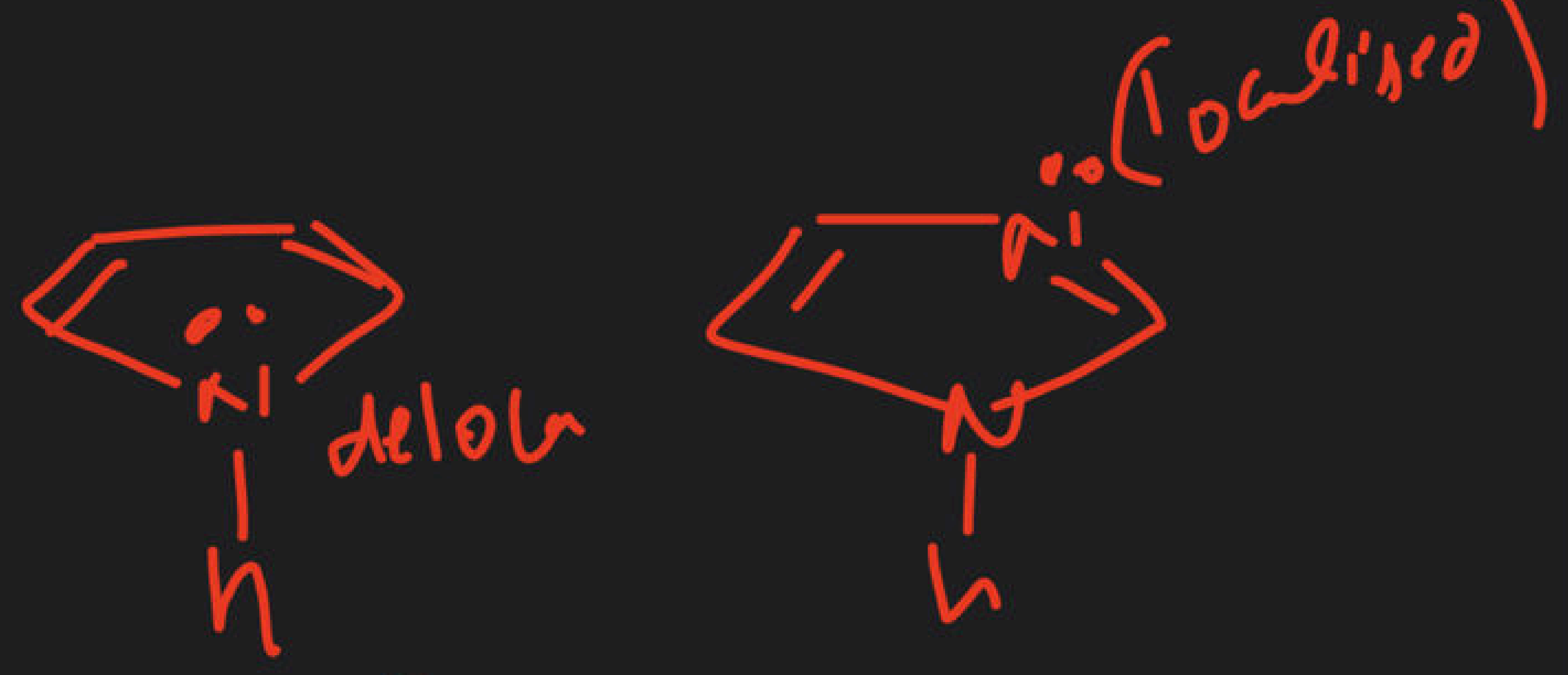
Structural Isomerism - Tautomerism - III

Course on Structural Isomerism & Geometrical Isomerism

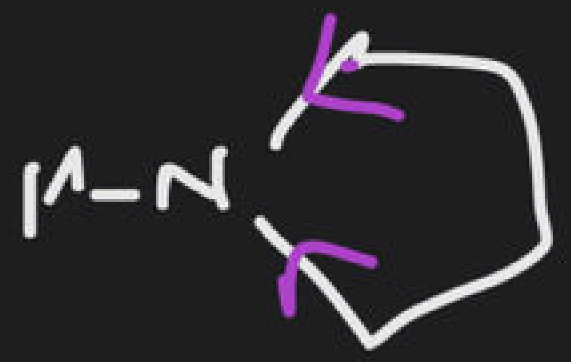
SURENDRA K MISHRA • Lesson 5 • Sept 21, 2021

MCQ (discussion)

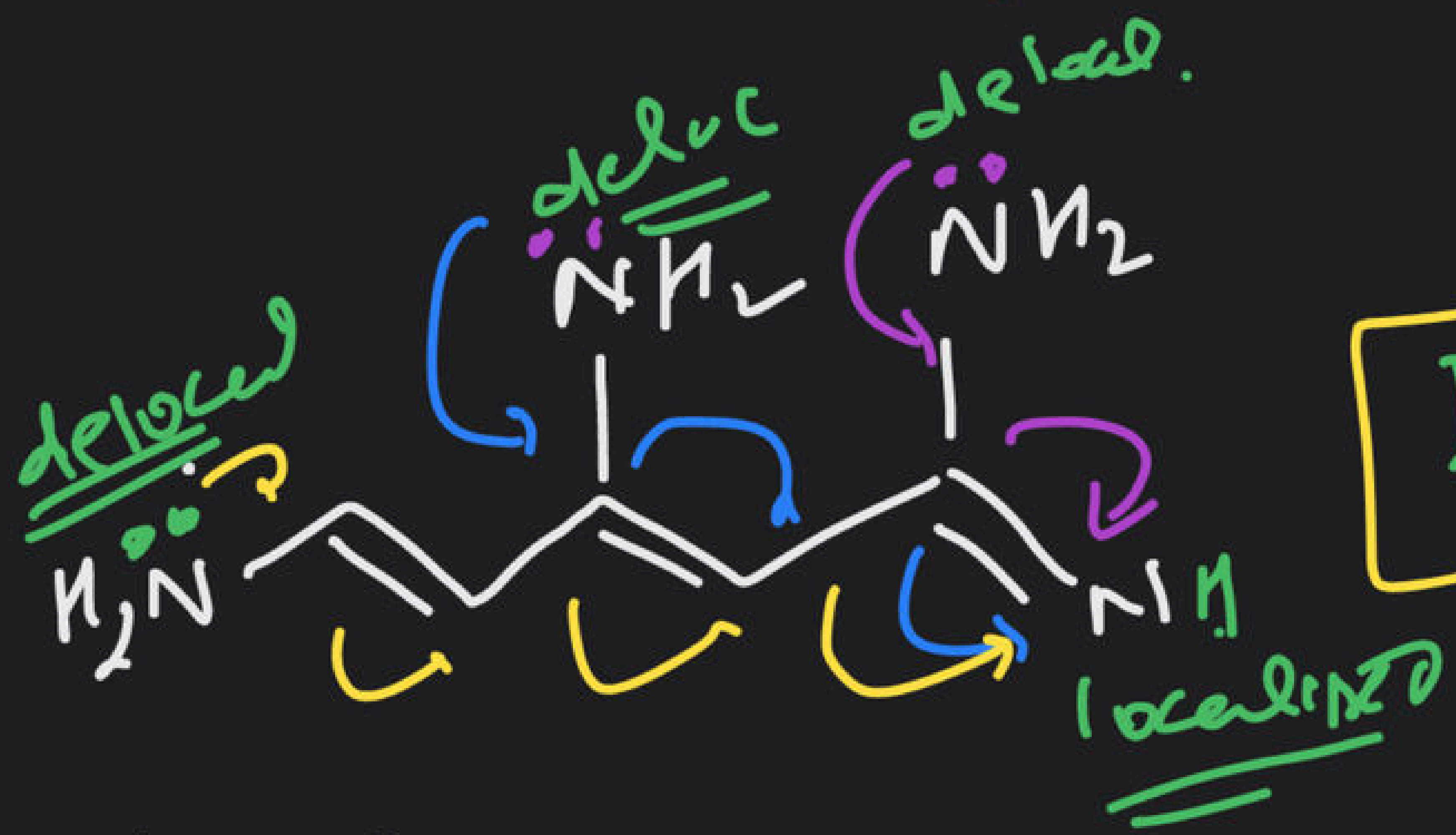
(20) Basic strength (2 > 1)



