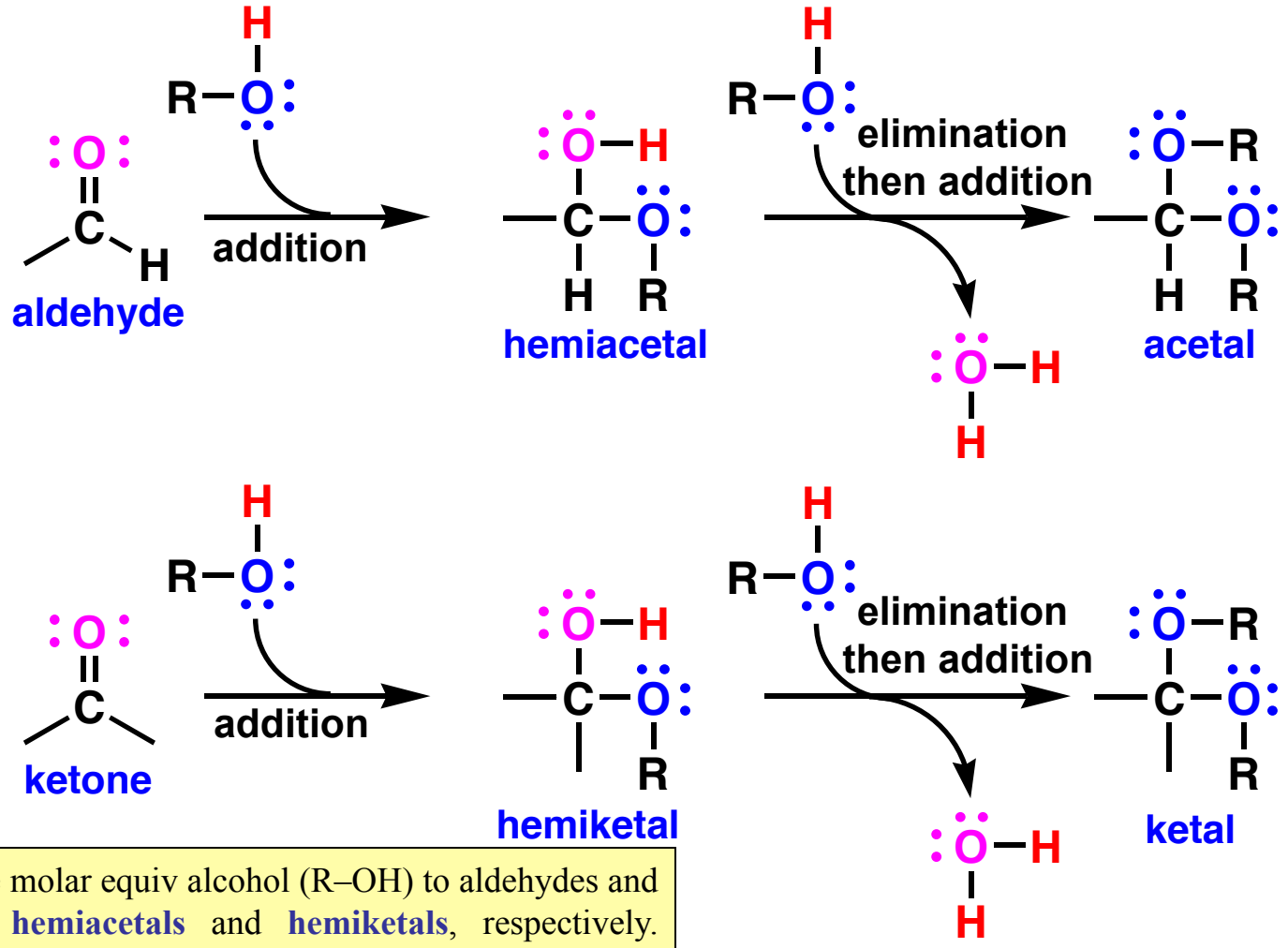
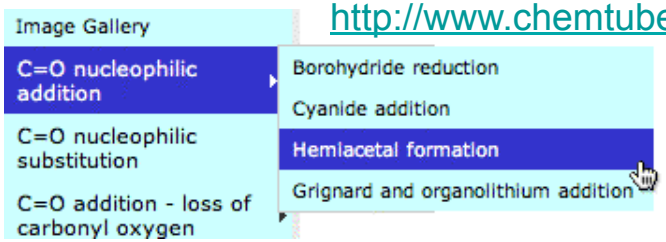
Substitution of the Carbonyl Oxygen in Ketones and Aldehydes with Two C–O Bonds: Acetals and Ketals



