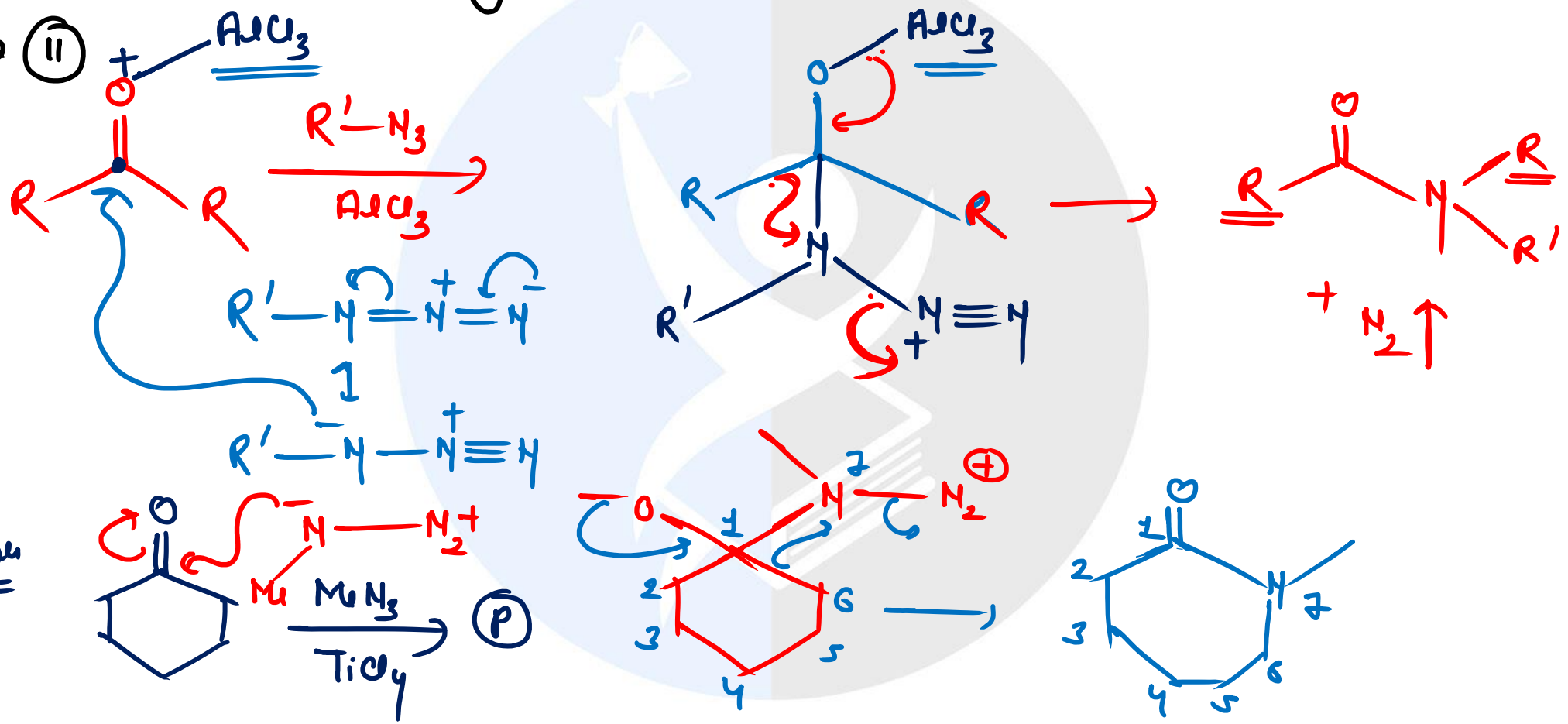
Schmidt Rearrangement

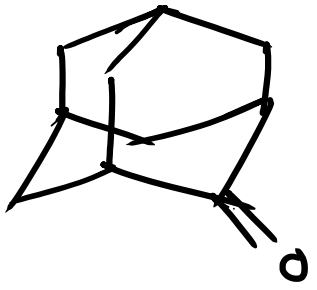
Nidrone

* Case (II)



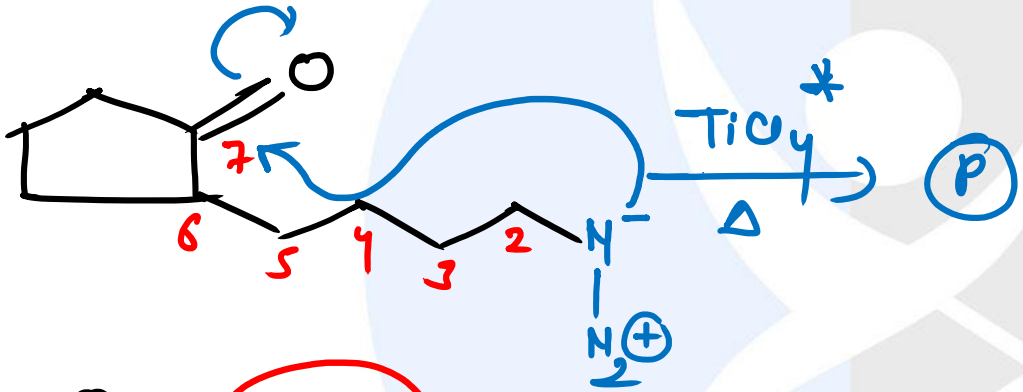
Q.

Ans



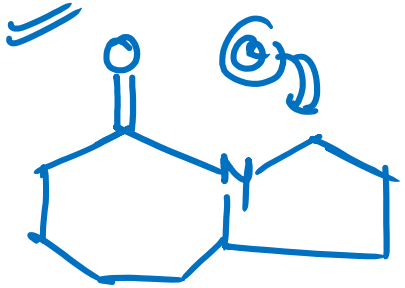
HN_3 / CF_3COOH → (P)

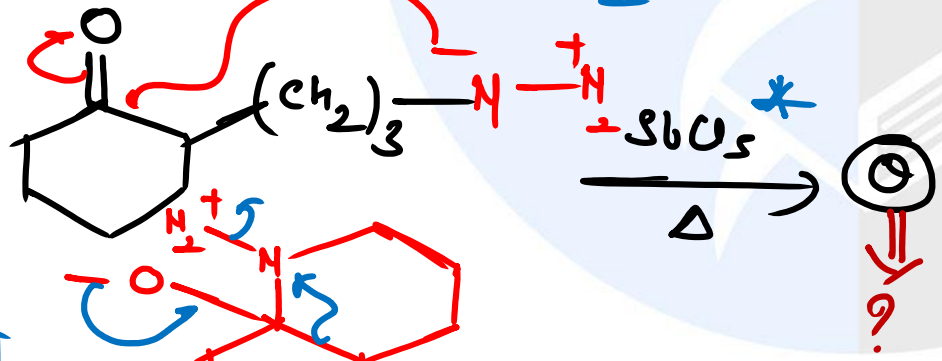
Q.



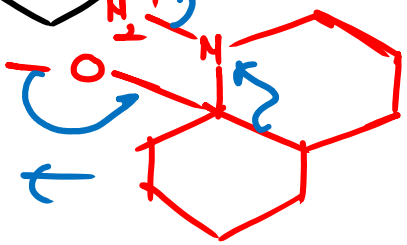
$TiCl_4$, Δ → (P)

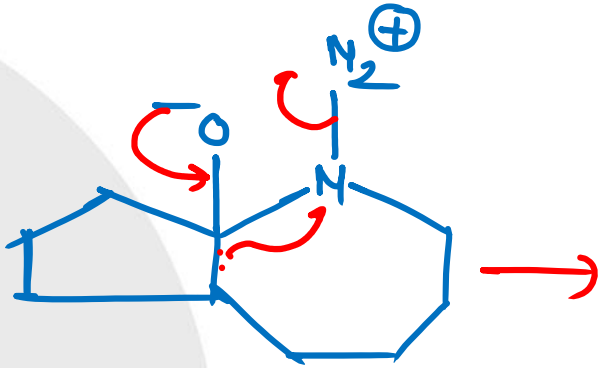
Q.

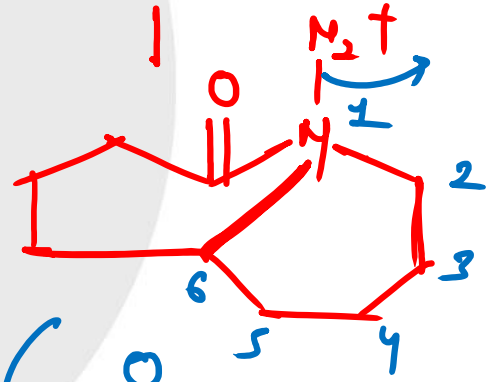


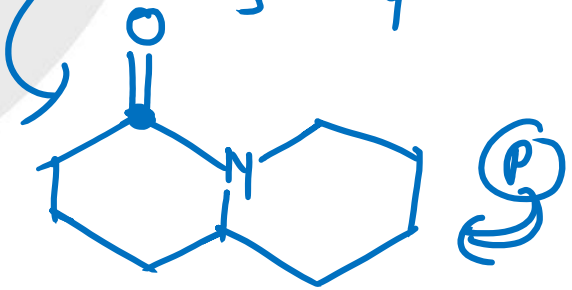


$SbCl_5$, Δ → ?

