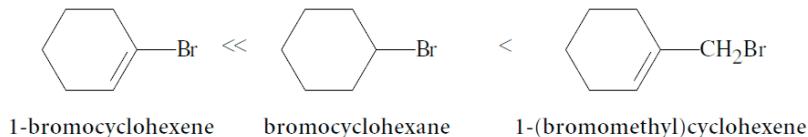


Chapter 18

The Chemistry of Aryl Halides, Vinylic Halides, and Phenols. Transition-Metal Catalysis

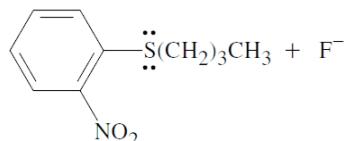
Solutions to In-Text Problems

- 18.1 (b) 1-Bromocyclohexene, a vinylic halide, does not react by the S_N2 mechanism; 1-(bromomethyl)cyclohexene, an allylic halide, reacts most rapidly. (See text Sec. 17.4, text p. 802.)



- 18.3 (b) The reactivity order is $B \ll C < A$. The reaction of compound B is slowest because vinylic halides are virtually inert in S_N1 reactions; and the reaction of compound A is fastest because its ionization gives a resonance-stabilized allylic carbocation.

- 18.4 (b) The product results from nucleophilic aromatic substitution by the thiolate group:



- 18.5 (b) The second compound, *p*-fluoronitrobenzene, reacts most rapidly because only in the reaction of this compound is the intermediate Meisenheimer complex stabilized by resonance interaction of an unshared electron pair with the nitro substituent.

- 18.7 (b) The PPh_3 ligands are L-type ligands; hence, there are no X-type ligands, and, because the charge on Pd is 0, the oxidation state of Pd is 0.

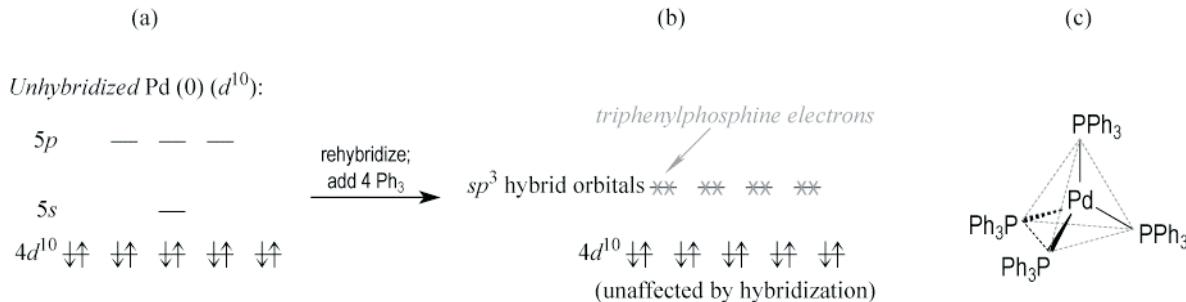


You might be wondering about the prefix *tetrakis* in the name of this complex. The prefixes *bis*, *tris*, and *tetrakis* are used as numerical prefixes instead of *di*, *tri*, and *tetra* when the group that is enumerated itself contains multiple substituents. Thus, the ligand triphenylphosphine has three phenyl groups on the phosphorus (thus the prefix *tri* in the name of this ligand). There are four triphenylphosphine ligands—thus the prefix *tetrakis*.

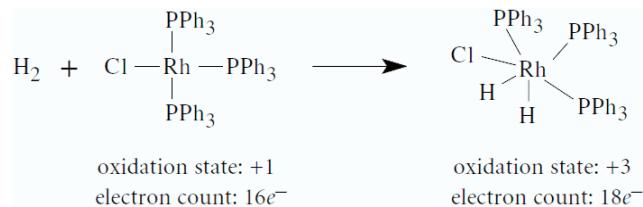
- 18.9 (b) Pd has ten valence electrons in the neutral atom. There are no charges and no X-type ligands in the complex; hence, this is a d^{10} complex. Using Eq. 18.24, text p. 836, with an oxidation state of 0, we get the same answer.

- 18.11 Neutral iron (Fe) has 8 electrons. Because CO is an L-type ligand, it is counted twice in the electron count. We simply solve for x in $8 + 2x = 18$ and obtain $x = 5$. $\text{Fe}(\text{CO})_5$, or pentacarbonyliron(0), is in fact a stable complex that can be purchased commercially.

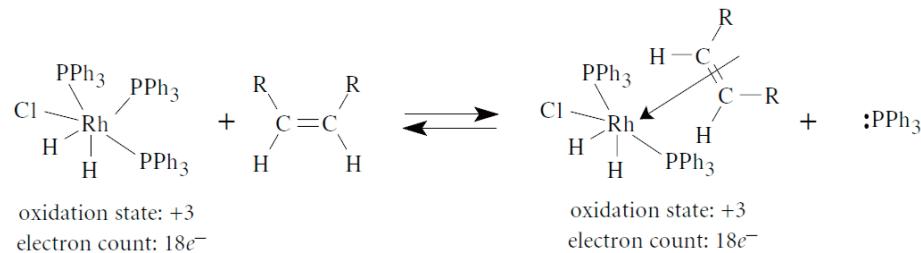
- 18.13 (b) Triphenylphosphine (PPh_3) is an L-type ligand. If we strip the four PPh_3 ligands from the Pd (palladium), a Pd (0) atom remains. From Fig. 18.3 on text p. 832, Pd has 10 valence electrons. This is exactly the number needed to fill all of the $4d$ orbitals with two electrons each. This leaves four valence orbitals—the $5s$ and the $5p$ orbitals—empty. These are hybridized to form more directed orbitals. (This situation is exactly like carbon hybridization in methane, except that we are using orbitals from period 5.) Hybridize one $5s$ and three $5p$ orbitals gives four sp^3 hybrid orbitals, which, as we know from methane, are directed to the corners of a regular tetrahedron. Each of these empty orbitals accepts a pair of electrons from a PPh_3 ligand. Thus, the $\text{Pd}(\text{PPh}_3)_4$ complex is tetrahedral.



