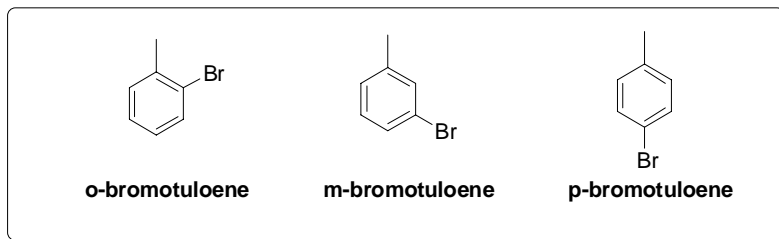


Chapter 16

16.1 Monobromination of toluene gives a mixture of three bromotoluene products. Draw and name them.

Solution:



16.2 How many products might be formed on chlorination of o-xylene (o-dimethylbenzene), m-xylene, and p-xylene?

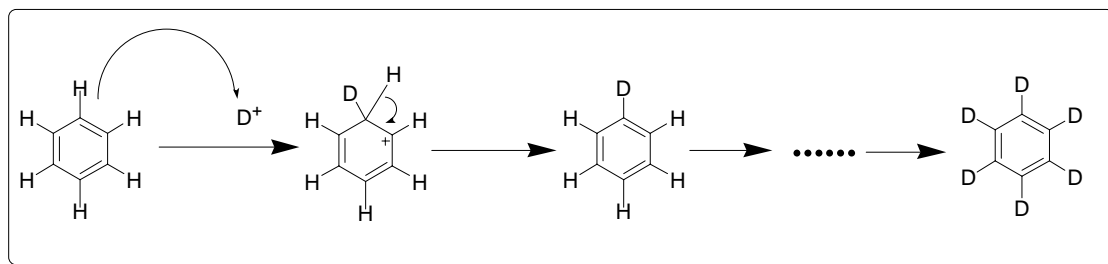
Solution: o-xylene: 2.

m-xylene: 3

p-xylene: 1

16.3 When benzene is treated with D_2SO_4 , deuterium slowly replaces all six hydrogens in the aromatic ring. Explain.

Solution: D^+ is used as an electrophile.



16.4 Which of the following alkyl halides would you expect to undergo Friedel-Crafts reaction without rearrangement? Explain.

(a) CH_3CH_2Cl

(b) $CH_3CH_2CH(Cl)CH_3$

(c) $CH_3CH_2CH_2Cl$

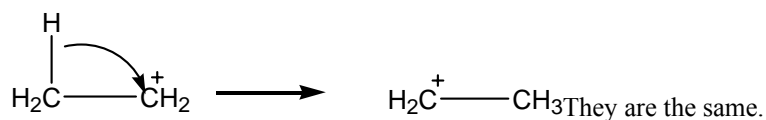
(d) $(CH_3)_3CCH_2Cl$

(e) Chlorocyclohexane

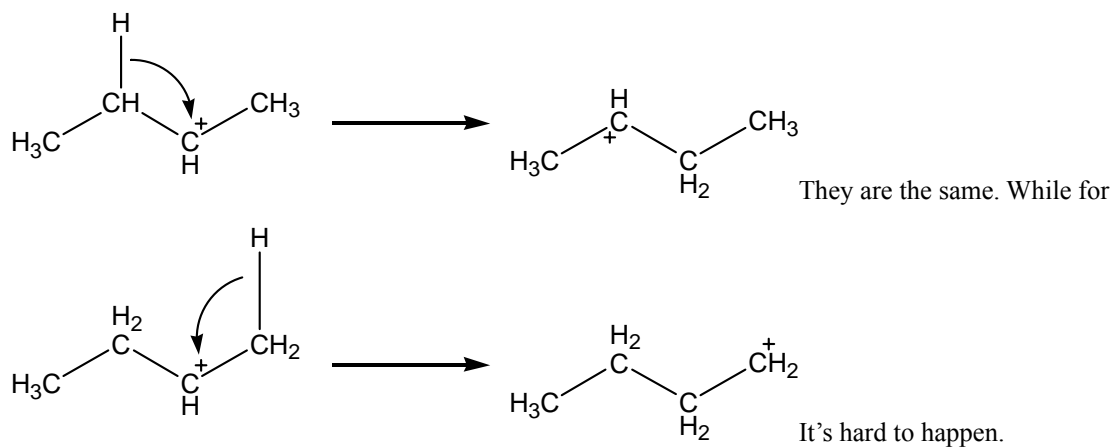
Solution:

(a),(b),(e)

Because for (a),



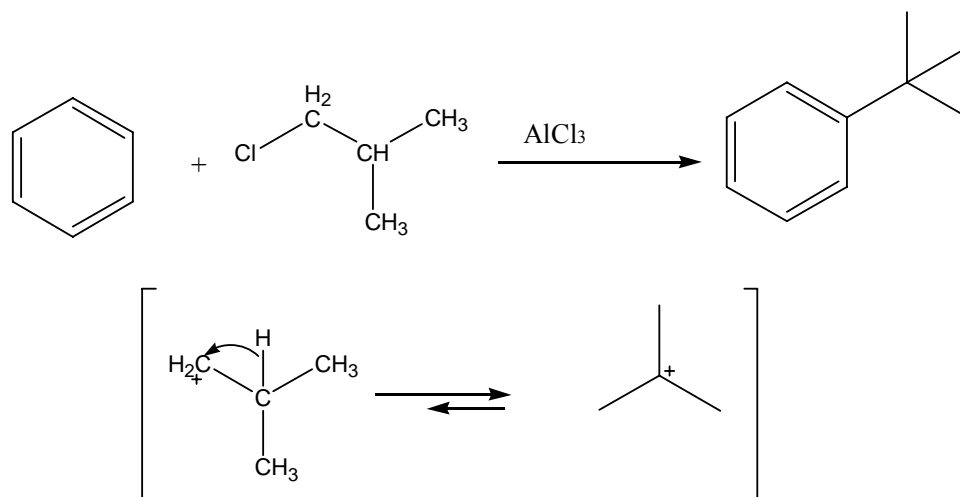
For (b)



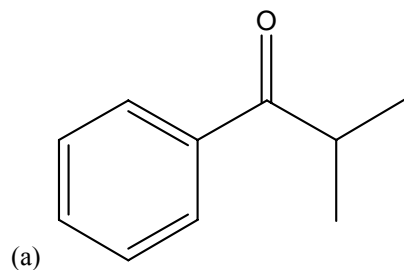
For (e) cyclohexyl carbocation doesn't rearrange.

16.5 What is the major monosubstitution product from the Friedel-Crafts reaction of benzene with 1-chloro-2-methylpropane in the presence of AlCl_3 ?

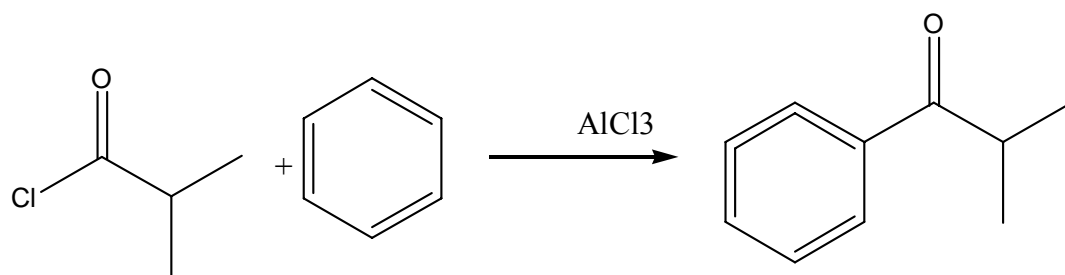
Solution:



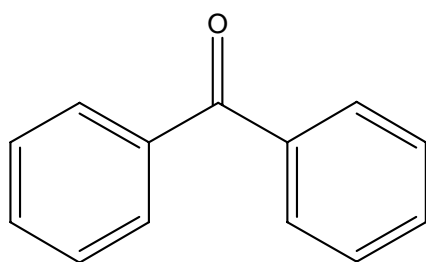
16.6 Identify the carboxylic acid chloride that might be used in a Friedel-Crafts acylation reaction to prepare each of the following acylbenzenes:



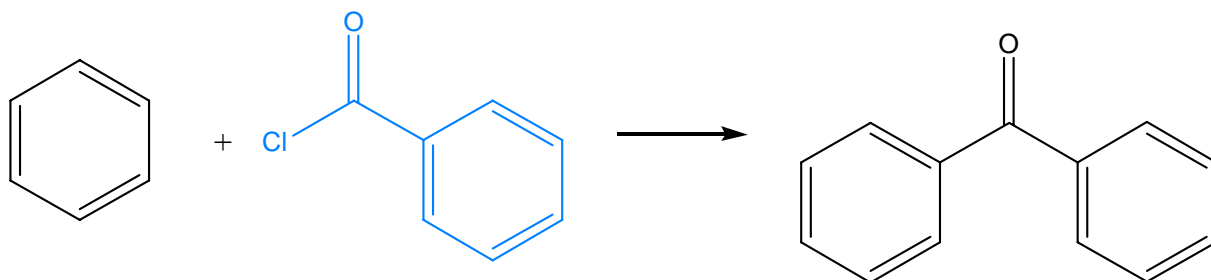
Solution:



(b)

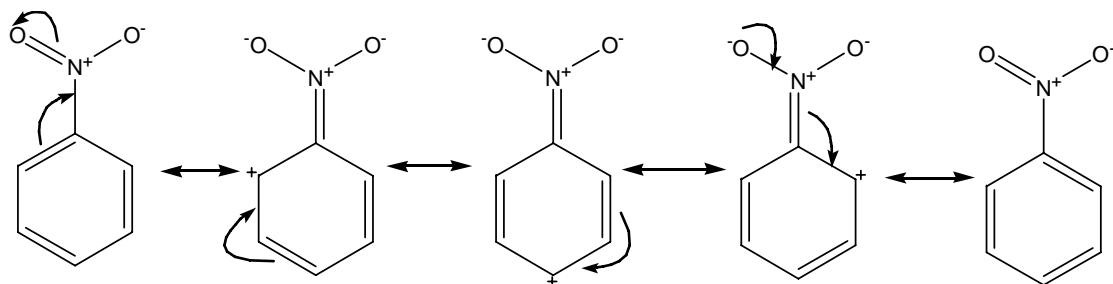


Solution:



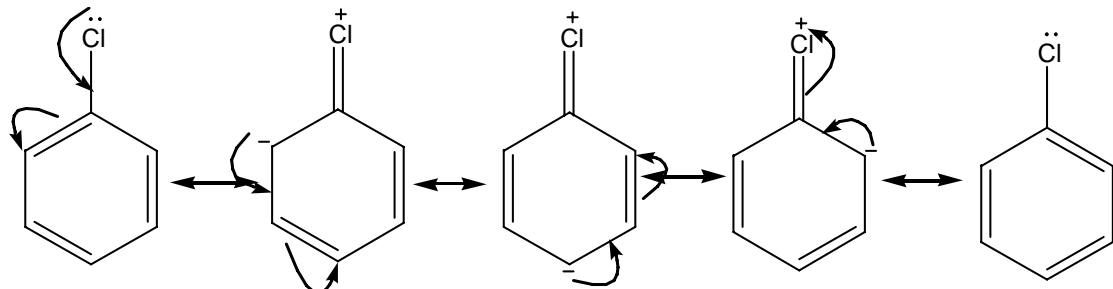
16.7 Write resonance structures for nitrobenzene to show the electron-withdrawing resonance effect of the nitro group.

Solution:



16.8 Write resonance structures for chlorobenzene to show the electron-donating resonance effect of the chloro group.

Solution:



16.9 Predict the major products of the following reactions:

- (a) Mononitration of bromobenzene (b) Monobromination of nitrobenzene
(c) Monochlorination of phenol (d) Monobromination of aniline

Solution:

- (a) It will be o, p orientation, but because of spacial effect, the p orientation product will be the major product.
(b) It will be meta orientation, and meta orientation is the major product.
(c) It will be o, p orientation, but because of spacial effect, the p orientation product will be the major product.
(d) It will be o, p orientation, but because of spacial effect, the p orientation product will be the major product. The reaction system should not have H^+ , otherwise the amino group will transfer to be a meta orientation group.

16.10 Rank the compounds in each group in order of their reactivity to electrophilic substitution:

- (a) Nitrobenzene, Phenol, toluene, benzene
(b) Phenol, benzene, chlorobenzene, benzoic acid
(c) Benzene, bromobenzene, benzaldehyde, aniline

Solution:

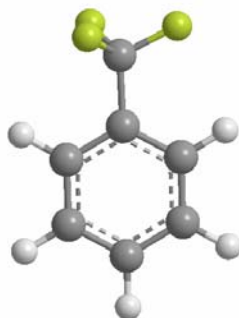
- (a), Phenol > toluene > benzene > Nitrobenzene
(b) Phenol > benzene > chlorobenzene > benzoic acid
(c) Aniline > Benzene > bromobenzene > benzaldehyde

16.11 Use figure 16.10 to explain why Friedel-Crafts alkylations often polysubstitution but Friedel-Crafts acylations do not.

Solution:

The alkyl groups activate the ring of benzene, however, the acetyl groups deactivate the benzene as electron withdraw groups.

16.12 An electrostatic potential map of (trifluoromethyl)benzene, $C_6H_5CF_3$, is showed below. Would you expect (trifluoromethyl)benzene to be more reactive or less reactive than toluene towards electrophilic substitution? Explain.



Solution:

The (trifluoromethyl) benzene is less reactive than toluene for the group $-CF_3$ is an electron withdraw

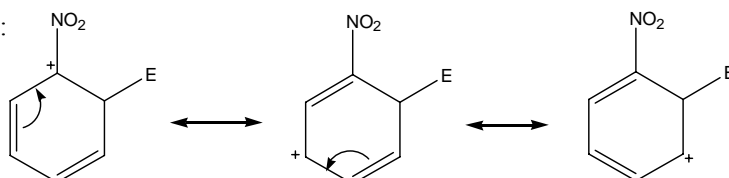
group.

16.13 Acetanilide is less reactive than aniline toward electrophilic substitution. Explain.

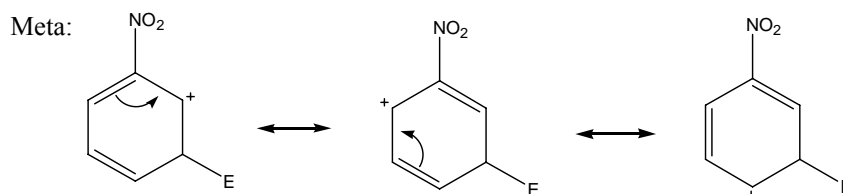
Solution: Because the nitrogen's lone-pair electrons are donated to the nearby carbonyl and are donated less to the ring.

16.14 Draw resonance structures for the intermediates from reaction of an electrophile at the ortho, meta, and para positions of nitrobenzene. Which intermediates are most stable?

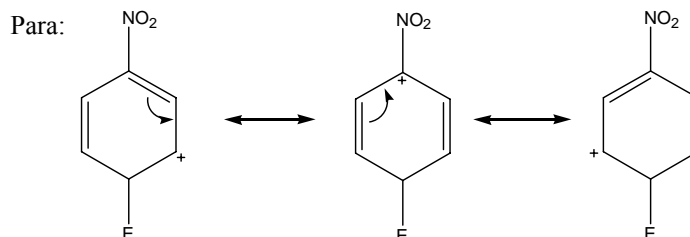
Solution: Ortho:



Meta:

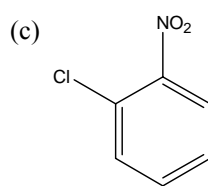
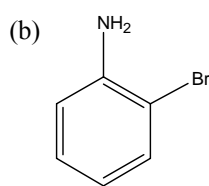
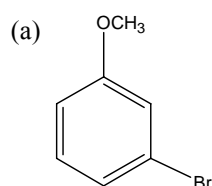


Para:

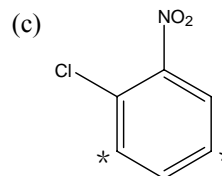
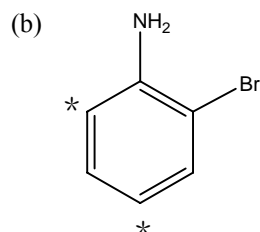
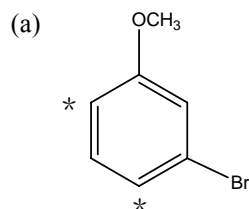


The meta intermediate is most favored.

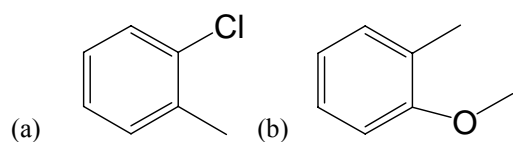
16.15 At what positions would you expect electrophilic substitution to occur in the following substances?



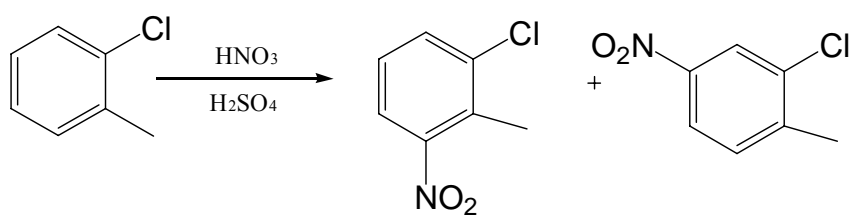
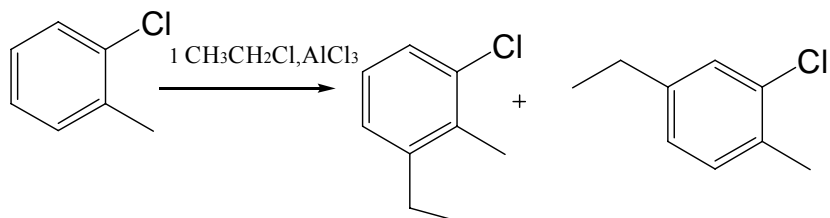
Solution: The substitutions will occur at the positions marked by asterisk



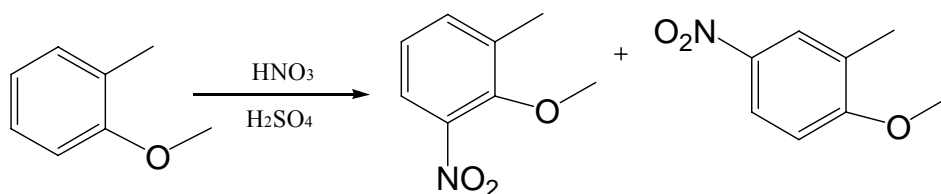
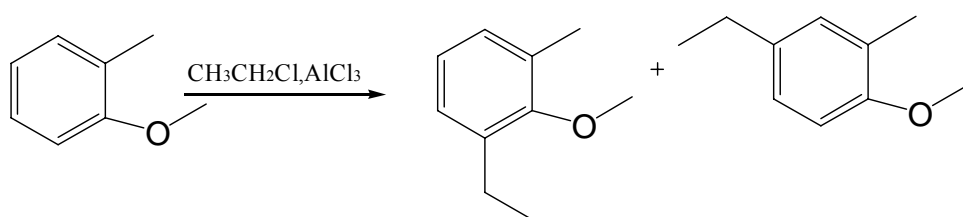
16.16 Show the major products from reaction of following substances with (i) $\text{CH}_3\text{CH}_2\text{Cl}$, AlCl_3 and (ii) $\text{HNO}_3, \text{H}_2\text{SO}_4$



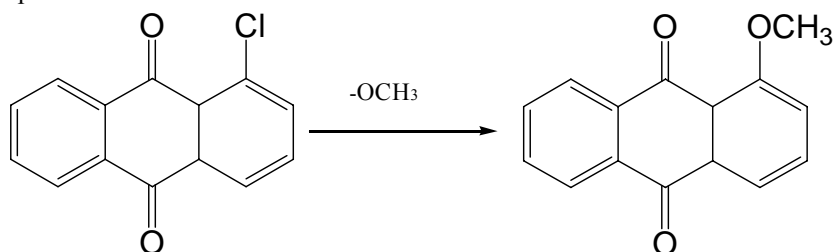
Solution: (a)



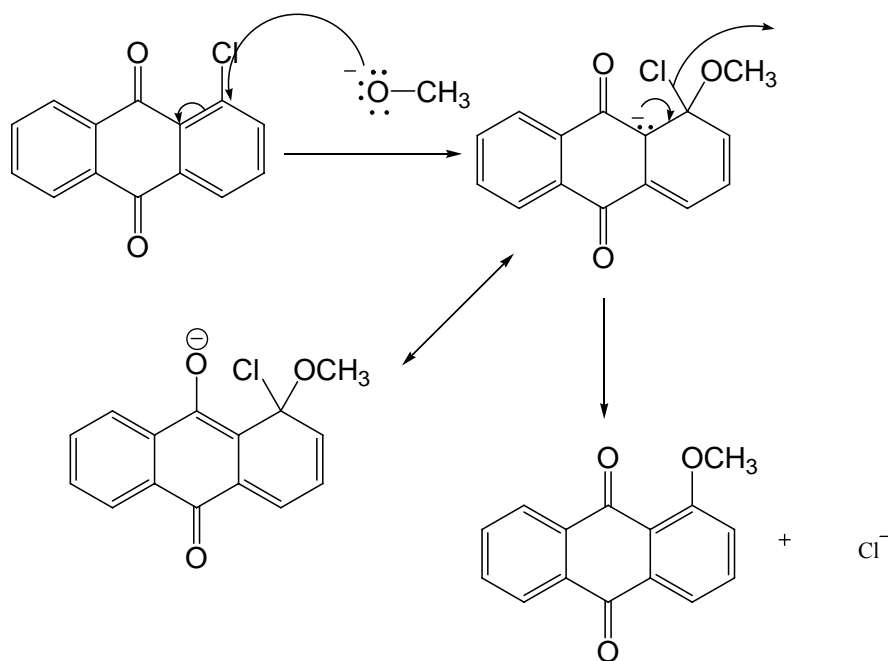
(b)



16.17 Propose a mechanism for the reaction of 1-chloroanthraquinone with methoxide ion to give the substitution product 1-Methoxyanthraquinone. Use curved arrows to show the electron flow in each step.

