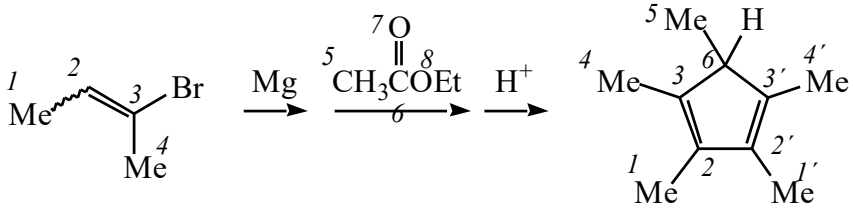
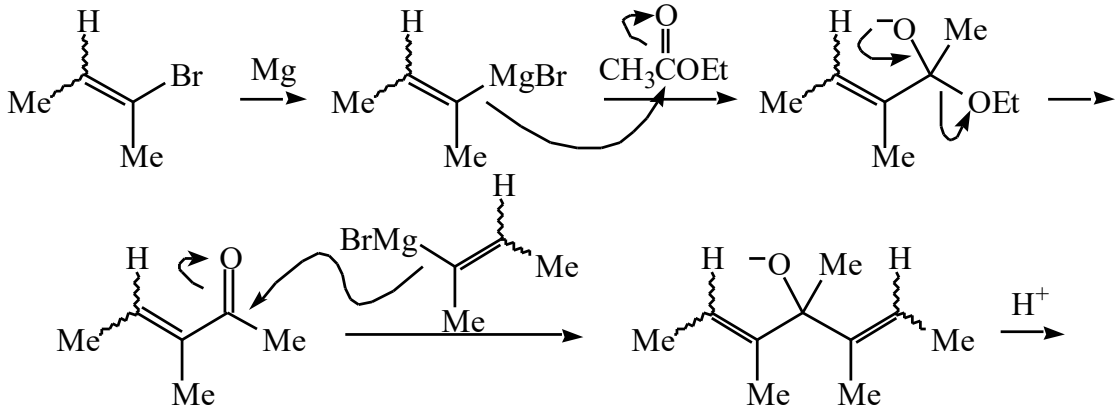
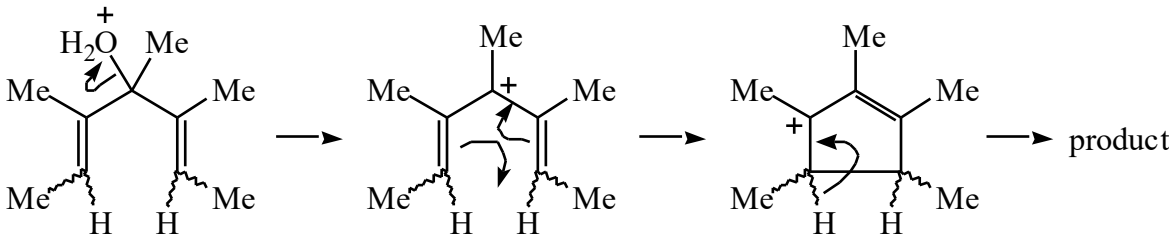
ANSWERS TO PROBLEMS IN BODY OF CHAPTER 4.

4.1. The numbering of the atoms is quite difficult in this problem. The number of Me groups in the product suggests that at least two equivalents of the bromide are incorporated into the product. But which ring atoms are C3 and which one is C6? And even if one of the ring carbons is arbitrarily chosen as C6, there is still the question of whether C3 or C2 becomes attached to C6. This problem is solved by noting that step 1 turns the bromide into a Grignard reagent, which is nucleophilic at C3, so it is likely to attack C6, and electrophilic atom. Make: C3–C6, C3′–C6, C2–C2′. Break: C6–O7, C6–O8, C3–Br, C3′–Br.

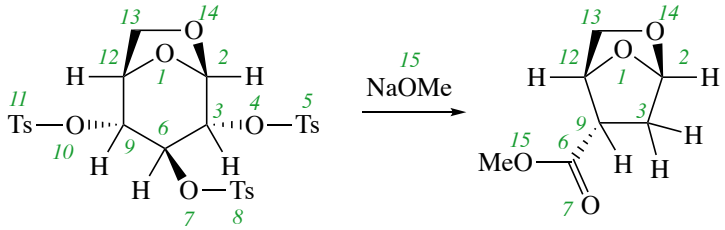


In the first step, the bromide is converted to a Grignard reagent. In the second step, two equivalents of the Grignard reagent react with the ester by addition–elimination–addition. (Remember, the ketone that is initially obtained from reaction of a Grignard reagent with an ester by addition–elimination is more electrophilic than the starting ester, so addition of a second Grignard reagent to the ketone to give an alcohol is faster than the original addition to give the ketone.) In the last step, addition of acid to the tertiary, doubly allylic alcohol gives a pentadienyl cation that undergoes electrocyclic ring closure. Loss of H^+ gives the observed product.

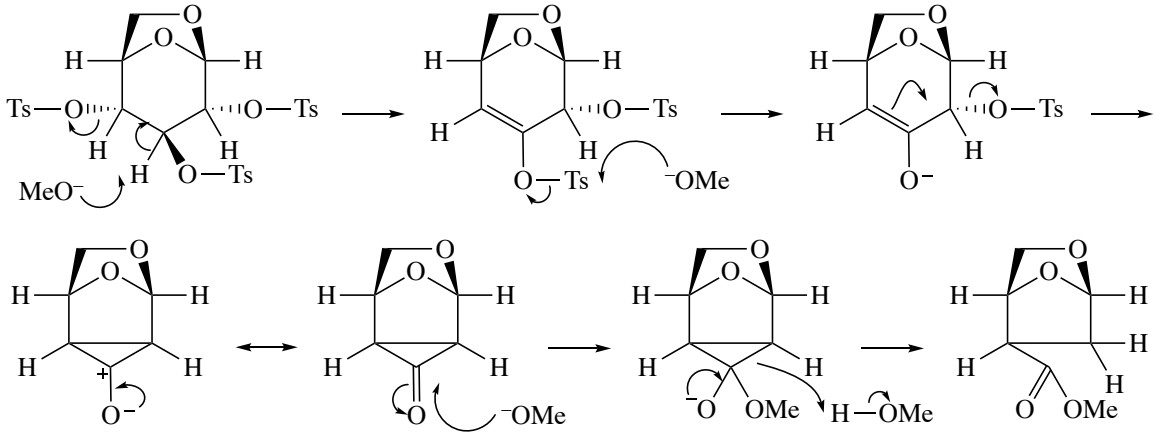




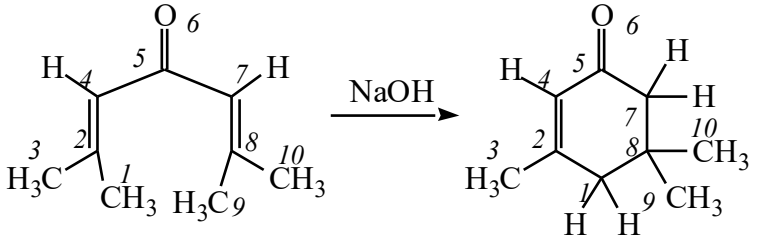
4.2. Make: C3–C9, C6–O15. Break: C3–O4, C3–C6, O7–Ts8, C9–O10. Note the somewhat unusual cleavage of the O7–Ts8 bond.



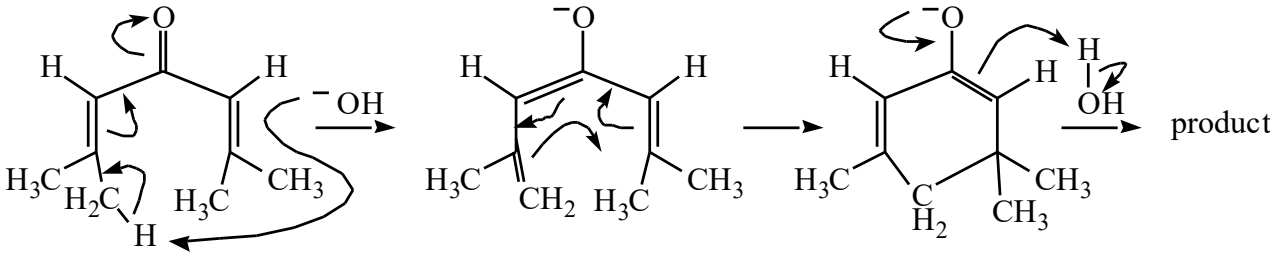
NaOMe is a base as well as a nucleophile, and OTs is a leaving group, so the ⁻OMe can promote E2 elimination of HOTs. (Either OTs group can be eliminated.) MeO⁻ can then attack Ts8 to cleave the C7–Ts8 bond and to give an enolate, the start of the Favorskii rearrangement. The enolate can undergo two-electron electrocyclic ring closing to give the cyclopropanone with a new C3–C9 bond, and addition of MeO⁻ to the carbonyl C followed by C3–C6 bond cleavage with concerted protonation of C3 gives the product.



4.3. Make: C1–C8. Break: none.

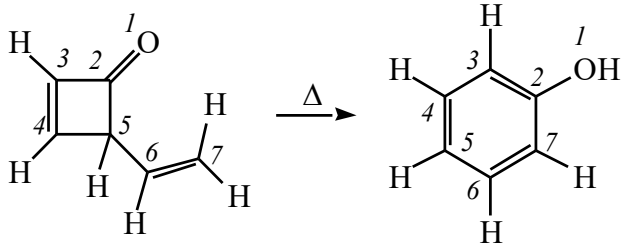


Deprotonation of C1 gives an enolate ion, which in this compound is actually a 1,3,5-hexatriene. As such it can undergo an electrocyclic ring closing. Protonation gives the product.

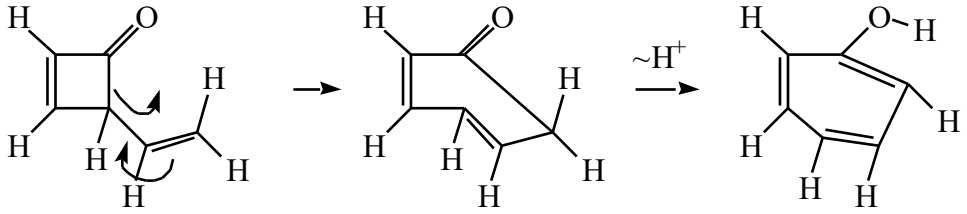


You may have been tempted to draw the C1–C8 bond-forming reaction as a conjugate addition. However, once C1 is deprotonated, the carbonyl group is no longer electrophilic, because it is busy stabilizing the enolate. It is much more proper to think of the bond-forming reaction as an electrocyclic ring closure. This problem illustrates why it is so important to consider *all* the resonance structures of any species.

4.4. Make: C2–C7. Break: C2–C5.

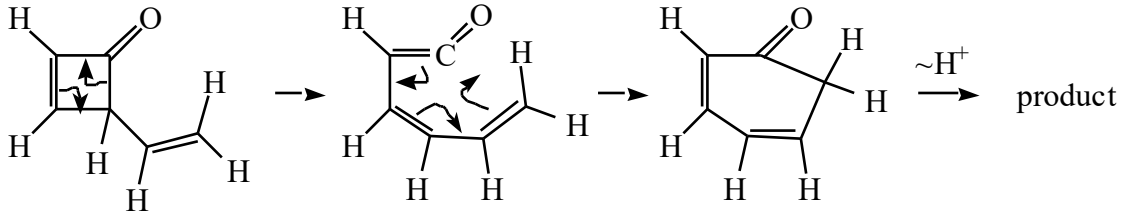


You may be very tempted to draw the following mechanism for the reaction:

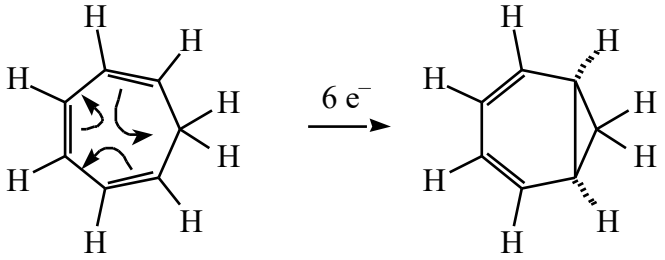


However, this mechanism is not correct. It is a [1,3]-sigmatropic rearrangement, and for reasons which are discussed in Section 4.4.2, [1,3]-sigmatropic rearrangements are very rare under thermal conditions. A much

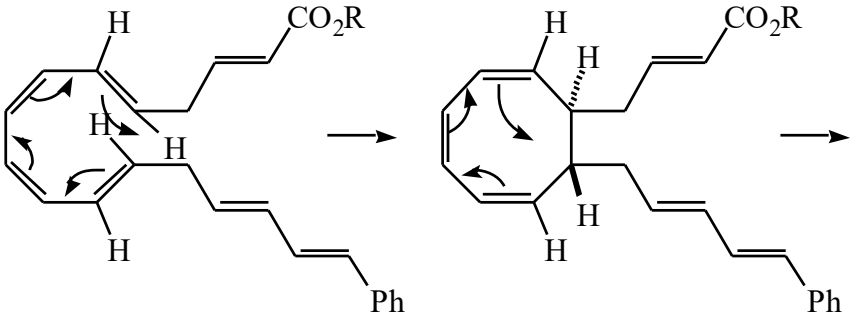
better mechanism can be written. The C2–C5 bond is part of a cyclobutene, and cyclobutenes open very readily under thermal conditions. After the electrocyclic ring opening, a 1,3,5-hexatriene is obtained, and these compounds readily undergo electrocyclic ring closure under thermal conditions. Tautomerization then affords the product.

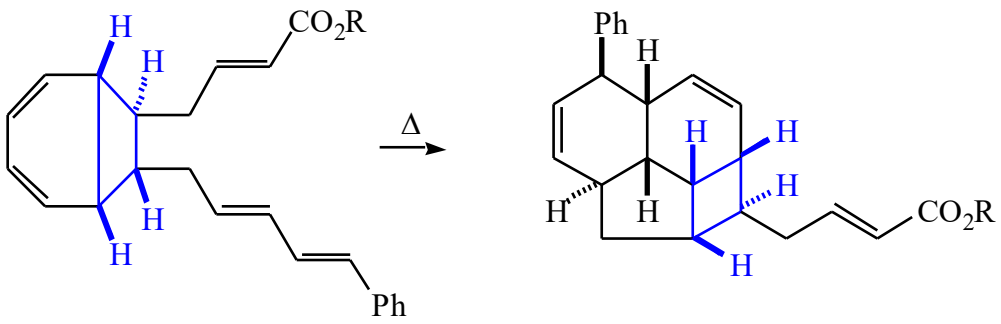


4.5. The product has a cis ring fusion.

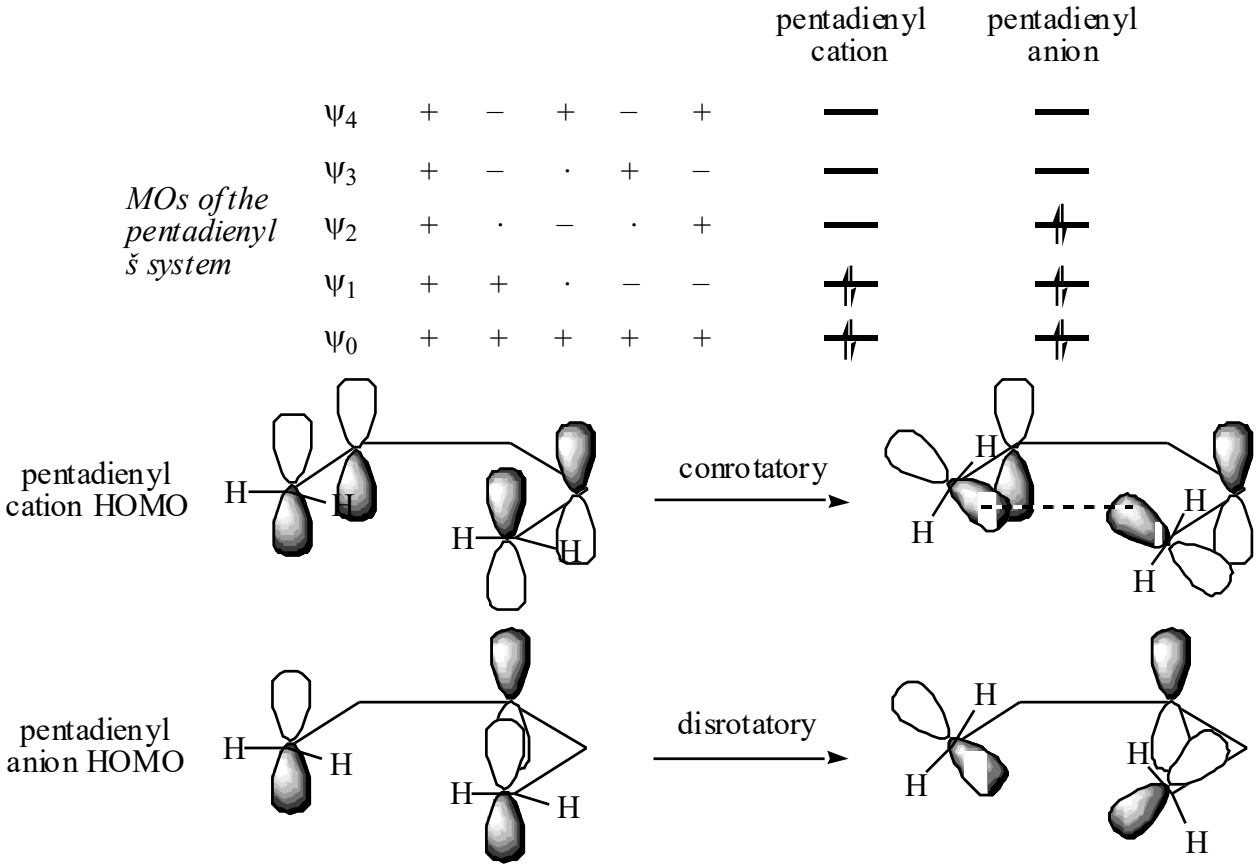


4.6. The first electrocyclic ring closure involves eight electrons, so it is conrotatory under thermal conditions, and the two hydrogen atoms at the terminus of the tetraene, which are both in, become trans. The second electrocyclic ring closure involves six electrons, so it is disrotatory under thermal conditions, and the two hydrogen atoms at the terminus of the triene, which are both out, become cis. This is the arrangement observed in the natural product.

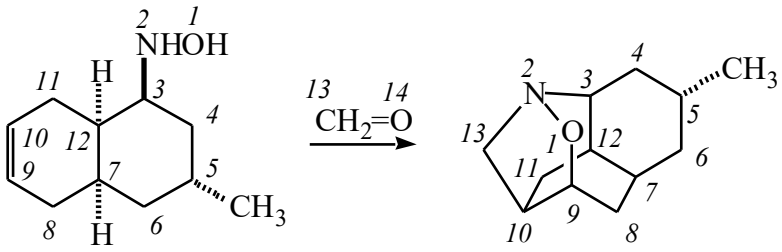




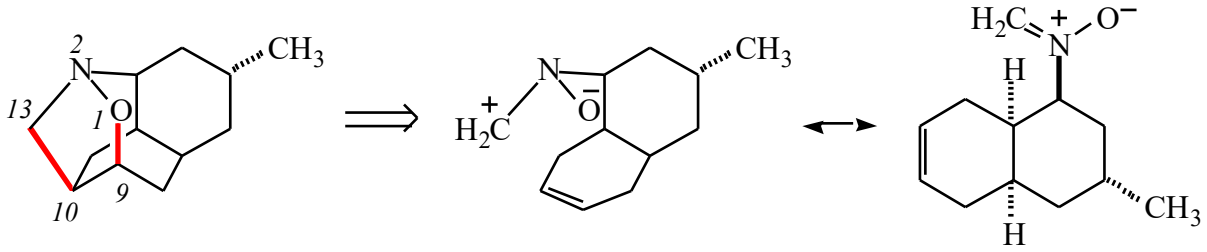
4.7. The HOMO of the pentadienyl cation is ψ_1, which is antisymmetric, so a conrotatory ring closure occurs, consistent with the four electrons involved in this reaction. The HOMO of the pentadienyl anion is ψ_2, which is symmetric, so a disrotatory ring closure occurs, consistent with the six electrons involved in this reaction.



