

Aromatic Electrophilic Substitution

3rd Sem
Lecture – 3
Paper – CC7

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Aromatic Electrophilic Substitution

summary of directing and activating affects

Electronic effect	Examples	Activating / Deactivating	Direction
Donation by conjugation ($+R \rightarrow I$)	$-O^-$, $-NR_2$, $-NHT_2$, $-OH$, $-NHCOOR$, $-OR$, $-OCOR$ -Ar etc	Very activating	ortho + para
Donation by I^- -effect and hyperconjugation	$-R$ (alkyl)	activating	mostly O _{dp} but some meta
Donation by conjugation but withdraw by $-I$ -effect	$-F$, $-Cl$, $-Br$, $-I$, $-NO_2$, $-CH=CH-NO_2$, $-CH_2 \times$ etc	deactivating	ortho + (mostly) Para
Withdrawal by Inductive effect	$-CF_3$, $-NR_3^+$	deactivating	meta-only
Withdrawal by Conjugation	$-NO_2$, $-CN$, $-COR$, $-SO_3H$, $-COOH$, $-COCl$, $-CHO$	very deactivating	meta only

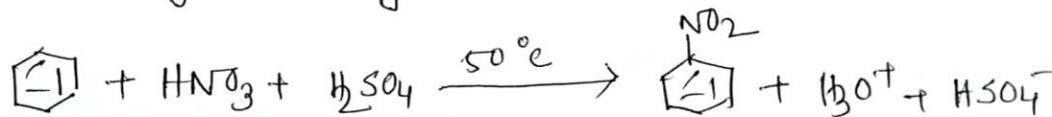
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Nitration

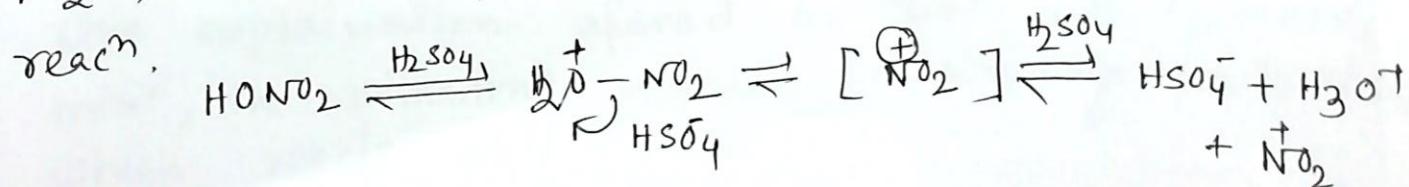
Generally nitration to the aromatic ring is done by following reagents.

- a) A mixr of Con. HNO_3 & Con. H_2SO_4 (M.A)
 - b) fuming HNO_3 in Ac_2O
 - c) HNO_3 in glacial AcOH
 - d) Dilute HNO_3

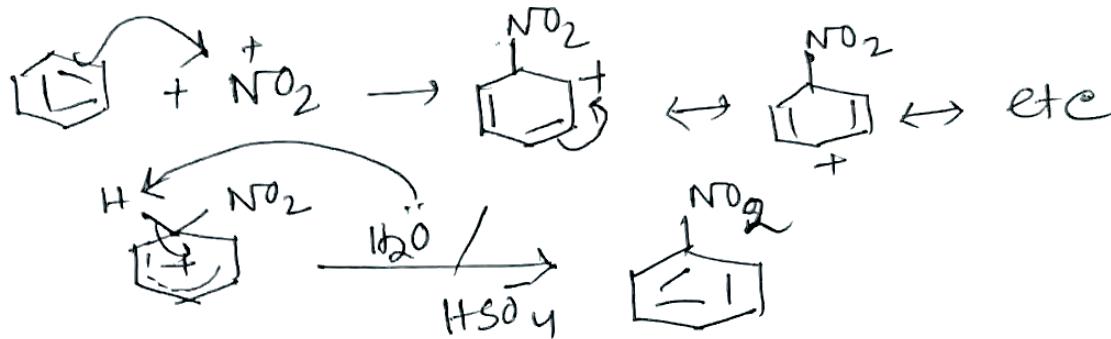
a) Mixed acid :- Benzene reacts slowly with conc. HNO_3 to yield nitrobenzene. But the reaction is much faster if it is carried out by heating with mix^r of conc. HNO_3 & conc. H_2SO_4 .



