



NBS or DEAD as effective reagents in α -thiocyanation of enolizable ketones with ammonium thiocyanate

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ABSTRACT

Ketones possessing α -hydrogen undergo smooth thiocyanation with ammonium thiocyanate in the presence of *N*-bromosuccinimide (NBS) at room temperature in acetonitrile under neutral conditions to produce the corresponding α -ketothiocyanates in excellent yields with high selectivity. The use of NBS makes this procedure simple, convenient and cost effective. In addition, diethyl azodicarboxylate (DEAD) was also found to promote this reaction under mild conditions.

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Alkyl thiocyanates are important intermediates for the synthesis of sulfur-containing organic compounds. They are frequently found in some biologically active natural products (Fig. 1).¹

Thiocyanato functionality can be used as a masked mercapto group or as a precursor for sulfur-containing heterocyclic compounds, such as thiazolidine and cyclic thioureas.² In particular, α -ketothiocyanates are useful intermediates in the synthesis of sulfur-containing heterocycles such as thiazoles.³ Some of these thiazoles exhibit herbicidal and other important biological activities.⁴ Thus, the direct thiocyanation of ketones is of prime importance. Generally, α -thiocyanato carbonyl compounds are prepared from α -halocarbonyl compounds⁵ or α -tosyloxycarbonyls⁶ or α -diazoketones⁷ and also by oxidative thiocyanation of enol ethers.⁸ However, the yields are typically low as a result of the poor nucleophilicity of the SCN anion. Subsequently, one-pot methods have been reported for the α -thiocyanation of enolizable ketones using a variety of reagents.^{9,10} However, many of these methods involve the use of toxic metal thiocyanates,⁸ expensive thiocyanating agents⁹ and a large excess of strong oxidizing agents¹⁰ and also result in low conversions due to the formation of complex mixtures of products. Therefore, the development of simple, convenient and efficient approaches for their synthesis is desirable.

In this Letter, we wish to report a metal-free thiocyanation of ketones using a readily available and inexpensive reagent, NBS.

Abbreviations: DEAD, diethyl azodicarboxylate; NBS, *N*-bromosuccinimide; NCS, *N*-chlorosuccinimide; NIS, *N*-iodosuccinimide; NTS, *N*-thiocyanatosuccinimide.

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Initially, we have attempted the thiocyanation of acetophenone (1) with ammonium thiocyanate (2) using NBS as a novel oxidant.

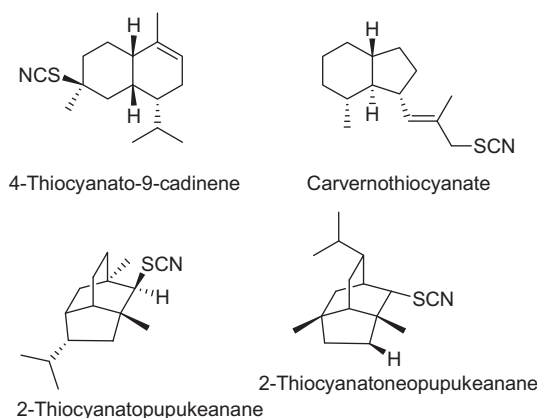
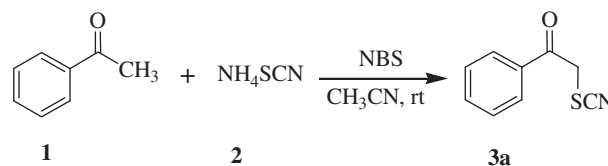


Figure 1. Examples of some natural products bearing thiocyanato functionality.



Scheme 1. α -Thiocyanation of acetophenone.

The reaction proceeded smoothly at room temperature under mild and neutral conditions to afford the 1-phenyl-2-thiocyanatoethanone **3a** in 85% yield (Scheme 1).

Similarly, other substituted acetophenones, such as *p*-bromo-, *p*-nitro- and 3,4-dimethoxyacetophenone derivatives underwent

smooth thiocyanation to furnish the corresponding α -thiocyanoketones in good yields (Table 1, entries b–d). The excellent reactivity of NBS in the thiocyanation of aryl methyl ketones prompted us to extend this method for other enolizable ketones. Interestingly, cyclic ketones, such as α -tetralone and 6-methoxy-1-tetralone gave

Table 1
NBS-promoted efficient synthesis of α -thiocyanatketones

Entry	Ketone	Product (3) ^a	Time (h)	Yield ^b (%)
a			4.0	85
b			7.0	75
c			5.0	72
d			6.0	85
e			7.0	80
f			7.0	85
g			4.5	80
h			4.5	75
i			6.0	70
j			5.0	85
k			6.0	76
l			5.0	70
m			5.0	75

^a All products were characterized by ¹H NMR, IR and mass spectroscopy.

^b Yield refers to pure products after chromatography.

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