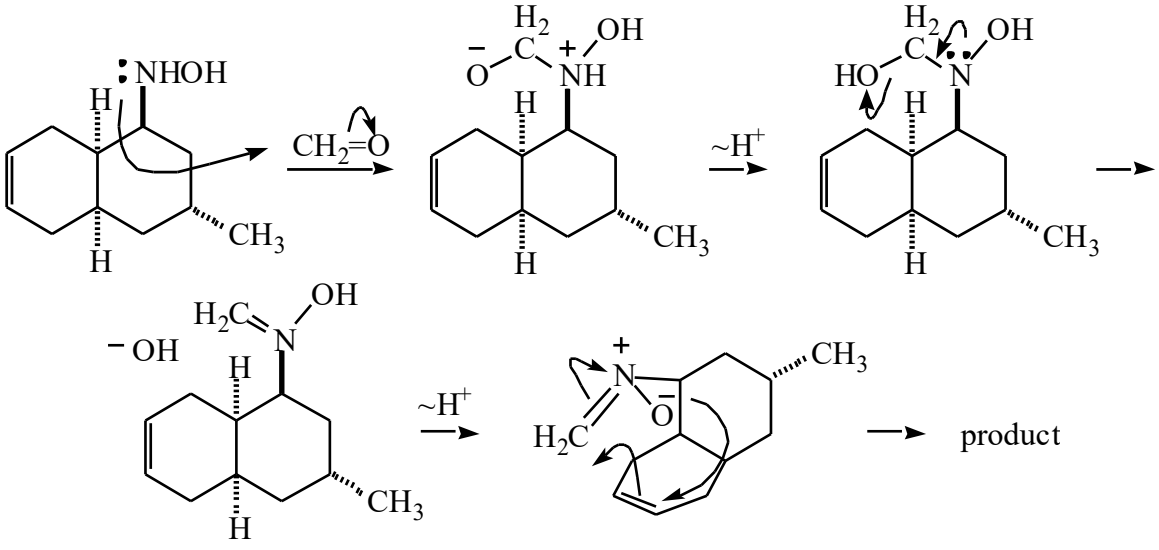
4.8. Make: O1–C9, N2–C13, C10–C13. Break: C13–O14.



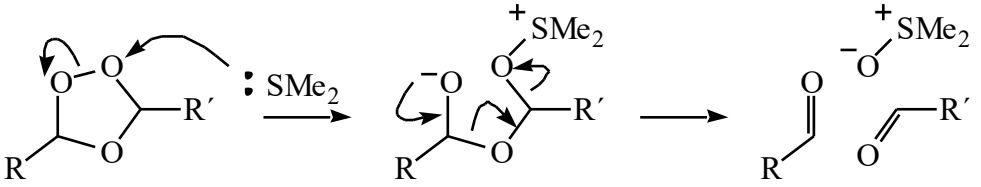
The new five-membered, heterocyclic ring clues you in to the fact that a 1,3-dipolar cycloaddition has occurred here to form bonds O1–C9 and C10–C13. Disconnect these bonds, putting a + charge on C13 and a – charge on O1, to see the immediate precursor to the product.



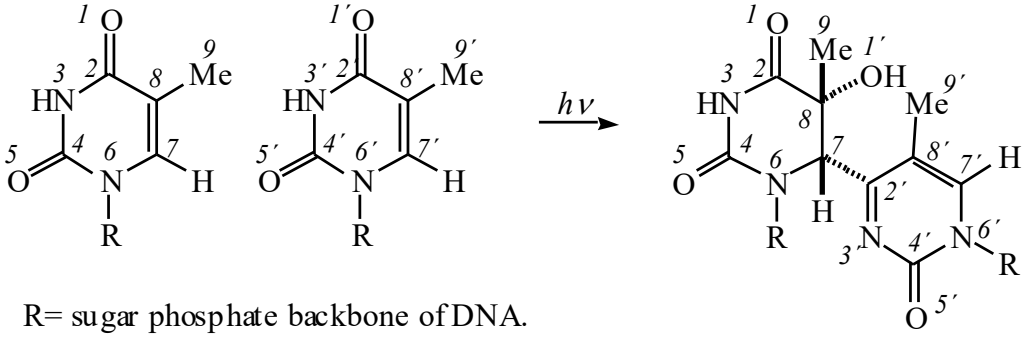
When this disconnection is written in the forward direction along with some curved arrows, it is the last step in the reaction. Now all you have to do is make N2–C13 and break C13–O14. This is easy to do: N2 attacks C13, proton transfer occurs, N2 expels O14, and deprotonation gives the nitrone.



4.9. Me_2S attacks one of the O atoms involved in the O–O bond, displacing O^-. Hemiacetal collapse to the carbonyl compounds then occurs.

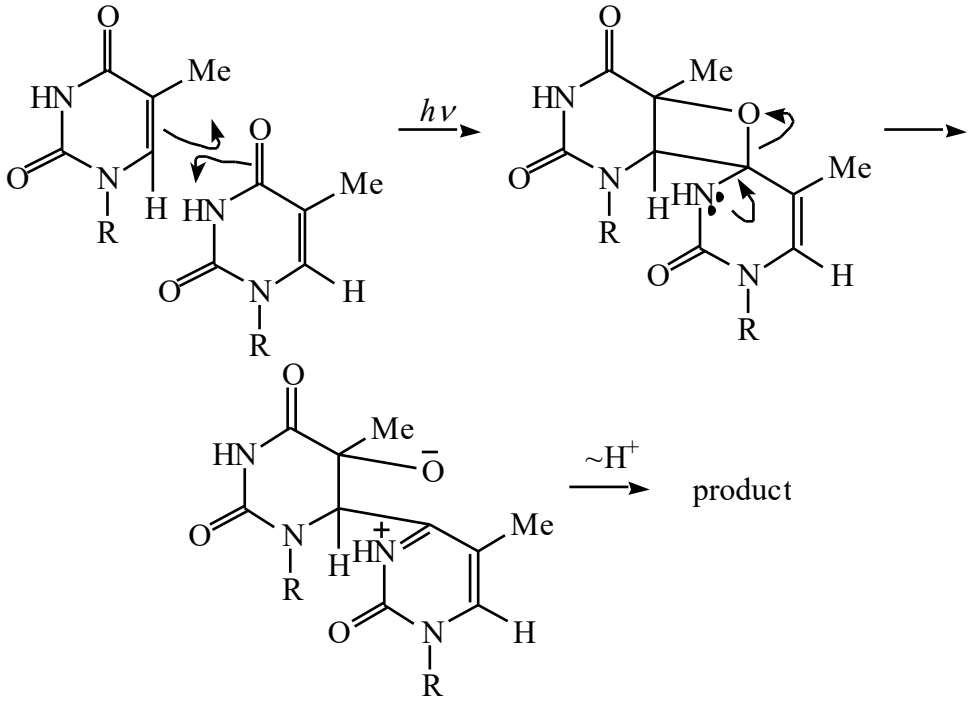


4.10. Make: C7–C2′, C9–O1′. Break: C2′–O1′.

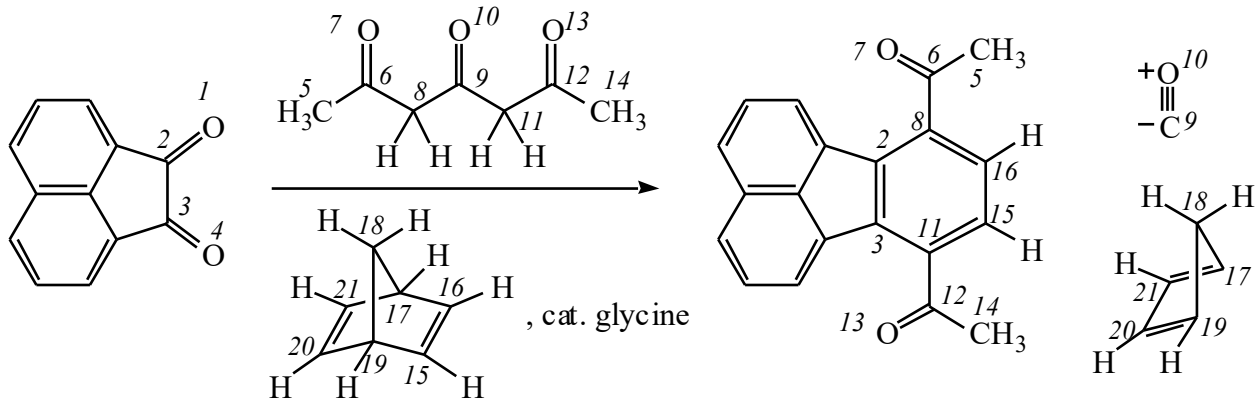


R= sugar phosphate backbone of DNA.

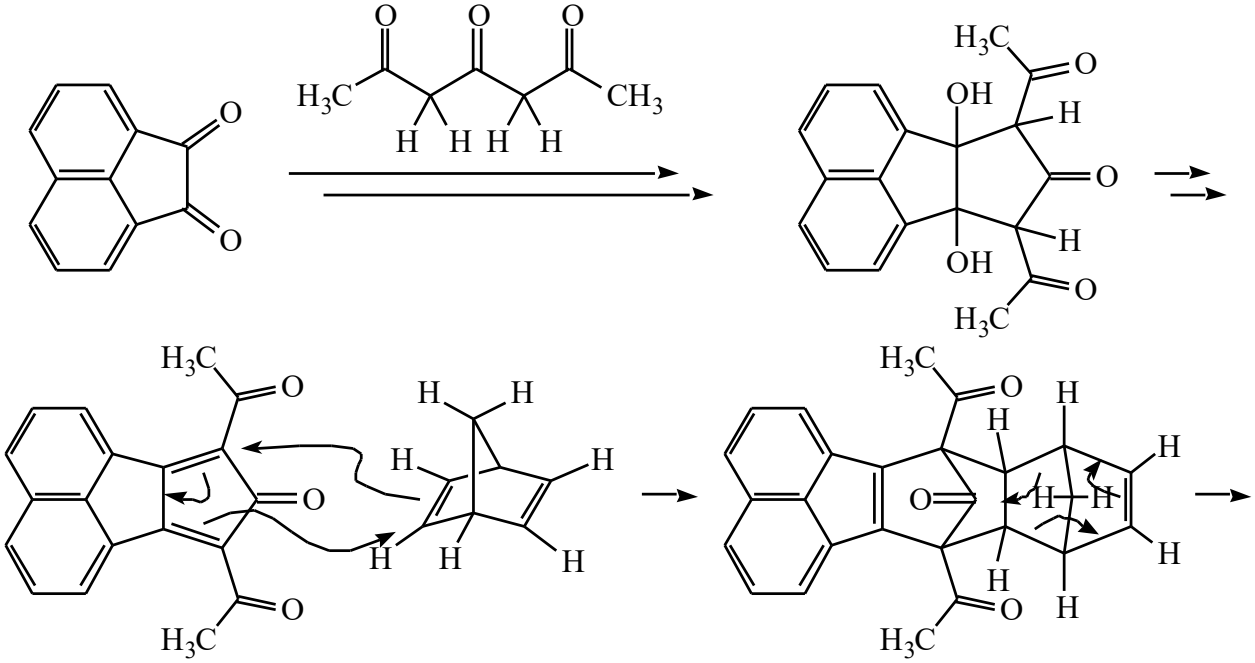
Making the C7–C2′ and C9–O1′ suggests a [2 + 2] photocycloaddition. Then the lone pair on N3′ expels O1′ from C2′ to give the observed product (after proton transfer).

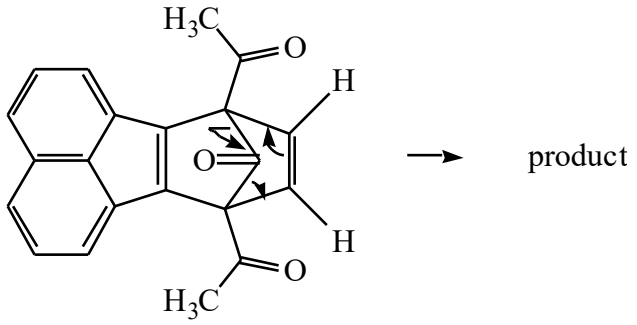


4.11. The numbering is not straightforward in this reaction, but if you draw in the H atoms you can see that the two CH groups in the new benzene ring in the product probably come from two CH groups in norbornadiene. Atoms unaccounted for in the written product include C9 and O10 (can be lost as CO), C17 to C21 (can be lost as cyclopentadiene), and O1 and O4 (can be lost as H_2O). Make: C2–C8, C3–C11, C8–C16, C11–C15. Break: O1–C2, C3–O4, C8–C9, C9–C11, C15–C19, C16–C17.

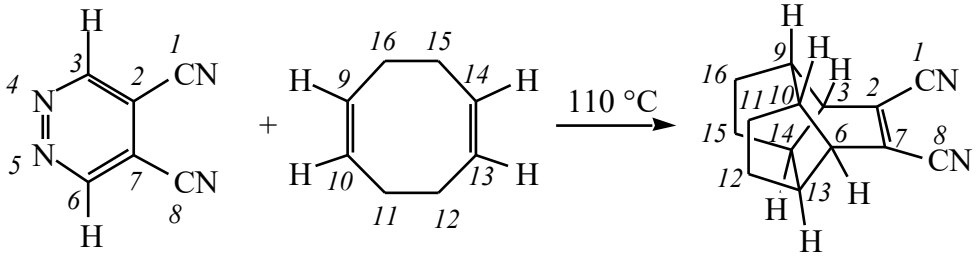


Glycine acts as an acid–base catalyst in this reaction. C8 and C11 are very acidic, and once deprotonated they are very nucleophilic, so they can attack C2 and C3 in an aldol reaction. Dehydration gives a key cyclopentadienone intermediate. (The mechanism of these steps is not written out below.) Cyclopentadienones are antiaromatic, so they are very prone to undergo Diels–Alder reactions. Such a reaction occurs here with norbornadiene. A retro-Diels–Alder reaction followed by a [4 + 1] retrocycloaddition affords the product.

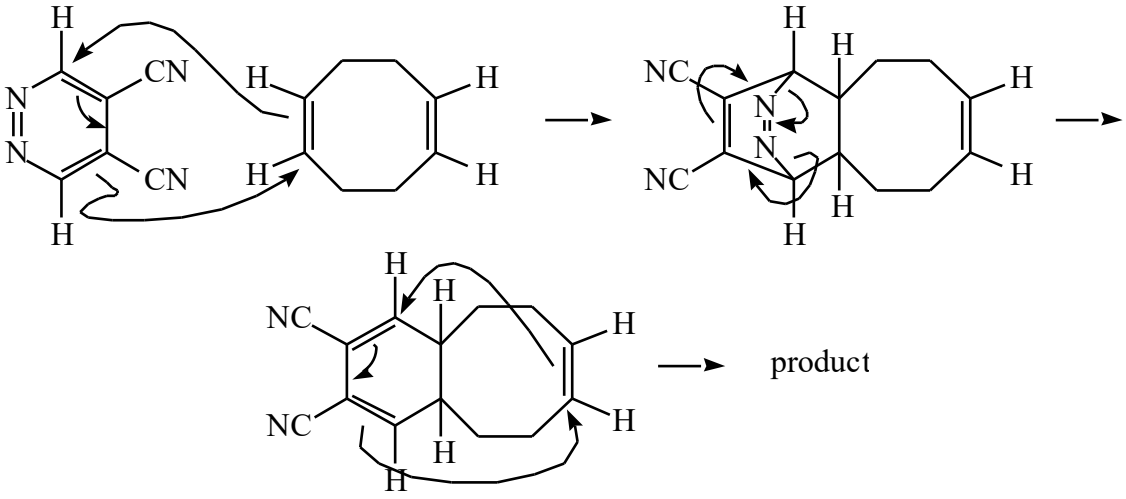




4.12. Make: C3–C9, C3–C14, C6–C10, C6–C13. Break: C3–N4, N5–C6.

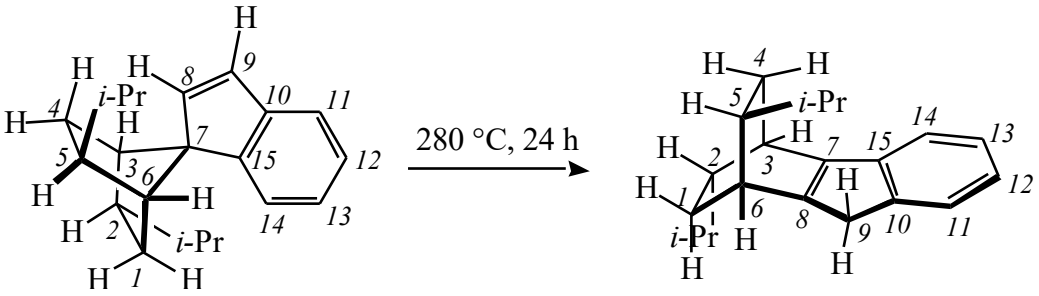


The C3–C9 and C6–C10 bonds can be made by a Diels–Alder reaction. Then loss of N_2 and cleavage of the C3–N4 and N5–C6 bonds can occur by a retro-Diels–Alder reaction. This step regenerates a diene, which can undergo another, intramolecular Diels–Alder reaction with the C13–C14 π bond to give the product.

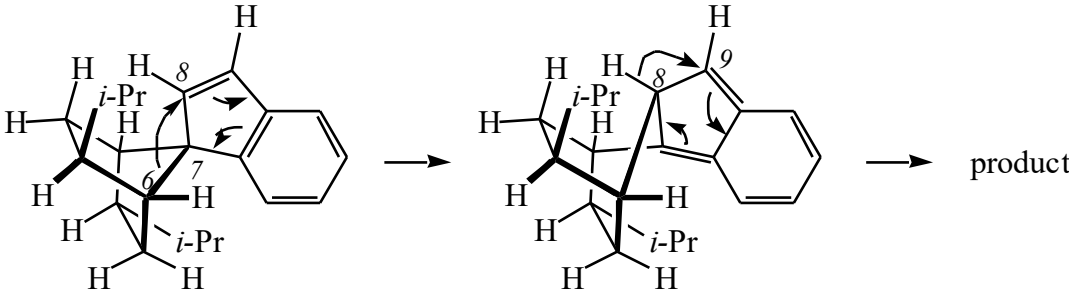


4.13. The [6+4] cycloaddition involves five pairs of electrons (an odd number), so it is thermally allowed. The [4+3] cationic cycloaddition involves three pairs of electrons, so it is also thermally allowed.

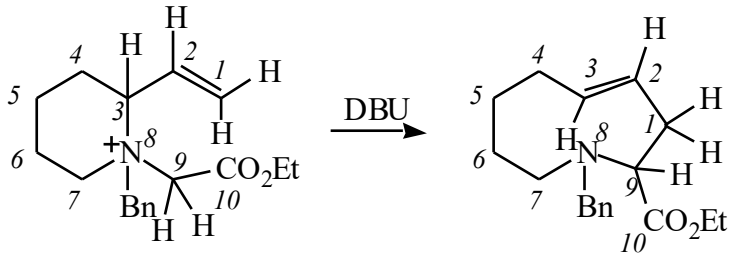
4.14. Make: C6–C8. Break: C6–C7.



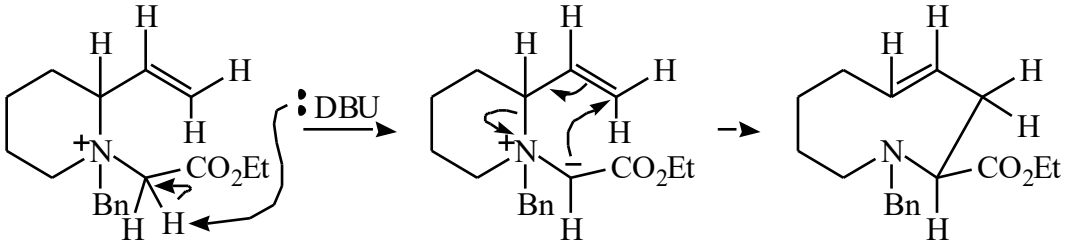
Making and breaking bonds to C6 suggests a [1,n] sigmatropic rearrangement, and a [1,5] sigmatropic rearrangement, one of the most common types, is possible here. Once the rearrangement is drawn, however, the mechanism is not complete, even though all bonds on the make & break list have been crossed off. C8 still has one extra H and C9 has one too few. Both these problems can be taken care of by another [1,5] sigmatropic rearrangement. This step, by the way, reestablishes the aromatic ring.



