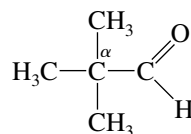


## CHAPTER 18

### ENOLS AND ENOLATES

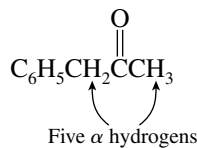
#### SOLUTIONS TO TEXT PROBLEMS

- 18.1 (b) There are no  $\alpha$ -hydrogen atoms in 2,2-dimethylpropanal, because the  $\alpha$ -carbon atom bears three methyl groups.



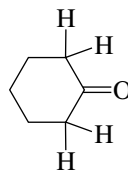
2,2-Dimethylpropanal

- (c) All three protons of the methyl group, as well as the two benzylic protons, are  $\alpha$  hydrogens.



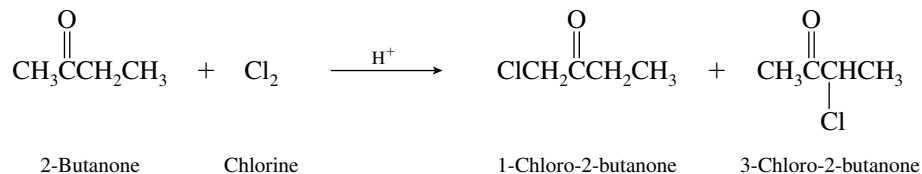
Benzyl methyl ketone

- (d) Cyclohexanone has four equivalent  $\alpha$  hydrogens.

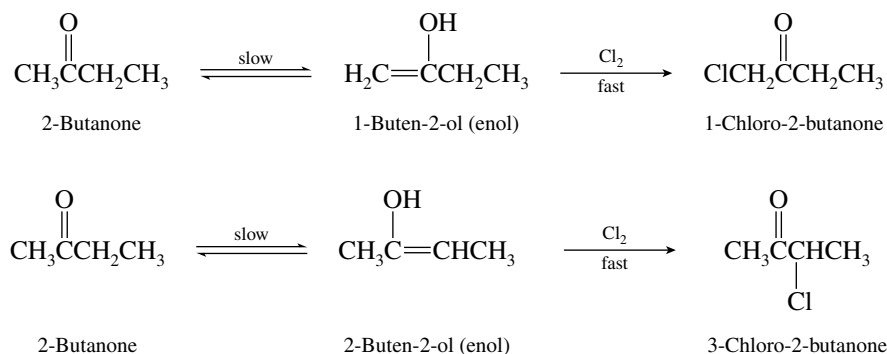


Cyclohexanone (the hydrogens indicated are the  $\alpha$  hydrogens)

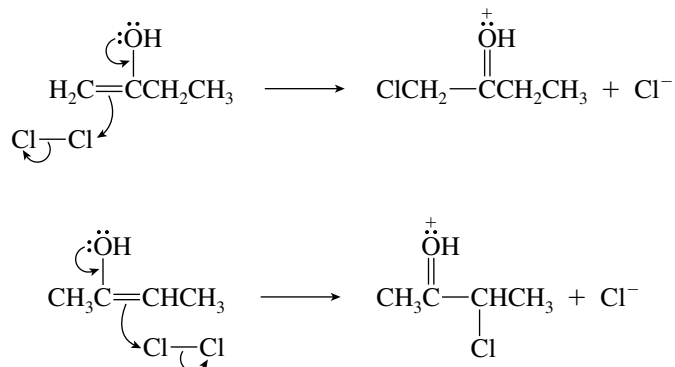
- 18.2** As shown in the general equation and the examples, halogen substitution is specific for the  $\alpha$ -carbon atom. The ketone 2-butanone has two nonequivalent  $\alpha$  carbons, and so substitution is possible at both positions. Both 1-chloro-2-butanone and 3-chloro-2-butanone are formed in the reaction.



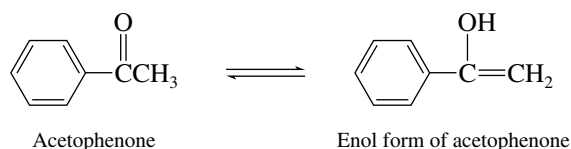
- 18.3** The carbon-carbon double bond of the enol always involves the original carbonyl carbon and the  $\alpha$ -carbon atom. 2-Butanone can form two different enols, each of which yields a different  $\alpha$ -chloro ketone.



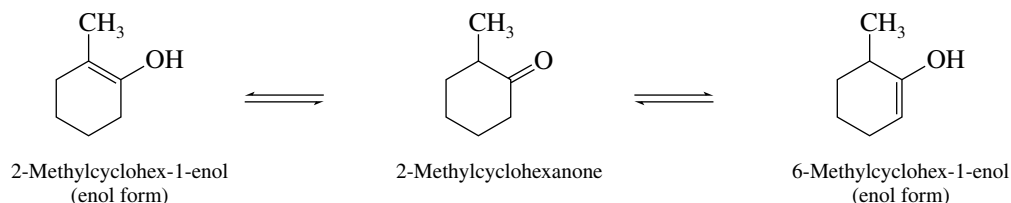
- 18.4** Chlorine attacks the carbon-carbon double bond of each enol.



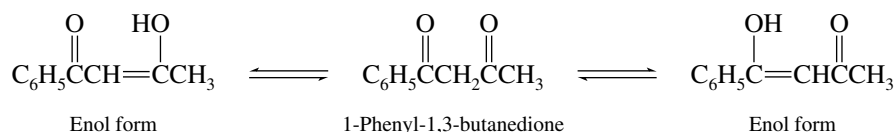
- 18.5** (b) Acetophenone can enolize only in the direction of the methyl group.



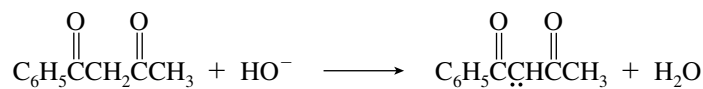
- (c) Enolization of 2-methylcyclohexanone can take place in two different directions.



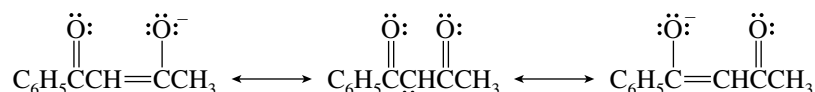
- 18.6 (b) Enolization of the central methylene group can involve either of the two carbonyl groups.



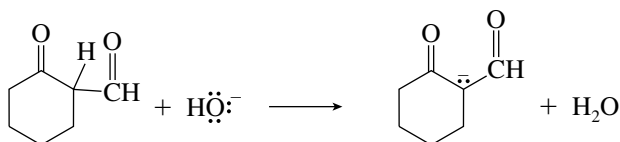
- 18.7 (b) Removal of a proton from 1-phenyl-1,3-butanedione occurs on the methylene group between the carbonyls.



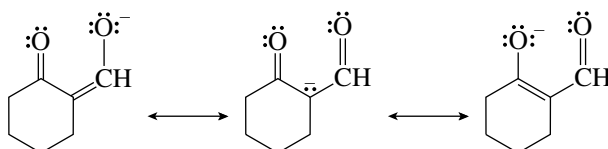
The three most stable resonance forms of this anion are



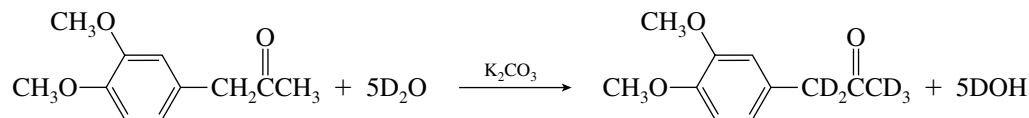
- (c) Deprotonation at C-2 of this  $\beta$ -dicarbonyl compound yields the carbanion shown.



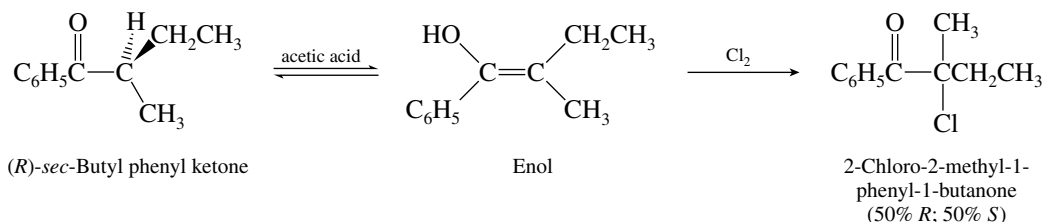
The three most stable resonance forms of the anion are:



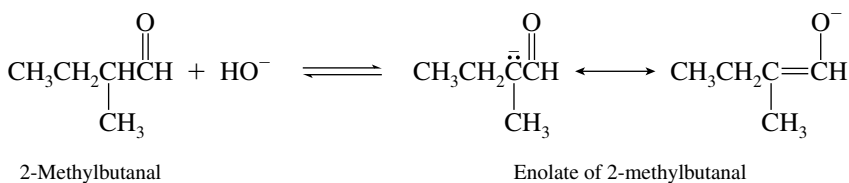
- 18.8 Each of the five  $\alpha$  hydrogens has been replaced by deuterium by base-catalyzed enolization. Only the  $\text{OCH}_3$  hydrogens and the hydrogens on the aromatic ring are observed in the  $^1\text{H}$  NMR spectrum at  $\delta$  3.9 ppm and  $\delta$  6.7–6.9 ppm, respectively.



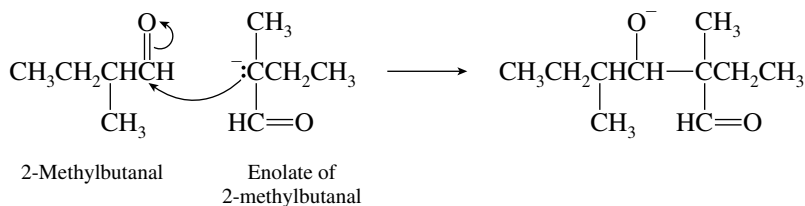
- 18.9  $\alpha$ -Chlorination of (*R*)-*sec*-butyl phenyl ketone in acetic acid proceeds via the enol. The enol is achiral and yields equal amounts of (*R*)- and (*S*)-2-chloro-2-methyl-1-phenyl-1-butanone. The product is chiral. It is formed as a racemic mixture, however, and this mixture is not optically active.



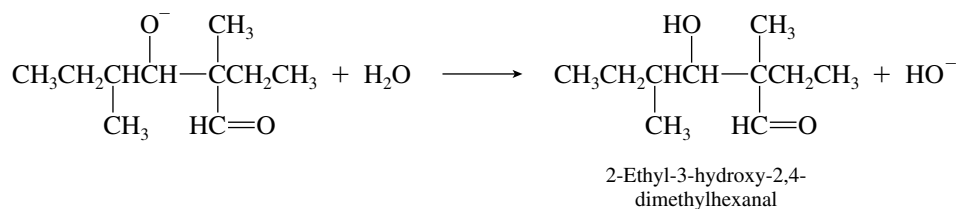
- 18.10 (b) Approaching this problem mechanistically in the same way as part (a), write the structure of the enolate ion from 2-methylbutanal.



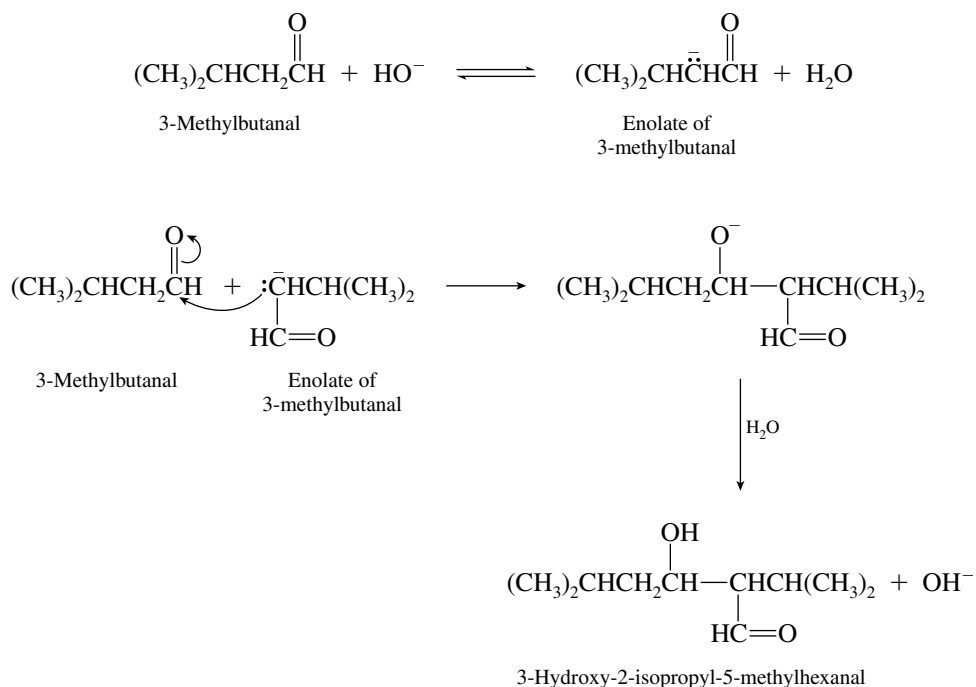
This enolate adds to the carbonyl group of the aldehyde.



