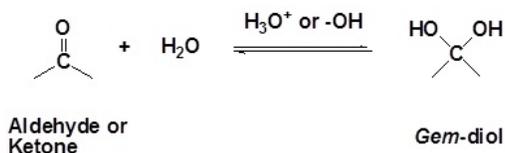
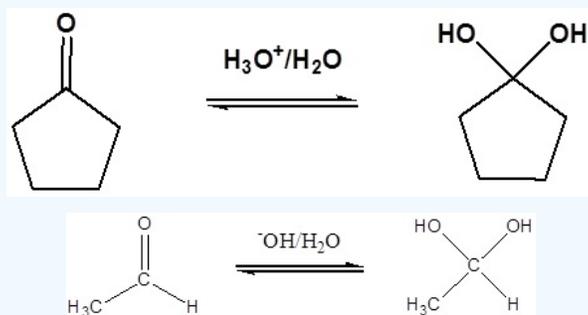


19.6: NUCLEOPHILIC ADDITION OF WATER (HYDRATION)

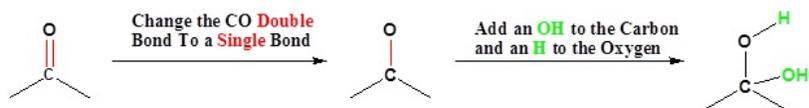
It has been demonstrated that water, in the presence of an acid or a base, adds rapidly to the carbonyl function of aldehydes and ketones establishing a reversible equilibrium with a **hydrate** (geminal-diol or *gem*-diol). The word geminal or gem comes from the Latin word for twin, *geminus*.



Example

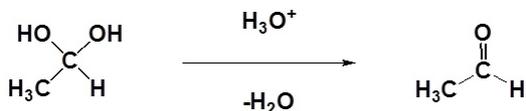


GOING FROM REACTANTS TO PRODUCTS SIMPLIFIED



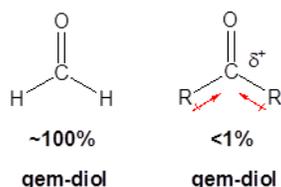
REVERSIBILITY OF THE REACTION

Isolation of *gem*-diols is difficult because the reaction is reversibly. Removal of the water during a reaction can cause the conversion of a *gem*-diol back to the corresponding carbonyl.

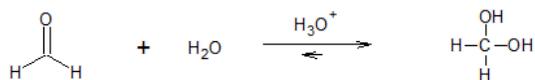
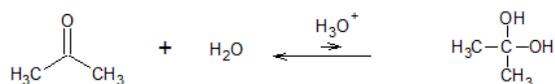


FACTORS AFFECTING THE GEM-DIOL EQUILIBRIUM

In most cases the resulting *gem*-diol is unstable relative to the reactants and cannot be isolated. Exceptions to this rule exist, one being formaldehyde where the weaker pi-component of the carbonyl double bond, relative to other aldehydes or ketones, and the small size of the hydrogen substituents favor addition. Thus, a solution of formaldehyde in water (formalin) is almost exclusively the hydrate, or polymers of the hydrate. The addition of electron donating alkyl groups stabilized the partial positive charge on the carbonyl carbon and decreases the amount of *gem*-diol product at equilibrium. Because of this ketones tend to form less than 1% of the hydrate at equilibrium. Likewise, the addition of strong electron-withdrawing groups destabilizes the carbonyl and tends to form stable *gem*-diols.



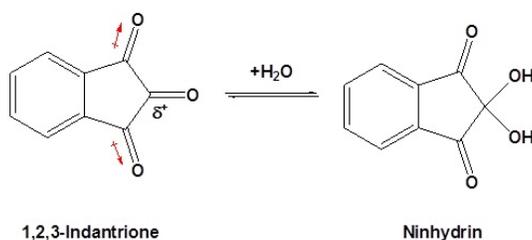
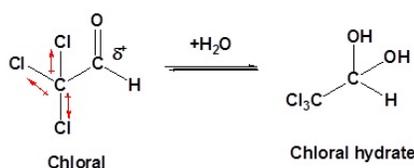
The relative equilibrium between the carbonyl and *gem*-diol builds understanding about steric effects in reaction mechanisms. This relationship is summarized below.



As the steric hindrance decreases around the carbonyl carbon

hydrate formation increases because there is more room for the tetrahedral geometry.

Two examples of this are chloral, and 1,2,3-indantrione. It should be noted that chloral hydrate is a sedative and has been added to alcoholic beverages to make a “Knock-out” drink also called a Mickey Finn. Also, ninhydrin is commonly used by forensic investigators to resolve finger prints.

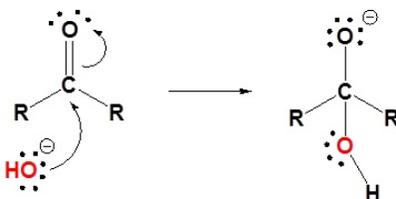


MECHANISM OF GEM-DIOL FORMATION

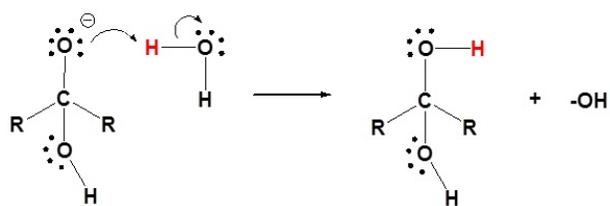
The mechanism is catalyzed by the addition of an acid or base. Note! This may speed up the reaction but it has no effect on the equilibria discussed above. Basic conditions speed up the reaction because hydroxide is a better nucleophile than water. Acidic conditions speed up the reaction because the protonated carbonyl is more electrophilic.

