

# A DIRECT SYNTHESIS OF ARYL THIOCYANATES USING CERIUM(IV) AMMONIUM NITRATE<sup>#</sup>

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## Abstract

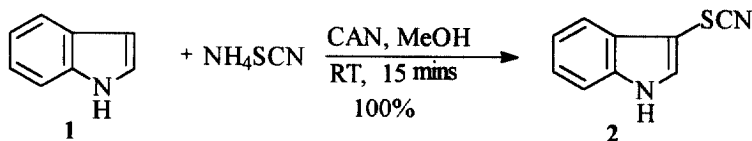
An easy method for the conversion of arenes to aryl thiocyanates in high yields as illustrated by the formation of 3-thiocyanato indole from indole in quantitative yield is described.

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*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

<sup>#</sup> 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 <sup>a</sup>
1		 99%
2		 84%
3		 88%  6%
4		 75%
5		 44%
6		 38%
7		 32(48b)%  6%

Reaction conditions: 2.3 equiv. CAN, 1.2 equiv.  $\text{NH}_4\text{SCN}$ , MeOH, RT.

(a) Isolated yield. (b) Yield based on reacted starting material.

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### References and notes

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