Organic Chemistry Concepts

LOKT.09.051

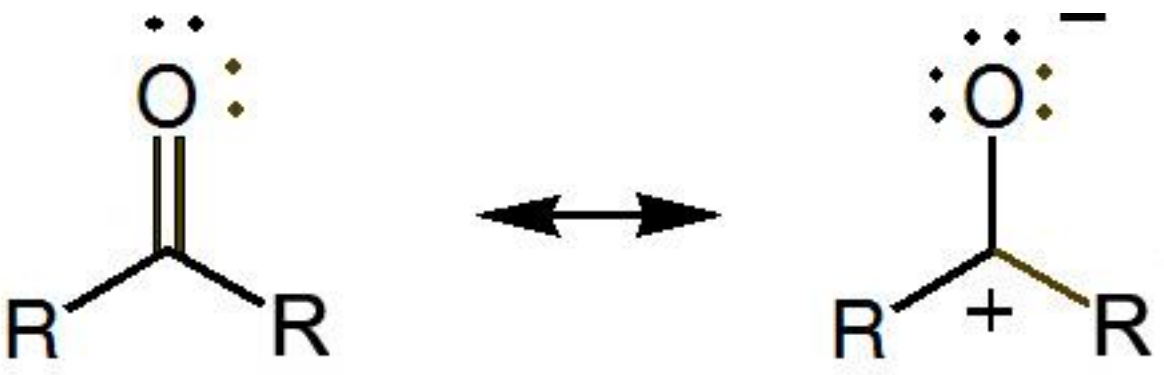
Polar π-bond reactivity

- C – C 83 - 85 kcal/mol
- C = C 146 – 151 kcal/mol
- C ≡ C 199 – 200 kcal/mol

- **C – O 85 – 91 kcal/mol**
- **C = O 173 – 181**

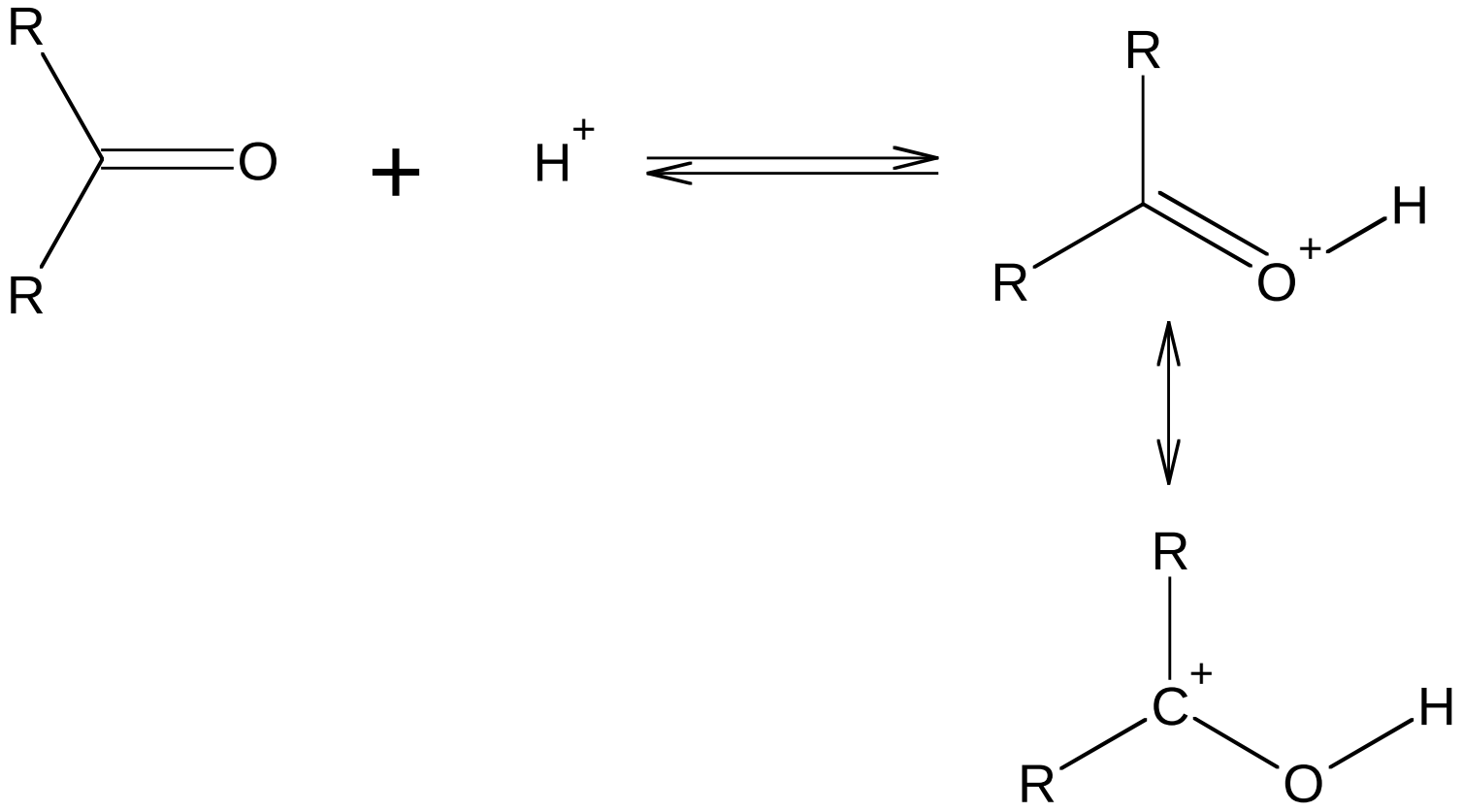
- **C – N 69 – 75 kcal/mol**
- **C = N 143 kcal/mol**
- **C ≡ N 204 kcal/mol**

