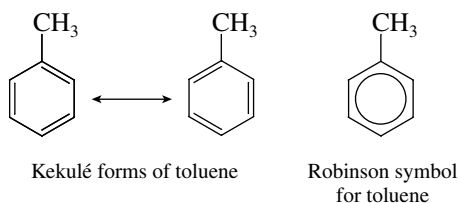


CHAPTER 11

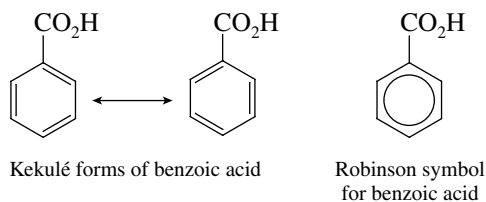
ARENES AND AROMATICITY

SOLUTIONS TO TEXT PROBLEMS

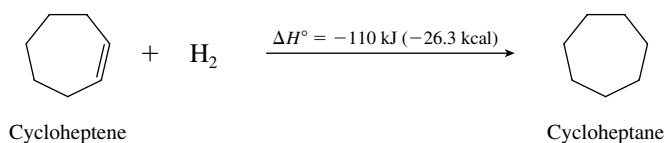
11.1 Toluene is $C_6H_5CH_3$; it has a methyl group attached to a benzene ring.



Benzoic acid has a $-CO_2H$ substituent on the benzene ring.

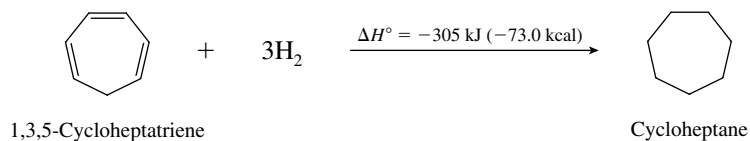


11.2 Given



and assuming that there is no resonance stabilization in 1,3,5-cycloheptatriene, we predict that its heat of hydrogenation will be three times that of cycloheptene or 330 kJ/mol (78.9 kcal/mol).

The measured heat of hydrogenation is

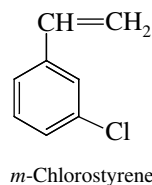


Therefore

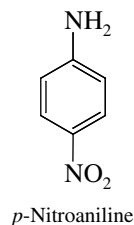
$$\begin{aligned}
 \text{Resonance energy} &= 330 \text{ kJ/mol (predicted for no delocalization)} - 305 \text{ kJ/mol (observed)} \\
 &= 25 \text{ kJ/mol (5.9 kcal/mol)}
 \end{aligned}$$

The value given in the text for the resonance energy of benzene (152 kJ/mol) is six times larger than this. 1,3,5-Cycloheptatriene is *not* aromatic.

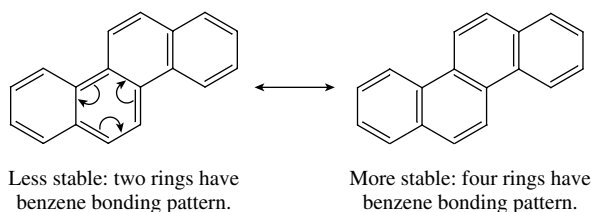
- 11.3 (b) The parent compound is styrene, $\text{C}_6\text{H}_5\text{CH}=\text{CH}_2$. The desired compound has a chlorine in the meta position.



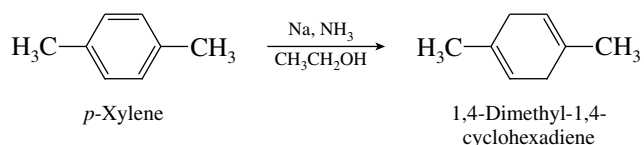
- (c) The parent compound is aniline, $\text{C}_6\text{H}_5\text{NH}_2$. *p*-Nitroaniline is therefore



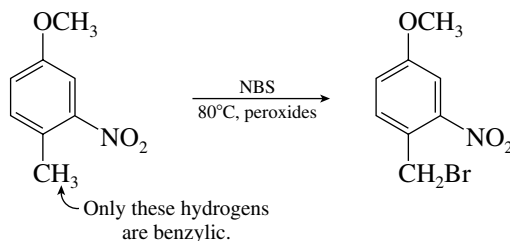
- 11.4 The most stable resonance form is the one that has the greatest number of rings that correspond to Kekulé formulations of benzene. For chrysene, electrons are moved in pairs from the structure given to generate a more stable one:



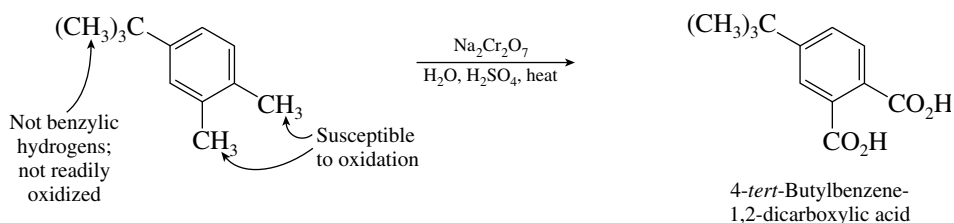
- 11.5 Birch reductions of monosubstituted arenes yield 1,4-cyclohexadiene derivatives in which the alkyl group is a substituent on the double bond. With *p*-xylene, both methyl groups are double-bond substituents in the product.



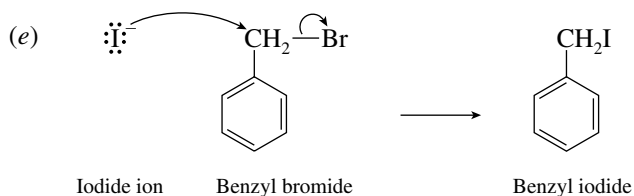
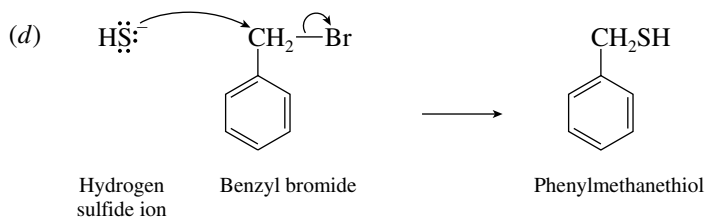
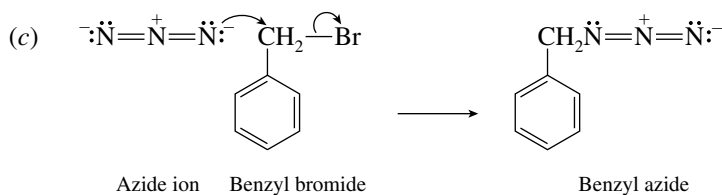
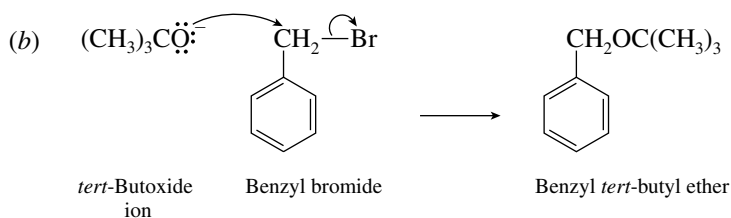
- 11.6 (b) Only the benzylic hydrogen is replaced by bromine in the reaction of 4-methyl-3-nitroanisole with *N*-bromosuccinimide.



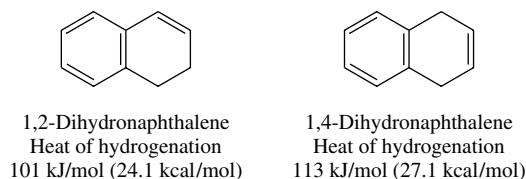
- 11.7 The molecular formula of the product is $C_{12}H_{14}O_4$. Since it contains four oxygens, the product must have two $-CO_2H$ groups. None of the hydrogens of a *tert*-butyl substituent on a benzene ring is benzylic, and so this group is inert to oxidation. Only the benzylic methyl groups of 4-*tert*-butyl-1,2-dimethylbenzene are susceptible to oxidation; therefore, the product is 4-*tert*-butylbenzene-1,2-dicarboxylic acid.



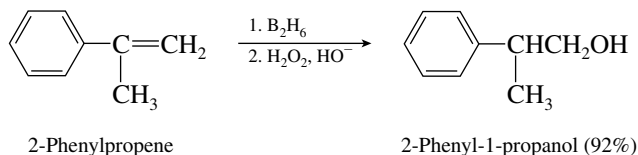
- 11.8 Each of these reactions involves nucleophilic substitution of the S_N2 type at the benzylic position of benzyl bromide.



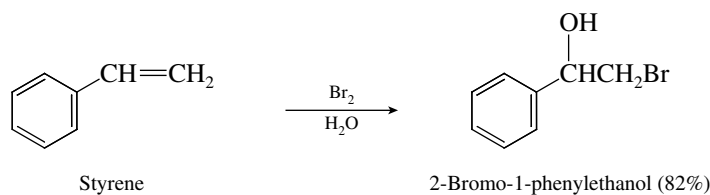
- 11.9 The dihydronaphthalene in which the double bond is conjugated with the aromatic ring is more stable; thus 1,2-dihydronaphthalene has a lower heat of hydrogenation than 1,4-dihydronaphthalene.



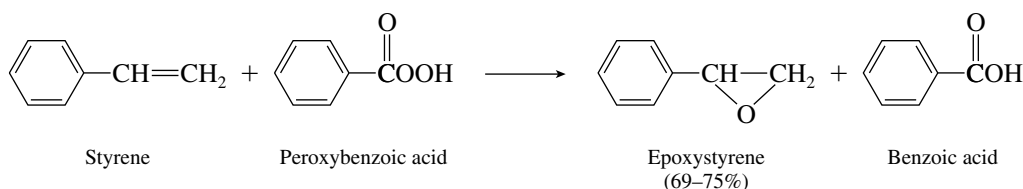
- 11.10 (b) The regioselectivity of alcohol formation by hydroboration–oxidation is opposite that predicted by Markovnikov’s rule.



