

## A Review on -Aryl Diazonium Compounds

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**ABSTRACT:** Aryldiazonium salt,  $\text{Ar-N}_2\text{Cl}$ , are highly reactive compounds in synthetic organic chemistry. Azo dyes of phenolic compounds are the largest class of industrial synthesized organic dyes due to their versatile skeleton, ease of preparation, and uses in many practical applications. They are characterized by the presence of one or more azo ( $-\text{N}=\text{N}-$ ) groups and are prepared by diazotizing an aromatic primary amine and coupled with a phenol or an aromatic amine. The aryl diazonium salt is a very useful and fascinating chemical salt, a vital intermediate. They are colourless, ionic, and crystalline by nature. They are mostly utilised in the dye and pigment industries and helpful in the synthesis of a wide range of chemical compounds like primarily aryl derivatives. Aryl diazonium ions are more stable than alkyl diazonium ions because aryl diazonium ions have more resonance due to alternative double bonds. Diazonium salt is a popular colour agent.

**Key words:** Diazotization, Aryldiazonium salt, Diazo coupling reactions, Azo compounds

### I. INTRODUCTION

In organic chemistry, there are several classes of chemicals such as aldehyde, ketone, nitrile, ester, lactone, anhydride, imine, and azo compounds, and aryl diazonium compounds play an essential part in synthetic organic chemistry.<sup>1</sup> Aryldiazonium salt,  $\text{Ar-N}_2\text{Cl}$ , is a highly reactive class of molecules in synthetic organic chemistry.<sup>2</sup> Aromatic diazonium salts (ADS) have been recognised for more than 150 years as one of the most versatile and important reagents in chemical synthesis.<sup>3</sup> Diazo and diazonium compounds are exceptionally flexible organic synthesis intermediates and reagents. Diazoalkanes are widely used alkylating reagents.<sup>4</sup> Diazo compounds have evolved into an indispensable class of small reactive molecules for a wide range of chemical transformations, from cycloaddition reactions for the synthesis of heterocycles and cyclopropanes to heteroatom H bond insertion reactions and, more recently,

enantioselective CH activation reactions.<sup>5</sup> The diazonium group triggers nucleophilic aromatic substitutions and provides a generic manner of introducing halogens, CN, OH, H, and other elements into an aromatic ring to generate a diverse spectrum of compounds. Furthermore, the reaction of diazonium salts with aromatic molecules ( $\text{ArO}$ ,  $\text{OH}$ ,  $\text{ArO NR}_2$ ) produces azo compounds with the general formulae  $\text{Ar-NQN-ArO}$ , which are extremely important as dyes. Azo-coupling is also an important reaction in analytical chemistry for determining nitrite ( $\text{NO}_2$ ) and nitroso species.<sup>6</sup>

Chemical functional groups containing nitrogen are common in the physical and biological sciences. Indeed, nitrogen and, in particular, the amine functional group can be found in a wide range of fine chemical products from commercial suppliers. However, it is worth noting that there are still very few methods for activating and using a C-N bond as a tool for the construction of more complex molecules, with the formation and use of diazo and diazonium compounds being the most widely used method.<sup>7</sup> Diazo compounds, depending on their stability and coexisting functional groups, might be difficult to prepare and isolate.<sup>8</sup>

Heterocyclic diazo compounds are extremely reactive and are employed in the synthesis of novel chemicals, including those with biological functions. For example, 5-diazoimidazole 4-carboxamide is a precursor to the anticancer medicines dacarbazine and temozolomide, both of which are used in clinical use.<sup>9</sup>

**Origin of Diazonium Salt:** In 1858, scientist "PETER GRIESS" predicted the reaction of aryl diazonium salt. He also identified a plethora of reactions involving these newly synthesised chemicals. Most diazonium salts are made by treating aromatic amines with nitrous acid and then adding another acid, such as hydrochloric acid.

