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Cerium(IV) Ammonium Nitrate Mediated Addition of Thiocyanate and Azide to Styrenes: Expeditious Routes to Phenacyl Thiocyanates and Phenacyl Azides

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This paper is dedicated with respectful regards to Professor Josef Fried on the occasion of his 85th birthday

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Abstract—An efficient synthesis of phenacyl thiocyanates and phenacyl azides is described here. Styrenes react with ammonium thiocyanate and sodium azide in the presence of cerium(IV) ammonium nitrate under an oxygen atmosphere to afford phenacyl thiocyanates and phenacyl azides respectively in good yields. © 2000 Published by Elsevier Science Ltd.

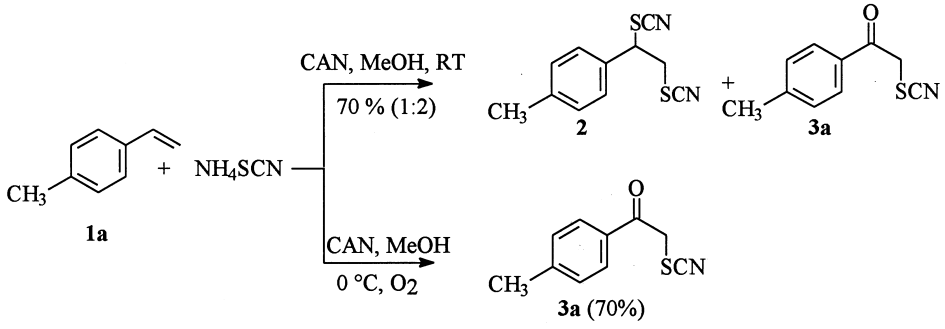
Introduction

In view of the current interest in the synthetic applications of cerium(IV) ammonium nitrate (CAN)[1,2] we have been exploring its potential use in carbon–heteroatom bond formation. Recently we have reported a very efficient CAN mediated addition of thiocyanate to styrenes and electron rich aromatics leading to the formation of 1,2-dithiocyanates and aryl thiocyanates respectively.[3] Subsequently we encountered a novel procedure for the synthesis of phenacyl thiocyanates directly from styrenes, using ammonium thiocyanate mediated by CAN. This strategy was found applicable to the synthesis of phenacyl azides also; these results are reported here. It is noteworthy that recently, iodine(III) reagents have been used for the thiocyanation of alkenes[4,5] and for the conversion of enol silyl ethers to α-thiocyanato ketones.[6]

Results and Discussion

Our initial experiment involved the reaction of 4-methylstyrene with ammonium thiocyanate in the presence of CAN in methanol, which led to an inseparable mixture of 1,2-dithiocyanate **2** and phenacyl thiocyanate **3a** in 1:2 ratio. With the reasonable assumption that oxygen takes part in the reaction leading to the phenacyl thiocyanate, the reaction of **1a** with CAN (2.3 equiv.) and ammonium thiocyanate (1.1 equiv.) was conducted in an atmosphere of oxygen. In this case the phenacyl thiocyanate was formed in 70% yield and no dithiocyanate was observed (Scheme 1).

Various substituted styrenes when subjected to similar experimental conditions afforded the corresponding phenacyl thiocyanates (Scheme 2, Table 1).



Scheme 1.

Keywords: cerium(IV) ammonium nitrate; phenacyl thiocyanate; phenacyl azide; styrene.

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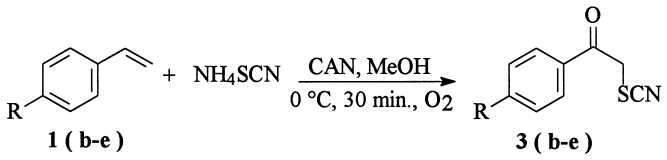


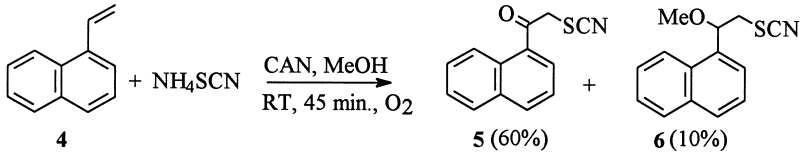
Scheme 2.

