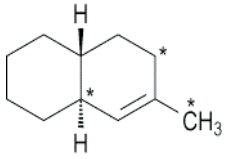
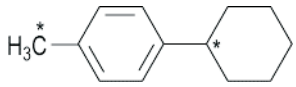
# Chapter 17
# Allylic and Benzylic Reactivity

## Solutions to In-Text Problems

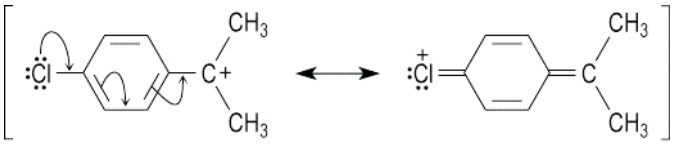
17.1 (b) The allylic carbons are indicated with an asterisk (*).



17.2 (b) The benzylic carbons are indicated with an asterisk (*).



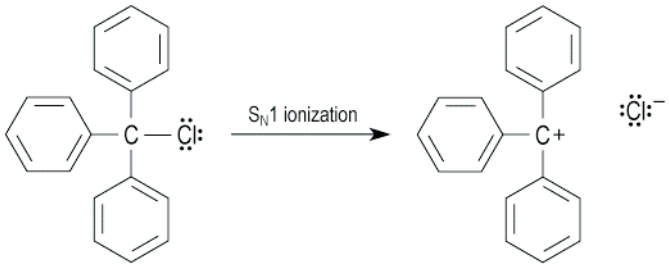
17.3 (b) The reactivity order is (2) < (3) < (1). The $S_N1$ reaction of compound (2) is slowest because the polar effect of the meta-chloro substituent destabilizes the intermediate carbocation. The reaction of compound (3) is faster because the resonance effect of the *para*-chloro group partially offsets its polar effect.



carbocation intermediate in the solvolysis of compound (3)

Compound (1) reacts most rapidly because the carbocation intermediate is not destabilized by the deactivating polar effect of a chloro substituent, which outweighs its resonance effect.

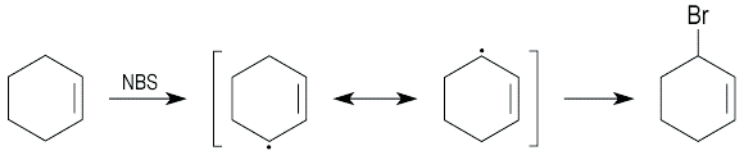
17.5 The carbocation formed when trityl chloride ionizes, the *trityl cation* ($Ph_3C^+$), is stabilized by delocalization of electrons from *all three* phenyl rings. This carbocation has more resonance structures than the carbocations formed from the other alkyl halides in the table, and is thus so stable that the transition state leading to its formation also has very low energy; consequently, it is formed very rapidly.




**trityl chloride (triphenylmethyl chloride)** **trityl cation (triphenylmethyl cation)**

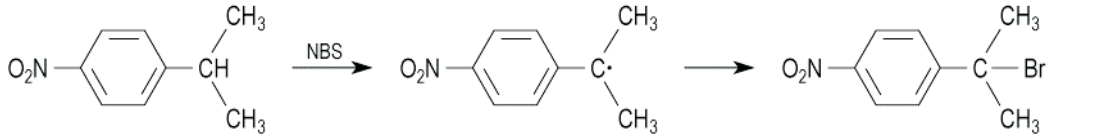
17.6 The number of products depends on (1) whether all of benzylic or allylic positions are equivalent, and (2) whether the resonance structures of the free-radical intermediate are identical.

(a) All allylic positions of cyclohexene are chemically equivalent, and the two resonance structures are identical. Hence, only one allylic bromination product is possible.



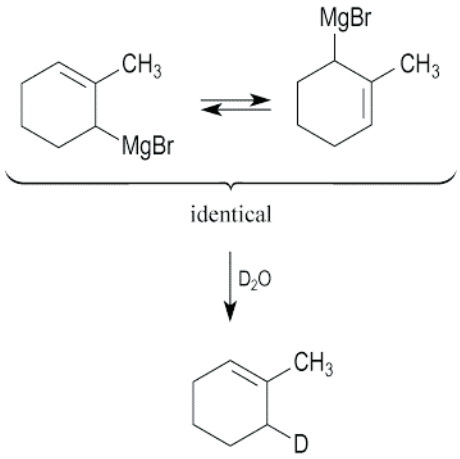

**cyclohexene** (starting material) — free-radical intermediate (identical resonance structures) — **3-bromocyclohexene** product

(e) A benzylic hydrogen is abstracted from the isopropyl group rather than a hydrogen of the two methyl groups because a more stable benzylic free-radical intermediate is obtained.

