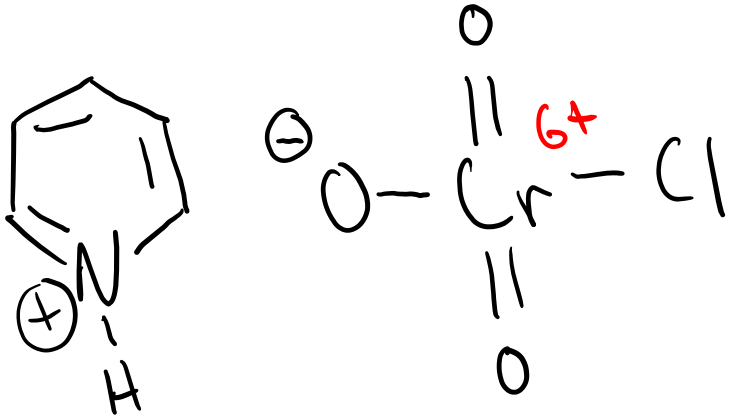
Oxidation State & Oxidation of Alcohols

2/3/2023

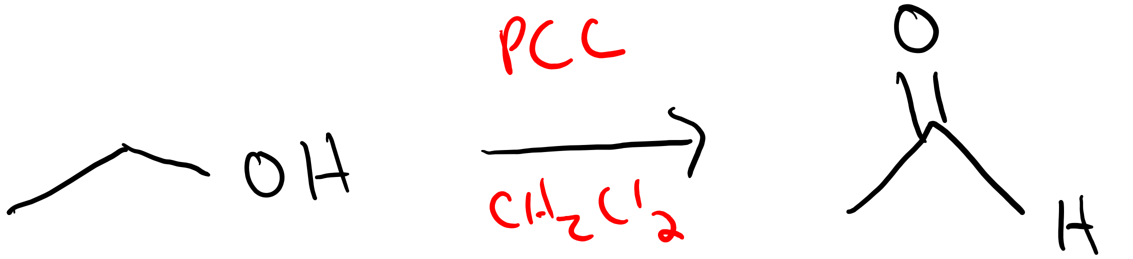
Chromium-based Reagents for Oxidizing Alcohols (12.10)

pyridinium chlorochromate



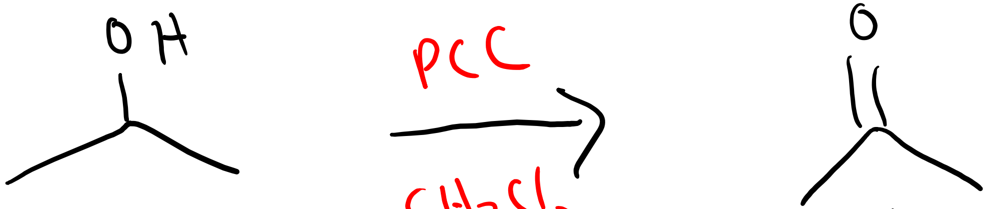
aka "PCC"

- requires anhydrous conditions - absolutely <u>no</u> H_2O! (CH_2Cl_2 solvent)
- extremely toxic + carcinogenic



1° alcohol

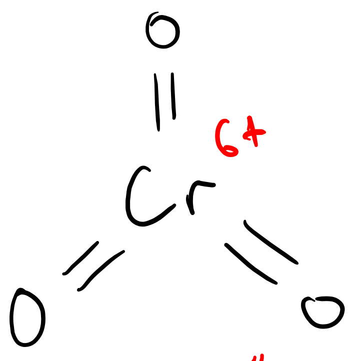
stops at aldehyde!



2°

ketone

Chromium-based Reagents for Oxidizing Alcohols (and aldehydes!!) (12.10)

