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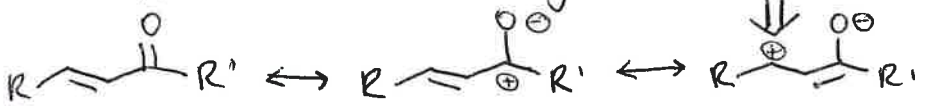
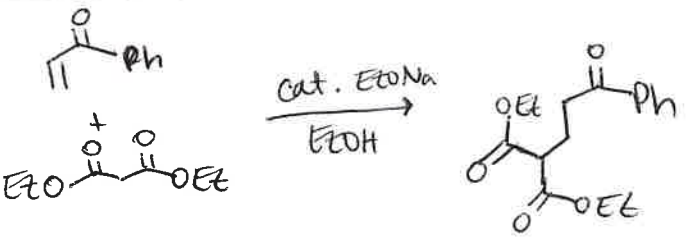
Recall: "conjugate addition" of nucleophiles to β carbon of α,β-unsat. carbonyl compounds



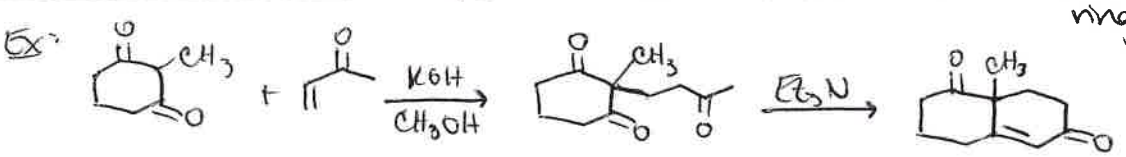
"Michael Addn" – enolate as nucleophile

Ex:

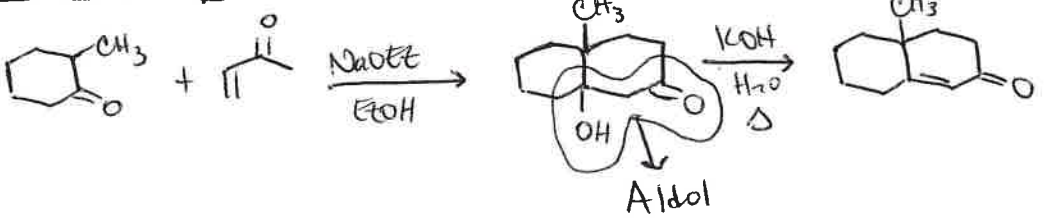


"Robinson annulation" – Michael addn. followed by aldol (to form a ring)

Ex:



One more example:



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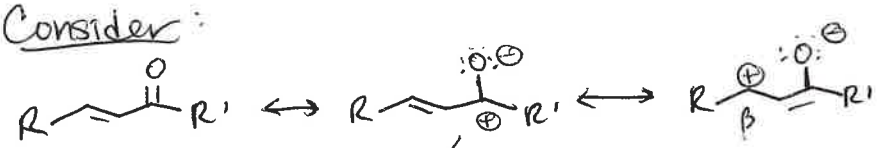
Consider:

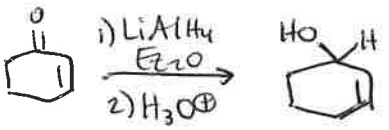


↳ select addn. here w/ irreversibly adding nucleophiles..

so far, weakly basic nucleophiles add selective @ β-position. (reversible

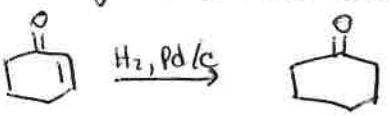
* what would be ~~[illegible]~~ irreversibly adding nucleophiles? (select addn @ carbonyl C)

- Hydride reagents ("$H:^{\ominus}$")

Ex: 

$NaBH_4$ – gives mixtures – not useful here

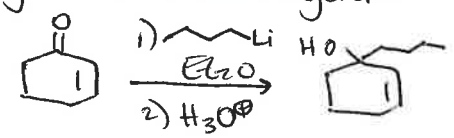
Note: Reagent choice determines product:



~~[illegible]~~.

