

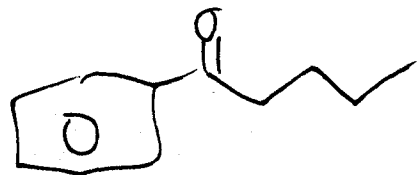
Redox Reactions (Reduction)

| Compound | Reagent (Reducing Agent) | Product |
|-----------------|--|------------|
| Acid Chloride | $\text{LiAlH}(\text{OtBu})_3/\text{ether}/-78^\circ; \text{H}_3\text{O}^+$ | Aldehyde |
| Ester | $\text{DIBAL}/\text{ether}/-78^\circ; \text{H}_3\text{O}^+$ | Aldehyde |
| Nitrile | $\text{DIBAL}/\text{ether}/-78^\circ; \text{H}_3\text{O}^+$ | Aldehyde |
| Acid Chloride | $\text{LiCuR}_2; \text{H}_3\text{O}^+$ | Ketone |
| Nitrile | $\text{RMgBr}/\text{ether}; \text{H}_3\text{O}^+$ | Ketone |
| Aldehyde | NaBH_4 or $\text{LiAlH}_4; \text{H}_3\text{O}^+$ | 1° Alcohol |
| Ketone | NaBH_4 or $\text{LiAlH}_4; \text{H}_3\text{O}^+$ | 2° Alcohol |
| Ester | $\text{LiAlH}_4; \text{H}_3\text{O}^+$ | 1° Alcohol |
| Carboxylic Acid | $\text{LiAlH}_4; \text{H}_3\text{O}^+$ | 1° Alcohol |

Redox Reactions (Oxidation)

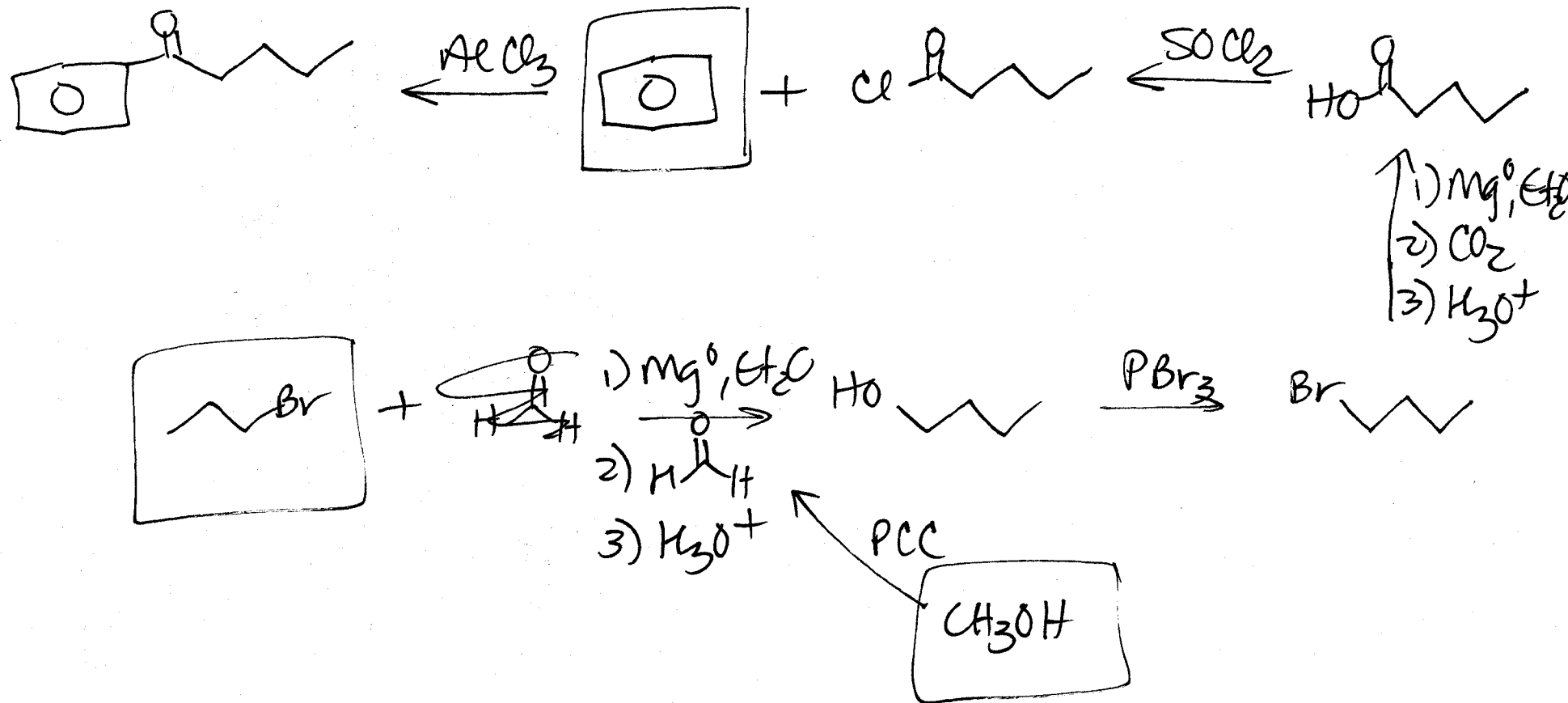
| Compound | Reagent (Oxidizing Agent) | Product |
|------------|---|--|
| 1° Alcohol | H_2CrO_4 or $\text{Na}_2\text{Cr}_2\text{O}_7/\text{H}_2\text{SO}_4$ | Carboxylic Acid (via aldehyde; not observed) |
| 1° Alcohol | PCC | Aldehyde |
| 2° Alcohol | PCC or H_2CrO_4 or $\text{Na}_2\text{Cr}_2\text{O}_7/\text{H}_2\text{SO}_4$ | Ketone |
| 3° Alcohol | Any of the above | NRX |
| Aldehyde | H_2CrO_4 or $\text{Na}_2\text{Cr}_2\text{O}_7/\text{H}_2\text{SO}_4$ | Carboxylic Acid |
| Aldehyde | | |

