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Review Article

Review in Synthesis and Biological Activities of Azo Compounds

Ghufran Th. Sadeek **Neam H. Saleem**
Department of Chemistry/ College of Education for Pure Science/ University of Mosul/ Mosul
Mohammed M. Ahmed
Directorate of Education/ Kirkuk/ Ministry of Education/ Iraq
Mohanad Y. Saleh
Department of Chemistry/ College of Education for Pure Science/ University of Mosul/ Mosul
Moayad J. Mohammd
Department of Pharmacy/ College Alnoor University/ Mosul

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corresponding author:
Mohanad Y. Saleh
mohanadalallaf@uomosul.edu.iq

ABSTRACT

In this research, we deal with azo compounds, which are organic compounds that contain in their structure one or more active groups, that are the bridge azo groups (-N=N-), which can bind with the alpha group, giving the formula (R-N=N-R) and they are called aliphatic azo compounds, and if associated with an aromatic group (Ar-N=N-Ar), they are called aromatic azo compounds.

We classified the azo compounds according to the groups attached to their ends (which included aliphatic compounds and aromatic compounds) the second class according to the number of azo groups (mono-, di-, tri-, and poly-azo), and the third class according to the type of rings associated with the azo groups (homocyclic azo compounds and heterocyclic azo compounds).

Methods for preparing azo compounds were indicated, including two methods: The direct method (which includes the reduction of aromatic nitro compounds in the presence of zinc, and this method is used in the preparation of the corresponding azobenzene compounds) or the indirect method, which includes two steps in this type of reaction. The first step is the nitrogenation reaction and the second step is the coupling reaction.

Reference was also made to the preparation of diazonium salts through the reaction of primary amines with nitrous acid, which was prepared simultaneously from the reaction of sodium nitrite with mineral acid, at a low temperature between (0-5 °C) because nitrous acid dissociates quickly, and we discussed the resonant forms of diazonium salts.

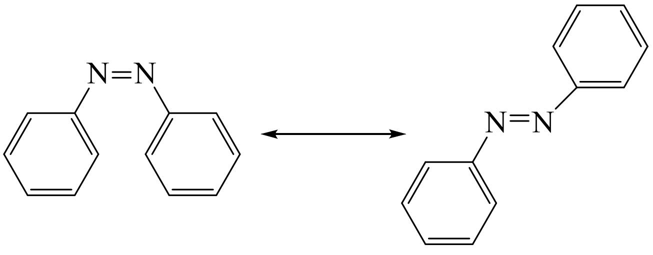
We also dealt with the preparation of azo compounds from the reaction of diazonium salt with an aromatic amine compound or phenol.

We have dealt with azo compounds that are prepared from different other types of compounds that well be illustrated in this review.

Keywords: Azo compounds, diazonium salt, organic reaction.

INTRODUCTION

Azo compounds are organic compounds that contain in their composition one or more active groups, which are the bridge azo groups (N=N) that bind with the alpha group, giving the formula (R-N=N-R) and they are called aliphatic azo compounds, which are non-widespread because it is unstable, it quickly decomposes into nitrogen and hydrocarbons. But if they are with an aromatic group (Ar-N=N-Ar), then they are called aromatic azo compounds. An example of this is azo benzene (Addnan, 2016), as shown in the Fig. below:



(*E*)-1,2-diphenyldiazene

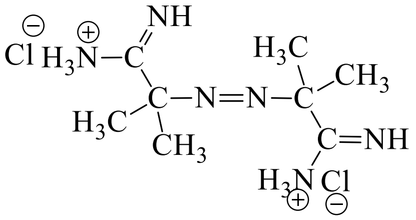
In addition to the azo group, azo compounds may contain electron donor groups called the color developing group, such as ($-NH_2$, -OH, -Cl, $-CH_3$, -SH, -Br) which have a major role in increasing the sensitivity of these compounds as they increase the color intensity and thus affect the stability of these compounds and their complexes, and have many uses in the industrial and biological fields. Due to the high sensitivity and selectivity of these compounds. In addition to its high stability, speed, and ease of preparation, it has been widely used in the field of analytical chemistry, especially in the field of quantitative and qualitative estimation using various techniques and the azo group (-N=N) that connects two carbon atoms with a SP^3 hybridization and is classified as one of the well-known compounds (Huang and Kosower, 1968).

Classification of azo compounds:

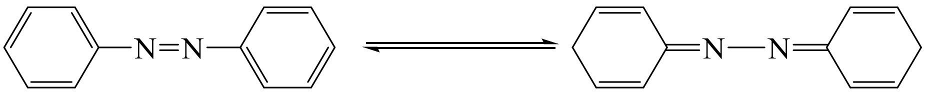
1. According to the aggregates attached to both ends of the azo group:

The simplest classification of azo compounds is to classify them as:

First class: Aliphatic azo compounds, as these compounds and their metallic complexes are considered to be of little spread due to their rapid dissociation into nitrogen and hydrogen composite example below (Garjani *et al.*, 2004).



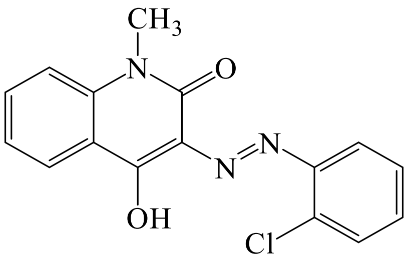
Second class: They are aromatic compounds that are characterized by their high stability due to the appearance of resonance formulas for the rings attached to both sides of the azo group, as shown in the azo compounds (diphenyl azo) (Starikova, 2013). As shown in the Fig. below:



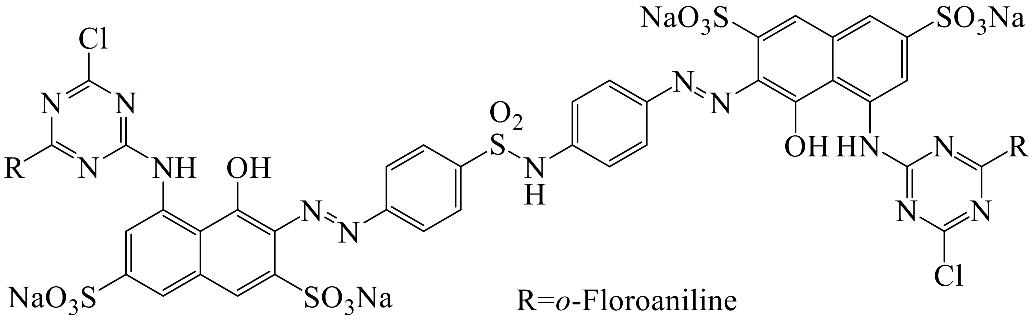
1,2-di(cyclohexa-2,5-dien-1-ylidene)hydrazine

2. According to the number of azo groups:

Mono azo compounds: They are compounds that contain one azo group and are called mono azo compounds, (Akwi and Watts, 2016) as in the Fig. below:

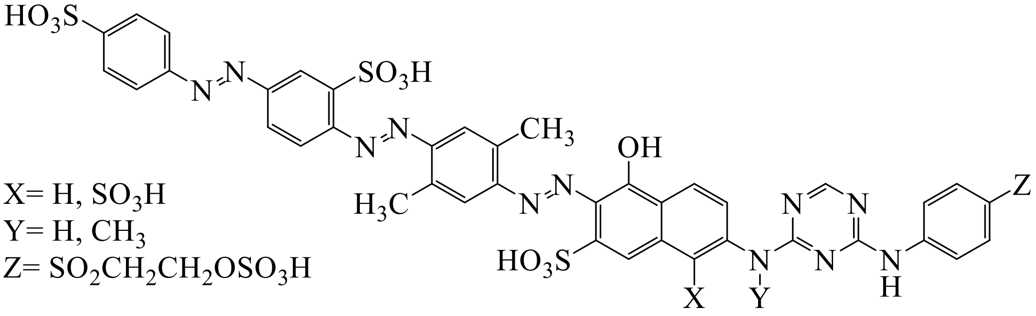


Diazo compounds: Contain two azo groups, (Al-Obaidi *et al.*, 2018) as in the Fig. below:



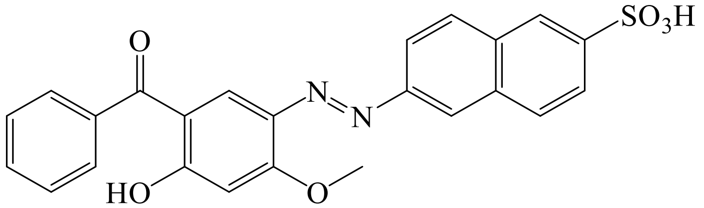
R=*o*-Floroaniline

Tri-azo compounds: These are compounds that contain three azo groups, as shown in the Fig. below (Jarad and Kadhim, 2015):



X= H, SO_3H
Y= H, CH_3
Z= $SO_2CH_2CH_2OSO_3H$

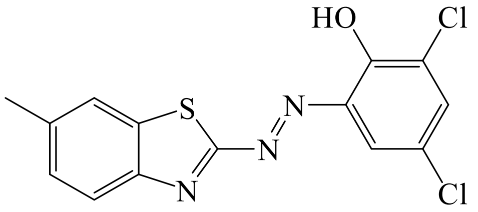
Polyazo compounds: These are compounds that contain more than three azo groups, as in the Fig. below (Heathcock and Streitwieser 1981):



3. Classification according to the type of ring attached to both ends of the azo group:

Homocyclic azo compounds: The aromatic rings in this type of compounds are linked to both ends of the azo group that do not contain hybrid atoms such as (S, N, O) as an example of the formula shown below (Asiri and Khan, 2011).

