Carbonyl Alpha Chem. I

- Keto/ Enol Tautomerism
- α H Acidity

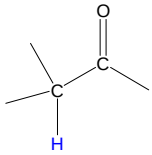
Halogenation Rxns

Ref 17: 1 - 3

Prob 17: 1 – 5; 37 - 39 (8th ed.)
17: 1 – 5; 36 - 38 (9th ed.)

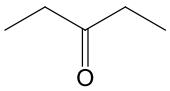
Adv Rdg 17: 7C; 19: 3 - 6

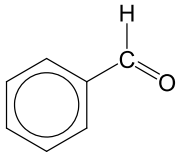
α Hydrogens

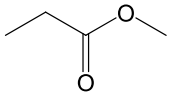


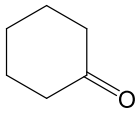
applies to any carbonyl cmpd

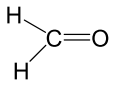
Practice: # of α H's

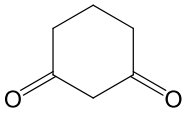
 4

 0

 2

 4

 0

 6

Tautomers

Def: • Isomers where location of α H as changed (normally, an acidic H)

• otherwise no change in connectivity (but single/double bond change may occur)

• generally, rapid equil. between tautomers

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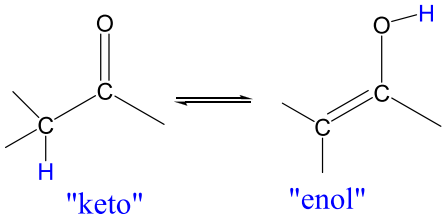
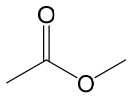
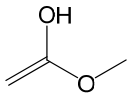
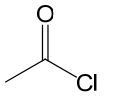
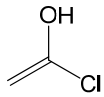
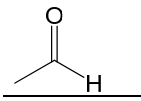
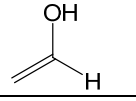
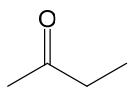
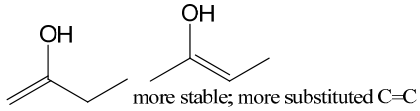
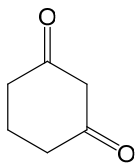
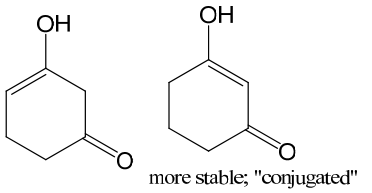
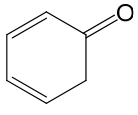
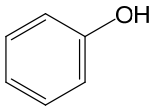
most important: **keto/ enol** tautomerism



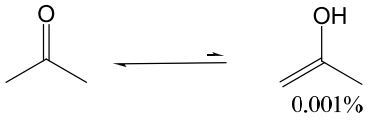
applies to any carbonyl cmpd with α H

Practice

"keto"	"enol"
	
	
	
	 more stable; more substituted C=C
	 more stable; "conjugated"
	

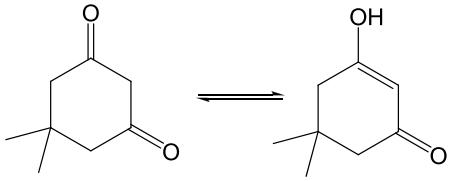
Extent of Enolization

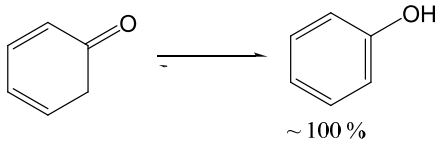
Normally: keto form more stable; e.g.



But enols, if stabilized by conjugation,

become more dominant; esp. **β-dicarbonyl**

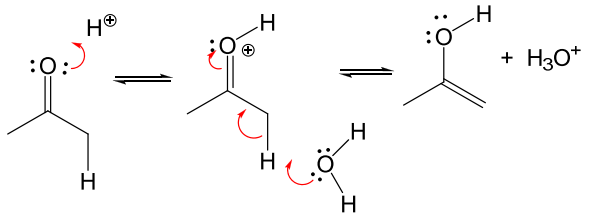




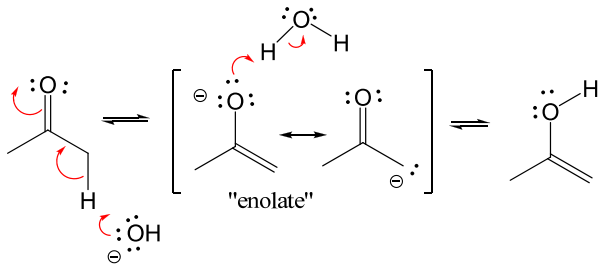
Rxn Mech.'s

enolization is catalyzed by a.) acid or b.)base

a.) acid

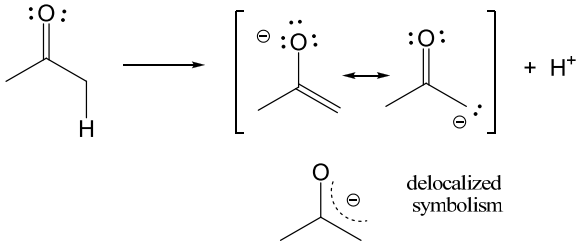


b.) base



Acidity

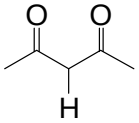
- "keto" cmpds are slightly acidic
- loose α H as H^+
- b/c enolate (= conj. base of "keto") is resonance stabilized



