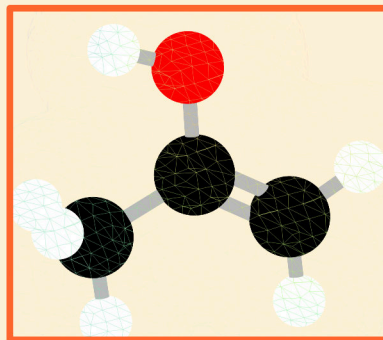


# HIGHLIGHTS

- Acid-catalyzed enol formation
- Base-catalyzed enolization (enol formation)
- Keto-enol tautomerization is the equilibrium between the ketone form and enol form
- Ketone tautomer normally favored
- Enol tautomer often favored with  $\beta$ -keto-carbonyl compounds
- More substituted enol favored
- Enols are nucleophiles and will react with strong electrophiles



Aldehydes and ketones are often in equilibrium with their enol form. The carbonyl compound undergoes tautomerization or enolization, where a proton is transferred from the  $\alpha$ -carbon to the oxygen atom and the  $C=O$   $\pi$  bond shifts to form a  $C=C$  double bond. Normally, this equilibrium favors the aldehyde or ketone to such an extent that the enol is not observable. Compounds with a  $\beta$ -carbonyl group often favor the enol form. Formation of the enol can be either base or acid catalyzed.

Invariably, the thermodynamically more stable, more substituted or Zaitsev enol is formed. Enols are nucleophiles and can react at both the oxygen or carbon atom. The latter is more common (and I haven't discussed the former in this summary). Enols react with strong electrophiles such as halogens or the nitronium ion to give  $\alpha$ -haloketones and aldehydes or dicarbonyl compounds.

## CHEMISTRY CLASSICS

# ENOLS AND ENOLATES

## PART I: FORMATION & REACTIONS OF ENOLS

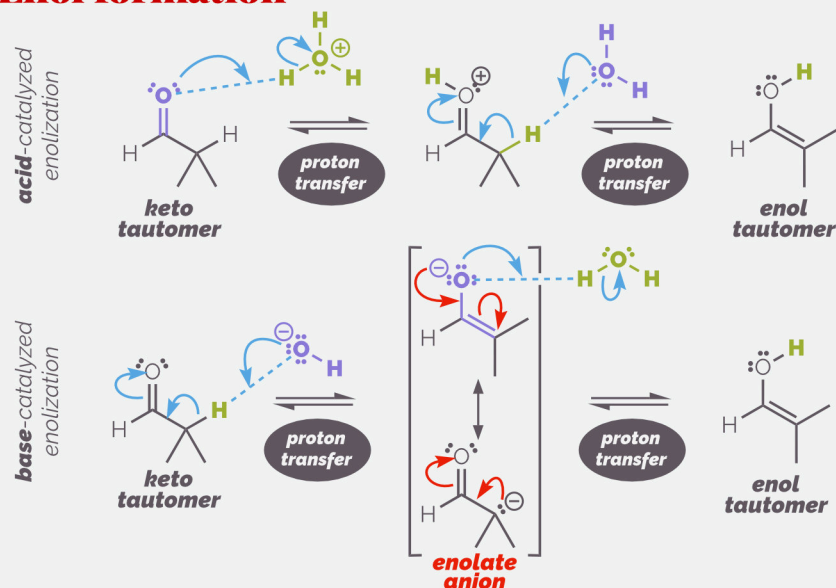


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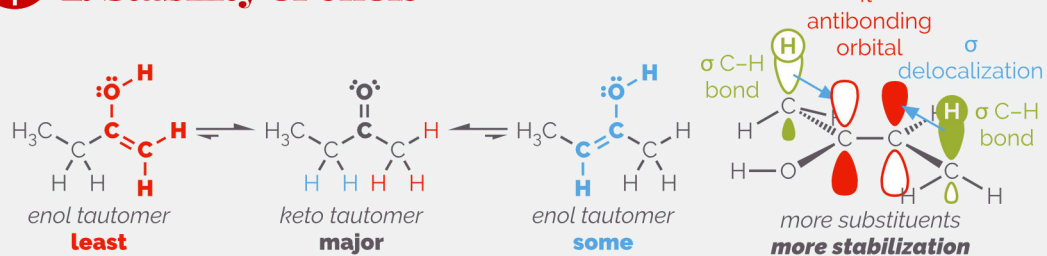
# Formation & Reactions of Enols

## 1. Enol formation

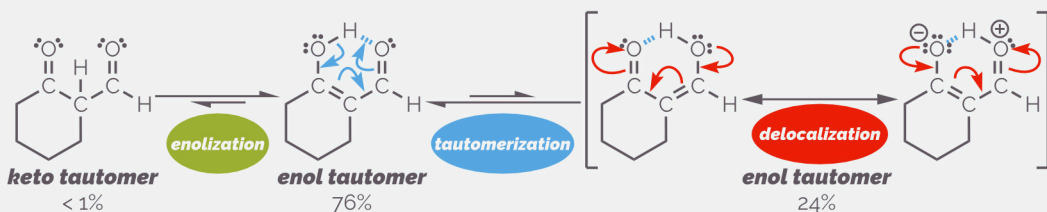


- **Tautomerization** or **enolization** of a carbonyl group leads to the enol form
- Requires  **$\alpha$ -proton** or proton on carbon adjacent to the carbonyl group

