

# Fundamentals of Chemistry, Module III: Organic Chemistry

Semester-1, CCF-2022 (NEP)

Course: CHEM-H-CC-2-2-TH

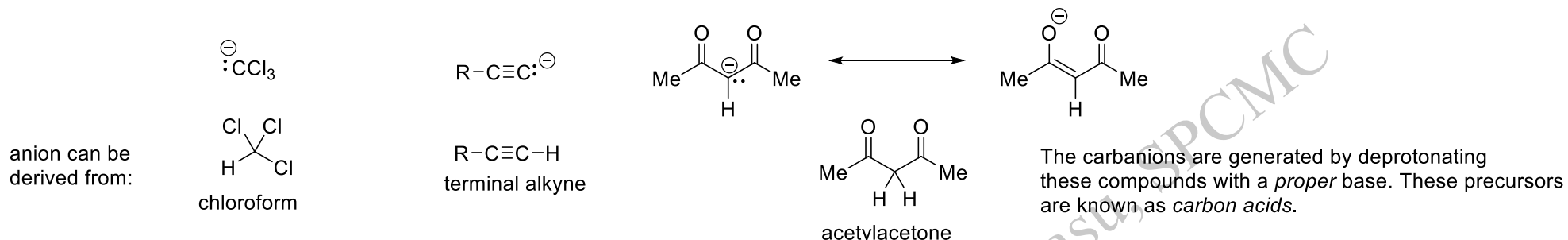
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Recommended texts:

1. Study Guide to Organic Chemistry, Volume 1, Second Ed., by Saha, Chakraborty, Saha & Basu, Techno World, ISBN 978-8192669564,
2. Organic Chemistry, Second Ed. by Clayden, Greeves & Warren, OUP, ISBN 978-0198728719

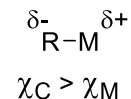
Carbanions: Generic name for anions containing an even number of electrons and having an unshared pair of electrons on a trivalent carbon atom or - if the ion is resonance-stabilized - having at least one significant contributing structure with an unshared pair of electrons on a trivalent carbon atom. For example:



Carbanion is a unit that contains a negative charge on a carbon atom, and is therefore a base/nucleophile depending upon the reaction conditions. The negative charge gives good nucleophilic properties to the unit that can be used in the formation of new carbon-carbon bonds. Carbanions are powerful Brønsted bases as well.

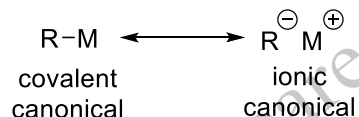
**The base-nucleophile dichotomy:**

A veritable source of carbanion is the organometallic compound class, where an electropositive metal is bonded to a carbon thereby conferring partial negative charge on the more electronegative carbon atom:



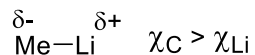
(dichotomy - a division or contrast between two things *that are or are represented as* being opposed or entirely different.)

We can draw one covalent and one ionic canonical for species such as these:



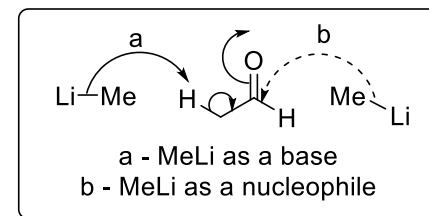
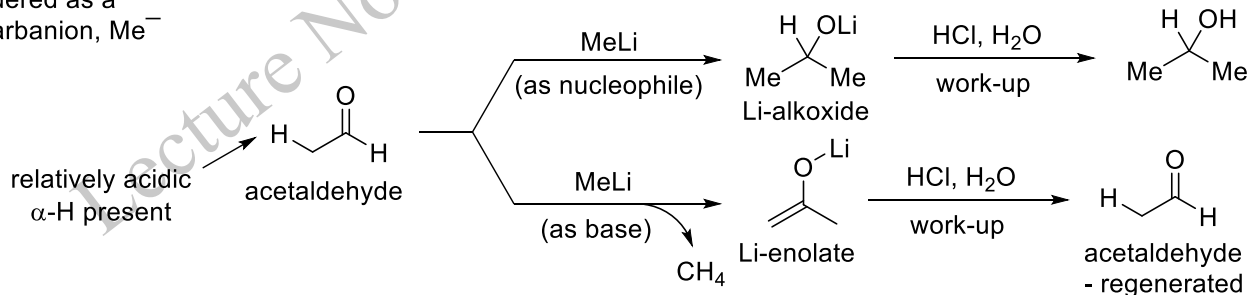
The negatively polarised carbon group (R) in the ionic canonical clearly indicates that organometallic compounds can be considered as sources of carbanion.

For example, take methyllithium



It can be considered as a source of methyl carbanion,  $\text{Me}^-$

When MeLi reacts with acetaldehyde, two things may happen - it can either abstract the  $\alpha$ -H of acetaldehyde (acting as a base), or it can directly attack the carbonyl carbon (acting as a nucleophile):



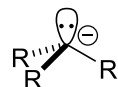
Carbanions therefore always have a dual reactivity - as a base and as a nucleophile. One behaviour may be promoted at the expense of the other by manipulating certain factors, as we will see later.

## Reactive Intermediates in Organic Chemistry:

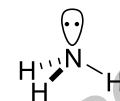
Structure and classification of carbanions:

Depending on the nature of the substituents present on the negatively charged carbon, carbanions can assume trigonal pyramidal, trigonal planar, bent, or linear geometry.

A] Simple alkyl anions: pyramidal in shape

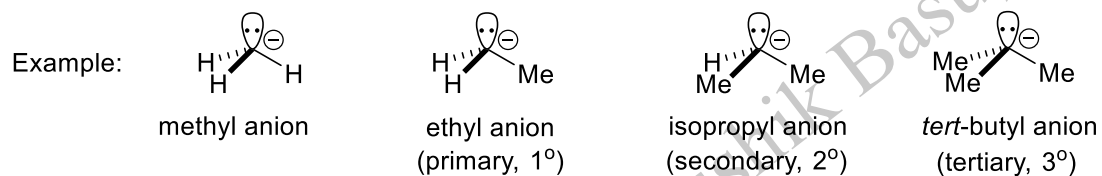


Recall the shape of ammonia molecule:



Why pyramidal?  
Think VSEPR!

hybridisation of negatively charged carbon:  $sp^3$   
orbital that carries the l.p. of e:  $sp^3$



The number of carbons that are attached to the negatively charged carbon:

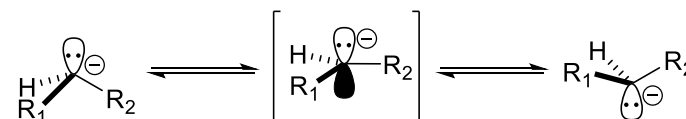
0

1

2

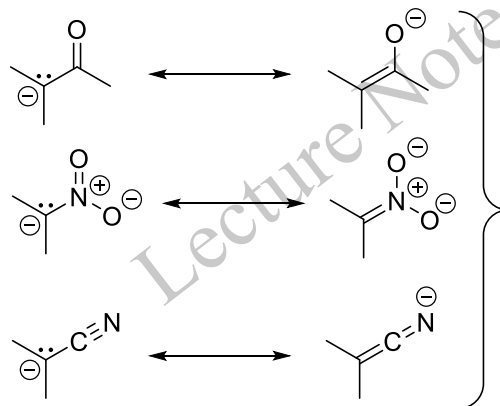
3

These anions undergo pyramidal inversion which in special cases leads to inversion of configuration at the carbanion centre, via a high-energy planar form:



The two pyramidal carbanions connected by the equilibrium are non-superposable mirror images to each other - enantiomers

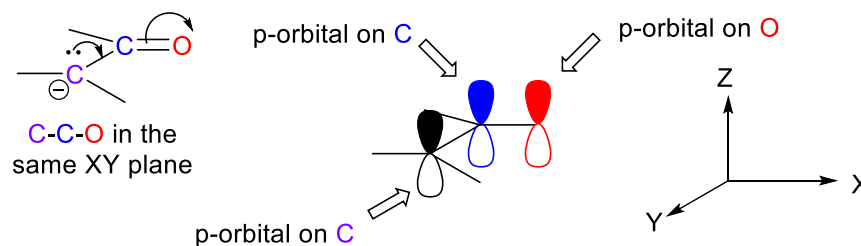
B] Carbanions conjugated to EWGs that can show -R effect:



The carbonyl, nitro and cyano groups - all are showing -R EW effect

In all these cases, the carbanionic carbon is  $sp^2$ -hybridised

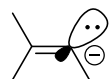
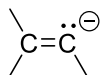
The l.p. of e is in a p orbital, parallel to the pi-network of these EW groups. This alignment helps in delocalising the excess e-density over these groups



## Reactive Intermediates in Organic Chemistry:

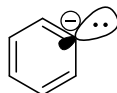
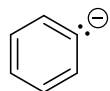
Structure and classification of carbanions:

C] Vinyl (alkenyl) and aryl anions:



secondary vinylic anion  
carbon bearing the negative charge:  $sp^2$   
l.p. of electrons housed in:  $sp^2$  orbital

This one is better (why?!)



aryl anion  
carbon bearing the negative charge:  $sp^2$   
l.p. of electrons housed in:  $sp^2$  orbital

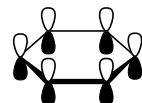
Alternative:



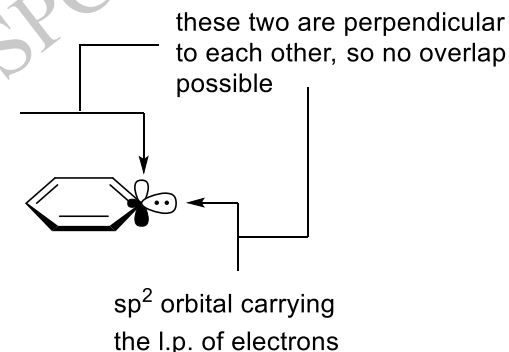
secondary vinylic anion  
carbon bearing the negative charge:  $sp$   
l.p. of electrons housed in:  $p$  orbital

Usually, the bent geometry is (slightly) more favoured than the linear one, at least for the secondary alkenyl carbanions

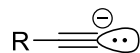
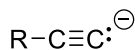
the  $\pi$ -network



$p_z$  orbital, part of the  $\pi$ -network

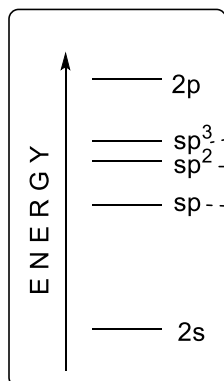
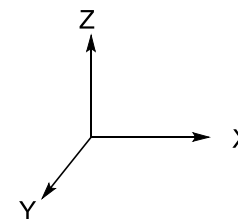
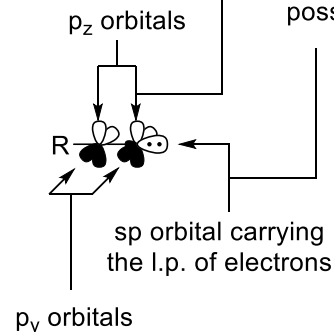


D] Acetylides and substituted acetylides (alkynyl anions): carbanions derived from acetylene and terminal alkynes



substituted acetylide ion  
carbon bearing the negative charge:  $sp$   
l.p. of electrons housed in:  $sp$  orbital

these two are perpendicular to each other, so no overlap possible (same for the  $p_y$  orbitals)



	% s-character	$\chi_c$
	25	2.5
	33	3.0
	50	3.3

hybrid orbital gets more compact in shape

% s-character increases

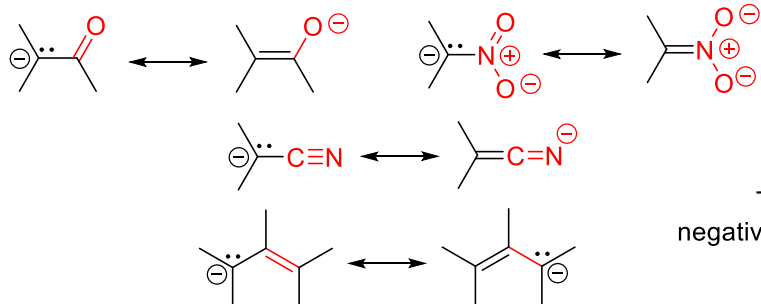
electronegativity increases

It is better to put electrons in an s-rich orbital, and on a  $sp$  carbon than on the other two hybridization schemes

Stabilisation of carbanions: Factors responsible

A] Presence of EWG adjacent to the carbon containing the l.p. of e: Delocalisation of negative charge

Groups that can show the -R and -I effect

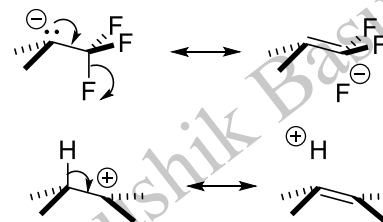


Groups that can show the -I effect



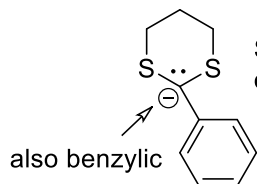
The CF<sub>3</sub> group offers stabilisation to an adjacent negative charge by hyperconjugation as well:

This is called negative hyperconjugation

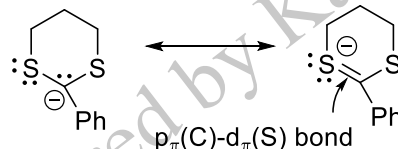


Compare with hyperconjugation seen in carbocations

Heteroatom adjacent to carbanions can stabilise the species:

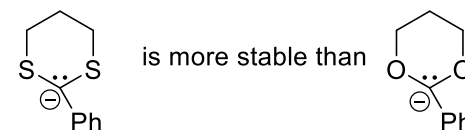


S stabilises the adjacent lone pair by delocalising it into its *vacant d orbital*:



$p_{\pi}(C)-d_{\pi}(S)$  bond

In addition to this, there is stabilisation from *negative hyperconjugation* by delocalising the lone pair into the vacant C-S  $\sigma^*$  MO. But we will discuss that factor later.



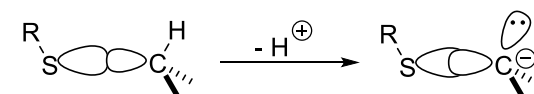
The stabilisation by S is so important that this anion is more stable than the corresponding oxygen analogue, although oxygen is more electronegative than sulfur and has a greater -I effect.

Another point that works in favour of S here is its *higher polarisability* compared to O (make sure that you understand why S is more polarisable than O). A more polarisable atom can stabilize an adjacent charge better than a less polarizable one, all other things being equal.

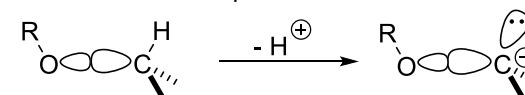
There is a size difference between the 3p orbitals of the S and 2p orbitals in the parent compound (from which the anion is generated). In the carbanion the C orbital increases in size, resulting in a more effective overlap and a stronger C-S sigma bond.

In an oxygen-substituted system the orbital mismatch is in the opposite direction: the orbital on oxygen is already smaller than that on carbon, and this size difference increases in the carbanion, leading to even poorer overlap, the C-O bond is weakened.

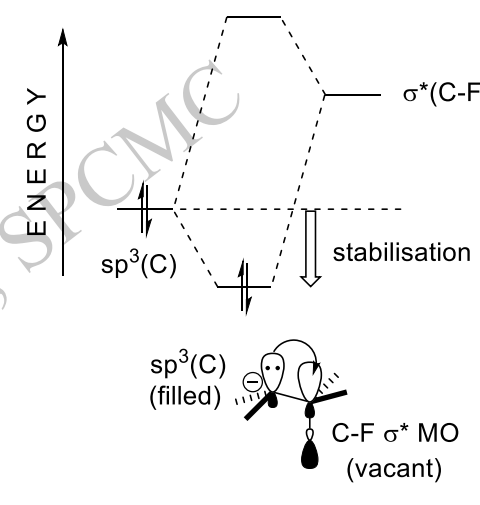
Finally, for the oxygen compound, there is probably a strong *interelectronic repulsion* between the l.p. on carbon and those on oxygen. Due to larger size of sulfur, this repulsion should be less in the sulfur analogue



for C-S bond, orbital sizes become compatible on deprotonation



for C-O bond, orbital sizes become even more incompatible on deprotonation



## Reactive Intermediates in Organic Chemistry:

### Stabilisation of carbanions: Factors responsible

A] Presence of EWG adjacent to the carbon containing the l.p. of e: Delocalisation of negative charge

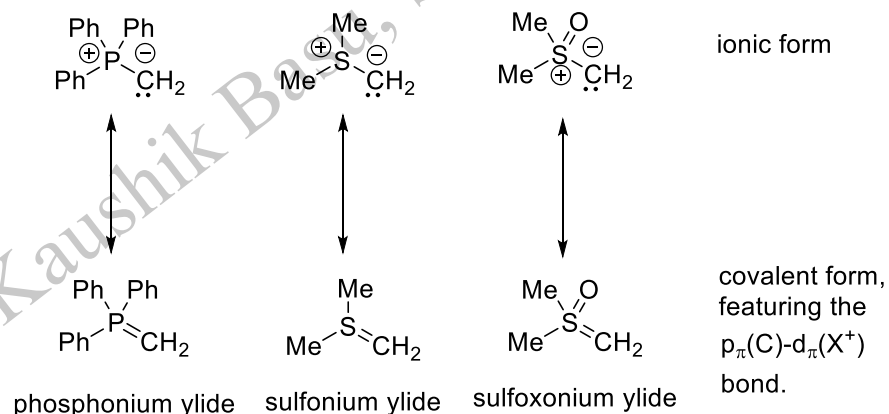
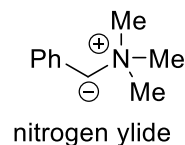
Heteroatoms bearing positive charge that are adjacent to carbanions can stabilise the species:

Compounds in which an anionic site  $Y^-$  (originally on carbon, but now including other atoms) is attached directly to a heteroatom  $X^+$  (usually nitrogen, phosphorus or sulfur) carrying a formal positive charge. They are thus 1,2-dipolar species of the type  $R_mX^+-Y^-R_n$ . If X is a saturated atom of an element from the second row of the periodic system, the ylide is commonly represented by a charge-separated form (ionic form); if X is a third, fourth, etc. row element uncharged canonical forms (covalent forms) are available  $R_mX=YR_n$  (X = S or P)

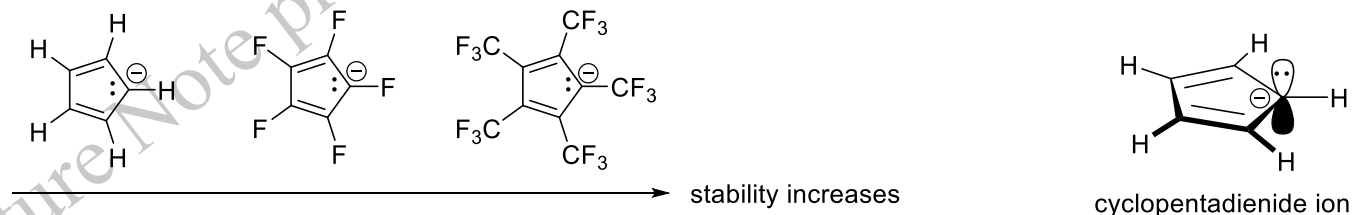
In ylide species, the carbanion is stabilised by both -I effect and the  $p_\pi(C)-d_\pi(X^+)$  bond where  $X^+$  is a positively charged heteroatom like P or S:

Alongwith the  $p_\pi(C)-d_\pi(X^+)$  bond, the carbanion here is also stabilised by the strong EW -I effect of the positively charged heteroatom.

There are also examples of nitrogen ylides, but in this case the stabilisation is by -I effect and not  $p_\pi-d_\pi$  bond, as N does not have any low-lying vacant d orbital available to delocalise the adjacent lone pair.



B] Aromaticity:



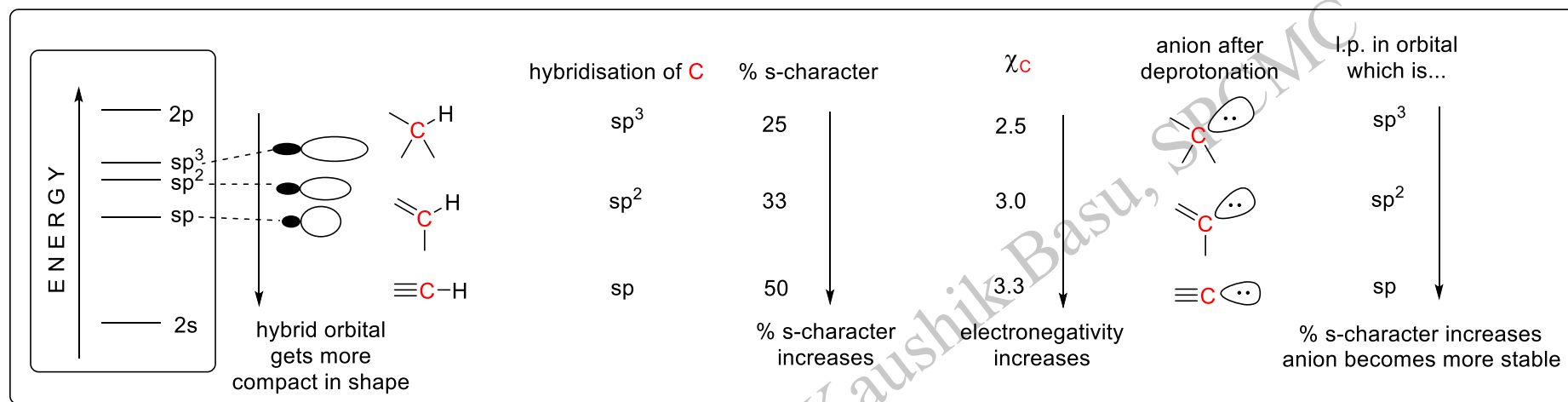
All the three carbanions are aromatic, each contain a five-membered ring with six  $\pi$ -electrons ( $4n+2$ ,  $n=1$ )

Additionally, the second ion benefits from EW -I effect of five F-atoms; however, it also suffers from l.p.(C)-l.p.(F) repulsions.

