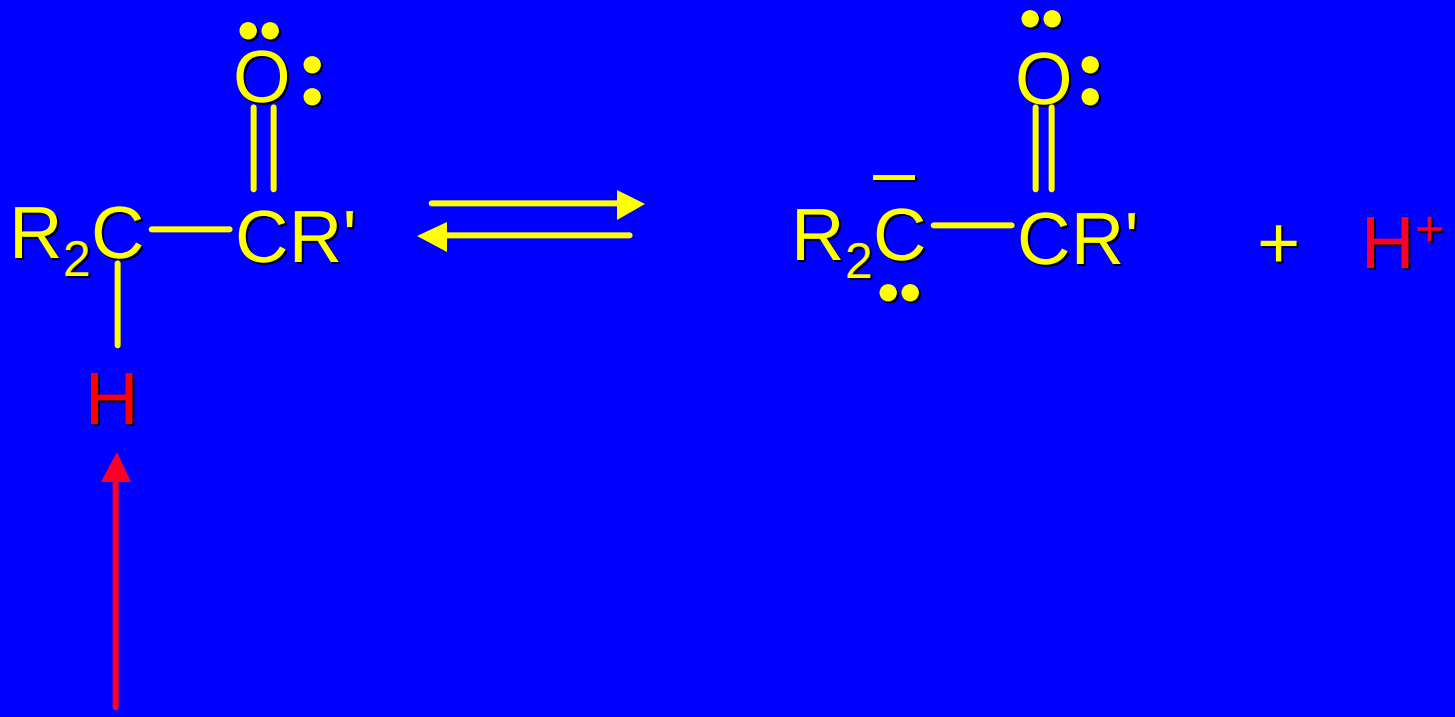
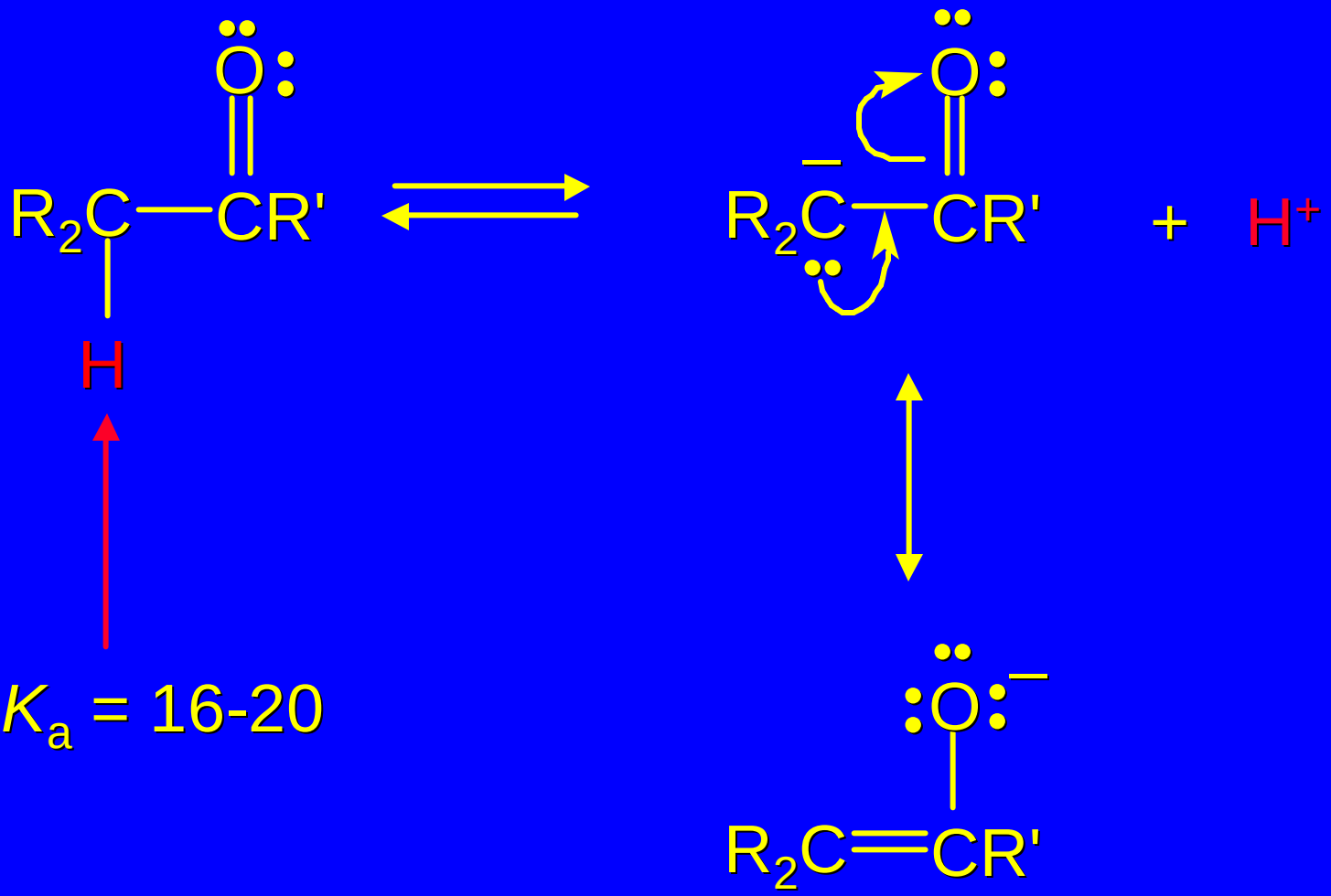
18.6
Base-Catalyzed Enolization: Enolate Anions

