

An Efficient and Green Route to Synthesize Azo Compounds through Methyl Nitrite

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Abstract

A clean preparation of aryl diazonium ions using methyl nitrite is described. Further reaction of the aryl diazonium ions with substituted benzenamine, substituted phenol and naphthol in different kinds of diazotization has been developed. In order to improve the water-solubility of the products, azo coupling reactions of sodium sulfanilate hydrochloride diazonium ions were also performed. The procedures are easy operations, environmentally benign conditions and high yields of the products with potential use as azo-dyes and pigments. Furthermore, no nitrous acid is produced during the diazotization which avoided the formation of dark decomposition products of the corresponding aromatic amine. Proposed mechanism is presented according to our procedure.

Keywords

Methyl Nitrite, Substituted Benzenamine, Diazotization, Azo Coupling, Dyes, Pigments, Environmentally Benign, Toxicological

1. Introduction

Aryl diazonium salts have been discovered in the middle of the 19th century by Johann Peter Griess who was working on azo-compounds as dyes and pigments [1]. Commonly, they are prepared by diazotization [2], a procedure in which a primary aromatic amine is treated with a source of nitrous acid (HNO_2). In spite of all precautions the formation of dark decomposition products due to the existence of nitrous acid and its aromatic amine is unavoidable, thus lowering the yield and also making the product difficult to isolate [3].

Environmental and toxicological concerns have resulted in increased interests in new diazotization reaction. Among them, the Sandmeyer Reaction is widely studied using either polymer supported acid [4] or polymer supported nitrite [5] to stabilize the aryl diazonium ions, which makes it easy to separate from the reaction mix-

ture. In addition, azo coupling reaction on clays was also carried out to prepare the azo-dyes [6]. But most of these reactions were carried out in a heterogeneous medium. As a potentially attractive alternative to the traditional methods, isoamyl nitrite, instead of nitrous acid, has also been reported to perform the diazotization. As the reaction undergoes a radical mechanism, a lot of organic solvents are used in many cases [7].

Based on our study of diazotizing reaction through methyl nitrite to prepare versatile intermediate 5,5'-methylene-bis(benzotriazole) [8], we have developed here a practical and clean diazotizing reagent and its further widely use in deferent kinds of diazotization. The procedures are very simple as methyl nitrite is a low boiling point gas (bp. -12°C ; mp. -17°C), which could be easily purified and bubbled through the reaction mixture and recovered through a cold-trap after the reaction. Furthermore, no nitrous acid is used during the diazotization which led to the procedure with easy operations, environmentally benign conditions and high yields of the products.

2. Results and Discussion

We began our efforts from methyl nitrite, which was easily prepared from sodium nitrite, methanol and hydrochloric acid, bubbled through a solution of 4-methylaniline via the gas tube, without further purification, 1,3-dimethyl-1,2,3-triazene was obtained with 96% of yield (Scheme 1). For the diazonium solution could not be stably existed in the solution of 4-methylaniline.

Upon further investigation, we found that the obtained aryl diazonium ions could be stably existed when aromatic amine hydrochloride, instead of aromatic amine, was used as substrate. Because the color center of the dye or pigment was the azo ($\text{N}=\text{N}$) group, azo coupling reactions of *N,N*-dimethyl benzenamine and 3,5-dimethylaniline, substituted phenol, naphthol with substituted aryl hydrochloride diazonium ions were performed in order to expand the diversity of the azo ($\text{N}=\text{N}$) group (Scheme 2). Results are described in Table 1.

The nature of the aromatic substituents on both sides of the azo group controls the colours of the azo compounds as well as the water-solubility of the dyes. In order to improve the water-solubility of the dyes, the sodium sulfanilate is common used in most case. In our procedure, azo coupling reactions of sodium sulfanilate hydrochloride diazonium ions with *N,N*-dimethyl benzenamine, substituted phenol and naphthol (Scheme 3) were also performed. Results are described in Table 2.

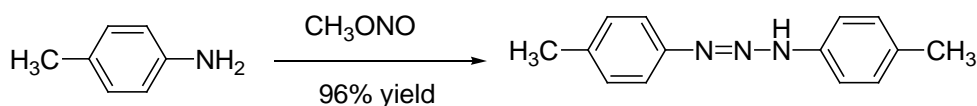
It was noteworthy that in our procedure no nitrous acid was used and proposed mechanism of the diazotization reaction was presented (Figure 1).

3. Experimental

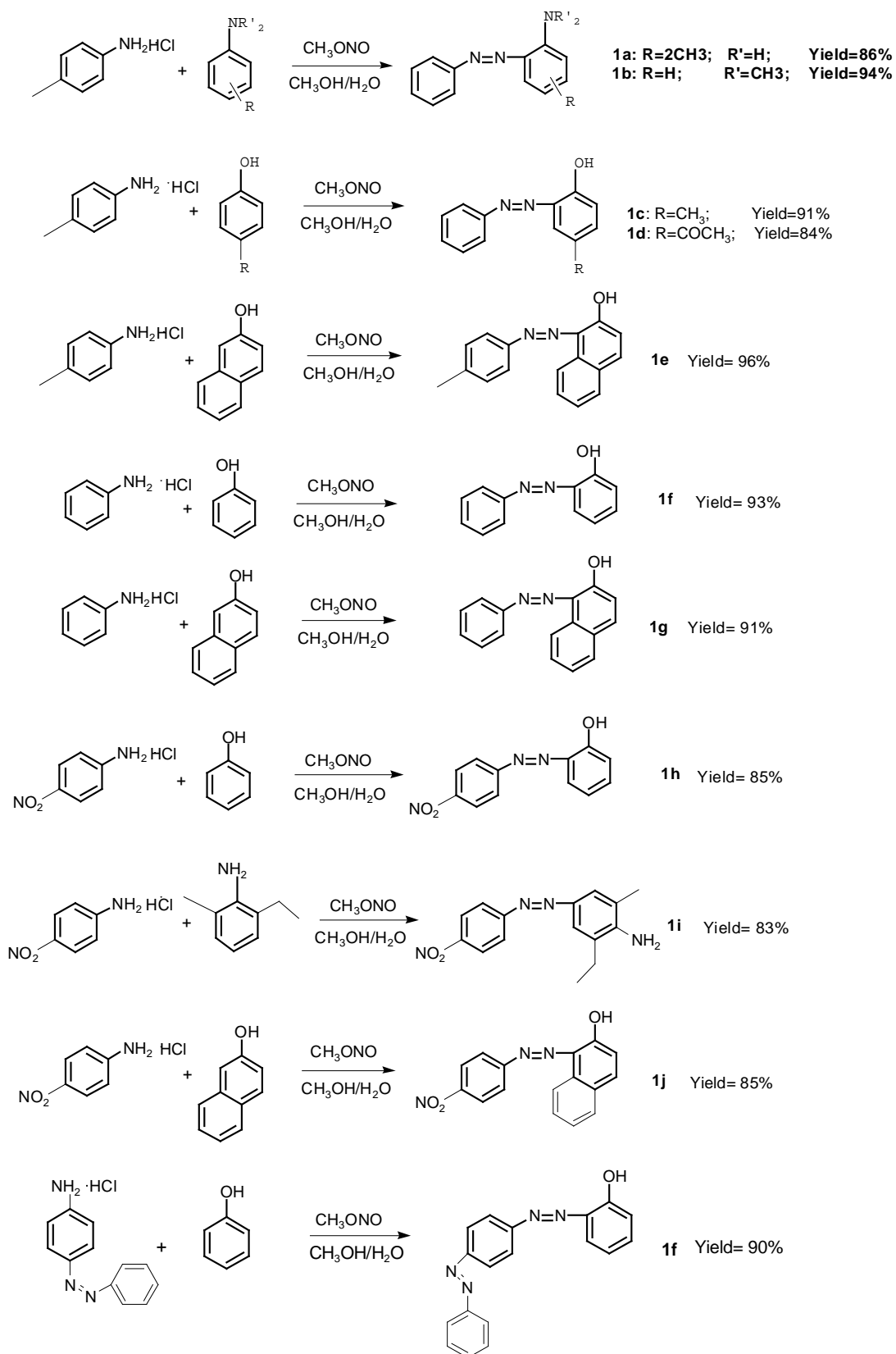
Starting materials were obtained from commercial suppliers and used without further purification. ^1H NMR (400 MHz or 500 MHz) and ^{13}C NMR (100 MHz) spectra were recorded on a Bruker Avance (400 MHz) spectrometer, using CDCl_3 or C_6D_6 or *d*-DMSO as the solvent and TMS as internal standard. Infrared spectra were recorded on a Bruker V-22 spectrometer. Elemental analyses were performed on a Flash EA1112 instrument.

Preparation of methyl nitrite: In a 500 mL round-bottomed flask, fitted with a pressure equalizing addition funnel filled with 110 mL 12 M hydrochloric acid, and a gas tube in a well ventilated hood, was placed 76.0 g (1.1 mol) of sodium nitrite, 60 mL methanol and 110 mL water. The temperature was raised to 35°C and hydrochloric acid was added dropwise over 1.5 h. The methyl nitrite evolved was passed through a water trap and a 10% sodium carbonate trap to remove acid and then bubbled through the reaction mixture below via the gas tube.

