Redox Reactions (Reduction)

Compound	Reagent (Reducing Agent)	Product
Acid Chloride	$LiAlH(OtBu)_3$/ether/-78°; H_3O^+	Aldehyde
Ester	DIBAL/ether/-78°; H_3O^+	Aldehyde
Nitrile	DIBAL/ether/-78°; H_3O^+	Aldehyde
Acid Chloride	$LiCuR_2$; H_3O^+	Ketone
Nitrile	RMgBr/ether; H_3O^+	Ketone
Aldehyde	$NaBH_4$ or $LiAlH_4$; H_3O^+	1° Alcohol
Ketone	$NaBH_4$ or $LiAlH_4$; H_3O^+	2° Alcohol
Ester	$LiAlH_4$; H_3O^+	1° Alcohol
Carboxylic Acid	$LiAlH_4$; H_3O^+	1° Alcohol

Redox Reactions (Oxidation)

Compound	Reagent (Oxidizing Agent)	Product
1° Alcohol	H_2CrO_4 or $Na_2Cr_2O_7/H_2SO_4$	Carboxylic Acid (via aldehyde; not observed)
1° Alcohol	PCC	Aldehyde
2° Alcohol	PCC or H_2CrO_4 or $Na_2Cr_2O_7/H_2SO_4$	Ketone
3° Alcohol	Any of the above	NRX
Aldehyde	H_2CrO_4 or $Na_2Cr_2O_7/H_2SO_4$	Carboxylic Acid
Aldehyde		

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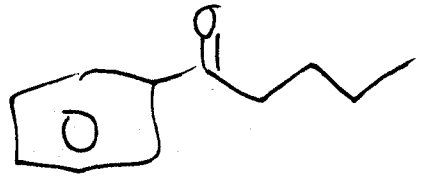
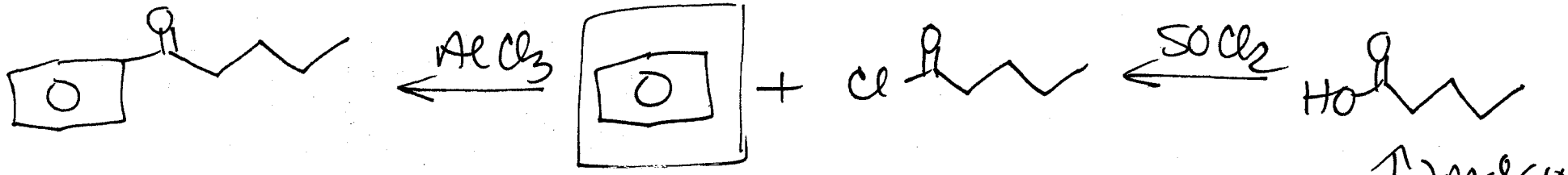
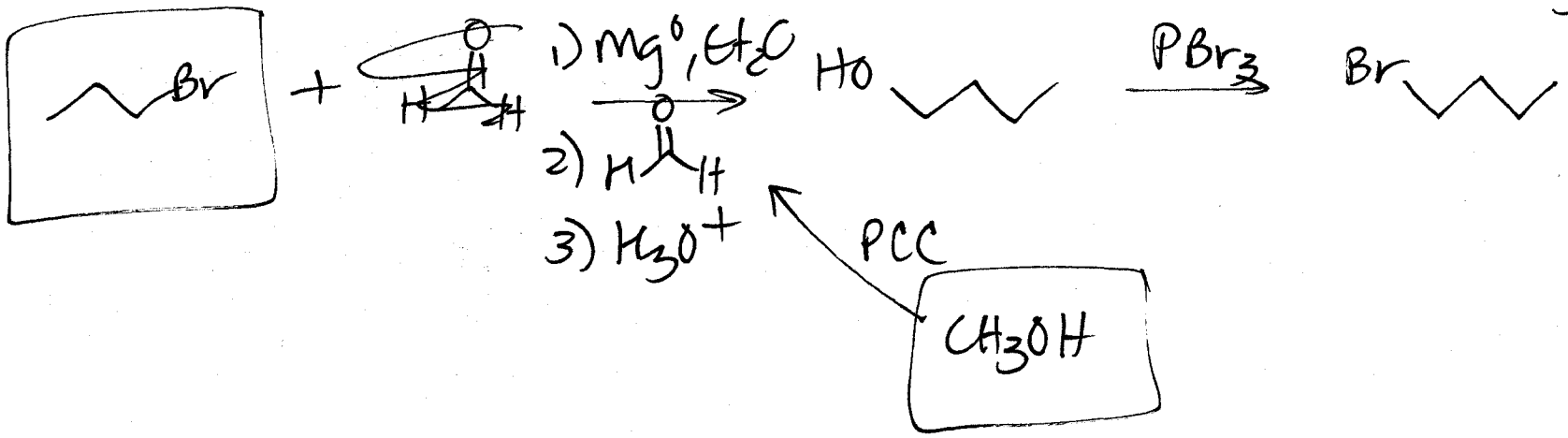
make: 

General rules:
start w/ benzene +
any 3-carbon or less
alcohol or alkyl halide
+ any inorganic reagent.

Solution #1





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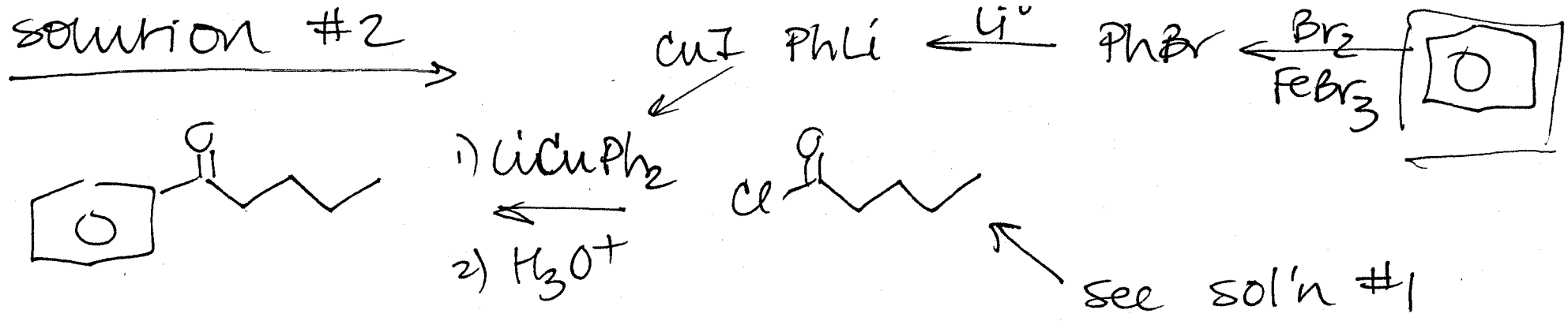

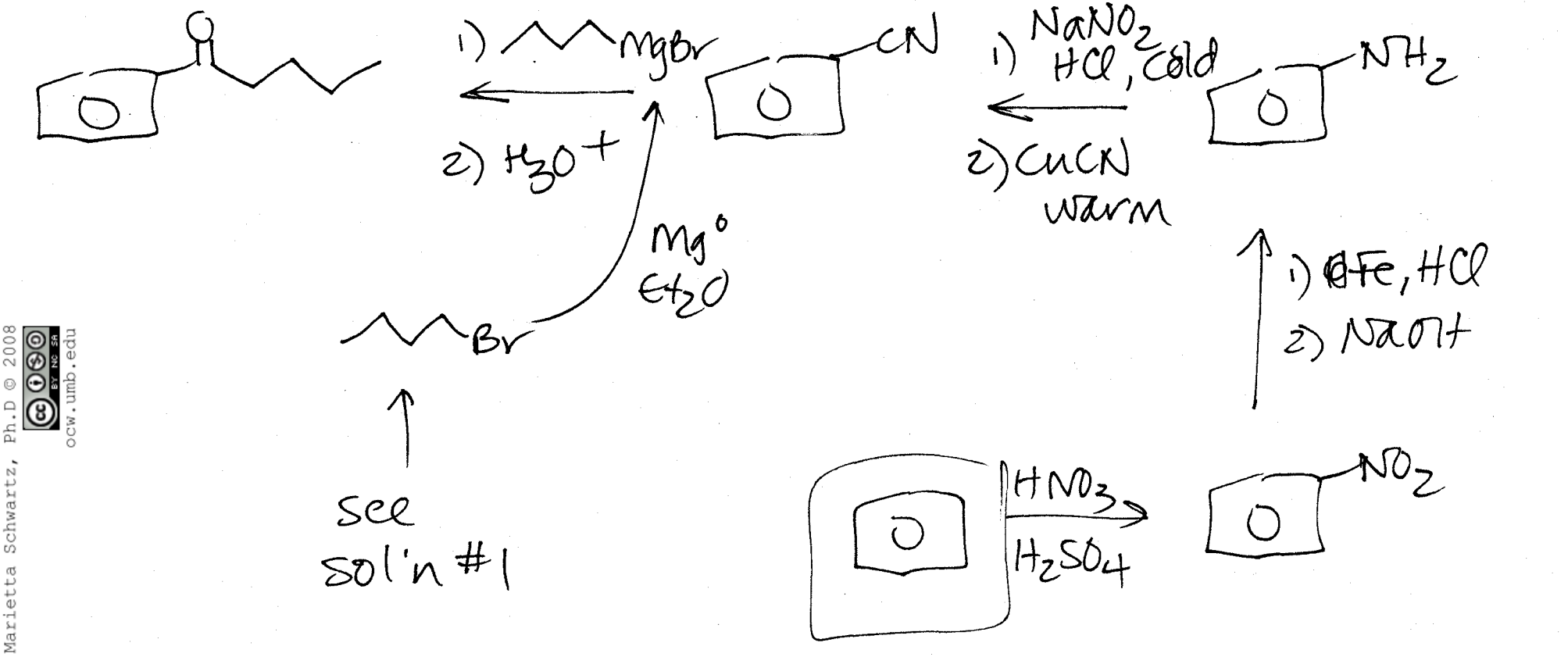

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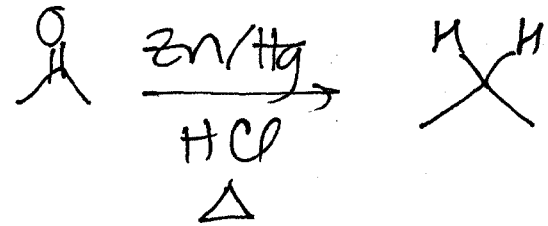
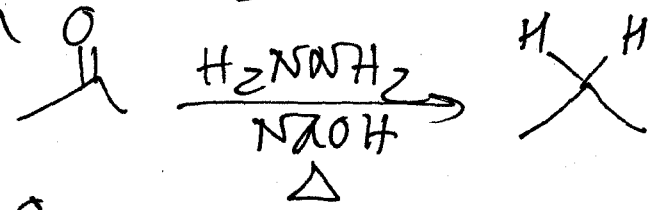
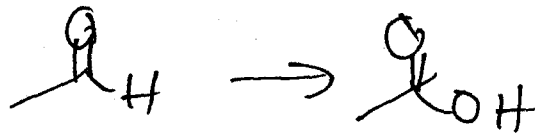
Reactions

1. Clemmensen reduction 

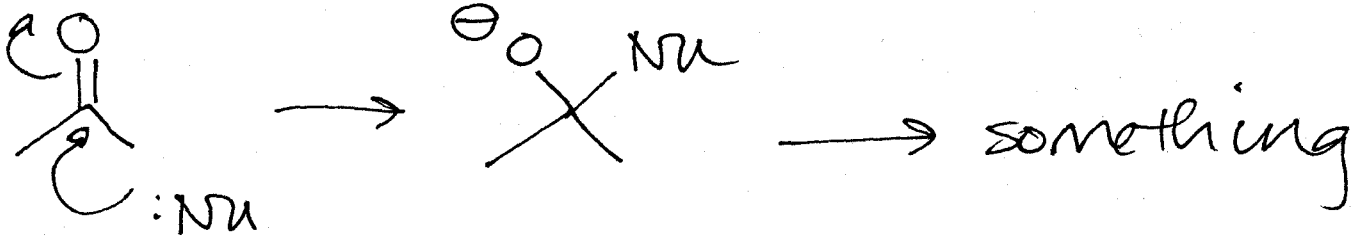
2. Wolff-Kishner reduction 

3. Oxidations –  CrO_3 or H_2CrO_4 or $Na_2Cr_2O_7$

4. Reductions w/ $NaBH_4$ or $LiAlH_4$ → alcohols

5. Grignard rxn

Look at #4 + #5 - nucleophile attacks C=O



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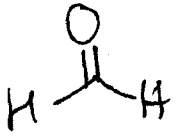
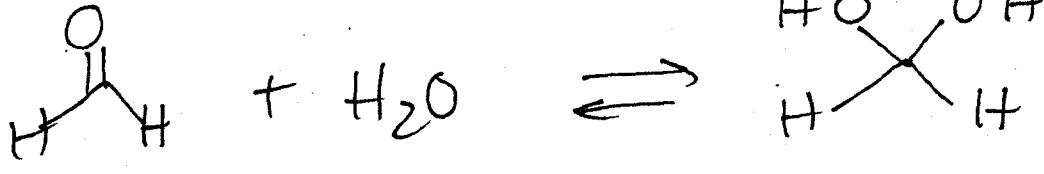


NMR: expect to see one peak ~9-10 ppm

However, if the solvent has any H_2O in it, we see a peak ~5 ppm instead.

Theory:



can't be isolated

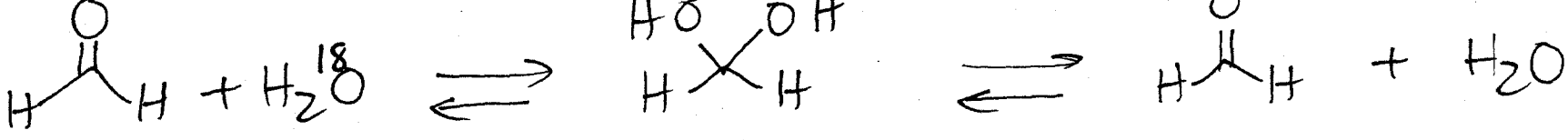
gem-diol

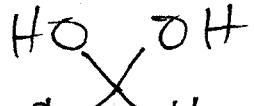
↑

geminal (on same C)

aka a hydrate b/c we have added water.

how do we know the hydrate is there?



(there are some stable hydrates: Cl_3C )

chloral hydrate

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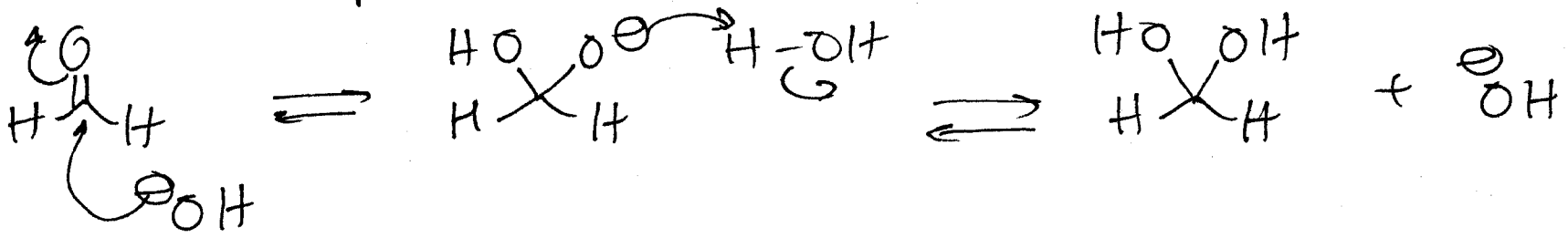
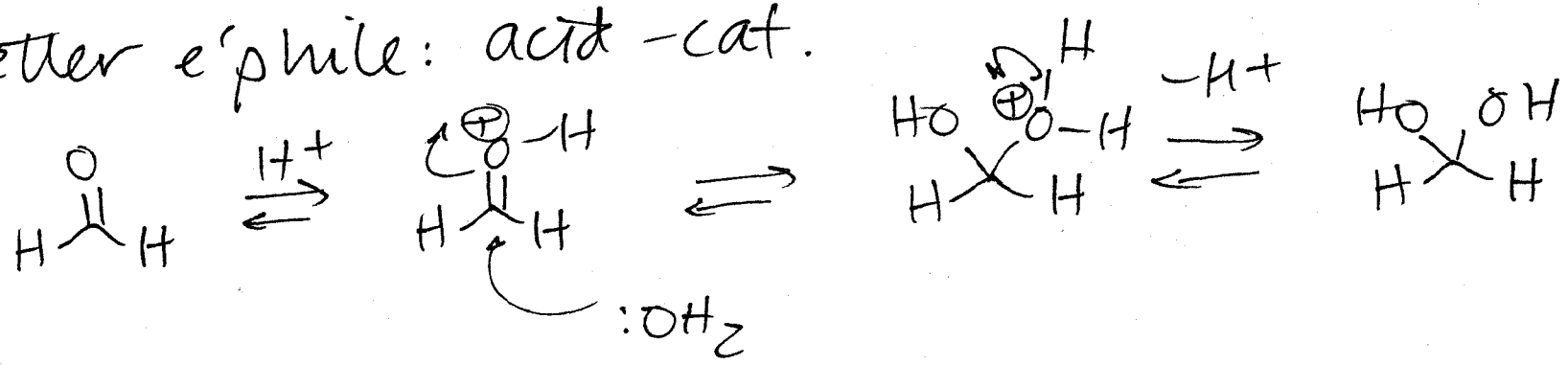
Formation of a hydrate is an equilibrium — takes time to establish the equilibrium.

How do we speed it up?

1) Better Nucleophile: base-cat.



2) Better e'phile: acid-cat.



If water will do something, generally alcohols will also. So let's try CH_3OH as nucleophile

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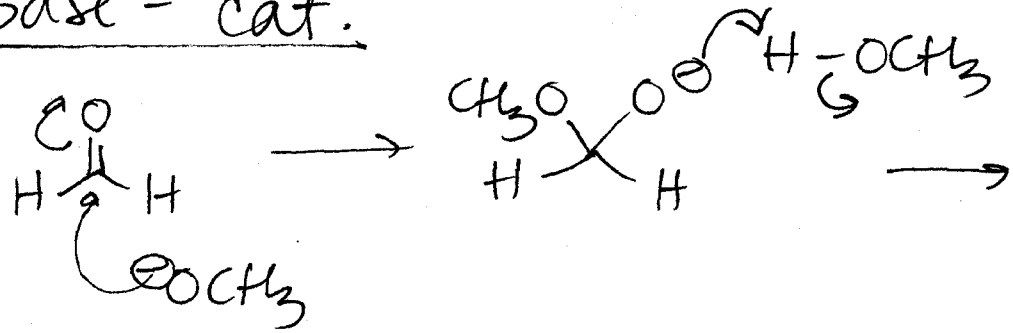
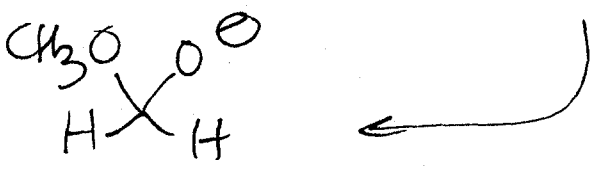
Base - cat.



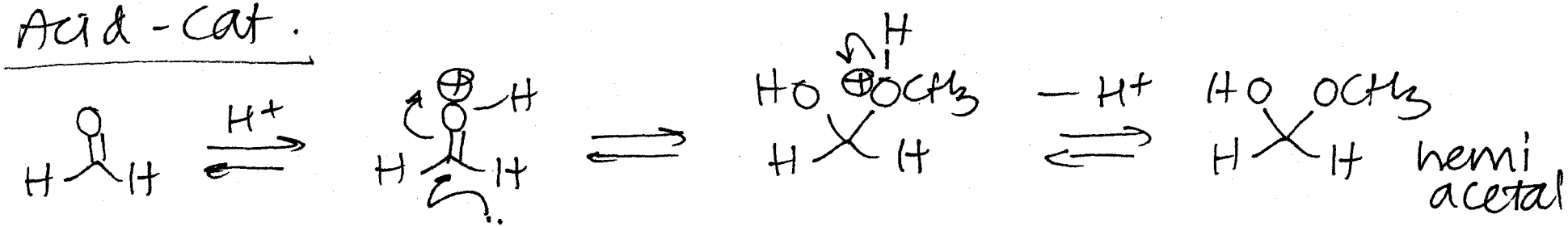
Add a 2nd equiv. of $NaOCH_3$

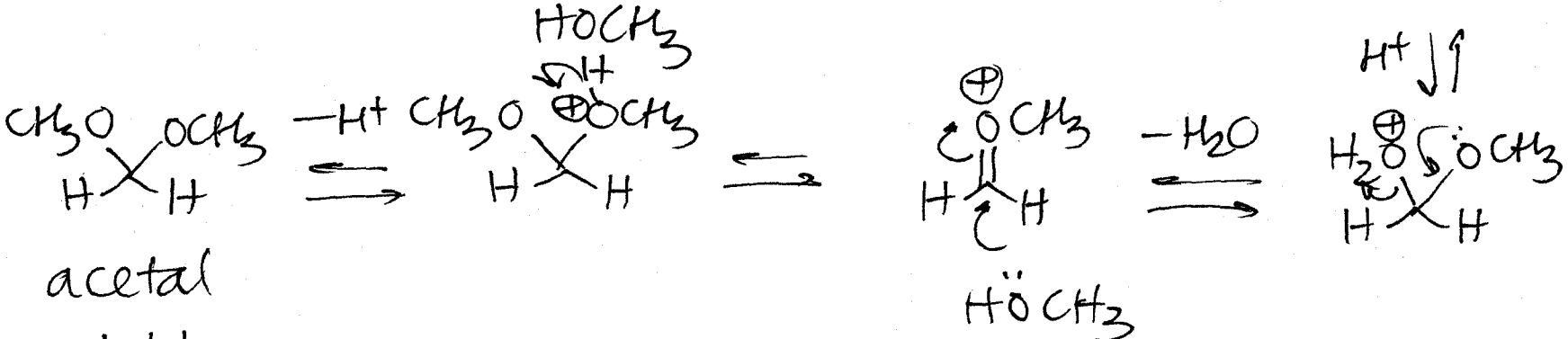


back again

stuck @ hemiacetal stage.

Acid - cat.





acetal

stable; unreactive except in aq. acid (CH_3O^+)

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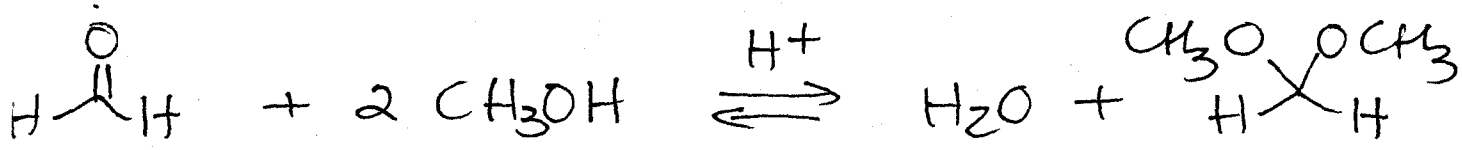
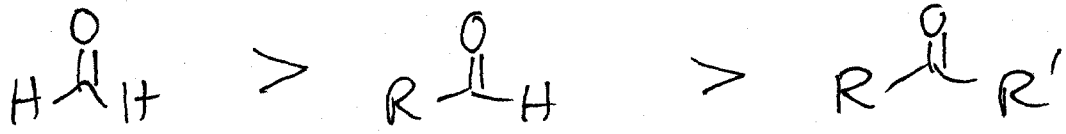
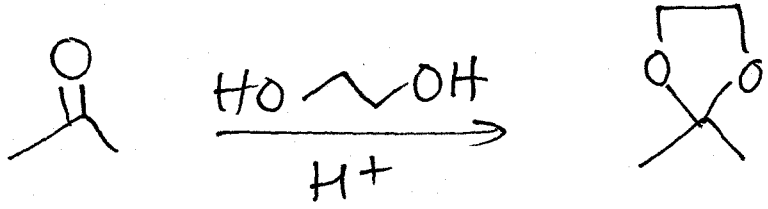


summary – relies on le Chatelier's Principle

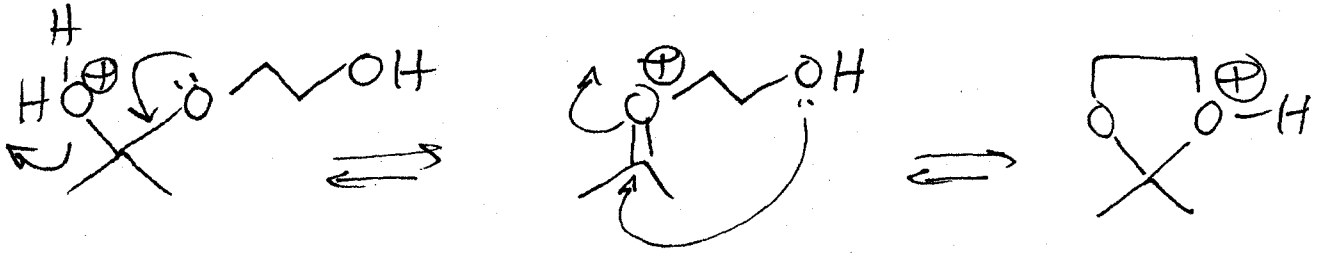
Sterics matter. The whole thing hinges on nucleophilic attack at the C=O.



Because ketones are less reactive, generally use diols to make their acetals.



cyclic acetal (5- + 6-membered rings preferred)



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