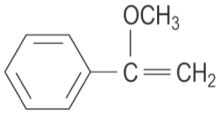



**1-isopropyl-4-nitrobenzene** — free-radical intermediate — **1-(2-bromoprop-2-yl)-4-nitrobenzene**

17.7 (b) Because the two Grignard reagents in rapid equilibrium are identical, only one product is obtained:

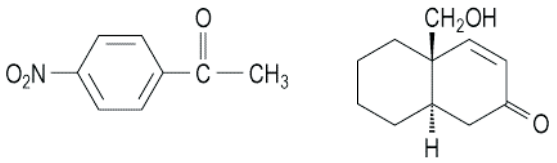



17.8 (b) The benzylic proton is abstracted; $\beta$-elimination gives a vinylic ether.

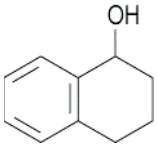



**(1-methoxyvinyl)benzene**
**($\alpha$-methoxystyrene)**

17.10 (b) (d)

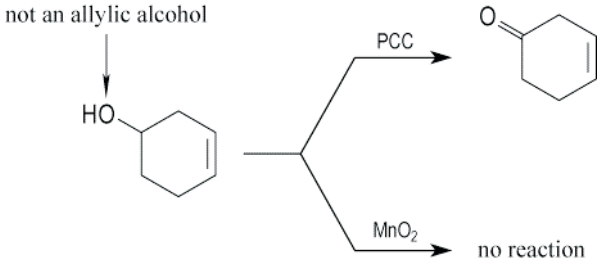


17.11 (b)

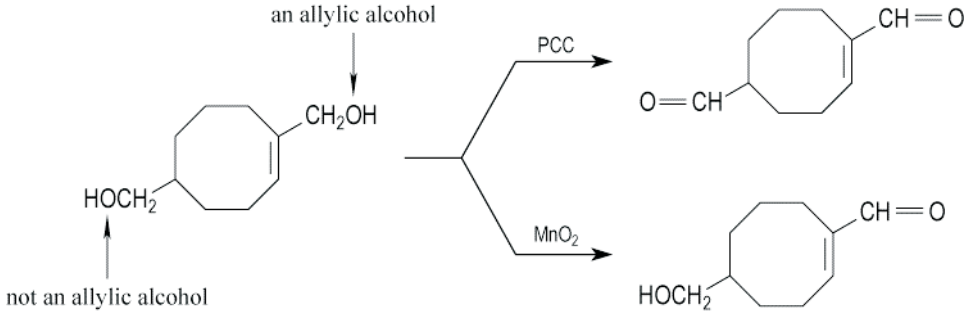



17.12 PCC oxidizes all primary alcohols to aldehydes and all secondary alcohols to ketones; $MnO_2$ oxidizes only allylic or benzylic alcohols (primary alcohols to aldehydes and secondary alcohols to ketones).

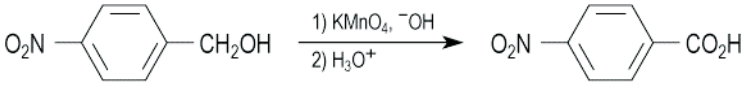
(b)




(d)

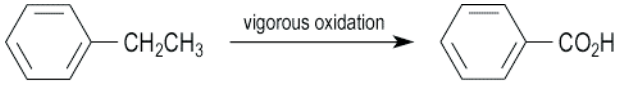



17.13 (a)



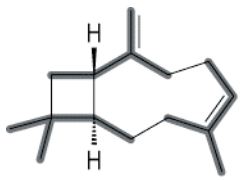

***p*-nitrobenzyl alcohol** ***p*-nitrobenzoic acid**

17.14 (b) Because one carbon is lost as a result of the oxidation, and because the benzene ring accounts for all four degrees of unsaturation, compound *B* must be ethylbenzene.