(21) 3 > 2 > 1



(22)

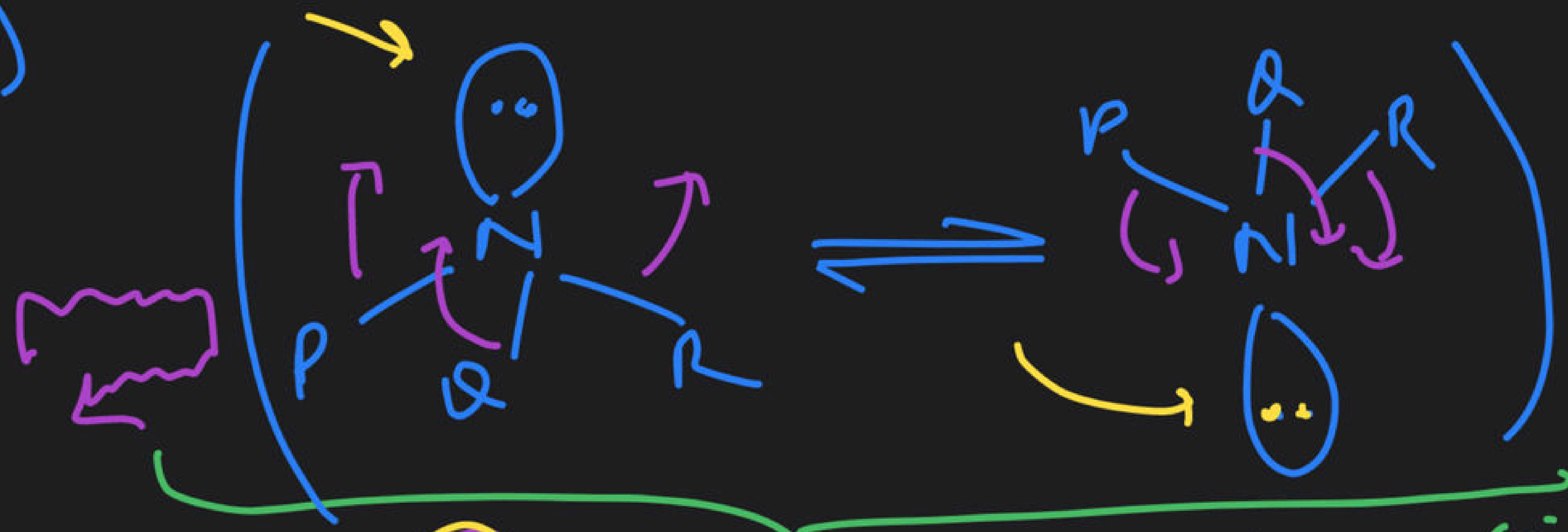


$\boxed{IV > III > II > I}$

(23) 1 > 2

localised. delocal

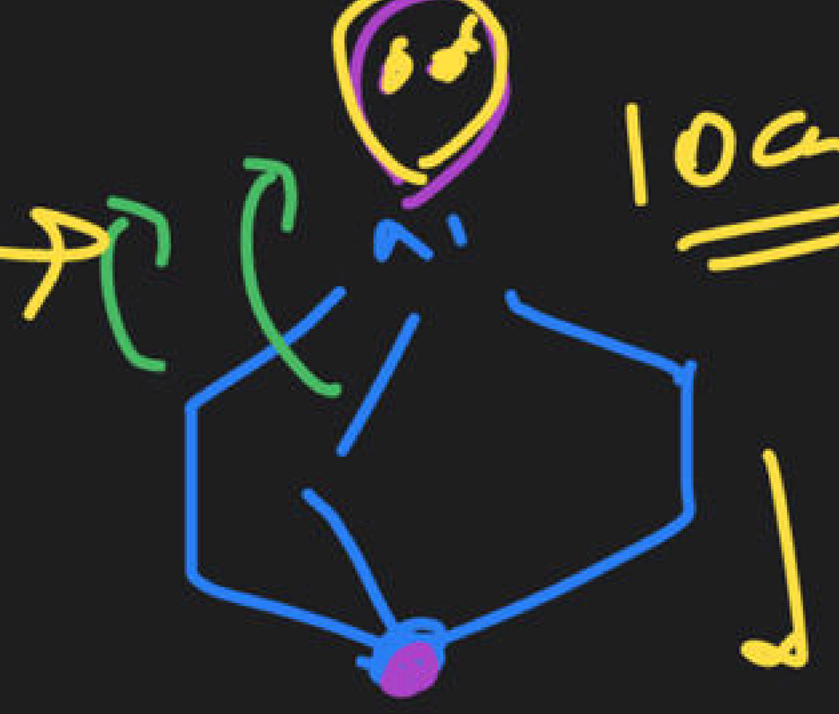
(24) (2 > 1)



f'lipiyg

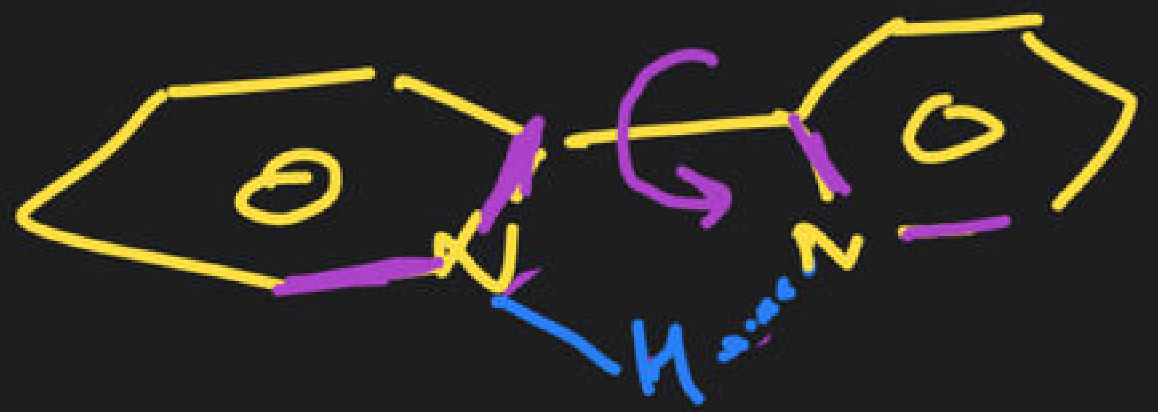
H^+

dispersing/delocalised



localised

(25)



(III > I > II)

(26) 2 > 1

(1) ______

(2) 1 > 2

(3) 1 > 2 > 3 > 4

(4) 1 > 2

(5) 1 > 2 > 3

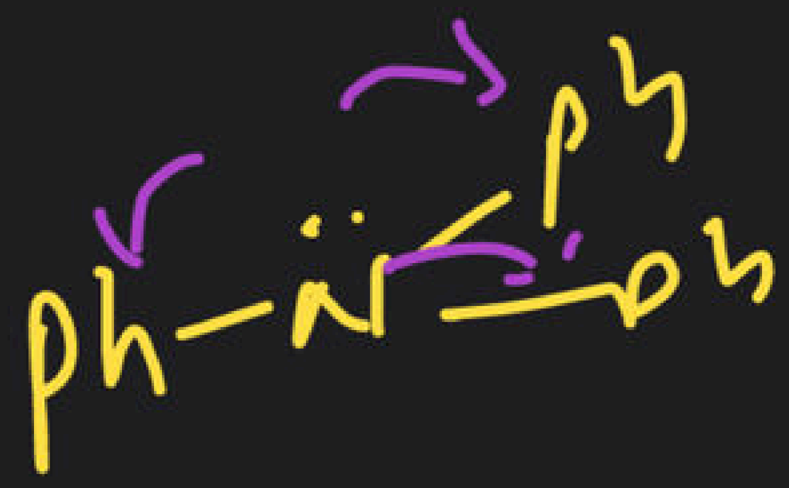
(6) ______

Basic
most

$\bar{C}H_3$ $\bar{N}H_2$ $\bar{C}N$ F^-
(unstable) (stable)

