VMC Vidyamandir Classes SINCE 1986

IIT JEE | MEDICAL | FOUNDATION

# Introduction to organic chemistry

# IOC

Topics included:

(1) Nomenclature

(2) GOC-1 ( Electronic displacement effects)

(3) GOC- II ( Stability of intermediates)

(3) GOC-III ( Acidity & Basicity)

(4) Isomerism

# Acidity / Acidic strength $\rightarrow$

$$\text{Acid} \xrightarrow{-H^+} \text{conjugate base}$$

$$HA \xrightarrow{-H^+} A^-$$

$$\text{Acidic strength} \propto \text{stab. of conjugate base}$$

$$\propto K_a \propto \frac{1}{pK_a}$$

$$\propto [H^+] \propto \frac{1}{pH}$$

stab. of conjugate base can be Increased by

EWG $\Rightarrow$ $-M > \text{Reso} > -I$

Conjugate base can be destabilise by EDG

$\Rightarrow$ $+M > H.C. > +I$

* In a period $L \rightarrow R \Rightarrow E.N. \uparrow$

$\Rightarrow$ stab. of conjugate base $\uparrow$

* In a group $\Rightarrow$ $T \rightarrow B \Rightarrow$ size $\uparrow$

$\Rightarrow$ stab. of conjugate base $\uparrow$

Q. Find order of acidic strength / $K_a$ ?

(1) $CH_4$ $\quad NH_3$ $\quad H_2O$ $\quad HF$

$CH_4 \downarrow CH_3^-$ $\quad NH_3 \downarrow {}^-NH_2$ $\quad H_2O \downarrow OH^-$ $\quad HF \downarrow F^-$

d > c > b > a

(2) $H_2O$ $\quad H_2S$ $\quad H_2Se$ $\quad H_2Te$

$H_2O \downarrow {}^-OH$ $\quad H_2S \downarrow {}^-SH$ $\quad H_2Se \downarrow {}^-SeH$ $\quad H_2Te \downarrow {}^-TeH$

d > c > b > a

(3) $HF$ $\quad HCl$ $\quad HBr$ $\quad HI$ $\quad$ d > c > b > a

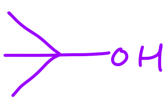
$NH_3$ $\quad PH_3$ $\quad AsH_3$ $\quad SbH_3$

(4) $R-NH-R$ $\quad R-NH_2$ $\quad NH_3$ $\quad H_2O$

$R-NH-R \downarrow R_2-N^{\ominus}$ (+I, +I) $\quad R-NH_2 \downarrow$ +I $R-\overset{\ominus}{N}H$ $\quad NH_3 \downarrow {}^{\ominus}NH_2$ $\quad H_2O \downarrow {}^{\ominus}OH$ $\quad$ d > c > b > a

(5) $\underbrace{CH_3-CH_2}_{+I}-OH$ $\quad \overbrace{CH_3-\underset{|}{C}H-CH_3}^{+I}$ OH $\quad CH_3-\underset{CH_3}{\overset{CH_3}{C}}-OH$ +I

a > b > C

(6)  $\quad NH_3$ $\quad H_2O$ $\quad CH_3-CH_2-OH$

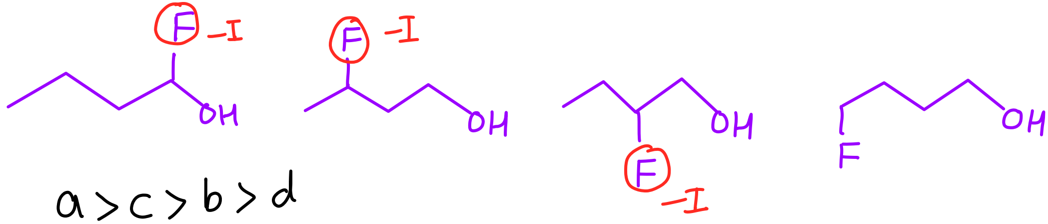
c > d > a > b

(7) $\underset{\underbrace{NO_2}_{-I}}{CH_2}-CH_2-OH$ $\quad \underset{\underbrace{\oplus NF_3}_{-I}}{CH_2}-CH_2-OH$ $\quad \underset{\underbrace{\oplus SR_2}_{-I}}{CH_2}-CH_2-OH$

$\underbrace{CH_3-CH_2-CH_2}_{+I}-OH$

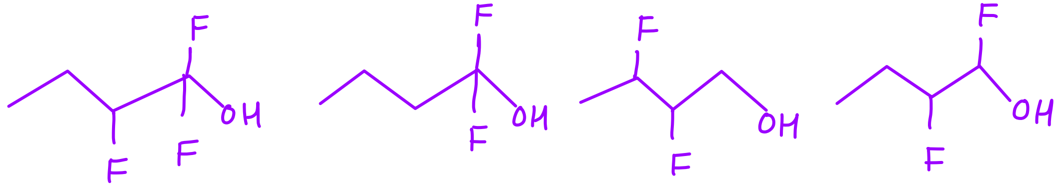
b > c > a > d

(8)




a > c > b > d

(9)




a > b > d > c

(10)

$CH\equiv CH \downarrow CH\equiv C^{\ominus}$ sp

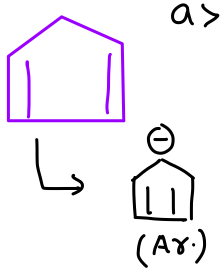
$CH_2=CH_2 \downarrow CH_2=\overset{\ominus}{C}H$ $sp^2$

$CH_3-C\equiv CH \downarrow \underbrace{CH_3}_{+I}-C\equiv C^{\ominus}$ sp

$CH_3-CH_3 \downarrow CH_3-\overset{\ominus}{C}H_2$ $sp^3$

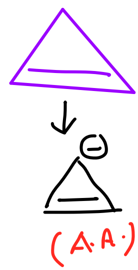
a > c > b > d

** (11)



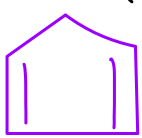

$CH\equiv CH \downarrow CH\equiv C^{\ominus}$

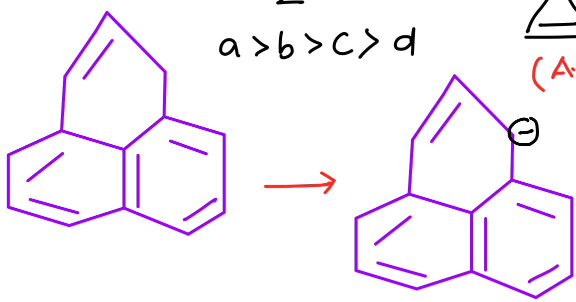
$CH_2=CH_2 \downarrow CH_2=\overset{\ominus}{C}H$




a > b > c > d

** (12)





b > a

** (13) $R-\overset{O}{\underset{O}{\overset{\|}{\underset{\|}{S}}}}-OH > R-\underset{O}{\underset{\|}{C}}-OH > Ph-OH > H_2O > CH_3-CH_2-OH$

$\downarrow$ $R-\overset{O}{\underset{O}{\overset{\|}{\underset{\|}{S}}}}-O^-$ 3eq.R.S

$\downarrow$ $R-\underset{O}{\underset{\|}{C}}-O^-$ 2eq R.S.

$\downarrow$ $Ph-O^-$ 5 R.S.

$\downarrow$ $\overset{\ominus}{O}H$

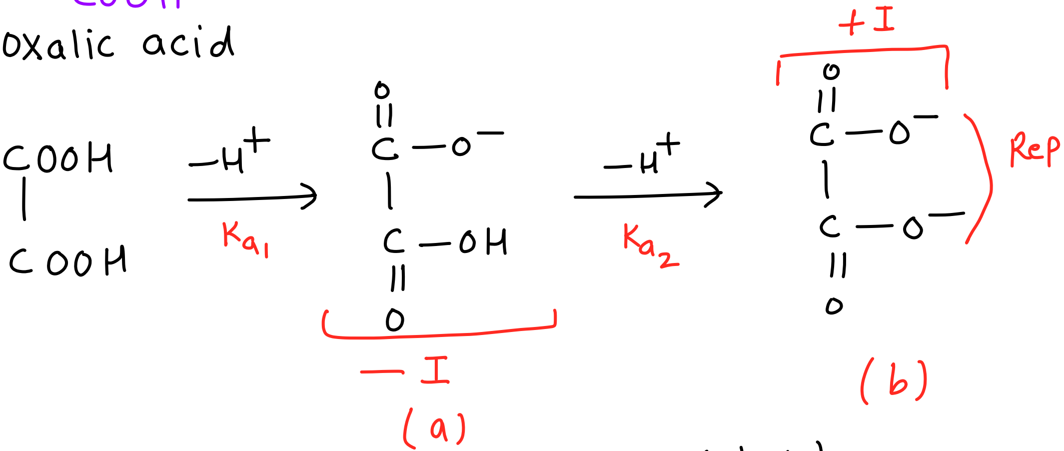
$\downarrow$ $CH_3-CH_2-\overset{\ominus}{O}$

(14) Exception $CH_3-OH > H_2O$

(15) 

Oxalic acid

Compare $K_{a_1}$ and $K_{a_2}$ ?

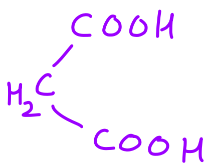



$a > b \longrightarrow$ (stab.)

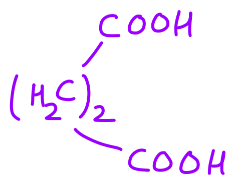
$K_{a_1} > K_{a_2}$

(16) 

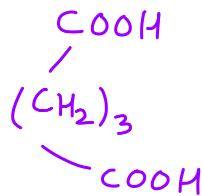
Oxalic acid



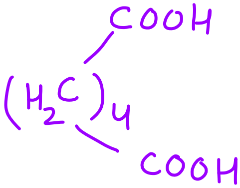
Malonic acid



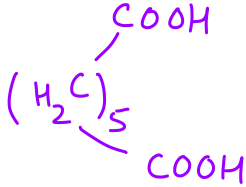
Succinic acid



Glutaric acid



Adipic acid



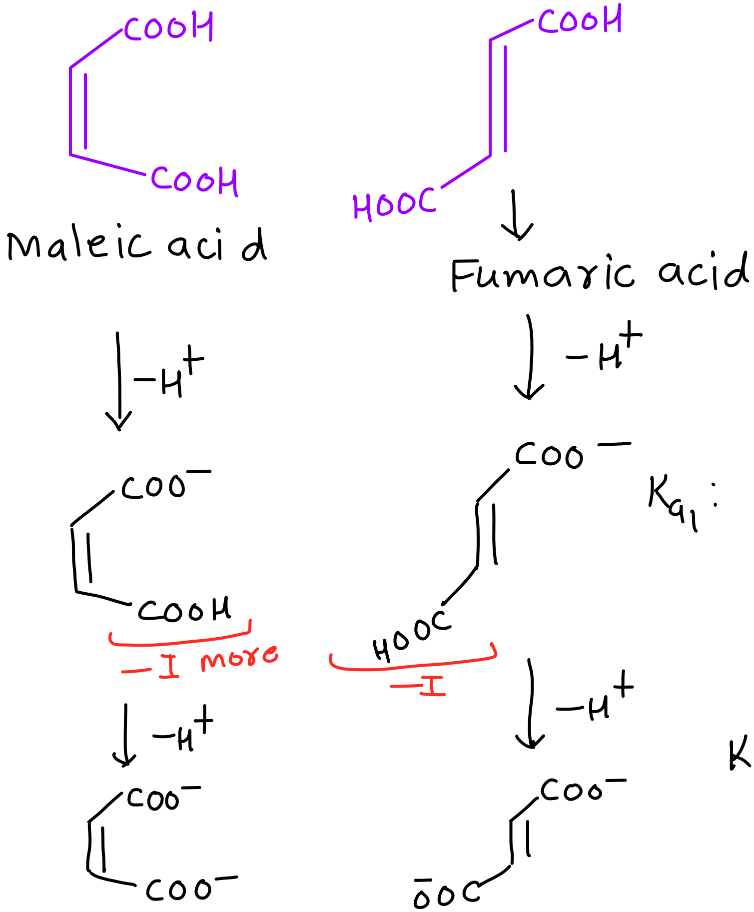
Pimelic acid

$K_{a_1}: O > M > S > G > A > P$

$K_{a_2}: O < M < S < G < A < P$

OMSGAP

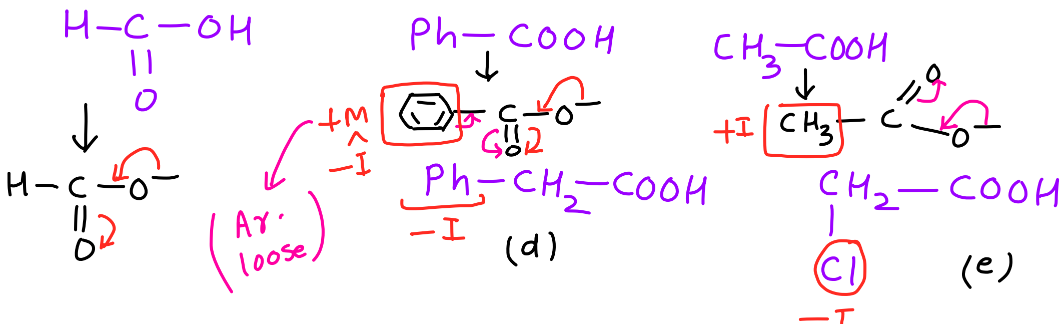
(17)




$K_{a_1}$: M > F

$K_{a_2}$: F > M

** (18) V.Imp.




e > a > b > d > c

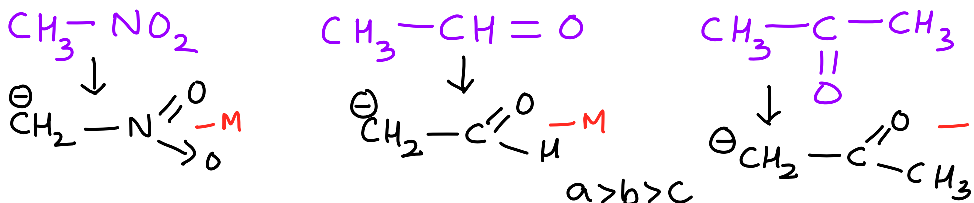
(19) $HCl \qquad \underbrace{F_3C}_{-I}-COOH \qquad \underbrace{Ph}_{+M<-I}-\underset{\underset{O}{\|}}{C}-OH \qquad \underbrace{CH_3}_{+I}-COOH$

a > b > c > d

(20) $\underbrace{F_3C}_{-I}-COOH \qquad \underbrace{Cl_3C}_{-I}-COOH \qquad \underbrace{Br_3C}_{-I}-COOH \qquad \underbrace{I_3C}_{-I}-COOH$

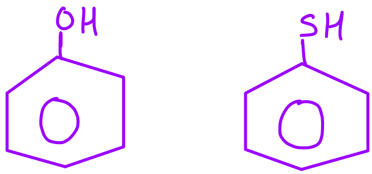
a > b > c > d

(21)




a > b > c

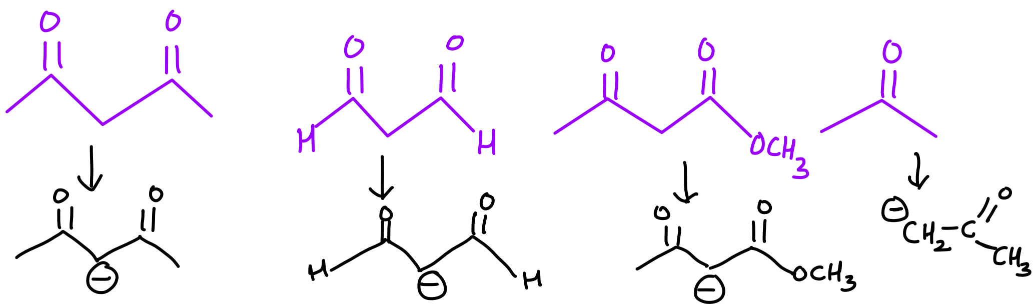
(22)



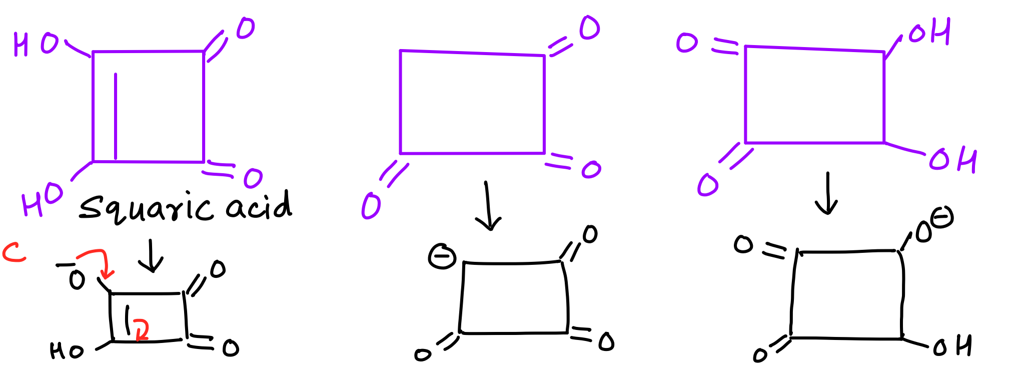

(b > a)

(23)

b > a > c > d

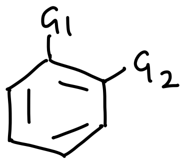


(24)




a > b > c

## Steric Inhibition of Resonance (SIR) ⟶



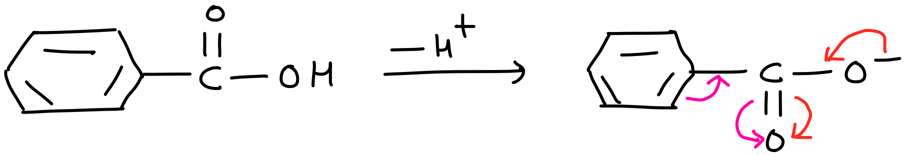

$G_1$ and $G_2$ are bulky groups.

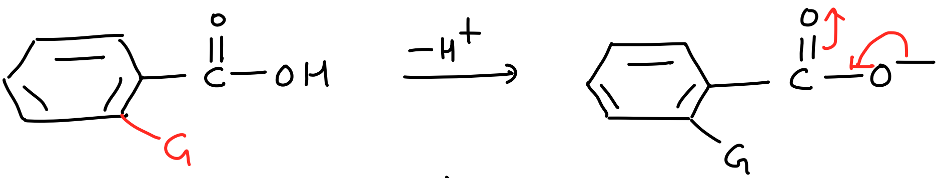
$G_1, G_2 \neq -H, -D, -T, -CN, -NH_2, -F, -C\equiv CH, -OH$

If $G_1, G_2$ are bulky $\Rightarrow$ Repulsion b/w $G_1$ and $G_2$ $\Rightarrow$ Planarity of p-orbitals of $G_1, G_2$ with benzene ring lost $\Rightarrow$ Resonance of $G_1$ and $G_2$ with benzene ring cut off.

$$SIR \propto \text{size of groups}$$

**ortho effect** ⟶ o-substituted benzoic acid are more acidic than its meta and para isomers and benzoic acid itself irrespective of electronic effect of any group (+M, −M, H.C., +I, −I etc.)

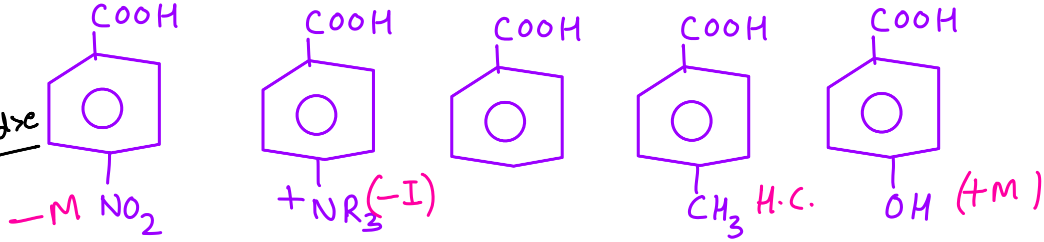


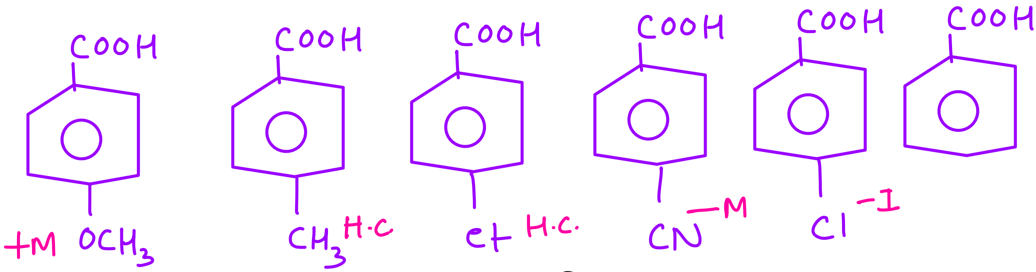

Effective conj. of $O^{\ominus}$ ⟵ (b > a) ⟶ cross conjugation of (=O)

(25)

a>b>c>d>e

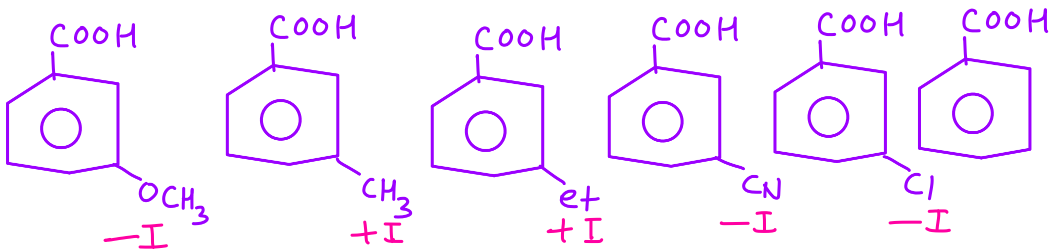



(26)



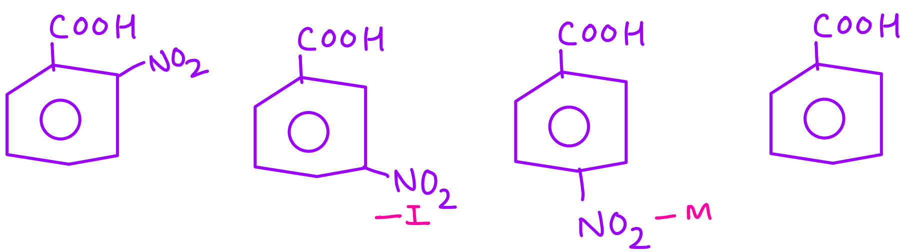

d > e > f > c > b > a

(27)



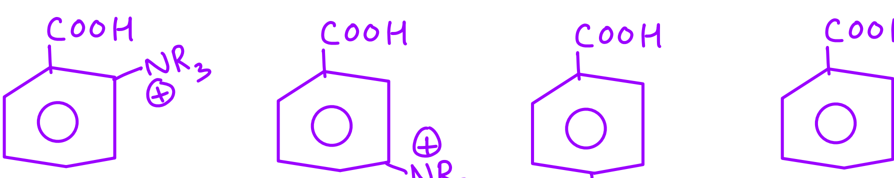

d > e > a > f > b > c

(28)

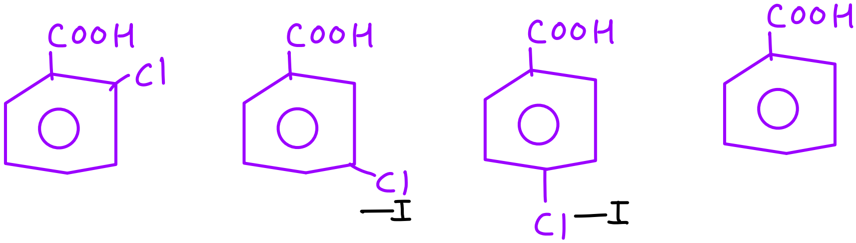



a > c > b > d

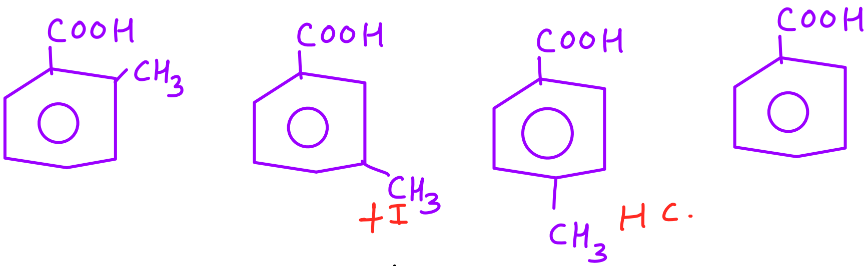
(29)



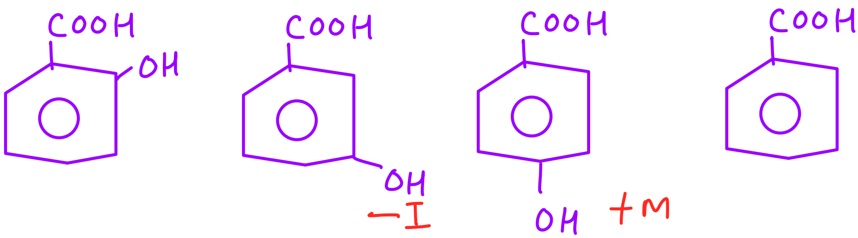

a > b > c > d

(30) 

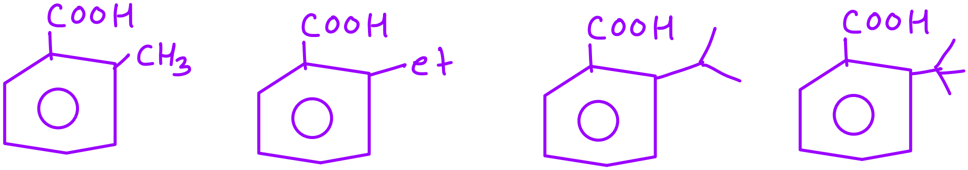

a > b > c > d

(31) 


a > d > b > c

(32) 

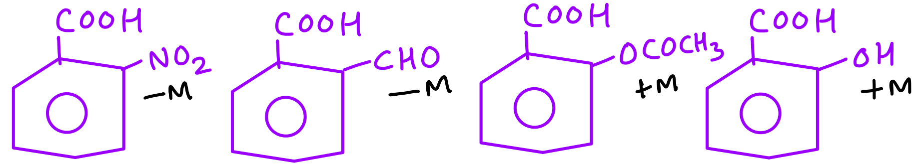

a > b > d > c

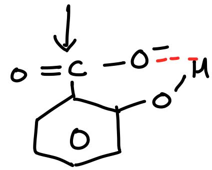
(33) 

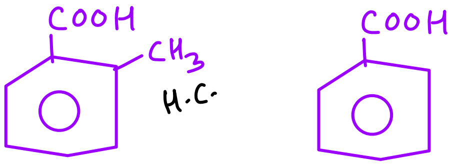

Acidity ∝ SIR ∝ size of group

d > c > b > a

(34)

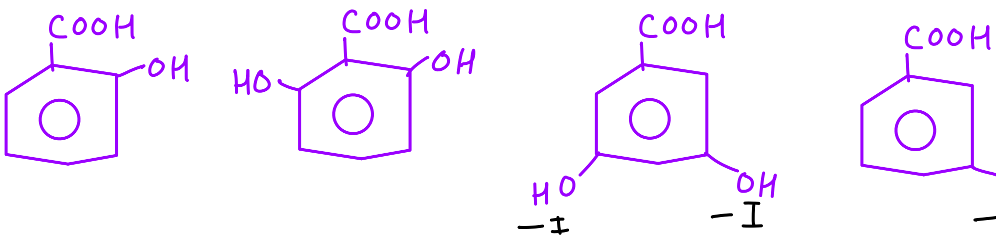


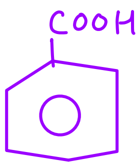




a > b > d > e > c > f

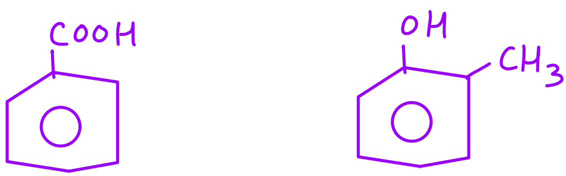
(35)



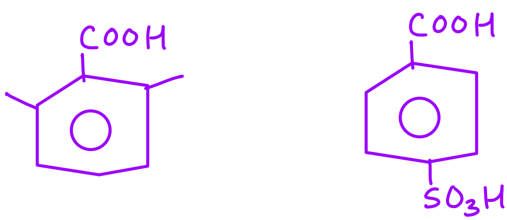

b > a > c > d > e

(36)




a > b

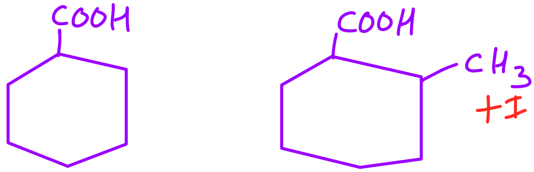
(37)




→ Acidic group

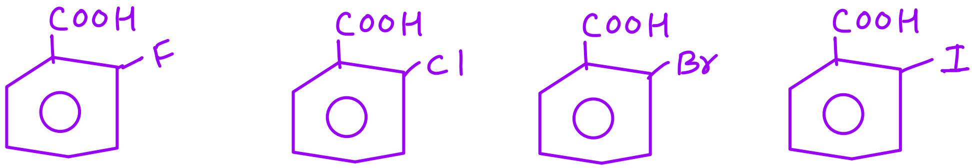
b > a

(38)



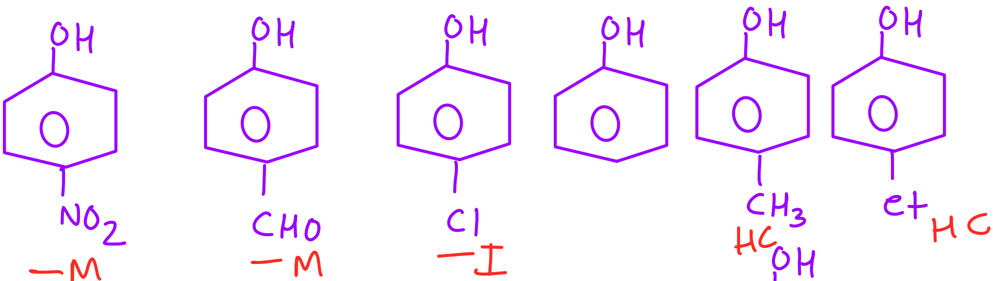

a>b

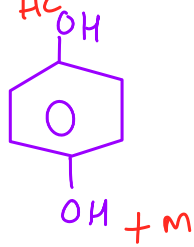
(39)




d > c > b > a

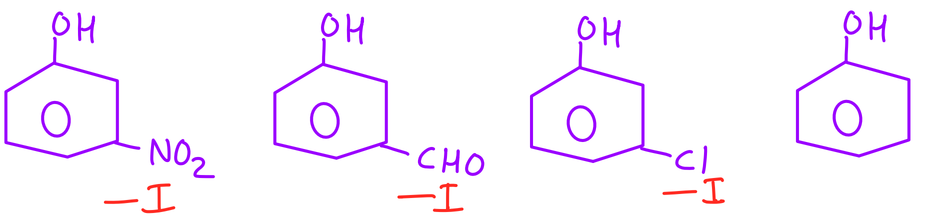
(40)

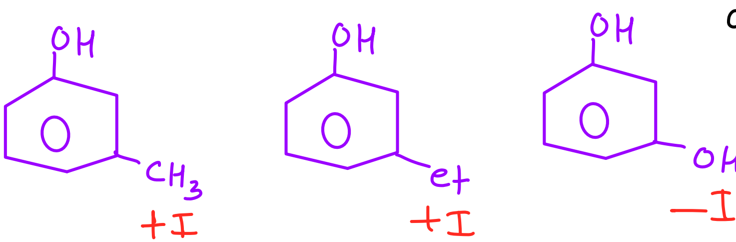



a > b > c > d > f > e > g

(41)

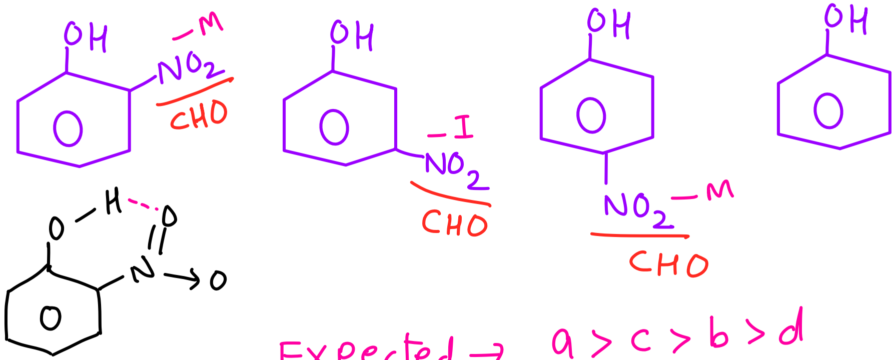



a > b > c > g > d >
e > f

Imp.

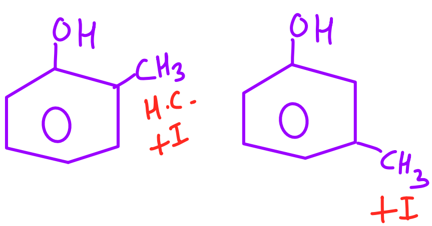
(42)

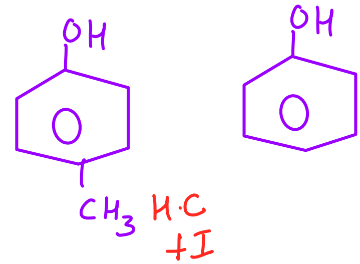



Expected → a > c > b > d

Actual → c > a > b > d

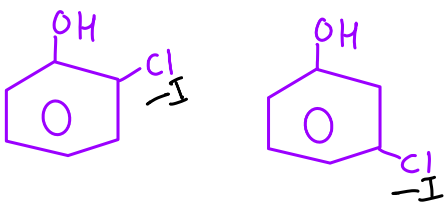
(43)

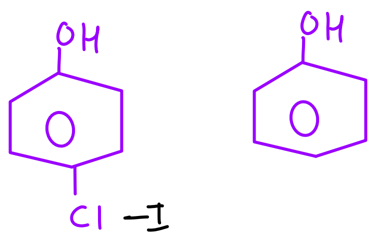



d > b > c > a

(44)

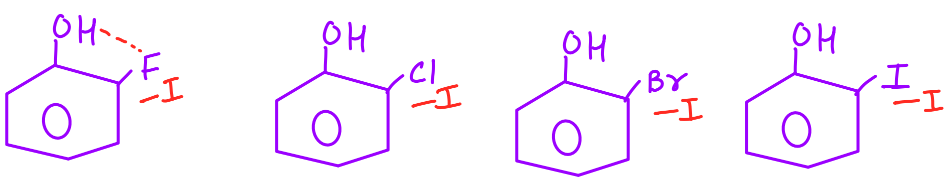



a > b > c > d

**

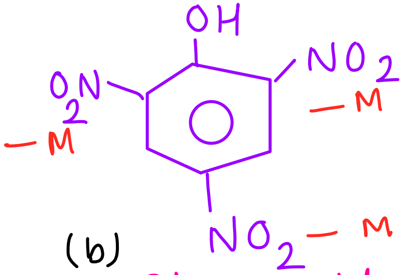
(45)




b > c > d > a

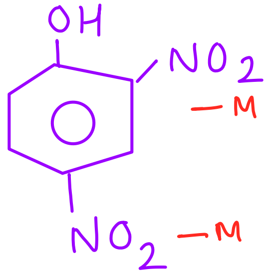
(46) R–COOH

(a)

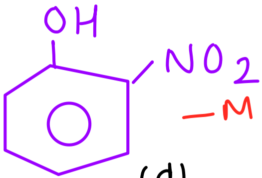



(b)

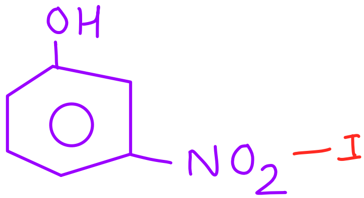
Picric acid




(c)



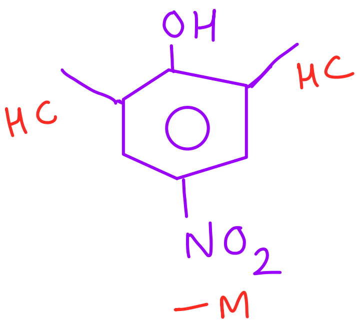

(d)

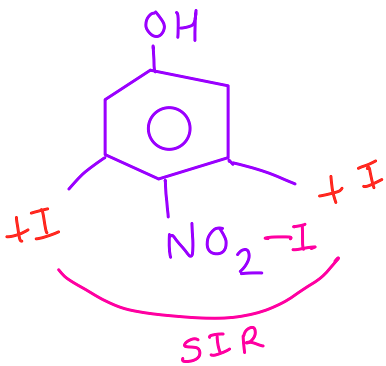



(e)

a > b > c > d > e

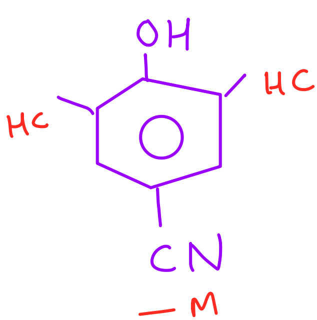
(47)

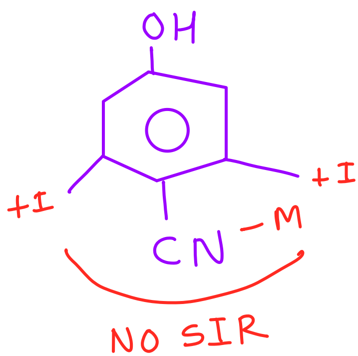



a>b

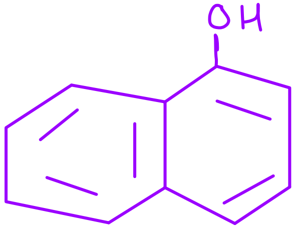
(48)




b>a

(49)



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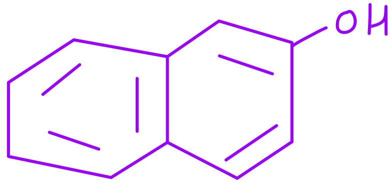


α– Naphthol

$\downarrow -H^+$

α– Naphthoxide

10 R.S.

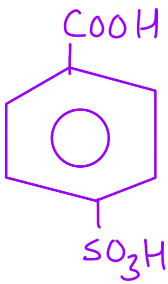
β– Naphthol

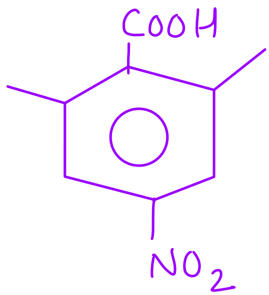
$\downarrow -H^+$

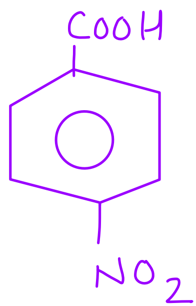
β– Naphthoxide

9 R.S.

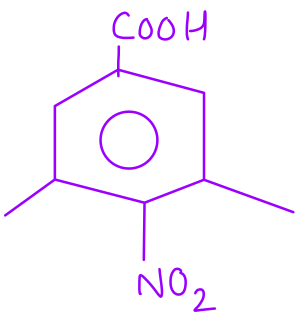
(50)







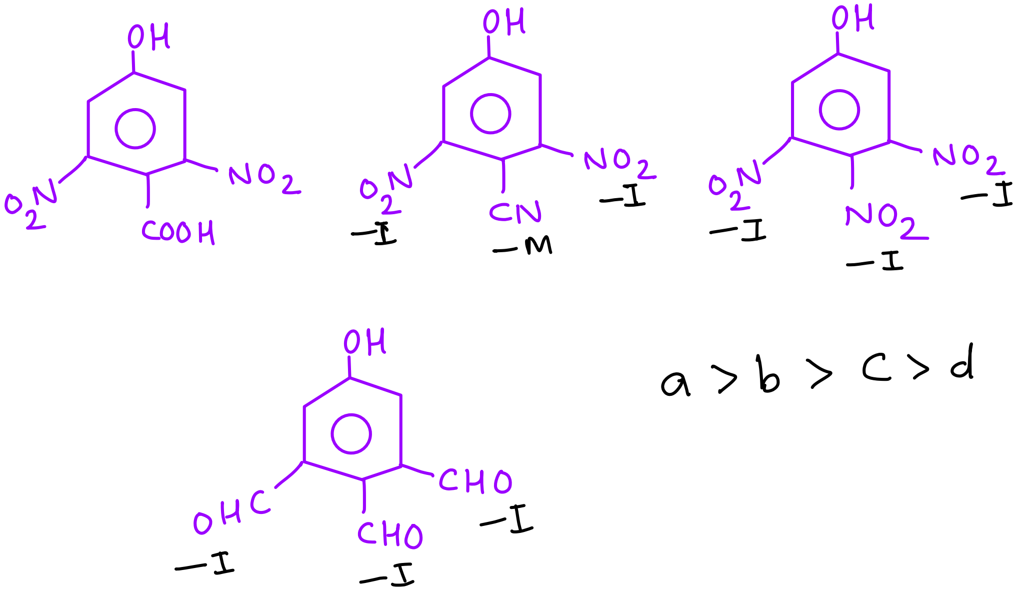
—M



—I

a > b > c > d

(51)




$a > b > c > d$

(52) $H_3O^+$ $H_2O$ $NH_4^+$ $NH_3$

$a > c > b > d$

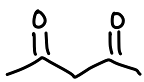
(53) $\underbrace{R}_{+I}-\overset{+}{N}H_3$ $\overset{+}{N}H_3$ $H_3O^+$

$c > b > a$

## Acidic strength order →

$HClO_4 > HI > HBr \simeq H_2SO_4 > HCl > Ph-\overset{O}{\overset{\|}{\underset{\underset{O}{\|}}{S}}}-OH >$

$H_3O^+ > HNO_3 > HF > HNO_2 > H-\underset{\underset{O}{\|}}{C}-OH > PhCOOH >$

$CH_3COOH > H_2CO_3 >$  $> HCN > NH_4^+ > Ph-OH$

$> CH_3-OH > H_2O > R-OH > CH\equiv CH > NH_3 >$

Toluene > benzene > $CH_2=CH_2 > CH_3-CH_3$