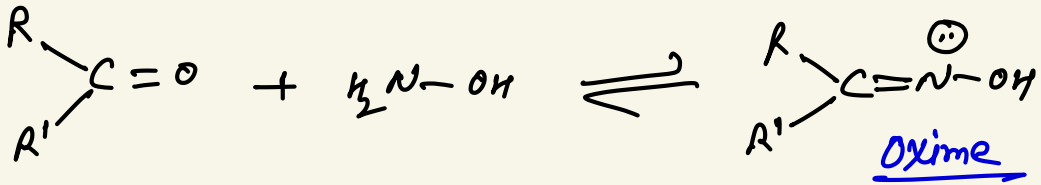
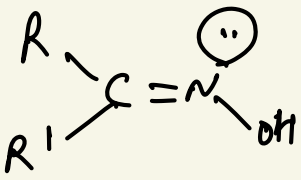
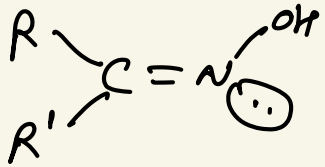

G
O
D
O
O
O
O
D

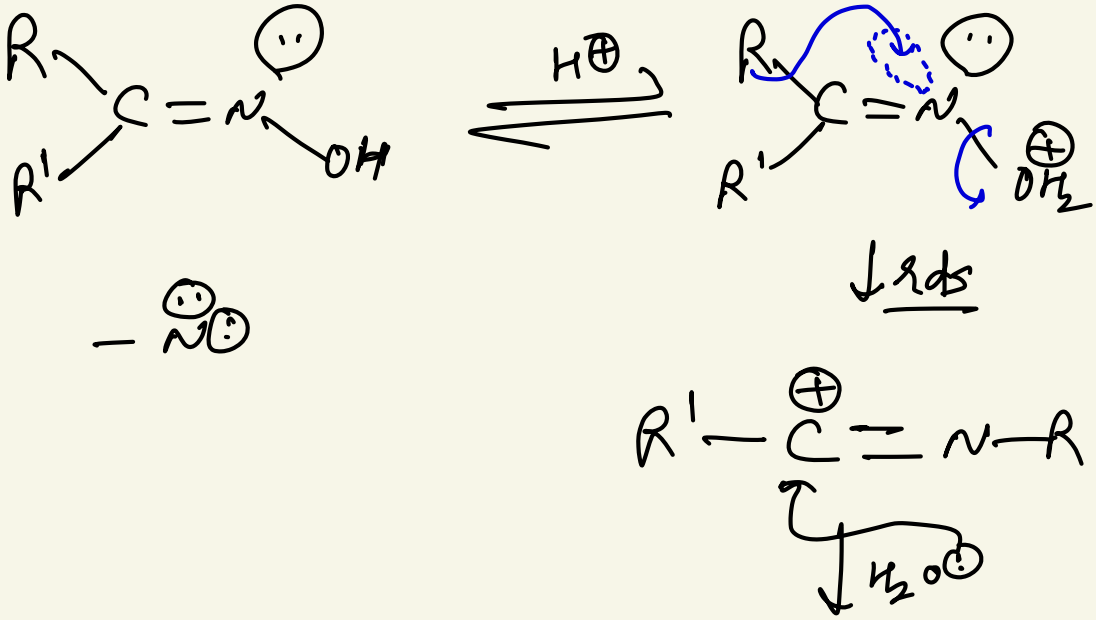
Backmann Rearrangement :-

ketoxime in presence of bronsted acid (Conc. H_2SO_4) or lewis acid (PCl_5, / P_4O_{10}) is converted into N- alkyl substituted amide. This Rxn is called backmann Rearrangement.

