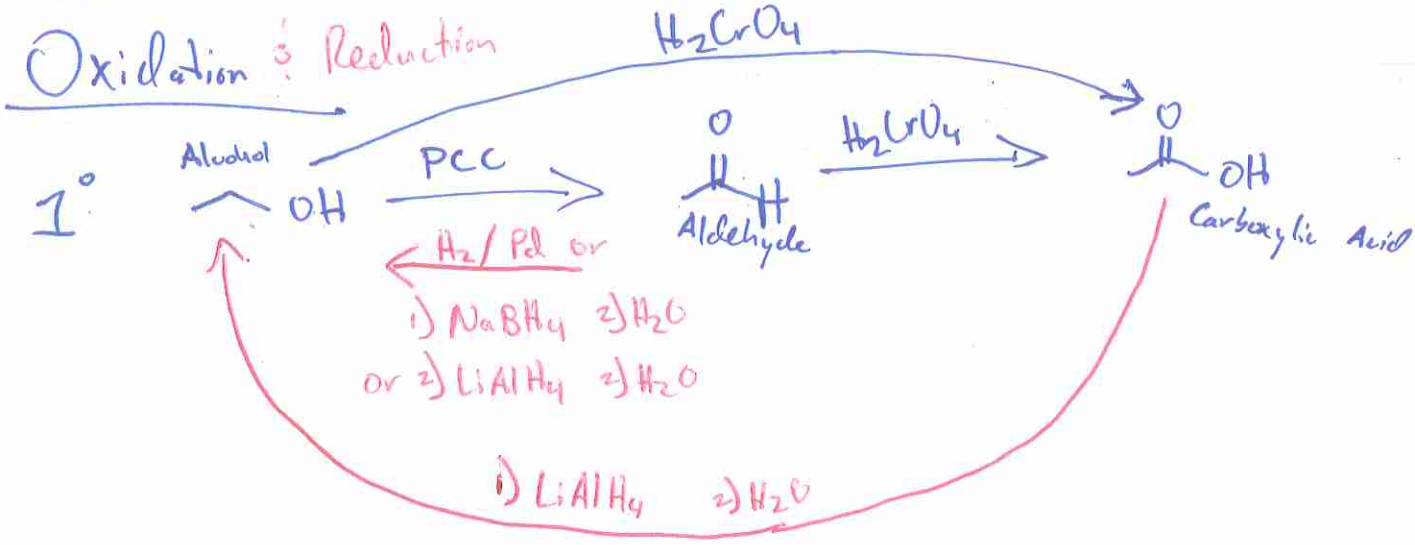
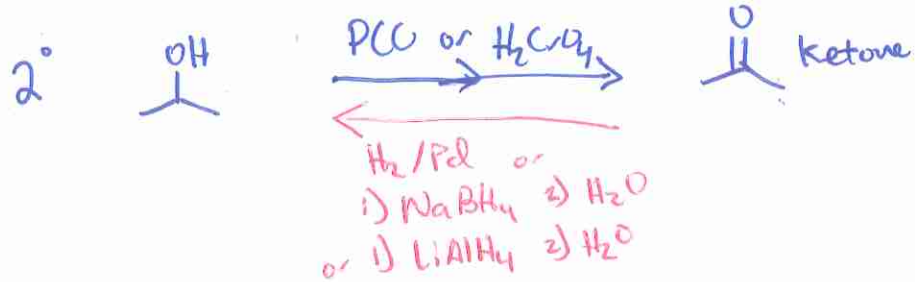
MTW 2/20/2017

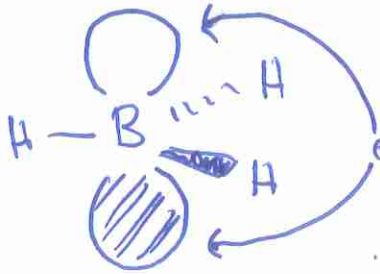
Oxidation & Reduction





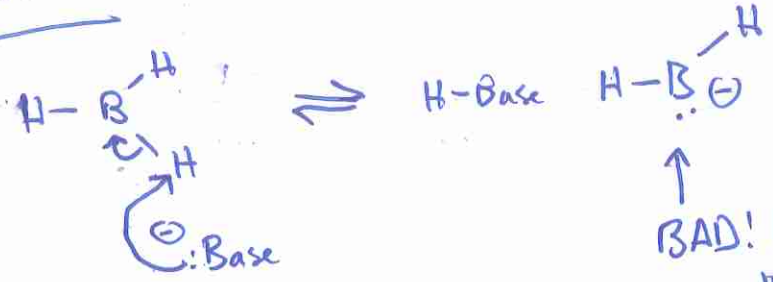
Boron (and Aluminum) Reagents

BH_3 → Neutral, 3 bonds, lacks full octet!



Reactivity

B.L. Acid?

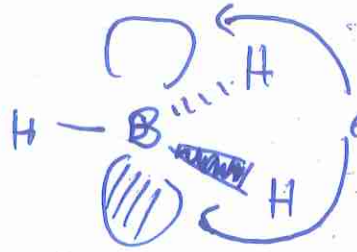


Not an Acid!

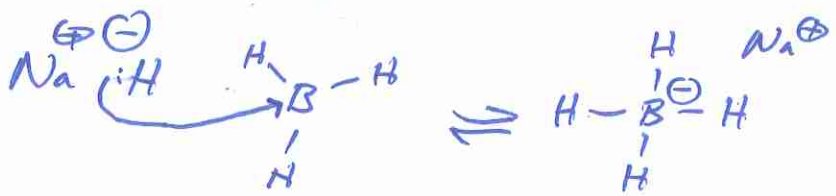
B.L. Base? → No - No lone pairs to grab protons ($H^{\oplus}$)

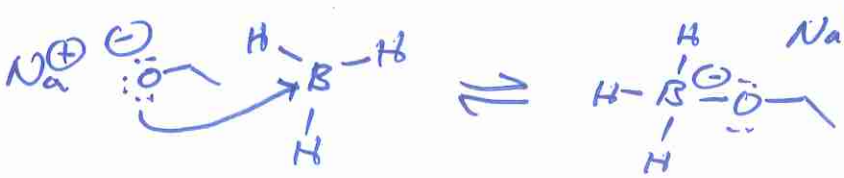
Nucleophile? → No! Same reason it's not a base!

Electrophile? Yes!



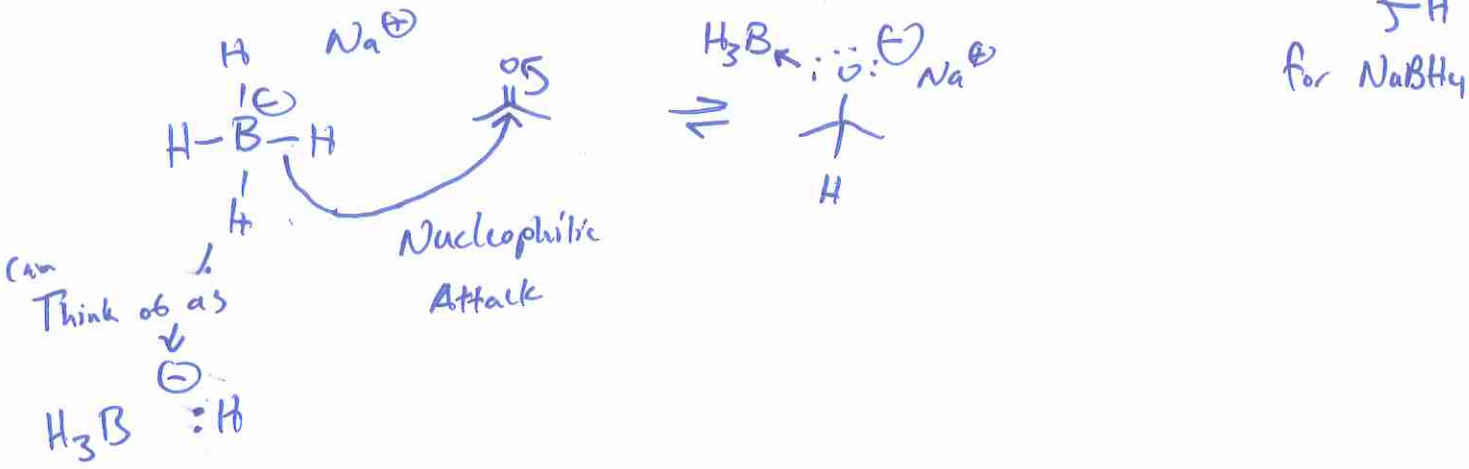
Examples:

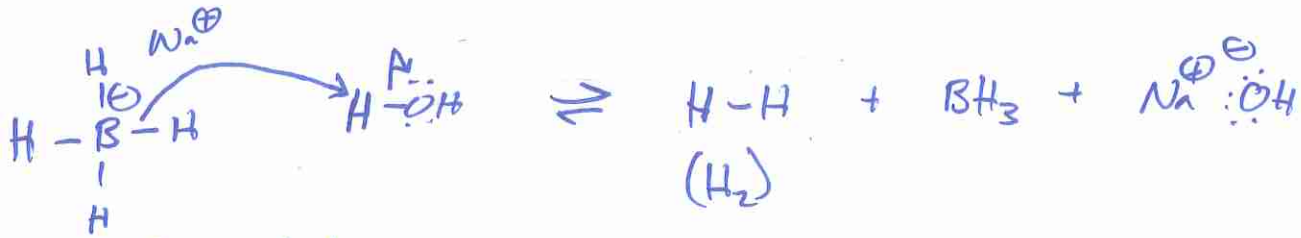




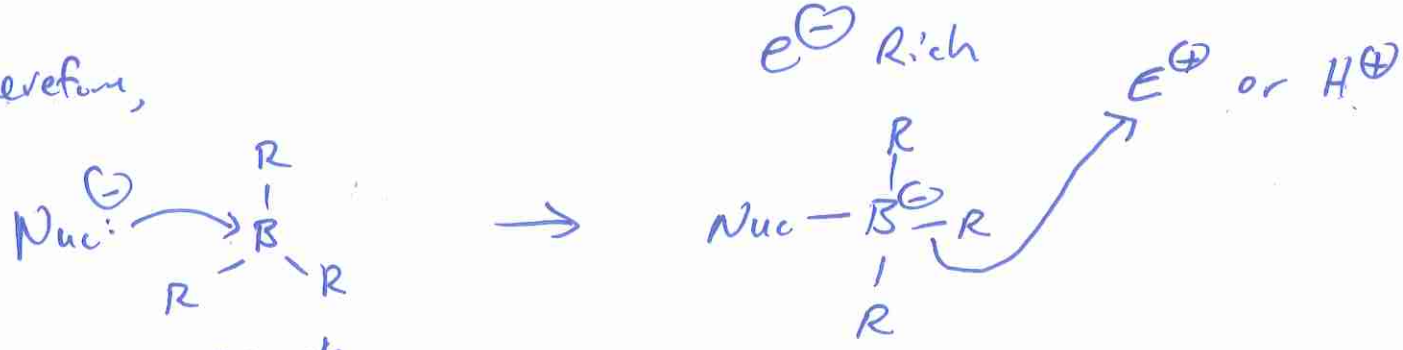
So what about $NaBH_4$?

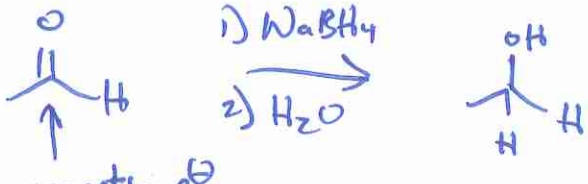
↳ Donates "$\ominus$ R" ← e.g. $\ominus$H for $NaBH_4$

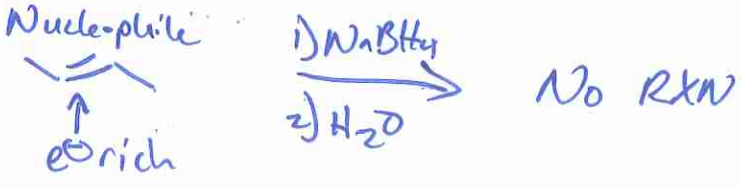




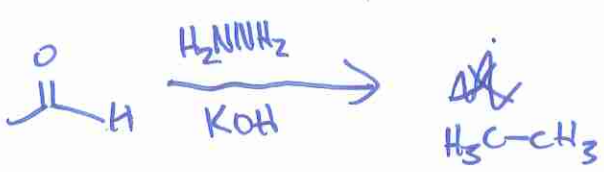
Therefore,



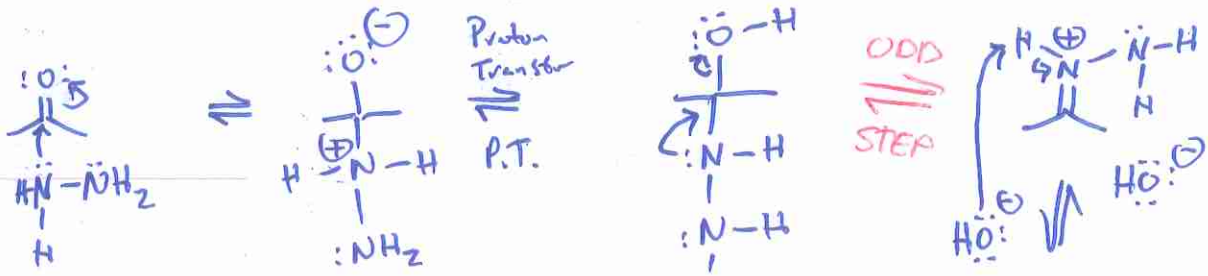




Wolff-Kishner Reaction

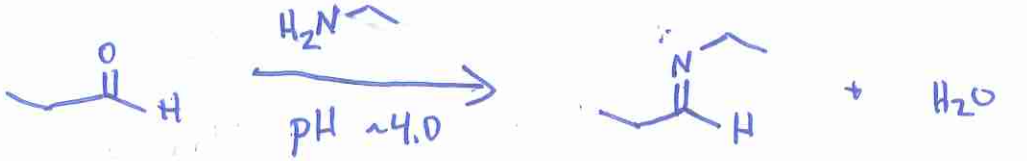


First Intermediate: SPECIAL IMINE formation (In Base!)



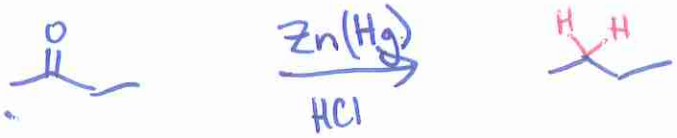
Several steps, see Mechanism packet

Imine Formation in general is in slightly acidic conditions



Clemmensen Reduction → No mech!

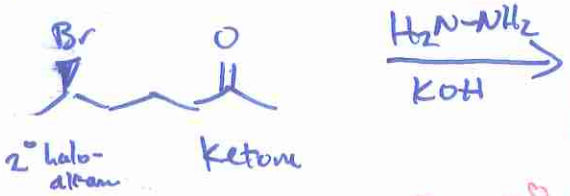
Aldehydes & ketones



Clemmensen vs. Wolff-Kishner

- Molecules w/ multiple functional groups

Can we do the following?

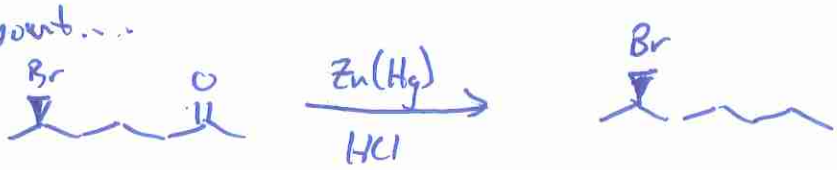


Reality → mixture of products

NO! → Why? 2° Haloalkanes eliminate in Rxn

So W.K. Reduction isn't good for this starting material!

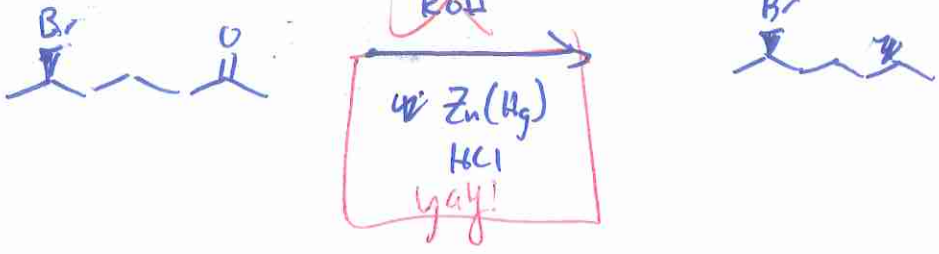
What about...



← Actual product

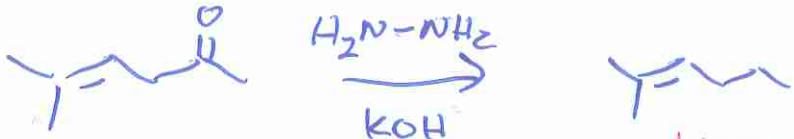
Yes! HCl doesn't react w/ 2° haloalkane

Therefore



Would this work?

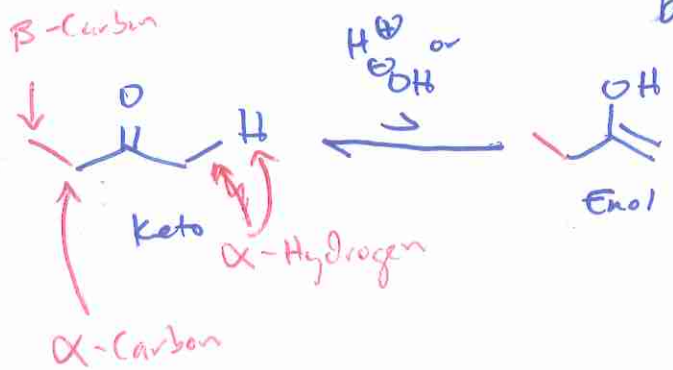
No reality is multiple products

But 

Yay

Keto-Enol Tautomerization → A proton moves

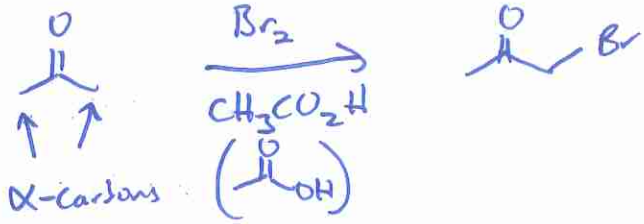
→ Both keto & Enol forms exist but much more keto than enol

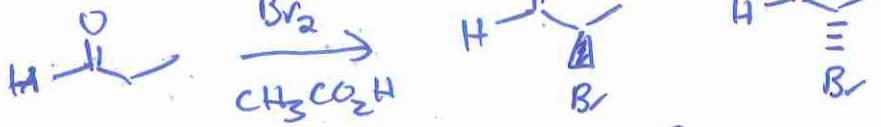


α-Hydrogens are relatively acidic

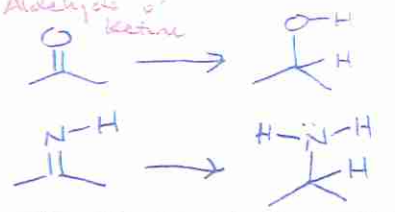
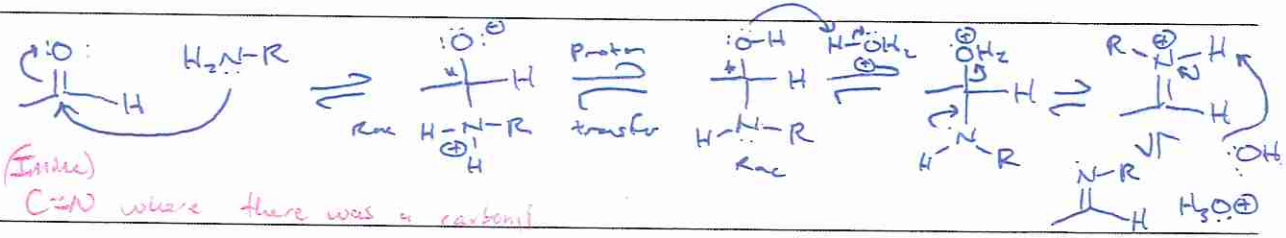
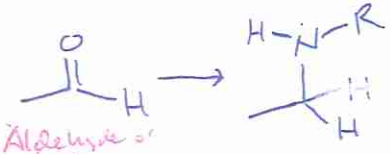
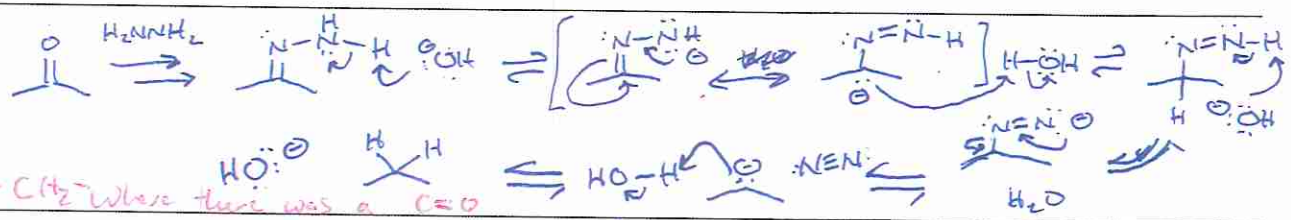
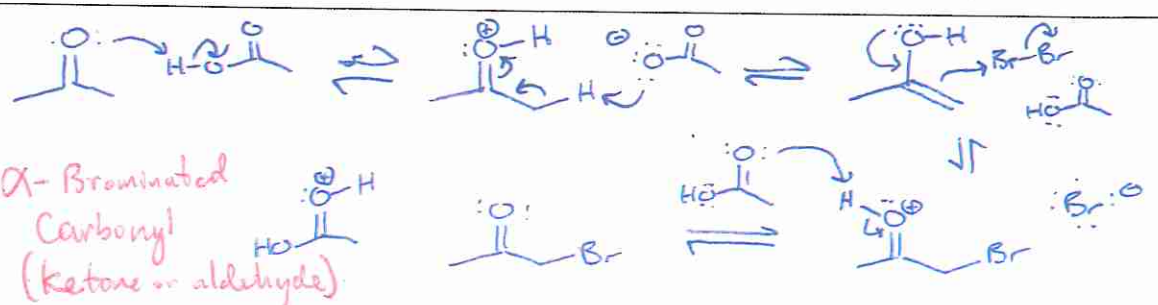
pka 18-20

X-Halogenation → Aldehyde or ketone



ex. 

Racemic

Aldehyde or ketone → 	H_2, Pd° -OR- 1) $NaBH_4$ or $LAlH_4$ 2) H_2O	NO MECH.
	1) $LiAlH_4$ 2) H_2O	NO MECH
Aldehyde or ketone → 	H_2N-R pH ~ 4.0	 (Imine) C=N where there was a carbonyl
Aldehyde or ketone → 	[H_2N-R, H_2, Pd°] ≠	NO MECH
Aldehyde or ketone → 	Basic H_2NNH_2, $NaOH$ -OR- Acidic (NO MECHANISM) $Zn(Hg)$, HCl	 $-CH_2-$ where there was a C=O
Aldehyde or Ketone → 	cat. $H^\oplus$ -OR- cat $^\ominus OH$	
Aldehyde or Ketone → 	[(CH_3CO_2H) Br_2]	 α-Brominated Carbonyl (ketone or aldehyde)