

3

Carbanions

3.1

Structure and Geometry of Carbanions

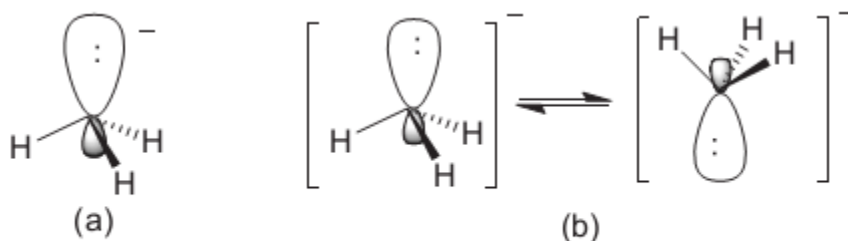


Figure 3.1 (a) sp^3 -Hybridized methanide anion; (b) inversion of configuration.

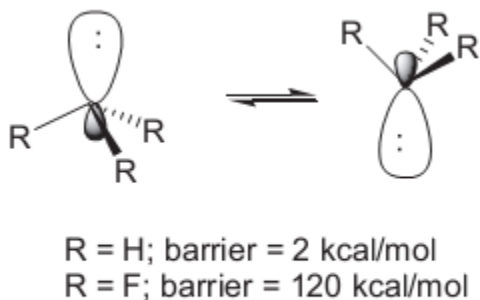


Figure 3.2 A barrier to inversion of carbanions.

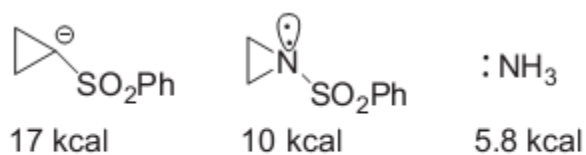
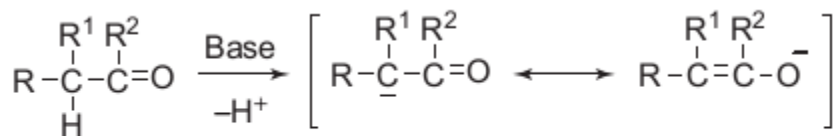
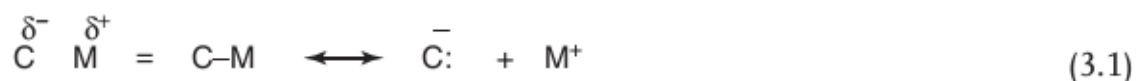


Figure 3.3 Comparison of rate of inversion.



Scheme 3.1 Electron delocalization resulting in a coplanar structure.

Carbanions in solution can be considered as resonance hybrids of two contributing structures, one purely covalent and one purely ionic (Eq. (3.1)):



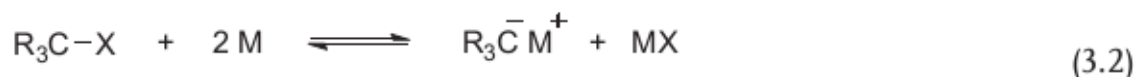
3.2

Generation of Carbanions

3.2.1

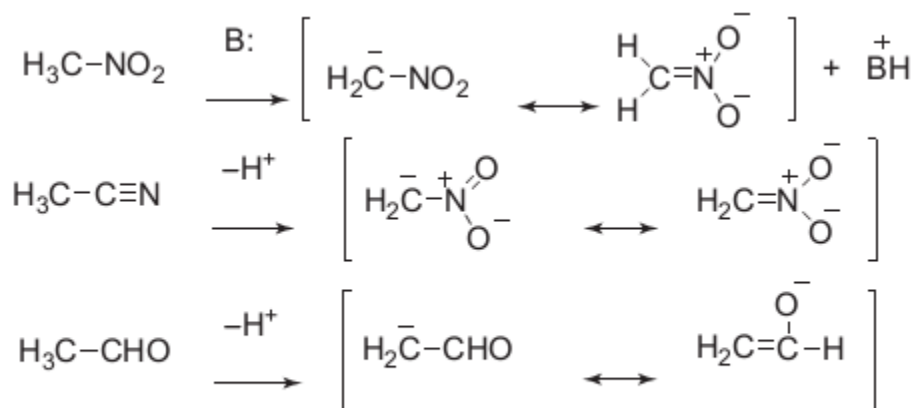
Reduction of C–X Bond with Metal

A common procedure for the synthesis of organometallic compounds is the reduction of a carbon–halogen bond with a metal (M), as illustrated in Eq. (3.2). This simple equation ignores the role of solvent molecules and aggregated species in some of these reactions:



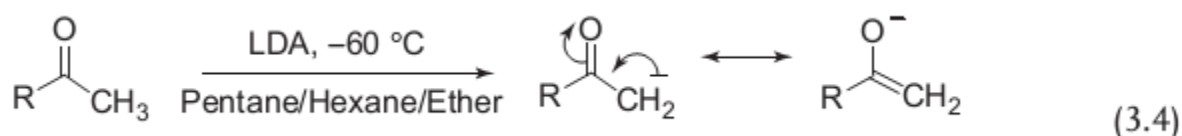
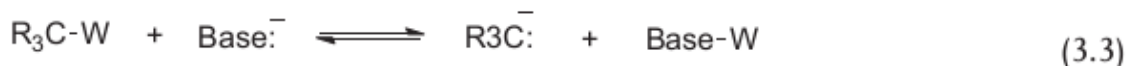
3.2.2

Deprotonation from a C–H Bond



Scheme 3.4 Generation of carbanion.

