

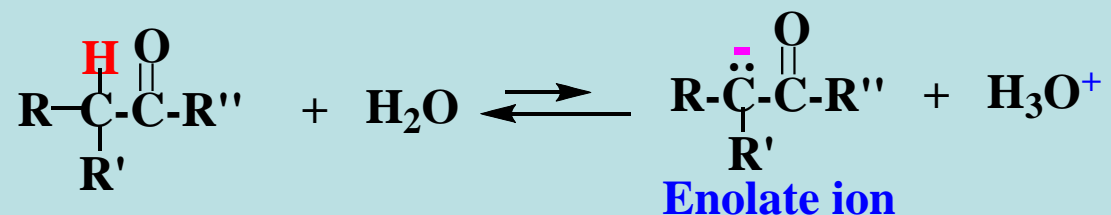
## Chapter 17

# Aldehydes and Ketones II: Enols and Enolates

Besides the ability of aldehydes and ketones to undergo nucleophilic addition, a second characteristic is the unusual acidity of their  **$\alpha$  hydrogens** (those on a carbon immediately attached to a carbonyl group, an  **$\alpha$  carbon**).

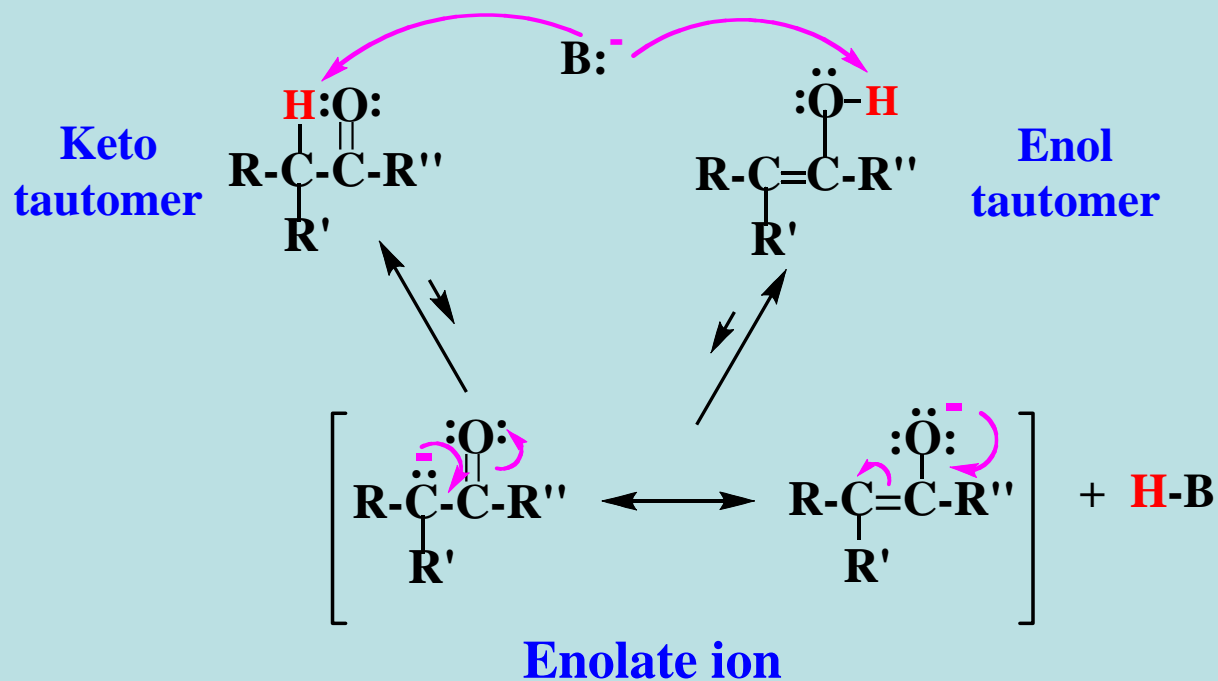


These hydrogens  **$\alpha$**  to the carbonyl group have  $\text{pK}_a$  values of 19-20. Thus they are **much more acidic** than ordinary aliphatic hydrogens, which have  $\text{pK}_a$  values of 40-50.



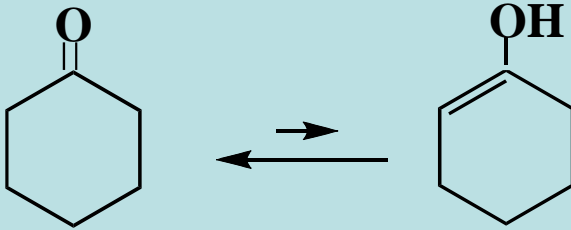
## The Keto-Enol Tautomers and the Enolate Anion

The anion formed by loss of a proton  $\alpha$  to a carbonyl group is called an **enolate anion** because it is the conjugate base of the carbonyl compound's **enol tautomer**. Enolate anions are **resonance stabilized** by delocalization of the negative charge.



# The Keto-Enol Equilibrium

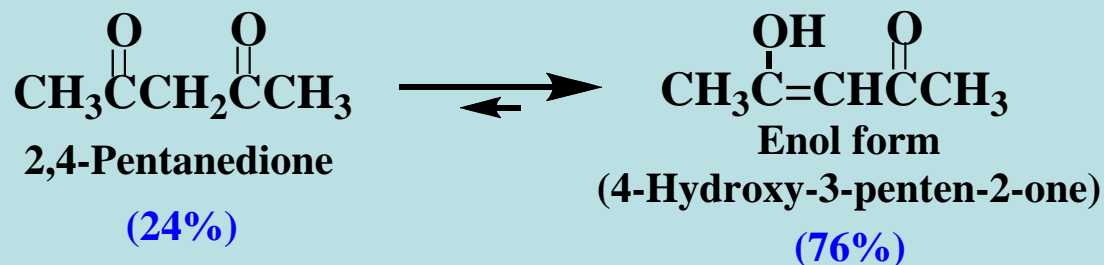
Keto and enol structures are **constitutional isomers** that are also called **tautomers**. They interconvert rapidly in the presence of catalytic amounts of acids or bases. This equilibration is referred to as **tautomerization**. The keto form, generally, is heavily favored in the equilibrium, as shown by the examples below.

Compound	Keto-enol equilibrium
Acetaldehyde	$\text{CH}_3\overset{\text{O}}{\parallel}\text{CH} \xrightleftharpoons{\quad} \text{CH}_2=\overset{\text{OH}}{\text{C}}\text{H}$ <p style="text-align: center;">~100%</p>
Acetone	$\text{CH}_3\overset{\text{O}}{\parallel}\text{CCH}_3 \xrightleftharpoons{\quad} \text{CH}_2=\overset{\text{OH}}{\text{C}}\text{CH}_3$ <p style="text-align: center;">&gt;99% <span style="margin-left: 150px;"><math>1.5 \times 10^{-4}\%</math></span></p>
Cyclohexanone	 <p style="text-align: center;">98.8% <span style="margin-left: 150px;">1.2%</span></p>

Keto form dominance reflects the **greater strength** of the carbonyl  $\pi$ -bond (~364 kJ/mol) compared to the alkene  $\pi$ -bond (~250 kJ/mol).

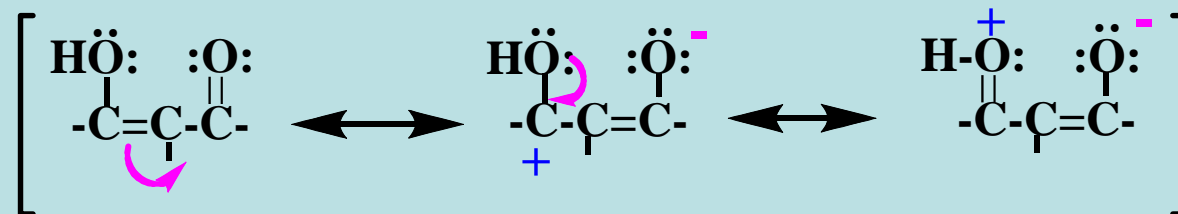
## The High Enol Content of $\beta$ -Dicarbonyl Compounds

In compounds with two carbonyl groups separated by one carbon atom,  **$\beta$ -dicarbonyls**, the amount of enol form present at equilibrium is much higher. The linking carbon must, of course, carry at least one hydrogen.

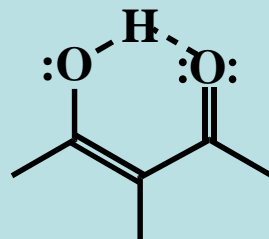


The high enol content is attributed to stabilization of the enol structure by two factors:

(1) *Resonance in the conjugated system:*

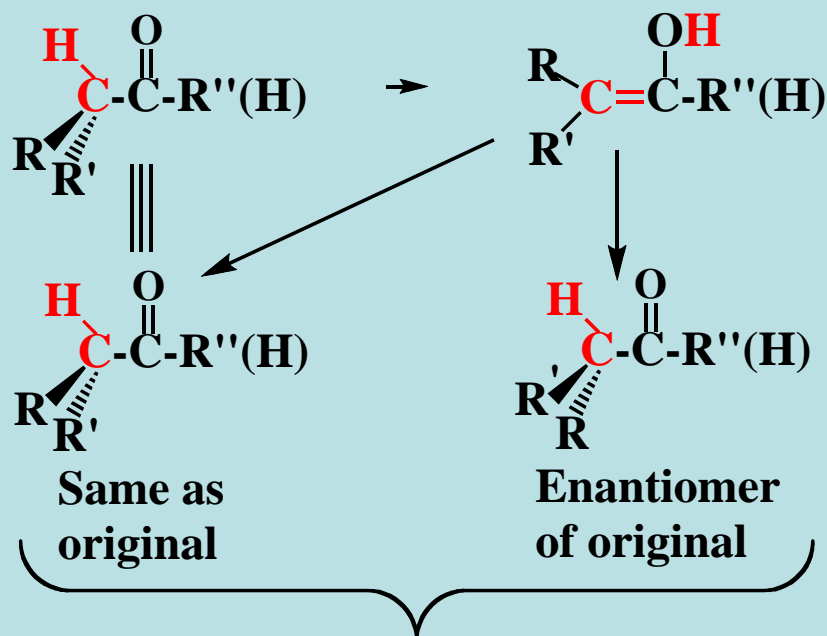


(2) *Intramolecular hydrogen bonding (when structurally permitted):*



## Racemization via Enols

The pure enantiomer of an aldehyde or ketone that has a **hydrogen-bearing  $\alpha$  carbon** as a chiral center, exemplified below, will easily racemize via its enol form:

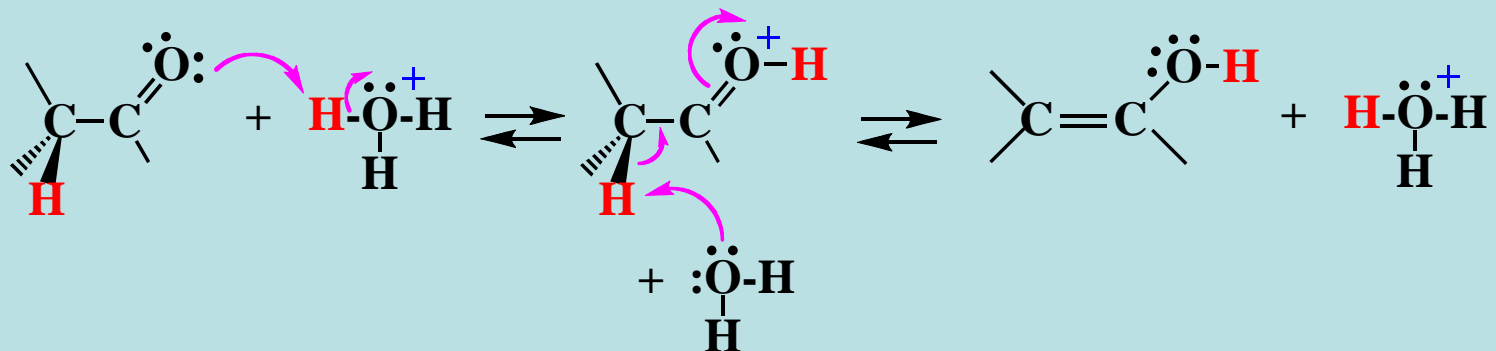


Racemization occurs because of addition of **H** to the top versus the bottom of the enol double bond.

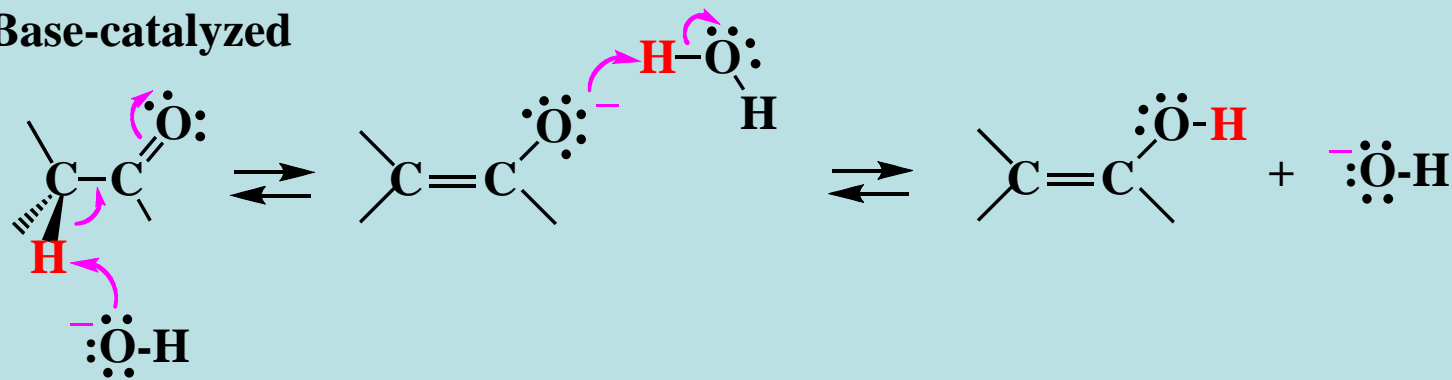
Racemization is hastened by the presence of either acid or base because they both catalyze formation of the intermediate enol form.

# Mechanism of Enolization

## (1) Acid-catalyzed



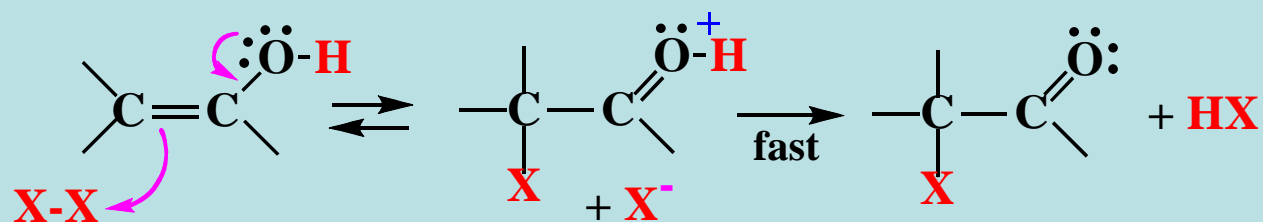
## (2) Base-catalyzed



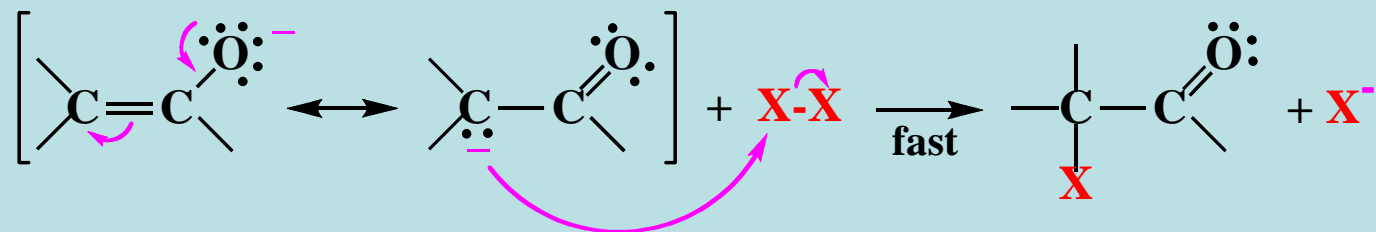
## Mechanism of Aldehyde and Ketone Halogenation

The initial rate of reaction is independent of halogen concentration, but it is increased in the presence of acid or base because either promotes enol formation.

(1) Under acidic conditions there is rapid reaction of the enol with halogen:

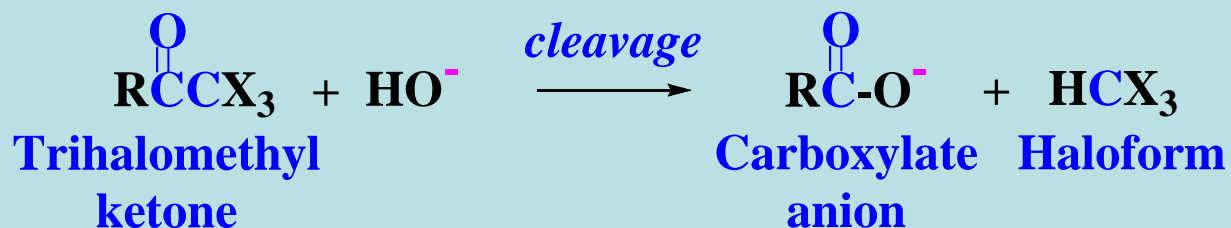
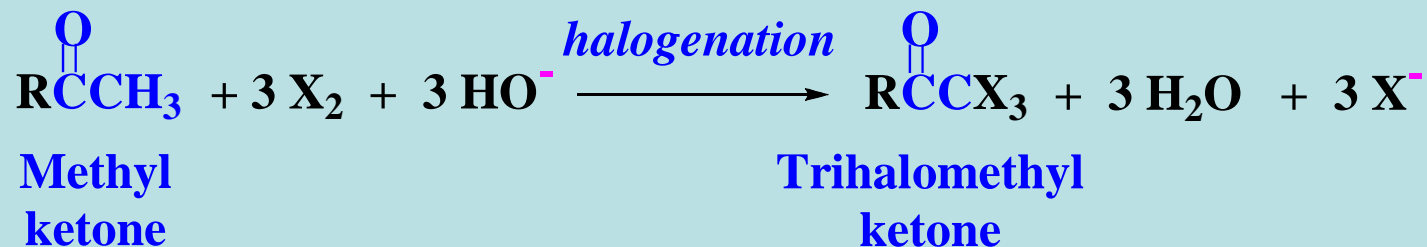


(2) Under basic conditions there is rapid reaction of enolate ion with halogen:



## The Haloform Reaction

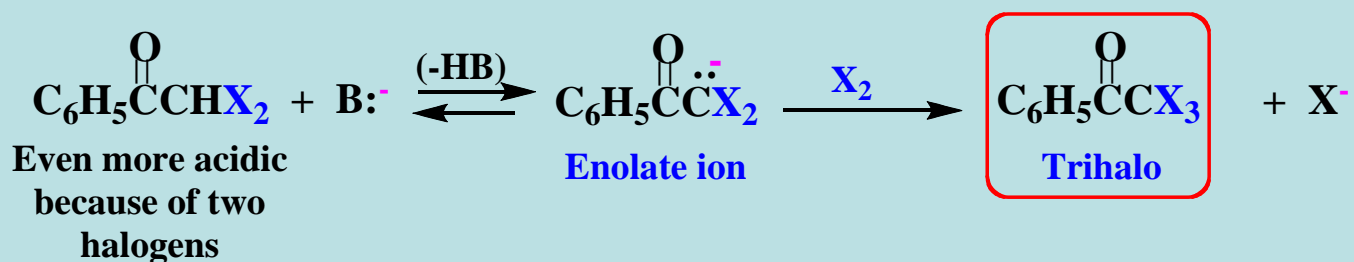
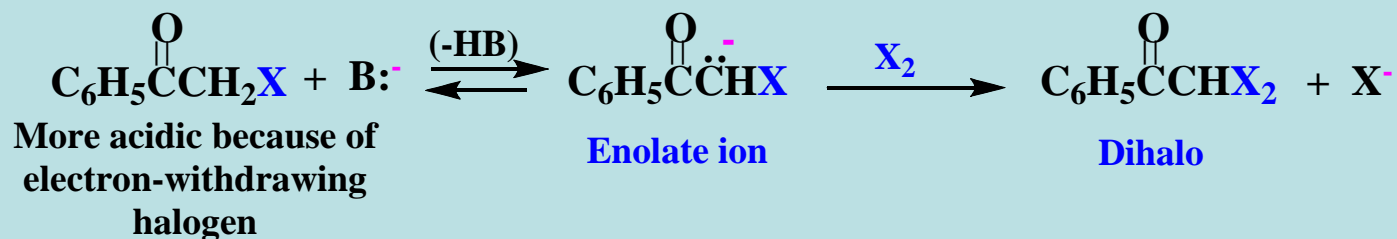
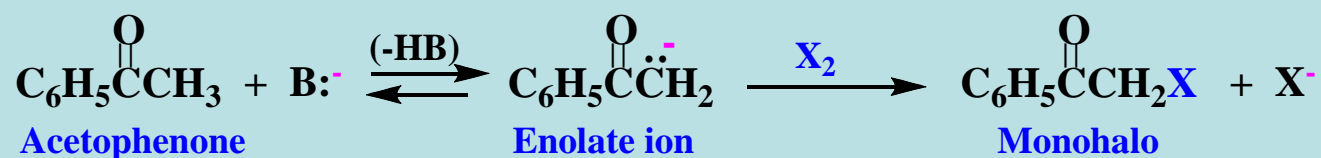
**Methyl ketones** ( $\text{RCCH}_3$ ) react with halogen in the presence of base to give multiple halogenation, eventually producing the trihalomethyl ketone, which cleaves to give a **carboxylate anion and haloform**.



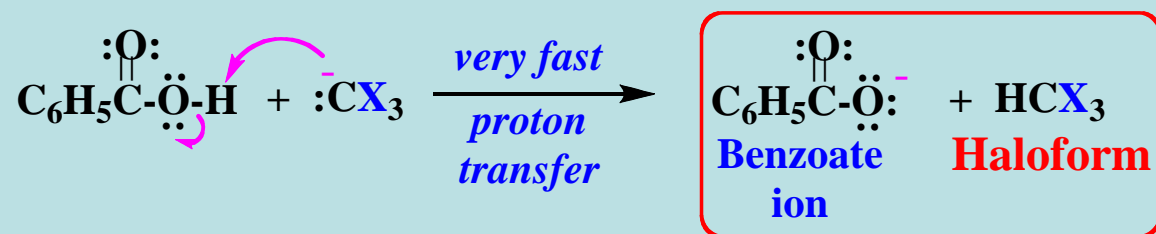
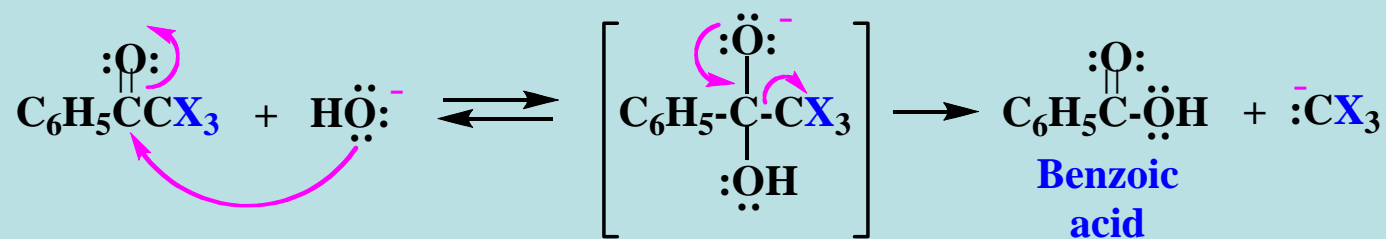
The haloform reaction has synthetic value as an **oxidative cleavage of methyl ketones to carboxylic acids**.

## EXAMPLE: The Haloform Reaction of Acetophenone

(1) **Trihalogenation**: In the presence of sufficient  $X_2$  and base, all three enolizable hydrogens are sequentially replaced by X.



## (2) Nucleophilic addition and cleavage

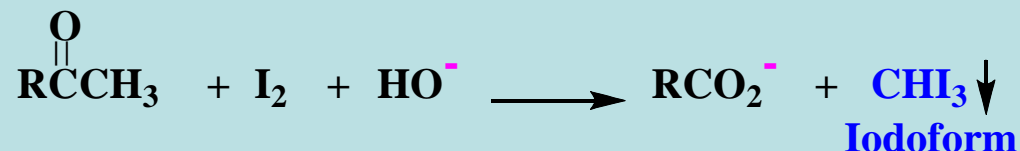


The reaction typically is carried out in an aqueous solution of sodium hydroxide and  $\text{X}_2$  ( $\text{Br}_2$ ,  $\text{I}_2$  or  $\text{Cl}_2$ ), in which an equilibrium is established that produces sodium hypohalite,  $\text{NaOX}$ . This solution is an oxidant.



## The Iodoform Test

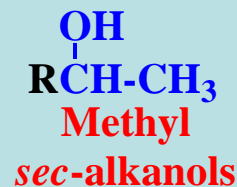
This visual test for identifying structural components uses iodine in the haloform reaction. A positive test is the appearance of the bright yellow solid iodoform,  $\text{CHI}_3$ .



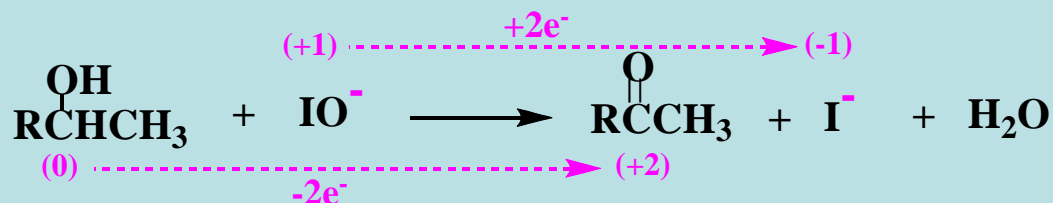
This classic chemical diagnostic is run on test tube scale and identifies both of these structural features:



and

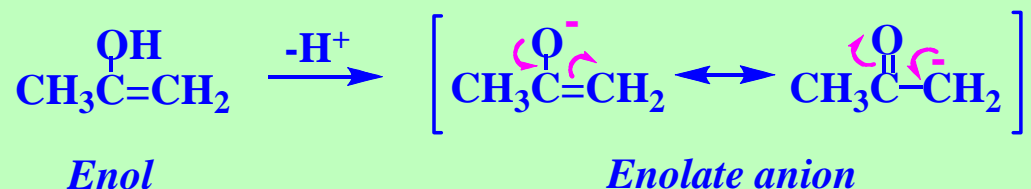


Because of the **oxidizing potential of hypoiodite**, methyl *sec*-alkanols are oxidized to methyl ketones, which explains why these alcohols give a positive iodoform test.



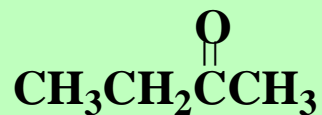
### Quiz 17.01

Draw the enol tautomer of acetone (2-propanone) and the resonance forms that contribute to the stability of its enolate anion (conjugate base).

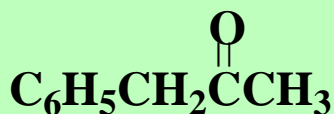


### Quiz 17.02

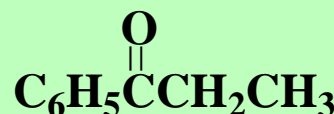
Which of the following compounds give positive iodoform tests?



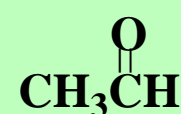
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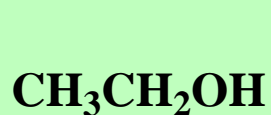
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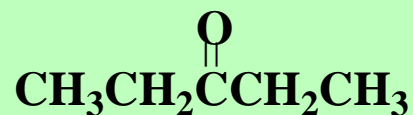
no



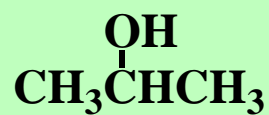
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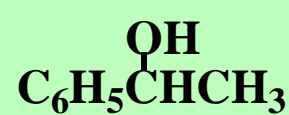
yes



no



yes



yes

### Quiz 17.03

For each reaction below, draw the structure of the principal product(s). (THF is a co-solvent to help solubilize the organic material.)