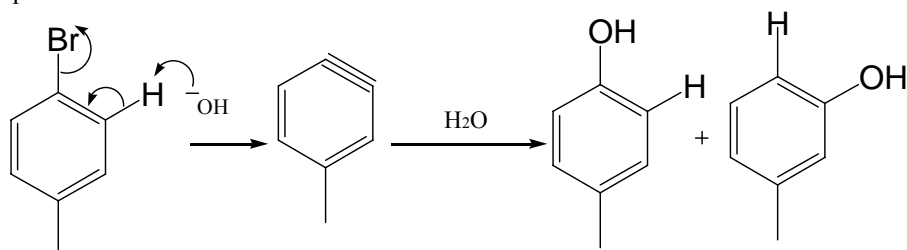


Solution:

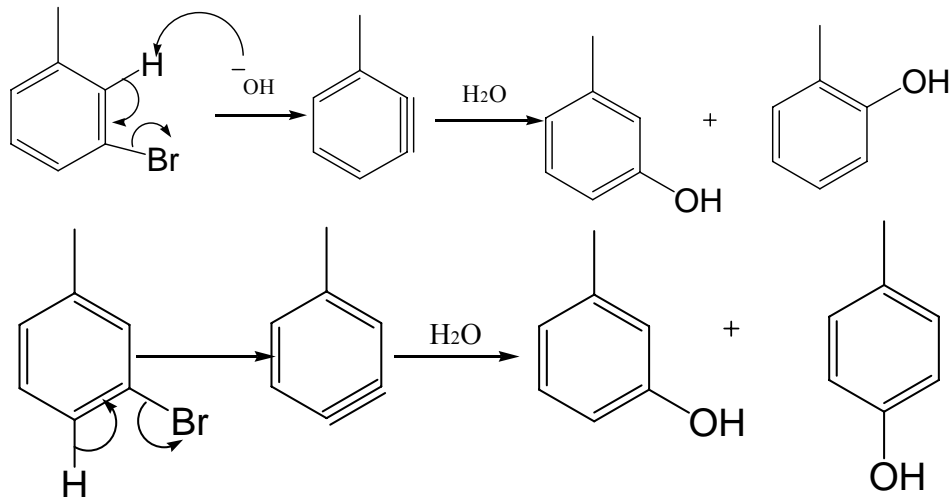


16.18 Treatment of p-bromotoluene with NaOH at 300°C yields a mixture of two products, but treatment of m-bromotoluene with NaOH yields a mixture of three products. Explain.

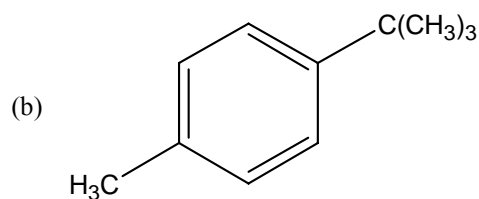
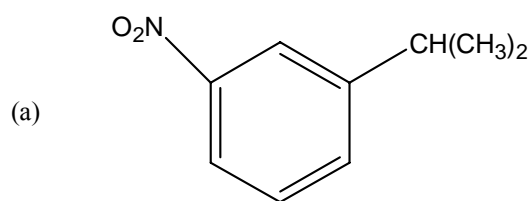
Solution: p-bromotoluene with NaOH :



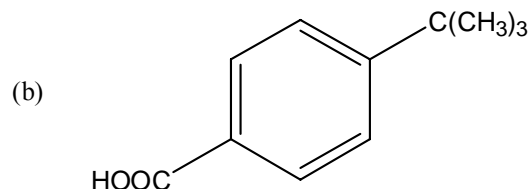
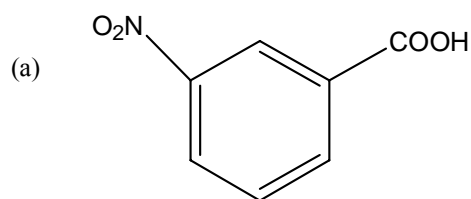
m-bromotoluene with NaOH:



16.19 What aromatic products would you obtain from the $KMnO_4$ oxidation of the following substances?



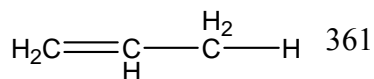
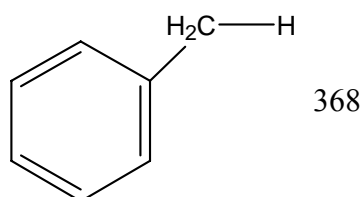
Solution:



16.20 Refer to Table 5.3 for a quantitative idea of the stability of a benzyl radical. How much more stable (in kJ/mol) is the benzyl radical than a primary alkyl radical? How does a benzyl radical compare in stability to an allyl radical?

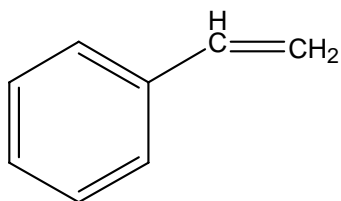
Solution:

Bond	D(kJ/mol)
$\text{C}_2\text{H}_5\text{---H}$	420

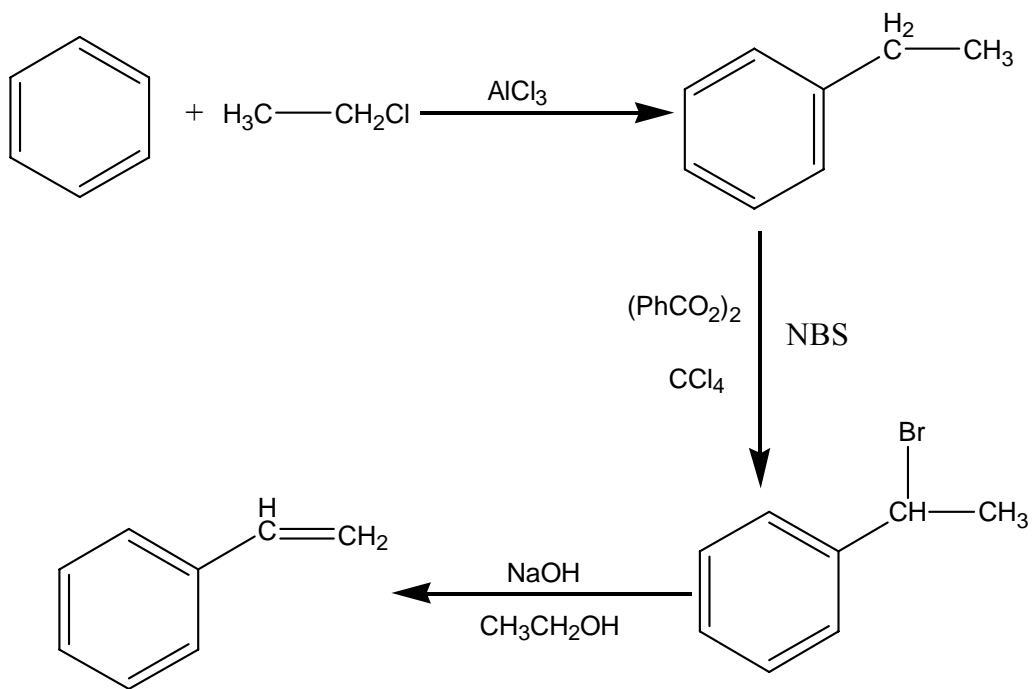


From the statistics showed above, benzyl radical is 52kJ/mol more stable than a primary alkyl radical and almost has the same stability as an allyl radical.

16.21 Styrene, the simplest alkenylbenzene, is prepared commercially for use in plastics manufacture by catalytic dehydrogenation of ethylbenzene. How might you prepare styrene from benzen using reactions you've studied?



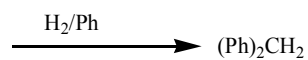
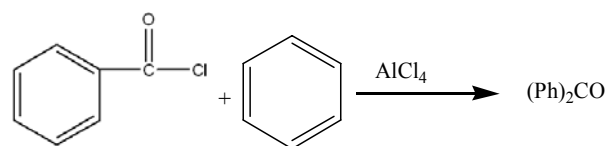
Solution:



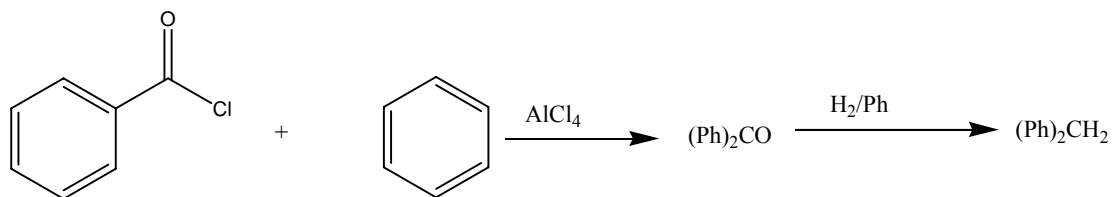
16.22: Show how you would prepare $(\text{Ph})_2\text{CH}_2$, from benzene and an acid chloride.

Solution:

1,



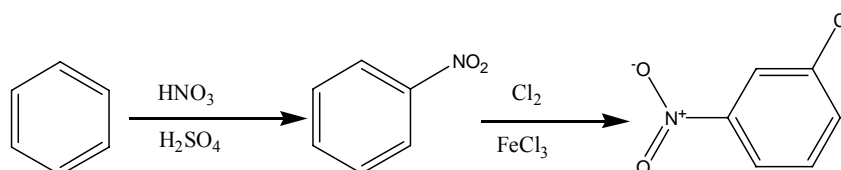
2,



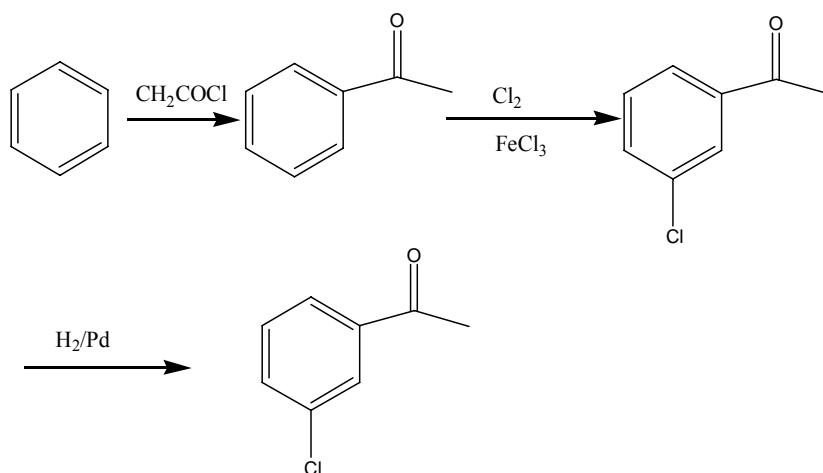
16.23: Propose syntheses of the following substances from benzene.

Solution:

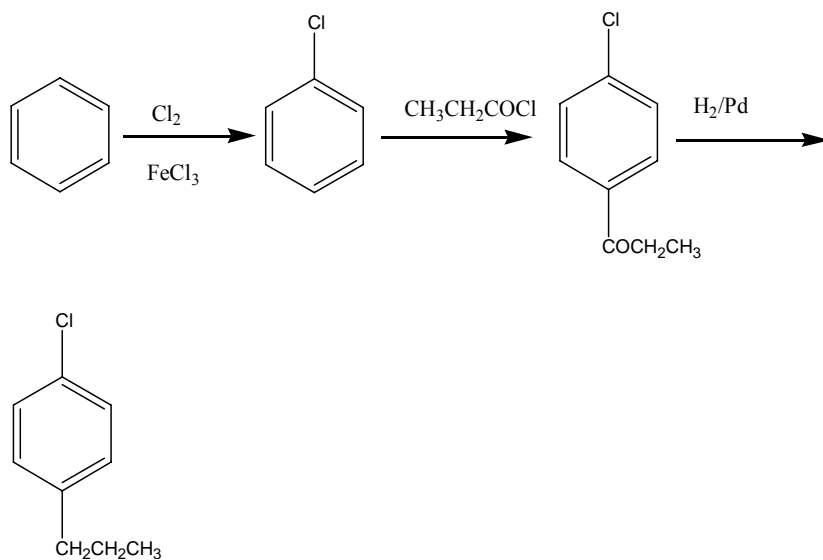
(a) m-Chloronitrobenzene:



(b) m-Chloroethylbenzene:

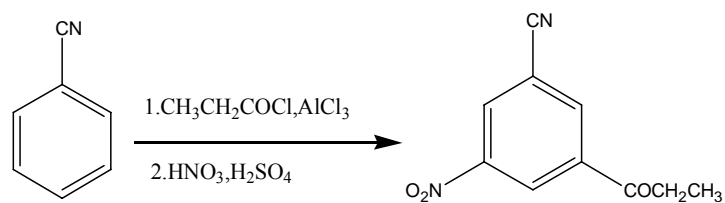


(c) p-Chloropropylbenzene:



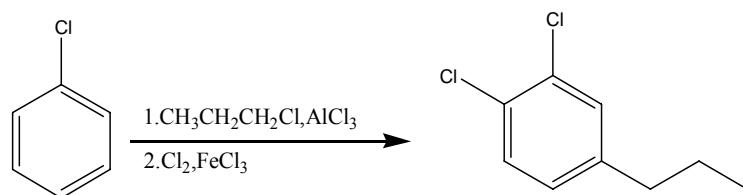
16.24: What is wrong with the following reaction.

Solution: (a):



Because of $-\text{CN}$, Ph-CN can not undergo Friedel-Crafts Reaction.

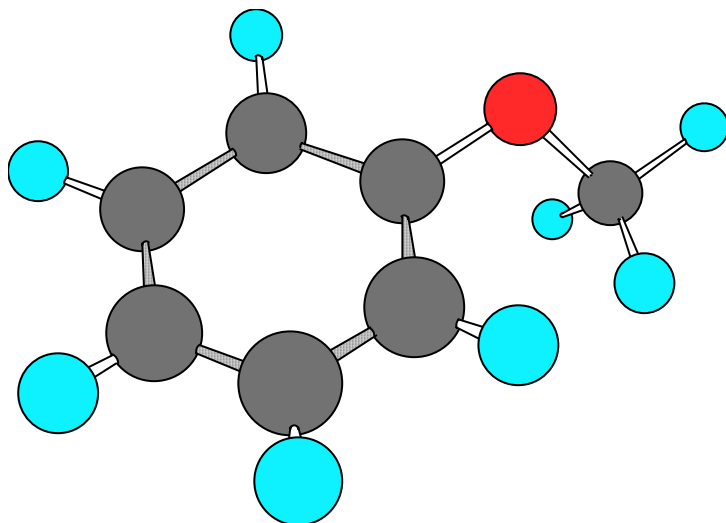
(b):



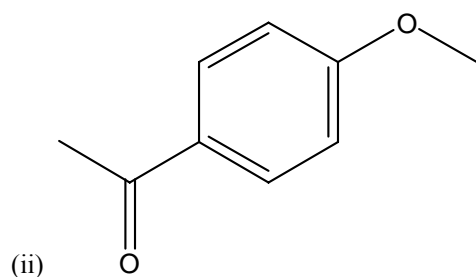
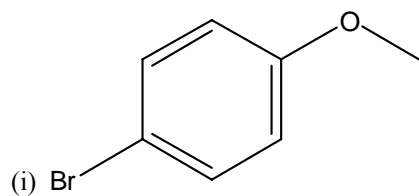
Rearrangement takes place.

16.25 Draw the product from reaction of each of the following substances with (i) Br_2 , FeBr_3 and (ii) CH_3COCl , AlCl_3 .

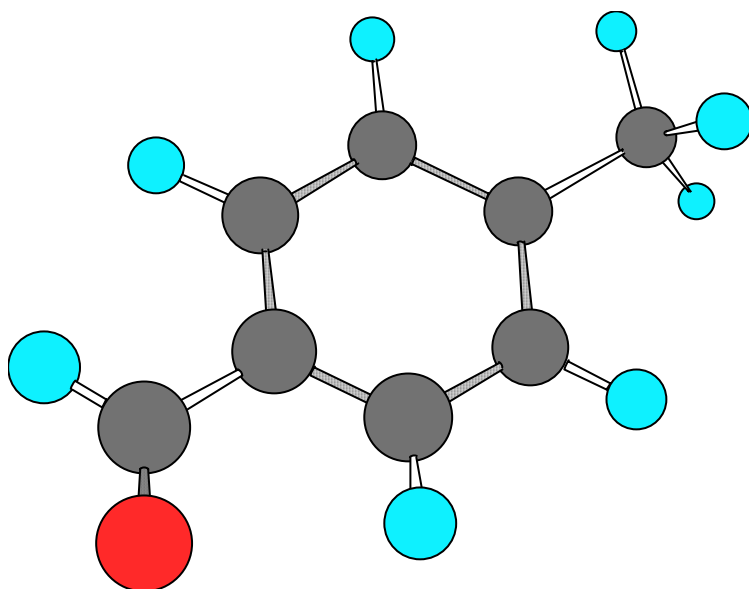
Solution:



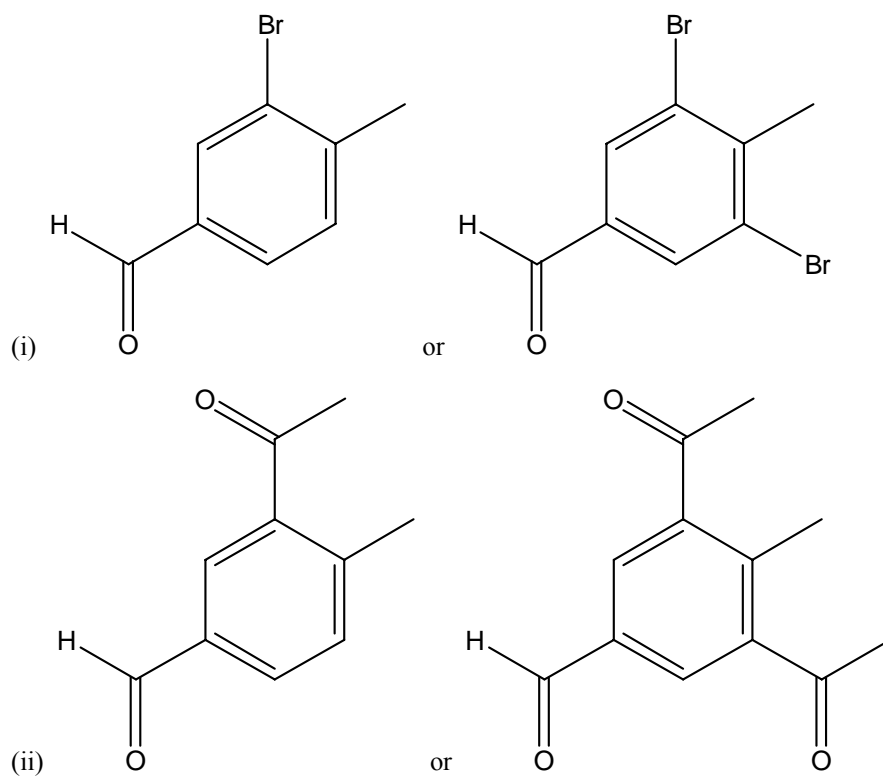
(a)



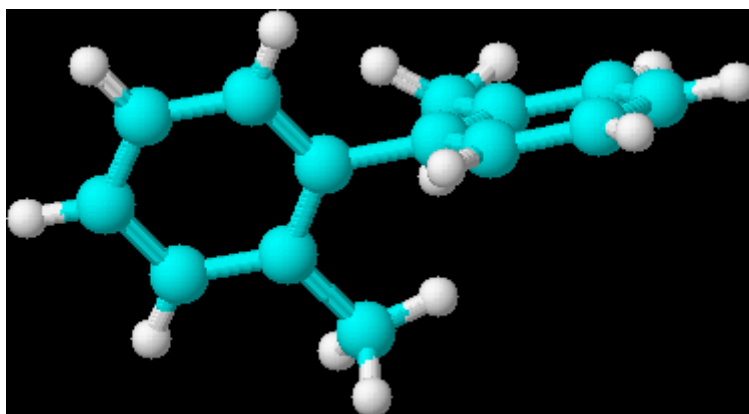
(ii)



(b)

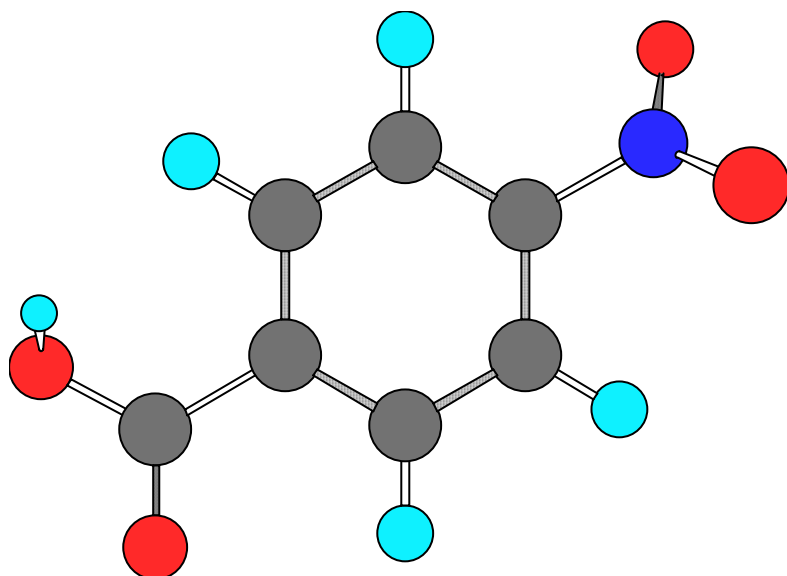


16.26 The following molecular model of a dimethyl-substituted biphenyl represents the lowest-energy conformation of the molecule. Why are the two benzene rings not in the same plane so that their p orbitals can overlap? Why doesn't complete rotation around the single bond joining the two rings occur?

