

Chapter 18

Enols and Enolates

Chapter 18 suggested problems: none

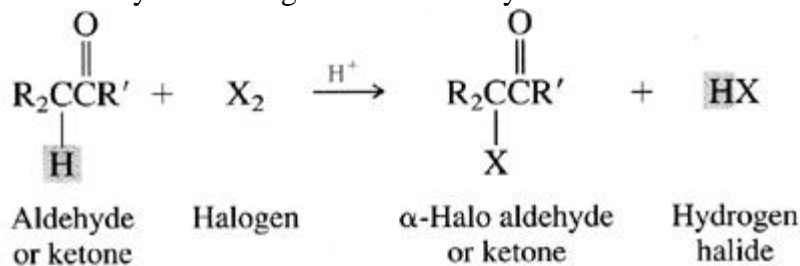
Class Notes

I. The hydrogens of α -carbons

A. Greek letter labeling of backbone carbon atoms

1. Alpha, beta, gamma, delta omega

B. Acid-catalyzed α -halogenation of aldehydes and ketones

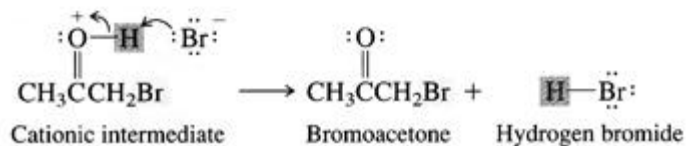
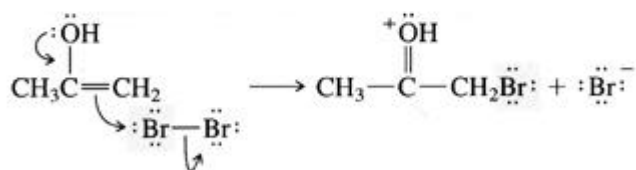
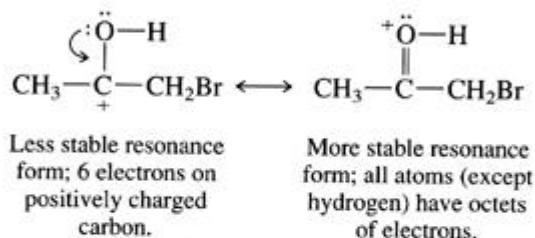
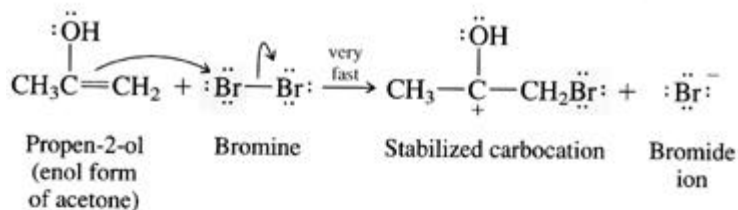


1. Aldehydes and ketones react with halogens by substituting an α -hydrogen for a halogen atom
2. The reaction is regiospecific for α -hydrogens; no other H atoms are affected
3. The reaction is acid-catalyzed, and since one of the products is an acid the reaction is autocatalyzed
4. Results limited to monohalogenation

C. Mechanism of bromination of acetone

1. Whether using iodine, bromine, or chlorine, the rate of reaction of acetone is independent of [halogen] and first order in [acetone]
2. This was the clue that something unexpected was going on

3. Mechanism of bromination of acetone



II. Keto-enol tautomerism

A. General

1. The reactive form of acetone in α -halogenation is not the keto form of acetone but its enol form
2. The interconversion between keto and enol forms is called keto-enol tautomerism



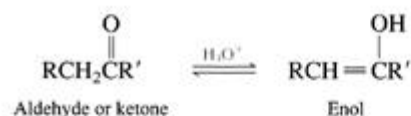
3. Tautomerism: the interconversion between two compounds based on the movement of a single atom or group
4. An eqb. exists between the keto and enol forms of compounds

- Enols are actual compounds and not just resonance structures equivalent with the keto form of the compound
- The concentration of enol is generally quite small, since the keto form is more stable by abt. 45-60 kJ/mol; i.e., C=O bonds are stronger than C=C bonds
- This is generally true of both ketones and aldehydes
- There is only one enol form of aldehydes and symmetrical ketones
- There are two enol forms of unsymmetrical ketones, but both are present in far smaller amounts combined than the keto form of the molecule