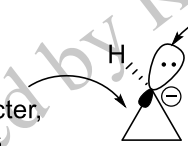
The third one benefits from -I effect and negative hyperconjugation of the five  $CF_3$  groups and free of any interelectronic repulsion.

Stabilisation of carbanions: Factors responsible

C] Hybridisation of carbon holding the lone pair of electrons and the s-character of the orbital that holds the l.p.:

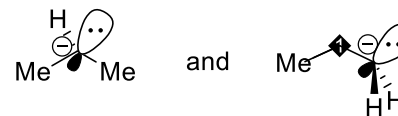


Similar logic dictates that:

 internal C-C bond has more than usual p-character,  
 internal angle is only 60 degrees which means...


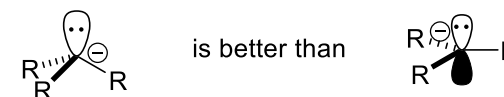
... the external orbitals have more than usual s-character

Thus this anion derived from cyclopropane is more stable than either of the following:

 In the last two cases, the lone pair is on a usual  $sp^3$  hybrid orbital with only 25% s-character. But the anion derived from cyclopropane has the lone pair in an orbital that has more than 25% s-character. The latter is thus more stable.


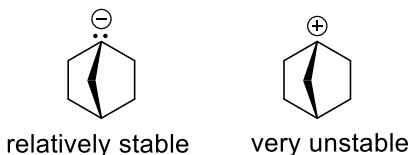
both of which are derived from propane

The relationship between high s-character and subsequent stabilisation of l.p. of electrons can also explain why carbanions (that do not enjoy any resonance stabilisation) prefer pyramidal structure and not the trigonal planar structure (like carbocations):


 lone pair is on  $sp^3$  hybrid;  
 33% s-character

lone pair is on unhybridised p orbital; no s-character at all

And pyramidal shape means carbanions are relatively stabilised at the bridgehead, completely opposite to such carbocations:



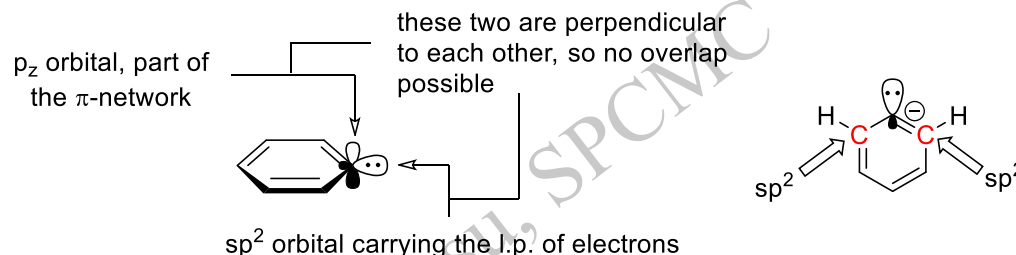
## Reactive Intermediates in Organic Chemistry:

Stabilisation of carbanions: Factors responsible

### C] Hybridisation and % s-character:

This also explains why aryl anions are relatively stable:

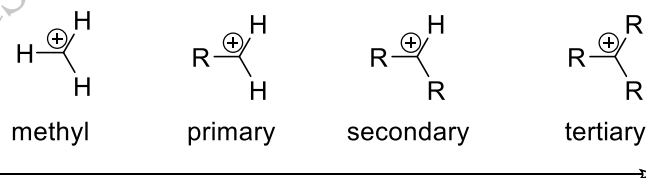
The negatively charged carbon is  $sp^2$ , the lone pair is also into an  $sp^2$  orbital. Both cases favourable with 33% s-character. You should also note that there is -I effect two adjacent  $sp^2$  hybridised ring carbons (*ortho*-carbons) - that also helps in stabilising the negative charge.



Point to note: phenyl cation is a really high energy, unstable species, for the same high percentage s-character of the positively-charged carbon and the vacant orbital.

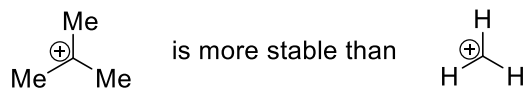
### D] Effect of alkyl substituents: Stability of alkyl anions

The alkyl substitution at the carbanionic site results in an intensification of the carbanion character because of the ER character of the alkyl groups (recall the +I effect). The order of stability in carbanions is thus the reverse of that of carbocations, that is:

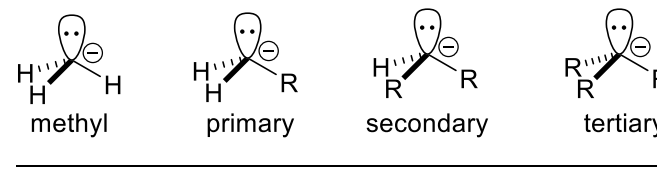
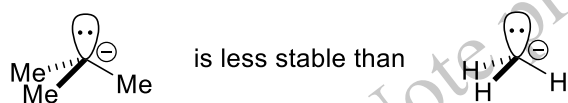


carbocation stability *increases* - positive charge gets increasingly delocalised as the number of ER alkyl groups on positively charged carbon increases

Thus,



but,



carbanion stability *decreases* - negative charge gets increasingly intensified as the number of alkyl groups on negatively charged carbon increases

However, the concept of inductive electron donation for alkyl groups is a rather simplified treatment of a rather complex issue. The carbanion stability order in solution and in gas phase are not same and not uniform, pointing to the fact that a simple inductive effect argument does not describe the picture completely. More analysis is required, taking the polarisability of the alkyl groups into consideration. But presently it is beyond our scope to delve into the details any further.

