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Fast, efficient and convenient method for the preparation of arylazo sulfides using aryl diazonium silica sulfates under mild and solvent-free conditions

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1. Introduction

ABSTRACT

An efficient, fast, and straightforward procedure for the synthesis of arylazo sulfides and arylazo thiosulfonates is described in the present paper by using aryl diazonium silica sulfates and sodium thiolates. Using the present method, different kinds of aryl diazonium silica sulfates, containing electron-withdrawing groups as well as electron-donating groups, were rapidly converted to the corresponding arylazo sulfides in good yield and short reaction time. These reactions were carried out at room temperature under mild and solvent-free conditions. The use of non-toxic and inexpensive materials, simple and clean work-up, short reaction times and good yields are the advantages of this method.

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Aryl diazonium salts have been prepared and studied as powerful intermediates in classical and modern organic synthesis due to their easy availability and high reactivity [1–4]. Therefore, there is always an interest in the field of aromatic diazonium salts. Arylazo sulfides have been studied from their thermal [5,6] and photochemical [7,8] behavior as well as their applications in organic synthesis [9-20]. For example, it is known that the thermolysis of these compounds is an important method for the preparation of arydiazenyl radicals [5,6]. Moreover, arylazo sulfides are one of the important precursors for S_{RN}1 reactions to produce a number of variously functionalized aromatic compounds [9–20]. Furthermore, some of the chlorinated phenylazo phenyl sulfides are used as agricultural pesticides and miticides. One of the useful procedures for the preparation of arylazo sulfides is the reaction of aryl diazonium salts with aryl mercaptans [21–24]. Although some of these methods are convenient protocols with good yields, some of them suffer from disadvantages such as the stench associated

with using aryl mercaptans, tedious work-up, and low yields because of disulfide formation. In continuation of our studies on the stabilization of diazonium salts on silica sulfuric acid and their applications in organic synthesis [25–28], we report herein an efficient, fast, and convenient procedure for the synthesis of arylazo sulfides employing aryl diazonium silica sulfates in the presence of sodium thiolates under solvent-free conditions. In spite of the traditional methods, these reactions were carried out at room temperature and there was no need to employ low temperature (Scheme 1).

2. Experimental

2.1. General

All reagents were purchased from Merck and Aldrich and used without further purification. Aryl diazonium silica sulfates were synthesized according to the previous works [25–28]. All yields refer to the isolated products after purification. The products were characterized by comparison with authentic samples and by spectroscopic data (IR, ¹H NMR, ¹³C NMR spectra and melting point). All melting points were taken on a Gallenkamp melting apparatus and were uncorrected. UV spectra were recorded on a JASCO V-570



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$$\operatorname{ArN}_{2}^{+} \operatorname{OSO}_{3}^{-} \operatorname{SiO}_{2} + \operatorname{RSNa} \xrightarrow{\text{Grinding}} \operatorname{ArN=NSR}$$

 $R = Ph, CH_{3}SO_{2}$

Scheme 1. An efficient, fast, and convenient procedure for the synthesis of arylazo sulfides employing aryl diazonium silica sulfates in the presence of sodium thiolates under solvent-free conditions.

UV/vis/NIR spectrophotometer. IR spectra were recorded on a JASCO FT/IR-680 PLUS spectrometer. ¹H NMR spectra were recorded on a Bruker 500 MHz.

2.2. General procedure for the synthesis of arylazo sulfides

Sodium thiolate (1.2 mmol, 0.161 g) was added to freshly diazonium silica sulfate (1 mmol) and the reaction mixture was ground with a pestle in a mortar at room temperature for the time specified in Table 1. The mixture was diluted with ethyl acetate (12 mL) and, after stirring, was filtered. The residue was extracted with ethyl acetate (3×10 mL) and the combined organic layers were washed with 5% NaOH solution and then dried over anhydrous Na₂SO₄. The solvent was evaporated and the crude product was purified by short column chromatography to afford the corresponding pure product.

2.3. The spectral data of new compounds

2.3.1. 4-Methylphenylazo methanethiosulfonate (Table 1, entry 15) Pale yellow solid; UV (λ_{max} in acetone): 325 nm. Mp 95–96 °C; FTIR (KBr) cm⁻¹: 3038, 3925, 1585, 1487, 1365, 1163, 970, 867, 762. ¹H NMR (500 MHz, CDCl₃) δ = 7.51 (2 H, d, *J* = 8.10 Hz), 7.20 (2 H, d, *J* = 8.10 Hz), 3.24 (3 H, s), 2.35 (3 H, s). ¹³C NMR (125 MHz, CDCl₃) δ = 147.30, 138.26, 128.28, 122.50, 35.28, 21.38. Anal. Calcd for C₈H₁₀N₂O₂S₂: C, 41.72; H, 4.38; N, 12.16; S, 27.85. Found: C, 41.65; H, 4.49; N, 12.05; S, 27.78.