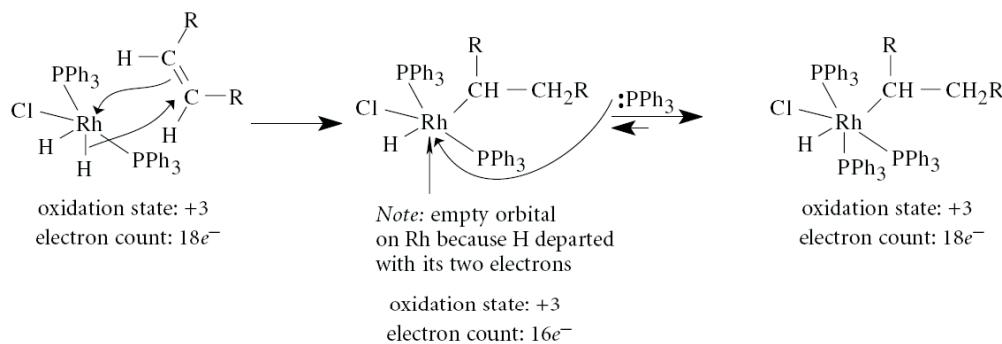
- 18.15 (a) *Oxidative addition of H_2 to the catalyst:*



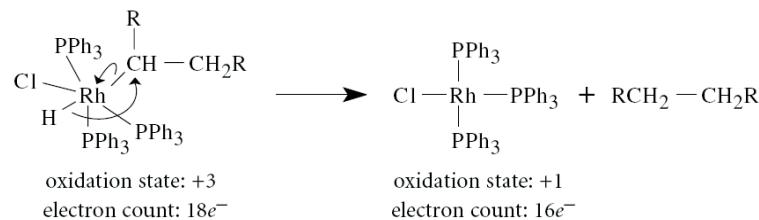
Ligand substitution of one PPh_3 by the alkene:



1,2-Insertion of the alkene into an Rh—H bond and addition of the previously expelled PPh_3 :



Reductive elimination of the product to regenerate the catalyst:



- 18.16 The steps in Eq. 18.42b, text p. 846, of the text are numbered for reference.

Step 1:

Fundamental process: oxidative addition

Oxidation state of Pd starting catalyst (PdL_2): 0

Electron count of Pd in the starting catalyst: $14e^-$. (Note that neutral Pd is a 10-electron atom.)

Oxidation state of Pd in the product: +2

Electron count of Pd in the product: $16e^-$

Step 2: (From here on, the reactant has the same properties as the product of the previous step.)

Fundamental process: ligand substitution

Oxidation state of Pd in the product: +2

Electron count of Pd in the product: $16e^-$

Step 3:

Fundamental process: 1,2-ligand insertion

Oxidation state of Pd in the product: +2

Electron count of Pd in the product: $14e^-$

Step 4:

Fundamental process: β -elimination

Oxidation state of Pd in the product: +2

Electron count of Pd in the product: $16e^-$

Step 5:

Fundamental process: ligand dissociation

Oxidation state of Pd in the product: +2

Electron count of Pd in the product: $14e^-$

Step 6:

Fundamental process: ligand association

Oxidation state of Pd in the product: +2

Electron count of Pd in the product: $16e^-$

(Steps 5 and 6 together result in a ligand substitution.)

Step 7:

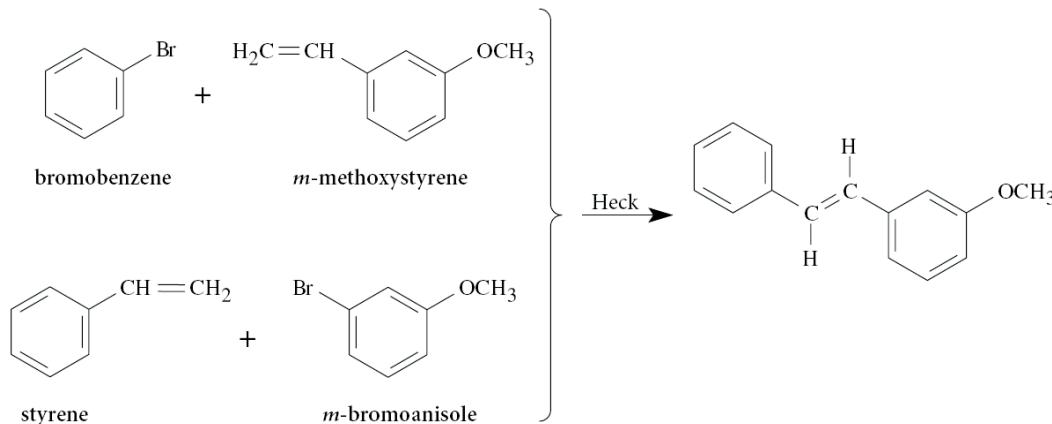
Fundamental process: reductive elimination

Oxidation state of Pd in the product: 0

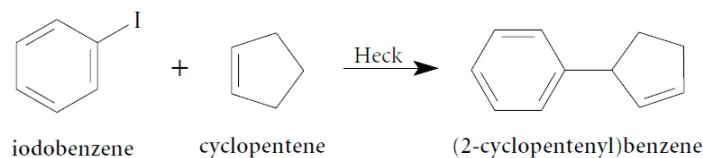
Electron count of Pd in the product: $14e^-$

(The catalyst is regenerated in this step.)

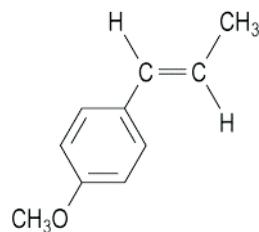
- 18.18 Either aryl substituent could originate from the aryl halide or from the alkene. Remember, if the alkene substituent is aryl (as in these cases), substitution occurs mainly at the less branched carbon.



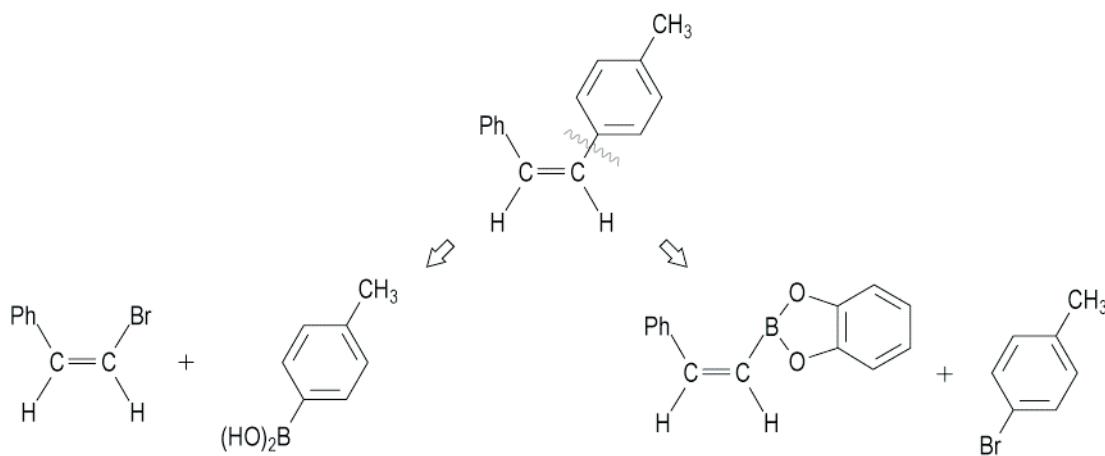
- 18.20 This is essentially like the cyclohexene case given in Eq. 18.43 (text p. 846) and subsequent discussion.