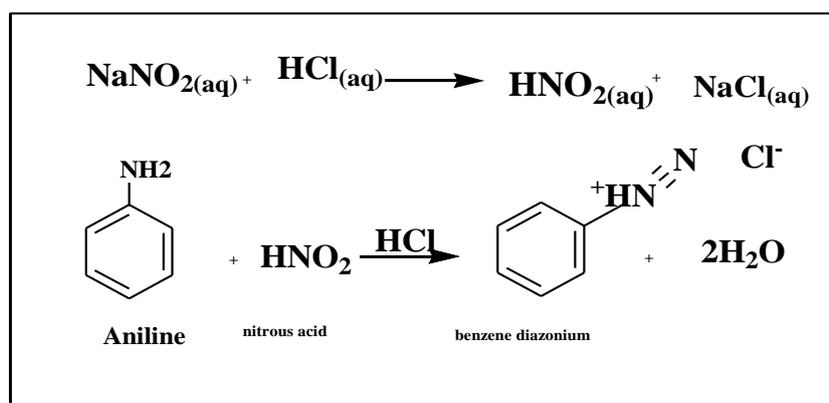
**DIAZOTIZATION:** Diazotization occurs when a primary aromatic amine interacts with sodium nitrate and hydrochloric acid in the presence of ice-

cold water at 0-5 degrees Celsius to generate diazonium salt.<sup>10</sup>

#### PREPARATION OF DIAZONIUM SALTS:

In a diazotation process in which a ice cold solution of sodium nitrate is introduced to a concentrated acid solution of aryl-amine (below 5 °C). The acid first interacts with sodium nitrate to generate an unstable nitrous acid. Nitrous acid then

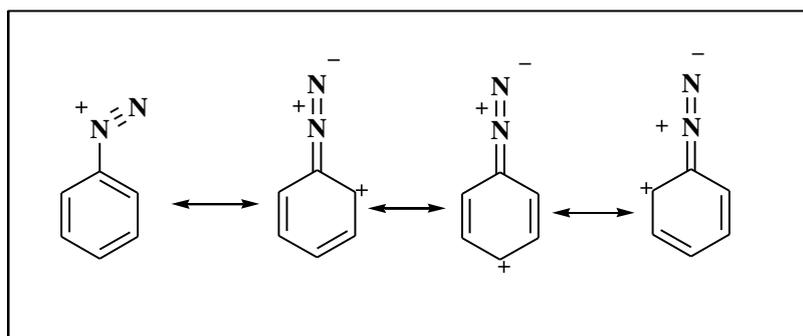
interacts with the aryl amine; diazonium salts are generated in icecold solutions. A diazonium salt is benzene-diazonium chloride: Benzene-diazonium chloride decomposes in aqueous solution above temperatures of 5 °C they are extremely unstable; the only stable diazonium salts are aromatic, and they are not particularly stable due to the presence of the benzene ring, which stabilises the group due to its high electron density.



#### Stability of benzene diazonium-cation

□The benzene diazonium-cation is more stable than the alkyl diazonium-cation (aliphatic)

due to the diazo group being part of the delocalized system with the benzene ring and hence the way in which the positive charge is spread about the ring.<sup>11</sup>