(7) 1 > 2

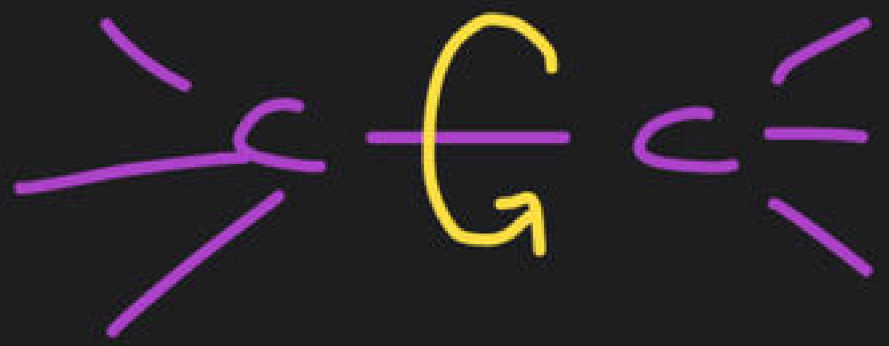
(8) 2 > 1



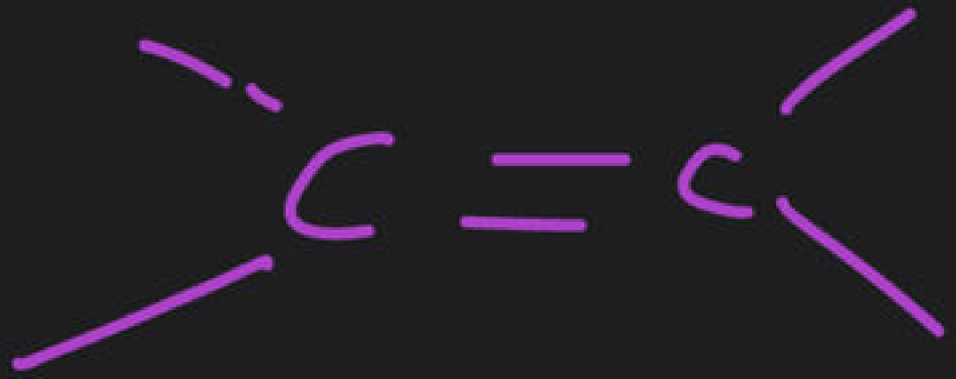
(9) 3 > 2 > 1

(10) 1 > 2 > 3

(#) Bond length, Bond strength, Bond dissocition Energy
Bond Rotation Energy Barrier



Single
character



Bond Rotation Energy Barrier ↓
Bond length ↑
Bond strength ↓
Bond diss. Energy ↓

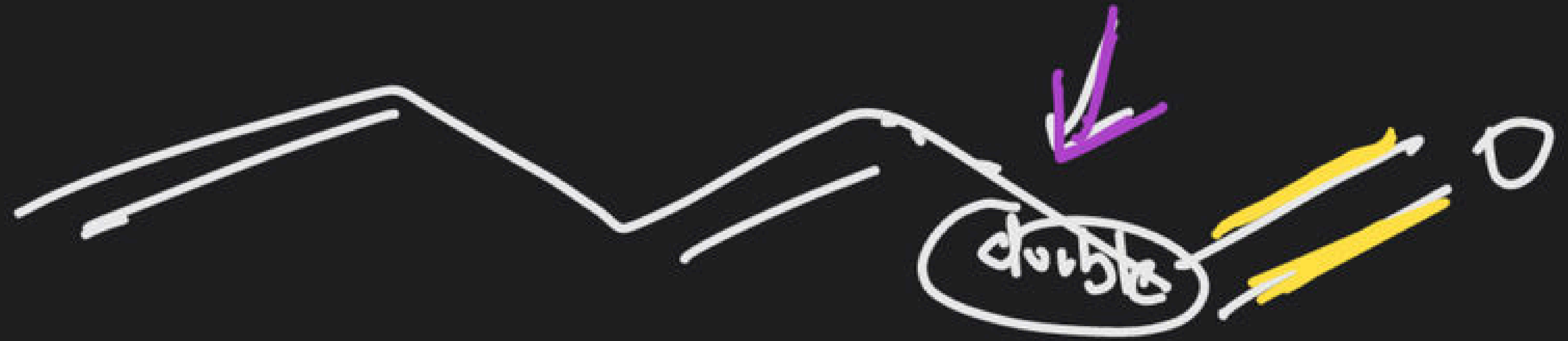
Bond Rotation Energy Barrier ↑
Bond length ↓
Bond strength ↑
Bond diss. En ↑

Bond length $\propto$ Extent of Resonance {If initially double bond}

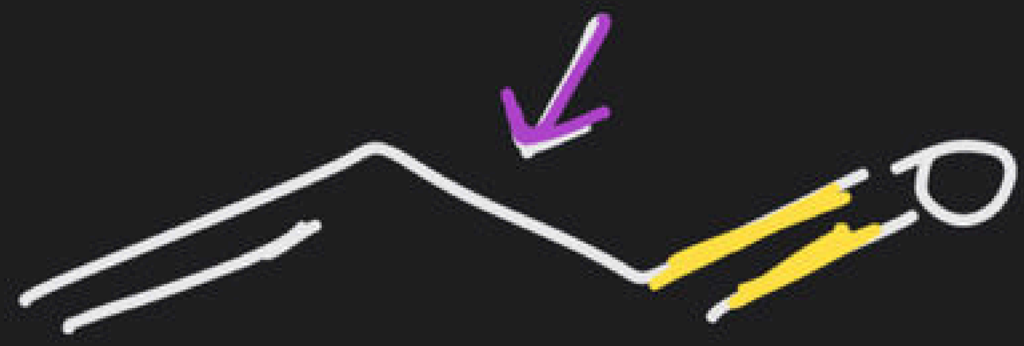
$\propto \dfrac{1}{\text{Extent of Resonance}}$ {If initiall Single bond chn}

$\propto \dfrac{1}{\text{Bond D.E}} \propto \dfrac{1}{\text{Bond Strength}} \propto \dfrac{1}{\text{Bond Rotn. E. Barr}}$

