

## Quiz CH206

### Organic Chemistry

#### Aldehydes and Ketones

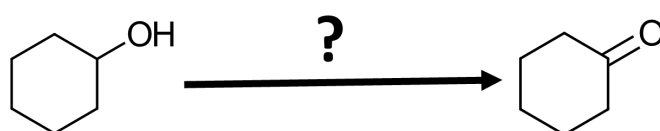
Lucas Monteiro Nogueira

#### ► PROBLEMS

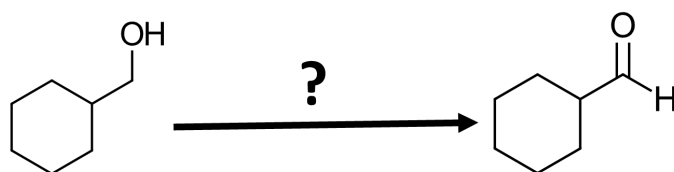
##### ► Problem 1

Let's begin by reviewing reactions used to prepare aldehydes and ketones. Identify reagents that can be used to achieve each of the following transformations.

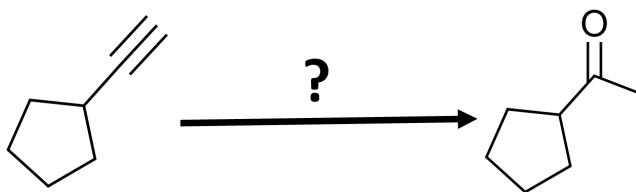
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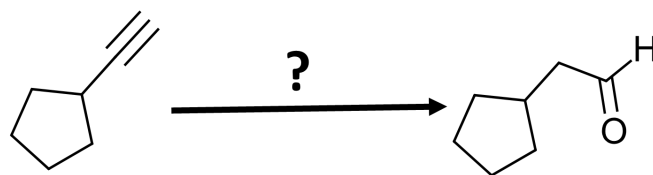
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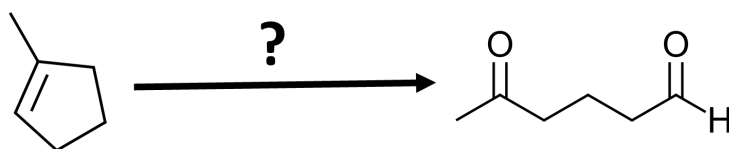
1.3.



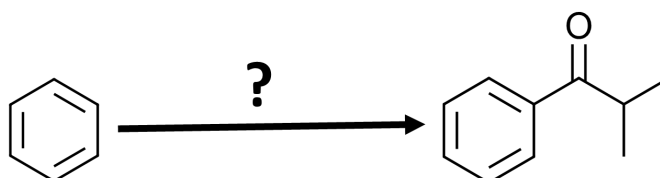
1.4.



1.5.



1.6.



► **Problem 2** (Wade and Simek, 2016)

Aldehydes and ketones can be synthesized from nitriles. Predict the products of the following reactions.

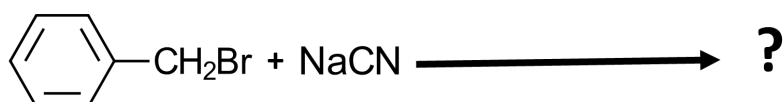
2.1.



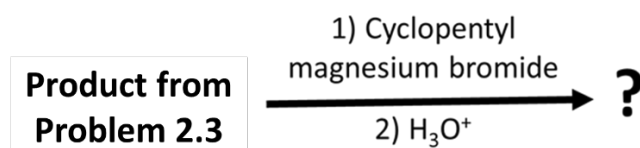
2.2. (DIBAL-H = Diisobutylaluminium hydride)



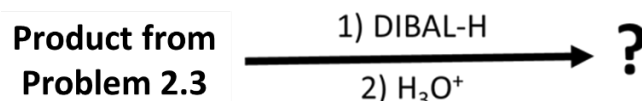
2.3.



2.4.



2.5.



► **Problem 3** (Carey, 2008, w/ permission)

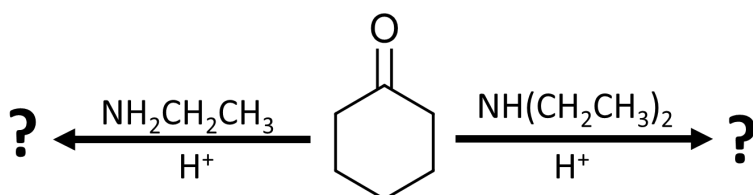
3.1. Write structural formulas and provide IUPAC names for all the isomeric aldehydes and ketones that have the molecular formula  $\text{C}_5\text{H}_{10}\text{O}$ . Include stereoisomers.

3.2. Which of the isomers in Problem 3.1 yield chiral alcohols on reaction with sodium borohydride?

3.3. Which of the isomers in Problem 3.1 yield chiral alcohols on reaction with methylmagnesium iodide?

► **Problem 4**

Show the products you would obtain by acid-catalyzed reaction of cyclohexanone with ethylamine,  $\text{CH}_3\text{CH}_2\text{NH}_2$ , and with diethylamine,  $(\text{CH}_3\text{CH}_2)_2\text{NH}$ .



► **Problem 5**

**Problem 5.1:** Predict the products of the reaction of phenylacetaldehyde with the following reagents.

5.1.1.  $\text{NH}_2\text{CH}_3$ ,  $\text{H}_3\text{O}^+$

5.1.2.  $\text{NaBH}_4$ , then  $\text{H}_3\text{O}^+$

5.1.3.  $\text{NH}_2\text{OH}$ , HCl catalyst

5.1.4.  $\text{CH}_3\text{MgBr}$ , then  $\text{H}_3\text{O}^+$

5.1.5. 2  $\text{CH}_3\text{OH}$ , HCl catalyst

5.1.6.  $\text{H}_2\text{NNH}_2$ , KOH

5.1.7.  $\text{Ph}_3\text{P}=\text{CH}_2$

5.1.8. HCN, KCN

**Problem 5.2:** Predict the products of the reaction of acetophenone with the following reagents.

**5.2.1.**  $\text{NH}_2\text{CH}_3$ ,  $\text{H}_3\text{O}^+$

**5.2.2.**  $\text{NaBH}_4$ , then  $\text{H}_3\text{O}^+$

**5.2.3.**  $\text{NH}_2\text{OH}$ , HCl catalyst

**5.2.4.**  $\text{CH}_3\text{MgBr}$ , then  $\text{H}_3\text{O}^+$

**5.2.5.** 2  $\text{CH}_3\text{OH}$ , HCl catalyst

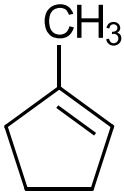
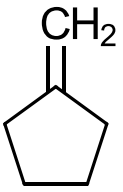
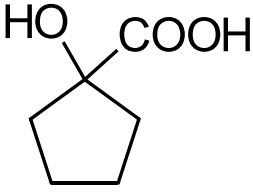
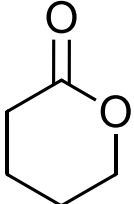
**5.2.6.**  $\text{H}_2\text{NNH}_2$ , KOH

**5.2.7.**  $\text{Ph}_3\text{P}=\text{CH}_2$

**5.2.8.** HCN, KCN

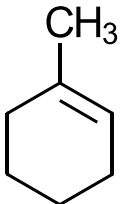
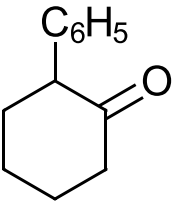
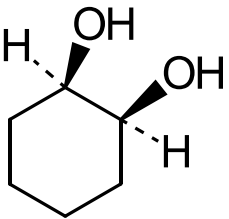
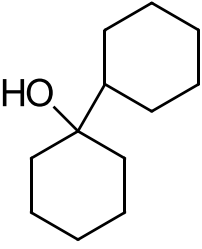
► **Problem 6**

Starting with cyclopentanone and using any other reagents of your choosing, identify how you would prepare each of the following compounds.

<p><b>6.1.</b> 1-Methylcyclopentene</p> 	<p><b>6.2.</b> 1-Methylenecyclopentane</p> 
<p><b>6.3.</b> 1-Hydroxycyclopentanecarboxylic acid</p> 	<p><b>6.4.</b> <math>\delta</math>-Valerolactone</p> 

► **Problem 7**

How would you synthesize the following compounds from cyclohexanone?

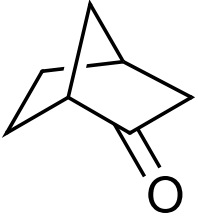
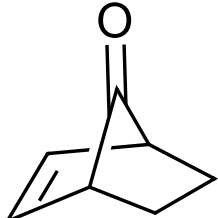
<p><b>7.1.</b> 1-Methylcyclohexene</p> 	<p><b>7.2.</b> 2-Phenylcyclohexanone</p> 
<p><b>7.3.</b> <i>Cis</i>-1,2-cyclohexanediol</p> 	<p><b>7.4.</b> 1-Cyclohexylcyclohexanol</p> 

► **Problem 8** (Carey, 2008, w/ permission)

Hydride reduction (with  $\text{LiAlH}_4$  or  $\text{NaBH}_4$ ) of each of the following ketones has been reported in the literature and gives a mixture of two diastereomeric alcohols in each case. Give the structures of both alcohol products for each ketone.

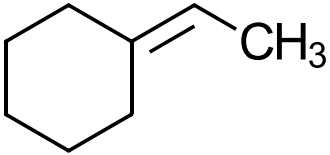
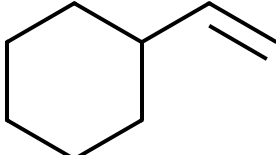
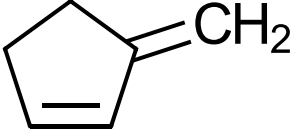
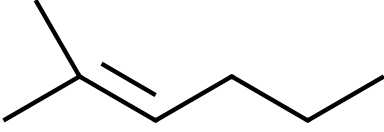
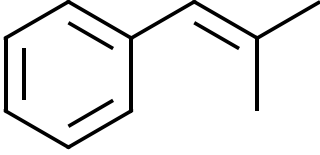
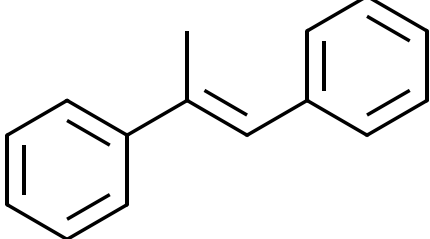
**8.1.** (*S*)-3-Phenyl-2-butanone

**8.2.** 4-*tert*-Butylcyclohexanone

<p><b>8.3.</b></p> 	<p><b>8.4.</b></p> 
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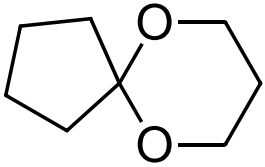
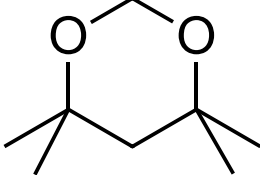
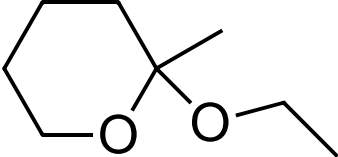
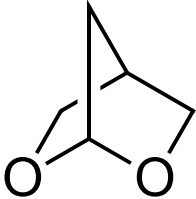
► **Problem 9**

What carbonyl compound and what phosphorus ylide might you use to prepare each of the following compounds?