Certain methyl groups can be deprotonated. For example, the acidity of the methyl groups in acetone (Me_2CO) is about 10^{20} more acidic than methane. The resulting carbanions are key intermediates in many reactions in organic synthesis and biosynthesis. Reagents such as *n*-butyllithium, methyllithium, and phenyllithium are commercially available. Carbanions can also be formed by an acid–base reaction involving heterolytic dissociation of a carbon–hydrogen bond, as illustrated by the hypothetical example in Eq. (3.3) (Scheme 3.4):



3.2.3

Reaction of a Metal with an Alkene

In some cases metals will react directly with alkenes (Eq. (3.5)), and alkenes sometimes form carbanions by addition of nucleophiles (Eq. (3.6)):

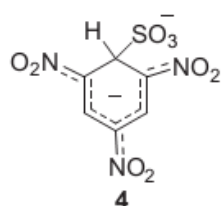
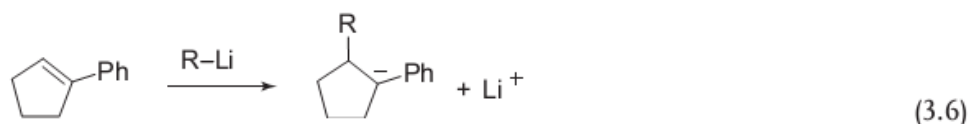
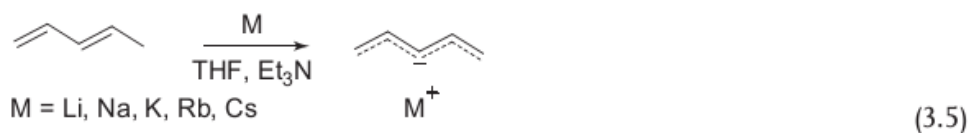


Figure 3.5 Jackson–Meisenheimer complex.

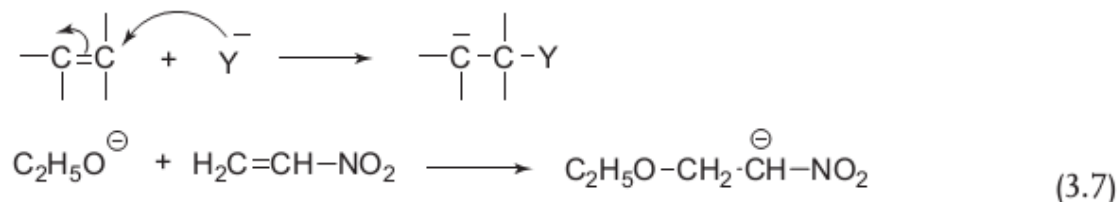


Addition of nucleophiles to aromatic compounds with several nitro or cyano groups leads to the formation of a resonance-stabilized carbanion known as a *Jackson–Meisenheimer complex*. For example, addition of sulfite ion to 1,3,5-trinitrobenzene leads to the complex 4 (Figure 3.5).

3.2.4

A Negative Ion Adds to a Carbon–Carbon Double or Triple Bond

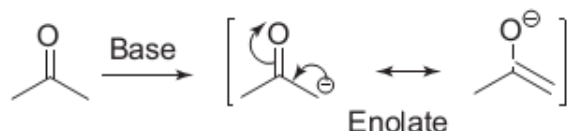
The addition of a negative ion to a carbon–carbon double or triple bond leads to a carbanion. The addition of a negative ion to a carbon–oxygen double bond does not give a carbanion, since the negative charge resides on the oxygen. Carbanions are also formed when a nucleophile adds to an α,β -unsaturated compounds (Eq. (3.7)):



3.3

Stability of Carbanions

The negative charge on a carbanion is stabilized by neighboring electron withdrawing groups (EWGs) such as carbonyl, nitro, cyano, and sulfone. Carbonyl functions are very effective in stabilizing an adjacent negative charge and when two carbonyl groups are present (as in diethyl malonate or acetylacetone) a very useful carbanionic intermediate is produced. The intermediate is called an *enolate* (Scheme 3.5). The dithiane system can stabilize the carbanion by dispersal of the charge into the d orbitals of the sulfur atoms.

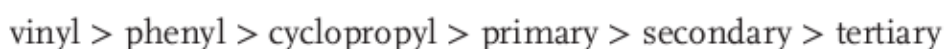


Scheme 3.5 Stabilization of carbanion through formation of enolate.

A carbanion works as a nucleophile when attacks any electron-deficient center except a proton. The stability and reactivity of a carbanion is determined by several factors. These include:

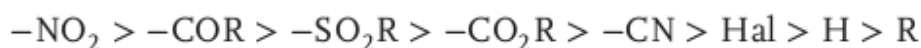
- The inductive effect: electronegative atoms adjacent to the charge will stabilize the charge.
- Hybridization of the charge-bearing atom: the greater the s-character of the charge-bearing atom the more stable the anion.
- The extent of conjugation of the anion: Resonance effects can stabilize the anion. This is especially true when the anion is stabilized as a result of aromaticity.

The alkyl substitution at the carbanionic site results in an intensification of the carbanionic character because of the electron-donating character of the alkyl groups. The order of stability in carbanions is the reverse of that of carbocations, that is:



ethylene. The carbanions can be stabilized by electron-withdrawing substituents, unlike the carbocations, which are stabilized by electron-donating substituents.

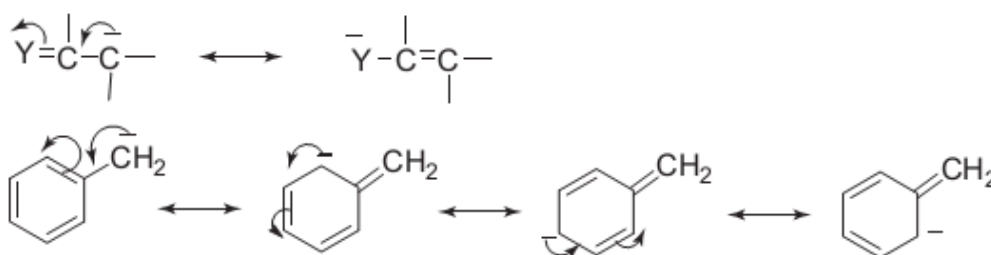
The order of effectiveness of various groups for stabilizing the carbanion is:



Many carbanions are more stable than the simple kind mentioned above due to certain structural features:

- 1) Conjugation of the unshared pair with an unsaturated bond:

Allylic and benzylic anions are about 59 kJ mol^{-1} (14 kcal mol^{-1}) more stable than their non-allylic and nonbenzylic counterparts. There are two reasons for the stabilities of these anions. The first is *resonance stabilization* and second is the *polar effect* of the double bond (Scheme 3.6).



