withdraw	b. donate
c. less	c. less	c. more
d. deactivate	d. deactivate	d. activate

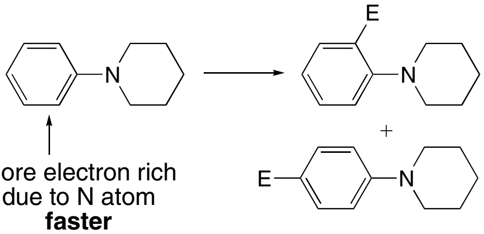
18.47

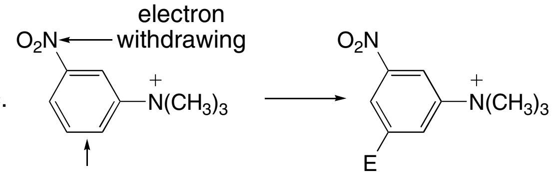
a.

more electron rich
due to O atom
more reactive

b.

more electron rich
due to CH_3 group
more reactive

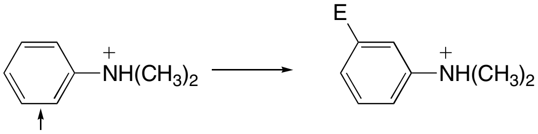
c.

more electron rich
due to C atom
more reactive

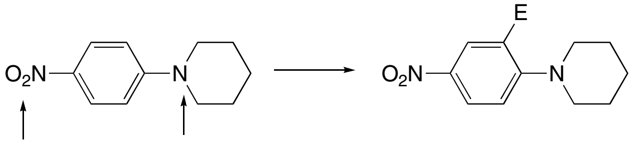
18.48

a.

more electron rich
due to N atom
faster

c.


less electron rich
due to (+) charge on N and
electron-withdrawing NO_2 group
slower

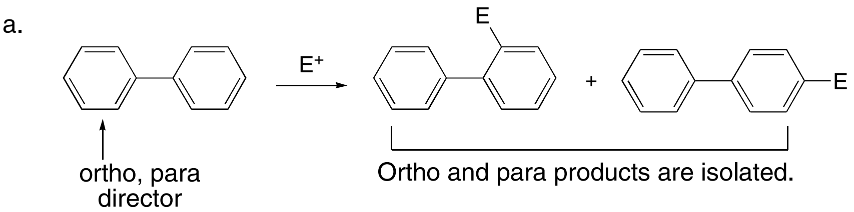
b.

less electron rich
due to (+) charge on N
slower

d.


Effects cancel out.
similar in reactivity to benzene

18.49

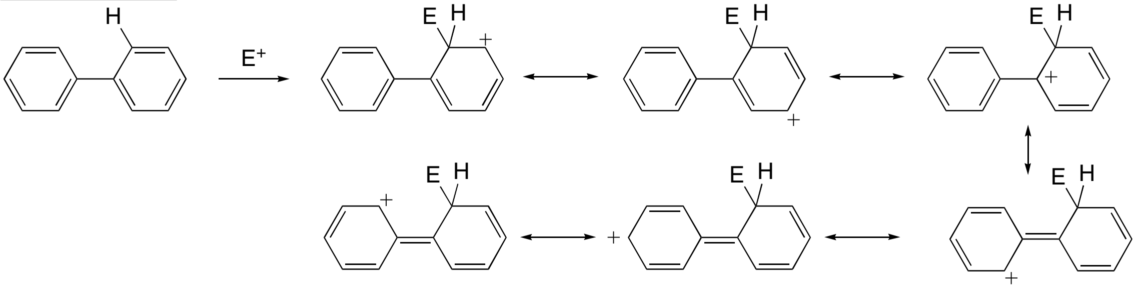
a.



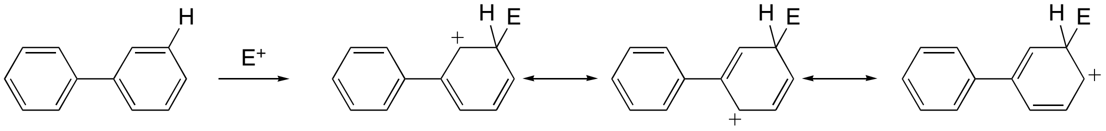
A benzene ring is an electron-rich substituent that stabilizes an intermediate positive charge by an electron-donating resonance effect. As a result, it activates a benzene ring toward reaction with electrophiles.

With ortho and para attack there is additional resonance stabilization that delocalizes the positive charge onto the second benzene ring. Such additional stabilization is not possible with meta attack.

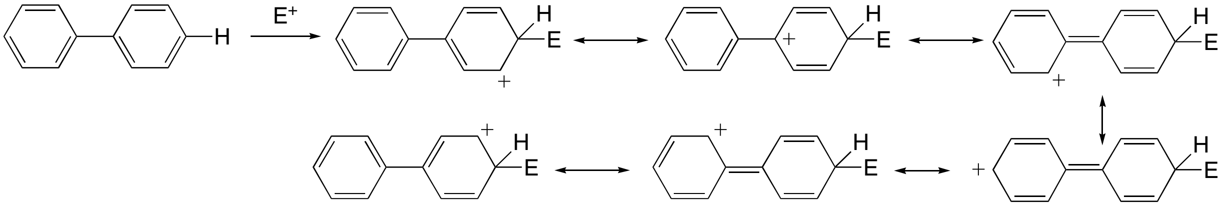
Ortho attack:



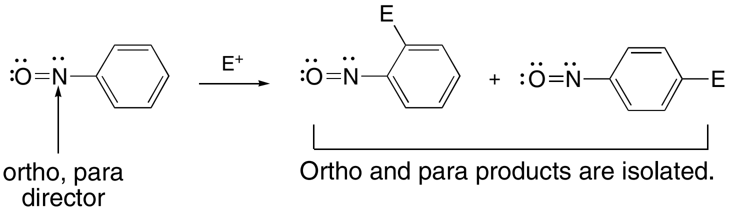
Meta attack:



Para attack:

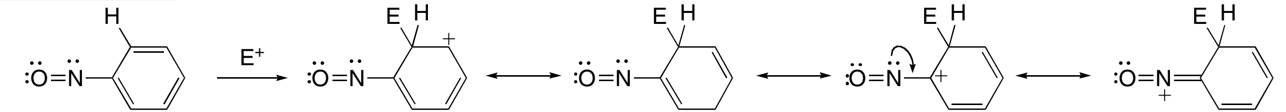


b.



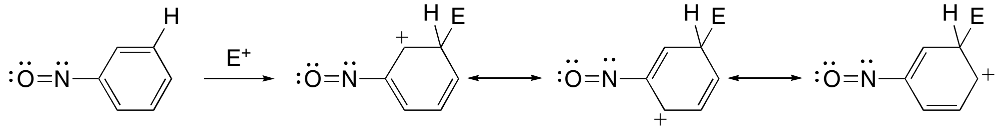
With ortho and para attack there is additional resonance stabilization that delocalizes the positive charge onto the nitroso group. Such additional stabilization is not possible with meta attack. This makes –NO an ortho, para director. Since the N atom bears a partial (+) charge (because it is bonded to a more electronegative O atom), the –NO group inductively withdraws electron density, thus deactivating the benzene ring towards electrophilic attack. In this way, the –NO group resembles the halogens. Thus, the electron-donating resonance effect makes –NO an o,p director, but the electron-withdrawing inductive effect makes it a deactivator.

Ortho attack:

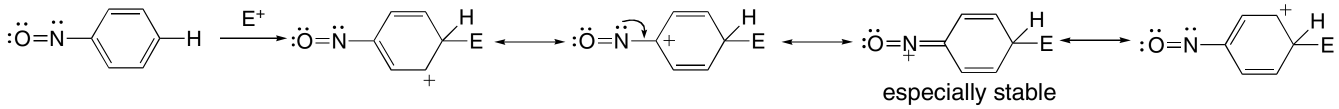


especially stable

Meta attack:

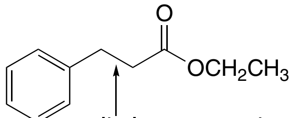


Para attack:

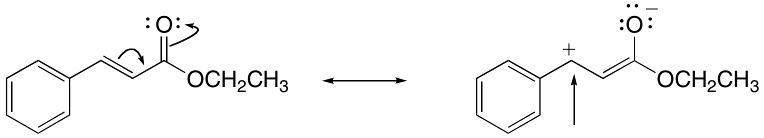


especially stable

18.50

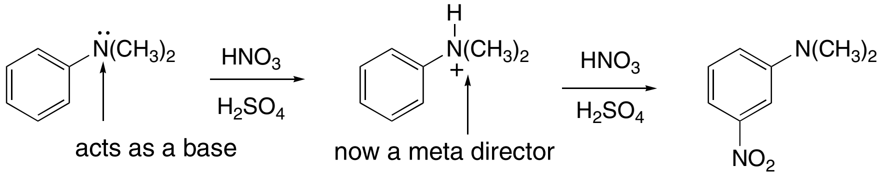


alkyl group on the benzene ring
R stabilizes (+) charges on the o,p positions by an electron-donating inductive effect. This group behaves like any other R group so that ortho and para products are formed in electrophilic aromatic substitution.



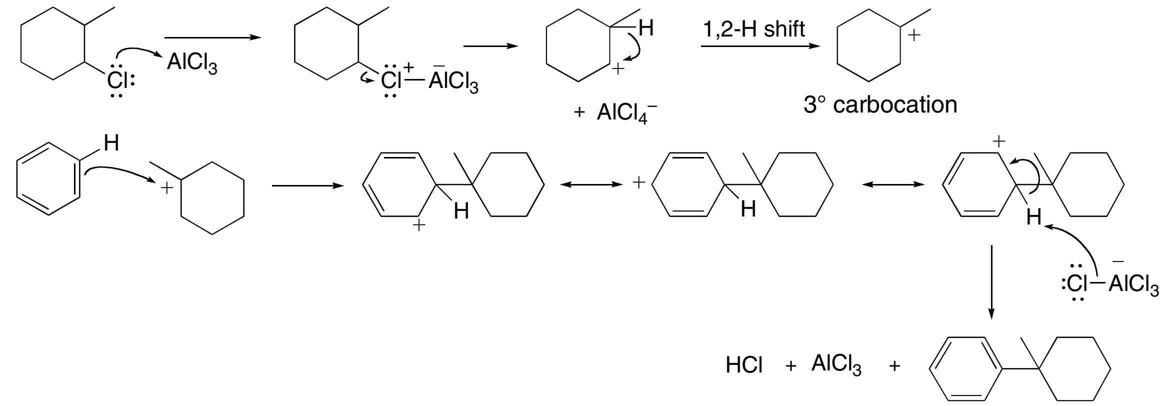
(+) charge on atom bonded to the benzene ring
Drawing resonance structures in electrophilic aromatic substitution results in especially unstable structures for attack at the o,p positions—two (+) charges on adjacent atoms. This doesn't happen with meta attack, so meta attack is preferred. This is identical to the situation observed with all meta directors.