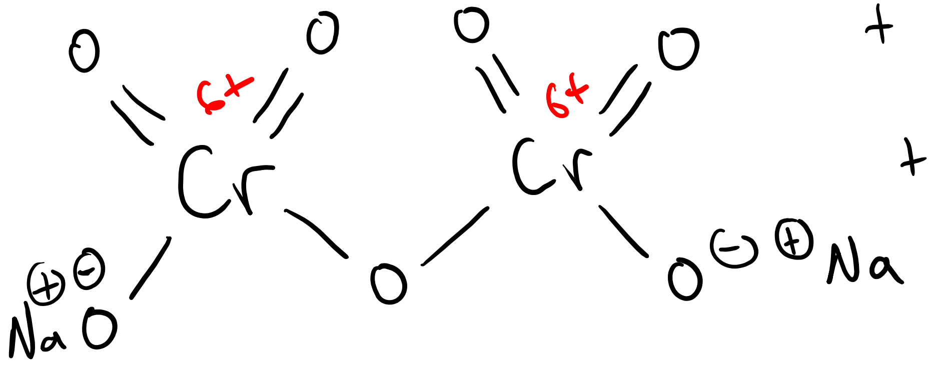


$+ H_2SO_4$

$+ H_2O$ (aqueous)

"CrO_3" aka Jones reagent

or

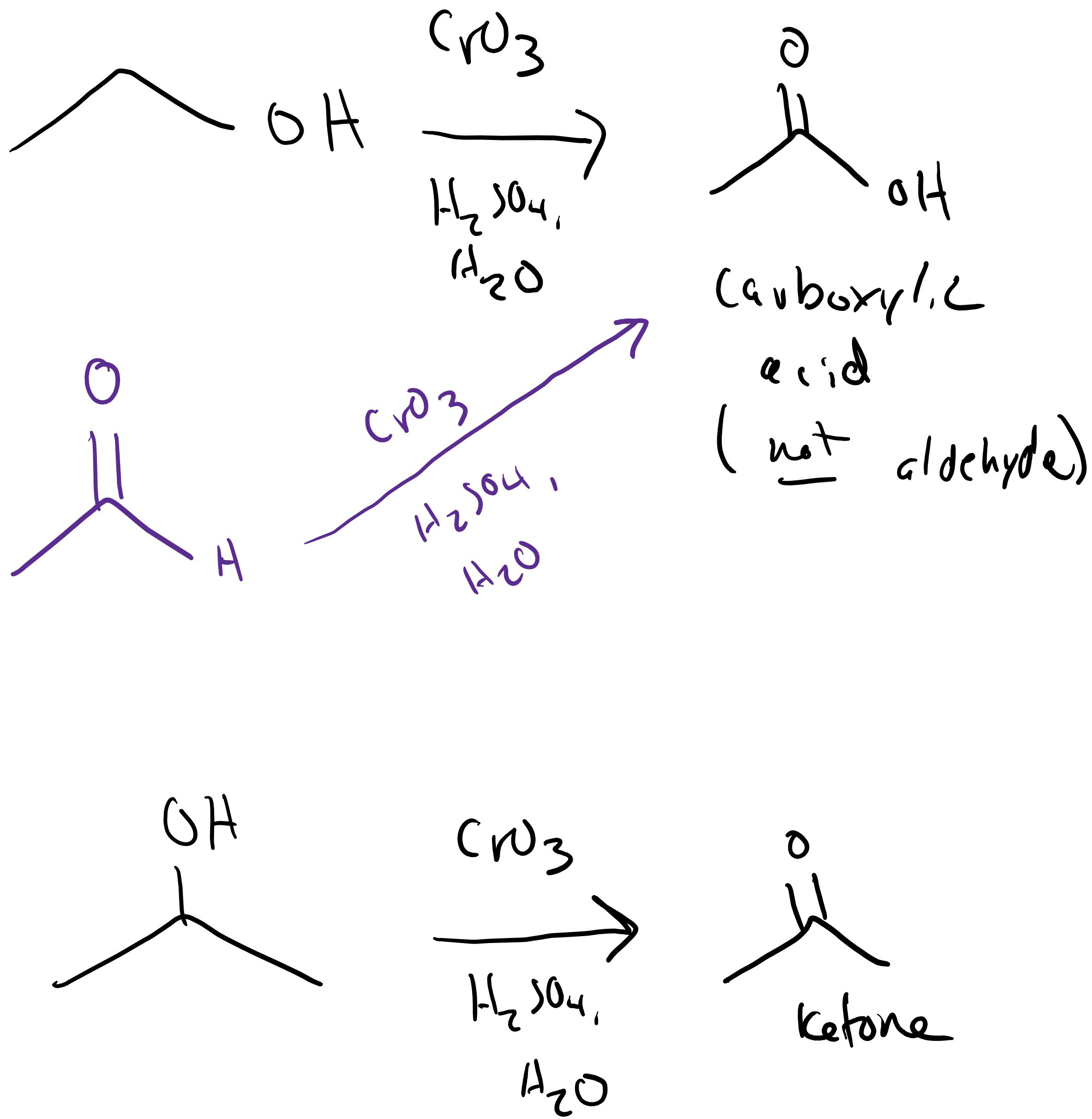


$+ H_2SO_4$