make:

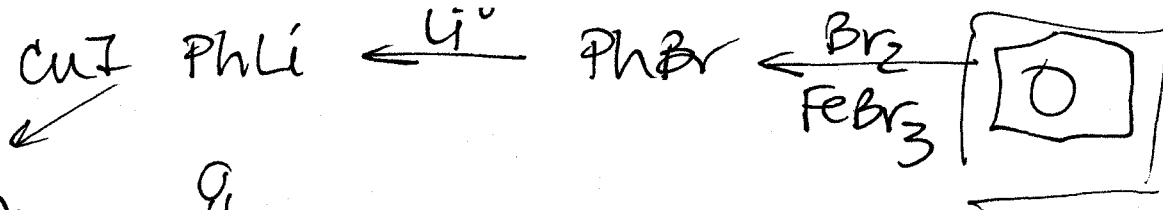
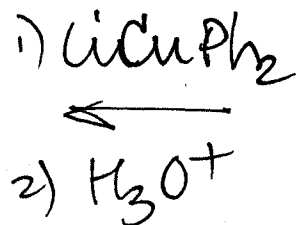
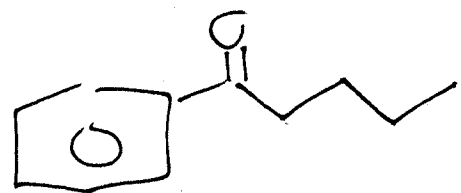


General rules:
start w/ benzene +
any 3-carbon or less
alcohol or alkyl halide
+ any inorganic reagent.