BASIC CONDITIONS

1) Nucleophilic hydroxide reacts with carbonyl carbon

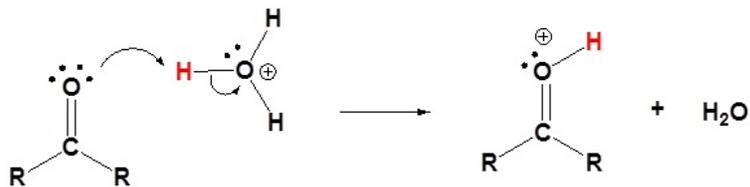


2) Protonation of the alkoxide

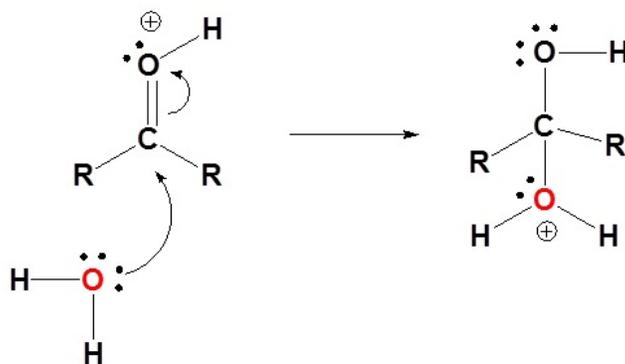


ACIDIC CONDITIONS

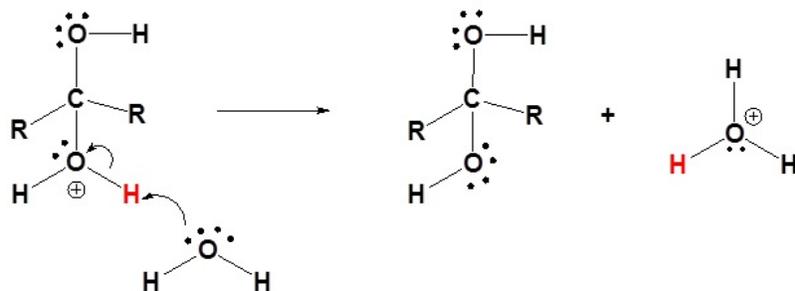
1) Protonation of the carbonyl



2) Nucleophilic water reacts with carbonyl carbon

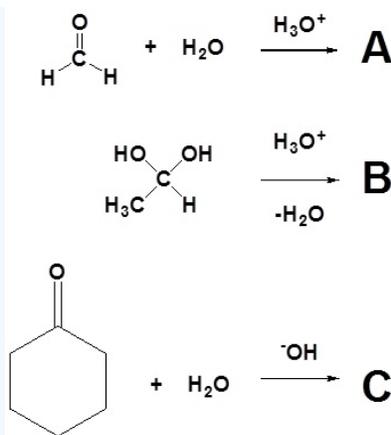


3) Deprotonation

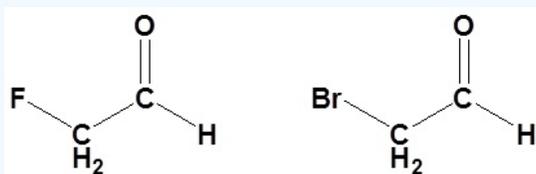


Exercise

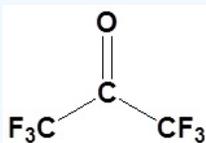
5. Draw the expected products of the following reactions.



6. Of the following pairs of molecules which would you expect to form a larger percentage of *gem*-diol at equilibrium? Please explain your answer.

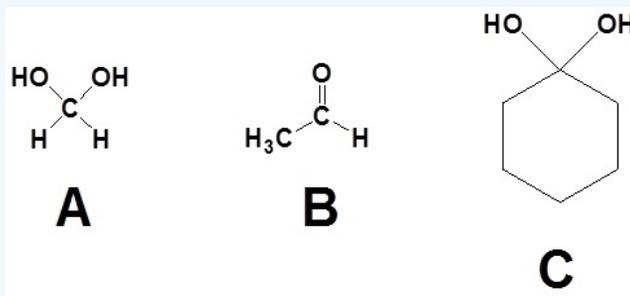


7. Would you expect the following molecule to form appreciable amount of *gem*-diol in water? Please explain your answer.



Answer

5.



6. The compound on the left would. Fluorine is more electronegative than bromine and would remove more electron density from the carbonyl carbon. This would destabilize the carbonyl allowing for more *gem*-diol to form.

7. Although ketones tend to not form *gem*-diols this compound exists almost entirely in the *gem*-diol form when placed in water. Ketones tend to not form *gem*-diols because of the stabilizing effect of the electron donating alkyl group. However, in this case the electron donating effects of alkyl group is dominated by the presence of six highly electronegative fluorines.

CONTRIBUTORS AND ATTRIBUTIONS

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- Prof. Steven Farmer ([Sonoma State University](#))
- William Reusch, Professor Emeritus ([Michigan State U.](#)), [Virtual Textbook of Organic Chemistry](#)

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