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A Research on Synthesis of Azo Derivatives of Some Primary Amines and Phenols

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Abstract: *The synthesis of Azo derivatives from primary amines and phenols plays a crucial role in the development of dyes, pigments, and biologically active compounds. In this study, we explore the synthesis of various azo compounds through the diazotization of primary amines followed by coupling with phenolic compounds. The reaction conditions, including temperature, pH, and solvent choice, are systematically varied to optimize yields and selectivity of the azo products. Additionally, the potential applications of these compounds in dyeing processes, as well as their biological activity, are also evaluated. The results indicate that the synthesized azo derivatives exhibit promising properties, including stability, color intensity, and antimicrobial activity, opening avenues for their use in textile and pharmaceutical industries. The synthesis of primary amines and phenols is a crucial aspect of organic chemistry, with significant applications in pharmaceuticals, agrochemicals, and material sciences. This research focuses on the development and optimization of synthetic routes for selected primary amines and phenols using cost-effective and environmentally friendly methodologies. Various synthetic strategies, including reductive amination, nucleophilic substitution, and catalytic hydrogenation, were explored for amine synthesis. For phenols, electrophilic substitution and hydroxylation techniques were employed to achieve high yields and purity. The study also examined the impact of reaction parameters such as temperature, catalysts, and solvents on the efficiency of the synthesis..*

Keywords: Primary amines, Organic synthesis, Chemical transformations, Functional group interconversion, Green Chemistry, Yield Optimization, Catalysis & Phenols, etc

I. INTRODUCTION

History of azo compounds

In early nineteenth, the dyes were obtained from natural sources for coloring the fabrics. Mauveine was the first synthetic dye synthesized in 1856. By 1970 nearly 60 % of the dyes available were synthetic and prepared by diazotization mechanism. Azo compounds influenced a largest portion of synthesized organic compounds as they are very successful in drugs, dye and cosmetics. These molecules are better stable in a wide range of pH than natural dyes and even thermo stable (Awale et al., 2013). Azo compounds are synthesized by diazotization reaction of a primary aromatic amine and coupled with one or more nucleophiles, mostly an amino, active methylene and hydroxyl group (Olayinka et al., 2013). They bear functional group R-N=N-R', where R and R' can be either an aryl or heteroaryl group. The -N=N- represents as azo group. The coloring properties of those azo molecules even lasts long often exposed to light and oxygen.

It was found to be observed from a lot of literatures that azo bearing ligands have modified therapeutic effect when they were combined with transition metallic ions (Abou-DobaraI et al., 2014; Esin, 2009). Cobalt, copper, nickel and zinc are the potentially used metal ions that form low molecular weight complexes which found to be effective against various diseases. Literature support even suggests that metal complexes are more active than their ligands because the metal complexes serve as vehicle for activation of the ligands as principal cytotoxic species (Petering, 1973; Hankare et al., 2001).

Biological aspects of metallic ligands depend upon the ease of cleaving the bond between metal ion and ligand. Hence it is necessary to study the relationship between ligand and metal ion in biological system (Zahid et al., 2010). The complexes of transition metal having significant biological actions including antibacterial, antifungal and anticancer

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activities (Refat et al., 2013). It is well known that metal present in complexes generally accelerate the drug action and efficacy of therapeutic agents and the pharmacological efficiencies of drug-based metal complexes depend upon nature of the metal ion and ligands
(Siddiqi et al., 2010).

"Synthesis and Pharmacological Activities of Azo Dye Derivatives": This review discusses the synthesis of heterocycle-incorporated azo dye derivatives, highlighting their potential as pharmaceutical scaffolds. It emphasizes the incorporation of heterocyclic moieties like imidazole, pyrazole, thiazole, and others into azo dye structures, enhancing their bioactive properties. (PMC.NCBI.NLM.NIH.GOV)

"Classifications, Properties, Recent Synthesis, and Applications of Azo Dyes": This article provides a chemical classification of azo dyes, detailing their structural characteristics and common synthesis methods, including the diazotization of primary aromatic amines and subsequent coupling with aromatic substrates. (PMC.NCBI.NLM.NIH.GOV)

"Review on Synthesis of Azo-Phenolic Derivatives, Their Applications, and Biological Activities": Focusing on the use of diazonium salts as intermediates, this review highlights the preparation of phenolic derivatives through coupling reactions, discussing their applications and biological activities. (RESEARCHGATE.NET)

"Recent Advances in the Synthesis of Aromatic Azo Compounds": This review summarizes significant progress in the synthesis of aromatic azo compounds, emphasizing new synthetic methods and the role of functional nanomaterials in the field. (MDPI.COM)

Azo dyes have attracted much attention as they are sensitive chromogenic reagents in addition to interesting complexing nature and have been used as reagents for spectrophotometric and extractive photometric determinations of many metal ions. Some of them are also proved to be particularly useful as indicators in complexometric titrations owing to the low stabilities of the metal indicator complexes. In the subsequent pages of this Chapter, an attempt has been made to outline a survey of relevant literature regarding the preparation, purification, mechanism, general complexing properties of azo dyes and applications of the heterocyclic azo dyes.