Solution #1

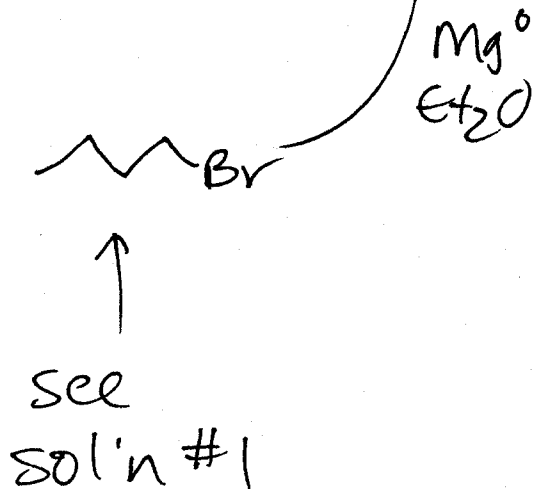
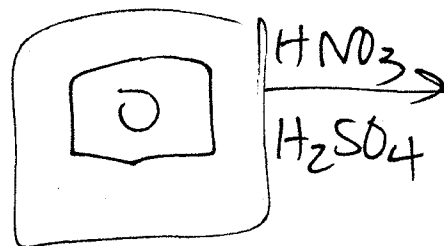
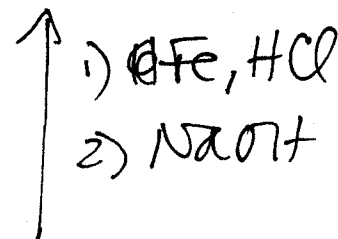
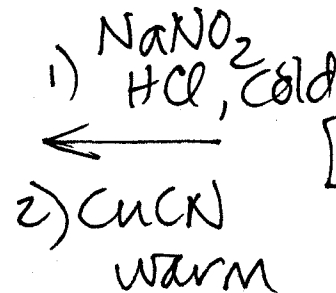
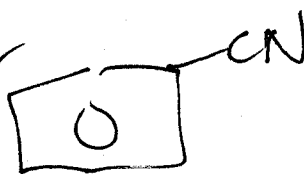
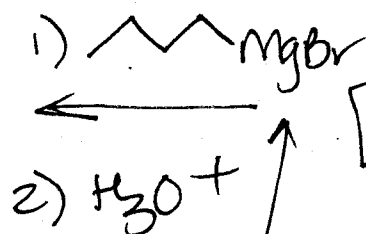
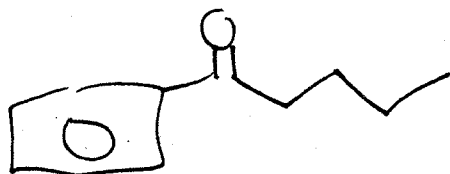


Solution #2


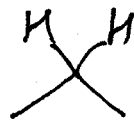

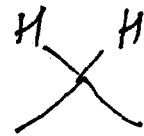
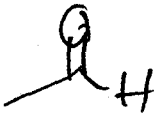
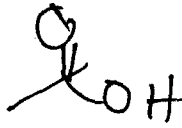


see sol'n #1

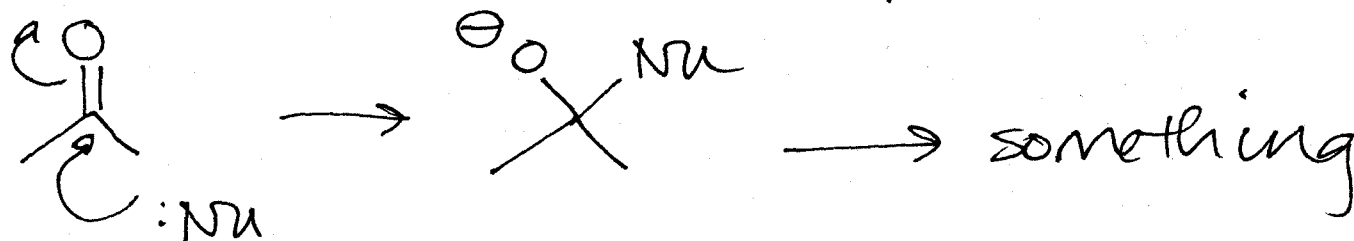
Solution #3

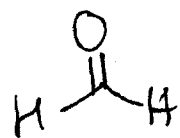


Reactions

1. Clemmensen reduction  $\xrightarrow[\text{HCl}]{\text{Zn/Hg}}$ 
2. Wolff-Kishner reduction  $\xrightarrow[\Delta]{\text{H}_2\text{NNH}_2, \text{NaOH}}$ 
3. Oxidations -  \rightarrow  CrO_3 or H_2CrO_4 or $\text{Na}_2\text{Cr}_2\text{O}_7$
4. Reductions w/ NaBH_4 or $\text{LiAlH}_4 \rightarrow$ alcohols
5. Grignard rxn