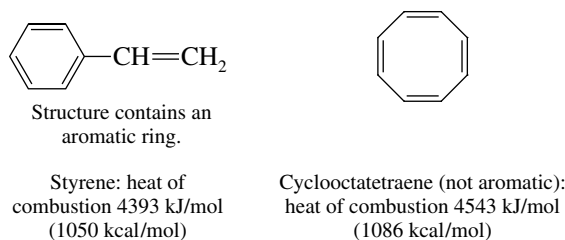
- (c) Bromine adds to alkenes in aqueous solution to give bromohydrins. A water molecule acts as a nucleophile, attacking the bromonium ion at the carbon that can bear most of the positive charge, which in this case is the benzylic carbon.



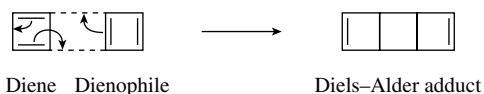
- (d) Peroxy acids convert alkenes to epoxides.



- 11.11 Styrene contains a benzene ring and will be appreciably stabilized by resonance, which makes it lower in energy than cyclooctatetraene.

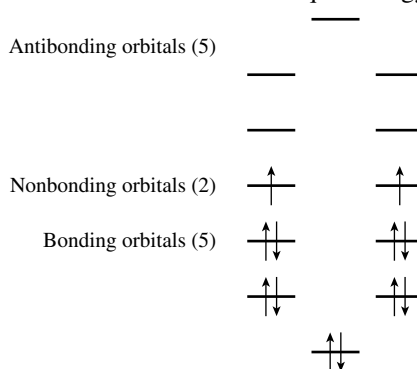


- 11.12 The dimerization of cyclobutadiene is a Diels–Alder reaction in which one molecule of cyclobutadiene acts as a diene and the other as a dienophile.



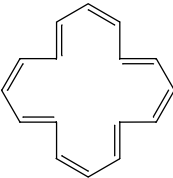
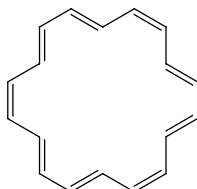


- 11.13 (b) Since twelve $2p$ orbitals contribute to the cyclic conjugated system of [12]-annulene, there will be 12π molecular orbitals. These MOs are arranged so that one is of highest energy, one is of lowest energy, and the remaining ten are found in pairs between the highest and lowest

energy orbitals. There are 12π electrons, and so the lowest 5 orbitals are each doubly occupied, whereas each of the next 2 orbitals—orbitals of equal energy—is singly occupied.

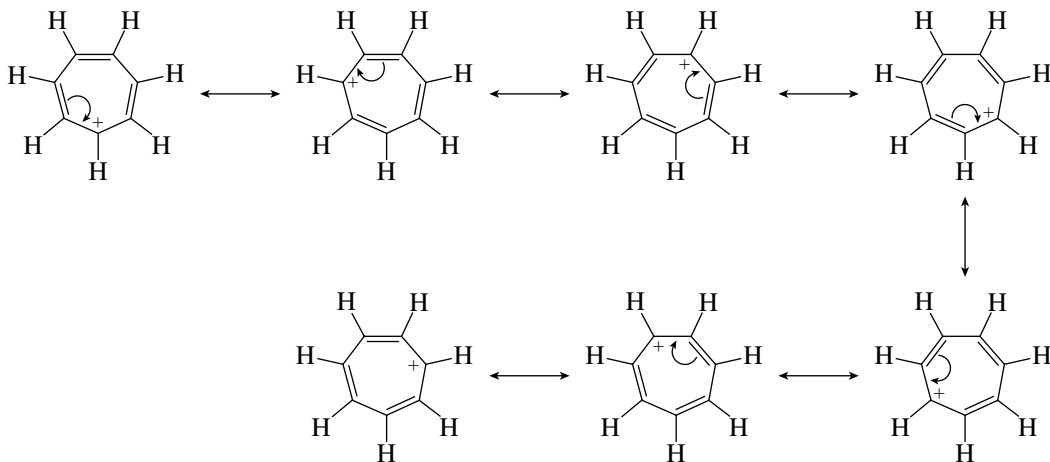


- 11.14** One way to evaluate the relationship between heats of combustion and structure for compounds that are not isomers is to divide the heat of combustion by the number of carbons so that heats of combustion are compared on a “per carbon” basis.

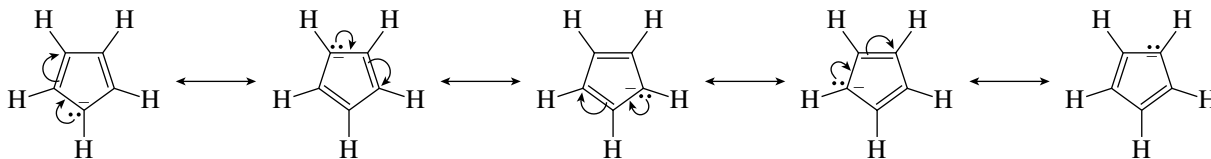
			
Benzene	Cyclooctatetraene	[16]-Annulene	[18]-Annulene
Heats of combustion: 3265 kJ/mol (781 kcal/mol)	4543 kJ/mol (1086 kcal/mol)	9121 kJ/mol (2182 kcal/mol)	9806 kJ/mol (2346 kcal/mol)
Heats of combustion per carbon: 544 kJ/mol (130 kcal/mol)	568 kJ/mol (136 kcal/mol)	570 kJ/mol (136 kcal/mol)	545 kJ/mol (130 kcal/mol)

As the data indicate (within experimental error), the heats of combustion *per carbon* of the two aromatic hydrocarbons, benzene and [18]-annulene, are equal. Similarly, the heats of combustion per carbon of the two nonaromatic hydrocarbons, cyclooctatetraene and [16]-annulene, are equal. The two aromatic hydrocarbons have heats of combustion per carbon that are less than those of the nonaromatic hydrocarbons. On a per carbon basis, the aromatic hydrocarbons have lower potential energy (are more stable) than the nonaromatic hydrocarbons.

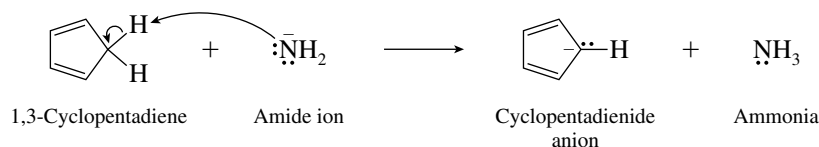
- 11.15** The seven resonance forms for tropylium cation (cycloheptatrienyl cation) may be generated by moving π electrons in pairs toward the positive charge. The resonance forms are simply a succession of allylic carbocations.



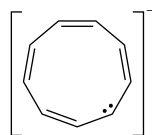
- 11.16** Resonance structures are generated for cyclopentadienide anion by moving the unshared electron pair from the carbon to which it is attached to a position where it becomes a shared electron pair in a π bond.



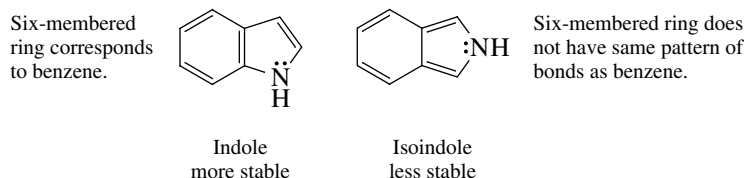
- 11.17** The process is an acid–base reaction in which cyclopentadiene transfers a proton to amide ion (the base) to give the aromatic cyclopentadienide anion. The sodium ion (Na^+) has been omitted from the equation.



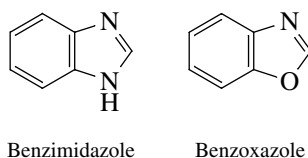
- 11.18** (b) Cyclononatetraenide anion has 10 π electrons; it is aromatic. The 10 π electrons are most easily seen by writing a Lewis structure for the anion: there are 2 π electrons for each of four double bonds, and the negatively charged carbon contributes 2.



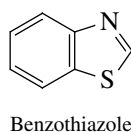
- 11.19** Indole is more stable than isoindole. Although the bonding patterns in both five-membered rings are the same, the six-membered ring in indole has a pattern of bonds identical to benzene and so is highly stabilized. The six-membered ring in isoindole is not of the benzene type.



- 11.20** The prefix *benz-* in benzimidazole (structure given in text) signifies that a benzene ring is fused to an imidazole ring. By analogy, benzoxazole has a benzene ring fused to oxazole.

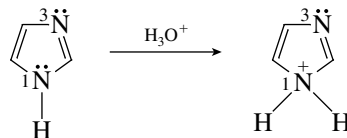


Similarly, benzothiazole has a benzene ring fused to thiazole.



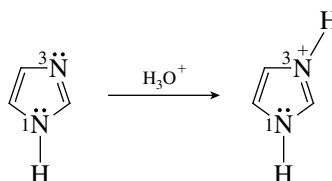
- 11.21 Write structural formulas for the species formed when a proton is transferred to either of the two nitrogens of imidazole.

Protonation of N-1:

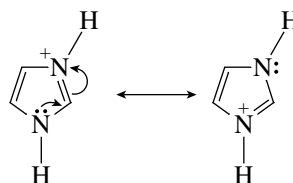


The species formed on protonation of N-1 is not aromatic. The electron pair of N-1 that contributes to the aromatic 6 π -electron system of imidazole is no longer available for this purpose because it is used to form a covalent bond to the proton in the conjugate acid.

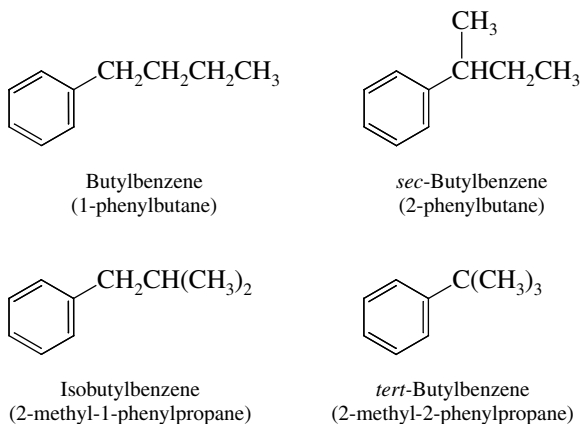
Protonation of N-3:



The species formed on protonation of N-3 is aromatic. Electron delocalization represented by the resonance forms shown allows the 6 π -electron aromatic system of imidazole to be retained in its conjugate acid. The positive charge is shared equally by both nitrogens.

