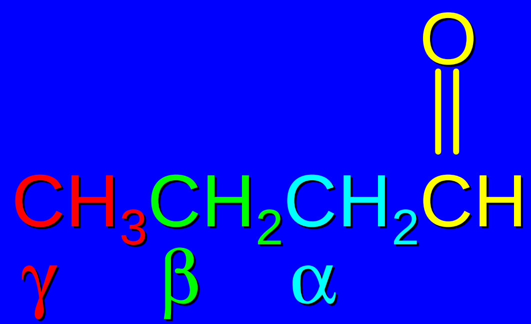
Chapter 18

Enols and Enolates

18.1

The α-Carbon Atom and its Hydrogens

Terminology



The reference atom is the carbonyl carbon.

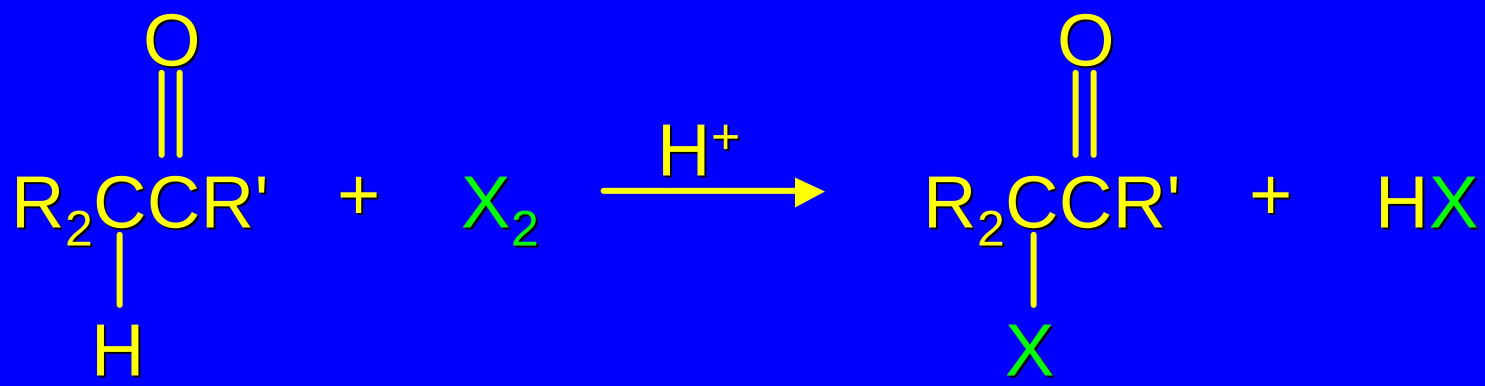
Other carbons are designated α, β, γ, etc. on the basis of their position with respect to the carbonyl carbon.

Hydrogens take the same Greek letter as the carbon to which they are attached.

18.2

α Halogenation of Aldehydes and Ketones

General Reaction



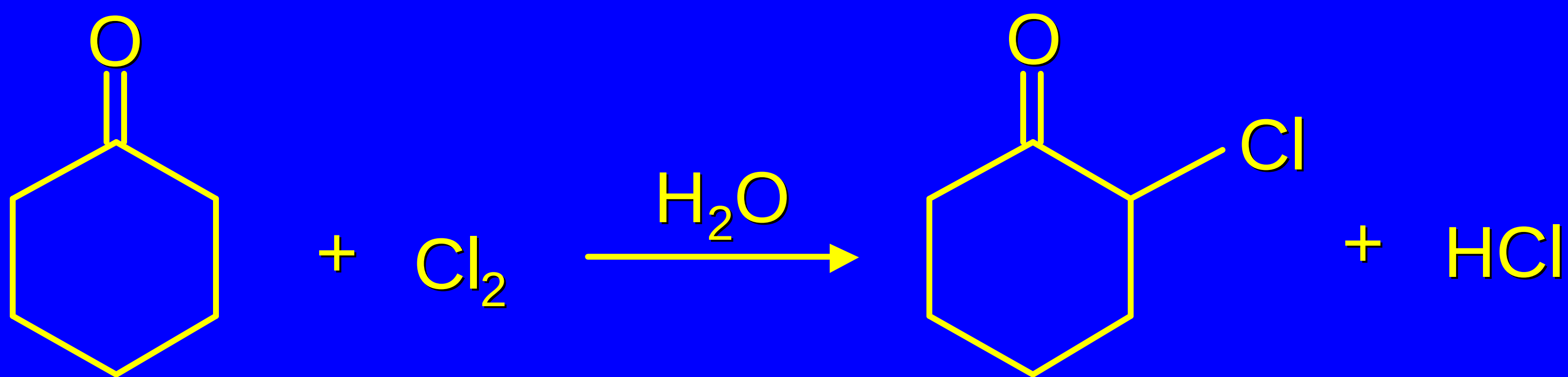
X_2 is Cl_2, Br_2, or I_2.

Substitution is specific for replacement of α hydrogen.

Catalyzed by acids. One of the products is an acid (HX); the reaction is *autocatalytic*.

