Course Chem 345 Lecturer Prof. Gellman

Day Monday Date 3/9/15

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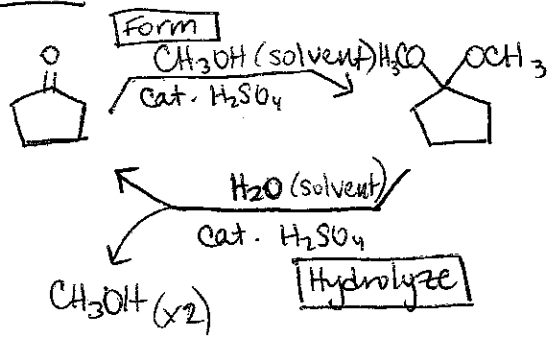
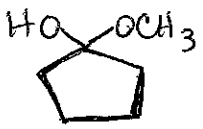
Recall: Acetals...

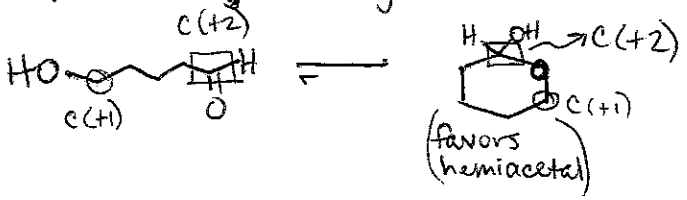


Mechanism of formation involves hemiacetal as intermediate:

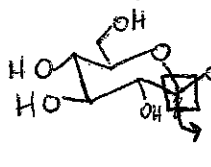


unstable

- Cyclic hemiacetals - especially w/5- or 6-membered rings - are stable
  - * exception to normally unstable hemiacetals



- * Carbohydrates -



Glucose

hemiacetal

- Acetals are often used as "protecting groups" for aldehydes / ketone C=O during multi-step synthesis
  - * b/c acetals formation is readily reversible

⇒ temporarily mask C=O reactivity

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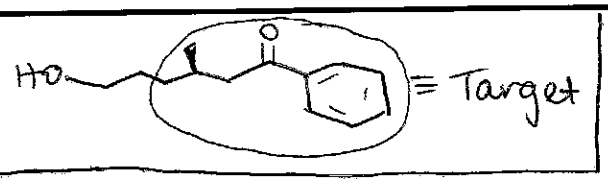
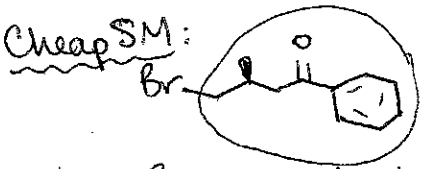
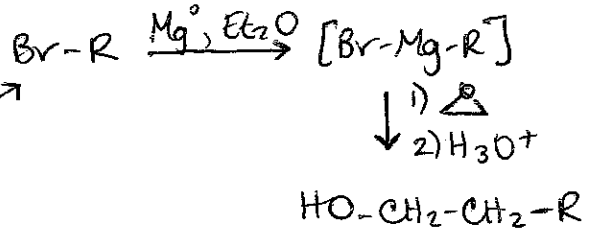


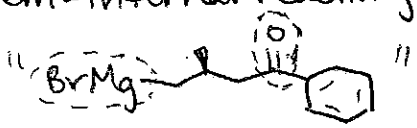
Recall:



* use Br as reactive handle to add 2 more C's and an OH



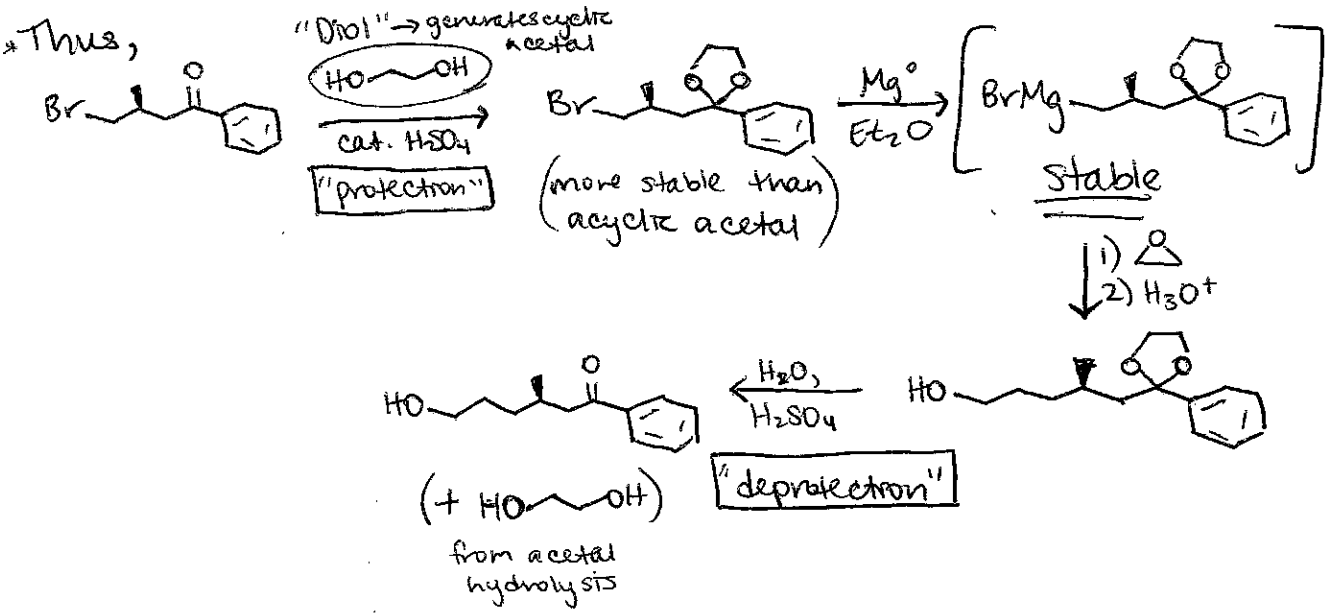
⇒ Problem - internal reactivity incompatibility:



self-destructs (Grignard will attack carbonyl)

⇒ Solve problem by temporarily "protecting" C=O as an acetal.

* Thus,



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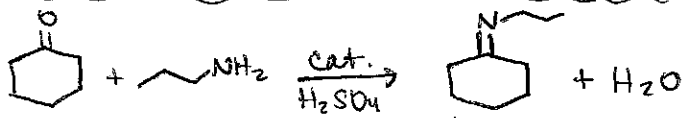
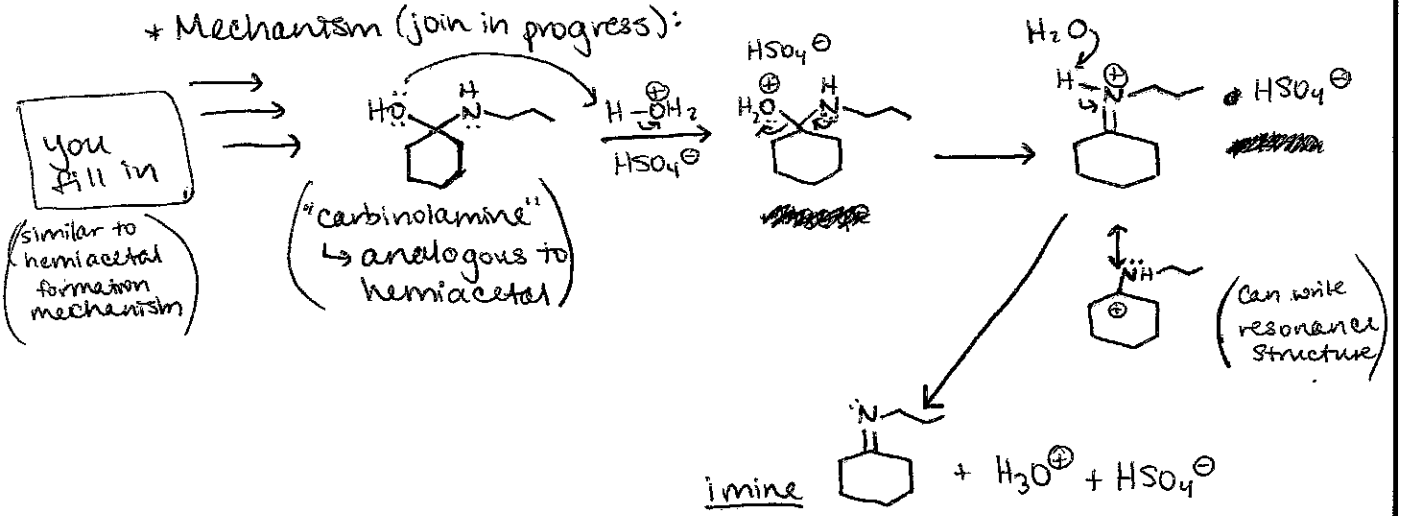
- Reactions of aldehydes and ketones with amines (revesible processes)