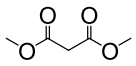
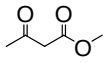
Generally, less acidic than ROH

can get more acidic

if keto cmpd has doubly activated α H;

esp., β-dicarbonyl 

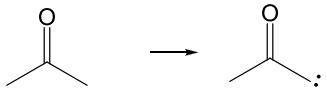
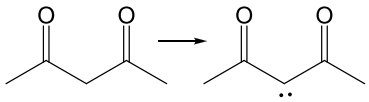
List of Acidity of Carbonyl Cmpds

cmpd	structure	pKa
amide		30
ester		25
ketone		19
aldehyde		17
1,3-diester		13
1,3-ketoester		11
1,3-diketone		9
For reference:		
	RCO_2H	5
		12
	ROH, H_2O	16
	NH_3	36
		40
	CH_3CH_3	60

Acidity Practice

Which base is needed
to effect the following conversion?

Answers

	OR^- ?	NH_2^- ?
	no	yes
	yes	yes

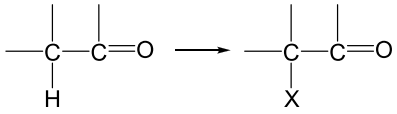
Recall:

"An acid will react
with the conj. base of a weaker acid"

or more simply

"Weaker acids and bases are formed"

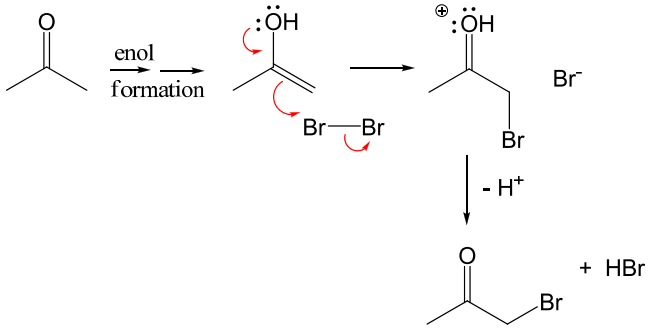
α Halogenation of A/K's



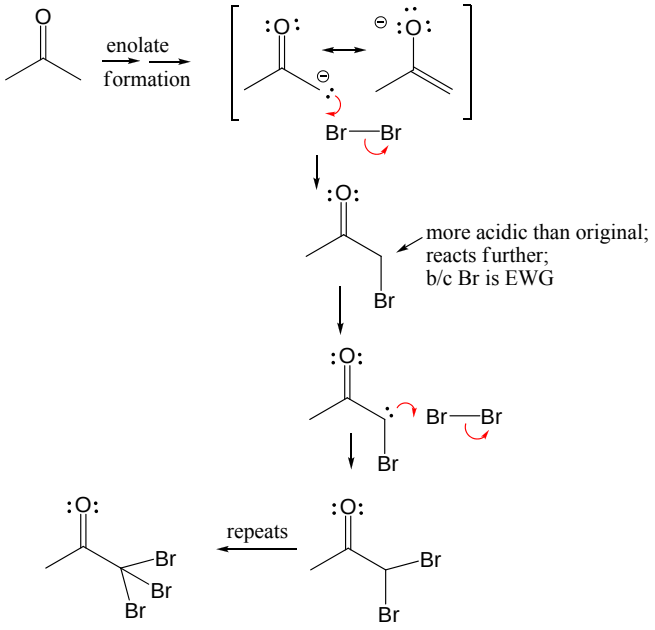
A.) Acidic

"keto" → enol → substituted "keto"

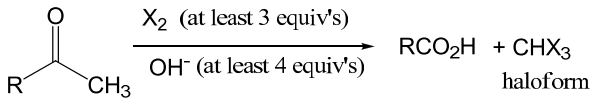
Ex.



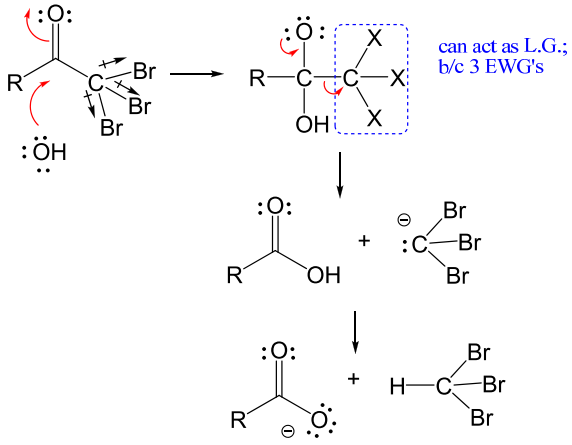
B.) Basic



C.) Haloform Rxn



Initially as under B.); then

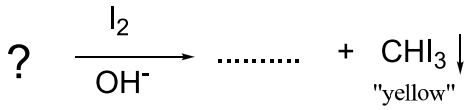


haloform ..

Applications:

1.) Prep. of acids from methylketones

2.) Analytical test for methyl ketones (traditional):
"iodoform test":



∴ If yellow precipitate is observed,
test indicates presence of methylketone