#### 1.Preparation of 1-(3-Methoxy-phenyl)azo-naphthalen-2-ol

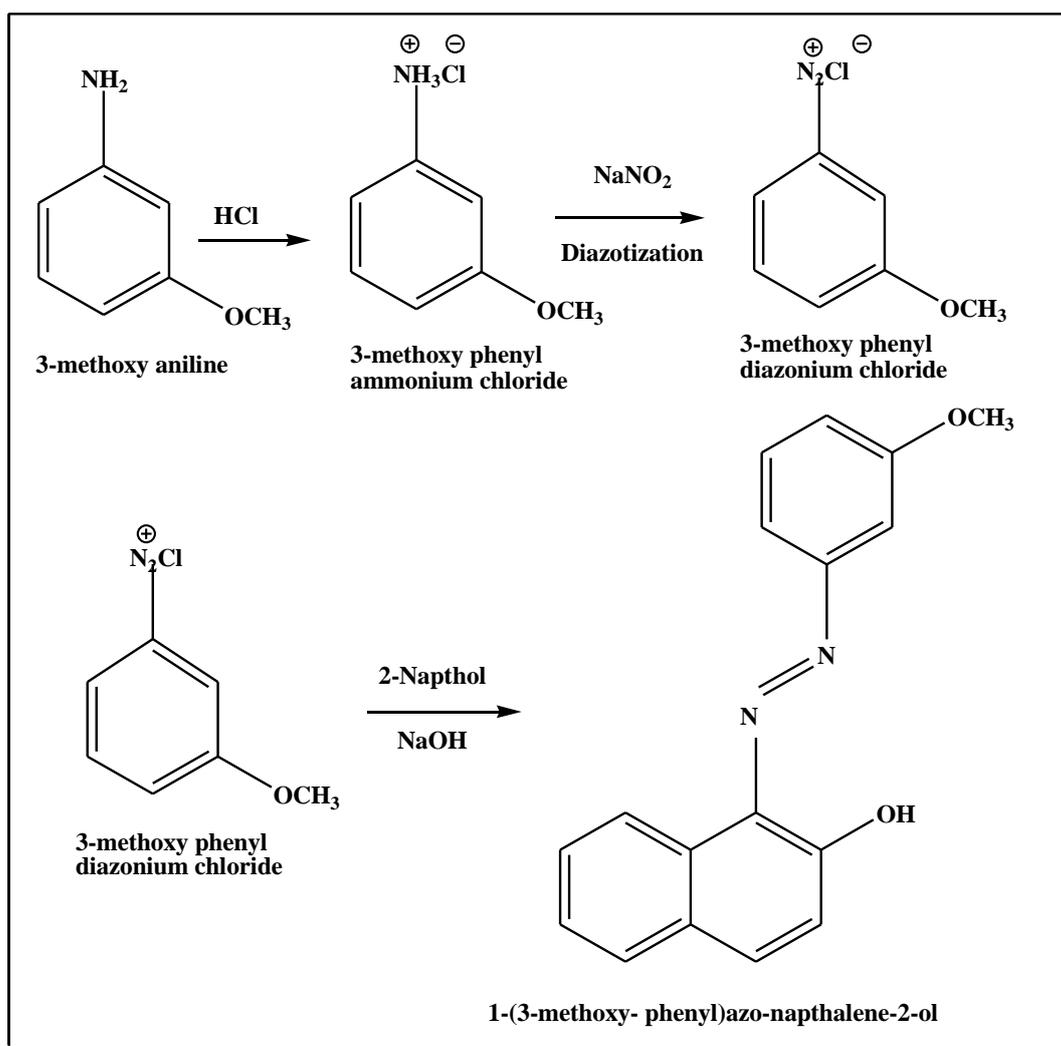
J. Patil et al., added 2 mL aniline (or its derivative) to a 100 mL beaker, then add a mixture of 5 mL conc. HCl and 10 mL water and stir with a glass rod to obtain a clear solution. Cool the solution to 0 °C by immersing it in an ice bath. Dissolve 1 gm sodium nitrite in 10 mL water. Cool the solution in an ice bath to 0 °C, then add sodium nitrite solution drop by drop into aniline hydrochloride (or derivatives) solution with

continual stirring (do not allow temperature to increase over 5 °C during addition). The reaction mixture passes the nitrous acid test on starch iodide paper (a blue colour is obtained on potassium iodide starch paper). Decompose the excess nitrous acid by adding a grain of salt then filtrate which is diazonium salt solution.

Prepare a solution of 1.5 gm 2-Naphthol (β-Naphthol) in 10 ml 10% NaOH and chill to 0 °C. Now, dropwise add diazonium salt solution into 2-naphthol in NaOH with constant stirring after

complete addition, allow reaction mixture to stand for 10 minutes in ice bath, filter the coloured azo dye 1 st wash it with cold water dry weight and note the yield of clear crude azo product is formed