Scheme 3.6 Resonance stabilization of carbanions.

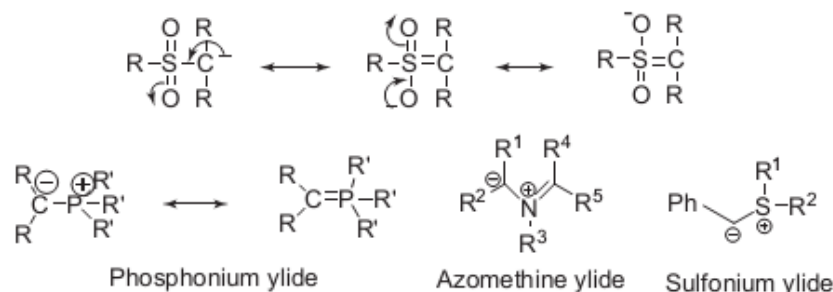
The order of decreasing acidity $\text{Ph}_3\text{CH} > \text{Ph}_2\text{CH}_2 > \text{PhCH}_3$ reflects the ability of each successive phenyl group to delocalize the negative charge on carbon and thereby stabilize the carbanion.

- 2) Carbanions increase in stability with an increase in the amount of s character at the carbanionic carbon. Thus the order of stability is:

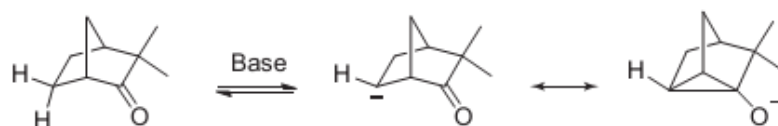


- 3) Stabilization by sulfur or phosphorus:

The second row elements, particularly phosphorus and sulfur, stabilize the adjacent carbanion. The cause of stability is due to delocalization of negative charge of carbanion by a vacant d-orbital ($p\pi-d\pi$ bonding) of phosphorus and sulfur, for example, sulfur and phosphorus ylides. Ylides are more stable than the corresponding simple carbanions (Scheme 3.7).



Scheme 3.7 Stabilization of carbanion by adjacent heteroatoms.



Scheme 3.8 Stabilization of carbanion by a nonadjacent π bond.

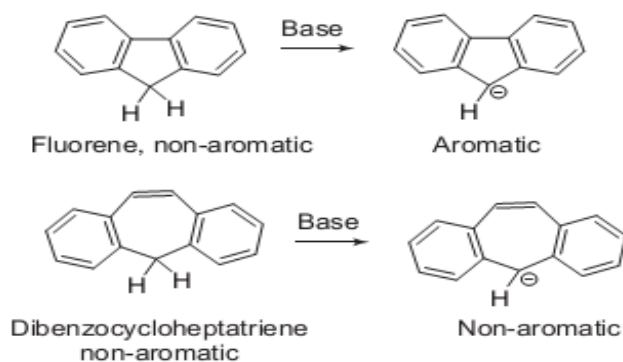
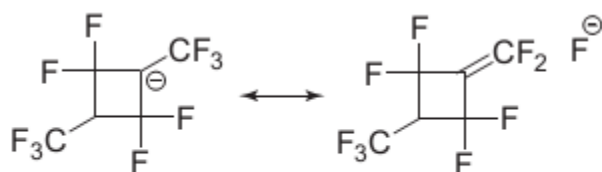


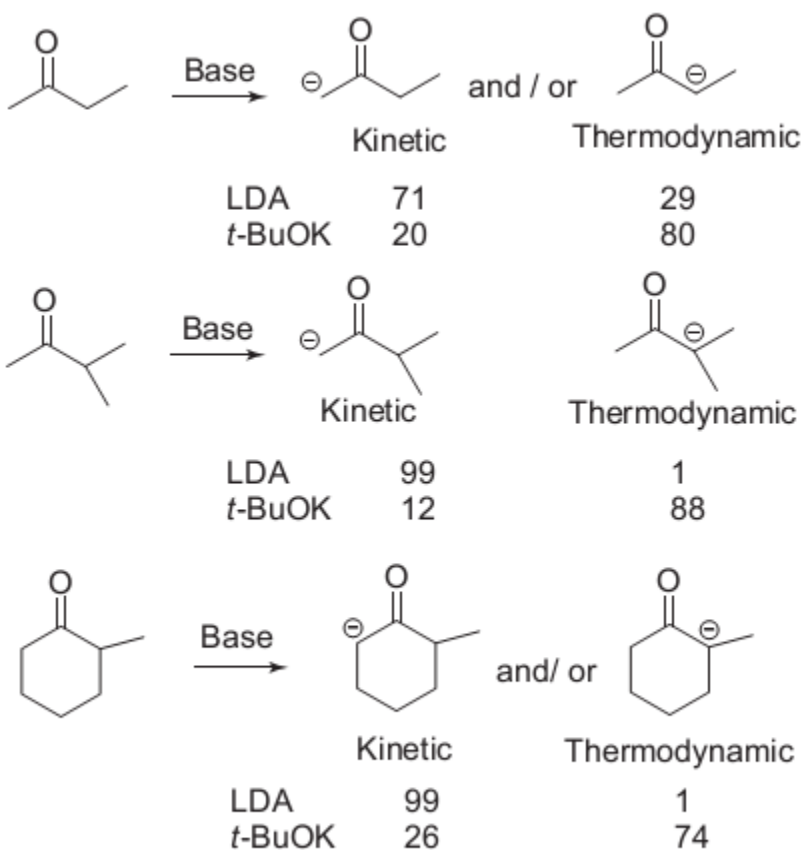
Figure 3.6 Stabilization through aromatization.

- 4) Stabilization by a nonadjacent π bond (Scheme 3.8):
- 5) Stabilization through aromatization:
 The much greater acidity of fluorine relative to dibenzocycloheptatriene reflects the aromatic stabilization of the cyclopentadienide ring in the fluorene anion (Figure 3.6).