$+ H_2O$

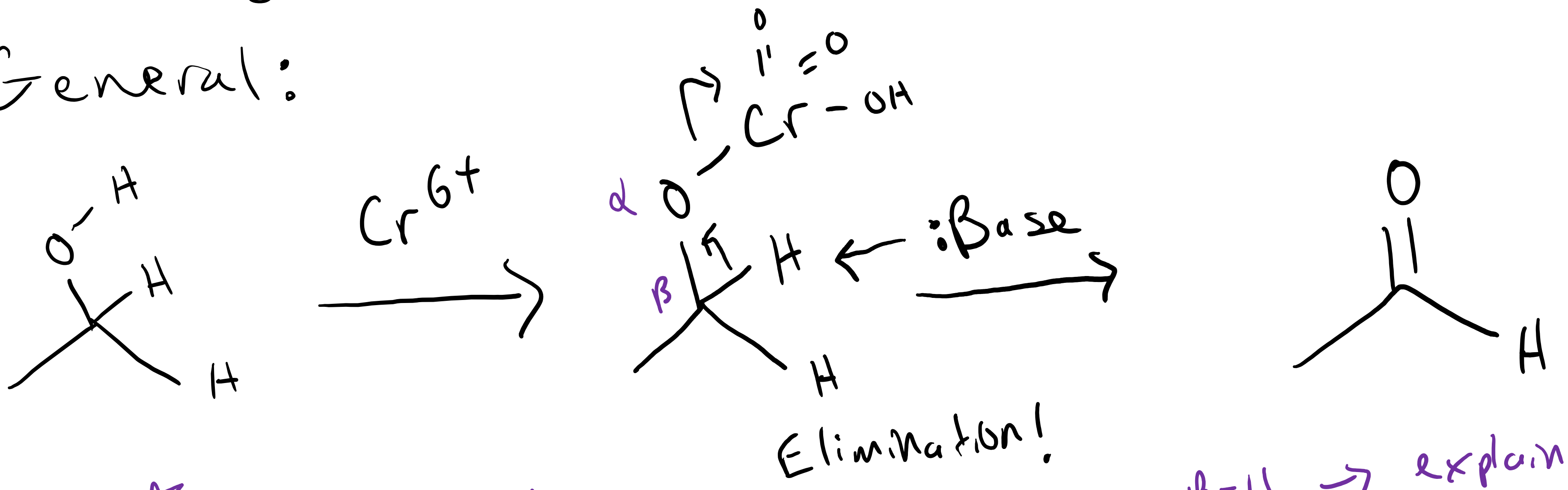
$Na_2Cr_2O_7$

sodium dichromate



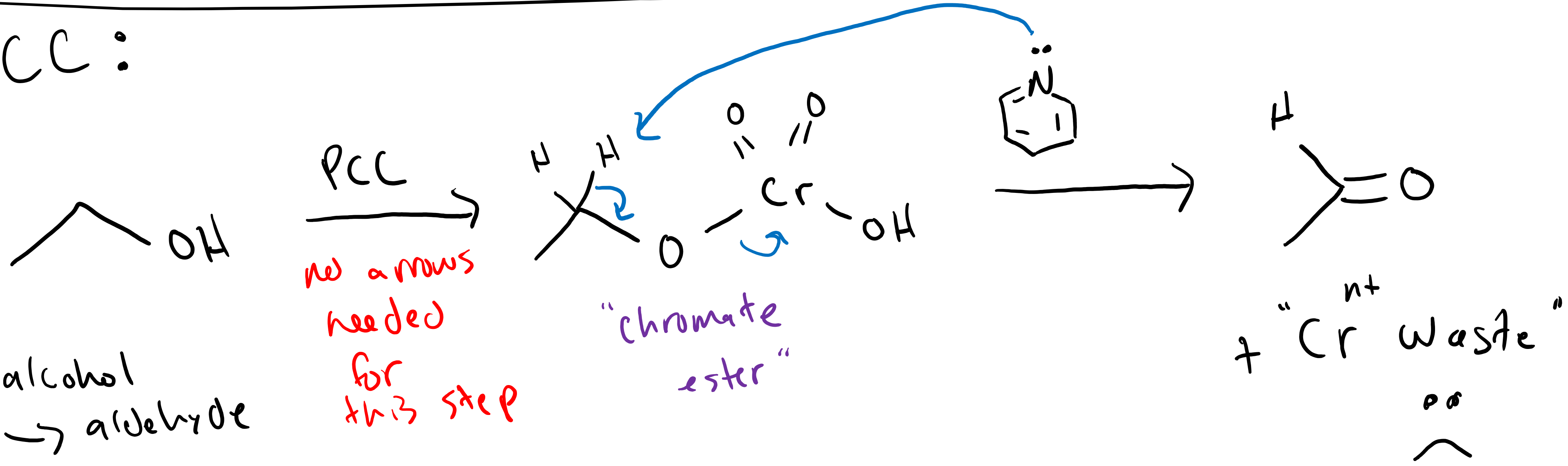
Oxidizing Alcohols with Chromium: Mechanism

General:



★ each oxidation step requires a β-H → explains 2° & 3° alcohol reactivity

PCC:

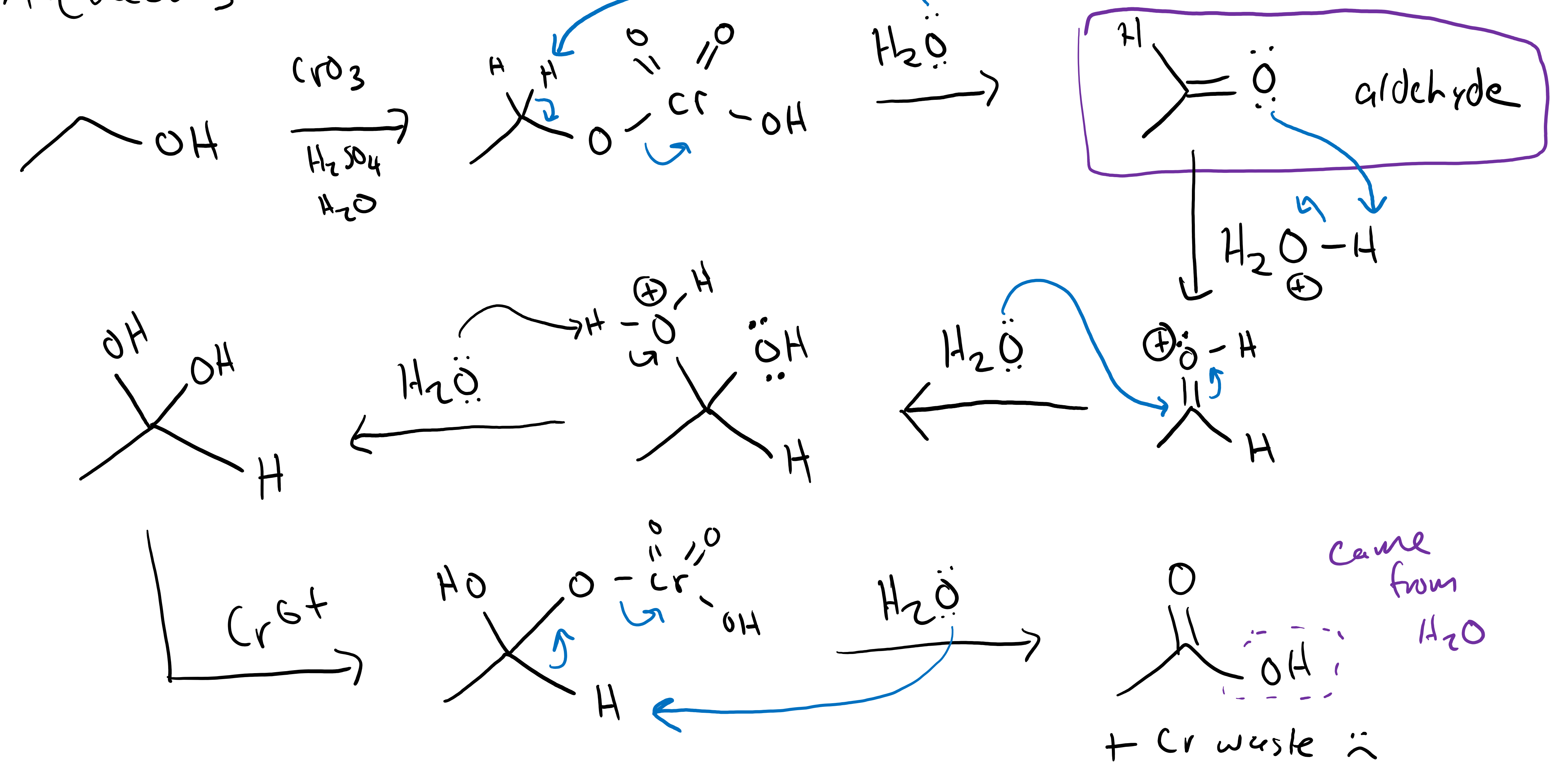


