

Student Study Guide and Solutions Manual

ORGANIC CHEMISTRY

THIRD EDITION



DAVID KLEIN

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Student Study Guide and Solutions Manual, 3e

for
Organic Chemistry, 3e

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Johns Hopkins University

WILEY

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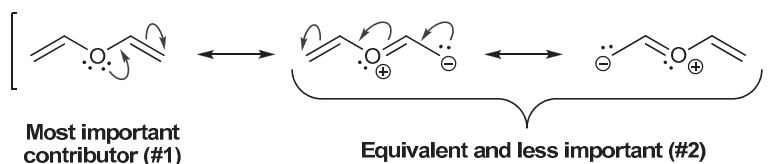
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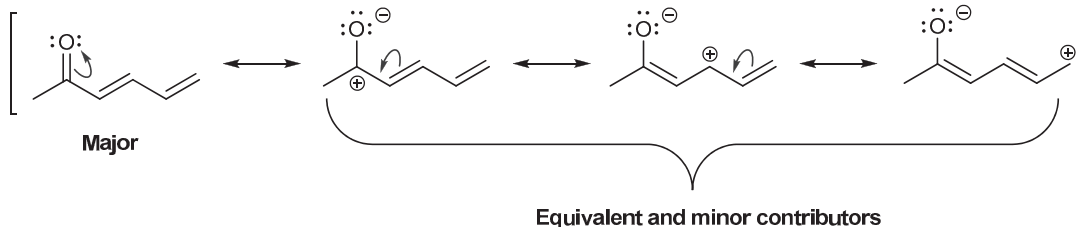
(b) Using the skills developed in the previous SkillBuilders, we begin by drawing all significant resonance structures, shown below. Both resonance structures have filled octets and a negative charge on an oxygen atom. Both resonance structures are equivalent and equally significant.



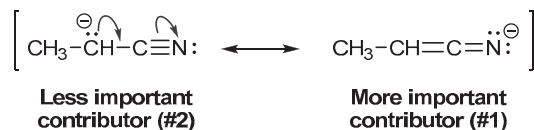
(c) Using the skills developed in the previous SkillBuilders, we begin by drawing all significant resonance structures, shown below. None of the three structures has an atom with an incomplete octet. The first resonance structure is the largest contributor because it has filled octets and no formal charges. The other two resonance structures are equivalent and less significant contributors because they contain formal charges.



(d) Using the skills developed in the previous SkillBuilders, we begin by drawing all significant resonance structures, shown below. The first resonance structure is the only major contributor because it is the only one with filled octets. Recall that a structure with filled octets and no formal charges is an ideal Lewis structure. The other three resonance structures are approximately equivalent and minor contributors because each one is missing an octet (they also have formal charges, but that is a less significant feature to consider when ranking resonance forms).



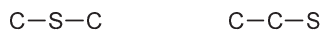
(e) Using the skills developed in the previous SkillBuilders, we begin by drawing all significant resonance structures, shown below. Neither resonance structure has an incomplete octet so they are both expected to be major contributors to the hybrid. The second resonance structure is the more significant contributor because it has the negative charge on the more electronegative nitrogen atom. The first resonance structure is less significant because the negative charge is on the less electronegative carbon atom.



(f) This cation has two different resonance patterns that can be employed, using the lone pair or the π bond to fill the vacancy on carbon, giving a total of three resonance structures. The middle resonance structure is the only major contributor because it is the only one with filled octets. The other two structures are equivalent (missing one octet and

values of the acids on either side of the equilibrium and we would arrive at the same conclusion. That is, the equilibrium will favor the products in this case because the equilibrium favors formation of the weaker acid (H_2O).

3.50. Each of the carbon atoms is tetravalent; the sulfur atom is divalent; and each of the hydrogen atoms is monovalent. We begin by connecting the atoms that have more than one bond (in this case, the two carbon atoms and the sulfur atom). There are only two different ways that these three atoms can be connected to each other, shown below:

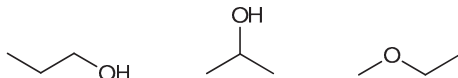


For each of these arrangements, we connect the hydrogen atoms, giving the following two constitutional isomers:

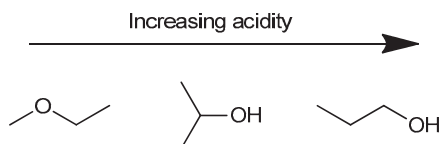


The second isomer is more acidic because deprotonation of that isomer gives a conjugate base with a negative charge on a sulfur atom. The first compound above is less acidic, because its conjugate base would have a negative charge on a carbon atom, which is much less stable (factor #1 of ARIO).