>C=O bond is polar

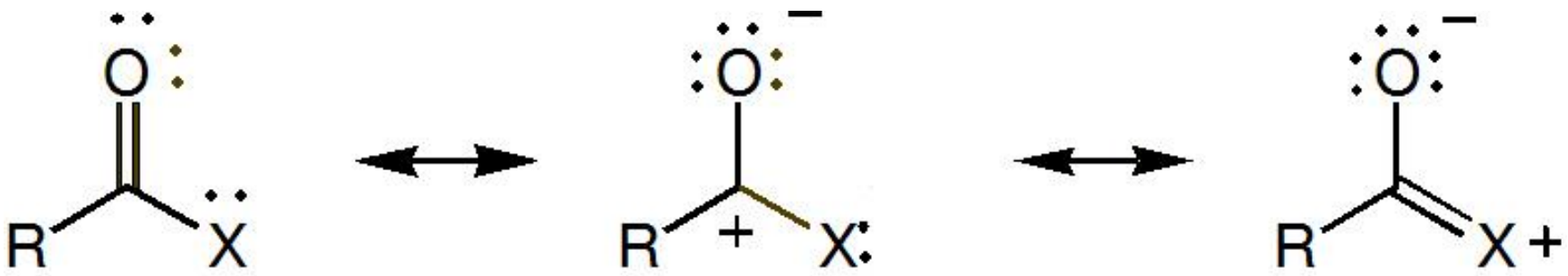


Carbon atom is electrophile

>C=O group is a base



>C=O group is conjugated with neighbour electron donating groups



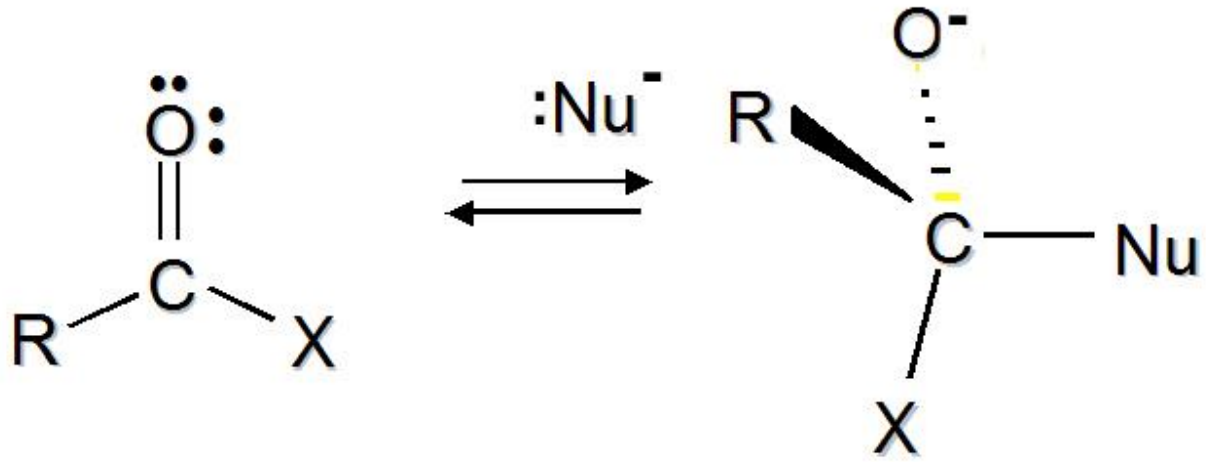
Summary of >C=O group reactions

Reactions with nucleophiles

Reactions with acids

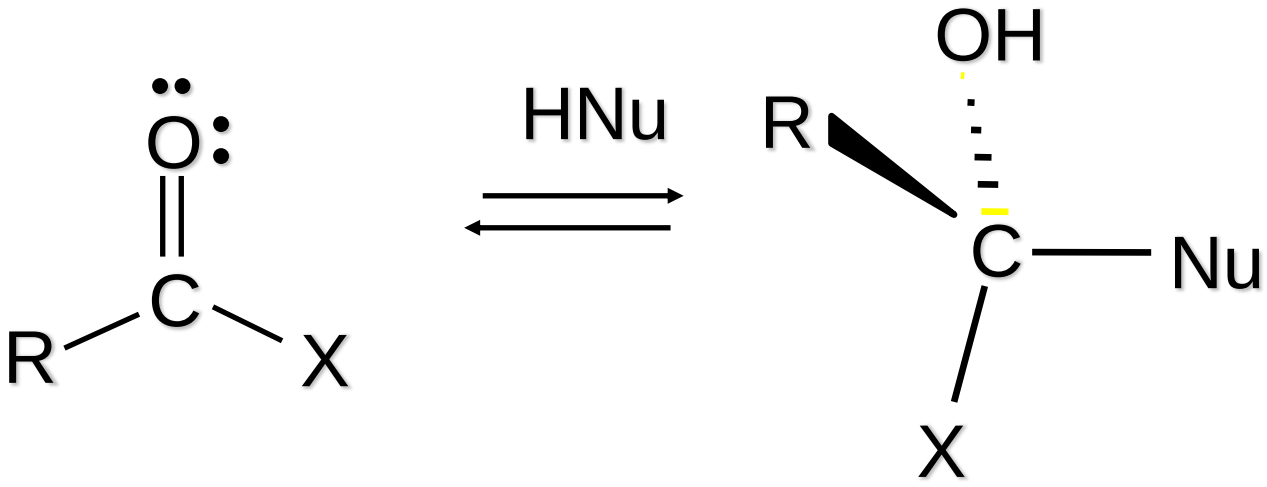
Stabilization of anions at a-carbon atom (CH acids