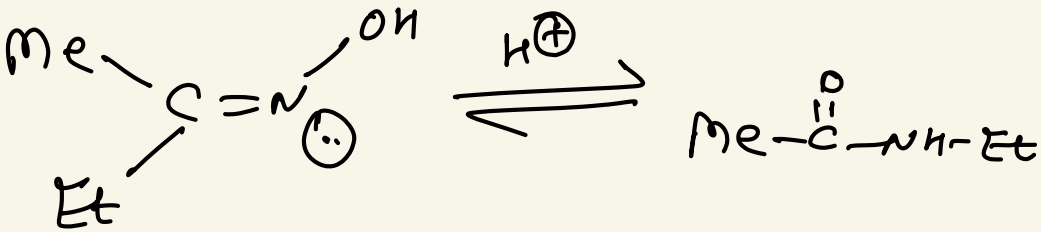




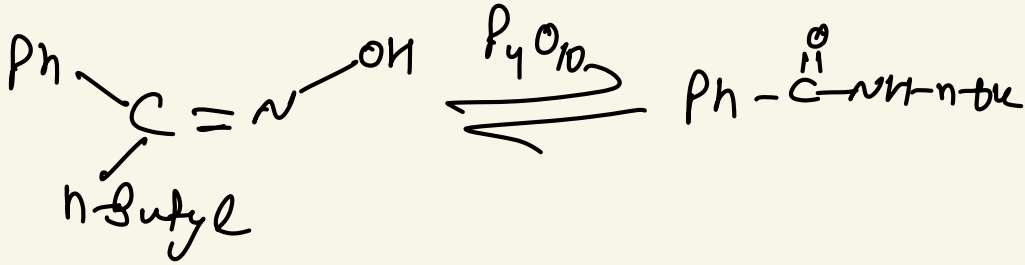



R
R'
C = N
OH
H⊕
OH2
rds
- N⊖
R' — C⊕ = N — R
H2O
R' — C(=O) — NH — R
R' — C(OH) = N — R

Q.

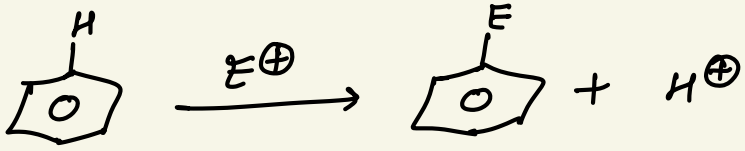

Me
Et
C = N
OH
H⊕
Me — C(=O) — NH — Et

Q.


Ph
n-Butyl
C = N
OH
P4O10
Ph — C(=O) — NH — n-Bu

Aromatic Compounds

Aromatic Rings Can Show aromatic electrophilic Substitution Reaction.



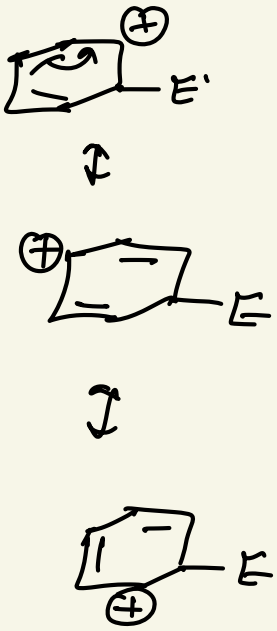
$E^{\oplus}$	
$NO_2^{\oplus}$	Nitration
$Cl^{\oplus}$	Chlorination
SO_3	Sulphonation
$R^{\oplus}$	friedal craft alkylation
$R-\overset{O}{\overset{\|}{C}}{}^{\oplus}$	friedal craft acylation
$N\overset{\oplus}{O}$	Nitrosation
$H-\overset{O}{\overset{\|}{C}}{}^{\oplus}$	formylation
$PhN_2^{\oplus}$	Diazo Coupling

Mechanism:-

σ-complex.