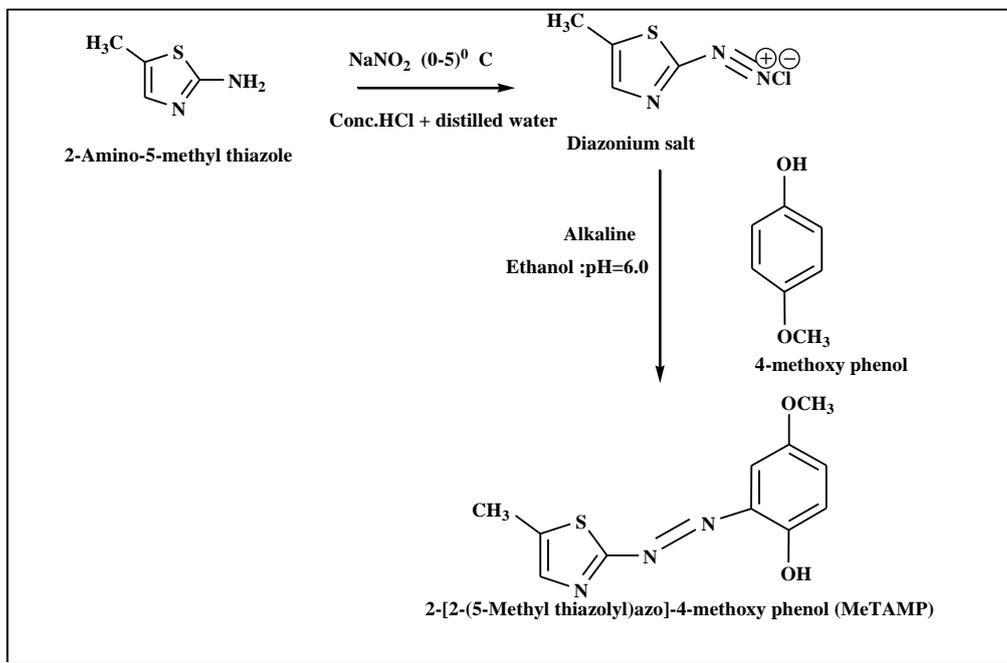
is recrystallised by using solvent ethanol. Record the dry weight and the colour with a physical constant, i.e. the compound's M.p. range.<sup>12</sup>



## 2.Preparation of 2-[2-(5-Methyl thiazolyl)azo]-4-methoxy phenol

AL-Adileetal., were synthesised the metal complexes by dissolved (0.499 gm, 0.002 mol) from ligand (MeTAMP) in hot ethanol (50 mL) and added dropwise with stirring to a stoichiometric amounts of 1:1 (ml) molar ratio with 0.272 gm (0.002 mol) of ZnCl<sub>2</sub> and 1:2 (ml) molar ratio (0.001 mol) with CrCl<sub>3</sub>·6H<sub>2</sub>O, MnCl<sub>2</sub>·4H<sub>2</sub>O, FeCl<sub>2</sub>·4H<sub>2</sub>O, FeCl<sub>3</sub>·6H<sub>2</sub>O, CoCl<sub>2</sub>·6H<sub>2</sub>O, NiCl<sub>2</sub>·6H<sub>2</sub>O and CuCl<sub>2</sub>·2H<sub>2</sub>O dissolved in the least amount of buffer solution (ammonium acetate) at optimal pH for each metal ions. After a 40-minute reflux, the reaction mixture was maintained

overnight. The isolated solid complexes were filtered, rinsed with distilled water until the solution turned colourless, and then washed with 10 mL of hot ethanolwater (1:1) to remove any unreacted components. The solid complexes were dried at 70 °C for several days. By combining 5-methyl thiazolylazonium chloride with 4-methoxy phenol in alkaline alcoholic solution, a novel Me TAMP (thiazolyl dye ligand 2-[2-(5-methyl thiazolyl)azo]-4-methoxyphenol) was produced. The structure of an azo dye ligand has been determined using techniques such as 1H-NMR, mass spectroscopy, FT-IR, UV-vis, and elemental analysis.<sup>13</sup>



### 3.Synthesis of 7-[2-(Benzimidazolyl) azo] 8-Hydroxy Quinoline

Alshamsi,etal., were synthesised BIAHQ metal complexes by gradually adding 0.289 g (0.002 mol) of ligand solution in 50 ml of 100% ethanol. The reaction mixture was heated for 50-60

$^\circ \text{C}$  at 30- 40 min, until solid complexes were precipitated, then left over night, the solid products formed were filtered off, washed with distilled water until the solution became colourless, and washed with 5 ml ethanol to remove traces of the unreacted materials.<sup>14</sup>

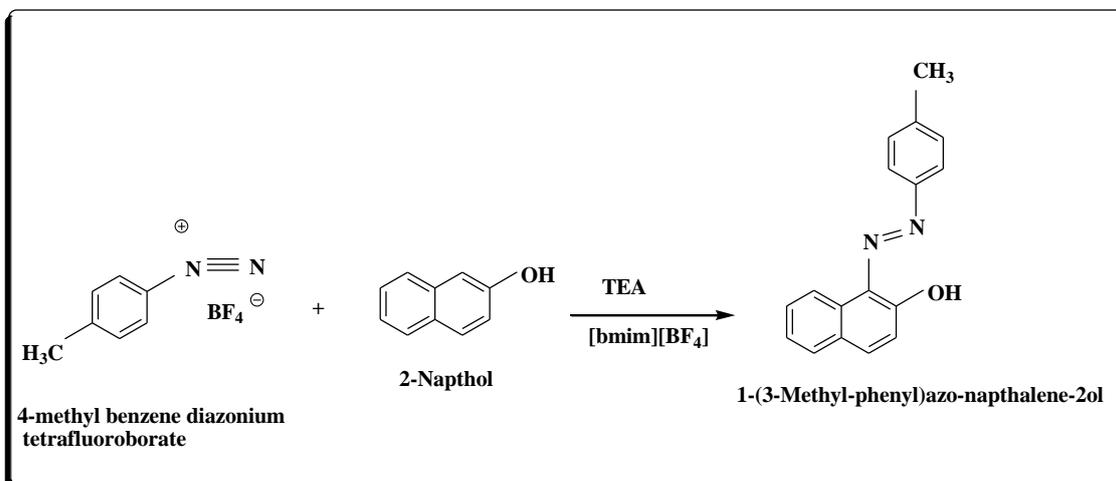


Scheme 2: Synthesis of azo dye ligand 7-[2-(Benzimidazolyl)azo] 8-Hydroxy Quinoline (BIAHQ)

### 4.Preparation of 1-(3-Methyl-phenyl) azo-naphthalene-2ol

The diazo-coupling reaction of 4-substituted benzenediazonium tetrafluoroborates with 2naphthol in [bmim][BF<sub>4</sub>] was studied at 25 C

in the presence of triethylamine (B) and triethylammonium tetrafluoroborate (BH) (1:1). The measured diazo-coupling rate constant (kobs) rose linearly with increasing triethylamine content was given by JiřHanusek etal.,<sup>15</sup>



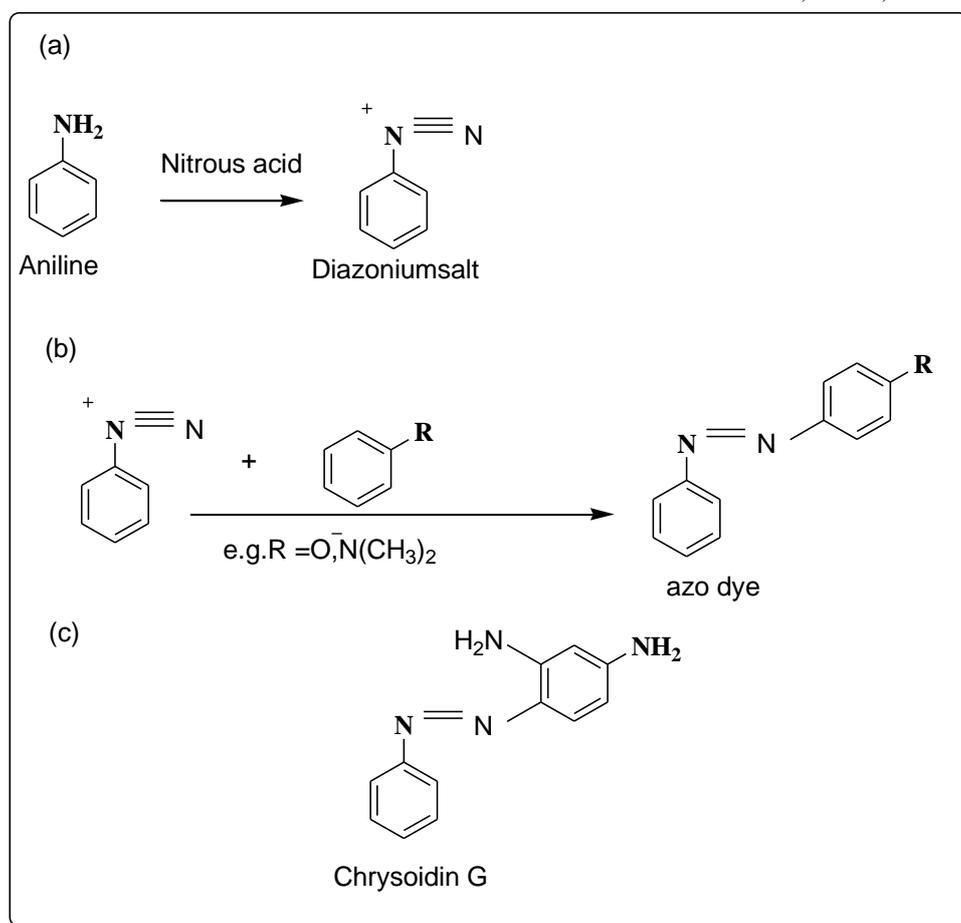
### 5.Preparation of Chrysoidin G

Yates et al., synthesised Chrysoidin G (chrysoidine), a basic azo dye by Diazotization.