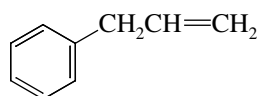


- 11.22 Since the problem requires that the benzene ring be monosubstituted, all that needs to be examined are the various isomeric forms of the C_4H_9 substituent.



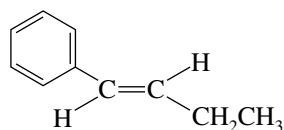
These are the four constitutional isomers. *sec*-Butylbenzene is chiral and so exists in enantiomeric *R* and *S* forms.

- 11.23 (a) An allyl substituent is $-\text{CH}_2\text{CH}=\text{CH}_2$.



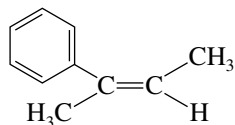
Allylbenzene

- (b) The constitution of 1-phenyl-1-butene is $\text{C}_6\text{H}_5\text{CH}=\text{CHCH}_2\text{CH}_3$. The *E* stereoisomer is



(*E*)-1-Phenyl-1-butene

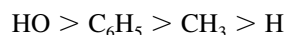
- The two higher ranked substituents, phenyl and ethyl, are on opposite sides of the double bond.
- (c) The constitution of 2-phenyl-2-butene is $\text{CH}_3\text{C}(\text{C}_6\text{H}_5)=\text{CHCH}_3$. The *Z* stereoisomer is



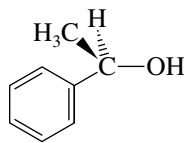
(*Z*)-2-Phenyl-2-butene

- The two higher ranked substituents, phenyl and methyl, are on the same side of the double bond.
- (d) 1-Phenylethanol is chiral and has the constitution $\text{CH}_3\text{CH}(\text{C}_6\text{H}_5)\text{OH}$. Among the substituents

attached to the stereogenic center, the order of decreasing precedence is

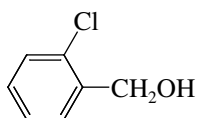


In the *R* enantiomer the three highest ranked substituents must appear in a clockwise sense in proceeding from higher ranked to next lower ranked when the lowest ranked substituent is directed away from you.

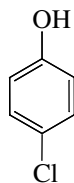


(*R*)-1-Phenylethanol

- (e) A benzyl group is $\text{C}_6\text{H}_5\text{CH}_2-$. Benzyl alcohol is therefore $\text{C}_6\text{H}_5\text{CH}_2\text{OH}$ and *o*-chlorobenzyl alcohol is

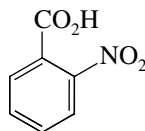


- (f) In *p*-chlorophenol the benzene ring bears a chlorine and a hydroxyl substituent in a 1,4-substitution pattern.



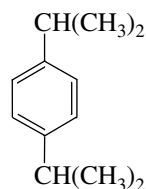
p-Chlorophenol

- (g) Benzenecarboxylic acid is an alternative IUPAC name for benzoic acid.

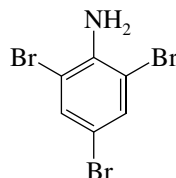


2-Nitrobenzenecarboxylic acid

- (h) Two isopropyl groups are in a 1,4 relationship in *p*-diisopropylbenzene.

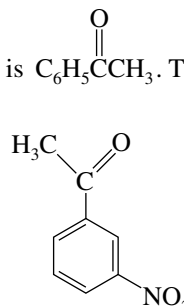
*p*-Diisopropylbenzene

- (i) Aniline is $C_6H_5NH_2$. Therefore

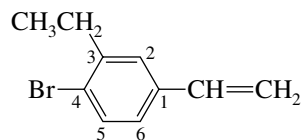


2,4,6-Tribromoaniline

- (j) Acetophenone (from text Table 11.1) is $C_6H_5C(=O)CH_3$. Therefore

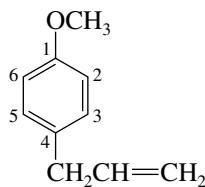
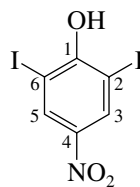
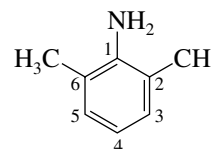
*m*-Nitroacetophenone

- (k) Styrene is $C_6H_5CH=CH_2$ and numbering of the ring begins at the carbon that bears the side chain.

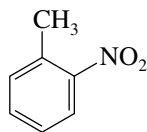


4-Bromo-3-ethylstyrene

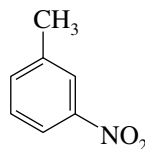
- 11.24** (a) Anisole is the name for $C_6H_5OCH_3$, and allyl is an acceptable name for the group $H_2C=CHCH_2-$. Number the ring beginning with the carbon that bears the methoxy group.
 (b) Phenol is the name for C_6H_5OH . The ring is numbered beginning at the carbon that bears the hydroxyl group, and the substituents are listed in alphabetical order.
 (c) Aniline is the name given to $C_6H_5NH_2$. This compound is named as a dimethyl derivative of aniline. Number the ring sequentially beginning with the carbon that bears the amino group.

Estragole
4-AllylanisoleDiosphenol
2,6-Diiodo-4-nitrophenol*m*-Xylidine
2,6-Dimethylaniline

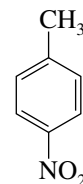
- 11.25 (a) There are three isomeric nitrotoluenes, because the nitro group can be ortho, meta, or para to the methyl group.



o-Nitrotoluene
(2-nitrotoluene)

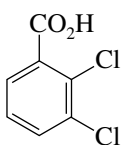


m-Nitrotoluene
(3-nitrotoluene)

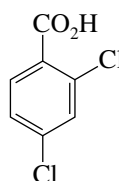


p-Nitrotoluene
(4-nitrotoluene)

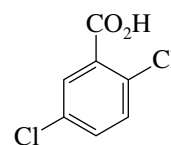
- (b) Benzoic acid is $C_6H_5CO_2H$. In the isomeric dichlorobenzoic acids, two of the ring hydrogens of benzoic acid have been replaced by chlorines. The isomeric dichlorobenzoic acids are



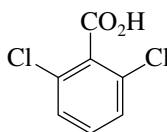
2,3-Dichlorobenzoic acid



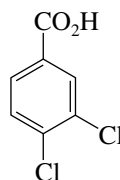
2,4-Dichlorobenzoic acid



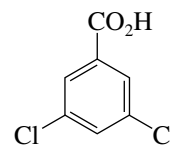
2,5-Dichlorobenzoic acid



2,6-Dichlorobenzoic acid



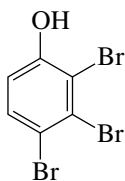
3,4-Dichlorobenzoic acid



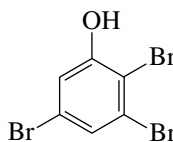
3,5-Dichlorobenzoic acid

The prefixes *o*-, *m*-, and *p*- may not be used in trisubstituted arenes; numerical prefixes are used. Note also that **benzenecarboxylic** may be used in place of **benzoic**.

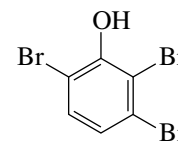
- (c) In the various tribromophenols, we are dealing with tetrasubstitution on a benzene ring. Again, *o*-, *m*-, and *p*- are not valid prefixes. The hydroxyl group is assigned position 1 because the base name is phenol.



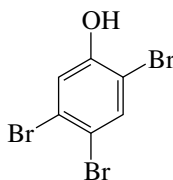
2,3,4-Tribromophenol



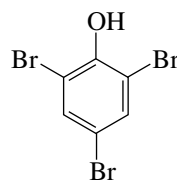
2,3,5-Tribromophenol



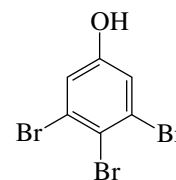
2,3,6-Tribromophenol



2,4,5-Tribromophenol

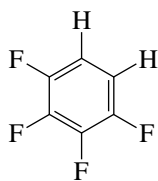


2,4,6-Tribromophenol

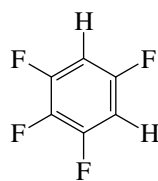


3,4,5-Tribromophenol

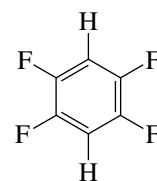
- (d) There are only three tetrafluorobenzenes. The two hydrogens may be ortho, meta, or para to each other.



1,2,3,4-Tetrafluorobenzene

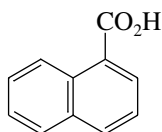


1,2,3,5-Tetrafluorobenzene

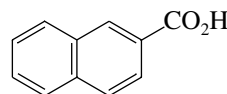


1,2,4,5-Tetrafluorobenzene

- (e) There are only two naphthalenecarboxylic acids.

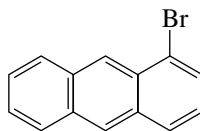


Naphthalene-1-carboxylic acid

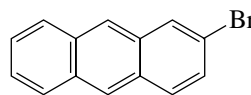


Naphthalene-2-carboxylic acid

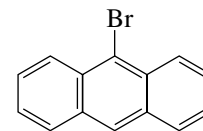
- (f) There are three isomeric bromoanthracenes. All other positions are equivalent to one of these.