<p>9.1.</p> 	<p>9.2.</p> 
<p>9.3.</p> 	<p>9.4.</p> 
<p>9.5.</p> 	<p>9.6.</p> 

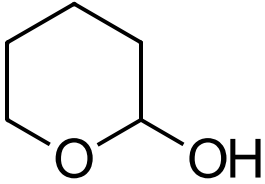
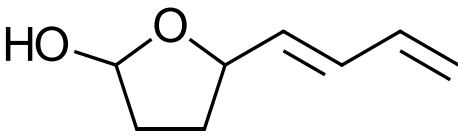
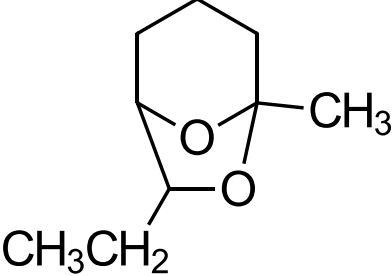
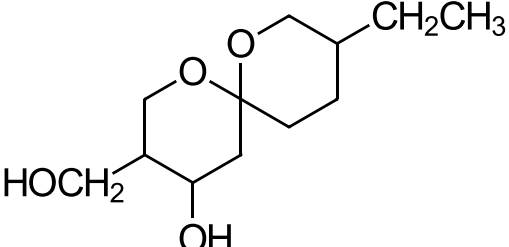
► **Problem 10**

Draw the products of hydrolysis of the following acetals.

<p>10.1.</p> 	<p>10.2.</p> 
<p>10.3.</p> 	<p>10.4.</p> 

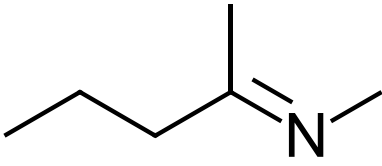
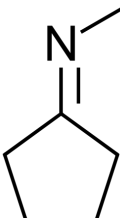
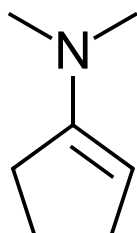
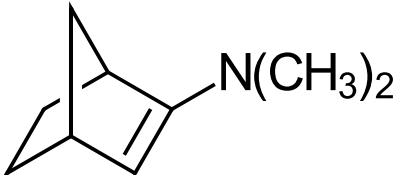
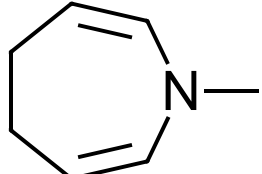
► **Problem 11** (Carey, 2008, w/ permission)

Compounds that contain both carbonyl and alcohol functional groups are often more stable as cyclic hemiacetals or cyclic acetals than as open-chain compounds. Examples of four of these are shown below. Deduce the structure of the open-chain form of each.

<p>11.1.</p> 	<p>11.2.</p> 
<p>11.3. Brevicomín</p> 	<p>11.4. Talaromycin A</p> 

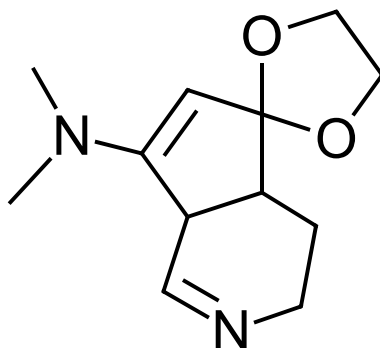
► **Problem 12**

Draw the products of hydrolysis of the following imines and enamines.

<p>12.1.</p> 	<p>12.2.</p> 
<p>12.3.</p> 	<p>12.4.</p> 
<p>12.5.</p> 	

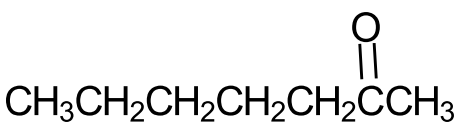
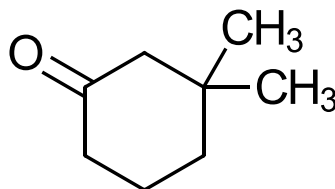
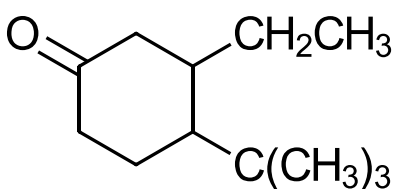
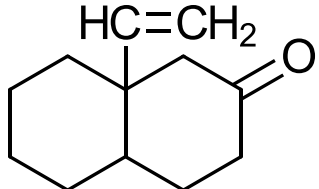
► **Problem 13** (Klein, 2017)

Identify all of the expected products when the compound below is treated with aqueous acid.



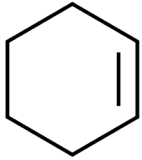
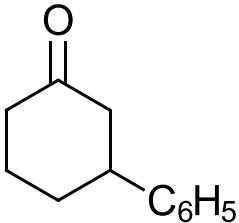
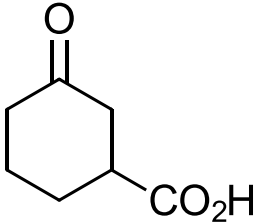
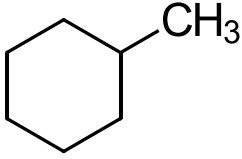
► **Problem 14** (McMurry, 2008, w/ permission)

How might conjugate addition reaction of lithium diorganocopper reagents be used to synthesize the following compounds?

<p>14.1.</p> 	<p>14.2.</p> 
<p>14.3.</p> 	<p>14.4.</p> 

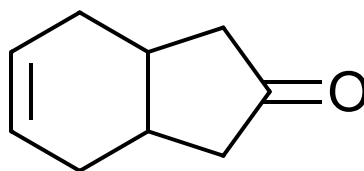
► **Problem 15**

How would you prepare the following substances from 2-cyclohexenone? Lithium diorganocopper reagents may be useful.

<p>15.1.</p> 	<p>15.2.</p> 
<p>15.3.</p> 	<p>15.4.</p> 

► **Problem 16** (Carey, 2008, w/ permission)

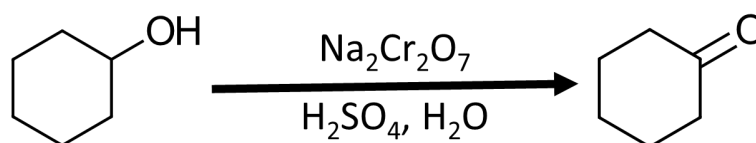
Wolff-Kishner reduction (hydrazine, KOH, ethylene glycol, 130°C) of the compound shown below gave compound A. Treatment of compound A with *m*-chloroperoxybenzoic acid gave compound B, which on reduction with lithium aluminum hydride gave compound C. Oxidation of compound C with chromic acid gave compound D (C<sub>9</sub>H<sub>14</sub>O). Identify compounds A through D in this sequence.



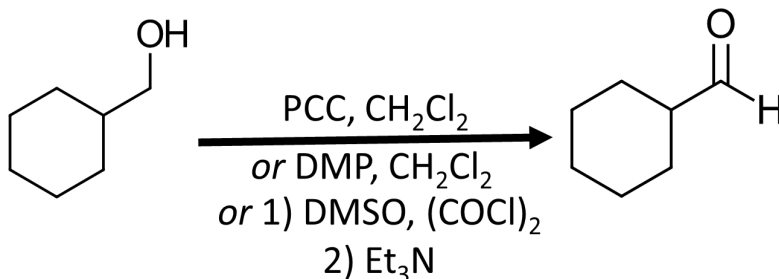
►► **SOLUTIONS**

**P.1** → **Solution**

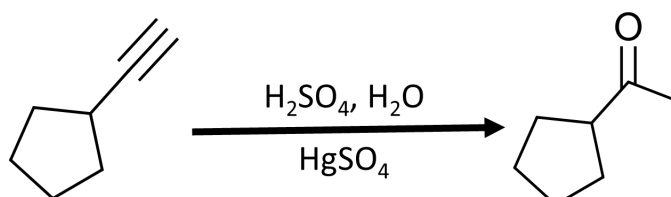
**1.1:** Oxidation of a secondary alcohol to a ketone can be achieved by treatment with chromic acid. PCC (pyridinium chlorochromate) and DMP (Dess-Martin periodinane) work just as well.



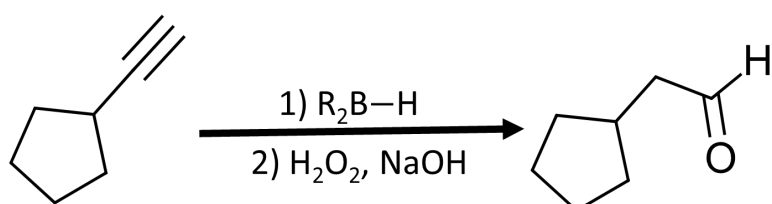
**1.2:** Oxidation of a primary alcohol to an aldehyde can be achieved by treatment with chromic acid. PCC (pyridinium chlorochromate) and DMP (Dess-Martin periodinane) work just as well.



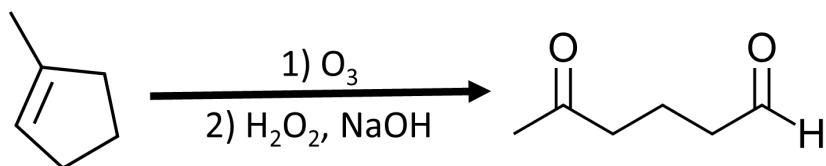
**1.3:** A terminal alkyne can be converted into a methyl ketone upon acid-catalyzed hydration in the presence of mercuric sulfate.



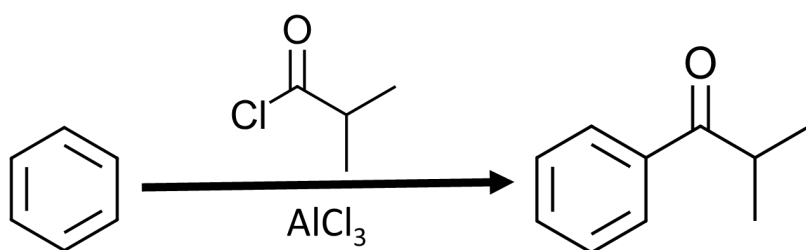
**1.4:** A terminal alkyne can be converted into an aldehyde via hydroboration-oxidation.



**1.5:** A  $C=C$  bond can be cleaved into two carbonyl groups via ozonolysis. In this case, the ring is opened to give an acyclic product.