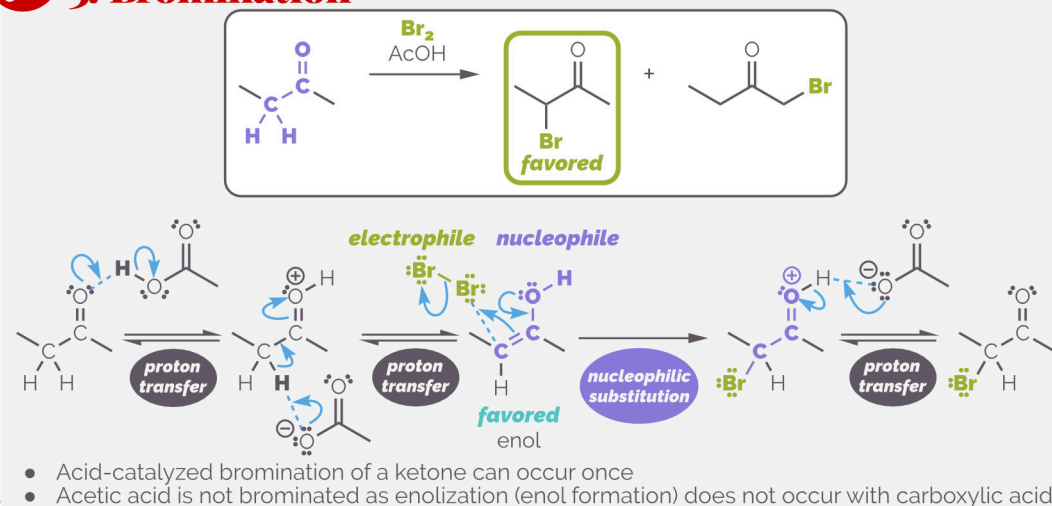
## 2. Stability of enols



- Normally the carbonyl-form is favored over enol
- Position of equilibrium is highly solvent dependent
- Generally, **more substituted enol favored** (more stable)
- **Delocalization** or **conjugation** can lead to the enol being **favored**

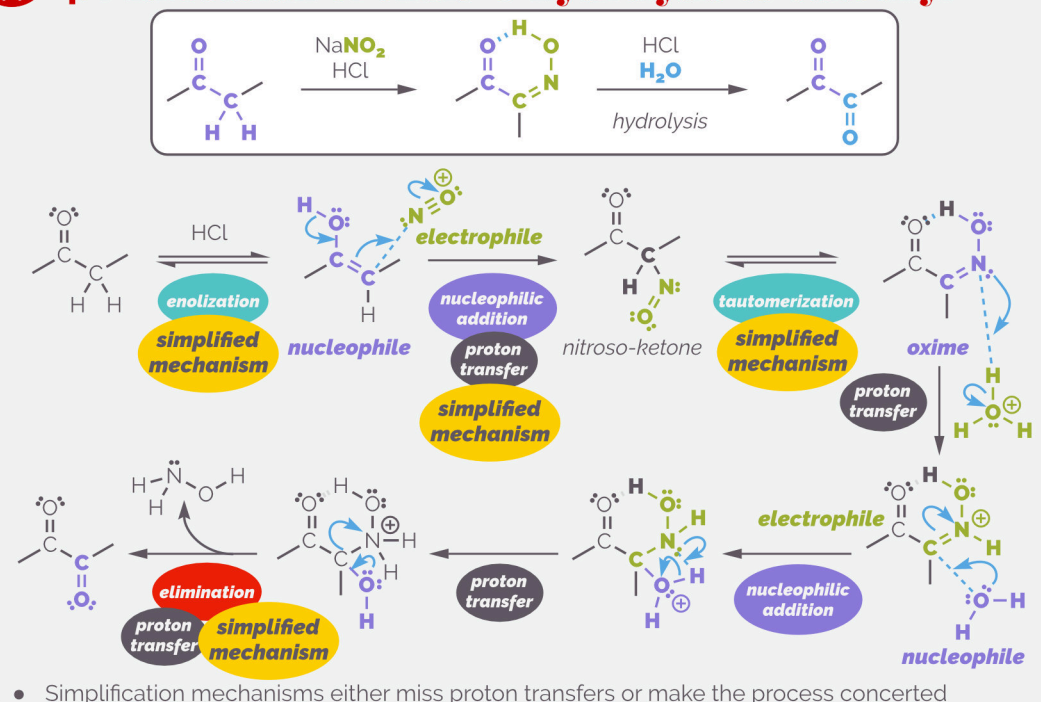


## 3. Bromination



- Acid-catalyzed bromination of a ketone can occur once
- Acetic acid is not brominated as enolization (enol formation) does not occur with carboxylic acid

## 4. Nitrosation of enols & hydrolysis to carbonyl



- Simplification mechanisms either miss proton transfers or make the process concerted