Acidity of a-Hydrogen

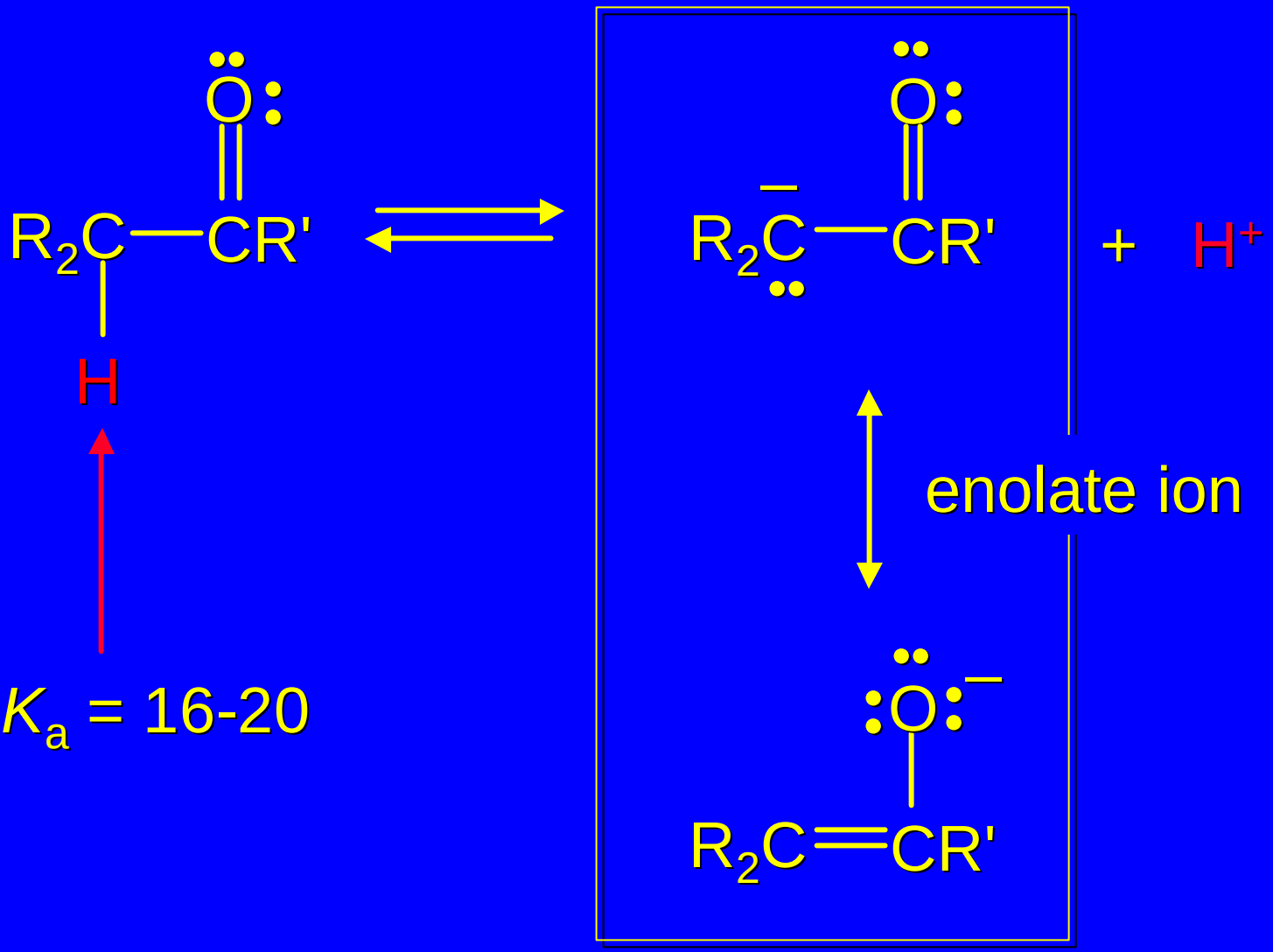


pK_a = 16-20

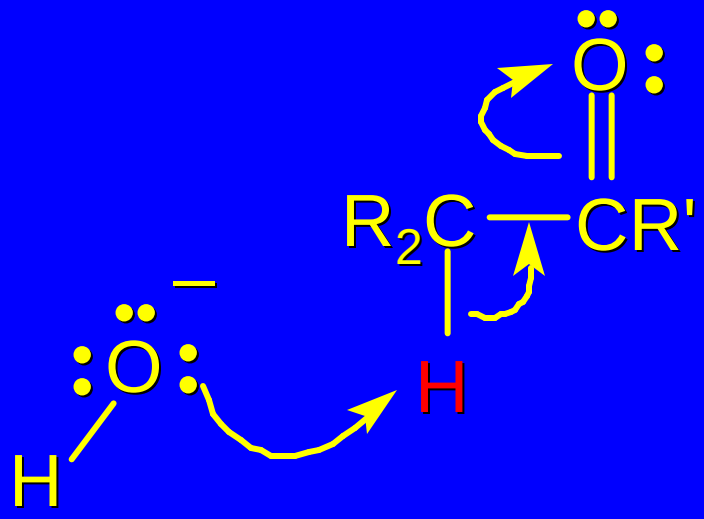
Acidity of a-Hydrogen



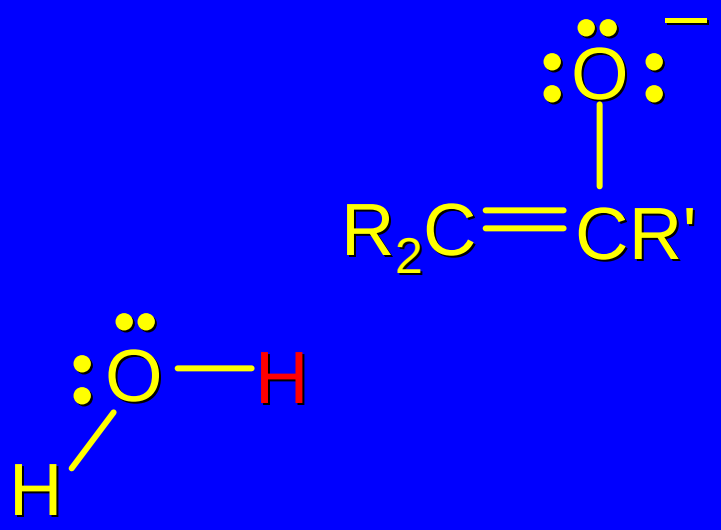
Acidity of a-Hydrogen



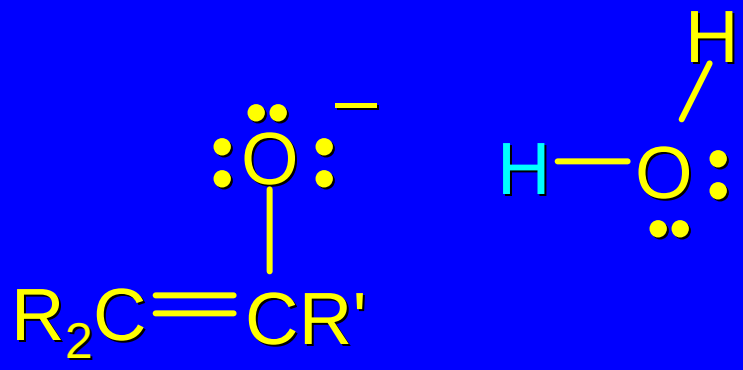
Mechanism of Enolization (Base-catalyzed)



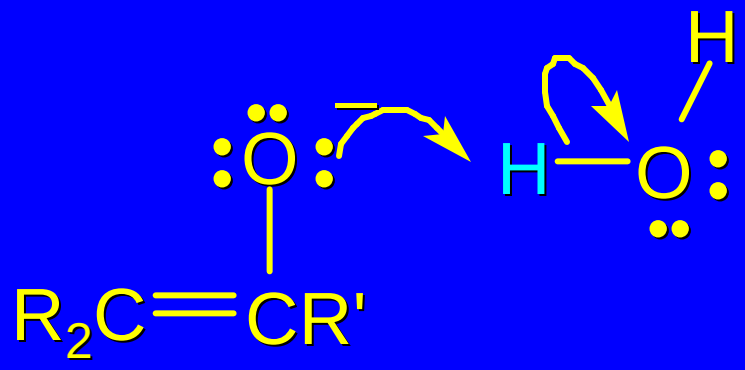
Mechanism of Enolization (Base-catalyzed)