Table 1. Synthesis of phenacyl thiocyanates

Entry	Substrate	R	Product	Yield[a] (%)
1	**1b**	OMe	**3b**	53
2	**1c**	OAc	**3c**	68
3	**1d**	Cl	**3d**	65
4	**1e**	NHAc	**3e**	57

[a] Isolated yield.

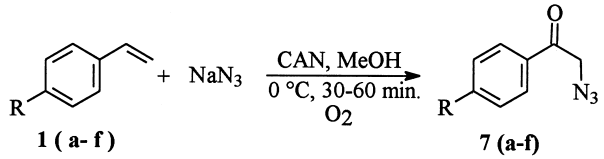
$Mn(OAc)_3$ leading to the corresponding diazides.[11,12] In this context, it may be recalled that iodosobenzene diacetate–azidotrimethylsilane[13] or CrO_3–$TMSN_3$[14] combination has been used in the conversion of styrenes to phenacyl azides. The formation of phenacyl azides from styrenes and azide mediated by CAN, however, has not been reported previously. In a procedure analogous to the one leading to phenacyl thiocyanates, the reaction of styrene



Scheme 3.

As expected, when the experiment was conducted under a deoxygenated atmosphere, the dithiocyanate was formed as the only isolable product and the formation of phenacyl thiocyanate was not observed. In the reaction of thiocyanate with 1-vinylnaphthalene **4**, although the major product was the expected keto thiocyanate **5**, a small amount of the β-methoxy thiocyanate **6** was also obtained (Scheme 3).

Prompted by the success of the above reaction, it was decided to explore the possibility of synthesizing phenacyl azides using a similar strategy. It is noteworthy that in his pioneering work in 1971 Trahanovsky reported that CAN mediated addition of azide to alkenes resulted in the formation of 1-azido-2-nitrates and diazides.[7,8] Subsequent work on CAN mediated azidation of glycals and triisopropylsilyl enol ethers is also well documented.[9,10] Mention may also be made of the azidation of alkenes and glycals using



Scheme 4.

Table 2. Synthesis of phenacyl azides

Entry	Substrate	R	Product	Yield[a] (%)
1	**1a**	Me	**7a**	76
2	**1b**	OMe	**7b**	95
3	**1c**	OAc	**7c**	75
4	**1d**	Cl	**7d**	69
5	**1e**	NHAc	**7e**	68
6	**1f**	H	**7f**	85

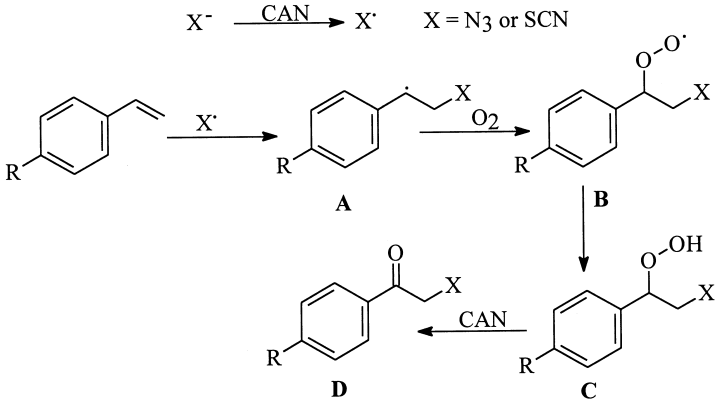
[a] Isolated yield.

1f and sodium azide in presence of CAN in methanol in oxygen atmosphere afforded phenacyl azide **7f** in 85% yield. Similar results were obtained with other styrenes also (Scheme 4, Table 2).

A mechanistic rationalization of the process leading to phenacyl thiocyanate or azide may be presented as follows (Scheme 5). Oxidation of the anion (thiocyanate or azide) by CAN would lead to the corresponding radical. Conceivably addition of the latter to the styrene will result in the benzylic radical **A**. This can trap oxygen[2b,15] to form the peroxy radical **B**, eventually leading to the hydroperoxide **C** by abstraction of a hydrogen from the solvent. Oxidative cleavage of **C** by CAN will result in the corresponding phenacyl thiocyanate or azide **D**.

In conclusion, we have uncovered a facile process for the synthesis of phenacyl thiocyanates and phenacyl azides. α-Thiocyanatoketones have been conventionally prepared from α-haloketones via nucleophilic displacement with thiocyanate or by the ring opening of epoxide using thiocyanate anion followed by oxidation.[16,17] These methods, however, often require drastic reaction conditions leading to low yields of products. Phenacyl azides are generally prepared from the corresponding bromides obtainable from acetophenone, by displacement with azide.[18,19] The instability and lachrymatory property of phenacyl bromides make this procedure inconvenient.

