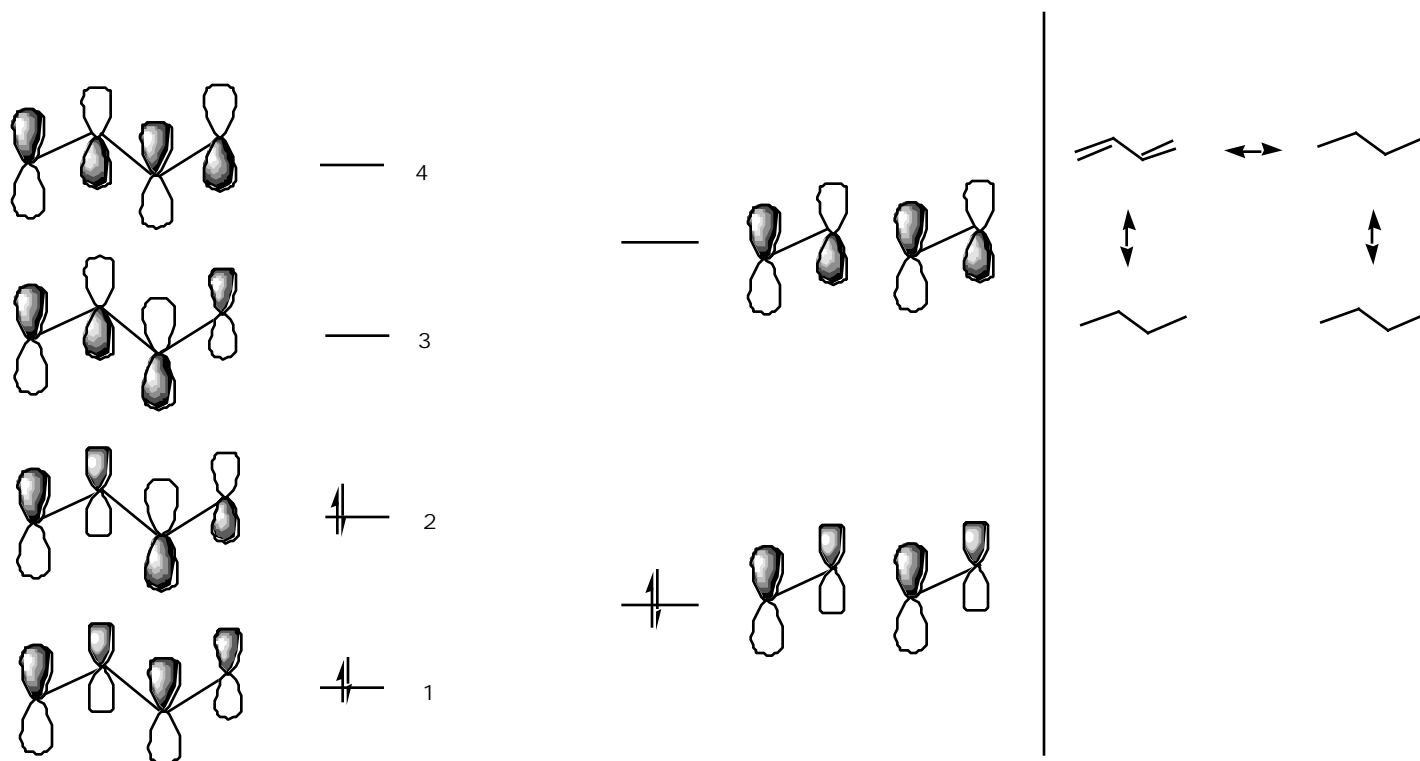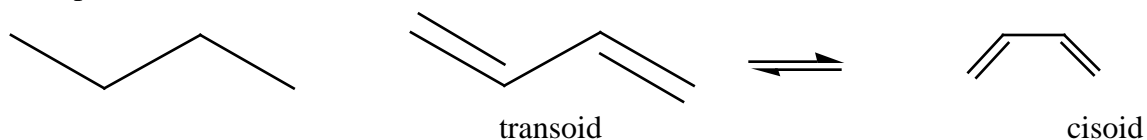**Aside: Laboratory Experiment on the Diels-Alder Reaction**: Jones pp 536-546

