

## Research Article



## Coupling Reactions Involving Reactions of Aryldiazonium Salt: Part-V. Chemoselective Synthesis of 1-(Substituted-phenyl)-azo-naphthalen-2-ol

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### ABSTRACT

The aryldiazonium salts are easily prepared and highly reactive and hence useful as starting material or active intermediate in varied synthetically important reactions. These reactions, either, losses nitrogen containing function or without loss of nitrogen function. They are specially used in nucleophilic substitutions, radical reactions and some cross coupling reactions. In the present piece of work we have reacted the aryldiazonium salt with a phenolic compound, 2-Naphthol. The final product formed has potential to use as azo dyes.

**Keywords:** Substituted Aniline, Sodium Nitrite, Diazotization, Aryldiazonium salt, Azo Coupling, Phenolic compound, Dyes and Pigments.

### INTRODUCTION

There are many classes of organic chemistry like carbonyl compounds viz. aldehyde<sup>1</sup> and ketone<sup>2</sup> and imine<sup>3-6</sup> compound etc. likewise aryldiazonium compounds also play an important role in synthetic organic chemistry. There are many chemical reactions like reduction<sup>4,6</sup>, oxidation<sup>5</sup>, hydrolysis, complexation, and coupling<sup>7-10</sup> etc. In the present piece of work we reacted the diazonium salt coupled with a phenolic compound, 2-Naphthol. These synthesized compounds will be useful for varied applications viz. for synthesis of newer chemicals and pharmaceuticals. Aryl diazonium salts have been discovered in the middle of the 19<sup>th</sup> century by Johann Peter Griess who was working on azo-compounds as dyes and pigments<sup>11</sup>. They are very easily prepared by diazotization<sup>12</sup>, a procedure in which a primary aromatic amine is treated with a source of nitrous acid (HNO<sub>2</sub>).

### Diazonium Salts

The general formula for Aromatic diazonium salt, is represented as Ar-N<sub>2</sub><sup>+</sup>X<sup>-</sup> and (arene diazonium halide) they are highly reactive compounds serves as intermediate in the synthesis of a wide variety of organic aromatic compound. In fact, they are comparable to Grignard reagent in there versatility that is ease of processing.

### Reaction of Diazonium Salt

The reaction involves loss of nitrogen and reaction involving retention of nitrogen.

Aryl diazonium salts are usually synthesized in the presence of a liquid acid dissolve in water at low temperature between 0°C and 10°C. An initial optimization of an amount of acid was performed by

diazotization of Substituted aniline as model substrate and diazo coupling with 2-Naphthol.

Replacement of diazonium group is the best general way of introducing F, Cl, Br, OH, and H into an aromatic ring diazonium salt are valuable in synthesis not only because they react to form so many classes. Diazonium salt is quite different from Grignard reagent. Recently, we have communicated the research work on the coupling of aryldiazonium salts with Active methylene compounds<sup>7a</sup> anilines<sup>7b</sup> and salicylic acid<sup>7c</sup> derivatives. Recently we have published three articles on the synthesis of azo compounds<sup>8-9</sup> including Sudan and its nitro derivatives<sup>10</sup>.

In the present work we have putforth coupling reaction of diazotized methyl and methoxy-substituted anilines with 2-Naphthol as shown in **Scheme-1**. These compounds are useful and important to the dye as well as other versatile type of industry.

### MATERIALS AND METHODS<sup>13</sup>

#### Stage 1

#### General Procedure for Preparation of Diazonium Salt

In 100 ml capacity beaker add 2 ml aniline (or its derivative) and to this add to it mixture of 5ml conc. HCl and 10 ml water and stir with the glass rod to get clear solution. Cool, the solution to 0°C by keeping in ice bath. Dissolve (1 gm) sodium nitrite in 10 ml water. Cool the solution in ice bath to 0°C, after attaining 0°C add sodium nitrite solution into aniline hydro chloride (or derivatives) solution drop wise with constant stirring (Do not allow to rise temperature above 5°C during addition). The reaction mixture shows the positive test of nitrous acid on starch iodide paper (blue colour is obtained on the potassium-iodide starch paper). Decompose the excess of nitrous



acid by adding pinch of urea filter the solution and collect the filtrate which is diazonium salt solution.

## Stage 2

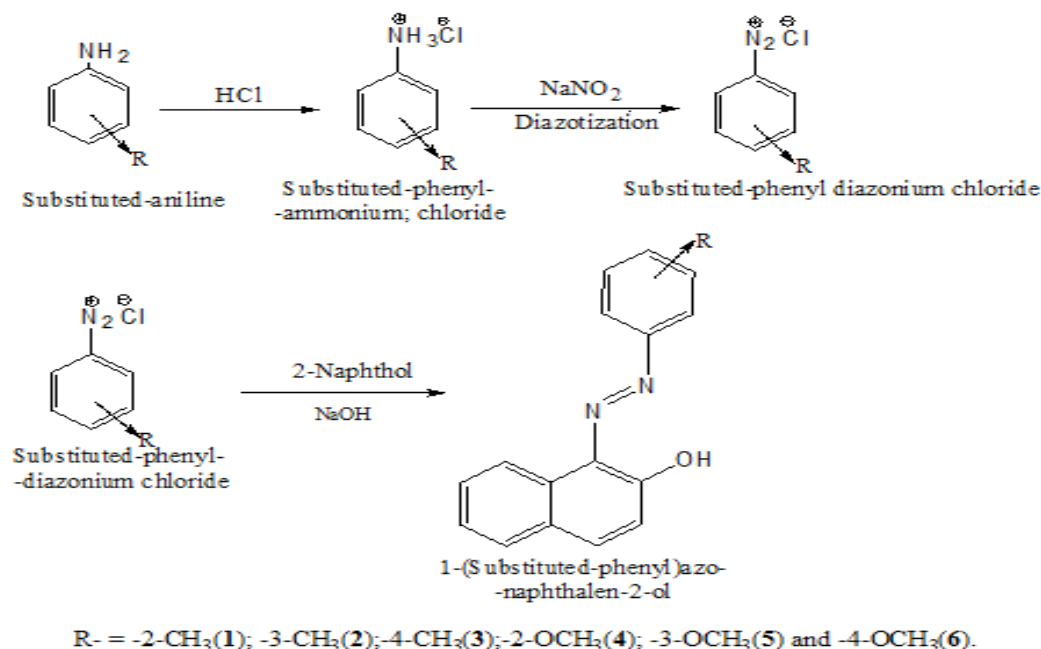
### General Procedure - Diazonium Coupling Reaction

Prepare a mixture of solution of 1.5 gm 2-Naphthol ( $\beta$ -Naphthol) in 10 ml 10% NaOH and solution of obtain cool to 0°C. Now add drop wise solution of diazonium salt into 2-naphthol in NaOH with constant stirring after complete addition allow reaction mixture to stand for 10 min in ice bath, filter the coloured azo dye 1<sup>st</sup> wash it with cold

water dry weight and note the yield of clear crude azo product is formed is recrystallised by using solvent ethanol. Record the dried weight and the colour with physical constant i.e. m.p. range of compound.

## RESULTS AND DISCUSSION

In the present study, diazonium intermediates of aniline and substituted anilines are synthesized reacted with 2-Naphthol ( $\beta$ -naphthol). All compounds were obtained in high purity. All compounds gave satisfactory elemental analysis as given in **Table 1**.



Scheme-1

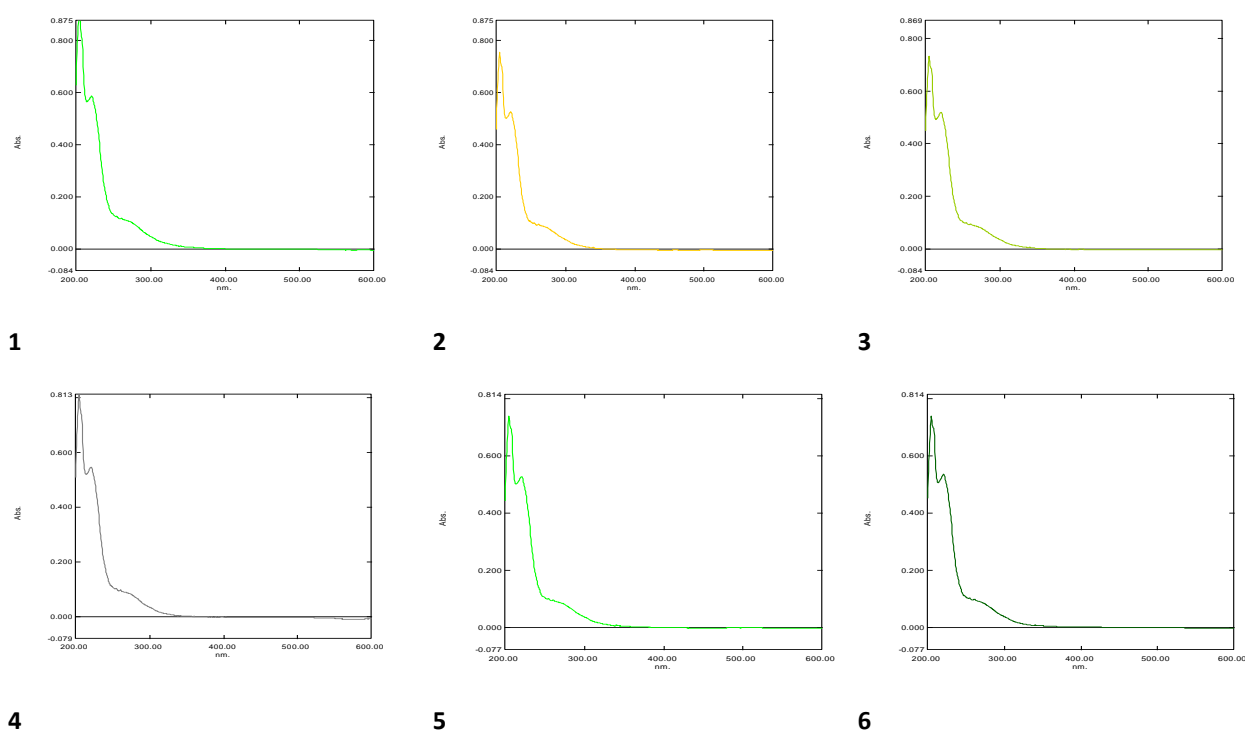
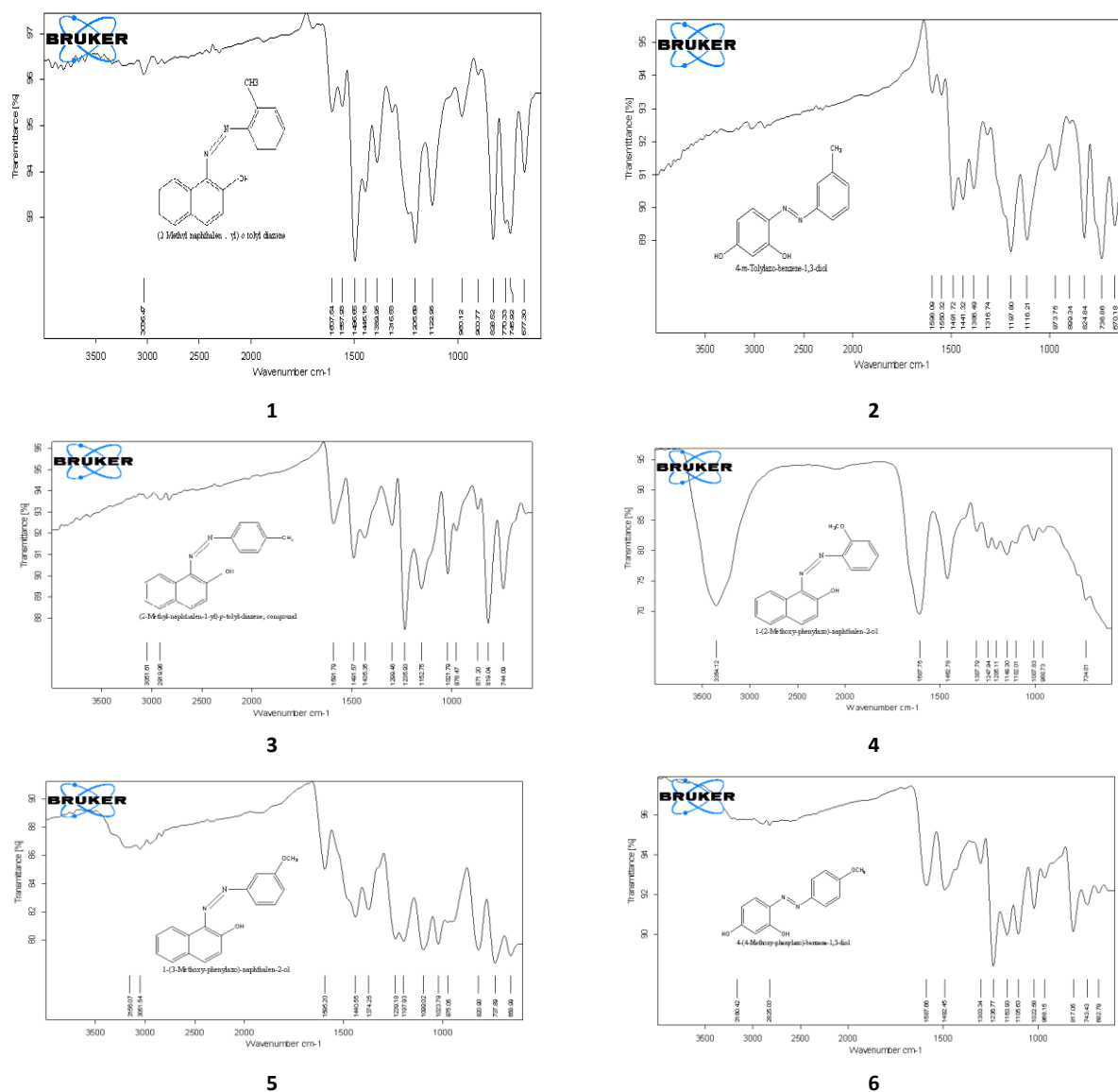


Figure 1: The UV-Vis Spectra (1 to 6) for 1-(Substituted-phenyl)azo-naphthalen-2-ol, 1 – 6.

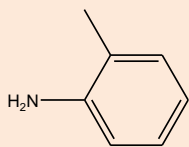
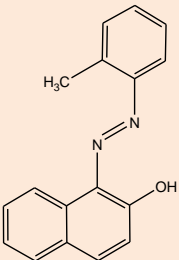
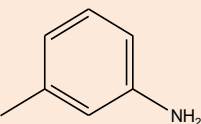
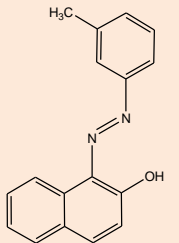
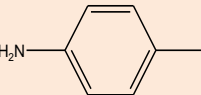
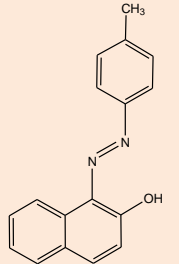
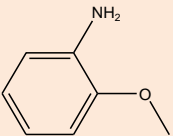
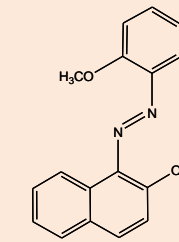
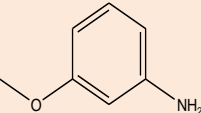
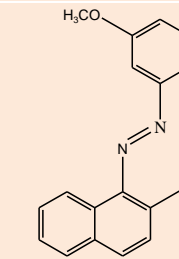
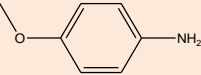
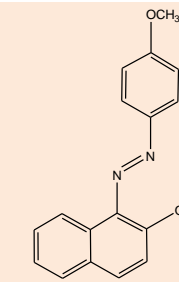


**Figure 2:** The FTIR Spectra (1 to 6) for 1-(Substituted-phenyl)azo-naphthalen-2-ol, 1 – 6.







**Table 1:** The Physical constants and the Elemental analysis data for Phenolic Azo Compounds, 1-6.

ID	Colour	m.p., °C	Results of TLC analysis	Micro-anal (Elemental) of Phenolic Azo Compound					
				% C		% H		% N	
				obs.	cal.	obs.	cal.	obs.	cal.
1	Brown red	77.2-78.1	Single Spot product	77.78	77.84	5.36	5.38	10.62	10.68
2	Light red	73.6-74.5	Single Spot product	77.86	77.84	5.39	5.38	10.64	10.68
3	Light Brown	85.8-86.9	Single Spot product	77.76	77.84	5.41	5.38	10.71	10.68
4	Brown	96.0-97.5	Single Spot product	73.38	73.37	5.06	5.07	10.06	10.07
5	Brown	81.5-82.6	Single Spot product	73.35	73.37	5.04	5.07	10.05	10.07
6	Brown red	110.0-111.5	Single Spot product	73.34	73.37	5.05	5.07	10.07	10.07

**Table 2:** The structures of varied Phenolic azo product, 1 – 6, obtained from differently Substituted-aniline.

Product Code	Starting Material	Probable Structure of Product	Mol. For. (Mol. Wt.)	% Yield
1		 1-(2-Methylphenyl)azo-naphthalen-2-ol	C <sub>17</sub> H <sub>14</sub> N <sub>2</sub> O (246.3)	51.0
2		 1-(3-Methylphenyl)azo-naphthalen-2-ol	C <sub>17</sub> H <sub>14</sub> N <sub>2</sub> O (246.3)	53.6
3		 1-(4-Methylphenyl)azo-naphthalen-2-ol	C <sub>17</sub> H <sub>14</sub> N <sub>2</sub> O (246.3)	54.0
4		 1-(2-Methoxyphenyl)azo-naphthalen-2-ol	C <sub>17</sub> H <sub>14</sub> N <sub>2</sub> O <sub>2</sub> (278.3)	60.0
5		 1-(3-Methoxy-phenylazo)-naphthalen-2-ol	C <sub>17</sub> H <sub>14</sub> N <sub>2</sub> O <sub>2</sub> (278.3)	46.0
6		 1-(4-Methoxyphenyl)azo-naphthalen-2-ol	C <sub>17</sub> H <sub>14</sub> N <sub>2</sub> O <sub>2</sub> (278.3)	43.0

**Table 3:** The Photographic Representation of the Phenolic Azo Compounds, 1 – 6.

S. No.	Name of Product / Compound ID	Purified Compound*
1	1-(2-Methyl-phenyl)azo-naphthalen-2-ol, 1	
2	1-(3-Methyl-phenyl)azo-naphthalen-2-ol, 2	
3	1-(4-Methyl-phenyl)azo-naphthalen-2-ol, 3	
4	1-(2-Methoxy-phenyl)azo-naphthalen-2-ol, 4	
5	1-(3-Methoxy-phenyl)azo-naphthalen-2-ol, 5	
6	1-(4-Methoxy-phenyl)azo-naphthalen-2-ol, 6	

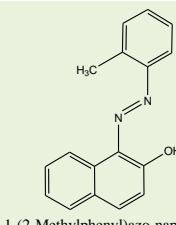
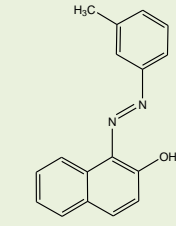
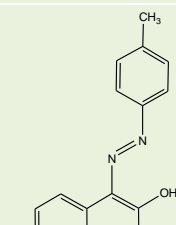
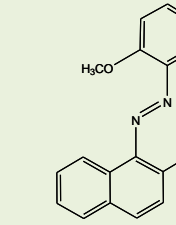
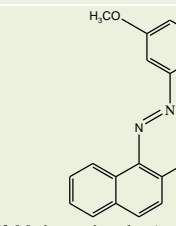
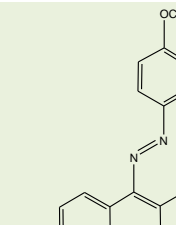
\*Solvent of recrystallisation: Ethanol

**Table 4:** The UV-Vis spectral data for Phenolic Azo Compounds, 1 - 6.

Compound ID	UV <sub>max</sub>	Concn.	Absorbance	ε, mol <sup>-1</sup> Lit <sup>-1</sup>
1	220.50	1.2 x 10 <sup>-5</sup>	2.898	2,41,500
	204.00		0.290	24,166
2	220.50	3.3 x 10 <sup>-6</sup>	0.525	1,59,091
	204.50		0.754	2,28,485
3	260.50	1.1 x 10 <sup>-6</sup>	0.095	86,363.6
	220.50		0.520	4,72,727
	204.50		0.753	6,87,273
4	220.50	1.0 x 10 <sup>-6</sup>	0.548	5,48,000

	204.50		0.811	8,11,000
5	260.50	$1.0 \times 10^{-6}$	0.097	97000
	220.50		0.0527	52700
	204.50		0.739	7,39,000
6	220.50	$1.0 \times 10^{-6}$	0.536	5,36,000
	204.50		0.780	7,80,000

**Table 5:** The FTIR Spectral data and Structural assignment of Phenolic Azo compounds, 1 to 6.

S. No.	Name of Compound, ID	Structure of Compound	FTIR Spectral absorbance frequency, $\text{cm}^{-1}$ .
1	1-(2-Methyl-phenyl)azo-naphthalen-2-ol, 1	 1-(2-Methylphenyl)azo-naphthalen-2-ol	$\nu$ -OH = 3035 $\nu$ -C=C = 1557 $\nu$ -C-N (aryl) = 1389.96 $\nu$ -C-H = 1316.58 $\nu$ -N=N = 1496.66
2	1-(3-Methyl-phenyl)azo-naphthalen-2-ol, 2	 1-(3-Methylphenyl)azo-naphthalen-2-ol	$\nu$ -OH = 3035 $\nu$ -C=C = 1557 $\nu$ -C-N (aryl) = 1389.96 $\nu$ -C-H = 1316.58 $\nu$ -N=N = 1496.66
3	1-(4-Methyl-phenyl)azo-naphthalen-2-ol, 3	 1-(4-Methylphenyl)azo-naphthalen-2-ol	$\nu$ -OH = 3051.51 $\nu$ -C=C = 1591.79 $\nu$ -C-N (aryl) = 1435.35 $\nu$ -C-H = 1299.45 $\nu$ -N=N = 1491.57
4	1-(2-Methoxy-phenyl)azo-naphthalen-2-ol, 4	 1-(2-Methoxyphenyl)azo-naphthalen-2-ol	$\nu$ -OH = 3035 $\nu$ -C-H = 1308.46 $\nu$ -C=C = 1607.75 $\nu$ -C-N (aryl) = 1307.78 $\nu$ -C-H = 1247.94 $\nu$ -N=N = 1462.78
5	1-(3-Methoxy-phenyl)azo-naphthalen-2-ol, 5	 1-(3-Methoxy-phenyl)azo-naphthalen-2-ol	$\nu$ -OH = 3156.07 $\nu$ -C=C = 1595.20 $\nu$ -C-N (aryl) = 1374.33 $\nu$ -N=N = 1440.55
6	1-(4-Methoxy-phenyl)azo-naphthalen-2-ol, 6	 1-(4-Methoxyphenyl)azo-naphthalen-2-ol	$\nu$ -OH = 3035 $\nu$ -C=C = 1580.54 $\nu$ -C-N (aryl) = 1492.54 $\nu$ -C-H = 1291.41 $\nu$ -N=N = 1492.45

The progress of reaction was monitored by TLC (silica gel-G), visualised by iodine vapour and UV cabinet. The purity of compound was ascertained by melting point determinations and TLC. The spectral data are in close agreement with the structures of the synthesized compounds. The TLC monitoring indicated the single spot. The probable structure of the product, molecular formula and the % of the yield obtained is depicted in **Table-2**. Similarly, **Table-3** depicts the Photographic representation of the synthesized azo compound.

The UV-Vis spectra of the synthesized azo compounds, **1** to **6**, indicated two to three peaks at about 205 nm, second at 220 nm and third at 260 nm and are respectively attributed to  $\pi \rightarrow \pi^*$  and  $n \rightarrow \pi^*$  transitions. The details of the UV-Vis spectra along with the absorbance  $\lambda_{\max}$  and the molar extinction coefficient,  $\epsilon$  are shown in **Table-4**.

In general the FTIR exhibits the expected features of standard FTIR spectra for this type of compound the spectra of the synthesized azo compounds, **1** to **6**, indicated absorption at about 3035- 3156  $\text{cm}^{-1}$  indicated  $\nu_{\text{OH}}$  absorption.; 1607 – 1557  $\text{cm}^{-1}$  indicated  $\nu_{\text{C}=\text{C}}$  (Arom.) group absorption; 1389  $\text{cm}^{-1}$  indicated  $\nu_{\text{C}-\text{N}}$  (aryl) absorption; 1316  $\text{cm}^{-1}$  indicated  $\nu_{\text{C}-\text{H}}$  (Arom.) group absorption and 1496  $\text{cm}^{-1}$  indicate presence of  $\nu_{\text{N}=\text{N}}$  group in azo compound.

The detailed FTIR data for respective compound, **1** to **6** is depicted in **Table-5**. The spectral data are in close agreement with the structures of the synthesized compounds. Similar remarks were made in the results mentioned earlier<sup>10</sup>.

### Applications

Azo comp have different colour red orange their fore they are used as dye are an commonly known as azo dye an example of which is disperse orange some azo compound e.g. Methyl orange used as acid base indicator due to different colour of their acid and salt for colour.

The aryl diazonium compound shows a lot of reaction, few to mentioned here are as discussed below.

The reaction either, losses nitrogen containing function or without loss of nitrogen function.

#### With loss of N-function

On replacement by Nitrogen group

Replacement by Cyno group

#### Without loss of N-function

Diazo coupling

Reaction with ester function

### CONCLUSION

The present study demonstrated the synthesis involving Aniline or substituted aniline to synthesize diazonium salt

and further reacted upon with 2-Naphthol(Beta-naphthol) to give 1-(Substituted-phenyl)azo-naphthalen-2-ol.

All the synthesized azo compounds were characterized on the basis of physical, analytical and spectral data.

These compounds will be useful as synthone or building block by budding researchers in organic chemistry, in the near future.

**Scope:** There is a future scope for using these compounds for the organic transformations and screening of these compounds against different microorganism and the data obtained will be useful for the society to study their further studies for Budding Organic and the other Researchers.

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Dr. Chandrashekhar has graduated from Pune university, INDIA and post graduated from Pune University of INDIA. He is having 14 years of experience in Industries of different types and capacity and 6.5 yrs of UG and 10 yrs of PG teaching experience at College level. Presently in service at Smt. G. G. Khadse College (UG and PG), Muktainagar. He served one and half year at M. J. College (PG), Jalgaon, and two academic years at A. S. C. College (PG), Chalisgaon. He has experience to handle many of the analytical sophisticated instruments and hands on experience for different reactions. He has completed two Research Project (one Industrial and the other UGC), one research project (VCRMS) is on-going, guided to 80 students to complete the 36 M.Sc. projects and presently 7 students are working for Ph.D. under his guidance. He has completed cGMP certification of a company in Pharma sector.