Addition of one molar equiv alcohol (R–OH) to aldehydes and ketones gives **hemiacetals** and **hemiketals**, respectively. Hemiacetals and hemiketals are not usually isolated. Elimination of water followed by addition of a second molar equiv of R-OH gives the corresponding **acetals** and **ketals**. Acetal and ketal derivatives are isolable compounds. Note: several [pt] steps assist the elimination of water.



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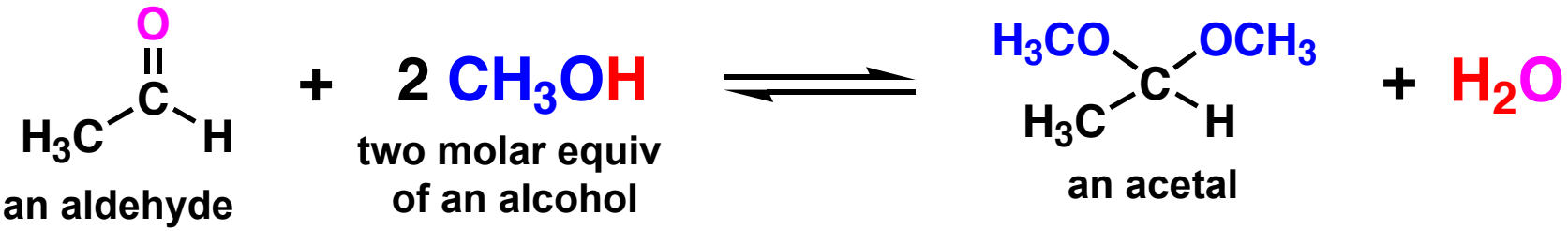
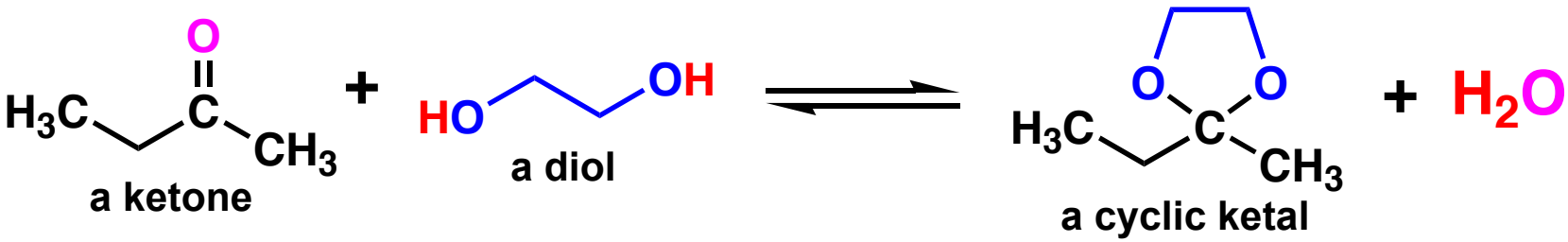
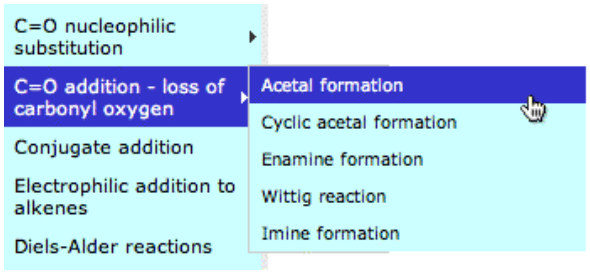
Examples of Acetal and Ketal Formation







