Carbanions:

A carbanion is an anion in which carbon has an unshared pair of electrons and bears a negative charge usually with three substituents for a total of eight valence electrons.

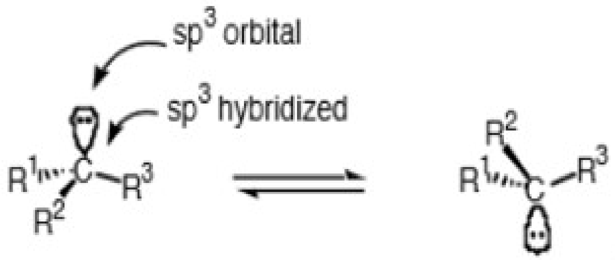
- Formally a carbanion is the **conjugate base** of a **carbon acid**.

$$R-\underset{|}{\overset{|}{C}}-H \rightleftharpoons R-\underset{|}{\overset{|}{C}}:^{-} + H^{+}$$

Carbanions are units that contain a negative charge on a carbon atom. The **negative charge** gives **good nucleophilic properties** to the unit that can be used in the **formation of new carbon-carbon bonds**. **Carbanions** thus **act as nucleophiles in substitution reactions**, **carbonyl addition** and **substitution reactions**, and **1,4-addition (Michael) reactions**.

structure:

A **carbanion** possesses an **unshared pair of electrons** and thus represents a **base**. The most likely description is that the **central carbon atom** is **sp^3 hybridized** with the **unshared pair** occupying one apex of the **tetrahedron**.



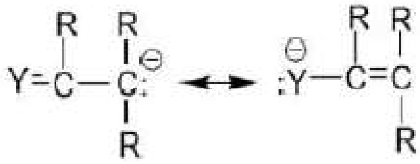
-rapid epimerization of stereogenic carbanions, except when R_1 = OR

Stability and structure:

The **stability** of the **carbanion** is **directly related to the strength of the conjugate acid**. The **weaker the acid**, the **greater the base strength** and the **lower the stability of the carbanion**.

Factors determining the stability and reactivity of a carbanion:

1- The **inductive effect**: **Electronegative atoms adjacent** to the **charge will stabilize the charge**.

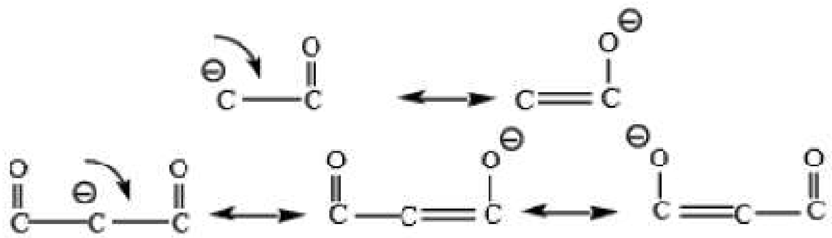


(Y=C, O or N)

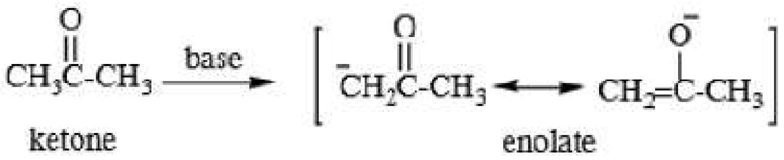
- The **negative charge** on a **carbanion** is **stabilized by neighboring electron-withdrawing groups** (**WEG**) such as **carbonyl**, **nitro**, and **sulfone.**