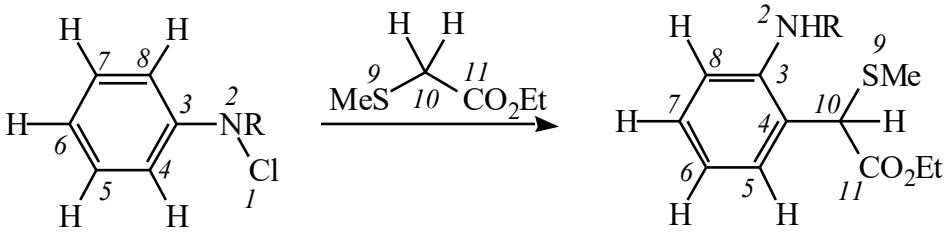
4.15. Make: C1–C9. Break: C3–N8.



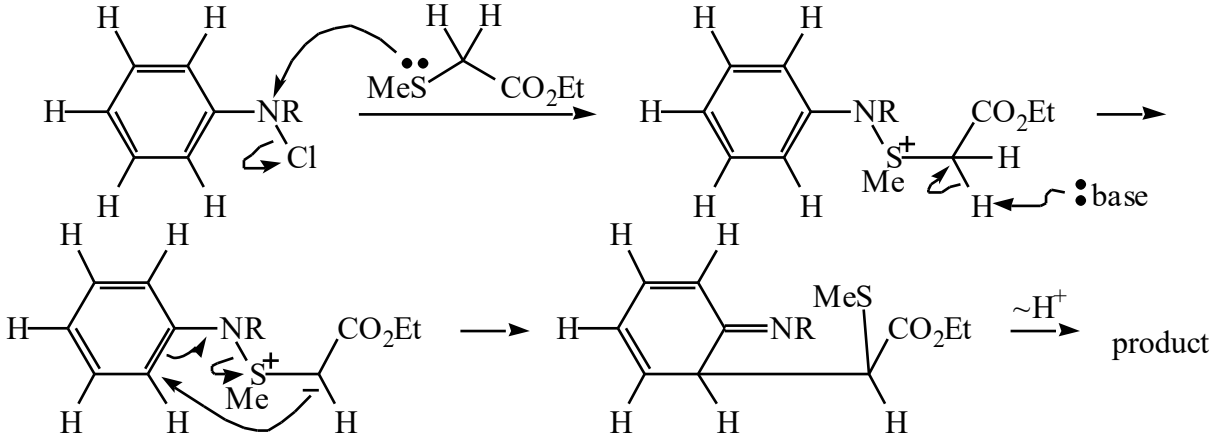
Deprotonation of C9 by DBU gives an ylide (has positive and negative charges on adjacent atoms that cannot quench each other with a π bond), a compound which is particularly prone to undergo [2,3] sigmatropic rearrangements when an allyl group is attached to the cationic center, as is the case here. Esters are not normally acidic enough to be deprotonated by DBU, but in this ester the N^+ stabilizes the enolate by an inductive effect.



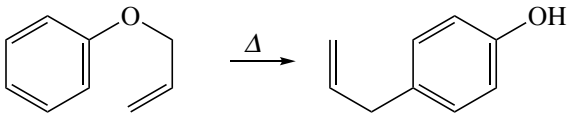
4.16. Make: C4–C10. Break: Cl1–N2.



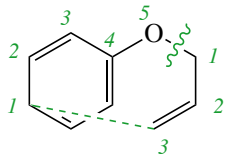
The most unusual bond in this system is the N–Cl bond. The nucleophilic substitution step must involve cleavage of this bond. No base is present, but S is an excellent nucleophile, even in its neutral form, so the first step probably entails formation of an S9–N2 bond. Now we have to make the C4–C10 bond and make the S9–N2 bond. Deprotonation of C4 gives an ylide, which as discussed in problem 4.15 is likely to undergo a [2,3] sigmatropic rearrangement. Tautomerization to rearomatize then gives the product.



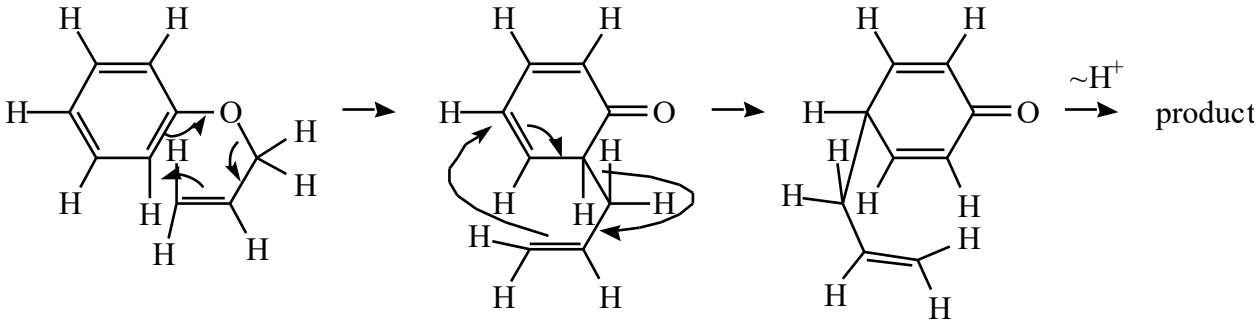
4.17. The reaction in question is:



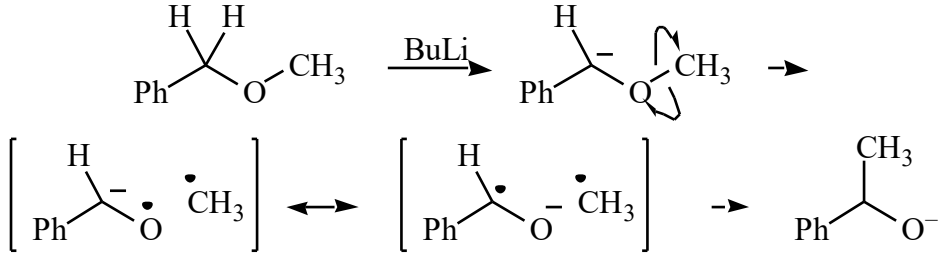
To name the reaction, draw a dashed line where the new bond is made, draw a squiggly line across the bond that is broken, and count the number of atoms from the termini of the dashed bond to the termini of the squiggly bond.



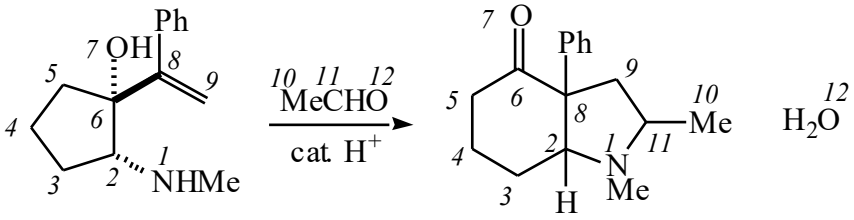
This reaction would be a [3,5] sigmatropic rearrangement, an eight-electron reaction, and hence would require that one component be antarafacial. Not likely! A more reasonable mechanism begins with the same [3,3] sigmatropic rearrangement that gives 2-allylphenol. However, instead of tautomerization to give the aromatic product, a second [3,3] sigmatropic rearrangement occurs. Then tautomerization gives the product.



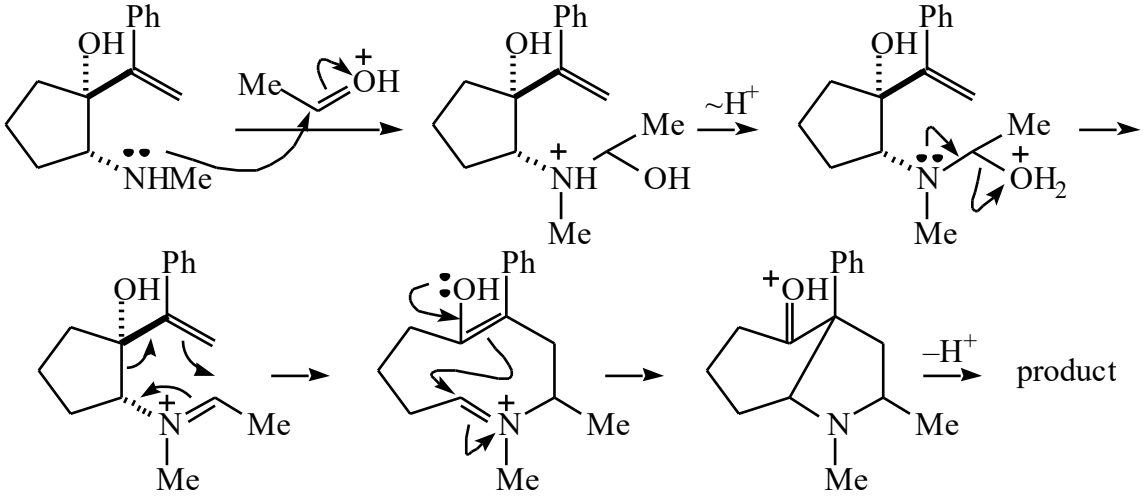
4.18. Both the Stevens rearrangement and the nonallylic Wittig rearrangement begin with deprotonation of the C atom next to the heteroatom followed by an anionic [1,2] sigmatropic rearrangement. Both involve four electrons, an even number of electron pairs, and hence if either is concerted then one of the two components of the reaction must be antarafacial. This condition is extremely difficult to fulfill, and hence it is much more likely that both reactions are nonconcerted. Both the Stevens rearrangement and the nonallylic Wittig rearrangement are thought to proceed by homolysis of a C–S or C–O bond and recombination of the C radical with the neighboring C atom.



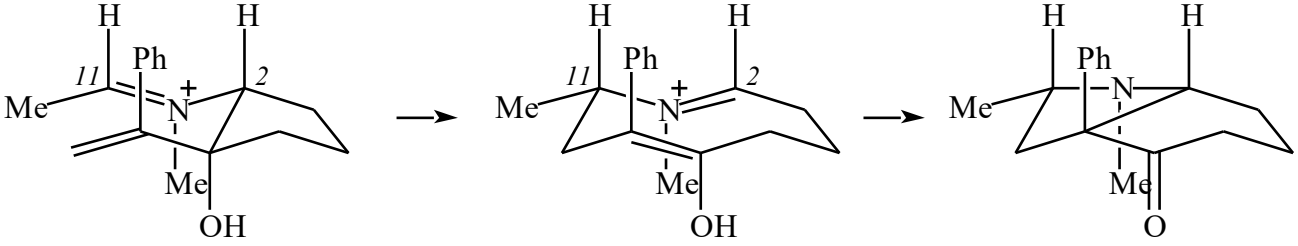
4.19. Make: N1–C11, C2–C8. Break: C2–C6, C11–O12.



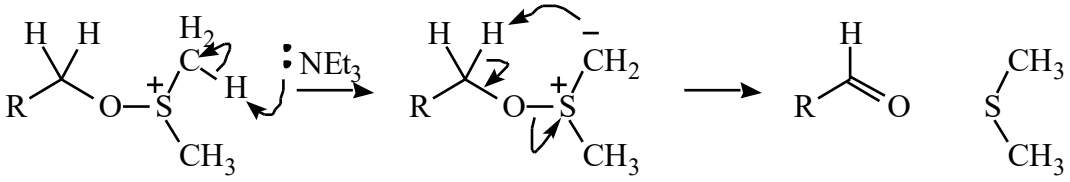
The N1–C11 bond is easily made first. Cleavage of the C11–O12 bond gives an iminium ion that is also a 1,5-(hetero)diene. The Cope rearrangement occurs to give a new iminium ion and an enol. Attack of the enol on the iminium ion (the Mannich reaction) affords the product.



Now the stereochemistry. Assume the thermodynamically more stable iminium ion forms (Me groups cis). The Cope rearrangement occurs from a chair conformation. This puts the Ph, H2, and H11 all pointing up both before and after the rearrangement. Assuming the Mannich reaction occurs without a change in conformation (a reasonable assumption, considering the proximity of the nucleophilic and electrophilic centers), the Ph, H2, and H11 should all be cis in the product.



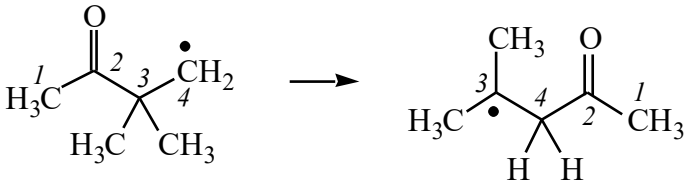
4.20. Deprotonation of one of the Me groups adjacent to S gives an ylide which can undergo a retro-hetero-ene reaction to give the observed products.



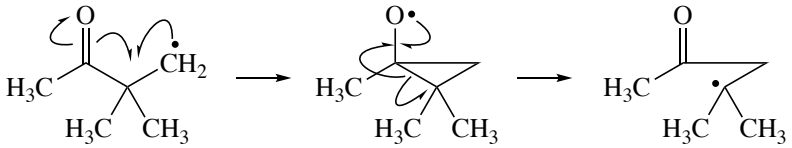
If $(CD_3)_2SO$ (deuterated DMSO) is used for the Swern reaction, the E2 mechanism predicts that the sulfide product should be $(CD_3)_2S$; the retro-hetero-ene mechanism predicts that it should be $(CD_3)S(CHD_2)$. Guess which product is actually found?

ANSWERS TO PROBLEMS IN BODY OF CHAPTER 5.

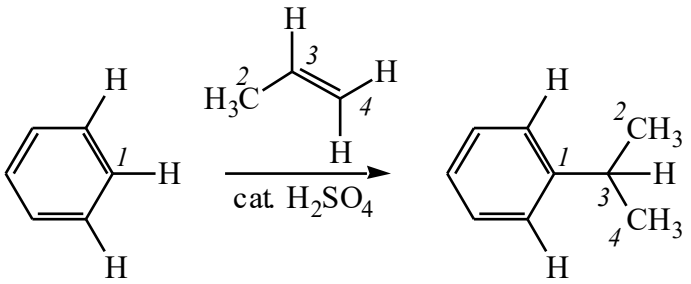
5.1. Make: C2–C4. Break: C2–C3.



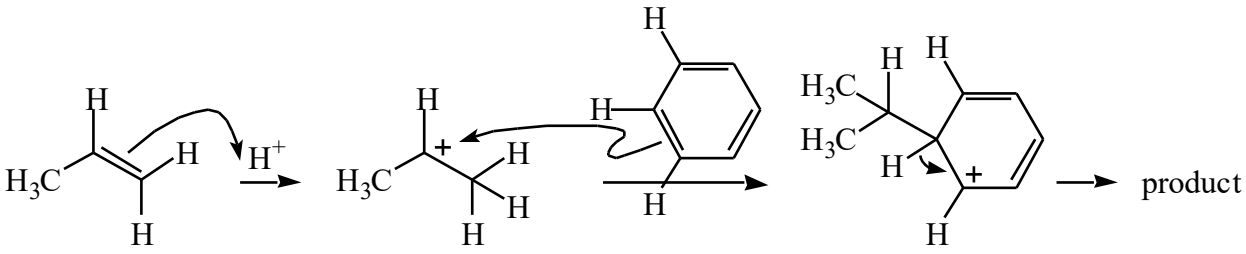
If this compound were not a radical, you might suspect a [1,2] sigmatropic rearrangement. However, radicals do not undergo such rearrangements. The C4 radical can make a bond to C2 by adding to the π bond. Then the C3–C2 bond can break by fragmentation.



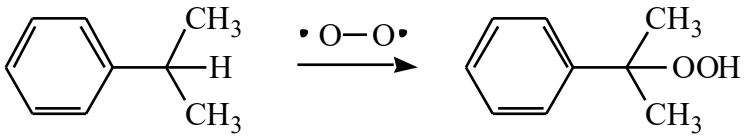
5.2. Step 1. Make: C1–C3. Break: none.



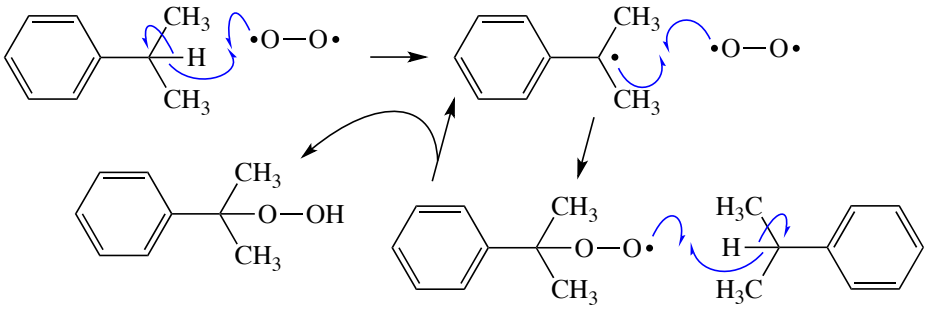
Note: This reaction involves a polar acidic mechanism, not a free-radical mechanism! It is a Friedel–Crafts alkylation, with the slight variation that the requisite carbocation is made by protonation of an alkene instead of ionization of an alkyl halide. Protonation of C4 gives a C3 carbocation. Addition to C1 and fragmentation gives the product.



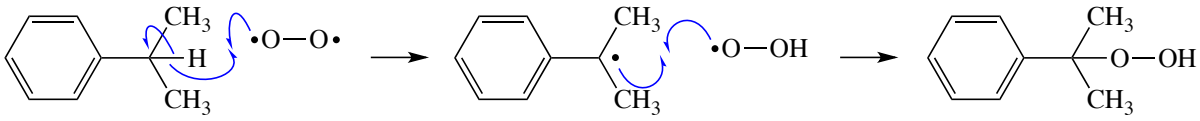
Step 2. Only a C–O bond is made.



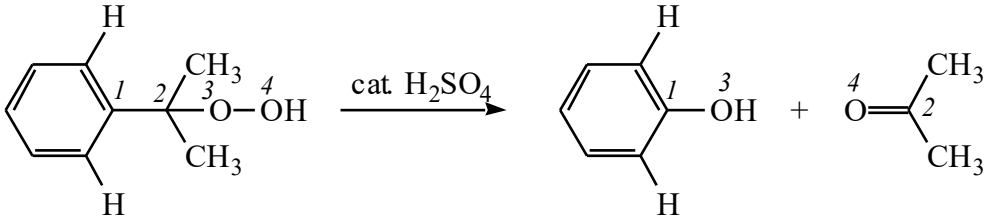
The presence of O_2 clues you in that this is a free-radical mechanism, specifically a free-radical substitution. Because it is an intermolecular substitution reaction, it probably proceeds by a chain mechanism. As such it has three parts: initiation, propagation, and termination. (We do not draw termination parts in this book.) The initiation part turns one of the stoichiometric starting materials into an odd-electron radical. This can be done here by abstraction of H· from C by O_2. The propagation part begins with the radical generated in the initiation part, and it continues until all the starting materials are converted into products. Every individual step in the propagation part must have an odd number of electrons on each side of the arrow, and the last step must regenerate the radical that was used in the first step. Here the C· radical combines with O_2 to give an O· radical, and this O· radical abstracts H· from starting material to regenerate the C· radical and to give the product.