Reaction with nucleophiles



This intermediate is unstable

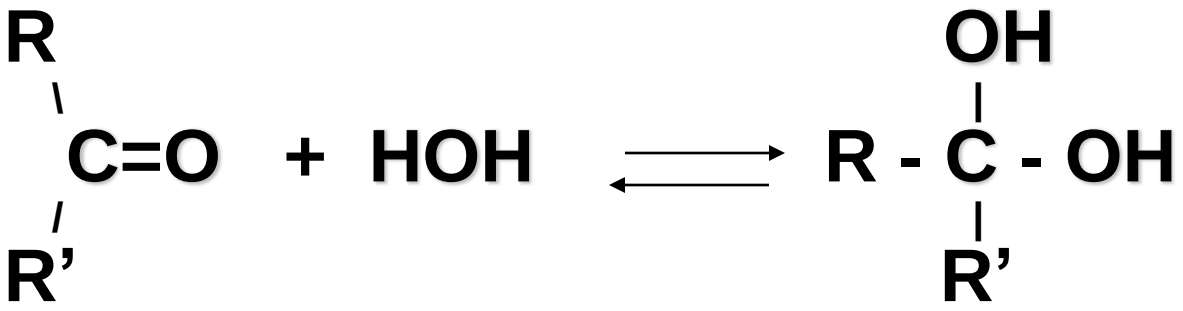
Addition to >C=O bond

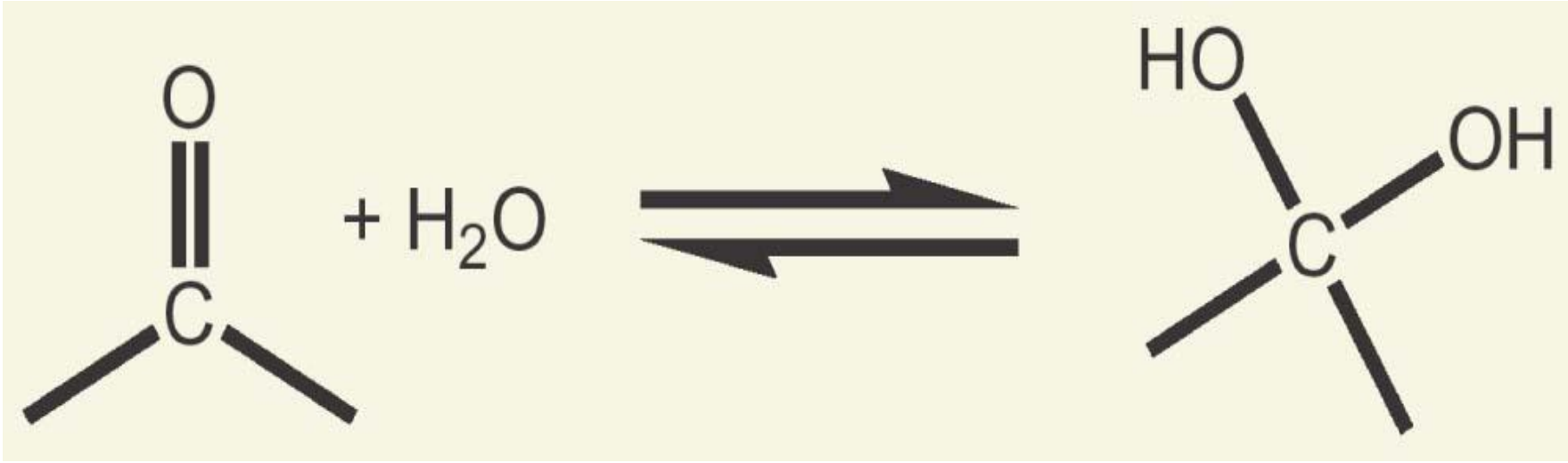


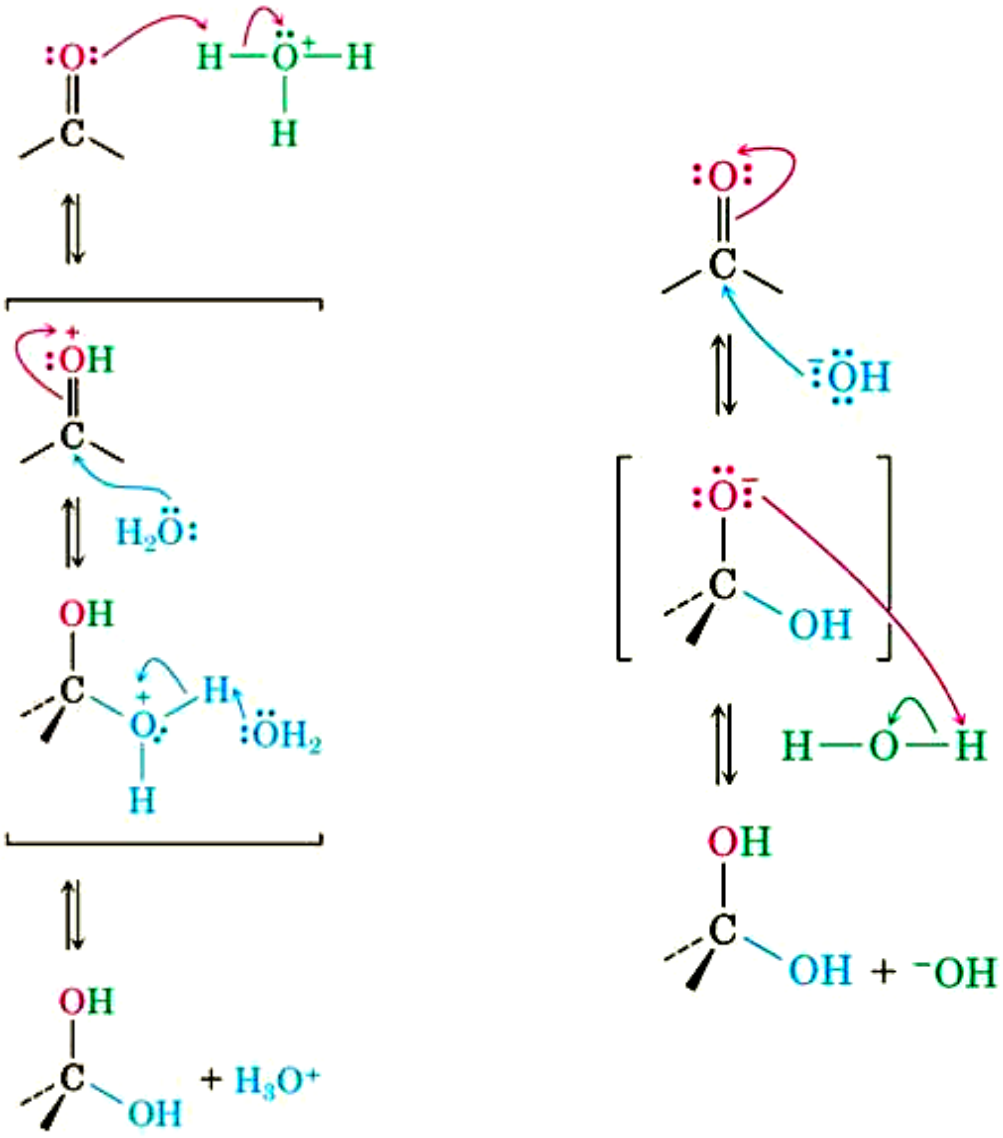
Some nucleophiles

- H_2O, R - OH
- NH_3, R - NH_2 etc
- H_2S, R - SH
- Carbanions, $C:^-$
- Hydride anion $H:^-$

