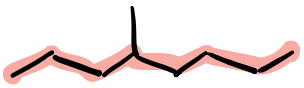
Chapter 19 Aldehydes & Ketones

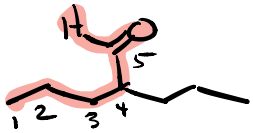
Nomenclature

butane

butanal



4-methyl octane

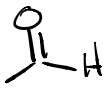


4-propylpentanal

formaldehyde

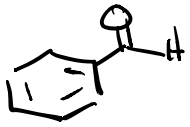
C-H

formal



acetaldehyde

⇒ ethanal



benzaldehyde

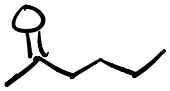
butane

butanone

hexane

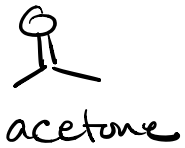
3-hexanone

ethyl propyl ketone

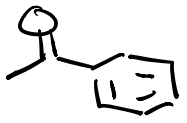


2-hexanone

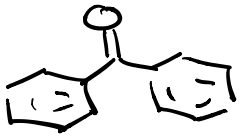
methyl butyl ketone



acetone



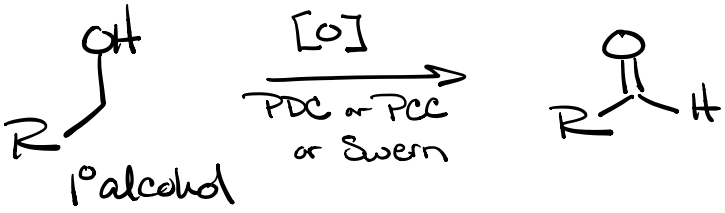
acetophenone

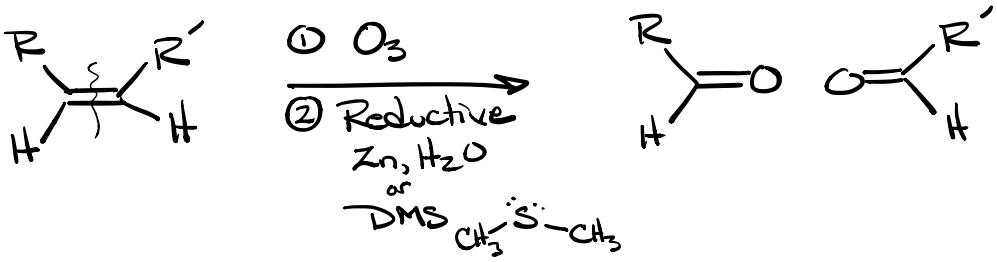


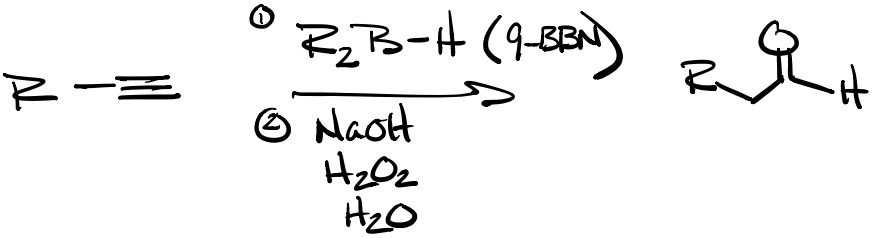
benzophenone

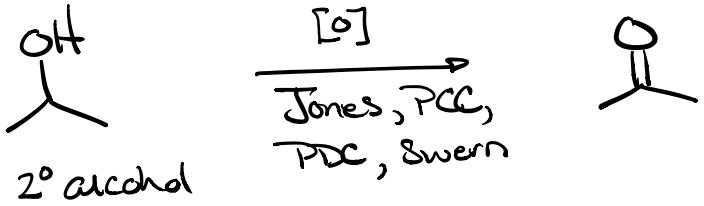
acet group

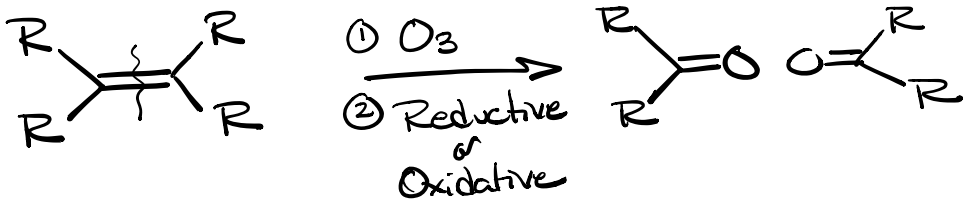
Formation of Aldehydes & Ketones

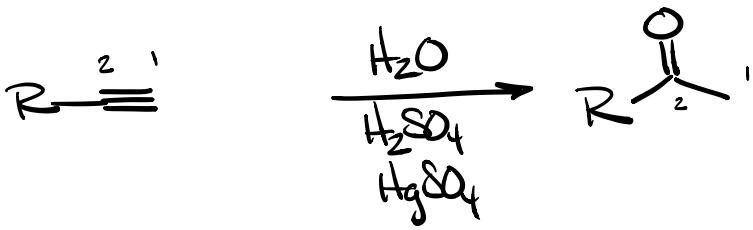


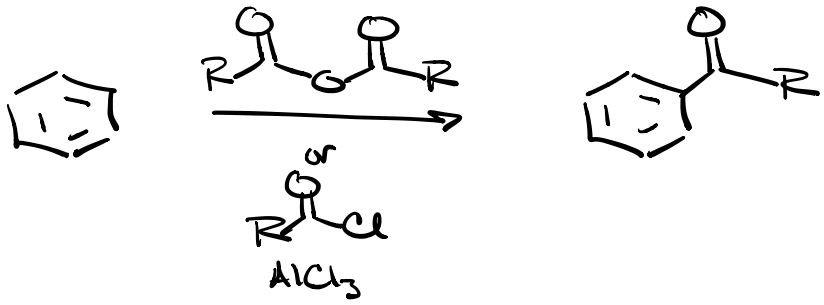


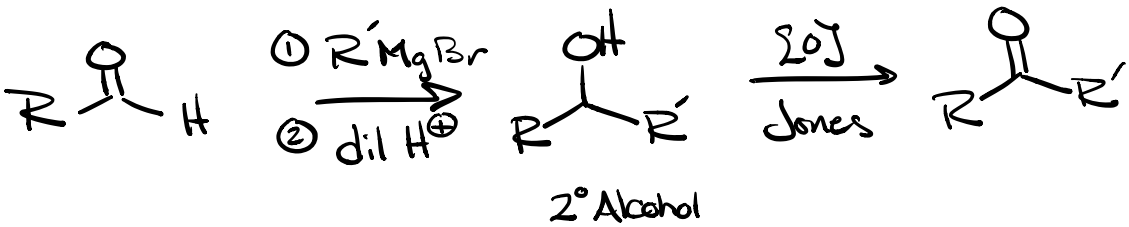


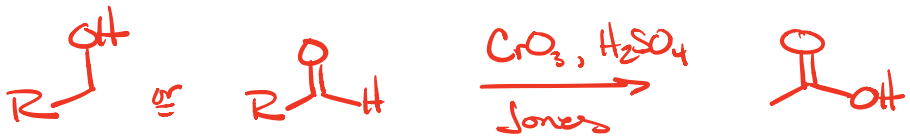

[O]
Jones, PCC,
PDC, Swern
2° alcohol

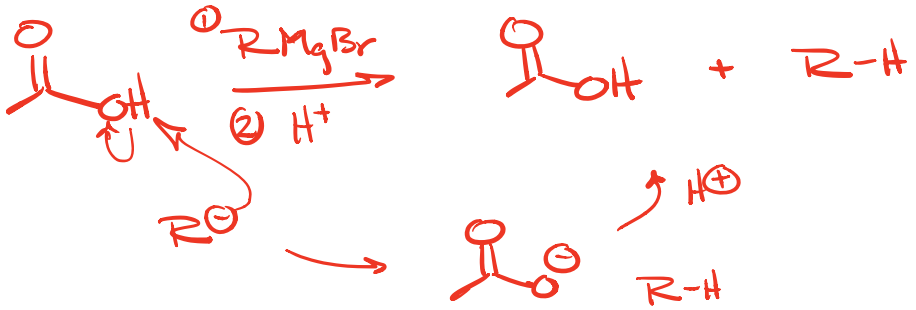

① O3
② Reductive
or
Oxidative


H2O
H2SO4
HgSO4

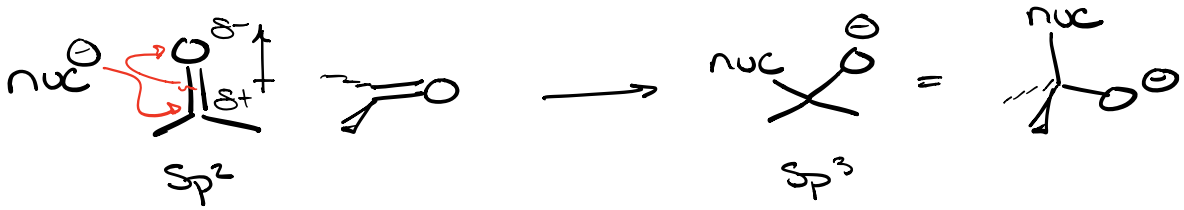

or
AlCl3

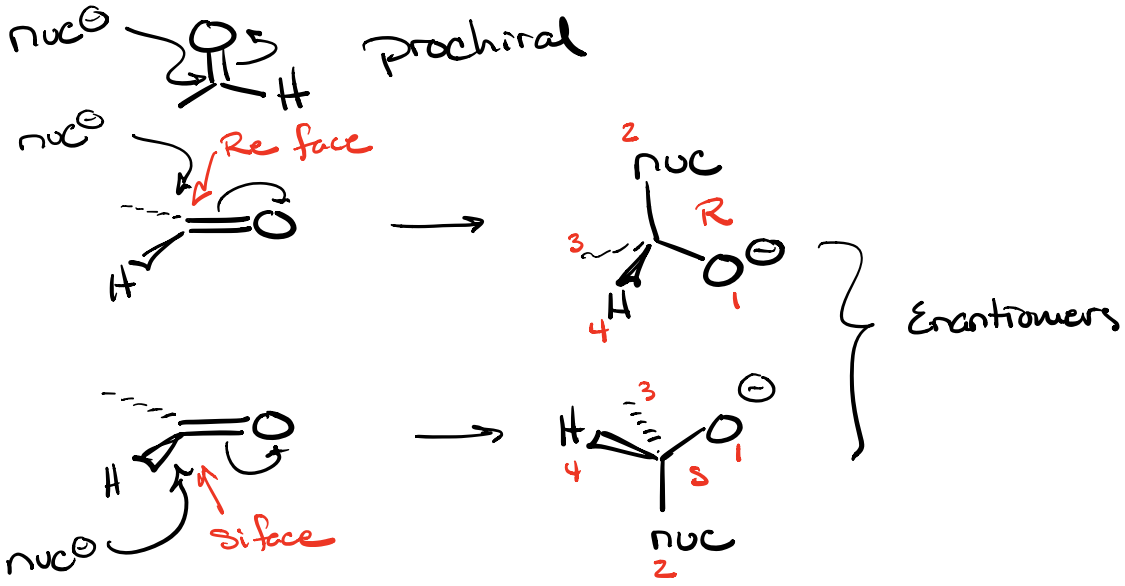

① R'MgBr
② dil H⊕
2° Alcohol
[O]
Jones


or
CrO3, H2SO4
Jones



Nucleophilic Addition to Carbonyl

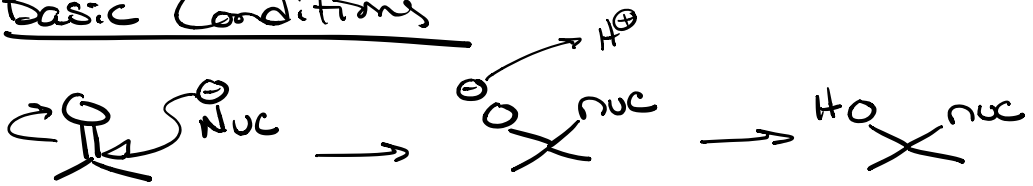




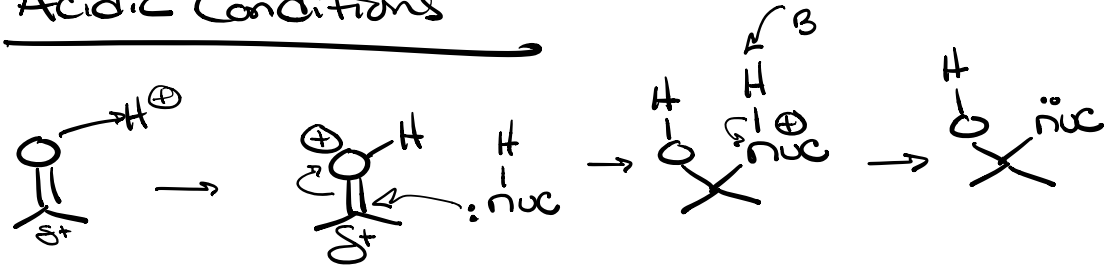
Many types of nucleophiles

Oxygen	Sulfur	Nitrogen	Hydrogen [H:]	Carbon
H_2O	H_2S	NH_3	$^{\ominus}BH_4$	R-MgBr
R-OH	thiols	$R-NH_2$	$^{\ominus}AlH_4$	$^{\ominus}CN$
HO OH	HS SH	R–N–H (R)		Ph, ⊕ ⊖, R; Ph–P–C–R; Ph; Wittig Reagent
				$^{\ominus}\equiv R$

Basic Conditions

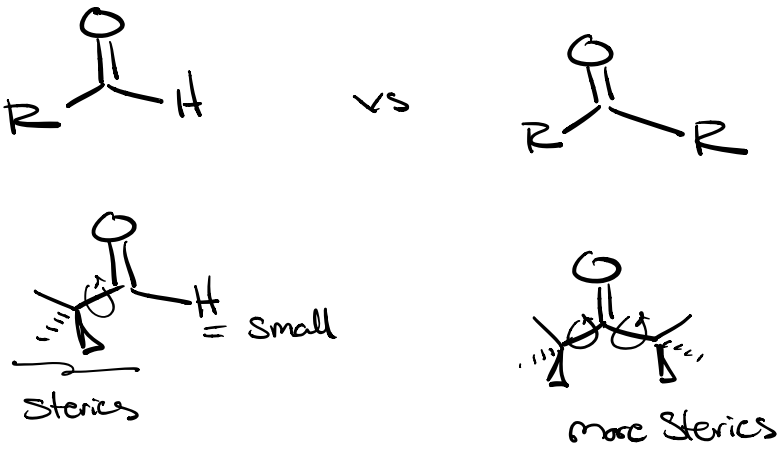


Acidic Conditions

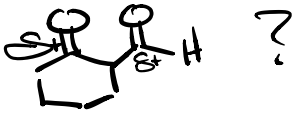


Reactivity of Aldehydes vs. Ketones

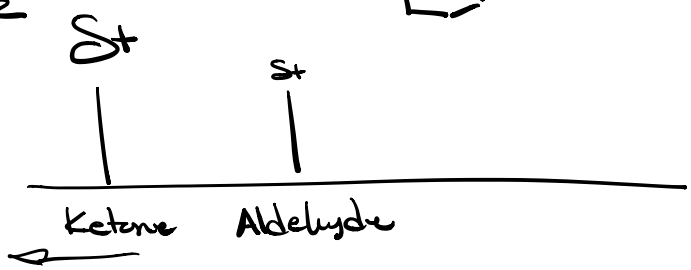
- Steric
- Electronic



Electronic



CNMR

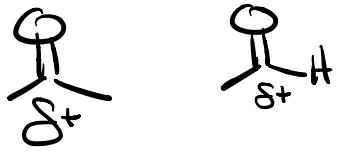


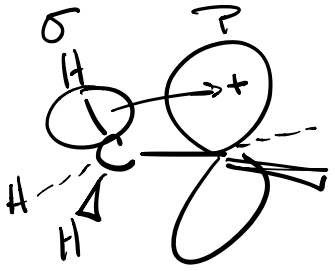
Fact

Book

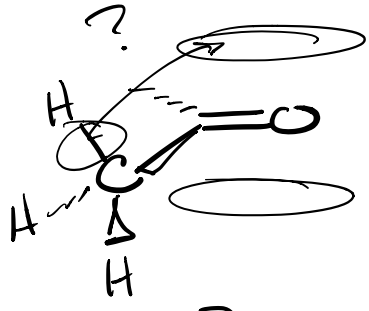
Wrong

Actually





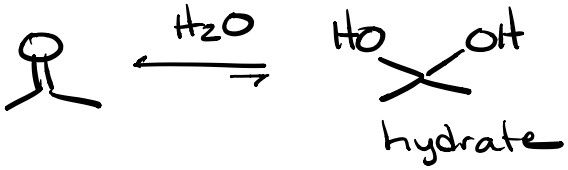
Hyperconjugation
⟹ Induction
Inductively donating



In absence of C^+
Alkyl groups are EWG

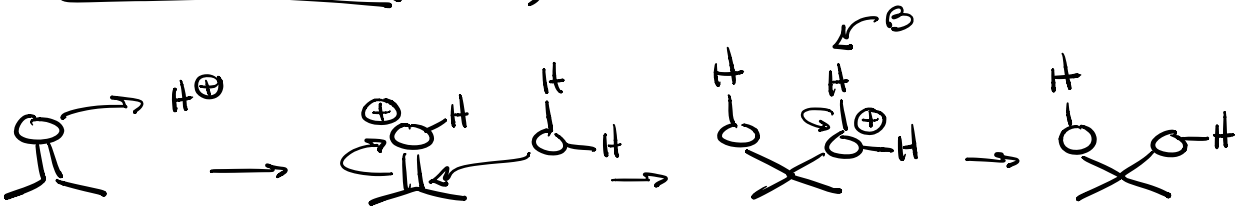
EWG ?

Hydration

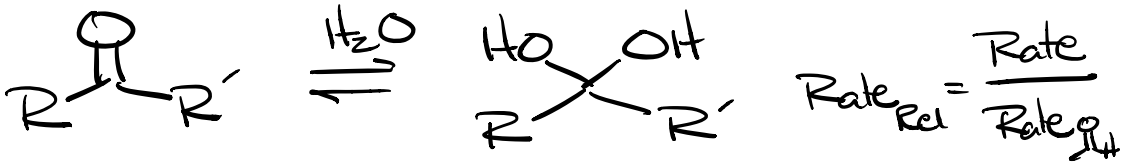


hydrate

Mechanism (Acidic)



hydrate



Rel Rate	22,000	2200	1	0.09	0.0018

Increasing St+ Electronics

Small Sterics

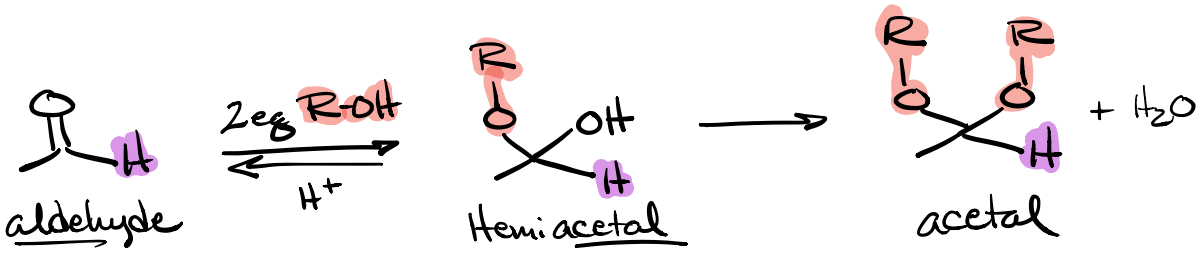
Sterics increasing

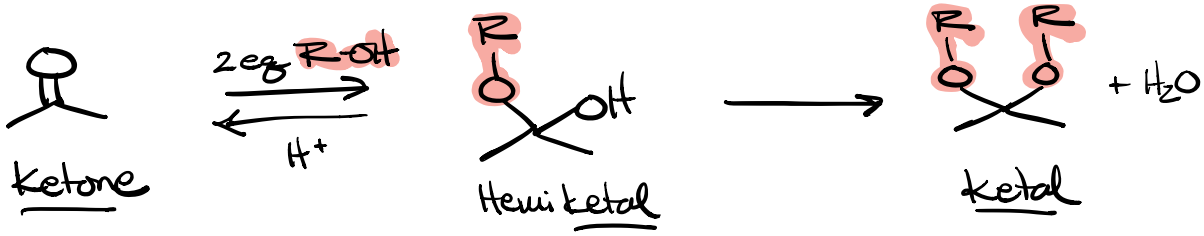
Sterics

In general ⇒ Aldehydes >> ketones

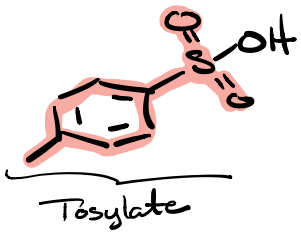
aldehydes much more Reactive than ketones due to lower Sterics.

Acetal/Ketal Formation



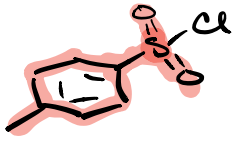


Acid



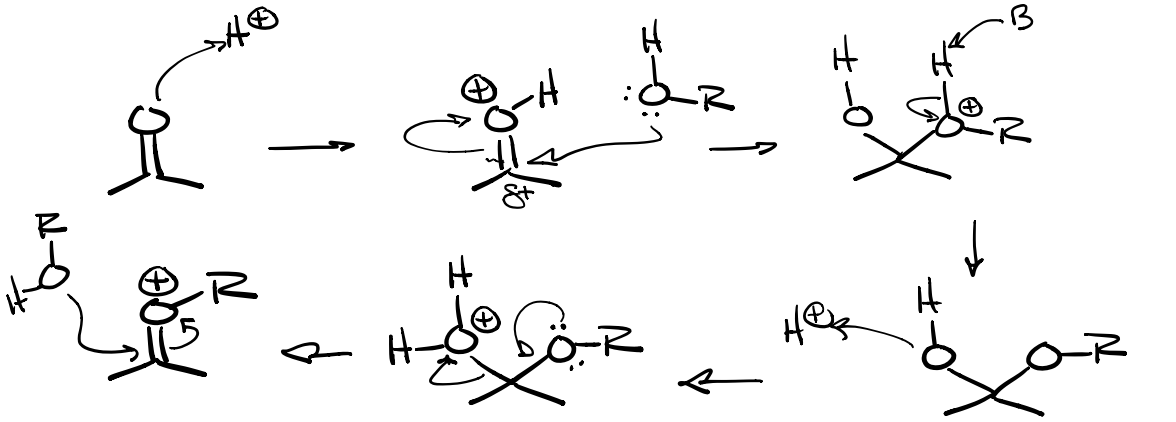
Para-toluLsulfonic acid

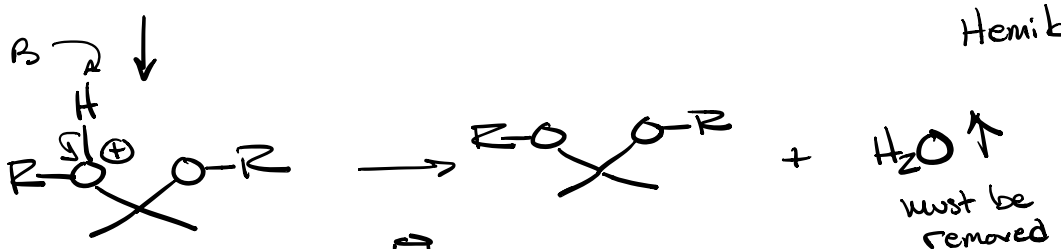
PTSA or TsOH

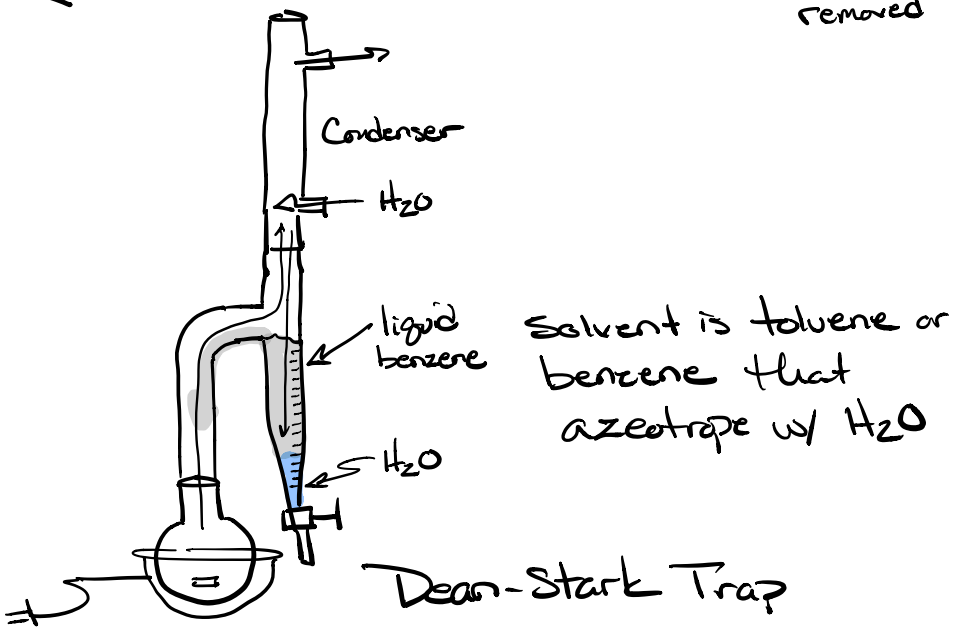


= TsCl

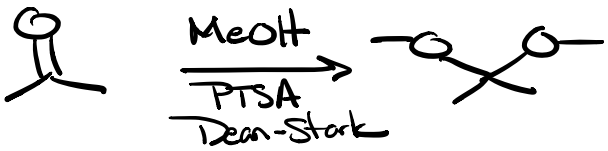
Mechanism

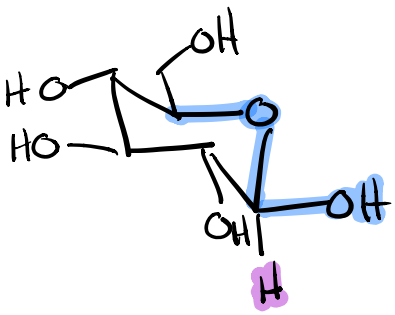






Solvent is toluene or benzene that azeotrope w/ H_2O



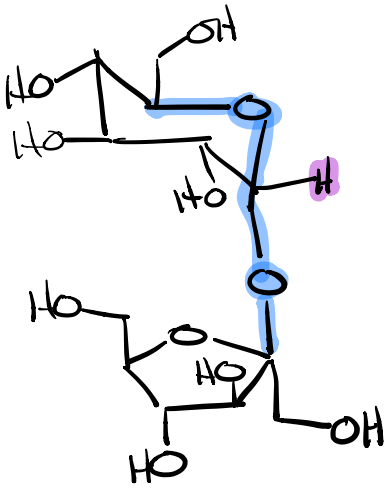


Hemiacetal

D-glucopyranose

D-glucose

monosaccharide



Acetal

Sucrose

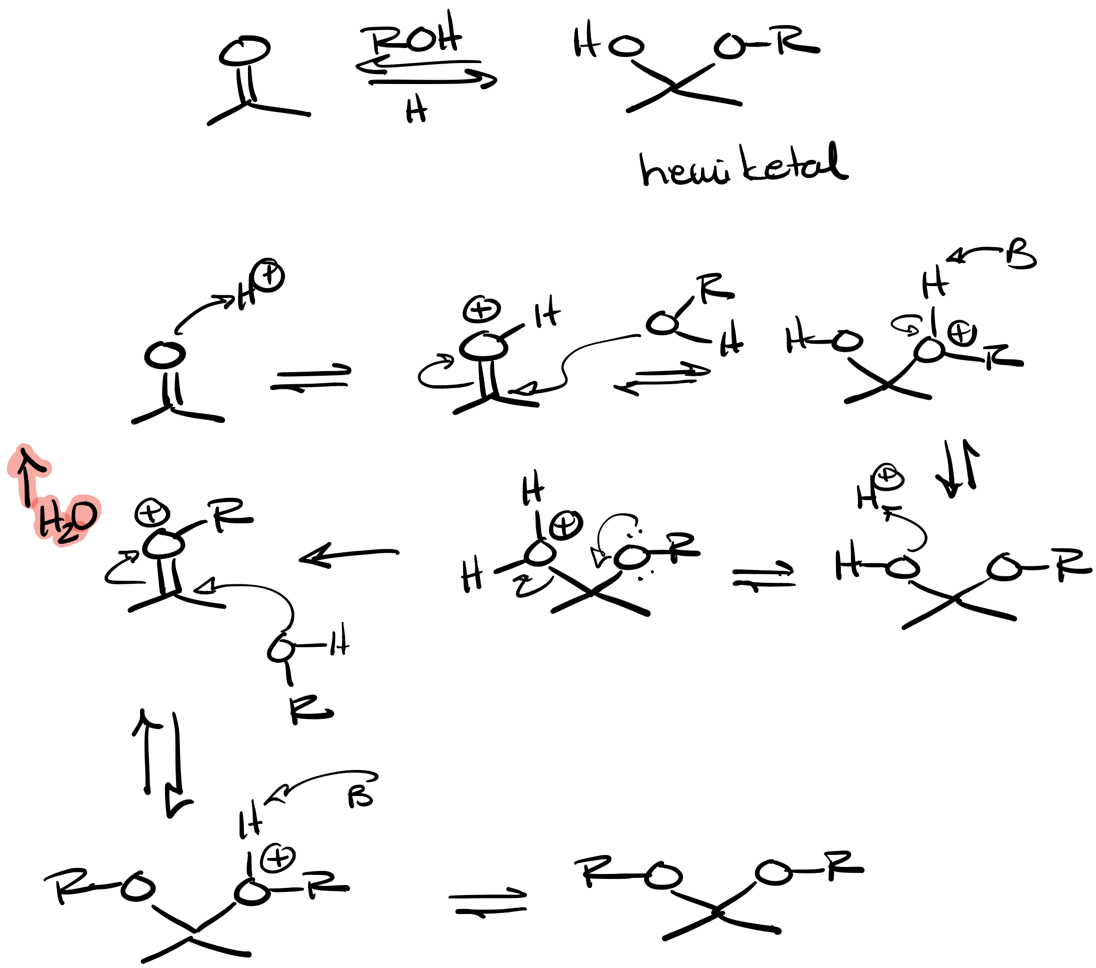
table sugar

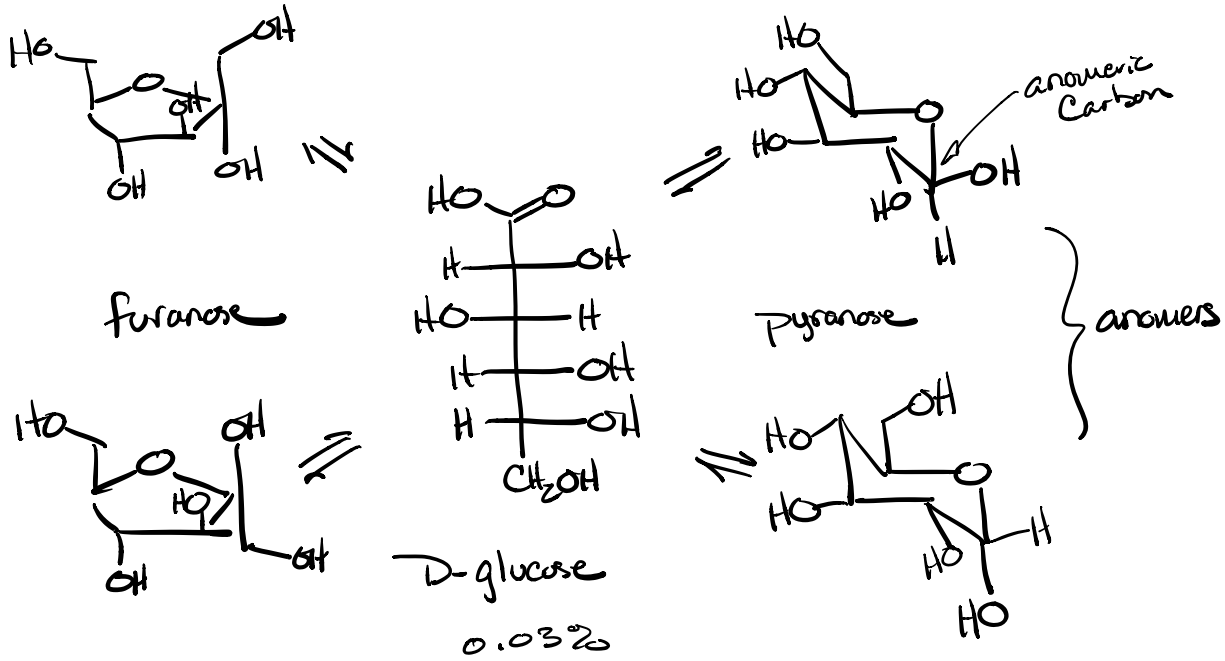
disaccharide

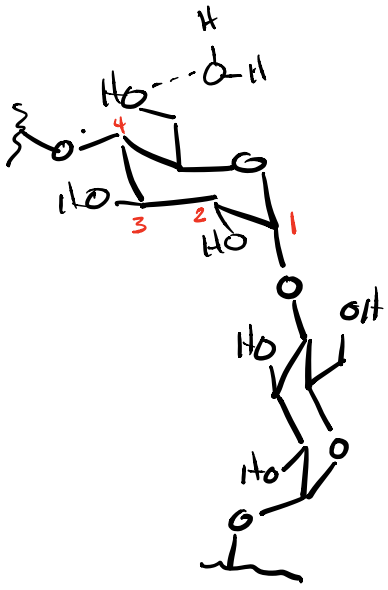
ketal

protecting

group


ROH
H
hemiketal
B
H_2O





β-1,4 glycosidic linkage

CO_2 $\xrightarrow{H_2O}$ CO_3H carbonic acid

M^+ + Acid