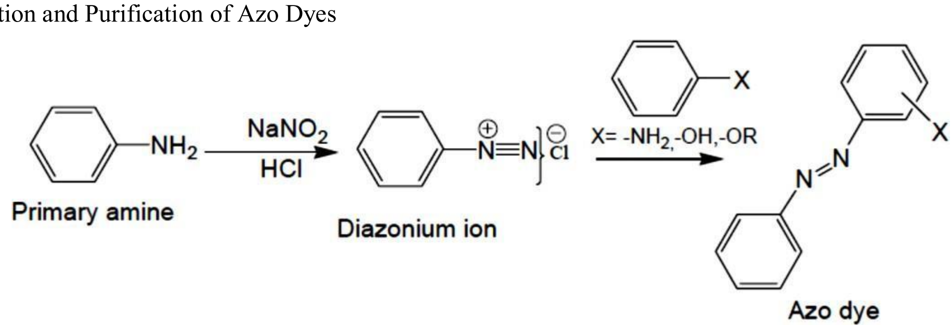
Background of Azo Compounds

Azo compounds contain the characteristic -N=N- functional group, making them useful in textile dyes, biological staining, and pharmaceutical agents. Their stability, color properties, and reactivity make them valuable in various application.

Objectives of the Research

- To synthesize azo derivatives from selected primary amines and phenols.
- To optimize reaction conditions such as pH, temperature, and reagent concentration.
- To characterize synthesized azo compounds using UV-Vis, IR, and NMR spectroscopy.
- To study the stability and potential applications of the synthesized derivatives.

Preparation and Purification of Azo Dyes

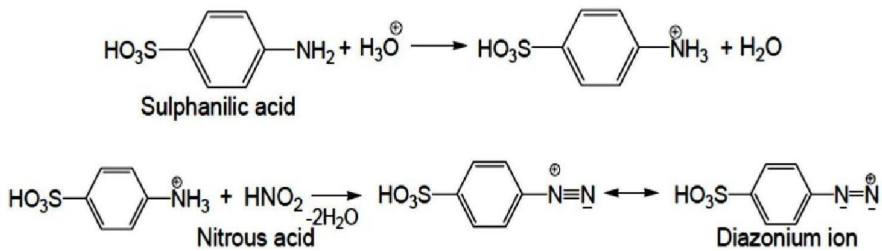


A primary amine (R-NH2) is converted into a diazonium salt and this is reacted with another aryl unit to yield azo dye. Usually, dyes are purified by repeated crystallizations from ethanol. Dissolution of the dye in alkali metal hydroxide solution, followed by extraction with diethyl ether and subsequent re-precipitation with dilute hydrochloric acid, has proved to be useful for purification of thiazole dyes. Some azo dyes are purified by sublimation under reduced pressure. Drying the dye over calcium chloride in desiccators or drying the dye at 120°C removes the water content. The azo dyes can be separated from impurities such as phenol and other azo dye derivatives by paper chromatography, thin layer chromatography and column chromatography [Havard R. Hovind, 1975].

II. LITERATURE REVIEW

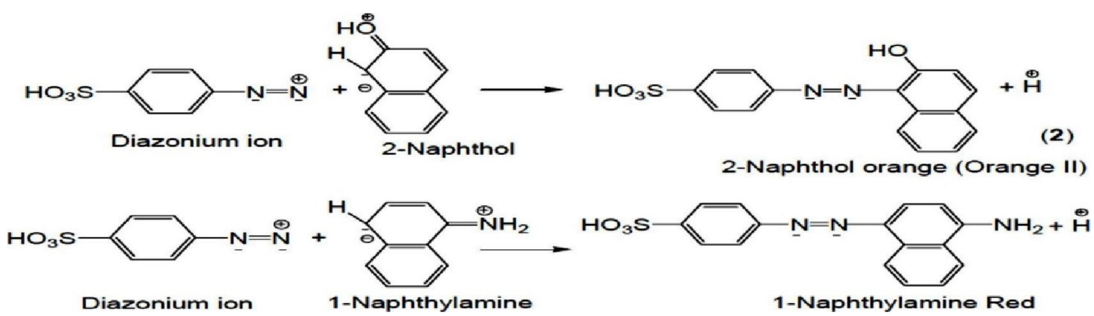
Mechanism of Azo Dye Formation

Step 1: Diazotization



When primary aryl amines react with nitrous acid (HNO2), generated from NaNO2 and HCl), a reaction occurs which makes a diazonium ion. The reaction takes place under 0-5°C conditions.

