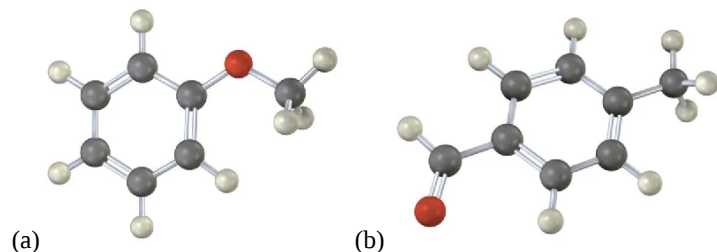


3.13: Additional Problems

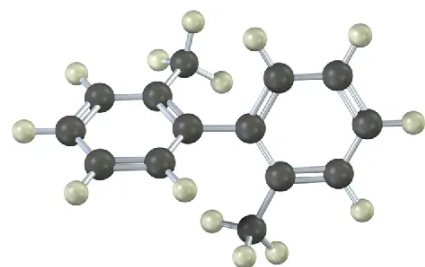
16 • Additional Problems

Visualizing Chemistry

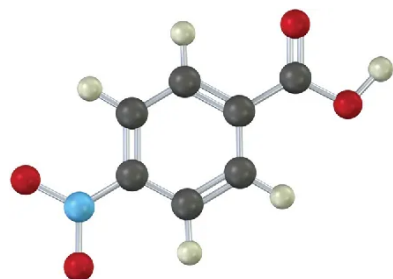
PROBLEM 3-24 Draw the product from reaction of each of the following substances with (1) Br_2 , FeBr_3 and (2) CH_3COCl , AlCl_3 .



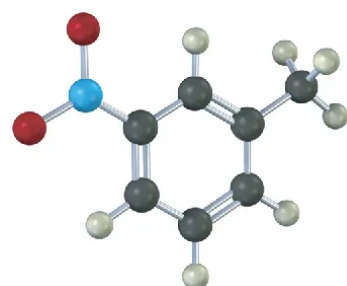
PROBLEM 3-25 The following molecular model of a dimethyl-substituted biphenyl represents the lowest-energy conformation of the molecule. Why are the two benzene rings tilted at a 63° angle to each other rather than being in the same plane so that their p orbitals overlap? Why doesn't complete rotation around the single bond joining the two rings occur?



PROBLEM 3-26 How would you synthesize the following compound starting from benzene? More than one step is needed.



PROBLEM 3-27 The following compound can't be synthesized using the methods discussed in this chapter. Why not?



Mechanism Problems

Mechanisms of Electrophilic Substitutions

PROBLEM 3-28 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.

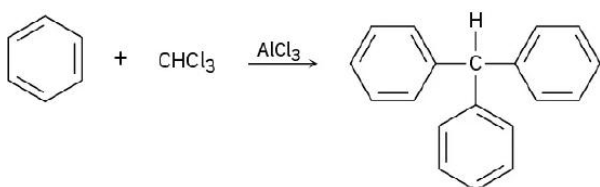
PROBLEM 3-29 The sulfonation of an aromatic ring with SO_3 and H_2SO_4 is reversible. That is, heating benzenesulfonic acid with H_2SO_4 yields benzene. Show the mechanism of the desulfonation reaction. What is the electrophile?

PROBLEM 3-30 The carbocation electrophile in a Friedel–Crafts reaction can be generated by an alternate means than reaction of an alkyl chloride with AlCl_3 . For example, reaction of benzene with 2-methylpropene in the presence of H_3PO_4 yields *tert*-butylbenzene. Propose a mechanism for this reaction.

PROBLEM 3-31 The *N,N,N*-trimethylammonium group, $-\text{N}^+(\text{CH}_3)_3$, is one of the few groups that is a meta-directing deactivator yet has no electron-withdrawing resonance effect. Explain.

PROBLEM 3-32 The nitroso group, $-\text{N}=\text{O}$, is one of the few nonhalogens that is an ortho- and para-directing deactivator. Explain this behavior by drawing resonance structures of the carbocation intermediates in ortho, meta, and para electrophilic reaction on nitrosobenzene, $\text{C}_6\text{H}_5\text{N}=\text{O}$.