The Special Chemistry of 1,3-Dienes
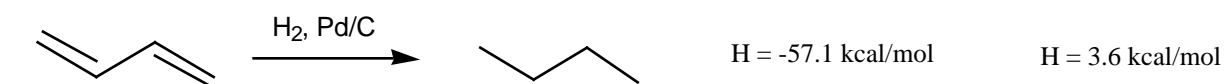

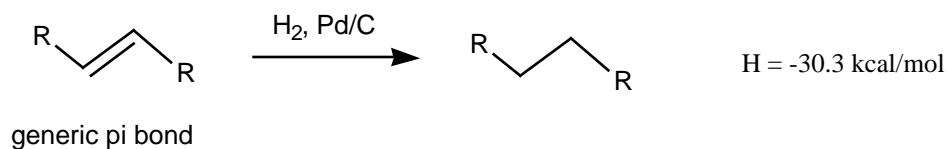
Effects of the adjacent pi bonds:
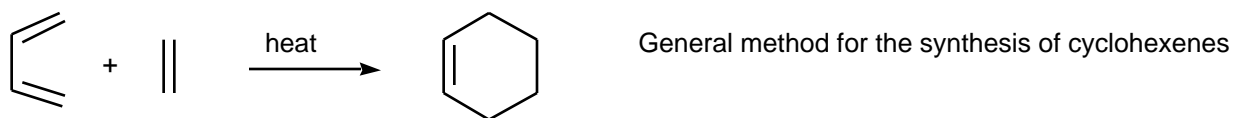
bond lengths
bond rotation

transoid   cisoid

Two explanations: p-p overlap increases delocatization--how much?
                      middle bond is overlap between sp^2 and sp^2 orbitals

Measure effects of conjugation by determining energy of removing the p orbitals--hydrogenation

H_2, Pd/C

$H = -30.3$ kcal/mol

generic pi bond

H_2, Pd/C

$H = -57.1$ kcal/mol $H = 3.6$ kcal/mol

General method for the synthesis of cyclohexenes

No nucleophile, no electrophile, no radical---what is the basis for the reactivity in this process?
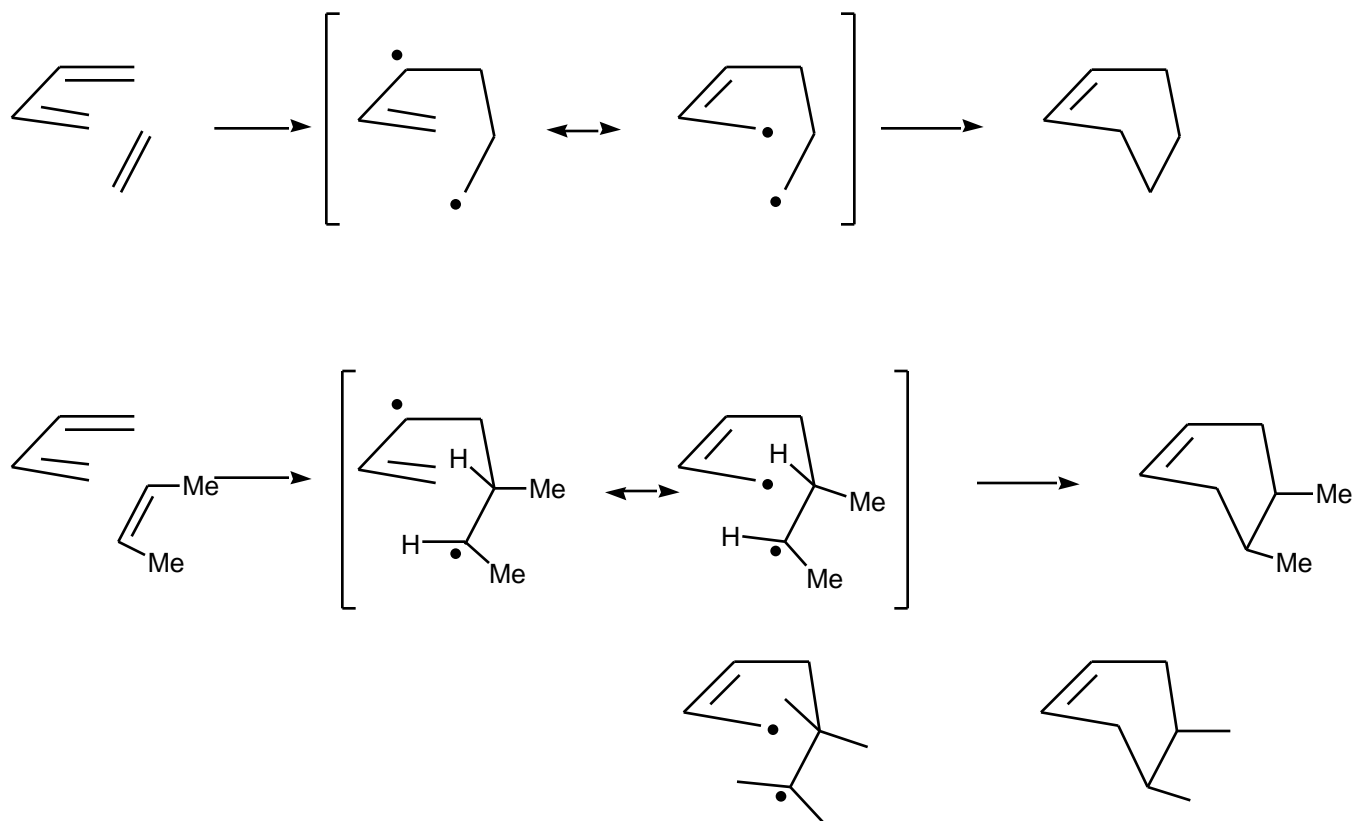
Collision between the reactants leads to orbital interaction, with precise geometry for "best" interaction.

