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Ammonium metavanadate/thiocyanate-triggered electrophilic thiocyanation of aromatic and heteroaromatic compounds in aqueous bisulfate and acetonitrile media

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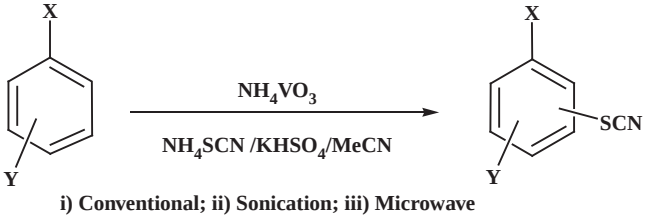
The ammonium metavanadate/thiocyanate system is used as an efficient reagent for regioselective thiocyanation of aromatic and hetero aromatic compounds under conventional and nonconventional conditions such as ultrasonically assisted and microwave-assisted reactions. The reactions proceeded smoothly and afforded good yields of products with high regioselectivity. Longer reaction times (about 8 h) observed under conventional conditions were reduced to 0.5 h/30 min under sonication and to 90 s in the case of microwave-assisted reactions.



i) Conventional; ii) Sonication; iii) Microwave
Where X = OH, NH_2, COOH, $COCH_3$, CHO
Y = EWG or EDG

Keywords: ammonium metavanadate; potassium thiocyanate; regioselective thiocyanation; sonication; microwave irradiation

1. Introduction

Thiocyanation of aromatic and heteroaromatic compounds is one of the most useful electrophilic substitution reactions in organic synthesis and provides a direct route for the formation of carbon–sulfur bonds despite the fact that nucleophilic attack of thiocyanate ion at aromatic nuclei is a difficult route to form thiocyanate compounds. The thiocyanate functional group is an interesting variant of organic thiocompounds because they can be readily transformed into pharmaceutically important entities.[1–5] This particular aspect has become the stimulus for the development of simple, safe, and fast synthetic protocols for the synthesis of thioaromatic systems.[6–17] Recently, Sajadifar and co-workers developed simple regioselective thiocynation protocols using H_2O_2,

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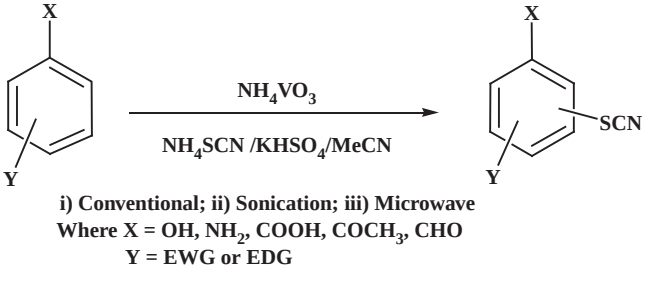
H_5IO_6, or silica boron sulfonic acid/hydrogen peroxide in the presence of Potassium thiocyanide (KSCN).[16,17] These procedures provided the target thiocyanate derivatives in short duration followed by good to excellent yields and high regioselectivity. However, some of these methods still suffer from the disadvantages such as the use of strongly acidic or oxidizing conditions, low yields, long reaction time and/or high temperature, and also the use of expensive reagents. These reasons together with the versatility of the thiocyanide (SCN) functionality stimulated us to take up the present study in which laboratory desktop chemicals such as ammonium metavanadate (NH_4VO_3) and ammonium thiocyanate (NH_4SCN) are used to achieve thiocyanation of aromatic and hetero aromatic compounds. In order to attain greenery of the study, we have used potassium hydrogen sulfate ($KHSO_4$) as a catalyst, because it has received considerable attention in several organic protocols as an inexpensive, eco friendly, highly reactive, easy to handle and non-toxic substance. Baghernejad's recent review[18] on this aspect provides an excellent literature survey on the use of $KHSO_4$ as a solid catalyst. Since preliminary results indicated longer reaction times, efforts were also made to increase the rate of the reactions. The success and advantages of ultrasound-assisted,[19–24] and microwave-assisted chemical reactions,[25–28] reported in earlier investigations prompted us to explore their utility in the present study to achieve effective thiocyanation.

2. Results and discussion

The thiocyanation of aromatic compounds with ammonium metavanadate (NH_4VO_3) as a catalyst in the presence of (0.10 mol) ammonium thiocyanate and $KHSO_4$ afforded thiocyanate derivatives in very good yield (Scheme 1).



Scheme 1. Thiocyanation of aromatic compounds in the presence of NH_4VO_3.

The reaction has been conducted using different concentrations of NH_4VO_3 (0.001–0.01 mol) in different solvents such as dichloromethane (DCM), dichloroethane (DCE), and acetonitrile (MeCN), in order to optimize the conditions. Table 1 shows reaction times and percentage (%) yields of thiocyanation of phenol under different reaction conditions. The reaction went smoothly in DCE when 0.005 mmol of NH_4VO_3 was used as a catalyst. Consequently, 0.001 mol of NH_4VO_3 is used throughout the study.

We have also performed control experiments under different conditions: (i) using $KHSO_4$ but excluding NH_4VO_3 and (ii) using NH_4VO_3 but excluding $KHSO_4$. In both cases the reactions were too sluggish even under drastic conditions. Practically no trace of the product was observed in these two cases.

A wide range of active, moderately active, and non-active aromatic compounds and heterocyclic compounds were chosen for thiocyanation under conventional and non-conventional conditions and the corresponding results are presented in Table 2. The data revealed that thiocyanation of aromatic compounds occurred smoothly with good regioselectivity and yields in the presence

Table 1. Effect of solvent and NH_4VO_3 on thiocyanation of phenol under conventional conditions.

S. No.	Solvent	NH_4VO_3 (mol)	Time (h)	Yield (%)
		0.001	6–8	75
		0.002	6–8	70
1	ACN	0.005	6–8	75
		0.01	6–8	75
		0.001	12–14	50
		0.002	12–14	55
2	DCE	0.005	12–14	60
		0.01	12–14	60
		0.001	12–14	50
3	DCM	0.002	12–14	55
		0.005	12–14	55
		0.01	12–14	55

Table 2. Ultrasonic and microwave-assisted thiocyanation of certain aromatic and heteroaromatic compounds using ($KHSO_4/NH_4VO_3/NH_4SCN$) in MeCN.

			Conventional (6–8 h)	Sonication (30–45 min)	MWAR (5–7 min)
S. No.	Substrate	Product	Yield (%)	Yield (%)	Yield (%)
1	Phenol	2-Thiocyanatophenol	75	77	80
2	*o*-Cresol	2-Methyl-4-thiocyanatophenol	79	82	83
3	*m*-Eresol	3-Methyl-4-thiocyanatophenol	79	80	80
4	4-Bromophenol	4-Bromo-2-thiocyanato-phenol	66	70	74
5	Aniline	4-Thiocyanatoaniline	78	79	80
6	*o*-Chlorophenol	2-Chloro- 4-thiocyanatoaniline	80	83	85
7	*m*-Methoxy-aniline	3-Methoxy-4-thiocyanato-aniline	79	80	80
8	N-Methylaniline	4-Thiocyanato-N-methylaniline	79	79	80
9	N,N-dimethylaniline	4-Thiocyanato-N,N-dimethylaniline	79	82	83
10	N,N-diethylaniline	4-Thiocyanato-N,N-diethylaniline	75	78	82
11	Diphenylamine	4-Thiocyanatodiphenylamine	69	73	76
12	Diphenylamine	Dithiocyanatodiphenylamine	80	83	87
13	Indole	3-Thiocyanato-1H-indole	75	78	86
14	1-Methyl-indole	1-Methyl-3-thiocyanatoindole	72	74	77
15	5-Bromo-indole	5-Bromo-3-thiocyanatoindole	85	86	86
16	Pyrrole	2-Thiocyanato-1H-pyrrole	77	79	81
17	Pyrrole	2,5-Dithiocyanato-1H-pyrrole	17	15	10
18	Thiophene	2-Thiocyanatothiophene	78	81	83
19	1-Methoxy naphthalene	1-Methoxy-4-thiocyanatonaphthalene	82	79	80
20	N-Methyl-indole	3-Thiocyanato-N-methyl-indole	80	78	79

of NH_4VO_3, but are associated with longer reaction times (8–12 h). It is of interest to note that *para*-substituted compounds underwent thiocyanation only at the *ortho* position, while *ortho*-substituted compounds afforded the para derivative in a very good yield. Even though, benzene failed to undergo thiocyanation; it is also of interest to note that aromatic hydrocarbons, such as α-methoxynaphthalene, underwent smooth thiocyanation with fairly good yields. When this protocol is extended to carbonyl compounds, thiocyanation went smoothly without oxidation or any other side reaction. The reaction was clean with no attack observed on the alkyl portion of the ketones. To further check the regioselectivity of the reaction, the reaction was carried out with different para-substituted aromatic carbonyl and related compounds, which afforded only *meta* thiocyanate products in good yields.

In an attempt to enhance the rates of the reactions they were also conducted with nonconventional activation techniques, such as ultrasonically assisted and microwave-assisted methods.

Ultrasonically assisted reactions (USAR) and microwave-assisted reactions (MWAR) have become popular with physical and organic chemists because of their immense importance to promote and enhance a broad spectrum of synthetic organic reactions.[25–28] The use of these non-traditional tools has been found to be of great help in overcoming most of the difficulties associated with conventional reactions related to their environmental shortcomings. We were extremely pleased to discover that all of the reactions underwent dramatic rate enhancements. In addition, the kinetically enhanced reactions maintained their desirable selectivity and ease of experimental manipulation. The reaction times were reduced from 8 to 12 h (under conventional conditions) to about 30–45 min in USA reactions and about 5–7 min in MWA reactions.

Rate accelerations of the ultrasonically assisted thiocyanation reactions (USNR) in the present study are due to cavitation, a physical process that creates, enlarges, and implodes gaseous and vaporous cavities in an irradiated liquid.[19–24] Cavitation is a process in which mechanical activation destroys the attractive forces of molecules in the liquid phase. Applying ultrasound, compression of the liquid is followed by rarefaction (expansion), in which a sudden pressure drop forms small, oscillating bubbles of gaseous substances. These bubbles expand with each cycle of the applied ultrasonic energy until they reach an unstable size; they can then collide and/or violently collapse. Cavitation induces very high local temperatures in the liquid and enhances mass transfer.

On the other hand, the observed rate and yield enhancements in MWA reactions [28] are probably due to a combination of thermal effects, arising from the heating rate, superheating or 'hot spots', and the selective absorption of radiation by polar substances, which ultimately causes bulk activation of molecules. It is important to note that the rate of the reaction has a direct dependence on the fraction of activated/energized species.

3. Conclusion

In summary, the authors have developed ammonium metavanadate/thiocyanate as an efficient reagent to trigger electrophilic thiocyanation of aromatic and heteroaromatic compounds in aqueous bisulfate medium under conventional and nonconventional, such as ultrasonically assisted (USA) and micro wave-assisted (MWA), conditions. These newly developed methods have several advantages such as the use of water as solvent, simple workup procedure, good selectivity, short reaction times, and high product yields. The longer reaction times of conventional methods (6–8 h) were remarkably reduced to about 30–45 min in sonicated and (5–7 min) in MW-assisted reactions.

4. Experimental

4.1. *General*

Chemicals were obtained from S.D fine Chemicals (India), Avra fine Chemicals (India), and Aldrich Chemical Company and used without further purification.

4.2. *A typical procedure*

In a typical experiment, a suspension of phenol (0.1 mol), ammonium metavanadate (0.001 mol), ammonium thiocyanate (0.1 mol), and aqueous $KHSO_4$ (0.1 mol), in about 20 mL solvent (MeCN) was stirred at room temperature. The progress of the reaction was monitored by thin-layer chromatography (TLC) (ethyl acetate:*n*-hexane 1:9). After completion of the reaction, the reaction

mixture was treated with DCE and dried over anhydrous Na_2SO_4 and concentrated to obtain the end product. The products were identified by IR, ^{1}H NMR, and MS spectra. IR spectra showed the characteristic peaks of the –SCN group between 2120 and 2150 cm^{-1} and the C–S stretching between 650 and 750 cm^{-1}. The regio-chemistry of substitution was deduced by interpretation of ^{1}H NMR spectra and by their comparison with the spectral and physical data of those of authentic samples.[4–18,29–34] Mass and ^{1}H NMR data for typical examples are given below:

Spectroscopic data of representative compounds

(1) *2-Thiocyanato phenol*: ^{1}H NMR ($CDCl_3$): δ 7.14 (d, $J = 8.1$ Hz, 1H), 6.73 (m, $J = 7.9$ Hz, 2H), 6.54 (d, $J = 8.1$ Hz, 1H), 4.83 (s, 1H), m/z = 151.

(2) *2-methyl-4-thiocyanato-phenol*: ^{1}H NMR ($CDCl_3$): δ 6.63–7.24 (m, 3H), 6.13 (brs, 1H), 3.26 (s, 3H), m/z = 165 (mp 70–74°C).

(3) *3-methyl-4-thiocyanato-phenol*: ^{1}H NMR ($CDCl_3$): δ 7.13 (d, $J = 7.9$ Hz, 1H), 6.93 (m, 2H), 4.84 (s, 1H), 2.32 (s, 1H), m/z = 165.

(4) *4-bromo-2-thiocyanato-phenol*: ^{1}H NMR ($CDCl_3$): δ 7.22 (s, 1H), 7.03 (d, $J = 8.1$ Hz, 1H), 6.53 (d, $J = 8.1$ Hz, 1H), 4.84 (s, 1H) m/z = 230.

(5) *4-Thiocyanatoaniline*: ^{1}H NMR ($CDCl_3$): δ 7.38 (d, $J = 8.7$ Hz, 2H), 6.66 (d, $J = 8.7$ Hz, 2H), 3.94 (brd s, 2H), ^{13}C NMR (75 Hz, $CDCl_3$): δ 148.7, 134.3, 116.1, 112.3, 109.5, m/z = 150 (m.p.51–54°C.)

(6) *2-Choloro-4-thiocyanatoaniline*: ^{1}H NMR ($CDCl_3$): δ 7.52 (d, $J = 8.2$ Hz, 2H), 7.26 (dd, $J = 8.1$ Hz, 1H), 6.76 (d, $J = 8.2$ Hz, 1H), 4.37 (brd s, 2H). m/z = 184 (m.p. 59–61°C).

(7) *3-Methoxy-4-thiocyanatoaniline*: ^{1}H NMR ($CDCl_3$): δ 7.29 (d, $J = 8.3$ Hz, 1H), 6.28 (dd, $J = 8.3$ Hz, 1H), 6.24 (d, $J = 8.2$ Hz, 1H), 3.98 (s, 2H), 3.87 (s, 3H). m/z = 180 (m.p. 99–101°C)

(8) *4-Thiocyanato-N-methylaniline*: ^{1}H NMR ($CDCl_3$): δ 7.37 (d, $J = 8.64$ Hz, 2H), 6.59 (d, $J = 8.68$ Hz, 2H), 4.11 (brd s, 1H), 2.85 (s, 3H). m/z = 164.

(9) *4-Thiocyanato-N, N-dimethylaniline*: ^{1}H NMR ($CDCl_3$): δ 7.44 (d, $J = 8.8$ Hz, 2H), 6.66 (d, $J = 8.8$ Hz, 2H), 3.02 (s, 6H), ^{13}C NMR (75 MHz, $CDCl_3$): 151.5, 134.3, 113.2, 112.9, 106.4, 40.2. m/z = 178 (m.p. 72–74°C).

(10) *4-Thiocyanato-N, N-diethylaniline*: ^{1}H NMR ($CDCl_3$): δ 7.5–7.35 (m, 2H), 7.2–7.11 (m, 1H), 6.62–6.60 (m, 1H), 3.38 (q, $J = 7.12$ Hz, 4H), 1.16 (t, $J = 5.4$ Hz, 6H). ^{13}C NMR($CDCl_3$): δ 149.2, 134.8, 125.3, 121.6, 112.8, 44.7, 12.3 (m/z) = 206 (M+) (mp 82–84°C).

(11) *4-Thiocyanatodiphenylamine*: ^{1}H NMR ($CDCl_3$): δ 7.43 (d, $J = 8.1$ Hz, 2H), 7.34 (t, $J = 8.2$ Hz, 2H), 7.14 (d, $J = 8.1$ Hz, 2H), 7.08 (t, $J = 8.2$ Hz, 1H), 7.03 (d, $J = 8.2$ Hz, 2H), 5.94 (brd s, 1H). m/z = 226 (m.p. 62–63°C).

(12) *Dithiocyanatodiphenylamine*: ^{1}H NMR ($CDCl_3$): δ 7.49 (d, $J = 8.4$ Hz, 4H), 7.13 (d, $J = 8.4$ Hz, 4H), 6.09 (brd s, 1H). m/z = 283 (m.p. 110–111°C).

(13) *3-thiocyanato-1H-indole*: ^{1}H NMR ($CDCl_3$): δ 7.30 (m, 2H, $J = 9.9$ Hz, $J = 6.9$ Hz), 7.42 (m, 1H, $J = 9.9$ Hz, $J = 7.2$ Hz), 7.48 (d, 1H, $J = 3$ Hz), 7.09 (dd, 1H, $J = 5.7$ Hz, $J = 3$ Hz), 8.72 (br s, 1H), ^{13} C NMR (75 MHz, $CDCl_3$): δ 135.9, 131.1, 127.4, 123.7, 121.8, 118.5, 112.3, 112.1, 91.53. m/z = 174 (mp 72–73°C).

(14) *1-Methyl-3-thiocyanatoindole*: ^{1}H NMR ($CDCl_3$): δ 7.83–7.36 (m, 5H), 3.74 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 137.2, 135.2, 128.4, 123.4, 121.6, 118.8, 112.1, 110.3, 33.4 (m/z) = 188. mp 79–81°C.

(15) *5-Bromo-3-thiocyanatoindole*: ^{1}H NMR ($CDCl_3$): δ 8.87 (br s, 1H), 7.92–7.15 (m, 5H). ^{13}C NMR ($CDCl_3$): δ 134.6, 132.2, 129.3, 123.1, 121.2, 115.4, 113.7, 111.9, 102.2 (m/z) = 251($M = 1$), 253 (M + 2) (mp 126–127°C).

(16) *2-thiocyanato-1H-pyrrole*: ^{1}H NMR ($CDCl_3$): δ 6.27 (dd, H, $J = 3$ Hz, $J = 6.3$ Hz), 6.64 (m, 1H, $J = 1.5$ Hz, $J = 3.6$ Hz, $J = 3.9$ Hz), 6.96 (m, 1H, $J = 1.5$ Hz, $J = 3$ Hz, $J = 4.5$ Hz), 8.9 (s, 1H), ^{13}CNMR(75 *MHz*, $CDCl_3$): δ 124.3, 120.1, 111.1, 110.9, 102.8. m/z = 124.

(17) *2, 5-dithiocyanato-1H-pyrrole*: ^{1}H NMR ($CDCl_3$) δ 1.49 (d, 2H, $J = 2.4$ Hz), 4.76 (s, 1H), ^{13}C NMR (75 Hz, $CDCl_3$): δ 121.2, 110.9, 109.4, m/z = 181 (mp 99–103°C).

(18) *2-Thiocyanatothiophene*: (Oil). ^{1}H NMR ($CDCl_3$): δ 7.45–8.10 (m, 3H).

(19) *1-Methoxy-4-thiocyanatonaphthalene*: ^{1}H NMR (300 *MHz*, $CDCl_3$): δ 4.07 (s, 3H), 6.72–6.74 (m, 1H), 7.60–8.31 (m, 5H) (mp 105–107°C).

4.3. *Procedure for USAR thiocyanation of organic compounds*

Methodology for USNR of organic compounds is similar to the one described above. A reaction flask containing a suspension of phenol (0.1 mol), ammonium metavanadate (0.001 mol), ammonium thiocyanate (0.1 mol), and aqueous $KHSO_4$ (0.1 mol), in about 20 mL solvent (MeCN) was placed in a sonicator and the progress of the reaction was monitored by TLC. After completion of the reaction, the reaction mixture was filtered and washed with water. The remaining work up was similar to the one adopted for the conventional approach. All products are characterized by comparison of their IR, ^{1}H-NMR, and mass spectra and also with their physical data.

4.4. *Procedure for microwave-assisted (MWAR) thiocyanation of organic compounds*

A CEM microwave reactor was used, which was equipped with temperature, pressure, and microwave power control units. An oven-dried microwave vial was charged with a mixture containing a suspension of phenol (0.1 mol), ammonium metavanadate (0.001 mol), ammonium thiocyanate (0.1 mol), aqueous $KHSO_4$ (0.1 mol), and silica gel slurry, and was irradiated in a microwave (power input 140 W) at 150°C for few minutes. After completion of the reaction, as ascertained by TLC, the reaction mixture was treated with sodium bicarbonate; the organic layer was diluted with DCM, and separated from the aqueous layer. The crude product mixture was purified by recrystallization with an ethyl acetate DCM mixture. The purity was checked with TLC. The products were identified by characteristic spectroscopic data.

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