Course Chem 345 Instructor Gellman
Day Monday Date 10 March 2014
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PLEASE COMPLETE NOTES IN INK AND DO NOT STAPLE.

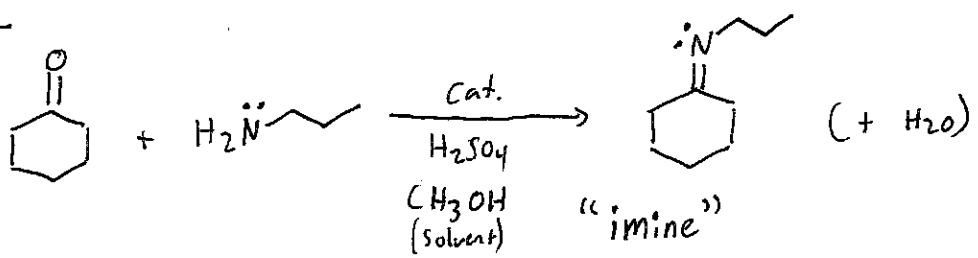
Recall: Reactions of Aldehydes & Ketones...

Reactions with amines, e.g. $:NH_3$

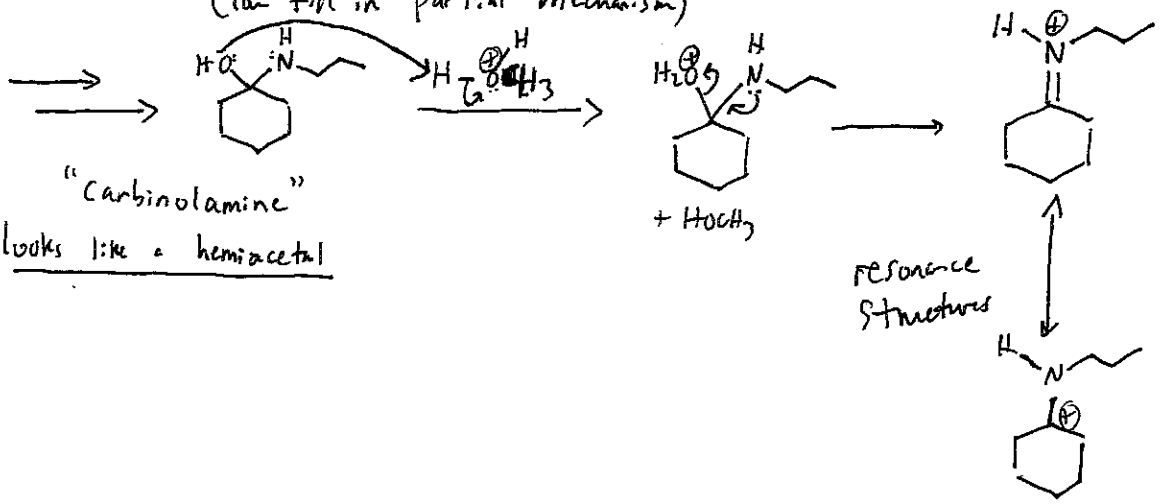
1) 1° amines + aldehyde/ketone ⟶ imine

(Note: $R-NH_2$ is a 1° amine
$R-\underset{R'}{N}-H$ is a 2° amine
$R-\underset{R'}{N}-R''$ is a 3° amine)

Ex.



Mechanism – related to acetal formation in initial steps
(You fill in partial mechanism)