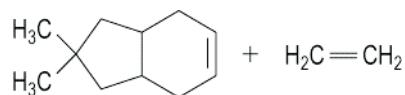
- 18.21 (b) As illustrated in Eq. 18.48, text p. 849, Suzuki coupling occurs with retention of the alkene stereochemistry.



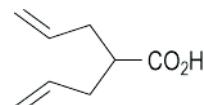
- 18.23 Start by breaking the compound at the bond between the aryl ring and the alkene; then place a bromine atom (Br) on one of the cleaved fragments and a boronic acid [$\text{B}(\text{OH})_2$] or catecholborane (see Eq. 18.50, text p. 849) on the other:



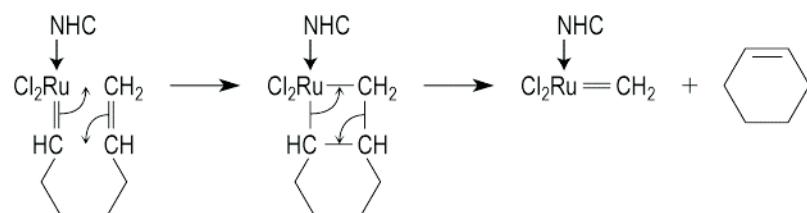
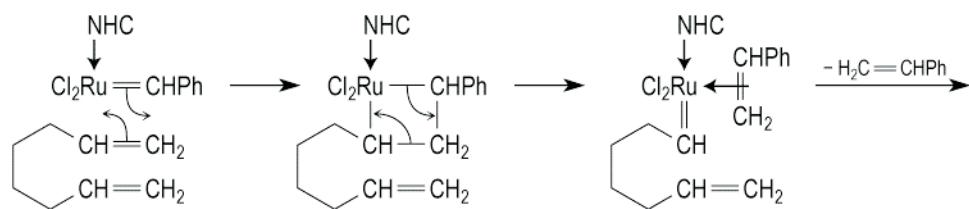
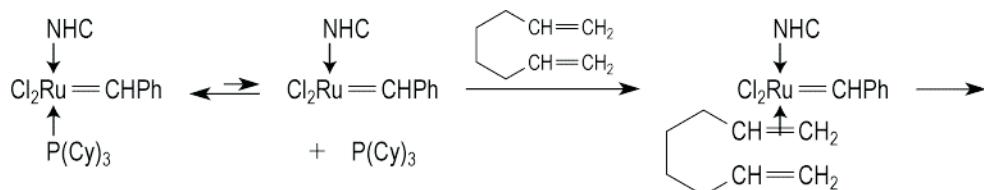
18.26 (b)



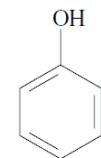
18.27 (b)



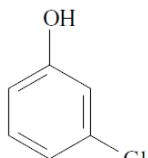
18.28



- 18.30 (b) *Meta*-chlorophenol is more acidic because the conjugate-base anion, *m*-chlorophenoxyde, is stabilized by the electron-withdrawing polar effect of the chloro substituent. The actual pK_a values are

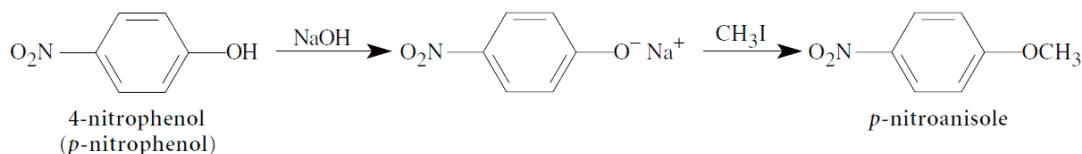


phenol
 $pK_a = 9.95$

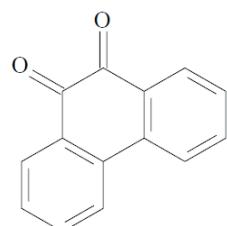


m-chlorophenol
 $pK_a = 9.02$

- 18.31 (a)

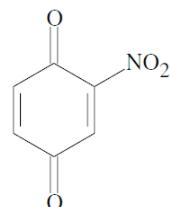


- 18.34 (a)

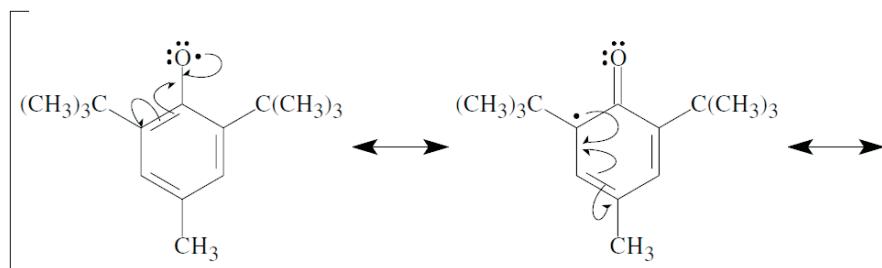


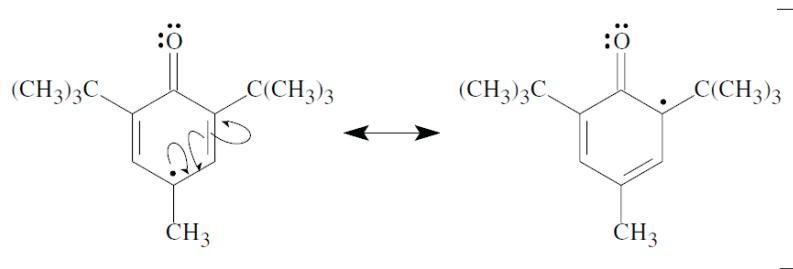
9,10-phenanthraquinone
(an *o*-quinone)

- 18.35 (a) A *para*-quinone is formed as in Eq. 18.69, text p. 862; the nitro group is unaffected.

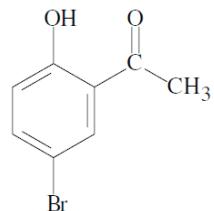


- 18.36 (b) As in part (a), the phenolic hydrogen atom is abstracted because a resonance-stabilized radical is formed.