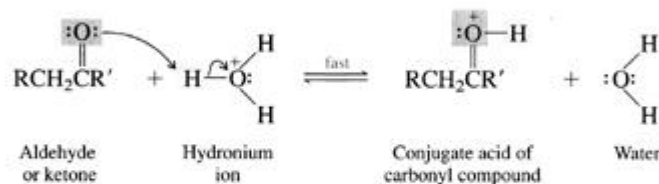
B. Mechanism in acidic solution

- The mechanism involves two separate proton transfer steps rather than a single step transfer

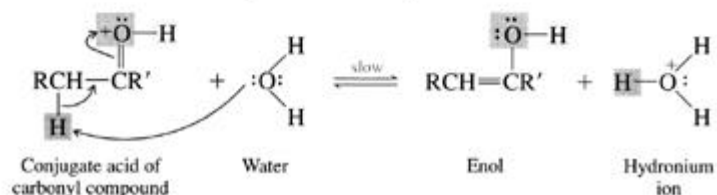
Overall reaction:



Step 1: A proton is transferred from the acid catalyst to the carbonyl oxygen.

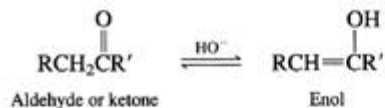


Step 2: A water molecule acts as a Brønsted base to remove a proton from the α carbon atom of the protonated aldehyde or ketone.

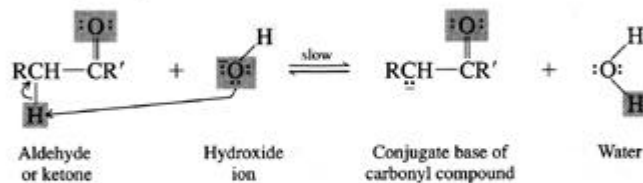


C. Mechanism in basic solution

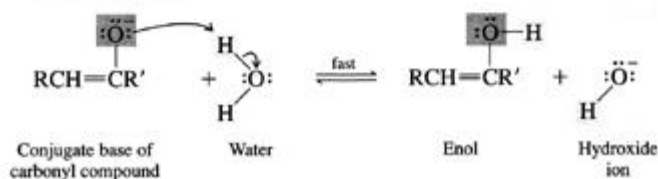
1. Overall reaction:



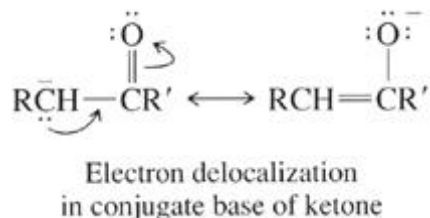
Step 1: A proton is abstracted by hydroxide ion from the α carbon atom of the carbonyl compound.



Step 2: A water molecule acts as a Brønsted acid to transfer a proton to the oxygen of the enolate ion.



2. The conjugate base at the beginning of Step 2. is a resonance form of the conjugate base at the end of Step 1.

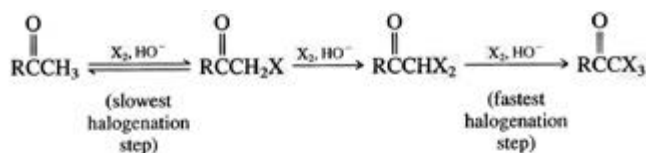


3. The structure with the negative charge on oxygen is the more significant of the two and is called an enolate ion

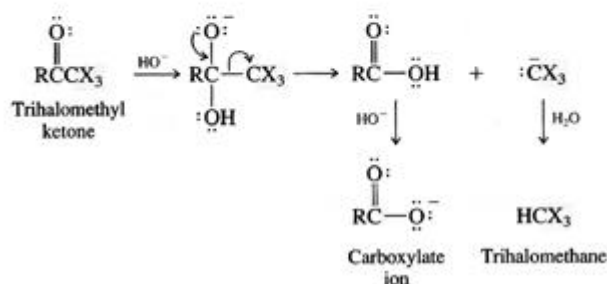
4. Enolate ions are the conjugate bases of the corresponding enols

III. The haloform reaction

- Base-catalyzed α -halogenation of aldehydes and ketones
- As in acid-catalyzed α -halogenation, the rate of reaction depends on [carbonyl] and is independent of [halogen]
- Unlike acid-catalyzed α -halogenation, there is often an exchange of all α -hydrogens for halogen atoms
- If the ketone is a methyl ketone, the trihalomethylketone undergoes hydrolysis and dissociates into a carboxylate ion and a trihalomethane molecule



The trihalomethyl ketone (RCCX_3) so formed then undergoes nucleophilic addition of hydroxide ion to its carbonyl group, triggering its dissociation.