One can draw arrows, but gives a misleading picture of two electrons flowing from high electron density location to low.
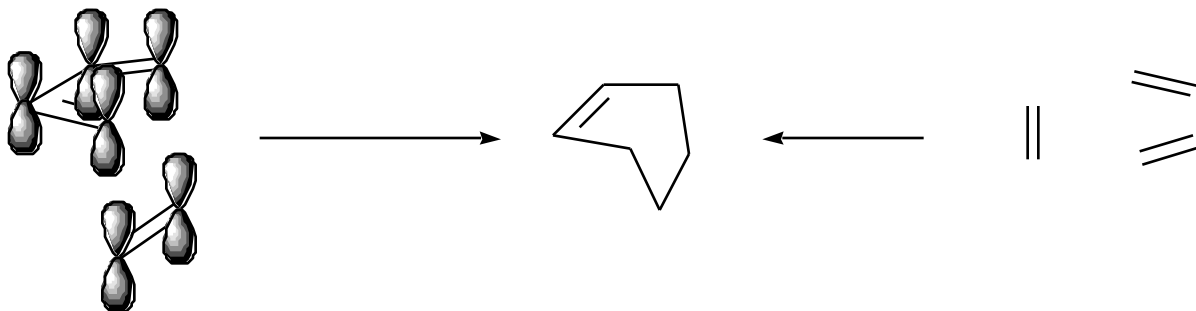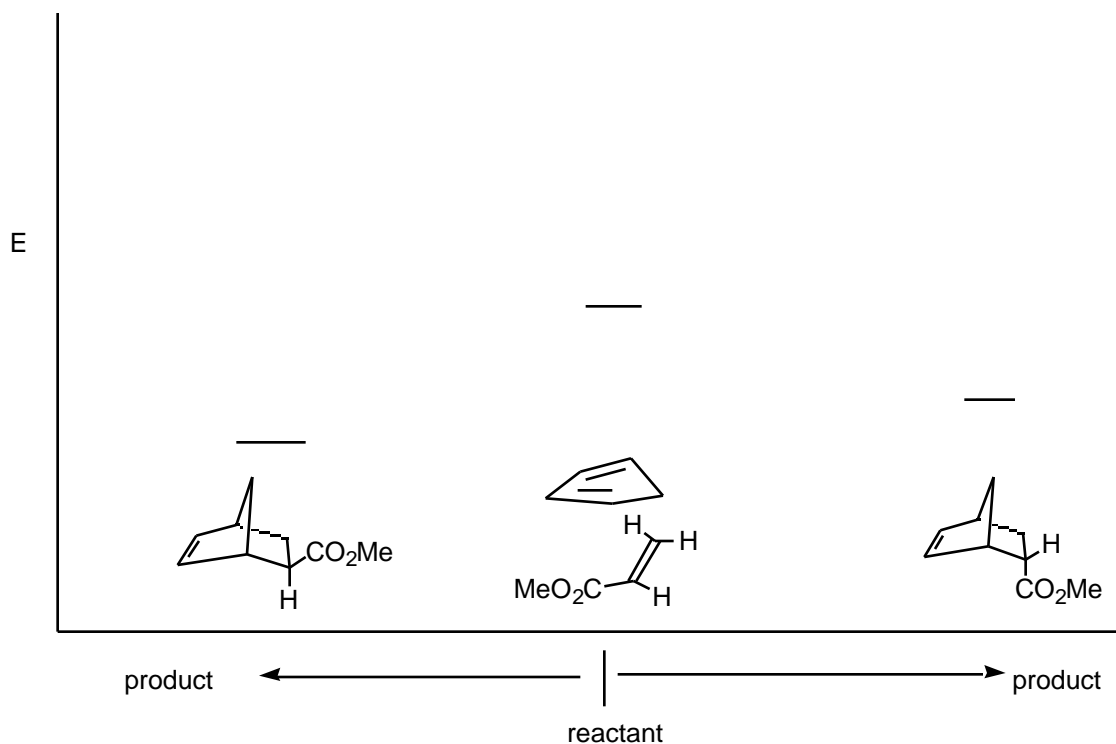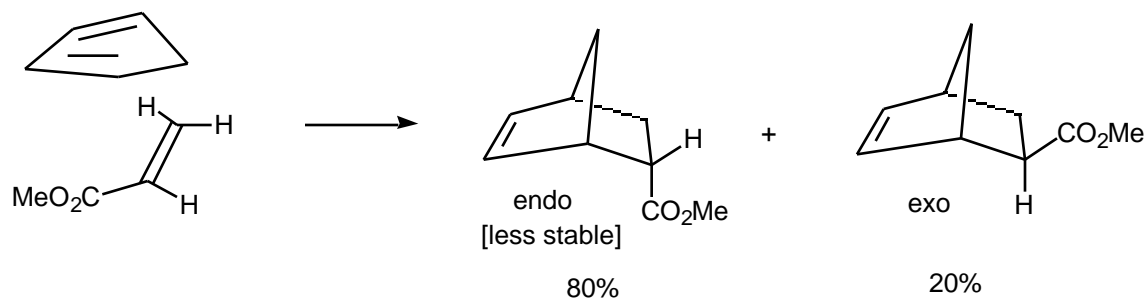
Classic example of the question of one-step or two-step mechanism:

Radical Two-step:

Generally highly stereospecific: Product retains geometry of alkene substituents.

Another element of stereoselectivity: ENDO   EXO

endo
[less stable]

80%

exo

20%

E

product ← | → product

reactant

Why ENDO favored kinetically, when not the most stable?
Transition State feels "secondary orbital overlap"
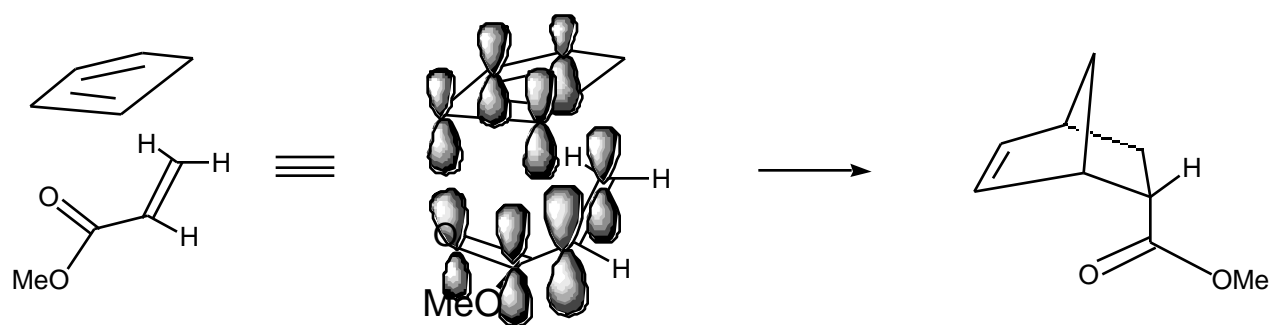
Endo leads through the more favorable transition state (lower energy) to give the less stable product.