- Alkyl addns to C=O vs. C=C

→ organolithium reagents

Ex: 

(Grignard reagents – product mix – not useful)

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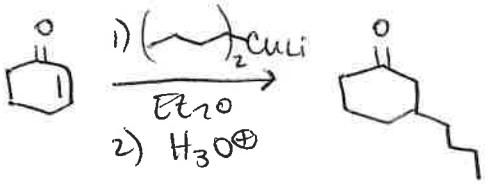
* specialized organometallic reagents for selective addn. of alkyl (and other) groups to β-position
= Lithium diorganocuprates

Ex: 

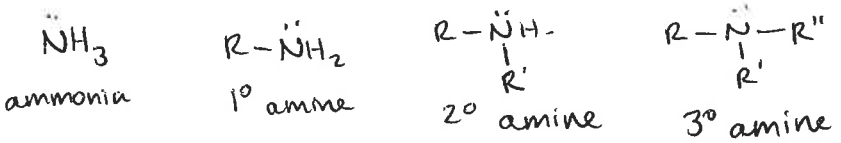
(Mechanism: studied by Herbert Goering (1921-1997))

• Read § 22.11 → conjugate addns. in synthesis

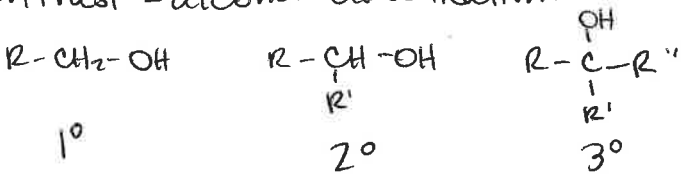
Chapter 23 - Amines

Recommended problems: 5-25, 30, 32-38, 39(except h), 40(except j), 41-46, 49-55, 56(except c), 57-60, 62, 64-74.

• Structural classification:



* contrast - alcohol classification:



↳ classify by # of substituents off of carbon adjacent to alcohol

↳ amines: classify by # of substituents off of nitrogen

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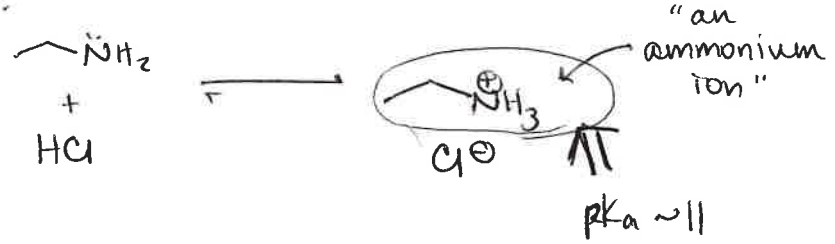
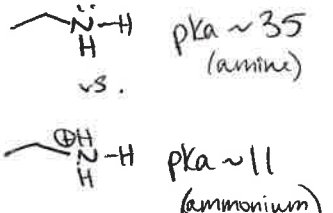
(§ 23.2 - 23.4 – spectroscopy of amines)

- Acid-base chemistry
  - * Amines are generally moderate bases...

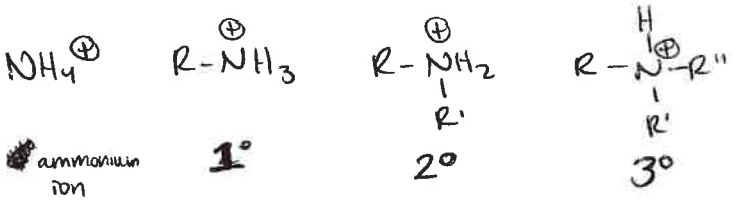
Ex:



Note (and do not confuse):



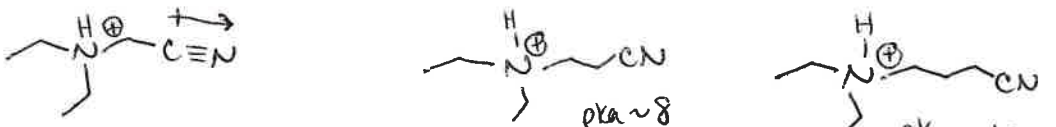
Note:



R, R', R" = alkyl pKa ~9-11

1) e- withdrawing substituents on "R" decrease basicity, i.e., lower pKa of ammonium

Ex:



3° pKa ~5 (compared to 9-11 range)

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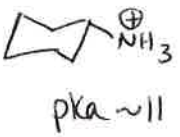
2) Effects of N lone pair conjugation

Ex:

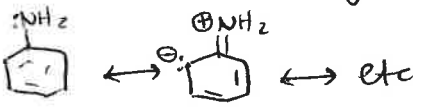


pKa ~11

pKa ~5

Rationale:

Lone pair of conjugate base is delocalized into ring.



= No delocalization of conjugate acid form

(no lone pair on N)