

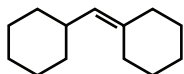
(d) **Schiff's Reagent:** It is a dilute solution of p-rosaniline hydrochloride. Its red colour has been discharged by passing SO_2 . Aldehyde restores red colour when treated with Schiff's reagent (Magenta solution in H_2SO_3).

5. USES OF ALDEHYDES AND KETONES

In the Chemical industry, aldehydes and ketones are used as solvents, and reagents for the synthesis of products. Formaldehyde is known as formalin (40%) solution used to preserve biological specimens and to prepare Bakelite, urea-formaldehyde glues and other polymeric products. Acetaldehyde is used primarily as a starting material in the manufacture of acetic acid, ethyl acetate, vinyl acetate, polymers and drugs. Benzaldehyde is used in perfumery and in dye industries. Many aldehydes and ketones, e.g. butyraldehyde, vanillin, acetophenone, camphor, etc. are well known for their odours and flavours.

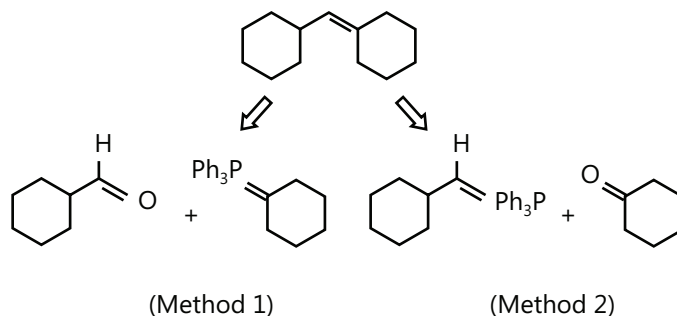
PROBLEM-SOLVING TACTICS

Problem 1: Identify the reagents to prepare the compound below using a witting reaction

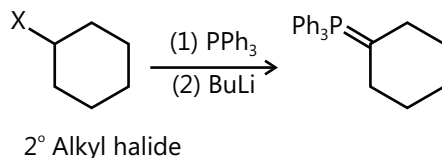


Sol: Begin by focusing on the carbon atom of the double bond. One carbon atom must be a carbonyl group, while the other must be the Wittig reagent. This gives two potential routes to us to explore.

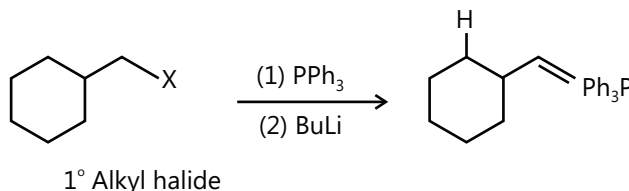
Step 1: Using a retrosynthetic analysis, determine the two possible sets of reactants that could be used to form the C=C bond



Let's compare these two methods, by focusing on the Wittig reagent in each case. Wittig reagent is prepared by an $\text{S}_{\text{N}}2$ process, and we therefore must consider steric factors during its preparation. Method 1 requires the use of a secondary alkyl halide.

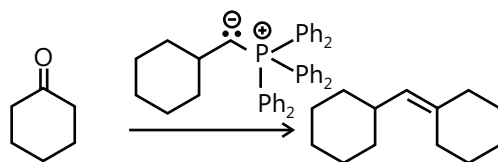


But method 2- requires the use of a primary alkyl halide

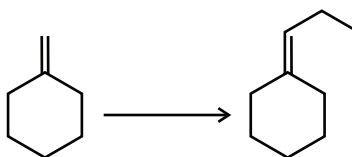


Step 2: Consider how you would make each possible Wittig reagent, and determine which method involves the substituted alkyl halide

Method 2 is likely to be efficient, because a primary alkyl halide will undergo S_N2 more rapidly than a secondary alkyl halide. Therefore, the following would be the preferred synthesis.



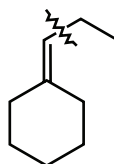
Problem 2: Propose an efficient synthesis for the following



Sol: Always begin a synthesis problem by asking the following two questions.

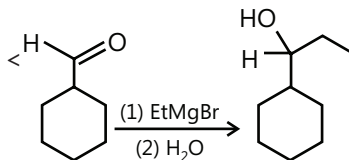
Step 1: Inspect whether there is a change in the carbon skeleton and /or a change in the identity or location of the functional group.