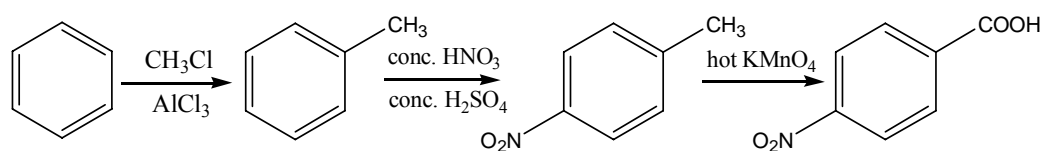


Solution: The two benzene rings are not in the same plane because they will have more steric strain because of the substituents. Complete rotation around the single bond joining the two rings doesn't occur because it is hindered by the substituents.

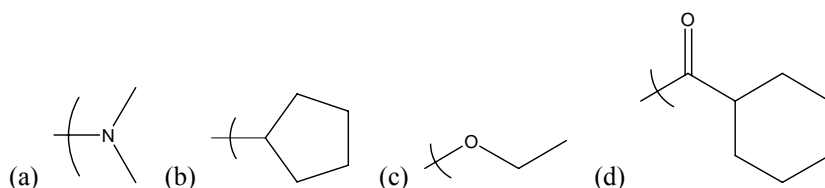
16.27 How would you synthesize the following compound starting from benzene? More than one step is needed.



Solution:



16.28: Identify each of the following groups as an activator or deactivator and as an o,p-director or m-director:



Solution: (a) As it is electron-donate, it is an activator, and is an o,p-director.

(b) As it is electron-donate, it is activator, and is an o,p-director.

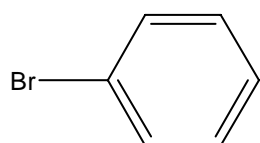
(c) It is electron-donate, it is activator, and is an o,p-director.

(e) It is electron-poor, it will absorb the electrons in the aromatic ring, so it is deactivator and m-director.

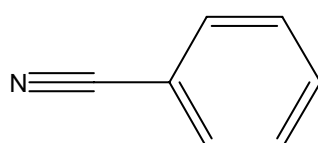
16.29: Predict the major product(s) of mononitration of the following substances. Which react faster than benzene, and which slower?

- | | | |
|------------------|--------------------------|--------------------|
| (a) Bromobenzene | (b) Benzonitrile | (c) Benzoic acid |
| (d) Nitrobenzene | (e) Benzenesulfonic acid | (f) Methoxybenzene |

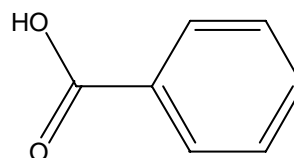
Solution:



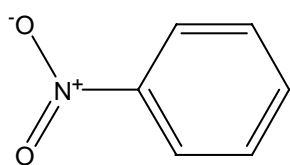
Bromobenzene



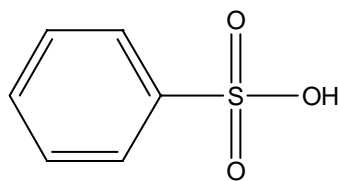
Benzonitrile



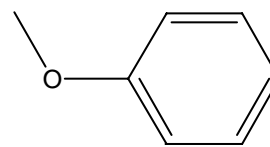
Benzoic acid



Nitrobenzene

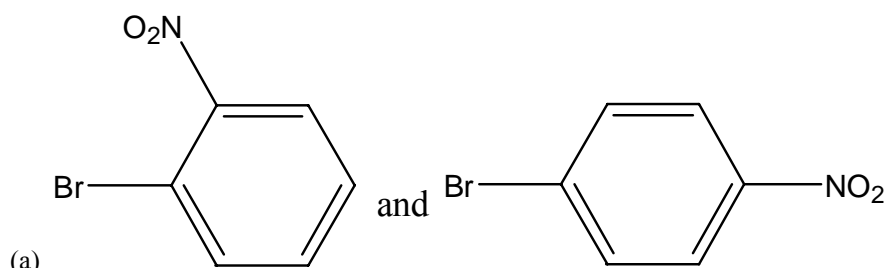


Benzenesulfonic acid

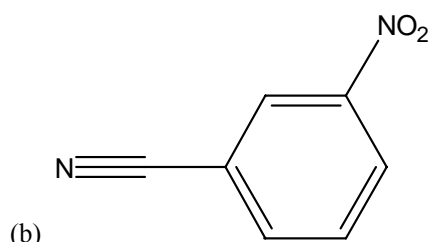


Methoxybenzene

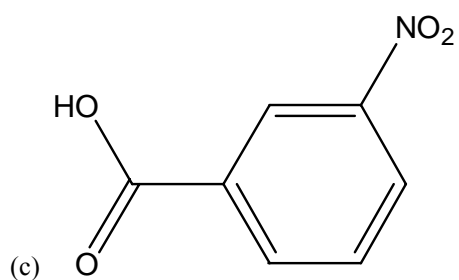
Follow the active figure 16.10 and table 16.1, the solutions are:



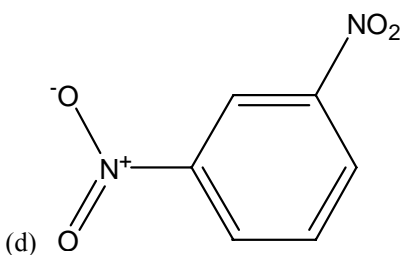
It react slower than the benzene.



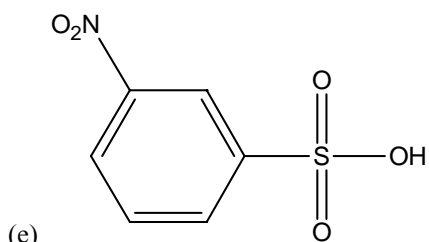
It react slower than benzene.



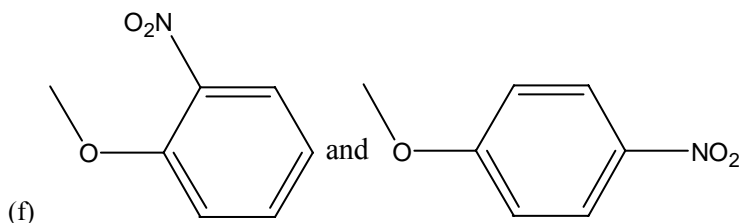
It react slower than benzene.



It react slower than benzene.



It reacts slower than benzene

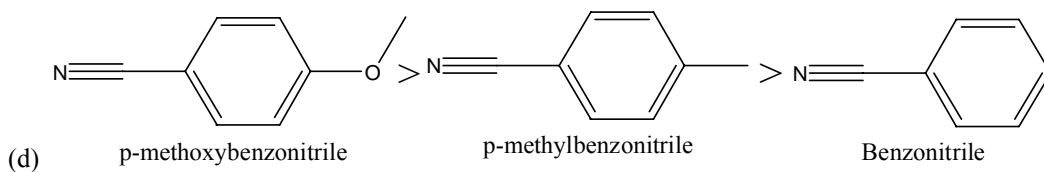
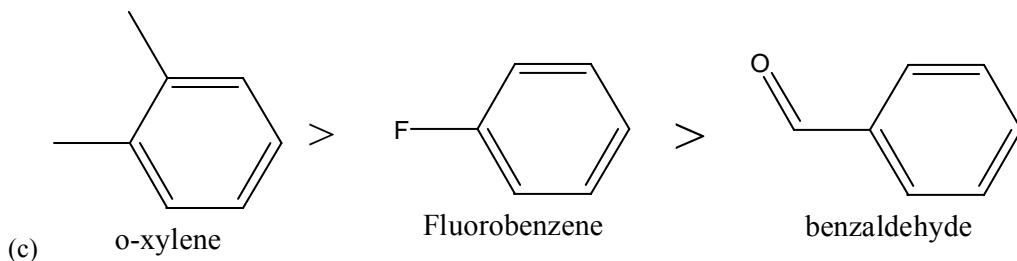
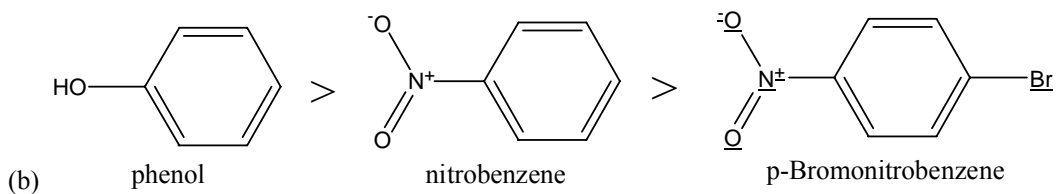
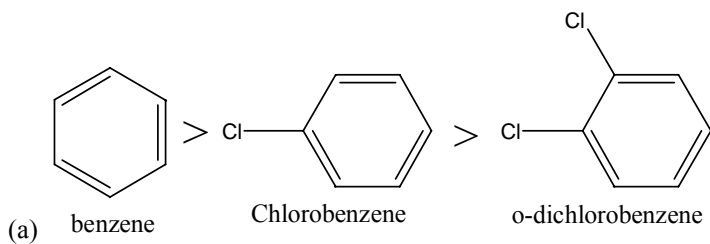


It reacts faster than benzene

16.30: Rank the compounds in each group according to their reactivity toward electrophilic substitution.

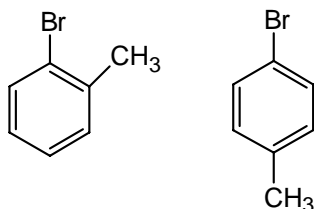
- (a) Chlorobenzene, o-dichlorobenzene, benzene
 (b) p-Bromonitrobenzene, nitrobenzene, phenol
 (c) Fluorobenzene, benzaldehyde, o-xylene
 (d) Benzonitrile, p-methylbenzonitrile, p-methoxybenzonitrile

Solution:



16.31 Predict the major monoalkylation products you would expect to obtain from reaction of the following substances with chloromethane and AlCl_3 :

- | | |
|----------------------------------|------------------------------|
| (a) Bromobenzene | (b) m-Bromophenol |
| (c) p-Chloroaniline | (d) 2,4-Dichloronitrobenzene |
| (e) 2,4-Dichlorophenol | (f) Benzoic acid |
| (g) p-Methylbenzenesulfonic acid | (h) 2,5-Dibromotoluene |

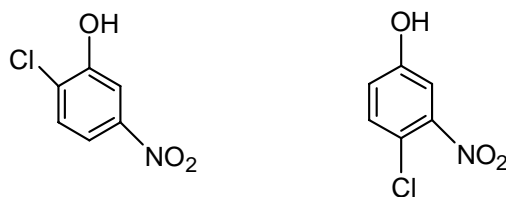


Solution: Major product: (a)

- | | |
|-----------------|--|
| | |
| (b) | |
| (c) No reaction | |
| (d) No reaction | |
| | |
| (e) | |
| (f) No reaction | |
| (g) No reaction | |
| | |
| (h) | |

16.32 Name and draw the major product(s) of electrophilic monochlorination of the following substances:

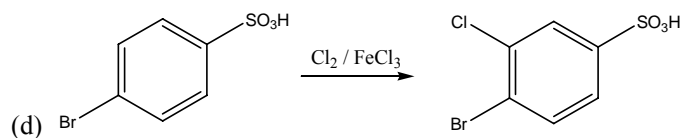
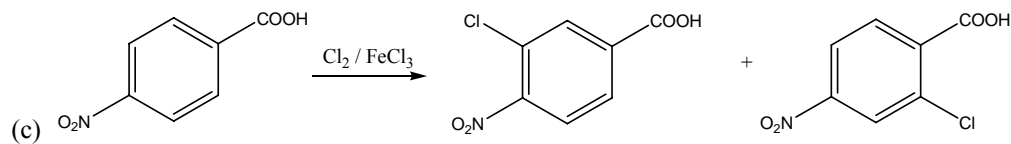
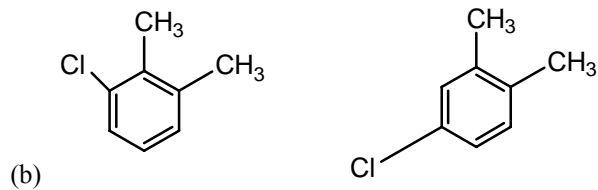
- | | |
|-------------------------|---------------------------------|
| (a) m-Nitrophenol | (b) o-Xylene |
| (c) p-Nitrobenzoic acid | (d) p-Bromobenzenesulfonic acid |



Solution: Major product(s): (a)

2-Chloro-5-nitrophenol

4-Chloro-3-nitrophenol



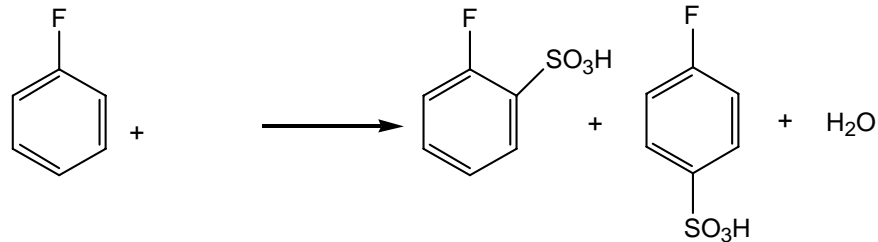
16.33 Predict the major product(s) you would obtain from sulfonation of the following compounds:

(a) Fluorobenzene

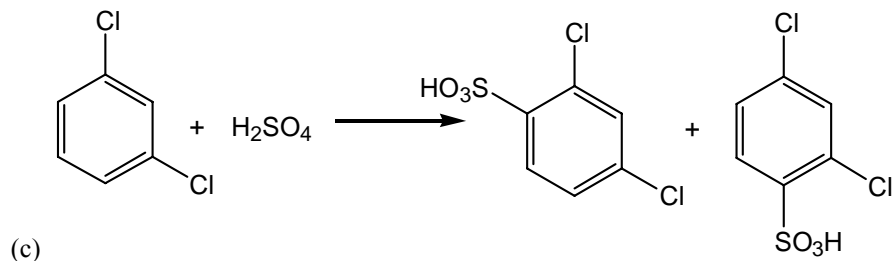
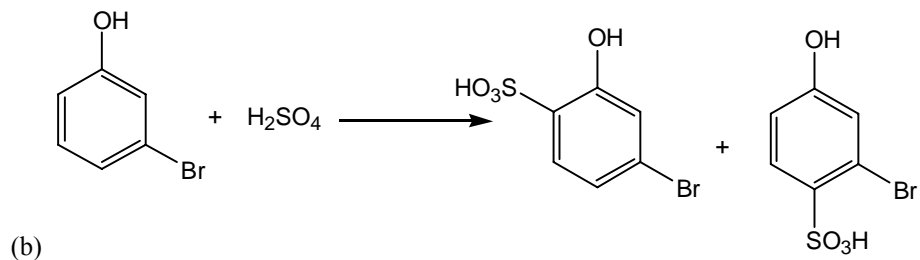
(b) m-Bromophenol

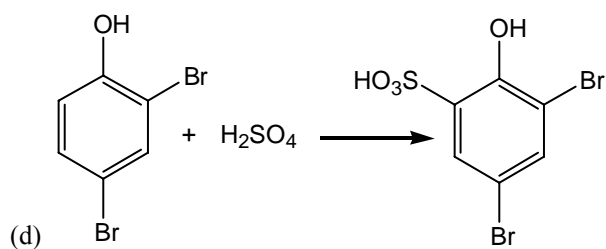
(c) m-Dichlorobenzene

(d) 2,4-Dibromophenol



Solution: (a)





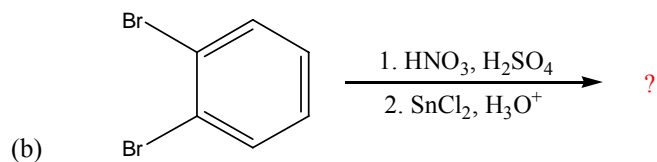
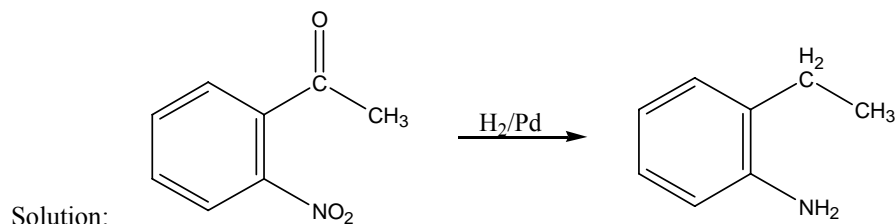
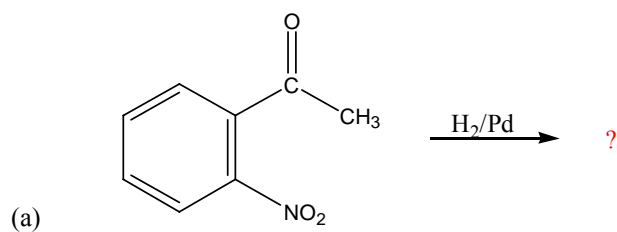
16.34 Rank the following aromatic compounds in the expected order of their reactivity toward Friedel-Crafts alkylation. Which compounds are unreactive?