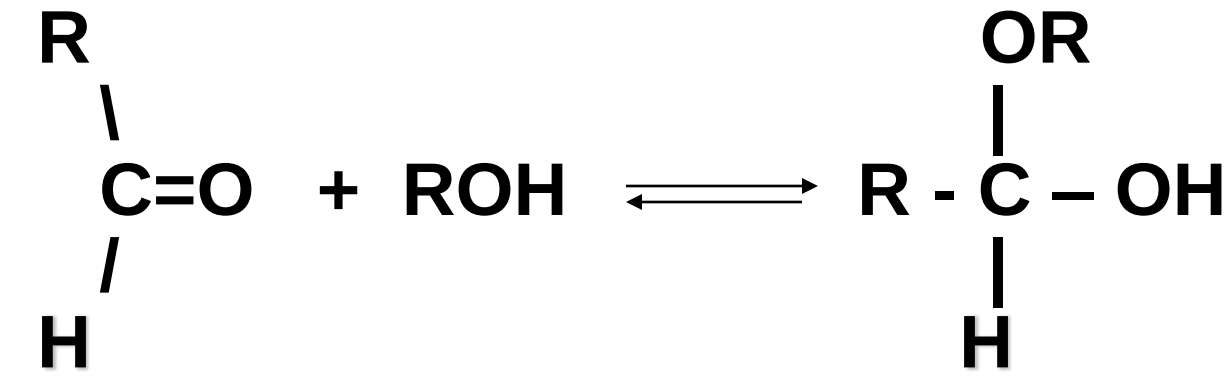
Hydratation

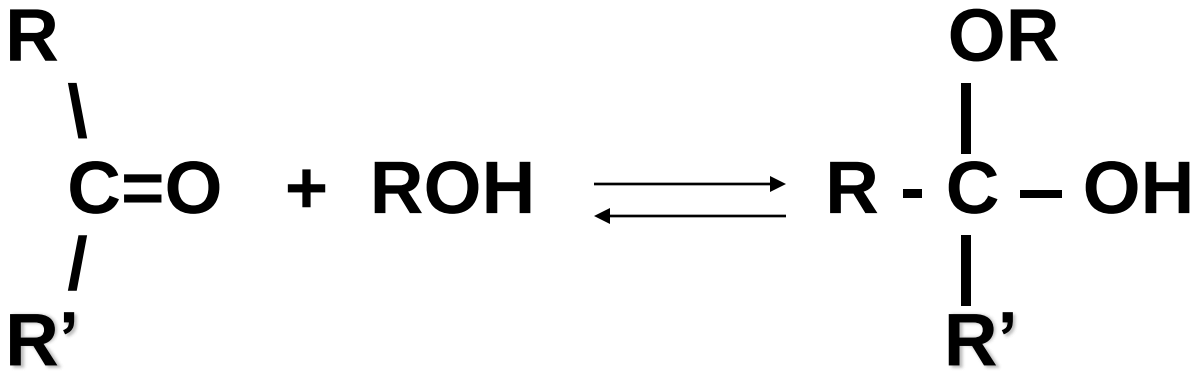



O
C
+ H2O
HO
OH
C

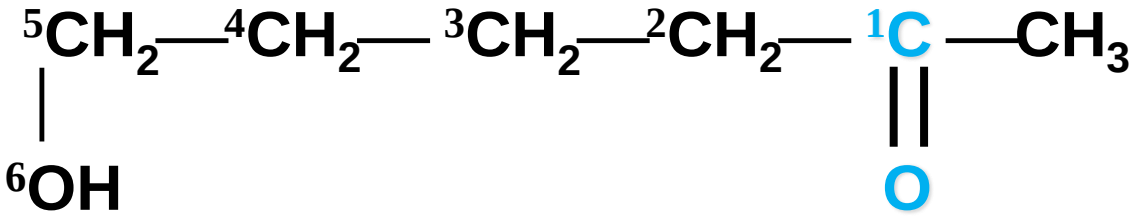

:O:
H—O+—H
H
C
:OH
H2O:
OH
H
:OH2
+ H3O+
:O:
:OH
:O:
OH
H—O—H
OH + −OH

Hemiacetals and hemiketals

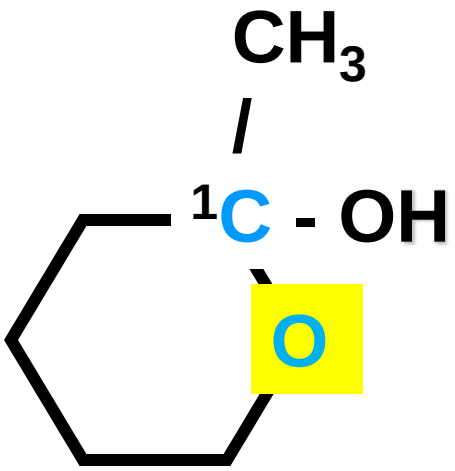


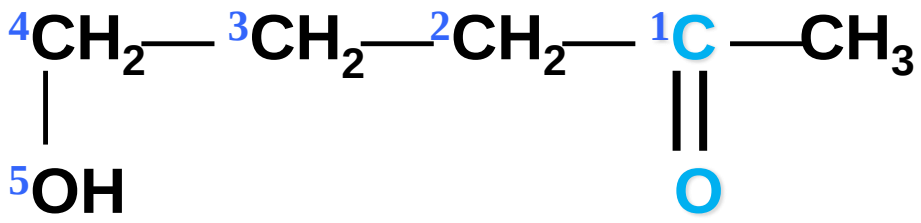