1° alcohol → aldehyde

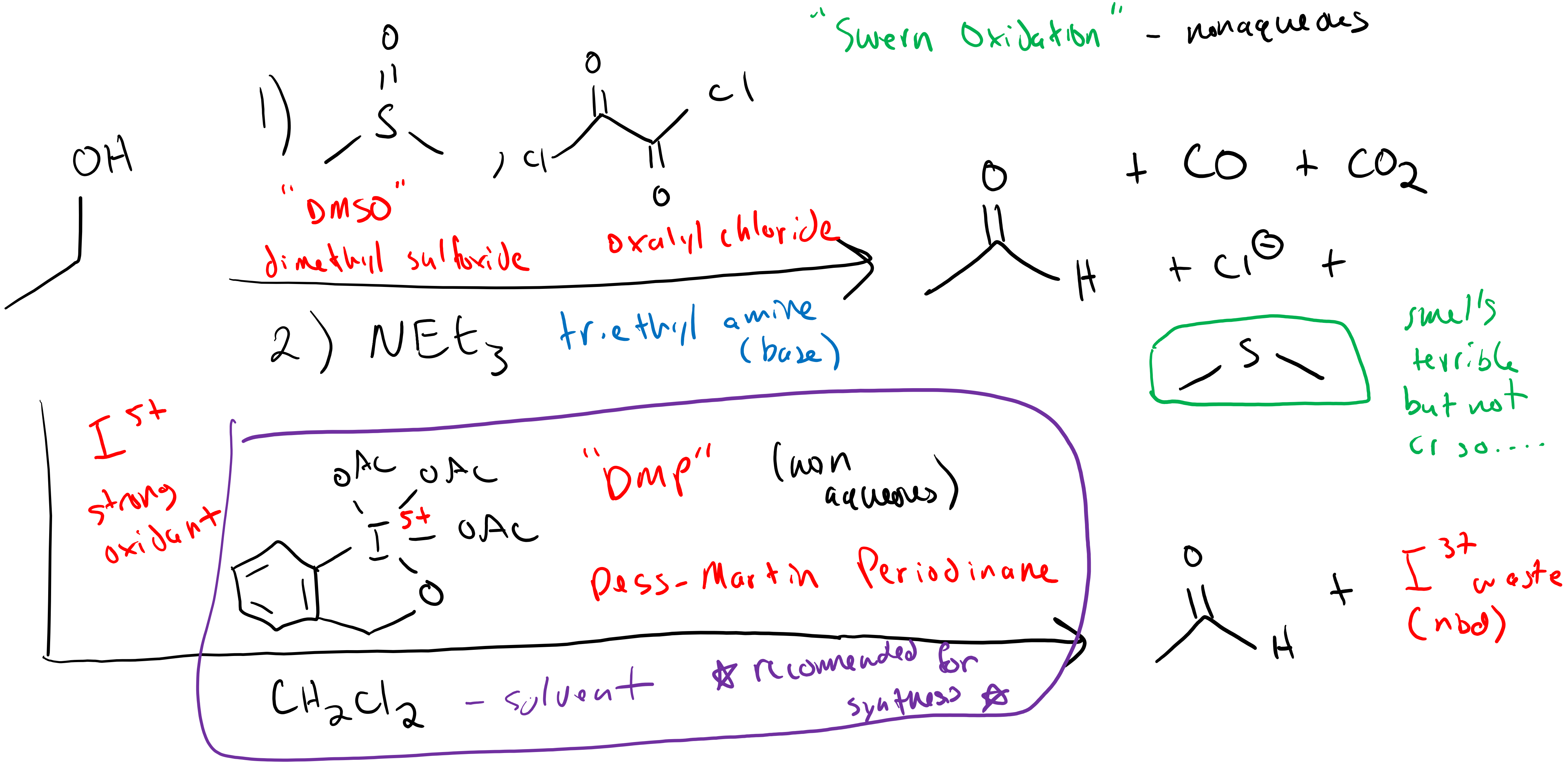
Oxidizing Alcohols with Chromium: Mechanism

Aqueous Cr^{6+}: 1° alcohol → carboxylic acid

mech starts here if reactant is aldehyde already



Organic Oxidizing Agents: "Greener" Alternatives



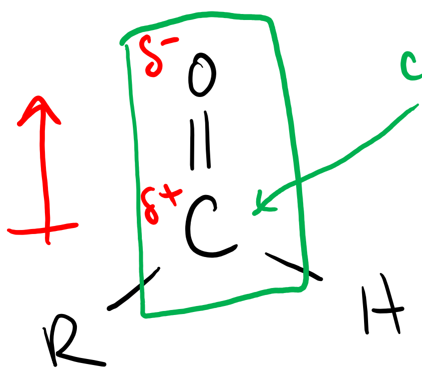
★ Both recipes will also convert 2° alcohol into ketone ★

Aldehydes and Ketones as Electrophiles (19.4)

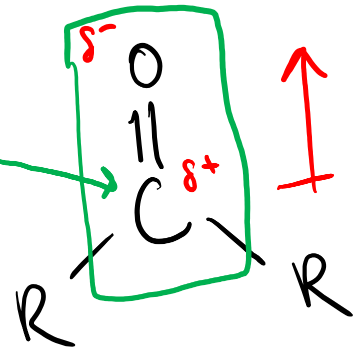
"carbonyl group"

less bulky (H is very small)

easier to attack



carbonyl carbon



more bulky

harder to attack

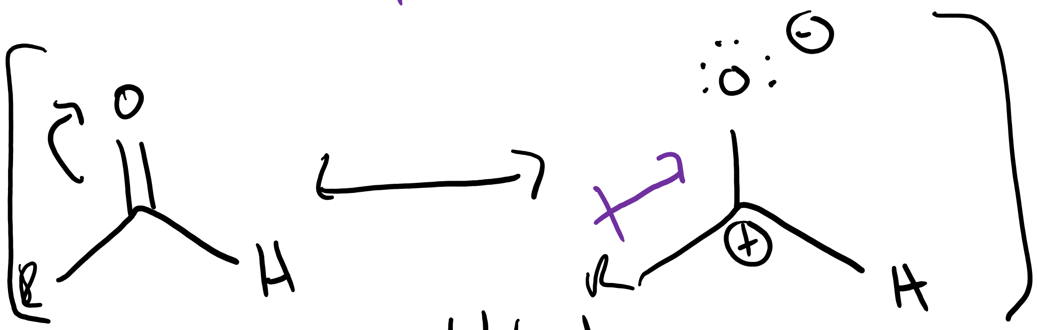
aldehyde

ketone

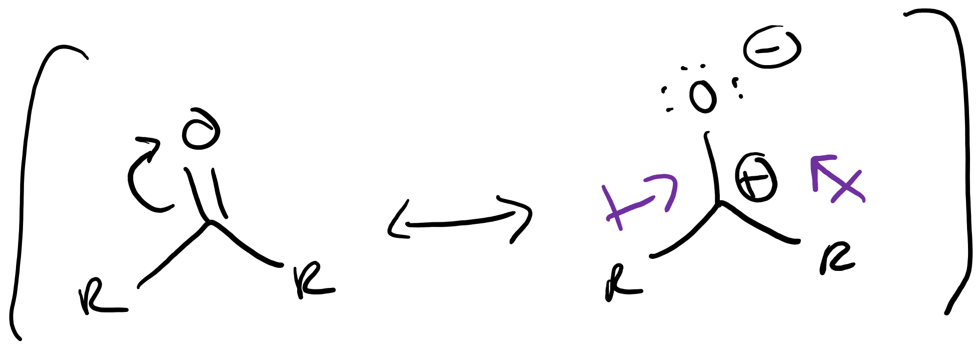
more E⊕ based on sterics AND electronics!

1 EDG stabilize C⊕

2 EDG stabilize C⊕



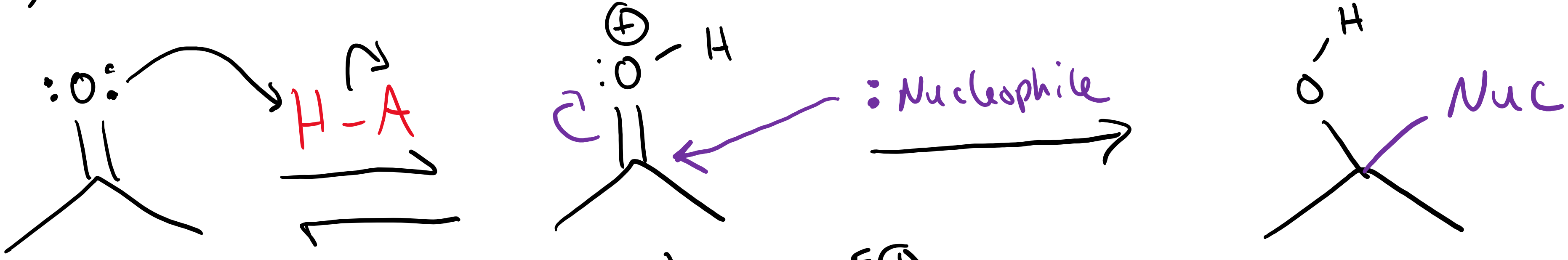
aldehyde



ketone

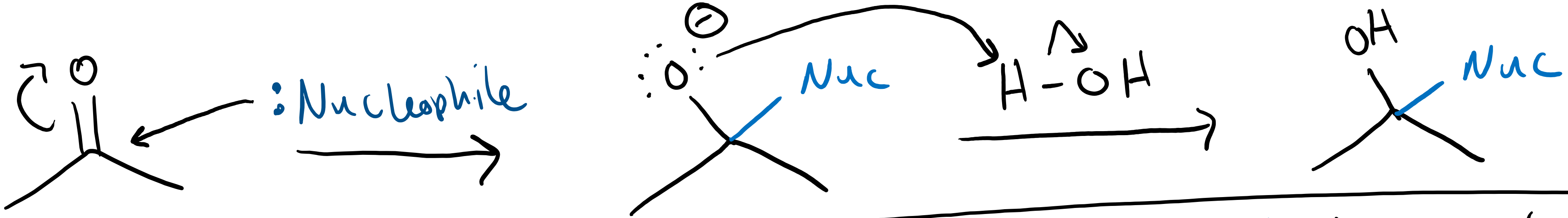
Nucleophilic Addition to Aldehydes and Ketones

A) Under acidic conditions (weak nucleophile)



even stronger E⊕

B) Under basic conditions (strong nucleophiles) (nucleophile is base)



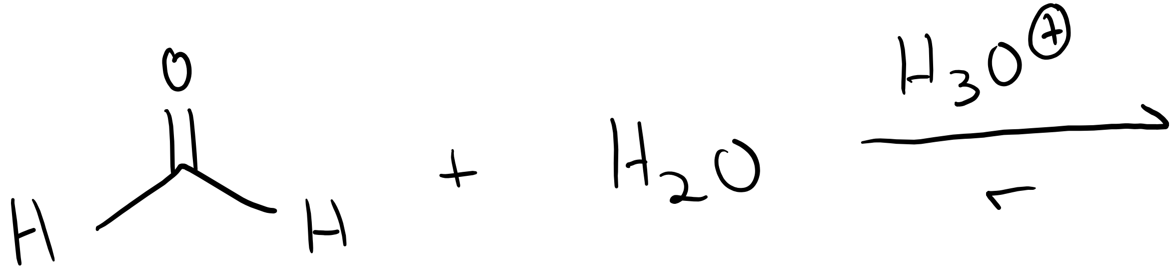
nucleophiles we will discuss:

Alcohols (weak)
Amines (moderate)
reversible

irreversible
Hydride ($H:^{\ominus}$) (strong)
Carbanion ($C^{\ominus}$) (strong)

Oxygen Nucleophiles (19.5)

Formation of hydrates:



mechanism: