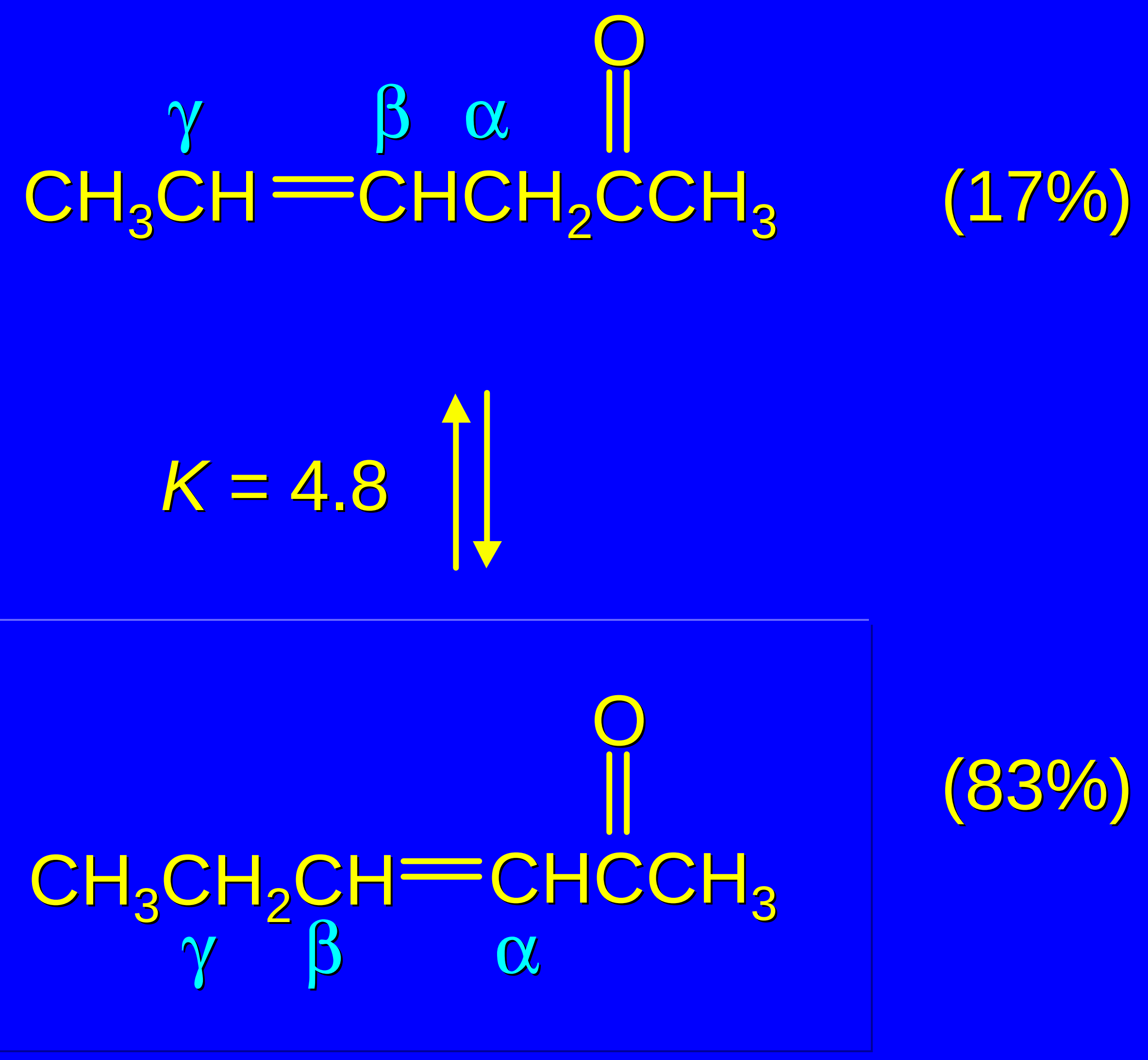
18.11
Effects of Conjugation in α,β-Unsaturated Aldehydes and Ketones

Relative Stability

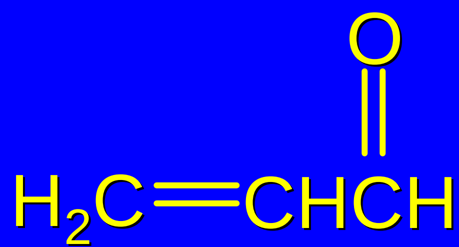
aldehydes and ketones that contain a carbon-carbon double bond are more stable when the double bond is conjugated with the carbonyl group than when it is not

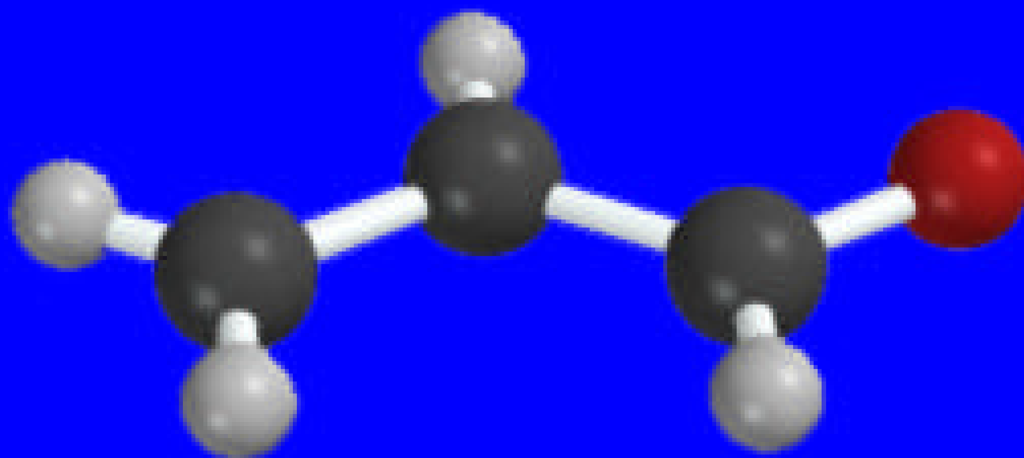
compounds of this type are referred to as α,β unsaturated aldehydes and ketones

