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FACILE SYNTHESIS OF 1-NAPHTHOL AZO DYES WITH NANO SiO_2/HIO_4 UNDER SOLVENT-FREE CONDITIONS

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ABSTRACT. Nano-silica supported periodic acid (nano-SPIA) has been utilized as a heterogeneous reagent for a highly efficient and one pot synthesis of azo dyes based on 1-naphthol under solvent-free conditions at room temperature. This method has some advantages, the reaction workup is very easy and the catalyst can be easily separated from the reaction mixture and one-pot procedure. The related products have been obtained in good to excellent yields, high purity and short reaction times. The structures of the products have been characterized by several techniques using UV-Vis, FT-IR, ^{1}H NMR, ^{13}C NMR and mass spectra.

KEY WORDS: Diazotization, Nano silica, Azo dyes, Solvent-free, Periodic acid

INTRODUCTION

In recent decades, organic color chemistry is undergoing very exciting development as a result of the opportunities presented by dye applications in high technology fields: electronic devices, linear and non linear optics, reprography, sensors and biomedical uses [1-4]. The acid-base catalyzed processes are effective for the near quantitative formation of desired products. But its main limitation is their environmental incompatibility, so nowadays the prohibition of the environmental pollution is main issue in global of the world [5]. Aromatic diazonium salts are important building blocks in the preparation of azo dyes which were synthesized *via* diazotization of aryl amines using nitrous acid. Sodium or potassium nitrites are used as nitrous acid sources because of the instability of free nitrous acid. Organic nitrite esters, such as *t*-butyl nitrite and ethyl nitrite have been used as alternative sources of nitrous acid in organic solvents [6, 7]. Recently HIO_4/Al_2O_3 has been reported by Khalilzadeh as a new system for iodination of activated aromatics and 1,3-dicarbonyl compounds [8]. There are a few reports for synthesis of stable diazonium salts at room temperature by using supported reagents [9, 10]. The solvent-free approach opens up numerous possibilities for conducting selective organic functional group transformations more efficiently and expeditiously using a variety of supported reagents on mineral oxides, inorganic substances or polymers [11]. Also azo dyes can be obtained under solvent free condition [10, 12-14]. Synthesis of azo compounds with nanosized iron-promoted reductive coupling of aromatic nitro compounds has been reported [15]. Here in, we wish to report a convenient and one-pot method for diazotization and diazo coupling reactions using nano silica supported periodic acid under solvent-free conditions at room temperature.

EXPERIMENTAL

Materials and instruments

Chemicals were purchased from Merck and Fluka chemical companies. All the products were known and were identified by comparison of their physical and spectroscopic data with those of authentic samples.

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IR spectra were recorded as KBr pellets on a Perkin-Elmer 781 spectrophotometer and an Impact 400 Nicolet FT-IR spectrophotometer. ^{1}H NMR and ^{13}C NMR spectra were recorded on a BrukerDRX-400 spectrometer with tetramethylsilane as internal reference. The scanning electron microscopy (SEM) of nano particles were determined with VEGA/TESCAN scanning electron microscope. Mass spectra were recorded on Micro Mass UKLTD spectra. The transmission electron microscopy (TEM) was recorded whit Philips CM10-HT100KV. The X-ray diffraction (XRD) patterns of materials were recorded by employing a Philips Xpert MPDdiffractometer equipped with a Cu Kα anode (λ = 1.54 Å) in the 2θ range from 5 to 80◦. Melting points obtained with a Yanagimoto micro melting point apparatus. The purity determination of the substrates and reaction monitoring were accomplished by TLC on silica-gel polygramSILG/UV 254 plates (Merck Company).

Preparation of nano silica supported periodic acid

10 mL of 70% aqueous solution HIO_4 was added to 1 g of nano silica gel and stirred for 30 min. After filtration from unreacted periodic acid, it was heated at 50 °C for 1 h under vacuum to afford nano-SPIA as a free flowing powder.

Typical procedure

A mixture of aniline (1 mmol, 0.093 g), nano-SPIA (0.05 g) and sodium nitrite (2 mmol, 0.138 g) were ground in a mortar for 10 min to obtain a homogeneous mixture. Then, a few drops of water were gradually added to this mixture and it was ground for 10 min until the gas evolution completely finished. 1-Naphthol (1 mmol, 0.144 g) was added to the diazonium salt and it was ground for 10 min. The reaction progress was monitored by thin layer chromatography (TLC) using a mixture of ethyl acetate and n-hexane (1:9 v/v) as solvent. Furthermore, purification of the product was performed by column chromatography using n-hexane and ethyl acetate. Corresponding azo dyes were obtained in 78% yield (product A, m.p.: 136 °C, lit. [16] 136 °C and product B, m.p.: 206 °C, lit. [16] 204 °C).