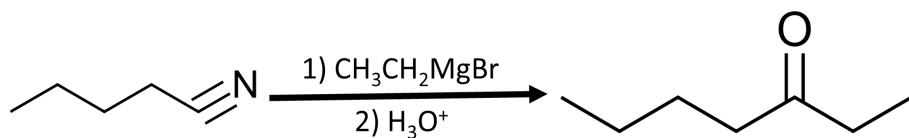


**1.6:** An acyl group can be installed via a Friedel-Crafts acylation, using the appropriate acyl halide.

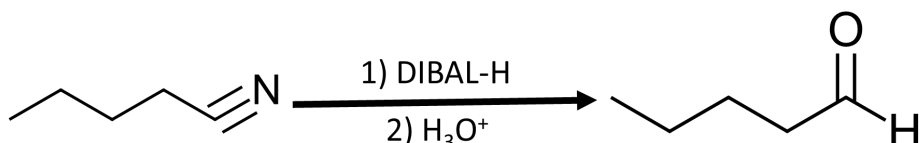


## P.2 → Solution

**2.1:** The Grignard reagent attacks the nitrile to give the magnesium salt of an imine. Then, acidic hydrolysis of the imine leads to a ketone. The product in this case is 3-heptanone.



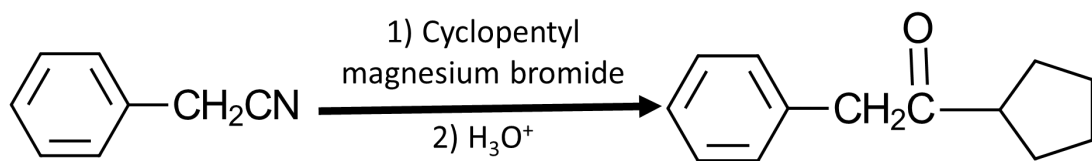
**2.2:** Treatment with DIBAL-H reduces a nitrile to the corresponding aldehyde. The product in this case is pentanal.



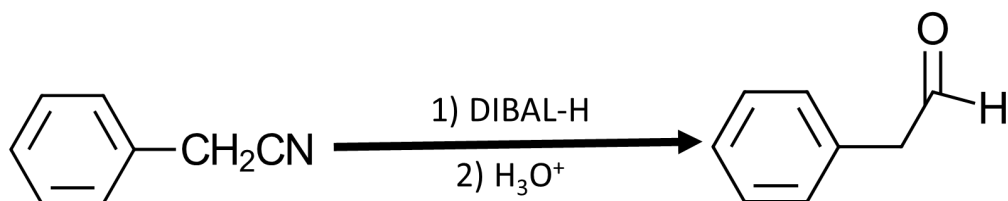
**2.3:** This is a simple  $S_N2$  substitution. The product is phenylacetonitrile.



**2.4:** This reaction is similar to that of Problem 2.1 and yields a ketone.

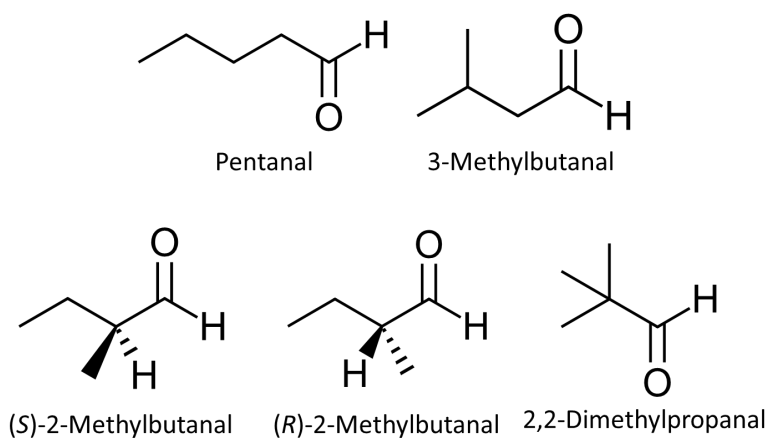


**2.5:** This reaction is similar to that of Problem 2.2 and yields phenylacetaldehyde.

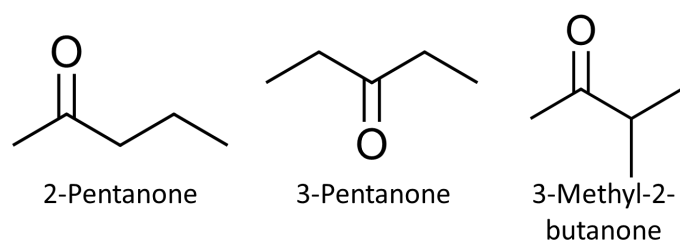


**P.3** → **Solution**

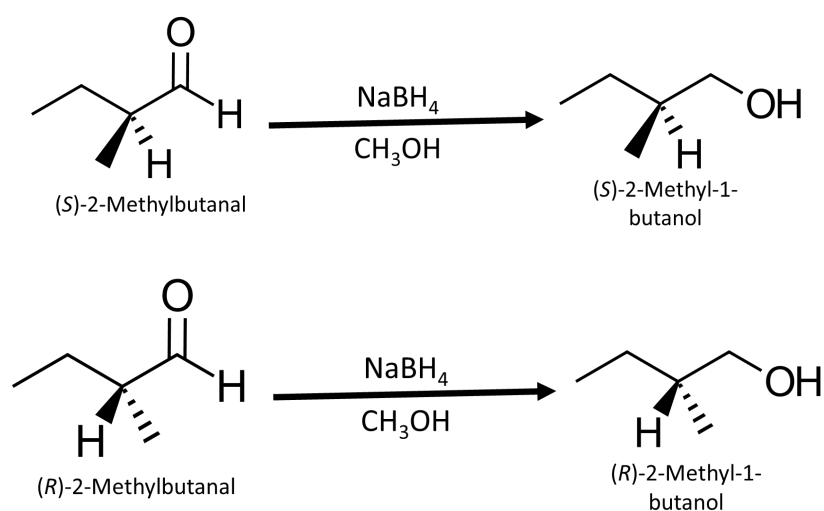
**3.1:** There are four aldehydes with the formula  $C_5H_{10}O$ ; one of them, 2-methylbutanal, occurs in two stereoisomeric forms.



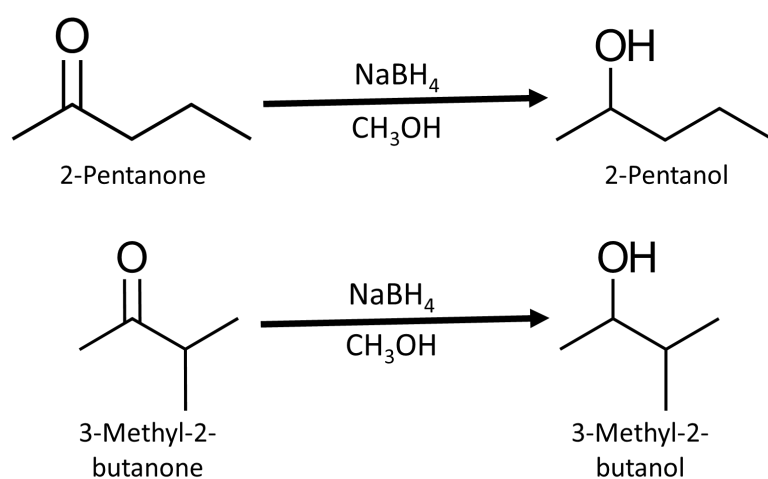
There are three isomeric ketones with the formula  $C_5H_{10}O$ .



**3.2:** Reduction of an aldehyde to a primary alcohol does not introduce a stereogenic center into the molecule. The only aldehydes that yield chiral alcohols on reduction are therefore those that already contain a stereogenic center.

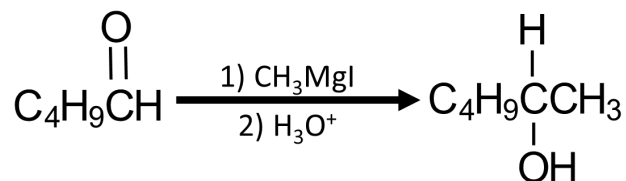


Among the ketones, 2-pentanone and 3-methyl-butanone are reduced to chiral alcohols.

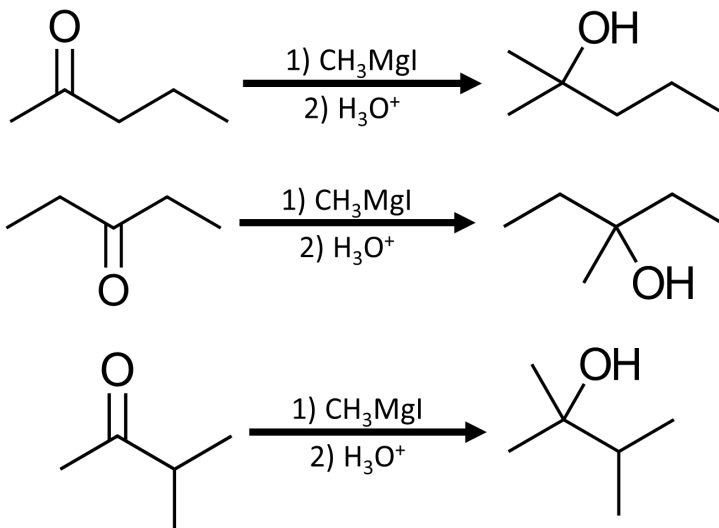


**3.3:** All five aldehydes yield chiral alcohols on reaction with methylmagnesium iodide, as shown in the next page.



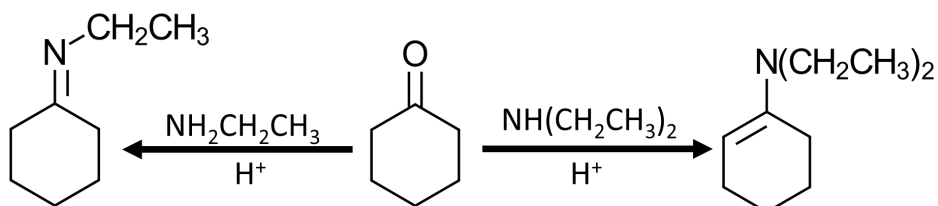


In contrast, none of the three ketones yield chiral alcohols.



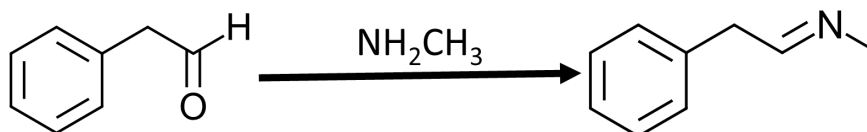
**P.4** → **Solution**

Reaction of a ketone or aldehyde with a primary amine yields an imine, in which C=O has been replaced by C=NR. Reaction of a ketone or aldehyde with a secondary amine yields an enamine, in which C=O has been replaced with C-NR<sub>2</sub>, and the double bond has moved.

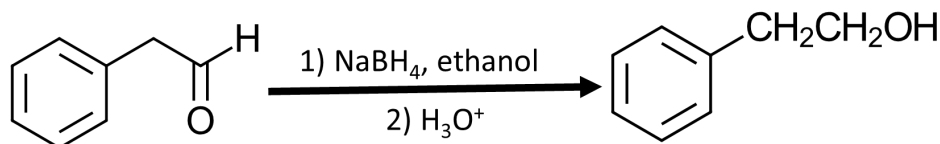


**P.5** → **Solution**

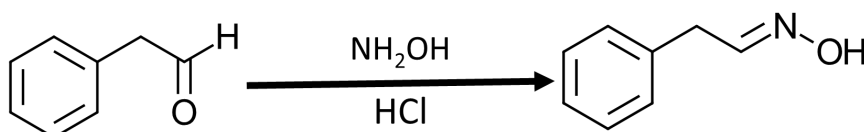
**5.1.1:** Addition of methylamine, a primary amine, leads to the formation of an imine.