Look at #4 + #5 - nucleophile attacks $\text{C}=\text{O}$

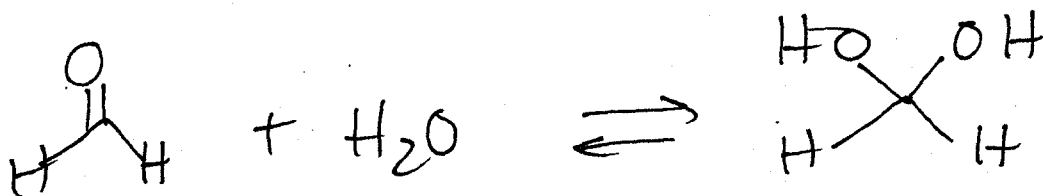




NMR: expect to see one peak $\sim 9-10$ ppm

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

Theory:

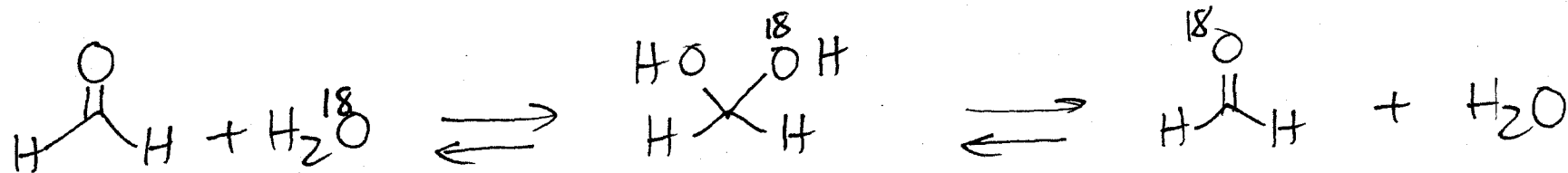


can't be isolated

gem-diol
↑
geminal (on same C)

How do we know the hydrate is there?

aka a hydrate
b/c we have added water.

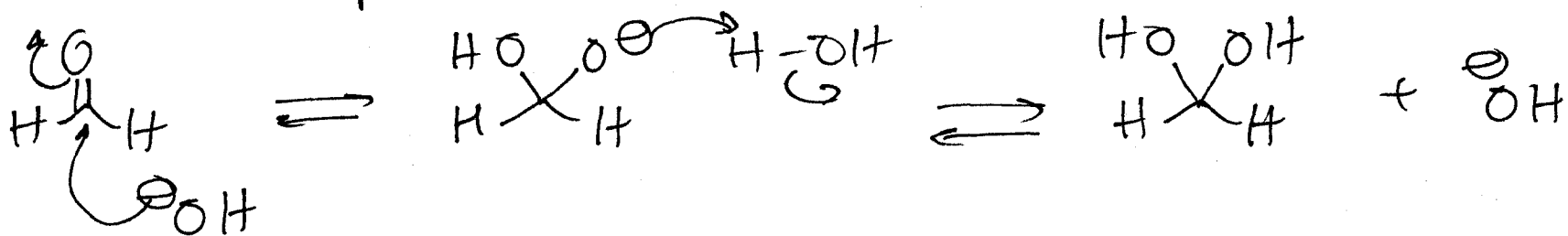


(there are some stable hydrates: $\text{Cl}_3\text{C}-\begin{array}{c} \text{HO} \quad \text{OH} \\ \diagdown \quad \diagup \\ \text{C} \\ \diagup \quad \diagdown \\ \text{H} \quad \text{H} \end{array}$)
chloral hydrate