1-Bromoanthracene

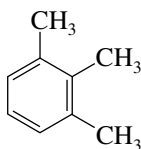


2-Bromoanthracene

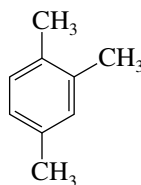


9-Bromoanthracene

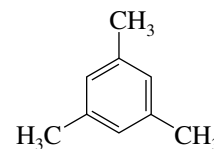
- 11.26 There are three isomeric trimethylbenzenes:



1,2,3-Trimethylbenzene



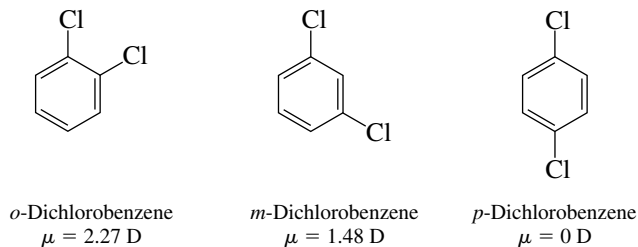
1,2,4-Trimethylbenzene



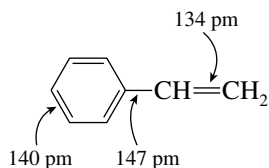
1,3,5-Trimethylbenzene

Their relative stabilities are determined by steric effects. Mesitylene (the 1,3,5-trisubstituted isomer) is the most stable because none of its methyl groups are ortho to any other methyl group. Ortho substituents on a benzene ring, depending on their size, experience van der Waals strain in the same way that *cis* substituents on a carbon-carbon double bond do. Because the carbon-carbon bond length in benzene is somewhat longer than in an alkene, these effects are smaller in magnitude, however. The 1,2,4-substitution pattern has one methyl-methyl repulsion between ortho substituents. The least stable isomer is the 1,2,3-trimethyl derivative, because it is the most crowded. The energy differences between isomers are relatively small, heats of combustion being 5198, 5195, and 5193 kJ/mol (1242.4, 1241.6, and 1241.2 kcal/mol) for the 1,2,3, 1,2,4, and 1,3,5 isomers, respectively.

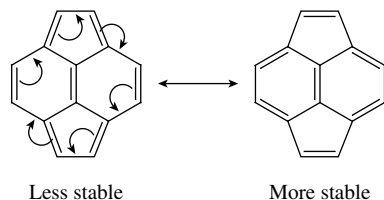
- 11.27 *p*-Dichlorobenzene has a center of symmetry. Each of its individual bond moments is balanced by an identical bond dipole oriented opposite to it. *p*-Dichlorobenzene has no dipole moment. *o*-Dichlorobenzene has the largest dipole moment.



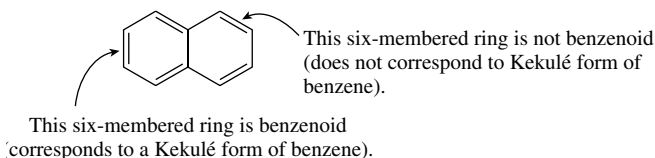
- 11.28 The shortest carbon–carbon bond in styrene is the double bond of the vinyl substituent; its length is much the same as the double-bond length of any other alkene. The carbon–carbon bond lengths of the ring are intermediate between single- and double-bond lengths. The longest carbon–carbon bond is the sp^2 to sp^2 single bond connecting the vinyl group to the benzene ring.



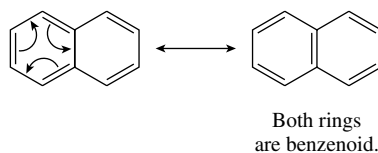
- 11.29 Move π electron pairs as shown so that both six-membered rings have an arrangement of bonds that corresponds to benzene.



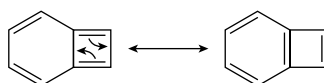
- 11.30 (a) In the structure shown for naphthalene, one ring but not the other corresponds to a Kekulé form of benzene. We say that one ring is **benzenoid**, and the other is not.



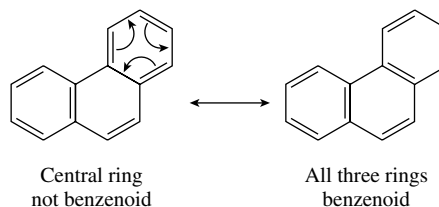
By rewriting the benzenoid ring in its alternative Kekulé form, *both* rings become benzenoid.



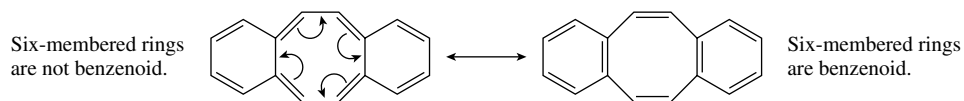
- (b) Here a cyclobutadiene ring is fused to benzene. By writing the alternative resonance form of cyclobutadiene, the six-membered ring becomes benzenoid.



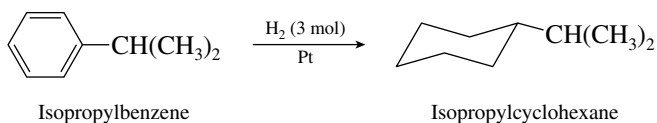
- (c) The structure portrayed for phenanthrene contains two terminal benzenoid rings and a non-benzenoid central ring. All three rings may be represented in benzenoid forms by converting one of the terminal six-membered rings to its alternative Kekulé form as shown:



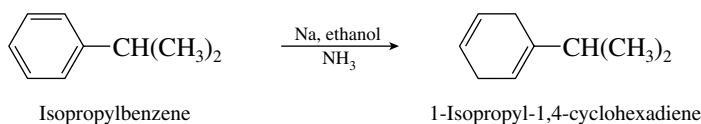
- (d) Neither of the six-membered rings is benzenoid in the structure shown. By writing the cyclo-octatetraene portion of the molecule in its alternative representation, the two six-membered rings become benzenoid.



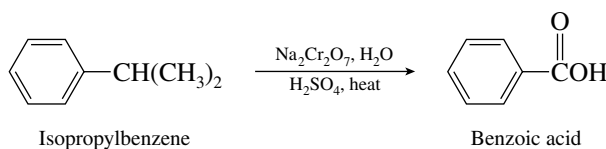
- 11.31** (a) Hydrogenation of isopropylbenzene converts the benzene ring to a cyclohexane unit.



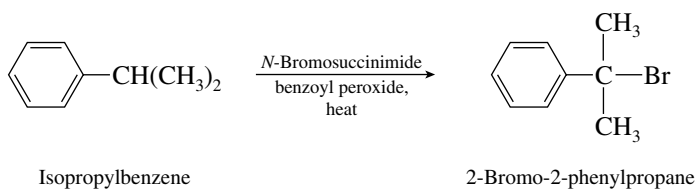
- (b) Sodium and ethanol in liquid ammonia is the combination of reagents that brings about Birch reduction of benzene rings. The 1,4-cyclohexadiene that is formed has its isopropyl group as a substituent on one of the double bonds.



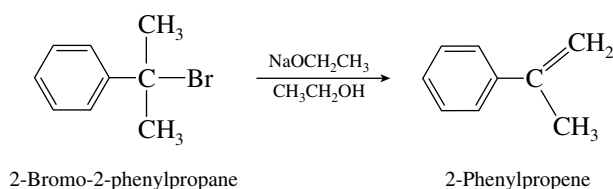
- (c) Oxidation of the isopropyl side chain occurs. The benzene ring remains intact.



- (d) *N*-Bromosuccinimide is a reagent effective for the substitution of a benzylic hydrogen.

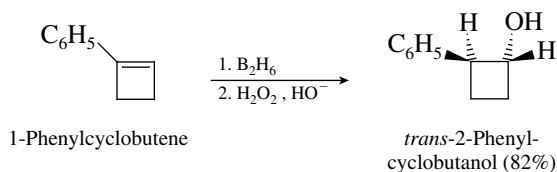


- (e) The tertiary bromide undergoes E2 elimination to give a carbon–carbon double bond.

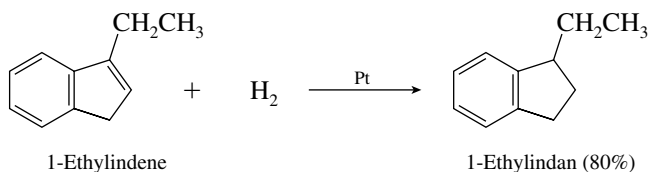


- 11.32** All the specific reactions in this problem have been reported in the chemical literature with results as indicated.

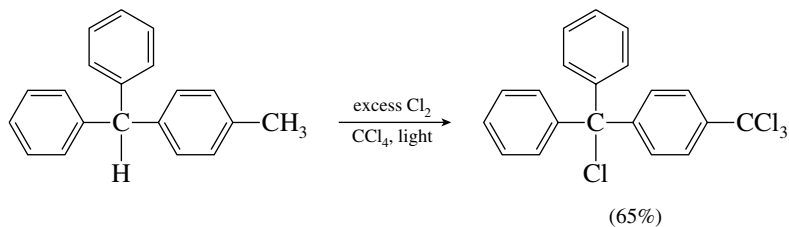
- (a) Hydroboration–oxidation of alkenes leads to syn anti-Markovnikov hydration of the double bond.



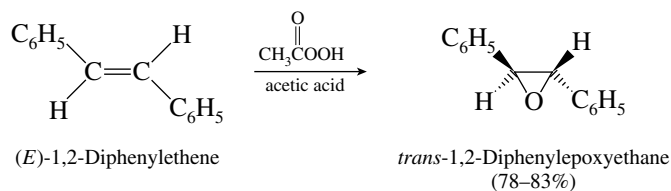
- (b) The compound contains a substituted benzene ring and an alkene-like double bond. When hydrogenation of this compound was carried out, the alkene-like double bond was hydrogenated cleanly.



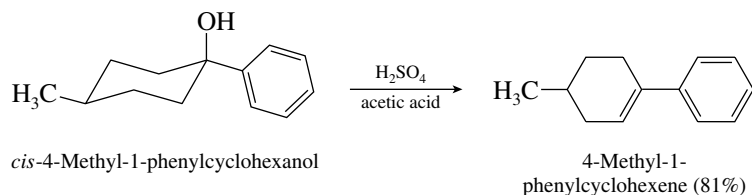
- (c) Free-radical chlorination will lead to substitution of benzylic hydrogens. The starting material contains four benzylic hydrogens, all of which may eventually be replaced.