- (a) Bromobenzene (b) Toluene (c) Phenol
 (d) Aniline (e) Nitrobenzene (f) p-Bromotoluene

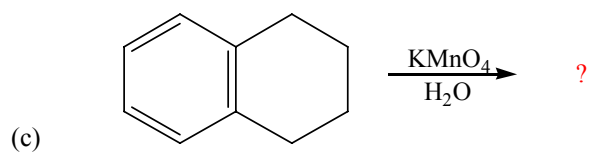
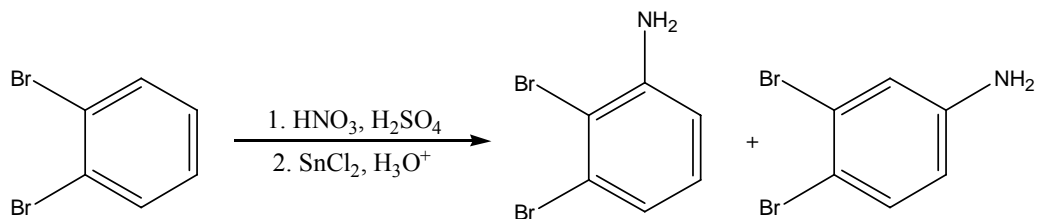
Solution: order: phenol > toluene > p-bromotoluene > bromobenzene

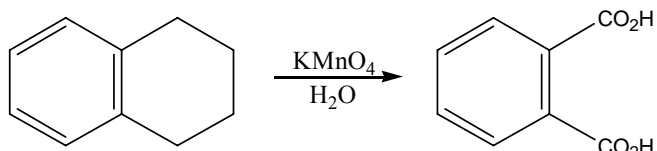
Unreactive: (d), (e)

16.35 What product(s) would you expect to obtain from the following reactions?

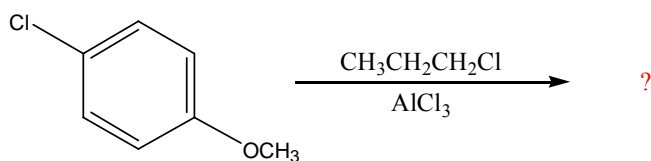


Solution:



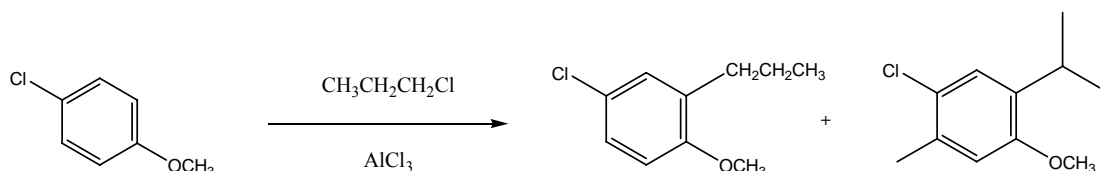


Solution:

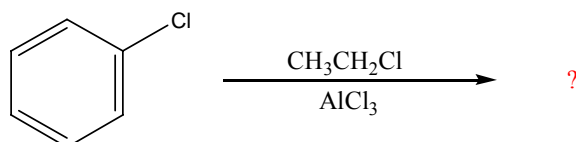


(d)

Solution:

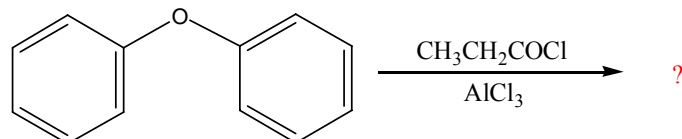
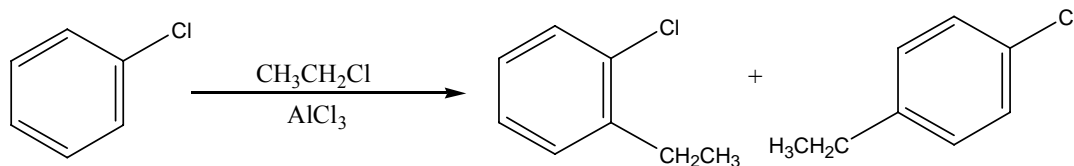


16.36 Predict the major product(s) of the following reactions:



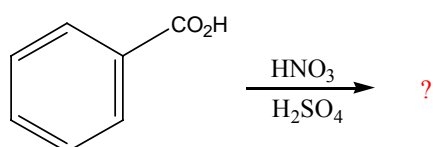
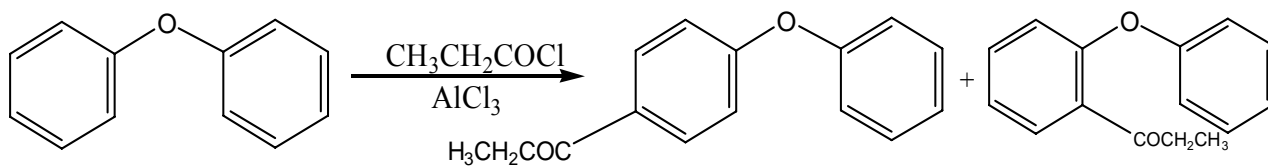
(a)

Solution:



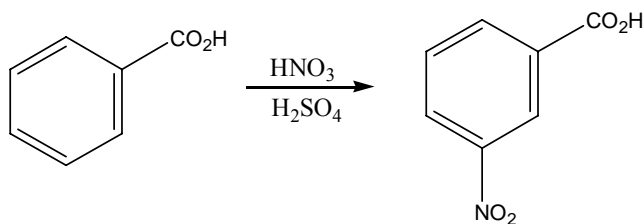
(b)

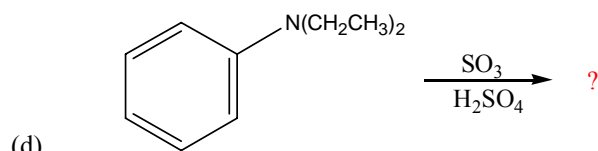
Solution:



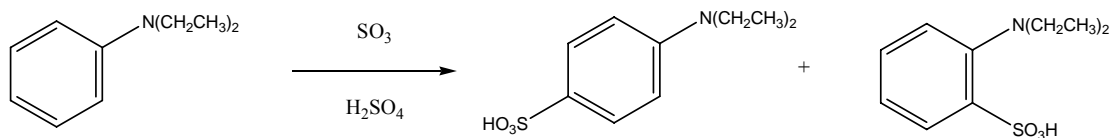
(c)

Solution:



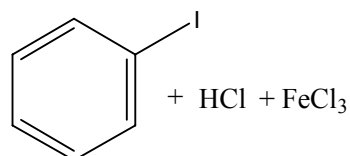
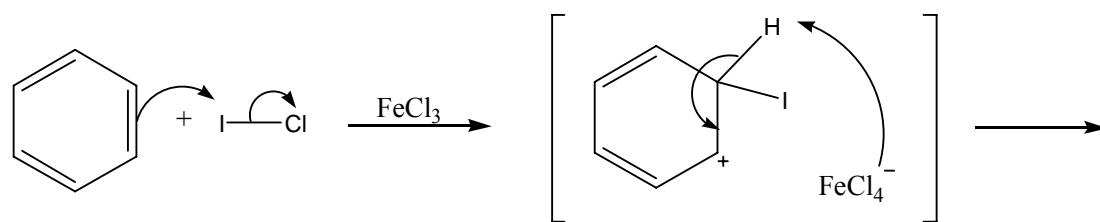
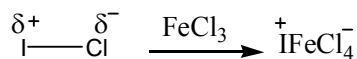
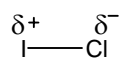


Solution:



16.37 Aromatic iodination can be carried out with a number of reagents, including iodine monochloride, ICl. What is the direction of polarization of ICl? Propose a mechanism for the iodination of an aromatic ring with ICl.

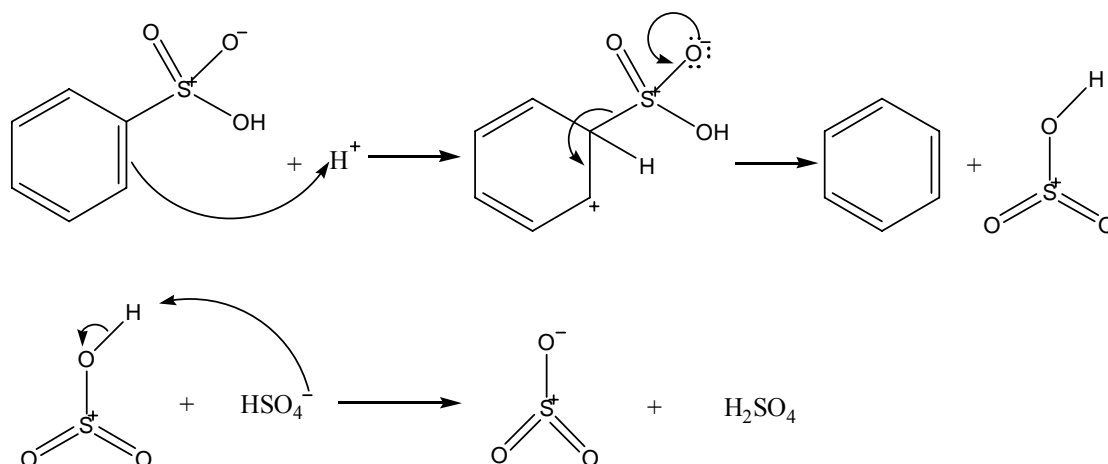
Solution:



16.38 The sulfonation of an aromatic ring with SO_3 and H_2SO_4 is a reversible reaction. That is, heating benzenesulfonic acid with H_2SO_4 yields benzene. Show the mechanism of the desulfonation reaction. What is the electrophile?

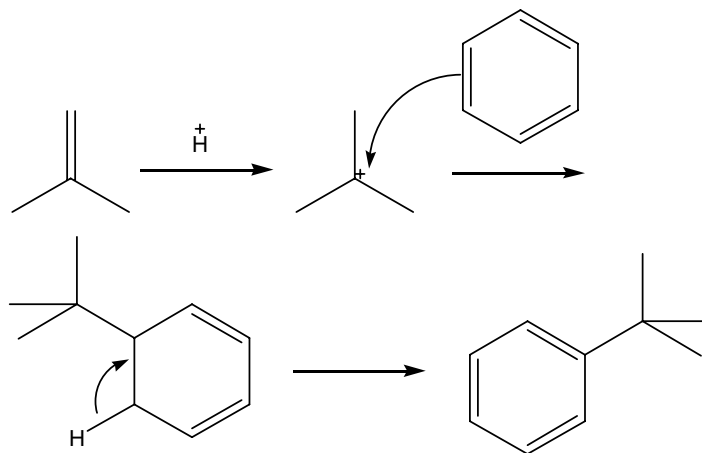
Solution:

H_2SO_4 supplies H^+ . And it is the electrophile.



16.39 The carbocation electrophile in a Friedel-Crafts reaction can be generated in ways other than by reaction of an alkyl chloride with AlCl_3 . For example, reaction of benzene with 2-methyl-propene in the presence of H_3PO_4 , yield tert-butylbenzene. Propose a mechanism for this reaction.

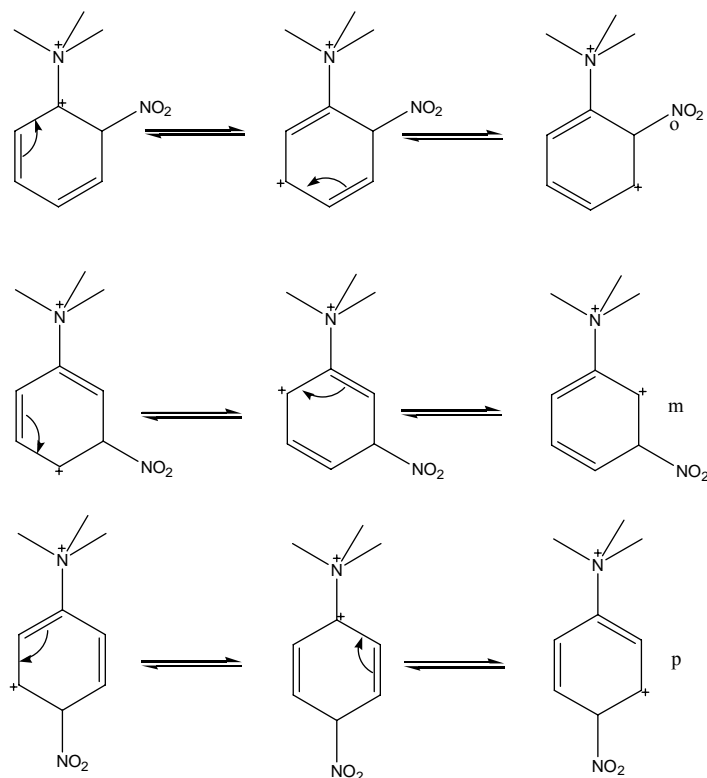
Solution:



16.40 The N,N,N-trimethylammonium group, $-\text{N}^+(\text{CH}_3)_3$, is one of the few groups that is a meta-deactivator yet has no electron-withdrawing resonance effect. Explain.

Solution:

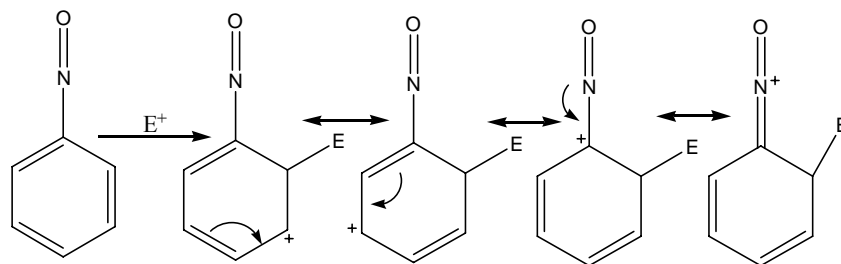
$-\text{N}^+(\text{CH}_3)_3$ is a positive charged group which reduce the electron cloud density of the benzene structure, so it is a deactivator. The N atom in the structure is positive charged so it doesn't have long-pair electrons, so it doesn't have the resonance structure. The resonance structure of o,m,p-carbocation is showed as follow:



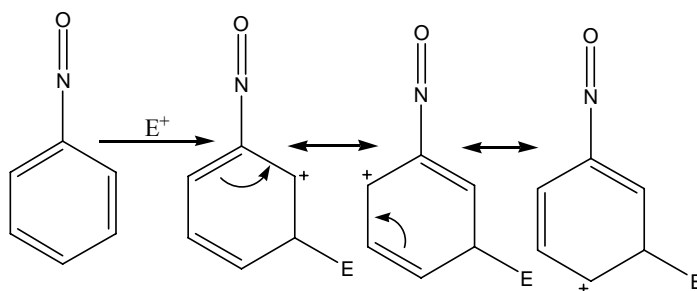
The structures of resonance forms tell us that the o,p-structures each has a resonance form that the carbocation centre is nearest to the positive N atom, so the structures is very unstable, but the m-structure doesn't have such a structure, so it is more stable than the o,p-structure.

16.41 The nitroso group, $-N=O$, is one of the few nonhalogens that is an ortho- and para-directing deactivator. Explain by drawing resonance structures of the carbocation intermediates in ortho, meta, and para electrophilic reaction on nitrosobenzene, $C_6H_5N=O$.

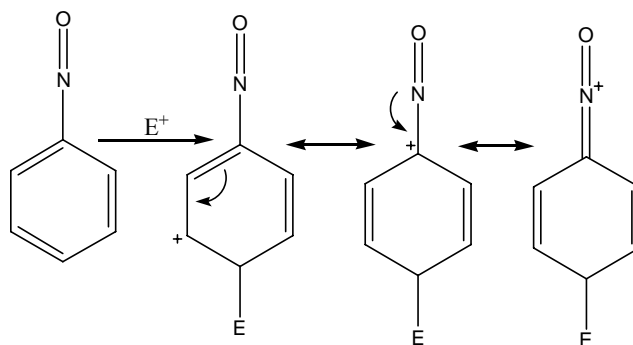
For ortho:



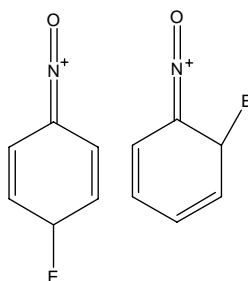
For meta



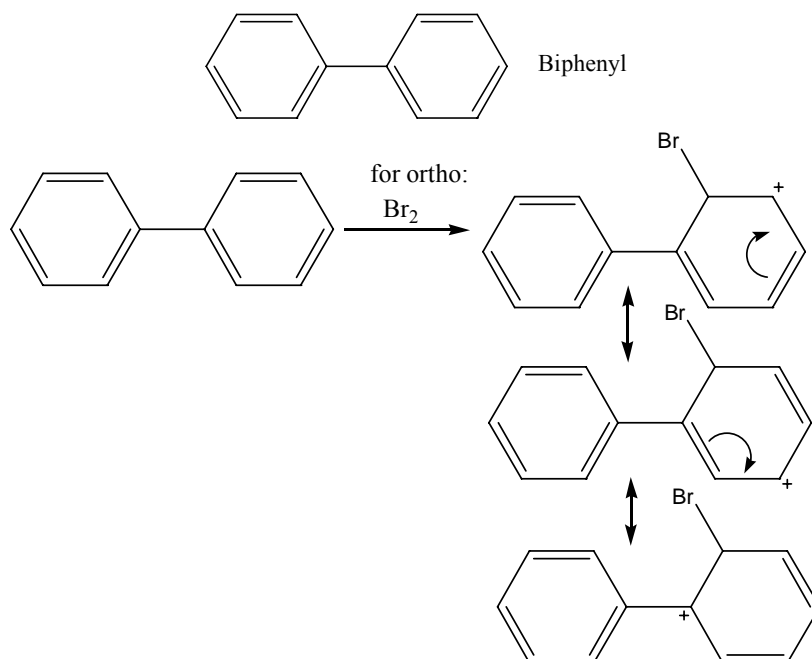
For para

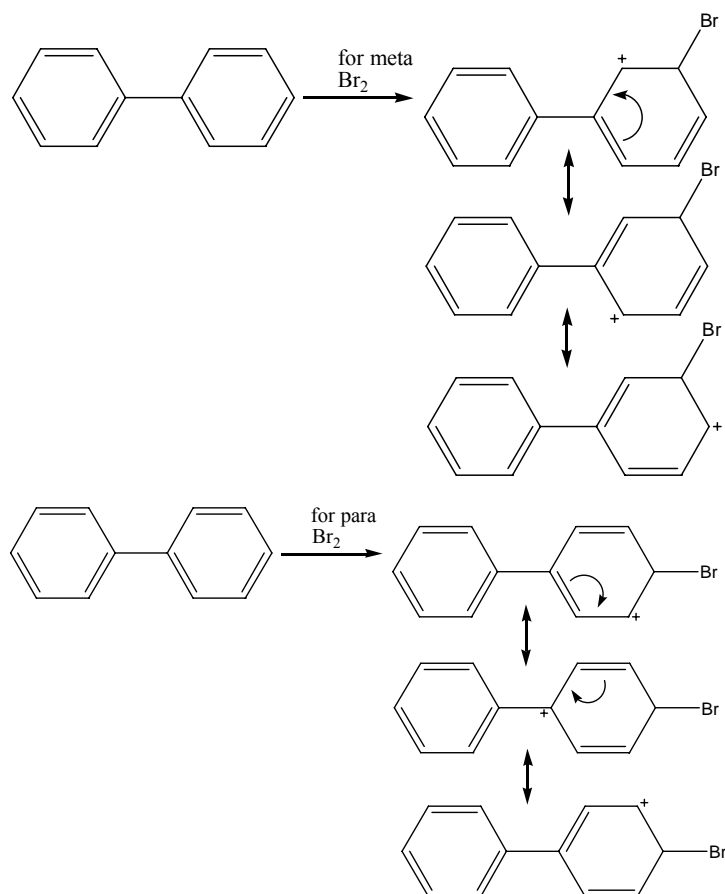


The following two structures are the most stable ones, so it is more likely to have ortho- and para- substitutions. The electronegativity of N is bigger than C, $-N=O$ is an electron withdrawing group, that is deactivating group. So $-N=O$ is an ortho- and para-directing deactivator.

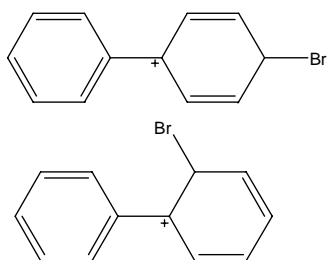


16.42 Using resonance structures of the intermediates, explain why bromination of biphenyl occurs at ortho and para positions rather than at meta.



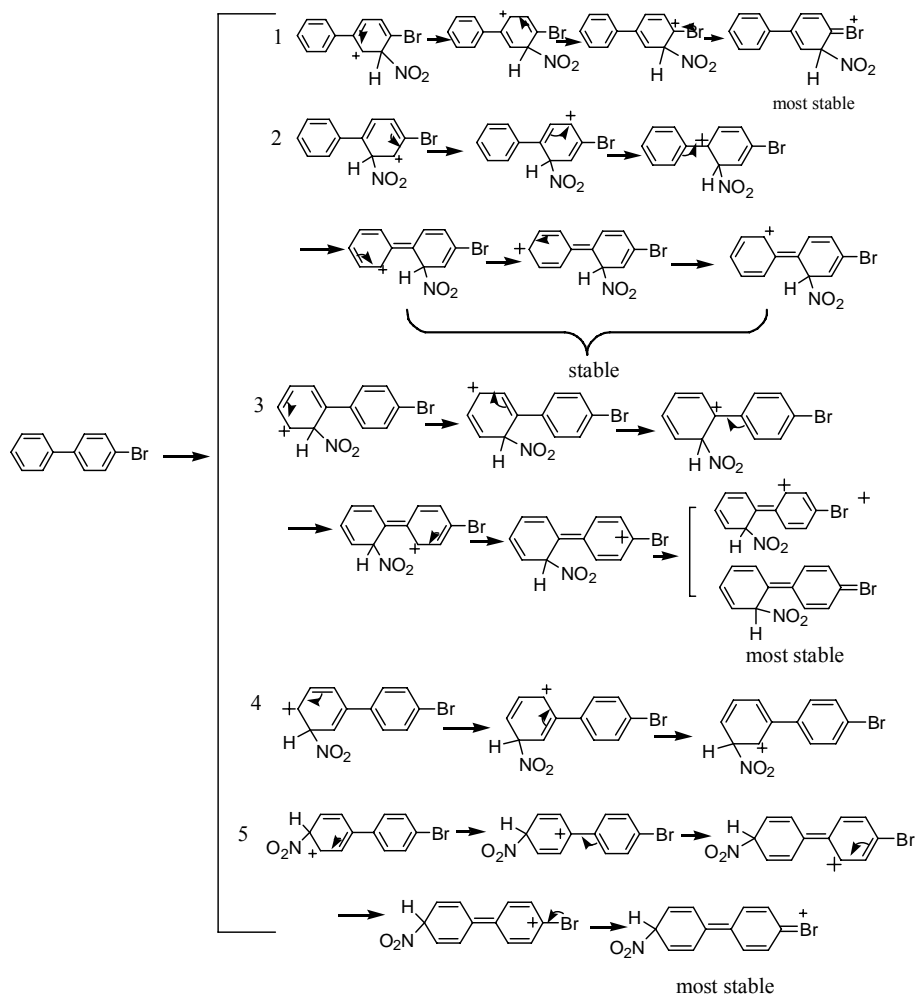


As we all know, phenyl is an electron donating group, so the following two structures are the most stable. They exist in the resonance of ortho and para positions. So bromination of biphenyl occurs at ortho and para positions rather than at meta.



16.43 At what position and on what ring do you expect nitration of bromobiphenyl to occur? Explain, using resonance structures of the potential intermediates.