The selected spectral data

2-(2-(4-Nitrophenyl)diazenyl) naphth-1-ol. UV-Vis: λ_{max} $CHCl_3$ = 498, 295 nm; IR (KBr): 3441, 3030, 2935, 1609, 1512, 1442, 1332, 1270, 1110, 756 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 16.15 (s, 1H), 8.41 (d, *J* = 7.6 Hz, 1 H), 8.33 (d, *J* = 8.8 Hz, 2H), 7.8 (d, *J* = 7.2 Hz, 1H), 7.7 (d, *J* = 8.8 Hz, 2H), 7.55 (t, *J* = 9.2 Hz, 1H), 7.45 (t, *J* = 9.2 Hz, 1H), 6.85 (d, *J* = 8.4 Hz, 1H), 6.71 (d, *J* = 8.4 Hz, 1H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 168.40, 143.59, 138.86, 138.36, 133.55, 130.19, 129.79, 128.59, 128.50, 128.03, 125.32, 124.00, 121.64, 119.18 ppm.

4-(2-(4-Nitrophenyl)diazenyl) naphth-1-ol. UV-Vis: λ_{max} $CHCl_3$ = 490, 315 nm; IR (KBr): 3441, 3033, 1635, 1444, 1526, 1352, 1188, 1266, 756, 827 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.53 (s,1 H), 8.4 (d, *J* = 7.6 Hz, 1H), 8.33 (d, *J* = 8.41 Hz, 2H), 8.09 (d, *J* = 9.6 Hz, 1H), 7.77 (d, *J* = 8.4 Hz, 1H), 7.58 (t, *J* = 9.2 Hz, 1H), 7.42 (t, *J* = 9.2 Hz, 1H), 7 (d, *J* = 8.41 Hz, 2H), 6.7 (d, *J* = 9.6 Hz, 1H) ppm; mass spectra: 294 (M^{+}+1, 10), 293 (M^{+}, 48), 263 (12), 171 (10), 143 (92), 115 (61), 92 (17), 76 (9), 65 (12) m/z.

2-(2-(4-Chlorophenyl)diazenyl) naphth-1-ol. IR (KBr) cm^{-1}: 3438, 3032, 1626, 1491, 1448, 1209, 1254, 1096, 822, 749 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 16.11 (s,1 H), 8.32 (d, *J* = 8.0 Hz, 1H) 7.77 (d, *J* = 8.8 Hz, 2H), 7.62 (d, *J* = 8.0 Hz, 1H), 7.38 (d, *J* = 8.8 Hz, 2H), 7.31-7.25 (m, 2H), 7.04-6.83 (dd, *J* = 9.6 Hz, 2H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 172.29, 145.75,

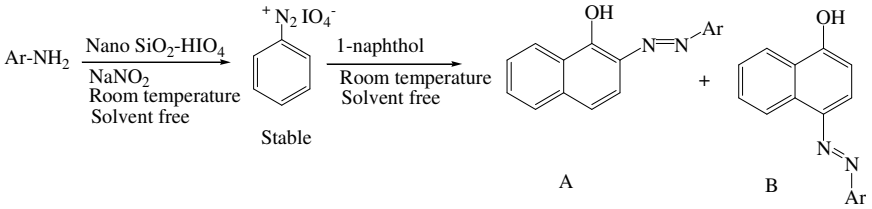
142.19, 131.69, 130.21, 127.63, 125.56, 124.75, 124.19, 123.62, 122.59, 120.73, 119.15, 116.53 ppm.

4-(2-(4-Chlorophenyl)diazenyl) naphth-1-ol. IR (KBr): 3438, 3032, 1618, 1491, 1448, 1209, 1254, 1096, 822, 749 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ: 8.83 (s, 1H), 8.32 (d, *J* = 8.0 Hz, 1H), 8.22 (d, *J* = 8.8 Hz, 1H), 7.77 (d, *J* = 8.8 Hz, 2H), 7.62 (d, *J* = 8.0 Hz, 1H), 7.38 (d, *J* = 8.8 Hz, 2H), 7.31-7.25 (m, 2H), 6.57 (d, *J* = 8.8 Hz, 1H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 170.59, 144.33, 140.10, 133.39, 133.01, 129.76, 128.94, 128.69, 128.19, 125.89, 124.33, 121.75, 119.93.