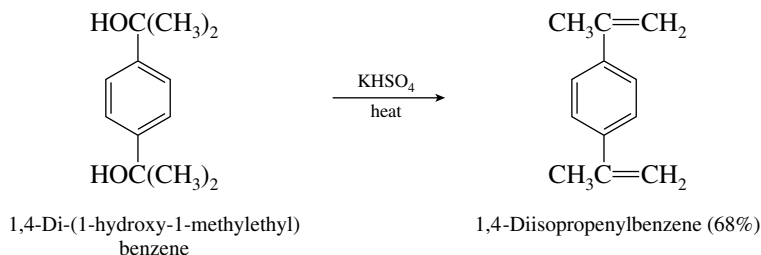
- (d) Epoxidation of alkenes is stereospecific.



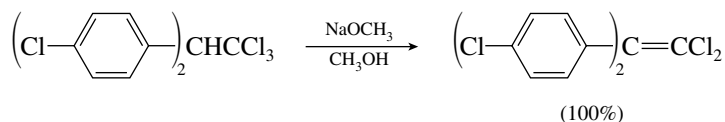
- (e) The reaction is one of acid-catalyzed alcohol dehydration.



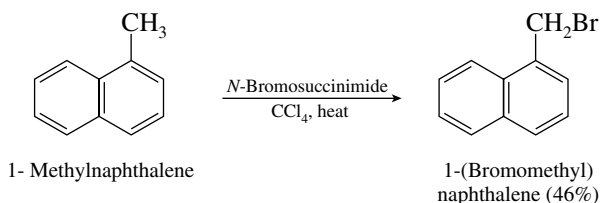
- (f) This reaction illustrates identical reactivity at two equivalent sites in a molecule. Both alcohol functions are tertiary and benzylic and undergo acid-catalyzed dehydration readily.



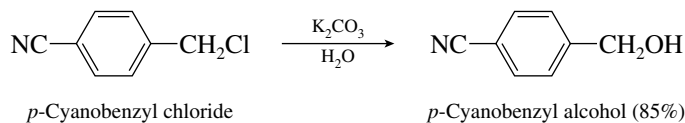
- (g) The compound shown is DDT (standing for the nonsystematic name **dichlorodiphenyl-trichloroethane**). It undergoes β -elimination to form an alkene.



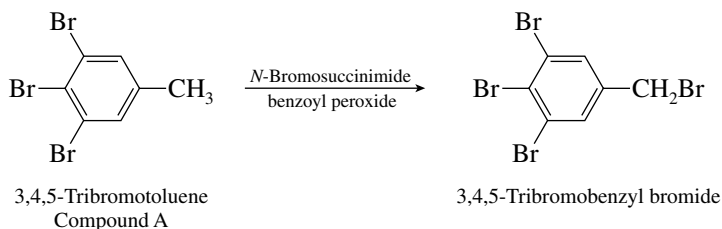
- (h) Alkyl side chains on naphthalene undergo reactions analogous to those of alkyl groups on benzene.



- (i) Potassium carbonate is a weak base. Hydrolysis of the primary benzylic halide converts it to an alcohol.

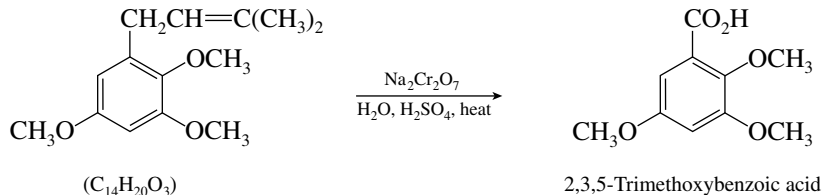


- 11.33** Only benzylic (or allylic) hydrogens are replaced by *N*-bromosuccinimide. Among the four bromines in 3,4,5-tribromobenzyl bromide, three are substituents on the ring and are not capable of being introduced by benzylic bromination. The starting material must therefore have these three bromines already in place.

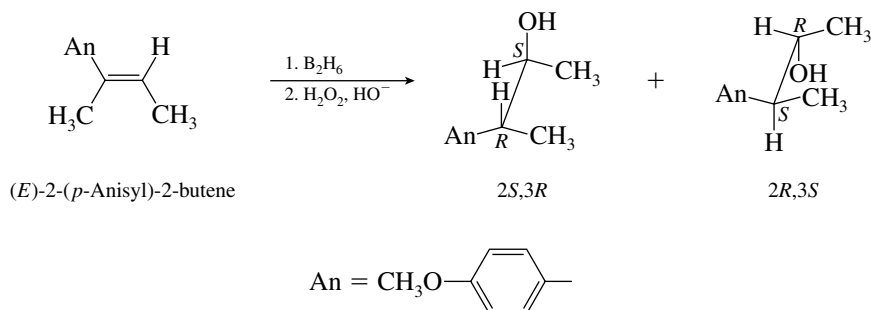


- 11.34** 2,3,5-Trimethoxybenzoic acid has the structure shown. The three methoxy groups occupy the same positions in this oxidation product that they did in the unknown compound. The carboxylic acid

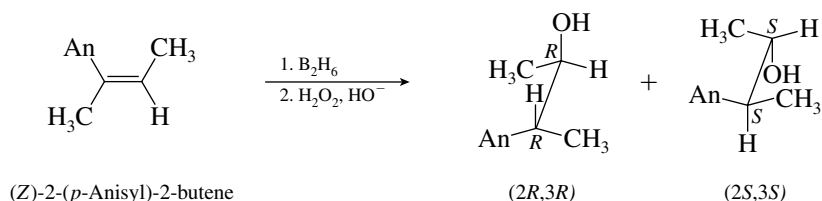
function must have arisen by oxidation of the $-\text{CH}_2\text{CH}=\text{C}(\text{CH}_3)_2$ side chain. Therefore



- 11.35** Hydroboration–oxidation leads to stereospecific syn addition of H and OH across a carbon–carbon double bond. The regiochemistry of addition is opposite to that predicted by Markovnikov’s rule. Hydroboration–oxidation of the *E* alkene gives alcohol A.

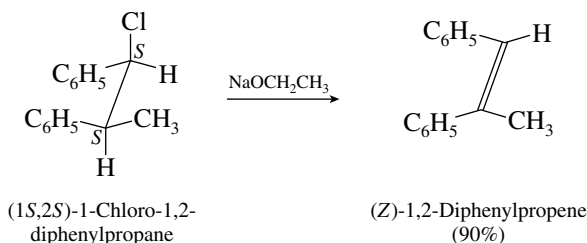


Alcohol A is a racemic mixture of the *2S,3R* and *2R,3S* enantiomers of 3-(*p*-anisyl)-2-butanol. Hydroboration–oxidation of the *Z* alkene gives alcohol B.



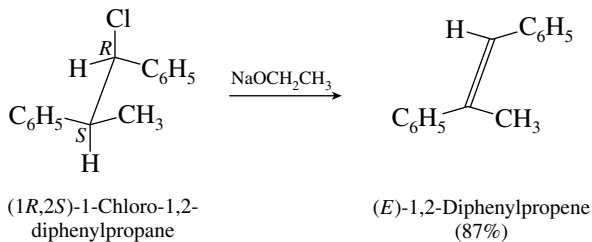
Alcohol B is a racemic mixture of the *2R,3R* and *2S,3S* enantiomers of 3-(*p*-anisyl)-2-butanol. Alcohols A and B are stereoisomers that are not enantiomers; they are diastereomers.

- 11.36** Dehydrohalogenation of alkyl halides is stereospecific, requiring an anti arrangement between the hydrogen being lost and the leaving group in the transition state. (*Z*)-1,2-Diphenylpropene must therefore be formed from the diastereomer shown.

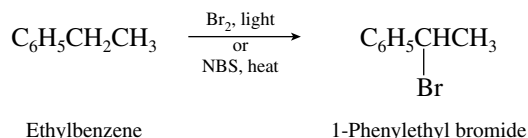


The mirror-image chloride, *1R,2R*, will also give the *Z* alkene. In fact, the reaction was carried out on a racemic mixture of the *1R,2R* and *1S,2S* stereoisomers.

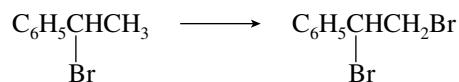
The *E* isomer is formed from either the 1*R*,2*S* or the 1*S*,2*R* chloride (or from a racemic mixture of the two).



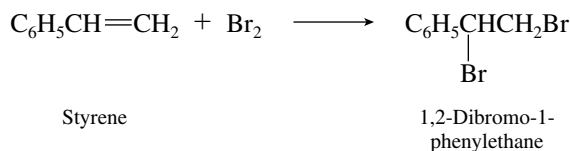
- 11.37 (a) The conversion of ethylbenzene to 1-phenylethyl bromide is a benzylic bromination. It can be achieved by using either bromine or *N*-bromosuccinimide (NBS).



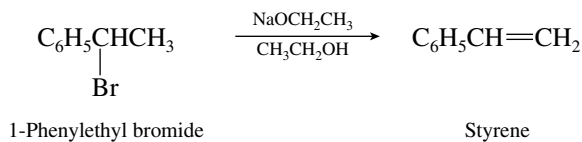
- (b) The conversion of 1-phenylethyl bromide to 1,2-dibromo-1-phenylethane



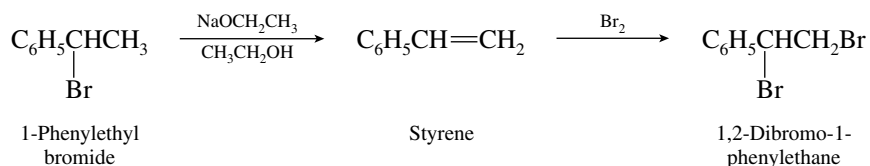
cannot be achieved cleanly in a single step. We must reason backward from the target molecule, that is, determine how to make 1,2-dibromo-1-phenylethane in one step from any starting material. Vicinal dibromides are customarily prepared by addition of bromine to alkenes. This suggests that 1,2-dibromo-1-phenylethane can be prepared by the reaction



The necessary alkene, styrene, is available by dehydrohalogenation of the given starting material, 1-phenylethyl bromide.

