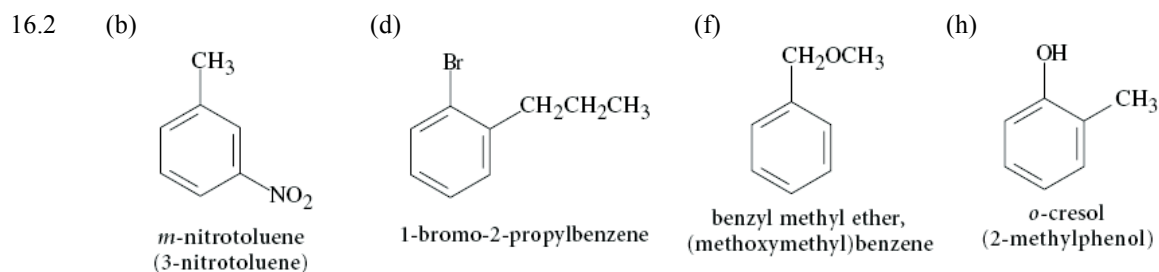


Chapter 16

The Chemistry of Benzene and Its Derivatives

Solutions to In-Text Problems

- 16.1 (b) *o*-Diethylbenzene or 1,2-diethylbenzene
(d) 2,4-Dichlorophenol
(f) Benzylbenzene or (phenylmethyl)benzene (also commonly called diphenylmethane)



16.3 Add about 25 °C per carbon relative to toluene (110.6 °C; see text p. 743):

- (b) propylbenzene: 161 °C (actual: 159 °C)

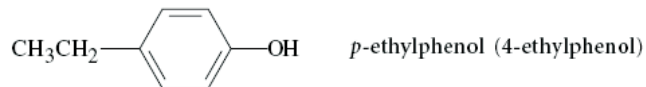
16.4 The aromatic compound has NMR absorptions with greater chemical shift in each case because of the ring current (Fig. 16.2, text p. 745).

- (b) The chemical shift of the benzene protons is at considerably greater chemical shift because benzene is aromatic and 1,4-cyclohexadiene is not.

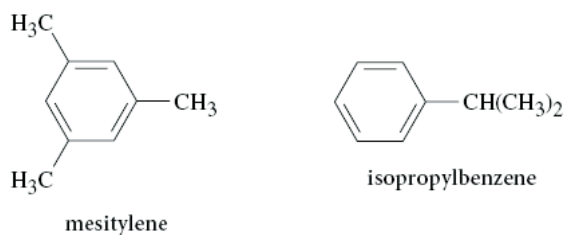
16.6 (b) Among other features, the NMR spectrum of 1-bromo-4-ethylbenzene has a typical ethyl quartet and a typical para-substitution pattern for the ring protons, as shown in Fig. 16.3, text p. 747, whereas the spectrum of (2-bromoethyl)benzene should show a pair of triplets for the methylene protons and a complex pattern for the ring protons. If this isn't enough to distinguish the two compounds, the integral of the ring protons relative to the integral of the remaining protons is different in the two compounds.



16.7 (b) The IR spectrum indicates the presence of an OH group, and the chemical shift of the broad NMR resonance (δ 6.0) suggests that this could be a phenol. The splitting patterns of the δ 1.17 and δ 2.58 resonances show that the compound also contains an ethyl group, and the splitting pattern of the ring protons shows that the compound is a para-disubstituted benzene derivative. The compound is *p*-ethylphenol.

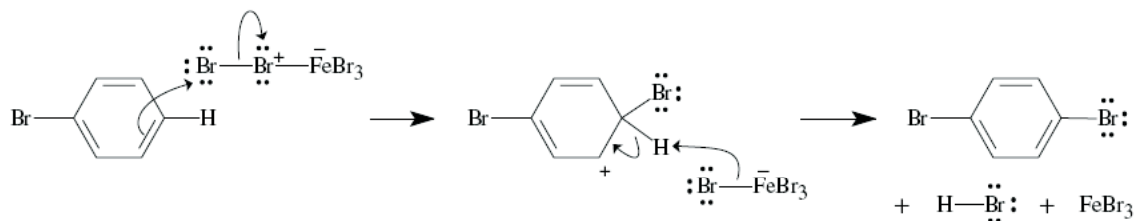


- 16.9 Count the resonances. Mesitylene has three resonances; isopropylbenzene has six.

