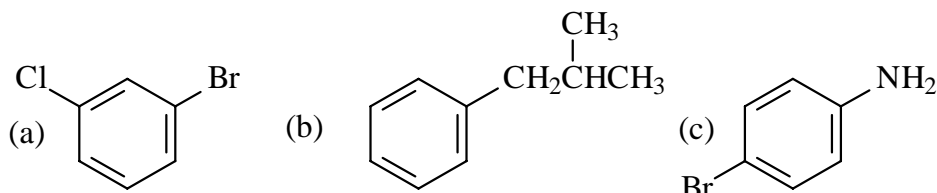


Chapter 5

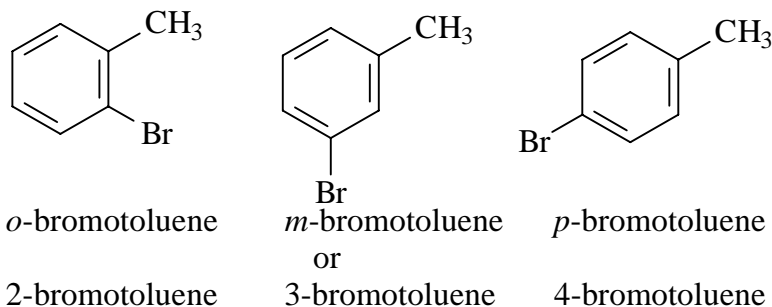
4. Give IUPAC names for the following compounds.



- (a) 1-bromo-3-chlorobenzene or *m*-bromochlorobenzene. (b) isobutylbenzene.
 (c) *p*-bromoaniline or 4-bromoaniline.

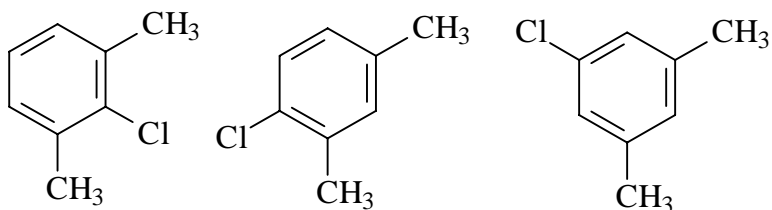
6. There are three products that might form on bromination of toluene. Draw and name them.

I am assuming here that the author means *monobromination*.



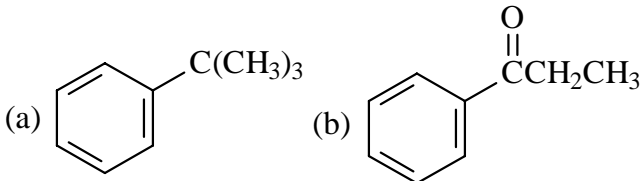
7. Show the mechanism of the reaction of benzene with nitric acid and sulfuric acid to yield nitrobenzene.
9. How many products might be formed on chlorination of *m*-xylene?

There are three. They are shown to the right.



12. What products would you expect to obtain from the reaction of benzene with the following reagents?

(a) $(\text{CH}_3)_3\text{CCl}$, AlCl_3 , (b) $\text{CH}_3\text{CH}_2\text{COCl}$, AlCl_3



13. Use Figure 5.9 to rank the compounds in each of the following groups in order of their reactivity to electrophilic aromatic substitution.