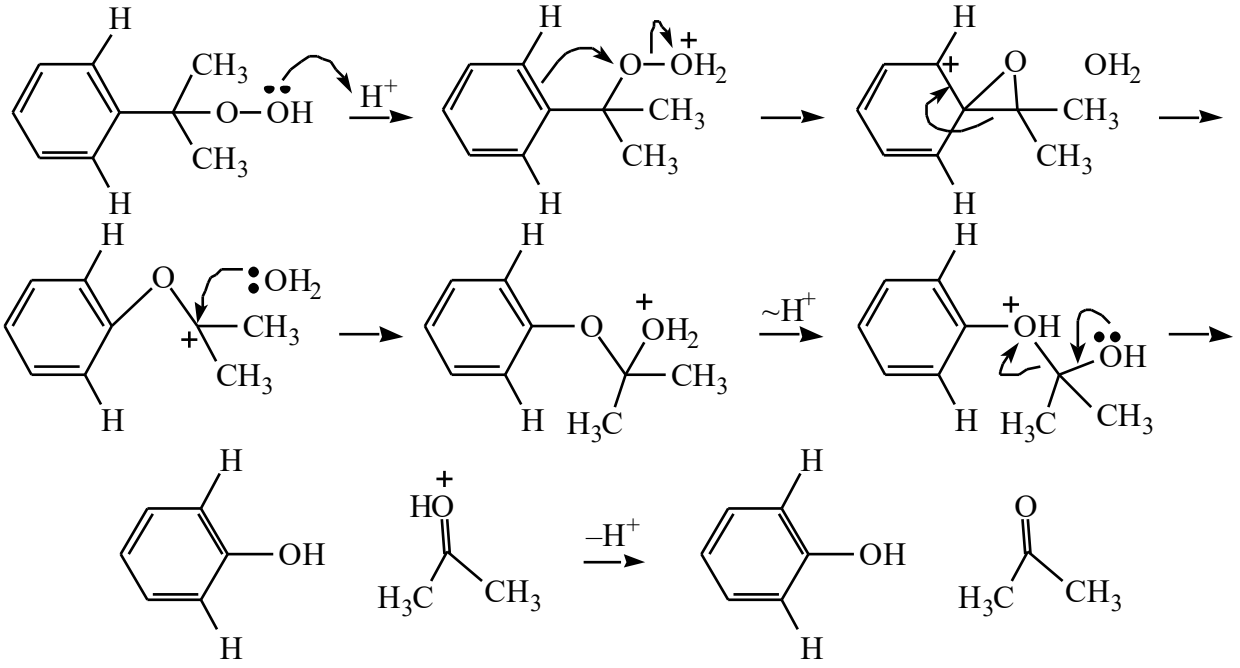
Although it is tempting to draw the following mechanism, the temptation should be resisted, because it is not a chain mechanism.



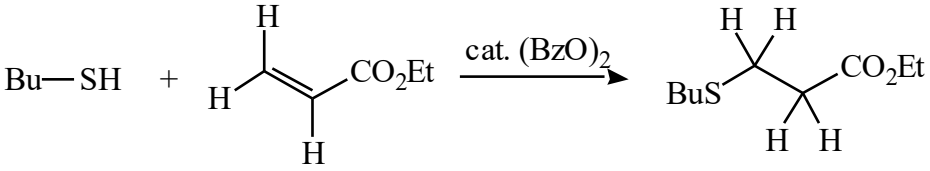
Step 3. The numbering of the atoms in this polar acidic mechanism is not straightforward, because it is not clear whether C1 ends up bound to O3 or O4. However, if it ends up bound to O3, then we can draw a 1,2-alkyl shift (break C1–C2, make C1–O3) with expulsion of a leaving group (break O3–O4). Then O4 can add to the new C2 carbocation, and the resulting hemiacetal can collapse to phenol and acetone.



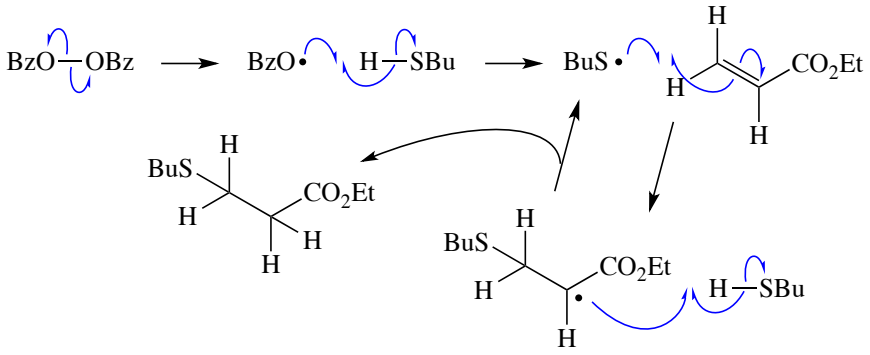
Actually, a two-step 1,2-alkyl shift has to be drawn, because Ph groups do not undergo concerted 1,2-shifts; instead their π bonds participate in an addition–fragmentation process.



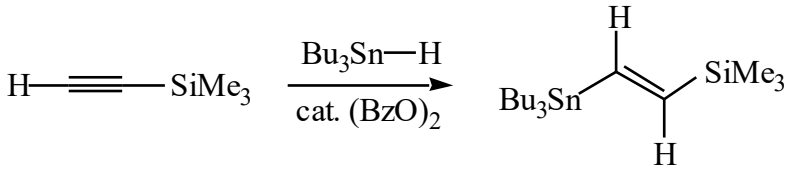
5.3. This addition reaction proceeds by a chain mechanism.



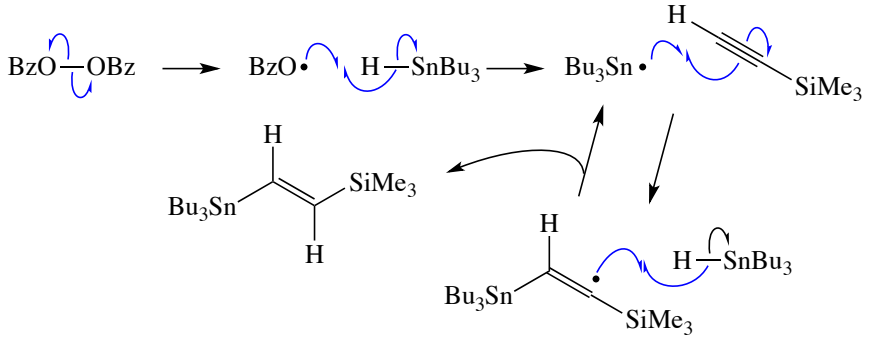
In the initiation part, one of the stoichiometric starting materials is converted into a free radical. The BzO· produced from $(BzO)_2$ can abstract H· from BuSH to give BuS·. In the propagation part, BuS· adds to the alkene to give an alkyl radical, which abstracts H· from BuSH to give the product and to regenerate the starting radical.



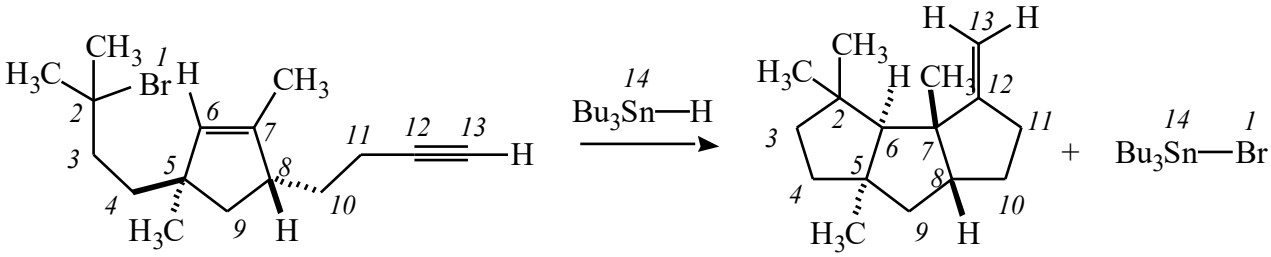
5.4. This addition reaction proceeds by a chain mechanism.



In the initiation part, the BzO· produced from $(BzO)_2$ can abstract H· from Bu_3SnH to give Bu_3Sn·. In the propagation part, Bu_3Sn· adds to the alkyne to give an alkenyl radical, which abstracts H· from Bu_3SnH to give the product and to regenerate the starting radical.

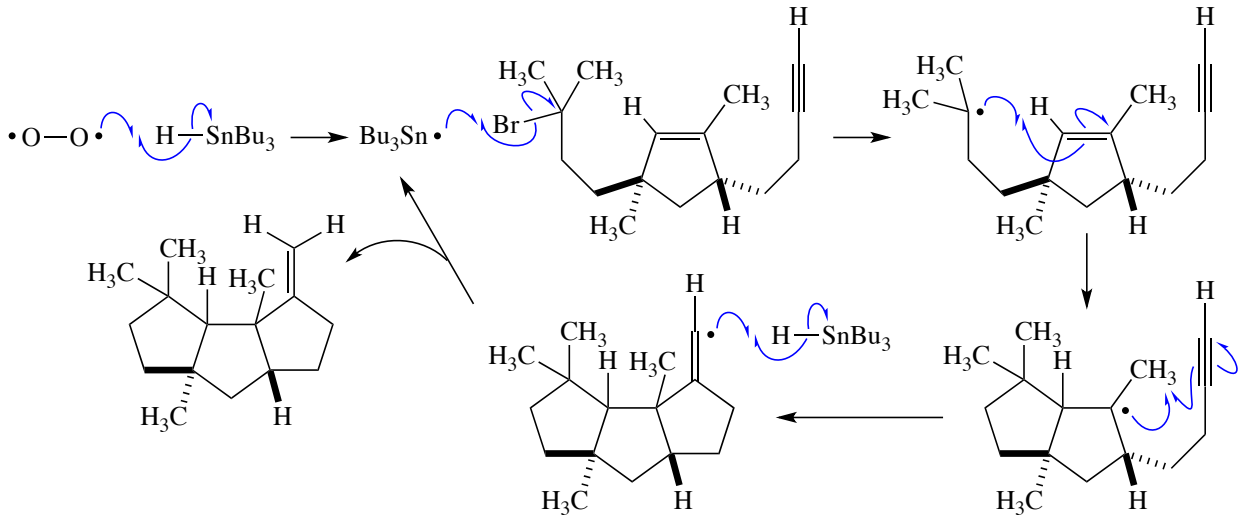


5.5(a). Make: Br1–Sn14, C2–C6, C7–C12. Break: Br1–C2.

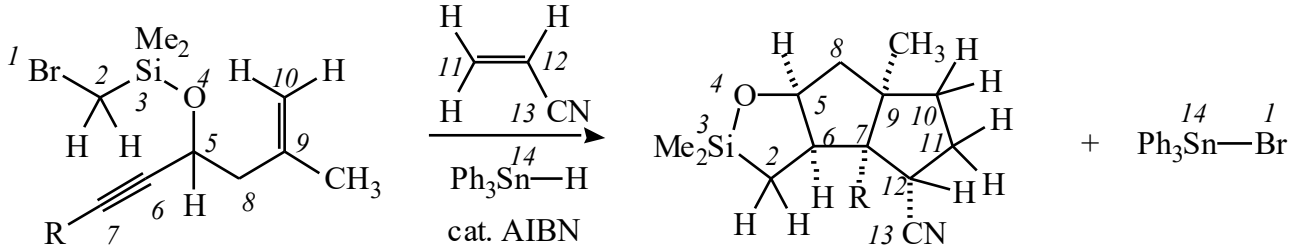


This is overall a substitution reaction — the C2–Br1 and Sn14–H σ bonds are swapped — so it is almost certainly a chain reaction. No initiator is listed, but it is likely that ambient air provides enough O_2 to abstract

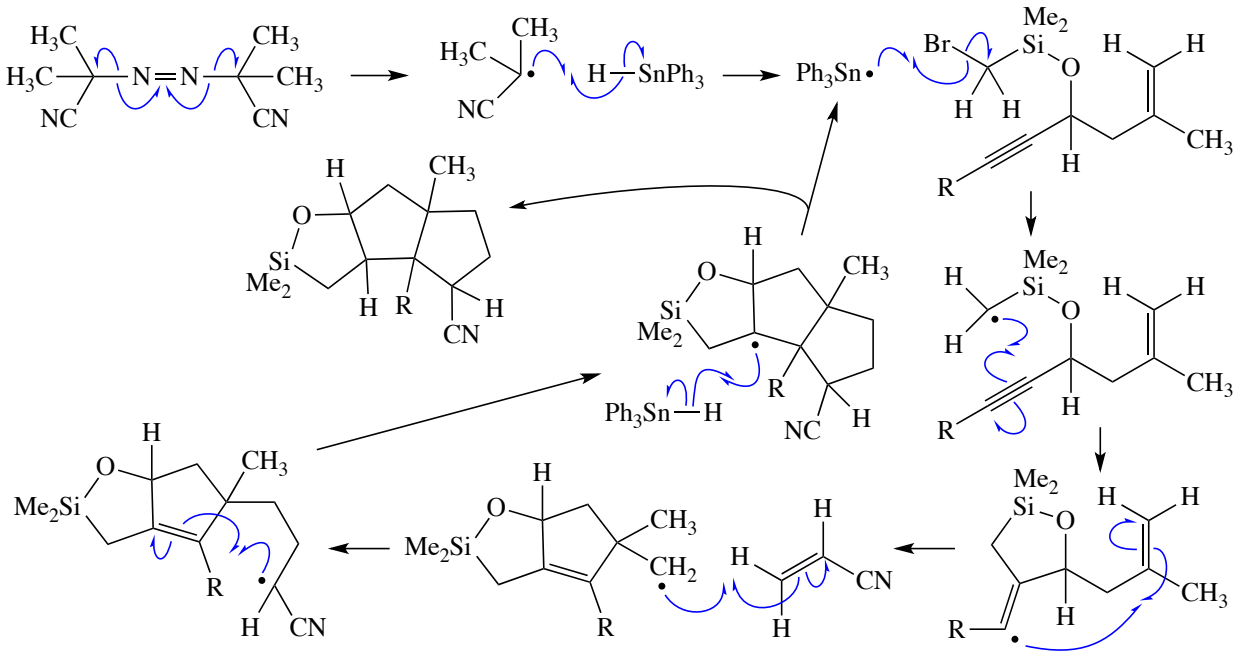
H· from Sn14. Bu_3Sn· abstracts Br1 from C2. The C2 radical then adds to C6 to give a C7 radical, which adds to C12 to give a C13 radical. The C13 radical abstracts H· from Bu_3SnH to give the product and regenerate Bu_3Sn·.



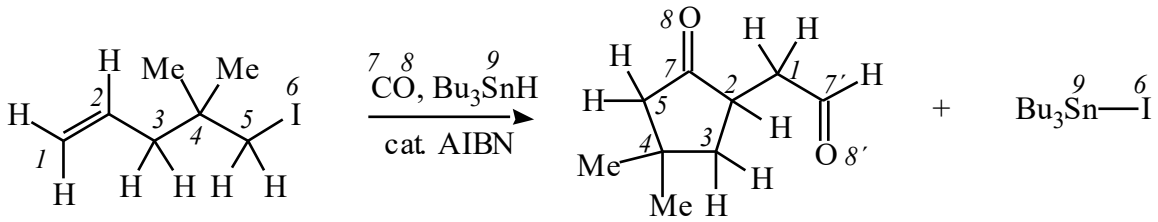
5.5(b). Make: Br1–Sn14, C2–C6, C7–C9, C7–C12, C10–C11. Break: Br1–C2.



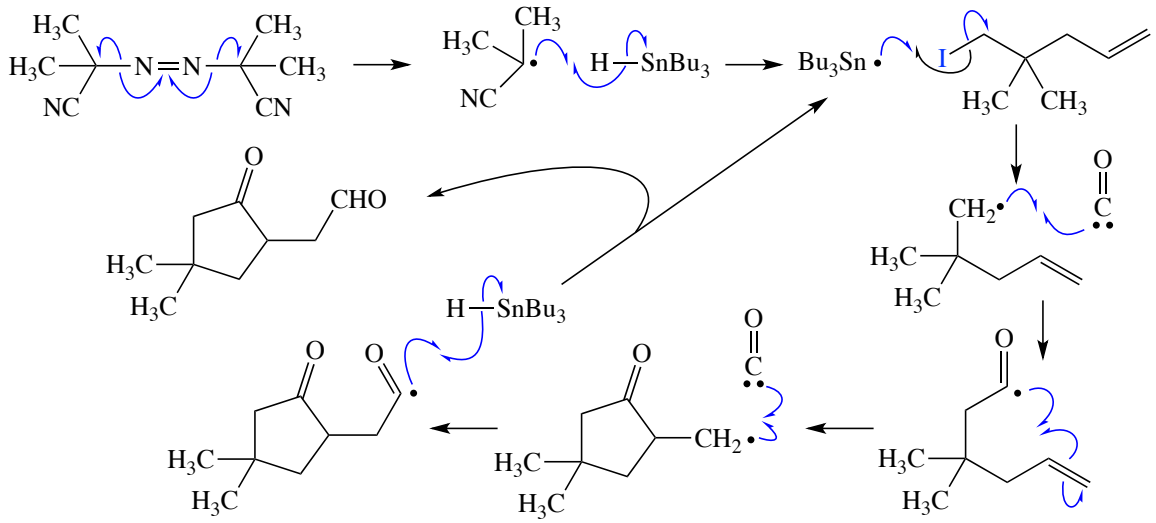
AIBN is a very common initiator of free radical reactions. The radical derived from its fragmentation abstracts H· from Ph_3SnH to give Ph_3Sn·. Ph_3Sn· abstracts Br1 from C2. The C2 radical then adds to C6 to give a C7 radical, which adds to C9 to give a C10 radical. (Why not have C7 add to C12 instead of C9 at this point? Because addition to C9 is intramolecular and forms a five-membered ring, making this addition very fast.) Now C10 adds to C11 to give a C12 radical, which can then add to C7 to give a C6 radical. C6 then abstracts H· from Ph_3SnH to give the product and regenerate Ph_3Sn·.



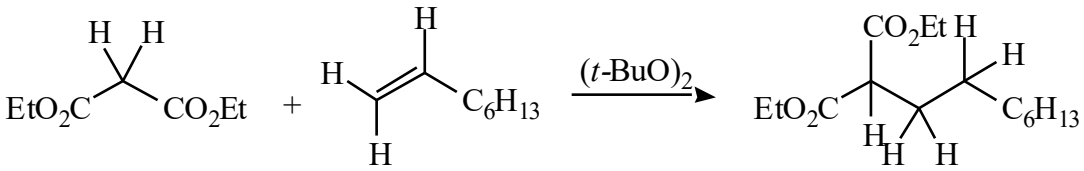
5.6. Make: C1–C7′, C2–C7, C5–C7, I6–Sn9. Break: C5–I6.



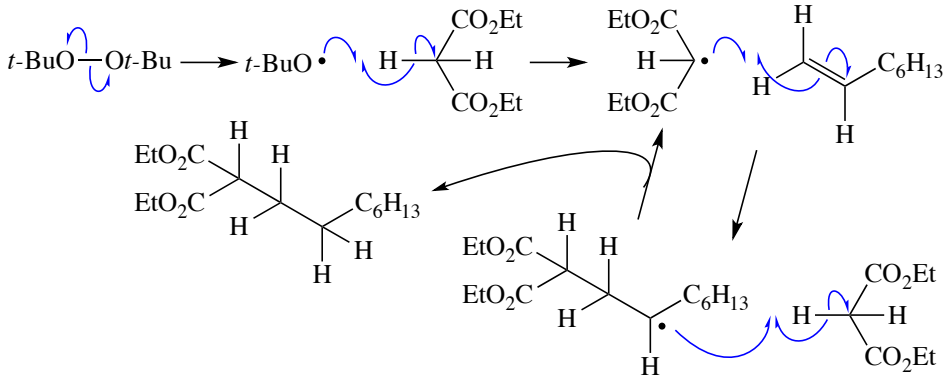
The initiation is the same as for 5.5(b). In the propagation part, $Bu_3Sn\cdot$ abstracts I· from C5. The C5 radical then adds to C7 of CO to make a new C7 radical. The C7 radical adds to C2 to make a C1 radical, which adds to C7′ of a second equivalent of CO to make a C7′ radical. C7′ then abstracts H· from Bu_3SnH to give the product and regenerate $Bu_3Sn\cdot$.