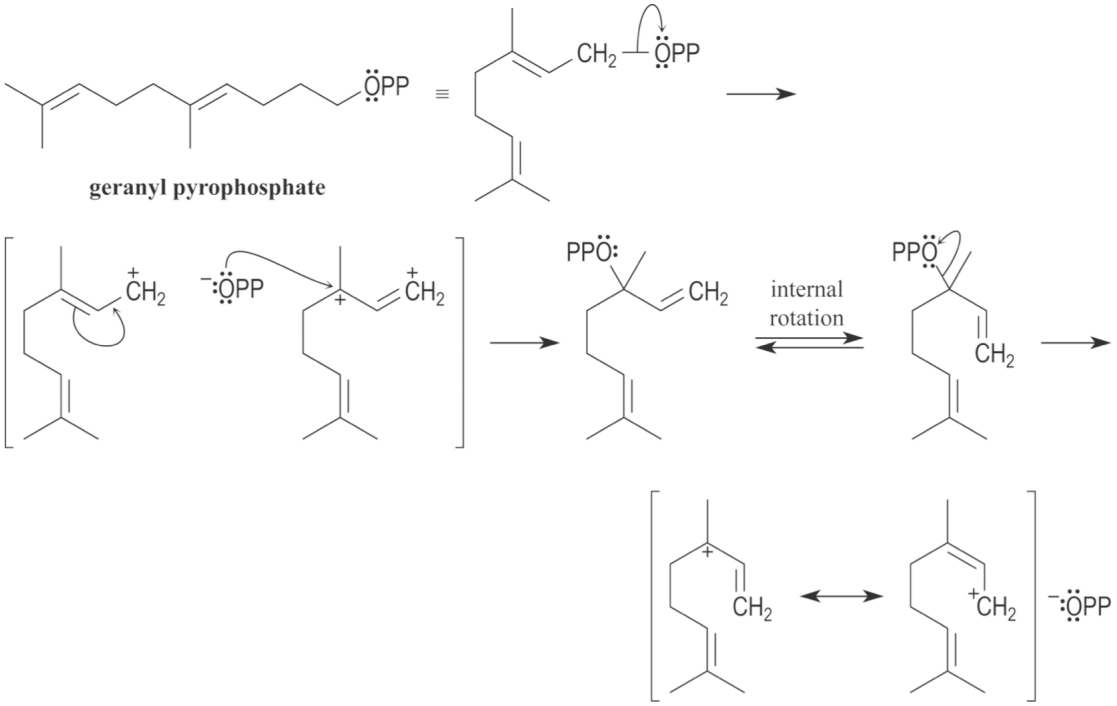

**ethylbenzene** **benzoic acid**

17.15 (b) Caryophyllene is a sesquiterpene because it contains three isoprene skeletons, which are shown as heavy bonds.

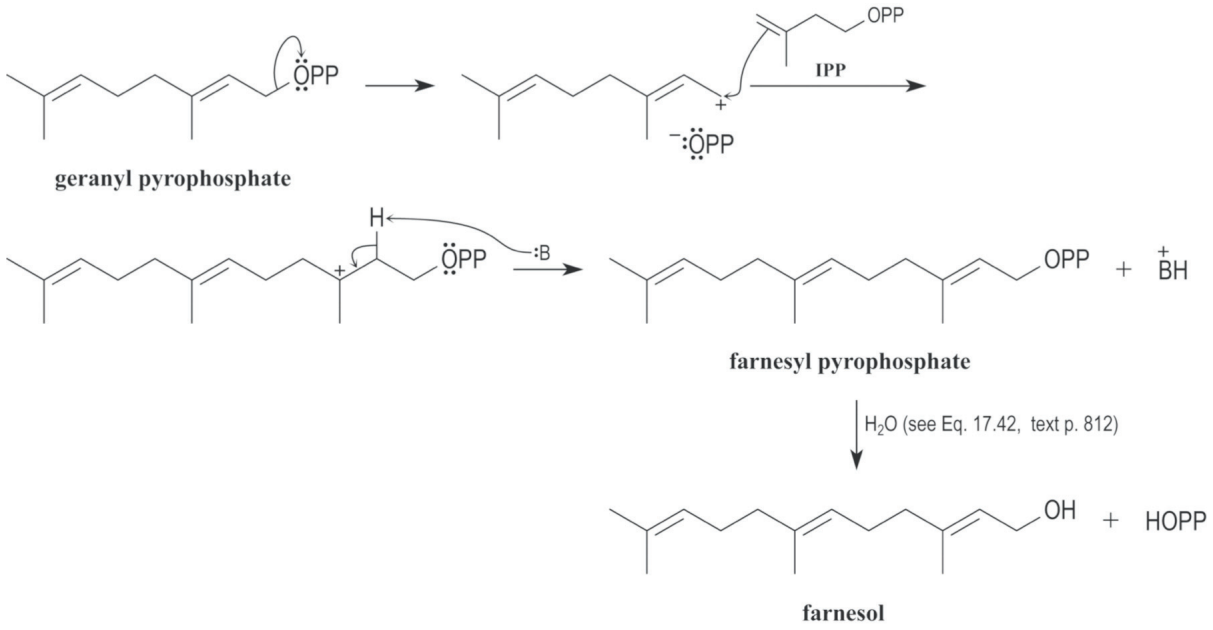



**caryophyllene**

17.16 (b) Ionization of geranyl pyrophosphate is followed by reaction with the pyrophosphate anion on the other electron-deficient carbon of the resonance-stabilized carbocation; rotation about a single bond is followed by ionization of pyrophosphate to give the desired carbocation.




17.17 (b) Geranyl pyrophosphate is converted into farnesyl pyrophosphate by a mechanism exactly analogous to the one shown in Eq. 17.38 on text p. 765. Then farnesyl pyrophosphate hydrolyzes to farnesol; see text Eq. 17.39.

