

ERRATA
Study Guide and Solutions Manual, Sixth Edition
by Jim Parise and Marc Loudon
to accompany
Organic Chemistry, 6th Edition, by Marc Loudon and Jim Parise
Date of this release: February 22, 2019

“How do I know what printing I have?” Look at the reverse side of the title page of your *Study Guide and Solutions Manual*, where you see all sorts of publication information. On the last line, you will see a series of digits. These digits will end with the number of your printing. Thus, 10 9 8 7 6 5 4 3 2 1 is a first printing; 10 9 8 7 6 5 4 3 2 is a second printing; and 10 9 8 7 6 5 4 3 is a third printing.

All items marked with ² were corrected in the second printing.
All items marked with ³ were corrected in the third printing.
All items marked with ⁴ will be corrected in the fourth printing.

Chapter 1

p. 11³ Figure SG1.5. In the figure, the part (b) antibonding MO and bonding MO H₂ should be H₂⁻.

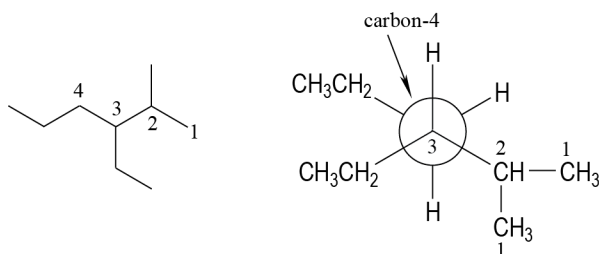
Chapter 2

p. 34³ Solution 2.26 (b), 3,4-dimethylhexane is another possible answer. [Credit: Sae Rome Choi, student, University of Notre Dame]

p. 37³ Solution 2.33 (b). Should read “Compound *B* is 3-ethyl-2-methyl**hexane**.” [Credit: Erin Jonasson, University of Notre Dame]

p. 37³ Solution 2.34 (b). This answer has been updated to reflect the correction to 2.33 (b). The corrected display and changes to the text are shown in bold below:

- (b) The **ethyl** group on carbon-4 has to be gauche to either the ethyl group or the isopropyl group **on carbon-3**. Because the isopropyl group is larger, the **ethyl** group is gauche to the **other** ethyl group in the most stable conformation.



The ambiguity in drawing the structure is that it has a mirror image, which is not the same, although it has the same energy. (The issue of mirror-image structures is considered in Chapter 6.) If you drew the mirror-image structure, it is equally correct. As noted in the solution to Problem 2.33(b), the name of this compound is 3-ethyl-2-methyl**hexane**.

[Credit: Erin Jonasson, University of Notre Dame]

p. 39³ Solution 2.38 (b). Should read “...viewing down the **C3–C4** bond.” [Credit: Bruce Ganem, Cornell University]

Chapter 3

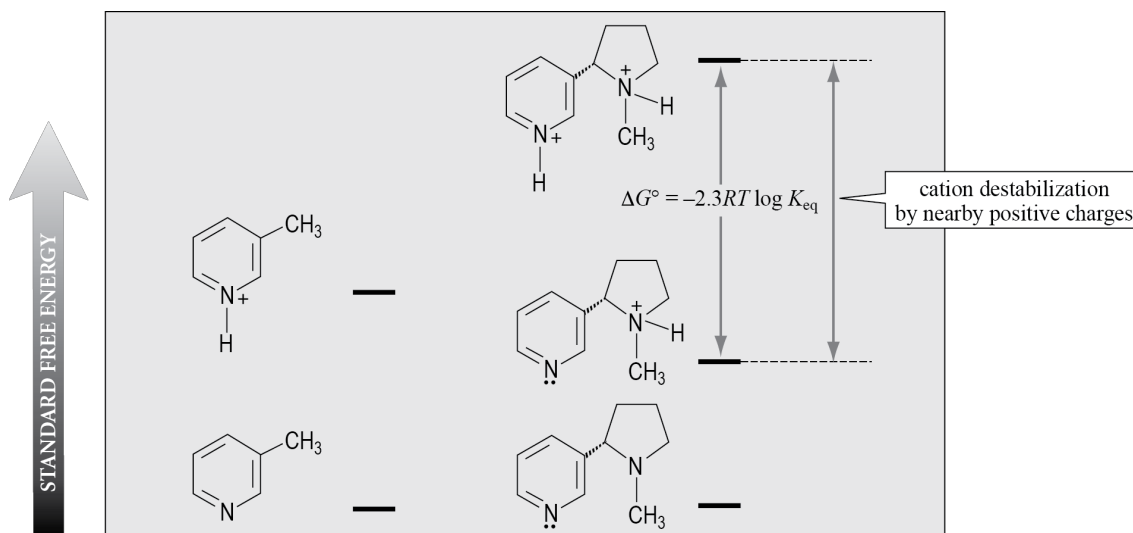
p. 66³Solution 3.53. The figure and caption to which this problem references is missing. It is shown below.

Figure SG3.2 Free-energy diagram to accompany the solution to Problem 3.53. The dication is destabilized by the two nearby positive charges. (The neutral compounds, are arbitrarily placed at the same energy for comparison purposes.)

