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STUDY THE NULEOPHILIC- DISPLACEMENT REACTIONS OF SOME AROMATIC COMPOUNDS AND THEIR APPLICATIONS TO AGRICULTURAL AND MEDICAL FIELDS

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Abstract:-Nucleophiles are the reactive species which are attacked to Carboniumion as substrate in presence of physical laboratory conditions, refractants and solvation to explain their mechanism how to displace the leaving group (s) as nucleophile(s). Nucleophile may be electron with drawing group by changing the environmental conditions. Few examples of nucleophiles are, $\bar{X}$, $\bar{C}N$, $\bar{O}H$ $\bar{N}H_2$, $\bar{C}H_2$, N= $N^{\ominus}$, $\bar{O}R$ etc. at higher temperature, under pressure, to study their Steriochemistry, inductive effect, mesomeric effect, conjugation hyper conjugation with σ and Π electrons of aromating ring. How they undergo nucleophilic displacement reactions readily. If a strong electron withdrawing group (s) is present at O, P, positions on Aromatic Compounds and their detail mechanism.

Keywords: Nucleophiles, Electrophiles, Carboniumion, Carbanions, displacement, Aromatic compounds, Mechanism, Electron releasing, Electron with drawing groups, π & σ bonds, resonance, inductive hyperconjugation effects, stability, Nitrogroup, Highertemperature, underpressure. Catalyst, Substitution, Agriculture, Medicalfields, O, P, M, Refractants, ArSN2, ArsN1.

INTRODUCTION:

Study the nucleophlic displacement reaction of some Aromatic Compounds, how the nucleophiles are displaced by changing the conditions on Aromatic compounds like Benzene, Pyridine etc. at the various positions Author has utilized by secondary data's to study the nucleophilic displacement reactions of some Aromatic Compounds and their Applications for Agriculture and Medical fields.

1.1 THE FORMATION OF AROMATICHALIDES AND THEIR MECHANISM :

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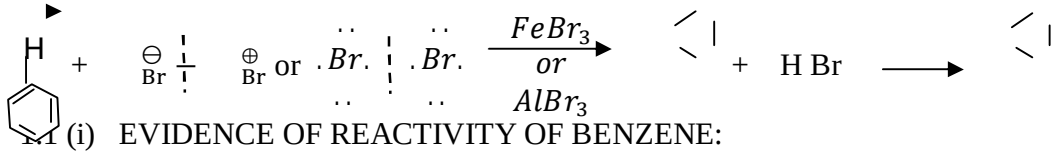
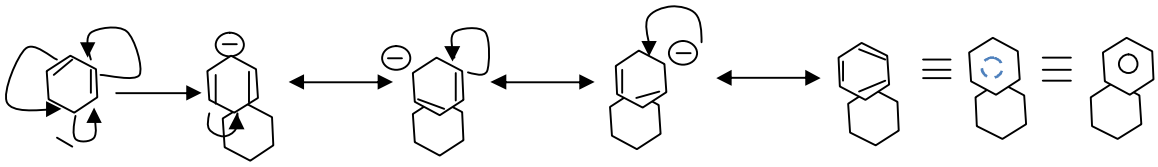


1.1 (i) EVIDENCE OF REACTIVITY OF BENZENE:

Benzene is highly reactive species, it contributes canonical structure by Bayer's theory. The movements of Π electrons towards a positive charge. It obyes the Hukel-Rule (in 1865) [4n + 2] Π electrons where n = 0, 1, 2, 3 …… etc. It is readily abstracted by $_{Br}^{+}$ to form bromobenzene. It follows electrophilic substitution as well as freeradical and nucleophilic substitution reaction.

i)

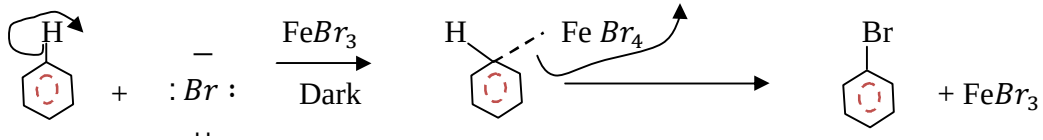


ii) $:\ddot{Br}. \quad \ddot{Br}: \xrightarrow[\text{or Lewisacid}]{\text{Uv light}} :\overset{\ominus}{\ddot{Br}}: + :\overset{\oplus}{\ddot{Br}}:$ Freeradicals are Generated