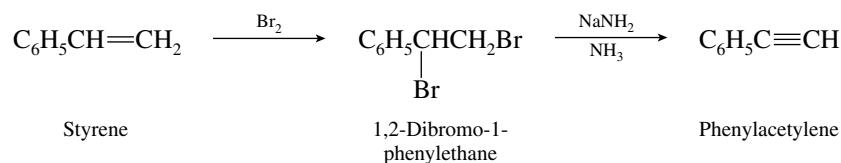


Thus, by reasoning backward from the target molecule, the synthetic scheme becomes apparent.

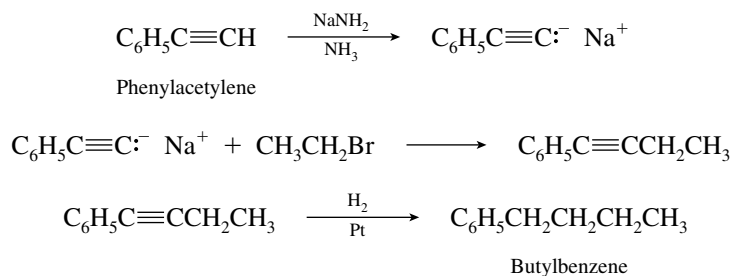


- (c) The conversion of styrene to phenylacetylene cannot be carried out in a single step. As was pointed out in Chapter 9, however, a standard sequence for converting terminal alkenes

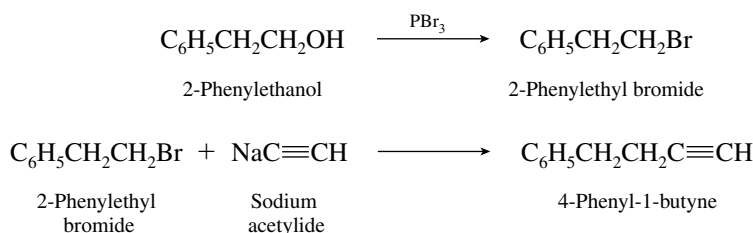
to alkynes consists of bromine addition followed by a double dehydrohalogenation in strong base.



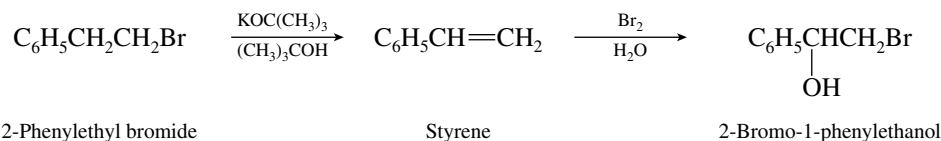
- (d) The conversion of phenylacetylene to butylbenzene requires both a carbon-carbon bond formation step and a hydrogenation step. The acetylene function is essential for carbon-carbon bond formation by alkylation. The correct sequence is therefore:



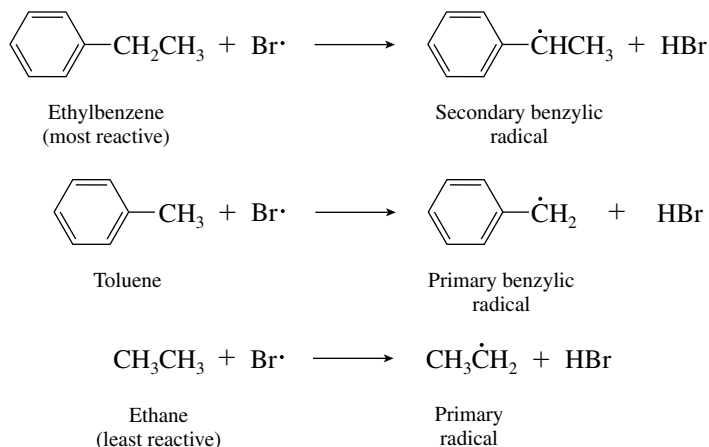
- (e) The transformation corresponds to alkylation of acetylene, and so the alcohol must first be converted to a species with a good leaving group such as its halide derivative.



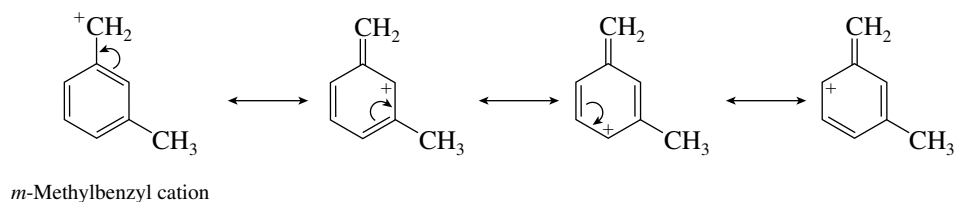
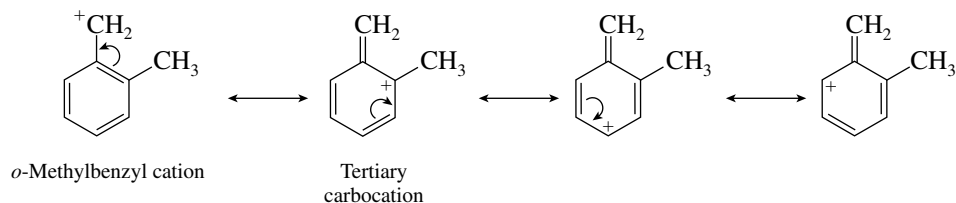
- (f) The target compound is a bromohydrin. Bromohydrins are formed by addition of bromine and water to alkenes.



- 11.38** The stability of free radicals is reflected in their ease of formation. Toluene, which forms a benzyl radical, reacts with bromine 64,000 times faster than does ethane, which forms a primary alkyl radical. Ethylbenzene, which forms a secondary benzylic radical, reacts 1 million times faster than ethane.

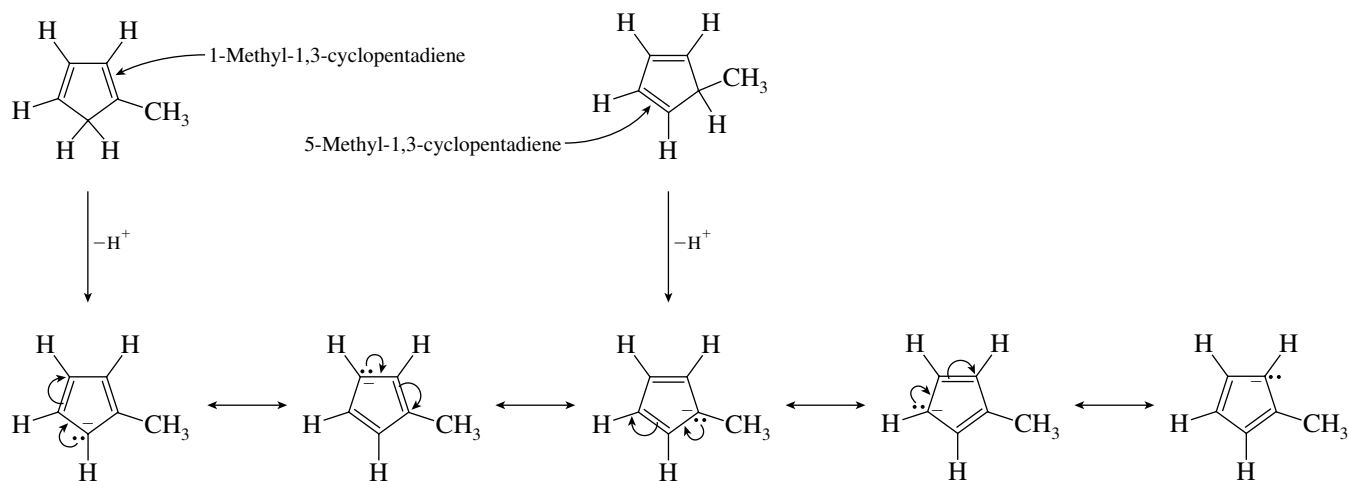


- 11.39** A good way to develop alternative resonance structures for carbocations is to move electron pairs toward sites of positive charge.

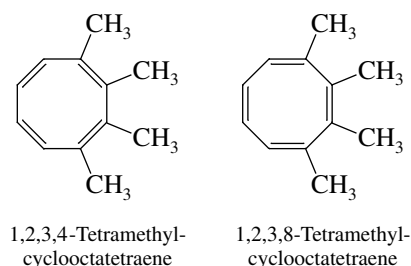


Only one of the Lewis structures shown is a tertiary carbocation. *o*-Methylbenzyl cation has tertiary carbocation character; *m*-methylbenzyl cation does not.

- 11.40** The resonance structures for the cyclopentadienide anions formed by loss of a proton from 1-methyl-1,3-cyclopentadiene and 5-methyl-1,3-cyclopentadiene are equivalent.

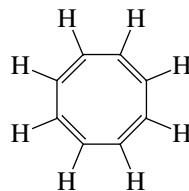


- 11.41** Cyclooctatetraene is not aromatic. 1,2,3,4-Tetramethylcyclooctatetraene and 1,2,3,8-tetramethylcyclooctatetraene are constitutional isomers.



Leo A. Paquette at Ohio State University synthesized each of these compounds independently of the other and showed them to be stable enough to be stored separately without interconversion.

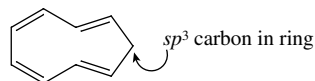
- 11.42 Cyclooctatetraene has eight π electrons and thus does not satisfy the $(4n + 2)$ π electron requirement of the Hückel rule.



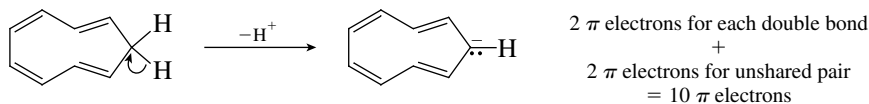
Cyclooctatetraene.
Each double bond contributes
2 π electrons to give a total of 8.

All of the exercises in this problem involve counting the number of π electrons in the various species derived from cyclooctatetraene and determining whether they satisfy the $(4n + 2)$ π electron rule.