(b) phenol, benzene, chlorobenzene, benzaldehyde, aniline

aniline > phenol > benzene > chlorobenzene > benzaldehyde

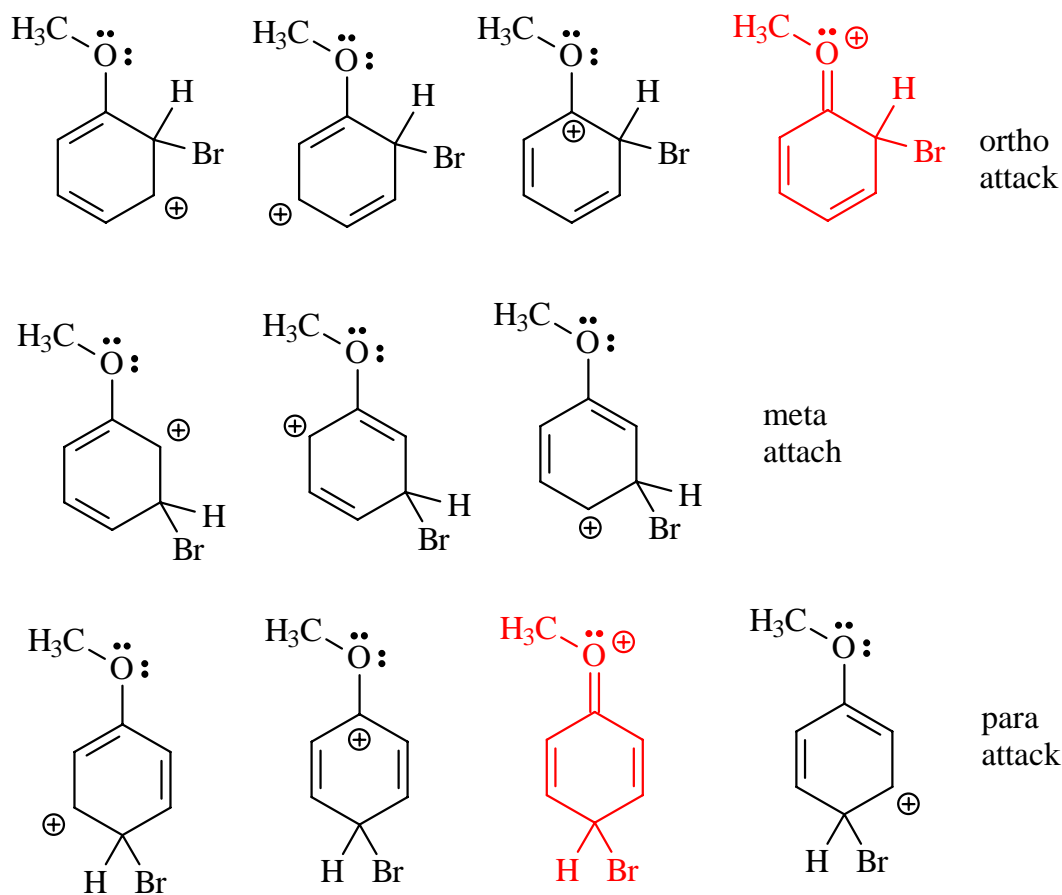
14. What product(s) would you expect from nitration of the following compounds?

(a) nitrobenzene, (b) bromobenzene, (c) toluene, (d) benzoic acid, (e) *p*-xylene

(a) *m*-dinitrobenzene, (b) *o*- and *p*-bromonitrobenzene, (c) *o*- and *p*-nitrotoluene, (d) *m*-nitrobenzoic acid, (e) 1,4-dimethyl-2-nitrobenzene.

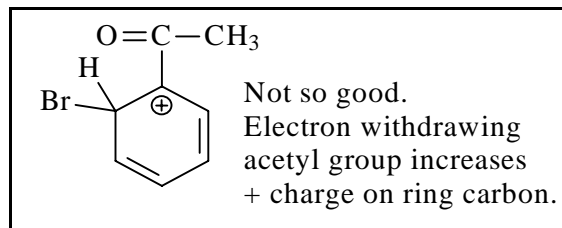
15. Draw resonance structures of the three possible carbocation intermediates to show how a methoxyl group ($-\text{OCH}_3$) directs bromination toward ortho and para positions.

The structures are shown below. Note that there are three good resonance structures for attack at the meta position while there are four good ones for attack at the ortho and para positions. More resonance structures means a more stable carbocation. Furthermore, the resonance structures for ortho and para attack shown in red are especially good in that every atom (except hydrogens) has an octet of electrons.

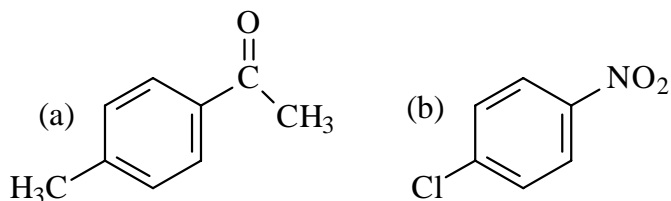


16. Draw resonance structures of the three possible carbocation intermediates to show how an acetyl group, $\text{CH}_3\text{C}=\text{O}$, directs bromination toward the meta position.

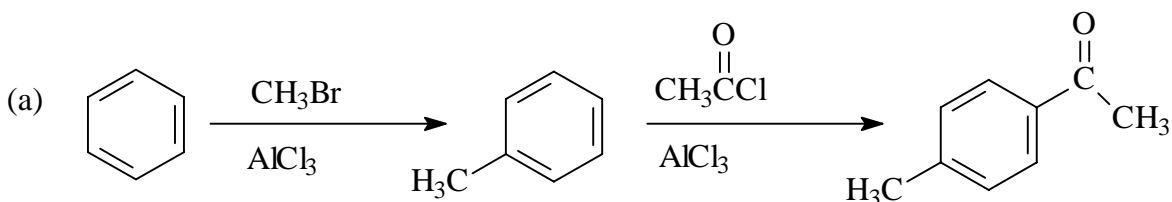
In this case, we can draw three reasonable resonance structures for each carbocation that would result by virtue of attack at each of the three possible positions. However, in the case of meta attack the positive charge is not held at all by the ring carbon that holds the electron withdrawing acetyl group. On the other hand, in the cases of ortho and para attack this ring carbon does hold positive charge as shown by the structure on the right (for ortho attack). This resonance structure is not as good as the others owing to the intensified positive charge on the ring carbon caused by the electron withdrawing group.