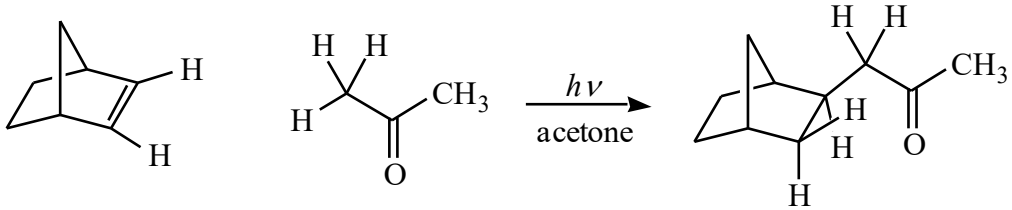
5.7(a). One C–C bond is made, and no bonds are broken.



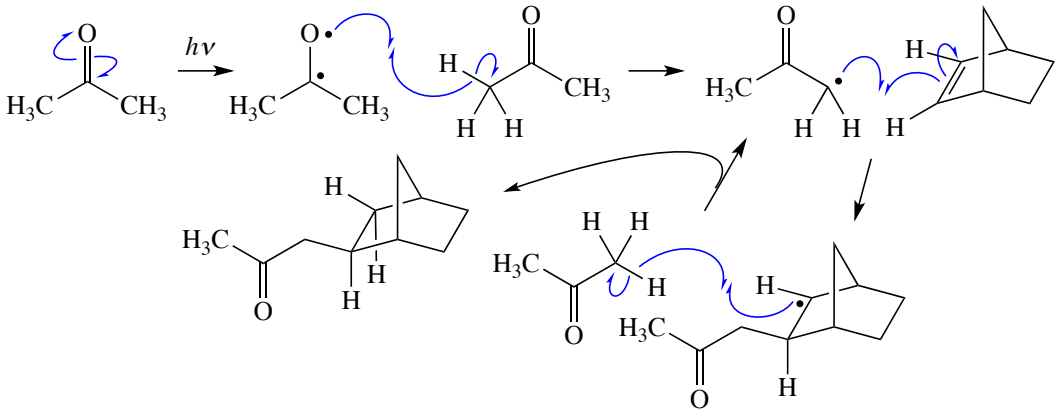
The *t*-BuO· abstracts H· from malonate in the initiation part. A free radical addition mechanism like the one in problem 5.3 ensues.



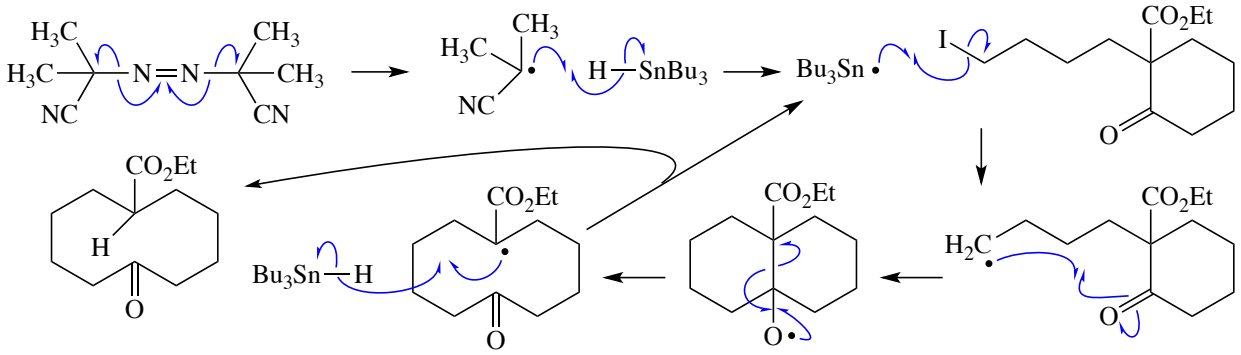
5.7(b). Again, one C–C bond is made, and no bonds are broken.



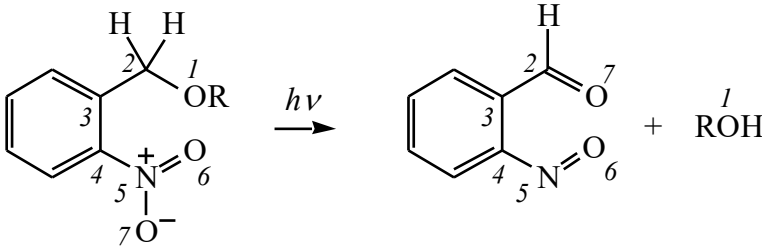
Intermolecular free-radical addition reactions almost always proceed by chain mechanisms. Here light photoexcites acetone, and O· then abstracts H· from the α-position of another molecule of acetone to complete the initiation. Propagation proceeds as in problem 5.7(a).



5.8. The initiation occurs the usual way to generate. As usual, Bu_3Sn· abstracts the halogen from the substrate to give a C· radical. This compound adds to the ketone C to generate a high-energy oxy radical, and this radical then undergoes a fragmentation reaction to put the radical on a C adjacent to a carbonyl group. The chain is completed by abstraction of H· from Bu_3SnH.

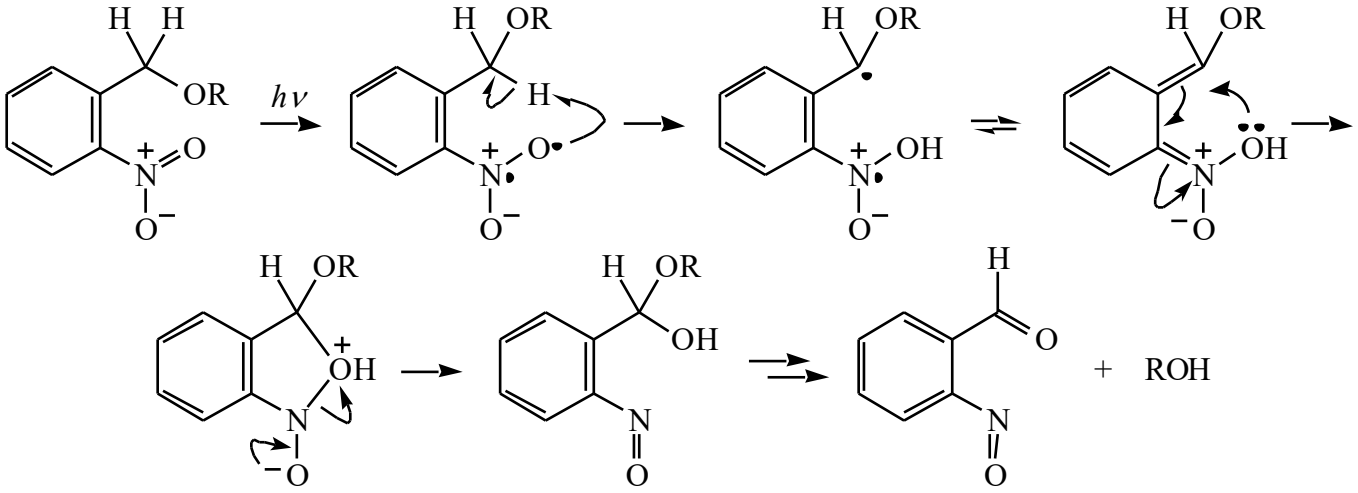


5.9. Make: C2–O7. Break: O1–C2, N5–O7. Note that O6 and O7 are equivalent.

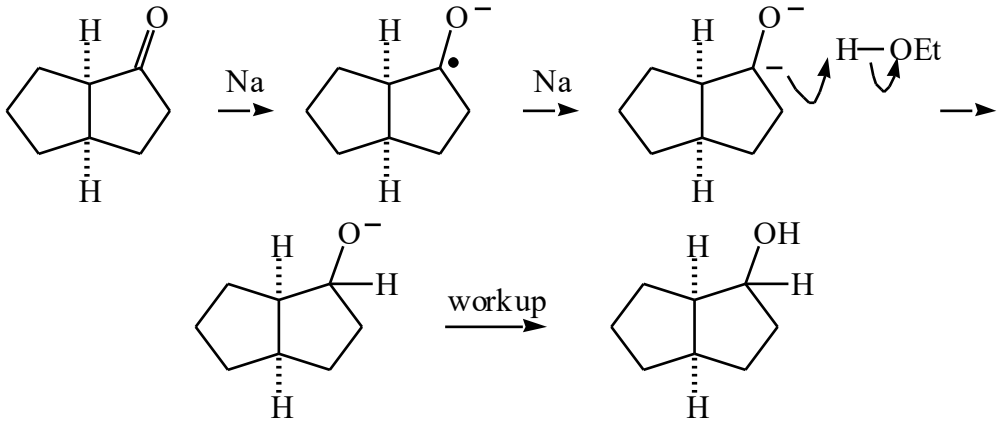


Unimolecular photochemical eliminations usually proceed by nonchain mechanisms. Photoexcitation gives an N5–O6 1,2-diradical. Abstraction of H· from C2 by O6 then gives a 1,4-diradical, which can collapse to an *o*-xylylene type of compound. Electrocyclic ring closure forms the O7–C2 bond and reestablishes aromaticity.

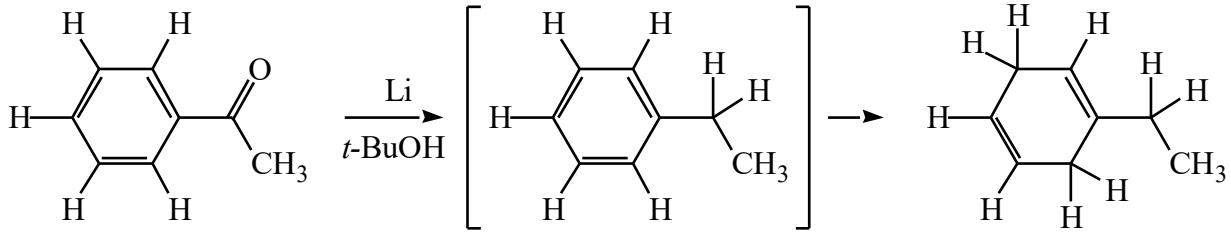
Cleavage of the N5–O7 bond then gives a hemiacetal, which undergoes cleavage by the usual acid- or base-catalyzed mechanism to give the observed products.



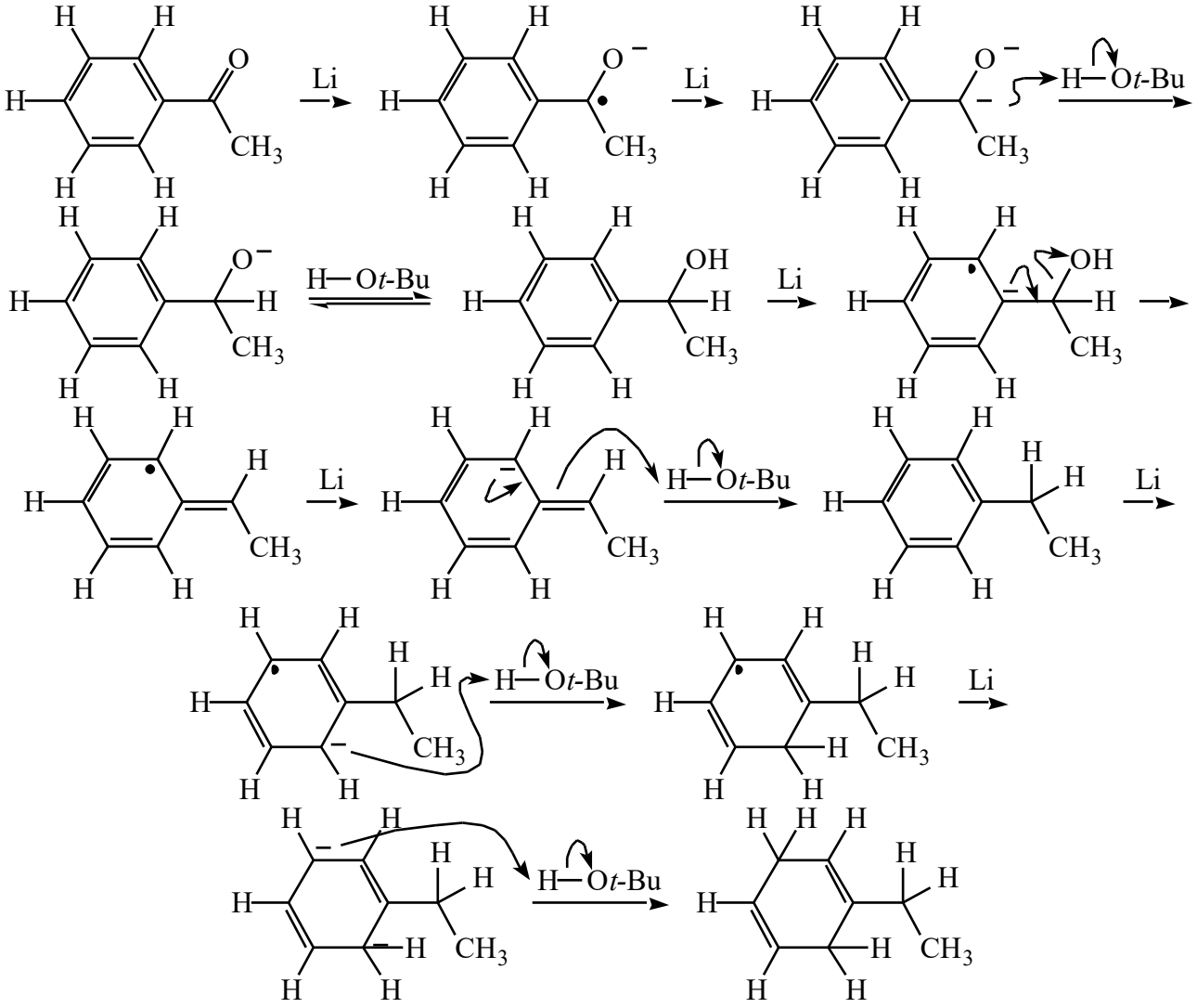
5.10. Addition of one electron to the ketone gives a ketyl (·C–O⁻), and addition of another electron gives a carbanion, which is protonated by EtOH. Workup then gives the reduced compound. Note how curved arrows are *not* used to show the movement of electrons in electron transfer steps.



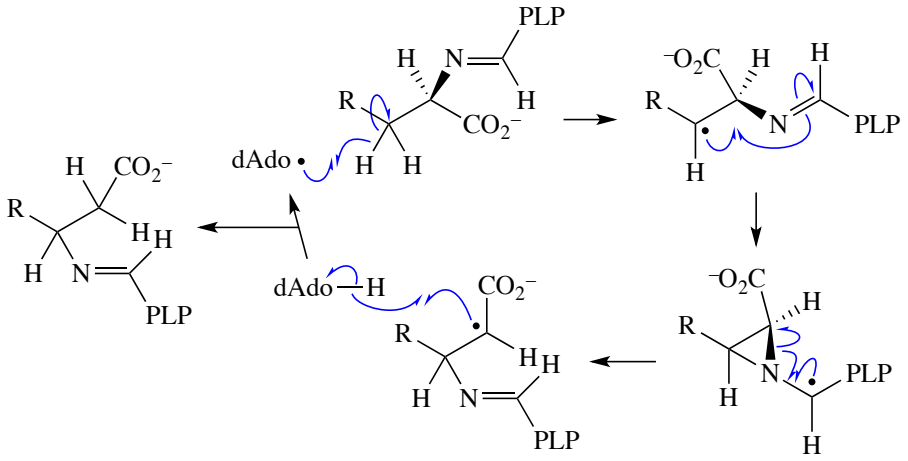
5.11. Only the C–O bond is cleaved, but several C–H bonds are made.



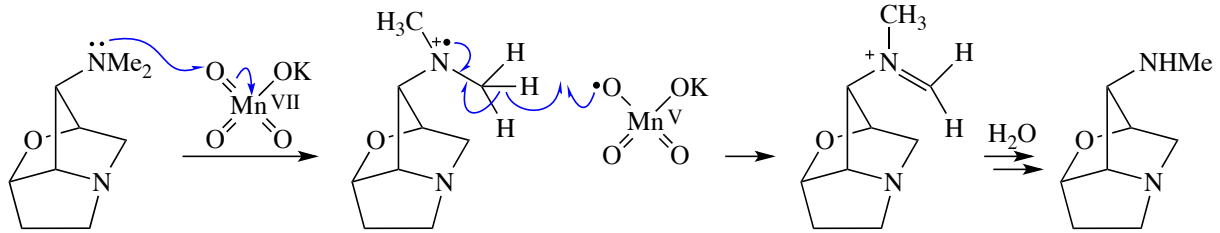
First the ketone is reduced to the alkoxide according to the mechanism shown in problem 5.9. This alkoxide is in equilibrium with the corresponding alcohol. Addition of another electron to the benzene π system gives a radical anion, which expels $^{-}$OH to give a radical. This radical is reduced again and then protonated to give ethylbenzene. Another electron is added, protonation occurs again, another electron is added, and protonation occurs once more to give the observed product.



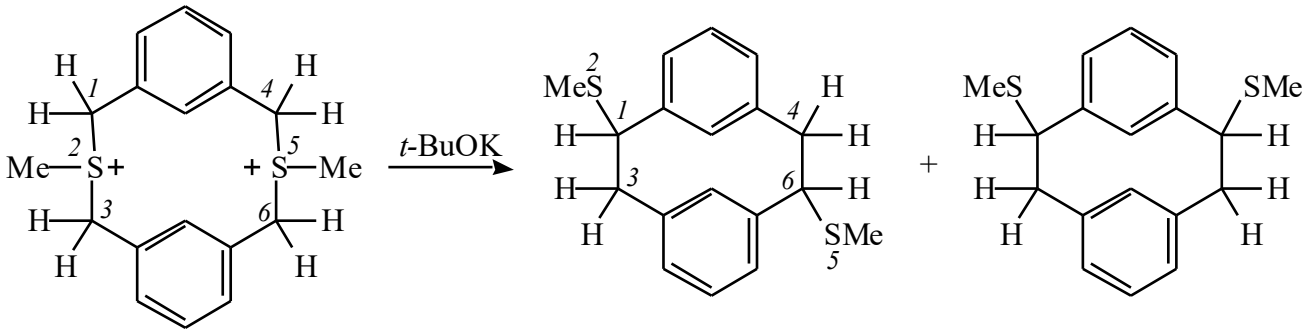
5.12. This reaction is *catalyzed* by dAdo·, so we have to regenerate the dAdo· at the end of the mechanism. The mechanism begins with dAdo· abstracting H· from C3 of the lysine. (The enzyme that catalyzes this reaction directs the dAdo· to this particular C atom.) The C3 radical adds to N to form an aziridine, and then the other C–N bond of the aziridine breaks to give a C2 radical, which finally abstracts H· back from the dAdoH formed in the first step.



5.13. The reaction begins by electron transfer from N to $KMnO_4$. Abstraction of an H atom from one of the C atoms neighboring the N atom then occurs to give an iminium ion, which reacts with water in the usual way to give the 2° amine. The ring N does not react in the same way because Bredt's rule prevents it from forming an iminium ion.

