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Synthesis and spectral analysis of some new phenolic azo dyes

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Abstract : Series of eight azo dyes were synthesized by diazotization process of eight aromatic amines using $NaNO_2$ and HCL, and coupling of these diazonium salts with o-nitrophenol. Newly synthesized azo dyes have been confirmed by FT-IR and H^1 NMR spectral data.
Key Words : Azo dyes, diazotization, o-nitrophenol.

Introduction:-

Azo compounds, with two phenyl rings separated by an azo (-N=N-) bond are versatile molecules and have received much attention in research areas both fundamental and applications. The strong electronic absorption maximum can be tailored by ring substitution to fall anywhere from the ultraviolet to red visible regions, allowing chemical fine tuning of color. This combined with the fact that these azo groups are relatively robust and chemically stable, has prompted extensive study of dyes and colorants.

Azo compounds are the most fundamental class of commercial dyes and are well colored that have been used as dyes and pigments[1, 2].Azo compounds are known to be involved in a number of biological reactions such as inhibition of DNA, RNA and protein synthesis, carcinogenesis and nitrogen fixation[3, 4], also known for their use as antibacterial[5-10], antifungal anti neoplastics, antidiabetics, antiseptics[11], anticancer[12], anti-inflammatory and other useful chemotherapeutic agents [13-16].These dyes are used in electro photographic or sensor applications for photoconductors, lasers[17], electro-optical devices and ink-jet printers. Due to their ability to absorb visible light, and ease of synthesis, have been extensively used in the textile, fiber, leather, paint and printing industries for more than a century. Azo dyes are widely used colorants in consumer products such as leather, textiles, agriculture, cosmetics and in laboratories as indicators.

In the present study o-nitrophenolis coupled with diazonium salt of eight different aromatic amines VIZ: Aniline, o-Nitro aniline, p-Toluedine, α-Naphthylamine, Sulphanilic acid, m-Nitro aniline, Benzedine and Anthranilic acid.

Methods and Materials:

All the chemicals used in these experiments were of analytical grade. All the melting points were determined by open capillary method and are uncorrected. The products were confirmed by ^{1}H NMR

(Burkeravernce II 400 NMR Specrtometer) and IR technique (Shimatzu). The products were recrystallized by ethanol as solvent.

General procedure for synthesis of azo compounds.

Substituted aromatic amines (0.01mole) were mixed with 2.5 ml conc. HCl and 2.5 ml (4N) cold solution of NaNO2 was added with the stirring. The temperature of the reaction was maintained up to 0-5^0 C. Diazonium salt solution prepared above was added drop wise to the alkaline solution of o-nitrophenol. The reaction mixture stirred for 10 – 20 minutes maintaining the temperature 5-10^0 C. The colored product so obtained is filtered washed with water and recrystallised from 80% ethanol. The general Scheme for the synthesis of azo dyes of o-nitrophenolis shown in figure (I).

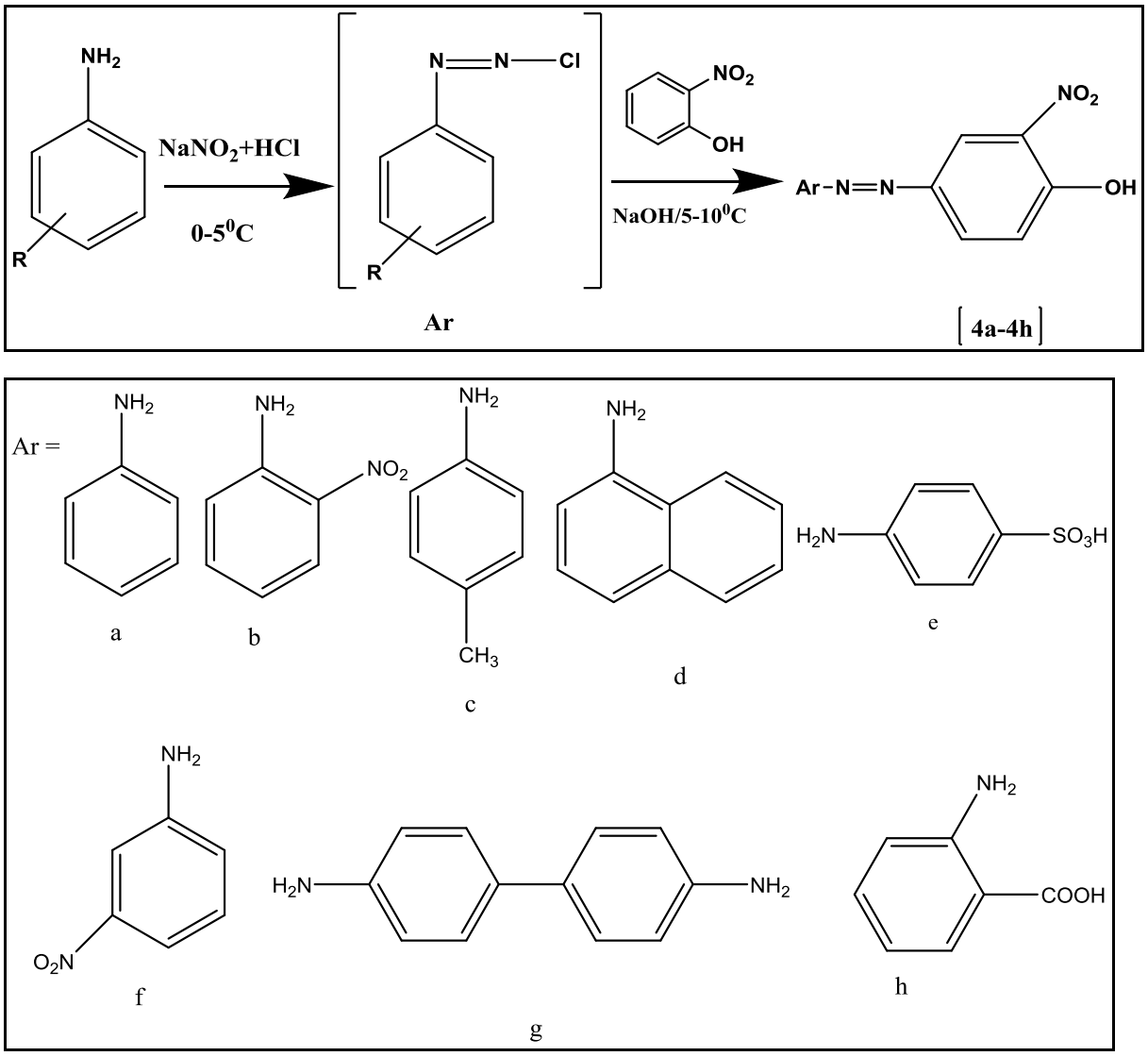

Figure I: General Scheme for the synthesis of azo dyes of o-nitrophenol.

Table (I): The code, compound name, molecular formula, molecular weight, melting point and percentage yield of synthesized compounds of o-nitrophenol.

Sr. No.	Structure	Molecular Formula	Mol. Wt.	Melting Point	Yield
4a	**2-nitro-4-(phenyldiazenyl)phenol**	$C_{12}H_9N_3O_3$	243	176^0 C	43%
4b	**2-nitro-4-((2-nitrophenyl)diazenyl)phenol**	$C_{12}H_8N_4O_5$	288	142^0 C	52%
4c	**2-nitro-4-(*p*-tolyldiazenyl)phenol**	$C_{13}H_{11}N_3O_3$	257	153^0 C	48%

4d	**4-(naphthalen-1-yldiazenyl)-2-nitrophenol**	$C_{16}H_{11}N_3O_3$	293	160^0 C	55%
4e	**4-((4-hydroxy-3-nitrophenyl)diazenyl) benzenesulfonic acid**	$C_{12}H_9N_3O_6S$	323	312^0 C	48%
4f	**2-nitro-4-((3-nitrophenyl)diazenyl)phenol**	$C_{12}H_8N_4O_5$	288	275^0 C	55%
4g	**4-((4'-amino-[1,1'-biphenyl]-4-yl)diazenyl) -2-nitrophenol**	$C_{18}H_{14}N_4O_3$	334	328^0 C	51%
4h	**2-((4-hydroxy-3-nitrophenyl)diazenyl) benzoic acid**	$C_{13}H_9N_3O_5$	287	282^0 C	40%

Result and Discussion:

The azo dyes synthesized were characterized by IR andNMR spectroscopic methods. IR and ^{1}H-NMR spectrashowedthe expected signals which correspond to variousgroups present in each compounds. The IR and ^{1}H-NMR spectral values for different synthesis dyes are shown in table II.

Table (II): FTIR AND ^{1}H NMR data of azo compounds of o-nitophenol.

Compound	Spectra	Spectoscopic Data
SDB 4a	IR (KBr. cm^{-1})	3232 (phenolic –OH streach), 1625 (C=C Aromatic), 1539 (N=N), 1261 (C-N Streach), 1328 (NO_2)
	NMR (δ ppm)	4.48 (s 1H of –OH), 7.07 to 8.42 (m 8H of Ar-H)
SDB 4b	IR (KBr. cm^{-1})	3603 (phenolic –OH streach), 1614 (C=C Aromatic), 1512 (N=N), 1261 (C-N Streach) , 1332 (NO_2)
	NMR (δ ppm)	3.63 (s 1H of –OH), 6.57to 8.47 (m 7H of Ar-H)
SDB 4c	IR (KBr. cm^{-1})	3194 (phenolic –OH streach), 1606 (C=C Aromatic), 1514 (N=N), 1255 (C-N Streach) , 2920 (C-H of CH_3), 1327 (NO_2)
	NMR (δ ppm)	3.74 (s 1H of –OH), 6.91 to 8.38 (m 7H of Ar-H), 2.39 (s 3H of $–CH_3$)
SDB 4d	IR (KBr. cm^{-1})	3595 (phenolic –OH streach), 1612 (C=C Aromatic), 1508 (N=N), 1255(C-N Streach), 1323 (NO_2)
	NMR (δ ppm)	4.16 (s 1H of –OH), 6.73 to 8.11 (m 10H of Ar-H)
SDB 4e	IR (KBr. cm^{-1})	3562 (phenolic –OH streach), 1618 (C=C Aromatic), 1535 (N=N), 1228 (C-N Streach) , 1340 (NO_2)
	NMR (δ ppm)	3.51 (s 1H of –OH), 7.31 to 8.44 (m 7H of Ar-H), 3.24 (s 1H of SO_3H)
SDB 4f	IR (KBr. cm^{-1})	3576 (phenolic –OH streach), 1620 (C=C Aromatic), 1531 (N=N), 1263 (C-N Streach) , 1344 (NO_2)
	NMR (δ ppm)	3.55 (s 1H of –OH), 6.65 to 8.48 (m 7H of Ar-H)
SDB 4g	IR (KBr. cm^{-1})	3273 (phenolic –OH streach), 1616 (C=C Aromatic), 1535 (N=N), 1253(C-N Streach) , 3074(N-H Streach), 1325 (NO_2)
	NMR (δ ppm)	3.57 (s 2H of $–NH_2$), 6.70 (s 1H of –OH), 7.28 to 8.40 (m 11H of Ar-H)
SDB 4h	IR (KBr. cm^{-1})	3277 (phenolic –OH streach), 1616 (C=C Aromatic), 1535 (N=N), 1236 (C-N Streach) , 1638 (C=O, Streach of COOH), 1319 (NO_2)
	NMR (δ ppm)	5.09 (s 1H of –OH), 7.10 to 8.10 (m 7H of Ar-H), 8.38 (s 1H of –COOH)

Conclusion:

In the present study azo dyes have been synthesized from different aromatic amines by simple diazotization process followed by their coupling with o-nitrophenol. Their structures were confirmed by FTIR

and 1HNMR Spectroscopic techniques. These compounds shows different shades of colors like red, orange, yellow and brown which can be used for the dying in industries as well as pharmaceutical industries.

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