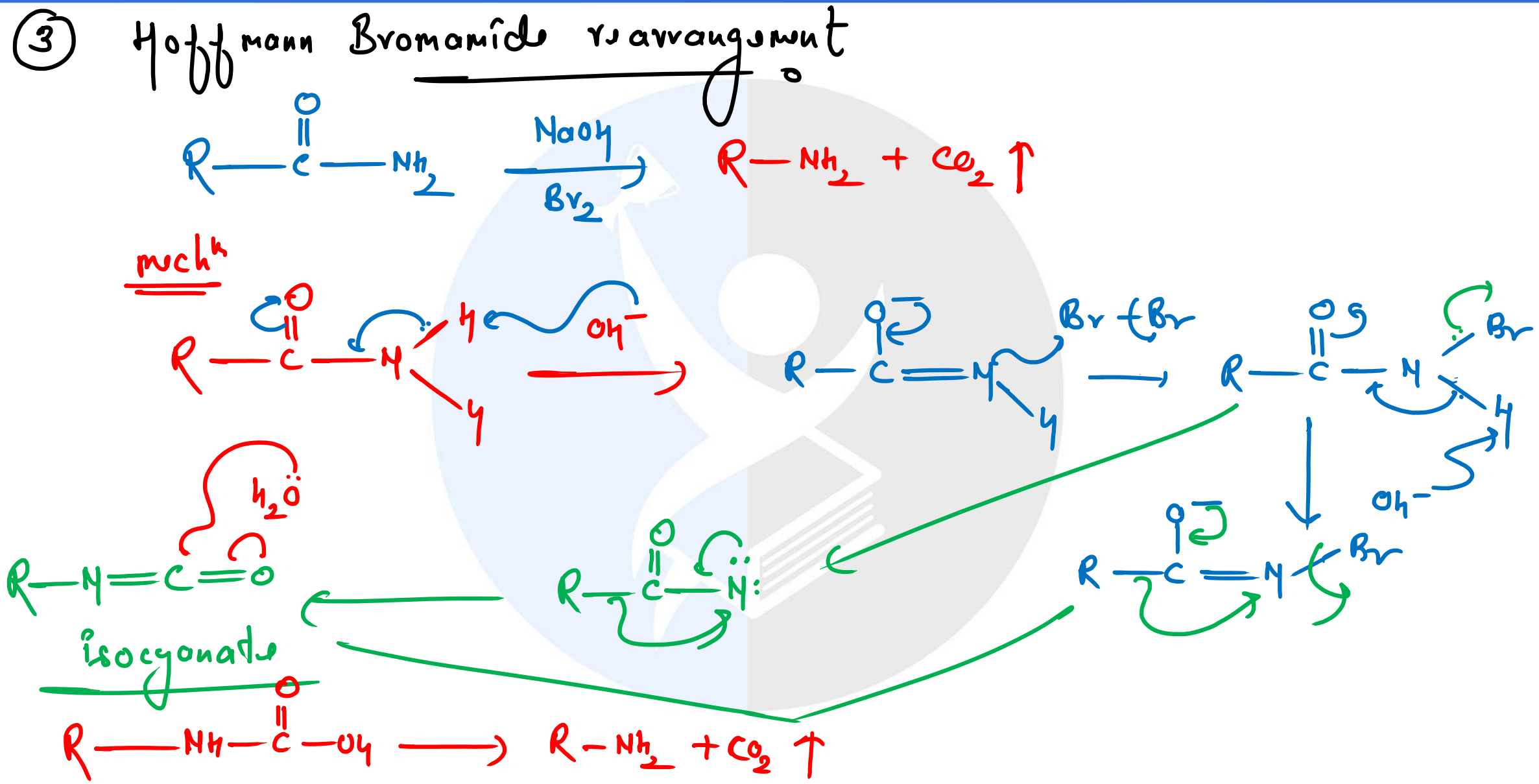


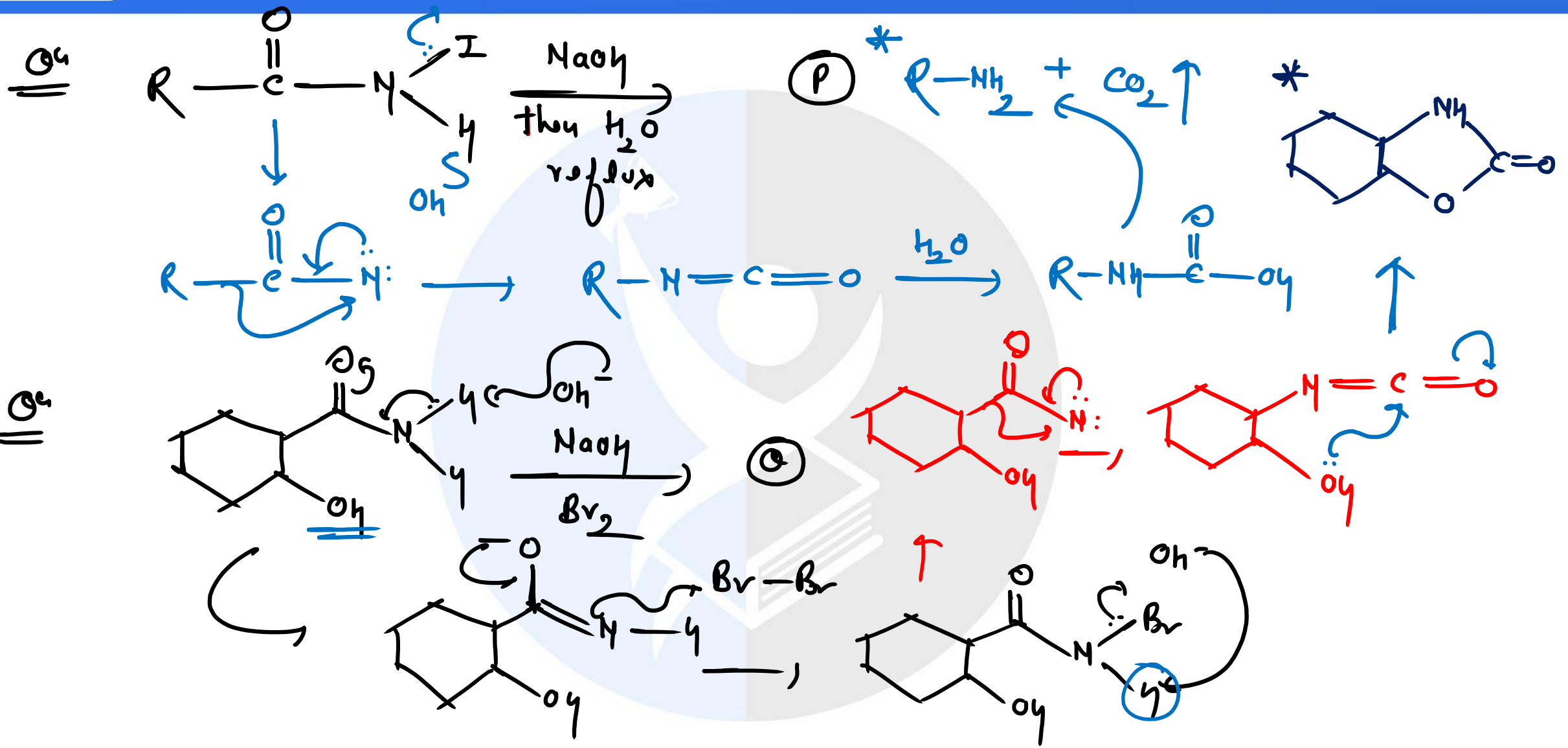


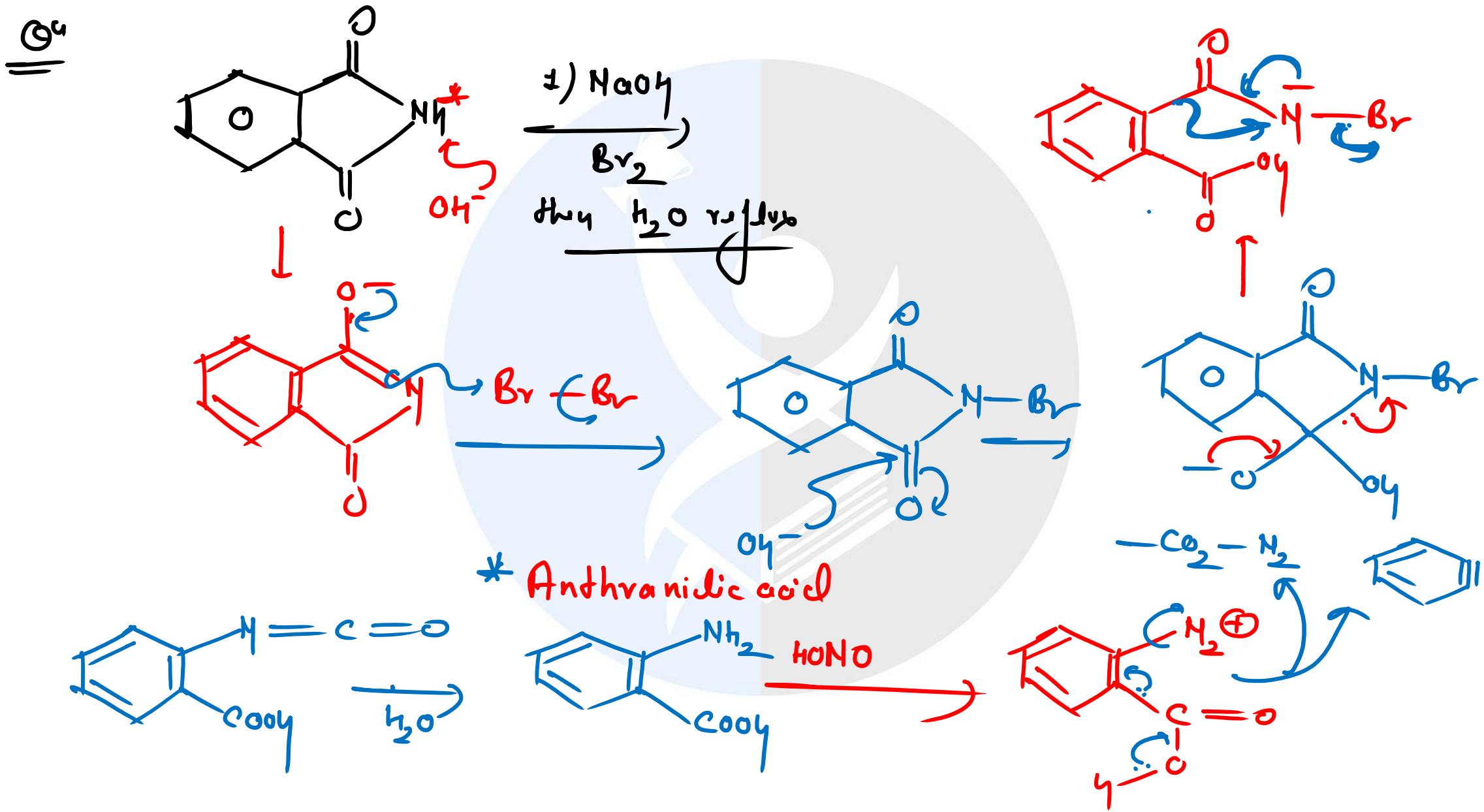




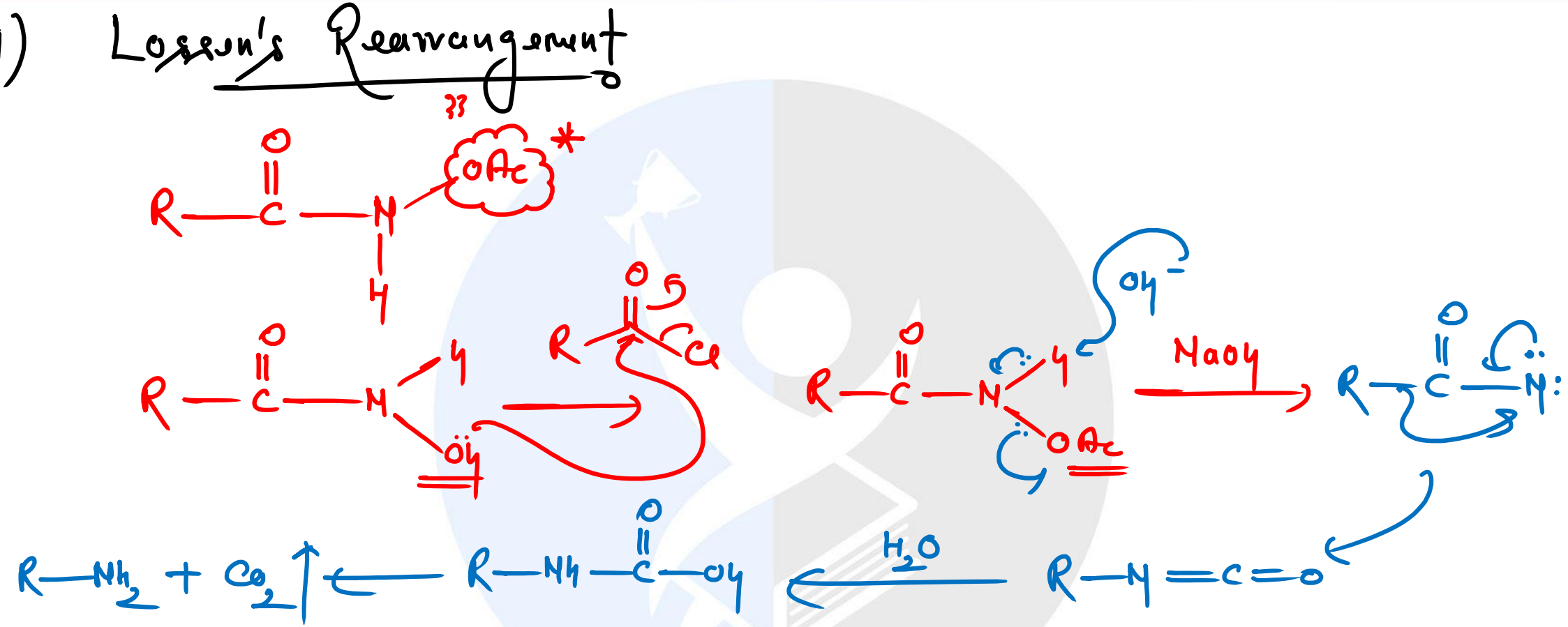
(3) Hoffmann Bromamide rearrangement




NaOH
Then H_2O
reflux
$R-NH_2$
CO_2
H_2O
NaOH
Br_2

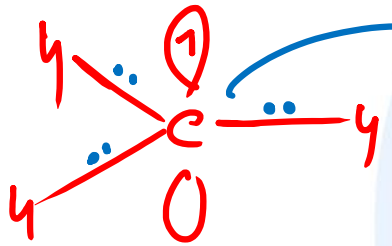

1) NaOH
Br2
thin H2O reflux
OH-
Br
Br
N—Br
* Anthranilic acid
NH2
HONO
COOH
H2O
—CO2 — N2