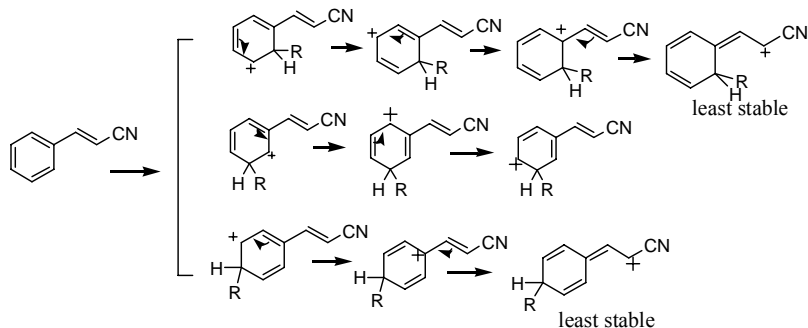
Solution:



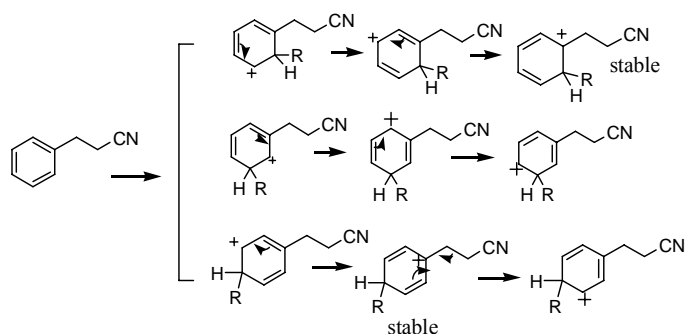
So the main product will be O=[N+]([O-])c1ccc(Br)cc1

16.44 Electrophilic substitution on 3-phenylpropanenitrile occurs at the ortho and para position, but reaction with 3-phenylpropanenitrile occurs at the meta position. Explain, using resonance structures of the intermediates.

Solution: for 3-phenylpropanenitrile, the reaction will be following:

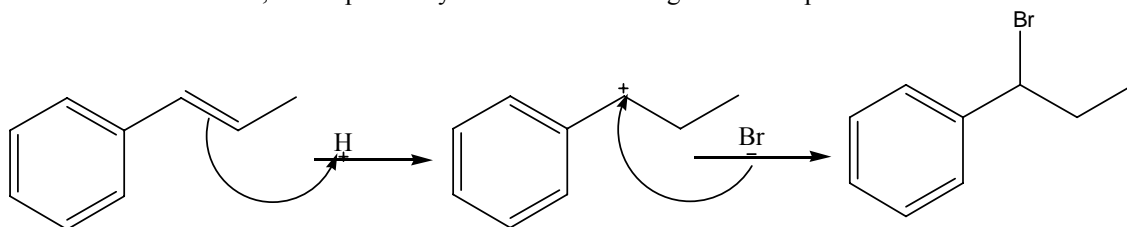


For 3-phenylpropanenitrile, the reaction will be following:



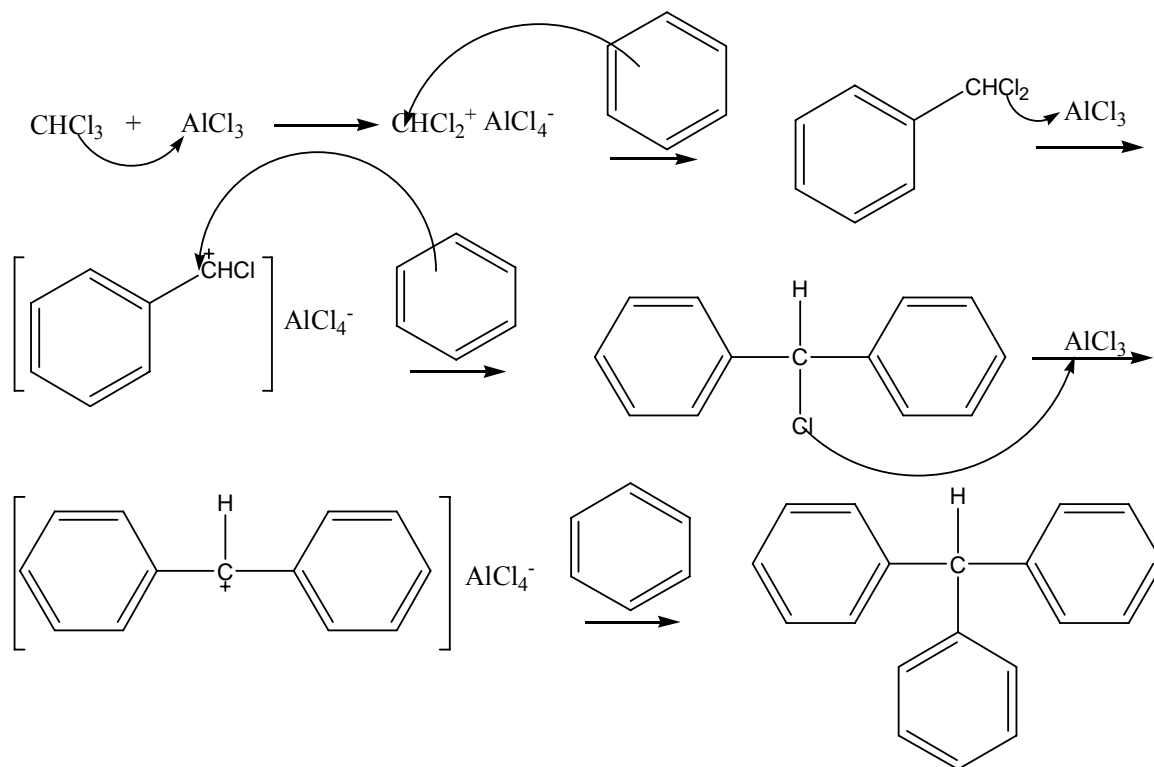
so the is ortho- and para-director by inductive effect, but is meta-director by conjugate effect.

16.45 Addition of HBr to 1-phenylpropene yields only (1-bromopropyl)benzene. Propose a mechanism for the reaction, and explain why none of the other regioisomer is produced.

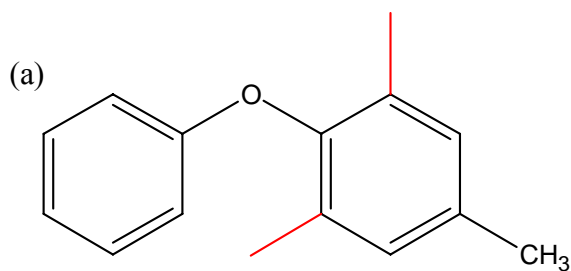


Because the intermediate: benzyl carbon cation is much more stable.

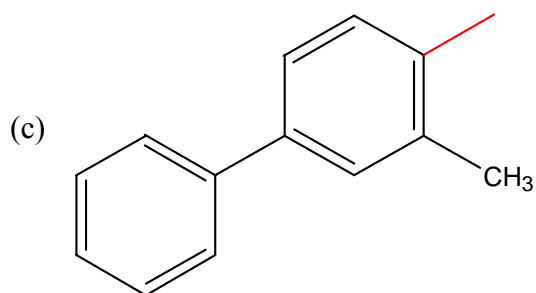
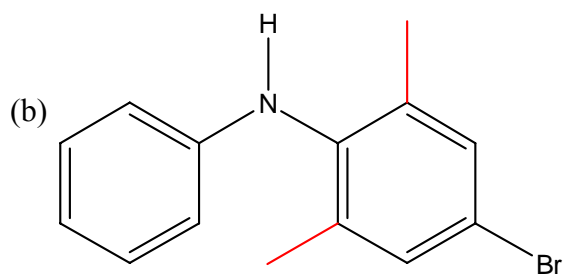
16.46 Triphenylmethane can be prepared by reaction of benzene and chloroform in the presence of AlCl_3 . Propose a mechanism for the reaction.



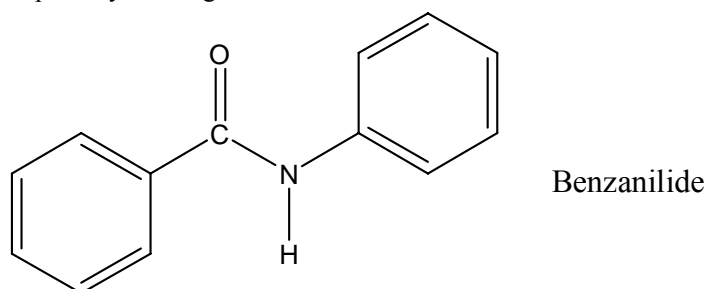
16.47: At what position, and on what ring, would you expect the following substances to undergo electrophilic substitution?

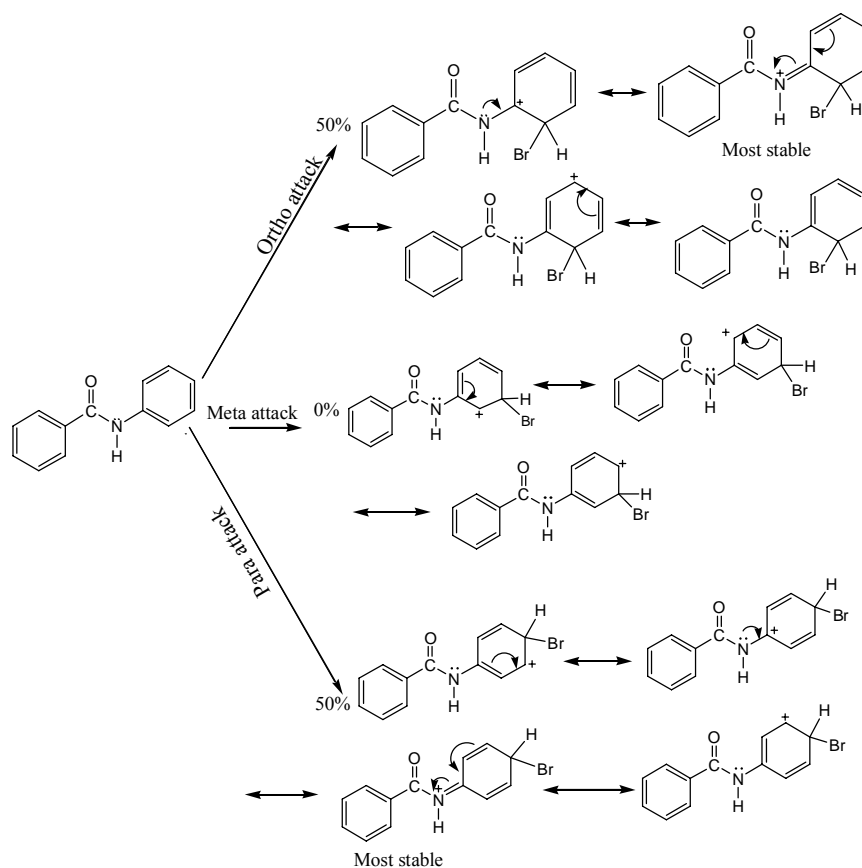


Solution:



16.48: At what position, and on what ring, would you expect bromination of benzanilide to occur? Explain by drawing resonance structures of the intermediates.

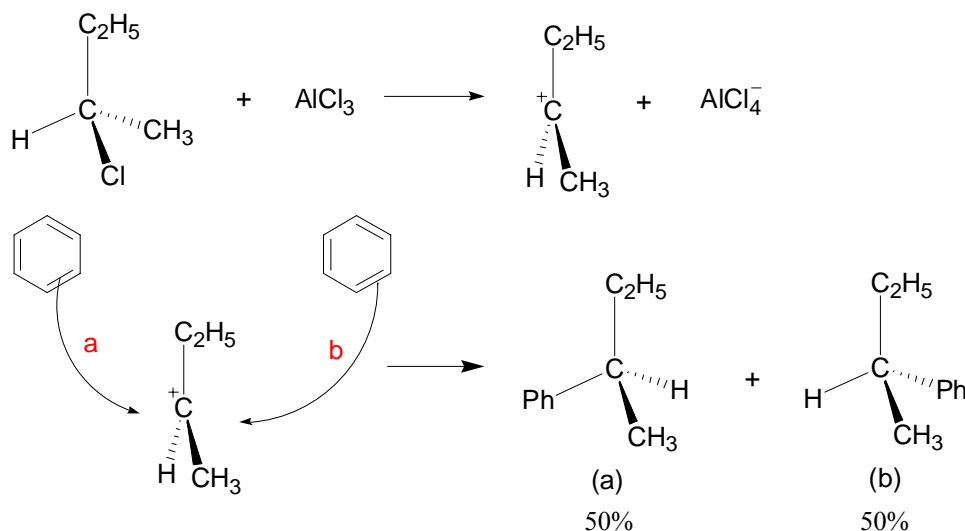




Solution:

16.49 Would you expect the Friedel-Crafts reaction of benzene with (R)-2-chloro-butane to yield optically active or racemic product? Explain.

Solution: The products are racemic, because the mechanism of the reaction is S_N1 . It occurs as below:

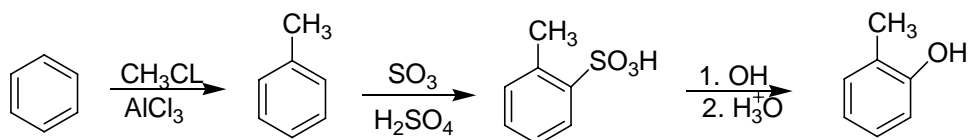


16.50 How would you synthesize the following substances starting from benzene? Assume that ortho-and para-substitution products can be separated.

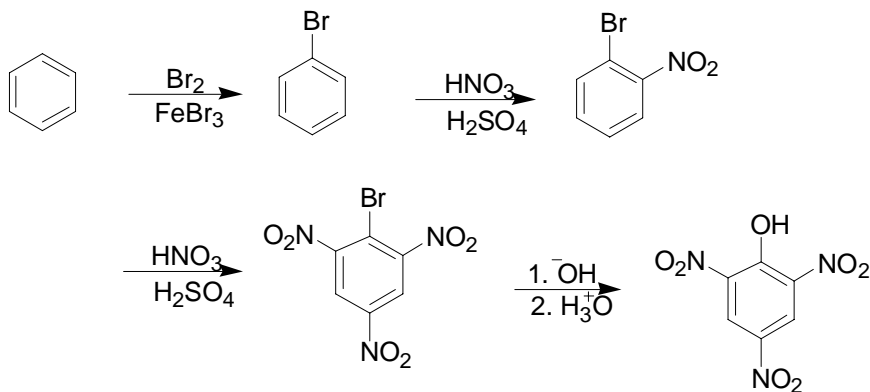
- (a) o-Methylphenol (b) 2,4,6-Trinitrophenol
(c) 2,4,6-Trinitrobenzoic acid (d) m-Bromoaniline

Solution:

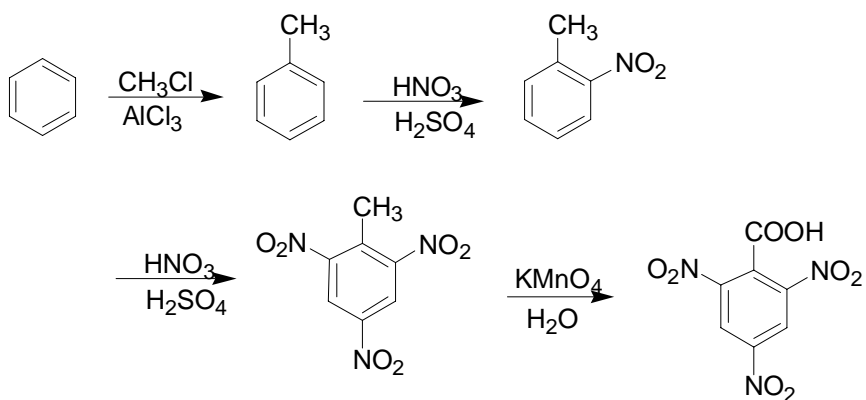
- (a)



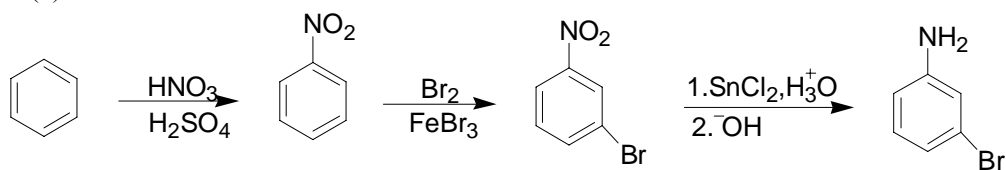
(b)



(c)



(d)



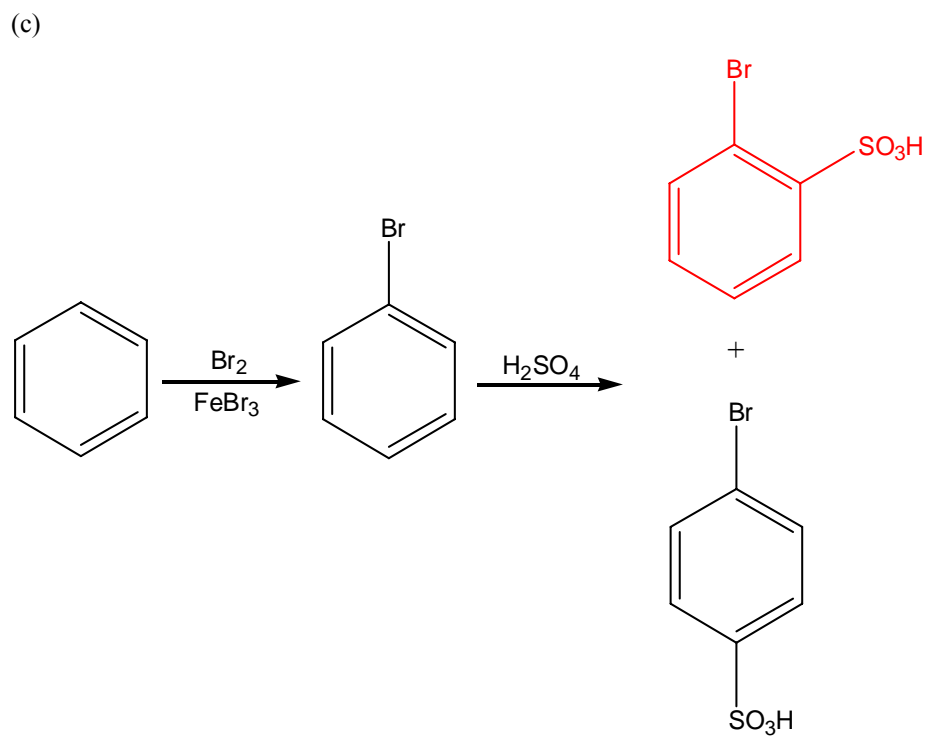
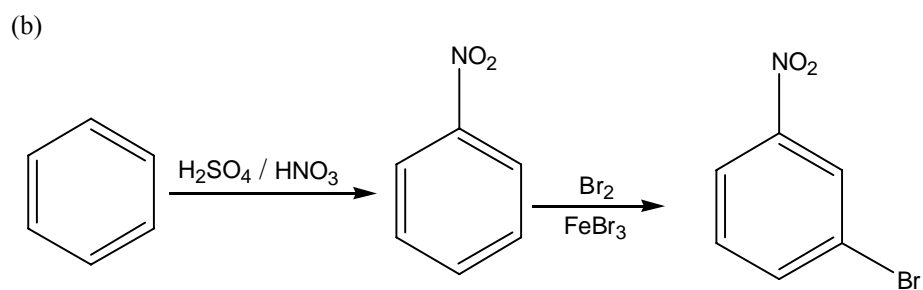
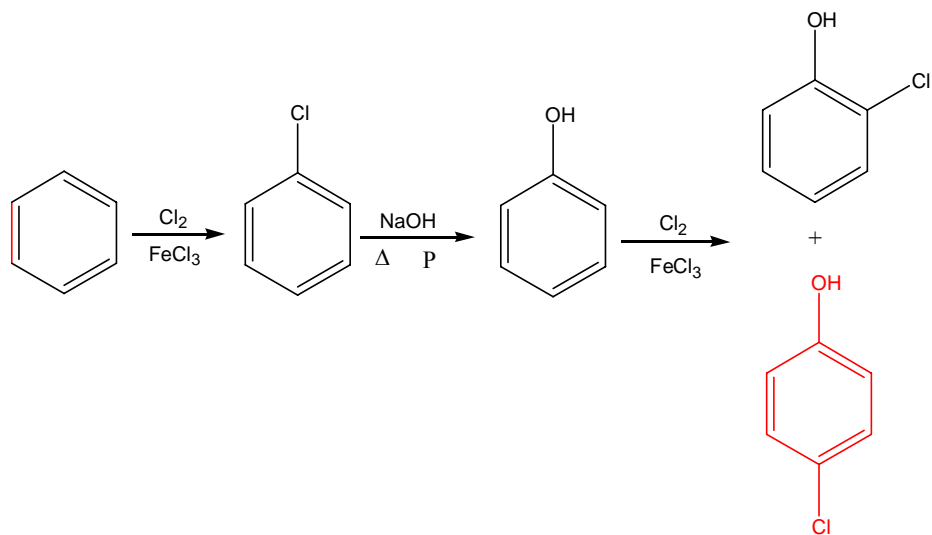
16.51 Starting with benzene as your only source of aromatic compounds, how would you synthesize the following substance? Assume that you can separate ortho and para isomers if necessary.

