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Mild and Efficient Method for α-Thiocyanation of Ketones and β-Dicarbonyl Compounds Using Bromodimethylsulfonium Bromide-Ammonium Thiocyanate

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MILD AND EFFICIENT METHOD FOR α-THIOCYANATION OF KETONES AND β-DICARBONYL COMPOUNDS USING BROMODIMETHYLSULFONIUM BROMIDE–AMMONIUM THIOCYANATE

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An efficient and convenient method for α-thiocyanation of ketones and β-dicarbonyl compounds has been developed using a reagent combination of bromodimethylsulfonium bromide (BDMS) and ammonium thiocyanate in acetonitrile. The developed method is mild and gave good yield of the products at room temperature.

Keywords: Ammonium thiocyanate; BDMS; β-dicarbonyl compounds; ketones; α-thiocyanation

Organosulfur chemistry of thiocyanates and their derivatives is of considerable importance. α-Thiocyanato carbonyl compounds are valuable precursors for synthesis of heterocyclic ring systems such as 2-amino-1,3-thiazines, thiazoles, and their derivatives,[1] some of which are associated with herbicidal and other biological activities.[2] Thiocynato group plays an important function in certain anticancer natural products formed by deglycosylation of glucosinolates derived from cruciferous vegetables.[3]

Thiocyanation is usually carried out via a nucleophilic reaction using the thiocyanate anion. Generally α-thiocyanato carbonyl compounds are prepared from α-halocarbonyl compounds[4] or α-tosyloxycarbonyls[5] or via nucleophilic epoxide ring opening using the thiocyanate anion.[6] Electrophilic or radical reactions using thiocyanogen and thiocyanogen chloride constitute other useful methods for thiocynations.[1c,7] α-Thiocyanation of enolizable carbonyl compounds can be effected using thiocyanatotrimethylsilane and SO_2Cl_2,[8] which may be considered to be an electrophilic method. α-Thiocyanation of carbonyl and β-dicarbonyl compounds are also carried out by using (dichloroiodo)benzene-lead(II) thiocyanate,[9] $K_2S_2O_8$-Cu/ammonium thiocyanate,[10] iodine/ammonium thiocyanate,[11a] and $FeCl_3$/ammonium thiocyanate.[11b]

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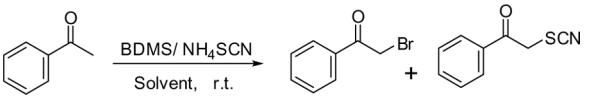
In recent years, the use of bromodimethylsulfonium bromide (BDMS) has gained attention in synthetic organic chemistry.[12] BDMS has been utilized for the transformation of alcohols to corresponding bromides,[13] oxidation of thiols to disulfides,[14] deprotection of dithioacetals,[15] preparation of α-bromoenones from the corresponding enones,[16] and regioselective α-bromination of β-keto esters and 1,3-diketones.[17] The reagent BDMS is readily accessible, can be conveniently stored, is less hazardous, and is easy to handle. Recently we have developed BDMS as an efficient and regioselective reagent for aromatic and heteroaromatic thiocyanation.[18] We have now explored its utility for α-thiocyanation of ketones and β-dicarbonyl compounds in combination with ammonium thiocyanate.

BDMS was prepared by following the literature procedure.[15] To optimize reaction conditions, acetophenone was taken as study substrate, and results are summarized in Table 1.

When acetophenone was added to a stirred mixture of BDMS and NH_4SCN in acetonitrile, it gave a mixture of α-bromoacetophenone (**2a**) and α-thiocynatoacetophenone (**3a**) with recovery of a small amount of unreacted starting material (Table 1, entry 1). By increasing the molar ratio of BDMS–NH_4SCN to 1:2, only α-thiocynatoacetophenone (**3a**) was obtained with a substantial amount of unreacted acetophenone (Table 1, entry 2). The sequence of addition was very critical for getting good yields and conversion; for example, when ammonium thiocynate was added to the stirred mixture of acetophenone and BDMS, only α-thiocynatoacetophenone (**3a**) was obtained in 90% yield with practically no recovery of unreacted acetophenone (Table 1, entry 4).