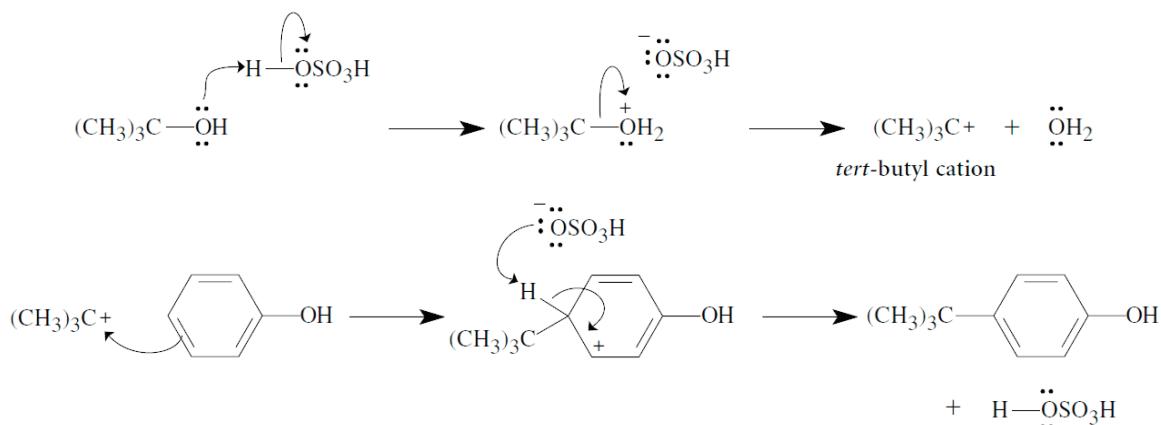




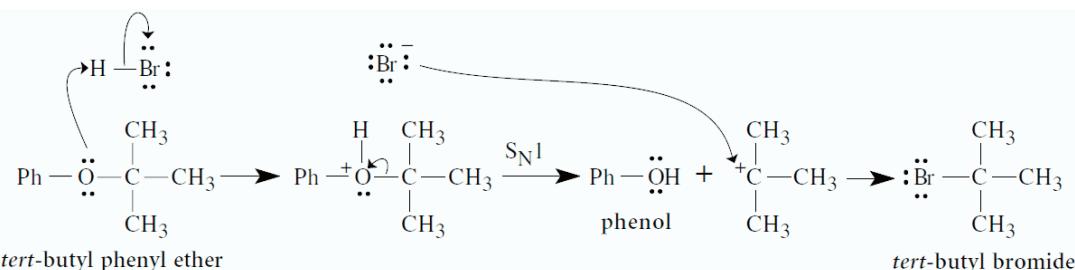
18.38 (c)



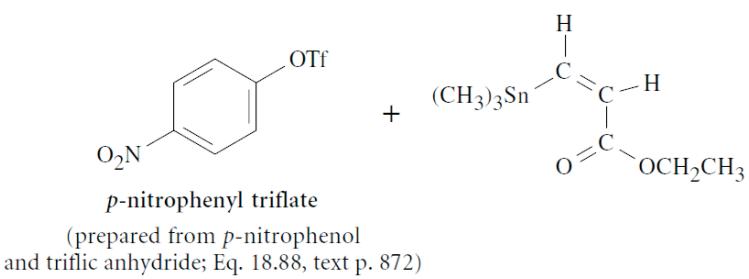
18.39 The electrophile is the *tert*-butyl cation, which is formed by protonation of the alcohol and the Lewis acid–base dissociation of water.



18.40 (b) Diphenyl ether does not cleave with hot, concentrated HBr, because such a cleavage would require either an S_N1 reaction or an S_N2 reaction at a phenyl–oxygen bond; as this section of the text shows, such reactions do not occur. In contrast, *tert*-butyl phenyl ether cleaves by an S_N1 mechanism involving protonation of the oxygen and loss of phenol to form a *tert*-butyl cation, which undergoes a Lewis acid–base association reaction with bromide ion to form *tert*-butyl bromide.

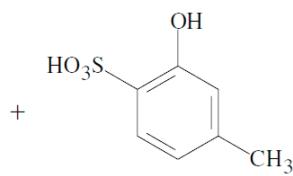
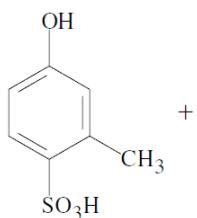


18.42 The triflate derivative of *p*-nitrophenol and the (*Z*)-stereoisomer of the appropriate trimethylstannylyl derivative would be required.

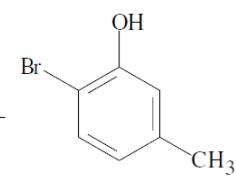
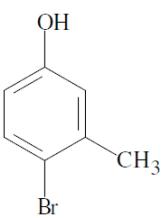


Solutions to Additional Problems

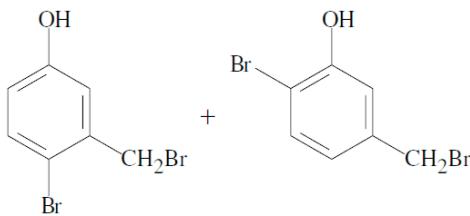
18.45 (a)



(b)

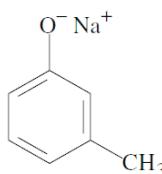


(c) Both benzylic bromination and ring bromination take place; see Eq. 18.75, text p. 867.

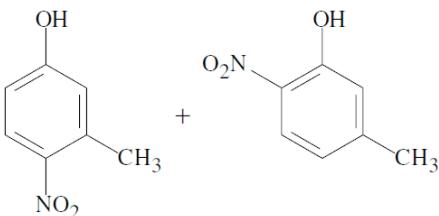


(d)

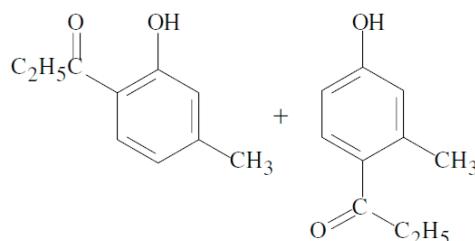
no reaction



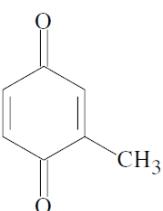
(f)



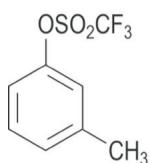
(g)



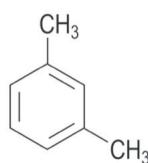
(h)



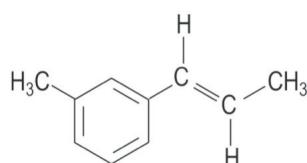
(i)



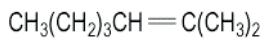
(j)



(k)

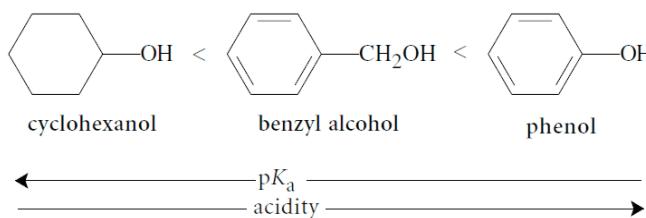


18.46 (b)