1



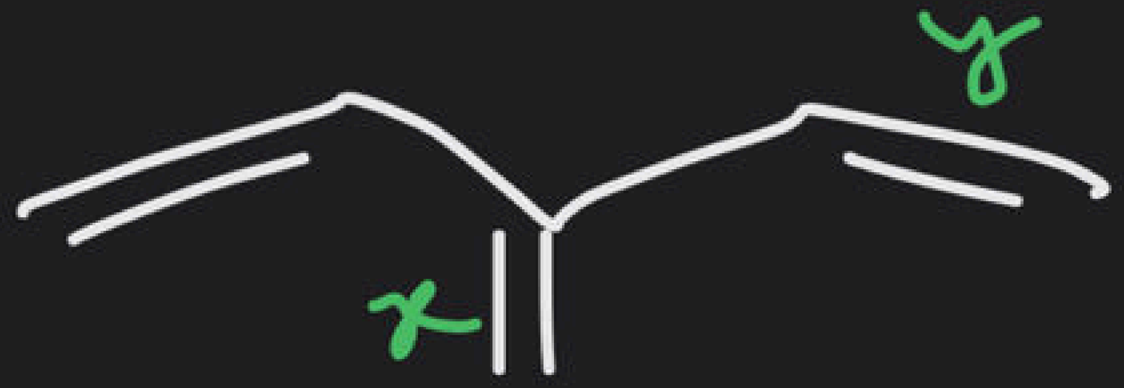
Bond length



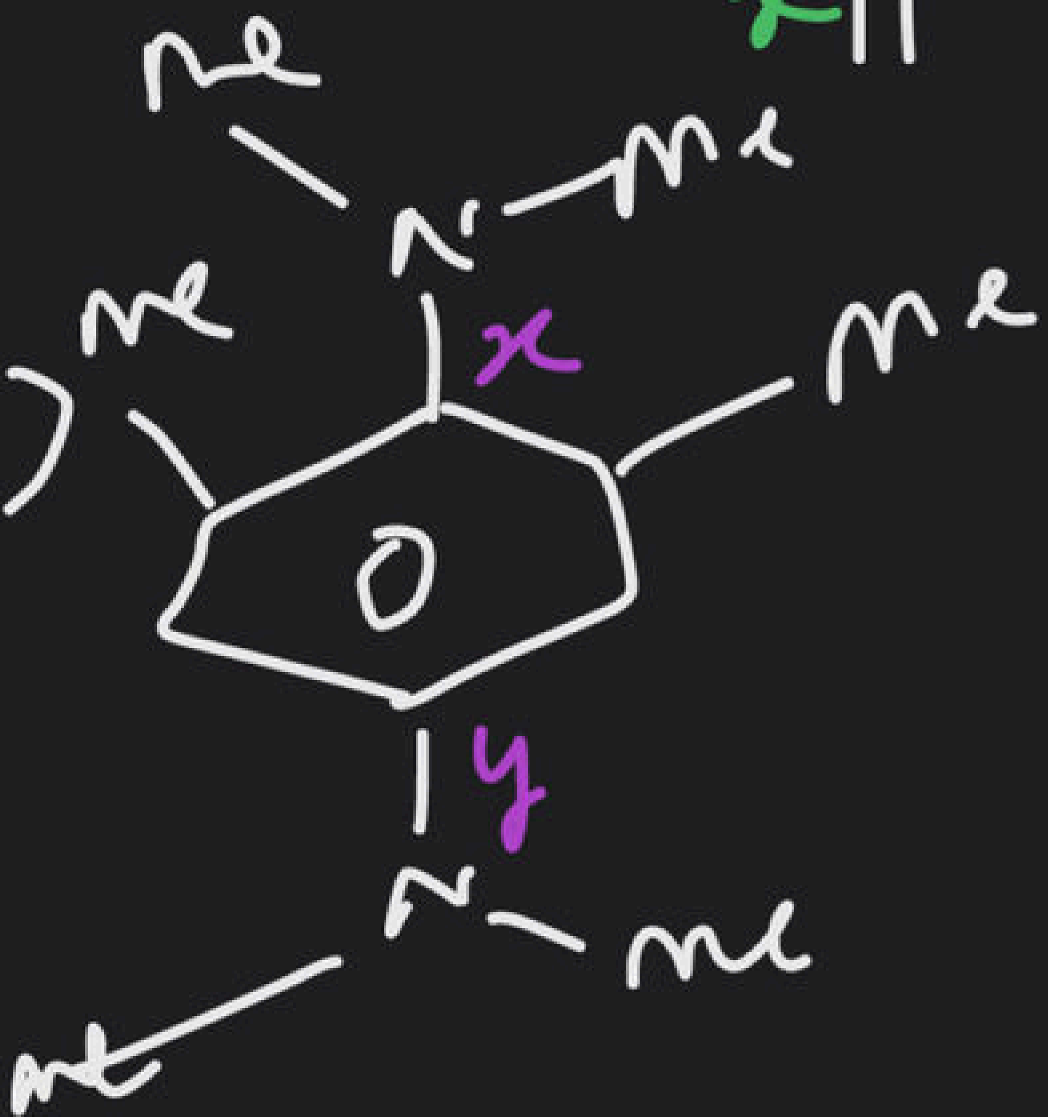
(2 > 1)

(2)

(3)

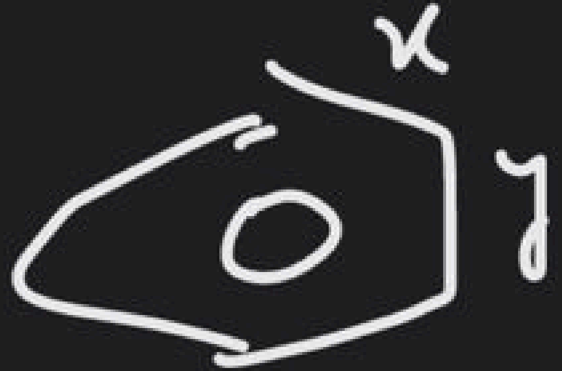


(4)



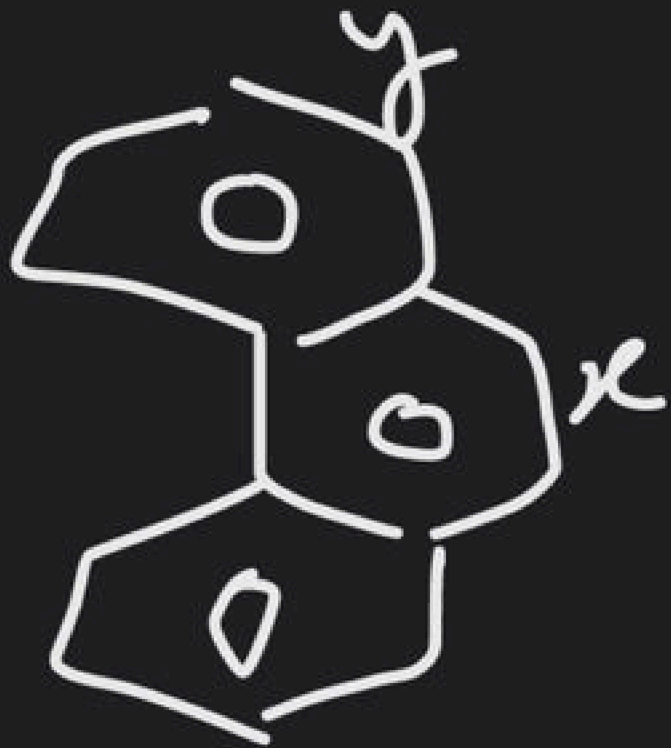
(5)

(6)

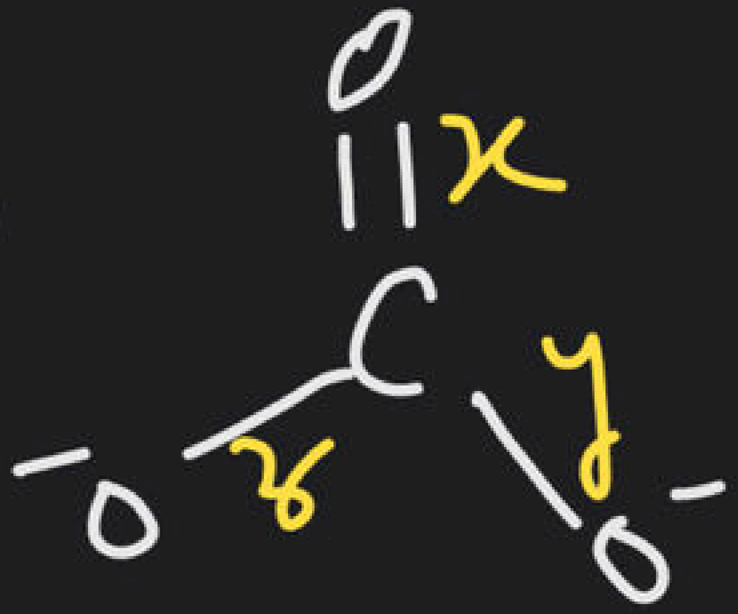


(7)

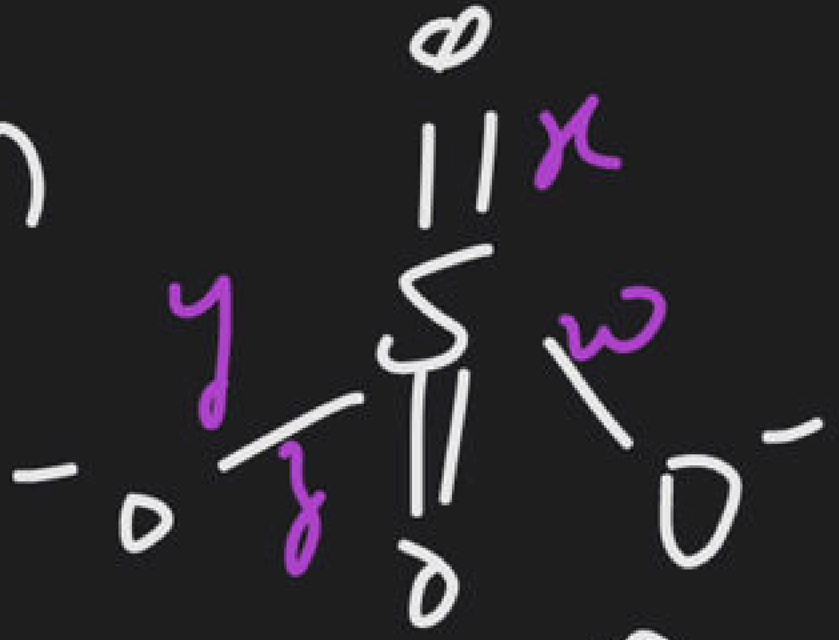
(8)