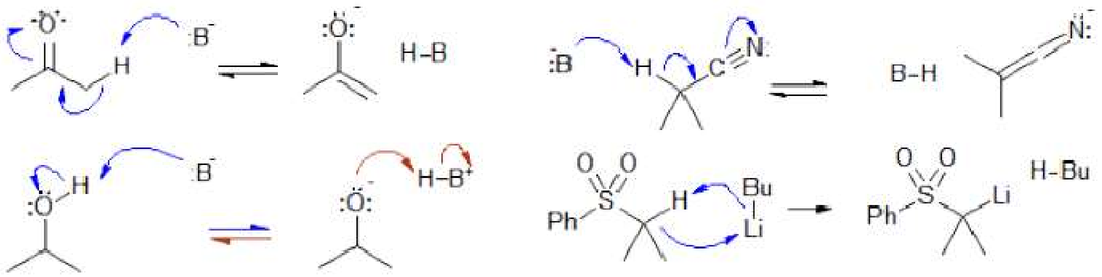
$$\boxed{EWG = C{=}O\,,\ NO_2\,,\ CN\,,\ SO_2}$$

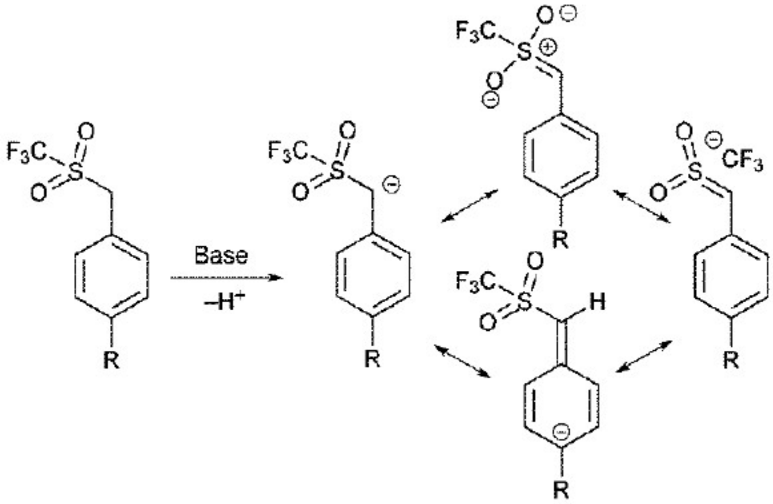
The **stabilizing dispersal** of the **electrons into the EWG** is shown in the examples below. **Carbonyl functions are very effective in stabilizing adjacent negative charge and when two carbonyl groups are present (as in diethyl malonate or acetylacetone) a very useful carbanionic intermediate is produced.** The **intermediate** is **called** an **enolate** (**a carbonyl group stabilizes** an **adjacent carbanion via the overlap of its pi bond with the nonbonding electrons of the carbanion**). The **dithane system** is capable of **stabilizing** the **carbanion by dispersal of the charge into the d orbitals of the sulfur atoms**.



Examples:







R	pKa (in DMSO)	pKa (in H_2O)
H	14.62	/
NO_2	9.46	/
SO_2CF_3	8.85	11.6
$S(O)(NSO_2CF_3)CF_3$	6.45	9.70

2- Hybridization of the charge-bearing atom: The **greater** the **s-character** of the **charge-bearing atom**, the **more stable the anion.**

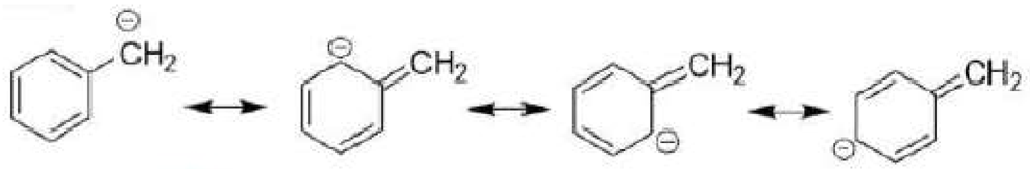
- **Carbanions increase** in **stability** with an **increase** in the **amount of s character** at the **carbanionic carbon.**

Stability:

$$RC{\equiv}C^- > R_2{=}CH^- \approx Ar^- > RCH_2^-$$

3- 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.**

- **Conjugation** of the **unshared pair of electrons** with an **unsaturated bond.**