18.51 Under the acidic conditions of nitration, the N atom of the starting material gets protonated, so the atom directly bonded to the benzene ring bears a (+) charge. This makes it a meta director, so the new NO_2 group is introduced meta to it.

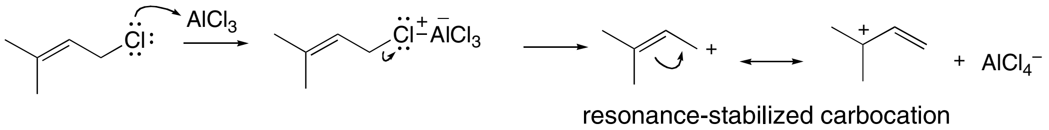


18.52

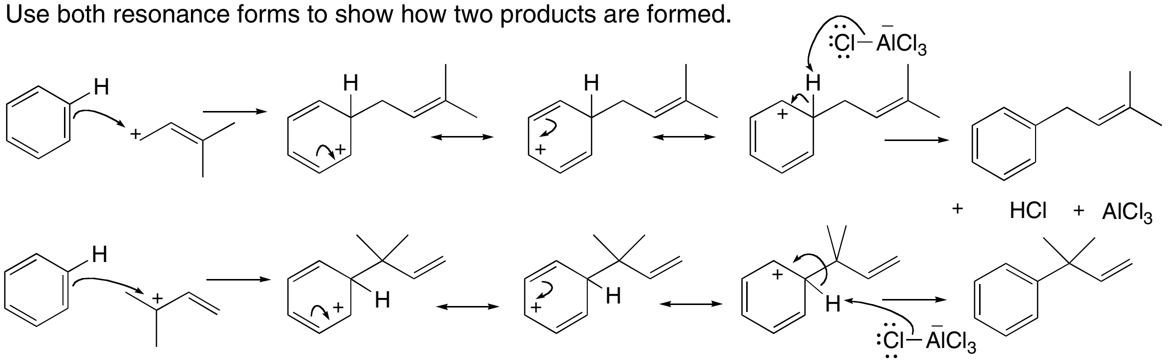
a.



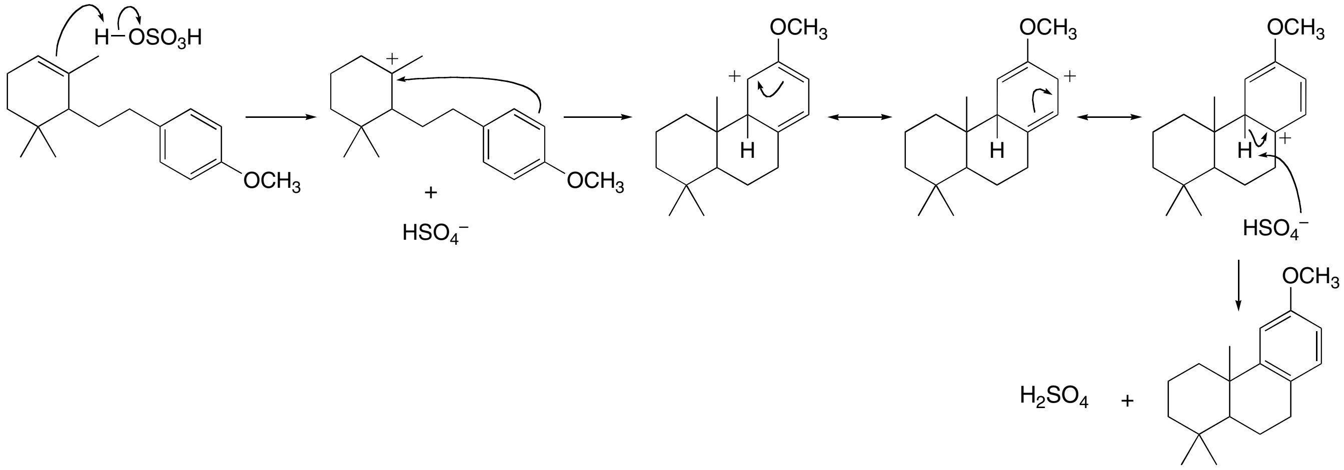
b.



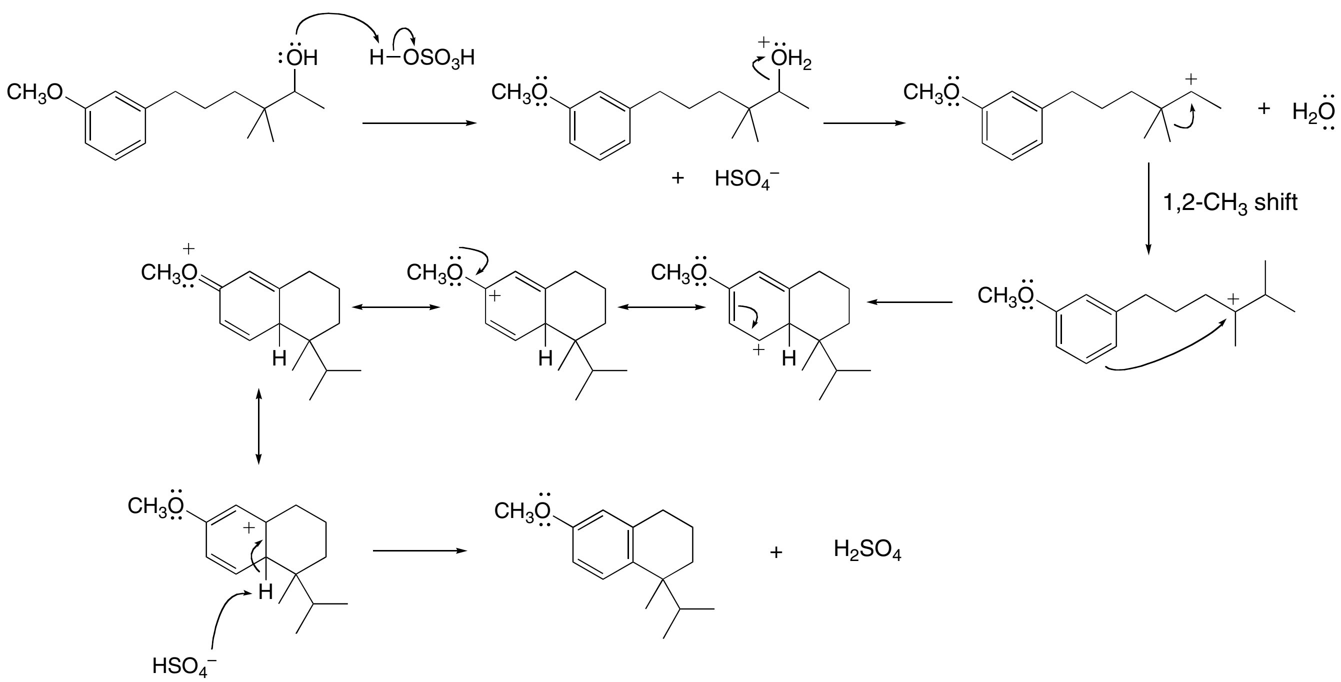
Use both resonance forms to show how two products are formed.



18.53

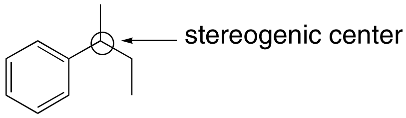


18.54

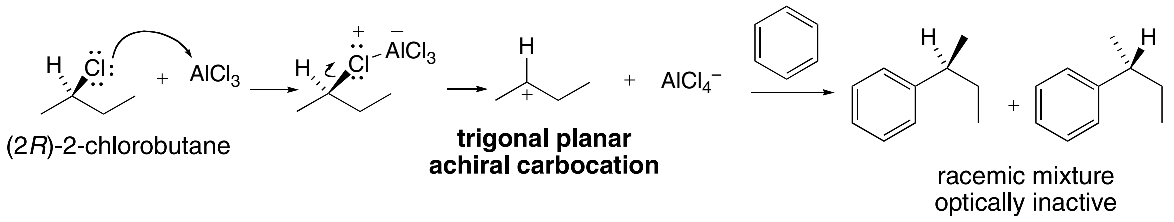


18.55

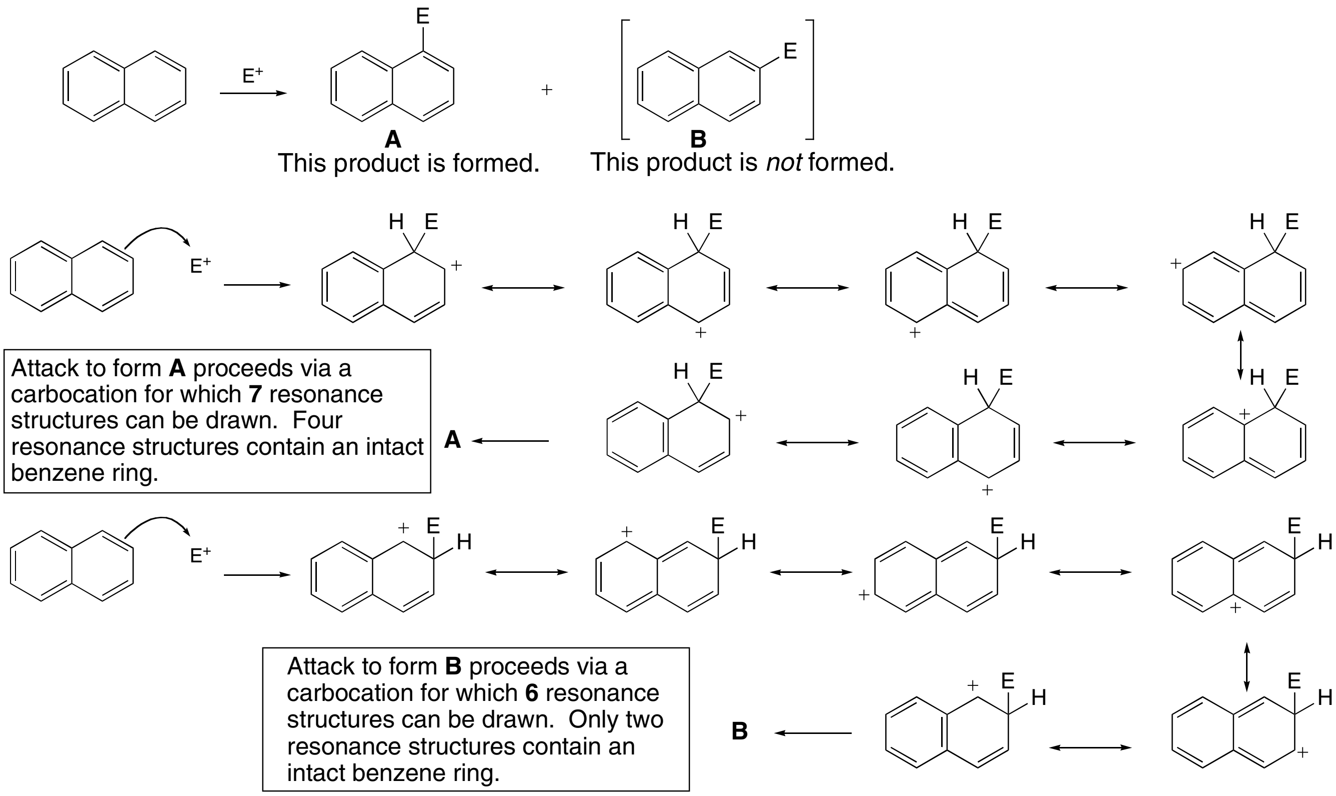
a. The product has one stereogenic center.



b. The mechanism for Friedel–Crafts alkylation with this 2° halide involves formation of a trigonal planar carbocation. Since the carbocation is achiral, it reacts with benzene with equal probability from two possible directions (above and below) to afford an optically inactive, racemic mixture of two products.