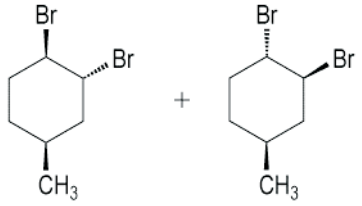


## Solutions to Additional Problems

17.19 The structure of the starting material is:

**4-methylcyclohexene**

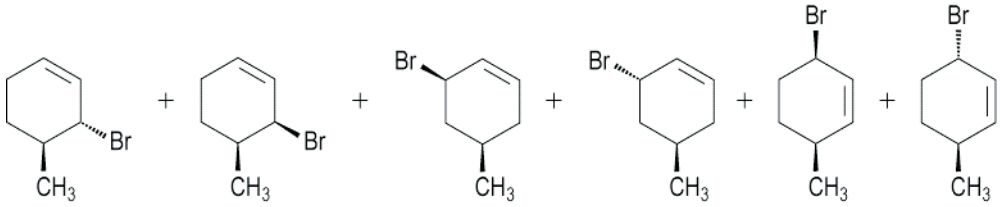
(a)



**(1*R*,2*R*,4*S*)-1,2-dibromo-4-methylcyclohexane** + **(1*S*,2*S*,4*S*)-1,2-dibromo-4-methylcyclohexane**

(and their enantiomers)

(b)

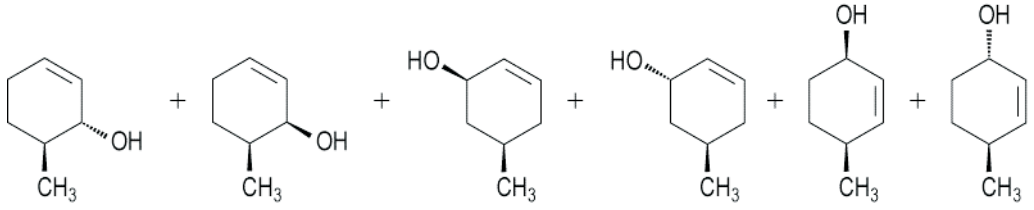


**3-bromo-4-methylcyclohexene** (two diastereomers and their enantiomers)

**3-bromo-5-methylcyclohexene** (two diastereomers and their enantiomers)

**3-bromo-6-methylcyclohexene** (two diastereomers and their enantiomers)

(c)

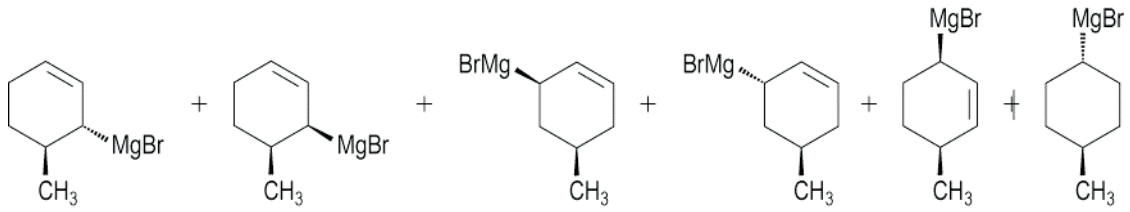


**6-methyl-3-cyclohexenol** (two diastereomers and their enantiomers)

**4-methyl-2-cyclohexenol** (two diastereomers and their enantiomers)

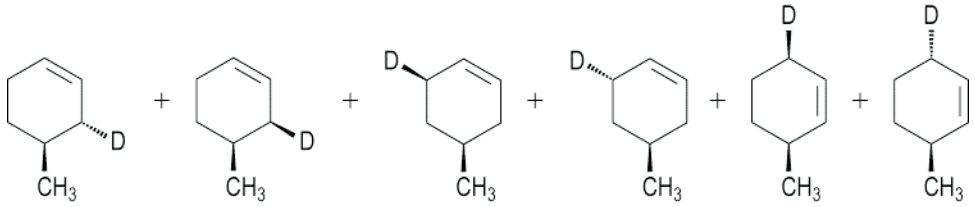
**4-methyl-2-cyclohexenol** (two diastereomers and their enantiomers)

(d) As in the previous parts, all four stereoisomers of each compound are formed.




Don't forget that Grignard reagents undergo a very rapid allylic rearrangement (Eq. 17.23, text p. 799).

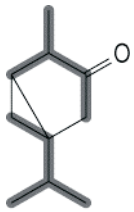
(e) As in the previous part, all four stereoisomers of each compound are formed.




17.20 Compound (d) is a terpene. The isoprene skeleton is shown with heavy bonds.

(b) Compound (b) is not a terpene.

(d) Compound (d) is a terpene. The isoprene skeleton is shown with heavy bonds.

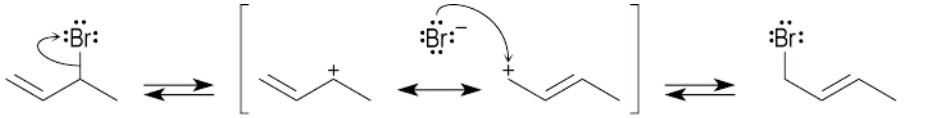



**b-thujone**

(f) Compound (f) is not a terpene.

17.23 (a) The allylic-rearrangement product *B* [(*E*)-1-bromo-2-butene] could be formed by ionization to a carbocation and bromide ion followed by reaction with the bromide ion on the other electron-deficient carbon.

(b) The curved-arrow notation is shown in the following scheme.

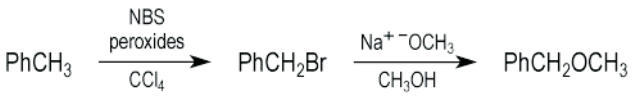



**3-bromo-1-butene**
(compound *A*)

**(*E*)-1-bromo-2-butene**
(compound *B*)

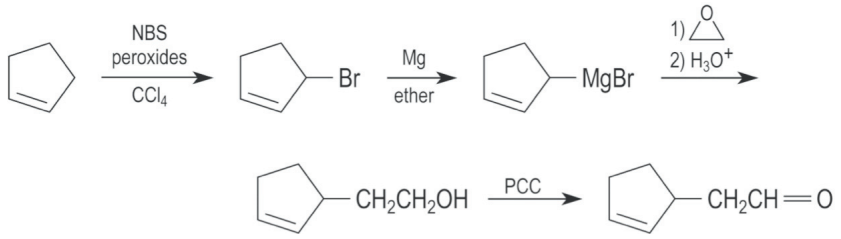
(c) Compound *B*, the rearrangement product, is favored at equilibrium because it has the double bond with the greater number of alkyl branches.

17.24 (a)

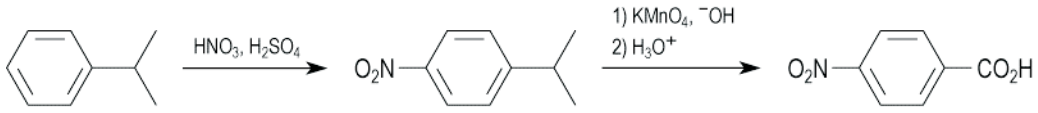



**benzyl methyl ether**

(d)



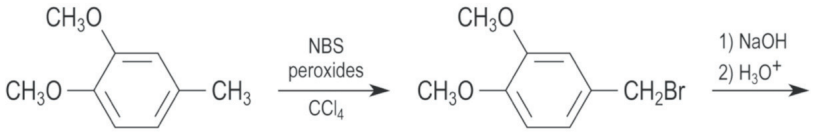

(f)



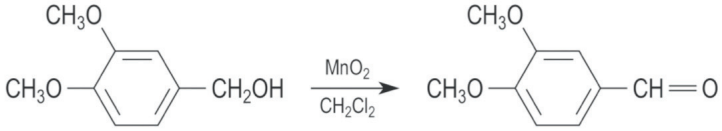

**cumene** **p-nitrobenzoic acid**

Compare the solutions to parts (e) and (f) and notice how reversing the sequence of the oxidation and nitration steps brings the directing effects of different substituents into play during nitration.

(g)

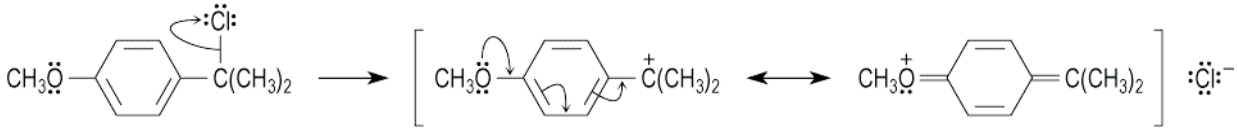



**1,2-dimethoxy-4-methylbenzene**

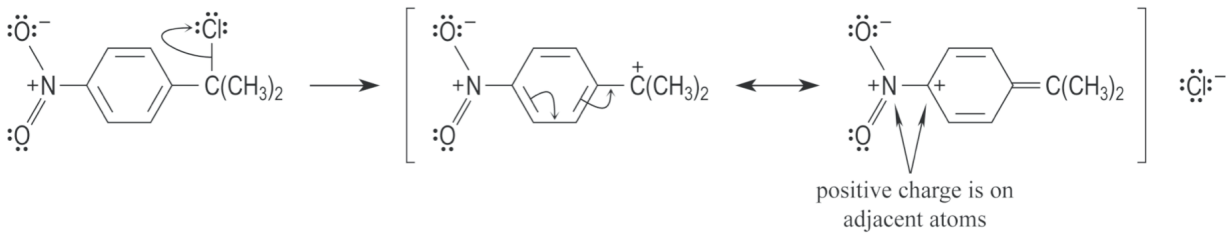



**3,4-dimethoxybenzaldehyde**

17.25 The compounds that give the most stable carbocation intermediates are the ones that undergo the most rapid solvolysis. This problem deals with the effect of substituent on the stability of the carbocation intermediate. The key is to analyze the balance of resonance and polar substituent effects just as you would for electrophilic aromatic substitution. The order of increasing reactivity is (4) < (1) < (3) < (2). Thus, compound (2) reacts most rapidly because the carbocation intermediate is stabilized by the *electron-donating resonance effect* of the *p*-methoxy substituent:

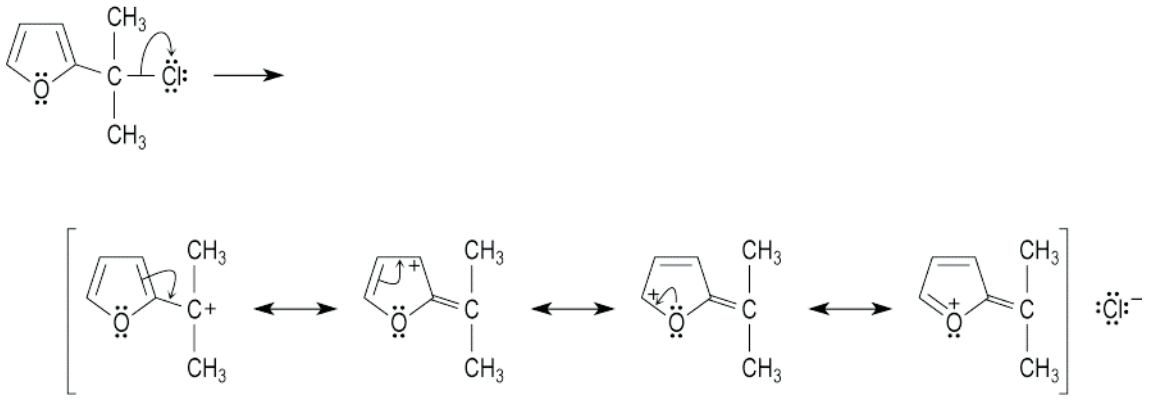



As in electrophilic substitution, the resonance effect of the *p*-methoxy group strongly outweighs its electron-withdrawing polar effect. In compound (3), there is a similar resonance effect; however, the polar effects of halogen substituents outweigh their resonance effects. Consequently, compound (3) reacts more slowly. The nitro group exerts no resonance effect in the carbocation intermediates derived from compounds (1) and (4); the question is then whether its polar effect is stronger from the meta or para position. As in electrophilic aromatic substitution, a *para*-nitro group destabilizes a carbocation intermediate more than a *meta*-nitro group because, in a *para*-nitro carbocation, positive charge is on adjacent atoms:



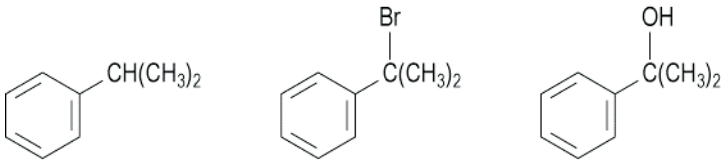

In the *meta*-nitro carbocation, positive charge does *not* reside on adjacent atoms. Consequently, the *meta*-nitro carbocation is more stable (or perhaps we should say *less unstable*) than the *para*-nitro carbocation, and *m*-nitro-*tert*-cumyl chloride solvolyzes more rapidly than *p*-nitro-*tert*-cumyl chloride.

17.28 The solution to this problem, like the previous three solutions, hinges on an analysis of the relative stabilities of the carbocation intermediates involved in the $S_N1$ reactions of the two compounds. The carbocation intermediate in the solvolysis of compound *A* is resonance-stabilized:



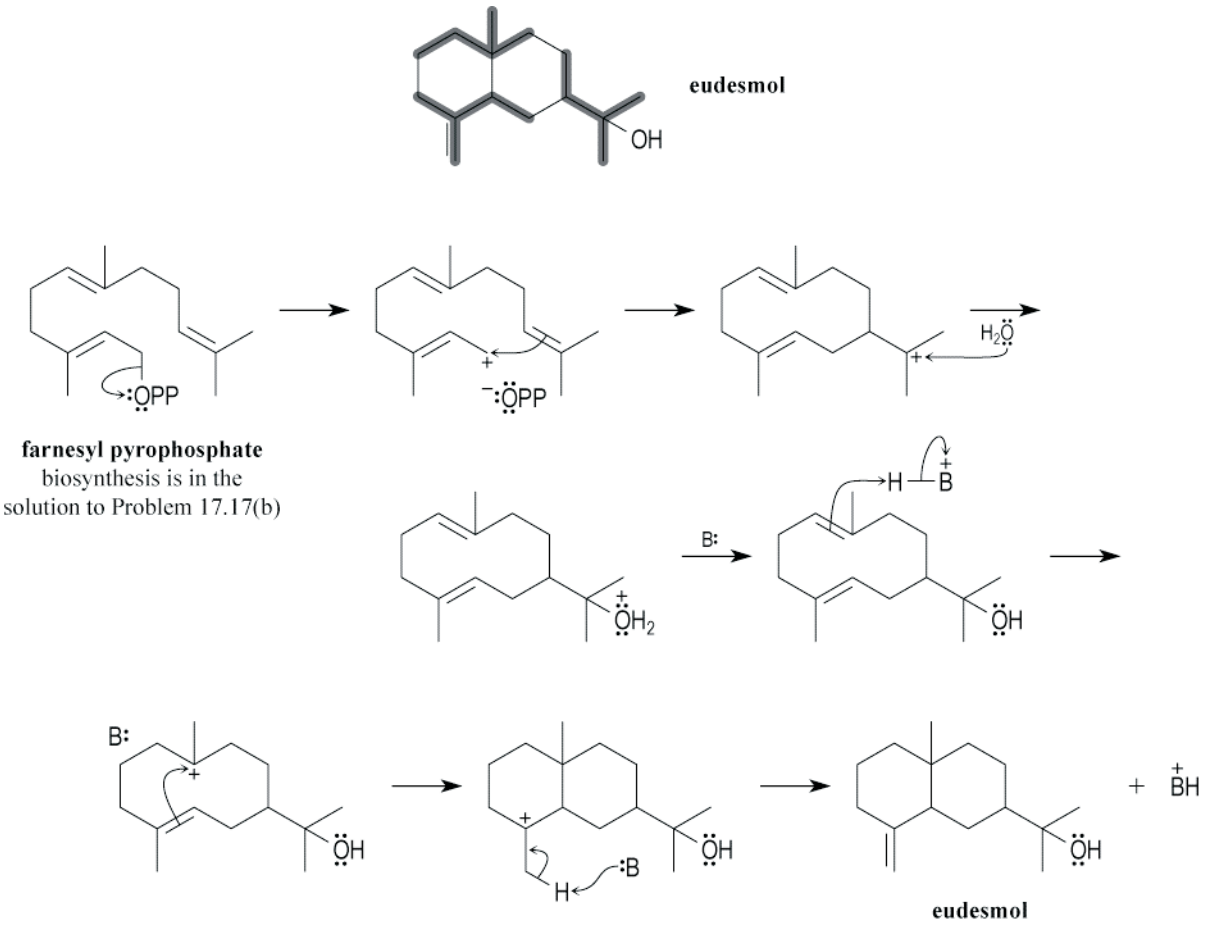
The carbocation intermediate involved in the solvolysis of compound *B* is not resonance-stabilized, and in fact is somewhat destabilized by the electron-withdrawing polar effect of the oxygen. The greater stability of the carbocation derived from compound *A* results in a greater solvolysis rate.

17.29 The fact that benzoic acid is obtained by chromic acid oxidation shows that all compounds contain a monosubstituted benzene ring. The NBS reaction is a benzylic bromination, and the alcohol produced by solvolysis of the resulting bromide must be tertiary, since it cannot be oxidized with $CrO_3$ and pyridine. The structures of compound *A*, *B*, and *C* are therefore as follows:

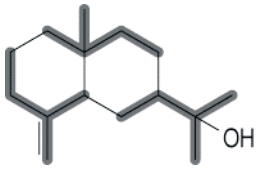


*A* *B* *C*

17.34 First analyze the relationship of the isoprene skeletons. Then use steps like the ones shown in Eqs. 17.40–17.42, text pp. 812, to assemble the parts from IPP and DMAP. Start with farnesyl pyrophosphate, the biosynthesis of which is shown in the solution to Problem 17.17(b), text p. 813. Note that B**:** = a base.




A different arrangement of isoprene units in eudesmol can also be envisioned:

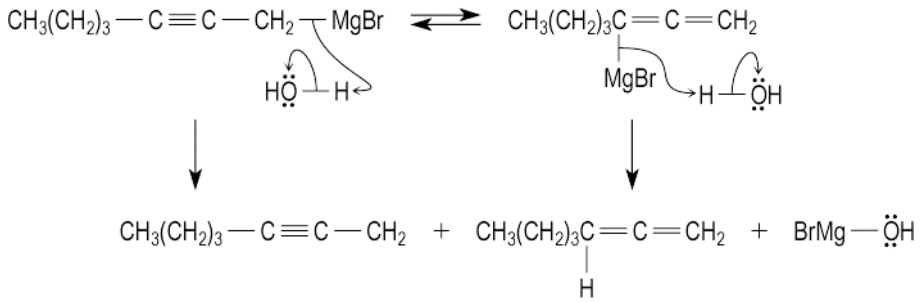



**eudesmol**
(alternate arrangement
of isoprene units)

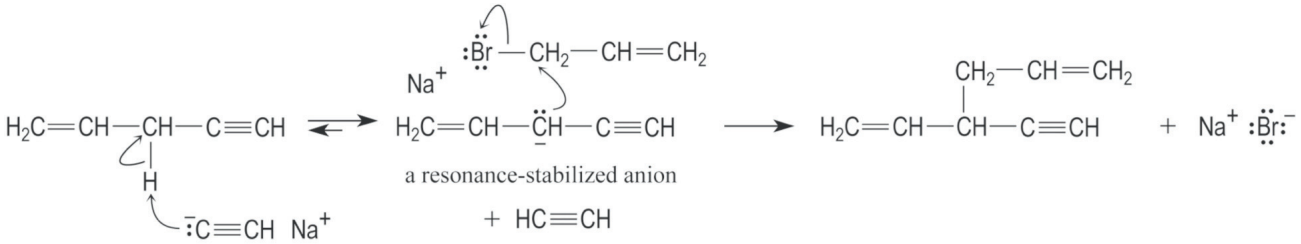
A biosynthetic scheme based on this arrangement would be an equally correct answer. An isotope-labeling experiment would be required to distinguish between the two arrangements.