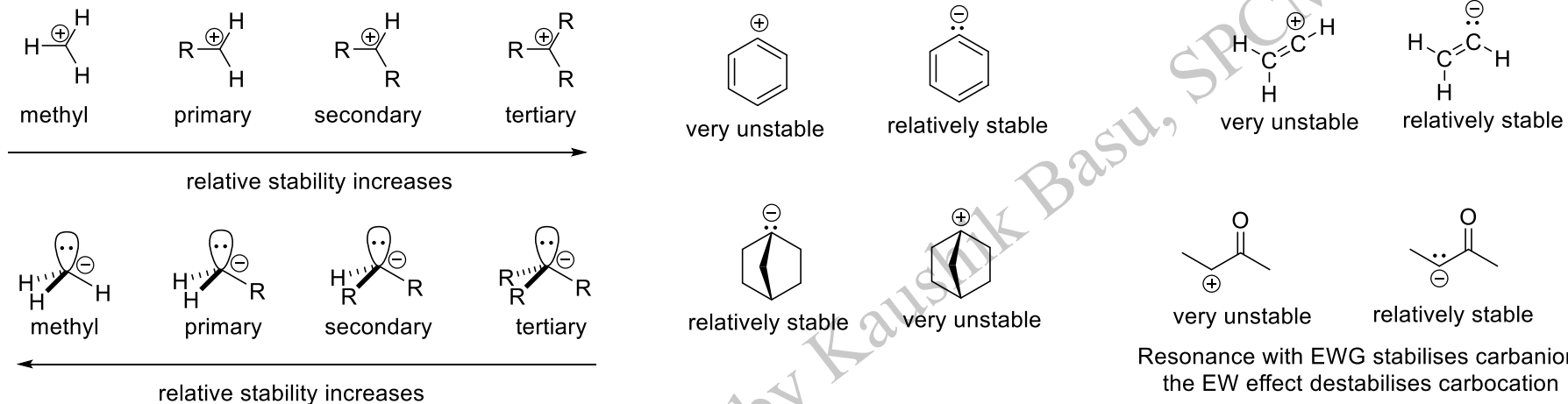


Stabilisation of carbanions: Factors responsible

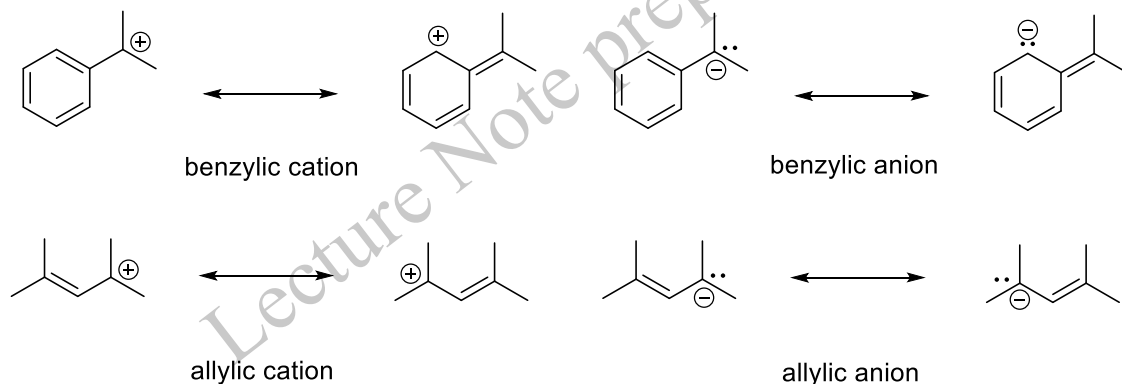
E] A structural feature that stabilises carbocation and carbanion both:

Till now, opposing trend is seen for the carbocation and carbanion stability order.

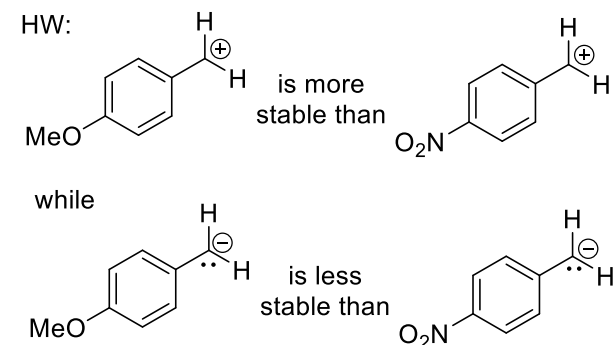
For example:



However, there are a few features which stabilise both carbocation and carbanion, the allylic and benzylic resonance:



All four systems are resonance-stabilised

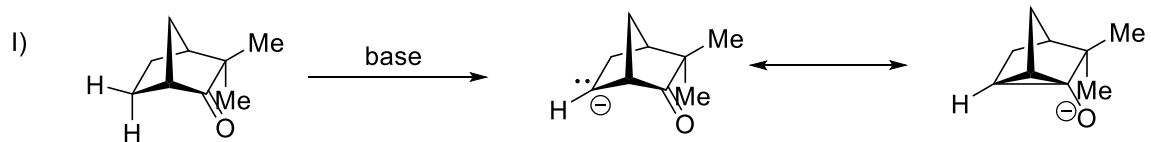


hint: Resonance with EWG stabilises carbanion destabilises carbocation

Resonance with ERG stabilises carbocation destabilises carbanion

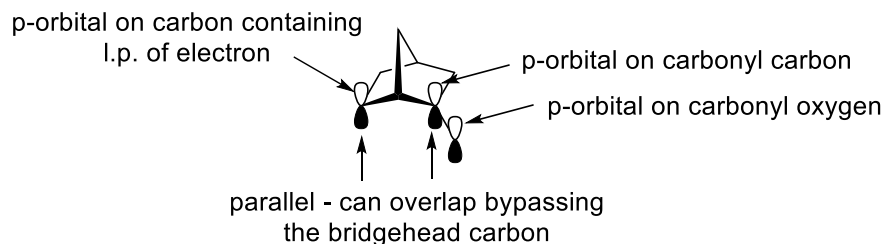
## Reactive Intermediates in Organic Chemistry:

Relative stability of carbanions - a few case studies:

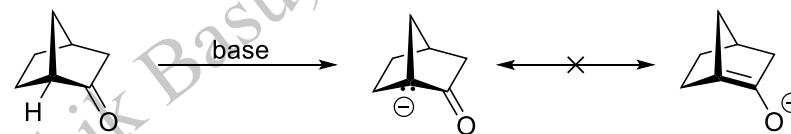


This should remind you of homoaromatic systems where cyclic p-orbital overlap takes place bypassing one or more saturated carbons

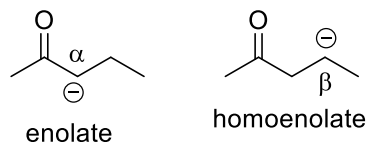
This anion is stabilised by conjugation with the non-adjacent C=O bond



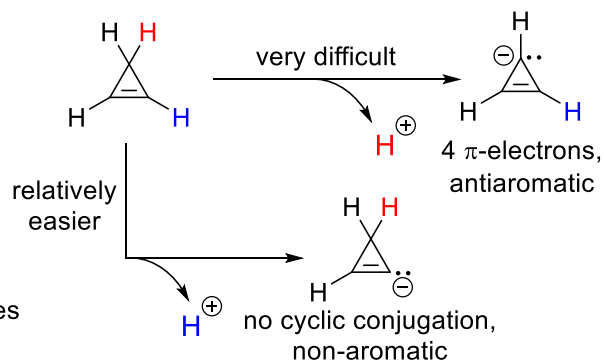
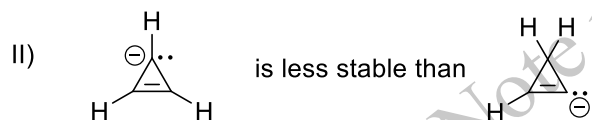
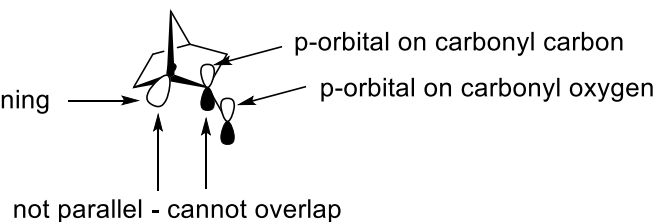
Also note, anion at the bridgehead position cannot take part in conjugation with the C=O, due to orbital alignment mismatch:



This is an example of a homoenolate ion, the "higher homologue" of enolate ion - where the  $\beta$ -carbon is anionic instead of the usual  $\alpha$ -carbon:



$sp^3$  hybrid orbital containing the l.p. of electron



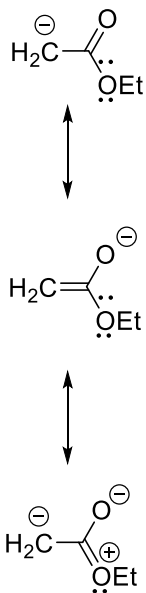
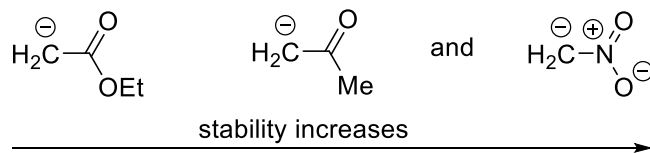
Thus, when cyclopropene is deprotonated, it the C(sp<sup>2</sup>)-H that is lost, and not the C(sp<sup>3</sup>)-H; this is an unusual result as C(sp<sup>2</sup>)-H bond is stronger than the C(sp<sup>3</sup>)-H bond (why is the former stronger, you think?)

Recall that all other things being equal, a non-aromatic species is more stable than an antiaromatic one.

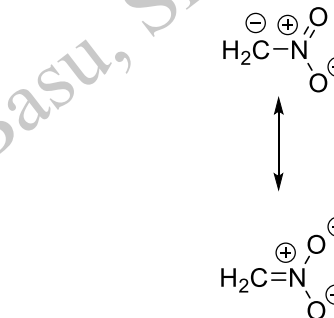
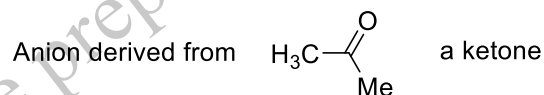
## Reactive Intermediates in Organic Chemistry:

Relative stability of carbanions - a few case studies:

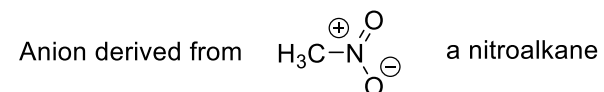
III)



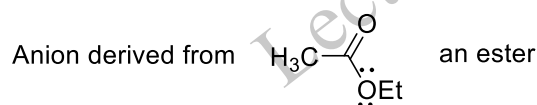
Me has both +I and hyperconjugation effect, both decreases the EW capacity of C=O, but the system is not cross-conjugated thus the keto carbonyl group's capacity to stabilise the adjacent negative charge is more than that of ester but less than that of nitro.



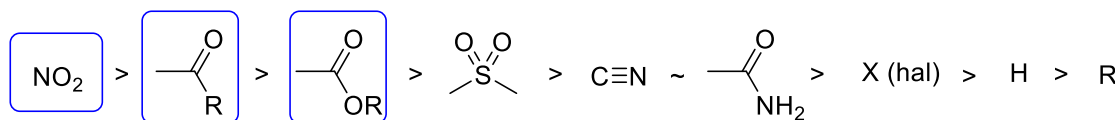
NO<sub>2</sub> has strong -I and -R effect, both helps to delocalise the adjacent negative charge is more than either CO<sub>2</sub>Et or COMe, this anion is most stable.



OEt has both -I and +R effect, -I effect increases the EW power of C=O, while the +R effect decreases it. The system is cross-conjugated, thus the carbonyl group's capacity to stabilise the adjacent negative charge is least among the series given.



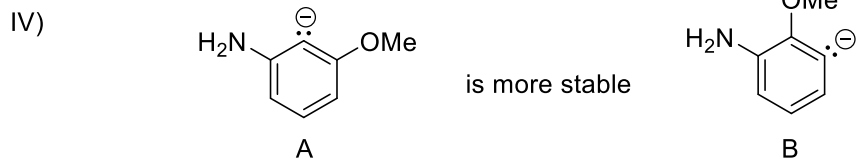
The greater the capacity of the substituent to delocalise the adjacent l.p. of electrons, greater is the stability of the anion. The approximate order of stabilising power by different substituents for a given carbanion is :



————— anion stabilising power decreases —————>

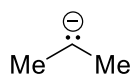
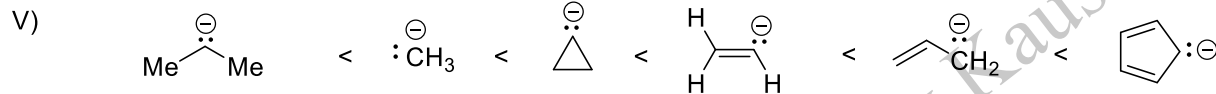
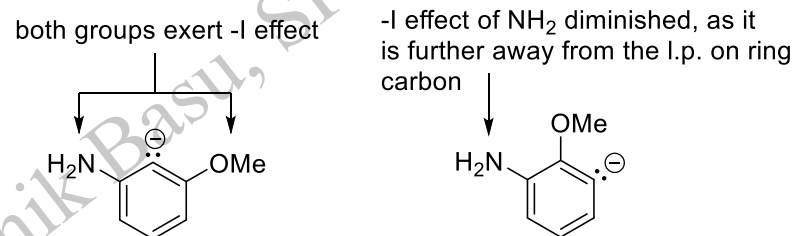
## Reactive Intermediates in Organic Chemistry:

Relative stability of carbanions - a few case studies:



These are aryl anions where the l.p. of electron is on a  $sp^2$  hybrid orbital. Therefore the heteroatom substituent can exert only their EW -I effect. No +R effect can operate as the  $sp^2$  orbital is perpendicular to the  $\pi$ -network. Recall, for manifestation of +R effect, we need to delocalise the heteroatom l.p. through the  $\pi$ -network.

Both OMe and  $NH_2$  has +R effect but those cannot operate here. These groups display their EW -I effect. As -I effect rapidly decreases with increasing distance, anion A is more stable than anion B. In the former, -I effect of both OMe and  $NH_2$  stabilise the l.p. to the maximum extent but in the latter, the -I effect of the  $NH_2$  is diminished due to the larger distance between the substituent and the  $sp^2$  orbital carrying the l.p.



