ERRATA
Study Guide and Solutions Manual, Sixth Edition
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to accompany
Date of this release: March 1, 2016

“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.

Chapter 2
p. 34
Solution 2.26 (b). 3,4-dimethylhexane is another possible answer. [Credit: Sae Rome Choi, student, University of Notre Dame]

p. 39
Solution 2.38 (b). Should read “…viewing down the C3–C4 bond.” [Credit: Bruce Ganem, Cornell University]

Chapter 3
p. 66
Solution 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. 84
Solution 4.8, parts (c) and (d) should be switched. Part (c) should begin “The prefix “cyclo”…” and part (d) should begin “The suffix “triene”…”.
Solution 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 $A$ ($C_{10}H_{20}N_3$), which would make it unreasonable.

Solution 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, are in equilibrium with their corresponding ketone or aldehyde forms.

[Credit: Meridith Balbach, student, University of Notre Dame]

Solution 4.52. The cis isomer of the second compound shown is also a correct answer. The updated display is shown below.

[Credit: Meridith Balbach, student, University of Notre Dame]

Solution 4.61 (c). The last line should read “…by between 14.2 and $6.6$ kJ mol$^{-1}$”.

Figure SG4.6. The second value, between 2-methyl-1-butene and 2-methyl-2-butene should be $-6.6$ kJ mol$^{-1}$, not $-14.2$. The corrected figure is shown below.
Chapter 6
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. 194² Solution 7.54 (a). The end of the second sentence should read “...whereas an anti-addition will lead to the observed 2S,3R product.”, not 2R,3R.
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.

\[
\begin{align*}
\text{H}_3C & \quad \text{Br} & \quad \text{H} & \quad \text{H} & \quad \text{H} & \quad \text{Br} \\
& & & & & + \\
\end{align*}
\]

bottom face blocked; HBr must approach from above

p. 204² Solution 7.72 (a). Line 7 in the first paragraph should read, “that of a methyl–hydrogen gauche-butane interaction be \(\Delta G^\circ\) (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 \(\Delta G^\circ\) for equation (2) is therefore 14.8 – 16.9 = –2.1 kJ mol\(^{-1}\).”
Chapter 8

p. 215 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]

```
CH₃CH₂CH₂CH₂CH₂OH  CH₃CH₂CH₃CH₂CH₃  CH₃CH₂CHCH₃CH₃
1-pentanol         2-pentanol         3-pentanol
(an achiral primary alcohol) (an achiral secondary alcohol) (an achiral primary alcohol)
```

p. 220 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. 220 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. 221 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. 236

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.

Chapter 10

p. 271

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

“Because all these methods have an $S_N2$ mechanism as their basis, alcohols with a significant amount of $\beta$-branching (that is, alkyl substituents at the $\beta$-position) will react more slowly or not at all, with one exception. The exception is $\text{Ph}_3\text{PBr}_2$, as described on p. 471, will react even with neopentyl alcohols.”

p. 289

Solution 10.49 (b). The reagent mentioned should be $\text{Ph}_3\text{PBr}_2$, not $\text{PBr}_3$.

p. 297

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 $\text{H}^+$ 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. 299

Solution 10.67 (c). Initially, the phosphorus should attack the bromine, not carbon, as shown below.
Chapter 11

p. 305

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.

\[
\begin{align*}
\text{O} & \quad \text{O} \\
\text{R}_2\text{C} & \quad \text{R}_2\text{C} \\
\text{O} & \quad \text{O} \\
\end{align*}
\]

\text{an osmotic ester}

p. 319

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

p. 328

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

\[
\begin{align*}
\text{H} & \quad \text{H} \\
\text{H} & \quad \text{H} \\
\text{CH}_3 & \quad \text{CH}_3 \\
\end{align*}
\]

\text{(1\textsuperscript{-})-trans-1-ethoxy-2-methylcyclopentane}

p. 334

Solution 11.57. Compounds \textit{A} and \textit{B} are mislabeled, and should be switched. The corrected display is shown below.

\[
\begin{align*}
\text{H}_2\text{C} & \quad \text{H} \\
\text{CH}_3 & \quad \text{CH}_3 \\
\text{H} & \quad \text{H} \\
\end{align*}
\]

\text{(3S,4S)-4-methoxy-3-methyl-1-pentene}

\text{compound A (meso; therefore achiral and optically inactive)}

\text{compound B (optically active)}

Chapter 12

p. 355

Solution 12.5. The answer should be 0.39, not \textit{--}0.39.

p. 366

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

\[
\begin{align*}
\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2 & \quad \text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2 \\
\text{CH}_2 & \quad \text{CH}_2 \\
\text{CH}_3\text{CH}_2\text{CH}_2 & \quad \text{CH}_2\text{CH}_2\text{CH}_2 \quad \text{CH}_2 & \quad \text{CH}_2 \\
\text{1-butyl radical} & \quad \text{allyl cation}
\end{align*}
\]

Chapter 13

p. 382

Solution 13.25. The \textit{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. 388

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-butyll group. This, plus the requirement for two chlorines and a partial structure CH₂—CH required by the splitting leaves only the following possibility:

(CH₃)₃C—CH₂—CH=CCl₂

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

p. 394

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

p. 397

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).

“The two doublets centered at δ 6.2 are assigned to the diene protons 1 and 2. These protons are split by each other, but not significantly by any other protons. (Coupling constants depend on dihedral angle, and the large splitting evidently suggests an anti relationship about the single bond.) The two resonances centered at δ 4.9 are assigned to the geminal alkene protons 3 and 4. These two protons are diastereotopic, and are therefore chemically nonequivalent. Their splitting, although not expanded, is evidently the small splitting typical of geminal alkene protons (Table 13.3, text. p. 647). The multiplet just below δ 4 is assigned to the α-alcohol methane proton 6. We are given no information about a D₂O shake, so the proton 5 is not identified; it is probably within the complex pattern between δ 1 and δ 3. Within the inset on the right, the doublet integrating for three protons probably corresponds to a methyl group. The only CH₂—CH group are the methyl protons 8. In the inset, the doublet of doublets corresponds to six protons, which corresponds to the two diastereotopic methyl groups 9 and 10, each split by the adjacent methine hydrogen and having slightly different chemical shifts. The resonance at δ 0.5 is due to an unsplit methyl group and must correspond to protons 7.”

p. 400

Solution 13.66 (c). The answer given is correct, but it should be calculated differently. It is calculated using the natural log equation for free energy, and given in kcal. The answer calculated using the log equation for free energy, and given in kilojoules, is shown below.

(c) One conformation is present in 3.39 times greater concentration than the other. The equilibrium constant, \( K_{eq} \), is the ratio of the two conformations, 3.39:1, or 3.39. Using this value, the temperature, \( T \), of 193 K (remember to convert Celsius to kelvins), and the gas constant of 8.314 x 10⁻³ kJ mol⁻¹ K⁻¹, we can solve for \( ΔG \).

\[
ΔG = -2.3RT \log K_{eq} \\
= -2.3(8.134 \times 10⁻³ \text{ kJ mol}⁻¹ \text{ K}⁻¹)(193 \text{ K}) \log 3.39 \\
= -1.96 \text{ kJ mol}⁻¹
\]
Chapter 14
p. 408  Solution 14.3d. The correct answer: \((E)-7\)-methoxy-3-propyl-5-hepten-1-yne

Chapter 15
p. 450  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.

\[
\Delta E = \frac{hc}{\lambda_1} - \frac{hc}{\lambda_2} = h\left(\frac{1}{\lambda_1} - \frac{1}{\lambda_2}\right) = (3.99 \times 10^{-13} \text{kJ mol}^{-1} \text{s})(3 \times 10^6 \text{ m s}^{-1})\left(\frac{1}{488} - \frac{1}{510}\right)
\]

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

Chapter 16
p. 476  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.

Chapter 17
p. 538  Solution 17.47. Part (e) should be deleted, and part (f) should be the answer to part (e).

Chapter 25
p. 920  Solution 25.1b. Should be **S-isopropyl butanethioate**.

p. 921  Solution 25.10. The text is irrelevant, and can be ignored. The reaction mechanism is correct.

p. 924  Solution 25.15a. The text is irrelevant, and can be ignored. The reaction mechanism is correct.

p. 926  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. 930  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. 930  Solution 25.30. The mechanism has been corrected, and is shown below:

\[
\begin{align*}
\text{CH}_3\text{O} &\text{PO} \text{OCH}_3 + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{O} \text{PO} \text{OCH}_3 + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{O} \text{PO} \text{OCH}_3 + \text{CH}_3\text{O} \text{PO} \text{OCH}_3
\end{align*}
\]

p. 930  Solution 25.32. The explanation has been revised for clarity, and should read as follows:

"Nitrate ion can react with hydroxide to form onitrate, 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.

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° would be more negative at pH = 11, and the reaction would be more favorable.”

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