1. Is there any change in the carbon skeleton? Yes. The product has two additional carbon atoms.
2. Is there any change in the functional groups? No. Both the starting material and the products have a double bond in the exact same location. If we destroy the double bond in the process of adding the two carbon atoms we will need to make sure that we do so in such a way that we can restore the double bond. Now, let's consider how we might install the additional two-carbon atoms. The following C–C bond is the one that needs to be made. In this chapter, we have seen a C–C bond-forming reaction, let's consider each one as possible.

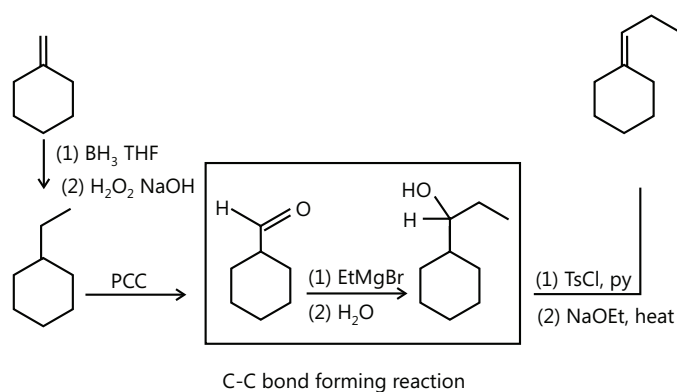


Step 2: When there is a change in the carbon skeleton, consider all of the C–C bond-forming reactions and all of the C–C bonds. Breaking the reaction that you have formed so far.

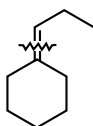
We can immediately rule out cyanohydrin formation, as that process installs only one carbon atom, not two. So, let's consider forming the C–C bond with either a Grignard reaction or a Wittig reaction. A Grignard reagent won't attack a C=C double bond into a functional group that can be attacked by a Grignard reagent, such as a carbonyl group.



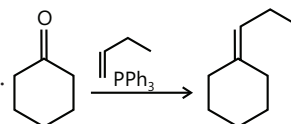
This reaction can indeed be used to form the crucial C–C bond. To use this method of C–C bond formation, we must first form the necessary aldehyde, then perform the Grignard reaction, and then finally restore the double bond in its proper location. This can be accomplished with the following reagents.



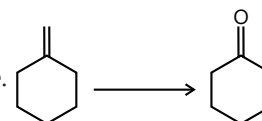
This provides us with a four-step procedure, and this answer is certainly reasonable. Let's now explore the possibility of proposing a synthesis with a Wittig reaction. Recall that a Wittig reaction can be used to form a C=C bond, so we focus on the formation of this bond



This bond can be formed if we start with a ketone and use the following Wittig reagent.

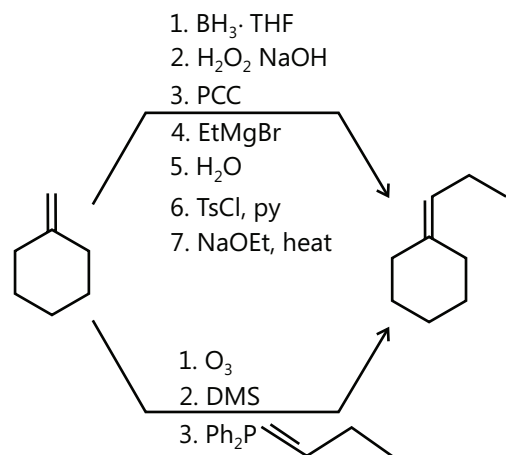


To use this reaction we must first form the necessary ketone from the starting alkene.

