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SYNTHESIS AND CHARACTERIZATION OF NEW SUBSTITUTED 2-(2-ARYL DIAZENYL) – *H* BENZO (d) –IMIDAZOLE DERIVATIVES

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ABSTRACT

A Series of new substituted 2-(2-aryl diazenyl)-*H* benzo(*d*)- imidazole derivatives were synthesized by the reaction of Substituted 2-[(1*H*) benzo(*d*)-imidazol-2-yl] anilines with 2- naphthol and phenol. The structures of the products were confirmed from ^{1}HNMR, ^{13}C-NMR and IR spectra.

KEYWORDS: 2-[(1*H*) benzo(*d*)-imidazol-2-yl] aniline, 2- naphthol, sodium nitrite, etc.

INTRODUCTION

Azo compounds are the oldest and largest class of industrial synthetic organic dyes due to their versatile application in various fields.[1-2] Dyes used before the nineteenth century were either of vegetables or animal origin and belonged to various chemical types such as flavonoids, anthraquinones and indigoids.[3] Azo dyes have been most widely used in dyeing textile fibres, biomedical studies, advanced application in organic synthesis and high technology areas like lasers, liquid crystalline displays, electrooptical devices and ink-jet printers.[4] There are about 3000 azo dyes currently in use all over the world. The great majority of them are mono azo compounds, which have the common structure unit of the azo chromophore N=N linking two aromatic systems. The textile industry is the largest consumer of dye stuffs.[5] They have some variety of interesting biological activities[6] including antimicrobial activity, antibacterial and pesticidal activities.[7]

The azo dyes possesses antiseptic and antiprotozoal and also promote wound healing properties. Azo compounds have received much attention due to their versatile use in many practical applications such as coloring, fiber, photoelectronic applications, printing systems,

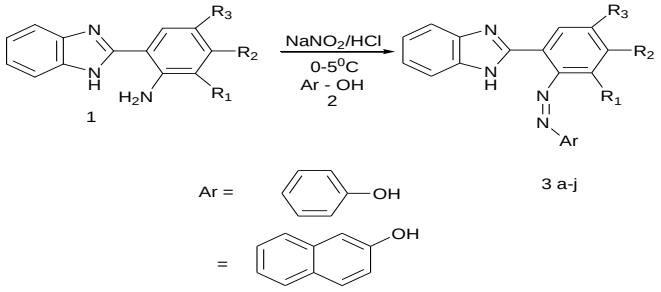
optical storage technology and in various analytical techniques.[8] Traditionally, azo dyes are the most important class of commercial dyes occupying more than half of the dye chemistry which contain phenols as intermediates.[9-15] Azo dyes have been reported to be good antibacterial agents.[16] Present work is focused on the synthesis and characterization of azo dyes containing phenol and β-napthol moieties. We have synthesized azo dyes using substituted 2-[(1*H*) benzo(*d*)-imidazol-2-yl] anilines and phenolic compounds such as phenol and beta naphthol following simple diazotization method. The dyes synthesized were characterized by IR, ^{1}HNMR and ^{13}CNMR spectra.

MATERIALS AND METHODS

All reagents were purchased from Sigma–Aldrich and Qualigens and are used without further purification. ^{1}H NMR spectra were recorded on a Bruker Spectrospin Avance DPX400 Ultrashield (400 and 300-MHz) spectrometer. IR spectra were recorded on FT-IR Bruker with KBr disc. All reactions were monitored by thin layer chromatography (TLC) on silica gel with chloroform–acetone as mobile phase. The newly synthesized products were also separated and purified by column chromatography.

Experimental Procedure

Substituted 2-[(1*H*) benzo(*d*)-imidazol-2-yl] anilines (0.05M) was dissolved in 16 ml. conc. HCl and 16 ml. water. (The temperature of the solution was maintained below 5^{0}c. The solution was diazotized by the addition of a solution of (0.05 gm.) of sodium nitrite in 20 ml. water. Then a solution of (0.05M) of phenol in 45 ml. of 10 % sodium hydroxide solution was prepared in 250 ml. beaker and it was also cooled below 5^{0}c in an ice-bath, assisted by the direct addition of about 25 gms. of crushed ice. Phenol solution was stirred vigoursly and the cold diazonium solution was added very slowly till a red color developed and red crystals of the compound get separated. After complete addition of diazonium salt solution, the mixture was allowed to stand in an ice-bath for 30 minutes with occasional stirring, then the solution was filtered, washed with water and recrystalized by using ethanol.



Scheme

RESULT AND DISCUSSION

Substituted 2-[2-(1*H*-Benzoimidazol-2-yl) phenyl azo]-phenols and Substituted 2-[2-(1*H*-Benzoimidazol-2-yl) phenyl azo]-naphthols are synthesized. Substituted 2-[(1*H*) benzo(*d*)-imidazol-2-yl] anilines are synthesized using substituted isatoic anhydrides and ortho phenylene diamine[17]. Substituted 2-[(1*H*) benzo(*d*)-imidazol-2-yl] anilines on reaction with sodium nitrite and HCl at 0-5^{0}C underwent diazotization reaction which on treatment with phenol and B-napthol undergo azo-coupling reaction to give the respected products. All these azo coupled products are synthesized by the usual method reported in literature to study the reactivity of Substituted 2-[(1*H*) benzo(*d*)-imidazol-2-yl] anilines. The melting points of the azo compounds are relatively close to each other and ranged between150-175^{0}C. Thus they are relatively high melting point azo dyes. The ^{1}HNMR spectra of products showed a singlet at δ 8.0-8.4 due to H of NH of benzimidazole proton and a singlet at δ 5.0-5.2 5 due to H of OH, it is the characteristic singlet of phenolic -OH. The multiplet at δ 6.8-9.00 is due to aromatic protons. This is suppored by the IR spectrum which indicates that the amino compound has successfully undergone the azo coupling reaction, as can be seen from the absorption by the azo functional group (-N=N-) in the region 1500-1600 cm^{-1}. ^{13}CNMR spectrum shows the characteristic peaks of the aromatic region.

Table 01: Analytical and physical data of substituted 2-(2-aryl diazenyl)-*H*-benzo(*d*)imidazole.

Sr. No.	M.F.	R_1, R_2, R_3	M.P.^{0}C	Yield %
3a.	$C_{19}H_{14}N_4O$	H, H, H	170	70
3b.	$C_{23}H_{16}N_4O$	H, H, H	182	65
3c.	$C_{19}H_{13}ClN_4O$	Cl, H, H	145	65
3d.	$C_{23}H_{15}ClN_4O$	Cl, H, H	160	60
3e.	$C_{20}H_{16}N_4O$	CH_3, H, H	152	62
3f.	$C_{24}H_{18}N_4O$	CH_3, H, H	168	60
3g.	$C_{19}H_{13}ClN_4O$	H, H, Cl	158	72
3h.	$C_{23}H_{15}ClN_4O$	H, H, Cl	162	60
3i.	$C_{19}H_{13}N_5O_3$	H, H, NO_2	150	62
3j.	$C_{25}H_{15}N_5O_3$	H, H, NO_2	169	60

SPECTRAL DATA

1. 2-[2-(1*H*-Benzoimidazol-2-yl)-phenylazo]-phenol

I.R. (Cm^{-1}): 3300 (NH), 1560 (-N=N), 3225 (Ar-OH), 3111(Ar-H).

^{1}H NMR: δ 5.4 (S,1H, OH), 6-5 -7.7(m,12H,Ar -H) 8.2 (S,1H,NH).

^{13}C-NMR: δ116.2, 118, 122, 124.2,125.6, 129.3, 131, 133, 134.5, 140, 152.6, 153.4, 155.

2. 2-[2-(1*H*-Benzoimidazol-2-yl)-phenylazo]-napthalen-1-ol

I.R. (Cm^{-1}): 3350 (NH), 1500 (-N=N), 3200 (Ar-OH), 3112(Ar-H).

^{1}H NMR: δ 5.5 (S,1H,OH), 6-5 -8.0(m,14H,Ar -H) 8.3 (S,1H,NH).

^{13}C-NMR: δ 116.1, 116.9, 122.3, 124, 127.4, 128.1, 129.5, 131.2, 133.6, 140.3, 152.3, 154.

3. 3-methyl, 2-[2-(1*H*-Benzoimidazol-2-yl)-phenylazo]-phenol

I.R. (Cm^{-1}): 3360 (NH), 1575 (-N=N), 3250 (Ar-OH), 3115(Ar-H), 2830 (CH_3).

^{1}H NMR: δ 5.5 (S,1H,OH), 6-5 -8.0(m,14H,Ar -H) 8.3 (S,1H,NH), 2.08 (S,3H, CH_3).

^{13}C-NMR: δ115, 118, 124, 125.2,126.6, 129.8, 131.4, 133.3, 134.5, 140.5, 152.5, 153.4, 156.

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