IMPORTANCE OF DIAZOTIZATION AND SYNTHESIS OF AZO COMPOUNDS BY GREEN ROUTE: A REVIEW

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Abstract: The paper represents the study of diazotization which exhibits considerable importance in dyestuff industries. Arene diazonium salts are common, easily prepared and highly useful intermediates in organic synthesis due to their rich reactivity. Diazonium salts obtained from diazotization reaction are important synthetic intermediates that can undergo coupling reactions to form azo dyes and substitution reaction to effect the functional group present on aromatic rings. The importance of temperature, moles of hydrochloric acid and other important parameters are described. Moreover a clean preparation of aryl diazonium ions using methyl nitrite is also summarized furthermore no nitrous acid is produced during the diazotization.

Keywords: Diazotization, Azo coupling, Arene diazonium salts, intermediates, Methyl nitrite, Nitrous acid

INTRODUCTION

Aryl diazonium salts have been discovered in the middle of the 19th century by Johann Peter Griess who was working on azo-compounds as dyes and pigments. Commonly, they are prepared by diazotization, a procedure in which a primary aromatic amine is treated with a source of nitrous acid (HNO₂). In spite of all precautions the formation of dark decomposition products due to the existence of nitrous acid and its aromatic amine is unavoidable, thus lowering the yield and also making the product difficult to isolate. Diazonium compounds, taught in almost every sophomore organic chemistry course, represent a large group of organic compounds with the general formula R–N≡N⁺ X⁻, in which R can be alkyl or aryl and X is an organic or inorganic anion such as a halogen. Diazonium salts, especially those where R is an aryl group, are important intermediates and have found wide applications in organic synthesis.

DIAZOTIZATION

By this process a second nitrogen atom is introduced in the primary aromatic amine by the action of nitrous acid (HNO₂) in the presence of mineral acid like HCl or H₂SO₄ at between 0 to 5 °C temperatures this process is called diazotization reaction.
Mechanism:

\[
\text{Ar-NH}_2 + \text{NaNO}_2 + 3\text{HCl} \rightarrow \text{Ar-} \overset{\oplus}{\equiv} \text{N Cl} + \text{NaCl} + 2\text{H}_2\text{O}
\]

Importance of temperature, pH and moles of HCl: In aqueous solution diazonium salts are unstable at temperatures above 5 °C; the \(-\overset{\oplus}{\equiv}\text{N}^-\) group tends to be lost as N\(_2\) (nitrogen gas). As a result proper dyeing does not take place and dye will wash with washing of cloth. In this reaction three moles of hydrochloric acid (HCl) is used, one mole of hydrochloric acid (HCl) is used to maintain the stability of diazonium salt, second mole for the preparation of nitrous acid (HNO\(_2\)) with sodium nitrite (NaNO\(_2\)) and the third mole is used to maintain the acidic condition (1 to 2 pH).

Diazotization of Aliphatic amine: Primary aliphatic amine [1.1] on treatment with nitrous acid (HNO\(_2\)) yields corresponding alcohols and unsaturated products with the involution of nitrogen gas.

Diazotization of Aromatic amine: Primary aromatic amine [1.2] on treatment with nitrous acid (HNO\(_2\)) at 0-5°C temperature yields diazonium salt with NaCl and H\(_2\)O. Secondary aromatic amine [1.3] gives nitroso amine on treatment with nitrous acid (HNO\(_2\)). Tertiary aromatic amine [1.4] gives p-Nitroso compound when treated with nitrous acid (HNO\(_2\)).
METHODS OF DIAZOTIZATION

1. Direct method
In this method one mole of primary aromatic amine is treated with three moles of hydrochloric acid (HCl) by maintaining the temperature about 0 to 5°C with constant stirring. After the completion of reaction slight excess of nitrous acid (HNO₂) can be analyzed by the starch iodide paper. Suppose the excess nitrous acid (HNO₂) is not analyzed properly then the coupling reaction is not giving quality product. Excess amount of nitrous acid (HNO₂) can be removed by addition of urea or sulfamic acid. [1.5]

\[
\text{Urea} + 2 \text{HNO}_2 \rightarrow \text{CO}_2 + 2 \text{N}_2 + 3 \text{H}_2\text{O}
\]

\[
\text{Sulfamic acid} + \text{HNO}_2 \rightarrow \text{N}_2 + \text{H}_2\text{SO}_4 + \text{H}_2\text{O}
\]  

[1.5]

2. Reverse method
In this method a solution of amine and a solution of sodium nitrite (NaNO₂) are added to the solution of acid. This method gives insoluble diazonium salts. Reaction is depend on the basicity of amines, that is decreases if amine contains electron withdrawing group such as –NO₂ and it is affect the quality of product.

3. Special method
In this process amine is dissolved in concentrated sulphuric acid (H₂SO₄) and run into phosphoric acid (H₃PO₄) with constant stirring. After 30 minutes the urea is added for removal of excess nitrous acid (HNO₂) and then the reaction mixture is poured into the ice, as a result clean solution of diazonium salt is obtained.