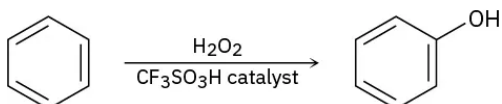
PROBLEM 3-33 Triphenylmethane can be prepared by reaction of benzene and chloroform in the presence of AlCl_3 . Propose a mechanism for the reaction.



PROBLEM 3-34 Using resonance structures of the intermediates, explain why bromination of biphenyl occurs at ortho and para positions rather than at meta.

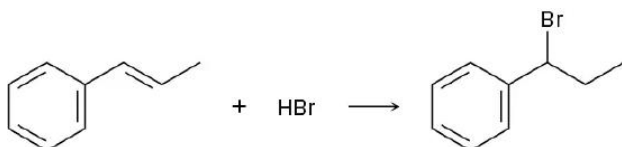


PROBLEM 3-35 Benzene and alkyl-substituted benzenes can be hydroxylated by reaction with H_2O_2 in the presence of an acidic catalyst. What is the structure of the reactive electrophile? Propose a mechanism for the reaction.

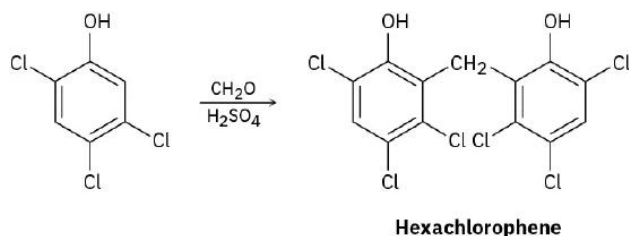


Additional Mechanism Practice

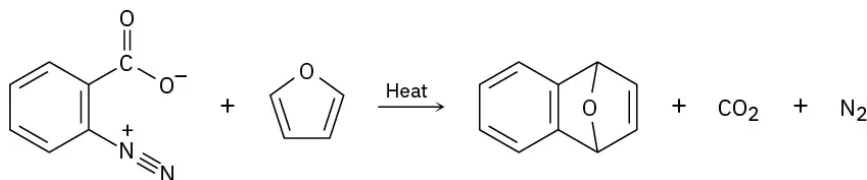
PROBLEM 3-36 Addition of HBr to 1-phenylpropene yields only (1-bromopropyl)benzene. Propose a mechanism for the reaction, and explain why none of the other regioisomer is produced.



PROBLEM 3-37 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.

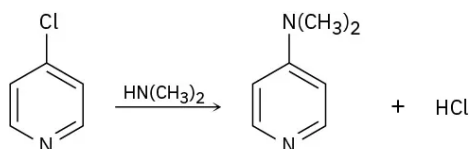


PROBLEM 3-38 Benzenediazonium carboxylate decomposes when heated to yield N_2 , CO_2 , and a reactive substance that can't be isolated. When benzene-diazonium carboxylate is heated in the presence of furan, the following reaction is observed:

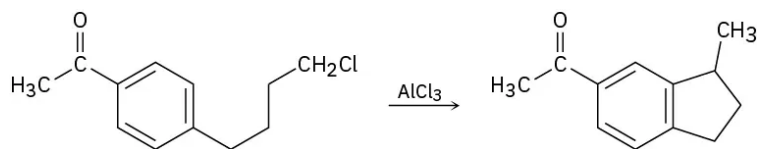


What intermediate is involved in this reaction? Propose a mechanism for its formation.

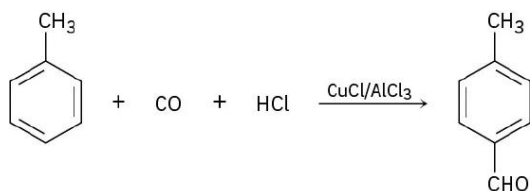
PROBLEM 3-39 4-Chloropyridine undergoes reaction with dimethylamine to yield 4-dimethylaminopyridine. Propose a mechanism for the reaction.



PROBLEM 3-40 Propose a mechanism to account for the following reaction:

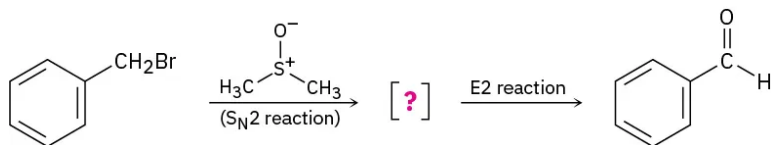


PROBLEM 3-41 In the *Gatterman-Koch reaction*, a formyl group ($-CHO$) is introduced directly onto a benzene ring. For example, reaction of toluene with CO and HCl in the presence of mixed $CuCl/AlCl_3$ gives *p*-methylbenzaldehyde. Propose a mechanism.