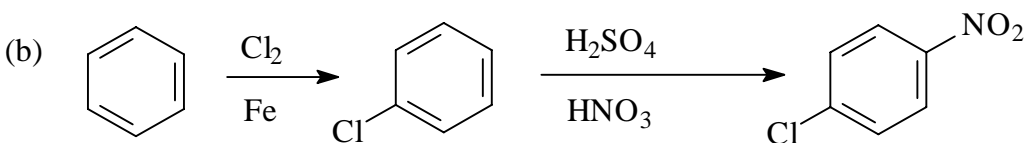
19. Propose a synthesis of each of the following substances from benzene.



Before we start slapping groups onto the benzene ring we need to think for a moment about a couple of things. First, some groups are ortho/para directing and others are meta directing. You want to have the right kind of group *on* the benzene ring to properly position the *incoming* group. Second, Friedel-Crafts reactions will not work if there is a group on the ring that is more deactivating than a halogen.



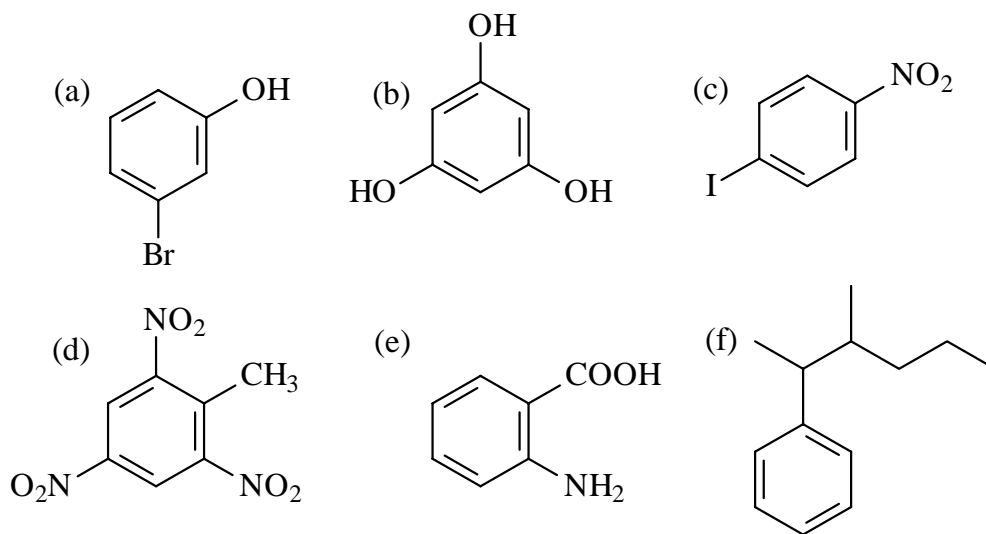
In this case we attached the methyl group first. This group is an activating ortho/para director. The acetyl group can then be placed in the para position.



In this case we attached the chloro group first. It is an ortho/para director so the incoming nitro group goes to the para (and ortho) position. If we had attached the meta directing nitro group first and then chlorinated, we would have gotten *m*-chloronitrobenzene.

23. Draw the structures corresponding to the following names.

- (a) *m*-bromophenol, (b) 1,3,5-benzenetriol, (c) *p*-iodonitrobenzene, (d) 2,4,6-trinitrotoluene, (e) *o*-aminobenzoic acid, (f) 3-methyl-2-phenylhexane



26. Propose structures for aromatic hydrocarbons meeting the following descriptions.
 (a) C_9H_{12} ; can give only one product on aromatic bromination.

OK. This is not a simple problem; so we will have to formulate a method of attack.

Basically, the situation is that there is a benzene ring and this uses up 6 of the 9 carbons. So, we have 3 carbons to work with.