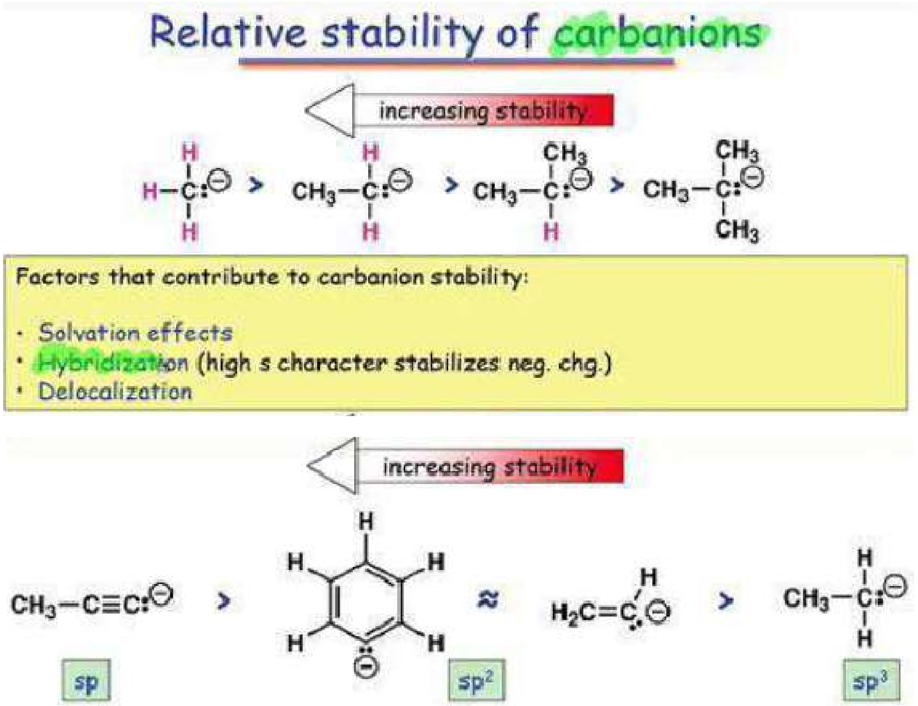


$$R{-}\underset{H}{C}{=}CH{-}\overset{\ominus}{C}H_2: \longleftrightarrow R{-}\underset{H}{C}{=}\overset{\ominus}{\ddot{C}}H{=}CH_2$$

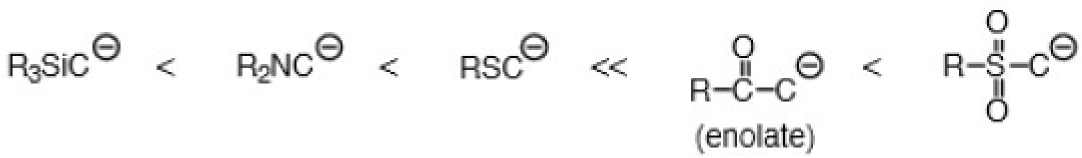
$3^o < 2^o < 1^o <$ allylic, benzylic

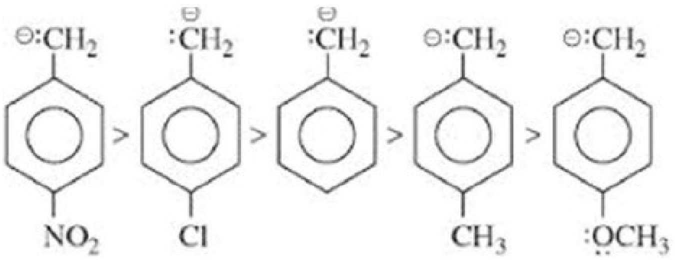
$sp^3 < sp^2 < sp$

[note: these trends are exactly <u>opposite</u> those of carbocations]

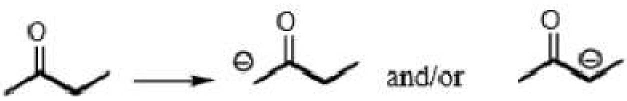


Examples:



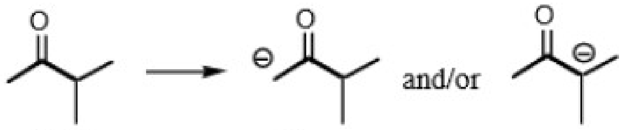


- When **carbanions** are **formed** in **unsymmetrical ketones**, **two carbanions are possible**. One, the **more substituted carbanion** and **more stable**, is **called** the **thermodynamic anion**; while the **least substituted** and **first formed anion** is **called** the **kinetic anion**. **LDA** is a base of choice for the formation of **kinetic products** while **hydroxide** and **alkoxides give** the **thermodynamic anion**.