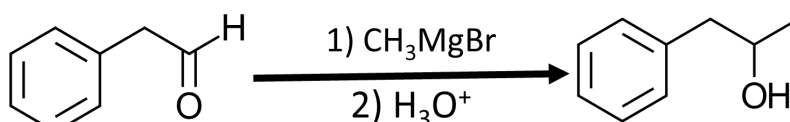
**5.1.2:** Treatment of phenylacetaldehyde with NaBH<sub>4</sub> leads to an addition of hydride, forming an alcohol. The product is phenethyl alcohol.



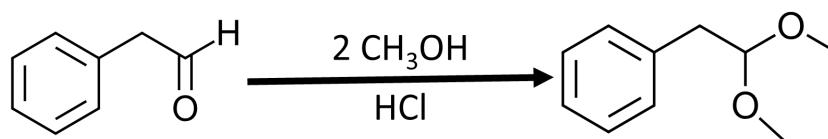
**5.1.3:** Reaction of phenylacetaldehyde with hydroxylamine yields phenylacetaldehyde oxime.



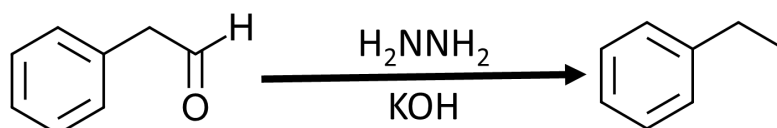
**5.1.4:** Reaction of an aldehyde with a Grignard reagent followed by acid treatment adds a hydroxyl group and an alkyl group to the carbonyl carbon. Reaction of acetaldehyde with methylmagnesium bromide yields 1-phenyl-2-ethanol.



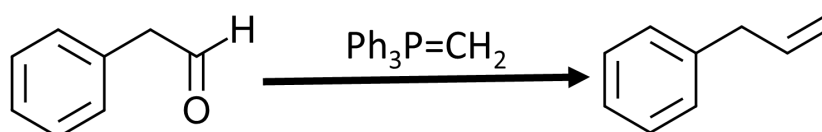
**5.1.5:** Addition of two equivalents of an alcohol to an aldehyde yields an acetal. The product of addition of alcohol to phenylacetaldehyde is (2,2-dimethoxyethyl)benzene.



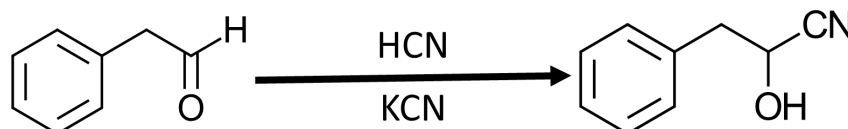
**5.1.6:** Reaction with hydrazine in the presence of KOH is the Wolff-Kishner process. Its structural effect is to convert carbonyl compounds to alkanes. In the present case, phenylacetaldehyde is converted to ethylbenzene.



**5.1.7:** Reaction of this phosphorus ylide with an aldehyde should attach the carbonyl carbon to a =CH<sub>2</sub> group. The product is allylbenzene (phenylpropene).

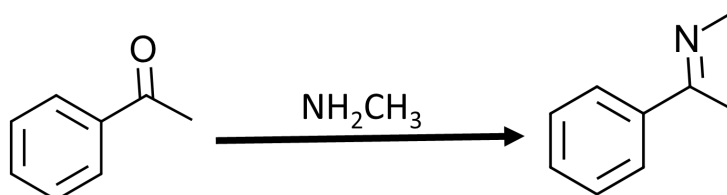


**5.1.8:** Nucleophilic addition of HCN produces a cyanohydrin. The product in the present case is 2-hydroxy-3-phenylpropanitrile.

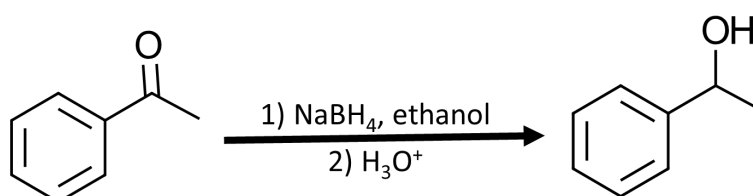


Problems 5.2.1 to 5.2.8 follow the same logic as the corresponding problems involving phenylacetaldehyde.

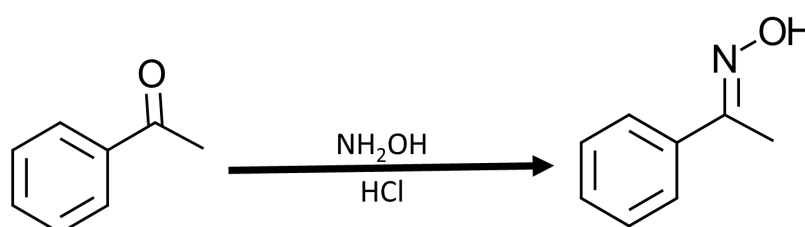
**5.2.1:** Acetophenone reacts with methylamine to form an imine.



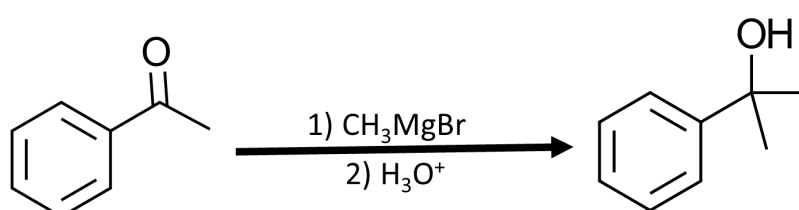
**5.2.2:** Acetophenone reacts with NaBH<sub>4</sub> and yields 1-phenyl-1-ethanol, a secondary alcohol.



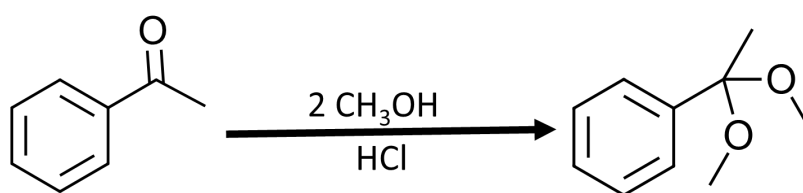
**5.2.3:** Reaction of acetophenone with hydroxylamine yields 1-phenyl-1-ethanone oxime.



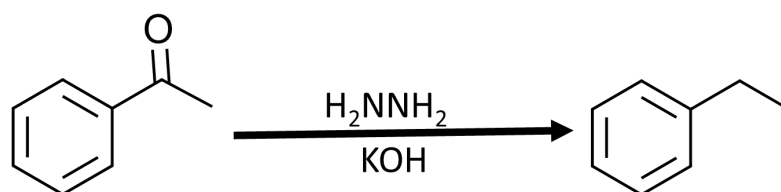
**5.2.4:** Reaction of acetophenone with methylmagnesium bromide followed by acid treatment yields 2-phenyl-2-propanol.



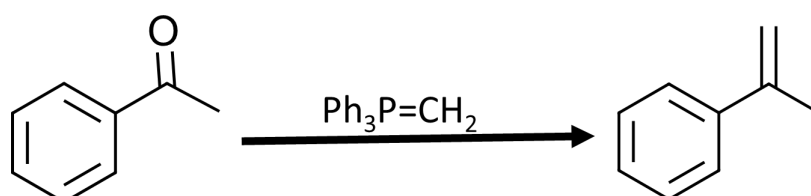
**5.2.5:** Reaction of acetophenone with 2 equivalents of methanol yields (1,1-Dimethoxyethyl)benzene.



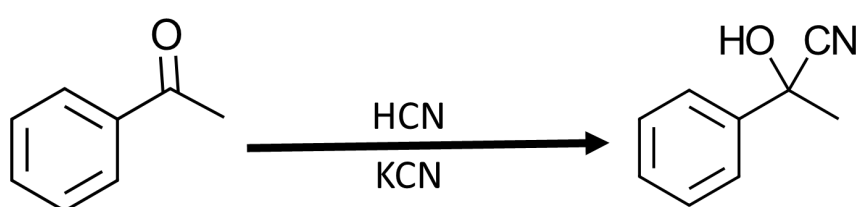
**5.2.6:** The product of a Wolff-Kishner reaction of acetophenone is no different from that of a similar process involving phenylacetaldehyde.



**5.2.7:** This Wittig reaction yields isopropenylbenzene.

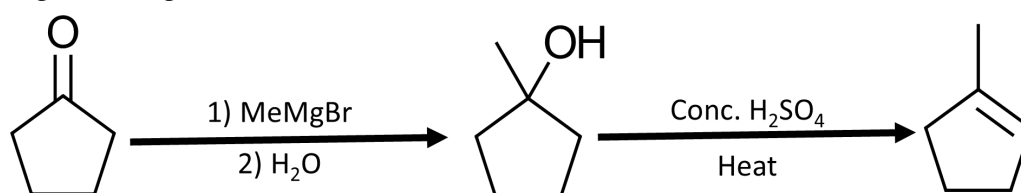


**5.2.8:** Treatment of acetophenone with HCN and KCN yields the following cyanohydrin.

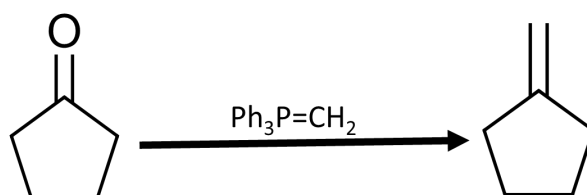


## P.6 → Solution

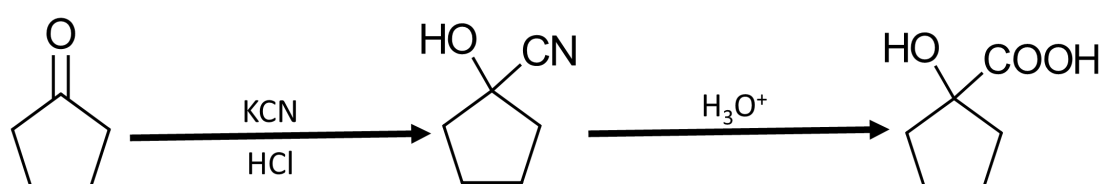
**6.1:** This transformation requires installation of a methyl group, which can be achieved by a Grignard reaction of the starting material with methyl magnesium bromide, followed by an aqueous workup. The resulting tertiary alcohol can be heated with concentrated sulfuric acid in an E1 process, generating the desired alkene.



**6.2:** Conversion of cyclopentanone into the desired alkene requires installation of a carbon atom, while converting the carbonyl group into a  $\text{C}=\text{C}$  bond. This can be achieved in a single step via a Wittig reaction.