Special method to Aminophenol and Amino naphthols
Because they are radly oxidized by HNO₂ to quinones, they are diazotized in presence of CuSO₄ and in absence of mineral acid. E.g. 1-amino2-naphthol-4-sulphonic acid is made into 25% solution and then the solution of NaNO₂ containing copper sulphate is added to it. Diazoxide is more stable than other diazo ions and can be subject to even further reaction such as nitration and halogenations. [1.5]

\[\begin{align*}
\text{NH}_2\text{CONH}_2 & + 2 \text{HNO}_2 \rightarrow \text{CO}_2 + 2 \text{N}_2 + 3 \text{H}_2\text{O} \\
\text{NH}_2\text{SO}_3\text{H} & + \text{HNO}_2 \rightarrow \text{N}_2 + \text{H}_2\text{SO}_4 + \text{H}_2\text{O} \\
\text{CuSO}_4 & \quad \text{Diazoxyde}
\end{align*}\]  

[1.5]

RECENT DEVELOPMENTS

Synthesis of azo compounds by green route using methyl nitrite.
Preparation of methyl nitrite: In a 500 mL round-bottomed flask, fitted with a pressure equalizing addition funnel filled with 110 mL 12 M hydrochloric acid, and a gas tube in a well ventilated hood, was placed 76.0 g (1.1 mol) of sodium nitrite, 60 mL methanol and 110 mL water. The temperature was raised to 35°C and hydrochloric acid was added dropwise over 1.5 h. The methyl nitrite evolved was passed through a water trap and a 10% sodium carbonate trap to remove acid and then bubbled through the reaction mixture below via the gas tube.
Preparation of the 4-methylaniline hydrochloride diazonium solution; (used in Scheme 1): In a 1 L round-bottomed flask, fitted with a mechanical stirrer, and a gas tube in a well-ventilated hood, was placed 143.7 g (1.0 mol) of 4-methylaniline hydrochloride and 300 mL methanol. Methyl nitrite (1.1 mol) was added through the tube for about 1.5 h. When the reaction was complete, the temperature was raised to 50°C and the mixture was stirred for another 20 min. to expel excess methyl nitrite, which was recovered through a cold-trap.

Scheme 1. Preparation of 1, 3-dimethyl-1, 2, 3-triazene.

Scheme 2. Preparation of the azo (N=N) group.
Scheme 3. Preparation of azo coupling reactions of sodium sulfanilate hydrochloride diazonium ions.

Table 1. Synthesis of azo compounds.

<table>
<thead>
<tr>
<th>Product</th>
<th>Substrate</th>
<th>Substrate</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>4-methylaniline</td>
<td>3,5-dimethylaniline</td>
<td>86</td>
</tr>
<tr>
<td>1b</td>
<td>4-methylaniline</td>
<td>N,N-dimethylaniline</td>
<td>94</td>
</tr>
<tr>
<td>1c</td>
<td>4-methylaniline</td>
<td>4-methylphenol</td>
<td>91</td>
</tr>
<tr>
<td>1d</td>
<td>4-methylaniline</td>
<td>4-hydroxyacetophenone</td>
<td>84</td>
</tr>
<tr>
<td>1e</td>
<td>4-methylaniline</td>
<td>2-naphthol</td>
<td>96</td>
</tr>
<tr>
<td>1f</td>
<td>aniline</td>
<td>4-methylphenol</td>
<td>93</td>
</tr>
<tr>
<td>1g</td>
<td>aniline</td>
<td>2-naphthol</td>
<td>91</td>
</tr>
<tr>
<td>1h</td>
<td>4-nitroaniline</td>
<td>phenol</td>
<td>85</td>
</tr>
<tr>
<td>1i</td>
<td>4-nitroaniline</td>
<td>6-ethyl-2-methylaniline</td>
<td>83</td>
</tr>
<tr>
<td>1j</td>
<td>4-nitroaniline</td>
<td>2-naphthol</td>
<td>85</td>
</tr>
<tr>
<td>1k</td>
<td>4-aminoazobenzene</td>
<td>phenol</td>
<td>90</td>
</tr>
</tbody>
</table>

Table 2. Synthesis of azo compounds with sulfanilate.

<table>
<thead>
<tr>
<th>Product</th>
<th>Substrate</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2a</td>
<td>N,N-dimethylaniline</td>
<td>83</td>
</tr>
<tr>
<td>2b</td>
<td>1,3-diphenol</td>
<td>82</td>
</tr>
<tr>
<td>2c</td>
<td>2-naphthol</td>
<td>88</td>
</tr>
<tr>
<td>2d</td>
<td>4-ethylphenol</td>
<td>87</td>
</tr>
<tr>
<td>2e</td>
<td>3,5-dimethylaniline</td>
<td>81</td>
</tr>
</tbody>
</table>

Figure 1. Possible mechanism of the diazotization.
CONCLUSION

In this review we have shown an importance of diazotization and number of synthetic applications of aryldiazonium salts. We have concluded that how the temperature, moles of hydrochloric acid and other important parameters are affect the diazotization reaction. Also we came to know that how the azo compounds are prepared by green route.

REFERENCES