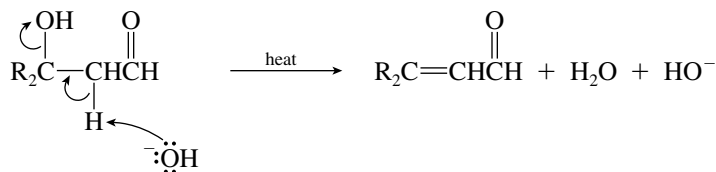
A proton transfer from solvent yields the product of aldol addition.



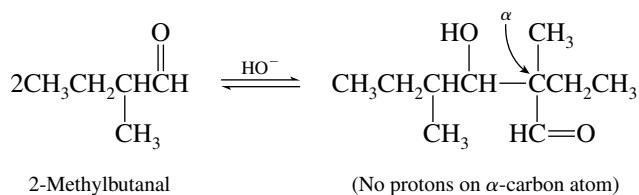
- (c) The aldol addition product of 3-methylbutanal can be identified through the same mechanistic approach.



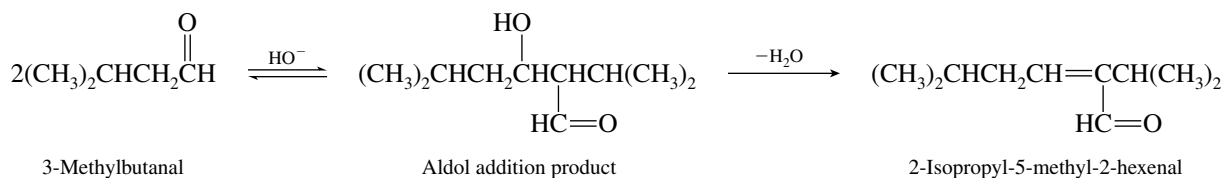
- 18.11 Dehydration of the aldol addition product involves loss of a proton from the  $\alpha$ -carbon atom and hydroxide from the  $\beta$ -carbon atom.



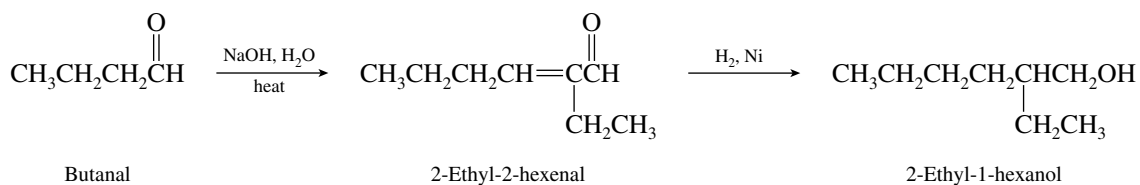
- (b) The product of aldol addition of 2-methylbutanal has no  $\alpha$  hydrogens. It cannot dehydrate to an aldol condensation product.



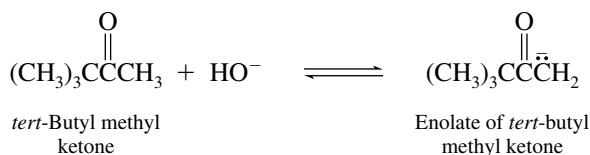
- (c) Aldol condensation is possible with 3-methylbutanal.



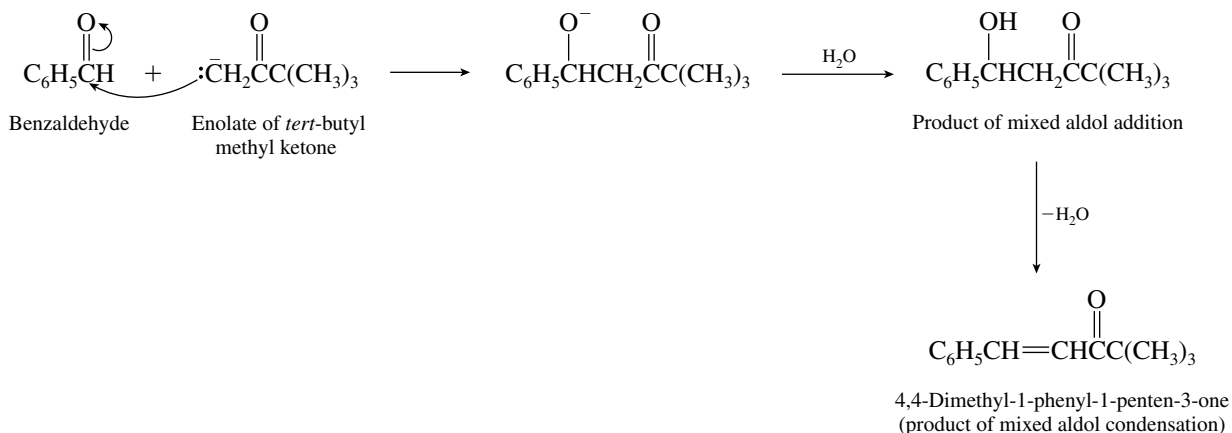
- 18.12 The carbon skeleton of 2-ethyl-1-hexanol is the same as that of the aldol condensation product derived from butanal. Hydrogenation of this compound under conditions in which both the carbon-carbon double bond and the carbonyl group are reduced gives 2-ethyl-1-hexanol.



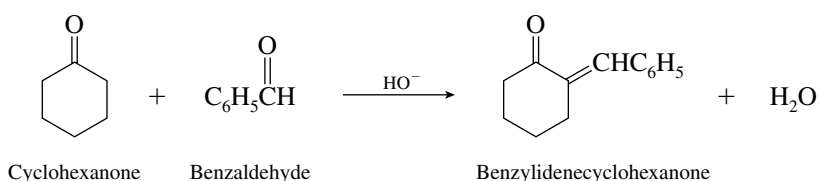
- 18.13 (b) The only enolate that can be formed from *tert*-butyl methyl ketone arises by proton abstraction from the methyl group.



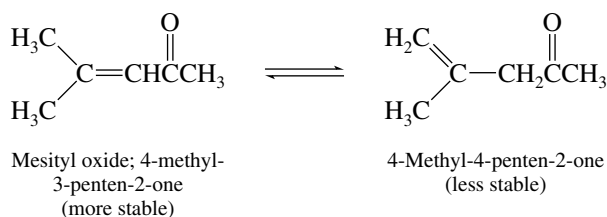
This enolate adds to the carbonyl group of benzaldehyde to give the mixed aldol addition product, which then dehydrates under the reaction conditions.



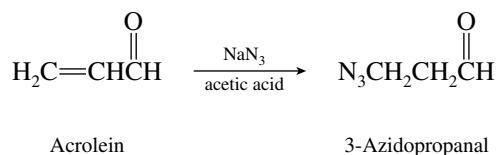
(c) The enolate of cyclohexanone adds to benzaldehyde. Dehydration of the mixed aldol addition product takes place under the reaction conditions to give the following mixed aldol condensation product.



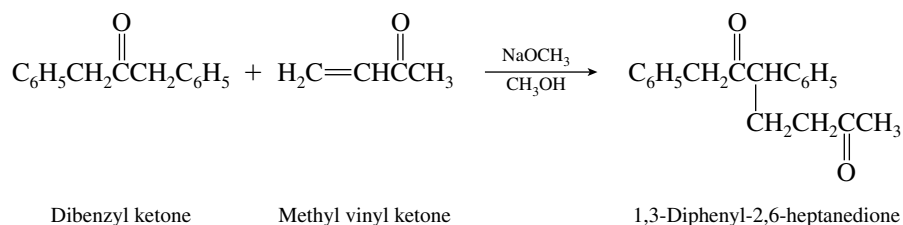
**18.14** Mesityl oxide is an  $\alpha,\beta$ -unsaturated ketone. Traces of acids or bases can catalyze its isomerization so that some of the less stable  $\beta,\gamma$ -unsaturated isomer is present.



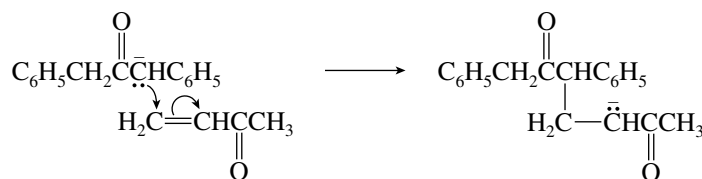
**18.15** The relationship between the molecular formula of acrolein ( $\text{C}_3\text{H}_4\text{O}$ ) and the product ( $\text{C}_3\text{H}_5\text{N}_3\text{O}$ ) corresponds to the addition of  $\text{HN}_3$  to acrolein. Because propanal ( $\text{CH}_3\text{CH}_2\text{CH}=\text{O}$ ) does not react under these conditions, the carbon-carbon, not the carbon-oxygen, double bond of acrolein is the reactive site. Conjugate addition is the reaction that occurs.



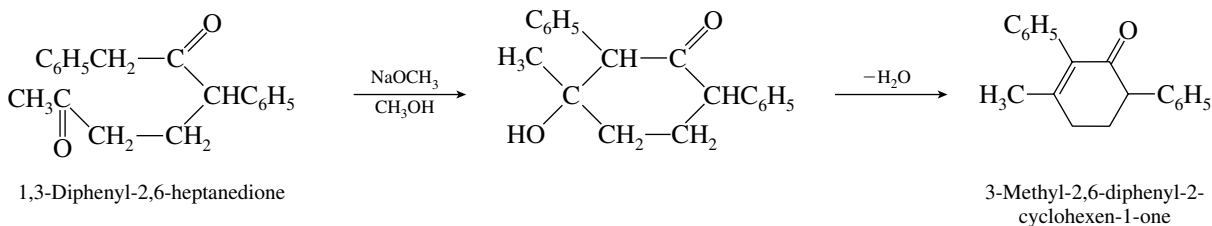
18.16 The enolate of dibenzyl ketone adds to methyl vinyl ketone in the conjugate addition step.



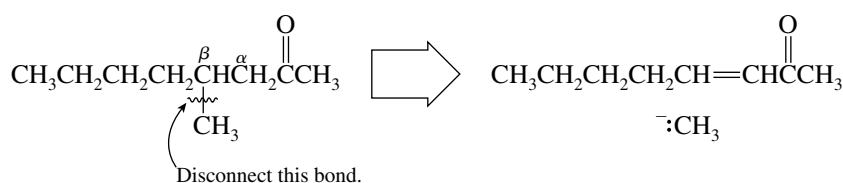
via



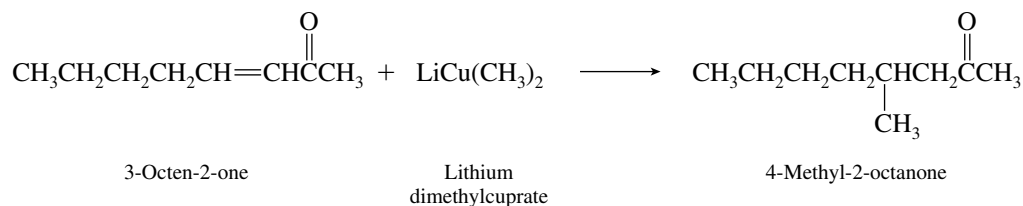
The intramolecular aldol condensation that gives the observed product is



18.17 A second solution to the synthesis of 4-methyl-2-octanone by conjugate addition of a lithium dialkylcuprate reagent to an  $\alpha,\beta$ -unsaturated ketone is revealed by the disconnection shown:

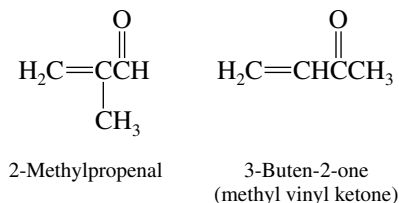
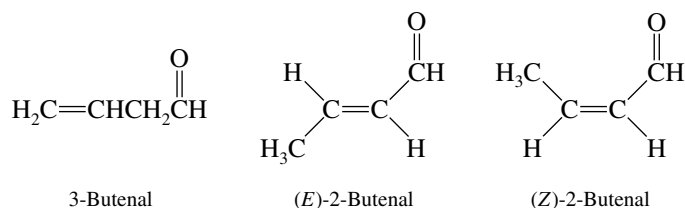


According to this disconnection, the methyl group is derived from lithium dimethylcuprate.