At higher temperature, the reaction can go rapidly backwards (and forwards), and "equilibrate" the products.
   The more stable product will dominate as equilibrium is established.
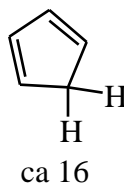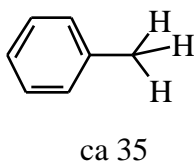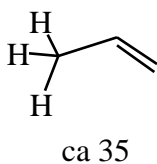
Note: Cisoid geometry required (see: text p 538)

_____

Back to acidity and basicity:

ca 35   ca 35   ca 16

Critical point: in the allyl structures (and in the carboxylate example), the negative charge is distributed equally
   at both of the terminal atoms and not at all at the central carbon. That means when the anion is quenched by
   addition of water, a proton can return to either end (but not the middle carbon)

Phenols

Inductive effects on the acidity of carboxylic acids:

$$CH_3\text{-}CO_2H \qquad FCH_2\text{-}CO_2H \qquad F_2CH\text{-}CO_2H \qquad CF_3\text{-}CO_2H$$

pK_a 4.8   2.7   1.2   0.2

$$CH_3CH_2 - \overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle Cl}{|}}{C}} - CO_2H \qquad CH_3 - \overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle Cl}{|}}{C}} - CH_2CO_2H \qquad H - \overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle Cl}{|}}{C}} - CH_2CH_2CO_2H \qquad CH_3CH_2CH_2CO_2H$$

$$\qquad 2.8 \qquad\qquad\qquad 4.1 \qquad\qquad\qquad\qquad 4.5 \qquad\qquad\qquad\qquad 4.8$$
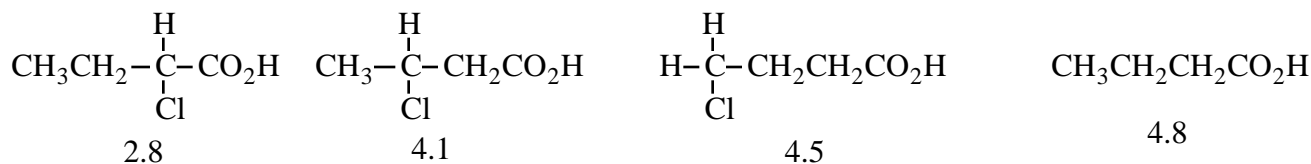
Summary: resonance and inductive effects rationalize acidity of organic compounds.

inductive effects depend on electronegativity of attached or nearby atoms

resonance effects depend on delocalization and stability of contributing structures

---

One more factor:

Especially in considering the acidity of hydrocarbons: $CH_4 \qquad [:CH_3]^- + H^+$

Consider the stability of the orbital in which the electron pair of the anion resides