18.56

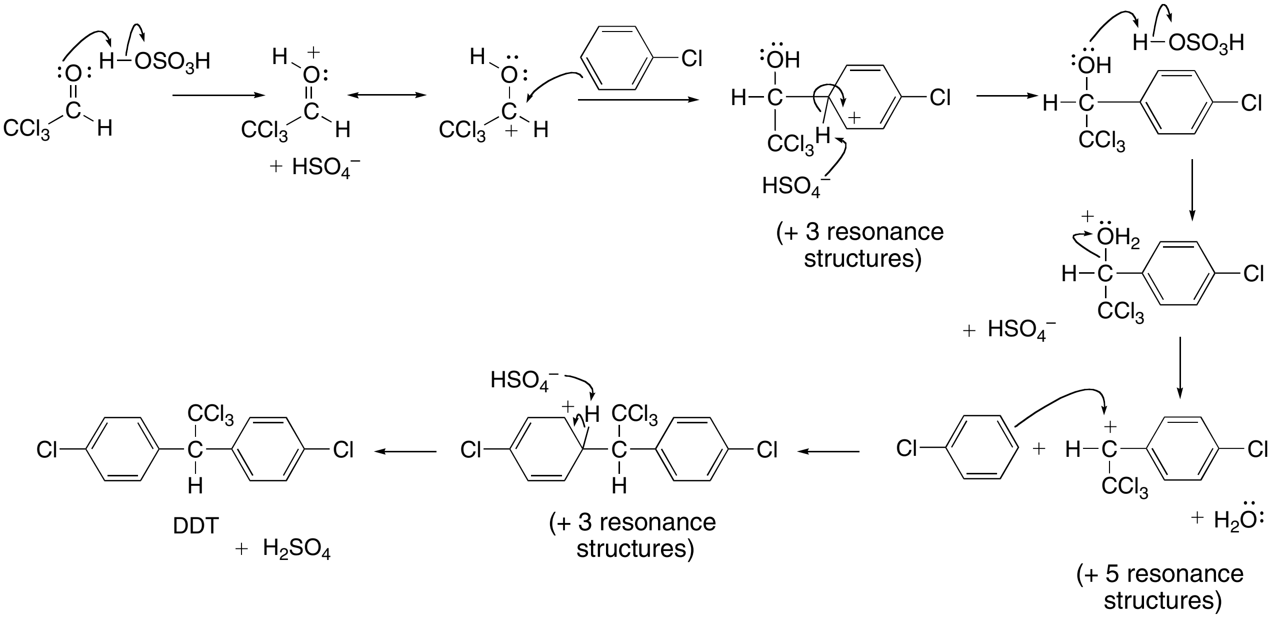


Attack to form **A** proceeds via a carbocation for which **7** resonance structures can be drawn. Four resonance structures contain an intact benzene ring.

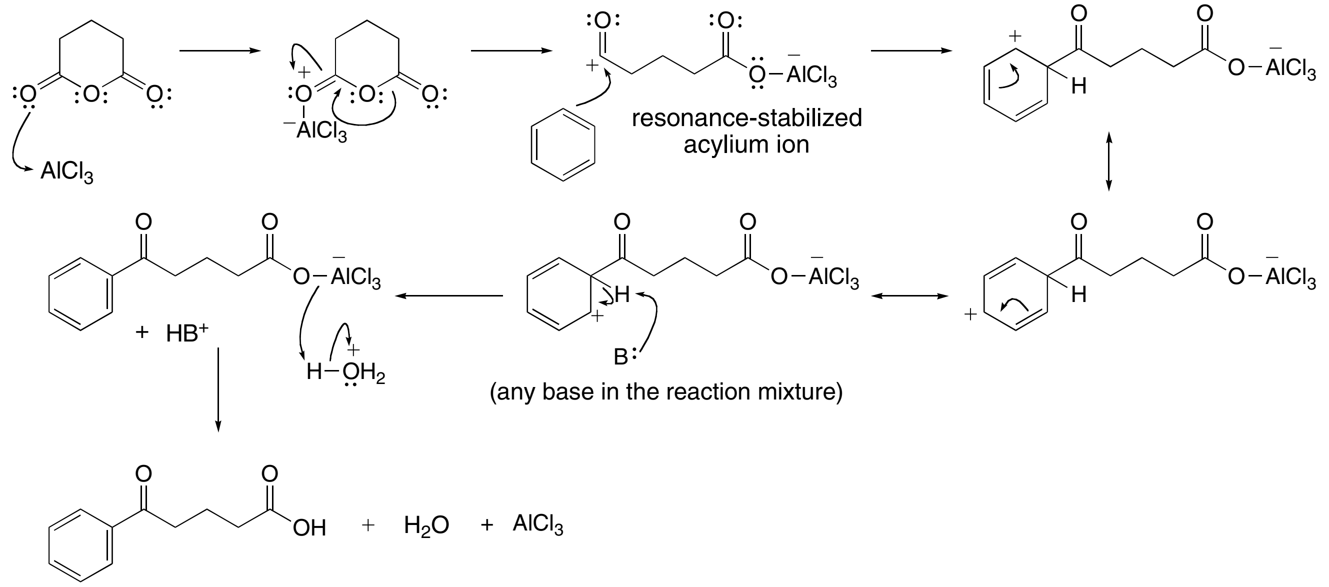
Attack to form **B** proceeds via a carbocation for which **6** resonance structures can be drawn. Only two resonance structures contain an intact benzene ring.

A reaction that occurs by way of the more stable carbocation is preferred so product **A** is formed.

18.57

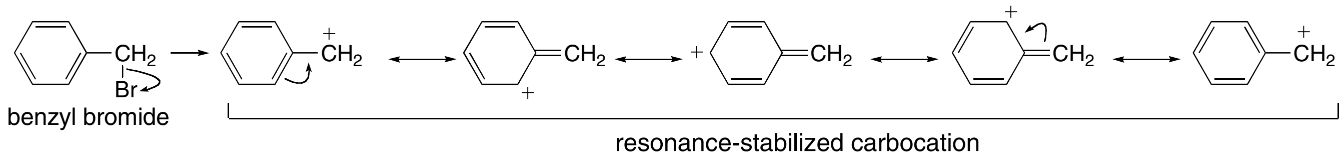


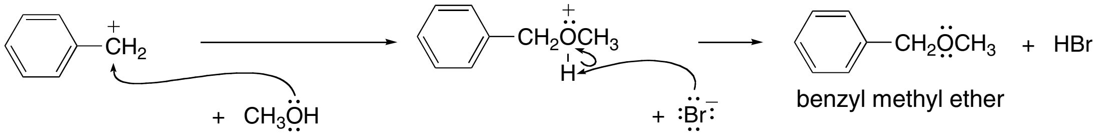
18.58

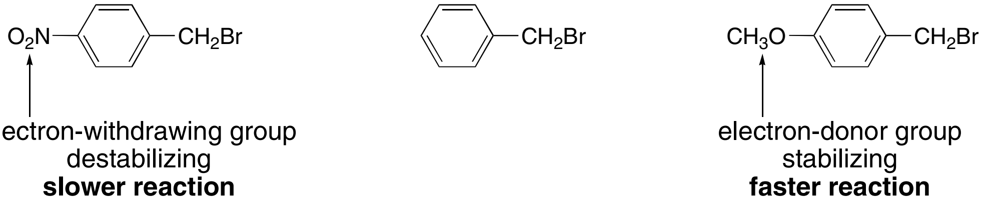


18.59 Benzyl bromide forms a resonance-stabilized intermediate that allows it to react rapidly under S_N1 conditions.

Formation of a resonance-stabilized carbocation:

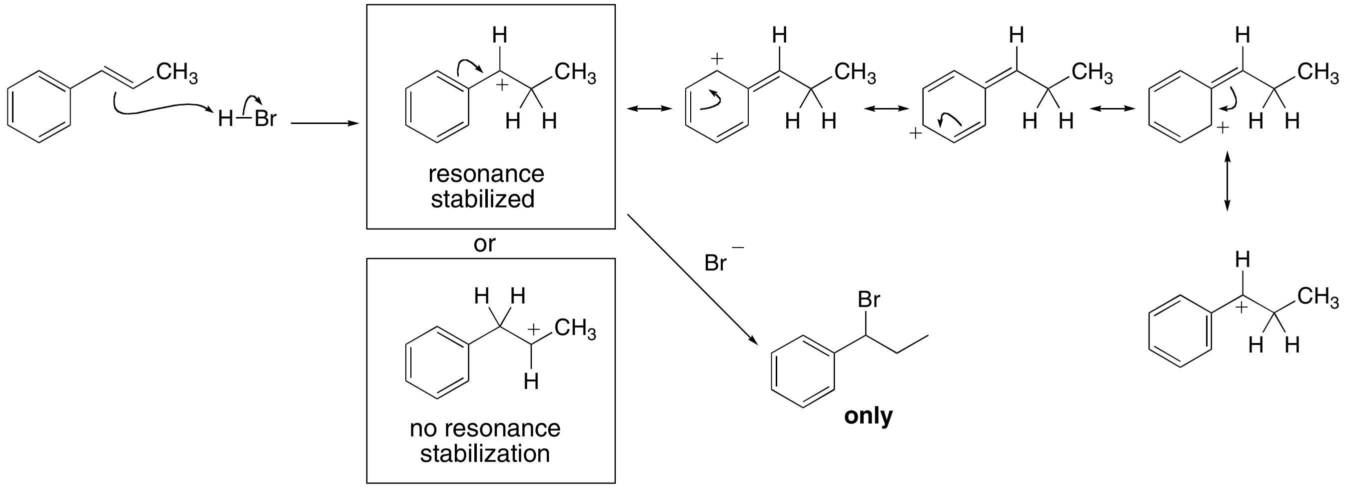






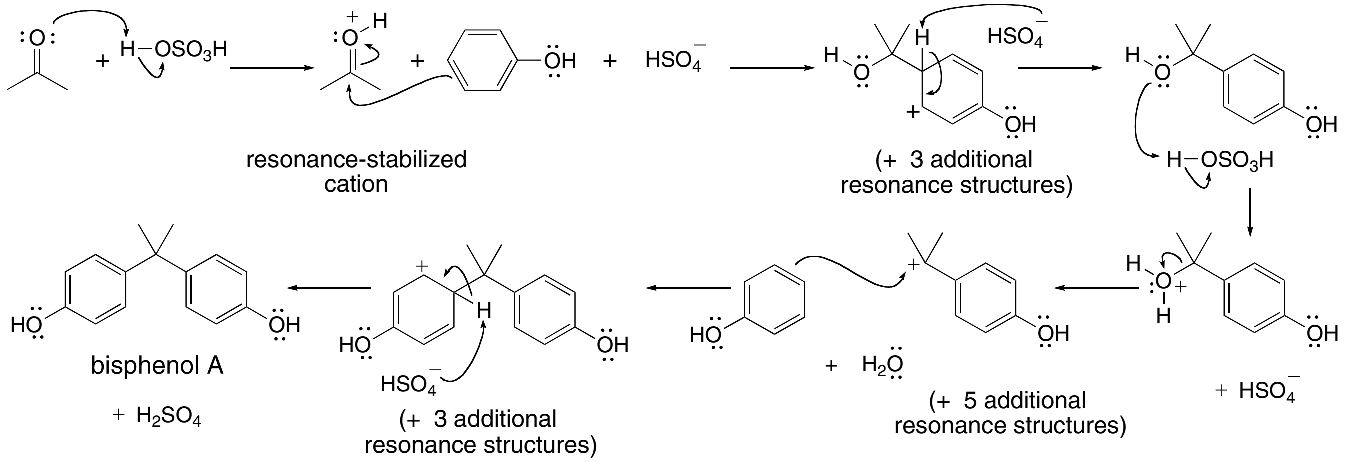
The electron-withdrawing NO_2 group will destabilize the carbocation so the benzylic halide will be less reactive, while the electron-donating OCH_3 group will stabilize the carbocation, so the benzylic halide will be more reactive.

18.60 Addition of HBr will afford only one alkyl bromide because the intermediate carbocation leading to its formation is resonance stabilized.



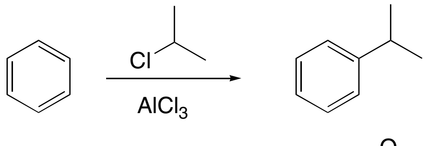
As a result, this carbocation does not form.

18.61

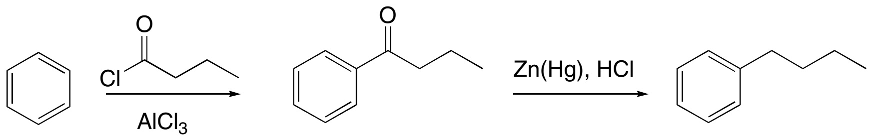


18.62

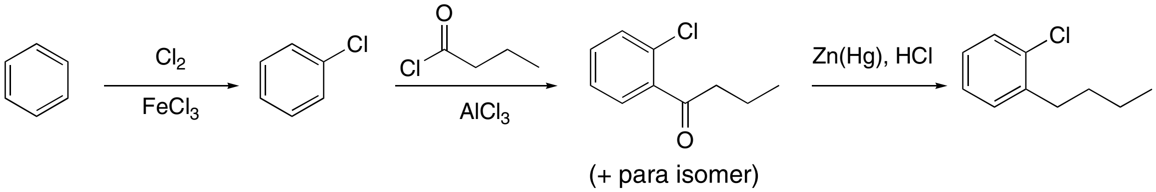
a.



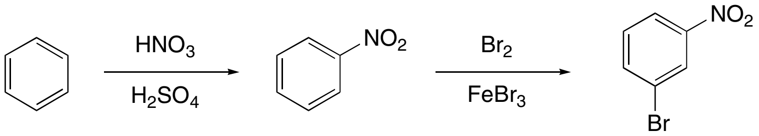
b.



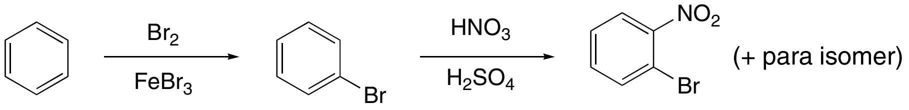
c.



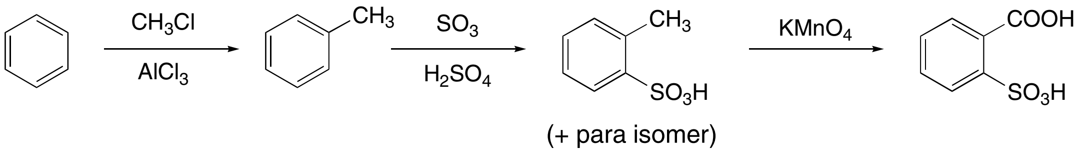
d.


HNO3
H2SO4
NO2
Br2
FeBr3
NO2
Br

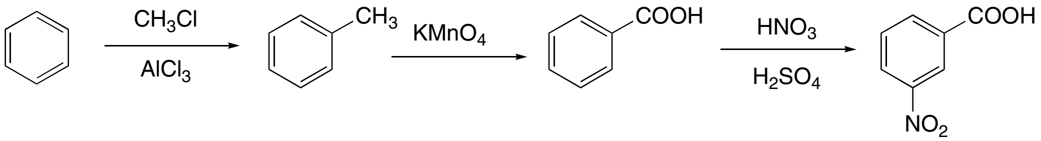
e.


Br2
FeBr3
Br
HNO3
H2SO4
NO2
Br
(+ para isomer)

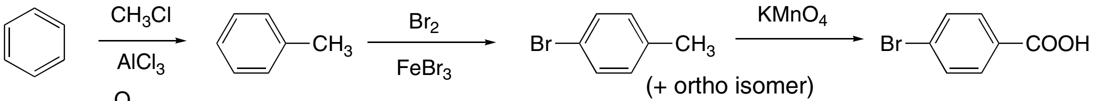
f.


CH3Cl
AlCl3
CH3
SO3
H2SO4
CH3
SO3H
(+ para isomer)
KMnO4
COOH
SO3H

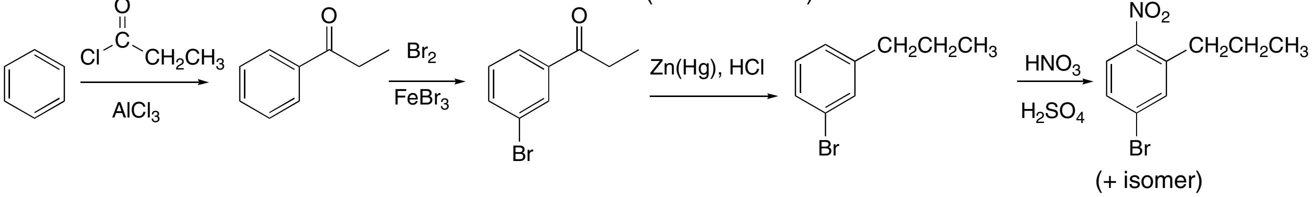
g.


CH3Cl
AlCl3
CH3
KMnO4
COOH
HNO3
H2SO4
COOH
NO2

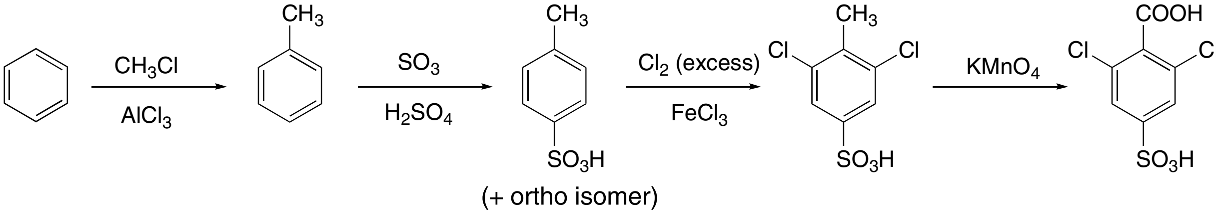
h.


CH3Cl
AlCl3
CH3
Br2
FeBr3
Br
CH3
(+ ortho isomer)
KMnO4
Br
COOH

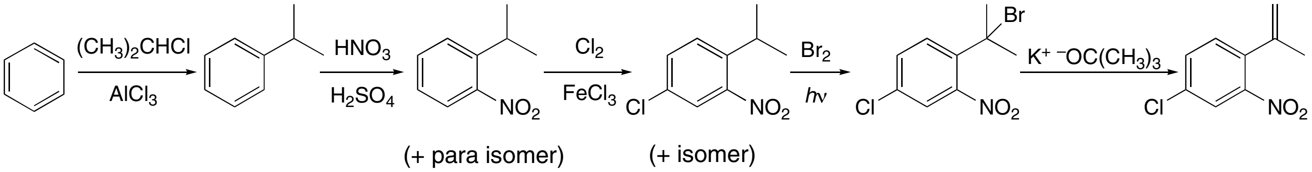
i.


O
Cl
C
CH2CH3
AlCl3
O
Br2
FeBr3
O
Br
Zn(Hg), HCl
CH2CH2CH3
Br
HNO3
H2SO4
NO2
CH2CH2CH3
Br
(+ isomer)

j.

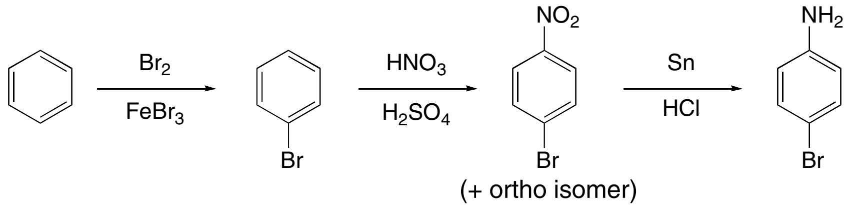

CH3Cl
AlCl3
CH3
SO3
H2SO4
CH3
SO3H
(+ ortho isomer)
Cl2 (excess)
FeCl3
CH3
Cl
Cl
SO3H
KMnO4
COOH
Cl
Cl
SO3H

k.

