







• Even though enols are difficult to isolate and are present to only a small extent at equilibrium, they are nevertheless critically important intermediates in the chemistry of carbonyl compounds

OH

0.000 001%

CH

H<sub>2</sub>C



Keto-enol tautomerism of carbonyl compounds is catalyzed by both acids and bases
Acid catalysis involves protonation of the carbonyl oxygen atom to give an intermediate cation that then loses H<sup>+</sup> from the a carbon to yield the enol

- Base-catalyzed enol formation occurs because the presence of a carbonyl group makes the hydrogens on the α carbon weakly acidic
- A carbonyl compound can act as an acid and donate one of its α hydrogens to the base. The resultant resonance-stabilized anion, an enolate ion, is then protonated to yield a neutral compound





 When an alkene reacts with an electrophile, such as Br<sub>2</sub>, addition of Br<sup>+</sup> occurs to give an intermediate carbocation that react with Br<sup>-</sup> to give the addition product

• When an enol reacts with electrophile, the addition step is the same but the intermediate cation loses the –OH proton to regenerate a carbonyl compound



















- The resonance forms in enolate ions differ from carboxylate ion, because the two resonance forms are not equivalent
- The resonance form with the negative charge on the enolate oxygen is lower in energy than the form with the charge on carbon





Cyclohexanone

Cyclohexanone enolate ion (100%)



Compound type	Compound	pK <sub>a</sub>	
Carboxylic acid	CH <sub>3</sub> COOH	5	Stronger acid
1,3-Diketone	$CH_2(COCH_3)_2$	9	A
3-Keto ester	$CH_3COCH_2CO_2CH_3$	11	
1,3-Diester	$CH_2(CO_2CH_3)_2$	13	
Water	НОН	15.74	
Primary alcohol	CH <sub>3</sub> CH <sub>2</sub> OH	16	
Acid chloride	CH <sub>3</sub> COCl	16	
Aldehyde	CH <sub>3</sub> CHO	17	
Ketone	CH <sub>3</sub> COCH <sub>3</sub>	19	
Ester	$CH_3CO_2CH_3$	25	
Nitrile	CH <sub>3</sub> CN	25	
Dialkylamide	CH <sub>3</sub> CON(CH <sub>3</sub> ) <sub>2</sub>	30	
Ammonia	NH <sub>3</sub>	35	Weaker acid







































- The only difference between an aldol condensation and a Claisen condensation involves the fate of the initially formed tetrahedral intermediate

   The tetrahedral intermediate in the aldol reaction is protonated to give stable alcohol
   The tetrahedral intermediate in the Claisen reaction expels a leaving group to yield an acyl substitutuion product
  - Aqueous base cannot be used because their use would result in hydrolysis of ester



- Begining with conversion of glucose from its cyclic hemiacetal form to its open-chain aldehyde form
- The aldehyde undergoes tautomerization to yield an enol, which undergoes another tautomerization to give the ketone frucose





• Fructose,  $\beta$ -hydroxy ketone, is then cleaved into two three-carbon molecules – one ketone and one aldehyde – by a retro aldol reaction CH<sub>2</sub>OH CH<sub>2</sub>OH Ċ=0  $\dot{C}=0$ CH<sub>2</sub>OH но-с-н + `c=0 н-H H-C-OH H-C-OH CH2OH CH2OH Fructose