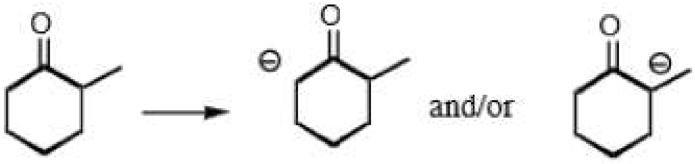


	kinetic	thermodynamic
LDA	71	29
t-BuOK	20	80

<u>Examples:</u>



LDA	99	1
t-BuOK	12	88



LDA	99	1
t-BuOK	26	74

4- Solvents and Bases:

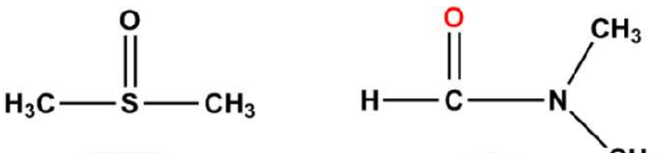
The **formation** of **carbanions** can occur in **several solvent systems. Very strong bases cannot be formed** in **protic solvents** because **they abstract a hydrogen atom from the solvent to form a hydrocarbon.**

Commonly Used Solvents:

1- Polar protic solvents (Water, Alcohols).

2- Covalent aprotic solvents (Ether, THF, Hexane).

3- Polar, aprotic solvents (DMSO, DMF, HMPA).



DMSO DMF

The **strongest bases** are **obtained from** the **reaction** of **metal** with **organohalogen compounds** to **give reagents** known as **Grignard reagents** (where carbon is bonded to metal lithium, potassium sodium, zinc, mercury, lead, thallium – almost any metal known. Whatever the **metal** it is **less electronegative than carbon**) or **organolithium reagents**.

Organolithium reagents:

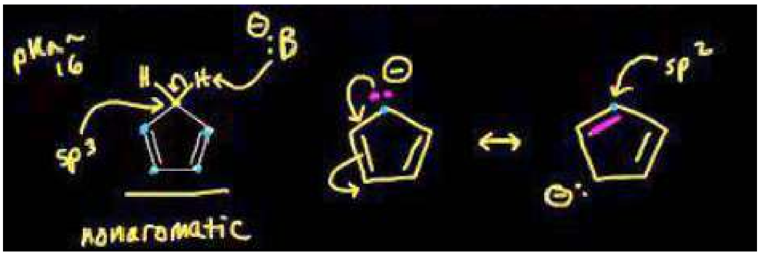
n-BuLi, PhLi and MeLi are commercially available.

t-BuLi > sec-BuLi>n-BuLi in base strength.

<u>Stability of Carbanion by aromatization:</u>

1- Contains a ring of continuously overlapping p orbitals.

2- Has **4n+2** (**Huckel's rule**) **pi electrons** in the ring.

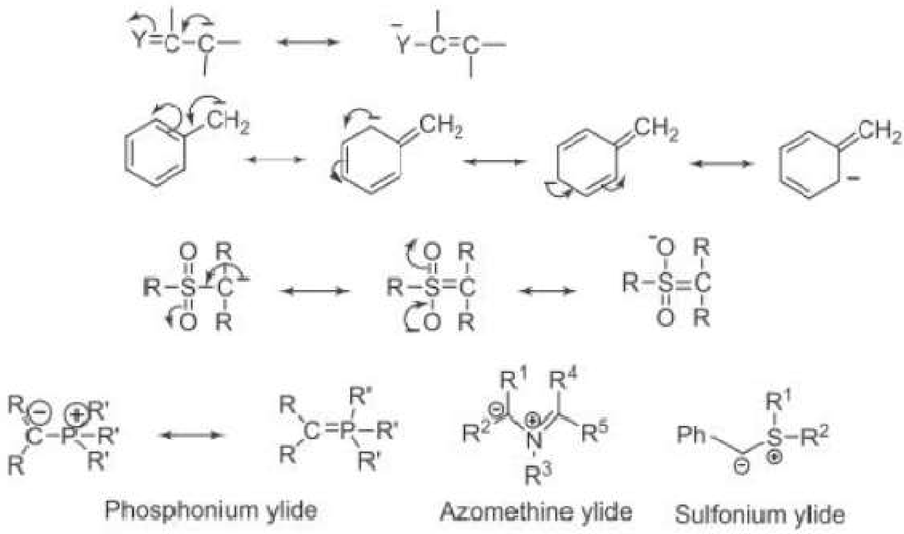


Summaries:

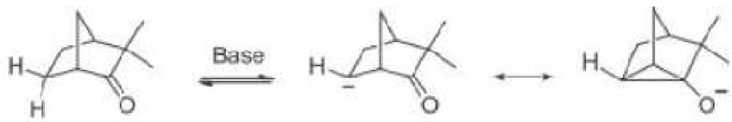
Stability of Carbanions

Stabilization of carbanion through formation of enolate.

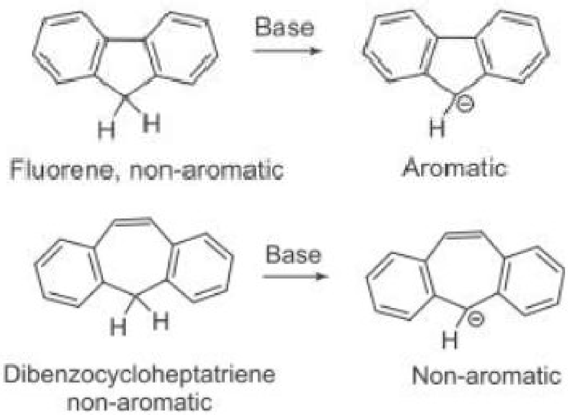
Conjugation



Stabilization of carbanion by adjacent heteroatoms.

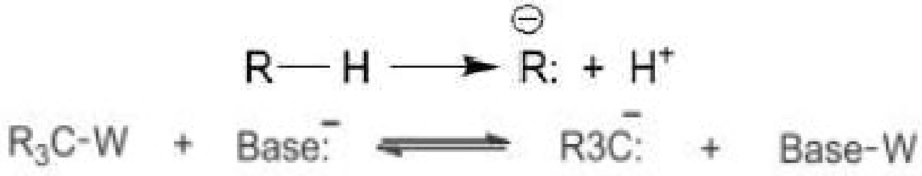


Stabilization of carbanion by a nonadjacent π bond.