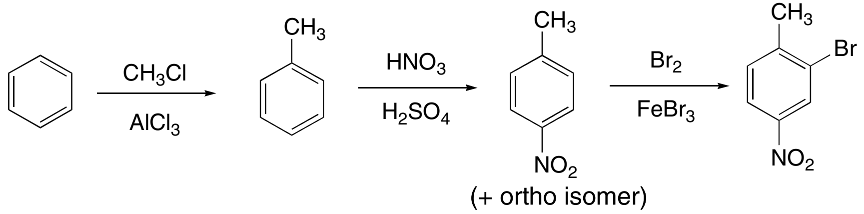

(CH3)2CHCl
AlCl3
HNO3
H2SO4
NO2
(+ para isomer)
Cl2
FeCl3
Cl
NO2
(+ isomer)
Br2
hν
Br
Cl
NO2
K+ −OC(CH3)3
Cl
NO2

18.63

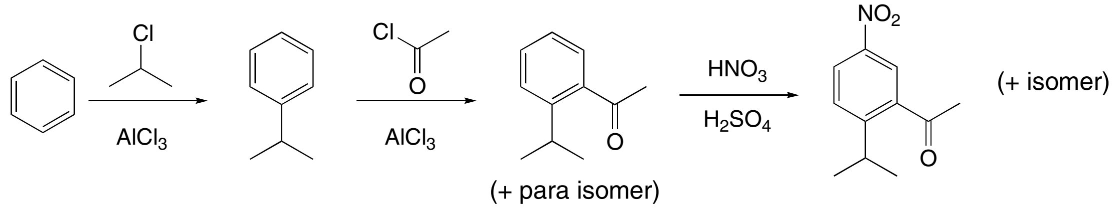
a.



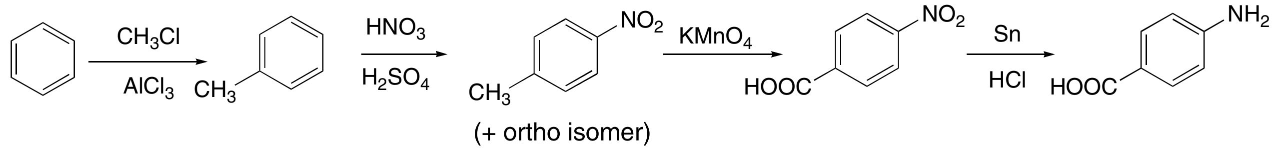
b.



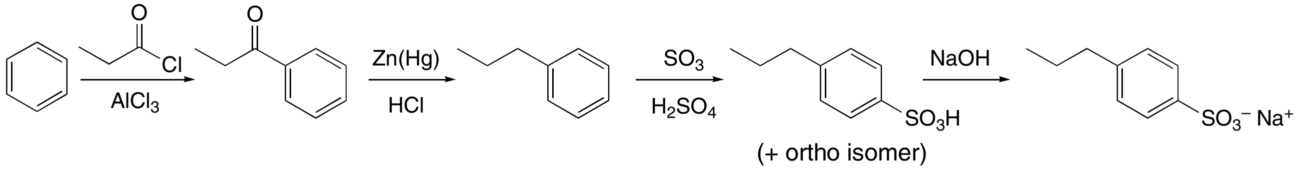
c.



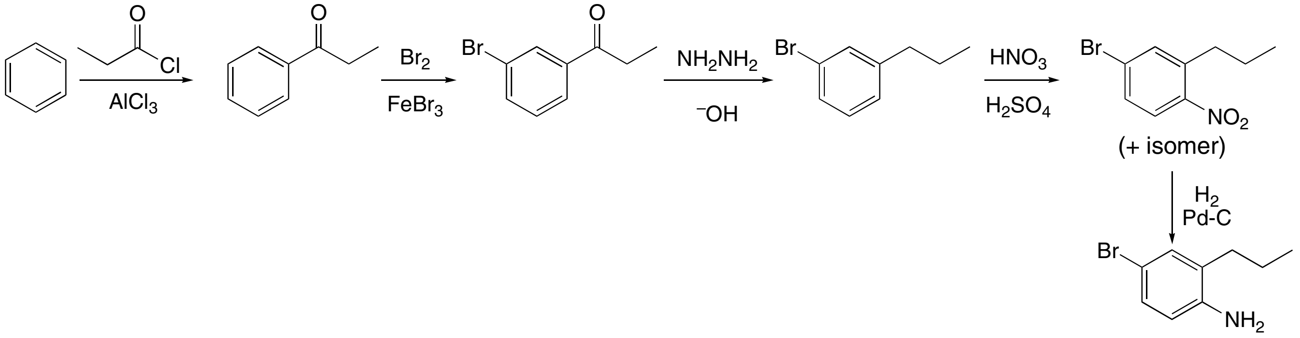
d.



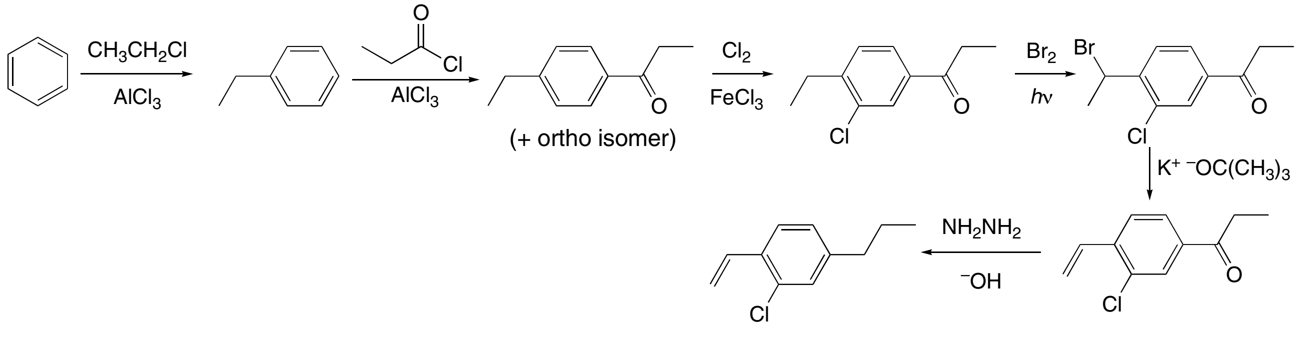
e.



f.

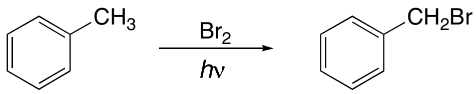


g.

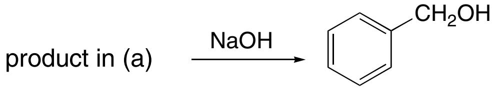


18.64

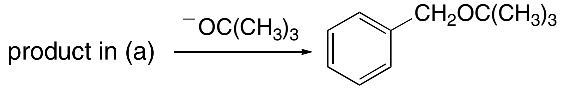
a.



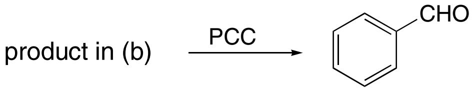
b.



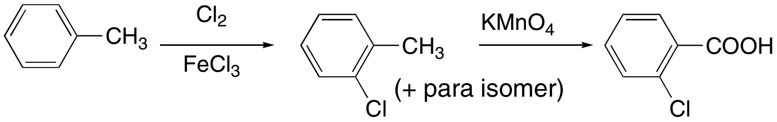
c.



d.

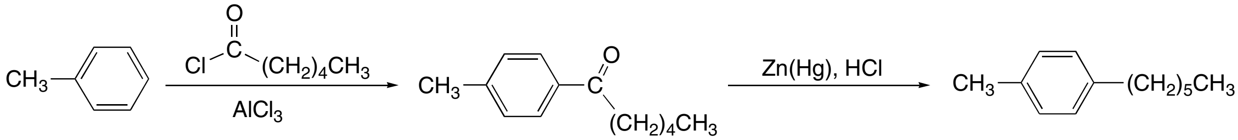


e.



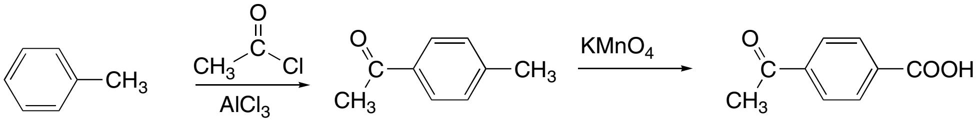
(+ para isomer)

f.



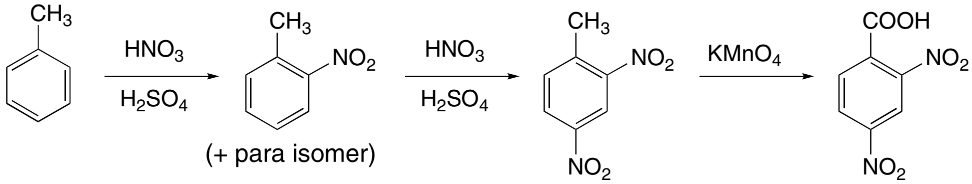
(+ ortho isomer)

g.



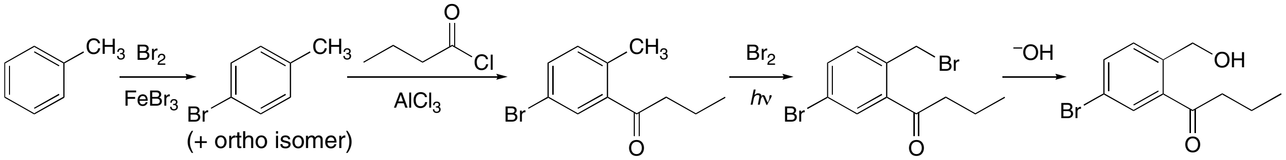
(+ ortho isomer)

h.



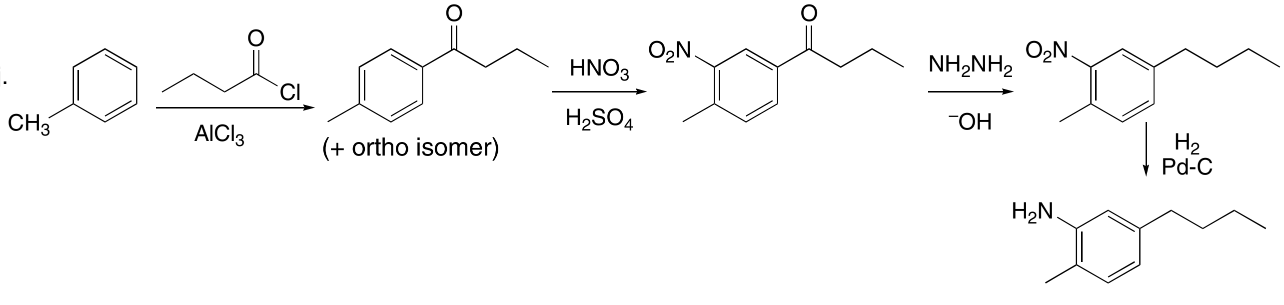
(+ para isomer)

i.