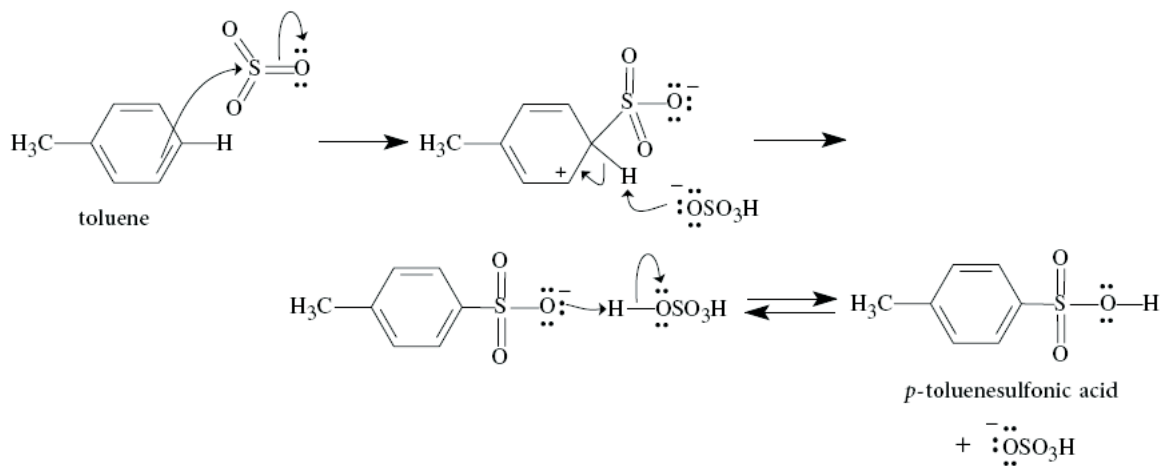


- 16.11 Because styrene has a double bond in conjugation with the ring and ethylbenzene does not, styrene has a greater λ_{\max} in its UV spectrum.

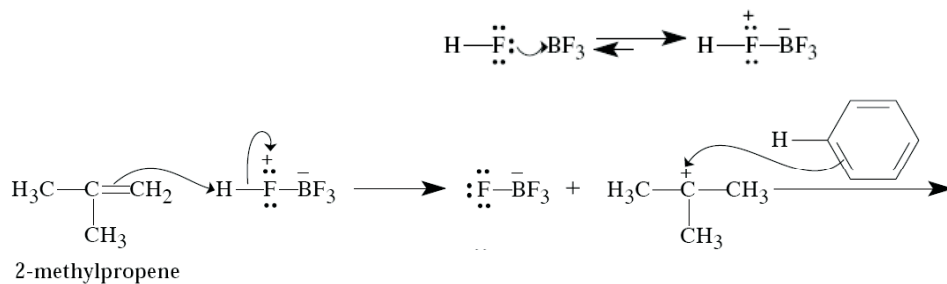
- 16.12 Apply the steps shown in Eqs. 16.6–16.7 on text p. 752 to the para position of bromobenzene.

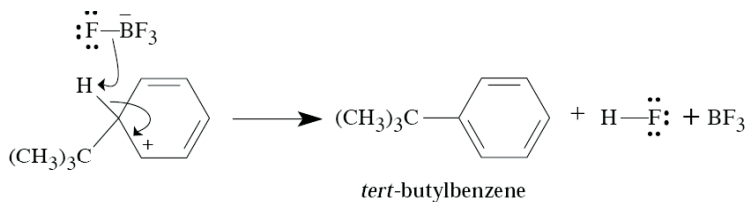


- 16.14 Apply the sulfonation mechanism shown in Eq. 16.13 on text p. 756 to the para position of toluene.

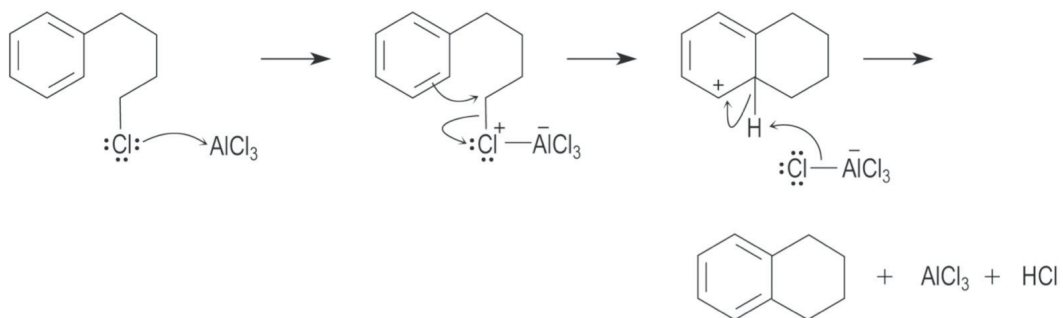


- 16.16 The product is *tert*-butylbenzene. The role of the Lewis acid BF_3 is to promote the ionization of HF. The mechanism of the reaction is as follows:

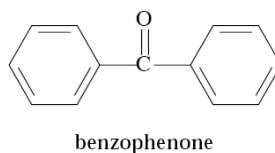




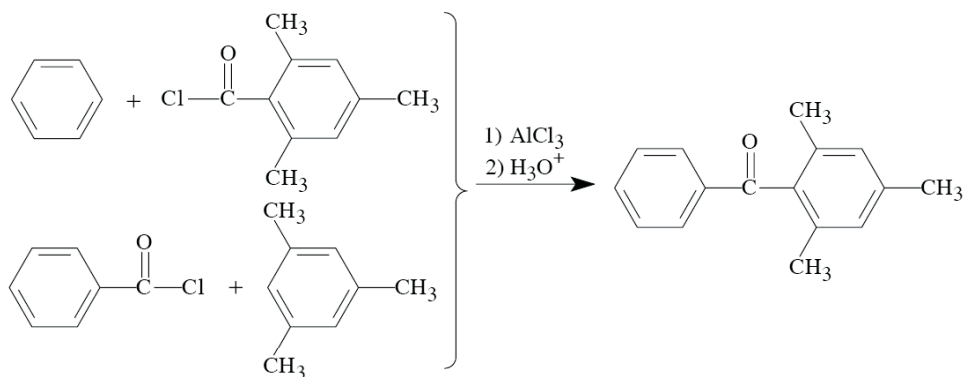
- 16.17 (b) This is another example of an intramolecular Friedel-Crafts reaction—in this case, one that forms a six-membered ring.



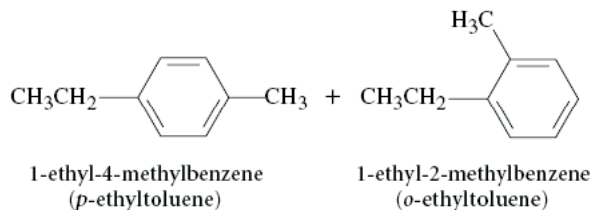
- 16.18 (b)



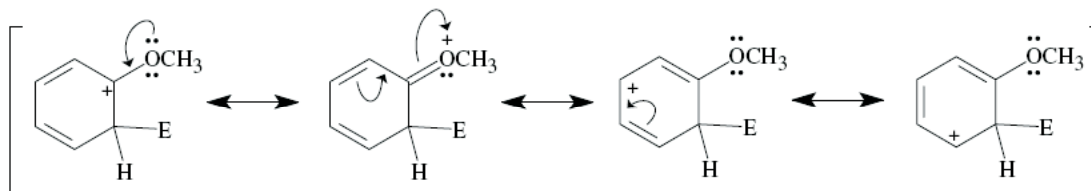
- 16.19 The two possible Friedel-Crafts reactions:



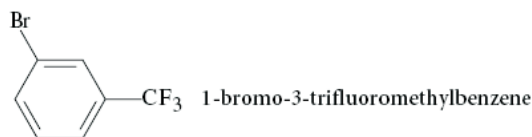
- 16.21 (b) Table 16.2 indicates that alkyl groups are ortho, para-directing groups, and the ethyl group is a typical alkyl group:



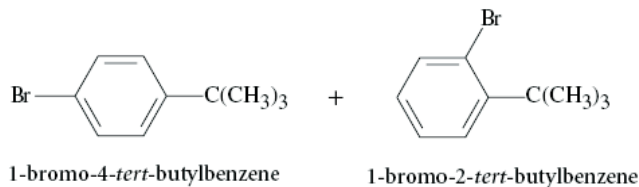
- 16.22 Let E^+ be a general electrophile. The four resonance structures of the carbocation intermediate that results from reaction of E^+ at the position ortho to the methoxy group of anisole are as follows:



- 16.24 (b) The three strong carbon-fluorine bond dipoles result in substantial positive charge on the carbon of the CF_3 group; consequently, this is a meta-directing group.