Homolysis.

iii) $:\overset{+}{Br}: + Fe\,Br_3 \xrightarrow{\text{Dark}} [FeBr_4^-]$

iv)



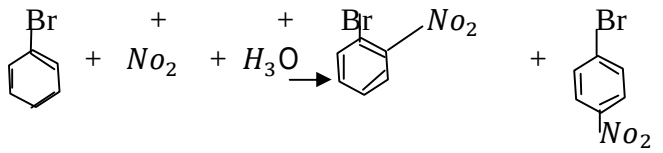
$\overset{\oplus}{Br}$ act as electrophile it displaces protonium ion from benzene to from Bromobenzene and bromide leaving.

1.1(ii) Nucleophile undergo nucleophilic displacement reactions readily. If a strong electron withdrawing group like Nitroniumion $(\overset{\oplus}{N}o_2)$ Present at O or P positions what happens ? First to know the formations of $\overset{\oplus}{N}o_2$ from nitrating mixture,

a) Ho-$\overset{\oplus}{N}o_2$ + $2H_2So_4 \underset{}{\overset{273^0K_1}{\rightleftharpoons}}$ 2 [$H So_4^-$] + $\overset{\oplus}{H_3}o$ + $\overset{\oplus}{N}o_2$

b) H_3o ⇌ H + H_2o

c) $HS\bar{o}_4$ + $\overset{\oplus}{H}$ ⇌ H_2So_4

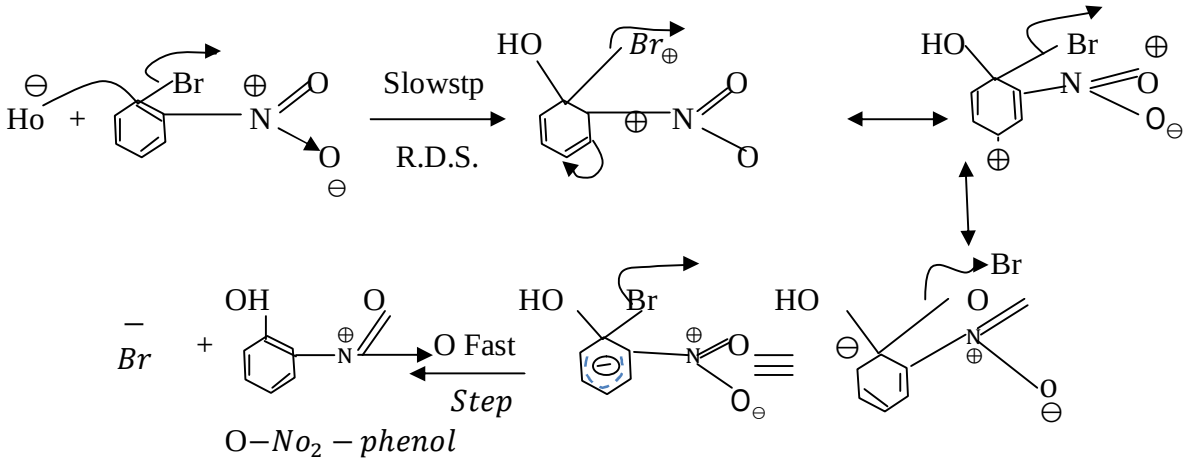
d) 

+ H_2o (Major pdt) P- $No_2 - Br -$ Benzene

Minor Pdt
O$-No_2 - Bromo\ Benzene$

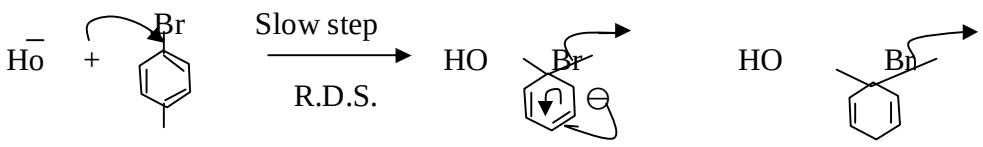
1.2. EFFECT OF No_2 GROUP ON HALOGEN SUBSTITUTED AROMETIC COMPOUND AS BASIC UNIT BENZENE:

1.2 i) If $\overset{\oplus}{No_2}$ group Substituted at O – position with (respective) related to bromogroup to the Benzene and its mechanism is as follows;



O$-No_2 - phenol$

1.2 (ii) If $\overset{\oplus}{No_2}$ group present at P-Position related to bromo group to the benzene and its mechanism is as follows.



