



Phenol Synthesis Part II

Assistant Lecturer Sahar Mohammed Shakir Assistant Lecturer

Abdul Hafeedh Hameed

Procedure :





Cool the soln. to 0 °C by replacing the beaker in an ice - bath & stir from time to time.





In another beaker, dissolve 5.5 g sodium nitrite in 25 ml H_2O .

> Temp. 0 °C Aniline, H2SO4 & H2O soln.

Transfer 22 ml of this NaNO₂ soln. to a separatory funnel . Add drop wisely the soln. of nitrite to the aniline sulfate solution with keeping temp. at 0 °C & shaking.



Add the remainder of the nitrite soln. until an immediate + ve test for excess of HNO2 with an external indicator - moist potassium iodide- starch paper is obtained.

 $2 \text{ HNO}_2 + 2 \text{ KI} + 2 \text{ H}_2 \text{SO}_4 \longrightarrow \text{I}_2 + 2 \text{ NO} + 2 \text{ H}_2 \text{O} + 2 \text{ K}_2 \text{SO}_4$

Starch - iodine complex

white \rightarrow blue-violet

25 ml H₉O

5.5 g NaNO2

Place the soln. of the prepared benzene diazonium bisulfate in a 250 ml round bottomed flask, attach an air condenser & heat on a hot plate until all the N_2 gas, formed from decomposition of diazonium salt, has evolved.



 H_2O (out)

The aqueous solution of the diazonium cpd. is warmed to about 50 °C since at higher temperature the reaction may become vigorous & lead to appreciable quantities of tarry compounds.





SALTING OUT,

In aqueous soln.s of organic molecules, salt is added to separate the organic material from the salty aqueous phase.



Combine the ethereal extracts, dry over anhydrous CaCl₂, (drying agent), which can remove dissolved water to ensure dryness. Anhydrous: CaCl₂ Dihydrate: CaCl₂ · 2H₂O Hexahydrate: CaCl₂ · 6H₂O



Transfer the remainder to a distilling flask, attach an air condenser and distill the phenol (for purification) Collect the fraction at 180 - 183 °C



Colorless crystals of phenol form, weigh & handle in yield of 6 - 7.5 g.

Notes :

The experimental conditions necessary for diazotization of an aromatic 1°- amine, are as follows: The amine is dissolved in a suitable volume of H_2O containing an excess of H_2SO_4 , the soln. is cooled in ice when the amine sulfate usually crystallizes. The temperature is maintained at 0-5 °C and an aqueous soln. of NaNO₂ is added portion - wise until, after allowing 3-4 minutes for reaction, the solution gives an immediate +ve test for excess of HNO₂ with an external indicator-moist potassium iodide-starch paper The precipitated amine sulfate dissolves during the diazotization to give a clear soln. of the highly soluble diazonium salt.

For acidification H_2SO_4 is used in preference to HCl since the presence of chloride ions give rise to small quantities of aryl chloride as a by-product.



Excess acid in diazotization of aniline is required for maintaining the proper condition of acidity required to stabilize the diazonium salt & hence to minimize secondary reactions, e.g.; the interaction of some of the diazonium salt with unchanged amine to form a diazoamino compound, a reaction occurs readily in neutral solution.

$$\underbrace{ NH_2 + }_{NH_2} + \underbrace{ NOSO_3H_{moderate-weak}}_{noderate-weak} \underbrace{ N=N-}_{p-Aminoazobenzene} NH_2$$

Unreacted aniline In moderate-low acidic medium

Couples rapidely

In high acidic medium Does not couple

Diazotization of a 1°-aromatic amine is of significant synthetic value while diazotization of 1° – aliphatic amines is not; since,

- •Difference in the stability of the prepared diazonium salt. (discussed earlier)
- •Difference in basicity of the aromatic and aliphatic amines.

Diazotization requires unprotonated amine whose lone pair of electrons nucleophilically attacks the electrophilic nitrosyl reagent.

Aliphatic amines are stronger bases so they are completely protonated at pH < 3 and present as ammonium ions & does not react.

While aromatic amines have weaker basicity than aliphatic amines & sufficient unprotonated aryl amine molecules remain for diazotization even in strong acidic solutions. So diazotization of aliphatic amines does not occur in strong acidic soln., as almost all amino groups are protonated and do not possess a lone pair of electron.

Aromatic amines are much weaker bases than aliphatic amines because of the resonance delocalization of unshared pair of electrons of nitrogen atom.



Test for phenol is done by taking 1-2 ml of the liquid and adding it to 1-2 ml of bromine water, a white ppt. indicates the presence of phenol.

During salting out the miscibility of phenol & water is reduced by the addition of many common salts such as alkali and alkaline - earth halides. The origin of this effect is the tendency of water molecules to associate with ions, hydrating them. So simple ions reduce the tendency of water to solvate phenol. During hydrolysis of diazonium salt, the solution must be acidic to avoid coupling reaction between the un-reacted diazonium salt and the phenol.





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