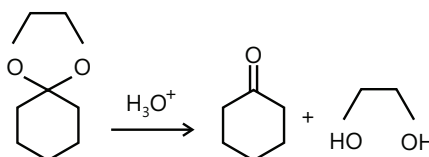


This can be accomplished with ozonolysis. This gives a two-step procedure for accomplishing the desired transformation: Ozonolysis followed by a Wittig reaction. This approach is different from our first answer. In this approach, we are not attaching a two-carbon chain, but rather, we are first expelling a carbon atom and then attaching a three-carbon chain

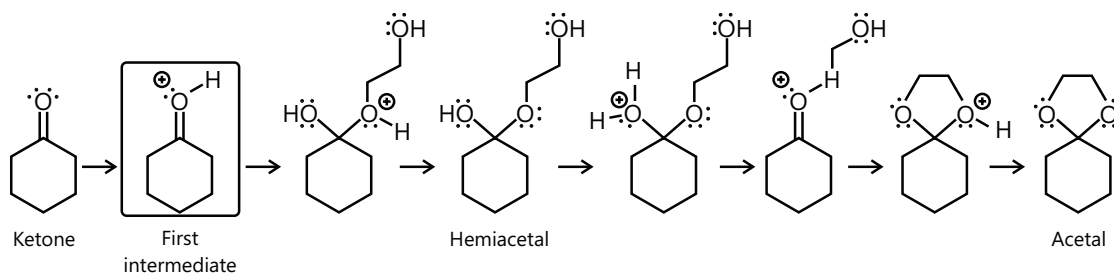
In short, there are two plausible methods have been discovered. Both methods are correct answers to this problem, however the method employing the Wittig reaction is likely to be more efficient, because it requires fewer steps.



Problem 3: Propose a mechanism for the following transformation:

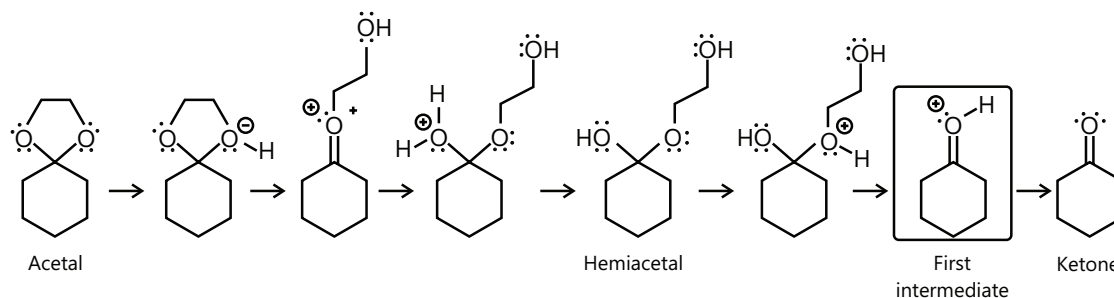


Sol: This is a hydrolysis reaction in which a cyclic acetal is opened to form a ketone. We therefore expect the mechanism to be the reverse of acetal formation. Begin by considering all of the intermediates in acetal formation

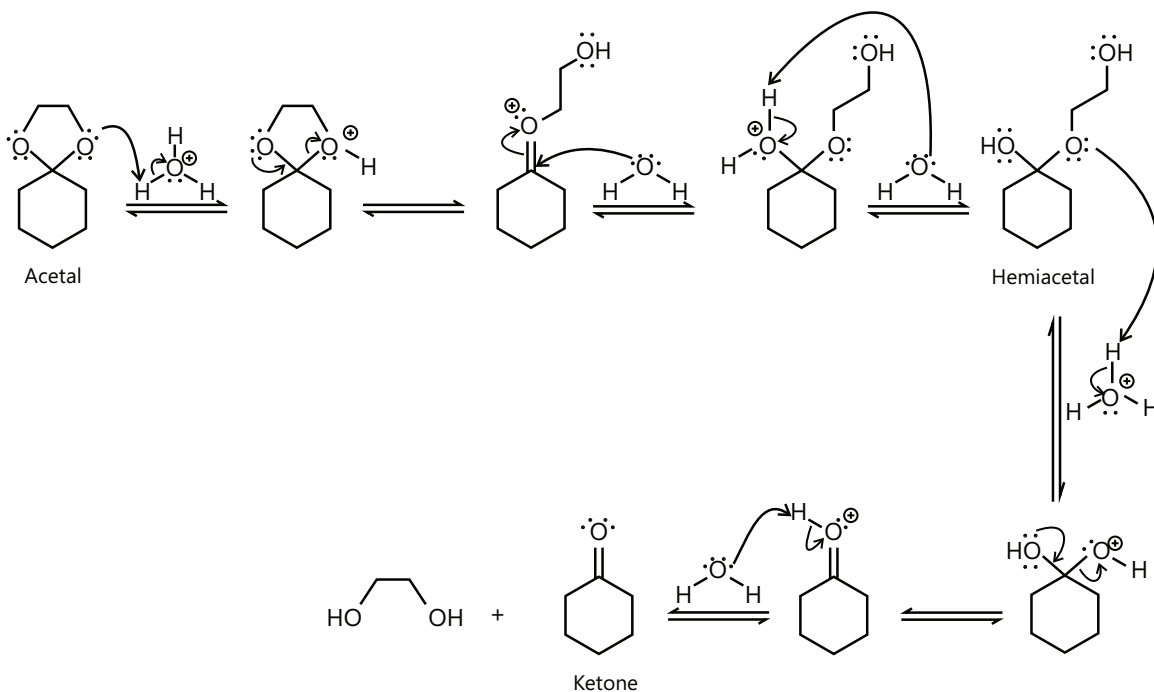


Step: 1 Draw all intermediates for acetal formation in reverse order

We simply draw all of these intermediates in reverse order so that the first intermediate above (Highlighted) becomes the last intermediate of the hydrolysis mechanism.



Hydrolysis of the acetal must involve these intermediates, in the order shown above. If any of the intermediates has a negative charge, then a mistake has been made. With the intermediates placed in the correct order, the final step is to draw the reagents and curved arrows that show how each intermediate is transformed into the next intermediate. Begin with the acetal, and work forward until reaching the ketone. Make sure to use only the reagents that are provided, and obey the master rule for proton transfer. For example this problem indicates that H_3O^+ is available. This means that H_3O^+ should be used for protonating, and H_2O should be used for deprotonating. Do not use hydroxide ions, as they are not present in sufficient quantity under acid-catalyzed conditions, Application of these rules gives the following answer?

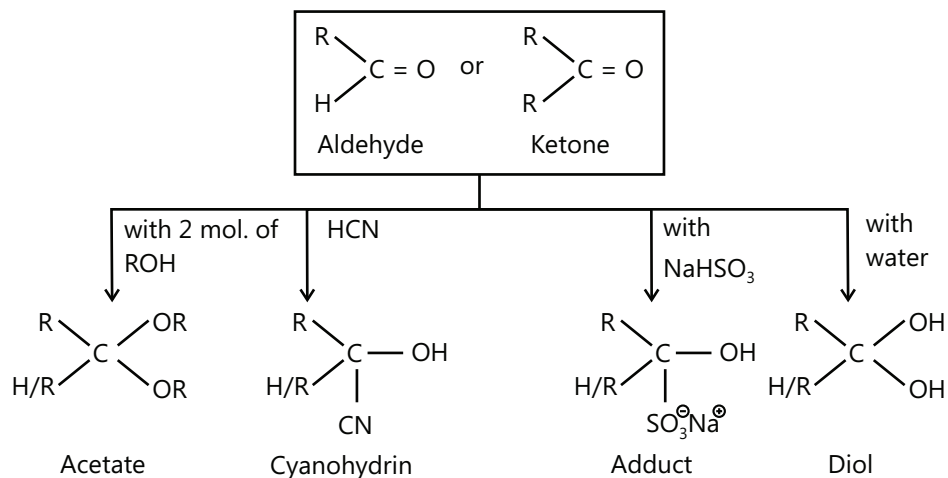


Step: 2 Draw the curved arrows and necessary reagents for each step of the mechanism

Notice the use of equilibrium arrows, because the process is governed by an equilibrium, as noted in the previous section.

POINTS TO REMEMBER

Nucleophilic Addition Reactions:



Reagents used to identify Aldehyde and Ketone:

No.	Reagent	Reactant	Product
1.	<p>Tollen's Reagent: (Ammoniacal solution of AgNO₃)</p> $[\text{Ag}(\text{NH}_3)_2]^+ \text{OH}^-$ <p>Also known as silver mirror Test.</p>	$\begin{array}{c} \text{O} \\ \\ \text{R}-\text{C}-\text{H} \rightarrow \end{array}$ <p>α, β -Unsaturated Aldehyde.</p> $\text{RCH}=\text{CH}-\text{CHO} \rightarrow$ <p>α -hydroxy ketone</p> $\text{R}-\begin{array}{c} \text{H} \\ \\ \text{C} \\ \\ \text{OH} \end{array}-\begin{array}{c} \text{C}-\text{R} \\ \\ \text{O} \end{array} \rightarrow$ <p>Ketone</p>	$\begin{array}{c} \text{O} \\ \\ \text{R}-\text{C}-\text{O}^- + \text{Ag} \\ \text{Silver mirror} \end{array}$ $\text{R}-\text{CH}=\text{CH}-\text{COO}^\ominus + \text{Ag mirror}$ $\text{R}-\begin{array}{c} \text{C} \\ \\ \text{O} \end{array} + \begin{array}{c} \text{C}-\text{R} \\ \\ \text{O} \end{array} + \text{Ag mirror}$ <p>No reaction</p>
2.	<p>Fehling's solution: Ammoniacal solution of CuSO₄ + Rochelle salt. i.e. – sodium potassium tartarate</p>	$\begin{array}{c} \text{O} \\ \\ \text{R}-\text{C}-\text{H} \rightarrow \end{array}$ <p>α, β -Unsaturated aldehyde</p> $\text{R}-\text{CH}=\text{CH}-\text{CHO} \rightarrow$ <p>α - hydroxyl ketone</p> $\text{R}-\begin{array}{c} \text{H} \\ \\ \text{C} \\ \\ \text{O} \end{array}-\begin{array}{c} \text{C}-\text{R} \\ \\ \text{O} \end{array}$ <p>Ketone</p>	$\text{RCOO}^- + \text{Cu}_2\text{O} \quad (\text{Red ppt})$ $\text{R}-\text{CH}=\text{CH}-\text{COO}^\ominus + \text{Cu}_2\text{O}$ $\text{R}-\begin{array}{c} \text{C} \\ \\ \text{O} \end{array}-\begin{array}{c} \text{C}-\text{R} \\ \\ \text{O} \end{array} + \text{Cu}_2\text{O}$ <p>No red ppt.</p>
3.	<p>Schiff's reagent Containing rosaniline hydrochloride in H₂O, whose red colours is decolourised with SO₂.</p>	<p>Schiff's reagent + Aldehyde</p>	<p>Red colour of dye is restored.</p>

No.	Reagent	Reactant	Product
4.	Benedict's solution: (Ammoniacal solution of CuSO_4 + sodium citrate) $[\text{Cu}(\text{NH}_3)_4]_2 + (\text{OH}^{2-})_2$	$\begin{array}{c} \text{O} \\ \\ \text{R}-\text{C}-\text{H} \end{array} \rightarrow$ α, β -Unsaturated aldehyde $\text{R}-\text{CH}=\text{CH}-\text{CHO} \rightarrow$ α -hydroxy ketone $\begin{array}{c} \text{R}-\text{C}-\text{H}-\text{C}-\text{R} \\ \quad \\ \text{OH} \quad \text{O} \end{array} \rightarrow$ Ketone	$\text{RCOO}^- + \text{Cu}_2\text{O}$ (Red ppt) $\text{R}-\text{CH}=\text{CH}-\text{COO}^- + \text{Cu}_2\text{O}$ (Red ppt) $\begin{array}{c} \text{R}-\text{C}-\text{C}-\text{R} \\ \quad \\ \text{O} \quad \text{O} \end{array} + \text{Cu}_2\text{O}$ (Red ppt) No reaction (No red ppt)
5.	Haloform or Iodoform or Hypohalite oxidation $\text{NaOH} + \text{x}_2$ Or $\text{KOH} \text{x}_2 = \text{I}_2$ Or $\text{Ca}(\text{OH})_2$	Aldehyde or ketone containing 3 α H atom (methyl ketone) $\begin{array}{c} \text{O} \\ \\ \text{CH}_3-\text{C}-\text{H} \end{array} \rightarrow$ $\begin{array}{c} \text{O} \\ \\ \text{CH}_3-\text{C}-\text{CH}_3 \end{array} \rightarrow$	$\begin{array}{c} \text{O} \\ \\ \text{CH}_3-\text{C}-\text{O}^- \end{array} + \text{CHI}_3$ (yellow) $\begin{array}{c} \text{O} \\ \\ \text{CH}_3-\text{C}-\text{O}^- \end{array} + \text{CHI}_3$ (yellow)

Important Reaction Flow Chart: