CSIR-NET GATE IIT JAM

NAME REACTIONS

L-03

Enolates and It's Generations

Vision Batch

Chiral Academy

- Subject – Organic Chemistry
- Topic - Enolates and Name Reactions

Lect - 03

Avinash Sir

Topics to be cover

#03

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1) Introduction to Enolates
2) Generation of Enolates
3) Alkylation of Enolates

Revision

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Enolization

70%

30%

30%

70%

1) Hyperconjugation
2) conjugation.
3) H-Bonding

* $\% \text{Enol} \propto \frac{1}{\text{Temp.}}$

Introduction to Enolates

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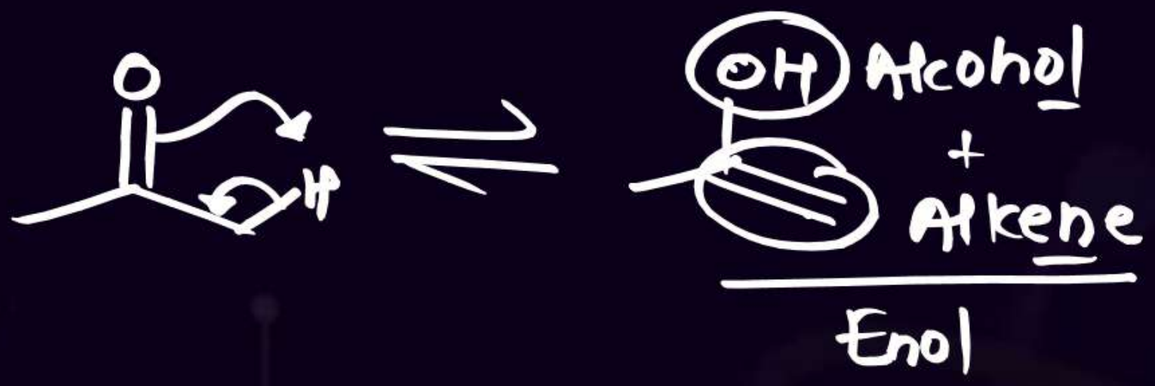
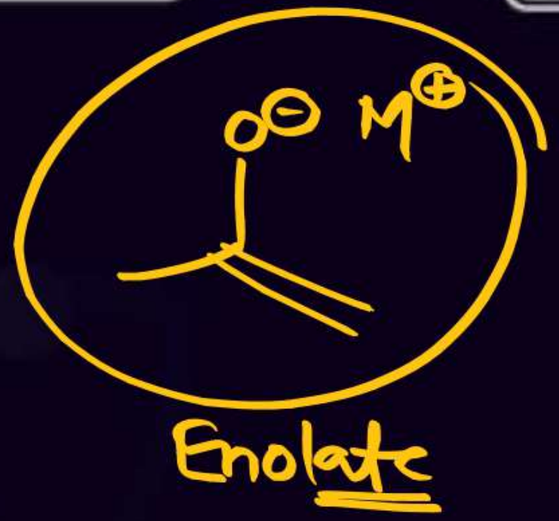
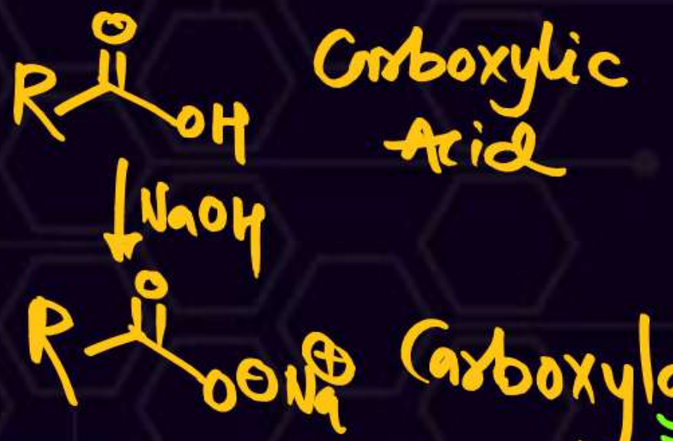
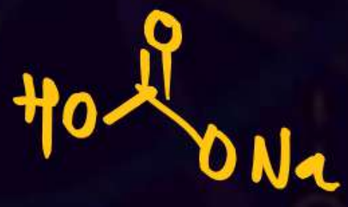






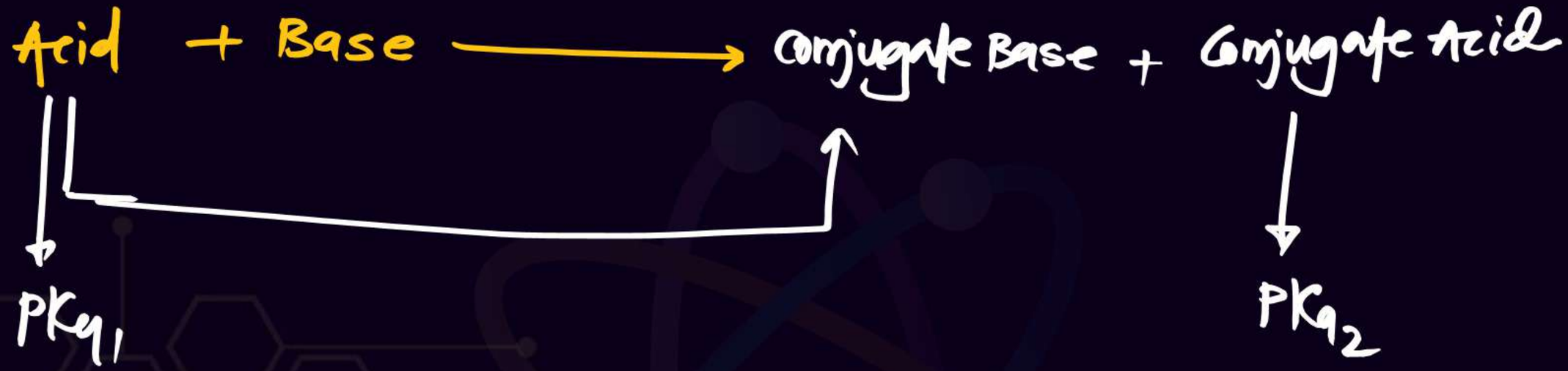


$R \rightleftharpoons P$ Equal Equilibrium

$R \rightleftharpoons P$ Rxn in Equilibrium, favour product

$R \rightleftharpoons P$ Rxn in Equilibrium, favour Reactant.

Acid Base



$$\Delta pK_a = pK_{a_2} - pK_{a_1}$$

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Reactant ⟶ Product

irreversible Rxn

$\Delta pKa = +>10$

Reactant ⇌ Product

Rerersible, But favour product

$pKa = 0-10$

Reactant ⇌ Product

Reversible, But favour Reactant

$\Delta pKa = -10$ to 0

Reactant ⟶ Product

No Rxn or very slow Rxn.