Chapter 4

p. 84²Solution 4.8, parts (c) and (d) should be switched. Part (c) should begin “The prefix “cyclo”...” and part (d) should begin “The suffix “triene”...”.p. 85³Solution 4.10 (a). Depending on which printing of the textbook you have, formula *D* may or may not be reasonable. The answer should read:

- (a) A way to tell whether a formula is reasonable is to calculate its unsaturation number using Eq. 4.7 on text p. 144. A formula that gives a negative or fractional unsaturation number is not possible. Formula *A* cannot be a correct formula, because a compound containing only C, H, and an odd number of nitrogens must have an odd number of hydrogens. Formula *C* also could not be the formula of an organic compound, because the maximum number of hydrogens possible in a compound containing 10 carbons, 3 nitrogens, and any number of oxygens is 25. Formulas *B* ($C_{10}H_{20}N_2O_2$) and *D* ($C_{10}H_{16}O_2$) are both reasonable, and could be organic compounds.

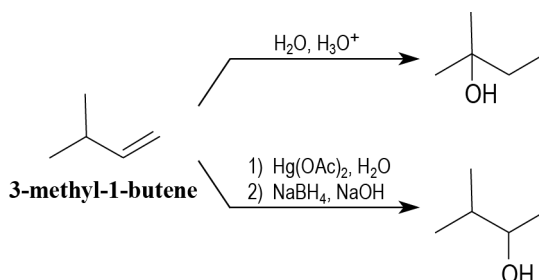


An early printing of the text had a formula *D* that was the same as formula *A* ($C_{10}H_{15}N$), which would make it unreasonable.

p. 85³Solution 4.10 (b). There are nine isomeric alcohols with the given formula. The answer should read:

- (b) There are nine isomeric alcohols and one ketone with the formula C_4H_8O . The first three alcohols are called enols and, as you will learn in Chapter 14, they are in equilibrium with their corresponding ketone or aldehyde forms.

- p. 124⁴ Solution 5.7 (d). In the product, the last carbon in the chain should be CH₃, not CH₂. [Credit: Madison McCracken, student, University of Notre Dame]
- p. 124³ Solution 5.5. The product of the first reaction, acid catalyzed hydration, has one too many carbons in it. The corrected display is below. [Credit: Karl Schlaht, student, University of Notre Dame]



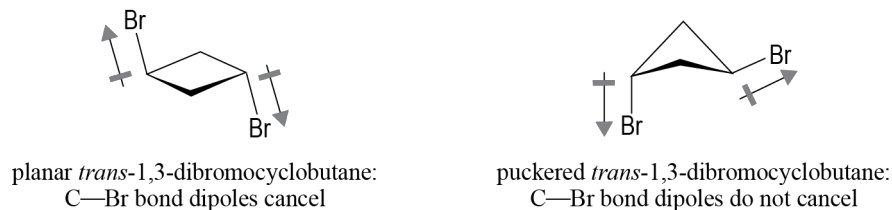
- p. 127³ Solution 5.14. The answers to parts (a) and (b) should be switched. Part (a) is *cis*- or *trans*-4-octene and (b) is 1-methylcycloheptene [Credit: Jori Goldberg and Clare Hannon, students, University of Notre Dame]
- p. 129⁴ Solution 5.20 (a). There is an extra methyl group attached to the carbon in the radical initiator (it should look like the product of Eq. 5.50 in the book) and the product (product should be NC–CH(CH₃)₂). [Credit: Chloe Hemm and Kyle Moon, students, University of Notre Dame]
- p. 134² Solution 5.32 (i). Hydrogenation of 3-ethyl-2-pentene (or 3-ethyl-1-pentene, not shown) would give the desired alkane.

Chapter 6

- p. 154⁴ Solution 6.10 (e). The units for the answer should be deg mL g⁻¹ dm⁻¹, not deg mL⁻¹ g⁻¹ dm⁻¹. [Credit: Erin Jonasson, University of Notre Dame]
- p. 158⁴ Solution 6.27. The four stereoisomers should be: (2*Z*,4*S*), (2*E*,4*S*), (2*Z*,4*R*), and (2*E*,4*R*). [Credit: Nick Rossiter, student, University of Notre Dame]
- p. 161³ Solution 6.40. Compounds *D* and *E* can be resolved into enantiomers. The explanations should be: “Compounds *D* and *E* can be resolved because they contain asymmetric carbons (the ones bearing the phenyl group in each).” [Credit: Lilia Escobedo, student, Cornell University]
- p. 163² Solution 6.46 (a). The first line should read “(See the solution to Problem **6.45**...)”

Chapter 7

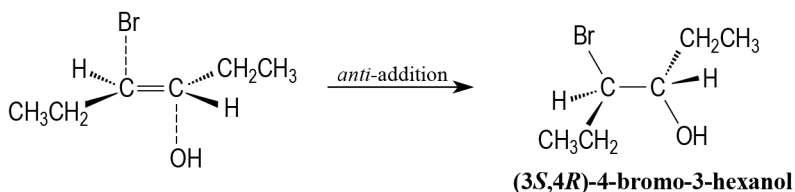
- p. 173² Further Exploration 7.4. First line should read “(p. **114** of this manual).”, not 107.
- p. 181⁴ Solution 7.16 (a). At the top of page 181, the caption under puckered *trans*-1,3-dibromocyclobutane should read C–Br bond dipoles do not cancel. [Credit: Erin Jonasson, University of Notre Dame]



