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Nanosilica/NaNO₂: Novel Heterogeneous System for Synthesis of Azo Compounds

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Various azo compounds are synthesized by electrophonic substitution reaction in the presence of Nanosilica/NaNO_2 as a catalyst.

Keywords azo compound, fumed SiO₂, nanomaterials, sodium nitrite, solid acids

INTRODUCTION

Azo compounds are chemical compounds that contain R-N=N-R' as a functional group. Derivatives containing aryl groups are more stable. Oxidation of hydrazine (R-NH-NH-R') is a method for the synthesizing of azo compounds. Aromatic azo compounds are more common and can be synthesized by azo coupling reaction, which is an electrophilic substitution reaction of diazonium salt on aromatic ring.^[1]

Because of the electron delocalization, many azo compounds are colored and have been utilized as the oldest and largest class of industrial organic dyes and analytical reagents.^[2] These compounds have more recently attracted increased attention by finding potential applications in various fields such as biomedicine,^[2,3] organic synthesis,^[4–6] and as materials with excellent optical and photoelectric properties.^[7]

Many methods for the synthesis of these compounds have been described in literature; however, most of them have disadvantages such as low productivity, insensitive reaction conditions, expensive reagents, and undesirable side reactions. Most of the processes for the large scale production of azo compounds use liquid acids, such as HCl, as catalyst,^[2] resulting in the generation of large amount of wastes that are environmentally hazardous and costly to treat.^[3]

In order to reduce or eliminate the use or generation of hazardous materials during the synthesis, and simplify the handling procedures in the production process, viable alternative manufacturing processes that use eco-friendly catalysts with lower toxicity and higher stability are under attention. Nanoparticles are sized between 1 and 100 nanometers. Nanoparticles may or may not exhibit size-related properties that differ significantly from those observed in fine particles or bulk materials.^[8]

Nanosilica (fumed SiO₂) as a stable acidic reagent (solid acid) effectively plays the role of HCl in the reaction, assisting the formation of diazonium species. Protection of transition compounds is a key factor in multi-step synthesis process; hence, due to the decomposition of diazonium salts at temperatures above 5°C, synthesis must take place in solution near ice temperatures. In addition to the elimination of HCl as a hazardous substance, using nanosilica as catalyst for synthesis of azo compounds possess many advantages such as mild reaction conditions; low energy consumption; high efficiency; and high selectivity.

EXPERIMENTAL

All chemicals were reagent grade quality obtained from Merck company and used as received. Melting points were measured by a MODEL digital melting point measurement apparatus. IR spectrometry was performed on a Galaxy FT-IR 500 spectrophotometer. ¹H NMR spectra were recorded on a Brucker 300 MHz spectrometer. Chemical shifts (ppm) were referenced to the internal standards tetramethylsilane (TMS). The reactions were monitored by thin layer chromatography using silicagel F_{254} aluminum sheets (Merck).

General Producer

Azo compounds were synthesized as follows: The required amounts of corresponding aniline or *p*-amino benzoic acid (0.054 mol), nanosilica (0.054 mole), water (15-20 mL), and NaNO₂ (0.054 mol) were mixed in a flask. After gentle grinding of the resultant mixture for 15 min, a basic solution of phenol (0.054 mol) in sodium hydroxide) was added drop wise to the flask (in a period of 15–20 min), and the mixture was stirred vigorously for 20 minutes. It was then filtered, and the resultant solid was washed with diethyl ether and then air dried. The crude product was recrystallized from acetic acid (or ethanol).

4-Ethyl-2(p-carboxyl azophenyl) phenol (2a)

mp: 171–173°C, yield% 92. IR (KBr): 3225 (OH), 3078 (CH aroma), 2962 (CH_{aliph}), 3300–2500 (COOH), 1683 (C=O),

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SCH. 1. Synthesis of Azo compounds

1593 (C=C) cm⁻¹. ¹H NMR (DMSO-d₆): δ = 1.02 (t, 3H, CH₃), 2.66 (q, 2H, CH₂), 7.07–7.99 (m, 7H, CH_{arom}), 8.01 (d, 1H, OH), 10.61 (bs, 1H, COOH).

4-(Azophenyl)-1-naphthol (2b)

m.p:165-168 °C, yield %95, IR (KBr): 3225.58 (OH), 3078 (CH_{arom}), 3300-2500 (COOH), 1683 (C=O), 1593 (C=C) cm⁻¹. ¹H NMR (DMSO-d₆): δ = 5.62–6.73 (m, 11H, CH_{arom}), 8.4 (s, 1H, OH).