3.51. There are three constitutional isomers with the molecular formula $\text{C}_3\text{H}_8\text{O}$, shown here:



One of these compounds lacks an O-H group, so that compound will be the least acidic (its conjugate base will have a negative charge on a carbon atom). Of the two remaining compounds, the compound with the least branching will be the most acidic, because its conjugate base is the most stable (due to steric effects, discussed in Section 3.7).

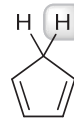


3.52.

(a) A carbon atom must have four sigma bonds in order to be sp^3 hybridized. There is only one such carbon atom in cyclopentadiene, highlighted below.

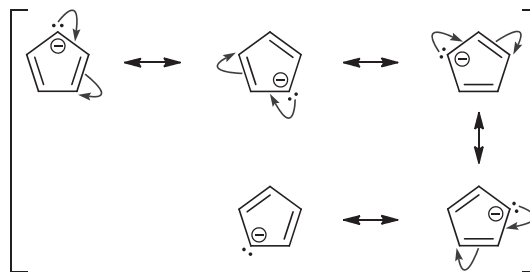


(b) The most acidic proton in cyclopentadiene is highlighted below:



The corresponding conjugate base is highly resonance stabilized (see the solution to Problem 3.15c). In addition, the conjugate base is further stabilized by yet another factor that we will discuss in Chapter 18.

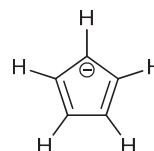
(c) Deprotonation of cyclopentadiene gives a conjugate base that is highly stabilized by resonance, as shown here:



(d) There are no sp^3 hybridized carbon atoms in the conjugate base. All five carbon atoms are sp^2 hybridized.

(e) All carbon atoms are sp^2 hybridized and trigonal planar. Therefore, the entire compound has planar geometry.

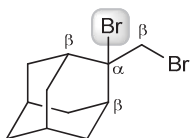
(f) There are five hydrogen atoms in the conjugate base.



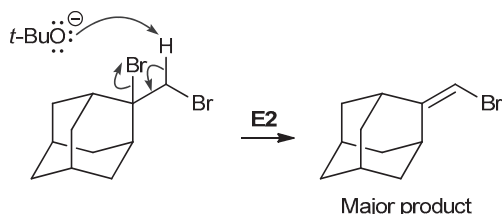
(g) As seen in the resonance structures (see the solution to part c of this problem), there is one lone pair in the conjugate base, and it is highly delocalized.

3.53. We begin by drawing the conjugate base of each compound and comparing them:

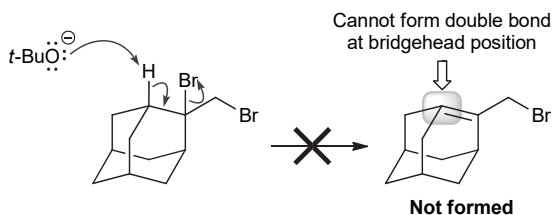




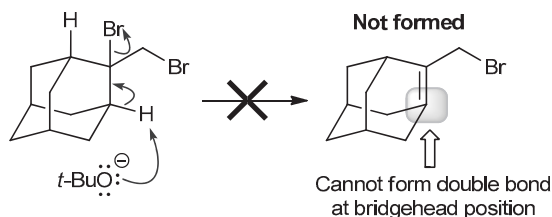
There are many β positions, but the base (*t*-butoxide) is sterically hindered, so we expect the Hofmann product (deprotonation of the less hindered beta hydrogen):



Regarding the other β positions, Bredt's Rule states that it is highly unlikely for a C–C double bond to be formed at a bridgehead carbon of a bicyclic system such as the one shown.