$\Delta pKa < -10$

Acid Base

$\Delta pK_a > +10$

Acid (pK_{a1}) + Base $\xrightarrow{\text{Irreversible}}$ Conjugate Base + Conjugate Acid (pK_{a2})

$\Delta pK_a = 0$ to $+10$

Acid (pK_{a1}) + Base $\xrightleftharpoons{\text{Rev.}}$ Conjugate Base + Conjugate Acid (pK_{a2})

$\Delta pK_a = -10$ to 0

Acid (pK_{a1}) + Base $\xleftrightharpoons{\text{Rev.}}$ Conjugate Base + Conjugate Acid (pK_{a2})

$\Delta pK_a < -10$

Acid (pK_{a1}) + Base $\not\longrightarrow$ Conjugate Base + Conjugate Acid (pK_{a2})

pKa_1 (19.2)

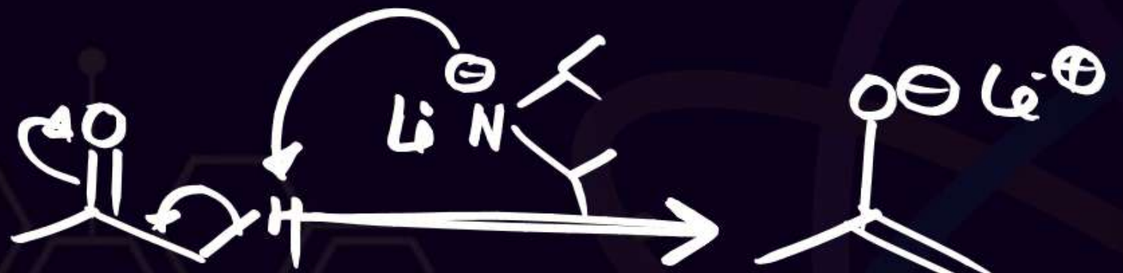
pKa_2

$$\Delta pKa = pKa_2 - pKa_1$$

$\Delta pKa = 16 - 19$

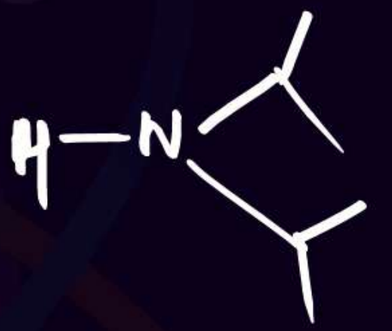
$= -3$ → Rxn Equilibrium, favour Reactant

-10 to 0 → Reactant favour in equilibrium



19

99%



~35

$\Delta pK_a = 35 - 19 = 14$

>+10

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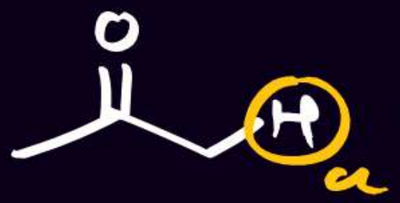
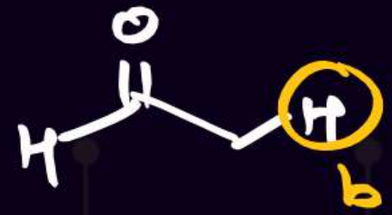
pKa



19.2



16.7

18.3

Acidity = $H_b > H_c > H_a$

EtOH = 16

tBuOH = 18

19.2

$EtO^{\ominus}$

$\Delta pK_a \simeq -3$

+ EtOH

+

15.9

19.2

Na-H

Irreversible Rxn

+ H_2

Gas

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①  + EtO⊖ ⇌ + EtOH

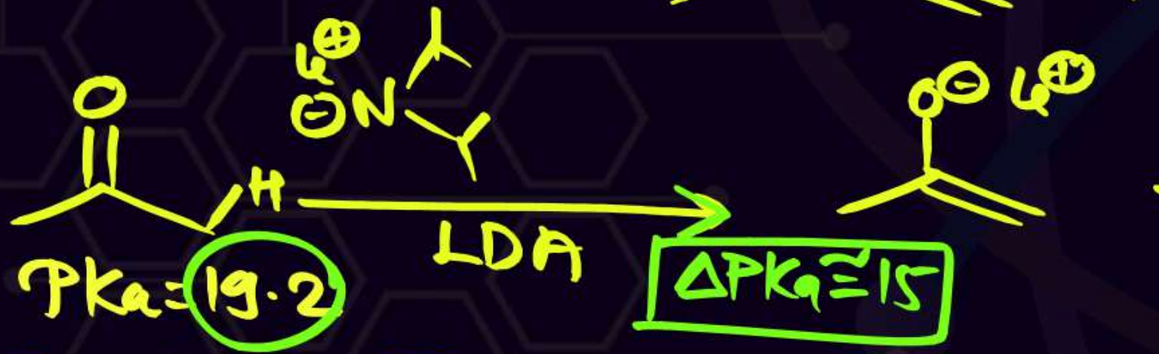
pKa = 19.2

pKa = 16

Reversible

②  + H₂↑

Irreversible

③  + 

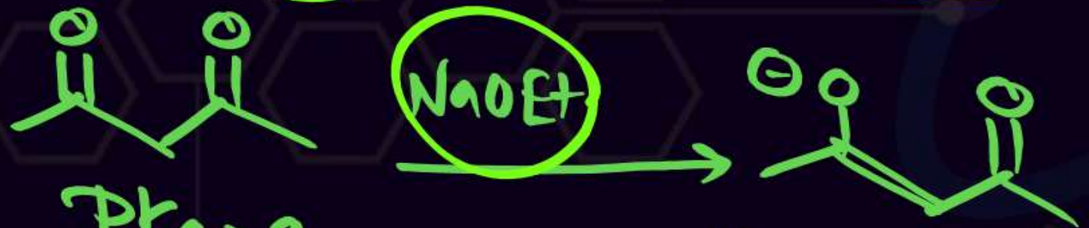
pKa = 19.2

LDA

ΔPKa ≅ 15

Diisopropylamine

pKa = 36

④  + EtOH

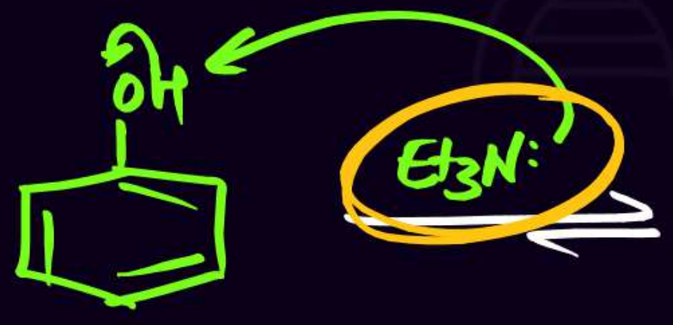
pKa = 9

99.9999%

pKa 16

← favour product

ΔPKa = 16 − 9 = 7



+ $Et_3\overset{\oplus}{N}-H$

pKa1 = 9.5

pKa = 10.5

$\Delta pKa = 10.5 - 9.5$

= +1

0 to +10

9.5

+ H_2O

16

$\Delta pKa = 16 - 9.5$

6.5

0 to +10

ΔPKa	
> +10	Irreversible
0 to +10	Reversible, product favour
−10 to 0	Reversible, Reactant favour
< −10	No Rxn.

