

Bi(NO₃)₃·5H₂O: An efficient acidic reagent for synthesis of azo dyes at room temperature

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Received 4 June 2012; received in revised form 8 November 2012; accepted 11 November 2012

ABSTRACT

An one-pot method has been developed for the synthesis of azo dyes *via* sequential diazotization–diazo coupling of aromatic amines with coupling agents at room temperature in the presence of Bi(NO₃)₃·5H₂O. Short reaction times, high yields, a clean process, simple methodology, easy work-up and green conditions are advantages of this protocol.

Keywords: Azo dye, Bi(NO₃)₃·SiO₂, Stable diazonium salts, One-pot synthesis

1. Introduction

Azo compounds are the most widely class of industrial synthesized organic dyes due to their versatile application in various fields such as dyeing textile fiber, biological–pharmacological activities and advanced application in organic synthesis [1]. Azo dyes have been synthesized *via* coupling of diazotized aromatic amines with activated aromatic compound. Previously, aromatic amines have been converted to diazonium salts in the presence of NaNO₂ and a mineral acid at 0-5°C [2].

Generally, a mixture of hydrochloric acid and NaNO₂ was used as diazotization reagent. Recently, ionic liquid nitrite source [3] and organosilane-based nitrite ionic liquid immobilized on silica [4] were applied for above mentioned purpose.

Bismuth (III) nitrate penta hydrate (Bi(NO₃)₃·5H₂O) [5-8] with favorable ecological behaviour have low toxicity, low cost, stability in air, commercial availability and ease of handling properties. In this article, we report a new protocol for synthesis of azo dyes using Bi(NO₃)₃·5H₂O at room temperature.

2. Experimental

2.1. Materials and methods

All chemicals were purchased from Fluka and Merck companies. Products were characterized by IR, ¹H-NMR and by comparison of their physical properties with those

reported in the literature. IR spectra were run on a Bruker, Eqinox 55 spectrometer. ¹H NMR spectra were obtained using a Bruker Avance 400 MHz spectrometer (DRX). Melting points were determined by a Buchi melting point B-540 B.V.CHI apparatus.

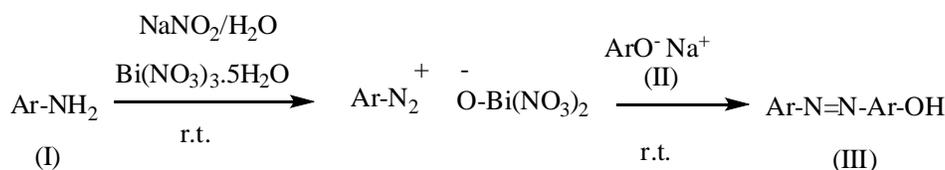
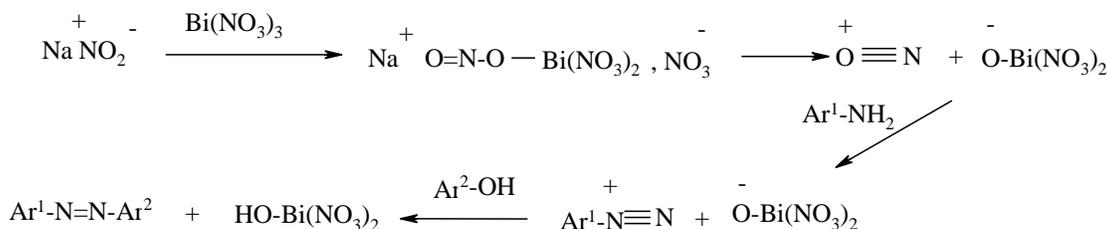
2.2. Synthesis of 12-(4-nitrophenyl)-9, 9-dimethyl 8, 9, 10, 12-tetrahydrobenzo(a)xanthenes -11-one (IV) in water

A mixture of 2-naphthol (1 mmol), 4-nitrobenzaldehyde (1 mmol), dimedone (1.2 mmol), Bi(NO₃)₃·5H₂O (0.05 g), 0.01 g of sodium dodecyl sulfate (SDS) and 2 mL water was heated at 45 °C in water bath. The progress of the reaction was monitored by TLC. After completion of the reaction, the mixture was charged in to isolating funnel and extracted with chloroform to isolation of product. The chloroform layer was evaporated carefully and the obtained solid was crystallized in ethanol: water (80:20) to afford the pure product [9].