18.18 (a) In addition to the double bond of the carbonyl group, there must be a double bond elsewhere in the molecule in order to satisfy the molecular formula  $\text{C}_4\text{H}_6\text{O}$  (the problem states that the

compounds are noncyclic). There are a total of five isomers:

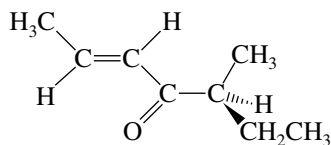


- (b) The *E* and *Z* isomers of 2-butenal are stereoisomers.  
 (c) None of the  $\text{C}_4\text{H}_6\text{O}$  aldehydes and ketones is chiral.  
 (d) The  $\alpha,\beta$ -unsaturated aldehydes are (*E*)- and (*Z*)- $\text{CH}_3\text{CH}=\text{CHCHO}$ ; and  $\text{H}_2\text{C}=\overset{\text{O}}{\parallel}\text{CCHO}$ .  
 $\begin{array}{c} \text{CH}_3 \\ | \\ \text{H}_2\text{C}=\overset{\text{O}}{\parallel}\text{CCHO} \end{array}$

There is one  $\alpha,\beta$ -unsaturated ketone in the group:  $\text{H}_2\text{C}=\overset{\text{O}}{\parallel}\text{CHCCH}_3$ .

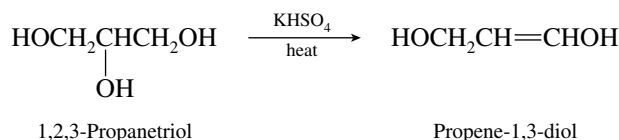
- (e) The *E* and *Z* isomers of 2-butenal are formed by the aldol condensation of acetaldehyde.

**18.19** The main flavor component of the hazelnut has the structure shown.

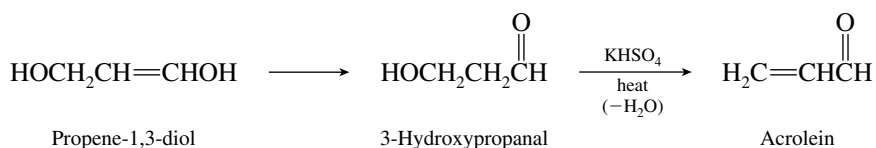


(2*E*,5*S*)-5-Methyl-2-hepten-4-one

**18.20** The characteristic reaction of an alcohol on being heated with  $\text{KHSO}_4$  is acid-catalyzed dehydration. Secondary alcohols dehydrate faster than primary alcohols, and so a reasonable first step is

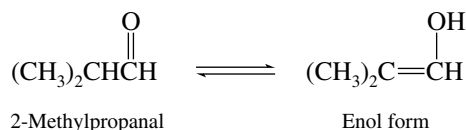


The product of this dehydration is an enol, which tautomerizes to an aldehyde. The aldehyde then undergoes dehydration to form acrolein.

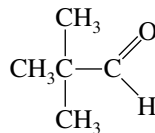




- 18.21 (a) 2-Methylpropanal has the greater enol content.

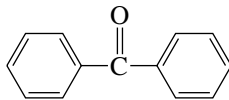


Although the enol content of 2-methylpropanal is quite small, the compound is nevertheless capable of enolization, whereas the other compound, 2,2-dimethylpropanal, cannot enolize—it has no  $\alpha$  hydrogens.



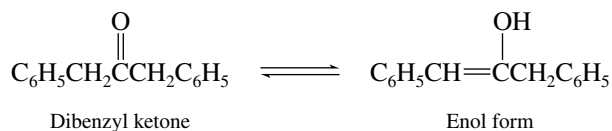
(Enolization is impossible.)

- (b) Benzophenone has no  $\alpha$  hydrogens; it cannot form an enol.

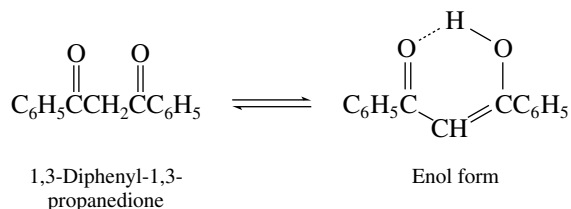


(Enolization is impossible.)

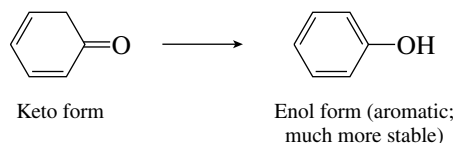
Dibenzyl ketone enolizes slightly to form a small amount of enol.



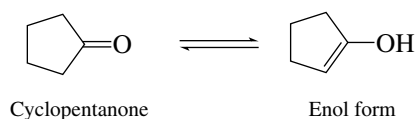
- (c) Here we are comparing a simple ketone, dibenzyl ketone, with a  $\beta$ -diketone. The  $\beta$ -diketone enolizes to a much greater extent than the simple ketone because its enol form is stabilized by conjugation of the double bond with the remaining carbonyl group and by intramolecular hydrogen bonding.



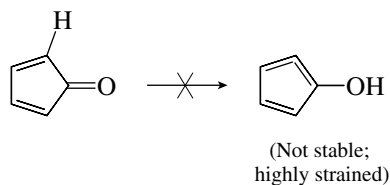
- (d) The enol content of cyclohexanone is quite small, whereas the enol form of 2,4-cyclohexadienone is the aromatic compound phenol, and therefore enolization is essentially complete.



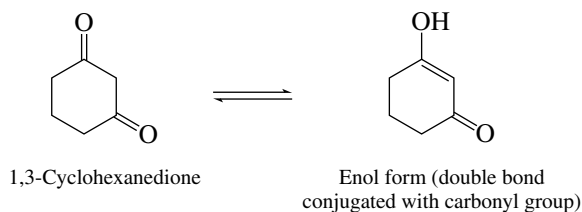
- (e) A small amount of enol is in equilibrium with cyclopentanone.



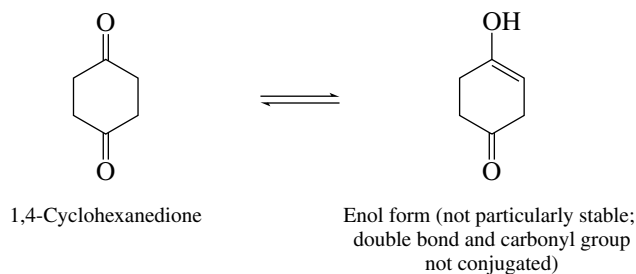
Cyclopentadienone does not form a stable enol. Enolization would lead to a highly strained allene-type compound.



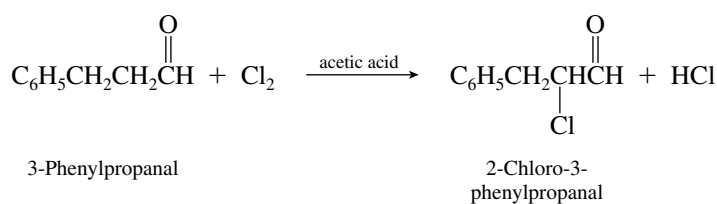
- (f) The  $\beta$ -diketone is more extensively enolized.



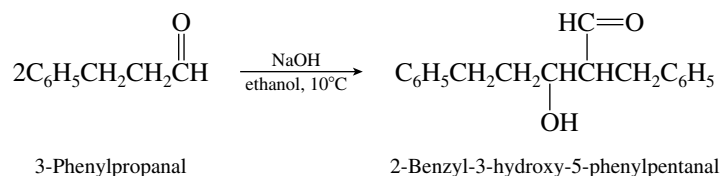
The double bond of the enol form of 1,4-cyclohexanedione is not conjugated with the carbonyl group. Its enol content is expected to be similar to that of cyclohexanone.



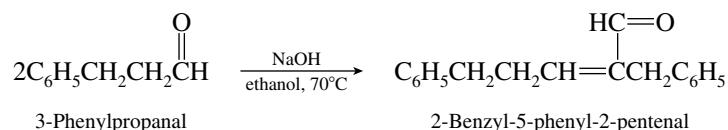
- 18.22 (a) Chlorination of 3-phenylpropanal under conditions of acid catalysis occurs via the enol form and yields the  $\alpha$ -chloro derivative.



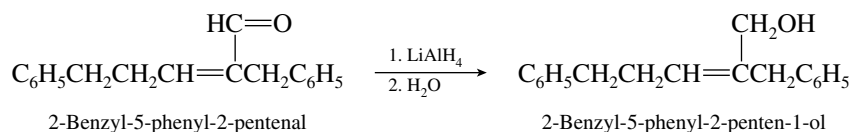
- (b) Aldehydes undergo aldol addition on treatment with base.



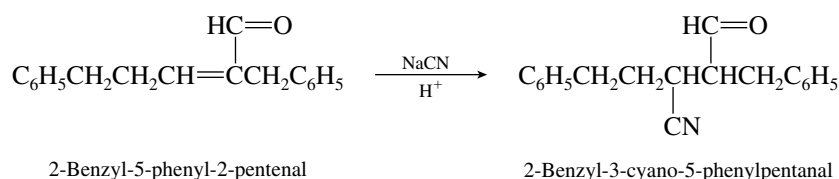
- (c) Dehydration of the aldol addition product occurs when the reaction is carried out at elevated temperature.



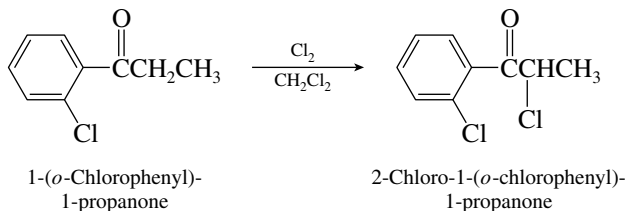
- (d) Lithium aluminum hydride reduces the aldehyde function to the corresponding primary alcohol.



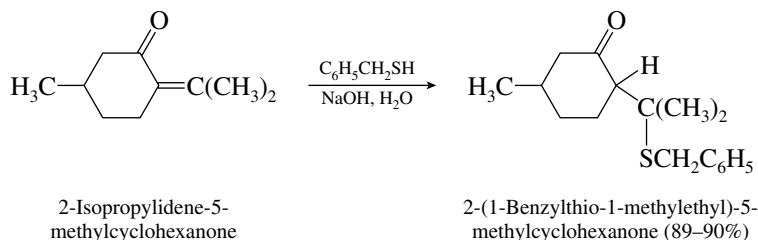
- (e) A characteristic reaction of  $\alpha,\beta$ -unsaturated carbonyl compounds is their tendency to undergo conjugate addition on treatment with weakly basic nucleophiles.



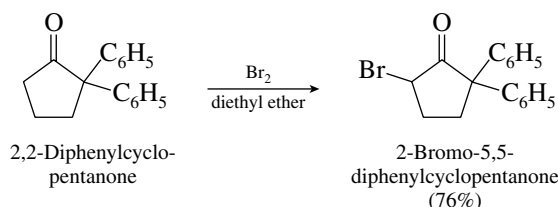
- 18.23** (a) Ketones undergo  $\alpha$  halogenation by way of their enol form.



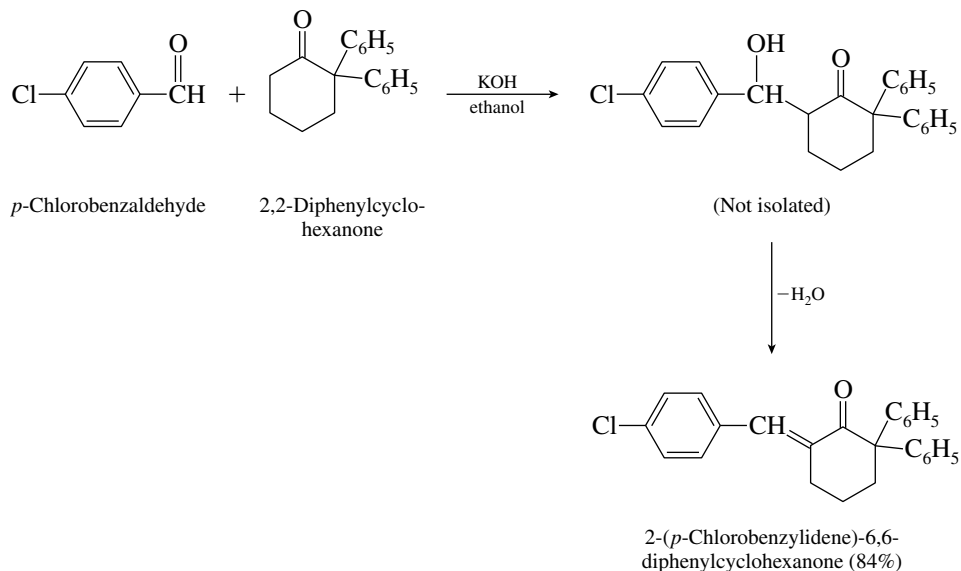
- (b) The combination of  $\text{C}_6\text{H}_5\text{CH}_2\text{SH}$  and  $\text{NaOH}$  yields  $\text{C}_6\text{H}_5\text{CH}_2\text{S}^-$  (as its sodium salt), which is a weakly basic nucleophile and adds to  $\alpha,\beta$ -unsaturated ketones by conjugate addition.