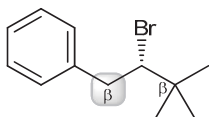
The same is true regarding deprotonation at the other beta position:



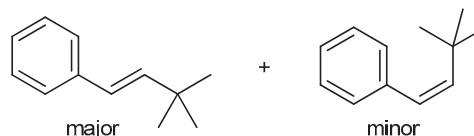
As a result, this reaction affords only one product.

7.21.

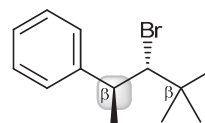
(a) The substrate has two β positions, but only one of these positions (highlighted) bears protons.



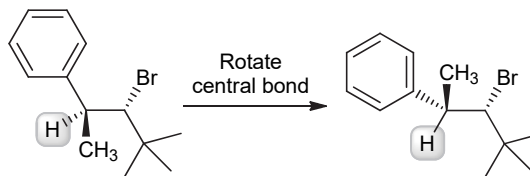
This β position has two protons, so the reaction will be stereoselective. That is, we expect both *cis* and *trans* isomers, with a preference for the *trans* isomer.



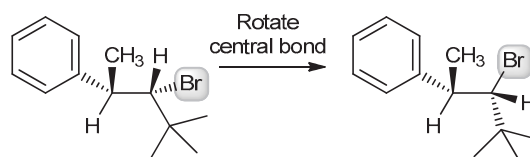
(b) The substrate has two β positions, but only one of these positions (highlighted) bears a proton.



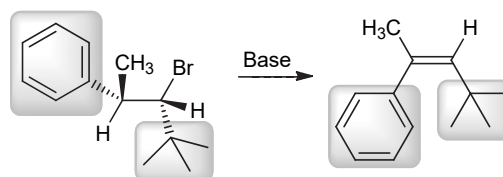
This β position has only one proton, so the reaction will be stereospecific. That is, only one particular stereoisomeric product will be obtained. To determine which product to expect, we must rotate the central C–C bond so that the β proton is *anti*-periplanar to the leaving group. We will do so in two stages. First, we rotate the central C–C bond in a manner that places the β proton in the plane of the page (rather than on a dash):



Then, we rotate the central C–C bond again, in a manner that places the leaving group (Br) in the plane of the page:

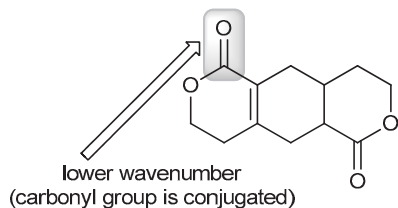


In this conformation, the proton and the leaving group are *anti*-periplanar. To draw the product, use the wedges and dashes as guides. In this case, the *tert*-butyl group and the phenyl group are both on wedges, so they will be *cis* to each other in the product:

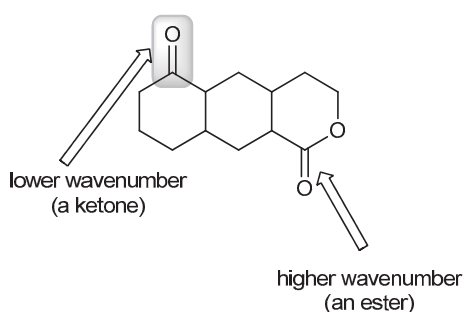


(c) The substrate has two β positions, but only one of these positions (highlighted) bears a proton.

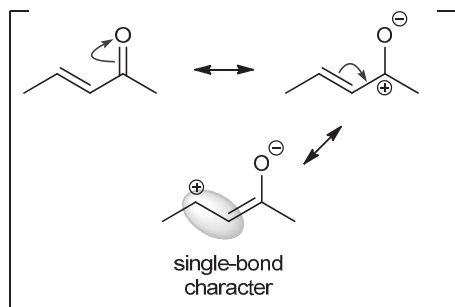
approximately 1740 cm^{-1} . The other carbonyl group (upper left) is conjugated to a $\text{C}=\text{C}$ π bond, so it is expected to produce a signal at approximately 1710 cm^{-1} .