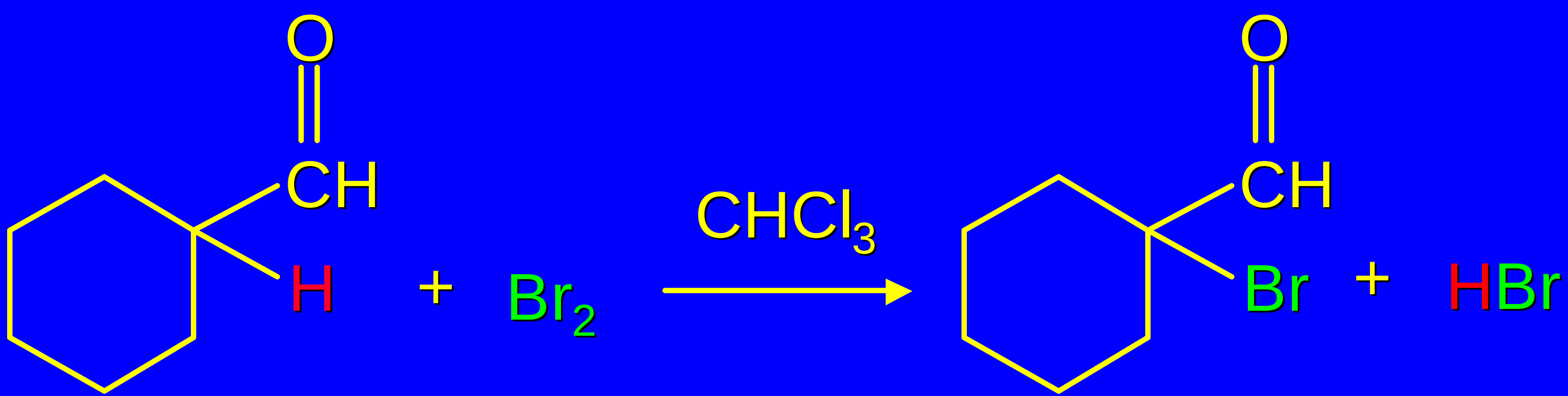
Not a free-radical reaction.

Example



(61-66%)

Example



(80%)

Notice that it is the proton on the α carbon that is replaced, not the one on the carbonyl carbon.

18.3

Mechanism of α Halogenation of Aldehydes and Ketones

Mechanism of α Halogenation

Experimental Facts

specific for replacement of H at the α carbon

equal rates for chlorination, bromination, and iodination

first order in ketone; zero order in halogen

Mechanism of α Halogenation

Experimental Facts

specific for replacement of H at the α carbon

equal rates for chlorination, bromination, and iodination

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Interpretation

no involvement of halogen until after the rate-determining step

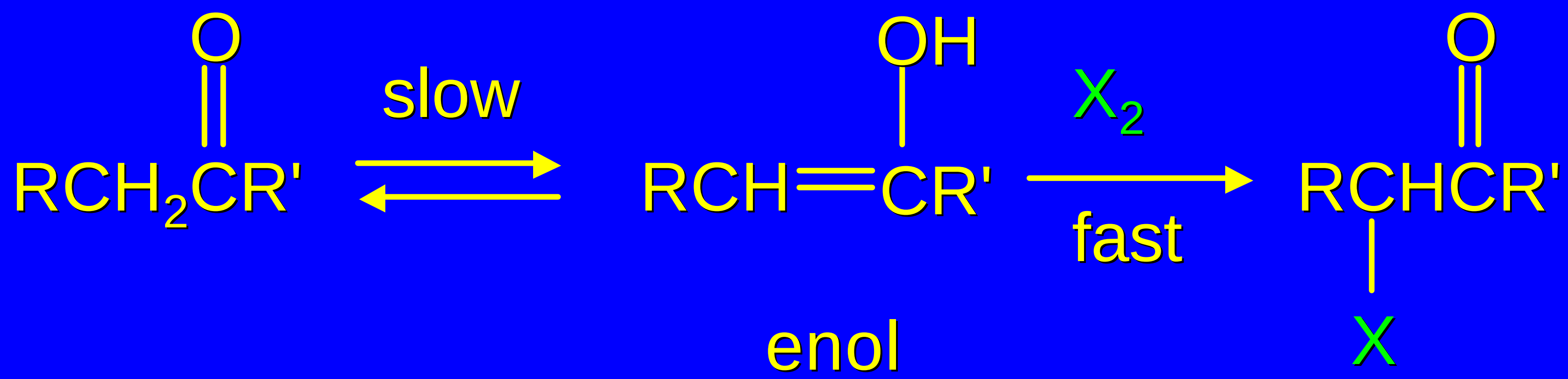
Mechanism of α Halogenation

Two stages:

first stage is conversion of aldehyde or ketone to the corresponding enol; is rate-determining

second stage is reaction of enol with halogen; is faster than the first stage

Mechanism of α Halogenation



Enol is key intermediate

Mechanism of α Halogenation

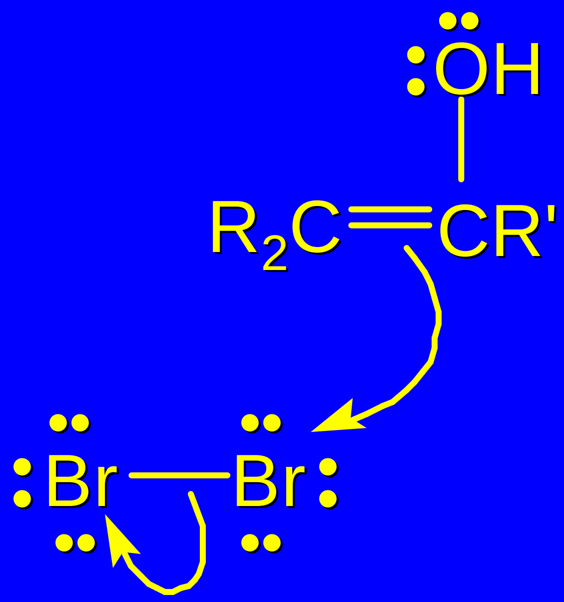
Two stages:

first stage is conversion of aldehyde or ketone to the corresponding enol; is rate-determining