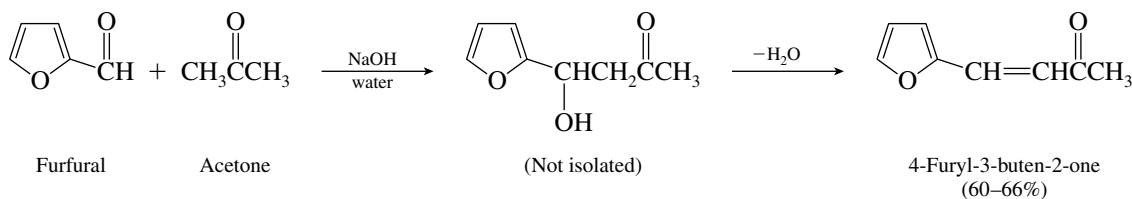
- (c) Bromination occurs at the carbon atom that is  $\alpha$  to the carbonyl group.



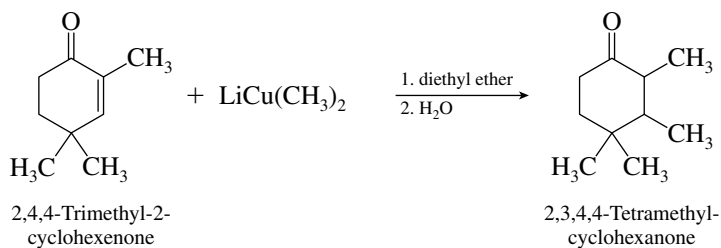
- (d) The reaction is a mixed aldol condensation. The enolate of 2,2-diphenylcyclohexanone reacts with *p*-chlorobenzaldehyde. Elimination of the aldol addition product occurs readily to yield the  $\alpha,\beta$ -unsaturated ketone as the isolated product.



- (e) The aldehyde given as the starting material is called **furfural** and is based on a furan unit as an aromatic ring. Furfural cannot form an enolate. It reacts with the enolate of acetone in a manner much as benzaldehyde would.

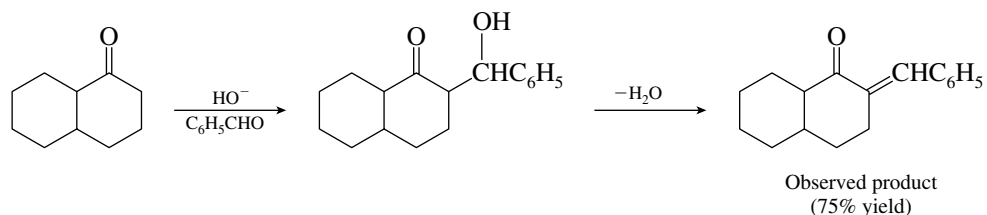


- (f) Lithium dialkylcuprates transfer an alkyl group to the  $\beta$ -carbon atom of  $\alpha,\beta$ -unsaturated ketones.

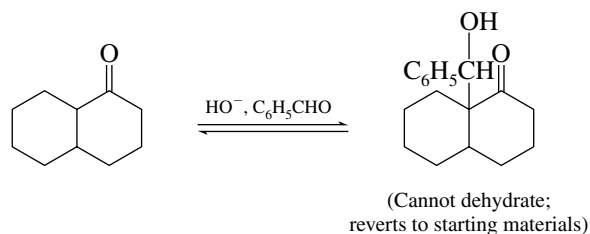


A mixture of stereoisomers was obtained in 67% yield in this reaction.

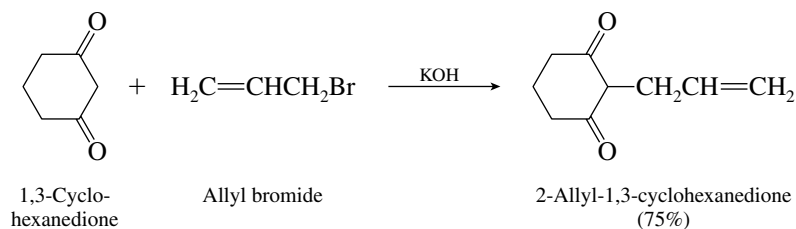
- (g) Two nonequivalent  $\alpha$ -carbon atoms occur in the starting ketone. Although enolate formation is possible at either position, only reaction at the methylene carbon leads to an intermediate that can undergo dehydration.



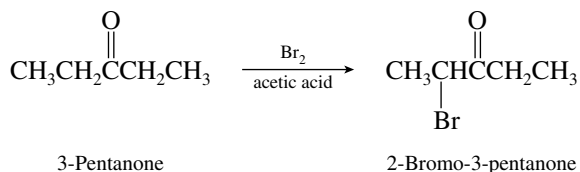
Reaction at the other  $\alpha$  position gives an intermediate that cannot dehydrate.



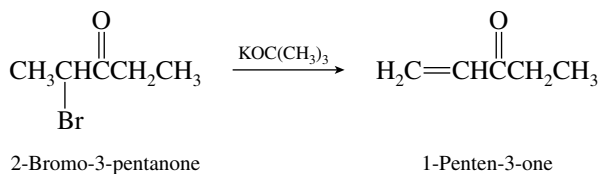
- (h)  $\beta$ -Diketones readily undergo alkylation by primary halides at the most acidic position, on the carbon between the carbonyls.



- 18.24 (a) Conversion of 3-pentanone to 2-bromo-3-pentanone is best accomplished by acid-catalyzed bromination via the enol. Bromine in acetic acid is the customary reagent for this transformation.

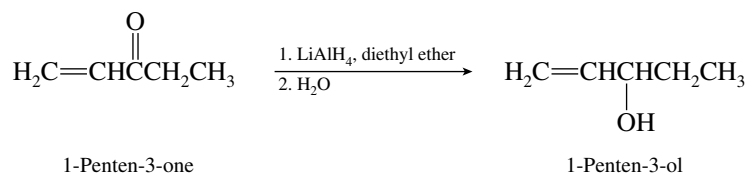


- (b) Once 2-bromo-3-pentanone has been prepared, its dehydrohalogenation by base converts it to the desired  $\alpha,\beta$ -unsaturated ketone 1-penten-3-one.



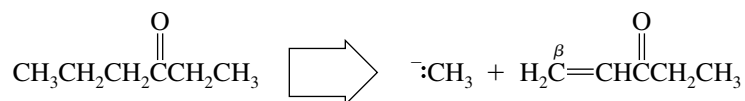
Potassium *tert*-butoxide is a good base for bringing about elimination reactions of secondary alkyl halides; suitable solvents include *tert*-butyl alcohol and dimethyl sulfoxide.

- (c) Reduction of the carbonyl group of 1-penten-3-one converts it to the desired alcohol.

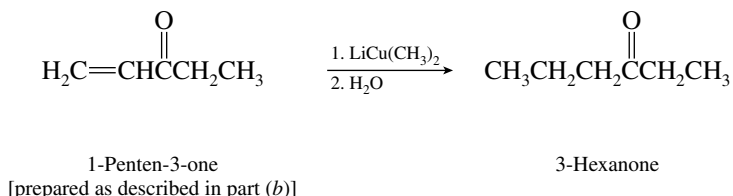


Catalytic hydrogenation would not be suitable for this reaction because reduction of the double bond would accompany carbonyl reduction.

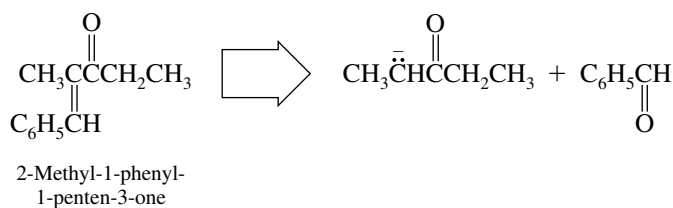
- (d) Conversion of 3-pentanone to 3-hexanone requires addition of a methyl group to the  $\beta$ -carbon atom.



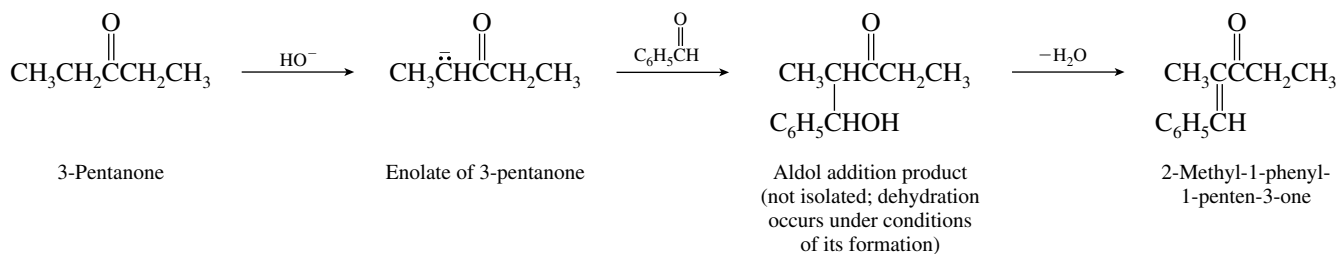
The best way to add an alkyl group to the  $\beta$  carbon of a ketone is via conjugate addition of a dialkylcuprate reagent to an  $\alpha,\beta$ -unsaturated ketone.



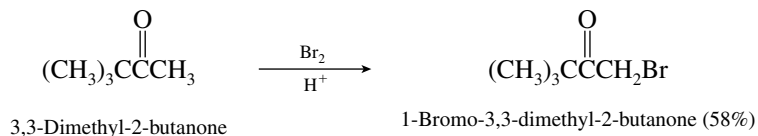
- (e) The compound to be prepared is the mixed aldol condensation product of 3-pentanone and benzaldehyde.



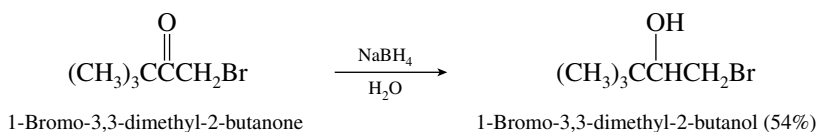
The desired reaction sequence is



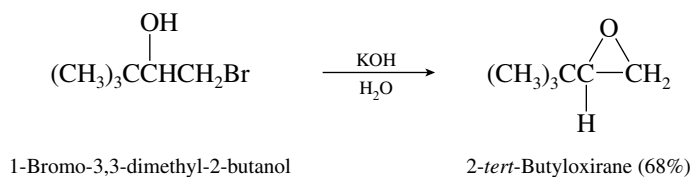
- 18.25 (a) The first step is an  $\alpha$  halogenation of a ketone. This is customarily accomplished under conditions of acid catalysis.



In the second step the carbonyl group of the  $\alpha$ -bromo ketone is reduced to a secondary alcohol. As actually carried out, sodium borohydride in water was used to achieve this transformation.



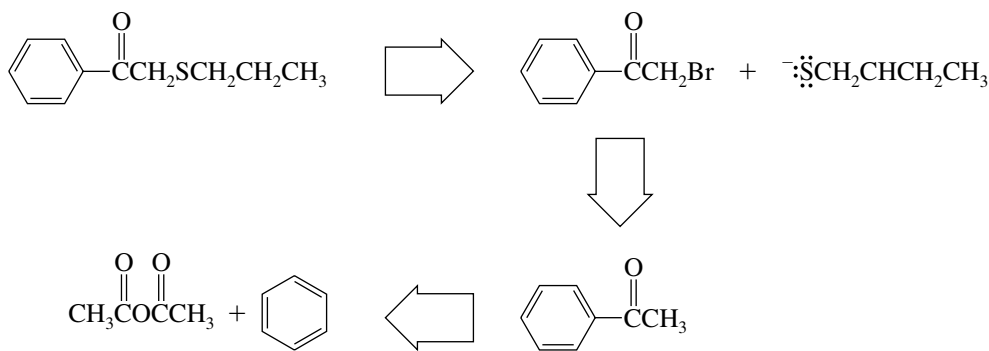
The third step is conversion of a vicinal bromohydrin to an epoxide in aqueous base.



