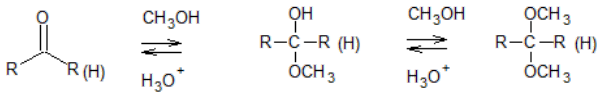
# 19.11: NUCELOPHILIC ADDITION OF ALCOHOLS (ACETAL FORMATION)

## INTRODUCTION

It has been demonstrated that water adds rapidly to the carbonyl function of aldehydes and ketones to form geminal-diol. In a similar reaction alcohols add reversibly to aldehydes and ketones to form hemiacetals (h*emi*, Greek, half). This reaction can continue by adding another alcohol to form an acetal. Hemiacetals and acetals are important functional groups because they appear in sugars.




hemiacetal acetal

To achieve effective hemiacetal or acetal formation, two additional features must be implemented. First, an acid catalyst must be used because alcohol is a weak nucleophile; and second, the water produced with the acetal must be removed from the reaction by a process such as a molecular sieves or a **Dean-Stark trap**. The latter is important, since acetal formation is reversible. Indeed, once pure hemiacetal or acetals are obtained they may be hydrolyzed back to their starting components by treatment with aqueous acid and an excess of water.

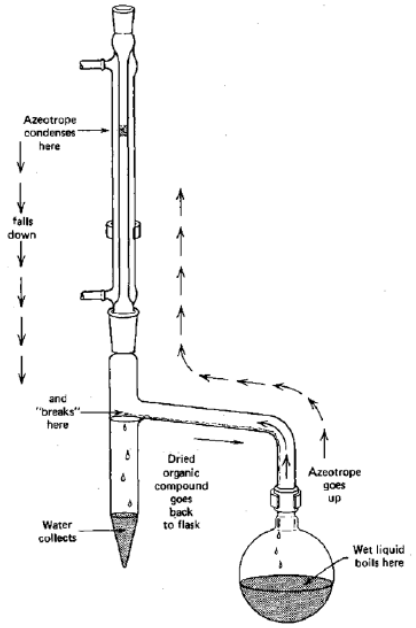
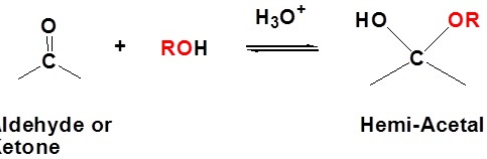
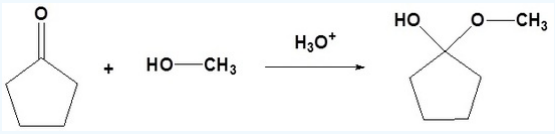



Figure: Dean-Stark Trap for Isolating Hemiacetals and Ketals

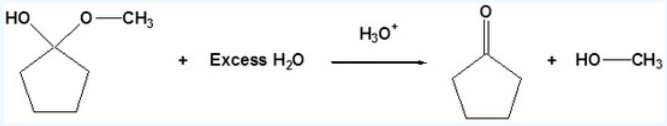
## FORMATION OF HEMIACETALS




### Example: Formation of Hemiacetals

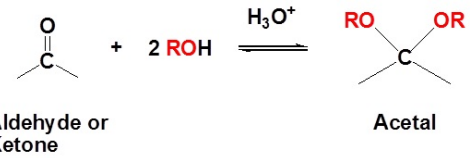


**Example: Hemiacetal Reversibility**

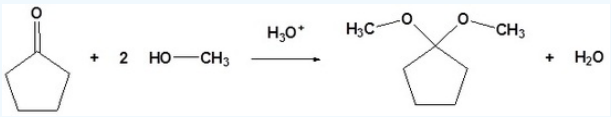



## FORMATION OF ACETALS

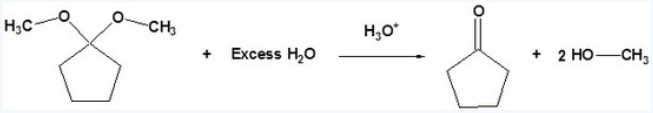
Acetals are geminal-diether derivatives of aldehydes or ketones, formed by reaction with two equivalents (or an excess amount) of an alcohol and elimination of water. Ketone derivatives of this kind were once called ketals, but modern usage has dropped that term. It is important to note that a hemiacetal is formed as an intermediate during the formation of an acetal.