(a) *p*-Chlorophenol. (b) *m*-Bromonitrobenzene.

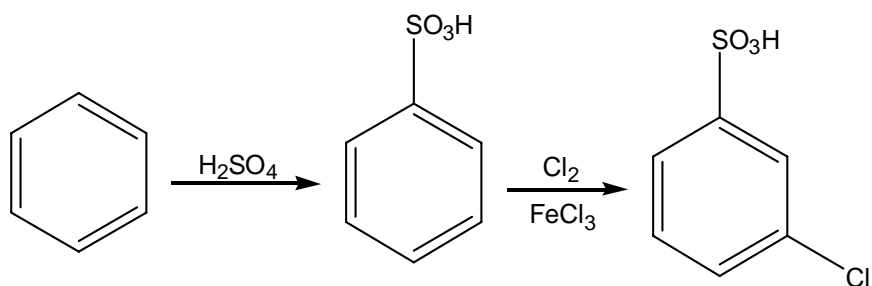
(c) *o*-Bromobenzenesulfonic acid. (d) *m*-Chlorobenzenesulfonic acid.

Solution:

(a)



(d)



16.52 Starting with either benzene or toluene, how would you synthesis the following substances?

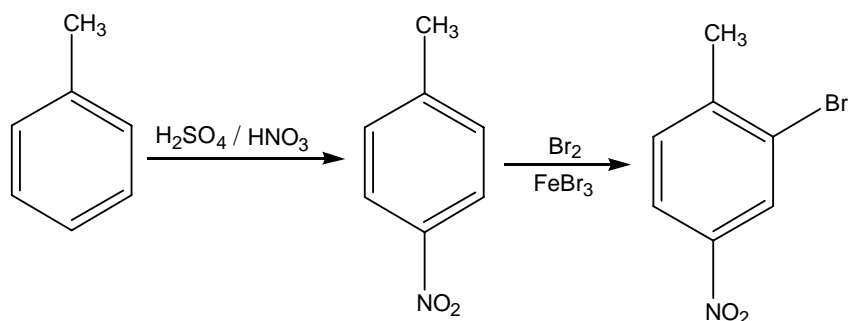
Assume that orho and para isomers can be sepatated.

(a) 2-Bromo-4-nitrotoluene. (b) 1,3,5-Trinitrobenzene.

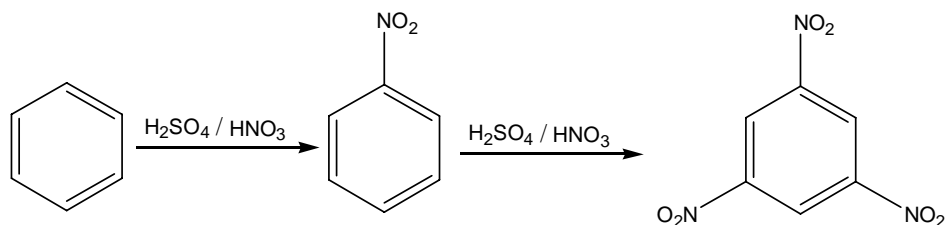
(c) 2,4,6-Tribromoaniline. (d) 2-Chloro-4-methylphenol

Solution:

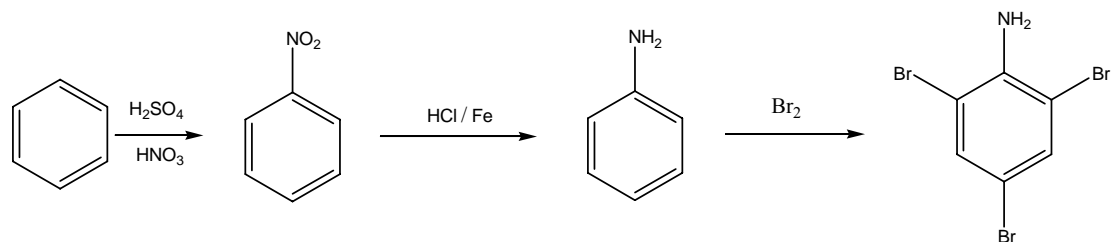
(a)



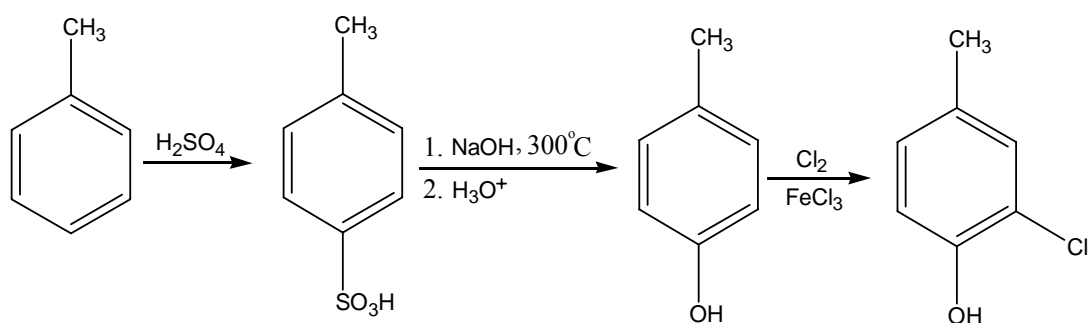
(b)



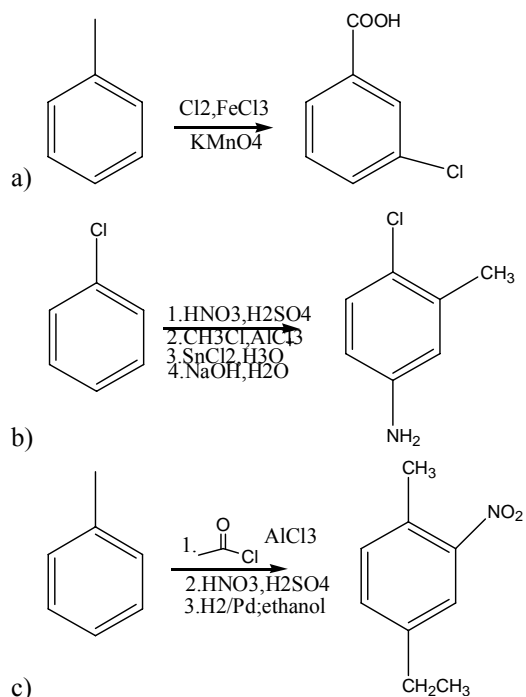
(c)



(d)



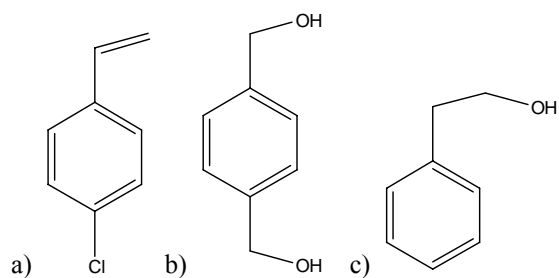
16.53 As written, the following syntheses have flaws. What is wrong with each?



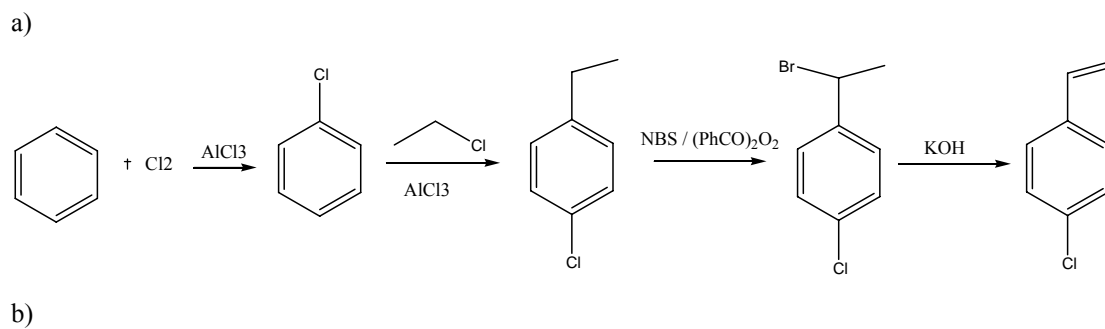
Solution:

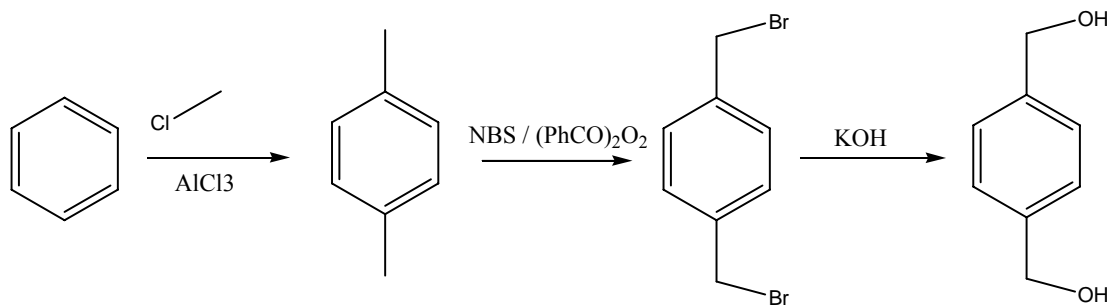
- a) Methyl is an o,p-director group, so the reaction should be:
- b) P-Chloronitrobenzene is inert to F-C reaction.
- c) The first two steps in the sequence is incorrect, but H₂ / Pd reduces the nitro group as well as the ketone.

16.54 How would you synthesize substances starting from benzene?

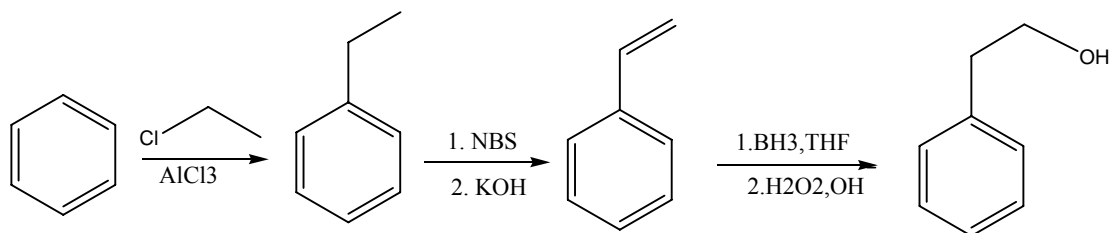


Solution:

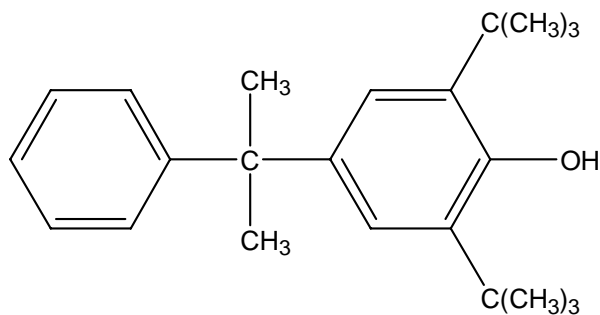




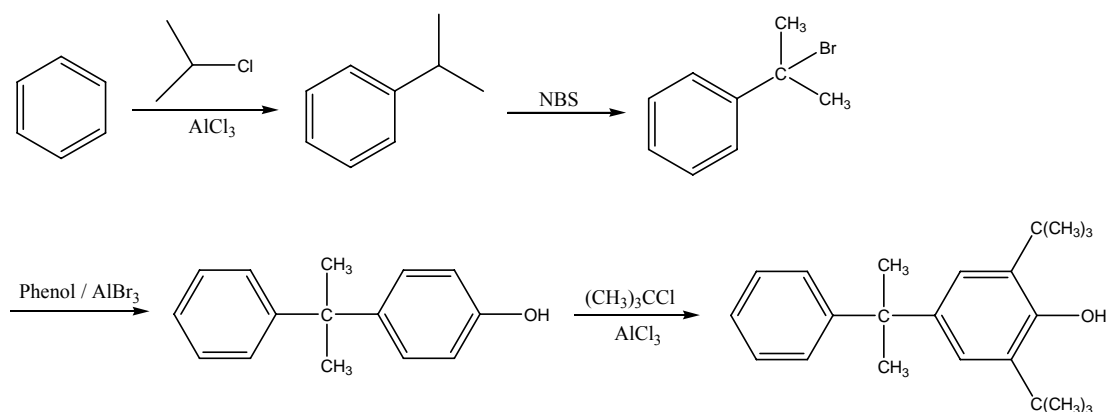
c)



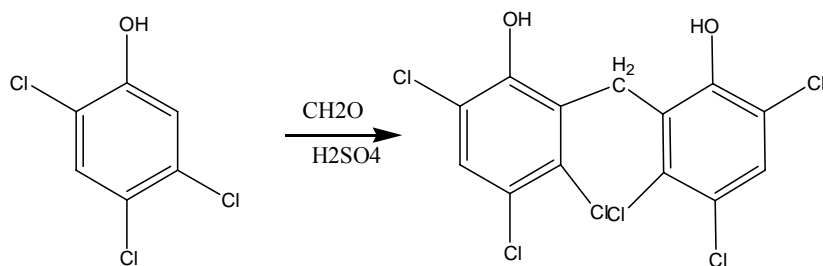
16.55. The compound MON-0585 is a nontoxic, biodegradable larvicide that is highly selective against mosquito larvae. Synthesize MON-1585 using only benzene as a source of the aromatic rings.



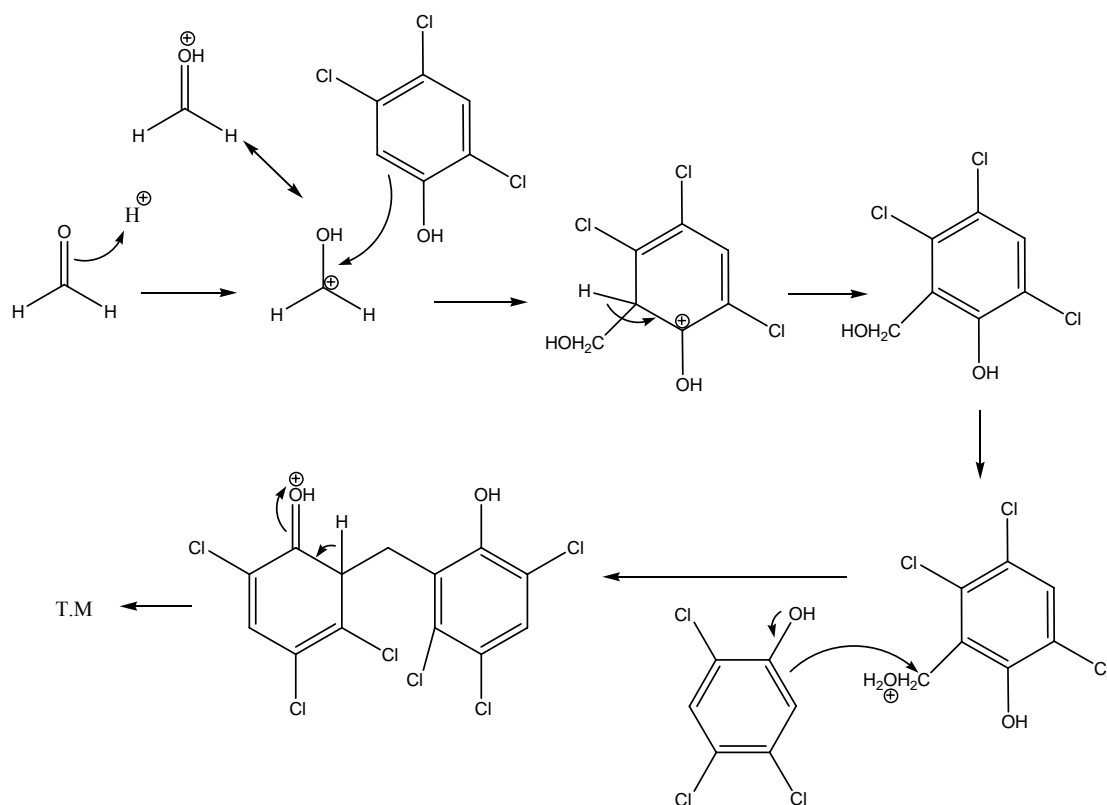
SOLUTION:



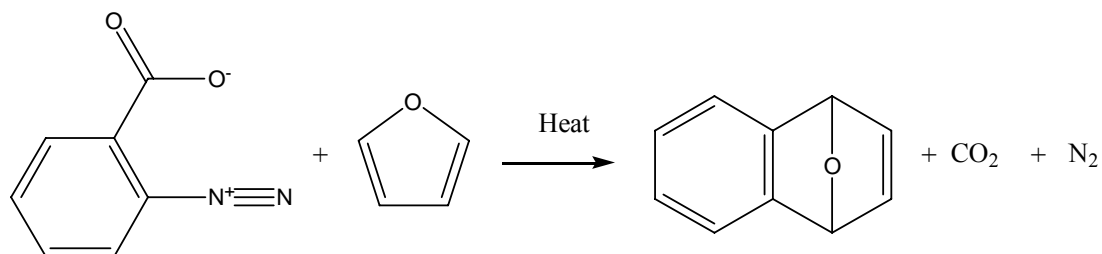
16.56 Hexachlorophene, a substance used in the manufacture of germicidal soaps, is prepared by reaction of 2, 4, 5-trichlorophenol with formaldehyde in the presence of concentrated sulfuric acid. Propose a mechanism for the reaction.



SOLUTION:



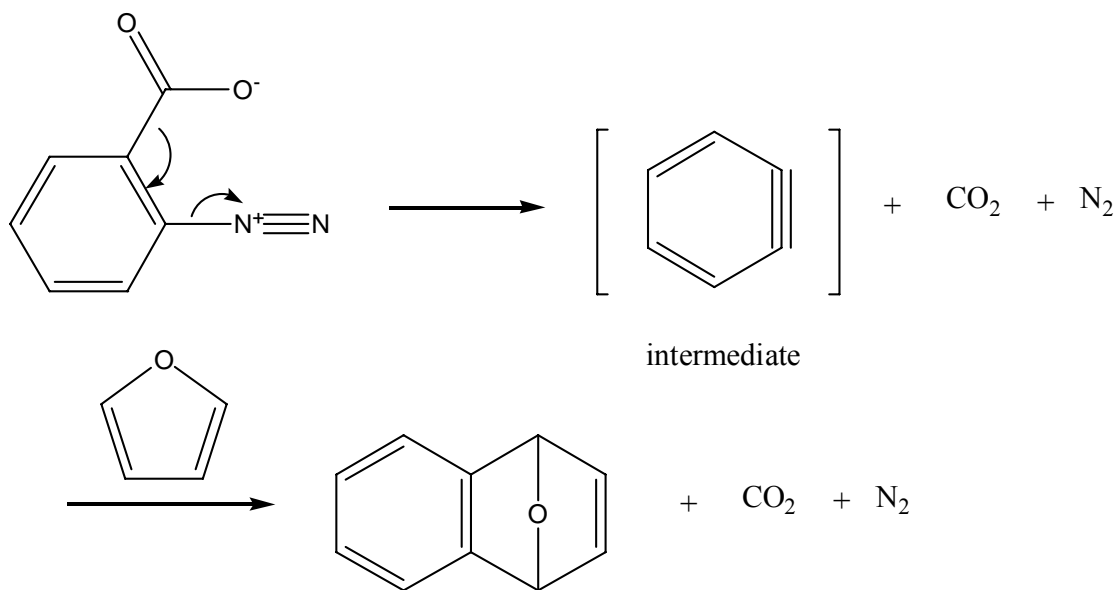
16.57 Benzenediazonium carboxylate decomposes when heated to yield N_2 , CO_2 , and a reactive substance that can't be isolated. When benzenediazonium carboxylate is heated in the presence of furan, the following reaction is observed:



Benzenediazonium carboxylate

What intermediate is involved in this reaction? Propose a mechanism for its formation.

Solution:



16.58 phenylboronic acid, $\text{C}_6\text{H}_5\text{B}(\text{OH})_2$, is nitrated to give 15% ortho-substitution product and 85% meta. Explain the meta-directing effect of the $-\text{B}(\text{OH})_2$ group.

Solution:

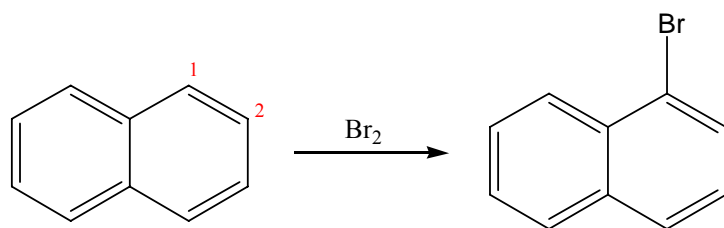
$-\text{B}(\text{OH})_2$ group on the aromatic ring withdraws electrons because the vacant p_z orbital of B causing electron-withdrawing resonance effect which is strong.

Meanwhile, it has a electron-donating inductive effect which is weak.