Heterocyclic azo compounds: Are so named because one or both of their rings sometimes contain hybrid atoms (S, N, O). (Dutta *et al.*, 2016; Fleming and Trost, 1993) It is considered one of the most important types of azo compounds because of its importance in various fields, the most important of which are medicine, science, technology and various industries, including the dye industry. Studies have shown that there are more than 6 million heterocyclic compounds that can be used in this type. The use of these compounds in the dye industry dates back to the year 1950, as shown in the Fig. below (Stuart, 2004).

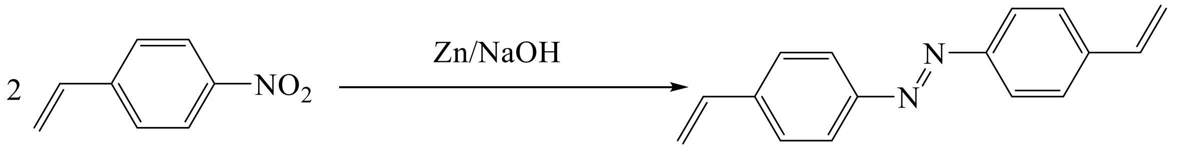


Also, the classification of azo compounds into acidic because they contain exomeromic groups of an acidic nature (SO_3H, -OH, -COOH-) and basic compounds if they contain groups such as (NR_2, -NRH, $-NH_2$), but if they contain both acidic and basic groups, then their classification depends on the number these aggregates and their strength (Dixit *et al.*, 2010).

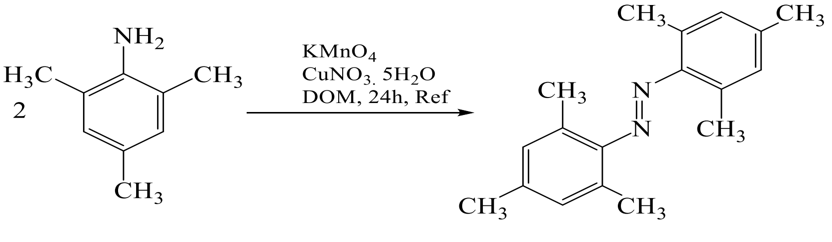
Methods to prepare azo compounds:

1. The direct method:

In this method, azo compounds are prepared by reducing aromatic nitro compounds in the presence of zinc or iron acetate as reducing agents. (Calvino *et al.*, 2006) If this method is used in the preparation of analogous azo benzene compounds. (Mo *et al.*, 2013) As in the reduction of the para-nitro styrene compound shown in the figure below:



Naureeldin and Bellegrade described how to prepare azo compounds by the direct oxidation method, using potassium permanganate and aqueous copper nitrate, as shown in the equation below (Noureldin and Bellegared, 1999).



2. The indirect method:

This method is carried out in two steps

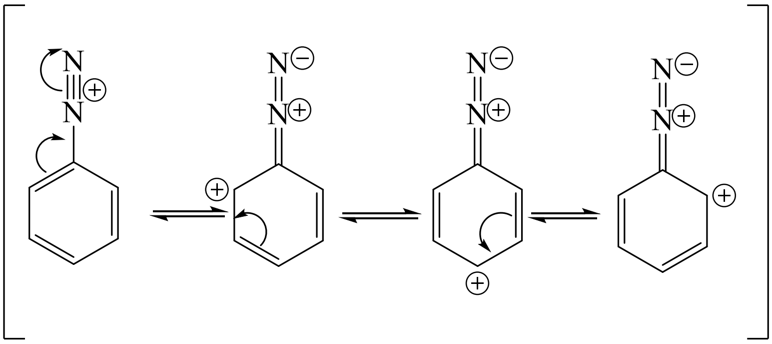
This step includes the reaction of sodium nitrite with a mineral acid such as hydrochloric or sulfuric acid using cooling at a temperature of [0-5°C] and this reaction is called azo coupled (Pan *et al.*, 2000) where it becomes the final equation for the preparation of diazonium salts (Forstinge *et al.*, 2000).

$$Ar-NH_2 + 2HX + NaNO_2 \xrightarrow{0\text{-}5^{o}C} Ar-\overset{\oplus}{N_2}\overset{\ominus}{X} + NaX + 2H_2O$$

$$X= Cl^-, SO_4^{-2}, NO_3^-$$

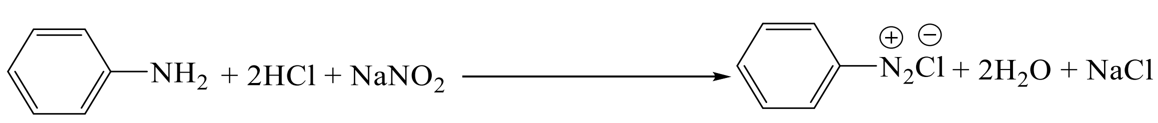
Diazonium salts:

Diazonium salts are formed through the reaction of aliphatic and aromatic primary amines with nitroso acid prepared automatically. Aliphatic diazonium salts are less stable than aromatic diazonium salts, and therefore both types decompose slowly at 0 degrees celsius. Most diazonium salts are used immediately after their preparation without resorting to separating them from their solution. The scientist Peter Grice discovered diazonium salts for the first time in 1858, when he gave them the structural formula R-N2+ With it. (Tao *et al.*, 2012) While alpha diazonium salts are less stable due to their ability to explode (Golka *et al.*, 2004).



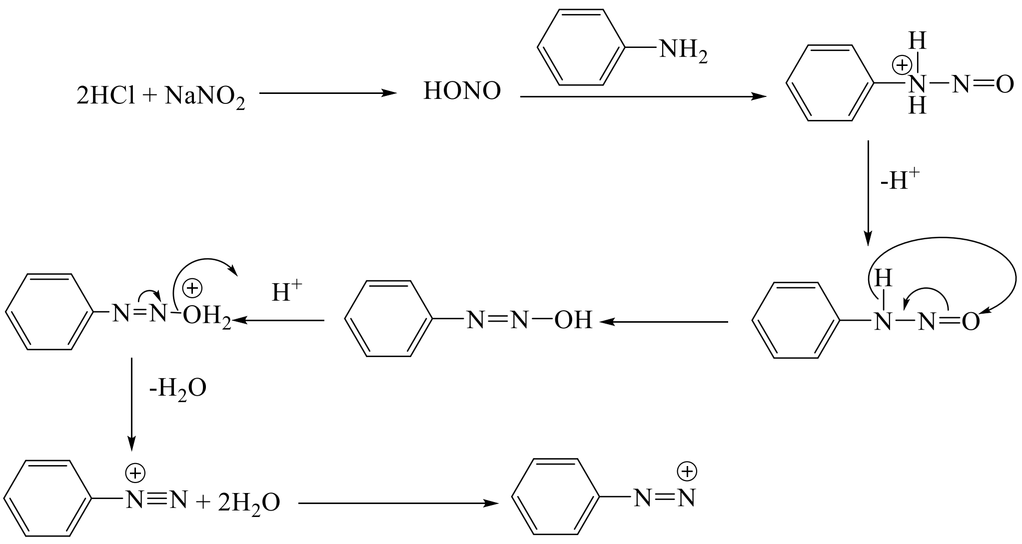
1. Diazonium salts are prepared:

In general, the reaction of the aromatic primary amine with sodium nitrite in the presence of a mineral acid of hydrochloric acid and at a temperature of zero degrees celsius (Guoxi *et al.*, 2011).



