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Efficient and Mild Oxidative Nuclear Thiocyanation of Activated Aromatic Compounds Using Ammonium Thiocyanate and Diacetoxyiodobenzene

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Abstract: A mild and general method for the nuclear thiocyanation of electron rich arenes has been developed by the reaction of NH₄SCN with diacetoxyiodobenzene as the oxidant.

Keywords: Ammonium thiocyanate, arenes, aryl thiocyanates, hypervalent iodine, oxidation

INTRODUCTION

Aryl thiocyanates are the valuable and versatile class of organic compounds useful for the transformations of the thiocyanato group into various sulfur functional groups^[1] as well as in the synthesis of sulfur-containing hetero-cycles.^[2] The synthesis of aryl thiocyanates is usually accomplished by the chemical oxidation of thiocyanate anion using heavy metal oxidants such as MnO₂, Pb(OAc)₄, CuSO₄,^[3–5] CuBr₂-Al₂O₃,^[6] NaBO₃,^[7] and cerric ammonium nitrate.^[8] The other methods for aryl thiocyanate preparation

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Scheme 1.

utilizes polymer-supported thiocyanogen ion,^[9] and the procedures based upon the reaction of NBS with alkali metal thiocyanates.^[10] Recently, the reaction of N-bromosulphonamides^[11] with thiocyanate anion has been used for aromatic electrophilic thiocyanation reactions. The thiocyanation of selected substrates such as phenols and phenol ethers using thiocyanating agents such as $Me_3SiNCS^{[12]}$ and $Pb(SCN)_2^{[13]}$ in combination with $PhI(OCOCF_3)_2$ and $PhICl_2$, respectively, has been previously reported. It was surprising that inexpensive and readily available NH_4SCN as a thiocyanating agent has not been utilized. In this article, we report the thiocyanation of electron-rich arenes by using NH_4SCN coupled with DIB as an oxidant (Scheme 1).

RESULTS AND DISCUSSION

Initially, we examined the model thiocyanation reaction of hydroquinone dimethyl ether (1 mmol) with NH_4SCN (3 mmol) in acetonitrile. When DIB (1.1 mmol) was added to this stirred reaction mixture, immediately the solution turned yellow and the thiocyanation product was obtained in 82% yield.

The mechanism of the reaction may involve the initial nucleophilic attack of thiocyanate anion on the fairly electrophilic DIB **3**, through a phenomenon of ligand exchange^[14] to form the intermediate **4**. The overwhelming tendency of intermediate **4** to expel iodobenzene^[15] is expected to generate the rather unstable thiocyanogen **5** required for aromatic electrophilic thiocyanation reaction (Scheme 2).

A variety of aromatic compounds including methoxybenzenes and heteroaromatics were successfully thiocyanated by using the DIB and NH_4SCN (Table 1). The electron density on the aromatic ring was shown to have considerable effect on the yield of thiocyanation reaction. Highly activated

$$\frac{\text{SCN}}{\text{PhI(OAc)}_2 + 2 \text{ NH}_4 \text{SCN}} \xrightarrow{-2 \text{ NH}_4 \text{OAc}} \text{Ph} \xrightarrow{|} \text{F} \text{Ph} \xrightarrow{-\text{PhI}} \text{SCN} \xrightarrow{-\text{PhI}} \text{SCN}_2}$$

$$3 \qquad 4 \qquad 5$$

Thiocyanation of Activated Aromatic Compounds

Entry	Substrate	Product	Yield ^b (%)	mp (lit) (°C)
1	MeO	MeO SCN	89	41 (33–44) ^[11]
2	MeOOMe	MeO	86	Oil
3	MeO	MeOSCN OMe	82	68 (68–69) ^[13]
4	OMe	SCN OMe	79	106 (106–107) ^[13]
5	OMe	NCS Mc	73	Oil
6	MeO MeO	MeO SCN	74	48 (49-50) ^[13]
7	Me ₂ N	Me ₂ N SCN	78	72 (73–74) ^[11]
8	$\langle s \rangle$		72	Oil
9	N Mc		69	91

Table 1. Electrophilic thiocyanation of activated aromatic substrates using NH_4SCN and DIB^a

^{*a*}All the reactions were carried out in CH_3CN solvent at room temperature and stirred for 2 h.

^bIsolated yields after chromatography.

methoxybenzenes (entries 1–6) underwent thiocyanation in good yields. It is noteworthy that only *para* substitution products are formed in the case of anisole (entry 1). The heteroaromatics such as thiophene (entry 8) and N-methyl indole yield thiocyanation products in moderate yields. The reaction of phenol and indole with the DIB/NH₄SCN combination gave a number of products. This may be attributed to the facile oxidation of phenols and amines with DIB.^[14]

In summary, we have found that aryl thiocyanates can be synthesized in high yields under mild conditions using readily available, inexpensive, ecofriendly, and recyclable DIB in combination with ammonium thiocyanate.

EXPERIMENTAL

General Procedure

To a solution of aromatic substrate (1 mmol), NH₄SCN (3 mmol) in acetonitrile (10 ml) was added diacetoxyiodobenzene (1.1 mmol). The reaction mixture was magnetically stirred for 2 h at room temperature. The progress of the reaction was monitored by TLC. After completion of the reaction, water (10 ml) was added and extracted with CH_2Cl_2 (2 × 10 ml). The combined organic extract was dried over anhydrous sodium sulphate, concentrated in vacuo, and chromatographed to give the thiocyanated product.

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