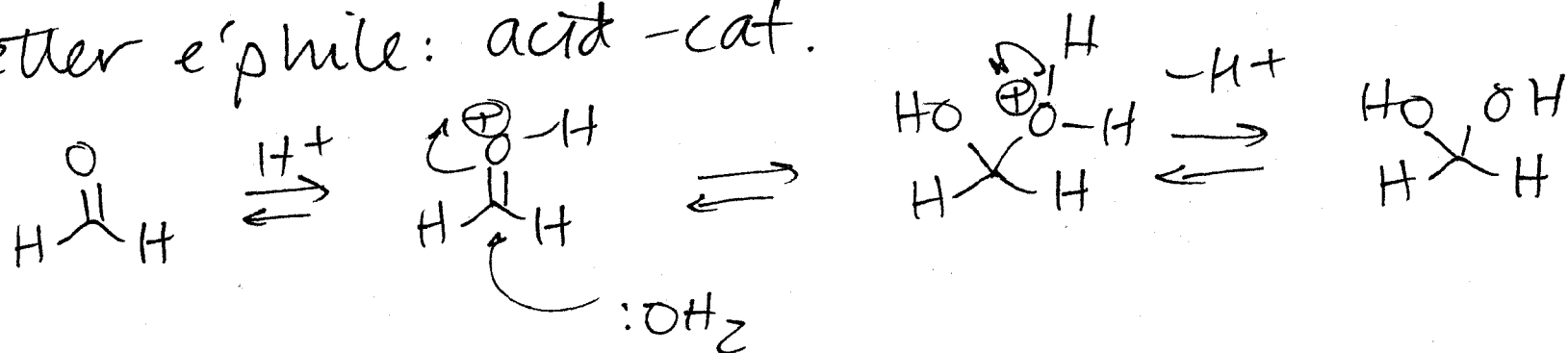
Formation of a hydrate is an equilibrium - takes time to establish the equilibrium.

How do we speed it up?

1) Better Nucleophile: base-cat.

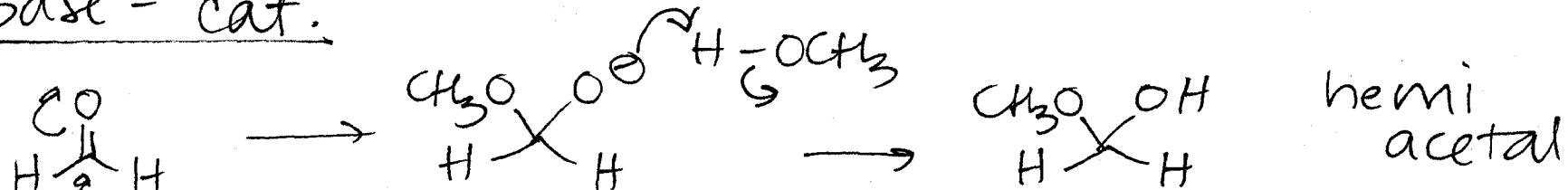


2) Better e'ophile: acid-cat.

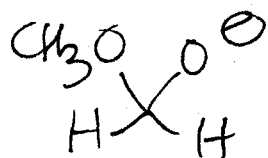


If water will do something, generally alcohols will also. So let's try CH_3OH as nucleophile

Base - cat.



