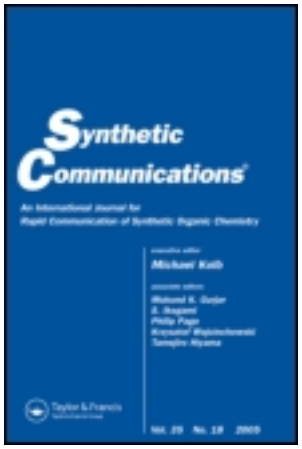

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2,2′-Azobenzothiazole as a New Recyclable Oxidant for Heterogeneous Thiocyanation of Aromatic Compounds with Ammonium Thiocyanate

Nasser Iranpoor [a], Habib Firouzabadi [a], Rezvan Shahin [a] & Dariush Khalili [a]

[a] Department of Chemistry, College of Sciences, Shiraz University, Shiraz, Iran

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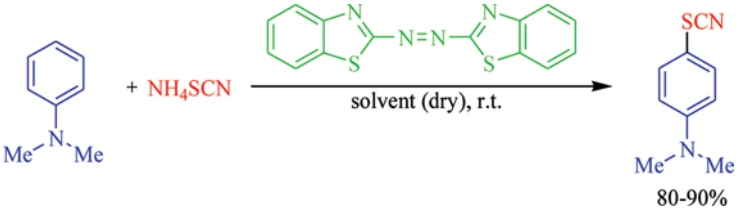
2,2′-AZOBENZOTHIAZOLE AS A NEW RECYCLABLE OXIDANT FOR HETEROGENEOUS THIOCYANATION OF AROMATIC COMPOUNDS WITH AMMONIUM THIOCYANATE

Nasser Iranpoor, Habib Firouzabadi, Rezvan Shahin, and Dariush Khalili

Department of Chemistry, College of Sciences, Shiraz University, Shiraz, Iran

GRAPHICAL ABSTRACT



Abstract *A simple synthesis of thiocyanated aromatics has been developed by using heteroaromatic azo compounds such as 2,2′-azobenzothiazole as a mild and heterogeneous oxidant. The reactions proceed at room temperature with good regioselectivity. The hydrazine by-product can be easily separated by filtration and recycled for further use.*

Keywords Aromatic compounds; azobenzothiazole; heterogeneous; thiocyanation

INTRODUCTION

Thiocyanation of aromatics and heteroaromatics is an important reaction in organic synthesis.[1] Aryl or heteroaryl thiocyanates are versatile intermediates in the synthesis of sulfur-containing heterocycles.[2] Moreover, aryl thiocyanates can be easily converted into various sulfur-bearing functionalities such as sulfides, aryl thioesters,[3a,b] and cyanothiolated compounds.[3c] Several methods for the thiocyanation of aromatic systems using a variety of reagents such as oxone,[4] iodine,[5] ferric chloride,[6] *N*-thiocyanatosuccinimide,[7] ceric ammonium nitrate,[8] acidic K-10 clay,[9] phenyliodine(III) bis(trifluoroacetate) (PIFA),[10] $PhICl_2$,[11] diacetoxyiodobenzene,[12] 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ),[13] iodic acid,[14] $Mn(OAc)_3$,[15] $Al_2O_3/MeSO_3H$,[16] I_2O_5,[17] and iodoxybenzoic acid (IBX),[18] have

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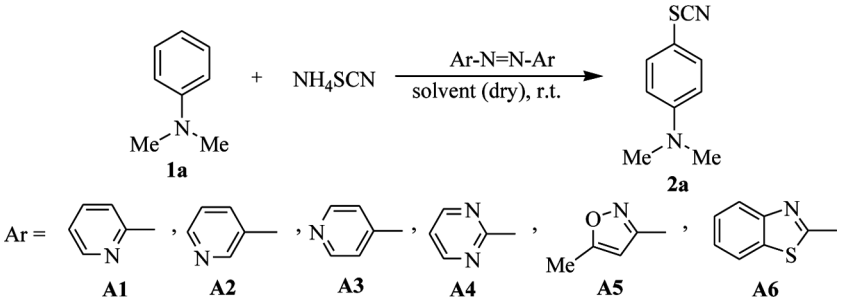
Address correspondence to Nasser Iranpoor or Habib Firouzabadi, Department of Chemistry, College of Sciences, Shiraz University, Shiraz 71454, Iran. E-mail: iranpoor@susc.ac.ir; firouzabadi@susc.ac.ir

been explored. Recently, we have reported on the use of diethylazodicarboxylate (DEAD) as an oxidant for this reaction.[19a] However, DEAD is explosive, photosensitive, toxic, shock sensitive, and thermally unstable.[19b] Because of these practical issues, there is a requirement to develop new efficient and simple routes for thiocyanation of aromatic and heteroaromatic compounds. In this context, we report a novel, simple, and efficient protocol for the thiocyanation of electron-rich arenes such as indoles, pyrrole, and aryl amines using NH_4SCN in conjunction with 2,2′-azobenzothiazole in CH_3CN at room temperature. This azo reagent has several advantages over the previous reagents and also DEAD including easy handling, simple synthesis, and heterogeneity. To have easily prepared oxidants, we first synthesized some heteroaromatic azo compounds **A1**–**A6**[20] and studied their applicability for thiocyanation of aromatic compounds. The reaction of *N,N*-dimethylaniline (1 eq) with ammonium thiocyanate (3 eq) in the presence of these azo compounds (**A1**–**A6**: 1.9 eq) at room temperature was chosen as a model reaction. Among these azo compounds, 2,2′-azobenzothiazole **A6** was found to be the most suitable oxidant for this reaction in acetonitrile (Table 1).

A major advantage of using 2,2′-azobenzothiazole **A6** is the heterogeneous nature of this azo and also its hydrazine, which facilitates the purification of the product. In addition, **A6** is readily prepared in one step by the treatment of 2-aminobenzothiazole with commercial sodium hypochlorite (aqueous 6–14%).[20a] The produced hydrazine (Fig. 1, **II**) can be easily removed by filtration and reoxidized to the original azo **A6** by oxidation with $PhI(OAc)_2$ in dimethylsufoxide (DMSO) at 60 °C. With the optimized reaction conditions in hand, we probed the scope of our reagent system for thiocyanation of various activated aromatic rings (Table 2).

Aniline (Table 2, entry 2) and some of its *N*-substituted derivatives (Table 2, entries 3–5) reacted efficiently with ammonium thiocyanate in the presence of

Table 1. Thiocyanation of *N,N*-dimethylaniline utilizing different heterocyclic azo compounds **A1**–**A6**



Entry	Azo	Yield of **2a** (%)[a]	Time (h)
1	**A1**	59	12
2	**A2**	45	12
3	**A3**	77	8
4	**A4**	60	5
5	**A5**	12	24
6	**A6**	87	2

[a]Isolated yields.

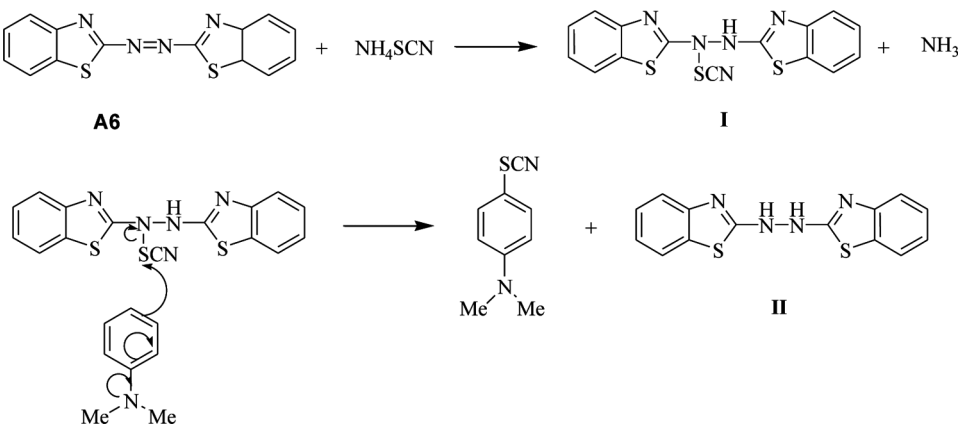
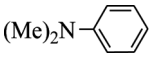
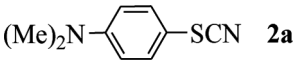
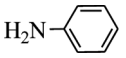
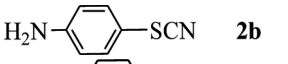
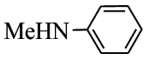
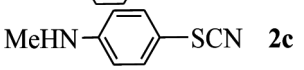
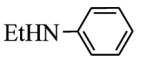
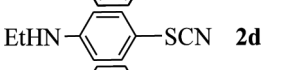
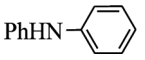
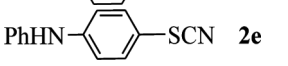
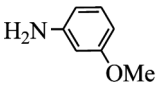
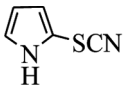
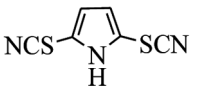
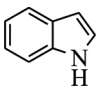
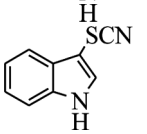
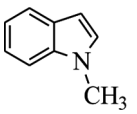
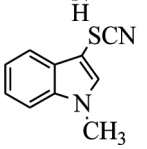
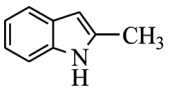
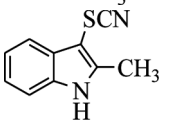
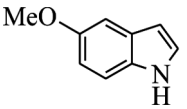
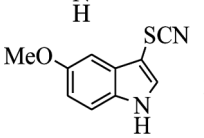
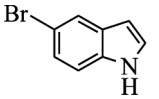
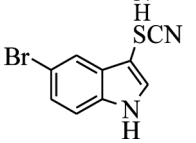
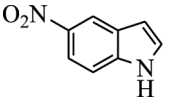
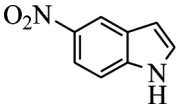


Figure 1. Proposed mechanism for the thiocyanation of aromatic amines with 2,2′-azobenzothiazole.

2,2′-azobenzothiazole **A6** and resulted in the formation of arene thiocyanates **2b–e** in good yields. Generation of ammonia in these reactions has no effect on the produced product. In the case of aryl amines **1a–e**, the products were obtained with excellent *para*-selectivity. Even under optimized condition, when 3-methoxyaniline **1f** was used, no reaction occurred and all the starting material was recovered after 24 h (Table 2, entry 6). Like *N,N*-dimethylaniline, pyrrole also afforded the corresponding 2-thiocyanatopyrroles **2g** in good yield (Table 2, entry 7). In the case of pyrrole, a minor amount of 2,4-dithiocyanatopyrrole **2g′** was formed, which increased with a longer reaction time. We also studied the conversion of indole (Table 2, entry 8) and its derivatives (Table 2, entries 8–13) to their corresponding thiocyanato indoles under similar reaction conditions. Substituted indoles such as *N*-methylindole (Table 2, entry 9), 2-methylindoles (Table 2, entry 10), 5-methoxyindole (Table 2, entry 11), 5-bromoindole (Table 2, entry 12), and 5-nitroindole predominantly gave the corresponding thiocyanato products. Indole with an electron-withdrawing group on the aryl ring affords a lesser product yield. Consistent with this observation, the product yield of 5-nitroindole is generally less than for 5-methoxyindole. No reaction took place when we used phenol and anisol as substrate (Table 2, entries 14 and 15). As in the present work, thiocyanation of aromatic amines with 2,2′-azobenzothiazole can be carried out under heterogeneous conditions, which provides easier workup, although its reactivity is comparable with those reagents that have been used for this reaction under homogeneous condition (Table 3).

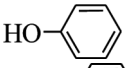
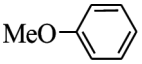
The proposed reaction mechanism is shown in Fig. 1. Addition of ammonium thiocyanate to azo **A6** produces the corresponding thiocyanato hydrazine **I**, and the red color of the reaction changes to dark green. In a subsequent reaction, aromatic amine reacts with **I** to furnish the end product together with the formation of hydrazine **II**. In addition to the formation of ammonia and isolation of the corresponding hydrazine **II**, to have more evidence in support of the proposed mechanism, we performed a ^{1}H and ^{13}C NMR study (in DMSO-d_6) of the reaction mixture of azo **A6** and ammonium thiocyanate prior to the addition of arene. The presence of the NH proton and N-S<u>C</u>N group at 8.46 ppm and 126.32 ppm supports the intermediacy of **I** in the proposed mechanism.

Table 2. Thiocyanation of activated arenes promoted by 2,2′-azobenzothiazole **A6** in the presence of NH_4SCN[a]

Entry	Arene	Product[b]	Time (h)	Yield (%)[c]
1	 **1a**	 **2a**	2[13b]	87
2	 **1b**	 **2b**	5[13b]	80
3	 **1c**	 **2c**	4[13b]	81
4	 **1d**	 **2d**	4[5]	85
5	 **1e**	 **2e**	5[5]	86
6	 **1f**	—	—	—
7[d]	 **1g**	 **2g**  **2g'**	5.5[13b]	80 5
8	 **1h**	 **2h**	2[8]	83
9	 **1i**	 **2i**	3[13b]	90
10	 **1j**	 **2j**	4.5[13b]	85
11	 **1k**	 **2k**	3[5]	83
12	 **1l**	 **2l**	5[13b]	80
13	 **1m**	 **2m**	6[9]	75

(*Continued*)

Table 2. Continued

Entry	Arene		Product[b]	Time (h)	Yield (%)[c]
14		**1n**	Unreacted starting material	—	—
15		**1o**	Unreacted starting material	—	—

[a]Molar ratio of arene: **A6**:NH_4SCN was 1:1.9:3.
[b]All the products are known compounds and were identified from their spectral data and comparison with known samples.
[c]Isolated yields.
[d]After 18 h, the *bis*-adduct was obtained in 12% yield.

In summary, we have developed a simple, convenient, and efficient protocol for the preparation of aryl and hetero aryl thiocyanates. The use of 2,2′-azobenzothiazole as a new, stable, and heterogeneous oxidant provides mild conditions for the regioselective electrophilic thiocyanation of aromatic and hetero-aromatic amines at room temperature. The simple preparation of this oxidant and ease of removal with the possibility of reoxidation of the produced hydrazine can be considered as other advantages of this system.

EXPERIMENTAL

All the solvents and reagents were purchased from Fluka or Merck chemical companies. The products were purified by column or prepartory thin-layer chromatographic (TLC) techniques and identified by comparison of their spectral data with those of known compounds. Fourier transform infrared (FTIR) spectra were recorded on a Shimadzu DR-8001 spectrometer. NMR spectra were recorded on a Brucker Avance DPX 250-MHz instrument. Elemental analyses were determined in our department using a ThermoFinnigan Flash EA 1112 series instrument.

Typical Procedure

The arene (1.0 mmol, 0.12) was added slowly in a dropwise manner to a stirred solution of ammonium thiocyanate (3 mmol, 0.23 g), and 2,2′-azobenzothiazole

Table 3. Comparison of the reactivity of 2,2′-azobenzothiazole for heterogeneous thiocynation of *N,N*-dimethylaniline and homogeneous thiocyanation using some other reagents

Entry	Oxidant	Condition	Time	Yield (%)	Reference
1	2,2′-Azobenzothiazole	Rt/CH_3CN	2 h	87	This work
2	DEAD	Rt/CH_3CN	1.5 h	81	19a
3	$PhI(OAc)_2$	Rt/CH_3CN	2 h	78	12
4	I_2	Rt/MeOH	20 min.	87	5
5	CAN	Rt/MeOH	15 min.	75	8
6	DDQ	Sonication/MeOH	15 min.	95	13b

(1.9 mmol, 0.56 g) in dry CH_3CN (5 mL), and the mixture was stirred at room temperature for the appropriate time (Table 2). After completion of the reaction as indicated by TLC (2 h), the reaction mixture was filtered to remove the hydrazine by-product. Evaporation of the filtrate and flash chromatography with EtOAc/*n*-hexane (1:5) gave *N,N*-dimethyl-4-thiocyanatoaniline **2a** in 87% yield (0.15 g).

Compound 2a

Mp 73–74 °C lit.[12b] 71–72 °C IR (KBr, cm^{-1}): 2158 (SCN). ^1H NMR (250 MHz, $CDCl_3$) δ: 7.33 (d, 2H, $J = 5.4$ Hz), 6.60 (d, 2H, $J = 5.5$ Hz), 2.91 (s, 6H). ^{13}C NMR (62.9 MHz, $CDCl_3$) δ: 151.6, 134.5, 113.1, 112.8, 106.7, 40.1. Anal. calcd. for $C_9H_{10}N_2S$: C, 60.64; H, 5.65; N, 15.72%. Found: C, 61.02; H, 5.11; N, 16.12%.

4-Thiocyanatoaniline (2b)

IR (KBr, cm^{-1}): 3366 (NH_2), 2145 (SCN). ^1H NMR (250 MHz, $CDCl_3$) δ: 7.43 (d, 2H, $J = 8.5$ Hz), 6.71 (d, 2H, $J = 8.5$ Hz), 3.94 (br, s, 2H, NH_2). ^{13}C NMR (62.9 MHz, $CDCl_3$) δ: 148.9, 133.5, 116.8, 112.4, 109.4. Anal. calcd. for $C_7H_6N_2S$: C, 55.97; H, 4.03; N, 18.65%. Found: C, 56.20; H, 4.19; N, 18.47%.

4-Thiocyanato-*N*-methylaniline (2c)

IR (KBr, cm^{-1}): 3380 (NH), 2140 (SCN). ^1H NMR (250 MHz, $CDCl_3$) δ: 7.35 (d, 2H, $J = 8.6$ Hz), 6.63 (d, 2H, $J = 8.6$ Hz), 4.09 (br, s, 1H, NH), 2.80 (s, 3H). ^{13}C NMR (62.9 MHz, $CDCl_3$) δ: 150.4, 131.7, 117.2, 115.0, 112.6, 29.8. Anal. calcd. for $C_8H_8N_2S$: C, 58.51; H, 4.91; N, 17.06%. Found: C, 58.75; H, 4.63; N, 17.42%.

3-Thiocyanato-1*H*-indole (2h)

IR (KBr, cm^{-1}): 3315 (NH), 2159 (SCN). ^1H NMR (250 MHz, $CDCl_3$) δ: 8.96 (br, s, 1H, NH), 7.81 (1H, d, $J = 9.1$ Hz), 7.43–7.28 (4H, m). ^{13}C NMR (62.9 MHz, $CDCl_3$) δ: 136.1, 131.3, 127.7, 123.8, 121.8, 118.6, 112.3, 112.1, 91.6. Anal. calcd. for $C_9H_6N_2S$: C, 62.05; H, 3.47; N, 16.08%. Found: C, 62.41; H, 3.17; N, 15.78%.

1-Methyl-3-thiocyanato-1*H*-indole (2i)

IR (KBr, cm^{-1}): 2148 (SCN). ^1H NMR (250 MHz, $CDCl_3$) δ: 7.81 (d, 1H, $J = 8.5$ Hz), 7.45–7.38 (m, 4H), 3.80 (s, 3H). ^{13}C NMR (62.9 MHz, $CDCl_3$) δ: 136.9, 133.0, 128.6, 122.3, 121.9, 120.8, 113.1, 112.3, 88.4, 37.1. Anal. calcd. for $C_{10}H_8N_2S$: C, 63.80; H, 4.28; N, 14.88%. Found: C, 63.56; H, 4.48; N, 14.79%.

2-Methyl-3-thiocyanato-1*H*-indole (2j)

IR (KBr, cm^{-1}): 3326 (NH), 2139 (SCN). ^1H NMR (250 MHz, $CDCl_3$) δ: 8.48 (br, s, 1H, NH), 7.82 (d, 1H, $J = 7.5$ Hz), 7.35 (d, 1H, $J = 7.63$ Hz), 7.29–7.20 (m, 2H), 2.62 (s, 3H). ^{13}C NMR (62.9 MHz, $CDCl_3$) δ: 138.4, 135.0, 128.6, 123.1,

120.8, 119.5, 112.2, 111.4, 86.6, 12.5. Anal. calcd. for $C_{10}H_8N_2S$: C, 63.80; H, 4.28; N, 14.88%. Found: C, 64.00; H, 4.07; N, 14.66%.

5-Methoxy-3-thiocyanato-1*H*-indole (2k)

IR (KBr, cm^{-1}): 3304 (NH), 3138, 2150 (SCN). ^1H NMR (250 MHz, $CDCl_3$) δ: 8.77 (br, s, 1H, NH), 7.42 (d, 1H, $J = 2.4$ Hz), 7.29 (d, 1H, $J = 8.5$ Hz), 7.14 (d, 1H, $J = 2.1$ Hz), 6.97 (dd, 1H, $J = 8.5$ Hz, $J = 2.8$ Hz), 3.93 (s, 3H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ: 157.1, 131.9, 130.5 127.9, 114.0, 113.0, 112.1, 98.9, 93.5, 55.5. Anal. calcd. for $C_{10}H_8N_2OS$: C, 58.80; H, 3.95; N, 13.72%. Found: C, 58.49; H, 3.76; N, 14.03%.

5-Bromo-3-thiocyanato-1*H*-indole (2l)

IR (KBr, cm^{-1}): 3318 (NH), 2135 (SCN). ^1H NMR (250 MHz, $CDCl_3$) δ: 8.69 (br, s, 1H, NH), 7.90 (s, 1H), 7.53 (d, 1H, $J = 2.8$ Hz), 7.37 (dd, 1H, $J = 8.5$, 1.6 Hz), 7.26 (d, 1H, $J = 8.5$ Hz). ^{13}C NMR (62.9 MHz, $CDCl_3$) δ: 137.7, 132.8, 129.5, 127.6, 123.1, 117.1, 113.8, 112.5, 93.4. Anal. calcd. for $C_9H_5BrN_2S$: C, 42.71; H, 1.99; N, 11.07%. Found: C, 42.55; H, 2.12; N, 11.30%.

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