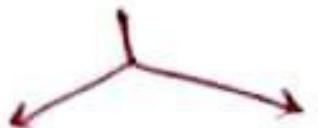


(15)

## [DEPTH OF BIOLOGY]

- Effect of substituent on acidity of phenol.

Effect due to nature of substituent



Effect due to position of substituent.

$e^-$  withdrawing &  $e^-$  releasing.

- Ortho<sup>& para</sup> position are more Influencing than meta. (In case of EWG)

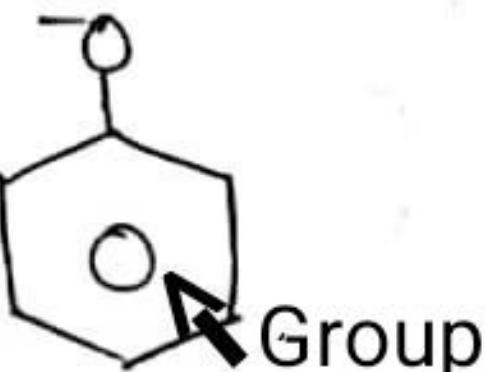
$\uparrow$  acidity



withdraw stabilize the phenoxide ion.

eg.  $\text{NO}_2$

$\downarrow$  acidity



$e^-$  releasing makes less stable phenoxide ion  
eg.  $\text{CH}_3$

## [DEPTH OF BIOLOGY]

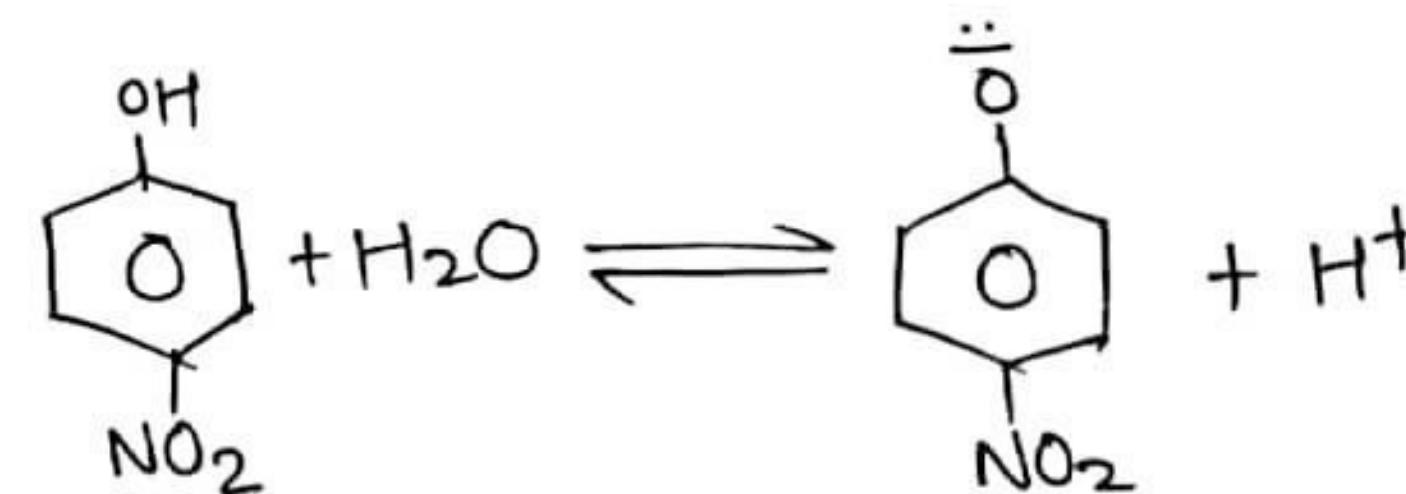
## [DEPTH OF BIOLOGY]

E.W.G =  $-\text{NO}_2$ ,  $-\text{CN}$ ,  $-\text{Cl}$ ,  $-\text{CHO}$ ,  $-\text{COOH}$ , etc., on the Aromatic ring.

- $\uparrow\uparrow$  the acidity of phenol  $\rightarrow$  it enable the ring to withdraw more  $e^-$  from the phenoxy oxygen (makes easy to leave  $\text{H}^+$ )



This  $\uparrow\uparrow$  stabilizes phenoxide ion still further & results in stronger acid eg: Nitrophenol is more acidic than phenol. [DEPTH OF BIOLOGY]

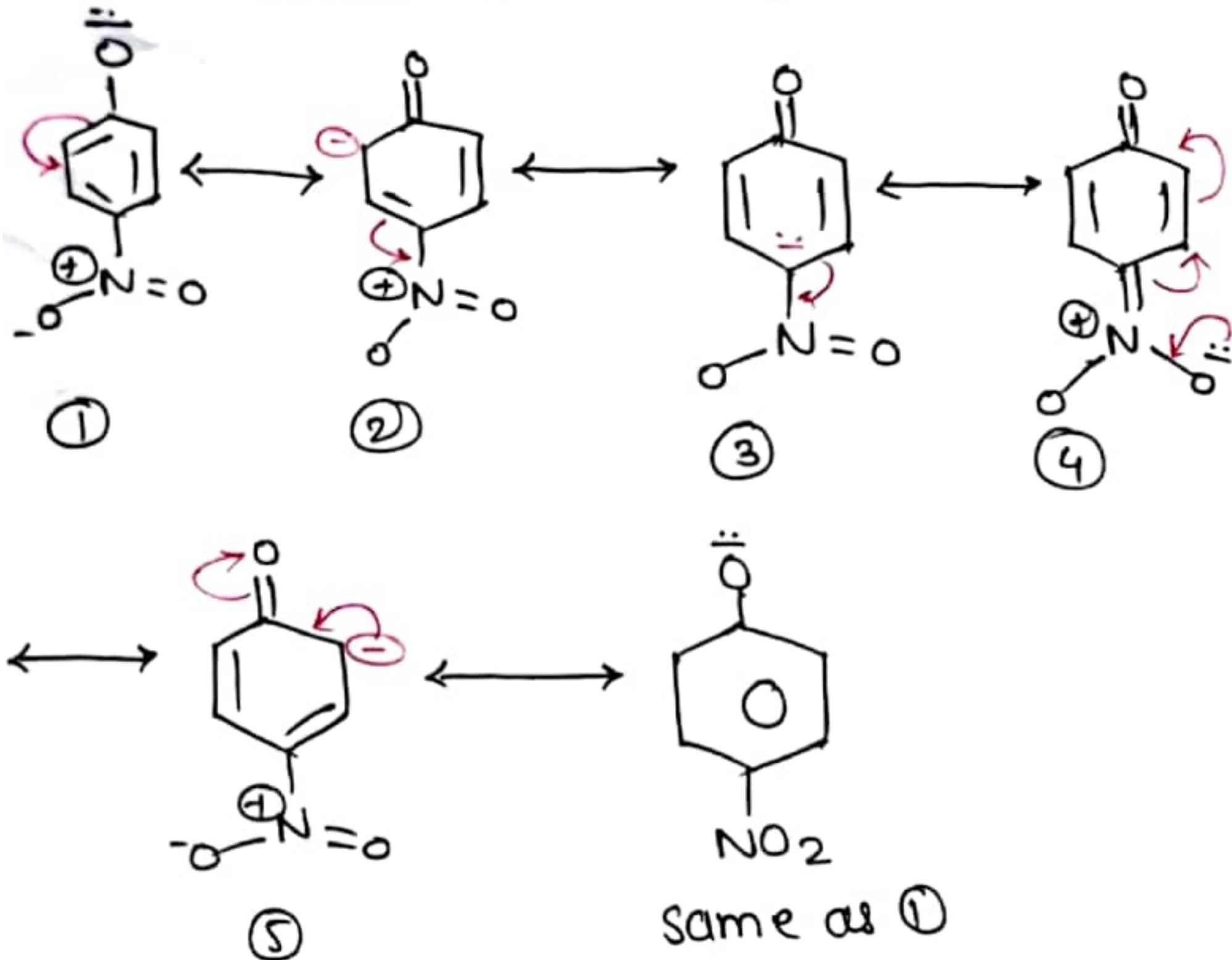


p-Nitrophenol

p-Nitrophenoxy Ion.