(9)

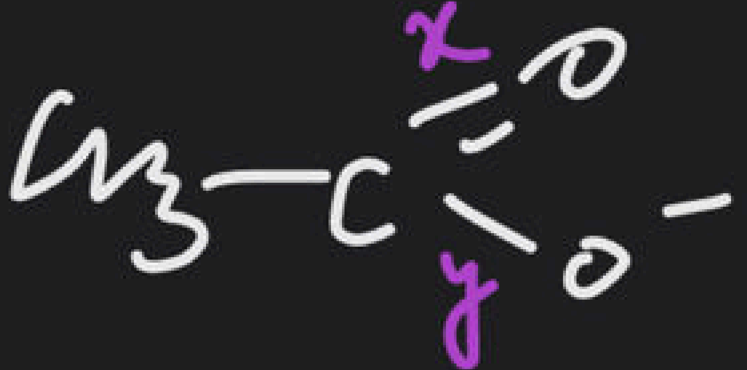


(10)

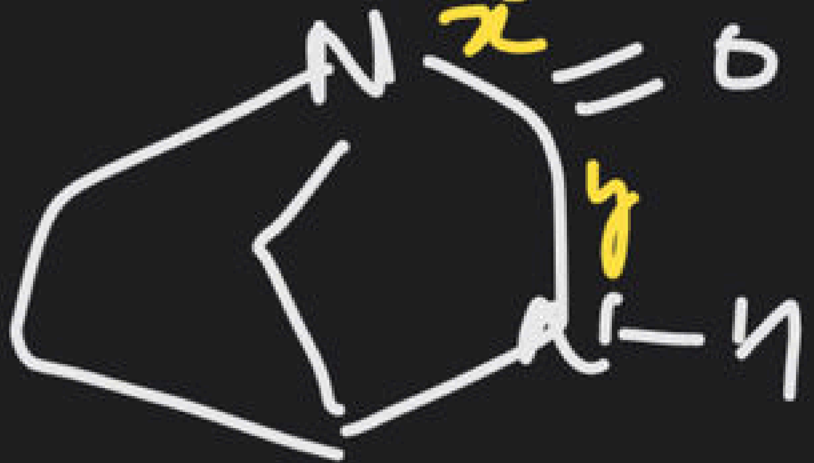


(11)

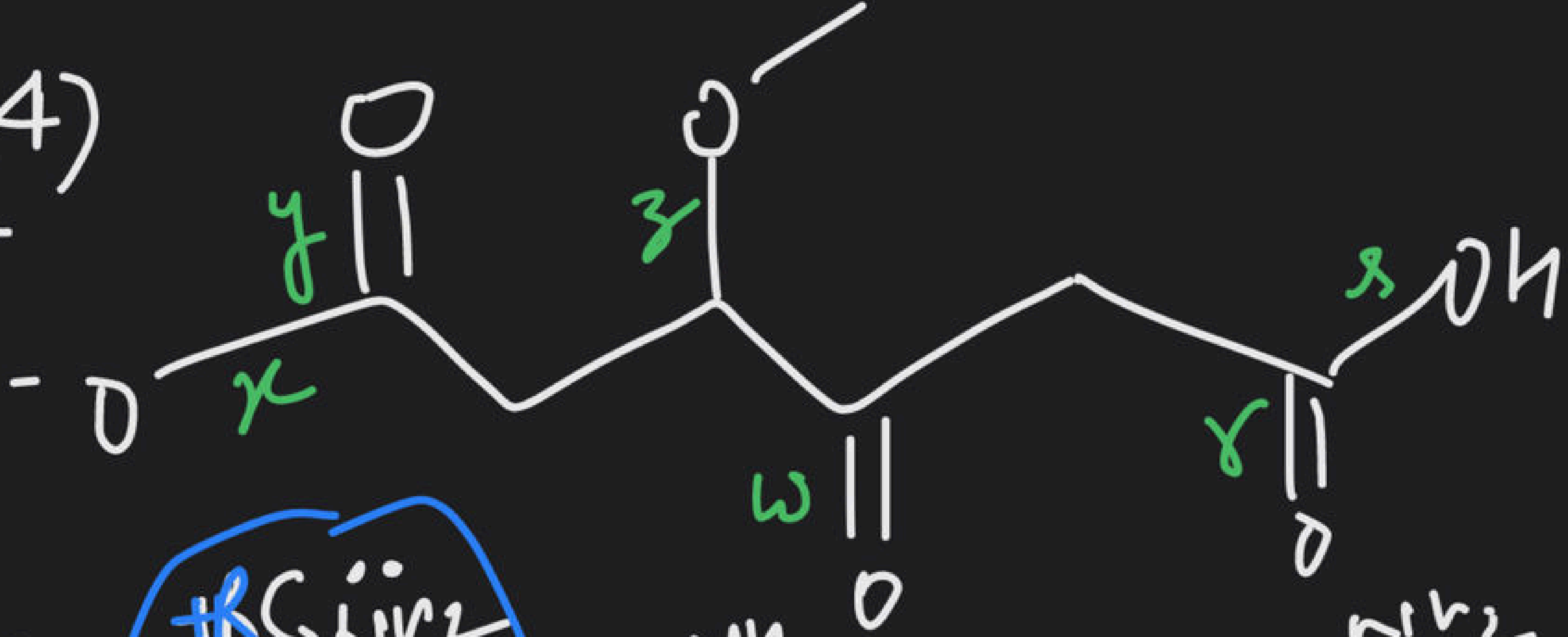
(12)



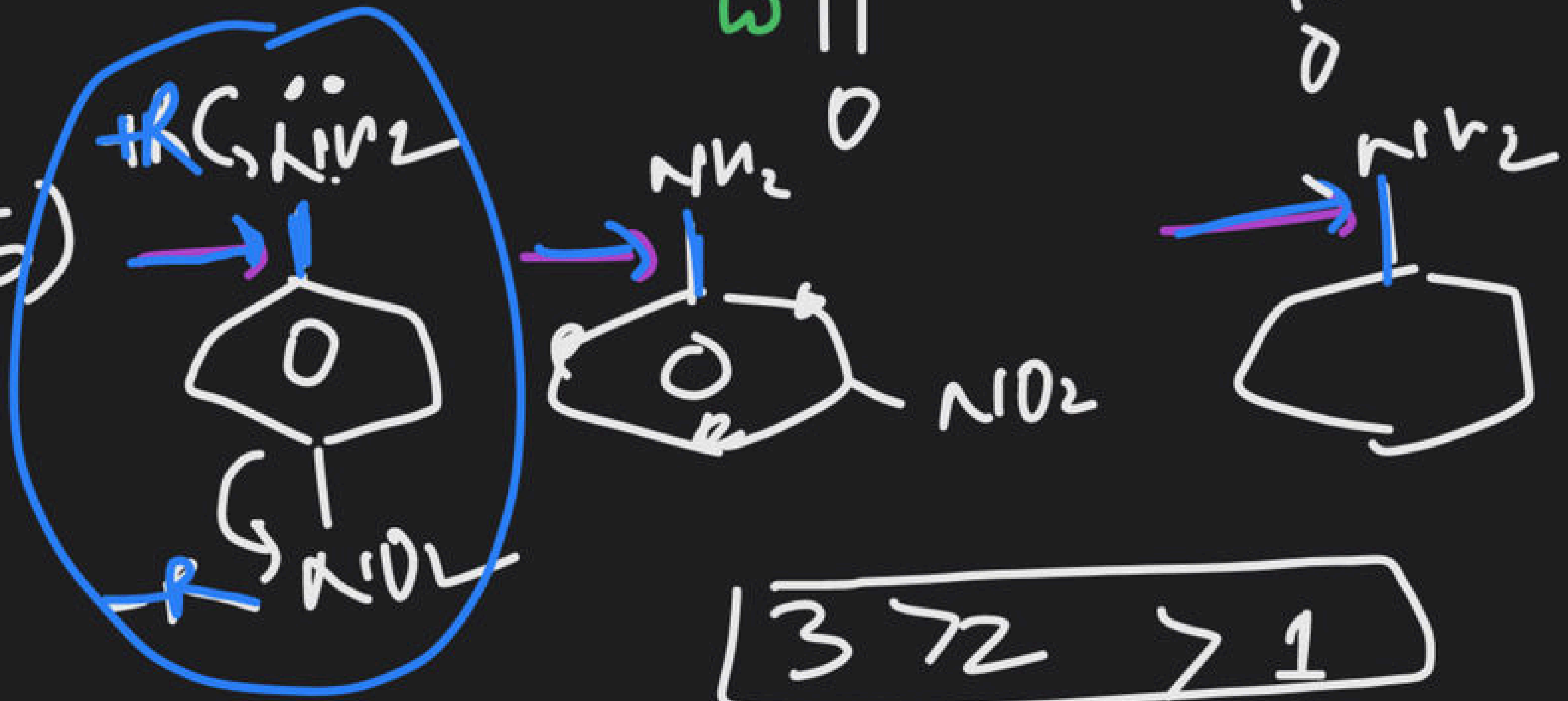
(13)



