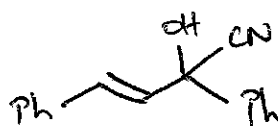
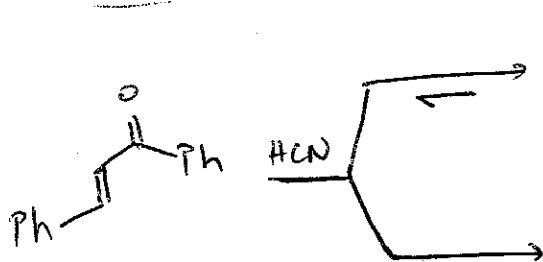
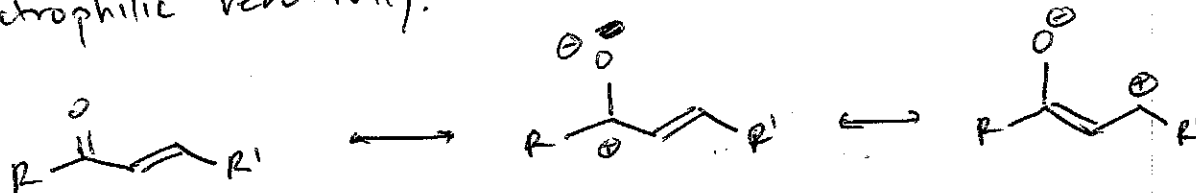
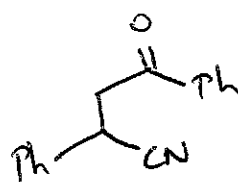


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Recall: for  $\alpha,\beta$ -unsaturated carbonyl, two sites of electrophilic reactivity.



kinetic product

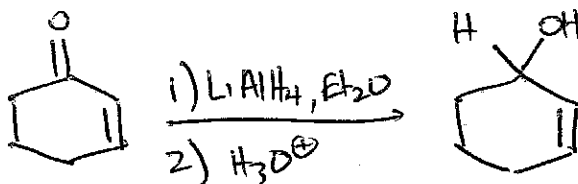


thermodynamic product  
(more stable)

- Reactions with weak bases form more stable conj. addn. products (addition to  $\beta$  carbon).

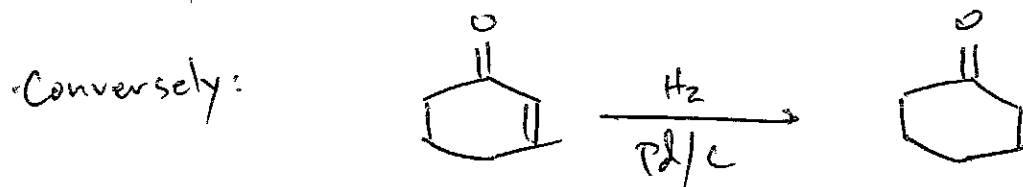
- contrast: nucleophiles that add irreversibly often react preferentially at carbonyl carbon

Example:  $\text{LiAlH}_4$



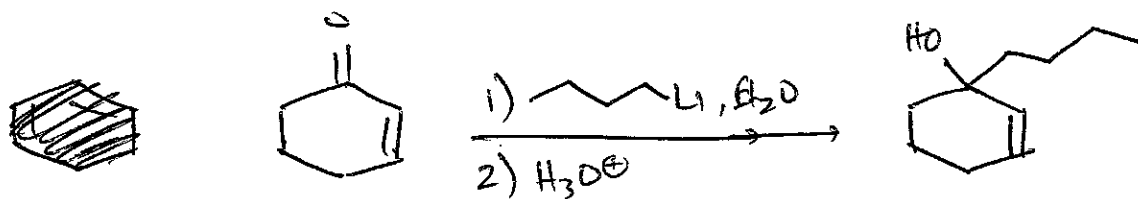
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\* Note:  $\text{NaBH}_4$  gives product mixtures w/  $\alpha, \beta$ -unsaturated ketones/aldehydes - not a useful reagent



The choice of reagents enables the chemist to achieve selective reduction at either  $\pi$  bond in  $\alpha, \beta$ -unsaturated aldehydes/ketones.

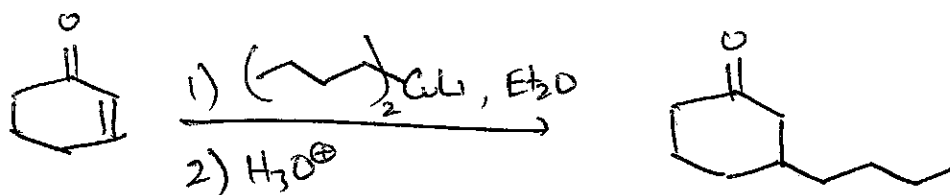
• Selective carbon nucleophile addition to  $\text{C}=\text{O}$



Note: Grignard reagents are not selective,  $\therefore$  not useful for addition to  $\alpha, \beta$ -unsat. ketones