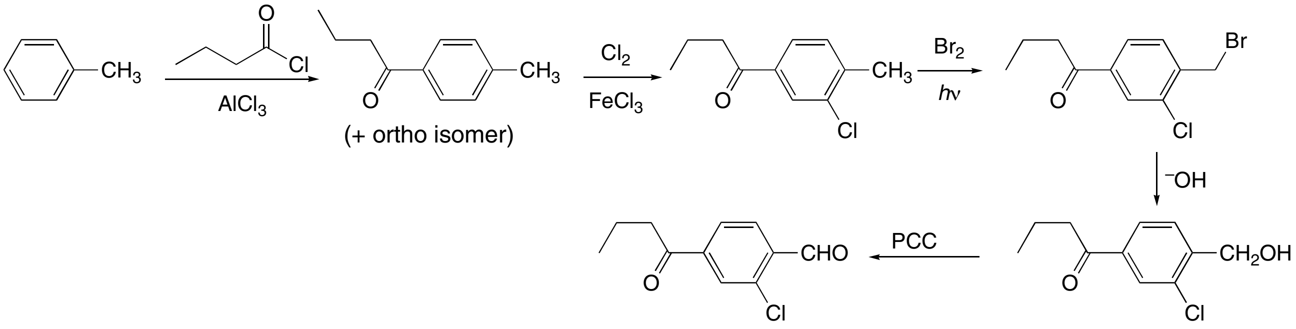
(+ ortho isomer)

j.



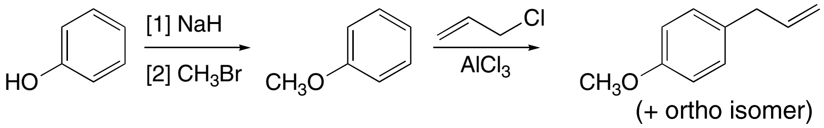
(+ ortho isomer)

k.

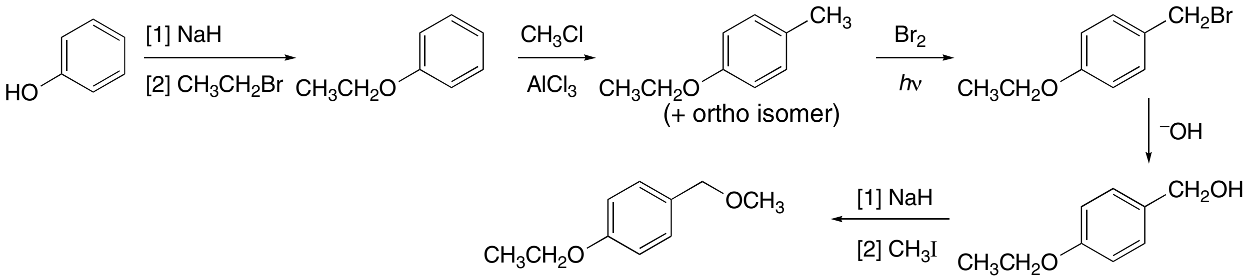


18.65

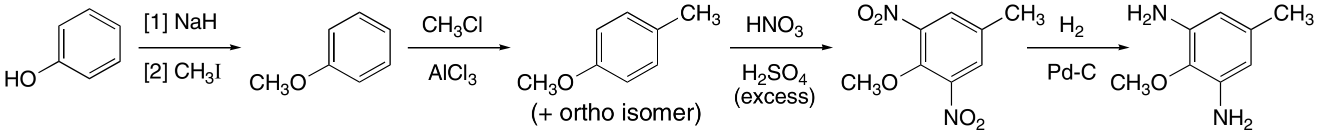
a.



b.

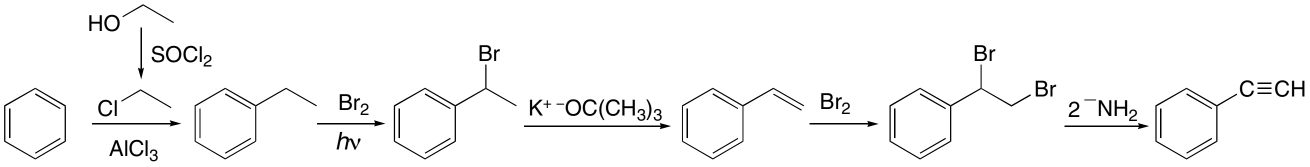


c.

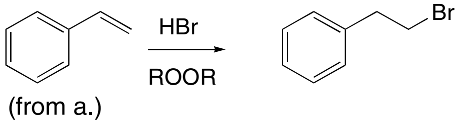


18.66

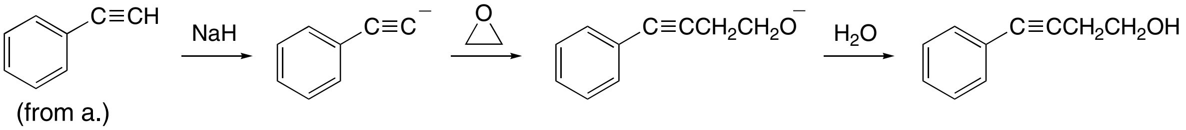
a.



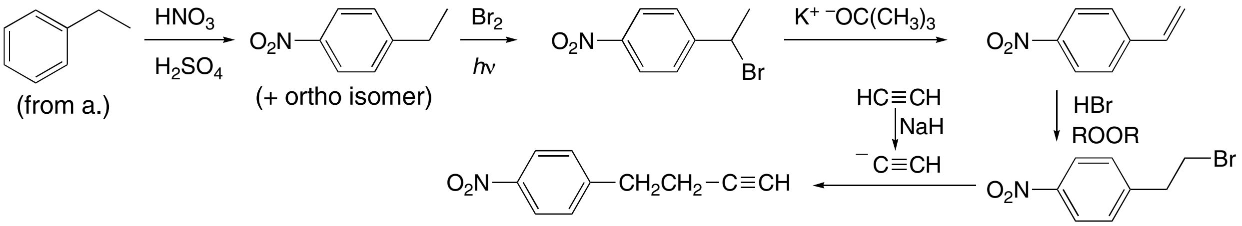
b.



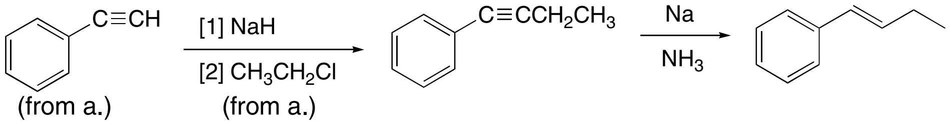
c.



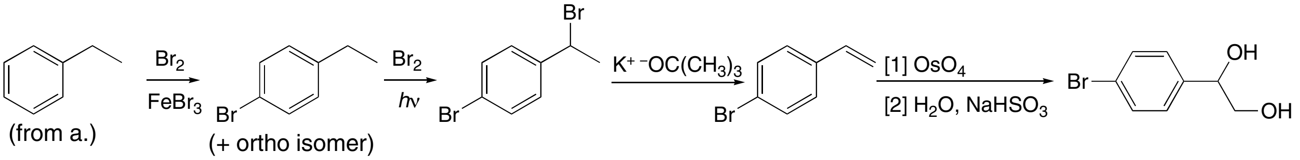
d.



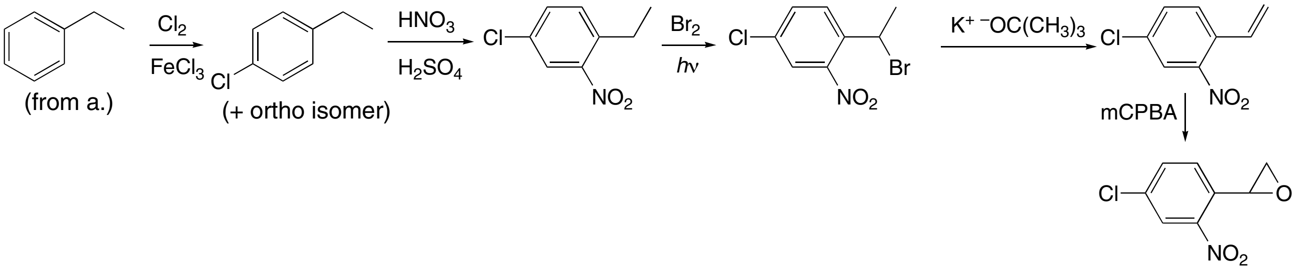
e.



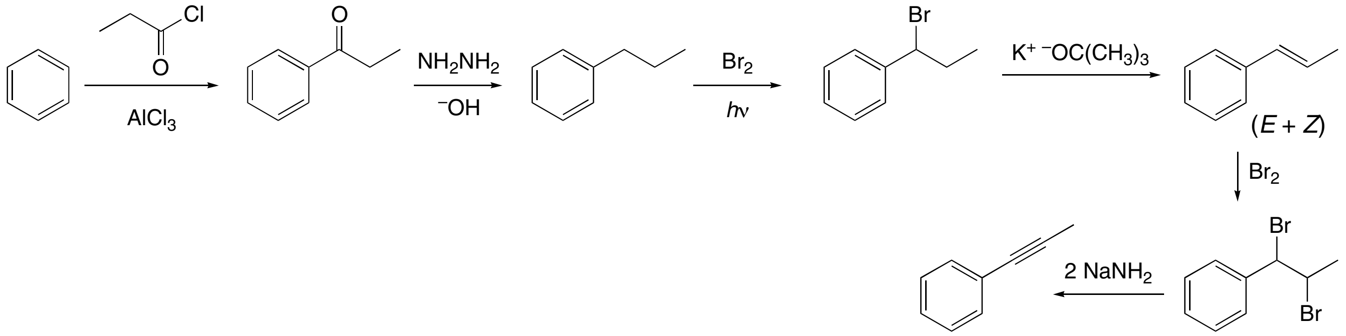
f.



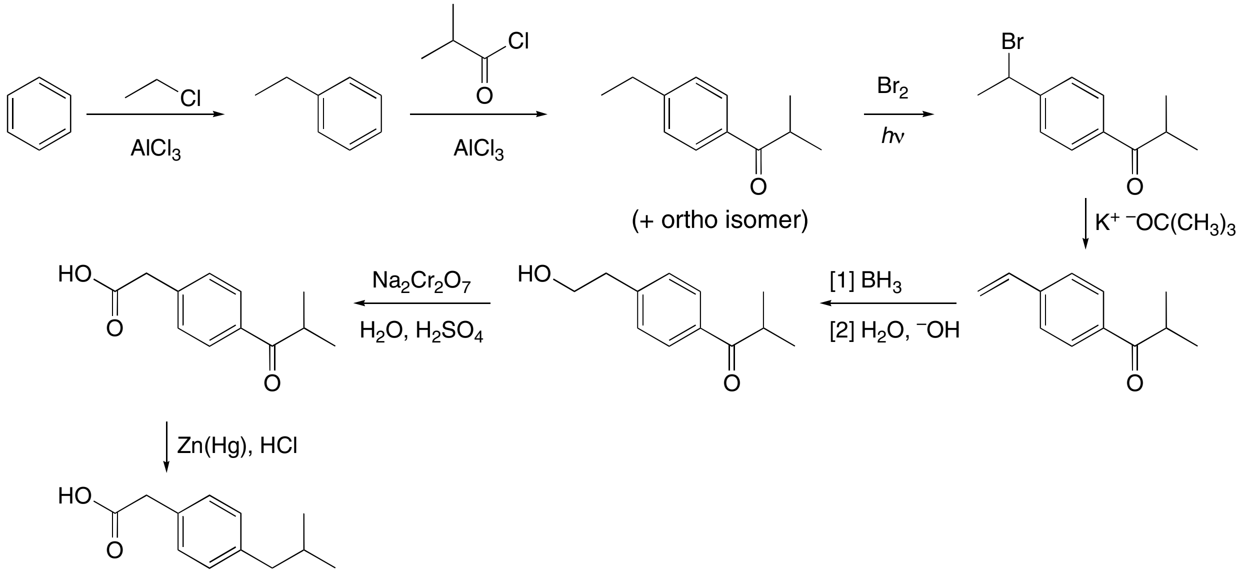
g.



