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LETTERS

A DIRECT SYNTHESIS OF ARYL THIOCYANATES USING CERIUM(IV) AMMONIUM NITRATE[#]

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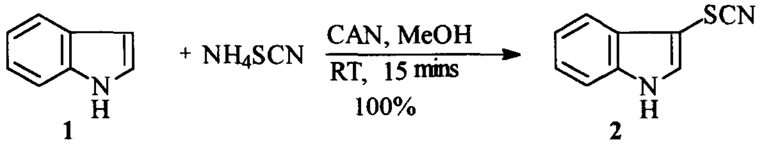
Abstract

An easy method for the conversion of arenes to aryl thiocyanates in high yields as illustrated by the formation of 3-thiocyanato indole from indole in quantitative yield is described.

Key words: Cerium(IV) ammonium nitrate; Thiocyanates; Arenes; Indoles

In the course of our exploration of the synthetic potential of cerium(IV) ammonium nitrate (CAN)[1], very recently we have found that it mediates a facile addition of thiocyanate to alkenes resulting in dithiocyanates[2]. As a logical extension of this work and in view of the versatility of the thiocyanato group in heterocyclic constructions[3], it was of interest to probe the direct thiocyanation of aromatic compounds. Nucleophilic thiocyanation of phenol ethers using hypervalent iodine(III) reagents has been reported recently[4]. Thiocyanation of arenes using *N*-thiocyanato succinimide was reported by Still [5].

Our initial work involved the reaction of ammonium thiocyanate with indole. A solution of indole **1** and ammonium thiocyanate in methanol on treatment with CAN in methanol at room temperature afforded **2** in quantitative yield as colorless crystalline solid [6,7].



Scheme 1

Experiments with a number of other aromatic compounds gave similar results and the reaction appears to be general. The results are summarized in table 1.

In conclusion, we have observed a facile and easy route to the synthesis of aryl thiocyanates mediated by cerium(IV) ammonium nitrate. The present procedure appears

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[#] Dedicated with best personal regards to Professor James P. Kutney.

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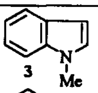
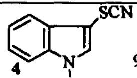
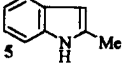
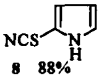
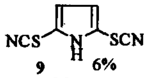
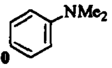
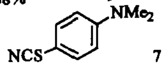
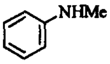
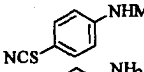
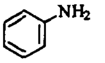
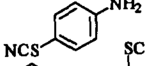
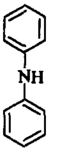
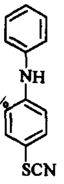
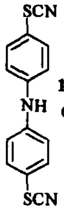
attractive for its experimental simplicity and generally high yields of products especially from heteroarenes. Further studies are in progress.

Table 1: Thiocyanation of arenes

Entry	Substrate	Products/ yields^a
1	 3	 4 99%
2	 5	 6 84%
3	 7	 8 88%  9 6%
4	 10	 11 75%
5	 12	 13 44%
6	 14	 15 38%
7	 16	 17 32(48^b)%  18 6%

Reaction conditions: 2.3 equiv. CAN, 1.2 equiv. NH_4SCN, MeOH, RT.
(a) Isolated yield. (b) Yield based on reacted starting material.

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References and notes

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[2] Nair V, Nair LG. Tetrahedron Lett. 1998;39:4585-4586.

[3] Review: (a)Wood JL. Organic reactions; Adams R. Ed.; John Wiley & Sons: NewYork, 1946;3:240-266. (b) Guy RG. The Chemistry of Cyanates and their Thio derivatives; Patai S. Ed.; John Wiley & Sons: NewYork, 1977; Part 2, Chapter 18:819-886.

[4] Kita Y, Takada T, Mihara S, Whelan BA, Tohma H. J. Org. Chem. 1995;60:7144-7148.

[5] Toste FD, Stefano VD, Still IW. J. Synth. Commun. 1995;25:1277-1286.

[6] Typical experimental procedure: The indole 1 (1 mmol) and ammonium thiocyanate (1.2 mmol) were dissolved in 5 mL methanol and treated with CAN (2.3 mmol) in methanol (25 mL) at room temperature The reaction mixture was stirred for 15 minutes. It was then diluted with water (100 mL) and extracted with dichloromethane (4x20 mL). The solvent was evaporated and the residue was purified by coloumn chromatography (ethyl acetate/ hexane as eluent) to afford 2 (100 %) as colorless crystalline solid which was then re-crystallised from CH_2Cl_2 / hexane, m p. 76 °C. IR (KBr): 3340, 2160 (SCN), 1418, 737 cm^{-1}.

[7] Grant MS, Snyder HR. J. Am. Chem. Soc. 1960;82:2742-2744.