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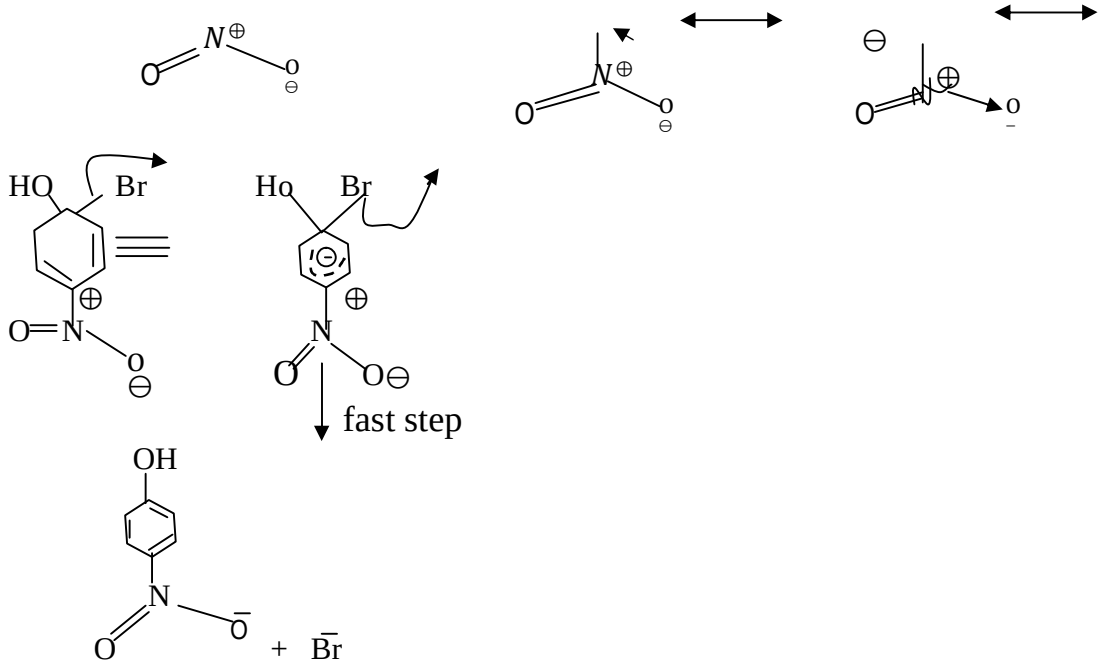
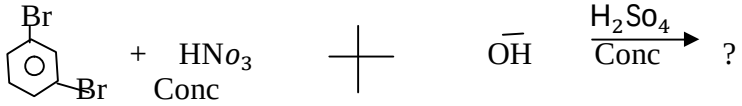


P-No_2 phenol 1

Both reactions follows ArSN2 Mechanism. In both above said reactions the Carbanions formed by the attack of nucleophile $\bar{O}H$, gets stabilized at O & P positions due to stronger electron with drawing No_2 group (s). Resonating structures do not have negative charge at meta position due to less electrondensity i.e 0.7, hence the presence of electron with drawing group at meta position no effect on reactivity this is due to the resonace and inductive effects.