**Example: Formation of Acetals**



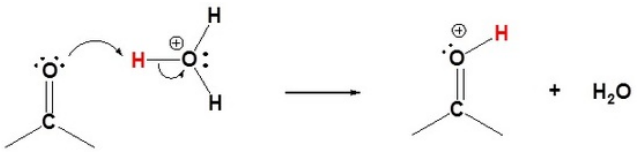

**Example: Acetal Reversibility**



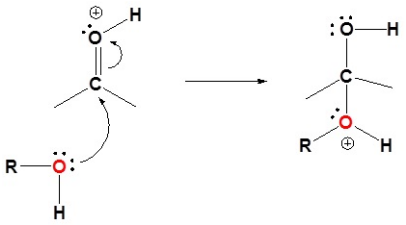

## MECHANISM FOR HEMIACETAL AND ACETAL FORMATION

The mechanism shown here applies to both acetal and hemiacetal formation

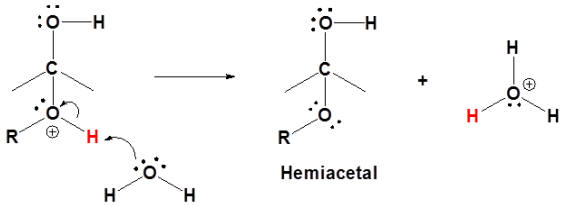
1) Protonation of the carbonyl



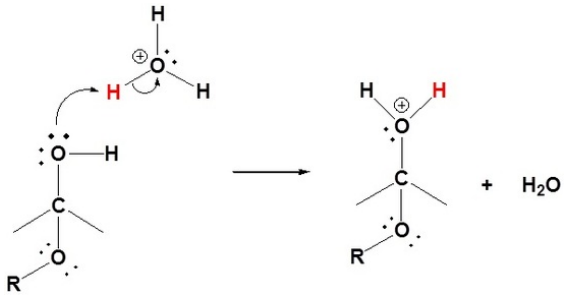

2) Nucleophilic additional reaction by the alcohol



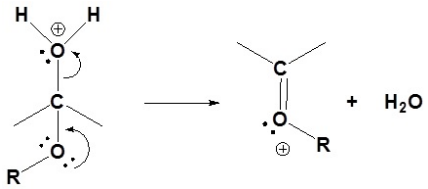

3) Deprotonation to form a hemiacetal



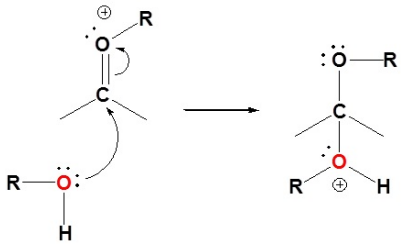

4) Protonation of the alcohol



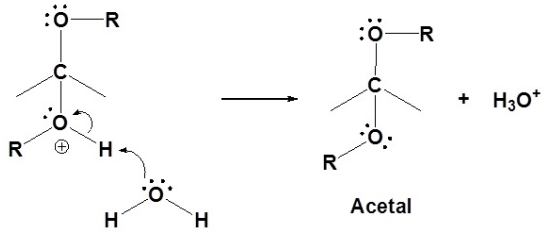
5) Removal of water



6) Nucleophilic addition reaction by the alcohol

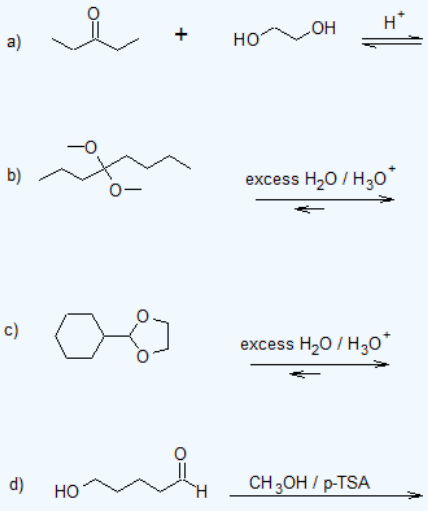


7) Deprotonation by water




## Exercise

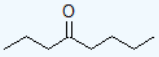
**18.** Draw the products for the following reactions.

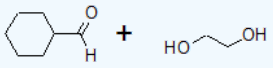



**Answer**

**18.**

a) 

b) 

c) 

d) 

## CONTRIBUTORS AND ATTRIBUTIONS

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- Prof. Steven Farmer (Sonoma State University)