(a) The formation of a diazonium salt by the reaction of aniline (or another aryl amine) and nitrous acid.

(b) The diazonium salt is then reacted with a variety of aromatic derivatives, including amines and phenols, to produce stable azo colours.

(c) Chrysoidin G (chrysoidine), a basic azo dye used to colour wool, cotton, leather, and silk.<sup>16</sup>



### 6.Preparation of Bromoxynil azo dye

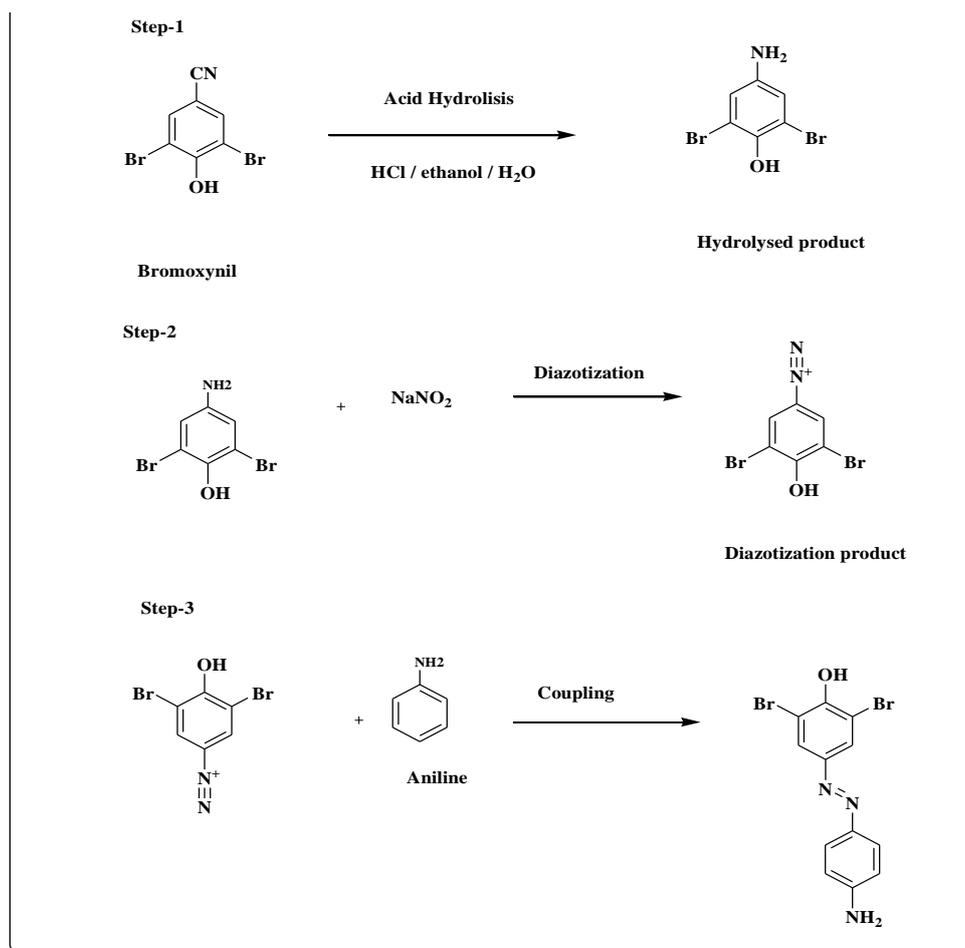
Rasul, Md. Mustanetal.; prepared diazotized bromoxynil in 50 mL volumetric flasks, 1 to 3 mL portions of a standard stock solution of bromoxynil (1 ppm) were taken, followed by the optimal volume of 0.15% nitrite solution (4 mL) and shaken thoroughly. The optimum volume of aniline 2% (6 mL) was added to these solutions and diluted to 50 mL with distilled water. After 12 minutes of equilibration, the absorbance of the resultant orange red dyes was measured at 500 nm with a UNICO UV-2100 spectrophotometer. In order to determine bromoxynil using the FIA system, nitrite solution (0.15%) and aniline solution (2%) were constantly injected into the FI manifolds. To create the diazonium ion, a hydrolyzed solution of bromoxynil was injected into a nitrite stream. This diazotized reagent was mixed with a coupling reagent before the dye was

fed through a flow cell of a spectrophotometer and the absorbance was continuously monitored at 500 nm.