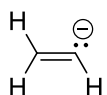
secondary alkyl anion, +I effect of two methyls most destabilised



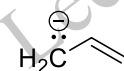
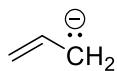
no +I effect, but no stabilisation either



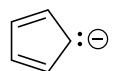
l.p. in orbital with unusually high s-character - somewhat stabilised



negatively charged carbon is  $sp^2$ , l.p. is also in an  $sp^2$  orbital, high s-character means stability for anion

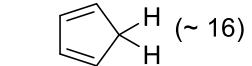
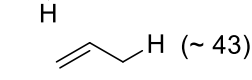
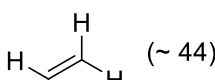
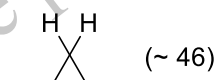
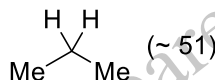


resonance stabilised



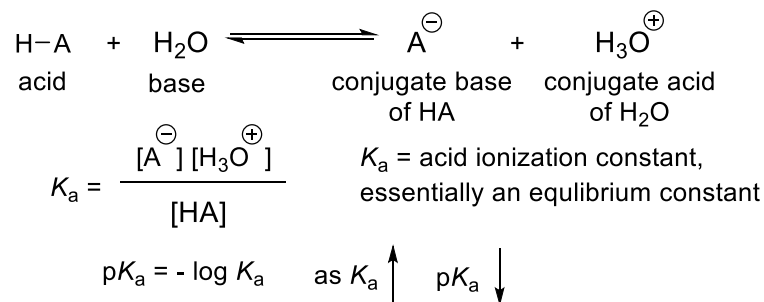
aromatic anion

conjugate acid ( $pK_a$ )



$pK_a$  decreases  
 anion stability increases

$pK_a$  is the quantity that is used to measure acidity of a species. It is defined in the following way:



Higher the acidity, more stable the anion  $A^{\ominus}$  is, more is HA ionised, greater is the  $K_a$ , smaller is the  $pK_a$

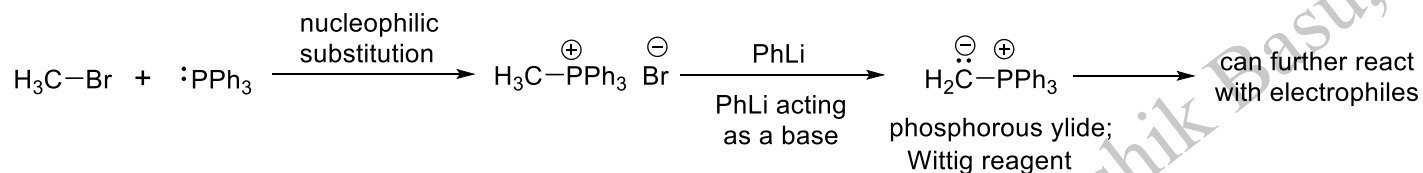
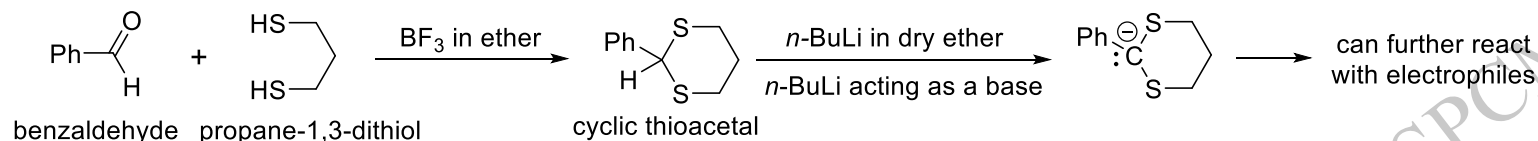
Between two acids, the one which has a lower  $pK_a$  is the stronger acid.

This means that  $pK_a$  can be used to measure the anion stability, lower the  $pK_a$  of the acid HA, more stable the conjugate base, anion  $A^{\ominus}$  is.

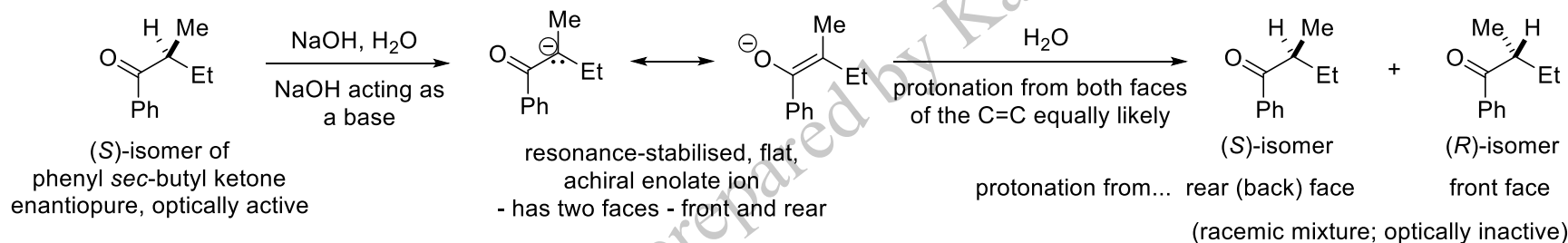
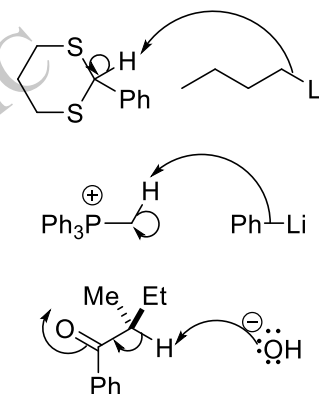
## Reactive Intermediates in Organic Chemistry:

Generation of carbanion:

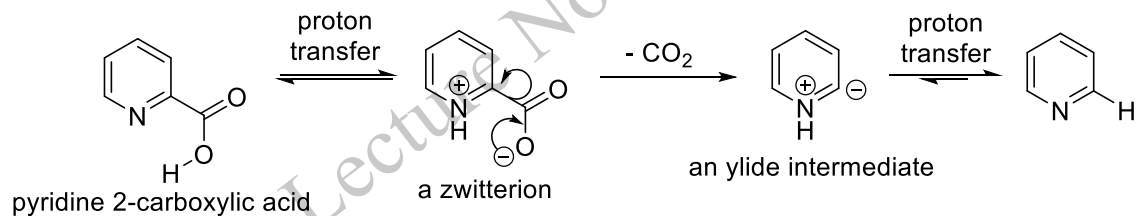
A] Deprotonation of carbon acids:



deprotonation step:



B] Decarboxylation can lead to carbanion formation:



Decarboxylation: Loss of  $\text{CO}_2$

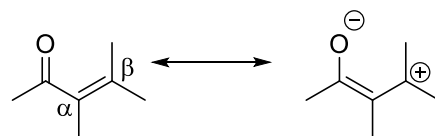
Recall that an ylide is a neutral dipolar molecule containing a negatively charged atom directly attached to a positively charged heteroatom, in which the negatively charged atom is a nucleophilic center and the onium group is usually a good leaving group.

