

Do Not Use Pencil

Do Not Staple, Please!

Course Chem 345

Lecturer Gellman

Day Friday

Date 4-15-16

Notes Taken by Lu Liu

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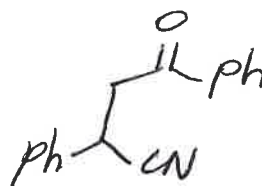
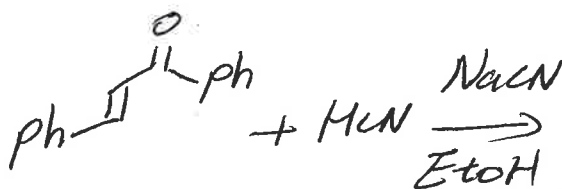
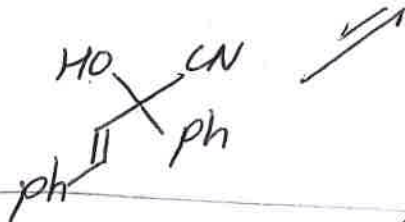
Recall: "conjugate addition" to  $\alpha, \beta$ -unsaturated

carbonyl compounds

General:



"cyanohydrin"

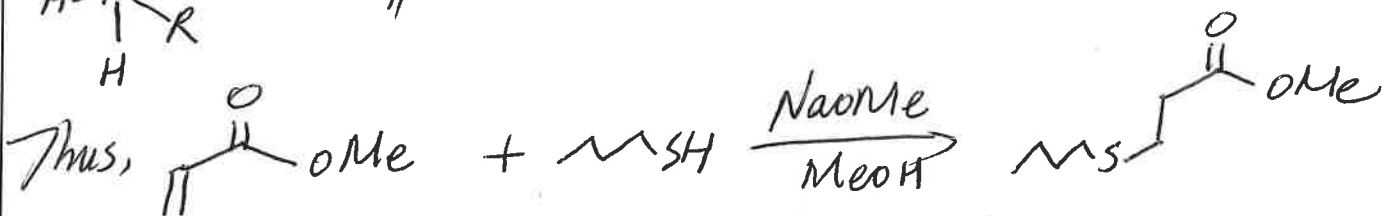


conjugate addn product favored. (C=C vs. C=O)

Weakly basic nucleophiles often favor conj. addn (vs. C=O addn)

H-CN pKa  $\sim 10$

H-SR "



Use of enolates as nucleophiles ...

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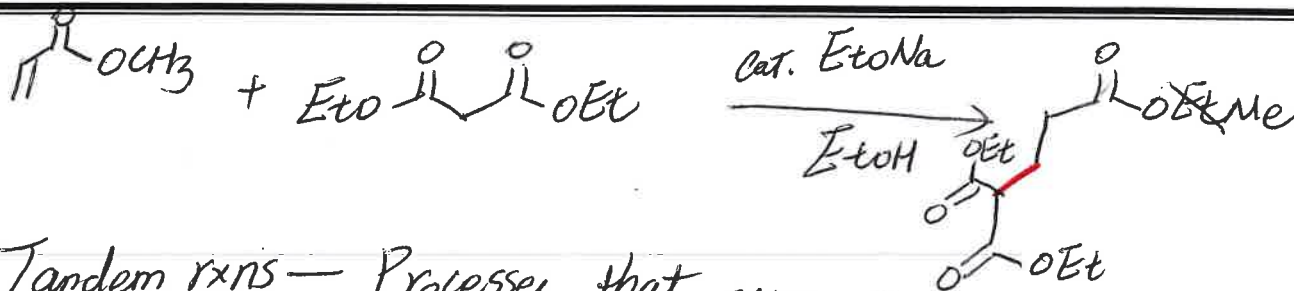
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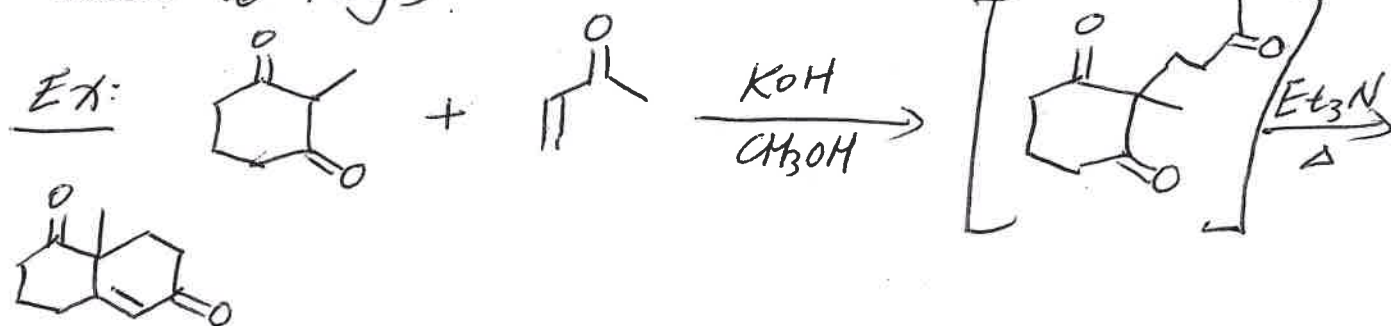
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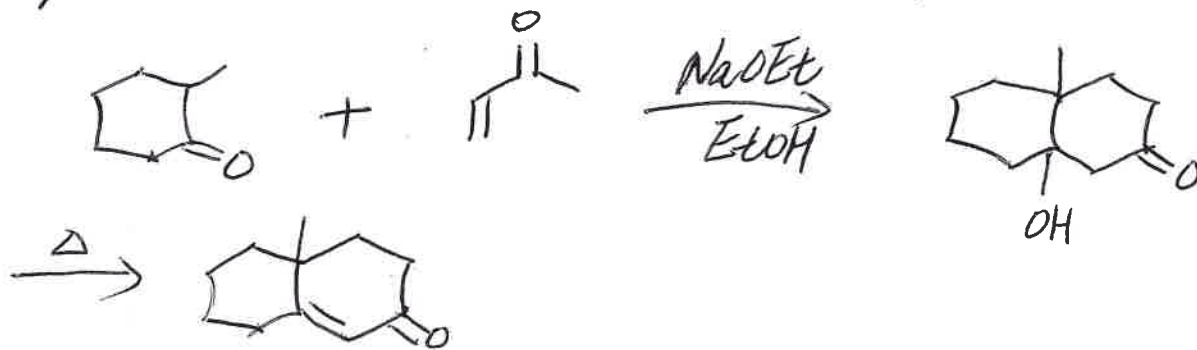