1) Reactions w/ 1° amines → form "imine"

Ex: 

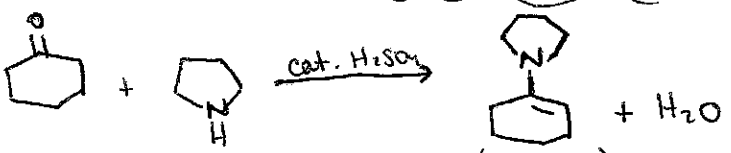
(imine)

* Mechanism (join in progress):



imine + $H_3O^{\oplus}$ + $HSO_4^{\ominus}$

2) Reactions w/ 2° amines → form "enamine"

Ex: 

(enamine)

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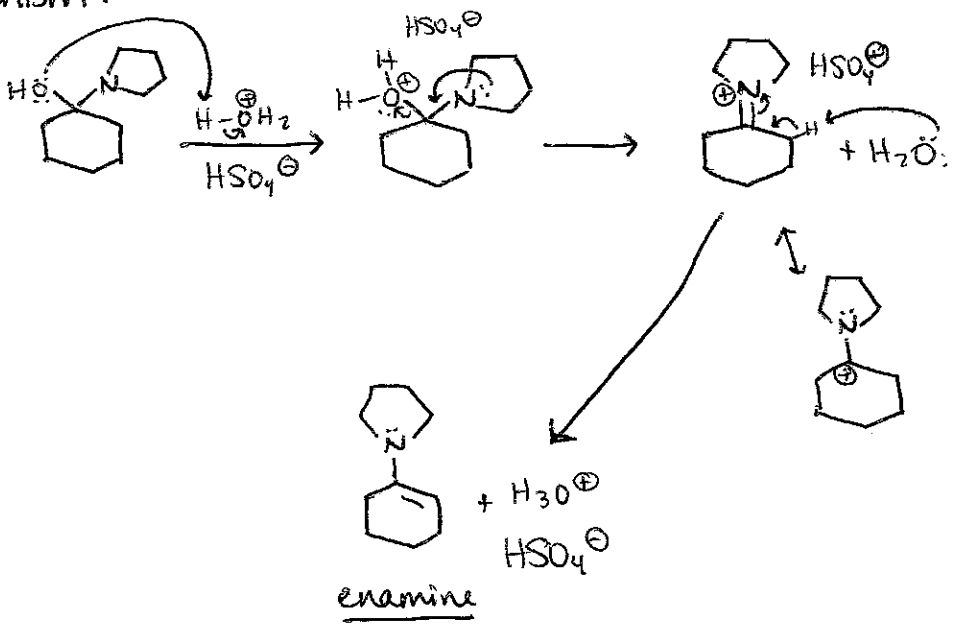
* Partial mechanism:

you fill in

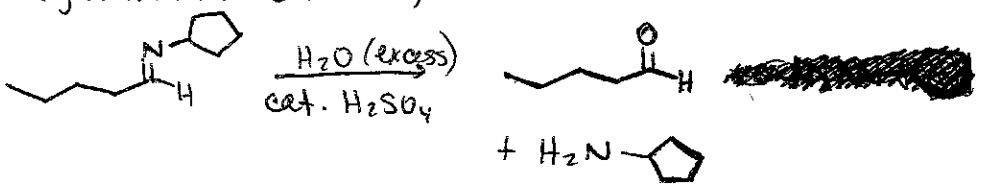
(similar to hemiacetal formation)



enamine

* Imines and enamines can be hydrolyzed to amine + aldehyde or ketone

Ex: (you fill in mechanism)



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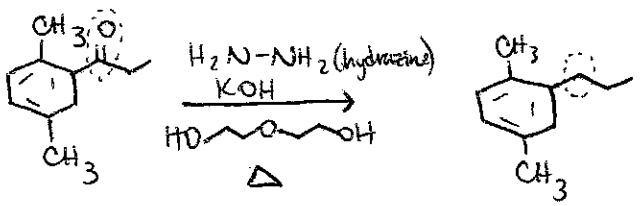
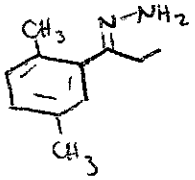
- Reductions of aldehydes and ketones (C=O to CH_2):
  - * going from C(+2) to C(+0)
  - * 2 Methods:
    1) Wolff-Kischner

Ex:



- Comments:
  - ① H_2N-NH_2 "Hydrazine"; Form imine-like intermediate



  - ② HO~O~OH ⇒ high-boiling alcohol (solvent that can withstand heat of reaction)