## [DEPTH OF BIOLOGY]

[DEPTH OF BIOLOGY]



[DEPTH OF BIOLOGY]

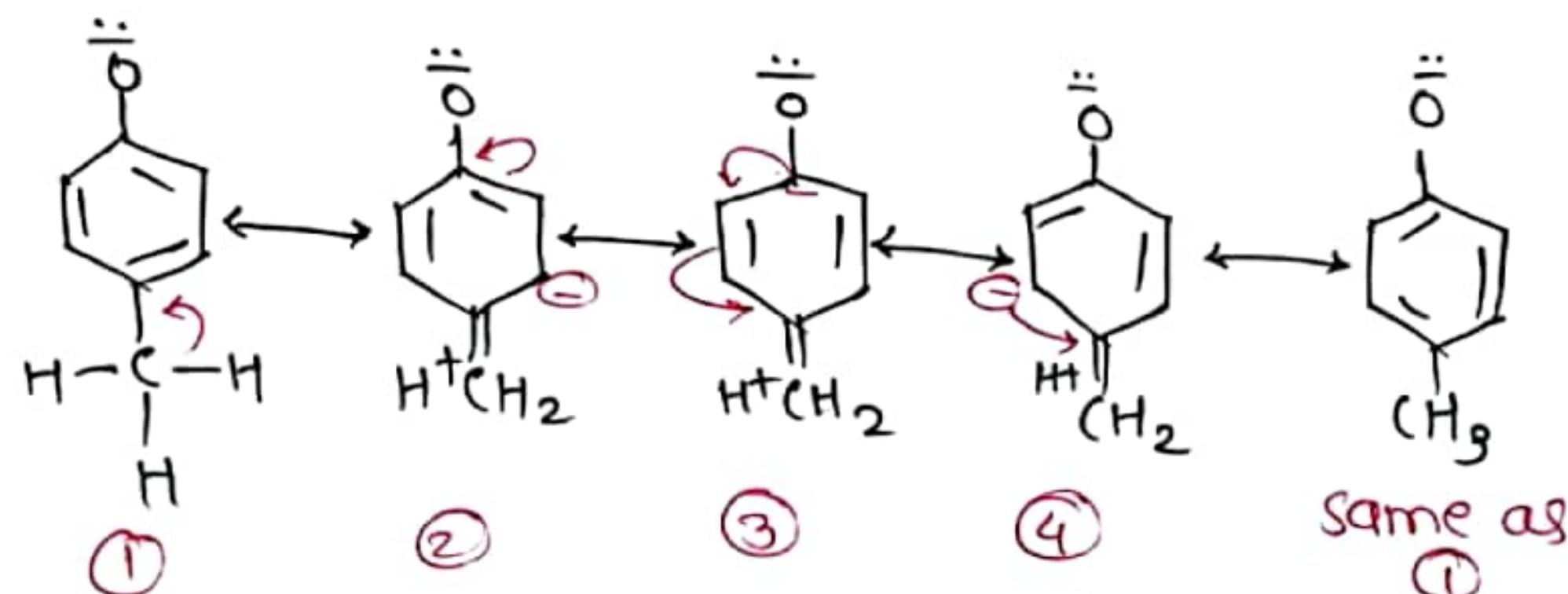
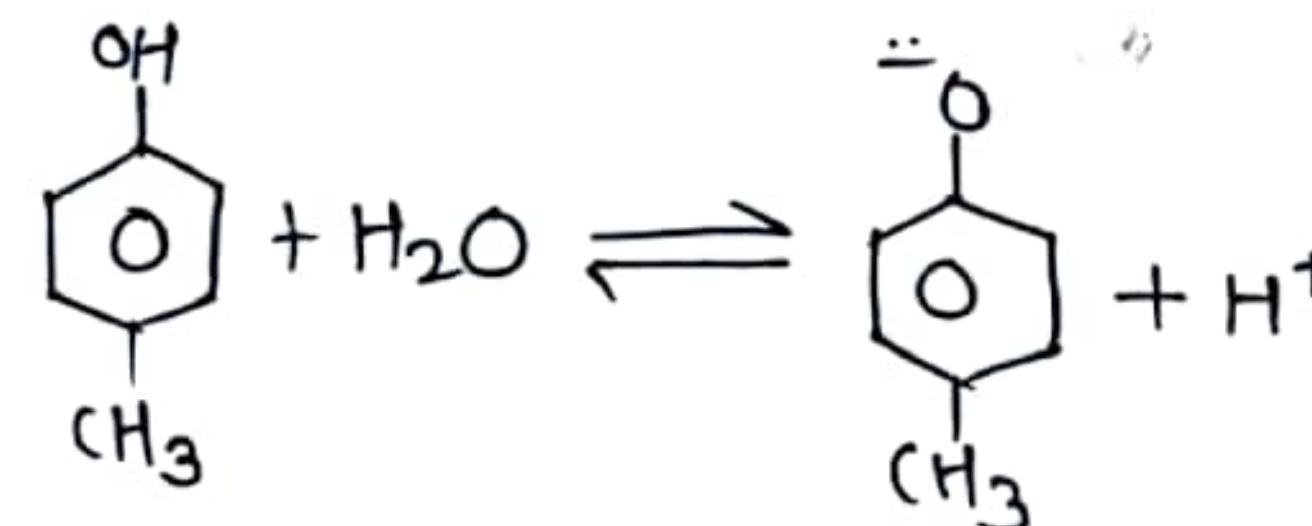
\* Effect of  $e^-$ -releasing Group:

- An  $e^-$ -releasing group like  $-\text{CH}_3$ ,  $-\text{OCH}_3$ ,  $-\text{OH}$ ,  $-\text{NH}_2$ , etc.,  $\downarrow\downarrow$  the acidity of phenol.
- They destabilised the phenoxide Ion by  $\uparrow\uparrow$  the  $-ve$  charge on oxygen & Inhibit the charge delocalisation by resonance.

[DEPTH OF BIOLOGY]

[DEPTH OF BIOLOGY]

eg: p-Cresol is less acidic than phenol.



[DEPTH OF BIOLOGY]

$\Rightarrow +I$  effect of  $\text{CH}_3$  group  $\uparrow\uparrow$  the magnitude & destabilises the ion.

\* Effect of position of substituent on Acidity.

- The presence of substituent at ortho & para position is more pronounced than the m-position.

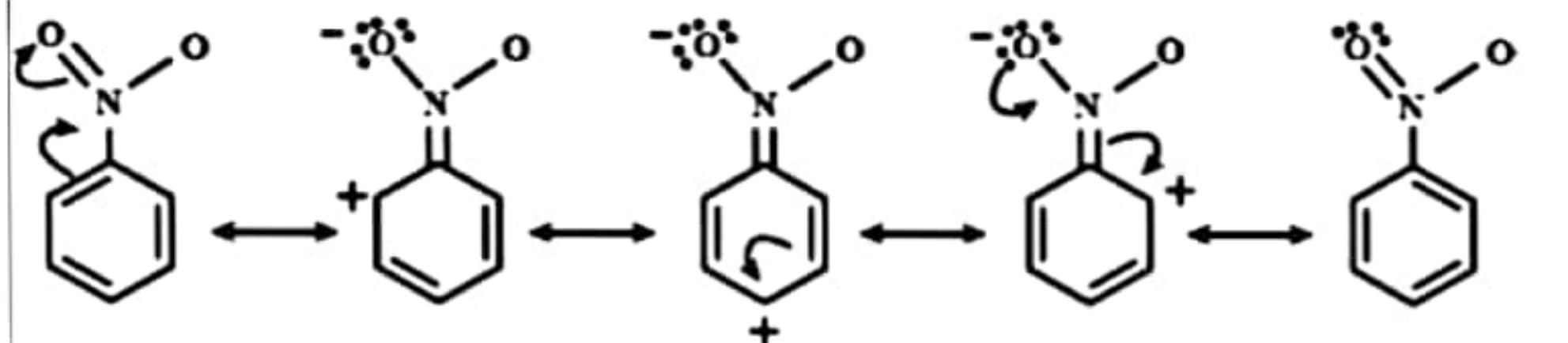
[DEPTH OF BIOLOGY]

[DEPTH OF BIOLOGY]

This is due to resonance effect and Involvement of group.

Ex:  $\text{NO}_2$  group at ortho & para position is more able to delocalise.