Cyclic hemiketal

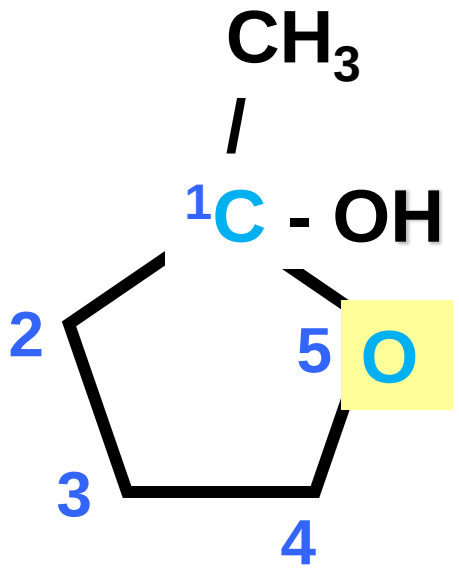


6-member cycle is stable



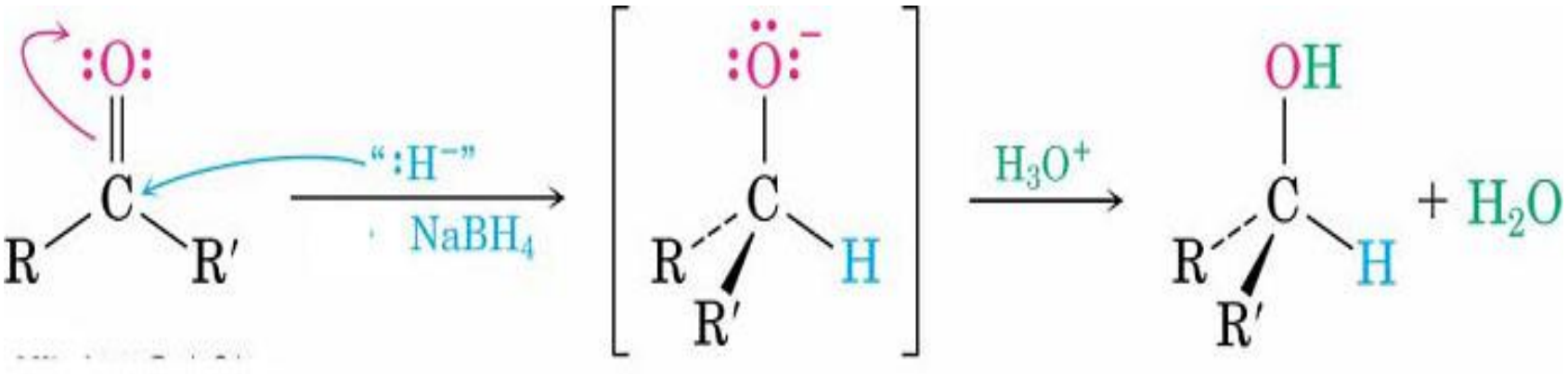


5-member cycle is stable

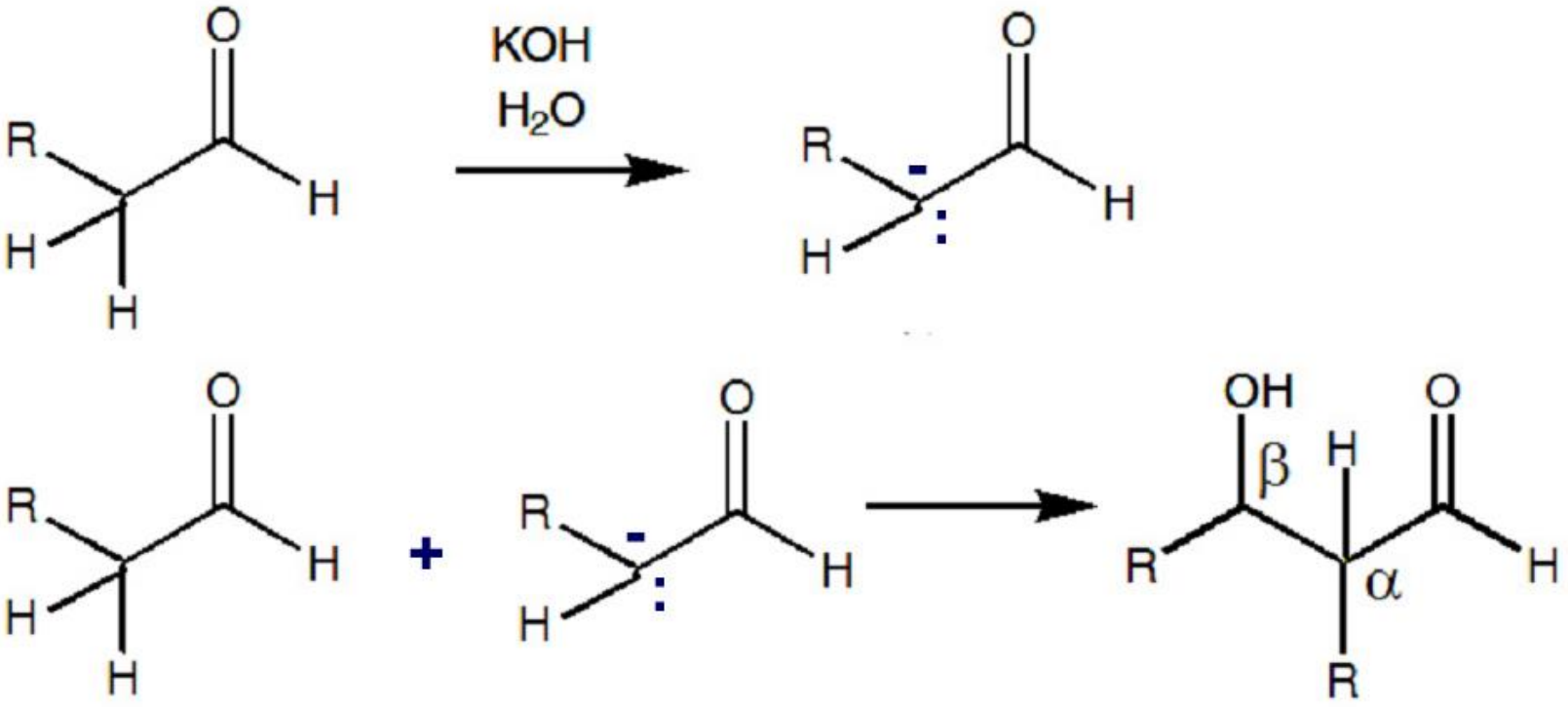


>C=O reduction

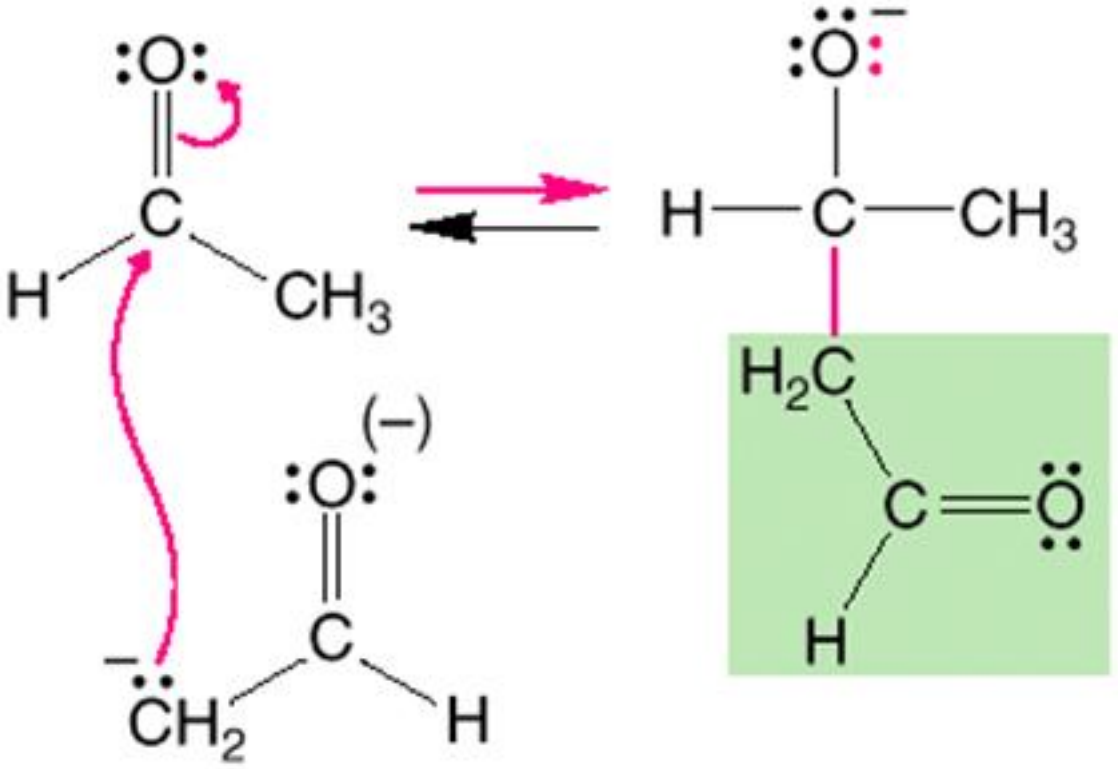
- Reaction with hydride ion H:$^-$
- Addition of proton