2.3. Synthesis of azo dyes in the presence of Bi(NO₃)₃·5H₂O at room temperature

In a mortar, a mixture of 0.14 g (2 mmol) of NaNO₂ and 0.2 g of Bi(NO₃)₃·5H₂O was grinded. Then, 2 mmol of aromatic amine was added and grinded. Then, 1 mL of water was gradually added to this mixture and ground for 2 min for evolution of all obtained gas. After formation of diazonium salt, a solution containing 2 mmol aromatic amine, sodium phenoxide or sodium naphthoxide was added and sufficiently grinded. The obtained azo dye was dissolved in ethanol and filtered to isolation of catalyst. The

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Scheme 1. Synthesis of azo dyes in the presence of $\text{Bi(NO}_3)_3 \cdot 5\text{H}_2\text{O}$.Scheme 2. A proposed mechanism for formation of azo dyes in the presence of $\text{Bi(NO}_3)_3 \cdot 5\text{H}_2\text{O}$.

ethanol solution of azo dye was concentrated. By addition of water to ethanol solution, the azo dye was separated in pure solid form.

Selected spectral data

4-(1-Naphthyl azo)-1-naphthylamine (Table 1, Entry 1): Dark brown, FT-IR (KBr, $\nu_{\text{max}}/\text{cm}^{-1}$): 3379, 3481, 1616, 1462, 1597, 1462, 1330, 828, 756. $^1\text{H NMR}$ (CDCl_3 , ppm) δ : 4.67 (s, 2H, NH_2), 6.87 (d, $J=8.4$ Hz, 1H), 7.56-7.71 (m, 6H, Ph), 7.84 (d, 1H), 7.95 (m, 2H), 8.11 (d, $J=8.4$ Hz, 1H), 9.04 (d, $J=8.4$ Hz, 1H), 9.18 (d, $J=8.4$ Hz, 1H) ppm. UV-vis (CHCl_3): $\lambda_{\text{max}}(\text{nm})= 271.21$ ($\pi\text{-}\pi^*$, Ar-H), 441.45 ($\pi\text{-}\pi^*$, N=N).

1-(*p*-Chlorophenyl azo)-2-naphthol (Table 1, Entry 2): Red solid, FT-IR (KBr, $\nu_{\text{max}}/\text{cm}^{-1}$): 3130-3300, 1598, 1510, 1438, 1243, 1091, 825, 749. $^1\text{H NMR}$ (CDCl_3 , ppm) δ : 7.1 (s, 1H), 7.35-7.70 (m, 5H), 8.56 (s, 1H), 9.55 (s, 3H), 16.1 (s, 1H, OH). UV-vis (CHCl_3): $\lambda_{\text{max}}(\text{nm})= 360.80$ ($\pi\text{-}\pi^*$, Ar-H), 482.40 ($\pi\text{-}\pi^*$, N=N).

1-(2-(2, 4-Dimethyl phenyl azo)-4, 6-dimethyl phenyl azo)-2-naphthol (Table 1, Entry 3): Red solid, m.p. 161-163°C, FT-IR (KBr, $\nu_{\text{max}}/\text{cm}^{-1}$): 3280-3570, 3028, 2977, 1612, 1497, 1443, 1383, 1206, 750. $^1\text{H NMR}$ (CDCl_3 , ppm) δ : 2.36 (s, 9H), 2.49 (s, 3H), 6.84 (d, $J=9.6$ Hz, 1H), 7.08-7.21 (m, 3H), 7.43 (t, $J=8$ Hz, 1H), 7.61-7.76 (m, 3H), 8.03 (s, 1H), 8.56 (d, $J=7.6$ Hz, 1H), 9.51 (s, 1H), 16.43 (s, 1H, OH). UV-vis (CHCl_3): $\lambda_{\text{max}}(\text{nm})= 368.48$ ($\pi\text{-}\pi^*$, Ar-H), 487.52 ($\pi\text{-}\pi^*$, N=N).

12-(4-(4-Hydroxyphenyl azo)phenyl)-9, 9-dimethyl-8, 9, 10, 12-tetrahydrobenzo[*a*]xanthen-11-one (Table 1, Entry 10): Yellow solid, m.p. 263-265°C. FT-IR (KBr, $\nu_{\text{max}}/\text{cm}^{-1}$): 3120-3350, 2954, 1628, 1616, 1590, 1503, 1466, 1439, 1370, 1266, 1238, 1226, 1184, 1032, 838, 828, 814, 744.

$^1\text{H NMR}$ (CDCl_3 , ppm) δ : 0.88 (s, 3H), 1.05 (s, 3H), 2.16 (d, $J=16.3$ Hz, 1H), 2.24 (d, $J=16$ Hz, 1H), 2.52 (s, 2H), 5.67 (s, 1H), 6.82 (d, $J=8.2$ Hz, 2H), 7.26-7.38 (m, 6H), 7.57 (d, $J=7.7$ Hz, 2H), 7.65 (t, $J=8.3$ Hz, 2H), 7.71 (t, $J=8.2$ Hz, 2H), 7.89 (d, $J=8.1$ Hz, 1H). UV-vis (CHCl_3): $\lambda_{\text{max}}(\text{nm})= 272.48$ ($\pi\text{-}\pi^*$, Ar-H), 353.12 ($\pi\text{-}\pi^*$, N=N).

14-(2-Hydroxy naphthyl azo) phenyl-14H-dibenzo [*a*,*j*] xanthen (Table 1, Entry 12): Red solid, m.p. 115-116°C. FT-IR (KBr, $\nu_{\text{max}}/\text{cm}^{-1}$): 3100-3500, 3386, 3059, 1621, 1595, 1552, 1510, 1458, 1431, 1400, 1248, 1112, 1143, 961, 829, 746, 609, 516. $^1\text{H NMR}$ (CDCl_3 , ppm) δ : 6.77 (s, 1H), 6.84 (s, 1H), 6.82 (s, 1H), 7.12 (s, 1H), 7.20-7.83 (m, 17H), 8.39 (s, 2H), 16 (s, 1H, OH).

14-(4-Hydroxy 2,6-dimethyl phenyl azo)phenyl-14H-dibenzo [*a*,*j*] xanthen (Table 1, Entry 13): Red solid, m.p. 98-100°C. FT-IR (KBr, $\nu_{\text{max}}/\text{cm}^{-1}$): 2900-3100, 1593, 1515, 1459, 1433, 1384, 1314, 1247, 963, 810, 745, 700, 512). $^1\text{H NMR}$ (CDCl_3 , ppm) δ : 2.27 (br, 6H), 6.78 (s, 1H), 6.98 (s, 1H), 7.10-8.00 (m, 16H), 8.40 (d, $J= 8.8\text{Hz}$, 2H).

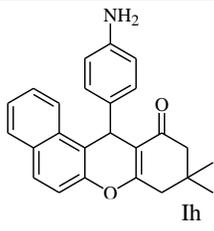
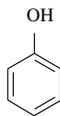
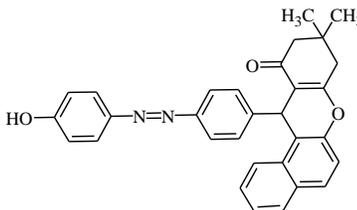
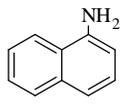
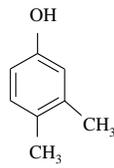
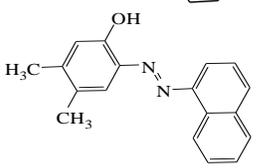
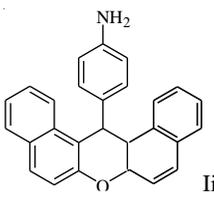
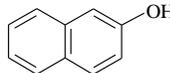
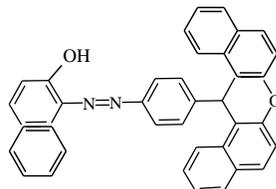
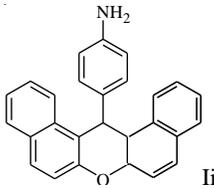
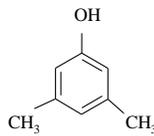
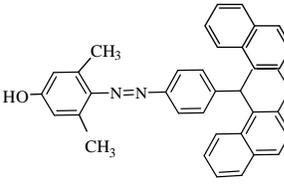
3. Results and Discussion

Previously, diazonium salts had poor thermal stability and were synthesized around 0-10°C. To avoid decomposition of them, they were handled below 0°C. In our investigation, the obtained aryldiazonium salts counteracting $\text{Bi(NO}_3)_3$ were sufficiently stable to be kept at room temperature in the dry condition. In our new methods, different kinds of aromatic amines, with electron-withdrawing groups as well as electron-donating groups, were rapidly converted to the corresponding azo dyes in the presence of NaNO_2 and $\text{Bi(NO}_3)_3 \cdot 5\text{H}_2\text{O}$ at room temperature (Scheme 1 and Table 1). Generally, an aromatic amine (2 mmol), $\text{Bi(NO}_3)_3 \cdot 5\text{H}_2\text{O}$

Table 1. Synthesis of azo dyes using $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ at room temperature.