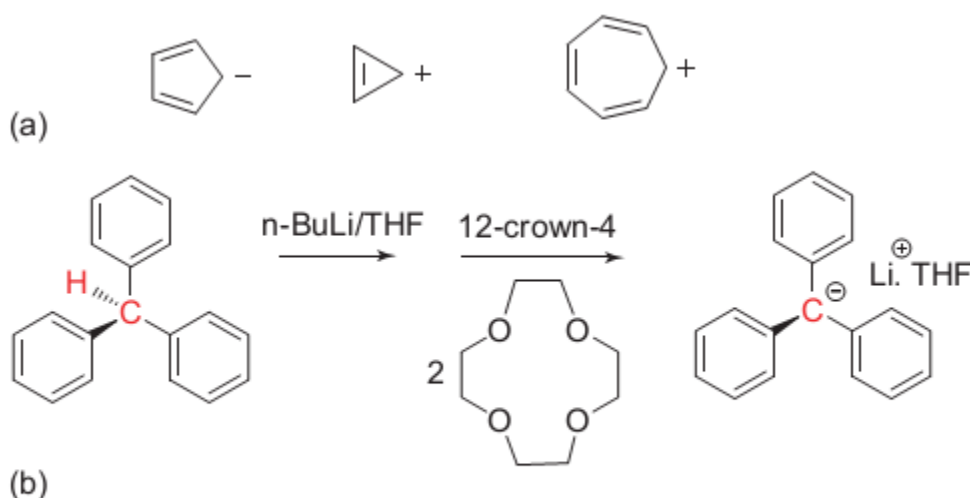
Scheme 3.9 Negative hyperconjugation.

Selective deprotonation in enolate forming



Scheme 3.10 Formation of kinetic and thermodynamic carbanions.

Both the carbanion and carbocations are stable provided they contain $(4n + 2)$ π electrons. For example, cyclopentadienyl anion, cyclopropenium cation, and tropylium cation exhibit unusual stability. Stable carbanions do, however, exist. In 1984 Olmstead presented the lithium crown ether salt of the diphenylmethyl carbanion from diphenylmethane, butyllithium, and 12-crown-4 at low temperatures. Addition of *n*-butyllithium to triphenylmethane in THF at low temperatures followed by 12-crown-4 resulted in a red solution and the salt complex precipitated at -20 °C. The central C–C bond lengths are 145 pm with the phenyl ring propelled at an average angle of 31.2° (Scheme 3.11).



Scheme 3.11 (a) cyclopentadienyl anion and cyclopropenium and tropylium cations; (b) formation of the triphenylmethane carbanion.

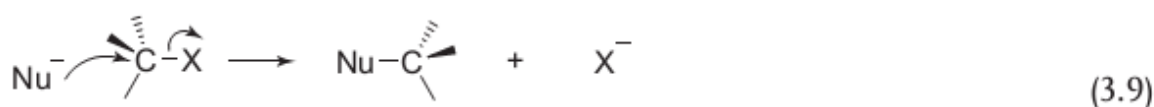
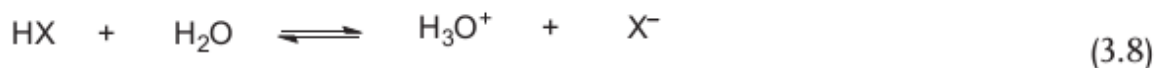
3.4

Reactions of Carbanions

A carbanion may act as base or nucleophile depending on the reaction conditions. Action as a base involves electron pair donation to H^+ , whereas nucleophilic reactions involve electron pair donation to other atoms such as carbon. Can we relate base strength to nucleophilic reactivity? Here are some comparisons:

base strength: $C_2H_5O^- > OH^- > CN^- > Cl^-$;

nucleophilic reactivity: $CN^- > C_2H_5O^- > OH^- > Cl^-$.



Carbanions are very useful intermediates for the formation of new carbon-carbon bonds. Thus carbanions participate in (i) $\text{S}_{\text{N}}2$ alkylation reactions, (ii) α -halogenation of ketones, (iii) 1,2 additions to carbonyl functions, and (iv) 1,4-additions such as Michael reactions. Fluorinated carbanions are very common useful intermediates for the synthesis of new fluorinated materials.

3.5

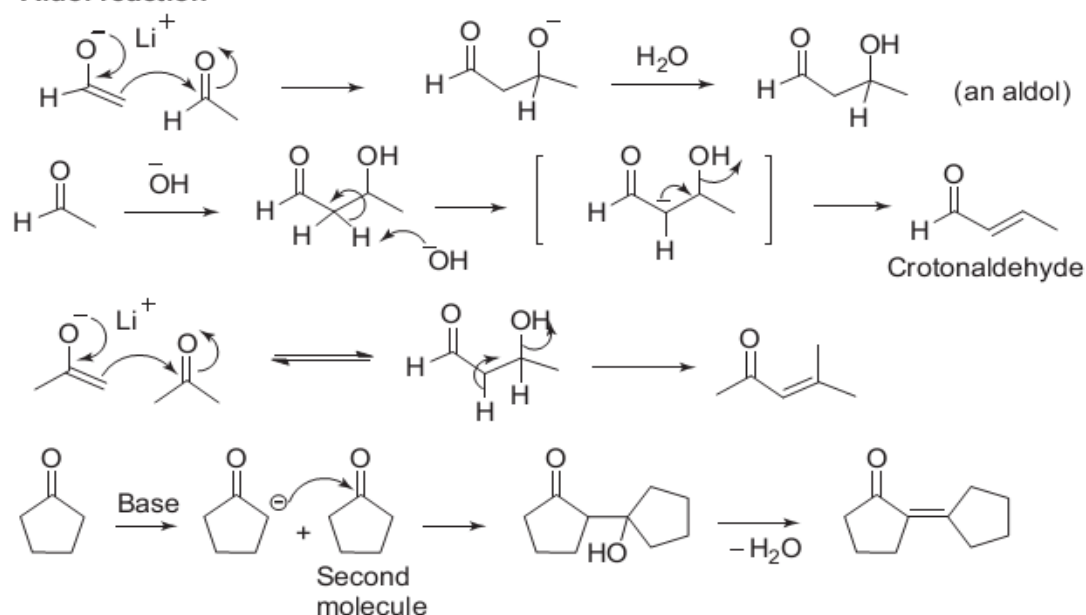
Enolate Reactions with Carbonyl Groups

Carbanions frequently add to the carbonyl double bond. The aldol reaction, Claisen reaction, Dieckmann reaction, Michael reaction, and Knoevenagel condensation are familiar examples of carbanions (as enolates) undergoing nucleophilic addition to carbon-oxygen double bonds.