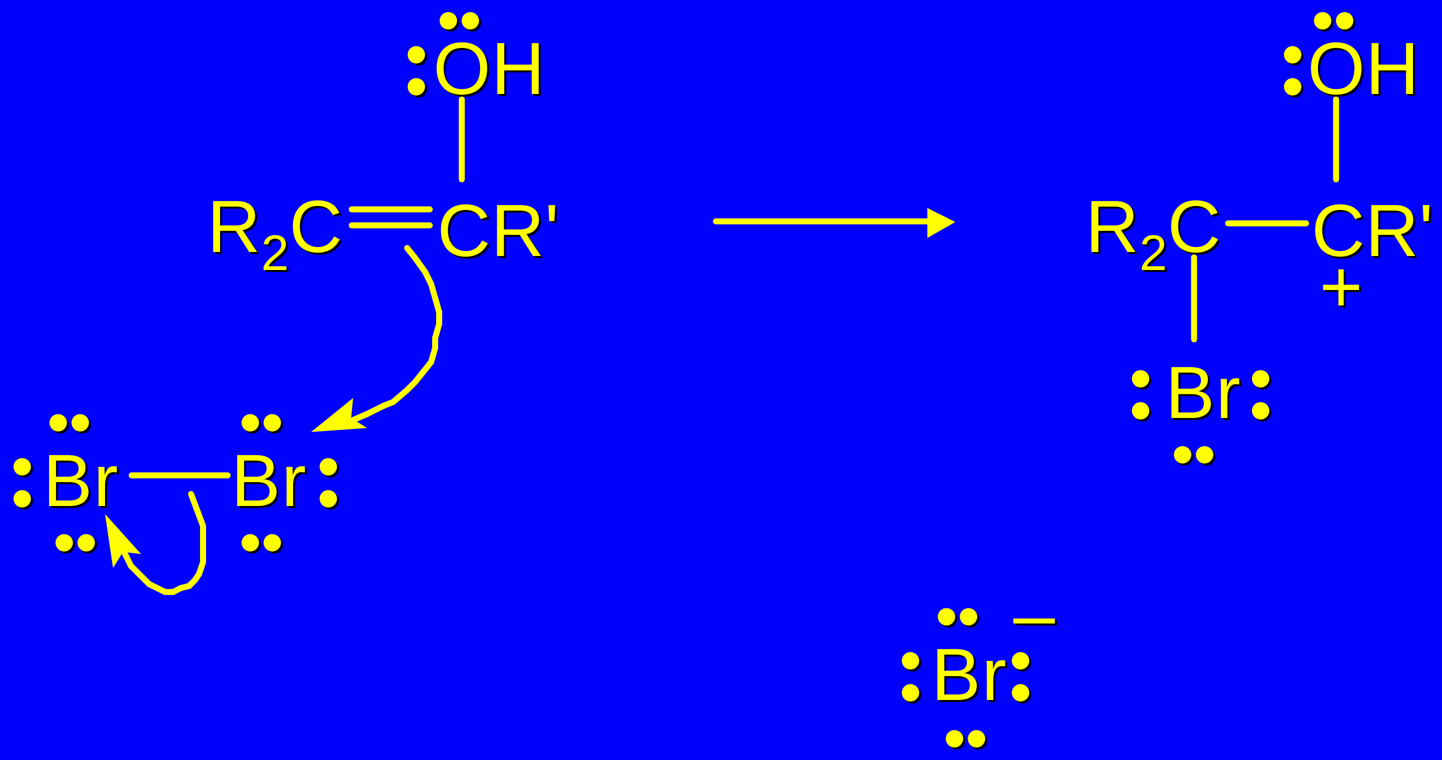
second stage is reaction of enol with halogen; is faster than the first stage