4-(2-Phenyl)diazenyl) naphth-1-ol. IR (KBr): 3441, 3033, 1635, 1444, 1526, 1352, 1188, 1266, 756, 827 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ: 15.69 (s, NH), 8.18 (d, *J* = 7.6 Hz, 1H), 8.11 (d, *J* = 9.2 Hz, 2H), 7.50 (m, 1H), 7.48 (t, *J* = 7.6 Hz, 1H). 7.43 (d, *J* = 9.2 Hz, 2H), 7.32 (t, *J* = 7.6 Hz, 1H), 6.89 (d, *J* = 9.6 Hz, 1H), 6.82 (d, *J* = 9.6 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 161.33, 160.67, 141.84, 136.71, 133.31, 129.53, 128.33, 128.15, 124.80, 122.19, 122.06, 121.61, 114.78, 55.64 ppm. Mass spectra: 249 (M^++1, 22), 248 (M^+, 95), 171 (25), 144 (14), 145 (88), 115 (59), 77 (31), 51 (10) m/z.

RESULTS AND DISCUSION

In continuation of our previous studies on the application of supported reagents in organic syntheses [17-30], we studied the conversion of primary aromatic amines to the corresponding azo dyes by using nano silica supported periodic acid as a acidic source for diazotization and diazo coupling with sodium nitrite under solvent-free conditions at room temperature (Scheme 1).



Scheme 1. General preparation procedure of azo dyes.

At first, we prepared nano-SPIA by reacting nano silica gel with a 70% aqueous solution of HIO_4. According to the SEM and TEM images and XRD pattern, the particle size of nano-SPIA is presented 35 nm (Figure 1).

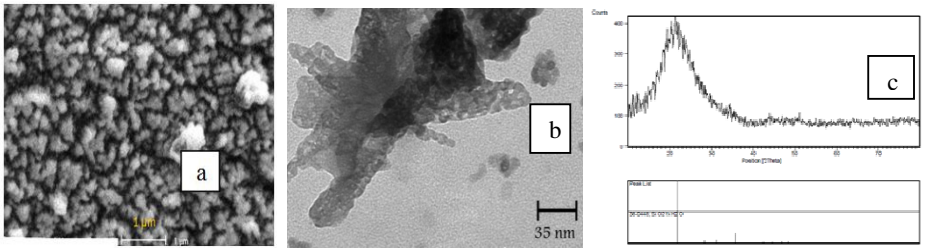


Figure 1. The SEM (a) and TEM (b) images and XRD (c) pattern of nano-SPIA.

Then mixture of *p*-nitro aniline (1 mmol) and sodium nitrite (1 mmol) in the presence of various amounts of nano-SPIA were ground, we have obtained the related diazonium salt in excellent yield using 0.05 g of nano-SPIA (Table 1).

Table 1. Preparation of phenyl diazonium periodate. In the presence of various amount of nano-SPIA[a].

Ent.	Time (min)	Catalyst (g)	Yield (%)
1	45	0.03	47
2	40	0.04	59
3	35	0.045	78
4	30	0.05	89
5	30	0.06	89

[a] *p*-nitroaniline (1 mmol) and sodium nitrite (2 mmol) were used.

After preparation of diazonium salt, 1-naphthol (1mmol) was added to them and stirred for 10 min. The whole process of diazotization was performed in 30 minutes. The crude product was extracted with dichloromethane. Then the solvent was evaporated by rotary evaporator at reduced pressure and the crude product was purified by flash column chromatography. By this procedure, 2-(2-(4-nitrophenyl)diazenyl) naphth-1-ol as product A and 4-(2-(4-nitrophenyl) diazenyl) naphth-1-ol as product B were obtained with 89% isolated yield. We used the same conditions for the conversion of other aromatic amines to the related azo dyes and we obtained the products in good to excellent yields (Table 2).

Table 2. Diazotization and diazo coupling reactions of some amines with 1-naphthol at room temperature.

Entry	Amines	Yield (%)[a]	Yield (%)[b]	Time (min)	M.p. (°C)	
					Found	Reported [16]
1	$C_6H_5NH_2$	78	78	30	A:136 B:206	A:136 B:204
2	*p*-$ClC_6H_4NH_2$	81	81	25	A:160 B:178	A:162 B: 176
3	*o*-$ClC_6H_4NH_2$	82	76	27	A:154 B:176	A:153 B:178
4	*o*-$NO_2C_6H_4NH_2$	80	76	23	A:174 B:286	A:175 B:284
5	*p*-$NO_2C_6H_4NH_2$	89	89	30	A:182 B:293	A:183 B:295
6	*p*-$MeOC_6H_4NH_2$	78	73	27	A:158 B:194	A:159 B:194
7	*p*-$BrC_6H_4NH_2$	75	67	26	A:189 B:265	A:188 B:269
8	*o*-$MeC_6H_4NH_2$	85	80	30	A:165 B:245	A:168 B:249
9	*p*-$MeC_6H_4NH_2$	77	70	28	A:178 B:289	A:180 B:285

[a,b]The ratio of amine (mmol), $NaNO_2$ (mmol), 1-naphthol (mmol) and nano-SPIA (g) was 1:2:1:0.05.

In ^{1}H NMR spectrum of 2-(2-(4-nitrophenyl)diazenyl) naphth-1-ol, the (NH/OH) signal around 16 ppm is deshielded more than those of other signals, due to bifurcated intramolecular hydrogen bonds which are examples of hydrogen bonds involving one proton and two acceptors. Also the ^{1}H NMR spectra of product B, the singlet peak around δ = 8.5 ppm may be attributed to bifurcated NH/N proton in azo-hydrazon forms.

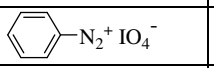
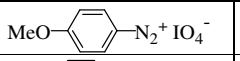
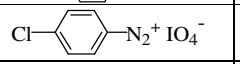
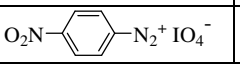
The reusability of nano-SPIA was investigated for several times which indicated no significant decrease in catalytic activity (Table 3).

Table 3. The reusability of catalyst

Reaction cycles	1	2	3	4	5
Yields (%)	89	89	78	59	47

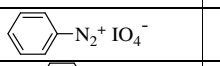
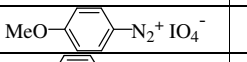
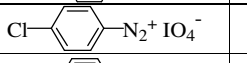
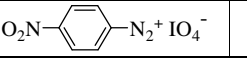
To determining the stability of the diazonium salts, some aryl diazoniumnano-silica periodates were stored in a desiccator at room temperature. After the specified times, 2-naphthol was added to each salt and the reaction mixture was ground at room temperature for 10 min. The products were extracted and the yields of azo dyes compared with the product provided with the corresponding fresh diazonium salts (Table 4). Aryl diazoniumnano-silica periodate with electron-withdrawing groups on aromatic ring are more stable than those with electron donating groups because of the instability of the resulting aryl cation (Table 4). Also, we have compared the stability of diazonium silica periodates *versus* diazonium nano-silica periodates and found that the diazonium silica periodates have less stability (Table 5).

Table 4. The stability study of some aryl diazoniumnano silica periodate at room temperature[a].

Diazonium salt	Product	Yield (%) after						
		30 min	1 day	2 days	3 days	4 days	5 days	6 days
	2a	91	88	85	80	75	52	35
	2b	90	85	80	76	61	50	30
	2c	93	90	86	81	77	70	65
	2d	96	93	90	85	79	73	69

[a]The yields refer to the isolated pure products after adding 2-naphthol into their corresponding diazonium salts within the specified time.

Table 5. The stability study of some aryl diazonium silica periodate at room temperature.

Diazonium salt	Product	Yield (%) after						
		30 min	1 day	2 days	3 days	4 days	5 days	6 days
	2a	85	73	50	43	25	20	-
	2b	80	75	43	32	22	-	-
	2c	83	78	74	70	48	37	24
	2d	89	80	73	69	51	30	25

[a]The yields refer to the isolated pure products after adding 2-naphthol into their corresponding diazonium salts within the specified times.

CONCLUSION

Various aromatic amines including electron-withdrawing and electron-donating groups were rapidly and efficiently converted to the related azo dyes under solvent-free conditions at room

temperature. Especially nano-SPIA proved to be a suitable catalyst affording the highest stability of diazonium salts and yields. One reason for this behavior may be related to the number of available active sites which in turn increases the catalytic activity. The solvent free conditions employed in the present method, which make it environmentally friendly and make it useful for industrial applications. Furthermore, it has other advantages such as mildness, low cost, the reusability of catalyst, ease handling, short reaction times and simple experimental procedure.

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