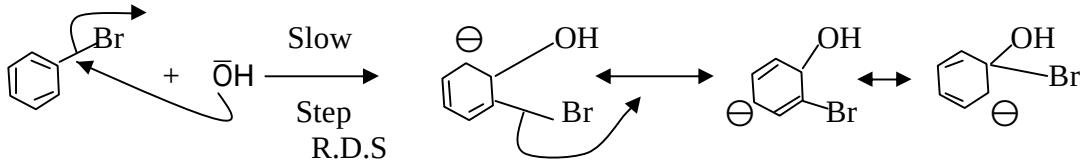
Greater the number of $\bar{e}$ (electron) withdrawing group (s) ($-No_2$) at 'O' and 'P' positions in bromobenzene greater the corresponding phenols due to hyper conjugation, resonace lonepair of $\bar{e}_{-s}$ (electrons) on Br atom in Benzenedibromide is in Conjugation with π $\bar{e}_{-s}$ of aromatic compounds - C- Br bond has trigonal hybridised (sp^2) having greater % s character (33.33%), shorter the bond length (169 pm) stronger is the bond and greater is the energy required to Benzenedibromide break the covalent bond. To break – C Br bond in (aryl halides) greater energy is required, hence (arylhalidesare) less reaction Benzenedibromide is less reactive.

The lone pair of electrons of Br atom in bromobenzene is in conjugation with π $\bar{e}_{-s}$ of the ring due to the resonance, the C-Br covalent bond in bromobenzene possesses unsaturated character. The ionization carboniumion produced due to the self ionization of C-Br in bromobenzene will not be stabilized by resonance which is rejected the possibility of ArSN1 mechanism because the backside attack of nucleophile is blocked by π $\bar{e}_{-s}$ of aromaticring which is ruled out ArSN2 mechanism. Greater the number of $\bar{e}$, withdrawing groups (-No_2) at O & P, Positions in dibromenzene greater is the reactivity.

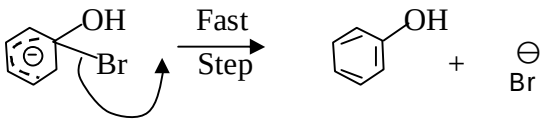
iii) THE SNAR MECHANISM:

1.2 iii) The SN Armechanism Consists of two steps.

Set P –I



Set P –II



First step slow, rate determining (R.D.S.). It is similarly the tetrahedralmechanism. In these cases the attacking spe̅cies OH forms a bond with the substrate the giving an intermediate and leaving group $\overset{\ominus}{Br}$ fascilitates. It is labeled by I.U.P.A.C. AN + DN Same as tetrahedral mechanism. AE + DE for the arenium mechanism. It is found where activating groups are present on the benzene ring.

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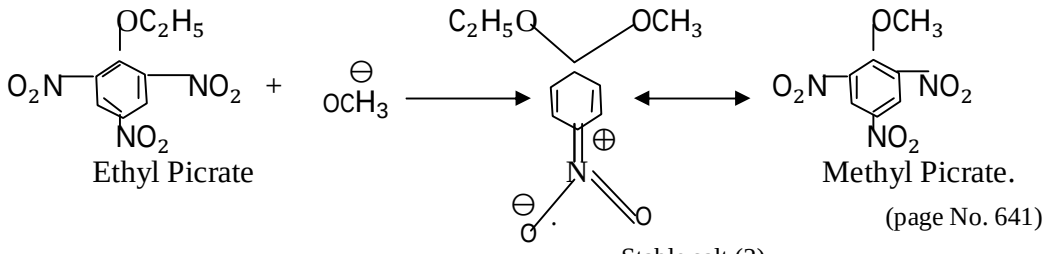
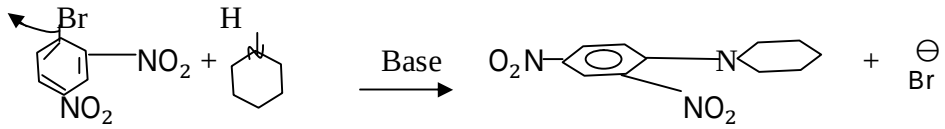
1.2 (iv) EVIDENCE FOR THE MECHANISM BY SOMMELET HAUSER, VONRI, CHTER SOMM, TSCHISCHIBABIN, MEISENHIERMOR, JAKSON & SMILERS ETALS :



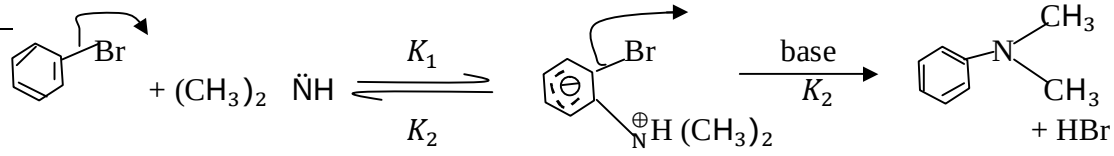
(page No. 641)

