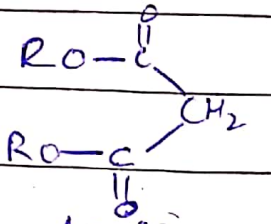
Date: / /2020 M T W T F S

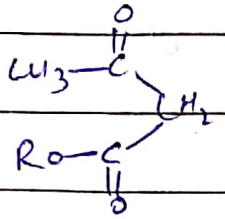
Generation of $Nu^{\ominus}$ carbon

⇒ Substrates:

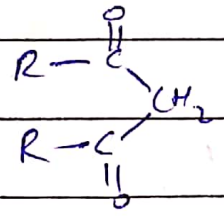
Many substrates can be used.



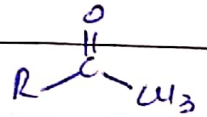
malonic ester

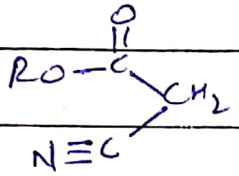


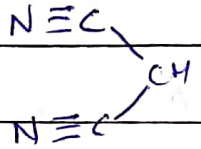
acetoacetic ester



ketones







Nitro group is most electron withdrawing. Nitro on alpha position is most effective.

proton attach to α-carbon is removed.

CH_3-NO_2 (Nitro methane is most common)

Note:

if EWG is not attach e.g $R-CH_3$, alkyl group is attach than $R-\bar{C}H_2$ or very good base is formed and take up ~~that~~ proton and reaction become backward and it becomes reversible.

To do reaction; in the reactants acid and base must be made strong.

⇒ Base :-

Base selection is very important Base should be strong and should not act as Nucleophile.
e.g. $R\bar{O}Na^+$ is strong base and it is easily synthesize.

Preparation:

$$ROH + NaOH \longrightarrow R\bar{O}Na^+ + H_2O$$

if $R\bar{O}Na^+$ is used as Base Than ROH is produce after capturing proton as conjugate acid.

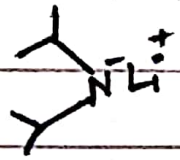
$$R\bar{O}Na^+ \xrightarrow{H^\oplus} ROH$$

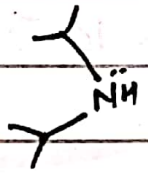
conjugate acid.

pyridine and triethyl amine are weak bases so, not used.

Base	conjugate Acid
PhO^-Na^+ weak base	PhOH phenol is formed strong acid
RO^-Na^+	ROH alcohol is formed
$tBuO^-K^+$	tBuOH is formed → weak acid
EtO^-Na^+	EtOH is formed → weak acid
available in market Na^+H^-	Hydrogen present ↑H_2 is formed which is easily removed. Not give reversible reaction.
available in market K^+H^-	in the form of Hydrid
$BuLi$	↑Butane gase is formed.
LDA Lithium di isopropyAmide	weakest conjugate acid is formed.

available in market



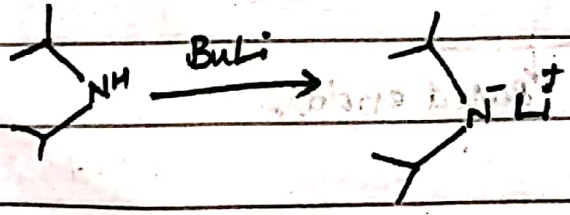


Formation of BuLi :-

$$BuX \xrightarrow{Li} BuLi$$

-exchange is on carbon, which is a less electronegative atom, so it easily gain/accept proton and become good/strong base.

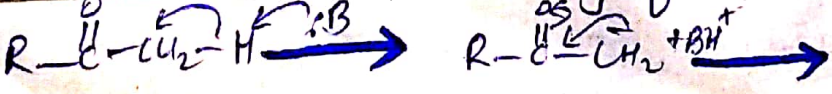
Formation of LDA :-



Nitrogen gain negative charge it becomes strong Base.

Important Note

- strong base
- reversible reaction not take place
- stability of carbanion.



Side Reaction:-

if Base can act as Nu: it may attack on the electrophillic carbon and side reaction takes place- To avoide this;

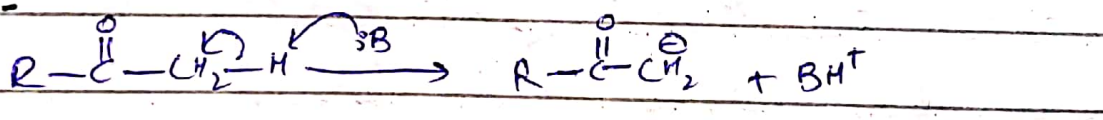
"The Base having larg size sterically hindered size can't act as Nucleophile. Thus became strong Base and used in the reaction e.g. LDA."