Both the phenacyl azides and thiocyanates are useful intermediates in organic synthesis. A recent example of the use of phenacyl azides in synthesis involves their conversion to formyl oxazoles by Vilsmeir reaction.[20] The thiocyanato group is an important functional group since it can be transformed into a number of other functionalities.[21,22] Its presence in several biologically active natural products is also noteworthy.[23,24] α-Thiocyanato ketones[25] serve as



Scheme 5.

intermediates in the synthesis of several types of heterocycles.[26]

Experimental

NMR spectra were recorded on a Bruker—300 MHz NMR spectrometer. Chemical shifts are reported (δ) relative to TMS (^{1}H) and $CDCl_3$ (^{13}C) as the internal standards. Elemental analyses were performed on a Hewlett–Packard 185-B CHN analyser. Mass spectra were recorded under EI/HRMS (at 5000 resolution) using Auto Spec. M mass spectrometer. Melting points were recorded on Büchi melting point apparatus and were uncorrected. Column chromatography was performed on silica gel (100–200 mesh). Solvents were distilled prior to use. The CAN used for the reactions was purchased from Aldrich Co. and was used without purification. Substituted styrenes were prepared from the corresponding aldehydes via Wittig olefination reaction.

General procedure for the synthesis of phenacyl thiocyanates

To a solution of styrene (1 mmol) and ammonium thiocyanate (1.1 mmol) in methanol saturated with oxygen, an oxygenated solution of CAN (2.3 mmol) in methanol was added dropwise at ice temperature, while the reaction mixture was continuously being purged with oxygen. After 30 min, the reaction mixture was diluted with distilled water (50 mL), extracted with dichloromethane (5×20 mL), washed with saturated brine, and dried over anhydrous sodium sulfate. The residue obtained after the removal of solvent was purified using a silica gel column to afford the corresponding phenacyl thiocyanates.

4′-Methyl-2-thiocyanatoacetophenone (3a). A mixture of 4-methylstyrene **1a** (0.118 g, 1 mmol) and ammonium thiocyanate (0.086 g, 1.1 mmol) in methanol (5 mL) was treated with CAN (1.26 g, 2.3 mmol) in methanol (10 mL) in an atmosphere of oxygen. The reaction mixture was worked up as usual and the residue on purification afforded **3a** as a colorless crystalline solid (0.134 g, 70%) which was recrystallized from $CHCl_3$–hexane, mp 105–107°C; IR (KBr)ν_{max}: 2985, 2153 (SCN), 1678 (CO), 1605 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 7.82 (d, 2H, J=7.7 Hz, Ar*H*), 7.31 (d, 2H, J=7.7 Hz, Ar*H*), 4.73 (s, 2H, COCH_2), 2.45 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$): δ 190.10, 145.77, 131.51, 129.72, 128.51, 111.63, 42.98, 21.76; Anal. Calcd for $C_{10}H_9NOS$: C, 62.82; H, 4.71; N, 7.32; S, 16.75. Found: C, 62.77; H, 4.78; N, 7.39; S, 16.82.

4′-Methoxy-2-thiocyanatoacetophenone (3b). Reaction of 4-methoxystyrene **1b** (0.136 g, 1 mmol) and ammonium thiocyanate (0.086 g, 1.1 mmol) with CAN (1.26 g, 2.3 mmol) in methanol under an oxygen atmosphere afforded **3b** as colorless crystals (0.110 g, 53%). It was recrystallized from $CHCl_3$–hexane; mp 122–125°C (lit.,[27] 121°C); IR (KBr)ν_{max}: 3063, 2982, 2840, 2160 (SCN), 1674 (CO), 1600 cm^{-1}.