2. Mechanism of preparation of diazonium salts:

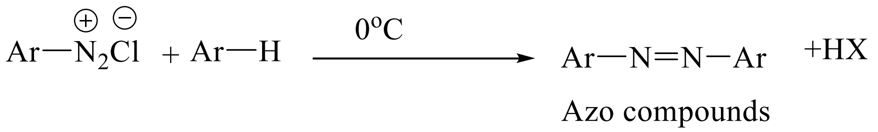
So a weak electrophile is formed, it is diazonium salt, and because of it possesses of these electrophilic properties, the possibility of coupling with compounds with high electrophilic density such as phenols or amines, which are considered nucleophiles through the mechanics of aromatic electrophilic substitution (Engel *et al.*, 2007).



The nitrification process takes place at temperatures as low as (0-5°C). (Hunger, 2002) And due to the extreme instability of the diazonium salts that are formed except at low degrees, they are used immediately after their formation (Husain *et al.*, 2013).

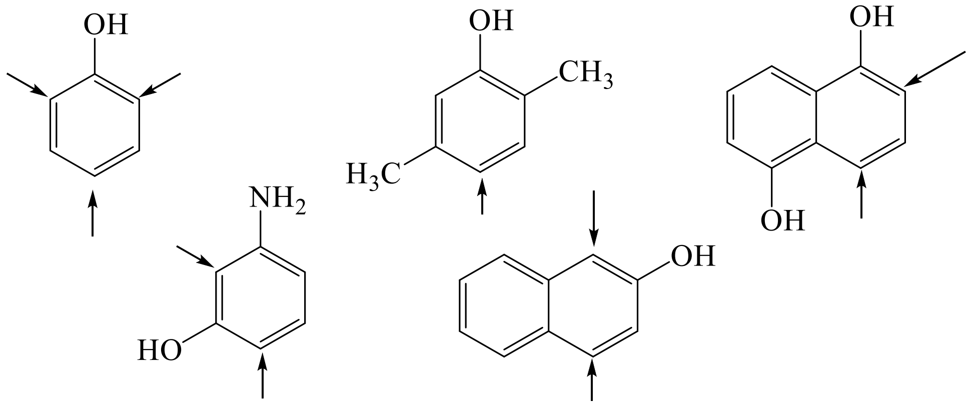
3. Conjugation reactions:

This occurs due to the type of reaction between the diazonium salt formed in the nitrogenation process with another aromatic compound (phenol or amine) under specific conditions (Mohammed and Mustapha, 2010).



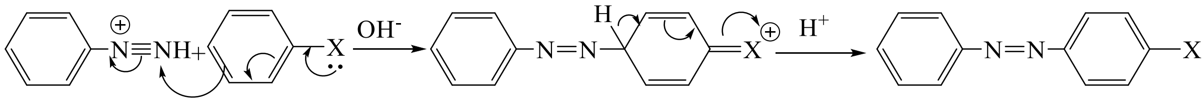
$$\mathrm{Ar{-}\overset{\oplus\ \ominus}{N_2Cl}} + \mathrm{Ar{-}H} \xrightarrow{0^{o}C} \underset{\text{Azo compounds}}{\mathrm{Ar{-}N{=}N{-}Ar}} \quad +HX$$

The reaction mostly takes place at specific sites on the aromatic ring concerning to the phenol or amine groups present on the ring, which are parasites or ortho sites if para is occupied (Stang *et al.*, 1982) as shown below, the preferred sites for conjugation to occur (the dark arrow indicates the preferred sites for conjugation to occur, and the other sites are indicated by the normal arrow).



Azo compound was obvious that the aromatic ring reacting with the diazonium salt must contain a strong electron donor group, such as hydroxyl groups (-OH) or amine groups (NH2-), (NR-), and (NR2-), and also because the reaction medium is acidic. In this case, the reaction medium must be modified by adding appropriate amounts of carbonate or sodium hydroxide (March, 1992).

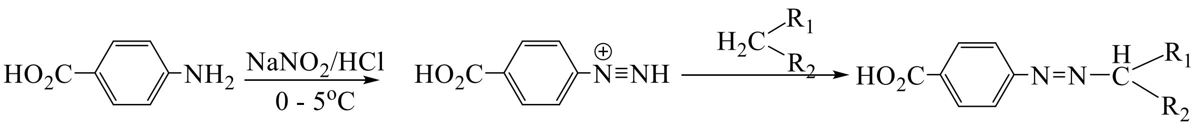
The coupling reaction can also be illustrated by the following example:



X = -OH , -NH$_2$

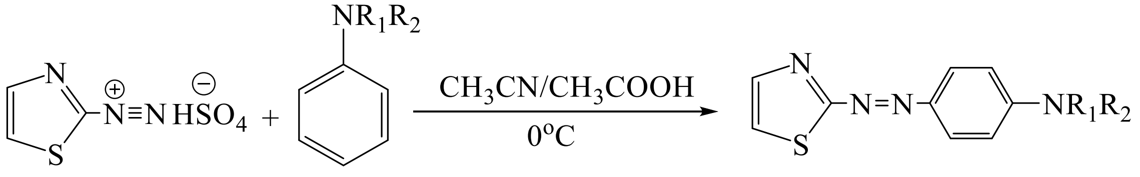
Preparation of azo compounds

Azo compounds were prepared by reacting the diazonium salt of the compound 4-amino benzoic acid with compounds containing active methyl groups such as (ethyl acetoacetate, ethyl cyanoacetate, malonitrile) (Nafis, 2010) as shown in the Fig. below:



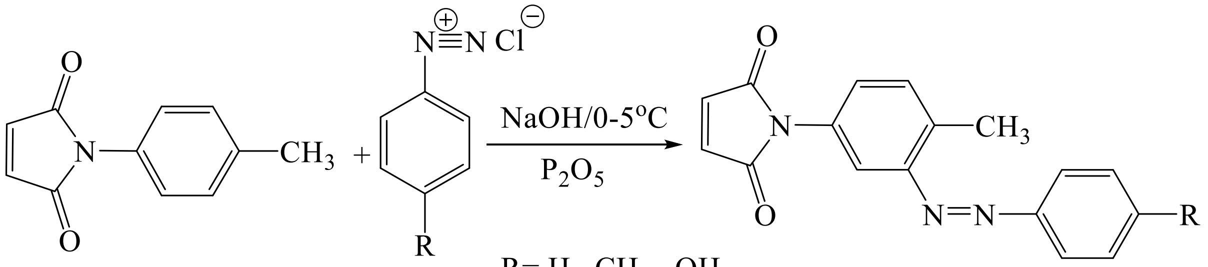
R1	R2
COCH$_3$	CO$_2$Et
CN	CO$_2$Et

A series of azo dyes were prepared through the coupling reaction of (N,N-diethyaniline, 2-anilinoethanol and N-Phenyl-2,2-iminodiethanol) with aminothiazolyl derivatives, and the ratio of these dyes was good (Mokhtari *et al.*, 2009):



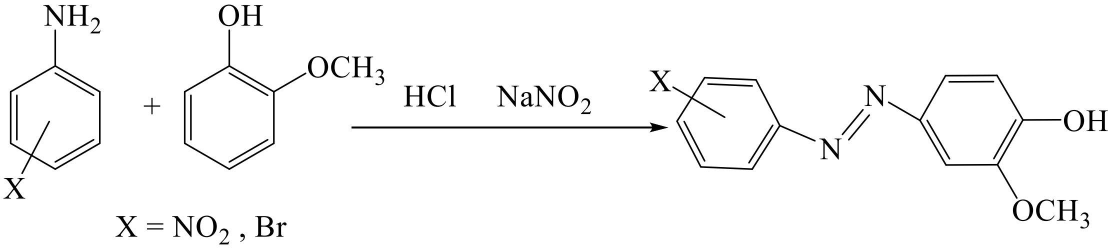
R$_1$ = C$_2$H$_4$OH , R$_1$=R$_2$= C$_2$H$_5$, R$_1$ = H , R$_2$ = C$_2$H$_4$OH

An azocyclic compound linked to a heterocyclic ring prepared from the reaction of the compound N-(4-methyl phenyl) maleimide with aminobenzene, or two compounds in the presence of a catalyst, diphosphorus (P$_2$O$_5$) (Mohammed and Mustapha, 2010).

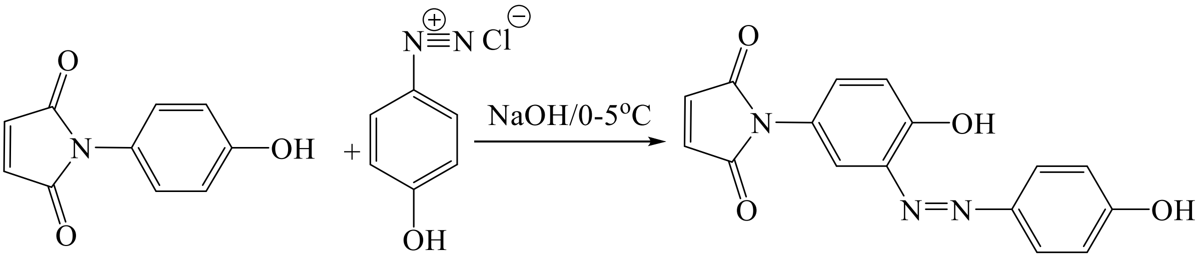


R= H , CH$_3$, OH

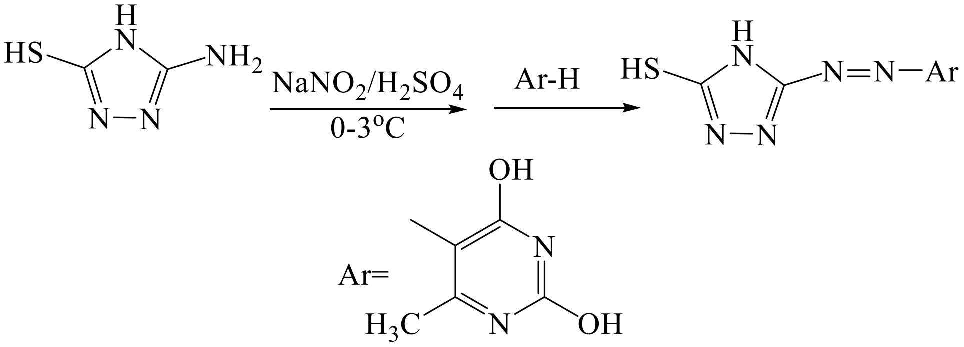
They also managed to prepare diazonium salts from the reaction of aniline substitutes with 2-methoxyphenol in the presence of sodium nitrate and hydrochloric acid. (Jayapal and Sreedhar, 2010).



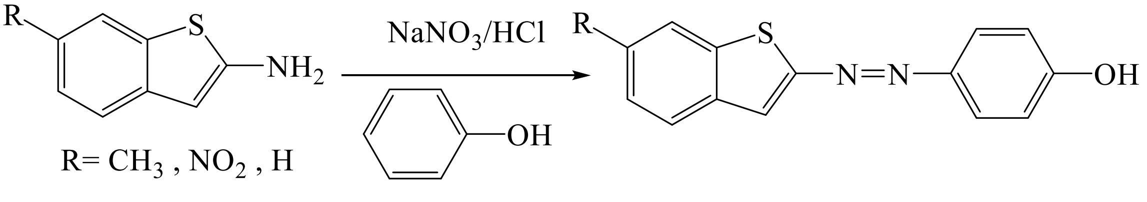
Generally speaking, preparing a cyclic azo dye and studying its properties and biological activity through the reaction of N-(4-hydroxy phenyl) maleimide was done with 4-aminophenol compound as shown in the equation below (Mohammed and Mustapha, 2010):



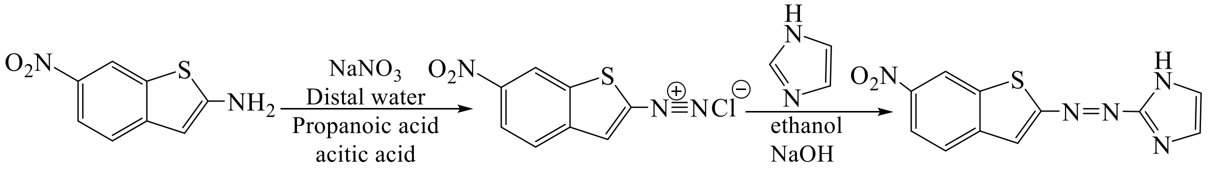
As well as preparing the compound 2,4-dihydroxy-6-methyl-5[5]-3thiazol-4,2,1-triazolyl]-azo-pyrimidine was prepared from -3amino-5-mercapto-1,2,4-triazole as shown in the following equation (Pratt *et al.*, 2001):



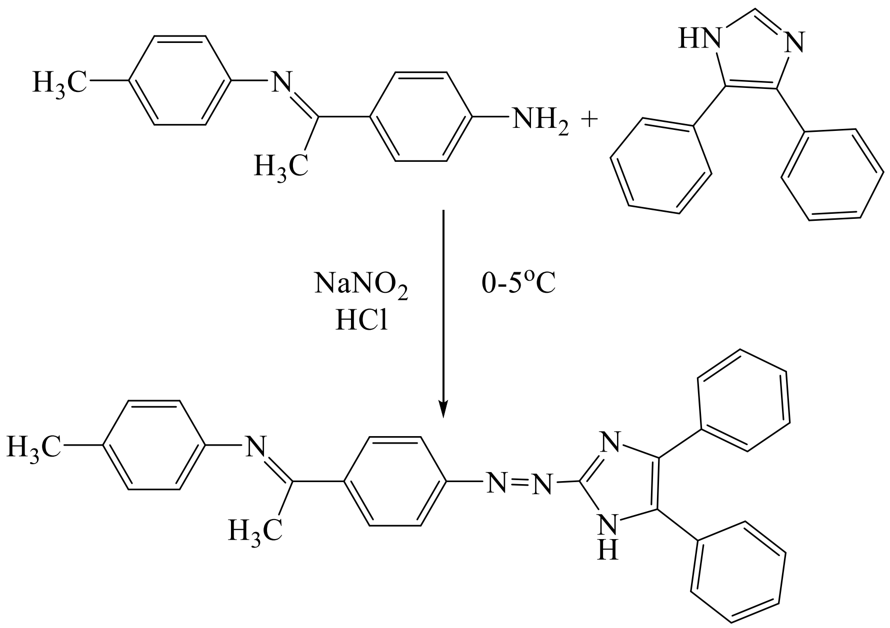
On the other hand, researchers were able to prepare diazonium salts from the reaction of 2-aminobenzthiazole substituents with phenol in the presence of sodium nitrite, hydrochloric acid, methanol, and potassium hydroxide (Karim *et al.*, 2013).



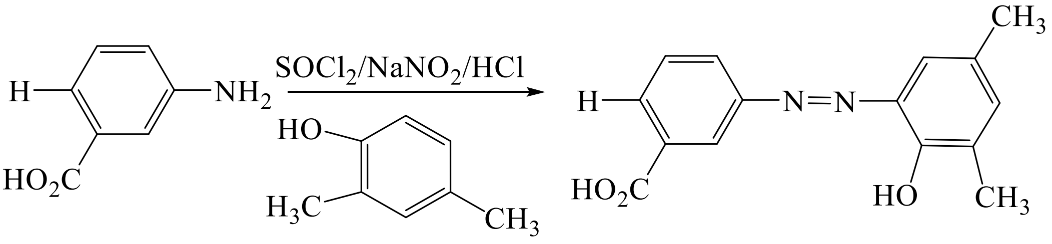
The researchers prepared a dye that includes an electron seeker substitution on position 2 of the imidazole domain, which is included in the structure of this dye (Al-Dilee *et al.*, 2013).



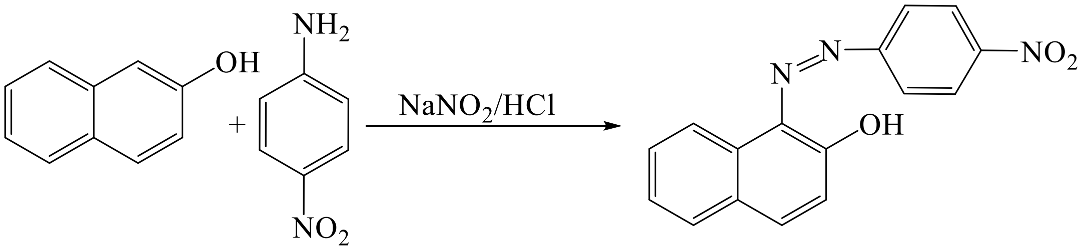
While other researcher also prepared azoimidazole with imidazole ring as in the following equation (Bani *et al*., 2005):



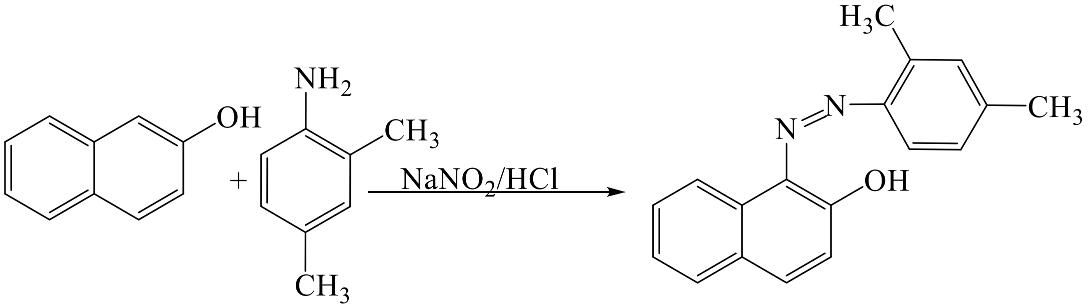
Also, preparation of diazonium salts from the reaction of 3-amino acid Benzoic with 2,4-dimethylphenol in the presence of sodium nitrite, thionyl chloride and acetone at ambient temperature. (0-5) C (Ana *et al*., 2008).



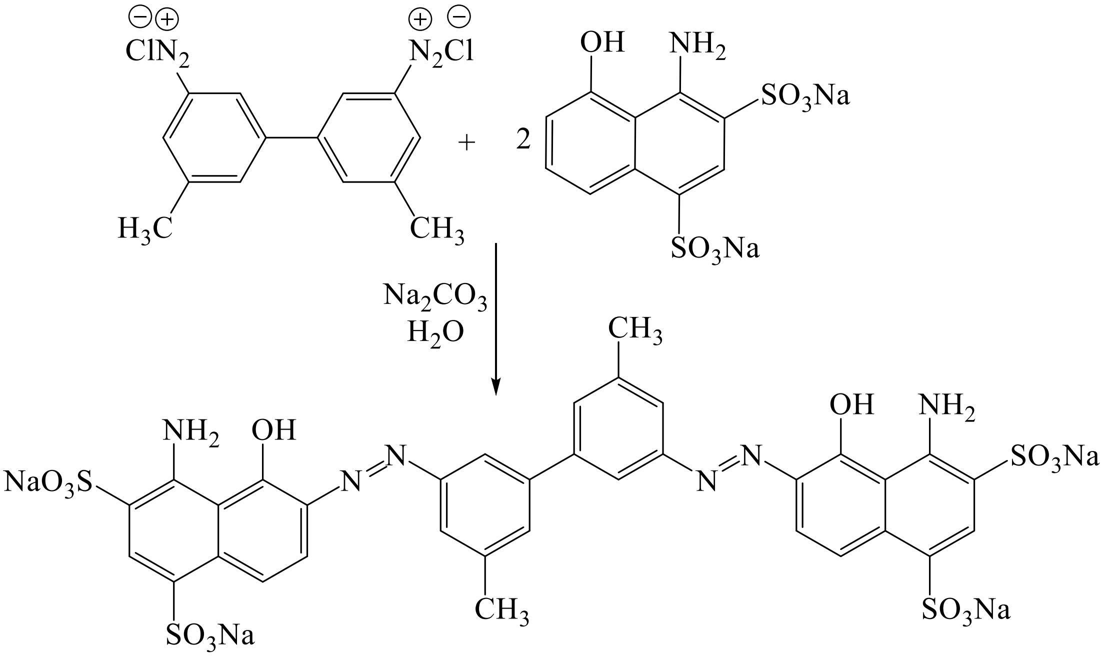
In a study conducted by researcher DeMagalhäes, it was shown that diazonium salts can be prepared by reacting beta-naphthol with 4-nitroaniline in the presence of sodium nitrite and hydrochloric acid at a temperature of (0-5) Celsius (DeMagalhães, 2007).



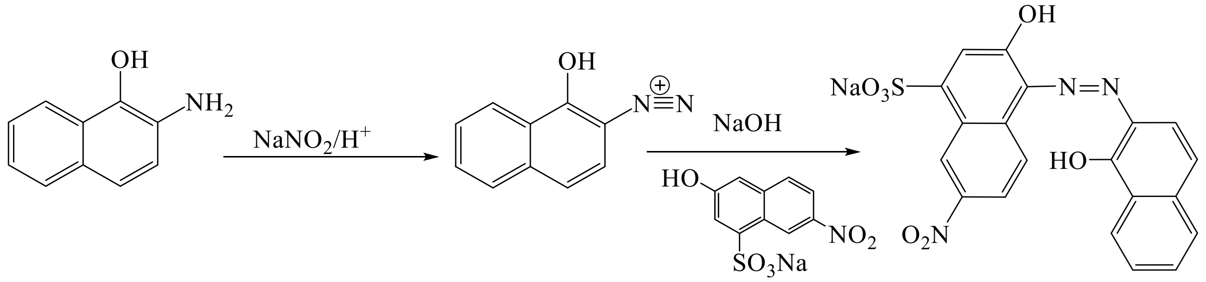
Some diazonium salts were prepared by reacting 2,4-dimethylaniline with 2-naphthol in the presence of sodium nitrite and hydrochloric acid (Kurahashi and Kawase, 1976).



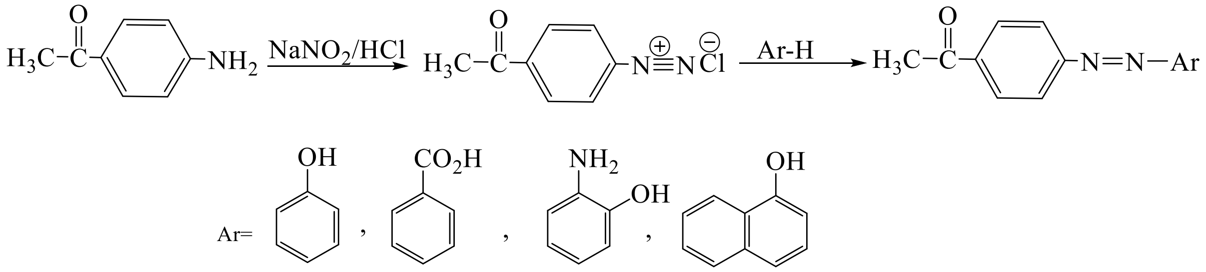
The scientists were able to prepare stable azo compounds and diazonium salts from 5,5-dimethyl-[1,1-biphenyl-3,3-diamine with 2 mol of 1,3-sodium sulfonate -4-amino-5-hydroxynaphthalene (Juma and Sage, 2013).



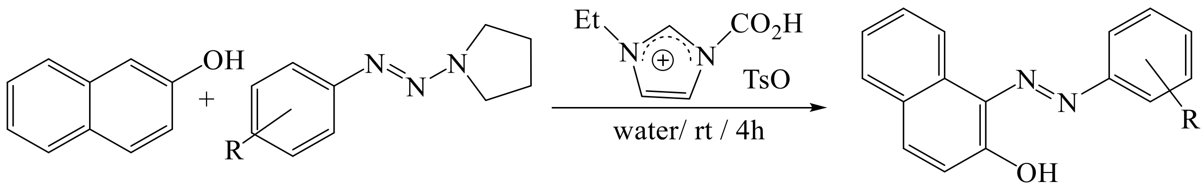
The azo compound was prepared by reacting 3-amino-4-hydroxyl-3-naphthalene and 3-nitro-7-hydroxyl-5-naphthalene sulfonic acid with sodium salt (Asniza *et al.*, 2011).



While researchers were able to prepare diazonium salts from the reaction of 4-aminoacetophenone with phenolbenzoic acid, 2-aminophenol, and naphthol in the presence of sodium nitrite and hydrochloric acid (Neifar *et al.*, 2011).

