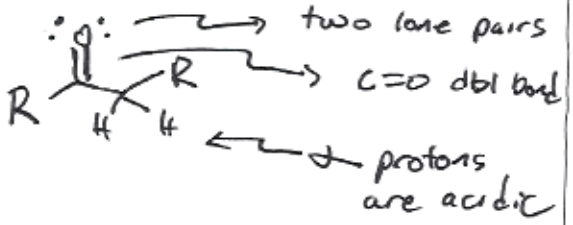
Carbonyl Chemistry – Chapter 16 – Week 7/8

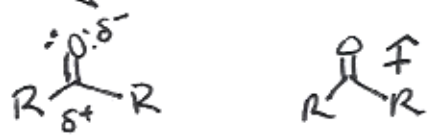
① Basic Parts



double bond = 1 σ + 1 π

②

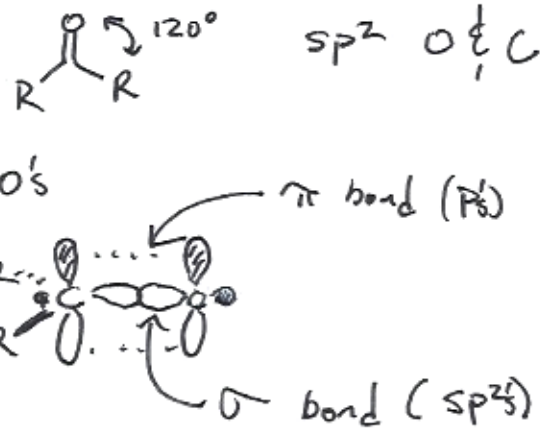
Strong dipole



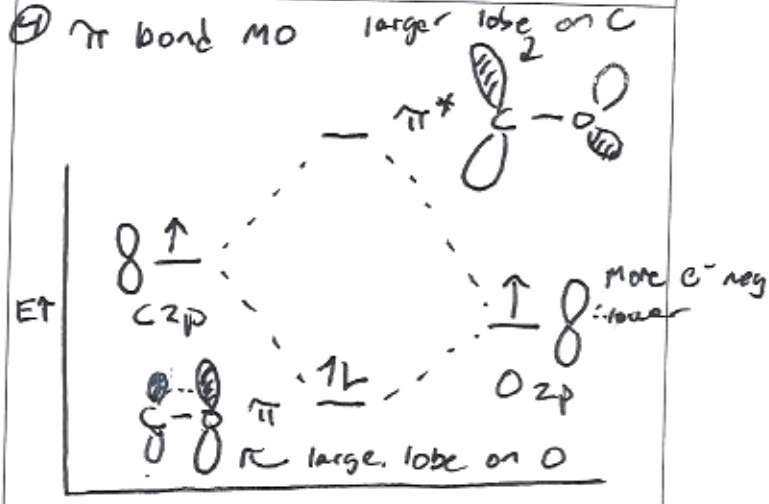
Strong Bond, yet reactive

C=O	C=C
1.2 Å	1.3 Å

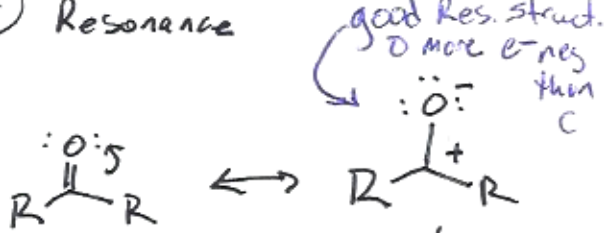
③ MO picture



④ π bond MO

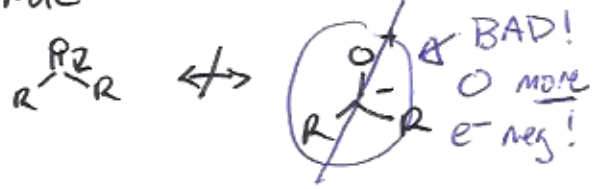


⑤ Resonance

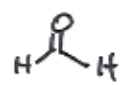


explains dipole & reactivity

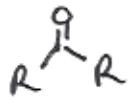
note



⑥ Nomenclature

Ⓐ  2 hydrogens — formaldyde

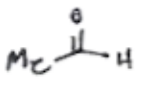
Ⓑ  1 carbon substituent — aldehyde

Ⓒ  2 carbon subs — ketone

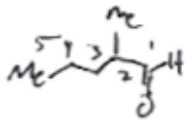
(7) Naming Aldehydes

1) drop e from alkane
2) add "al"
3) aldehyde group = #1 carbon
4) 2 aldehydes, keep "e", "dial"

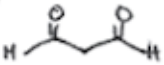
ex



Ethanal



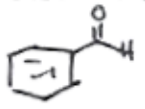
2-methylpentanal



propanedial

also called acetaldehyde

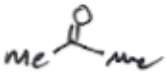
exception



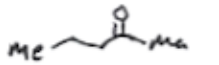
benzaldehyde

(8) Naming ketones

1) drop "e" from alkane
2) add "one"
3) If not highest priority ketone becomes "oxo" group



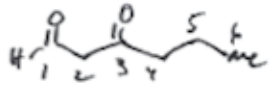
propanone (acetone)



2-pentanone

1,4 cyclohexanedione

acetophenone (aromatic ketone)

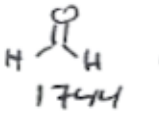


3-oxohexanal

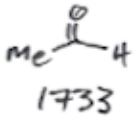
(9) Spectroscopy

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

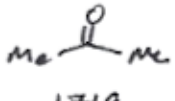
ex



1744

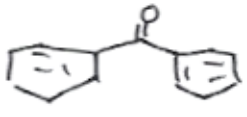


1733



1719

1691

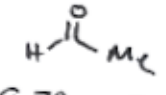


1666

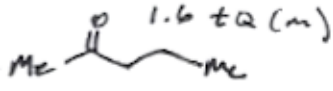
Question - why trend?

~~lower~~ higher freq = ~~weaker~~ stronger bond
stabilization of δ^+ on C!

(10) ^{1}H NMR



9.79 (~s) 2.20 (s)



1.6 tq (m)

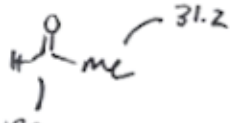
2.1 (s) 2.4 (t) 0.9 ppm (t)

Take home

aldehyde 9-11 ppm

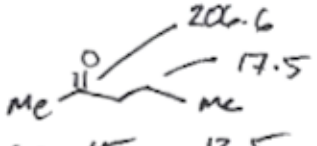
α proton deshielded ~2-3 ppm

(11) ^{13}C NMR



31.2

199.6 ppm



206.6

17.5

29.3 45.2 13.5

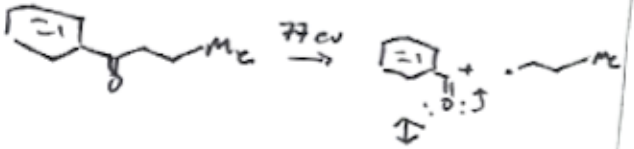
Take home

carbonyl ~200 ppm

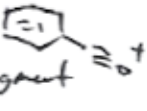
α carbons deshielded

(12) MS

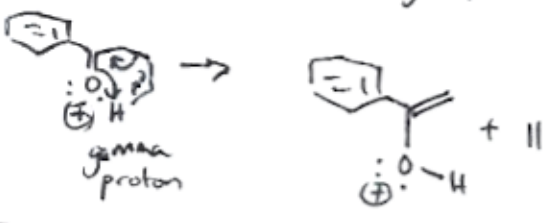
a)



77 eV



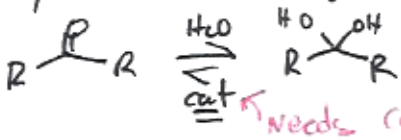
b) McLafferty Rearrangement



gamma proton

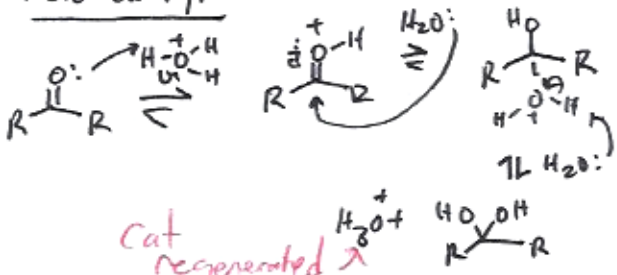
(13) Addition Rxns

(A) Hydration of carbonyls



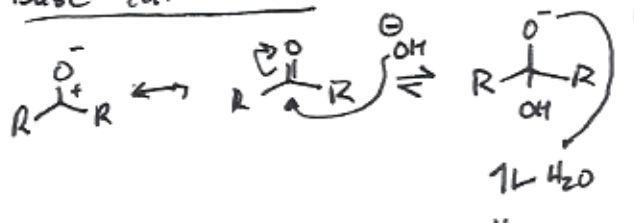
Needs cat

Acid catalysis



Cat regenerated

(14) Base cat Rxns



Neutral H_2O

Recall

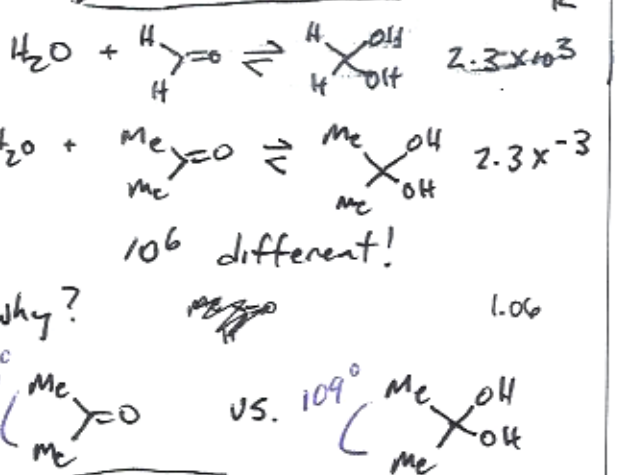
$H_2O \rightleftharpoons H^+ + OH^-$

At pH 7

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

Can use either mech at pH 7

(15) Equilbra => sterics

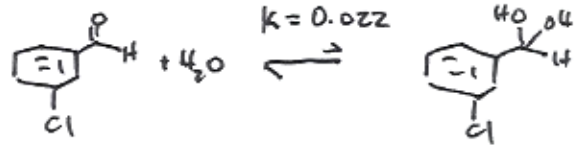


10^6 different!

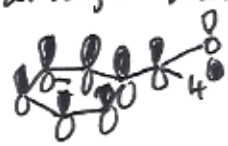
Why?

SP3 is more crowded bc w/ large groups

(16) Substituent effects

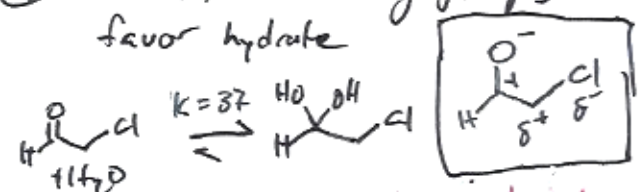


Carbonyl stabilized by arene

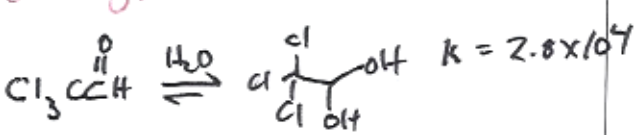


Can also explain w/ resonance see text

(17) Electron withdrawing groups favor hydrate

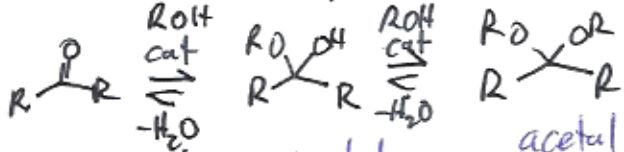


Charge / charge repulsion destabilizes carbonyl



"Mickey Finn" knockout drops

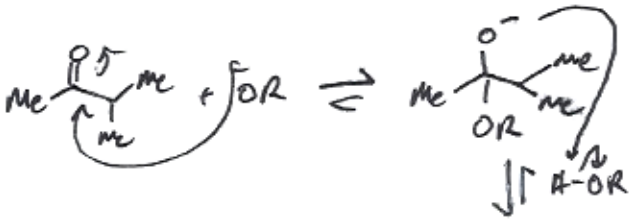
(18) (B) Hemiacetal / Acetal formation



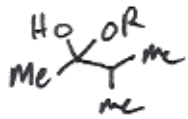
hemiacetal acetal

Note sometimes also called "ketals" when carbonyl is a ketone

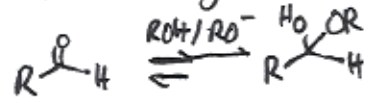
(19) Base cat - hemiacetal formation

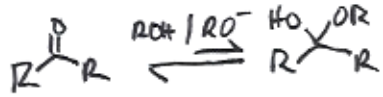


Note: why no acetal formation? (see p 757 text)



(20) Hemiacetal stability

Aldehydes  K>1

ketones  K<1

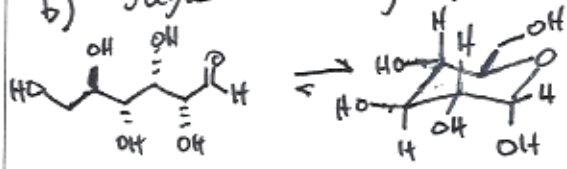
Why? sterics - see above

Note: hemiacetals hard to isolate

(21) Exceptions - isolable

a) cyclic hemiacetals

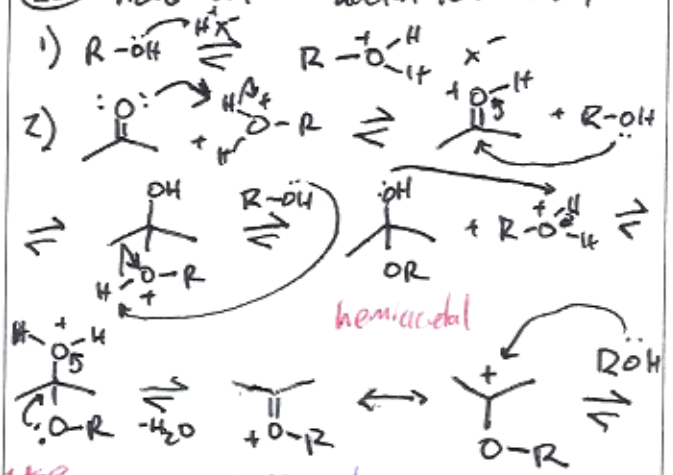
b) sugars - mainly cyclic



α - D-glucose

(more on sugars later)

(22) Acid cat - acetal formation

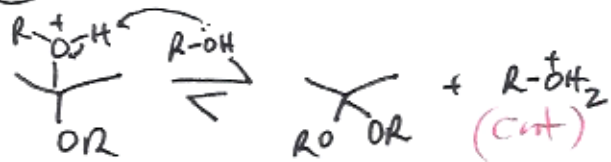


hemiacetal

use lone pairs

oxo carbenium ion

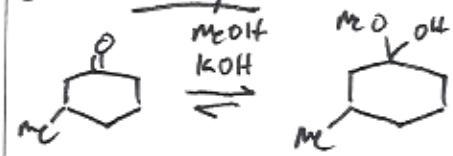
(23) Acid cat mech cont.



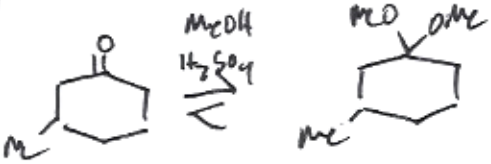
note: using lone pairs to form oxo carbenium ion says "I understand this is a special & stable cation"

must know this mech

(24) examples



hemiacetal

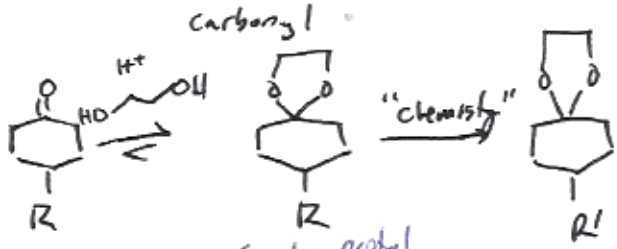


acetal

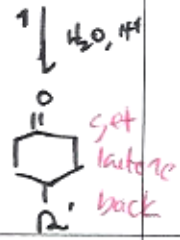
(25) Note: Acetal formation- Reversible

Acetals as protecting groups

carbonyl



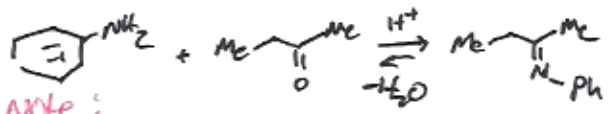
Cyclic acetal



(Note: ketone can also protect diols..)

(26) (C) Nitrogen Nucleophiles

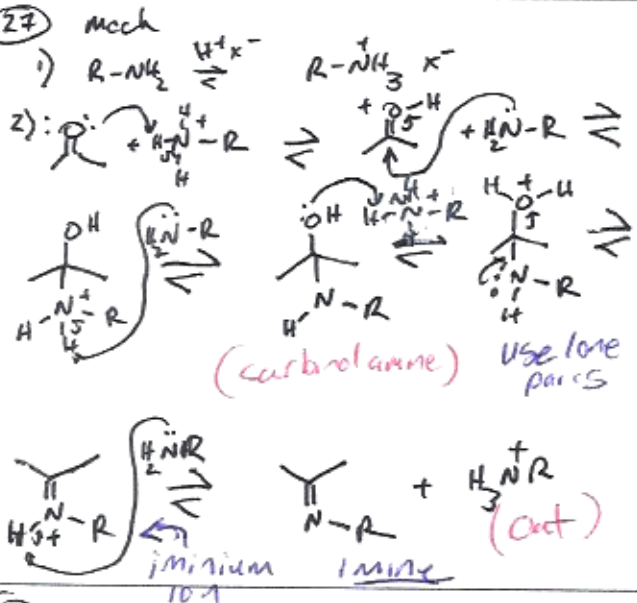
Primary amine ⇒ Imines



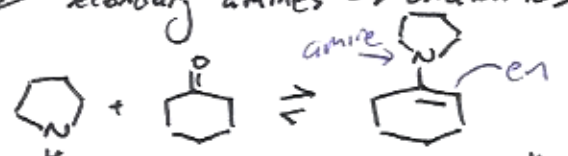
Note: 2 hydrogens

imine (Schiff base)

(27) mech

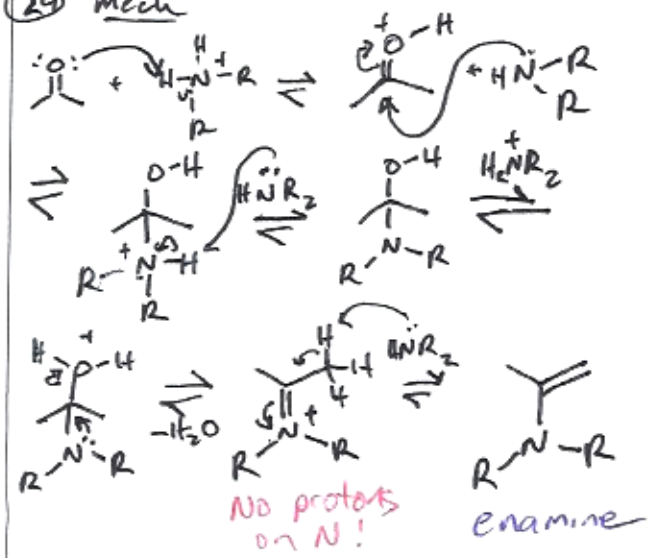


(28) Secondary amines ⇒ enamines

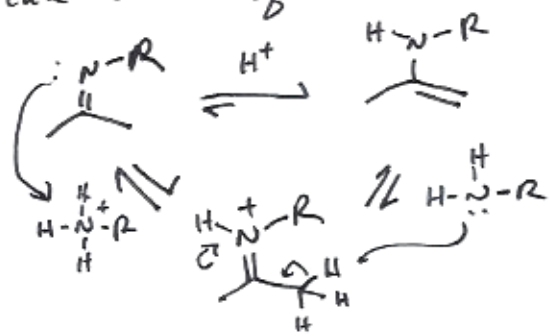


Note only one proton!

(29) mech



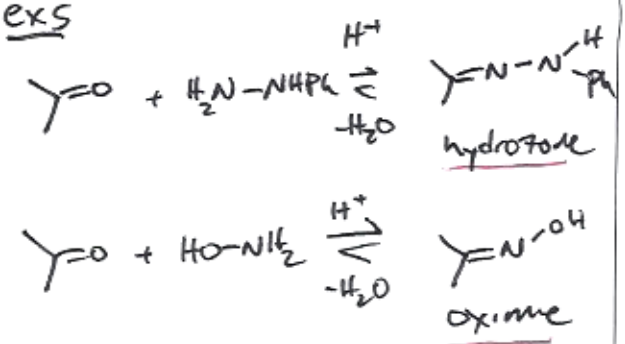
(30) Note: Enamine & Imines can lie in equilibrium



imines generally more stable

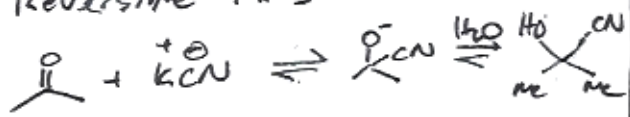
(31) Many related examples
See p 793 text

exs



(32) D Carbon Nucleophiles

Reversible rxns

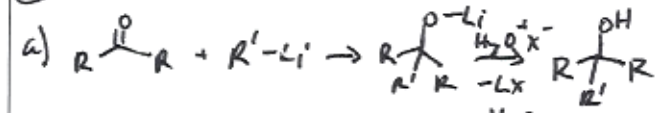


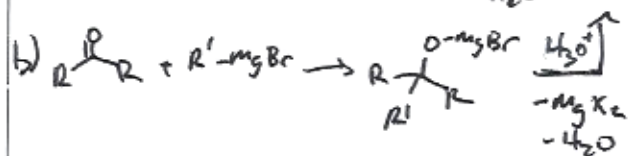
pka HCN ~9.4

ie ^-CN not very basic & is fairly stable ∴ Rxn is reversible

note: all rxn up to this point have been reversible

(33) Irreversible rxns

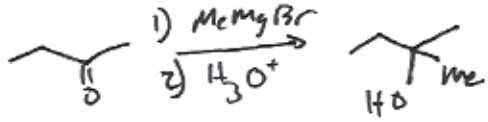
a) 

b) 

Note pka R'-H ~ 50-55

$R'^{\ominus}$ not stable ∴ rxn exothermic & does not want to go backwards.

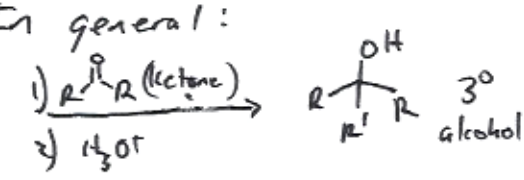
(34) write as

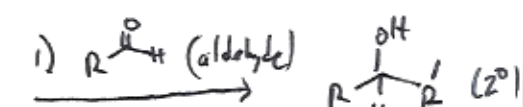


Note workup is important

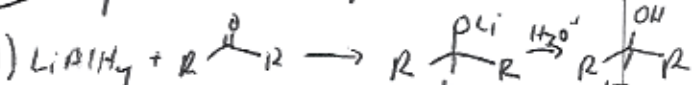
(35) In general:

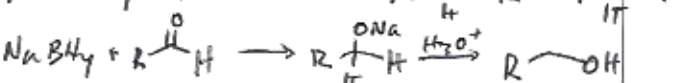
R'-Li or R'-MgBr





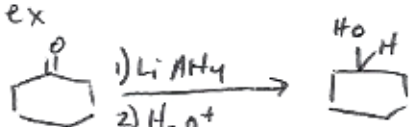
(36) Hydride Nucleophiles (Reduction)

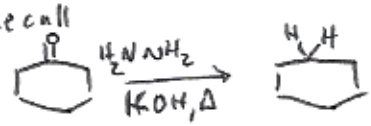
A) 

B) 

NaBH4 more mild than LiAlH4

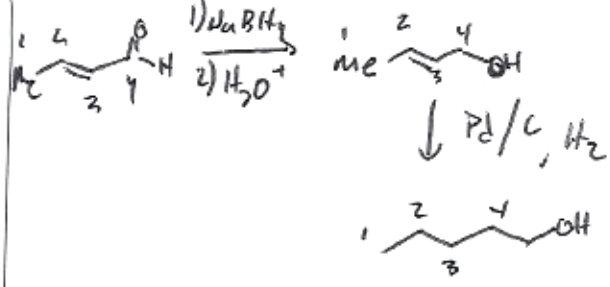
ex



Recall 

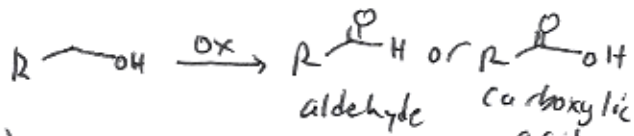
Red to alkane

(37) 2nd example

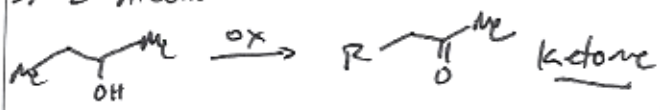


(38) Oxidation of alcohols

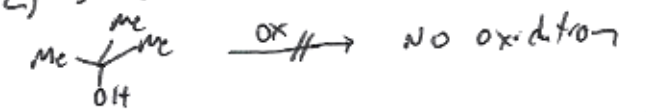
a) 1° Alcohols



b) 2° Alcohol



c) 3° alcohol



(39) Oxidants

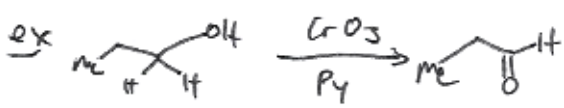
a) CrO_3,  (chromium trioxide)

No water

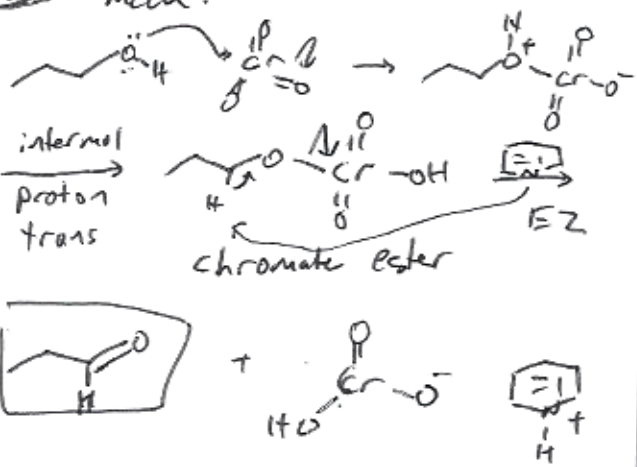
1° alcohols ⟶ aldehydes

2° alcohols ⟶ ketones

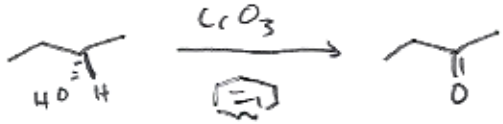
ex



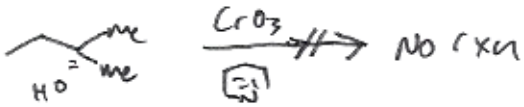
(40) Mech:



(41) ex



2° alcohol



3° alcohol NO hydrogen atom vicinal (next to) alcohol

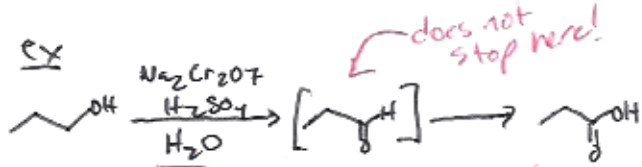
(42)

B) $Na_2Cr_2O_7$, H_2SO_4, H_2O (sodium dichromate)

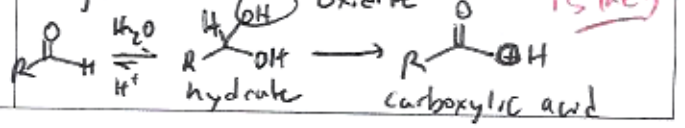
1° alcohol ⟶ carboxylic acid

2° alcohol ⟶ ketone

ex



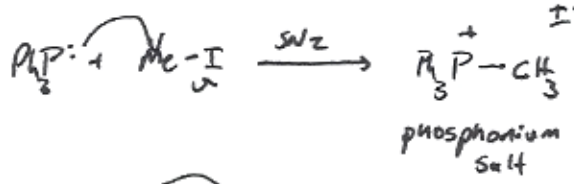
Why?

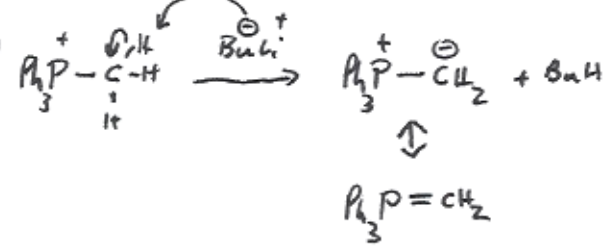


water is key

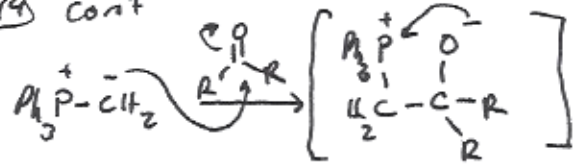
(43) The Wittig Rxn (Nobel Pr. 7c 1979)

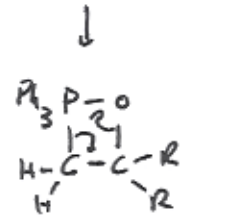
C=O ⟶ C=C

a) 

b) 

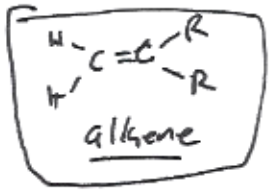
(44) cont'd



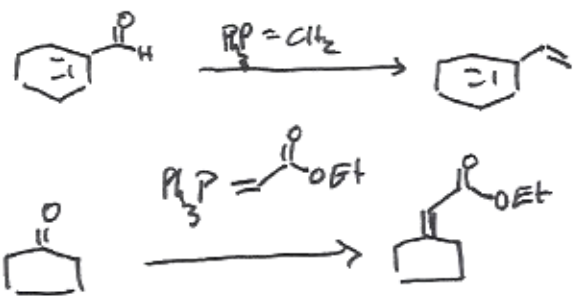


triphenylphosphine oxide

$Ph_3P{=}O$



(45) examples



Ch 16 problem

10, 31 – 43, 46–52, 55–60, 62–64, 67.