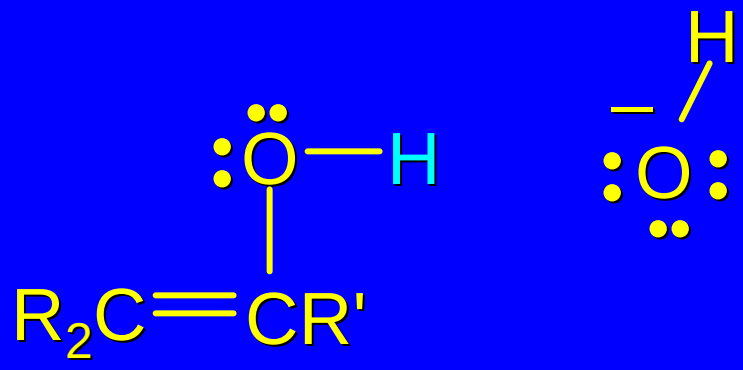
Mechanism of Enolization (Base-catalyzed)



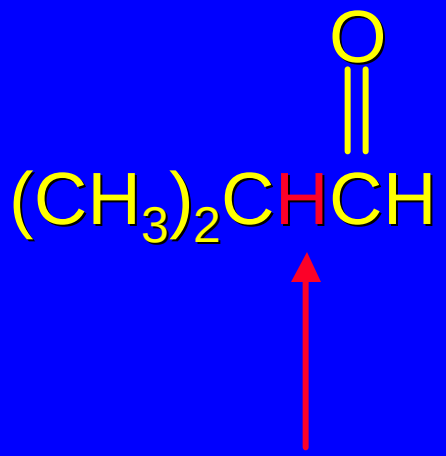
Mechanism of Enolization (Base-catalyzed)



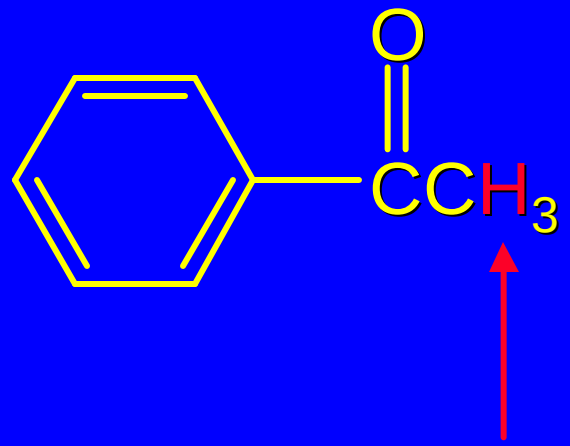
Mechanism of Enolization (Base-catalyzed)



