

BF₃.SiO₂: an efficient catalyst for the synthesis of azo dyes at room temperature

Bi Bi Fatemeh Mirjalili^{a*}, Abdolhamid Bamoniri^b and Ali Akbari^a

^aDepartment of Chemistry, College of Science, Yazd University, Yazd, P.O.Box 89158-13149, I. R. Iran

^bDepartment of Organic Chemistry, Faculty of Chemistry, University of Kashan, Kashan, I.R.Iran

ARTICLE INFO

Article history:

Received May 30, 2012
Received in Revised form
June 2, 2012
Accepted 24 June 2012
Available online
24 June 2012

Keywords:

Azo dye
BF₃.SiO₂
Stable diazonium salts
Diazotization
Lewis acid

ABSTRACT

A rapid 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 BF₃.SiO₂ as acidic catalyst. The obtained aryl diazonium salts bearing silica supported boron tri-fluoride counter ion was sufficiently stable to be kept at room temperature in the dry state.

© 2012 Growing Science Ltd. All rights reserved.

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 fiber¹, biological–pharmacological activities². Azo dyes have been synthesized via coupling of diazotized aromatic amines with activated aromatic compounds. Previously, aromatic amines have been converted to diazonium salts in the presence of NaNO₂ and a mineral acid at 0–5 °C.

Boron tri-fluoride.etherated (BF₃.OEt₂), as thin, coloured and fuming liquid, is used in industry and organic synthesis. Since, BF₃.OEt₂ is liquid that fumes in air and reacts with the moisture to form HF, the handling and the usability of it as liquid form is laborious and the supported form is indeed preferable. Silica supported boron tri-fluoride (BF₃.SiO₂)^{3–7} is a bench-top catalyst which is reusable,

* Corresponding author.

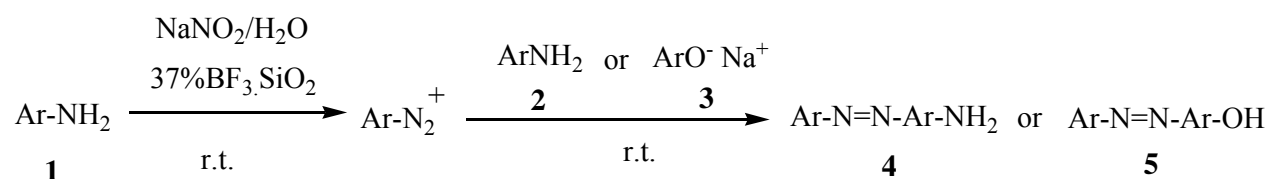
E-mail addresses: fmirjalili@gmail.com (B. B. Mirjalili)

cheap, readily available, eco-friendly, versatile and efficient for promotion of many acid catalyzed organic reactions. This catalyst does not need special precautions for preparation, handling or storage, and it can be stored at ambient temperature for months without losing its catalytic activity.

In this article, we report a new protocol for synthesis of azo dyes in the presence of 37% $\text{BF}_3 \cdot \text{SiO}_2$, at room temperature.

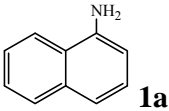
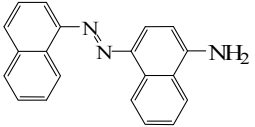
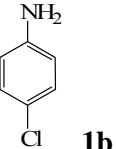
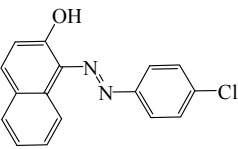
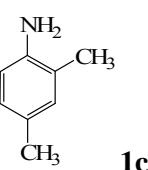
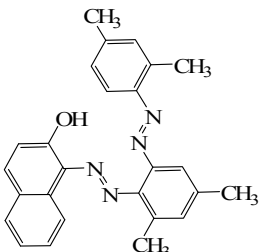
2. Results and Discussion