The reaction involves electrophilic attack of nitronium ion NO_2^+ , which is produced under the condition of HgSO_4 .



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Role of H_2SO_4 :-

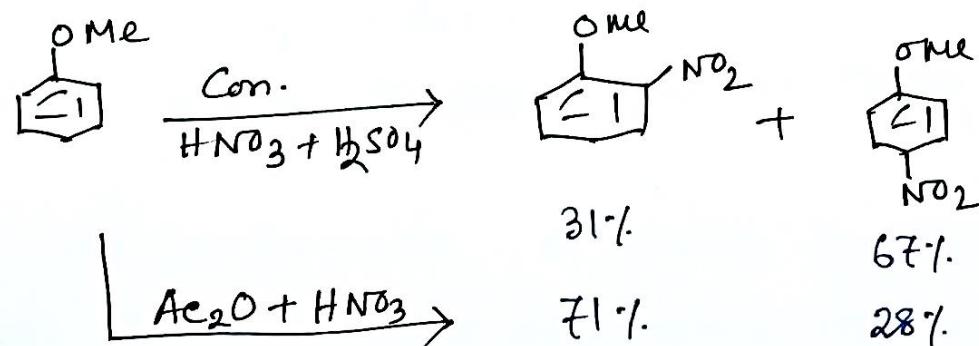
- (i) To facilitate the formation of NO_2^+ by making the medium strongly acidic
- (ii) The bisulphate ion (HSO_4^-) which is produced in the reactⁿ mixr acts as a base to remove proton from σ -complex.

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5) Mix^r of Con. HNO_3 in Ac_2O :-

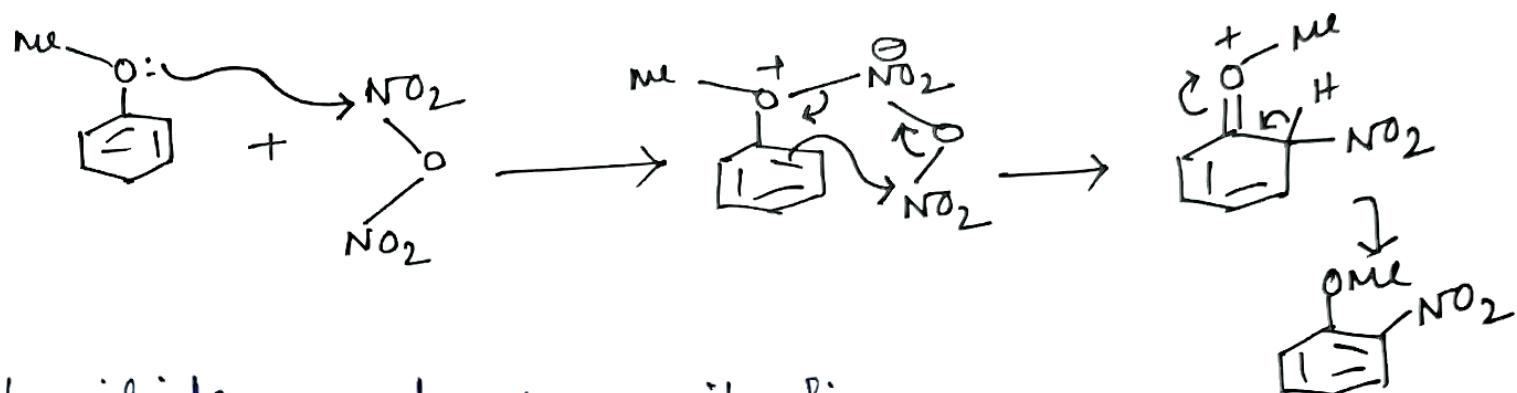


An interesting feature of this reagent is usually high proportion of ortho-isomer that is obtained when the side chain contains a hetero atom.



One explanation offered is that with $\text{Ac}_2\text{O} + \text{HNO}_3$ mix^r, the nitrating species is dinitrogen pentoxide, which reacts as follows.

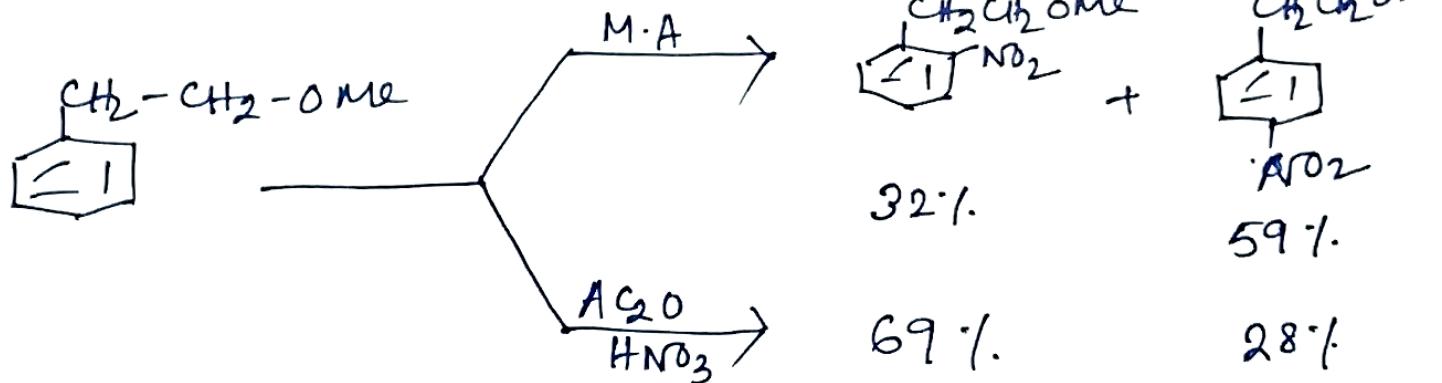
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Q.1 Acetanilide undergoes nitration by $\text{Ac}_2\text{O} - \text{HNO}_3$ predominantly at the sterically hindered ortho position. Explain.

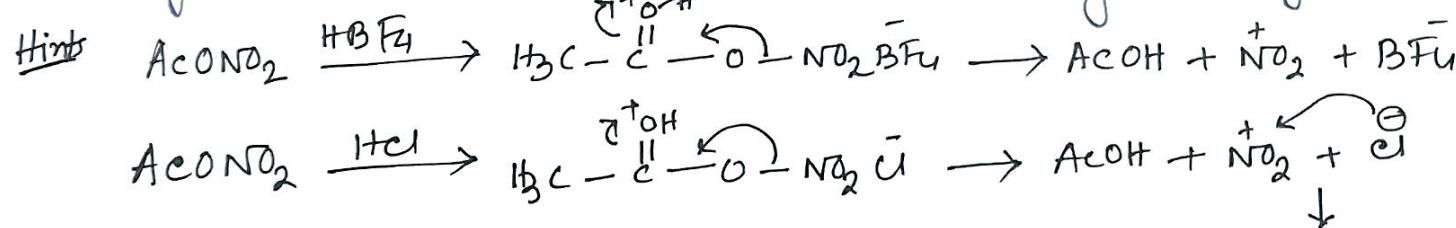
Q.2

Explain:
the observation
→



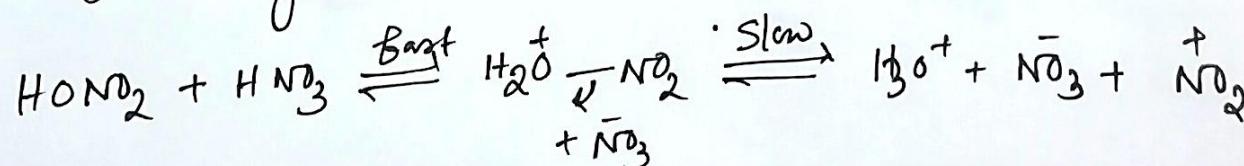
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Q.3 Why is nitration with acetyl nitrate accelerated by addition HBF_4 but retarded by adding HCl ?



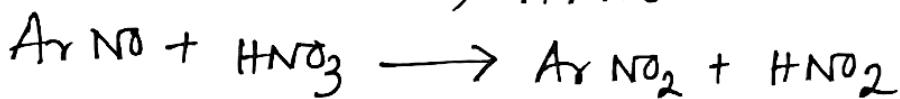
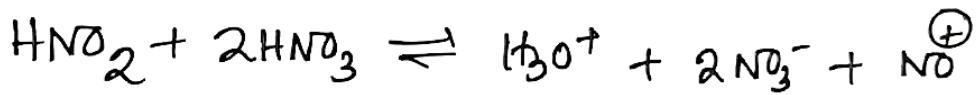
BF_4^- is non nucleophilic it does not react with NO_2^+ , but Cl^- is nucleophilic, it reacts with NO_2^+ to form nitryl chloride. Hence the concentration of NO_2^+ in HCl is lower than HBF_4

Conc. HNO_3 :- The performance of c. HNO_3 in the nitration of benzene is poor. The electrophile NO_2^+ is obtained in poor amount by the dissociation of HNO_3 by the following two steps.



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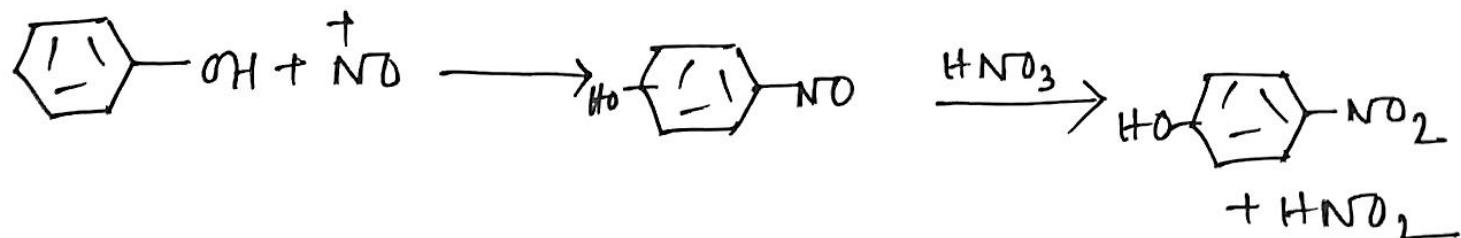
Dilute HNO_3 :- Dilute HNO_3 contains a negligible concⁿ of the nitrous acid (HNO_2) and it gives rise to the nitrosonium ion (NO^+), which nitrosates the aromatic ring. The nitro compd is oxidised by nitric acid to the nitro compd which generates more nitrous acid to continue the chain reacⁿ.



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* Highly reactive aromatic compd such as phenol, amine are found to undergo nitration by dil. HNO_3

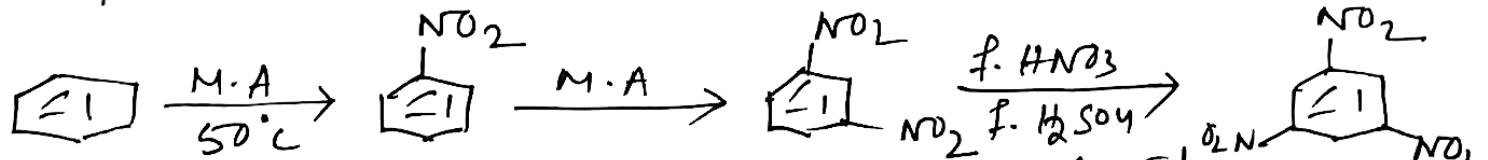
It has been found that the nitration of phenol and amine is accelerated by the presence of HNO_2 . Evidence for this is based on the observation that when phenol is nitrated in the presence of little HNO_2 of P nitrophenols are formed in the ratio of 7:3. When large amount of HNO_2 is added, then the ratio becomes 1:9. It is therefore believed that the nitrous compd is formed first and this is then oxidised to the nitro compound.



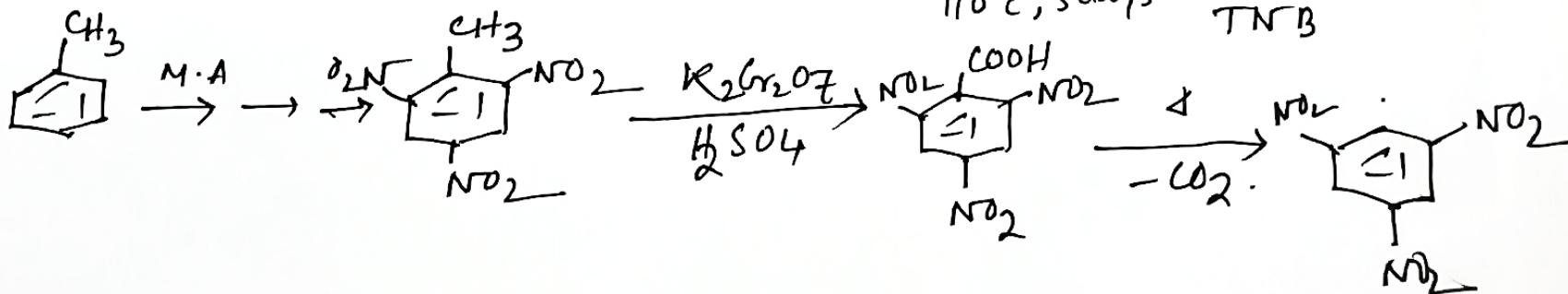
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Different nitration procedure for the synthesis of various compound.

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BnT



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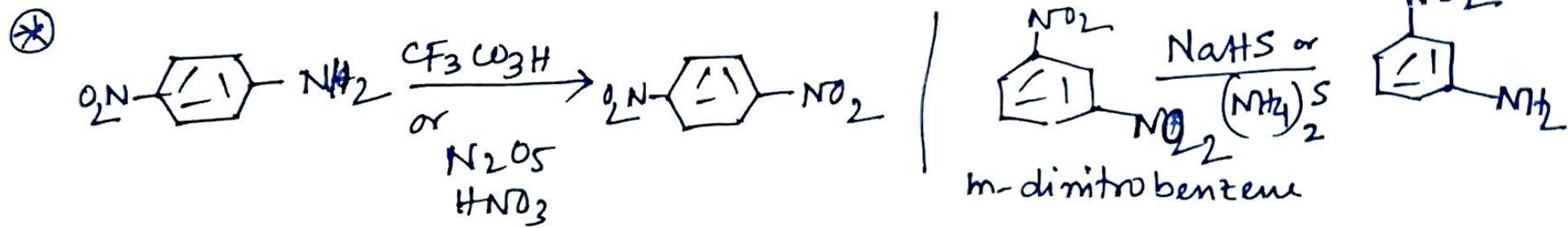
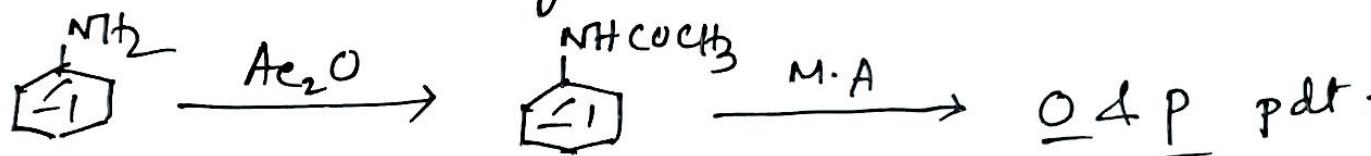
Nitration of aniline by M.A. is difficult because

- (i) $-\text{NH}_2$ group is strongly activating, under M.A. condition the ring becomes oxidised, ~~by~~ The yields are poor.

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(ii) Under acidic condition $-\text{NH}_2$ gr. becomes protonated and hence converted to $-\text{NH}_3^+$ which is strongly deactivating. Therefore we used less acidic condition.

But if we protected the $-\text{NH}_2$ gr by acetylation then nitration by M.A will be easier.