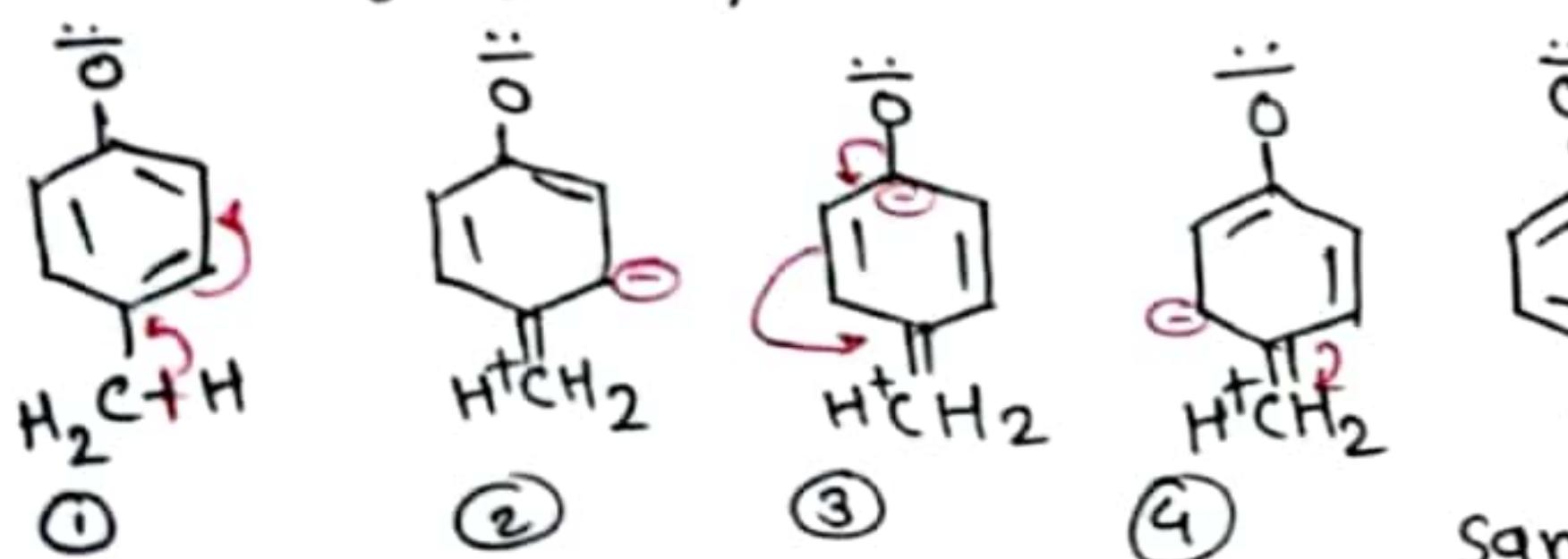
- The change on phenoxide ion then meta position.



- \* m-cresol is more acidic than ortho & para cresol, this is due to Hyper-conjugation (special resonance).

[DEPTH OF BIOLOGY]

- \* In the case of  $e^-$  releasing the m-position effect is opposite to  $e^-$  withdrawing group.

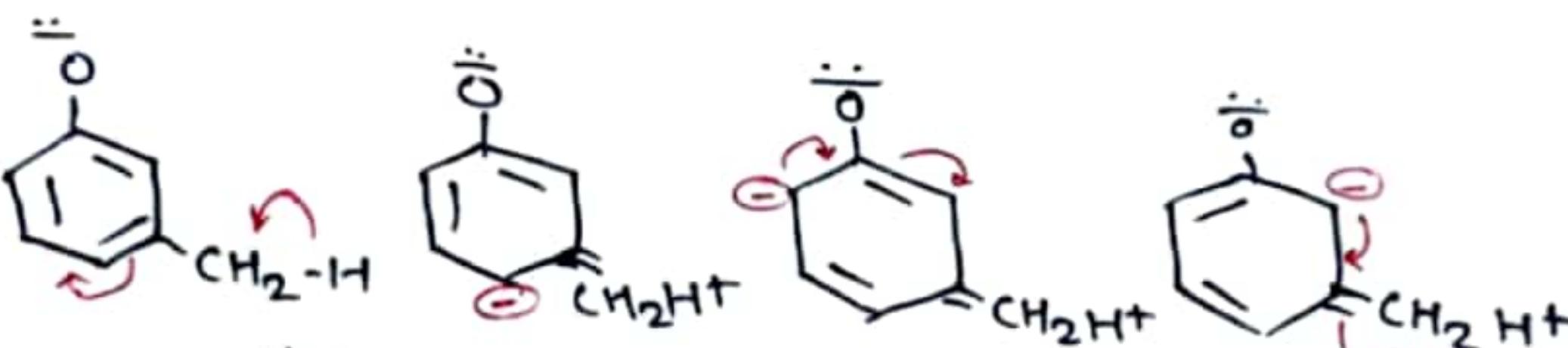


same as ①

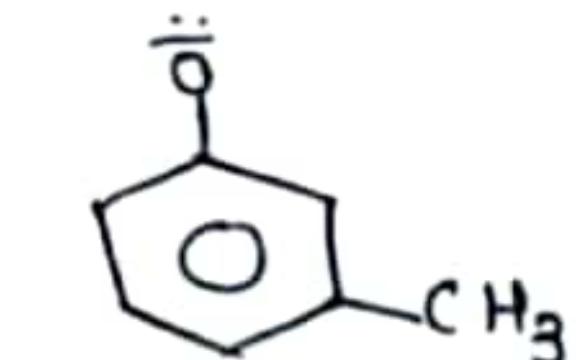
[DEPTH OF BIOLOGY]

[DEPTH OF BIOLOGY]

In case of meta:



m-cresoxide Ion.

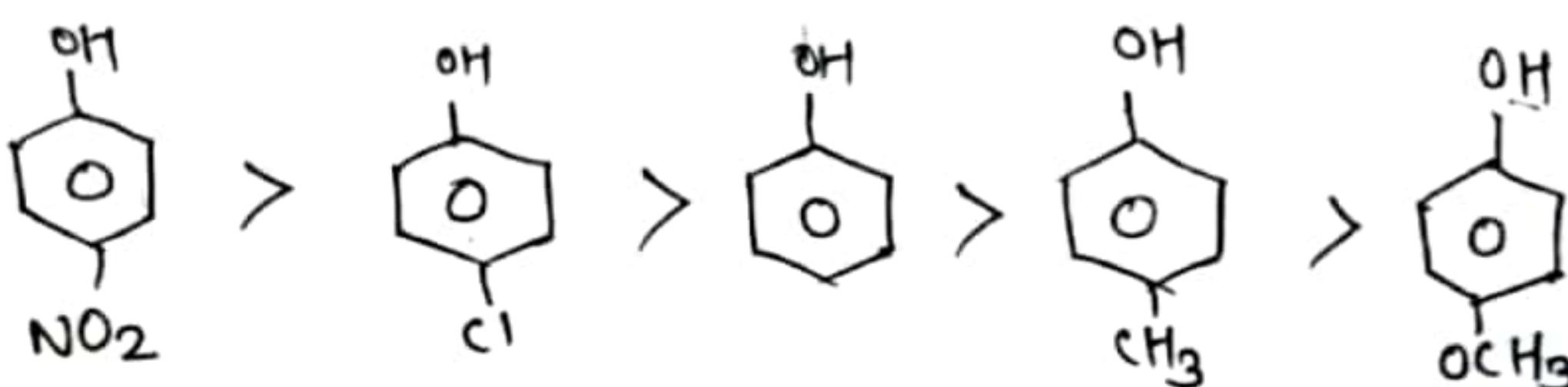


same as ①

more stable than ortho and para position.

- m-cresoxide Ion is more stable than ortho & para cresoxide Ion due to  $\ominus$  ve charge on phenoxide carbon. Thus m-cresol is more acid.

we can say that,



[DEPTH OF BIOLOGY]

## [DEPTH OF BIOLOGY]

Imp:

- acid strength of phenol also affect by  
(no. of  $e^-W.G / e^-R.G$ )
- ② Tri Nitrophenol  $>$  oNitrophenol  
(picric acid) (Acidic)
- ③ some phenol with o  $e^-W.G$  are weaker acid than p-substituted (group)  
(same group).
- ① o-  $NO_2$  phenol weaker than para.
- ② o- Fluoro phenol weaker than para.