examine second stage first

Reaction of enol with Br_2

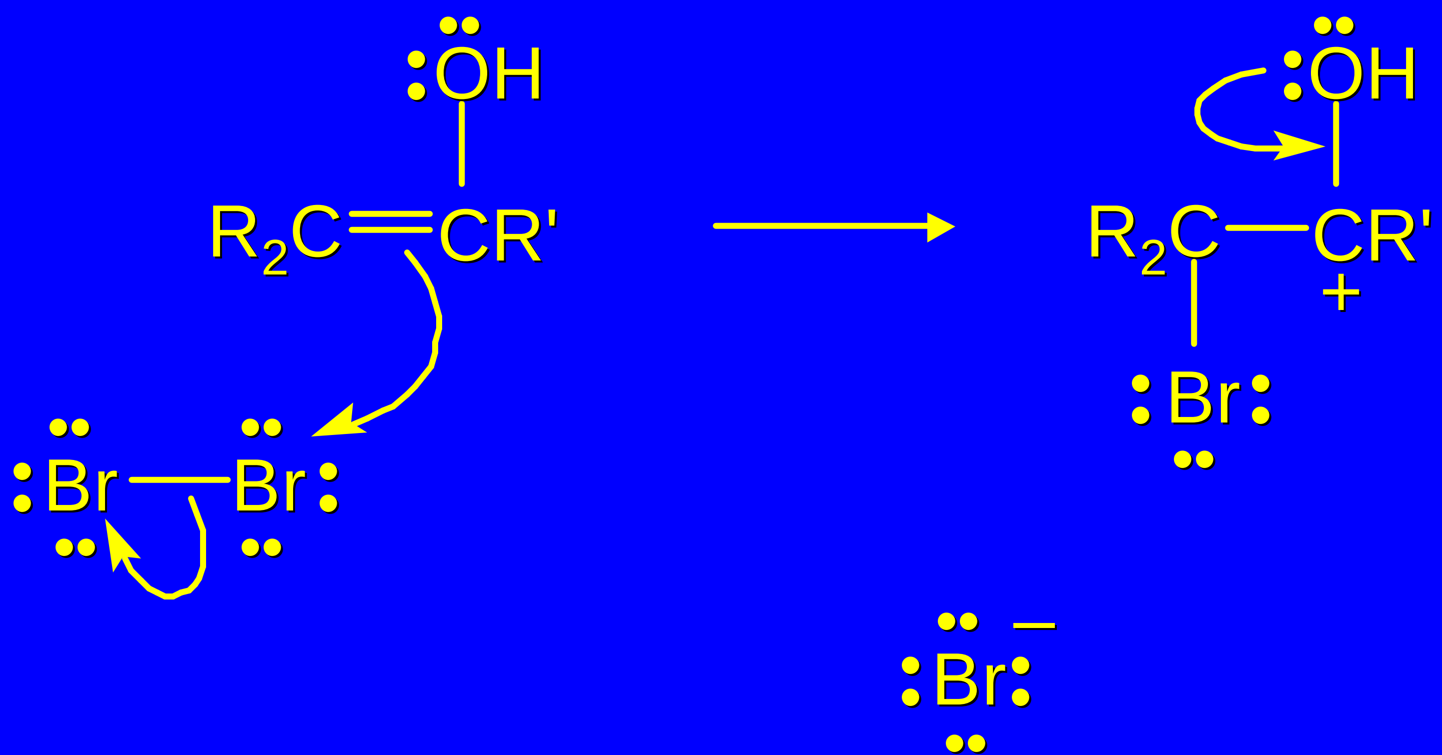


Reaction of enol with Br_2



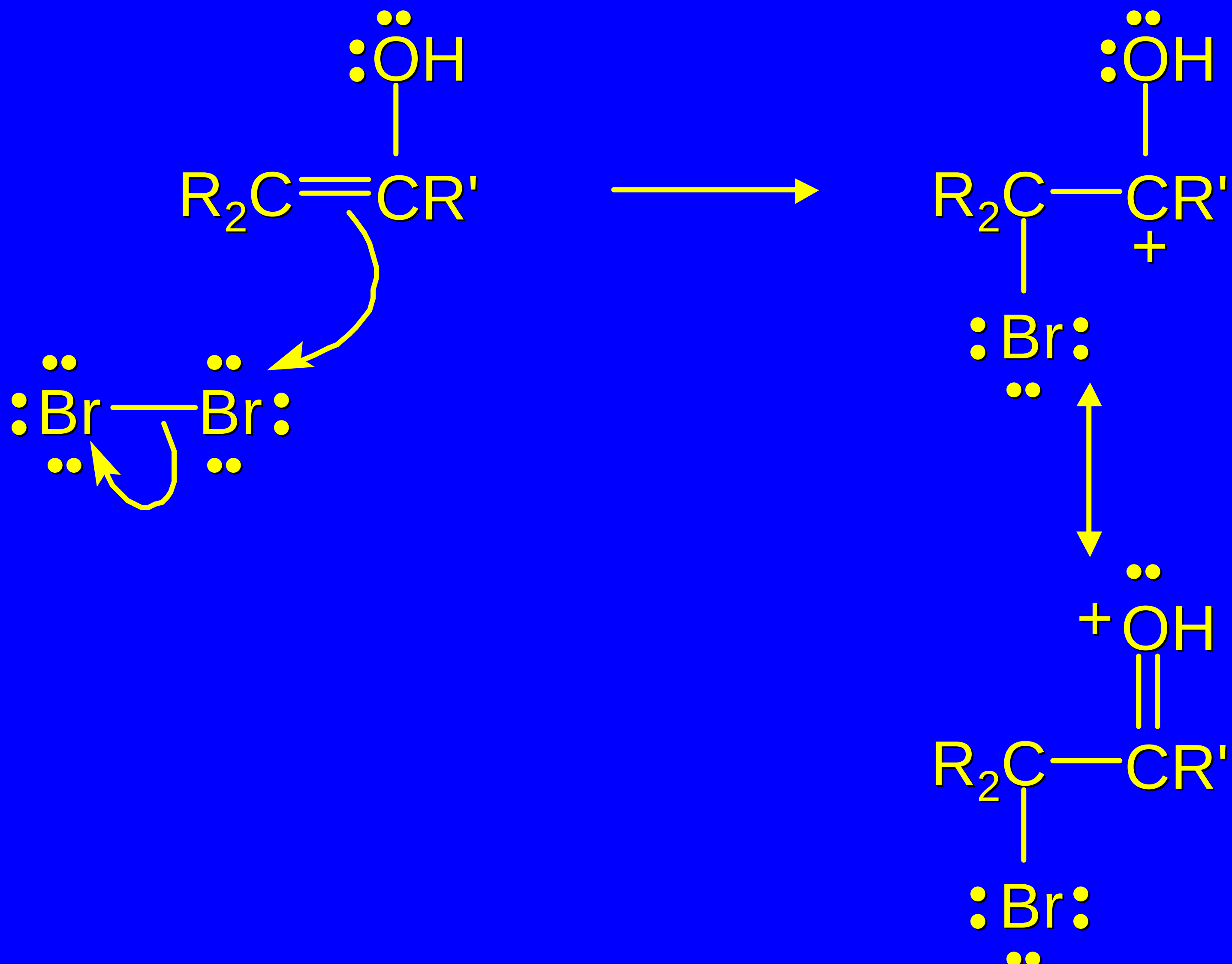
carbocation is stabilized by electron release from oxygen

Reaction of enol with Br_2

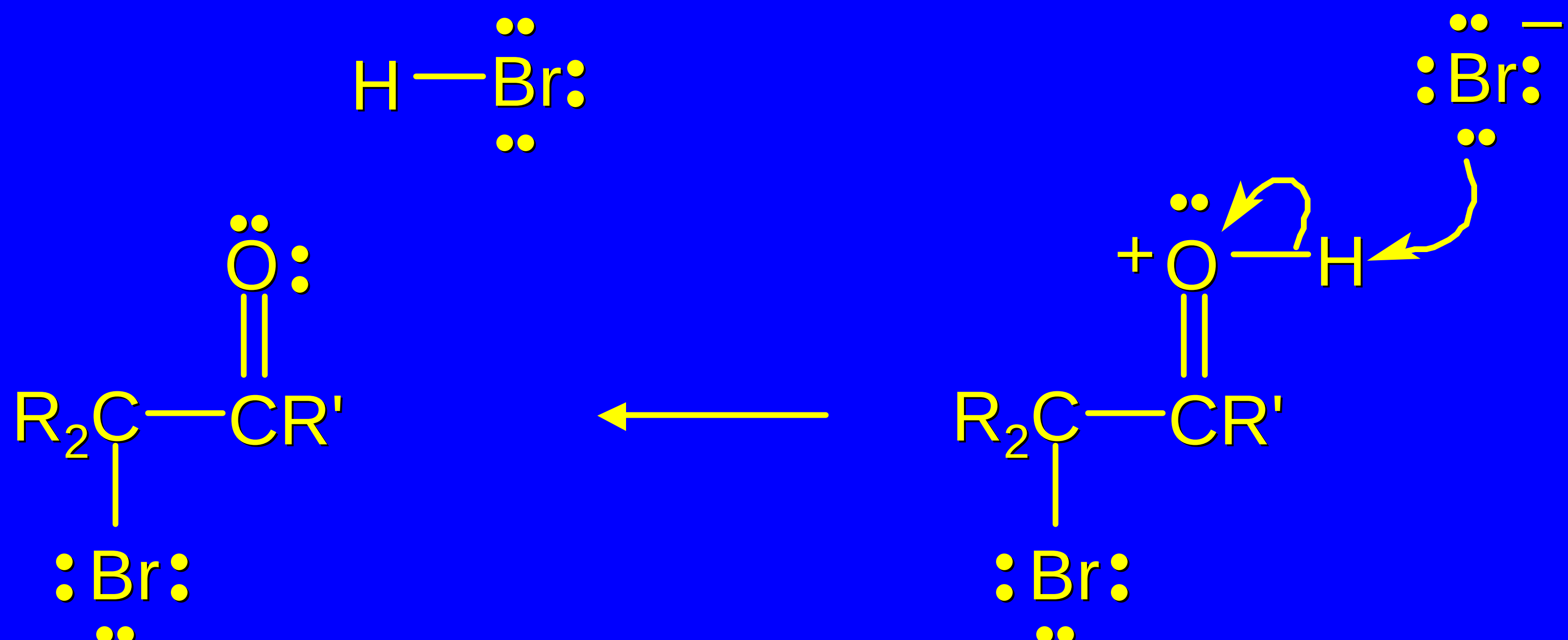


carbocation is stabilized by electron release from oxygen

Reaction of enol with Br_2



Loss of proton from oxygen completes the process



18.4

Enolization and Enol Content

Mechanism of α Halogenation

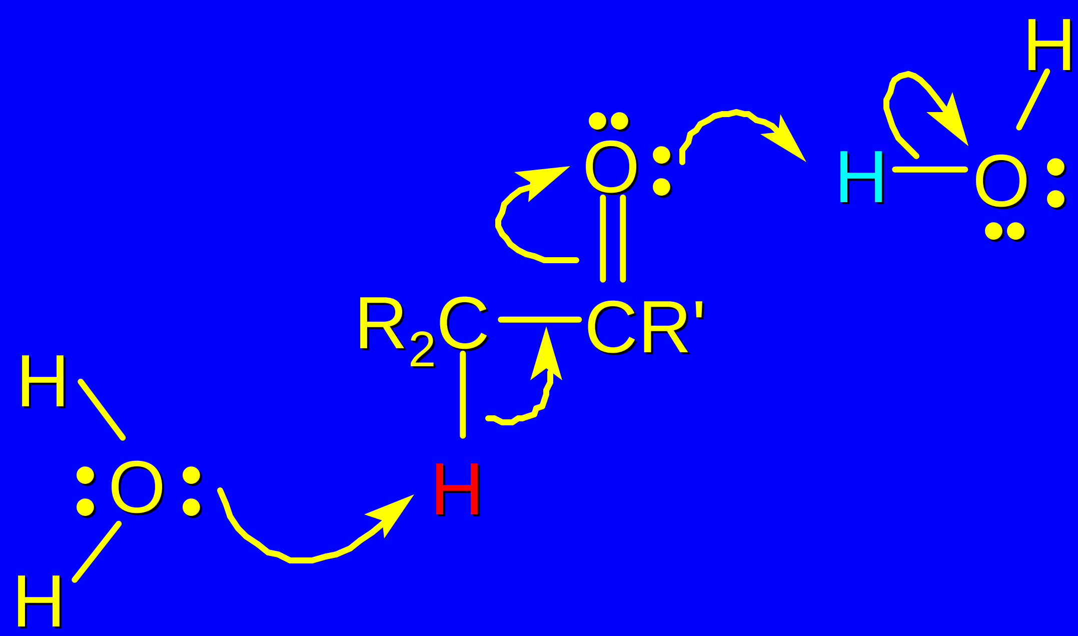
Two stages:

first stage is conversion of aldehyde or ketone to the corresponding enol; is rate-determining

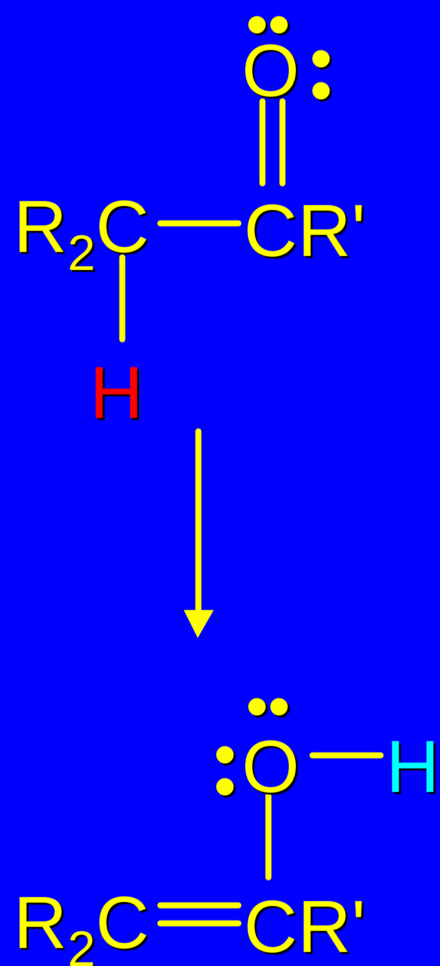
second stage is reaction of enol with halogen; is faster than the first stage

now examine first stage

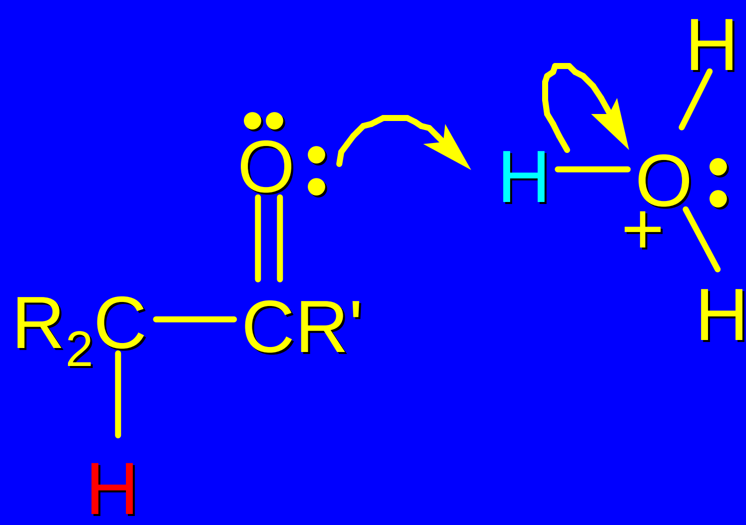
Mechanism of Enolization (In general)



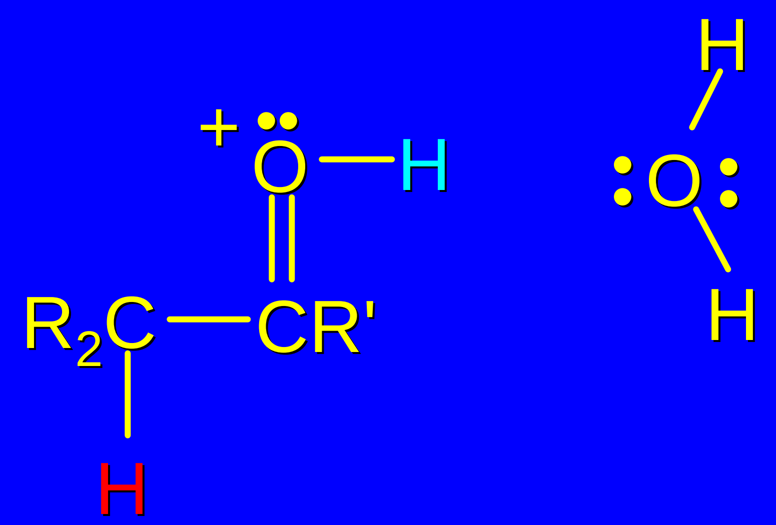
Mechanism of Enolization
(In general)



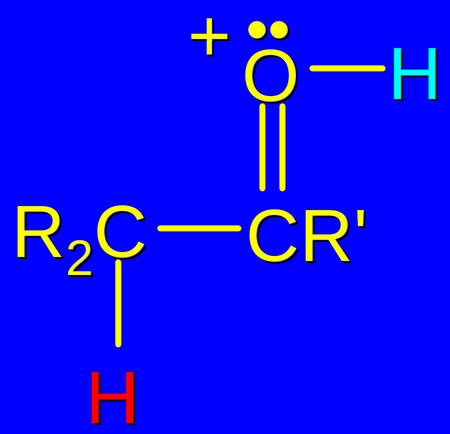
Mechanism of Enolization (Acid-catalyzed)



Mechanism of Enolization (Acid-catalyzed)



Mechanism of Enolization
(Acid-catalyzed)



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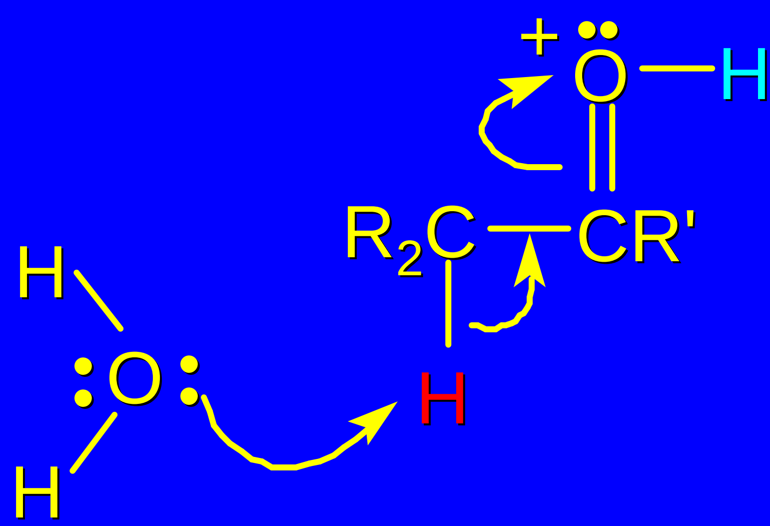
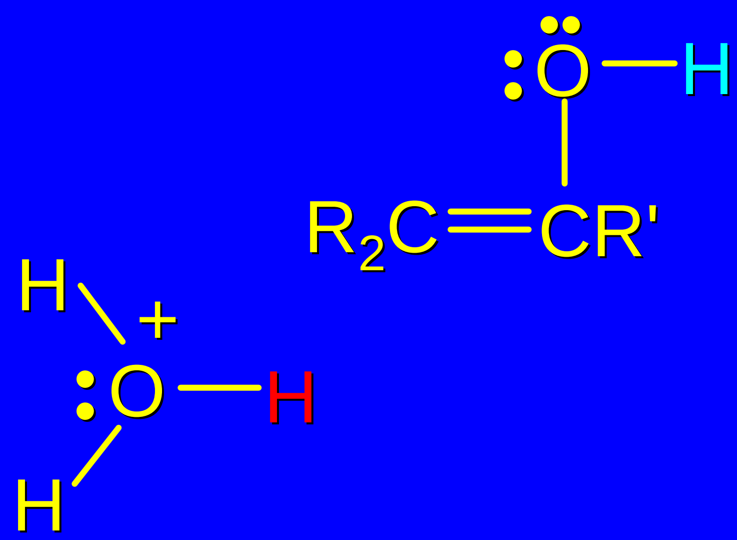
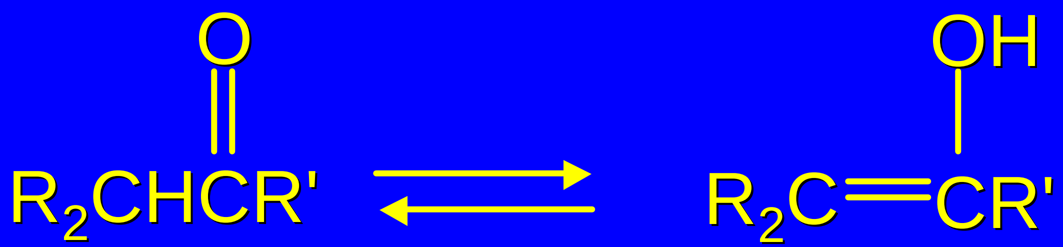


Mechanism of Enolization (Acid-catalyzed)



Enol Content



keto enol

percent enol is usually very small

keto form usually 45-60 kJ/mol more stable than enol

Enol Content

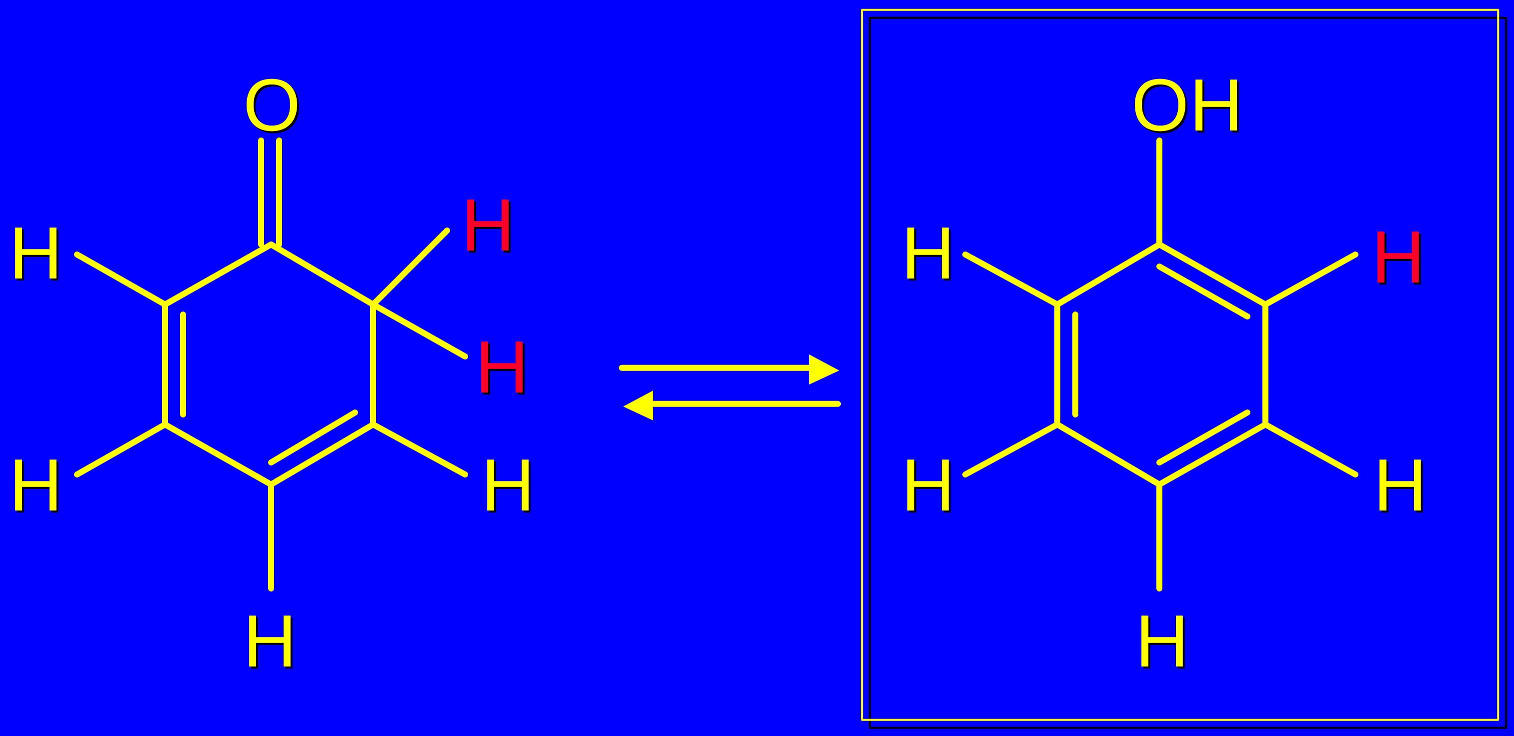
$$CH_3\overset{O}{\overset{\|}{C}}H \rightleftharpoons H_2C{=}\overset{OH}{\overset{|}{C}}H \qquad K = 3 \times 10^{-7}$$

$$CH_3\overset{O}{\overset{\|}{C}}CH_3 \rightleftharpoons H_2C{=}\overset{OH}{\overset{|}{C}}CH_3 \qquad K = 6 \times 10^{-9}$$

18.5

Stabilized Enols

2,4-Cyclohexadienone



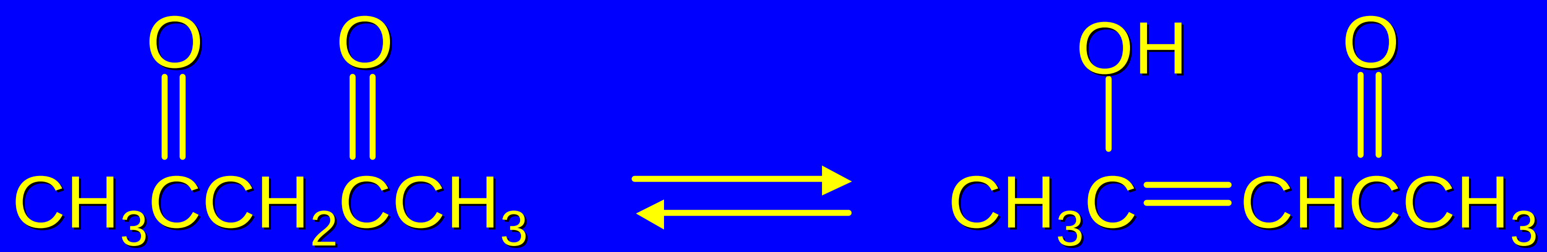
keto form is less stable than enol form

keto form is not aromatic

enol form is aromatic

1,3-Diketones
(also called b-diketones)

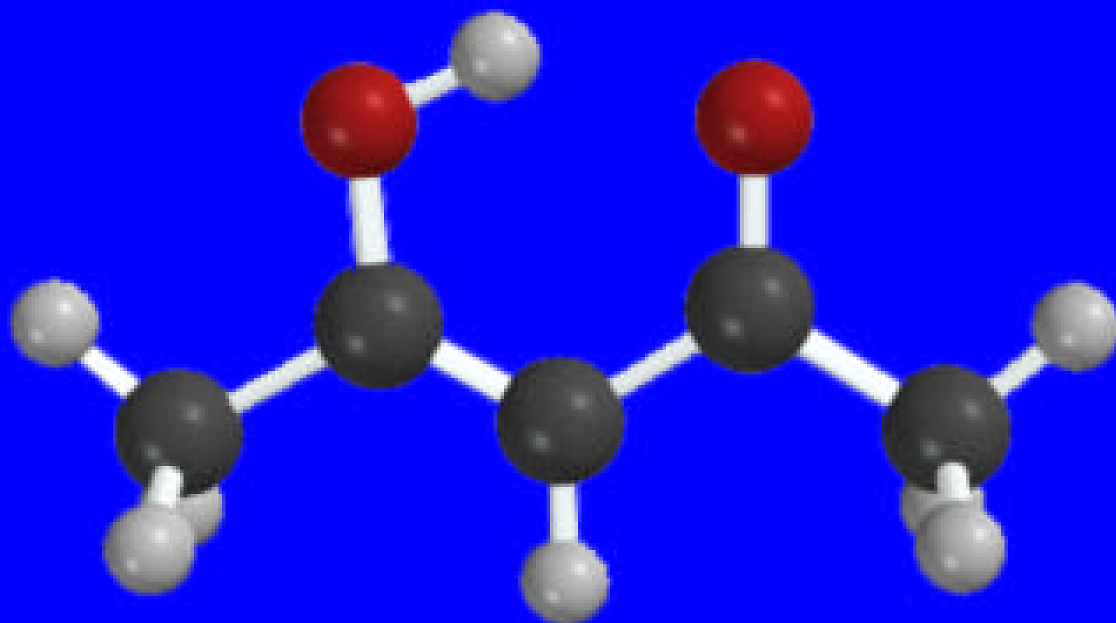
Example: 2,4-pentanedione



(20%) (80%)

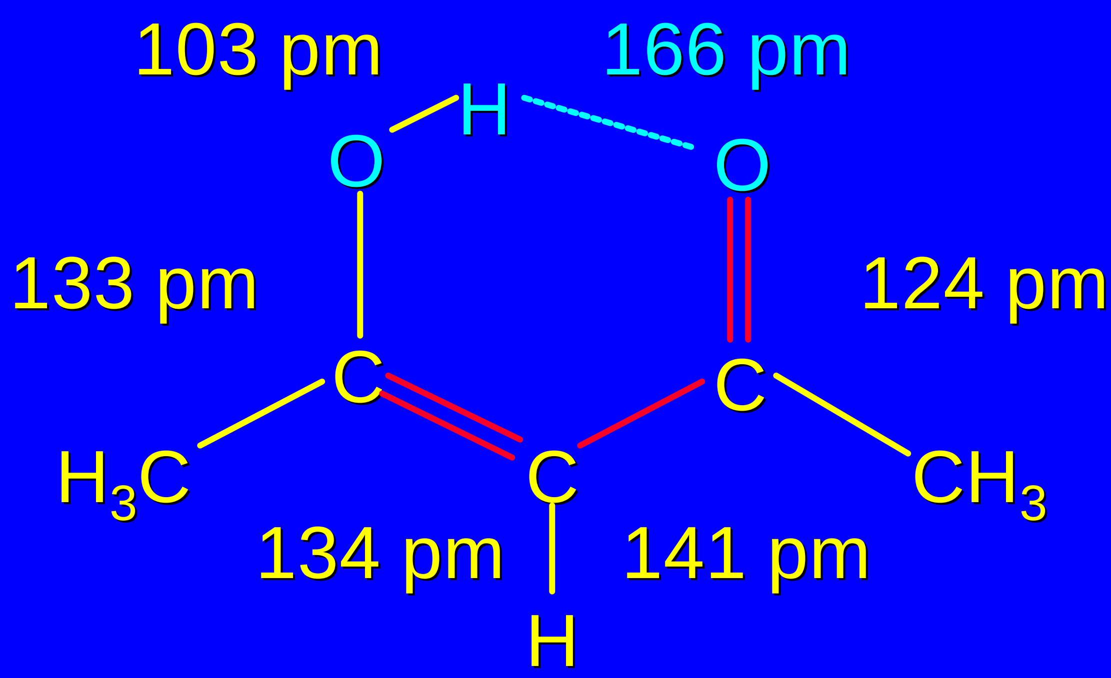
keto form is less stable than enol form

Enol form of 2,4-pentanedione



Enol form of 2,4-pentanedione

intramolecular hydrogen bond



C=C and C=O are conjugated