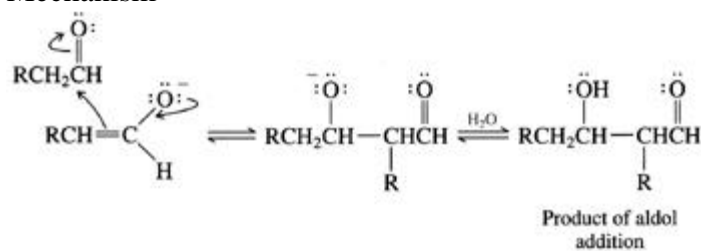


- E. This reaction can be used to prepare carboxylic acids but if both α -carbons have α -hydrogens then the yield of the acid will drop drastically

IV. Aldol additions and aldol condensations

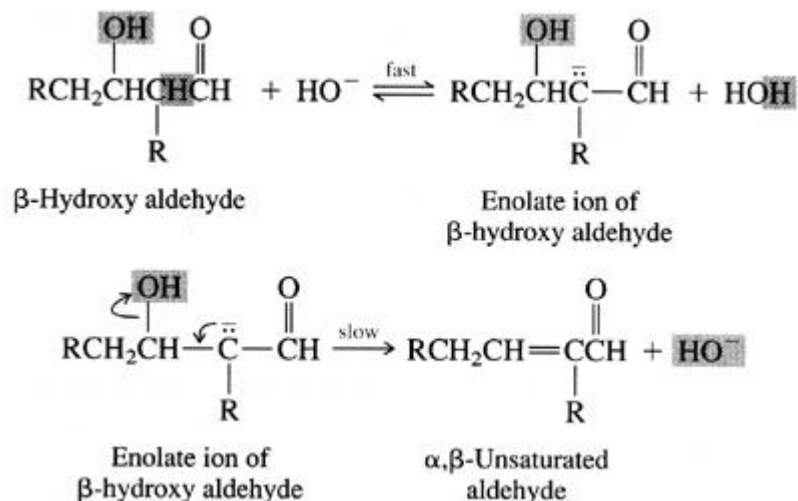
- A. Aldol: a compound that contains both an aldehyde and a hydroxyl group
- B. Aldol addition: in a solution that contains both an aldehyde (or ketone) and its enol, the enol can undergo nucleophilic addition to the aldehyde at its carbonyl carbon

1. Mechanism



2. Note that this results in carbon-carbon bond formation and a hydroxyl group beta to the carbonyl
 3. The carbon not bonded to oxygen in the enol attacks the carbonyl carbon of the aldehyde
- C. Aldol condensation: a reaction in which two molecules of an aldehyde combine to form an α,β -unsaturated aldehyde and a molecule of water
1. β -Hydroxy aldehydes undergo dehydration on the application of heat to form α,β -unsaturated aldehydes

2. Mechanism



3. Can occur with aldehydes or ketones, can be acid or base catalyzed

D. Notes on aldol condensation from March (p. 829 - 834)

1. Aldol condensation: the α -carbon of one aldehyde or ketone adds to the carbonyl carbon of another
2. The base most often used is hydroxide although stronger bases, such as alkoxides, can be used (e.g. aluminum tert-butoxide)
3. Hydroxide ion is not a strong enough base to convert all of the carbonyl compound to its corresponding enol, but enough enolate ion is produced for the reaction to proceed
4. The product is a β -hydroxy aldehyde (aldol) or ketone (ketol), which may be spontaneously dehydrated during the course of the reaction to an α,β -unsaturated aldehyde or ketone (product may be dehydrated independent of reaction)
5. Five possible types of aldol condensations
 - a. Two molecules of the same aldehyde: eqb lies with the product
 - b. Two molecules of the same ketone: eqb lies with the reactants and must be shifted, rather laborious
 - c. Two different aldehydes: if both aldehydes have α -hydrogens then a mixture of four products will be formed (eight including alkenes); if one aldehyde does not have an α -hydrogen then a mixture of two products will be formed
 - d. Two different ketones: seldom attempted, laborious

- e. Aldehyde and a ketone: usually feasible, esp. when the aldehyde has no α -hydrogens, since there is no competition from the ketone condensing with itself; even when the aldehyde has an α -hydrogen it is the α -carbon of the ketone that adds to the carbonyl of the aldehyde and not the other way around

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