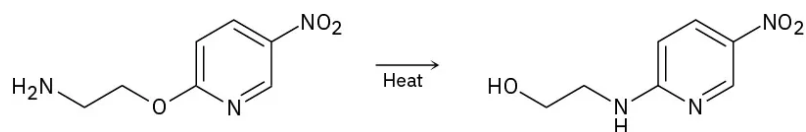


PROBLEM 3-42 Treatment of *p*-*tert*-butylphenol with a strong acid such as H_2SO_4 yields phenol and 2-methylpropene. Propose a mechanism.

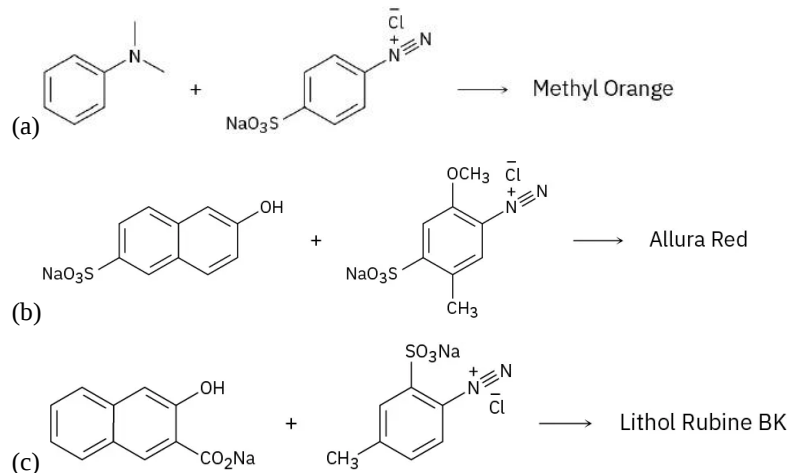
PROBLEM 3-43 Benzyl bromide is converted into benzaldehyde by heating in dimethyl sulfoxide. Propose a structure for the intermediate, and show the mechanisms of the two steps in the reaction.



PROBLEM 3-44 Propose a mechanism for the *Smiles rearrangement* below.

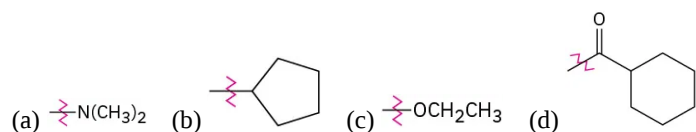


PROBLEM 3-44 Because of their conjugation, azo dyes are highly colored compounds and the major artificial color source for textiles and food. Azo dyes are produced by the reaction of aryl diazonium salts with a second aromatic compound. In the product, the aromatic rings are linked by a diazo bridge ($-N=N-$). From the reactants provided, propose a structure for each azo dye and draw the electron-pushing mechanism.



Reactivity and Orientation of Electrophilic Substitutions

PROBLEM 3-46 Identify each of the following groups as an activator or deactivator and as an *o*,*p*-director or *m*-director:



PROBLEM 3-47 Predict the major product(s) of nitration 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) ethoxybenzene

PROBLEM 3-48 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

PROBLEM 3-49 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

PROBLEM 3-50 Name and draw the major product(s) of electrophilic chlorination of the following compounds:

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

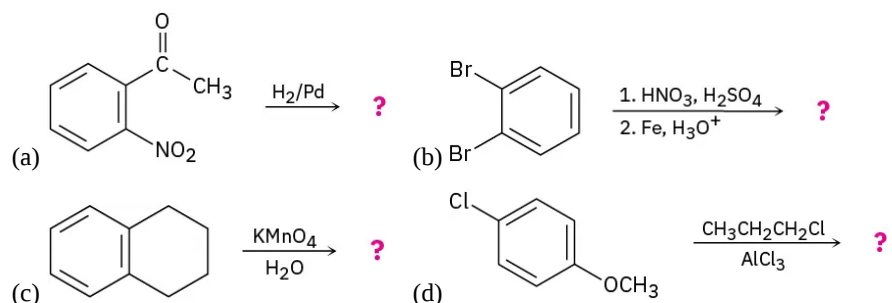
PROBLEM 3-51 Predict the major product(s) you would obtain from sulfonation of the following compounds:

(a) Fluorobenzene (b) *m*-Bromophenol (c) *m*-Dichlorobenzene (d) 2,4-Dibromophenol

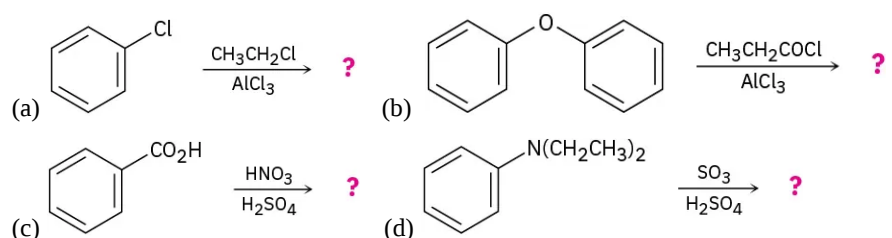
PROBLEM 3-52 Rank the following aromatic compounds in the expected order of their reactivity toward Friedel–Crafts alkylation. Which compounds are unreactive?

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

PROBLEM 3-53 What product(s) would you expect to obtain from the following reactions:



PROBLEM 3-54 Predict the mayor product(s) of the following reactions:



Organic Synthesis

PROBLEM 3-55 How would you synthesize the following substances starting from benzene or phenol? Assume that ortho- and para-substitution products can be separated. (a) *o*-Bromobenzoic acid (b) *p*-Methoxytoluene (c) 2,4,6-Trinitrobenzoic acid (d) *m*-Bromoaniline

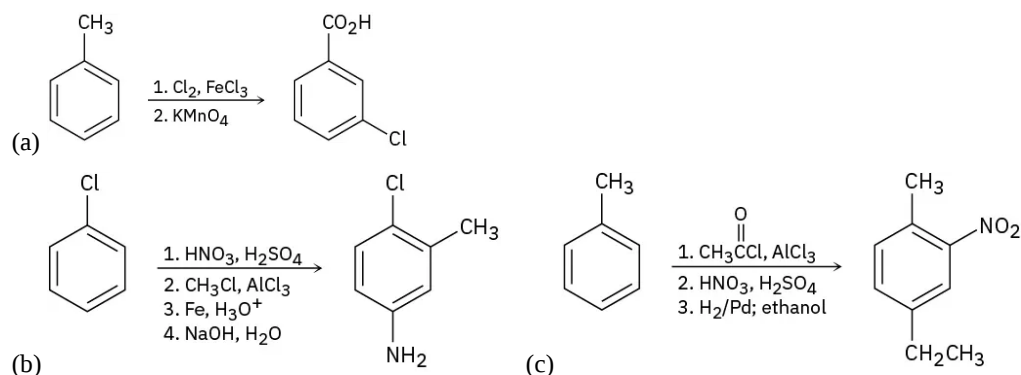
PROBLEM 3-56 Starting with benzene as your only source of aromatic compounds, how would you synthesize the following substances? Assume that you can separate ortho and para isomers if necessary.

(a) *p*-Chloroacetophenone (b) *m*-Bromonitrobenzene (c) *o*-Bromobenzenesulfonic acid (d) *m*-Chlorobenzenesulfonic acid

PROBLEM 3-57 Starting with either benzene or toluene, how would you synthesize the following substances: Assume that ortho and para isomers can be separated.

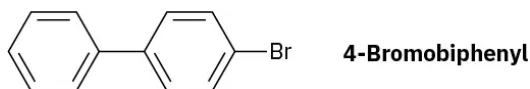
(a) 2-Bromo-4-nitrotoluene (b) 1,3,5-Trinitrobenzene (c) 2,4,6-Tribromoaniline (d) *m*-Fluorobenzoic acid

PROBLEM 3-58 As written, the following syntheses have flaws. What is wrong with each?



General Problems

PROBLEM 3-59 At what position and on what ring do you expect nitration of 4-bromo-biphenyl to occur? Explain, using resonance structures of the potential intermediates.