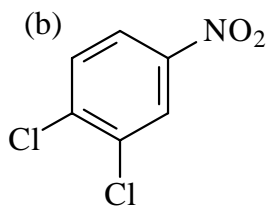
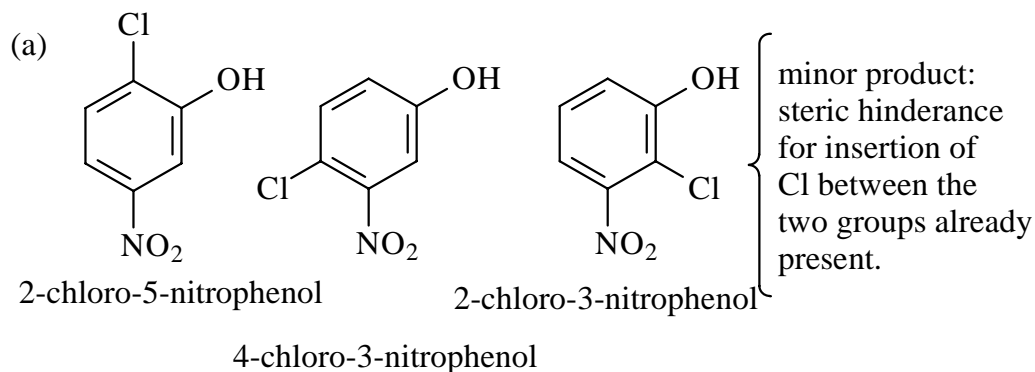
Suppose we make one group of the three carbons – propyl (C_3H_7), for example – and attach this to the benzene ring. This would make [C_6H_5 (phenyl) + propyl (C_3H_7)] C_9H_{12} . Bromination of this compound would lead to ortho, meta, and para products. So, one group on the ring is a loser.

OK. Let's go for two groups. Since we have three carbons, this would have to be methyl and ethyl. If the methyl and ethyl are ortho or meta to each other we can draw four monobromo isomers. **Draw them!** If the methyl and ethyl are para to each other two isomers would result upon bromination – one with the bromine ortho to the methyl, the other with the bromine ortho to the ethyl. Can't win for losing.

OK. Let's go for three groups. These must all be methyl. The only arrangement that will give only one bromination product is 1,3,5-trimethylbenzene. **Draw the various arrangements to convince yourself of this.**

32. The orientation of electrophilic aromatic substitution on a disubstituted benzene ring is usually controlled by whichever of the two groups already on the ring is the more powerful activator. Name and draw the structure(s) of the major product(s) of electrophilic chlorination of these substances.

(a) *m*-nitrophenol, (c) *p*-chloronitrobenzene



The Cl is an ortho/para director and the NO₂ is a meta director, so the two groups initially on the ring direct the incoming Cl to the same position.

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

(a) bromobenzene, (b) toluene, (c) anisole (C₆H₅OCH₃), (d) nitrobenzene, (e) *p*-bromotoluene

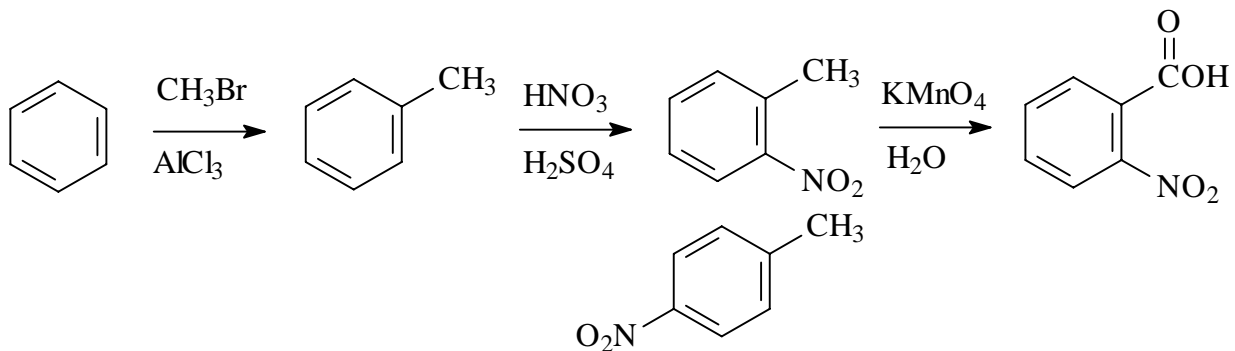
In order of decreasing reactivity: c > b > e > a > d. This is based on the list in the text or the one in the lecture notes. Nitrobenzene would be unreactive in a Friedel-Crafts reaction.

41. Starting from any aromatic hydrocarbon of your choice, how would you synthesize the following substances? Ortho and para isomers can be separated if necessary.

(a) *o*-nitrobenzoic acid, (b) *p*-*tert*-butylbenzoic acid

(a) *o*-Nitrobenzoic acid has two meta directing groups on the benzene ring. Consequently, you cannot have either of these groups on the ring and expect to be able to place a second group ortho to it. As we scratch our heads over this conundrum it dawns on us that the carboxylic acid group was probably not placed on the ring directly since we do not know how to do that. It is much more likely that the -COOH group got there through oxidation of an alkyl group, methyl, for example.

Now, alkyl groups are ortho/para directors. So, what we need to do is methylate the benzene ring, then nitrate it in the ortho/para positions, and then oxidize the methyl to a -COOH.



43. We said in Section 4.11 that allylic carbocations are stabilized by resonance. Draw resonance structures to account for a similar stabilization of benzylic carbocations.