Tandem rxns — Processes that occur in a predictable sequence. "Robinson Annulation"

= Conj. Addn of enolate followed by intramolecular aldol (6-rings)



(R.A.) This Tandem process proceeds w/ simple enolate nucleophiles as well:



"Reversible" Nucleophiles  $\rightarrow$  "irreversible" nucleophiles  
(carbonion-like or ~~to~~ hydride)  $\text{LiAlH}_4$  = "clean" carbonyl reduction

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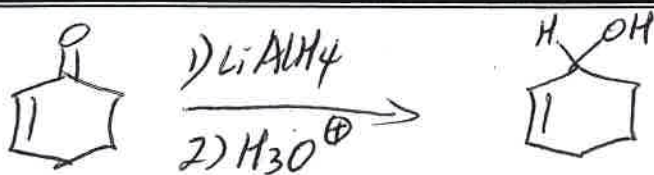
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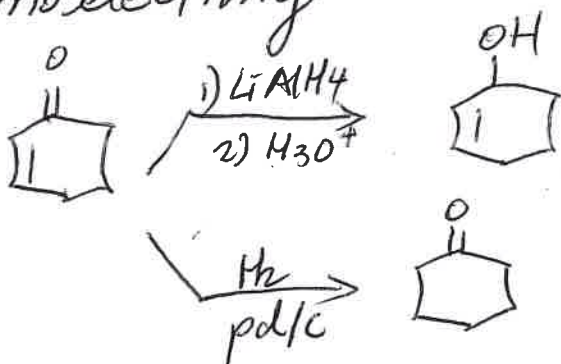
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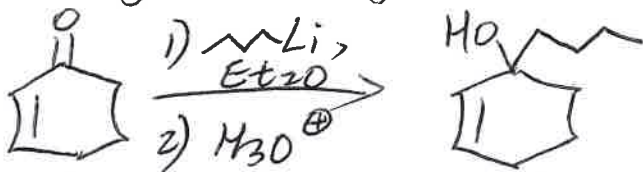


Note: NaBH<sub>4</sub> not synthetically useful - product mixtures.

"Chemoselectivity"

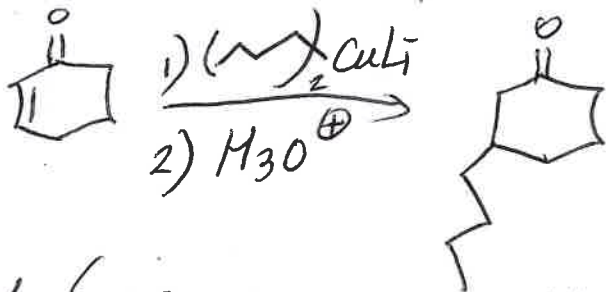


C-C bond formation from  $\alpha, \beta$ -unsat. carbonyl compounds



Note: Grignard reagents tend to give product mixtures not synthetically useful.

Selective addn to  $\beta$  carbon via cuprate reagents.



Read § 22.12 - conj. addn rxns from synthetic perspective.

