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Review Article

COUPLING REACTIONS INVOLVING ARYLDIAZONIUM SALT: PART-IX. REVIEW ON SYNTHESIS OF AZO-PHENOLIC DERIVATIVES, THEIR APPLICATIONS AND BIOLOGICAL ACTIVITIES

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ABSTRACT

Aryl diazonium salts are easily prepared, common and highly applicable intermediates in the synthetic organic chemistry because of their high reactivity and varied reactions. They are synthesized starting from primary aromatic amines by diazotization and coupling with aromatics like phenols (or primary aromatic amines). Azo dyes are industrially very important for technical purposes. Azo compounds have many applications like acts as pigments, antioxidants, the polymeric biodegradable pro-drugs and many used in food, cosmetics and drug industry as synthetic colorants. The present review highlights the literature involving diazonium salts as active intermediate for preparation of synthetically useful phenolic derivatives used up to 2010 with their applications and biological activities.

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INTRODUCTION

The azo compounds or dyes are characterized by the presence of the azo moiety ($-N=N-$) in their structure, conjugated with two, distinct or identical, mono- or polycyclic aromatic or hetero-aromatic systems. Because of their specific physico-chemical properties and biological activities, they have found a broad application viz. in pharmaceutical, cosmetic, food, dyeing or textile industry and analytical chemistry.

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 pigments¹. Since the discovery of aryl diazonium salts¹⁻³ in 1858 many developments in dye and other organic industry have benefited for more than a century in 1884, scientist, Sandmeyer treated copper(I) chloride with benzenediazonium salt to convert to chlorobenzene⁴⁻⁵. Thereafter, varied workers highlighted uses of aryl diazonium salts. Gomberg and Bachmann (1924)⁶⁻⁸, Meerwein (1939)⁹ showed reaction of α,β -unsaturated carbonyl compound-Meerwein arylation. In 1977, Doyle et. al.,¹⁰⁻¹¹ reported no need of aqueous acid for the formation of this intermediate. After the work of Kikukawa and Matsuda (1977)¹² in the next 50 years the coupling reactions of C-C and C-B bonds have

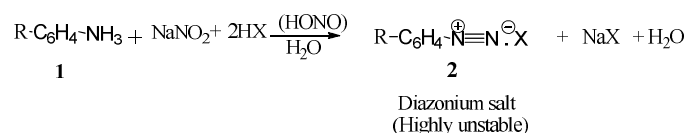
been well elaborated. The structures of compounds were studied to confirmation their structure using different type of data (analytical and the spectroscopic) using techniques like UV-Vis, FTIR, ¹H NMR. Commonly, they are prepared by diazotization², a procedure in which a primary aromatic amine is treated with a source of nitrous acid (HNO_2). 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 isolate¹⁰.

In addition to dye and pigment industry¹⁵ the azo compounds are applicable for biocidal treatment of textile materials because they exhibit biological activity. Azo compounds are well known for their medicinal importance and are recognized for their applications as – antiseptics⁴, antineoplastics¹⁶, antibacterial¹⁷⁻¹⁸ antidiabetics¹⁹ and antitumor²⁰. They are involved in a many biological reactions such as inhibition of carcinogenesis, protein synthesis and nitrogen fixation²¹. Azo compounds are valuable in the medicinal and pharmaceutical fields²² and probably the azo-imine linkage might be responsible for the biological activities displayed by some Schiff bases as reported²³⁻²⁴.

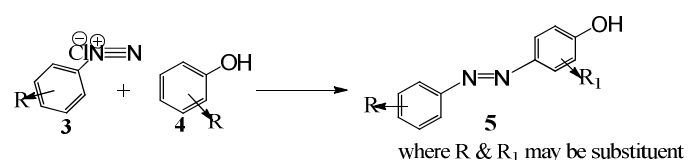
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Some of the azo compounds are studied as HIV inhibitors of viral replications²⁵. The existence of azo moiety show antibacterial and pesticidal activities. The diazonium salt reacts with other arene(coupling agents) to show diazocoupling reaction²⁶. The azo group containing compounds, as antimicrobial agents has been the subject of many reports²⁷⁻³⁷. Synthesis of most azo compounds involves diazotization of a primary aromatic amine, followed by coupling with coupling agents²⁶ viz. ethylacetate²⁷, pentane-2,4-dione(or acetylacetone)²⁸⁻²⁹, phenols³⁰⁻³⁵ or anilines³⁶. Thus, phenolic, salicylic and naphtholic compounds undergo diazotization reactions and because of variety applications of the azo compounds, it is interesting to study synthesis of such phenolic azo compounds. Literature shows studies on their derivatives in order to explore the newer potentials of similar compounds. Few times azo compounds are often described as a chromogen in the literature³². The hydroxy-³⁰⁻³⁵ and or amino-³⁶ groups are common functional group of organic compounds used as coupling agents³⁷. The emergence of diverse classes of synthetic dyes³⁸ including azo dyes occurred due to constant effort to find specific dye for application in diverse materials of industrial importance which include, but not limited to textile fabric³⁹, silk, wool and nylon⁴⁰ fabrics also. Furthermore, azo compounds also have a many applications in photo-industry such as photodynamic therapy, photographic or electro-photographic systems and are dominant organic photoconductives^{9,32}. Recently, no nitrous acid is used during the diazotization which led to the procedure with easy operations, environmentally benign conditions and high yields of the products⁴¹. Recently a review on azo compounds of salicylic acid and its biological activities has been reported⁴². Reaction of primary aromatic amine, **1** with nitrous acid formed from sodium nitrite and hydrochloric acid at 0-5°C forms a diazonium salt, **2** which is highly unstable and hence very reactive moiety. **Scheme-1** shows the general reaction of formation of diazonium salt, **2**. The **Scheme-2** shows the general reaction of diazonium chloride, **3** with phenolic compound, **4** to form the phenolic-azo compound, **5**.



Scheme-1: General Reaction Mechanism of Diazonium salt formation.



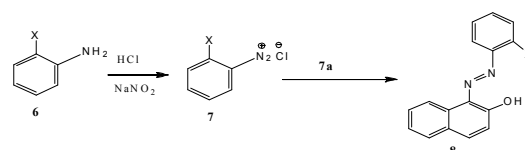
Scheme-2: General Reaction of Diazonium salt with Phenolic compound.

Some aromatic amines (e.g. 2-Naphthylamine, o-Toluidine, o-Anisidine and 2,4-Diaminotoluene) are used to prepare the tattoo ink. The Body moisturizer, hair dye and nail polish contains varied amount of p-aminophenol and 1,3-Diaminotoluene. All these causes potential carcinogenicity.