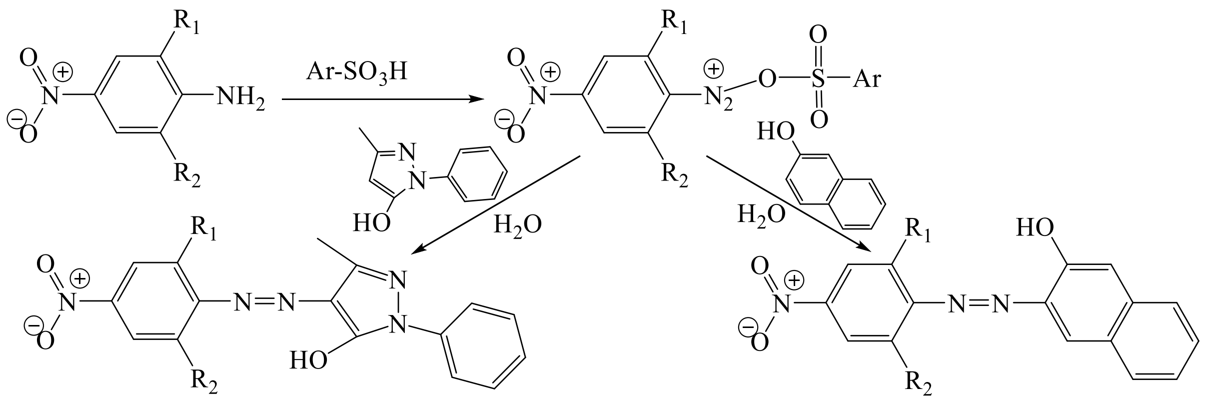


An environmentally friendly and effective method for the synthesis of azo compounds from aryltrisol and -2-naphthol using Brönstedt acid as a catalyst and water as a solvent at room temperature (Yazdanbakhsh *et al.*, 2010).



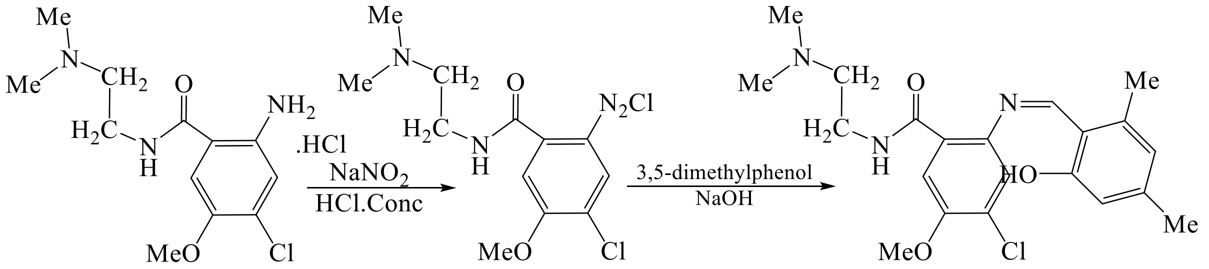
R = H , F , Cl , CH_3, iso-Pr, t-Bu, OCH_3

Azo compounds were also prepared from the reaction of highly stable diazoinum salts prepared from weak basic amines and aromatic hydroxyl compounds (Alam *et al.*, 2009):

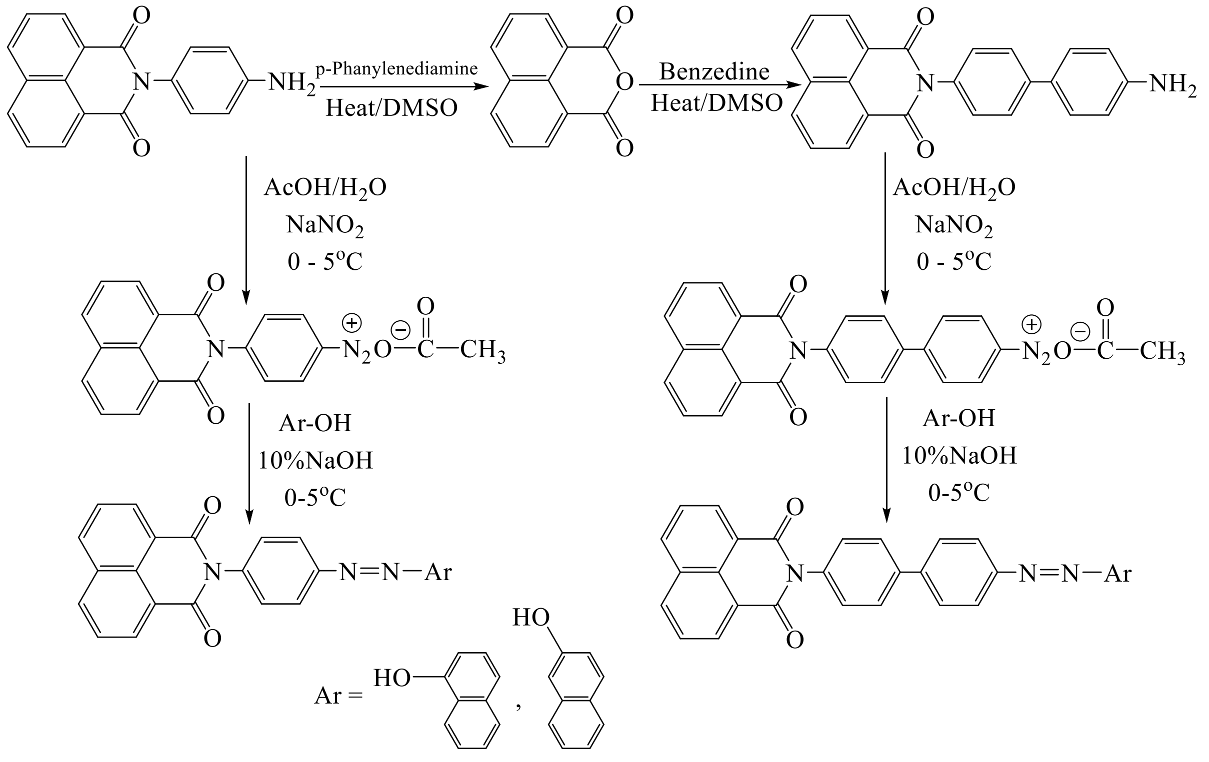


$R_1 = R_2 = H$, CN , NO_2 , Cl , Br

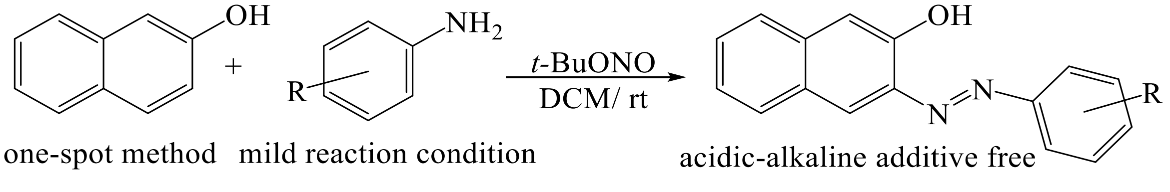
The researcher managed from the preparation of azo compounds, as in the following equation (Weiger, 1988):



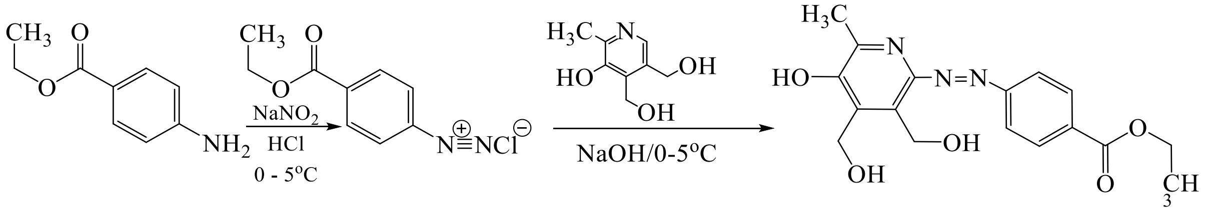
The world empowered from the preparation of azo compounds as well in the following scheme (Obaid *et al.*, 2020):



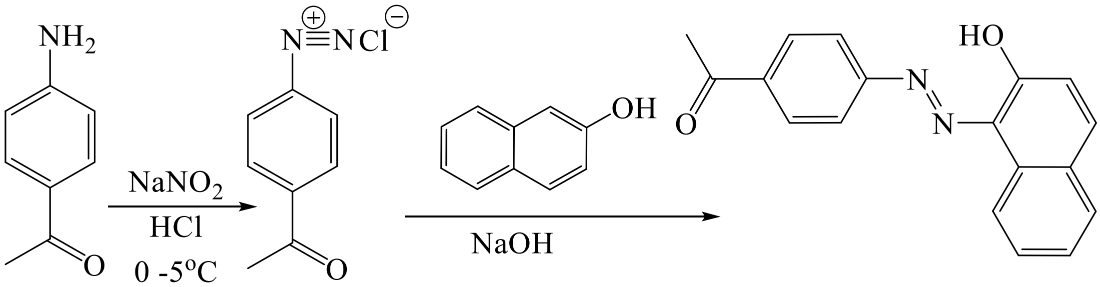
Researcher can preparation of azo compounds, according to the following equation. (Al-Majidi and Al-Khuzaie, 2019):



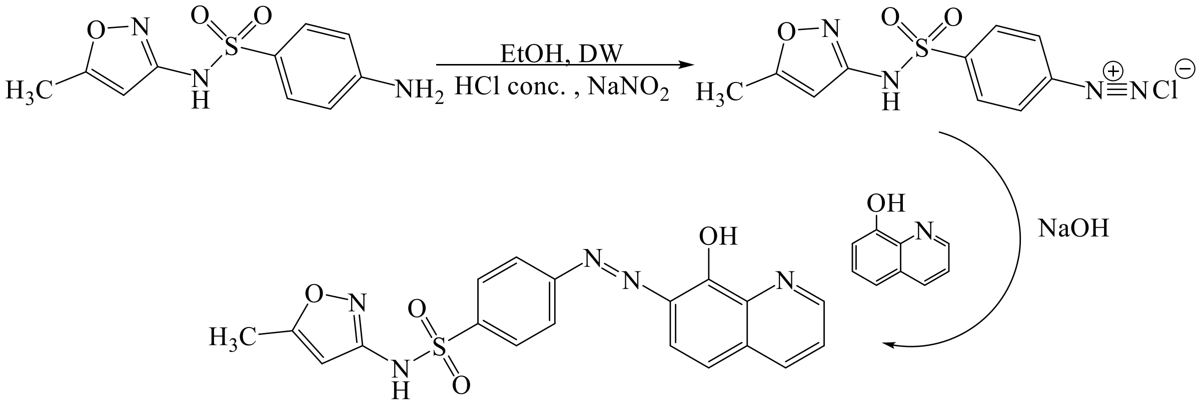
Preparation of azo compounds according to the following equation (Al-Rufaie, 2016):



In a recent study conducted, researchers were able to prepare a series of nitrogenous compounds as in the following equation (Abdulrazzaq and Al-Hamdani, 2023):



The researcher was able to prepare some azo compounds, as shown in the following equation (Hassan *et al.*, 2023):



Schiff basis:

These compounds were named after their discoverer, Hugo Schiff, and thanks to him, the preparation of the first organic compound containing in its composition the azomethine group (-CH=N) from the reaction of condensation of some carbonyl derivatives with primary amines in different solvents that have a role in drawing water molecules as a result of the said reaction. Schiff bases have been widely used in various fields, because they have physical and chemical properties that qualify them to bind with many metal ions to form complexes, these have proven useful in many practical applications in various fields. In recent years, the researchers' work focused on an effective biological study of this type of compound when used as a catalyst in the field of organic chemistry. The effectiveness of Schiff bases is attributed to the non-bonding electron pair of the hybridization (SP^2) of a nitrogen atom of the azomethine group. Schiff bases derived from aldehydes have their general form ('NR=RHC'), as each of (R and 'R') represent homogeneous or heterogeneous alkyl or aryl groups substituted and non-compensated by groups of different structures and characteristics on the part of electronic withdrawal and push, and accordingly different names are given to them, including amines Imines, Anils, Benzamil's, or Azomethenes, while ketimines are called Schiff bases derived from ketones (Mohammed and Mustapha, 2010).

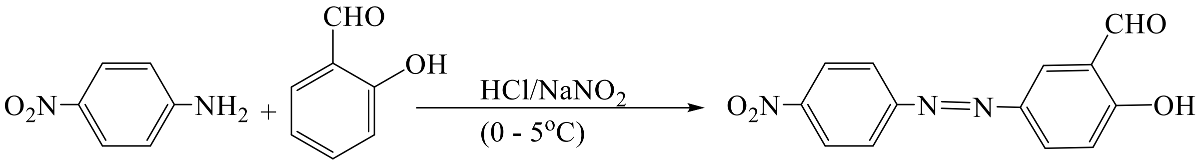
Azo compounds -Schiff's Basis:

This type of organic compound gained its name from its chemical composition, which includes the (azo bridge) group added to the (azo methine) group. This class of vehicles is relatively recent. When compared with the compounds of each of the azo and Schiff bases. Both of the mentioned groups contain a nitrogen atom with a non-electronic double electron that gives it many of its physical and chemical properties (Mohammed and Mustapha, 2010).

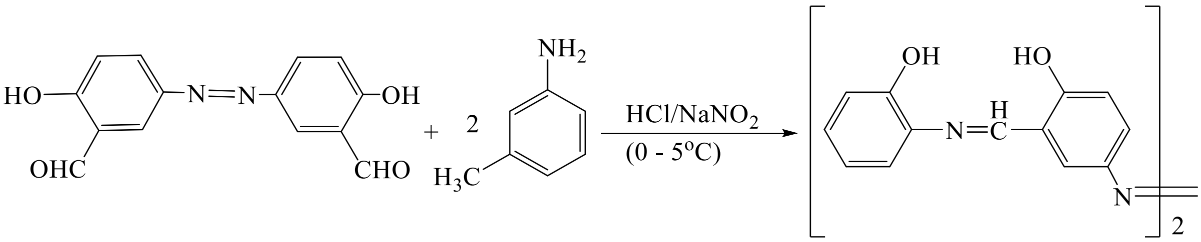
And azo compounds-Schiff bases prepared through the reaction between diazonium salts with Schiff bases prepared previously, which contain substitutes (hydroxide or amine) in different locations (Patel *et al.*, 2005).

Preparing the azo-Schiff's rules:

Azo compounds Schiff's bases are organic compounds of great importance in organic chemistry that were first introduced by the researcher (Botrus, 1977). These compounds are characterized by their beautiful and distinctive colors. There are many compounds prepared by the same researcher (Al-Haidari, 1992).



Researcher generally prepared a several of azo-Schiff bases with a many of different aromatic amines using sublimation and in the presence of an ethanol solvent (Palleros, 2004).



The researcher (Patai, 1978) and his group preparation of Schiff's azo-bases using microwave irradiation.

Chalcones:

Chalcones are chemical compounds containing a group (Ph-CH=CH-COPh) and has many biological effects, including against bacteria and against fungi (Qiu *et al.*, 2019). Chalcones are prepared by aldol condensation with sodium hydroxide (Hu *et al.*, 2002; Mahdi *et al.*, 2022; Botros, 1977) or use an acid medium (Nafis, 2010) or use thionyl chloride or potassium fluoride chalcones can be prepared using microwave technology (Rudyk *et al.*, 2003).

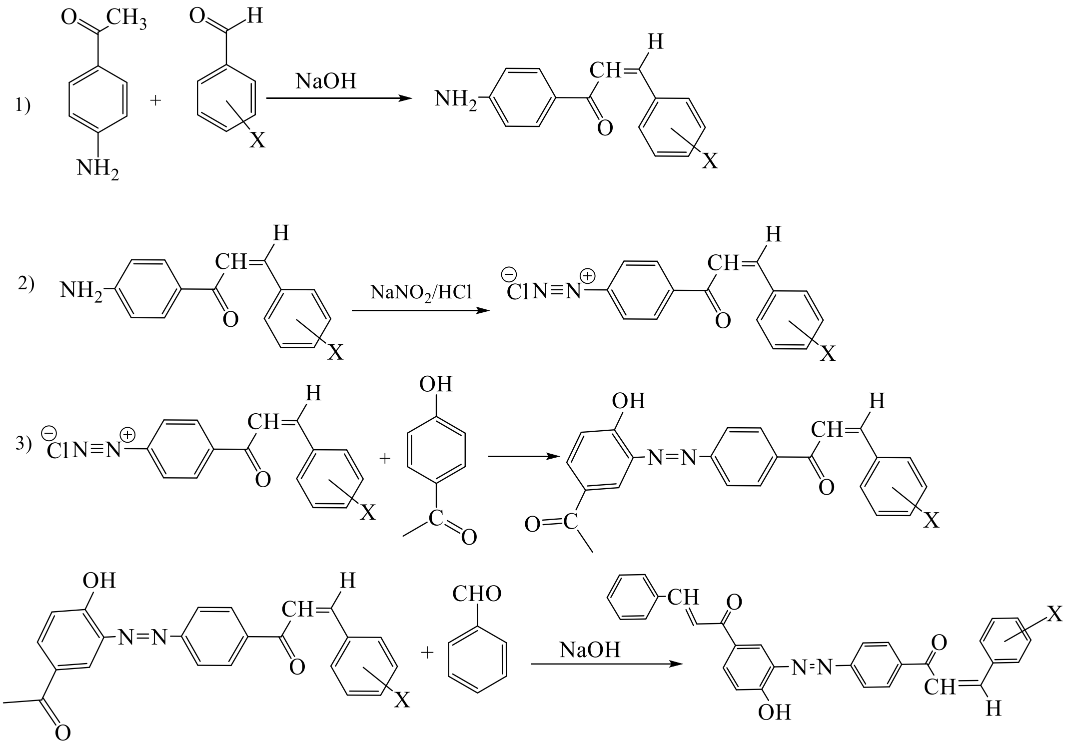
But dichalcones are prepared by using binary aldehydes in aromatic compounds or aromatic compounds containing two acetyl groups (-CO-CH3) (Bondock *et al.*, 2006).

Azo-Chalcone compounds

They are chalcone compounds linked to an azo-phenyl group, and are prepared by the reaction between the diazonium salt containing the acetyl group with different aromatic aldehydes (Nasser, 2011).

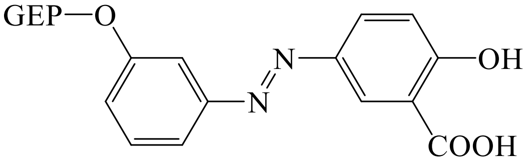
Preparation of Azo-Chalcone

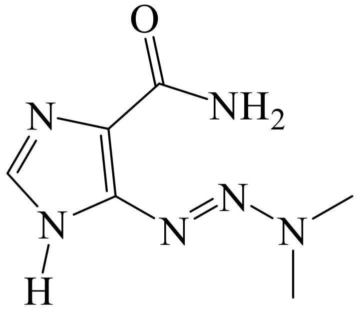
A study was conducted by researcher Shatha and his group in 2020 to prepare some azo-chalcone compounds (Obaid *et al.*, 2020), as shown in the diagram below:



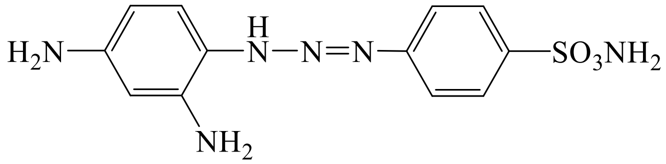
Biological activity:

Scientists were interested in preparing azo compounds that have biological effectiveness, as they exploited the biological effectiveness of azo compounds in terms of their use as important drugs because of their antibacterial role. (Solankee *et al.*, 2010) Among these germs is the gouty colon germ, and the bacteria that cause chronic bowel disease and cancer aminosalicylic acid immobilized on polyethylene glycol-5 was used as an anti-inflammatory, as in the following Fig.:

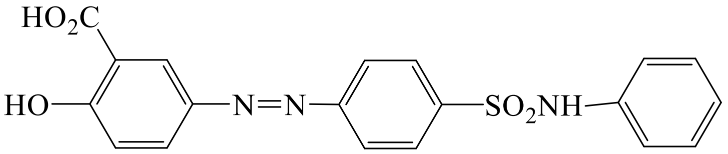




The compound 5-(3,3-dimethyltriazoeno) midazole-4-carboxamide, known as (Dacarbazine), is a drug used to treat some cancerous tumors. It works to break down the DNA structure in some stages of the life cycle of the cancer cell, which stops its growth and causes death (Li *et al.*, 2005). As shown in Fig.:

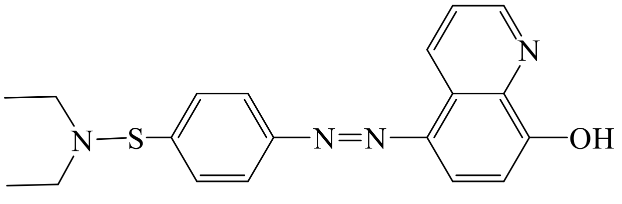


It was also found that the compound azo-4-(parasulfamide phenyl azo)-1,3-diaminobenzene known as (Ptontsil) has a therapeutic effect on streptococcus infection, it had an effective role in stopping the growth of this type of bacteria, and we explain below the formula of the aforementioned compound (Zhang *et al.*, 2018).

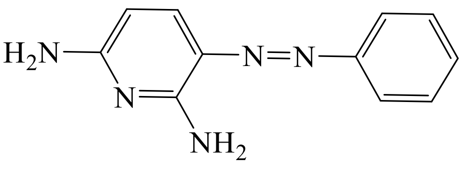


Among the azo compounds with a therapeutic effect is the compound 5-[Para (2-permethylsulfamil) phenyl azo] salicylic acid. It is known medically as (Azulfidine), which is used to treat ulcers of the colon (ulceration colitic) because it is absorbed slowly and suffers from cleavage at the azo site to produce the compound 5-amino salicylic acid, which has an effective effect in the treatment of ulcers of the colon. Below is the structural formula of the azo compound mentioned.

In a study of (5-DSAQ) N,N-(4-Diethyaminosulfonylphenyl azo) hydroxyquinoline was found to have antifungal properties, but the complexes of this dye with binary ions such as Cu, Zn, Ni, Co, and Mn showed more effective on antifungals.



It has been found that when using 3-Dyldiamine-2,6-phenylazopyridine as an analgesic for urinary system pain, it also helps to provide comfort and reduce the pain and burning resulting from frequent urination (Eliel and Wilen, 1994).



CONCLUSIONS

It is known the great importance of azo compounds, and what increased their importance is their association with highly stable chalcone compounds. Therefore, the aim of the study in the work was that we classified the azo compounds according to the groups attached to their ends (which included aliphatic compounds and aromatic compounds). The second class according to the number of azo groups (mono-, di-, tri-, and multiple). Azo the third class depends on the type of rings attached to the azo groups (homocyclic azo compounds and heterocyclic azo compounds).

The most important methods of synthesis of compounds were highlighted, as well as their wide uses.

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دراسة مراجعة تخليق لمركبات الآزو وتقييم الأنشطة البيولوجية لها

غفران ذنون صديق **نعم حازم سليم**
قسم الكيمياء/ كلية التربية للعلوم الصرفة/ جامعة الموصل
محمد محمود أحمد
مديرية تربية كركوك/ وزارة التربية العراقية
مهند يقضان صالح
قسم الكيمياء/ كلية التربية للعلوم الصرفة/ جامعة الموصل
مؤيد جاسم محمد
كلية الصيدلة/ جامعة النور

الملخص

مركبات الآزو وهي مركبات عضوية تحتوي في بنيتها على مجموعة نشطة وهي الآزو الجسرية (−N=N−)، والتي يمكن أن ترتبط مع مجموعة ألفاتية مما يعطي الصيغة (R-N=N-R) وتسمى مركبات الآزو الأليفاتية، وإذا ارتبطت بمجموعة اروماتية (Ar-N=N-Ar) تسمى مركبات الآزو الاروماتية.

قمنا بتصنيف مركبات الآزو حسب المجموعات الملحقة بأطرافها (والتي شملت المركبات الأليفاتية والمركبات الاروماتية) الصنف الثاني حسب عدد مجموعات الآزو (أحادية وثنائية وثلاثية ومتعددة الآزو) الدرجة الثالثة حسب نوع الحلقات المرتبطة بمجموعات الآزو (مركبات الآزو الحلقية المتجانسة ومركبات الآزو الحلقية غير المتجانسة).

وتمت الإشارة إلى طرق تحضير مركبات الآزو ومنها طريقتان: الطريقة المباشرة (التي تتضمن اختزال مركبات النيترو الاروماتية في وجود الزنك، وتستخدم هذه الطريقة في تحضير مركبات الآزوبنزين المقابلة) أو الطريقة غير المباشرة والتي يتضمن خطوتين في هذا النوع من التفاعل. الخطوة الأولى هي تفاعل النيتروجين والخطوة الثانية هي تفاعل الاقتران.

كما تمت الإشارة إلى تحضير أملاح الديازونيوم من خلال تفاعل الأمينات الأولية مع حامض النتروز، الذي يتم تحضيره بشكل متزامن من تفاعل نتريت الصوديوم مع حامض المعدن، عند درجة حرارة منخفضة تتراوح بين (0−5 درجة مئوية) لأن حامض النتروز يتفكك بسرعة، وناقشنا الأشكال الرنينية لأملاح الديازونيوم.

كما تناولنا تحضير مركبات الآزو من تفاعل ملح الديازونيوم مع مركب الأمين الاروماتي أو الفينول.

لقد تعاملنا مع مركبات الآزو التي يتم تحضيرها من أنواع أخرى مختلفة من المركبات والتي سيتم توضيحها جيدًا في هذه المراجعة.

الكلمات الدالة: مركبات الآزو، ملح الديازونيوم، التفاعل العضوي.