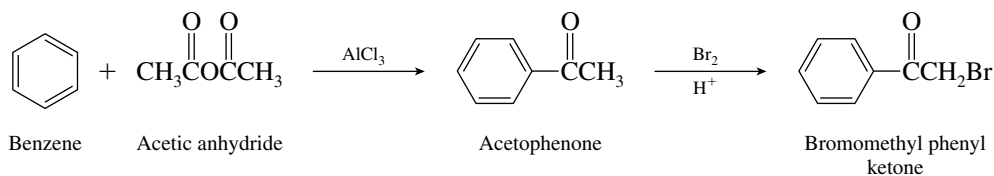
(b) The overall yield is the product of the yields of the individual steps.

$$\begin{aligned}
 \text{Yield} &= 100(0.58 \times 0.54 \times 0.68) \\
 &= 21\%
 \end{aligned}$$

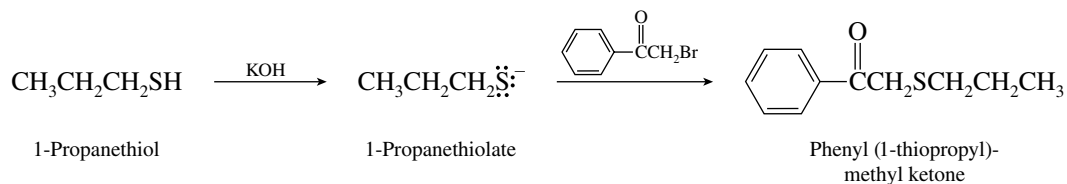
**18.26** The product is a sulfide (thioether). Retrosynthetic analysis reveals a pathway that begins with benzene and acetic anhydride.



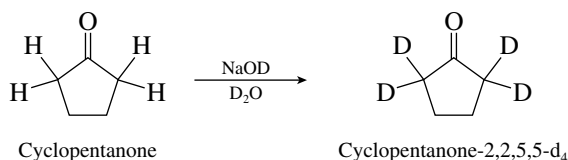
The desired synthesis can be accomplished with the following series of reactions:



The synthesis is completed by reacting bromomethyl phenyl ketone with 1-propanethiolate anion.

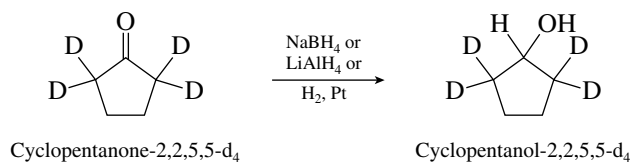


**18.27** All these problems begin in the same way, with exchange of all the  $\alpha$  protons for deuterium (Section 18.8).

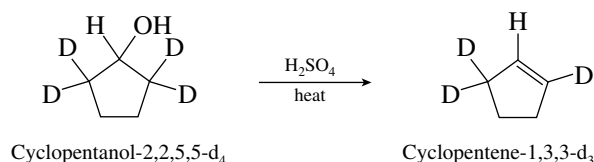


Once the tetradeuterated cyclopentanone has been prepared, functional group transformations are employed to convert it to the desired products.

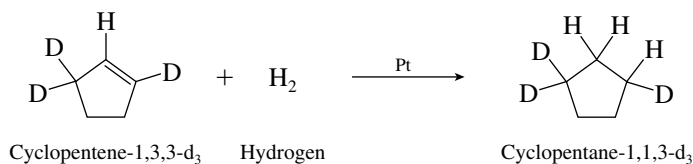
- (a) Reduction of the carbonyl group can be achieved by using any of the customary reagents.



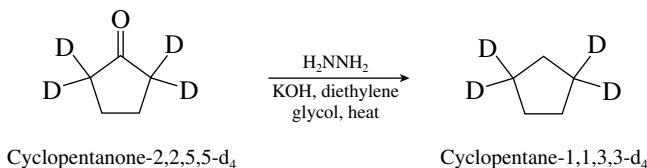
- (b) Acid-catalyzed dehydration of the alcohol prepared in part (a) yields the desired alkene.



- (c) Catalytic hydrogenation of the alkene in part (b) yields cyclopentane-1,1,3,3-d<sub>3</sub>.

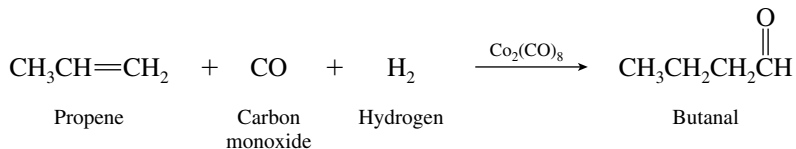


- (d) Carbonyl reduction of the tetradeuterated ketone under Wolff–Kishner conditions furnishes the desired product.

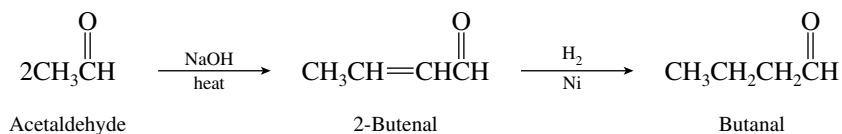


Alternatively, Clemmensen reduction conditions (Zn, HCl) could be used.

- 18.28** (a) Hydroformylation converts alkenes to aldehydes having one more carbon atom by reaction with carbon monoxide and hydrogen in the presence of a cobalt octacarbonyl catalyst.



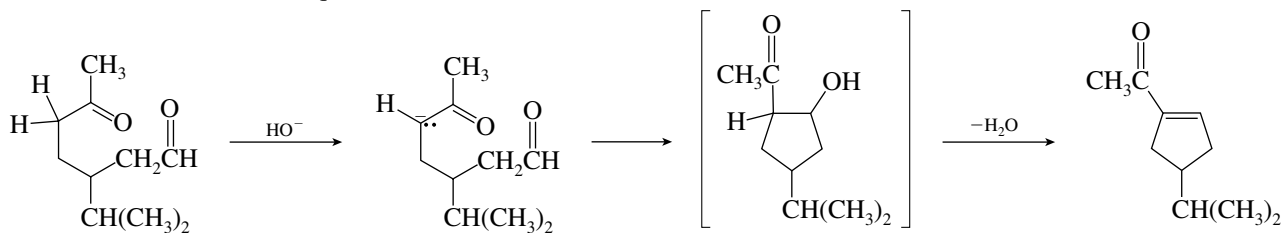
- (b) Aldol condensation of acetaldehyde to 2-butenal, followed by catalytic hydrogenation of the carbon–carbon double bond, gives butanal.



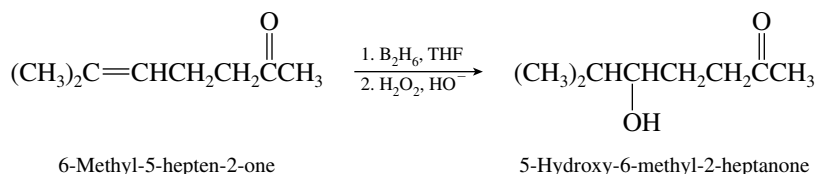




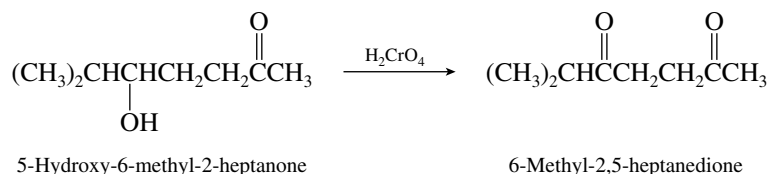
Cyclization of the resulting keto aldehyde is an intramolecular aldol condensation. Base is required.



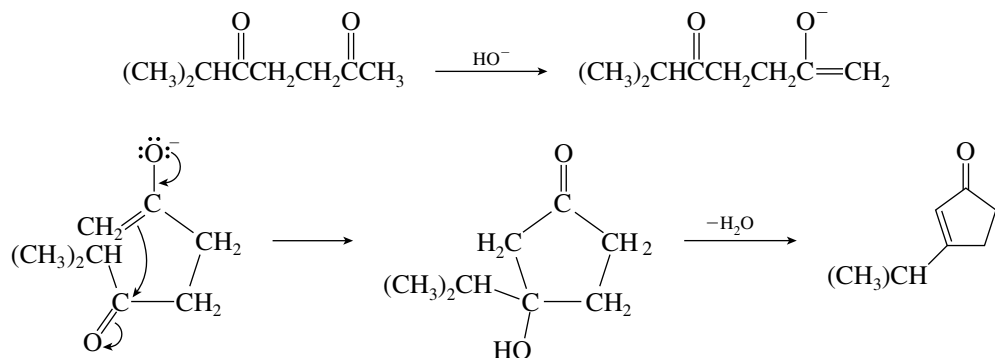
- (d) The first step in this synthesis is the hydration of the alkene function to an alcohol. Notice that this hydration must take place with a regioselectivity opposite to that of Markovnikov's rule and therefore requires a hydroboration–oxidation sequence.



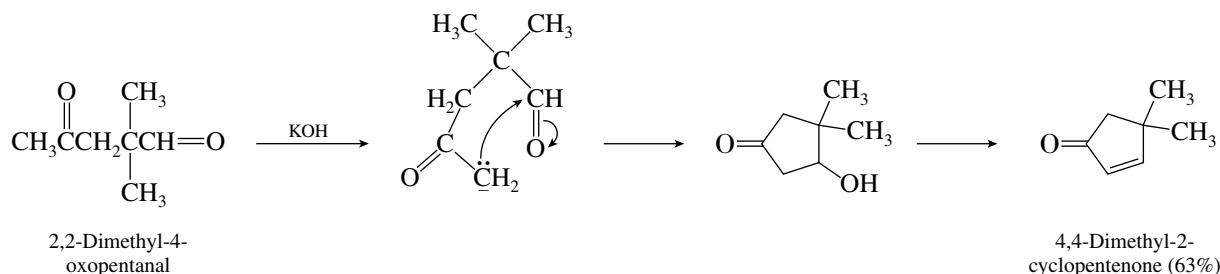
Conversion of the secondary alcohol function to a carbonyl group can be achieved with any of a number of oxidizing agents.



Cyclization of the dione to the final product is a base-catalyzed intramolecular aldol condensation and was accomplished in 71% yield by treatment of the dione with a 2% solution of sodium hydroxide in aqueous ethanol.

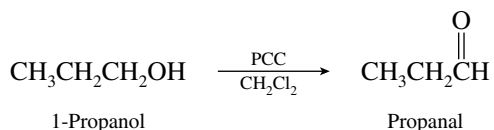
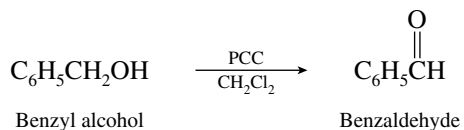


- 18.30** Intramolecular aldol condensations occur best when a five- or six-membered ring is formed. Carbon–carbon bond formation therefore involves the aldehyde and the methyl group attached to the ketone carbonyl.

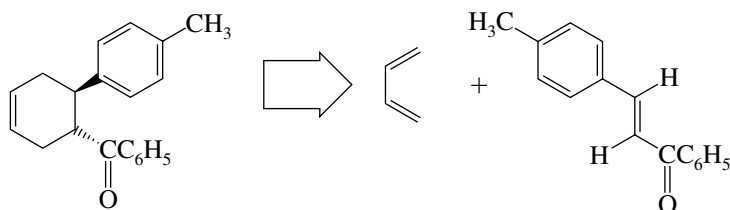




The starting materials for the mixed aldol condensation—benzaldehyde and propanal—are prepared by oxidation of benzyl alcohol and 1-propanol, respectively.