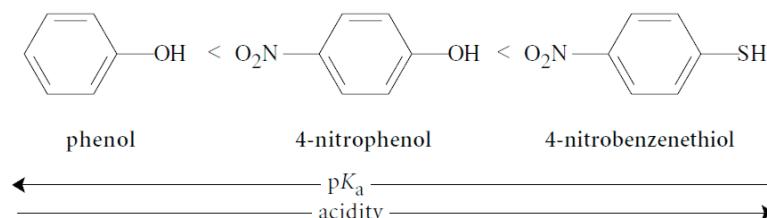
**2-methyl-2-heptene**

18.47 (b)

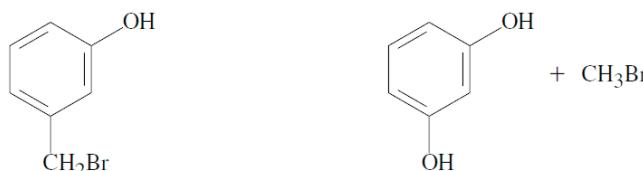
Phenol is most acidic because its conjugate-base anion is stabilized by both the polar and resonance effects of the phenyl group. The conjugate-base anion of benzyl alcohol is stabilized by the polar effect of the phenyl group. The conjugate-base anion of cyclohexanol has none of these stabilizing contributions. The acidity order is



- (d) 4-Nitrophenol is more acidic than phenol (see text p. 859), and benzenethiols are more acidic than phenols (element effect.) The acidity order is

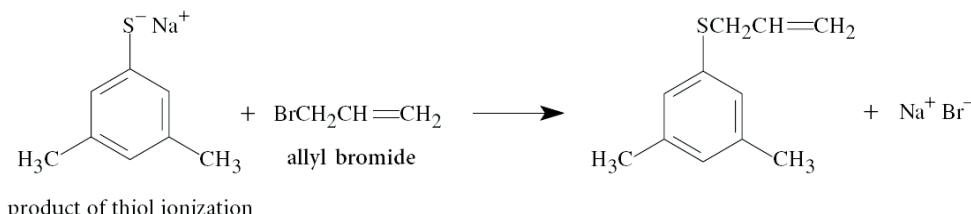


- 18.52 The phenol group is unaffected in both compounds (except for a small amount of protonation of the phenol oxygen); the alcohol and ether groups react.



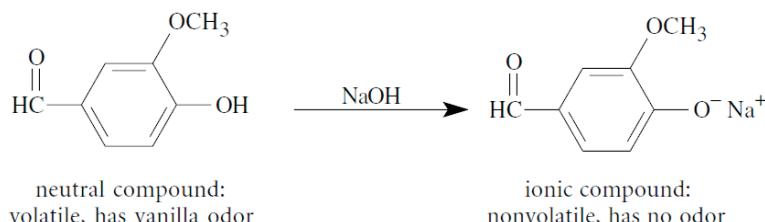
- 18.54 Sodium ethoxide converts the thiol completely into its conjugate-base thiolate ion.

- (a) The thiolate ion is alkylated. (Remember from Sec. 17.4, text p. 802, that allyl bromide is a particularly reactive alkylating agent.)

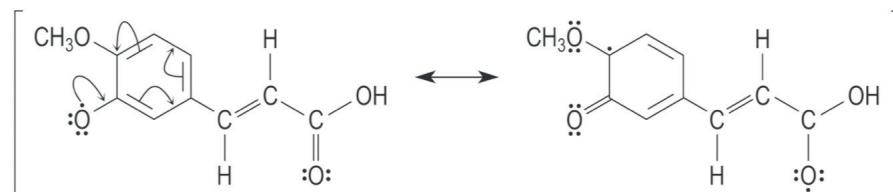
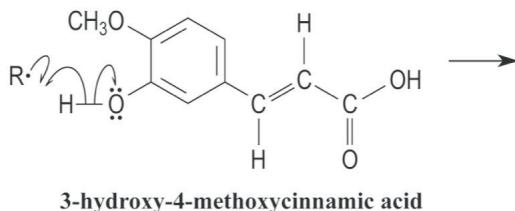


- (b) No further reaction of the thiolate occurs because bromobenzene, an aryl halide, is inert to nucleophilic substitution and elimination reactions. (Sec. 18.1, text p. 823.)

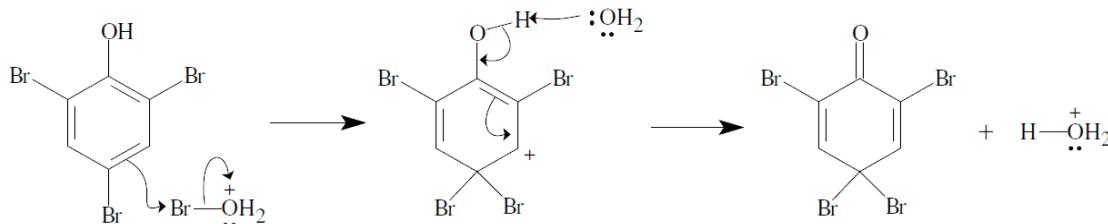
- 18.57 It is the *un-ionized* form of vanillin that has the typical odor. In NaOH solution, the phenol group of vanillin ionizes to its conjugate-base phenoxide ion; because vanillin is no longer present, and because ionic compounds such as the conjugate-base phenoxide are not volatile, the odor disappears. (A compound has to be volatile—that is, it must have a significant vapor pressure—to enter the gas phase and thus reach the nostrils.) Acidification of the solution brings about protonation of the phenoxide and regeneration of vanillin and, hence, the characteristic odor.



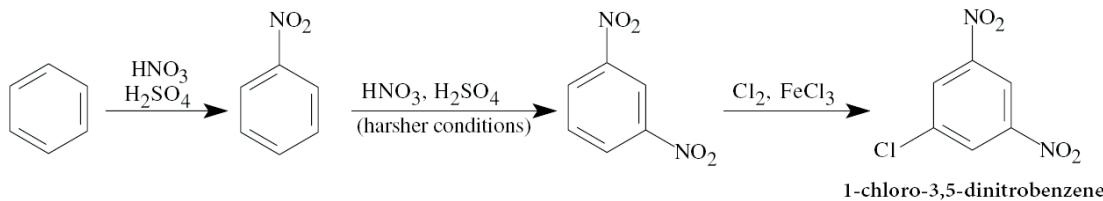
- 18.59 (a) Because the S_N2 reaction requires approach of the nucleophile from the backside of the C—Br bond, and because this would require approach of the nucleophile along the axis of the triple bond, the S_N2 reaction is impossible.
- (b) 1-Haloalkynes cannot undergo an S_N1 reaction. Such a reaction would require that a carbocation be formed at an *sp*-hybridized carbon. Yet carbocations optimally require *sp*² hybridization, which, in turn, requires trigonal planar geometry. An alkyne carbon cannot achieve this geometry because its three bonds are connected to the same atom. Hence, the *sp*² hybridization required for carbocation formation is impossible.
- 18.60 (b) No. The phenolic group is meta to the alkene and carboxylic acid groups and the radical that is formed from proton abstraction cannot delocalize to the alkene and carboxylic acid groups.