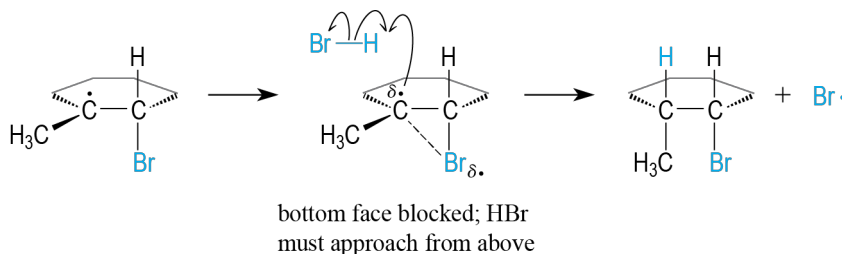
- p. 189⁴ Solution 7.41 (a,b). The structures are correct, but compounds *D* and *C* should be named as cyclopentanols, not cyclohexanol)s. [Credit: Erin Jonasson, University of Notre Dame]

p. 194² Solution 7.54 (a). The end of the second sentence should read "...whereas an anti-addition will lead to the observed **2*S*,3*R*** product.", not *2*R*,3*R**.

p. 195³ Solution 7.55 (b). The second product should contain an OH group (circled, below), not a second Br. [Credit: Leigh Campbell, student, University of Notre Dame]



p. 203² Solution 7.69 (b). The last sentence of the paragraph should read "...unusual **cyclic bromonium radical** (similar to...)", not ion. In the display, the bromine should bear a "partial electron", not a partial positive charge. The corrected display is shown below.



p. 204² Solution 7.72 (a). Line 7 in the first paragraph should read, "that of a methyl–hydrogen *gauche*-butane interaction be $\Delta G^\circ(\text{gauche}) = 3.7 \text{ kJ mol}^{-1}$," not 2.8. Using this value, the first equation should be:

$$\Delta G^\circ(\text{eq}) = \Delta G^\circ(B) - \Delta G^\circ(A) = 8.4 = 7.4 + 3.7 + \Delta G^\circ(\text{Me–Me}) - 17.6$$

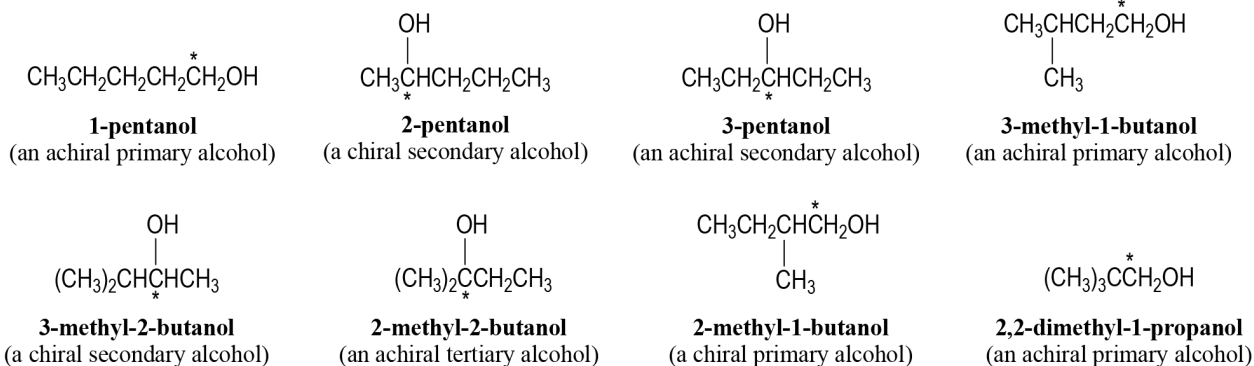
And solving for $\Delta G^\circ(\text{Me–Me})$ then gives:

$$\Delta G^\circ(\text{Me–Me}) = 14.9 \text{ kJ mol}^{-1} (3.6 \text{ kcal mol}^{-1})$$

p. 205² Solution 7.73 (b). The last paragraph should be:
 "In Equation (2), two Ph–H diaxial interactions (13.2 kJ mol^{-1}) and a *gauche*-butane interaction (3.7 kJ mol^{-1}) on the left side are balanced against four methyl–hydrogen diaxial interactions on the right (14.8 kJ mol^{-1}). The overall ΔG° for equation (2) is therefore $14.8 - 16.9 = -2.1 \text{ kJ mol}^{-1}$."

Chapter 8

p. 215² Solution 8.28. The fourth structure, 3-methyl-1-butanol, has an extra hydrogen on carbon-3. The correct display should be as follows. [Credit: Alison Ou, student, Purdue University]

p. 220²

Solution 8.47. This solution has been expanded for clarity:

“The structure of propofol is largely hydrocarbon-like, even though it contains a polar OH group, which is why it is insoluble in water. The lecithin/soybean oil mixture forms phospholipid vesicles. The propofol is incorporated into the vesicles near the aqueous interface so that the OH group can H-bond to solvent water and the apolar portion can interact with the apolar region of the vesicles.”

p. 220²

Solution 8.51 (c). This solution has been expanded for clarity:

“As the hint suggests, the boiling point is a measure of the tendency of a molecule to escape from its liquid state. The solubility in water is a combination of the escaping tendency from the pure alcohol phase and solvation in the aqueous phase. Both of these factors work in the same direction. The tertiary alcohol has a greater escaping tendency *and* requires a less negative entropy of solvation in water.”

p. 221²

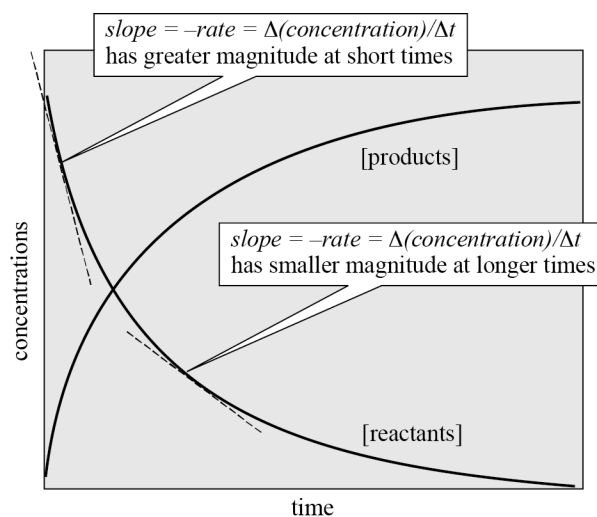
Solution 8.52 (d). This solution has been expanded for clarity:

“As described in the solution to 8.51 (c), solubility in water is composed of two factors: escape of a molecule from its own liquid phase *and* solvation by water. Although 1-pentanol can be both a hydrogen bond donor and acceptor, this favorable interaction must be outweighed by the fact that the molecules are attracted to each other through hydrophobic interactions of the five-carbon alkyl chain. The relative boiling points tell us that the intrinsic escaping tendency of the ether from its own liquid phase is much greater than that of the alcohol. Even though the alcohol can donate hydrogen bonds, it seems that the escaping tendency is more important. Thus, diethyl ether, with its hydrogen bond-accepting ability, smaller alkyl chains, and lower boiling point, is more soluble in water.”

Chapter 9

p. 236²

Figure SG9.1. The description of the lower curve should read “has **smaller magnitude at longer times.**” The corrected figure is shown below.



p. 247

Solution 9.46 (e). The text reference page is missing. It should refer to **text p. 191.**

p. 248⁴

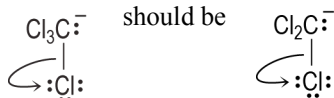
Solution 9.48 (a). The last sentence in the explanation should read, “The only one that gives only **one chiral monochlorinated product and one achiral monochlorinated product** is 2,3-dimethylbutane.” The structures are correct. [Credit: Daniel Staros, student, Bloomsburg University]

p. 248⁴

Solution 9.52 (c). The answer should have one additional carbon than what is shown: $\text{Na}^+ \text{ } ^-\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OCH}_3$ [Credit: Hannah Choset, student, Cornell University]

p. 263⁴

Solution 9.87 (a). On the second line of the reaction mechanism, the carbon has one too many chlorines.



[Credit: Susan Li, student, University of Notre Dame]

Chapter 10

p. 271²

Reaction Review II. B. 5. is incomplete. It should read as follows:

“Because all these methods have an $\text{S}_{\text{N}}2$ mechanism as their basis, alcohols with a significant amount of β -branching (that is, alkyl substituents at the β -position) will react more slowly or not at all, with one exception. **The exception is Ph_3PBr_2 , as described on p. 471, will react even with neopentyl alcohols.**”

p. 284³

Solution 10.33 (e). H^a and H^c (and H^b and H^d) are enantiotopic, not homotopic. The second sentence should read, “ H^a and H^c are **also** constitutionally equivalent and **enantiotopic**, as are H^b and H^d .” [Credit: Alexander Seed, Kent State University]

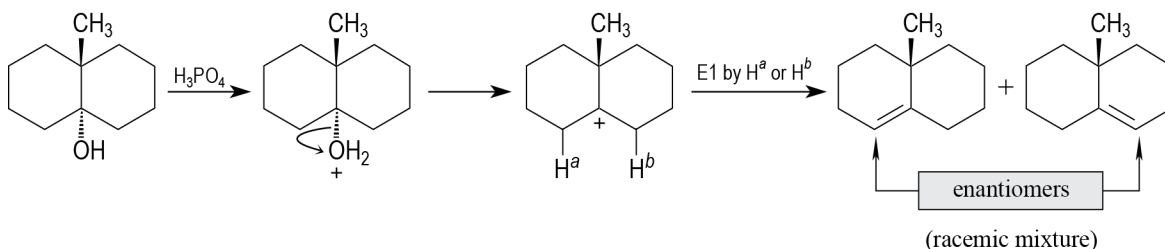
p. 289²

Solution 10.49 (b). The reagent mentioned should be **Ph_3PBr_2** , not PBr_3 .

p. 294³

Solution 10.59 (f). This reaction proceeds by E_1 , not E_2 . The solution should read:

- (f) Treatment of the alcohol with strong acid protonates the hydroxy group making it a good leaving group. Once the water leaves, there are two different but equivalent protons adjacent to the positively charged carbon. Since there is an equal opportunity to remove either one leading to one of two enantiomers, a racemic mixture of E1 elimination products is generated.

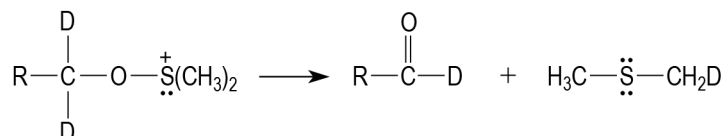


[Credit: Albert Wang, student, Cornell University]

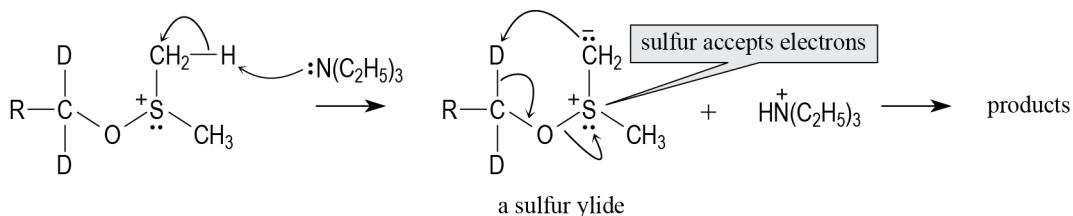
p. 295³

Solution 10.61 (c). This part of the answer is incomplete; it doesn't take into account the details given in the problem involving deuterium. The corrected answer is shown below.