"Any alkyl group on N makes it good Base rather than good Nucleophile."

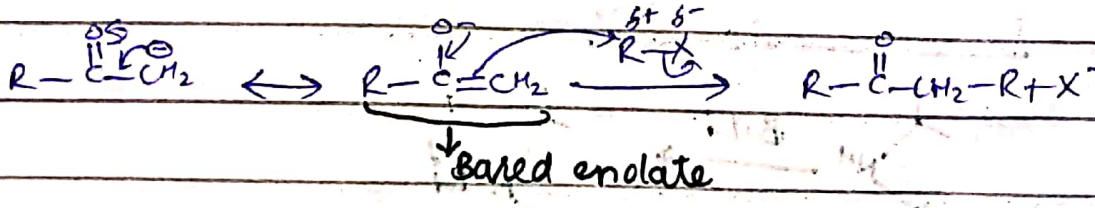
Solvent Selection:-

Solvent selection is most important for example if ethanol (a protic solvent) is used it gives proton and reaction become reversible- As reaction takes place in two steps:-

Step 1:-

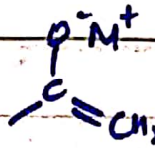


Step 2:-



Based enolate

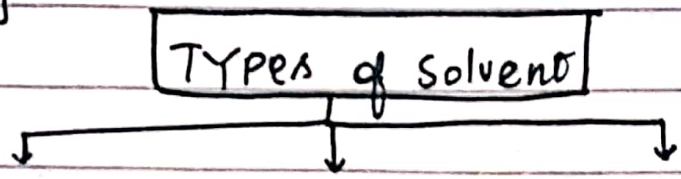
The enolate formed actually oriented as;



metal is present it attack with oxygen. Thus enolate not exist independently- The solvents are used to creat;

1) solvation (dissociation)

2) solvolysis



Protic polar:-

Have polarization, cause polarization. In this case metal is attach to oxygen as $R-\overset{\delta-M^{+}}{C}=CH_2$ and thus polar solvent may be used. They are;

Cation solvator:- Negative part of the solvent is used. like in alcohol OH is used.

Anion solvator:- positive part of solvent solvate the anion part of enolate.

Examples:-

ROH, H_2O

Advantage: These are good cation and anion solvator.

Draw Back:-

Give proton and make reaction reversible.

They remove metal ion but give proton to the negativily charge oxygen of enolate

"So in this reactions protic solvents are not used. Even traces of protic solvents are not used."

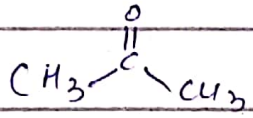
Aprotic Solvent:-

They don't have proton to give, But they have polarity-

Example:-

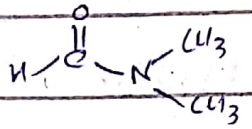
DMSO

DiMeThyl Sulfonyl Oxide



DMF

DiMethyl Foramide



Properties:-

Labil proton are not present have high dielectric constant

They are most polar even than H_2O and alcohol-

They are **cation solvator**

So They can easily dissociat enolate-

Draw back:-

1) Although they are poor ~~ed~~ anion generator not cause reversibility. But They have high boiling point.

2) They are not used because of this, due to they after they reaction they are not easy to remove-

3) As high temp may not exceed at lab and it may decompose the product-

4) Determination using NMR is also very Hectic-

Medium polar:-

1) They have medium dielectric constant.
2) Provide slow and safe reaction comparatively.
3) Good cation solvator but poor anion solvator.
4) Boiling point is lower can be easily removed by using **rotar vaporizer** (Boil solvent at reduce pressure)

Example:-

THF

Diethyl ether

Non-Polar :-

1) Not have labil polar Hydrogen. They have carbon–Hydrogen bond.
2) They not have cationic solvator and anionic solvator part.
3) Thus They are not used in this reactions.

Example:- Toulene, benzene, hexane.

Success of Using "Medium polar Solvents":-

i) Not give proton to cause reversibility.
ii) Have low Boiling point so can be easily removed.
iii) Cause medium dissociation.

Reversibility :-

→ Reaction Must Not Be Reversible