(c) The carbonyl group of a ketone is expected to produce a signal at approximately 1720 cm^{-1} , while the carbonyl group of an ester is expected to produce a signal at approximately 1740 cm^{-1} .

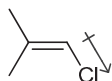


14.4. The $\text{C}=\text{C}$ π bond in the conjugated compound produces a signal at lower wavenumber (1600 cm^{-1}) because it has some single bond character, as seen in the third resonance structure below. This additional single bond character renders the $\text{C}=\text{C}$ π bond weaker (relative to the $\text{C}=\text{C}$ π bond of the other compound, which does not exhibit any single bond character).



14.5.

(a) The second compound has an electronegative chlorine atom, which withdraws electron density via induction.



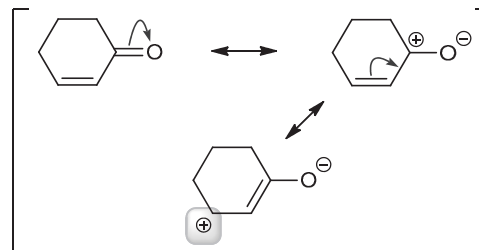
This causes the two vinylic positions to experience different electronic environments. The vinylic position connected directly to the chlorine atom is expected to be more electron-poor (δ^+) than the other vinylic position

(which is not directly connected to the chlorine atom). Therefore, the $\text{C}=\text{C}$ bond in this compound has a larger dipole moment than the $\text{C}=\text{C}$ bond in the other compound. As a result, we expect the chloroalkene to be more efficient at absorbing IR radiation (thereby producing a stronger signal).

(b) The $\text{C}=\text{C}$ bond in the compound shown below will have a larger dipole moment because one vinylic position is connected to two chlorine atoms while the other vinylic position is not directly connected to any chlorine atoms. As a result, the two vinylic positions are in very different electronic environments, giving rise to a large dipole moment. We therefore expect this $\text{C}=\text{C}$ bond to be more efficient at absorbing IR radiation (and therefore produce a stronger signal).

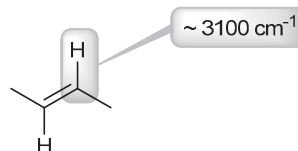


14.6. If we draw all significant resonance structures of 2-cyclohexenone, we see that one of the vinylic positions is electron-deficient (highlighted in the third resonance structure):



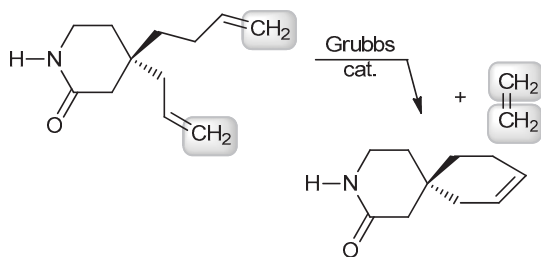
As a result, the two vinylic positions experience very different electronic environments, giving rise to a large dipole moment. With a large dipole moment, this $\text{C}=\text{C}$ bond is expected to be very efficient at absorbing IR radiation, thereby producing a strong signal.

14.7. The vinylic $\text{C}-\text{H}$ bond should produce a signal at approximately 3100 cm^{-1} .

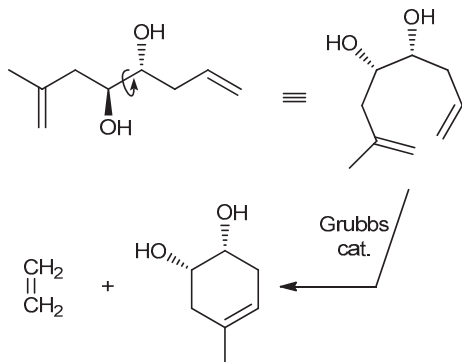


14.8. The narrow signal is produced by the $\text{O}-\text{H}$ stretching in the absence of a hydrogen bonding effect. The broad signal is produced by $\text{O}-\text{H}$ stretching when hydrogen bonding is present. Hydrogen bonding effectively lowers the bond strength of the $\text{O}-\text{H}$ bonds, because each hydrogen atom is slightly pulled away from the oxygen atom to which it is connected. A longer bond length (albeit temporary) corresponds with a weaker bond, which corresponds with a lower wavenumber.