Relative Stability

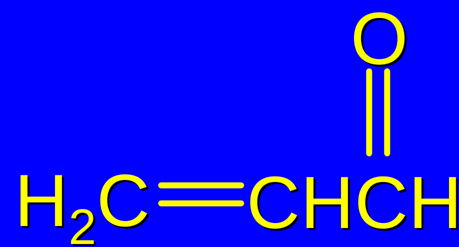


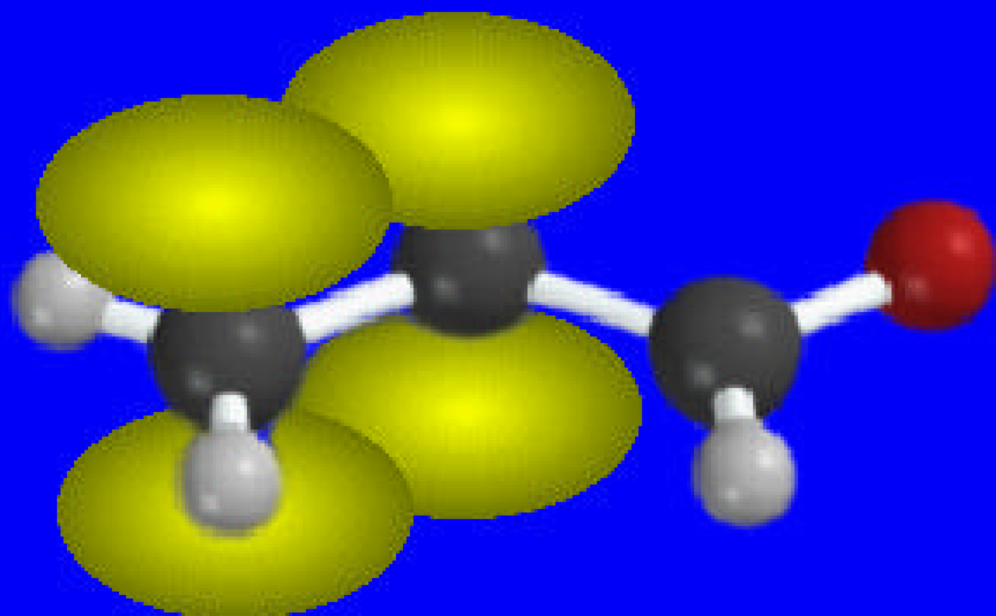
Acrolein



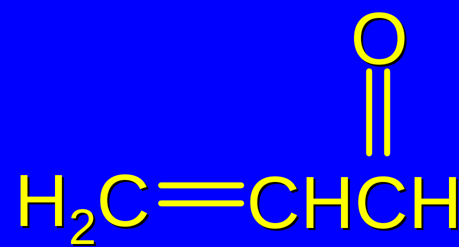


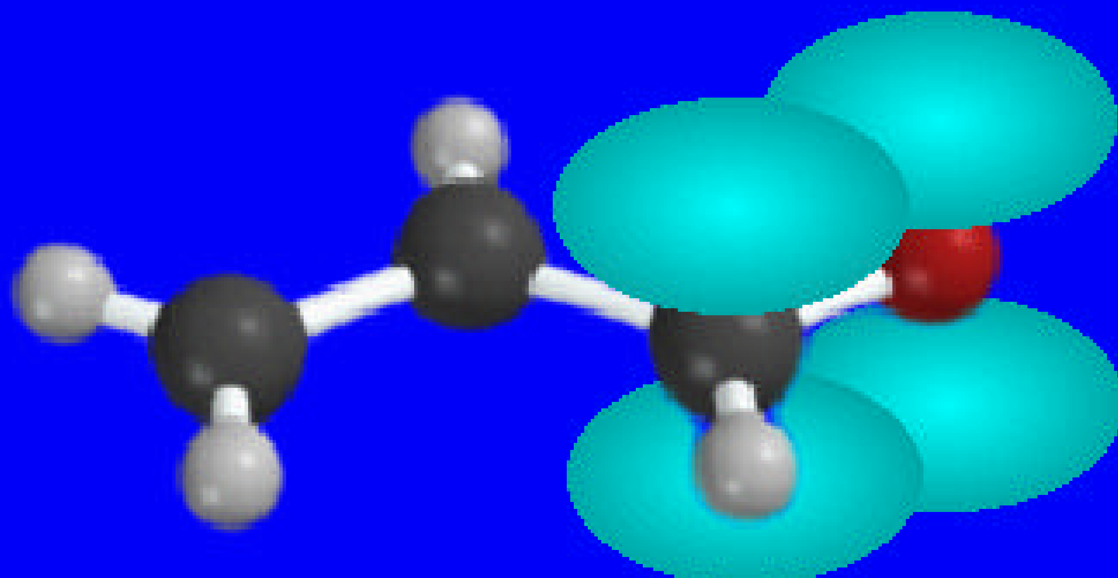
Acrolein



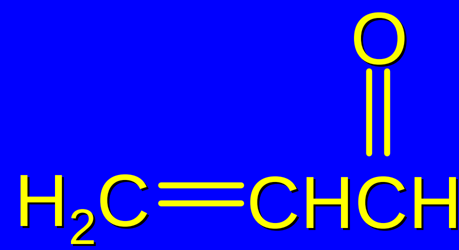


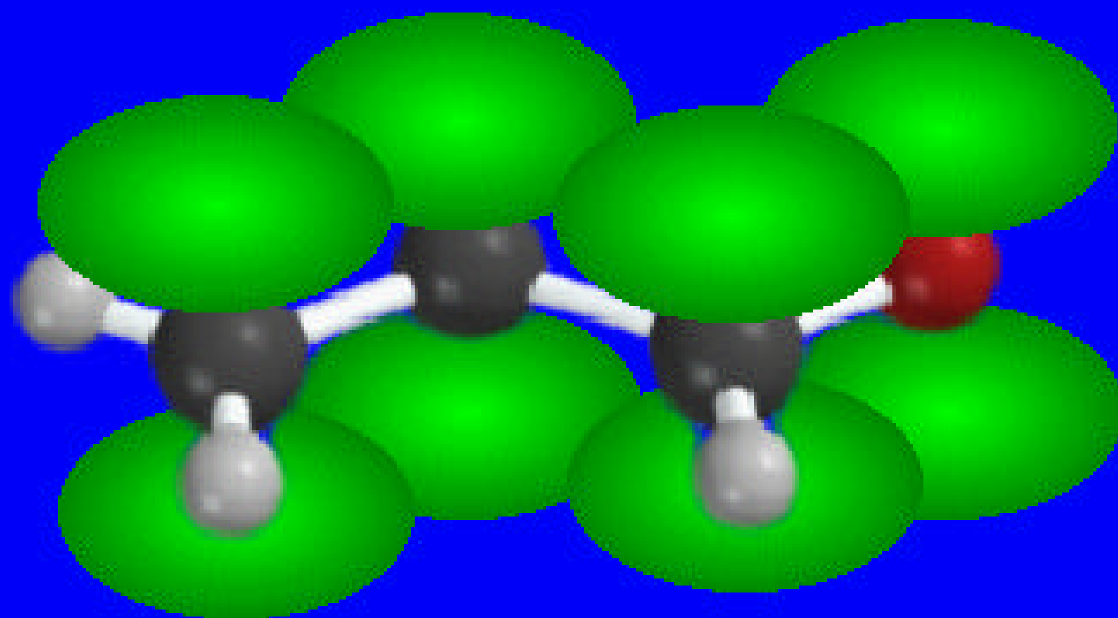
Acrolein



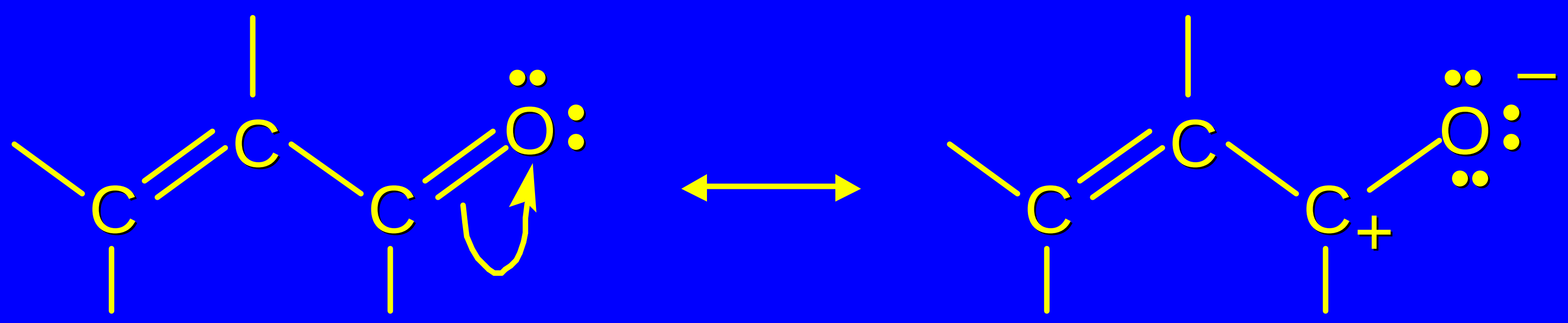


Acrolein

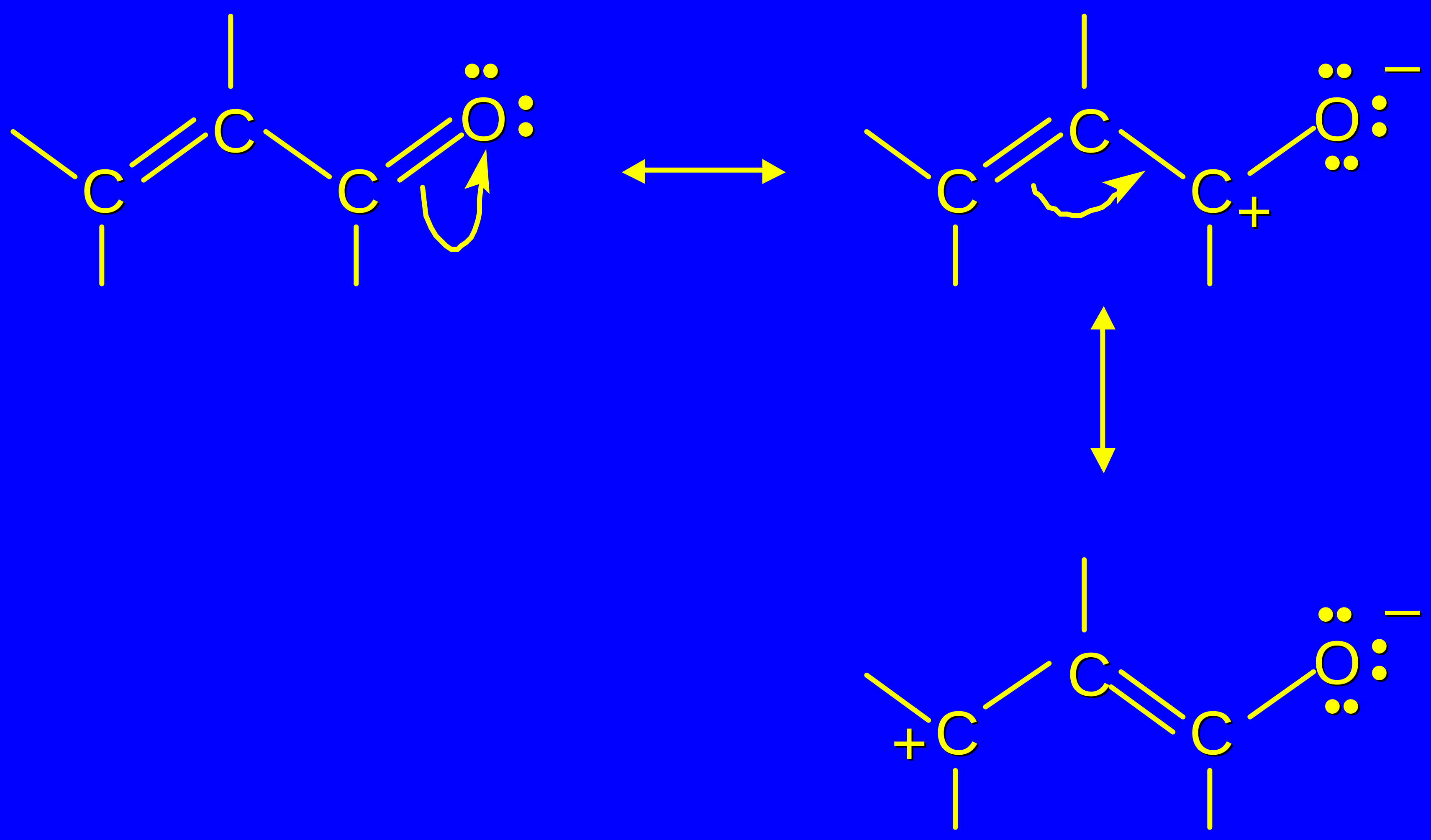




Resonance Description



Resonance Description



Properties

α,β-Unsaturated aldehydes and ketones are more polar than simple aldehydes and ketones.