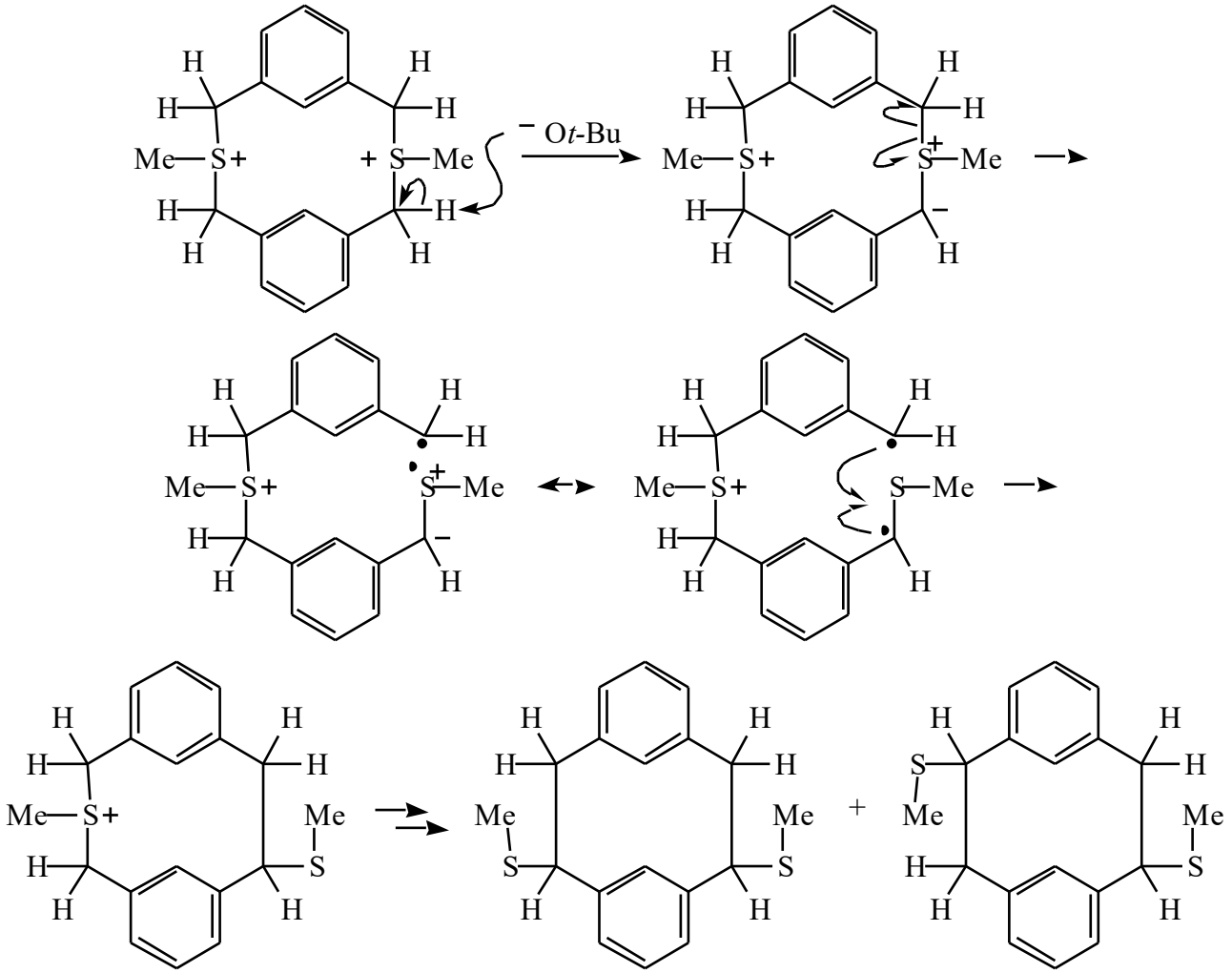


5.14. Make: C1–C3, C4–C6. Break: S2–C3, C4–S5.



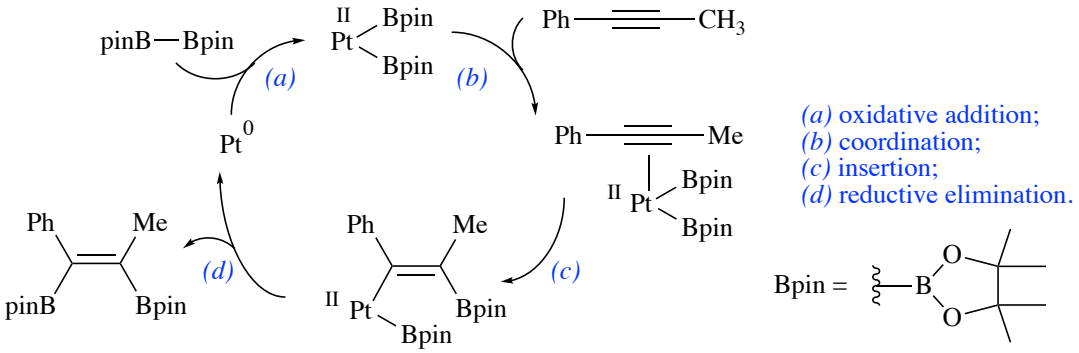
Deprotonation of C6 gives an ylide , which undergoes a 1,2-shift (break C4–S5, make C4–C6). This 1,2-shift occurs in two steps: the C4–S5 bond homolyzes to give a radical and a radical cation, and recombination of C4 and C6 occurs to give an intermediate ring-contracted by one atom. The same process is repeated on the other

side to give the observed product. Whether one or the other regioisoemr is obtained depends on whether C1 or C3 is deprotonated for the second ring contraction.

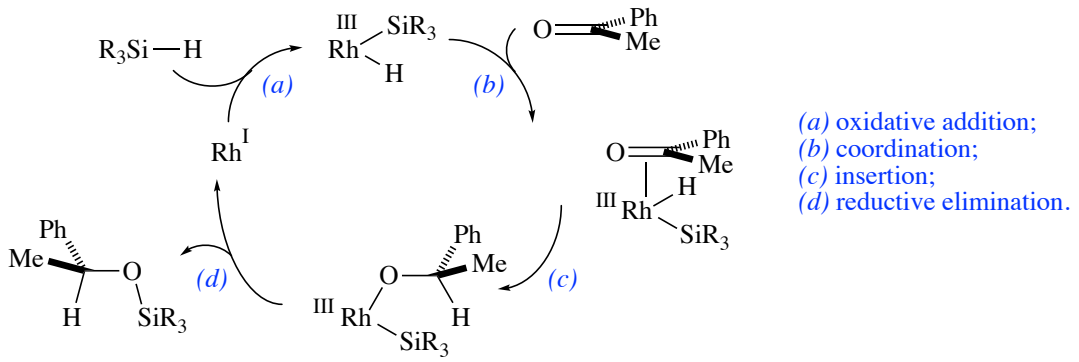


ANSWERS TO PROBLEMS IN BODY OF CHAPTER 6.

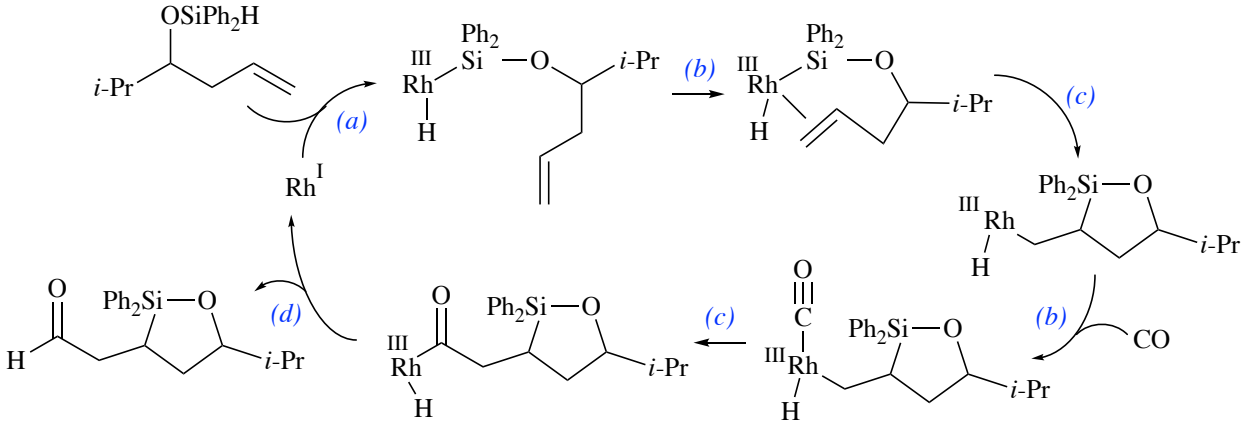
6.1.



6.2.

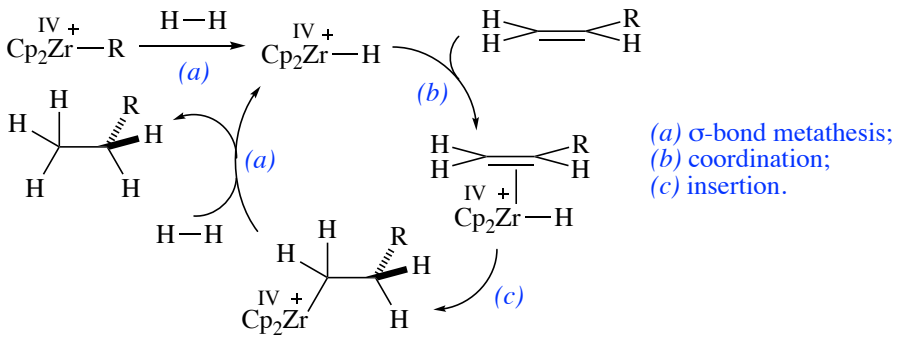


6.3.

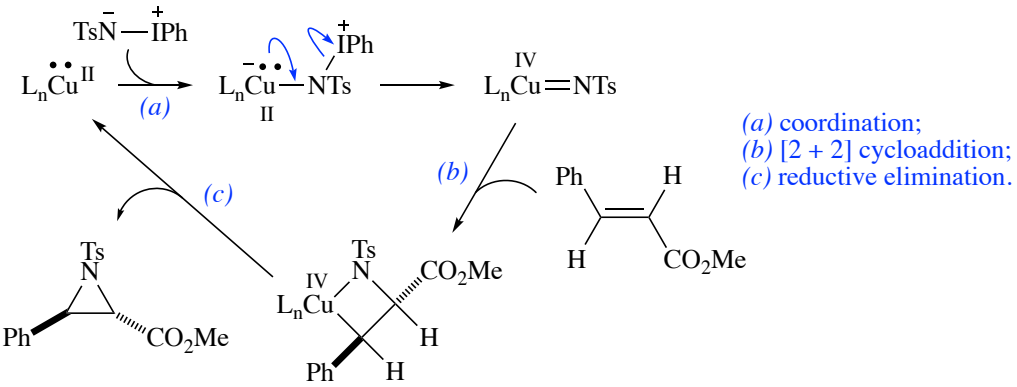


6.4. Because the Zr–C(sp^2) bond is much stronger than the Zr–C(sp^3) bond, and because alkynes are higher n energy than alkenes.

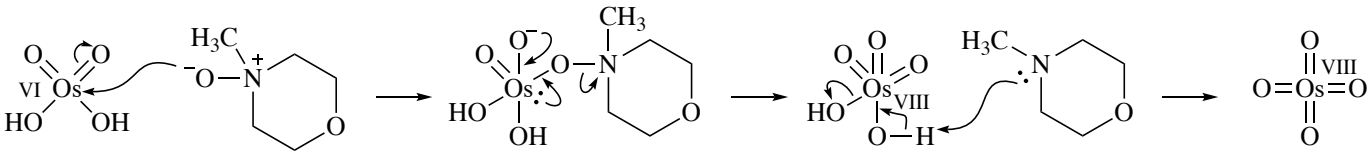
6.5.


(a) σ-bond metathesis;
(b) coordination;
(c) insertion.

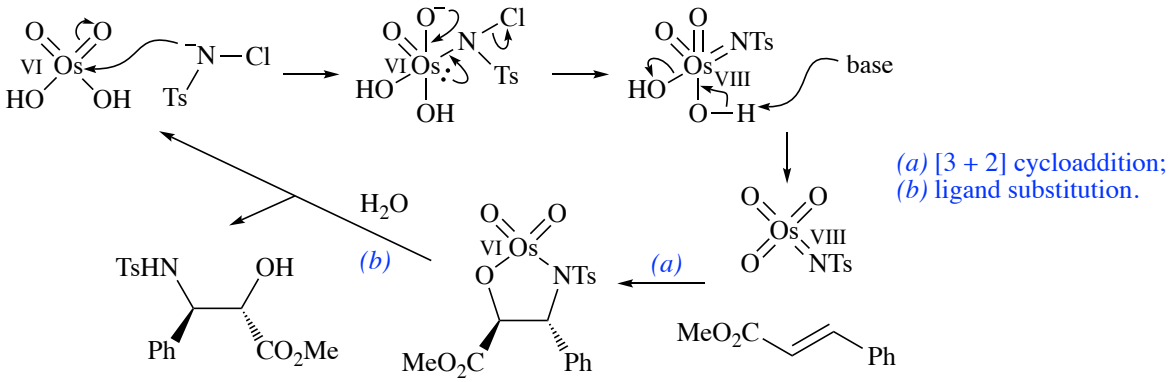
6.6.


(a) coordination;
(b) [2 + 2] cycloaddition;
(c) reductive elimination.

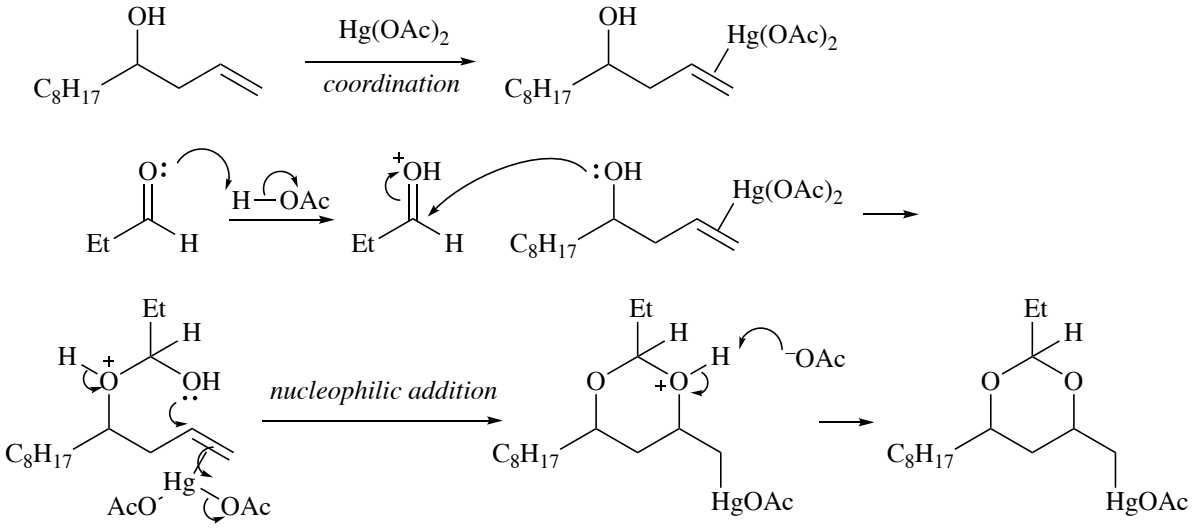
6.7.



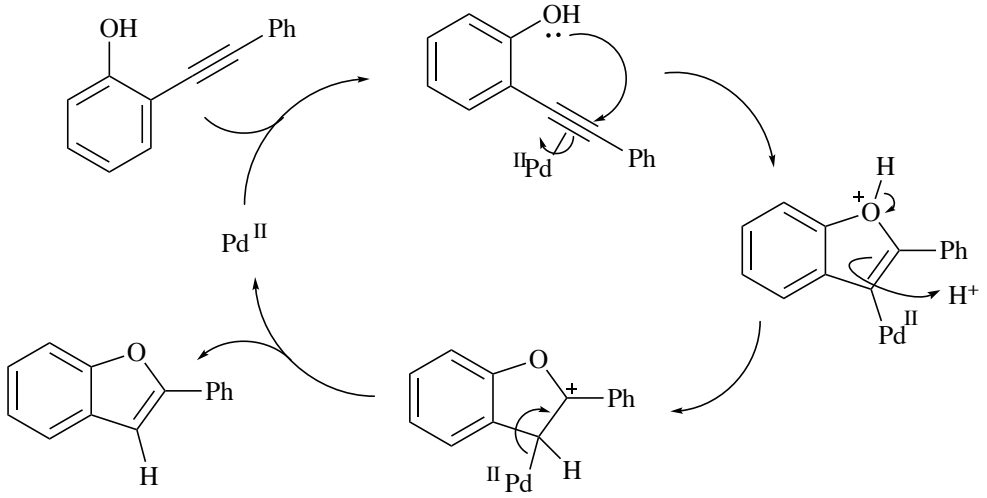
6.8.


(a) [3 + 2] cycloaddition;
(b) ligand substitution.

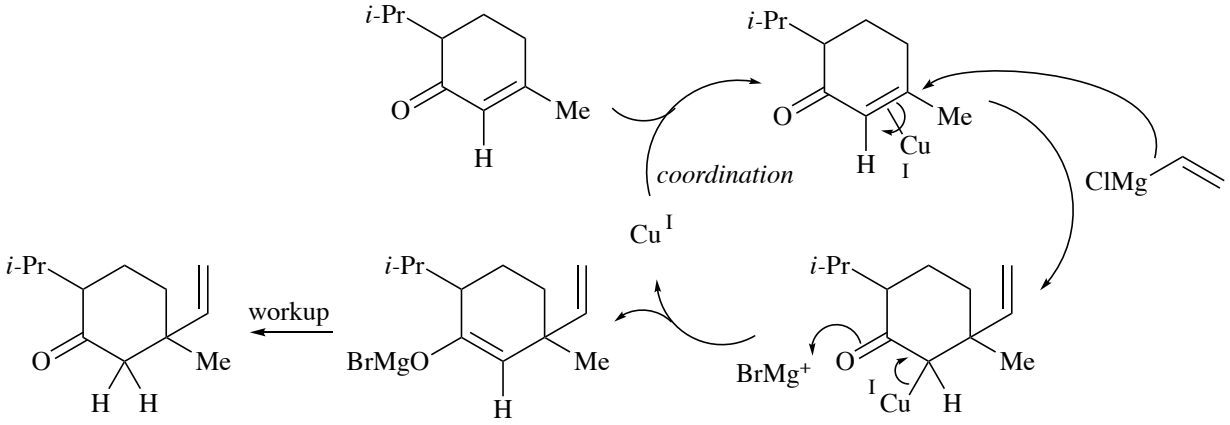
6.9. A coproduct of the reaction is AcOH, so the reaction conditions for formation of the hemiacetal are acidic.



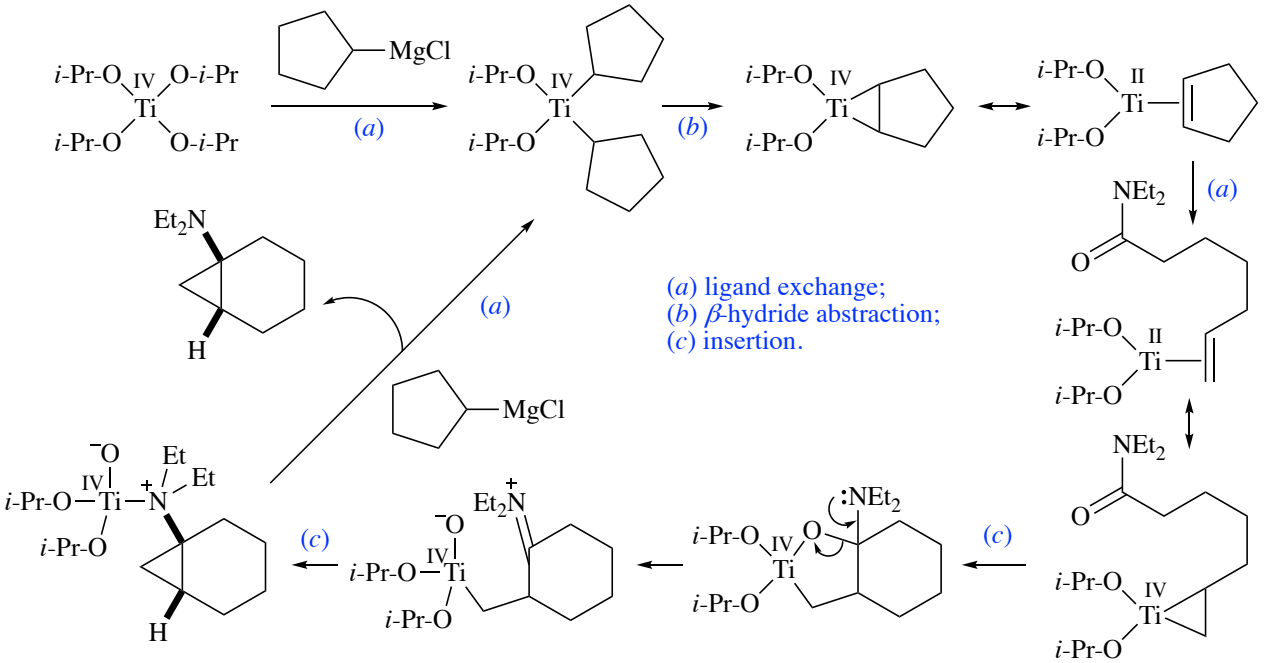
6.10. In the proposal below, the C–H bond forms and the C–Pd bond breaks via an electrophilic aromatic substitution mechanism. Alternatively, one could protonate the Pd atom and then have the resulting complex undergo reductive elimination, but this process would involve a Pd(IV) intermediate, which is unlikely.



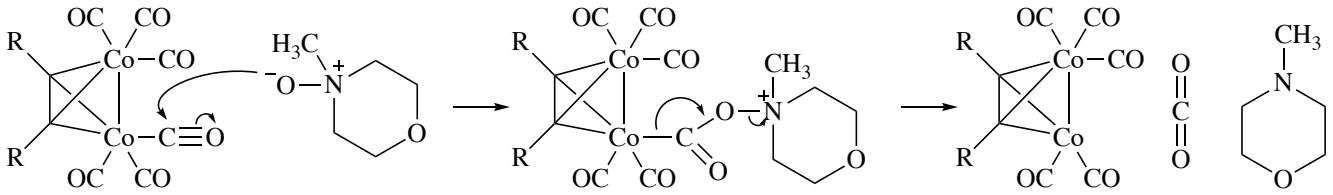
6.11.



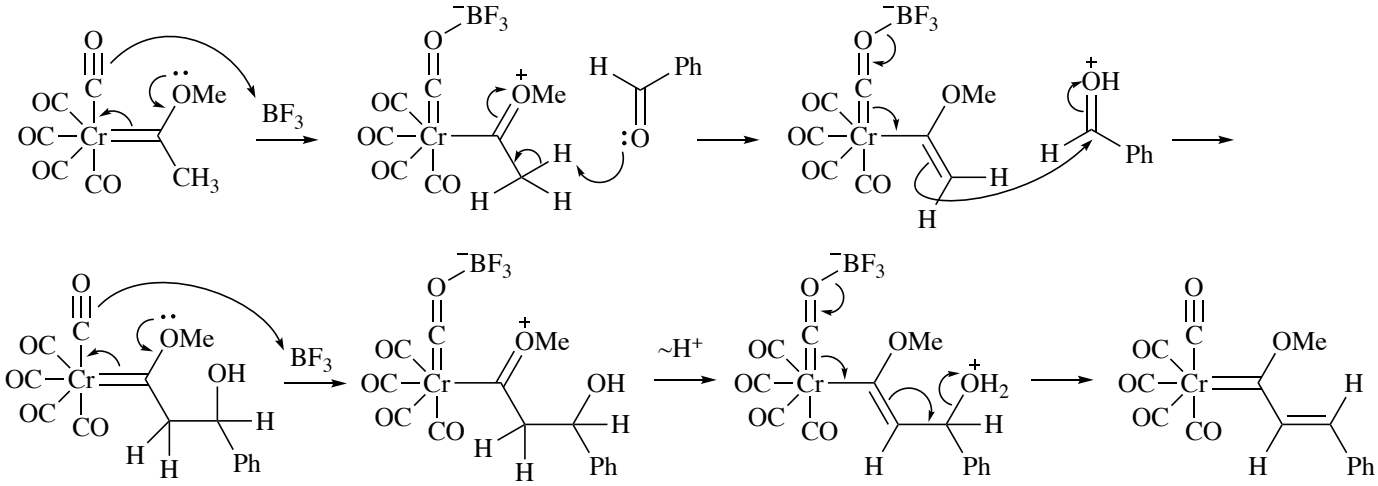
6.12. The Grignard reagent reduces the Ti(IV) to a Ti(II) π complex, which can undergo ligand exchange with the alkene. Redrawing this complex in its metallacyclopropane resonance form, the carbonyl group can now insert into one of the Ti–C σ bonds. The aminal expels O^- to give an iminium ion, and then insertion of the iminium ion into the remaining Ti–C bond occurs to give the aminocyclopropane complexed to Ti(IV). Ligand exchange with the Grignard reagent frees the product and completes the catalytic cycle.



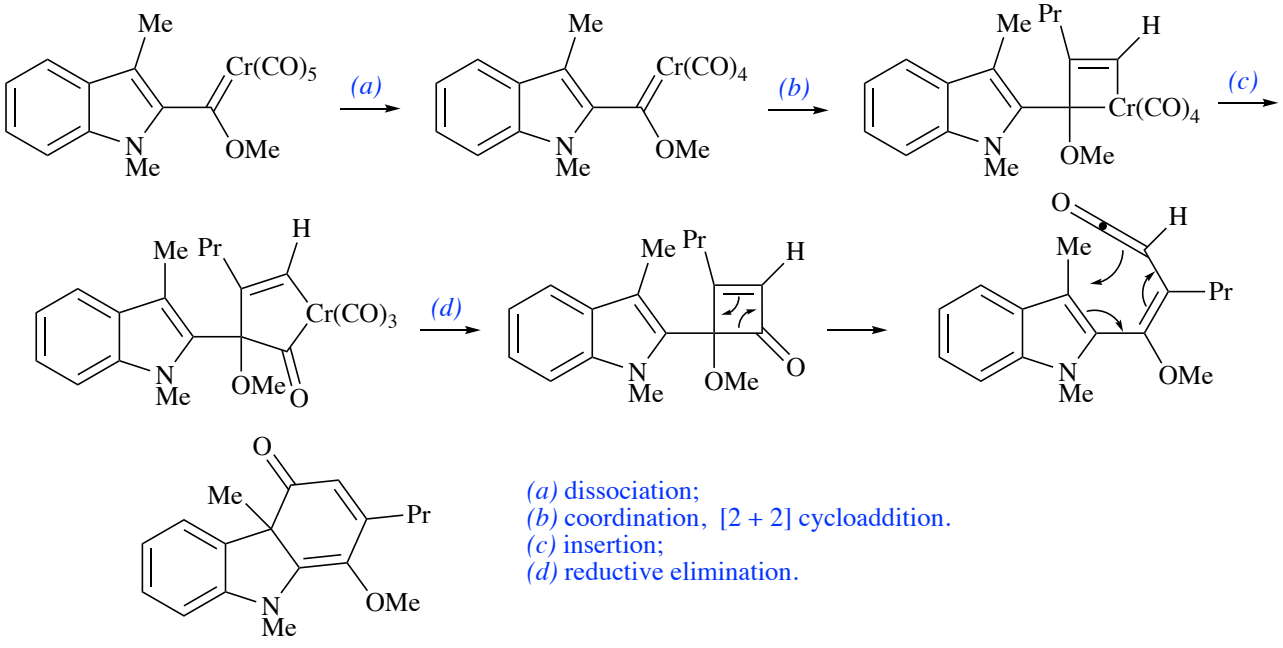
6.13.



6.14.

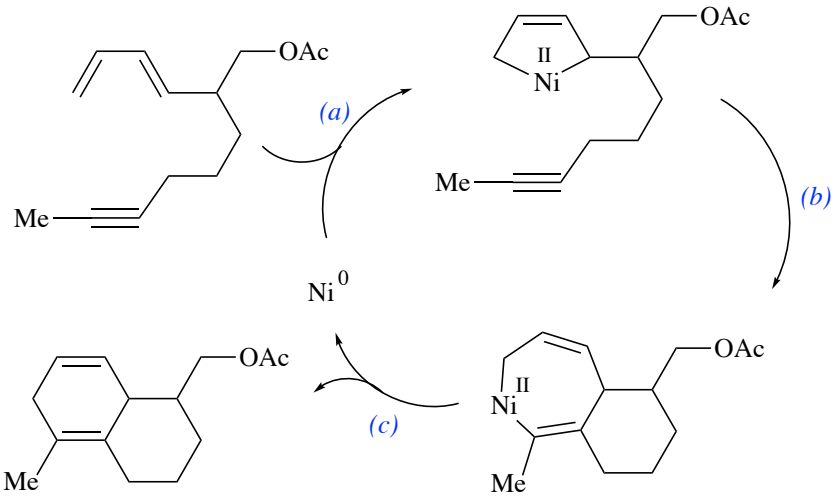


6.15. After the metallacyclobutane forms, there are several possibilities for the remainder of the mechanism. This answer shows one of them.



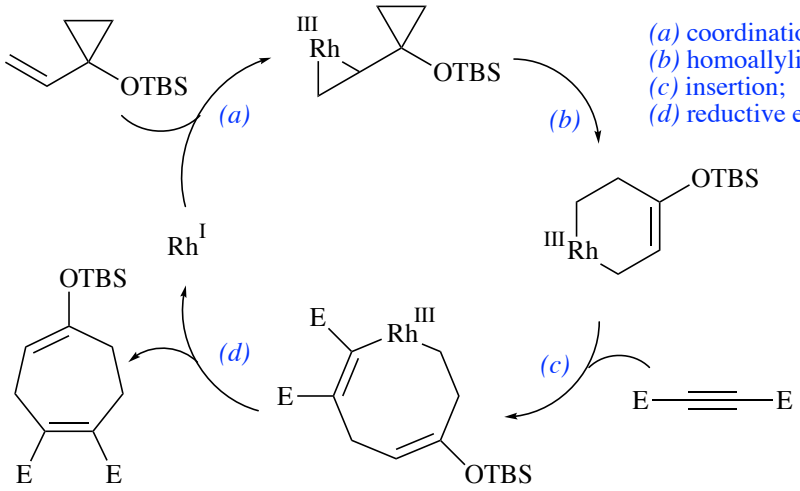
(a) dissociation;
(b) coordination, [2 + 2] cycloaddition.
(c) insertion;
(d) reductive elimination.

6.16.



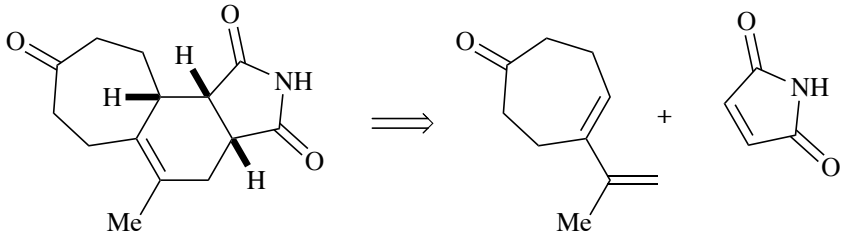
(a) coordination;
(b) insertion;
(c) reductive elimination.

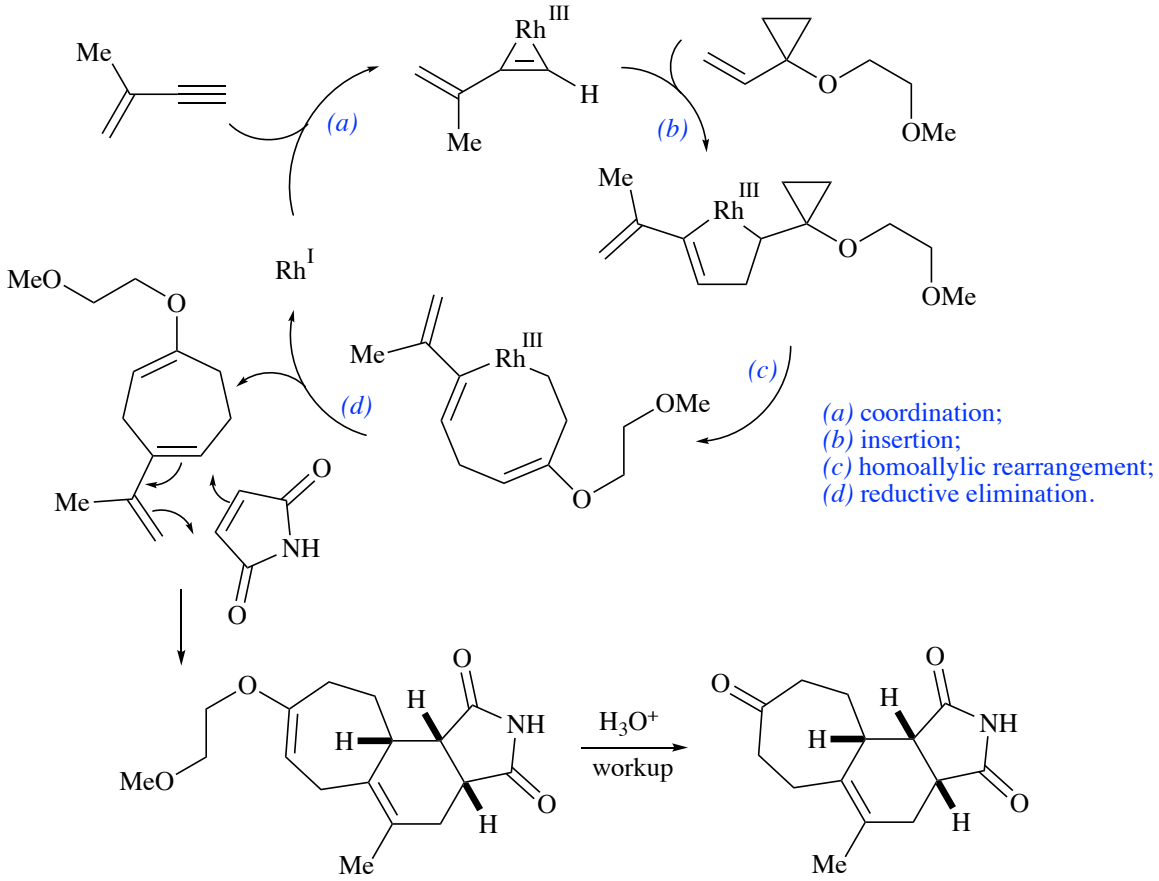
6.17.



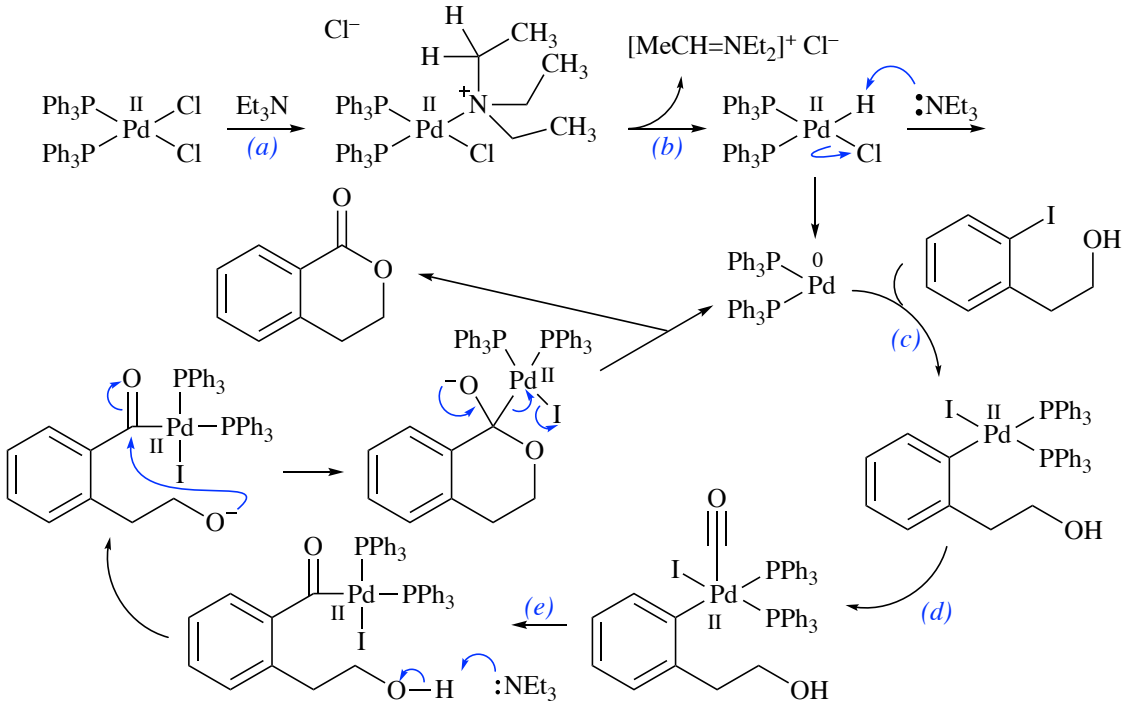
(a) coordination;
(b) homoallylic rearrangement;
(c) insertion;
(d) reductive elimination.

6.18. The last step of the mechanism involves a Diels–Alder reaction of the maleimide, so we only need to figure out how to form the alkenylcycloheptenone from the other two starting materials.

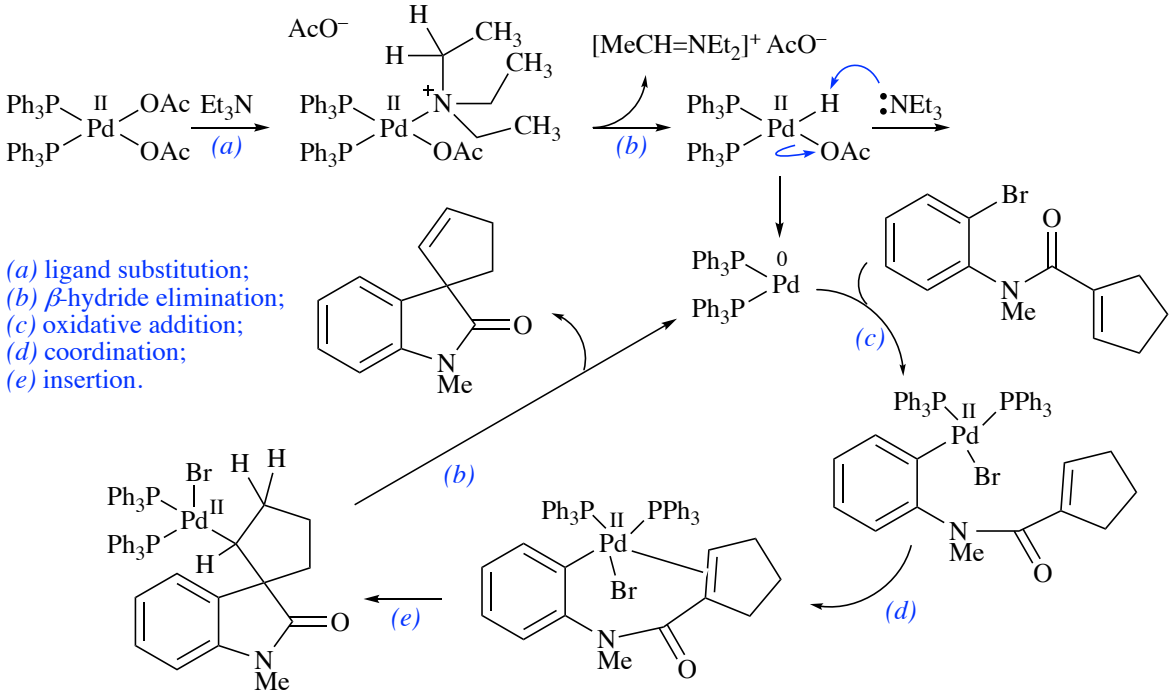



(a) coordination;
(b) insertion;
(c) homoallylic rearrangement;
(d) reductive elimination.
H3O+
workup

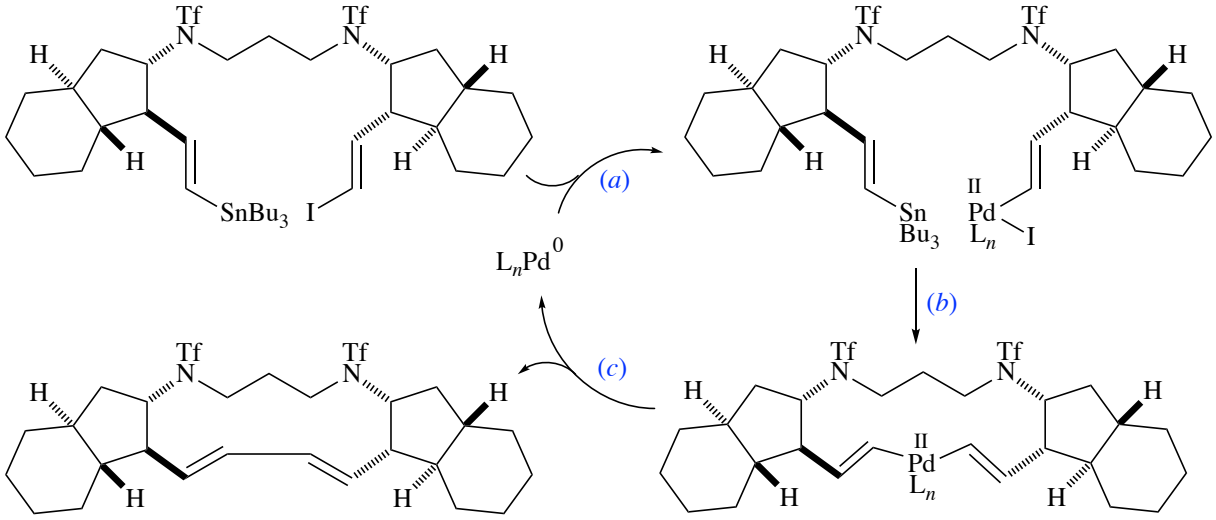
6.19.