- (c) To solve this problem, first write out the reaction that occurs with deuterium-labeled alcohol:



Since deuterium ends up incorporated into one of the methyl groups on sulfur, one of those hydrogens must have been removed at some point. Use triethylamine to remove a proton, generating an intermediate called a sulfur ylide. The sulfur ylide then can react *intramolecularly* to remove a deuterium from the nearby carbon, oxidizing that carbon, and eliminating dimethyl sulfide containing deuterium. The sulfur ultimately accepts electrons so it is oxidized, as noted in the solution to part (b).



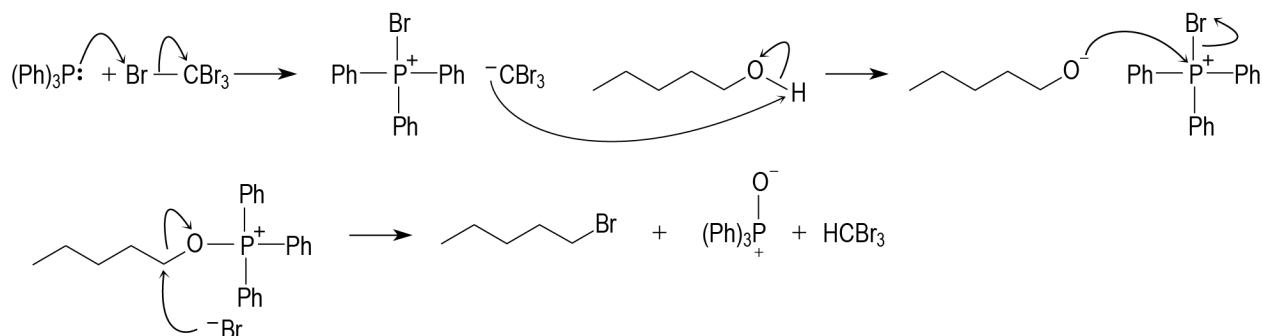
p. 297²

Solution 10.64 (a). This reaction is two-electron oxidation, not one. The solution should read:

“Following the steps in Sec. 10.5A, we can balance the equation. First, we don't need to add any water because no oxygens are involved. Next, we add one H⁺ to the right side to replace the one that was lost from serotonin. Finally, we add **two** electrons to the right side to cancel the plus charges. Thus, **two** electrons were lost, or, we can say this reaction is a **two**-electron oxidation.”

p. 299³

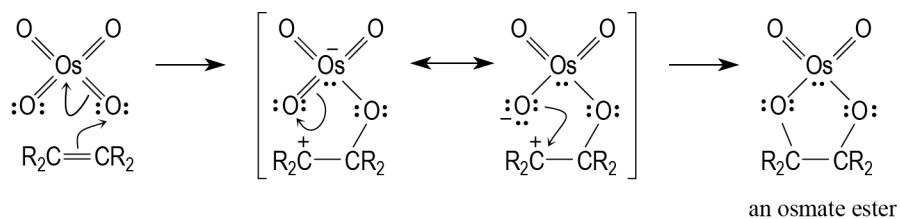
Solution 10.67 (c). Initially, the phosphorus adds to the bromine, then the displaced CBr₃⁻ deprotonates the alcohol, as shown below.



Chapter 11

p. 305²

Further Exploration 11.1. At the top of p. 305, the osmium in the second resonance structure should be neutral, not negative. The corrected display is shown below.



p. 319²

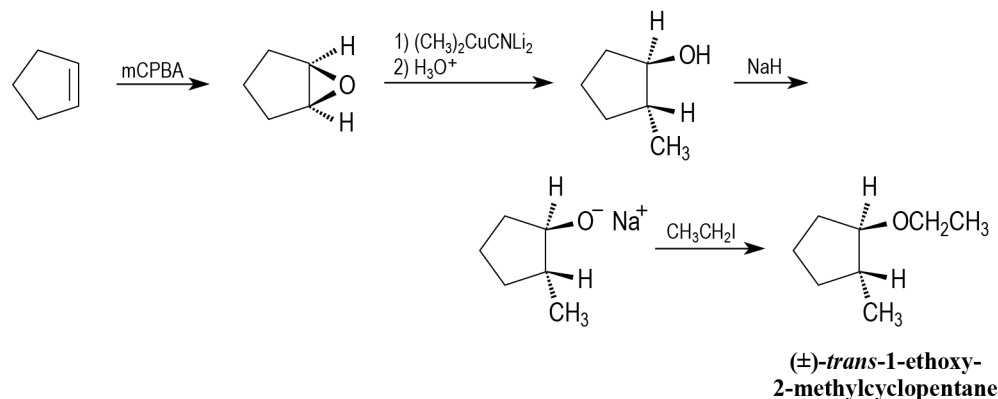
Solution 11.16 (d). The reference in this problem should be to Sec. 11.1, text p. 512.

p. 323⁴

Solution 11.27 (b). The structure of **phenylacetaldehyde** should be **PhCH₂CH=O**, not PhCH₂=O. [Credit: Jamieson Abrams, student, University of Notre Dame]

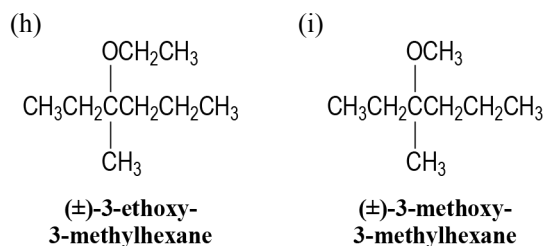
p. 328²

Solution 11.40 (d). In the last two structures, the lower ethoxy groups should be methyl groups. The corrected display is shown below.



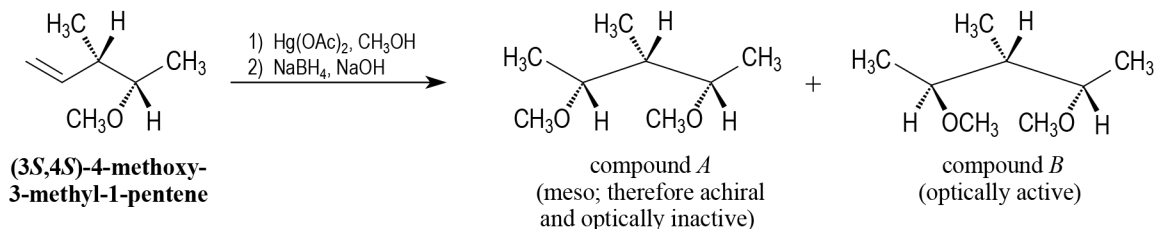
p. 330³

Solution 11.45 (h,i). Corrected structures and/or names are shown below.



p. 334²

Solution 11.57. Compounds **A** and **B** are mislabeled, and should be switched. The corrected display is shown below.

p. 337³

Solution 11.61 (l). The final reagent in the sequence should be H₂O₂, not 1) O₂; 2) H₂O.

Chapter 12

p. 352⁴

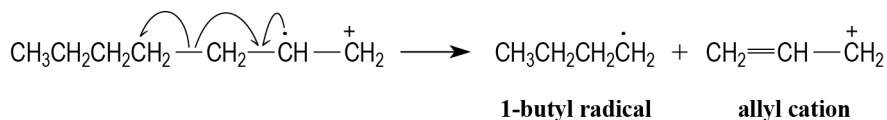
Second to last paragraph. Should read “But Eq. **SG12.4** states that...”.

p. 355²

Solution 12.5. The answer should be **0.39**, not -0.39.

p. 366²

Solution 12.44 (c). The explanation given is inappropriate for this part, and should be ignored. The correct answer is shown by the mechanism below.



Chapter 13

p. 382²

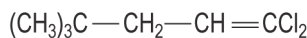
Solution 13.25. The first paragraph of this solution should read:

“The two protons in the δ 4.6–4.8 region are vinylic protons, and they are not chemically equivalent. Their very small splitting is consistent only with geminal (that is, H₂CA) protons. Thus, we have the partial structure”

p. 388²

Solution 13.40 (f). Ignore the first sentence. The second line, containing chemical shifts and integrations, can also be ignored because it is just a restatement from the problem and unnecessary for the solution. This solution should read simply as follows:

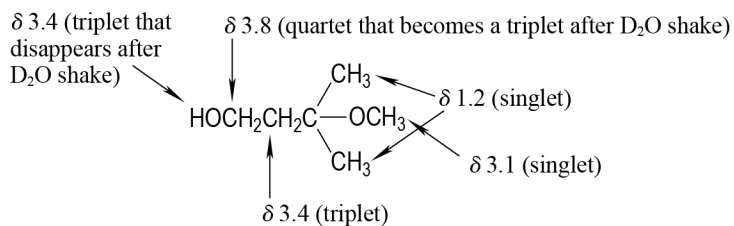
- (f) The compound has one degree of unsaturation and a *tert*-butyl group. This, plus the requirement for two chlorines and a partial structure CH₂—CH required by the splitting leaves only the following possibility:



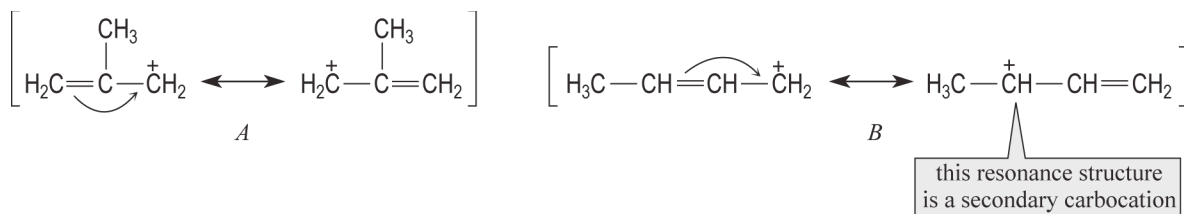
1,1-dichloro-4,4-dimethyl-1-pentene

p. 394²

Solution 13.52 (a). The structure is incorrect, and should be as is shown below. The explanation is correct.

p. 397²

Solution 13.58. The first paragraph at the top of the page should be replaced with the following, which contains a few minor changes (noted in **bold**).



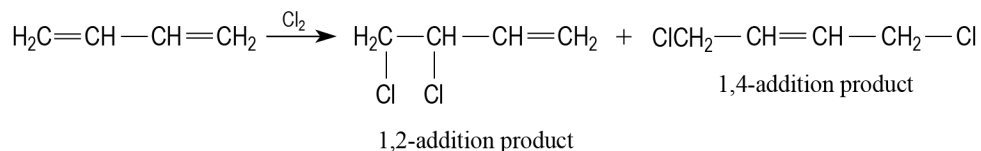
p. 450² Solution 15.55. The correct answer is as follows:

The energy difference between the two waves can be calculated using Eq. 15.3. The 109 term at the end of the solution is to convert the difference in reciprocal wavelengths from nm to m.

$$\Delta E = \frac{hc}{\lambda_1} - \frac{hc}{\lambda_2} = hc \left(\frac{1}{\lambda_1} - \frac{1}{\lambda_2} \right) = (3.99 \times 10^{-13} \text{ kJ mol}^{-1} \text{ s}) (3 \times 10^8 \text{ m s}^{-1}) \left(\frac{1}{488} - \frac{1}{510} \right)$$

$$= (12 \times 10^{-5} \text{ kJ mol}^{-1}) (8.8 \times 10^{-5} \text{ nm}^{-1}) (10^9 \text{ nm m}^{-1}) = 10.6 \text{ kJ mol}^{-1}$$

p. 458⁴ Solution 15.71. The 1,4-addition product is missing a carbon. The correct display is below.



[Credit: Leigh Campbell, student, University of Notre Dame]

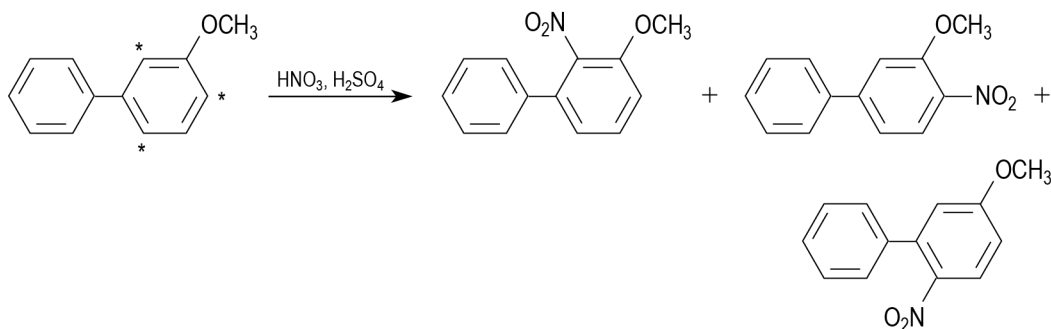
Chapter 16

p. 476² Solution 16.2. Parts (f) and (h) are should be switched; i.e. (f) should be benzyl methyl ether, and (h) should be *o*-cresol.

p. 481⁴ Solution 16.16. The *tert*-butyl groups in the last two structures should be (CH₃)₃C-, not (CH₃)C-.
[Credit: Katie Adlaka, student, University of Notre Dame]

p. 491⁴ Solution 16.43 (g). The name of the product should be 2,6-dibromo-4-nitrotoluene, not 2,6-dibromo-1-nitrotoluene. [Credit: AJ Lepore, PhD student, University of Notre Dame]

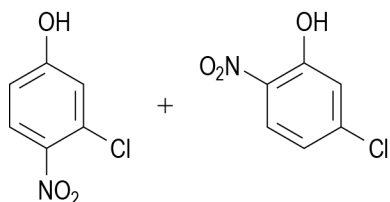
p. 493⁴ Solution 16.45 (d). The final structure is incorrect, the nitro group should be ortho to the phenyl ring and para to the methoxy group. The correct display is shown below. [Credit: Leigh Campbell, student, University of Notre Dame]



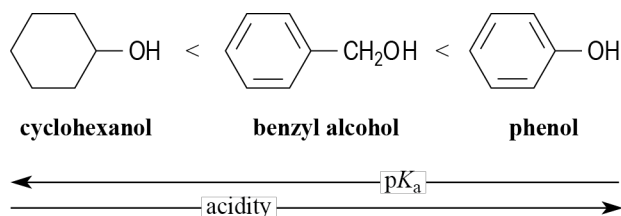
Chapter 17

p. 538² Solution 17.47. Part (e) should be deleted, and part (f) should be the answer to part (e).

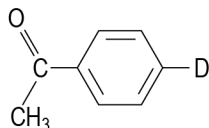
Chapter 18

p. 550⁴Reaction Review I.A.1. The alkyne in the product has an extra H on the left carbon.p. 575⁴Solution 18.40 (b). The second product is incorrect. The two products should be:

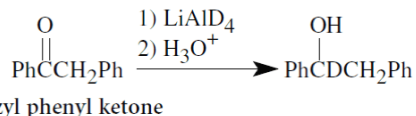
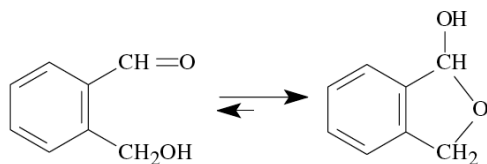
[Credit: Corinne O'Connor, student, University of Notre Dame]

p. 579⁴Solution 18.49 (b). The benzyl alcohol structure is missing double bonds. The corrected display is:

Chapter 19

p. 646⁴Solution 19.52 (m). The final product should contain CH₃, not CD₃:p. 646⁴

Solution 19.69 (b) is missing. It should be as follows.

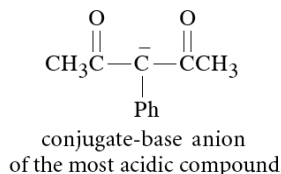
(b) Allow benzyl phenyl ketone to react with LiAlD₄.p. 657⁴Solution 19.70 (c). The corrected solution is:(c) Compound *A* exhibits a very weak carbonyl stretch in IR because very little of it is in the aldehyde form; rather, the molecule exists largely as a cyclic hemiacetal.

Chapter 20

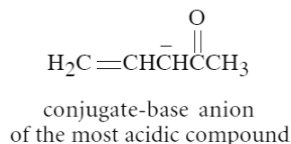
p. 689⁴Solution 20.51 (a). In the last step, the reference over the arrow (Eqs. 19.18a–b) is incorrect and should be ignored. The correct reference is in the solution text: **Eqs. 19.20a–b.**

Chapter 22

p. 797⁴ Solution 22.64 (a). The second structure in part (b), shown below, should be associated with part (a).



p. 797⁴ Solution 22.64 (b). Only the first structure (shown below) should be associated with part (b). The second structure belongs with part (a).



p. 801⁴ Solution 22.74 (c). In the first step, the reference over the arrow (Problem 22.63) is incorrect and should be ignored. The correct reference is in the solution text: **Problem 22.73.**

Chapter 23

p. 840⁴ Solution 23.8 is missing. It should be:

23.8 From Table 23.1, text p. 1190, we see that the basicity order is as follows:

$$A < B < C$$

The basicities of all these amines are reduced by resonance interaction of the nitrogen unshared electron pair with the ring. The electron-withdrawing polar effect of the nitro group lowers basicity further, and resonance interaction of the nitrogen unshared pair with the *p*-nitro group stabilizes *p*-nitroaniline and lowers its basicity even more. (Resonance structures depicting this interaction are shown in the solution to Problem 23.3(a) on p. 838 of this manual.)

[Credit: Maeve Flatley, student, University of Notre Dame]

p. 849⁴ Solution 23.35 is mislabeled as 23.29. The solution given is correct.

Chapter 25

p. 920² Solution 25.1b. Should be **S-isopropyl butanethioate**.

p. 921² Solution 25.10. The text is irrelevant, and can be ignored. The reaction mechanism is correct.

p. 924² Solution 25.15a. The text is irrelevant, and can be ignored. The reaction mechanism is correct.

p. 926² Solution 25.19. The answer is incorrect. It should be **-48.29 kJ/mol**. The solution should read as follows:

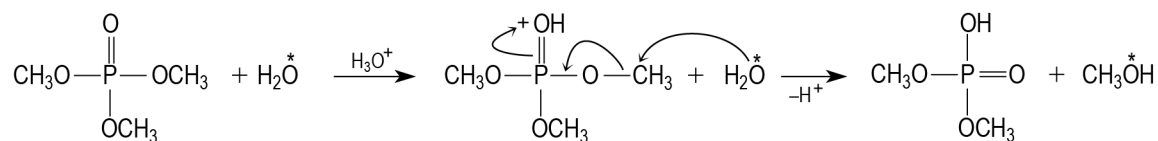
If the concentrations of ATP, ADP, and phosphate are all 0.001 mM, then by Eq. 25.37 on text p. 1318, $\Delta G^\circ = -48.29 \text{ kJ mol}^{-1}$ (see Study Problem 25.1 for a similar example).

p. 930² Solution 25.29. The solution has been expanded. After the reaction mechanisms, additional explanation is as follows:

“Now consider the final part of the question. Sulfonate ions are much less basic than carboxylate ions, and are therefore better leaving groups than carboxylate ions, which is why the nucleophile reacts with the methyl group in reaction (a) and with the carbonyl in reaction (b). For reaction (c), the reaction could occur at either phosphorus (Sec. 25.7A) or the methyl group (Sec. 25.7C). Since we know that the isotope is

incorporated into compound *F*, we could argue that steric interference of the isopropyl groups precludes reaction at the phosphorus, and reaction at the methyl carbon is preferred.”

p. 930² Solution 25.30. The mechanism has been corrected, and is shown below:



p. 930² Solution 25.32. The explanation has been revised for clarity, and should read as follows:

“Nitrate ion can react with hydroxide to form orthonitrate, but the reaction is unfavorable. Nitrate ion is stabilized by resonance, which distributes the negative charge around to all three oxygen atoms equally. After reaction with hydroxide at the nitrogen, the product is very unstable for a few reasons. First, the resonance of the nitrate ion is lost—it is tetrahedral and the three oxygens bear three formal negative charges because no delocalization is possible. Also, its formation is unfavorable, because approach of the hydroxide is repelled by the nearby negative charges on the oxygens. Additionally, the product has a 2– charge, with negative charges localized on three oxygens. Finally, the three negative charges are pushed closer together in a tetrahedral arrangement than in the trigonal planar nitrate ion, further destabilizing the product.”

p. 932² In problem 25.38 of the text, the first sentence should read: “The pKa of the thiol group of CoASH is 9.6.” (if you have the third printing of the text or later, this problem has been corrected.)

Solution 25.38. The solution for this problem has been corrected to match the corrected wording of the problem in the text, and should read as follows:

“As noted in Sec. 25.5A, thioesters are about as reactive as the corresponding oxygen esters, that is, not very reactive. At pH = 7, hydrolysis can proceed only with water, which is not a very good nucleophile, and the rate of the reaction is very slow. At pH = 10, hydroxide is present, and it is a much more reactive nucleophile than water. Additionally, after reaction at the carbonyl and expulsion of the leaving group, CoAS[–] reacts with the acetic acid which drives the equilibrium to the right (see Eq. 25.3, text p. 1291, and Sec. 21.7A, text p. 1061). Therefore, ΔG^o would be more negative at pH = 11, and the reaction would be more favorable.”

p. 932² Solution 25.39b. The text in this part is irrelevant, and can be ignored. The reaction mechanism is correct.