α,β-Unsaturated aldehydes and ketones contain two possible sites for nucleophiles to attack

carbonyl carbon

β-carbon

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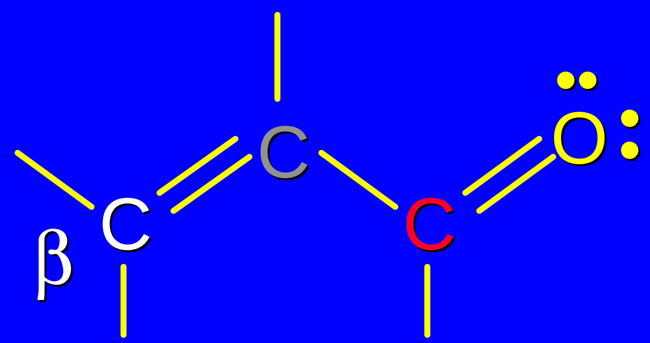
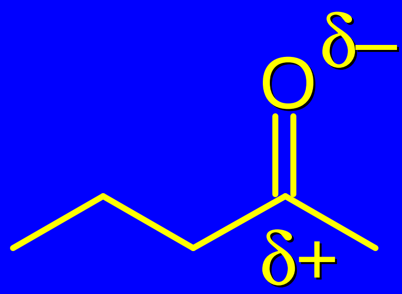
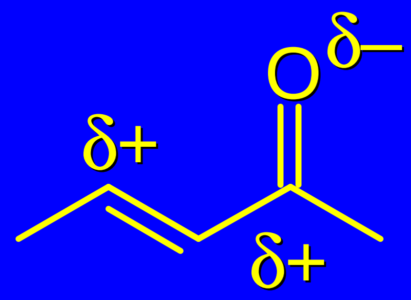
carbonyl carbon

β-carbon



Dipole Moments





μ = 2.7 D

Butanal

μ = 3.7 D

trans-2-Butenal

greater separation of positive and negative charge

18.12

Conjugate Addition to α,β-Unsaturated Carbonyl Compounds

Nucleophilic Addition to α,β-Unsaturated Aldehydes and Ketones

1,2-addition (direct addition)

nucleophile attacks carbon of C=O

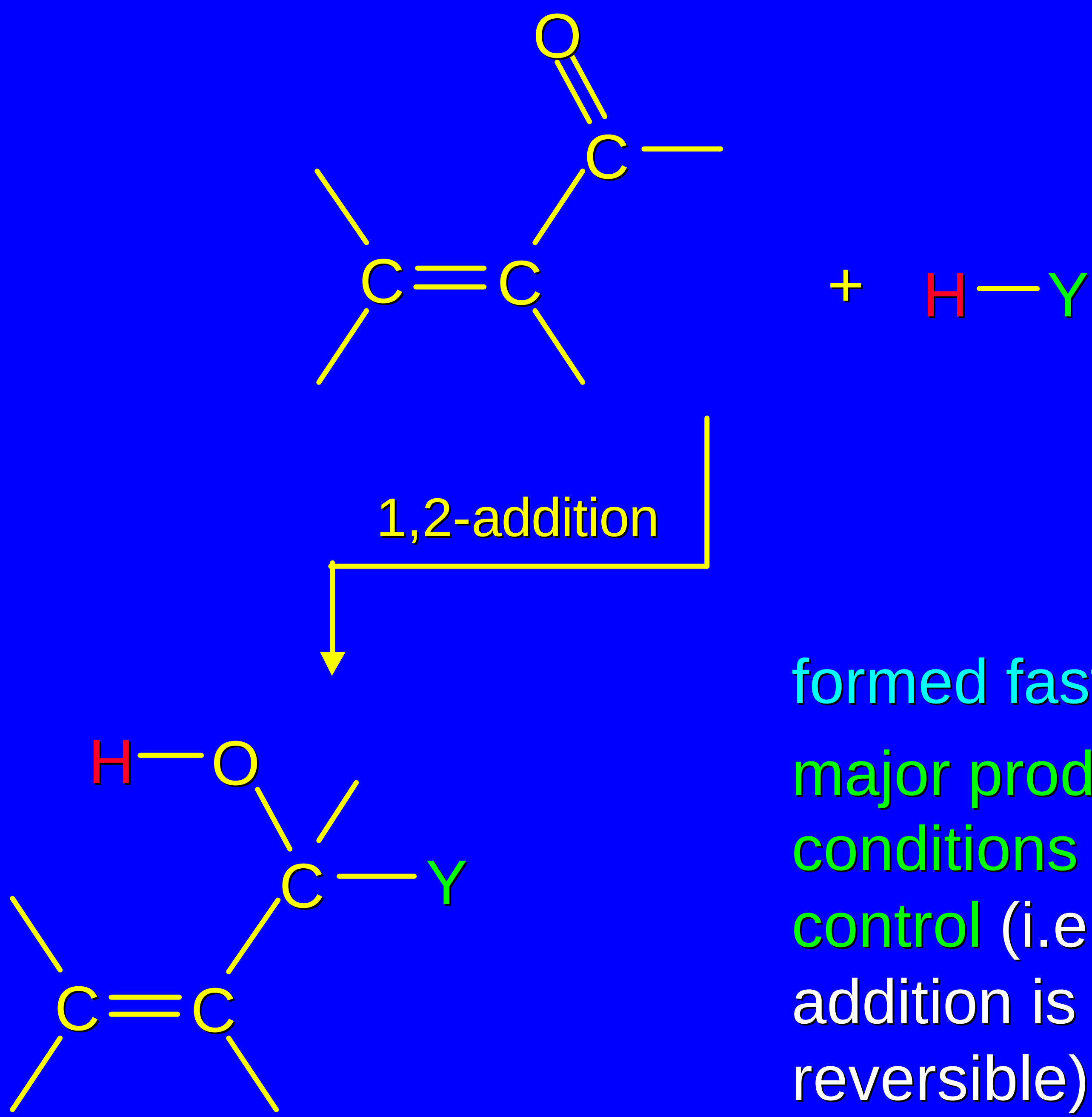
1,4-addition (conjugate addition)