They are also present in food and food packaging⁴³. These compounds (and the other mentioned in this review) were characterized by elemental, IR, ¹H NMR, ¹³C NMR and mass spectra.

LITERATURE SURVEY AND DISCUSSION

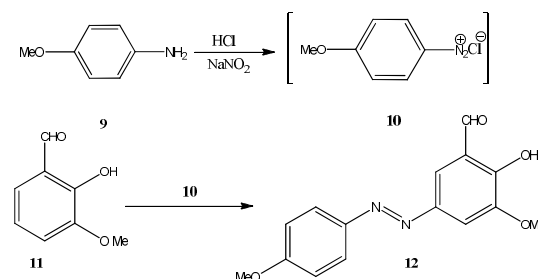
The series of azo compounds, **8** were synthesized via the diazotization of different aromatic amines followed by coupling with 2-naphthol²⁵, **7a**. These compounds were characterized by IR, ¹H NMR and ¹³C NMR spectra. Synthesized compounds(**Scheme-3**) have been tested to assess their antimicrobial properties using disk diffusion method. The minimum inhibitory concentrations (MIC) were also determined by the broth micro-dilution technique. Some of the products exhibited comparable activity with known standard drugs at same concentration.

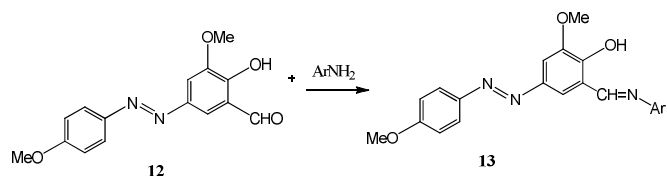


Scheme-3: Azo coupling reaction with □-Naphthol.

Two novel azo dyes were reported by A. Chakraborty et. al.⁴⁰ by coupling of diazo solutions of 4-anisidine and 2-nitro-aniline with sodium-2-naphtholate followed by acidification in ice cold condition. Resultant azo phenolic dyes were analysed by UV-Vis, IR, (¹H ¹³C) NMR and Mass spectra. It is evaluated on silk, wool and nylon fabrics. Also, antibacterial properties were evaluated. Dyes from 2-nitro-aniline showed more antibacterial potency than for 4-anisidine.

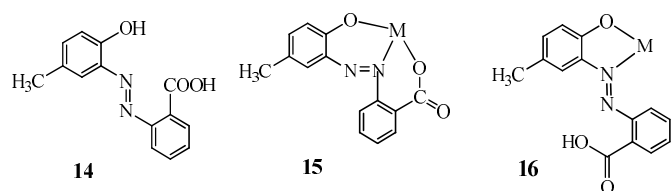
The condensation of different aromatic amine, p-anisidine, **9** and a new azoaldehyde, 2-hydroxy-3-methoxy-5-(4-methoxyphenylazo) benzaldehyde, **12** by two different methods⁴⁴ formed ten new azo Schiff bases, **13**. All new compounds (**Scheme-4**) were tested against five microorganisms: *S. aureus* (Gram positive and methicillin resistant), *B. subtilis* (Gram positive), *K. pneumonia*, *P. aeruginosa* and *E. coli* (Gram negative). Compounds **12**, **13a**, **13c**, **13d** and **13g** were moderately active against *S. aureus* and *B. subtilis*. Compound **SO₂** was highly active against *B. subtilis* and moderately active against *S. aureus*. Other compounds were inactive against these strains of bacteria. The antifungal activities of these compounds were also tested against eight different fungal species. None of them were active against the fungi species tested.



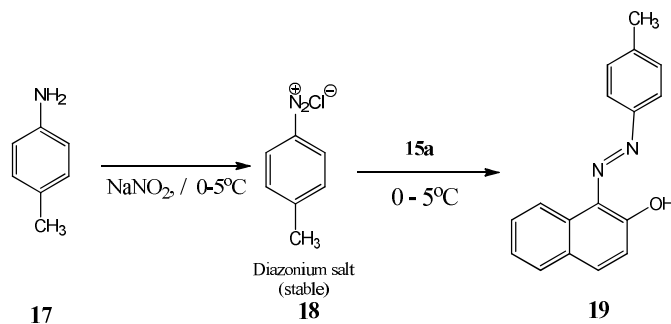


Scheme-4: Formation of Azo-aldehyde(9-12) and condensation with aromatic amine(12-13).

Reaction of 2-(2'-carboxyphenylazo)-4-methylphenol, **14** with [M(PPh₃)₂Cl₂] (M = Pd, Pt) affords mixed-ligand complexes⁴⁵ of type [M(PPh₃)(L)]. Structures of both the complexes have been determined by X-ray crystallography. Both the complexes are square planar, where the 2-(2'-carboxyphenylazo)-4-methylphenol, **14** is coordinated to the metal center, via dissociation of the two acidic protons, as a dianionic tridentate O,N,O-donor, and the fourth position is occupied by the triphenylphosphine. These complexes show intense metal-ligand-CT transitions in the visible region.

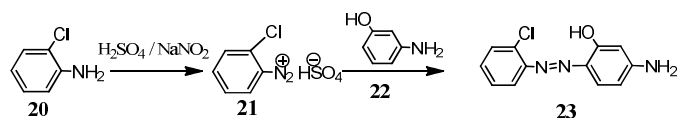


In **Scheme-5** Azo-2-naphthol and 2-naphthol⁴⁶ were tested against 5 microorganisms: *S. aureus*, *E. coli*, *B. subtilis*, *P. aeruginosa* and *S. faecalis*. 2-Naphthol was slightly active while azo-2-naphthol was highly active against all the bacteria species tested. The presence of azo group contributed more than 60% of the antibacterial activities exhibited by azo-2-naphthol on all the bacteria tested.



Scheme-5: Azo coupling reaction with β-Naphthol.

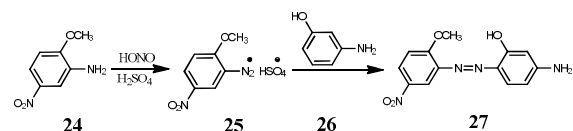
In **Scheme-6**, 2-Chloroaniline (carbocyclic) monoazo dye analogs, **23** was also used as an intermediate⁴⁷ synthesize disazo dyes in order to compare fastness properties.



Scheme-6: Synthesis of Monoazo dye intermediate, **23** from 2-Chloroaniline.

A series of monoazo dyes intermediate containing nitro and methoxy groups was an intermediate⁴⁸ **27** for the synthesis of dyes used for dyeing of polyester fibre. The intermediate having the methoxy and nitro groups were prepared (**Scheme-7**) and coupled with the corresponding coupling components to

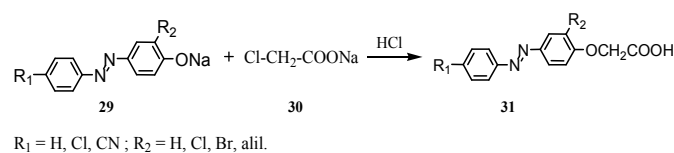
give 2-methoxy-5-nitrophenylazo-2-hydroxy-4-aminobenzene dyes. The absorption maxima of the final dyes were dependent upon the substituents and coupling components. The final dyes showed excellent wash fastness and sublimation fastness on polyester substrate.



Scheme-7: Synthesis of Monoazo dye intermediate, **27** from 2-Methoxy-5-nitroaniline.

In 2010 azo dye 4-(4'-Hydroxy-phenylazo)-benzointrile was investigated⁴⁹ by means of differential thermal analyses (DTA) and thermogravimetry (TG) in comparison with electron impact (EI) mass spectral (MS) fragmentation at 70 eV.

Literature shows the experimental data regarding the synthesis⁵⁰ and the antimicrobial activity of new 4-phenylazo-phenoxyacetic acids, **31** (**Scheme-8**). These compounds were tested for their antibacterial activity against *S. aureus*, *S. pyogenes*, *E. coli*, *P. aeruginosa*, *P. vulgaris* and for their antifungal activity against *C. albicans* by disk diffusion method.



Scheme-8: Synthesis of 4-Phenylazo-phenoxyacetic acid.

Several azo compounds were synthesized by using simple diazotization reaction pathway. The synthesized compounds contains drug⁵¹ moiety of paracetamol which shows excellent antimicrobial activity.

As part of a general study of the crystal chemistry of dyes and to provide templates for molecular modelling studies, the crystal structure of the title compound(I), a yellow dye containing a 4-methoxy group, has been determined. The title compound, C₁₅H₁₆N₂O, has a trans configuration⁵² with respect to the diazene double bond, and is approximately planar in the solid state. In the crystal structure, the molecules are linked to one another, head-to-head, by the hydroxyl groups, forming intermolecular O-H...O hydrogen bonds.

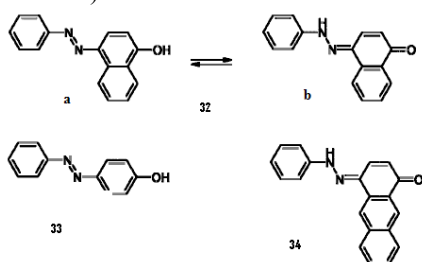
The tautomerism between azophenolic and hydrazone structures of 4-(2',4'-dinitrophenylazo)alkylphenols in tetrachloroethylene solution has been studied by IR. The tautomeric composition varies between 0-100 percent hydrazone according to the alkyl substitution. The alkyl groups increase the hydrazone proportion apparently by inductive effects. Large group in both meta positions to hydroxyl sterically prevent formation of the hydrazone and destabilize the azo form. The corresponding 4-(2'-nitrophenylazo)-alkylphenols parallel the dinitro series, but with slightly lower contents of hydrazone. The main conditions for stabilising⁵³ the hydrazone form appear to be the presence of a 2'-nitro group, and the presence of one or better two alkyl groups ortho to hydroxyl. Appreciable amounts of hydrazone are not formed unless both conditions are fulfilled. The IR spectra indicate that many solid 4-(2',4'-dinitrophenylazo)alkylphenols exit as

tautomeric mixtures with alkyl-1,4-benzoquinone-2',4'-dinitrophenylhydrazones. There is also some indication that both tautomers⁵⁴ are packed into a common crystal lattice. 2,5-Diisopropylquinone-2',4'-dinitrophenylhydrazone was isolated in two interconvertible, solid modifications of seemingly different tautomeric composition.

UV-Vis spectra of the hydrazone tautomer of 4-(2',4'-dinitrophenylazo)alkylphenols show two distinct absorption maxima, at about 383–402 and 417–440 nm, in tetrachloroethylene solution. The shorter wavelength band occurs in the same region as the main band of the azo tautomer⁵⁵, and thus interferes with the detection of that form. Similar spectra are given by quinone 2'-nitrophenylhydrazones, and by the N-methyl derivatives of quinone 2'- and 4'-nitro and 2',4'-dinitrophenylhydrazones. The longer wavelength maximum is tentatively assigned to the degenerate transitions of the NH nitrogen lone pair to the nitro groups and the quinone oxygen, and the shorter-wavelength band is proposed to be the displaced, next-lower band among the four commonly found in dinitrophenylhydrazone. It has been found that metalliferous azo-dye stuffs⁵⁶ can be produced by treating with agents yielding azo dyestuffs of the general formula as substituted phenyl-azo-1-naphthol derivative with Chloro-, bromo- group as substituent.

Novel acid mono azo and mordent acid mono azo dyes were synthesized by the coupling of diazonium salt solution of different aromatic amines with 2-hydroxy-4-methoxybenzophenone⁵⁷. The dyeing performance of all the dyes was evaluated on wool and silk fabrics. The dyeing of chrome pre-treated wool and silk fabrics showed better hues on mordented fabrics. The dyed fabrics showed excellent to very good light, washing, perspiration, sublimation and rubbing fastness. The results of antibacterial studies of chrome pre-treated fabrics revealed that the toxicity of mordented dyes against *Escherichia coli*, *Staphylococcus aureus*, *Salmonella typhi*, *Bacillus subtilis* bacteria was fairly good.

Segmented polyurethanes⁵⁸ containing azo aromatic groups in the main chain were synthesized by reaction of 3,3'-azobis(6-hydroxybenzoic acid), 5-[4-(hydroxyphenyl)azo] salicylic acid and 5-[1-hydroxynaphthyl]azo] salicylic acid with hexamethylenediisocyanate. All the synthesized azo polymers showed good thermal stability. The synthesis of azo compounds containing thymol⁵⁹ moiety. Thymol, azo monoterpenoids is also reported. The tautomeric constants of a series of azo dyes were estimated in the gas phase^{60a} by using electron ionization mass spectrometry and it was shown that the relative amount of the keto tautomer increases from 4-phenylazo-1-phenol to 4-phenylazo-anthracen-1-ol, thus confirming the quantum-chemical predictions (Scheme-9, compounds 32a-32b).

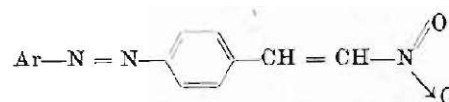


Scheme-9: Tautomerism in Azo-naphthol (32a – 32b).

The relative strength of the intramolecular hydrogen bonding (IHB) in the **Scheme-9**, compounds **32a-32b**, has been investigated by means of ab initio quantum chemical calculations, UV-Vis spectral study and linear solvation energy relationship analysis (LSER) of the obtained tautomeric constants. It was marked that in acetone (and in all used solvents with substantial proton acceptor abilities) the tautomeric constant in the azonaphthol^{60b} compound is lower than could be expected. The fact is explained with the breakage of the IHB and the coexistence of closed and open enol tautomers.

Novel addition curable phenolic resins bearing terminal ethynyl groups anchored to benzene ring through a phenyl azo linkage⁶¹ were realized by the coupling reaction between novolac and 3-ethynyl phenyl diazonium salt. The apparent molecular weight, determined from gel permeation chromatography showed a downward drift with increase in degree of acetylene substitution. The thermal stability and anaerobic char yield of the polymers increased proportional to the crosslinking and were considerably superior to those of a conventional resole.

The aim of our present work was to synthesize a number of azodyes⁶² possessing the structure:



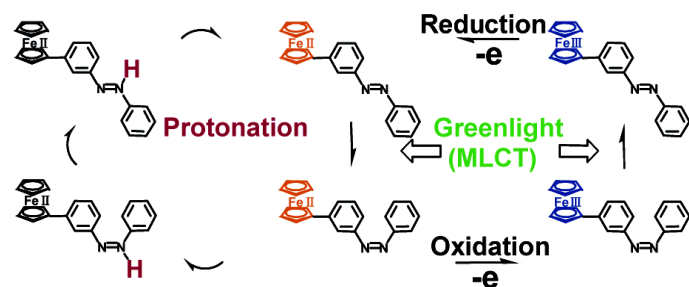
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The characteristic feature of this type of compounds consists in the presence of \square -nitrovinyl group. It was believed that two conjugated double bonds, which exist outside one of the aromatic rings, may produce dyes possessing interesting properties.

Synthesis of azo compounds was reported by using simple diazotization reaction pathway. The synthesized compounds contains drug moiety of m-cresol⁶³ which shows excellent antimicrobial activity.

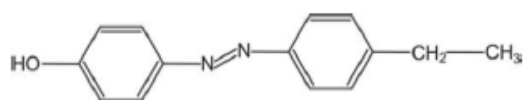
The electrochemical behaviour of 3-allyl-4-hydroxyazobenzene⁶⁴ was studied at RT. In this study, the electrode reactions for the azo compound were investigated using SWV, DPP, DCP and CV. The reduction of the azo group to amino group in acidic media and hydrazo step in neutral and basic media was observed. From the observation an electrode reaction mechanism has been suggested for the compound.

3-, 4-, 2-Ferrocenylazobenzenes, were synthesized and their photon-, electron- and proton-induced trans-cis isomerization behaviors⁶⁵ were examined. Compound 1 undergoes reversible trans to cis isomerization with a single green light source and the $\text{Fe}^{\text{III}}/\text{Fe}^{\text{II}}$ redox change. The oxidized form of 2 undergoes facile cis to trans thermal isomerization. Both 1 and 2 undergo facile protonation and show proton-catalyzed cis-to-trans isomerization (Scheme-10).



Scheme-10: Proton catalysed Cis – trans isomerisation.

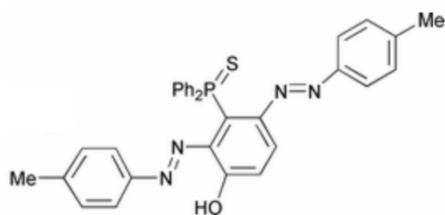
The crystal structure of **41** determined at 100 K, indicate that the molecules are not planar in the solid state, in contrast to other azobenzene⁶⁶ (diazene) derivatives. The molecules are linked by intermolecular O—H·····N hydrogen bonds, forming an infinite one-dimensional chain. Azobenzenes are widely used as dyes, but also as photochemical switch using photoisomerization by UV light to induce a conformational change from trans to cis and back.



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Tertiary phosphines containing an azo linkage⁶⁷ have been synthesized for the first time and one has been characterized by a single crystal X-ray diffraction study of its oxide.

p-HO-Ph(Ph₂P(E)) (E = S, Se) reacts with the diazonium salts [4-R-PhN≡N][BF₄] (R = H, Me, Et, ⁱPr, ^tBu, NMe₂, NO₂) to afford the new compounds⁶⁸ [1-HO-2-(4-R-PhN≡N)-4-Ph₂P(E)C₆H₃] (E = S, R = H; Me; Et; ⁱPr; ^tBu; NMe₂; NO₂; E = Se, R = H; Me) in acceptable yield. Similarly *m*-HO-Ph(Ph₂P(S)) reacts with two molar equivalents of the diazonium salts [4-R-PhN≡N][BF₄] (R = H, Me, NMe₂, NO₂) to give the new compounds 1-HO-2,4-(4-R-PhN≡N)-3-Ph₂P(S)-C₆H₂ (R = H; Me; NMe₂; NO₂). These data have been compared to those obtained from analogous coupling reactions between *m*-cresol and one and two molar equivalents of [4-Me-PhN≡N][BF₄] which afford 1-HO-3-CH₃-4-(4-Me-PhN≡N)C₆H₃ and 1-HO-3-CH₃-2,4-(4-Me-PhN≡N)C₆H₂ respectively.

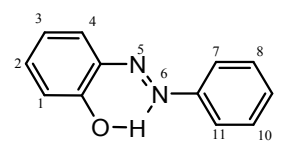


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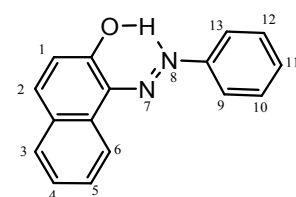
The enol imine ⇌ enamino tautomerization constants, *K*_T, and thermodynamic parameters, Δ*H*_T and Δ*S*_T, of 1-hydroxy-2-naphthaldehyde Schiff bases are determined by UV-Vis spectroscopy⁶⁹. Polar solvents shift the equilibrium toward the quinone form (for the unsubstituted derivative. In apolar solvents, for all the studied derivatives, the enol imine ⇌ enamino equilibria are endergonic but exothermic. Linear solvation energy relationships allow extrapolation of Δ*G*_T to the gas phase. The results obtained for these compounds are compared with tautomeric properties of the isomeric

naphthaldehyde anils, the monocyclic analogues, the corresponding azo derivatives and the N-alkyl derivative.

In connection with studies of nuclear shielding parameters⁷⁰ in strong hydrogen bonds have been made on a series of compounds of the basic skeleton as



43



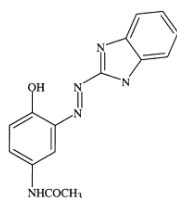
44

The isolation of the hydrogen-bonding species in an inert solvent such as CCl₄ enables a nuclear shielding parameter for an undissociated intramolecular hydrogen bond⁷⁰.

The synthesis, evaluation, and structure–activity relationships of a series of phenylazobenzenesulfonamides as potent and selective COX-2 inhibitors⁷¹ are described. Extensive structure–activity relationships (SAR) were studied within this series. When the para position is already occupied⁷¹, ortho substitution takes place. The pH of solution was important both for amine and phenol. The use of an aromatic amine needed a mildly acidic or neutral solution. If the solution was too acidic, the reaction did not occur because the concentration of free amine became too small. Phenol was not active enough for the reaction, but, in slightly alkaline solution, the more reactive phenoxide ion afforded the target azobenzene⁷¹. Neither amines nor phenols, however reacted in moderately alkaline solution because the diazonium ion was converted into the corresponding diazo hydroxide⁷¹.

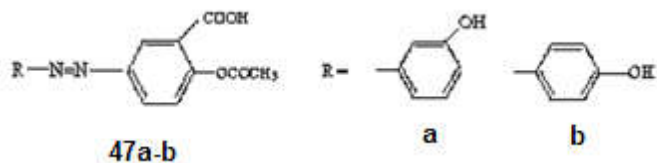
Charge transfer properties of a series of substituted arylazonaphthols⁷² are shown to correlate with the Hammett's substituent constant σ. For both contact charge exchange of the dyes to metal and field assisted, photostimulated charge transfer from the dyes into nonpolar fluids, the amount of charge transferred is found to increase with increasing σ. However, the efficiency of charge transfer into fluids does not change with σ. In addition the energies of the highest filled and lowest unoccupied molecular levels are shown (by measurement of oxidation and reduction potentials) to decrease as σ increases. The correlations establish a relationship between charge exchange phenomena and the energy levels of the dyes.

The preparation and structural identification of new Fe(III), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) complexes of 2-(2-benzimidazolylazo)-4-acetamidophenol⁷³ are studied on the basis of their analytical, spectroscopic, magnetic and conductance data. The dissociation constant of the 2-(2-benzimidazolylazo)-4-acetamidophenol as well as the stability constant of its metal complexes have been determined by spectrophotometric methods.



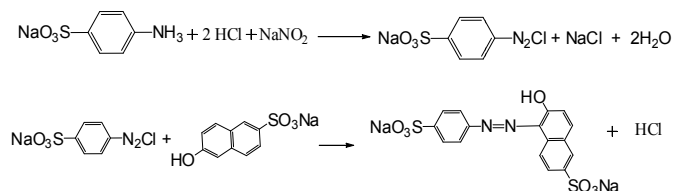
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Several azo compounds⁷⁴ were synthesized by using simple diazotization reaction pathway. The synthesized compound contains drug moiety⁷⁴ of aspirin which shows excellent antimicrobial activity. Structure of the two compounds was confirmed by ¹H NMR and IR spectral data.



Thirty-seven monoazo isomeric dyestuffs⁷⁵ were synthesized and the change in properties of these dyestuffs⁷⁵ produced by a shift in the position of the hydroxyl and sulfonic acid groups was studied. Conclusions have been drawn concerning the effect of these changes in position on the color, visible absorption spectra, and exhaustive properties of the dyestuffs and on their fastness to light and washing when applied to wool fabric. The presence of two sulfonic acid groups in the naphthol nucleus does not seem to decrease the fastness of the dyestuff.

The dyestuff was prepared by the usual method of diazotization and coupling, the amine being converted into the corresponding Diazonium compound and this Diazonium compound being allowed to react with the selected Naphthol sulphonic acid. An example of the reaction involved is given below:



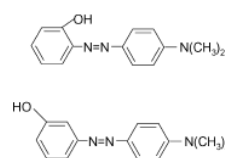
Scheme-11: Coupling of Diazonium salt with Naphthol sulphonic acid.

A polymerized film of 2-hydroxy-1-(1-hydroxynaphthyl-2-azo)-naphthalin-4-sulfonic acid⁷⁶ was prepared at the surface of a glassy carbon electrode by electropolymerization. The modified electrode was used for the simultaneous determination of dopamine and uric acid. The electrochemical behaviors of the compounds at the surface of the modified electrode were studied using CV, chronoamperometry and SWV. Alternative substrates were synthesized⁷⁷ to allow direct and continuous spectrophotometric assay of both monooxygenase (cresolase) and oxidase (catecholase) activities of mushroom tyrosinase. Using azo derivatives of phenol⁷⁷, 4-[(4-methoxybenzo) azo]-phenol, 4-[(4-methylphenyl) azo]-phenol, 4-(phenylazo)-phenol, and 4-[(4-hydroxyphenyl)azo]-benzenesulfonamide, and azo derivatives of catechol 4-[(4-methylbenzo)azo]-1,2-benzenediol, 4-(phenylazo)-1,2-benzenediol, and 4-[(4-sulfonamido) azo]-1,2 benzenediol, as substrates allows measurement of the rates of the

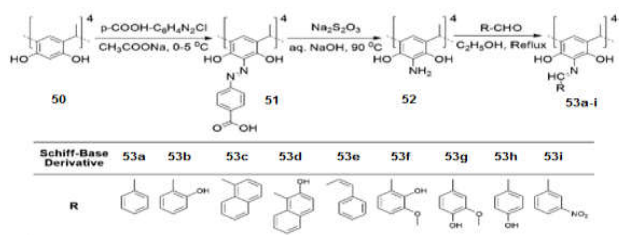
corresponding enzymatic reactions through recording of the depletion rates of substrates at their $k_{max}(s)$ with the least interference of the intermediates or products absorption.

Synthesis and characterization of novel-azo containing polymethacrylates bearing spiroacetal-norbornene moiety and methylene spacers was reported⁷⁸.

This follow-up study tended to provide a systematic comparison for how the variation of functional groups and molecular structures present in model azo dyes⁷⁹ affects color removal capability of *P. luteola*. As sulfo group at methyl orange (p-MO) or carboxyl group at 4-(4-dimethylaminophenylazobenzoic acid) sodium salt (denoted p-MR) were both *para* to azo bond, the ranking of decolorization rate was p-MO > p-MR due to the stronger electron-withdrawing effect of the sulfo group. Azo dyes with different properties of substituent on aromatic ring could affect the efficiency of biodecolorization of *P. luteola*. Moreover, the relative position (e.g., *ortho*, *meta*, *para*) of the substituent to azo bond could also influence the capability of biodecolorization of *P. luteola*. Regarding the electronic effect, azo dyes with stronger electron-withdrawing group (e.g., sulfo group) at specific positions (e.g., at *para*) could be more easily biodecolored than those with a carboxyl group.



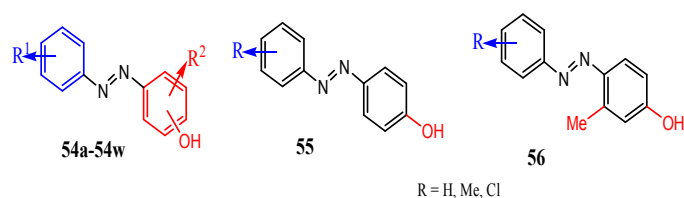
An interesting series of mononuclear organoruthenium⁸⁰ complexes of formulation $[Ru(CO)(PPh_3)_2(ap-R)]$ (where ap-R = -H, -Cl, -Me, -OMe, -OEt) have been synthesized from the reaction of five 2-(aryloxy)phenol⁶⁷ ligands with ruthenium(II) precursor $[RuH(Cl)(CO)(PPh_3)_3]$ in benzene under reflux. The 2-(aryloxy)phenolate ligands behave as dianionic tridentate ligand and are coordinated to ruthenium through C, N and O by dissociation of the phenolic and phenyl proton at the *ortho* position of the phenyl ring forming two five-membered chelate rings. The free ligands and their ruthenium complexes have also been screened for their antibacterial and antifungal activities, which have shown great promise in inhibiting the growth of both Gram +ve and Gram -ve bacteria *Staphylococcus aureus* and *Escherichia coli* and fungus *Candida albicans* and *Aspergillus niger*. These results made it desirable to delineate a comparison between free ligands and their complexes. Synthesis of new "upper rim" functionalized calix[4] resorcinarene⁸¹ Schiff-bases has been carried out by reacting tetraaminocalix [4] resorcinarene with different aromatic aldehydes in ethanol at reflux temperature. The tetraaminocalix [4] resorcinarene, which can serve as very good precursor for various derivatizations at the extra annular position, was synthesized (**Scheme-12**) for the first time through tetra-azo intermediate, by first introducing the azo functionality at the upper rim, and subsequent reduction with $Na_2S_2O_4$ in aq. NaOH.



Scheme-12: Synthesis of polymeric azo compounds and Schiff bases.

Aza-derivatives of phenols such as Schiff bases are an important and interesting group of chemical compounds. They exhibit a number of biological activities and play an important role in the regulation of many biochemical processes. Due to these properties, these compounds⁸² are potentially useful for the design and production of novel anticancer, antimalaria, antivirus and antimicrobial drugs. The primary aim of the present review is to compare selected groups of phenol-derivatives containing azo-, heterocyclic, aromatic, alkyl and sugar moieties in view of their potential use and undesired effects, since some of them are widely used as dyes in the industry.

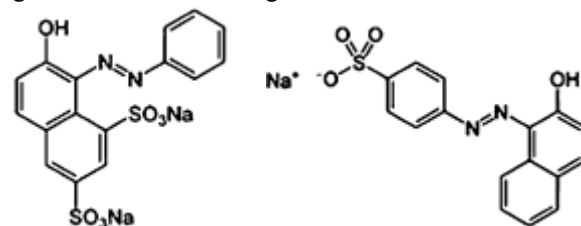
As compared with a commercially available agricultural fungicide hymexazol, some phenyl-azo phenol⁸³ derivatives (e.g., **54a**, **54b**, **54f**, **54n**, **54q**, **54u**, and **54v**) exhibited the more promising and pronounced antifungal activities *in vitro* against seven phytopathogenic fungi. It seemed that 4-((un)substituted phenylazo)-phenol and 4-((un)substituted phenylazo)-3-methylphenol might be considered as new lead structures for further design of agricultural fungicides. Among of all the compounds **54a–w**, 4-((un)substituted phenylazo)-phenol **55** and 4-((un)substituted phenylazo)-3-methylphenol **56** might be considered as new promising lead candidates for further design and synthesis of agricultural fungicides.



Several diaryl ethers⁸⁴ were synthesized and tested *in vitro* against seven phytopathogenic fungi, namely *Fusarium graminearum*, *Alternaria alternate*, *Helminthosporium sorokinianum*, *Pyricularia oryzae*, *Fusarium oxysporum* f. sp. *vasinfectum*, *Fusarium oxysporum* f. sp. *cucumarinum* and *Alternaria brassicae*. Compared to a commercial agricultural fungicide, hymexazol, especially compounds a, b, e, g and k were found to be more effective at 50 µg/ml against *F. graminearum*, *F. oxysporum* f. sp. *vasinfectum* and *F. oxysporum* f. sp. *cucumarinum*. Meantime, some structure-activity relationships were also observed.

Novel acid azo and mordent acid⁸⁵ azo dyes have been prepared by the coupling of diazo solution of different aminonaphthol sulphonic acids⁸⁵ and aromatic amino acids with 2,4-dihydroxybenzophenone. The resultant dyes were characterized by elemental analysis as well as IR and ¹H NMR spectral studies. The UV-Visible spectral data have also been discussed in terms of structure property relationship. The dyeing assessments of all the dyes were evaluated on wool and

silk textile fibers. The result shows that better hue was obtained on mordented fiber. Dyeing on wool and silk fibers resulted in yellowish pink to reddish brown colourations having excellent light fastness and washing fastness.



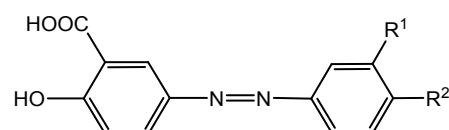
57 Orange

58 Acid orange

A series of conformationally rigid half-sandwich organoruthenium(II) complexes⁸⁶ with the general formula [(g6-p-cymene) RuCl(L)] (where L = mono anionic 2-(naphthylazo) phenolato ligands) have been synthesized from the reaction of [(g6-p-cymene)RuCl]2-(I-Cl)₂ with a set of 2-(naphthylazo) phenolato O,N-donor ligands. All the ruthenium complexes were fully characterized by FT-IR, ¹H NMR, and UV-Vis spectroscopy as well as elemental analysis. Electrochemical data of all the ruthenium complexes show a two metal centered voltammetric responses with respect to Ag/AgCl at scan rate 100 mVs⁻¹. Further, the complex efficiently catalyzes the oxidation of a wide range of alcohols to their corresponding carbonyl compounds in the presence of N-methylmorpholine-N-oxide up to 97%. The *o,o'*-dihydroxyazodye, 1-(2-hydroxy-4-methylphenylazo)-2-naphthol⁸⁷, and its metal complexes (Cr, Co and Fe) having the ligand to metal ratio 2:1 were synthesized, but manganese forms a 1:1 complex.

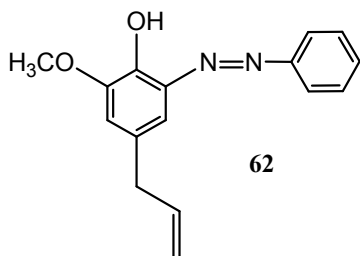
Preparation and properties of a series of azo dye⁸⁸ derived from p-aminophenol is described. The influence on colour, dyeing fastness properties of the dye on synthetic polymer fibers is reported. It is marked that the structural variation significantly affected the nature of substrate. So these dyes can be useful in textile as well as automobile industry.

The protective and anti-inflammatory effects of azo and azo-linked polymeric prodrugs of 5-ASA on acetic acid induced colitis in rats were investigated. Three azo prodrugs⁸⁹, 4,4'-dihydroxy-azobenzene-3-carboxylic acid **59**, 4-hydroxy-azobenzene-3,4'-dicarboxylic acid **60**, 4,4'-dihydroxy-3'-formyl-azobenzene-3-carboxylic acid, **61** and their polyethylene glycol (PEG 6000) derivatives were synthesized. Histological examinations also indicated a marked reduction in tissue injury and inhibition in neutrophil infiltration in rats treated with azo compound, **61** and PEG conjugates of azo compounds **60** and **61**. Results of this investigation provide experimental evidence supporting new cytoprotective, anti-inflammatory and anti-edema properties of the azo derivatives of 5-ASA and their PEGylated prodrugs.

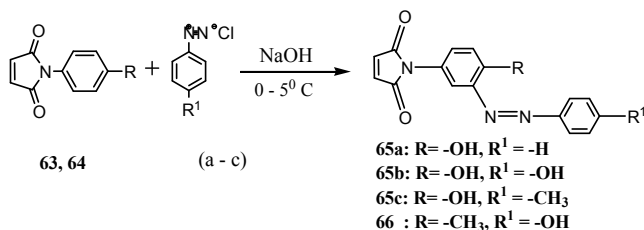


59: R¹ = H, R² = OH; **60:** R¹ = H, R² = COOH and **61:** R¹ = CHO, R² = OH

The synthesis of azo compounds from eugenol has been carried out and reported⁹⁰ by diazotization reaction. The reaction of benzenediazonium chloride with eugenol gave 4-allyl-2-methoxy-6-hydroxyazobenzene, **62** in 34.27% yield. The derivative of azo compound was dissolved in ethanol and then the color changing was observed in range of pH 9.8-11.1 from yellow to red. Application for titration indicator for acetic acid titrated with sodium hydroxide showed error less than 3.20 % compared with phenol phtaline indicator.

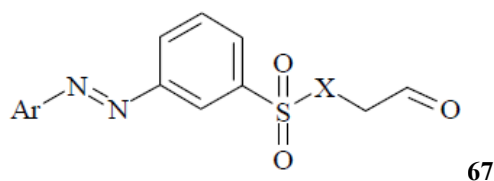


Maleic anhydride was reacted with *p*-aminophenol and *p*-toluidine in the presence of di-phosphorus pentoxide as a catalyst⁹⁰ to produce two compounds: *N*-(4-hydroxyphenyl) maleimide and *N*-(4-methylphenyl)maleimide. The new azo compounds were prepared⁹⁰ by the reaction of the two compounds with three different aromatic amines, namely aniline, *p*-aminophenol and *p*-toluidine (Scheme-13).



Scheme-13: Synthesis of azo compounds containing five member substituent.

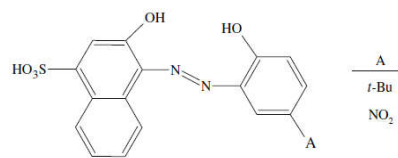
In the literature there are reports on the synthesis of new optical sensors⁹¹ for determination of pH and chloride ions in reinforced concrete. The reactive azo dyes can be represented by the following general formula,



General formula of the synthesized reactive azo dyes

Where, X is methylene or amidomethylene and Ar - *p*-cresol, α - or β -naphthol. The *m*- position of the sulphone acceptor was preferred because of weak conjugation to the hydroxyl group and, consequently, resulted in dyes, which are weak acids. This allows a shift of their colour change to the pH-range from 9 to 13.

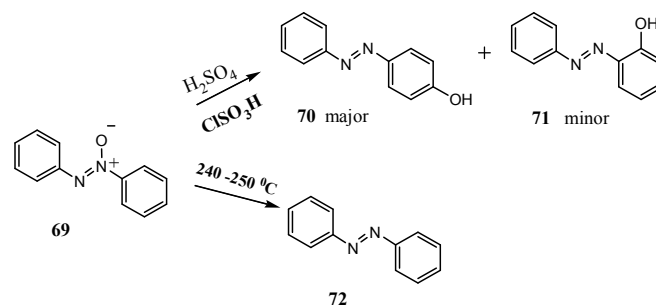
Synthesis and characterization of azo dyes⁹² containing *o*,*o*-dihydroxy groups and their azo-metal(II) [Cu, Co, Ni, Zn] chelates by ¹H N.M.R., IR, AAS, UV-VIS, magnetic susceptibility and thin-layer chromatography techniques are reported. The synthesized azo dyes and azo-metal chelate dyes were applied on wool fabric.



68

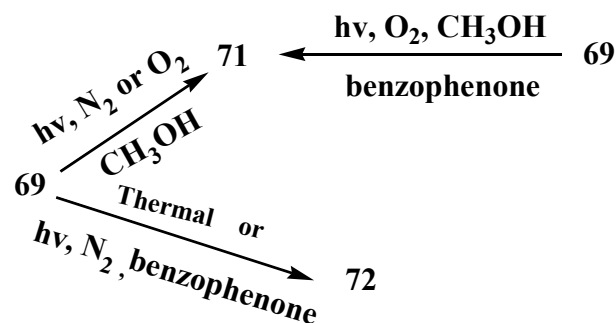
This reaction was first reported by Wallach and Belli⁹³ in 1880. It is a strong acid promoted conversion of azoxybenzene and its derivatives into 4-hydroxyazobenzene and the corresponding substituted hydroxyazobenzenes, and is generally known as the Wallach rearrangement

It was notable that the Wallach rearrangement using sulfuric acid induced the direct conversion of azoxybenzene **69** into the corresponding 4-hydroxyazobenzene, **70**⁹³⁻⁹⁶ (Scheme-14).



Scheme-14: Wallach rearrangement using H₂SO₄.

Acidic zeolites HY and CaY catalyse the Wallach rearrangement⁹⁶ (Scheme-15) of azoxybenzene, **69** leading mainly to the formation of *para*-hydroxyazobenzene, **70** and *ortho*-hydroxyazobenzene, **71** and deoxygenation in presence of nitrogen and benzophenone yields **72**.



Scheme-15: Thermal and photochemical Wallach rearrangement of azoxybenzene.

A convenient, rapid, one-pot method for the synthesis of azo dyes⁹⁷ has been developed by the sequential diazotization-diazo coupling of aromatic amines with NaNO₂, silica sulfuric acid and coupling agents under solvent-free conditions at room temperature. Using this method, several types of aromatic amine, containing electron-withdrawing groups as well as electron-donating groups, were rapidly converted to the corresponding azo dyes in good yield. The ensuing aryldiazonium salts supported on silica sulfuric acid (aryl diazonium silica sulfates), ArN₂-p-OSO₃-SiO₂, were sufficiently stable to be kept at room temperature in the dry state. The use of mild reaction conditions and an inexpensive procedure are further advantages of this method.

Two (from phenol and β -naphthol) series of dyes⁹⁸ were synthesized. These components are the most commonly utilized phenols and they represent, two different forms of azo compounds in the solution. It has been predicted that the phenolic azo dyes exist in azo form while β -naphthol dye exists in hydrazone form.

Synthetic dyes based on toxicological considerations, a group of premetallized iron complexed monoazo dyes⁹⁹ were synthesized as potential alternatives to presently used high volume Cr and Co-containing monoazo acid dyes for nylon and wool. This approach took the advantage of environmentally friendly property of Fe, and draws from the established utility of Fe complexes as brown dyes for certain protein substrates. Which led to two black Fe complexes having fastness properties comparable to the Cr analogs on both wool and nylon.

Novel rearrangement products¹⁰⁰ viz. 2-alkyl-5-(p-alkylphenylazo) phenols and 2-alkyl-4-(p-alkylphenylazo) phenols, in some cases 4-(p-alkylphenylazo) phenols were formed from the reaction of 4,4'-dialkylazoxybenzenes with sulphuric acid. Also a small amount of 5-alkyl-2-(p-alkylphenylazo) phenols was a normal Wallach rearrangement products.

The relative strength¹⁰¹ of the intramolecular hydrogen bonding (IHB) in the title compounds was studied by means of ab initio quantum chemical calculations, UV-Vis spectral study and linear solvation energy relationship analysis (LSER) of the obtained tautomeric constants. It is reported that in acetone (and in all used solvents with substantial proton acceptor abilities) the tautomeric constant in the azo-naphthol compound is lower than could be expected. It is explained with the breakage of the IHB and the coexistence of closed and open enol tautomers. table 1

ABBREVIATIONS:

<i>A. alternata</i>	: <i>Alternaria alternata</i>
<i>A. brassicae</i>	: <i>Alternaria brassicae</i>
<i>A. niger</i>	: <i>Aspergillus niger</i>
<i>B. subtilis</i>	: <i>Bacillus subtilis</i>
<i>C. albicans</i>	: <i>Candida albicans</i>
<i>E. coli</i>	: <i>Escherichia coli</i>
<i>E. faecalis</i>	: <i>Enterococcus faecalis</i>
<i>F. graminearum</i>	: <i>Fusarium graminearum</i>
<i>F. oxysporum</i> f. sp. <i>vasinfectum</i>	: <i>Fusarium oxysporum</i> f. sp. <i>vasinfectum</i>
<i>F. oxysporum</i> f. sp. <i>cucumarium</i>	: <i>Fusarium oxysporum</i> f. sp. <i>cucumarium</i>
<i>H. sorokinianum</i>	: <i>Helminthosporium sorokinianum</i>
<i>K. pneumonia</i>	: <i>Kelebsiella pneumonia</i>
<i>S. aureus</i>	: <i>Staphylococcus aureus</i>
<i>S. faecalis</i>	: <i>Streptococcus faecalis</i>
<i>S. pyogenes</i>	: <i>Streptococcus pyogenes</i>
<i>P. aeruginosa</i>	: <i>Pseudomonas aeruginosa</i>
<i>P. luteola</i>	: <i>Pseudomonas luteola</i>
<i>P. oryzae</i>	: <i>Pyricularia oryzae</i>
<i>P. vulgaris</i>	: <i>Proteus vulgaris</i>
HIV	: Human Immunodeficiency Virus
MIC	: minimum inhibitory concentrations
SAR	: Structure Activity relationship
5-ASA	: 5-Aminosalicylic acid

CCl ₄	: Carbon Tetra Chloride
PEG	: Poly Ethylene Glycol
σ	: Substituent constant (Hammett equation)
CT	: Charge Transfer
DC	: Direct Current
RT	: Room temperature
UV-Vis	: Ultra Violet Visible
IR	: Infra Red
FTIR	: Fourier Transform Infra Red
NMR	: Nuclear Magnetic Resonance
AAS	: Atomic Absorption Spectroscopy
DTA	: Differential Thermal Analyses
TG	: Thermo Gravimetry
EI	: Electron Impact
MS	: Mass Spectra
CV	: Cyclic Voltammetry
SWV	: Square Wave Voltammetry
DPP	: Differential Pulse Polarography
DCP	: Direct Current Polarography

CONCLUSION

The present review paper gives an overview or detailed account of azo-phenols synthesized and used in various reactions. The compounds synthesized from the azo derivatives of azo-phenols are useful for many applications such as colours of azo dyes include different shades of yellow, red, orange, brown, and blue used for textile, dyeing industry, for the chelation ion-exchanging properties of the polymers. These type of compounds have antibacterial, antifungal, activities and for antioxidant activities. Azo derivatives of phenol serve as a building block for many intermediates.

Future Scope: Thus, this review may be useful to many researchers for further developments of azo-phenol and their varied reactions to form different applied derivatives in near future.

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