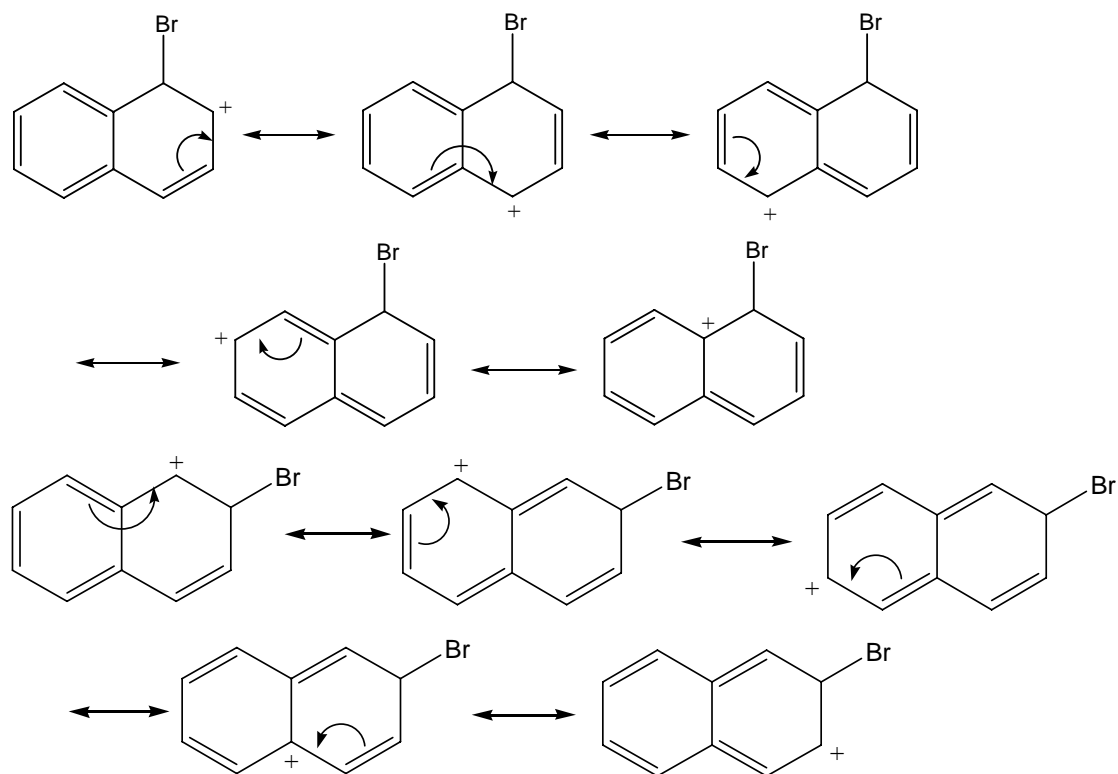
So the electron-withdrawing resonance effect dominates and deactivate ortho and para positions.

As a result, $-\text{B}(\text{OH})_2$ group is a meta-directing deactivator.

16.59 Draw resonance structures of the intermediate carbocations in the bromination of naphthalene, and account for the fact that naphthalene undergoes electrophilic substitution at C1 rather than C2.



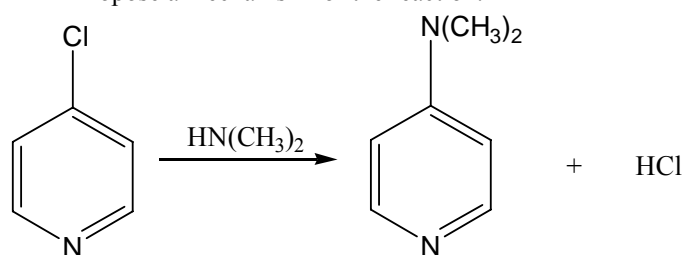
Solution:



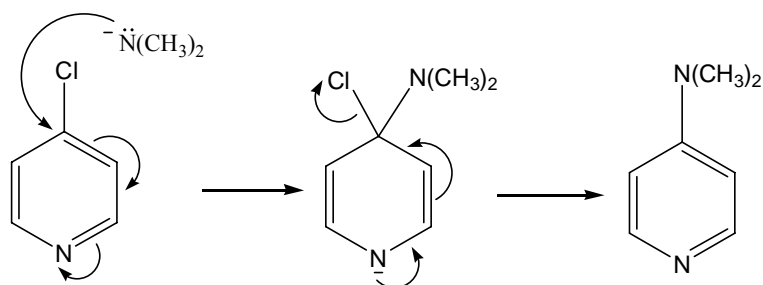
Because the first two resonance structures for a-substitution are stable forms, while there is only one stable resonance form for the b-substitution.

16.60 4-Chloropyridine undergoes reaction with dimethylamine to yield 4-dimethyl-aminopyridine.

Propose a mechanism for the reaction.



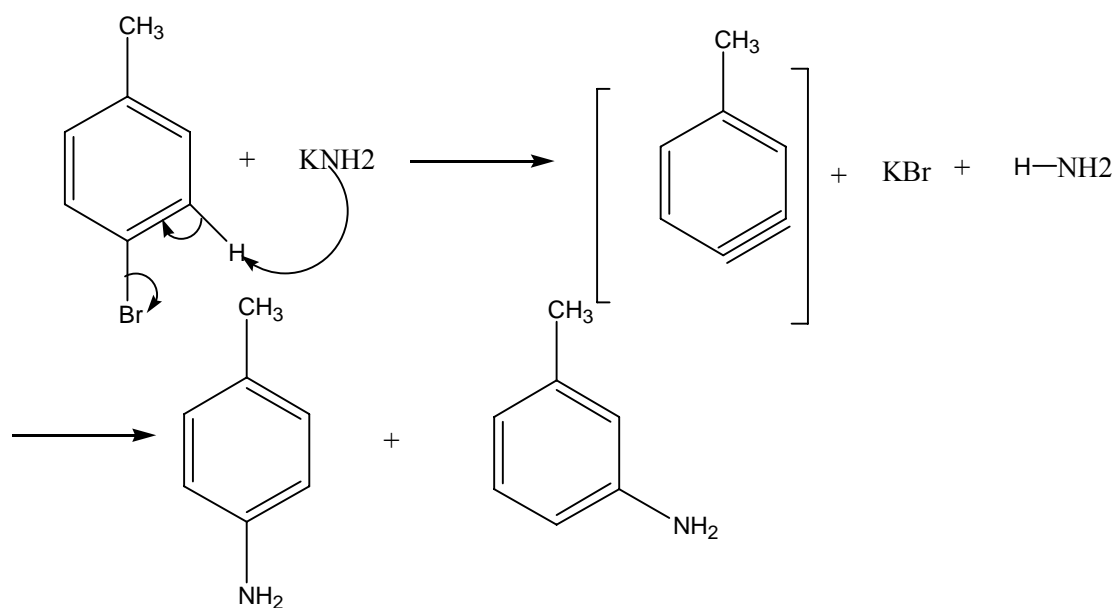
Solution:



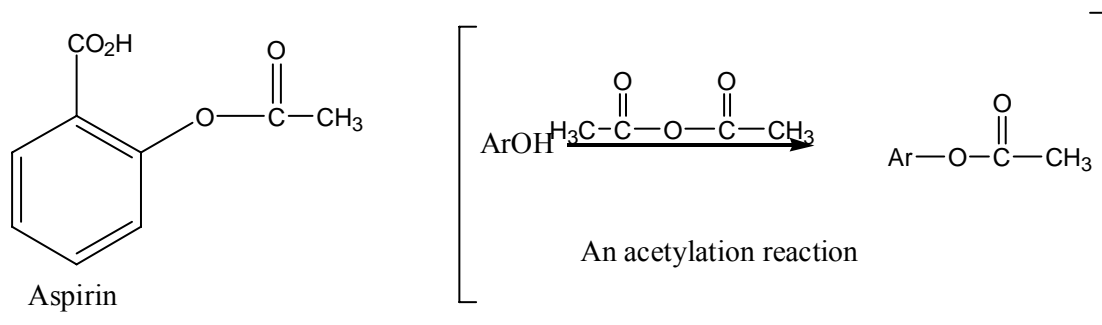
16.61 p-Bromotoluene reacts with potassium amide to give a mixture of m- and p-methylaniline.

Explain.

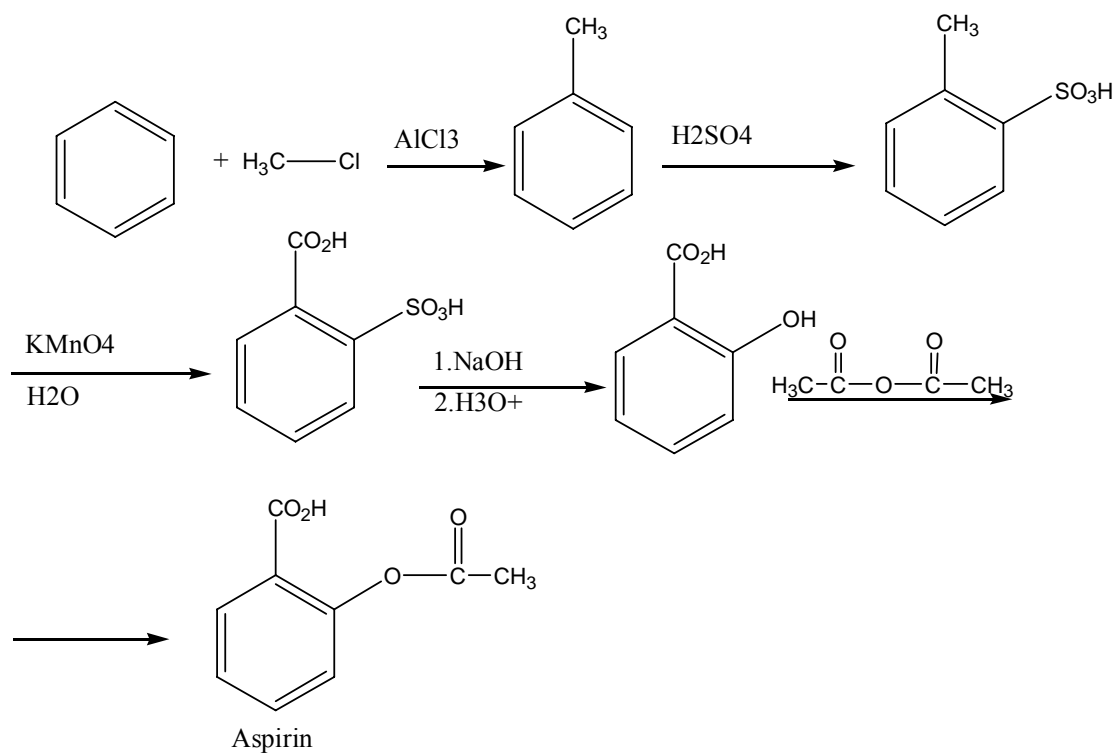
Solution:



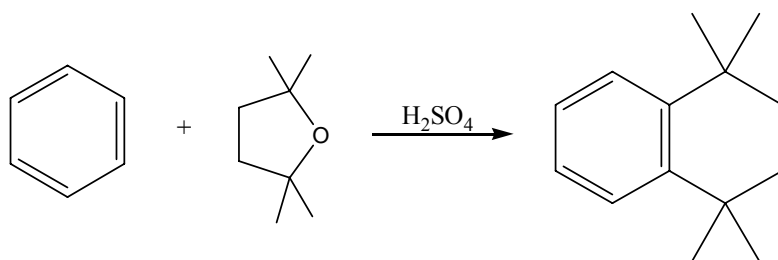
16.62 Propose a synthesis of aspirin (acetylsalicylic acid) starting from benzene. You will need to use an acetylation reaction at some point in your scheme.



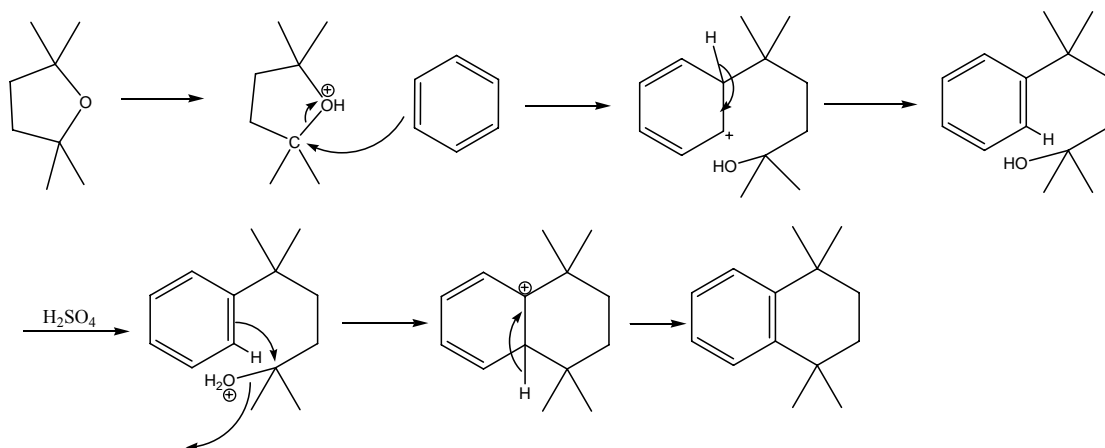
Solution:



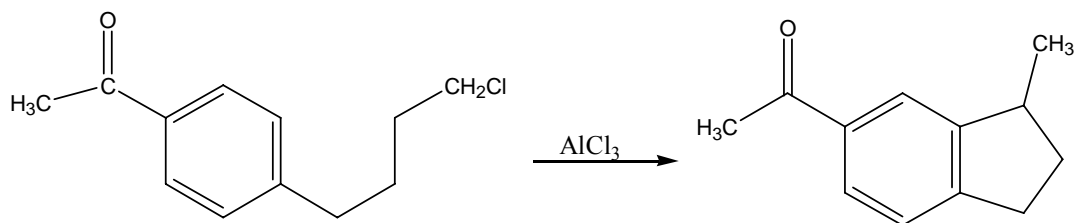
16.63 Propose a mechanism to account for the reaction of benzene with 2,2,5,5-tetramethyltetrahydrofuran.



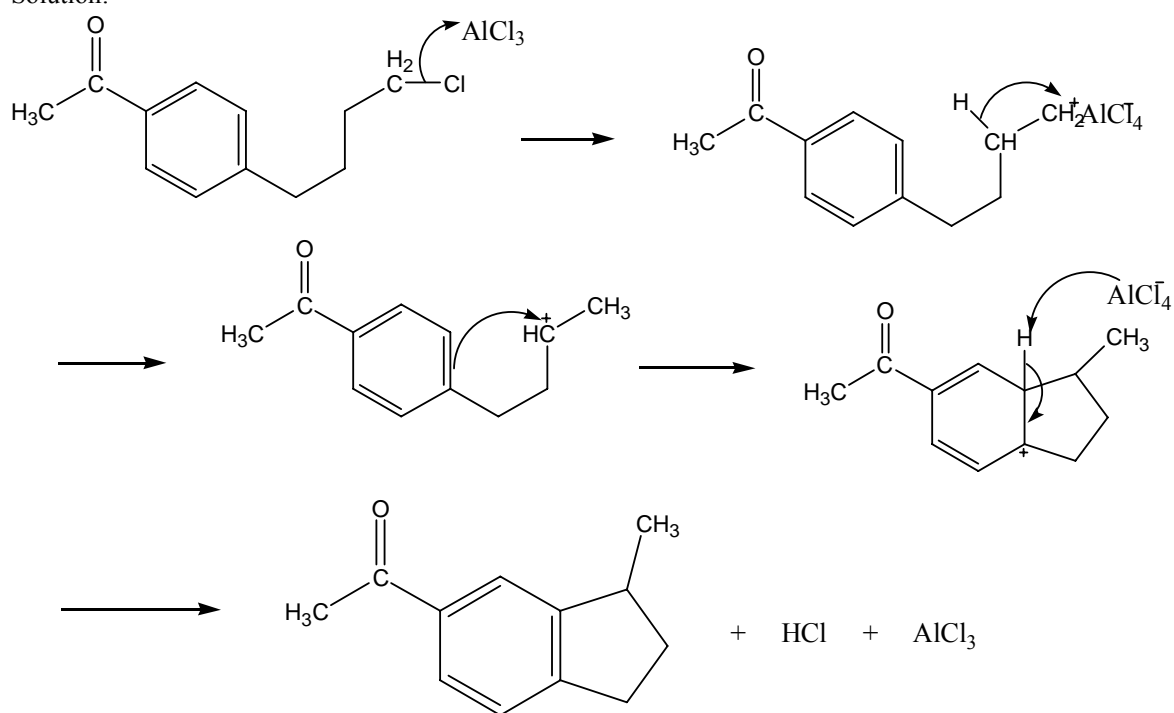
Solution:



16.64 Propose a mechanism to account for the following reaction:

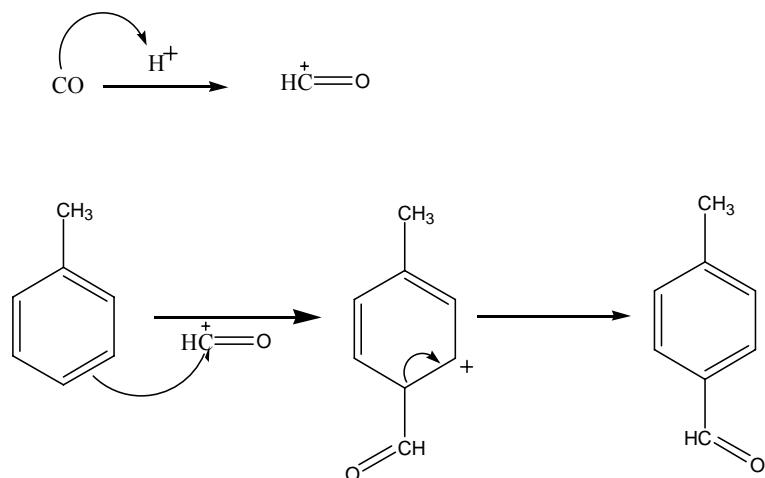


Solution:



16.65 In the gatterman-koch reaction, a formyl group is introduced directly onto a benzene ring. Propose a mechanism.

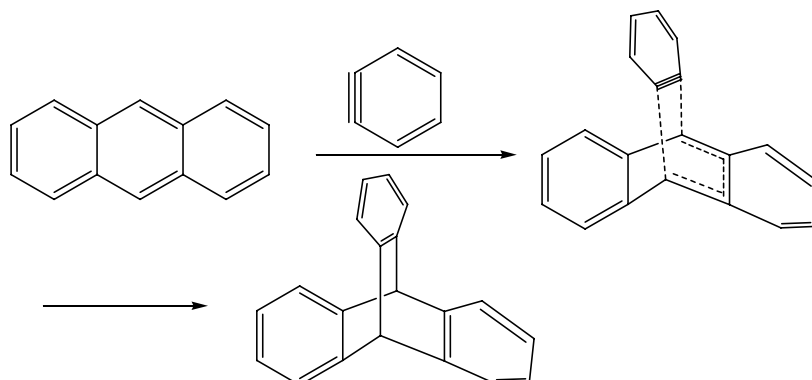
Answer:



16.66 Triptycene is an unusual molecule that has been prepared by reaction of benzyne with

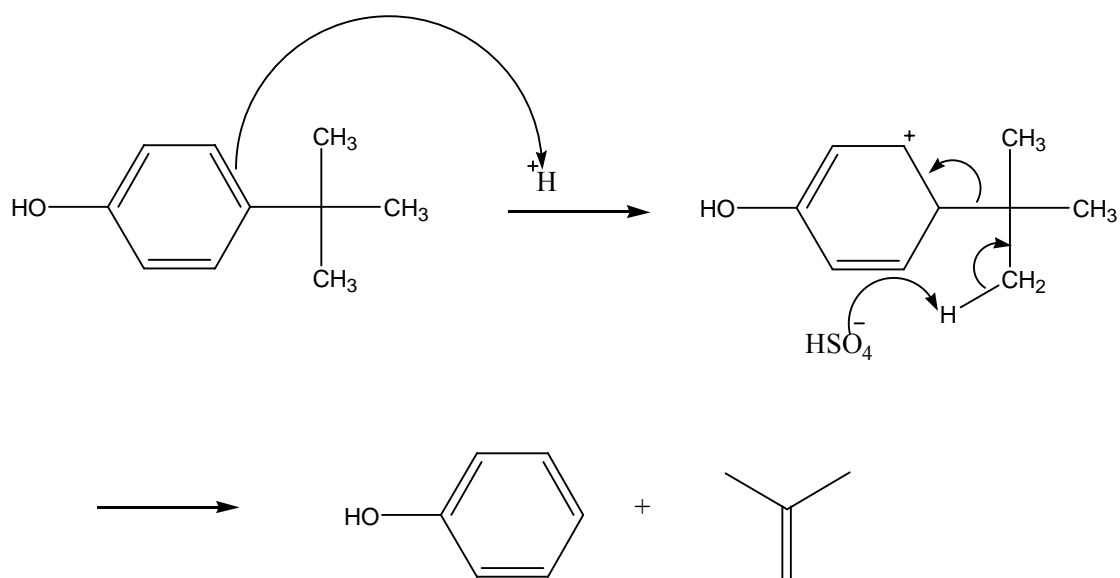
anthracene. Show the mechanism.

