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Transition-Metal-Free C-S Bond Formation. Aqueous Synthesis of s-Aryl Dithiocarbamates by Use of Stable Arenediazonium Salts Mediated by Nano-Magnetic Supported Silica Sulfonic Acid

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Green synthesis of S-aryl dithiocarbamates

TRANSITION-METAL-FREE C-S BOND FORMATION. AQUEOUS SYNTHESIS OF *S*-ARYL DITHIOCARBAMATES BY USE OF STABLE ARENEDIAZONIUM SALTS MEDIATED BY NANO-MAGNETIC SUPPORTED SILICA SULFONIC ACID Firouzeh Nemati^{a,*}, Ali Elhampour^a, Soghra Zulfaghari^a ^aDepartment of Chemistry, Semnan University, Semnan, Iran, Zip Code: 35131-19111, Tel.: +98

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Abstract

A convenient and transition-metal-free method for the synthesis of *S*-aryl dithiocarbamates based on the reaction of stable arenediazonium nano-magneto silica sulfates $(ArN_2^+ \ OSO_3^- SiO_2@Fe_3O_4)$ with dithiocarbamic acid at room temperature was studied. Avoiding the use of any hazardous transition metal, simple procedure, low cast and short reaction time are noteworthy advantages of this methodology.



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Keywords

Diazotization; Magnetic Nanoparticles; S-Aryl Dithiocarbamates, Diazonium salts; Transitionmetal-free.

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INTRODUCTION

Sulfur-containing compounds are found in many biological, pharmaceutical, and material products.¹⁻⁶ The formation of a carbonósulfur (CóS) bond is a fundamental approach to introduce sulfur into organic compounds. Traditionally, various metal-based catalysts in combination with different ligands are generally used for the CóS bond formation by cross coupling of their halides.⁷⁻¹² But most of these synthetic methods involve designed ligands or catalysts, which may increase the cost and limit the scope of their applications. Thus, the investigation of new protocols for $C_{(aryl)}$ óS bond generation, especially under õgreenö conditions, which can lead to the discovery of less expensive and more efficient synthetic methods for the preparation of organo-sulfur compounds has attracted much attention in recent years.¹³⁻¹⁵

Dithiocarbamates are vital structural motifs occurring in numerous natural products¹⁶, pharmaceuticals and agrochemicals.¹⁷ They are also used as linkers in solid phase organic synthesis,¹⁸ protecting groups in peptide synthesis¹⁹ and in the synthesis of ionic liquids.²⁰ Thus the development of novel protocols for the synthesis of dithiocarbamates, which are practical, cheap and environmentally benign, is highly desirable. The synthetic methods for the formation of *S*-aryl dithiocarbamates are somewhat limited. The most commonly used conventional method is the reaction of amines with thiophosgene or isothiocyanates.²¹ However, these methods have limited application because costly and toxic reagents are used. Other methods applied for the synthesis of *S*-aryl dithiocarbamates are the reaction of hypervalent iodine compounds with sodium salts of dithiocarbamic acids,²² the reaction of certain organometallic reagents with tetramethyllitium disulfide,²³ coupling of sodium dithiocarbamates with aryl iodides catalyzed by CuI in the presence of a ligand in DMF(dimethyl formamide).²⁴ These methods suffer from one

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or more disadvantages such as the use of expensive and toxic reagents or difficulty in preparing the reagent. Ranu et al. previously described the synthesis of *S*-aryl dithiocarbamates via two green routes: the condensation of arenediazonium fluoroborate, carbon disulfide and an amine in water,²⁵ and coupling of aryl iodides with carbon disulfide and an amine catalyzed by Cu nanoparticles.²⁶ Even though they are considered as highly useful synthetic method, their only disadvantage is the need for expensive starting materials such as arenediazonium fluoroborate, or aryl iodide. Despite these advances, the above drawbacks need to be overcome, and the development of a convenient and efficient method using cheap and benign reagents for the synthesis of *S*-aryl dithiocarbamates is attracting considerable attention. We have recently reported the synthesis of nano-Fe₃O₄@SiO₂-SO₃H and its application in green protocols.^{27,29} It has been identified as the ideal heterogeneous solid acid due to its excellent stability as well as its great accessibility and low cost.³⁰ It can be directly separated from the reaction mixture using an external magnet and be reused several times without a significant decrease of activity.

RESULTS AND DISCUSSION

In light of the above facts and in continuation of our studies on the application of stable arenediazonium salts for organic transformations^{31,32} and as a part of our recent endeavors in the use of nano-Fe₃O₄@SiO₂-SO₃H, we developed an efficient and metal-free reaction for the synthesis of *S*-aryl dithiocarbamates. Nano-Fe₃O₄@SiO₂-SO₃H can be used as acid source for the generation of stable diazonium salts from the corresponding anilines that are widely available commercially or generated by the reduction of the corresponding nitroarene, which may serve as a protected amine in a synthetic route.³³ It is well-known that arenediazonium salts with the bulky sulfate anion are stable and non-explosive.³⁴⁻³⁶ So, because of environmental issues, the

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protocol was carried out using the reaction of stable arenediazonium nano-magneto silica sulfates $(ArN_2^+ OSO_3 - SiO_2 @Fe_3O_4)$ with carbon disulfide and a secondary aliphatic amine without the need of any transition metal in water at room temperature in a short reaction time (Scheme 1).

 $Fe_3O_4@SiO_2-SO_3H$ was prepared according to our previously reported procedure with some modification.²⁷ The X-ray diffraction (XRD) pattern of Fe_3O_4 , $Fe_3O_4@SiO_2$ and $Fe_3O_4@SiO_2-SO_3H$ are depicted in Fig. 1. The XRD pattern of Fe_3O_4 clearly matches well with the literature data.²⁹ Six peaks at 30.24, 35.60, 43.24, 53.7, 57.6 and 62.8 can be assigned to the (220), (311), (400), (422), (511) and (440) planes of Fe_3O_4 that indexed to the crystalline cubic inverse spinal structure of MNPs. The crystallite size of the nanoparticles was calculated to be around 10 nm from the XRD results using the Debye-Scherrer equation.

In the XRD pattern of $Fe_3O_4@SiO_2$ the same peaks were also observed, and in addition the broad peak at 2 = 12.5 is referred to amorphous silica. Notably, the same peaks were also revealed in XRD spectra of $Fe_3O_4@SiO_2-SO_3H$, which indicate the structural stability of MNPs after modification with chlorosulfonic acid.

The morphology and structure of the prepared samples were characterized by FE-SEM. Figure 2a shows that the Fe₃O₄ MNPs are spherical in shape, and it has a marked tendency to form large clusters. Fig. 2b shows that the Fe₃O₄@SiO₂ nanoparticles are spherical with larger particle size and smoother surface. The SEM images of Fe₃O₄@SiO₂-SO₃H demonstrate that there is no change in the shape of MNPs after being functionalized with sulfonic acid and also the surface morphology being retained (Fig. 2c).

In order to optimize the reaction condition, as a model reaction, aniline (1 mmol) was homogenized by mixing 0.8 g of $Fe_3O_4@SiO_2-SO_3H$ and 0.2 mL water into a mortar with a

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pestle until the aniline had disappeared as monitored by TLC. Then sodium nitrite (2 mmol) was added with continues grinding; the diazotation proceeded in few minutes and stable phenyldiazonium nano-magneto silica sulfate was prepared (Scheme 1, step 1). Next, the stable phenyl nano-magneto silica sulfate was added to a suspension of piperidine (1.2 mmol) and carbon disulfide (2.5 mmol) in 3 mL water. The mixture was then stirred at room temperature for 10 min. After the completion of the reaction, the crude product was extracted with ethyl acetate and Fe₃O₄@SiO₂-SO₃H simply separated with an external magnet. The solvent was evaporated and the raw product was purified by flash chromatography.

Further studies revealed that 0.8 g Fe₃O₄@SiO₂-SO₃H that equals to 0.25 mmol H⁺ loading was sufficient to generate ArN_2^+ -OSO₃-SiO₂@Fe₃O₄ in high yield. The usage of lower amounts of nano-magnetic reagent reduced the yield of arenediazonium salts.

The scope of this convenient procedure was investigated using diversely substituted aromatic amines. The results are summarized in Table 1. The stable arenediazonium nanomagneto silica sulfates were formed in short reaction times of 5-10 min. Then, they underwent reactions with carbon disulfide and a secondary aliphatic amine to produce the corresponding products. A broad range of *S*-aryl dithiocarbamates was thus synthesized in good to excellent yields. Both electron-donating (Table 1, entries 4-11) and electron-withdrawing (Table 1, entries 12-16) substrates gave similar high yields. The *ortho-* and *meta-*substituents also provided good results (Table 1, entries 12, 13).

Based on the literature reports,^{25,37} and considering the substituent effect, we can outline a $S_N 2Ar$ reaction pathway for the preparation of *S*-aryl dithiocarbamates (Scheme 2). In the first step, **I** could be formed from the diazotization of aniline derivatives in the presence of wet

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Fe₃O₄@SiO₂-SO₃H and NaNO₂. Nano-magneto silica sulfate as a bulky counter ion with high surface not only increases the stability of the diazonium salts but also increases the reaction rate, so that these salts can be used under mild conditions.³⁴⁻³⁷ Then, it is thought that the *in situ*-generated dithiocarbamate unit (II) attacks C-1 of the aryldiazonium magneto silica sulfate to form the transient intermediate III, which through elimination of N₂ forms the *S*-aryl dithiocarbamates.

In an attempt to study the stability of arenediazonium silica sulfate salts, the reaction condition was investigated for the model reaction after the time specified in Table 2. As shown in Table 2, the addition of dithiocarbamate to the stored diazonium sulfate salts (stored in a desiccator at room temperature) provided almost the same yield of the product as that from freshly prepared salt. Obviously, because of the instability of aryl cations, the arenediazonium salts with electron-withdrawing groups are more stable than those with electron-donating groups.³⁸

To demonstrate the efficiency of the present protocol for the synthesis of *S*-aryl dithiocarbamates, we compared it with the previously published procedures. The results summarized in Table 3 show that this methodology is superior to others in terms of reaction time, readily available starting materials, avoidance of the use of toxic solvent, and simple procedure.

CONCLUSION

In summary, a new methodology for the synthesis of synthetically important S-aryl thiocarbamates in a green protocol has been developed. For the first time, nano-Fe₃O₄@SiO₂-SO₃H was employed as a nanomagnetic heterogeneous Brønsted acid, in the synthesis of stable

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diazonium salts and afterwards, the transition-metal-free C-S bond formation. The promising points for the presented protocols are simple procedure, short reaction time at ambient temperature, use of stable and readily available starting material without requirement of any metal, ligand or organic solvent, which makes this procedure better alternative to existing ones.

EXPERIMENTAL

Chemical reagents in high purity were purchased from Merck and Aldrich and were used without further purification. Melting points were determined in open capillaries using an Electrothermal 9100 without further corrections. ¹H NMR and ¹³C NMR spectra were recorded using a Bruker DRX-400 spectrometer at 400 and 100 MHz respectively. FT-IR spectra were obtained with KBr pellets in the range of 40064000 cm⁻¹ using a Shimadzu 8400s spectrometer. The elemental analysis (C, H, N) was performed on a Perkin-Elmer CHN analyzer, 2400 series II. The purity of the compounds synthesized was monitored by TLC on commercial aluminumbacked plates of silica gel 60 F254, visualizing with ultraviolet light. X-Ray diffraction (XRD) was detected by Bruker D4 ENDEAVOR X-ray diffractometer using Cu-K_{α} radiation of wavelength 1.54Å. Scanning electron Microscopy, SEM, analysis was performed using Tescan vega II XMU Digital Scanning Microscope. Samples were coated with gold at 10 mA for 2 min prior to analysis. The Supplemental Materials contains sample ¹H NMR spectra for some products (Figures S 1 6 S 6)

Preparation of nano magneto silica sulfuric acid

The Fe₃O₄@SiO₂óSO₃H was prepared in accordance to our earlier report.²⁷

Typical procedure for the synthesis of 4-nitro-phenyl piperidine-1-carbodithioate (14a).

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4-Nitroaniline (0.13 g, 1 mmol) was homogenized by mixing of Fe₃O₄@SiO₂-SO₃H (0.8 g) and water (0.2 mL) into a mortar with a pestle. Next, NaNO₂ (0.136 g, 2 mmol) was added and grinding was continued *mildly* for 8 min (as monitored by TLC), until the aromatic amine had disappeared. 4-Nitrophenyl nano-magneto silica sulfate was added to a freshly prepared solution of dithiocarbamic acid. [The dithiocarbamic acid was prepared in a separate vessel by drop-wise addition of piperidine (0.102 g, 1.2 mmol) to a suspension of CS_2 (0.19 g, 2.5 mmol) in water (3 mL) at 0-5 °C for 5 min]. The mixture was stirred at room temperature for 15 min (Table 1). After completion of the reaction, EtOAc (10 mL) was added to the reaction mixture. The nano magnetic reagent was simply separated by an external magnet and the organic layer was dried over anhydrous Na₂SO₄. After evaporation of the solvent, the crude product was purified by flash chromatography (n-hexane: EtOAc, 95:5). 14a was obtained as a yellowish solid (0.25 g, 95%). M.p.: 158-159 °C; IR: 2943, 2856, 1582, 1531, 1350 cm⁻¹; ¹H NMR (CDCl₃): 1.77 (6H, s), 4.00 (2H, s, br), 4.28 (2H, s, br), 7.62-7.66 (2H, m), 8.19-8.27 (2H, m); ¹³C NMR (CDCl₃): 25.38, 53.72, 56.87, 123.9, 125.6, 136.5, 137.8, 139.0, 148.8, 193.6; Anal. calcd. for C₁₂H₁₄N₂O₂S₂: C, 51.06; H, 4.96; N, 9.92; Found: C, 51.21; H, 4.71; N, 10.06.

Reusability of catalyst

After the completion of a reaction, the nano magnetic reagent was removed by use of an external magnet, washed exhaustively with diethyl ether and methanol and dried at 90° C for 1h. It could be reused in subsequent reactions after treating it with the appropriate amount of chlorosulfonic acid.

Acknowledgment

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Product		Time Diazotization/C-S bond formation/min	Yield/% ^a	M.p./°C (Lit.)
1a	S S S	5/10	87	113-116 (113-116) ²⁶
2a	S S	5/12	80	93-95 (93-94) ²⁶
3a	S S S	5/12	71	44-46 (44-45) ²⁶
4 a	H ₃ C S N	5/15	87	118-120 (118-119) ²⁵
5a	H ₃ C S N	5/15	82	131-132 (131-133) ²⁵
6a	H ₃ C	5/20	79	111-112 (111-112) ²⁵
7a	H ₃ C	5/17	78	76-78(75-76) ²⁵
8a	H ₃ CO S S	5/15	85	101-102 $(102-103)^{25}$
9a	H ₃ CO S N	5/15	88	133-135 (133-135) ²⁵
10a	H ₃ CO S N	5/12	75	91-93(92-93) ²²

 Table 1. Synthesis of S-aryl dithiocarbamates.

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^a The yield is based on the aniline starting material

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Diazonium salt	Immediately	After 12	After 24	After 48
		h(%)	h(%)	h(%)
$\operatorname{Fe_3O_4}@\operatorname{SiO_2}-\operatorname{SO_3}^-+\operatorname{N_2}$	87	87	81	69
$\operatorname{Fe_3O_4@SiO_2-SO_3^-+N_2}$ NO ₂	95	95	89	80
$\operatorname{Fe_3O_4@SiO_2-SO_3^-+N_2}$ OMe	85	85	78	63

Table 2.	The stability	v of nano-n	nagnetic	arenediazo	nium s	silica	sulfate	salts a	t room	temperature.	a
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^a materials: diazonium salt, piperidine, carbon disulfide.

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Table 3. Comparison of published procedures for synthesis of S-aryl dithiocarbamtes with this

work

Entry	Substrates	Reaction conditions	Time	Yield (%)
1^{26}	ArI, CS ₂ , HNR ₂	Nano-Cu, H ₂ O, Reflux	8-9 h	75-94
2^{25}	ArN ₂ ⁺ ⁻ BF ₄ , CS ₂ , HNR ₂	H_2O , r.t.	3 h	74-94
3 ²⁴	ArI, $R_2 NCS_2^- Na^+$	CuI, Ligand ^a , K ₂ CO ₃ , DMF, N ₂	22 h	71-95
4^{22}	$R_2NCS_2^-Na^+$, ArI^+ArX^-	<i>t</i> -BuOH, 70°C	4-18 h	46-86
5 ³⁹	ArN_2^+ $^-BF_4$, CS_2 , HNR_2	Basic alumina, ball milling	15-20 min	77-86
6 ⁴	ArI, $R_2NCS_2^-Na^+$	CuI, ligand ^a , DMF, 110 °C	22 h	55-90
7 ^b	ArNH ₂ , CS ₂ , HNR ₂	Fe ₃ O ₄ @SiO ₂ - SO ₃ H, NaNO ₂ , H ₂ O, r.t.	15-32 min	75-95

^a N,N-dimethylglycine

^b This work

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Figure 1. XRD patern of (a) Fe_3O_4 (b) Fe_3O_4 @SiO₂ and (c) Fe_3O_4 @SiO₂-SO₃H.

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Figure 2. The FE-SEM images of (a) Fe₃O₄ (b) Fe₃O₄@SiO₂ and (c) Fe₃O₄@SiO₂-SO₃H.

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Scheme 1. Steps of protocol

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Scheme 2. A plausible mechanism

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