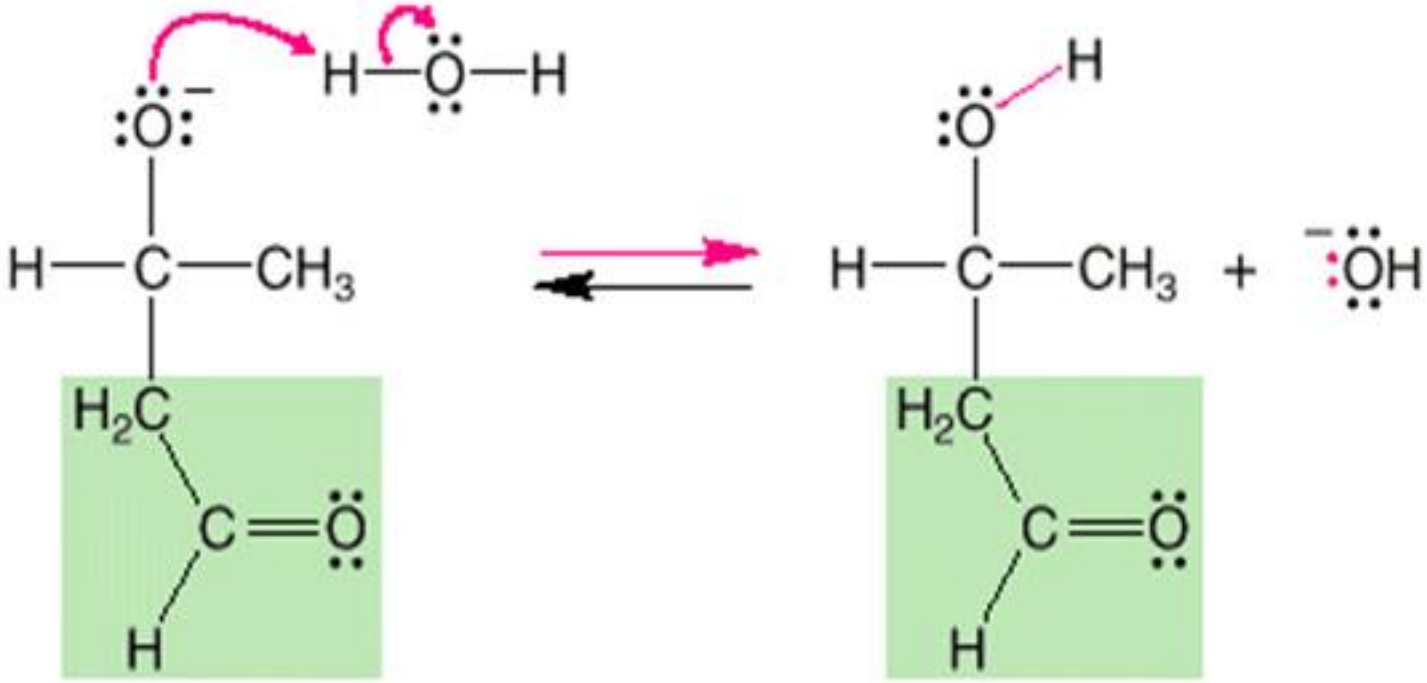


Carbonyl α-carbon reactions

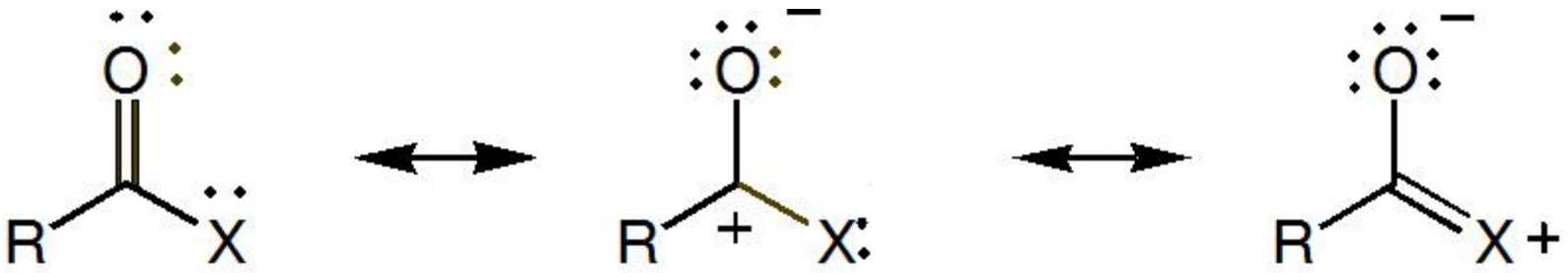


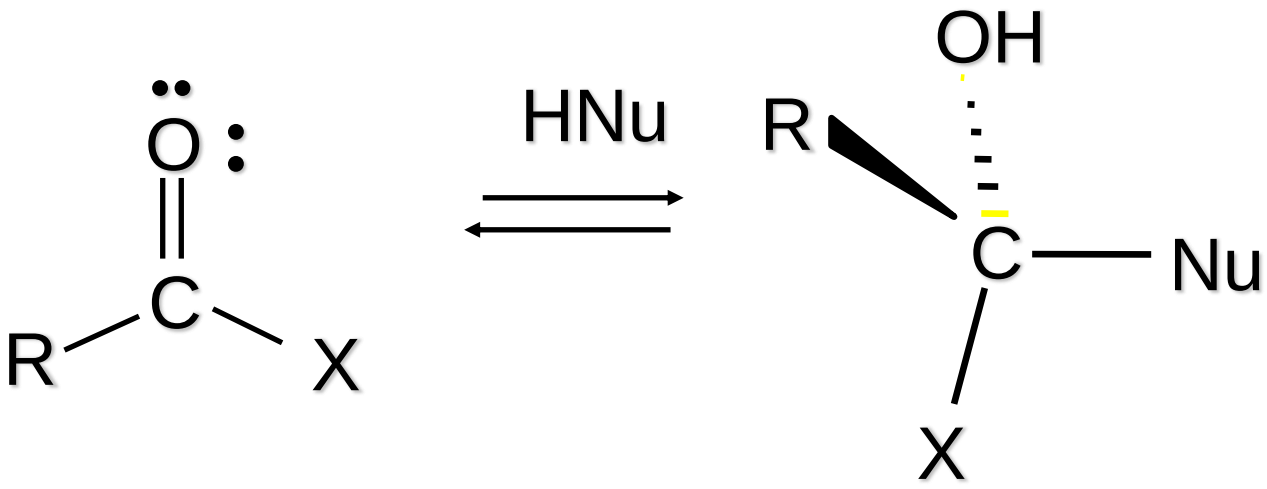
Condensation reaction

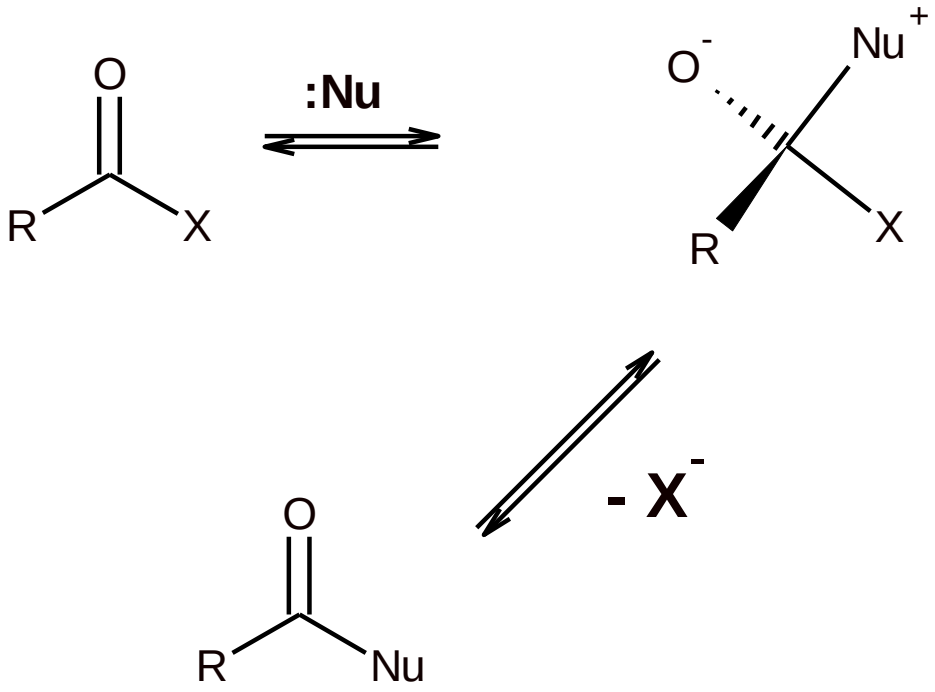




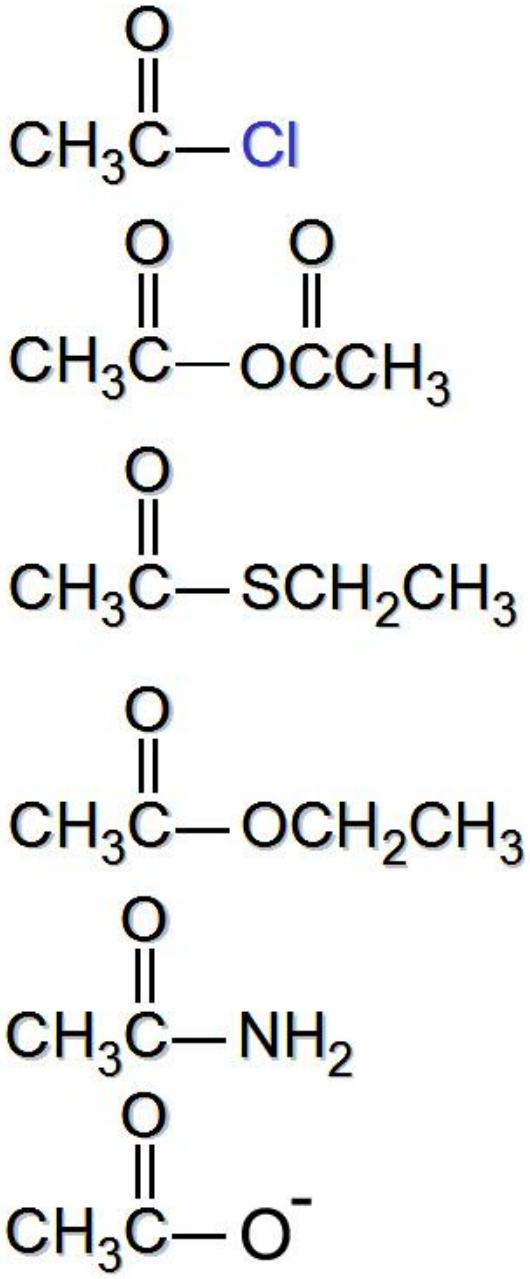
>C=O group stabilization by conjugation