The soluble salt (2) called meisenheimer or Meisenheimer Jackson salts (1902). The structures of several of these intermediates have by nmr, x-ray, Crystallography. They follows SN1 mechanism as like primary and t-alkylhalides leaving group [X = Br or Cl] not have much effect on the reaction rate. In the reaction (iv)

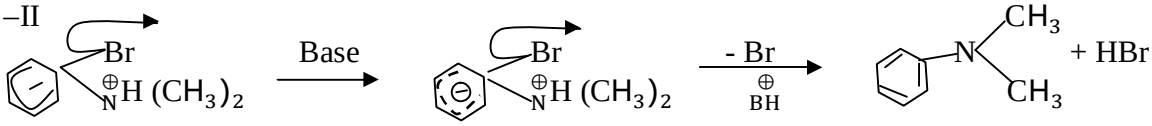
1.2. (v)



Setp –I



Step –II

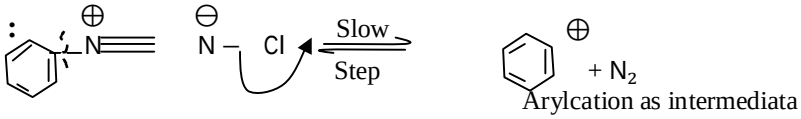


bases couldnot Catalyze step 1.2 (V) , but if amines are nucleophiles, bases can catalyses step (v). Base catalysis is found precisely in those cases where the amine moity cleaves easily but Br does not, so that K_{-1} is large and Step-1.2 (I) (II) is rate determing which leads two steps. It is

only low concentration of base. At low base concentration (0.1M, .01M, 0.01M etc) in creases the Step-II. Step-I is R.D.S. Step-II followed by rapid loss of leaving group Br and that bases Catalyze the reaction by increasing the rate of the deprotonation in presence aprotic Solvents. This mechanism is confirmed by using isotopic effect.

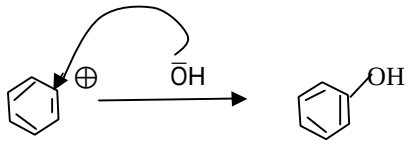
1.3 vi) : Benzenediazonium chloride Mechanism.

Step I :



Arylcation as intermediata

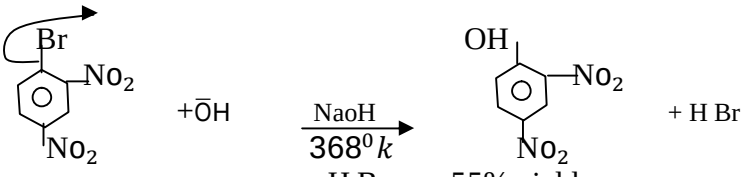
Step II



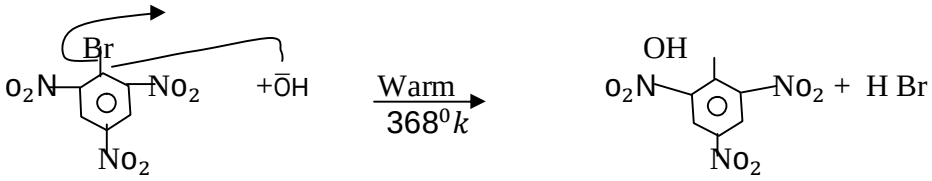
This reaction follows a unimolecular(ArSN1) mechanism. This is denoted by I.U.P.A.C: DN + AN.