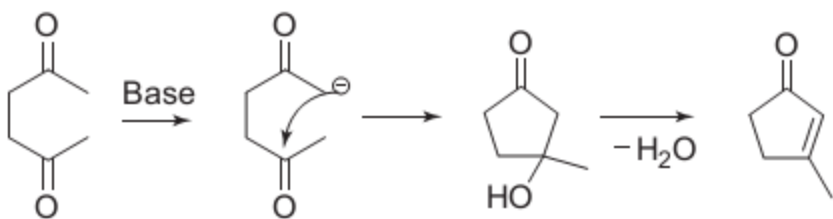
3.5.1

Aldol Condensation

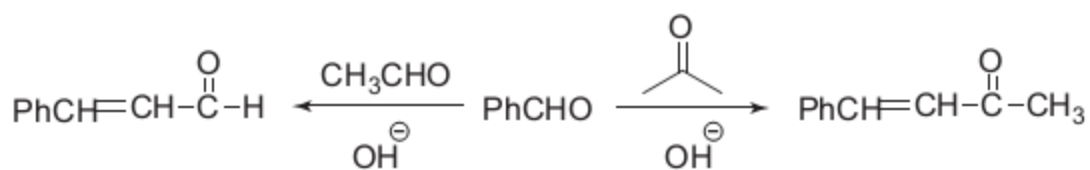
Aldol reaction



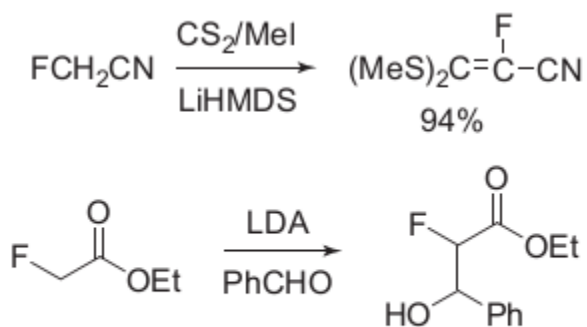
Intramolecular aldol condensation



Scheme 3.12 Aldol reactions.

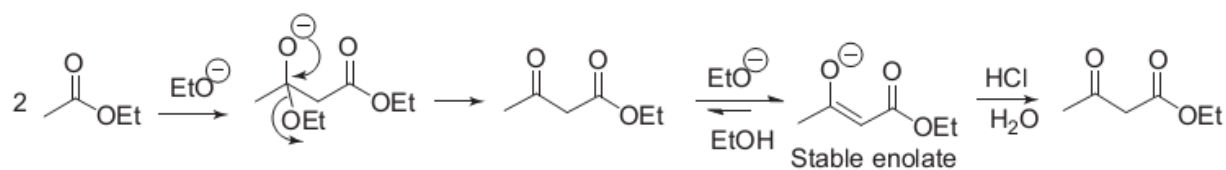


Scheme 3.13 Aldol condensation.

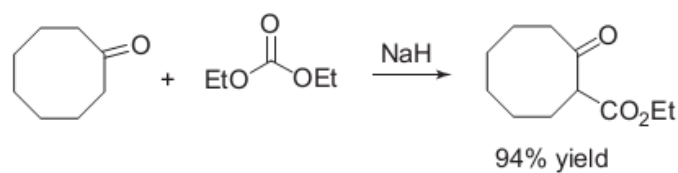
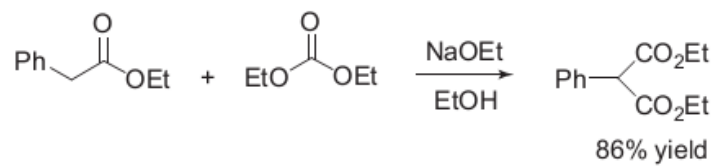


Scheme 3.14 Cross-aldol reaction.

Claisen ester condensation



Crossed Claisen ester condensation



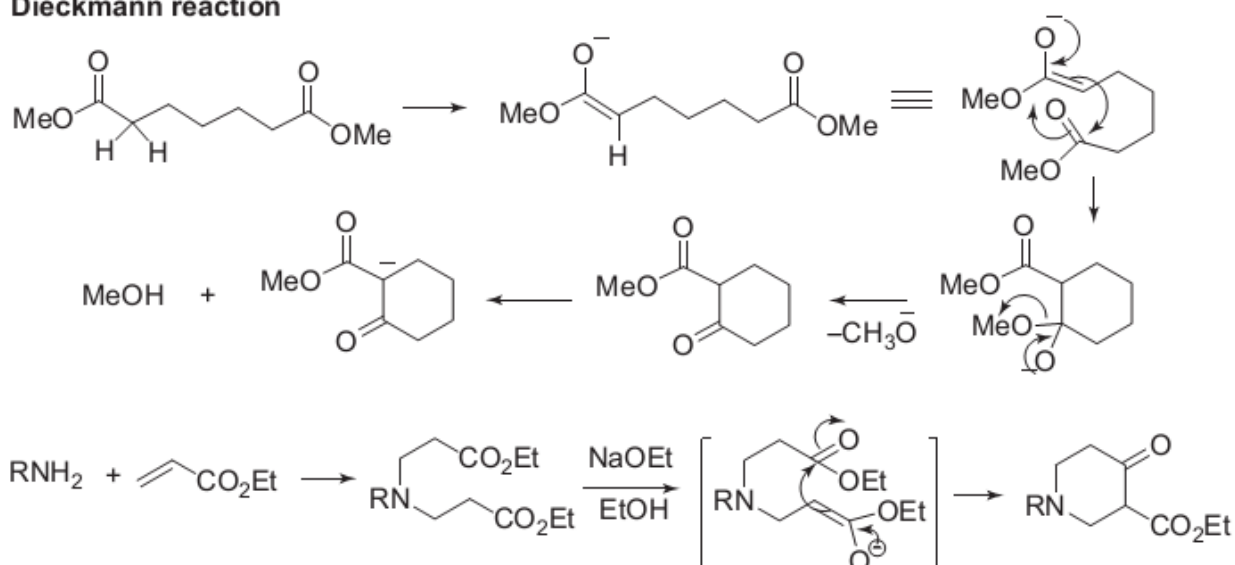
Scheme 3.15 Claisen condensation.



