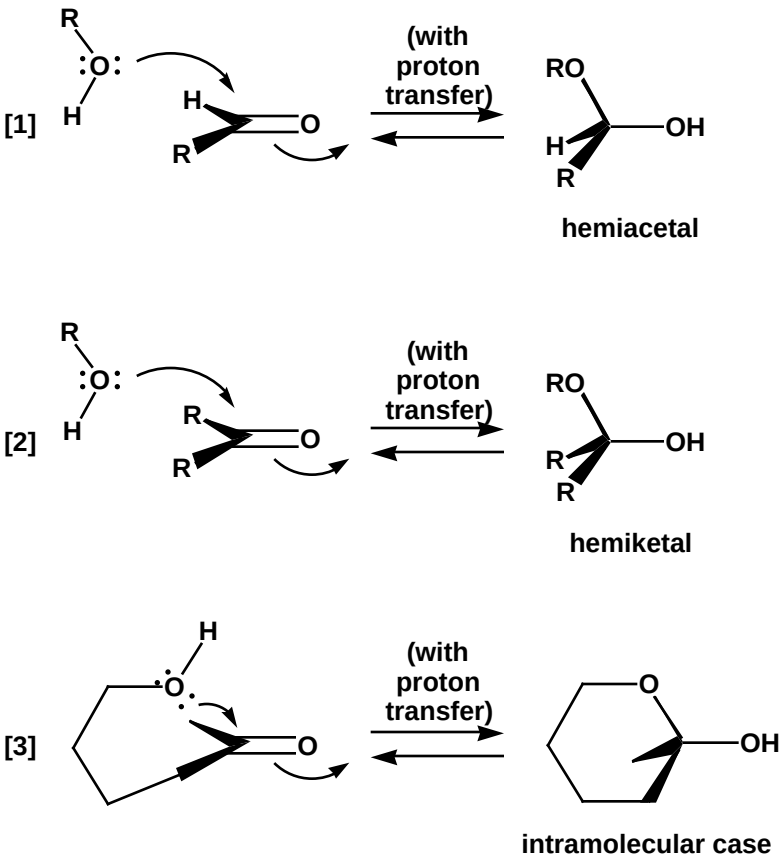
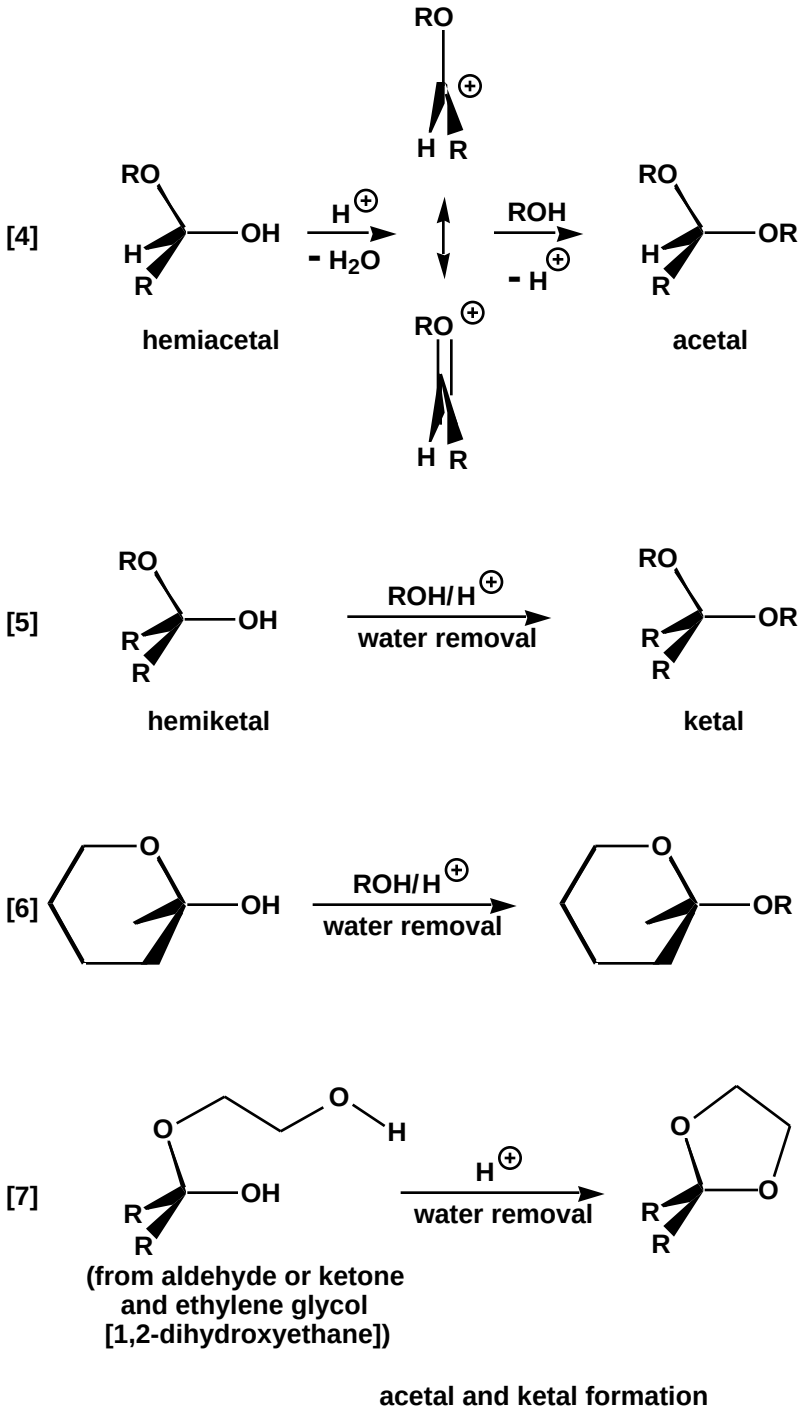
Text Related to Segment 18.02 ©2002 Claude E. Wintner