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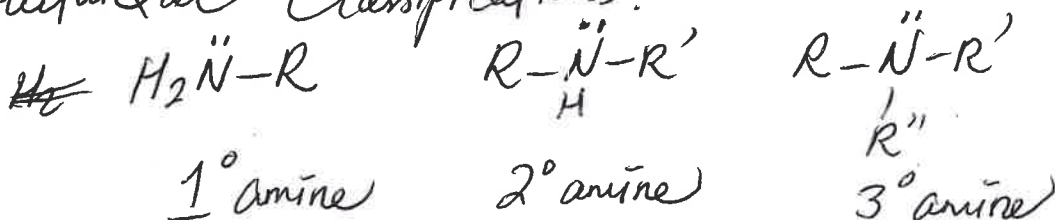
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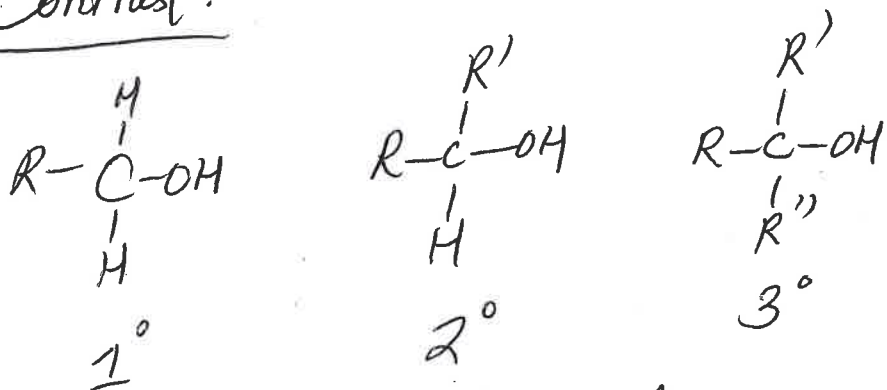
## Chap. 23 — Amines

Rec. Problems — (Partial) : 5-8, 12-26, 29, 30, 35, 36, 42 (not C).

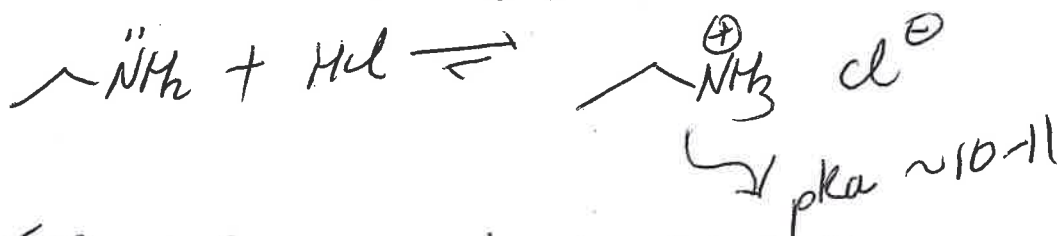
### Structural Classifications.



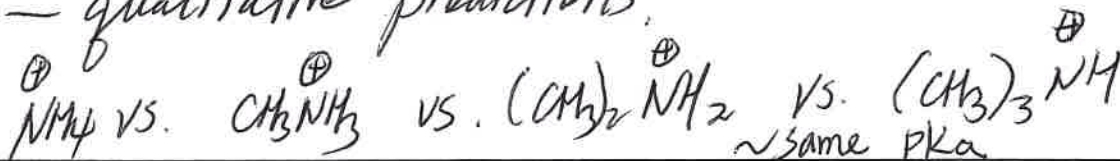
### Contrast:



### Acid-Base reactivity of amines



Effects of amine structure variation on acid-base behavior — qualitative predictions.





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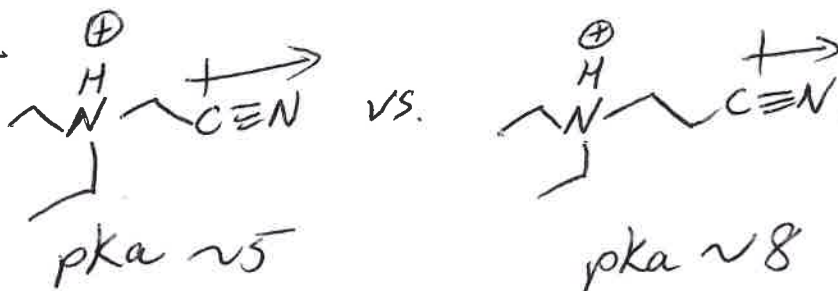
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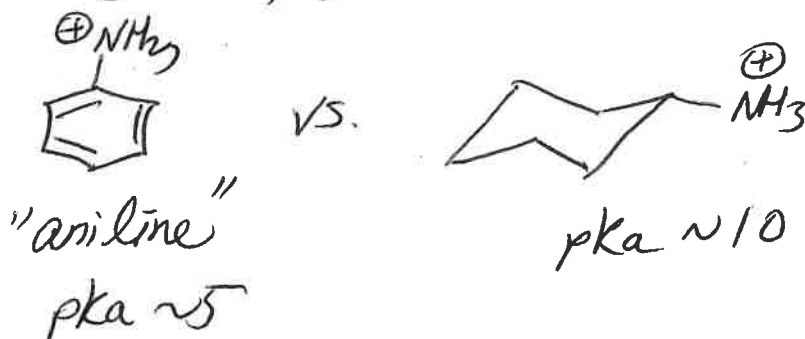
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$e^-$ -withdrawing groups dampen basicity\* (raise acidity of ~~ammonium~~ ammonium) \* of amine.

Ex:



Effects of conjugation



Aniline: lone pair conjugated to arom  $\pi$ -system.