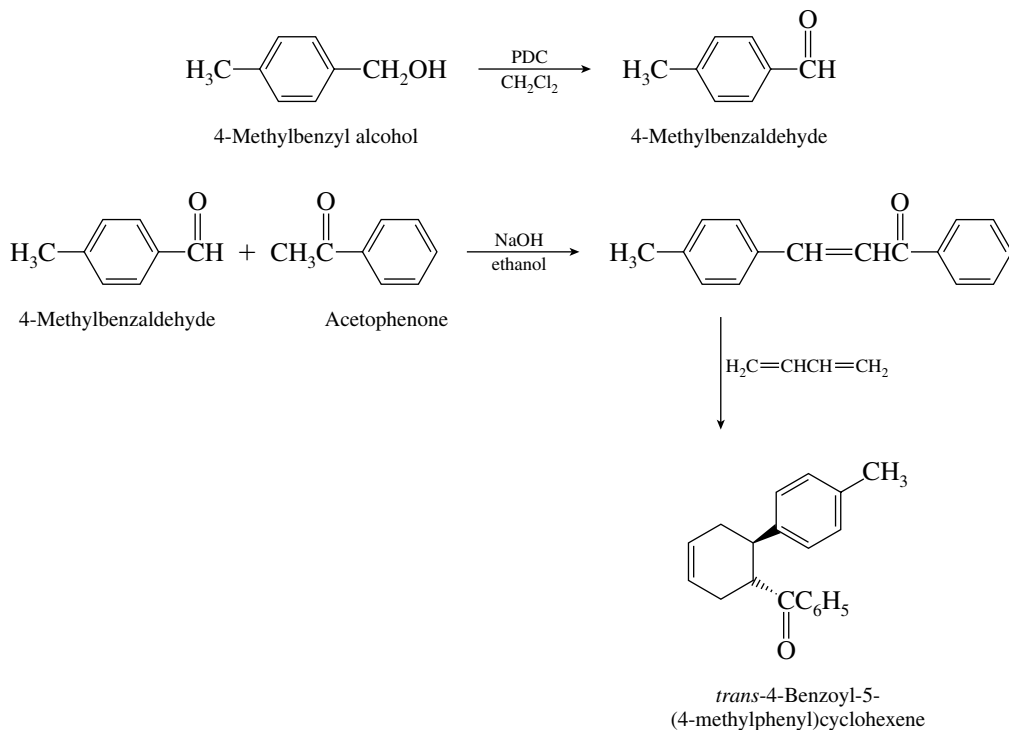
(c) The cyclohexene ring in this case can be assembled by a Diels–Alder reaction.



1,3-Butadiene is one of the given starting materials; the  $\alpha,\beta$ -unsaturated ketone is the mixed aldol condensation product of 4-methylbenzaldehyde and acetophenone.

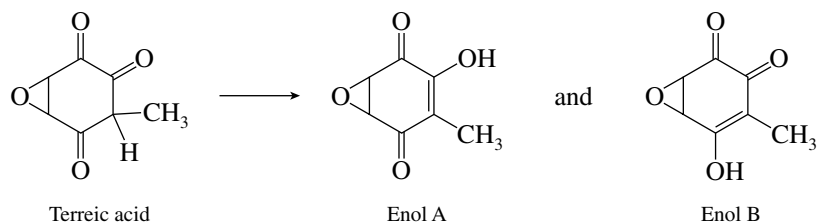


The complete synthetic sequence is



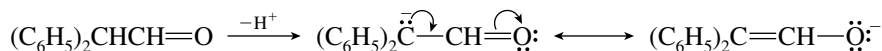
$\alpha,\beta$ -Unsaturated ketones are good dienophiles in Diels–Alder reactions.

- 18.32 It is the carbon atom flanked by two carbonyl groups that is involved in the enolization of terreic acid.

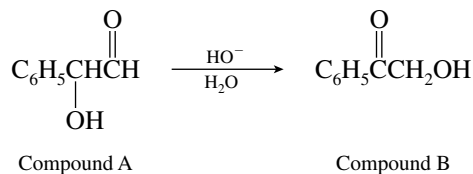


Of these two structures, enol A, with its double bond conjugated to two carbonyl groups, is more stable than enol B, in which the double bond is conjugated to only one carbonyl.

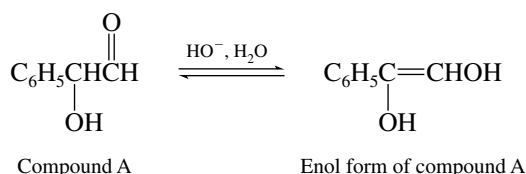
- 18.33 (a) Recall that aldehydes and ketones are in equilibrium with their *hydrates* in aqueous solution (Section 17.6). Thus, the principal substance present when  $(\text{C}_6\text{H}_5)_2\text{CHCH}=\text{O}$  is dissolved in aqueous acid is  $(\text{C}_6\text{H}_5)_2\text{CHCH}(\text{OH})_2$  (81%).
- (b) The problem states that the major species present in aqueous base is *not*  $(\text{C}_6\text{H}_5)_2\text{CHCH}=\text{O}$ , its enol, or its hydrate. The most reasonable species is the **enolate ion**:



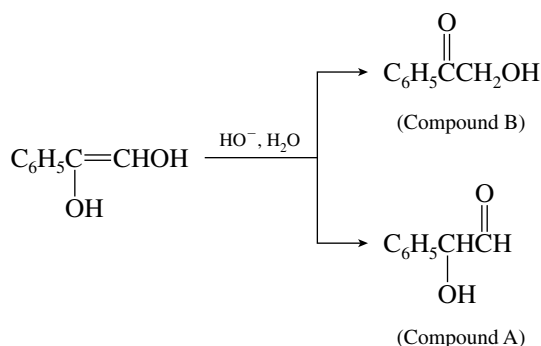
- 18.34 (a) At first glance this transformation seems to be an internal oxidation–reduction reaction. An aldehyde function is reduced to a primary alcohol, and a secondary alcohol is oxidized to a ketone.



Once one realizes that enolization can occur, however, a simpler explanation, involving only proton-transfer reactions, emerges.

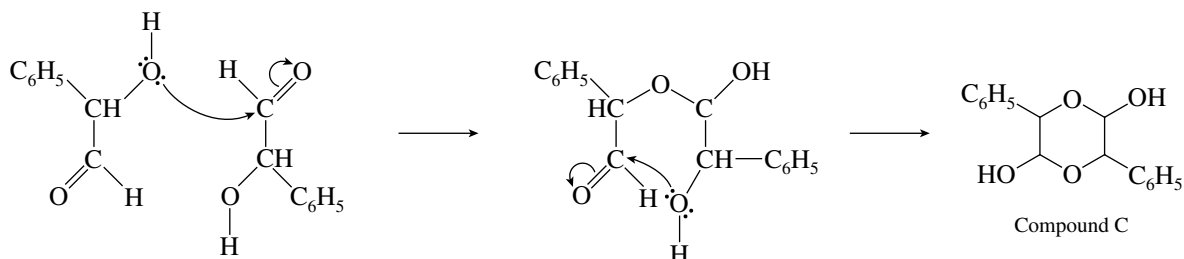


The enol form of compound A is an enediol; it is at the same time the enol form of compound B. The enediol can revert to compound A or to compound B.

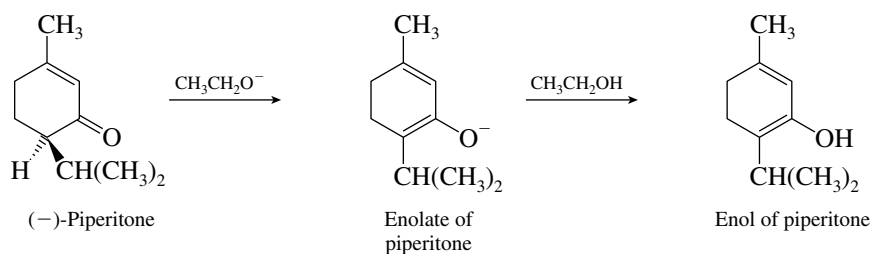


At equilibrium, compound B predominates because it is more stable than A. A ketone carbonyl is more stabilized than an aldehyde, and the carbonyl in B is conjugated with the benzene ring.

(b) The isolated product is the double hemiacetal formed between two molecules of compound A.

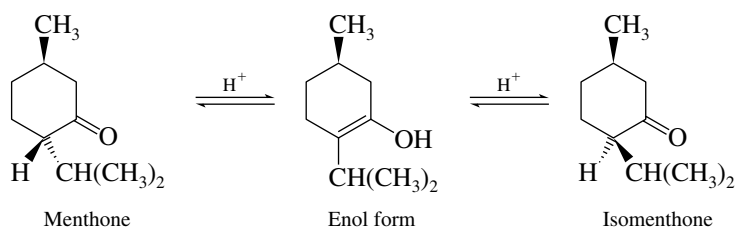


18.35 (a) The only stereogenic center in piperitone is adjacent to a carbonyl group. Base-catalyzed enolization causes this carbon to lose its stereochemical integrity.



Both the enolate and enol of piperitone are achiral and can revert only to a racemic mixture of piperitones.

(b) The enol formed from menthone can revert to either menthone or isomenthone.

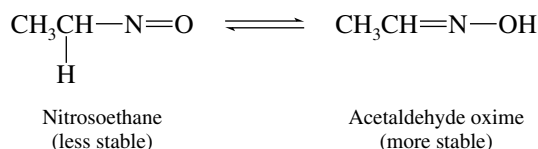


Only the stereochemistry at the  $\alpha$ -carbon atom is affected by enolization. The other stereogenic center in menthone (the one bearing the methyl group) is not affected.

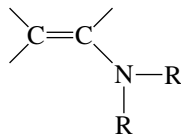
18.36 In all parts of this problem the bonding change that takes place is described by the general equation



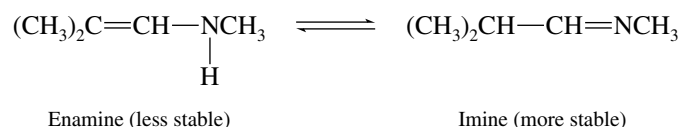
(a) The compound given is nitrosoethane. Nitrosoalkanes are less stable than their oxime isomers formed by proton transfer.



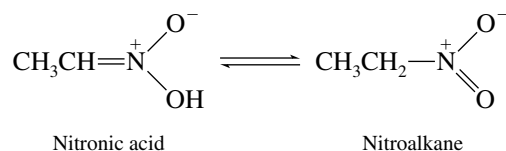
- (b) You may recognize this compound as an enamine. It is slightly different, however, from the enamines we discussed earlier (Section 17.11) in that nitrogen bears a hydrogen substituent. Stable enamines are compounds of the type



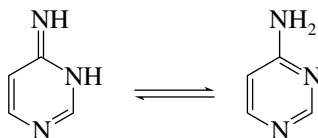
where neither R group is hydrogen; both R's must be alkyl or aryl. Enamines that bear a hydrogen substituent are converted to imines in a proton-transfer equilibrium.



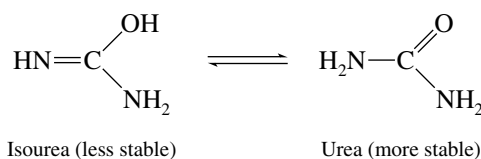
- (c) The compound given is known as a **nitronic acid**; its more stable tautomeric form is a nitroalkane.



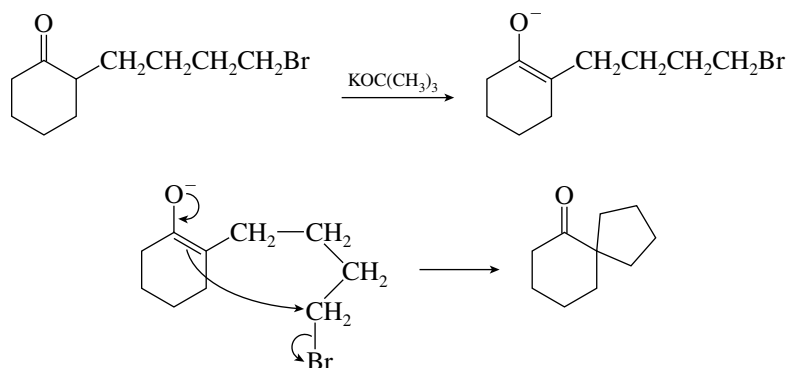
- (d) The six-membered ring is aromatic in the tautomeric form derived from the compound given.



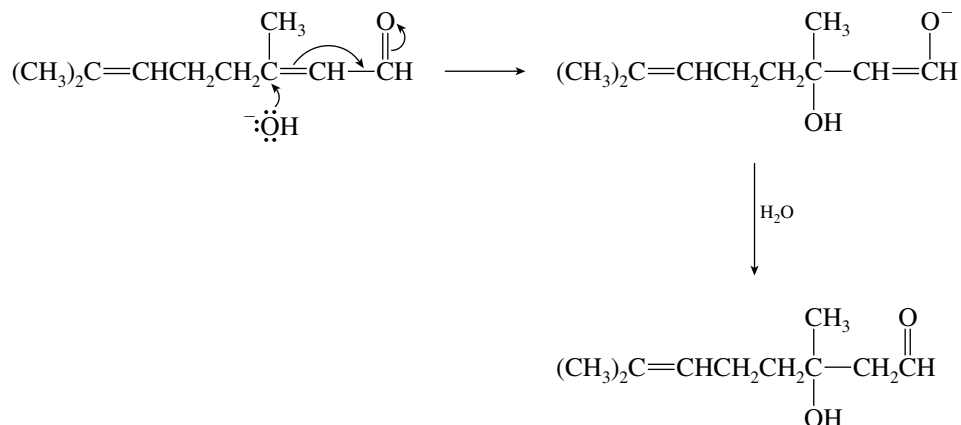
- (e) This compound is called **isourea**. Urea has a carbon-oxygen double bond and is more stable.