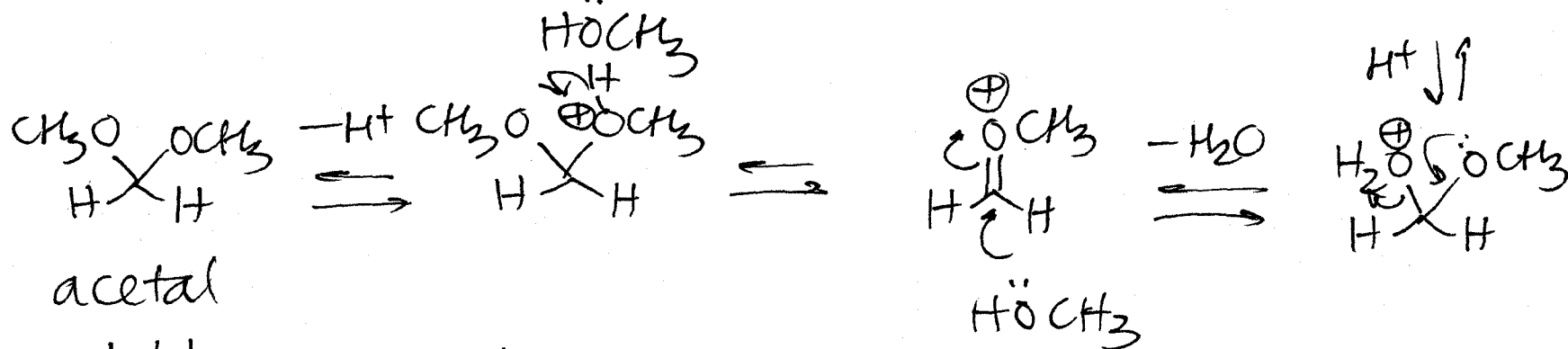
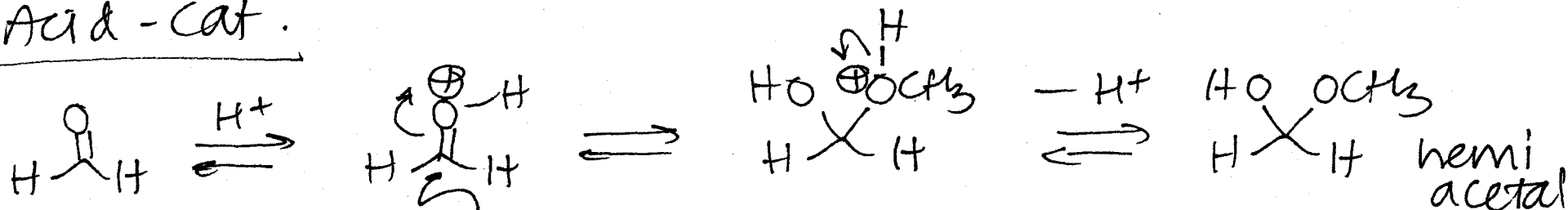
stuck @
hemiacetal
stage.



back again

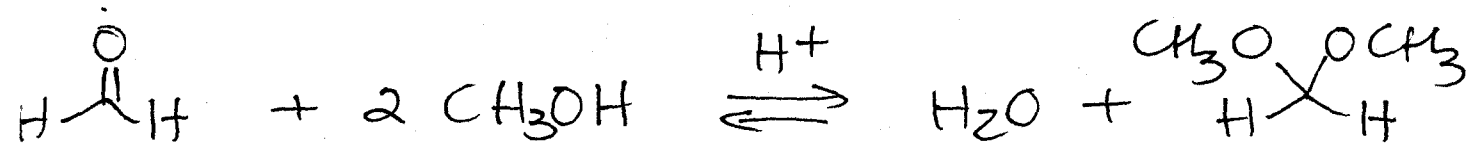
Add a 2nd equiv.
of NaOCH₃

Acid - cat.



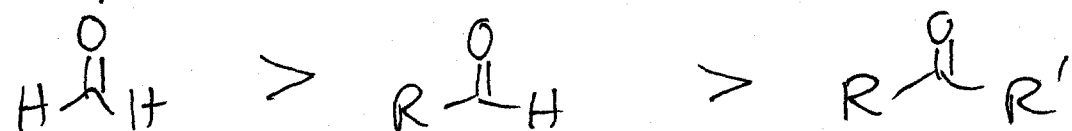
acetal

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

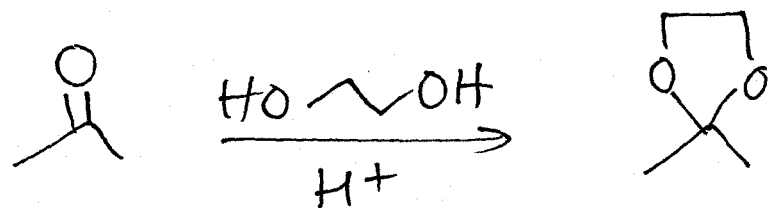


summary - relies on Le Chatelier's Principle

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)