Answer:

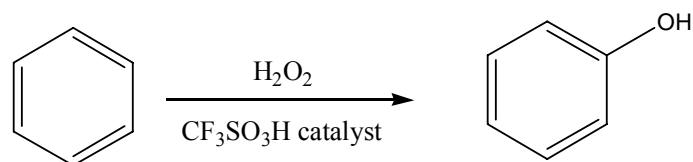


16.67. Treatment of p-tert-butylphenol with a strong acid as H_2SO_4 yields phenol and 2-methylpropene. Propose a mechanism.

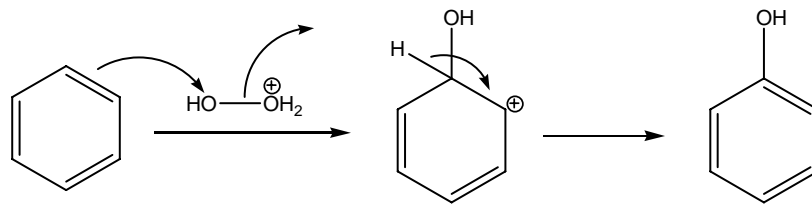
Solution:



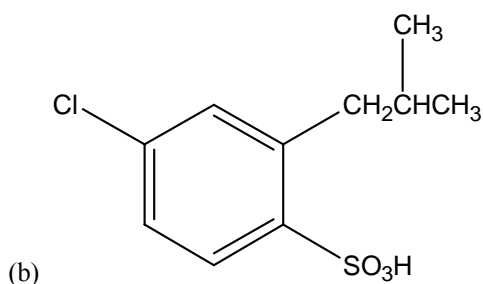
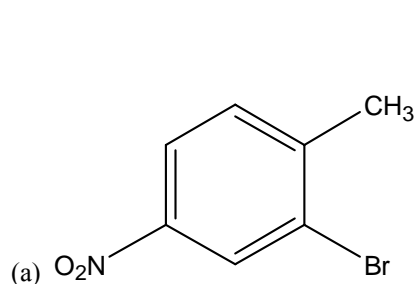
16.68. Benzene and alkyl-substituted benzenes can be hydroxylated by reaction with H_2O_2 in presence of an acidic catalyst. What is the structure of the reactive electrophile? Propose a mechanism for the reaction.



Solution:

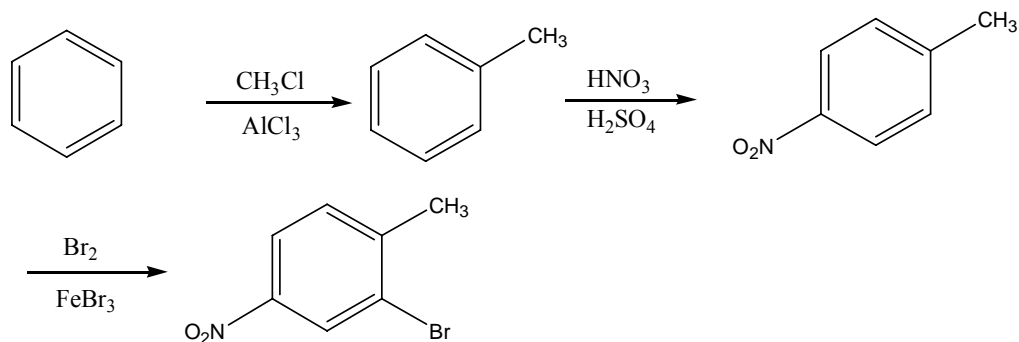


16.69 How would you synthesize the following compounds from benzene? Assume that ortho and para isomers can be separated.

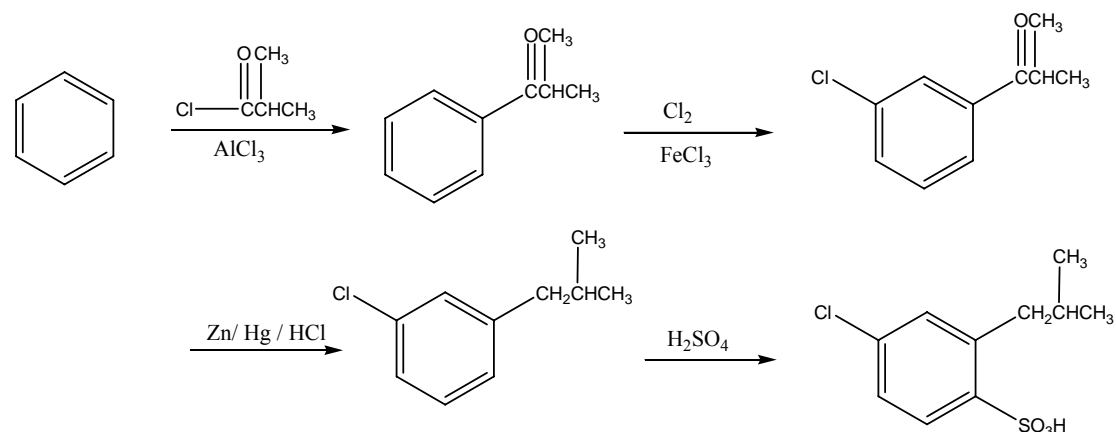


Solution:

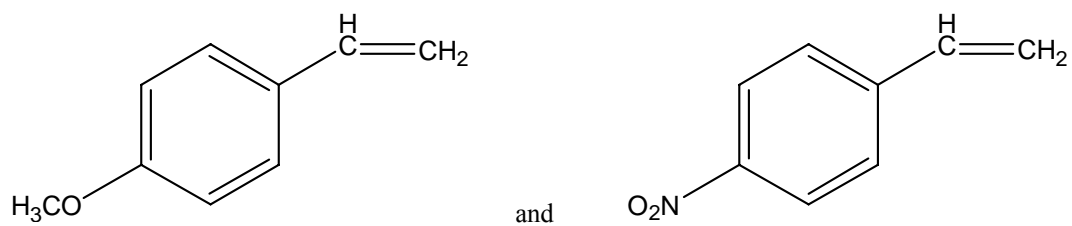
(a)



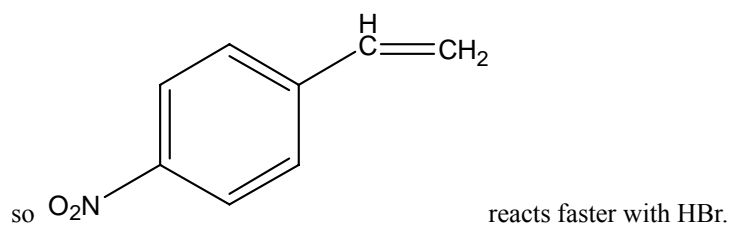
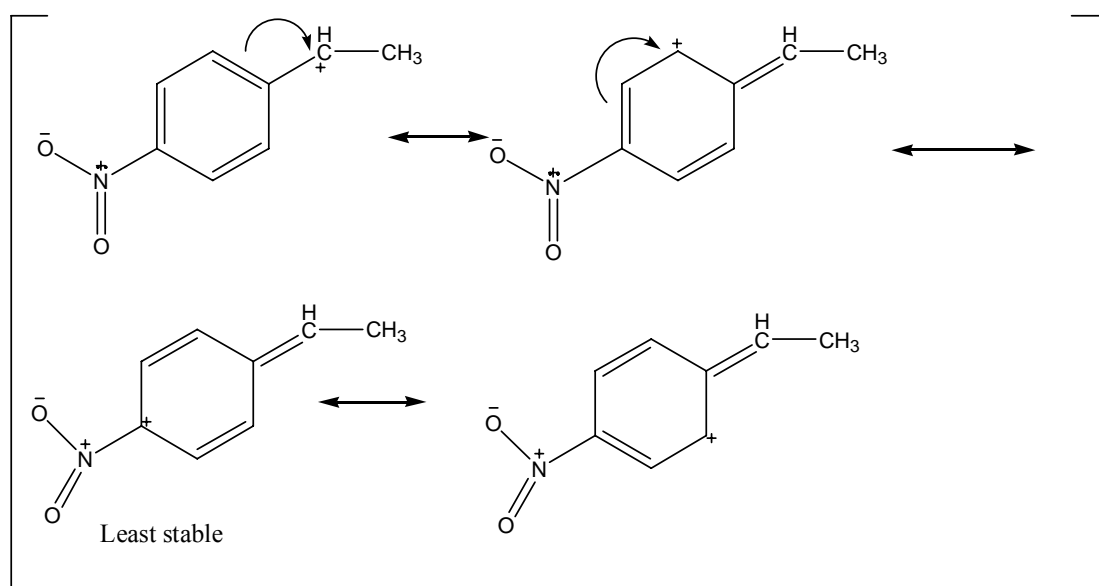
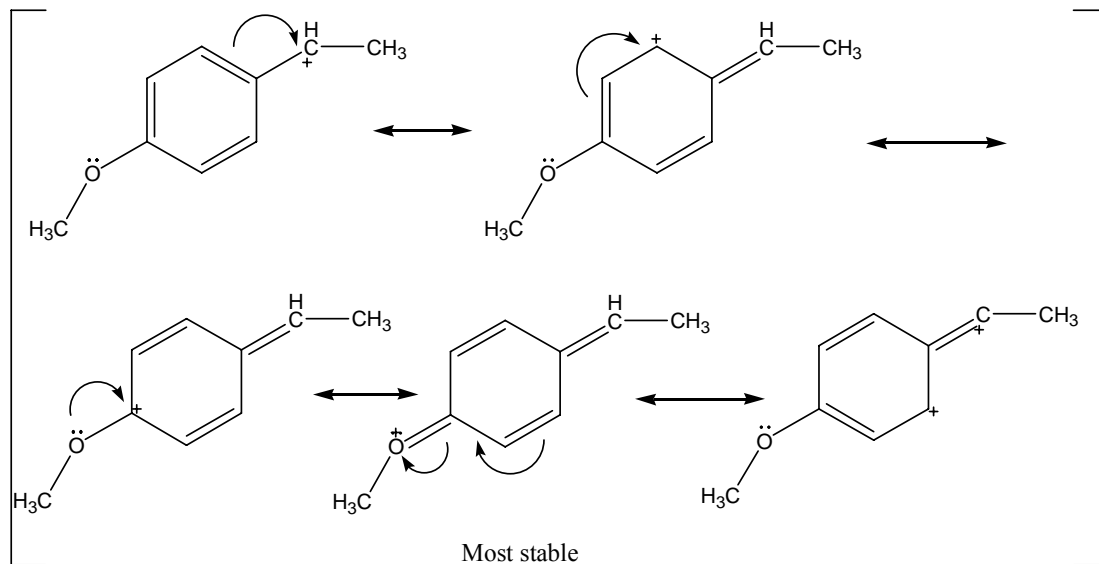
(b)



16.70 You know the mechanism of HBr addition to alkenes, and you know the effects of various substituent groups on aromatic substitution. Use this knowledge to predict which of the following two alkenes reacts faster with HBr. Explain your answer by drawing resonance structures of the carbocation intermediates.



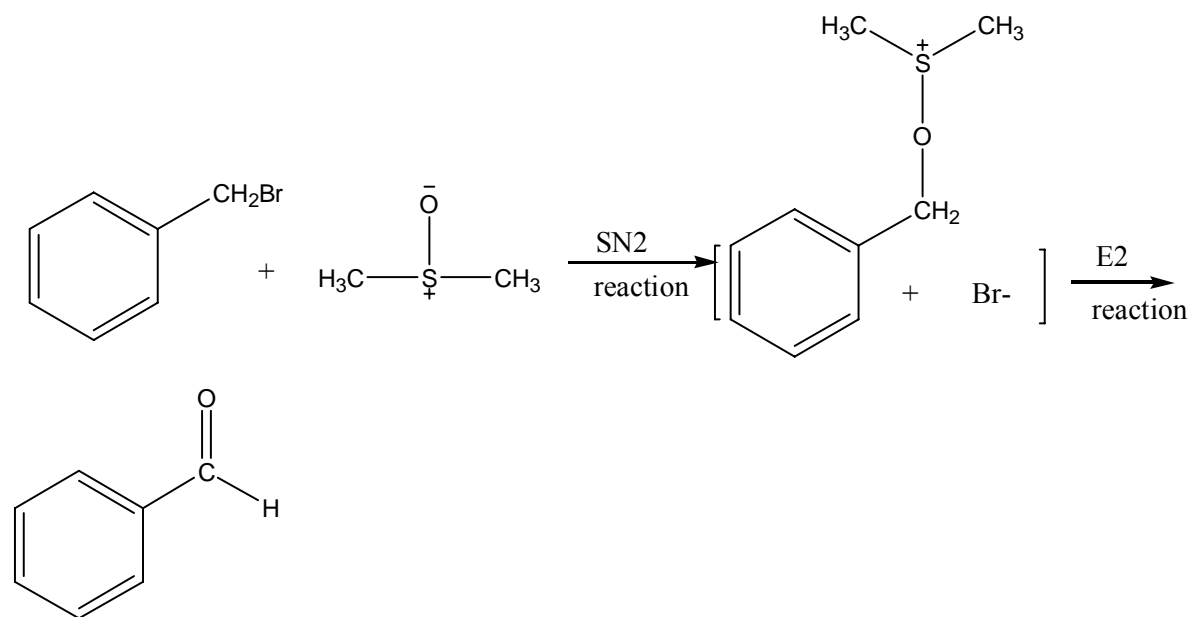
Solution:



16.71 Benzyl bromide is converted into benzaldehyde by heating in dimethyl sulfoxide. Propose a

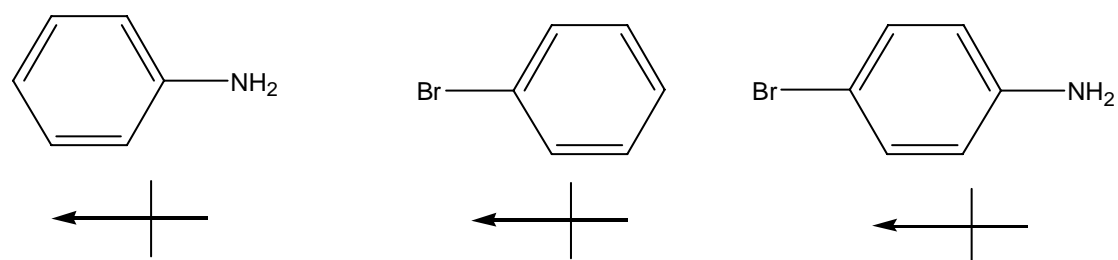
structure for the intermediate, and show the mechanisms of the two steps in the reaction.

Solution:



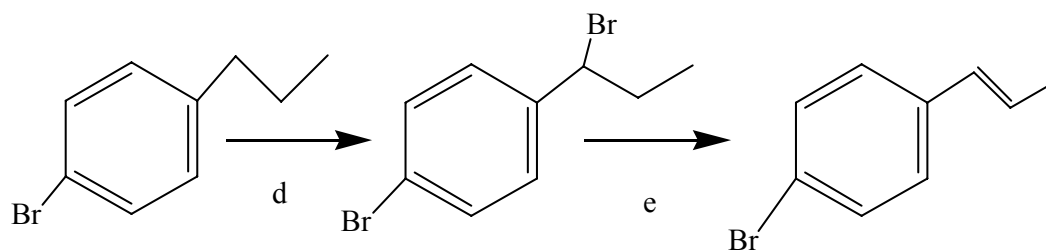
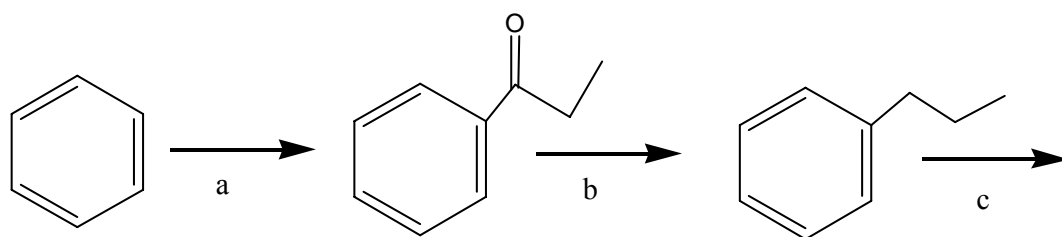
16.72 Use your knowledge of directing effects, along with following data, to deduce the directions of dipole moments in aniline and bromobenzene.

Solution:

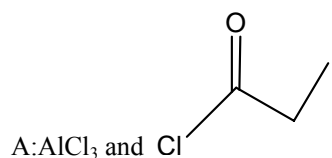


In the aniline molecule, because the lone-pair electrons of nitrogen atom and 6 electrons in the benzene molecule forms a Π_7^8 . But in the bromobenzene molecule, the inductive effect is more important than the conjugating effect, so the direction of the whole molecule is opposite to aniline. As a whole, the p-Bromoaniline show its dipole moments like the third figure.

16.73 Identify the reagent represented by the letters a-e in the following scheme:



Reasoning and solutions :



A: AlCl_3 and Cl

B: Pt and H_2

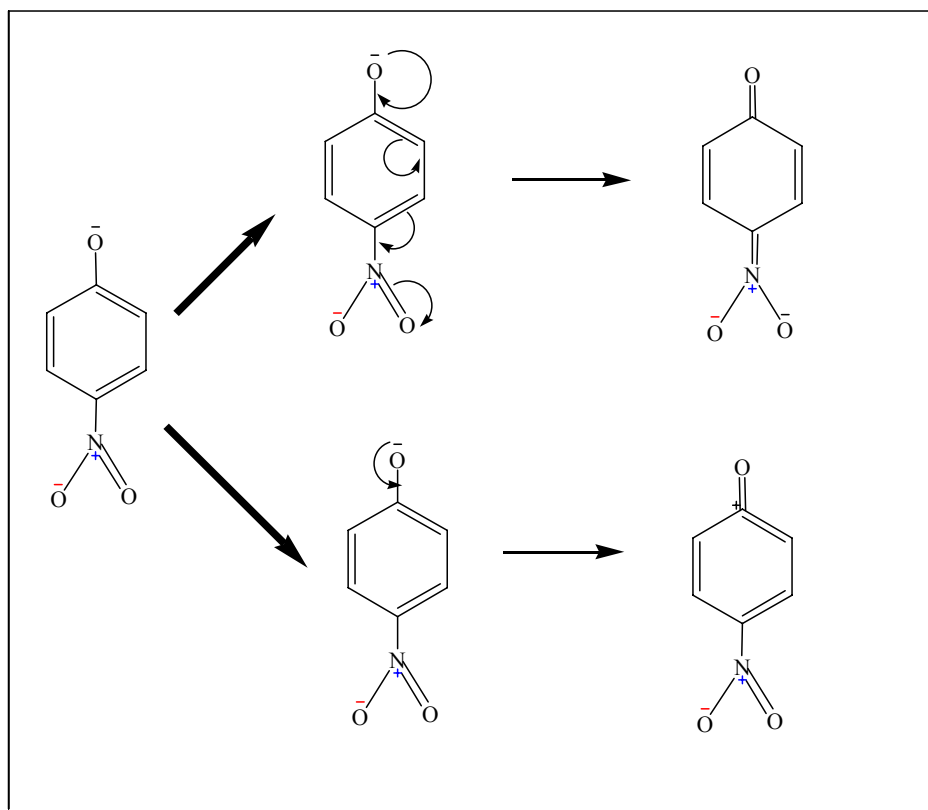
C: Br_2 and FeBr_3 (as a catalyst)

D: NBS and CCl_4 (as a solvent)

E: NaOH

16.74: Phenols (ArOH) are relatively acidic, and the presence of a substituent group on the aromatic ring has a large effect. The PK_a of unsubstituted phenol, for example, is 9.89, while that of *p*-nitrophenol is 7.15. Draw resonance forms of the corresponding phenoxide anions and explain the data.

Solutions :



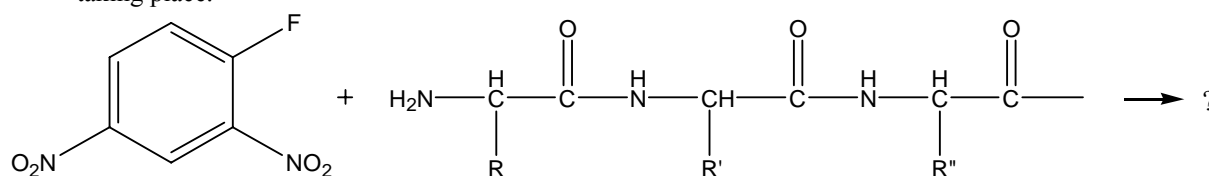
Because the acidity associates with two facts (1), the dissociation (2) the inductive effects. With a nitro group, it is easier to be solvated by water. What is more, it is a electron withdraw group. So it is more acidic.

16.75 Would you expect p-methylphenol to be more acidic or less acidic than unsubstituted phenol? Explain.

Solution:

Substituted phenols can be either more acidic or less acidic than phenol itself. Phenol with an electron-withdrawing substituent are generally more acidic because these substituents delocalize the negative charge. Therefore, p-methylphenol is less acidic than phenol.

16.76 One method for determining the sequence of amino acids in a large protein molecule involve treatment for the protein with *Sanger's reagent*, 2,4-dinitrofluorobenzene. The reaction involves the -NH_2 group at the end of protein chain. Predict the product, and tell what kind of reaction is taking place.



Solution:

Nucleophilic substitution reaction:

