

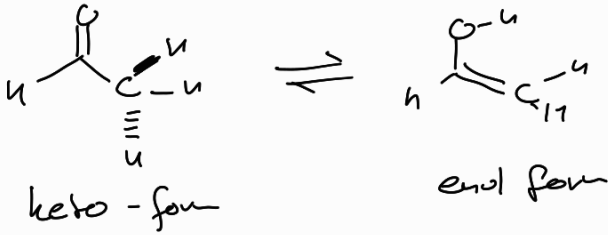
Today

- Keto-enol tautomerisation (acid/base)
- Reactivity
- Li and Si enolates stability
- C-C bonds with condensations (Aldol and Claisen condensation)

Keto-enol

Ch. 20 Enols and enolates

ex

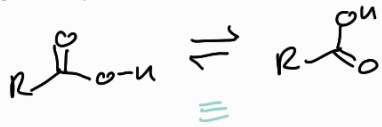


Equilibrium between two constitutional isomers

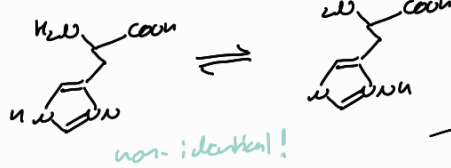
= Same formula but different bond order; connectivity and are convertible

ex for different constitutional isomers

Carboxylic acid

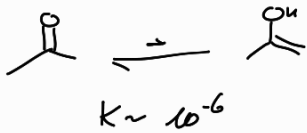


Indole ring



\Rightarrow Generally the Keto form is more stable

ex

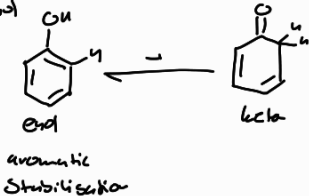


why? \rightarrow Bond strength

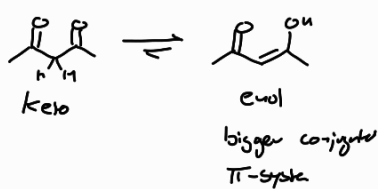
	EE (kJ/mol)	
C-H	440	} 1160
C=O	720	
O-H	500	} 1120
C=C	620	

Exceptions

1) Phenol

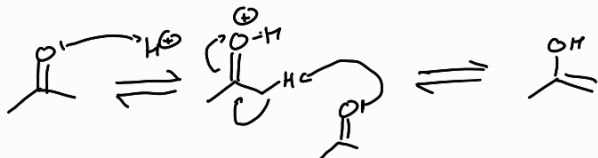


2) 1,3 Dicarbonyl compounds

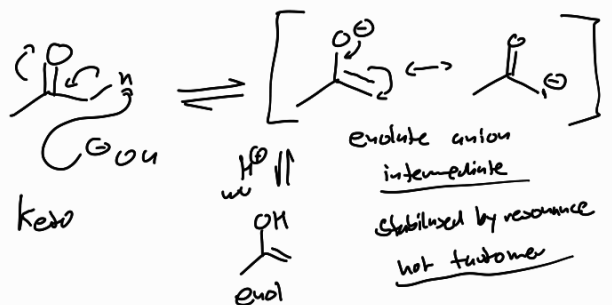


Catalysis

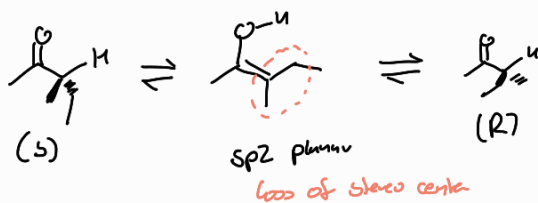
Acid



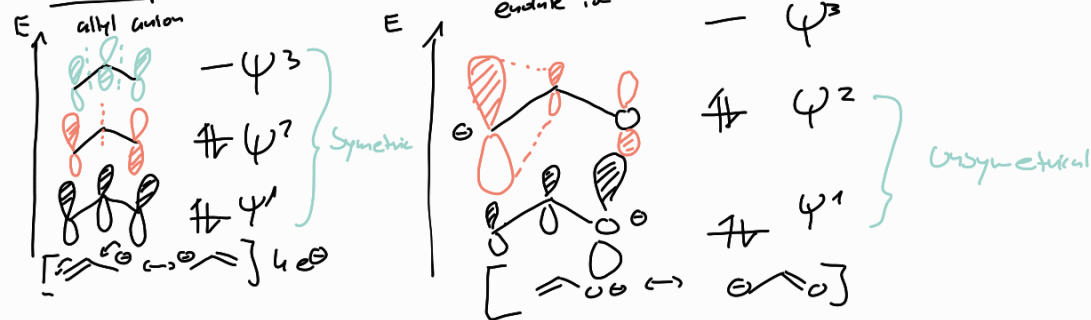
Base



Consequence: α -carbons enyclic migrate



Orbital perspective



ψ is a MO for >3 p-orbitals
(π is MO for 2 p-orbitals)