Diethyl oxalate Ethyl formate Diethyl carbonate Ethyl benzoate

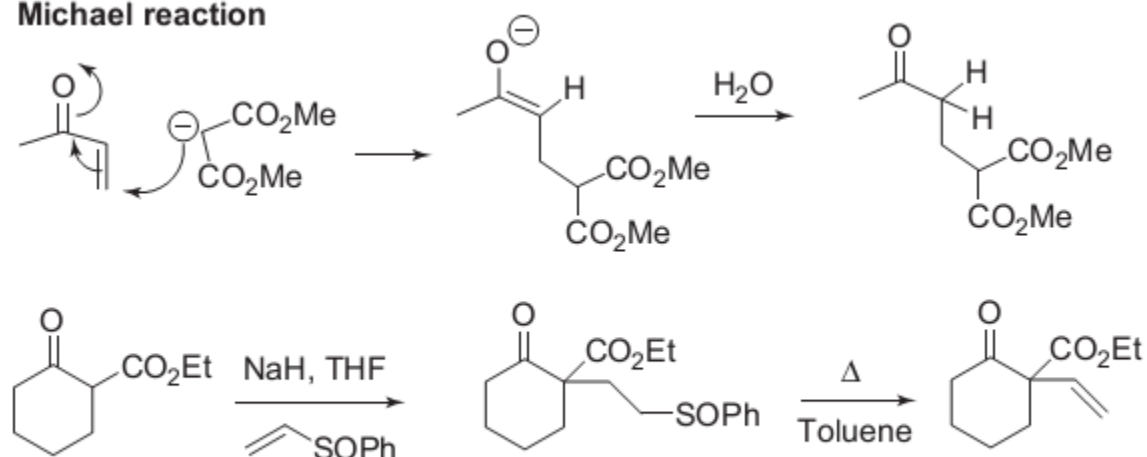
Intramolecular Claisen condensations go by the name of Dieckmann condensations and are useful for the preparation of five- and six-membered rings (Scheme 3.16).

Dieckmann reaction



Scheme 3.16 Dieckmann reaction.

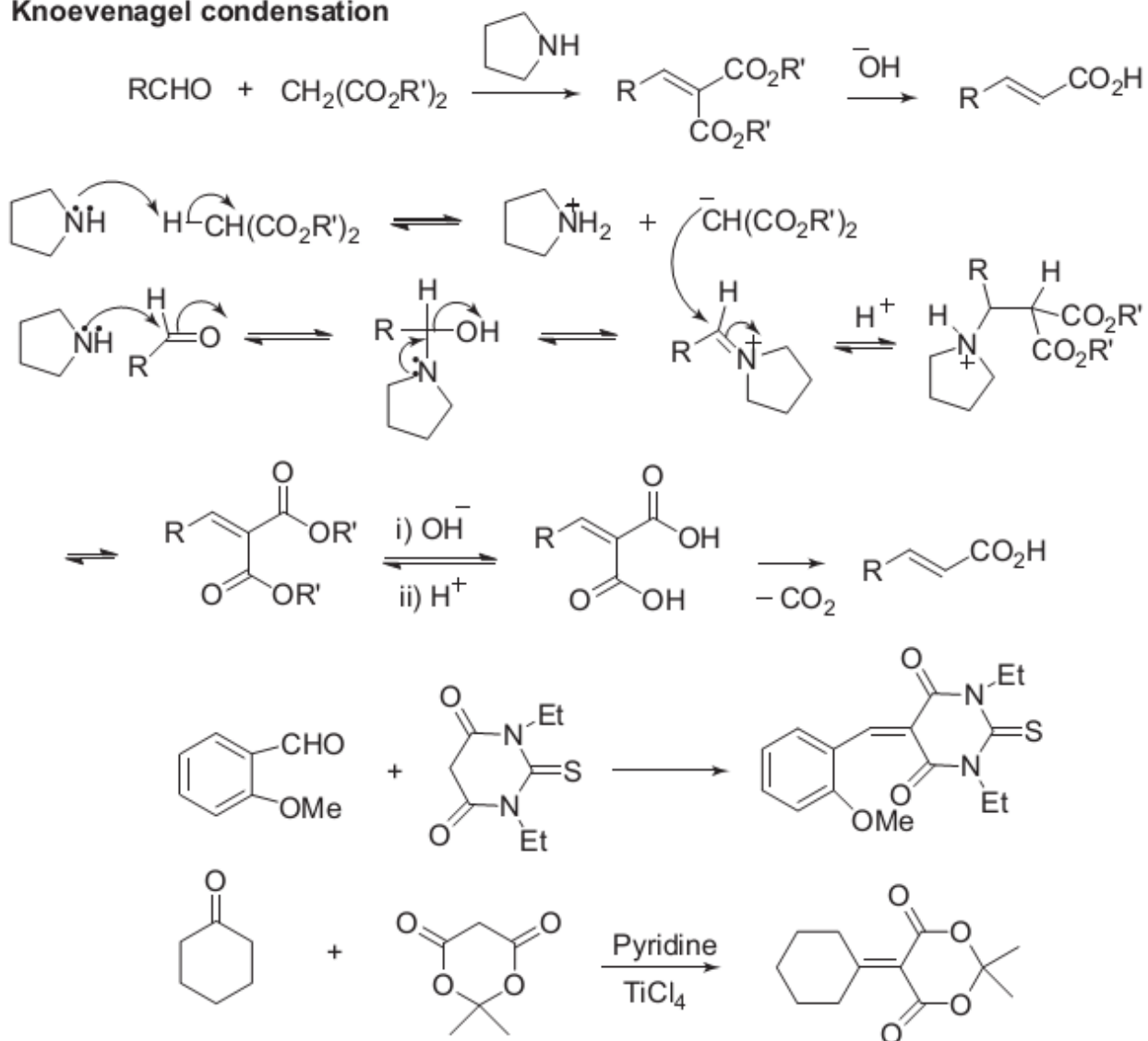
Michael reaction



Scheme 3.17 Michael reaction.