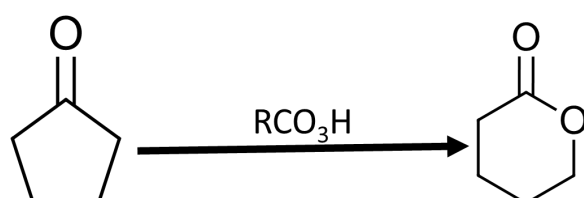


**6.3:** This transformation can be achieved in two steps. First, we convert the ketone into a cyanohydrin. Then, we hydrolyze the cyano group to obtain a carboxylic acid.



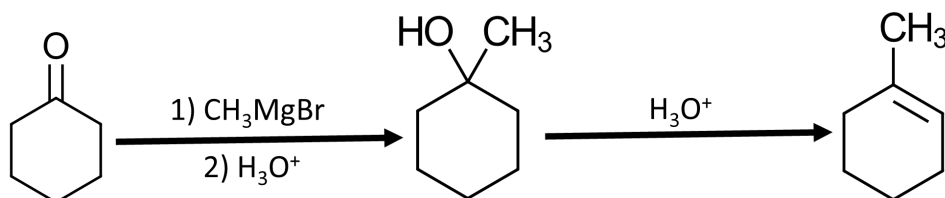
**6.4:** This transformation involves insertion of an oxygen atom next to the carbonyl group of a ketone, thereby converting the ketone into a cyclic

ester. This can be accomplished with a Baeyer-Villiger oxidation, which requires use of a peroxyacid.

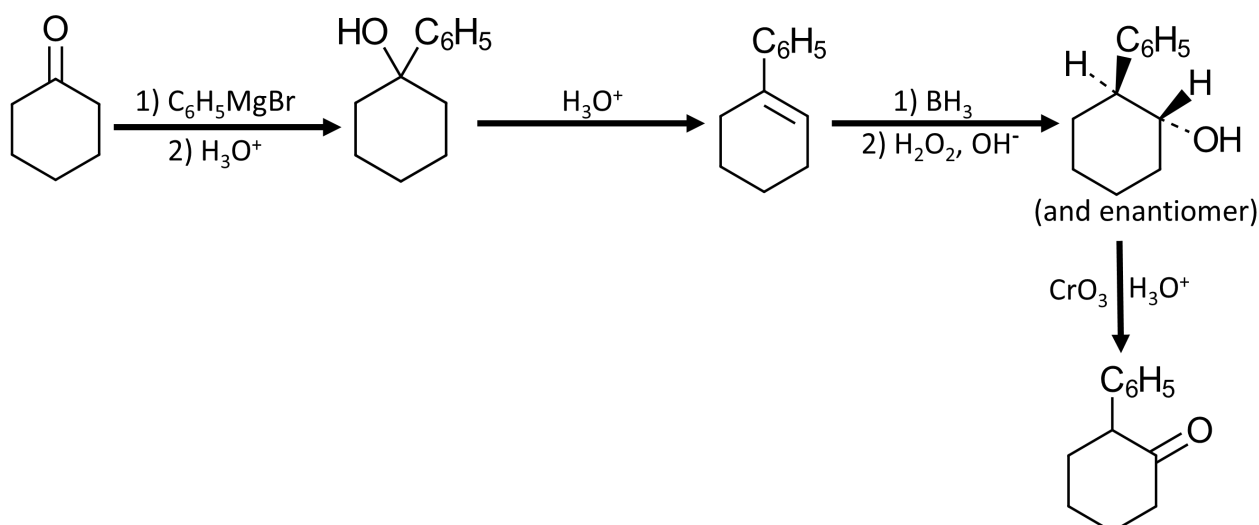


**P.7** → **Solution**

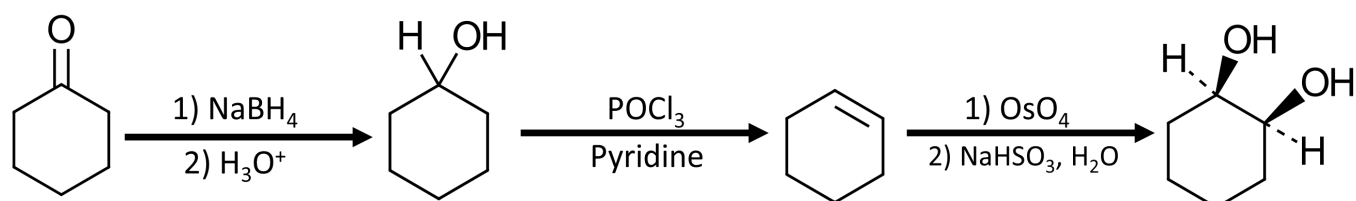
**7.1:** Similarly to Problem 6.1, we begin by reacting the ketone with a Grignard reagent. Next, we dehydrate the ensuing alcohol.



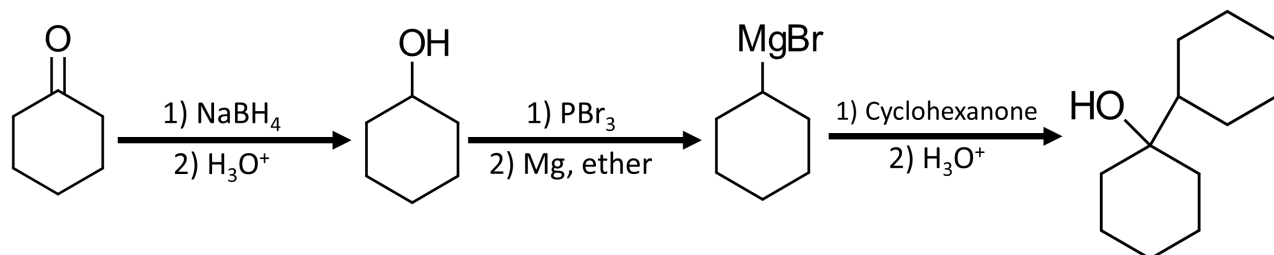
**7.2:** Reaction with phenylmagnesium bromide yields a tertiary alcohol that we can easily dehydrate. The resulting double bond can be treated with  $\text{BH}_3$  to give an alcohol, which is then oxidized to produce the desired ketone.



**7.3:** We first reduce cyclohexanone with  $\text{NaBH}_4$ . Then, we dehydrate the ensuing alcohol. Lastly, we dihydroxylate the alkene obtained in the previous step with  $\text{OsO}_4$ .

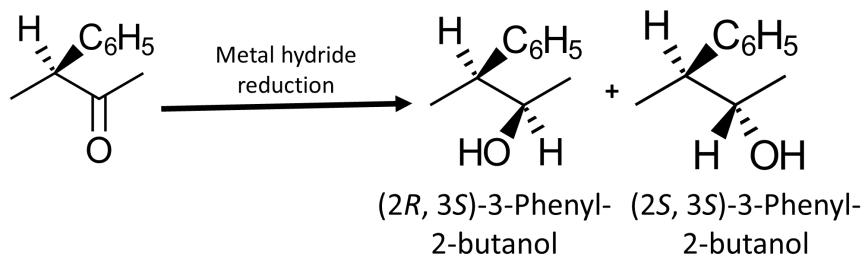


**7.4:** We start by reducing cyclohexanone to an alcohol, as we did in the beginning of the previous problem. Next, we treat this alcohol with phosphorus tribromide and magnesium to convert it to a Grignard reagent. Finally, we react the Grignard reagent with cyclohexanone to add hydroxyl and cyclohexyl groups to the hexane ring.

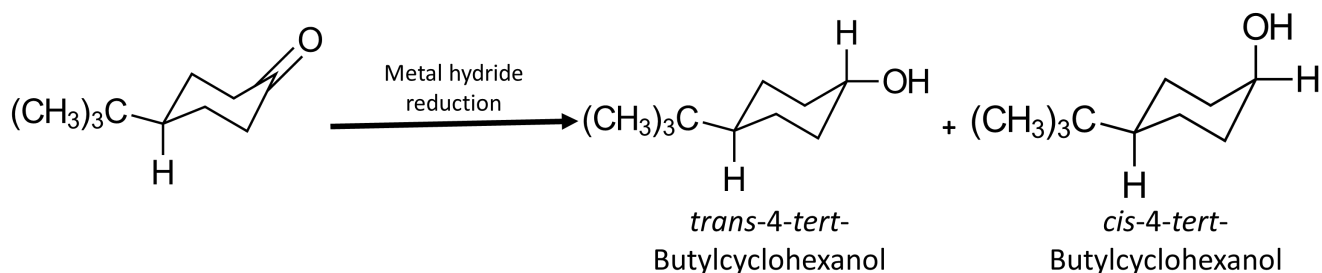


**P.8** → **Solution**

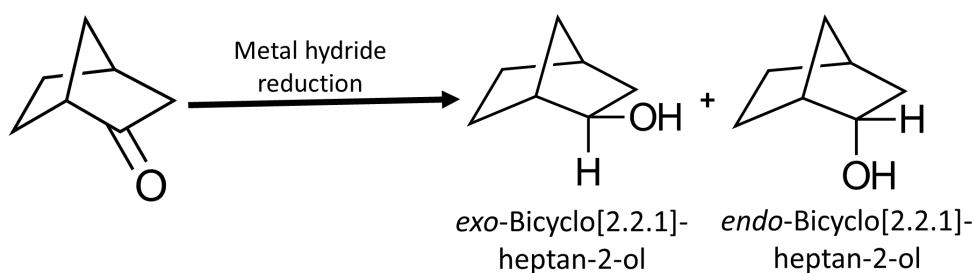
**8.1:** Below, the products of metal hydride reduction of (S)-3-phenyl-2-butanone are shown in stereochemical detail. Reduction of the ketone introduces a new chiral center, which may have either R or S configuration. The configuration of the original chiral center is unaffected. Carey notes that in practice the 2R,3S diastereoisomer is observed to form in greater amounts than the 2S,3S (ratio 2.5:1 for  $\text{LiAlH}_4$  reduction).



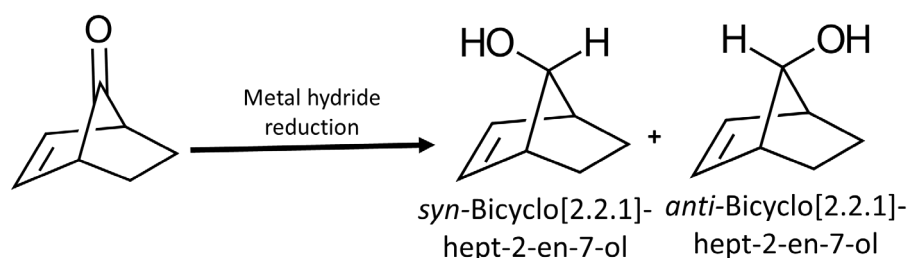
**8.2:** Below, the products of metal hydride reduction of 4-*tert*-butylcyclohexanone are shown in stereochemical detail. Carey states that the major product obtained on reduction with either lithium aluminum hydride or sodium borohydride is the *trans* alcohol (*trans/cis* = 9:1).



**8.3:** The two reduction products are the *exo* and *endo* alcohols. The major product is observed to be the *endo* alcohol (*endo/exo* = 9:1) for reduction with NaBH<sub>4</sub> or LiAlH<sub>4</sub>. The stereoselectivity observed in this reaction is due to decreased steric hindrance to attack of the hydride reagent from the *exo* face of the molecule, giving rise to the *endo* alcohol.