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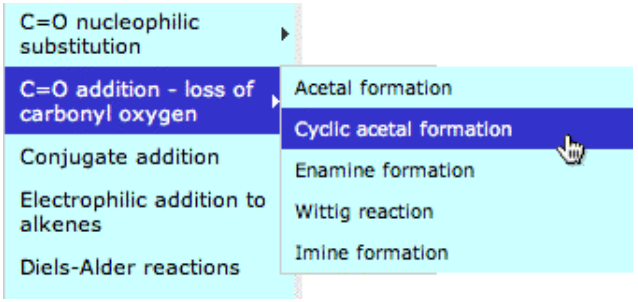
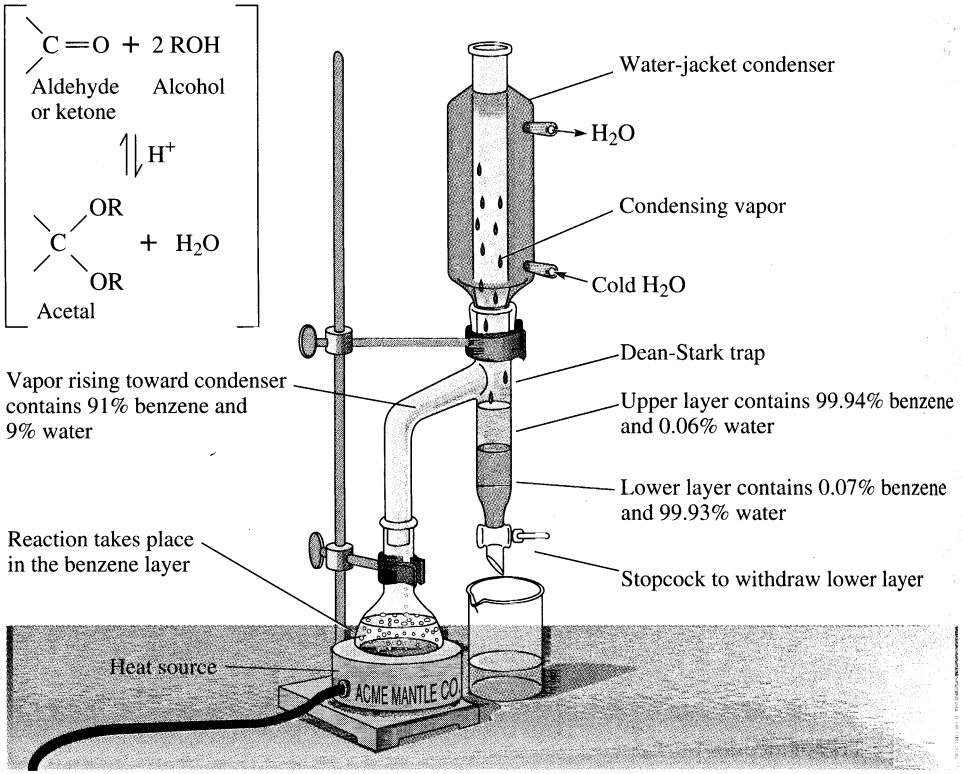


Removal of Water to Shift Equilibria

Reactions such as ester, imine, enamine, and acetal formation are reversible equilibria that generate water as a byproduct. The equilibria constants for these reactions are near unity, meaning that at equilibrium approximately equal quantities of reactants and products are present. To obtain high yields, the reaction must be driven to the right. **Le Chatelier's principle** suggests a useful strategy for driving these equilibria is to remove water. The apparatus below is called a Dean-Stark trap and is a practical device for removing water to shift chemical equilibria. Benzene is a commonly used solvent for these reactions. When heated to boil, benzene vapor forms an azeotropic mixture with the water that is generated in the reaction.



The azeotropic vapor phase is relatively rich in water content. When this vapor condenses it separates into immiscible liquid fractions, one rich in benzene and the other rich in water. In the receiver arm, the liquid benzene phase floats above the more dense water fraction. The benzene-rich fraction spills back into the pot, ready again to carry over more water. The water-rich phase sinks to the bottom of the receiver arm, withdrawn as needed. The Dean-Stark trap works because of the benzene-water density difference and because benzene and water are more compatible as vapors than they are as liquids.

Manipulating the Equilibrium

http://wps.prenhall.com/wps/media/objects/725/743131/0085f.html

Mechanism of Ketal (Acetal) Formation