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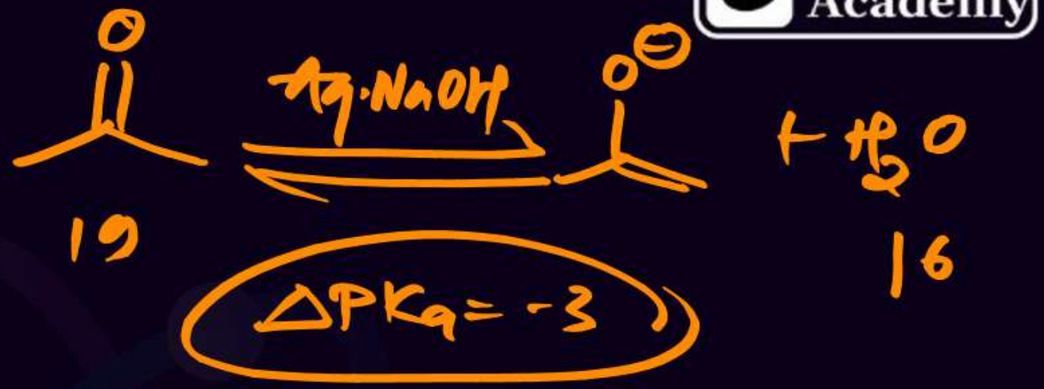
What are Enolates



100%

80%

20%

ΔPKa = 17

Generation of Enolates

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X = H → Aldehyde

= OMe → Ester

= $-NH_2$ → Amide

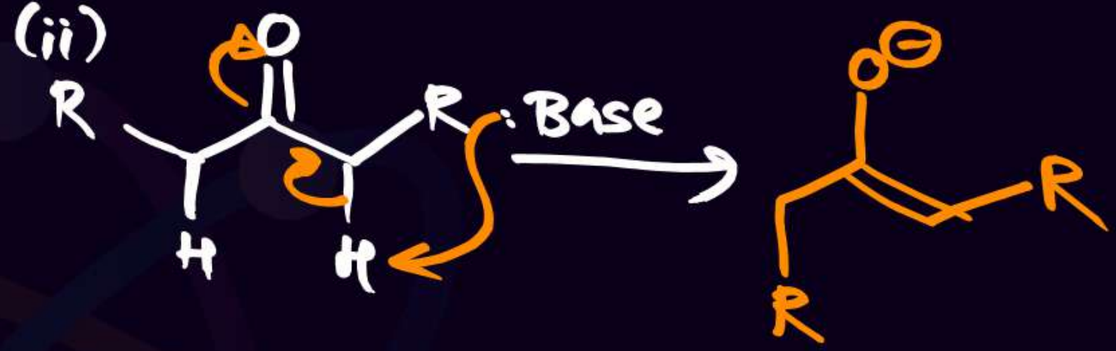
= −Cl → Acid chloride.

* 

* 

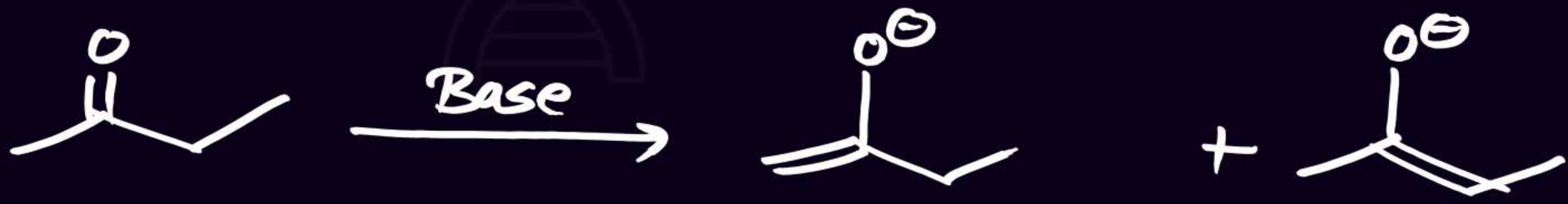
* Enolate of Ketones

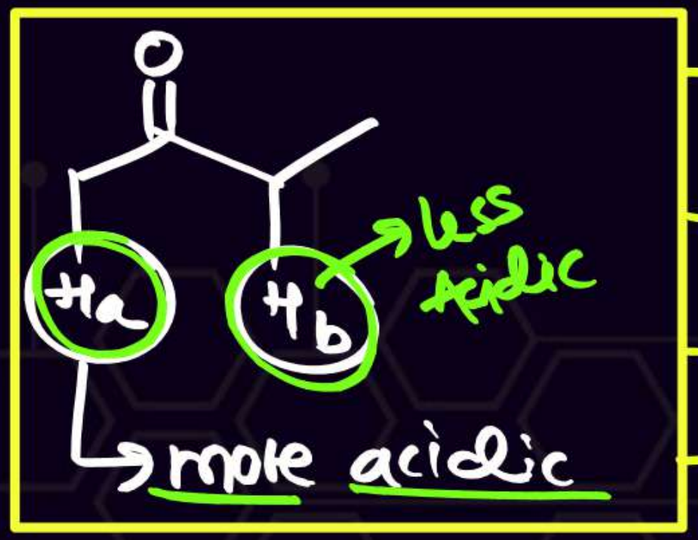
1) symmetrical Ketone :-



2) Unsymmetrical Ketones :-

→ less substituted → More substituted.





→ Less substituted	→ More substituted
→ Less stable	→ More stable
→ Less exn time	→ More exn time
→ Kinetic Enolate.	→ Thermodyanmic enolate
→ Bulkier Organic bases.	→ Inorganic bases
→ At Low temp.	→ At high temp.

Bases

Organic / Bulkier

LDA

LICA

LiTMP

MHMDS

LiHMDS

NaHMDS

KHMDS

LiTMDPS

$Ph_3C^{\ominus}\ Li^{\oplus}$

−78°C

LDA : 78°

Kinetic

General Kinetic Enolate.

Inorganic Bases

→ KH, NaH, KOH, NaOH, $Ca(OH)_2$

→ $CaCO_3$, Na_2CO_3, K_2CO_3

→ R-OH + NaH → $RO^{\ominus}$

→ EtOH + NaOH → $EtO^{\ominus}$

→ tBuOH + NaOH → $tBuO^{\ominus}$

→ $NaNH_2$

$Ph_3C^{\ominus}\ Li^{\oplus}$, 0°C

LDA

> 0°C

Thermodynamic.

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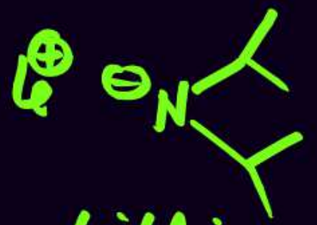
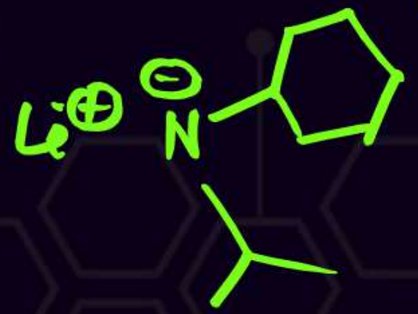
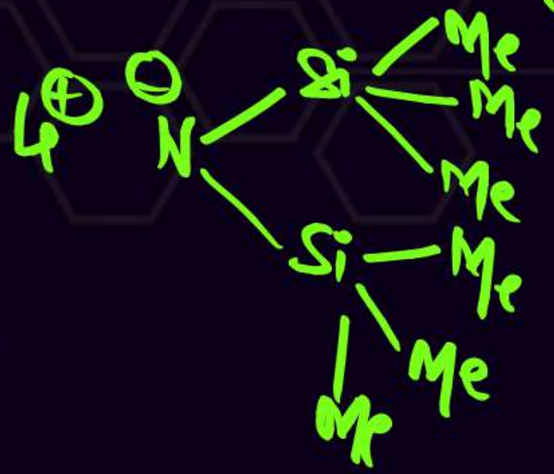
LDA = Lithium Diisopropyl Amide



LICA = Lithium Isopropyl cyclohexyl Amide



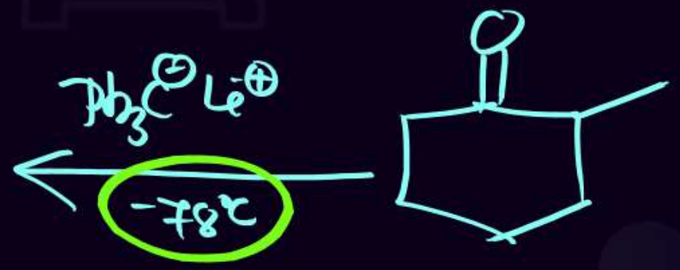
LiHMDS = Lithium Hexamethyl Disilyl Amide

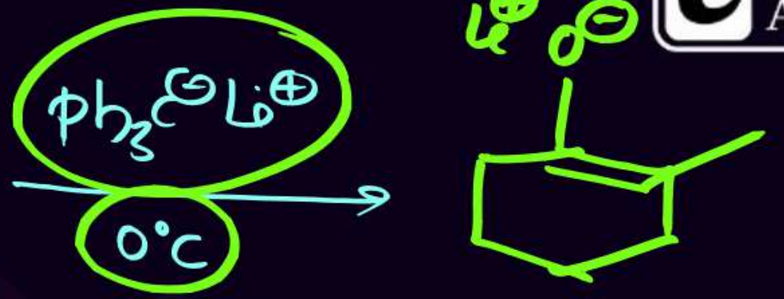


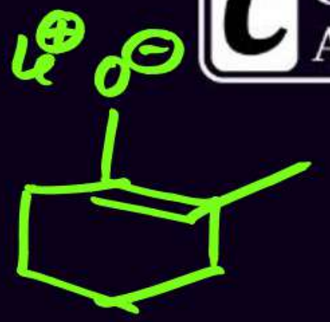
$M^{\oplus} = Na^{\oplus}$ NaHMDS

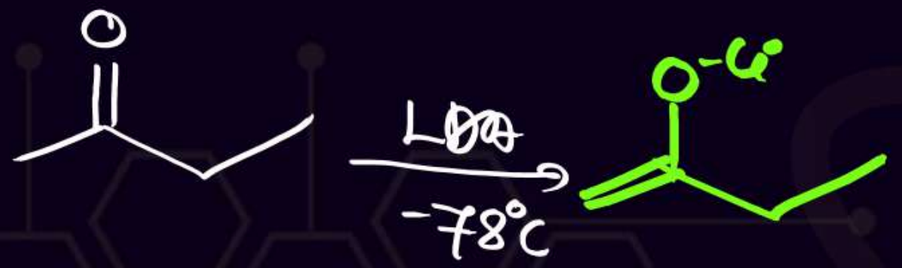
$M^{\oplus} = K^{\oplus}$ KHMDS

Carruthers







1) 

2) 

3) 

4) 

5) 

Only for WEP-GATE

Dale. Boger

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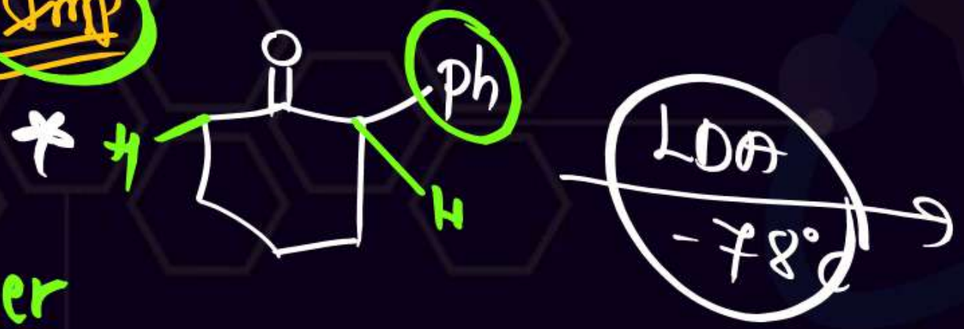
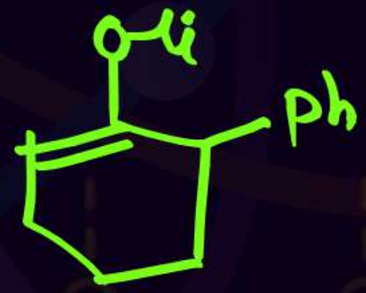
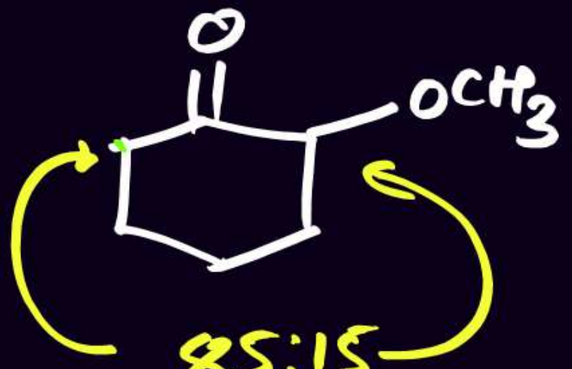
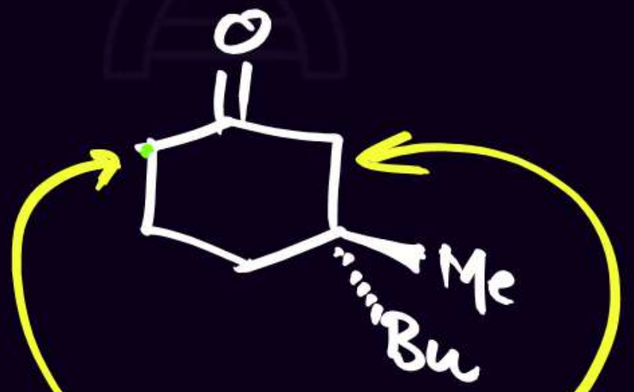
Bruckner