(14)



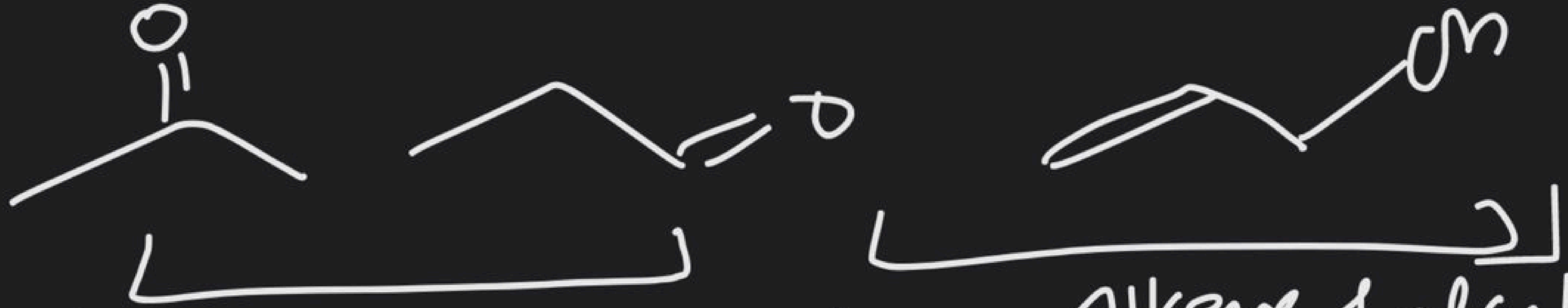
(15)



$\boxed{3 > 2 > 1}$

(#) Isomerism (hw)

(2)



F. Isomer

Alkene & alcohol

F gr	Ketone	Aldehyde
	di H-	
M.F	C_3H_6O	C_3H_6O

(3) F.I (Nitro nitrite)

(4) ______

(5) F.I (double, Triple)

(6) AB → F·I (Primary & sec. Amine)

AC → F I (Primary & Ter! Amine)

BC → F·I (sec & Tertn Amine)

(7) AB → F·I { ~~P~~ ——————— Acid Amide)

AC → F·I (——————— '')

BC → F·I (——————— '')

(8) AB → Anisole & Benzyl Alcohol (Ether & alcohol)

AC → (Ether & phenol)

BC → (alcohol & phenol)

(9) F·I (Acid Amide   Oxime   . Amine & Aldehyde)

(10) F.F (Ketone & Halide , Acid halide)

(11) F.I (Acid , Ester)

(12) F.I (Ketone & Ether , Ester & Ketone , Acid anhydride)

(13) F.I (~~Cyno~~ , ~~isocyno~~)

(A) Identical F.I

(B)

(14) F.I (Sulphonic Acid Sulpho ester)

(15) F.I (thiol thio Ether) (A) F.I

(16) F.I (Keton, Ether & Ester)

(17) F.I (Amine , Imine)

(18) F.F (Amine Cynide)

(5) metamer

(6) meta

(7) meta

Soln (1):

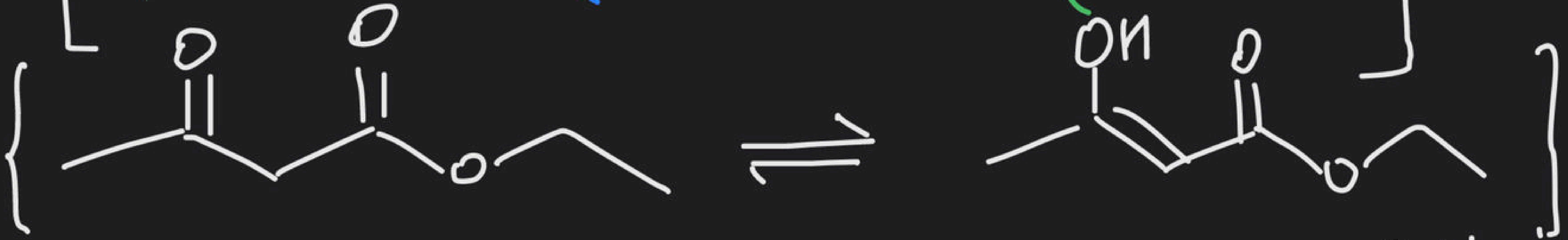
M.F $C_6H_{10}O_3$

(a) "+" test at $(-OH)$

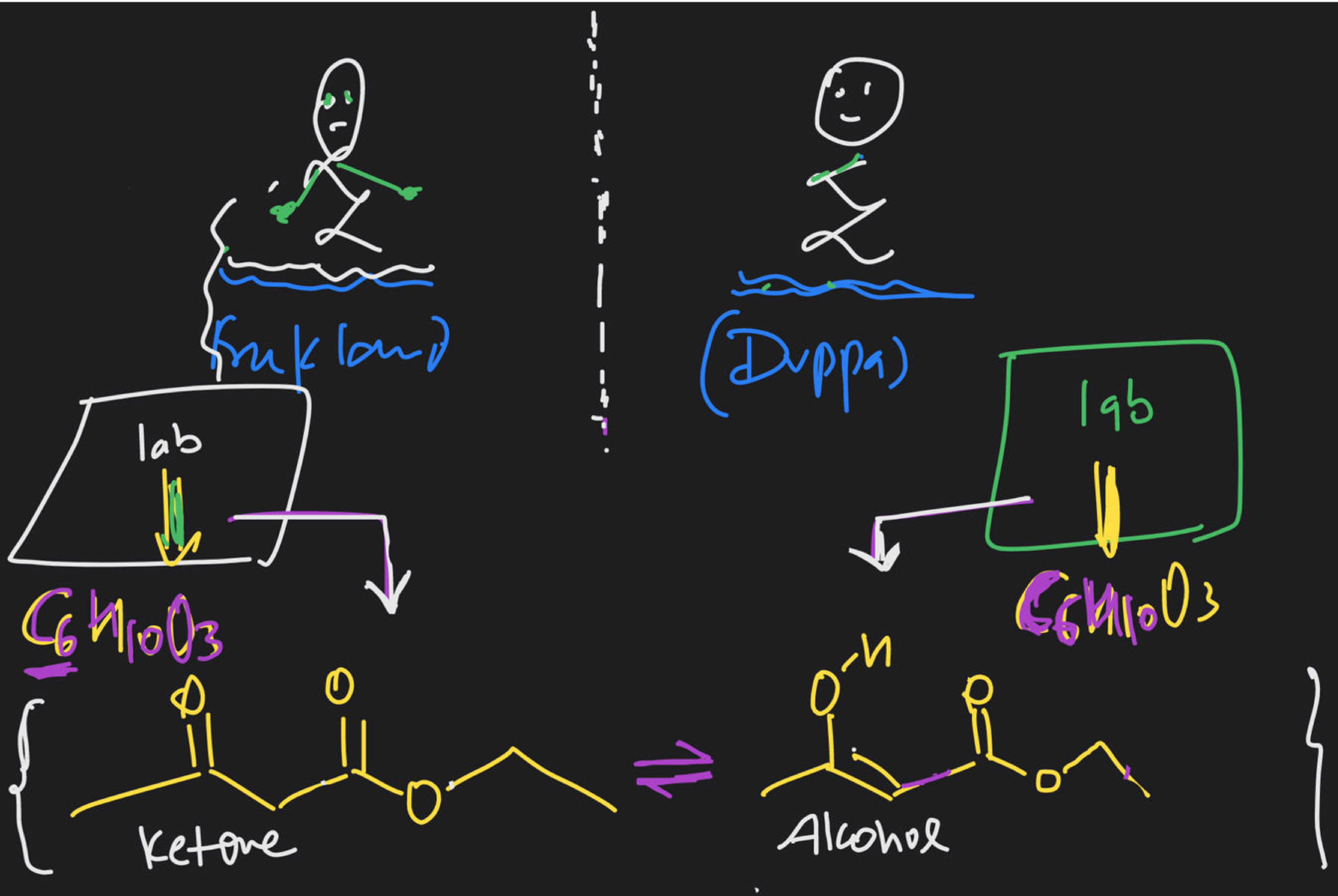
(b) ———————— $(-\overset{O}{\overset{\|}{C}}-)$

(c) ———————— $(-\overset{O}{\overset{\|}{C}}-O-)$

[(b & c) $\rightleftharpoons$ (a & c)]



Both isomers must be present together & it is possible when they are in equilibrium in a Reversible Reaction.


lab
(Duppa)
lab
C6H10O3
C6H10O3
Ketone
Alcohol

at equilibrium ($r_f = r_b$)

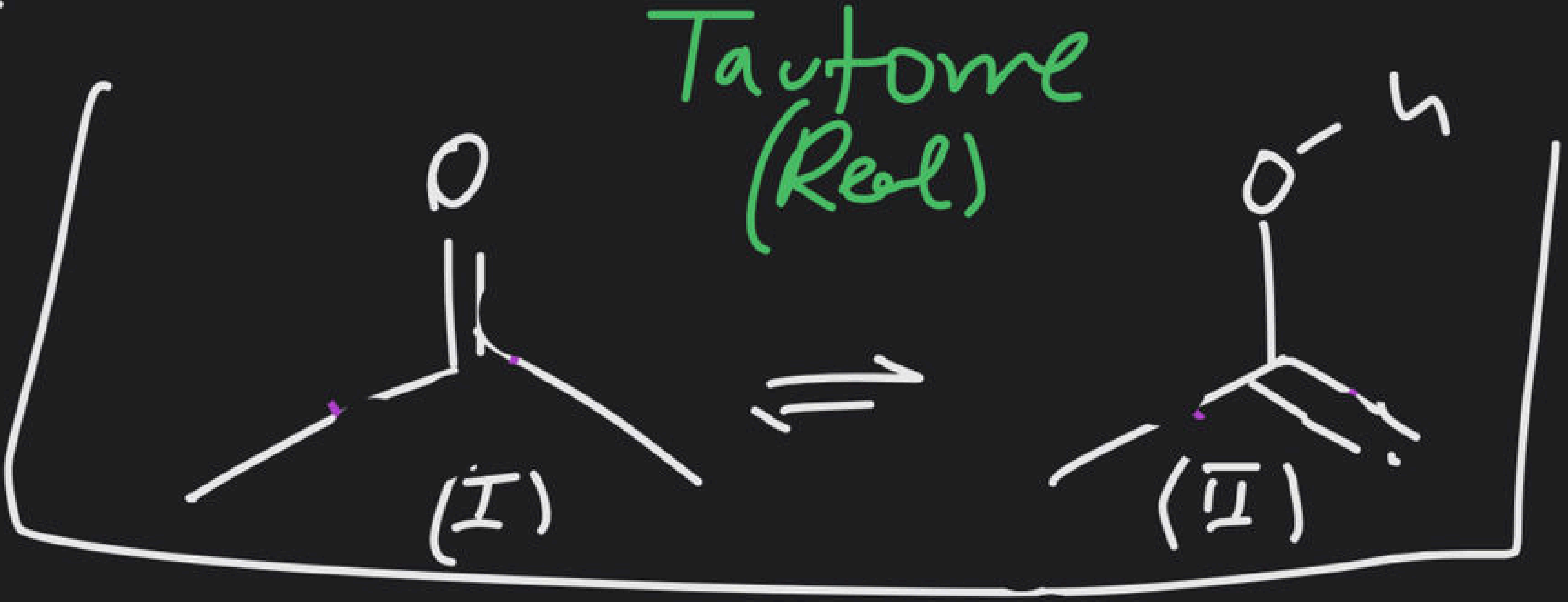
⇒ Tautomers

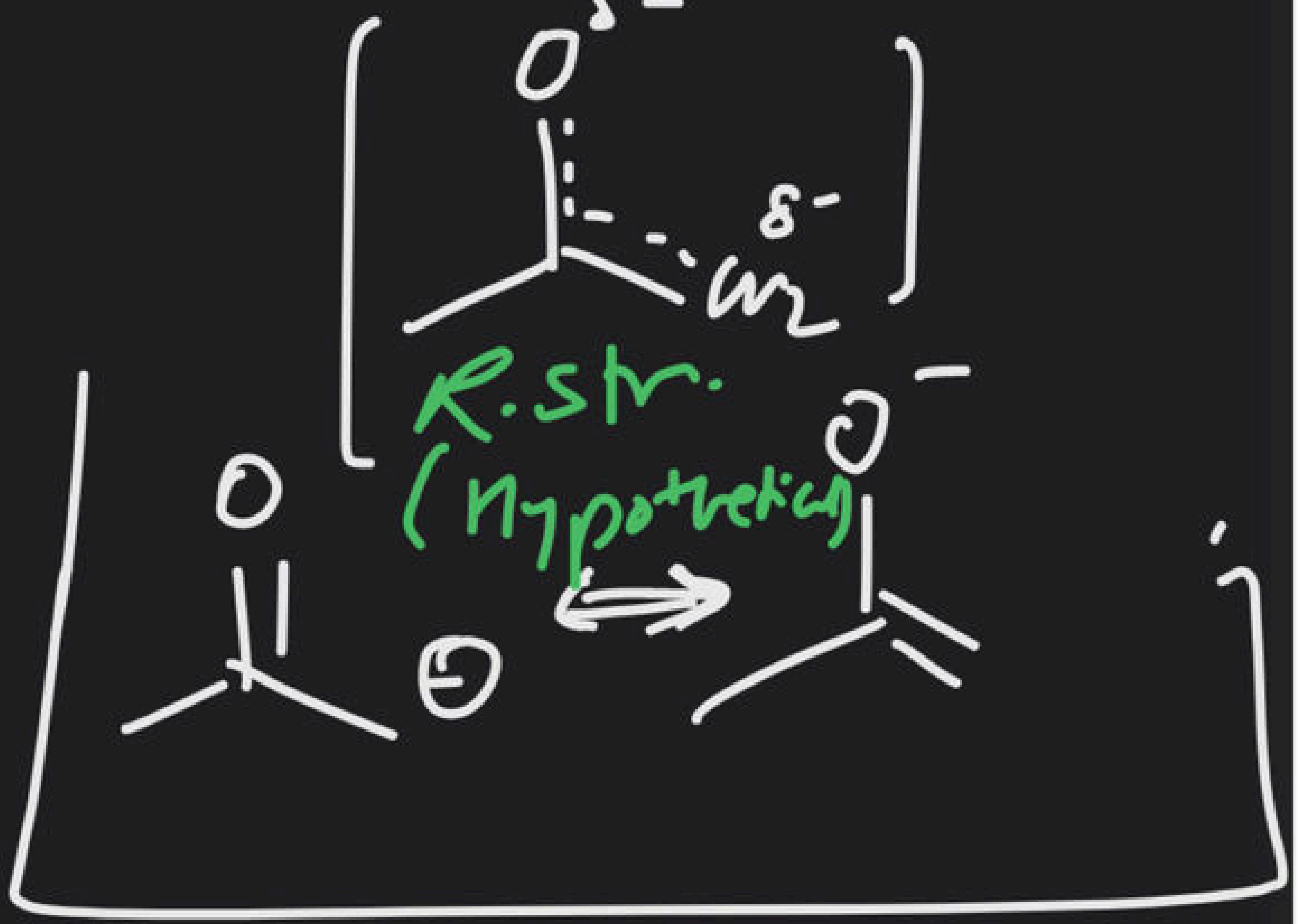
⇒ Tautomers are in dynamic equilibrium

Such kind of Isomerism arises due to oscillation of monovalent atom (−H) & structure obtained are known as Tautomers.

⇒ Tautomers can't be seprated at Room T^n.

Ex:-





first contained contains
2 compounds (I) & (II)

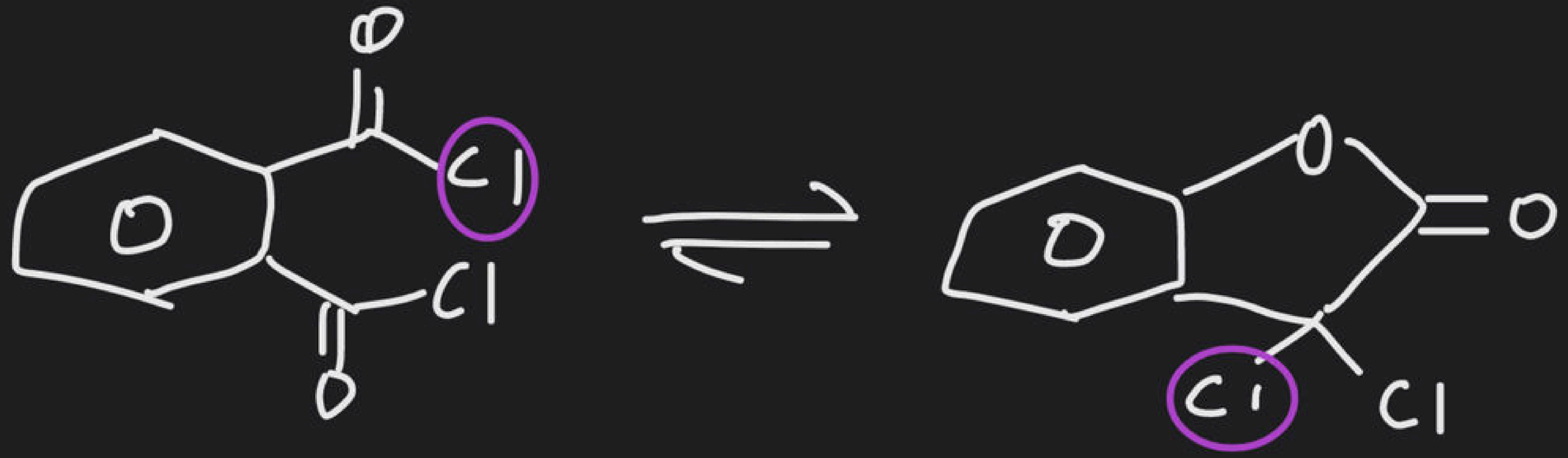
II
Contained contains
only single carbanion

Type of Tautomerism

These are two type of tautomerism

NOT in IIT JEE

(a) Anionotropy tautomerism: when oscillating atom is anion tautomerism is known as anionotropy tautomerism.



(b) Cationotropy tautomerism:

When oscillating atom is cation, tautomerism is known cationotropy tautomerism.

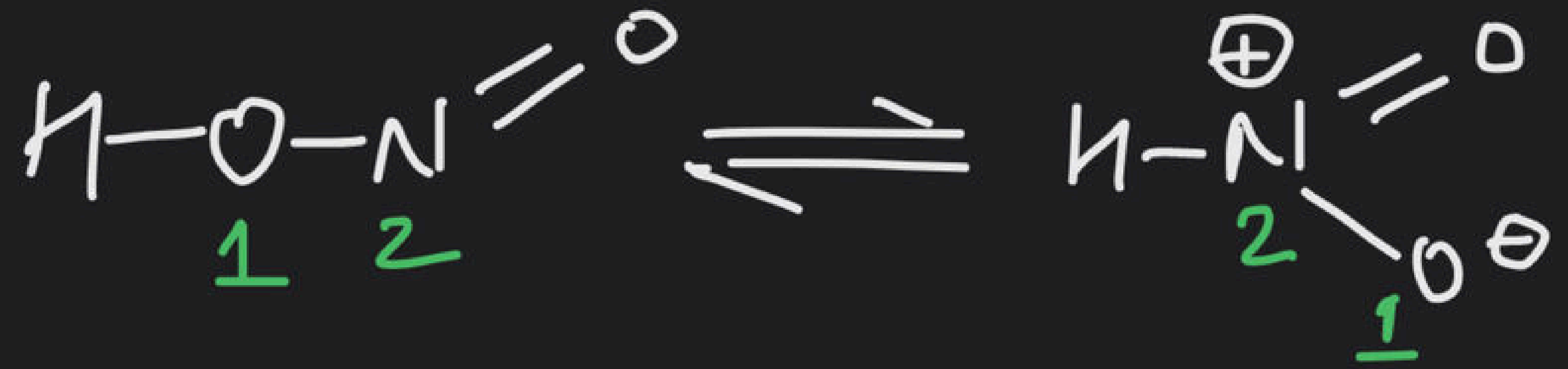
Type of tautomeric system.

(1) Diad system:

When oscillating atom oscillate between atom (1 to 2) & (2 to 1) system is known as diad system.

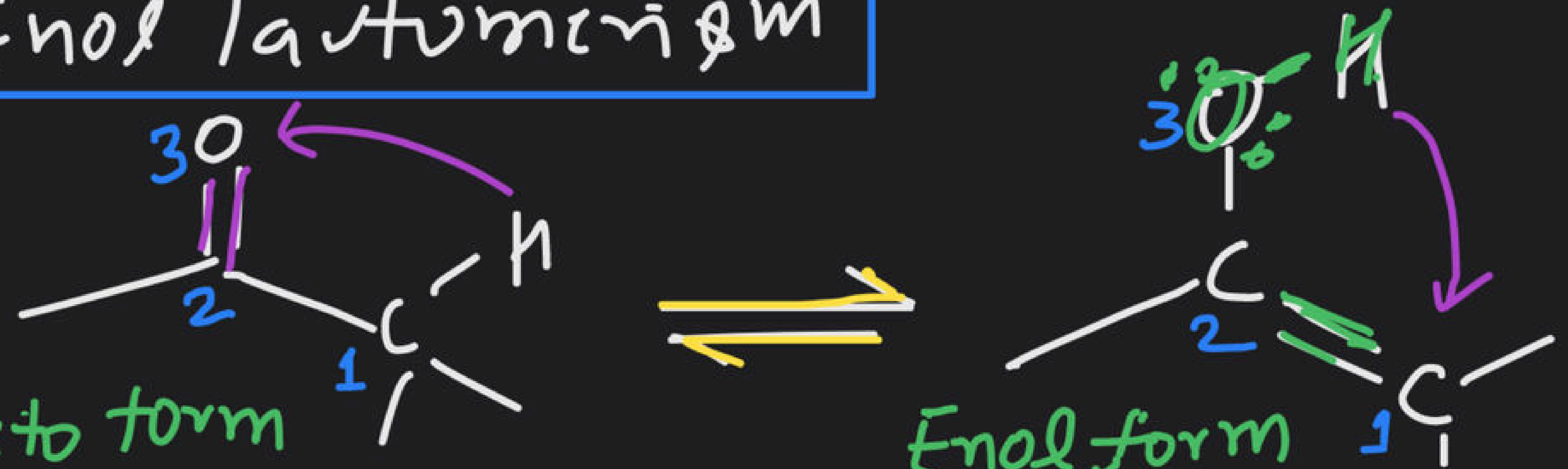
Ex-1: $H-\overset{1}{C}\equiv\overset{2}{N} \rightleftharpoons H-\overset{\oplus}{\underset{2}{N}}\equiv\overset{\ominus}{\underset{1}{C}}$

Ex-2



(2) **Triad System:** When oscillating atom oscillate between atom no. 1 to 3 & 3 to 1 then system is known as triad system.

Ex-1:- $\boxed{\text{Keto-Enol Tautomerism}}$



$$K_{eq} = \frac{[\text{Enol}]}{[\text{keto}]}$$

Since $BE_{\text{keto}} > BE_{\text{Enol}}$

hence Keto is more stable than enol & hence dominates over % Enol at Equilibrium.

$$[\text{keto}] > [\text{Enol}]$$

$$\Rightarrow \quad 1 > \frac{[\text{Enol}]}{[\text{keto}]}$$

$$\Rightarrow \quad \boxed{1 > K_{eq}}$$