17.36 (a) Although the conjugate-base anion of 1,4-pentadiene is doubly allylic and resonance-stabilized, the conjugate-base anion of 1,3-cyclopentadiene is in addition aromatic. (See text p. 726 for a discussion of this case.) Consequently, much less energy is required for the ionization of 1,3-cyclopentadiene, and its p$K_a$ is therefore much lower. (The p$K_a$ difference between these two compounds is estimated to be 10–15 units.)

17.38 (a) Propargylic Grignard reagents, like allylic Grignard reagents, are an equilibrium mixture of two constitutional isomers. Each reacts with $H_2O$.

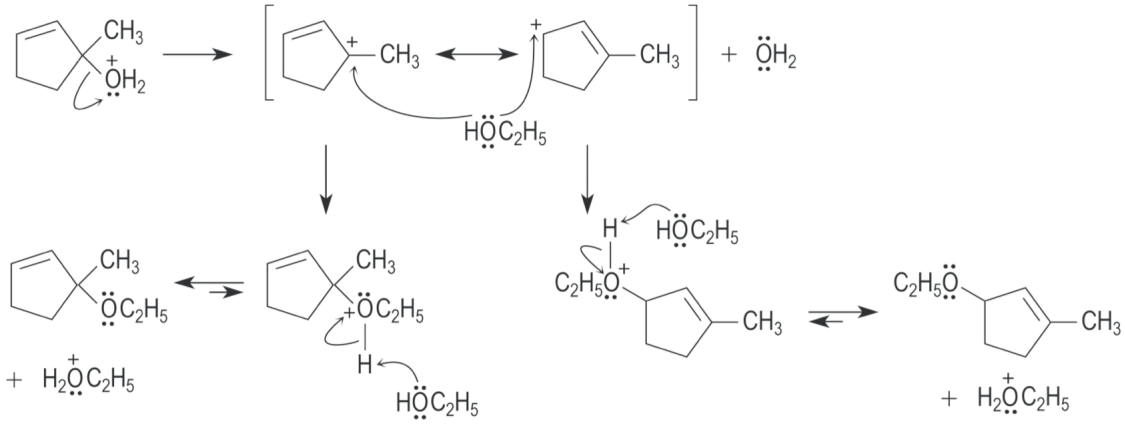


(c) A hydrogen on the central carbon is more acidic than an acetylenic hydrogen because the conjugate-base anion resulting from removal of the central hydrogen is both allylic and propargylic, and is therefore doubly resonance-stabilized. The conjugate-base anion is alkylated by allyl bromide.

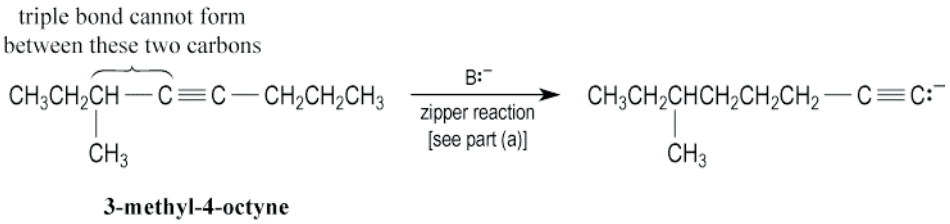



In the resonance structures of the anion intermediate, the negative charge is delocalized to two other carbons. (Draw these structures.) While the mechanism above shows why the indicated product is reasonable, it does not explain why products derived from the other possible resonance structures are not observed (or reported).

(d) Protonation of the alcohol and loss of water give an allylic carbocation that can react with ethanol at either of two electron-deficient carbons to give a mixture of two constitutionally isomeric ethyl ethers. The following mechanism begins with the protonated alcohol.



17.39 (b) The question is whether the triple bond migrates to the end of the carbon chain nearer to the methyl branch or to the end of the chain farther from the methyl branch. Once we consider the mechanism shown in part (a), the answer becomes clear. The migration of the triple bond occurs *away* from the methyl branch, because the mechanism of the reaction requires a stepwise migration of the triple bond, and a triple bond cannot form at a carbon that bears a branch because a carbon have no more than four bonds.




**3-methyl-4-octyne**

17.41 The equilibrium lies to the right because the double bond has four alkyl substituents whereas, in the starting material, it has three. Recall that alkyl substitution at double bonds is a stabilizing effect (Sec. 4.5B, text pp. 144–146). The mechanism involves simply protonation of the double bond to give the benzylic cation and loss of a proton to give the product.