HYBRIDIZATION: "s character" effects

methane

$pK_a > 55$

ethylene

ca 42

benzene

ca 42

an acetylene

25

39
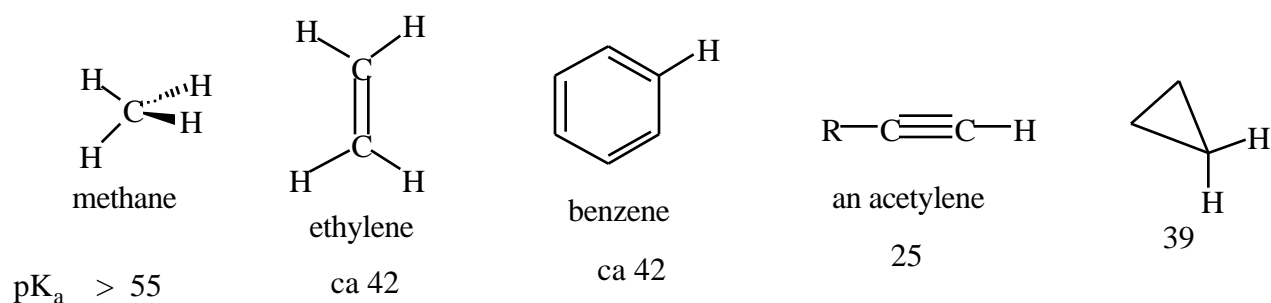
Now: BASICITY

Lewis base: Capable of donating a pair of electrons to a Lewis acid (or H^+)

More readily donated--stronger base

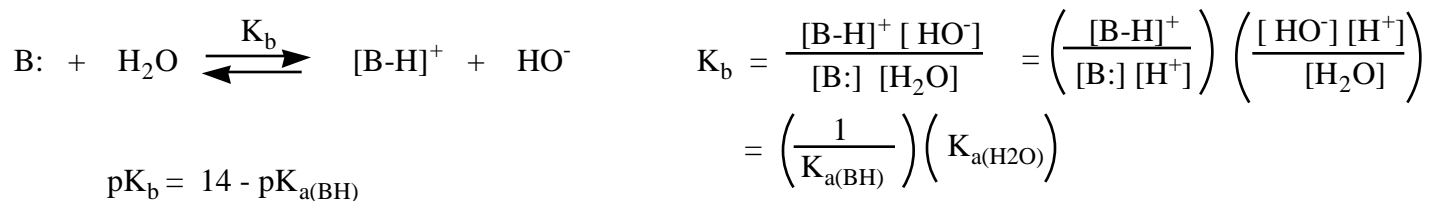less strongly held---more readily donated

Occupying higher energy MO--less strongly held

$$B: \quad + \quad H^+ \qquad\qquad [H\text{-}B]^+$$

$$:B^- \quad + \quad H^+ \qquad\qquad [H\text{-}B] \qquad \text{Less stabilized charge--Stronger base}$$

(a) related to pK_a of the conjugate acid (higher pK_a = stronger base)
    i.e., pK_a of [H-B] relates to the base strength of :B⁻.
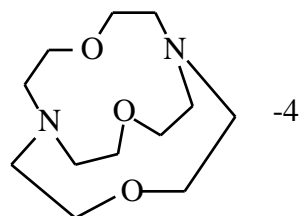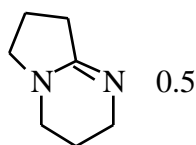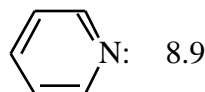(b) can define pK_b which relates directly to base strength in water

$$B: + H_2O \xrightleftharpoons{K_b} [B-H]^+ + HO^-$$

$$K_b = \frac{[B-H]^+ [HO^-]}{[B:] [H_2O]} = \left(\frac{[B-H]^+}{[B:] [H^+]}\right)\left(\frac{[HO^-] [H^+]}{[H_2O]}\right)$$

$$= \left(\frac{1}{K_{a(BH)}}\right)\left(K_{a(H2O)}\right)$$

$$pK_b = 14 - pK_{a(BH)}$$

Amines are the most common organic bases:

Data: pK_b
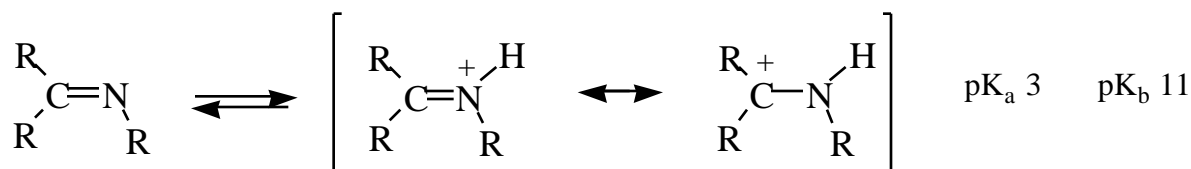
:NH₃	4.7
$(CH_3)NH_2$	3.4

 N: 8.9

 0.5

 -4

Hybridization effects: *extreme in nitriles*

$$R-C\equiv N \xrightleftharpoons{H^+} R-C\equiv \overset{+}{N}-H$$

pK_a -10
pK_b 24!