looks like a hemiacetal

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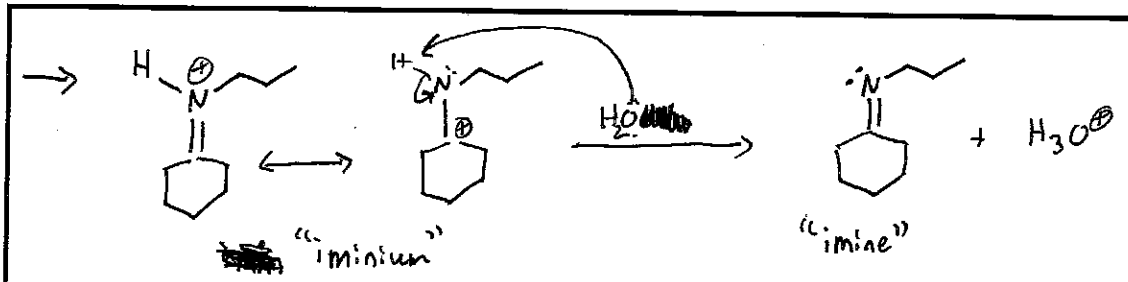
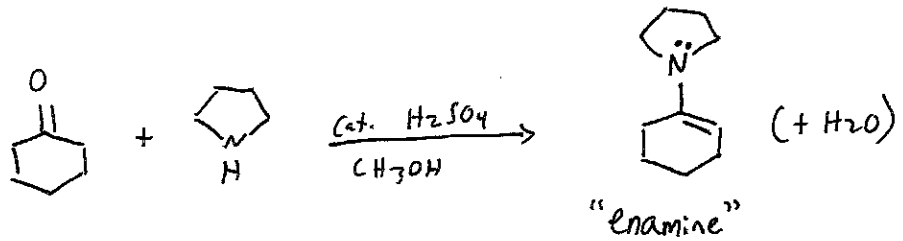
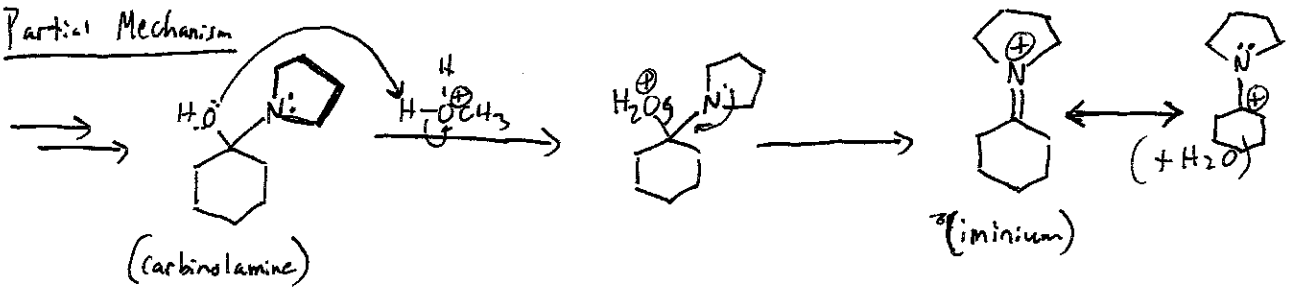


2) 2° Amine + aldehyde/ketone ⟶ enamine

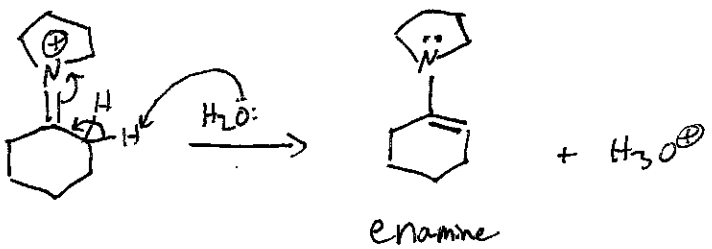
Ex:



Partial Mechanism



Now, deviation from the 1° amine mechanism:



These reactions are reversible! Thus, it is possible to hydrolyze an imine or enamine to generate the corresponding carbonyl compounds + amine.

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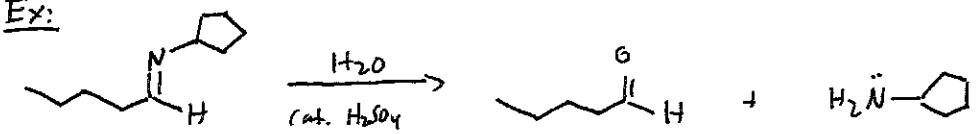
Hydrolysis Process (reverse reaction), acidic aqueous solution

Ex:



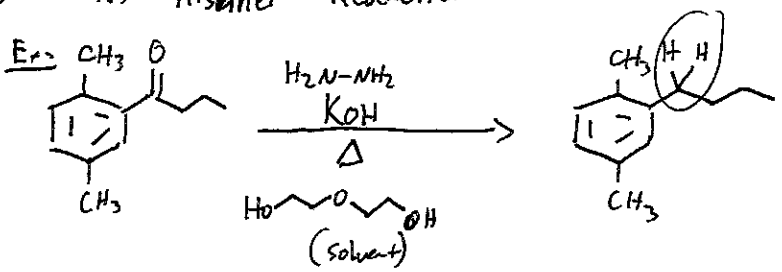
[You fill in mechanism]

Reduction of aldehyde/ketone C=O to CH_2

C (+2) ⟶ C (Ø)

2 methods: ① Wolff-Kishner Reduction

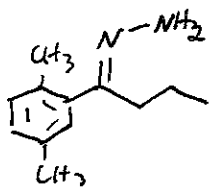
Ex:



Comments:

a) H_2N-NH_2 ≡ hydrazine

Intermediate formed ≡ "hydrazone"



b) Ho~O~OH = high-boiling alcohol (~OH, bp = 78°C; Ho~O~OH, bp = 278°C)

c) Mechanism is complex.

Note: H_2N-NH_2 is converted to N_2

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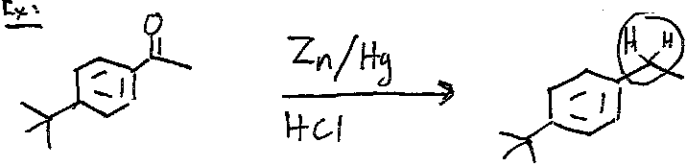
(2) Clemmensen Reduction

Ex:



Comments:

a) Mechanism unclear.

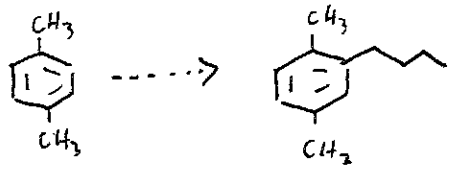
b) Zn/Hg is a zinc amalgam (mixture — zinc (solid) dissolved in mercury)

Perspective (Synthetic applications)

1) Harsh conditions! Requires simple substrates/starting materials.

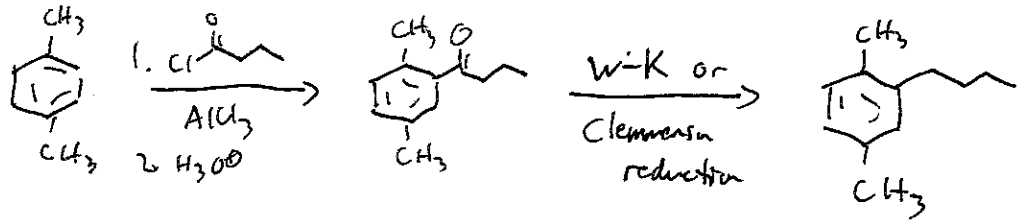
2) These reactions solve a problem in aromatic compound synthesis.

Recall:



FC alkylation is not useful because the product is more reactive than the starting material. (over alkylation)

Solution: 2-steps instead.



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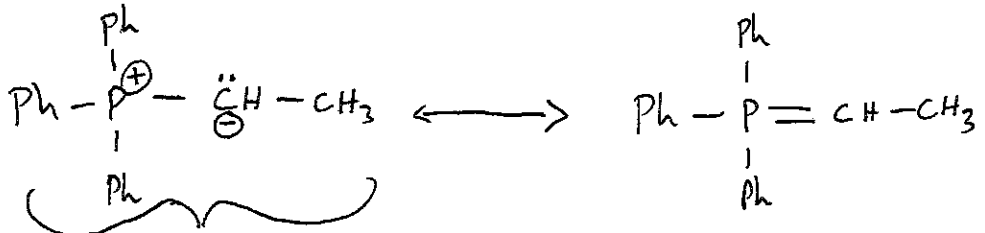
Synthesis of alkenes from Aldehydes / Ketones ("Wittig Reaction")