2.3.2. 4-Chlorophenylazo methanethiosulfonate (Table 1, entry 16)

Yellow solid; UV (λ_{max} in acetone): 330 nm. Decomposed at 111 °C; FTIR (KBr) cm⁻¹: 3091, 3039, 2932, 1574, 1484, 1404, 1331, 1161, 1142, 1089, 953, 887, 844, 794. ¹H NMR (500 MHz, CDCl₃) δ = 7.93 (2 H, d, *J* = 8.65 Hz), 7.59 (2 H, d, *J* = 8.65 Hz), 3.26 (3 H, s). ¹³C NMR (125 MHz, CDCl₃) δ = 147.78, 142.23, 130.28, 126.21, 35.31. Anal. Calcd for C₇H₇ClN₂O₂S₂: C, 33.53; H, 2.81; N, 11.17; S, 25.58. Found: C, 33.49; H, 2.90; N, 11.25; S, 25.53.

2.3.3. 3-Chlorophenylazo methanethiosulfonate (Table 1, entry 17)

Pale yellow solid; UV (λ_{max} in acetone): 325 nm. Mp 66–68 °C; FTIR (KBr) cm⁻¹: 3071, 3019, 2936, 1574, 1480, 1456, 1336, 1317, 1161, 1145, 1065, 960, 923, 817, 790. ¹H NMR (500 MHz, CDCl₃) δ = 7.94 (1 H, s), 7.88 (1 H, d, *J* = 8.00 Hz), 7.65 (1 H, d, *J* = 8.00 Hz), 7.55 (1 H, t, *J* = 8.00 Hz), 3.25 (3 H, s). ¹³C NMR (125 MHz, CDCl₃) δ = 149.70, 135.92, 134.88, 130.81, 123.63, 123.61, 34.90. Anal. Calcd for C₇H₇ClN₂O₂S₂: C, 33.53; H, 2.81; N, 11.17; S, 25.58. Found: C, 33.45; H, 2.88; N, 11.08; S, 25.49.

2.3.4. 4-Bromophenylazo methanethiosulfonate (Table 1, entry 18)

Orange solid; UV (λ_{max} in acetone): 336 nm. Decomposed at 127 °C; FTIR (KBr) cm⁻¹: 3086, 3038, 2930, 1582, 1571, 1481, 1400, 1328, 1160, 1141, 1060, 954, 893, 842, 831, 789, 724. ¹H NMR (500 MHz, CDCl₃) δ = 7.82 (2 H, d, *J* = 8.65 Hz), 7.73 (2 H, d, *J* = 8.65 Hz), 3.23 (3 H, s). ¹³C NMR (125 MHz, CDCl₃) δ = 148.14, 133.60, 131.00, 126.26 35.32. Anal. Calcd for C₇H₇BrN₂O₂S₂: C, 28.48; H, 2.39; N, 9.49; S, 21.73. Found: C, 28.52; H, 2.45; N, 9.41; S, 21.70.

2.3.5. 3-Nitrophenylazo methanethiosulfonate (Table 1, entry 19)

Orange solid; UV (λ_{max} in acetone): 334 nm. Decomposed at 121 °C; FTIR (KBr) cm⁻¹: 3084, 2935, 1607, 1531, 1493, 1356, 1335, 1160, 1086, 916, 872, 819, 793, 741. ¹H NMR (500 MHz, CDCl₃) $\delta = 8.71$ (1 H, s), 8.48 (1 H, d, J = 7.87 Hz), 8.25 (1 H, d, J = 7.77 Hz), 7.80 (1 H, t, J = 8.04 Hz), 3.25 (3 H, s). ¹³C NMR (125 MHz, CDCl₃) $\delta = 149.65$, 149.41, 131.40, 130.09, 129.16, 35.48. Anal. Calcd for C₇H₇N₃O₄S₂: C, 32.18; H, 2.70; N, 16.08; S, 24.54. Found: C, 32.11; H, 2.77; N, 15.99; S, 24.45.

2.3.6. 2-Nitrophenylazo methanethiosulfonate (Table 1, entry 20)

Orange solid; UV (λ_{max} in acetone): 338 nm. Mp 74–76 °C; FTIR (KBr) cm⁻¹: 3070, 3022, 2940, 1599, 1525, 1339, 1199, 957, 893, 857, 778, 746. ¹H NMR (500 MHz, CDCl₃) δ = 8.14 (1 H, d, *J* = 7.62 Hz), 7.88-7.83 (2 H, m), 7.71 (1 H, d, *J* = 7.14 Hz), 3.23 (3 H, s). ¹³C NMR (125 MHz, CDCl₃) δ = 147.60, 142.27, 134.86, 134.43, 125.48, 118.53, 34.94. Anal. Calcd for C₇H₇N₃O₄S₂: C, 32.18; H, 2.70; N, 16.08; S, 24.54. Found: C, 32.15; H, 2.81; N, 16.05; S, 24.58.

2.3.7. 4-(2-(Methylthiosulfonyl)diazenyl) benzoic acid (Table 1, entry 21)

Pale yellow solid; UV (λ_{max} in acetone): 327 nm. Decomposed at 137 °C; FTIR (KBr) cm⁻¹: 3100–2555, 1685, 1480, 1427, 1333, 1290, 1164, 1146, 966, 900, 871, 775. ¹H NMR (500 MHz, CDCl₃/DMSO-d₆) δ = 7.98 (2 H, d, *J* = 8.80 Hz), 7.63 (2 H, d, *J* = 8.80 Hz), 3.24 (3 H, s). ¹³C NMR (125 MHz, CDCl₃/DMSO-d₆) δ = 166.28, 148.23, 136.22, 130.56, 126.27, 35.30. Anal. Calcd for C₈H₈N₂O₄S₂: C, 36.91; H, 3.10; N, 10.76; S, 24.64. Found: C, 36.88; H, 3.15; N, 10.79; S, 24.56.

3. Results and discussion

Aromatic diazonium salts have been prepared and studied for years. These salts are important building blocks in classical and modern organic synthesis. These salts, however, have a serious drawback in their intrinsic instability. Therefore, these compounds are usually synthesized at around 10 °C, and to avoid their decomposition, they are handled below 0 °C. Moreover, because of this instability, subsequent reactions with diazonium salts must be carried out under similar conditions to which they are produced. These problems restrict chemists for approaching potentially important transformations of these salts. Thus, new diazonium salts with high stability and versatility that can be easily made and stored under solid state conditions with explosion proof properties, are desired and necessary [29–33]. Recently, we have reported an efficient, fast, and convenient method for the preparation of aryl diazonium salts supported on the surface of silica sulfuric acid (aryl diazonium silica sulfates) [25-28]. We found that these new aryl diazonium salts, $ArN_2^{+-}OSO_3$ -SiO₂, were sufficiently stable and could be kept at room temperature under anhydrous conditions. In the present work, different kinds of aromatic amines were rapidly converted to their corresponding arylazo sulfides in good to high yields under mild conditions (Table 1, entries 1-14). The crude products were extracted with ethyl acetate, and if necessary, were purified by short column chromatography.

Aromatic amines with electron-withdrawing groups or electron-donating groups reacted effectively. The steric effects of *ortho* substituents and electronic effects of functional groups on the aryl amine rings had relatively little influence on the yields of the products (Table 1). The corresponding disulfides and phenol derivatives were formed in trace yields as the by-products. Unlike the traditional methods, these reactions were carried out under solvent-free conditions at room temperature. We also studied the solvent effect on these reactions. Using water, methanol, or dimethyl sulfoxide as the solvent, under the same conditions, led to lower yields of the corresponding arylazo sulfides because the

Table 1

 Preparation of (E)-arylazo sulfides by using aryl diazonium silica sulfates and sodium thiolates at room temperature.^a

Entry	Sodium thiolates	Aromatic amines	Products	Time (min)	Yield (%)	Mp (°C)	
						Found	Reported
1	PhSNa	4-MePhN2 ⁺⁻ OSO3-SiO2	Me N=N-S-Ph	5	81	48-49	49-50 [24]
2		2-MePhN ₂ ⁺⁻ OSO ₃ -SiO ₂	N=N-S-Ph Me	5	78	Oil	19–20 [7]
3		2-MeOPhN ₂ ⁺⁻ OSO ₃ -SiO ₂	N=N-S-Ph OMe	5	75	33–34	31–33 [16]
4		4-MeOPhN2 ⁺⁻ OSO3-SiO2	MeO-N=N-S-Ph	5	78	47–48	46–47 [24]
5		2-BrPhN ₂ ⁺⁻ OSO ₃ -SiO ₂	N=N-S-Ph Br	5	79	45-46	44–45 [7]
6		4-ClPhN ₂ ⁺⁻ OSO ₃ -SiO ₂	Cl-N=N-S-Ph	5	87	57–58	59–60 [7]
7		2-CIPhN ₂ ⁺⁻ OSO ₃ -SiO ₂	N=N-S-Ph	5	82	45-46	46–47 [7]
8		4-NCPhN2 ⁺⁻ OSO3-SiO2	NC-N=N-S-Ph	5	82	106–108	110–111[11]
9		4-MeCOPhN2 ⁺⁻ OSO3-SiO2	H_3C-C $N=N-S-Ph$	5	85	34–35	31–33 [16]
10		4-PhCOPhN2 ⁺⁻ OSO3-SiO2	Ph-C-N=N-S-Ph	5	83	70–71	71–72 [12]
11		$4\text{-NO}_2\text{PhN}_2^{+-}\text{OSO}_3\text{-SiO}_2$	O ₂ N-N=N-S-Ph	5	84	94–95	95–97 [11]
12		$3-NO_2PhN_2^{+-}OSO_3-SiO_2$	N=N-S-Ph	5	86	47–48	48–49 [11]
13		$2\text{-NO}_2\text{PhN}_2^{+-}\text{OSO}_3\text{-SiO}_2$	N=N-S-Ph NO ₂	5	81	56–57	57–58 [11]
14		4-HOCOPhN2 ⁺⁻ OSO3-SiO2	HO-C-N=N-S-Ph	5	82	98–100	101 [21]
15	MeSO ₂ Na	4-MePhN ₂ ⁺⁻ OSO ₃ -SiO ₂	$Me \longrightarrow N = N - S \longrightarrow CH_3$	10	80	95–96	-
16		4-ClPhN2 ⁺⁻ OSO3-SiO2	CISSCH ₃	10	81	111 Decomposed	_

Table 1 (continued)

Entry	Sodium thiolates	Aromatic amines	Products	Time (min)	Yield (%)	Mp (°C)	
						Found	Reported
17		3-CIPhN2 ⁺⁻ OSO3-SiO2	N=N-S-CH ₃	10	79	66–68	_
18		4-BrPhN ₂ ⁺⁻ OSO ₃ -SiO ₂	$Br \longrightarrow N = N - S - S - CH_3$	10	83	127 Decomposed	_
19		3-NO ₂ PhN ₂ ⁺⁻ OSO ₃ -SiO ₂	$N=N-S-S-CH_3$	10	82	121 Decomposed	_
20		2-NO ₂ PhN ₂ ⁺⁻ OSO ₃ -SiO ₂	NO2	10	77	74–76	_
21		4-HOCOPhN2 ⁺⁻ OSO3-SiO2	HO-C-C-N=N-S-S-CH ₃	10	80	137 Decomposed	_

^a The yields refer to isolated pure products which were characterized from their spectral data by comparison with authentic samples.

yields of the corresponding disulfides and phenol derivatives increased as the by-products. It is known that replacement of aryl diazonium groups with an appropriate nucleophile is usually carried out by a $S_{RN}1$ mechanism. It is a chain process involving the coupling of an aryl radical with an anionic nucleophile [9,34]. Most of these reactions are carried out in solvents that can undergo electron transfer reactions. These electron transfer reactions can be carried out between solvent/substrate and solvent/nucleophile which lead to produce a number of by-products. In the present work, by omitting the solvent, the formation of by-products was reduced to trace yields. In contrast with the conventional methods, the reaction rate increased because by supporting the aryl diazonium salt on silica sulfuric acid, the surface area of the reaction increased [25–28,35].

We also studied the synthesis of arylazo methanethiosulfonates as a new derivation of arylazo sulfides (Table 1, entries 15–21). By using the present method, different kinds of arylazo methanethiosulfonates were easily synthesized in good yields and short reaction times by treating aryl diazonium salts in the presence of sodium methanethiosulfonate. Finally, after completion of the recycled [25–28]. In addition, the present procedure for the preparation of arylazo sulfides was shown to be safe and nonexplosive because by supporting aryl diazonium salts on the surface of silica sulfuric acid as a bulky support, the stability of these salts increased [25,36].

4. Conclusion

To sum up, what has been done in the present study can be considered as an efficient, rapid, experimentally simple, and environmentally benign method for the preparation of arylazo sulfides and arylazo methanethiosulfonates using aryl diazonium silica sulfates. These reactions proceed at room temperature under mild conditions in good to high yields. Among the notable advantages of this method, we can mention the following: operational simplicity, generality, availability of reactants, short reaction times, and easy work-up.

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