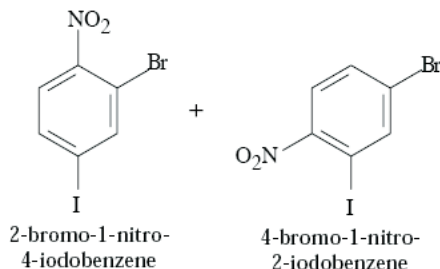
- (d) The *tert*-butyl group, like all other alkyl groups, is an ortho, para-directing substituent.



- 16.25 (b) The reaction-free energy profiles for electrophilic substitution of benzene, nitrobenzene at the meta position, and nitrobenzene at the para position are shown in Fig. IS16.1. Notice that nitrobenzene is less reactive than benzene because the nitro group is a deactivating substituent. Notice also that meta-substitution reactions on nitrobenzene are faster than para-substitution reactions because the nitro group is a meta-directing group.

- 16.27 Bromination of *N,N*-dimethylaniline is faster because nitrogen has an unshared electron pair that can stabilize the carbocation intermediate by resonance. As in the case of oxygen, the electron-withdrawing polar effect of nitrogen is much less important than its electron-donating resonance effect.

- 16.28 (b) As in part (a), each substituent is an ortho, para-directing group. Two products satisfy the directing effects of both groups.



- 16.29 (b) The order is anisole < toluene < chlorobenzene. Chlorobenzene requires the harshest conditions because chlorine is a deactivating group. Anisole requires the mildest conditions because the methoxy group is more activating than the methyl group of toluene. (See Table 16.2 on text p. 763.)

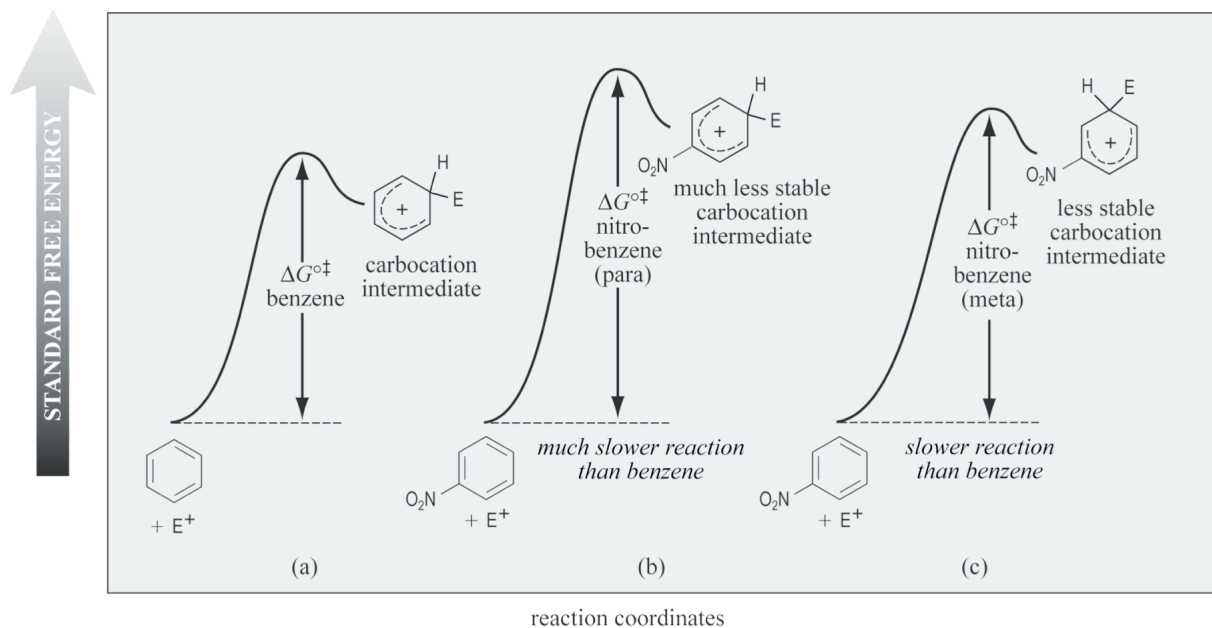
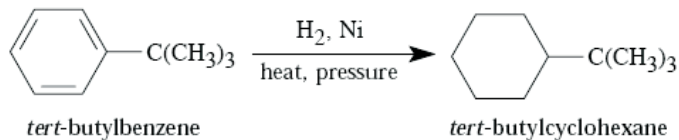