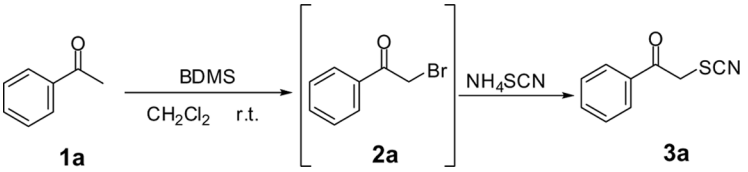
Table 1. Optimization of reaction conditions for α-thiocyanation[a]



1a **2a** **3a**

Entry	Molar ratio[b] wrt. **1a**	Solvent	Time	Product (%)[f] **2a**	Product (%)[f] **3a**	Recovered (%)[f] **1a**
1	1.1:1.1[c]	CH_3CN	5 h	70	10	15
2	1.1:2.2[c]	CH_3CN	5 h	—	40	55
3	1.5:3.0[c]	CH_3CN	5 h	—	50	45
4	1.1:2.2[d]	CH_3CN	5 h	—	90	Nil
5	1.1:2.2[c]	MeOH	5 h	—	80	15
6	1.1:2.2[c]	$CHCl_3$	5 h	70	25	—
7	1.1:2.2[c]	CH_2Cl_2	5 h	60	30	—
8	1.1:2.2[e]	CH_2Cl_2	20 min	—	95	Nil

[a]Reaction was performed on 5 mmol scale.
[b]**1a** (1 equiv): BDMS–NH_4SCN.
[c]Reaction carried out using a mixture of BDMS and NH_4SCN.
[d]Addition sequence is acetophenone, BDMS, and NH_4SCN.
[e]NH_4SCN was added after complete consumption of **1a** to form **2a**.
[f]By gas chromatography.



Scheme 1. α-Thiocyanation of acetophenone.

The results of solvent study revealed that dichloromethane and methanol were also viable for this transformation; however, in dichloromethane, α-bromination was the major product (Table 1, entries 5–7).

With these results in hand, the reaction was conducted in two stages (Scheme 1) using dichloromethane as solvent. Initially acetophenone **1a** was reacted with 1.1 equiv of BDMS and the reaction mixture was stirred at room temperature until complete consumption of starting material and formation of α-bromoketone **2a** as observed by thin-layer chromotography (TLC). This was followed by addition of 2.2 equiv of NH_4SCN. By this modification, the reaction was completed within an overall time of 20 min and gave of α-thiocyanatoacetophenone **3a** in 95% yield (Table 1, entry 8).

This developed protocol was applied to a wide range of acetophenones **1**, which underwent α-thiocyanation smoothly to afford α-thiocyanato products in 87–95% yields (Table 2, entries 1–8). The protocol was extended to cyclic ketones such as cyclohexanone and cyclopentanone and corresponding α-thiocyanato ketones were obtained in good yields (Table 2, entries 9 and 10). In the case of 1-phenylpropan-2-one **3k**, thiocyanation occurred as expected, predominantly at the benzylic position (Table 2, entry 11). The thiocyanato products **3a–k** were characterized by ^{1}H NMR and infrared (IR) spectroscopy and are in agreement with the reported values.

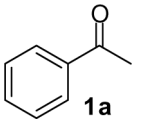
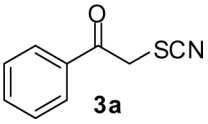
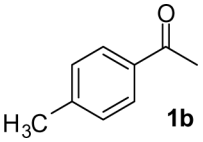
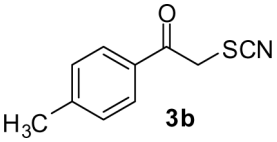
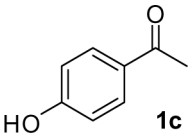
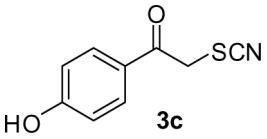
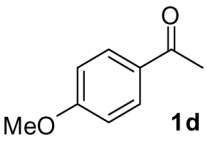
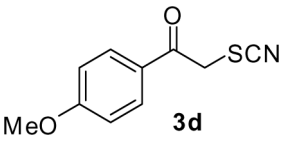
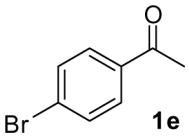
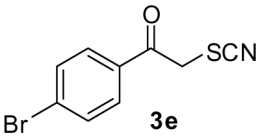
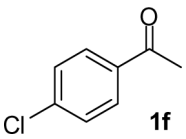
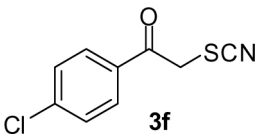
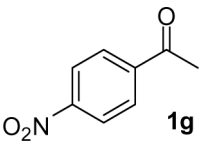
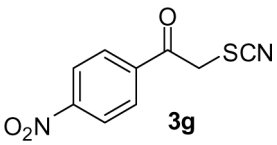
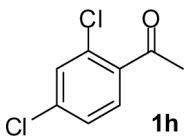
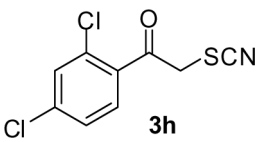
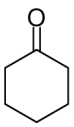
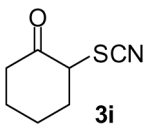
After establishing the reaction with ketones, α-thiocyanation of β-dicarbonyl compounds was studied. The reaction was carried out on acetylacetone in acetonitrile and gave 96% of 3-thiocyanatopentan-2,4-dione as a solid product in 10 min (Table 3, entry 1). The ^{1}H NMR and IR spectral data were in agreement with the reported values. Being relatively unstable, its shelf life at room temperature was short, and slow decomposition was observed.

Under the same conditions, α-thiocyanation of benzoylacetone, ethyl acetoacetate, and ethyl benzoylacetate proceeded to completion (as indicated by TLC and IR of the crude product) (Table 3, entries 2–4); however, it was not possible to isolate pure products because of their ready decomposition into a complex mixture.[9,20]

In contrast, α-substituted β-dicarbonyl compounds reacted smoothly to give α-thiocyanato derivatives (Table 3, entries 5 and 6). These are nonenolizable and quite stable crystalline solids.

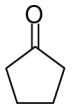
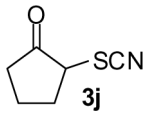
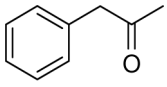
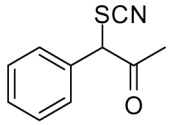
In summary, we have developed a simple, fast, and mild method for α-thiocyanation of ketones and β-dicarbonyl compounds to give corresponding α-thiocyanato products in excellent to good yields. The reaction can be conducted at room temperature. The reagents used are not hazardous and are easy to handle.

Table 2. α-Thiocyanation of ketones

Entry	Substrate **1**	Product **3**	Time (min)	Yield (%)[a]
1	 **1a**	 **3a**	20	95
2	 **1b**	 **3b**	20	92
3	 **1c**	 **3c**	25	88
4	 **1d**	 **3d**	20	91
5	 **1e**	 **3e**	25	87
6	 **1f**	 **3f**	25	87
7	 **1g**	 **3g**	35	88
8	 **1h**	 **3h**	40	88
9	 **1i**	 **3i**	30	65

(*Continued*)

Table 2. Continued

Entry	Substrate **1**	Product **3**	Time (min)	Yield (%)[a]
10	 **1j**	 **3j**	30	60
11	 **1k**	 **3k**	35	80

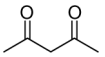
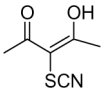
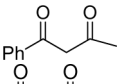
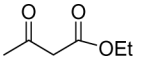
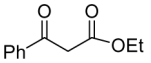
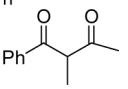
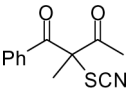
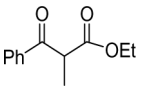
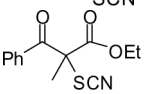
[a]Isolated yield by column chromatography.

EXPERIMENTAL

General Procedures

α-Thiocyanato ketones (3a–3k). Substrate ketone (5 mmol) was added to a yellow suspension of BDMS (1.22 g, 5.5 mmol) in CH_2Cl_2 in one portion. The reaction mixture was stirred at room temperature. After complete consumption of the starting material as observed by TLC (about 10 min), NH_4SCN (0.83 g, 11 mmol) was added and stirring continued. After completion of reaction (monitored on TLC), the solid was removed by filtration and washed with ethyl acetate (50 ml).

Table 3. α-Thiocyanation of β-dicarbonyl compounds[a]

Entry	Substrate	Product	Time (min)	Yield[b] (%)
1			10	96
2		—	180	—[c]
3		—	120	—[c]
4		—	150	—[c]
5			300	90
6			300	92

[a]Reactions were carried out on 5-mmol scale at rt using 1.5 equiv of BDMS and 3.0 equiv of NH_4SCN in acetonitrile.

[b]Yield by column chromatographically isolated compounds.

[c]A mixture of decomposed product was obtained.

The combined organic layer was washed with saturated solution of sodium bicarbonate (50 ml) and brine (50 ml), dried over anhydrous sodium sulfate, and concentrated under reduced pressure to give crude thiocyanato product. Pure product was obtained after column chromatography (silica gel, mesh size 60–120, eluent ethyl acetate–hexane 10:90).

Caution: Reaction should be carried out in an efficient fume hood.

Thiocyanation of β-dicarbonyl compounds. A substrate (5 mmol) was added immediately to a yellow suspension of BDMS (1.66 g, 7.5 mmol) and ammonium thiocyanate (1.14 g, 15 mmol) in 50 ml of dry acetonitrile in one portion. The reaction mixture was stirred at room temperature until complete consumption of starting material as observed by TLC. After completion of the reaction, solid residue was removed by filtration, and the residue was washed with ethyl acetate. The combined organic layer was washed with saturated solution of sodium bicarbonate (50 ml) and brine (50 ml), dried over anhydrous sodium sulfate, and concentrated under reduced pressure to give crude thiocyanato product. Pure product was obtained after column chromatography (silica gel, mesh size 60–120, eluent ethyl acetate–hexane 10:90).

Caution: Reaction should be carried out in an efficient fume hood.

Spectral Data for Selected Compounds

1-Phenyl-2-thiocyanatoethanone (3a). Solid. Mp 70–72°C (lit.[11b] 67–69°C). ^{1}H NMR (60 MHz, $CDCl_3$): δ 4.73 (s, 2H), 7.26–7.62 (m, 3H), 7.88–8.01 (m, 2H) ppm. IR (KBr): ν_{max} 2926, 2154 (–SCN), 1677, 1591, 1201, 996 cm^{-1}.

2-Thiocyanato-p-tolylethanone (3b). Solid. Mp 103–106°C (lit.[19a] 105–107°C). ^{1}H NMR (60 MHz, $CDCl_3$): δ 2.45 (s, 3H), 4.71 (s, 2H), 7.32 (d, $J = 7.8$ Hz, 2H), 7.84 (d, $J = 7.8$ Hz, 2H) ppm. IR (KBr): ν_{max} 2936, 2148 (–SCN), 1677, 1591, 1201, 996 cm^{-1}.

1-(4-Hydroxyphenyl)-2-thiocyanatoethanone (3c). Solid. Mp 159–161°C (lit.[11b] 160–162°C). ^{1}H NMR (60 MHz, $CDCl_3$): δ 4.68 (s, 2H), 6.94 (d, $J = 7.8$ Hz, 2H), 7.88 (d, $J = 7.8$ Hz, 2H) ppm. IR (KBr): ν_{max} 3500, 2156 (–SCN), 1678, 1596, 1205, 997 cm^{-1}.

1-(4-Methoxyphenyl)-2-thiocyanatoethanone (3d). Solid. Mp 121–125°C (lit.[19a] 122–125°C). ^{1}H NMR (60 MHz, $CDCl_3$): δ 3.91 (s, 3H), 4.70 (s, 2H), 6.98 (d, $J = 9.0$ Hz, 2H), 7.93 (d, $J = 9.0$ Hz, 2H) ppm. IR (KBr): ν_{max} 2930, 2153 (–SCN), 1666, 1598, 1208, 829 cm^{-1}.

1-(4-Bromophenyl)-2-thiocyanatoethanone[19b] (3e). Solid. Mp 123–125°C. ^{1}H NMR (60 MHz, $CDCl_3$): δ 4.67 (s, 2H), 7.66 (d, $J = 10.2$ Hz, 2H), 7.82 (d, $J = 10.2$ Hz, 2H) ppm. IR (KBr): ν_{max} 2926, 2155 (–SCN), 1669, 1584, 1202, 998 cm^{-1}.

1-(4-Chlorophenyl)-2-thiocyanatoethanone (3f). Solid. Mp 132–134°C (lit.[19a] 132–135°C). ^{1}H NMR (60 MHz, $CDCl_3$): δ 4.69 (s, 2H), 7.35 (d, $J = 10.2$ Hz, 2H), 7.92 (d, $J = 10.2$ Hz, 2H) ppm. IR (KBr): ν_{max} 2978, 2148 (–SCN), 1669, 1588, 1203, 998 cm^{-1}.

1-(4-Nitrophenyl)-2-thiocyanatoethanone (3g). Solid. Mp 119–120°C (lit.[21] 118.5°C). ^{1}H NMR (60 MHz, $CDCl_3$): δ 4.71 (s, 2H), 8.11 (d, $J = 9.0$ Hz, 2H), 8.40 (d, $J = 9.0$ Hz, 2H) ppm. IR (KBr): ν_{max} 2980, 2153 (–SCN), 1677, 1601, 1531, 1348, 1198, 1000 cm^{-1}.

1-(2,4-Dichlorophenyl)-2-thiocyanatoethanone[1b] (3h). Solid. Mp 88–90°C. ^{1}H NMR (60 MHz, $CDCl_3$): δ 4.73 (s, 2H), 7.46–7.98 (m, 3H) ppm. IR (KBr): ν_{max} 2985, 2152 (–SCN), 1674, 1594, 1200, 996 cm^{-1}.

2-Thiocyanatocyclohexanone (3i). Oil (lit.[9] oil). ^{1}H NMR (60 MHz, $CDCl_3$): δ 1.59–2.87 (m, 8H), 4.13–4.39 (m, 1H) ppm. IR (neat): ν_{max} 2948, 2155 (–SCN), 1713, 1449, 1302, 1127 cm^{-1}.

2-Thiocyanatocyclopentanone (3j). Oil (lit.[9] Oil). ^{1}H NMR (60 MHz, $CDCl_3$): δ 1.65–2.87 (m, 6H), 3.75–3.89 (m, 1H) ppm.

IR (neat): ν_{max} 2954, 2156 (–SCN), 1750, 1458, 832 cm^{-1}.

1-Phenyl-1-thiocyanatopropan-2-one (3k). Oil. ^{1}H NMR (60 MHz, $CDCl_3$): δ 2.14 (s, 3H), 5.26 (s, 1H), 7.23–7.45 (m, 5H) ppm.

IR (neat): ν_{max} 2924, 2156 (–SCN), 1713, 1595, 1254 cm^{-1}. Anal. calcd. for $C_{10}H_9NOS$: C, 62.80; H, 4.74; N, 7.32. Found: C, 62.70; H, 4.63; N, 7.25.

4-Hydroxy-3-thiocyanatopent-3-en-2-one. Solid. Mp 78–80°C (lit.[9] 79–81). ^{1}H NMR (60 MHz, $CDCl_3$): δ 2.51 (s, 6H), 17.18 (s, 1H, enol OH) ppm. IR (KBr): ν_{max} 3414, 2159 (–SCN), 1711, 1586, 1409, 1365, 1000 cm^{-1}.

2-Methyl-1-phenyl-2-thiocyanatobutane-1,3-dione. Oil. ^{1}H NMR (60 MHz, $CDCl_3$): δ 1.23 (s, 3H), 2.24 (s, 3H), 7.12–7.85 (m, 5H) ppm.

IR (neat): ν_{max} 2938, 2156 (–SCN), 1722, 1674, 1596, 1449, 1211, 952 cm^{-1}. Anal. calcd. for $C_{12}H_{11}NO_2S$: C, 61.78; H, 4.75; N, 6.0. Found: C, 61.67; H, 4.79; N, 6.1.

Ethyl 2-methyl-3-oxo-3-phenyl-2-thiocyanatopropanoate. Oil. ^{1}H NMR (60 MHz, $CDCl_3$): δ 1.21 (t, $J = 6.6$ Hz, 3H), 1.57 (s, 3H), 4.20 (q, $J = 6.6$ Hz, 2H), 7.32–7.96 (m, 5H) ppm. IR (neat): ν_{max} 2980, 2159 (–SCN), 1738, 1670, 1594, 1449, 1281, 1021 cm^{-1}. Anal. calcd. for $C_{13}H_{13}NO_3S$: C, 59.39; H, 4.98; N, 5.32. Found: C, 59.35; H, 4.87; N, 5.42.

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