4) Lossen's Rearrangement



"Radicals"

Carbon Radicals



sp^2

* Trigonal planar
* 7 $\bar{e}$ (ET)
* Homolytic cleavage

* Eg - $\dot{C}$, $\dot{O}$, $\dot{N}$, $\dot{F}$

* Carbon-free radicals

Formation of * carbon - free radicals

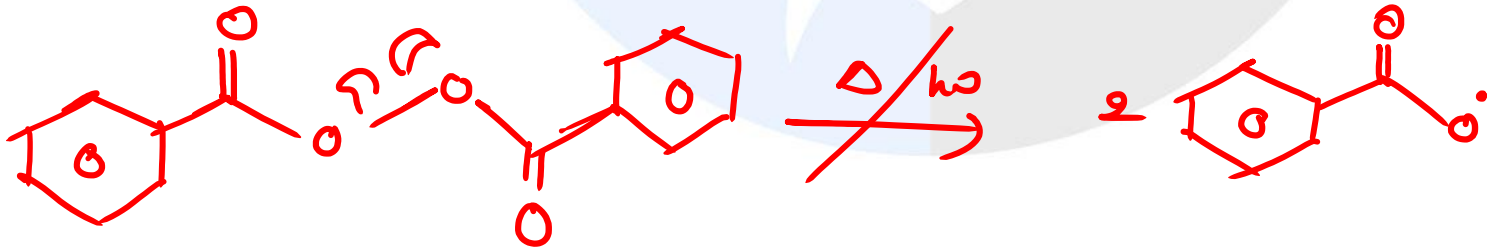
1) From halogens.

$Cl_2 \xrightarrow[h\upsilon]{\Delta} Cl—Cl \longrightarrow 2Cl^{\cdot}$

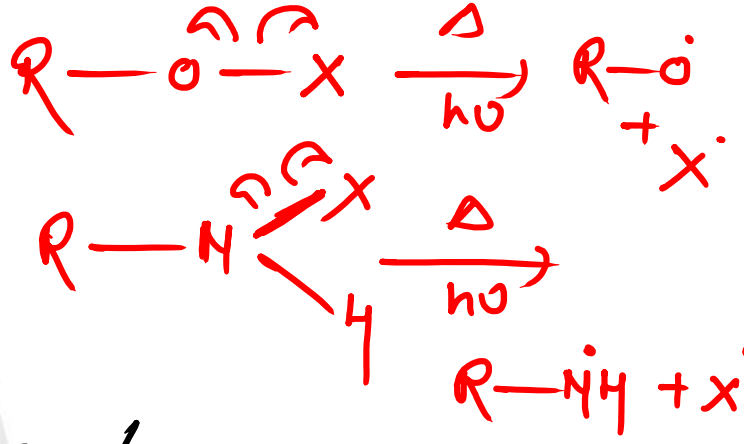
$Br_2 \xrightarrow[h\upsilon]{\Delta} Br—Br \longrightarrow 2Br^{\cdot}$

2) Peroxide molecule

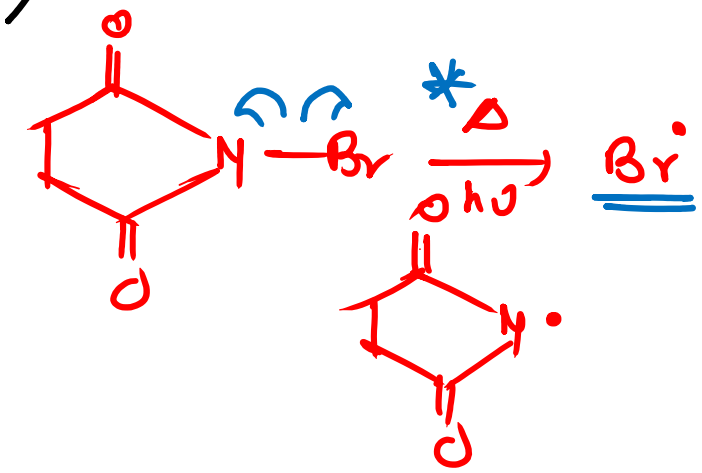
$H_2O_2 \longrightarrow H—O—O—H \xrightarrow{\Delta/h\upsilon} 2OH^{\cdot}$



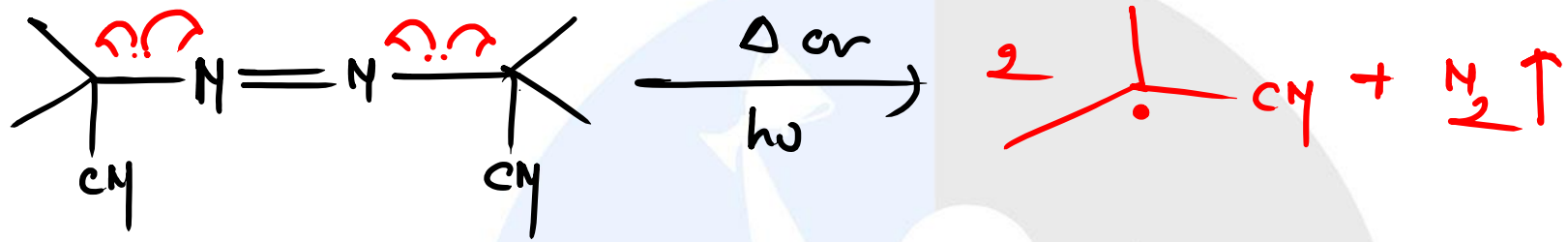
*3)

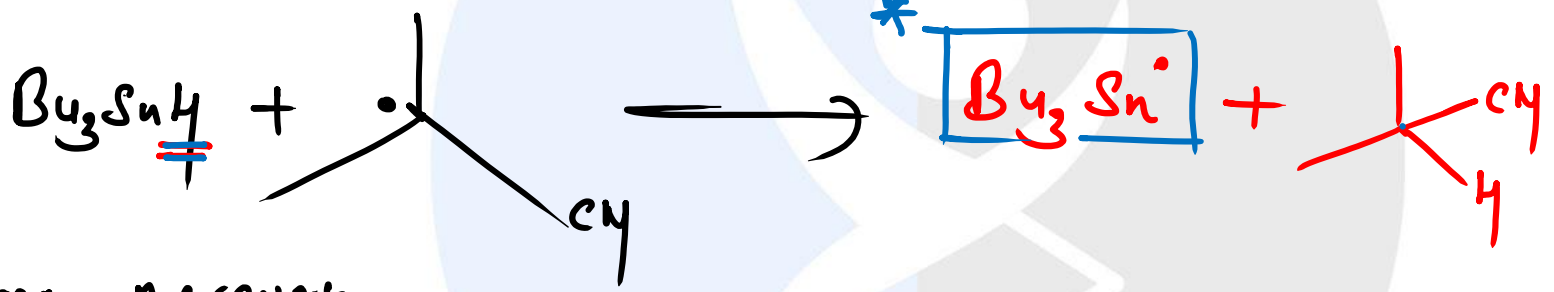


*4) NBS / hυ

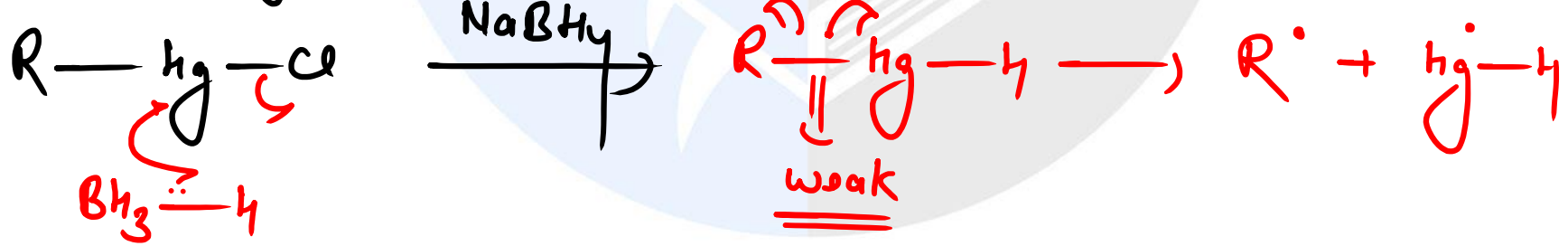


5) AIBN ≡ Azo bis isobutyronitrile — AIBN / Bu_3SnH



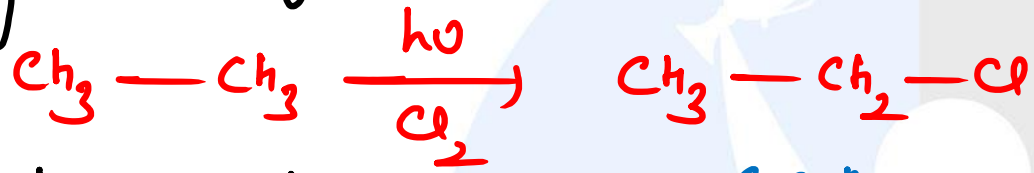


6) From mercury

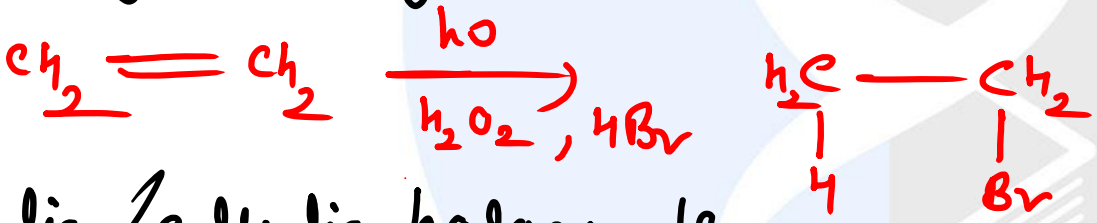


Basic Reactions

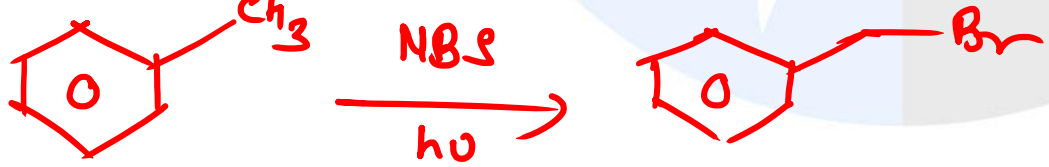
1. Halogenation of alkanes



2. Hydrohalogenation of alkene (R_2O_2 mech^n)



3. Benzylic / allylic halogenation



4. Kolbe Electrolysis.
5. Hundsdiecker R_2^n
6. Wurtz R_2^n
7. Wurtz-Fittig R_2^n

(1) Halogenation

Step (I) Initiation

$$Cl - Cl \xrightarrow{h\nu} Cl^{\cdot} + Cl^{\cdot}$$

step (II) Propogation

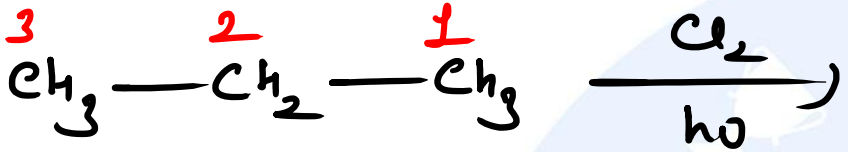
$$CH_3 - CH_2 - H + Cl^{\cdot} \longrightarrow {}^{*}CH_3 - \dot{C}H_2 + HCl$$