- Benzenediazonium chloride (salt) independent of the concentration of ŌH nucleophile.
- If high concentrations of chloride salts are added but product independent of the added salt.
- The effect of Benzenering substituents on the rate are consistent with a unimolecular rate determining cleavage. This is explained by using 2,4, dinitro, bromo, benzene and 2,4,6 tritnitro bromo benzene, reacts with the strong nucleophile like ŌH which displaces Br̄ as nuclerphile to give the corresponding 2,4, dinitro phenol (50% yield) and 2,4,6 T.N.P (Picricacid)

1.2 (vii)



55% yield



93% yield

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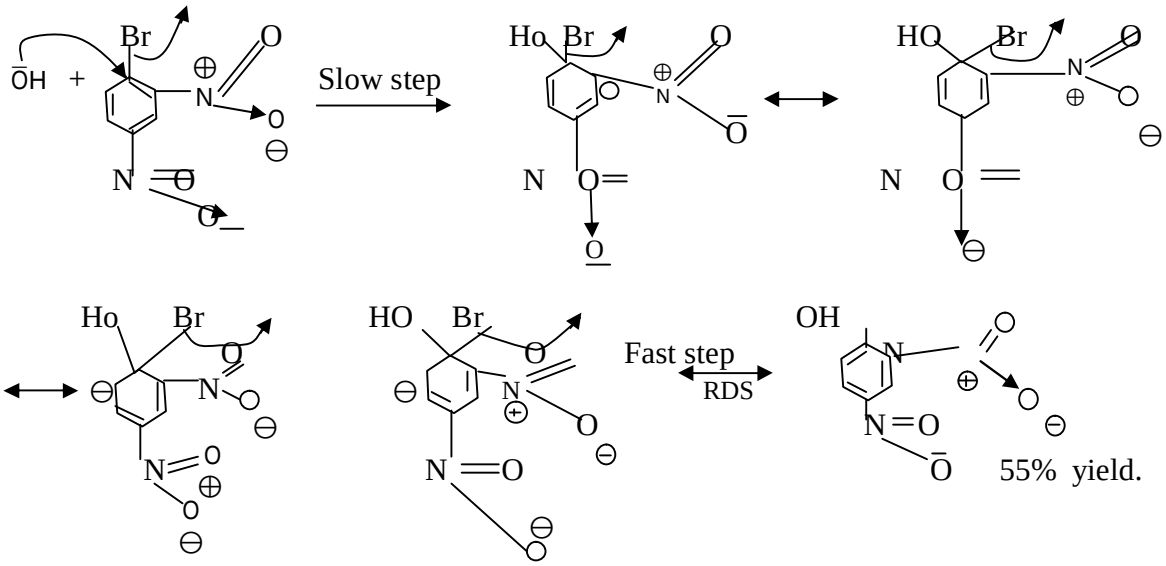
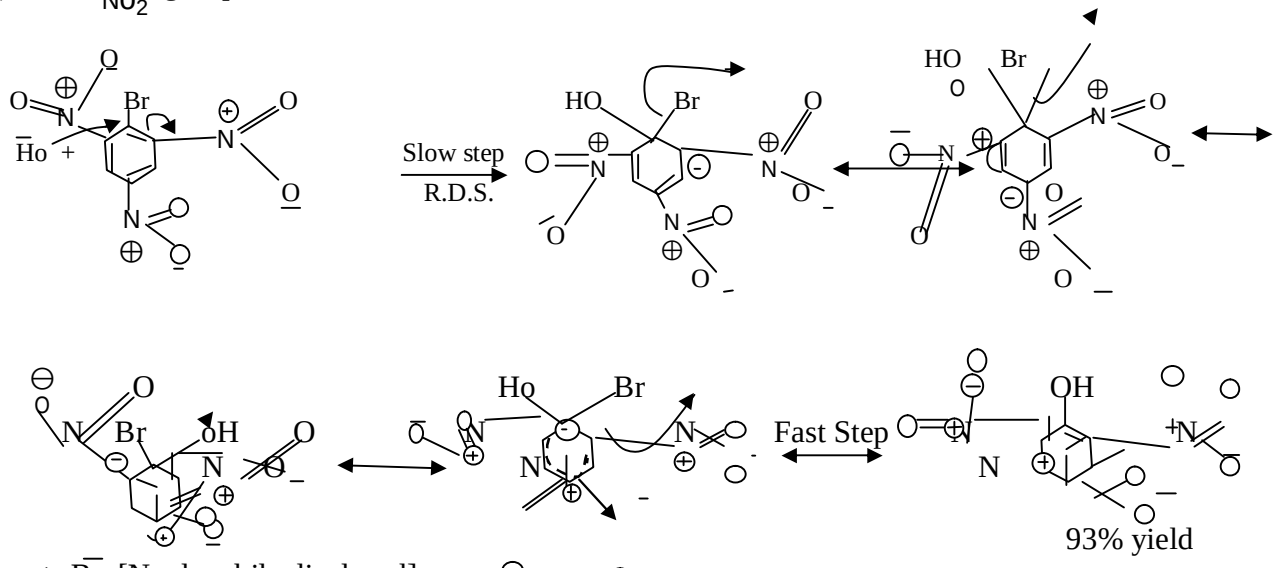
(This follows SN2Ar Machanism)

1.4 (viii)

1) If $\overset{\oplus}{NO_2}$ groups present at O & P, Positions of bromobenzene and its mechanism is as follows.



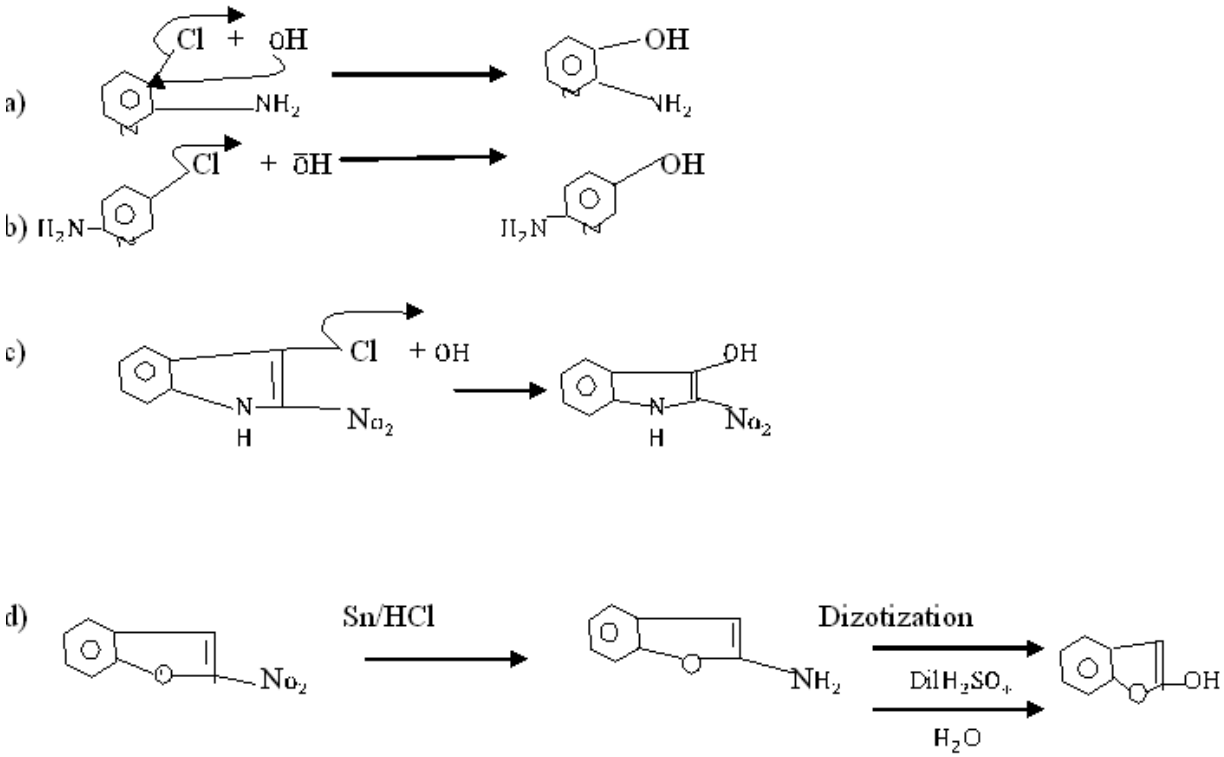
2) If $\overset{\oplus}{NO_2}$ groups are present at, O', P, Positions of bramobenzene its mechanism is as follows.



+ $\bar{Br}$ [Nucleophile displaced]

CONCLUSIONS AND SUGGESTIONS

The formation of Picricacid (2, 4,6 trinitrophenol) from 2,4,6, Trinitrobenzene $\bar{O}H$ as a strong nucleophile displaced by leaving group $Br\bar{}$ due to stearic effect. The nitrogroup (nitroniumgp) which is strong electron withdrawing which are deactivates π electroncloudes in benzene nucleus, more electrondensities on $\overset{\oplus}{NO_2}$ group which increasing the polarity and nucleophile, electron with drawing groups which are causes the displacement of nucleophile as a 'Br' from the aromatic nucleus. Therefore reaction set II gives 93% yield, but in case of O and P- NO_2 Phenol there is no electron with drawing group $\overset{\oplus}{NO_2}$ is present on O' hence it gives only 55% yield and electron- densities at O,P are 0.8 and 0.9. Similarly other nucleophlic is displacement reaction are like $\bar{C}N$, NH_2 , $O\bar{H}$ by alogens $\bar{X}$ by NH_2 , OCH_3 , $\bar{O}C_2H_5$, $Ph_3\bar{C}$ etc. same nucleophilic displacement reaction and there is observed in Heteroyclic Compounds like Pyridine, Indole, Benzofuran etc.



- Cine Substitution easily observed
- Bromobenzene having no hydrogen Ortho to the Br does not react under the same conditions example is 2,4,6, trimethyl, bromobenezene in KNH_2 & NH_3 no reaction takes-place.
- Effect of substrate structure. SN2Ar or ArSN2. Reactions are accelerated by electron with drawing groups at the O and P positions to the leaving group Br and retard by electron donating groups. The decreasing order of activating power of some group (s) in ArSN2:

  NH_3 > NO_2 > CF_3 > CN > SO_3 > CHO > CO > COOH > COOR > $CONH_2$ > F > Cl > Br > I

  Effect of leaving group: decreasing (approximate) order of leaving power

  F > NO_2 > OT_s > So_3Ph > Cl > Br > I > N_3 > $\overset{\oplus}{NR_3}$ > OAR, OR, SR, NH_2

Effect of the attacking nucleophile: The following decreasing order of nucleophilicity.

$\overset{\oplus}{NH_2} > \overset{\ominus}{Ph_3C} > \overset{\ominus}{Ph\_NH} > \overset{\ominus}{ArS} > \overset{\ominus}{RO} > R_2NH > Ar\bar{O} > \bar{O}H >$

$ArNH_2 > NH_2 > \bar{I} > \bar{B}r > \bar{C}l > H_2O >$ ROH

- Investigator should be able to study the Pyridine derivatives, properties related to N.D. reactions
- Environmental effects and their industrial applications, Medical, Agricultural fields.
- Partial factor > 1 activated by the substituent and partial factor < 1 deactivated the substituent by the Holleman product rule.
- The addition of the nitronium to the neucleus followed by the explusion of a Proton by Melander (1949, 1950) substitution occur in by the addition of nitroniumion and the Proton explusion be R.D.S.

  Rate = K [Substrate] [$\overset{\oplus}{NO2}$]

  = K [Br (1) $No_2(4)\, C_6H_4$ Br (1) No_2^{II}] [$\overset{\oplus}{No_2}$]
- Substitution or displacement depends upon the electrondensity as well as attacking reagent and functional group is on Benzene nucleus.
- σ Complex of Benzonium cations with NO_2^+ takeplace. During the NU.D.R., synchronous fornation of $-C-N$ and breaking of CH by Ingold (1937), wheland (1942).
- The band langth of $-C-C$ 1.54 A^0 $-C=C-$ is 1.33 A^0 same as ethylene linkage by Brown etal (1956, 1958) and proved by Hamett (1937).
- Nu. D. reaction / N.U.Sub. are depends upon the electron density, Rate of the reaction, they follows, ArSN1, ArSN2 respectively.

APPLICATIONS:

1) Ideal solvents for many Organic Compounds.
2) Fumigant pesticide.
3) Insecticide against malaria.
4) Healing agents, antiseptic, dressing of wounds, sores, disinfectants.

5) Soaps and detergents.
6) Kill dangerous insects, mosquitoes due to high specific toxicity, Tranquilizers, Antibiotics.

Which are effective against a widerange of grampositive and gramnegative bacterias inflammation, antirhuematic, edema, antipyretics, antiseptics, antifertility, drugs.

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