The **Knoevenagel condensation** reaction is a reaction of an enolate with an aldehyde or ketone named after Emil Knoevenagel. It is a modification of the aldol condensation. A Knoevenagel condensation is a nucleophilic addition of an active hydrogen compound to a carbonyl group followed by dehydration (Scheme 3.18).

Knoevenagel condensation

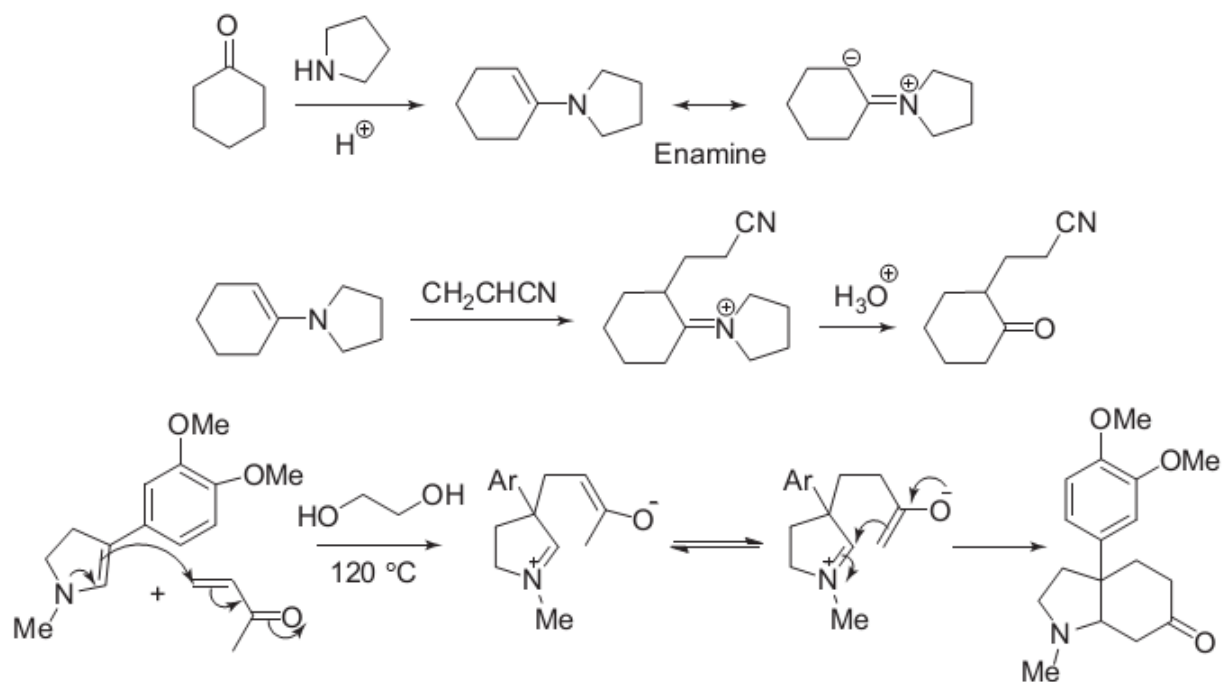


Scheme 3.18 Knoevenagel reaction.

3.5.2

Enamine Additions

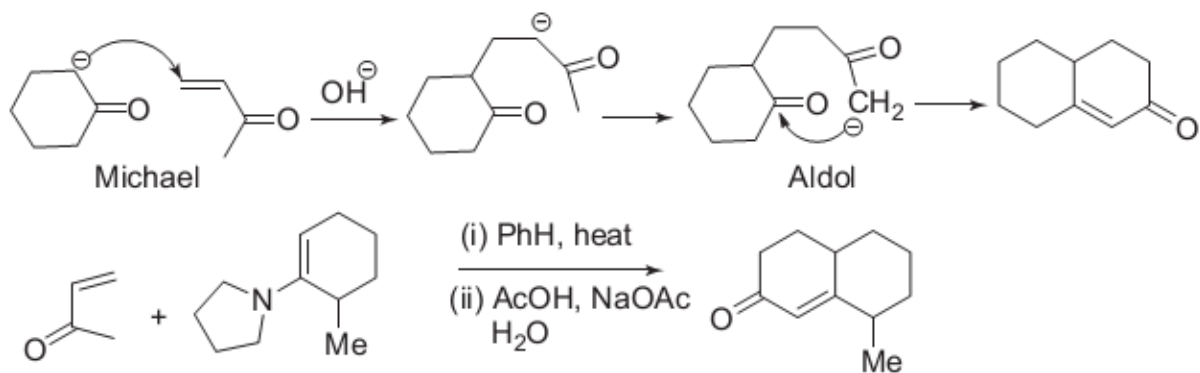
Enamines, the products of the acid-catalyzed addition of secondary amines to aldehydes or ketones, can be viewed as weakly nucleophilic enolate anions. Enamines react with α,β -unsaturated carbonyl systems in a Michael-type reaction, introducing new carbon-carbon bonds adjacent to the carbonyl group.