To determine bromoxynil in a commercial formulation, bromoxynils were isolated from

MCPA (2-methyl-4-chlorophenoxy acetic acid), which is present in commercial products in a 1:1 ratio using cyclohexane. This was accomplished by diluting 0.5 mL of the material to 20 mL and extracting it twice with 10 mL of cyclohexane using a separatory funnel. The extract was then evaporated over a hot water bath, and the residue was dissolved in ethanol, diluted with distilled water to volume, and hydrolyzed with 0.4 M hydrochloric acid.

The resultant solution was diazotized, and the colour was created in the same manner as before. At 500 nm, the absorbance of the coloured solutions was measured.<sup>17</sup>



### Reaction mechanism for the diazotization of bromoxynil

### Azo dyes

Griss discovered the azo coupling reaction in 1858 and created the first azo dye, Aniline Yellow. <sup>18</sup>Azo bond linkage (-N = N-) may be present more than once, mono azo dyes have one azo linkage.

While, there are two linkages in diazo dyes and three in tria dyes respectively. <sup>19</sup>

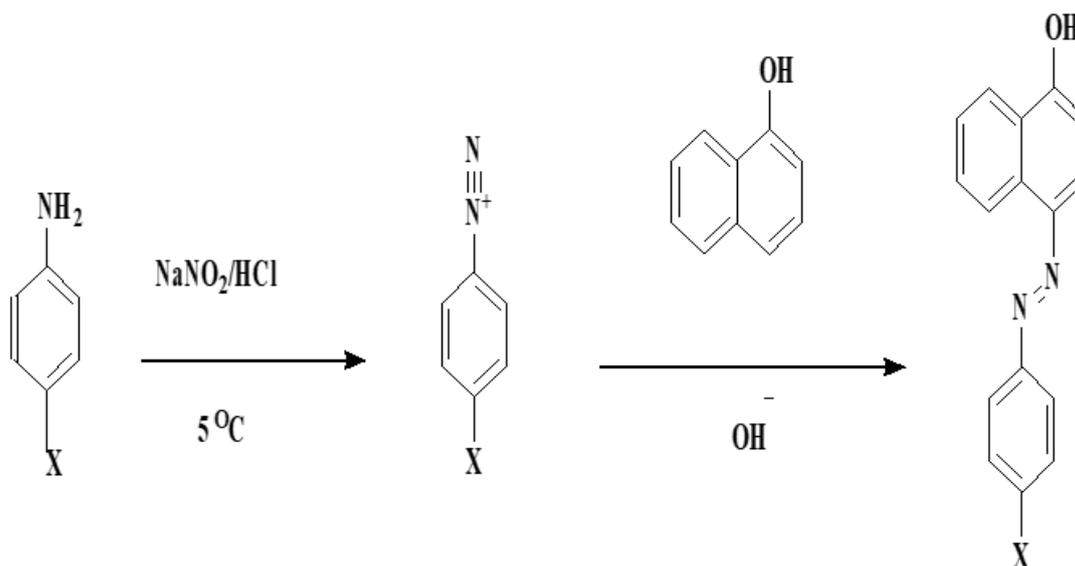
Azo dyes currently account for the majority of dye chemistry production volume, and their importance may rise in the future. They play an important part in the dye and printing market's governance. These dyes are created using a straightforward diazotization and coupling technique. To get the appropriate colour characteristics, yield, and particle size of the dye for better dispersibility, many approaches and modifications are used. <sup>20</sup>Azo dyes are among the most important synthetic coloring agents but are

regarded as potential carcinogens due to their metabolism; the reduction of the azo group affects their toxicity, mutagenicity, and carcinogenicity. <sup>21</sup>

### General experimental procedure for azo coupling for coupling reaction.

One mole equivalent of a coupler was taken and 1-2 moles equivalent of 10% NaOH solution (for alkaline coupling) or 1 mole equivalent of acetic 4 acid (for acidic coupling) were added.