O
C
R
X
HNu
OH
R
C
Nu
X

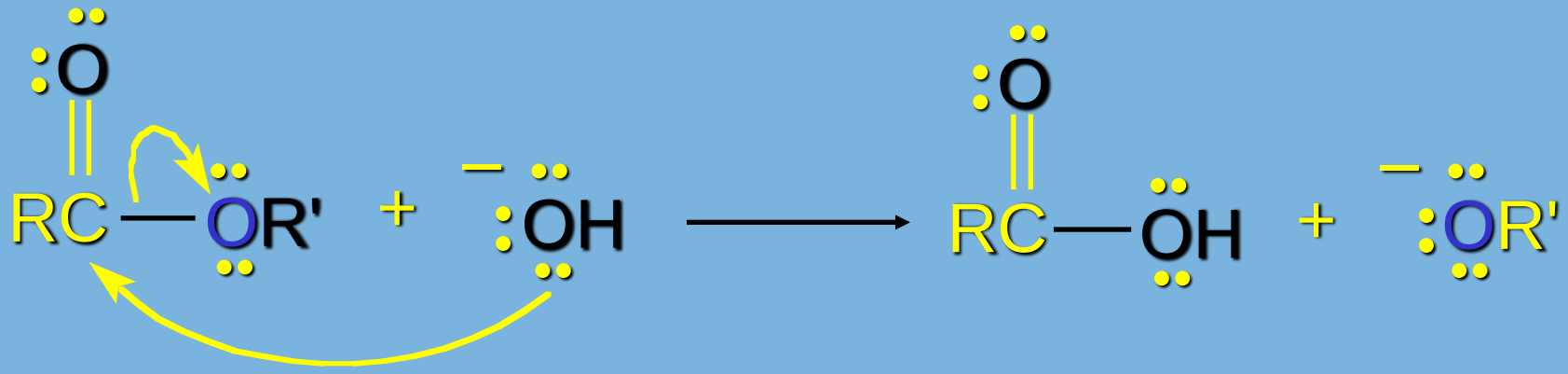

O
R
X
:Nu
O-
Nu+
R
X
- X-
O
R
Nu

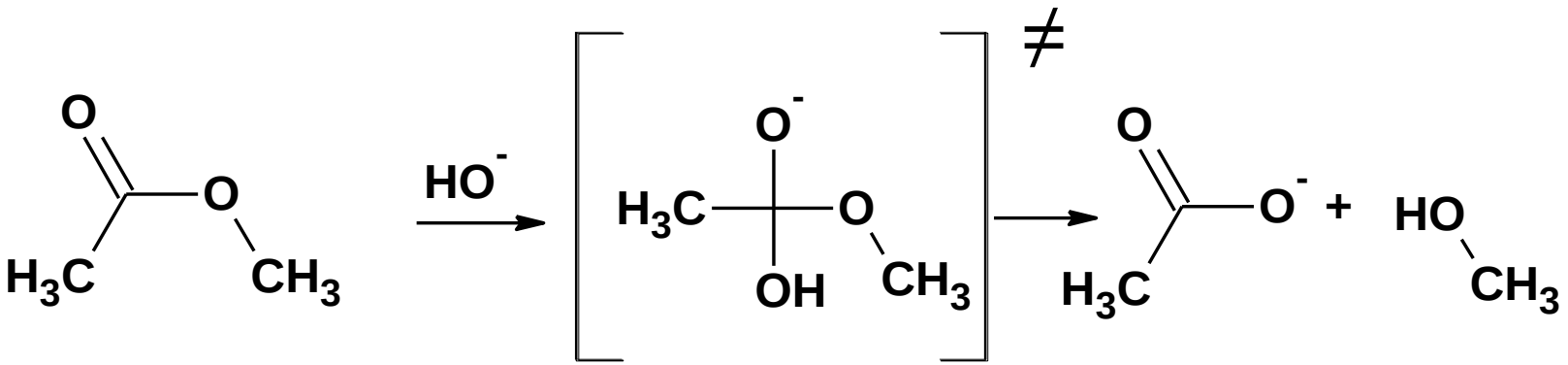
Inreasing reactivity

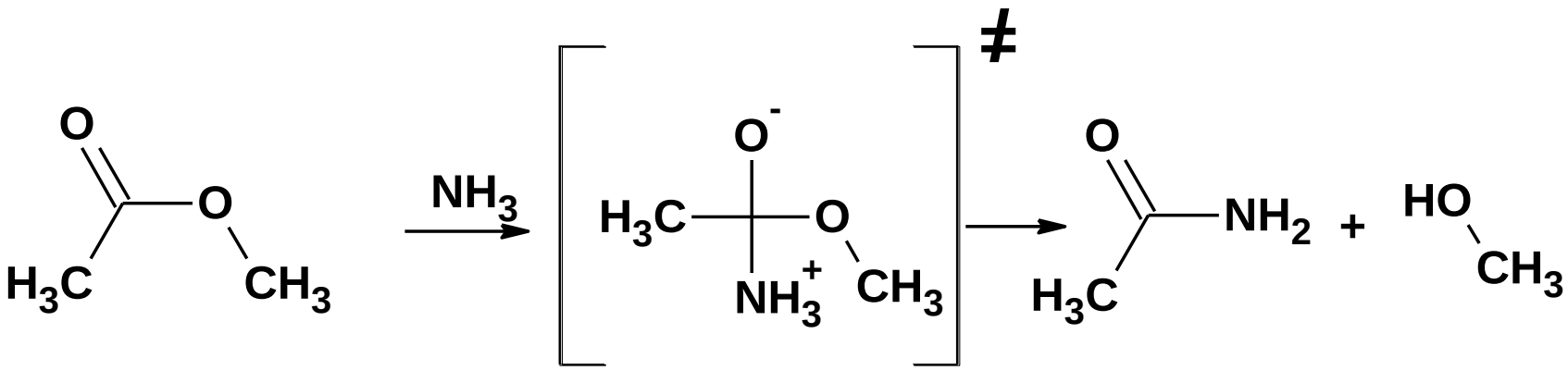


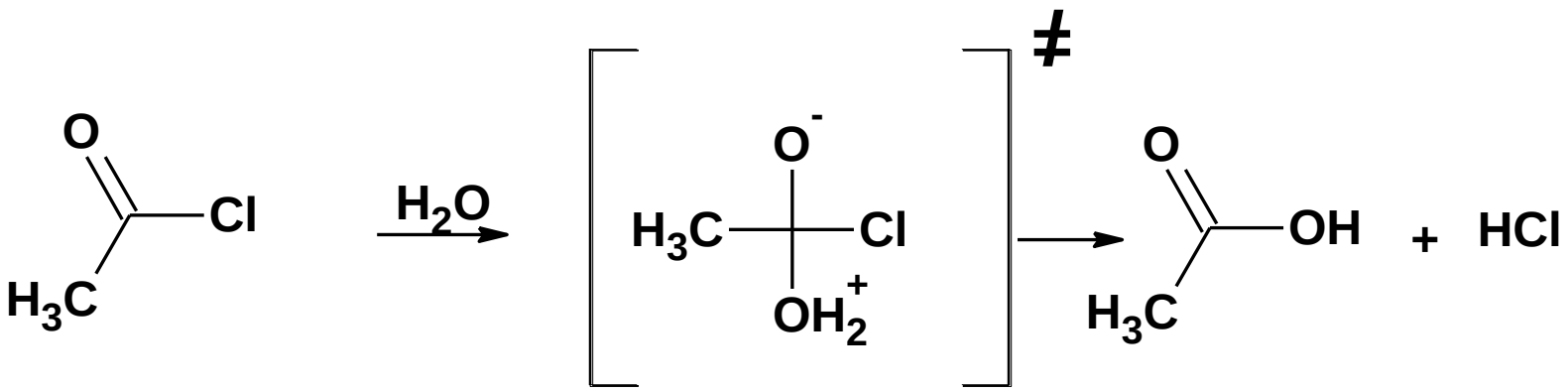
Initial state stabilization