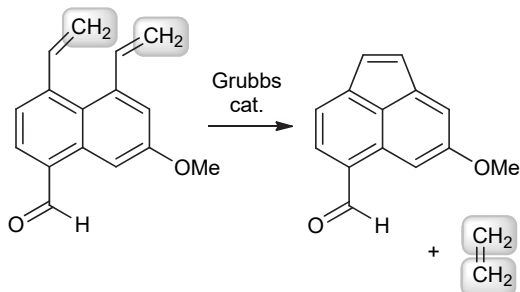
gas). We then draw a double bond between the remaining vinyl positions, giving the following product:



(b) The starting material has two C=C units that can undergo a ring-closing metathesis upon treatment with a Grubbs catalyst. To draw the metathesis product, we first redraw the starting material so that the C=C units are in close proximity. Then, we remove a methylene group from each C=C unit (these methylene groups ultimately combine to give ethylene gas). We then draw a double bond between the remaining vinyl positions, giving the following product:

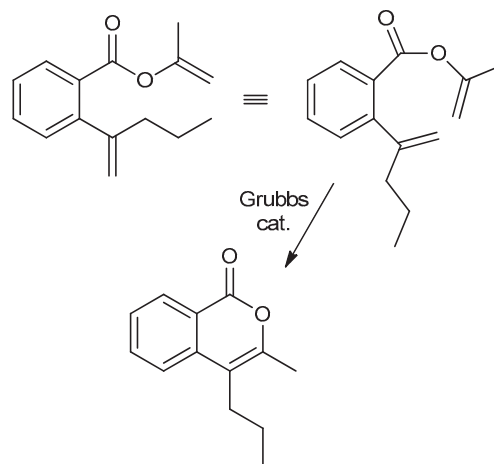


(c) The starting material has two C=C units that can undergo a ring-closing metathesis upon treatment with a Grubbs catalyst. To draw the metathesis product, we remove a methylene group from each C=C unit (these methylene groups ultimately combine to give ethylene gas). We then draw a double bond between the remaining vinyl positions, giving the following product:



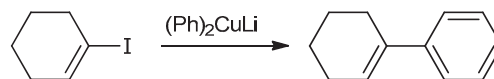
(d) The starting material has two C=C units that can undergo a ring-closing metathesis upon treatment with a Grubbs catalyst. To draw the metathesis product, we remove a methylene group from each C=C unit (these methylene groups ultimately combine to give ethylene

gas). We then draw a double bond between the remaining vinyl positions, giving the following product:

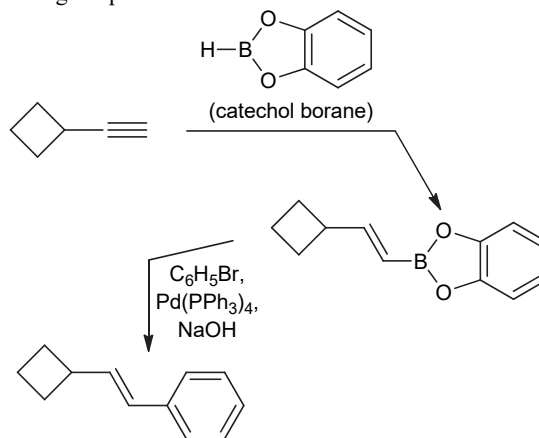


23.40.

(a) Lithium diphenyl cuprate is a Gilman reagent, and it will react with the following vinyl iodide to give a coupling product, as shown here:



(b) Upon treatment with catechol borane, the alkyne is converted into a vinyl boronic ester with the *E* configuration. This compound then serves as a coupling partner in a Suzuki coupling reaction with bromobenzene. The carbon atom connected directly to the bromine atom will be joined with the carbon atom connected directly to boron in the organoboron compound. Notice that the *E* configuration is preserved during the process:



(c) The starting materials are a vinyl iodide and a vinyl boronic ester, indicating a Suzuki coupling reaction. The carbon atom connected directly to the iodide group will be joined with the carbon atom connected directly to boron in the organoboron compound, giving the product shown. The coupling partners have been rotated in order to draw the coupling product more easily. Notice that