$$CH_3 - \dot{C}H_2 + Cl^{\cdot} \longrightarrow \boxed{CH_3 - CH_2 - Cl}$$

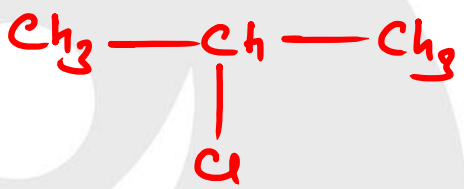
step (III) Termination

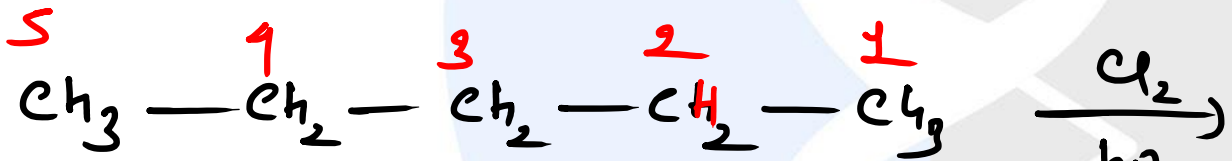
$$Cl^{\cdot} + Cl^{\cdot} \longrightarrow Cl_2$$

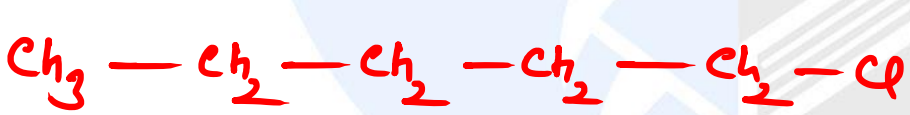
Q. No. of possible "structural isomers"?

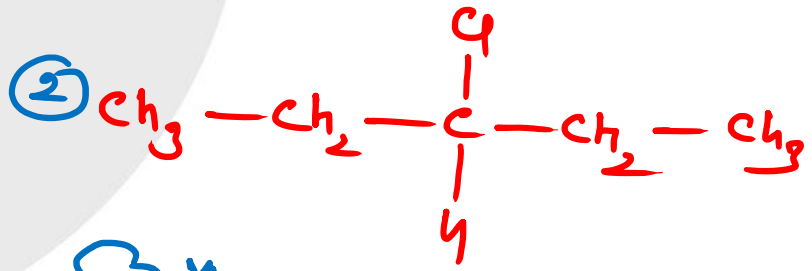


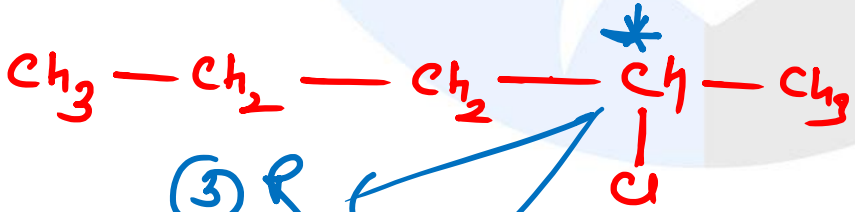
(2) *



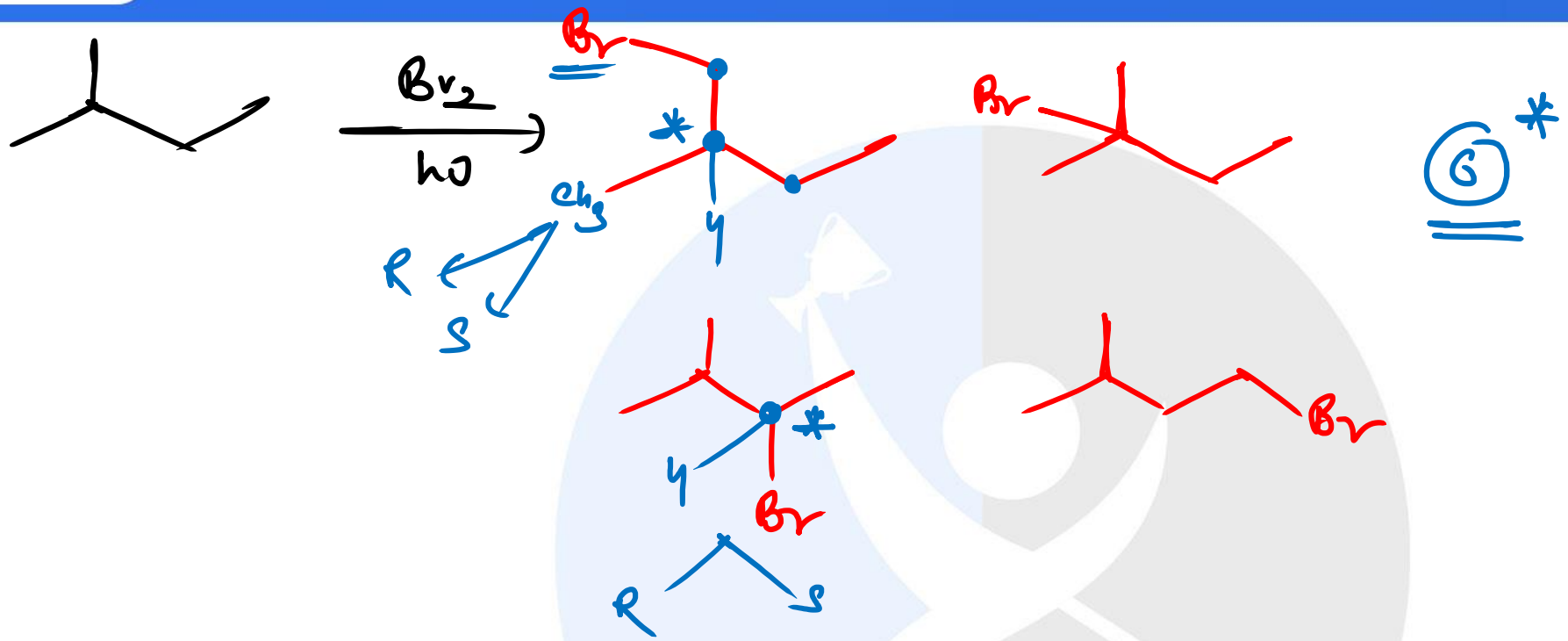


(1) 

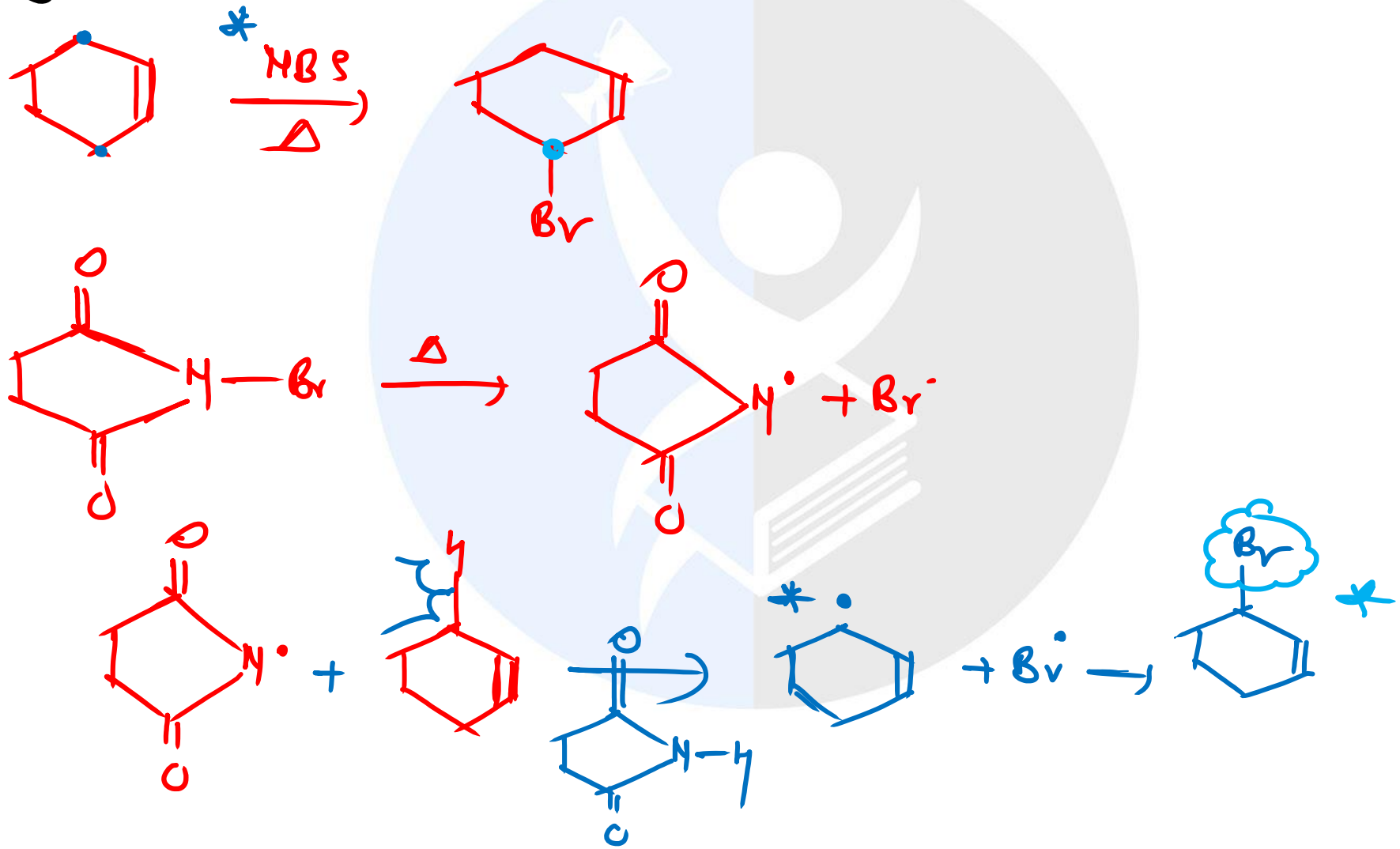
(2) 