In equilibria analogous to those for hydrate formation, aldehydes and ketones in the presence of alcohols form addition products called hemiacetals [1] and hemiketals [2], the position of the equilibrium varying for individual cases. For simplicity of communication the following figure sketches these changes only in terms of functional outcome. The mechanisms may be thought of as corresponding to those outlined for hydrates in the previous segment. If the carbonyl and alcohol functionalities are incorporated in the same molecule, and in a sterically favorable manner, an *intra*molecular addition reaction is the likely result [3]:



hemiacetal and hemiketal formation

As is summarized in the next figure, hemiacetals and hemiketals can react further in *acidic* alcohol solution to form acetals [4] and ketals [5]):



acetal and ketal formation

Protonation of the alcohol function of the hemiacetal or hemiketal, and subsequent loss of water, leads to a delocalized cation that gains considerable stabilization by means of the donation of an electron pair from oxygen to the adjacent electrophilic carbon atom. The quenching of this cation by the alcohol solvent, followed by loss of a proton, then yields the acetal or ketal product. It will be noted that during the course of the transformation water is lost; chemical or physical removal of water from such a system serves to help drive the reaction in the forward direction. Conversely, while acetals and ketals are stable to aqueous base (and do not form in base), in aqueous *acid* they readily are hydrolyzed back to hemiacetals and hemiketals, and thus ultimately to the original carbonyl compounds and alcohols, by a mechanism which is exactly the reverse of the forward sense of the figure, that is, protonation of one of the ether functions, loss of alcohol to a delocalized cation, and finally addition of water to the cation and loss of a proton.

Beyond the possibility of the intramolecular cyclic case of acetal or ketal formation [6], which is the completion of a sequence that commences with [3], *both* alcohol functions may be obtained from a *single* difunctional alcohol (diol). Such a scenario using ethylene glycol (1,2-dihydroxyethane) is outlined in [7]. This is a commonly used, reversible method for protecting an aldehyde or ketone functionality against unwanted reactions in base.