Communication

Hypervalent Iodine(III) Sulfonate Mediated Synthesis of α-Thiocynanatoketones in a Task-specific Ionic Liquid [bmim]SCN

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The task-specific ionic liquid (TSIL) and 1-n-butyl-3-methylimidazolium thiocynanate, ([bmim]SCN) were used as the medium as well as the reactant for the synthesis of α-thiocynanatoketones by the reaction with α-sulfonyloxy aryl ketones. Significant rate enhancements and improved yields have been observed.

Keywords: Hypervalent iodine; α-Thiocynanatoketones; Ionic liquid.

INTRODUCTION

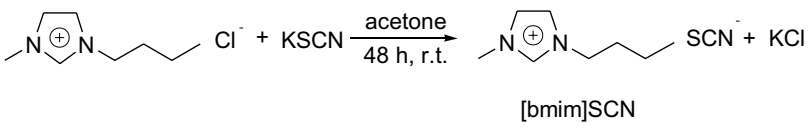
Alkyl thiocyanates are important synthetic precursors for the preparation of sulphur-containing organic compounds. This functional group can be used as a masked mercapto group or as a precursor for sulphur-containing heterocyclic compounds. Additionally, α-thiocyanatoketones are intermediates for a preferred synthetic route to several types of thiazoles.[1] Thiocyanation is generally carried out via nucleophilic substitution using thiocyanate anions. The low nucleophilicity of the NCS-ion requires rather harsh reaction conditions. Metal thiocyanates and organic halides or sulfonates are generally used to introduce the thiocyanate functionality into an organic molecule.[2] However, the thiocyanate group is not that stable when heated or under acidic conditions. Chromatography on silica gel or prolonged heating over 50 °C can cause intramolecular rearrangement to the thermodynamically favored isothiocyanate isomers.[3] Furthermore, thiocyanates have been obtained from alcohols,[4] silyl ethers[5] or amines[6] using $Ph_3P(SCN)_2$. However, many drawbacks have been observed for these thiocyanation methodologies.[7]

Recently, ionic liquids have been attracted a considerable attention as an environmental-friendly reaction media for the various organic transformations. Ionic liquids can serve as environmentally benign alternatives to the conventional volatile organic solvents due to their interesting properties such as very low volatility, high chemical stability, and nonflammability.[8]

The ionic liquid, 1-*n*-butyl-3-methyl imidazolium thiocyanate [bmim]SCN was prepared by the anion exchange of 1-*n*-butyl-3-methyl imidazolium chloride[9] with KSCN in acetone for 48 h at room temperature (Scheme I).[10]

Hypervalent iodine(III) sulfonates have been received continuous attention due to their versatile utilities in organic synthesis, ready availability, and relatively non-toxic properties.[11] In view of the easy accessibility of α-[(2,4-dinitrobenzene)sulfonyl]oxy ketone intermediates from readily available ketones and hypervalent iodine reagent, [hydroxyl(2,4-dinitrobenzenesulfonyloxy)iodo]benzene (HDNIB).[11(o)] We now report a facile and efficient method for the synthesis of α-thiocynanatoketones by the reaction of α-sulfonyloxy aryl ketones with [bmim]SCN under mild

Scheme I



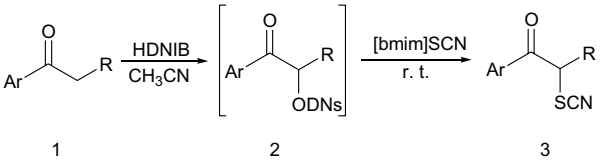
conditions.

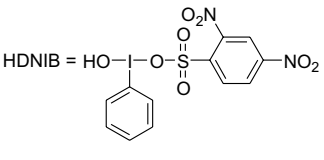
RESULTS AND DISCUSSION

The 2,4-dinitrobenzenesulfonyloxy group located at the α position to a carbonyl group represents an increasingly important entity in both mechanistic and synthetic organic chemistry. One reason for this importance is that 2,4-dinitrobenzenesulfonyloxy group is a good leaving group, and this accounts for the considerable synthetic utility associated with these groups in functionalization of carbonyl compounds.

As shown in Scheme II, our experiments involving a one-pot procedure for the preparation of α-thiocyanatoketones (**3**) by reaction of arylketones (**1**) with HDNIB (**2**) in CH_3CN at 80°C for 1 h. After completion of the formation of α-sulfonyloxy aryl ketone intermediates (**2**), [bmim]SCN (2 mL) was added to the reaction mixture and stirring was continued at room temperature for 10 min to give the desired α-thiocynanatoketones (**3**) in good yields. The results are summarized in the Table 1. When the reaction was carried out by reacting α-sulfonyloxy aryl ketone (**2a**) in ionic liquid, 1-butyl-3-methylimidazolium tetrafluoroborate, [bmim]BF_4 with KSCN, the preparation of 1-phenyl-2-thiocynanatoethanone (**3a**) needs stirring for 6 h at room temperature. This indicated that the nucleophilicity of the SCN anion is much higher in [bmim]SCN compared to KSCN in [bmim]BF_4.

Scheme II





a) Ar= Ph, R= H
b) Ar= 4-MeC6H4, R= H
c) Ar= 4-OMeC6H4, R=H
d) Ar = 4-ClC6H4, R= H
e) Ar = 4-BrC6H4, R= H
f) Ar = 2-Furyl, R= H
g) Ar = 2-Thienyl, R= H
h) Ar= Ph, R= Me
i) Ar= R= Ph

In conclusion, we have described a novel and efficient method for the synthesis of α-thiocynanatoketones using [bmim]SCN as reaction medium as well as reactant. This new efficient and facile method might be served as a useful alternative to existing methods, since it does not require α-haloketones or α-tosyloxyketones substrates as starting materials.

Table 1. Synthesis of α-thiocynanatoketones **3a-i**

Entry	Product	Ar	R	Yield (%)
1	3**a**	Ph	H	82
2	3**b**	4-MeC_6H_4	H	86
3	3**c**	4-$MeOC_6H_4$	H	85
4	3**d**	4-ClC_6H_4	H	72
5	3**e**	4-BrC_6H_4	H	75
6	3**f**	2-Furyl	H	73
7	3**g**	2-Thienyl	H	74
8	3**h**	Ph	Me	80
9	3**i**	Ph	Ph	79

EXPERIMENTAL SECTION

All melting points are uncorrected. The IR spectra were recorded on a Shimadzu IR-27 G spectrophotometer. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian Unity Plus 400 MHz. Chemical shifts (δ) were measured in ppm with respect to TMS. MS were obtained on a JEOL JMS D-300 instrument.

1-Phenyl-2-thiocynanatoethanone (3a); Typical procedure

To a solution of acetophenone (**1a**) (120 mg, 1.0 mmol) in CH_3CN (20 mL) was added HDNIB (561 mg, 1.2 mmol) and stirred for 1 h at 80 °C. Then [bmim]SCN (2 mL) was added to the reaction mixture and stirring was continued for 10 min at room temperature. After completion of the reaction, the reaction mixture was diluted with water, and the product was extracted with ethyl acetate. The collected organic fractions were dried over $MgSO_4$, and the solvent was evaporated under vacuum. The resulting residue was chromatographed on silica gel column eluting with AcOEt: n-hexane (1:1) to give **3a**, mp 69-70 °C (lit.[12] 71-72 °C). IR (KBr) ν: 2150, 1674 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 4.75 (s, 2H), 7.52-7.56 (m, 2H), 7.66-7.70 (m, 1H), 7.93-7.95 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 42.9, 111.8, 128.4, 128.4, 129.1, 129.1, 133.8, 134.7, 190.7; EI-MS *m/z* (relative intensity) 177 (M^+, 0.47), 105 (100), 76 (21).

1-*p*-Tolyl-2-thiocyanatoethanone (3b)

mp 100-102 °C (lit.[13] 102-103 °C). IR (KBr) ν: 2152, 1664 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 2.48 (s, 3H), 4.73 (s, 2H), 7.33 (d, J = 7.6 Hz, 2H), 7.84 (d, J = 8.0 Hz,

2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 21.8, 43.0, 128.5, 128.5, 129.8, 129.8, 131.4, 146.0, 190.3; EI-MS *m/z* (relative intensity) 191 (M^+, 0.26), 119 (100), 91 (30).

1-(4-Methoxyphenyl)-2-thiocyanatoethanone (3c)

mp 120-121 °C (lit.[14] 121 °C). IR (KBr) ν: 2147, 1660 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 3.90 (s, 3H), 4.71 (s, 2H), 6.99 (d, *J* = 8.8 Hz, 2H), 7.90 (d, *J* = 8.8 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 42.9, 55.6, 112.1, 114.3, 114.3, 126.9, 130.9, 130.9, 164.8, 189.1; EI-MS *m/z* (relative intensity) 207 (M^+, 1), 136 (9), 135 (100), 77 (10).

1-(4-Chlorophenyl)-2-thiocyanatoethanone (3d)

mp 132-134 °C (lit.[15] 135-136 °C). IR (KBr) ν: 2065, 1629 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 4.69 (s, 2H), 7.53 (d, *J* = 8.4 Hz, 2H), 7.88 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 42.6, 111.5, 129.5, 129.5, 129.8, 129.8, 132.2, 141.5, 189.6; EI-MS *m/z* (relative intensity) 213 (M^++2, 0.18), 211 (M^+, 0.50), 141 (33), 139 (100).

1-(4-Bromophenyl)-2-thiocyanatoethanone (3e)

mp 138-140 °C (lit.[16] 146 °C). IR (KBr) ν: 2065, 1665 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 4.69 (s, 2H), 7.69 (d, *J* = 8.4 Hz, 2H), 7.79 (d, *J* = 8.8 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 42.5, 111.5, 129.8, 129.8, 130.3, 132.5, 132.5, 132.6, 189.8; EI-MS *m/z* (relative intensity) 257 (M^++2, 0.40), 255 (M^+, 0.40), 185 (100), 183 (99).

2-(2-Thiocyanatoacetyl)furan (3f)

mp 93-94 °C (lit.[17] 101-103 °C). IR (KBr) ν: 2153, 1650 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 4.44 (s, 2H), 6.65 (dd, *J* = 3.6, 1.6 Hz, 1H), 7.38 (dd, *J* = 3.6, 0.8 Hz, 1H), 7.67 (dd, *J* = 1.6, 0.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 40.4, 111.2, 113.2, 119.2, 147.7, 150.4, 179.4; EI-MS *m/z* (relative intensity) 167 (M^+, 4), 95 (100), 53 (4).

2-(2-Thiocyanatoacetyl)thiophene (3g)

mp 86-88 °C (lit.[18] 88 °C). IR (KBr) ν: 2151, 1642 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 4.56 (s, 2H), 7.21 (dd, *J* = 4.8, 4.0 Hz, 1H), 7.77 (dd, *J* = 4.0, 0.8 Hz, 1H), 7.79 (dd, *J* = 4.8, 0.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 41.6, 111.4, 128.7, 133.6, 136.1, 140.4, 183.2; EI-MS *m/z* (relative intensity) 183 (M^+, 0.34), 112 (6), 111 (100).

1-Phenyl-2-thiocyanato-propan-1-one (3h)

mp 42-43 °C (lit.[19] 43-44 °C). IR (neat) ν: 2149, 1681 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 1.87 (d, *J* = 7.2 Hz, 3H), 5.09 (q, *J* = 7.2 Hz, 1H), 7.52-7.56 (m, 2H), 7.65-7.69 (m, 1H), 7.92-7.94 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 19.8, 49.9, 111.4, 128.8, 128.8, 129.1, 129.1, 133.1, 134.5, 194.7; EI-MS *m/z* (relative intensity) 191 (M^+, 100), 121 (53), 105 (50), 77 (52).

1,2-Diphenyl-2-thiocyanatoethanone (3i)

mp 106-108 °C (lit.[20] 109-110 °C). IR (KBr) ν: 2359, 1676 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 5.95 (s, 1H), 7.25-7.35 (m, 5H), 7.37-7.41 (m, 2H), 7.50-7.54 (m, 1H), 7.90-7.93 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 76.1, 127.7, 127.7, 128.5, 128.5, 128.6, 128.6, 129.1, 129.1, 129.9, 133.4, 133.9, 138.9, 198.9; EI-MS *m/z* (relative intensity) 253 (M^+, 39), 105 (100), 77 (77).

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