The solution was thoroughly mixed before adding water and allowing it to cool to 0-5 °C. Couplers such as N, N-dimethylaniline, N, N-diethyl aniline, and -naphthol were used. To obtain the colours, a synthetic diazo solution was added drop by drop to the coupler solution under cold circumstances. <sup>22</sup> Azo dyes are made by reacting aryl diazonium ions with an activated aromatic molecule. <sup>23</sup>

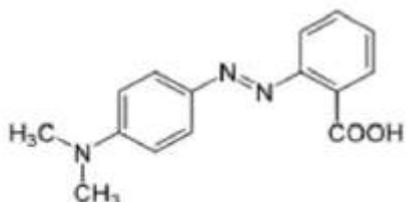
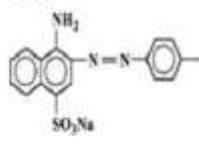


### General route for the synthesis of azo dyes

### Uses of Azodye

Azo dyes are widely utilised in a variety of industries such as textile, dyeing, printing, and cosmetics. <sup>24</sup>

### Azo dye structure and characteristics of methyl red and congo red

|                          |   |                          |  |
|--------------------------|---|--------------------------|--|
| <b>Name</b>              | <b>Methyl Red</b>   | <b>Name</b>              | <b>Congo Red</b>   |
| <b>Other Name</b>        | Acid red-2  | <b>Other Name</b>        | Direct red 28  |
| <b>Color</b>             | Red   | <b>Color</b>             | Red  |
| <b>Structure</b>         |  | <b>Structure</b>         |           |
| <b>Molecular Formula</b> | C <sub>15</sub> H <sub>15</sub> N <sub>3</sub> O <sub>2</sub>                     | <b>Molecular Formula</b> | C <sub>32</sub> H <sub>22</sub> N <sub>6</sub> Na <sub>2</sub> O <sub>6</sub> S <sub>2</sub> |
| <b>Molecular Weight</b>  | 269.29  | <b>Molecular Weight</b>  | 696.66   |
| <b>Melting Point</b>     | 179 to 182 °C   | <b>Melting Point</b>     | >360 °C  |

### Applications

The original application of diazonium salts was to manufacture water-fast coloured fabrics by immersing the fabric in an aqueous solution of the diazonium compound, followed by immersion in a solution of the coupler (the electron-rich ring that undergoes electrophilic substitution). The dye and pigment industries continue to be the most important users of diazonium compounds.

### Other uses

1. Diazonium compounds are common reagents used in the synthesis of chemical molecules, particularly aryl derivatives. Diazonium salts are photosensitive and degrade when exposed to near UV or violet light. This feature has led to their application in document replication. Paper or film is treated with a diazonium salt during this process. With an aqueous solution of coupler, the residual diazo is converted to a stable azo dye after contact exposure to light. A more popular method employs a paper coated with diazo, a coupler, and an acid to impede coupling; following exposure, the picture is developed by a vapour mixture of ammonia and water, which forces coupling.<sup>25</sup>

2. Many fillers' properties have been improved by diazonium salt modification. These fillers have found application in a wide range of polymers. Fillers that form covalent connections with the polymer, as well as those that do not appreciably increase composite characteristics. Thermal conductivity, thermal stability, and mechanical properties (e.g., interfacial shear strength,

compressive strength) have all been increased by the inclusion of a modified filler. Modified filler materials are projected to be widely used, for example, in controlled medication release, antistatic coatings, electrode materials, photocatalysts, bone tissue engineering scaffolds, fuel cell applications, abrasive tools, and electromechanical strain sensors.<sup>26</sup>

### II. CONCLUSION:

This review mainly indicates the formation of various diazonium salts by diazotization reaction and these azo dyes are synthetic compounds with an azo bond -N=N- that are derived primarily from aromatic amine, nitro, and nitroso substrates. The utilisation of an appropriate oxidative/reductive reaction or diazotization/coupling reaction is required for synthesis. They have found widespread application in a variety of industries due to the presence of the unique system of conjugated bonds exhibiting absorption in the visible light range. Based on the large amount of azo dyes discharged into the environment and their toxicity, new biodegradation processes must be improved and developed. Despite their toxicity, many of these chemicals show medicinal potential. According to the information provided, they contain antibacterial and antifungal activities, are protease inhibitors (enzymes that play roles in many clinical illnesses), and have anti-HIV effectiveness.

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