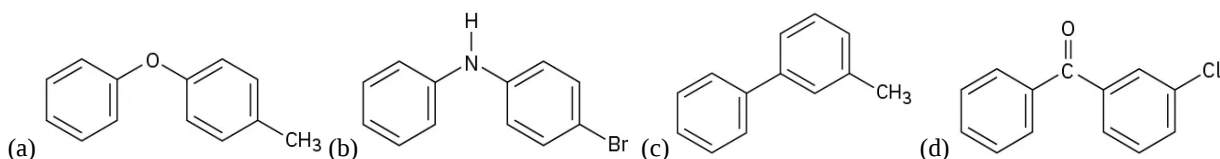
PROBLEM 3-60 Electrophilic substitution on 3-phenylpropanenitrile occurs at the ortho and para positions, but reaction with 3-phenylpropenenitrile occurs at the meta position. Explain, using resonance structures of the intermediates.



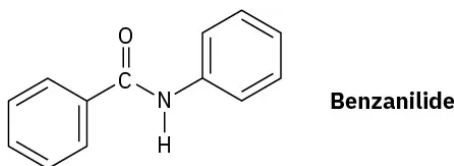
3-Phenylpropanenitrile

3-Phenylpropenenitrile

PROBLEM 3-61 At what position, and on what ring, would you expect the following substances to undergo electrophilic substitution?

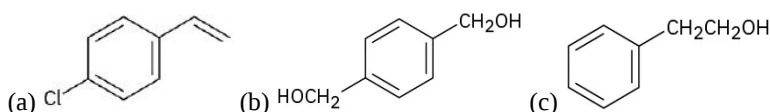


PROBLEM 3-62 At what position, and on what ring, would you expect bromination of benzanilide to occur? Explain by drawing resonance structures of the intermediates.

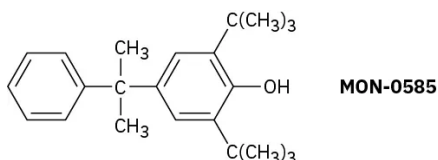


PROBLEM 3-63 Would you expect the Friedel–Crafts reaction of benzene with (*R*)-2-chlorobutane to yield optically active or racemic product? Explain.

PROBLEM 3-64 How would you synthesize the following substances starting from benzene?

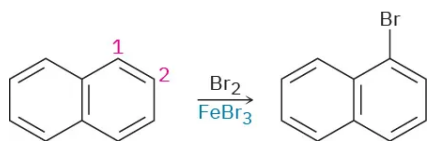


PROBLEM 3-65 The compound MON-0585 is a nontoxic, biodegradable larvicide that is highly selective against mosquito larvae. Synthesize MON-0585 using either benzene or phenol as a source of the aromatic rings.

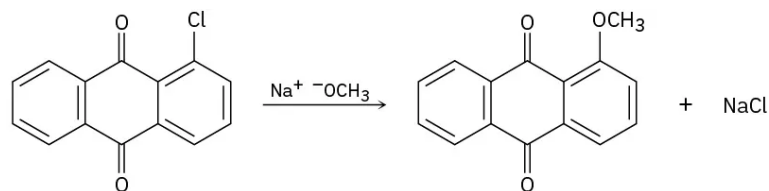


PROBLEM 3-66 Phenylboronic acid, $C_6H_5B(OH)_2$, is nitrated to give 15% ortho-substitution product and 85% meta. Explain the meta-directing effect of the $-B(OH)_2$ group.

PROBLEM 3-67 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.



PROBLEM 3-68 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.

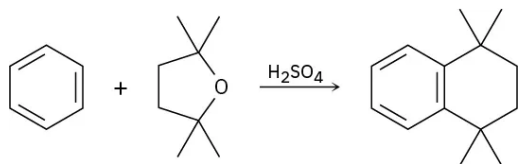


1-Chloroanthraquinone

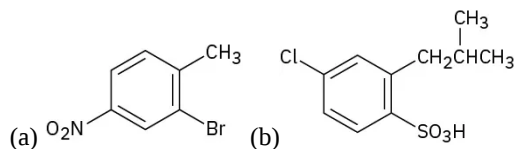
1-Methoxyanthraquinone

PROBLEM 3-69 *p*-Bromotoluene reacts with potassium amide to give a mixture of *m*- and *p*-methylaniline. Explain.