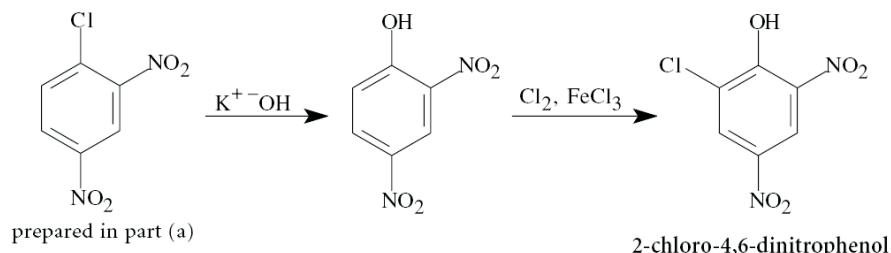
- 18.62 By loss of a proton from the hydroxy group, the carbocation intermediate becomes the neutral compound that precipitates. (Formation of the electrophile is shown in Eq. 18.77, text p. 868.)



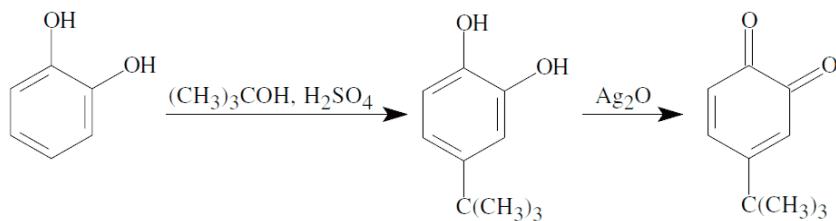
- 18.64 (b)



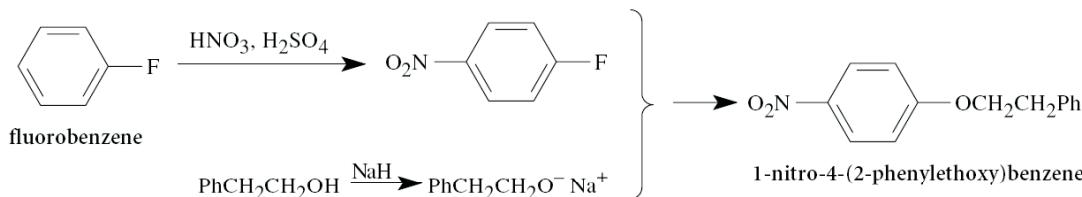
(e)



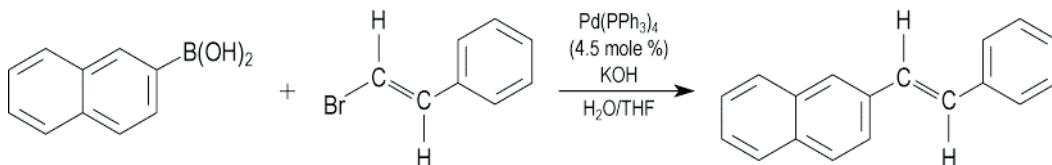
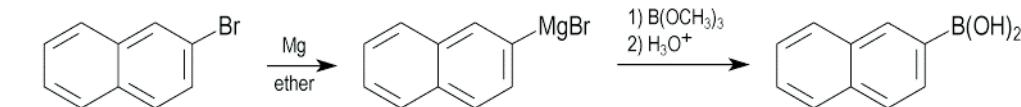
(g)



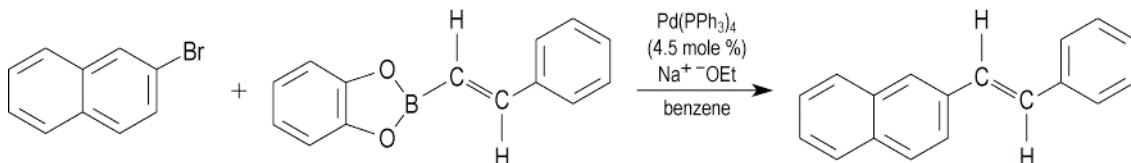
(i)



- (k) First, prepare the Grignard reagent from the aryl bromide, and use it to prepare the corresponding aryl boronic acid. Couple the resulting aryl boronic acid with (*E*)-1-bromo-2-phenylethene in the presence of a Pd(0) catalyst and aqueous base (Suzuki coupling).



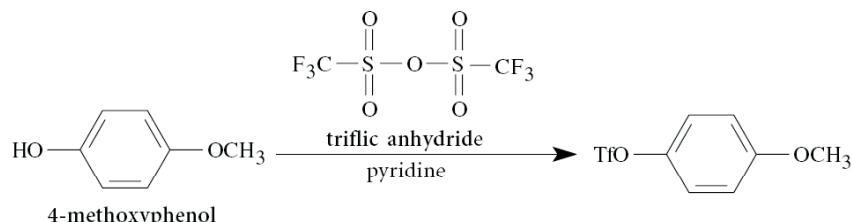
Alternatively, couple the aryl bromide with (*E*)-1-catecholboranyl-2-phenylethene in the presence of a Pd(0) catalyst, sodium ethoxide, and a non-aqueous solvent (Suzuki coupling)—water would hydrolyze the catecholboranyl reagent.



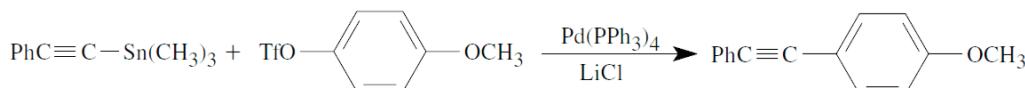
- (m) First, prepare the Grignard reagent from the alkyne, and use it to prepare the corresponding stannane.



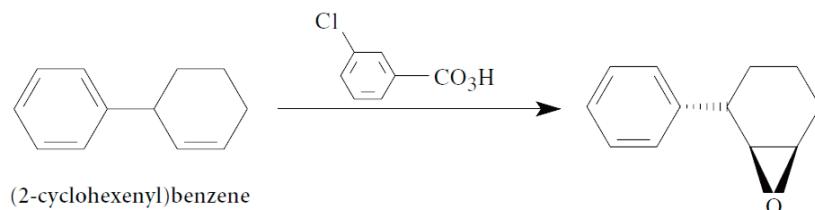
Next, prepare the triflate of the phenol.