## Reactive Intermediates in Organic Chemistry:

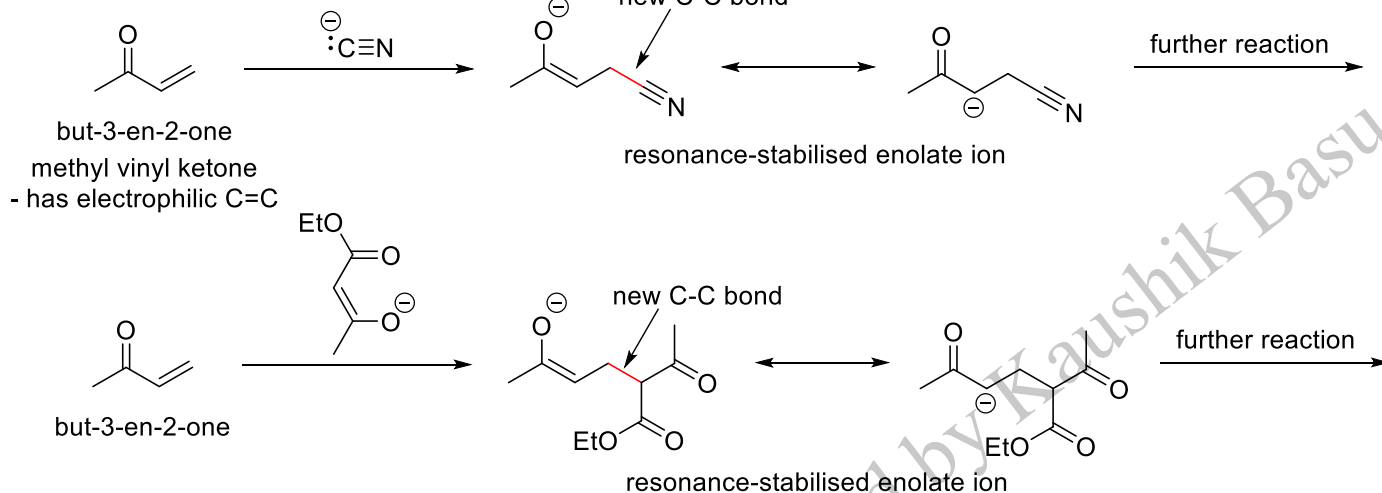
Generation of carbanion:

C] Addition of a nucleophile to an electrophilic C=C:

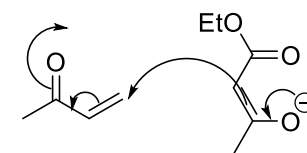
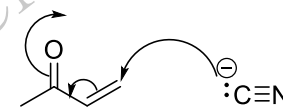
electrophilic C=C - alkene conjugated with EWG



$\alpha,\beta$ -unsaturated carbonyl -  $\beta$ -carbon is susceptible to nucleophilic attack

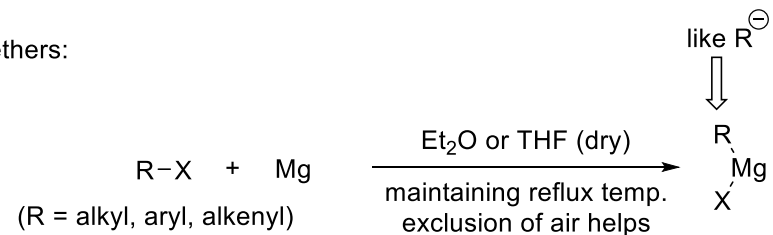
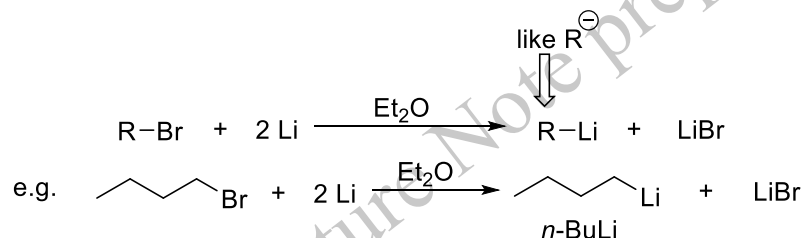


The nucleophilic addition reaction proceeds via:



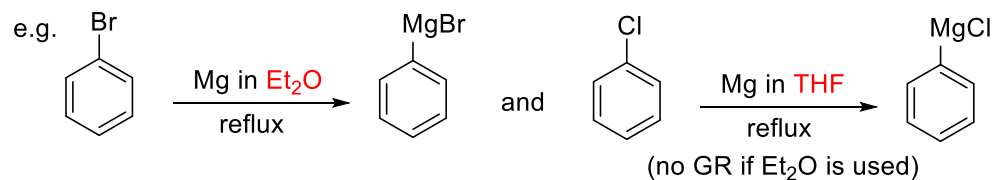
D] Preparation of organometallic compounds:

From metals and organic halides: simplest method, use unreactive solvent such as ethers:



We cannot use protic solvents here, as the carbanion generated is a very strong base and will immediately attack the acidic proton of the solvent and itself will get protonated.

Recall that both THF and  $Et_2O$  are non-polar, non-protic solvents.



(BP of THF 66 °C, BP of  $Et_2O$  35 °C, C-Br weaker than C-Cl)

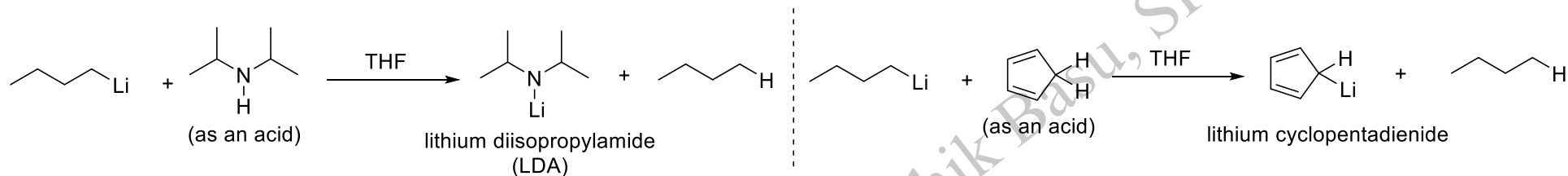
## Reactive Intermediates in Organic Chemistry:

Fates of a carbanion:

A] Reaction as a base: Protonation

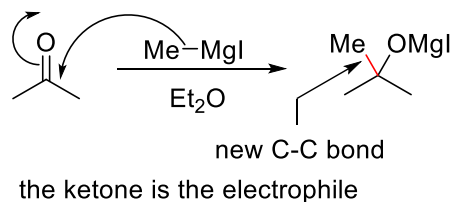


Water acting as an acid in both cases. This is why we cannot use protic solvents like water or alcohols while preparing these organometallic reagents.

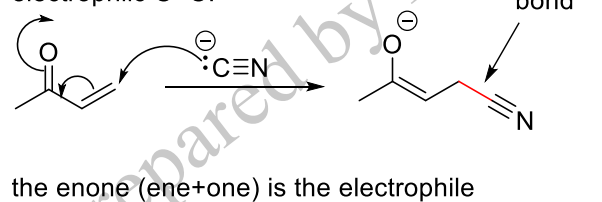


B] Reaction as a nucleophile:

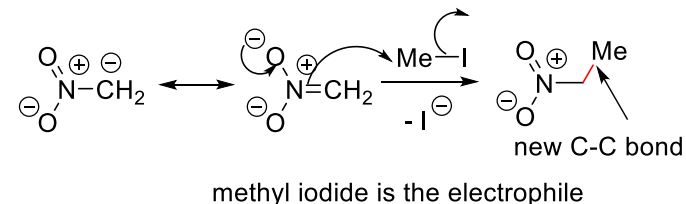
Nucleophilic addition to carbonyl:



Nucleophilic addition to electrophilic C=C:



Nucleophilic substitution:



The base-nucleophile dichotomy: That which can act as a base, can also act as a nucleophile and *vice versa*.