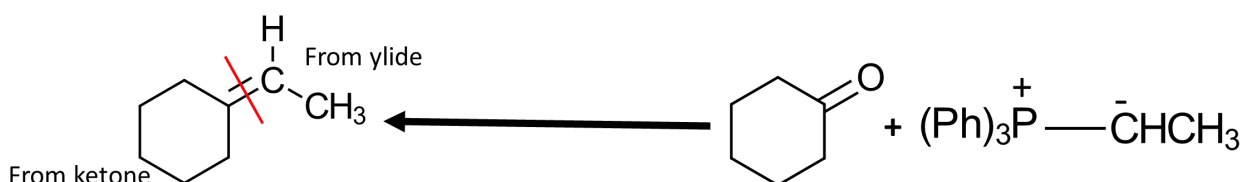
**8.4:** The hydroxyl group may be on the same side as the double bond or on the opposite side. The *anti* alcohol is observed to be formed in greater amounts (85:15) on reduction of the ketone with LiAlH<sub>4</sub>. Steric factors governing attack of the hydride reagent again explain the major product observed.



### P.9 → Solution

McMurry suggests the following strategy. Locate the double bond that is formed by the Wittig reaction. The simpler or less substituted component comes from the ylide, and the more substituted component comes from the aldehyde or ketone. Triphenylphosphine oxide is a byproduct of all these reactions.

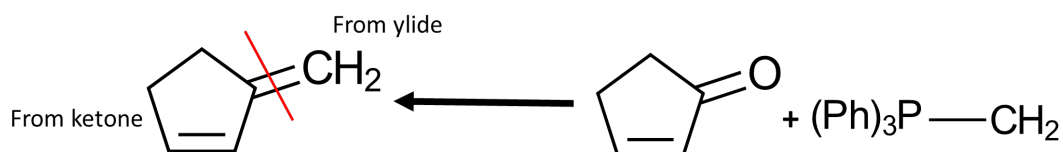
**9.1:** This compound can be synthesized with cyclohexanone.



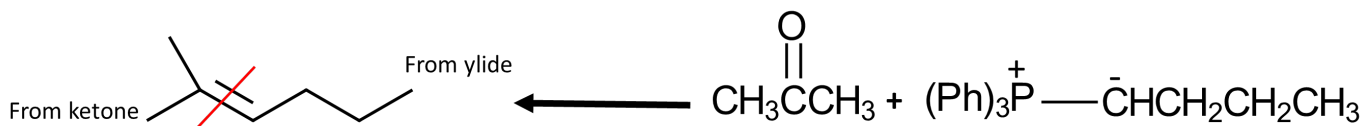
**9.2:** This compound can be synthesized with cyclohexanecarbaldehyde.



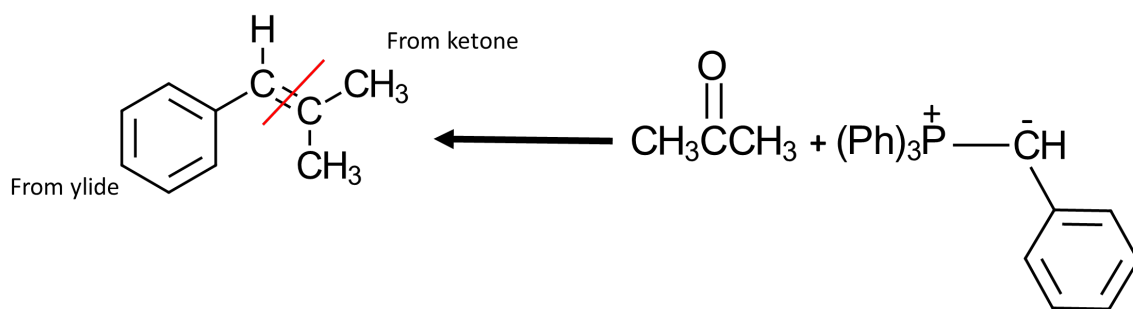
**9.3:** This compound can be synthesized with 2-cyclopenten-1-one.



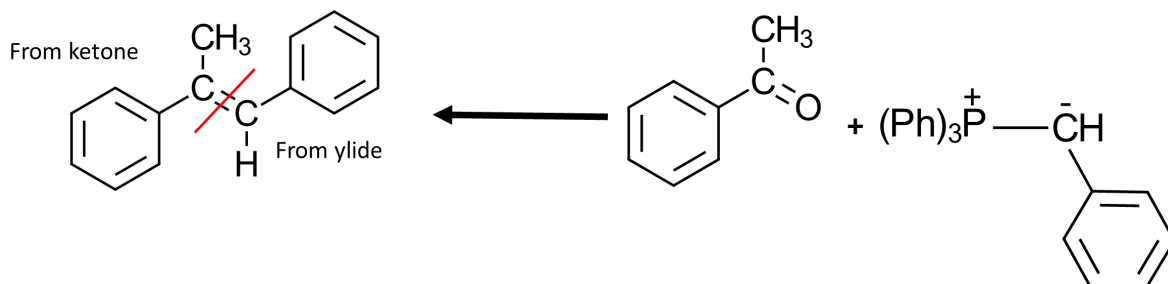
**9.4:** This compound can be synthesized with acetone.



**9.5:** Much like the previous compound, the molecule in question can be synthesized with acetone.

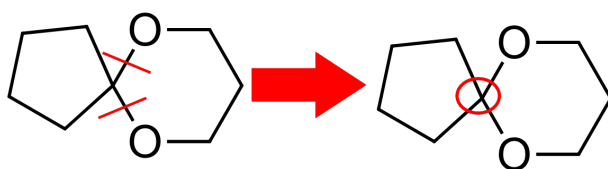


**9.6:** This compound can be synthesized with 1-phenyl-1-ethanone.

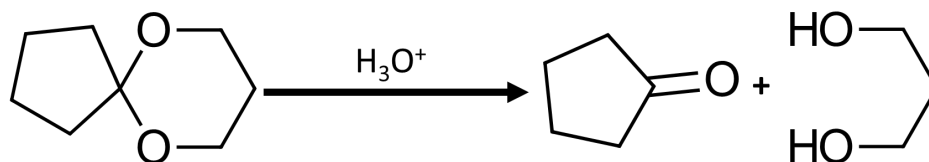


**P.10**  $\rightarrow$  **Solution**

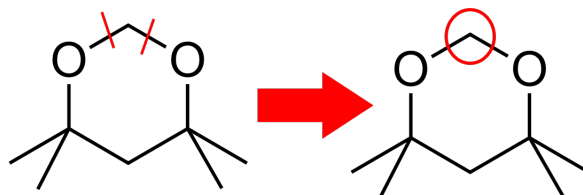
**10.1:** We first identify the bonds that will undergo cleavage. When an acetal undergoes hydrolysis, cleavage occurs in the C–O bonds of the acetal group, as highlighted below. Thus, the carbon circled below will be converted to a carbonyl group.



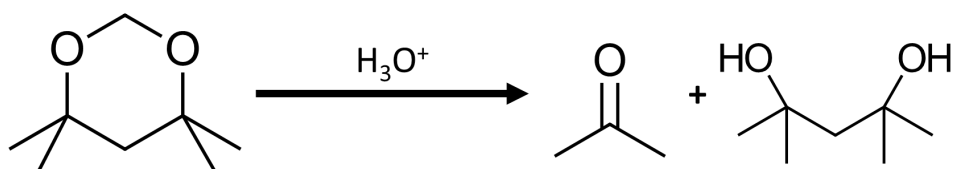
The products of hydrolysis are shown below. Clearly, the acetal in question can be decomposed into cyclopentanone and 1,3-propanediol.



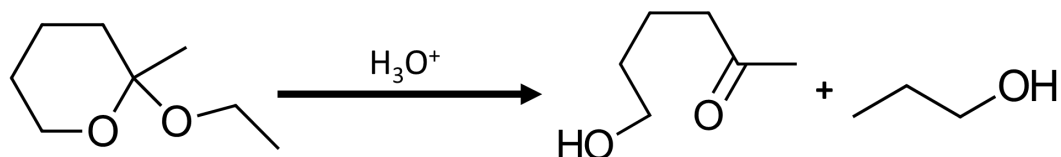
**10.2:** As before, we first identify the bonds that will undergo cleavage. The carbon circled below is converted to a carbonyl group.



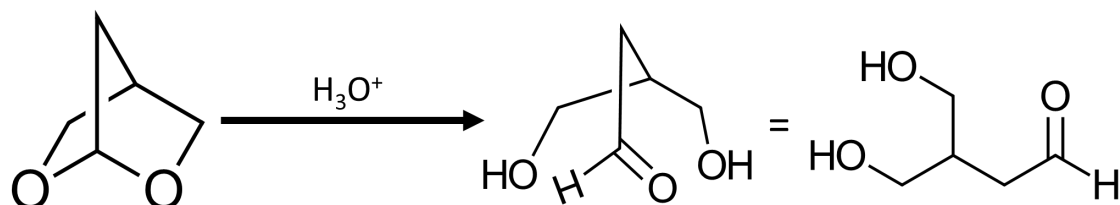
The products of hydrolysis are shown below. As can be seen, the acetal in question can be decomposed into formaldehyde and 2,4-dimethyl-2,4-pentanediol.



**10.3:** Hydrolysis of this acetal yields 6-hydroxy-2-hexanone and ethanol.

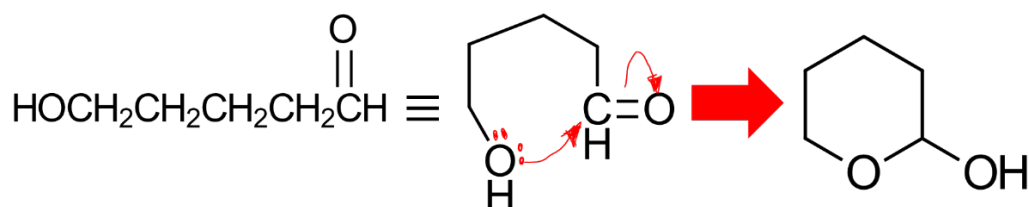


**10.4:** As usual, the carbonyl group comes from the carbon originally bonded to the two acetal oxygens. Hydrolysis of this bicyclic aldehyde yields 4-hydroxy-3-(hydroxymethyl)butyraldehyde.

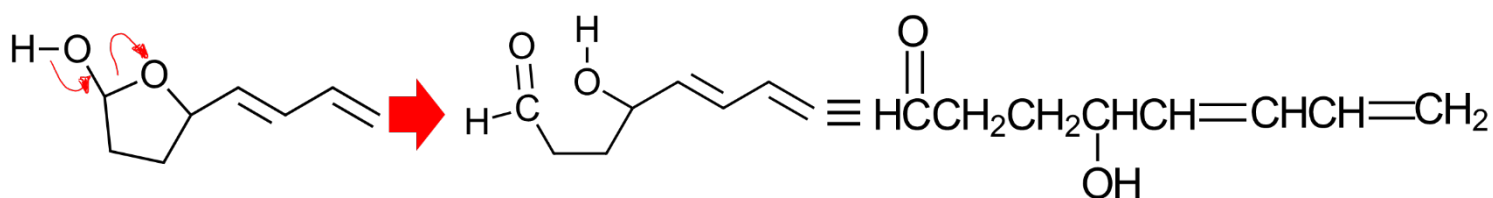


**P.11** → **Solution**

**11.1:** This compound is the cyclic hemiacetal of 5-hydroxypentanal.

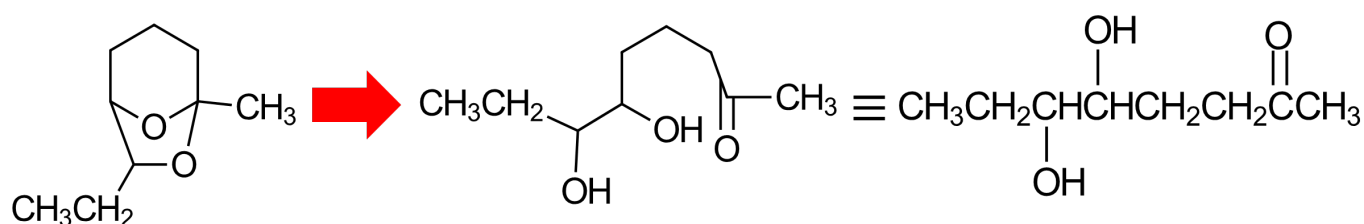


**11.2:** This compound is the aldehyde 4-hydroxy-5,7-octadienal.

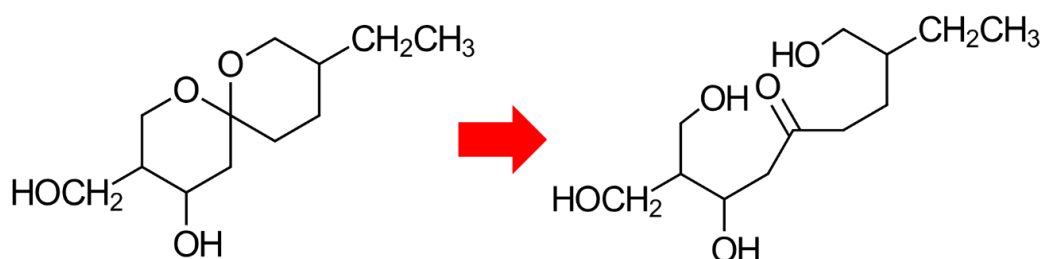


The compounds involved in problems 11.3 and 11.4 are cyclic acetals.

**11.3:** The original carbonyl group is identifiable as the one that bears two oxygen substituents, which originate as hydroxyl oxygens of a diol. The corresponding compound is 6,7-dihydroxy-2-nonanone.

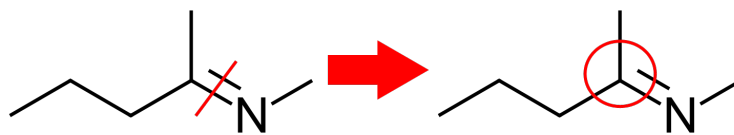


**11.4:** The corresponding compound is 2,8-di(hydroxymethyl)-1,3-dihydroxy-5-decanone.

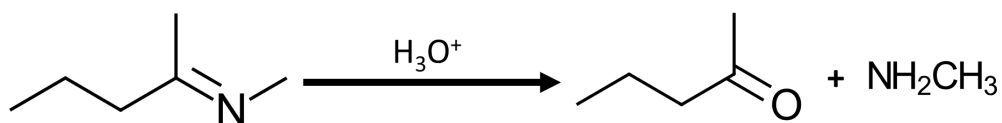


**P.12** → **Solution**

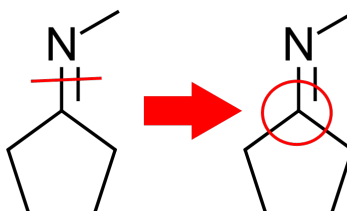
**12.1:** The starting compound is an imine. We first identify the bond that will undergo cleavage. When an imine undergoes hydrolysis, cleavage occurs in the  $\text{C}=\text{N}$  bond. The circled carbon will be converted to a carbonyl group.



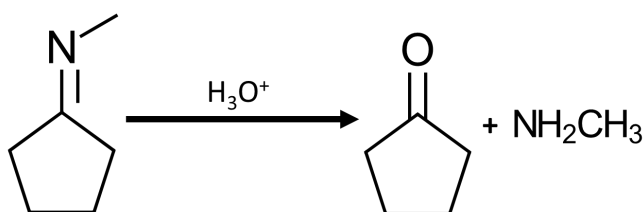
As a result of cleavage of the C=N bond, the carbon atom becomes a carbonyl group, and the nitrogen atom will accept two protons to generate a primary amine. The hydrolysis products are 2-pentanone and methylamine.



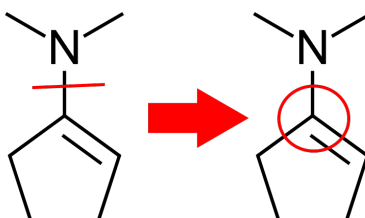
**12.2:** The starting compound is an imine. We first identify the bond that will undergo cleavage. Hydrolysis of imines occurs with cleavage of the C=N bond. The circled carbon will be converted to a carbonyl group.



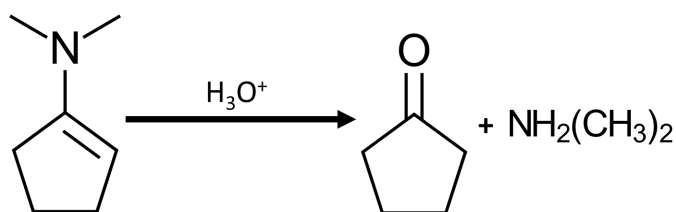
Following cleavage of the C=N bond, the carbon atom becomes a carbonyl group, and the nitrogen atom will accept two protons to produce a primary amine. The hydrolysis products are cyclopentanone and methylamine.



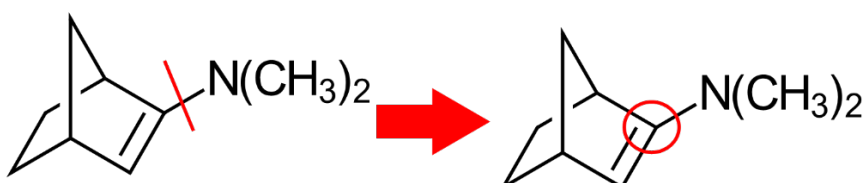
**12.3:** The starting compound is an enamine. We first identify the bond that will undergo cleavage. When an enamine undergoes hydrolysis cleavage occurs in the bond between the nitrogen atom and the  $sp^2$ -hybridized carbon atom to which it is attached. The circled carbon will be converted to a carbonyl group.



Following the C–N bond cleavage, the carbon atom becomes a carbonyl group, while the nitrogen atom will accept a proton to generate a secondary amine. The hydrolysis products are cyclopentanone and dimethylamine.

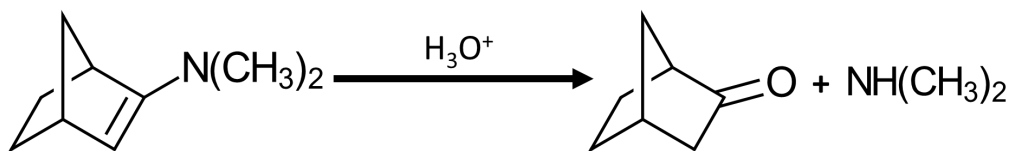


**12.4:** The starting compound is an enamine. We first identify the bond that will undergo cleavage. As we noted in the preceding problem, when an enamine undergoes hydrolysis cleavage occurs in the bond between the nitrogen atom and the  $sp^2$ -hybridized carbon atom to which it is attached. The circled carbon will be converted to a carbonyl group.

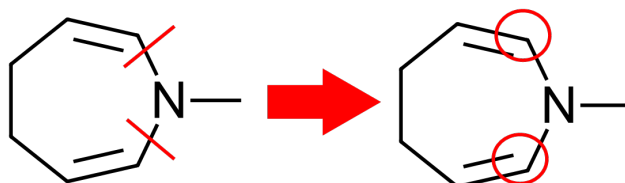




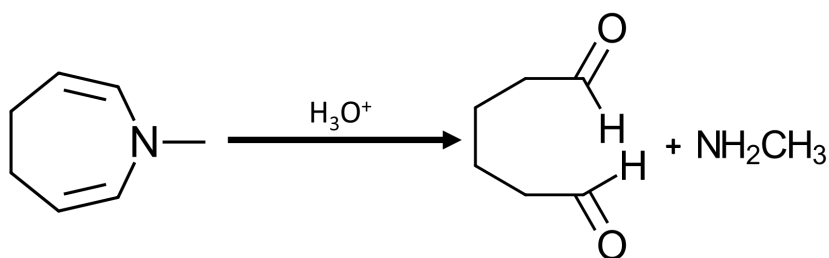
As a result of the C–N bond cleavage, the carbon atom becomes a carbonyl group, while the nitrogen atom will accept a proton to generate a secondary amine. The hydrolysis products are norcamphor and dimethylamine.



**12.5:** The carbons circled below will become carbonyl groups.

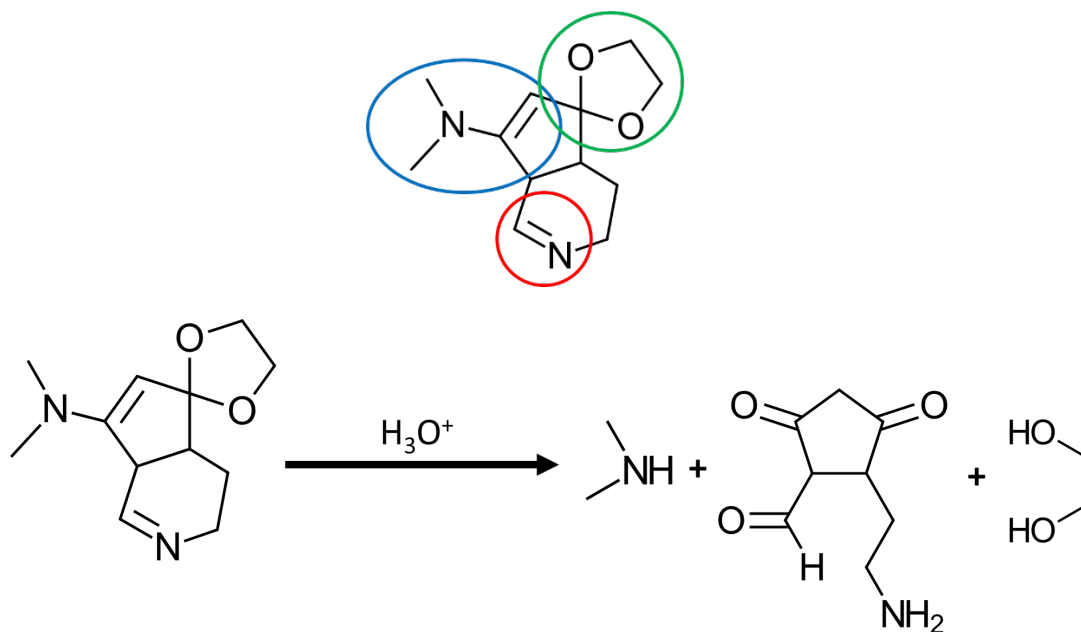


The C–N bonds are cleaved and the carbons are converted to carbonyl groups, while the nitrogen atom accepts two protons to yield a primary amine. The hydrolysis products are adipaldehyde and methylamine.