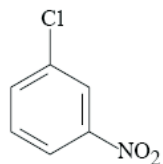
Figure IS16.1 Reaction-free energy profiles to accompany the solution to Problem 16.25(b)

- 16.31 (b) Hydrogenate *tert*-butylbenzene, which, in turn, is prepared by Friedel–Crafts alkylation as shown in Eq. 16.18 on text p. 758 or by the reaction shown in the solution to Problem 16.16.



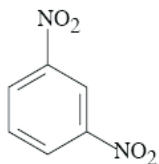
Solutions to Additional Problems

16.33 (a)



1-chloro-3-nitrobenzene

(b)

1,3-dinitrobenzene or
m-dinitrobenzene

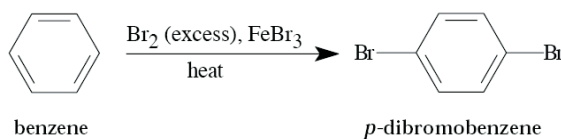
- (c) No electrophilic aromatic substitution reaction takes place. Friedel–Crafts acylation does not take place on any benzene derivative less reactive than the halobenzenes. In fact, nitrobenzene can be used as an inert solvent for Friedel–Crafts acylation.

16.37 Ethylbenzene has a three-proton triplet and, at somewhat greater chemical shift, in the benzylic proton region, a two-proton quartet. *p*-Xylene has a six-proton singlet in the benzylic region. Styrene, Ph—CH=CH₂, has no protons in the benzylic region.

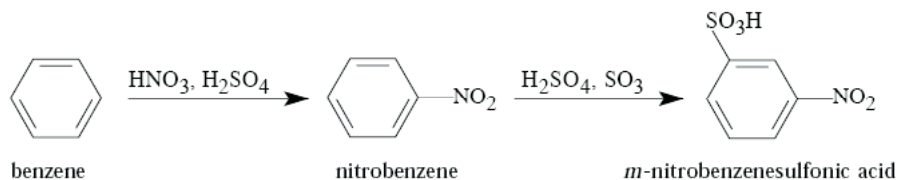
16.38 (b) Fig. 16.2 on text p. 745 shows that aromatic protons located in the plane of the ring and outside of the ring experience an augmented local field and thus a greater chemical shift. However, in the region above and below the ring, the induced field has the opposite direction, and consequently protons located in this region experience a reduced local field and thus a smaller chemical shift. Such is the case with the methyl group in the problem; the local field at this group is so small that its resonance occurs at nearly 1.7 ppm *smaller* chemical shift than that of TMS.

16.40 In each synthesis that involves substitution on a benzene derivative that contains an ortho, para-directing group, only the product resulting from para substitution is shown.

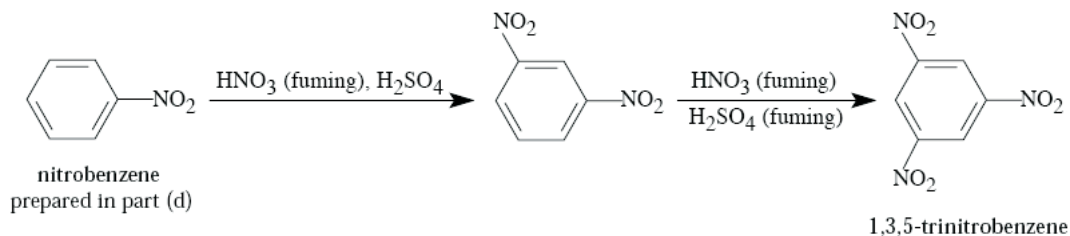
(b)



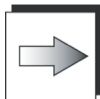
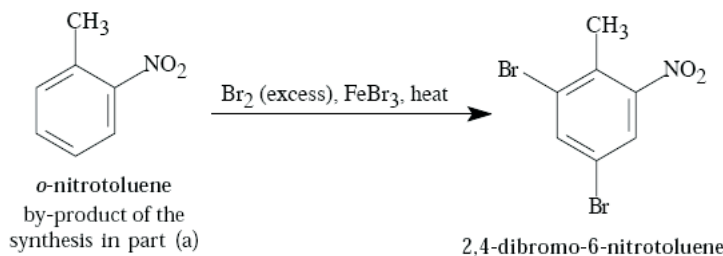
(d)