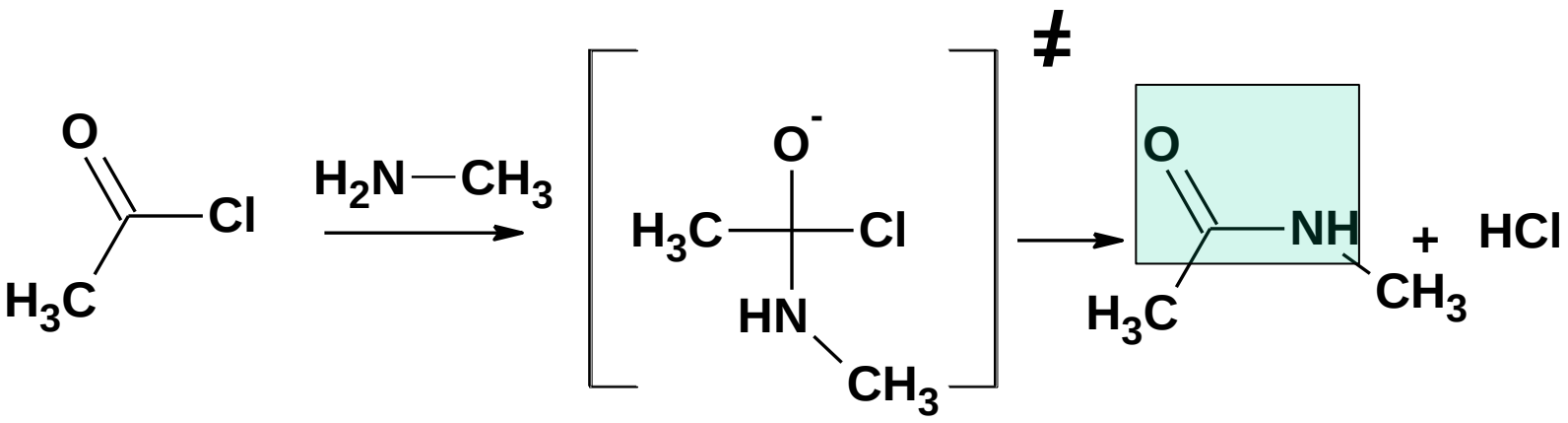
Ester alkaline hydrolysis




O
O
H3C
CH3
HO-
O-
H3C
O
OH
CH3
≠
O
O-
H3C
+
HO
CH3


O
O
H3C
CH3
NH3
O-
H3C
O
NH3+
CH3
≠
O
NH2
H3C
+
HO
CH3


O
Cl
H3C
H2O
O-
H3C
Cl
OH2+
≠
O
OH
H3C
+
HCl


O
Cl
H3C
H2N—CH3
O-
H3C
Cl
HN
CH3
≠
O
NH
+
HCl
H3C
CH3