Acidity of α-Hydrogen

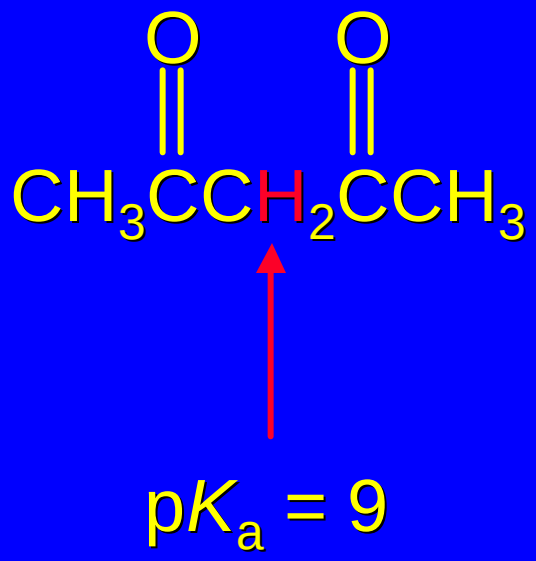


pK_a = 15.5

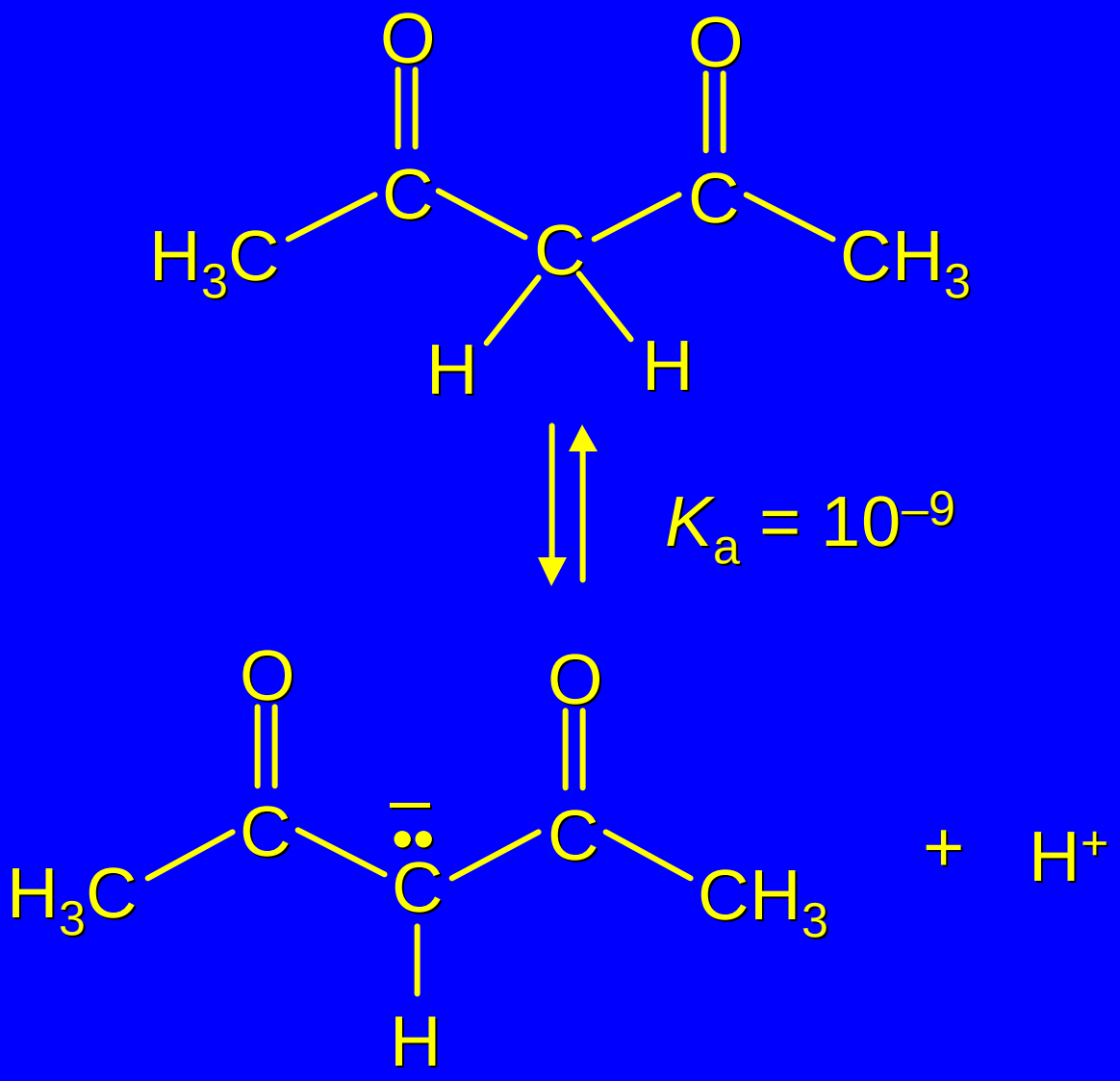


pK_a = 15.8

b-Diketones are much more acidic

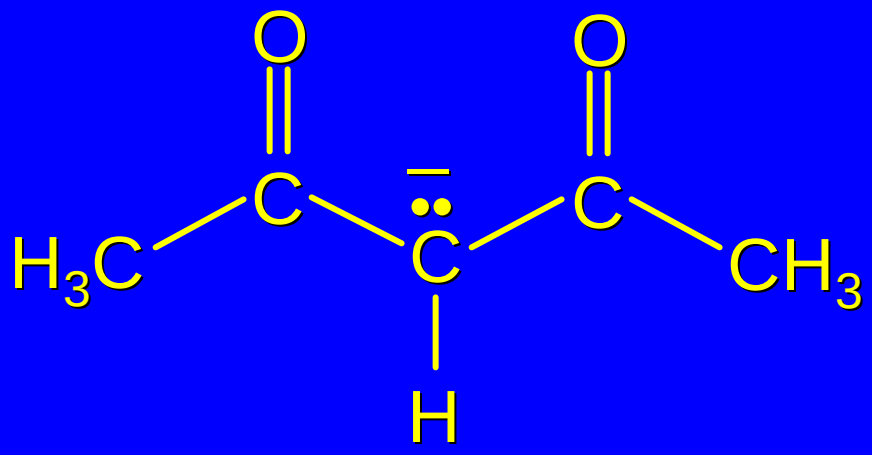


b-Diketones are much more acidic

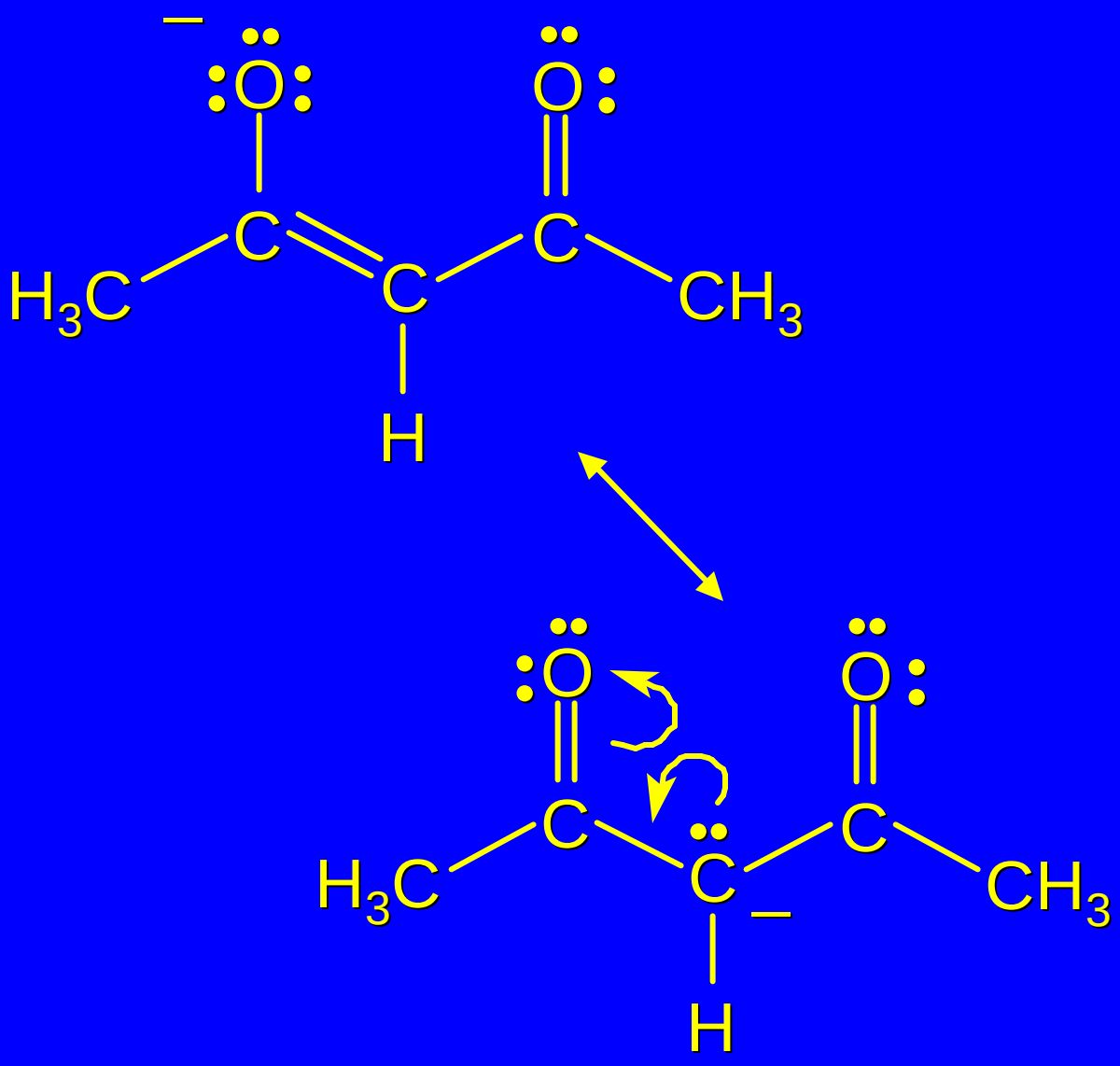


b-Diketones are much more acidic

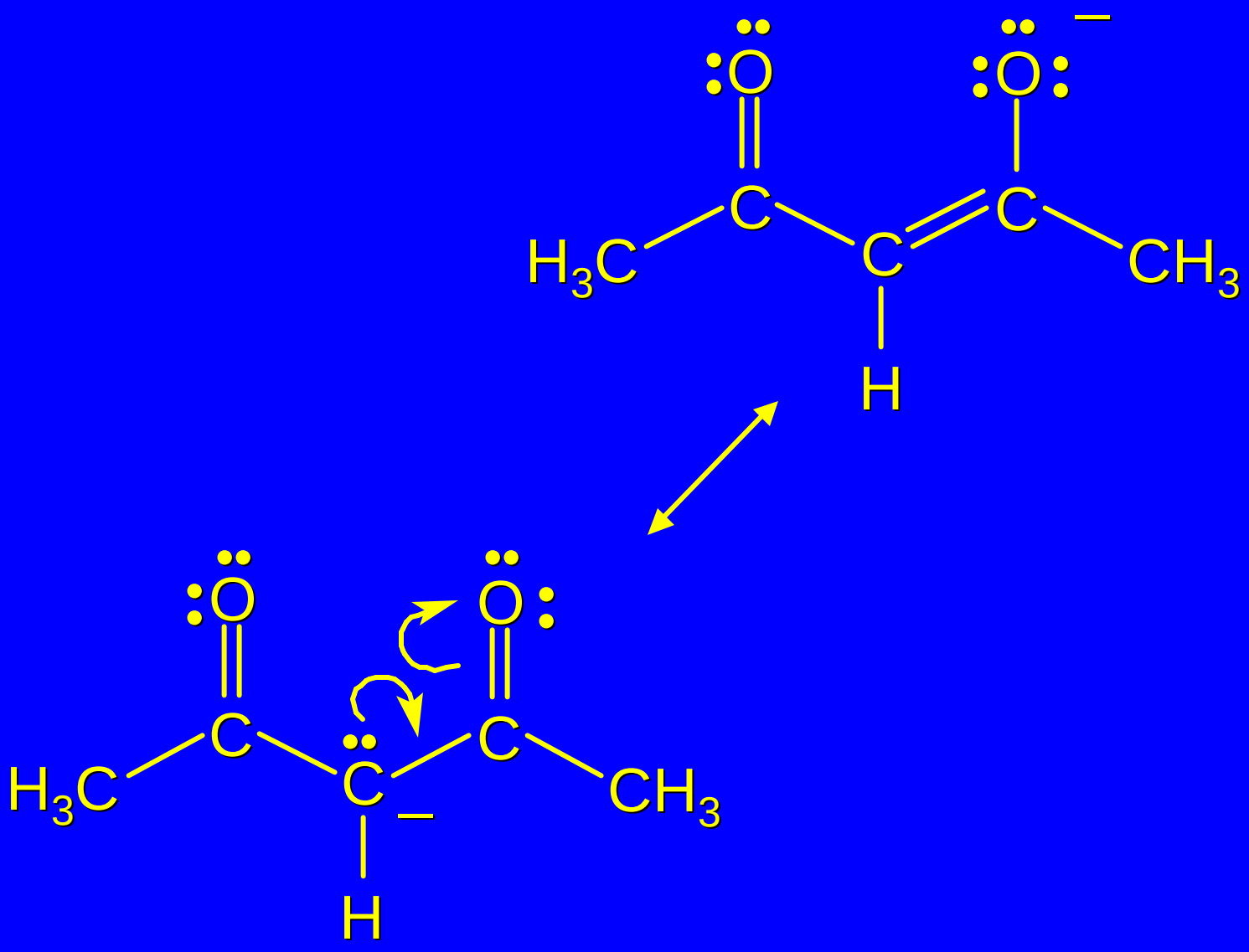
enolate of β-diketone is stabilized; negative charge is shared by both oxygens



b-Diketones are much more acidic



b-Diketones are much more acidic



18.7

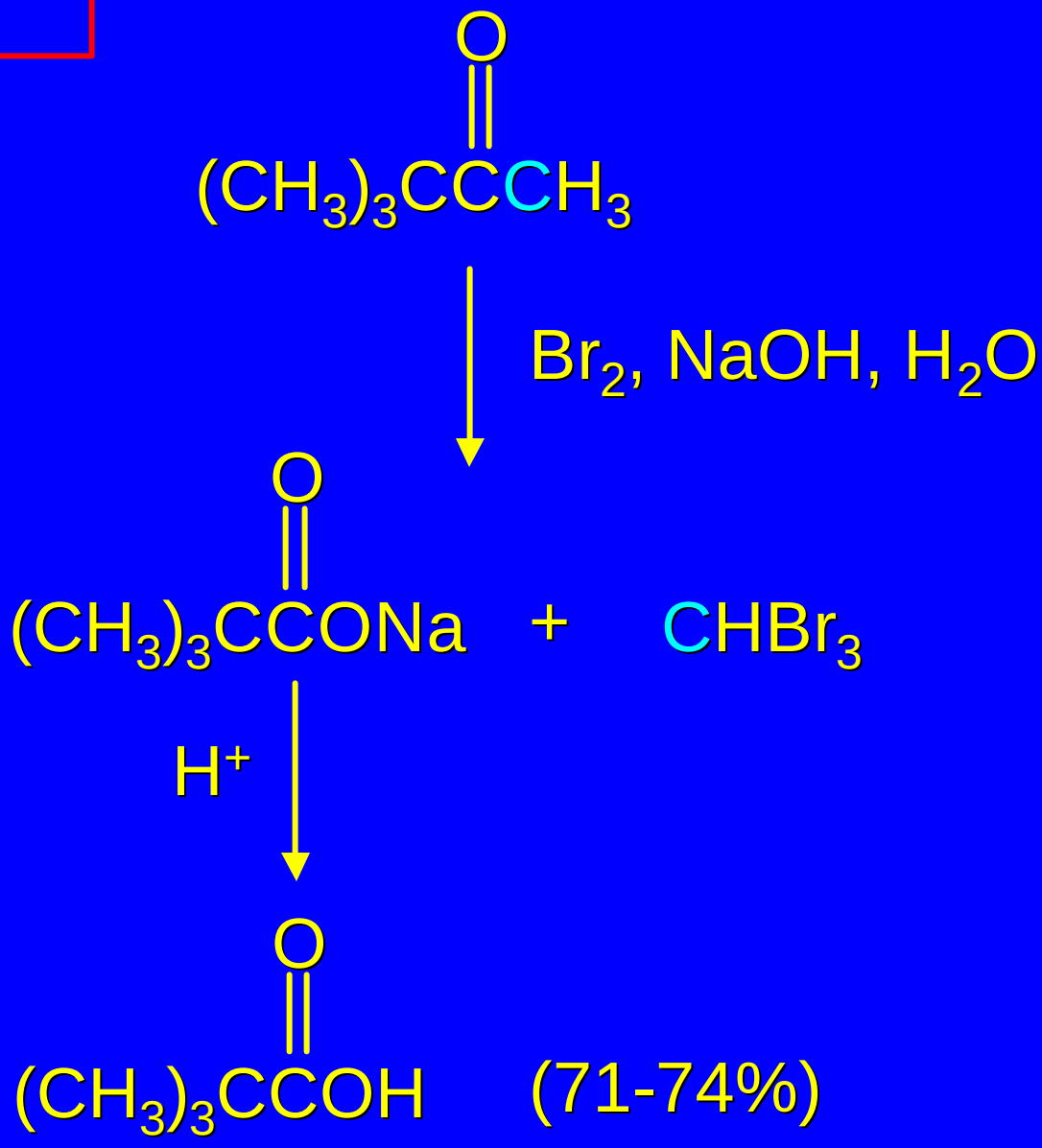
The Haloform Reaction

The Haloform Reaction

Under basic conditions, halogenation of a methyl ketone often leads to carbon-carbon bond cleavage.

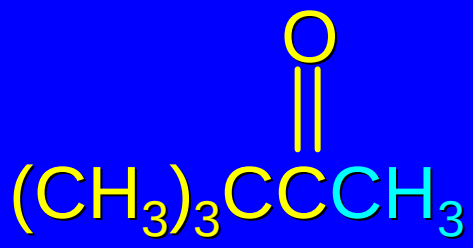
Such cleavage is called the haloform reaction because chloroform, bromoform, or iodoform is one of the products.

Example

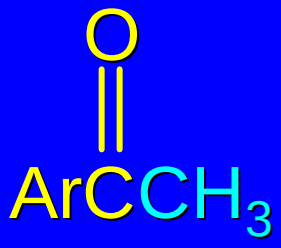


The Haloform Reaction

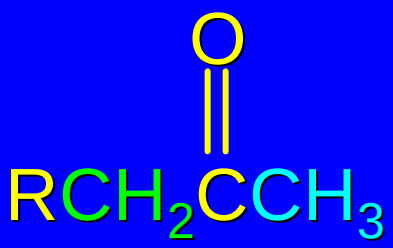
The haloform reaction is sometimes used as a method for preparing carboxylic acids, but works well only when a single enolate can form.



yes



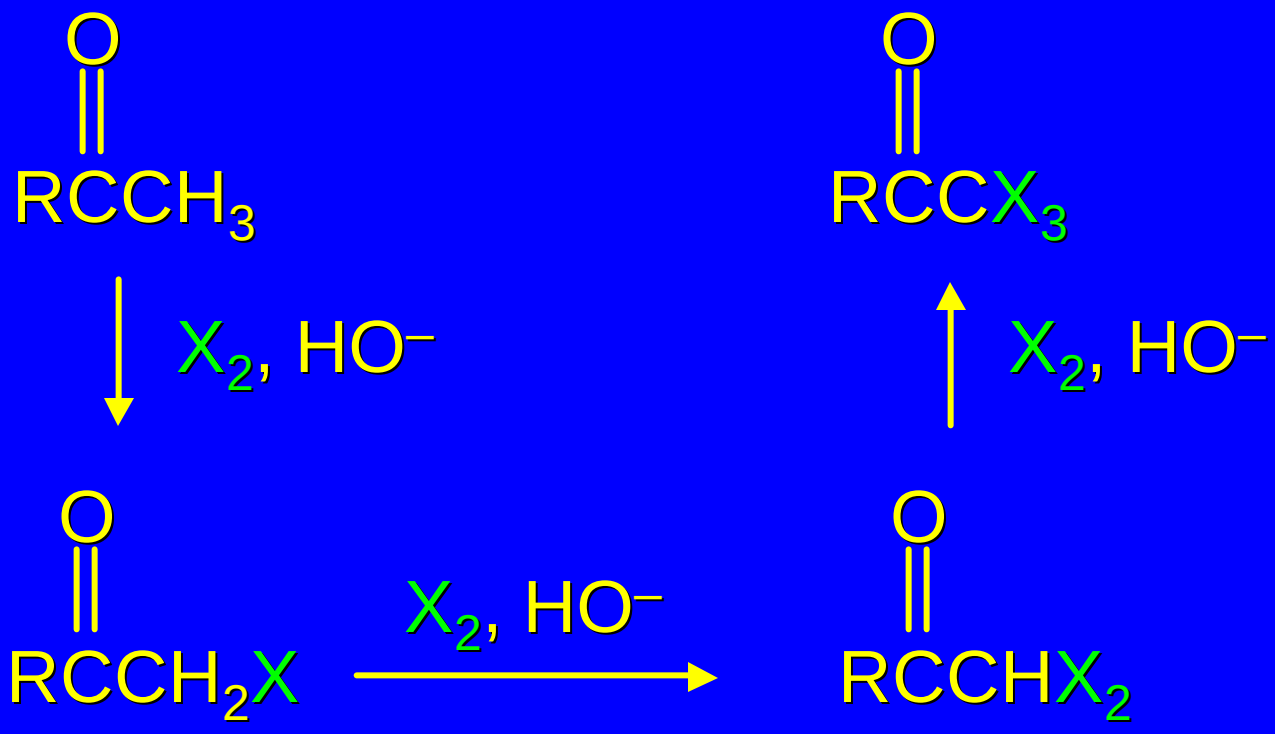
yes



no

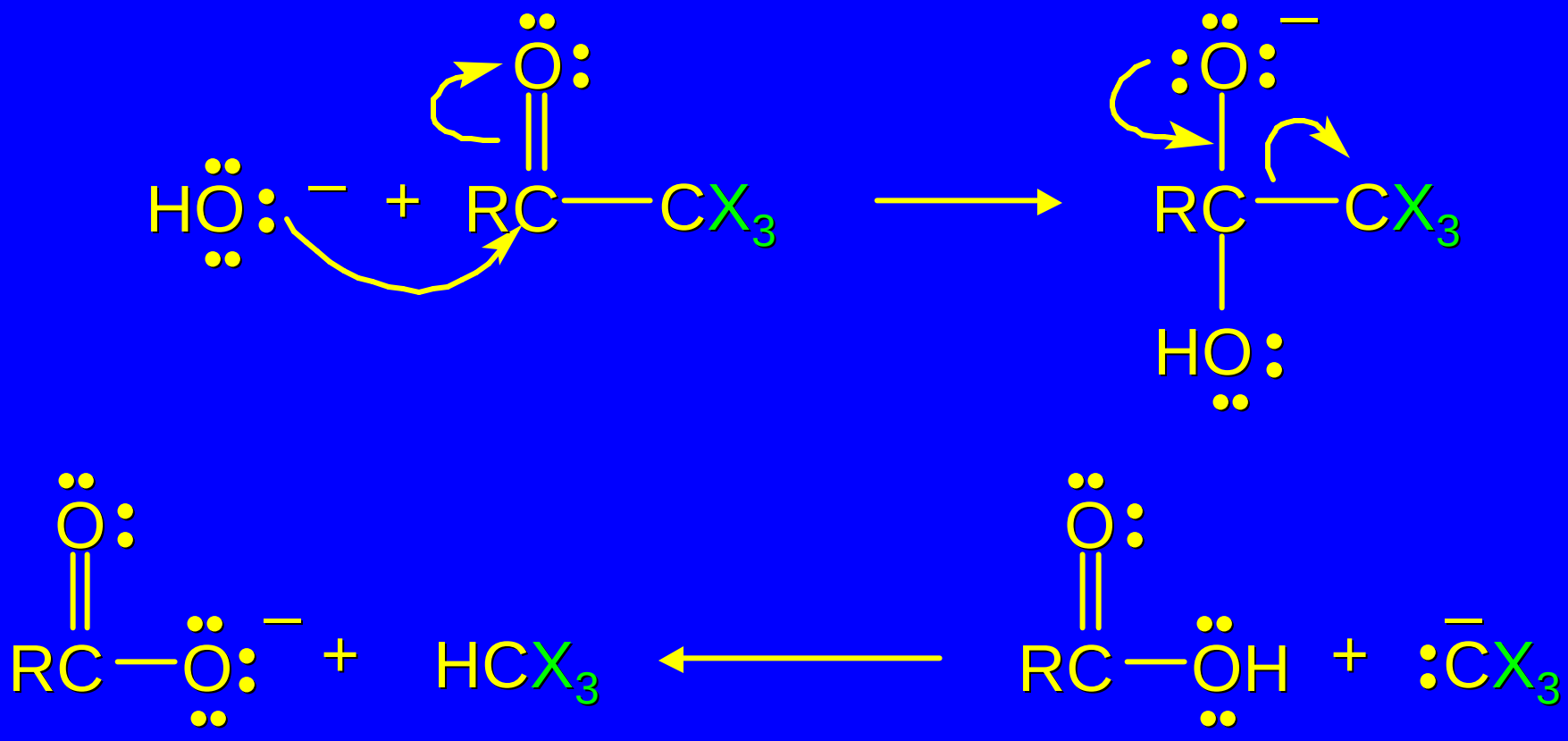
Mechanism

First stage is substitution of all available α hydrogens by halogen



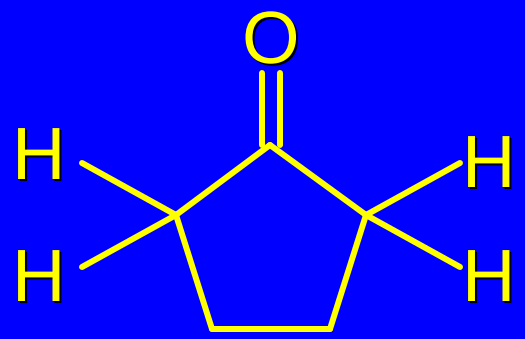
Mechanism

Formation of the trihalomethyl ketone is followed by its hydroxide-induced cleavage



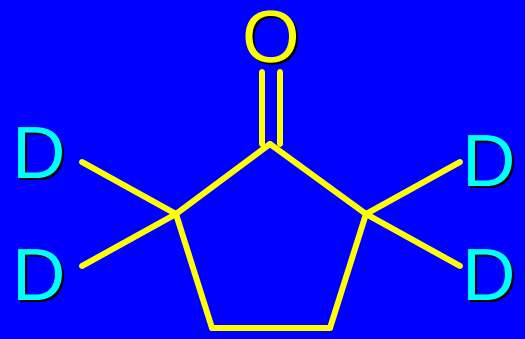
18.8
Some Chemical and Stereochemical Consequences of Enolization

Hydrogen-Deuterium Exchange



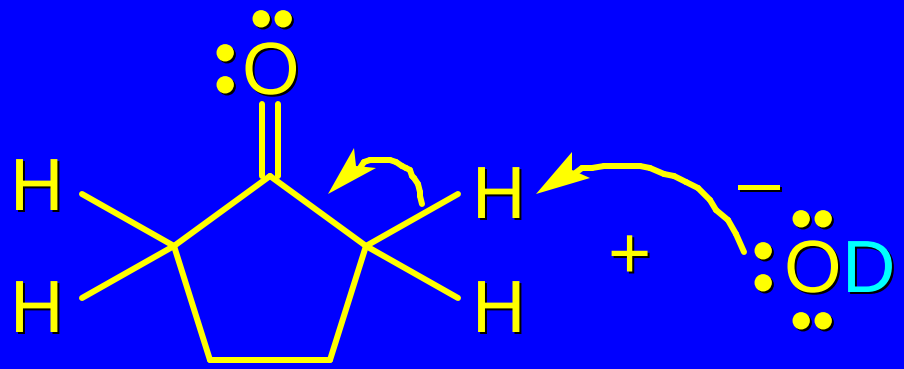
+ $4D_2O$

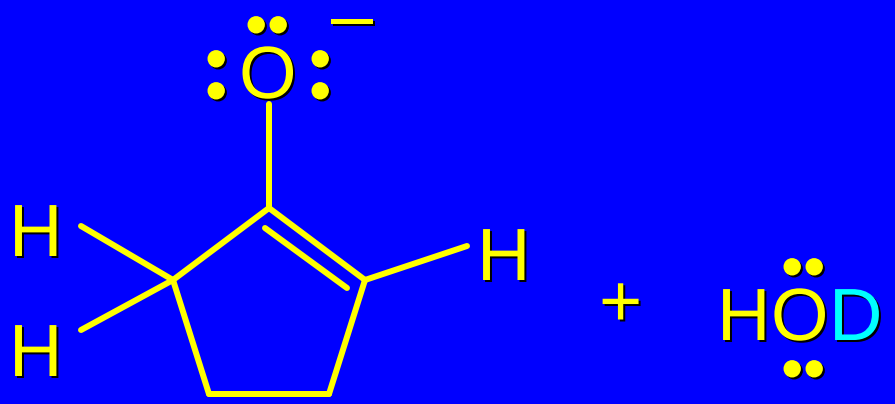
KOD, heat



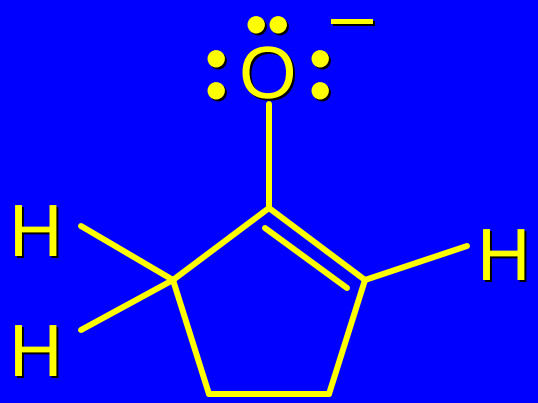
+ 4DOH

Mechanism

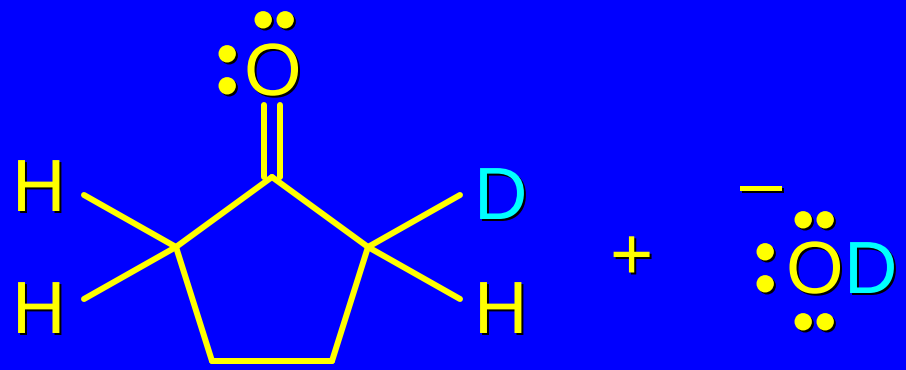


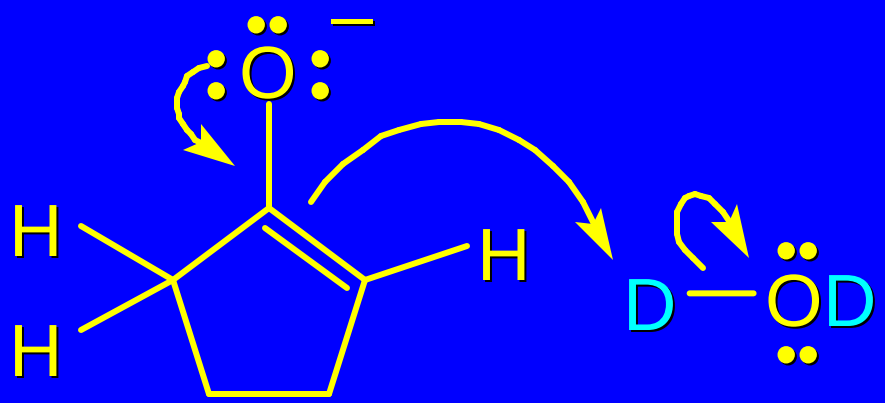


Mechanism

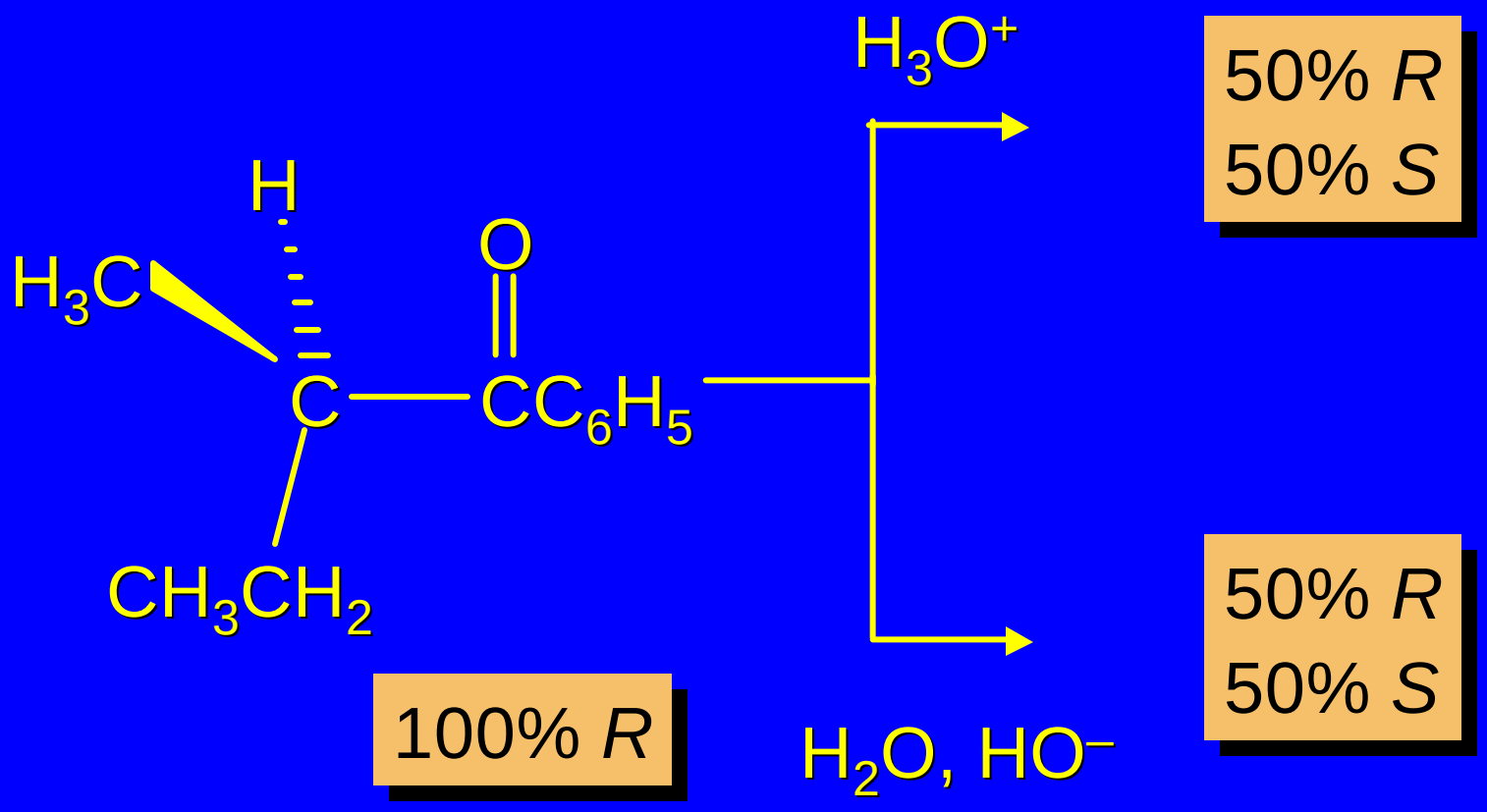


Mechanism

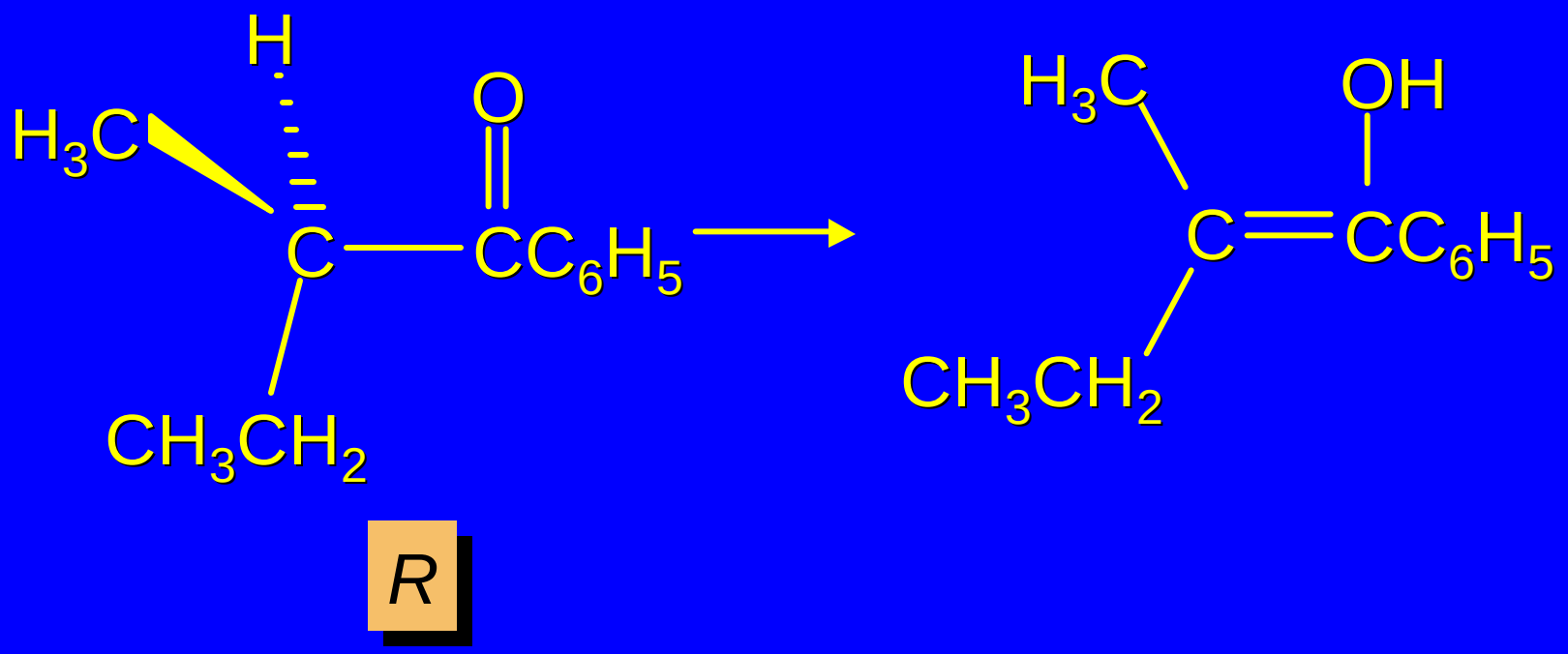




Stereochemical Consequences of Enolization

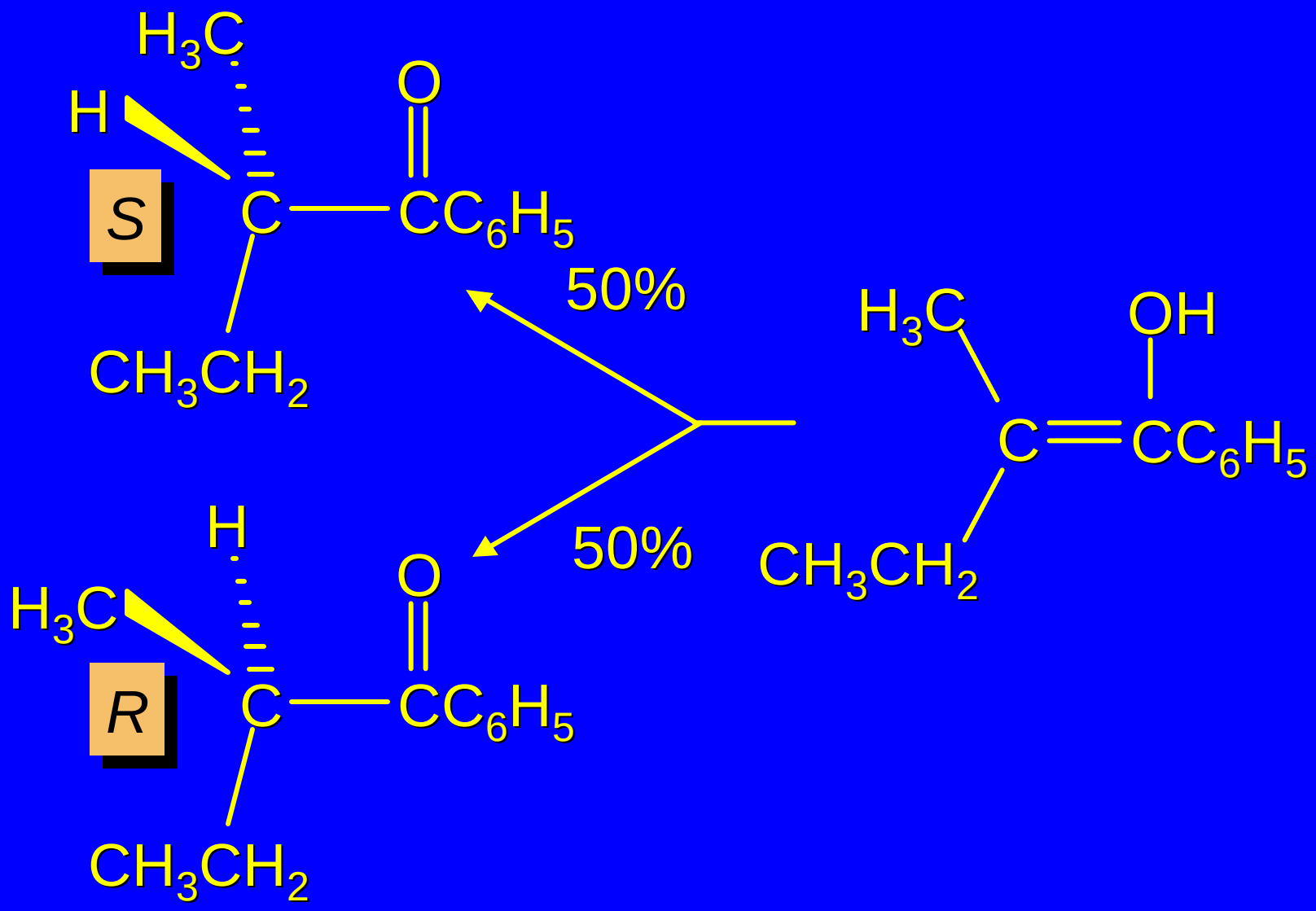


Enol is achiral

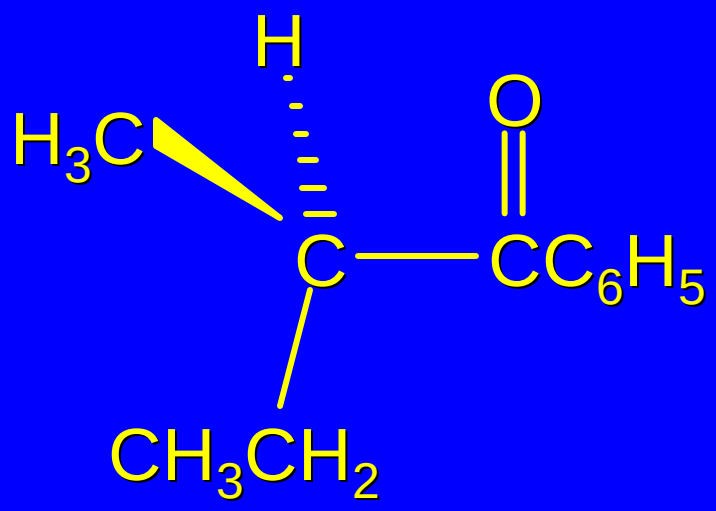


R

Enol is achiral



Results of Rate Studies



Equal rates for:

racemization

H-D exchange

bromination

iodination

Enol is intermediate and its formation is rate-determining