Finally, couple the triflate and the stannane in a Stille reaction.

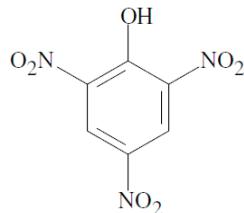


- (o) Start with (2-cyclohexenyl)benzene, which is prepared from iodobenzene and cyclohexene by a Heck reaction as shown in Eq. 18.43, text p. 846.

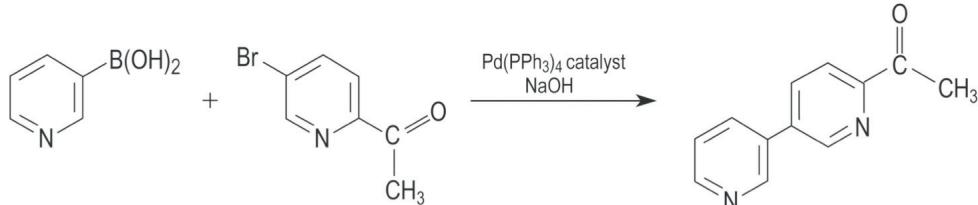


It is reasonable to suppose that epoxidation will occur at the face of the ring opposite to that occupied by the bulky phenyl group. (As noted in the problem, the product is a racemate because the reagents are achiral.)

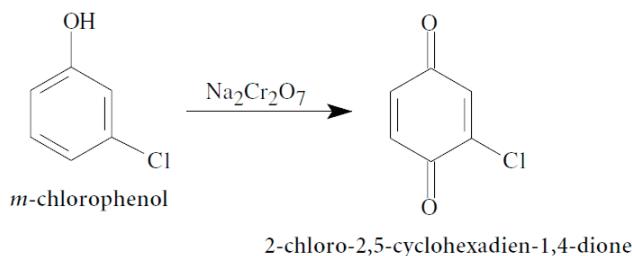
- 18.65 (b) The product is formed by a nucleophilic aromatic substitution reaction in which chloride is displaced by hydroxide ion. The product is ionized by -OH present in the reaction mixture; addition of acid (H_3O^+) forms the neutral phenol.



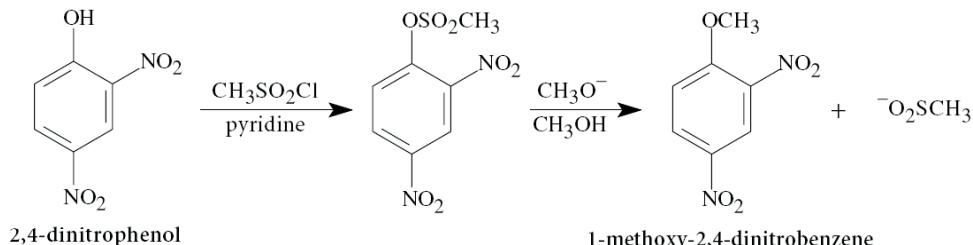
- (d) No reaction occurs under the mild conditions.
 (e) This is a Suzuki coupling reaction in which pyridine derivatives are used instead of benzene derivatives.



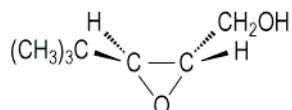
- (k) Oxidation occurs to give the quinone.



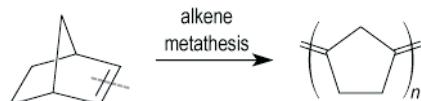
- (I) The methanesulfonate derivative of 2,4-dinitrophenol undergoes a nucleophilic substitution reaction in which the methanesulfonate group is displaced by methoxide.



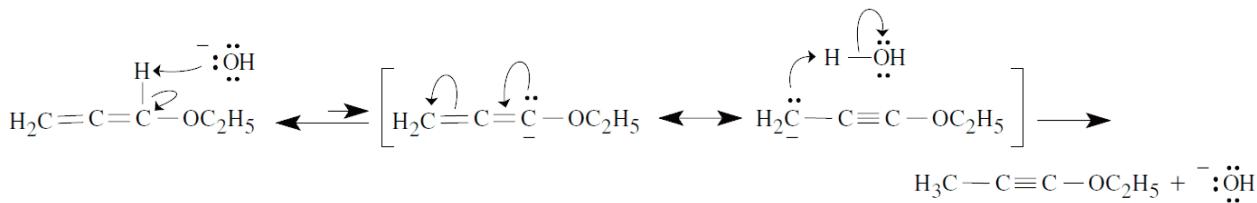
- (o) Alkene metathesis produces the more stable trans alkene; asymmetric epoxidation (see Sec. 11.10, text p. 522) produces the epoxide shown (see Eq. 11.74a, text p. 523, for an equivalent reaction).



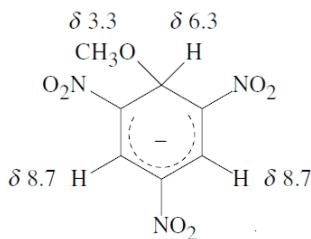
18.66 (b)



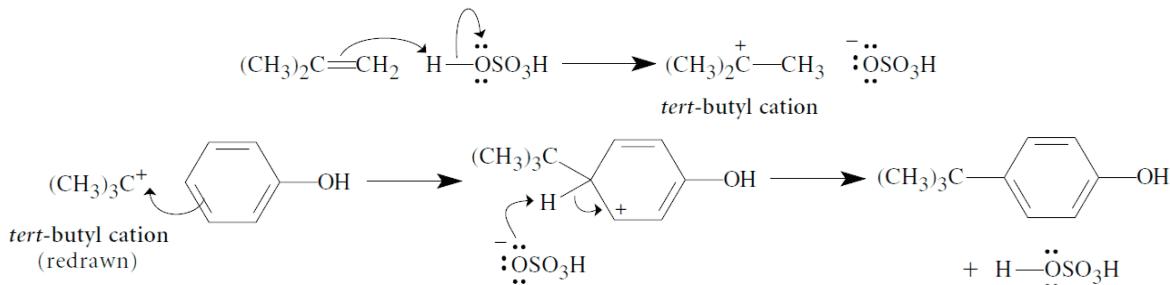
- 18.68 The basic principle needed to understand the results is that elimination is most rapid when it occurs with anti stereochemistry. In the first reaction, *anti*-elimination leads to the observed product. In the second reaction, formation of the alkyne requires a slower *syn*-elimination; hence, another process can compete, namely, elimination of a methyl hydrogen and the bromine to form the allene. In the first reaction, elimination of the methyl hydrogen to form the allene is a slower process because allenes are not so stable as alkynes. The transition state for elimination is destabilized by its allene-like character. (The methyl hydrogens are approximately as acidic as the vinylic hydrogens because they are allylic.) It is also possible that the allene is the only product formed in the second reaction and that the alkyne is formed by a base-catalyzed isomerization of the allene:



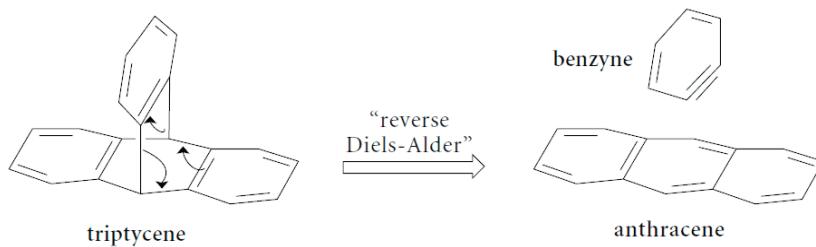
- 18.70 The spectrum is consistent with the formation of an anionic intermediate—a stable Meisenheimer complex. (The dotted lines symbolize resonance delocalization of the negative charge.) If you draw out the resonance structures for this ion, you will see that charge is delocalized to the carbons bearing the nitro groups, and it can also be delocalized into the nitro groups. However, charge is *not* delocalized to the other carbons. Hence, the protons on these carbons do not show the smaller chemical shift that would be expected if there were high electron density on these carbons.



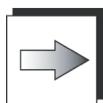
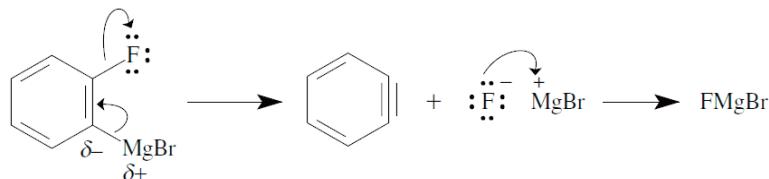
- 18.73 (b) Protonation of 2-methylpropene gives the *tert*-butyl cation, which serves as the electrophile in an electrophilic aromatic substitution reaction.



- 18.77 Deduce the structure of the “very interesting intermediate” by mentally imagining a “reverse Diels–Alder” reaction of triptycene that yields anthracene and the intermediate, which is benzyne:

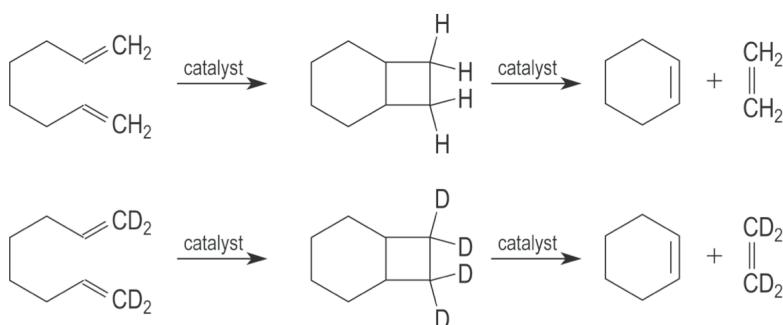


The Grignard reagent has carbanion character, and this “carbanion” is a strong base. Elimination of the weaker base fluoride gives benzyne:

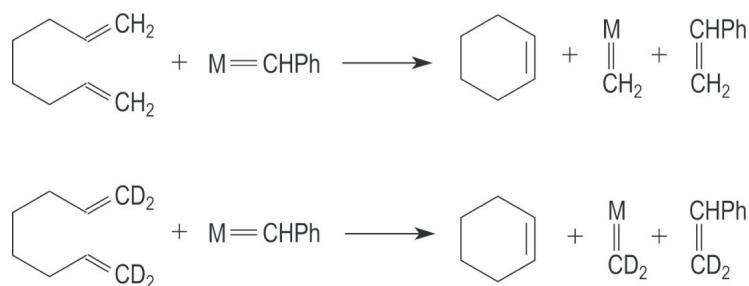


Because alkynes require linear geometry, it is difficult to incorporate them into six-membered rings. Therefore, benzyne is highly *strained* and, although it is a neutral molecule, it is very unstable. (Benzyne is about 205 kJ mol^{-1} (49 kcal mol $^{-1}$) more unstable than an ordinary alkyne.) Indeed, benzyne has been too reactive to isolate except at temperatures near absolute zero. (See also the solution to Problem 18.76 in the Study Guide and Solutions Manual.)

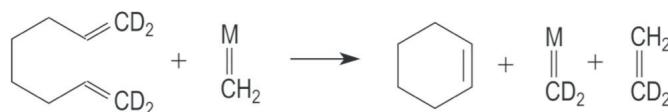
- 18.81 (b) The pairwise mechanism can only give ethylene and ethylene- d_4 , because at no point in the mechanism does one of the CH_2 (or CD_2) groups become detached from its parent molecule:



To see the results of the metallacycle mechanism, note that $\text{M}=\text{CH}_2$ and $\text{M}=\text{CD}_2$ (where M = the ruthenium and its ligands) are formed in the first catalytic cycle. (We leave it to you to fill in the details.)



Now, ethylene- d_2 can form in *two ways*: by the reaction of $\text{M}=\text{CH}_2$ with the d_4 -diene starting material, or by the reaction of $\text{M}=\text{CD}_2$ with the undeuterated diene:



However, ethylene- d_4 can form in only one way—the reaction of $\text{M}=\text{CD}_2$ with the d_4 -diene starting material; and ethylene- d_0 can form in only one way—the reaction of $\text{M}=\text{CH}_2$ with the undeuterated diene starting material. Consequently, the formation of ethylene- d_2 enjoys a two-fold statistical advantage, and the ratio of the three ethylenes is therefore $\text{H}_2\text{C}=\text{CH}_2 : \text{H}_2\text{C}=\text{CD}_2 : \text{D}_2\text{C}=\text{CD}_2 = 1 : 2 : 1$. The result of this very elegant experiment was that the three ethylenes were formed in this statistical ratio.

- 18.85 Whether the nucleophile occurs in biological systems or in the laboratory, nucleophilic substitution does not occur on aryl derivatives (see Sec. 18.1, text p. 823) unless the ring is activated by electron-withdrawing groups (such as carbonyl groups or nitro groups) that stabilize the Meisenheimer complex in nucleophilic aromatic substitution. (See Sec. 18.4, text p. 828.) Furthermore, both fluoride and cyanide are fairly strong bases (see Table 3.1, text p. 103) and are therefore very poor leaving groups.