New type of reagent: phosphorus ylide

Ex:



[Ph ≡ phenyl ≡ ]

This is a phosphorus ylid. ("ill-idd")

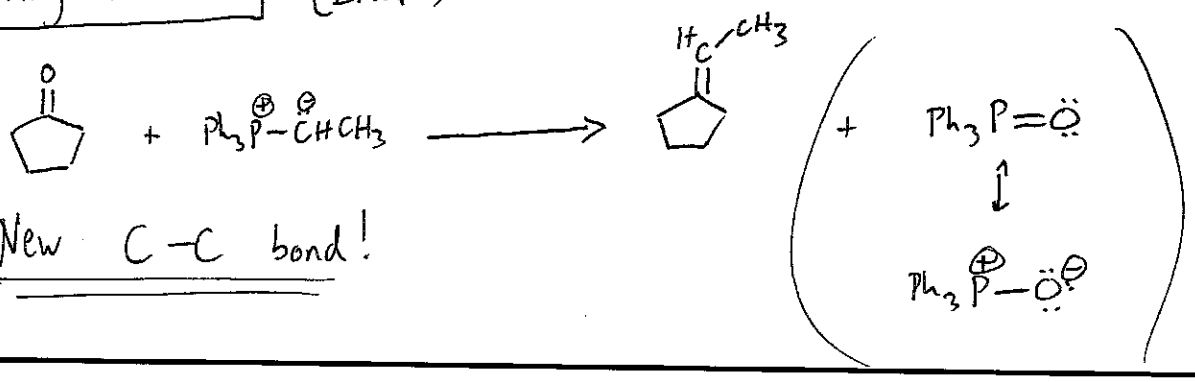
Ylid Synthesis: 2 steps

i) $Ph_3P: + I-CH_2-CH_3 \xrightarrow{S_N2} Ph_3\overset{\oplus}{P}-CH_2-CH_3\ I^{\ominus}$ (phosphonium ion)

ii) $Ph_3\overset{\oplus}{P}-CH_2CH_3\ I^{\ominus} \xrightarrow[Et_2O]{L:} Ph_3\overset{\oplus}{P}-\overset{\ominus}{C}HCH_3$ (+ butane + L:I)

(acid-base)

Wittig Reaction (Example)



New C-C bond!

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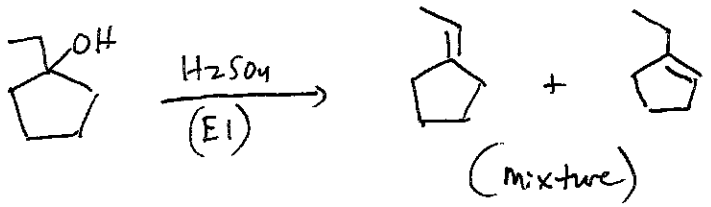
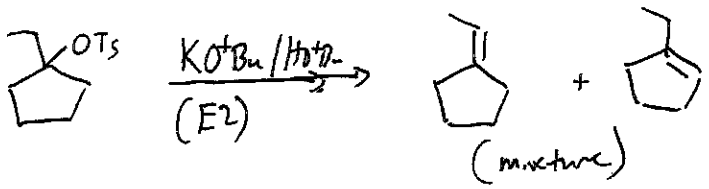
Note: the C=C bond is formed with complete regiocontrol.

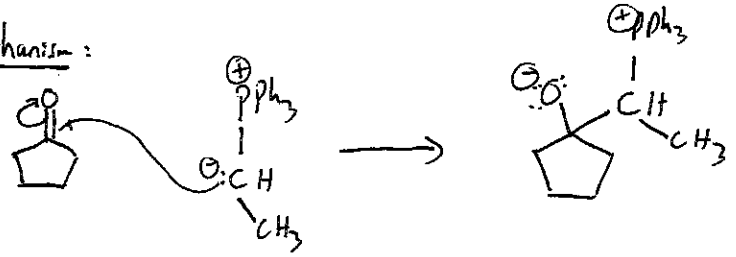
Recall:





But with the Wittig reaction, we have control over where the alkene ends up.

Mechanism:



To be continued...