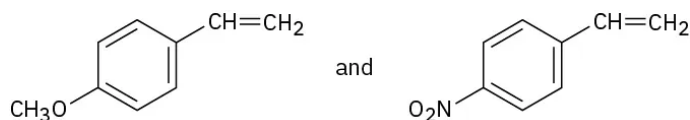
PROBLEM 3-70 Propose a mechanism to account for the reaction of benzene with 2,2,5,5-tetramethyltetrahydrofuran.



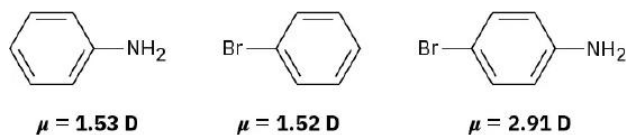
PROBLEM 3-71 How would you synthesize the following compounds from benzene? Assume that ortho and para isomers can be separated.



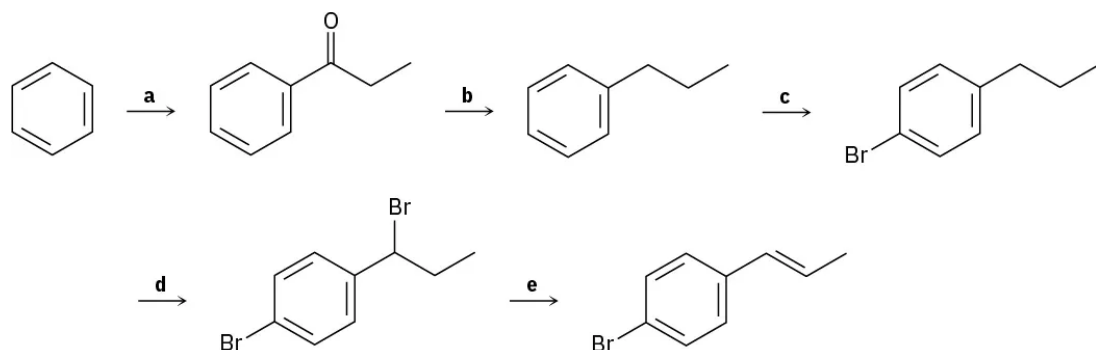
PROBLEM 3-72 You know the mechanism of HBr addition to alkenes, and you know the effects of various substituent groups on aromatic substitution. Use this knowledge to predict which of the following two alkenes reacts faster with HBr. Explain your answer by drawing resonance structures of the carbocation intermediates.



PROBLEM 3-73 Use your knowledge of directing effects, along with the following data, to deduce the directions of the dipole moments in aniline, bromobenzene, and bromoaniline.



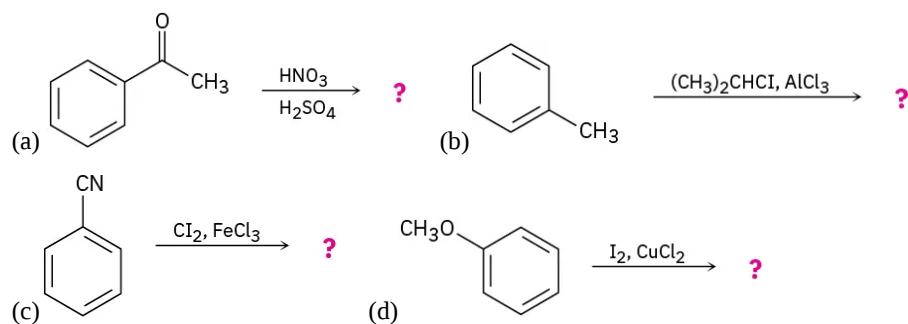
PROBLEM 3-74 Identify the reagents represented by the letters **a–e** in the following scheme:



PROBLEM 3-75 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 structures of the corresponding phenoxide anions and explain the data.

PROBLEM 3-76 Would you expect *p*-methylphenol to be more acidic or less acidic than unsubstituted phenol? Explain. (See PROBLEM 3-75.)

PROBLEM 3-77 Predict the product(s) for each of the following reactions. In each case, draw the resonance forms of the intermediate to explain the observed regiochemistry.



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