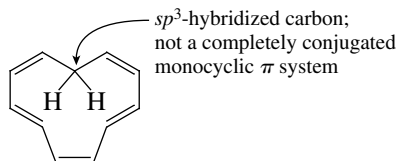
- (a) Adding 1 π electron gives a species (C_8H_8^-) with 9 π electrons. $4n + 2$, where n is a whole number, can never equal 9. This species is therefore **not aromatic**.
- (b) Adding 2 π electrons gives a species ($\text{C}_8\text{H}_8^{2-}$) with 10 π electrons. $4n + 2 = 10$ when $n = 2$. The species $\text{C}_8\text{H}_8^{2-}$ **is aromatic**.
- (c) Removing 1 π electron gives a species (C_8H_8^+) with 7 π electrons. $4n + 2$ cannot equal 7. The species C_8H_8^+ **is not aromatic**.
- (d) Removing 2 π electrons gives a species ($\text{C}_8\text{H}_8^{2+}$) with 6 π electrons. $4n + 2 = 6$ when $n = 1$. The species $\text{C}_8\text{H}_8^{2+}$ **is aromatic**. (It has the same number of π electrons as benzene.)
- 11.43 (a, b) Cyclononatetraene does not have a continuous conjugated system of π electrons. Conjugation is incomplete because it is interrupted by a CH_2 group. Thus (a) adding one more π electron or (b) two more π electrons will **not** give an aromatic system.



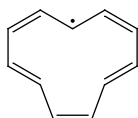
- (c) Removing a proton from the CH_2 group permits complete conjugation. The species produced has 10 π electrons and is aromatic, since $4n + 2 = 10$ when $n = 2$.



- (d) Removing a proton from one of the sp^2 -hybridized carbons of the ring does not produce complete conjugation; the CH_2 group remains present to interrupt cyclic conjugation. The anion formed is **not** aromatic.
- 11.44 (a) Cycloundecapentaene is **not aromatic**. Its π system is not conjugated; it is interrupted by an sp^3 -hybridized carbon.

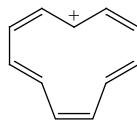


- (b) Cycloundecapentaenyl radical is **not aromatic**. Its π system is completely conjugated and monocyclic but contains 11 π electrons—a number not equal to $(4n + 2)$ where n is an integer.



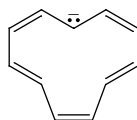
There are 11 electrons in the conjugated π system.
The five double bonds contribute 10 π electrons;
the odd electron of the radical is the eleventh.

- (c) Cycloundecapentaenyl cation is **aromatic**. It includes a completely conjugated π system which contains 10 π electrons (10 equals $4n + 2$ where $n = 2$).



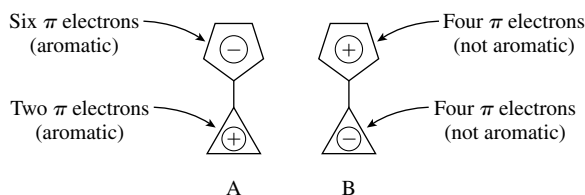
Empty p orbital is conjugated with 10-electron π system.

- (d) Cycloundecapentadienide anion is **not aromatic**. It contains 12 π electrons and thus does not satisfy the $(4n + 2)$ rule.

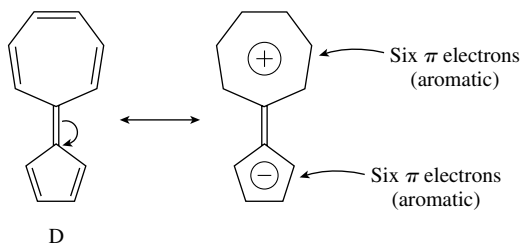


There are 12 π electrons. The five double bonds contribute 10; the anionic carbon contributes 2.

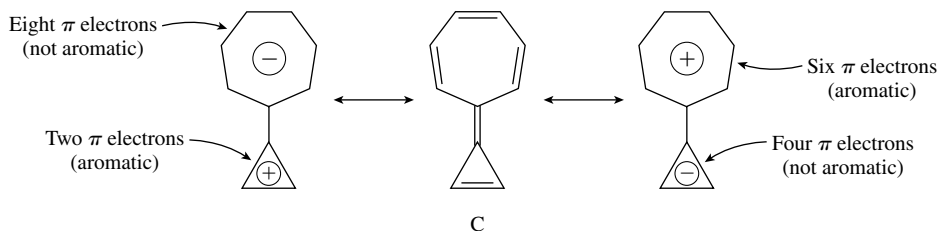
- 11.45 (a) The more stable dipolar resonance structure is A because it has an aromatic cyclopentadienide anion bonded to an aromatic cyclopropenyl cation. In structure B neither ring is aromatic.



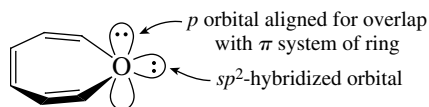
- (b) Structure D can be stabilized by resonance involving the dipolar form.



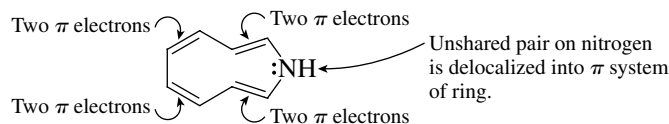
Comparable stabilization is not possible in structure C because neither a cyclopropenyl system nor a cycloheptatrienyl system is aromatic in its anionic form. Both are aromatic as cations.



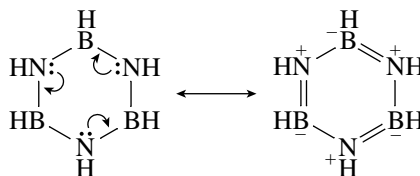
- 11.46 (a) This molecule, called **oxepin**, is **not aromatic**. The three double bonds each contribute 2 π electrons, and an oxygen atom contributes 2 π electrons to the conjugated system, giving a total of 8 π electrons. Only one of the two unshared pairs on oxygen can contribute to the π system; the other unshared pair is in an sp^2 -hybridized orbital and cannot interact with it.



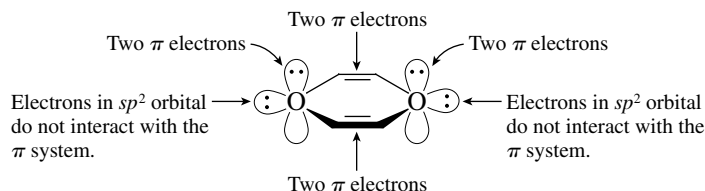
- (b) This compound, called **azonine**, has 10 electrons in a completely conjugated planar monocyclic π system and therefore satisfies Hückel's rule for $(4n + 2)$ π electrons where $n = 2$. There are 8 π electrons from the conjugated tetraene and 2 electrons contributed by the nitrogen unshared pair.



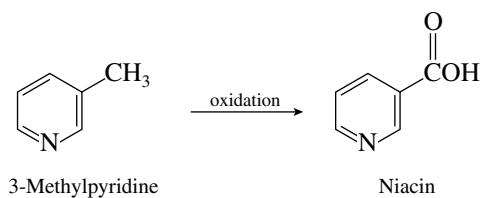
- (c) Borazole, sometimes called **inorganic benzene**, is **aromatic**. Six π electrons are contributed by the unshared pairs of the three nitrogen atoms. Each boron contributes a p orbital to maintain the conjugated system but no electrons.



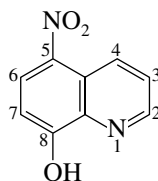
- (d) This compound has 8 π electrons and is **not aromatic**.



- 11.47** The structure and numbering system for pyridine are given in Section 11.21, where we are also told that pyridine is aromatic. Oxidation of 3-methylpyridine is analogous to oxidation of toluene. The methyl side chain is oxidized to a carboxylic acid.



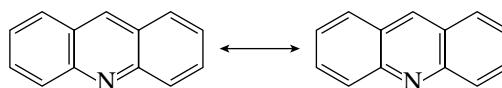
- 11.48** The structure and numbering system for quinoline are given in Section 11.21. **Nitroxoline** has the structural formula:



5-Nitro-8-hydroxyquinoline

- 11.49** We are told that the ring system of **acridine** ($C_{13}H_9N$) is analogous to that of anthracene (i.e., tricyclic and linearly fused). Furthermore, the two most stable resonance forms are equivalent to each other.

The nitrogen atom must therefore be in the central ring, and the structure of acridine is



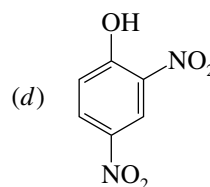
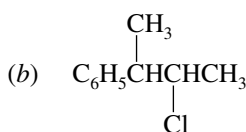
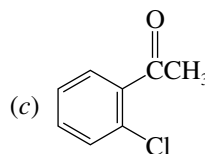
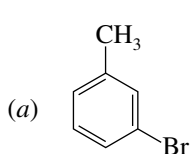
The two resonance forms would not be equivalent if the nitrogen were present in one of the terminal rings. Can you see why?

- 11.50 Solutions to molecular modeling exercises are not provided in this *Study Guide and Solutions Manual*. You should use *Learning By Modeling* for these exercises.

SELF-TEST

PART A

A-1. Give an acceptable IUPAC name for each of the following:



A-2. Draw the structure of each of the following:

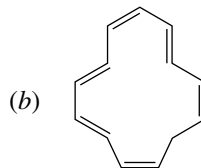
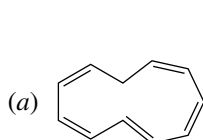
(a) 3,5-Dichlorobenzoic acid

(c) 2,4-Dimethylaniline

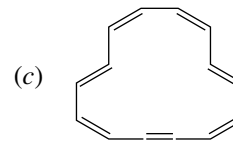
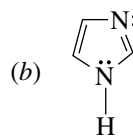
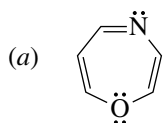
(b) *p*-Nitroanisole

(d) *m*-Bromobenzyl chloride

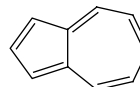
A-3. Write a positive (+) or negative (−) charge at the appropriate position so that each of the following structures contains the proper number of π electrons to permit it to be considered an aromatic ion. For purposes of this problem ignore strain effects that might destabilize the molecule.