(f)

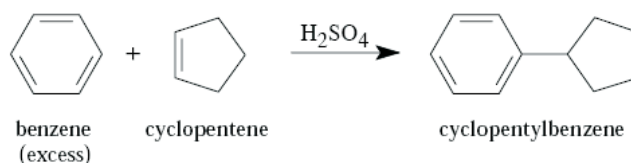


(h)



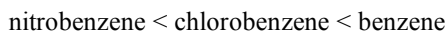
Nitration of toluene actually gives more ortho isomer than para isomer of toluene, and the two nitrotoluene isomers are readily separated by fractional distillation. (See text p. 768.) *o*-Nitrotoluene is a good starting material for a number of ortho-substituted benzene derivatives.

(j)

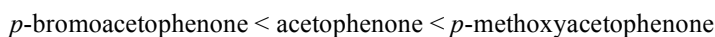


Cyclopentanol may be substituted for cyclopentene in this synthesis, or chlorocyclopentane and AlCl_3 catalyst may be used instead of cyclopentene and H_2SO_4 . Note that each of these possible starting materials serves as a source of the same carbocation, the cyclopentyl cation.

- 16.41 (b) The reactivity order follows from the relative activating effects of the substituents. (See the last column of Table 16.2 on text p. 763.)

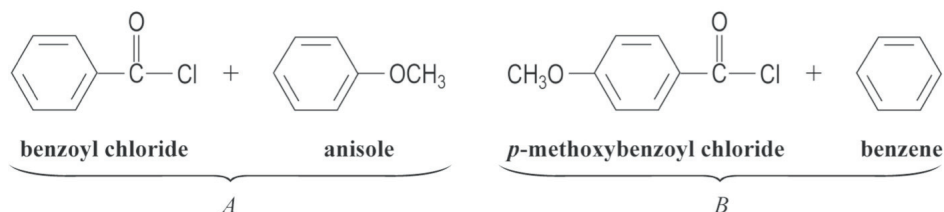


- (d) The reactivity order follows from the relative activating effects of the substituents. (See the last column of Table 16.2 on text p. 763.)



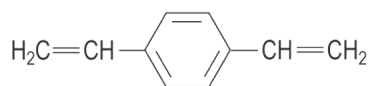
- 16.43 The reactivity order is $A < B < D < C$. Compound *C* is most reactive because the substituent has an unshared electron pair that can be used to stabilize the intermediate carbocation by resonance. Compounds *B* and *D* have alkyl substituents, which stabilize carbocations; however, the alkyl group of compound *B* contains a positively charged group that would interact unfavorably with a carbocation, offsetting the stabilizing effect of the alkyl carbon. Compound *A* has a positively charged, electronegative substituent attached directly to the ring that would interact most unfavorably with the carbocation. (See the solution to Problem 16.42b.) Compounds *C* and *D* undergo bromination at the ortho and para positions; compound *A* undergoes bromination at the meta position; and the position of substitution in compound *B* depends on the balance of the stabilizing effect of the alkyl group and the destabilizing effect of the positive charge. (In fact, this compound brominates in the ortho and para positions.)

- 16.45 The two possibilities are the acylation of anisole by benzoyl chloride (pair *A*), or the acylation of benzene by *p*-methoxybenzoyl chloride (pair *B*). Because the methoxy group activates electrophilic substitution at the *ortho* and *para* positions, the Friedel-Crafts reaction of pair *A* should occur under the milder conditions.



(Both reactions would work, however; and the use of pair *B* avoids the possibility of *ortho* substitution, although, with the Friedel–Crafts reaction, this does not generally occur to a great extent.)

- 16.47 Any compound must have an unsaturation number of 6 and must contain a benzene ring.