OR

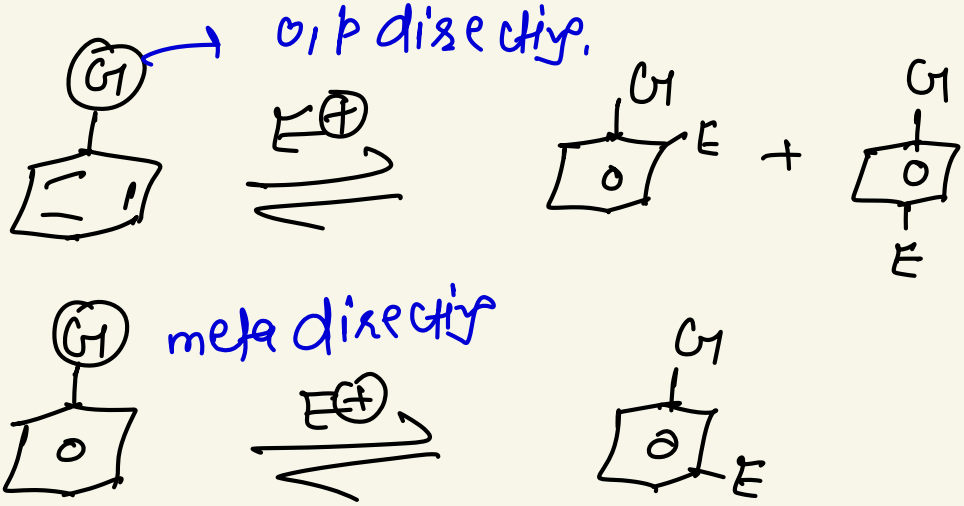
Wheland intermediate



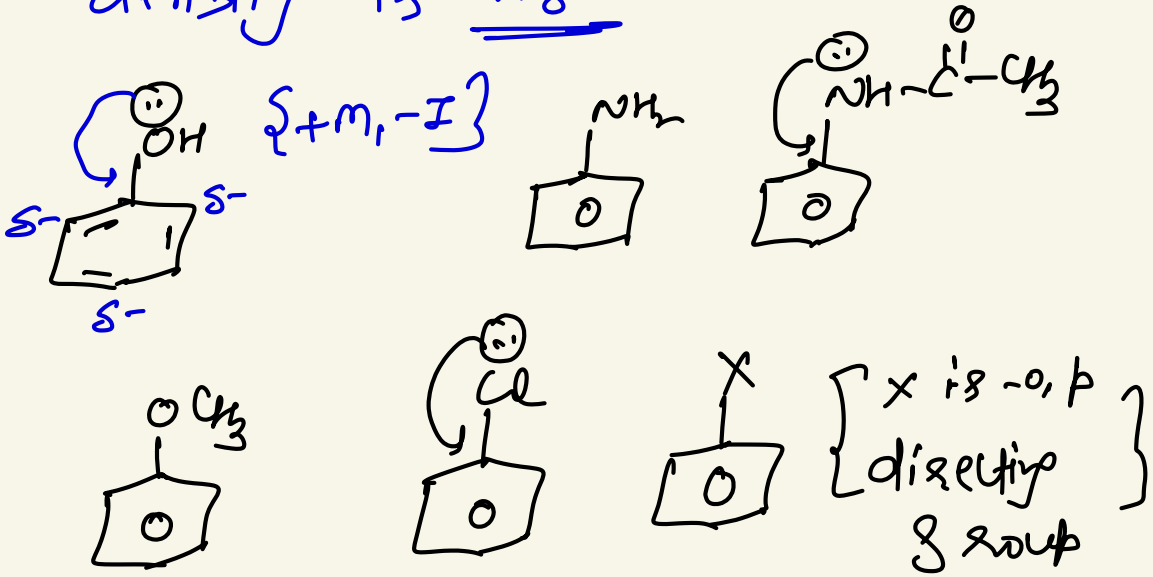
1st step is R.D.S.

$C^{\oplus}$ forms in R.D.S.

* E.D.G. Connected to benzene ring shows faster $E^{\oplus}Ar_{SE}$ Rxn than benzene as intd. is more stable in the former one.



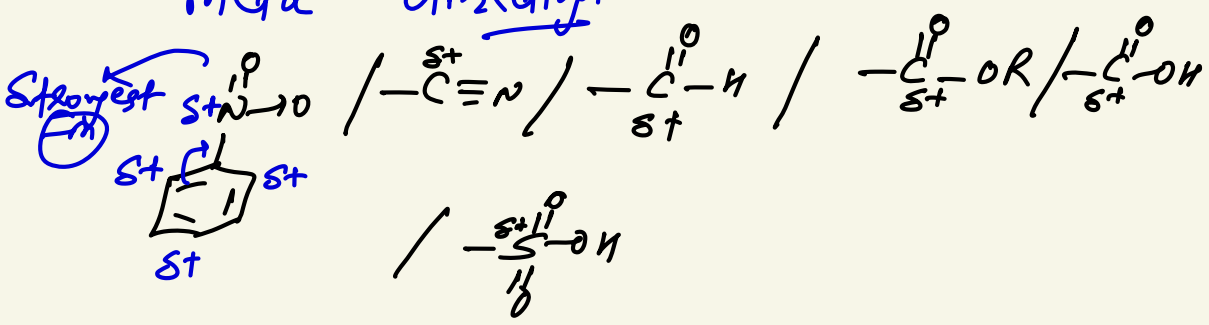
$E^{\oplus}$ attacks that position where e^- density is High.



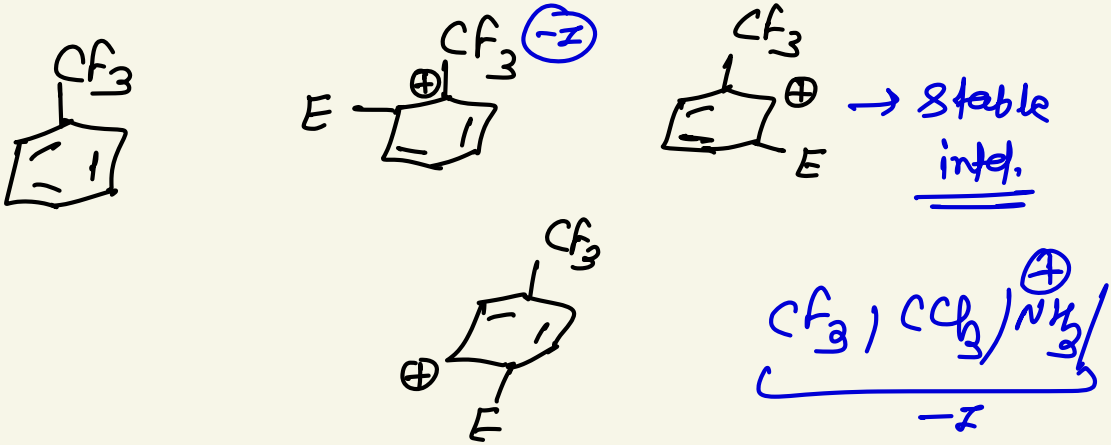
Groups having +R effects are -o/p directing.

Groups having −R effects are meta directing.

Strongest (−R)



Groups showing only −I effect are also meta directing.



→ Stable int.

CF_3, CCl_3, $\overset{\oplus}{N}H_3$ (−I)

Groups showing (+I, +H) are −o, p directing.

Activating Groups:-

Groups which increases e⊖ density in the ring or increase e⁻ density at some position of benzene ring are activating groups.

{ +R, +I, +H } → activating groups.

$-O^{\ominus}$, $-OH$, $-NH_2$, $-NH-\overset{\oplus}{C}-CH_3$,

NR_2, $-OR$, $-O-\overset{\oplus}{C}-CH_3$, $-CH_3$,

$-C_2H_5$, $-CMe_3$

Deactivating Groups:

Groups which overall decrease e⁻ density from the ring:-

{-M, -I}

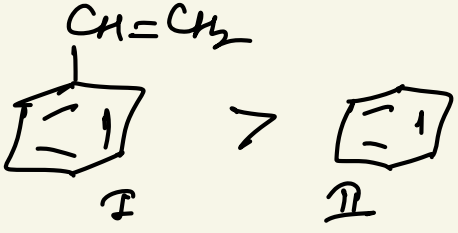
$-NO_2$, $-\overset{\overset{O}{\|}}{C}-H$, $-CN$, $-\overset{\oplus}{P}H_3$,

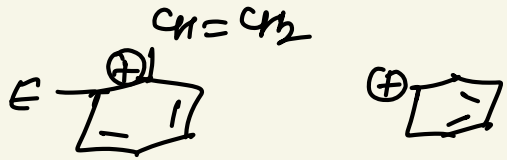
$-\overset{\overset{O}{\|}}{C}-OH$, $-\overset{\overset{O}{\|}}{C}-O-\overset{\overset{O}{\|}}{C}-R$, $-\overset{\overset{O}{\|}}{C}-Cl$,

$-CCl_3$, $-CF_3$, $-\overset{\oplus}{N}H_3$,

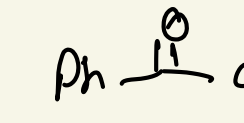
$-Cl$ / $-X$ {-I > +M} deactivating. -o,p directing.

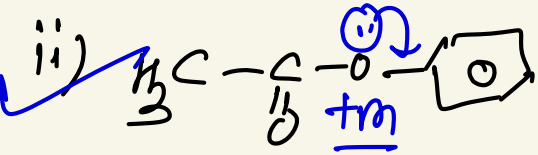
$-CH=CH_2$

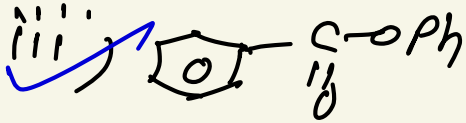


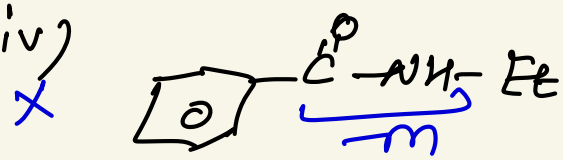


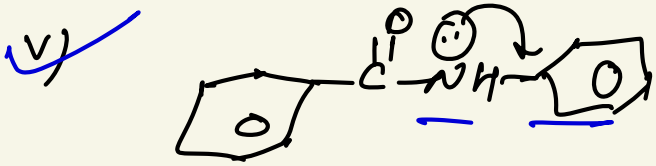
Q. find No. of compounds which are more reactive than benzene towards $E^{\oplus}$ Sub^{n} Rx^{n} ?

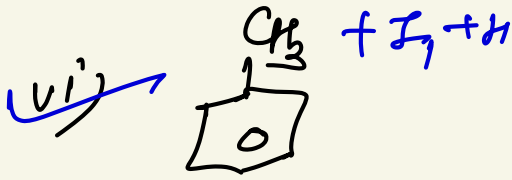
i)  −m

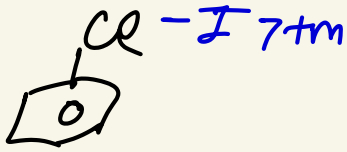
ii)  +m

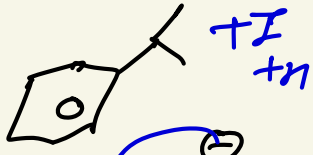
iii) 

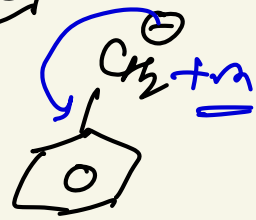
iv)  ✗

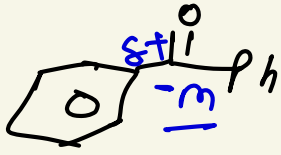
v) 

vi)  +I, +H

vii)  ✗

viii)  +I, +m

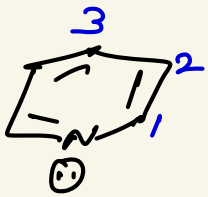
ix)  +m

x)  ✗

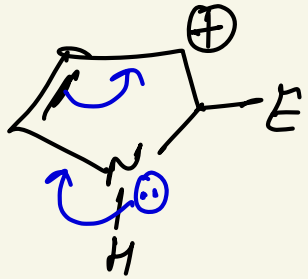
Q. Attacking $E^{\oplus}$ site :-

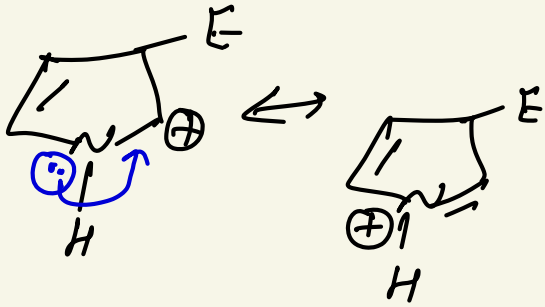
Pyrrole

furan.

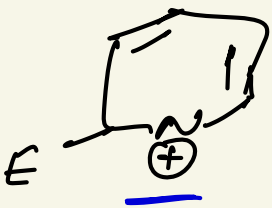


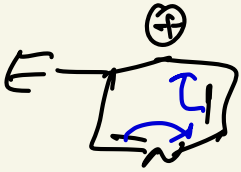
Pyridine

* 

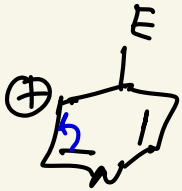


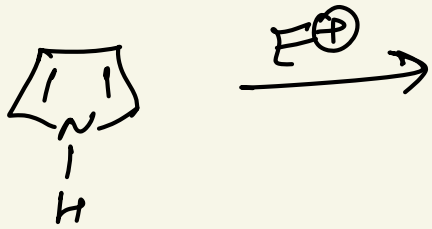
more stable intd.

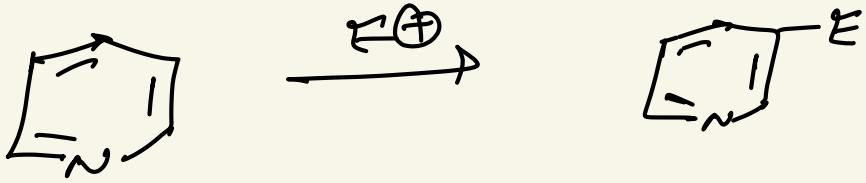


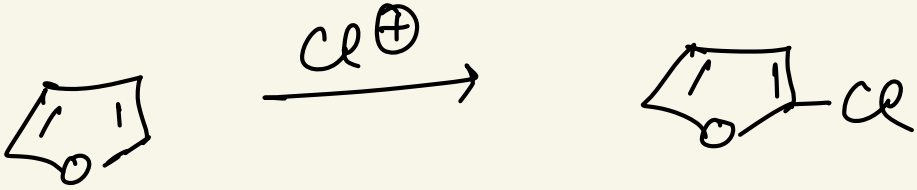


more stable intd.