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• Selective nucleophile addition to  $C=C$  ( $\beta$ -position) can be achieved with cuprate reagents.



synthetic complementarity to organolithiums

- mechanism is complex

- Key work: ~~Harlan~~ Harlan Goering (1921-1997)

• So, for alkylation of  $\alpha,\beta$ -unsaturated carbonyls:

→ organolithiums add to  $C=O$

→ cuprate reagents add to  $C=C$  ( $\beta$ -position)

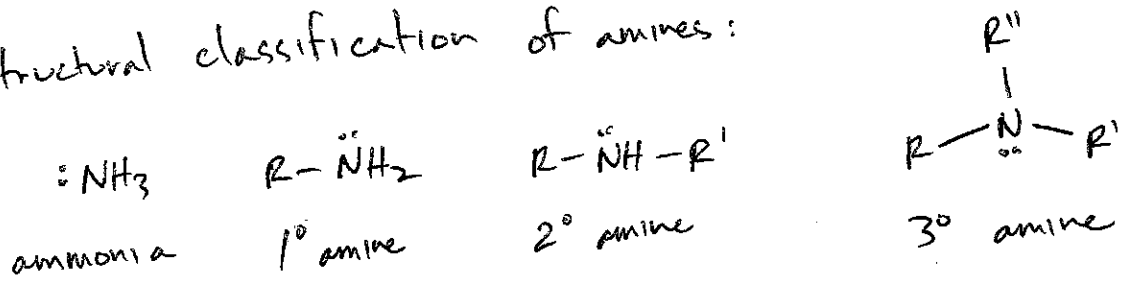
Read 22.11 on conj. addition in synthesis

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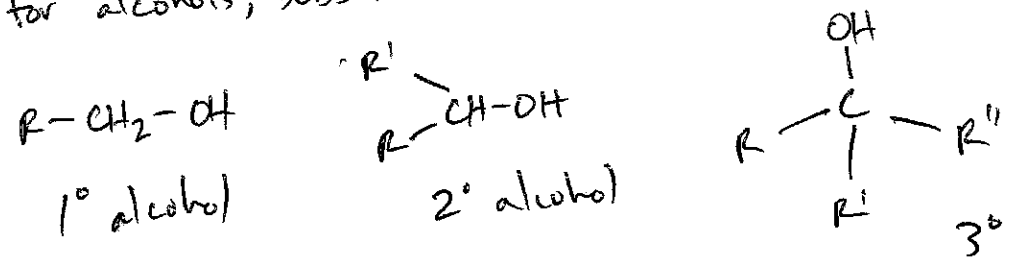
Chapter 23 - Amines

Rec. 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 of amines:



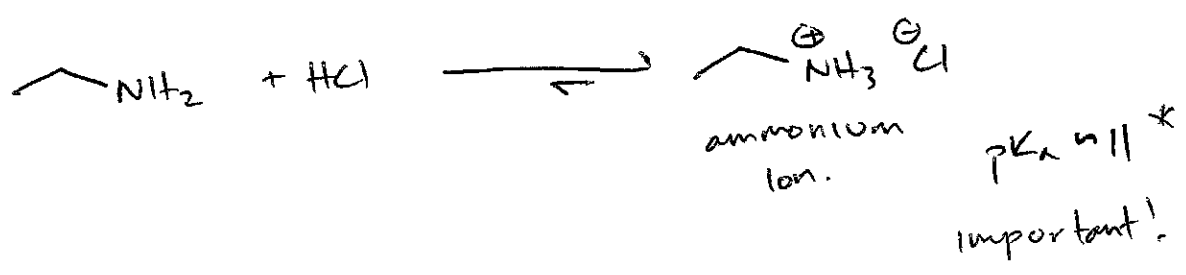
\* for alcohols, substituents on C determine classification



Read § 23.2 - 23.4 for spectroscopy, phys. properties  
 of amines

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Acid-base chemistry of amines



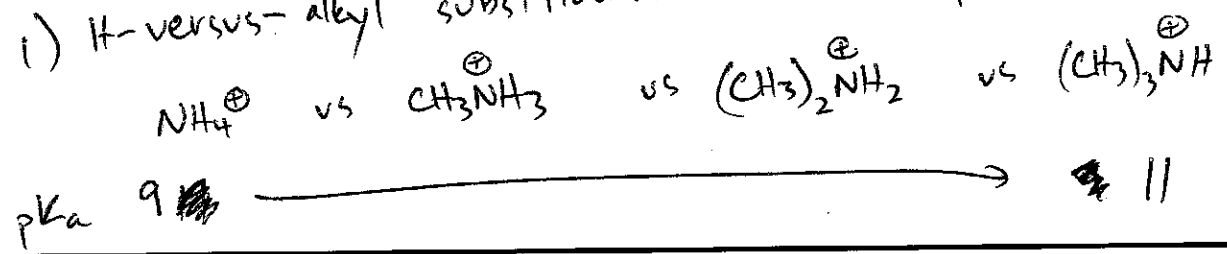
Note: Language precision is crucial in amine chemistry

" $pK_a$  of  $\text{CH}_3\text{CH}_2\text{NH}_2$ "  $\approx 35$

" $pK_a$  of  $\text{CH}_3\text{CH}_2\text{NH}_3^+$ "  $\approx 11$

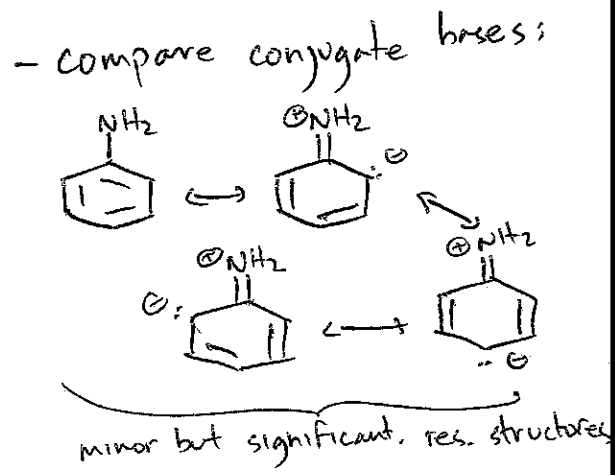
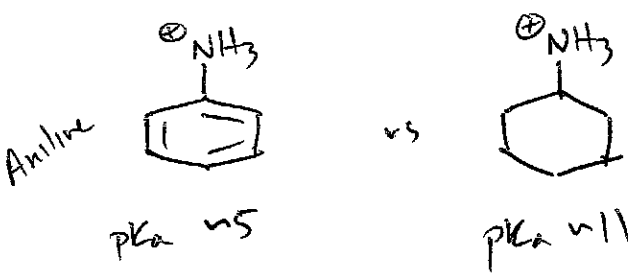
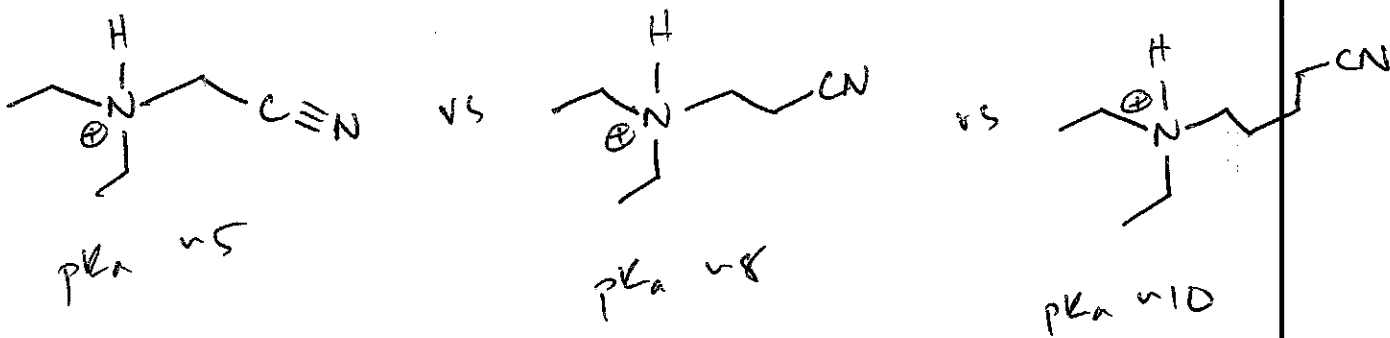
\* Principles of molecular structure already discussed can be extended to amines  
 - impact of variations in structure on acid-base properties (qualitative predictions)

i) H-versus-alkyl substituents: minor impact



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2) Electron-withdrawing substituents lower basicity  
 (i.e., lowers  $pK_a$  of conjugate acid)  
 - inductive effect



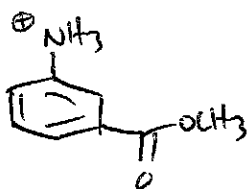
• Lone pair of aniline N is involved in resonance interactions with  $\pi$ - $\pi$  system, which lowers its basicity relative to the alkylamine

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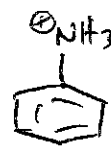
This understanding allows us to predict impact of substituents



vs

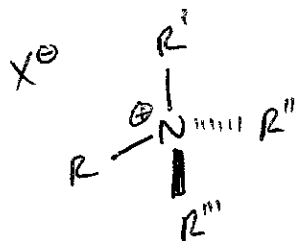


vs



—————▶ Increasing  $pK_a$

Quaternary ammonium ions



Net charge =  $\oplus$ , but charge can be  
 "coated in grease" if R groups are  
 large  
 → ions soluble in nonpolar solvents

Utility: "phase-transfer catalysis"