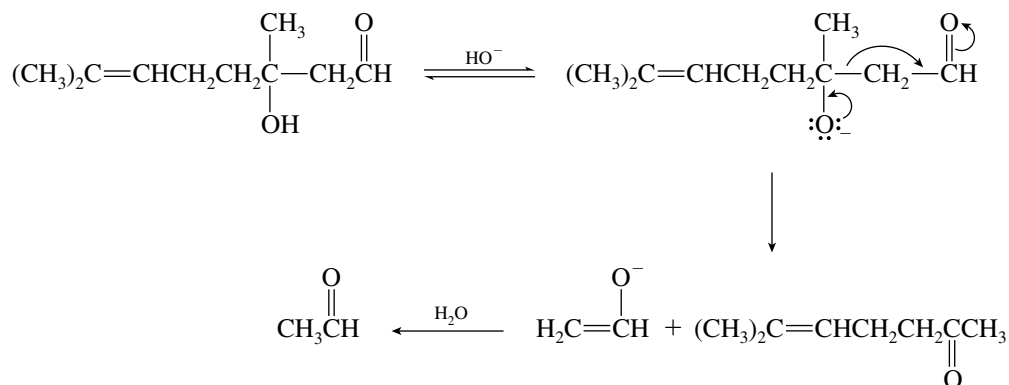
- 18.37** (a) This reaction is an intramolecular alkylation of a ketone. Although alkylation of a ketone with a separate alkyl halide molecule is usually difficult, **intramolecular** alkylation reactions can be carried out effectively. The enolate formed by proton abstraction from the  $\alpha$ -carbon atom carries out a nucleophilic attack on the carbon that bears the leaving group.



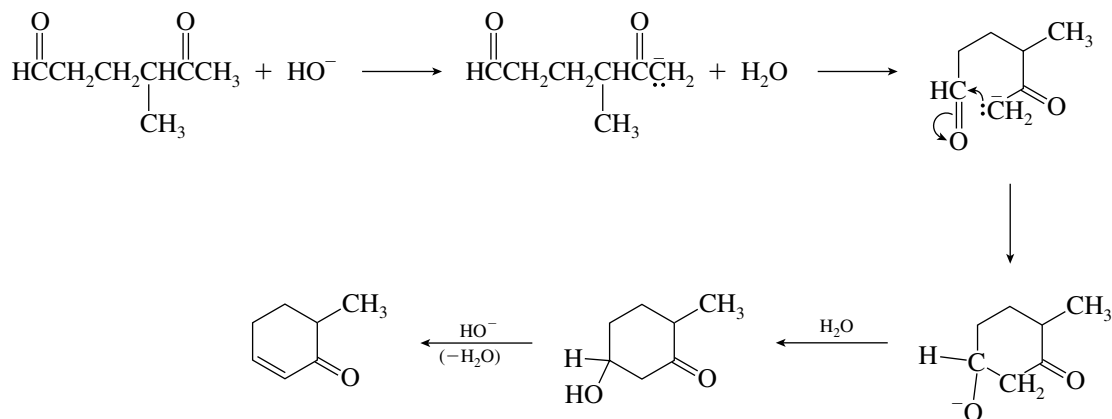
- (b) The starting material, known as **citral**, is converted to the two products by a reversal of an aldol condensation. The first step is conjugate addition of hydroxide.



The product of this conjugate addition is a  $\beta$ -hydroxy ketone. It undergoes base-catalyzed cleavage to the observed products.



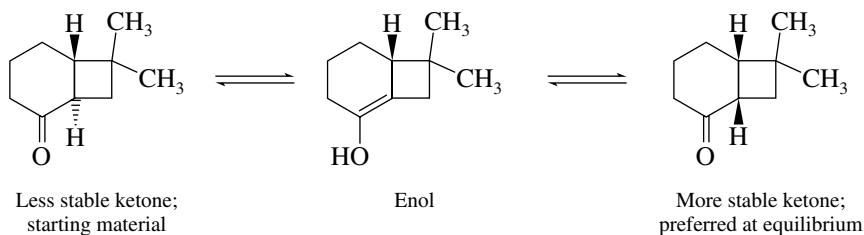
- (c) The product is formed by an intramolecular aldol condensation.



- (d) In this problem stereochemical isomerization involving a proton attached to the  $\alpha$ -carbon atom of a ketone takes place. Enolization of the ketone yields an intermediate in which the

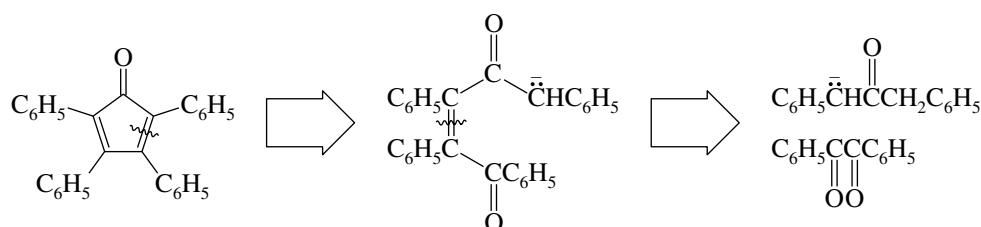


stereochemical integrity of the  $\alpha$  carbon is lost. Reversion to ketone eventually leads to the formation of the more stable stereoisomer at equilibrium.

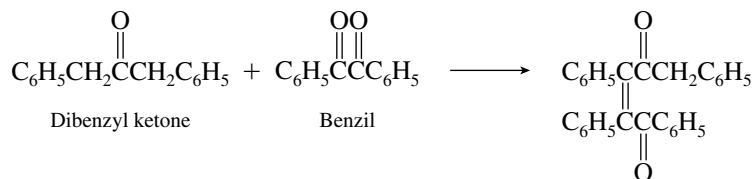


The rate of enolization is increased by heating or by base catalysis. The *cis* ring fusion in the product is more stable than the *trans* because there are not enough atoms in the six-membered ring to span *trans*-1,2 positions in the four-membered ring without excessive strain.

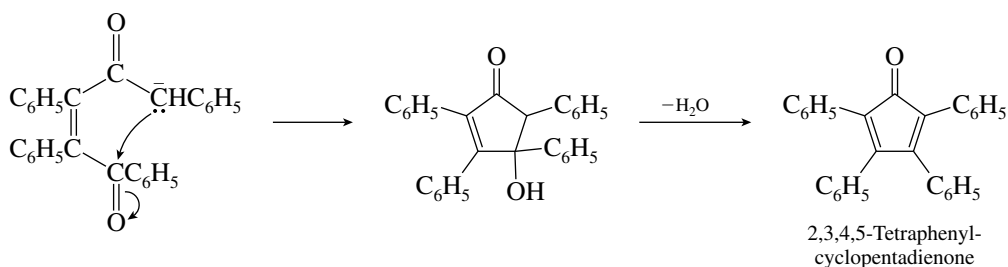
- (e) Working backward from the product, we can see that the transformation involves two aldol condensations: one intermolecular and the other intramolecular.



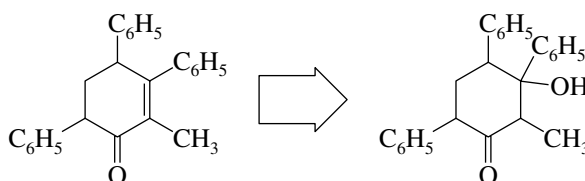
The first reaction is a mixed aldol condensation between the enolate of dibenzyl ketone and one of the carbonyl groups of the dione.



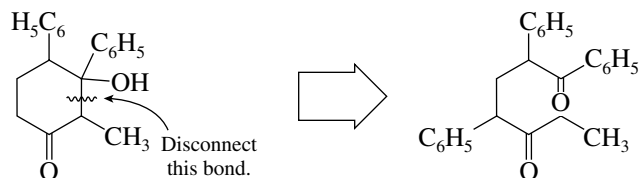
This is followed by an intramolecular aldol condensation.



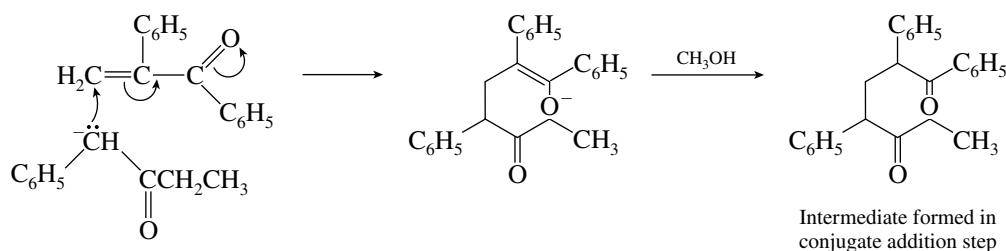
- (f) This is a fairly difficult problem because it is not obvious at the outset which of the two possible enolates of benzyl ethyl ketone undergoes conjugate addition to the  $\alpha,\beta$ -unsaturated ketone. A good idea here is to work backward from the final product—in effect, do a retrosynthetic analysis. The first step is to recognize that the enone arises by dehydration of a  $\beta$ -hydroxy ketone.



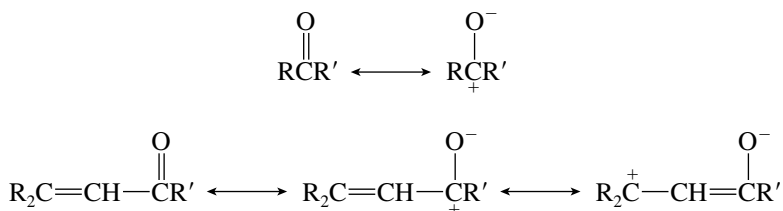
Now, mentally disconnect the bond between the  $\alpha$ -carbon atom and the carbon that bears the hydroxyl group to reveal the intermediate that undergoes intramolecular aldol condensation.



The  $\beta$ -hydroxy ketone is the intermediate formed in the intramolecular aldol addition step, and the diketone that leads to it is the intermediate that is formed in the conjugate addition step. The relationship of the starting materials to the intermediates and product is now more evident.

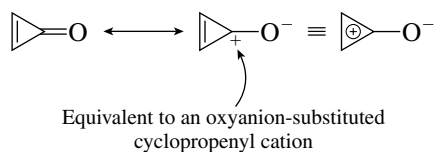


- 18.38 (a) The reduced  $\text{C}=\text{O}$  stretching frequency of  $\alpha,\beta$ -unsaturated ketones is consistent with an enhanced degree of single bond character as compared with simple dialkyl ketones.

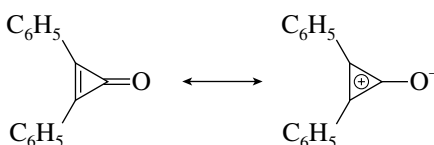


Resonance is more important in  $\alpha,\beta$ -unsaturated ketones. Conjugation of the carbonyl group with the carbon-carbon double bond increases opportunities for electron delocalization.

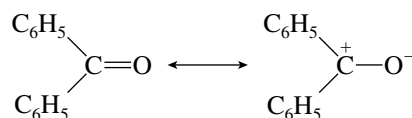
- (b) Even more single-bond character is indicated in the carbonyl group of cyclopropenone than in that of typical  $\alpha,\beta$ -unsaturated ketones. The dipolar resonance form contributes substantially to the electron distribution because of the aromatic character of the three-membered ring. Recall that cyclopropenyl cation satisfies the  $4n + 2$  rule for aromaticity (text Section 11.20).



- (c) The dipolar resonance form is a more important contributor to the electron distribution in diphenylcyclopropenone than in benzophenone.



is more pronounced than

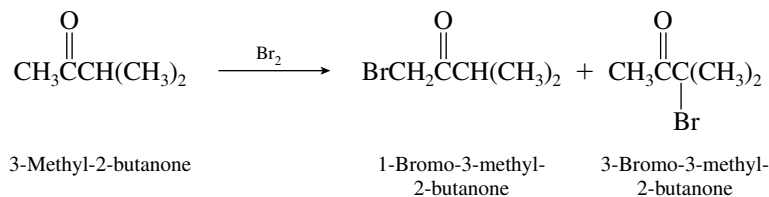


The dipolar resonance form of diphenylcyclopropanone has aromatic character. Its stability leads to increased charge separation and a larger dipole moment.

