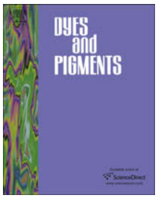
Dyes and Pigments 81 (2009) 240–244

Contents lists available at ScienceDirect

Dyes and Pigments

journal homepage: www.elsevier.com/locate/dyepig



Short communication

Rapid and efficient diazotization and diazo coupling reactions on silica sulfuric acid under solvent-free conditions

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ARTICLE INFO

Article history:
Received 23 June 2008
Received in revised form
13 October 2008
Accepted 13 October 2008
Available online 25 October 2008

Keywords:
Diazotization
Diazo coupling
Azo dyes
Silica sulfuric acid
Solvent-free conditions

ABSTRACT

A convenient, rapid, one-pot method for the synthesis of azo dyes has been developed by the sequential diazotization–diazo coupling of aromatic amines with $NaNO_2$, silica sulfuric acid and coupling agents under solvent-free conditions at room temperature. Using this method, several types of aromatic amine, containing electron-withdrawing groups as well as electron-donating groups, were rapidly converted to the corresponding azo dyes in good yield. The ensuing aryldiazonium salts supported on silica sulfuric acid (aryl diazonium silica sulfates), $ArN_2^{+-}OSO_3–SiO_2$, were sufficiently stable to be kept at room temperature in the dry state. The use of mild reaction conditions and an inexpensive procedure are further advantages of this method.

1. Introduction

Diazonium salts are useful synthetic building blocks in organic synthesis because these compounds can be linked to methine or aromatic sp^2-hybridized C-atoms. The diazotization and diazo coupling reactions are usually carried out with protonation of nitrous acid under strongly acidic conditions, and azo coupling carried out at low temperature in the presence of nucleophilic coupling components, the reactivity of a nucleophilic substrate increases with increasing basicity [1,2]. These conventional acid–base catalyzed processes are effective for the near quantitative formation of the desired azo-products. However the main limitation of such synthetic processes is their environmental incompatibility. The acidic and basic effluents from the laboratory and industry result in permanent damage to the environment and disturb the ecological balance [3]. In recent years, wide attention has been directed toward the application of solid acids in organic synthesis because such reagents not only simplify purification processes but also help to prevent release of reaction residues into the environment [4,5]. Recently, various solid acids have been used for the preparation of azo dyes [6,7]. Although satisfactory yields of products are usually obtained, the diazotization and diazo coupling reactions are complicated by numerous competing reactions [8]. For example, reaction temperatures above 10 °C generally promote phenol formation in aqueous media, and subsequent coupling of the phenol with undecomposed diazonium salts produces azo-phenols. In a continuation of our studies on the application of silica sulfuric acid (SSA) [9–14], herein, we wish to report a convenient and rapid one-pot method for diazotization and diazo coupling reactions using silica sulfuric acid under solvent-free conditions at room temperature (Fig. 1).

2. Experimental

2.1. General

Silica sulfuric acid was prepared according to previous work [13,14]. All reagents were purchased from Merck and Aldrich and used without further purification. The products were characterized by comparison with authentic samples and by spectroscopic data (FT-IR, ^{1}H NMR, UV, CHN and mp). UV spectra were recorded on a JASCO V-570 UV/vis/NIR spectrophotometer. IR spectra were recorded on a JASCO FT/IR-680 PLUS spectrometer. ^{1}H NMR spectra were recorded on a Bruker 250 MHz spectrometer.

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doi:10.1016/j.dyepig.2008.10.011

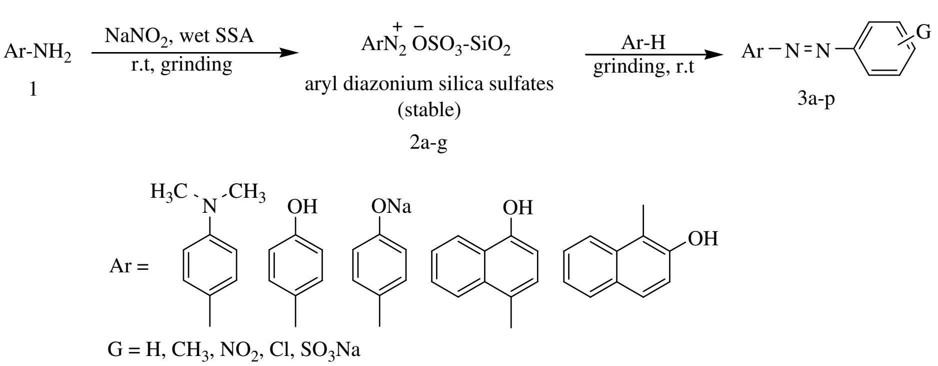


Fig. 1. One-pot method for diazotization and diazo coupling reactions using silica sulfuric acid under solvent-free conditions.

2.2. *Typical procedure for the preparation of 4-diethylaminoazobenzene*

Aniline (2 mmol, 0.19 mL), silica sulfuric acid (1.35 g) and sodium nitrite (4 mmol, 0.276 g) were ground in a mortar with a pestle for a few minutes to obtain a homogeneous mixture. Then, a few drops of water were gradually added to this mixture and the whole was ground for 10 min until the gas evolution ceased. Diethylaminobenzene (2 mmol, 0.32 mL) was added to the diazonium salt and grinding continued for 10 min. The crude product was extracted with acetone (4 × 15 mL). The solvent was evaporated by rotary evaporator and the crude product was purified by recrystallization in EtOH/H_2O. 4-Diethylaminoazobenzene was obtained in 80% yield (0.4 g), mp 95–97 °C, literature 97–98 °C [15].

2.3. *The spectral data of some representative products*

4-Dimethylamino-4′-nitroazobenzene (Table 1, **3a**): IR (KBr) cm^{-1}: 3060, 2924, 1618, 1530, 1351, 1235, 1054, 850. UV (λ_{max} in CH_2Cl_2): 479 nm. ^1H NMR ($CDCl_3$/DMSO-d_6): δ_H 8.6 (2H, d, $J = 8.9$ Hz), 8.2 (2H, d, $J = 8.9$ Hz), 8.1 (2H, d, $J = 9.5$ Hz), 6.94 (2H, d, $J = 9.5$ Hz), 3.25 (6H, s). Anal. Calcd for $C_{14}H_{14}N_4O_2$: C, 62.22; H, 5.18; N, 20.74%. Found: C, 61.96; H, 5.28; N, 21.05%.

4-Dimethylamino-2′-nitroazobenzene (Table 1, **3b**): IR (KBr) cm^{-1}: 3058, 2926, 1612, 1534, 1355, 1238, 1060, 813, 736. UV (λ_{max} in CH_2Cl_2): 428 nm. ^1H NMR ($CDCl_3$/DMSO-d_6): δ_H 8.15 (1H, d, $J = 9$ Hz), 8.08–7.6 (5H, m), 6.85 (2H, d, $J = 9.5$ Hz), 3.15 (6H, s). Anal. Calcd for $C_{14}H_{14}N_4O_2$: C, 62.22; H, 5.18; N, 20.74%. Found: C, 61.88; H, 5.32; N, 20.68%.

Sodium 4-(4-hydroxyphenylazo)benzenesulfonate (Table 1, **3h**): IR (KBr) cm^{-1}: 3460, 1595, 1439, 1365, 1280, 1170, 1134, 840, 755. UV (λ_{max} in EtOH): 357 nm. ^1H NMR (DMSO-d_6): δ_H 10.5 (1H, s, –OH), 8.16 (2H, d, $J = 8.6$ Hz), 7.9 (2H, d, $J = 8.6$ Hz), 7.86 (2H, d, $J = 8.8$ Hz), 6.96 (2H, d, $J = 8.8$ Hz). Anal. Calcd for $C_{12}H_9N_2NaO_4S$: C, 48; H, 3; N, 9.33. Found: C, 48.22; H, 3.1; N, 9.12%.

4-Dimethylaminoazobenzene (Table 1, **3j**): IR (KBr) cm^{-1}: 3035, 2915, 1598, 1500, 1400, 1370, 1220, 1140, 820, 750, 690. UV (λ_{max} in CH_2Cl_2): 411 nm. ^1H NMR ($CDCl_3$/DMSO-d_6): δ_H 8.28–8.08 (4H, m), 7.85–7.6 (3H, m), 6.96 (2H, d, $J = 9.3$ Hz), 3.18 (6H, s). Anal. Calcd for $C_{14}H_{15}N_3$: C, 74.66; H, 6.22; N, 18.66%. Found: C, 75.1; H, 6.45; N, 18.37%.

4-Diethylaminoazobenzene (Table 1, **3k**): IR (KBr) cm^{-1}: 3040, 2920, 1600, 1498, 1375, 1222, 1138, 823, 755, 692. UV (λ_{max} in CH_2Cl_2): 420 nm. ^1H NMR ($CDCl_3$/DMSO-d_6): δ_H 8.05–7.85 (4H, m), 7.8–7.4 (3H, m), 6.7 (2H, d, $J = 9.2$ Hz), 3.47 (4H, q, $J = 7.4$ Hz), 1.2 (6H, t, $J = 7.4$ Hz). Anal. Calcd for $C_{16}H_{19}N_3$: C, 75.89; H, 7.5; N, 16.6%. Found: C, 76.1; H, 7.63; N, 16.32%.

4-Dimethylamino-2′-chloroazobenzene (Table 1, **3n**): IR (KBr) cm^{-1}: 3055, 2924, 1617, 1498, 1595, 1544, 1383, 1220, 1190, 1109, 842, 748. UV (λ_{max} in CH_2Cl_2): 428 nm. ^1H NMR ($CDCl_3$/DMSO-d_6): δ_H 8.05 (1H, d, $J = 8.9$ Hz), 7.85–7.35 (5H, m), 6.85 (2H, d, $J = 9.4$ Hz), 3.15 (6H, s). Anal. Calcd for $C_{14}ClH_{14}N_3$: C, 64.74; H, 5.39; N, 16.18%. Found: C, 65.12; H, 5.68; N, 16.34%.

4-Dimethylamino-3′-chloroazobenzene (Table 1, **3o**): IR (KBr) cm^{-1}: 3059, 2922, 1619, 1597, 1548, 1352, 1179, 833, 768, 693. UV (λ_{max} in CH_2Cl_2): 422 nm. ^1H NMR ($CDCl_3$/DMSO-d_6): δ_H 8.25 (1H, s), 8.15–7.95 (2H, m), 7.75–7.55 (3H, m), 6.95 (2H, d, $J = 9.4$ Hz), 3.2 (6H, s). Anal. Calcd for $C_{14}ClH_{14}N_3$: C, 64.74; H, 5.39; N, 16.18%. Found: C, 64.96; H, 5.45; N, 15.97%.

4-Dimethylamino-2′-methylazobenzene (Table 1, **3p**): IR (KBr) cm^{-1}: 3038, 2925, 1597, 1510, 1405, 1372, 1215, 1125, 820, 745, 690. UV (λ_{max} in CH_2Cl_2): 410 nm. ^1H NMR ($CDCl_3$/DMSO-d_6): δ_H 8.15–7.7 (3H, m), 7.5–7.35 (3H, m), 6.85 (2H, d, $J = 9.3$ Hz), 3.15 (6H, s), 2.68 (3H, s). Anal. Calcd for $C_{15}H_{17}N_3$: C, 75.31; H, 7.11; N, 17.57%. Found: C, 75.11; H, 7.48; N, 17.31%.

3. Results and discussion

Diazonium salts are versatile compounds in organic chemistry. However, their poor thermal stability limits the application of these derivatives. Usually these compounds are synthesized around 10 °C and to avoid their decomposition they are handled below 0 °C. In this new method, different kinds of aromatic amines, with electron-withdrawing groups as well as electron-donating groups, were rapidly converted to the corresponding of azo dyes in good yields under solvent-free conditions at room temperature (Table 1).

Generally, an aromatic amine (2 mmol), silica sulfuric acid (1.35 g) and sodium nitrite (4 mmol) are ground in a mortar with a pestle for a few minutes to obtain a homogeneous mixture. Then, a few drops of water are gradually added to this mixture and then the reaction mixture is ground for 10–20 min until the gas evolution completely stops. Then, coupling agent (2 mmol) is added to the diazonium salt and grinding continues for 10 min. the whole process of diazotization and diazo coupling takes 20–30 min (Table 1). The crude product is extracted with ethanol or acetone and the solvent is evaporated by rotary evaporator and the crude product is purified by recrystallization or short column chromatography. The steric effect of *ortho*-substituents has relatively little influence on the reaction time and yields (Table 1, entries 2, 14, 16). As shown in Table 1, phenol is the weakest nucleophilic coupling component amongst those coupling agents used and as such the product is obtained in negligible yield (Table 1, entry 12). Therefore, we used sodium phenoxide instead of phenol to improve the yield of the product (Table 1, entries 4, 8, 13). In the traditional methods of azo dye synthesis reaction temperatures above 10 °C generally promote phenol formation in aqueous media, and subsequent coupling of the phenol with undecomposed diazonium salts produces azophenols as side reactions [8]. However, by using this method, the corresponding phenol derivatives were only formed in trace amounts which constitute another advantage of this procedure. The effect of water and

Table 1
Diazotization and diazo coupling reactions of some aromatic amines on silica sulfuric acid under solvent-free conditions at room temperature[a,b]

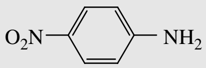
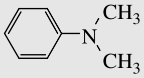
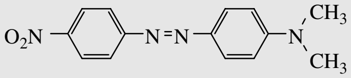
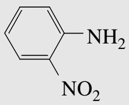
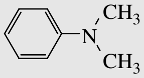
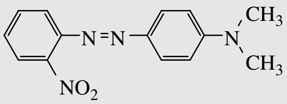
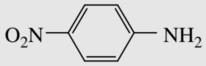
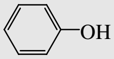
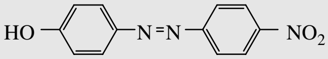
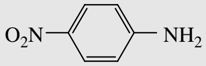
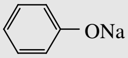
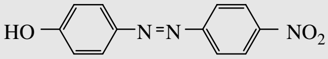
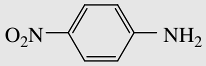
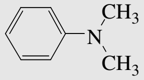
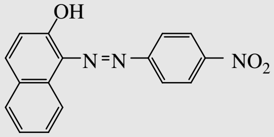
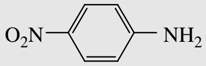
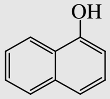
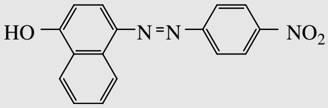
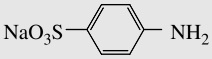
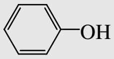
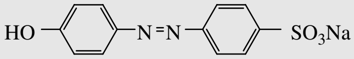
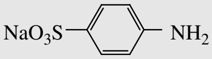
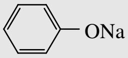
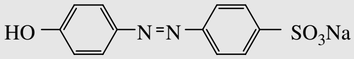
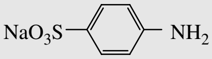
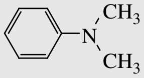
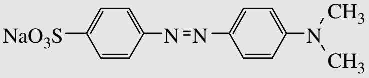
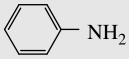
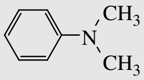
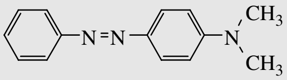
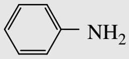
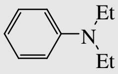
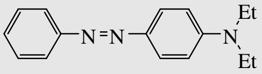
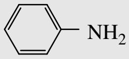
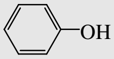
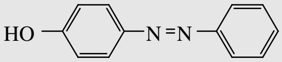
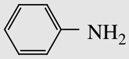
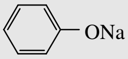
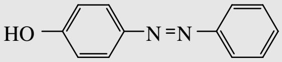
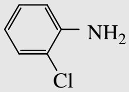
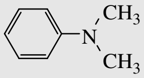
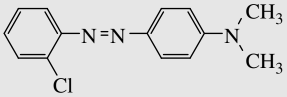
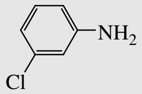
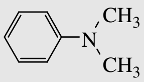
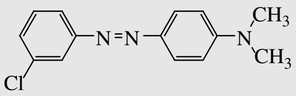
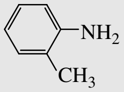
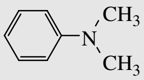
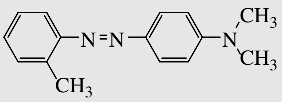
Entry	Amine	Coupling agent	Time (min)	Product	Structure number	Yield (%)
1			30		**3a**	85
2			30		**3b**	81
3			30		**3c**	60
4			30		**3d**	86
5			30		**3e**	83
6			30		**3f**	80
7			30		**3g**	55
8			30		**3h**	84
9			30		**3i**	83
10			20		**3j**	81
11			20		**3k**	80
12			20		**3l**	trace
13			20		**3m**	82
14			25		**3n**	79

Table 1 (*continued*)

Entry	Amine	Coupling agent	Time (min)	Product	Structure number	Yield (%)
15			25		**3o**	82
16			20		**3p**	77

[a] The yields refer to the isolated pure products.

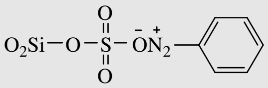
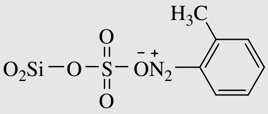
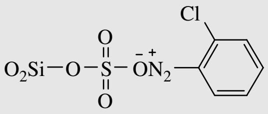
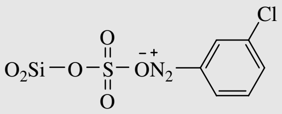
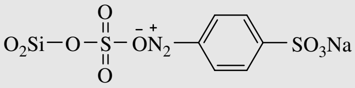
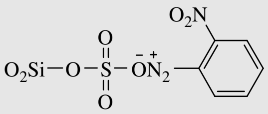
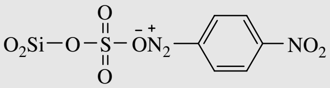
[b] The products were characterized from their spectral data (IR, ^{1}H NMR, UV, CHN and mp) and compared with authentic samples.

acetonitrile on these diazotization–diazo couplings was also studied. We found that in contrast to solvent-free conditions, the yields of azo dyes in these solvents are lower. For example, by using this method, 4-dimethylamino-4′-nitroazobenzene (Table 1, **3a**) was obtained in 85% yield under solvent-free conditions. However, this product was obtained in 60% yield in water and 30% yield in acetonitrile at room temperature under the same conditions. It should be highlighted that the reaction requires a small amount of water for the formation of moist conditions and the addition of water must be carried out in stepwise manner to ensure good yields.

The diazonium salts (Table 2, **2a**–**g**) supported on silica sulfuric acid (aryl diazonium silica sulfates), $\mathrm{ArN_2^{+}{}^{-}OSO_3{-}SiO_2}$, were sufficiently stable to be kept at room temperature in a dried state. To determine the stability of these salts, the aryl diazonium silica sulfates were stored in a desiccator at room temperature. After the times specified in Table 2, dimethylaminobenzene was added to

Table 2

The stability study of some aryl diazonium silica sulfates at room temperature[a,b]

Entry	Diazonium salt	Structure number	Yield after 6 h (%)	Yield after 24 h (%)	Yield after 48 h (%)	Yield after 72 h (%)
1		**2a**	91	77	55	23
2		**2b**	90	75	53	20
3		**2c**	96	89	81	72
4		**2d**	95	87	80	70
5		**2e**	94	88	82	73
6		**2f**	98	94	86	77
7		**2g**	97	93	85	75

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

[b] Each yield of the product was compared with the product provided with the corresponding fresh diazonium salt.

each salt and the reaction mixture was ground at room temperature for 10 min. The product was extracted and the yield of azo dyes compared with the product provided with the corresponding fresh diazonium salt. For example, *p*-nitrophenyldiazonium silica sulfate was kept in a desiccator at room temperature. After 24 h, the addition of dimethylaminobenzene to this salt provided 93% yield of 4-dimethylamino-4′-nitroazobenzene prepared with fresh *p*-nitrophenyldiazonium silica sulfate (Table 2, **2g**). As shown in Table 2, aryl diazonium silica sulfates with electron-withdrawing groups on aromatic rings, are more stable than those with electron-donating groups because of the instability of the resulting aryl cation [16]. In addition, all aryldiazonium silica sulfates prepared with this procedure are stable and non-explosive because the reactivity of these aryldiazonium salts decrease when they are supported on silica sulfuric acid as a bulky solid support [17,18]. In our hands the diazotization and diazo coupling method was found to be safe and the grinding of these aryldiazonium salts was not found to be hazardous.

In contrast with the traditional methods, by using this method the reaction rate of diazotization–diazo coupling increases. We think that by supporting these aryldiazonium salts on silica sulfuric acid, these salts are well dispersed on the surface of silica sulfuric acid so that it can lead to significant improvements in reactivity [4]. Besides, solvent-free conditions at room temperature can be another cause for increasing the rate of these reactions because the higher concentration of reactants in the absence of solvents usually leads to more favorable kinetics than in solution [19,20].

4. Conclusion

In summary, we have developed an efficient experimentally simple and relatively environmentally benign method for the diazotization and diazo coupling reactions of aromatic amines on silica sulfuric acid. These reactions proceed at room temperature under virtually solvent-free conditions. The resulting diazonium salts are stable and react rapidly with coupling agents to produce azo dyes in good yields. Our new method has some advantages over traditional methods which include mild reaction conditions at room temperature, short reaction time and easy experimental work-up procedure. Further investigations on new applications of this method are ongoing in our laboratories due to the stability of these diazonium salts and the ease of their synthesis.

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