[MeCH=NEt2]+ Cl−
Et3N
:NEt3
(a) ligand substitution; (b) β-hydride elimination; (c) oxidative addition; (d) coordination; (e) insertion.

6.20. Because the α-carbon of the carbonyl bears no H atoms, the β-hydride elimination occurs away from the carbonyl to give a β,γ-unsaturated product.

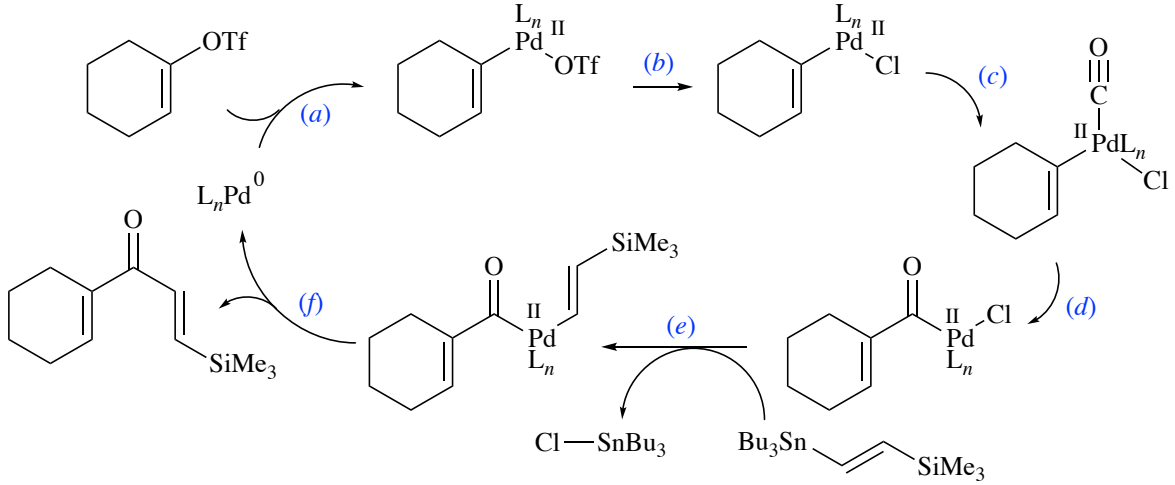


6.21.



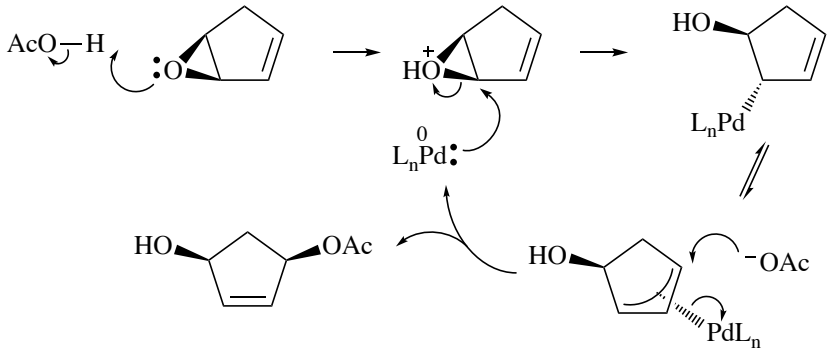
(*a*) oxidative addition; (*b*) transmetallation; (*c*) reductive elimination.

6.22. The mechanism is just the same as that of a regular Stille coupling, but with an additional coordination and insertion of CO. In this particular example, there is also an exchange of Cl^- for ^-OTf; perhaps the transmetallation step is slow when the Bu_3Sn needs to make a bond to OTf.

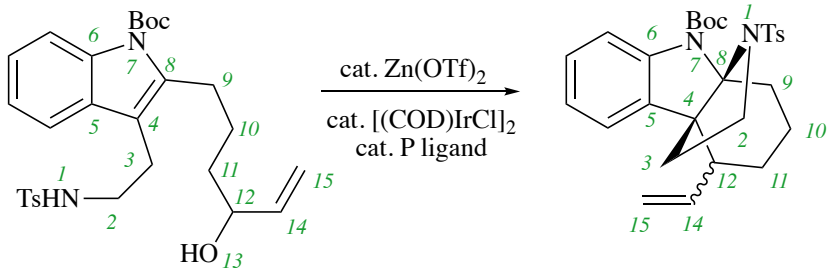


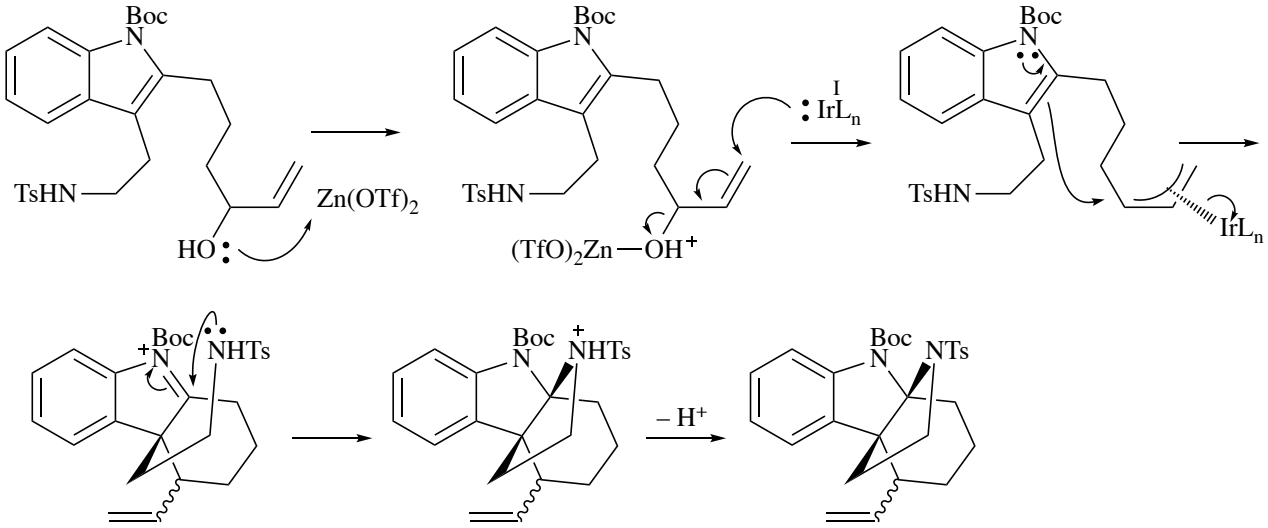
(*a*) oxidative addition; (*b*) ligand substitution; (*c*) coordination; (*d*) insertion; (*e*) transmetallation; (*f*) reductive elimination.

6.23.



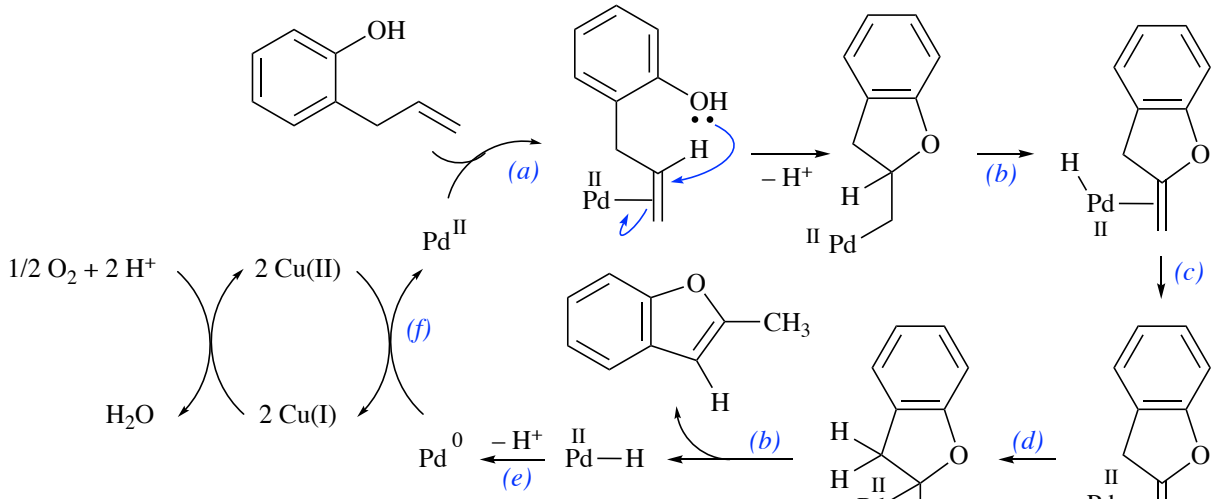
6.24. Make: N1–C8, C4–C12. Break: C12–O13. The $Zn(OTf)_2$ coordinates to the OH and makes it a better leaving group, allowing the Ir(I) to make the π-allyl complex.





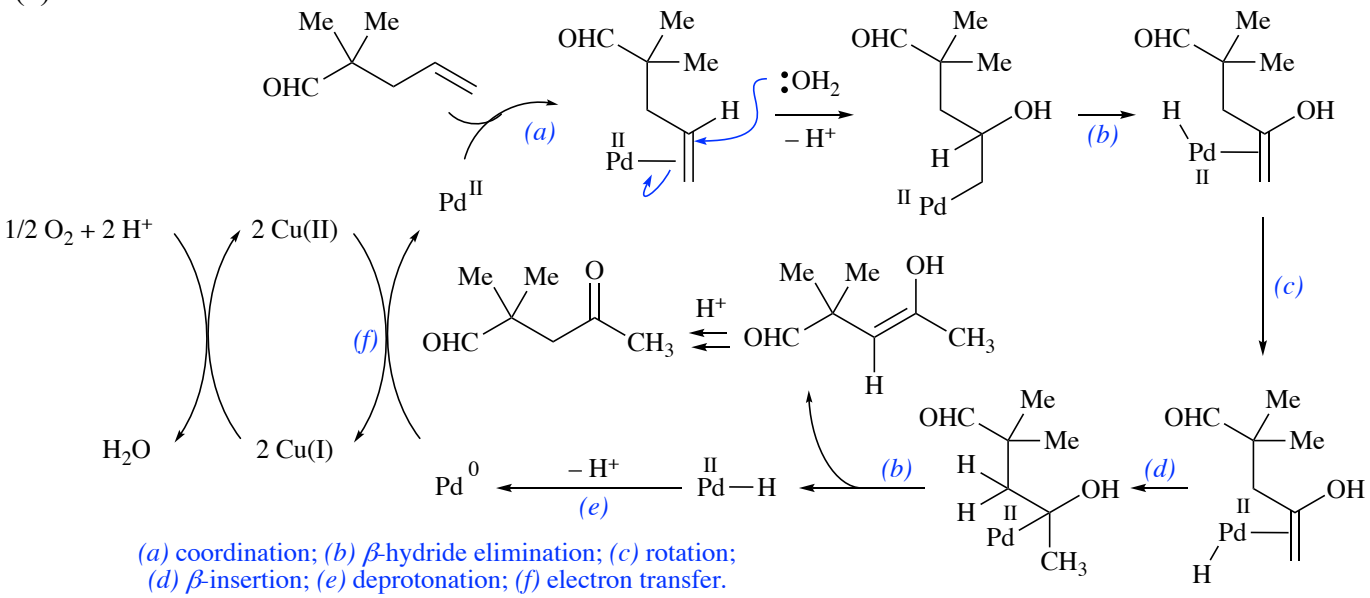
6.25.

(a)



(a) coordination; *(b)* β-hydride elimination; *(c)* rotation; *(d)* β-insertion; *(e)* deprotonation; *(f)* electron transfer.

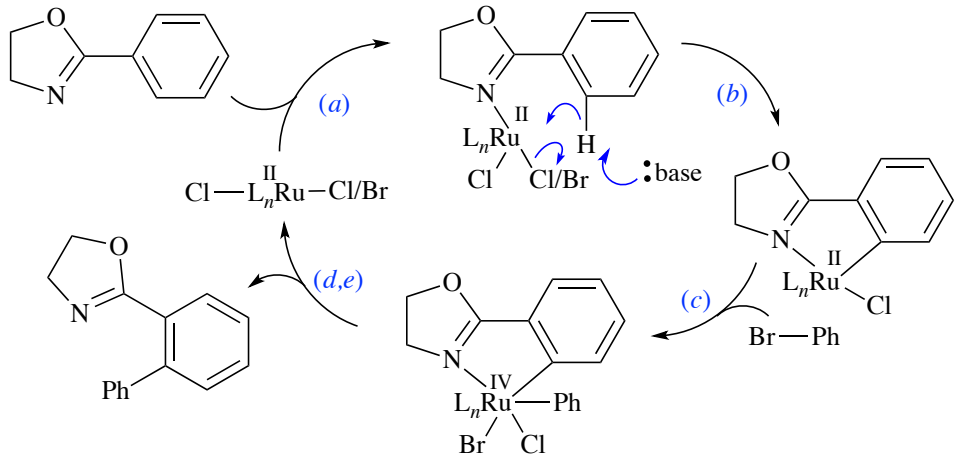
(b)



(a) coordination; *(b)* *β*-hydride elimination; *(c)* rotation; *(d)* *β*-insertion; *(e)* deprotonation; *(f)* electron transfer.

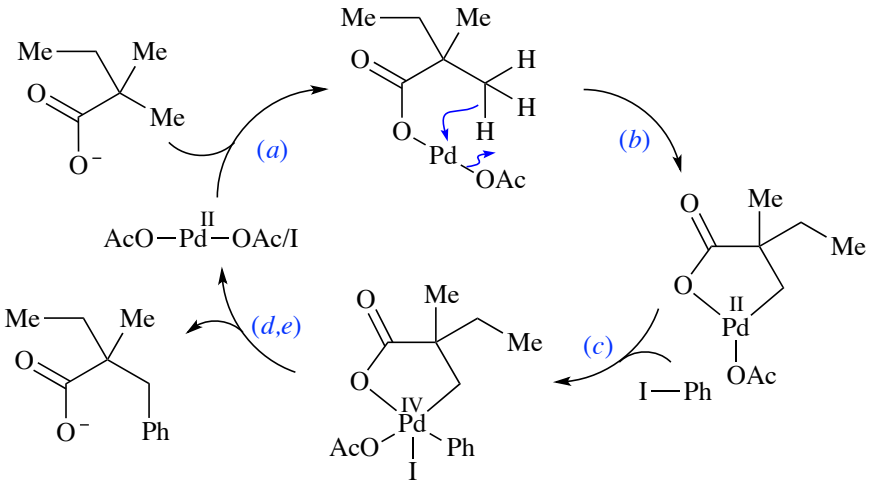
6.26.

(a) The reaction conditions here include base, which probably assists the *δ*-hydride abstraction reaction, either by helping remove the H^+ (as shown) or by first substituting for halide on Ru.



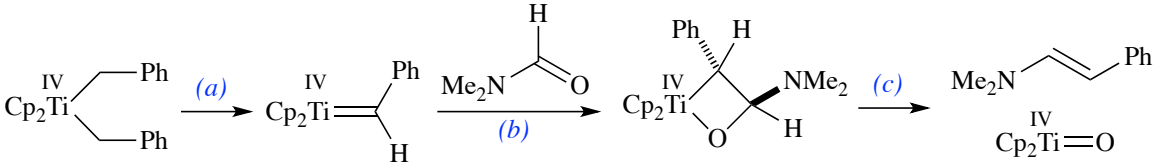
(*a*) coordination; (*b*) concerted metallation–deprotonation; (*c*) oxidative addition; (*d*) reductive elimination; (*e*) dissociation.

(b)



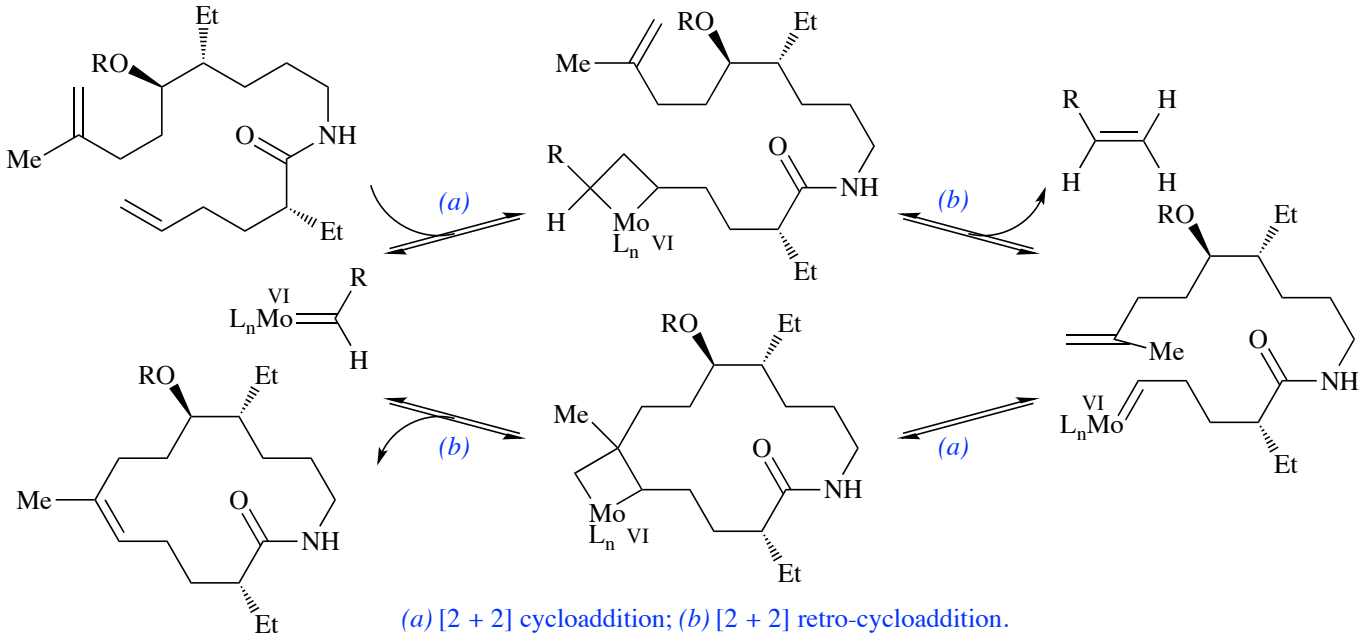
(*a*) coordination; (*b*) concerted metallation–deprotonation; (*c*) oxidative addition; (*d*) reductive elimination; (*e*) dissociation.

6.27.



(a) α-hydride abstraction; *(b)* [2 + 2] cycloaddition; *(c)* retro [2 + 2] cycloaddition.

6.28. In the first catalytic cycle, R = $CPhMe_2$; in subsequent cycles, R = H.



(a) [2 + 2] cycloaddition; *(b)* [2 + 2] retro-cycloaddition.

6.29. In the first catalytic cycle, R = H; in subsequent cycles, R = the growing polymer chain. Each cyclopentane is always trans-disubstituted, but the relationship of one cyclopentane's configuration to the next is random.