18.67

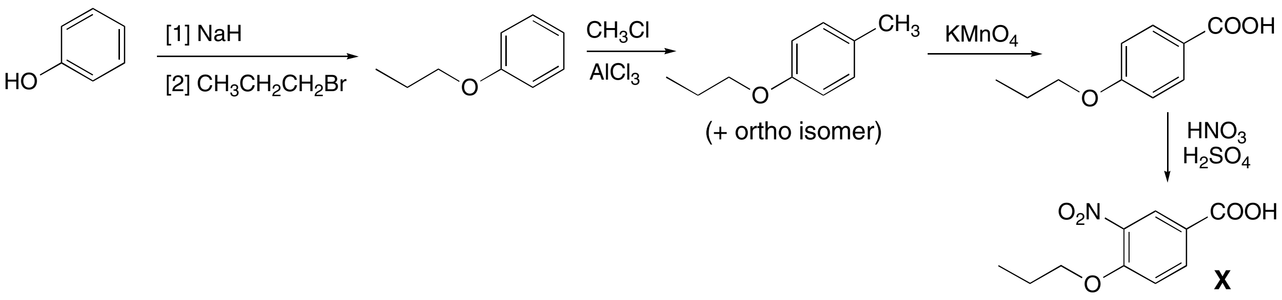


18.68 One possibility:



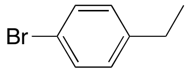
ibufenac

18.69

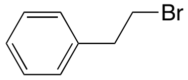


18.70 Use integration data and the molecular formula to determine the number of H's that give rise to each signal (Section 14.5, *How To*).

^{1}H NMR data of compound **A** (C_8H_9Br):

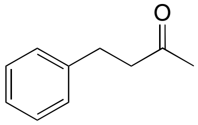
Absorption	**ppm**	**# of H's**	**Explanation**	**Structure:**
triplet	1.2	3	3 H's adjacent to 2 H's	
quartet	2.6	2	2 H's adjacent to 3 H's	
two signals	7.1 and 7.4	2 + 2	para disubstituted benzene	

^{1}H NMR data of compound **B** (C_8H_9Br):

Absorption	**ppm**	**# of H's**	**Explanation**	**Structure:**
triplet	3.1	2	2 H's adjacent to 2 H's	
triplet	3.5	2	2 H's adjacent to 2 H's	
multiplet	7.1–7.4	5	monosubstituted benzene	

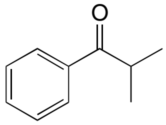
18.71 IR absorption at 1717 cm^{-1} means compound **C** has a C=O.

^{1}H NMR data of compound **C** ($C_{10}H_{12}O$):

Absorption	**ppm**	**# of H's**	**Explanation**	**Structure:**
singlet	2.1	3	3 H's	
triplet	2.8	2	2 H's adjacent to 2 H's	
triplet	2.9	2	2 H's adjacent to 2 H's	
multiplet	7.1–7.4	5	monosubstituted benzene	

18.72

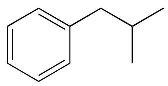
^{1}H NMR data of compound **X** ($C_{10}H_{12}O$):

Absorption	**ppm**	**# of H's**	**Explanation**	**Structure:**
doublet	1.3	6	6 H's adjacent to 1 H	
septet	3.5	1	1 H adjacent to 6 H's	
multiplet	7.4–8.1	5	monosubstituted benzene	

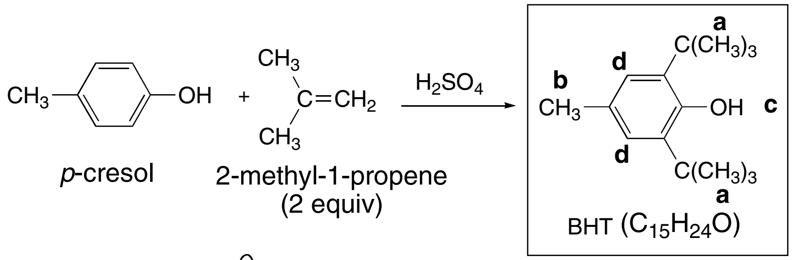
^{1}H NMR data of compound **Y** ($C_{10}H_{14}$):

Absorption	**ppm**	**# of H's**	**Explanation**
doublet	0.9	6	6 H's adjacent to 1 H
multiplet	1.8	1	1 H adjacent to many H's
doublet	2.5	2	2 H's adjacent to 1 H
multiplet	7.1–7.3	5	monosubstituted benzene

Structure:

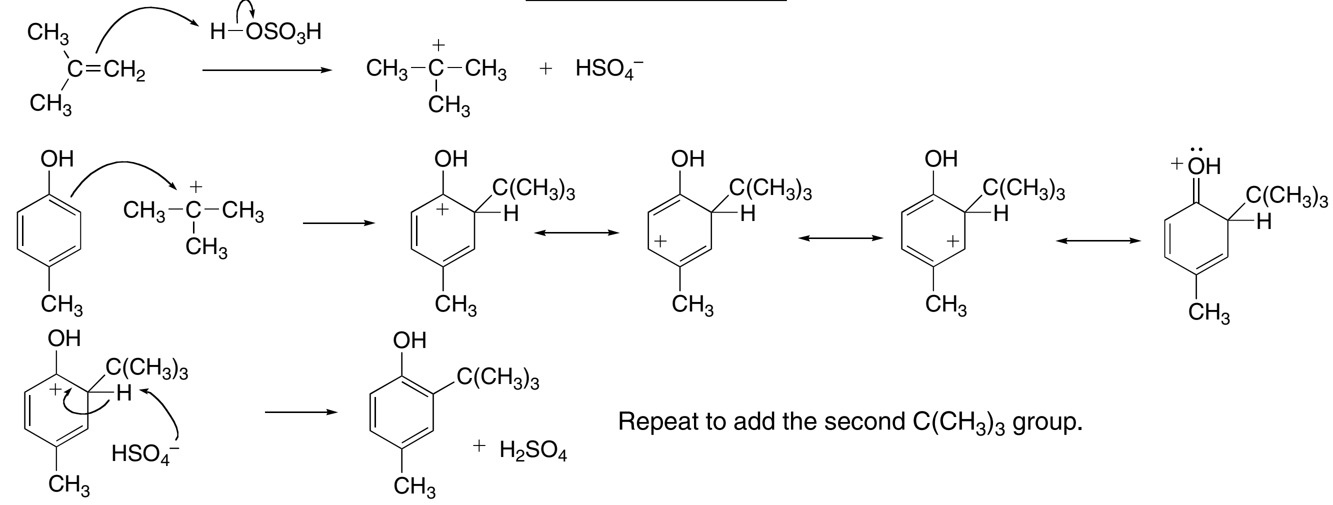


18.73



^{1}H NMR spectral data:

1.4 (singlet, 18 H) (a)
2.27 (singlet, 3 H) (b)
5.0 (singlet, 1 H) (c)
7.0 (singlet, 2 H) (d) ppm



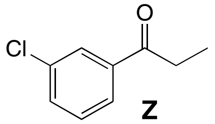
Repeat to add the second $C(CH_3)_3$ group.

18.74

Molecular formula (**Z**): C_9H_9ClO
IR absorption at 1683 cm^{-1}: C=O
^{1}H NMR spectral data:

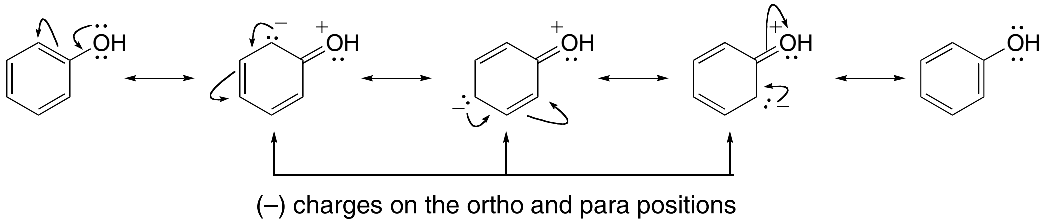
Absorption	**ppm**	**# of H's**	**Explanation**
triplet	1.2	3	3 H's adjacent to 2 H's
quartet	2.9	2	2 H's adjacent to 3 H's
multiplet	7.2–8.0	4	disubstituted benzene

Structure:



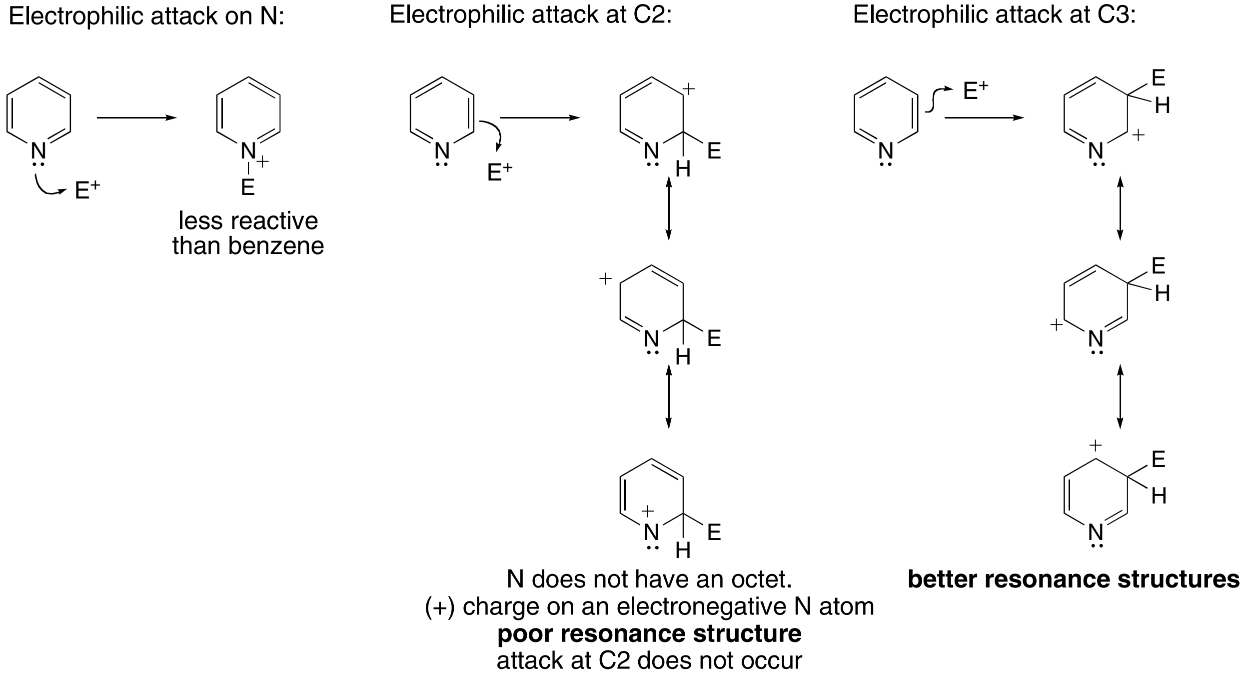
Z

18.75 Five resonance structures can be drawn for phenol, three of which place a negative charge on the ortho and para carbons. These illustrate that the electron density at these positions is increased, thus shielding the protons at these positions, and shifting the absorptions to lower chemical shift. Similar resonance structures cannot be drawn with a negative charge at the meta position, so it is more deshielded and absorbs farther downfield, at higher chemical shift.