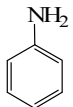
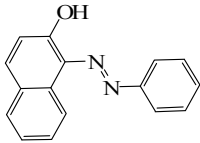
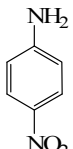
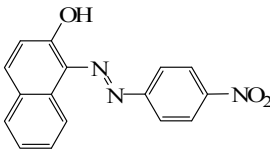
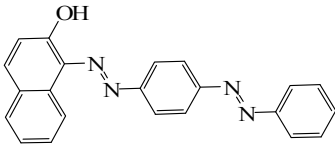
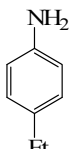
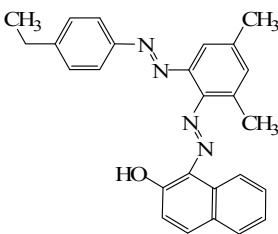
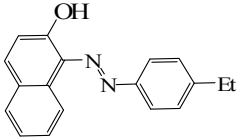
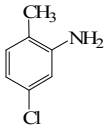
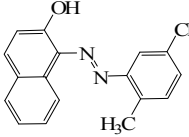
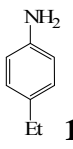
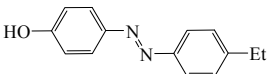
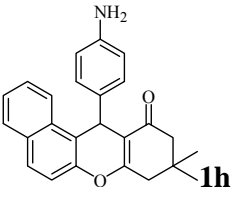
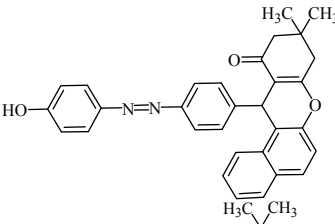
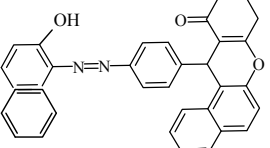
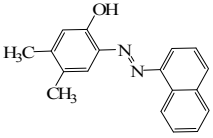
Due to the poor thermal stability of diazonium salts, they were previously synthesized around 0–10 °C and were handled below 0 °C. In our investigation, the obtained aryl diazonium salts bearing silica supported boron tri-fluoride counter ion was sufficiently stable to be kept at room temperature in the dry state. In our new method, 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 37% $\text{BF}_3 \cdot \text{SiO}_2$ at room temperature (Scheme 1 and Table 1). Generally, a mixture of an aromatic amine (2 mmol), 37% $\text{BF}_3 \cdot \text{SiO}_2$ (0.2 g) and sodium nitrite (2 mmol) was 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 mixed for 2 min. 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 re-crystallization in ethanol.

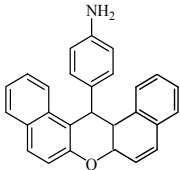
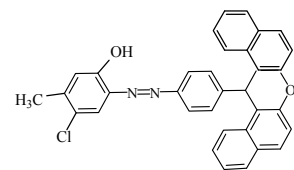
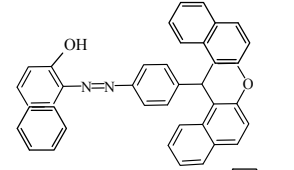
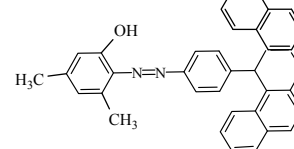


Scheme 1: Synthesis of azo dyes in the presence of silica supported boron tri-fluoride

Table 1. Synthesis of azo dyes in the presence of 37% $\text{BF}_3 \cdot \text{SiO}_2$ at room temperature.

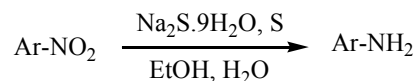
Entry	Amine (1)	Azo dye (4 or 5)	Yield ^a	m.p.(°C)
1	 1a		85	123-125
2	 1b		88	73-76
3	 1c		87	161-163

4	 1d	 Sudan I	86	129-131
5	 1e	 Para Red	82	183-185
6	1d	 Sudan III	82	103-105
7	 1f		82	89-91
8	1f		84	75-77
9	 1g		89	118-120
10	 1f		87	74-77
11	 1h		88	263-265
12	1h		85	123-126
13	1a		84	123-125

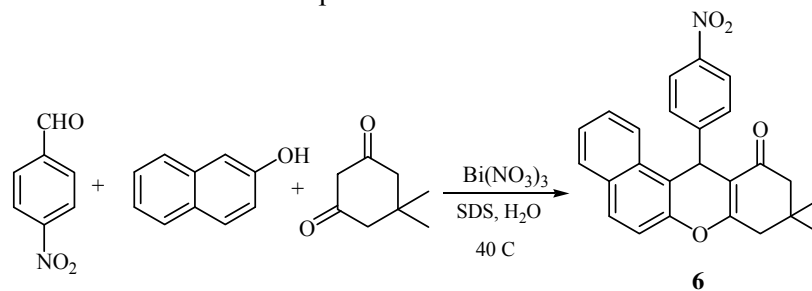
14			88	90-91
15	1i		89	115-116
16	1i		93	98-100

^a The ratio of amine (mmol): NaNO₂ (mmol): 37% BF₃.SiO₂ (g): coupling agent (mmol) is equal to 2:2:0.2:2

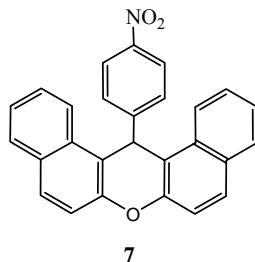
The amines **1h**, and **1i** were obtained by reduction of corresponding nitro compounds **6** and **7** in the presence of Na₂S · 9H₂O and sulfur⁸ (Scheme 2). The substance **6** was synthesized via condensation of β-naphthol, dimedone and 4-nitrobenzaldehyde in the presence of Bi(NO₃)₃.SiO₂ and sodium dodecyl sulfate (SDS) in water at 40 °C (Scheme 3). The diarylxanthene **7** (Scheme 4) was synthesized via reaction between 4-nitrobenzaldehyde and 2-naphthol in the presence of 37% BF₃.SiO₂³.



Scheme 2: reduction of aromatic nitro compounds



Scheme 3. Synthesis of **6** via condensation of β-naphthol, dimedone and 4-nitrobenzaldehyde



Scheme 4. The structure of nitro diarylxanthene **7**

3. Conclusion

We have demonstrated simple method for the synthesis of azo dyes using BF₃.SiO₂, as heterogeneous and efficient catalyst. Short reaction times, high yields, a clean process, simple methodology, easy work-up and green conditions are advantages of these protocols.

Acknowledgements

The Central Iron Ore and Strategic of Research Centre gratefully acknowledged for the financial support for this work.

Experimental

Materials and Methods

All chemicals were purchased from Fluka and Merck companies. Products were characterized by IR, $^1\text{H-NMR}$ and by comparison of their physical properties with those reported in the literature. IR spectra were run on a Bruker, Equis 55 spectrometer. $^1\text{H NMR}$ spectra were obtained using a Bruker Avans 400 MHz spectrometer (DRX). Melting points were determined by a Buchi melting point B-540 B.V.CHI apparatus.

Synthesis of 12-(4-nitrophenyl)-9, 9-dimethyl 8, 9, 10, 12-tetrahydrobenzo(a)xanthenes -11-one (**6**) in water

A mixture of 2-naphthol (1 mmol), 4-nitrobenzaldehyde (1 mmol), dimedone (1.2 mmol), $\text{Bi}(\text{NO}_3)_3 \cdot \text{SiO}_2$ (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 poured into a separator funnel to isolate the product. The chloroform layer was evaporated carefully and the obtained solid was crystallized from ethanol : water (80:20) to afford the pure product.

Synthesis of azo dyes in the presence of $\text{BF}_3 \cdot \text{SiO}_2$ at room temperature:

A mixture of 0.14 g (2 mmol) of NaNO_2 and 0.2 g 37% $\text{BF}_3 \cdot \text{SiO}_2$ was grounded in a mortar. Then, 2 (mmol) of aromatic amine was added and grinded. After formation of diazonium salt, a solution containing 2 mmol sodium phenoxide or naphthoxide was added and sufficiently grounded. The obtained azo dye was dissolved in ethanol and filtered to isolate of catalyst. The ethanol solution of azo dye was concentrated. By addition of water to ethanol solution, the azo dye was separated in pure solid form.

Physical and spectral data of some represented products

4-(2-(naphthalen-1-yl)diazen-1-yl)naphthalen-1-amine (Table 1, entry 1)

Dark brown, FT-IR: $\nu_{\text{max}}(\text{KBr}) = 3379, 3481, 1616, 1462, 1597, 1462, 1330, 828, 756 \text{ cm}^{-1}$. $^1\text{H NMR}(\text{CDCl}_3)$: 4.67 (s, 2H, NH_2), 6.89 (d, $J=8.4 \text{ Hz}$, 1H, CH_3), 8.28 7.52-7.98 (m, 9H, Ph), 8.12 (d, $J=8.4 \text{ Hz}$, 1H), 9.05 (d, $J=8.4 \text{ Hz}$, 1H, CH_2), 9.19 (d, $J=8.4 \text{ Hz}$, 1H, CH_2) ppm. UV-Vis (CHCl_3): $\lambda_{\text{max}} = 271.21 (\pi-\pi^*, \text{Ar-H}), 441.45 (\pi-\pi^*, \text{N=N}) \text{ nm}$.

1-(4-chlorophenylazo)-2-naphthol (Table 1, entry 2)

Orange red solid, FT-IR (KBr): ν_{max} : 3130-3300, 1598, 1510, 1438, 1243, 1091, 825, 749 cm^{-1} . $^1\text{H NMR}$ (400 MHz, CDCl_3): $\delta = 6.9$ (s, 1H), 7.35-7.70 (m, 9H), 9.53 (s, 1H, OH), 16.1 (s, 1H, NH) ppm. UV-Vis (CHCl_3): $\lambda_{\text{max}}(\text{nm}) = 360.80 (\pi-\pi^*, \text{Ar-H}), 482.40 (\pi-\pi^*, \text{N=N})$.

1-(2-(2, 4-dimethyl phenyl azo)-4, 6-dimethyl phenyl azo)-2-naphthol (Table 1, entry 3)

Dark red solid, mp $161-163^\circ\text{C}$, FT-IR (KBr): ν_{max} : 3280-3570, 3028, 2977, 1612, 1497, 1443, 1383, 1206, 750 cm^{-1} . $^1\text{H NMR}$ (400 MHz, CDCl_3): $\delta = 2.36$ (s, 9H), 2.49 (s, 3H), 6.84 (d, $J=9.6 \text{ Hz}$, 1H), 7.08-7.21 (m, 4H), 7.43 (t, $J=8 \text{ Hz}$, 1H), 7.61-7.76 (m, 3H), 8.03 (s, 1H), 8.56 (d, $J=7.6 \text{ Hz}$, 1H),

9.51 (s, OH), 16.43 (s, 1H) ppm. UV-Vis (CHCl₃): λ_{\max} = 368.48 (π - π^* , Ar-H), 487.52 (π - π^* , N=N) nm.

12-(4-(4-hydroxyphenylazo)phenyl)-9, 9-dimethyl-8, 9, 10, 12-tetrahydrobenzo(a)xanthen-11-one (Table 1, entry 11)

Yellow solid, mp 263-265 °C. FT-IR (KBr): ν_{\max} : 3120-3350, 2954, 1628, 1616, 1590, 1503, 1466, 1439, 137, 1266, 1238, 1226, 1184, 1032, 838, 828, 814, 744. ¹H NMR (500 MHz, CDCl₃, DMSO): 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) ppm. UV-Vis (CHCl₃): λ_{\max} (nm) = 272.48 (π - π^* , Ar-H), 353.12 (π - π^* , N=N).

12-(4-(2-hydroxynaphthylazo)phenyl)-9, 9-dimethyl-8,9,10,12-tetrahydrobenzo(a)xanthen-11-one (Table 1, entry 12)

Orange red solid, mp 123-126 °C. FT-IR (KBr): ν_{\max} : 3200-3535, 3058, 2956, 2875, 1652, 1621, 1596, 1467, 1502, 1459, 1372, 1225, 1180, 1026, 839, 813, 748 cm⁻¹. ¹H NMR (500 MHz, CDCl₃, DMSO): δ = 1.02 (s, 3H), 1.17 (s, 3H), 2.30 (d, J=16.3 Hz, 1H), 2.37 (d, J=16.3 Hz, 1H), 2.63 (s, 2H), 5.80 (s, 1H), 6.88 (d, J=9.3 Hz, 1H), 7.35-7.47 (m, 7H), 7.49 (d, J=8.4 Hz, 2H), 7.60 (t, J=6.4 Hz, 1H), 7.71 (d, J=9.4 Hz, 2H), 7.80-7.84 (m, 2H), 8.01 (d, J=8.3 Hz, 1H), 8.52 (d, J=8.1 Hz, 1H) ppm. UV-Vis (CHCl₃): λ_{\max} (nm) = 269.92 (π - π^* , Ar-H), 490.08 (π - π^* , N=N).

14-(2-hydroxy-4-methyl-5-chloro-phenyl azo)phenyl-14H-dibenzo(a,j)xanthenes (Table 1, entry 14)

Orange red solid FT-IR: ν_{\max} (ATR, neat) = 2900-3100, 1593, 1514, 1478, 1459, 1431, 1400, 1247, 1163, 810, 746, 1H NMR (400 MHz, CDCl₃): δ = 2.31(s, 3H), 6.57(s, 1H), 6.60(d, J= 8.8Hz, 1H), 6.71(s, 1 H), 6.82(s, 1H), 7.17(d, J= 8.8Hz, 1H), 7.39(t, J= 7.6Hz, 2H), 7.51(d, J= 8.8Hz, 2H), 7.6 (m, 3H), 7.66 (m, 1H), 7.77(s, 1H), 7.84(t, J= 8.8Hz, 4H), 8.37(d, J= 8.8Hz, 2H) ppm.

References

- Karci, F.; Demircali, A.; Sener, I.; Tilki, T. (2006) Synthesis of 4-amino-1H-benzo[4,5]imidazo[1,2-a]pyrimidin-2-one and its disperse azo dyes. Part 1: Phenylazo derivatives, *Dyes and Pigments* 71, 90-96.
- Sharma, P.; Rane, N.; Gurram, V. K. (2004) Synthesis and QSAR studies of pyrimido[4,5-d]pyrimidine- 2, 5-dione derivatives as potential antimicrobial agents, *Bioorg. Med. Chem. Lett.* 14, 4185-4190.
- Sadegi, B.; Mirjalili, B. F.; Hashemi, M. M. (2008) BF₃.SiO₂: An efficient reagent system for the one-pot synthesis of 1,2,4,5-tetrasubstituted imidazoles, *Tetrahedron Lett.* 49, 2575-2577.
- Mirjalili, B.F.; Bamoniri, A.; Akbari, A. (2008) BF₃.SiO₂: An efficient alternative for the synthesis of 14-aryl or alkyl-14H-dibenzo[a,j]xanthenes, *Tetrahedron Lett.* 49, 6454-6456.
- Mirjalili, B. F.; Bamoniri, A.; Akbari, A. (2011) Nano-BF₃.SiO₂: a reusable and eco-friendly catalyst for synthesis of quinoxalines, *Chem. Heterocycl. Comp.*, 47, 487-491.
- Mirjalili, B. F.; Bamoniri, A.; Akbari, A. (2011) One-Pot Synthesis of 3,4-Dihydropyrimidin-2(1H)-ones (Thiones) Promoted by Nano-BF₃.SiO₂, *J. Iran. Chem. Soc.*, 8, S135-S140.
- Mirjalili, B. F.; Bamoniri, A.; Akbari, A. (2011) Nano-BF₃.SiO₂: Areusable and eco-friendly catalyst for thioacetalization and trans-thioacetalization reactions, *Iranian J. Catal.* 1, 87-92.
- Pourjavadi, A., Mirjalili, B. F., Entezami, A. A.; Zohuriaan-Mehr, M. J. (2001), Novel azo containig polymethacrylates bearing spiroacetalmoieity and methylene spacers: synthesis and characterization, *Eur. Poly. J.* 37, 2111-2121.