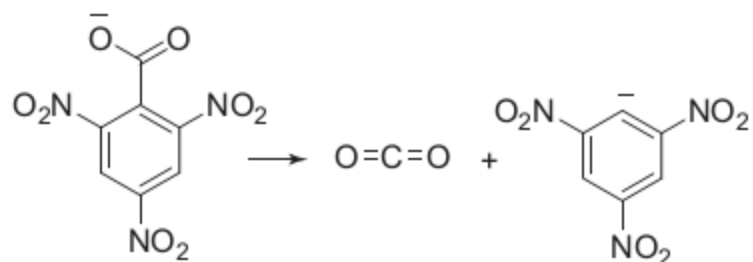
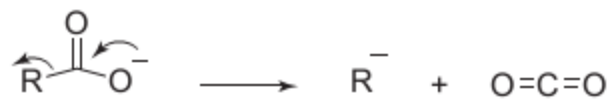
Scheme 3.19 Michael-type reaction.

3.5.3

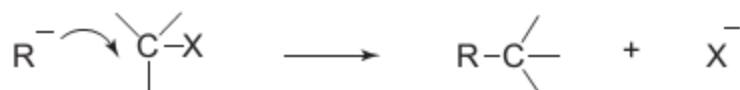
Robinson Ring-Forming Reaction



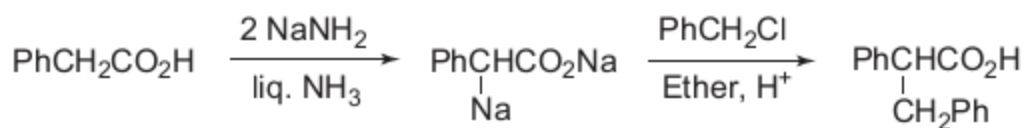
Scheme 3.20 Robinson ring-forming reaction.



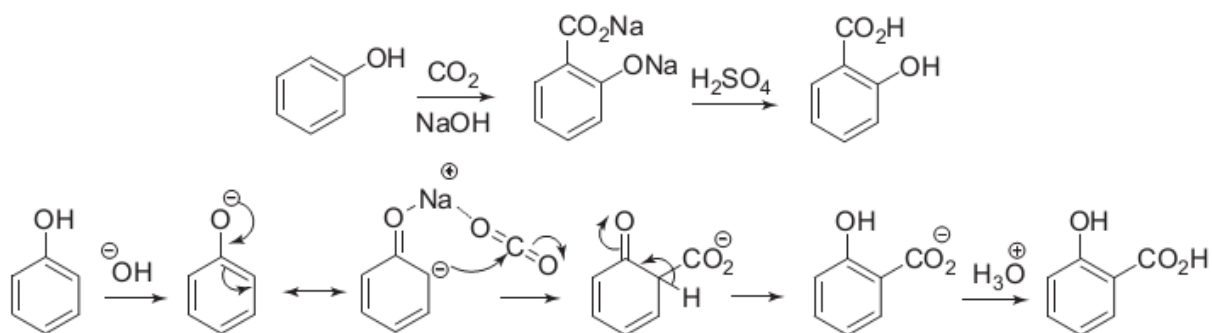
Scheme 3.22 Decarboxylation of carboxylic acid.



Scheme 3.23 Carbanion acting as nucleophile.



Scheme 3.24 Carbanion as nucleophile in $\text{S}_{\text{N}}2$ reaction.



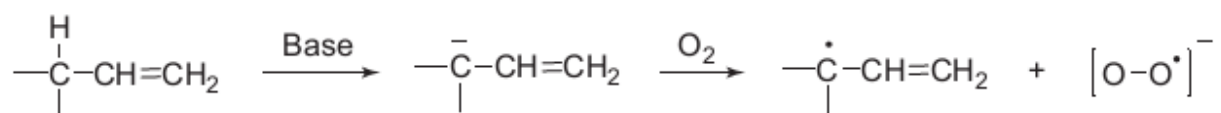
Scheme 3.25 Kolbe-Schmidt reaction.



The triphenylmethyl carbanion is oxidized slowly by air to give the triphenyl methyl free radical (Eq. (3.11)):



Carbanions react with O_2 in alkaline medium to give a radical (Scheme 3.26).



Scheme 3.26 Oxidation of a carbanion.

3.6

Rearrangements of Carbanions

3.6.1

Homoallylic Rearrangements

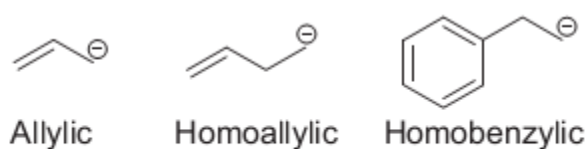
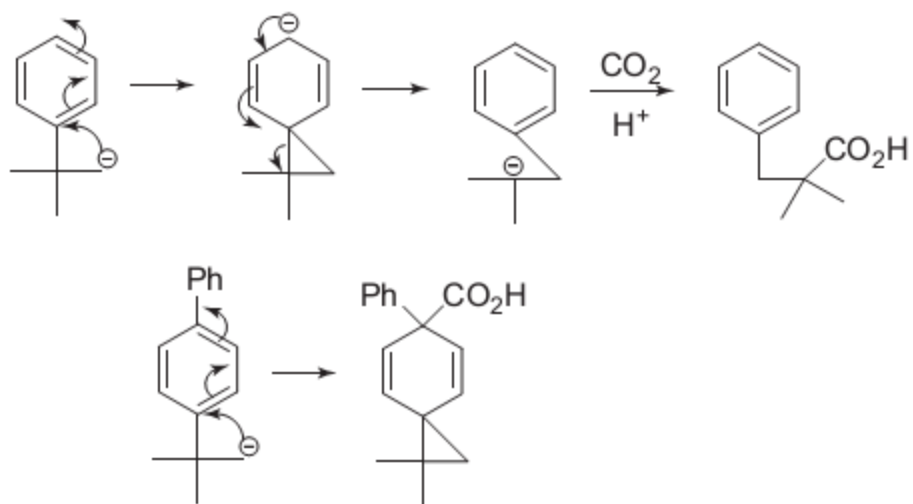


Figure 3.7 Structures of allylic, homoallylic, and homobenzylic carbanions.



Scheme 3.32 Homobenzylic rearrangement.