4-Flouro-2-(Azophenyl) Phenol (2c)

m.p:101–103°C, yield %85. IR (KBr):3205.89 (OH), 3159.58 (CH_{arom}), 1610.25 (C=C) cm⁻¹. ¹H NMR (DMSO-d₆): δ = 7.07–7.99 (m, 8H, CH_{arom}), 8.01 (d, 1H, OH).

2,3-Dichloro-4-(Azophenyl) Phenol (2d)

m.p: 230–233°C, yield %65. IR (KBr): 3213 (OH), 3061 (CH_{arom}), 1591 (C=C) cm⁻¹. ¹H NMR (DMSO-d₆): δ = 6.33–6.51 (m, 2H, CH_{arom}), 7.43–7.68 (m, 5H, CH_{arom}), 7.85(d, 2H, OH).

2, 6-Dichloro-4-(Azophenyl) Phenol (2e)

m.p: 142–144°C, yield %90. IR (KBr): 3508 (OH), 3084 (CH_{arom}), 1570 (C=C).¹H NMR (DMSO-d₆): δ = 6.33-6.51 (m, 2H, CH_{arom}), 7.43–7.68 (m, 5H, CH_{arom}), 7.85(d, 2H, –OH).

2-Hydroxy-3-(Azophenyl) Benzaldehyde (2f)

m.p: 151–153°C, yield %95. IR (KBr): 3207 (OH), 3040 (CH_{arom}), 1591 (C=C) cm⁻¹. ¹H NMR (DMSO-d₆): 6.89-6.96 (m, 3H, CH_{arom}), 7.48–7.53 (m, 2H, CH_{arom}), 7.77–7.85 (m, 2H, CH_{arom}), 11.31 (bs, 2H, OH, CHO).

4-Chloro-2-(Azophenyl) Phenol (2g)

m.p:161–163°C, yield %72. IR (KBr): 3311 (OH), 3057 (CH_{arom}), 1591. (C=C) cm⁻¹. ¹H NMR (DMSO-d₆): 7.10 (d, 1H, CH_{arom}), 7.43–7.64 (m, 5H, CH_{arom}), 7.99 (s, 2H, CH_{arom}), 10.85 (bs, 1H, OH).

2, 6-Dihydroxy-1-(Azo Phenyl) Benzene (2h)

m.p:152–155°C, yield %95. IR (KBr): 3213.61 (OH), 3061 (CH_{arom}), 1591 (C=C) cm⁻¹. ¹H NMR (DMSO-d₆): 6.08–6.11 (m, 2H, CH_{arom}), 6.32–6.73(m, 6H, CH_{arom}), 8.79 (s, 2H, OH).

TABLE 1 Azo compounds

Entrance	Ar	Ar'
4a	4-ethyl phenol	<i>p</i> -carboxyl phenyl
4b	1-naphthol	phenyl
4c	4-flourophenol	phenyl
4d	2,3-dichlorophenol	phenyl
4e	2, 6-dichlorophenol	phenyl
4f	2-hydroxybenzaldehyde	phenyl
4g	4-chlorophenol	phenyl
4h	1, 3-dihydroxy benzene	Phenyl

RESULTS AND DISCUSSION

Scheme 1 shows the reaction between a phenol derivative and an appropriate aniline compound in the presence of nanosilica as catalyst. The reaction takes place at mild condition with suitable yield.

The authors' studies on nanomaterials for finding appropriate solid acids led to nanosilica, which is exhibited. Nanosilicas have different properties based on their size. Nanosilica (fumed silica), also known as pyrogenic silica, is a non-crystalline, fine-grain, low density, and high surface area. Silica is also known as microsilica. Fumed silica (10–15 nm) has acidic properties with pH = 4.2.

As shown in Table 1, the substitutes in the phenol compounds of the reaction have an effective role. Electron-withdrawing group on phenol compounds decreased the yield of reaction compared to the electron-releasing groups and the substitute group; its position on phenol ring affects the color of the final azo compounds.

The ¹H NMR data of the synthesized compounds are shown as follows. The ¹H NMR data of all synthesized compounds are consistent with the expected structures. The ¹H-NMR spectra of **2a** shows two broad singles at 10.61 ppm, which is attributed to the resonance of the carboxylic group. Seven aromatic protons related to two aromatic rings appeared as a multiple at the 7.07–7.99 ppm range. Protons of CH₂ and CH₃ groups appeared as quartet and triplet at 2.66 and 1.02 ppm, respectively.

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