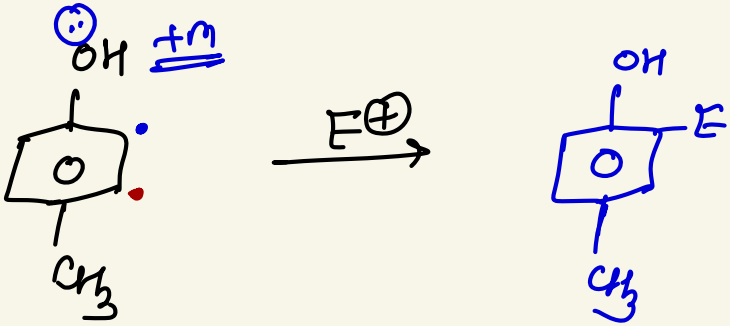




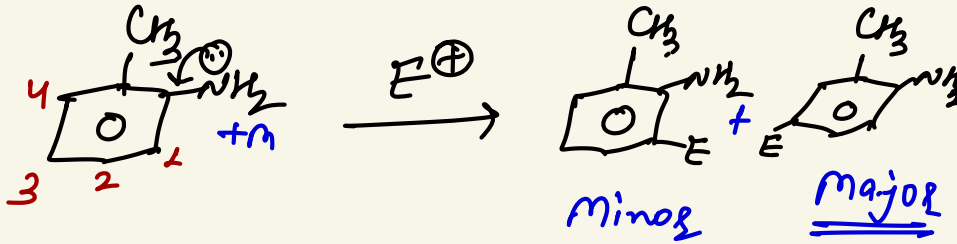




Q-



Q-

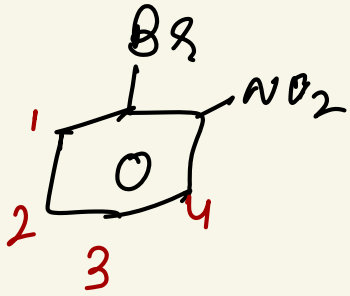


Minor

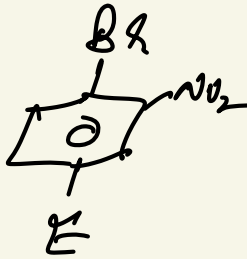
Steric Crowding

Major

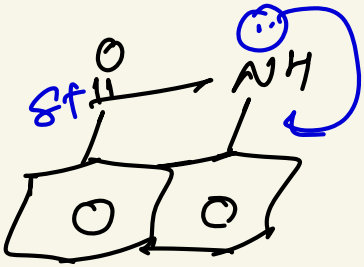
Q.



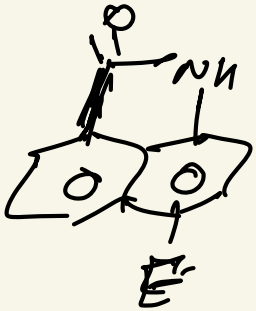
$E^{\oplus}$



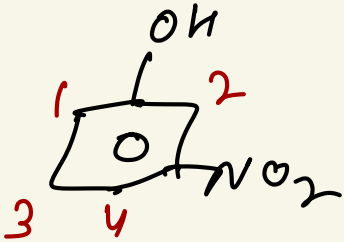
Q.



$E^{\oplus}$



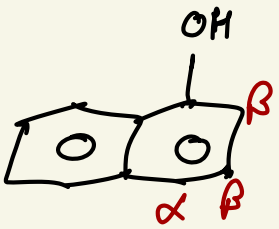
Q.



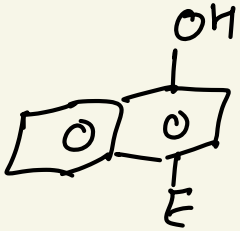
$E^{\oplus}$

1, 4

Q.

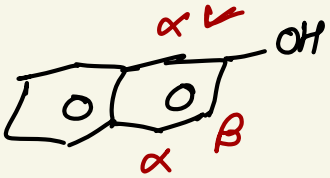


$E^{\oplus}$

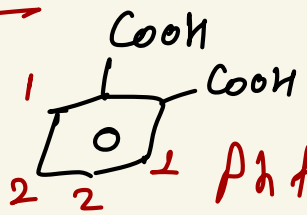


α-Naphthol

Q.



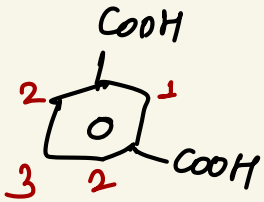
Q.



$E^{\oplus}$ ⟶ (2)

Phthalic acid

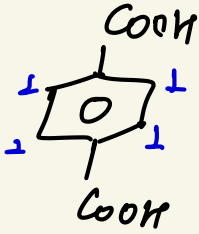
Q.



(3)

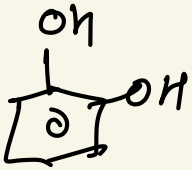
Isophthalic

Q.



(1)

Terephthalic



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