18.76 a. Pyridine: The electron-withdrawing inductive effect of N makes the ring electron poor. Also, electrophiles E^+ can react with N, putting a positive charge on the ring. This makes the ring less reactive with another positively charged species.

To understand why substitution occurs at C3, compare the stability of the carbocation formed by attack at C2 and C3.



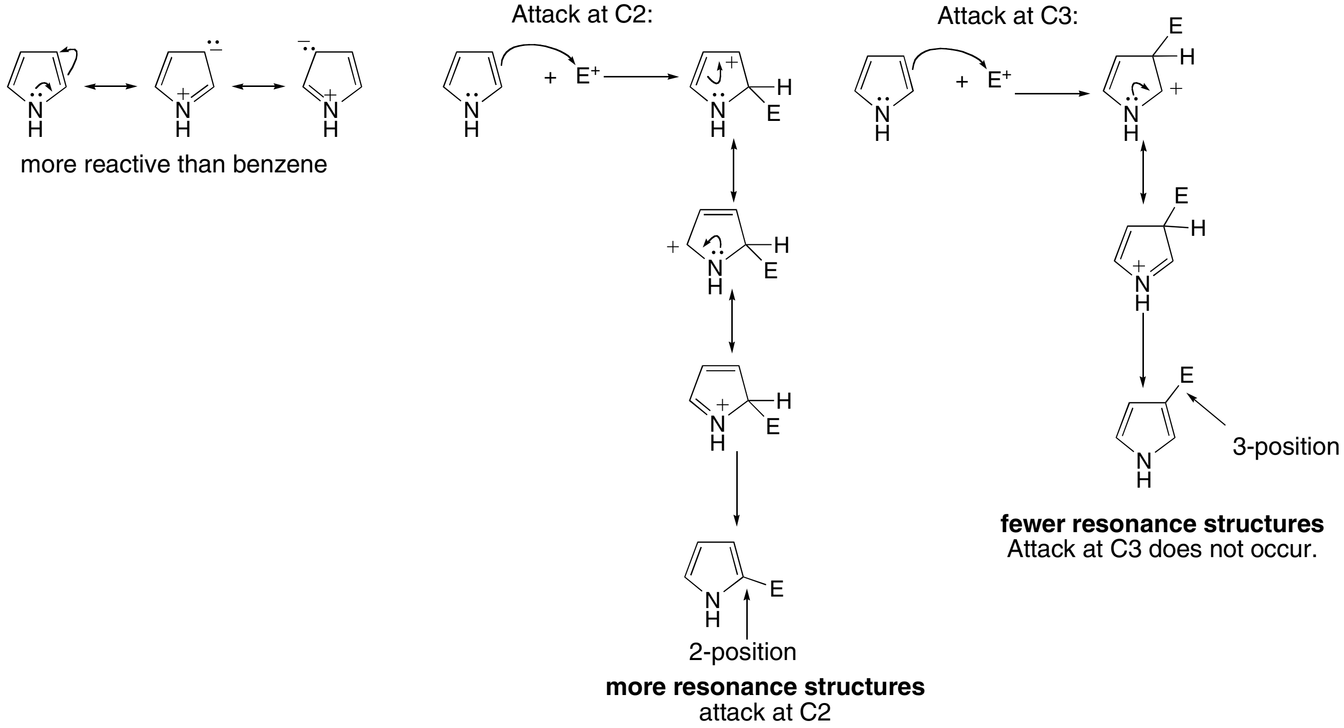
less reactive than benzene

N does not have an octet.
(+) charge on an electronegative N atom
poor resonance structure
attack at C2 does not occur

better resonance structures

Since attack at C3 forms a more stable carbocation, attack at C3 occurs. Attack at C4 generates a carbocation of similar stability to attack at C2, so attack at C4 does not occur.

b. Pyrrole is more reactive than benzene because the C's are more electron rich. The lone pair on N has an electron-donating resonance effect.

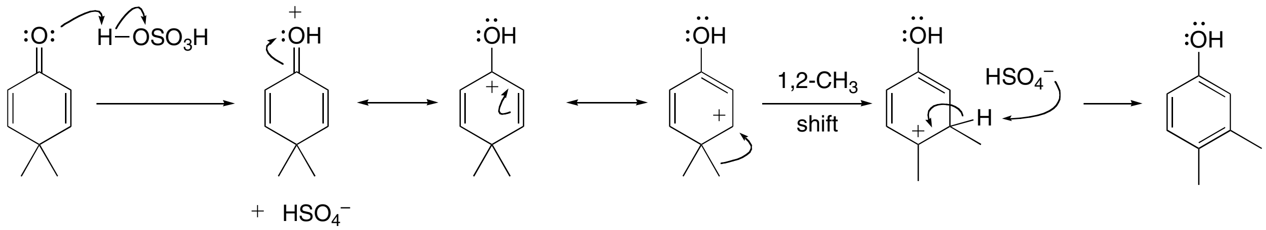


more resonance structures
attack at C2

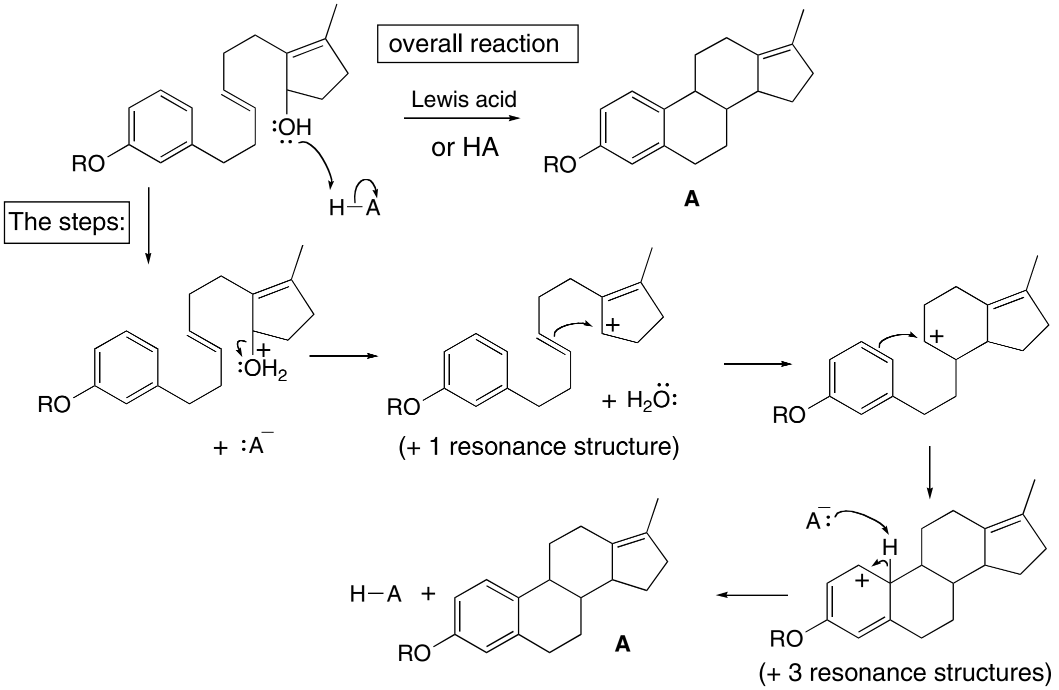
fewer resonance structures
Attack at C3 does not occur.

Since attack at C2 forms a more stable carbocation, electrophilic substitution occurs at C2.

18.77

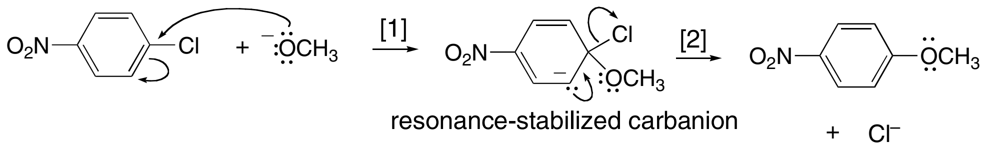


18.78 Draw a stepwise mechanism for the following intramolecular reaction, which was used in the synthesis of the female sex hormone estrone.

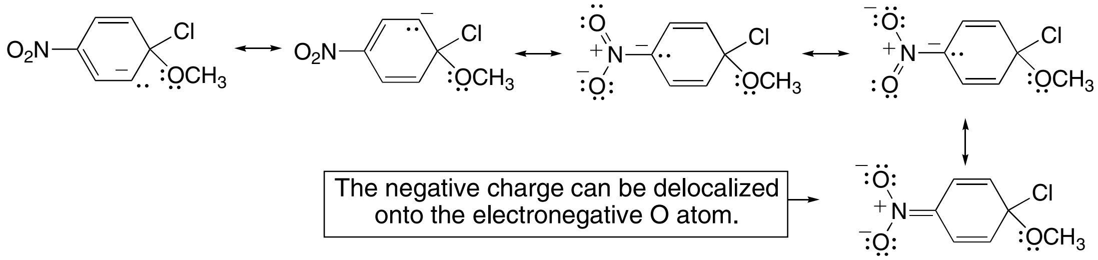


18.79

a. The reaction could follow a two-step mechanism: [1] addition of the nucleophile to form a carbanion, followed by [2] elimination of the leaving group.



b. The NO_2 group stabilizes the negatively charged intermediate by an electron-withdrawing inductive effect and by resonance.



c. *m*-Chloronitrobenzene does not undergo this reaction because no resonance structure can be drawn that delocalizes the negative charge of the reactive intermediate onto the O atom of the NO_2 group.