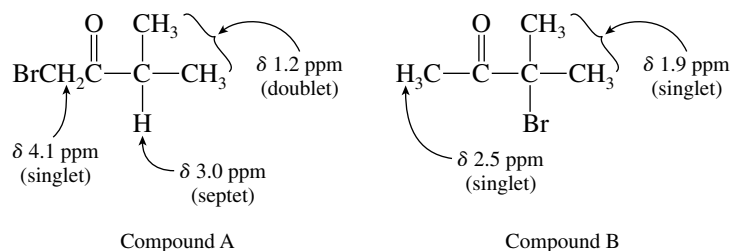
- (d) Decreased electron density at the  $\beta$  carbon atom of an  $\alpha,\beta$ -unsaturated ketone is responsible for its decreased shielding. The decreased electron density arises from the polarization of its  $\pi$  electrons as represented by a significant contribution of the dipolar resonance form.



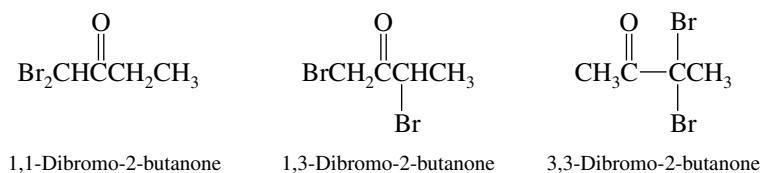
- 18.39 Bromination can occur at either of the two  $\alpha$ -carbon atoms.



The  $^1\text{H}$ NMR spectrum of the major product, compound A, is consistent with the structure of 1-bromo-3-methyl-2-butanone. The minor product B is identified as 3-bromo-3-methyl-2-butanone on the basis of its NMR spectrum.



- 18.40 Three dibromination products are possible from  $\alpha$  halogenation of 2-butanone.



The product is **1,3-dibromo-2-butanone**, on the basis of its observed  $^1\text{H}$  NMR spectrum, which showed two signals at low field. One is a two-proton singlet at  $\delta$  4.6 ppm assignable to  $\text{CH}_2\text{Br}$  and the other a one-proton quartet at  $\delta$  5.2 ppm assignable to  $\text{CHBr}$ .

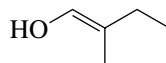
- 18.41 Solutions to molecular modeling exercises are not provided in this *Study Guide and Solutions Manual*. You should use *Learning By Modeling* for this exercise.

## SELF-TEST

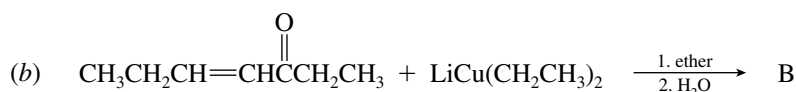
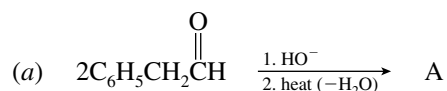
## PART A

A-1. Write the correct structure(s) for each of the following:

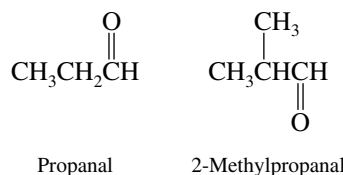
- The two enol forms of 2-butanone
- The enolate ion derived from reaction of 1,3-cyclohexanedione with sodium methoxide
- The carbonyl form of the following enol



A-2. Give the correct structures for compounds A and B in the following reaction schemes:

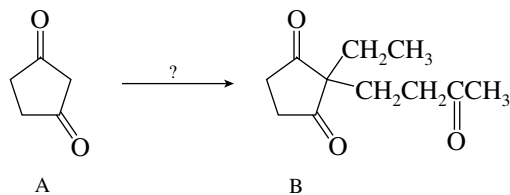


A-3. Write the structures of all the possible aldol addition products that may be obtained by reaction of a mixture of propanal and 2-methylpropanal with base.

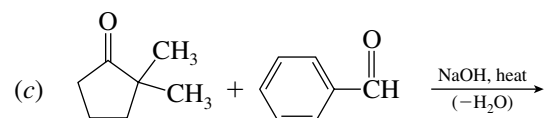
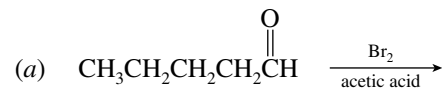


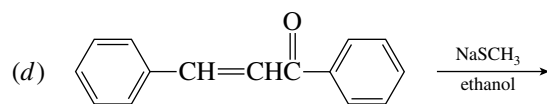
A-4. Using any necessary organic or inorganic reagents, outline a synthesis of 1,3-butanediol from ethanol as the only source of carbons.

A-5. Outline a series of reaction steps that will allow the preparation of compound B from 1,3-cyclopentanedione, compound A.

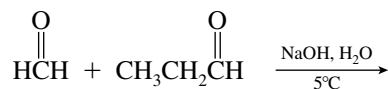


A-6. Give the structure of the product formed in each of the following reactions:

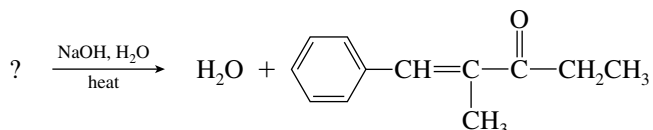




**A-7.** Write out the mechanism, using curved arrows to show electron movement, of the following aldol addition reaction.

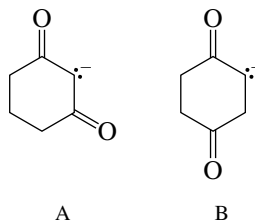


**A-8.** Identify the two starting materials needed to make the following compound by a mixed aldol condensation.



## PART B

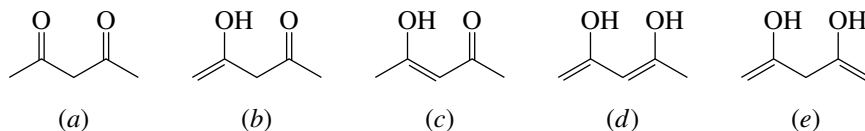
**B-1.** When enolate A is compared with enolate B



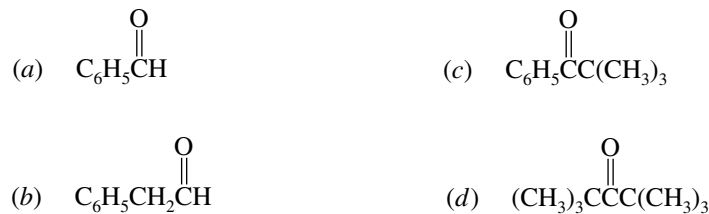
which of the following statements is true?

- A is more stable than B.
- B is more stable than A.
- A and B have the same stability.
- No comparison of stability can be made.

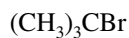
**B-2.** Which structure is the most stable?



**B-3.** Which one of the following molecules contains deuterium ( $^2\text{H} = \text{D}$ ) after reaction with NaOD in  $\text{D}_2\text{O}$ ?



**B-4.** Which of the following RX compounds is (are) the best alkylating agent(s) in the reaction shown?



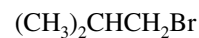
1



2



3



4

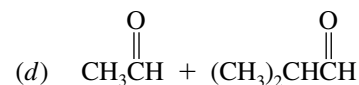
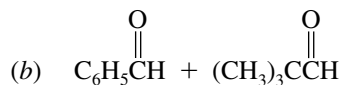
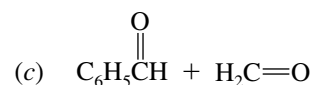
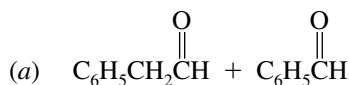
(a) 1 and 4

(c) 2 and 4

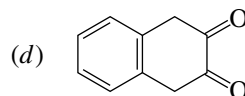
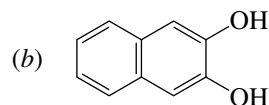
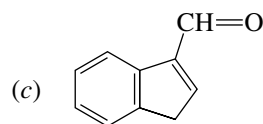
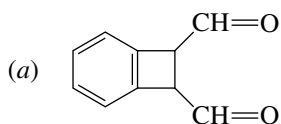
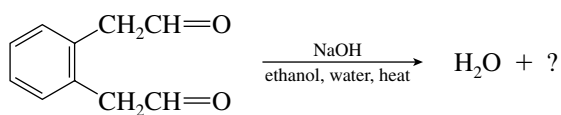
(b) 4 only

(d) 1, 3, and 4

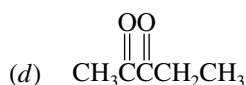
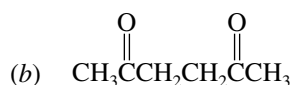
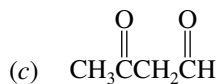
**B-5.** Which of the following pairs of aldehydes gives a single product in a mixed aldol condensation?



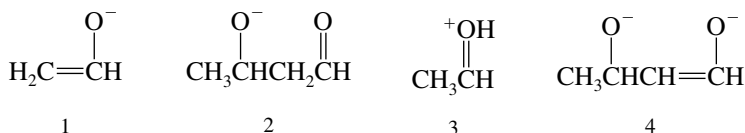
**B-6.** What is the principal product of the following reaction?



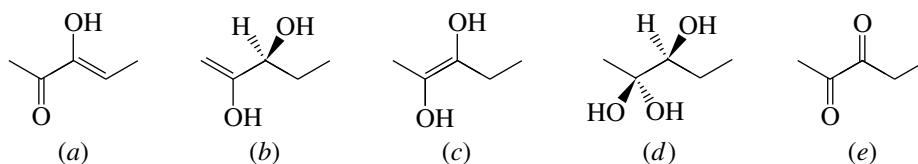
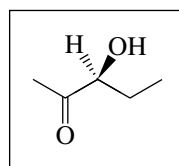
**B-7.** Which of the following forms an enol to the greatest extent?



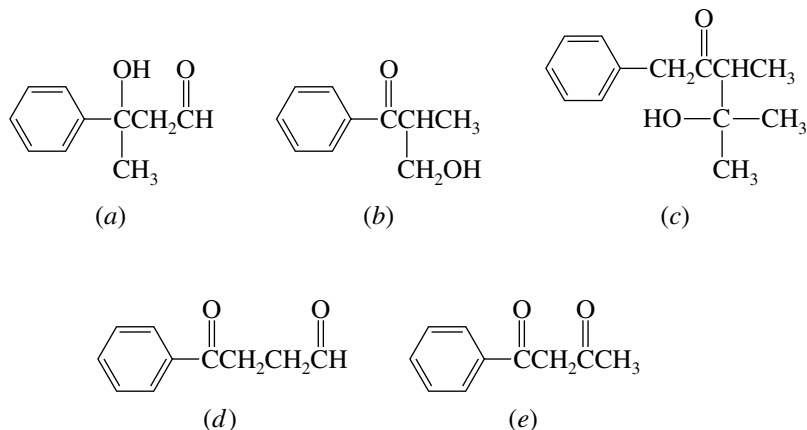
- B-8.** Which of the following species is (are) *not* intermediates in the aldol condensation of acetaldehyde (ethanal) in aqueous base?



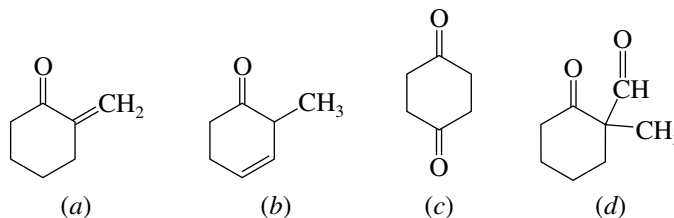
- (a) 1 and 2                      (c) 4 only                      (e) 3 and 4  
 (b) 3 only                      (d) 2 and 3
- B-9.** The compound shown in the box undergoes racemization on reaction with aqueous acid. Which of the following structures best represents the intermediate responsible for this process?



- B-10.** Which one of the following compounds is the best candidate for being prepared by an efficient mixed aldol addition reaction?



- B-11.** Which one of the following undergoes 1,4-addition with  $\text{CH}_3\text{SK}$  (in ethanol)?



**B-12.** Benzalacetone is the mixed aldol condensation product formed between benzaldehyde ( $\text{C}_6\text{H}_5\text{CH}=\text{O}$ ) and acetone [ $(\text{CH}_3)_2\text{C}=\text{O}$ ]. What is its structure?