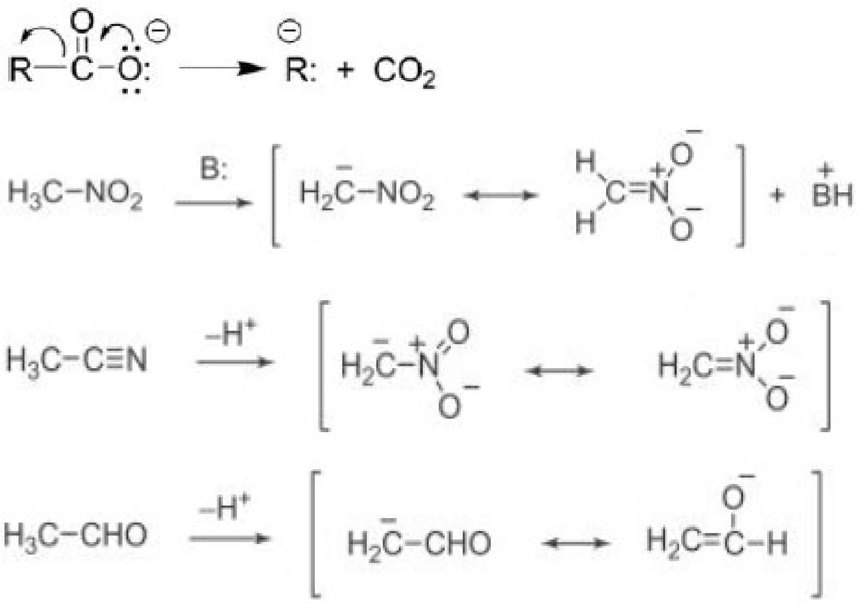


Formation of Carbanions:

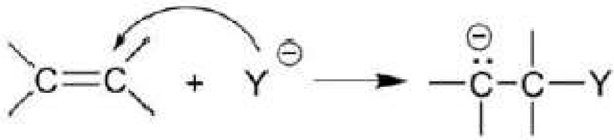
1- **Deprotonation from a C-H bond**: A **group attached** to a **carbon leaves without** its **electron pair**.



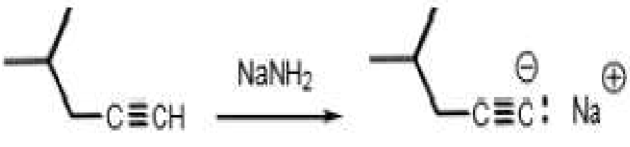
Examples:



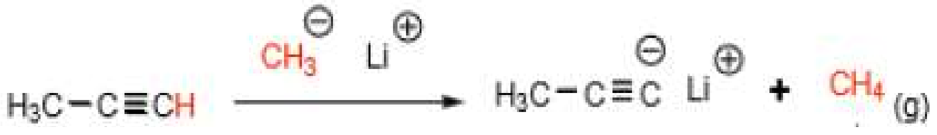
2- A **negative ion adds** to a **carbon-carbon double** or **triple bond**.



Examples:

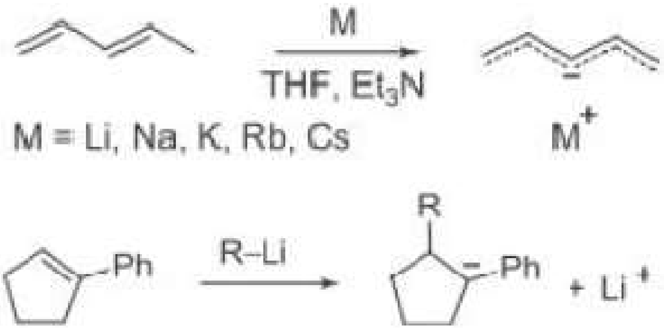


The first step is an acid-base reaction which produces the alkyne conjugate base, or alkynide ion (a nucleophile).



3- **Reaction of a metal with an alkene**:

Examples:



4- **Reduction of σ bonds**: Any **preparation** of **organic-alkali-metal** compounds is a **source** of **carbanions**. The **reaction** of **organic compounds containing atoms** of **chlorine**, **bromine**, or **iodine** with **alkali metals** is **one** of the **most often used methods**.

$R—X$	+	$2M$	$\longrightarrow$	R^-M^+	+	M^+X^-
organic halide		metal atoms		carbanion-metal ion pair		metal ion-halide ion pair

In which R is an organic group; X is an atom of chlorine, bromine, or iodine; and M is an atom of an alkali metal.

- The **conversion** of **one carbanion** into **another** can be **accomplished** with either **hydrocarbons** or **organic halides**, as shown by the equations below:

$R—H$	+	R'^-M^+	$\longrightarrow$	R^-M^+	+	$R'—H$
hydrocarbon		carbanion-metal ion pair		carbanion-metal ion pair		hydrocarbon

$R—H$	+	R'^-M^+	$\longrightarrow$	R^-M^+	+	$R'—H$
hydrocarbon		carbanion-metal ion pair		carbanion-metal ion pair		hydrocarbon