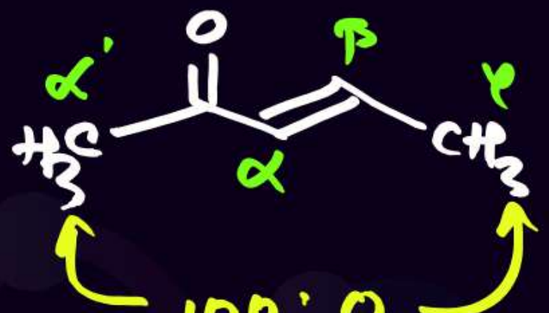




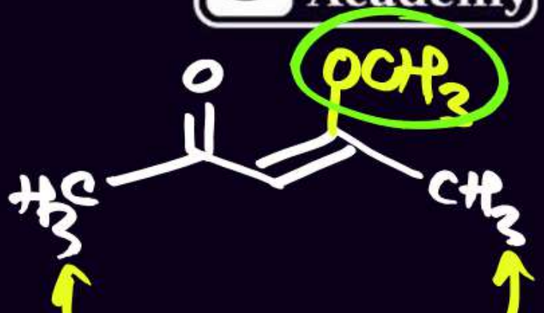
85:15
LDA, -78°C



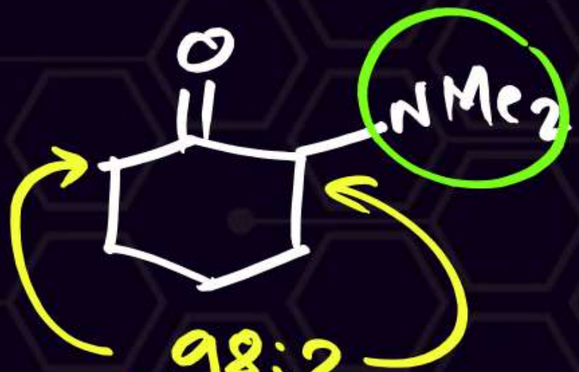
91:9
LDA, -78°C



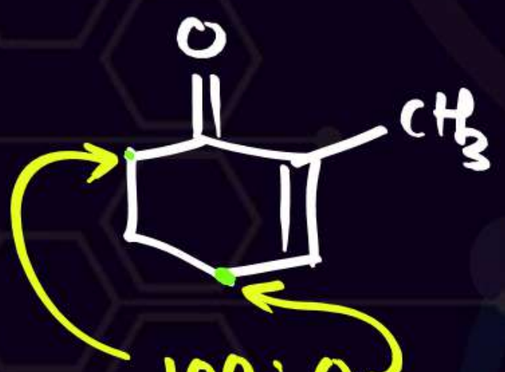
100:0
LDA, -78°C



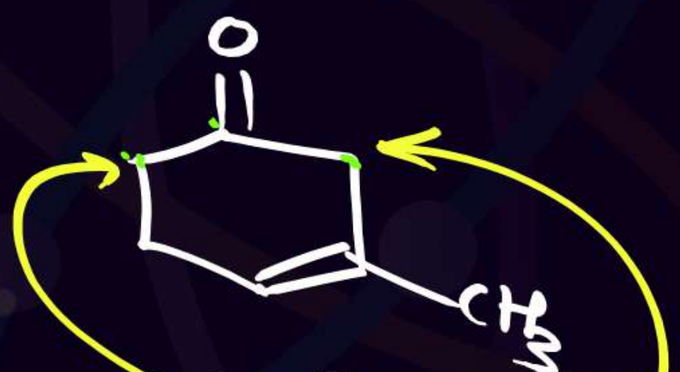
100:0
LDA, -78°C



98:2
LDA, -78°C



100:0
LDA, -78°C



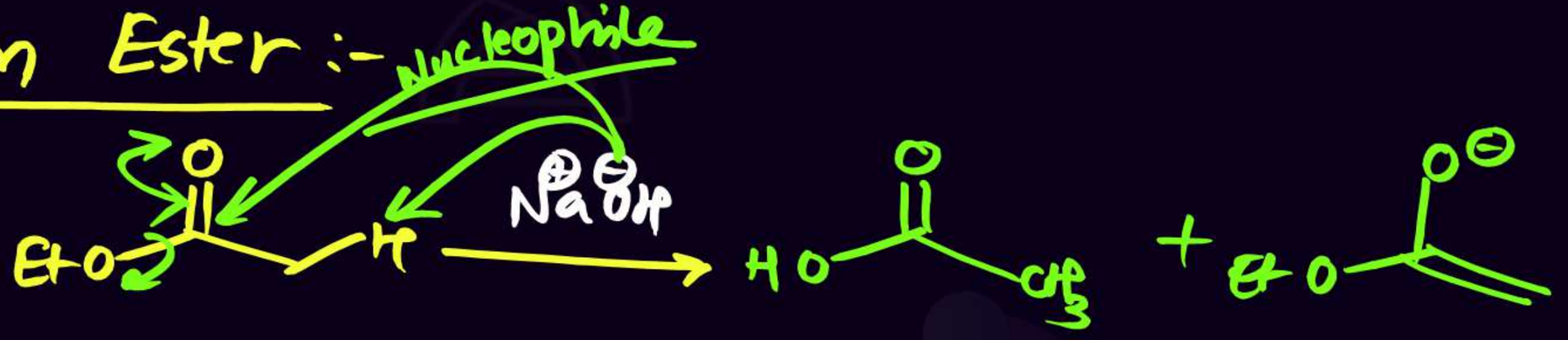
20:80
LDA, -78°C

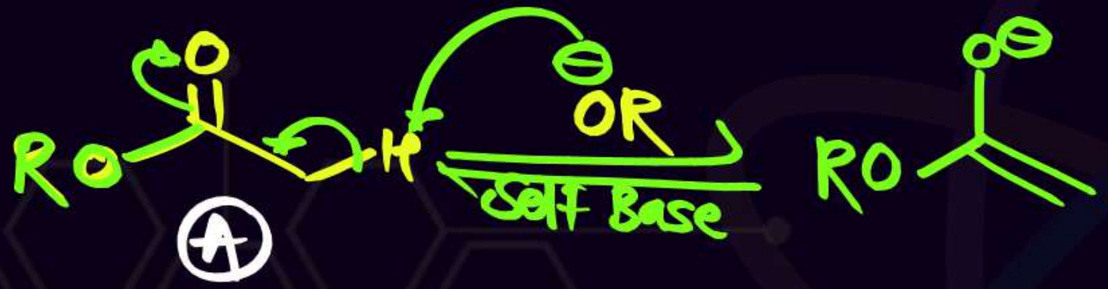
* Generations of Enolates :-

① From Aldehyde

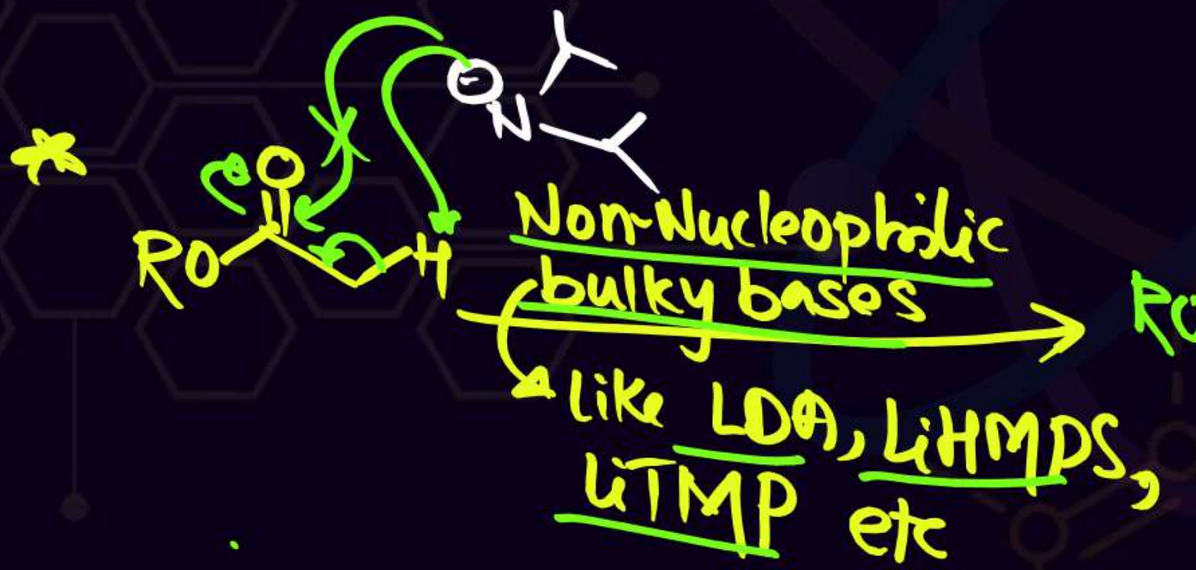
② From Ketone

③ From Ester :-





→ Reversible



→ Irreversible.

④ From Amide

⑤ From Acetic Anhydride :

⑥ From α,β-Unsaturated Carbonyl Compound :-

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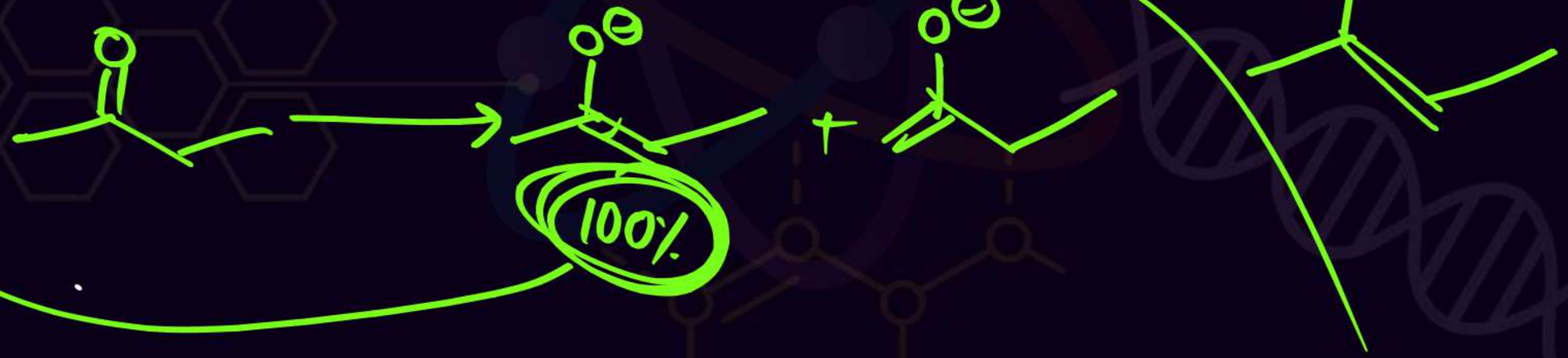
1) By Using Na/liq.NH_3

2) By Using R_2CuLi

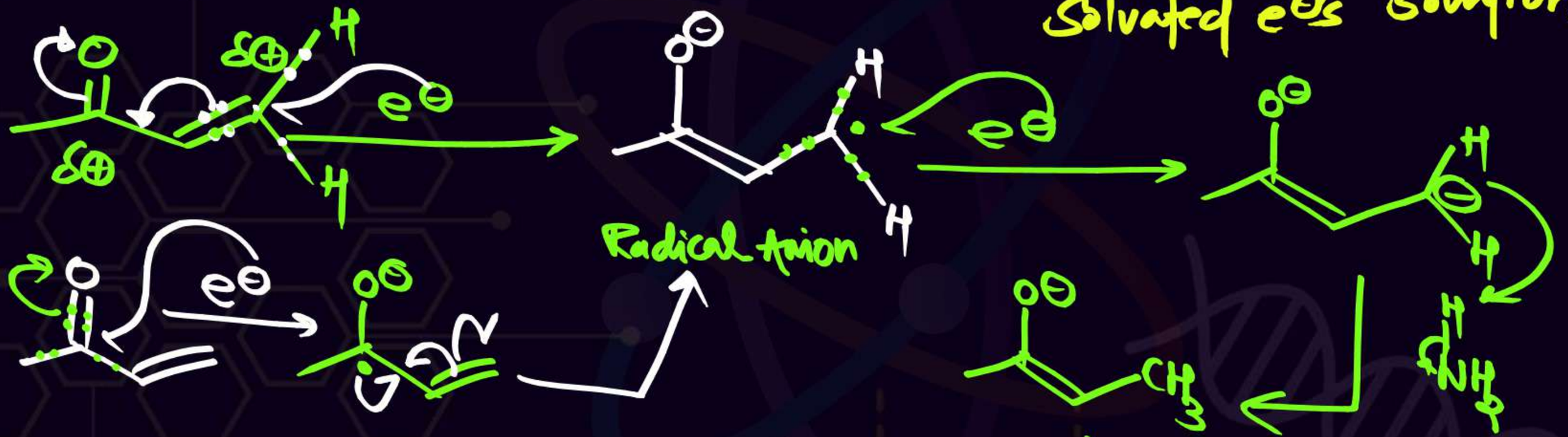
3) By Using Selecteides.



ⓐ by Using Na/Li/K in Liq. NH_3 :-

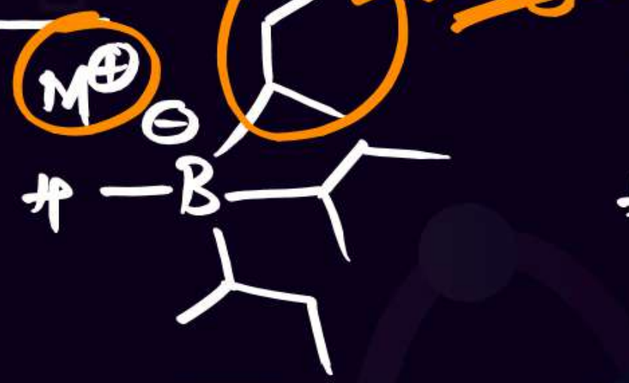
$$\text{Liq.}NH_3 + Na/Li/K \longrightarrow Na^{+}/K^{+}/Li^{\oplus} + e^{\ominus}(NH_3)$$

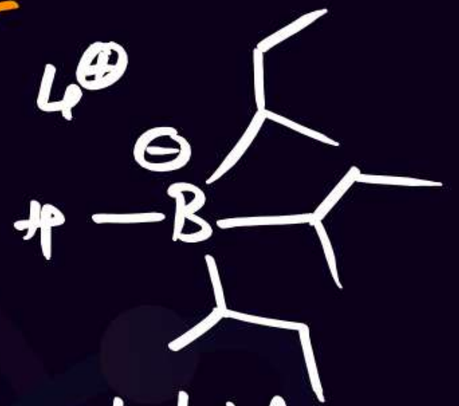
Solvated $e^{\ominus}$s solution



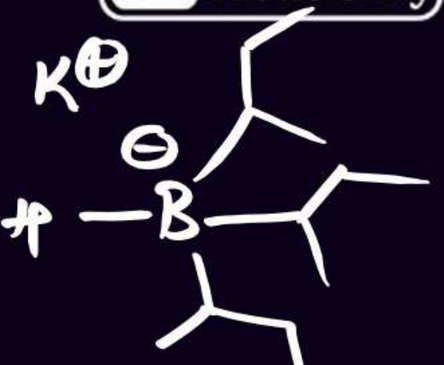
* By Using Selecteides :-

Selecteides =

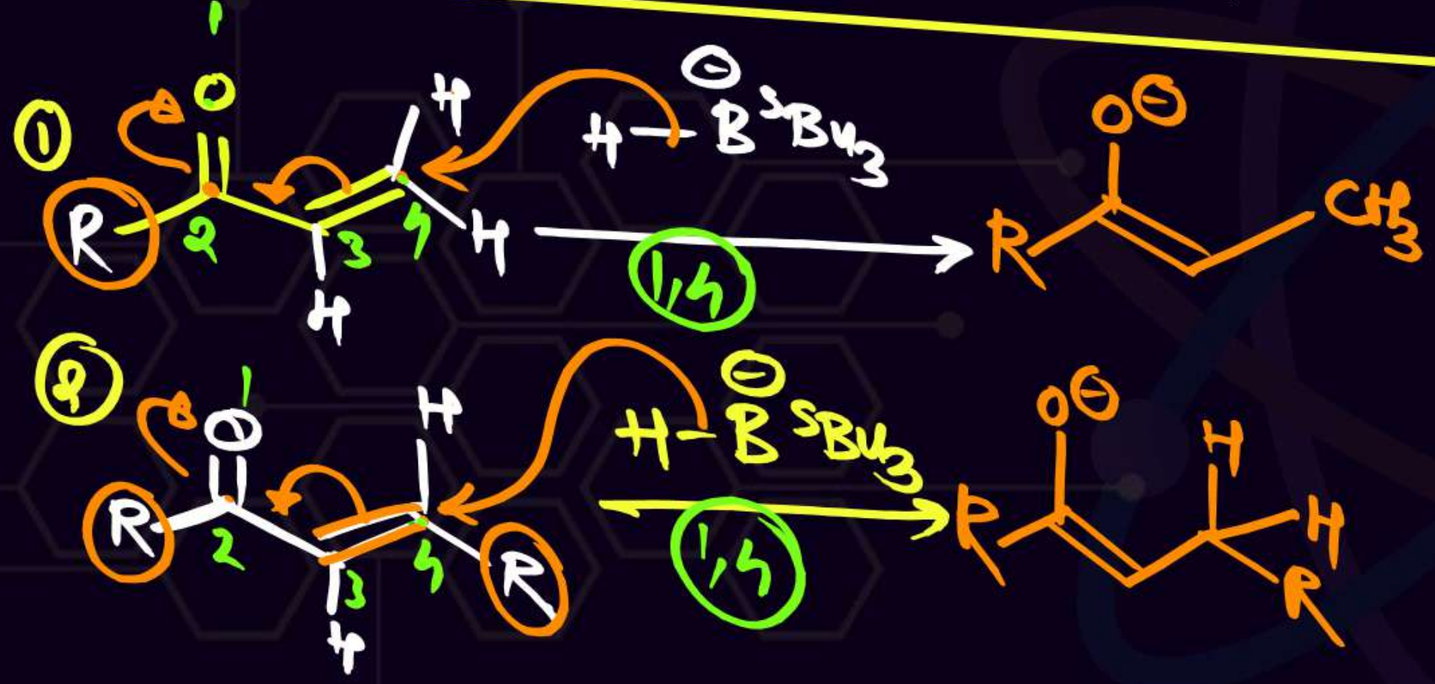


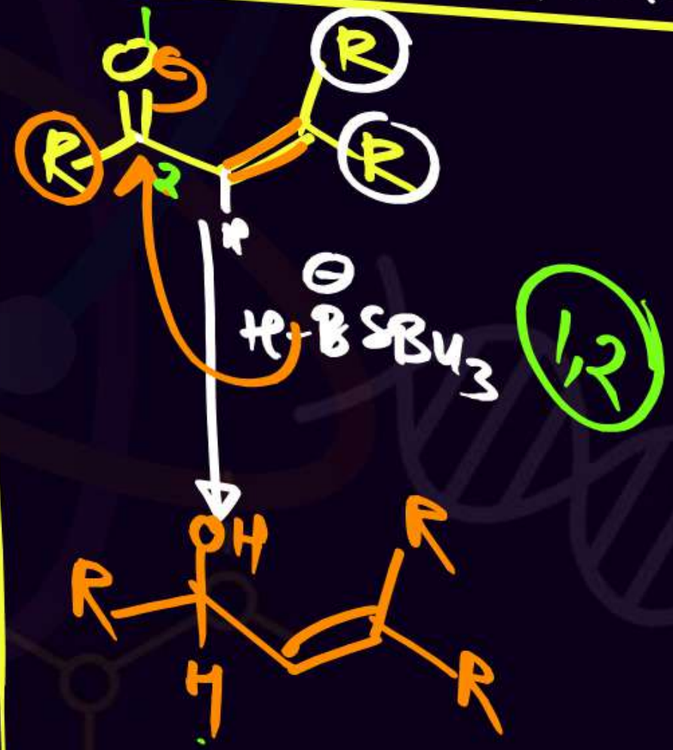


L-Selecteide

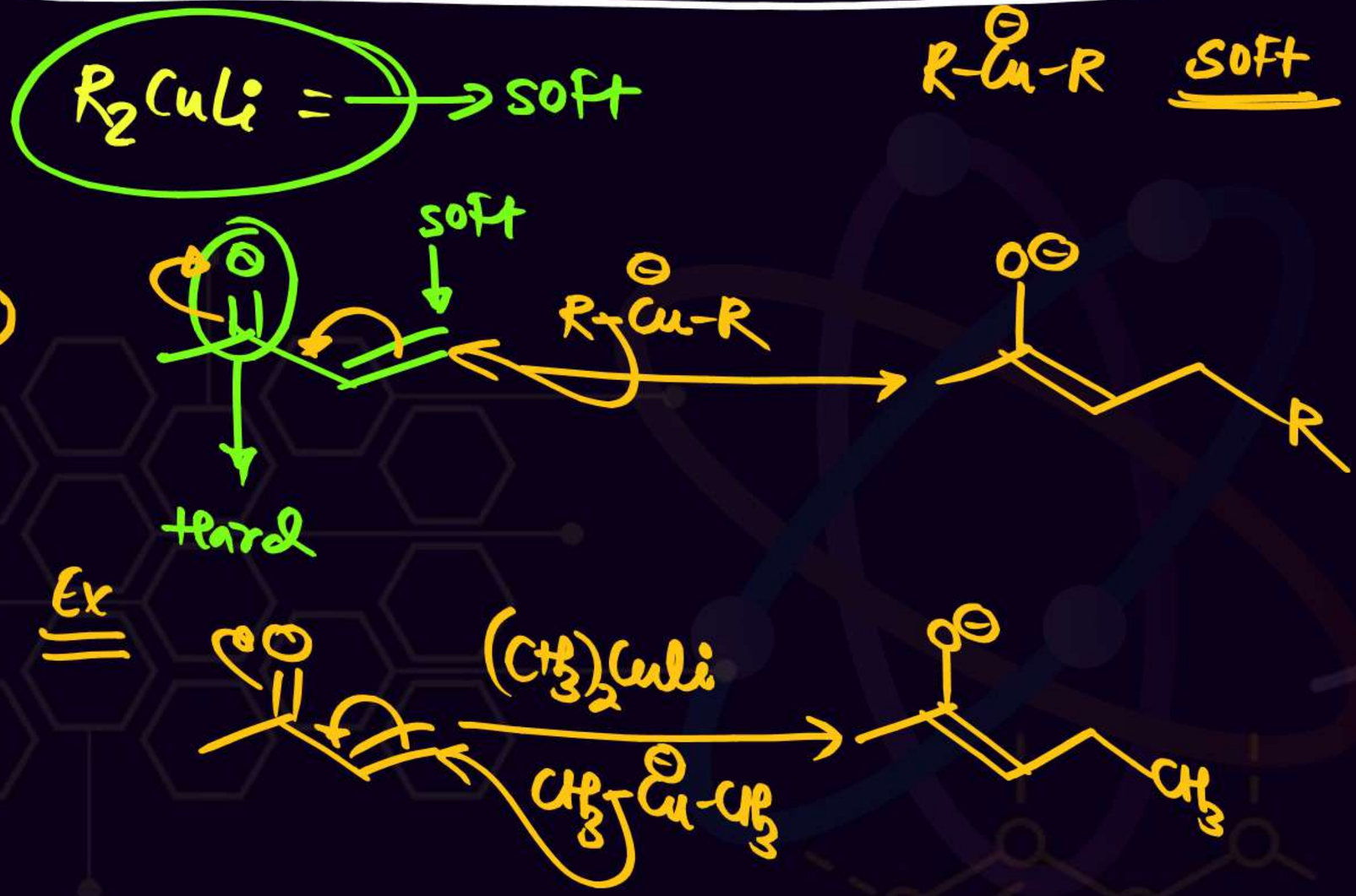


K-Selecteide





9) By Using Gilman Reagent (R_2CuLi)



SUMMARY


1)
Base


2)
Base


3)
Base
+

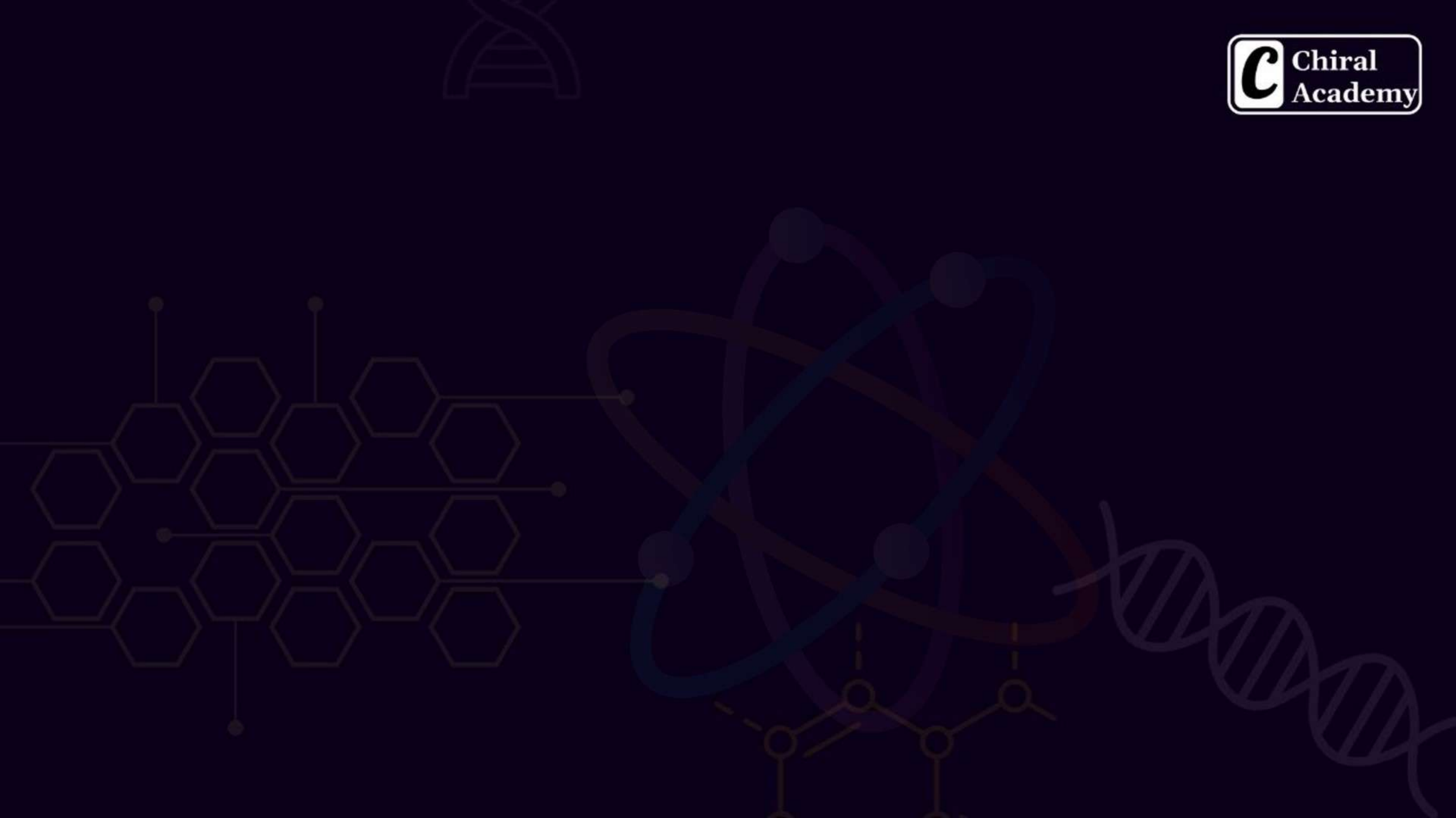

4)
RO⊖
or NNB
5)
NR2


6)
NaOAc


7)
Na/liq NH3


8)
Selectrides
Li BH-SBu3


9)
R2CuLi
R


Chiral
Academy


Chiral
Academy
Thank you