sp hybridization,
non-bonding electrons tightly held: weak base
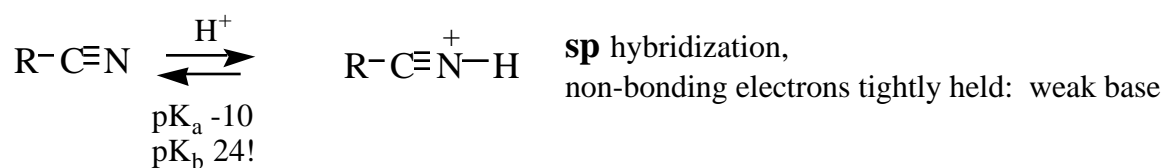
intermediate in imines: sp² hybridization

                    pK_a 3 pK_b 11
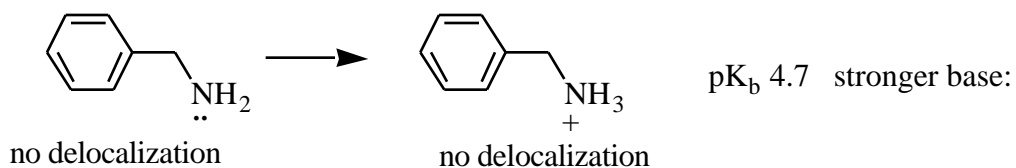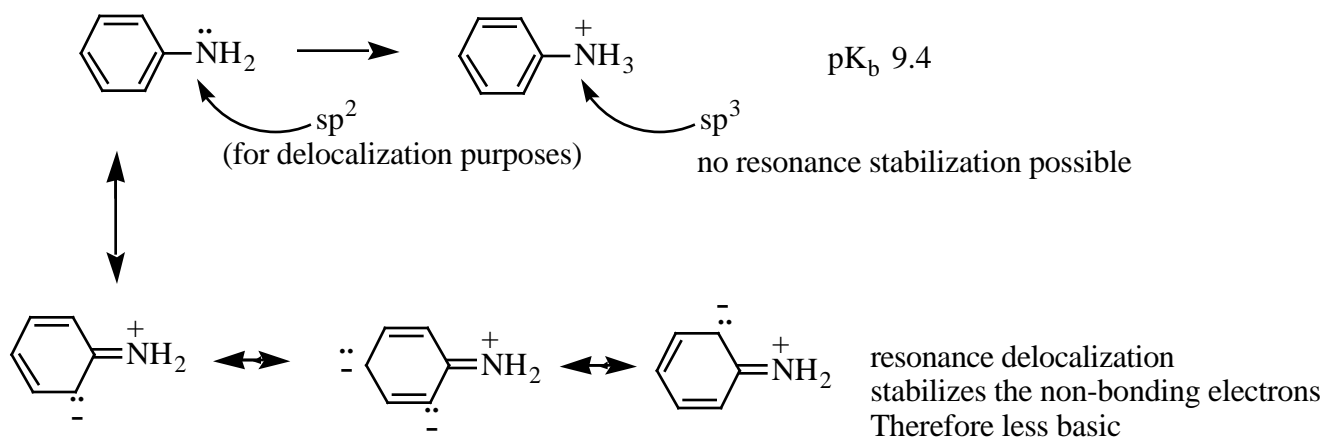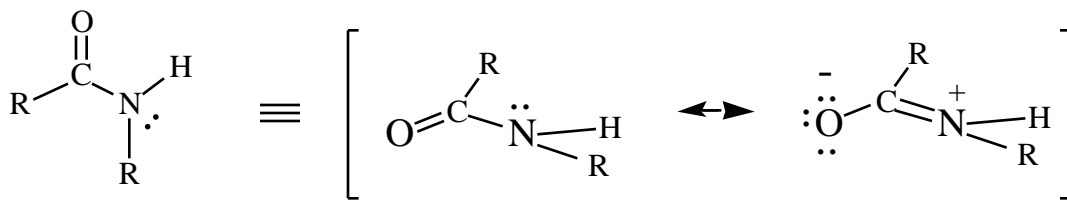
pK_a -2