(4) *

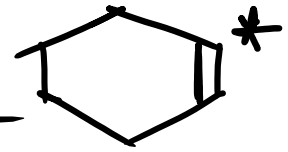

Br2
hυ
Br
*
CH3
H
R
S
Br
6
*
H
*
Br
R
S
Br

③ Allylic / Benzylic halogenation



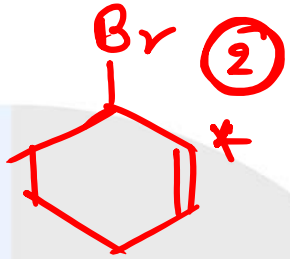
Or

CSIR - NET

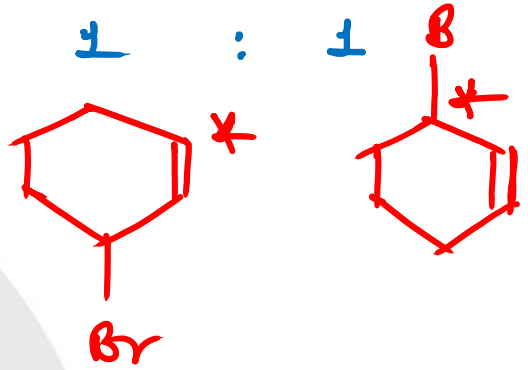


NBS, Δ

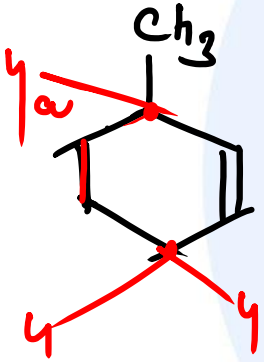
1) 2 : 1 : 1
2) 1 : 2 : 1
3) 1 : 1 : 2



2) 1 : 1 : 1

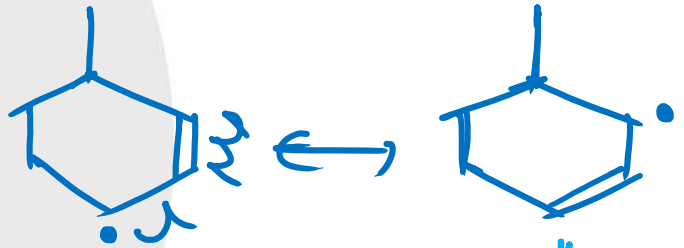


Or

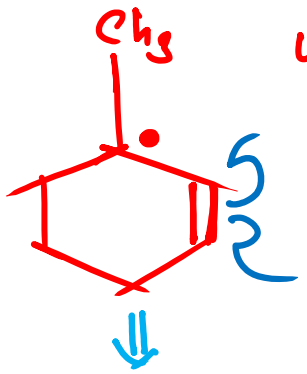


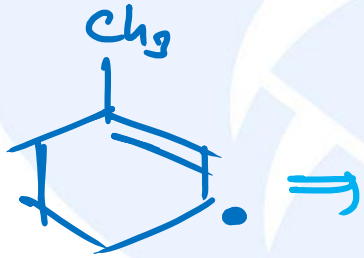
NBS, Δ

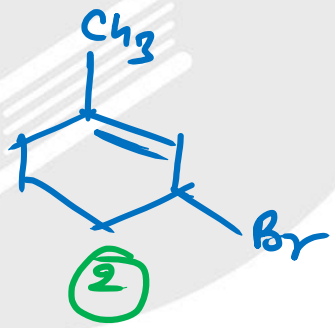
H_b (1)



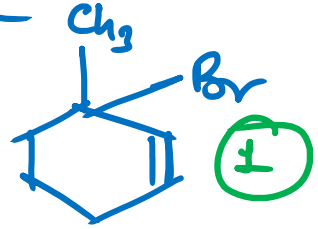
H_a (1)





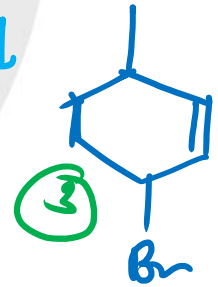


(2)

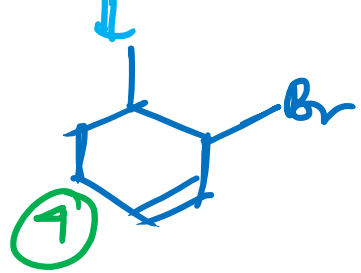


(1)

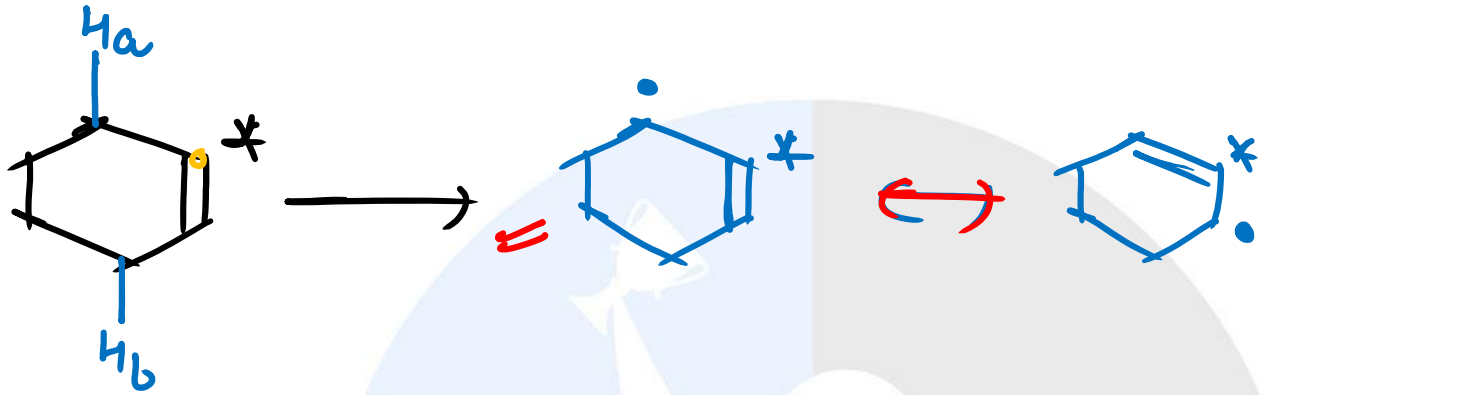
(4)*



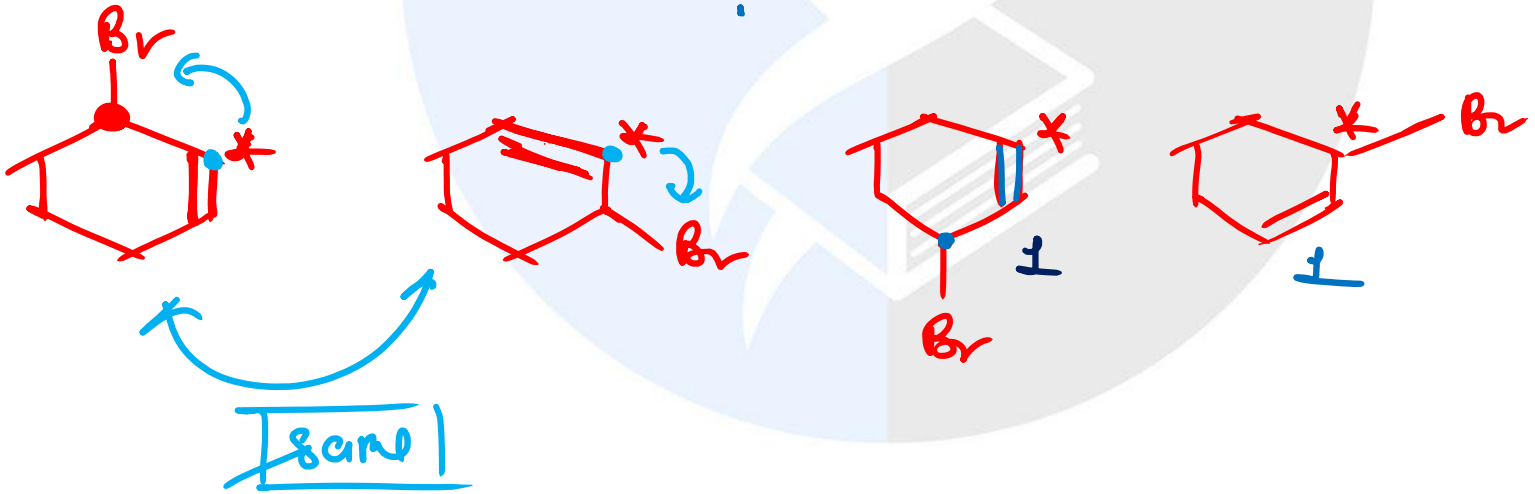
(3)



(4)



10 min



SCN1

Advanced Rxn of Radicals

- Imp
  - Dehalogenation
    - $R-X \xrightarrow[Bu_3SnH]{AIBN} R-H$
    - $C-C-X \xrightarrow{"} C-C-H$
    - $C=C-X \longrightarrow C\equiv C-H$
  - Dehydroxylation
    - $R-OH \xrightarrow{1)\ NaH} R-H$ (2) CS_2, then MeI, (3) Bu_3SnH, AIBN
- Miscellaneous

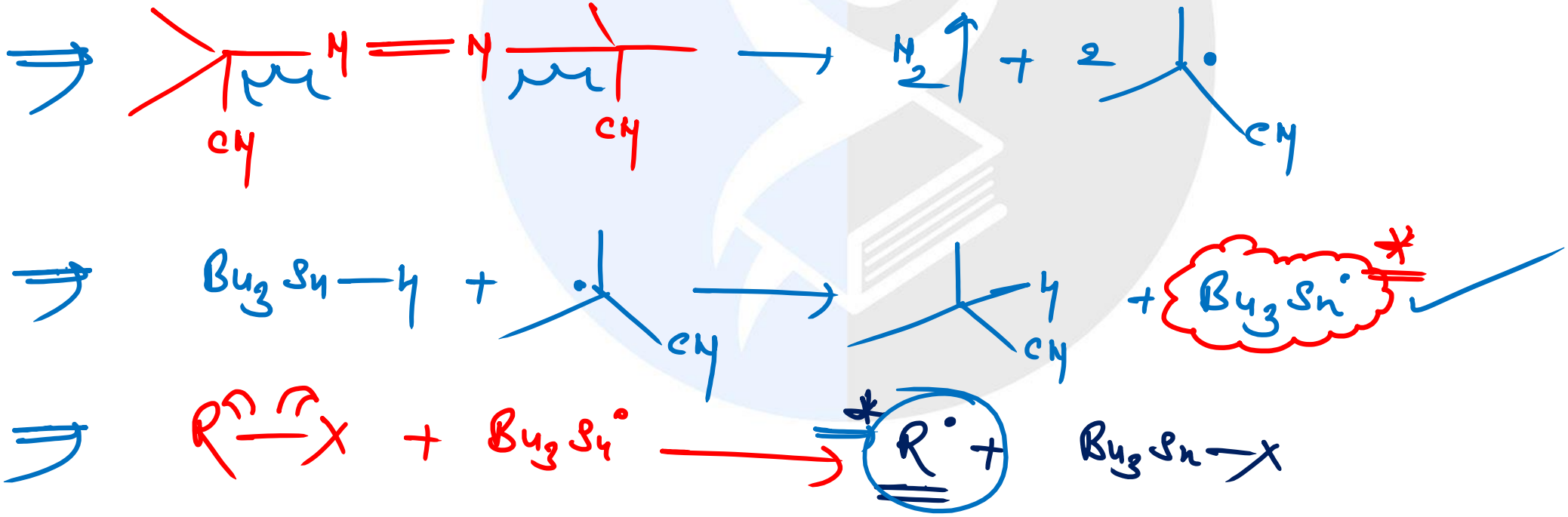
Dehalogenation

Level - ①

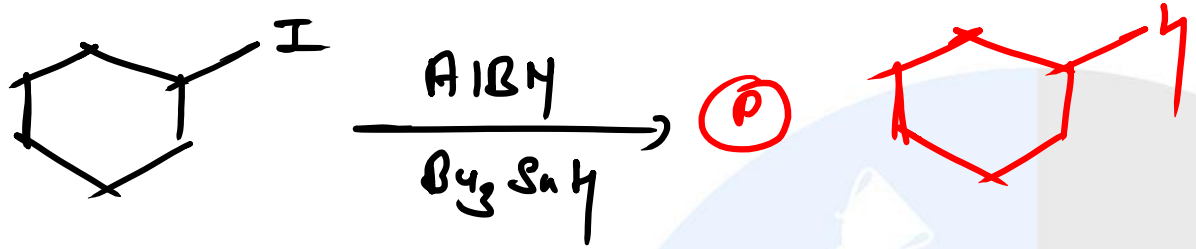
$R-X \xrightarrow[Bu_3SnH\ (1.02\,eq)]{AIBN\ (0.05\,eq)} R-H$

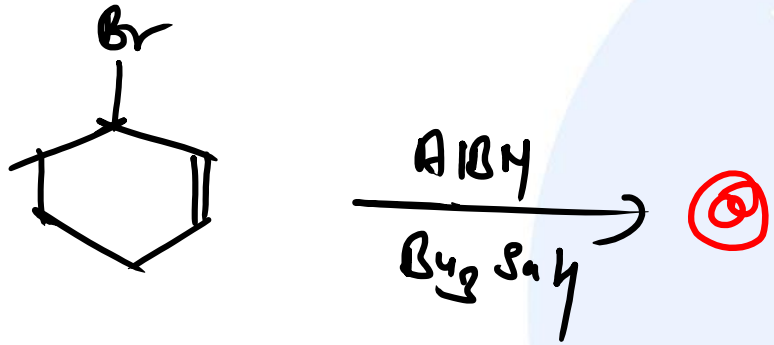
$\Rightarrow R^{\circ} + Bu_3SnH \longrightarrow R-H + Bu_3Sn^{\circ}$

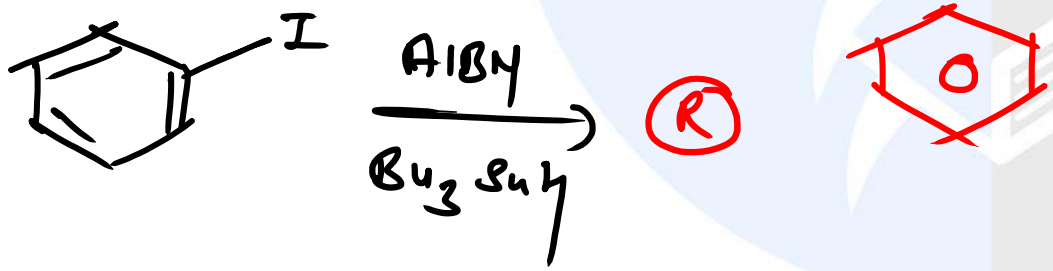
mech^{n}

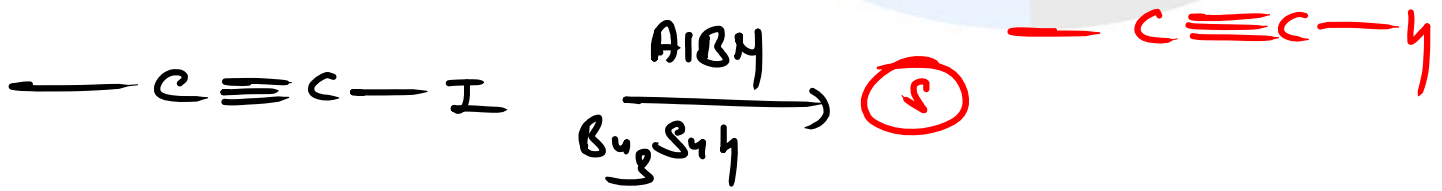


Q4

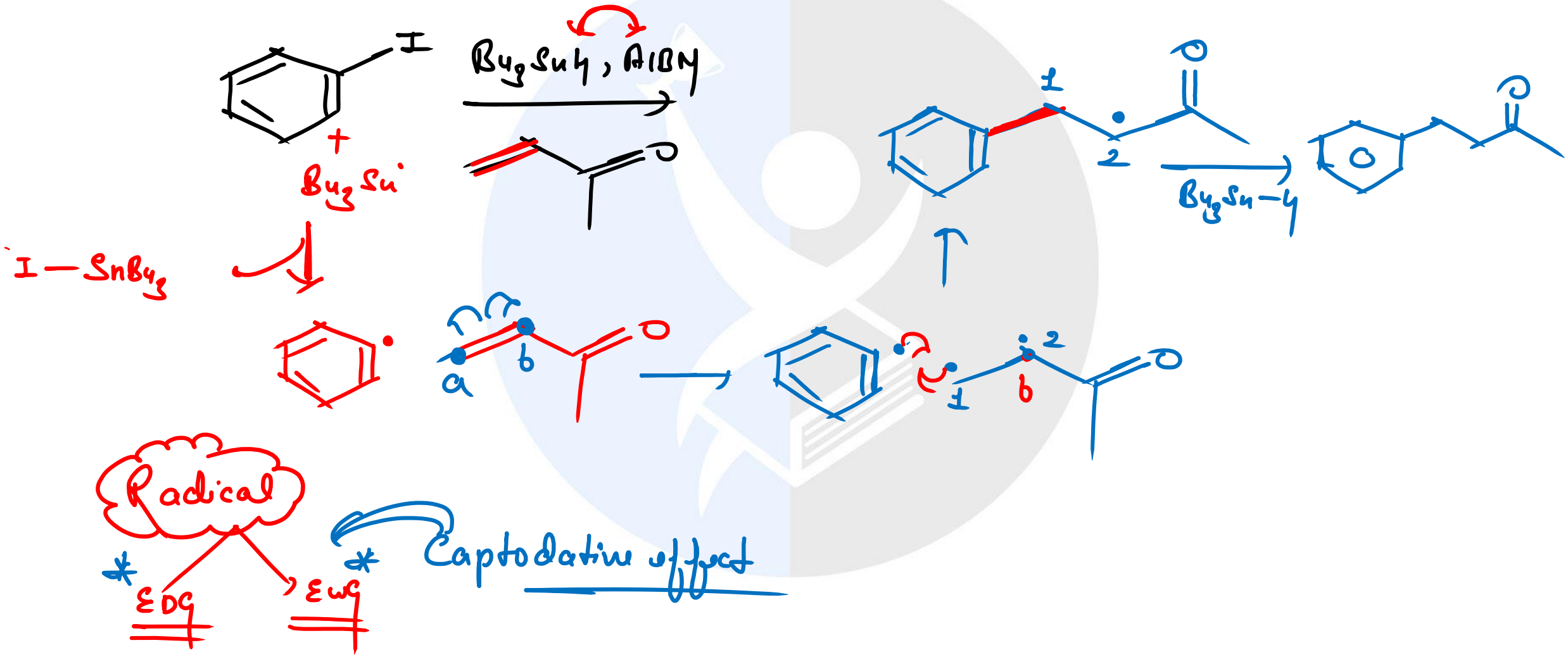

I
AIBN
Bu3SnH
P
H


Br
AIBN
Bu3SnH
Q
H


I
AIBN
Bu3SnH
R
O

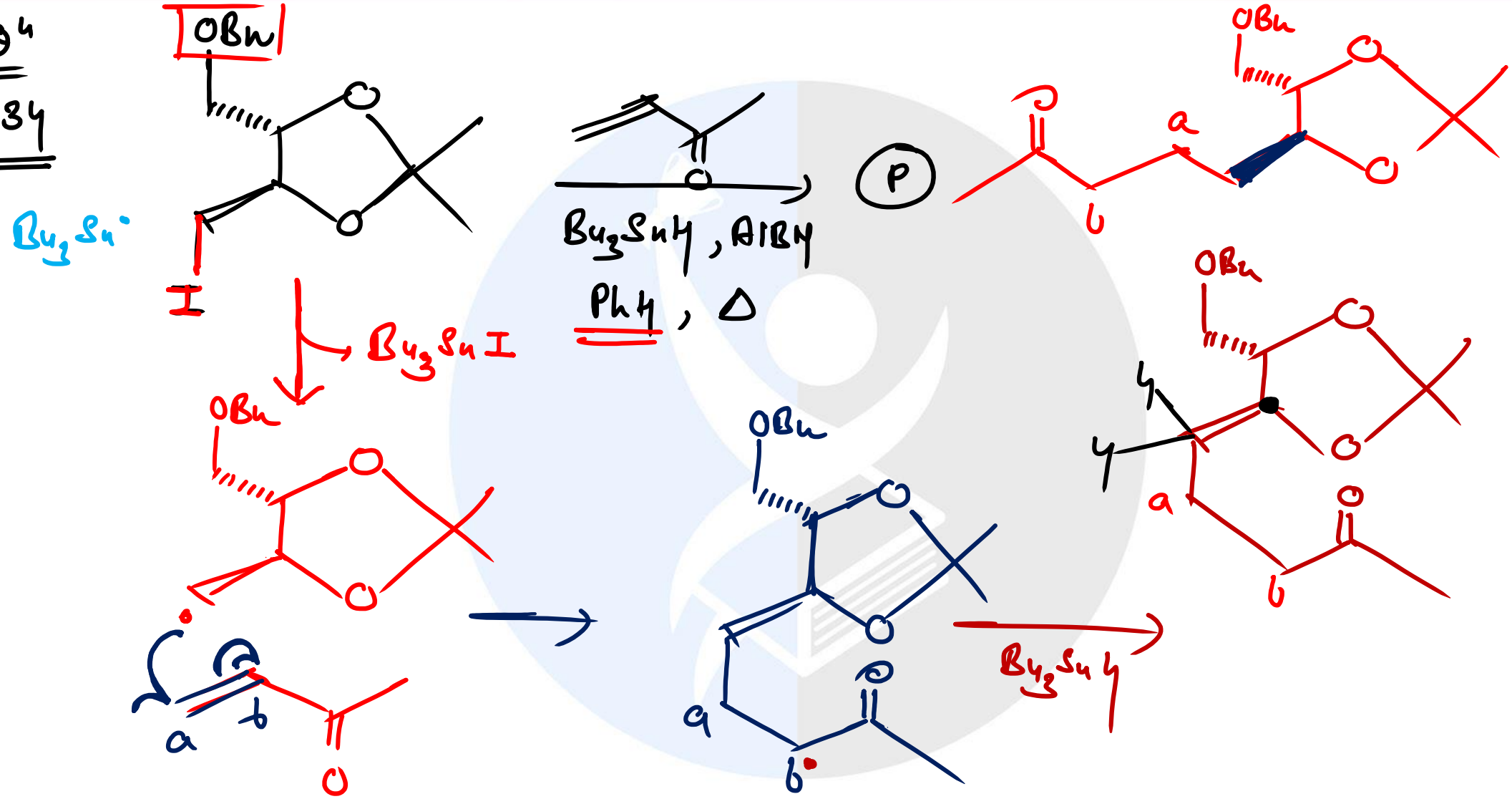

— C≡C — I
AIBN
Bu3SnH
S
— C≡C — H

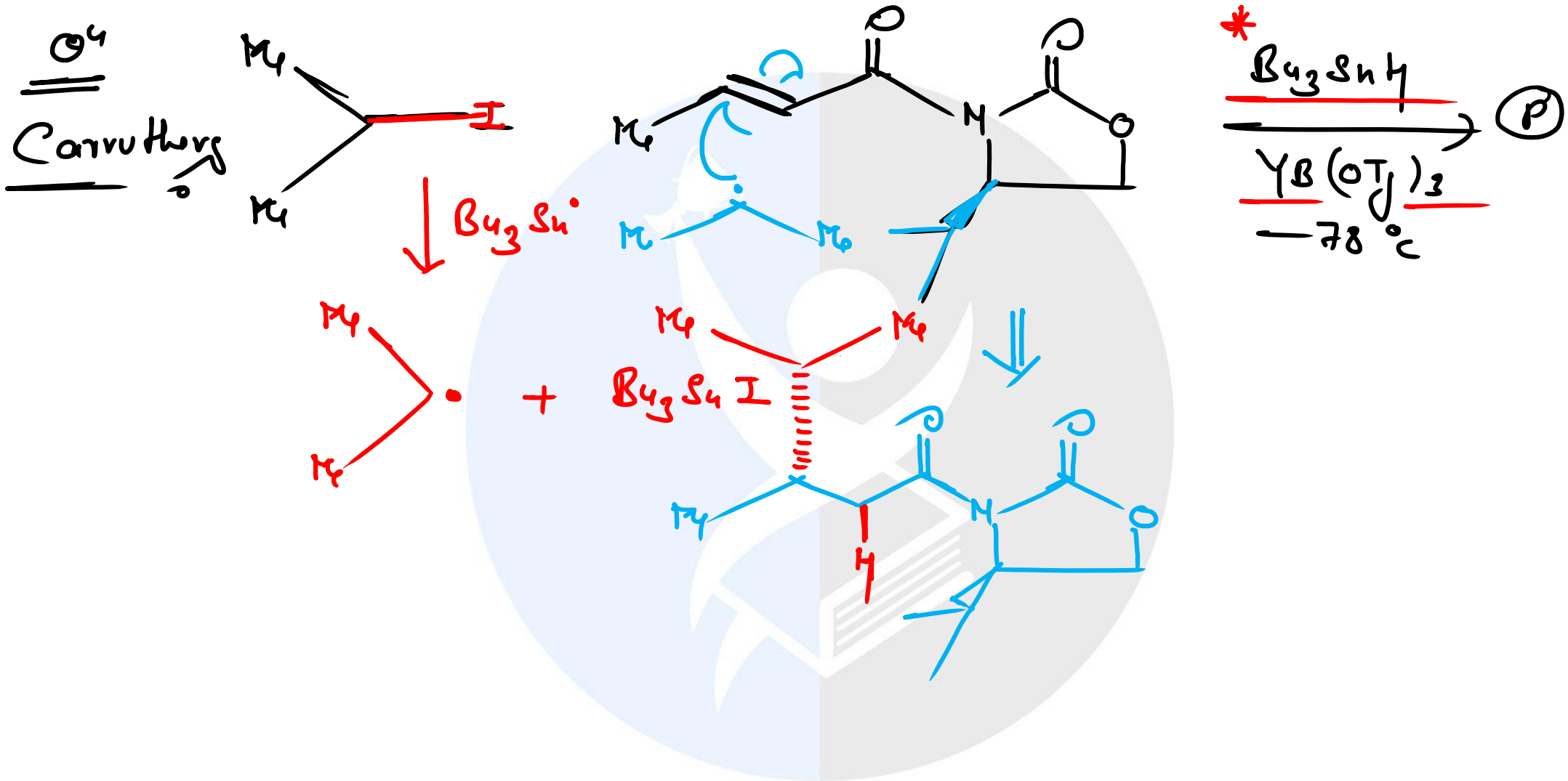
Level - ② Radicals addition Rxn *



Q4

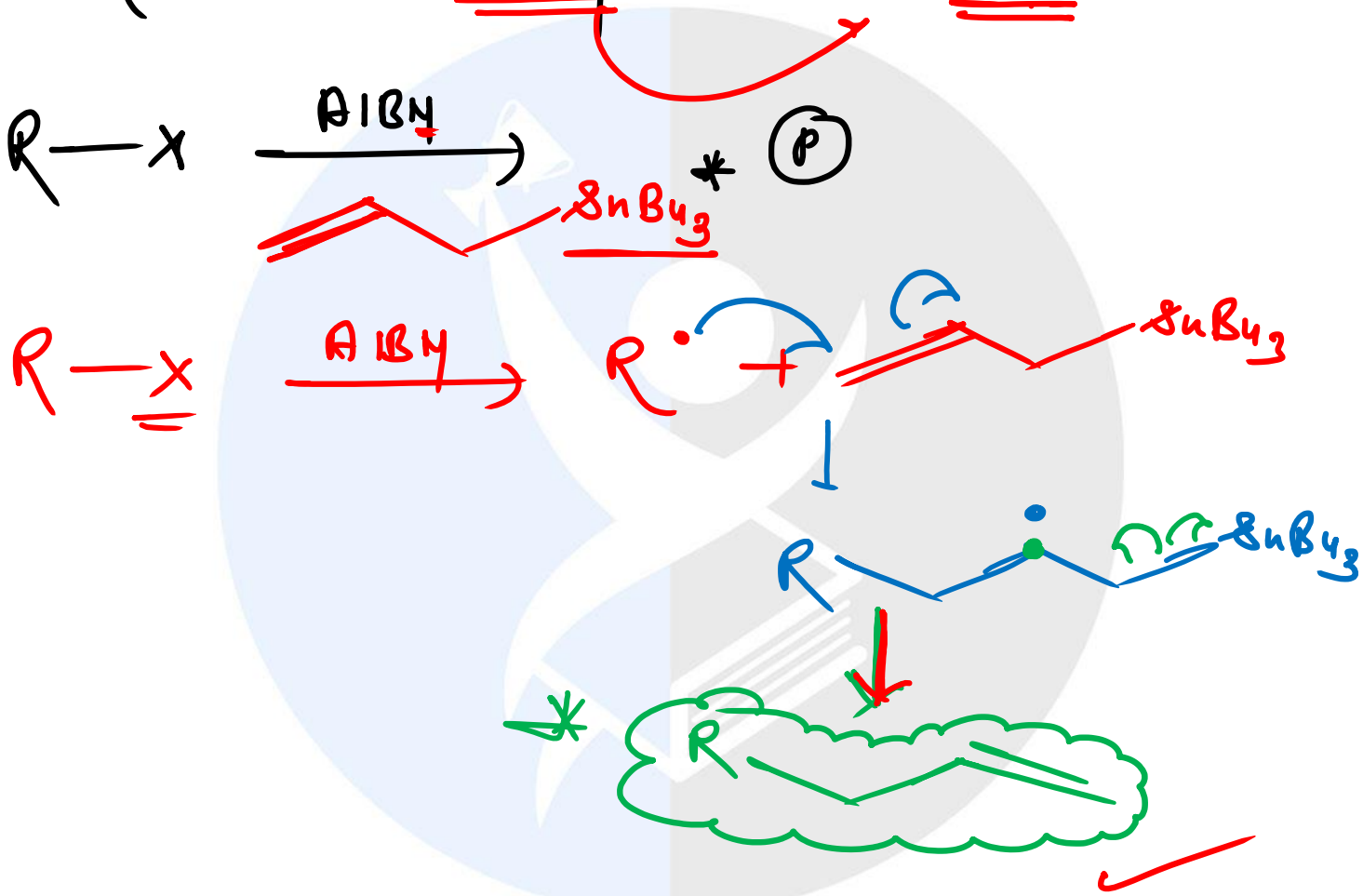
4·34


OBn
I
Bu3Sn•
Bu3SnI
Bu3SnH, AIBN
PhH, Δ
P
OBn
a
b
OBn
a
b
OBn
a
b
Bu3SnH


Carruthers
$Bu_3Sn^{\bullet}$
Bu_3SnI
Bu_3SnH
$Yb(OTf)_3$
−78 °C
P

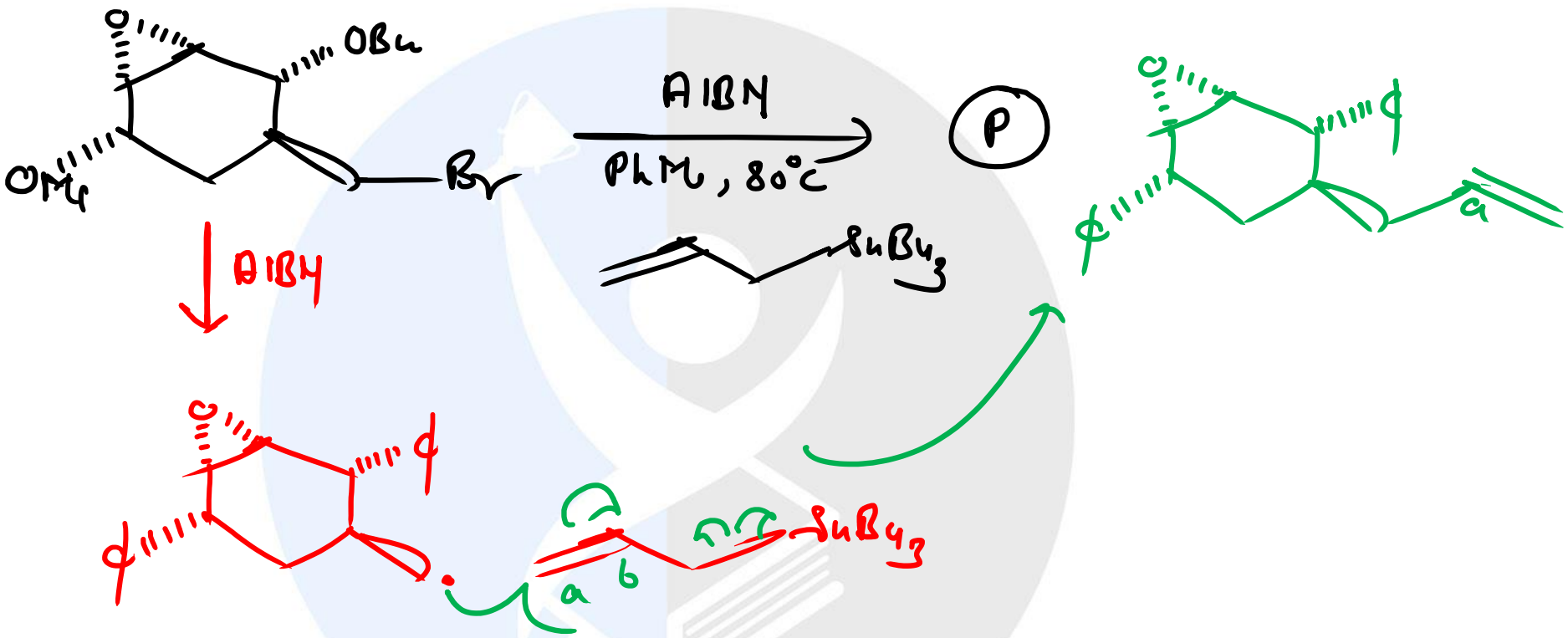
Level - ⑤

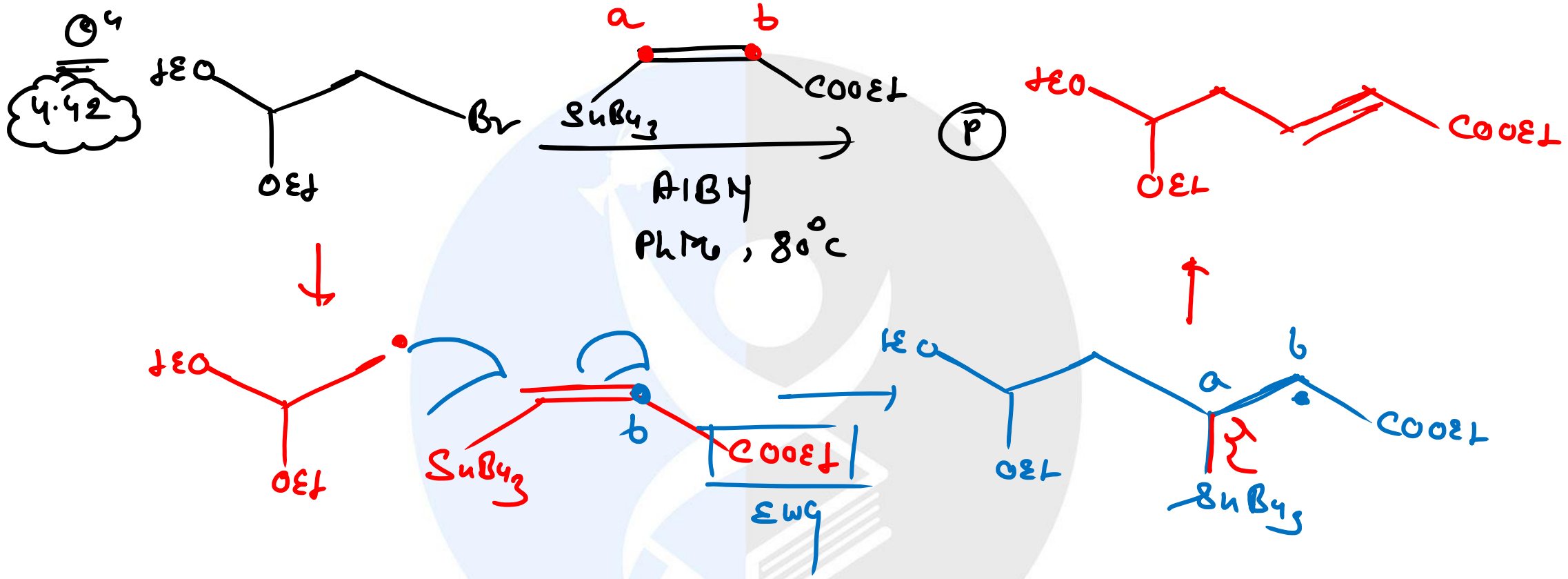
Radical addition then elimination

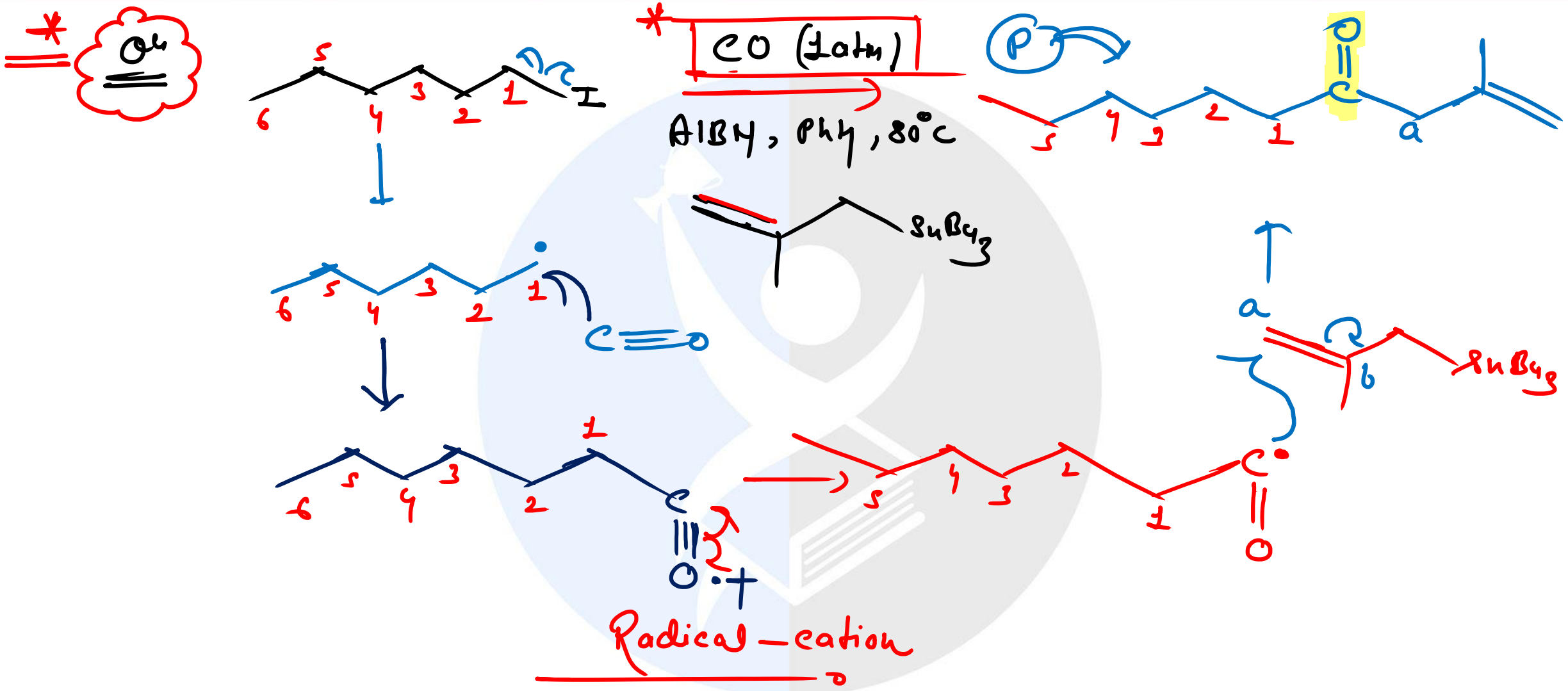


Q4

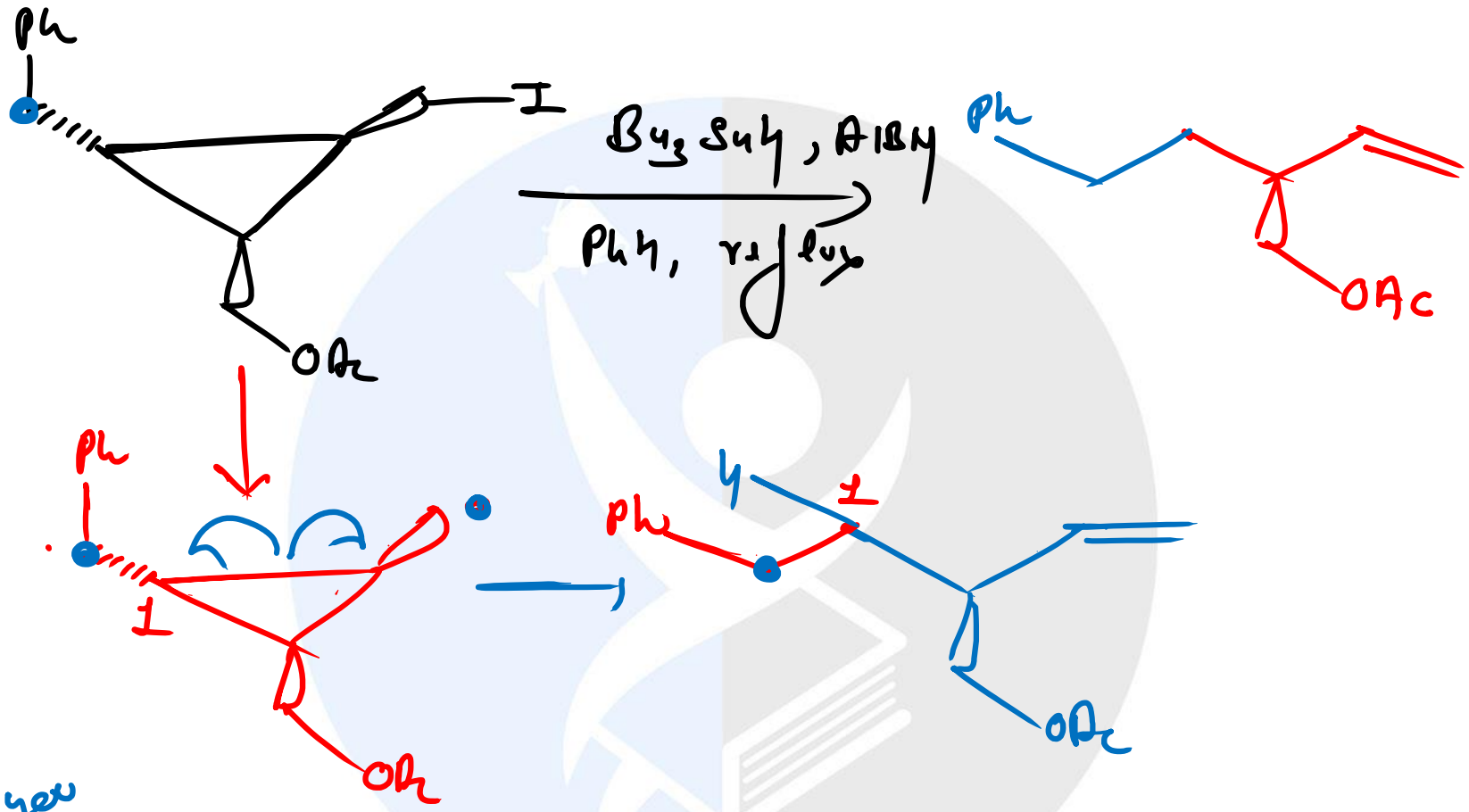
4·39




4·42
EtO
OEt
Br
a
b
SnBu3
COOEt
AIBN
PhMe, 80°C
P
EtO
OEt
COOEt
EtO
OEt
SnBu3
b
COOEt
EWG
EtO
OEt
a
b
COOEt
SnBu3


CO (1atm)
AIBN, PhH, 80°C
SnBu3
Radical – cation

Q.
4.49



Thank you.