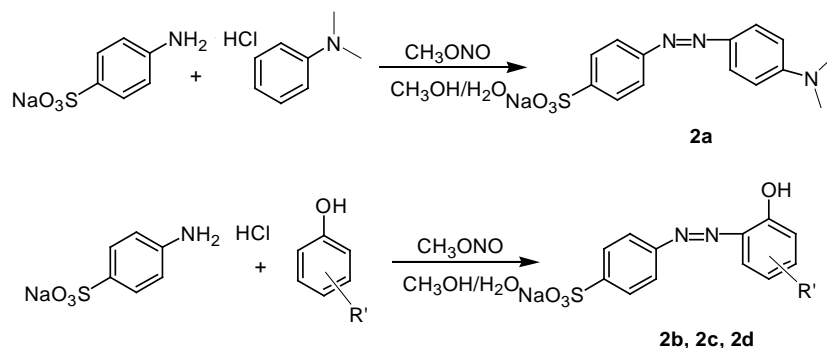
Preparation of the 4-methylaniline hydrochloride diazonium solution; (used in Scheme 1): In a 1 L round-bottomed flask, fitted with a mechanical stirrer, and a gas tube in a well-ventilated hood, was placed 143.7 g (1.0 mol) of 4-methylaniline hydrochloride and 300 mL methanol. Methyl nitrite (1.1 mol) was added through the tube for about 1.5 h. When the reaction was complete, the temperature was raised to 50°C and the mixture was stirred for another 20 min. to expel excess methyl nitrite, which was recovered through a cold-trap.



Scheme 1. Preparation of 1,3-dimethyl-1,2,3-triazene.



Scheme 2. Preparation of the azo (N=N) group.



Scheme 3. Preparation of azo coupling reactions of sodium sulfanilate hydrochloride diazonium ions.

Table 1. Synthesis of azo compounds.

Product ^a	Substrate	Substrate	Yield (%) ^b
1a	4-methylaniline	3,5-dimethylaniline	86
1b	4-methylaniline	N,N-dimethylaniline	94
1c	4-methylaniline	4-methylphenol	91
1d	4-methylaniline	4-hydroxyacetophenone	84
1e	4-methylaniline	2-naphthol	96
1f	aniline	4-methylphenol	93
1g	aniline	2-naphthol	91
1h	4-nitroaniline	phenol	85
1i	4-nitroaniline	6-ethyl-2-methylaniline	83
1j	4-nitroaniline	2-naphthol	85
1k	4-Aminoazobenzene	phenol	90

^aAll the products were characterized by IR, ¹H NMR, ¹³C NMR and MS spectroscopy. ^bIsolated yield.

Table 2. Synthesis of azo compounds with sulfanilate.

Product ^a	Substrate	Yield (%) ^b
2a	N,N-dimethylaniline	83
2b	1,3-dilphenol	82
2c	2-naphthol	88
2d	4-methylphenol	87
2e	3,5-dimethylaniline	81

^aAll the products were characterized by IR, ¹H NMR, ¹³C NMR and MS spectroscopy. ^bIsolated yield.

Preparation of 3,5-dimethyl-4-(p-tolyldiazenyl)aniline (1a): To a solution of 121.1 g (1.0 mol) 3,5-dimethylaniline in 300 mL methanol, the above 4-methylaniline hydrochloride diazonium solution was added dropwise for 4 h at 0 °C. Then the precipitated crystals were collected, recrystallized from 60 mL of ethanol and dried in vacuo to afford 205.5 g (86%) of the product as a red solid; mp. 90 °C - 92 °C.

1a: IR ν_{\max} (cm⁻¹): 822, 852, 1029, 1165, 1328, 1426, 1597, 1619; ¹H NMR (CDCl₃): δ 2.41 (3 H, s), 2.45 (6 H, s), 3.29 (2 H, b), 6.42 (2 H, s), 7.27 (2 H, d, *J* = 8.0 Hz), 7.73 (2 H, d, *J* = 8.0 Hz); ¹³C NMR (CDCl₃): δ 20.3, 21.3, 115.3, 122.0, 129.5, 135.3, 139.9, 142.8, 147.0, 151.5; MS *m/z*: 91 (40), 120 (100), 148 (20), 239 (M⁺, 95); Elemental analysis. Calcd for C₁₅H₁₇N₃, C 75.28; H 7.16; N 17.56; Found C 75.07; H 7.27; N 17.66.

Preparation of N,N-dimethyl-4-(p-tolyldiazenyl)aniline (1b): To a solution of 121.1 g (1.0 mol) N,N-dimethylaniline in 300 mL methanol, the above 4-methylaniline hydrochloride diazonium solution was added dropwise for 2 h. Then the precipitated crystals were collected, recrystallized from 60 mL of ethanol and dried