pK_a -2

pK_a -6
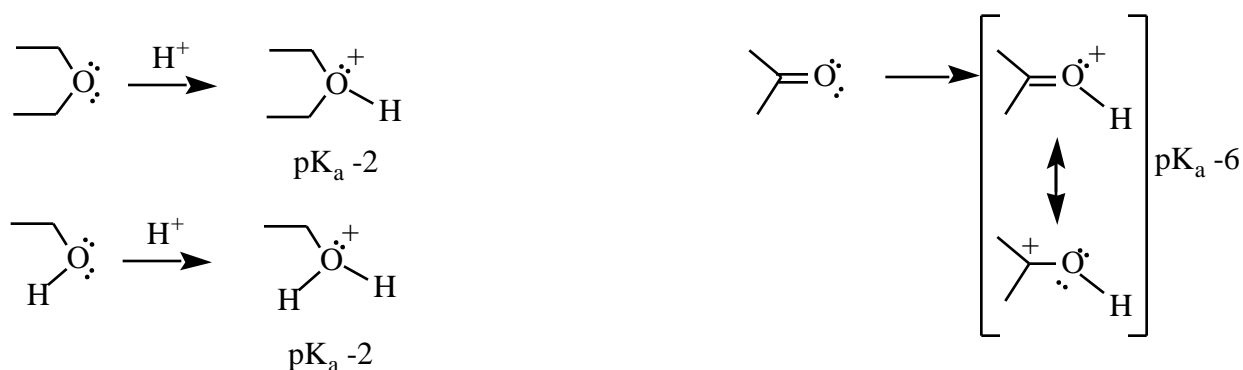
Reasons for the differences in pK_a not simple--solvent effects, ambiguous hybridization, etc.
Most important conclusion is that the oxygen in an ether, alcohol, or carbonyl group can serve as a (very)
weak base. This will be important in considering reactions of these groups.

Special cases:

a. aniline derivatives

pK_b 9.4

sp^2
(for delocalization purposes)

sp^3
no resonance stabilization possible

resonance delocalization
stabilizes the non-bonding electrons
Therefore less basic

pK_b 4.7   stronger base:

no delocalization

no delocalization

b. amides

relatively non-basic
pK_a ca 0 to -1
pK_b ca 14-15

c. Nitrogen anions:

NH_3 + strong base $\longrightarrow$ $^-NH_2$ amide anion (e.g., sodium amide)
pK_a ca 35 pK_b ca -21

 NH + strong base $\longrightarrow$ N^- diisopropylamide anion

pK_a >35 pK_b ca -23 to -25
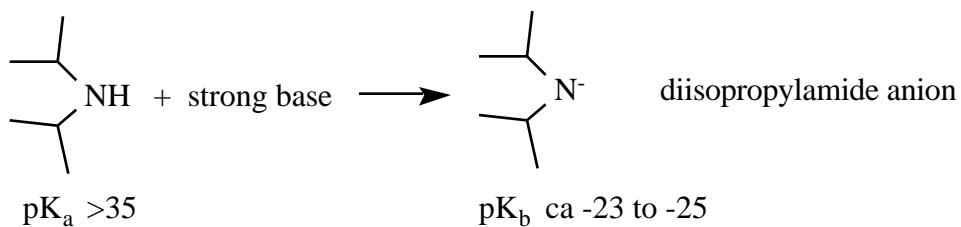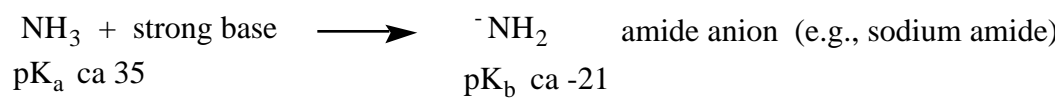
e.g., lithium diisopropyl amide, LDA

Back to Dienes: Read chapter 12.