\Rightarrow Consequences:

Enolate is 'distorted' or unsymmetrical

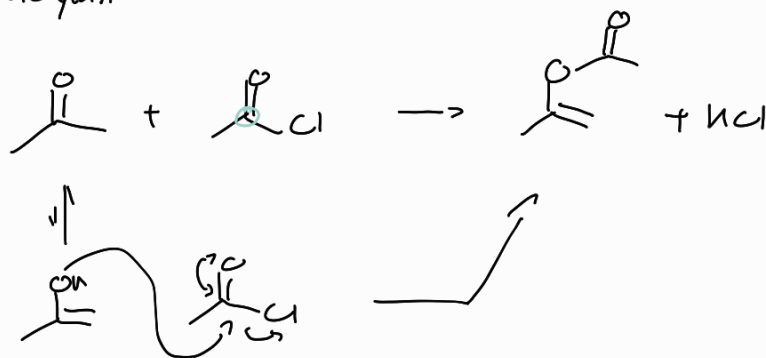
- Higher EUMO leads to lower ψ^1 energy (compared to allyl)
- HOMO ψ^2 has large coefficient on α -carbon

\Rightarrow O more electronegative, but C more HOMO

\Rightarrow Two cases of reactions with electrophiles

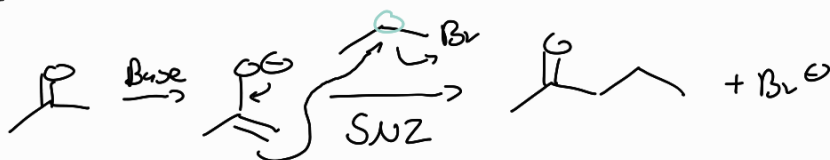
1) Hard electrophiles = electrostatically driven \Rightarrow reacts with O

ex acylation



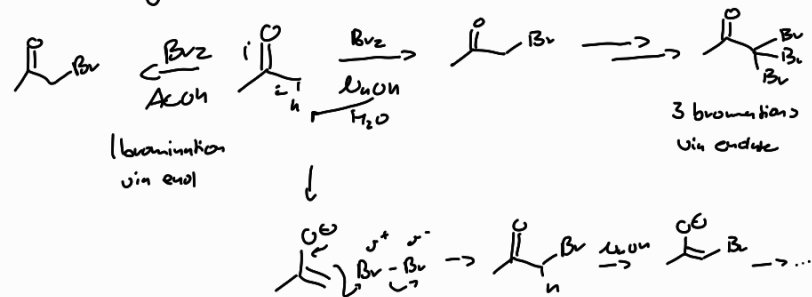
2) Soft electrophiles react orbital-guided via HOMO

ex alkylation



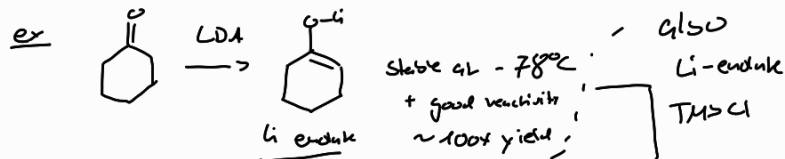
Reactions involving enolates

3) Halogenation

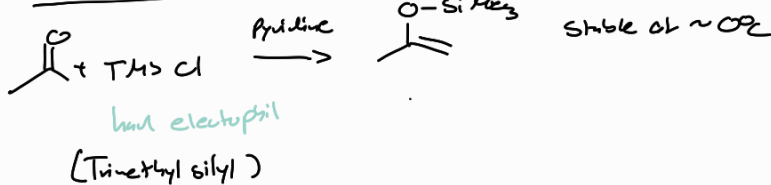


4) Stable Li enolates with strong Br₂

\Rightarrow LDA Li diisopropyl amide



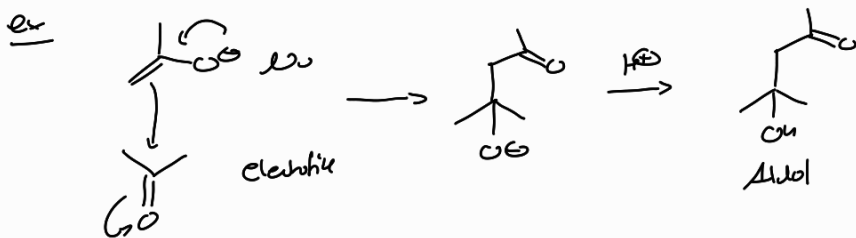
5) Silyl-enolates



Enolate alkylations CH 25

Note Carbonyls are electrophiles and nucleophiles

\Rightarrow Condensations are possible! Ex aldol and Claisen condensation



Alkylations with alkyl halides