**P.13** → **Solution**

This compound contains three different functional groups that will each undergo hydrolysis. The enamine (highlighted in blue) is hydrolyzed to give a ketone and a secondary amine. The imine (highlighted in red) is hydrolyzed to give an aldehyde and an amino group (tethered together). Lastly, the cyclic acetal (highlighted in green) is hydrolyzed to give a ketone and ethylene glycol, as shown.

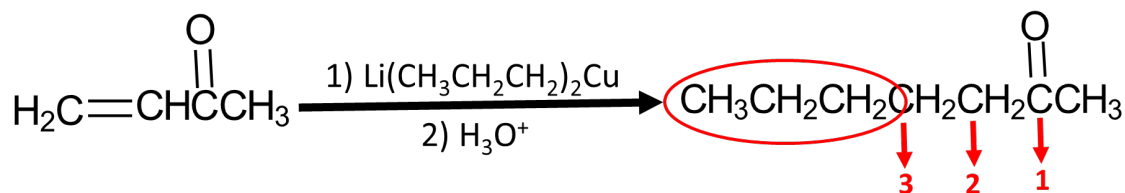


**P.14** → **Solution**

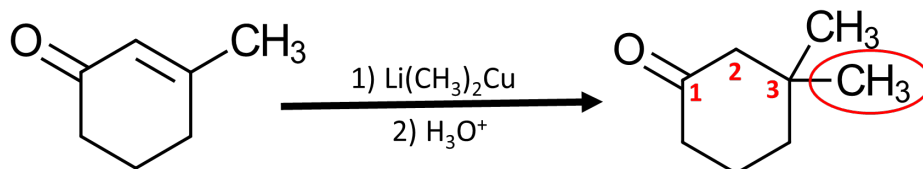
To choose the reactants that form a conjugate addition product, McMurry recommends following two steps:

1. Give to the aldehyde or ketone carbon the number “1,” and count two carbons away from the carbonyl carbon. The double bond in the  $\alpha,\beta$ -unsaturated starting material connected the carbons numbered “2” and “3.”
2. The grouping bonded to the “3” carbon came from the alkyllithium reagent and appears circled in the reactions below.

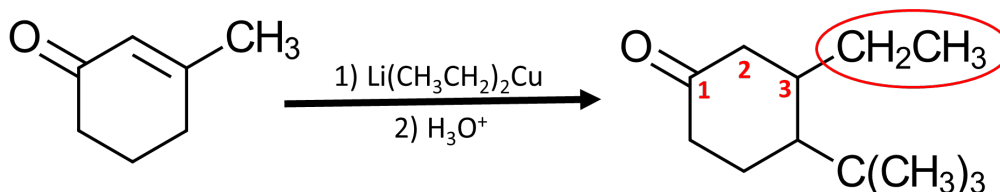
**14.1:** The ketone in question can be prepared by treating 3-buten-2-one with the appropriate alkyllithium reagent.



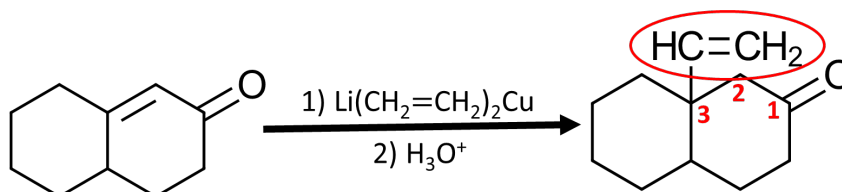
**14.2:** The cyclic ketone in question can be prepared by treating 3-methyl-2-cyclohexen-1-one with the appropriate alkyllithium reagent.



**14.3:** The cyclic ketone in question can be prepared by treating 4-(tert-butyl)-2-cyclohexen-1-one with the appropriate alkyllithium reagent.

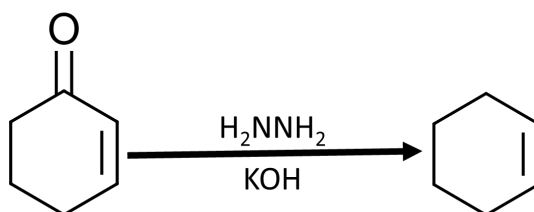


**14.4:** The ketone in question can be prepared by treating the following bicyclic ketone with the appropriate alkyllithium reagent.

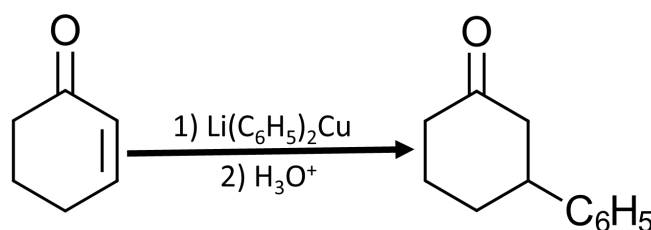


**P.15** → **Solution**

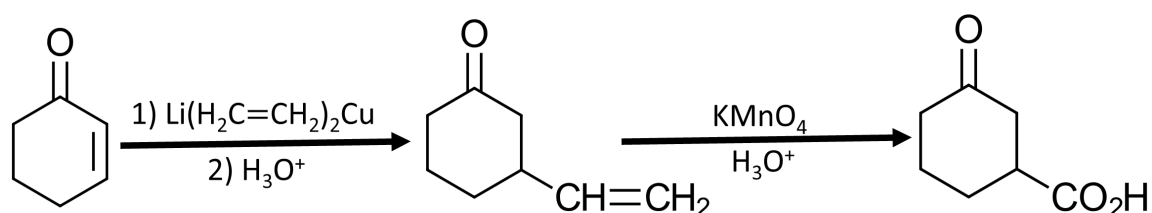
**15.1:** Cyclohexene can be prepared by performing a Wolff-Kishner reaction on 2-cyclohexenone, thereby eliminating the ketone group.



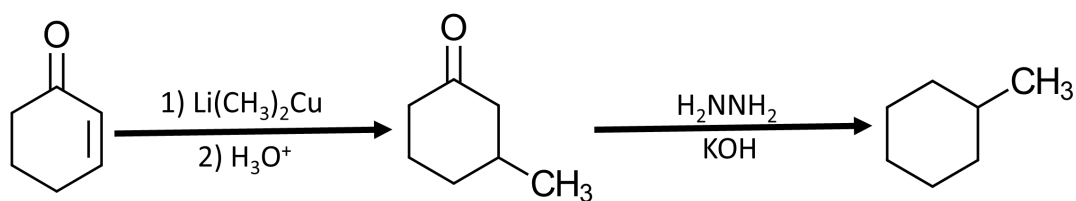
**15.2:** To synthesize this compound, we must desaturate 2-cyclohexenone and attach an aromatic ring 2 carbons away from the carbonyl carbon. Both modifications can be achieved if we react 2-cyclohexenone with the appropriate lithium diorganocopper reagent, followed by an acidic workup.



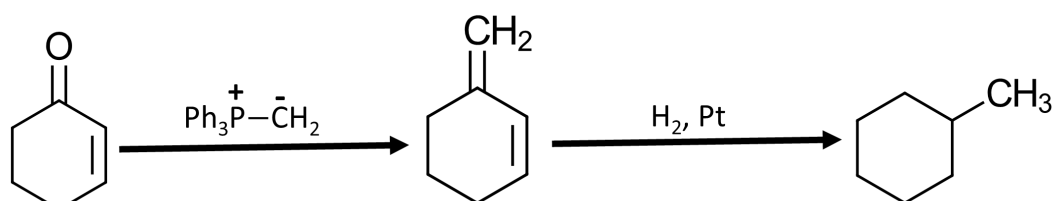
**15.3:** We begin by performing a conjugate addition to 2-cyclohexenone with the lithium diorganocopper reagent indicated below; this suppresses the double bond and attaches a  $\text{CH}=\text{CH}_2$  group to a carbon located 2 carbons away from the carbonyl group. Then, we oxidize the double bond of the  $\text{CH}=\text{CH}_2$  group with acid  $\text{KMnO}_4$ , yielding a carboxylic acid group.



**15.4:** We begin by eliminating the double bond of 2-cyclohexanone and adding a methyl group to the ring via treatment with lithium dimethylcuprate. Next, we perform a Wolff-Kishner reaction to extinguish the carbonyl group. The final product is methylcyclohexane, as desired.

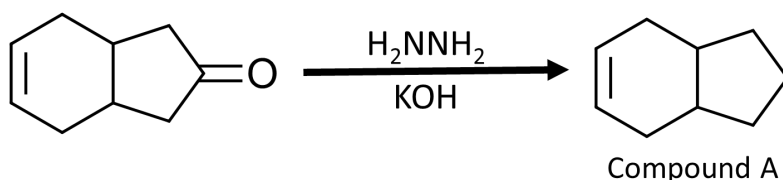


A second method to convert 2-cyclohexanone to methylcyclohexane is to perform a Wittig reaction and then hydrogenate the ensuing alkene.

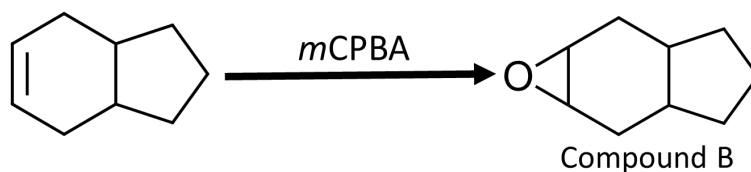


**P.16** → **Solution**

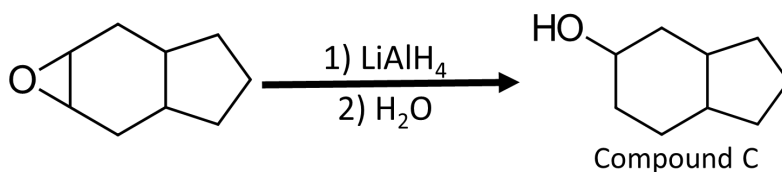
Wolff-Kishner reduction converts a carbonyl group to a methylene group, yielding compound A.



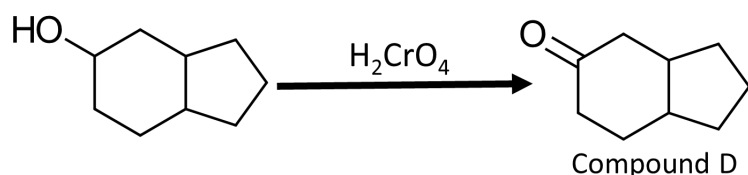
Treatment of the alkene with *m*-chloroperoxybenzoic acid produces an epoxide, compound B.



Epoxides undergo reduction with lithium aluminum hydride to form alcohols.



Chromic acid oxidizes the alcohol to a ketone.



►► **REFERENCES**

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