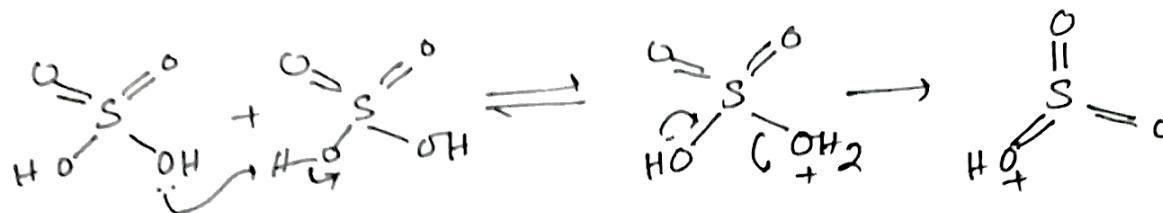


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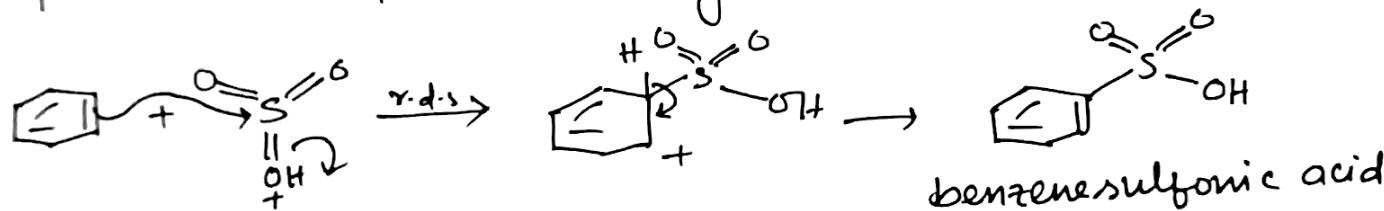
Sulfonation

Benzene itself reacts slowly with H_2SO_4 but rapidly with oleum ($H_2S_2O_7$) or by SO_3 in inert solvents.

With H_2SO_4 : - The reacⁿ starts with the protonation of one molecule of H_2SO_4 by another and loss of a H_2O molecule. Similar to the first step in nitration.

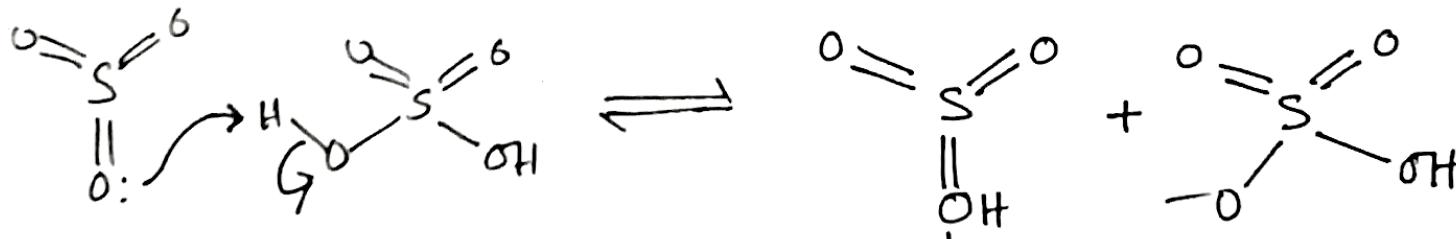


The cation produced is very reactive and combines with benzene by the same mechanism as in nitration, slow addition to the aromatic π -system followed by rapid loss of proton to regenerate the aromaticity.



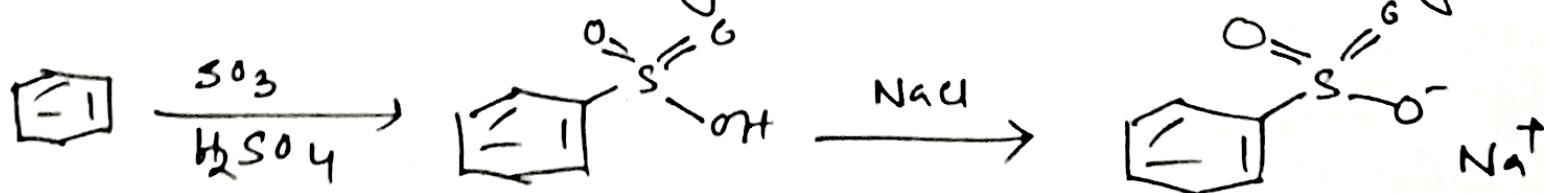
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with $\text{H}_2\text{S}_2\text{O}_7$ (SO_3 in H_2SO_4) $\ddot{\text{o}}^-$



2nd step is similar as above

- * Sulfonic acid are strong acids, about as strong as $\text{H}_2\text{S}_2\text{O}_7$



Crystalline sodium benzene sulfonate.

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