# Sodium Monobromoisocyanurate: A New Catalyst for Direct Synthesis of Aryl Thiocyanates

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# Abstract

An efficient and highly selective methods for the preparation of arylthiocyanates by thiocyanation with ammonium Thiocyanates in the presence of sodium mono bromoisocyanurate as a catalyst in methanol under mild conditions to afford the corresponding aryl and para substituted thiocyanates. The use of sodium mono bromoisocyanurate is simple and more convenient.

Keywords: Aromatic system, Aryl thiocyanates, Sodium monobromoisocyanurate (SMBI), Thiocyanation

# 1. Introduction

The thiocyanation of aromatics and hetero aromatics is an important carbon-hetero atom bond formation in organic synthesis. It was of interest to probe the direct thiocyantion of aromatic and hetero aromatic compounds. (Roberto, Margarita. 2000) Nucleophilic thiocyanation of phenol ethers using hypervalent iodine (III) reagents has been reported recently, thus thiocyanation of aromatic systems is of importance. Consequently several methods have been developed for the thiocyanation of arenes using a variety of reaction conditions. In contrast only a limited number of reagents such as N-Chlorosucinamide (NCS), N-Bromosuccinamide (NBS), (Yadav, J, Reddy, B. V. S, 2004) Ferric (III) chloride-promted efficient thiocyanation of aryl alkenes. (Nair, V. George., 1999; Grant, M. S, Snyder, H. R. 1960) Ceric ammonium nitrate (CAN) etc. have reported for thiocyanation of indoles and arenes.

# 2. Experimental

Our preliminary studies were carried out with indole (1) (3 equivalents) and of ammonium thiocyanate (3 equivalents) and sodium monobromoisocyanurate (SMBI) (1.0 equivalent) in the required minimum volume of methanol at 50  $^{\circ}$ C for 6 hours as a model substrate in order to establish the best reaction conditions. The reaction went to completion within 6 hrs at 50  $^{\circ}$ C and the products 3-thiocyanato indole (2) was obtained in 85-90% yield (scheme 1 Table 1, entry a).

Like indoles, isatins also worked under similar conditions to give 5-thiocyanato derivatives (Table 1, entries C). Similarly anilines in the presence of SMBI and ammonium thiocyanate resulted also in the formation of aryl thiocyanates in high yield (entries d, e, and f Table 1, Scheme 2)

In the case of aryl amines, the products were obtained with high para selectivity. In all cases the products were characterized by <sup>1</sup>H NMR, IR and mass spectroscopic data and also by comparison with authentic samples.

In conclusion we have developed an efficient and improved procedure for thiocyanation of indoles and aryl compounds using sodium monobromoisocyanurate: The mild reaction condition, easy isolation of products, high yields (80-90 %), economically viability of the catalyst and wide applicability for various reactants and wide applicability of various reactants are important features of this protocol.

Melting Points were recorded Buchi R-535 apparatus and are uncorrected.IR spectra were recorded on Perkin-Elmer FT/IR-2400 spectrometer with KBr optics. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Varian Gemini – 200 spectrometer in CDCl3 using TMS as an internal standard. Mass spectra were recorded an Finnigan MAT 1020 Mass spectrum operating at 70 eV.

## **3. General Procedure**

The indole 1(1mmol) and ammonium thiocyanate (3 mmol) were dissolved in minimum amount of methanol and treated with SMBI (3 mmol) in methanol (50 mL) at 50 °C for 6 hrs. It was then distilled of then diluted with water (100ml) and extracted with  $CH_2Cl_2$  (5 x25mL). The solvent was evaporated and the residue was then recrystallised from Chloroform: Methanol.

# 4. Results and Discussion

#### 3-Thiocyanato - 1H- indole (2a)

Solid; mp 125-127° C

IR(KBr):3341,3107,2924,2853,2157,1618,1503,1455,1217,758,668,589 cm-1.

<sup>1</sup>H NMR (200 MHz, CDCl3) = 7.23-7.45(m, 4H), 7.80(d, 1H, J = 8.0Hz).

EIMS: *m/z* (%) : 174 (M<sup>+</sup>,30)155 (25),141(30),97(20),85(27),71(36),57(94),43(100).

## 2-Methyl-3-thiocyanato-1H-indole (2b)

Solid; mp 102-103° C

IR(KBr):3324,2933,2151,1618,1543,1408,1229,740,651 cm-1.

<sup>1</sup>H NMR (200 MHz, CDCl3) = 2.48(s, 3H) 7.15(m, 3H), 7.70(d, J = 8.1Hz 1H).8.48 (brs, 1H, NH)

EIMS: *m/z* (%): 188 (M<sup>+</sup>, 100)156 (18), 77(14).

#### 5-Thiocyanato-2, 3-indolidine (2c)

Solid; mp 203-204° C

IR(KBr):3447, 2924, 2165, 1618, 1460, 771 cm-1.

<sup>1</sup>H NMR (200 MHz, DMSO-d6) = 7.05 (d, 1H, J = 8.1Hz, 1H), 7.65-7.75(m, 2H) 11.35 (brs, 1 H, NH)

EIMS: m/z (%) : 204 (M<sup>+</sup>,20)180 (80),176(35),135.(30),109(10),88(100),71(60),43(50).

# 2-Chloro – 3-methyl-4-thiocyanatoaniline (2d)

Solid; mp 112-113° C

IR(KBr):3382,2148,1632,1578,1461,1394,1302,1109,811,593 cm-1.

<sup>1</sup>H NMR (200 MHz,CDCl<sub>3</sub>) = 2.45(,3H), 3.85(brs,2H,NH2), 6.60(d,J=8.2Hz,1H), 7.35(d,J=8.2Hz,1H)

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Scheme 2

Entry	Indole	Product <sup>a</sup>	Time	Yields
	1	2	(h)	(%) <sup>b</sup>
a	ZI	SCN H	6.0	80
b	CH <sub>3</sub>	SCN CH <sub>3</sub>	9.0	90
с		NCS H	12.0	80
d	NH <sub>2</sub> Cl CH <sub>3</sub>	CI CI CH <sub>3</sub>	5.5	75
e	NMe <sub>2</sub>	NMe <sub>2</sub> SCN	6.0	80
f	NH2 NO2	NH <sub>2</sub> NO <sub>2</sub> SCN	3.0	80

Table 1. Thiocyanation of aryl and hetero aromatic compounds

<sup>a</sup> All products were characterized by <sup>1</sup>H NMR,IR and mass spectroscopy.

<sup>b</sup> Isolated yields