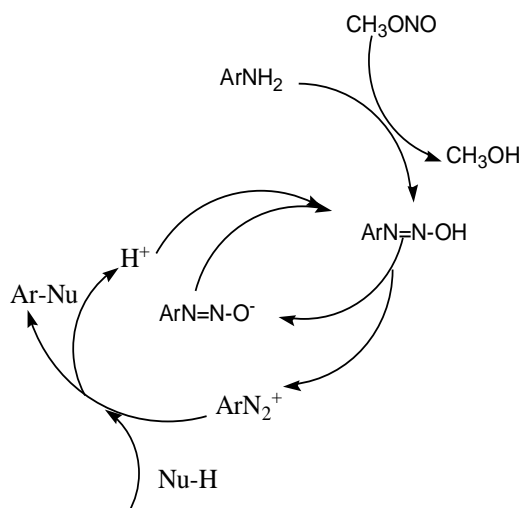
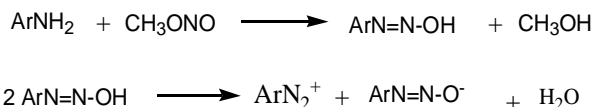


Figure 1. Possible mechanism of the diazotization.

in vacuo to afford 224.7 g (94%) of the product as an orange red solid; mp. 151°C - 152°C, lit. [7] mp. 151°C - 152°C. **1b**: IR ν_{max} (cm^{-1}): 823, 946, 1137, 1366, 1517, 1558, 1597; ^1H NMR (CDCl_3): δ 2.39 (3 H, s), 3.02 (6 H, s), 6.72 (2 H, d, $J = 8.8$ Hz), 7.25 (2 H, d, $J = 7.2$ Hz), 7.75 (2 H, d, $J = 7.6$ Hz), 7.86 (2 H, d, $J = 8.4$ Hz); ^{13}C NMR (CDCl_3): δ 21.4, 40.3, 111.5, 122.2, 124.7, 129.6, 139.6, 143.7, 151.3, 152.2; MS m/z 120 (100), 239 (M^+ , 85); Elemental analysis. Calcd for $\text{C}_{15}\text{H}_{17}\text{N}_3$, C 75.28; H 7.16; N 17.56; Found C 75.15; H 7.28; N 17.47.

Preparation of 4-methyl-2-(p-tolyldiazenyl)phenol (1c): To a mixture of 108.0 g (1.0 mol) 4-methylphenol, 69.5 g (0.50 mol) of potassium carbonate and 400 mL methanol, the above 4-methylaniline hydrochloride diazonium solution was added dropwise for 5 h at 0°C. Then the mixture was poured into 800 mL water and the precipitated crystals were collected and dried *in vacuo* to afford 205.8 g (91%) of the product as an orange red solid; mp. 112°C - 113°C, lit. [9] mp. 113°C. An analytical sample for EA was prepared by recrystallization from ethanol. **1c**: IR ν_{max} (cm^{-1}): 808, 829, 1268, 1428, 1491, 1597, 1621; ^1H NMR (CDCl_3): δ 2.37 (3 H, s), 2.42 (3 H, s), 6.91 (1 H, d, $J = 8.4$ Hz), 7.13 (1 H, d, $J = 8.4$ Hz), 7.29 (2 H, d, $J = 8.0$ Hz), 7.71 (1 H, s), 7.75 (2 H, d, $J = 8.0$ Hz), 12.73 (1 H, b); ^{13}C NMR (CDCl_3): δ 20.3, 21.5, 117.8, 122.1, 129.0, 130.0, 132.7, 133.8, 136.9, 141.6, 148.6, 150.5; MS m/z 91 (100), 135 (25), 226 (M^+ , 90); Elemental analysis. Calcd for $\text{C}_{14}\text{H}_{14}\text{N}_2\text{O}$, C 74.31; H 6.24; N, 12.38; Found C 74.22; H 6.31; N 12.29.

Preparation of 4-hydroxy-3-(p-tolyldiazenyl)acetophenone (1d): To a mixture of 136.0 g (1.0 mol) 4-hydroxyacetophenone, 69.5 g (0.50 mol) of potassium carbonate and 400 mL methanol, the above 4-methylaniline hydrochloride diazonium solution was added dropwise for 5 h at 10°C. Then the mixture was poured into 800 mL water and the precipitated crystals were collected, recrystallized from 70 mL of ethanol and dried *in vacuo* to afford 213.5 g (84%) of the product as a red solid; mp. 95°C - 96°C. **1d**: IR ν_{max} (cm^{-1}): 704, 817, 1168, 1274, 1356, 1439, 1490, 1597, 1664; ^1H NMR (CDCl_3): δ 2.45 (3 H, s), 2.64 (3 H, s), 7.07 (1 H, d, $J = 8.8$ Hz), 7.34 (2 H, d, $J = 8.0$ Hz), 7.79 (2 H, d, $J = 8.0$ Hz), 7.99 (1 H, d, $J = 8.8$ Hz), 8.55 (1 H, s), 13.46 (1 H, b); ^{13}C NMR (CDCl_3): δ 21.5, 26.3, 118.6, 122.3, 129.8, 130.1, 132.6, 134.2, 136.0, 142.7, 148.1, 157.0, 196.0; MS m/z 91 (100), 119 (23), 135 (20), 254 (M^+ , 55); Elemental analysis. Calcd for $\text{C}_{15}\text{H}_{14}\text{N}_2\text{O}_2$, C 70.85; H 5.55; N 11.02; Found 70.56; H 5.43; N 10.93.

Preparation of 1-(p-tolyldiazenyl)-2-naphthol (1e): To a mixture of 144.0 g (1.0 mol) 2-naphthol, 69.5 g (0.50 mol) of potassium carbonate and 400 mL methanol, the above 4-methylaniline hydrochloride diazonium solution was added dropwise for 5 h at 0°C. Then the mixture was poured into 800 mL water and the precipi-

tated crystals were collected and dried *in vacuo* to afford 251.5 g (96%) of the product as an orange red solid; mp. 130°C - 132°C, lit. [10] mp. 130°C - 132°C. An analytical sample for EA was prepared by recrystallization from methanol. **1e**: IR ν_{\max} (cm⁻¹): 750, 813, 986, 1144, 1171, 1207, 1268, 1501, 1552, 1616; ¹H NMR (CDCl₃): δ 2.41 (3 H, s), 6.92 (1 H, d, *J* = 8.8 Hz), 7.28 (2 H, d, *J* = 8.0 Hz), 7.38 (1 H, t, *J* = 7.6 Hz), 7.55 (1 H, t, *J* = 7.6 Hz), 7.62 (1 H, d, *J* = 8.0 Hz), 7.67 (2 H, d, *J* = 8.4 Hz), 7.72 (1 H, d, *J* = 9.2 Hz), 8.60 (1 H, d, *J* = 7.6 Hz), 16.17 (1 H, b); ¹³C NMR (CDCl₃): δ 21.2, 119.1, 121.6, 123.9, 125.3, 128.0, 128.4, 128.5, 129.6, 130.1, 133.5, 138.3, 138.8, 143.5, 168.4; MS *m/z* 91 (50), 115 (53), 143 (85), 262(M⁺,100); Elemental analysis. Calcd for C₁₇H₁₄N₂O, C 77.84; H 5.38; N 10.68; Found 77.56; H 5.49; N 10.82.

Preparation of Aniline diazonium salt (B)

HCl was added dropwise to a mixture of Aniline and methanol in a 100 mL round-bottomed flask, fitted with a mechanical stirrer, and a gas tube in a well-ventilated hood until pH = 2. Methyl nitrite was added through the tube under an icebath for about 2 h. When the reaction was complete, the mixture was stored in fridge as standby material.

Preparation of 4-methy-2-(phenylazoyl) phenol (1f) [11]: In a 100 ml round-bottomed flask, fitted with a mechanical stirrer, and a gas tube in a well-ventilated hood, was placed 1.24 g (10 mmol) of 4-methylphenol and 15 mL methanol. After the mixture was dissolved under stirring, Material B was added dropwise under an icebath temperature. Some buffer-solution (Na₂CO₃-AcOH) was added until the solution pH = 8. The mixture was stirred under the same situation for 30 min, before some HCl was allowed to add for keeping the mixture pH = 6. The precipitate (2.26 g, 93%) of the mixture was collected and dried over vacuum. An analytical sample for EA was prepared by recrystallization from methanol. mp. 106°C - 108°C.

1f: 4-methy-2-(phenylazoyl) phenol ¹H NMR (500 MHz, CDCl₃): δ 12.73 (s, 1 H), 7.89 (m, 2 H), 7.78 (d, *J* = 1.6 Hz, 1 H), 7.58 - 7.53 (m, 2 H), 7.50 (m, *J* = 7.3, 3.5, 1.2 Hz, 1 H), 7.20 (m, *J* = 8.4, 2.0 Hz, 1 H), 6.97 (d, *J* = 8.4 Hz, 1 H), 2.42 (s, 3 H). ¹³C NMR (126 MHz, CDCl₃): δ 150.68, 150.54, 137.08, 134.29, 133.01, 131.03, 129.35, 129.21, 122.20, 117.88, 20.31.

Preparation of 1-(phenylazoyl) naphthyl-2-ol (1g): In a 100 ml round-bottomed flask, fitted with a mechanical stirrer, and a gas tube in a well-ventilated hood, was placed 1.60 g (10 mmol) of naphthyl-2-ol and 10 mL methanol. After the mixture was dissolved under stirring, Material B was added dropwise under an icebath temperature. Some buffer-solution (Na₂CO₃-HOAc) was added until the solution pH = 8. The mixture was stirred under the same situation for 40 min, then some HCl was added to keep the mixture pH = 6. The precipitate (2.5 g, 91%) of the mixture was collected and dried over vacuum. An analytical sample for EA was prepared by recrystallization from methanol. mp. 131°C - 133°C.

1g: ¹H NMR (500 MHz, CDCl₃): δ 8.59 (d, *J* = 8.2 Hz, 1 H), 7.76 (m, 3 H), 7.63 (d, *J* = 7.8 Hz, 1 H), 7.58 (m, *J* = 11.3, 4.1 Hz, 1 H), 7.51 (t, *J* = 7.9 Hz, 2 H), 7.42 (m, 1 H), 7.33 (t, *J* = 7.4 Hz, 1 H), 7.29 (s, 1 H), 6.90 (d, *J* = 9.4 Hz, 1 H); ¹³C NMR (126 MHz, CDCl₃): δ 171.83, 144.81, 140.05, 133.61, 130.08, 129.59, 128.86, 128.62, 128.07, 127.43, 125.72, 124.81, 121.73, 118.61.

Preparation of 4-nitroaniline diazonium salt (C)

HCl was added dropwise to a mixture of 4-nitroaniline and methanol in a 100 mL round-bottomed flask, fitted with a mechanical stirrer, and a gas tube in a well-ventilated hood until pH = 2. Methyl nitrite was added through the tube under an icebath for about 2 h. When the reaction was complete, the mixture was stored in fridge as standby material.

Preparation of 4-(4-nitrophenylazoyl)-phenol (1h): In a 100 ml round-bottomed flask, fitted with a mechanical stirrer, and a gas tube in a well-ventilated hood, was placed 0.98 g (10 mmol) of phenol and 10 mL methanol. After the mixture was dissolved under stirring, Material C was added dropwise under an icebath temperature. Some buffer-solution (Na₂CO₃-HOAc) was added until the solution pH = 8. The mixture was stirred under the same situation for 2h, then some HCl was added to keep the mixture pH = 6. The precipitate (2.15 g, 85%) of the mixture was collected and dried over vacuum. An analytical sample for EA was prepared by recrystallization from methanol. mp. 119°C - 120°C.

1h: ¹H NMR (500 MHz, CD₃OD_SPE): δ 8.38 - 8.34 (m, 2 H), 7.99 - 7.95 (m, 2 H), 7.90 - 7.86 (m, 2 H), 6.97 - 6.92 (m, 2 H); ¹³C NMR (126 MHz, CD₃OD_SPE): δ 162.17, 156.12, 148.15, 146.16, 125.47, 124.31, 122.63, 115.59.

Preparation of 2-methyl-6-ethyl-4-(4-nitrophenylazoyl)aniline (1i): In a 100 ml round-bottomed flask, fitted with a mechanical stirrer, and a gas tube in a well-ventilated hood, was placed 2 g (10 mmol) of phenol and 10 mL methanol. After the mixture was dissolved under stirring, HCl was added to keep the mixture pH = 2.

Material C was added dropwise under an icebath temperature. The mixture was stirred under the same situation for 3 h. The precipitate (3.4 g, 83%) of the mixture was collected and dried over vacuum.

1i: $^1\text{H NMR}$ (500 MHz, CDCl_3): δ 13.13 - 13.06 (m, 2 H), 12.69 - 12.62 (m, 2 H), 12.33 (s, 2 H), 7.33 (q, $J = 7.4$ Hz, 2 H), 6.95 (s, 3 H), 5.96 (t, $J = 7.4$ Hz, 3 H). Elemental analysis. Calcd for $\text{C}_{16}\text{H}_{16}\text{N}_4\text{O}_2$, C 63.28; H 5.47; N 19.58; Found 63.38; H 5.63; N 19.72.

Preparation of 1-(4-nitrophenylazoyl)naphthyl-2-ol (1j): In a 100 ml round-bottomed flask, fitted with a mechanical stirrer, and a gas tube in a well-ventilated hood, was placed 1.60 g (10 mmol) of phenol and 10 mL methanol. After the mixture was dissolved under stirring, Material C was added dropwise under an icebath temperature. Some buffer-solution ($\text{Na}_2\text{CO}_3\text{-HOAc}$) was added until the solution pH = 8. The mixture was stirred under the same situation for 40 min, then some HCl was added to keep the mixture pH = 6. The precipitate (2.76 g, 85%) of the mixture was collected and dried over vacuum. An analytical sample for EA was prepared by recrystallization from methanol. mp. $251^\circ\text{C} - 254^\circ\text{C}$.

1j: $^1\text{H NMR}$ (500 MHz, CDCl_3): δ 16.14 (s, 1 H), 8.45 (d, $J = 8.0$ Hz, 1 H), 8.35 (d, $J = 8.9$ Hz, 2 H), 7.72 (t, $J = 7.8$ Hz, 3 H), 7.58 (dd, $J = 17.0, 7.7$ Hz, 2 H), 7.46 (t, $J = 7.2$ Hz, 1 H), 6.73 (d, $J = 9.0$ Hz, 1 H).

Preparation of disperse Yellow RGFL (1k): In a 100 ml round-bottomed flask, fitted with a mechanical stirrer, and a gas tube in well-ventilated hood, was placed 1.97 g (10 mmol) of p-Aminoazobenzene and 15 mL methanol. After the mixture was dissolved under stirring, HCl was added to keep the mixture pH = 2. Methyl nitrite was added through the tube under an icebath for about 3 h. When the reaction was complete, the mixture was stored in fridge as standby material (D).

In another 100 ml round-bottomed flask, fitted with a mechanical stirrer, and a gas tube in a well-ventilated hood, was placed 1.0 g (10 mmol) of phenol and 10 mL methanol. After the mixture was dissolved under stirring, Material D was added dropwise under an icebath temperature. Some buffer-solution ($\text{Na}_2\text{CO}_3\text{-HOAc}$) was added until the solution pH = 8. The mixture was stirred under the same situation for 1.5 h, the precipitate (2.9 g, 90%) of the mixture was collected and dried over vacuum. An analytical sample for EA was prepared by recrystallization from methanol. mp. $222^\circ\text{C} - 225^\circ\text{C}$.

1k: $^1\text{H NMR}$ (400 MHz, DMSO): δ 10.47 (s, 1 H), 8.08 - 8.02 (m, 2 H), 8.00 (d, $J = 8.6$ Hz, 2 H), 7.93 (d, $J = 6.2$ Hz, 2 H), 7.86 (d, $J = 8.6$ Hz, 2 H), 7.60 (d, $J = 6.7$ Hz, 3 H), 6.98 (d, $J = 8.7$ Hz, 2 H).

Preparation of 4-aminobenzenesulfonic acid diazonium salt (E): In a 100 ml round-bottomed flask, fitted with a mechanical stirrer, and a gas tube in a well-ventilated hood, was placed 2.1 g (10 mmol) of 4-Aminobenzenesulfonic Acid and 15 mL 5% NaOH. After the mixture was dissolved under stirring. Methyl nitrite was added through the tube under an icebath for about 5 h. When the reaction was complete, the mixture was stored in fridge as standby material (E).

Preparation of 4-(N,N-dimethyl benzene amino azo)-benzene sulfonic acid (2a): In another 100 ml round-bottomed flask, fitted with a mechanical stirrer, and a gas tube in a well-ventilated hood, was placed 1.2 g (10 mmol) of N,N-dimethylaniline and 10 mL glacial acetic acid. After the mixture was dissolved under stirring, Material E was added dropwise under an icebath temperature. The mixture was stirred under the same situation for 1.5 h, the precipitate (2.49 g, 83%) of the mixture was collected and dried over vacuum. An analytical sample for EA was prepared by recrystallization from methanol.

2a: $^1\text{H NMR}$ (400 MHz, DMSO): δ 7.80 (d, $J = 8.9$ Hz, 2 H), 7.77 - 7.69 (m, 4 H), 6.83 (d, $J = 9.0$ Hz, 2 H), 3.06 (s, 6 H); $^{13}\text{C NMR}$ (101 MHz, DMSO): δ 152.96, 152.58, 149.16, 142.93, 126.93, 125.20, 121.59, 111.92, 40.21. Elemental analysis. Calcd for $\text{C}_{14}\text{H}_{15}\text{N}_3\text{SO}_3$, C 55.08; H 4.92; N 13.77; Found C 54.88; H 4.86; N 13.66.

Preparation of 4-(2,4-dihydroxy phenyl azo)-benzene sulfonic acid (2b): In another 100 ml round-bottomed flask, fitted with a mechanical stirrer, and a gas tube in a well-ventilated hood, was placed 1.5 g (10 mmol) of m-dihydroxybenzene and 10 mL methanol. After the mixture was dissolved under stirring, Material D was added dropwise under an icebath temperature. Some buffer-solution (NaOH-HOAc) was added until the solution pH = 8. The mixture was stirred under the same situation for 2 h, then some HCl was added to keep the mixture pH = 6. the precipitate (3.3 g, 82%) of the mixture was collected and dried over vacuum. An analytical sample for EA was prepared by recrystallization from methanol [12].

2b: $^1\text{H NMR}$ (400 MHz, DMSO): δ 12.40 (s, 1 H), 10.80 (s, 1 H), 7.80 (d, $J = 8.4$ Hz, 2 H), 7.74 (d, $J = 8.5$ Hz, 2 H), 7.66 (m, $J = 8.6, 4.1$ Hz, 2 H), 6.52 (m, $J = 8.8, 2.4$ Hz, 1 H), 6.41 (d, $J = 2.2$ Hz, 1 H); $^{13}\text{C NMR}$ (101 MHz, DMSO): δ 163.70, 156.97, 150.92, 149.26, 132.72, 130.15, 127.11, 121.52, 109.69, 103.38. Elemental analysis. Calcd for $\text{C}_{12}\text{H}_{10}\text{N}_2\text{SO}_5$, C 49.98; H 3.40; N 9.52; Found C 49.84; H 3.26; N 9.48.

Preparation of 4-(2-hydroxyl naphthyl azo)-benzene sulfonic acid (2c):

In another 100 ml round-bottomed flask, fitted with a mechanical stirrer, and a gas tube in a well-ventilated hood, was placed 1.8 g (10 mmol) of naphthyl-2-ol and 15 mL methanol. After the mixture was dissolved under stirring, Material D was added dropwise under an icebath temperature. Some buffer-solution (NaOH-HOAc) was added until the solution pH = 8. The mixture was stirred under the same situation for 2 h, then some HCl was added to keep the mixture pH = 6. The precipitate (3.6 g, 88%) of the mixture was collected and dried over vacuum. An analytical sample for EA was prepared by recrystallization from methanol.

2c: ^1H NMR (400 MHz, DMSO): δ 15.84 (s, 1 H), 8.53 (d, J = 8.1 Hz, 1 H), 7.95 (d, J = 9.4 Hz, 1 H), 7.84 - 7.79 (m, 2 H), 7.76 (d, J = 7.7 Hz, 3 H), 7.61 (t, J = 7.6 Hz, 1 H), 7.46 (t, J = 7.4 Hz, 1 H), 6.89 (dd, J = 9.4, 4.7 Hz, 1 H), 1.05 (t, J = 7.0 Hz, 1 H). ^{13}C NMR (101 MHz, DMSO): δ 170.63 (d, J = 8.3 Hz), 147.52 (d, J = 8.5 Hz), 144.93 (d, J = 9.2 Hz), 140.79, 133.05, 129.76, 129.55, 129.31, 128.21, 127.55, 126.39, 124.60 (d, J = 6.8 Hz), 121.81 (d, J = 7.0 Hz), 118.35 (d, J = 11.8 Hz). Elemental analysis. Calcd for $\text{C}_{16}\text{H}_{12}\text{N}_2\text{SO}_4$, C58.54; H 3.64; N8.54; Found C 58.48; H 3.56; N 8.47.

Preparation of 4-(2-hydroxy-5-methyl phenyl azo)-benzene sulfonic acid (2d): In another 100 ml round-bottomed flask, fitted with a mechanical stirrer, and a gas tube in a well-ventilated hood, was placed 1.1 g (10 mmol) of 4-methylphenol and 15 mL methanol. After the mixture was dissolved under stirring, Material D was added dropwise under an icebath temperature. Some buffer-solution (NaOH-HOAc) was added until the solution pH = 8. The mixture was stirred under the same situation for 2 h, then some HCl was added to keep the mixture pH = 6. The precipitate (2.58 g, 87%) of the mixture was collected and dried over vacuum. An analytical sample for EA was prepared by recrystallization from methanol [13].

2d: ^1H NMR (400 MHz, DMSO): δ 7.92 - 7.94 (d, 2 H), 7.76 - 7.78 (d, 2 H), 7.57 (s, 1 H), 6.64 - 6.68 (d, 2 H), 6.62 - 6.64 (d, 1 H), 2.29 (t, 3 H) Elemental analysis. Calcd for $\text{C}_{13}\text{H}_{12}\text{N}_2\text{SO}_4$, C53.42; H 4.10; N9.59; Found C 53.28; H 3.97; N 9.47.

Preparation of 4-(4-amino-2,6-dimethyl phenyl azo)-benzene sulfonic acid (2e): In another 100 ml round-bottomed flask, fitted with a mechanical stirrer, and a gas tube in a well-ventilated hood, was placed 1.1 g (10 mmol) of 2,6-dimethylaniline and 15 mL methanol. After the mixture was dissolved under stirring, Material E was added dropwise under an icebath temperature. Some buffer-solution (NaOH-HOAc) was added until the solution pH = 8. The mixture was stirred under the same situation for 2 h, then some HCl was added to keep the mixture pH = 6. The precipitate (2.4 g, 81%) of the mixture was collected and dried over vacuum. An analytical sample for EA was prepared by recrystallization from methanol [14].

2e: ^1H NMR (400 MHz, CDCl_3): δ 7.67 - 7.67 (d, 2 H), 7.41 - 7.44 (m, 4 H), 6.47 - 6.49 (d, 2 H), 2.71 (s, 6 H). Elemental analysis. Calcd for $\text{C}_{14}\text{H}_{15}\text{N}_3\text{SO}_3$, C55.08; H4.92; N13.77; Found C 55.18; H 5.06; N 13.8.

4. Conclusion

In conclusion, we have developed a clean preparation of aryl diazonium ions using methyl nitrite. The processes were easy operations, environmentally benign conditions and high yields of the products. We believe that such a simple and safe methodology would initiate a growing interest for the chemistry of diazonium salt and introduce its further practical use as azo dyes and pigments.

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