Entry	Amine (I)	Coupling agent	Azo dye (III)	Yield ^a	m.p. (°C) [Ref]
1			 CAS No: 2835-61-2	90	123-125 [12]
2				87	73-76 [13]
3				86	161-163 [13]
4			 Sudan I	88	129-131 [13]
5			 Para Red	79	183-185 [14]
6			 Sudan III	87	193-195 [13]
7				83	75-77 [13]
8				85	118-120 [13]
9				83	74-77 [15]

Table 1. (Continued)

10				88	263-265 [13]
11				89	123-125 [13]
12				82	115-116 [13]
13				84	98-100 [13]

^aThe ratio of amine (mmol): NaNO₂ (mmol): Bi(NO₃)₃·5 H₂O (g): coupling agent (mmol) is equal to 2:2:0.2:2.

(0.2 g) and sodium nitrite (2 mmol) were ground in a mortar for 2-3 minutes at room temperature to obtain a homogeneous mixture. Then, 1 mL of water was gradually added to this mixture and ground for 2 min for evolution of all obtained brown NO₂ gas. Then, coupling agent (2 mmol) was added to the diazonium salt and ground for 2 min. the whole process of diazotization and diazo coupling takes 6–7 minutes. The crude product was dissolved in chloroform and filtered to isolation of catalyst. The crude product was purified by recrystallization in ethanol.

A proposed mechanism for formation of azo dyes in the presence of Bi(NO₃)₃·5H₂O as an Lewis acid reagent is shown in Scheme 2.

The amines (Ih and Ii) were obtained by reduction of corresponding nitro compounds (IV-V) in the presence of Na₂S·9H₂O and sulfur [10]. The substance (IV) was synthesized via condensation of β-naphthol, dimedone and 4-nitrobenzaldehyde in the presence of Bi(NO₃)₃·SiO₂ and sodium dodecyl sulfate (SDS) in water at 40 °C. The diarylxanthene (V) was synthesized via reaction between 4-nitrobenzaldehyde and 2-naphthol in the presence of 37% BF₃·SiO₂ [11] (Scheme 3).

4. Conclusion

We have demonstrated a simple method for the synthesis of

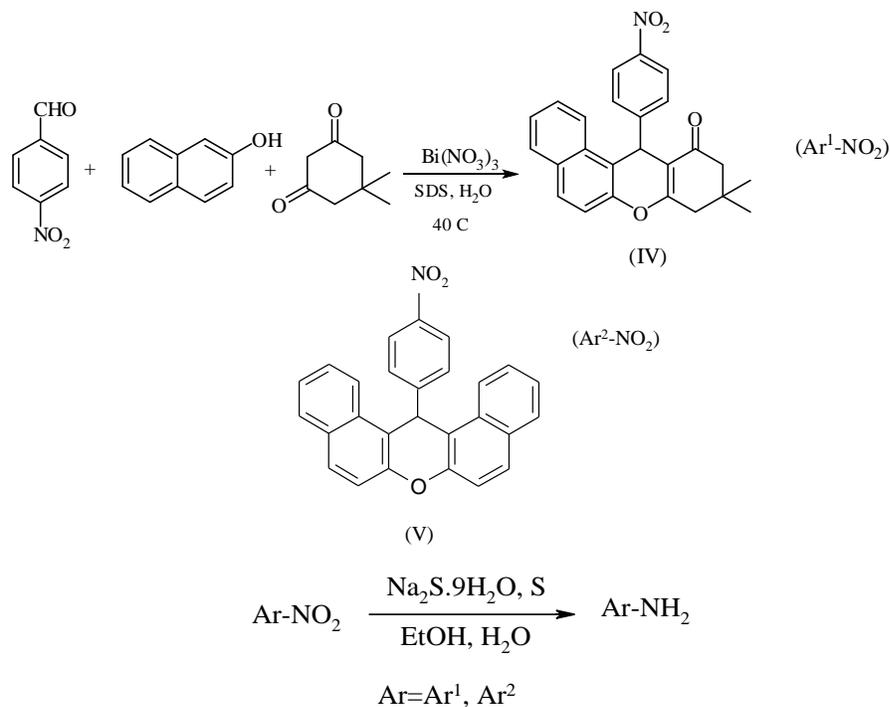
azo dyes using Bi(NO₃)₃·5H₂O as efficient reagent. Short reaction times, high yields, a clean process, simple methodology, easy work-up and green conditions are advantages of this protocol.

Acknowledgements

The Research Council of Yazd University is gratefully acknowledged for the financial support of this study.

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Scheme 3. Synthesis and reduction of aromatic nitro compounds.

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