4′-Acetoxy-2-thiocyanatoacetophenone (3c). Reaction of 4-acetoxystyrene **1c** (0.162 g, 1 mmol) and ammonium thiocyanate (.086 g, 1.1 mmol) with CAN (1.26 g, 2.3 mmol) in methanol under an oxygen atmosphere afforded **3c** as a colorless solid (0.160 g, 68%) and recrystallized from $CHCl_3$–hexane; mp 99–102°C; IR (KBr)ν_{max}: 2935, 2160, 1762, 1688, 1550 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 7.97 (d, 2H, J=8.6 Hz, Ar*H*), 7.27 (d, 2H, J=8.6 Hz, Ar*H*), 4.72 (s, 2H, COCH_2), 2.34 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$): δ 189.32, 168.16, 155.52, 131.39, 130.06, 122.33, 111.35, 42.79, 21.02. Anal. Calcd for $C_{11}H_9NO_3S$: C, 56.16; H, 3.86; N, 5.96; S, 13.60. Found: C, 55.92; H, 3.89; N, 5.81; S, 13.48.

4′-Chloro-2-thiocyanatoacetophenone (3d). A mixture of 4-chlorostyrene **1d** (0.138 g, 1 mmol) and ammonium thiocyanate (0.086 g, 1.1 mmol) in methanol was treated with a solution of CAN (1.26 g, 2.3 mmol) in methanol under an oxygen atmosphere to afford **3d** as colorless crystals (0.138 g, 65%). It was recrystallized from $CHCl_3$–hexane; mp 132–135°C (lit.,[27]135°C). IR (KBr)ν_{max}: 3097, 2987, 2153, 1667, 1580, 1485 cm^{-1}.

4′-Acetamido-2-thiocyanatoacetophenone (3e). Reaction of **1e** (0.162 g, 1mmol) and ammonium thiocyanate (0.086 g, 1.1 mmol) with CAN (1.26 g, 2.3 mmol) in methanol under an oxygen atmosphere afforded **3e** as pale yellow powder (0.133 g, 57%) which was recrystallized from acetone–hexane. Mp 192–194°C (lit.,[28] 193°C). IR (KBr)ν_{max}: 3306, 2153, 1688, 1640, 1600, 1539 cm^{-1}.

1-(1-Naphthyl)-2-thiocyanatoethanone (5) and 1-methoxy-1-(1-naphthyl)-2-thiocyanatoethane (6)

To a stirred mixture of 1-vinylnaphthalene **4** (0.154 g, 1 mmol) and ammonium thiocyanate (0.086 g, 1.1 mmol) in methanol (5 mL), CAN (1.26 g, 2.3 mmol) in methanol (10 mL) was added dropwise. The reaction mixture on work up and purification afforded **5** as a colorless solid (0.136 g, 60%) and **6** (.024 g, 10%) as a yellow viscous liquid.

Data of 1-(1-naphthyl)-2-thiocyanatoethanone (5). Mp 89–90°C; IR (KBr) ν_{max}: 2916, 2155, 1669 cm^{-1}. ^1H NMR ($CDCl_3$): δ 8.80 (d, 1H, J=8.5 Hz, Ar*H*), 8.08 (d, 1H, J=8.2 Hz, Ar*H*), 7.94–7.87 (m, 2H, Ar*H*), 7.67–7.49 (m, 3H, Ar*H*), 4.81 (s, 2H, CH_2SCN); ^{13}C NMR ($CDCl_3$): δ 193.14, 135.24, 134.03, 131.03, 130.33, 129.81, 129.17, 128.70, 127.12, 125.66, 124.18, 111.71, 45.04; Anal. Calcd for $C_{13}H_9NOS$: C, 68.70; H, 3.99; N, 6.16; S, 14.11. Found: C, 68.81; H, 3.95; N, 6.09; S, 14.15.

Data of 1-methoxy-1-(1-naphthyl)-2-thiocyanatoethane (6). IR (CH_2Cl_2) ν_{max}: 2934, 2830, 2149, 1103; ^1H NMR ($CDCl_3$): δ 8.06 (d, 1H, J=8.1 Hz, Ar*H*), 7.86–7.78 (m, 2H, Ar*H*), 7.57–7.43 (m, 4H, Ar*H*), 5.15 (dd, 1H, J=3.3, 9.0 Hz, C*H*OMe), 3.35 (s, 3H, O*Me*), 3.30–3.18 (m, 2H, CH_2SCN). ^{13}C NMR ($CDCl_3$): δ 133.90, 133.49, 130.52, 129.20, 129.11, 126.71, 125.85, 125.30, 124.24, 122.07, 112.19, 79.58, 57.36, 40.00; HRMS Calcd for $C_{14}H_{13}NOS$: 243.0717. Found: 243.0725.

General procedure for the synthesis of phenacyl azides

To a solution of styrene **1a**–**f** (1 mmol) and sodium azide (1.5 mmol) in methanol saturated with oxygen, an oxygenated solution of CAN (2.3 mmol) in methanol was added dropwise at ice temperature, while the reaction mixture was continuously being purged with oxygen. After 30–45 min, the reaction mixture was diluted with distilled water (50 mL), extracted with dichloromethane (5×20 mL), washed with saturated brine, and dried over anhydrous sodium sulfate. The residue obtained after the removal of solvent was purified on a silica gel column to afford the corresponding phenacyl azide **7a**–**f**.

2-Azido-4′-methylacetophenone (7a). Reaction of 4-methylstyrene **1a** (0.118 g, 1 mmol) and sodium azide (0.097 g, 1.5 mmol) with CAN (1.26 g, 2.3 mmol) in methanol (10 mL) under an oxygen atmosphere afforded **7a** (0.133 g, 76%) as a colorless solid. It was recrystallized from CH_2Cl_2–hexane; mp 60–61°C (lit.,[18] 59–62°C); IR (KBr) ν_{max}: 2903, 2101, 1690, 1227 cm^{-1}.

2-Azido-4′-methoxy-acetophenone (7b). Reaction of 4-methoxystyrene **1b** (0.136 g, 1 mmol) and sodium azide (0.097 g, 1.5 mmol) with CAN (1.26 g, 2.3 mmol) in methanol under an oxygen atmosphere afforded **7b** as colorless solid, (0.181 g, 95%). It was recrystallized from CH_2Cl_2–hexane; mp 71–72°C (lit.,[18] 71–73°C); IR (KBr) ν_{max}: 2903, 2843, 2126, 1684, 1602, 1240 cm^{-1}.

2-Azido-4′-acetoxyacetophenone (7c). Reaction of 4-acetoxystyrene **1c** (0.162 g, 1 mmol) and sodium azide (0.097 g, 1.5 mmol) with CAN (1.26 g, 2.3 mmol) in methanol under an oxygen atmosphere afforded **7c** as a colorless oil (0.165 g, 75%). It was recrystallized at 0°C from CH_2Cl_2–hexane; mp 54–56°C; IR (KBr) ν_{max}: 2921, 2099, 1755, 1694, 1607, 1499, 1371, 1196 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ 7.89 (d, 2H, J=8.5 Hz, Ar*H*), 7.18 (d, 2H, J=8.5 Hz, Ar*H*), 4.48 (s, 2H, COCH_2N_3), 2.28 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 191.76, 168.37, 155.04, 131.89, 129.58, 122.20, 54.71, 21.10; Anal. Calcd for $C_{10}H_9N_3O_3$: C, 55.07; H, 4.00. Found: C, 54.79; H, 4.14.

2-Azido-4′-chloroacetophenone (7d). Reaction of 4-chlorostyrene **1d** (0.138g, 1 mmol) and sodium azide (0.097 g, 1.5 mmol) with CAN (1.26 g, 2.3 mmol) in methanol under an oxygen atmosphere afforded **7d** (0.135 g, 69%) as a colorless solid. It was recrystallized from CH_2Cl_2–hexane; mp 68–70°C (lit.,[18] 67–70°C); IR (KBr) ν_{max}: 2903, 2100, 1693, 1217 cm^{-1}.

2-Azido-4′-acetamidoacetophenone (7e). Reaction of 4-acetamidostyrene **1e** (0.161 g, 1 mmol) and sodium azide (0.097 g, 1.5 mmol) with CAN (1.26 g, 2.3 mmol) in methanol under an oxygen atmosphere afforded **7e** (0.150 g, 68%) as colorless powder, which got decomposed at 165–166°C (lit.,[29] 167°C); IR (KBr) ν_{max}: 3335, 3195, 2113, 1675, 1653, 1596, 1535 cm^{-1}.

2-Azidoacetophenone (7f). Reaction of styrene **1f** (0.104 g, 1 mmol) and sodium azide (0.097 g, 1.5 mmol) with CAN (1.26 g, 2.3 mmol) in methanol under an oxygen atmosphere afforded **7f**[30] as a pale yellow viscous liquid, (0.136 g, 85%). IR (CH_2Cl_2) ν_{max}: 3063, 2921, 2106, 1694, 1593, 1452, 1283 cm^{-1}.

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