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HETEROPOLY ACIDS AS HETEROGENEOUS AND REUSABLE CATALYST FOR α -THIOCYANATION OF KETONES

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Simple, efficient, and mild method for α -thiocyanation of ketones in presence of heteropolyacid has been developed. This methodology offered α -oxothiocyanates in good to excellent yields at room temperature in a highly selective manner. The catalyst could be efficiently recovered from the reaction and reused.

Keywords: Ketones; α-oxothiocyanates; phosphomolybdic acid; thiocyanation

INTRODUCTION

Organic thiocyanates are obtained by deglycosylation of glucosinolates, derived from cruciferous vegetables, and are biologically important natural products.^[1] α -Oxothiocyanates are important intermediates in the synthesis of sulfur-containing heterocycles such as thiazoles and 2-amino-1,3-thiazines.^[2–4] Some of these compounds exhibit herbicidal and other important biological activities.^[5,6] Several methods have been reported for α -thiocyanation of ketones, using a wide variety of reagents under diverse reaction conditions.

Different thiocyanogens were used as catalysts in heterolytic and homolytic conditions.^[7–10] Dichloroiodobenzene–lead(II) thiocyanates^[11] have been used for direct thiocyanation of carbonyl compounds. However, these methods involve harsh reaction conditions, excess use of oxidizing agents, use of toxic metal thiocyanates, and multistep processes, which in turn practically affect the yield.

Heteropolyacids (HPAs) have both acidic and oxidative properties.^[12–14] In the past two decades, the broad utility of HPAs as catalysts in solution as well as in the solid state for various industrial processes has been demonstrated for a wide variety of synthetically useful transformations of organic substrates.^[15,16] HPAs are stronger than the usual mineral acids such as H_2SO_4 , HCl, and HNO₃.^[17] Solid HPAs are also

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Scheme 1. Synthesis of 2-oxo cyclohexyl thiocyanate.

stronger than conventional solid acids such as SiO_2/Al_2O_3 , H_3PO_4/SiO_2 , and HX or HY zeolites.^[18]

Considering the properties and importance of the HPAs as the catalysts in organic synthesis, we herein report α -thiocyanation of ketones using a catalytic amount of HPA. HPA not only oxidized the ammonium thiocyanate to thiocyanogen [(SCN)₂] but also enolized the carbonyl group to get α -thiocyanate. Cyclohexanone (1 mmol), ammonium thiocyanate (2 mmol), and phosphomolybdic acid in ethylene dichloride were stirred for 20 min at room temperature to get 2-oxo cyclohexyl thiocyanate (Scheme 1). At the end of the reaction, the catalyst could be recovered by filtration. The recovered catalyst was washed with dichloromethane and reused.

We studied the effects of various organic solvents on the yield of product and rate of the reaction. Organic solvents [viz., dichloromethane, tetrahydrofuran (THF), ethylene dichloride, methanol, chloroform, carbon tetrachloride, and acetonitrile] were selected for the study. It was observed that maximum yields were obtained when ethylene dichloride was used as solvent (Table 1). Solubility of HPA in a few organic solvents did not show significant effect on the outcome of the reaction.

Considering the effectiveness of the HPA, we decided to generalize the protocol by treating a broad range of ketones with ammonium thiocyanate in the presence of HPA. All the selected ketones afforded corresponding α -oxothiocyanates in good to excellent yields. Thiocyanation of cyclic ketones occurred with excellent yields, whereas that of β -dicarbonyl compounds occurred in moderate yields. The presence of a heteroatom in the ring did not affected the yield of α -oxothiocyanates. Physical and spectral data of known compounds are in agreement with those reported in the literature^[19,20] (Table 2).

Entry	Solvent	Time (min)	Yield (%)
1	CHCl ₂	25	75
2	THF	30	70
3	ClCH ₂ CH ₂ Cl	20	86
4	MeOH	30	75
5	CHCl ₃	25	82
6	CCl ₄	30	78
7	CH ₃ CN	20	80

 Table 1. Solvent effects on the reaction of cyclohexanone and ammonium thiocyanate catalyzed by HPA

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Entry	Carbonyl compound	α-Oxothiocyanates	Time (min)	Yield (%)
1		SCN	20	86
2		SCN	35	75
3			35	68
4	CH3	SCN	30	73
5	MeO CH ₃	MeO	45	68
6	Br CH ₃	Br SCN	40	68
7	CI O CH ₃	CI O SCN	30	75
8	HO CH3	HO	40	65

Table 2. HPA-catalyzed α -thiocyanation of ketones

(Continued)

Entry	Carbonyl compound	α-Oxothiocyanates	Time (min)	Yield (%)
9	o	SCN	30	78
10	мео	MeO SCN	40	80
11		SCN	35	70
12	MeO		40	65
13	O O Ph	SCN O Ph	30	75
14	S S	SCN	30	75
15	MeO	MeO O SCN	35	65
16		SCN	45	65

Table 2. Continued

(Continued)

Entry	Carbonyl compound	α-Oxothiocyanates	Time (min)	Yield (%)
17		SCN SCN	45	60
18	OC ₂ H ₅ OC	OC ₂ H ₅ SCN	40	70

Table 2. Continued

EXPERIMENTAL

All commercial reagents were used as received without purification, and all solvents were of reagent grade. The reaction was monitored by thin-layer chromatography (TLC) using 0.25-mm E. Merck silica-gel 60 F_{254} precoated plates, which were visualized with ultraviolet light. Melting points were observed using open capillaries. The infrared (IR) spectra were recorded on a Perkin-Elmer 257 spectrometer using KBr discs. ¹H NMR and ¹³C NMR spectra were recorded on a VXR 300-MHz instrument using tetramethylsilane (TMS) as internal standard.

General Experimental Procedure

A mixture of ketone (1 mmol), ammonium thiocyanate (2 mmol), and phosphomolebdic acid (0.0002 mol) with a pinch of $CuCl_2$ in ethylene dichloride (15 ml) was stirred at room temperature for the appropriate time, as indicated in Table 2. After completion of reaction, as monitored by TLC, the solution was filtered, and the filtrate was dried on sodium sulfate and concentrated under reduced pressure. The product obtained was purified by column chromatography.

Representative Spectral Data for Products

Compound 1. IR (KBr): 3045, 2851, 2156, 1705, 1690, 1438, $1120 \text{ cm}^{-1.1}\text{H}$ NMR CDCl₃ (δ ppm): 4.42–4.47 (m, 1H), 2.82–2.87 (m, 1H), 2.56–2.62 (m, 1H), 2.28–3.34 (m, 1H), 1.82–2.23 (m, 5H). ¹³C NMR CDCl₃(δ ppm): 24.13, 26.18, 34.09, 40.21, 50.47, 112.14, 206.80.

Compound 6. IR (KBr): 3058, 2960, 2927, 2125, 1685, 1585, 1520, 792, 650 cm⁻¹. ¹H NMR CDCl₃ (δ ppm): 8.12 (s, 1H), 7.87 (d, J = 7.0 Hz, 1H), 7.52 (d, J = 7.0 Hz, 1H), 7.28(t, 1H, J = 7.0 Hz), 4.70 (s, 2H). ¹³C NMR CDCl₃ (δ ppm): 42.96, 111.32, 125.87, 128.20, 131.10, 132.25, 134.80, 138.15, 189.70.

Compound 16. IR (KBr): 3040, 2849, 2110, 1715, 1645. ¹H NMR CDCl₃ (δ ppm): 2.48 (s, 6H), 4.90 (s, 1H). ¹³C NMR CDCl₃ (δ ppm): 29.10, 61.78, 112.12, and 202.69.

CONCLUSION

In conclusion, we have developed an alternative and simple protocol for the synthesis of α -oxothiocyanates using HPA as an ecofriendly, reusable, inexpensive, and efficient catalyst. Excellent yields, relatively short reaction times, and easy workup are some of the advantages of this protocol.

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