A-4. For each of the following, determine how many π electrons are counted toward satisfying Hückel's rule. Assuming the molecule can adopt a planar conformation, is it aromatic?

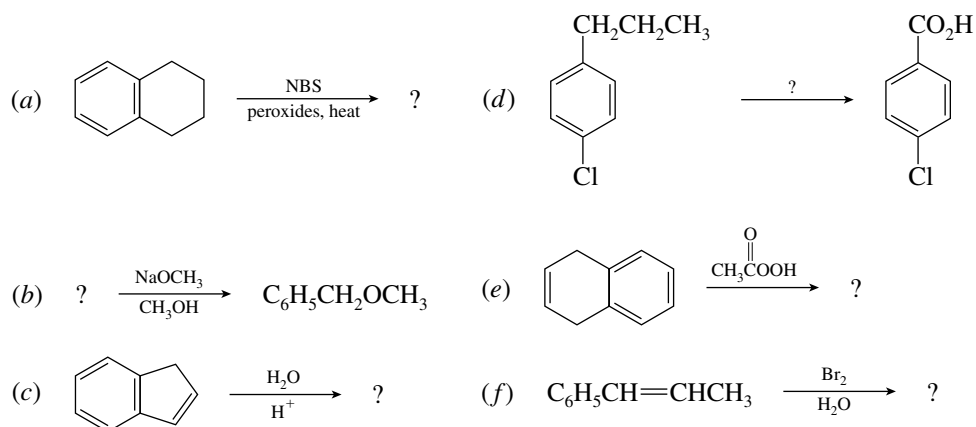


A-5. Azulene, shown in the following structure, is highly polar. Draw a dipolar resonance structure to explain this fact.



Azulene

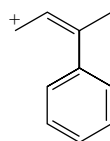
A-6. Give the reactant, reagent, or product omitted from each of the following:



A-7. Provide two methods for the synthesis of 1-bromo-1-phenylpropane from an aromatic hydrocarbon.

A-8. Write the structures of the resonance forms that contribute to the stabilization of the intermediate in the reaction of styrene ($C_6H_5CH=CH_2$) with hydrogen bromide in the absence of peroxides.

A-9. Write one or more resonance structures that represent the delocalization of the following carbocation.



A-10. An unknown compound, $C_{12}H_{18}$ reacts with sodium dichromate ($Na_2Cr_2O_7$) in warm aqueous sulfuric acid to give *p-tert*-butylbenzoic acid. What is the structure of the unknown?

PART B

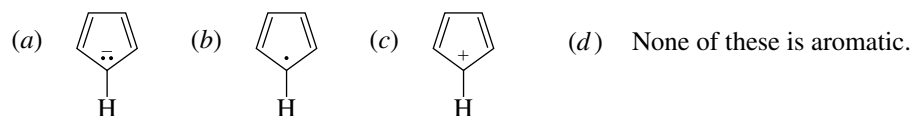
B-1. The number of possible dichloronitrobenzene isomers is

- (a) 3 (c) 6
(b) 4 (d) 8

B-2. Which of the following statements is correct concerning the class of reactions to be expected for benzene and cyclooctatetraene?

- (a) Both substances undergo addition reactions.
(b) Both substances undergo substitution reactions.
(c) Benzene undergoes substitution; cyclooctatetraene undergoes addition.
(d) Benzene undergoes addition; cyclooctatetraene undergoes substitution.

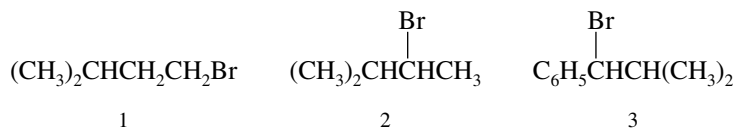
B-3. Which, if any, of the following structures represents an aromatic species?



B-4. Which of the following compounds has a double bond that is conjugated with the π system of the benzene ring?

- (a) *p*-Benzyltoluene (c) 3-Phenylcyclohexene
(b) 2-Phenyl-1-decene (d) 3-Phenyl-1,4-pentadiene

B-5. Rank the following compounds in order of increasing rate of solvolysis (S_N1) in aqueous acetone (slowest \rightarrow fastest):

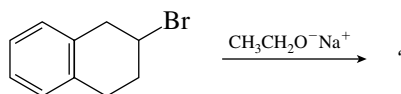


- (a) $1 < 2 < 3$ (b) $2 < 1 < 3$ (c) $3 < 2 < 1$ (d) $1 < 3 < 2$

B-6. When comparing the hydrogenation of benzene with that of a hypothetical 1,3,5-cyclohexatriene, benzene _____ than the cyclohexatriene.

- (a) Absorbs 152 kJ/mol (36 kcal/mol) more heat
 (b) Absorbs 152 kJ/mol (36 kcal/mol) less heat
 (c) Gives off 152 kJ/mol (36 kcal/mol) more heat
 (d) Gives off 152 kJ/mol (36 kcal/mol) less heat

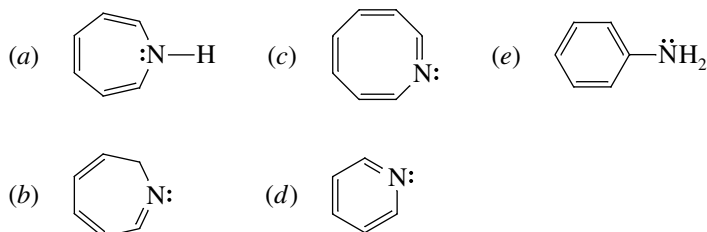
B-7. The reaction



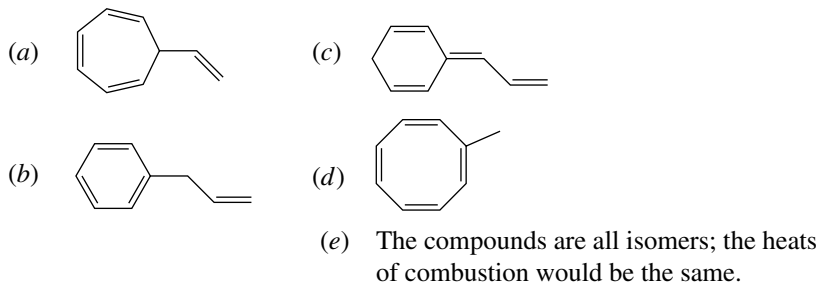
gives as the major elimination product

- (a) (b) (c) Equal amounts of (a) and (b)
 (d) Neither (a) nor (b)

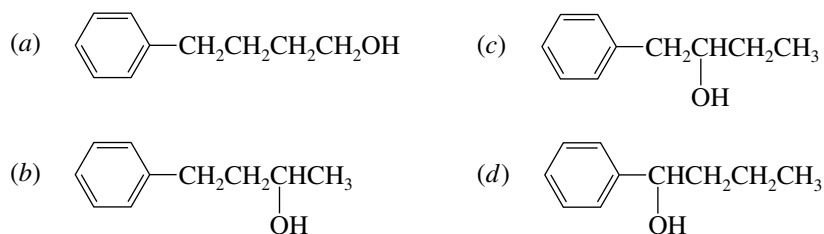
B-8. Which one of the following is best classified as a **heterocyclic aromatic** compound?



B-9. Which of the following has the smallest heat of combustion?



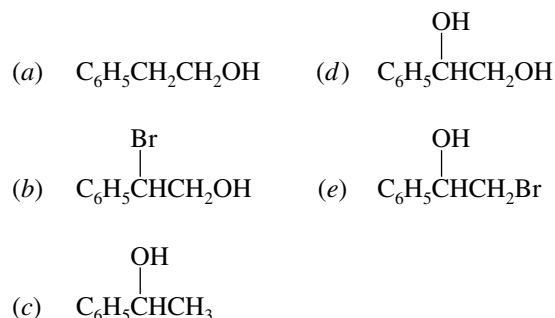
B-10. Which one of the following alcohols undergoes dehydration at the *fastest* rate on being heated with sulfuric acid? (The potential for rearrangement does not affect the rate.)



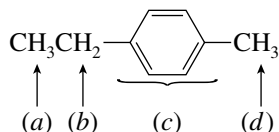
B-11. Ethylbenzene is treated with the reagents listed, in the order shown.

1. NBS, peroxides, heat
2. $\text{CH}_3\text{CH}_2\text{O}^-$
3. B_2H_6
4. $\text{H}_2\text{O}_2, \text{HO}^-$

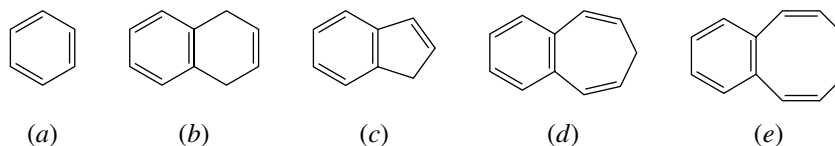
The structure of the final product is:



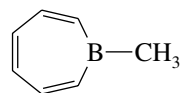
B-12. Which of the following hydrogens is most easily abstracted (removed) on reaction with bromine atoms, $\text{Br}\cdot$?



B-13. All the hydrocarbons shown are very weak acids. One, however, is far more acidic than the others. Which one is the strongest acid?

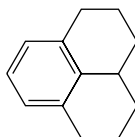


B-14. The compound shown is planar, and all the carbon–carbon bond lengths are the same. What (if anything) can you deduce about the bonding of boron from these observations?



- (a) The boron is sp^2 -hybridized, and the p orbital contains an unshared pair of electrons.
- (b) The boron is sp^3 -hybridized, and a hybrid orbital contains an unshared pair of electrons.
- (c) The boron is sp^3 -hybridized, and a hybrid orbital is vacant.
- (d) The boron is sp^2 -hybridized, and the p orbital is vacant.
- (e) Nothing about the bonding of boron can be deduced from these observations.

B-15. How many benzylic hydrogens are present in the hydrocarbon shown?



- (a) 3 (b) 4 (c) 5 (d) 6 (e) 8