Step 2: Coupling reaction



The diazotized sulphanilic acid reacts with 2-naphthol and 1-naphthyl-amine to produce an acidic and basic azo dye respectively. The azo coupling reaction represents an electrophilic aromatic substitution. The diazonium cation is a relatively weak electrophile. So, the aromatic ring which attacks must have an activating group such as -OH, -NH2. Electron withdrawing groups on the aromatic rings of the diazonium ion facilitate the substitution reaction. Electrophilic substitution of 2-naphthol occurs preferentially at the 1-position. The -NH2 group in 1-naphthylamine activates the 2- and 4-positions.

In azo compounds the -N=N- group is part of an extended delocalized electron system involving the aromatic rings, called - chromophore. Groups such as -OH and -NH2 attached to chromophores modify the colors of the dyes.

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General properties of azo dyes

Generally azo dyes are red, violet or brownish in their crystalline state and few are readily soluble in water, most of them being only partly soluble or insoluble. However, their solubility can be increased by the addition of organic solvents, e.g., chloroform, cyclohexane and butan-1-ol, then in water.

Complexing properties of azo dyes

Dyes give colored complexes with most of the metals; stable chelates being, especially with some of the transition metals. In acidic and slightly acidic solutions, the metals form complexes with a metal to ligand ratio of 1:1 or mixture of complexes 1:1 and 1:2 in alkaline solutions, the equilibrium usually displaces towards the 1:2 complex [Venkatraman K., 1970].

Among the various available azo dyes, heterocyclic azo dyes are well known for their outstanding photometric sensitivities, constitute an important class amongst the various organic reagents used in the determination of metal ions [Anderson R.G. et al., 1967; Shibata S. et al., 1972; Sandell E.B. et al.,1978; Chauhan O.S. et al., 1980.

Future Scope

1. Advanced Functional Materials

Development of smart azo materials with photochromic and thermochromic properties for applications in optical switches, sensors, and molecular memory devices.

Exploration of azo compounds in liquid crystal technologies and organic semiconductors.

2. Biomedical & Pharmaceutical Applications

Investigation of azo derivatives as potential antibacterial, antifungal, and anticancer agents due to their bioactive properties.

Use of azo compounds in drug delivery systems, particularly for targeted colon drug delivery, as azo bonds can be selectively cleaved by gut microbiota.

3. Eco-friendly & Sustainable Synthesis

Development of green chemistry approaches using eco-friendly catalysts and solvents (such as water-based or ionic liquid-mediated synthesis).

Use of bio-catalysis and enzymatic methods to produce azo derivatives with high specificity and reduced environmental impact.

4. Enhanced Dyeing & Pigment Properties

Modification of azo dyes to enhance their lightfastness, wash fastness, and stability in textiles, leather, and food industries.

Design of biodegradable and non-toxic azo dyes to replace hazardous synthetic dyes in various industries.

5. Applications in Nanotechnology & Sensors

Functionalization of azo derivatives for chemo-sensors and biosensors to detect metal ions, pollutants, and biological molecules.

Integration of azo compounds with nanomaterials for applications in nanomedicine and catalysis.

6. Computational & Theoretical Studies

Utilization of quantum chemical calculations and molecular modeling to predict and optimize the properties of new azo derivatives.

Machine learning-based approaches for predicting synthetic pathways and bioactivity of azo compounds.

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III. CONCLUSION

The result of the experiment is that we get an idea about the Chromophore and Auxochrome interaction due to the change in the colour of the compound which gives us an idea about the Auxochrome and Chromophore interaction. p-nitroaniline + β-naphthol gives you a para red colour & p-chloroaniline + β- naphthol gives you an orange colour.

The synthesis of azo derivatives of primary amines and phenols remains a significant area of research due to their wide-ranging applications in dyes, pharmaceuticals, and advanced materials. This study has successfully explored the synthesis and characterization of these compounds, highlighting their structural properties and potential functionalities.

The findings indicate that azo derivatives exhibit remarkable stability, tunable electronic properties, and potential biological activity, making them valuable candidates for industrial and biomedical applications. The use of different primary amines and phenols allows for structural modifications, leading to derivatives with enhanced color properties, solubility, and reactivity.

Future advancements in green chemistry approaches, nanotechnology, and computational modeling will further refine the synthesis processes, making them more sustainable and efficient. Additionally, expanding research into biomedical applications, eco-friendly dyes, and functional materials will enhance the practical significance of azo compounds.

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