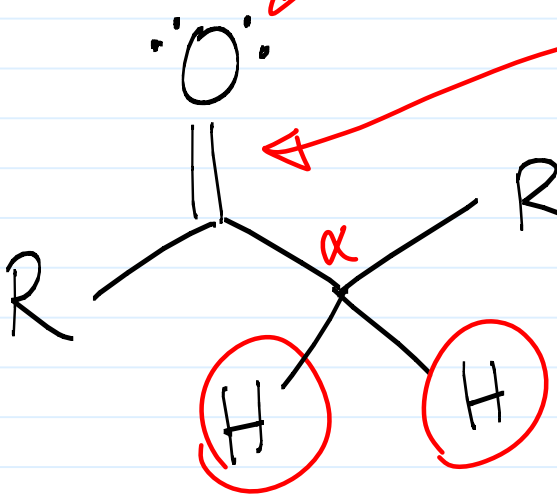
Carbonyl Chemistry

Note Title 3/27/2014



2 lone pairs (Brønsted + Lewis basic)

C=O double bond
↳ σ + π

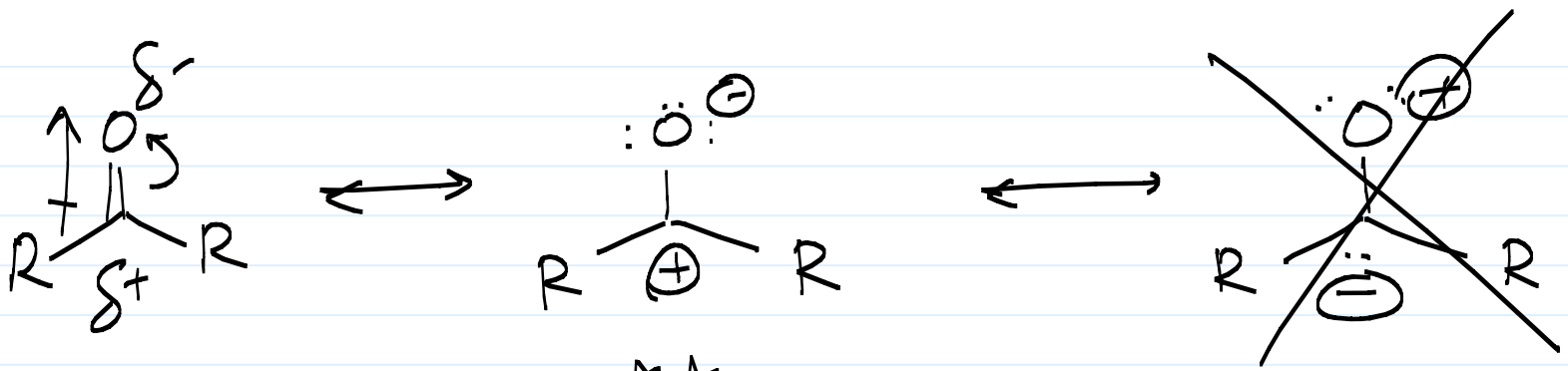
What does this do?

α-protons = acidic → they can be deprotonated

Very strong bond:

C=C 1.3 Å vs. C=O 1.2 Å

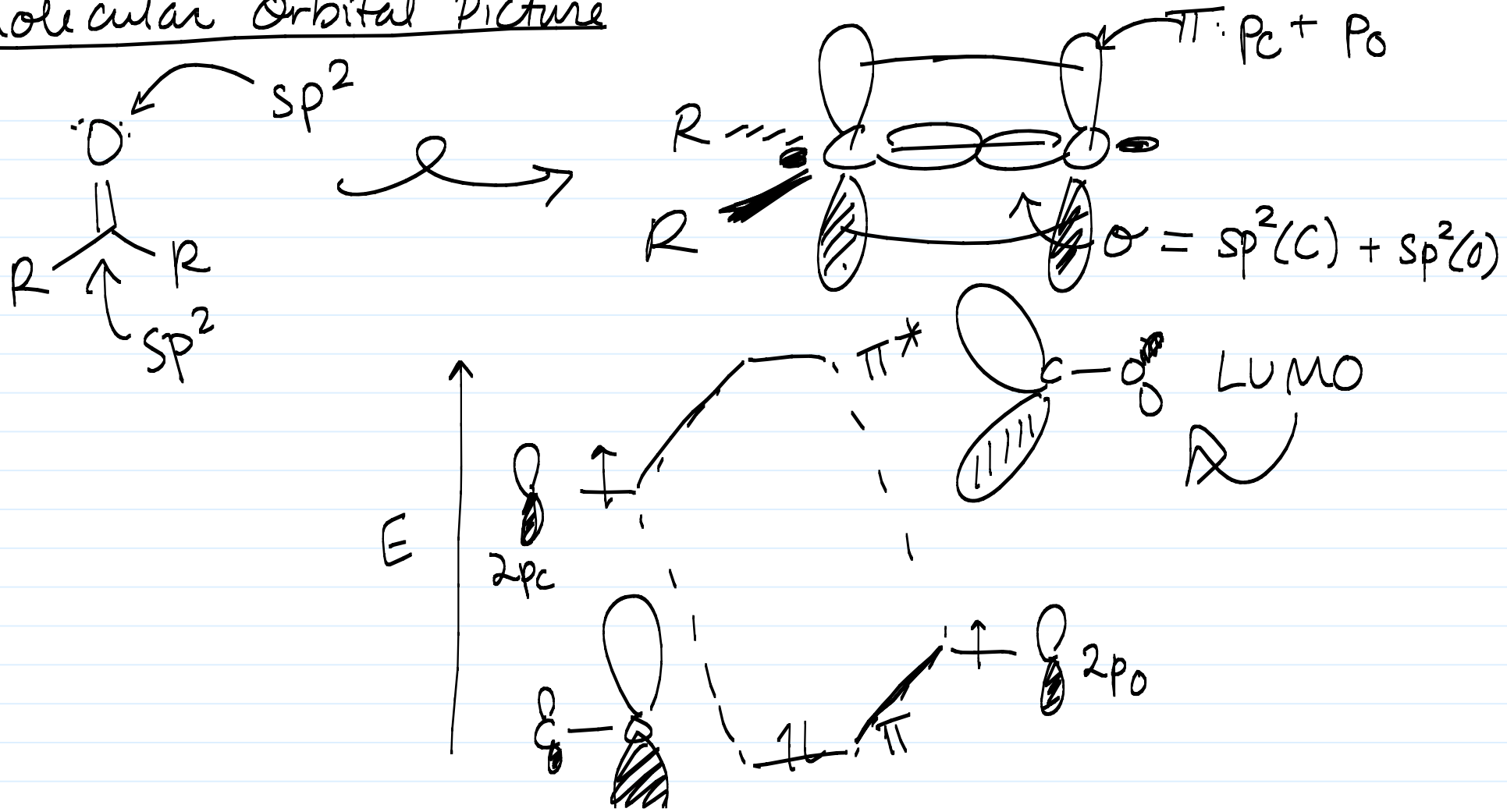
But also reactive:



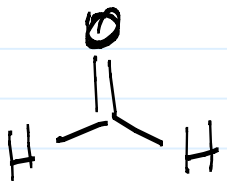
Electrophilic @ C

↑ will be attacked by nucleophiles.

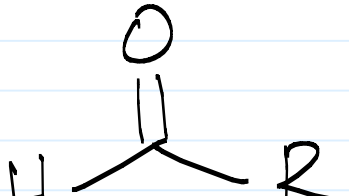
Molecular Orbital Picture



Nomenclature : Aldehydes & Ketones

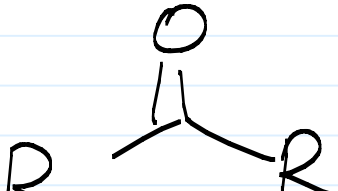


formaldehyde



aldehyde

carbon substituent

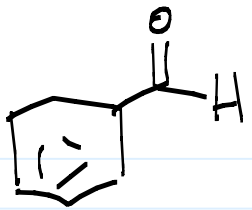


ketone

Naming Aldehydes

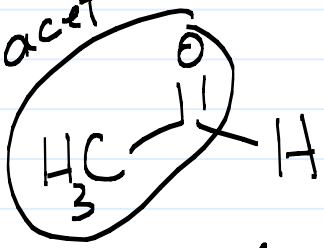
1) Drop "e" from alkane
2) Add "al"
3) Aldehyde group = #1 carbon
4) If 2 aldehydes, keep "e" and "dial"

exception:



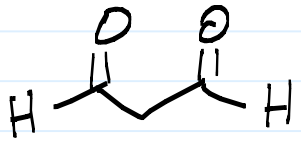
benzaldehyde

ex:



ethanal
(acetaldehyde)

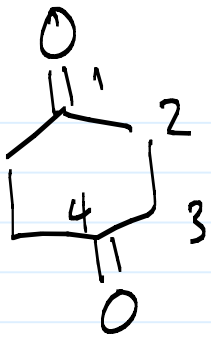
2-methylpentanal



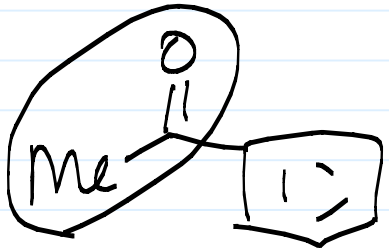
1,3-propane dial

Naming Ketones:

1) Drop "e" from alkane
2) Add "one"
3) If not highest priority, ketone becomes "oxo" group.

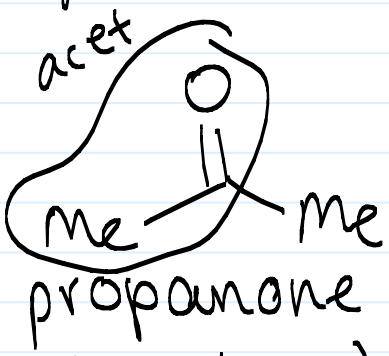


1,4-cyclohexadione

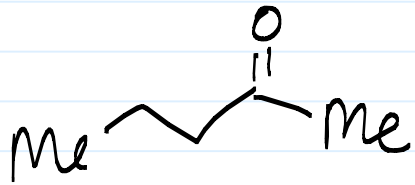


acetophenone
(aromatic ketone)

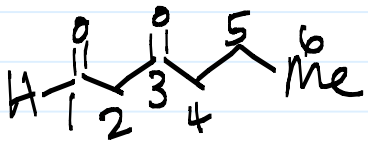
ex:



propanone
(acetone)



2-pentanone

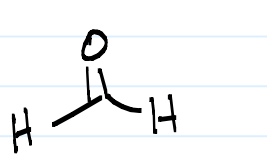


3-oxohexanal

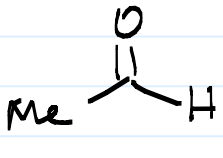
Spectroscopy

IR C=O ~1700 cm^{-1} (strong peak)

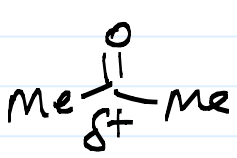
ex:



1744 cm^{-1}

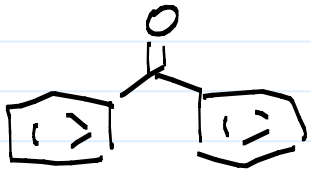


1733

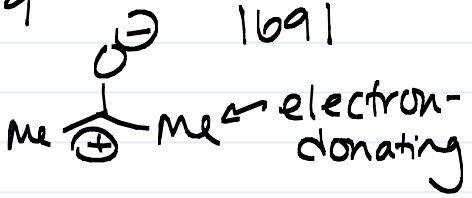


1719

1691



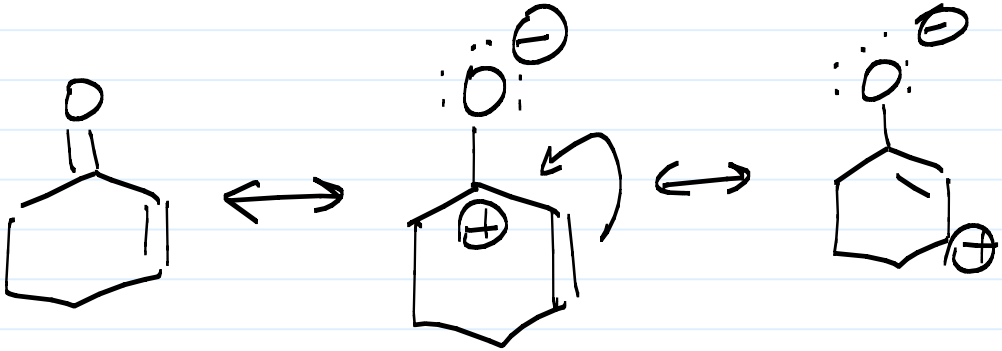
1666

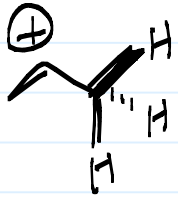


lower frequencies

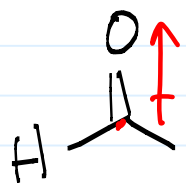
⇓

weaker C=O bonds.



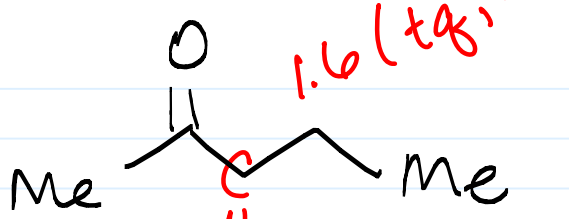


^1H NMR



9.79 (s)

2.20 (s)



1.6 (tq, m)

2.1 (s)

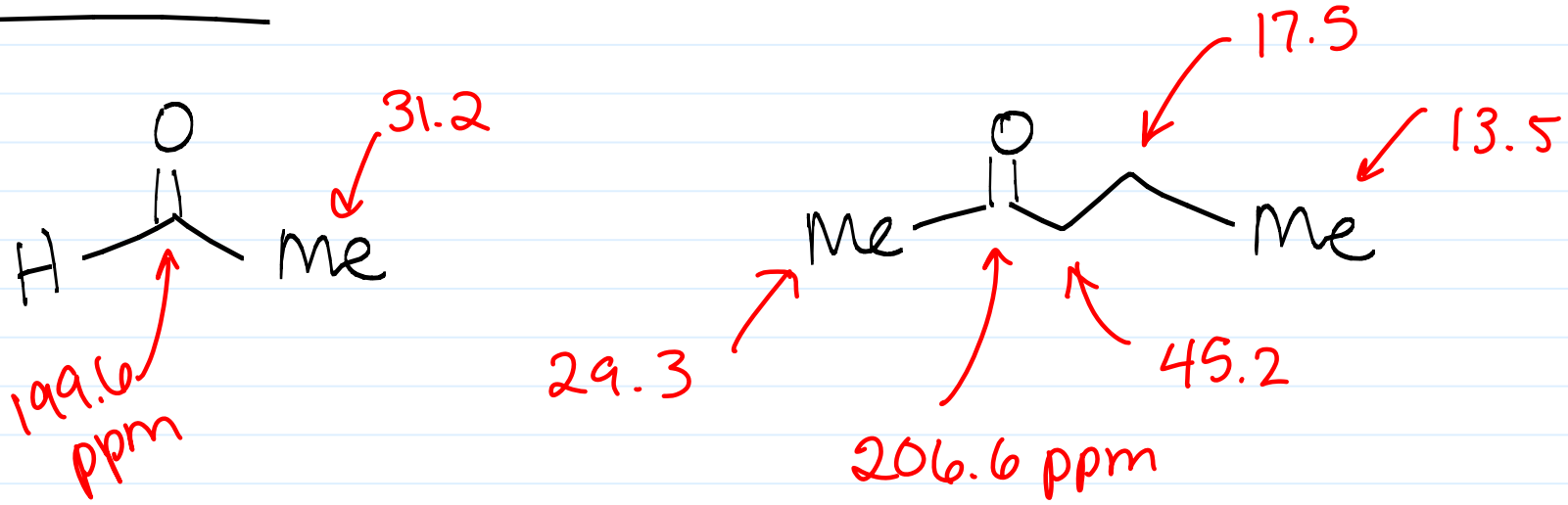
2.4 (t)

0.9 (t)

** Aldehyde H 9-11 ppm ** (very diagnostic!)

α-protons deshielded ~ 2-3 ppm

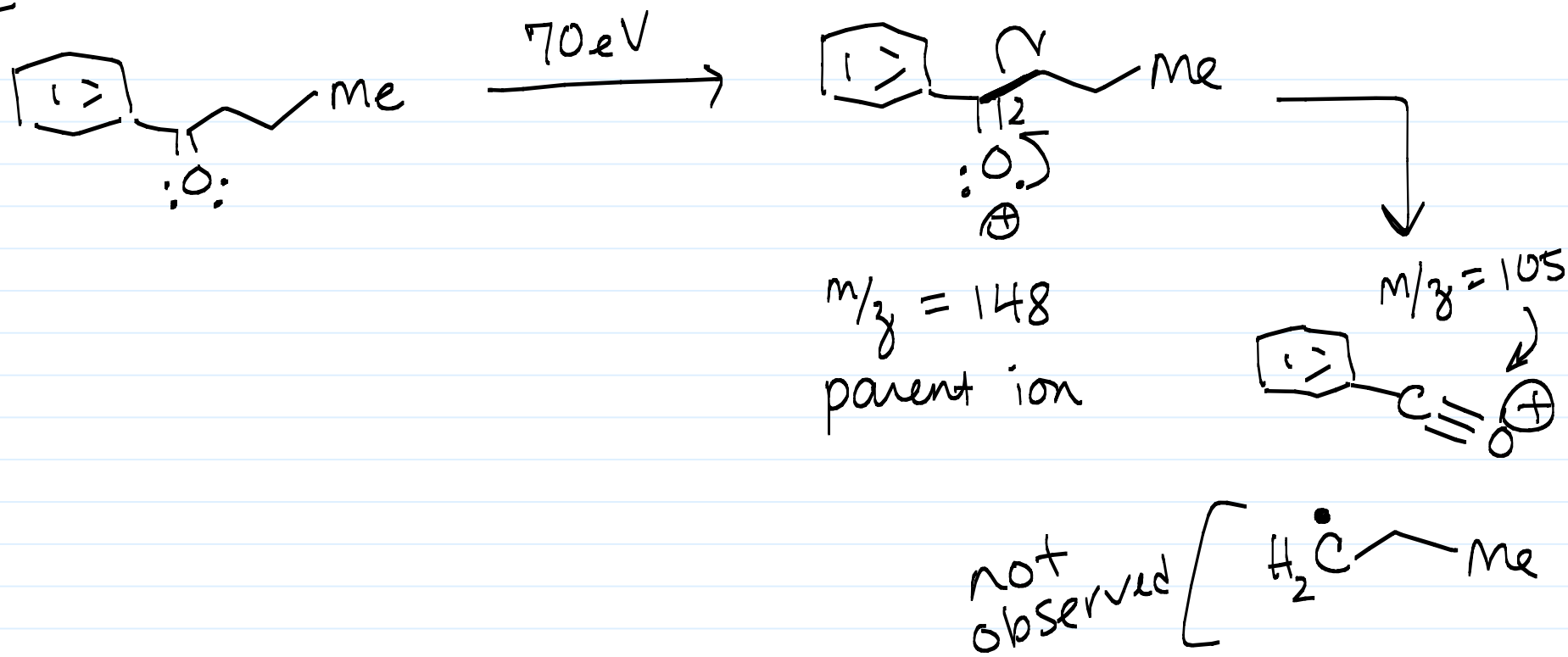
^{13}C NMR



* C=O * ~200 ppm * Very diagnostic.

α-C's deshielded.

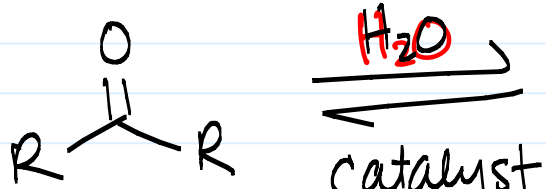
MS:



REACTIONS

Addition Reactions

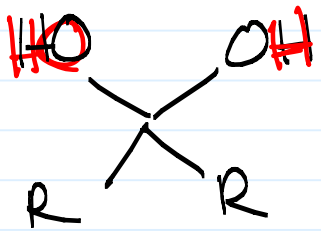
(A) Hydration



H_2O

catalyst

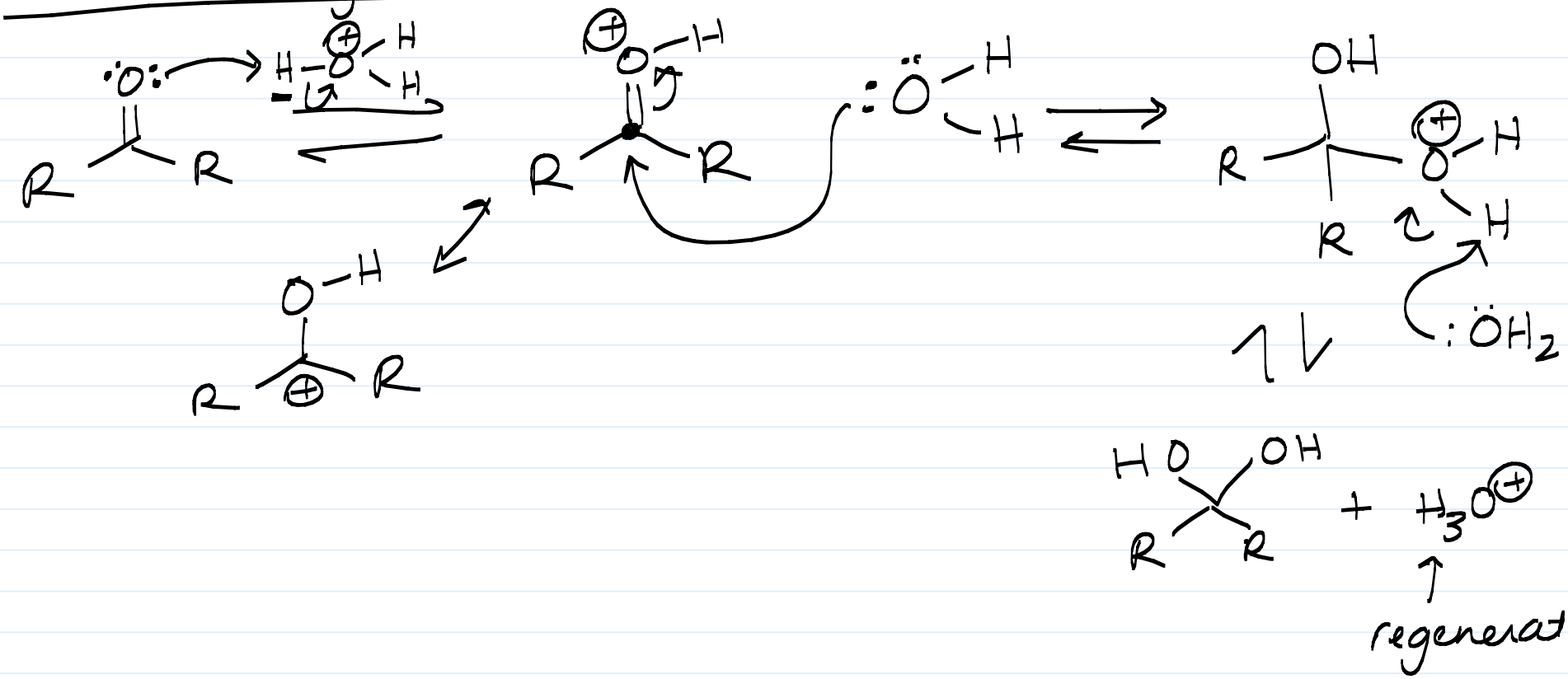
Requires acid or base



"hydrate"

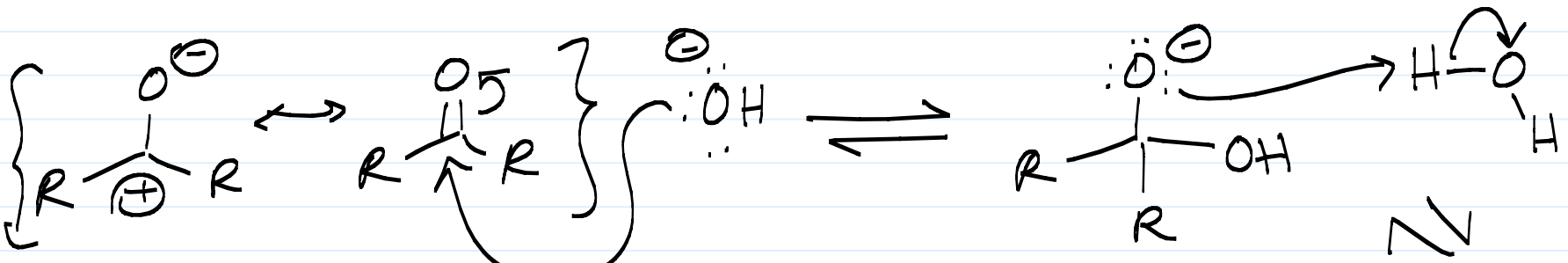
Reversible

Acid catalysis → "Soup" up the electrophile



Base Catalysis

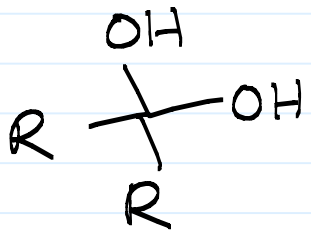
$H_2O + {}^{\ominus}OH \rightleftharpoons {}^{\ominus}OH + H_2O$



In neutral H_2O:

Recall: $H_2O \rightleftharpoons {}^{\ominus}OH + H_3O^{\oplus}$ ← can use either mech @ pH 7!

@ pH 7: $[H^+] = [OH^-] = 10^{-7}$ M



+ ${}^{\ominus}OH$

regenerated ↑