nucleophile attacks β-carbon

Kinetic versus Thermodynamic Control

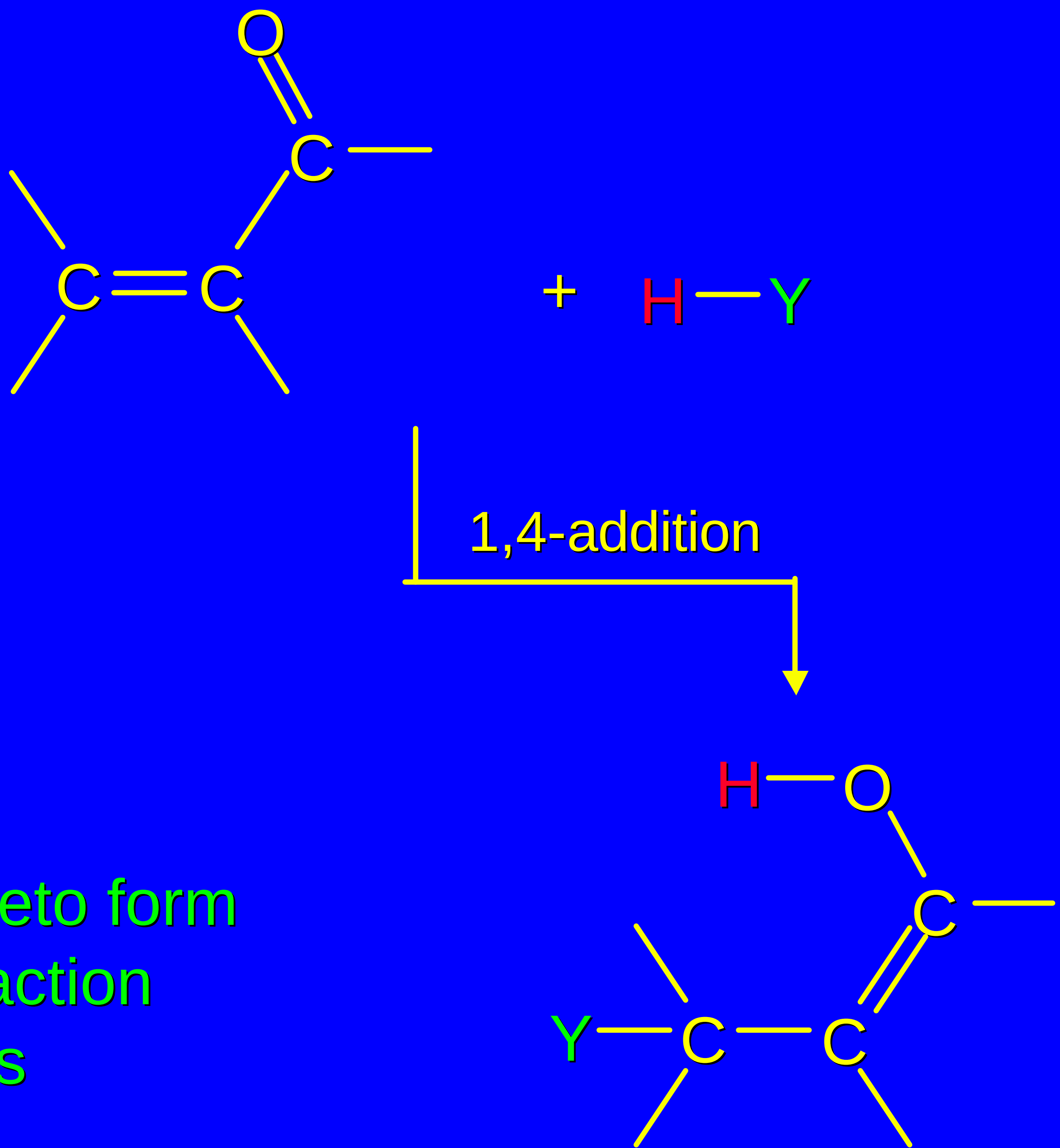
attack is faster at C=O

attack at β-carbon gives the more stable product



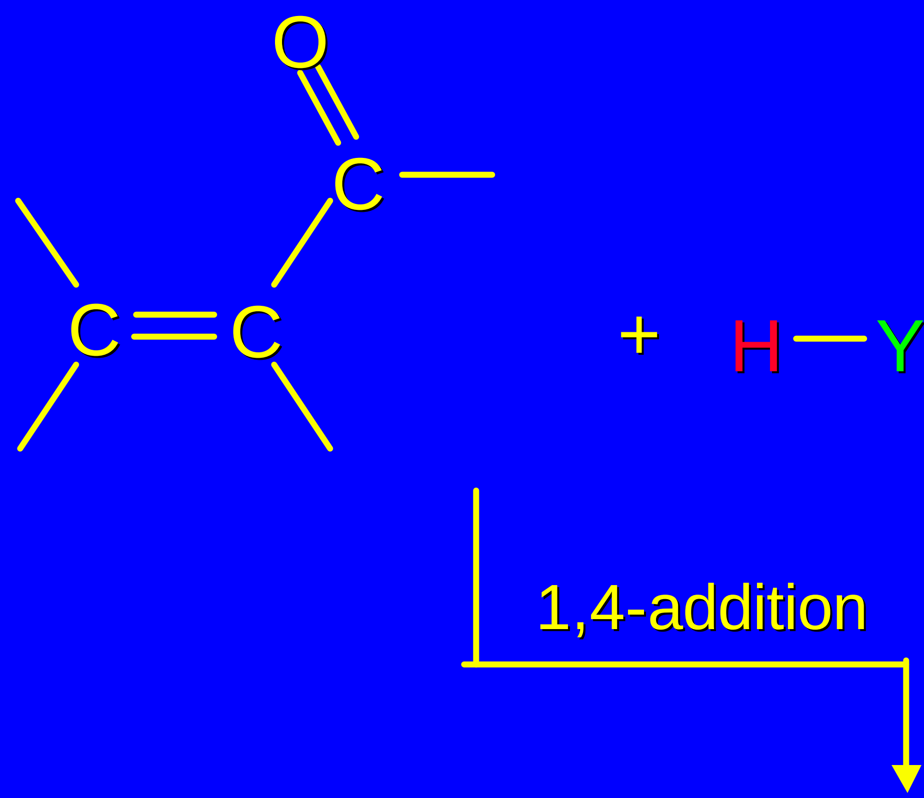
formed faster

major product under conditions of kinetic control (i.e. when addition is not readily reversible)



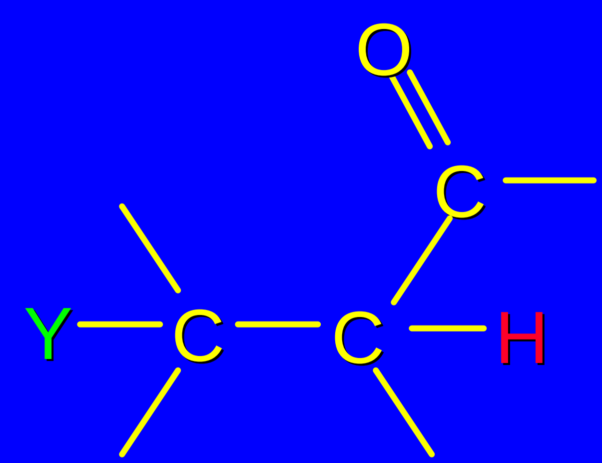
enol

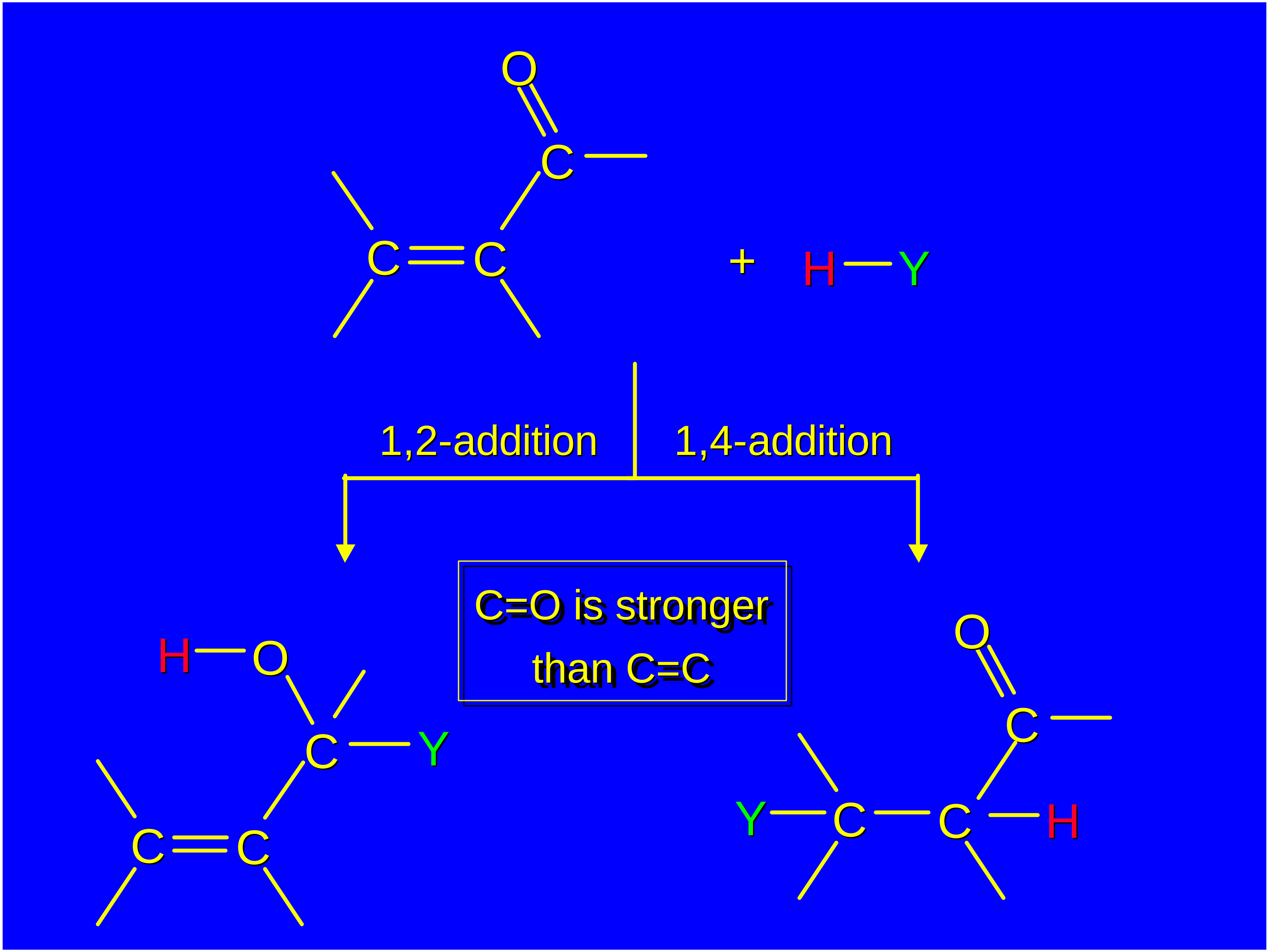
goes to keto form
under reaction
conditions



keto form is isolated
product of 1,4-addition

is more stable than
1,2-addition product




O
C
C C
+ H Y
1,2-addition
1,4-addition
C=O is stronger
than C=C
H O
C Y
C C
O
C
Y C C H

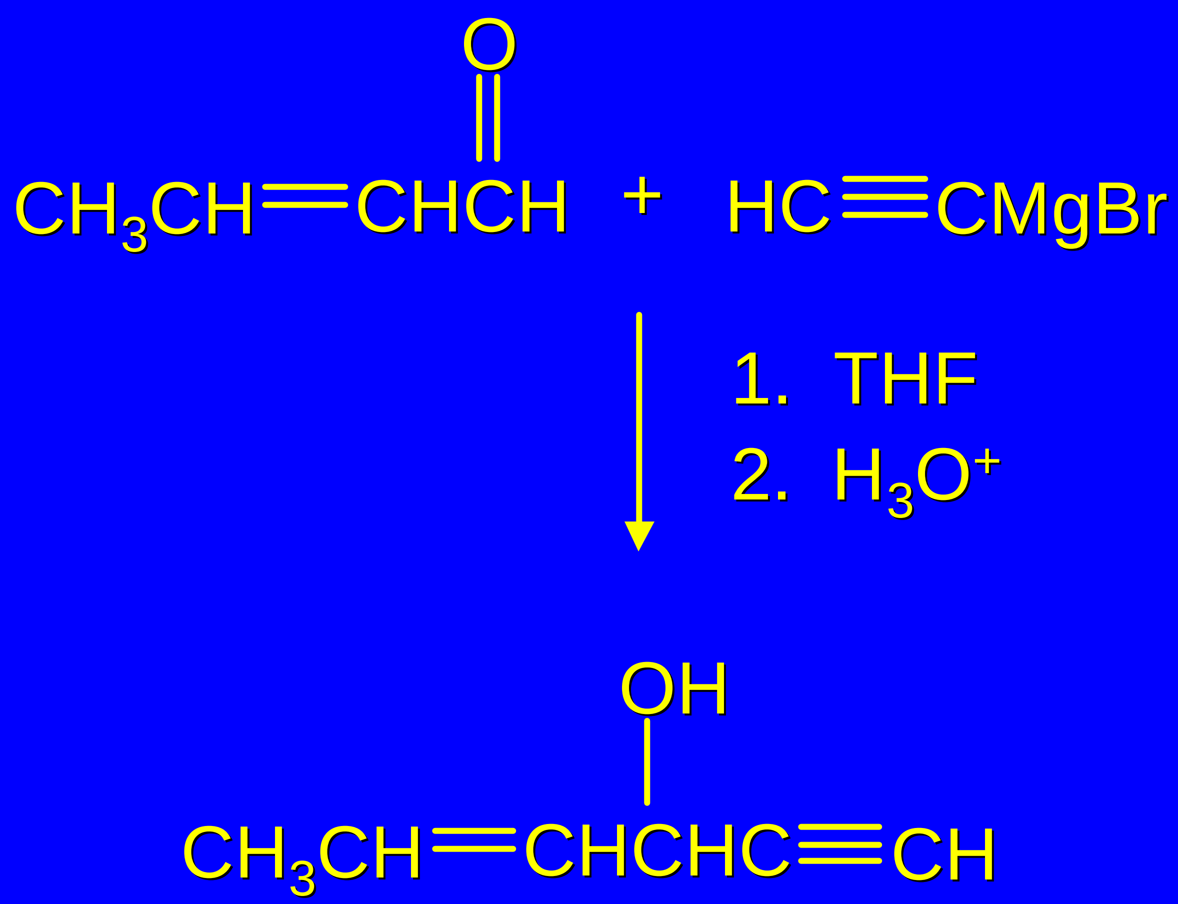
1,2-Addition

observed with *strongly* basic nucleophiles

- Grignard reagents
- $LiAlH_4$
- $NaBH_4$
- Sodium acetylide

strongly basic nucleophiles add irreversibly

Example



(84%)

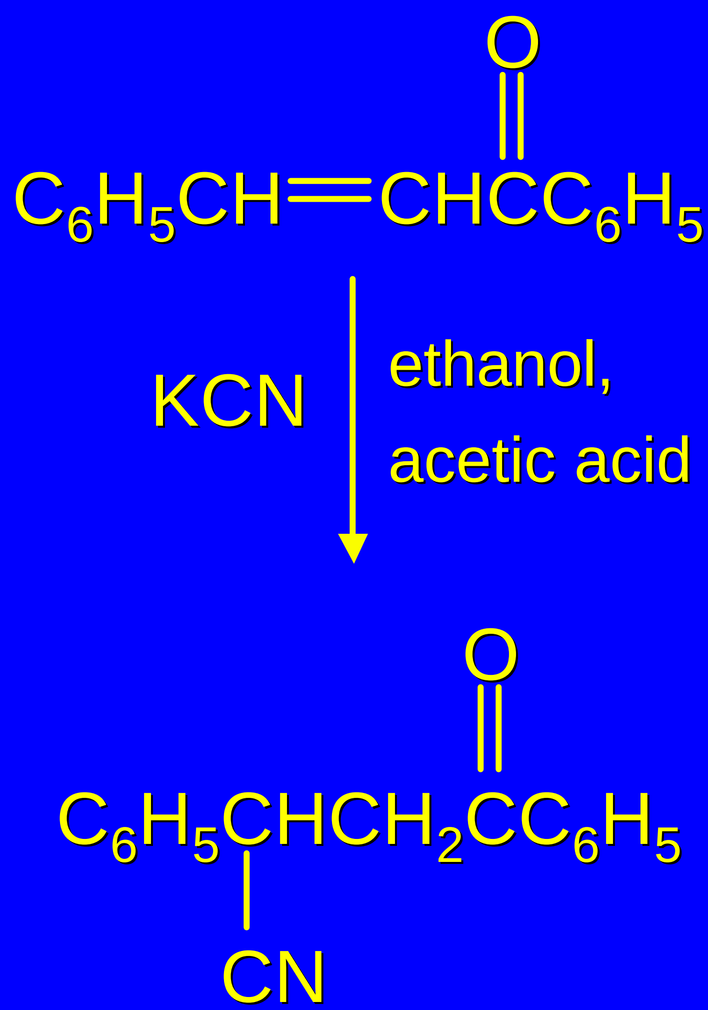
1,4-Addition

observed with *weakly* basic nucleophiles

- cyanide ion (CN^-)
- thiolate ions (RS^-)
- ammonia and amines
- azide ion (N_3^-)

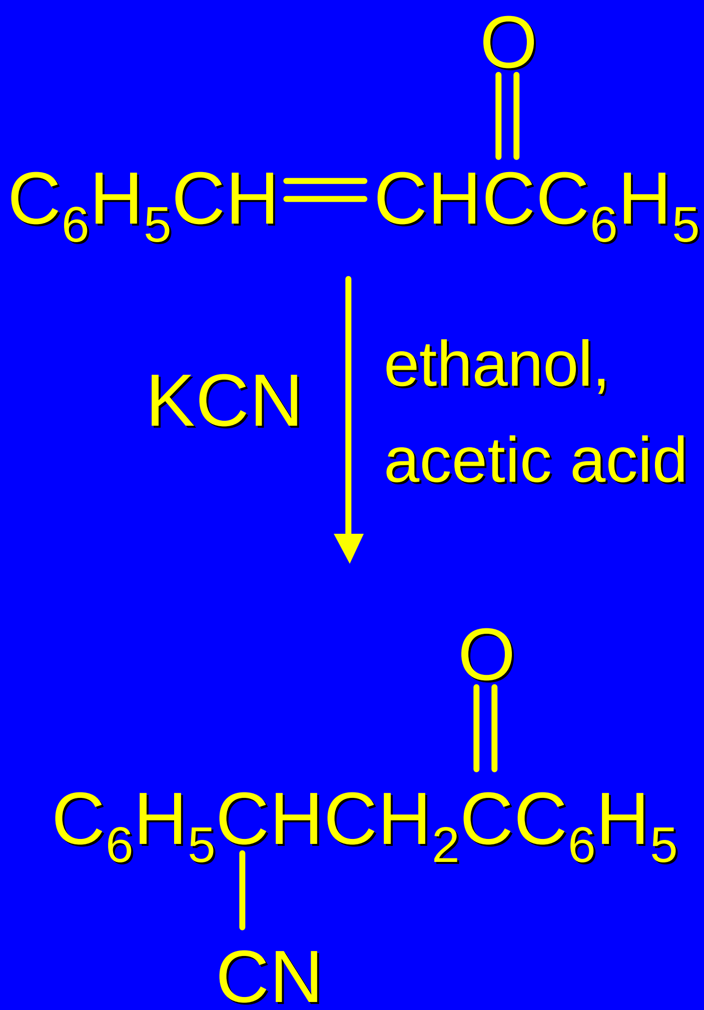
weakly basic nucleophiles add reversibly

Example



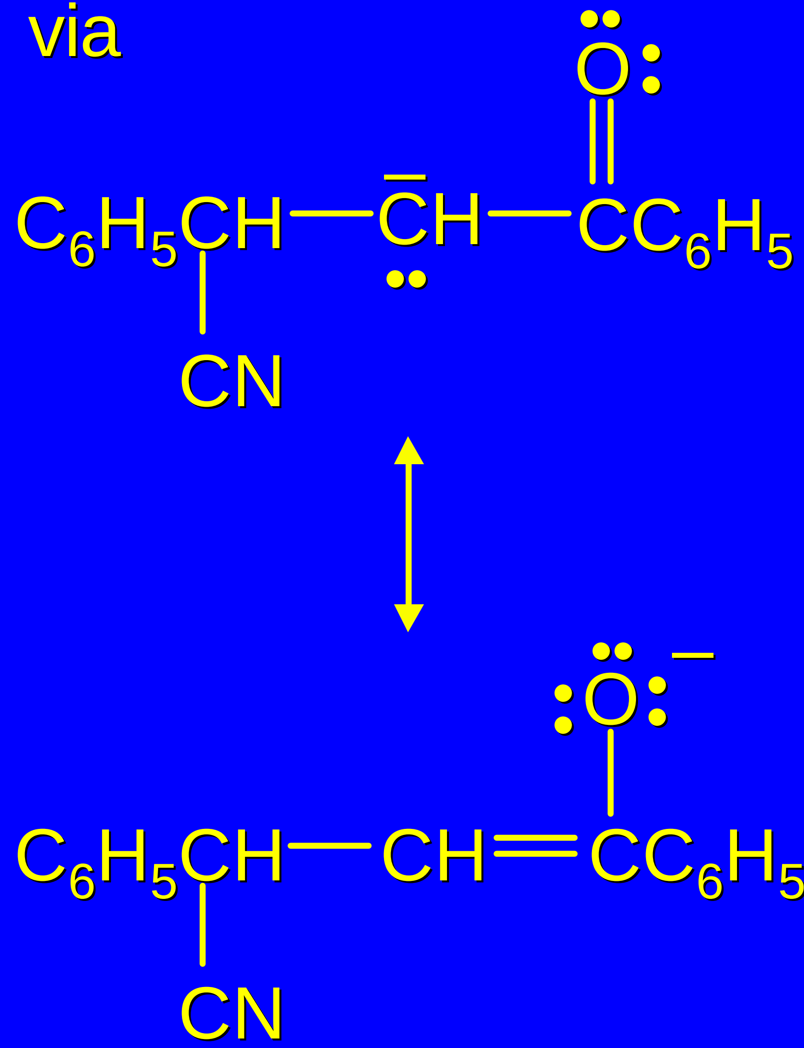
(93-96%)

Example

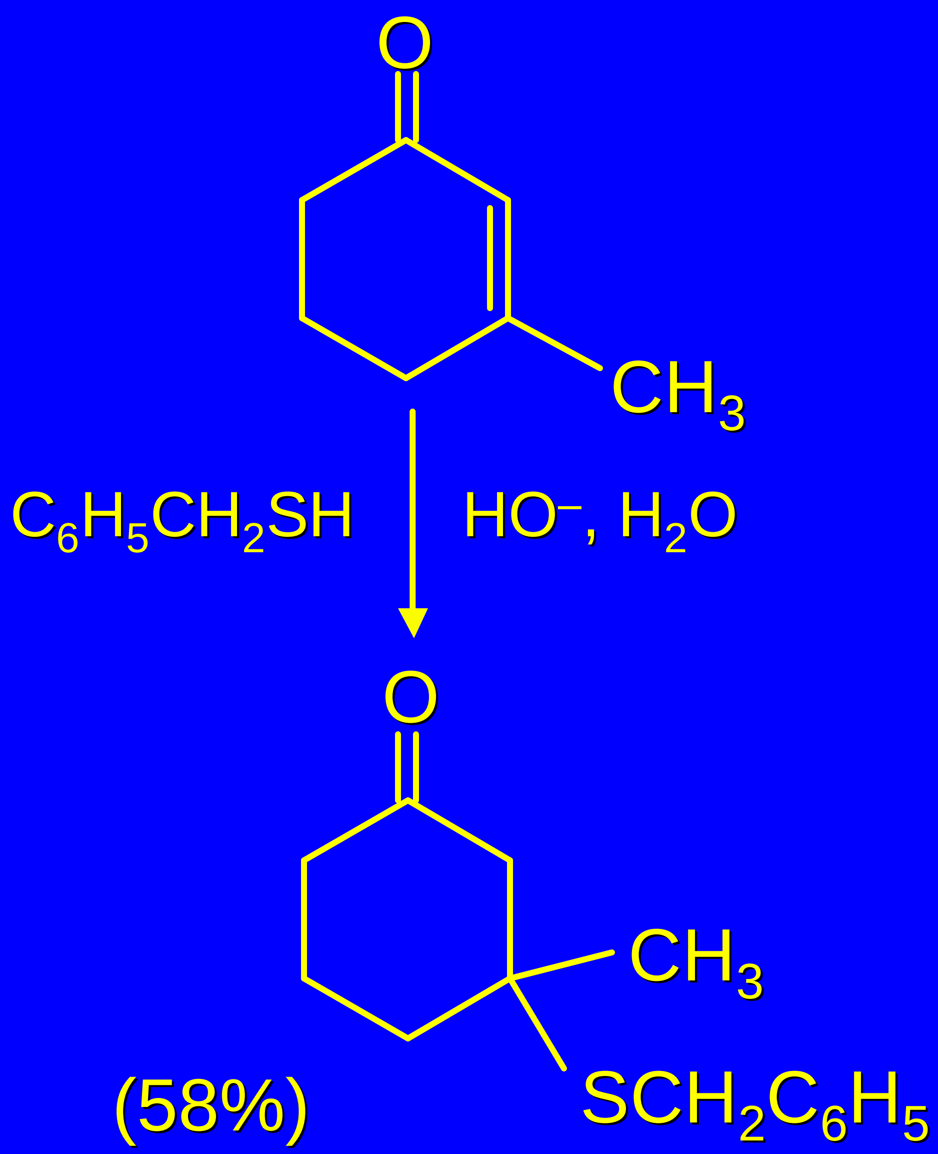


(93-96%)

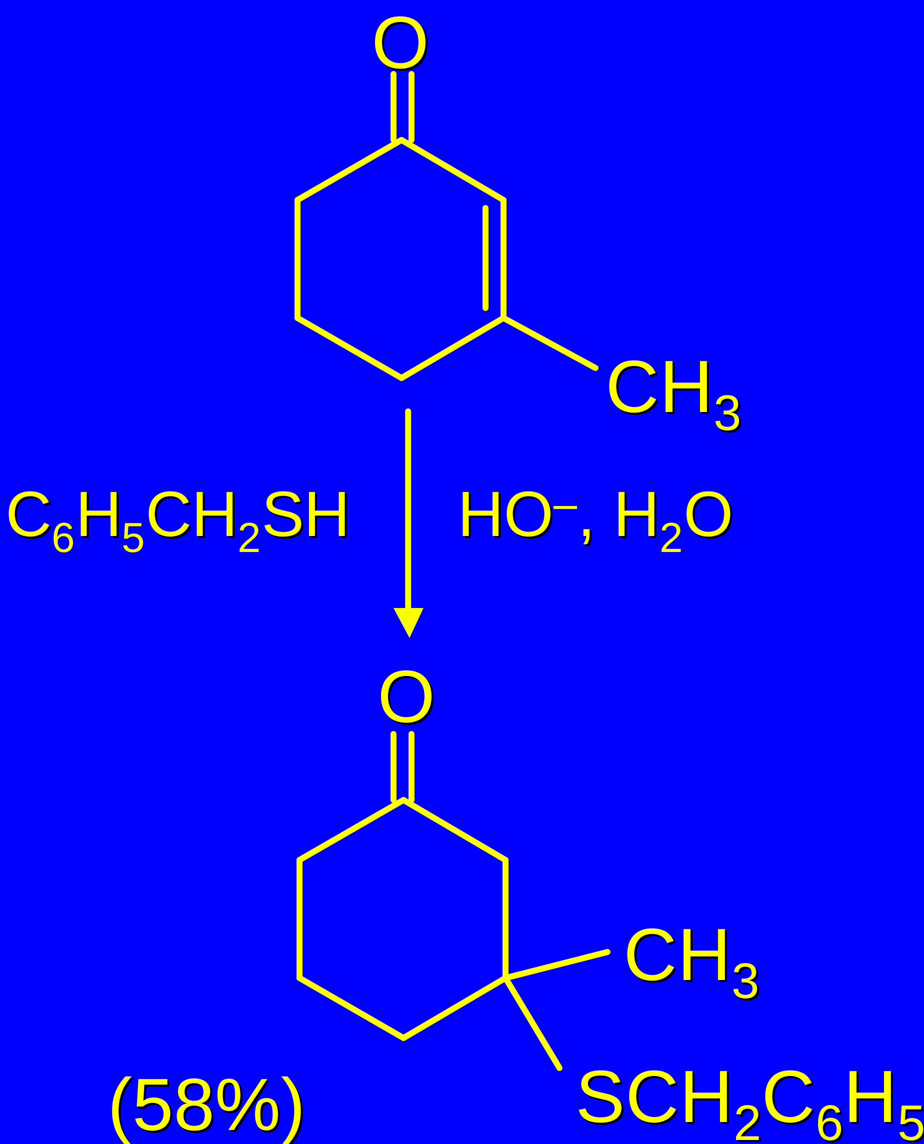
via



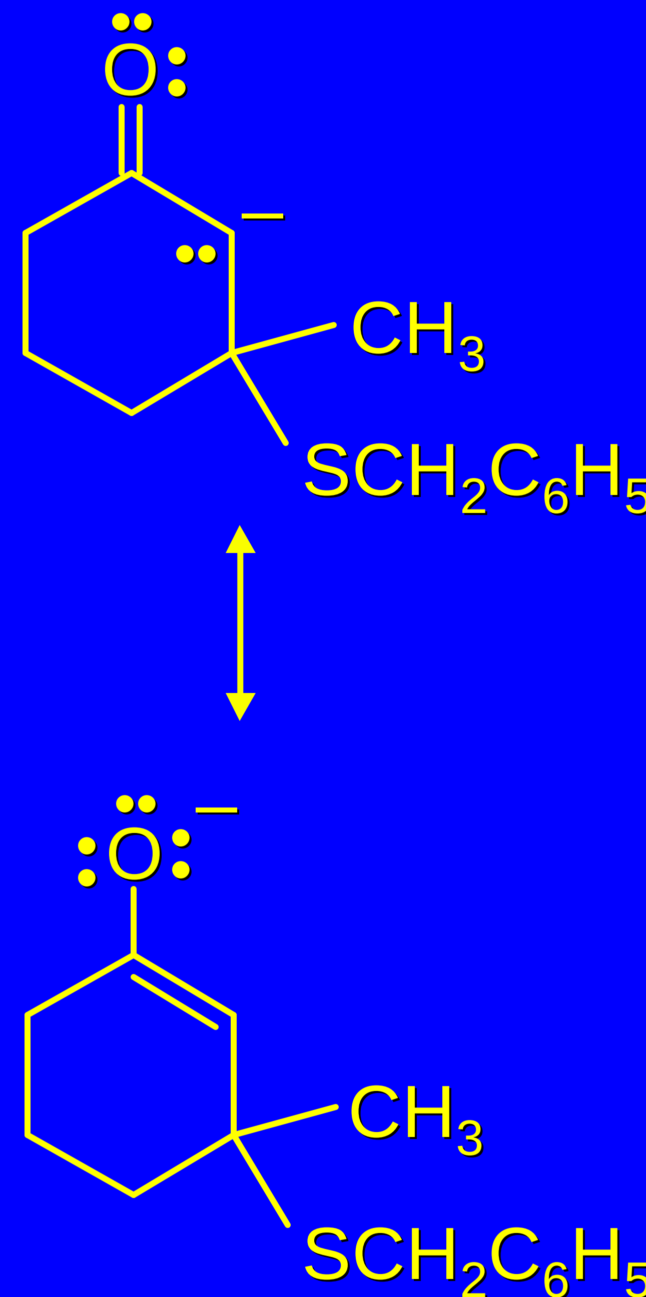
Example



Example


O
CH3
C6H5CH2SH
HO–, H2O
O
CH3
SCH2C6H5
(58%)

via

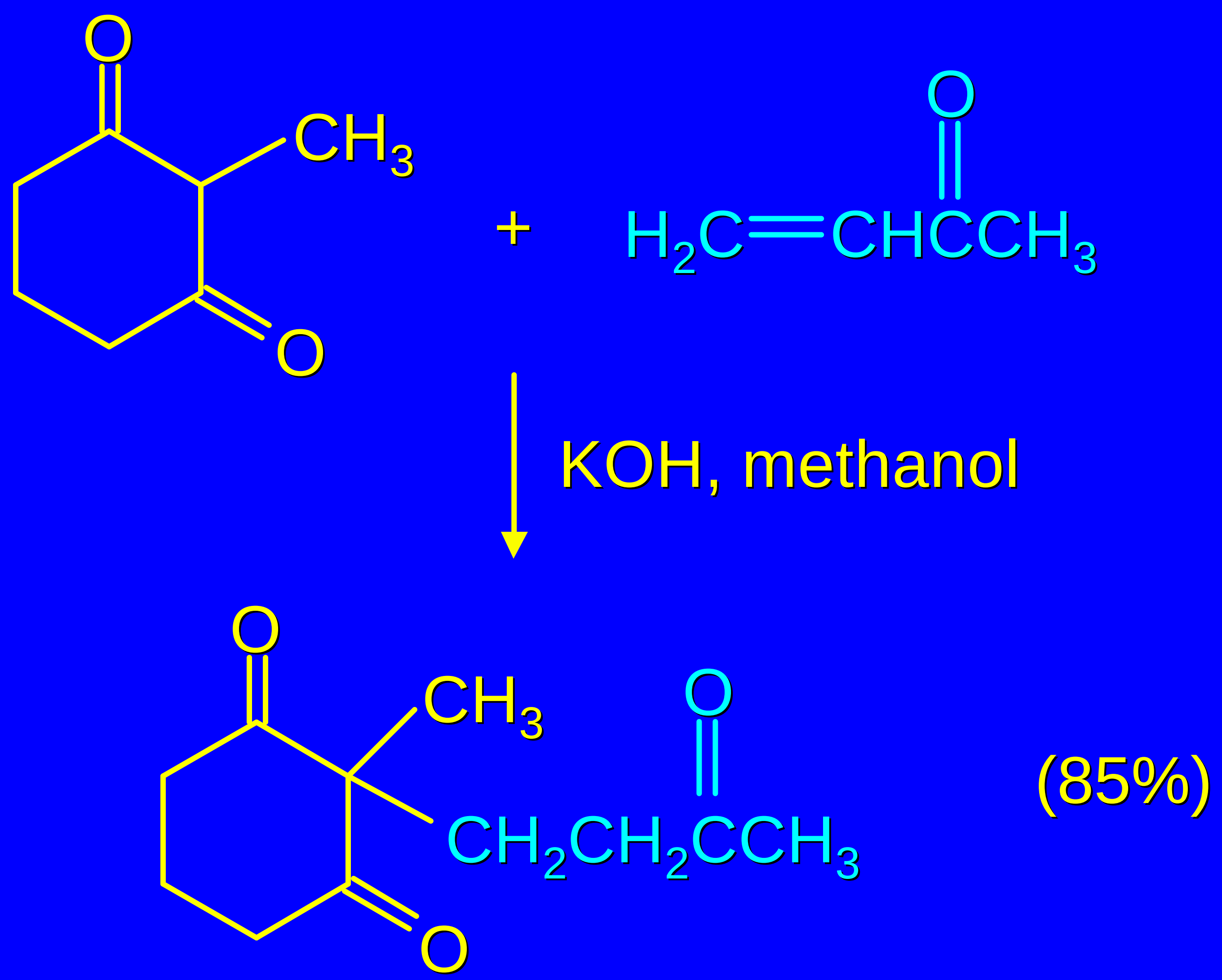

O
CH3
SCH2C6H5
O
CH3
SCH2C6H5

18.13
Addition of Carbanions to
α,β-Unsaturated Carbonyl Compounds:
The Michael Reaction

Michael Addition

Stabilized carbanions, such as those derived from β-diketones undergo conjugate addition to α,β-unsaturated ketones.

Example

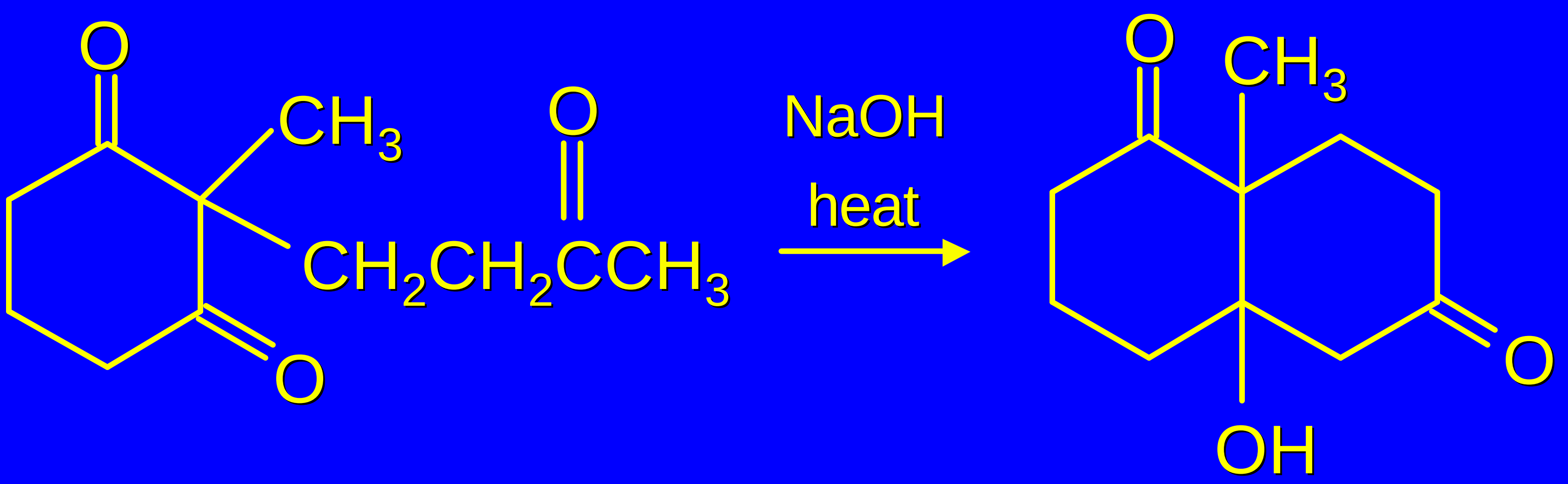


Michael Addition

The Michael reaction is a useful method for forming carbon-carbon bonds.

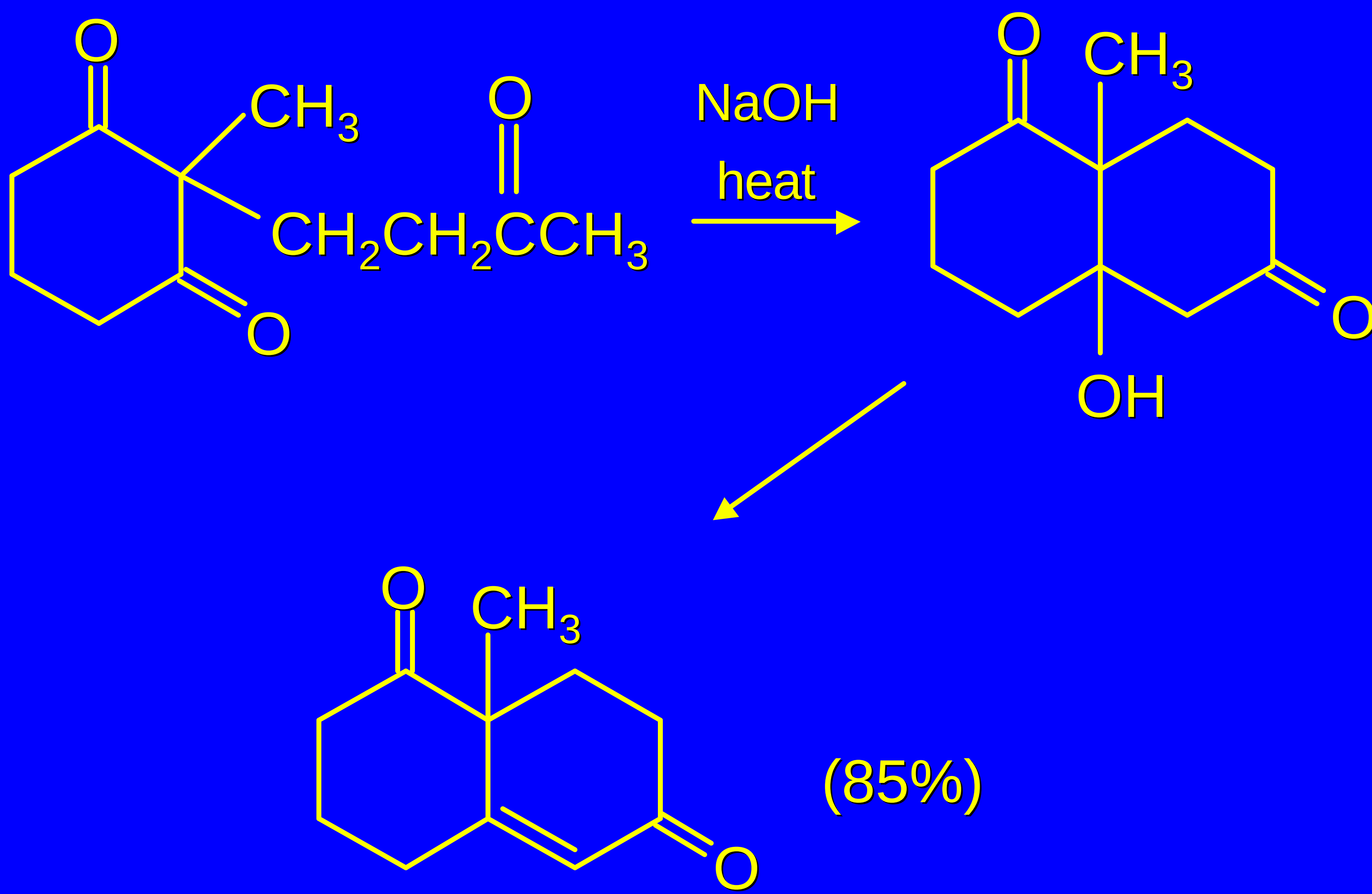
It is also useful in that the product of the reaction can undergo an intramolecular aldol condensation to form a six-membered ring. One such application is called the Robinson annulation.

Example



not isolated;
dehydrates under
reaction conditions

Example



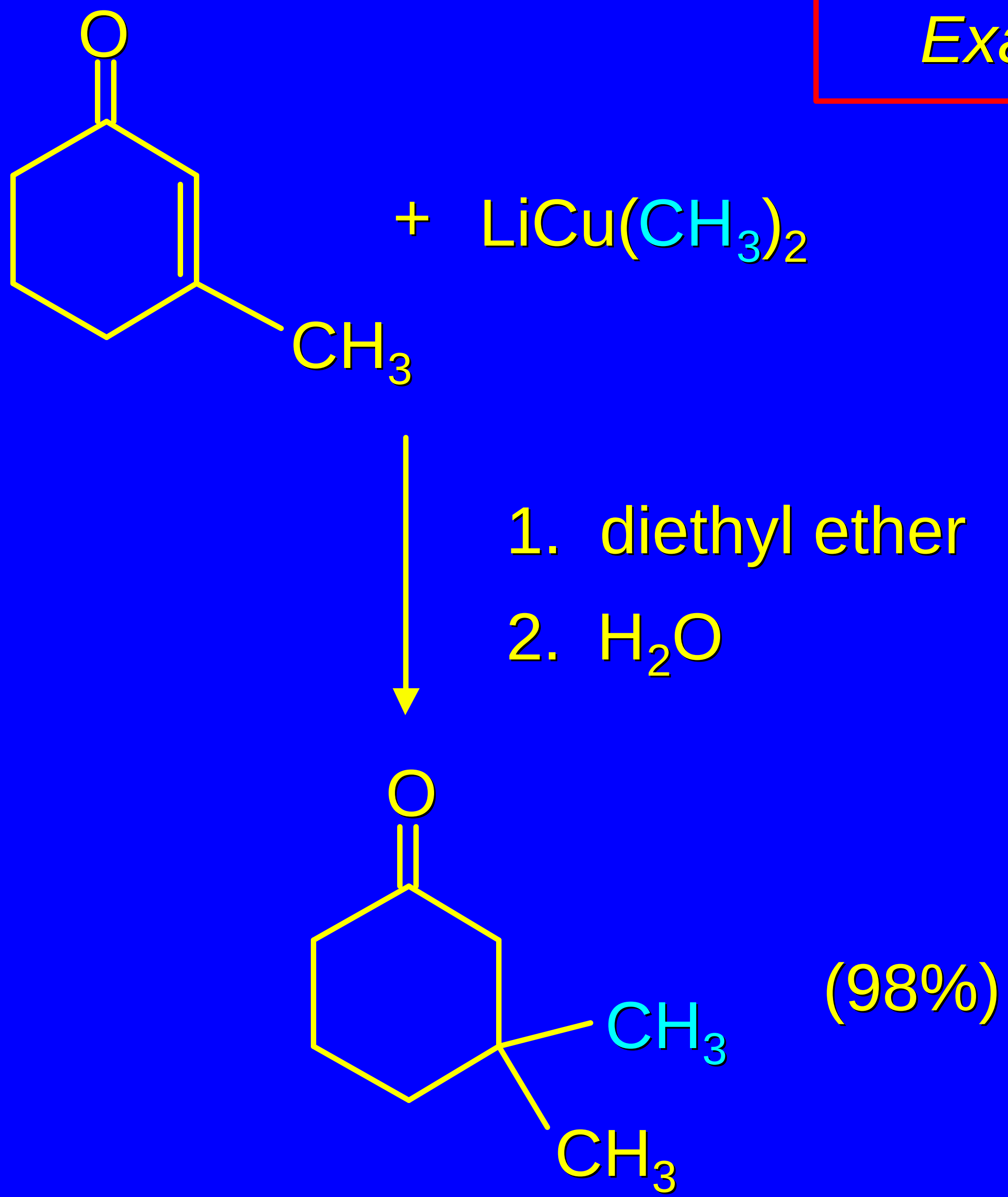
18.14

Conjugate Addition of Organocopper Reagents to α,β-Unsaturated Carbonyl Compounds

Addition of Organocopper Reagents to a,b-Unsaturated Aldehydes and Ketones

The main use of organocopper reagents is to form carbon-carbon bonds by conjugate addition to α,β-unsaturated ketones.

Example



18.15

Alkylation of Enolate Anions

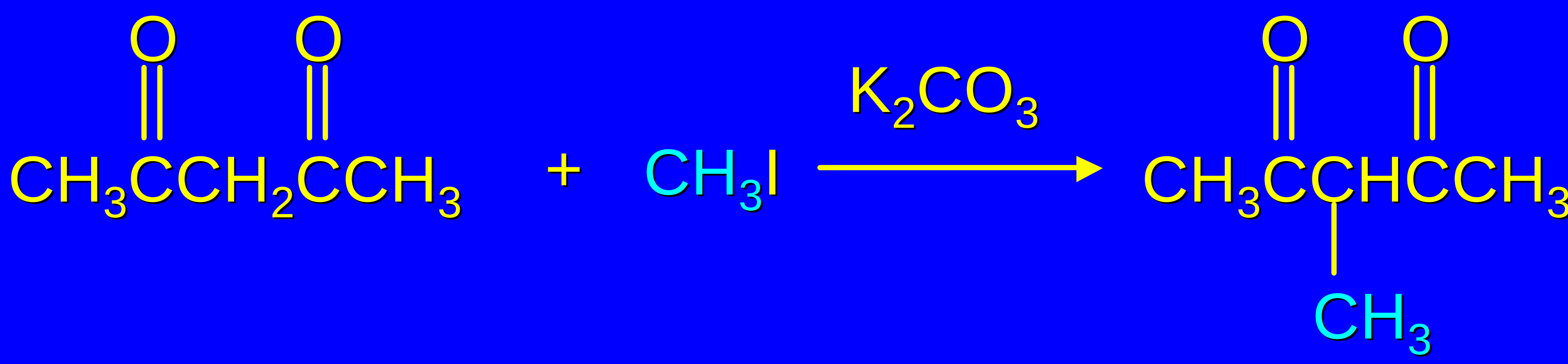
Enolate Ions in S_N2 Reactions

Enolate ions are nucleophiles and react with alkyl halides.

However, alkylation of simple enolates does not work well.

Enolates derived from β-diketones can be alkylated efficiently.

Example



(75-77%)