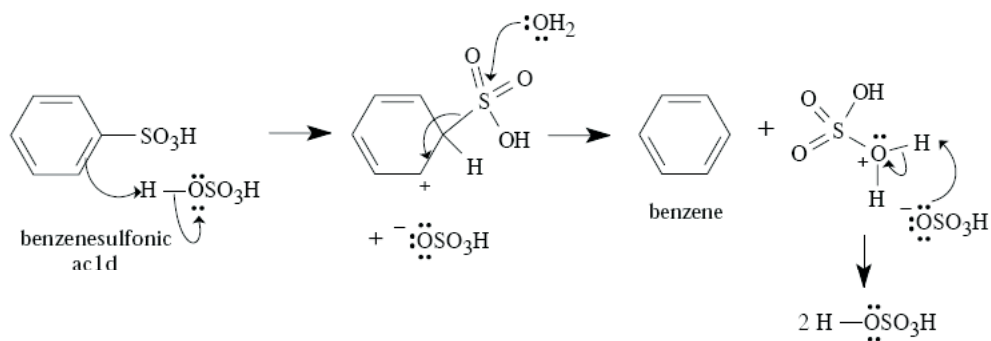
p-divinylbenzene



structures such as this without a benzene ring would hydrogenate to *cis*-1,4-diethylcyclohexane

Structures such as the one on the right that do not contain a benzene ring do not meet the criterion, because they would undergo hydrogenation of the ring double bonds.

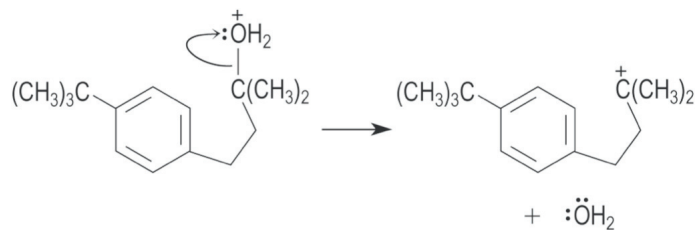
- 16.50 Run the electrophilic aromatic substitution reaction in reverse.



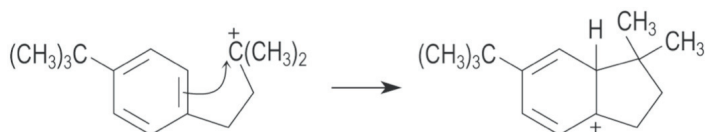
There are several variations on this mechanism. For example, SO_3H could be lost from the carbocation intermediate to give protonated SO_3 (that is, $^+\text{SO}_3\text{H}$; see Problem 16.13 on text p. 756) which could react with water to give SO_3 (sulfur trioxide) and H_3O^+ . Sulfur trioxide reacts vigorously with water to give H_2SO_4 (sulfuric acid). The important aspect of the mechanism is the protonation of the ring and loss of a species which would serve as an electrophile in the reverse reaction.

- 16.52 (a) and (b)

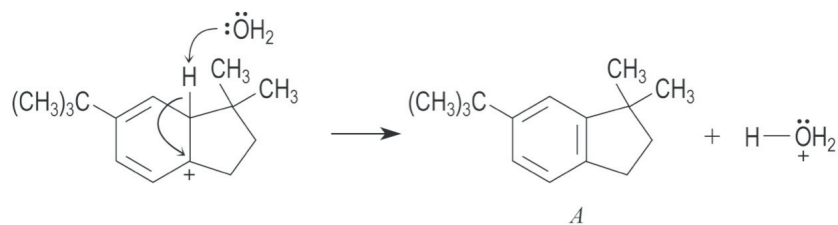
Generation of the electrophile: The electrophile is the carbocation generated by protonation of the alcohol oxygen and loss of water.



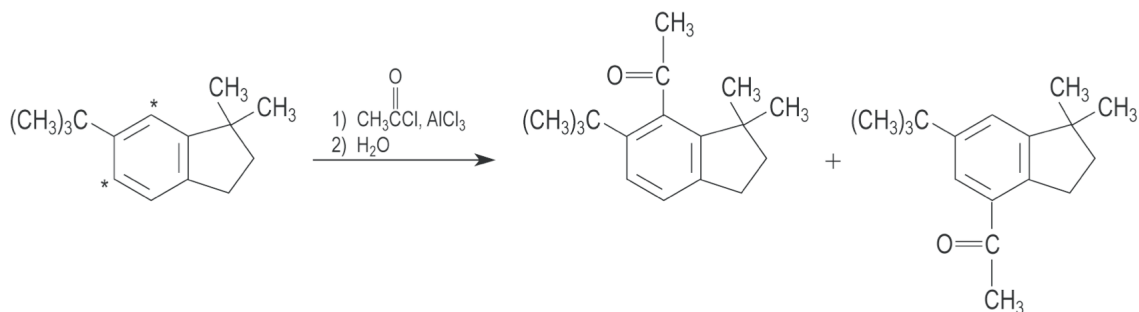
A Lewis acid–base association reaction of the benzene π electrons with the electrophile to generate another carbocation:



Loss of a β -proton to the Brønsted base H_2O to form the new aromatic compound:

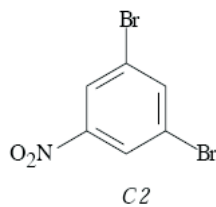
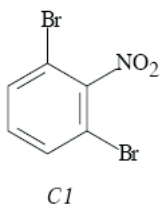


- (c) The aromatic ring of compound *A* has three alkyl substituents. Two of them—the *tert*-butyl group and one of the ring bonds—direct substitution by their electronic effects to the positions indicated by the asterisk:

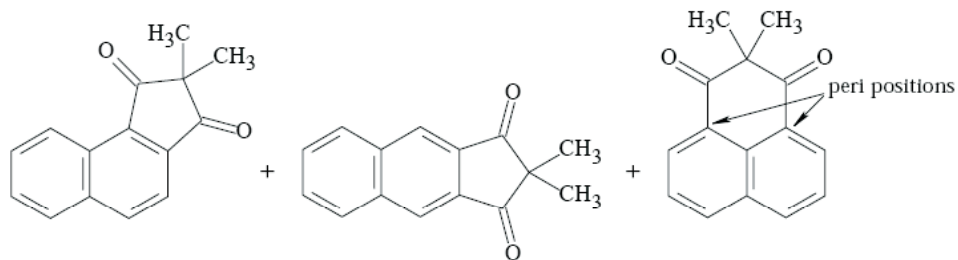


Electrophilic substitution might have occurred at either of these positions to give either or both of the compounds shown in the foregoing equation. Both of these positions, however, are ortho to the very large *tert*-butyl group, and one of them is ortho to *two* highly branched groups. For steric reasons substitution cannot occur at these very congested positions. Hence, it occurs at the remaining position. Note that ring position meta to alkyl substituents are not deactivated; they are simply less activated than positions that are ortho and para to alkyl substituents. Furthermore, the remaining ring position is activated by one alkyl substituent.

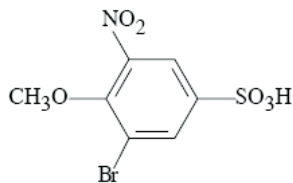
- 16.58 (c) The following two products derived from nitration of compound *C* were probably formed in smallest amount. In the formation of compound *C1*, the nitro group and the two bromines are involved in severe van der Waals repulsions; and the formation of compound *C2* satisfies the directing effect of neither bromine substituent.



- 16.59 (b) The formula indicates that successive electrophilic aromatic substitution reactions have occurred; the product is triphenylmethane, Ph_3CH .
- (d) Comparison of the formula of the product to that of naphthalene shows that one molar equivalent of the acylating agent has been introduced. Since there is no chlorine in the product, the reaction must involve a double acylation of the naphthalene ring by both ends of the acid chloride. The only way that this can occur with the formation of rings of reasonable size is for the acylation to occur across ortho positions of one benzene ring, or across the peri positions, which are the two positions on either side of the ring junction. These three possibilities account for the three products:

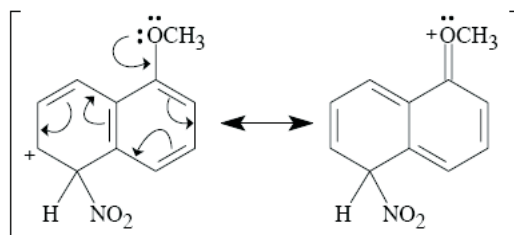


- (g) The nitro group is directed by both substituents to the position ortho to the methoxy group, and the bromine in the second reaction is directed to the other position ortho to the methoxy group.



3-bromo-4-methoxy-5-nitrobenzenesulfonic acid

- 16.60 (b) When nitration occurs at carbon-5, the unshared electrons of the oxygen can be used to stabilize the carbocation intermediate by resonance; consequently, nitration at carbon-5 of 1-methoxynaphthalene is faster than nitration of naphthalene itself.



- 16.64 In this reaction a *tert*-butyl cation is lost rather than a proton from the carbocation intermediate. The electrophile, a nitronium ion $^+\text{NO}_2$, is generated by the mechanism shown in Eqs. 16.11a–d on text p. 755.

